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OIL FIELD BRINE POLLUTION IN
NORTH CENTRAL OKLAHOMA

BY

THOMAS MICHAEL SIMMONS

Bachelor of Science

Emporia State University

Emporia, Kansas

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OIL FIELD BRINE POLLUTION IN
NORTH CENTRAL OKLAHOMA

Thesis Approved:

Richard N. DeVries
Thesis Adviser

AWHounslow

Vernon C. Mast

Norman N. Durham
Dean of Graduate College

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TABLE OF CONTENTS

Chapter Page

I. INTRODUCTION. 1

II. LITERATURE REVIEW AND THEORY. 5

Oil Field Brines 5
Chemical Analysis. 9
Identification of Oil Water. 14
Ground Water Flow and the Darcy Equation 16
Additional Contaminants. 19

III. STATEMENT OF PROBLEM AND METHODS. 22

Purpose of Study 22
Problem Area and Methods 22
Water Analysis Concentrations. 30
Identification of Brine Water by Ionic Ratios. 31
Identification of Brine Water with Patterns. 36
Long Term Effects. 38
Large Scale Study. 42
Garfield County. 46
Kay County 48
Osage County 48

IV. CONCLUSIONS AND RESULTS 51

V. RECOMMENDATIONS FOR FUTURE WORK 54

BIBLIOGRAPHY. 56

APPENDIX A - LISTING OF COMPUTER PROGRAMS 58

APPENDIX B - BRINE WATER ANALYSIS 61

APPENDIX C - GEOLOGICAL MAP EXPLANATION 63

APPENDIX D - WATER QUALITY DATA FOR HIGH CHLORIDE AREAS 65

LIST OF TABLES

Tables . . . Page

I. Analysis of Brine Water from Cushing Field. 7

II. Analysis of an Oklahoma Oil Field Brine 11

III. Various Additives Used in Drilling Muds 20

IV. Scale Inhibitors Used in Brine Treatment. 21

V. Water Analysis for Monitoring Wells 30

VI. Brine Analysis Skinner Formation. 34

VII. Water Analysis in North East Osage County 50

LIST OF FIGURES

Figure Page

1. Area of Study 4

2. Concentration of Chloride with Depth. 8

3. Concentration of Bicarbonate with Depth 10

4. Water Analysis Reresented by Pecentages of Cations and Anions. 17

5. Three Dimensional Representation of Brine Polluted Area . . . 24

6. Structural Contour Map of Underlying Strata 25

7. Topography of Study Area. 27

8. Potentiometric Surface of Upper Aquifer 28

9. Potentiometric Surface of Lower Aquifer 29

10. Map of Chloride Concentration in Upper Aquifer. 32

11. Map of Chloride Concentration in Lower Aquifer. 33

12. Sodium to Chloride Ratio versus Degree of Contamination . . . 35

13. Calcium to Sulfate Ratio versus Degree of Contamination . . . 37

14. Percent Cation-Anion Representation of Skinner Brine in Comparison with Fresh and Polluted Waters 39

15. Contour of Chloride Concentration in Milligrams per Liter . . 43

16. Chloride Concentration and Oil Fields 44

17. Chloride Concentration and Water Flooding Projects. 45

18. Geologic Map of Study Area. 47

CHAPTER I

INTRODUCTION

Many surface and ground waters in Oklahoma have been contaminated by the presence of salt water originating from the disposal of oil field brines associated with the production of petroleum. In normal production for this state each barrel of oil pumped from the producing zone is usually accompanied by one or more barrels of formation brine water which contain chloride concentrations up to seven times that of sea water. By the time a well reaches a point on its production decline curve where profits become marginal it may be pumping as much as 200 or more barrels of brine per barrel of oil.

During the early days of production, due to lack of regulation, these waters were left to drain over the surface into rivers and streams or placed in earthen evaporation pits which allowed seepage into the ground water. In the 1920's at the Cushing oil field in Creek County it was found that pumping the salt water down a dry or abandoned hole increased the production in nearby wells. This method of disposal or "water flooding" became a profitable means of disposing oil field brines and by 1949 water flooding had been tried in 25 Oklahoma counties, with the injection of approximately 449 million barrels of water (Powell and Johnston, 1951). Today there are 9,000 injection wells being used in Oklahoma for secondary recovery of oil (Corporation Commission, 1985). However, with the presence of leaky surface casing and numerous unplugged wells the injected water may leak directly into fresh water zones or increased formation pressures may push salt water up the unplugged wells and into the fresh water zones. Even wells that were plugged in accordance with State regulation may still be thought of as potential polluters. In 1909 Oklahoma required operators to plug wells by inserting a six foot pine pole into the well bore. This type of plug would last about two years (Enright, 1963).

While many brines were being disposed of in injection wells during the 1930's through the 1950's, earthen pits were still being used in areas where there were no water flooding projects, especially by the small or independent oil companies. Legislation was passed in May of 1955 granting the Oklahoma Corporation Commission the power to order storage of salt water in an earthen pit stopped if it was proven in a hearing to be polluting the fresh water supplies. At that time however, the state legislation, specifically limited the Corporation Commission from prohibiting the use of earthen pits altogether (Hallman, 1957). The storage of oil field brines in an earthen evaporation pit is still legal today, but is seldom used and is regulated by the Corporation Commission rules and regulations 3-104.

The magnitude of contamination by oil field brines is manifested by consideration of the chloride concentrations involved. Data taken from a well in north central Oklahoma shows that in a ten year period of operation it produced approximately 10,731,000 gallons of salt water which was stored in an earthen evaporation pit. The salt water contained a chloride concentration of 163,000 milligrams per liter (mg/l). This amounts to 7,304 tons of chloride. The Environmental Protection Agency (E.P.A.) maximum recommended allowable concentration of chloride in domestic water supplies is 250 mg/l. A simple mass balance of the accumulated chloride concentration shows that 700 million gallons of fresh water will eventually be polluted beyond EPA standards as seepage and leaching of the chlorides occur from the pit.

The problem seems relatively clear, but in actuality it is just beginning to take shape. Much time and energy have been spent in the past on ways to curtail pollution of surface and ground waters by oil field brines. Indeed, through the evolution of techniques and regulation the problem of additional contamination has been prevented to a great extent, but the long term effects of past practices are still haunting us today. The brine water evaporation pit example previously mentioned is still continuing to turn fresh ground water in the vicinity into a deleterious saline flow killing all protective vegetation in its path, twenty five years after it was abandoned.

Each year the Corporation Commission receives hundreds of complaints pertaining to salt water contamination. In the 1985 fiscal year alone 600 complaints were referred for legal action.

The oil boom of Oklahoma is over but the remnant is left behind for Oklahomans to clean. Most of this will be ordered through the courts of law.

A study of oil production and its effects on ground water chemistry in North Central Oklahoma is presented in this report. Emphasis is placed on a detailed study of a brine water disposal pit within the study area used from 1951 to 1961 which still persists in flushing 92,000 milligrams per liter chloride into the local ground water. The confines of the study are shown in Figure 1.

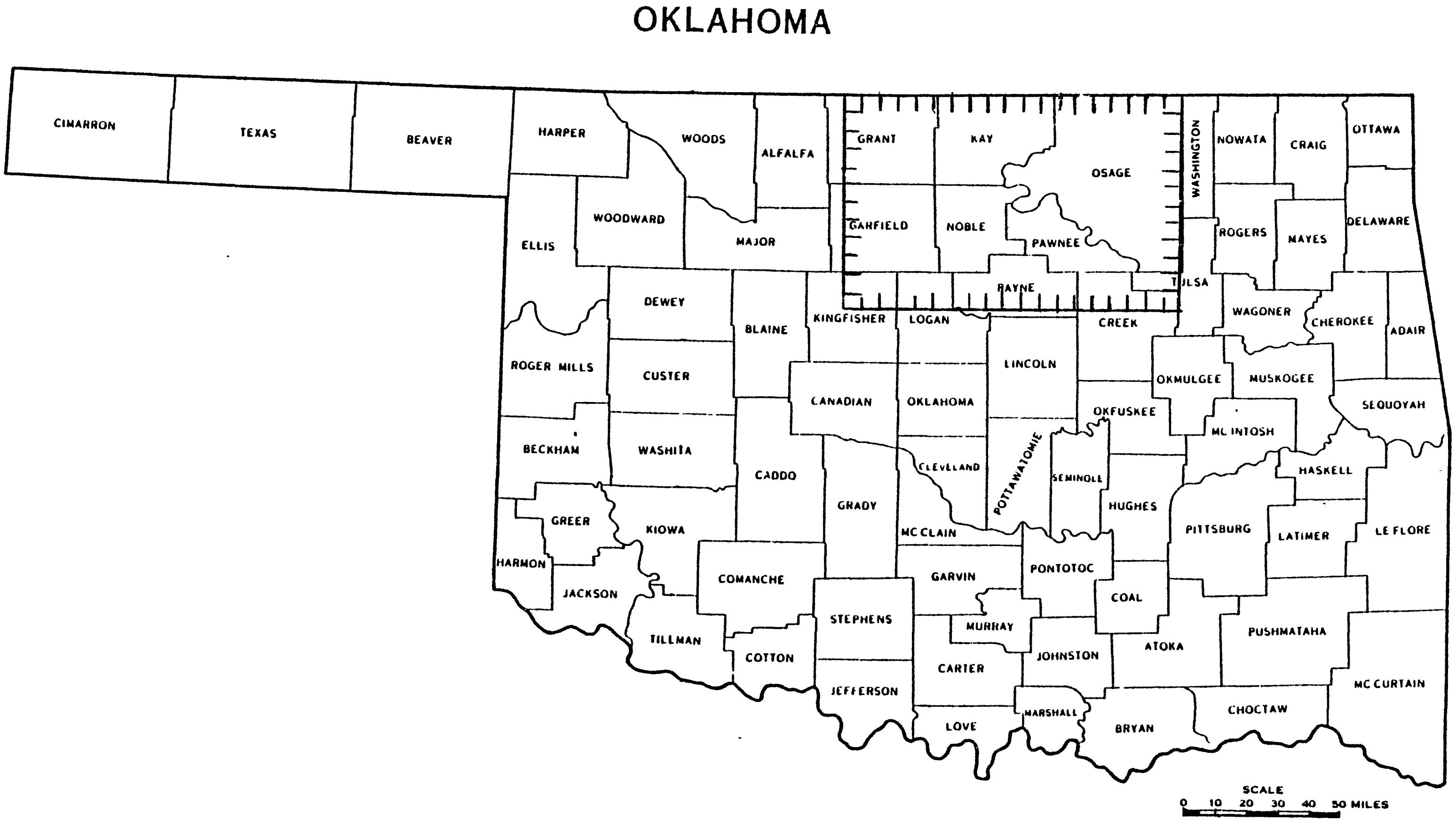


Figure 1. Area of Study

CHAPTER II

LITERATURE REVIEW AND THEORY

Oil Field Brines

Oil waters, which are produced from the oil bearing zones conventionally have been referred to as Connate waters. Connate waters are those that were entrapped in the sediments at the time they were deposited (Freeze and Cherry, 1979). White (1957) later redefined connate water as "fossil" water because of its tendency to migrate from its original pore space. As the sediments were buried compaction and expulsion caused these waters to migrate from their source and it is believed that their migration has played an important role in the transport and subsequent accumulation of oil in stratified traps.

Through long periods of geologic time the waters have been out of the atmosphere. Their high concentrations of dissolved solids are due to the long residence time and their increased solubility with respect to the formation rock because of the high temperatures at those depths (Hem, 1975).

Kreiger (1957), has defined a brine water as one with 35,000 milligrams per liter or more of total dissolved solids (TDS). The major constituent elements in oil waters are sodium, potassium, magnesium, calcium, chloride, sulfate and bicarbonate. Oil field brines are characteristically low in bicarbonate and sulfate however. Trace elements such as lithium, rubidium, strontium, bromide, barium and iodide are often found in significant amounts in oil field brines.

Each oil producing formation will produce a brine with differing concentrations of individual ions, though they may change laterally in the formation. Brines can therefore be identified according to their chemical analysis. Furthermore, according to Reistle (1950), the brine waters will not change chemically to a great extent with production. A sample was taken from a well head at Cushing field in Oklahoma in December 1922 and another in June of 1923 and the two waters were virtually the same. An analysis of both are shown in Table I.

TABLE I

ANALYSIS OF BRINE WATER FROM CUSHING FIELD

CONCENTRATION IN PARTS PER MILLION (ppm)

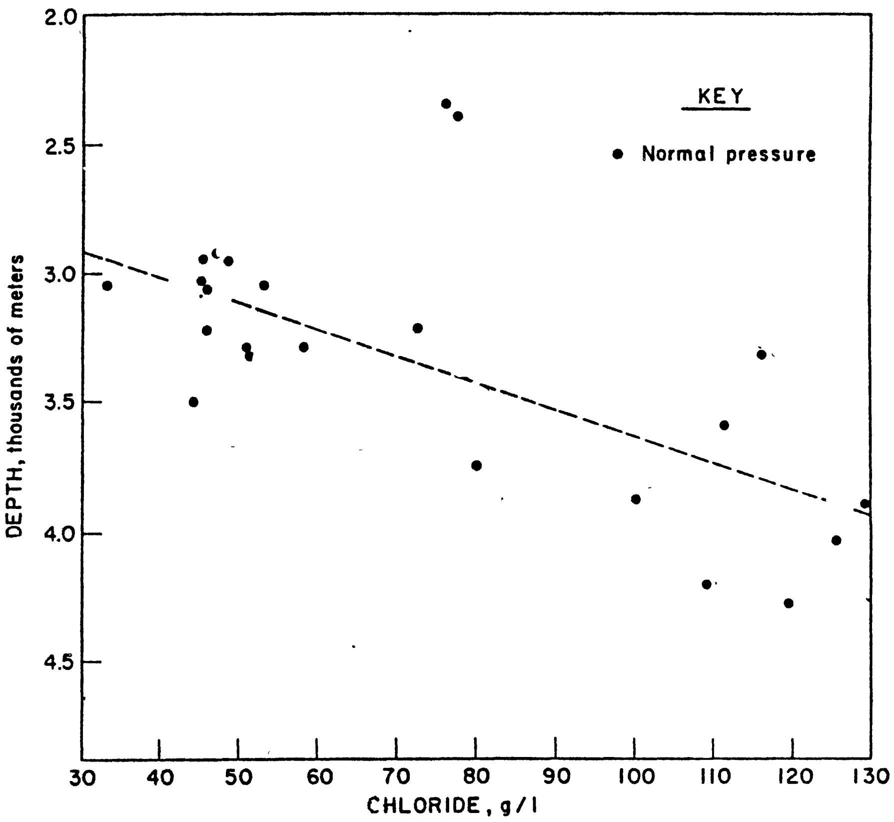
Dec. 12, 1922		Jun. 5, 1923	
Na	8,470	Na	8,420
Mg	55	Mg	54
Ca	2,160	Ca	2,157
Al	1,220	Al	1,243
Cl	21,624	Cl	21,624
SO_4	293	SO_4	290

SOURCE: C. E. Reistle, "Identification of Oil Field Waters by Chemical Analysis," Bureau of Mines (1950).

A well producing for a number of years may bring a larger change but data has not been located.

Dissolved solids generally increase with depth. Figure 2 shows Chloride, which is generally used as an indication of the degree of total dissolved solids, plotted against depth for 24 brine water samples from various oil fields in Louisiana.

Bicarbonate however generally shows a reverse relationship and decreases in concentration with depth. This however would agree with Chebotarev's (1955) evolution of groundwater chemistry which states



SOURCE: A.G. Collins, "Geochemistry of Oil Field Waters." Elsevier Scientific Publishing Co., New York, 1975.

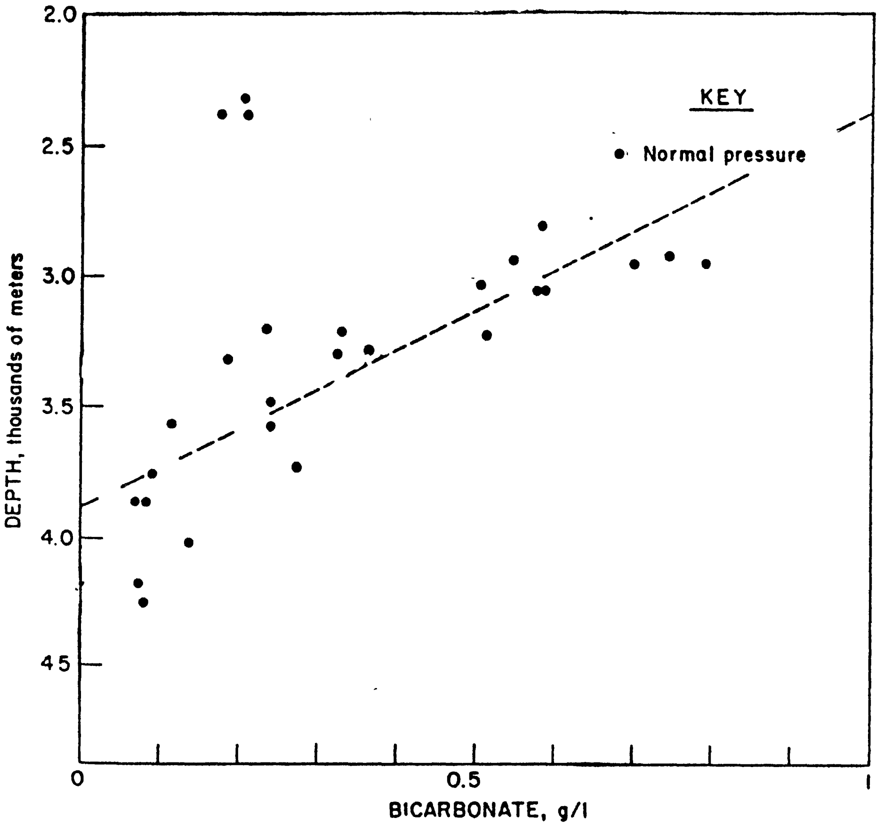
Figure 2. Concentration of Chloride with Depth

that water evolves chemically from HCO_3 - SO_4 - Cl type with depth and age. Figure 3 shows a plot of bicarbonate versus depth from the same data as in Figure 2.

Chemical Analysis

The most commonly used forms of water analysis are milligrams per liter (mg/l) and parts per million (ppm). Because many forms of analysis reporting such as hypothetical combinations and the Palmer system can be misleading, Reistle (1950) holds that all reporting of chemical data should always include either mg/l or ppm.

Parts per million (ppm) will be the same value as milligrams per liter (mg/l) if the density of the water is 1.0 g/ml. If the density is greater than this, mg/l will be divided by the water density to obtain ppm. An example of a brine analysis from North Central Oklahoma is shown in Table II. Using both mg/l and ppm.



SOURCE: A.G. Collins, "Geochemistry of Oil Field Waters." Elsevier Scientific Publishing Co., New York, 1975.

Figure 3. Concentration of Bicarbonate with Depth

TABLE II

ANALYSIS OF AN OKLAHOMA OIL FIELD BRINE

Density = 1.157 g/ml

	mg/l	ppm
Na	75,899	65,600
Ca	20,363	17,600
Mg	3,505	3,030
Cl	163,137	141,000
SO_4	223	193
HCO_3	53	46

SOURCE: Dwights Energy Data Service. Norman, Oklahoma, 1985.

Milliequivalents per liter (meq/l) and equivalents per million (epm) are both used in pattern representations of chemical analysis such as the Stiff, Piper and block diagrams. Milliequivalents per liter are calculated by dividing the expression in mg/l by the combined weight of the ion. The combined weight is the molecular weight of the ion divided by its valence charge.

ION	Valence	mg/l	combined wt.	meq/l
Na	+1	75899	/ (23/1)	3300
Ca	+2	20363	/ (40/2)	1018
Mg	+2	3505	/ (24.3/2)	288

Cl	-1	163137	/ (35.45/1)	4602
SO_4	-2	223	/ (96/2)	4
HCO_3	-1	53	/ (61/1)	1

Equivalents per million (epm) are used to express equivalent weight when the concentrations are reported as parts per million instead of milligrams per liter. The calculation is the same as for meg/l.

ION	Valence	ppm		epm
Na	+1	65600	/ (23/1) =	2852
Ca	+2	17600	/ (40/2) =	880
Mg	+2	3030	/ (24.3/2) =	249
Cl	-1	141000	/ (35.45) =	3977
SO_4	-2	193	/ (96/2) =	4
HCO_3	-1	46	/ (61/1) =	1

After a water sample has been analyzed, and before expressing it in any other form, a cation-anion balance should be made to ensure the analysis itself is acceptable. This can be done with either form of equivalent weights, meq/l or epm. The equation used is

$$\frac{(\text{cation} - \text{anion})}{(\text{cation} + \text{anion})} \times 100$$

CATION (epm)		ANION (epm)	
Na	2852.2	Cl	3977.4
Ca	880.0	SO_4	4.0
Mg	249.4	HCO_3	0.7
Tot	3981.6	Tot	3982.1

$$\text{BALANCE} = \frac{(3981.6 - 3982.1)}{(3981.6 + 3982.1)} \times 100 = 0.006\%$$

A brine analysis should have no more than a 2% difference in the cation-anion balance (Collins, 1975).

A widely used form of reporting water analysis, especially in the older literature, is hypothetical combinations. This form according to Reistle (1950) is not acceptable for identification of brines because there are several different hypothesis used to combine the ions. If the hypothesis is not given from each of several sources, the analyses cannot be compared.

Most often the ions are combined in the following order.

Calcium	Bicarbonate
Magnesium	Sulfate
Sodium	Chloride
Potassium	Nitrate

Calcium is combined with bicarbonate until one of the two is exhausted. The remainder is combined with the next ion down in the opposite column. The procedure is as follows.

Start with milliequalents per liter or equivalents per million. An example is shown using the epm values calculated previously.

Cation	epm	Anion	epm
Ca	880	HCO_3	0.7
Mg	249.4	SO_4	4.0
Na	2852.2	Cl	3977.4
Tot	3981.6	Tot	3978.5

Reacting value distribution

Ca as Calcium carbonate	0.7
Ca as Calcium sulfate	4.0
Ca as Calcium chloride	875.3
Mg as Magnesium chloride	249.4
Na as Sodium chloride	2852.2
	3981.6

The reaction values are then multiplied by the combination factors for each compound. A combination factor for Ca to $CaCO_3$ is calculated below as an example.

$$\text{Combination factor} = \frac{\text{Molecular wt. CaCO3}}{\text{Valence Ca}} = \frac{100}{2} = 50$$

	Reaction Value		Combination Factor		Hypothetical Combination
Ca-CO_3	0.7	x	50	=	35 ppm $CaCO_3$
Ca-SO_4	4.0	x	68	=	272 ppm $CaSO_4$
Ca-Cl	875.3	x	55.5	=	48579.1 ppm $CaCl_2$
Mg-Cl	249.4	x	47.6	=	11871.4 ppm $MgCl_2$
Na-Cl	2852.2	x	58.4	=	166568.5 ppm NaCl

Identification of Oil Water

Two major problems are encountered when identifying a high chloride contaminant source. First there is the possibility of naturally occurring brine from water migration in evaporate beds. Concentrations of chloride may be very high in parts of Western Oklahoma where salt beds are abundant. Secondly, in areas where there are many abandoned and producing wells on the same tract of land, identification of the source may be very difficult. Mast (1985) has reported significant results using ionic mixing curves to differentiate naturally occurring evaporate brines from oil field brines.

Ionic ratios, especially sodium to Chloride (Na/Cl), have been used in "fingerprinting" a brine source. In the literature, ionic ratios are reported directly as (mg/l)/(mg/l) or in the equivalent form as (meq/l)/(meq/l). The latter mainly being used to compare the ratio against probable rock dissolution. For instance if the water were migrating through an evaporate salt bed the equivalent ratio of Na/Cl would or should be approximately 1 to 1.

Whitmore and Pollock (1978) have found that oil field brines in Kansas have consistent ratios of Na to Cl of 0.5 ± 0.1 in the mg/l form. Fryberger (1972) however, maintains that chemical fingerprinting of brines is a rather dubious matter in that the ratios with respect to chloride will change substantially when the brine is diluted with fresh water.

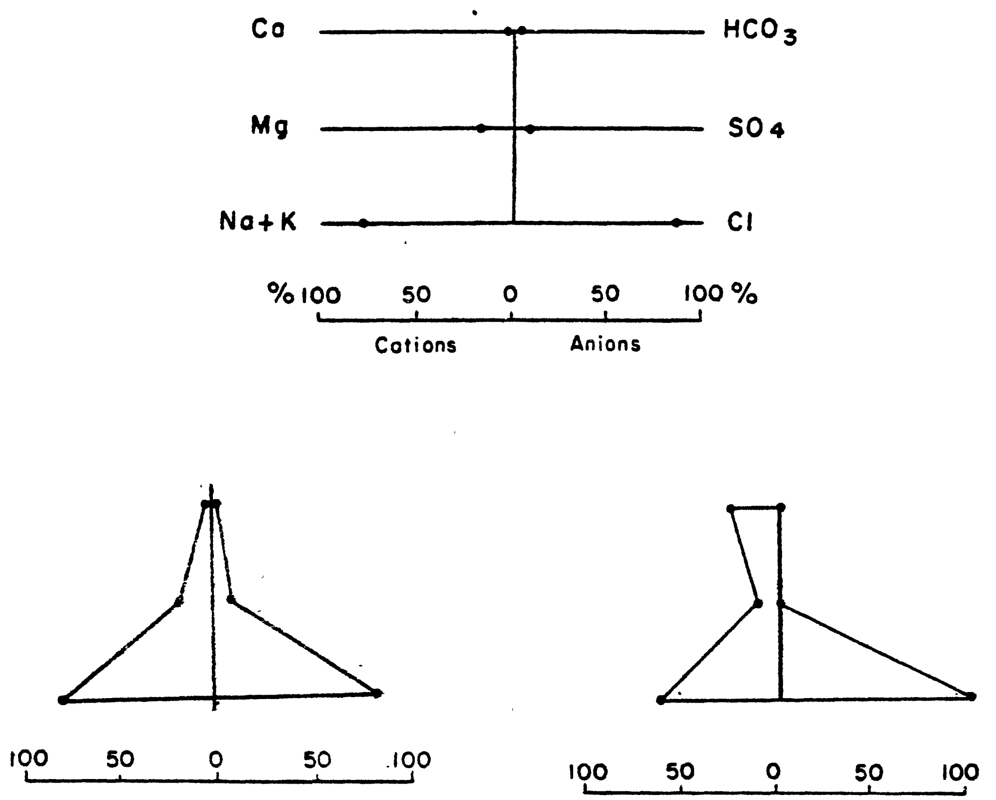
Taking into account that specific brine ionic ratios will change in the fresh water flow path due to water mixing and the exchange properties of the soil, most brine waters however are still in the order of 1000 times greater in dissolved solids than the fresh water. The brine water, even though somewhat diluted and appears totally different in a water analysis or particular ionic ratios, can still be identified when viewed by its character or type alone. This method entails removing the confusion of magnitudes in weight per volume and expressing the analysis in terms of percent of individual ions to the total ions. What makes this expression of data so valuable in identification of brine contaminant is that brine waters have a distinct pattern unlike shallow groundwaters and they change only slightly when diluted with fresh water. Examples using this method for shallow bicarbonate type, sea water and brine water are shown in Figure 4.

Ground Water Flow and the Darcy Equation

When brines enter the fresh water zones and are detected in domestic or irrigation wells, surface waters, or even at their source, methods must be taken to trace the plume back to the source or to delineate the flow path away from the source.

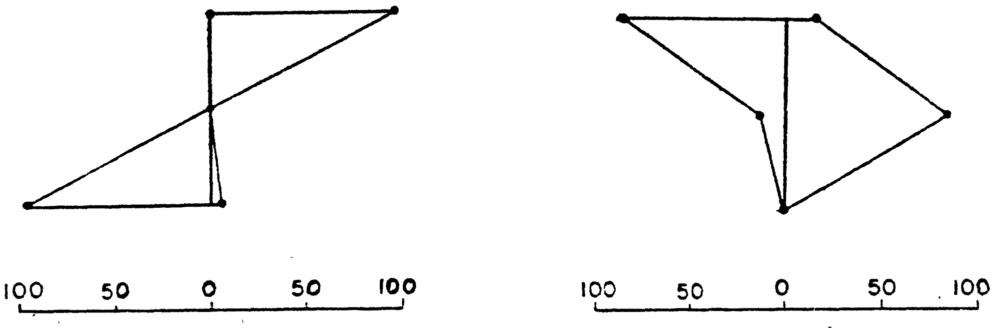
Groundwater flow is dependent upon the media permeability, impervious boundaries such as clay or shale layers, and an energy gradient. The flow direction is always in the direction of high energy to low energy. The total energy at any point in an aquifer is a total of the kinetic (velocity) and potential (pressure and elevation) energies. Ground water flow is very slow so that the kinetic energy contribution is negligible. Therefore the energy gradient will depend on the pressure and elevation distribution in the aquifer.

Hydrologists use the term hydraulic head to express the total energy at any one place in the aquifer. If the aquifer is unconfined the water surface will be at atmospheric pressure and the hydraulic head will merely be the elevation of the water surface (z) above some arbitrary datum. If the aquifer is confined between two impermeable boundaries then the hydraulic head will also account for the pressure.



Sea Water

Brine water



Sodium bicarbonate water

Calcium Sulfate (Gypsum) Water

SOURCE: C.E. Reistle, "Identification of Oil Field Waters by Chemical Analysis," Bureau of Mines (1950).

Figure 4. Water Analysis Represented by Percentages of Cations and Anions

$$h = z + \frac{P}{\rho g} \qquad (2\text{-}1)$$

where

P = pressure

ρ = density of water

g = gravity

Note that z and $P/\rho g$ are both in units of length. Therefore the hydraulic head in a confined aquifer can be measured by the height of which water will rise in a piezometer tube that penetrates the confined aquifer.

The hydraulic gradient (i) is the change in hydraulic head (dh) over the change in distance (dl) through the aquifer

$$i = \frac{dh}{dl} \qquad (2\text{-}2)$$

The Darcy equation which expresses flow rate through an aquifer is

$$Q = KAi \qquad (2\text{-}3)$$

where

Q = flow rate L^3/T

K = Coefficient of Permeability (Hydraulic Conductivity) L/T

A = Area of Aquifer Perpendicular to flow direction L^2

i = Hydraulic Gradient

The hydraulic gradient exists for two reasons, recharge and discharge. For shallow, near surface groundwaters, topographic relief plays a major role in flow direction. Topographic highs tend to be recharge areas and topographic lows tend to be discharge areas. In the case of confined aquifers the flow is most often in the direction of dip of the confining strata unless pressure dictates otherwise.

Brine water, because of its greater density than fresh water will reside beneath the fresh water and will tend to move along the base of the aquifer in the direction of structural lows (Fryberger, 1972).

Additional Contaminants

A point that must be kept in mind is that other contaminants in addition to the brine itself will be introduced into the formation waters. Drilling, production and disposal practices will introduce additives in each phase that will show up in conjunction with the brine.

In the drilling phase, most of these will be incorporated in the drilling mud. The principle make up of drilling muds are Bentonite ("gel"), Caustic soda, lignosulfonate, lignite and Barite. Bentonite is used as the primary mud addition to produce favorable drilling conditions and removal of cuttings. Barite is added to produce weight in the mud and increases hydrostatic pressures in the annulus equal to or greater than the formation pressures to prevent blow out and loss of circulation. Lignosulfonates and lignite are used as dispersing agents and to form a more stable mud. Caustic soda is used to neutralize the mud. Various muds used in petroleum drilling are listed in Table III.

TABLE III

VARIOUS ADDITIVES USED IN DRILLING MUDS

Quebracho extract
Lignosulfonates, calcium and chrome derivatives
Acrylonitrites (such as hydrolyzed polyacrylonitrite)
Sodium salts of meta and pyrphosphoric acid
Natural gums
Tannins
Molecularly dehydrated phosphates
Subbituminous products
Protocatechuic acid
Barite
Lignins (such as humic acids)
Bentonite
Sugar cane fibers
Lime
Granular material, such as ground nutshells
Corn starch
Salt water
Soluble caustic/lignin product
Carboxy methyl cellulose
Crude oil
Sulfonated crude oil
Oil emulsions
Sodium chromate
Anionic and nonionic surfactants
Organophylic clay
Soaps of long-chain fatty acids
Phospholipids (e.g., lecithin)
Asbestos

SOURCE: A. G. Collins, "Geochemistry of Oil Field Waters." Elsevier Scientific Publishing Co., New York, 1975.

To enhance well production the formation is often acidized to increase permeability of the reservoir rock. The acids most commonly used are Hydrochloric, nitric, sulfuric, formic and acetic. A well may be acidized using any where from 7500 to 45000 gallons of acid.

Scale inhibitors are often added to brines to prevent precipitation of the dissolved solids. Some of these are listed below in Table IV.

TABLE IV

SCALE INHIBITORS USED IN BRINE TREATMENT

Ethylenediamine tetraacetic acid salts

Nitrilotriacetic acid salts

sodium hexametaphosphate

sodium carboxymethyl cellulose

aminotrimethylene phosphate.

SOURCE: A. G. Collins, "Geochemistry of Oil Field Waters." Elsevier Scientific Publishing Co., New York, 1975.

CHAPTER III

STATEMENT OF PROBLEM AND METHODS

Purpose of Study

Oil field brine disposal practices, especially the earlier ones have no doubt caused many local ground and surface waters to be polluted beyond use. Special attention is given to one such case in the study area used for this report.

Through monitoring well data and surface reconnaissance, a brine polluted, 160 acre tract of land was studied to determine the brine source, its flow path and subsequent damage. The information and insight gained from this study was then used for a large scale study of north central Oklahoma's major water bearing formations and the effects of brine disposal on their water quality.

Problem Area and Methods

Salt water containing a chloride content of 1,410 mg/l was detected in a domestic house water well in 1982. 1500 ft west of the house is an abandoned, unlined earthen brine disposal evaporation pit, that had been in use from 1951 to 1961. Directly north of the pit is an abandoned oil well that produced from 1951 to 1974. Approximately one half mile south of the pit is an abandoned salt water disposal well used in the 1960's after the brine pit was abandoned. One producing well still remains just south of the house water well.

A surface inspection of the area showed scar faces along a north south striking terrace deposit where salt water had been seeping out of the ground destroying the vegetation. As a result gullies had formed due to erosion and are presently still widening. A pond was built along the bed of one of the gullies to curtail salt movement towards the house water well. It has been found to contain 1217 mg/l chlorides. Other water seeping from the terrace deposit contains over 10,000 mg/l chloride. A monitoring well was drilled north of the pit and next to the abandoned N.W. oil well. It was discovered that two fresh water zones occurred separated by a twenty five foot thick shale layer. Eight other monitoring wells were drilled with four of the wells being "nested" as to sample the shallow and deep aquifers separately. Figure 5 is a three dimensional view of monitoring wells, general topography and structure of the study area.

The regional dip of the layers was studied by a collection of oil well logs within four square miles of the polluted area. A structural contour map was made from gamma and spontaneous potential logs of a continuous zone approximately 400 ft below ground surface. This map is shown in Figure 6.

The rock layers are dipping to the north west across the polluted zone, however a structural high with North-South orientation truncates this trend along the western edge of the study area. This effect causes a trough right under the brine pit and will greatly influence the ground water flow away from the pit, especially in the lower confined aquifer.

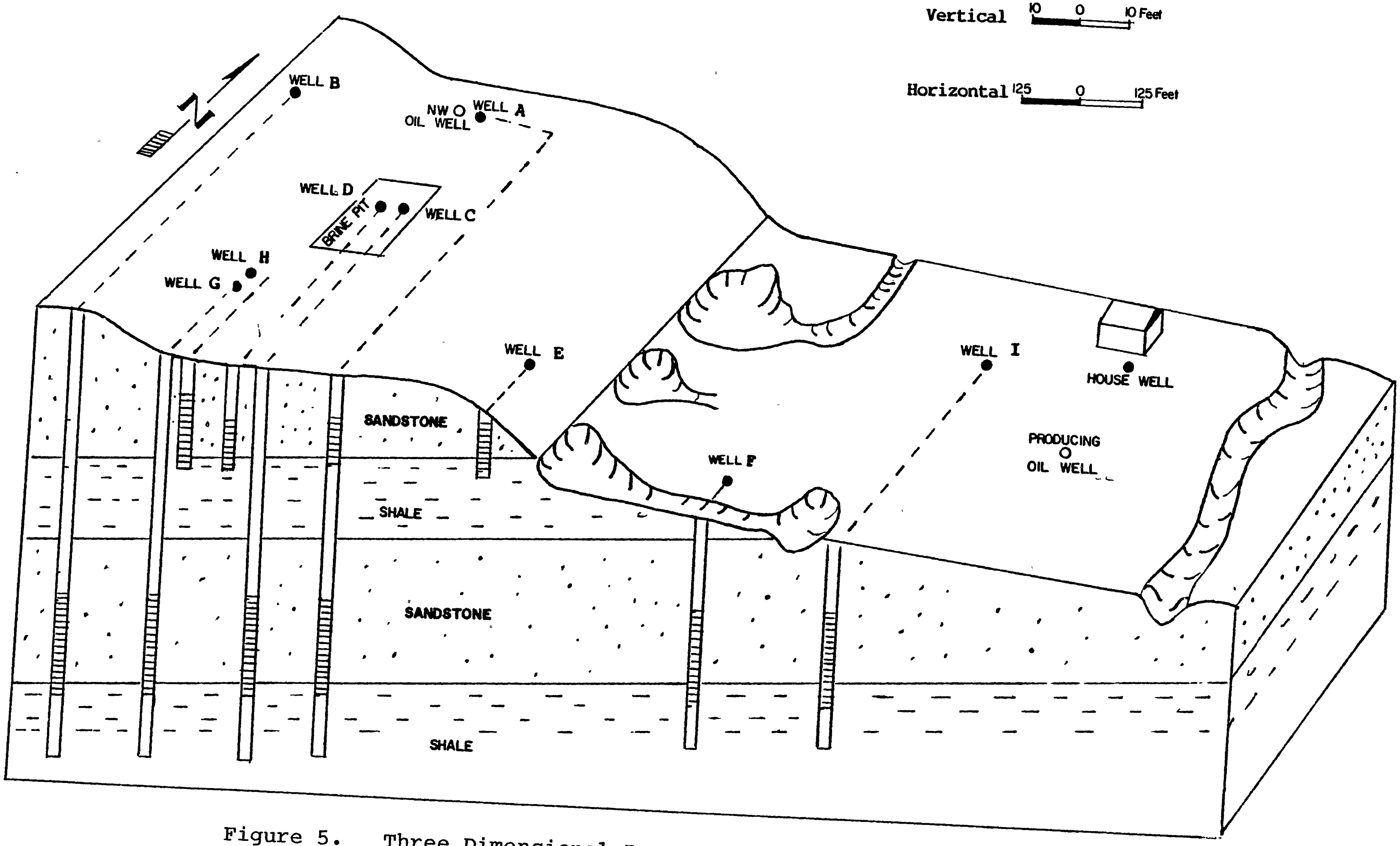


Figure 5. Three Dimensional Representation of Brine Polluted Area

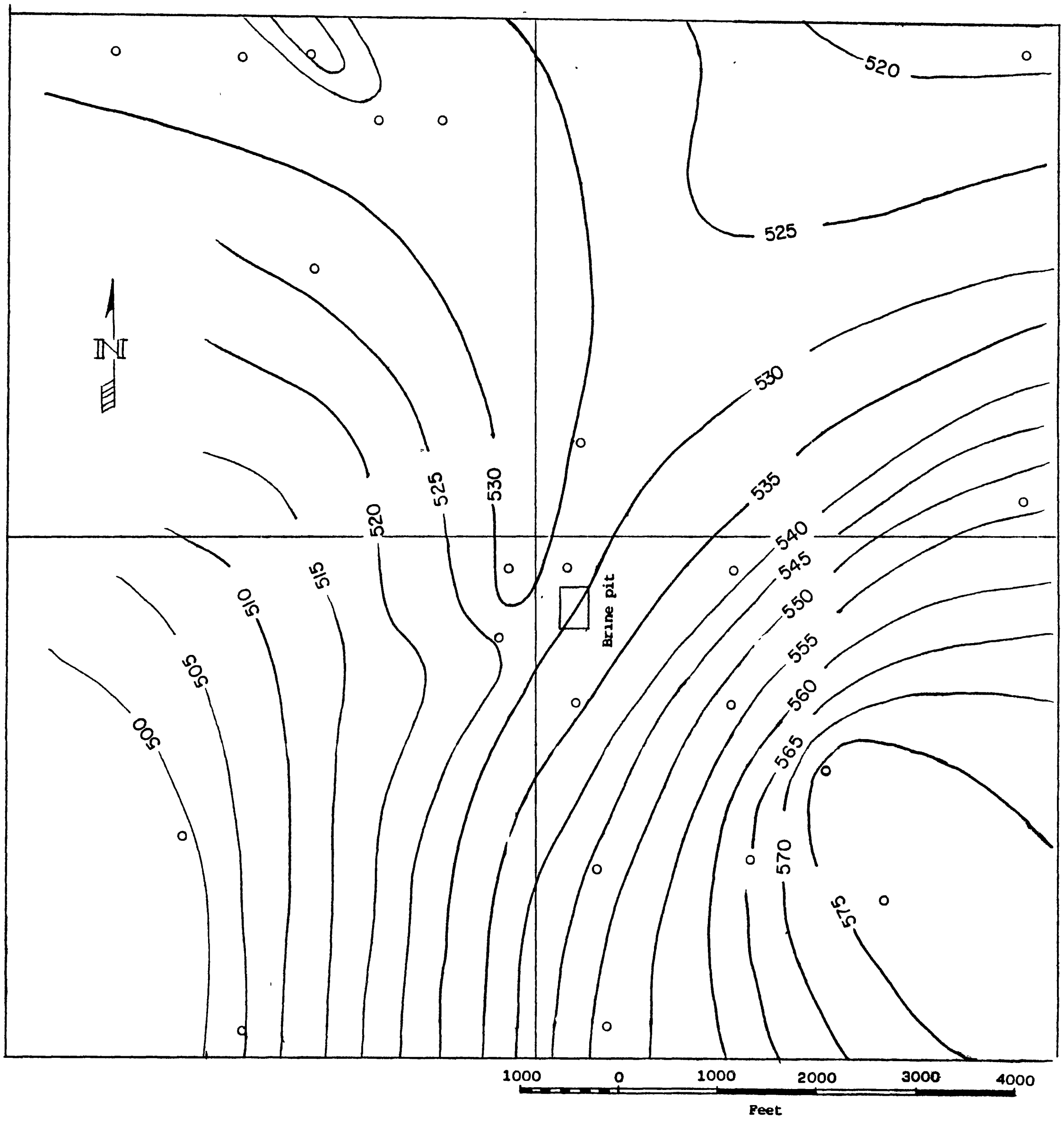


Figure 6. Structural Contour Map of Underlying Strata

Surface topography plays the greatest roll in the upper sandstone flow direction. A topographic map is shown in Figure 7.

The brine pit is located on a topographic high within a sandstone outcrop making the area a recharge zone. The ground surface slopes to the east as part of the Salt Creek drainage area, so the ground water flow is very interesting due to the reverse dip of the rocks with respect to the surface topography.

Keeping in mind that two aquifer systems with different compelling drive forces of topography and rock dip are interacting beneath the pit, a water surface potentiometric map was drawn for each aquifer using data from the monitoring wells.

The upper unconfined sandstone layer shows that the ground water flow away from the pit is almost directly east and is shown in Figure 8. It then surfaces along the sandstone-shale interface in the scar area where the shale layer outcrops. The water then partially runs off to the north along a gully and partially into the pond.

On several occasions the water flowing toward the pond has been seen to reenter the ground, supposedly into the second sand layer between Well E and Well F. Chloride concentrations in Well F may be explained from this fact and will be discussed later.

The lower aquifer potentiometric surface has been drawn using all monitoring wells that intersect the lower aquifer, these being A, B, C, F, G, and I and is shown in Figure 9.

The lower aquifer flow is to the west until it intersects the trough under the pit that was depicted on the geological structure map. The high water surface at Well B blocks it from any further westward movement. Water levels in Wells A, C, and G indicate a south west

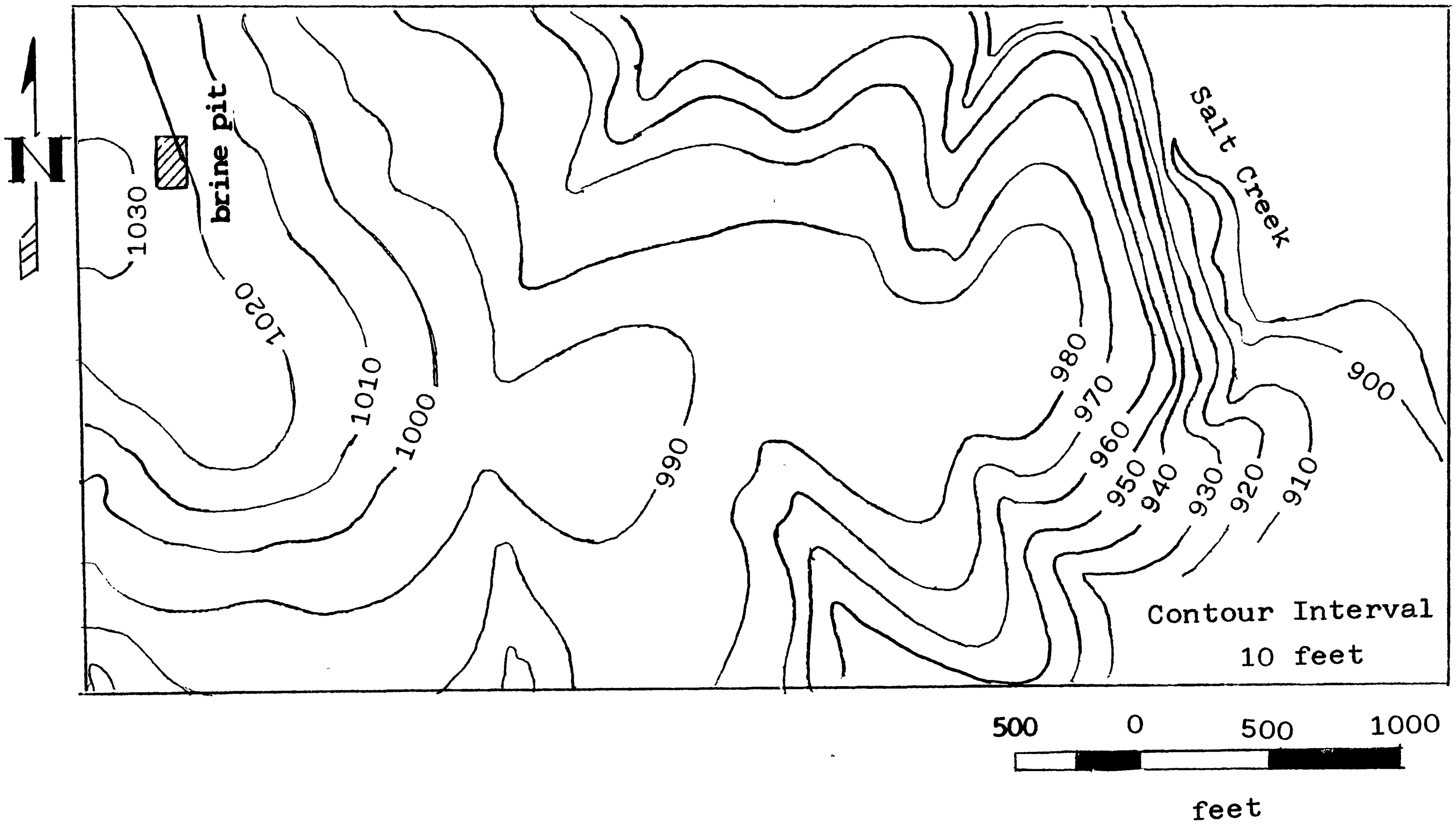


Figure 7. Topography of Study Area

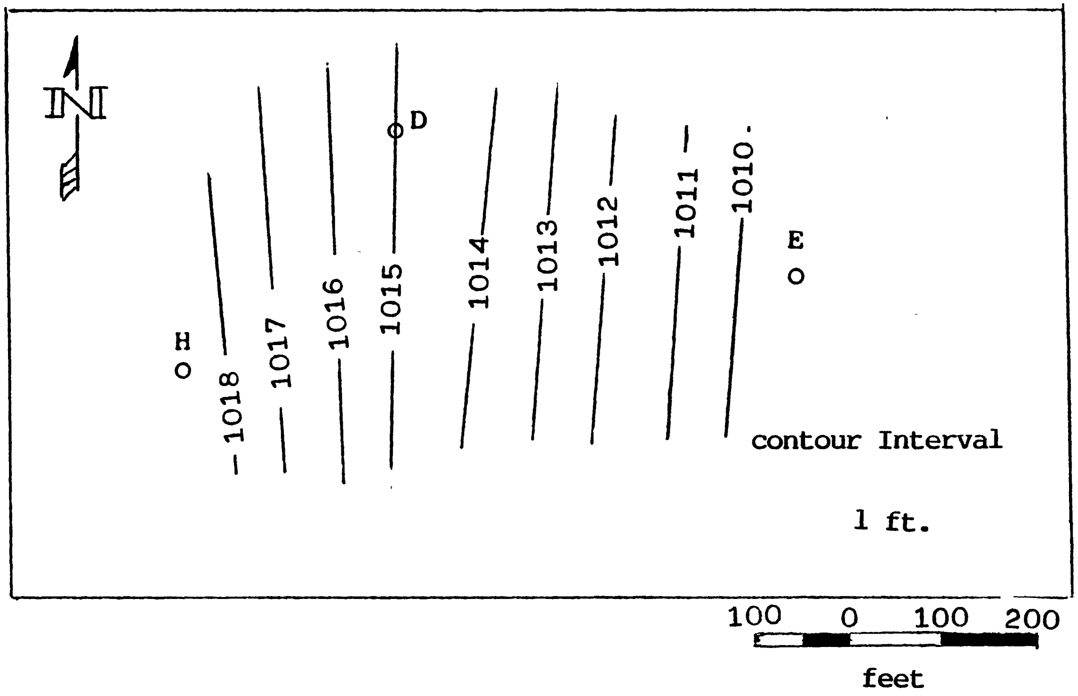


Figure 8. Potentiometric Surface of Upper Aquifer

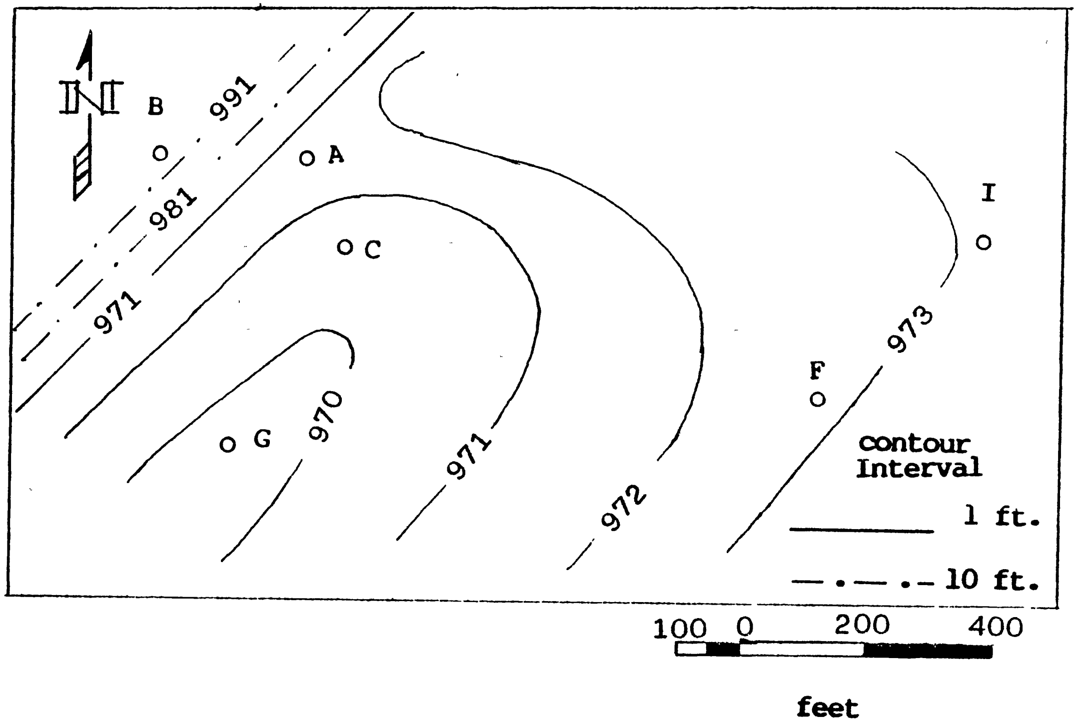


Figure 9. Potentiometric Surface of Lower Aquifer

direction, but concentrations in Well G show little or no contamination from the brine.

The evidence from the potentiometric surfaces show that the upper aquifer flows unobstructed to the east away from the pit and the lower aquifer flows westward towards the pit. At this point however the flow direction is inconclusive in the lower aquifer. It may be that the flow is stagnated due to the mound in structure and water level from Well B west of the pit. Dissolved solids in Well A north of the pit indicate that the flow may angle off towards the north in the lower aquifer.

Water Analysis Concentrations

The monitoring well analyses are listed in Table V.

TABLE V

WATER ANALYSIS FOR MONITORING WELLS

Concentration in Milligrams per Liter

ION	A	B	C	D	E	F	G	H	I
Na	257	15	8227	43578	42737	10053	98	40	68
Ca	259	66	2141	2941	1398	1236	140	47	61
Mg	23	17	525	6643	5931	1807	11	14	6
Cl	653	23	17941	92059	85882	22941	185	76	129
SO_4	38	22	30	26	45	26	108	19	10
HCO_3	265	176	153	94	129	165	194	53	94
CO_3	0	0	0	0	0	0	0	35	0

Chloride, being the most unreactive ion, was used to indicate the brine plume in the upper and lower sandstones in Figures 10 and 11 respectively.

Note the configuration of the plume in the lower aquifer. From the pit it advances northward towards Well A with 653 mg/l Cl. However the highest concentrations of dissolved solids are found in Well F with 22,941 mg/l chloride. Well C directly under the pit contains only 17,941 mg/l chloride. This, together with the fact that Well I is relatively clean with only 129 mg/l, indicates that much of the water from the upper sandstone is seeping into the lower sand near Well F and flowing back westward towards the pit. In other words the contaminant plume seems to be making a round trip from the pit to Well F and back to the pit in the lower sand.

Identification of Brine Water by Ionic Ratios

The suspected brine source is the oil water connected with the production zone (Skinner Formation) in which the oil was produced. A water sample was obtained at the well head from the north west oil well in 1954. Its water analysis is listed in Table VI.

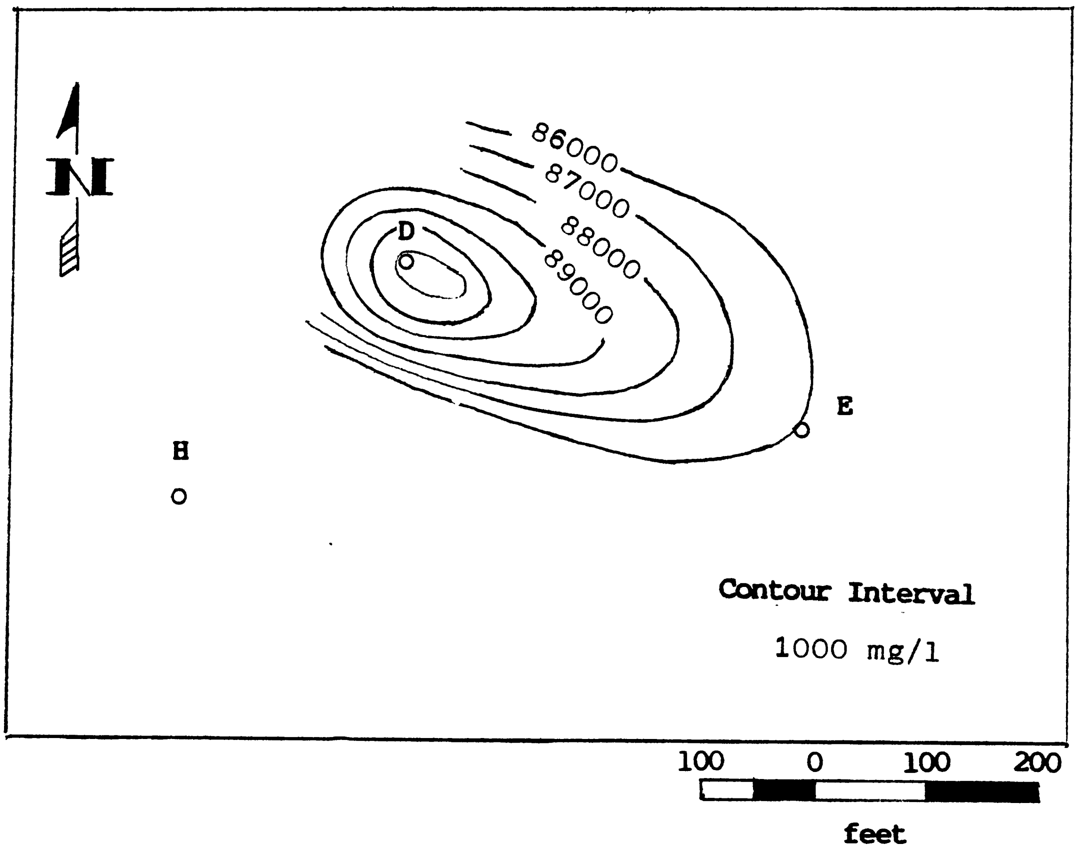


Figure 10. Map of Chloride Concentration in Upper Aquifer

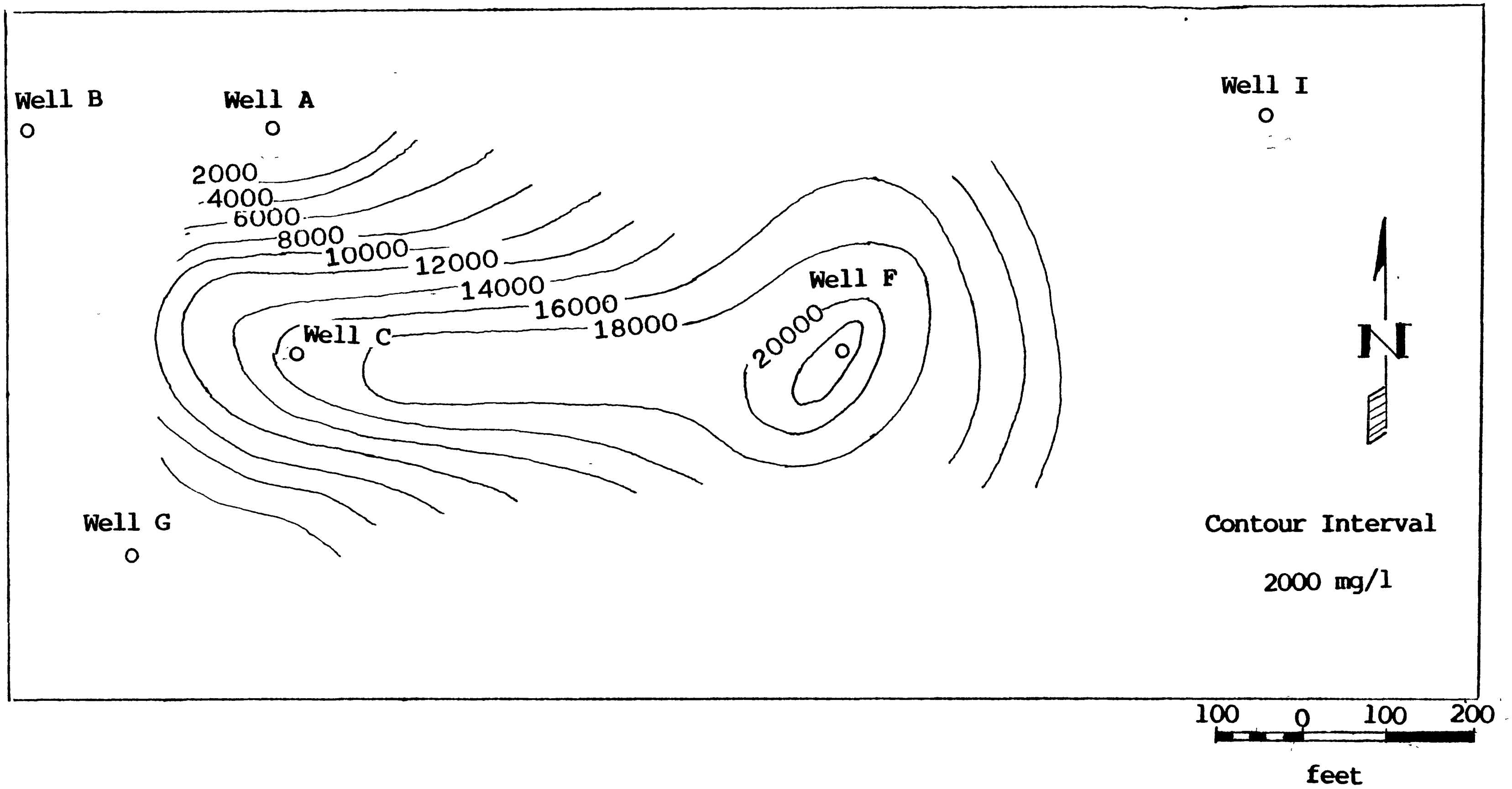


Figure 11. Map of Chloride Concentration in Lower Aquifer

TABLE VI

BRINE ANALYSIS SKINNER FORMATION

DATE 5/19/54	
Na	75,899 mg/l
Ca	20,363 mg/l
Mg	3,505 mg/l
Cl	163,137 mg/l
SO_4	223 mg/l
HCO_3	53 mg/l
Ba	13 mg/l

SOURCE: Dwight Energy Data Inc.
Norman, Oklahoma, 1985.

The ionic ratio Na/Cl was calculated for the Skinner brine water and monitoring well data. Figure 12 shows that the less polluted Wells B, G, H, and I tend towards a 0.65 (mg/l) ratio. In fact Well B which has the least amount of dissolved solids is 0.65 which would be expected for most unpolluted fresh ground waters. As the chloride concentrations increase, ionic ratios close in about the Skinner brine water ratio of 0.46.

Monitoring Well A has a very low ratio and obviously does not follow the trend. However this is probably due to the orientation of Well A in the flow pattern. The order of decreasing chloride concentration is

Well D -- Well E -- Well F -- Well C -- Well A.

This indicates that Well A is contaminated only after the flow has traveled east in the upper aquifer and west through the lower aquifer. Therefore the low ratio of Na/Cl is probably due to a deficit of sodium rather than an abundance of chloride since chloride is an unreactive ion where sodium is prone to cation exchange as it travels through the soil.

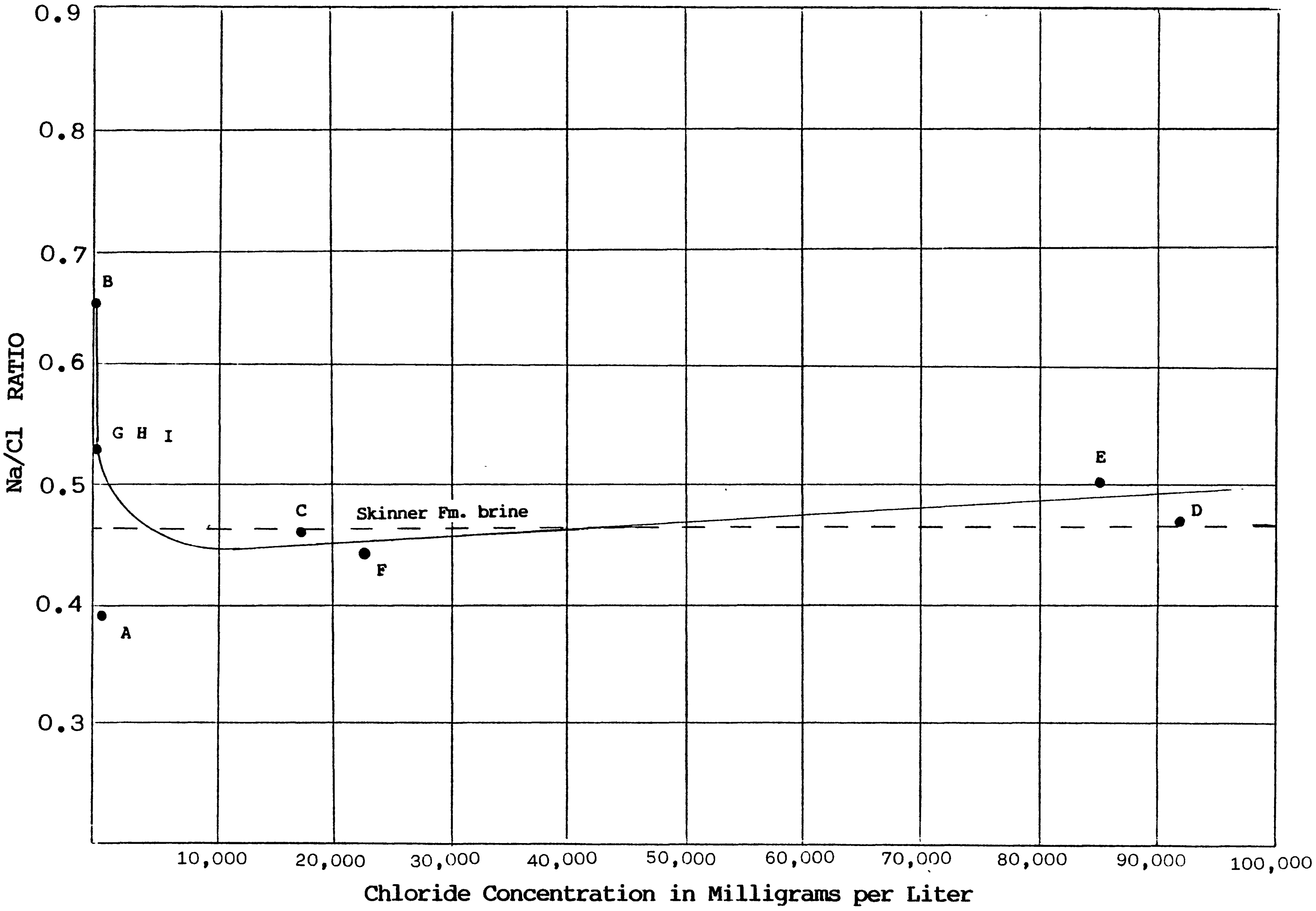


Figure 12. Sodium to Chloride Ratio versus Degree of Contamination

The ionic ratio, calcium to sulfate (Ca/SO_4) showed no correlation with increased chloride content of the water samples, Figure 13. This could be due to the fact that sulfate is relatively low in oil field brine waters which makes it too close to the fresh background water concentration. Another factor that is influencing the Ca/SO_4 ratio in this particular case is that the calcium concentration is much too low in the three highly contaminated Wells D, E and F with respect to the brine source. Also the magnesium concentration in these wells is much too high. It appears that a calcium - magnesium exchange is taking place in the soil.

$$Ca^{+2} + MgCLAY \longrightarrow Mg^{2+} + CaCLAY$$

This is probably the case because the soil in this area has an average exchange capacity of about 10 milliequivalents per 100 grams of soil and calcium and magnesium are the most active extractable bases.

Identification of Brine Water with Patterns

An identification of the brine waters was attempted using a pattern of percent anions and percent cations. A computer program, shown in Appendix A, was made to calculate the milliequivalents of all the ions in the sample. The percent of each cation, calcium, magnesium and sodium plus potassium, of the total cations was calculated. The same procedure was used for the anions, chloride, sulfate and carbonate plus bicarbonate. Using the calculated percentages, patterns were drawn for the background (unpolluted) samples of Well H in the upper sand and Well B for the lower sand. A pattern for the Skinner formation brine water, the polluted Well C under the pit and the house well was also drawn.

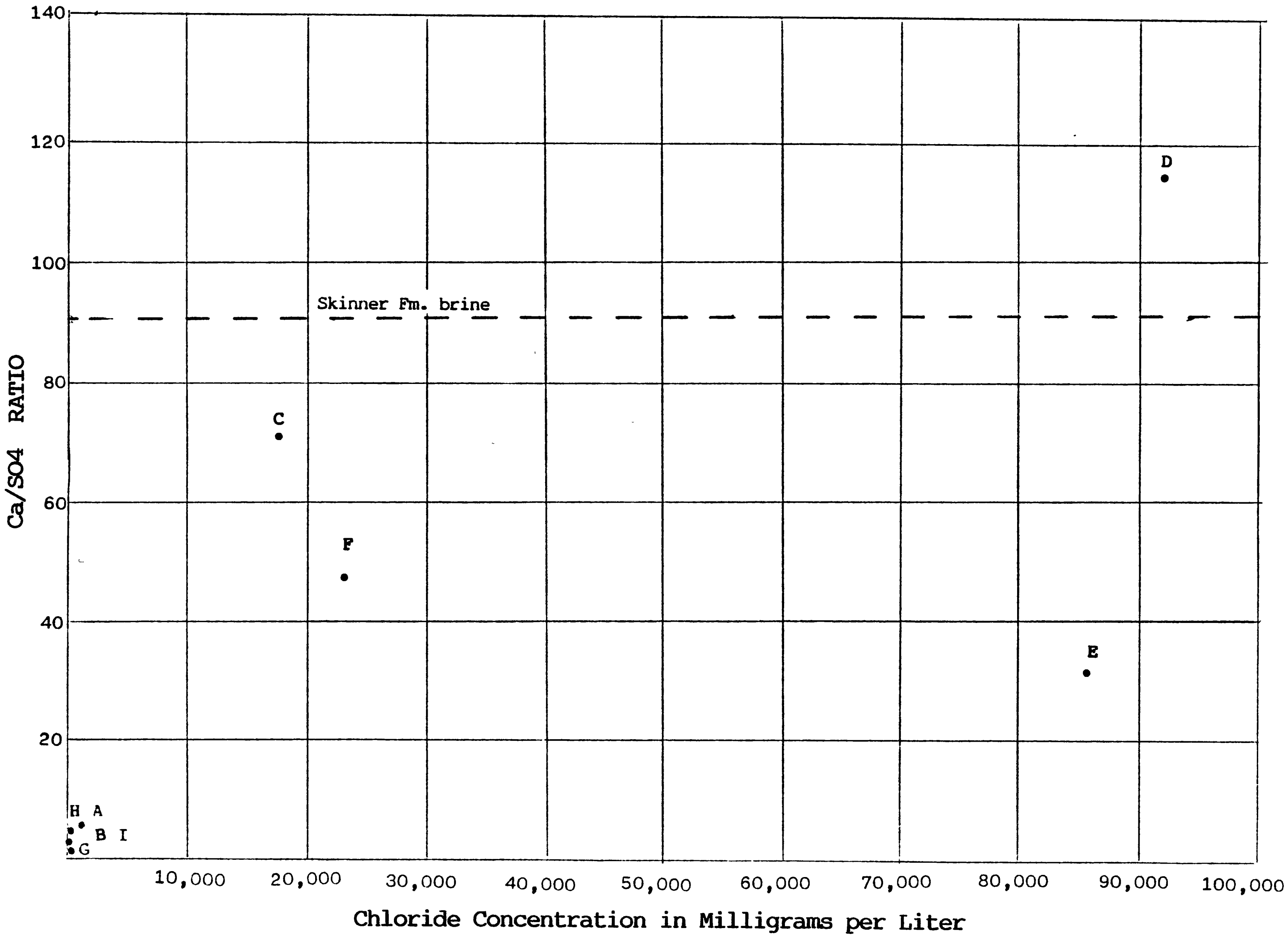


Figure 13. Calcium to Sulfate Ratio versus Degree of Contamination

Figure 14 shows the difference between the fresh and polluted waters.

It should be noted that the sample from the house well was diluted to a chloride concentration of 0.48 percent and a sodium concentration of 0.44 percent of the original Skinner Formation brine water concentrations. Again the observation is pointed out that brine waters have concentrations three orders of magnitude larger than that of fresh ground waters and their identity may still be found even if they are greatly diluted in the ground water system.

Long term effects

In the ten years that brine water was dumped into the pit it was estimated that 6,626,809 kilograms of chloride had accumulated by the following data and calculations

Data

Brine Production	1951	54 Barrels/day
Brine Production	1974	128 Barrels/day
Brine placed in pit	1951 to 1961	

Calculations

Avg. barrels per day in 1961 estimated by a straight line.

$$y = mx + b \qquad (3\text{-}1)$$

where

y = barrels per day in 1961

m = slope of line, $(128-54)/(1974-1951)$

x = $(1961-1951)$ yrs

b = y intercept, 54 barrels per day

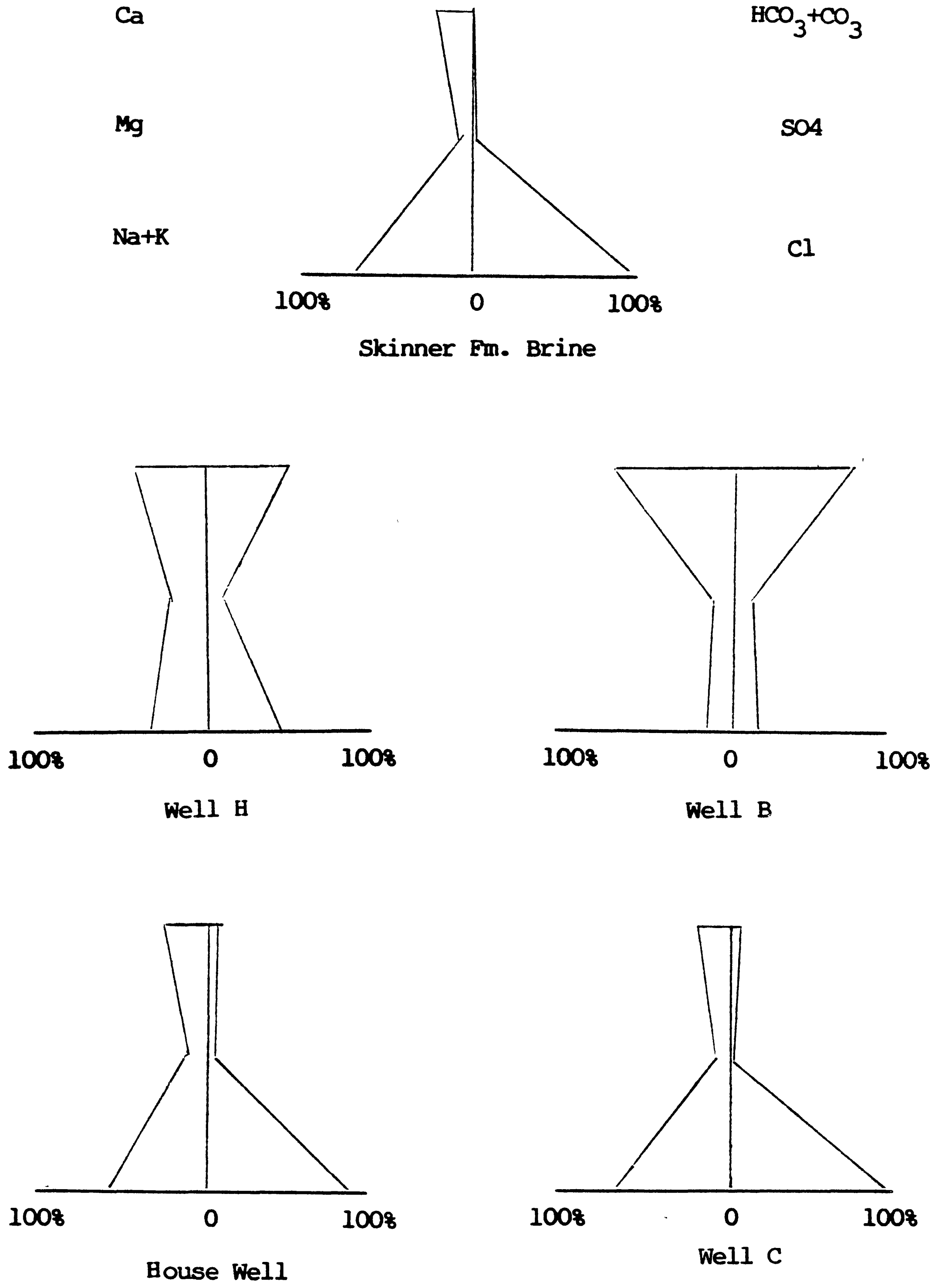


Figure 14. Percent Cation-Anion Representation of Skinner Brine in Comparison with Fresh and Polluted Waters

therefore production in 1961 was estimated to be

$$y = (3.217)(10) + 54$$

$$y = 86 \text{ barrels per day}$$

Averaging 54 and 86 gives 70 barrels per day average between 1951 and 1961. Knowing the brine contained 163137 mg/l chloride, the total amount of chloride was calculated to be 6,626,809 kilograms.

With the assumption that the only method of which the dissolved solids will be removed from the aquifer is with natural flushing, a computer program was developed to mix the background water with the brine water. The chloride concentration in the water directly under the pit was simulated by mixing background fresh water with the brine water. The percentage of background and brine waters mixed to produce the existing polluted water was used in conjunction with the Darcy flow equation to produce a mass balance of chloride concentrations into and out of the system. The control volume for the system consists of the pit dimensions laterally and the height of saturated aquifer vertically.

From the mixing program, shown in Appendix A, it was determined that the polluted water under the pit sampled from Well D could be simulated by mixing 43.6% background water from Well H with 56.4% brine water from the Skinner Formation.

From the Darcy equation, aquifer characteristics and monitoring well data, the time for the aquifer to flush the chloride introduced from the pit is calculated by

$$t = \frac{M}{(1000)(\%B)KAiC} \qquad (3\text{-}2)$$

where

t = time days d

K = Hydraulic conductivity m/d

A = Area saturated aquifer under pit (m^2)

i = Hydraulic gradient

C = Concentration of initial brine (kg/l)

M = total mass of chloride introduced to the pit (kg)

$\%B$ = percent of original brine concentration being flushed

The Coye-Zaneis soil which outcrops the area has a hydraulic conductivity range of 0.37 to 1.2 meters per day giving an average of 0.78 m/day (Soil Conservation Service, 1984). The pit was measured to be sixty meters in length from a Soil Conservation Service (S.C.S.) aerial photo and the depth of saturated aquifer under the pit is 3.9 meters. The area of saturated aquifer perpendicular to flow is then 234 square meters. The hydraulic gradient measured from water levels in Well D and Well E is 0.008.

The flow rate calculated from the Darcy equation is

$$Q = KAi = (0.78\ m/d)(234m^2)(0.008) = 1.46\ m^3/d$$

$$= 1.46\ x.10^3\ l/d$$

Replacing KAi with Q from equation 3-2 the time in days for the aquifer to flush out the chlorides is calculated by

$$t = \frac{M}{1000(\%B)\ Q\ C} \qquad (3\text{-}3)$$

$$= \frac{6626809kg}{(1000l/m^3)(.564)(1.46m^3/d)(0.163137Kg/l)}$$

$$= 49331 \text{ days}$$

It is estimated that the brine removal from the pit area will take 135 years.

The term "removal" is actually a misnomer when considering the fate of the contaminants. The brine pit acts as a source and the flushing only displaces the chloride into other areas. As was seen from the potentiometric maps, the contaminated water, where it does not run off, enters into the lower aquifer system and will migrate elsewhere. Much of the runoff water will reenter the ground or be carried into other surface water bodies. A landowner to the north east of this tract of land has already become vocal about high chlorides in his domestic water well and ponds.

Large Scale Study

Chloride content in the ground waters of nine north western Oklahoma counties were investigated to detect any possible oil field brine contamination. This was done by mapping chloride concentration in milligrams per liter for these counties using water quality data published by the United States Geological Survey. Water quality data for the high chloride areas is listed in Appendix D. This map was then superimposed onto two other maps. The first being a map of oil and gas fields in the area and the second being a plot of secondary oil production through water flooding in these counties.

Figures 15, 16, and 17 show the chlorides map, the superimposed oil field map, and the areas of water flooding respectively.

High chloride concentration does not necessarily mean there is oil field brine pollution, therefore areas with high chloride concentration were studied using three criteria. These being geological outcropping, early well water quality data presented by Gould (1905), and oil field brine analyses obtained for the major oil production areas in each county.

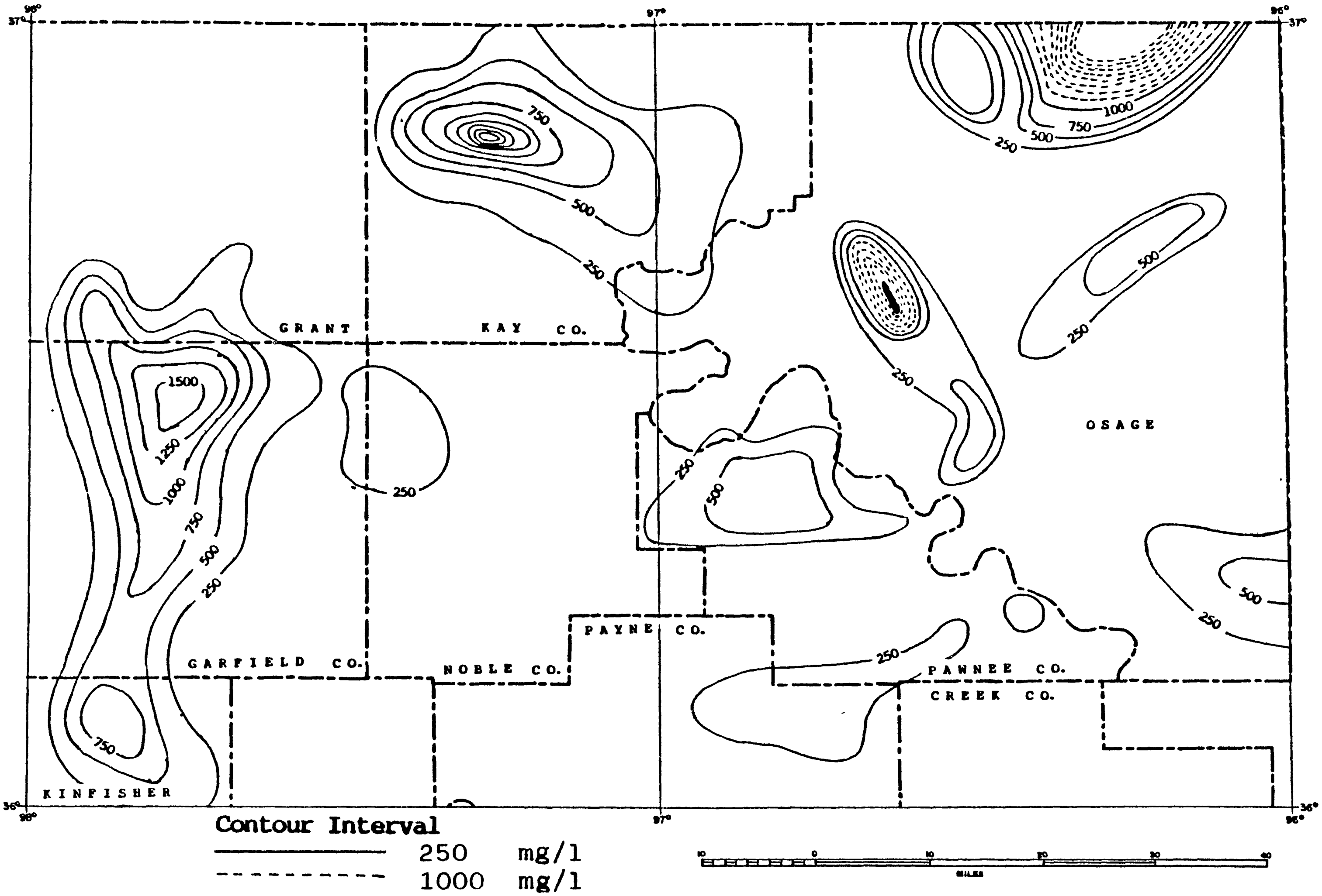


Figure 15. Contour of Chloride Concentration in Milligrams per Liter

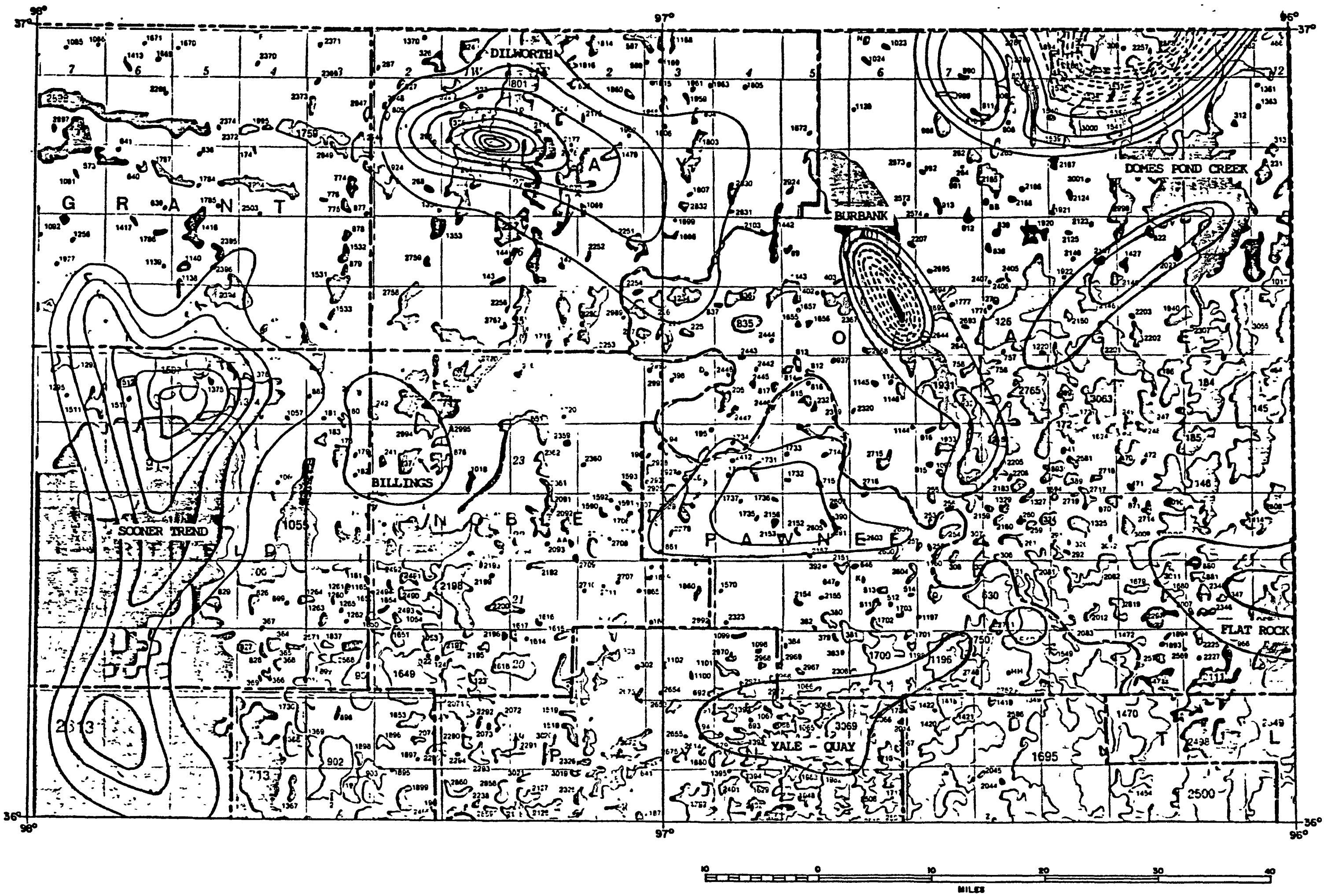


Figure 16. Chloride Concentration and Oil Fields

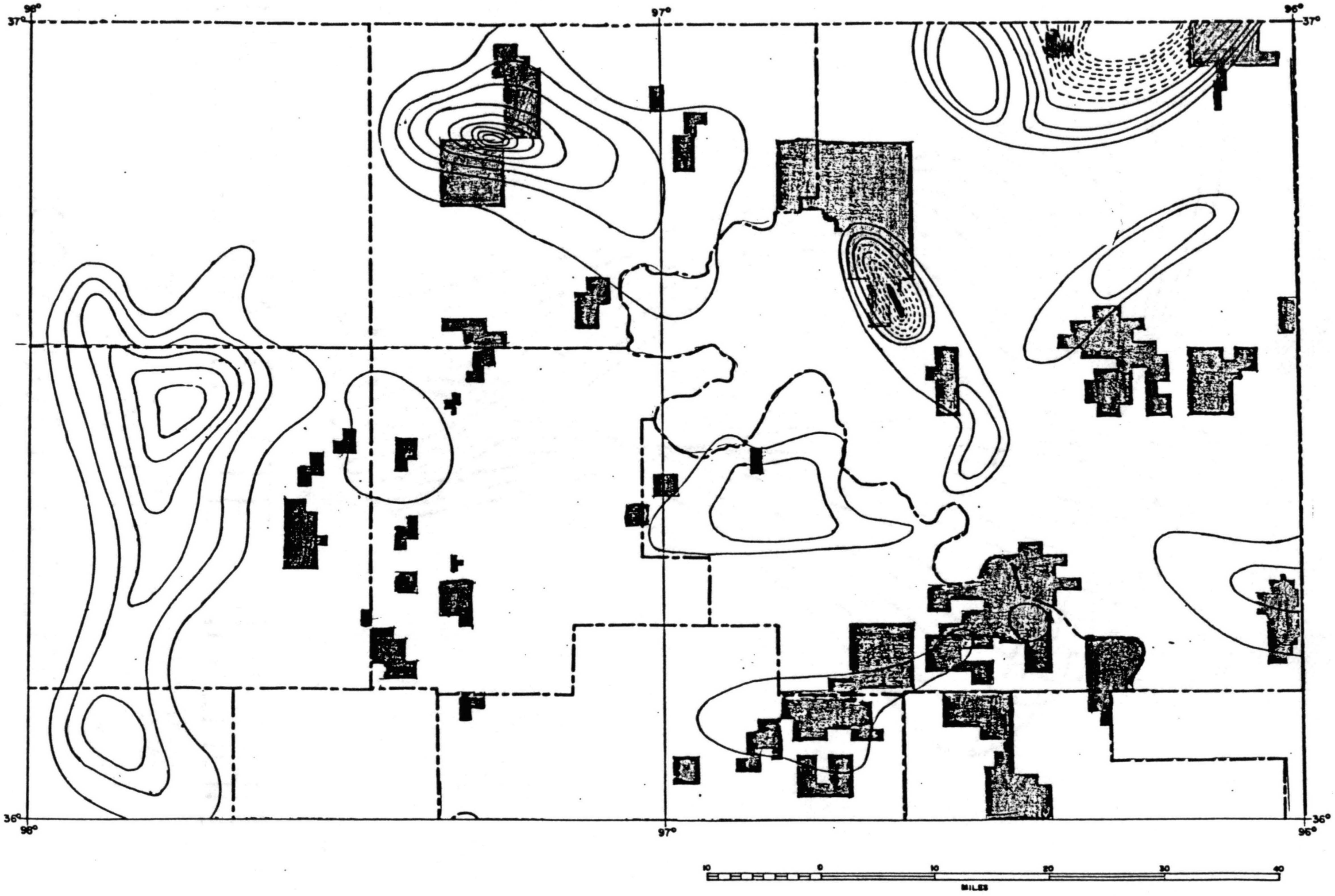


Figure 17. Chloride Concentration and Water Flooding Projects

Figure 18 is a geological map of the study area and will be used for outcrop information. The explanation for the geologic map is in Appendix C. Fifteen oil field brine analyses from Oklahoma oil fields are listed in Appendix B.

The particularly high chloride areas, from west to east, are in Garfield and Kingfisher counties, Northern Kay County, Western Osage County and Northern Osage County.

Garfield County

Chloride concentrations reach 1600 milligrams per liter in Garfield County. The area of high concentration corresponds to the "Sooner Trend" production area almost exactly. However, much of the ground water supply from this area comes from red beds containing gypsum and salt beds causing water in some places to be high in chloride and sulfate. Also a look at the Geological map shows that the Salt Plains Formation outcrops at the same location with the same orientation as the high chloride.

Oil field brine water chemistry data for Garfield County show that the sodium to chloride ratios are 0.48 + 0.01 in the Sooner Trend oil fields. The ground water quality data for this high chloride area show the sodium to chloride ratio to be 0.68 in the mg/l form. This would be 1.05 in the equivalent form. Therefore the high chloride concentration is probably due to dissolution of evaporate salt rather than oil field brine pollution.

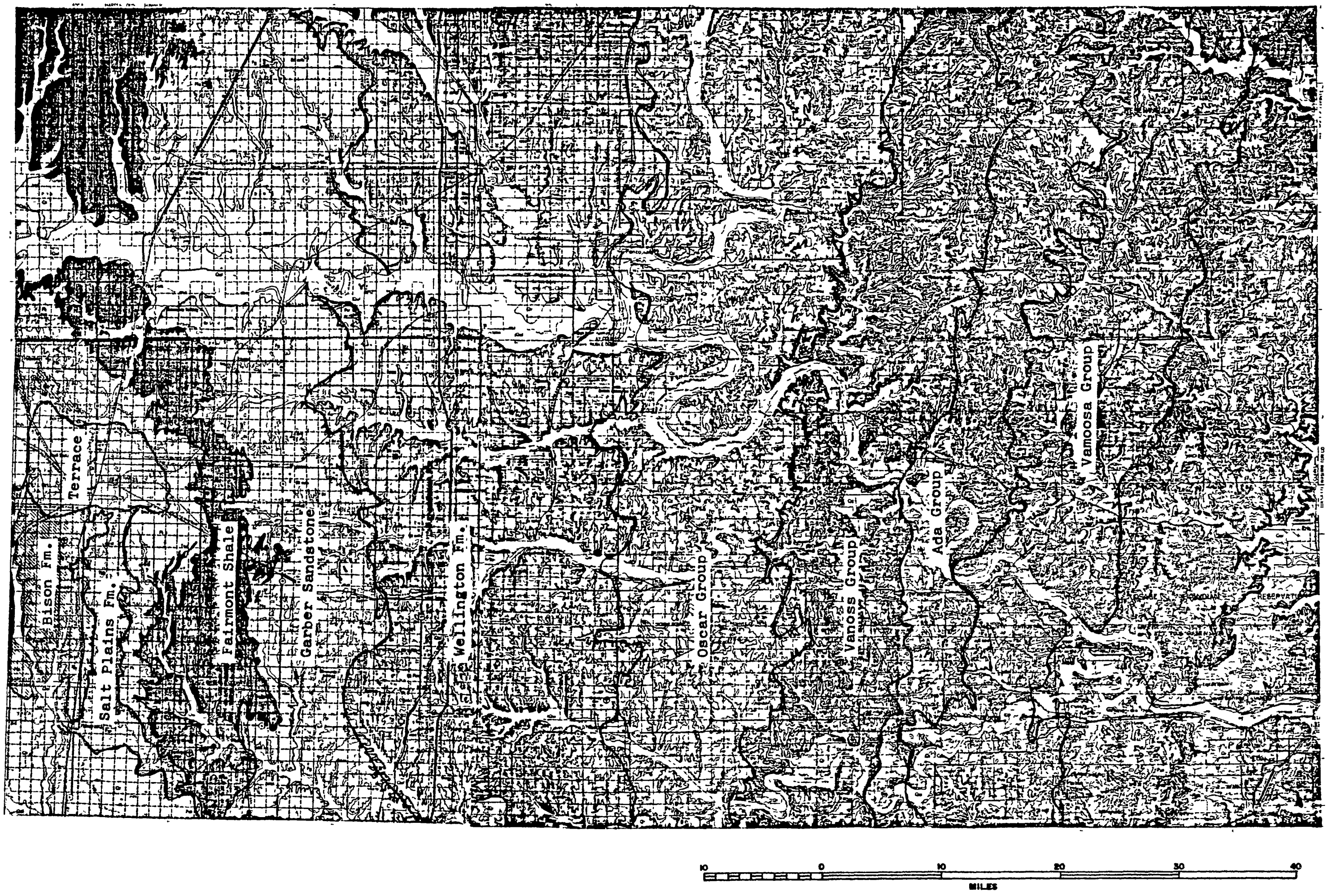


Figure 18. Geologic Map of Study Area

Kay County

Chloride concentrations reach 2,500 milligrams per liter in Northern Kay County. This is in the Dilworth Oil Field area. The Dilworth is one of Oklahoma's oldest oil fields. The first commercial oil well was drilled in 1913. Water flooding projects have been practiced in this area using reinjected brine as the source water. The oil field brine water produced here has a sodium to chloride (mg/l) ratio of 0.49.

Ground water supply in this area is from the Wellington Formation and is found at an average depth of 60 ft. Red Beds in Kay County contain some evaporate minerals and produce hard to salty water in some areas. The high chloride ground waters found have a Na/Cl ratio of 0.36. This much more represents an oil field brine rather than evaporate dissolution. Also the contaminated ground waters in this location have a much higher calcium concentration than sulfate concentration which again indicates oil field brine contamination rather than evaporite dissolution. The Dilworth field near Blackwell therefore shows probable signs of oil field brine contamination.

Osage County

Chloride concentrations as high as 65,000 milligrams per liter were found in Western Osage County near the Burbank field. This is another of Oklahoma's older fields and has been producing since 1920.

The regional ground water in this area is produced from the Vamoosa Formation, Oscar group and the Arkansas River alluvial deposits. The lithology is predominantly sandstone and limestones which produce a calcium bicarbonate type water. The salt water contaminated area has a sodium to chloride ratio of 0.48, which is the average ratio for oil field brines in the study area.

As the natural ground water in this area averages about 500 mg/l of total dissolved solids (T.D.S.) and is generally of good quality regionally, the immediate area around Burbank appears to be contaminated with oil field brines.

Northern Osage also shows high chlorides near the Domes Pond Creek field. Concentrations reach 9,400 milligrams per liter chloride in this area. Ground water in this region comes from the Vamoosa formation and alluvium and is of good quality.

Domes Pond Creek and the Duck Creek field adjacent to the west, are both older fields. This area has been producing oil since 1905. Brine waters from these fields have a sodium to chloride ratio of 0.49. Both of these fields have had water flooding projects starting from before 1950.

A contaminated ground water analysis is shown in Table VII.

TABLE VII

Water Analysis in North East Osage County

Concentrations in Milligrams Per Liter	
Na	2500
Ca	1400
Mg	200
Cl	9400
HCO_3	0
SO_4	120

Source: U.S. Geological Survey. Ground Water Records for Eastern Oklahoma. Open File Report 78-357, 1978.

The Sodium to Chloride ratio is 0.27. This ratio is too low for the brine and much too low for a fresh water sample. The cation-anion balance has a 15.8 percent difference so this particular analysis is questionable and no conclusion will be made as to the source of contaminant. However this particular area does contain high chlorides where the Vamoosa aquifer should yield good quality water. There is a good chance that these fields are contaminating fresh water supplies.

CHAPTER IV

CONCLUSIONS AND RESULTS

The purpose of this study was to investigate a localized oil field brine contaminated area by identifying the source, determining the characteristic flow pattern and the estimated time of natural flushing clean up. The second part of the study was a correlation of high chloride content in the major aquifers of North Central Oklahoma and the oil producing areas.

It was found that the ionic ratio of sodium to chloride approximated that of the original oil field brine within plus or minus 0.05 when the concentration of the contaminated water reached 75 milliequivalents per liter or 2650 milligrams per liter. It would take a 98.5 percent background and a 1.5 percent brine water mix to produce this. Therefore the ionic ratio of Na/Cl should be a fairly good "fingerprint" even in highly diluted brines.

The calcium to sulfate ratio does not lend itself well to the identification of oil field brines. Data from the three most polluted monitoring wells shows a scatter of values that would make even the most imaginative hard pressed to correlate them. The Ca/SO_4 ratio fails in this respect due to the characteristic small sulfate concentration in oil field brines which is too near that of fresh ground water.

By drawing the pattern of percent cations and percent anions the difference between fresh water and brine polluted waters was seen fairly well. It was shown that the original brine water kept its shape even after it had been diluted to 0.5 percent of its original value of dissolved solids. It is concluded that this method works because all the patterns are of the same size, it views the water in its entirety rather than specific ions, and because of the extreme difference in concentrations between oil field brines and fresh water.

The flow direction of the contaminant plume for the most part followed the path of the natural ground water. However, in the lower sand, it was found that Well A north of the pit showed evidence of brine pollution with 653 milligrams per liter chloride even though the well was upgradient of the flow direction. This occurrence was most likely due to the fact that the aquifer basal shale layer was dipping to the north under the pit area and the heavier brine water followed this route rather than the hydraulic gradient to the south toward Well G.

The method of water mixing combined with the Darcian flow rate gave an estimate of natural flushing of the disposed brine to be 135 years. This estimate is probably on the conservative side in that it treats the dissolved species as a normal parcel of water moving at the Darcy flow rate with no retardation factor (Kd). Also, as capillary forces pull the brine water upward from below the pit, layers of salt are formed on and near the surface and will only be flushed by rain fall.

The fate of the contaminants will be divided into the runoff portion in the gullies, and the amount that seeps into the lower sand aquifer. The runoff portion will be carried along erosion channels to the east and to the north. The runoff portion will eventually make its way to

Salt Creek and its tributaries. The portion that seeps directly into the lower aquifer will flow westward back towards the pit and veer off to the north east which is the direction of structural dip of the rocks.

In any event the contaminants will be displaced from the pit area, and though they may be diluted, they will continually be degrading near by water supplies for decades to come. As we keep in mind that this specific pollution problem is due to the disposal of salt water from one well one can imagine the degradation of water supplies around the larger fields, especially the older ones.

High chlorides were found in several counties in the study area. The particularly high concentration areas were in Garfield near the Sooner Trend oil producing area, Northern Kay County near Dilworth field and in Osage County near Burbank and Domes Pond Creek oil fields.

The chlorides in Garfield County were probably due to evaporites in the red beds. The three older oil fields, Burbank, Dilworth and Domes Pond Creek, which have produced since around 1910 showed good indications of contaminating the surrounding water supplies.

CHAPTER V

RECOMMENDATIONS FOR FUTURE WORK

Debasement of fresh water from oil field brine disposal does not occur as blatantly as it did in earlier times, however it still occurs in the forms of pipeline leaks, injection well casing leaks, blow outs and unplugged wells. The list could go on, however the point is that salt water pollution exists from past and present disposal and is now, as it was in the past, mostly due to the lack of regulation and inspection. Some recommendations in the form of regulation and inspection are:

1. All drilling muds and additives used and their amounts should be documented and filed in a state agency.
2. A water analysis be made of the producing formation brine and also filed in a state agency.
3. A fresh water monitoring well be drilled near disposal sites so that background water analyses can be compared to future analyses for early detection of contamination.
4. The state, aided with past plugging and well spacing records should inspect areas near injection wells and disposal wells for unplugged wells. Aerial photographs may be used to help locate past well sites.

5. Land owners, especially those near oil producing areas should periodically have a water analysis of the primary ions done on their well water. Also the analysis should include a trace metal particular to the brines produced in that area. Brine water analyses may be found in various petroleum information services.

Future studies for locally brine contaminated areas should include differential rates of movement of the brine components and their exchange properties in the local soil. Evidence shows that the brine water does not exactly follow the direction of decreasing hydraulic gradient. This may be the result of density differences between the brine and fresh waters. Water with greater density will show a lower piezometric surface than surrounding fresh water simply because the column is heavier and will have more pressure per foot of water. Therefore studies in delineation of the brine flow should be made with this consideration. Especially in confined flow where differential pressures are important.

On the larger scale, water quality maps should be made for previous, present and future data to detect aquifer deterioration caused by oil field brine waters and to determine the rate in which they are being affected.

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APPENDIX A

LISTING OF COMPUTER PROGRAMS

Cation Anion Balance and Percent Ion Program

```
10 LPRINT "This program takes input water quality data as mg/l and computes
20 LPRINT "ionic concentrations in mm/l and meq/l. total anions and cations"
30 LPRINT "in meq/l , total dissolved solids and computes the anion cation"
40 LPRINT "balance."
50  LPRINT "********************************************************************"
51  REM
52  REM                    VARIABLES ENCOUNTERED
53  REM
54  REM             SUMCAT:         TOTAL CATIONS
55  REM             SUMANI:         TOTAL ANIONS
56  REM             TOTION:         TOTAL IONS
57  REM             TDS:            TOTAL DISSOLVED SOLIDS
58  REM             MEQ:            MILLIEQUIVALENTS PER LITER
59  REM             MMC:            MILLIMOLES PER LITER
60  REM             PERION:         PERCENT ION
61  REM             PERCAT:         PERCENT CATION
62  REM             PERANI:         PERCENT ANION
63  REM             BALANCE"        CATION - ANION BALANCE
64  REM  *****************************************************************
65 DIM W$(9), X(9), Y(9)
70 INPUT "sample location", S$
80 INPUT "date", D$
90 INPUT "temperature", T$
100 INPUT "ph", P$
110 INPUT "conductivity", COND$
120 TDS = 0
130 SUMCAT = 0
140 SUMANI = 0
150 LPRINT
160 LPRINT"*********************************************************************"
170 LPRINT
180 LPRINT "SAMPLE LOCATION" TAB(20) "DATE" TAB(29) "TEMPERATURE" TAB(44) "PH" T
AB(50) "CONDUCTIVITY"
190 LPRINT S$ TAB(20) D$ TAB(30) T$ TAB(43) P TAB(50) COND$
200 LPRINT
210 LPRINT
220 LPRINT "   ION" TAB(20) "mg/l" TAB(40) "mm/l" TAB(60) "meq/l"
230 LPRINT
240 FOR I = 1 TO 9
250 READ W$(I), X(I), Y(I)
260 PRINT W$(I)
270 INPUT "conc", C
280 MMC = C/X(I)
290 MEQ(I) = MMC* ABS(Y(I))
300 PRINT TAB(3) W$(I) TAB(18) C TAB(38) MMC TAB(58) MEQ(I)
310 LPRINT TAB(3) W$(I) TAB(18) C TAB(38) MMC TAB(58) MEQ(I)
320 IF Y(I) > 0 THEN SUMCAT = SUMCAT + MEQ(I)
```

```
330 IF Y(I) < 0 THEN SUMANI = SUMANI + MEQ(I)
340 TDS = TDS + C
350 NEXT I
360 BALANCE =ABS(((SUMCAT - SUMANI)/(SUMCAT + SUMANI))* 100)
370 LPRINT
380 LPRINT
390 LPRINT
400 LPRINT "*****************************************************************"
410 LPRINT
420 LPRINT TAB(3)"CATION" TAB(18) "% CATION"
430 LPRINT
440 FOR I = 1 TO 4
450 PERCAT = (MEQ(I)/SUMCAT)*100
460 LPRINT TAB(3) W$(I) TAB(18) PERCAT
470 NEXT I
480 LPRINT
490 LPRINT "*****************************************************************"
500 LPRINT
510 LPRINT TAB(3)"ANION" TAB(18) "% ANION"
520 LPRINT
530 FOR I = 5 TO 8
540 PERANI =(MEQ(I)/SUMANI)*100
550 LPRINT TAB(3) W$(I) TAB(18) PERANI
560 NEXT I
570 LPRINT
580 LPRINT "*******************************************************************"
590 LPRINT
600 LPRINT TAB(3)"ION"TAB(18) "%ION"
610 LPRINT
620 FOR I = 1 TO 9
630 PERION = (MEQ(I)/(SUMCAT + SUMANI))*100
640 LPRINT TAB(3) W$(I) TAB(18) PERION
650 NEXT I
660 TOTION = SUMANI + SUMCAT
670 LPRINT
680 LPRINT "TOTAL ANIONS", SUMANI, "meq/l"
690 LPRINT "TOTAL CATIONS",SUMCAT , "meq/l"
700 LPRINT "TOTAL   IONS", TOTION, "meq/l"
710 LPRINT "TOTAL DISSOLVED SOLIDS" TAB(25) TDS TAB(35) "mg/l"
720 LPRINT "CATION, ANION BALANCE" BALANCE TAB(35) "%"
730 DATA "Ca",40,2,"Mg",24.3,2,"Na",23,1,"K",39,1,"SO4",96,-2,"Cl",35.4,-1
740 DATA "CO3",60,-2,"HCO3",61,-1,"SiO2",60,0
750 LPRINT "________________________________________________________________"
760 LPRINT "________________________________________________________________"
770 LPRINT
780 LPRINT
790 END
```

Water Mixing Program

```
11  LPRINT "water mixing program"
12  LPRINT "****************************************
21  REM THIS PROGRAM TAKES A CONTAMINANT WATER SOURCE AND MIXES IT WITH
22  REM BACKGROUND WATER TO PRODUCE THE EXISTING POLLUTED STATE. EACH ION
23  REM IS TREATED SEPARATELY.
24  REM
25  REM                   VARIABLES ENCOUNTERED
26  REM       ION:                 ION TO BE MIXED
27  REM       BG:                  BACKGROUND UNPOLLUTED WATER
28  REM       BW$:                 LOCATION OF BACKGROUND WATER
29  REM       BR:                  CONTAMINATED WATER SOURCE
30  REM       BL$:                 LOCATION OF CONTAMINATED WATER SOURCE
31  REM       EM$:                 LOCATION OF EXISTING POLLUTED WATER
32  REM       FM:                  COMPUTED EXISTING MIX SIMULATION
33  LPRINT "**************************************************************"
40  LPRINT
50  INPUT "brine from ?",BL$
60  INPUT "background water from ?",BW$
70  INPUT "existing mix from ? ",EM$
80  LPRINT "brine water from" TAB(30)BL$
90  LPRINT "background water from" TAB(30)BW$
100 LPRINT  "existing mix from"TAB(30)EM
110 LPRINT
120 INPUT  "ion mixed",ION$
130 INPUT   "ion to be mixed" TAB(30) ION$
140 INPUT  "brine conc.",BR
150 INPUT  "background concentration",BG
160 INPUT  "existing mix",FM
170 LPRINT
180 LPRINT
190 LPRINT
200 LPRINT "brine concentration" TAB(25) "back ground conc." TAB(50) "existing m
ix conc."
210 LPRINT BR TAB(25) BG TAB(50) FM
220 IF BR < BG GOTO 440
221 IF FM < BG THEN  LPRINT "mix can not be made from waters given"
222 IF FM < BG THEN GOTO  740
223 IF FM > BR THEN  LPRINT "mix can not be made from waters given"
224 IF FM > BR THEN GOTO 740
230 A = .05
240 B = .95
250 FOR I = 1 TO 20
260     MIX = (A*BR) + (B*BG)
270     IF MIX < FM THEN A = A + .05
280     IF MIX > FM THEN A = A - .05
290     B = 1 - A
300 NEXT I
310 FOR I = 1 TO 10
320     IF MIX > FM THEN A = A - .01
330     IF MIX < FM THEN A = A + .01
340     B = 1 - A
350     MIX = (A*BR) + (B*BG)
360 NEXT I
370 FOR I = 1 TO 10
380     IF MIX < FM THEN A = A + .001
400     B = 1 - A
410     MIX = (A*BR) + (B*BG)
420 NEXT I
421 FOR I = 1 TO 10
422     IF MIX < FM THEN A = A + .0001
423     IF MIX > FM THEN A = A - .0001
424     B = 1 - A
425     MIX = (A*BR) + (B*BG)
426 NEXT I
430 GOTO 660
440 IF BG < FM THEN LPRINT "mix can not be made from waters given"
450 IF BG < FM THEN GOTO 740
451 IF FM < BR THEN LPRINT"mix can not be made from waters given"
452 IF FM < BR THEN GOTO 740
460 A = .95
470 B = .05
480 FOR I = 1 TO 20
490     IF MIX < FM THEN A = A - .05
500     IF MIX > FM THEN A = A + .05
510     B = 1 - A
520     MIX = (A*BR) + (B*BG)
530 NEXT I
540 FOR I = 1 TO 5
550     IF MIX < FM THEN A = A - .01
560     IF MIX > FM THEN A = A + .01
570     B = 1 - A
580     MIX = (A*BR) + (B*BG)
590 NEXT I
600 FOR I = 1 TO 10
610     IF MIX < FM THEN A = A - .001
620     IF MIX > FM THEN A = A + .001
630     B = 1 - A
640     MIX = (A*BR) + (B*BG)
650 NEXT I
651 FOR I = 1 TO 10
652     IF MIX < FM THEN A = A - .0001
653     IF MIX > FM THEN A = A + .0001
654     B = 1 - A
655 NEXT I
660 LPRINT
670 LPRINT
680 A = A*100
690 B = B*100
700 LPRINT "% brine concentration"  TAB(30) A
710 LPRINT "% back ground concentration" TAB(30) B
720 LPRINT
723 LPRINT
730 LPRINT "existing mix simulation" TAB(30) MIX TAB(40) "mg/l"
740 LPRINT "_________________________________________________________"
750 LPRINT "_________________________________________________________"
760 LPRINT
770 LPRINT
771 LPRINT
772 LPRINT
773 LPRINT
774 LPRINT
775 LPRINT
776 LPRINT
780 END
```

APPENDIX B

BRINE WATER ANALYSIS

Brine Analysis

Concentration in mg/l

County	Field	Location	Na	Ca	Mg	Cl	SO4	HCO3	Na/Cl
Creek	Mannford	T19N R9E	34213	6820	1664	69500	53	45	0.49
Garfield	Enid NE	T23N R6W	61600	14800	2410	128000	277	0	0.48
Garfield	Hunter South	T23N R4W	27200	6520	935	56000	169	203	0.48
Grant	Deer Creek	T26N R6E	62627	17000	2360	134800	370	46	0.46
Kay	Dilworth	T29N R1E	68152	16329	2280	140117	615	77	0.49
Kay	Tonkawa	T24N R1W	59827	9662	6633	120935	93	-	0.49
Osage	Domes Pond Ck.	T29N R11E	34225	6760	1649	69504	45	15	0.49
Osage	Flatrock	T20N R12E	62040	13197	2707	127464	90	-	0.49
Osage	Wildhorse	T22N R10E	51167	12400	2100	107000	130	-	0.48
Pawnee	Watchorn	T22N R3E	74260	16158	2589	150126	641	76	0.49
Payne	March	T18N R5E	59136	11177	2688	118720	107	146	0.50
Payne	March	T18N R5E	60745	13636	2964	126224	250	103	0.48
Payne	Ramsey	T18N R2E	21254	3947	640	41565	95	32	0.51
Payne	Ripley	T18N R4E	62588	14200	2176	127800	132	47	0.49
Payne	Yale Quay	T19N R5E	39583	9986	2022	83475	1552	40	0.47

SOURCE: Dwights Energy Data Service. Norman, Oklahoma, 1985.

APPENDIX C

GEOLOGICAL MAP EXPLANATION

Geological Map Explanation

Alluvium

Sand, silt, clay, and locally gravel. Maximum thickness ranges from 30 to 80 feet (9 to 24 m) along major streams and from 0 to 60 feet (0 to 18 m) along minor streams.

Terrace deposits

Sand, silt, clay, and gravel. Maximum thickness, about 75 feet (23 m) along major streams.

Cedar Hills Sandstone

Mainly orange-brown, fine-grained quartzose sandstone. Thickness, about 180 feet (55 m).

Bison Formation

Mainly red-brown shale and greenish-gray and orange-brown calcitic siltstone with minor sandstone in Garfield County. Thickness, about 120 feet (35 m).

Salt Plains Formation

Mainly red-brown shale with several thin beds of orange-brown, fine-grained sandstone Thickness, about 160 feet (50 m).

Kingman Siltstone

Mainly red-brown with several thin layers of greenish-gray and orange-brown calcitic siltstone. Thickness, about 70 feet (20 m).

Fairmont Shale

Mainly red-brown shale with many thin layers of calcitic siltstone in upper 60 feet (18 m). Thickness, about 150 feet (45 m).

Garber Sandstone

Mostly orange-brown, fine- to medium-grained quartzose sandstone and conglomerate, grading northward into shale and calcitic siltstone. Thickness, about 600 feet (180 m).

Wellington Formation

Mostly red-brown shale to north, grading into fine-grained sandstone and mudstone conglomerate southward into Logan County. Thickness, about 850 feet (260 m).

Oscar Group

Mainly shale with many layers of limestones that pinch out southward, where fine-grained arkosic sandstones are thicker and more numerous. Near Kansas border, sequence is (descending). *Herington Limestone* (20 feet thick) at top, *Enterprise Shale* (45 feet thick), *Winfield Limestone,* IPowi (8 feet thick), *Gage Shale* (80 feet thick), *Towanda Limestone* (3 feet thick), *Holmesville Shale* (25 feet thick), *Fort Riley Limestone,* IPofr (30 feet thick) and underlying *Florence Flint,* IPofr (8 feet thick), *Blue Springs Shale* (60 feet thick), *Kinney Limestone* (5 feet thick), *Wymore Shale* (22 feet thick), *Wreford Limestone,* IPowr (25 feet thick), *Speiser Shale* (38 feet thick), *Funston Limestone* (4 feet thick), *Blue Rapids Shale* (15 feet thick), *Crouse Limestone* (6 feet thick), *Easly Creek Shale* (12 feet thick), *Bader Limestone* (5 feet thick), *Stearns Shale* (10 feet thick), *Morrill Limestone* (2 feet thick), *Florena Shale* (6 feet thick), *Cottonwood Limestone,* IPoc (3 feet thick), *Eskridge Shale* (65 feet thick), and *Neva Limestone* (25 feet thick) at base. Total thickness, about 400 feet (120 m).

Vanoss Group

Alternating layers of limestone and shale to north, grading southward into limestone, shale, and fine-grained arkosic sandstone. Locally group contains thin coal seams. Near Kansas border, group includes (descending): *Salem Point Shale* (12 feet thick) at top, underlain by *Burr Limestone* (8 feet thick), *Legion Shale* (4 feet thick), *Sallyards Limestone* (3 feet thick), *Roca Shale* (15 feet thick), *Red Eagle Limestone,* IPvre (20 feet thick), *Johnson Shale* (35 feet thick), *Long Creek Limestone,* IPvlc (10 feet thick), unnamed shale (3 feet thick), *Hughes Creek Limestone* (15 feet thick),unnamed shale (5 feet thick), *Americus Limestone,* IPvam (12 feet thick), *Oaks Shale* (3 feet thick), *Houchen Creek Limestone* (8 feet thick), *Stine Shale* (20 feet thick), *Five Point Limestone* (3 feet thick), unnamed shale (12 feet thick), *Brownville Limestone,* IPvb (8 feet thick), *Pony Creek Shale* (40 feet thick), *Grayhorse Limestone,* IPvg (5 feet thick), unnamed shale (12 feet thick), *Nebraska City Limestone* (5 feet thick), *French Creek Shale* (12 feet thick), *Jim Creek Limestone* (3 feet thick), *Friedrich Shale* (30 feet thick), *Grandhaven Limestone* (2 feet thick), *Dry Shale* (25 feet thick), *Dover Limestone* (30 feet thick), *Willard-Langdon Shale* (110 feet thick), *Elmont Limestone,* IPve (10 feet thick), *Stonebreaker Shale* (20 feet thick), and *Reading Limestone* (20 feet thick) at base. Total thickness, about 500 feet (150 m).

Ada Group

Mainly shale with many limestone layers that are thinner and pinch out southward, where fine-grained sandstones are thicker and more numerous. Near Kansas border, group includes (descending): *Auburn Shale* (50 feet thick) at top, underlain by *Wakarusa Limestone,* IPaw (2 feet thick), unnamed shale (40 feet thick), *Rulo Limestone* (3 feet thick), unnamed shale (18 feet thick), *Happy Hollow Limestone* (2 feet thick), unnamed shale and sandstone (60 feet thick), *Bird Creek Limestone,* IPab (2 feet thick; = *Church Limestone* of Kansas), *Severy-Aarde Shale* (70 feet thick), *Turkey Run Limestone,* IPat (2 feet thick; = *Coal Creek Limestone* of Kansas), unnamed shale (30 feet thick), *Pearsonia Limestone* (3 feet thick), unnamed shale (15 feet thick), *Little Hominy Limestone* (22 feet thick), unnamed shale (15 feet thick), *Deer Creek Limestone* (15 feet thick), unnamed shale (10 feet thick), *Plummer Limestone* (2 feet thick), unnamed shale (35 feet thick), and *Beil Limestone Member* (10 feet thick) of *Lecompton Limestone* at base. Total thickness, about 400 feet (120 m).

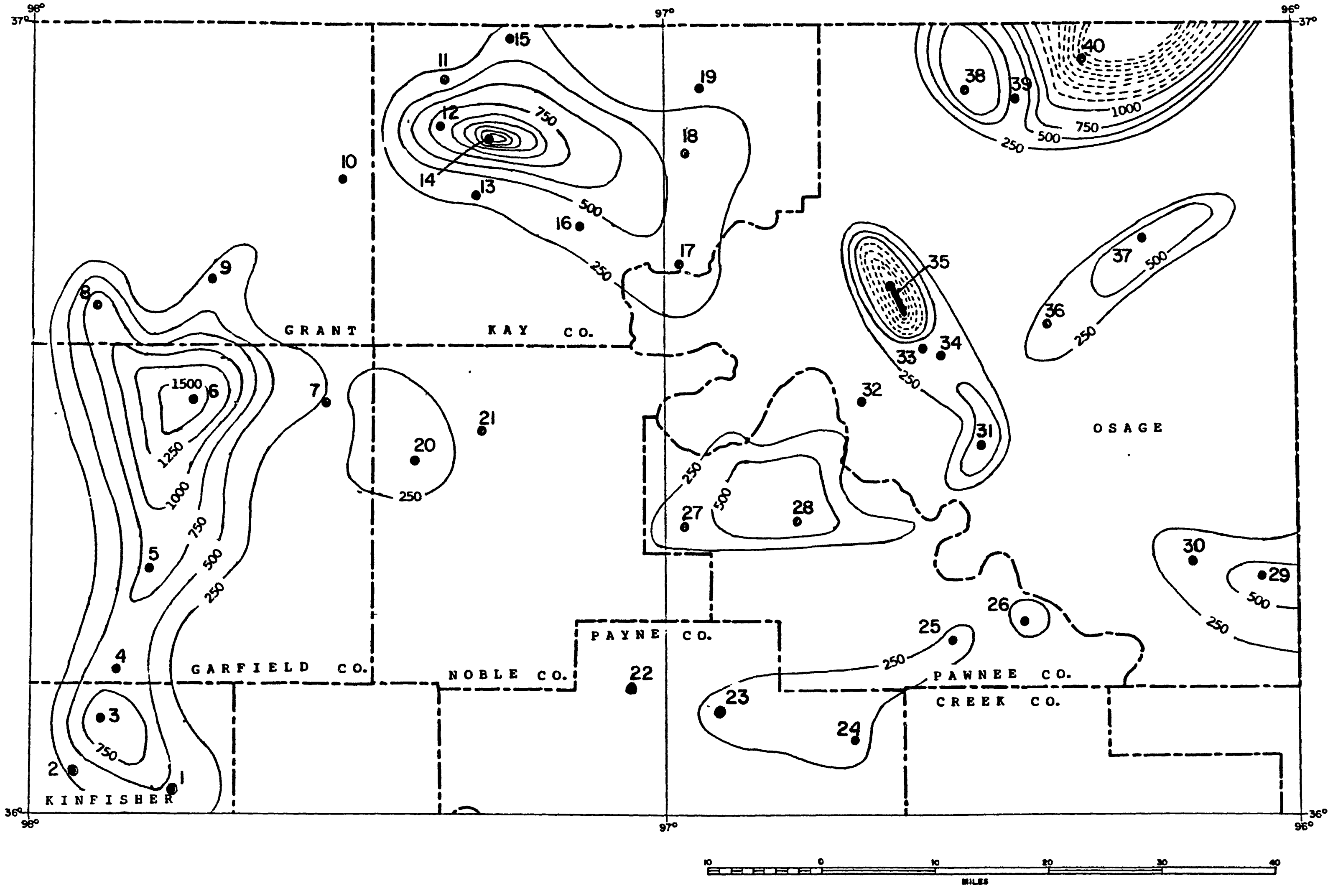
Vamoosa Group

Alternating layers of shale and fine to coarse-grained sandstone, with some thin limestones. Sandstone layers are thicker, coarser grained, and more numerous southward. Group near Kansas border includes (descending): unnamed shale and sandstone (160 feet thick) at top, *Plattsmouth Limestone,* IPvap (14 to 23 feet thick), unnamed shale and sandstone (15 to 90 feet thick), *Leavenworth Limestone,* IPvale (4 feet thick), unnamed shale and sandstone (170 feet thick), *Labadie Limestone,* IPval (6 to 23 feet thick; = ?*Haskell Limestone),* unnamed shale and sandstone (60 to 100 feet thick), *Bowring Limestone,* IPvab (2 feet thick; = ?*Westphalia Limestone),* unnamed shale (5 to 10 feet thick), and basal *Cheshewalla Sandstone* (7 to 20 feet thick; = *Tonganoxie Sandstone).* Total thickness, about 630 feet (190 m).

SOURCE: U.S. Geological Survey. "Reconnaissance of the Water Resources of the Enid Quadrangle, North Central Oklahoma, by R.H. Bingham and D.L. Bergman, (1980).

APPENDIX D

WATER QUALITY DATA FOR HIGH CHLORIDE AREAS


98°
37°
97°
96°
37°
36°
98°
97°
96°
36°
GRANT
KAY CO.
OSAGE
GARFIELD CO.
NOBLE CO.
PAYNE CO.
PAWNEE CO.
CREEK CO.
KINFISHER
1
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3
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36
37
38
39
40
1500
1250
1000
750
500
250
10
0
10
20
30
40
MILES

Water Well Data

Concentration in mg/l

Data Pt.	County	Na	Ca	Mg	Cl	SO4	HCO3
1	Kingfisher	300	-	-	487	75	152
2	Kingfisher	92	-	-	266	24	268
3	Kingfisher	655	-	-	1382	465	305
4	Garfield	560	-	-	682	288	200
5	Garfield	483	-	-	762	302	390
6	Garfield	1092	-	-	1595	773	335
7	Garfield	287	-	-	230	105	720
8	Grant	747	-	-	877	470	866
9	Grant	391	-	-	266	154	738
10	Grant	140	-	-	124	283	457
11	Kay	204	-	-	257	293	262
12	Kay	320	-	-	1100	380	366
13	Kay	85	-	-	250	720	324
14	Kay	910	-	-	2550	720	384
15	Kay	207	-	-	275	312	262
16	Kay	241	-	-	337	1680	305
17	Kay	92	-	-	354	105	366
18	Kay	33	201	103	370	193	340
19	Kay	200	26	16	150	61	344

Data Pt.	County	Na	Ca	Mg	Cl	SO4	HCO3
20	Noble	110	150	96	410	110	365
21	Noble	130	120	57	130	150	482
22	Payne	1460	62	24	190	2740	301
23	Payne	150	207	121	355	139	132
24	Payne	110	120	26	265	50	286
25	Pawnee	-	390	13	270	970	413
26	Pawnee	102	-	-	360	58	150
27	Pawnee	470	-	-	340	200	482
28	Pawnee	580	-	-	540	110	506
29	Osage	414	101	61	618	281	266
30	Osage	210	-	-	420	45	276
31	Osage	140	220	57	570	120	176
32	Osage	150	150	18	210	30	563
33	Osage	161	-	-	434	225	280
34	Osage	533	-	-	301	91	860
35	Osage	31800	6710	1670	65000	19	11
36	Osage	150	180	41	470	24	253
37	Osage	600	11	2	640	-	447
38	Osage	860	8	3	860	220	560
39	Osage	440	5	2	440	20	411

Data Pt.	County	Na	Ca	Mg	Cl	SO4	HCO3
40	Osage	2500	1400	200	9400	120	0

SOURCE: U.S. Geological Survey. "Reconnaissance of the Water Resources of the Enid Quadrangle, North Central Oklahoma, by R.H. Bingham and D.L. Bergman, (1980).

SOURCE: U.S. Geological Survey. Ground Water Records for Eastern Oklahoma. Open File Report 78-357, 1978.

VITA

Thomas Michael Simmons

Candidate for the Degree of

Master of Science

Thesis: OIL FIELD BRINE POLLUTION IN
NORTH CENTRAL OKLAHOMA

Major Field: Civil Engineering

Biographical:

Personal Data: Born in Fort Worth, Texas, February 23, 1955, the son of Dayton Joseph and Marguerite Simmons.

Education: Graduated from El Dorado High School, El Dorado, Kansas, in May, 1973; Received Bachelor of Science Degree in Earth Science from Emporia State University in December, 1977; Studied Undergraduate Civil Engineering at the University of Texas January, 1981 to September, 1984; Completed requirements for the Master of Science degree at Oklahoma State University in December, 1985.

Professional Experience: Manager of Geophysical Seismograph Survey for Western Geophysical in Pakistan and Egypt, April, 1978 to December, 1979; Research Assistant for Bureau of Economic Geology, June, 1981, to August, 1984, Teaching Assistant, Department Civil Engineering, Oklahoma State University, January, 1985, to May, 1985.

Professional and Honorary Organizations: Chi Epsilon.