

IDENTIFICATION OF THE SOURCES OF
HIGH CHLORIDE CONCENTRATIONS
IN THE FRESH WATER AQUIFERS
OF CENTRAL OKLAHOMA

BY

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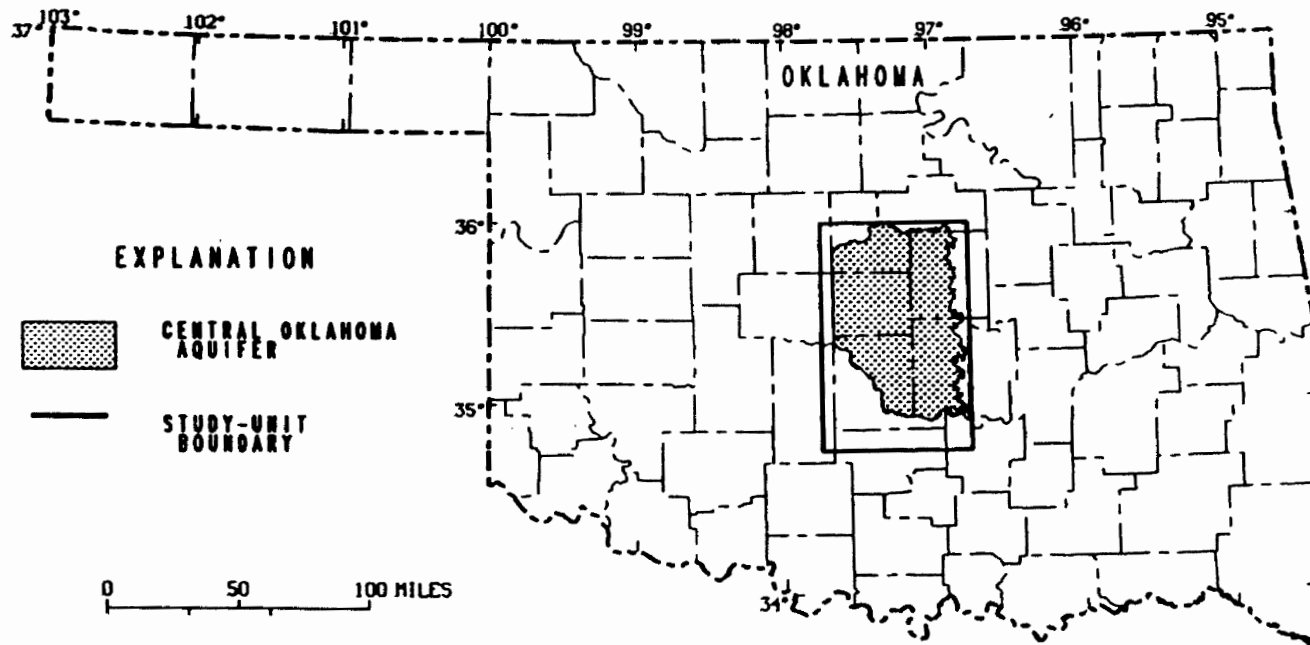
CHAPTER I

INTRODUCTION AND OBJECTIVE

Introduction

The Central Oklahoma aquifer underlies approximately 3,000 square miles of central Oklahoma (Figure 1) and consists of aquifers in the Permian bedrock units and overlying Quaternary-age alluvium and terrace deposits. The Permian-age Garber Sandstone and Wellington Formation are the main aquifers in the region and have been the subject of numerous hydrogeological and general geochemical studies. Higher than normal chloride levels often are present in the waters of the Central Oklahoma aquifer. Possible sources of these elevated chloride concentrations are: oil field brines, deeper natural saline ground waters, solution of natural halite, saline seeps, agricultural activities (primarily due to irrigation and fertilization), and road salts. Differentiation among these sources of chloride sometimes is possible using ion ratios and mixing curves of both major constituents and trace elements.

Figure 1. Location of the Central Oklahoma Aquifer and the Study Unit (from Parkhurst and others, 1989).



Objective of Study

The main objective of this study was to determine the sources of the higher chloride concentrations that often are present in the waters of the Central Oklahoma aquifer of Oklahoma. This study was based on recently performed water analyses from 202 existing water wells. From this data set, 42 wells were selected that exhibited relatively high chloride levels. Their chemical constituents and geochemical relationships as well as their physical and geographical characteristics were reviewed to determine the possible sources of this chloride and to establish what parameters are most useful in differentiating these sources.

Due to the large amount of past and present oil industry activity in the area, the focus of this study will be placed on differentiating oil field brine contaminated waters from non-oil field brine contaminated waters.

CHAPTER II

BACKGROUND

Description and Hydrogeology of the Study Unit

Parkhurst and Christenson (1989) defined the Central Oklahoma aquifer as follows:

The Central Oklahoma aquifer consists of those geologic units that yield substantial volumes of water to wells from the extensive, continuous flow system centered around Cleveland, Lincoln, Logan, Oklahoma, and Pottawatomie Counties. Ground water in this flow system originates as recharge from precipitation on the aquifer and circulates in the Quaternary-age alluvium and terrace deposits along major streams; the Permian-age Garber Sandstone and Wellington Formation; and the Permian-age Chase, Council Grove, and Admire Groups.

Parkhurst and others (1989) referred to the Central Oklahoma aquifer as a study unit rather than a study area, since it is defined by both depth and areal extent. The northern and southern boundaries of the study unit are the Cimarron River and the Canadian River, respectively. The eastern boundary is the eastern limit of the Oscar Group outcrop and the western boundary is approximately near the Oklahoma-Canadian County line where the fresh water circulation in the aquifer becomes negligible and the dissolved-solids concentrations increase to greater than

5,000 mg/L. The lower boundary of the Central Oklahoma aquifer is defined as the lower limit of the fresh ground water containing less than 5,000 mg/L dissolved solids. The depth to the base of the fresh ground water is approximately 1000 feet near Midwest City. The base of the fresh ground water gradually becomes shallower and is approximately 100 feet from the surface near the north, south, and east boundaries of the study unit. It is approximately 200 feet from the surface near the west boundary (Parkhurst and others, 1989).

The Central Oklahoma aquifer includes Quaternary-age alluvium and terrace deposits and the underlying Permian-age bedrock units (Table 1). The Quaternary deposits overlie the older Permian beds as these lower beds subcrop across the study unit (Figure 2). The Permian unit dips uniformly to the west with a slope of approximately 50 feet per mile; the only major exception to this is the structure that is present over the Oklahoma City Field which shows surface structural relief of approximately 100 feet (Gatewood, 1970). The source of recharge for the Central Oklahoma aquifer is precipitation (Bingham and Moore, 1975). The principal source of discharge for the Central Oklahoma aquifer is ground water discharge into streams. In addition, there is a deep, slow moving flow system that

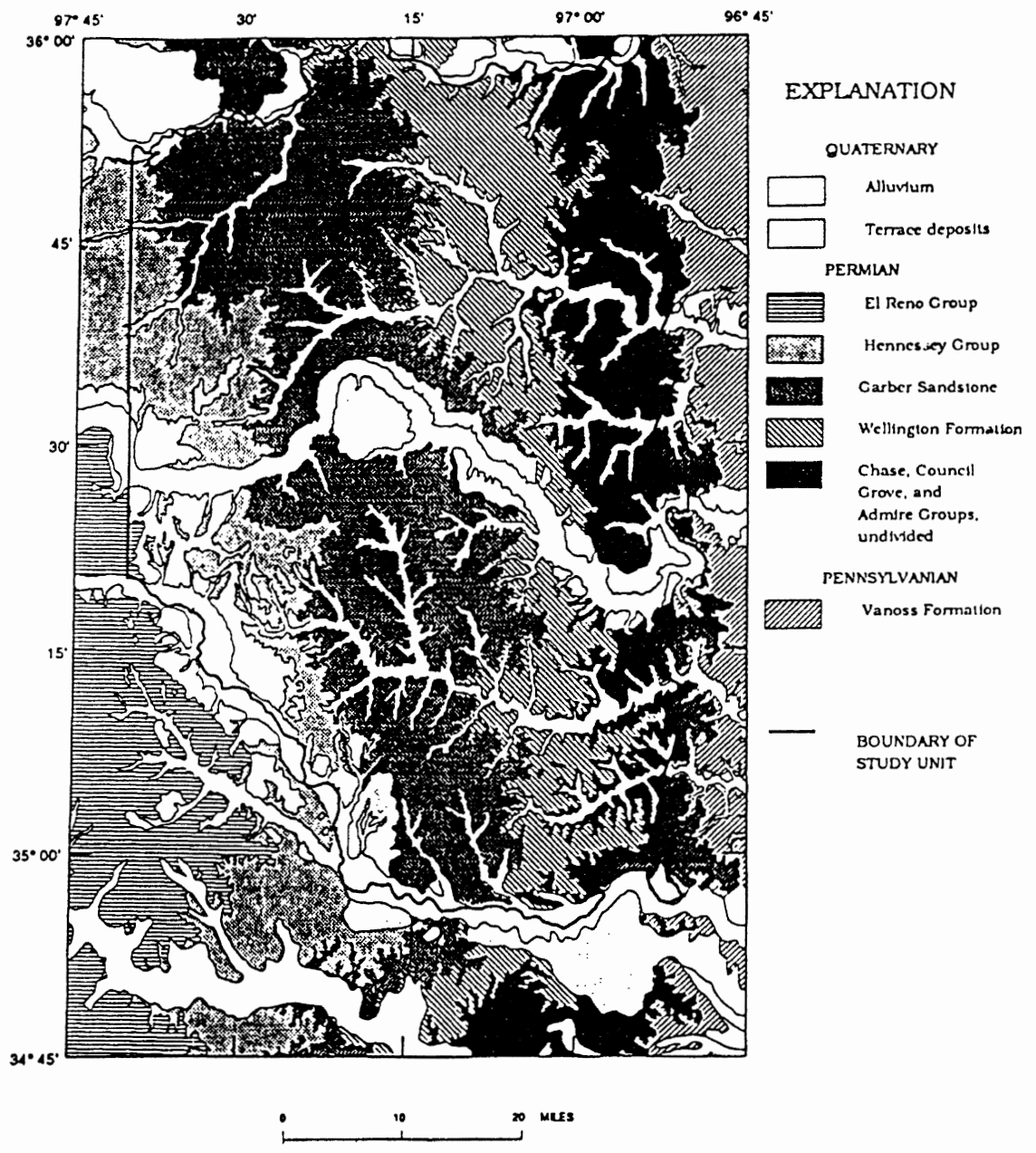
first flows to the west under the confining Hennessey Group and then flows north and discharges into streams (Christenson, 1992).

TABLE 1
MAJOR CHRONOSTRATIGRAPHIC UNITS AND
ROCK-STRATIGRAPHIC UNITS
IN CENTRAL OKLAHOMA

Erathem	System	Geological Unit
Cenozoic	Quaternary	Alluvium Terrace Deposits
Paleozoic	Permian	El Reno Group Hennessey Group Garber Sandstone Wellington Formation Chase Group* Council Grove Group* Admire Group*
	Pennsylvanian	Vanoss Formation

* Collectively referred to as the "Oscar Group"

Figure 2. Geological Map of Central Oklahoma (from Ferree and others, 1992, modified from Bingham and Moore, 1975, and Hart, 1974).



Most large-capacity municipal water wells are completed in the Permian bedrock units of the Central Oklahoma aquifer and typically range from 100 to 800 feet in depth. Domestic water wells are completed in the bedrock, alluvium, or terrace deposits and are typically 30 to 150 feet in depth. Central Oklahoma aquifer ground water withdrawals, aside from domestic use, were estimated to have peaked in 1985 at 13,900 million gallons per day. This number had declined to 7,860 million gallons per day by 1989 (Christenson, 1992). The Garber Sandstone and Wellington Formation are by far the most significant aquifers within the Central Oklahoma aquifer study unit and their geology and hydrogeology have been reviewed in detail in numerous studies. The following is a brief geological review of each group which comprises the Central Oklahoma aquifer.

Quaternary Alluvium and Terrace

Deposits (Quaternary)

The Quaternary alluvium and terrace deposits are located along streams and consist of lenticular beds of unconsolidated clay, silt, sand, and gravel. The thickness of the alluvium and terrace deposits ranges from 0 to 100 feet in the study unit (Parkhurst and others, 1989).

El Reno Group (Permian)

The El Reno Group, which crops out only in the very southwest corner of Oklahoma County, is the youngest consolidated unit in the study unit (Figure 2). The El Reno Group provides sufficient yields of water for domestic use. However, Parkhurst and others (1989) did not include it as part of the Central Oklahoma aquifer because it is separated from the other Permian units by the Hennessey Group which is considered to be a confining unit. The El Reno Group consists of red-brown fine grained sandstone, mudstone conglomerates, and shale.

Hennessey Group (Permian)

The Hennessey Group overlies the Garber Sandstone and is present in the western one-third of the study unit (Figure 2). It primarily consists of shale, siltstone, and thin beds of very fine grained sandstone. It is as thick as 500 feet along the western edge of Oklahoma County (Carr and Marcher, 1977). Units within the Hennessey Group in descending order are the Bison Formation, Salt Plains Formation, Kingman Siltstone, and Fairmount Shale. Because of the Hennessey Group's low transmissivity, Parkhurst and others (1989) considered it to be a confining unit and not part of the Central Oklahoma aquifer. However, numerous shallow domestic wells have been completed in this group along the western edge of the study unit.

The Hennessey Group is important in this study for two reasons. First, the Hennessey Group dramatically affects water quality in the units below it. Garber Sandstone and Wellington Formation water wells that are completed in the upper parts of these units and that are overlain by the Hennessey Group typically show increased levels of sulfate and, to a lesser extent, elevated levels of other ion concentrations (Na^+ , Ca^{++} , and Cl^-). These increased concentrations are the result of gypsum dissolution in the Hennessey Group (Parkhurst, 1992). Second, it appears that several of the water analyses from wells reported as producing from only the Quaternary alluvium and terrace deposits in the western part of the study unit are likely from wells that have these units commingled with units of the Hennessey Group. The water quality of those wells appears to be dramatically affected by the Hennessey Group's waters.

Garber Sandstone and Wellington Formation (Permian)

The Garber Sandstone and Wellington Formation are the main aquifers from the Cimarron River south to the Canadian River, and westward from Lincoln and Pottawatomie counties to the western border of Oklahoma County (Carr and Marcher, 1977). These two units are made up of interfingering beds of sandstone, siltstone, shale, and mudstone. The Garber Sandstone and Wellington Formation have a combined maximum thickness of about 1600 feet. The percent of sand relative

to the total thickness of these two units varies from over 70 percent in the area of greatest thickness and decreases to about 40 percent near their boundaries (Christenson, 1992). These deposits have been interpreted to be of deltaic origin (Christenson, 1992). Thus, individual beds in these units are virtually impossible to correlate for more than short distances because lithologies change abruptly and strata are commonly lenticular.

These two units outcrop in the middle of the study unit (Figure 2) and can be mapped separately on the surface. However, they appear indistinguishable in the subsurface due to similar lithologies and the lack of key markers or index fossils. Furthermore, the two units have similar hydrologic properties and are hydrologically interconnected. For these reasons, the water-bearing unit comprising all or parts of the Garber Sandstone and Wellington Formation in the study unit is considered to be a single aquifer (Woods and Burton, 1968) and herein is referred to as the Garber-Wellington aquifer.

A Garber-Wellington aquifer water well typically has yields ranging from 200 to 400 gallons per minute when designed for maximum yield (Christenson, 1992). While this aquifer's properties are highly variable, the following data are reported in the literature:

Transmissivity:

5000 gal/day per ft (Woods and Burton, 1968)

3300 gal/day per ft (Wickersham, 1979)

Storage Coefficient (confined portion):

2×10^{-4} (Woods and Burton, 1968)

Specific yield:

0.2 (Christenson and Rea, 1992)

Water table conditions generally exist in the upper 200 feet of this aquifer in the area where it outcrops.

Confined aquifer conditions generally exist below a depth of 200 feet or where the Garber-Wellington is overlain by the Hennessey Group and the aquifer is fully saturated (Carr and Marcher, 1977).

Another characteristic of this Permian bedrock aquifer is that the water is more mineralized with depth (Parkhurst and others, 1989). The fresh water zone overlies the saline water present in this aquifer.

Chase, Council Grove, and Admire Groups (Permian)

The Permian Chase, Council Grove, and Admire Groups are below the Wellington Formation. These groups are aquifers in the eastern half of the study unit, having a combined thickness of as much as 600 feet (Figure 2). These rock-stratigraphic units are commonly referred to as the "Oscar Group" and a few authors have assigned these units to the Pennsylvanian System. However, both the USGS (Parkhurst and others, 1989) and the Oklahoma Geological Survey (Johnson,

1993) presently interpret these units to belong to the Permian System. These units consist of beds of sandstone, shale, and thin limestone. Wells that are completed in these units generally yield 10 to 100 gallons of water per minute (Christenson, 1992).

Vanoss Formation (Pennsylvanian)

The Vanoss Formation mainly consists of shale and a few thin, fine-grained sandstone beds. This Pennsylvanian formation is found along the eastern boundary of the study unit (Figure 2). Parkhurst and others (1989) considered it to be a confining unit and therefore did not include it as part of the Central Oklahoma aquifer, but several of the wells in the USGS data base were completed from this formation.

Previous Geochemical Studies

The early studies of the water chemistry in the study unit only dealt with the descriptive characteristics of the aquifer (inorganic species concentration, pH, etc.). Subsequently, McBride (1978) and Scott (1988) reviewed the hydrogeochemical processes and the ground water-rock interactions that result in the various identifiable ground water facies that are present in the Central Oklahoma aquifer.

McBride (1978) described the fresh water section of the Garber-Wellington aquifer as generally enriched either in $\text{Ca}^{++}\text{-Mg}^{++}\text{-HCO}_3^-$ or $\text{Na}^+\text{-HCO}_3^-$, with intermediate waters locally high in $\text{Ca}^{++}\text{-SO}_4^-$ and $\text{Na}^+\text{-Cl}^-$. McBride also reviewed the occurrences of selenium and other trace elements and their possible sources. Scott (1988) described four distinct hydrochemical ground water facies ($\text{Ca}^{++}\text{-HCO}_3^-$, $\text{Na}^+\text{-HCO}_3^-$, $\text{Na}^+\text{-HCO}_3^-$ with intermediate SO_4^- , and $\text{Na}^+\text{-HCO}_3^-/\text{SO}_4^-$) in wells located in Cleveland County and reviewed seasonal effects on the saturation states of the carbonate phases using thermodynamics.

Parkhurst and others (1989) conducted a water quality study of the Central Oklahoma aquifer using information available through 1987. They evaluated regional variations in major ion chemistry, calculated summary statistics of the water quality, and mapped the locations of wells from which samples were taken that did not meet water quality standards. Using analyses from 711 Central Oklahoma aquifer wells, they found that 7% exceeded the U.S. Environmental Protection Agency's SMCL (secondary maximum contaminant level) of 250 mg/L of chloride. They also found that the analyses that exceeded this SMCL were distributed equally among the different geohydrologic categories of the Central Oklahoma aquifer (i.e.: alluvium and terrace deposit wells, shallow Garber-Wellington wells, medium depth Garber-Wellington wells, etc.).

Parkhurst (1992) described the following geochemical observations of the Central Oklahoma aquifer:

Generally, $\text{Ca}^{++}\text{-Mg}^{++}\text{-HCO}_3^-$ ground water is found in the unconfined part of the Garber Sandstone and Wellington Formation; $\text{Na}^+\text{-HCO}_3^-$ ground water is found in the confined part of the Garber Sandstone and Wellington Formation and in the Chase, Council Grove, and Admire Groups; SO_4^{--} -rich ground water is found in and, in places, below the Hennessey Group; and $\text{Na}^+\text{-Cl}^-$ ground water is found below the fresh water throughout the study unit.

Parkhurst (1992) stated that:

...in many parts of the shallow, unconfined aquifer, ground water is undersaturated with dolomite and calcite.... In all other parts of the aquifer the ground water is saturated with dolomite and calcite....

Parkhurst (1992) also stated the predominant geochemical reactions that control the ground water compositions are the following:

- 1) uptake of carbon dioxide.
- 2) dissolution of dolomite and, to a lesser extent, calcite.
- 3) cation exchange of calcium and magnesium onto clay minerals with the release of sodium.
- 4) dissolution of gypsum.
- 5) dispersion of fresh water with pre-existing brines.

Parkhurst (1992) also noted that: (1) the Br^-/Cl^- ratios of the natural saline ground waters of the Lower Garber-Wellington indicate that they are derived from seawater, and (2) similar Br^-/Cl^- ratios indicate that these deeper natural saline ground waters may be the source of the chloride in the fresh water. Christenson and Rea(1992)

studied the USGS data base used in this report to review ground water quality in the Oklahoma City urban area and the effect of urban land use on the quality of water in the Central Oklahoma aquifer. They noted the following: (1) there was a statistically significant difference in ground water quality between the urban and non-urban land uses (Table 2), (2) the urban area analyses showed elevated median levels of numerous organic and inorganic constituents, and (3) the elevated concentrations of chloride could not be attributed to one single source, and therefore the observed contamination probably results from multiple sources.

Data Base

The data used in this report is part of a pilot study of the National Water-Quality Assessment (NAWQA) Program. The data was collected and analyzed by the USGS between June, 1987 and September, 1990. This data base is unique for it included analyses for numerous trace elements. The purpose, scope, sampling network design, sampling procedures, and quality-assurance controls all are reviewed in detail in the report by Ferree and others (1991).

TABLE 2

MEDIAN VALUES OF SELECTED COMMON CONSTITUENTS,
NUTRIENTS, AND TRACE ELEMENTS IN SELECTED
HYDROGEOLOGICAL UNITS
(Modified from Christenson and Rea, 1992).

Constituents and Properties	Sampling Network			
	Urban	Permian Geologic Units		Alluvium and Terrace Deposits
		Shallow	Intermediate-Depth	
pH (standard units)	7.2	6.9	7.3	7.2
Oxygen, dissolved (mg/L)	5.2	4.9	6.9	2.3
Alkalinity, total (mg/L)	310.	259.	280.	258.
Calcium, dissolved (mg/L)	88.	42.	54.	55.
Magnesium, dissolved (mg/L)	42.	21.	26.	20.
Sodium, dissolved (mg/L)	72.	30.	30.	39.
Potassium, dissolved (mg/L)	1.9	1.1	1.0	1.3
Bicarbonate, total (mg/L)	378.	315.	342.	315.
Carbonate, total (mg/L)	0.	0.	0.	0.
Sulfate (mg/L)	37.	18.	22.	34.
Chloride (mg/L)	76.	19.	20.	22.
Fluoride, dissolved (mg/L)	0.2	0.3	0.3	0.3
Nitrite plus nitrate (mg/L)	2.0	0.75	0.93	0.87
Arsenic, dissolved ($\mu\text{g/L}$)	1.	<1.	1.	<1.
Barium, dissolved ($\mu\text{g/L}$)	150.	180.	240.	230.
Cadmium, dissolved ($\mu\text{g/L}$)	<1.	<1.	<1.	<1.
Chromium, dissolved ($\mu\text{g/L}$)	<5.	<5.	<5.	<5.
Copper, dissolved ($\mu\text{g/L}$)	<10.	<10.	<10.	<10.
Iron, dissolved ($\mu\text{g/L}$)	16.	5.	3.	11.
Lead, dissolved ($\mu\text{g/L}$)	<10.	<10.	<10.	<10.
Manganese, dissolved ($\mu\text{g/L}$)	1.	<1.	<1.	6.
Mercury, dissolved ($\mu\text{g/L}$)	<0.1	<0.1	<0.1	<0.1
Selenium, dissolved ($\mu\text{g/L}$)	1.	<1.	<1.	<1.
Silver, dissolved ($\mu\text{g/L}$)	<1.	<1.	<1.	<1.
Gross-alpha particle activity (pCi/L)	9.1	3.4	5.0	3.1
Radon, total (pCi/L)	200.	150.	120.	200.
Uranium, dissolved (pCi/L)	3.05	1.09	0.96	1.51
Number of wells in network	41	25	35	42

mg/L, milligrams per liter.
 $\mu\text{g/L}$, micrograms per liter.
 pCi/L, picocuries per liter.

The data base consists of chemical analyses from water wells in four different sampling networks: a "low-density bedrock survey network," a "low-density alluvium and terrace survey network," a "targeted urban (Oklahoma City) survey network," and a "geochemical survey network." The "low-density bedrock survey network" was comprised of 25 shallow wells (less than 100 feet in depth), 35 intermediate wells (100 to 300 feet in depth), and 27 deep wells (greater than 300 feet in depth). The "low-density alluvium and terrace survey network" was comprised of 42 wells located along fluvial systems. The "targeted urban survey network" was comprised of 41 wells in the urban area of Oklahoma City. The "geochemical survey network" was comprised of 37 wells that were selected due to their locations along suspected flow paths. Often well pairs, consisting of a deep well and a shallow well, were tested together at the same location in the "geochemical survey network." The locations of all of the wells in these four networks are shown respectively in Figures 3, 4, 5, and 6.

With the exception of the "geochemical survey network," the well data was gathered with an attempt to obtain a random and unbiased sampling of the aquifers in these networks. It is important to note, however, that only wells that were operational with installed pumps were tested. Should a known water-quality problem exist in an area, it is unlikely that an operational well still would be present at

Figure 3. Locations of Wells Sampled in the "Low-Density Bedrock Survey Network" (from Ferree and others, 1992).

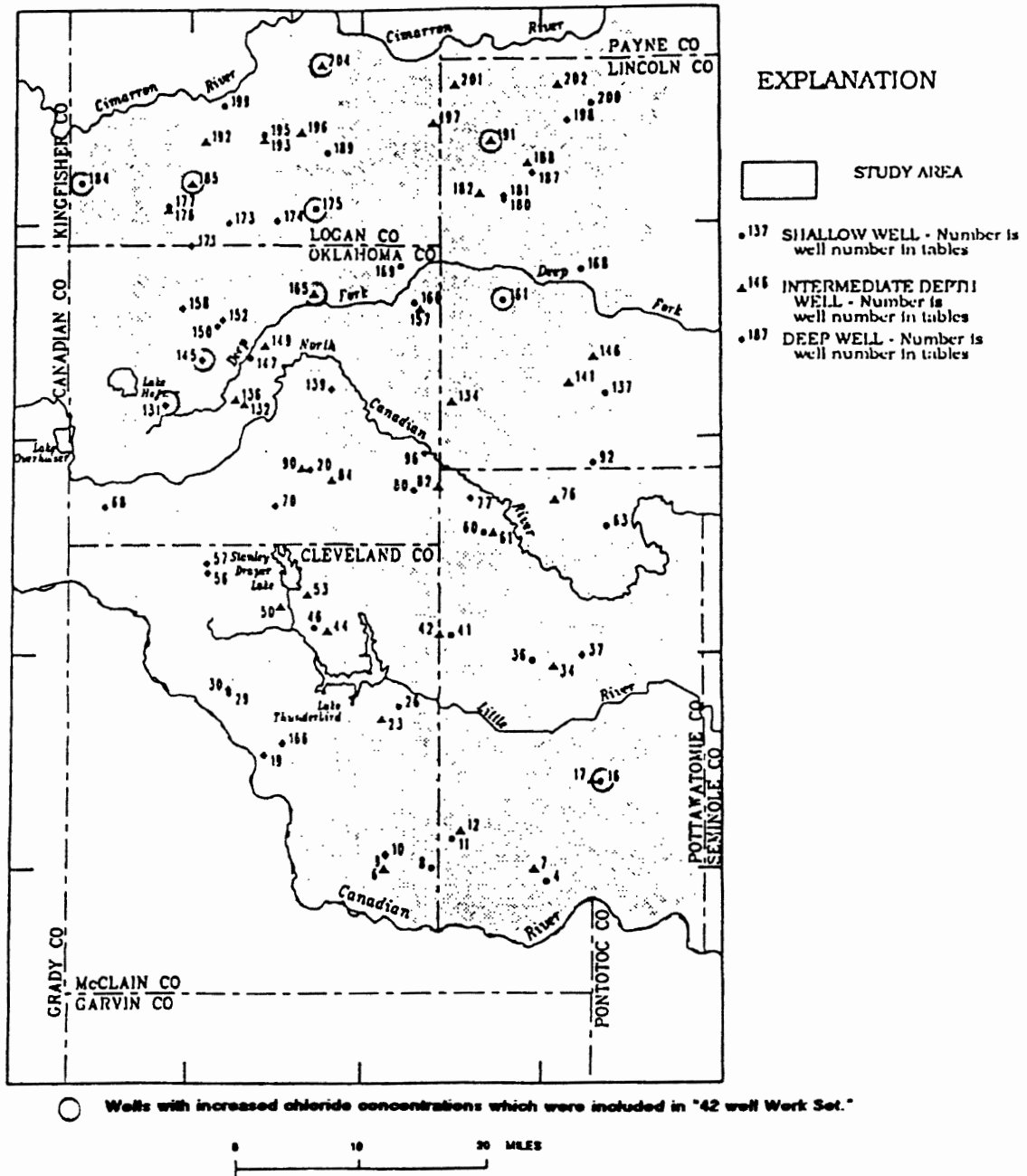


Figure 4. Locations of Wells Sampled in the "Low-Density Alluvium and Terrace Survey Network" (from Ferree and others, 1992).

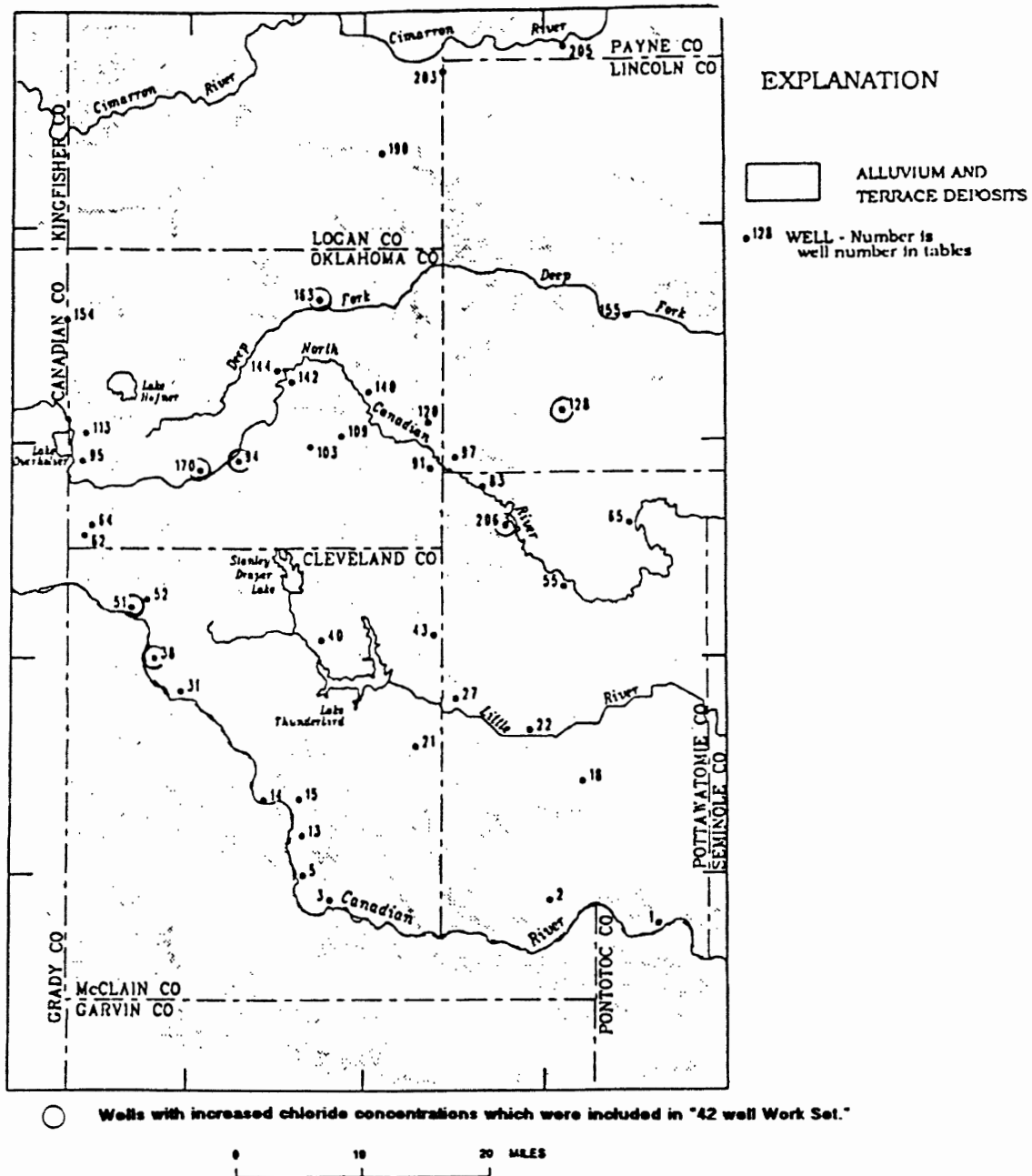
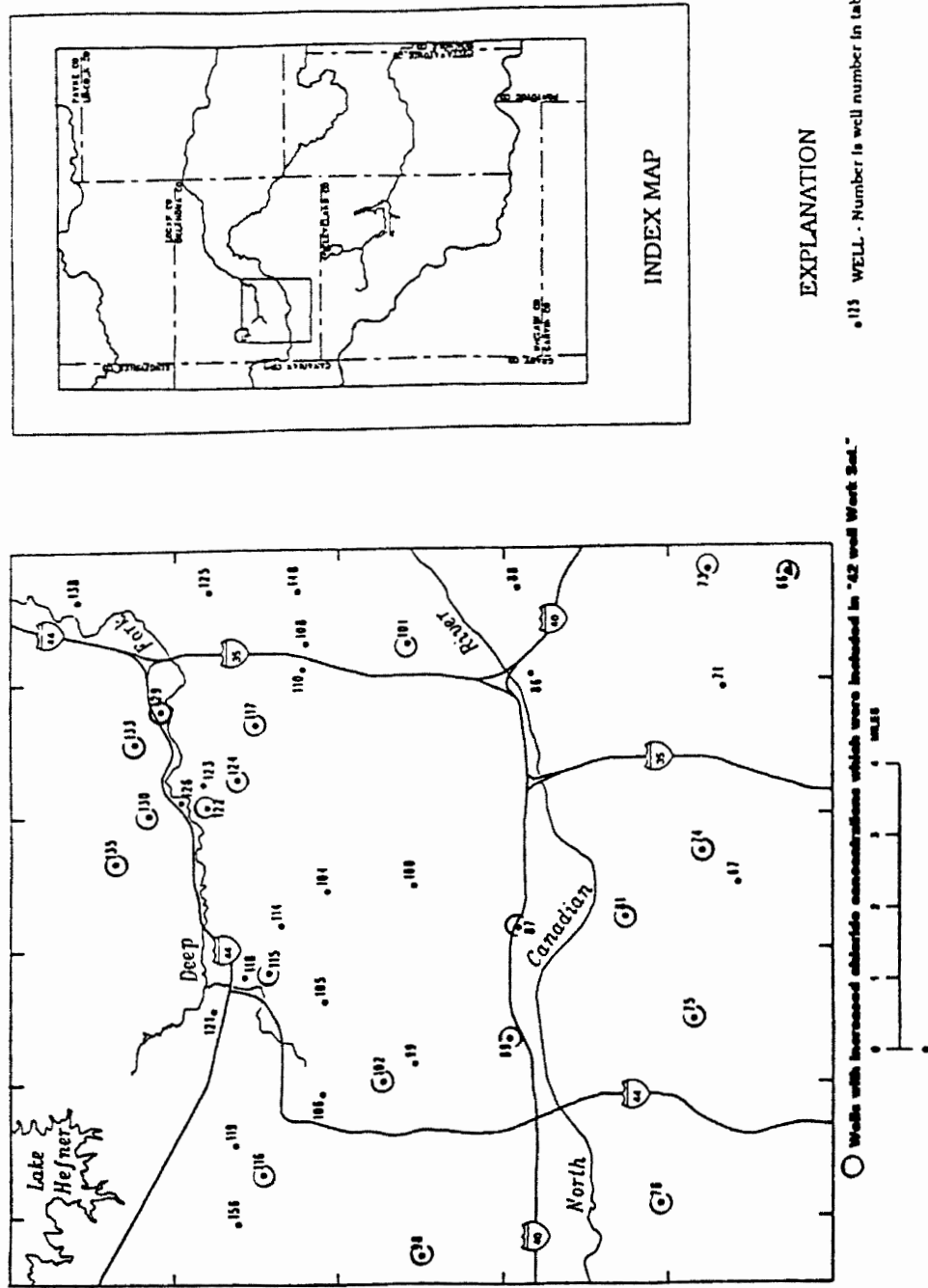


Figure 5. Locations of Wells Sampled in the "Targeted Urban Survey Network" (from Ferree and others, 1992).



EXPLANATION

○ 113 WELL - Number is well number in tables

○ Wells with increased nitrate concentrations which were included in "42 well Work Set."

that location. Therefore, there is a bias in the data toward wells of better water quality (lower amounts of TDS, chloride, SO_4^- , etc.).

Each analysis included a large suite of categories: physical properties, common constituents, nutrients, trace elements, radionuclides, and organic constituents (Appendix I).

Potential Sources of High Chloride Concentrations

Richter and Kreitler (1991) interpreted that there are seven major sources that can cause increased chloride concentrations on a regional scale. These sources are: (1) oil field brines, (2) deeper natural saline ground waters, (3) solution of natural halite, (4) saline seeps, (5) agricultural activities of irrigation and fertilization, (6) road salts, and (7) sea-water intrusion. The geographic location of the study unit eliminates sea-water intrusion as a possible source for consideration in this study.

Oil Field Brines

Oil field brine contamination is one of the primary topics of concern due to the large amount of oil field activity that has taken place in Oklahoma. Oil and gas exploration has been active in Oklahoma since the first commercial oil well was discovered in Oklahoma in 1897 (Oklahoma Historical Society, 1993). The largest field in the study unit is the Oklahoma City Field which was

discovered by the Indian Territory Illuminating Oil Company and Foster Petroleum Company #1 Oklahoma City well (SE of Section 24-T11N-R3W) in 1928. The rapid development of this giant oil field, a field with recoveries in excess of 500,000,000 barrels of oil, continued through the 1930's. The field eventually covered over a 32 square mile area. Oil field drilling and operations have continued in this area, and to date over 13,000 oil and gas wells have penetrated the Central Oklahoma aquifer (Christenson and Rea, 1992).

There are numerous mechanisms by which oil field brine contamination can occur. Seepage from a surface waste pit, defective well casing, defective well plugging, water-flooding operations, or improper brine disposal can cause contamination of a fresh water aquifer by oil field brines. During the initial period of oil exploration in Oklahoma, there was little regulation of the industry. Oil field brines commonly were spread on the land surface or placed in unlined surface pits. Today strict regulations are required to protect the fresh water aquifers. However, a large percentage of the wells drilled in the study unit pre-date these strict regulations.

Typically, most oil field brines have high concentrations of chloride, sodium, calcium, and magnesium, and show signs of reverse softening ($\text{Na}^+ < \text{Cl}^-$, moles). The number of hydrocarbon-producing zones within the study unit precludes any attempt to set median chemical concentrations

for the waters of individual formations as over 30 zones were productive in the Oklahoma City Field. Combining all of the producing formations, Parkhurst and Christenson (1987) derived median concentrations for the major ions in brines from typical oil and gas wells in Oklahoma County (Table 3). In addition, eight analyses of oil field brines from oil and gas wells located within this region were acquired through the Oklahoma Geological Survey from the Natural Resource Information System (NRIS) data base. This data set contained analyses which included numerous trace elements (Appendix II). Graphs of each trace element versus chloride were done to determine if linear relationships existed (Appendix III). Where no linear relationship existed, a mean value for the data set was calculated. Where a linear relationship was present, a best fit line was constructed. From these best fit lines, estimated concentrations of the trace elements at chloride concentrations of 146,0000 mg/L were derived (Table 4). These values were used to determine both mixing relationships and geochemical processes that have occurred as a result of oil field brines mixing with the fresh waters of the Central Oklahoma aquifer.

TABLE 3

MEDIAN CONCENTRATIONS OF MAJOR IONS OF BRINES
 FROM OIL AND GAS WELLS IN OKLAHOMA COUNTY
 From Christenson and Rea (1992) and
 Parkhurst and Christenson (1987)

pH	6.3
Alkalinity	46.4 mg/L as CaCO ₃
Ca ⁺⁺	13,000 mg/L
Mg ⁺⁺	2,510 mg/L
Na ⁺	75,500 mg/L
Cl ⁻	146,000 mg/L
SO ₄ ⁼	232 mg/L
Total dissolved solids	237,000 mg/L

TABLE 4

ESTIMATED MEAN CONCENTRATIONS OF TRACE ELEMENTS
 OF BRINES FROM OIL AND GAS WELLS IN LINCOLN,
 LOGAN, AND OKLAHOMA COUNTIES

(at a chloride concentration of 146,000 mg/L)

Strontium	1150 mg/L
Lithium	14 mg/l
Barium	5.45 mg/l
Boron	5.71 mg/L
Bromide	635 mg/L

Derived from data from NRIS data base.
 Strontium, lithium, boron, and bromide mean values were
 derived from best fit lines on bivariate plots of the
 trace element versus chloride. See Appendixes II and
 III.

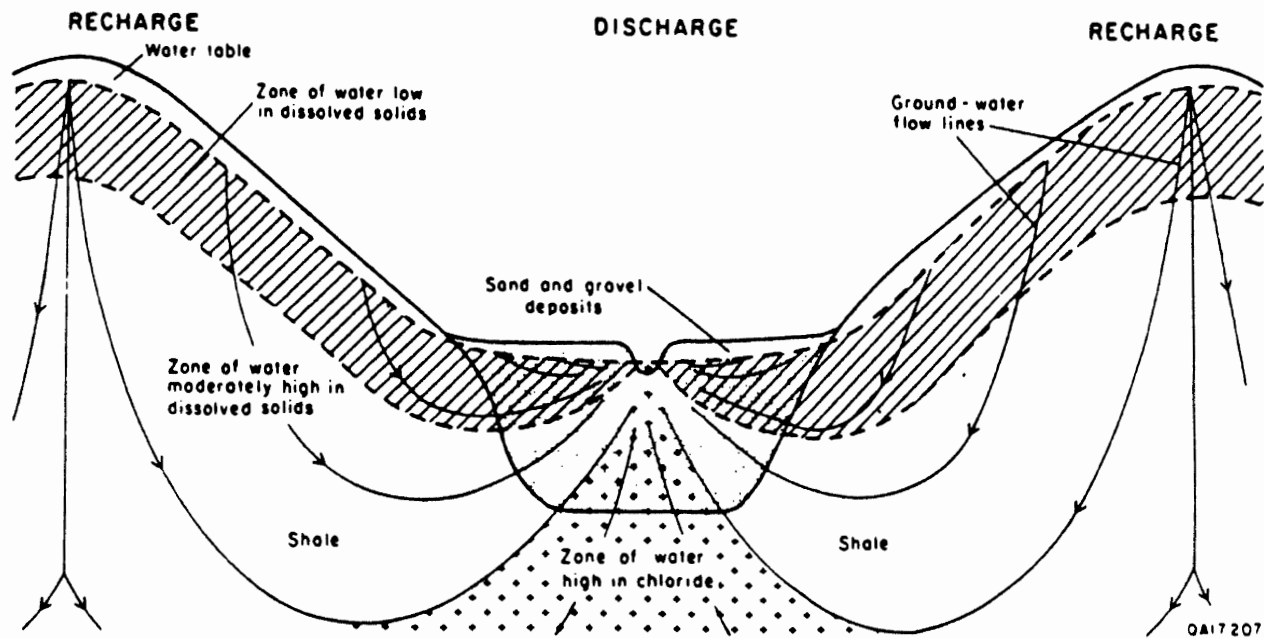
Deeper Natural Saline Ground Waters

For this report, deeper natural saline ground water will refer to the natural saline ground water which underlies the fresh water in the Central Oklahoma aquifer and is defined as having greater than 5,000 mg/L of total dissolved solids. As described previously, the water in the Central Oklahoma aquifer increases in salinity with depth. The depth to that transition zone which separates the shallower fresh water from the deeper saline water varies from 100 to 1000 feet from the surface in the study unit.

Contamination by the deeper natural saline ground water occurs because of both anthropogenic and nonanthropogenic activities. Pumping-induced mixing (upconing) and the upward migration of natural saline ground waters along boreholes drilled through the fresh water section into the saline section of the aquifer are both anthropogenic mechanisms by which this form of contamination can occur.

Several analyses from shallow wells located along the river systems show a deterioration of water quality. This deterioration appears in part to be the result of the natural saline ground water of the Central Oklahoma aquifer moving upward along natural flow paths and mixing with the fresh water portion of the aquifer as they discharge into the river system (Figure 7). Analysis 163 is an example of this type of nonanthropogenic activity which causes elevated chloride levels. Analyses 163 and 165 are from two wells

Figure 7. Relationship between Ground Water Quality and Discharge Areas
(from Kantrowitz, 1970).



located near each other along the Deep Fork River. However, analysis 163 is from an alluvium well that is 60 feet deep, and analysis 165 is from a bedrock well that is 220 feet deep. Both analyses have very similar water compositions including elevated chloride levels of greater than 480 mg/L, indicating that locally a gaining stream system is resulting in the mixing of the deeper natural saline ground water with the shallower fresh water.

As was done with the oil field brines, an attempt was made to determine a typical end member chemistry composition of the deeper natural saline ground water. Very little data is available on the chemistry of the natural saline ground water of the Central Oklahoma aquifer from which to assess the typical concentration ranges for the major ions and trace elements. Schlottmann and Funkhouser (1991) reported water sample analyses acquired through core hole data from two sands in the deeper part of the Garber-Wellington. The collection of these samples was done in a manner to prevent them from mixing with other waters. Therefore, these two samples represent the true water chemistry of these zones. These two analyses had TDS values of greater than 5,000 mg/L with very high concentrations of sodium and sulfate, variable amounts of chloride, and elevated levels of the trace elements bromide, boron, and fluoride (Table 5). Since these samples were taken immediately below the fresh water, it is assumed that these analyses represent the water

TABLE 5

MAJOR CONSTITUENTS AND SOME TRACE ELEMENTS OF TWO
ANALYSES FROM CORED TEST HOLES DRILLED IN THE
CENTRAL OKLAHOMA AQUIFER
(Modified from Schlottmann and Funkhouser, 1991).

WELL	DEPTH feet	COND	PH	TEMP	O2 mg/L	HARDNESS mg/L	SUM										
							ALK mg/L	OF mg/L	CON mg/L	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	HCO3 mg/L	CO2 mg/L	SO4 mg/L	Cl mg/L
NOTS 5 OF 3-8N-3E	131	11600	7.9	18.0	0.1	240	156	9783	29	40	3100	7	190	0	5100	1300	17
NOTS 5 OF 3-8N-3E	183	8210	8.2	18.0	0.1	140	186	7442	19	22	2300	5	227	0	4700	150	19

WELL	TRACE ELEMENTS					
	F mg/L	Br mg/L	B ug/L	Bo ug/L	Li ug/L	Sr ug/L
NOTS 5 OF 3-8N-3E	2.30	4.10	<100	7400	100.00	3600
NOTS 5 OF 3-8N-3E	2.30	0.57	<100	6700	80.00	2100

chemistry of the upper part of the saline water section of the Garber-Wellington aquifer and therefore will be used as representative end members.

In addition to these core hole analyses, analyses 128 and 159 in the USGS data base showed very unusual chemical characteristics when compared to the other water analyses. Their chemical compositions are very similar to the two above-mentioned core hole analyses. In addition, these analyses did not contain detectable tritium (less than .3 picocuries per liter). The presence of detectable tritium has been used to infer that post-1952 recharge waters are entering a subject well (Fetter, 1980). The lack of detectable tritium in analyses 128 and 159 indicates that the waters from these two analyses have not mixed with any meteoric water which has entered the Central Oklahoma aquifer since the late 1950's-early 1960's. Though this does not prove that analyses 128 and 159 are representative of a possible end member for the natural saline ground water, it does signify that neither analysis is located in a position where active recharge is occurring. Sample 159 was taken from a well that is 600 feet deep, further supporting the possibility that the analysis could be representative of a natural saline ground water end member. Sample 128 was taken from a well that is 54 feet deep, and as such makes this conclusion more suspect. It should be noted, however, that sample 128 was taken from an alluvium well located along the eastern edge of the Central Oklahoma aquifer. As

stated earlier, near the eastern edge of the study unit the depth to the base of the fresh water zone is as shallow as 100 feet. In addition, as stated earlier, there are gaining stream systems present in areas of the study unit that move the deeper natural saline ground water upward along flow paths near fluvial systems. These two factors could result in analysis 128 being a sample close in composition to the true end member composition.

Though this data is limited, these four analyses are considered examples of natural saline ground water end members. The two core hole analyses are shown as such on all graphs.

Solution of Natural Halite

The solution of naturally occurring halite is a common cause of elevated chloride levels in aquifers. The solution of halite by a fresh water will produce a water with a somewhat predictable composition. Depending on the depositional history of the halite, it often will be associated with other chloride salts and evaporites. Halite dissolution brines characteristically will show Na^+/Cl^- and $\text{Ca}^{++}/\text{SO}_4^{--}$ molar ratios that are close to unity and Br^-/Cl^- weight ratios that are less than 10×10^{-4} . Since the dissolution of halite frequently is associated with other

evaporites, the resulting water compositions commonly have high $\text{SO}_4^{2-}/\text{Cl}^-$ ratios.

Halite is common in western Oklahoma, where halite dissolution is indicated by salt springs and shallow saline ground water as documented by Leonard and Ward (1962) and the Oklahoma Water Resources Board (1975). However, no halite has been described in the study unit.

Johnson and others (1977) summarized the requirements necessary for the dissolution of halite as being: (1) a supply of water undersaturated with respect to halite, (2) a deposit of salt through which or against which the fresh water flows, (3) an outlet that will accept the resultant brine, and (4) hydrostatic head to cause the flow of water through the system. The absence of documented halite in this area eliminates natural halite solution as a possible source of the elevated chloride levels in this study unit.

Saline Seeps

Saline seeps are defined by Bahis and Miller (1975) as "recently developed saline soils in nonirrigated areas that are wet some or all of the time, often with white salt crusts, and where crop or grass production is reduced or eliminated." The evaporation from a shallow water table causes increased levels of salinity in the ground water. Richter and Kreitler (1991) stated that the following conditions are required for the development of a saline seep: (1) excess percolation recharge water, (2) soluble

soil or aquifer minerals, (3) low-permeability unit at a relatively shallow depth, (4) an internally drained flow system, and (5) evaporation.

Saline seep chemistry will reflect an evaporation trend on constituent graphs. At low salinities, the increased chloride levels are characterized by more constant constituent ratios of major ions such as $\text{Ca}^{++}/\text{Cl}^-$, $\text{Mg}^{++}/\text{Cl}^-$, or $\text{SO}_4^{--}/\text{Cl}^-$. With increasing salinity, mineral precipitation will change these ratios as carbonates and sulfates begin to form.

Most of the reported cases of saline seeps have been in the Northern Great Plains states of Montana, North Dakota, and South Dakota. Saline seeps also have been reported in the Central Rolling Red Plains of Texas. Berb and others (1987) described the effect of saline seeps in Harper County, Oklahoma.

The study unit has higher amounts of annual precipitation than most areas where saline seeps have been documented. In addition, water tables are typically at depths greater than 10 feet within the study unit. These factors indicate that this source of elevated chloride levels is not a major factor in the study unit.

Agricultural Activities

The contamination of ground water with chloride can be associated with several agricultural activities. Irrigation can deteriorate ground water quality in two ways. As discussed earlier, heavy pumpage associated with irrigation wells can cause the upconing of deeper natural saline ground waters. In addition, often the return flow associated with irrigation becomes concentrated in chloride by evapotranspiration, solution minerals, and solution of agricultural residues such as fertilizers, herbicides, and insects which are leached from the soil and then concentrated in the water table. Aside from irrigation, large feedlot operations can produce enough animal waste to cause elevated chloride concentrations in the ground water. Though irrigation and feedlot operations are present in the study unit, neither could be considered common practice. When present, they are normally small in scale when compared to their use in other parts of the country.

Typically, elevated chloride levels due to agricultural activities are associated with increased levels of nitrate and, to a lesser extent, ammonia and potassium. Nitrate and ammonia levels were slightly higher in several of the analyses which showed elevated chloride concentrations (Figures 8a and 8b). However, these higher levels of nitrate and ammonia are also scattered among all of the analyses (Figures 9a and 9b). Christenson and Rea (1992)

FIGURE 8a. XY-Graph: Nitrite+Nitrate vs Cl

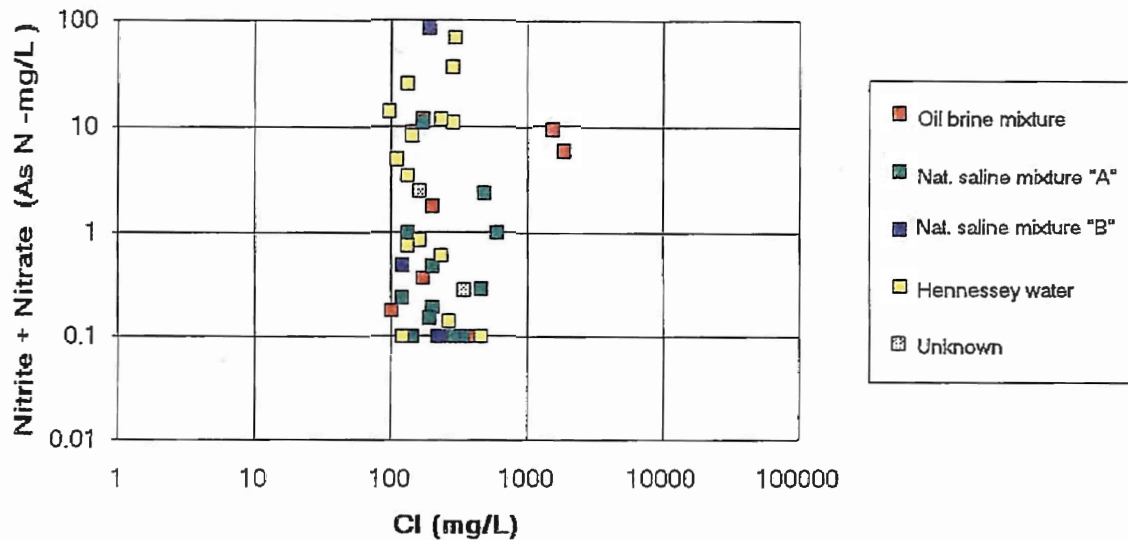


FIGURE 8b. XY- Graph: Ammonia+Organic Nitrogen vs Cl

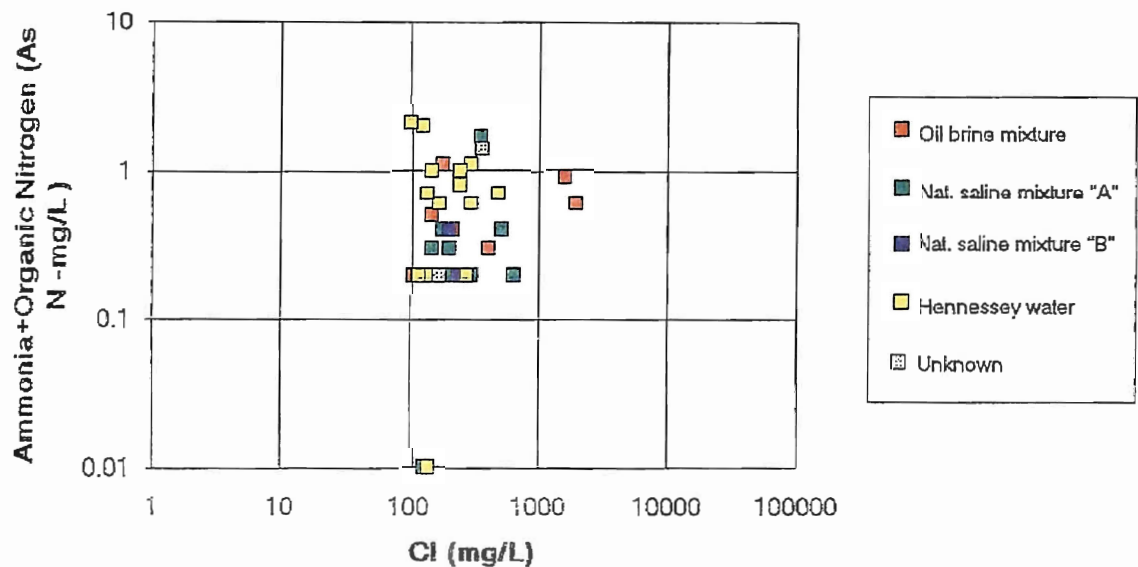


FIGURE 9a. XY - Graph: Nitrite+Nitrate vs Cl
(all 202 wells)

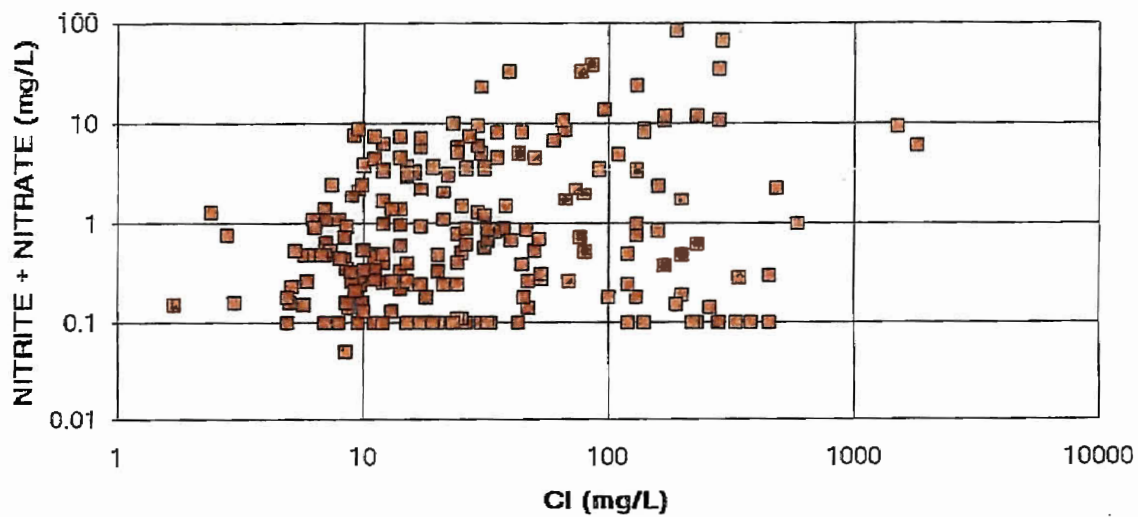
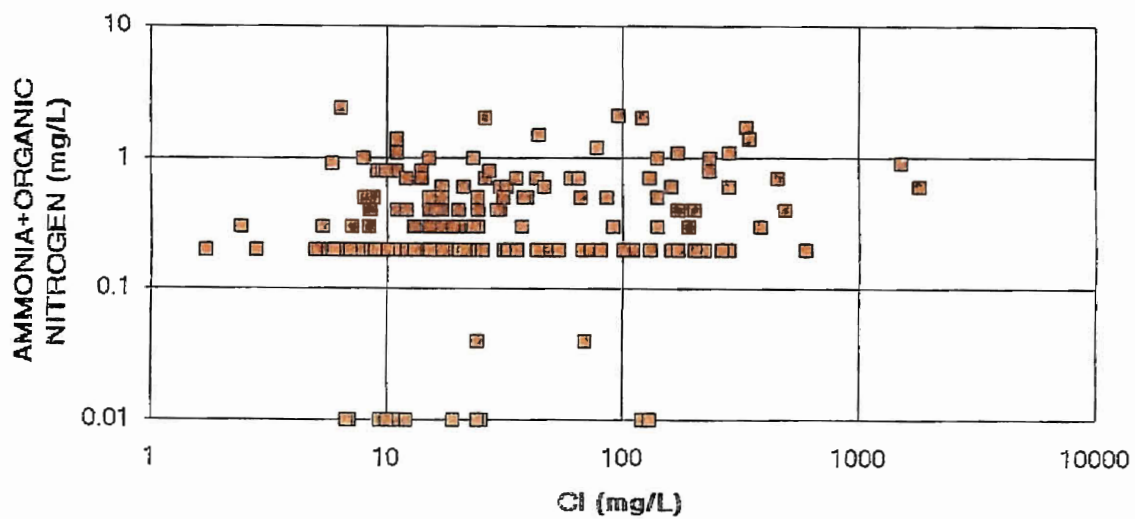


FIGURE 9b. XY- Graph: Ammonia+Organic Nitrogen vs Cl
(all 202 wells)



calculated the median concentration levels of nitrate in the "targeted urban survey network" and for the shallow wells of the "low-density bedrock survey network" as being 2.0 and 0.75 mg/L, respectively. The median concentration value of nitrate in the 42 wells in this study which showed higher chloride levels was 0.92 mg/L. Therefore, while agricultural activities might have contributed to the elevated chloride levels in a few cases, this source does not appear to be a primary one.

Road Salts

The dissolution of road salts is a major concern where the practice of de-icing roads is done for safer travel. Numerous cases have been reported in the northern United States where elevated chloride levels were attributed to the use of road salts. NaCl and CaCl₂ are the most commonly used road salts. Reported compositions of road salts used in Oklahoma (Richter and Kreitler, 1991 and Christian and Rea, 1992) indicate that NaCl type road salt has been the only one used significantly within the study unit. Geochemically, brines derived from a NaCl type road salt would have compositions with a Na⁺/Cl⁻ molar ratio close to unity and a low Br⁻/Cl⁻ ratio.

Table 6 shows the amount of road salt that has been used in each state and the reported contamination cases attributed to its use (Richter and Kreitler, 1991). It

TABLE 6

REPORTED USE* (IN TONS) OF ROAD SALTS AND
 ABRASIVES DURING 1966-67, 1981-82, AND
 1982-83 (FROM RICHTER AND KREITLER,
 1991).

State	NaCl			CaCl ₂	Contamination
	1966-67	1981-82	1982-83	1966-67	
Arkansas	1,000	2,510	856	-	
California	11,000	13,600	-	-	
Colorado	7,000	22,460	10,896	-	yes
Connecticut	101,000	103,201	51,934	3,000	yes
Delaware	7,000	8,913	7,053	1,000	yes
Idaho	1,000	11,000	11,000	-	
Illinois	249,000	304,184	206,000	10,000	yes
Indiana	237,000	313,365	116,650	6,000	yes
Iowa	54,000	64,000	60,400	2,000	
Kansas	25,000	35,490	31,630	2,000	
Kentucky	60,000	73,275	32,960	1,000	
Maine	99,000	51,676	49,202	1,000	yes
Maryland	132,000	155,758	82,499	1,000	yes
Massachusetts	190,000	262,000	178,500	6,000	yes
Michigan	409,000	397,000	229,000	7,000	yes
Minnesota	398,000	118,587	127,957	14,000	
Missouri	34,000	90,963	75,111	3,000	
Montana	4,000	2,817	3,245	-	
Nebraska	10,000	22,221	24,899	-	
Nevada	4,000	8,500	9,831	-	
New Hampshire	118,000	138,692	93,813	-	yes
New Jersey	51,000	138,692	35,700	6,000	yes
New Mexico	7,000	16,000	23,000	-	
New York	472,000	443,000	300,000	5,000	yes
North Carolina	17,000	45,264	36,573	2,000	yes
North Dakota	2,000	8,222	8,719	1,000	yes
Ohio	511,000	401,285	184,341	12,000	yes
Oklahoma	7,000	9,300	18,770	-	
Oregon	1,000	-	456	-	
Pennsylvania	592,000	500,010	231,000	45,000	yes
Rhode Island	47,000	56,280	29,297	1,000	yes
South Dakota	2,000	4,345	3,697	1,000	
Texas	3,000	-	-	-	
Utah	28,000	79,540	79,720	-	
Vermont	89,000	71,904	65,647	1,000	yes
Virginia	77,000	178,500	95,000	22,000	yes
Washington	2,000	10,000	7,500	-	
West Virginia	55,000	90,636	52,709	9,000	yes
Wisconsin	225,000	236,790	229,803	3,000	yes
Wyoming	1,000	5,000	6,340	-	

* States not included are due to unavailability of data.

should be noted that there has not been a reported case of contamination of a fresh water aquifer in Oklahoma, Kansas, Missouri, Arkansas, Texas, or New Mexico due to road salt use. This problem has been limited primarily either to far northern states or to those states located in major mountain ranges.

Christenson and Rea (1992) reported elevated levels of chloride in the urban area of Oklahoma City. However, the lack of correlatable patterns between major highway systems, wells that exhibited increased chloride levels, and Br^-/Cl^- and Na^+/Cl^- ratios typical of road salt brines indicate that this source is not a major contributor to these elevated chloride levels in the study unit.

CHAPTER III

DISCUSSION

Method of Analysis

From the original USGS data base of 202 water wells, 42 wells were selected to be reviewed in detail (Table 7 and Figure 10). These wells were selected because they showed signs of reverse softening which often is indicative of a brine mixing with a fresh water aquifer, or they exhibited elevated chloride concentrations. The wells selected had at least one of the following characteristics:

Number of wells:	Characteristics:
19 wells	$\text{Na}^+ \leq \text{Cl}^-$ (moles) and $\text{Cl}^- > 85$ mg/L
23 wells	$\text{Cl}^- > 107$ mg/L (3 meq/L)

These 42 wells became the "Work Set." The WATEVAL Computer Program (Hounslow and Goff, 1991) was used to indicate possible data analysis problems within the "Work Set" analyses. This program checks the data using ion balance equations and some general "rule of thumb" relationships pertaining to commonly occurring constituents. It also compares calculated and measured values of these

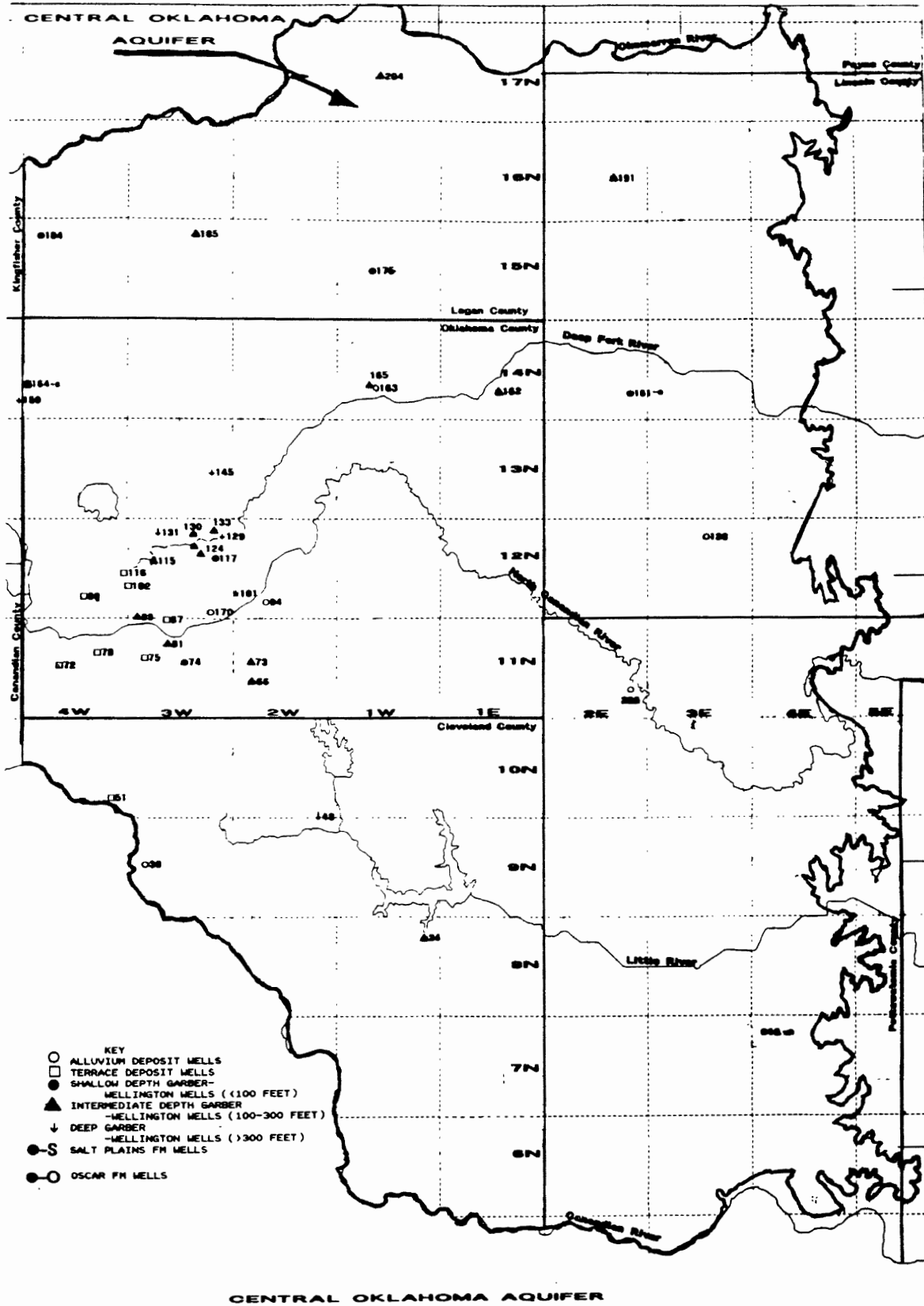
TABLE 7

"Work Set" Selected for Review

$\text{Na}^+ \leq \text{Cl}^-$ and $\text{Cl}^- > 85 \text{ mg/L}$, or $\text{Cl}^- > 107 \text{ mg/L}$

WELL ID #	LOCATION	COUNTY	WELL#
353915097403901	14N-05W-25 DDC 1	CANADIAN	159
351106097155201	08N-01W-12 BCB 1	CLEVELAND	24
351501097325301	09N-03W-18 DDA 1	CLEVELAND	38
351729097221302	10N-02W-36 CCC 2	CLEVELAND	48
351832097345101	10N-04W-25 CBC 1	CLEVELAND	51
353207096583301	12N-03E-10 BAB 1	LINCOLN	128
353938097031101	14N-02E-26 ADD 1	LINCOLN	161
355039097041401	16N-02E-22 DAA 1	LINCOLN	191
354605097185901	15N-01W-21 BBA 1	LOGAN	175
354755097392001	15N-04W-05 CCC 1	LOGAN	184
354758097295201	15N-03W-03 DDD 1	LOGAN	185
355614097183001	17N-01W-21 ACB 1	LOGAN	204
352433097262401	11N-02W-20 CCB 1	OKLAHOMA	66
352527097380501	11N-04W-16 CCB 1	OKLAHOMA	72
352531097262101	11N-02W-17 CBC 1	OKLAHOMA	73
352535097303301	11N-03W-15 CBA 1	OKLAHOMA	74
352541097330301	11N-03W-18 ADC 1	OKLAHOMA	75
352605097354801	11N-04W-14 BBA 1	OKLAHOMA	78
352631097313101	11N-03W-09 CBA 1	OKLAHOMA	81
352749097314101	11N-03W-04 BBB 1	OKLAHOMA	87
352755097332002	12N-03W-31 DCC 1	OKLAHOMA	89
352844097254001	12N-02W-29 DDC 1	OKLAHOMA	94
352859097363501	12N-04W-27 DBC 1	OKLAHOMA	98
352910097272501	12N-02W-30 BCC 1	OKLAHOMA	101
352927097335801	12N-04W-25 AAD 1	OKLAHOMA	102
353051097322001	12N-03W-17 CAA 1	OKLAHOMA	115
353055097352201	12N-04W-14 ACD 1	OKLAHOMA	116
353101097283701	12N-03W-14 ADD 1	OKLAHOMA	117
353136097295101	12N-03W-10 DAC 1	OKLAHOMA	122
353141097293001	12N-03W-14 BBA 1	OKLAHOMA	124
353210097282401	12N-03W-12 BBA 1	OKLAHOMA	129
353219097295801	12N-03W-03 DCD 1	OKLAHOMA	130
353223097320501	12N-03W-05 DCA 1	OKLAHOMA	131
353229097285301	12N-03W-02 DBD 1	OKLAHOMA	133
353532097285601	13N-03W-23 ABD 1	OKLAHOMA	145
353947097111501	14N-01E-27 BDA 1	OKLAHOMA	162
353958097185001	14N-01W-28 BBA 1	OKLAHOMA	163
354007097395401	14N-04W-19 CDD 1	OKLAHOMA	164
354008097190901	14N-01W-20 DDD 1	OKLAHOMA	165
352805097290101	12N-03W-35 DBC 1	OKLAHOMA	170
350603096550801	07N-04E-07 ABA 1	POTTAWATOMIE	16
352410097031401	11N-02E-25 BBC 1	POTTAWATOMIE	206

Figure 10. Location of "Work Set" Wells within Study Unit



properties. All checks indicated reasonable analyses. This study then utilized geochemical relationships along with physical and geographical aspects to identify and differentiate among the various sources of chloride contamination in the study unit. Graphical techniques were used to illustrate chemical trends which might help to identify these sources. The steps involved in the analysis of the above data and the order in which they are reviewed in this study are as follows:

Step 1:

The first step was the development of the key graphic relationships. All major cations, major anions, and trace elements were plotted against chloride, sulfate, and bromide in an attempt to reveal mixing relationships that could be useful in determining the source of the higher chloride concentrations. In addition, previously published graphic relationships were employed to help in this differentiation. The graphic relationships reviewed in this paper are limited to those which were most significant by consistently differentiating among the sources and to those which indicated the occurrence of geochemical reactions (ion exchange, precipitation, and/or dissolution of minerals).

Step 2:

With the above information, new geochemical relationships were developed to assist in the determination of the elevated chloride source.

Step 3:

The physical and geographical characteristics of each well were considered in this study to aid in the determination of the source of the high chloride concentration. Individual well data such as the depth of the well and the producing aquifer was reviewed. In addition, the location of the well relative to locations of anthropogenic sources of contamination (presence or absence of oil field activity, land use, etc.) also was considered.

**Major Sources Interpreted to Have Caused
the Elevated Chloride Concentrations**

Three major sources were interpreted to have caused the elevated chloride concentrations in the study unit. Table 8 summarizes the reviewed wells and the interpreted primary sources of their elevated chloride concentrations. All but two of the wells could be categorized under the following groups. The three major sources are:

Oil Field Brines

Oil field brines have mixed with the fresh waters of the Central Oklahoma aquifer. These oil field brine/fresh water mixtures will be referred to as "oil brine mixtures."

TABLE 8
 INTERPRETATION OF THE SOURCES OF THE ELEVATED
 CHLORIDE CONCENTRATIONS IN THE
 "WORK SET" WELLS

WELLS	SOURCE	Cl ⁻ (mg/L)
73	OIL BRINE MIXTURE	1800
74	OIL BRINE MIXTURE	1500
94	OIL BRINE MIXTURE	380
122	OIL BRINE MIXTURE	200
66	OIL BRINE MIXTURE	170
124	OIL BRINE MIXTURE	170
81	OIL BRINE MIXTURE	140
130	OIL BRINE MIXTURE	100
165	NATURAL SALINE MIXTURE -"A"	590
163	NATURAL SALINE MIXTURE -"A"	480
24	NATURAL SALINE MIXTURE -"A"	450
38	NATURAL SALINE MIXTURE -"A"	330
161	NATURAL SALINE MIXTURE -"A"	280
48	NATURAL SALINE MIXTURE -"A"	200
131	NATURAL SALINE MIXTURE -"A"	200
145	NATURAL SALINE MIXTURE -"A"	190
175	NATURAL SALINE MIXTURE -"A"	170
206	NATURAL SALINE MIXTURE -"A"	140
115	NATURAL SALINE MIXTURE -"A"	130
162	NATURAL SALINE MIXTURE -"A"	120
159	NATURAL SALINE MIXTURE -"B"	230
128	NATURAL SALINE MIXTURE -"B"	220
191	NATURAL SALINE MIXTURE -"B"	190
185	NATURAL SALINE MIXTURE -"B"	120
170	HENNESSEY WATER	450
72	HENNESSEY WATER	290
184	HENNESSEY WATER	280
117	HENNESSEY WATER	280
89	HENNESSEY WATER	260
87	HENNESSEY WATER	230
78	HENNESSEY WATER	230
101	HENNESSEY WATER	160
116	HENNESSEY WATER	140
102	HENNESSEY WATER	130
164	HENNESSEY WATER	130
133	HENNESSEY WATER	130
129	HENNESSEY WATER	130
51	HENNESSEY WATER	120
75	HENNESSEY WATER	110
98	HENNESSEY WATER	96
16	UNKNOWN SOURCE	340
204	UNKNOWN SOURCE	160

Deeper Natural Saline Ground Waters

Deeper natural saline ground waters have mixed with the fresh water of the Central Oklahoma aquifer. These natural saline ground water/fresh water mixtures will be referred to as "natural saline mixtures." The compositions of the natural saline mixtures vary from a high saline water with minor sulfate to a high $\text{Na}^+\text{-SO}_4^-$ saline water with minor chloride. The end member analyses reviewed in the Deeper Natural Saline Ground Waters section (page 27) of this report appear to be representative of the high $\text{Na}^+\text{-SO}_4^-$ variety. No end member analysis from the high $\text{Na}^+\text{-Cl}^-$ variety could be located.

These natural saline ground water/fresh water mixtures will be referred to as "natural saline mixture 'A'" for those mixtures that result in the a high $\text{Na}^+\text{-Cl}^-$ saline water, and as "natural saline mixture 'B'" , for those mixtures that result in the high $\text{Na}^+\text{-SO}_4^-$ saline water.

Hennessey Group - Associated Waters

Some of the increased chloride levels detected in the analyses are related to the presence of the Hennessey Group. Shallow wells which are completed in the upper part of the Central Oklahoma aquifer where the Hennessey Group is present typically show increased levels of sulfate which has been interpreted to be the result of the dissolution of the gypsum existing in the Hennessey (Parkhurst, 1992).

Increases in chloride concentrations to levels ranging in value from 120 to 230 mg/L often are associated with this sulfate. Waters with increased chloride concentrations due to their association with the Hennessey Group will be referred to as "Hennessey waters."

Parkhurst and others (1989) used the SMCL (a concentration of chloride equal to or greater than 250 mg/L) to check for a statistical correlation between increased chloride concentrations and different geohydrologic units of the Central Oklahoma aquifer. Since the elevated chloride concentrations detected in the Hennessey waters in this area are typically less than 250 mg/L, they did not observe any statistical correlation.

The possible origin of the chloride in the Hennessey-associated chloride waters are reviewed in a later section.

Graphic Relationships

The following graphic relationships proved to be the most significant in consistently differentiating among the various sources of the elevated chloride concentrations in the waters of the Central Oklahoma aquifer. Several relationships suggest that ion exchange and/or precipitation has occurred in these waters; these relationships are noted in each graph's individual review and are discussed in detail in the Geochemical Reaction Processes section of this report.

Br⁻ versus Cl⁻

Figures 11a and 11b

The importance of Br⁻/Cl⁻ ratios in the evaluation of brine sources has been well documented (Whittemore, 1988; Whittemore and others, 1979; Richter and Kreitler, 1991). Next to chloride, dissolved bromide generally is considered to be the most conservative of natural inorganic constituents in water. Oxidation-reduction reactions, adsorption on mineral surfaces, and precipitation of minerals appreciably do not affect its concentration in most ground waters.

A general linear relationship between Br⁻ and Cl⁻ existed in all of the analyses. Because of this linear relationship, a graph of any constituent against chloride shows the same general trend as if the constituent were plotted against bromide (ie: the Na⁺ versus Cl⁻ graph shows the same relationship as the Na⁺ versus Br⁻ graph). Therefore, no other graphs using only bromide as an axis are reviewed in this study.

Whittemore (1988) showed that significant differences in Br⁻/Cl⁻ ratios exist between most halite-solution brines and oil field brines (Figure 11a), allowing for the generation of site-specific mixing curves for the local oil field brines and the natural saline brines. One limitation of this method is that high concentrations of chloride are required to differentiate among the sources.

FIGURE 11a. XY- Graph: Br/Cl x 10000 vs Cl for Kansas Freshwaters and Brines
(Modified from Whitmore, 1988)

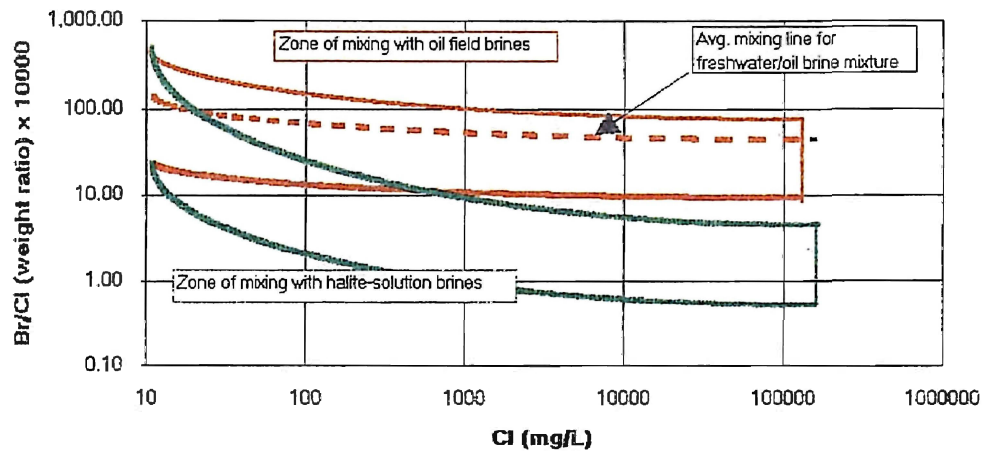
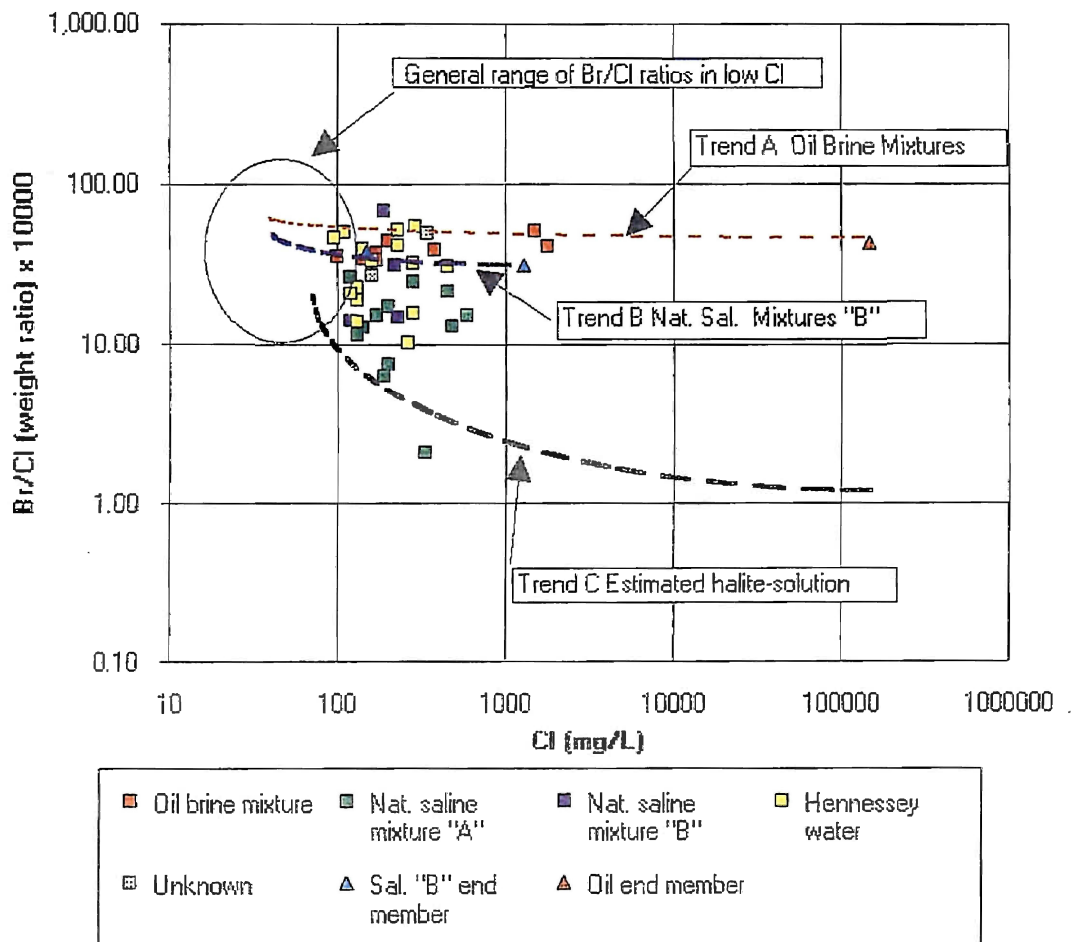


FIGURE 11b. XY- Graph: Br/Cl x 10000 vs Cl



The method described by Whittemore (1988) was used to examine the different potential sources of elevated chloride in the study unit by using a $\text{Br}^-/\text{Cl}^- \times 10000$ (weight ratio) versus Cl^- (mg/L) mixing curve (Figure 11b). Trend A is the site-specific mixing curve for a typical oil field brine and fresh water of the Central Oklahoma aquifer. Water analyses from wells 73 and 74 graph as "classic" oil brine mixtures along this curve. The remaining analyses have chloride concentrations that are too low to conclusively provide any indication of their source. However, the analyses which have been interpreted to be examples of oil brine mixtures by other relationships described in this paper all plot in the correct region of the graph.

It is interesting to note that Morton (1986), in an evaluation of oil brine contamination in east central Oklahoma, found that Br^-/Cl^- weight ratios of approximately 48×10000 were indicative of oil brine mixtures in that part of the state. The interpreted oil brine mixtures of the "Work Set" analyses all have weight ratios near this value.

Trends B and C in Figure 11b are site-specific mixing curves for the natural saline mixtures "B" and a typical halite-solution brine, respectively. The high Br^-/Cl^- weight ratios of the natural saline mixture "B" end members do not support a halite-solution brine origin.

As stated above, the remaining water analyses in the "Work Set" have chloride concentrations that are too low

to conclusively determine their chloride source by using this method. However, this graph indicates that at higher levels of chloride ($\text{Cl}^- > 1000 \text{ mg/L}$), the differentiation of oil brine mixtures from the other elevated chloride waters should be possible.

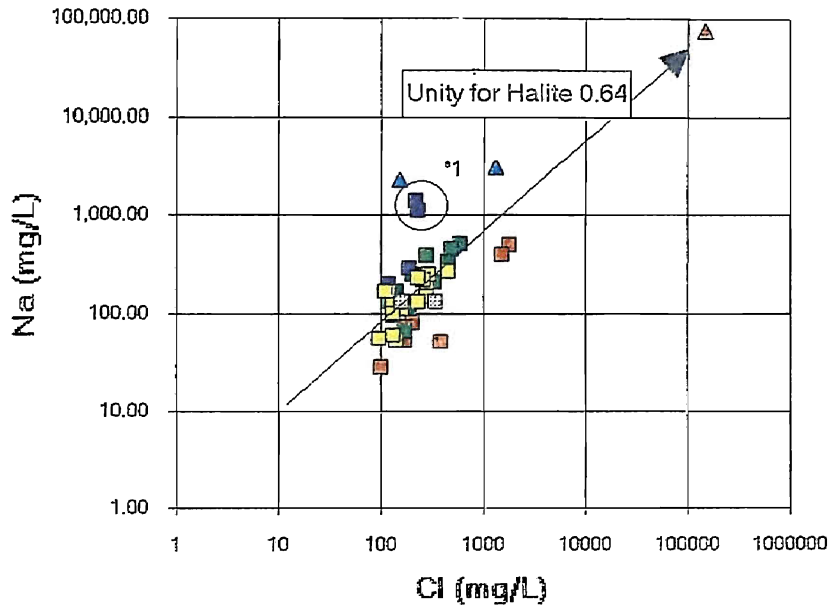
Na^+ Versus Cl^-

Figures 12a and 12b

Oil field brines and halite-solution brines typically will show strong linear relationships between sodium and chloride concentrations on a graph. Leonard and Ward (1962) reviewed oil field brines from Oklahoma, Kansas, and Texas and found that a Na^+/Cl^- (mg/L) ratio of about 0.5 was indicative of those brines. The oil field brines from wells in Oklahoma County conform to this relationship (Table 3). Morton (1986), in evaluating oil field contamination in east-central Oklahoma, reported that Na^+/Cl^- (mg/L) ratios of approximately 0.46 were characteristic of those oil brine mixtures. A solution of pure halite will result in a Na^+/Cl^- weight ratio of 0.648 (mg/L).

The Figure 12a (Na^+ vs Cl^-) illustrates that all of the interpreted sources show linear relationships between sodium and chloride. In addition, the graph shows that oil brine mixtures typically have lower Na^+/Cl^- ratios (averaging 0.3 mg/L) than the other sources.

FIGURE 12a. Na vs Cl



*1- Assumed analyses compositions are very close to the Sal."B" end members composition. Refer to discussion of Deeper Natural Saline Ground Water Section .

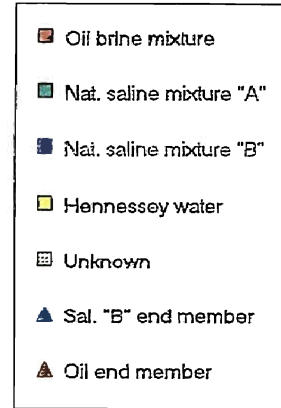
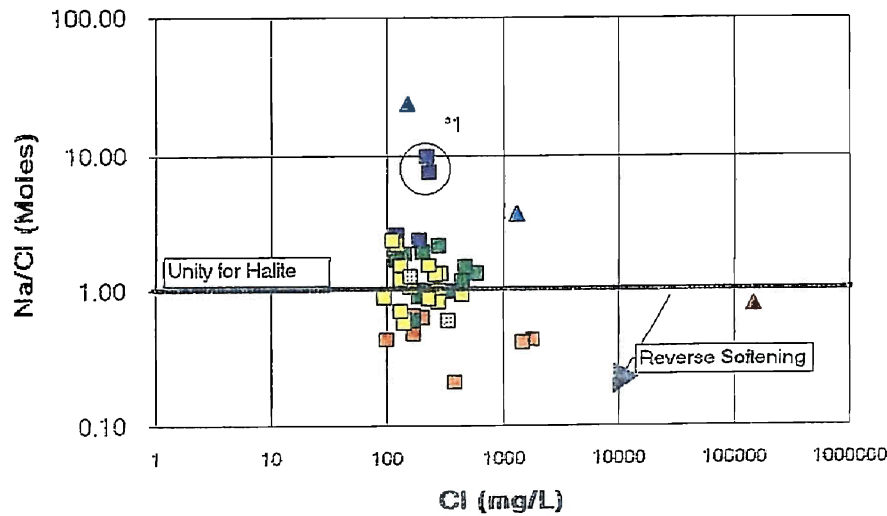
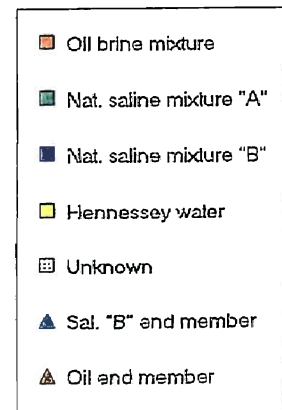


FIGURE 12b. Na/Cl(Moles) vs Cl



*1- Assumed analyses compositions are very close to the Sal."B" end members composition. Refer to discussion of Deeper Natural Saline Ground Water Section .



The Figure 12b (Na^+/Cl^- (Moles) vs Cl^-) incorporates the same data but displays it in a different format. This graph clearly shows the effects of reverse softening on the oil field brine and the oil brine mixtures.

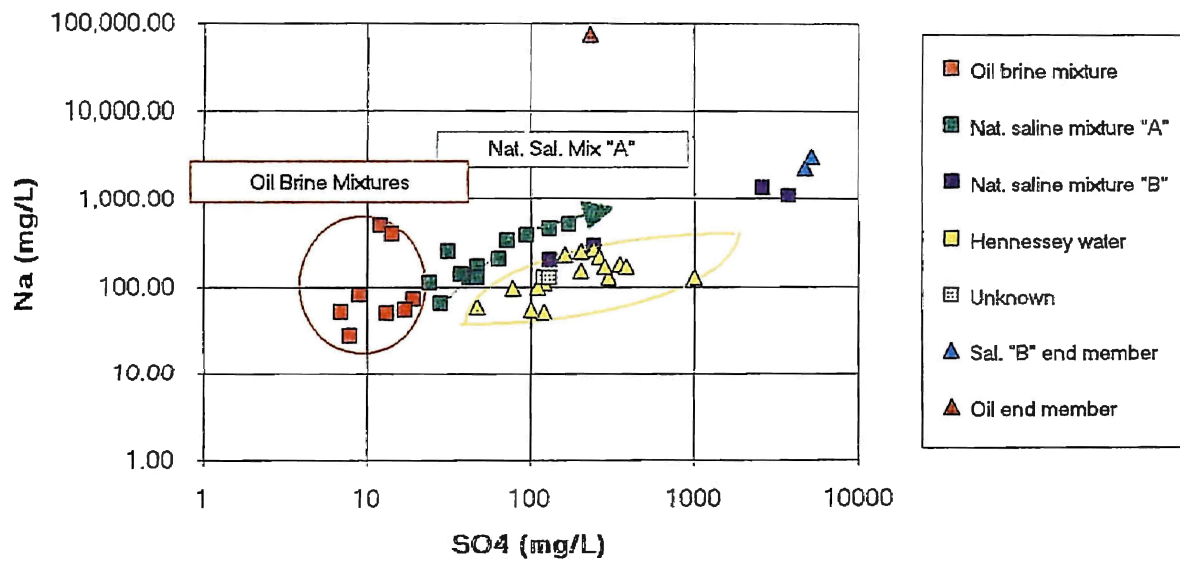
Both graphs show that the oil brine mixtures and natural saline mixtures "B" have Na^+/Cl^- ratios less than those of their interpreted end members. Assuming no secondary sources of chloride are present, these relationships indicate that sodium is being removed from the aquifer as mixing occurs.

Na^+ versus SO_4^-

Figure 13

This graph also does an excellent job of distinguishing among the chloride sources. The oil brine mixtures are characterized by high $\text{Na}^+/\text{SO}_4^-$ ratios with low sulfate concentrations (less than 20 mg/L). The natural saline mixtures "A" have intermediate $\text{Na}^+/\text{SO}_4^-$ ratios with sulfate ranging from 20 to 200 mg/L. The Hennessey waters and the natural saline mixtures "B" have the lowest $\text{Na}^+/\text{SO}_4^-$ ratios with the highest sulfate concentrations (generally greater than 100 mg/L). At low sulfate concentrations (less than 100 mg/L), an excellent linear relationship is exhibited between sodium and sulfate for the natural saline mixtures "A." At higher SO_4^- concentrations, the linear trend curves, suggesting that ion exchange, precipitation, and/or

FIGURE 13. XY-Graph: Na vs SO4



dissolution is occurring in the natural saline mixtures "A" and changing the concentration of either sodium or sulfate.

SO₄⁻ versus Cl⁻

Figures 14a and 14b

Typically, oil field brines have low sulfate concentrations relative to chloride. The oil field brines from wells in Oklahoma County conform to this relationship (Table 3). Mast (1982) used this relationship to plot theoretical mixing curves for a fresh water potentially mixing with both a typical oil field brine and a lower natural saline brine in Kansas. Mast's theoretical mixing curve of fresh water and the Kansas oil brine is shown on Figure 14a. The USGS data plotted on this graph shows a trend plotting in a similar fashion to what Mast had projected for an oil field brine/fresh water mixture plot. A comparison of this graph against the Br⁻/Cl⁻ mixing curve indicates that in addition to water analyses from wells 73 and 74, water analyses from wells 94, 122, 66, and 130 likely are examples of a fresh water aquifer that has been mixed with an oil field brine. Thus, assuming that no secondary source of sulfate is present, the SO₄⁻ versus Cl⁻ graph allows for the determination of oil brine mixtures when the chloride levels are too low to utilize the Br⁻/Cl⁻ method.

In addition, one of the most obvious geochemical differences between natural saline mixtures "A" and other

sources of increased chloride concentrations is illustrated on Figure 14a. Both the Hennessey waters and the natural saline mixtures "B" have high levels of sulfate and only slightly elevated chloride levels. The natural saline mixtures "A" have similar chloride levels and only slightly elevated sulfate levels.

The Figure 14b [$\text{SO}_4^{2-}/(\text{Cl}^- + \text{SO}_4^{2-})$ vs Cl^-] incorporates the same data in a different format. This graph dramatically separates the oil brine mixtures and natural saline mixtures "A" from the natural saline mixtures "B" and Hennessey water groups.

Both graphs show that the $\text{SO}_4^{2-}/\text{Cl}^-$ ratios are lower in the natural saline mixtures "B" than in their interpreted end members. Assuming no secondary sources of chloride are present, this decrease in sulfate suggests that it is being removed in the natural saline water mixtures "B." This same relationship appears to be present in the oil brine mixture group.

FIGURE 14a. XY-Graph: SO4 vs Cl

HS: Average halite solution end member in South Central Kansas

*1- Assumed analyses compositions are very close to the Sal."B" end members composition. Refer to discussion of Deeper Natural Saline Ground Water Section .

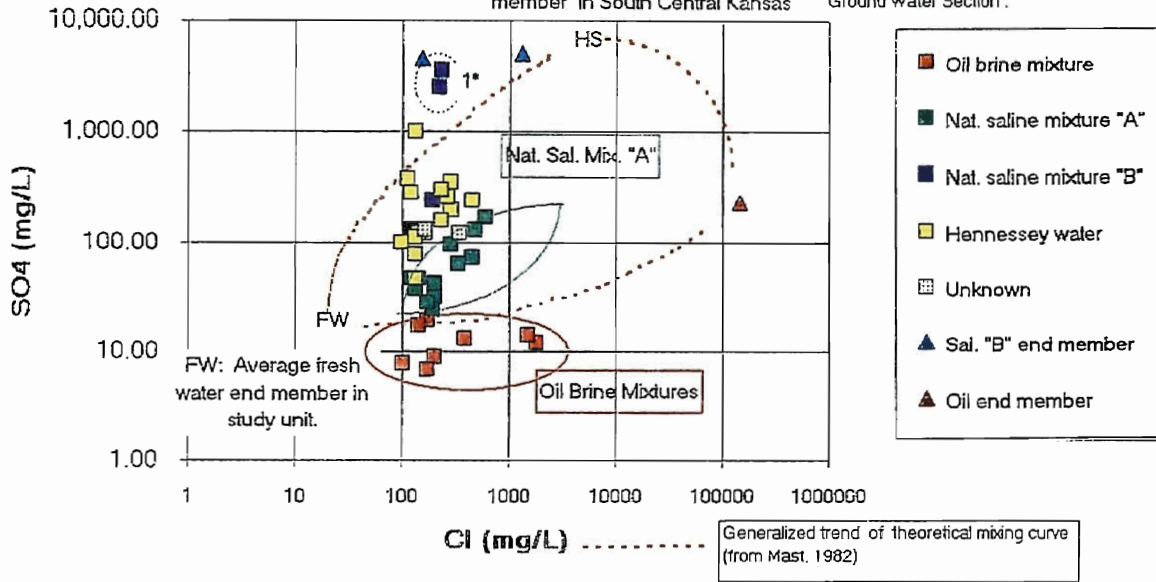
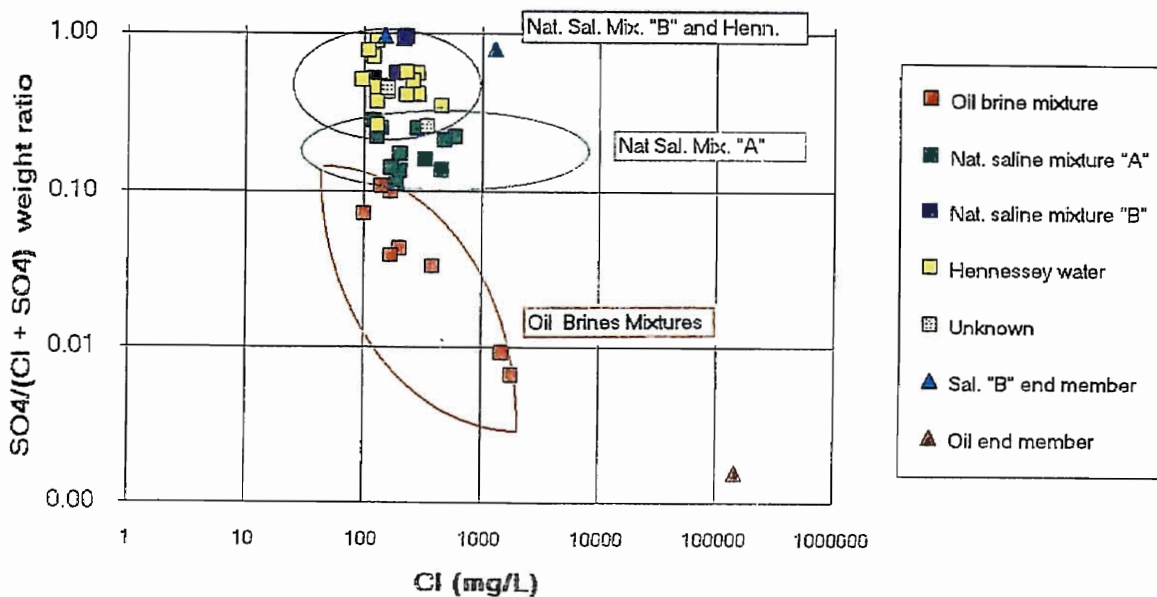


FIGURE 14b. XY-Graph: SO4/(Cl + SO4) vs Cl



Ca⁺⁺ versus SO₄⁻

Figure 15

This relationship can be utilized for the separation of oil brine mixtures, Hennessey waters, and natural saline mixtures "B." Oil brine mixtures have Ca⁺⁺/SO₄⁻ ratios of greater than 1 due to their low concentrations of sulfate. The Hennessey waters show a linear relationship between calcium and sulfate. This linear relationship suggests that dissolution of gypsum is the source of the sulfate. Their average Ca⁺⁺/SO₄⁻ (mg/L) ratio of 0.6 is only slightly above unity (0.41 mg/L) which further supports this conclusion.

Typically, both the oil brine mixtures and the natural saline mixtures "B" have ratios greater than those observed in their end members. These increased ratios suggest that either calcium is being added to the solutions or sulfate is being removed from the solutions when their sources are mixed with the fresh waters of the Central Oklahoma aquifer.

B³⁺ versus Cl⁻

Figure 16

This graph shows that a lack of boron is indicative of an oil brine mixture in this area. Both natural saline mixtures "A" and "B" show elevated levels of boron. The Hennessey waters show slightly elevated boron concentrations.

Figure 15. XY-Graph : Ca vs SO4

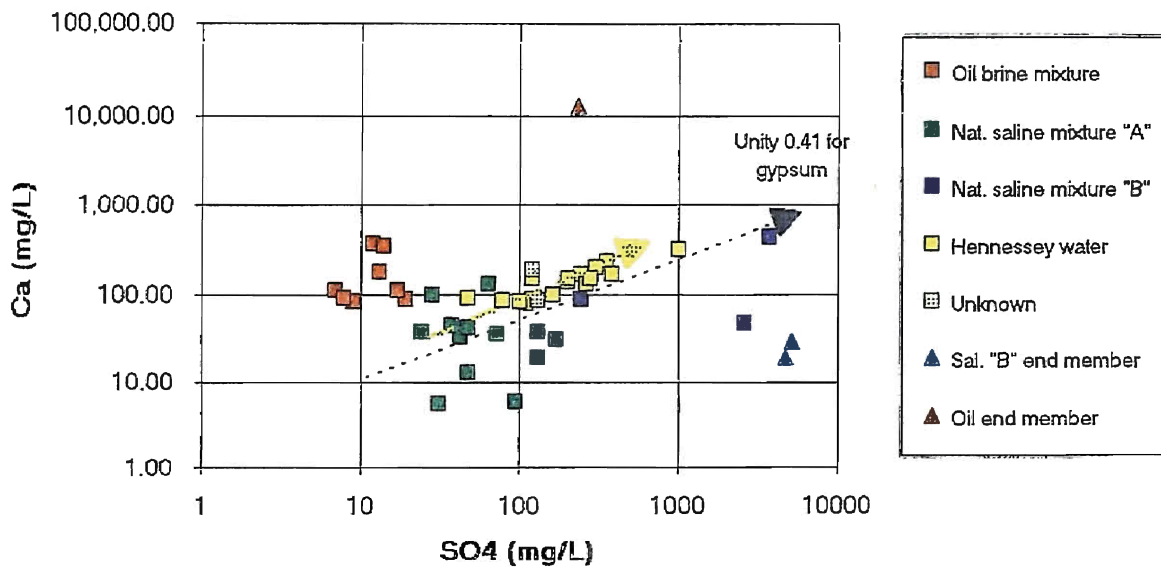
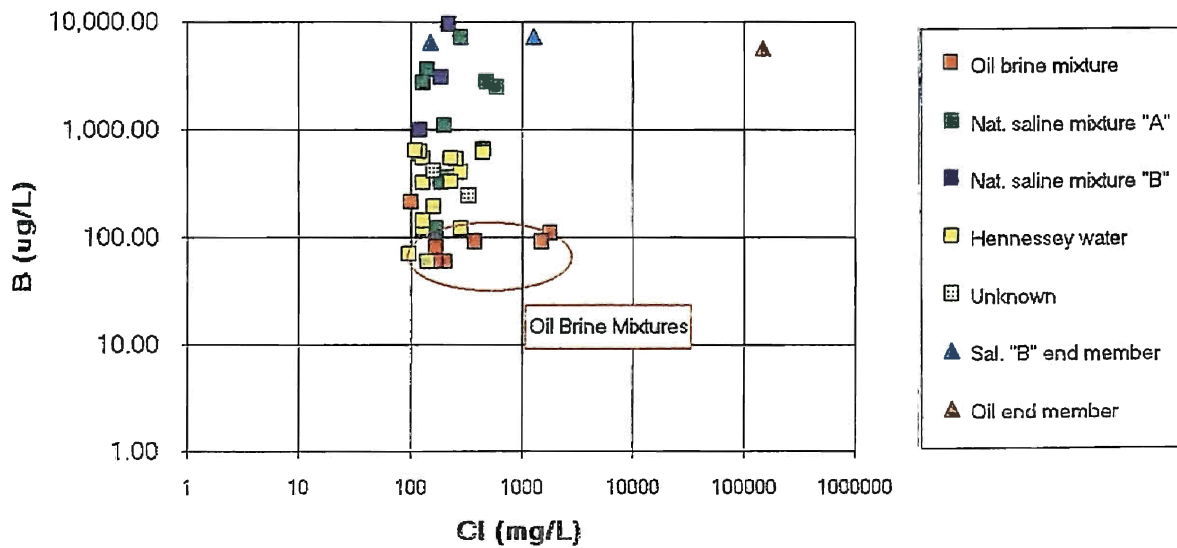


FIGURE 16. XY-Graph: B vs Cl



Ba⁺⁺ versus Cl⁻ and Ba⁺⁺ versus SO₄⁻

Figures 17a and 17b

The Ba⁺⁺ versus Cl⁻ graph (Figure 17a) shows that increased levels of barium are present in the oil brine mixtures. These elevated barium levels are greater than the levels that would be expected from mixing a typical oil field brine with a fresh water. Assuming no secondary sources of chloride are present, these increased barium concentrations suggest that either: (1) the estimate of barium in the end member is incorrect or (2) a secondary source of this trace element is present. Possible secondary sources of barium are drilling muds, ion exchange, or the dissolution of minerals. Fairchild and Knox (1985) reported the results of an in-depth study of the environmental implication of offsite disposal pits for drilling fluid waste at a site in Oklahoma. In that study, the water in the disposal pit had barium and chloride concentrations as high as 195 mg/L and 1,103 mg/L, respectively.

The Ba⁺⁺ versus SO₄⁻ curve (Figure 17b) shows a good separation of the oil brine mixtures from the other mixtures. This graph also shows a linear relationship between increasing sulfate and decreasing barium for the natural saline mixtures "B" and Hennessey waters.

FIGURE 17a. XY-Graph: Ba vs Cl

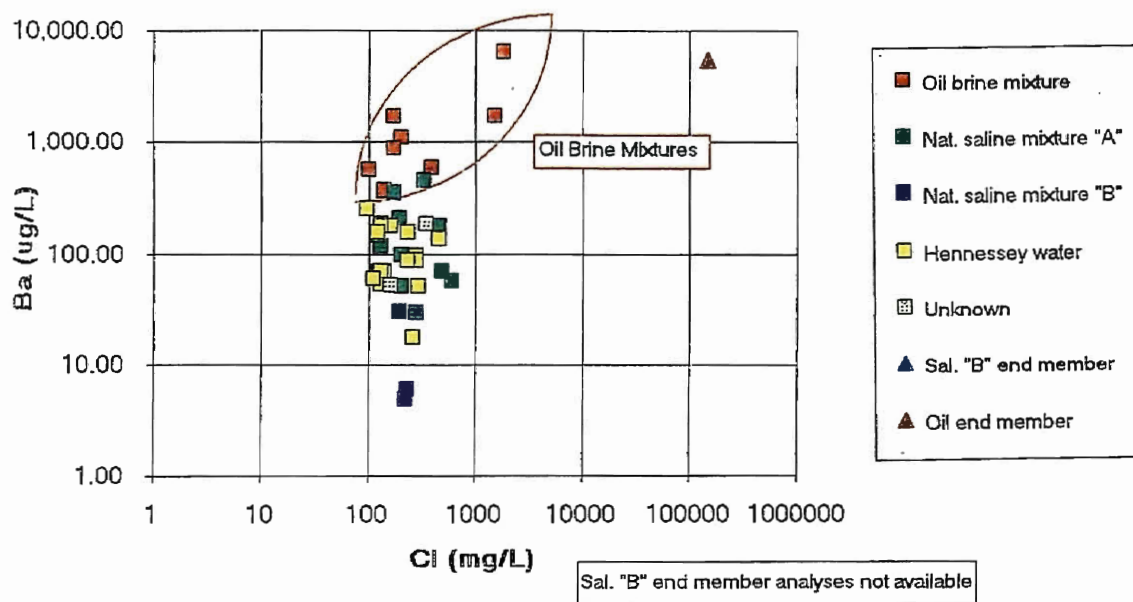
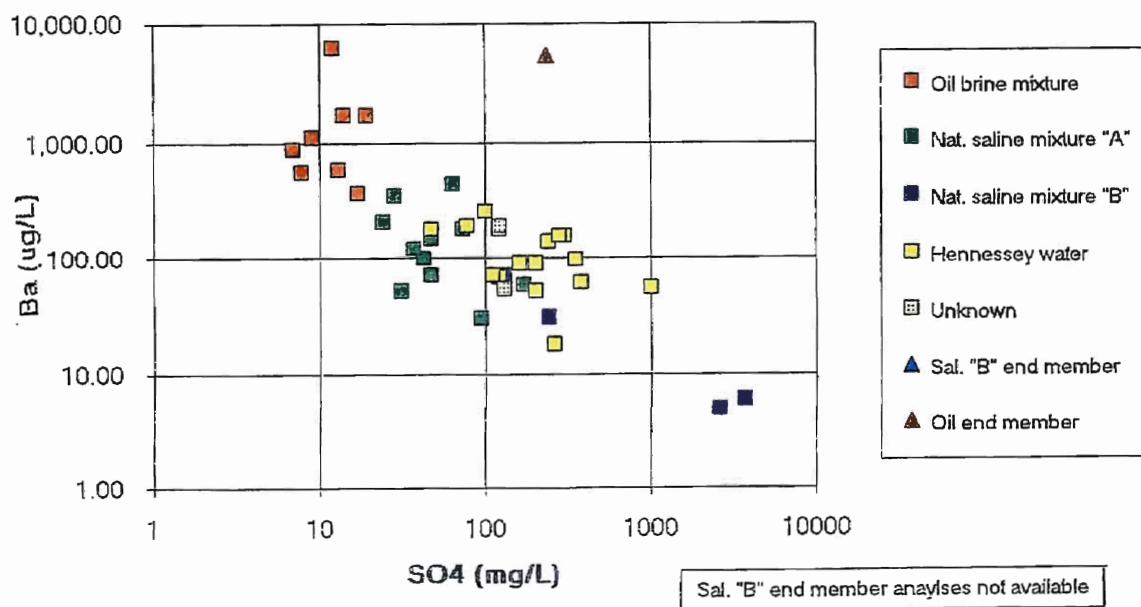


FIGURE 17b. XY-Graph: Ba vs SO4



Sr⁺⁺ versus SO₄⁻

Figure 18

This graph illustrates that higher strontium concentrations are related to increases in sulfate concentrations. It appears that the strontium is being released into solution with gypsum dissolution. Therefore, increases in strontium and sulfate concentrations with a slight increase in chloride levels is characteristic of the Hennessey waters.

Li⁺ versus SO₄⁻

Figure 19

Lithium is a conservative element often used in salinity studies. However, plotting Li⁺ versus Cl⁻ failed to show any useful relationships. The Li⁺ versus SO₄⁻ graph shows a linear relationship between lithium and sulfate in the Hennessey waters group. The other sources of elevated chloride concentrations do not show this relationship.

FIGURE 18. XY- Graph: Sr vs SO4

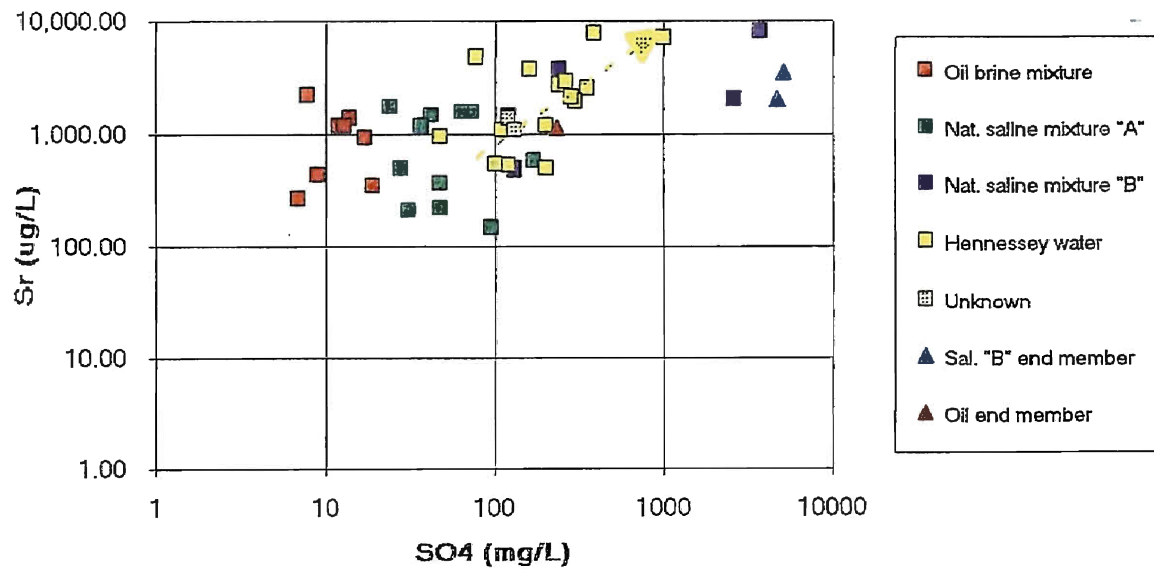
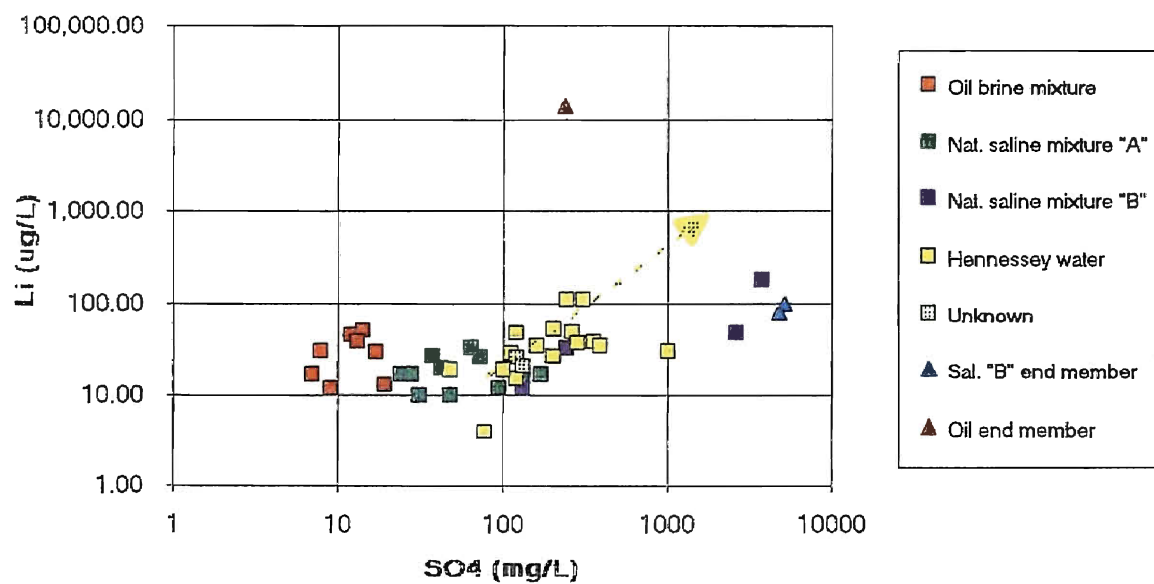


FIGURE 19. XY- Graph: Li vs SO4



Other Important Relationships

Multiple Component Plots

Figures 20, 21, 22a, 22b, 23a, 23b, and 24

Graphically plotting multiple components has long been used to differentiate waters based on chemistry. When end member water compositions are available, these types of multiple component plots are useful in determining a source of contamination in a sample. Nativ (1988) used this concept to differentiate between contamination caused by a saline lake water and an oil field brine in the Ogallala in Texas and New Mexico.

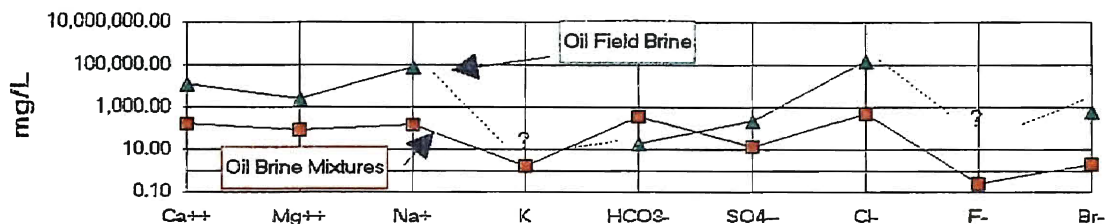
A line graph was created for each of the interpreted waters. In Figure 20, the line graphs show good correlations between both the mean oil brine mixture and the mean natural saline mixture "B" and their interpreted end members.

In addition, piper diagrams showing all of the interpreted water analyses were created (Figures 21, 22a, 22b, 23a, and 23b). By comparing concentrations of the major ions, a piper diagram illustrates the relative percentage of each major ion in a sample. The piper diagram shows the linear trends which are indicative of ion exchange and mixing relationships.

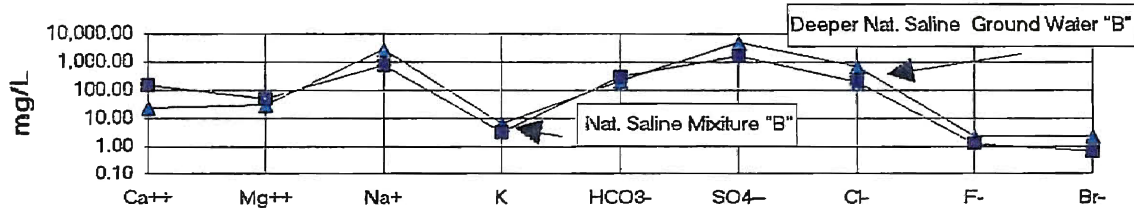
Stiff diagrams (Figure 24) also are provided for all of the interpreted water analyses with chloride concentrations of greater than 200 mg/L.

FIGURE 20. Salinity Diagrams

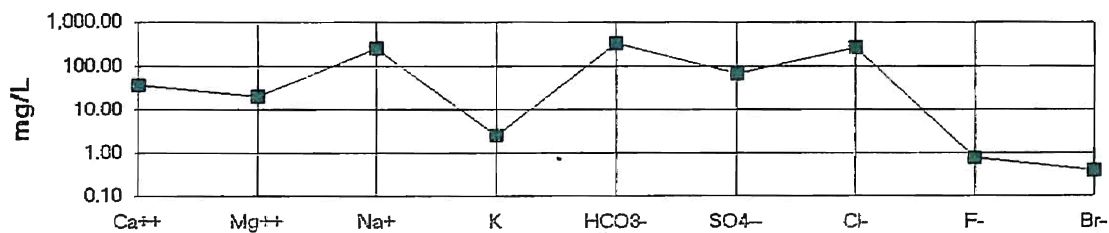
Mean Oil Field Brine and Mean Oil Brine Mixture



Mean Deeper Natural Saline Ground Water "B" and Mean Natural Saline Mixture "B"



Mean Natural Saline Mixture "A"



Mean Hennessey Water

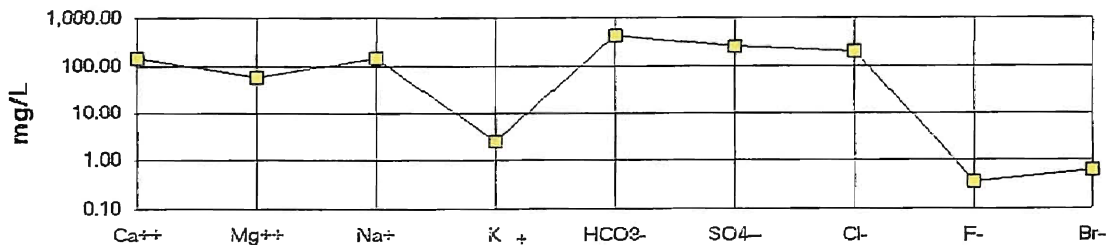
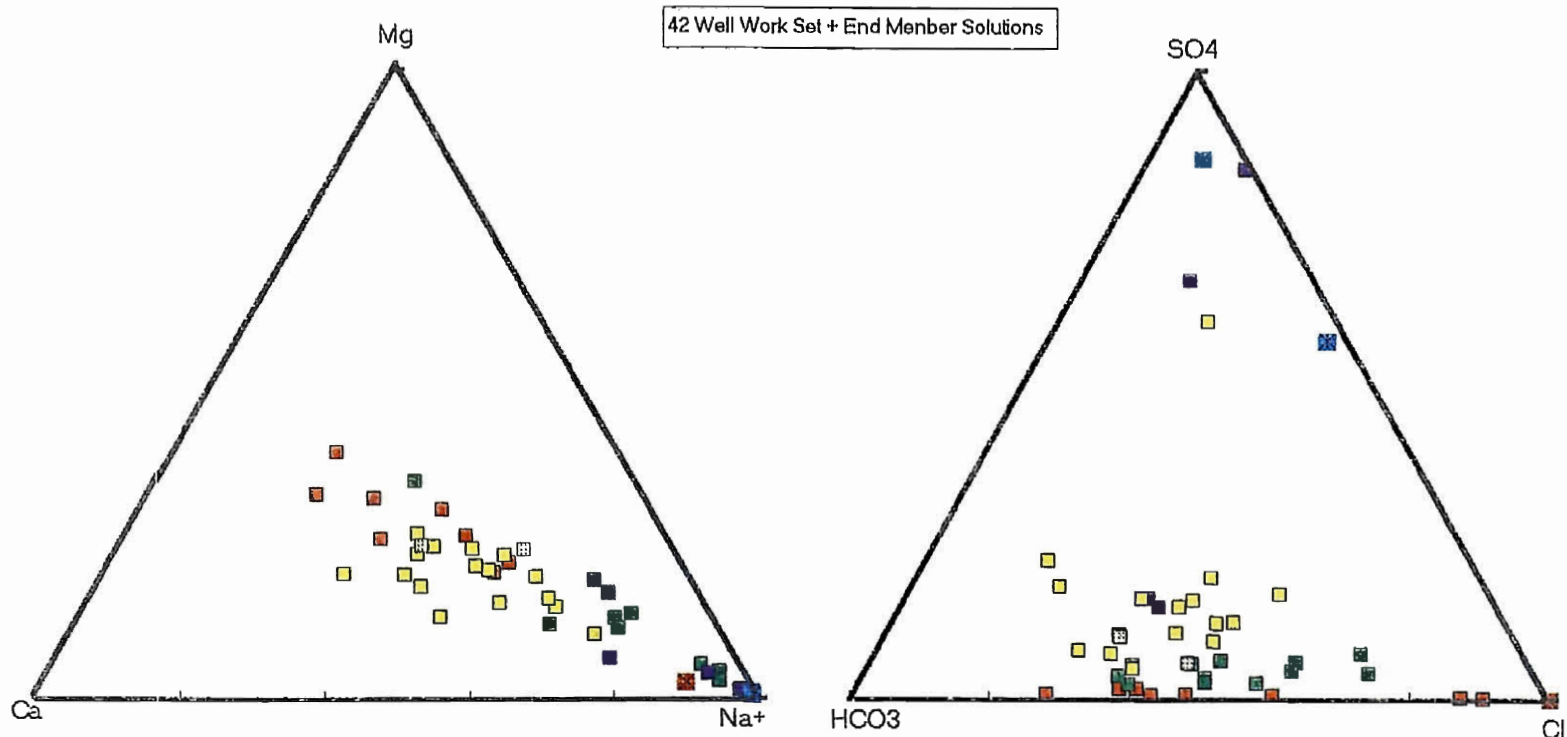


Figure 21. Piper Diagram



Graphic technique-Hounslow, 1992

- | | | | |
|---------------------|---------------------------|---------------------------|-------------------|
| ■ Oil brine mixture | ■ Nat. saline mixture "A" | ■ Nat. saline mixture "B" | ■ Hennessey water |
| ⊠ Unknown | ■ Sal. "B" end member | ■ Oil end member | |

Figure 22a. Piper Diagram - Oil Brine Mixtures

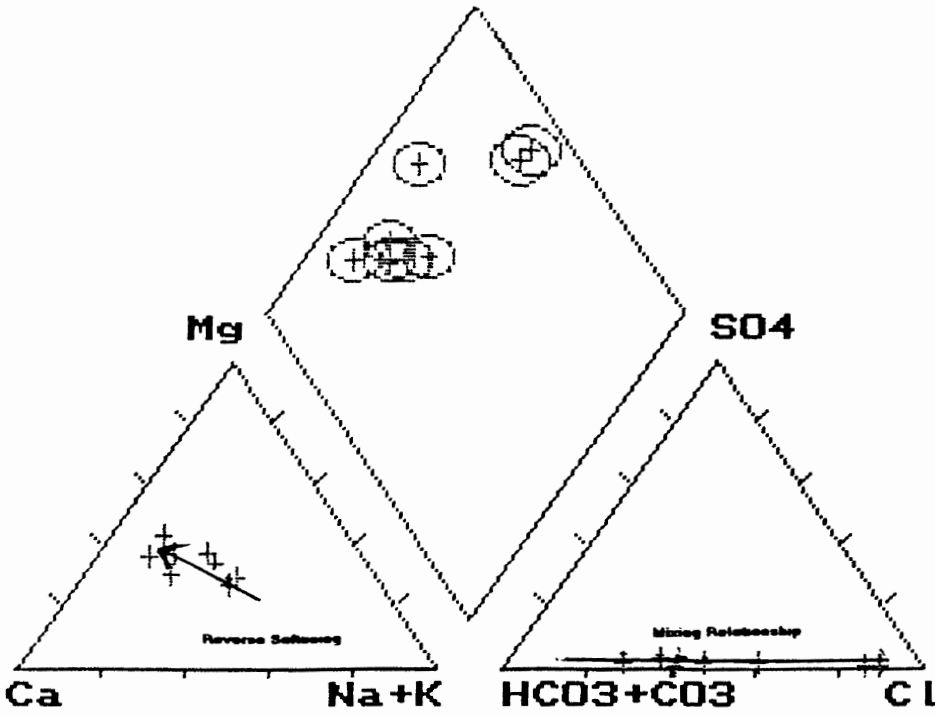


Figure 22b. Piper Diagram - Natural Saline Mixtures "A"

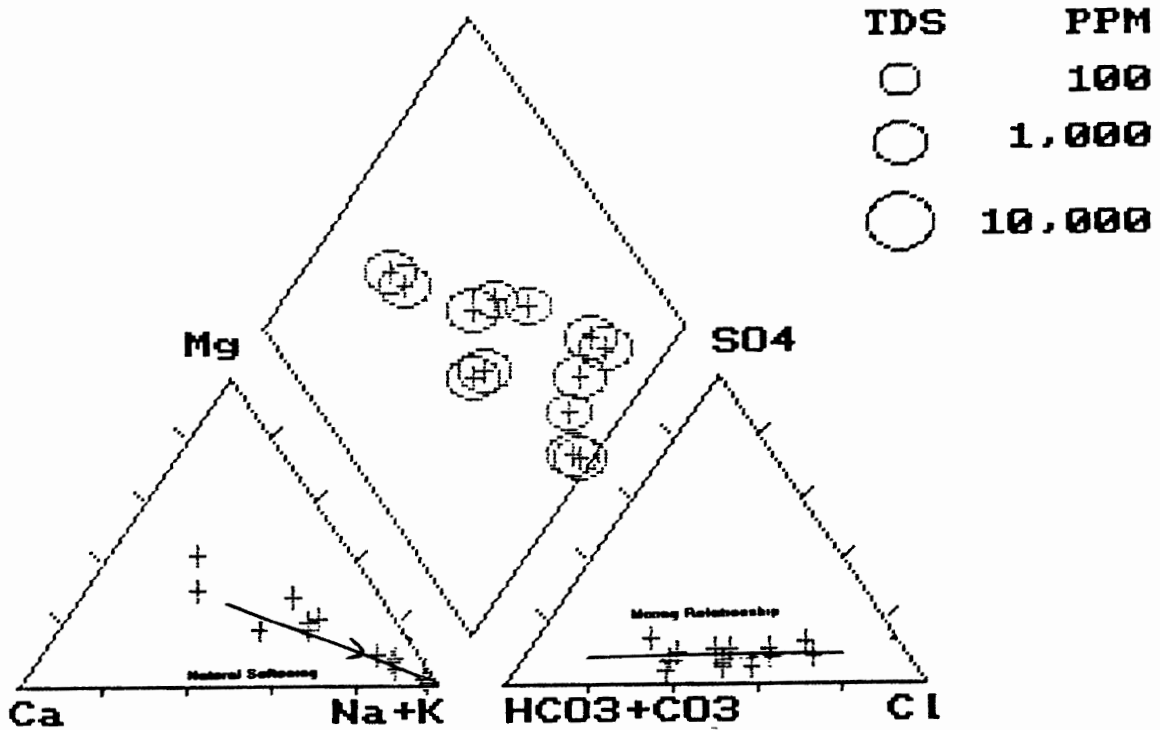


Figure 23a. Piper Diagram - Natural Saline Mixtures "B"

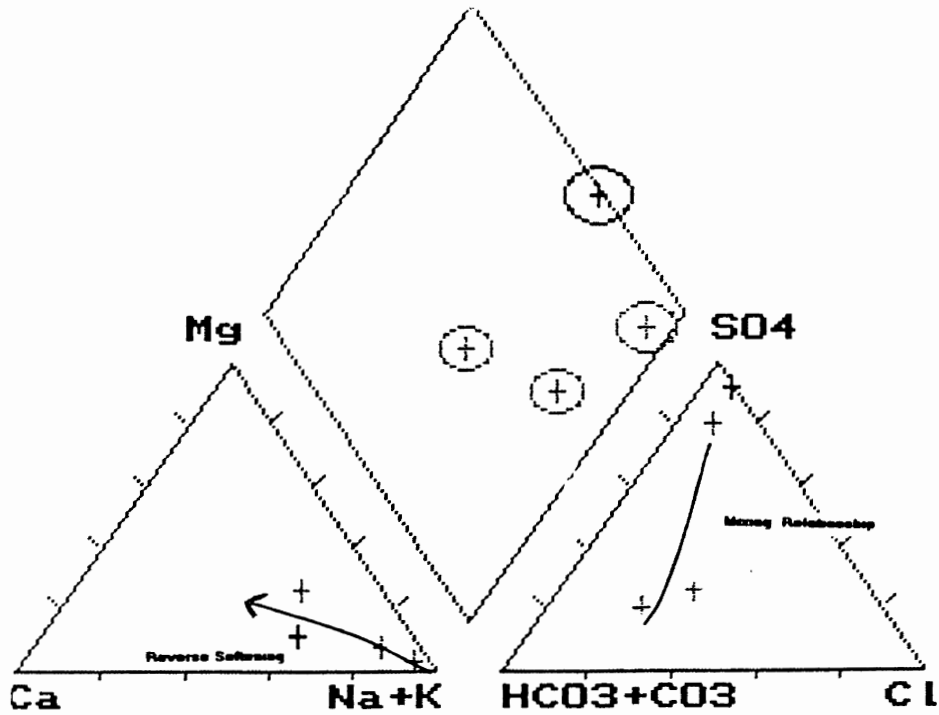


Figure 23b. Piper Diagram - Hennessey Waters

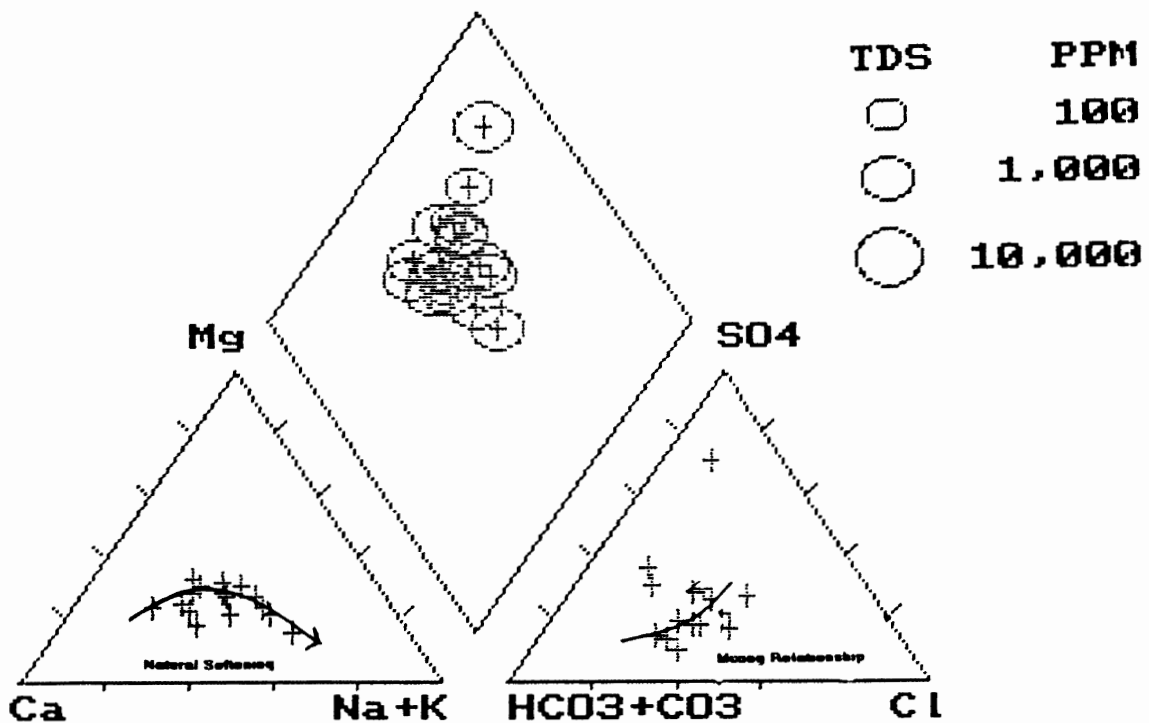
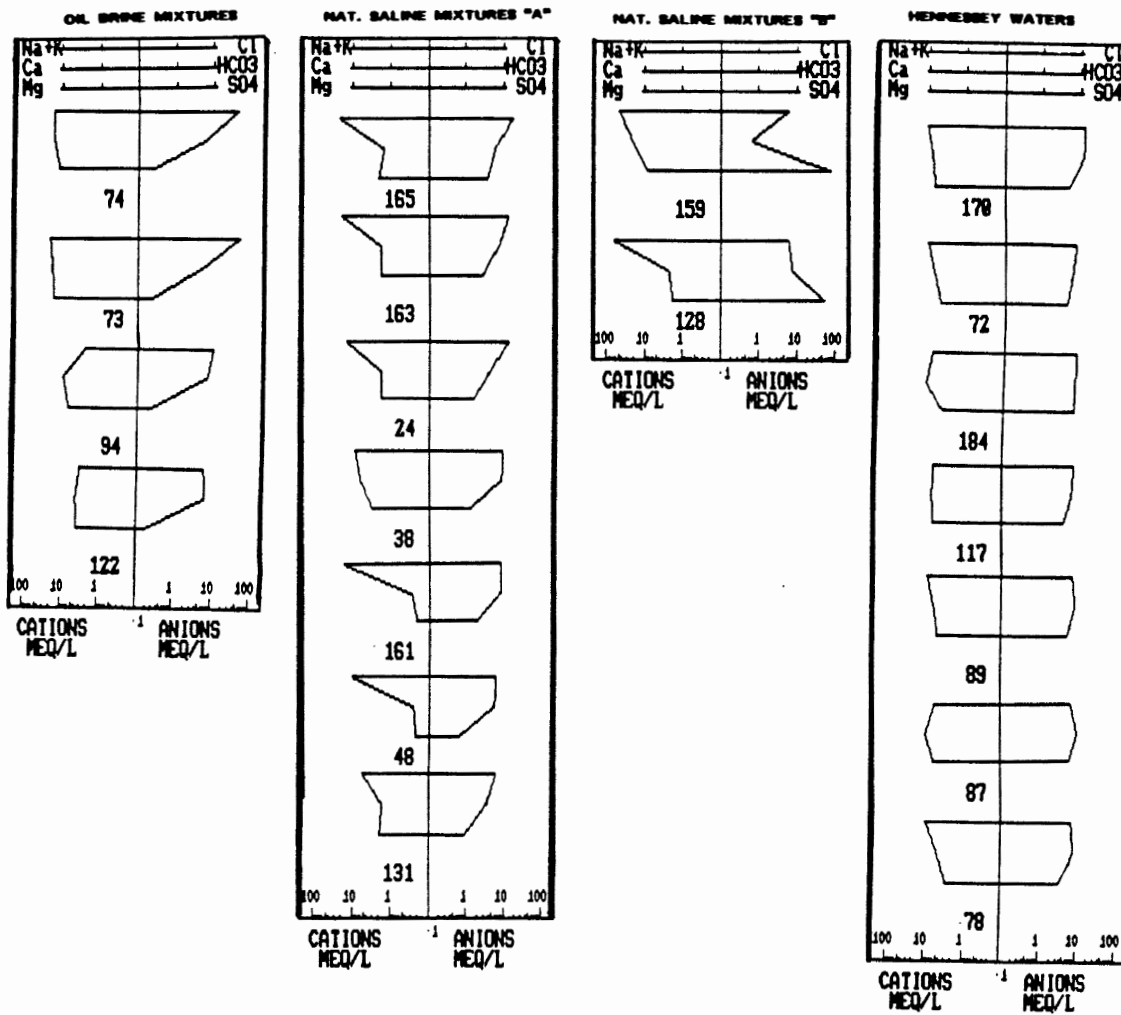


Figure 24. Stiff Diagrams



$\text{Ca}^{++}/(\text{Ca}^{++}+\text{SO}_4^{-})$ versus $\text{Na}^{+}/(\text{Na}^{+}+\text{Cl}^{-})$

and

$(\text{Ca}^{++}+\text{Mg}^{++})/\text{SO}_4^{-}$ versus $\text{Na}^{+}/\text{Cl}^{-}$

Figures 25 and 26

Hounslow and Goff (1991) used the graphic relationship illustrated in Figure 25 to aid in determining the origin of brines. Since oil field brines typically are low in sulfate relative to calcium and low in sodium versus chloride, an oil brine mixture normally will plot in the top left corner of the graph. Molar ratios near unity for $\text{Ca}^{++}/(\text{Ca}^{++}+\text{SO}_4^{-})$ versus $\text{Na}^{+}/(\text{Na}^{+}+\text{Cl}^{-})$ suggest a halite-solution source for a brine. As anticipated, the oil brine mixtures plot in the top left corner of the graph. The natural saline mixtures "A" and Hennessey waters plot roughly in the area where a halite-solution brine would plot.

Richter and Kreitler (1986 a,b) used a similar graphic relationship shown in Figure 26. This graph incorporates magnesium into a molar relationship with sulfate. As in the above graph, the oil brine mixtures plot in the top left corner of the graph. Molar ratios using $(\text{Ca}^{++}+\text{Mg}^{++})/\text{SO}_4^{-}$ versus $\text{Na}^{+}/\text{Cl}^{-}$ are close to unity for both natural saline mixtures "A" and Hennessey waters and again suggest a possible halite-solution source for those brines.

FIGURE 25. XY-Graph: $\text{Ca}/(\text{Ca}+\text{SO}_4)$ vs $\text{Na}/(\text{Na}+\text{Cl})$
 (Graphic method from Hounslow and Goff, 1991)

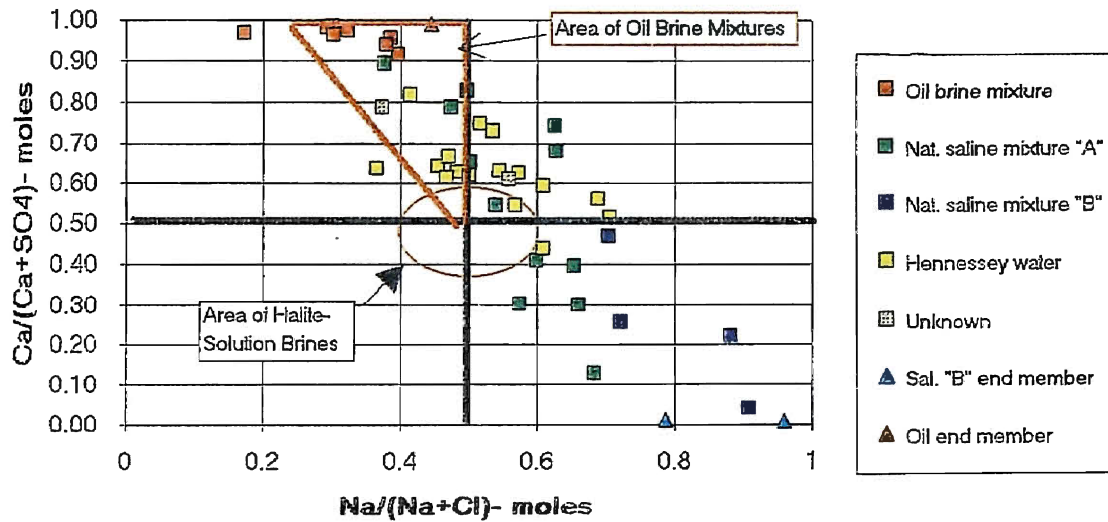
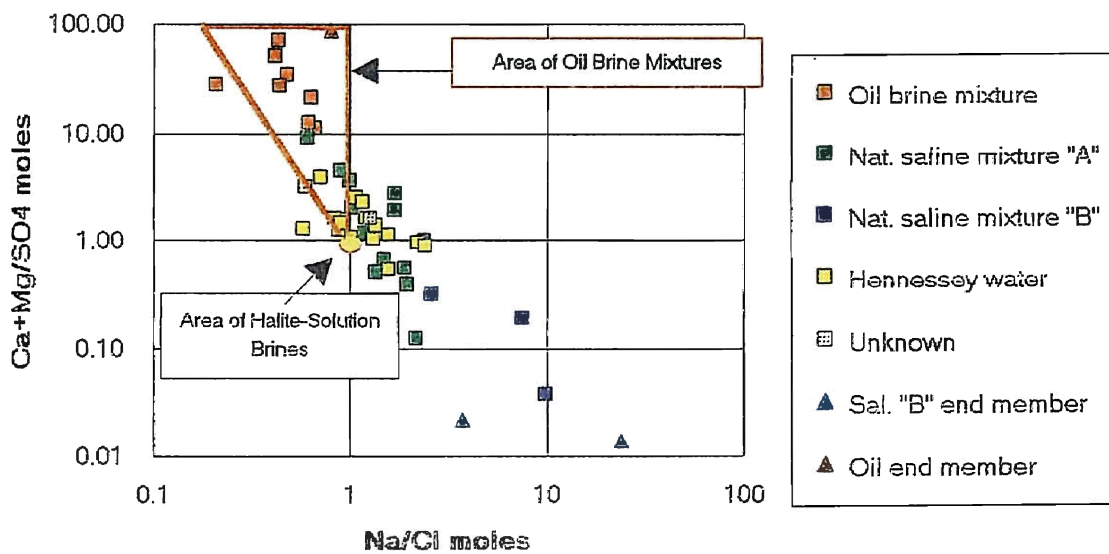


FIGURE 26. XY-Graph: $(\text{Ca}+\text{Mg})/\text{SO}_4$ vs Na/Cl
 (Graphic method from Richter and Kreitler, 1986a,b)



**Additional Graphic Relationships Derived to
Determine Oil Field Brine Contamination**

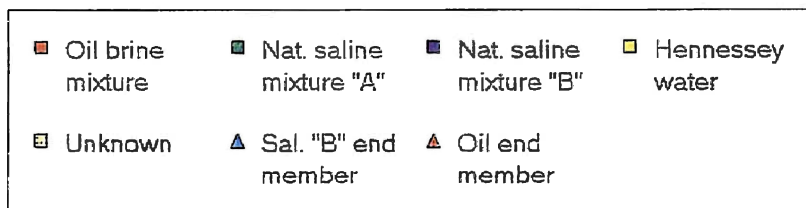
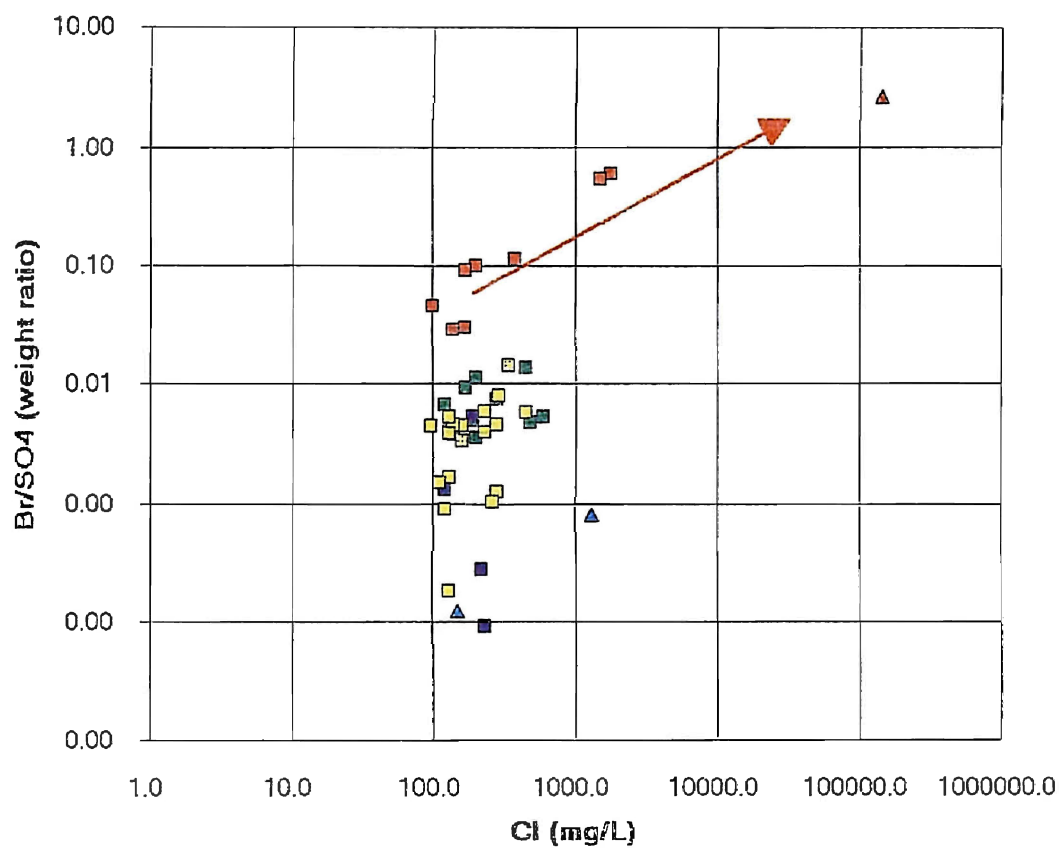
Based on the above graphical analyses and data, new methods were derived using multiple component plots to aid in the determination of the sources of the elevated chloride levels in this area. These derived methods combine previously discussed bivariate plots to produce more direct methods to differentiate among these sources.

Br⁻/SO₄⁻ versus Cl⁻

Figure 27

This derived graphic method appears to be one of the simplest and most accurate methods to quickly evaluate if an oil brine has mixed with a fresh water of the Central Oklahoma aquifer. This mixing relationship utilizes the fact that oil brines are high in bromide and low in sulfate concentrations relative to the other chloride sources in this study unit. A good linear relationship is reflected by the oil brine mixtures which allows for the separation of these waters from the non-oil brine mixtures. This mixing curve relationship appears to delineate chlorides derived from oil brine contamination from non-oil brine contamination at very low concentrations of chlorides, and therefore could prove to be more useful than the Br⁻/Cl⁻ versus Cl⁻ mixing curve (page 50).

FIGURE 27. XY- Graph: Br/SO4 vs Cl



Br⁻/SO₄⁼ versus SO₄⁼/Cl⁻

Figure 28

This graph incorporates the previously discussed relationships illustrated in the Br⁻ versus Cl⁻ and SO₄⁼ versus Cl⁻ graphs. This new graph successfully separates the various interpreted sources of the elevated chloride levels in this area.

Na⁺/Cl⁻ versus SO₄⁼/Cl⁻

Figure 29

Due to the apparent reverse softening which has occurred in the oil brine mixtures (Na⁺ < Cl⁻) and their very low sulfate concentrations, the oil brine mixtures plot in the bottom left corner of this graph. The lower linear trend is made up of primarily Hennessey water analyses. The upper linear trend is comprised of wells associated with natural saline mixtures. The difference in these two trends is a function of the natural saline mixtures having a much larger percentage of non-halite sodium (Na⁺/Na⁺+Cl⁻) relative to sulfate concentrations than found in the Hennessey waters.

Ca⁺⁺/SO₄⁼ versus SO₄⁼/Cl⁻

Figure 30

This new graph successfully separates the various interpreted sources of the elevated chloride levels in this area. All of the interpreted oil brine mixtures plot in the

FIGURE 28. XY-Graph: Br/SO4 vs SO4/Cl

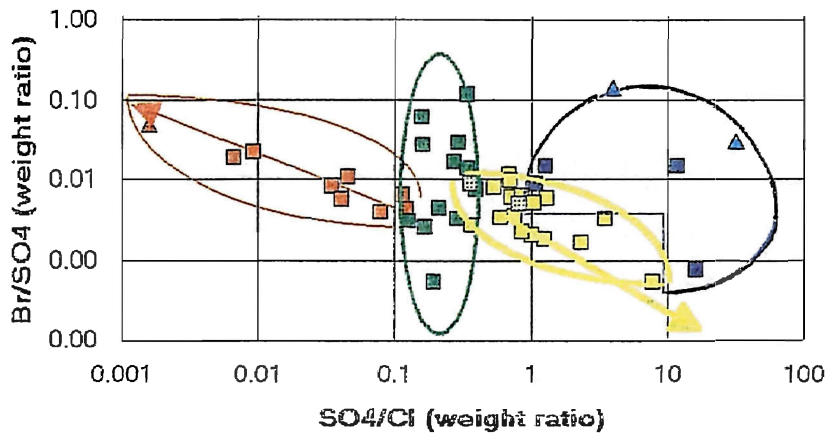
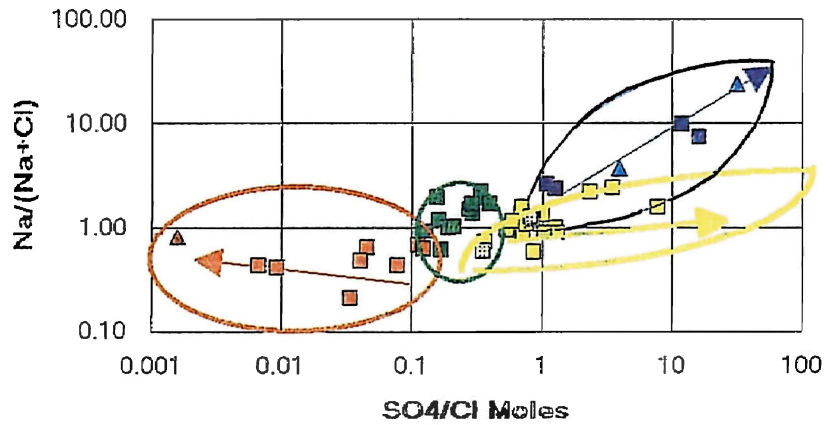
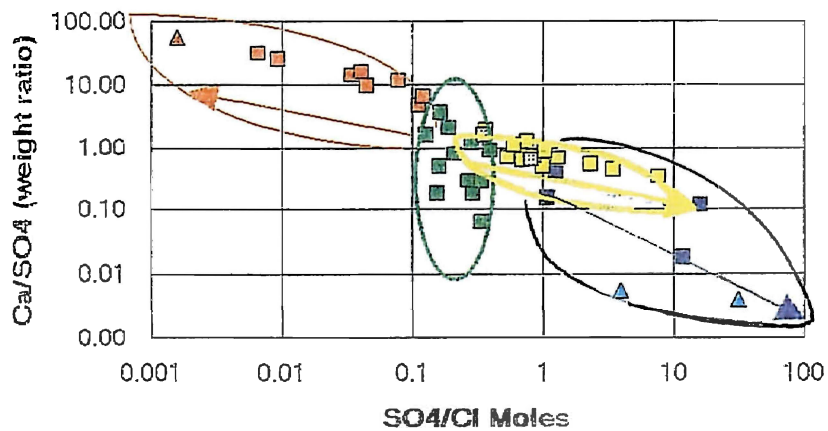


FIGURE 29. XY-Graph: Na/(Na+Cl) vs SO4/Cl



- Oil brine mixture
- Nat. saline mixture "A"
- Nat. saline mixture "B"
- Hennessey water
- Unknown
- Sal. "B" end member
- Oil end member

FIGURE 30. XY-Graph: Ca/SO4 vs SO4/Cl



upper left corner of this graph due to their low sulfate concentrations as well as their low sulfate relative to calcium ratios.

Physical and Geographical Characteristics of the Sources

The physical and geographical characteristics of each well were considered in this study to aid in the determination of the source of the elevated chloride concentration.

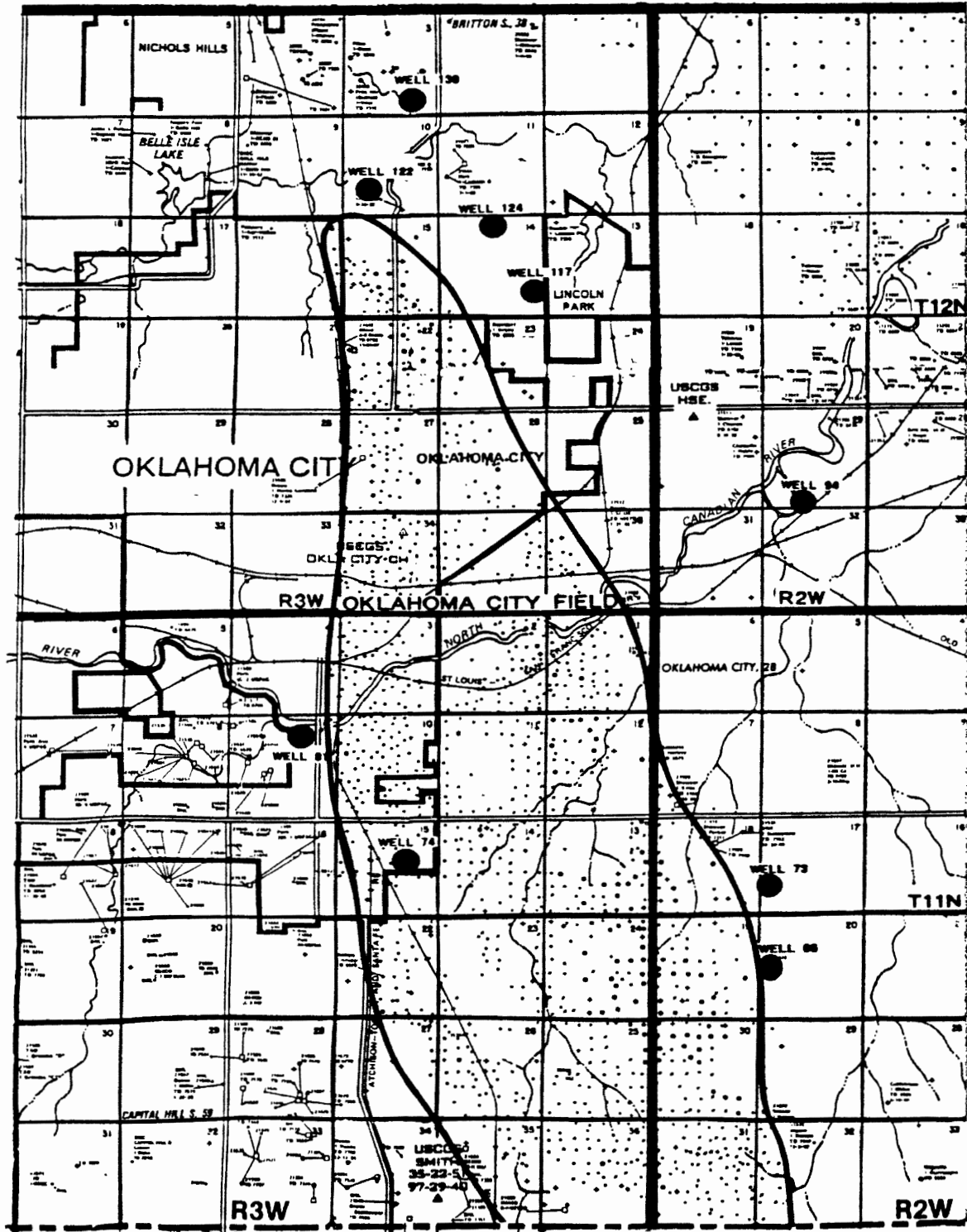
Oil Brine Mixtures

All of the wells which geochemically indicated contamination from oil field brines are associated with old oil field activity. Figure 31 shows the locations of these wells relative to oil field activities.

Well 74 is located in the central portion of the original Oklahoma City Field. Wells 73, 94, 122, 124, 66, and 81 are adjacent to the Oklahoma City Field and lie in the interpreted flow paths of the ground water that is moving away from the oil field area (Figure 32).

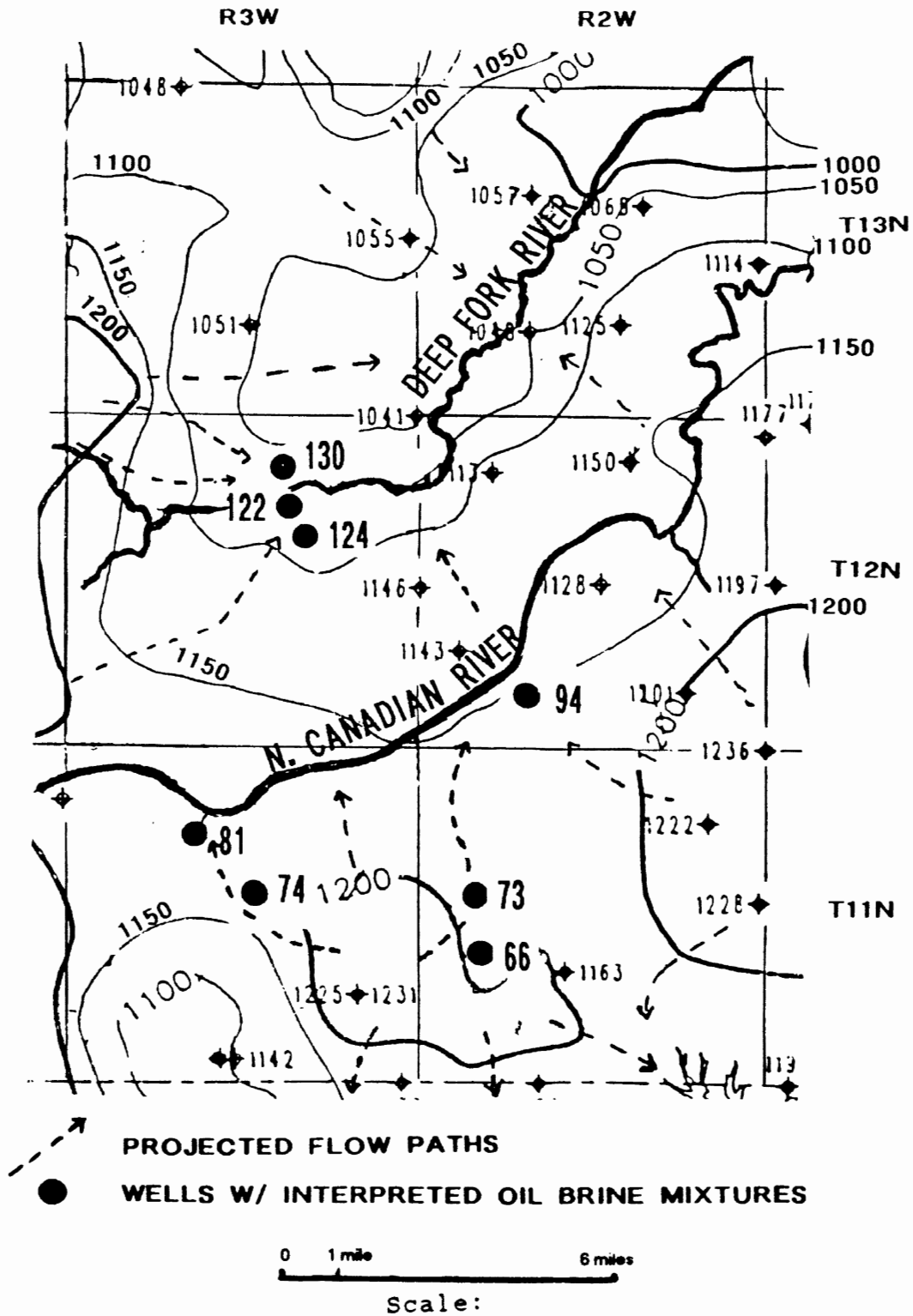
Well 130 appears to reflect contamination from oil field activity which had taken place in the Nichols Hills area of Oklahoma County. Harrington and Simpson (1988) made reference to higher levels of chloride present in the unconfined section of the Garber-Wellington aquifer in the

Figure 31, Oklahoma City Field and Interpreted Wells with Oil Brine Mixtures



● Wells with oil brine mixtures

Figure 32. Top of Water Table in the Central Okla. Aquifer in the Area of Oklahoma City Field, with Projected Flow Paths (Unconfined Section) (modified from Christenson and others, 1990).



area around Sections 3 and 4 of T12N-R3W, and had interpreted this increase to be the result of a brine plume caused by oil field contamination.

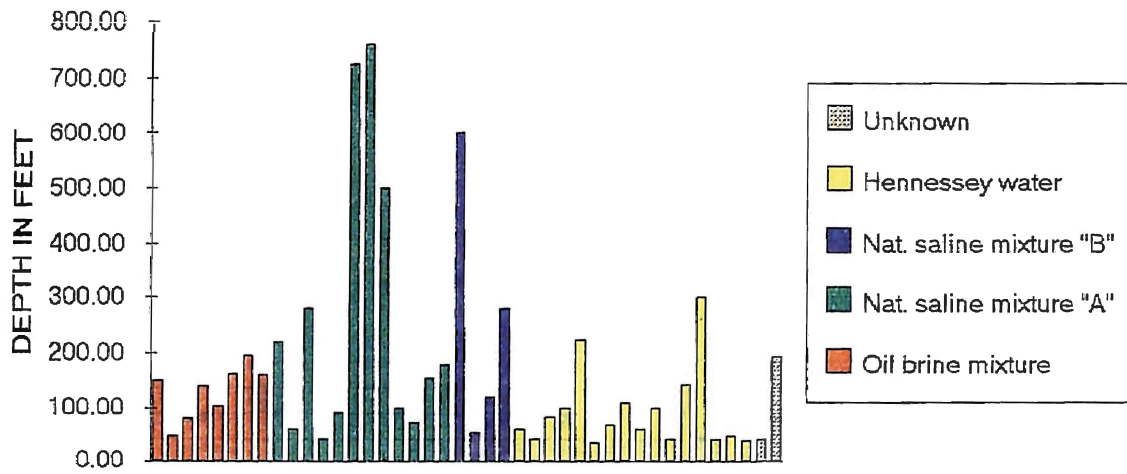
The fact that the analyses interpreted to be oil brine mixtures by geochemical relationships are from wells located in or in close proximity to an old "Giant Oil Field" further supports the conclusion that the higher chloride levels observed in these wells are likely the result of oil field activity.

All of the interpreted oil brine mixtures are from wells completed from depths of less than 200 feet and therefore it is unlikely that the upconing of deeper natural saline ground waters is present (Figure 33). In addition, with the exception of well 94, these wells are not located next to fluvial systems, thus eliminating the possibility that these elevated chloride levels are caused by the natural upflow associated with a gaining stream system.

Natural Saline Mixtures

Approximately half of the analyses interpreted geochemically to be natural saline mixtures are producing from wells with depths of greater than 200 feet (Figure 33). These analyses are the result of upconing of the deeper natural saline ground water of the aquifer. This is independent of whether the Hennessey Group is present or absent.

FIGURE 33. Bar Graph: Depth of Well vs Interpreted Source of Chloride

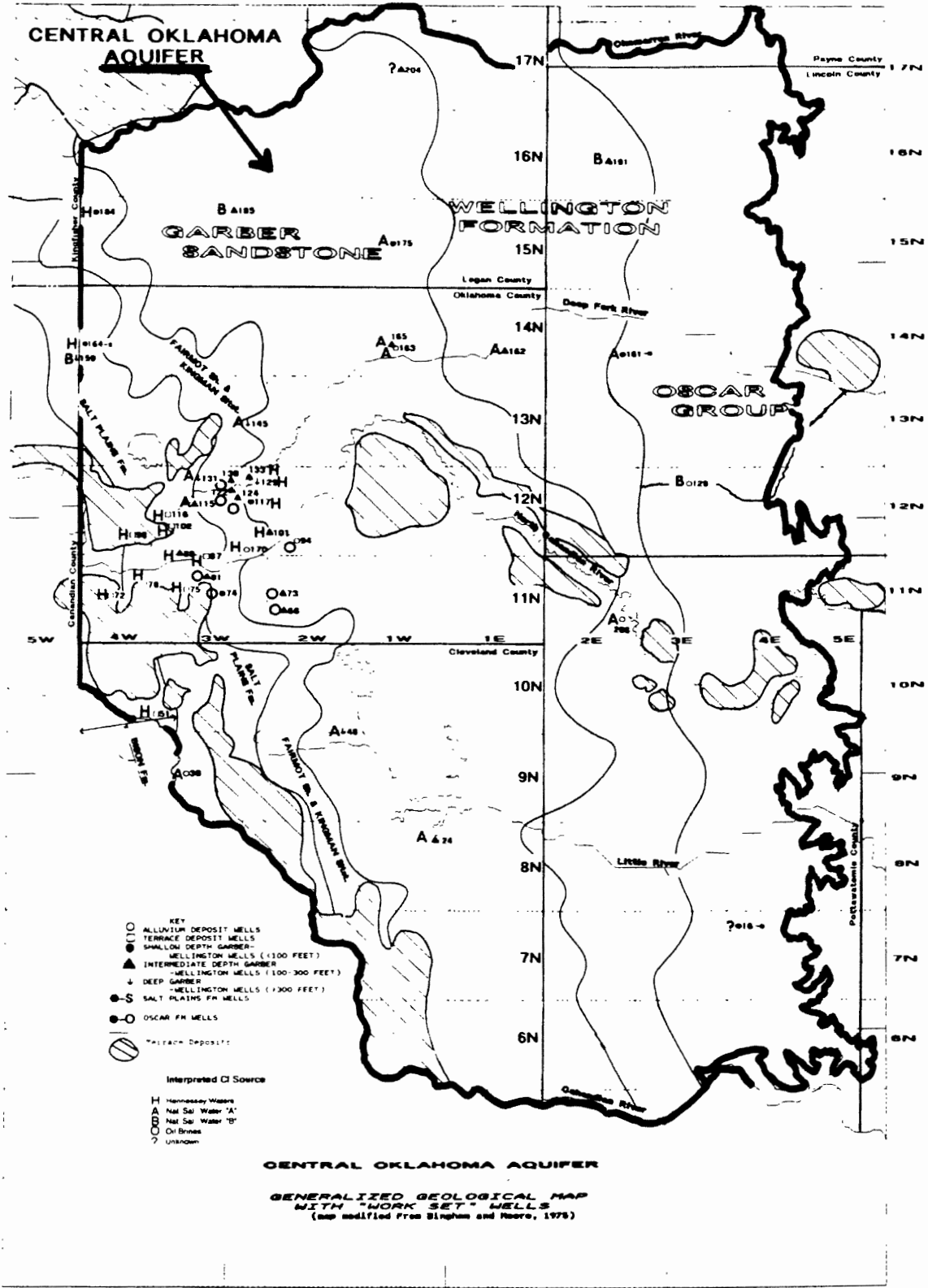


The remaining analyses interpreted geochemically to be natural saline mixtures are from wells located in the alluvium and terrace deposits or are from shallow wells located in the bedrock aquifer near major streams. As described earlier, there is a relationship between ground water quality and discharge areas. The upward flow path of deeper aquifer waters and their subsequent mixing with the shallower waters increases chloride levels in active discharge areas. This appears to be the case for these shallow wells, where the natural ground water flow in a gaining stream system is causing the deeper, more saline water to migrate upward, resulting in elevated chloride levels.

Hennessey Waters

All of the wells thought to reflect Hennessey waters are located in the western portion of the study unit. These wells have the Hennessey Group present in the area or are located along the truncation of the Hennessey Group (Figure 34). These characteristically are shallow wells, with 10 out of the 12 being less than or equal to 100 feet in depth.

Figure 34. Generalized Geological Map with "Work Set" Wells



Other Miscellaneous Relationships

Abandoned Oil Field Surface Waste Pits

Well 73 is potentially different from the other oil field brine contaminated wells. This well is only 52 feet deep; this shallow depth indicates that a high concentration of chloride is present immediately at the top of the fresh water aquifer.

A similar situation was reported in the Valley Brook city water well that is approximately 3 miles southeast of this well (personal communication with Christenson, 1992). The Valley Brook city well produced from the deeper, confined section of the Garber-Wellington Formation. This well showed a sudden increase in chloride concentration. It was discovered that the increased salinity was the result of a hole which had developed in the casing near the top of the fresh water zone within the unconfined section of the aquifer. As in well 73, higher amounts of chloride were present near the top of the aquifer.

Both of these wells are located in the center of the old Oklahoma City Field. The use of surface waste pits for the disposal of drilling mud and brine was common during the field's early development. The presence of a brine zone near the surface of the water table suggests that this higher level of chloride could be the result of an abandoned surface waste pit located in the immediate area. The high barium value associated with well 73 could be the result of

drilling muds (Refer to Ba^{++} versus Cl^{-} section, page 61). Additionally, barium could enter the ground water through ion exchange or dissolution of minerals as the oil brine leaching from the pit moved through the vadose zone.

Tritium and Fluoride

Figures 35a and 35b

The presence of detectable tritium has been used to infer that post-1952 recharge waters are entering a subject well (Fetter, 1988). Figure 35a shows the relationship between the absence of detectable tritium and elevated fluoride concentrations in the "Work Set" data. Figure 35b shows all of the analyses in the original data base (202 analyses) that have high fluoride concentrations (>2 mg/L). All of the analyses with high fluoride concentrations (>2 mg/L) lack detectable levels of tritium. Therefore, if tritium data is not available, a high fluoride concentration could be used to infer that no post-1952 recharge waters are present in this portion of the Central Oklahoma aquifer.

Summary Flow Chart

A detailed flow chart (Figure 36) was created to offer a workable procedure for determining the possible source of an elevated chloride concentration in a water from the Central Oklahoma aquifer. This flow chart summarizes what

**FIGURE 35a. Bar Graph: Fluoride and Tritium Concentrations
42 Well Work Set**

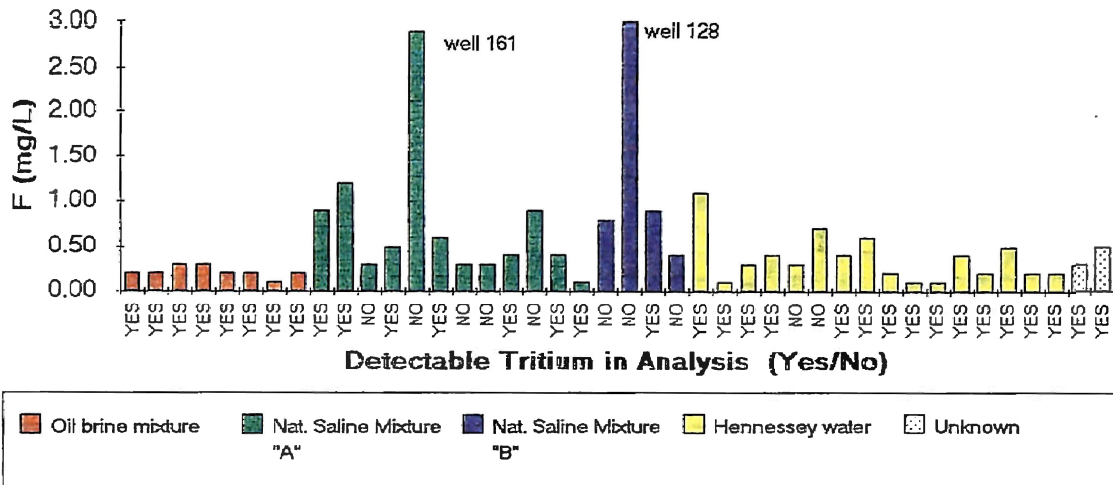


FIGURE 35b. Bar Graph: Fluoride and Tritium Concentrations for All Wells with > 2 mg/L Fluoride

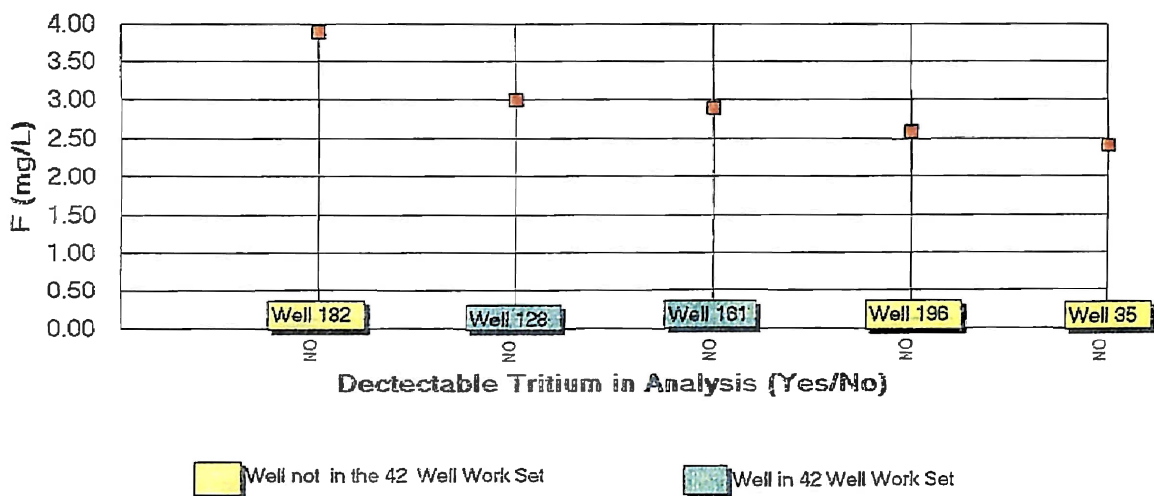
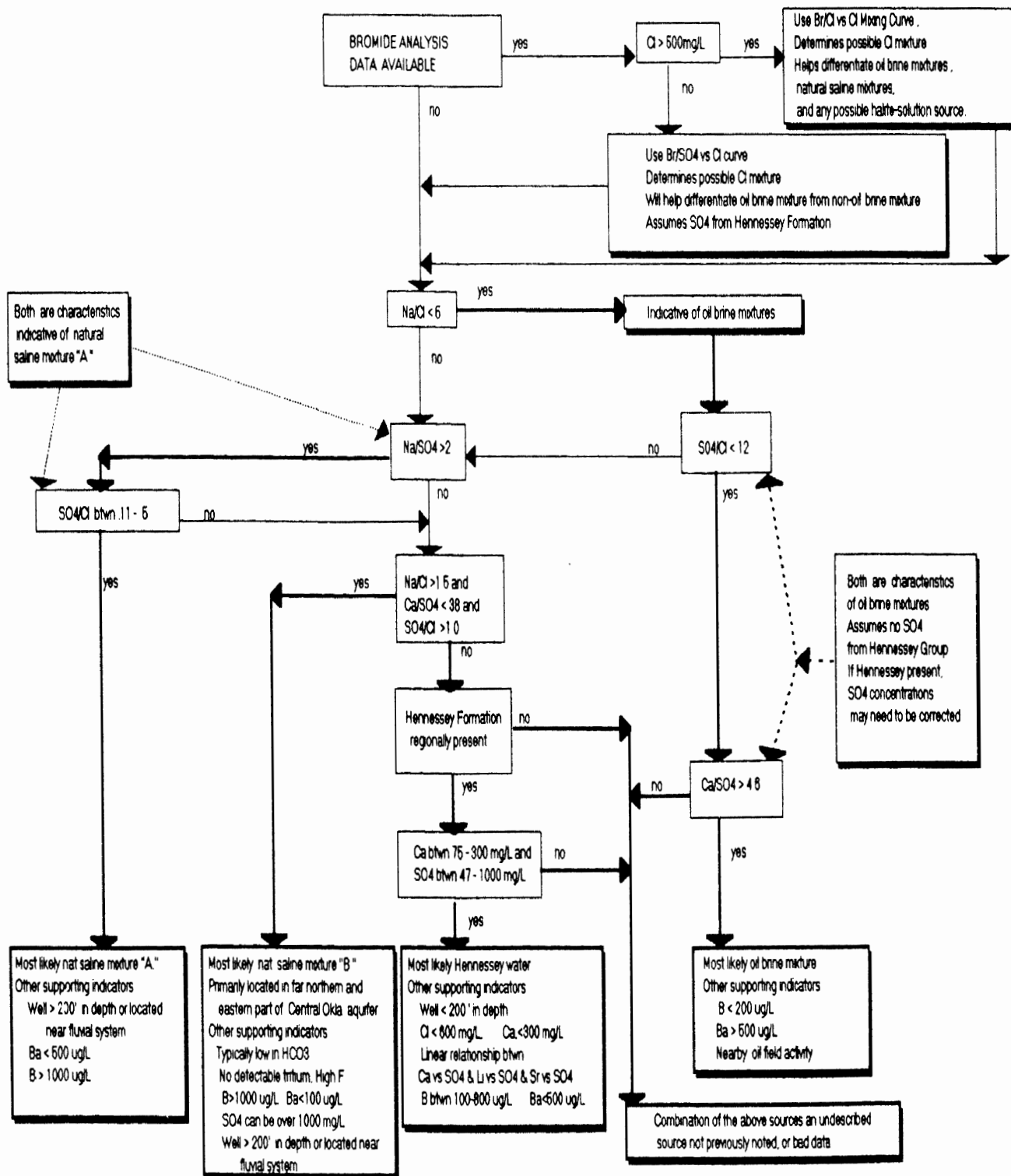


Figure 36. Summary Flow Chart to Determine Possible Source of Increased Chloride Concentration in the Central Oklahoma Aquifer

All units are in -mg/L



were interpreted to be the more diagnostic geochemical relationships, as well as physical and geographical characteristics studied in this thesis. Since most water analyses do not include the numerous trace elements that were available in this study, the main body of the flow chart was limited to the use of major constituents. However, the availability of trace element data greatly improves one's interpretation. This is especially true in the western part of the study unit where the Hennessey Formation will cause elevated sulfate levels. In this case, trace element data provides information that is useful for an interpretation.

Geochemical Reaction Processes

Several of the previous graphs indicate that ion exchange and/or the precipitation or dissolution of minerals possibly occurred in the oil brine mixtures and the natural saline mixtures "B."

It is assumed that no significant secondary sources of chloride are present in the analyses. The possibility of additional chloride derived from halite dissolution (naturally occurring halite or NaCl road salt) being a secondary source is eliminated by the very low Na^+/Cl^- ratios present in the analyses. Mixing with a halite solution would derive a mixture with a Na^+/Cl^- ratio closer to unity. Non-halite salts (KCl and CaCl_2) are commonly used in oil field completion practices such as cementing and

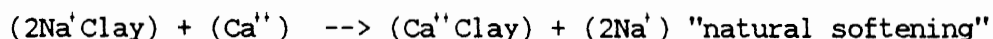
loading casing. However, the analyses are too uniform in chemical composition over a large areal extent for this to be a likely secondary source. Therefore, in the following discussion, it is assumed that no secondary source of chloride is present.

Ion Exchange

Under certain conditions in an aqueous solution, ions attracted to a solid surface may be exchanged for the solid's ions. This process is known as ion exchange. Divalent ions are more strongly bonded and tend to replace monovalent ions (Fetter, 1988). A generalized ordering of cation exchangeability for common ions in ground water is:



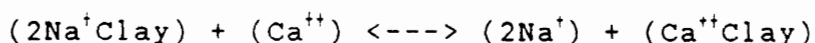
In the process of natural softening, the following illustration commonly is used to show the loss of calcium in the solution and the release of sodium:



However, it is a reversible reaction and at high ion strengths, the monovalent ions can replace divalent ions. An example of this process, referred to as reverse softening, can be found in home water softeners. Regeneration is accomplished by passing a concentrated NaCl solution through the system and the typical ion exchange process is reversed (Krauskopf, 1970).

The equilibrium of the softening process may be displaced in one direction or the other by a change in the

relative concentrations of sodium and calcium:



-----> natural softening

<----- reverse softening

The Na^+ versus Cl^- graphs (Figures 12a and 12b) show that both the oil brine mixtures and natural saline mixtures "B" have less sodium relative to chloride than their respective end members. This indicates that sodium has been removed from these solutions by reverse ion exchange. Reverse ion exchange is common in oil field brines (Collins, 1975). It also has been documented in the advancing fronts of salt-water intrusions (Richter and Kreitler, 1991, and Poland and others, 1959) and, under certain conditions, it can occur in irrigated areas (Hem, 1989). It seems logical that when the sodium-rich oil field brines and the deeper natural saline waters "B" enter the low sodium fresh waters, natural softening could cease and reverse softening could occur.

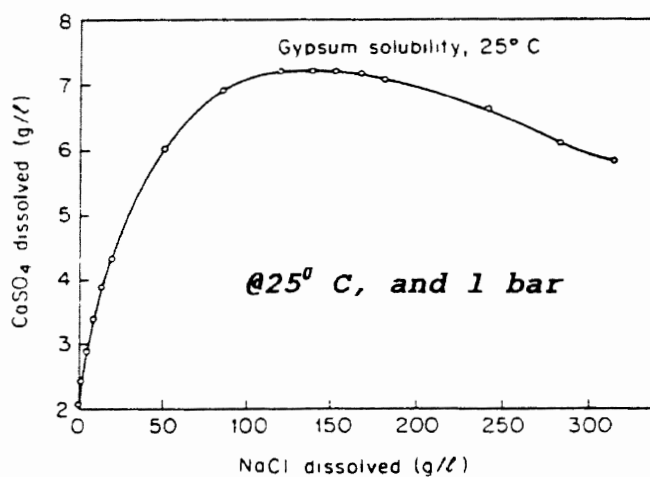
Precipitation of Gypsum, Anhydrite, and Barite

The SO_4^{2-} versus Cl^- graphs (Figures 14a and 14b) show a decrease in the $\text{SO}_4^{2-}/\text{Cl}^-$ ratio in both the oil brine mixtures and the natural saline mixtures "B" when compared to their end members. This decrease could be the result of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), anhydrite (CaSO_4), or barite (BaSO_4) precipitation. Past work has shown that the Central Oklahoma aquifer is undersaturated with respect to gypsum and anhydrite, while calcite, aragonite, and dolomite

concentrations vary from supersaturated to undersaturated (Parkhurst, 1992, and Scott, 1985). WATEQF, a computer program which calculates chemical equilibria, was used to calculate the saturation indices for various mineral species. The subject analyses conform to this previous work. However, these calculated saturation indices are not reflective of the conditions at the point of mixing.

The occurrence of either of the following two processes could change the equilibrium of the aquifer. First, the dilution of NaCl-rich oil brine or NaCl-rich deeper natural saline ground water "B" will reduce the ionic strength of the solution and therefore reduce the solubility of gypsum, anhydrite, and barite in the solution. Figure 37 illustrates how the solubility of gypsum is greatly reduced by lowering ionic strength (Freeze and Cherry, 1979). Second, reverse softening could appreciably increase the concentration of calcium in the mixture and result in increased saturation indices for gypsum and anhydrite. Thus, by mixing an oil field brine or deeper natural saline ground water "B" with the fresh water aquifer, the mixed waters could possibly become saturated in respect to either gypsum, anhydrite, or barite near the point of mixing. This would allow for the removal of sulfate and calcium or barite from solution through precipitation and account for the loss of sulfate relative to chloride in these mixtures.

Figure 37. Solubility of Gypsum in Aqueous Solutions of Different NaCl Concentrations
(from Freeze and Cherry, 1979)



The XY Graph of Ca^{++} vs SO_4^{-} (Figure 15) has a good curvilinear trend exhibited by the natural saline mixtures "A" analyses at high sulfate concentrations. The natural saline mixtures "A" analyses curve toward the end members for the natural saline mixtures "B". If, in fact, gypsum and/or anhydrite is precipitating out as described in the above situations, the curvilinear trend could suggest that the end member for the natural saline mixtures "A" could have a composition very similar to deeper natural saline "B" ground water but with the high concentration of sulfate subsequently removed upon mixing by the precipitation of gypsum and/or anhydrite.

Sources of the Chloride Associated with the Hennessey Group

Due to a maximum chloride concentration of only 450 mg/L in these Hennessey water analyses, the origin of the elevated chloride levels in the Hennessey-associated waters could not be conclusively concluded. A review of the land surface at many of the wells producing Hennessey waters did not yield any obvious anthropogenic origin for this chloride. Nitrate and ammonia were slightly higher in several of these wells, suggesting that fertilization could have contributed in part to these higher chloride levels.

However, a very consistent pattern exists between the production of ground waters from the Salt Plains Formation, Kingman Siltstone, and Fairmount Shale units of the

Hennessey Group and increased chloride levels (Figure 34). These units are described regionally as containing shale, siltstone, and some fine grained sandstone (Bingham and Moore, 1975). The beds within these units have very low transmissivities and are laterally discontinuous. The stratigraphically equivalent members of these units are known to contain halite approximately 50 miles west of the study unit (Johnson and others, 1989). In addition, Jordan and Vosburo (1962) described a very salty shale in the lower section of the Permian in Blaine County located immediately to the west of this area.

As discussed in the "Solution of Natural Halite" section of this study, no halite has been described in the study unit. Therefore, it appears that these higher salinities could be the result of a remnant halite solution brine, the dissolution of scattered pockets of halite, or the dissolution of interstitial halite that is present in the shale and siltstone. A more detailed study would be required to identify the source of the chloride in the Hennessey Group-associated waters.

CHAPTER IV

CONCLUSIONS

CONCLUSION 1:

Three major chloride sources were interpreted to have caused the elevated chloride concentrations in the waters of the Central Oklahoma aquifer. The three major sources are:

Oil Field Brines

It was interpreted that oil field brines have mixed with the fresh waters of the Central Oklahoma aquifer. These oil field brine/fresh water mixtures, referred to as "oil brine mixtures," exhibit the following characteristics in the study unit:

- At high Cl^- concentrations (>500 mg/L), site specific Br^-/Cl^- versus Cl^- mixing curves can be used to identify oil field brine contamination (Page 50)
- At low Cl^- concentrations (<500 mg/L), $\text{Br}^-/\text{SO}_4^{2-}$ versus Cl^- mixing curves can be used to identify oil field brine contamination (Page 74)
- Have low Na^+/Cl^- weight ratios ($<.5$) (Page 53)
- Have low $\text{SO}_4^{2-}/\text{Cl}^-$ weight ratios ($<.12$) (Page 58)
- Have high $\text{Ca}^{++}/\text{SO}_4^{2-}$ weight ratios (>4.6) (Page 60)

CONCLUSION 1 (continued):

- Frequently have low concentrations of boron (<200 µg/L) (Page 60)
- Frequently have high concentrations of barium (>500 µg/L) (Page 62)
- Wells are located near oil field activity

Deeper Natural Saline Ground Waters

It was interpreted that deeper natural saline ground waters have mixed with the fresh waters of the Central Oklahoma aquifer. These deeper natural saline ground water/fresh water mixtures were subdivided into:

- A high Na^+ - Cl^- saline water, referred to as "natural saline mixture 'A,'" and
- A high Na^+ - SO_4^{2-} saline water, referred to as "natural saline mixture 'B.'"

The characteristics of each are reviewed below:

Natural Saline Mixtures "A":

Natural saline mixtures "A" in the study area display the following characteristics:

- Have $\text{Na}^+/\text{SO}_4^{2-}$ weight ratios (>2.0) with sulfate concentrations ranging from 20 to 200 mg/L (Page 55)
- Have intermediate $\text{SO}_4^{2-}/\text{Cl}^-$ weight ratios (>.11 to <.5) (Page 58)
- Typically natural saline mixtures "A" are limited to either deep wells (>200 feet in depth) or to wells located near a fluvial system

CONCLUSION 1 (continued):

- Frequently have high concentrations of boron ($>1000 \mu\text{g/L}$) and exhibit a good linear relationship between boron and chloride (Page 60)
- Frequently have low concentrations of barium ($<500 \mu\text{g/L}$) (Page 62)

Natural Saline Mixtures "B":

Natural saline mixtures "B" in the study area have the following characteristics:

- At high Cl^- concentrations ($>500 \text{ mg/L}$), Br^-/Cl^- versus Cl^- mixing curves can be used to identify natural saline mixtures "B" (Page 50)
- Have high $\text{SO}_4^{2-}/\text{Cl}^-$ weight ratios (>1) (Page 58)
- Have Na^+/Cl^- weight ratios of greater than 1.5 with low $\text{Ca}^{++}/\text{SO}_4^{2-}$ weight ratios ($<.38$) (Pages 53 and 60)
- Have high concentrations of boron ($>1000 \mu\text{g/L}$) and exhibit a good linear relationship between boron and chloride (Page 60)
- Typically natural saline mixtures "B" are limited to either deep wells (>200 feet in depth) or to wells located near a fluvial system
- Frequently display relatively high fluoride concentrations
- Frequently display no detectable tritium concentrations
- Frequently display relatively low bicarbonate concentrations

CONCLUSION 1 (continued):

- Frequently have low concentrations of barium (<100 µg/L)(Page 62)

Hennessey Group-Associated Water

Some of the elevated chloride levels detected in the water analyses are related to the presence of the Hennessey Group and are referred to as "Hennessey waters." These Hennessey waters exhibit the following characteristics in the study unit:

- Have $\text{SO}_4^{2-}/\text{Cl}^-$ weight ratios $>.36$ (Page 58)
- Have Na^+/Cl^- weight ratios of less than 1.5 or $\text{Ca}^{++}/\text{SO}_4^{2-}$ weight ratios $>.38$ (Pages 53 and 60)
- Have Ca^{++} concentrations between 75-300 mg/L and SO_4^{2-} concentrations between 47-1000 mg/L (Page 60)
- Hennessey waters are located in the western portion of the study unit where the Hennessey Group is present locally (Page 83)
- Typically are from shallow wells (<200 feet in depth)
- Frequently display linear relationships between Ca^{++} versus SO_4^{2-} (Page 60)
 Li^+ versus SO_4^{2-} (Page 64)
 Sr^{++} versus SO_4^{2-} (Page 64)

CONCLUSION 1 (continued):

- Frequently have the following constituent concentrations:

Boron between 100-600 µg/L (Page 60)

Ba⁺⁺ > 500 µg/L (Page 62)

Cl⁻ < 600 mg/L (Page 53)

CONCLUSION 2:

Several graphic relationships were derived to assist in the interpretation of the source of the elevated chloride concentrations in this study unit. It appears that the simplest and best graphic method to delineate if the higher chloride was derived from an oil brine rather than a non-oil brine source is the following graphic relationship:

- Br⁻/SO₄⁼ versus Cl⁻

Other graphic relationships derived to assist in the determination of the source of the elevated chloride concentrations are:

- Br⁻/SO₄⁼ versus SO₄⁼/Cl⁻
- Na⁺/Cl⁻ versus SO₄⁼/Cl⁻
- Ca⁺⁺/SO₄⁼ versus SO₄⁼/Cl⁻

CONCLUSION 3:

Previously published multiple component plots can help to distinguish oil field brine contamination from non-oil field brine contamination in the study unit:

Ca⁺⁺/(Ca⁺⁺+SO₄⁼) vs Na⁺/(Na⁺+Cl⁻) (Hounslow and Goff, 1991)

(Ca⁺⁺+Mg⁺⁺)/SO₄⁼ vs Na⁺/Cl⁻ (Richter and Kreitler, 1986a,b)

CONCLUSION 4:

When oil field brine or natural saline ground water "B" mixes with the fresh water of the Central Oklahoma aquifer, the previously documented natural softening process which typically occurs in the aquifer ceases and the process of reverse softening occurs. Typically, oil brine mixtures and natural saline mixtures "B" have less sodium relative to chloride than their respective end members. This suggests that sodium has been removed from these mixtures by reverse ion exchange.

CONCLUSION 5:

Agricultural activities might have contributed to the elevated chloride levels in a few cases. However, this source does not appear to be one of the primary causes of the high chloride concentrations in the waters of the Central Oklahoma aquifer.

CONCLUSION 6:

The dissolution of road salts does not appear to be a major source of the elevated chloride concentrations in the Central Oklahoma aquifer. This conclusion is supported by the fact that there is a lack of correlatable patterns between major highway systems, wells that exhibited increased chloride levels, and Br^-/Cl^- and Na^+/Cl^- ratios which would conform to road salt dissolution.

CONCLUSION 7:

The elevated chloride concentration in analysis 73 likely is the result of precipitation percolating through an abandoned oil field surface waste pit located in the immediate area. (See "Abandoned Oil Field Surface Waste Pit" section)

CONCLUSION 8:

A good correlation exists between the absence of detectable tritium and elevated fluoride concentrations. All of the reviewed analyses that have high concentrations of fluoride (>2 mg/L) lack detectable levels of tritium. Therefore, if tritium data is not available, a high fluoride concentration could be used to infer that no post-1952 recharge waters are present in this portion of the Central Oklahoma aquifer.

CONCLUSION 9:

Several graphic relationships suggest that when oil field brines or natural saline ground waters "B" mix with the fresh waters of the Central Oklahoma aquifer, the mixtures become saturated with respect to gypsum, anhydrite, and barite resulting in the removal of sulfate and calcium or barium through precipitation.

CONCLUSION 10:

A more detailed study is required to identify the origin of the chloride in the Hennessey Group-associated water.

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APPENDIXES

APPENDIX A

**CONSTITUENTS ANALYZED AND REPORTING LEVELS FOR
EACH SAMPLING NETWORK**

Appendix I
From Ferree and others, 1992.
Page 1 of 5

Constituents analyzed and reporting levels for each sampling network

[, Network: Geoghem: geochemical network; Bedrock, low-density survey sampling bedrock network; Urban, targeted sampling urban network; Alliter, low-density survey sampling alluvium and terrace network; X, sampled in every well in this network; X, geochemical network chromium data were produced using an atomic absorption graphite furnace method which has a reporting level of 1 µg/L; §, for bedrock network wells, only those greater than 300 feet deep were sampled for ²/1 hydrogen and ¹⁸/¹⁶ oxygen isotopes; *, only selected sites were analyzed for picloram and dicamba in the targeted sampling urban network; \$, only in samples analyzed for organophosphorus compounds after January, 1990; °C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 °C; Reporting level: these values represent the minimum reporting value for the method used for each constituent. The actual minimum reporting value for any given constituent in the report may be higher than that value if analytical conditions, at the time of analysis, were not ideal. Dual reporting levels(--/--) reflect reporting levels for samples with specific conductance less than 2,000 µS/cm, and greater than 2,000 µS/cm respectively; mg/L, milligrams per liter; µg/L, micrograms per liter; pCi/L, picocuries per liter; Percent modern, 0.7 percent, or better, modern carbon at the 10,000 year age; δ-value, delta value; permil, ((isotope ratio in sample minus ratio in standard) divided by ratio in standard) multiplied by 1,000; PDB, Peedee belemnite; SMOW, Standard Mean Ocean Water; CDT, Canyon Diablo Troilite; DDD, 1,1-dichloro-2,2-bis (p-chlorophenyl) ethane; DOE, dichlorodiphenyldichloroethylene; DDT, dichlorodiphenyltrichloroethane; PCB's, polychlorinated biphenyls; 2,4-D, (2,4-dichlorophenoxy)-acetic acid; 2,4-DP, 2-(2,4-dichlorophenoxy)-propionic acid (±)2-(2,4-dichlorophenoxy)-propanoic acid; 2,4,5-T, 2,4,5-trichlorophenoxy-acetic acid. Synthetic organic chemical names are from Meister, (1988).]

Network			
G	B	U	A
e	e	r	i
o	d	b	i
c	r	e	&
h	o	n	t
e	c	e	
m	k	r	
		Reporting level	Constituent
Properties			
X	X	X	X
		0.1	Specific conductance, (µS/cm)
X	X	X	X
		0.1	pH (standard units)
X	X	X	X
		0.5	Water temperature, (°C)
X	X	X	X
		0.1	¹⁸ / ¹⁶ oxygen, dissolved (mg/L)
X	X	X	X
		1	Hardness, total (mg/L as calcium carbonate)
X	X	X	X
		1	Alkalinity, whole water, incremental titration, field, total, (mg/L as calcium carbonate)
Dissolved Solids			
X	X	X	X
		1	Solids, sum of constituents, dissolved (mg/L)
Major Ions			
X	X	X	X
		0.02/0.06	Calcium, dissolved (mg/L)
X	X	X	X
		0.01/0.03	Magnesium, dissolved (mg/L)
X	X	X	X
		0.2/0.6	Sodium, dissolved (mg/L)
X	X	X	X
		1	Sodium, percent
X	X	X	X
		0.1	Potassium, dissolved (mg/L)
X	X	X	X
		1	Bicarbonate, whole water, incremental titration, field (mg/L)
X	X	X	X
		1	Carbonate, whole water, incremental titration, field (mg/L)
X	X	X	X
		1	Sulfate, dissolved (mg/L)
X	X	X	X
		0.1	Chloride, dissolved (mg/L)
X	X	X	X
		0.01	Fluoride, dissolved (mg/L)
X	X	X	X
		0.01	Bromide, dissolved (mg/L)
X	X	X	X
		0.03	Silica, dissolved (mg/L)

*Constituents analyzed and reporting levels
for each sampling network—Continued*

<u>Network</u>					
G e o c r o n o m	B e r l i n g h o n t e r n e t	U n i t e d S t a t e s	A m e r i c a n I n d i c a t o r	Reporting level	Constituent
Nutrients					
X	X	X	X	0.001	Nitrite, dissolved (mg/L as nitrogen)
X	X	X	X	0.1	Nitrite plus nitrate, dissolved (mg/L as nitrogen)
X	X	X	X	0.002	Ammonia, dissolved (mg/L as N)
X	X	X	X	0.2	Ammonia plus organic nitrogen, dissolved (mg/L as nitrogen)
X	X	X	X	0.001	Phosphorous, orthophosphate, dissolved (mg/L as phosphorous)
Carbon					
X	X		X	0.1	Carbon, organic, dissolved (mg/L)
Trace Elements					
X	X	X	X	10	Aluminum, dissolved ($\mu\text{g/L}$)
	X	X	X	1	Antimony, dissolved ($\mu\text{g/L}$)
X	X	X	X	1	Arsenic, dissolved ($\mu\text{g/L}$)
X	X	X	X	2/6	Barium, dissolved ($\mu\text{g/L}$)
X	X	X	X	0.5/1.5	Beryllium, dissolved ($\mu\text{g/L}$)
X	X	X	X	10	Boron, dissolved ($\mu\text{g/L}$)
X	X	X	X	1/3	Cadmium, dissolved ($\mu\text{g/L}$)
X	X	X	X	5/15	Chromium, dissolved ($\mu\text{g/L}$)
	X			1	Chromium, hexavalent, dissolved ($\mu\text{g/L}$)
X	X	X	X	3/9	Cobalt, dissolved ($\mu\text{g/L}$)
X	X	X	X	10/30	Copper, dissolved ($\mu\text{g/L}$)
X	X	X	X	3/9	Iron, dissolved ($\mu\text{g/L}$)
X	X	X	X	10/30	Lead, dissolved ($\mu\text{g/L}$)
X	X	X	X	4/12	Lithium, dissolved ($\mu\text{g/L}$)
X	X	X	X	1/3	Manganese, dissolved ($\mu\text{g/L}$)
	X	X	X	0.1	Mercury, dissolved ($\mu\text{g/L}$)
X	X	X	X	10/30	Molybdenum, dissolved ($\mu\text{g/L}$)
X	X	X	X	10/30	Nickel, dissolved ($\mu\text{g/L}$)
X	X	X	X	1	Selenium, dissolved ($\mu\text{g/L}$)
X	X	X	X	1/3	Silver, dissolved ($\mu\text{g/L}$)
X	X	X	X	0.5/1.5	Strontium, dissolved ($\mu\text{g/L}$)
X	X	X	X	6/18	Vanadium, dissolved ($\mu\text{g/L}$)
X	X	X	X	3	Zinc, dissolved ($\mu\text{g/L}$)
Radionuclides					
	X	X	X	0.4	Gross alpha, dissolved (pCi/L as $^{230}\text{thorium}$)
	X	X	X	0.4	Gross alpha, dissolved ($\mu\text{g/L}$ as U-natural)
	X	X	X	0.4	Gross beta, dissolved (pCi/L as $^{137}\text{cesium}$)
	X	X	X	0.4	Gross beta, dissolved (pCi/L as $^{90}\text{strontium}/^{90}\text{yttrium}$)
X				0.02	$^{226}\text{Radium}$, dissolved (pCi/L)
X				1.0	$^{228}\text{Radium}$, dissolved (pCi/L)
X	X	X	X	80	$^{222}\text{Radium}$, total (pCi/L)

Constituents analyzed and reporting levels
for each sampling network—Continued

Network			
O B U A		Reporting	Constituent
e e r i		level	
o d b l			
o r e &			
h o n t			
e e e			
m k r			
Radionuclides—Continued			
X X X X	0.3		Tritium, total (pCi/L)
X X X X	0.1		²³⁴ Uranium, dissolved, (pCi/L)
X X X X	0.1		²³⁵ Uranium, dissolved, (pCi/L)
X X X X	0.1		²³⁸ Uranium, dissolved, (pCi/L)
X X X X	0.2		Uranium, natural, dissolved (µg/L)
Isotopic Ratios			
X	0.70		¹⁴ Carbon, percent modern
X	+/- 0.3		¹³ / ¹² Carbon, δ-value relative to PDB (permil)
X #	+/- 1.5		² / ¹ Hydrogen, δ-value relative to SMOW (permil)
X #	+/- 0.15		¹⁸ / ¹⁶ Oxygen, δ-value relative to SMOW (permil)
X	+/- 0.3		³⁴ / ³² Sulfur, δ-value relative to CDT (permil)
Volatile Organic Compounds			
X X X	0.20		Benzene, total (µg/L)
X X X	0.20		Bromobenzene, whole water, total (µg/L)
X X X	0.20		Bromoform, total (µg/L)
X X X	0.20		Chlorobenzene, total (µg/L)
X X X	0.20		1,2-Dichlorobenzene, total (µg/L)
X X X	0.20		1,3-Dichlorobenzene, total (µg/L)
X X X	0.20		1,4-Dichlorobenzene, total (µg/L)
X X X	0.20		Ethyl benzene, total (µg/L)
X X X	0.20		Carbontetrachloride, total (µg/L)
X X X	0.20		Chloroform, total (µg/L)
X X X	0.20		Chloroethane, total (µg/L)
X X X	0.20		1,2-Dibromoethane, whole water, total (µg/L)
X X X	0.20		1,1-Dichloroethane, total (µg/L)
X X X	0.20		1,2-Dichloroethane, total (µg/L)
X X X	0.20		1,1,1,2-Tetrachloroethane, whole water, total (µg/L)
X X X	0.20		1,1,2,2-Tetrachloroethane, total (µg/L)
X X X	0.20		1,1,1-Trichloroethane, total (µg/L)
X X X	0.20		1,1,2-Trichloroethane, total (µg/L)
X X X	0.2		1,2-Dichloroethene, whole water, recoverable (µg/L)
X X X	0.20		1,1-Dichloroethylene, total (µg/L)
X X X	0.20		Tetrachloroethylene, total (µg/L)
X X X	0.2		Trichloroethylene, total (µg/L)
X X X	0.20		Chlorodibromomethane, total (µg/L)
X X X	0.20		Dibromomethane, whole water, recoverable (µg/L)
X X X	0.20		Dichlorobromomethane, total (µg/L)
X X X	0.20		Dichlorodifluoromethane, total (µg/L)
X X X	0.20		Trichlorofluoromethane, total (µg/L)
X X X	0.20		Methyl bromide, total (µg/L)
X X X	0.20		Methyl chloride, total (µg/L)
X X X	0.20		Methylene chloride, total (µg/L)
X X X	0.20		1,2-Dichloropropane, total (µg/L)

*Constituents analyzed and reporting levels
for each sampling network—Continued*

<u>Network</u>			
G e o c h e m	B e r l i n g t o n e r	U d e s t r i c h e n s e	A l l i a n c e
	Reporting level	Constituent	
Volatile Organic Compounds—Continued			
X X X	0.20	1,3-Dichloropropane, whole water, total ($\mu\text{g/L}$)	
X X X	0.20	2,2-Dichloropropane, whole water, total ($\mu\text{g/L}$)	
X X X	0.20	1,2,3-Trichloropropane, whole water, total ($\mu\text{g/L}$)	
X X X	0.2	1,1-Dichloropropene, whole water, total ($\mu\text{g/L}$)	
X X X	0.20	cis-1,3-Dichloropropene, total ($\mu\text{g/L}$)	
X X X	0.20	trans-1,3-Dichloropropene, total ($\mu\text{g/L}$)	
X X X	0.2	Styrene, total ($\mu\text{g/L}$)	
X X X	0.20	Toluene, total ($\mu\text{g/L}$)	
X X X	0.20	ortho-Chlorotoluene, whole water, total ($\mu\text{g/L}$)	
X X X	0.20	para-Chlorotoluene, whole water, total ($\mu\text{g/L}$)	
X X X	0.20	Vinyl chloride, total ($\mu\text{g/L}$)	
X X X	0.2	Xylene, total, whole water, total recoverable ($\mu\text{g/L}$)	
Carbamate Insecticides			
X X X	0.5	Aldicarb, total ($\mu\text{g/L}$)	
X X X	0.5	Aldicarb sulfone, total ($\mu\text{g/L}$)	
X X X	0.5	Aldicarb sulfoxide ($\mu\text{g/L}$)	
X X X	0.5	Carbofuran, total ($\mu\text{g/L}$)	
X X X	0.5	3-Hydroxycarbofuran, total ($\mu\text{g/L}$)	
X X X	0.5	Methiocarb, total ($\mu\text{g/L}$)	
X X X	0.5	Methomyl, total ($\mu\text{g/L}$)	
X X X	0.5	1-Naphthol, total ($\mu\text{g/L}$)	
X X X	0.5	Oxamyl, total ($\mu\text{g/L}$)	
X X X	0.5	Propham, total ($\mu\text{g/L}$)	
X X X	0.5	Propoxur, total ($\mu\text{g/L}$)	
X X X	0.5	Sevin, total ($\mu\text{g/L}$)	
Organochlorine Compounds			
X X X	0.010	Aldrin, total ($\mu\text{g/L}$)	
X X X	0.010	Chlordane, total ($\mu\text{g/L}$)	
X X X	0.010	DDD, total ($\mu\text{g/L}$)	
X X X	0.010	DOE, total ($\mu\text{g/L}$)	
X X X	0.010	DDT, total ($\mu\text{g/L}$)	
X X X	0.010	Dieldrin, total ($\mu\text{g/L}$)	
X X X	0.010	Endosulfan, total ($\mu\text{g/L}$)	
X X X	0.010	Endrin, total ($\mu\text{g/L}$)	
X X X	0.010	Heptachlor, total ($\mu\text{g/L}$)	
X X X	0.010	Heptachlor epoxide, total ($\mu\text{g/L}$)	
X X X	0.010	Lindane, total ($\mu\text{g/L}$)	
X X X	0.01	Methoxychlor, total ($\mu\text{g/L}$)	
X X X	0.01	Mirex, total ($\mu\text{g/L}$)	
X X X	0.01	PCB's, total ($\mu\text{g/L}$)	
X X X	0.10	Naphthalenes, polychlorinated ($\mu\text{g/L}$)	
X X X	0.1	Perthane, total ($\mu\text{g/L}$)	
X X X	1	Toxaphene, total ($\mu\text{g/L}$)	

Page 5 of 5

*Constituents analyzed and reporting levels
for each sampling network—Continued*

<u>Network</u>				
G e o c h e m	B e r l i n g n e t	U n i t e d S t a t e s	A & t e r r i t o r i a n	
		Reporting level	Constituent	
Chlorophenoxy Acid Herbicides, with Dicamba and Picloram				
	•	X	0.01	Dicamba, total ($\mu\text{g/L}$)
	•	X	0.01	Picloram, total ($\mu\text{g/L}$)
X	X	X	0.01	Slivex, total ($\mu\text{g/L}$)
X	X	X	0.01	2,4-D, total ($\mu\text{g/L}$)
X	X	X	0.01	2,4-DP, total ($\mu\text{g/L}$)
X	X	X	0.01	2,4,5-T, total ($\mu\text{g/L}$)
Organophosphorus Insecticides				
\$	\$	\$	0.01	Def, total ($\mu\text{g/L}$)
X	X	X	0.01	Diazinon, total ($\mu\text{g/L}$)
\$	\$	\$	0.01	Disulfoton, total ($\mu\text{g/L}$)
X	X	X	0.01	Ethion, total ($\mu\text{g/L}$)
X	X	X	0.01	Trithion, total ($\mu\text{g/L}$)
X	X	X	0.01	Malathion, total ($\mu\text{g/L}$)
X	X	X	0.01	Methyl parathion, total ($\mu\text{g/L}$)
X	X	X	0.01	Methyl trithion, total ($\mu\text{g/L}$)
X	X	X	0.01	Parathion, total ($\mu\text{g/L}$)
\$	\$	\$	0.01	Phorate, total ($\mu\text{g/L}$)
Triazines and Other Nitrogen-Containing Herbicides				
X	X	X	0.10	Alachlor, total recoverable ($\mu\text{g/L}$)
X	X	X	0.10	Ametryne, total ($\mu\text{g/L}$)
X	X	X	0.10	Atrazine, total ($\mu\text{g/L}$)
X	X	X	0.1	Bromacil, total ($\mu\text{g/L}$)
X	X	X	0.1	Butachlor, total ($\mu\text{g/L}$)
X	X	X	0.1	Butylate, total ($\mu\text{g/L}$)
X	X	X	0.1	Carboxin, total ($\mu\text{g/L}$)
X	X	X	0.10	Cyanazine total ($\mu\text{g/L}$)
X	X	X	0.1	Cycloate, total ($\mu\text{g/L}$)
X	X	X	0.1	Diphenamid, total ($\mu\text{g/L}$)
X	X	X	0.1	Hexazinone, total ($\mu\text{g/L}$)
X	X	X	0.1	Metolachlor, whole water, total recoverable ($\mu\text{g/L}$)
X	X	X	0.1	Metribuzine, whole water, total recoverable ($\mu\text{g/L}$)
X	X	X	0.1	Prometon, total ($\mu\text{g/L}$)
X	X	X	0.1	Prometryne, total ($\mu\text{g/L}$)
X	X	X	0.1	Propachlor, total ($\mu\text{g/L}$)
X	X	X	0.10	Propazine, total ($\mu\text{g/L}$)
X	X	X	0.10	Simazine, total ($\mu\text{g/L}$)
X	X	X	0.1	Simetryne, total ($\mu\text{g/L}$)
X	X	X	0.1	Terbacil, total ($\mu\text{g/L}$)
X	X	X	0.10	Trifluralin, total recoverable ($\mu\text{g/L}$)
X	X	X	0.1	Vernolate, total ($\mu\text{g/L}$)

APPENDIX B

**SUMMARY OF NRIS DATA FOR OIL AND GAS WELLS IN
LINCOLN, LOGAN, AND OKLAHOMA COUNTIES WITH
KEY TRACE ELEMENTS AS CONSTITUENTS**

**APPENDIX B
SUMMARY OF ENRIS DATA FOR OIL AND GAS WELLS
IN LINCOLN, LOGAN, AND OKLAHOMA COUNTIES
WITH KEY TRACE ELEMENTS AS CONSTITUENTS**

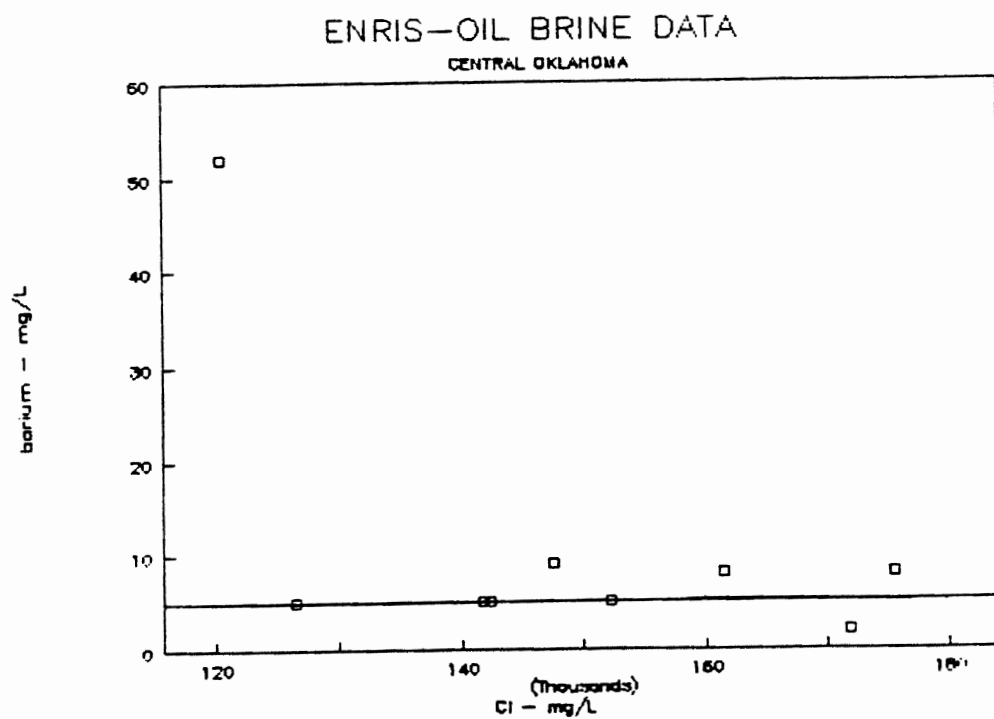
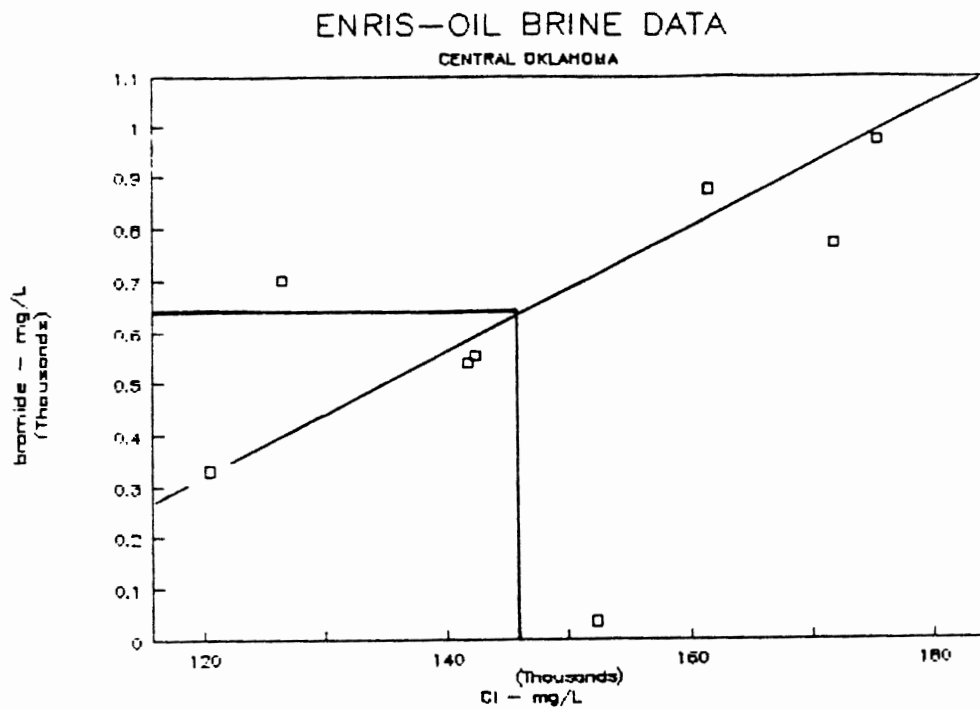
Well Loc.	ID #	County	Formation	Well Name
31-17n-4e	35007927	Lincoln	Checkerboard	W. Ag Cleve. sd Unite #2
33-16n-4w	35002775	Logan	Miss. Lime	Lucille #1
5-19n-2w	35002789	Logan	Cleveland	Bulling "A" #1
29-19n-4w	35002862	Logan	Layton	Cromer #1
32-20-4w	35009158	Logan	Cleveland	Mahler #1
20-11n-2w	35002780	Oklahoma	Pure	Prosperity Acres #1
3-11n-3w	35002861	Oklahoma	Wilcox	Bisbee #1
21-14n-2w	35002777	Oklahoma	Wilcox	Walnut Grove #2

Well Loc.	TDS mg/L	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	HCO3 mg/L	SO4 mg/L	Cl mg/L	Br mg/L	Sr mg/L	Ba ug/L	B ug/L	Li ug/L
31-17n-4e	194800	9450	3105	61000	160	24	0	120500	330	518	52000	6000	5000
33-16n-4w	119331	15298	0	54300	713	0	267	126468	702	1410	5000	9000	
5-19n-2w	245451	18551	970	61000	361	183	262	161426	877	1515	8000	6000	15000
29-19n-4w	239107	17189	2315	44550	400	0	182	171839	771	1516	2000	3000	14000
32-20-4w	254424	20500	4740	49100	682	0	658	175450	973	1590	8000	6000	30000
20-11n-2w	222825	15866	2310	50050	535	0	362	152307	34	810	5000	5000	25000
3-11n-3w	251960	12667	4635	89400	957	0	0	142400	554	898	5000	0 00	20000
21-14n-2w	229524	14687	1465	67650	885	31	220	141825	541	1765	5000	5000	10000
				Median Calc	Value			147353	628	1463	5000	5500	15000

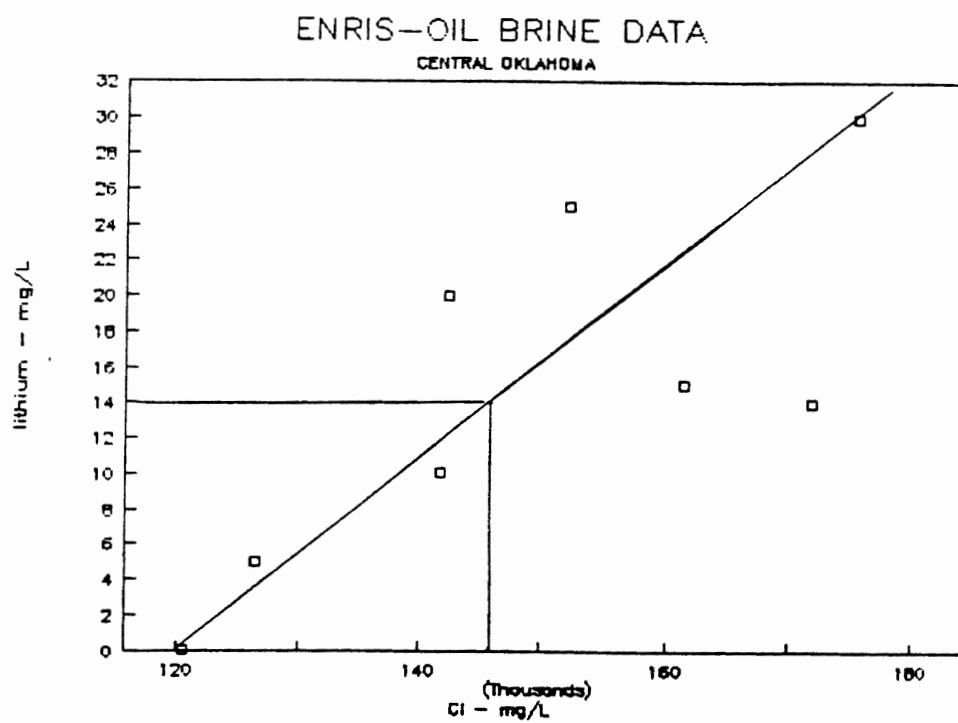
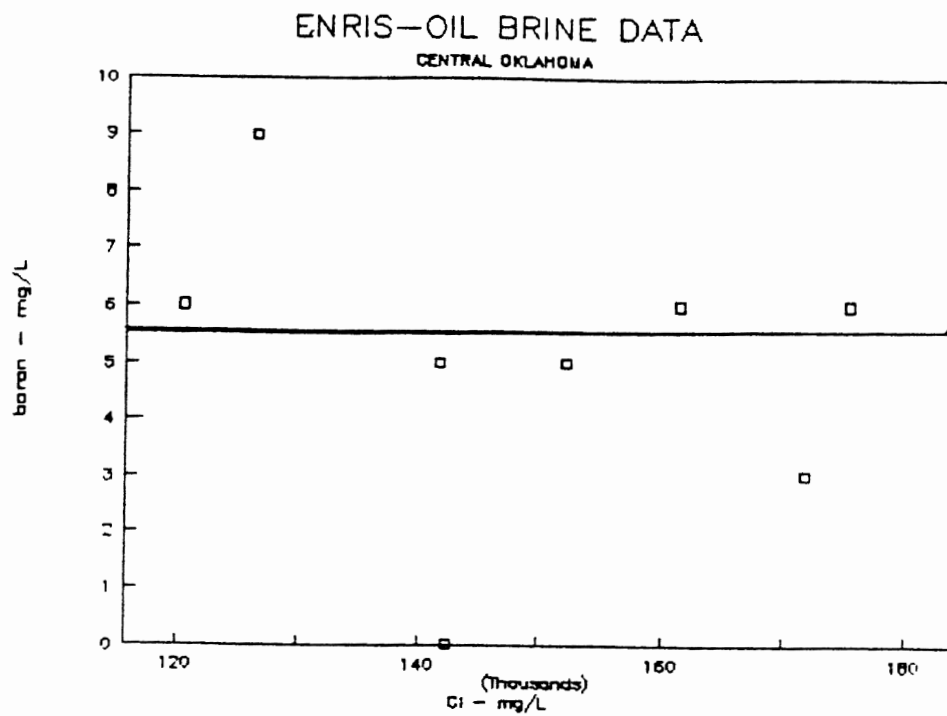
APPENDIX C

GRAPHS OF NRIS TRACE ELEMENTS VERSUS Cl^-

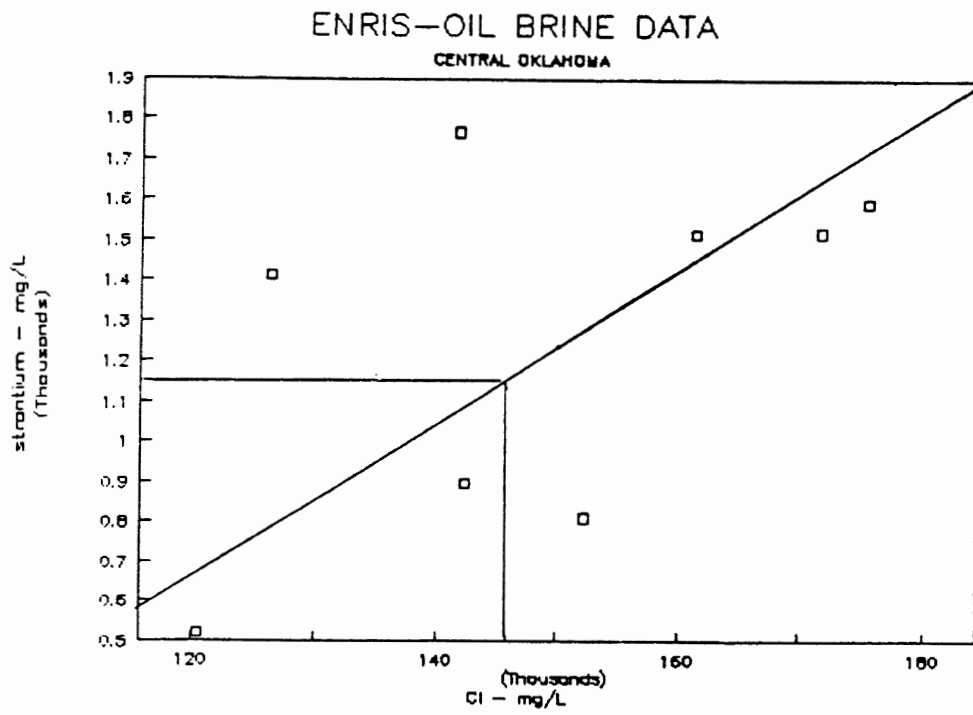
Appendix III: Graphs of NRIS trace element data versus Cl
Page 1 of 3



Graphs of NRIS trace element data versus Cl - continued
Page 2 of 3



Graphs of NRIS trace element data versus Cl - continued
Page 3 of 3



APPENDIX D

ANALYSES OF 42 WELL "WORK SET" AND END MEMBER DATA

ANALYSES OF 42 WELL "WORK SET" AND END MEMBER DATA
Page 1 of 5

WELLS	INTERPRETED SOURCE OF INCREASED Cl	Principle Aquifer	Depth of Well	Top of water	Detectable Tritium	Specific Conductance uS cm	PH	Temp C
			feet					
73	OIL BRINE	GW	150		YES	6160	6.8	17.5
74	OIL BRINE	GW	49	30	YES	5180	6.9	17.0
94	OIL BRINE	AL	80	17	YES	1800	7.1	17.0
122	OIL BRINE	GW	141	65	YES	1190	7.3	17.0
66	OIL BRINE	GW	104	55	YES	1190	7.0	17.0
124	OIL BRINE	GW	162	58	YES	1040	7.2	17.5
81	OIL BRINE	GW	196		YES	1080	7.2	17.0
130	OIL BRINE	GW	160	35	YES	945	7.2	17.0
165	NATURAL SALINE WATER -"A"	GW	220	120	YES	2700	7.6	18.0
163	NATURAL SALINE WATER -"A"	AL	60	10	YES	2350	7.6	17.0
24	NATURAL SALINE WATER -"A"	GW	280	24	NO	1960	8.6	18.0
38	NATURAL SALINE WATER -"A"	AL	42	3	YES	1910	7.3	17.0
161	NATURAL SALINE WATER -"A"	OS	91		NO	1800	8.3	17.0
48	NATURAL SALINE WATER -"A"	GW	725	142	YES	1250	9.0	17.0
131	NATURAL SALINE WATER -"A"	GW	760	278	NO	1040	8.0	18.0
145	NATURAL SALINE WATER -"A"	GW	500	180	NO	973	7.7	17.0
175	NATURAL SALINE WATER -"A"	GW	100	67	YES	1300	7.2	17.0
206	NATURAL SALINE WATER -"A"	AL	71	17	NO	867	8.2	17.5
115	NATURAL SALINE WATER -"A"	GW	155	38	YES	988	7.6	18.0
162	NATURAL SALINE WATER -"A"	WI	178		YES	911	7.6	16.5
159	NATURAL SALINE WATER -"B"	GW	600		NO	6440	8.4	20.5
128	NATURAL SALINE WATER -"B"	AL	54	13	NO	6010	8.6	17.5
191	NATURAL SALINE WATER -"B"	WI	119	39	YES	2350	7.5	17.0
185	NATURAL SALINE WATER -"B"	GW	280	40	NO	1050	8.3	17.5
170	HENNESSEY WATER	AL	60	14	YES	2630	7.0	18.0
72	HENNESSEY WATER	TP	40	9	YES	2360	7.1	17.0
134	HENNESSEY WATER	GW	91		YES	2210	7.0	18.0
117	HENNESSEY WATER	GW	100		YES	1810	7.1	18.0
89	HENNESSEY WATER	GW	223	214	NO	1890	7.2	19.0
87	HENNESSEY WATER	TR	35	25	NO	1950	7.1	19.0
78	HENNESSEY WATER	TR	67	17	YES	1730	7.4	16.5
101	HENNESSEY WATER	GW	109	77	YES	1560	7.1	17.5
116	HENNESSEY WATER	TR	60	11	YES	931	6.3	18.5
132	HENNESSEY WATER	TR	100	18	YES	2550	6.9	18.5
164	HENNESSEY WATER	SP	42		YES	1110	7.3	18.0
133	HENNESSEY WATER	GW	143	37	YES	992	7.4	17.5
129	HENNESSEY WATER	GW	300		YES	1140	7.3	17.5
51	HENNESSEY WATER	AL	41	0	YES	1660	7.3	17.0
75	HENNESSEY WATER	TR	49	26	YES	1890	7.0	18.0
98	HENNESSEY WATER	TR	38	24	YES	861	6.3	17.0
15	UNKNOWN	OS	40		YES	2190	6.9	17.0
204	UNKNOWN	GW	195		YES	1390	7.2	19.5
CH	CORE HOLE UNMIXED SAL WATER					11600	7.9	18.0
CH	CORE HOLE UNMIXED SAL WATER					8210	8.2	18.0
OB	MEAN OIL BRINE - OKLA COUNTY							6
FW	MEAN FRESH WATER							6.9

AL = Alluvium
TP = Terrace
SP = Salt Plains
GW = Garber-Wellington
WI = Wellington Formation
OS = Oscar Group

ANALYSES OF 42 WELL "WORK SET" AND END MEMBER DATA - CONTINUED
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ANALYSES OF 42 WELL "WORK SET" AND END MEMBER DATA - CONTINUED

WELLS	Oxygen Dissolved mg/L	Hardness as CaCO3 mg/L	Alkalinity as CaCO4 mg/L	Sum of Constit mg/L	Calcium mg/L	Magnesium mg/L	Sodium mg/L	Potassium mg/L	Bicarbonate mg/L
73	7.4	1800	268	3140	380.0	210.0	500.0	1.6	327.0
74	2.5	1600	310	2700	350.0	160.0	400.0	2.0	378.0
94	0.4	780	352	941	180.0	79.0	51.0	2.5	429.0
122	8.8	410	306	635	84.0	48.0	81.0	0.7	373.0
66	8.4	510	318	661	110.0	57.0	52.0	0.7	388.0
124	2.2	450	346	634	88.0	56.0	72.0	0.8	422.0
81	4.0	450	316	623	110.0	43.0	55.0	1.4	386.0
130	2.6	460	364	533	91.0	56.0	28.0	3.6	444.0
165	3.5	190	280	1520	31.0	26.0	510.0	1.6	342.0
163	0.2	190	360	1380	38.0	22.0	460.0	1.3	452.0
24	3.1	180	210	1080	36.0	22.0	340.0	4.7	232.0
38	0.1	500	452	1080	130.0	41.0	210.0	2.6	551.0
161	4.9	25	412	1040	5.9	2.5	390.0	1.5	483.0
48	13.2	26	272	674	5.6	2.9	250.0	4.5	298.0
131	2.9	190	161	547	33.0	25.0	130.0	2.1	196.0
145	0.7	230	192	532	38.0	33.0	110.0	2.9	234.0
175	11.0	530	366	723	100.0	69.0	66.0	1.1	446.0
206	0.0	56	174	499	13.0	5.6	170.0	1.9	212.0
115	5.2	220	300	588	45.0	26.0	140.0	2.6	366.0
162	2.0	190	256	533	42.0	21.0	130.0	2.3	312.0
159	0.2	1500	34	5610	440.0	100.0	1100.0	4.3	41.0
128	4.7	220	368	4540	48.0	23.0	1400.0	5.0	420.0
191	0.2	530	380	1510	89.0	73.0	290.0	2.7	464.0
185	6.8	88	222	630	19.0	9.8	200.0	1.1	271.0
170	0.1	820	580	1620	170.0	94.0	270.0	4.6	708.0
72	5.5	600	326	1460	140.0	60.0	250.0	1.5	398.0
184	3.6	810	365	1520	240.0	51.0	180.0	2.2	445.0
117	4.8	700	354	1140	150.0	79.0	150.0	1.6	432.0
89	9.8	580	419	1210	130.0	60.0	220.0	3.4	511.0
87	0.0	620	481	1070	200.0	78.0	130.0	4.1	588.0
78	6.6	390	376	1060	98.0	35.0	230.0	2.5	459.0
101	1.1	650	496	944	150.0	67.0	110.0	3.3	605.0
114	4.1	330	211	555	84.0	27.0	51.0	1.4	137.0
102	1.5	1200	162	1910	330.0	84.0	130.0	1.3	198.0
164	3.6	390	321	681	87.0	40.0	96.0	0.9	392.0
133	8.5	400	276	574	90.0	42.0	59.0	1.7	337.0
129	7.4	390	310	675	79.0	46.0	100.0	3.0	378.0
51	0.1	580	441	1100	150.0	49.0	170.0	3.2	600.0
75	2.9	750	540	1280	170.0	76.0	170.0	0.9	659.0
98	3.1	310	142	544	84.0	24.0	55.0	0.2	173.0
16	0.2	810	516	1200	190.0	82.0	130.0	0.8	629.0
204	8.4	460	376	827	85.0	59.0	130.0	1.1	459.0
CH	0.1	240.0	156		29.0	40.0	3100.0	7.3	190.0
CH	0.1	140.0	186		19.0	22.0	2300.0	5.4	227.0
OB			46	237000	13000	2510	75500		20
FW	5.2		259		42.0	21.0	30.0	1.1	315.0

ANALYSES OF 42 WELL "WORK SET" AND END MEMBER DATA - CONTINUED
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WELLS	Carbonate mg/L	Sulfate mg/L	Chloride mg/L	Fluoride mg/L	Bromide mg/L	Silica mg/L	Nitrite mg/L	Nitrite +	Ammonia mg/L	Organic mg/L	Phos mg/L
								Nitrate as N mg/L			
73	0.0	12.0	1800.0	0.20	7.30	18.00	0.01	6.00	0.12	0.60	0.01
74	0.0	14.0	1500.0	0.20	7.70	23.00	0.01	9.30	0.08	0.90	0.01
94	0.0	13.0	380.0	0.30	1.50	20.00	0.01	0.10	0.03	0.30	0.01
122	0.0	9.0	200.0	0.30	0.90	18.00	0.02	1.80	0.02	0.40	0.01
66	0.0	6.9	170.0	0.20	0.64	18.00	0.01	12.00	0.02	1.10	0.01
124	0.0	19.0	170.0	0.20	0.58	16.00	0.01	0.37	0.01	0.20	0.01
81	0.0	17.0	140.0	0.10	0.49	25.00	0.01	8.90	0.02	0.50	0.01
130	0.0	7.8	100.0	0.20	0.36	24.00	0.01	0.18	0.01	0.20	0.01
165	0.0	170.0	590.0	0.90	0.91	12.00	0.01	1.00	0.02	0.20	0.01
163	0.0	130.0	480.0	1.20	0.63	14.00	0.01	2.40	0.06	0.40	0.01
24	12.0	72.0	450.0	0.30	0.98	21.00	0.01	0.29	0.02		0.01
38	0.0	63.0	330.0	0.50	0.07	23.00	0.01	0.10	1.90	1.70	0.13
161	10.0	94.0	280.0	2.90	0.70	8.90	0.01	0.10	0.04	0.20	0.01
48	17.0	31.0	200.0	0.60	0.35	11.00	0.01	0.48	0.01		0.16
131	0.0	42.0	200.0	0.30	0.15	15.00	0.01	0.19	0.01	0.20	0.01
145	0.0	24.0	190.0	0.30	0.12	16.00	0.01	0.15	0.01	0.30	0.01
175	0.0	28.0	170.0	0.40	0.26	19.00	0.01	11.00	0.04	0.40	0.07
206	0.0	47.0	140.0	0.90	0.18	12.00	0.02	0.10	0.07	0.30	0.01
115	0.0	37.0	130.0	0.40	0.15	18.00	0.01	1.00	0.01	0.20	0.01
162	0.0	47.0	120.0	0.10	0.32	15.00	0.01	0.24	0.01	0.01	0.50
159	0.0	3700.0	230.0	0.80	0.34	8.80	0.01	0.10	0.18		0.02
128	14.0	2600.0	220.0	3.00	0.70	9.10	0.01	0.10	0.11	0.20	0.01
191	0.0	240.0	190.0	0.90	1.30	14.00	0.01	85.00	0.08	0.40	0.01
185	0.0	130.0	120.0	0.40	0.17	12.00	0.01	0.49	0.01		0.01
170	0.0	240.0	450.0	1.10	1.40	28.00	0.01	0.10	0.65	0.70	0.02
72	0.0	200.0	290.0	0.10	1.60	21.00	0.01	68.00	0.02		0.01
184	0.0	350.0	280.0	0.30	0.44	36.00	0.01	36.00	0.09	0.60	0.04
117	0.0	200.0	280.0	0.40	0.92	19.00	0.01	11.00	0.03	1.10	0.01
89	0.0	260.0	260.0	0.30	0.27	21.00	0.01	0.14	0.14	0.20	0.01
87	0.0	300.0	230.0	0.70	1.20	29.00	0.01	0.61	0.61	0.80	0.12
78	0.0	160.0	220.0	0.40	0.96	16.00	0.01	12.00	0.02	1.00	0.05
101	0.0	120.0	160.0	0.60	0.54	28.00	0.01	0.84	0.29	0.60	0.01
116	0.0	120.0	140.0	0.20	0.56	21.00	0.02	8.40	0.02	1.00	0.20
100	0.0	1000.0	130.0	0.10	0.18	20.00	0.01	25.00	0.07	0.70	0.01
164	0.0	77.0	120.0	0.10	0.30	36.00	0.01	3.50	0.01	0.01	1.30
105	0.0	47.0	170.0	0.40	0.05	21.00	0.01	3.50	0.01	0.20	0.01
129	0.0	110.0	120.0	0.20	0.19	16.00	0.01	0.75	0.01	0.20	0.01
51	0.0	280.0	120.0	0.50	0.25	27.00	0.01	0.10	0.10	0.20	0.01
75	0.0	380.0	110.0	0.20	0.56	21.00	0.01	5.00	0.04	0.20	0.08
96	0.0	100.0	96.0	0.20	0.45	1.00	0.01	14.00	0.02	2.10	0.04
16	0.0	120.0	340.0	0.30	1.70	18.00	0.01	0.28	1.00	1.40	0.17
204	0.0	130.0	160.0	0.50	0.44	23.00	0.01	2.50	0.06	0.20	0.01
CH	0.0	5100.0	1300.0	2.30	4.10	17.00	0.01	0.01	1.50		0.01
CH	0.0	4700.0	150.0	2.30	0.57	19.00	0.01	0.01	0.72		0.01
OE		230.0	146000.0		635.0						
FW	0.0	18.0	19.0	0.30							

ANALYSES OF 42 WELL "WORK SET" AND END MEMBER DATA - CONTINUED
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WELLS	Carbon	Aluminum	Antimony	Arsenic	Barium	Beryllium	Boron	Cadmium	Chromium	Cobalt	Copper	Iron
	mg/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
73		10	1	2	6400	0.50	110	1	5	3	10	14
74		10	1	1	1700	0.50	90	1	5	3	10	47
94	0.50	10	1	1	590	0.50	90	1	5	3	10	110
122		10	1	2	1100	0.50	60	1	5	3	10	18
66		10	1	1	870	0.50	80	1	5	3	10	8
124		10	1	1	1700	0.50	60	1	5	3	10	3
81		10	1	2	370	0.50	120	1	5	3	10	6
130		10	1	1	560	0.50	210	1	5	3	10	37
165	1.20	10	5	2	59	2.00	2500	3	30	9	30	9
163	0.70	10	1	1	72	1.00	2800	2	20	6	20	17
24	0.40	20		1	180	0.50	650	1	50	3	10	3
38	2.80	10	1	1	450	0.50	240	1	5	3	10	1500
161	0.90	10	1	1	30	0.50	7200	1	5	3	10	16
48	2.10	40		28	52	0.50	1100	1	80	3	30	10
131	0.60	10	1	2	100	0.50	360	1	7	3	10	30
145	0.60	10	1	1	210	0.50	320	1	9	3	10	31
175	1.50	10	1	1	350	0.50	120	1	5	3	10	49
206		10	1	1	72	0.50	3600	1	5	3	10	4
115		10	1	1	120	0.50	2700	1	7	3	10	22
162		10		1	150	0.50	580	1	20	3	10	5
159	0.40			4	6	2.00		3	0	9	30	970
125	0.40	10	1	1	5	3.00	9600	5	30	20	50	27
191	2.80	10	1	1	31	2.00	3100	1	5	3	10	22
185	0.40	10	1	9	70	0.50	1000	1	40	3	10	4
170	2.60	10	1	4	140	1.00	610	5	10	6	20	3400
72	1.90			2	52	0.50		1	1	3	10	30
184	1.90	10	1	3	97	0.50	400	1	5	3	10	3
117		10	1	1	89	0.50	120	2	5	3	40	100
89		10	1	1	18	0.50	530	2	5	3	10	70
87		10	1	4	160	0.50	330	2	5	3	10	1900
78		20	1	2	90	0.50	540	1	5	3	10	15
101		10	1	17	180		190	1	5	3	10	200
116		10	1	1	69	0.50	60	1	5	3	10	9
102		10	1	1	55	0.50	540	5	5	3	10	60
164		10		4	190	0.50	320	1	5	3	10	5
103		10	1	1	180	0.50	120	1	5	3	10	78
129		10	1	1	71	0.50	140	1	5	3	10	13
51	5.50	10	1	1	160	0.50	630	1	5	3	10	2000
75		10	1	1	61	0.50	640	1	5	3	10	23
98		10	1	1	260	0.50	70	1	5	3	10	16
15	1.00	10	1	1	190	0.50	240	1	5	3	10	1400
204	1.30	10	1	1	54	0.50	410	1	5	3	10	3
CH	0.80	10.00			<100	0.50	7400	1		3	48	30
CH	0.70	10.00			<100	0.50	6700	1		3	1	80
OB					5450		5710					
FW							180					

VITA

Dan J. Kennedy

Candidate for the Degree of

Master of Science

**Thesis: IDENTIFICATION OF THE SOURCES OF HIGH CHLORIDE
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