DISTRIBUTION AND POTENTIAL SOURCES OF PERCHLORATE IN THE HIGH PLAINS REGION OF TEXAS

FINAL REPORT

By

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EXECUTIVE SUMMARY

A large scale sampling program was led by the Texas Tech University Water Resources Center (TTUWRC) to determine the source and distribution of perchlorate in northwest Texas groundwater. This sampling program included public water system (PWS), private, irrigation, and USGS monitoring wells over an area of 52,900 mi^2 in 54 four Texas counties. Ten wells were sampled in the two eastern counties of New Mexico (Lea and Roosevelt) adjacent to the Texas study area, covering 6,800 square mi^2. Three well clusters were installed in Bailey (2 wells), Gaines (3 wells), and Martin (3 wells) counties to show possible vertical variations in perchlorate concentration. Grab samples of the sediments were collected at 5-ft intervals in both unsaturated and saturated zones for geologic logging and perchlorate extraction. In addition to the well clusters, unsaturated zone soil samples were obtained from one site in Carson County and two individual USGS monitoring wells from Bailey and Cochran counties. Groundwater samples were collected from the two USGS wells in Bailey and Cochran counties and from two USGS deep nested well systems in Hale and Castro counties. The wells in the fifty six-county study area in Texas and New Mexico represent five different aquifers, including the Edwards-Trinity (Plateau), Cenozoic Pecos Alluvium, Dockum (known locally as the Santa Rosa), Seymour, and High Plains Aquifer system (referred to locally as the Ogallala).

Perchlorate detections were widespread across the study area. Among the 560 PWS wells sampled in the 54 Texas counties, 256 (46%) contained perchlorate (>0.5 ppb), of which 102 (18%) contained perchlorate equal to or greater than 4 ppb. Reanalysis of 114 PWS samples that were originally reported as below the 0.5 ppb

detection limit by HPLC/MS found that 81 (71%) did test positive for perchlorate. Of the 76 private wells, 36 (47%) had detectable perchlorate (>0.5 ppb), and 23 (30%) had perchlorate concentrations at or above 4 ppb. Forty-two of the 100 irrigation wells had detectable perchlorate, with 30 at or above 4 ppb. All 10 New Mexico wells had detectable perchlorate (>0.5 ppb) and 6 (60%) had perchlorate concentration at or above 4 ppb.

The concentration of perchlorate varied vertically in all nested/clustered wells in which perchlorate was detected. There was a definite decreasing trend in perchlorate concentration with increase in depth at each TTU well cluster, and perchlorate concentrations ranged from 1.16 ppb in Bailey County to 179 ppb in Gaines County. The perchlorate concentrations in the saturated zone of the USGS wells sites ranged from 0.21 ppb to 6.0 ppb in Hale County, while none of the other wells contained any detectable perchlorate. In addition tritium data indicates that in some cases perchlorate is present in water which is older than modern atmospheric testing of nuclear weapons (~1950).

The unsaturated zone sampling sites (TTUWRC well clusters, Carson County archived samples, and USGS well systems) aligned roughly north-south, spanning 210 miles (65%) of the 370-mi length of the study area. The unsaturated zone thicknesses ranged from 40 ft in Gaines County to 270 ft in Carson County. Of the 201 unsaturated soil samples from TTUWRC wells, 66 (33%) had detectable perchlorate, ranging from 1 □g/kg to 116 □g/kg (dry soil weight) in the unsaturated zone Of the 296 unsaturated soil samples collected from the two USGS wells, only 25 (8.5%) had detectable perchlorate, ranging from 0.64 □g/kg to 14.6 □g/kg (dry soil weight). Sediment samples from the northernmost location (Carson County) were positive for perchlorate in 19 of 78 (24%)

samples with a range of 0.2 □g/kg to 7 □g/kg (dry soil weight).

It was possible to estimate the total mass of perchlorate in the saturated zone for 45 counties (those lying with in the region of the High Plains Aquifer system) with adequate data was available for saturated thickness distribution. The county masses ranged from 970 kg in Dickens County to 250,000 kg in Gaines County, and the total mass of perchlorate in the 45 counties estimated at 1,800,000 kg. The total mass of perchlorate in the unsaturated zone was estimated for the five counties from which unsaturated soil samples were available. The masses of perchlorate in the unsaturated zones were of similar magnitude as the masses in the saturated zone, ranging from 24,000 kg in Bailey County to 490,000 kg in Martin County.

After review of the collected data, it is apparent that no single anthropogenic source could have caused the widespread occurrence of perchlorate. Perchlorate seems to be fairly ubiquitous at very low concentrations in the saturated and unsaturated zone. While no single piece of data collected or calculated was able to definitively identify the source of perchlorate in the study area, it is the strong opinion of this research team that atmospheric production and/or surface oxidative weathering is the source of the perchlorate. The mass of perchlorate produced/deposited per year appears to be concentrated in the unsaturated zone by evapotranspiration during dry periods and flushed to the water table during wet periods. This process has led to higher concentration in groundwater where the water table is relatively shallow, and in areas with lower saturated thickness and thus less available dilution. Agricultural irrigation may have accelerated this process in some areas. Evidence supporting this hypothesis primarily relates to the vertical distribution of perchlorate in the unsaturated zone, co-occurrence of the higher perchlorate in groundwater with areas of low saturated thickness and shallow depth to water, presence of perchlorate in water older than ~1950, and lack of any other viable surface source.

Extended Research Needs

Significant progress has been made in defining both the extent and source of perchlorate in northwest Texas groundwater. However, two significant issues still exist and must be pursued. First, the survey of potentially affected groundwater sources in arid and semi-arid areas of the state must be extended. Second, we must evaluate future impacts of current land and water use practices on perchlorate and other significant contaminants of concern (As, Se, F, NO_3).

Sampling in Phases I and II focused on counties located primarily in the High Plains region of Texas, with additional coverage off the eastern Caprock escarpment and in the Trans-Pecos to the south. However, the results of this study indicate that it is likely any groundwater resources in arid or semi-arid areas with limited recharge will accumulate perchlorate. This conclusion is supported by detections of perchlorate in the Seymour, Edwards-Trinity, and Cenozoic-Pecos Alluvium aquifers. Most of West Texas is sparsely populated with few large PWSs and many residents who utilize private well water. These residents are highly dependent on single wells or small well fields, likely unable to mix multiple water sources. In addition, they are unlikely to be aware of or test for drinking water contaminants. A wider survey of water resources should be conducted to more fully characterize population with potential exposure to perchlorate. These areas should, at minimum, include all counties underlain by the Cenozoic-Pecos Alluvium, Edwards-Trinity, and Seymour aquifers. The region’s minor aquifers, such as the

Rustler, Capitan Reef, Blaine, Hickory, and Marathon, must also be investigated.

The impact of perchlorate in groundwater resources is currently significant and will most likely increase in the near future. The results of this study highlight the potential for increasing concentrations of perchlorate and other groundwater contaminants as the quantity of groundwater in storage decreases and the pace of evaporative salinization accelerates (see Figure 1).. As water levels decline in west and northwest Texas, influx of chemicals of concern will have a greater effect on the overall groundwater concentrations. In addition, evaporative processes such as surface irrigation can increase concentrations of chemicals of concern in the unsaturated zone during periods of low precipitation. During relatively rare high precipitation periods, those residual chemicals are flushed downward toward the water table. Better understanding of these processes is required to mitigate future degradation of groundwater quality.

It is likely that the National Academy of Science will agree with the EPA and recommend the lower RFD and hence an MCL of 6 ppb for perchlorate. If an MCL near this value is adopted, many small PWSs will have to treat some portion of their produced water for perchlorate. In the Southern High Plains, they may also be forced to simultaneously treat for F, As, and Se. These requirements encourage research on current economically viable technologies that can be applied by small PWSs. This effort should include surveys of currently used processes as well as those in development. Cost consideration, required technical level, waste disposal, and overall water efficiency should be considered.

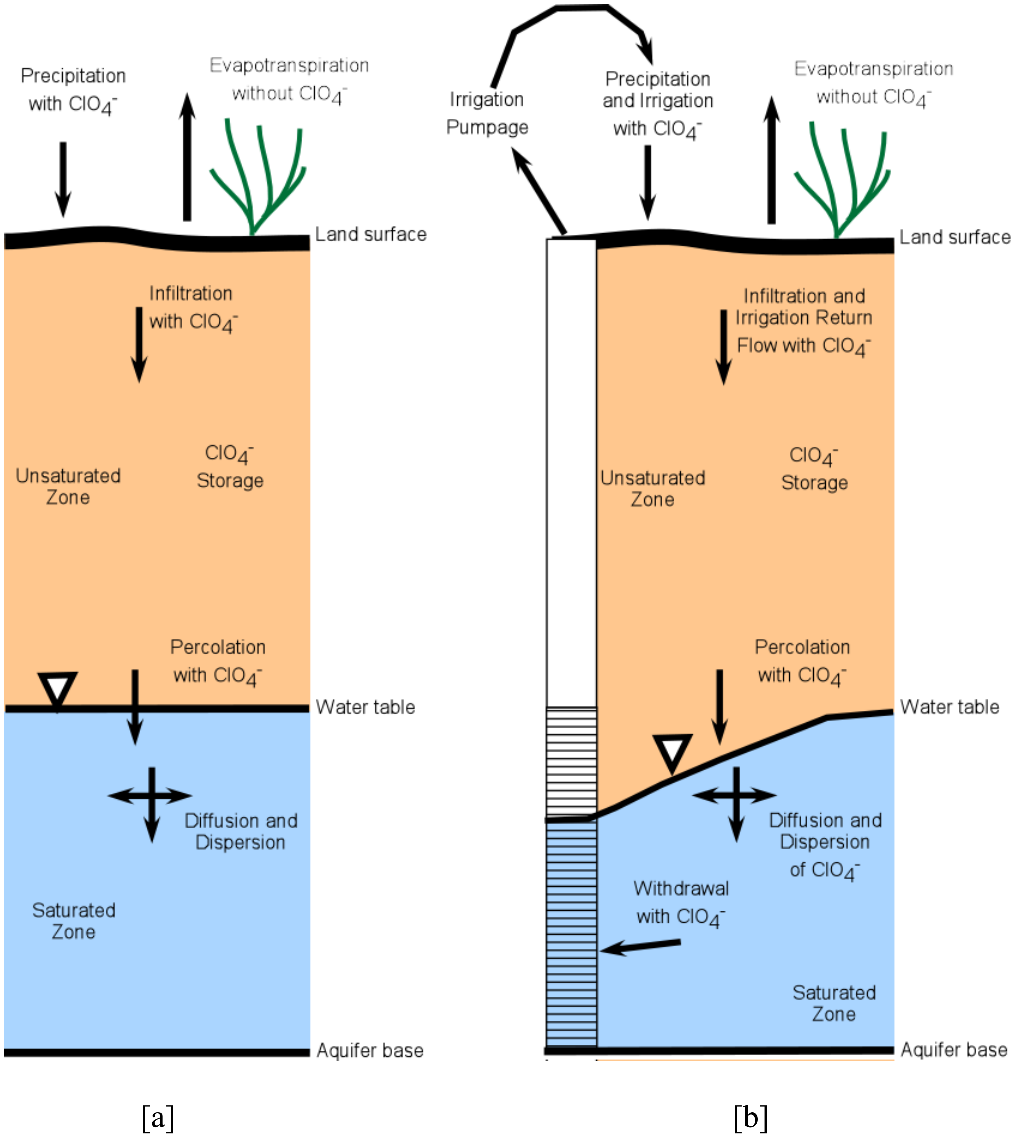

Figure 1. Schematic of perchlorate transport through unsaturated zone in [a] natural conditions and [b] irrigated conditions

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Chapter I

Introduction

In the spring of 2002, the Texas Commission on Environmental Quality (TCEQ) determined that perchlorate (ClO_4^-) was present in ground water from the McMillan and Paul Davis well fields that supply potable water for the City of Midland. Researchers began a large-scale sampling program to determine the source(s) and distribution of perchlorate in the area's ground water. This program included public water system (PWS) wells and private wells in Andrews, Borden, Dawson, Ector, Gaines, Glasscock, Howard, Martin, and Midland counties, which occupy a total area of 23,960 km^2. Water samples were tested for perchlorate and a suite of common ions. From the total of 254 wells sampled in the nine counties, 179 wells (70%) had detectable perchlorate concentrations (>0.5 ppb), and 88 wells (35%) had perchlorate concentrations at or above 4 ppb. The highest perchlorate concentration found at a private well was 58.8 ppb in Dawson County, while the highest concentration detected for a well in public water system (PWS) was 45.6 ppb in City of Midland, Midland County. Perchlorate positively correlated ($\alpha<0.0001$) with Cl^-, F^-, Br^-, SO_4^{2-}, Mg^{2+} and K^+, but not with NO_2^-, NO_3^-, Na^+, or Ca^{+2}. The most likely sources were thought to be [1] a natural mineralogical impurity, [2] agricultural fertilizers containing perchlorate, [3] in situ generation of perchlorate by electrochemical reactions, or [4] some combination of the three. The results of this research were reported to TCEQ (Phase I Final Report) in April of 2003. Following this effort, TTUWRC researchers initiated an additional sampling and research program through funding provided by TCEQ.

The program (Phase II) included several objectives, each with associated specific tasks, intended to resolve the general study questions of the distribution and source of perchlorate present in the High Plains area of Texas. The objectives of Phase II are stated in the following list.

Objective 1. Determine if perchlorate is present in water wells supplying public water systems in an additional 45 counties north, south, and west of the Phase I county region. The counties included Armstrong, Bailey, Briscoe, Carson, Castro, Cochran, Crane, Crosby, Dallam, Deaf Smith, Dickens, Donley, Floyd, Garza, Gray, Hale, Hansford, Hartley, Hemphill, Hockley, Hutchinson, Kent, Lamb, Lipscomb, Lubbock, Lynn, Mitchell, Moore, Ochiltree, Oldham, Parmer, Potter, Randall, Reagan, Roberts, Scurry, Sherman, Sterling, Swisher, Terry, Upton, Ward, Wheeler, Winkler, and Yoakum in Texas and Lea and Roosevelt in New Mexico.

Objective 2. Determine if perchlorate is present in unsaturated and/or saturated sediments and whether the presence of perchlorate is depth dependent within the saturated thickness.

Objective 3. Determine the potential source(s) of perchlorate in the groundwater for all areas where perchlorate is present.

Objective 4. Modeling of present and future contaminant movement and possible recharge through infiltration

This report is organized by these driving research questions and not only contains all the data produced from Phase II but also that from Phase I regarding occurrence and distribution (e.g. the data from the original 9 county area). Chapter 2 focuses on the frequency, distribution, and magnitude of perchlorate concentrations in groundwater in the study area. Chapter 3 describes the vertical distribution of perchlorate in the unsaturated zone of the study area. Chapter 4 summarizes the geology of the study area and any implications in relation to the occurrence of perchlorate. Chapter 5 presents the modeling of present and future contaminant movement and possible recharge through infiltration. Chapter 6 describes the possible sources of perchlorate, including analytical and historical information to aid in determining the likelihood of each source. Finally, Chapter 7 is a summary of the overall conclusions of this project with recommendations for additional work.

Chapter 2

Extent of Perchlorate in Saturated Zone

This chapter specifically discusses the distribution of perchlorate in the upper saturated zone (primary utilized water bearing formation) of fifty-four counties (Andrews, Armstrong, Bailey, Borden, Briscoe, Carson, Castro, Cochran, Crane, Crosby, Dallam, Dawson, Deaf Smith, Dickens, Donley, Ector, Floyd, Gaines, Garza, Glasscock, Gray, Hale, Hansford, Hartley, Hemphill, Hockley, Howard, Hutchinson, Kent, Lamb, Lipscomb, Lubbock, Lynn, Martin, Midland, Mitchell, Moore, Ochiltree, Oldham, Parmer, Potter, Randall, Reagan, Roberts, Scurry, Sherman, Sterling, Swisher, Terry, Upton, Ward, Wheeler, Winkler, and Yoakum) in Texas (from both Phase I and Phase II) and two counties (Lea and Roosevelt) in New Mexico. A number of well types were sampled including PWS and Private; in addition, through co-operative agreements with the USGS and the High Plains Water District, additional data are available from select counties.

2.1 Approach

2.1.1 Sampling

TCEQ records were used to identify all PWS wells in the fifty-four counties. PWS examples include cities, water utilities, mobile home parks, rural convenience stores, and industrial water producers. An appropriate subset of the identified wells was selected to provide adequate geographical coverage. The TTUWRC team considered the locations of all the available wells before selecting 560 wells for sampling and analyses in order to obtain an acceptable geographical distribution. As it turned out, some of the 560 wells originally chosen were not available for sampling due to access or mechanical problems (well no longer in service). Where possible, when an originally selected well could not be sampled, another well in the same area was used to replace the original well. In addition to the PWS wells, a limited number of private wells were sampled to gain a better overall geographical distribution of well locations. Water samples were also obtained from 29 USGS monitoring wells (screened at the top of the water table) and 100 High Plains Water District wells.

Sampling was conducted using flow-through cells to insure representative samples. Data collected at the time of sampling included pH, total dissolved solids (TDS), conductivity, temperature, dissolved oxygen (DO), and oxidation-reduction potential (ORP). Details of the sampling procedure are found in the Quality Assurance Project Plan (QAPP). In general, after well stabilization, 5 samples were collected from each well in 250-mL containers. One container was shipped to the Groundwater Analysis Laboratory (GAL) at The Institute of Environmental and Human Health (TIEHH) for perchlorate analysis, one container was shipped to the TTUWRC Environmental Science Laboratory (ESL) for anion analysis, one container was preserved with nitric acid and shipped to the Geosciences Laboratory for cation analysis, one container was preserved with EDA and was shipped to the TTUWRC Environmental Science Laboratory (ESL) for perchlorate byproduct analysis, and the final container was held in reserve. Occasionally (as needed) the reserve container was shipped to the GAL for a duplicate perchlorate analysis. A small number of reserve samples were also shipped to Exygen Labs for liquid chromatography-mass spectrometer/mass spectrometer (LC-MS/MS) analysis (as required by the contract) to further confirm detections of perchlorate. All wells sampled by TTU were analyzed for perchlorate, Cl^-, F^-, Br^-, NO_3^-, SO_4^{2-}, PO_4^{3},

HCO_3^- as alkalinity, Na^+, Mg^{2+}, K^+, Ca^{2+}, Sr, Fe, As, and Pb. Analytical procedures used are briefly described in the following section.

2.1.2 Instrumental Analyses

Perchlorate ion was analyzed using a Dionex DX-320 ion chromatograph (IC). Standard procedure according to EPA Method 314.0 (USEPA,1999) was used to analyze the samples. A Dionex DX-500 ion chromatograph (IC) equipped with an AS14A column, and 8 mM Na_2CO_3 / 8 mM $NaHCO_3$ eluent was used to determine the concentration of anions like NO_3^-, SO_4^-, Br^-, Cl^-, and $NO2^-$. The method was based on EPA 300.1 (USEPA, 1997) to measure inorganic anions. Cation concentrations (Na^+, Mg^{2+}, K^+, Ca^{2+}, Sr, Fe, and Pb) were measured using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) following EPA Method 200.7 (USEPA, 1994). Arsenic was measured using Graphite Furnace Atomic Absorption Spectrometry following EPA Method 200.9 (USEPA, 1994). Alkalinity was measured as $CaCO_3$ in the water samples according to an EPA standard test method (EPA 310.1).

2.2 Perchlorate Results

This section is a discussion of [1] the frequency and distribution of perchlorate in the study area (PWS wells, Private wells, USGS wells, and HPWD wells), [2] perchlorate confirmation (LC-MS/MS) results, and [3] comparison of the duplicate and field blank analyses. All other water quality data will be discussed in later sections or are available in Appendix A.

2.2.1 Frequency and Magnitude of Perchlorate in the Study Area

2.2.1.1 PWS Wells

From the 560 PWS wells sampled in the fifty-four counties, 314 wells (56%) had no detectable perchlorate (< 0.5 ppb), 246 wells (44%) had detectable perchlorate concentrations (>0.5 ppb), of which 100 wells (18%) had perchlorate concentrations that were equal to or above 4 ppb, and 26 wells (5 %) had perchlorate concentration equal to or greater than 10 ppb (Figure 2.2.1). The concentrations of perchlorate for all wells tested are presented in Appendix A along with the sample number, PWS name, PWS water source (TCEQ well number), well stabilization parameters (e.g. temperature, dissolved oxygen, pH, TDS, etc.), anions, cations, and GIS Locations (Latitude and Longitude) arranged by county.

Of the fifty-three counties analyzed for PWS wells, twenty one counties had no detectable perchlorate, while seven counties had detectable perchlorate in all the wells analyzed. Fifteen counties had detectable perchlorate in less than 50% of the wells analyzed, while eleven counties had detectable perchlorate in more than 50% of the wells analyzed. All of the counties with no detectable perchlorate lie in the Northern half and southeastern part of the study area, while the counties in other categories appear to be sporadically spread throughout the study area (Figure 2.2.2).

The percentage of wells with perchlorate above 4 ppb was smaller, but five counties (Cochran, Dawson, Gaines, Garza, and Kent) still had over 50% of the tested PWS wells with perchlorate greater than 4 ppb, while ten counties (Andrews, Bailey, Briscoe, Ector, Lamb, Lubbock, Lynn, Martin, Midland, and Yoakum) had less than 40% of the tested PWS wells with perchlorate greater than 4 ppb (Table 2.2.1). Most of the high perchlorate detections were found in the south central portion of the study area (Figure 2.2.3).

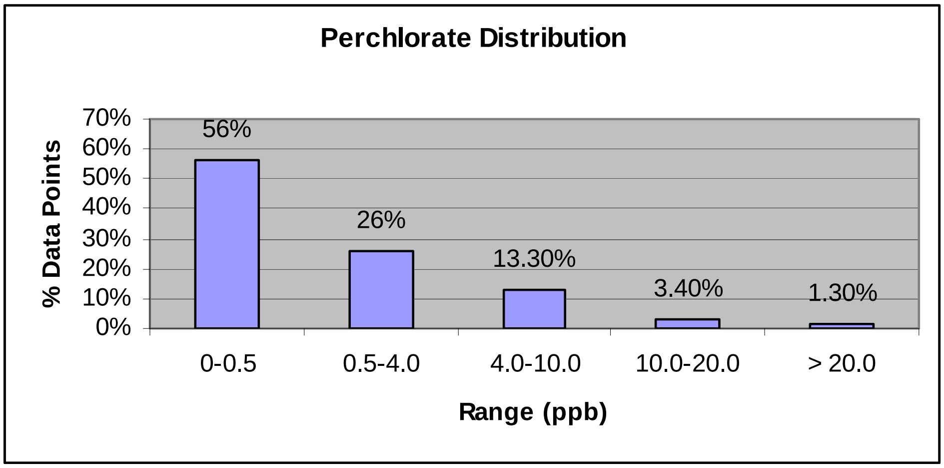

Figure 2.2.1 Frequency of Perchlorate Distribution (PWS wells) in the Study Area.

Table 2.2.1 Frequency of Perchlorate (PC) Detections in PWS Wells by County

County	PWS Wells		Number with PC		Percent with PC	
	Total	Tested	>0.5 ppb	>4 ppb	>0.5 ppb	>4 ppb
Andrews	24	17	17	5	100	29
Armstrong	7	3	0	0	0	0
Bailey	24	5	5	2	100	40
Borden	0	0	0	0	0	0
Briscoe	8	3	1	1	33	33
Carson	23	11	1	0	9	0
Castro	21	5	0	0	0	0
Cochran	15	6	5	3	83	50
Crane	59	9	6	1	67	11
Crosby	6	3	1	0	33	0
Dallam	12	4	0	0	0	0
Dawson		12	11	8	91	67
Deaf Smith	44	10	0	0	0	0
Dickens	4	2	0	0	0	0
Donley	15	2	1	0	50	0
Ector		46	20	2	43	4
Floyd	3	2	0	0	0	0
Gaines		38	38	25	100	66

Table 2.2.1 Frequency of Perchlorate (PC) Detections in PWS Wells by County cont..

County	PWS Wells		Number with PC		Percent with PC	
	Total	Tested	>0.5 ppb	>4 ppb	>0.5 ppb	>4 ppb
Garza	43	3	2	2	67	67
Glasscock		4	1	0	25	0
Gray	59	23	5	1	22	4
Hale	14	8	1	0	13	0
Hansford	6	7	0	0	0	0
Hartley	8	2	0	0	0	0
Hemphill	48	5	0	0	0	0
Hockley	56	7	0	0	0	0
Howard	15	8	3	0	38	0
Hutchinson	12	8	0	0	0	0
Kent		1	1	1	100	100
Lamb	31	15	7	3	47	20
Lipscomb	9	3	0	0	0	0
Lubbock	301	61	44	11	72	18
Lynn	18	5	3	2	60	40
Martin	42	22	17	6	77	27
Midland	85	65	45	27	69	42
Mitchell	16	3	0	0	0	0
Moore	32	15	0	0	0	0
Ochiltree	15	7	0	0	0	0
Oldham	16	7	1	0	14	0
Parmer	35	5	0	0	0	0
Potter	122	27	0	0	0	0
Randall	58	9	1	0	11	0
Reagan	19	4	1	0	25	0
Roberts	2	7	4	0	57	0
Scurry	9	3	0	0	0	0
Sherman	6	2	2	0	100	0
Sterling	3	2	0	0	0	0
Swisher	18	5	3	0	60	0
Terry	23	3	3	0	100	0
Upton	17	6	0	0	0	0
Ward	40	12	3	0	25	0
Wheeler	20	9	4	0	44	0
Winkler	22	6	2	0	33	0
Yoakum	53	3	3	1	100	33

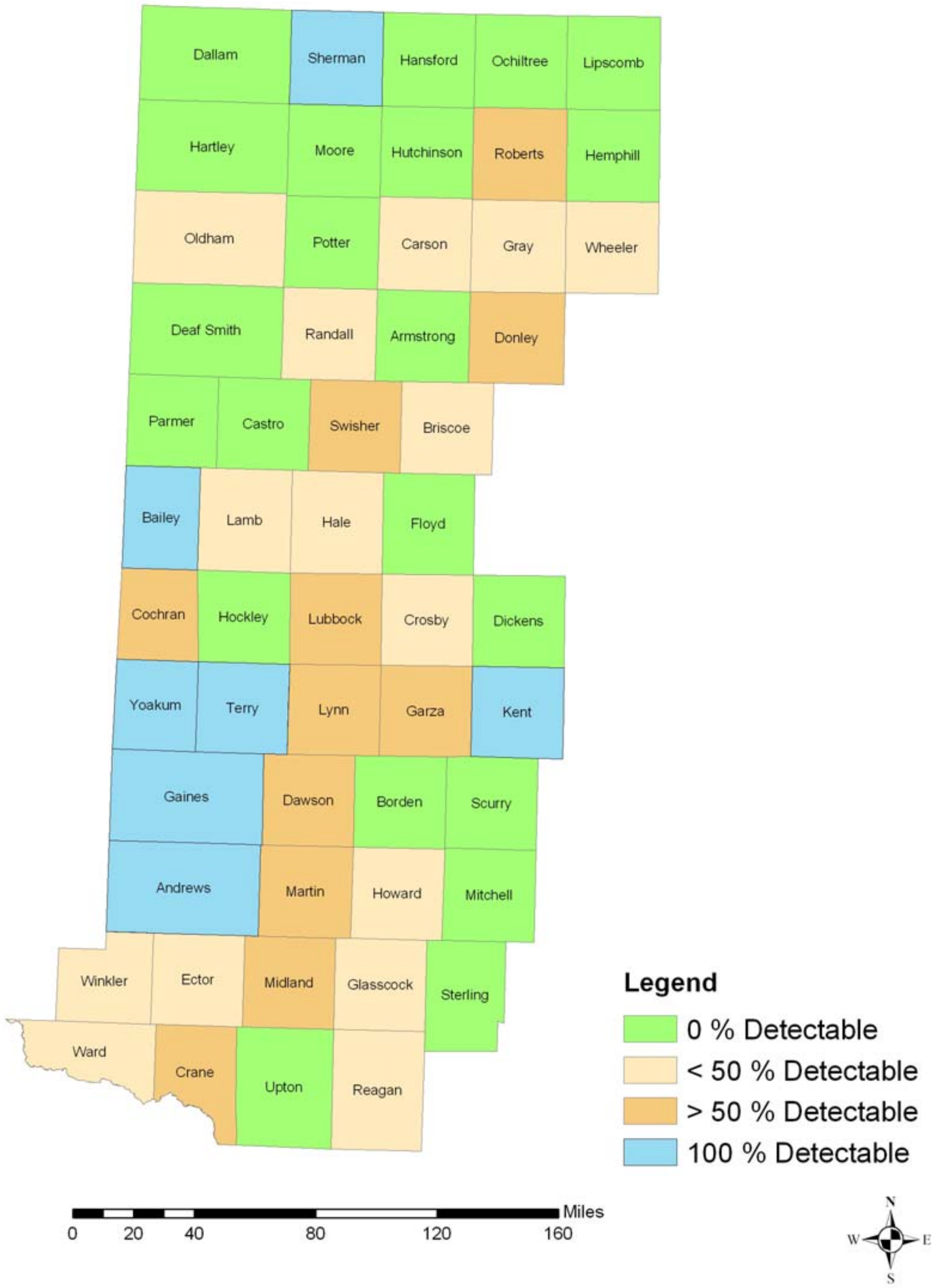

Figure 2.2.2 Frequency of Perchlorate Detections (PWS wells) in the Study Area.

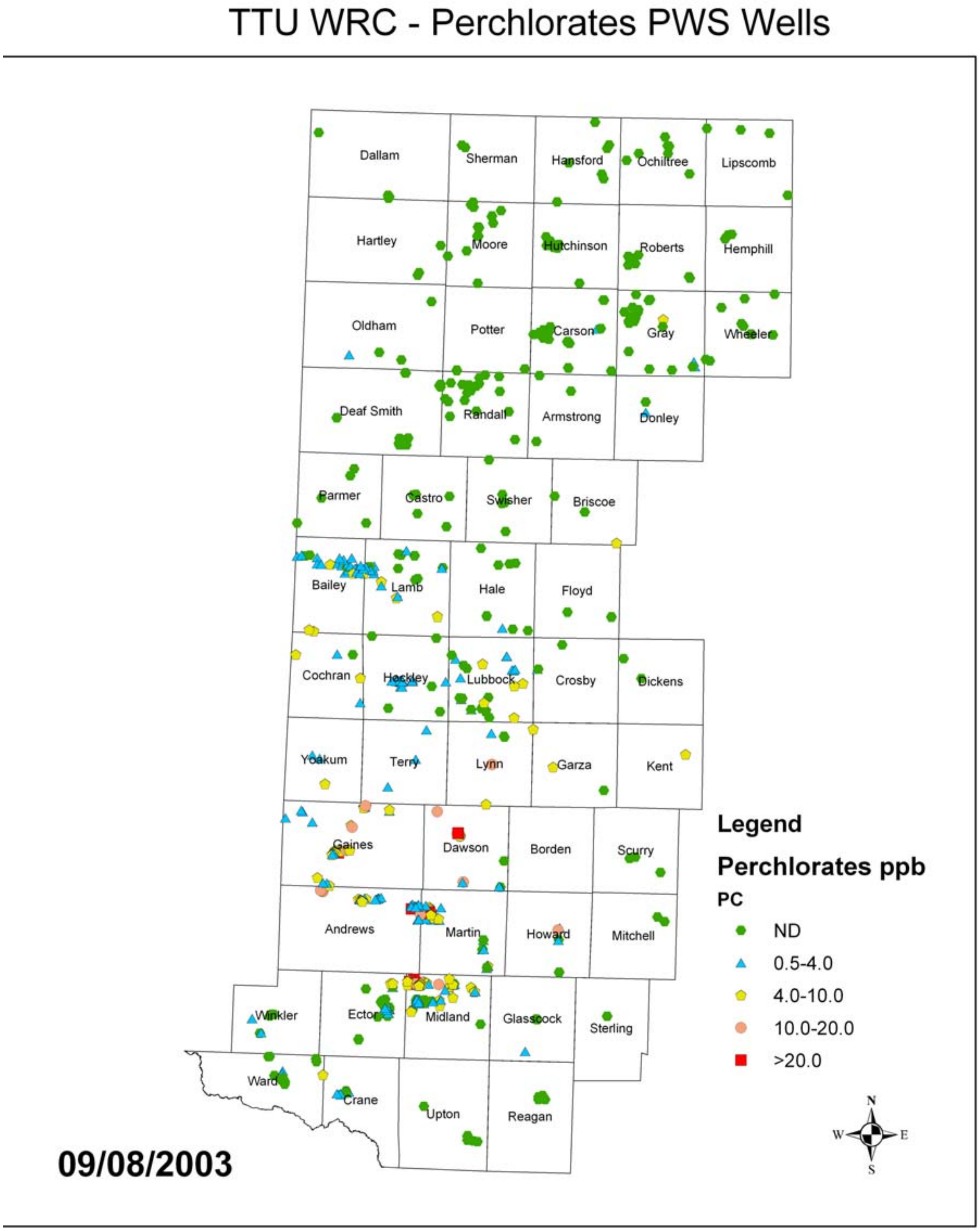

Figure 2.2.3 PWS well distribution and perchlorate concentrations in study area.

2.2.1.2 Private Wells

Private wells were sampled to obtain more data in areas that were not represented well by the PWS sampling effort. Examples of private wells include drinking water wells for homes and livestock (windmills). The concentrations of perchlorate for all private wells tested are presented in Appendix A along with the sample number, well stabilization parameters (e.g. temperature, dissolved oxygen, pH, TDS etc.), anions, cations, and GIS Locations (Latitude and Longitude) arranged by county.

Of the 76 private wells tested (both Phase I and Phase II) in Texas, 36 (47%) had detectable perchlorate (>0.5 ppb), 23 (30%) had perchlorate concentration at or above 4 ppb (Table 2.2.2), and 10 wells (13%) had perchlorate concentrations equal to or greater than 10 ppb (Figure 2.2.4). Of the ten wells sampled in New Mexico, all had detectable perchlorate (>0.5 ppb), 6 (60%) had perchlorate concentrations at or above 4 ppb, and 3 (30%) had perchlorate concentration greater than 10 ppb.

Of the twenty-three counties where private wells were analyzed, seven counties had no detectable perchlorate, while five counties had detectable perchlorate in all the wells analyzed. Seven counties had detectable perchlorate in less than 50% of the wells analyzed, while four counties had detectable perchlorate in more than 50% of the wells analyzed. Of the two counties analyzed for perchlorate in New Mexico, both had 100% perchlorate detections (Figure 2.2.5). Like PWS wells, all the high detections of perchlorate were found in the southern part of the study area in Texas, while all the detections in northern part of the study area were less than 4 ppb (Figure 2.2.6).

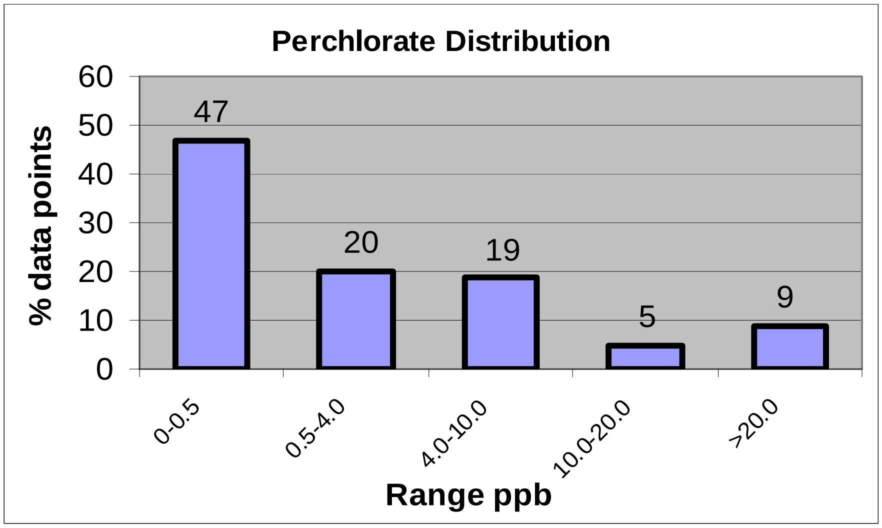

Figure 2.2.4 Frequency of Perchlorate Distribution (private wells) in the Study Area.

Table 2.2.2 Frequency of Perchlorate (PC) Detections in Private Wells by County

County	Private Wells Tested	Number with PC		Percent with PC	
		>0.5 ppb	>4 ppb	>0.5 ppb	>4 ppb
Andrews	6	5	2	83	33
Borden	8	1	1	13	13
Carson	1	1		100	0
Dallam	1	0	0	0	0
Dawson	4	4	2	100	50
Ector	3	1	0	33	0
Gaines	3	2	2	67	67
Glasscock	4	1	0	25	0
Gray	1	0	0	0	0
Hansford	1	0	0	0	0
Howard	5	4	3	80	60
Kent	5	1	1	20	20
Lynn	2	2	2	100	100
Martin	4	4	3	100	75
Midland	2	0	0	0	0
Mitchell	2	0	0	0	0
Potter	5	2	0	40	0
Randall	1	0	0	0	0
Reagan	3	0		0	0
Scurry	4	1	1	25	25
Terry	3	2	2	67	67
Upton	3	1	0	33	0
Winkler	2	2	2	100	100

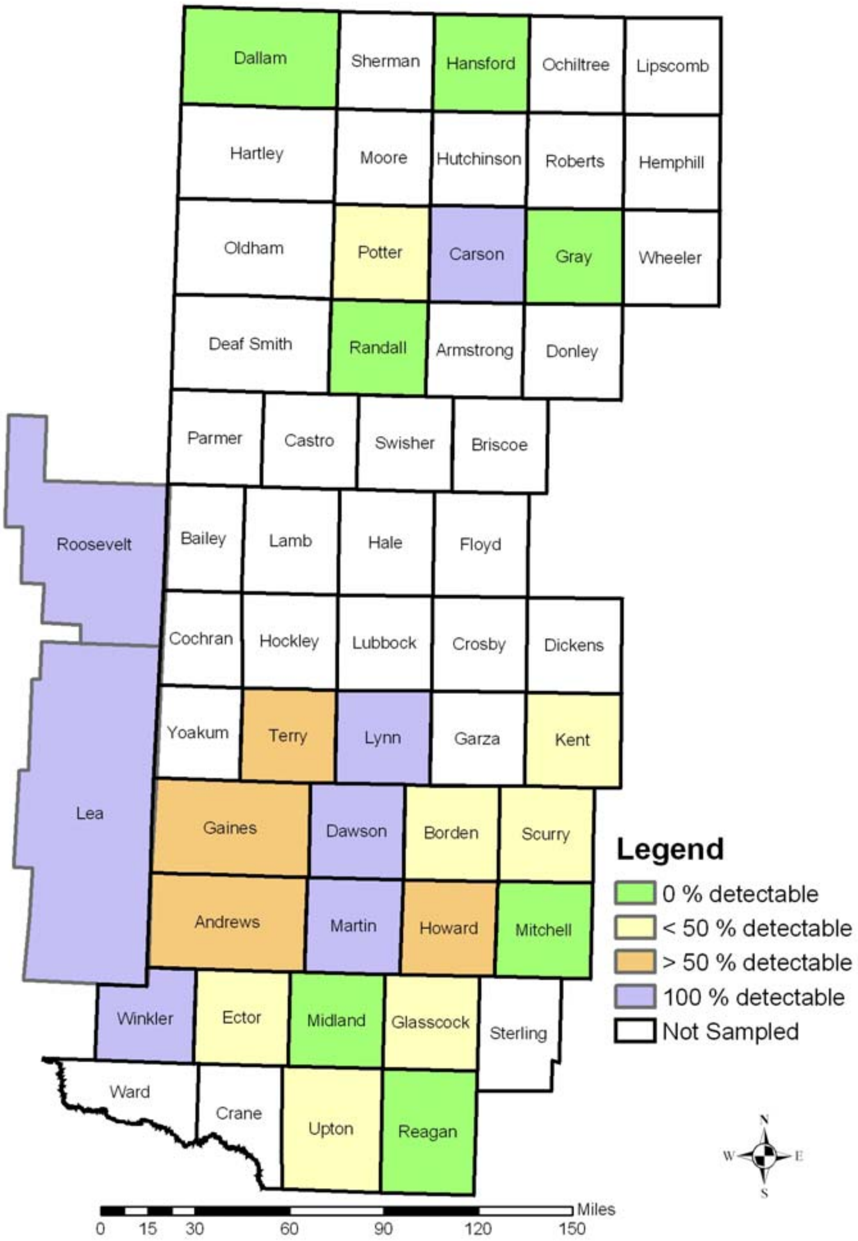

Figure 2.2.5 Frequency of Perchlorate Detections (private wells) in the Study Area.

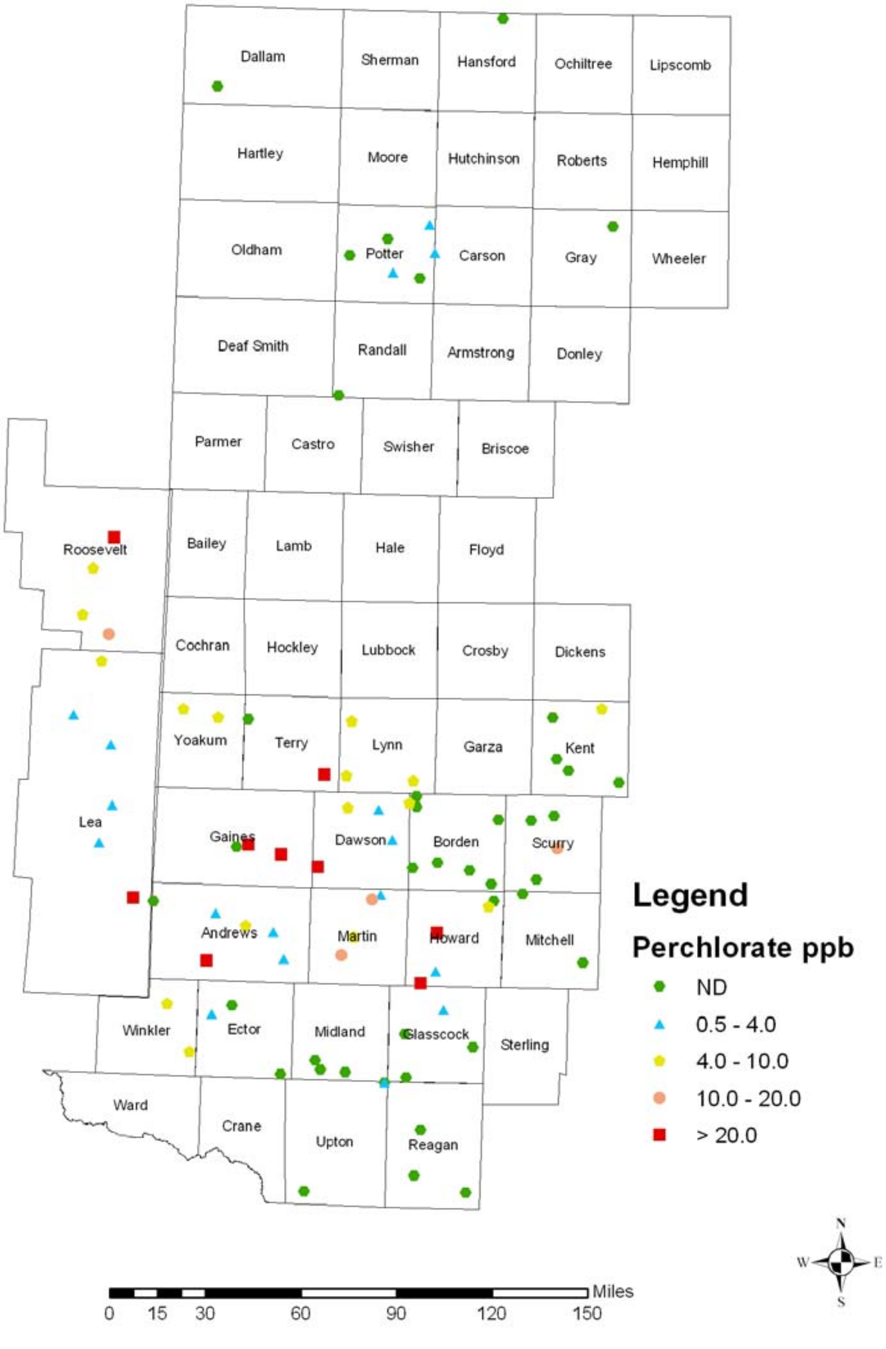

Figure 2.2.6 Private well distribution and perchlorate concentrations in study area.

2.2.1.3 High Plains Water District Wells

Water samples from 99 High Plains Water District (HPWD) wells were shipped to TTUWRC by HPWD for perchlorate analysis. These wells were located in Castro, Cochran, Deaf Smith, and Lamb counties. Of the 99 HPWD wells analyzed, 42 (42%) had detectable perchlorate (>0.5 ppb), 30 (30%) had perchlorate concentration at or above 4 ppb, and 4 wells (4%) had perchlorate concentrations greater than 10 ppb (Figure 2.2.7). Samples from Castro county had no detectable perchlorate. Deaf Smith and Lamb counties had detectable perchlorate concentrations in less than or equal to 50% of the wells analyzed, while Cochran county had perchlorate concentrations > 4 ppb in more than 50% of the wells analyzed (Table 2.2.3). Owner names, State ID, anions, cations, well stabilization data, and location (latitude, longitude) information were obtained from HPWD and are presented along with perchlorate data in Appendix A.

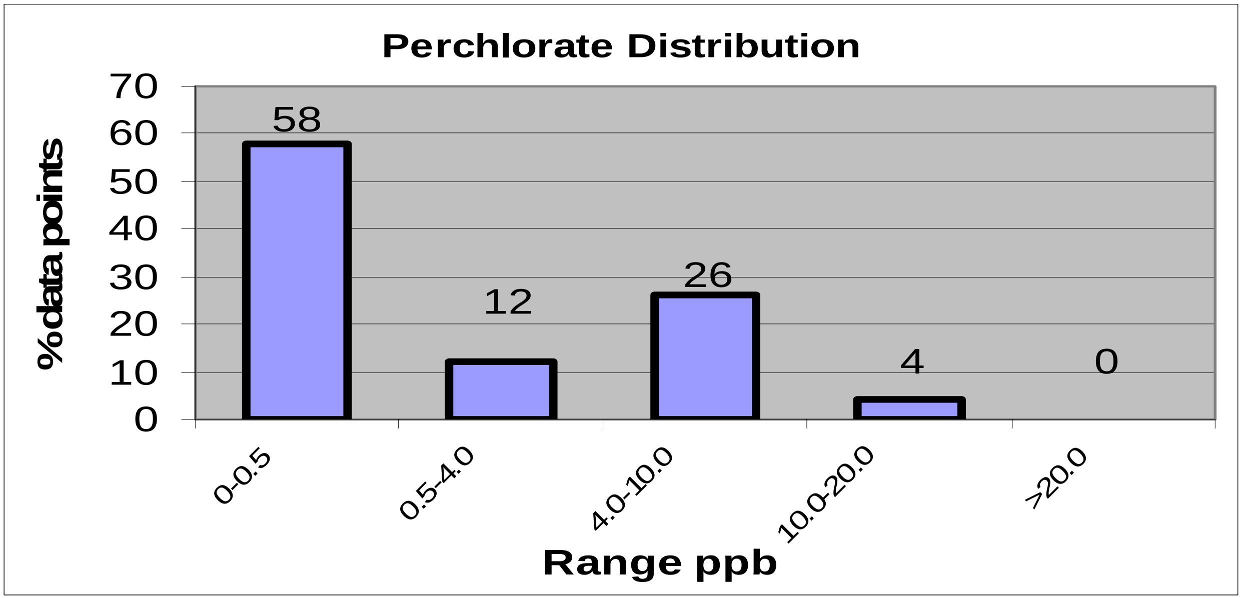

Figure 2.2.7 Frequency of Perchlorate Distribution (HPWD wells) in the Study Area.

Table 2.2.3 Frequency of Perchlorate (PC) Detections in HPWD Wells by County.

County	**HPWD Wells Tested**	**Number with PC**		**Percent with PC**	
		>0.5 ppb	**>4 ppb**	**>0.5 ppb**	**>4 ppb**
Castro	28	0	0	0	0
Cochran	28	24	19	86	68
Deaf Smith	4	2	1	50	25
Lamb	39	16	10	41	26

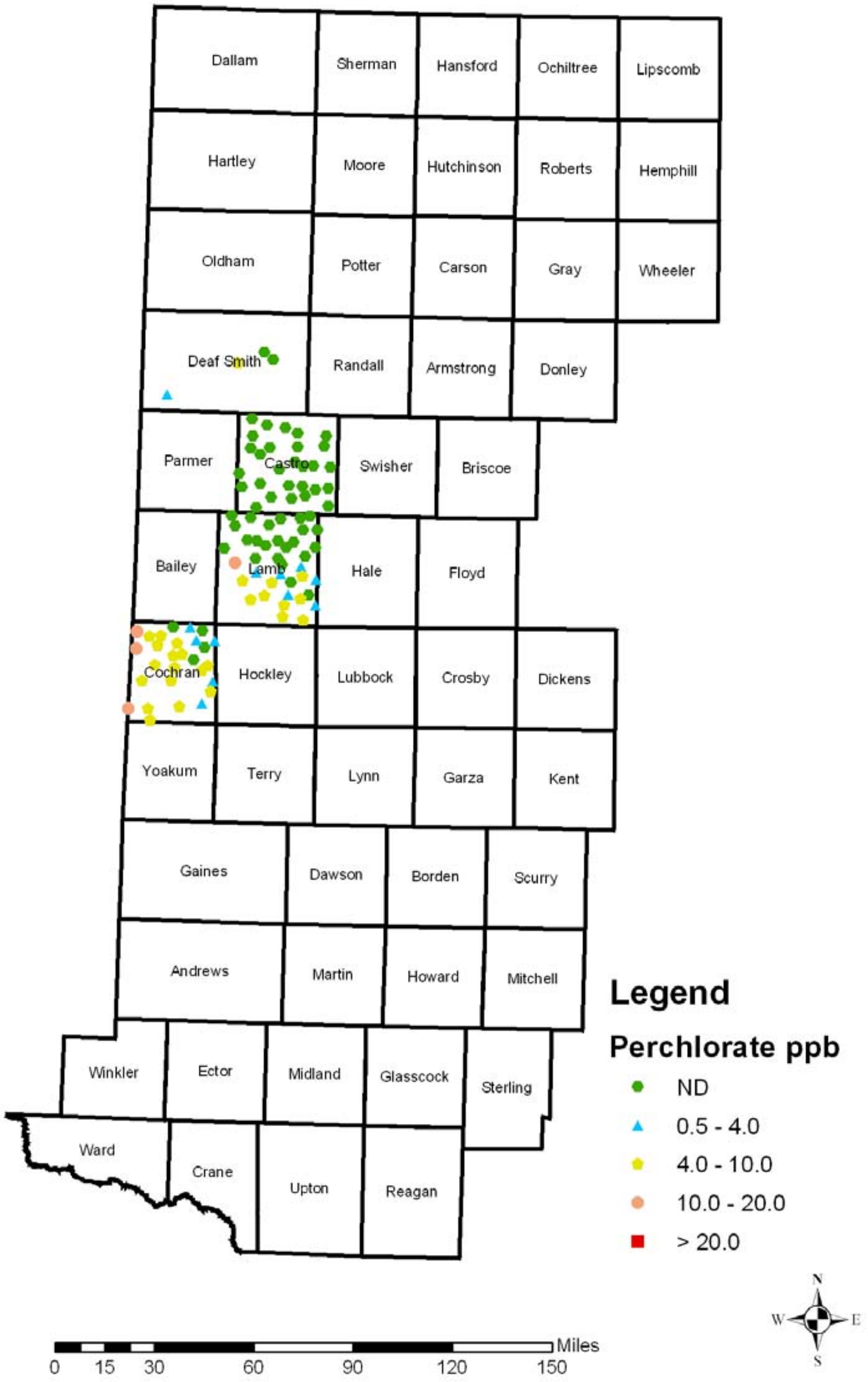

Figure 2.2.8 HPWD well distribution and perchlorate concentrations in study area.

2.2.1.4 United States Geological Survey (USGS) Wells

Water samples from 29 USGS wells were shipped to TTUWRC by USGS for perchlorate analysis. The USGS wells were monitoring wells screened at or near the water table. Of the 29 USGS wells analyzed, 20 wells (69%) had detectable perchlorate (>0.5 ppb), 12 (41%) had perchlorate concentrations at or above 4 ppb, and 4 wells (14%) had perchlorate concentrations equal to or greater than 10 ppb (Figure 2.2.9). The ten counties where USGS wells were sampled occur in the center of the study area. Nine of the ten counties had detectable perchlorate in more than 50% of the wells sampled while five counties had detectable perchlorate in all the wells sampled (Figure 2.2.10)

Seven of the ten counties had perchlorate concentrations greater than 4 ppb in more than 50% of the wells sampled (Table 2.2.4). The small number of data points spread over a large area does not show any trend (Figure 2.2.11). Site id, site name, depth to water, sample depth, anions, cations, well stabilization data, and location (latitude, longitude) information were obtained from USGS and are presented along with perchlorate data and TTU ID in Appendix A.

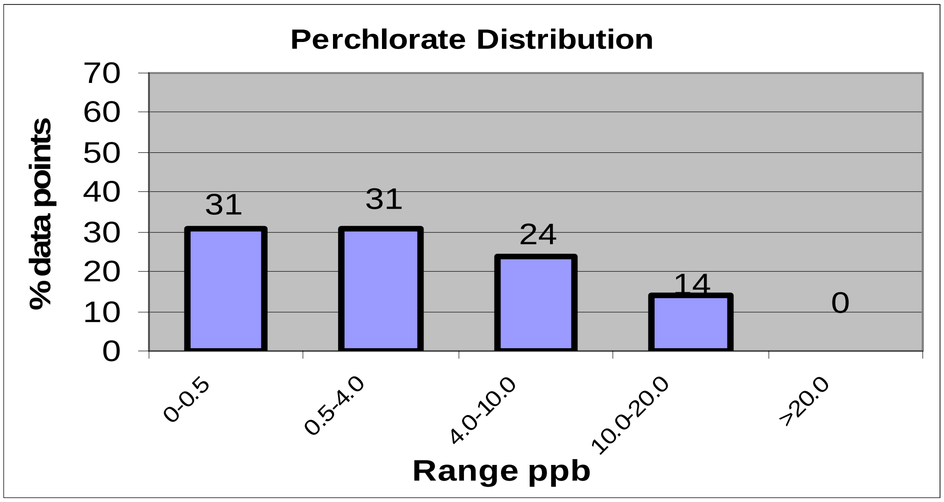

Figure 2.2.9 Frequency of Perchlorate Distribution (USGS wells) in the Study Area.

Table 2.2.4 Frequency of Perchlorate (PC) Detections in USGS Wells by County.

County	**Private Wells Tested**	**Number with PC**		**Percent with PC**	
		>0.5 ppb	**>4 ppb**	**>0.5 ppb**	**>4 ppb**
Castro	1	1	1	100	100
Cochran	5	4	3	80	60
Gaines	3	3	0	100	0
Hale	1	1	1	100	100
Hockley	4	2	0	50	0
Lamb	8	5	4	63	50
Lubbock	4	2	2	50	50
Swisher	1	1	1	100	100
Terry	1	1	1	100	100
Yoakum	1	0	0	0	0

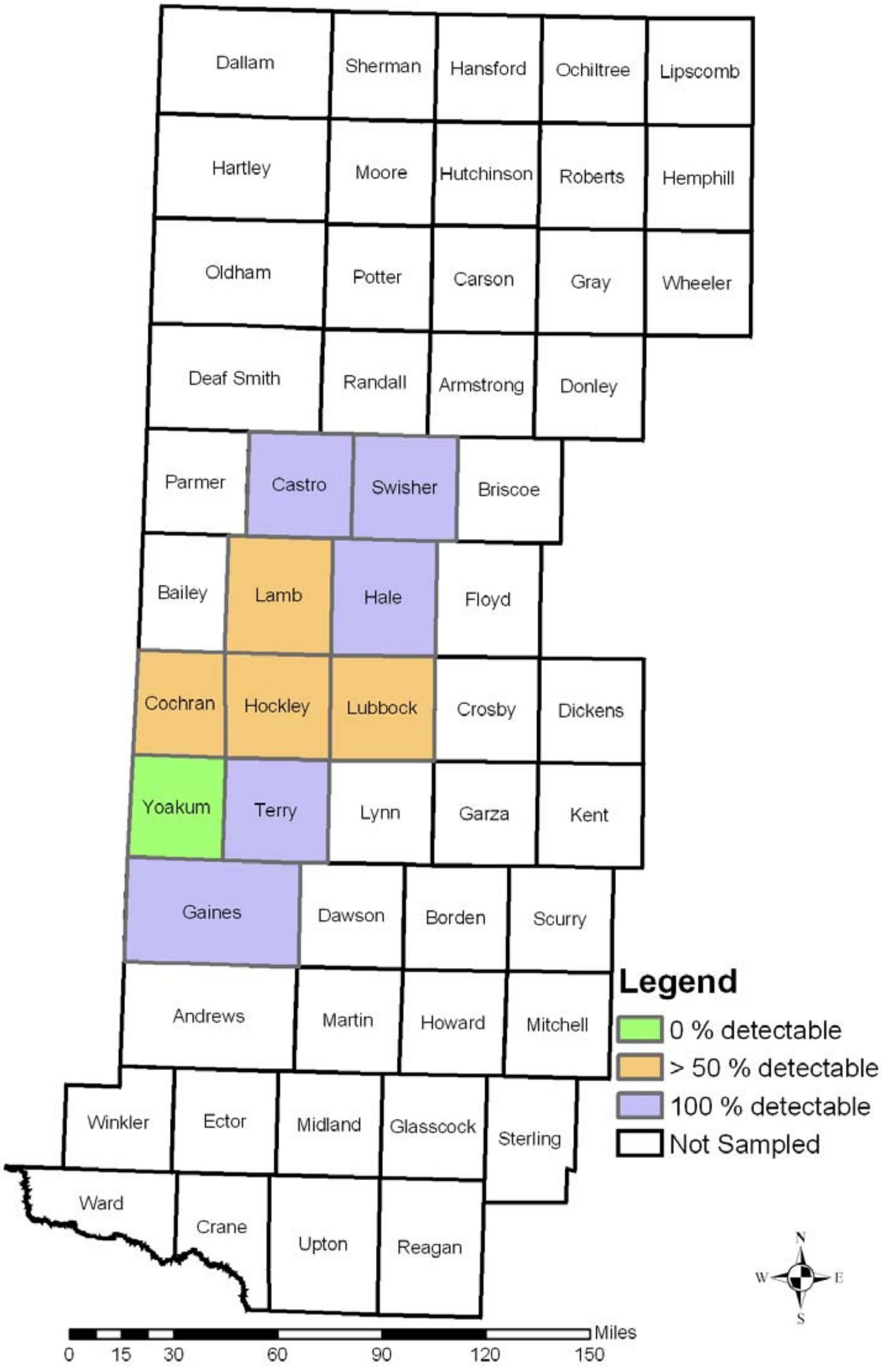

Figure 2.2.10 Frequency of Perchlorate Detections (USGS wells) in the Study Area.

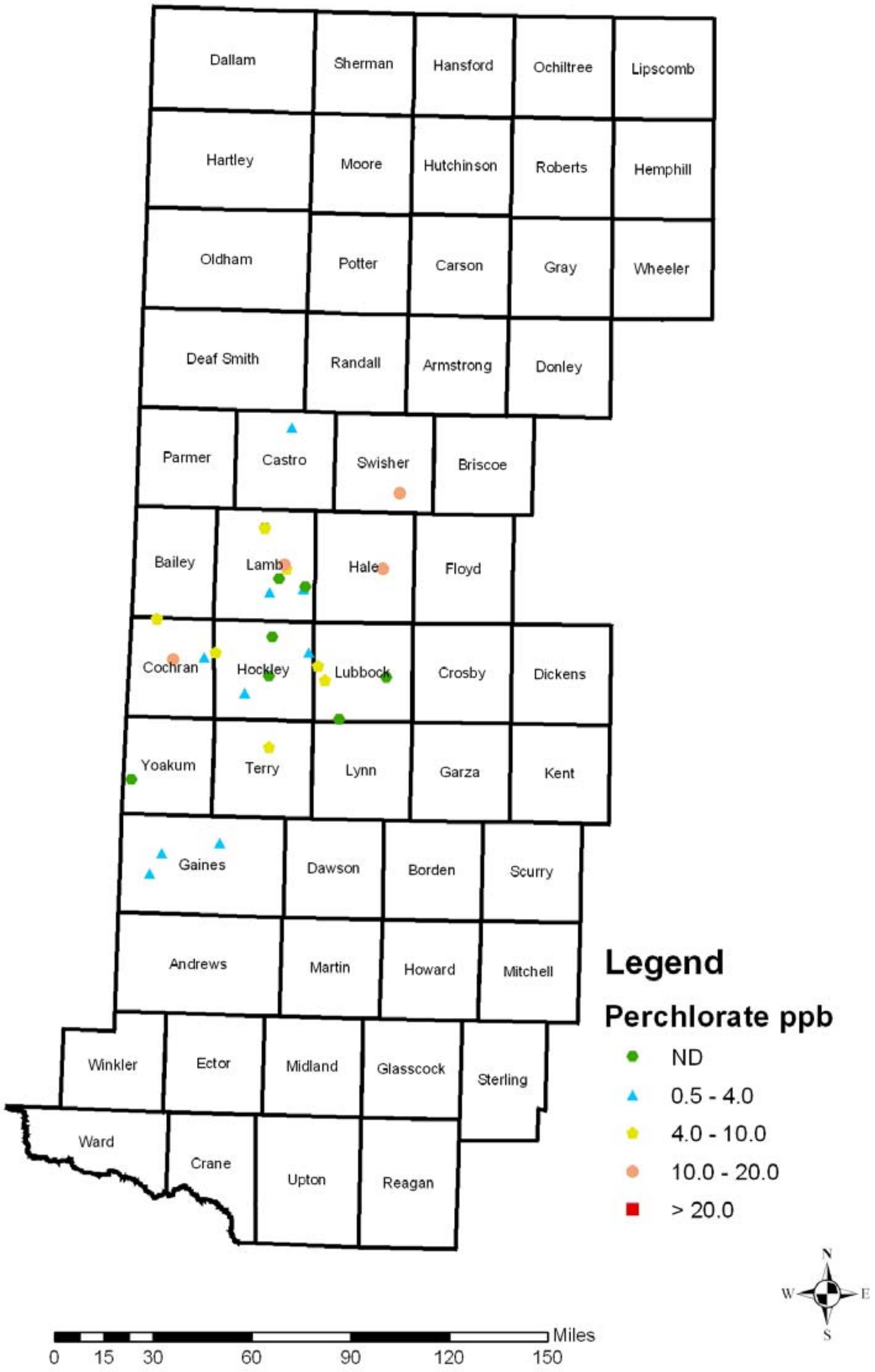

Figure 2.2.11 USGS wells distribution and perchlorate concentrations in study area

2.2.1.5 Low-Level Detection Analysis

About 424 (55%) of 765 wells analyzed were found to be non-detect or in general < 0.5 ppb. While for regulatory purposes there is probably not a driving interest in whether the wells and area represented by the non-detect results are truly free of perchlorate, the information is very important in determining the source of perchlorate. Therefore, 115 samples from 25 counties that were initially determined to be below detection for perchlorate using Method 314 were reanalyzed using a different method (Tian et al., 2003) able to achieve a lower detection limit (0.1 ppb). This method compares favorably to the current EPA Method 314, but provides better information on perchlorate in samples with high salinity. More than 90% of the wells reanalyzed were in the northern half of the study area, with less than 10% of wells in the southernmost counties of the study area (Figure 2.2.12). Of the115 wells that were reanalyzed, 82 (71% of the reanalyzed wells) wells had detectable perchlorate (>0.1 ppb). After considering the reanalysis results, 423 wells (55%) out of 765 wells analyzed had detectable perchlorate concentrations (>0.1 ppb) while 165 (22 %) of the 765 wells had perchlorate concentrations greater than 4 ppb, and 44 wells (6% of the total wells) had perchlorate concentrations greater than 10 ppb (Figure 2.2.13). Since reanalysis was not performed on all the wells that were initially classified as non-detects by the original method, some of these wells might actually have a detectable perchlorate concentrations, if they were analyzed using the lower detection method. Of the 309 wells that were not analyzed using this method about 219 wells (71%) may have a perchlorate concentration greater than 0.1 ppb. Of the 765 wells analyzed, 642 (84%) could potentially have detectable perchlorate.

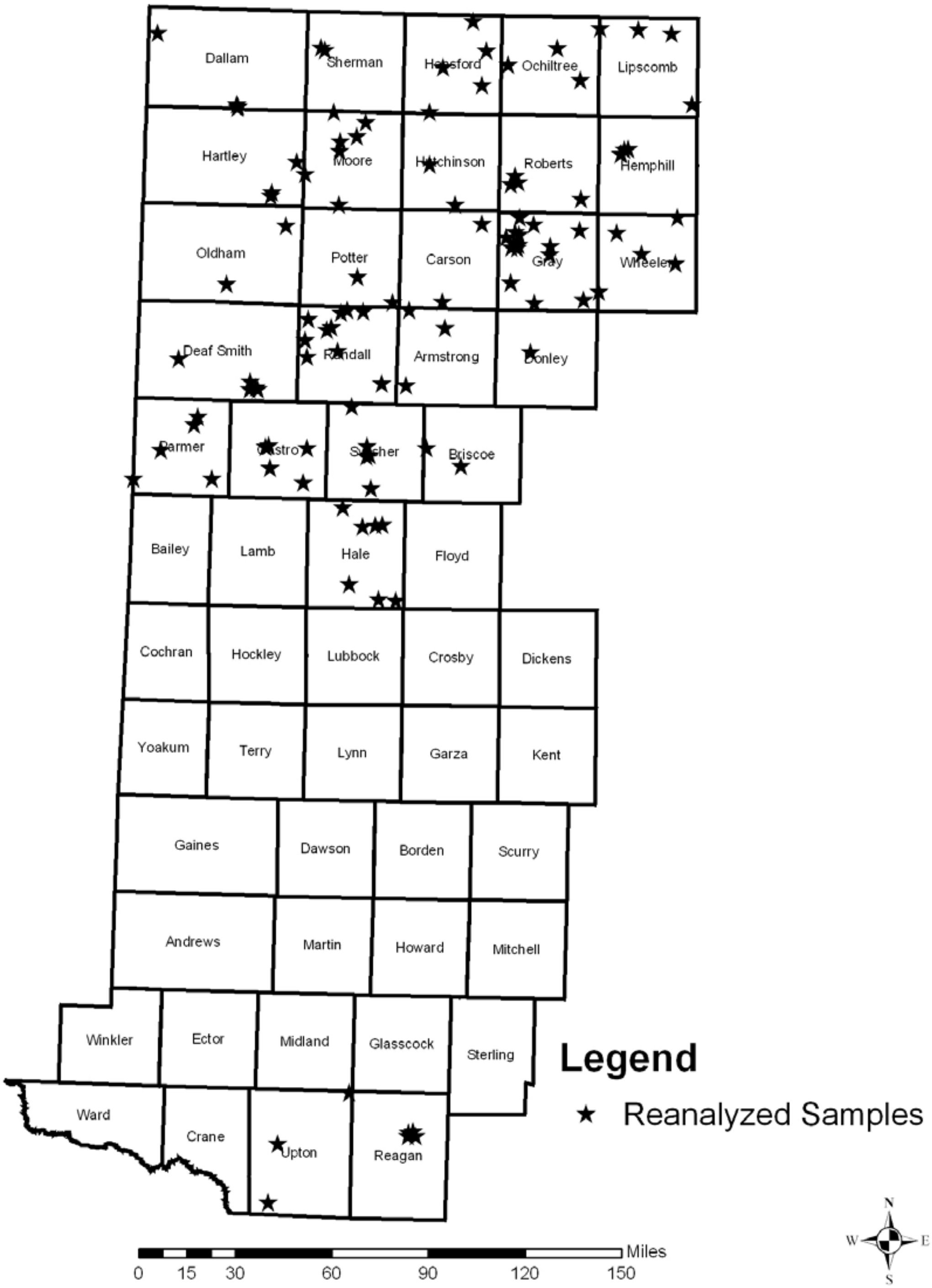

Figure 2.2.12 Location of Reanalyzed PWS wells in the Study Area that were initially below 0.5 ppb.

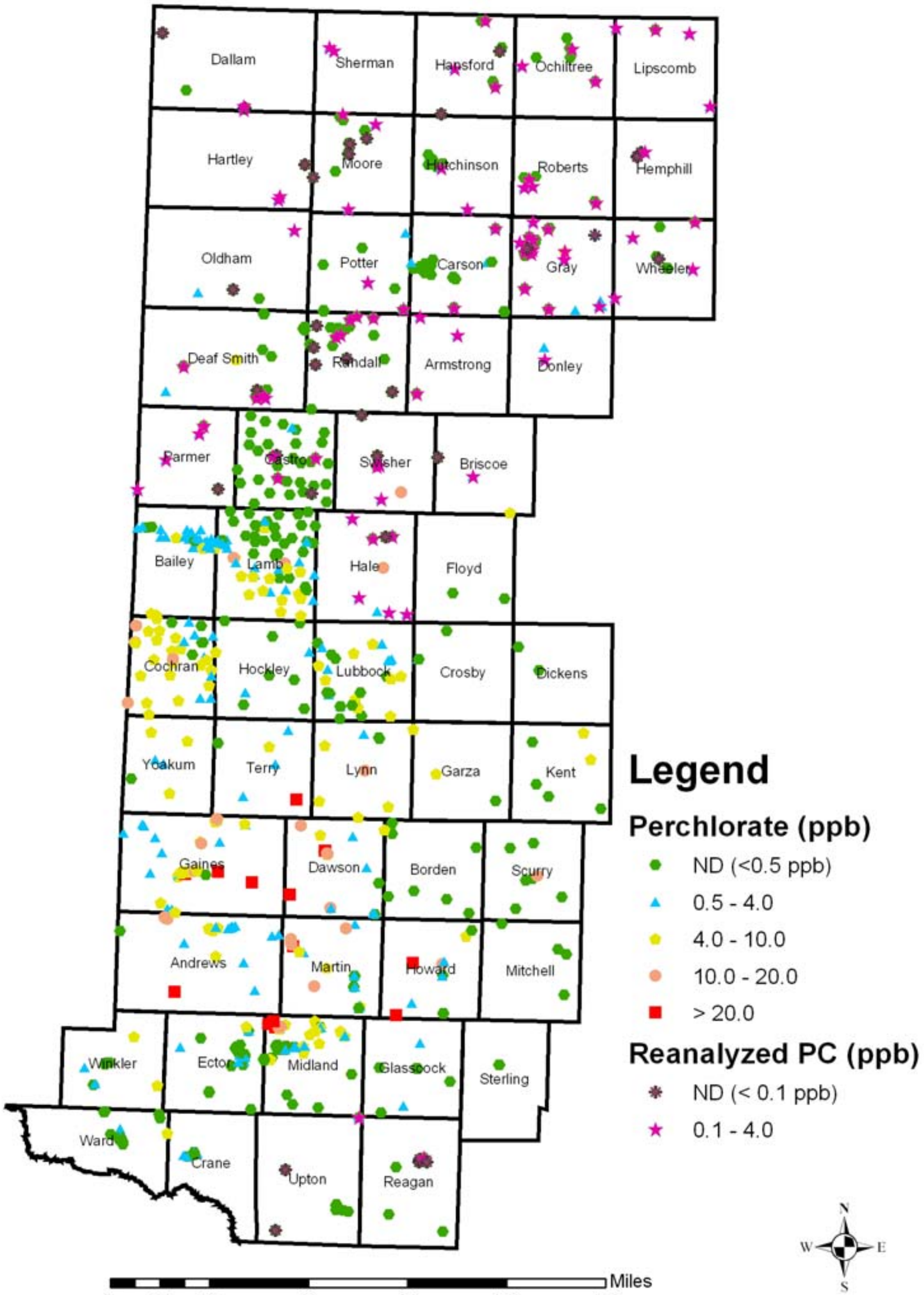

Figure 2.2.13 Perchlorate Concentrations in PWS wells after Reanalysis.

2.2.2 Distribution

A more detailed analysis of the distribution of perchlorate reveals few major trends and somewhat perplexing patterns (Figure 2.2.14). For the most part, the sampling efforts adequately represent each county spatially. More than 90% of the study area contains groundwater with detectable perchlorate (>0.1 ppb). A widespread phenomenon appears to be most likely, such as subsurface mineralogy or infiltration from surface sources, either natural or man made. An extensive discussion on sources is given in Chapter 5.

2.2.2.1 Distribution with Depth and Aquifer

Further analysis of distribution shows that perchlorate concentration is loosely related to depth to the water table from ground surface (Figure 2.2.16). The depth to water table map was prepared from Water Level Data for wells in the study area obtained from the TCEQ database. The perchlorate concentration distribution data were overlaid with the depth to water table map to study the relation between them. It appears that there is an inverse correlation between the concentration of perchlorate and depth to groundwater (e.g. the shallower the groundwater, the higher the perchlorate concentration). This could be explained if a surface source is the cause of perchlorate contamination. Perchlorate would leach towards the water table causing higher concentrations near the surface. At greater depths, perchlorate may be more diluted or may be degraded under potentially anaerobic conditions. The high perchlorate detections (> 20 ppb) were found in the southern tip of the Ogallala aquifer. Wherever the perchlorate concentration was greater than 20 ppb, the depth to water table was found to be less than 100 ft, while if the perchlorate concentrations are greater than 10 ppb, the depth to water table was found to be less than 150 ft. Most of the non detects were found in regions where depth to water table was greater than 250 ft.

There are four major aquifer systems and two minor aquifer systems in the study area from which water samples were obtained (Figure 2.2.17). More detailed description of the aquifer systems are given in Chapter 4. More than 70% of the wells that were not in the Ogallala Aquifer had no detectable perchlorate. All the aquifers tested positive for perchlorate. (Table 2.2.5).

Table 2.2.5 Frequency of Perchlorate Detection and Distribution in Aquifer Systems.

		% Perchlorate Distribution		
Aquifer Name	**# wells**	**detects**	**>4 ppb**	**> 10 ppb**
Ogallala	634	61	25	7
Edwards Trinity	67	27	1	0
Dockum	24	13	8	4
Cenozioc	29	45	10	0
Seymour	7	43	43	0
Blaine	1	100	0	0
Others	3	0	0	0
Total	765	55	22	6

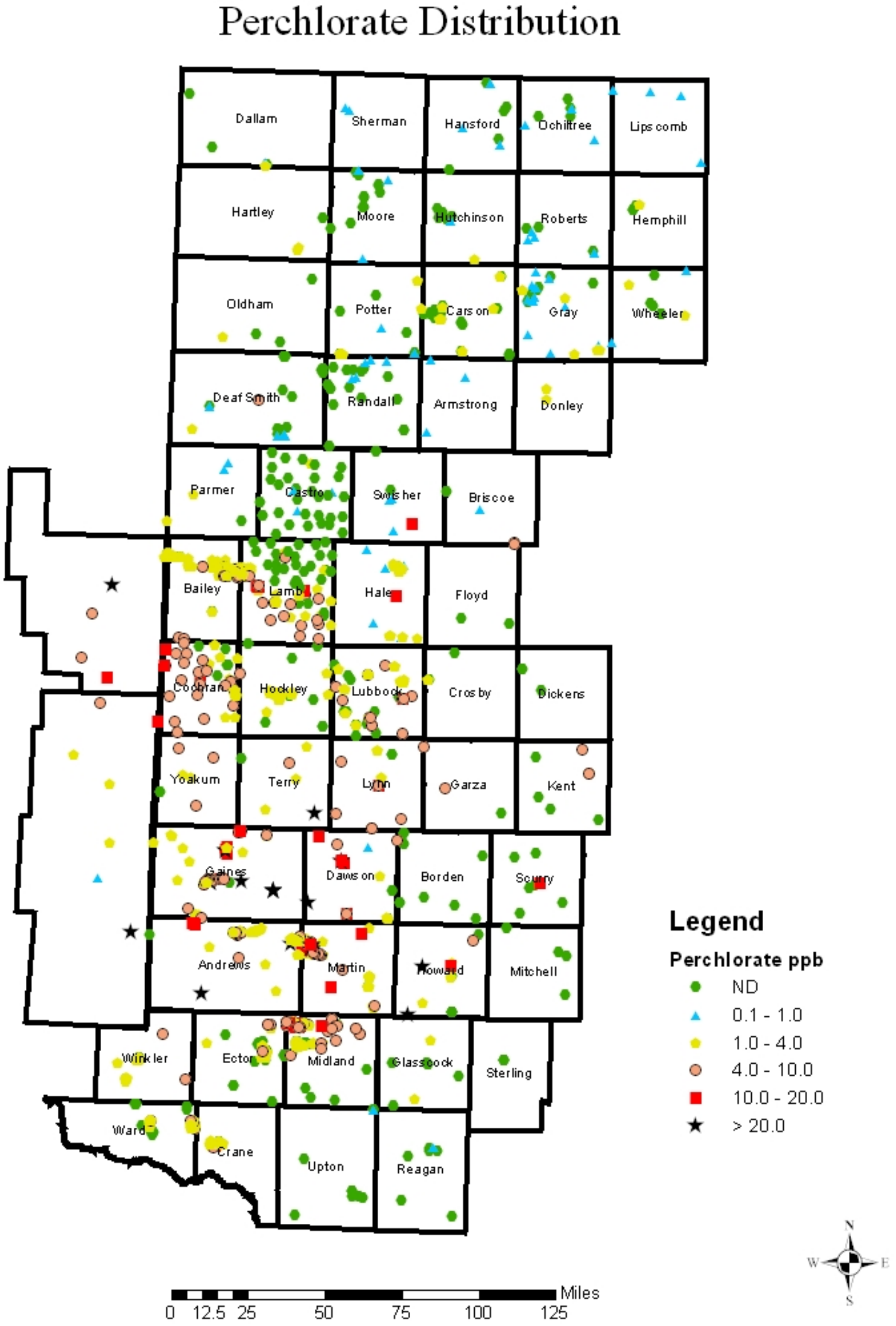

Figure 2.2.14 Distribution of Perchlorate in the Study Area (All Wells).

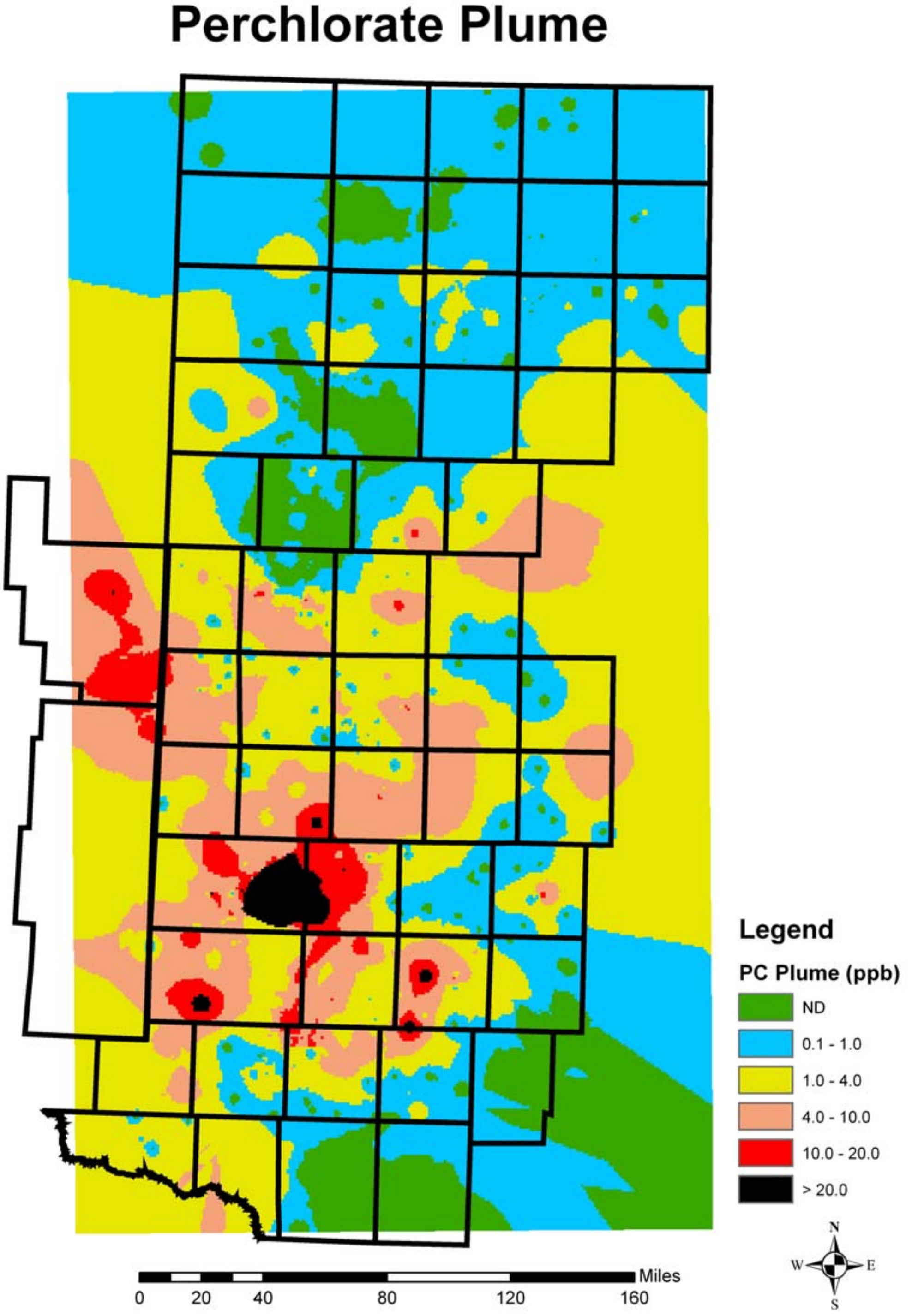

Figure 2.2.15 Perchlorate Plume in the Study Area (All Wells).

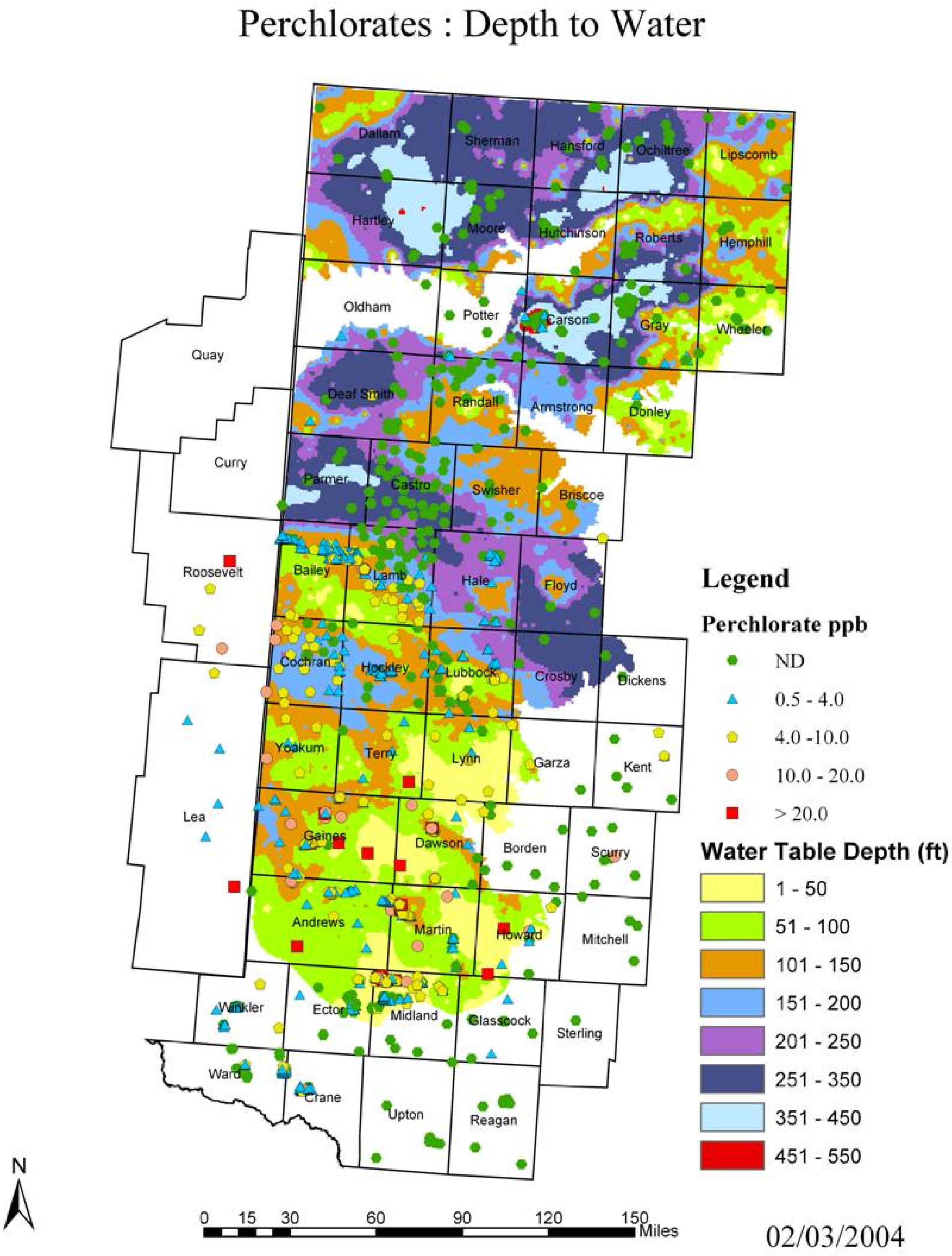

Figure 2.2.16 Distribution of Perchlorate with respect to Depth to Water Table.

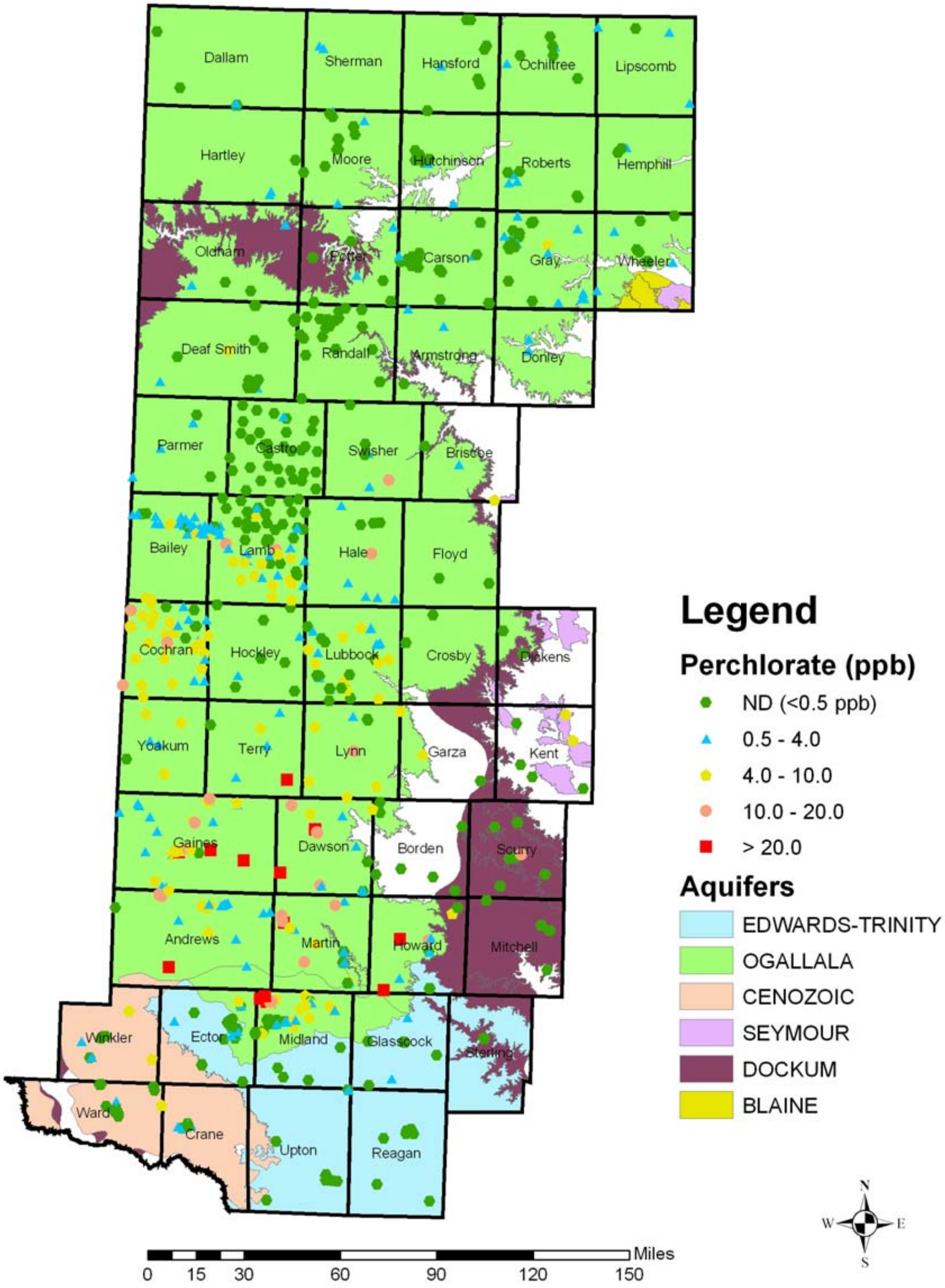

Figure 2.2.17 Aquifers Present in the Study Area.

2.2.3. Temporal Stability of Perchlorate

In order to determine the stability of perchlorate concentrations in wells with reported detections, 123 wells were sampled twice. 33 wells were previously sampled during 4/23/02-10/22/02 by TCEQ and analyzed by their lab, then sampled again during 9/11/02-6/25/03 by TTUWRC researchers for analysis in this project. 89 wells were sampled during 8/13/02- 6/4/2003 by the TTUWRC team, then sampled again on 9/27/02 – 10/9/2003 by TCEQ staff. Time difference between the sampling events ranged from 9 days to 373 days for the wells. Table 2.3.2.1 presents the perchlorate concentrations of wells which were re-sampled. The perchlorate concentration in each well is remarkably stable, with all but nine samples varied within 100% of each other, and all samples varied within a 1000% of each other

Table 2.2.6 Temporal Stability of Perchlorate

Water Source	Initial Sampling		Second Sampling		PC ppb
	Date	PC, ppb	Date	PC, ppb	Diff
G0020001D	9/10/2002	7.82	11/12/2002	7.7	0.12
G0020001H	9/10/2002	2.81	11/12/2002	2.88	0.07
G0020001J	9/10/2002	3.4	11/12/2002	3.7	0.3
G0020001K	9/10/2002	3.1	11/12/2002	3.6	0.5
G0020001L	9/10/2002	3	11/12/2002	2.4	0.6
G0020001M	9/10/2002	2.6	11/12/2002	2.3	0.3
G0020001N	9/10/2002	2.9	11/12/2002	2.8	0.1
G0020001P	9/10/2002	2.38	11/12/2002	1.96	0.42
G0020001Q	9/10/2002	2.5	11/12/2002	2.7	0.2
G0020001R	9/10/2002	3	11/12/2002	2.3	0.7
G0020001T	9/10/2002	2.3	11/12/2002	3.2	0.9
G0230002A	4/10/2003	9.54	6/25/2003	5	4.54
G0520001AA	6/3/2003	0	8/7/2003	< 4	0
G0520001AF	6/3/2003	2.63	8/6/2003	< 4	0
G0520001AM	6/3/2003	3.54	8/8/2003	2.6	0.94
G0520001AT	6/3/2003	5.2	8/8/2003	3.43	1.77
G0520001H	6/3/2003	0	8/7/2003	< 4	0
G0520001P	6/3/2003	0	8/7/2003	< 4	0

Table 2.2.6 Temporal Stability of Perchlorate cont..

Water Source	Initial Sampling		Second Sampling		PC, ppb
	Date	PC, ppb	Date	PC, ppb	Diff
G0520001U	6/3/2003	1.76	8/8/2003	< 4	0
G0520001X	6/3/2003	1.95	8/7/2003	< 4	0
G0680195A	5/21/2002	4.3	8/19/2002	4.46	0.16
G0830012A	8/13/2002	5.06	9/27/2002	3.93	1.13
G0830012C	8/13/2002	23.4	9/27/2002	25.2	1.8
G0830012D	8/13/2002	5.16	9/27/2002	10	4.84
G0830012E	8/13/2002	8.23	9/27/2002	7.5	0.73
G0830012F	8/13/2002	4.82	9/27/2002	6.4	1.58
G0830012H	8/13/2002	6.71	9/27/2002	7.5	0.79
G0830012J	8/13/2002	10.7	9/27/2002	5.1	5.6
G0830012L	8/13/2002	8.09	9/27/2002	8.9	0.81
G0830012N	8/13/2002	5.58	9/27/2002	8.2	2.62
G0830012O	8/14/2002	3.06	9/27/2002	4.7	1.64
G0830012P	8/14/2002	1.93	9/27/2002	1.95	0.02
G0830012Q	8/14/2002	5.16	9/27/2002	4.7	0.46
G0830012S	8/14/2002	9.46	9/27/2002	9.2	0.26
G0830012T	8/14/2002	2.1	9/27/2002	2.8	0.7
G0830012U	8/14/2002	3.54	9/27/2002	3.78	0.24
G0830019A	8/13/2002	14.4	10/11/2002	4.8	9.6
G0950001D	3/13/2003	2.45	4/10/2003	< 4	0
G0950004L	3/18/2003	0	7/7/2003	< 4	0
G1320001A	4/28/2003	4.81	7/17/2003	3.27	1.54
G1400005A	5/22/2003	9.05	10/9/2003	2.1	6.95
G1400005B	5/22/2003	1.21	6/26/2003	10.5	9.29
G1400006B	5/21/2003	5.5	6/25/2003	6.2	0.7
G1400006E	5/21/2003	3.62	6/25/2003	3.91	0.29
G1520001C	5/7/2003	2.04	6/26/2003	< 4	0
G1520002DG	5/13/2003	1.43	7/9/2003	< 4	0
G1520002DM	5/13/2003	1.28	7/9/2003	< 4	0
G1520002DP	5/13/2003	0	7/9/2003	< 4	0
G1520002DV	5/13/2003	2.23	7/9/2003	< 4	0
G1520002EF	5/13/2003	1.46	7/8/2003	< 4	0
G1520002EN	5/13/2003	1.14	7/8/2003	2.82	1.68
G1520002EP	5/13/2003	2.45	7/9/2003	< 4	0
G1520002EU	5/13/2003	2.49	7/9/2003	2.06	0.43

Table 2.2.6 Temporal Stability of Perchlorate cont..

Water Source	Initial Sampling		Second Sampling		PC ppb
	Date	PC, ppb	Date	PC, ppb	Diff
G1520002FA	5/13/2003	3.92	7/8/2003	5.1	1.18
G1520002FR	5/13/2003	3.62	7/8/2003	2.81	0.81
G1520002FX	5/13/2003	1.57	7/8/2003	< 4	0
G1520002FY	5/13/2003	1.94	6/27/2003	1.85	0.09
G1520002GG	5/13/2003	3.51	7/8/2003	3.97	0.46
G1520002GJ	5/13/2003	9.15	6/27/2003	7.9	1.25
G1520002GU	5/12/2003	1.54	7/8/2003	< 4	0
G1520002HD	5/12/2003	2.05	6/27/2003	< 4	0
G1520002HG	5/12/2003	0	6/27/2003	< 4	0
G1520002HS	5/12/2003	2.23	7/9/2003	< 4	0
G1520002HW	5/12/2003	3.07	7/9/2003	2.32	0.75
G1520002HX	5/12/2003	6.84	7/9/2003	6	0.84
G1520002IA	5/12/2003	1.72	7/9/2003	< 4	0
G1520002IB	5/12/2003	1.61	7/9/2003	< 4	0
G1520002IE	5/12/2003	2.16	6/27/2003	< 4	0
G1520002IG	5/12/2003	3.15	6/27/2003	3.57	0.42
G1520002IL	5/13/2003	6.73	7/8/2003	2.99	3.74
G1520002IN	5/12/2003	1.21	7/9/2003	< 4	0
G1520002JA	5/12/2003	1.94	7/10/2003	< 4	0
G1520062A	5/7/2003	3.39	6/26/2003	2.05	1.34
G1520067A	4/30/2003	4.44	6/25/2003	2	2.44
G1520079A	5/7/2003	2.04	7/17/2003	3.24	1.2
G1520079B	5/7/2003	3.24	7/17/2003	< 4	0
G1520123D	4/30/2003	10	6/25/2003	8.2	1.8
G1520159B	5/6/2003	4.51	7/16/2003	3	1.51
G1530001A	3/12/2003	5.16	4/9/2003	5.7	0.54
G1530011A	3/12/2003	2.18	4/10/2003	< 4	0
G1590002E	9/18/2002	1.6	9/27/2002	< 4	0
G1590002H	9/18/2002	2	9/27/2002	< 4	0
G1590002I	9/18/2002	0	9/27/2002	< 4	0
G1650001A	5/1/2002	1.1	9/11/2002	2.4	1.3
G1650001AH	5/1/2002	4	9/11/2002	2.8	1.2
G1650001AO	5/1/2002	1.5	9/11/2002	2.3	0.8
G1650001AR	4/23/2002	9	9/18/2002	11	2
G1650001AU	4/29/2002	9.1	9/18/2002	13	3.9

Table 2.2.6 Temporal Stability of Perchlorate cont..

Water Source	Initial Sampling		Second Sampling		PC ppb
	Date	PC, ppb	Date	PC, ppb	Diff
G1650001AV	4/29/2002	15	9/18/2002	20	5
G1650001BA	4/23/2002	20	9/18/2002	47	27
G1650001BG	4/23/2002	13	9/18/2002	14	1
G1650001BH	4/23/2002	19	9/18/2002	20	1
G1650001BM	4/29/2002	6.6	9/18/2002	6	0.6
G1650001D	5/1/2002	3.4	9/11/2002	4.6	1.2
G1650001L	5/1/2002	11	9/11/2002	22	11
G1650001O	5/1/2002	9.9	9/11/2002	17	7.1
G1650001S	5/1/2002	7.1	9/11/2002	11	3.9
G1650001U	5/1/2002	7.8	9/11/2002	15	7.2
G1650002A	5/10/2002	< 4	9/24/2002	0	0
G1650002B	5/10/2002	< 4	9/24/2002	0	0
G1650002C	5/10/2002	< 4	9/24/2002	0	0
G1650002D	5/10/2002	< 4	9/24/2002	0	0
G1650002E	5/10/2002	< 4	9/24/2002	0	0
G1650002F	5/10/2002	< 4	9/24/2002	0	0
G1650002G	5/10/2002	< 4	9/24/2002	0	0
G1650002H	5/10/2002	< 4	9/24/2002	0	0
G1650002I	5/10/2002	< 4	9/24/2002	0	0
G1650070A	4/25/2002	3.6	11/8/2002	3.34	0.26
G1650070B	4/30/2002	4.6	11/8/2002	6.94	2.34
G1650070C	4/25/2002	5.4	11/8/2002	6.01	0.61
G1650070D	4/25/2002	6.7	11/8/2002	6.19	0.51
G1650096A	5/10/2002	9.3	10/1/2002	8.31	0.99
G1880001CI	6/18/2003	0	10/22/2002	< 4	0
G1880001DD	6/18/2003	0	10/22/2002	< 4	0
G1880032A	6/17/2002	< 4	6/25/2003	0	0
G1880032B	6/17/2002	< 4	6/25/2003	0	0
G2380002C	6/4/2003	3.48	7/30/2003	3.22	0.26
G2480001G	6/3/2003	0	7/29/2003	< 4	0
G2480001H	6/3/2003	0	7/29/2003	< 4	0
G2480001L	6/3/2003	0	7/29/2003	< 4	0
G2480002D	6/3/2003	0	7/28/2003	< 4	0
G2480002E	6/3/2003	3.06	7/28/2003	2.06	1
G2480007B	6/3/2003	2.93	7/29/2003	2.55	0.38

2.2.4 Confirmation Sampling

Results of the confirmation sampling by Exygen Labs (State College, PA) were (in general) in close agreement with the reported values from the ESL lab (Table 2.2.7). In all cases, perchlorate identified by the ESL lab was confirmed as perchlorate by LC-MS/MS analysis.

Table 2.2.7 Confirmation Analytical Results by LC-MS/MS

ESL Lab Sample ID	**PC, ppb**	
	Exygen (LC-MS/MS)	**GWL (IC)**
9753	23.2	23.4
9860	11.6	10.5
9869	20.2	23.3
9901	17.4	22.3
10063	7.81	4.57
10088	2.83	3.07
10106	1.39	1.68
10229	0.163	ND
10239	3.43	2.02
10240	4.34	6.04
10480	0.844	ND
10489	2.17	3.15
10501	7.00	9.15

2.2.5 Total Mass of Perchlorate in Saturated Zone

Total mass of perchlorate in the saturated zone of the Ogallala aquifer within the fifty-four county study area was estimated. The entire study area was divided into approximately 40 square miles area grids (0.1 latitude X 0.1 longitude). Mass of perchlorate was calculated on the basis of saturated thickness and perchlorate concentrations in each of these grids. Total mass of perchlorate for each county was calculated as the sum of perchlorate mass in grids within each county.

2.2.5.1 Saturated thickness and perchlorate concentration

The 1997 saturated thickness of the Ogallala aquifer in these fifty-four counties was obtained from United States Geological Survey (USGS). USGS took water table elevation and aquifer base data from 1,085 wells to determine the saturated thickness of the entire Ogallala aquifer. This saturated thickness was represented in the form of ranges of 0 to 50 ft, 50 to 100 ft, 100 to 200 ft, 200 to 400 ft, and 400 to 600 ft (Figure 2.2.18). Average saturated thicknesses of 25 ft, 75 ft, 150 ft, 300 ft, and 500 ft were used for calculation purposes. A porosity range of 0.3 was assumed for calculations across the entire study area. The concentrations of perchlorate in the Ogallala aquifer across the study area were obtained from TTU-WRC. TTU-WRC conducted ground water sampling in the study area during the period starting from 13th August 2002 to 1st July 2004. A concentration contour plot for the entire study area was interpolated based on the concentration of perchlorate in individual wells. The grid maps for saturated thickness and perchlorate contours are given in Appendix C.

2.2.5.2 Formulation of solution

The entire study area comprising of fifty-four counties was divided into square cells of equal area (40 square miles). The saturated thickness and the perchlorate concentration in each of these squares were determined. If a square had more than one saturated thicknesses or concentration contour, the average value of the same was used. Mass of perchlorate in each of the areas was calculated by multiplying the area of the square with the saturated thickness and perchlorate concentration in that square. Similarly the perchlorate mass was calculated for all the squares in the study area. By adding up the perchlorate mass in each square in a county, the mass of perchlorate in that county was

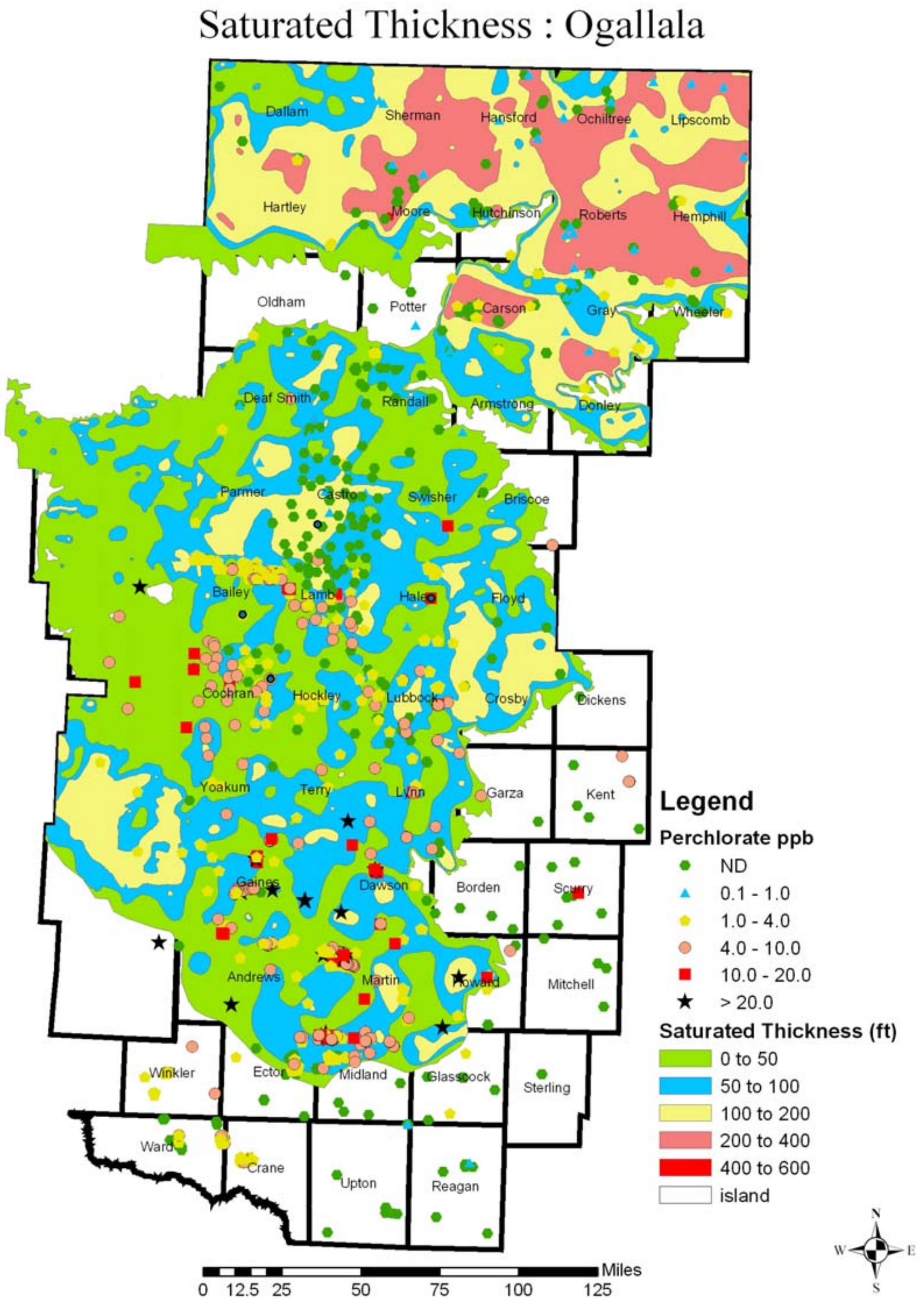
Saturated Thickness : Ogallala

Figure 2.2.18 Saturated Thickness of Ogallala Aquifer in Study Area.

determined. A sample calculation for this model is shown below. The saturated thickness in the cell was 75ft and the perchlorate concentration in that cell was 2µg/L. The porosity (n) of the soil was assumed to be 0.3. Therefore the mass of perchlorate concentration was calculated as follows:

Mass of perchlorate M (Kg) = Area of cell (m^2) X Saturated thickness in that cell (m) X Porosity X Perchlorate concentration in that cell(□g/L)

$$M = \left(40\, mi^2\right) \times \left[2589988\ \frac{\mathrm{m}^2}{\mathrm{mi}^2}\right] \times \left(75\ ft\right) \times \left[\frac{0.3048\, m}{1\, ft}\right] \times \left(0.3\right) \times \left(2\, \frac{\mu g}{L}\right) \times \left[1000\ \frac{L}{m^3}\right] \times \left[10^{-9}\ \frac{Kg}{\mu g}\right]$$

$Mass =$ **1420 Kg**

The mass of 1400 kg in one 40 sq mile area comes to only 2 ppb of perchlorate concentration in the water. Total mass of perchlorate in the counties in the study area ranged from 0 kg (where there was no saturated thickness of Ogallala was available) to 250,000 kg in Gaines County (Table 2.2.8). Total mass of perchlorate in the study area was estimated at 1.8 million Kg. Although the mass may look large, it is not quiet so large when mass per unit area (13 mg/m^2) is considered as the total study area is 53,000 sq miles.

Table 2.2.8 Perchlorate Mass in Saturated zone

County	Total Area (Acres)	Perchlorate Mass x 1000 Kg
Andrews	956915	220
Armstrong	583673	15
Bailey	528294	49
Borden	577779	5
Briscoe	577726	3
Carson	592097	23
Castro	575780	6
Cochran	495026	36
Crane	502680	0
Crosby	575173	33
Dallam	966963	17
Dawson	575342	100
Deaf Smith	958893	24
Dickens	578929	0.97
Donley	597023	28
Ector	575702	25
Floyd	634092	77
Gaines	958419	250
Garza	572646	24
Glasscock	574996	13
Gray	597366	20
Hale	641933	47
Hansford	591645	15
Hartley	938227	33
Hemphill	585649	26
Hockley	580959	50
Howard	576347	50
Hutchinson	574311	11
Kent	574589	0
Lamb	650432	35
Lipscomb	599788	27
Lubbock	575602	52
Lynn	569399	59
Martin	583628	180
Midland	574629	28
Mitchell	584314	0
Moore	583551	13
Ochiltree	590741	17
Oldham	962240	5
Parmer	565842	13
Potter	590356	5
Randall	589848	7
Reagan	748762	0
Roberts	592214	21
Scurry	578602	0
Sherman	592858	13
Sterling	588325	0
Swisher	576658	8
Terry	568126	35
Upton	789555	0
Ward	533061	0
Wheeler	585504	24
Winkler	535367	0
Yoakum	509805	54

2.3 Summary

A large scale sampling of PWS wells and private wells in the study area (fifty- four counties in Texas and two counties in New Mexico) covering six different aquifers was performed by TTU WRC researchers. Additional samples were obtained from USGS and HPWD through cooperative agreements. The samples were analyzed for perchlorate, arsenic, and a suite of anions and cations along with field measured parameters like DO, pH, TDS, etc. 765 samples were analyzed for perchlorate by IC using a detection limit of 0.5 ppb, while 115 wells (15%) that had no detectable perchlorate were reanalyzed using a lower level detection (0.1 ppb) by a preconcentration method. After considering the reanalysis results, 423 wells (55%) out of 765 wells analyzed had detectable perchlorate concentrations (>0.1 ppb) while 165 (22%) of the 765 wells had perchlorate concentrations greater than 4 ppb, and 44 wells (6%) of the total wells had perchlorate concentrations greater than 10 ppb. The authors have identified a weak relationship between perchlorate concentration and depth to the water table from surface. The closer the water table to ground surface, the higher the perchlorate concentration and vice versa. The perchlorate concentrations in wells were also analyzed at different times to study the temporal stability of perchlorate in ground water. Perchlorate was found to be remarkably stable. Total mass of 1.8 million kg of perchlorate was estimated in the study area, which is not large for the 53,000 sq. miles of the study area.

Chapter 3

Vertical Distribution of Perchlorate

The aerial distribution of perchlorate discussed previously is important for understanding the current distribution and potential impact to drinking water resources. However, this data does not illuminate the distribution of perchlorate vertically within the water bearing formations nor does it provide any information on the presence of perchlorate in the unsaturated zone. This vertical distribution is important as it directly bears on the potential source of the perchlorate (surface vs. upwelling) as well as provides information to estimate the potential for continued occurrence if the source is surface infiltration. Three nested well systems were installed under the supervision of TTUWRC in Martin, Gaines, and Bailey counties. These locations were selected for there land use and location within affected areas as discussed below. During installation of the nested well unsaturated sediment samples were collected as described below. Supplementing these nested wells, a number of nested well systems previously installed by USGS, were also sampled and in some cases archived sediment were also available from these wells. Lastly, unsaturated samples were also available from an undeveloped portion of the Pantex Plant. Figure 3.1 shows the locations of the nested well systems and other wells from which soil samples were obtained. Well construction and sample preparation method for analysis are described in the following section. In general, sediment samples were extracted in DDI water and the extract analyzed for a suite of cations and anions as well as for perchlorate. Full details of the procedure used for sediment processing and analysis as well as sampling of the nested well systems are described below for each location.

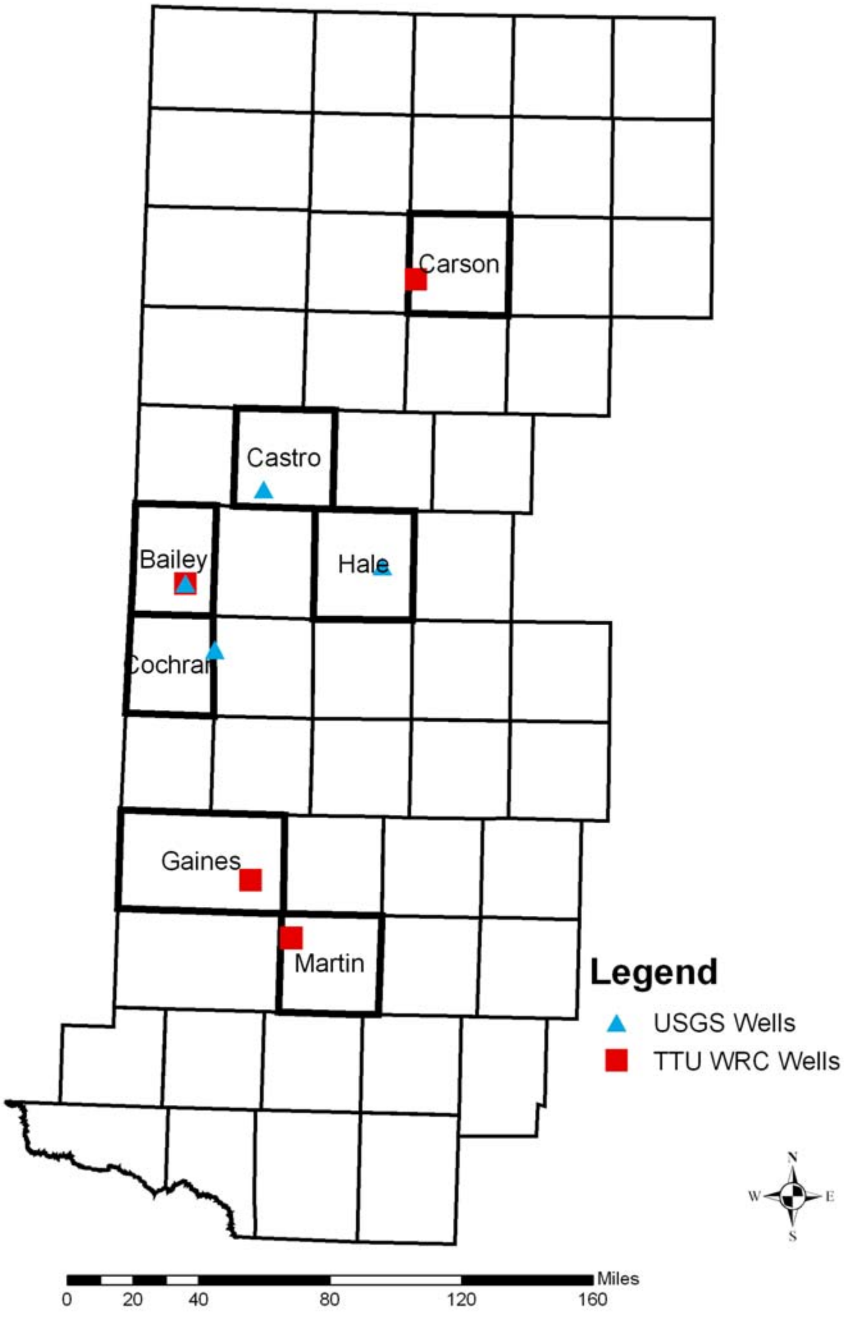

Figure 3.1 Location of Monitoring Wells

3.1 TTU WRC Wells

The three well systems drilled by TTUWRC lie in a rough North South direction covering 240 miles (65%) of the 370 mile length of the study area and spanning 3 counties (90 miles) in the East West direction. The depth of the unsaturated zone ranges from 40 ft in Gaines County to 130 ft in Martin County. Of 103 points sampled 31 (30%) sampling points had detectable perchlorate in the unsaturated zone. The detectable perchlorate concentration ranges from 1 ppb to 113 ppb in the unsaturated zone. The unsaturated zone samples from the undeveloped portion of the Pantex plant (Carson County) had an unsaturated zone of 260 ft. Of the 78 samples analyzed in Carson County 19 (24%) contained detectable perchlorate. The perchlorate concentrations range from 0.45 ppb to 7 ppb in the unsaturated zone. The following section describes the site locations, soil profile, and analytical results in each of the counties.

3.1.1 Martin County

3.1.1.1 Site Location

Three monitoring wells were installed in Martin County. These wells are located 20 miles West of Lenorah, Texas (Figure 3.1). High concentrations of perchlorate were detected in the wells surrounding this monitoring well site. This site is located on the edge of the Paul-Davis Well field and a currently irrigated area.

3.1.1.2 Well Installation

Two wells designated as MW 1 and MW 2 were drilled by air rotary in both saturated and unsaturated zone, while the third well (MW 3) was drilled by air rotary in the unsaturated zone and by mud rotary in the saturated zone. Unsaturated soil samples were collected at 5ft intervals during drilling by grab sampling approximately 0.1-1 kg of material. PVC casing and screens were used for the wells. The nested wells were screened at different levels to study the distribution of perchlorate with depth. Well MW1 was screened for the depth interval of 137 ft – 157 ft from ground surface, while well MW2 was screened from 119 ft to 127 ft, and well MW3 was screened from 157 ft to 177 ft (Figure 3.1.1). After the casings and screens were placed the bore hole was filled with gravel around the screens and bentonite slurry and cement mixtures in other places. These monitoring wells were developed using a jetting method.

3.1.1.3 Sample Preparation

To analyze the soil sample for ions, the ions must be leached from the soil into DDI water. For this about 15 grams of soil was added to 30 ml of DDI water in a centrifuge tube and the centrifuge tubes were then kept in a tumbler for 24 hours in order to leach the ions from the soil samples into water. The samples were than centrifuged at a speed of 10,000 rpm in a Avanti® J-E centrifuge using a JA-17 rotor for 25 – 30 minutes.

After centrifuging, the samples were filtered using 0.2 micron syringe filter. About 20 to 25 ml of the original 30 ml was recovered for each of the samples. Of this 5 ml was used for perchlorate analysis, another 5 ml was used for anion analysis, and 10 ml was preserved with10μL nitric acid (high purity, 1% final conc.) as soon as the samples were filtered for cation analysis. Perchlorate and anions were analyzed using Ion Chromatography (IC) and cations were detected using Inductively Coupled Plasma (ICP) by methods discussed in Chapter 2.

3.1.1.4 Soil Profile

The unsaturated zone for Martin County consists of Quaternary Eolian and Lacustrine sediments and a part of Ogallala Formation. The Quaternary Eolian and Lacustrine sediments are calcareous very fine sandy clay that grades downward to silty very fine sand which is highly calcareous throughout the unsaturated zone. These sediments are underlain by the Ogallala Formation. The Ogallala consists of the top zone that is highly laminated sandy caliche called as the Caprock caliche. The Ogallala Formation includes a fine-grained interval in the unsaturated zone consisting of silty to very fine medium sand with soft caliche in the upper part, and extends to the saturated zone (Figure 3.1.1).

3.1.1.5 Perchlorate Results

Soil samples to the depth of 120 ft were considered as the unsaturated zone as the water table at the site measured at 120 ft below ground surface. These samples were extracted and analyzed for perchlorate and other suite of ions. Perchlorate, other anions, and cations were analyzed by methods stated in Section 2.1.2. Well MW1 was analyzed for perchlorate by low level detection (preconcentration) method (Tian et al, 2003). Of the three wells in Martin County, the well designated as MW1 had no detectable perchlorate (>0.1 ppb) in the unsaturated zone while well MW2 had detectable perchlorate (>0.5 ppb) in 7 (30%) of 24 samples tested in the unsaturated zone and well MW3 had detectable perchlorate in 8 (33%) of 24 samples tested in the unsaturated zone. Well MW2 had a perchlorate concentration of 114 ppb (dry weight of soil) at a depth of 5 ft and less than 5 ppb (dry weight of soil) at all other sampling depths. The concentration of perchlorate is randomly distributed with respect to depth, but a weak trend of decreasing perchlorate concentration with an increase in depth seems to occur (Figure 3.1.2). The perchlorate concentration ranged from 1.6 to 3.3 ug/kg (dry weight of soil) in well MW3. The results of other ionic concentrations are given in Appendix B.

All three monitoring wells in Martin County had detectable perchlorate (>0.5 ppb) in the saturated zone (in ground water). The water samples in these wells were analyzed on two different time periods (12/17/2003 and 06/30/2004) for perchlorate, arsenic, other anions, and cations by methods stated in section 2.1.2. Perchlorate was highest (23.7-22.7 ppb) in the well screened at the shallowest interval (119-127ft BGS) and fairly similar (15.7-19.2 and 17.0-17.0 ppb respectively) for the deeper screens (137-157 and 157-177 ft BGS) (Figure 3.1.2).

Water samples in Martin County wells were analyzed for tritium isotope by USGS (Fahlquist 2004) to estimate the age of water in the site. The shallow well MW2 had relatively new water (after 1960's) with a tritium level of 4.8 pCi/L +/- 0.64 pCi/L, while the deeper wells MW1 and MW3 had relatively old water (pre 1960's) with tritium level of 0.32 pCi/L +/- 0.64 pCi/L and 0.96 pCi/L +/- 0.64 pCi/L respectively. Perchlorate concentration is evenly distributed throughout the Ogallala formation (figures 3.1.1 and 3.1.2) in both old and new waters. Anthropogenic sources of perchlorate cannot have caused the contamination in the Martin County site as the tritium would have also diffused with perchlorate, if perchlorate leached from surface.

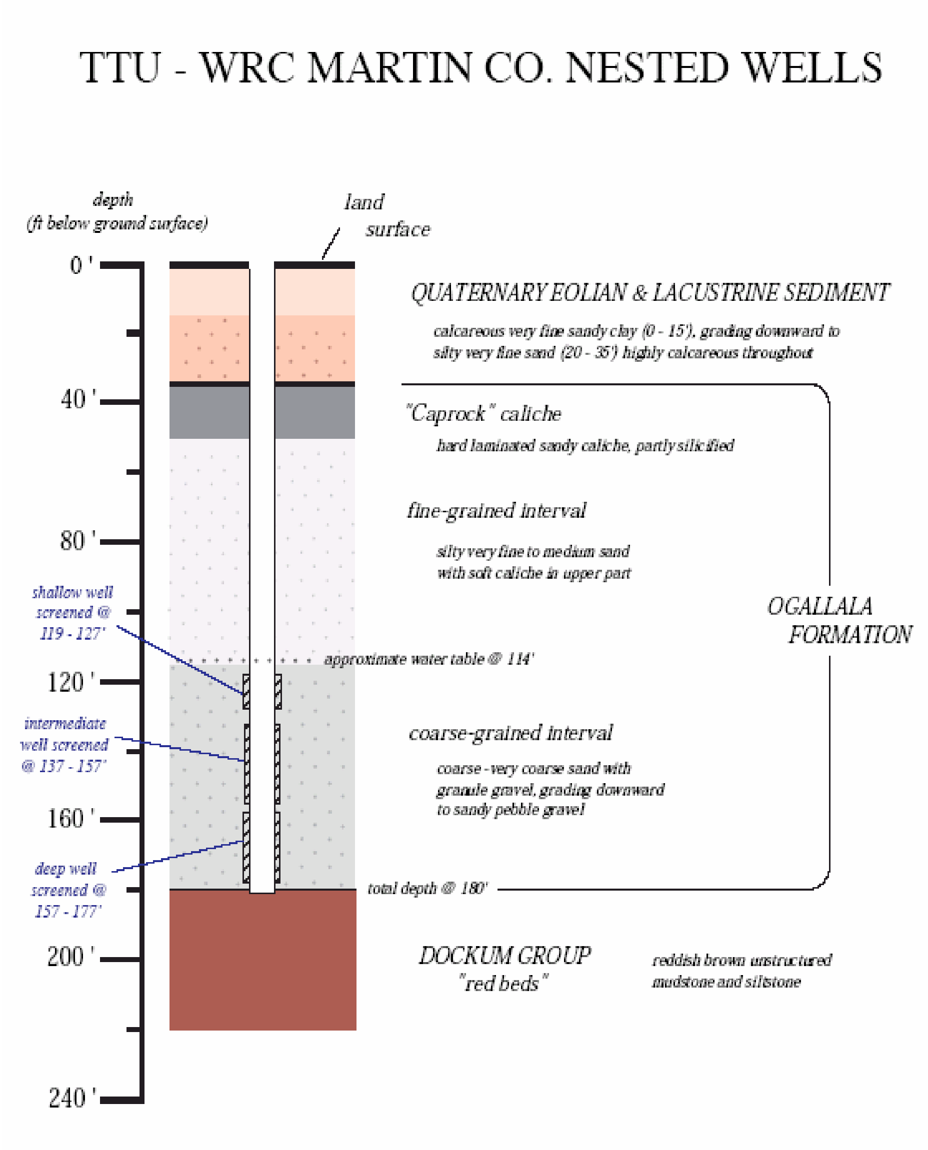

Figure 3.1.1 Subsurface Soil Profile for the Martin County Site

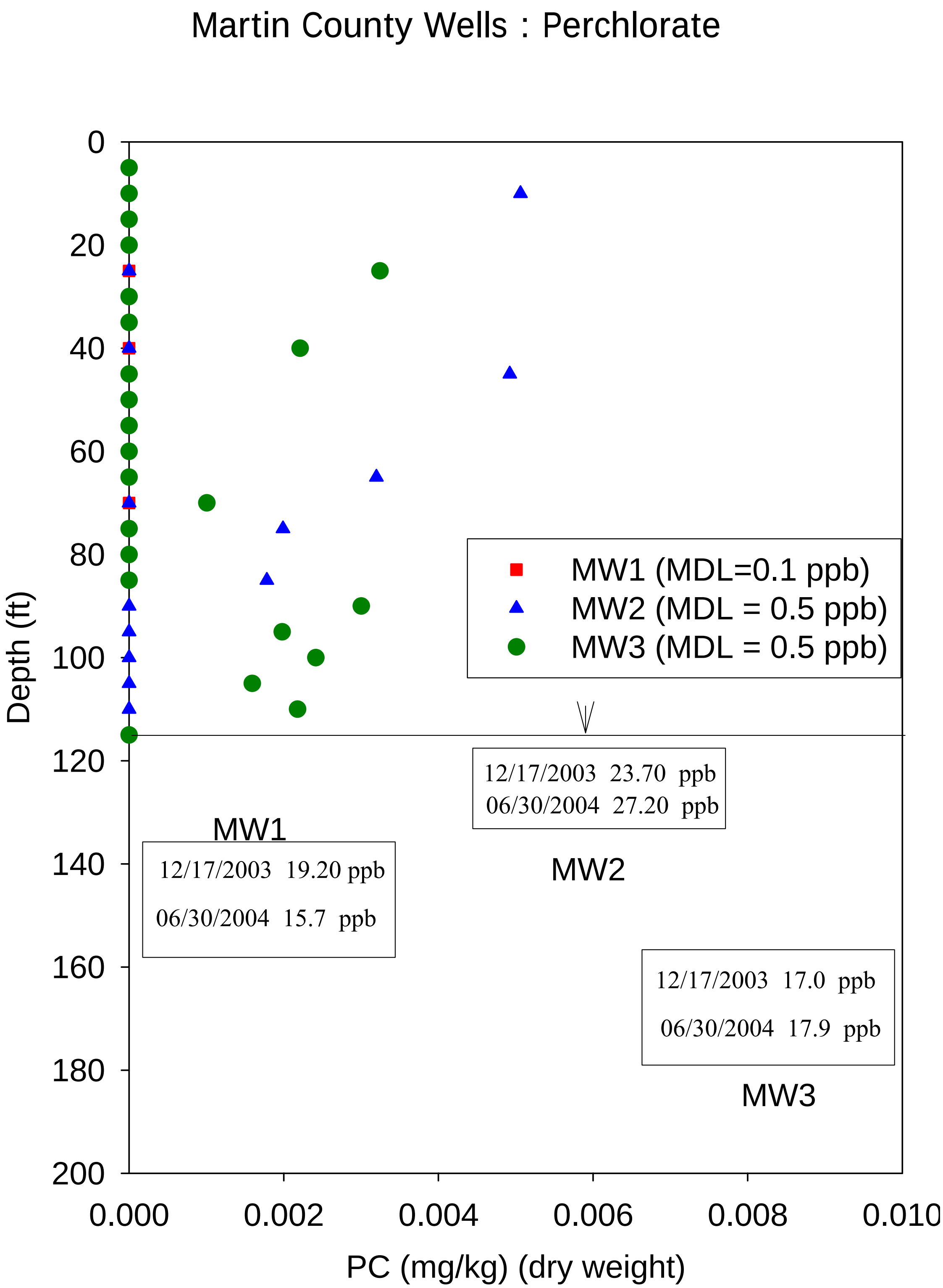

Figure 3.1.2 Perchlorate Distribution with Depth in Martin County Site

3.1.2 Gaines County

3.1.2.1 Site Location

The three nested wells in Gaines County are located six miles west of Seminole, Texas. The monitoring well site is located at less than half a mile from a groundwater well that recorded a perchlorate concentration of 30 ppb. Agriculture was practiced at the site until about 1990, after which the site came under a Conservation Recovery Plan. Intensive irrigated agricultural still occurs within a few hundred meters of the site.

3.1.2.2 Well Installation

All the monitoring wells in Gaines County were drilled by air rotary method. Unsaturated soil samples were collected at 5 ft intervals during drilling. Soil samples from well GW3 were not analyzed. Well GW1 was screened for the depth interval of 198– 218 ft, while well GW2 was screened from 25 ft to 45 ft, and well GW3 was screened from 100 ft to 120 ft (Figure 3.1.3). After the casings and screens were placed the bore hole was filled with gravel around the screens and bentonite slurry and cement mixtures in other places. The samples were prepared according to procedure given in section 3.1.1.3

3.1.2.3 Soil Profile

The unsaturated zone for Gaines County consists of the Blackwater Draw Formation. The Blackwater Draw Formation consists of very fine silty sand and caliche grading downward to fine to medium fine with recovered caliche fragments. The Blackwater Draw Formation extends in the saturated zone and is underlain by Kiamchi formation, Antlers Sandstone, and Dockum group respectively (Figure 3.1.3). The approximate water table in this county is at depth of about 30 feet.

3.1.2.4 Perchlorate Results

Samples were extracted and analyzed for perchlorate and other suite of ions. Perchlorate, other anions, and cations were analyzed by methods stated in Section 2.1.2. Both the TTUWRC wells in Gaines County, where unsaturated soil samples were collected had detectable perchlorate (> 0.5 ppb) almost through to water table. For well GW1, 5 (71%) samples out of 7 samples tested in the unsaturated zone contained detectable perchlorate (> 0.5 ppb); and for well GW2, 6 (86%) samples of the 7 samples tested contained detectable perchlorate. The perchlorate concentration ranged from 1.47 to 11.1 ug/kg (dry weight of soil). The perchlorate concentration increased with an increase in depth (Figure 3.1.4). The results of other tested parameters are given in Appendix B.

All three monitoring wells in Gaines County had detectable perchlorate (>0.5 pbb) in the saturated zone (in ground water). The water samples in these wells were analyzed for perchlorate, arsenic, other anions, and cations by methods stated in section 2.1.2. Wells screened at depths of 25 ft – 45, 100-120, and 198-218 ft tested positive for perchlorate at concentrations of 179, 111, and 98 ug/l respectively (Figure 3.1.4). The perchlorate concentration in the saturated zone clearly showed an increase from the top of the water table downward as in the Martin Well Site. Water samples in Gaines County wells were analyzed for tritium isotope by USGS (Fahlquist 2004) to estimate the age of water in the site. The groundwater in Gaines County appears to be well mixed with all the three wells having relatively new water (post 1960's). Tritium values ranged from 5 pCi/L to 11 pCi/L.

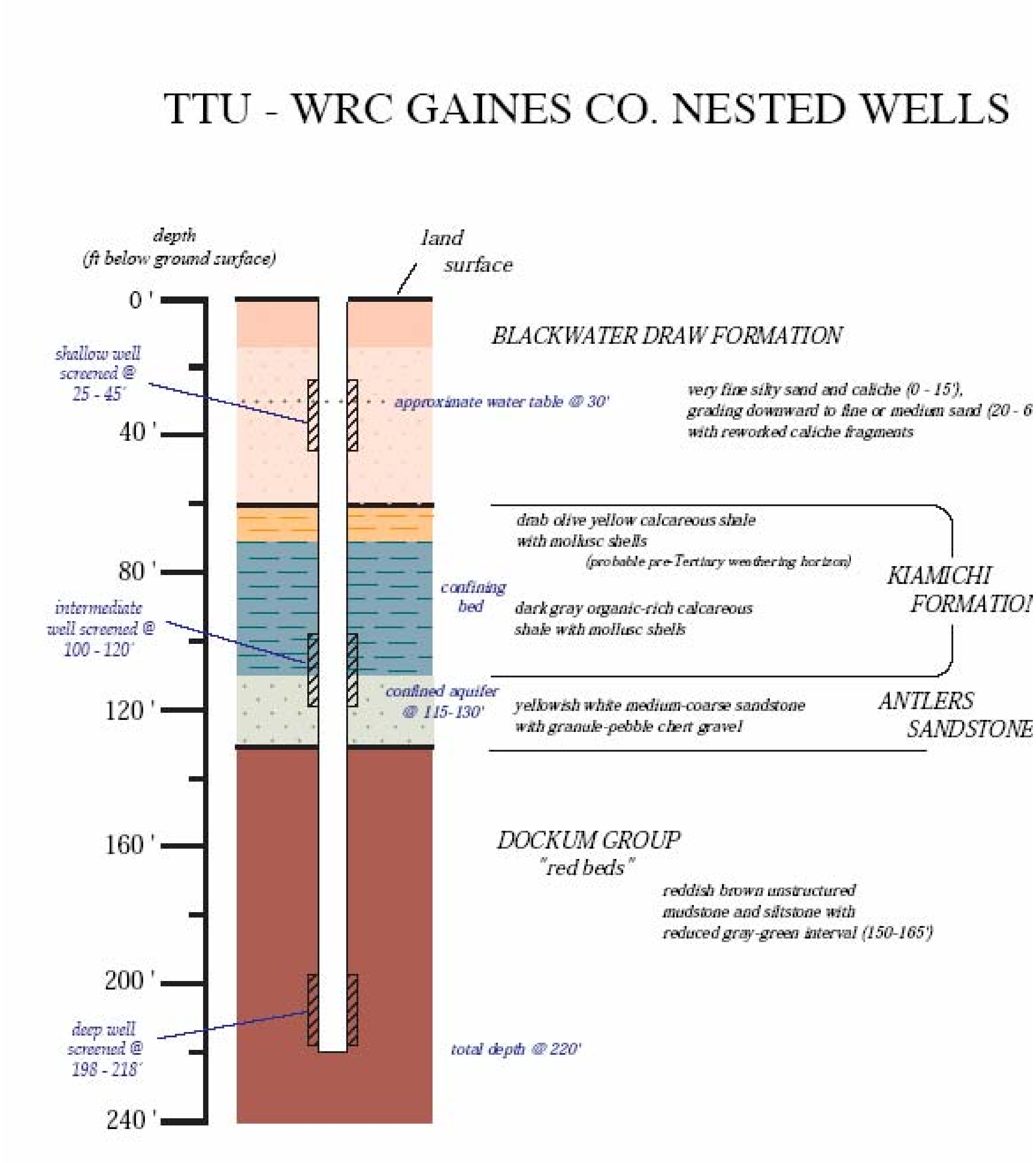

Figure 3.1.3 Subsurface Soil Profile in Gaines County Site

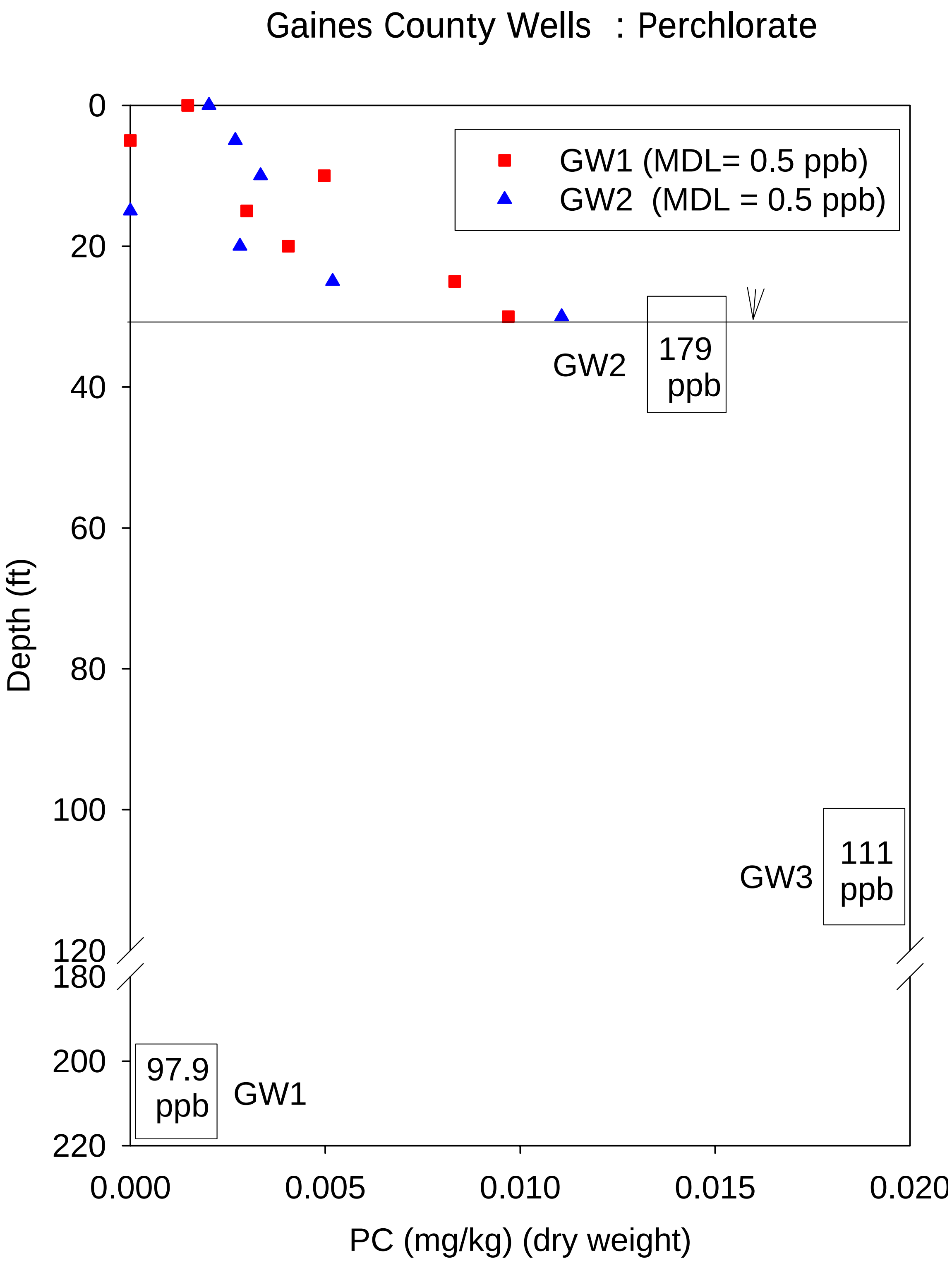

Figure 3.1.4 Perchlorate Distribution with Depth in Gaines County Site

3.1.3 Bailey County

3.1.3.1 Site Location

Two monitoring wells were installed by TTUWRC in Bailey County inside the Muleshoe National Wildlife Refuge. This Wildlife Refuge is located 15 miles South of Muleshoe, Texas. The location gains importance due to the fact that no recorded agricultural activity or industrial activity ever occurred on the site.

3.1.3.2 Well Installation

In Bailey County, one well (BW2) was drilled by air rotary method in both saturated and unsaturated zone while the other well (BW1) was drilled by air rotary method in unsaturated zone and mud rotary method in saturated zone. Unsaturated soil samples were collected at every 5ft interval during drilling by grab sampling. PVC casing and screens were used for the wells. The nested wells were screened at different levels to study the distribution of perchlorate with depth. Well BW1 was screened for the depth interval of 158 ft – 178 ft from ground surface, while well BW2 was screened from 66 ft to 86 ft (Figure 3.1.5). The samples from BW2 were prepared using the procedure given in section 3.1.1.3. For samples from well BW1 100 g of soil was added to 100 ml of water in a centrifuge tube and was mixed well using a tumbler for 24 hours to leach the ions into water. The samples were than centrifuged at a speed of 10,000 rpm in a Avanti® J-E centrifuge using a JLA-16.250 rotor for 40 minutes. The rest of the procedure was same as that stated in Section 3.1.1.3.

3.1.3.3 Soil Profile

The unsaturated zone in Bailey County consists of Blackwater Draw Formation and a part of the Ogallala Formation. The Blackwater Draw Formation consists of organic rich sand grading downward to very fine sand and caliche. This formation is underlain by top Caprock caliche of the Ogallala Formation, which is a hard laminated sandy caliche that is partly silicified. The caprock caliche is underlain by fine-grained interval of silty to very fine sand with soft caliche in the upper part (Figure 3.1.5)

3.1.3.4 Perchlorate Results

Soil samples to the depth of 60 ft were considered as the unsaturated zone. These samples were extracted and analyzed for perchlorate and other ions. For Well BW2 Perchlorate, other anions, and cations were analyzed by methods stated in Section 2.1.2. Well BW1 was analyzed for perchlorate by low level detection (pre-concentration) method (Tian et al, 2003), while other anions and cations were analyzed as in Section 2.1.2. Sediments from well BW2 contained no detectable perchlorate (> 0.5 ppb), while sediments from well BW1, 5 (39%) of 13 samples contained detectable perchlorate (>0.1 ppb). Four of the five detections were in the first fifteen feet of the soil; the other detection was at a depth of 35 feet (Figure 3.1.6). The perchlorate concentration ranged from 1.18 ug/kg to 2.62 ug/kg (dry weight of soil). The results of other ion concentrations are given in Appendix B. Of the two wells in Bailey County, only the shallower well screened at depth of 66 ft – 86 ft had a detectable perchlorate concentration of 1.16 ppb. Water samples in Bailey County wells were analyzed for tritium isotope by USGS (Fahlquist 2004) to estimate the age of water in the site. The ground water in Bailey county is relatively old (pre 1960’s) with tritium values ranging from 0 +/- 0.64 pCi/L to

0.96 +/- 0.64 pCi/L. Anthropogenic sources of perchlorate cannot have caused the contamination in the Bailey County site.

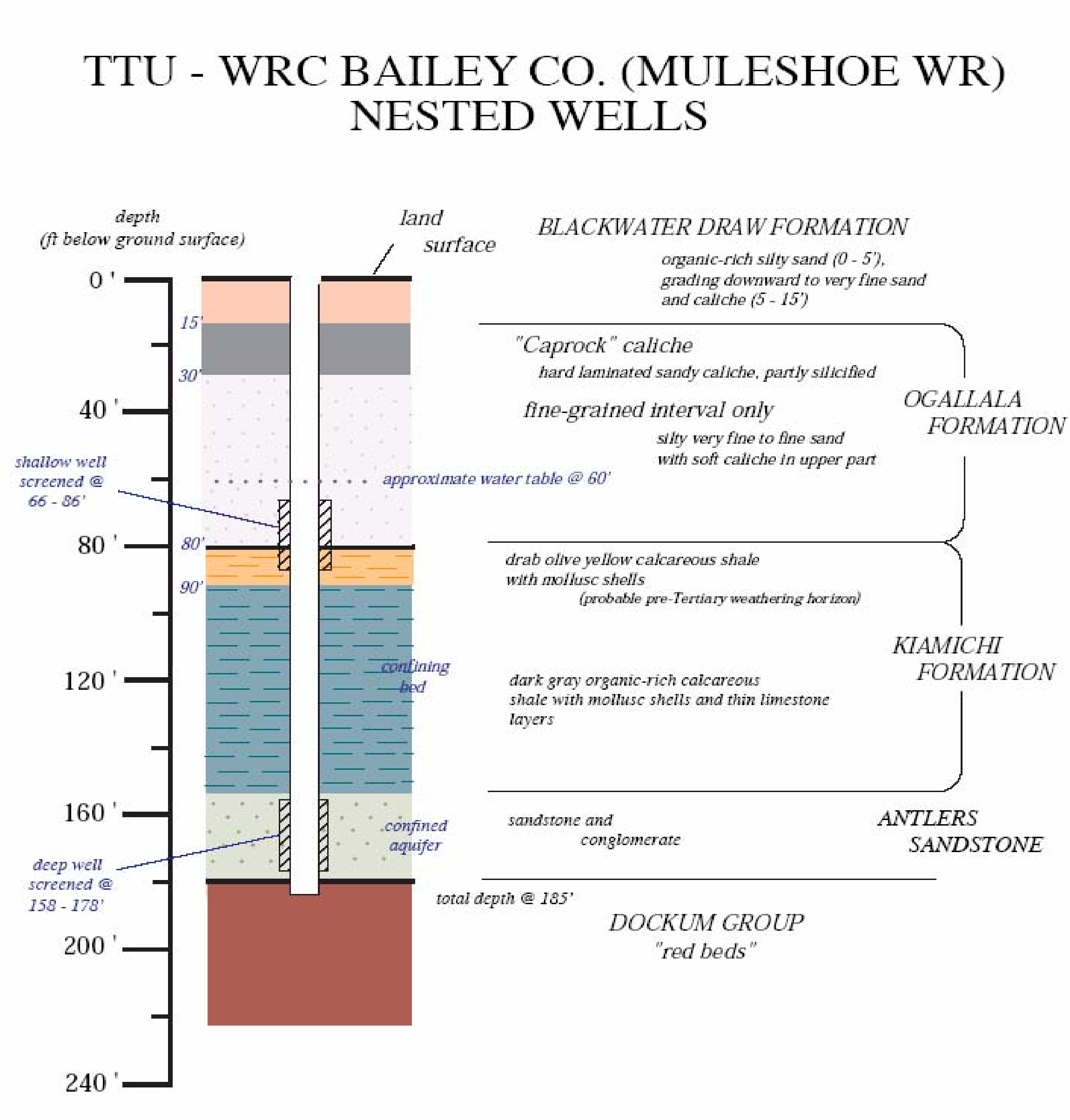

Figure 3.1.5 Subsurface Soil Profile in Bailey County Site.

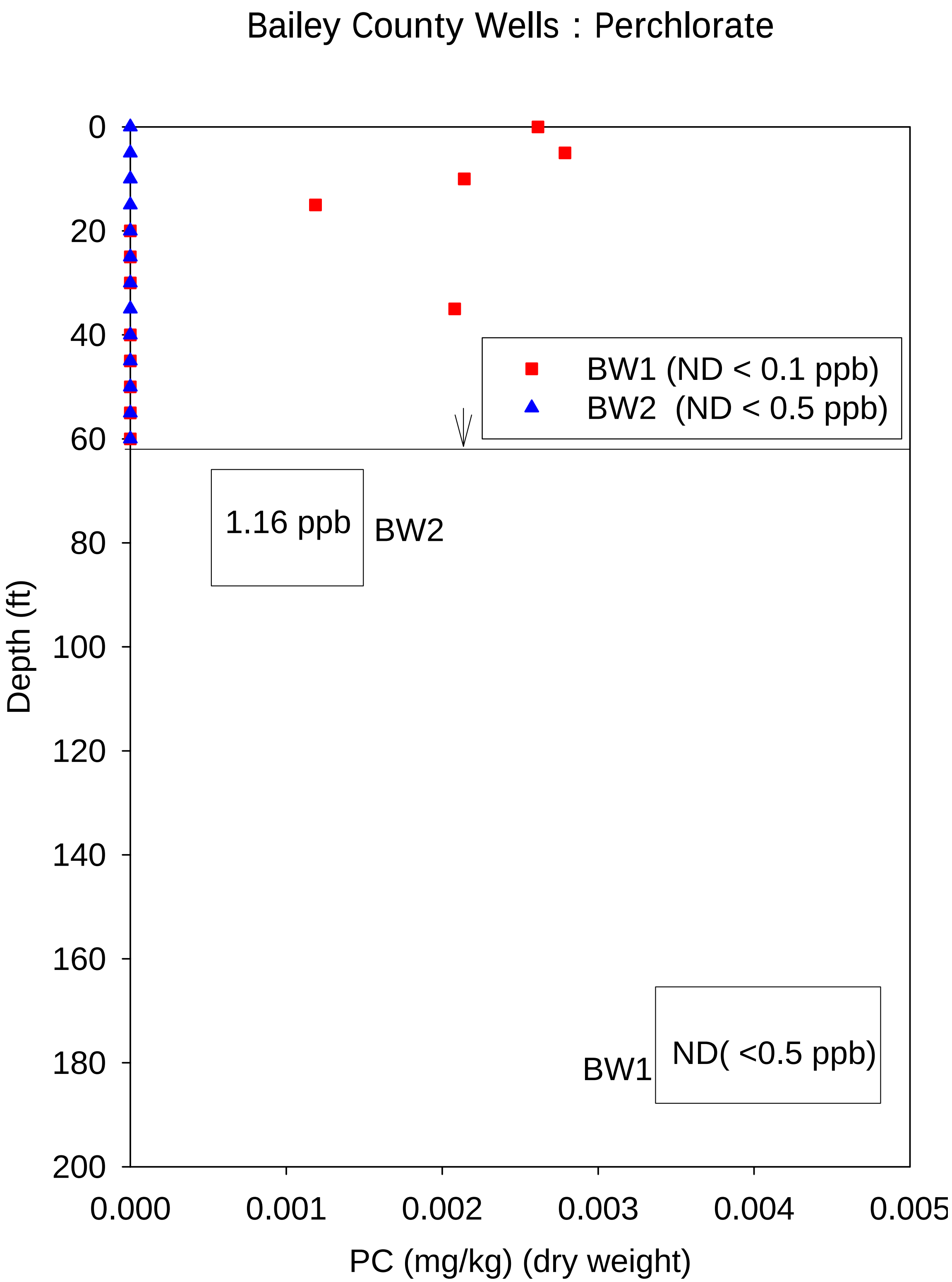

Figure 3.1.6 Perchlorate Distribution with Depth for the Bailey County Site

3.1.4 Carson County

3.1.4.1 Site Location

Unsaturated soil samples from a test hole (# PTX06-1016) drilled by U.S. Army Corps of Engineers in Carson County was obtained for determining the extent of perchlorate and other ions in the unsaturated zone. The well was located in Northern part of Zone 12 in "Pantex Superfund Site" 17 miles Northeast of Amarillo, TX. The water table in the site was at depth of about 270 ft.

3.1.3.2 Well Installation

In Carson County, the well was drilled by air rotary method. Unsaturated soil samples were collected at every 2.5 ft interval during drilling. The soil was core sampled from the augur. The core samples were ground to form a fine powder. The ground samples were prepared using the procedure given in section 3.1.1.3

3.1.3.3 Soil Profile

The land surface in the vicinity of the Pantex Plant is relatively flat and is dominated by shallow ephemeral lakes called playas. Surficial deposits in the Pantex area are composed of Quaternary and Recent Eolian deposits (well sorted, fine grained sands and clays) that contain concentrations of clay and carbonate. Two aquifers, the Dockum Group aquifer and the Ogallala aquifer, are present in the region. The Dockum Group aquifer occurs at depths varying between 350 and 700 feet below ground surface in the region. The Ogallala aquifer occurs in permeable sediments comprising the basal portion of the Ogallala Formation. The Ogallala aquifer is unconfined in this region and occurs at depths between 280 and 460 feet with overall thicknesses of 50 to more than 350 feet in the Pantex vicinity. A perched aquifer, averaging about 10 to 30 feet thick, occurs at approximately 270 feet below ground surface in Pantex site.

3.2.6.3 Perchlorate Results

Soil samples to a depth of 270 ft were considered to sample the unsaturated zone. These samples were extracted and analyzed for perchlorate by preconcentration method and other ions by methods stated in Section 2.1.2. Of the 76 sediment samples analyzed from this location 19 (25%) contained detectable perchlorate (>0.1 ppb). The perchlorate concentration ranged from 0.45 ug/kg to 7.2 ug/kg (dry weight of soil). Most of the perchlorate was detected in the top 50 ft of the unsaturated zone (Figure 3.1.7). The results of other ion concentrations are given in Appendix B.

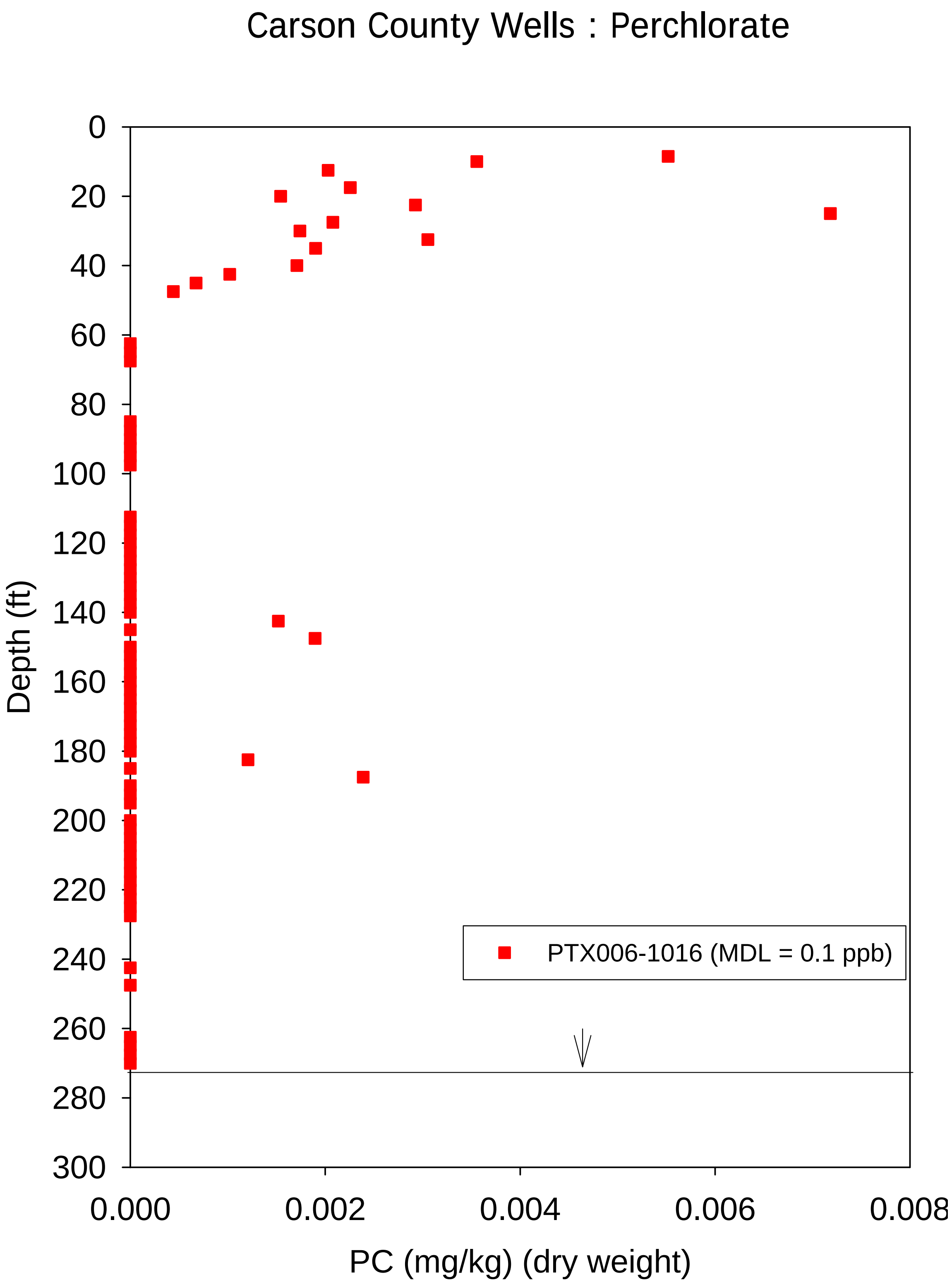

Figure 3.1.7 Perchlorate Distribution with Depth for the Carson County Site

3.2 USGS Wells

Archived sediment was available from two USGS wells located in Bailey and Cochran Counties (Figure 3.1). Of the 296 unsaturated samples collected from the two USGS wells only 25 (8.5%) had detectable perchlorate. The unsaturated zone depth ranges from 130 ft in Bailey County to 170 ft in Cochran County. Water samples were available for two nested well systems from Hale and Castro counties, and the two individual wells in Bailey and Cochran Counties. The detectable perchlorate concentration ranges from 0.64 ppb to 14.6 ppb in the unsaturated zone. The following section describes the site locations, soil profile, and analytical results in each of the counties.

3.2.1 Bailey County

3.2.1.1 Site Location

Soil samples from one USGS well (State ID#: 335830102444201) in Bailey County inside the Muleshoe National Wild Life Refuge were analyzed for perchlorate and other suite of ions. This Wild Life Refuge is located 15 miles South of Muleshoe, Texas. This well is in close vicinity to the TTUWRC monitoring wells. The water table is approximately 60 ft below ground surface.

3.2.1.2 Well Installation

In Bailey County, the USGS well was drilled by air percussion method. Unsaturated soil samples were collected at 1 ft intervals during drilling. Well screen, casing, and well development details are not available. The samples were prepared using the procedure given in section 3.1.1.3

3.2.1.3 Soil Profile

Unsaturated zone in Bailey County consists of Blackwater Draw Formation and a part of the Ogallala Formation. The Blackwater Draw Formation consists of organic rich sand grading downward to very fine sand and caliche. This formation is underlain by top Caprock caliche of the Ogallala Formation, which is a hard laminated sandy caliche that is partly silicified. The caprock caliche is underlain by fine-grained interval of silty to very fine sand with soft caliche in the upper part. The fine grained interval is underlain by Duck Creek formation which is yellowish brown silty clay stone/shale with mollusk shells and thin layers of very fine sandstone. The duck creek formation is underlain by dark olive gray organic-rich calcareous shale with mollusc shells and thin limestone of Kiamichi Formation. The Kiamichi formation was not penetrated by this well (Figure 3.2.1).

3.2.1.4 Perchlorate results

Soil samples to a depth of 60 ft were considered as the unsaturated zone. These samples were extracted and analyzed for perchlorate and other ions. The samples were analyzed for perchlorate by low level detection (pre-concentration) method (Tian et al, 2003), while other ions were analyzed as in Section 2.1.2. No perchlorate was detected in any of the samples(>0.1 ppb). In addition, water sampled from this location was also below detection for perchlorate (< 0.5 ppb). The results of other ionic concentrations are given in Appendix B.

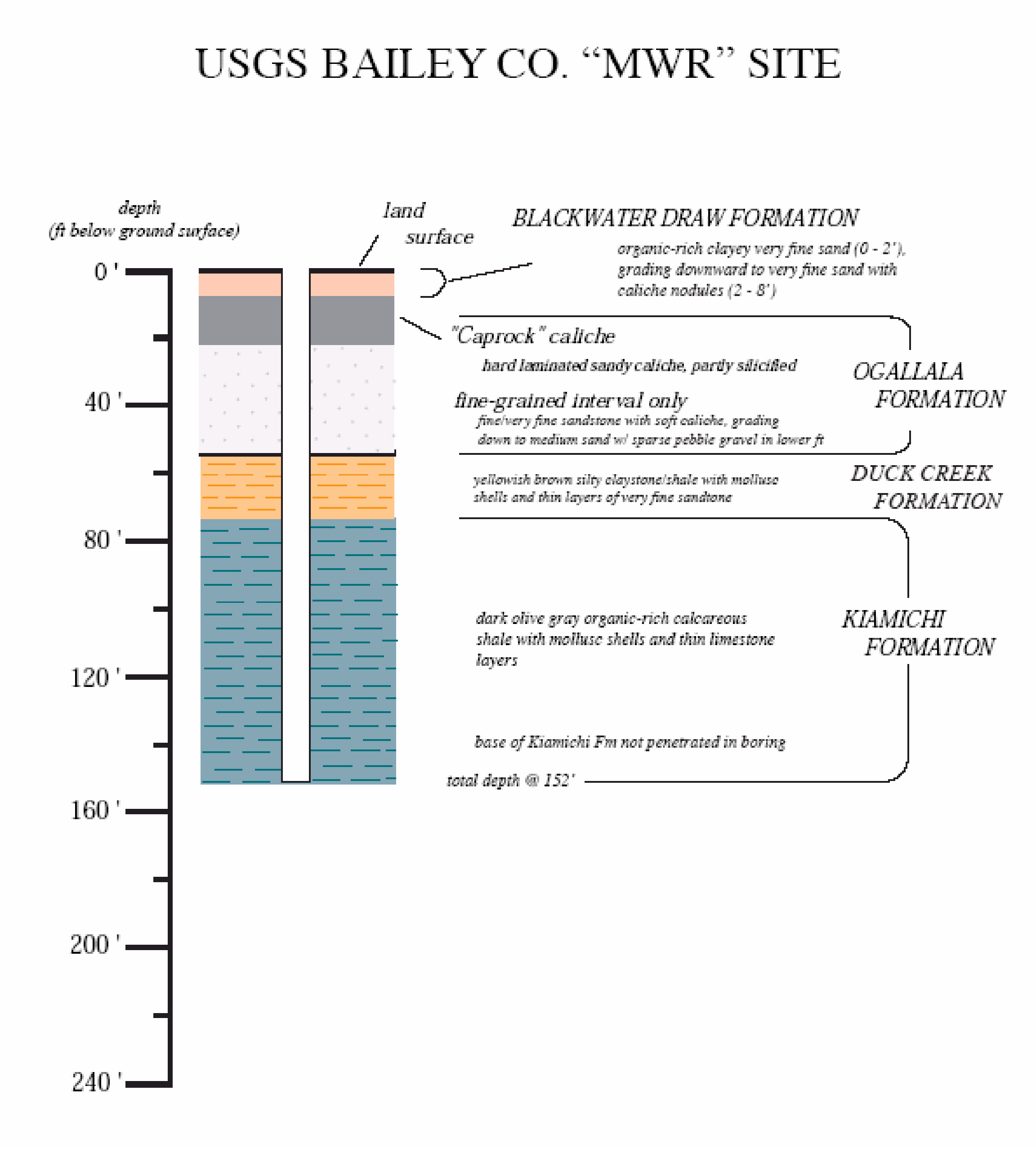

Figure 3.2.1 Subsurface Soil Profile in Bailey County (USGS) Site.

3.2.2 Cochran County

3.2.2.1 Site Location

Unsaturated soil samples from one monitoring well drilled by USGS (State ID# 334043102365501) on 6/21/01 at a site called "JRW Site" in Cochran County near Whiteface, TX was obtained for determining the extent of perchlorate and other ions in the unsaturated zone. The water table at this site was at a depth of about 151 ft.

3.2.2.2 Well Installation

In Cochran County, the USGS well (JRW) was drilled by air percussion method (Fahlquist, 2004). Unsaturated soil samples were collected at every 1 ft interval during drilling. The soil was grab sampled. PVC casing and screens were used for the wells. Well JRW was screened 155.5–165.5 ft BGS. After the casings and screens were placed the bore hole was filled with gravel around the screens and bentonite slurry and cement mixtures in other places. The samples were prepared using the procedure given in section 3.1.1.3

3.2.2.3 Soil Profile

The unsaturated zone in Cochran County consists of upper Quaternary eolian deposits, underlain by Ogallala Formation. The eolian deposits are very pale grayish orange colored undifferentiated sediments extending from 3 to 6 ft. the Ogallala forms the most of the unsaturated zone of in this county. The Ogallala consists of the upper Caprock caliche underlain by upper and fine grained intervals. The upper fine grained interval consists of Aeolian facies and ranges form pale brown to light brown in color. The lower coarse grained interval consists mainly of the fluvial facies and extends to the saturated zone with pale yellowish brown sediments (Figure 3.2.2)

3.2.6.3 Perchlorate Results

Of the 148 samples analyzed from this well 21 (14%) had detectable perchlorate in it. The perchlorate concentration was sporadically distributed with respect to depth and is present in all formations (Figure 3.2.3). The perchlorate concentration ranged from 0.68 ppb to 13.1 ug/kg (dry weight of soil) in the unsaturated zone, while there was perchlorate concentration of 9.6 ppb in the saturated zone. Water sample in Cochran County well was analyzed for tritium isotope by USGS (Fahlquist 2004) to estimate the age of water in the site. The ground water in Cochran county is relatively new (post 1960's) with tritium value of 36.8 pCi/L.

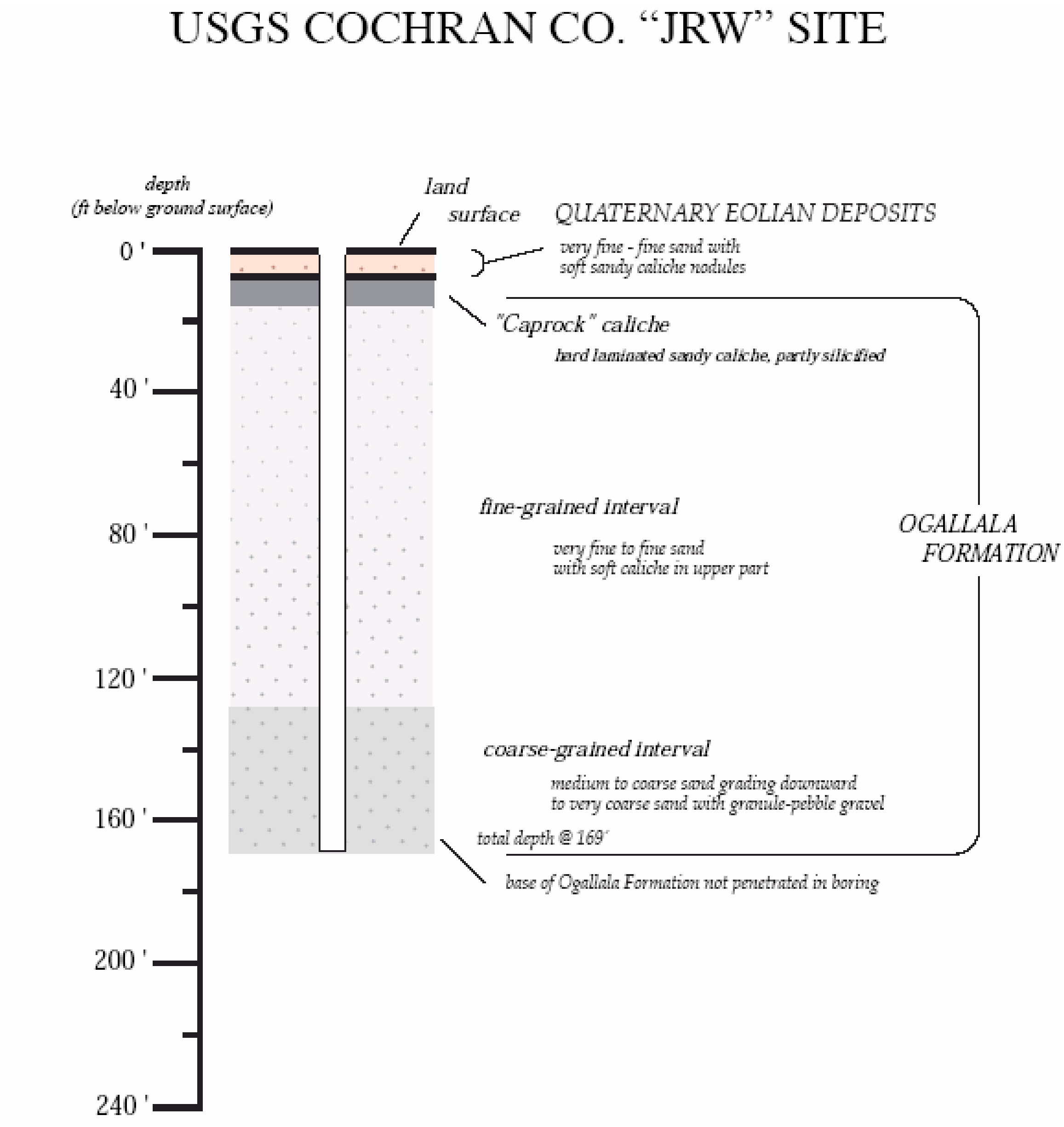

Figure 3.2.2 Subsurface Soil Profile in Cochran County (USGS) Site.

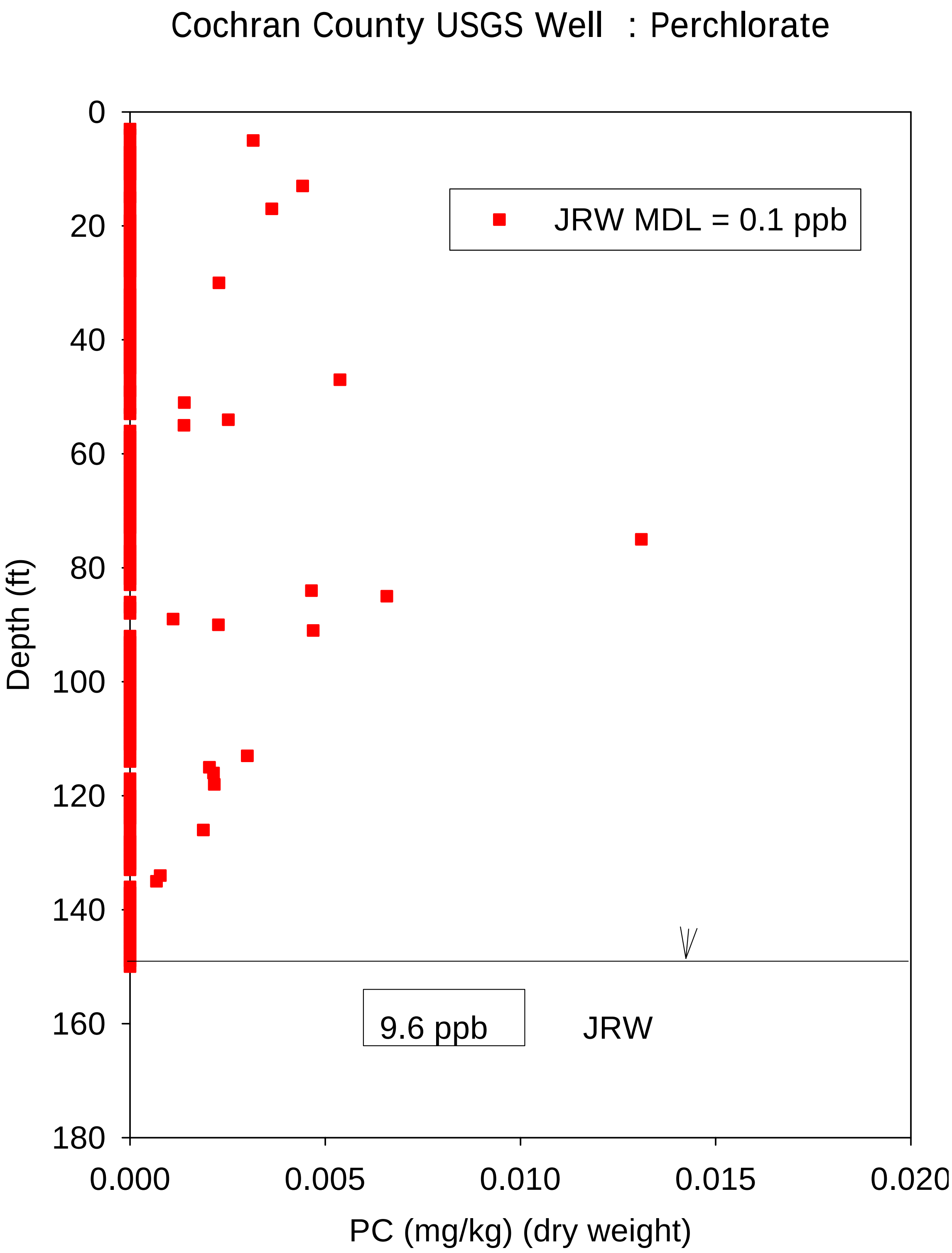

Figure 3.2.3 Perchlorate Distribution with Depth in Cochran County Site

3.2.3 Castro County

3.2.3.1 Site Location

Water samples from a nested well system with four wells drilled by USGS in Castro County was obtained for determining the extent of perchlorate and other ions in the saturated zone. The site was located in SW ¼ SECTION 32, near Hart, TX, Castro County. The water table in the site was at depth of about 220 ft.

3.2.3.2 Well Installation

In Castro County, the USGS well from which sediment was available was drilled by hydraulic rotary method (Fahlquist, 2004). PVC casing and screens were used for well construction. The nested wells in Castro County were screened at depth intervals of 231 ft – 241 ft (State ID#: 342313102174404), 320 ft – 330 ft (State ID# 342313102174403), 370 ft – 380 ft (State ID# 342313102174402), and 417 ft – 427 ft (State ID# 342313102174401) BGS respectively. The water samples were obtained from each of the wells representing different depth zones.

3.2.3.3. Soil Profile

Castro County geological data indicates that the unsaturated zone consists of the thin layer of playa deposits of the Blackwater Draw Formation underlain by Ogallala Formation. The Blackwater draw formation consists of dark muddy playa deposits (0 - 5') grading downward to very fine/fine sand (5 - 15') with soft sandy caliche (15 - 20'). A very weakly developed, hard laminated sandy Caprock caliche (20 - 30') separates Blackwater Draw formation and Ogallala formation. Ogallala formation consists of very fine to fine sandstone with soft caliche in upper part, grading downward to fine/medium sandstone in upper fine grained interval (upto 240 ft). Ogallala consist of coarse grained sandstone grading to granular material from 240 ft – 430 ft. The Dockum group starts from 430 ft depth and consist of reddish brown mudstone with thin intervals of micaceous siltstone and very fine sandstone to a depth 0f 495 ft (Figure 3.2.4).

3.2.3.4 Perchlorate Results

Water samples were analyzed for perchlorate and other suite of anions. There were no detectable perchlorate concentrations throughout the saturated zone. The results of other ionic concentrations are given in Appendix B.

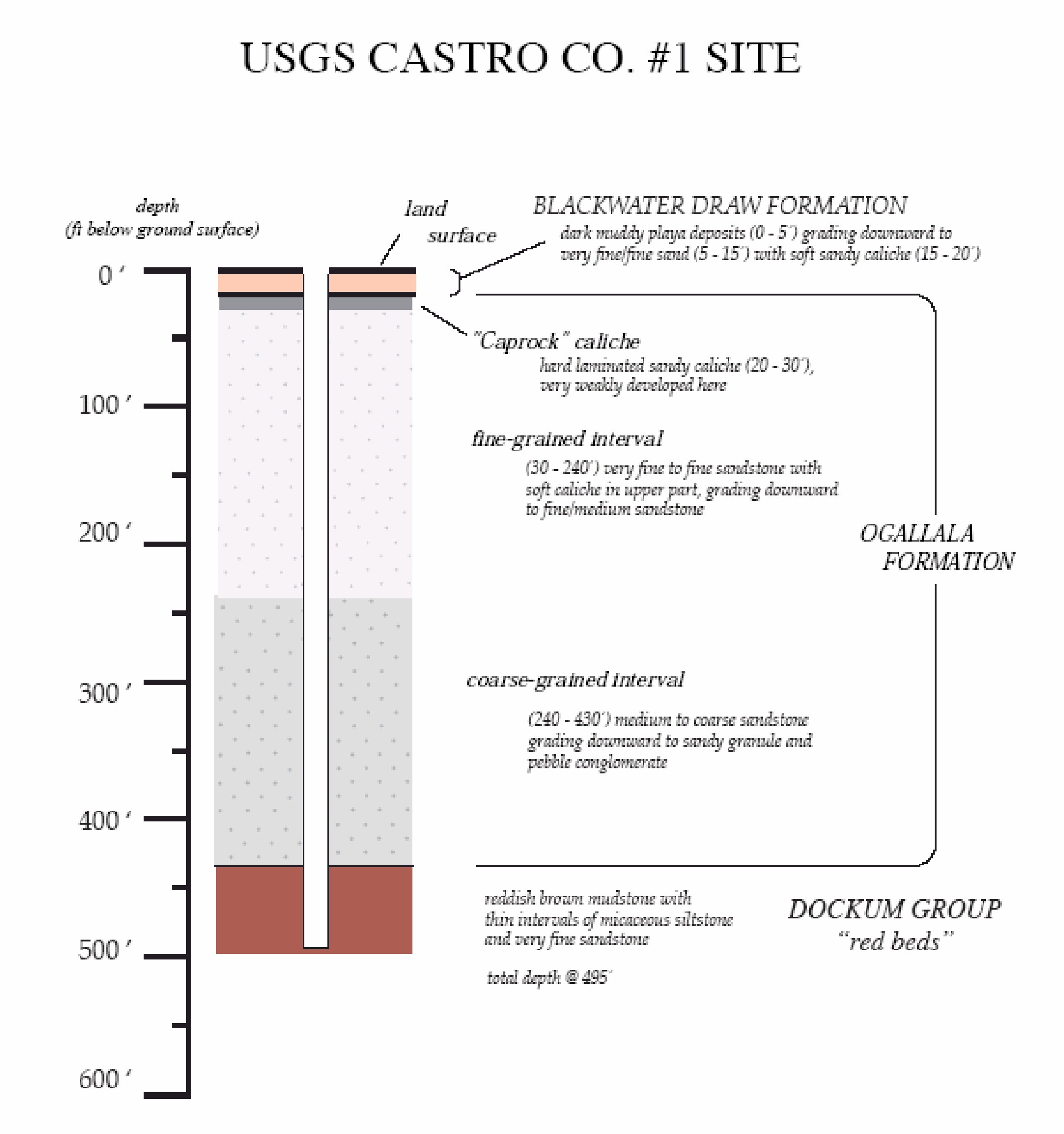

Figure 3.2.4 Subsurface Soil Profile in Castro County (USGS) Site.

3.2.4 Hale County

3.2.4.1 Site Location

Water samples from a nested well system with four wells drilled by USGS in Hale County was obtained for determining the extent of perchlorate and other ions in the saturated zone. The site was located in NE ¼ SECTION 141, near Petersburg, TX, Hale County. The water table in the site was at depth of about 220 ft.

3.2.3.2 Well Installation

In Hale County, the USGS well was drilled by hydraulic rotary method (Fahlquist, 2004). PVC casing and screens were used for well construction. The nested wells in Hale County were screened at depth intervals of 245 ft – 255 ft (State ID# 335028101365004), 330 ft – 340 ft (State ID# 335028101365003) , 390 ft – 400 ft (State ID# 335028101365002), and 459.5 ft – 489.5 ft (State ID# 335028101365001) BGS, respectively. After the casings and screens were placed the bore hole was filled with gravel around the screens and bentonite slurry and cement mixtures in other places.

3.2.3.3 Soil profile

Hale County geological data indicates that the unsaturated zone consists of the thin layer of playa deposits of the Blackwater Draw Formation underlain by Ogallala Formation. The Blackwater draw formation consists of dark muddy playa deposits (0 – 10 ft) grading downward to very fine/fine sand (10 ft – 20 ft) with soft sandy caliche (20 ft - 40ft). A hard laminated sandy Caprock caliche (40 ft – 50 ft) separates Blackwater Draw formation and Ogallala formation. Ogallala formation consist of massive jointed red claystone grading downward to siltstone/very fine sandstone with inter-bedded claystone in upper fine grained interval (50 ft – 100 ft) . Ogallala consist of coarse grained sandstone grading to granular material from 100 ft – 410 ft. The Dockum group starts from 410 ft depth and consist of reddish brown mudstone with thin intervals of micaceous siltstone and very fine sandstone to a depth of 500 ft (Figure 3.2.5).

3.2.3.4 Perchlorate Results

Of the four nested wells in the Hale County, wells designated as Hale 255 and Hale 400 were analyzed for perchlorate by preconcentraion method (MDL =0.1 ppb), while the other two wells were analyzed by standard method EPA 314.0 (MDL = 0.5 ppb). The shallow well (Hale 255) had a detectable perchlorate concentration of 6 ppb, while well Hale 400 had a perchlorate concentration of 0.21 ppb. The other two wells may have perchlorate concentrations that are less than the MDL of 0.5 ppb.

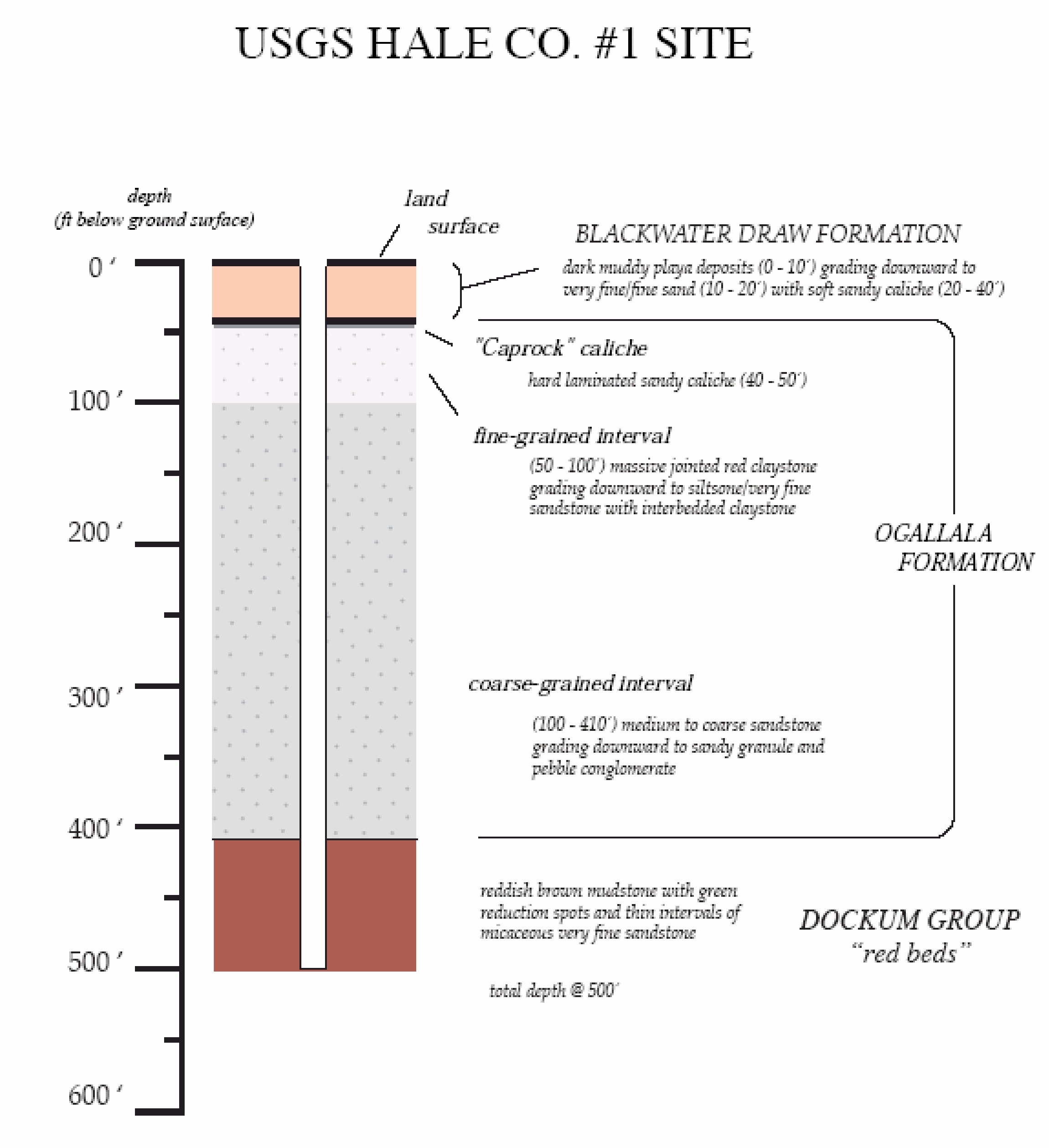

Figure 3.2.5 Subsurface Soil Profile in Hale County (USGS) Site.

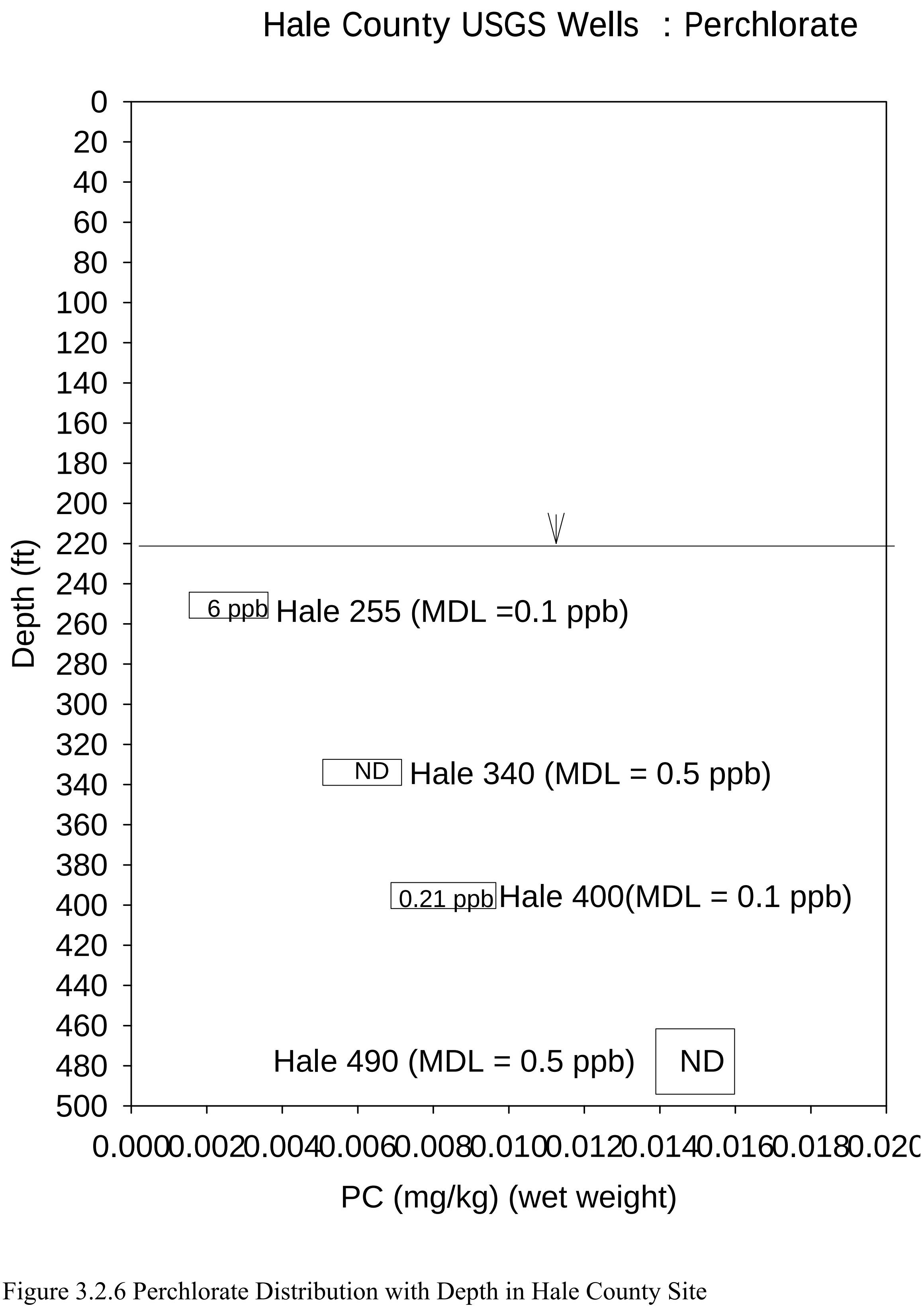

Figure 3.2.6 Perchlorate Distribution with Depth in Hale County Site

3.3 Mass of Perchlorate in Unsaturated Zone

Total mass perchlorate in the unsaturated zone for the counties that had unsaturated soil samples was estimated. For this perchlorate concentration of the soil extract was converted to perchlorate concentration (mg/kg) in soil. A soil density of 2.65 g/cc was assumed to convert the perchlorate mass for unit volume of soil (mg/cu.ft). Mass of perchlorate for unit area of soil was calculated by multiplying the perchlorate concentration with the depth interval between samples and summing up the perchlorate mass for one hole. If there were more than one hole per county average mass per sq.ft was calculated. Total mass of perchlorate in the unsaturated zone for a county was calculated by multiplying area of the county with perchlorate mass for unit area. Figure 3.3.1 shows the perchlorate mass for the counties with monitoring wells.

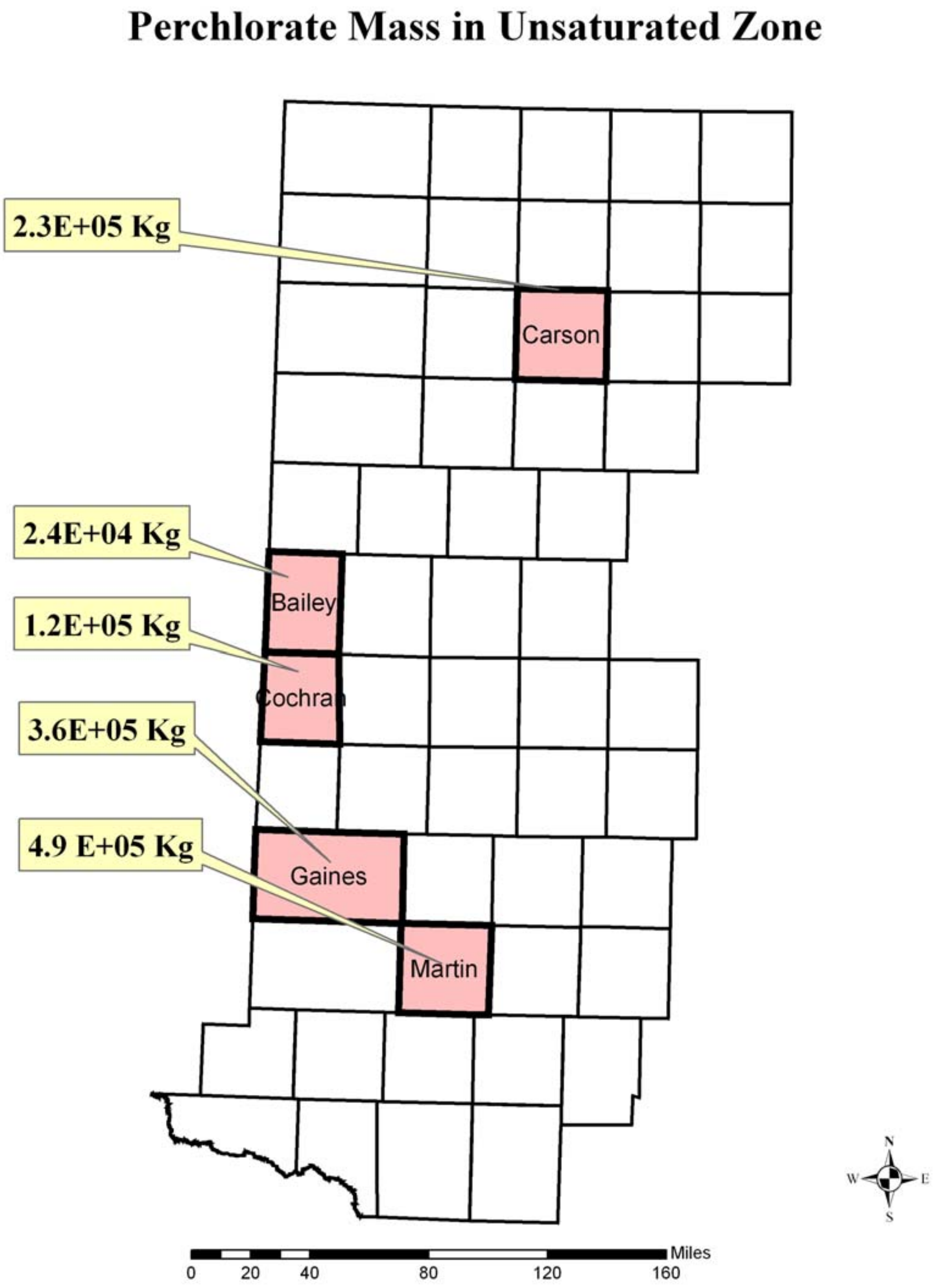

Figure 3.3.1 Mass of Perchlorate in Unsaturated Zone

3.4 Summary

Unsaturated soil samples were collected from seven counties for analysis of perchlorate, other anions, and cations. Five of the seven counties had water samples from nested well systems, while three counties had both soil and water samples from nested well system. Three counties had soil and water samples from individual wells. Unsaturated soil samples were collected from ten well holes, while water samples were collected from eighteen wells. Water samples from nested well systems allowed the study of relationship between perchlorate concentration and depth. There were detectable perchlorate concentrations in seven of the ten holes analyzed in the unsaturated zone, while nine out of eighteen wells analyzed for perchlorate in saturated zone had detectable perchlorate concentrations in them.

CHAPTER 4

AQUIFER STRATIGRAPHY IN THE STUDY AREA

Two major aquifer systems, as well as several minor ones, are present within the study area. The “High Plains Aquifer” and “Edwards-Trinity (Plateau) Aquifer” are the two principle aquifer systems Figures 2.2.17 and 6.3.1. The “Cenozoic Pecos Alluvium Aquifer,” the “Dockum Aquifer,” and “Seymour Aquifer” are also present in the study area, but are of limited extent and/or exploited to a limited degree in this region (e.g., Ashworth and Hopkins, 1995).

4.1 Aquifers in the Study Area

4.1.1 High Plains Aquifer

The “High Plains Aquifer” (or “Ogallala” Aquifer) is typical of the Southern High Plains, extensive over most of the study area, and is present to some extent in most counties sampled. In the High Plains Aquifer, sandstone and conglomerate of the Late Tertiary (Miocene-Pliocene) Ogallala Formation are overlain by a surficial veneer of permeable Pleistocene and Holocene eolian deposits including the Blackwater Draw Formation and younger dune sands (e.g., mapped as Qcs, Qs, and Qsu; Geologic Atlas of Texas, 1976; Holliday, 1989). The distribution and character of the Ogallala Formation in the region are well known (e.g., Cronin, 1961; 1969) and documented in numerous reports (e.g., reviewed by Gustavson, 1990 and Gustavson et al., 1991).

Overlying all pre-Quaternary strata in the High Plains region is a thick bed of hard pedogenic limestone often referred to informally as the “Caprock” Caliche. It is usually mapped as the uppermost unit in the Ogallala Formation. However, the term “Caprock” Caliche has not been accepted as a formally recognized stratigraphic unit, because in many areas it consists of several superimposed caliche beds that formed at different times, and includes caliche that formed earlier during deposition of the Ogallala Formation, as well as in more recent times, long after the end of Ogallala deposition (Gustavson et al., 1991). Caliche developed on the surface of older Cretaceous rocks (e.g., on the Edwards Plateau) is mapped simply as "caliche" (shown as "Qcc" on the Geologic Atlas of Texas, 1976), and not as part of the Ogallala Formation although it is identical in composition and morphology to the "Caprock" Caliche and likely formed at the same time. The term "Caprock" Caliche is used here in quotation marks to reflect this informal status and uncertain correlation.

The Ogallala Formation thins southward across the High Plains. It is typically 300 to 600 ft thick in northern counties (e.g., Dallam, Hartley) and locally over 800 ft in thickness (e.g., Carson), and typically 100 to 200 feet in central counties of the study area (e.g., Yoakum, Terry), thinning to less than 100 ft along the southern border of the High Plains (e.g., Ector, Midland). Areas where the Ogallala is relatively thick (exceeding 300 ft) are primarily fluvial paleo-valley fill deposits that trend southeastwardly across the High Plains (Seni, 1980). The paleo-valley fill deposits have a high percentage of coarse sand and gravel, and correspond to areas having the greatest saturated thickness in the aquifer and highest yields to water wells. More extensive areas where the Ogallala Formation is relatively thin represent "interfluve" or upland regions between the paleo-valley axes, where fine-grained eolian sediments predominate. These areas correspond to regions having lower saturated thickness in the aquifer and lower yields to water wells (e.g. Peckham and Ashworth, 1993; Nativ and Smith, 1987; Seni, 1980).

Over the southern part of the study area, Lower Cretaceous (Comanchean) strata lie beneath the Ogallala Formation, and vary in thickness owing to erosional relief prior to deposition of the Ogallala Formation. Where the Ogallala Formation is thickest (e.g., along the paleo-valley axes), Cretaceous strata were entirely removed by erosion prior to deposition of the Ogallala, and the Ogallala Formation rests directly on strata of the underlying Triassic Dockum Group. The regional characteristics and distribution of Cretaceous strata in the Southern High Plains region were described by Brand (1953), and more recently in some detail by Fallin (1988, 1989) and Nativ and Gutierrez (1988). Two intervals within the Cretaceous section are aquifers, and are generally saturated with fresh to moderately saline ground water. For the most part these strata appear to be in hydraulic continuity with the Ogallala Formation, and are usually included with the Ogallala within the "High Plains Aquifer," although the nature of cross-formational flow between these units is not well established. Because in most regional ground-water studies, the Cretaceous aquifers are not separated from the Ogallala Formation, and because these units are often difficult to discriminate in typical water well drillers' logs, in areas where both occur, the exact thickness and distribution of each is not well established.

There are two widely distributed aquifers within the Cretaceous section, one in the basal sandstone and conglomerate of the Antlers Sandstone (also referred to as the Trinity or Paluxy Sandstone by some authors; typically less than about 50 ft thick), and the other in jointed limestone of the Comanche Peak Limestone and Edwards Limestone (collectively about 100 ft thick). The water-bearing intervals within the Cretaceous section are separated by thin low-permeability or semi-permeable shale confining layers, but are collectively referred to as the "Edwards-Trinity (High Plains) Aquifer" (e.g., Knowles et al., 1984; Ashworth et al., 1991; Peckham and Ashworth, 1993). The limestone units thin and gradually pinch out to the west-northwest beneath the High Plains, where they are replaced by the Kiamichi and Duck Creek Formations, which consist predominantly of shale. These shale units typically act as aquitards, although thin sandstone beds, primarily in the Duck Creek Formation, yield small amounts of water locally (e.g., Fallin, 1989). In a small part of western Dallam and Hartley counties, a minor aquifer known locally as the "Rita Blanca Aquifer" (e.g., Ashworth and Hopkins, 1995) also occurs in the basal sandstone of the Cretaceous section. This unit is similar in composition and water production to the Antlers Sandstone farther south, but in that region is identified as the Dakota Sandstone.

4.1.2 Edwards-Trinity (Plateau) Aquifer

The "Edwards-Trinity (Plateau) Aquifer" extends northward from the Edwards Plateau into the southernmost counties of the study area (Reagan, Upton, Sterling, and parts of Glasscock, Midland, Ector, Winkler, and Crane counties; see e.g., Anaya, 2001; Ashworth et al., 1991; Walker, 1979). The aquifer includes all Cretaceous strata from the base of the Trinity Group (Antlers Sandstone) up to the top of the Washita Group (e.g., Georgetown Formation). However, in the study area the Edwards Group ("Edwards Limestone" or Fort Terrett and Segovia Formations) are the uppermost units present.

The "basal sand" of the Cretaceous section is usually identified as the Antlers Sandstone, but in older literature is also referred to as the Trinity Sandstone, or the Paluxy Sandstone (Fisher and Rodda, 1967). This unit consists of weakly cemented fine to medium-grained quartz sandstone and locally coarse chert-pebble conglomerate. Within the study area, this unit ranges from about 50 to 200 ft in thickness (e.g.,Walker, 1979). Although detailed data are limited, the Antlers Sandstone appears to be present continuously beneath the southernmost part of the study area where it yields small to moderate amounts of water to wells. Thick areas occur in linear belts trending approximately southeastwardly across the study area, where the Antlers Sandstone fills erosional channels incised into the underlying "red beds" of the Dockum Group (e,g., Fallin, 1989). In most areas, the Antlers Sandstone is overlain by a thin interval of shale or argillaceous limestone (Walnut Formation and/or Comanche Peak Limestone; typically about 20 to 50 ft thick) which may act as a confining layer separating the Antlers Sandstone from water-bearing limestones of the overlying Edwards Group. The Edwards "Limestone" (Fort Terrett and Segovia Formations) consists of thickly bedded cherty dolomitic limestone, and is typically less than 200 ft thick in the study area. The limestone beds have interconnected solution cavities, fractures, and bedding plane joints, and comprise an important aquifer farther south on the Edwards Plateau. The Edwards Limestone and the Antlers ("Trinity") Sandstone are generally thought to comprise a single aquifer; however, in Ector, Midland, and Glasscock counties, the zone of saturation is below the limestones and fresh ground water is typically confined to the Antlers Sandstone, while farther south in Upton and Reagan counties, the water table is higher, within the Edwards Limestone (e.g.,Walker, 1979). Within the study area, water levels within the Edwards-Trinity (Plateau) Aquifer declined as a result of pumpage, primarily for irrigation prior to 1980 (e.g., Ashworth and Hopkins, 1995).

4.1.3 Cenozoic Pecos Alluvium Aquifer

The “Cenozoic Pecos Alluvium Aquifer” extends northward from the Pecos River Valley into Crane and Ward counties and parts of Ector, Winkler and Andrews County in the southwestern part of the study area (Jones, 2001; Ashworth and Flores, 1991). These deposits consist of unconsolidated sand and gravel overlain by windblown sand (shown as Qs, Qsu, and Qsd on the Geologic Atlas of Texas, 1976), and are in part equivalent in age to the Ogallala Formation, but have typically been identified informally as the “Cenozoic Basin Fill” (Maley and Huffington, 1953) or “Cenozoic Pecos Alluvium” (Ashworth and Flores, 1991). They are at least in part equivalent to the Gatuna Formation in the upper Pecos River Valley (Powers and Holt, 1993; Kelley, 1980). Some of these deposits have also been mapped as Ogallala Formation (Nicholson and Clebsch, 1961; shown as “To” on the Geologic Atlas of Texas, 1976), but may more logically be included with the Gatuna Formation, as suggested by Hawley (1993).

The Pecos River Valley subsided in response to subsurface salt dissolution. A peripheral zone of subsurface (Permian) salt dissolution surrounds the High Plains, with its inner boundary generally coincident with the present escarpment of the High Plains (Gustavson and Simpkins, 1989). This peripheral belt of subsurface salt dissolution underlies the Pecos River Valley. A curvilinear belt of subsurface salt dissolution also coincides with the buried Permian Capitan Reef trend surrounding the Delaware Basin. Salt dissolution occurred over the buried summit of the artesian reef aquifer (Uliana, 2001; Baumgardner et al., 1982; Reeves, in Gustavson et al., 1991). The Capitan Reef Aquifer itself contains water of poor quality, used primarily for oil reservoir water-flooding operations and some irrigation of salt-tolerant crops (Ashworth and Hopkins, 1995). The extensive salt dissolution within the Permian strata resulted in subsidence of the “Monument Draw Trough” in Winkler and Ward counties, and similar subsidence in the “Pecos Trough” over the Delaware Basin farther west in Loving and Reeves counties (Jones, 2001; Maley and Huffington, 1953). The two depressions are now filled with “Cenozoic Basin Fill,” along the southwestern border of the study area. In western Winkler and Ward counties, the alluvial fill exceeds 1500 ft in thickness; however, the deposits thin abruptly eastward where they are typically less than 100 ft thick. Separate groundwater flow systems are found within the alluvial fill of the Monument Draw and Pecos troughs (e.g., Jones, 2001).

The Cenozoic Pecos Alluvium Aquifer is primarily utilized as a source of irrigation water to the west and south of the study area in Reeves and Pecos counties, and for industrial and public supply uses in Ward and Winkler counties (e.g., Ashworth and Hopkins, 1995). Some water is exported eastward, for example to the city of Odessa by the Colorado River Municipal Water District (Jones, 2001).

4.1.4 Dockum Aquifer

The distribution and regional characteristics of the Triassic Dockum Group were recently reviewed by Lehman (1994a, 1994b). The Dockum Group consists of five formations; in ascending order these are the Santa Rosa, Tecovas, Trujillo, and Cooper Canyon Formations. In older literature, and water development board reports, the upper parts of the Dockum Group (all strata above the Santa Rosa Sandstone) are identified as the Chinle Formation.

The Dockum Group is present beneath most of the study area, and so underlies the High Plains, Edwards-Trinity, Cenozoic Pecos Alluvium, and “Seymour” aquifers. The

Dockum Group is widely exposed at the land surface along the borders of the High Plains where it is typically less than 500 ft thick; however, these strata approach 2000 ft in thickness in the subsurface. In most areas, the upper part of the Dockum Group (Cooper Canyon Formation) consists primarily of thick beds of red mudstone (identified as "red beds" on most driller's logs), and forms the regional aquitard below surficial permeable strata of the High Plains, Edwards-Trinity, and Pecos Alluvium aquifers. However, the base (Santa Rosa Sandstone) and middle (Trujillo Sandstone) of the Dockum Group consist largely of sandstone and conglomerate beds that are permeable water-bearing units. These are sometimes referred to as the "lower Dockum" and "upper Dockum" aquifers; however, any water-bearing interval within the Dockum Group may locally be identified as the "Santa Rosa aquifer" regardless of its position (e.g., Dutton and Simpkins, 1986; Bradley and Kalaswad, 2001).

The water-bearing sandstone intervals are typically less than 200 ft thick. Ground water in the Dockum Aquifer is under confined or partially confined conditions, and is generally of poor quality, except near the outcrop belt where recharge occurs (e.g., by downward leakage from the Ogallala, Edwards, and Cenozoic Pecos Alluvium aquifers; Dutton and Simpkins, 1986; Bradley and Kalaswad, 2001). As a result, municipal use of the Dockum Aquifer is found primarily along the outer borders of the study area (e.g., cities of Happy, Hereford, and Tulia along the northern and eastern border of the High Plains and cities of Barstow, Kermit, Pecos, and Colorado City on the southern border). Elsewhere, the poor water quality, deep pumping depths, and low yields discourage its use (Bradley and Kalaswad, 2001). Relatively few wells within the study area utilize groundwater from the Dockum Aquifer.

4.1.5 “Seymour” Aquifer

Relatively thin deposits of Quaternary alluvium occur in the drainages of the Red, Brazos, and Colorado river valleys and their tributaries along the eastern border of the study area. Remnants of more extensive Quaternary alluvial deposits are also found on the drainage divides between tributaries. Although in some areas, these sediments are identified and mapped as the Seymour Formation, in most parts of the study area, such deposits are mapped variously as alluvium (Qal), windblown sand (Qs and Qsd), fluviatile terrace deposits (Qt), and other Quaternary deposits (Qao) in the Geologic Atlas of Texas (1976). Most of these deposits are not actually equivalent in age to the Seymour Formation, and in the study area those that are likely equivalent are assigned instead to the Lingos Formation (Gustavson et al., 1991). Nevertheless, in many Texas Water Development Board reports, these deposits are said to comprise the “Seymour Aquifer” (e.g., Ashworth and Hopkins, 1995) and are discussed collectively in that manner here, using quotation marks to convey their uncertain correlation. These varied deposits of sand and gravel with local lenses of silt and clay accumulated in stream channels, lakes and ponds, and in eolian sand sheets and dunes. They rest on the underlying Triassic Dockum Group along the border of the High Plains escarpment, and on Permian strata farther east. Their thickness varies markedly, but is typically less than 100 ft. Water quality and production varies markedly in these isolated accumulations, but over much of the Rolling Plains region the water is widely used for irrigation as well as for domestic supply and locally for municipalities (e.g., Duffin and Beynon, 1992). Groundwater within the isolated accumulations of the “Seymour” Aquifer generally flows toward adjacent stream drainages where it discharges at the land surface. Where these deposits overlie permeable sandstones, downward leakage of groundwater recharges the Dockum Aquifer.

4.1.6 Interaquifer Flow

The boundary between the High Plains and Edwards-Trinity (Plateau) aquifers is not precisely defined. Cretaceous strata within the High Plains Aquifer are contiguous with Cretaceous strata of the Edwards Plateau to the south. Although the nature of cross-formational flow between the Ogallala and Cretaceous aquifers is not well established, comparable water level elevations across the High Plains/Edwards Plateau boundary and comparable ground water flow directions suggest that they are in hydraulic continuity. In contrast, a regional ground water divide likely separates the High Plains and Edwards aquifers on the north and east from the Cenozoic Pecos Alluvium Aquifer on the southwest. Ground water flow in the Cenozoic Pecos Alluvium Aquifer is to the southwest, toward the Pecos River (Jones, 2001; Nicholson and Clebsch, 1961); while flow in the High Plains and Edwards aquifers is to the southeast (Knowles et al., 1984; Walker, 1979). Ground water flow within the Dockum ("Santa Rosa") Aquifer is also generally to the southeast (Dutton and Simpkins, 1986; Bradley and Kalaswad, 2001). Downward leakage from the Ogallala, Cenozoic Pecos Alluvium, Edwards-Trinity, and "Seymour" aquifers recharges the Dockum Aquifer where permeable sandstone intervals occur locally in the Dockum subcrop beneath them. This occurs in the southwestern part of the study area (e.g., Dutton and Simpkins, 1986; Nativ and Gutierrez, 1988; Bradley and Kalaswad, 2001) and in the eastern and southeastern part of the study area (Walker, 1979).

4.2 Occurrence of Perchlorate in Relation to Aquifer Stratigraphy

4.2.1 Primary area of Occurrence

The main area where perchlorate was detected in groundwater extends along the southwestern border of the High Plains in Texas from Bailey and Lamb counties on the north to Ector and Midland counties on the south, and into adjacent Lea and Roosevelt counties in New Mexico. Within this area, perchlorate was found primarily in groundwater produced from the High Plains (Ogallala) Aquifer, and primarily from that region where the Ogallala Aquifer overlies Cretaceous strata (the Edwards-Trinity (High Plains) Aquifer of Ashworth and Hopkins, 1995). Because of the limited geological data contained in most available water well driller's logs, it is not possible to determine precisely whether groundwater containing perchlorate in this area is produced solely from the Ogallala Aquifer or from the underlying Edwards-Trinity (High Plains) Aquifer in this area, or from both aquifers. Furthermore, the screened intervals are not known for many wells, and many wells probably produce water from both aquifers. However, perchlorate was detected in some wells that appear to produce water exclusively from the Ogallala Formation, as well as in some wells that produce exclusively from Cretaceous (Edwards-Trinity) strata. Two of the nested well sets completed for the present study (Gaines and Bailey nested wells), sample water independently from both the Ogallala and Edwards-Trinity (High Plains) aquifers, and in one case water produced from the Ogallala was found to contain perchlorate while that produced from the Edwards-Trinity (in both cases the Antlers Sandstone) did not while in the other both wells contained perchlorate as well as the lower well producing strictly from the Dockum.

4.2.2 Minor areas of Occurrence

Perchlorate was also detected in groundwater at isolated sites outside the main area of occurrence described above. In these isolated areas, perchlorate was typically found at concentrations lower than those measured in the main area of occurrence.

1 – Perchlorate was detected in isolated wells (nine or ten) farther north on the High Plains in Oldham, Potter, Carson, Gray, Donley, Deaf Smith, and Randall counties where water is produced exclusively from the Ogallala (High Plains) Aquifer. These isolated wells reflect geological conditions similar to that observed within the main area of perchlorate occurrence; however, these areas are well beyond the northern limits of the Cretaceous subcrop.

2 - Perchlorate was detected in several wells (five or six) producing water from the Edwards-Trinity (Plateau) Aquifer in Ector, Howard, and Glasscock counties. It should be noted, as described above, that the boundary between the High Plains and Edwards-Trinity (Plateau) aquifers is not precisely defined, and that it is possible that some or many additional wells (e.g., in the Midland and Odessa areas) included here with the High Plains aquifer may actually be producing water from the Edwards-Trinity (Plateau) aquifer (see Ashworth and Hopkins, 1995).

3 - Perchlorate was detected in several wells (four or five) producing water from the Cenozoic Pecos Alluvium Aquifer in Crane, Ward, and Winkler counties.

4 - Perchlorate was detected in several wells (four or five) producing water from the "Seymour" Aquifer and/or other similar shallow alluvial aquifers in Briscoe, Kent, and Howard counties. Because of the limited geological data available for these wells, and because the thin alluvial aquifers in these areas rest directly on the outcrop of the

Dockum Group, it is possible that some of these wells actually produce water in part from the Dockum Aquifer. This is possible particularly for the well in Howard County. However, samples from two wells producing water from the Dockum Aquifer in Borden County, and one well in Andrews County were not found to contain perchlorate. Only twenty four wells (total) producing water from the Dockum Aquifer were sampled in the study area.

Chapter 5

Transport Modeling

The investigation of potential sources of perchlorate in this region was supported by analytical and computer modeling of flow and transport in the unsaturated and saturate zones at the three locations at which the TTUWRC installed new clusters of monitoring wells. The modeling approaches connected to different source scenarios. First, a numerical computer model, CHEMFLO (Nofziger and Wu, 2000) was used to estimate the movement of infiltrating water through the unsaturated zone. The Bailey County site at the Muleshoe National Wildlife Refuge (MNWR) has never been developed or cultivated, so infiltration of rainfall is the only possible transport mechanism that could move perchlorate through the unsaturated zone, whether the perchlorate was originally in the rainfall or in the unsaturated soil matrix. Both the Gaines and Martin county sites are located in previously cultivated sections that are currently in the Conservation Reserve Program (CRP), so both rainfall infiltration and irrigation return flow could have been active in the past. The unsaturated zone transport could move the perchlorate to the water table. Second, the potential for diffusion of perchlorate due to concentration gradient across the saturated zone was estimated with a one-dimensional analytical relationship. Diffusion could assist downward movement from the water table if a recent man-made source was active, as well as upward diffusion from more saline groundwater in the Cretaceous or Dockum water-bearing zones. Third, the combined effects of advection and dispersion for downward transport from the water table near a hypothetical surface source downward across the saturated zone. A three-dimensional analytical solution for a distributed source in a regional flow field was applied to typical conditions at the sites.

5.1 Unsaturated Zone Flow and Transport

5.1.1 CHEMFLO Description

CHEMFLO 2000 is an interactive software PROGRAM developed by Nofziger and Wu (2000) of the Plant and Soil Sciences Department of Oklahoma State University. CHEMFLO is a simple but robust mathematical model that simulates one-dimensional water and contaminant movement in a single homogeneous unsaturated soil type. The software is written in Java and runs either as a stand-alone application or as a Java Web Start package. Flow and transport equations in CHEMFLO were solved using finite difference methods, so the user must discretize the subsurface solution domain. Initial conditions specified by the user determine the values of the matric potential at these mesh points at the beginning of the simulation. The Richards equation provides a partial differential flow equation for the matric potentials at each point over time. Soil characteristic curves that relate matric potential, moisture content, and unsaturated hydraulic conductivity may be chosen from those developed by Brooks and Corey (1964), Simmons (1979), or Van Genuchten (1980). Reactive transport of a single solute can consider molecular diffusion, dispersion, sorption, and first-order decay. CHEMFLO output includes volumetric moisture content (referred to as water content), matric potential, hydraulic conductivity, flux density and cumulative flux at all solution points and at different time steps.

5.1.2 CHEMFLO Application

The primary interest of the simulation was to approximate typical travel times through the unsaturated zones at the three monitoring well sites in Bailey, Gaines, and Martin counties. It was recognized that the unsaturated soil conditions were not completely homogeneous at any of the three sites, but the model allowed useful approximation of the flow conditions. The conceptual application considered rainfall applied at the soil surface and evaporation also active at the surface. Rainfall and evaporation data encompassing 26 years, starting from 1975 and ending with 2000, were used as part of the model input. This time period was selected due to the uninterrupted availability of rainfall data during that time period. Daily rainfall data were obtained from the National Climatic Data Center (NCDC) data collection sites nearest to the monitoring well sites (NOAA, 2003). It was assumed that the nearby sites, although actually separated from the monitoring well locations, represented appropriate ranges of weather conditions that fit the needs of this study. The evaporation data were obtained from Texas Water Development Board (TWDB) lake evaporation database (TWDB, 2004). The spatial distribution of evaporation data in this database corresponds to each one degree quadrangles, so the evaporation data for the quadrangle for each well site selected. Daily values of both precipitation and evaporation were used as model input. The output values obtained from CHEMFLO were used to achieve the desired objectives. Numerical experiments involving dispersion/diffusion equations were carried out to determine the movement of perchlorate in the Ogallala aquifer beneath the monitoring well locations.

5.1.3 Site-Specific Conditions

Table 5.1 summarizes useful information about the monitoring well locations. The depth to the water table was used as the total unsaturated zone vertical dimension. The perchlorate values were from the initial sampling event at each site.

5.1.3.1 Bailey County

Two monitoring wells were installed at the MNWR. Depth to the water table from the ground surface at this site was 60 ft (18.3 m). The soil type throughout this depth ranges from organic-rich silty sand to very fine sand (TTUWRC, 2003). Rainfall data from City of Muleshoe weather observation station, which is nearest to the monitoring well site, were used for CHEMFLO simulation. The monitoring well site is located in Quadrangle 305 of the TWDB evaporation database

Table 5.1 Monitoring Well Site Descriptions

County	Well	Depth to Screen Top (ft)	Depth to Screen Bottom (ft)	Depth to Static Water Table (ft)	Perchlorate (ppb)
Bailey	Shallow	66	86	60	1.1
	Deep	158	178	60	nd
Gaines	Shallow	25	45	30	179.0
	Intermediate	100	120	30	111.0
	Deep	198	218	30	97.9
Martin	Shallow	115	125	119	27.2
	Intermediate	133	153	119	15.7
	Deep	145	165	119	17.9

5.1.3.2 Gaines County

The three monitoring wells in Gaines County were located six miles east of Seminole, Texas. The monitoring well site was located less than half a mile distance from an existing groundwater well that recorded a perchlorate concentration of 30 ppb. Depth to the water table from the ground surface in this site was 30 ft (9 m). The entire cross-section of the unsaturated zone is predominantly composed of sand varying from very fine silty sand in the top to fine or medium sand in the bottom (TTUWRC, 2003). Rainfall data were obtained for the City of Seminole, the nearest weather observation station, as well as evaporation data corresponding to TWDB Quadrangle 505.

5.1.3.3 Martin County

The three monitoring wells were located 20 miles west of Lenorah, Texas. High concentrations of perchlorate were detected in the wells surrounding this monitoring well site. Depth to the water table from the ground surface in this site is 115 ft (35 m). The cross-section of the unsaturated zone is composed of calcareous very fine sandy clay, silty very fine sand, hard laminated sandy caliche, and silty very fine to medium sand (TTUWRC, 2003). Rainfall data came from the Lenorah weather observation station and evaporation for TWDB Quadrangle.

5.1.4 Model Assembly

CHEMFLO 2000 was used in this project to model the movement of water through the unsaturated layer above the High Plains aquifer in West Texas. Perchlorate has a high aqueous solubility and can readily migrate with infiltrating precipitation. The cross-section of the unsaturated layer in all three monitoring well sites is composed of different types of soils that include very fine sandy clay, silty very fine sand, hard laminated sandy caliche, and silty very fine to medium sand, but most of the material was sand. In the CHEMFLO modeling for each , the unsaturated soil matrix was selected as sand, and the soil characteristic curve parameters were assigned from the program's database. Mesh size for the finite difference model in all three sites was 2.60 cm (1 in) while the time step length was 0.63 hr. Maximum relative mass balance error for CHEMFLO modeling was set to 5 percent. The default system of units in CHEMFLO is metric, so metric units are shown in the discussion below.

CHEMFLO uses the Richards equation for water flow as

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x}\left[K(h)\left(\frac{\partial h}{\partial x} - \sin(A) \right) \right] \qquad [5.1]$$

where θ = volumetric moisture content, h = matric potential (cm), x = distance (cm), K(h) = hydraulic conductivity (cm/hr), t = time (d), and A = angle relative to vertical. The required soil hydraulic properties are defined by specifying the θ(h) and K(h) functions in Equation 5.1. In this project, the Van Genuchten equation related K(h) as

$$\begin{aligned} K(h) &= \frac{\left[1 - (-\alpha h)^{n-1}\left(1 + \{-\alpha h\}^{n} \right)^{-m} \right]^{2}}{\left[1 + (-\alpha h)^{n} \right]^{m/2}} \text{ for } h < 0 \\ K(h) &= K_s \text{ for } h \geq 0 \end{aligned} \qquad [5.2]$$

where

$$m = 1 - \frac{1}{n} \qquad [5.3]$$

and α, n , and K_s are defined in Table 5.2. The Simmons equation related θ(h) as

$$\begin{aligned} \theta(h) &= \alpha\theta_s - \ln\left[(-h)^{n} \right] \text{ for } h < 0 \text{ and } \theta_r \geq \theta(h) \\ \theta(h) &= \theta_s \text{ for } h \geq 0 \end{aligned} \qquad [5.4]$$

where α, n , and θ_s are defined in Table 5.3.

Table 5.2 Van Genuchten Parameters

Symbol	Description	Range	Value
K(h)	Hydraulic conductivity at matric potential h	$0 \leq K(h) \leq K_S$	Calculated variable
K_S	Saturated hydraulic conductivity	$0 < K_S$	29.7 cm/hr
α	Empirical constant	~0.002 ≤ α ≤ ~0.15	0.145 cm^{-1}
n	Empirical constant	~1.25 ≤ n ≤ ~3.0	2.68

Table 5.3 Simmons Parameters

Symbol	Description	Range	Value
$\theta(h)$	Volumetric water content at matric potential h	$\theta_r \leq \theta(h) \leq \theta_S$	Calculated variable
θ_r	Irreducible water content	$0.00 \leq \theta_r \leq \sim 0.15$	0.08
θ_S	Saturated water content	$\sim 0.25 \leq \theta_S \leq \sim 0.60$	0.35 or 0.40
α	Empirical constant	$\sim 1.15 \leq \alpha \leq \sim 1.25$	1.2
n	Empirical constant	$\sim 0.025 \leq n \leq \sim 0.1$	0.071

The initial matric potential of the sand was set at -36.00 cm H_2O (Mualem, 1978) throughout the solution domain. This matric potential value was assumed to be uniform throughout the entire cross-section of the unsaturated layer at the start of simulations. The default values assigned by CHEMFLO to sand were used for the variables K_S, α and n in the Van Genuchten equation. In the Simmons equation, default values were used for variables θ_r and α, while different values were used for variables θ_S and n. The saturated moisture content (θ_S) usually represents the porosity of the soil. The porosity of the soil in West Texas generally ranges from 0.35 to 0.40, and hence these two values were assigned for θ_S. Appropriate value for n in Simmons equation was selected by trial and error to obtain a convergent solution in CHEMFLO. Various values within the range 0.025 to 0.10 were specified as input until error-free convergence of the CHEMFLO simulation was obtained at a value of 0.071.

The boundary condition at the bottom of the unsaturated zone (at the water table) was always set as free drainage. At the top of the unsaturated zone (at the ground surface) two different boundary conditions were set, which were [1] a rainfall boundary condition and [2] a mixed-type boundary condition. When there was a rainfall event, the rainfall rate in cm/hr for the particular day was set as the boundary condition. On the remaining days, when there was no rainfall, a mixed-type boundary condition was set.

The mixed-type boundary condition is a combination of a negative flux and critical matric potential. The evaporation process can remove water from the soil only up to the critical matric potential (h_c), which can be related to the residual moisture content (θ_r) of the soil by

$$\theta(h) = \alpha\theta_s - \ln\left[(-h_c)^n\right] \qquad [5.5]$$

In this equation, $\theta(h)$ was replaced with θ_r to calculate the critical matric potential (h_c). The calculated values for 0.35 and 0.40 saturated moisture contents were -120 cm and -280 cm, respectively

Hydrologic input data for CHEMFLO included rainfall rate and evaporation rate. These data were collected for a 26-year period starting from 1975 to 2000. Daily rainfall amounts (inches) for the monitoring well sites were obtained from NCDC database. The rainfall data obtained from this database is a sum of rainfall inches as well as melted snow for a 24-hour period. Evaporation data were obtained from the TWDB evaporation database. These values are available as total lake evaporation amount (inches) for every month. Rainfall and evaporation data were made CHEMFLO-compatible by converting them into metric rainfall and evaporation rates (cm/hr). Rainfall rate was used as net input value on all rainfall days, neglecting any effects of evaporation. On all other days the evaporation rate was used as the net input value. Part of the input dataset for the year 1975, for the Martin County monitoring well site is shown as a sample in Table 5.4.

Table 5.4 CHEMFLO Input Dataset (Martin County site, 1975)

Date	Precipitation (in/d)	Precipitation (cm/hr)	Evaporation (in/d)	Evaporation (cm/hr)	Net (cm/hr)
1/1/1975	0.00	0.00	0.10	0.01	-0.01
1/2/1975	0.20	0.02	0.10	0.01	0.02
1/3/1975	0.00	0.00	0.10	0.01	-0.01
1/4/1975	0.00	0.00	0.10	0.01	-0.01
1/5/1975	0.00	0.00	0.10	0.01	-0.01
1/6/1975	0.00	0.00	0.10	0.01	-0.01
1/7/1975	0.00	0.00	0.10	0.01	-0.01
1/8/1975	0.00	0.00	0.10	0.01	-0.01
1/9/1975	0.00	0.00	0.10	0.01	-0.01
1/10/1975	0.00	0.00	0.10	0.01	-0.01
1/11/1975	0.00	0.00	0.10	0.01	-0.01
1/12/1975	0.08	0.01	0.10	0.01	0.01
1/13/1975	0.00	0.00	0.10	0.01	-0.01
1/14/1975	0.00	0.00	0.10	0.01	-0.01
1/15/1975	0.00	0.00	0.10	0.01	-0.01
--	--	--	--	--	--
--	--	--	--	--	--
--	--	--	--	--	--
12/24/1975	0.74	0.08	0.09	0.01	0.08
12/25/1975	0.00	0.00	0.09	0.01	-0.01
12/26/1975	0.00	0.00	0.09	0.01	-0.01
12/27/1975	0.00	0.00	0.09	0.01	-0.01
12/28/1975	0.00	0.00	0.09	0.01	-0.01
12/29/1975	0.00	0.00	0.09	0.01	-0.01
12/30/1975	0.00	0.00	0.09	0.01	-0.01
12/31/1975	0.00	0.00	0.09	0.01	-0.01

5.1.5 Model Results

Values for the output variables from the CHEMFLO simulations were obtained at the end of each year for selected mesh points. The first six years of the simulation were used to dampen any effects of the assumed initial matric potential and moisture distributions. The results for 1981 to 2000 were examined for moisture content distribution, cumulative flux at the soil surface and water table, and flux density, which served as an indication of velocity. Using the values for these parameters, further calculations were done to determine the time taken by water to reach the water table.

CHEMFLO outputs were obtained as tables and graphs. Graphs can be used to view the movement of water through the unsaturated zone. One such graph generated using the moisture content results for 1975 to 1979 at the Martin County site is shown below in Figure 5.1 as a sample of movement of water in unsaturated zone.

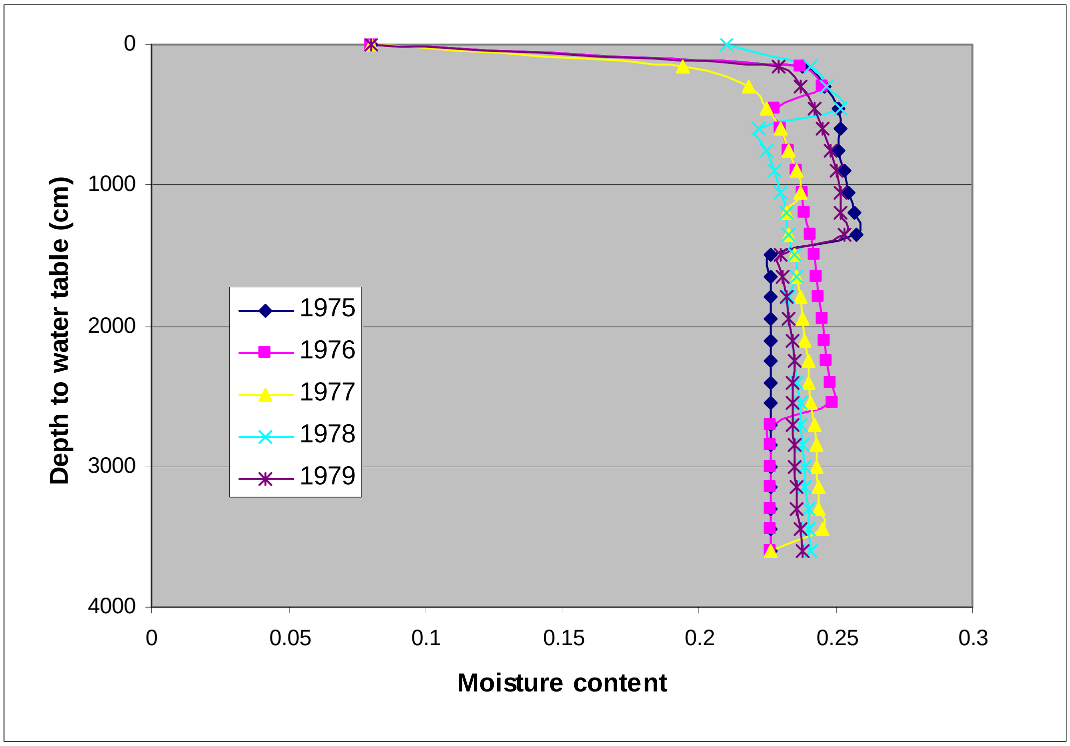

Figure 5.1 Moisture content with depth (1975-1979, Martin County, 0.40 porosity)

Typical travel time through the unsaturated zone was found from the results for flux density, F_d, and moisture content, θ. The velocity, v, at a point in the solution domain can be found by

$$v = \frac{F_d}{\theta} \quad [5.6]$$

Figure 5.2 shows the velocities for Martin County on five-year increments. The average travel time, T, through the unsaturated zone thickness, L, can be found using the mean velocity, v_{avg}, averaged across all points in the solution domain, by

$$T = \frac{L}{v_{avg}} \tag{5.7}$$

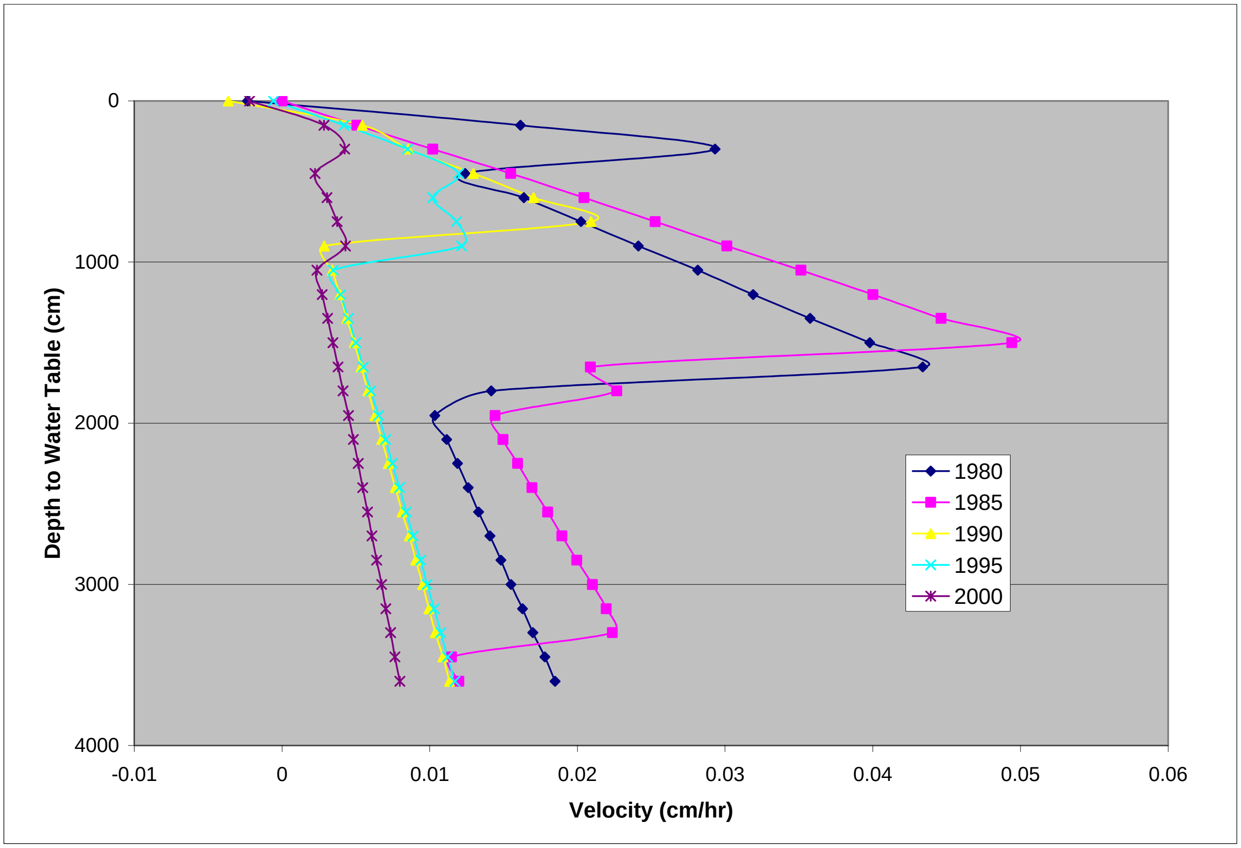

Figure 5.2 Velocity distributions in Martin County, porosity=0.35

Table 5.5 Velocity Calculation, 1980, Martin County, porosity = 0.35

Position (cm)	Flux Density (10^{-3} cm/hr)	Water Content (cm^3/cm^3)	Velocity (10^{-2} cm/hr)
0.00	-0.19	0.08	-0.23
150.80	3.05	0.19	1.61
299.00	5.75	0.20	2.93
449.80	2.31	0.19	1.24
600.60	3.10	0.19	1.64
748.80	3.89	0.19	2.02
899.60	4.68	0.19	2.41
1050.40	5.52	0.20	2.81
1201.20	6.32	0.20	3.19
1349.40	7.12	0.20	3.58
1500.20	7.96	0.20	3.98
1651.00	8.76	0.20	4.34
1799.20	2.62	0.19	1.42
1952.60	1.90	0.18	1.03
2100.80	2.05	0.18	1.11
2249.00	2.20	0.19	1.19
2399.80	2.34	0.19	1.26
2550.60	2.49	0.19	1.33
2698.80	2.63	0.19	1.41
2849.60	2.79	0.19	1.48
3000.40	2.93	0.19	1.55
3151.20	3.08	0.19	1.63
3299.40	3.23	0.19	1.70
3450.20	3.38	0.19	1.78
3601.00	3.53	0.19	1.85
	Average Velocity		1.93

A sample calculation for determining the average velocity of groundwater in the unsaturated zone of Martin County monitoring well site using selected point values at the end of 1980 is given in Table 5.5. The average velocity was calculated at the end of 1980, 1985, 1990, 1995, and 2000, and these five values were then averaged to get a representative travel time for each site. Porosities of 0.35 and 0.40 were considered. Table 5.6 shows the results of the calculations.

Table 5.6 Travel Times

County	Water Table Depth (m)	Porosity	Average Velocity (10^{-2} cm/hr)	Average Travel Time (yr)
Bailey	18.3	0.35	1.49	14
		0.40	0.95	22
Gaines	9.0	0.35	1.36	8
		0.40	0.97	11
Martin	36.0	0.35	1.21	34
		0.40	0.67	62

The results of the CHEMFLO simulation indicate that the estimated travel times through the unsaturated zones in Bailey, Gaines, and Martin counties were on the order of 20, 10, and 30 to 60 years, respectively. These travel times were based on the conservative selection of sand to represent the unsaturated soil matrix, and on climatic conditions approximated by nearby measurements. CHEMFLO only allows a single soil type in each simulation, so sand was selected as a worst case for fastest infiltration. Inclusion of finer grained soil types would certainly increase the travel times, but that effort would require more complex modeling that was beyond the scope of the current project.

5.2 Saturated Zone Transport

Diffusion, advection, and hydrodynamic dispersion are the major mechanisms responsible for the movement of any non-reactive solute in groundwater. Molecular diffusion is caused by concentration gradients within the saturated porous medium. Advection is defined as the transport of a dissolved solute in groundwater by the bulk movement of the groundwater at its average linear velocity. Hydrodynamic dispersion of the solute in groundwater is caused by the combination of molecular diffusion and mechanical dispersion due to mixing caused by the tortuous flow paths within the porous medium. In this project, two different scenarios were considered at each site to represent transport of perchlorate as a conservative solute in the saturated zone. In the first scenario, diffusion was assumed to be the only cause of perchlorate movement in groundwater. In the second scenario, advection and hydrodynamic dispersion both influenced perchlorate migration in groundwater. Both scenarios allowed estimation of the movement of perchlorate across the vertical dimension of the local aquifer system. That movement could be downward from the water table due to a perchlorate source above the water table, or upward from a perchlorate source in more saline groundwater beneath the aquifer of interest.

5.2.1 Diffusion Only

Diffusion of perchlorate in groundwater by diffusion is dependent on its molecular diffusion coefficient, D*, in water and the tortuosity, □, of the porous medium. The effective molecular diffusion coefficient, D, is given by

$$D = \tau D^{*} \qquad [5.8]$$

The one-dimensional diffusion equation is

$$\frac{C(x,t)}{C_o} = erfc\left(\frac{z}{2\sqrt{Dt}}\right) \qquad [5.9]$$

where C_0 = continuous source concentration (ppb), C(z,t) = concentration at time t at a distance x from the source (ppb), z = saturated thickness (m), D = effective molecular diffusion coefficient (m^2/d), and t = time (d). The value of D is 1.55 x 10^{-4} m^2/day (Lide, 2001), while τ ranges from 0.01 to 0.5 (Freeze and Cherry, 1979). Both the extreme values were used in the calculations.

Equations 5.8 and 5.9 were applied to each screened interval at the three well cluster sites. The value of x was taken as the distance from the water table to the bottom of the screened interval. Table 5.7 shows the result of these calculations for t = 60, 100, 1000, and 10000 yr.

The calculated C/C_o values indicate the ratio between the concentration at the bottom of the screened interval at that time and the source concentration. It can be seen that for the low D values, diffusion is not able to transport solute from the source more that a few meters, even over 10000 yr. For the high D values, it takes 1000 to 10000 yr for significant diffusion from the source. These findings imply that one-dimensional diffusion from a recent, manmade source could not cause the observed vertical distribution of perchlorate concentrations observed at the monitoring sites.

Table 5.7 Results of Diffusion Only Analysis for t = 60 to 10000 yr

County	Well	ClO_4^- (ppb)	z (m)	C/C_o (60) Low D	C/C_o (60) High D	C/C_o (100) Low D	C/C_o (100) High D	C/C_o (1000) Low D	C/C_o (1000) High D	C/C_o (10000) Low D	C/C_o (10000) High D
Bailey	Shallow	1.1	7.9	0.000	0.000	0.000	0.001	0.000	0.292	0.018	0.739
	Deep	nd	36.0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.130
Gaines	Shallow	179.0	4.6	0.000	0.013	0.000	0.055	0.000	0.543	0.174	0.848
	Intermediate	111.0	27.4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.249
	Deep	97.9	57.3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.016
Martin	Shallow	27.2	1.8	0.000	0.321	0.000	0.442	0.085	0.808	0.587	0.939
	Intermediate	15.7	10.4	0.000	0.000	0.000	0.000	0.000	0.168	0.002	0.663
	Deep	17.9	14.0	0.000	0.000	0.000	0.000	0.000	0.062	0.000	0.555

5.2.2 Advection and Dispersion

Advection and dispersion from a two-dimensional source was simulated with a solution provided by Domenico and Robbins (1985). This solution considers a planar source in the y,z-plane orthogonal to the uniform regional flow field in the x-direction, as shown in Figure 5.3. This approach allowed estimation of dispersion effects across the saturated thickness as well as along the flow path. The analytical solution is given by

$$\frac{C(x,y,z,t)}{C_o}=\frac{1}{8}erfc\left[\frac{(x-vt)}{2(\alpha_x vt)^{1/2}}\right]\left\{erf\left[\frac{(y+Y/2)}{2(\alpha_y x)^{1/2}}\right]-erf\left[\frac{(y-Y/2)}{2(\alpha_y x)^{1/2}}\right]\right\}$$
$$\left\{erf\left[\frac{(z+Z/2)}{2(\alpha_z x)^{1/2}}\right]-erf\left[\frac{(z-Z/2)}{2(\alpha_z x)^{1/2})}\right]\right\} \qquad [5.10]$$

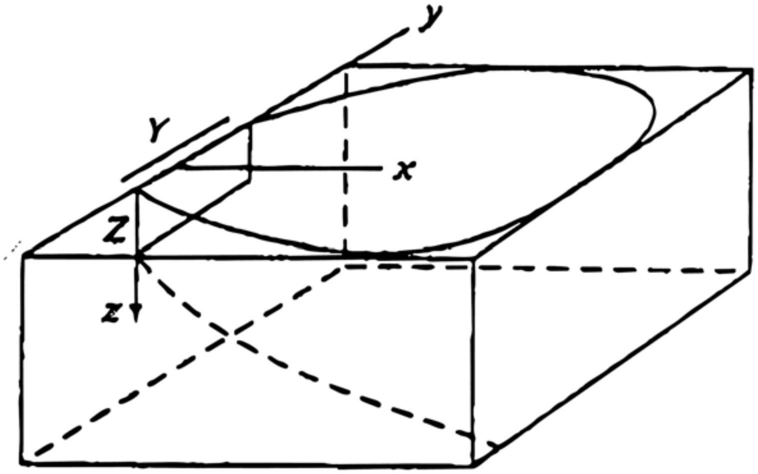

Figure 5.3 Planar source geometry for Domenico and Robbins (1985) solution

where v = uniform regional flow velocity, x, y, and z are measured from the top center of the planar source, Y = horizontal dimension of the source orthogonal to the flow direction, Z = vertical dimension of the source orthogonal to the flow direction, α_x, α_y, and α_z = dispersivities in the component directions, and other variables are as previously defined. The longitudinal dispersivity is given by

$$\alpha_x = 0.83(\log x)^{2.414} \qquad [5.11]$$

The transverse dispersivities were estimated to be one-tenth of the longitudinal value, as

$$\alpha_y = \alpha_z = 0.1\alpha_x \qquad [5.12]$$

The average velocity was estimated using Darcy's Law as

$$v=\frac{K}{\theta_s}\frac{dh}{dl} \qquad [5.13]$$

where K = aquifer hydraulic conductivity, and dh/dl = regional head gradient. With typical values of K, θ_S, and dh/dl at 7.1 m/d, 0.35, and 0.0052, respectively (Stovall et al., 2001), the average velocity was 0.11 m/d. The Y and Z dimensions of the planar source were set at 500 m and 1 m, respectively, so that the source would be at the water table and that tracking the vertical mixing from the x-axis downward would not be affected by the Y dimension edge effects.

The calculations were carried out for the various z values within the saturated thicknesses at the three sites, using only the upper saturated zone at Bailey County MNWR site (8 m), and the complete saturated zones at the Gaines (57 m) and Martin County (18 m) sites. Down-gradient distances of 10, 50, 100, 200, 300, 400, and 500 m were used with time values of 10, 20, 30, 40, 50, 60, and 100 yr. The total distance of 500 m was selected to represent a significant travel distance, as the cultivated cropland in the three counties is not uniformly distributed. The results were plotted as graphs of relative concentration C/C_o versus x. The calculated values of C/C_o stabilized for times of 20 years or more, as ample time had elapsed for the water from the source to completely traverse the 500-m longitudinal distance. Figures 5.4, 5.5, and 5.6 show the stabilized C/C_o plots for the Bailey, Gaines, and Martin sites, respectively. For all three sites, the relative concentration values trend down to less than two percent of the source concentration within 200 m of the source. Mixing across the saturated thickness is relatively complete in the 8-m Bailey site after 200 m, while at the 18-m thick Martin saturated thickness the mixing is almost complete at 500 m down-gradient from the source. The much thicker saturated zone at the Gaines County site shows mixing is much

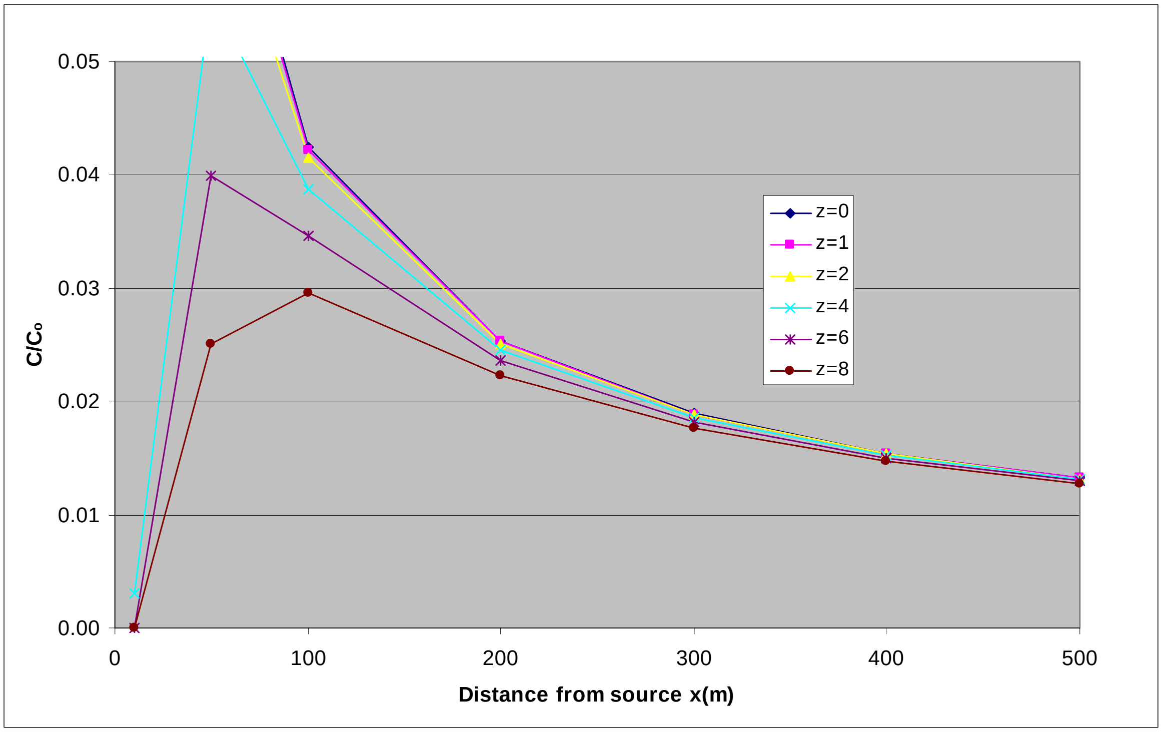

Figure 5.4 Bailey County Advection Dispersion Results

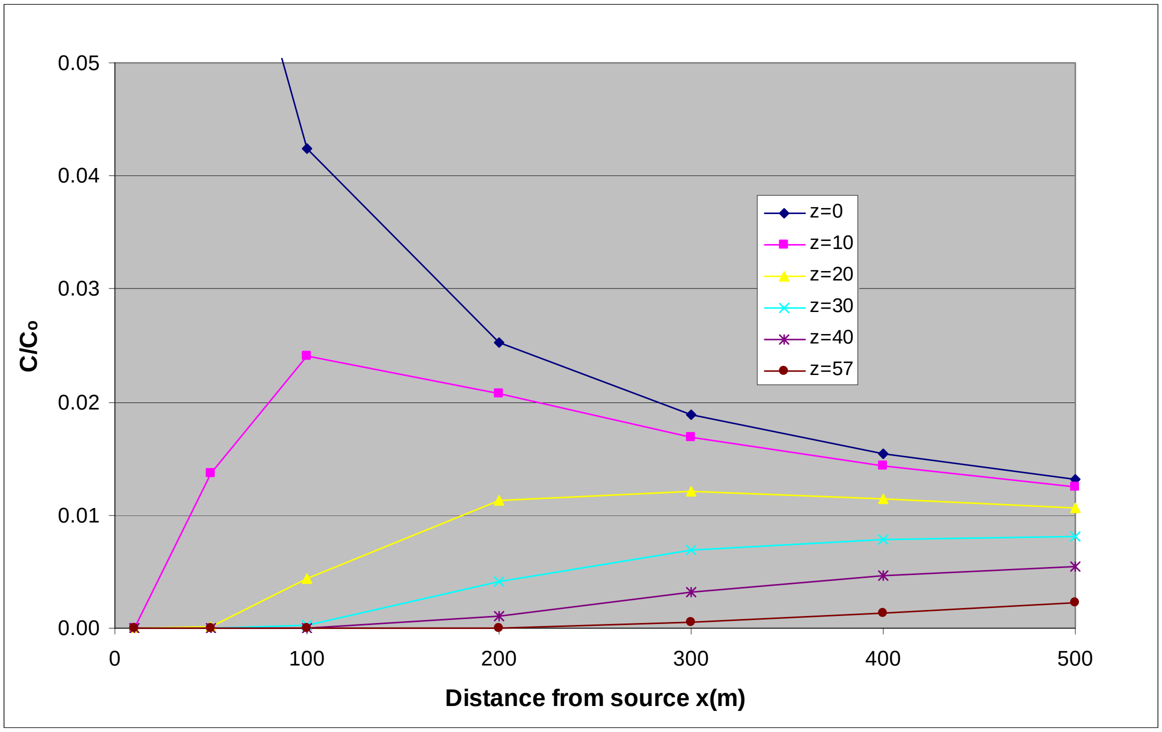

Figure 5.5 Gaines County Advection Dispersion Results

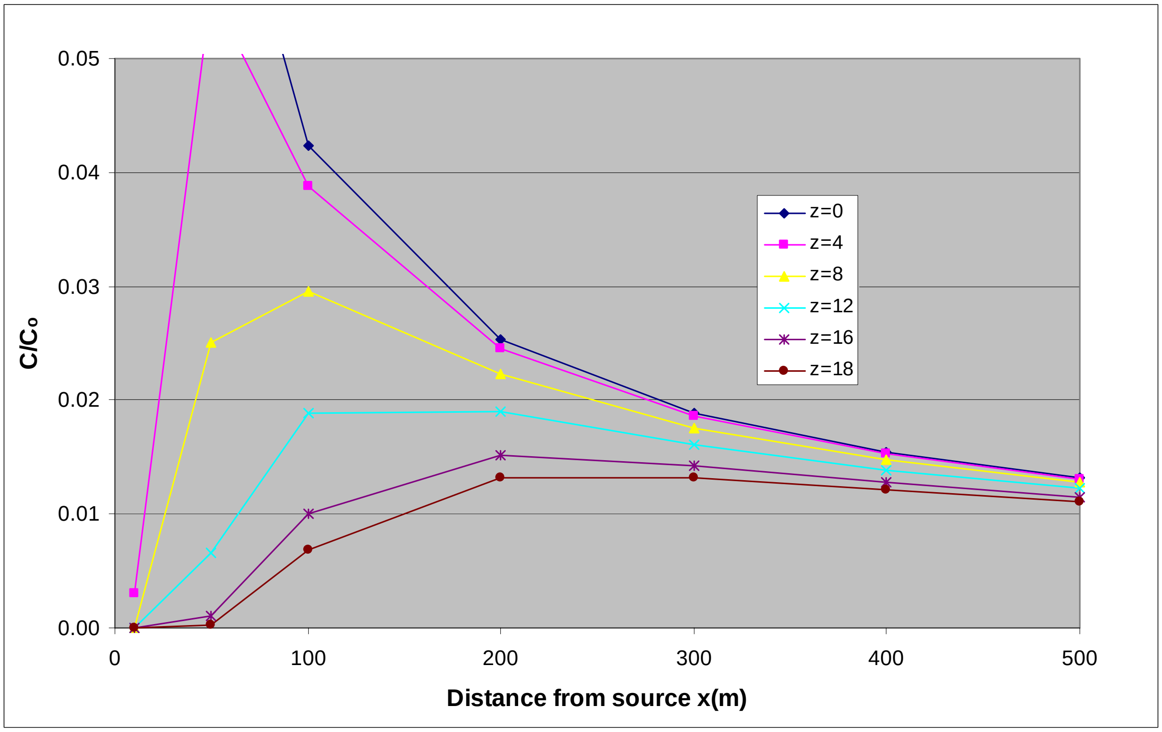

Figure 5.6 Martin County Advection Dispersion Results

less complete at 500 m from the source, with the relative concentration at z = 0 m approximately 6 times that at z = 57 m.

The contribution of the advection-dispersion analysis is to provide a general feel for mixing within the saturated zone based on typical regional aquifer conditions. In all three cases, the source concentration would have to be 50 to 100 times the observed concentration if the monitoring wells were at least 200 m from a planar source at the water table. The required continuous single source concentrations would be on the order of 100 ppb, 10000 ppb, and 2000 ppb for the Bailey, Gaines, and Martin sites, respectively. If such single sources existed, they could be associated with cropland that might have been fertilized with perchlorate- containing fertilizer, and the perchlorate could have been transported through the unsaturated zone by irrigation return flow or infiltrating precipitation. As the Domenico and Robbins (1985) solution is for a linear partial differential equation, it would be possible to superimpose multiple sources and accumulate their impacts at any downstream location. Although such conditions can be postulated, they cannot account for the presence of perchlorate in other parts of the Southern High Plains where such activities have not taken place.

5.3 Summary of Transport Modeling Results

The primary purpose of these tasks was to estimate flow and transport within the unsaturated zone that could affect perchlorate migration. The CHEMFLO application demonstrated that the times of travel through the unsaturated zones at the three drilling sites are on the order of 10 to 60 yr, which implies that human activities during the last 60 yr could have reached the water table if perchlorate was being applied at the surface within fertilizer. The diffusion only analysis demonstrated that molecular diffusion by itself would not be sufficient to move perchlorate from the water table downward across the entire saturated thickness in less than 10000 yr. The advection-dispersion analysis shows that typical values of saturated thickness, regional flow velocity, and dispersivities could allow for transport of perchlorate across the saturated thickness in a decade or two, but the concentration would fall off drastically within a short distance from the source. In sum, these results imply that human perchlorate applications at the surface could not account for the widespread concentration distributions observed in this field study. It is recognized that all the calculations were limited by the assumed values of many of the parameters. However, the assumed parameters were selected to represent conservative or "worst-case" situations.

CHAPTER 6

EVALUATION OF POTENTIAL PERCHLORATE SOURCES IN THE STUDY AREA

There are numerous possible sources/causes for the perchlorate present in much of the High Plains Aquifer System in the fifty four-county study area. In order to determine the actual source/cause, a number of tasks were performed including: [1] a comprehensive literature review, [2] correlation of ionic data (presence of various cations and/or anions) with presence or absence of perchlorate, [3] construction of appropriate cross-sections to relate perchlorate concentrations with specific geologic/hydrologic formations or conditions, [4] correlation of perchlorate occurrence to specific land uses, and [5] investigation of potential natural occurrence of perchlorate in the study region. This chapter provides a general discussion of possible sources based on existing scientific literature, application of that information to the currently available data from the target area, and a summary of the conclusions and recommendations that can be made at the present time.

6.1 Possible Sources

There are many possible sources that could be responsible for the perchlorate present in the affected groundwater. These possibilities can be separated into five main categories, including [1] industrial wastes, [2] military activities, [3] agricultural activities, [4] indirect formation, and [5] natural occurrence or deposition. Background literature and available data are discussed for each hypothetical source.

6.1.1 Industrial Wastes

Numerous industries are known to historically or currently use, produce, or process perchlorate salts and perchloric acid. By far the most common use of perchlorate is as a solid oxidant in items such as rockets, matches, fireworks, energetics, and flares. It is also found as a waste product in industries processing mined nitrate, one example of which is the Apache Powder Site (Arizona). Industries involved in the manufacture or packaging of such products are responsible for some very large-scale releases that led to contamination of significant groundwater resources in California, Nevada, and Arizona, as well as surface water resources, most notably Lake Mead and the Colorado River. In most of these cases, groundwater contamination by these activities is expressed as traditional finite plumes that begin at the perchlorate source and migrate down-gradient with groundwater flow. Perchlorate can also be used as a gas drying agent or a chemical reagent as a perchlorate salt or as perchloric acid. No widespread industrial production or packaging facilities other than the Pantex nuclear weapons assembly and disassembly plant, which has not been identified as a significant point of release for perchlorate, are known to be located in the fifty-four county region. It is possible that some other small manufacturing or processing facilities may have been located in the region, but it is also highly unlikely that they could be responsible for the presence of perchlorate in groundwater over such a large unindustrialized area.

Highway safety flares are known to contain significant amounts of perchlorate (Silva, 2003). A single standard 20-minute unburned flare could leach up to 3.5 grams of perchlorate ion within 4 hours of contact with water and a fully burned flare could leach up to 1.95 mg of perchlorate ion. Large amounts of these flares are used regularly by the Department of Transportation, and these flares could be a potential source of perchlorate in the groundwater. Assuming that these flares are solely responsible for perchlorate contamination found in the high plains, the number of burned and unburned flares required to cause this contamination in each of the fifty-four counties was estimated. Table 6.1 shows the number of burned and unburned flares required to account for the perchlorate mass found in the high plains and clearly indicates the unlikely possibility of flares as the source of perchlorate.

Table 6.1 Highway Safety Flares : Perchlorate Contamination

Perchlorate Mass Range	Avg Perchlorate	Burned flares	unburned flares	# of Counties
Kg	Mass (Kg)	X 10^6	X 10^6	
>100,000	150000	77,000	43	4
10,000 - 100,000	50000	26,000	14	33
1,000 - 10,000	5000	2,600	1.4	7
0-1,000	150	77	0.043	10

One widespread industry in the area that is generally known to use some perchlorate- containing products is the petroleum industry. Perchlorate is known to be an ingredient in a few of the many types of explosives (e.g. Magnagel) used in seismic surveys. To date, we have been unsuccessful in our attempts to gather specific information of the brands of explosives or the timing of their applications in seismic exploration on the Southern High Plains and Permian Basin. Other reported but unsubstantiated uses of perchlorate in the oil industry include use of perchloric acid down-hole and as an explosive to increase permeability in the oil-producing zone. To date, we have collected information on the distribution of historical/current petroleum related activities from the Railroad Commission (RRC). A set of geographic information system (GIS) coverages that included all boreholes/wells in the study area was obtained from the RRC (RRC, 2003). Locations in this database are defined as any drilling activity, whether test hole or well (abandoned or active for production, injection, or other purposes). These data were spatially referenced and overlaid on the study region with the associated distribution of perchlorate (Figure 6 .1.1). As can easily be seen, there has been a large amount of petroleum-related drilling activity in the area, with most of the counties showing significant locations. No obvious relation was observed between well location and perchlorate detection and it appears highly unlikely that this activity would be responsible, given the general lack of oil field activity in counties (e.g. Bailey) which have a significant presence of perchlorate or perhaps more importantly the general lack of perchlorate in counties with significant oil field activity (e.g. Reagan, Upton, Scurry). However, this distribution represents all known wells and test holes. It is possible that a hypothetical link between specific well activities and perchlorate in groundwater may be discernable. Specific characteristics might include age of the activity, active/inactive condition, casing type, production or injection, perforation procedure, or others. However, it is unlikely that oil field activity is responsible for the widespread distribution of perchlorate in the region, though it might be responsible for specific localized instances not identified here.

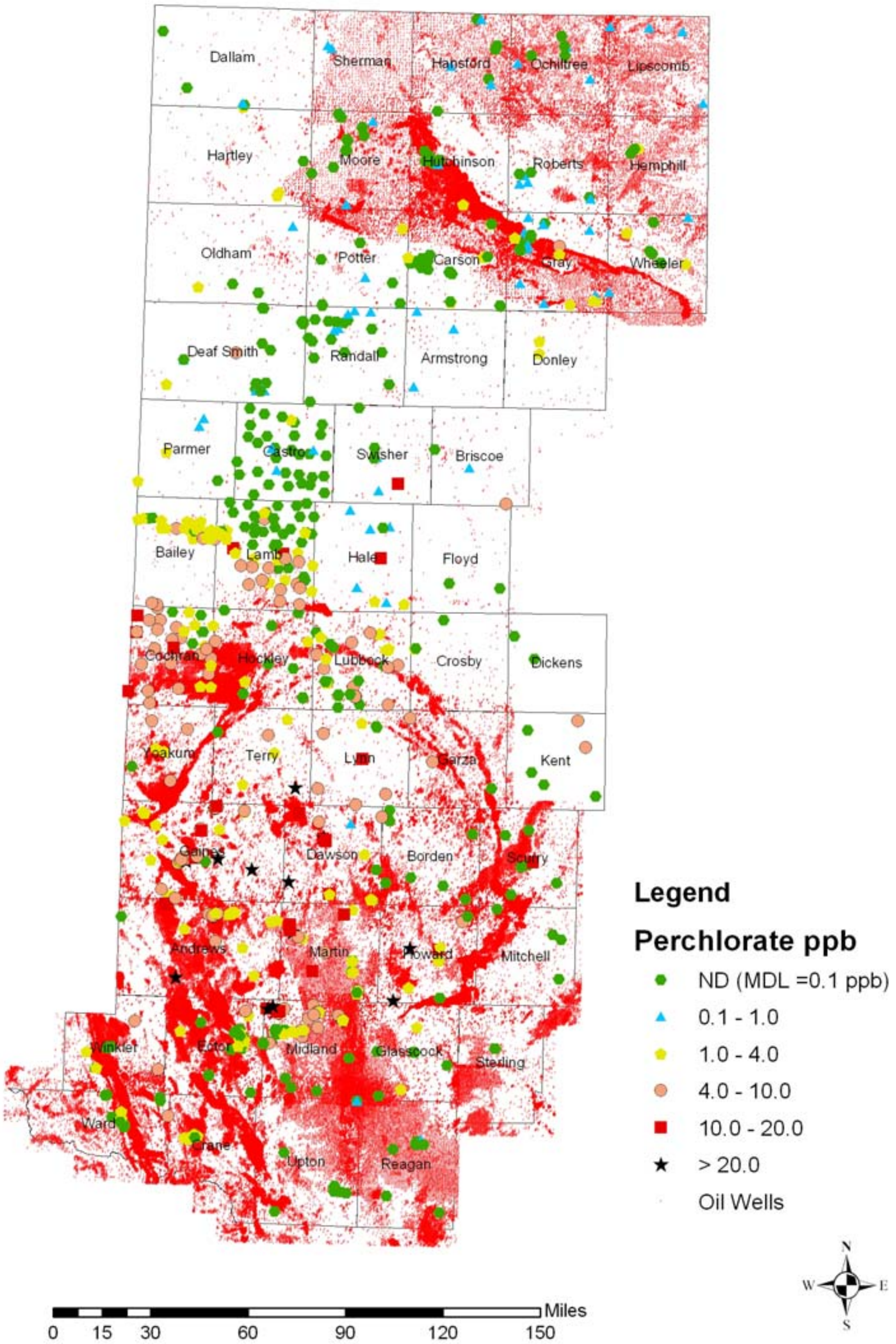

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Figure 6.1.1 Distribution of Oil and Gas Well Locations Overlaid on the Distribution of Perchlorate.

6.1.2 Agricultural Activities

Agriculture is another important industry in the study area. Perchlorate salts are not used as primary chemicals for any agricultural purpose. However, perchlorate can exist as an impurity or byproduct in two common agricultural products, mined nitrate fertilizers primarily from Chile and chlorate defoliants. For many years perchlorate was thought to only occur in Chilean nitrate deposits in the Atacama Desert, the most documented occurrence of natural perchlorate (e.g. Ericksen, 1983). Other known and suspected sources of perchlorate are discussed in the *Natural Sources* subsection of this chapter. While there is some controversy over the current concentration of perchlorate in Chilean fertilizers, certainly it can be said that these fertilizers historically contained perchlorate at varying concentrations. A study by Urbansky et al. (2001) found certain lots of $NaNO_3$ fertilizer to contain over 0.1% of ClO_4^-. Further, an earlier study (Tollenaar and Martin, 1972) reported 0.12-0.26% perchlorate in Chilean nitrate deposits. A more recent study, however, showed that changes made by the fertilizer industry have significantly reduced the concentration of perchlorate in commercial Chilean nitrate fertilizer. However, widespread perchlorate in groundwater in this study area would more likely represent historical releases and not more recent events.

Irrigated acreage for the study area for over a period of 42 years was available from a Texas Water Development Board (TWDB) report (TWDB, 2001). The earliest available data, for the year of 1958, was used to estimate if fertilizer use could be the reason for the widespread presence of perchlorate in the study area. This year was chosen based on the results of modeling (Chapter 5) which showed significant travel times for perchlorate infiltration from the surface to groundwater. In addition, through oral communication with local crop scientist and extension officials, it was concluded that no widespread use of nitrate fertilizers has been practiced for the last 30 years. Total mass of perchlorate in the saturated zone for each county was used to estimate a loading rate of fertilizers required to cause the entire perchlorate occurrence in the study area. A perchlorate concentration of 0.1% in the fertilizer was assumed. This loading rate was compared to the actual loading rate assumed (280 kg/acre/yr) for this objective. Results indicate that for many counties the application of fertilizer for 1 year could account for the estimated mass of perchlorate. However for 16 counties, it would require 10 years of Chilean nitrate application, and for 5 counties it would require 100 years or greater of Chilean nitrate application to account for the mass of perchlorate found (Figure 6.1.2). It should be noted that if the mass of perchlorate estimated in the unsaturated zone is included these numbers would double as estimates for the unsaturated zone are similar to saturated zone estimate (Figure 3.3.1).

Land use and land cover data for the irrigated acreage in the study area in 1980 was provided by the USGS (USGS, 1990) and overlaid on the study area with perchlorate results (Figure 6.1.3). Some counties with high irrigated acreage (e.g. Gaines, Floyd, and Lamb) have high perchlorate mass in the saturated zone, while others (e.g. Randall and Castro) have very low occurrence. More interestingly, counties with significant perchlorate occurrence have little if any irrigated acreage (e.g. Ward, Crane, and Winkler).

Chlorates are commonly used as defoliants and other limited applications. Chlorates are produced by electrolytic processes, and this process is theorized to also produce perchlorate in smaller amounts. No data are available on the concentration of perchlorate in chlorates, however information obtained from the Texas A&M Agricultural Experiment Station (Lubbock) indicated that chlorate was used on less than 5% of the total acreage of the High Plains. Combining this information with the low aerial application rates makes it highly unlikely that chlorates are the source of perchlorate in the Southern High Plains.

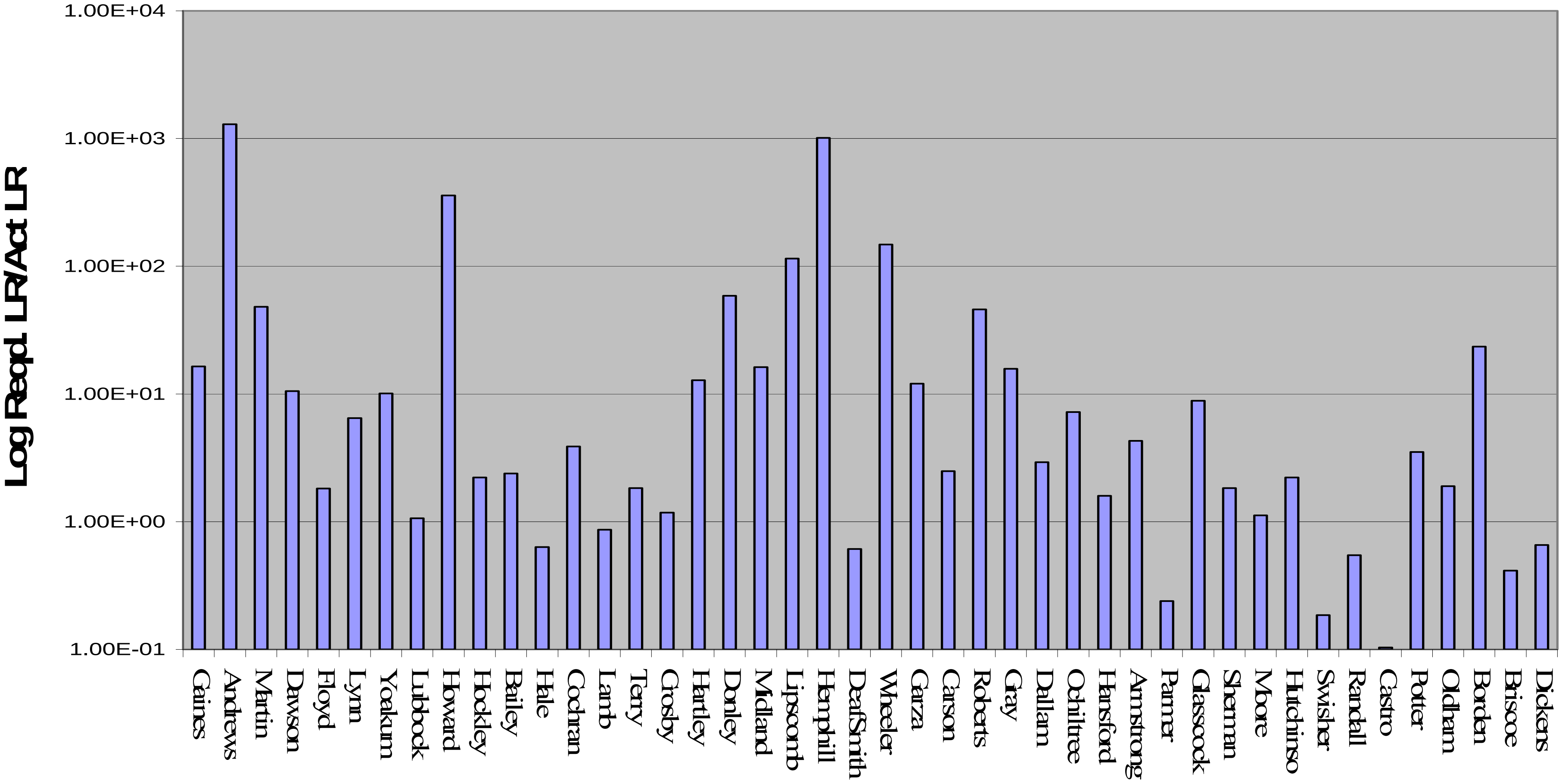

Figure 6.1.2 Potential Perchlorate Contribution by Fertilizers

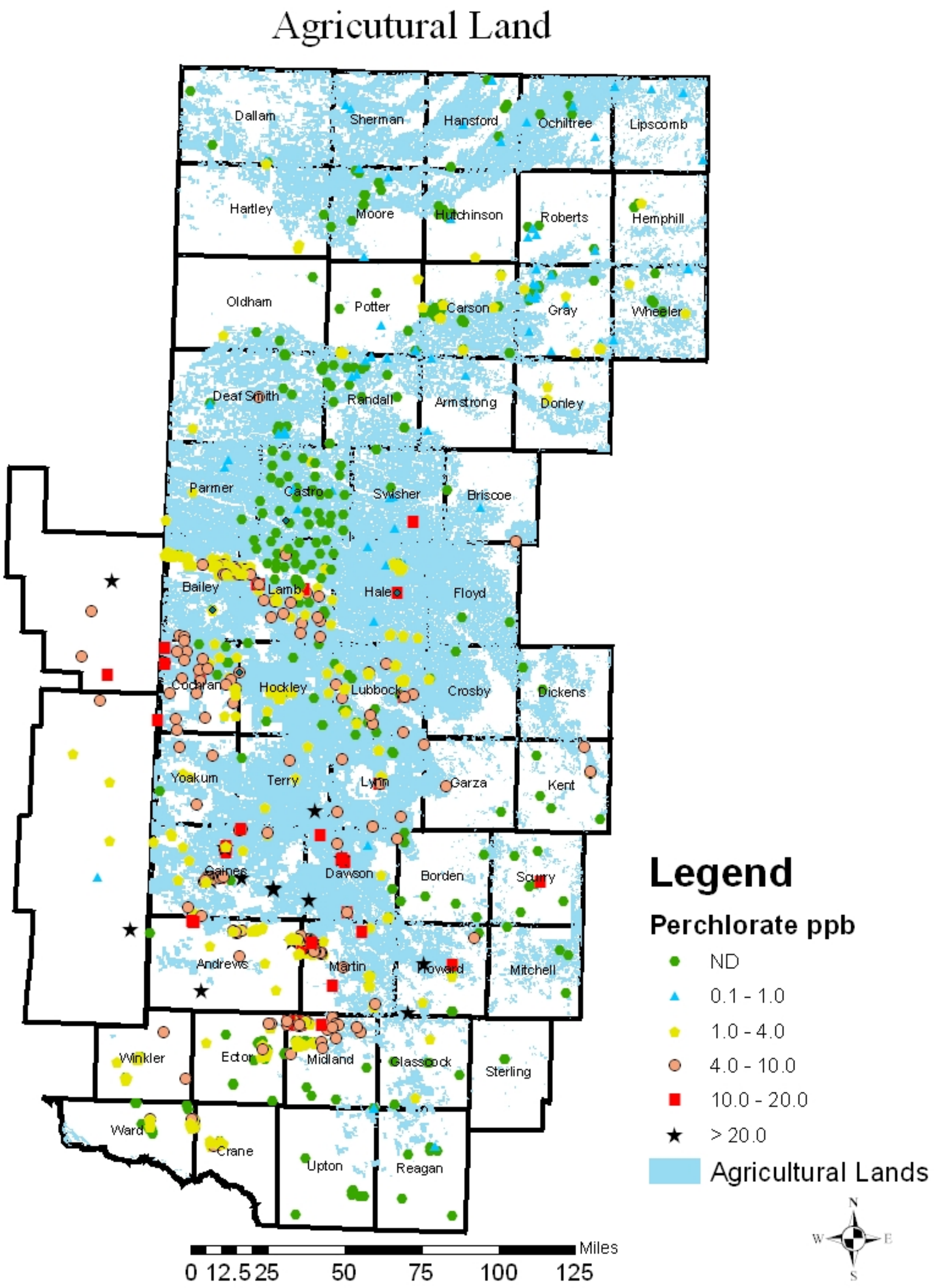

Figure 6.1.3 Distribution of Irrigated Farmland Overlaid on the Distribution of Perchlorate.

6.1.3 Indirect Production

One possible previously unreported source is the production of perchlorate within saturated and unsaturated sediments due to electrochemical reactions. This electrochemical reaction would be due to applied current. One current source could be lightning strikes on buried metallic objects such as wells, pipelines, or tanks. A second current source could be cathodic protection systems for oil wells, water wells, pipelines, and underground storage tanks. It is also well known that galvanic cells can exist in water supply wells that include steel well screen, steel well casing, steel discharge pipes, and electrical submerged well pumps. Certainly, given the number of buried metallic structures, there is an abundance of candidates that may have cathodic protection and thus could participate in the production reaction. Production rates (Jackson et al., 2004) indicate that this is highly unlikely to be the source of perchlorate given the high volume production of water and thus short retention time of most of the PWS wells.

6.1.4 Military Sites

Military sites are commonly found to be contaminated by a variety of chemicals, occasionally including perchlorate. The study area in question does contain a number of Formerly Used Defense Sites (FUDS). These sites were used as bombing practice ranges, and were reported to be all closed by the end of WWII (Corps of Engineers Documentation). In most cases only practice bombs were dropped, some of which may have had a spotting charge. In fewer instances, explosives were used due to the presence of impact craters. One practice bomb known to be used was the M38A2 which contained approximately 3 lbs of black powder (74% KNO_3, 11% sulfur, 15% charcoal). It is certainly possible that the nitrate used to make the black powder could have come from

Chilean deposits and thus contained a small percentage of perchlorate.

The distribution of these sites is indicated in Figure 6.1.4, which combines the fifty-four county region, FUDS location and size, and the perchlorate observations. It should be noted that actual shapes and orientations of the practice ranges were not provided by the cited reference. Seven of the nine counties contain FUDS, and the FUDS data for the forty-five counties of Phase II were not available. No FUDS were found to exist in either Gaines or Dawson counties, and only one very small site (0.32 acres) was located in Howard County. The known distribution of these sites and the apparent absence of these sites up-gradient in two of the most affected counties make it unlikely that these FUDS are responsible for the widespread perchlorate distribution. It is still possible that multiple sources are responsible for the distribution of perchlorate and if so, FUDS may be responsible for some of the detections.

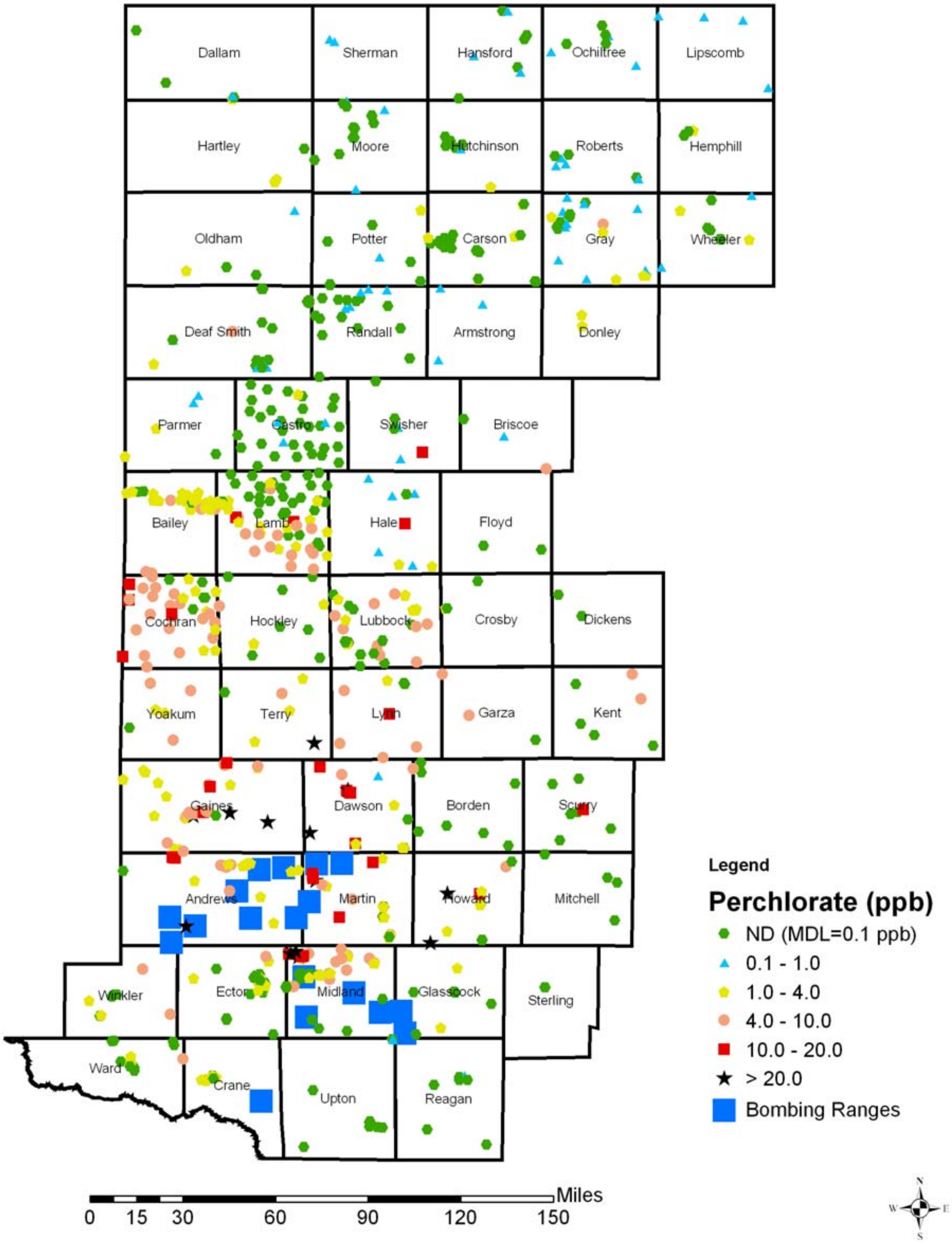

Figure 6.1.4 Distribution of FUDS and Wells Tested for Perchlorate.

6.1.5 Natural Sources of Perchlorate

Until recently, the prevailing opinion was that perchlorate was only found naturally in the Atacama Dessert. However, numerous unpublished (as of this date) but credible communications have found that perchlorate is commonly found in evaporite minerals throughout the Western hemisphere. Greta Orris of the USGS, has tested numerous potashes, evaporites, and other minerals and found many to contain perchlorate in small amounts (Orris et al, 2003). This work substantiates older studies in which other natural sources of perchlorate were reported (e.g. Becking et al., 1958). Minerals of prime interest include sylvinite, sylvite, and langbeinite. However, much more work is needed to assess the overall abundance and frequency of perchlorate in these minerals as well as other perchlorate-bearing minerals. In addition, a better understanding of the formation of perchlorate in natural conditions would also aid in determination of the likelihood of perchlorate being present in geologic formations. Preliminary experiments have shown that perchlorate is present in rainwater for a high percentage of events and that the presence of ozone, UV, or electrical discharge can produce perchlorate (data not shown). If the source is natural there are 3 mechanisms to affect groundwater including: 1) atmospheric generation followed by deposition and infiltration (surface source), 2) historical presence as a mineral in the subsurface, and 3) upwelling of brines.

6.1.5.1 Brine Water Infiltration

Brine water, formation water, or produced water is the waste component of oil production and refinement. Brine water is produced along with oil and natural gas pumped from oil wells. Due to geological formation of oil wells, the water and oil are saline. The brine water may naturally upwell and contaminate the aquifer. Moreover, a part of the brine water produced is pumped back into the ground so that it maintains the underground pressure and brings oil and gas to the surface (Mills, 2001).

Following the work of Wood and Jones (1990), solute ratios were calculated for Cl^-/Br^-, Na^+/K^+, and Cl^-/SO_4^{2-}. These ratios were used by Wood and Jones (1990) to identify possible sources of the solutes present in the saline lakes of the Southern High Plains of Texas. The average Cl^-/Br^-, Na^+/K^+, and Cl^-/SO_4^{2-} ratios of the High Plains Aquifer have been reported as 140, 7, and 1, respectively. Comparably, the Deep-Basin Brine aquifer (Paleozoic in age) has ratios of 290 (Cl^-/Br^-), 170 (Na^+/K^+), and 190 (Cl^-/SO_4^{2-}). In the present study these ratios (for all the wells sampled) closely match the previously reported High Plains Aquifer values, at 179 (Cl^-/Br^-), 14 (Na^+/K^+), and <1 (Cl^-/SO_4^{2-}).

The average aquifer ratios (Na^+/K^+ and Cl^-/SO_4^{2-}) were calculated for each county in the study area from the water quality data of individual wells sampled in the Ogallala aquifer. The same ratios were calculated for brine water in counties where brine data were available. The brine water quality data were obtained from USGS provisional database on produced water quality entitled Produced Water Compositional Database (USGS, 2002). The Cl^-/Br^- ratio was not used in the study as no bromide value was available in the brine water database. The volume of brine water required to cause the increase in the aquifer ratios was estimated by assuming the aquifer water should have ratios as stated by Wood and Jones (1990) and any increase in the ratios was caused by brine water infiltration. Total volume of water in the aquifer was calculated from the saturated thickness, porosity, and area of the counties. The perchlorate concentration in brine water required to cause the present amount of perchlorate contamination in each county was estimated from perchlorate masses calculated from Section 2.2.5 and volume of brine water (Tables 6.1.2 and 6.1.3).

Table 6.1.2 Estimation of Brine Infiltration required Using (Na^+/K^+) ratio

County	**(Na^+/K^+)w**	**(Na^+/K^+) b**	**Vt**	**Vb**	**PC mass**	**PC-brine**
	ppm/ppm	**Ppm/ppm**	**x10^9 L**	**x10^9 L**	**Kg**	**ppb**
Andrews	16.44	86.75	54885	6497	217192	33
Cochran	8.66	37.87	26237	1410	35627	25
Dawson	17.27	95.64	40025	4635	103211	22
Ector	14.41	70.81	15315	1779	24648	14
Gaines	12.84	91.21	71982	4988	247633	50
Garza	11.60	108.82	33710	1525	23625	15
Glasscock	14.72	330.14	5526	132	13378	101
Gray	9.71	69.76	123696	5340	19555	4
Hemphill	13.19	174.91	155252	5724	25555	4
Howard	31.21	166.77	14431	2187	50247	23
Lipscomb	10.26	120.67	164287	4714	27127	6
Lubbock	7.40	109.61	52451	206	52053	253
Midland	31.24	100.54	43118	11174	27601	2
Swisher	25.65	665.54	27918	791	8302	10
Terry	15.73	75.81	31681	4017	34856	9
Wheeler	10.29	82.35	108799	4753	23834	5
Yoakum	14.90	76.55	26038	2957	54151	18
Armstrong	3.50	-	76890	-	14947	-
Bailey	10.54	-	59951	-	49167	-
Borden	22.73	-	9505	-	4598	-
Briscoe	28.99	-	8462	-	3191	-
Carson	3.57	29.63	107634	0	22761	-
Castro	5.91	-	54775	-	5818	-
Crane	13.31	67.37	-	-	-	-
Crosby	4.68	156.92	80347	0	33016	-
Dallam	3.21	-	138375	-	17272	-
Deaf Smith	17.52	-	65736	-	24153	-
Dickens	13.87	-	3726	-	965	-
Donley	8.10	-	99434	-	28480	-
Floyd	5.82	-	31364	-	76549	-
Hale	4.85	174.49	54081	0	47156	-
Hansford	6.49	324.80	153710	0	15397	-
Hartley	2.27	337.71	198546	0	32897	-
Hockley	6.93	58.49	42548	0	49647	-
Hutchinson	4.28	172.18	104967	0	10867	-
Kent	18.58	-	2084	-	-	-

County	(Na^+/K^+)w	(Na^+/K^+) b	Vt	Vb	PC mass	PC-brine
	ppm/ppm	Ppm/ppm	$x10^9$ L	$x10^9$ L	Kg	ppb
Lynn	13.27	-	56380	-	58818	-
Martin	141.53	60.98	40086	0	176694	-
Mitchell	53.93	215.83	-	-	-	-
Parmer	5.79	-	43797	-	13497	-
Potter	12.29	-	23666	-	5399	-
Randall	35.63	-	30664	-	7266	-
Reagan	19.96	92.88	-	-	-	-
Roberts	4.36	365.10	189012	0	21362	-
Scurry	35.53	87.67	-	-	-	-
Sherman	3.22	-	128354	-	12857	-
Sterling	17.00	64.91	-	-	-	-
Upton	743.45	94.64	-	-	-	-
Ward	15.72	96.20	-	-	-	-
Winkler	21.07	105.02	-	-	-	-

Table 6.1.3 Estimation of Brine Infiltration required Using (Cl^-/SO_4^{2-}) ratio

County	(Cl^-/SO_4^{2-})w	(Cl^-/SO_4^{2-}) b	Vt	Vb	PC mass	PC-brine
	ppm/ppm	ppm/ppm	$x10^9$ L	$x10^9$ L	Kg	ppb
Andrews	1.37	68.05	54885	302	217192	720
Borden	1.16	71.33	9505	21	4598	214
Gaines	1.04	34.04	71982	90	247633	2745
Gray	1.52	2092.66	123696	31	19555	641
Hale	1.96	203.81	54081	255	47156	185
Hemphill	2.04	403.25	155252	403	25555	63
Howard	1.89	27.49	14431	487	50247	103
Lamb	1.03	23.06	78825	93	35383	381
Lipscomb	2.50	226.99	164287	1093	27127	25
Lynn	1.05	120.72	56380	23	58818	2544
Martin	1.08	67.28	40086	47	176694	3758
Midland	1.12	611.17	43118	8	27601	3374
Ochiltree	1.72	408.99	152929	271	17002	63
Roberts	1.44	546.75	189012	152	21362	141
Armstrong	0.39	-	76890	-	14947	-
Bailey	1.21	-	59951	-	49167	-
Briscoe	0.68	45.69	8462	0	3191	-
Carson	0.51	993.55	107634	0	22761	-
Castro	0.73	143.12	54775	0	5818	-
Cochran	0.76	65.89	26237	0	35627	-
Crane	2.70	116.33	-	-	-	-
Dallam	0.30	-	138375	-	17272	-
Dawson	0.91	108.60	40025	0	103211	-

County	**(Cl^-/SO_4^{2-})w**	**(Cl^-/SO_4^{2-}) b**	**Vt**	**Vb**	**PC mass**	**PC-brine**
	ppm/ppm	**ppm/ppm**	**$x10^9$ L**	**$x10^9$ L**	**Kg**	**ppb**
Dickens	0.76	-	3726	-	965	-
Donley	0.53	-	99434	-	28480	-
Ector	0.93	63.06	15315	0	24648	-
Glasscock	0.62	66.71	5526	0	13378	-
Hansford	0.45	402.96	153710	0	15397	-
Hartley	0.58	40.65	198546	0	32897	-
Hockley	0.77	134.01	42548	0	49647	-
Hutchinson	0.44	311.85	104967	0	10867	-
Kent	0.18	-	2084	-	-	-
Lubbock	0.60	206.06	52451	0	52053	-
Mitchell	0.59	3459.01	-	-	-	-
Moore	0.33	116.01	136012	0	12727	-
Oldham	0.41	-	21142	-	5131	-
Parmer	2.74	-	43797	-	13497	-
Potter	0.51	117.44	23666	0	5399	-
Randall	0.67	-	30664	-	7266	-
Reagan	0.51	1139.03	-	-	-	-
Scurry	0.67	51.08	-	-	-	-
Sherman	0.36	45.24	128354	0	12857	-
Sterling	0.96	1628.11	-	-	-	-
Swisher	0.78	192.71	27918	0	8302	-
Terry	0.54	212.08	31681	0	34856	-
Upton	1.31	224.58	-	-	-	-
Ward	1.09	144.02	-	-	-	-
Wheeler	0.53	4728.74	108799	0	23834	-
Winkler	1.18	56.31	-	-	-	-
Yoakum	0.84	45.60	26038	0	54151	-

Of the fifty-four counties in the study area, only twenty-four counties (17 by Na^+/K^+ method, 14 by Cl^-/SO_4^{-2} method, and 7 counties from both the methods) could have been possibly affected by brine water infiltration. This analysis was restricted as the brine water data were available only for 42 counties in the study area, and total volume of water in the aquifer (calculated from saturated thickness data) was available for forty-six counties in the study area that wholly or partly lie over Ogallala aquifer. The average aquifer ratio of Cl^-/SO_4^{-2} in the study area was less than the average ratio stated by Wood and Jones (1990) in 34 counties, while the average ratios of Na^+/K^+ in the study area was less than the average Na^+/K^+ ratio stated by Wood and Jones (1990) in 18 counties. In these counties, the aquifer ratios are in the wrong direction for brine water to have infiltrated the aquifer and be a source for perchlorate. In the seven counties that were analyzed using both the aquifer ratios, there were one to three orders of magnitude difference between the estimated required perchlorate concentrations in brine by the two methods stated above. This may mean that the aquifer ratios are inconsistent with the hypothesis that the aquifer was infiltrated by brine water. Although the study was interesting, the results indicate that the brine water is an unlikely source to cause the perchlorate contamination in most of the counties in the study area.

6.2 Geochemistry

6.2.1 General Chemistry of Perchlorate

The chemical behavior of perchlorate in aqueous media has been presented in some detail by Gu et al. (2000) and Urbansky (1998). For completeness, a brief summary of perchlorate chemistry is included here. Perchlorate salts are extremely soluble, and most frequently enter the environment as ammonium or sodium perchlorate. Although perchlorate is a strong oxidizing agent, it is kinetically inert (very slow to react) in many redox reactions, and is typically non-complexing with metal ions. These properties result in perchlorate ions being exceedingly mobile in subsurface soil environments; moreover, the ions may persist for many decades in ground and surface waters.

Perchlorate is a large, poorly hydrated anion in comparison to most other ions found in groundwaters, such a Cl^-, HCO_3^-, and NO_3^- (Table 6.2.1). However, some of the minor anions have very similar ionic radii; for example, MnO_4^- and IO_4^-, and SO_4^{2-} and CrO_4^{2-}, although the latter two have different ion charges. The similarity in ion radii between some of the more exotic anions and perchlorate, may potentially result in ionic substitution in the salts of these various anions (Ericksen, 1983).

Due to the soluble nature of perchlorate, common cations do not typically precipitate perchlorate, as apparent by the solubility of $NaClO_4$ and $KClO_4$ being 6-8 M and 0.12 M, respectively. The lower solubility of $KClO_4$ relative to $NaClO_4$ perhaps accounts for perchlorate having been found, in a few instances, in association with the evaporate minerals Langbeinite ($K_2Mg_2(SO_4)_3$) and sylvite (KCl).

Table 6.2.1 Anion Radii in □

Anion	Ion Radii (□)
NO_3^-	1.79
NO_2^-	1.92
Cl^-	1.81
$HClO_3^-$	1.56
IO_4^-	2.49
MnO_4^-	2.40
ClO_4^-	2.40
SO_4^{2-}	2.30
CrO_4^{2-}	2.40

6.2.2 Mineralogy

The mineralogy of the Southern High Plains Aquifer System is fairly well known from the many published studies (e.g. Diffendal et al., 1990) and unpublished theses and dissertations (e.g. Potratz, 1980). In summary, the predominant minerals present in the Ogallala Formation include quartz (SiO_2), calcite ($CaCO_3$), microcline and orthoclase ($[K,Na]AlSi_3O_8$), and plagioclase ($NaAlSi_3O_8$-$CaAl_2Si_2O_8$). In addition, the Ogallala Formation also comprises minor minerals and clay minerals, including hematite (Fe_2O_3), magnetite (Fe_3O_4), muscovite ($KAl_3Si_3O_{10}(OH)_2$), kyanite and sillimanite (Al_2SiO_5), zircon ($ZrSiO_4$), sphene ($CaTiSiO_5$), apatite ($Ca_5(PO_4)_3OH$), hornblende, tourmaline, garnet, biotite, epidote, smectite, illite, kaolinite, and palygorskite. The primary source of solutes within the High Plains Aquifer are likely derived directly from the dissolution and weathering of these mineral phases.

It is unlikely that perchlorate would be present within the crystal structure of any of the minerals typically found in the High Plains Aquifer System. However, anion-exchange reactions of perchlorate over other anions in an aqueous system may occur within the clay minerals (Gu et al., 2000).

6.2.3 Discussion of Chemical Data

The water sample analyses included field measurements along with laboratory analyses of anion, cation, and trace metal concentrations. The field data comprised measurements such as water temperature (7 to 30 °C), pH values (mostly near neutral, 6 to 9), dissolved oxygen values (0.01 to 16.21 mg/L), and specific conductivity (0.238 to 3.22 μS/cm, with some outliers to 9 μS/cm). The water samples comprised fairly high levels of total dissolved solids, which varied from 0.11 to 6.31 g/L. For the statistical analysis, well data from PWS wells, private wells, HPWD wells, and USGS wells were considered. Two correlations were performed for the field analysis data. One of the correlation analyses considered all the sampled well data points (765 samples), while the other analyses considered only the wells that had detectable perchlorate concentrations (423 samples). A slight positive correlation existed between perchlorate and DO, conductance, sp. Cond, and TDS when all data points were considered (Table 5.2.2), while conductance and TDS only had a slight positive correlation with perchlorate when non detects were excluded (Table 6.2.3).

The perchlorate data were correlated with the individual anions, cations, and trace metals for all data points and data points from wells that had detectable perchlorate concentrations. Very slight positive (increasing anion/cation and increasing ClO_4^-) statistically significant correlations are discernible between ClO_4^- and all the ions analyzed with the exception of Nitrite (Table 6.2.2) when all the data points were considered, while, statistically significant correlations are discernible between ClO_4^- and all the ions analyzed with the exception of Nitrite and Calcium (Table 6.2.3) when only the data points with detectable perchlorate was considered. While statistically significant correlations were found, the low coefficients indicate that the relationship is quite weak and possibly of little environmental relevance.

Table 6.2.2 Correlation Results with Perchlorate for All Data Points

Dependent Variable	Linear Regression		Statistics		Number of data points
	a0	a1	r^2	P value	
Field Data					
DO mg/L	6.10	0.08	0.02	<0.0001	663.00
Cond mS/cm	1.00	0.08	0.18	< 0.0001	636.00
Sp. Cond	1.13	0.09	0.17	< 0.0001	664.00
TDS g/L	0.69	0.06	0.16	< 0.0001	761.00
Alk as CaCO3 mg/L	231.23	-1.14	0.01	0.01	736.00
Anions					
NO_2 mg/L	0.03	0.00	0.00	0.25	765.00
NO_3 mg/L	2.25	0.11	0.04	< 0.0001	765.00
F^- ppm	1.95	0.09	0.09	< 0.0001	765.00
Cl^- ppm	116.91	20.36	0.15	< 0.0001	765.00
Br^- ppm	0.47	0.14	0.25	< 0.0001	765.00
SO_4^{-2} ppm	147.41	22.28	0.15	< 0.0001	765.00
Total anions ppm	285.95	43.25	0.19	< 0.0001	765
Cations					
Na^+ ppm	92.16	11.62	0.05	< 0.0001	765.00
K^+ ppm	8.00	0.42	0.12	< 0.0001	765.00
Ca^{++} ppm	108.30	7.72	0.03	< 0.0001	765.00
Mg^{++} ppm	42.00	8.04	0.17	< 0.0001	765.00
Sr ppm	1.50	0.24	0.22	< 0.0001	765.00
Transition Metals					
Mn ppm	0.02	0.00	0.00	0.78	765.00
Fe ppm	0.08	0.02	0.01	0.0056	765.00
Aquifer Ratios					
Br^- vs Cl^-	0.09	0.00	0.68	< 0.0001	765.00
SO_4^{-2} vs Cl^-	89.17	0.69	0.37	< 0.0001	765.00
Na^+ vs K^+	8.31	0.01	0.09	< 0.0001	765.00

Table 6.2.3 Correlation Results with Perchlorate for Detectable Data Points

Dependent Variable	Linear Regression		Statistics		Number of data points
	a0	a1	r2	P value	
Field Data					
DO mg/L	6.80	0.03	0.01	0.10	423.00
Cond mS/cm	1.09	0.08	0.21	< 0.0001	281.00
Sp. Cond	4.55	0.09	0.00	0.86	280.00
TDS g/L	0.64	0.06	0.24	< 0.0001	420.00
Alk as CaCO3 mg/L	225.04	-0.07	0.01	0.15	409.00
Anions					
NO_2 mg/L	0.03	0.00	0.00	0.29	423.00
NO_3 mg/L	2.31	0.10	0.06	<0.0001	423.00
F^- ppm	1.95	0.08	0.10	< 0.0001	423.00
Cl^- ppm	117.09	20.22	0.16	< 0.0001	423.00
Br^- ppm	0.43	0.14	0.24	< 0.0001	423.00
SO_4^{-2} ppm	111.05	25.14	0.24	< 0.0001	423.00
Total anions ppm	232.87	45.69	0.20	< 0.0001	423.00
Cations					
Na^+ ppm	99.61	10.84	0.03	0.0003	423.00
K^+ ppm	8.15	0.40	0.12	< 0.0001	423.00
Ca^{++} ppm	128.84	5.88	0.02	0.0035	423.00
Mg^{++} ppm	46.38	7.63	0.13	< 0.0001	423.00
Sr^{++} ppm	1.26	0.26	0.24	< 0.0001	423.00
Transition Metals					
Mn ppm	0.01	0.00	0.01	0.0396	423.00
Fe ppm	-0.02	0.03	0.04	< 0.0001	423.00
Aquifer Ratios					
Br^- vs Cl^-	0.03	0.01	0.75	< 0.0001	423.00
SO_4^{-2} vs Cl^-	84.85	0.69	0.46	< 0.0001	423.00
Na^+ vs K^+	9.25	0.01	0.09	< 0.0001	423.00

Some of the significant correlations may be due to the clustering of data points, which may lead to some of the false positive results. More rigorous statistical analysis such as multi variant analysis and analysis after removing the clustering of data are to be performed.

6.3 Relation of Perchlorate Distribution in Ground-Water to Geologic and Hydrogeologic Features on the Southern High Plains

The distribution of perchlorate in High Plains ground-water coincides with several surface and subsurface geological and hydrogeological features. These are, 1) the areal distribution of Quaternary saline lake basins on the High Plains surface, 2) the subcrop distribution of Cretaceous strata beneath the Tertiary and Quaternary sedimentary cover of the High Plains, 3) the subcrop distribution of salt deposits in the Permian Salado/Tansill Formations beneath the High Plains, 4) areas with thin sandy surface soils, 5) shallow depth to the water table and thin saturated interval, and 6) low precipitation and high evapotranspiration rates. A geological cross-section of the High Plains (Figure 6.3.1) illustrates the basic relationship of the High Plains aquifer to underlying strata discussed below, and a generalized cross-section of the aquifer (Figure 6.3.2) depicts perchlorate occurrence in relation to basic aquifer stratigraphy.

All six of the geological features listed above exhibit a spatial distribution that generally corresponds with the area of high perchlorate concentration in ground-water. This coincidence may reflect a generic linkage between one or more of these features and the source of perchlorate introduced to the groundwater, or instead may provide a mechanism whereby perchlorate introduced from other sources may be concentrated above detection limits.

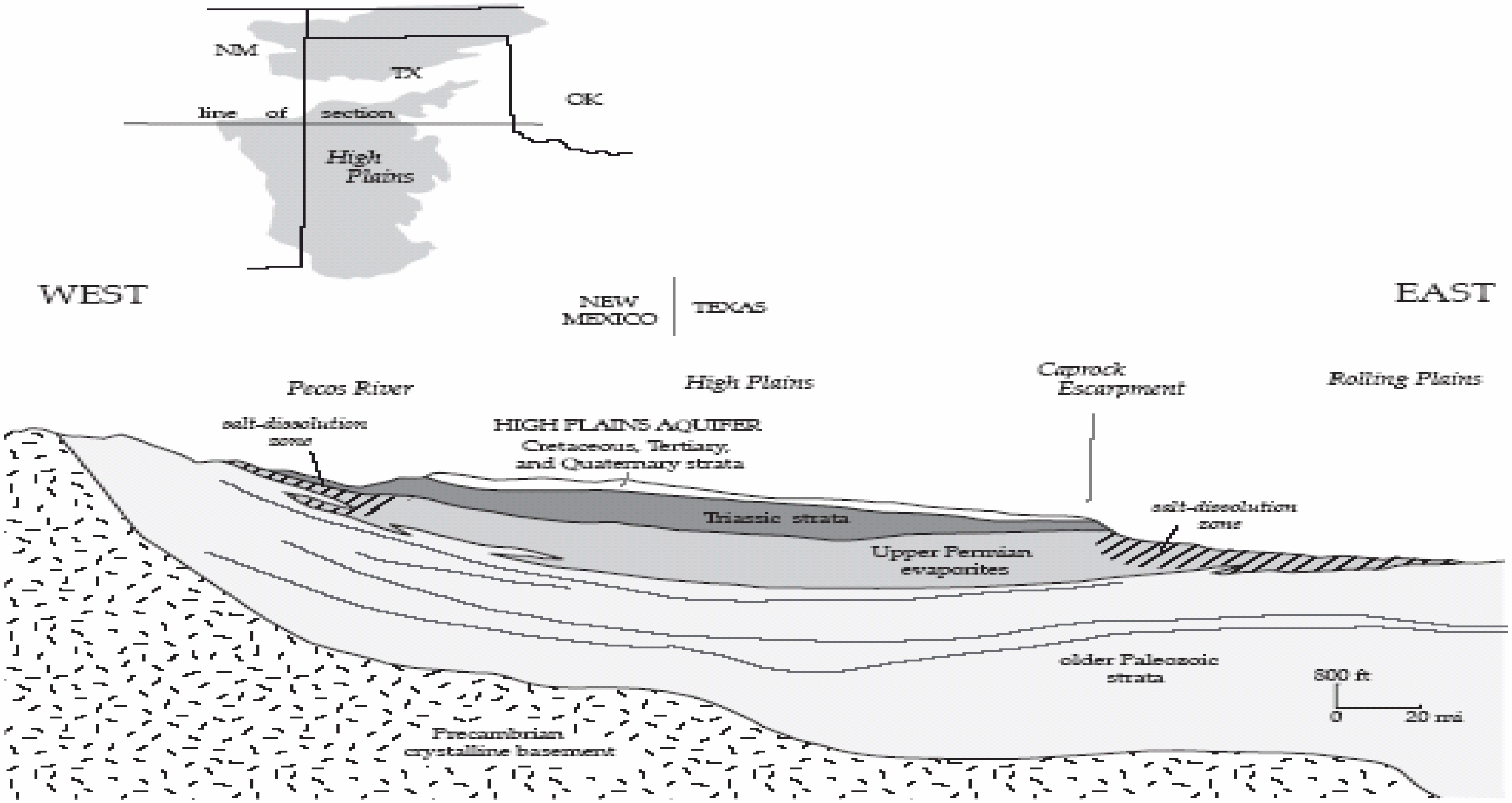

Figure 6.3.1 Generalized geological cross-section of the Southern High Plains region, showing the relationship of the High Plains aquifer to underlying strata (modified from Fisher and Kreitler, 1987).

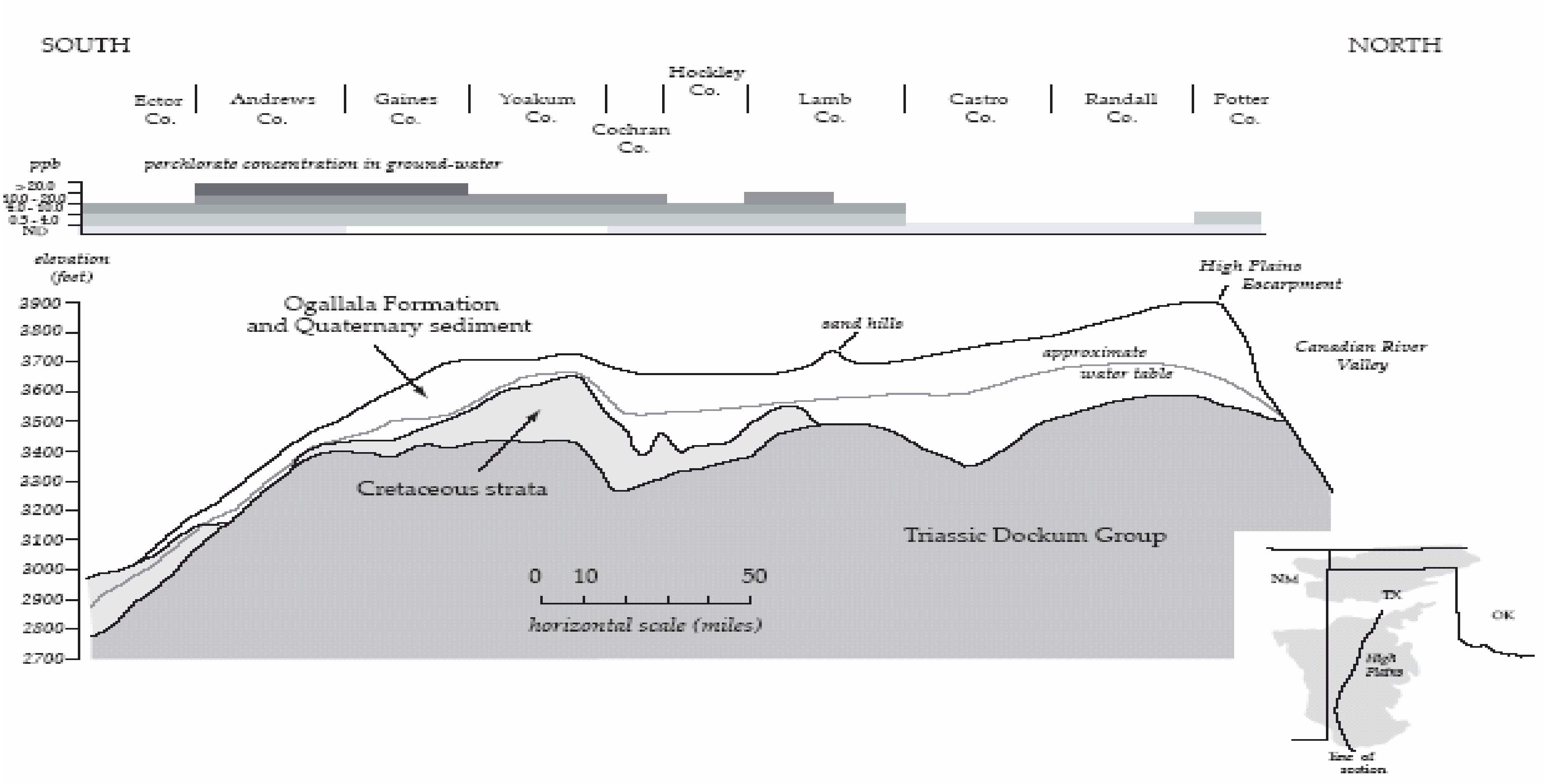

Figure 6.3.2 Generalized geological cross-section of the Southern High Plains regions, showing the basic stratigraphy of the High Plains aquifer (modified from Fallin, 1989) and general distribution and concentration of perchlorate in groundwater.

6.3.1 Geological Features in Study Area

6.3.1.1 Quaternary Saline Lake Basins

The saline lake basins of the High Plains occur within the area where perchlorate is generally present above detection limits in the underlying High Plains aquifer (Figure 6.3.3). The saline lakes are known to be areas where groundwater in the High Plains aquifer discharges to the land surface and is concentrated by evaporation (e.g., Wood and Jones, 1990). It seems unlikely that the lakes themselves could be the original source of perchlorate, because they appear only to concentrate groundwater discharged there and do not introduce a new source of water to the aquifer. In contrast, the much more numerous and more widely distributed playa lake basins on the High Plains are known to concentrate meteoric water by surface run-off, and to be important aquifer recharge sites, but do not bear any spatial association with groundwater perchlorate concentration. In fact, perchlorate concentration is highest where playa basins are least numerous.

If however, perchlorate is introduced to the aquifer regionally via some broader surface or subsurface source, the saline lakes would provide a mechanism for concentrating perchlorate in groundwater to higher values, assuming it does not precipitate with a mineral phase in the lake basins. Regional southeastward flow in the aquifer may then convey the perchlorate through mixing down-gradient from the lakes over time. Whether or not perchlorate may actually precipitate as a constituent in some mineral within the lacustrine sediment is as yet unknown. However, if this does occur, desiccation of the lakes, along with exposure and eolian deflation of the lake sediment could provide an additional means to distribute perchlorate to the land surface more broadly, downwind from the lakes as airborne dust (e.g., Wood and Sanford, 1995).

Even if the perchlorate were simply adsorbed or held in water bound to clay mineral

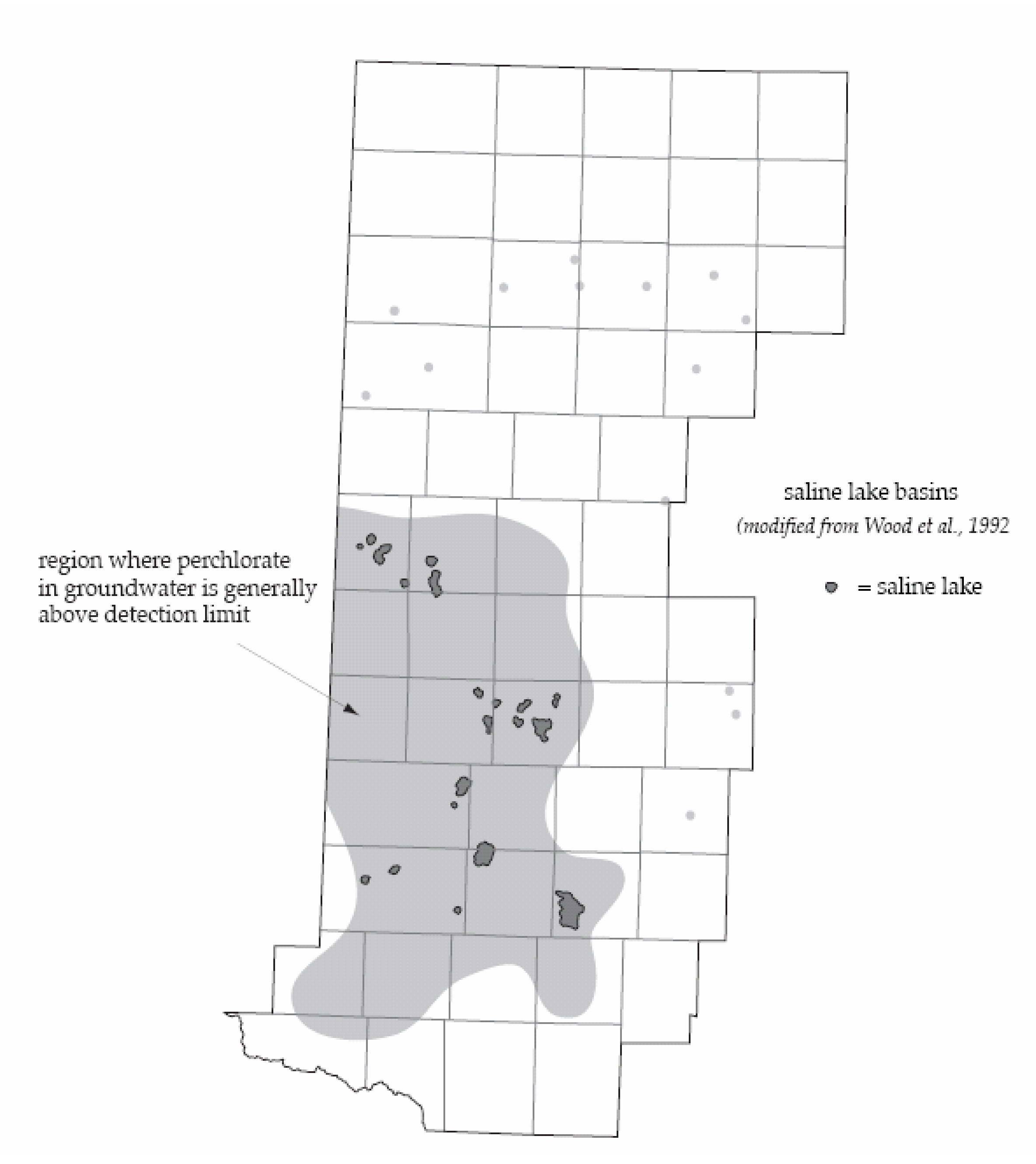

Figure 6.3.3 Map showing counties where groundwater was sampled for perchlorate and those areas where perchlorate was detected (shaded) in relation to the areal distribution of Quaternary saline lake basins on the High Plains (modified from Wood et al., 1992).

particles (rather than present by ionic substitution within a mineral crystal structure), its transport as dust could provide for broader dispersal downwind, presumably in a readily soluble form that could later be reintroduced to the groundwater by infiltration. If the saline lake basins concentrate perchlorate in groundwater, then there should be some correlation between perchlorate presence and/or concentration and total dissolved solids in groundwater, which should be higher in those areas subject to evaporative concentration. Indeed, groundwater in the southwestern part of the High Plains generally has higher total dissolved solids (1000 – 3000 mg/l tds; e.g., Ashworth et al., 1991). Samples of surface water from several saline lakes, however, have not yielded detectable perchlorate although the detection limit is quite high for these samples due to the high TDS.

6.3.1.2 Subcrop of Cretaceous Strata

The subsurface distribution of Cretaceous strata (Trinity, Fredricksburg, and Washita Groups) beneath the High Plains shows a remarkable correspondence with perchlorate distribution in groundwater (Figure 6.3.4). Perchlorate is generally not present above detection limits in areas where the High Plains aquifer is underlain by Triassic or Permian strata (Figure 6.3.4). Within the High Plains region, the Cretaceous strata have two or three water-bearing intervals that together with the Ogallala Formation constitute the High Plains aquifer system (Fallin, 1988; 1989). How or if groundwater in the Cretaceous aquifers interacts with that in the Ogallala Formation, and/or the rate of exchange of waters between the aquifers, are poorly understood. However, water in the Cretaceous aquifers differs in composition somewhat from that in the Ogallala aquifer (e.g., Nativ and Smith, 1987; Nativ and Gutierrez, 1988) suggesting limited or slow mixing between the two. We are as yet unaware of any perchlorate-bearing mineral phase or other source of perchlorate that might be present within the Cretaceous strata. These rocks consist primarily of limestone, shale, and sandstone, comparable in stratigraphy and composition to those found widely throughout the Edwards Plateau, Grand Prairie, and "Hill Country" of Texas (e.g., Anaya, 2001; Walker, 1979), where perchlorate has either not been reported in groundwater, or if present may be found below detection limits. It seems unlikely therefore that the Cretaceous strata beneath the High Plains could be the actual source of perchlorate, in spite of the close geographic correspondence.

Reeves (e.g., Reeves, 1990) and others have long maintained that a generic linkage exists between the presence of subsurface Cretaceous bedrock "highs" and the later origin of the High Plains saline lake basins during Quaternary time. One theory (e.g., Wood et al., 1992) suggests that high water tables induced by regional groundwater flow over the bedrock "highs" inhibited the formation of "caprock" caliche in those areas following the deposition of the Ogallala Formation. The absence of "caprock" in such areas made them readily subject to eolian deflation during Quaternary time, and this led to the initial formation of the saline lakes. Hence, the geographic correspondence between the saline lakes and underlying Cretaceous strata may reflect only this process, and may have little to do with the actual source of perchlorate.

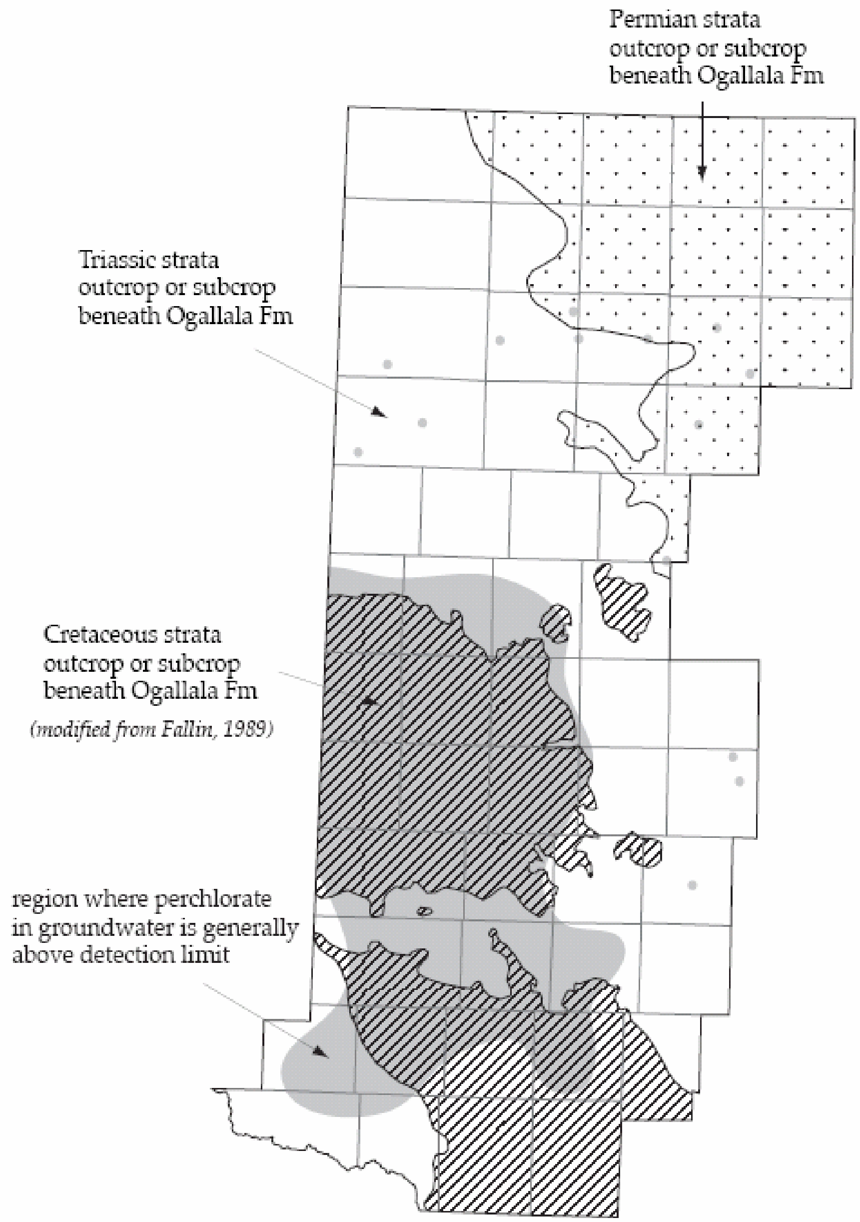

Figure 6.3.4 Map showing counties where groundwater was sampled for perchlorate and those areas where perchlorate was detected (shaded) in relation to areas where Cretaceous, Triassic, and Permian strata subcrop beneath the Ogallala Formation on the High Plains (modified from Fallin, 1989).

6.3.1.3 Subcrop of Permian Salt Deposits

Upper Permian (Ochoan) evaporite deposits are present in the subsurface Permian Basin region beneath the High Plains. Although gypsum, anhydrite, and halite beds are more widely distributed both geographically and stratigraphically throughout middle (Guadalupian) and late (Ochoan) Permian strata, the sylvite and bittern salt facies are largely restricted to the Ochoan Salado and Tansill formations (e.g., Sellards et al., 1932; McGillis and Presley, 1981). The salt beds within these formations exhibit a subsurface distribution broadly coincident with perchlorate occurrence in groundwater within the overlying High Plains aquifer (Figure 6.3.3).

The Salado/Tansill salt deposits are typically found at depths of 1500 to 2500 feet below the land surface of the High Plains, and are separated from the High Plains aquifer by 1000 to 2000 feet of “red beds” assigned to the Triassic Dockum Group (see Figure 6.3.1; e.g., Davis, 1953). The Dockum red beds consist largely of mudstone and are generally thought to act as an aquiclude or aquitard that separates the fresh groundwater in the High Plains aquifer from saline formation water in the Permian strata below. Several intervals within the Dockum Group (Santa Rosa Sandstone and Trujillo Sandstone) are locally important aquifers, particularly around the margins of the High Plains where the Dockum Group is exposed at the land surface and where recharge likely takes place (Dutton and Simpkins, 1986; Bradley and Kalaswad, 2001). However, over most of the High Plains, the Dockum Group aquifers contain saline groundwater (typically 5,000 to 20,000 mg/l TDS; Dutton and Simpkins, 1986).

If the bittern salts in the Permian Salado and Tansill formations are the source of perchlorate in the High Plains aquifer, then some more permeable subsurface connection must exist that spans the thickness of the intervening Dockum Group. Reeves (1970) suggested that such a connection may exist in the form of vertical fractures that cut through all of the surficial stratified rocks of the High Plains. Such fractures are well documented in outcrops of Permian and Triassic strata around the margins of the High Plains (e.g., Collins, 1984; Collins et al., 1986), and are suggested by geomorphic features such as drainage lineaments and alignment of playa basins on the land surface (Reeves, 1970; Finley, 1981). If these fractures are sufficiently spaced, connected, and open, they could provide a hydraulic connection between the High Plains aquifer and the deep Permian salt deposits.

There may be insufficient hydraulic head in underlying Permian brine aquifers, and/or insufficient fracture permeability to allow for upward flow through the Permian salts (e.g., Fisher and Kreitler, 1987); however, the fracture connections might allow for upward ionic diffusion even in the absence of flow. Reeves (1990) theorized that fortuitous intersections of fractures provided just such a permeable connection, and that this allowed for local dissolution of Permian salt beds beneath the High Plains. The salt dissolution ultimately led to subsidence of the land surface and formation of saline lake basins. Evidence for modern and ancient subsurface dissolution of Permian salt beds has since been well documented around the High Plains (e.g., Gustavson et al., 1990; 1991). Discharge of salt springs and land surface subsidence around the margins of the High Plains suggests that this process is active today (Figure 6.3.1; Gustavson and Simpkins, 1989).

Introduction of perchlorate from Permian salt to the High Plains aquifer via upward diffusion from local fracture connections might explain the very patchy distribution and wide local concentration variation of perchlorate within the region where it has been detected.

6.3.1.4 Thin Sandy Surface Soils

The unconsolidated windblown "cover sands" that blanket the High Plains surface are assigned to the Blackwater Draw Formation (e.g., Gustavson et al., 1990; Holliday, 1989; 1990). These deposits are overlain locally by younger dune sands (e.g., Muhs and Holliday, 2001). The modern soils have formed on the surface of these varied Quaternary windblown deposits. As a result of prevailing winds, the surficial Quaternary sediments of the High Plains vary in texture and thickness, generally becoming finer grained and thicker to the northeast (Godfrey et al., 1973).

Over the southwestern part of the High Plains, the surficial sediments consist predominantly of sand, typically of fine to very fine grade (0.05 to 0.1 mm). In the same region, these sediments are relatively thin (typically less than 10 ft) and in many areas are completely absent (where the "caprock" caliche of the Ogallala Formation is exposed at the land surface; e.g., Geologic Atlas of Texas, Hobbs Sheet 1976). The region where perchlorate has been detected in groundwater broadly coincides with this area of thin sandy soils (Figure 6.3.1.4). To the north and east of this area, the surficial sediments become increasingly finer grained (loamy to clayey) and thicker (typically 30 to 70 ft thick).

If perchlorate is or was deposited via some atmospheric or surficial source, then the thin sandy soils over the southwestern part of the High Plains, with their higher permeability and shorter transit time to the water table, would offer less impedance of infiltration to groundwater. In contrast, the thicker clayey soils to the north and east, with lower permeability and longer transit time to the water table, along with the possibility for adsorption of perchlorate with water in clays, might provide a more effective barrier to perchlorate entering the groundwater.

The detection of perchlorate at isolated locations outside the main area of occurrence along the southwestern margin of the High Plains, could reflect limited areas where conditions are similar (i.e., thin sandy surficial deposits above a shallow water table).

6.3.1.5 Shallow Depth to Water Table and Thin Saturated Interval

Over the southwestern part of the High Plains, the water table in the aquifer is found at relatively shallow depth (typically less than 100 feet) and the saturated thickness of the aquifer is relatively low (less than 100 feet). To the north and east, both the depth to the water table (typically greater than 100, up to 400 feet) and saturated thickness (greater than 100 ft) increase (e.g., Knowles et al., 1984). The northeastward increase in thickness of the saturated interval reflects the fact that the Ogallala Formation thickens to the northeast (Seni, 1980), and therefore the depth to underlying "red beds" of the Dockum Group is greater. The corresponding increase in depth to the water table to the northeast could reflect any of several phenomena. If recharge rates are broadly comparable over the surface of the High Plains, then the increase in depth to the water table could simply reflect the increase in depth to the base of the aquifer. The greater depth to the water table might also reflect the prevalence of irrigated agriculture and resulting greater regional drawdown of the water table in those areas due to pumping. Because the saturated interval is thin over the southwestern part of the High Plains, much of that land has remained grassland, fallow, or non-irrigated cropland and so the water table remains at shallow depth.

As in the case of section 6.3.1.4 above, if perchlorate is or was deposited via some atmospheric or surficial source, then the shallow depth to groundwater in the southwestern part of the High Plains would allow for a shorter transit time to the water table. In contrast, the greater depth to the water table to the north and east would result in a longer transit time for infiltrating groundwater. This factor alone might only be expected to affect perchlorate concentration in groundwater if the source of perchlorate were introduced relatively recently, and infiltrating water had not yet reached the water table where it lies at great depth. This seems unlikely because water in the upper part of the aquifer in some northern counties (e.g., Hale, Castro) is known to have been recharged since 1953 (tritium dating reported by McMahon et al., in review). However, if the greater depth to the water table in those areas reflects historic drawdown, it is possible that the absence of perchlorate in groundwater there could reflect removal of water by pumping and its application at the land surface via irrigation. This would require that the perchlorate had originally been concentrated only in the upper part of the aquifer, and that this water was preferentially removed by pumping. Again, this seems unlikely in view of the fact that many water wells are screened at greater depth in the aquifer, and that drawdown of the water table alone would not be expected to result in removal of perchlorate.

6.3.1.6 Precipitation and Evapotranspiration Rates

The southwestern part of the High Plains receives the lowest mean annual precipitation (generally less than 16 inches; Figure 6.3.5) and has the lowest minimum annual precipitation (less than 6 inches) in the region, and most of the precipitation falls during the warm season (April-September) when evapotranspiration rates are highest (Dugan and Zelt, 2000; their figures 20, 21). Although mean daily solar radiation does not vary substantially from north to south across the Southern High Plains, the cool season (October-March) solar radiation is notably higher over the southwestern part of this area (Dugan and Zelt, 2000; their figure 7). The mean annual potential evapotranspiration (about 66 inches) and actual evapotranspiration (about 15 inches) are high compared to precipitation rates. Hence, the mean annual potential groundwater recharge rate is very low (about 1 percent of annual precipitation; Dugan and Zelt, 2000; their figure 35).

The low annual precipitation and high evapotranspiration on the southwestern part of the High Plains may combine to concentrate perchlorate in groundwater if perchlorate was or is introduced via some atmospheric or other surface source. Higher rainfall and lower evapotranspiration rates over the northeastern part of the High Plains may allow for dilution of perchlorate in groundwater to below detection limits and/or its more rapid flushing through the aquifer.

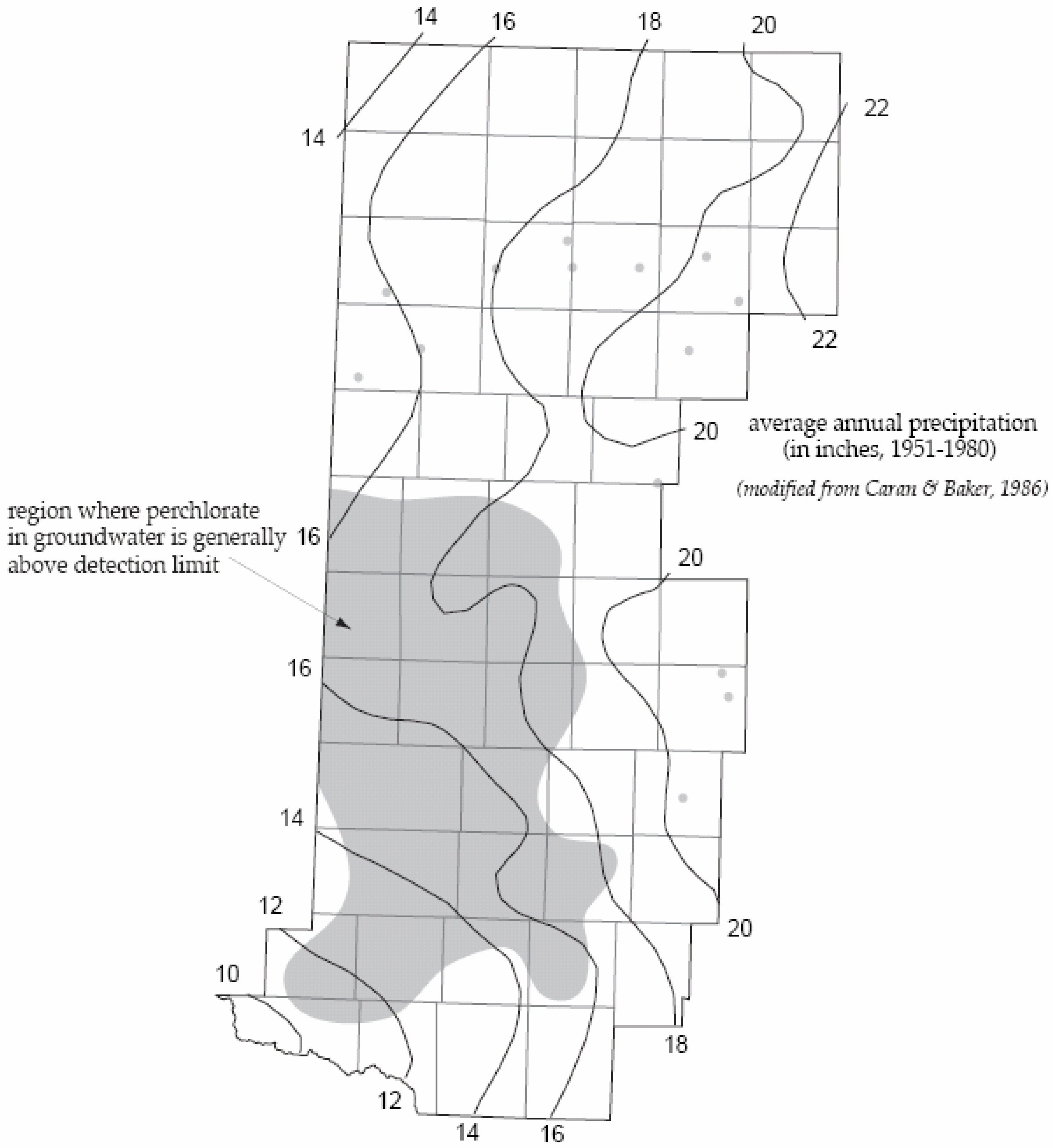

Figure 6.3.5 Map showing counties where groundwater was sampled for perchlorate and those areas where perchlorate was detected (shaded) in relation to average annual precipitation on the High Plains (modified from Caran and Baker, 1986).

6.3.2 Theories on the Origin of Perchlorate in High Plains Groundwater

The large amount of perchlorate documented in groundwater of the High Plains precludes its origin through any known human activities (e.g., military, oil field industrial, or agricultural). Therefore, perchlorate may now or in the past have been introduced to groundwater via some natural source. Three theories are considered below; these are 1) a deep source of perchlorate in Permian salt beds, 2) a shallow source of perchlorate in Cretaceous strata, and 3) an atmospheric source of perchlorate.

6.3.2.1 Perchlorate from Permian Salt Beds

Perchlorate is known to occur in some evaporite minerals in the Permian Salado and/or Tansill formations exposed in the Carlsbad Mining District of New Mexico (Orris et al, 2003). These evaporite deposits continue beneath the High Plains where they are typically found at a depth of 1500 to 2500 feet. Fractures that cut the Permian rocks as well as overlying Triassic and Tertiary strata may allow a hydraulic connection between the High Plains aquifer and the Permian salt beds. Upward diffusion or flow (less likely) via these fractures may result in dissolution (or partial dissolution) of the salt beds at depth and subsequent migration of perchlorate in solution to the High Plains aquifer. The subsurface limits of the Permian Salado and Tansill formations generally coincide with the observed distribution of perchlorate in groundwater. The isolated occurrences of perchlorate in groundwater at sites well outside the limits of Salado-Tansill salt deposits (Figure 6.3.6) could result from discharge of salt springs around the periphery of the High Plains.

The patchy distribution and highly variable local concentration of perchlorate could reflect its introduction via limited subsurface fracture paths. However, if this mechanism were operative, one might expect the concentration of perchlorate within the aquifer to be greatest at depth in the saturated zone and lowest at the water table. Such a concentration gradient is not observed; in fact the opposite may be true. (See Chapter 3) But, pumping of groundwater, its application to the land surface with irrigation, and return via infiltration through the unsaturated zone could result in vertical mixing of groundwater such that any original concentration gradient may be altered or obscured. Furthermore, samples of formation brine from Permian oil fields beneath the High Plains aquifer have yielded no detectable perchlorate.

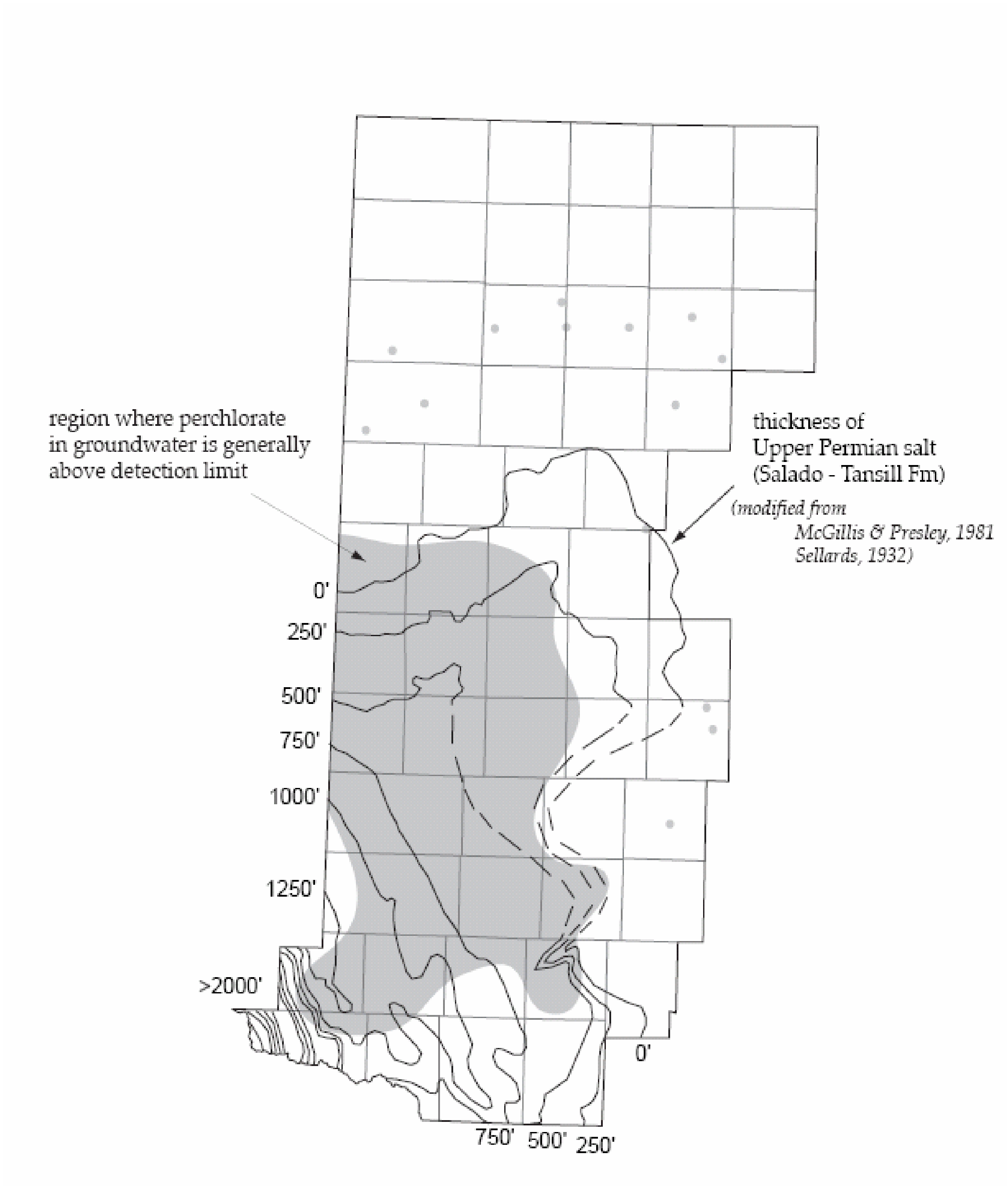

Figure 6.3.6 Map showing counties where groundwater was sampled for perchlorate and those areas where perchlorate was detected (shaded) in relation to the thickness of Upper Permian salt deposits in the Salado and Tansill Formations at depth (1500 to 2500 feet) below the High Plains aquifer (modified from Sellards et al., 1932; McGillis and Presley, 1981).

6.3.2.2 Perchlorate from Aquifers in Cretaceous Strata

The observed distribution of perchlorate in groundwater coincides closely with the subsurface distribution of Cretaceous strata beneath the Ogallala Formation. Within the Cretaceous strata, the Antlers Sandstone, Edwards Limestone, and to a limited extent the Duck Creek Formation are aquifers. The nature and rates of interaquifer flow between the Ogallala and Cretaceous aquifers are not well established. The Cretaceous strata contain no known perchlorate source, and no evaporite minerals that could theoretically provide a source. Further, these strata are widely exposed in central Texas where they are also important aquifers, and where perchlorate has not been found in groundwater. The hypothesis that perchlorate may enter the groundwater as a result of exchange with Cretaceous aquifers is based solely on the close geographic correspondence between the two. No additional evidence has been found to support this hypothesis. Samples of Cretaceous sediment obtained from the High Plains aquifer (drill cuttings) and groundwater samples obtained solely from Cretaceous units within the aquifer, have yielded no detectable perchlorate. Furthermore, perchlorate was detected in groundwater at isolated sites well outside the region of Cretaceous subcrop (Figure 6.3.4), and such occurrences could not reflect exchange with water in Cretaceous strata.

6.3.2.3 Perchlorate from an Atmospheric Source

Perchlorate may be present as a dissolved phase in precipitation or in particulate form, and could be deposited at the land surface with meteoric water or as dust fall. Some observations support this possibility. If perchlorate is deposited from an atmospheric source, its distribution in groundwater would be widespread unless a) the atmospheric source was local (e.g., dust derived from Permian evaporite exposures in the lower Pecos River valley); b) its concentration in precipitation is normally below detection limits and evaporative concentration of groundwater is necessary to produce detectable amounts (e.g., saline lake basins), or c) local vegetation or some soil constituent(s) intercept and/or adsorb perchlorate before it is able to enter groundwater (e.g., thick clayey soils).

Perchlorate concentrations are high in the southwestern part of the High Plains, coincident with an area having saline lake basins, thin sandy soils, a shallow water table, a thin saturated interval, and where rainfall is low, evapotranspiration rates are high, recharge rate is low, and there has been little regional lowering of the water table due to pumping. These factors may combine to concentrate perchlorate originally present in very low amounts in meteoric water later in groundwater, whereas in areas to the north and east it remains diluted below detection limits or is intercepted before reaching the water table. The isolated occurrences of perchlorate outside the southwestern part of the High Plains (Figure 6.3.7) could reflect local sites where conditions are favorable. Alternatively, if perchlorate is present in particulate form, it may be delivered to the soil surface only in those areas immediately downwind from a surface source of perchlorate. For example, surface soils in the Pecos River valley developed on Permian evaporite deposits could conceivably provide windblown dust with low amounts of perchlorate. In a soluble phase, it could then be released and transported by infiltration to the groundwater. Either mechanism would require a very extended period of operation in order to concentrate perchlorate to the levels observed. Either of the two mechanisms might result in greater concentrations of perchlorate at the water table compared to lower depths in the zone of saturation, particularly if the atmospheric source of perchlorate was active only recently. Prolonged operation of either, however, might produce no vertical concentration gradient, and pumping combined with evaporation and return of irrigation water via infiltration could also result in higher perchlorate concentration at the water table.

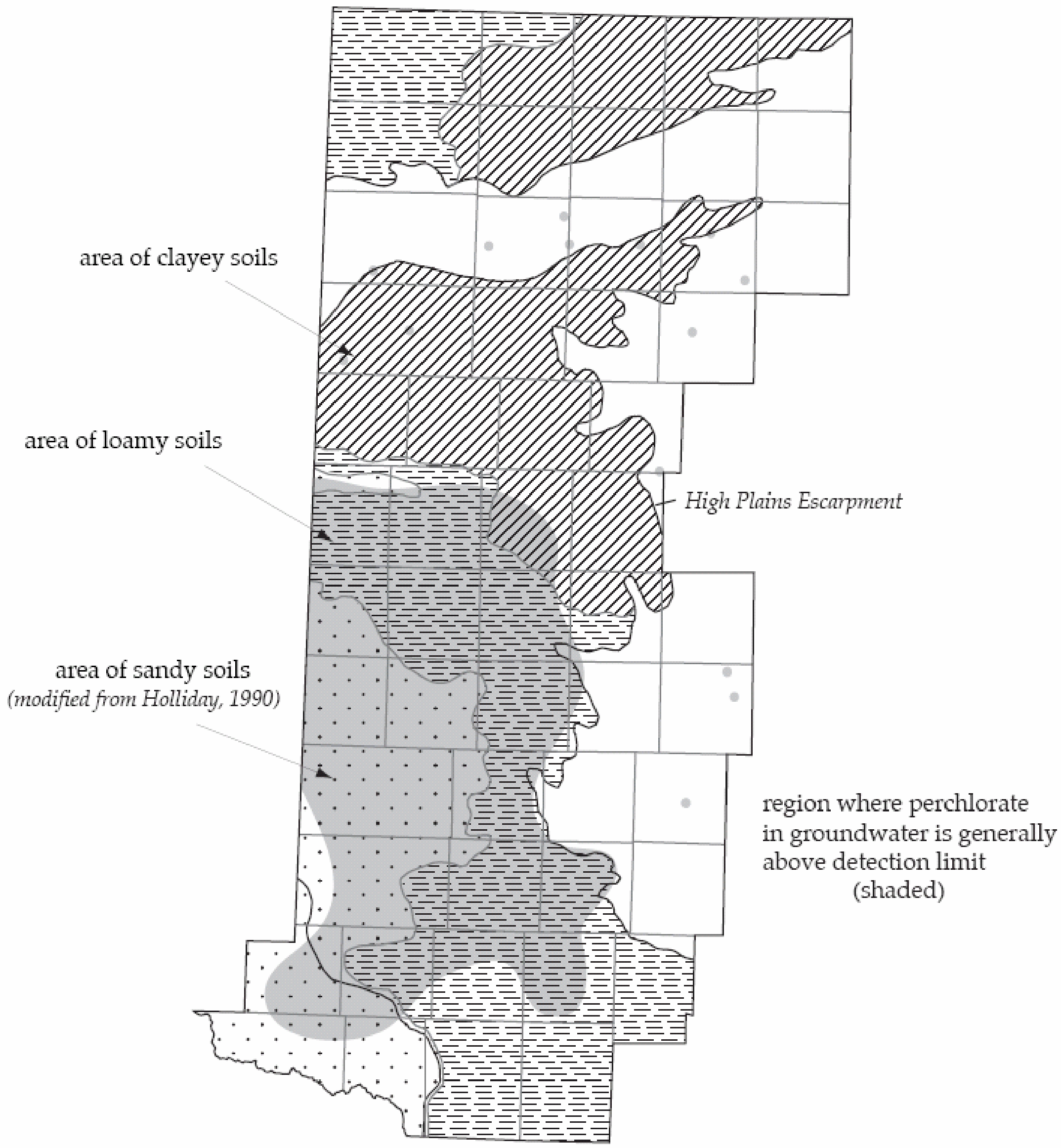

Figure 6.3.7 Map showing counties where groundwater was sampled for perchlorate and those areas where perchlorate was detected (shaded) in relation to the texture of surface soils in the unsaturated zone above the High Plains aquifer
(modified from Holliday, 1990)

6.4 Summary

While no single piece of data collected or calculation is able to definitively define the source of perchlorate in the study area, it is the strong opinion of this research team that atmospheric production and/or surface oxidative weathering is the source of the perchlorate. The mass of perchlorate produced/deposited per year would be concentrated in ground water by evaporation, thus leading to higher concentrations in groundwater where the depth to water is shallower and in areas with lower saturated thickness and thus less dilution is available. The influence of modern agricultural practices (irrigation) may have had a significant influence in some areas by greatly accelerating this process. Evidence supporting this hypothesis is numerous but primarily relates to the vertical distribution of the perchlorate (surface source), co-occurrence of the higher concentration distribution with areas of low saturated thickness and shallow depth to water, lack of any other viable surface source, and modeling of the travel times and distribution within the aquifer. Other data to support this hypothesis which were not available at the time this report was produced are the age of the groundwater in the nested wells and the isotopic signature of the perchlorate.

CHAPTER 7

SUMMARY

A large scale sampling program was led by the Texas Tech University Water Resources Center (TTUWRC) to determine the source and distribution of perchlorate in northwest Texas groundwater. This sampling program included public water system (PWS), private, irrigation, and USGS monitoring wells over an area of 52,900 mi^2 in 54 four Texas counties. Ten wells were sampled in the two eastern counties of New Mexico (Lea and Roosevelt) adjacent to the Texas study area, covering 6,800 square mi^2. Three well clusters were installed in Bailey (2 wells), Gaines (3 wells), and Martin (3 wells) counties to show possible vertical variations in perchlorate concentration. Grab samples of the sediments were collected at 5-ft intervals in both unsaturated and saturated zones for geologic logging and perchlorate extraction. In addition to the well clusters, unsaturated zone soil samples were obtained from one site in Carson County and two individual USGS monitoring wells from Bailey and Cochran counties. Groundwater samples were collected from the two USGS wells in Bailey and Cochran counties and from two USGS deep nested well systems in Hale and Castro counties. The wells in the fifty six-county study area in Texas and New Mexico represent five different aquifers, including the Edwards-Trinity (Plateau), Cenozoic Pecos Alluvium, Dockum (known locally as the Santa Rosa), Seymour, and High Plains Aquifer system (referred to locally as the Ogallala).

Perchlorate detections were widespread across the study area. Among the 560 PWS wells sampled in the 54 Texas counties, 256 (46%) contained perchlorate (>0.5

ppb), of which 102 (18%) contained perchlorate equal to or greater than 4 ppb. Reanalysis of 114 PWS samples that were originally reported as below the 0.5 ppb detection limit by HPLC/MS found that 81 (71%) did test positive for perchlorate. Of the 76 private wells, 36 (47%) had detectable perchlorate (>0.5 ppb), and 23 (30%) had perchlorate concentrations at or above 4 ppb. Forty-two of the 100 irrigation wells had detectable perchlorate, with 30 at or above 4 ppb. All 10 New Mexico wells had detectable perchlorate (>0.5 ppb) and 6 (60%) had perchlorate concentration at or above 4 ppb.

The concentration of perchlorate varied vertically in all nested/clustered wells in which perchlorate was detected. There was a definite decreasing trend in perchlorate concentration with increase in depth at each TTU well cluster, and perchlorate concentrations ranged from 1.16 ppb in Bailey County to 179 ppb in Gaines County. The perchlorate concentrations in the saturated zone of the USGS wells sites ranged from 0.21 ppb to 6.0 ppb in Hale County, while none of the other wells contained any detectable perchlorate. In addition tritium data indicates that in some cases perchlorate is present in water which is older than modern atmospheric testing of nuclear weapons (~1950).

The unsaturated zone sampling sites (TTUWRC well clusters, Carson County archived samples, and USGS well systems) aligned roughly north-south, spanning 210 miles (65%) of the 370-mi length of the study area. The unsaturated zone thicknesses ranged from 40 ft in Gaines County to 270 ft in Carson County.   Of the 201 unsaturated soil samples from TTUWRC wells, 66 (33%) had detectable perchlorate, ranging from 1 g/kg to 116 g/kg (dry soil weight) in the unsaturated zone Of the 296 unsaturated soil samples collected from the two USGS wells, only 25 (8.5%) had detectable perchlorate, ranging from 0.64 □g/kg to 14.6 □g/kg (dry soil weight). Sediment samples from the northernmost location (Carson County) were positive for perchlorate in 19 of 78 (24%) samples with a range of 0.2 □g/kg to 7 □g/kg (dry soil weight).

It was possible to estimate the total mass of perchlorate in the saturated zone for 45 counties (those lying with in the region of the High Plains Aquifer system) with adequate data was available for saturated thickness distribution. The county masses ranged from 970 kg in Dickens County to 250,000 kg in Gaines County, and the total mass of perchlorate in the 45 counties estimated at 1,800,000 kg. The total mass of perchlorate in the unsaturated zone was estimated for the five counties from which unsaturated soil samples were available. The masses of perchlorate in the unsaturated zones were of similar magnitude as the masses in the saturated zone, ranging from 24,000 kg in Bailey County to 490,000 kg in Martin County.

After review of the collected data, it is apparent that no single anthropogenic source could have caused the widespread occurrence of perchlorate. Perchlorate seems to be fairly ubiquitous at very low concentrations in the saturated and unsaturated zone. While no single piece of data collected or calculated was able to definitively identify the source of perchlorate in the study area, it is the strong opinion of this research team that atmospheric production and/or surface oxidative weathering is the source of the perchlorate. The mass of perchlorate produced/deposited per year appears to be concentrated in the unsaturated zone by evapotranspiration during dry periods and flushed to the water table during wet periods. This process has led to higher concentration in groundwater where the water table is relatively shallow, and in areas with lower saturated thickness and thus less available dilution. Agricultural irrigation may have accelerated this process in some areas. Evidence supporting this hypothesis primarily relates to the vertical distribution of perchlorate in the unsaturated zone, co-occurrence of the higher perchlorate in groundwater with areas of low saturated thickness and shallow depth to water, presence of perchlorate in water older than ~1950, and lack of any other viable surface source.

Extended Research Needs

Significant progress has been made in defining both the extent and source of perchlorate in northwest Texas groundwater. However, two significant issues still exist and must be pursued. First, the survey of potentially affected groundwater sources in arid and semi-arid areas of the state must be extended. Second, we must evaluate future impacts of current land and water use practices on perchlorate and other significant contaminants of concern (As, Se, F, NO_3).

Sampling in Phases I and II focused on counties located primarily in the High Plains region of Texas, with additional coverage off the eastern Caprock escarpment and in the Trans-Pecos to the south. However, the results of this study indicate that it is likely any groundwater resources in arid or semi-arid areas with limited recharge will accumulate perchlorate. This conclusion is supported by detections of perchlorate in the Seymour, Edwards-Trinity, and Cenozoic-Pecos Alluvium aquifers. Most of West Texas is sparsely populated with few large PWSs and many residents who utilize private well water. These residents are highly dependent on single wells or small well fields, likely unable to mix multiple water sources. In addition, they are unlikely to be aware of or test for drinking water contaminants. A wider survey of water resources should be conducted to more fully characterize population with potential exposure to perchlorate. These areas should, at minimum, include all counties underlain by the Cenozoic-Pecos Alluvium, Edwards-Trinity, and Seymour aquifers. The region's minor aquifers, such as the Rustler, Capitan Reef, Blaine, Hickory, and Marathon, must also be investigated.

The impact of perchlorate in groundwater resources is currently significant and will most likely increase in the near future. The results of this study highlight the potential for increasing concentrations of perchlorate and other groundwater contaminants as the quantity of groundwater in storage decreases and the pace of evaporative salinization accelerates (see Figure 1).. As water levels decline in west and northwest Texas, influx of chemicals of concern will have a greater effect on the overall groundwater concentrations. In addition, evaporative processes such as surface irrigation can increase concentrations of chemicals of concern in the unsaturated zone during periods of low precipitation. During relatively rare high precipitation periods, those residual chemicals are flushed downward toward the water table. Better understanding of these processes is required to mitigate future degradation of groundwater quality.

It is likely that the National Academy of Science will agree with the EPA and recommend the lower RFD and hence an MCL of 6 ppb for perchlorate. If an MCL near this value is adopted, many small PWSs will have to treat some portion of their produced water for perchlorate. In the Southern High Plains, they may also be forced to simultaneously treat for F, As, and Se. These requirements encourage research on current economically viable technologies that can be applied by small PWSs. This effort should include surveys of currently used processes as well as those in development. Cost consideration, required technical level, waste disposal, and overall water efficiency should be considered.

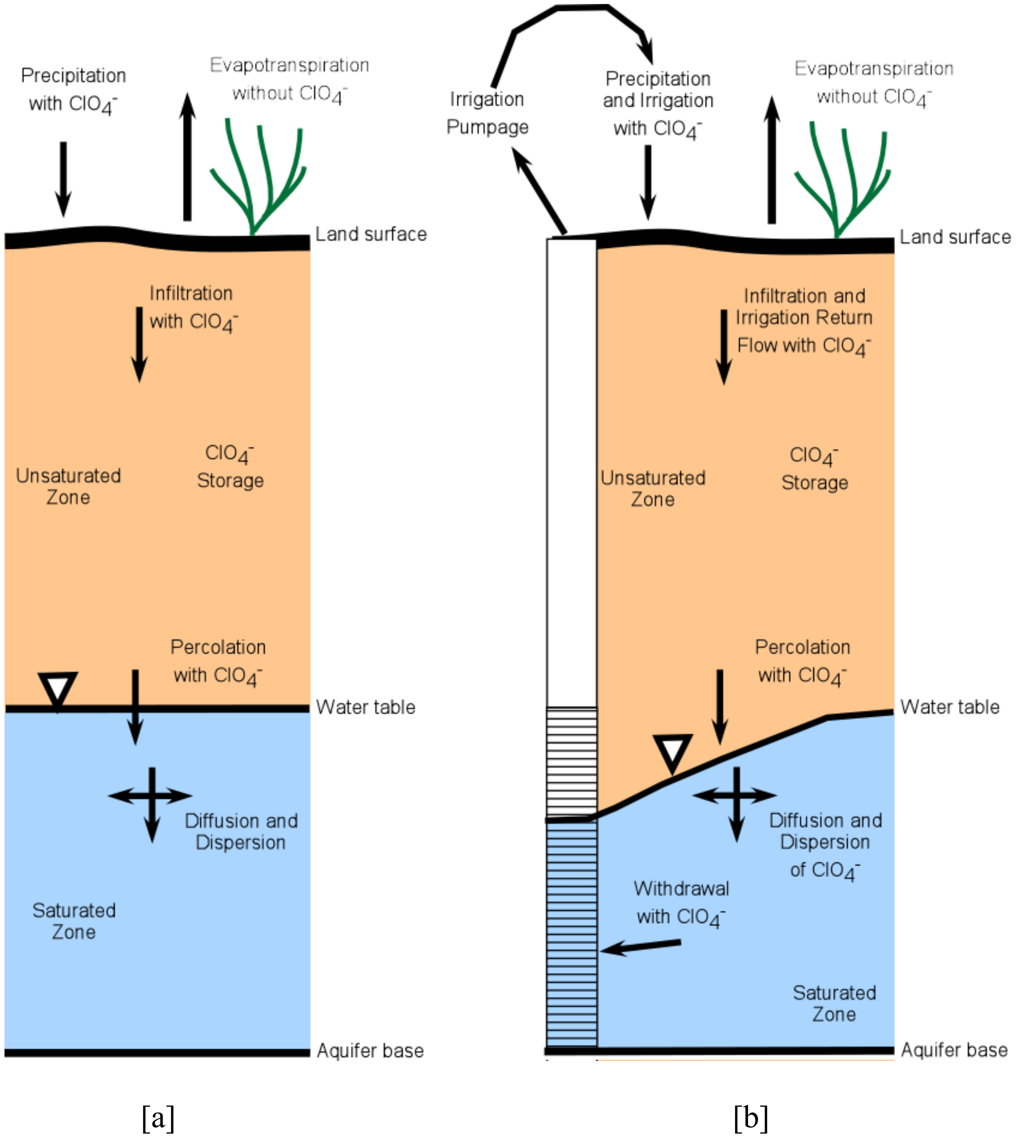

Figure 7.1 Schematic of perchlorate transport through unsaturated zone in [a] natural conditions and [b] irrigated conditions

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