GEOCHEMICAL CHARACTERIZATION AND SALINIZATION OF THE CLEO SPRINGS WELL FIELD IN WOODS AND MAJOR COUNTIES, OKLAHOMA

By

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CHAPTER I

INTRODUCTION AND BACKGROUND

In 1982 the City of Enid developed the Cleo Springs well field in response to an increasing need for water. The well field is located north of the Cimarron River in Townships 22 and 23 North and Ranges 12 and 13 West in Woods and Major counties, in western Oklahoma (fig. 1).

A preliminary study conducted for the City of Enid by Engineering Enterprises Incorporated (EEI) (1982), investigated the long term water-supply potential of the Cimarron Terrace and Alluvium (CMTA) in proximity to the City of Cleo Springs, to determine a suitable location for the well field. In addition to well yield, water quality was considered an important factor, because use would be primarily for public supply. Groundwater samples taken in the well field showed elevated concentrations of chloride (Cl) and total dissolved solids (TDS) in the eastern and western parts (figs. 2 and 3). The investigators stated that the elevated concentrations of chloride were "***probably a result of aquifer contamination from oil well drilling." (EEI, 1982), but no geochemical evidence was given to support this statement.

The City of Enid expressed a concern for the quality of groundwater in the well field and its potential for salinization in the future. This project was in part a response to this concern, with its primary purpose to determine the source of salinization to the alluvial aquifer in the well field. Financial support for this project was provided jointly by the U.S. Geological Survey and the City of Enid.

Purpose and Scope

The purpose of this report is to:

(1) discuss the potential sources of salinization to the Cleo Springs well field;

(2) show where groundwater in the well field has been affected by increased salinization, and where it exceeds the secondary maximum concentration levels (SMCL) for chloride, sulfate, and TDS and the maximum concentration level (MCL) for nitrogen as nitrate in drinking water;

(3) geochemically characterize the groundwater from the alluvial aquifer in well field;

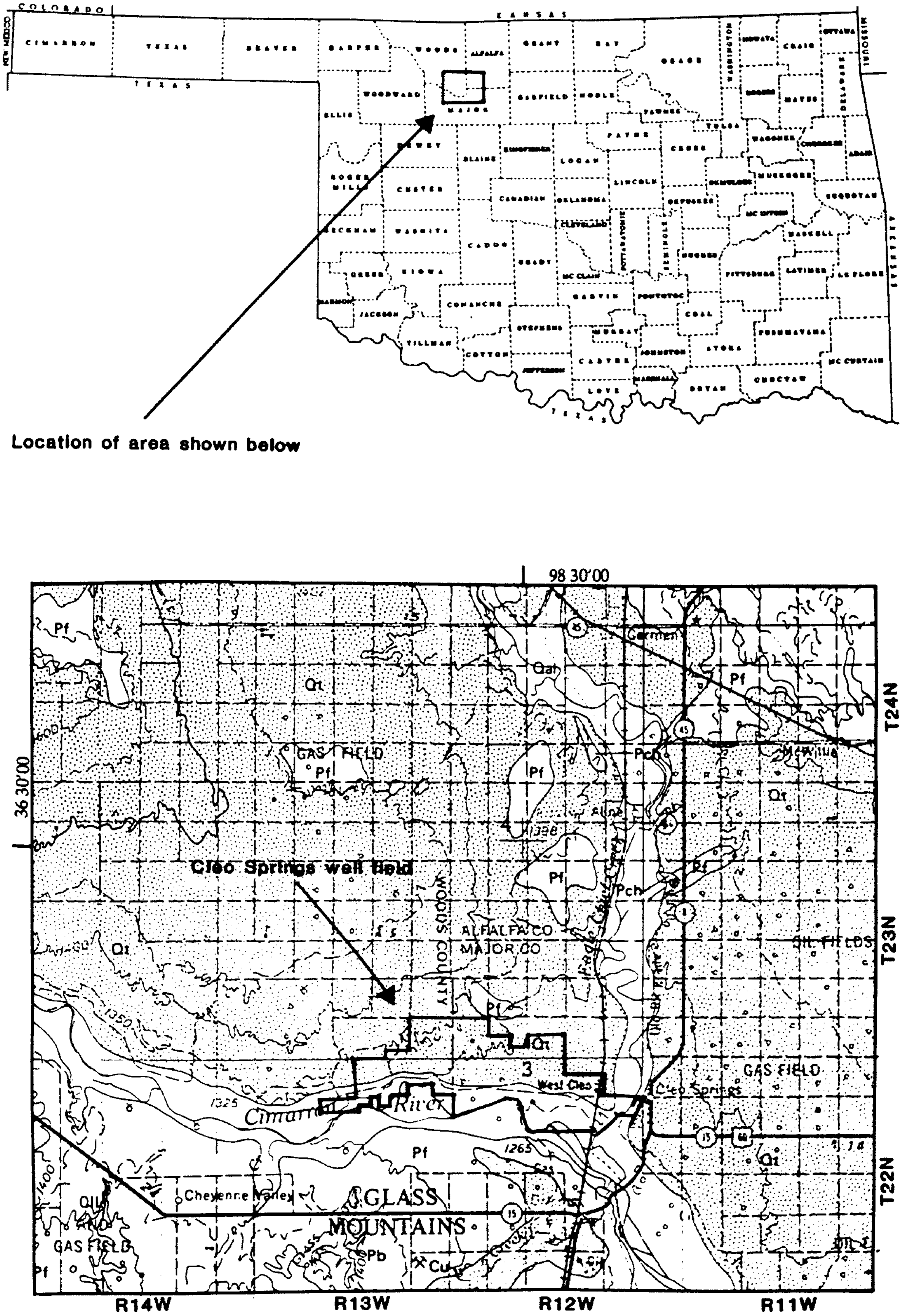

Location of area shown below

Figure 1. Location of the Cleo Springs well field.

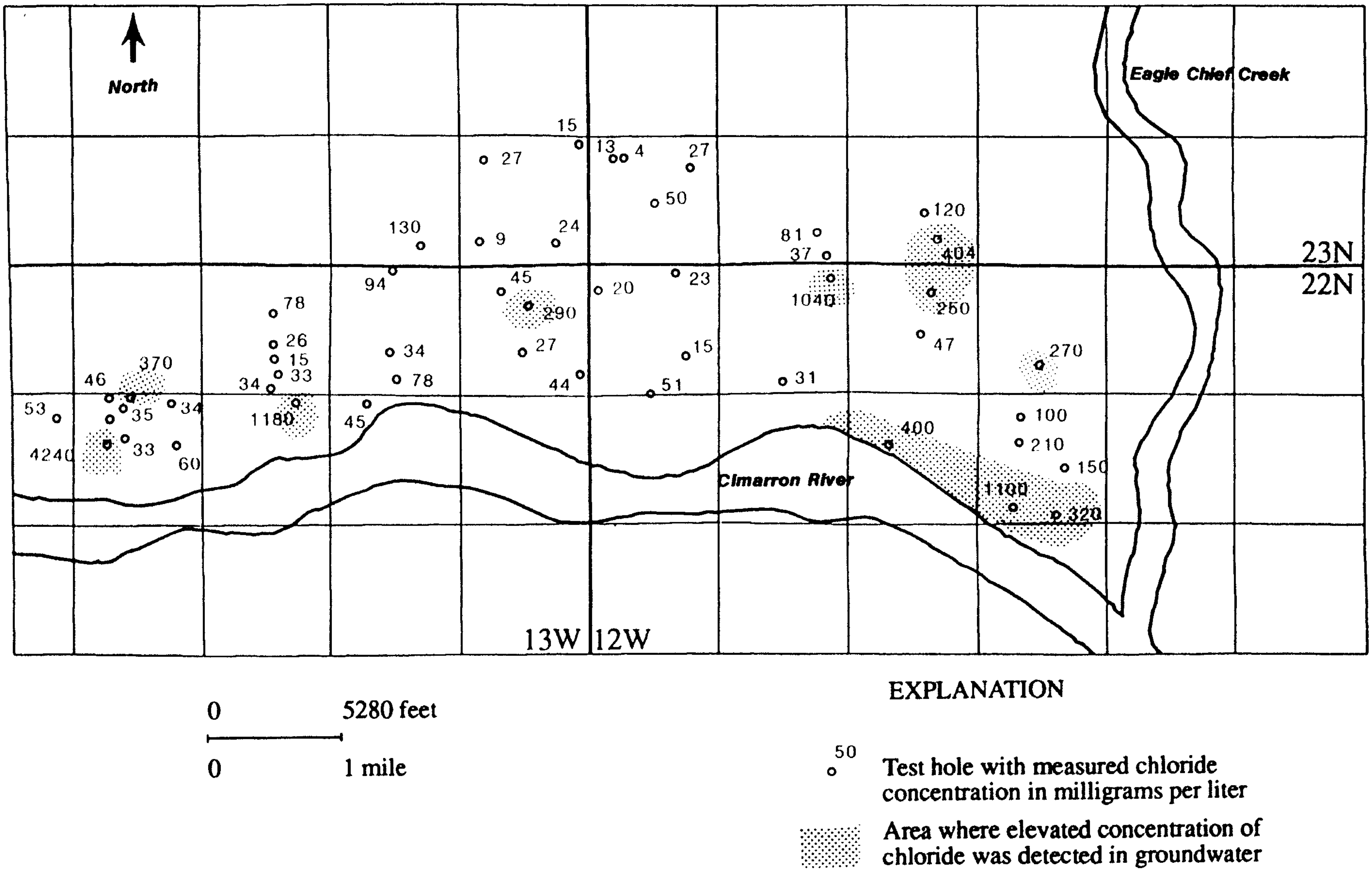


Figure 2. Chloride-concentration map of the Cleo Springs well field area from 1982 investigation [Data source: EEI, 1982].

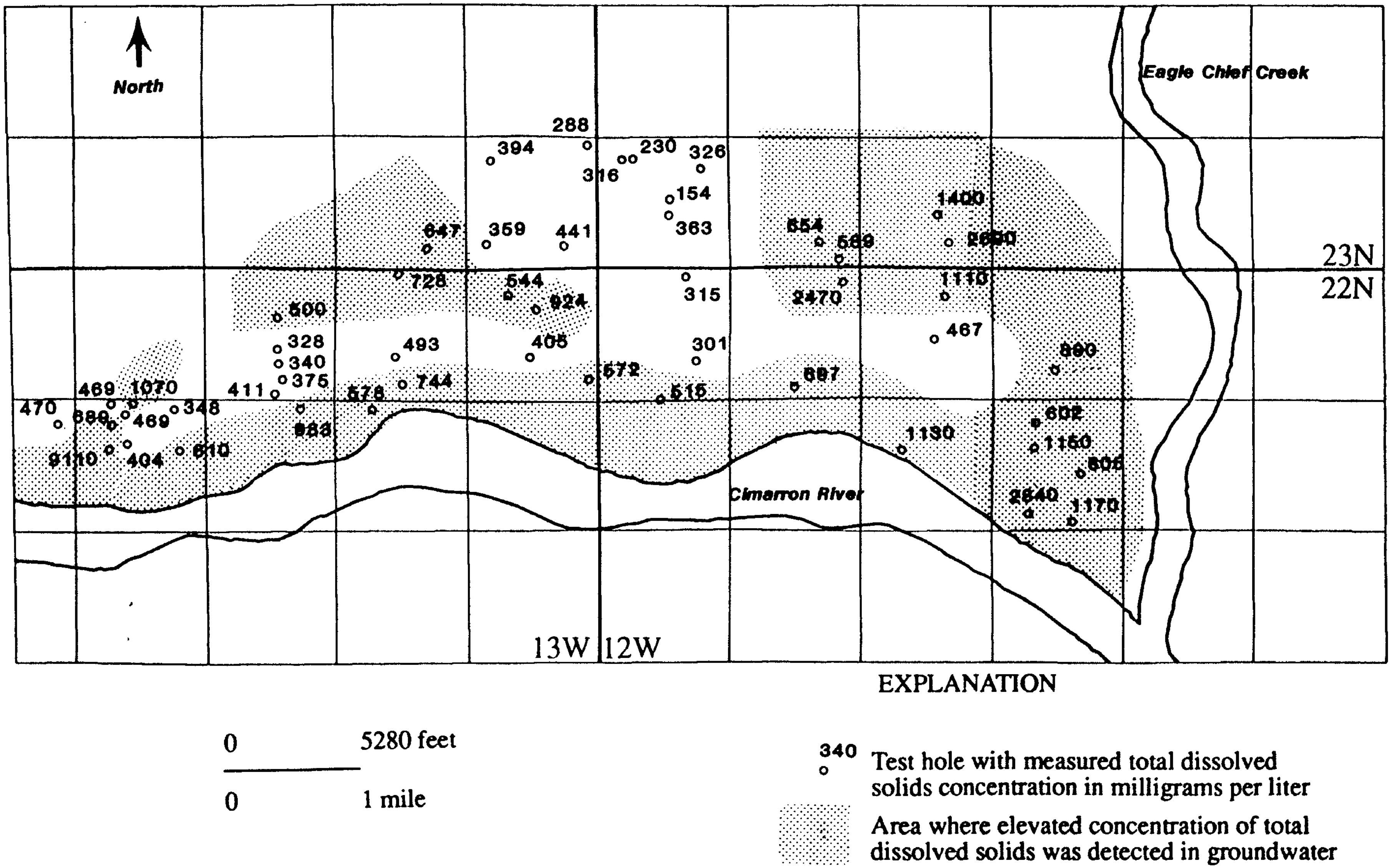


Figure 3. Total dissolved solids concentration map of the Cleo Springs well field area from 1982 investigation [Data source: EEI, 1982].

(4) use available hydrogeologic information and graphic plots of the major ions and bromide, iodide, and strontium, to determine the source of salinization to the well field.

The scope of the study entailed the acquisition of water-quality data from several sources and from water samples taken from the Cleo Springs well field and the potential sources of salinization.

Previous Investigations in the Cleo Springs Vicinity

The water-bearing properties of the CMTA and Flowerpot Shale have been studied in detail over the past 70 years. In 1914 A.T. Schwennesen published a brief report concerning groundwater in the Enid area. In 1924 B.C. Renick, in a study concerning future groundwater supplies for the City of Enid, mapped the terrace deposits around Enid and an area west of Ringwood. He analyzed several groundwater samples and commented on terrace-deposit stratigraphy and well yields. In 1944, E.T. Archer and Co., Consulting Engineers evaluated several possible sources for additional groundwater supplies for the City of Enid, and recommended the CMTA for future water-well locations. Reed (1952) studied the groundwater resources of the CMTA in Alfalfa, Garfield, Kingfisher, and Major Counties. In this comprehensive investigation groundwater from the alluvial deposits and underlying bedrock were evaluated in occurrence, quantity and quality to determine the feasibility of future development for exploitation. The report concluded that the alluvial deposits can supply an adequate amount of good-quality water in comparison to the underlying bedrock.

In 1982 EEI investigated the Cleo Springs area for long-term groundwater-supply potential for the City of Enid. The hydrologic data gathered from this study helped determine the present location of the well field.

Geology

Regional Geology

Orogenic episodes during the Pennsylvanian had pronounced effects on western Oklahoma. An array of mountains extending from southern Oklahoma to the Texas Panhandle was uplifted, forming a partial barrier to the encroachment of epicontinental seas. By Late Permian, western Oklahoma was the site of a broad, shallow, hypersaline sea in which were deposited redbeds and evaporite facies of anhydrite and halite. These strata extended westward and southward across the Amarillo uplift, and northward into Kansas (fig. 4) (Johnson, 1989).

The study area, located on the northern flank of the Anadarko Basin, appears to have been situated on a depositional hingeline receiving more clastics than evaporites as compared to the deeper basin to the west. Jordan and Vosberg (1963) gave some indication of this in their mapping and stated, "In a general way the evaporites occur as wedging tongues that increase in thickness down dip to the west away from the eastern land areas and shore lines. (Pg. 9)" Their study found that Permian sedimentary strata on the north limb of the Anadarko basin dipped toward the south at 9 to 40 feet per mile, averaging 20 feet per mile.

Post-Permian sedimentary rocks in the study area were removed by erosion. Quaternary alluvium and terrace deposits along with wind-blown sand overlie the Permian bedrock in the study area.

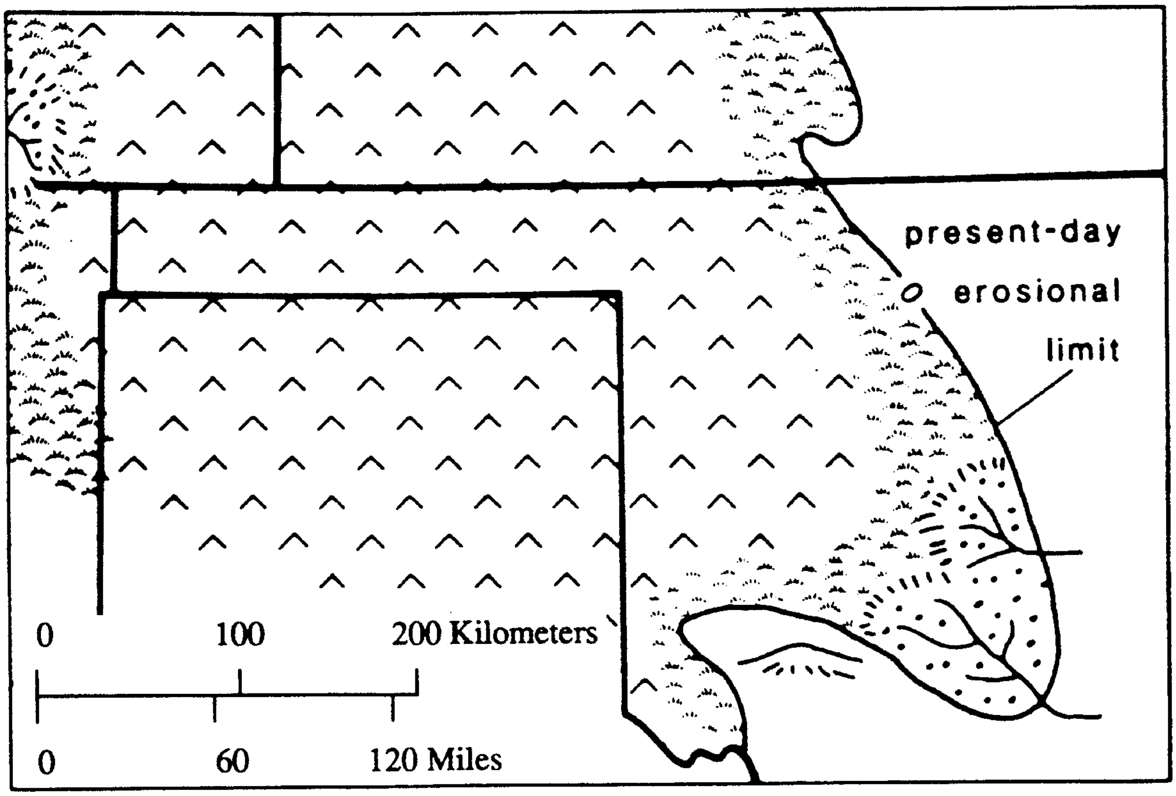
Stratigraphy

Several stratigraphers have studied the surficial bedrock and subsurface counterparts of western Oklahoma. Miser (1954) and Fay (1965) studied the surficial geology of northwestern Oklahoma. Morton's (1980) hydrologic atlas gives a comprehensive overview of the Permian strata exposed in the well field and surrounding region. Figure 5 is a geologic map of the study area.

Jordan and Vosberg (1963) published an in-depth study on the subsurface Permian evaporites in western Oklahoma. Vague statigraphic contacts and facies changes can make correlation between subsurface and surface strata difficult. Figure 6 is a stratigraphic column showing surficial nomenclature from Morton (1980) and counterpart subsurface nomenclature from Jordan and Vosberg (1963).

Alluvium

Quaternary alluvial deposits in the well field consist of river alluvium and overlapping terrace deposits. They are similar in composition, and are lenticular, interfingering deposits of gravel, sand, silt, and clay that are generally light tan to gray (Morton, 1980). Alluvial deposits are generally thicker in the northern half of the well field, averaging 60 feet (ft). Towards the Cimarron and Eagle Chief Creek they average 18 ft in thickness. Dune sands form a strip on the northeastern side of the Cimarron River 7 to 10 miles wide.



EXPLANATION OF ENVIRONMENTS

▨ Shale and sandstone

▨ Fluvial deposits

▨ Evaporites (salt, gypsum and anhydrite)
and redbeds

Figure 4. Geologic setting of western Oklahoma during Late Permian [Reproduced and modified from Johnson, 1989].

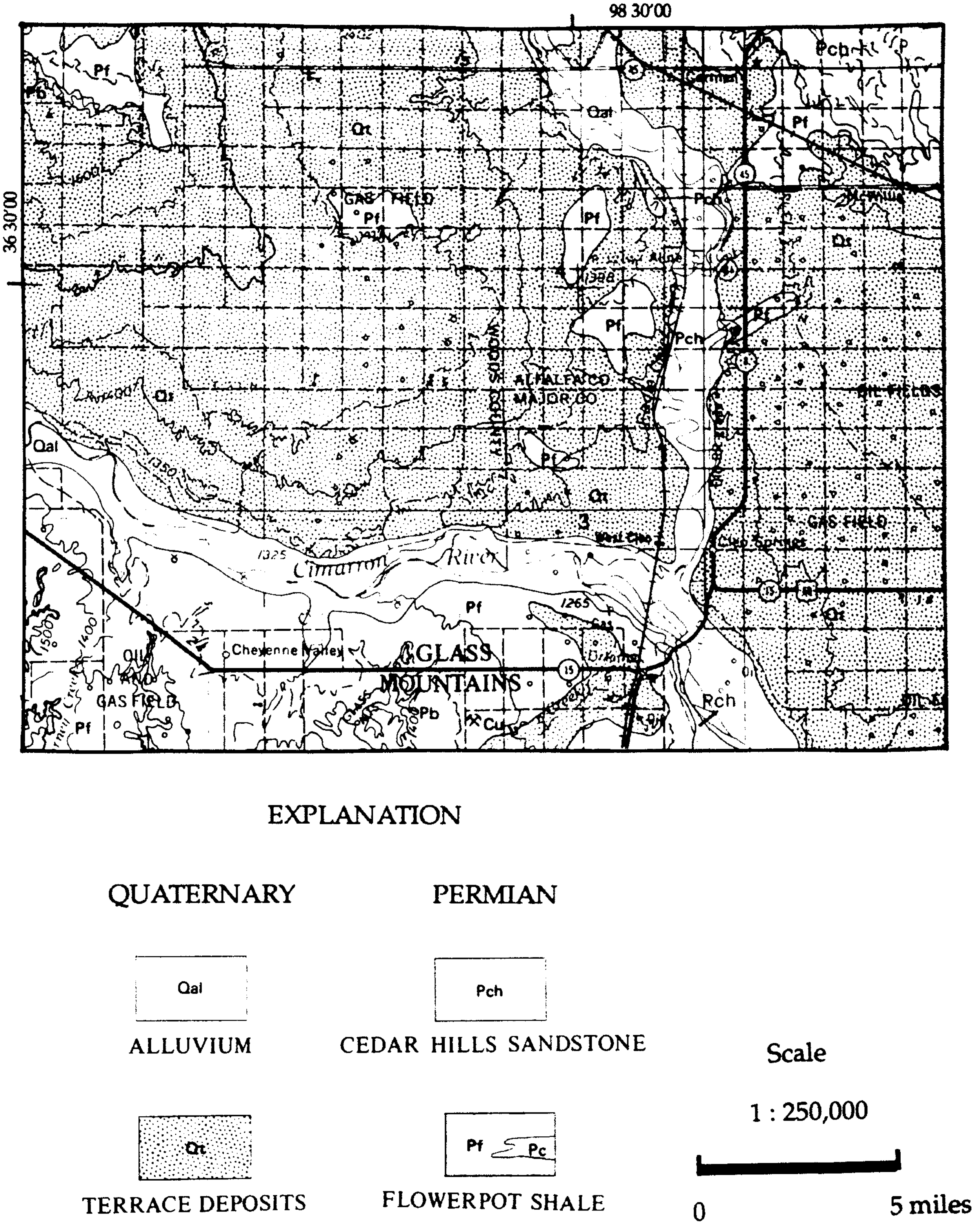


Figure 5. Geologic map of the Cleo Springs well field and vicinity [Reproduced from Morton, 1980; sheet 1].

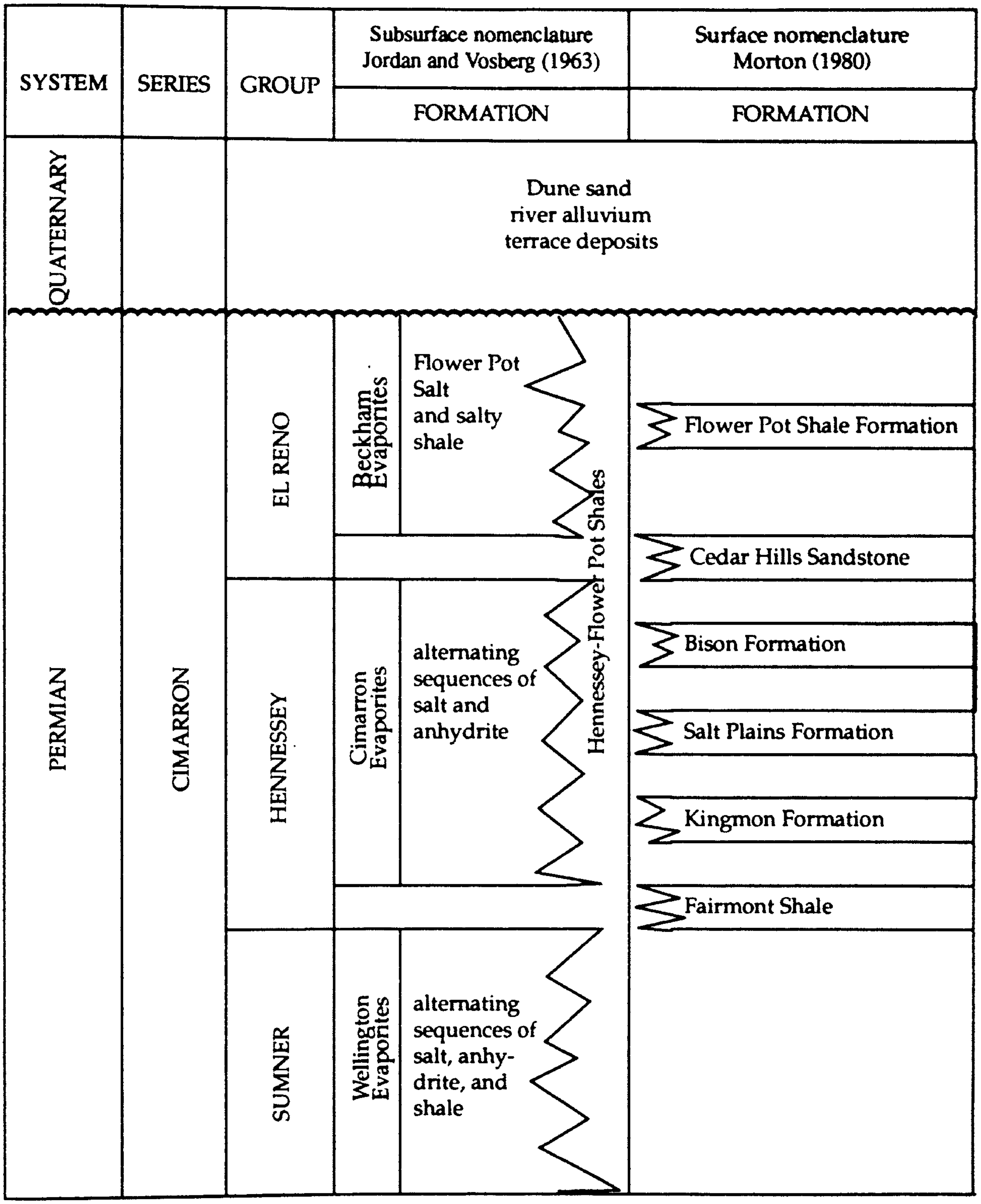


Figure 6. Stratigraphic column of the Cleo Springs well field and vicinity.

Flowerpot Shale and Associated Evaporites

The Flowerpot is in the upper section of a series of evaporite units that wholly or partially underlie the well field. Jordan and Vosberg (1963) divided the Permian stratigraphic section into three evaporite units and two intervening shales and called them in ascending order: Wellington Evaporites, Hennessey Shales, Cimarron Evaporites, Flowerpot-Hennessey Shales, and Beckham Evaporites. They state

> "Each evaporite sequence is widely distributed, occurring as eastward-thinning tongues or wedges within the framework of Permian clastic sediments. Together the evaporites have a maximum thickness of 2,500 ft. The evaporite strata, excluding clastics, consist of halite (about 80 percent), anhydrite and thin beds of dolomite (less than 5 percent)."

Jordan and Vosberg state that the Flowerpot Shale "is a surface term, referring to shale and siltstone strata lying below the Blaine Formation and above the Cedar Hills Sandstone." They found that when this sequence is traced into the subsurface, the clastic beds grade into salt and salty shale, which they gave the subsurface name of the Flowerpot Salt. Their work shows that the upper beds of halite in the Flowerpot Shale, which give rise to the Big Salt Plains and Little Salt Plains in Woods County, wedge out eastward and possibly are absent in the well field with only the lower section of silty shale containing beds of anhydrite/gypsum present. A cross section by Jordan and Vosberg shown in figure 7, illustrates their interpretation of the distribution of the three evaporite sequences in vicinity of the well field.

Morton (1980) described the regional lithofacies of the Flowerpot as red- brown silty shale with thin gypsum and dolomite beds, with the middle and upper parts of the formation containing 50 feet or more of halite.

In proximity to the well field, as described by Fay (1965), the Flowerpot along Eagle Chief Creek is about 356 feet thick and consists of "***red-brown gypsiferous shale and thin greenish-gray shales, with interbedded orange-brown to greenish-gray gypsiferous sandstones and siltstones, 1 to 7 feet thick." South of the Cimarron River resistant beds of gypsum in the Flowerpot give rise to the Glass Mountains (Morton 1980).

Engineering Enterprises Inc. drilled approximately 350 feet of the Flowerpot in the southeastern part of the well field and described the bedrock as containing "***numerous gypsum lenses [which were] evident in the drill cuttings throughout the formation from 75' to total depth."

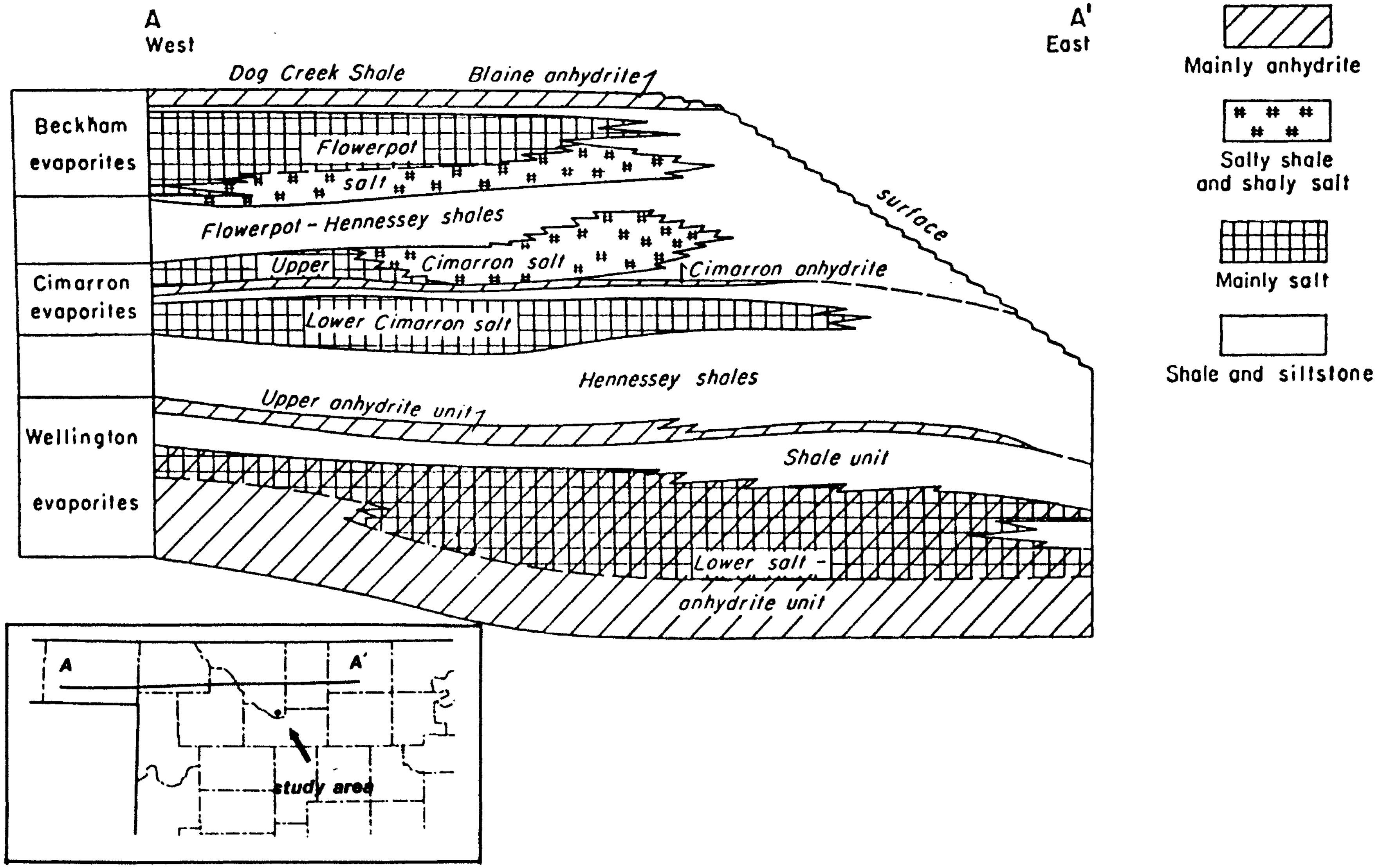


Figure 7. Cross section showing distribution of Permian evaporites in vicinity of the Cleo Springs well field [Reproduced and unmodified from Jordan and Vosberg, 1963].

As shown on the bedrock elevation map in figure 8, the meanderings of the Cimarron have left the surface of the Flowerpot scalloped and uneven in the well field, with a south to southeasterly slope towards the Cimarron and Eagle Chief Creek.

Physiography

Undulating sand dunes characterize the land surface in parts of the well field. Soils of the overlying Tivoli Series are described by the U.S. Department of Agriculture (USDA) (1950) as "grayish-brown, sandy soils with a yellowish- brown, fine sand subsoil". Both are extremely porous and permeable having drainage patterns that are nonexistent to poorly developed over most of the well field. The rolling topography and porous unconsolidated sediments allow for rapid infiltration and minimal runoff of precipitation. In the northern section of the well field close to Eagle Chief Creek, streams have developed a dendritic drainage patterns.

The type and distribution of vegetation in and surrounding the well field are dependent upon the soil characteristics. Most of the dunes are stabilized by vegetation. According to the USDA (1950) this region of Oklahoma is dominated by grasses, with numerous species of forbs and a few woody shrubs and trees. On the river bottom a wide variety of plants grow, including elm, cottonwood, locust, willow, and sumac in addition to various grasses. Salt grass is found in areas of the river bottom where soils are high in salinity (USDA, 1950).

Land usage in the well field is principally for grazing of livestock. Cattle are an important industry in this region, with almost all farms having some livestock.

The climate of the well field and region is described by the USDA (1950) as "continental, temperate and subhumid." The average annual precipitation is approximately 26 inches (Pettyjohn et al., 1983), with January being the driest month and May the wettest (Oklahoma Climatological Survey, 1984). The higher temperatures are in the summer months of July and August and average 83 degrees Fahrenheit. The lower temperatures are in January and average 31 degrees Fahrenheit (Pettyjohn et al., 1983).

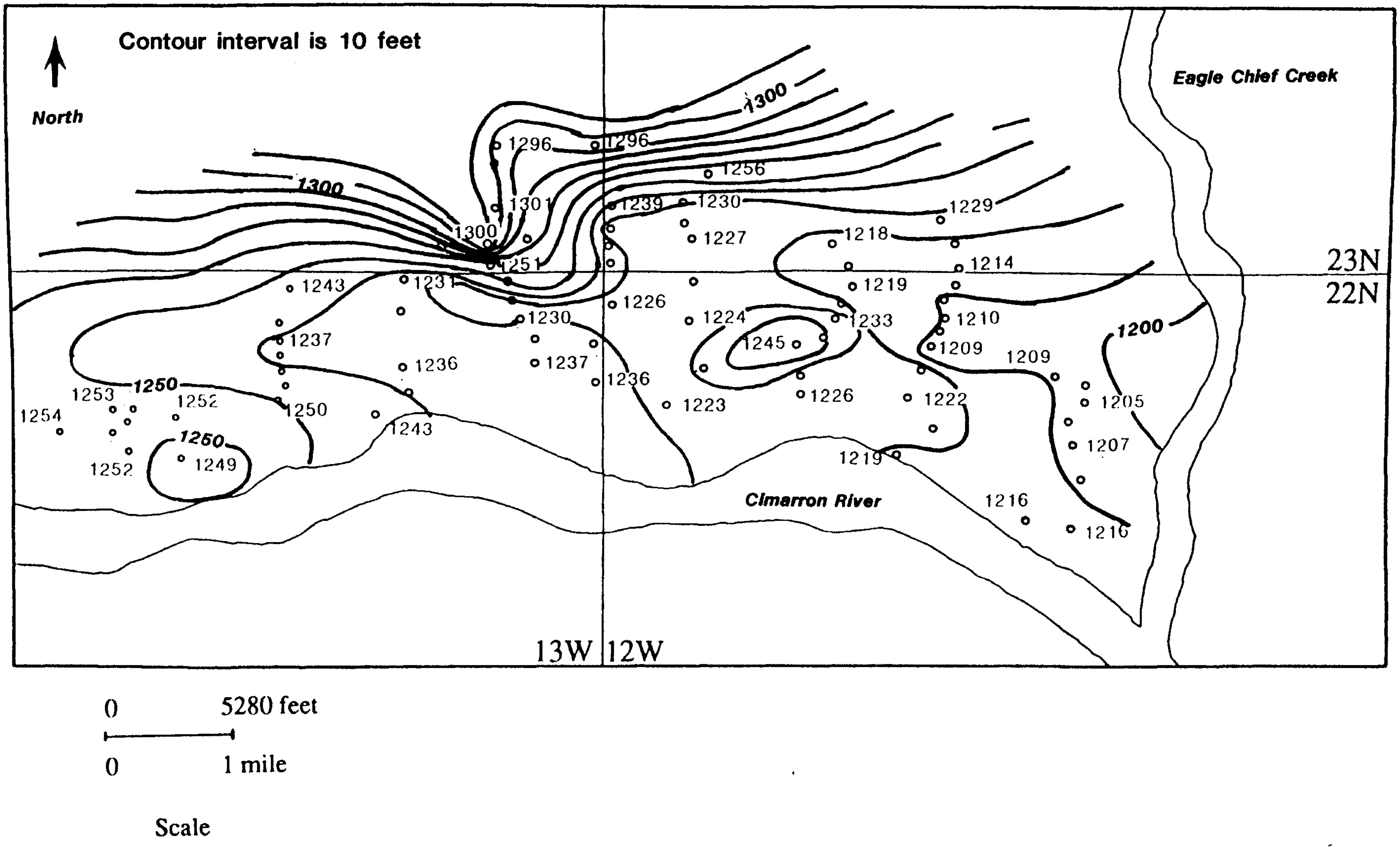


Figure 8. Bedrock elevation map of the Cleo Springs well field area [Data source: EEI, 1982].

Hydrogeology

Cleo Springs Well Field

The alluvial deposits in the well field transmit groundwater under predominately unconfined conditions, with a south and southeasterly slope towards the Cimarron and Eagle Chief Creek as shown by the elevation of the potentiometric surface on figure 9.

The morphology of the alluvial aquifer in the well field is typically heterogeneous and anisotropic. Lenses of silts and clays underlie permeable sands creating locally perched water tables. The zones with the highest yield potential are the coarser sands and gravels that are generally near the base of the fluvial sequence.

Measurements of transmissivity and storativity were made by EEI (1982) from four short-duration aquifer tests in the well field. Variation in lithology and hydraulic properties is shown in the range of values calculated from the tests; transmissivity ranged from 4,500 to 32,700 gallons per day per foot, storage coefficient ranged from 4.9×10^{-5} to 0.1621.

Precipitation is the primary source of recharge to the alluvial aquifer in the well field. Water that is not lost by surface runoff or evapotranspiration infiltrates to recharge the aquifer.

Cimarron River and Eagle Chief Creek

The Cimarron River and Eagle Chief Creek at the well field are both gaining streams as shown by stream-gauge measurements taken during periods of base flow (fig. 10). Stream-gauge measurements of Eagle Chief Creek, adjacent to the well field, show an increase of discharge in Eagle Chief Creek from 2.1 million gallons per day (MGPD) to 11.2 MGPD over a distance of approximately 12 miles.

Stream-gauge measurements of the Cimarron taken during August 1982 during low-flow conditions also show an increase of flow from west to east of 10.2 to 13.5 MGPD indicating a gain in base flow from groundwater discharge at the well field.

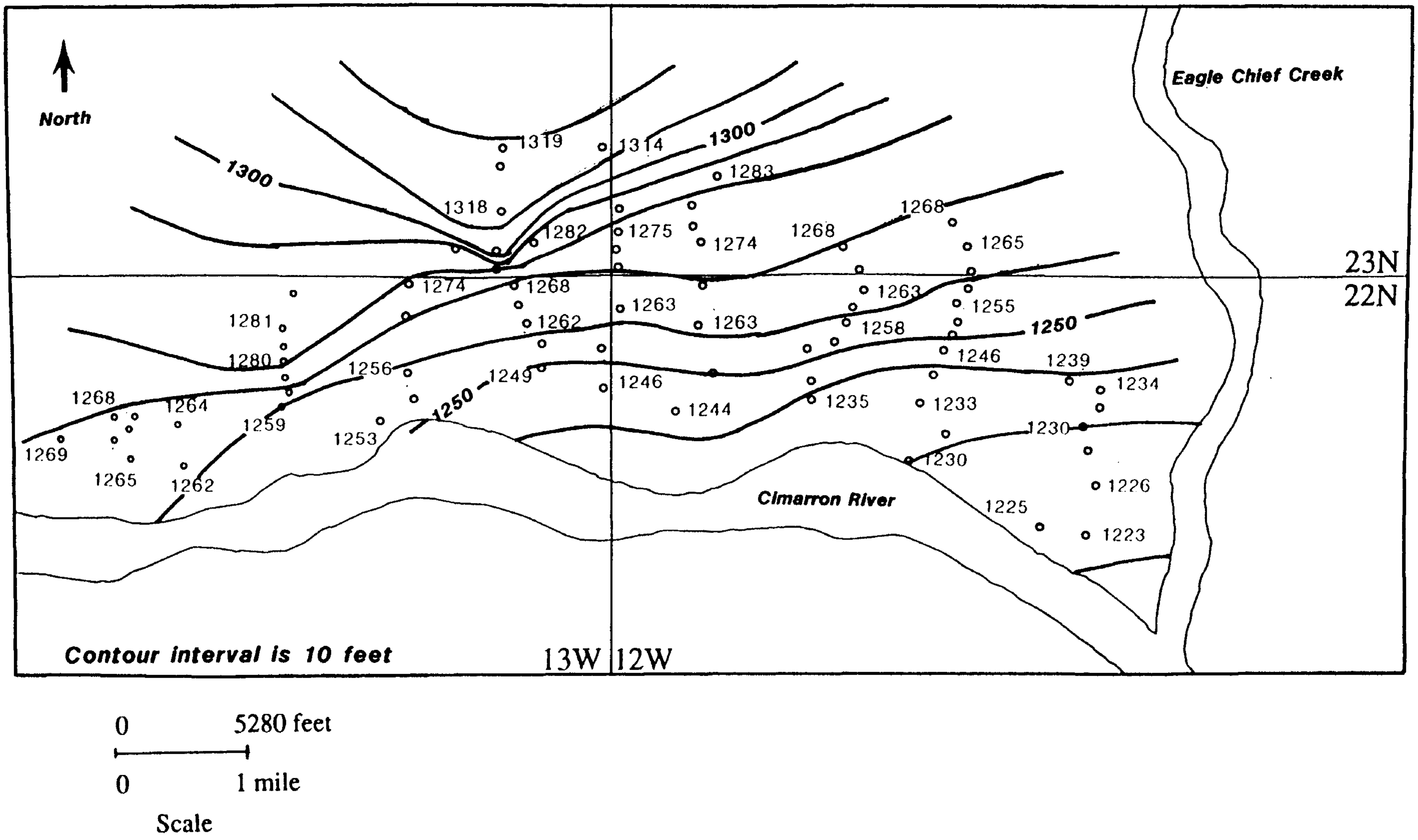


Figure 9. Potentiometric map showing direction of groundwater movement in the alluvial aquifer in the Cleo Springs well field [Data source: EEI, 1982].

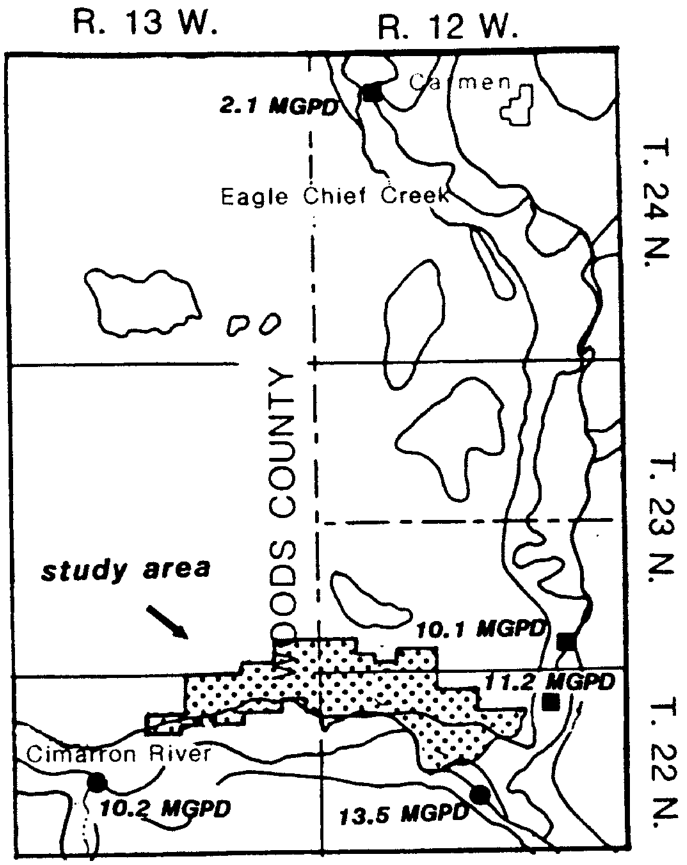


Figure 10. Stream-gauge measurements of the Cimarron River and Eagle Chief Creek showing gaining-stream conditions during periods of base flow [Source: Cimarron River, EEI 1982; Eagle Chief Creek, Reed and others, 1952; MGPD, million gallons per day].

CHAPTER II

POTENTIAL SOURCES OF SALINIZATION

Degradation of water quality by an increase in dissolved solids occurs by natural processes and from activities associated with man. In the Cleo Springs well field there are three potential sources of salinization; deep formation brines from oil and gas production, formation water from the Flowerpot and associated evaporite units, and the Cimarron River. Other common sources of increased salinization in groundwater include: (1) sea-water intrusion, (2) road salting, (3) saline seep, and (4) agricultural effluents. The likelihood of these sources causing increased TDS in the well field is nonexistent. Sea-water intrusion is not a source due to geographical location of the well field. Road salt is not used in the well field. A saline seep is 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." Saline seeps such as these are not a source of salinization in the well field because: (1) the water table averages 15 to 20 feet below ground surface (Enid Water Production Department, 1991, personal commun.) and (2) the alluvium is primarily composed of unconsolidated dune sand and as a result is well drained. Contamination from agricultural effluents would be improbable since irrigation is nonexistent and the use of fertilizers and pesticides is rare.

Flowerpot Shale and Associated Evaporites

Drill cuttings described by EEI (1982) indicate gypsum/anhydrite is a major constituent of the Flowerpot underlying the well field. A vertical hydraulic interconnection would allow mixing of formation water and fresher groundwater of the alluvial aquifer, with the direction of groundwater movement dependent upon the difference in potential head of the two systems. Engineering Enterprises Inc. (1982) measured groundwater levels in nested wells at two locations to determine direction of groundwater movement (fig. 11). At both locations one well was completed in the alluvial aquifer and another was completed in the Flowerpot. At site 2, measurements indicated decreasing potential with depth; thus the groundwater tends to flow downward at this site.

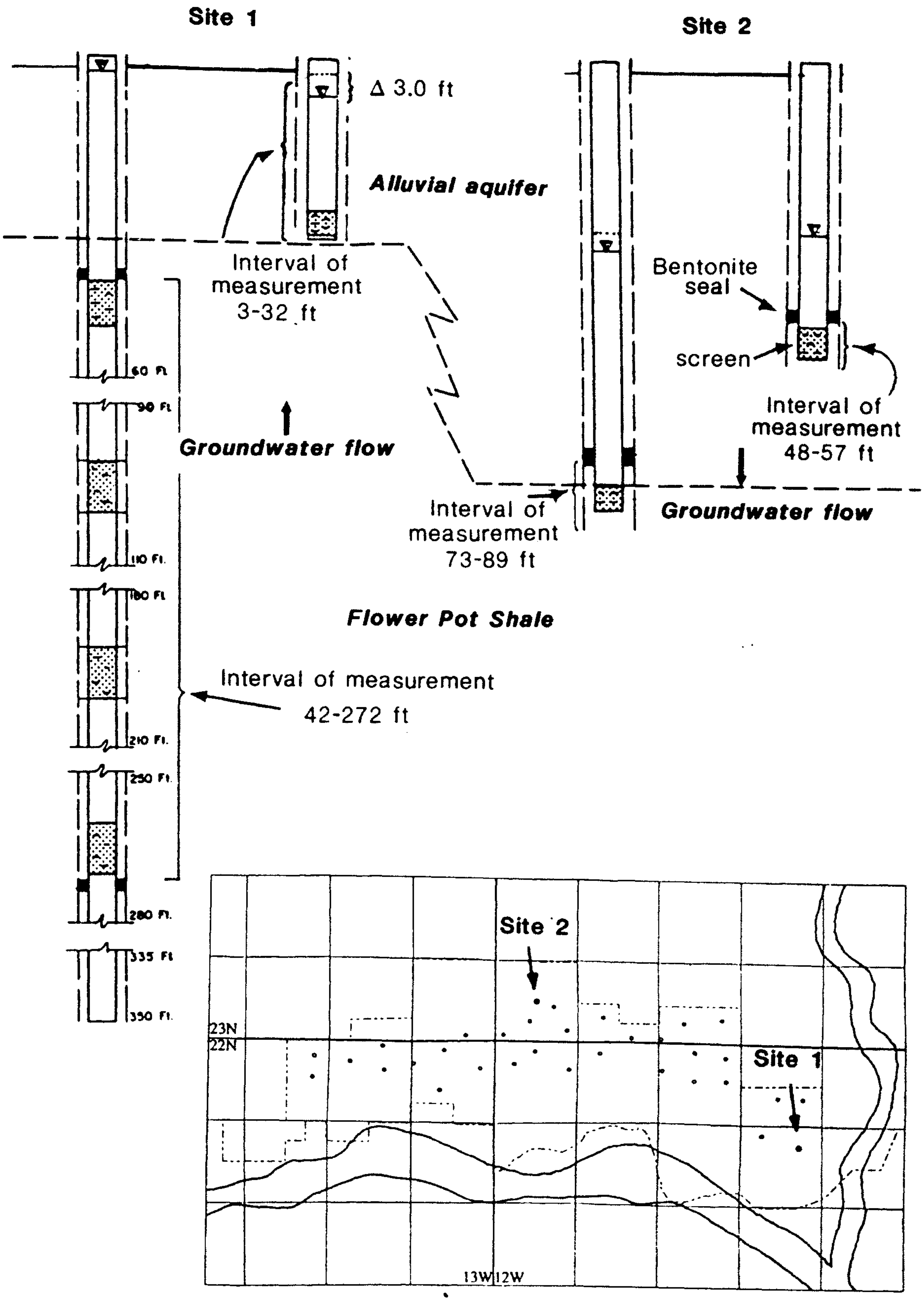


Figure 11. Diagram showing vertical distribution of fluid potential between the alluvial aquifer and the Flowerpot Shale at two nested-well sites in the Cleo Springs well field [Reproduced and modified from EEI, 1982].

However at site 1, the groundwater level measured in the deeper well (350 feet) was 3 feet higher than the adjacent well screened in the alluvium; indicating increasing potential with depth. Consequently, formation water can flow upward at this location if fractures or dissolution features are present.

Oil and Gas Production

Oil and gas production has been an important industry in this part of Oklahoma for over 40 years. Contamination of alluvial aquifers from brine associated with oil and gas production is a major concern because of the many older wells located in areas where cities and towns depend upon groundwater for drinking. An example is the City of Cresent; elevated concentrations of chloride in the CMTA were studied by the Oklahoma Water Resources Board (1975). The source of contamination was determined to be deep formation brines from oil and gas production in the Cresent Oil Field.

Several common mechanisms can allow mixing of oil and gas brine with fresh groundwater in the alluvial aquifer. These mechanisms include: defective oil-well casing, improper completion practices, improper plugging, brine-injection wells, and improper brine and drilling mud disposal practices. There are 54 oil and gas wells in the well field (fig. 12). Fifty-two wells are producing or have produced from formations representing four geologic periods: Silurian, Devonian, Mississippian, and Pennsylvanian. The majority of the oil and gas production is from Mississippian-aged limestones and Pennsylvanian-aged sandstones. Exploration and drilling began in the area in the late 1950's with the majority of the wells drilled in the late 1970's.

Cimarron River

The Cimarron is a composite of the many waters that discharge into it. However, brine created from the dissolution of halite has the greatest influence on the river's water quality. In a study by SYN-AC (1979) the total load was measured at various locations on the Cimarron. Measurements taken in December 1976 during low-flow conditions showed that the Big and the Little Salt Plains contributed approximately 3,740 tons per day of sodium and chloride (SYN-AC, 1979, figs. 38 and 39). This measurement is questionably high, but it gives an indication of the large amount of dissolved solids contributed by this source.

The Cimarron could be a potential source during periods at high stage or if the well field

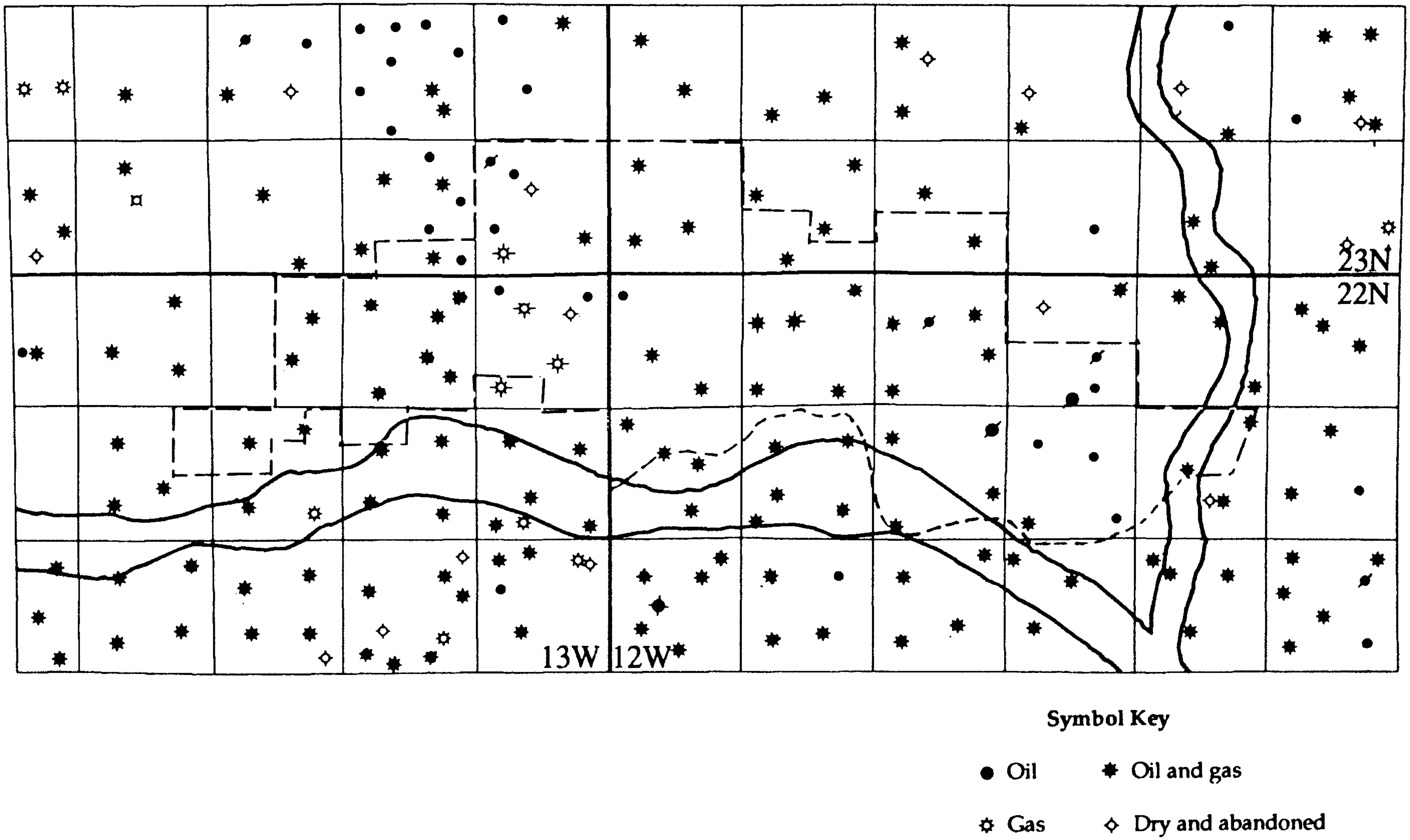


Figure 12. Oil and gas production in the Cleo Springs well field and vicinity.

was improperly managed by excessively pumping the wells. Both circumstances could reverse the direction of groundwater flow between the river and the alluvial aquifer.

CHAPTER III

DATA SOURCES

Ground- and surface-water analyses used in this study were gathered from outside sources and from an August 1991 sampling program. An analysis was considered acceptable if the major ions, calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), chloride (Cl^{-}), and sulfate (SO_4^{2-}) were measured and if the anion-cation balance was 7% or less. Occasionally, a major ion is not measured in a water sample and, if it does not constitute a major percentage of the solution, the analysis will still balance. Several oil and gas analyses used in this study lacked selected major-ion analyses.

When more than two analyses were available for a potential source, the median concentration for each ion was used to create an endmember analysis. For this report, the term "endmember" is used to refer to a water type, representing a source, that is a component of a mixture.

Cleo Springs Well Field

Groundwater samples from the 31 water wells in the well field were collected during August 1991. The water wells sampled are designated CLEO 1-31 and their respective locations are shown on figure 13. The groundwater analyses for the well field are given in table 1. Sampling methods and materials used are described in Appendix A.

Flowerpot Shale

Unfortunately, groundwater samples or analyses from the Flowerpot at the well field and vicinity were not available. As a result, the endmembers were derived from two sample locations west of the well field. Three analyses constituting one endmember are from wells sampled in August 1991 at the Cargill Solar Salt Company, located approximately 50 miles northwest of the well field. These analyses represent water from the Salt Member of the Flowerpot and are designated FP-HB. The major ions and the trace elements bromide (Br), iodide (I), and strontium (Sr)

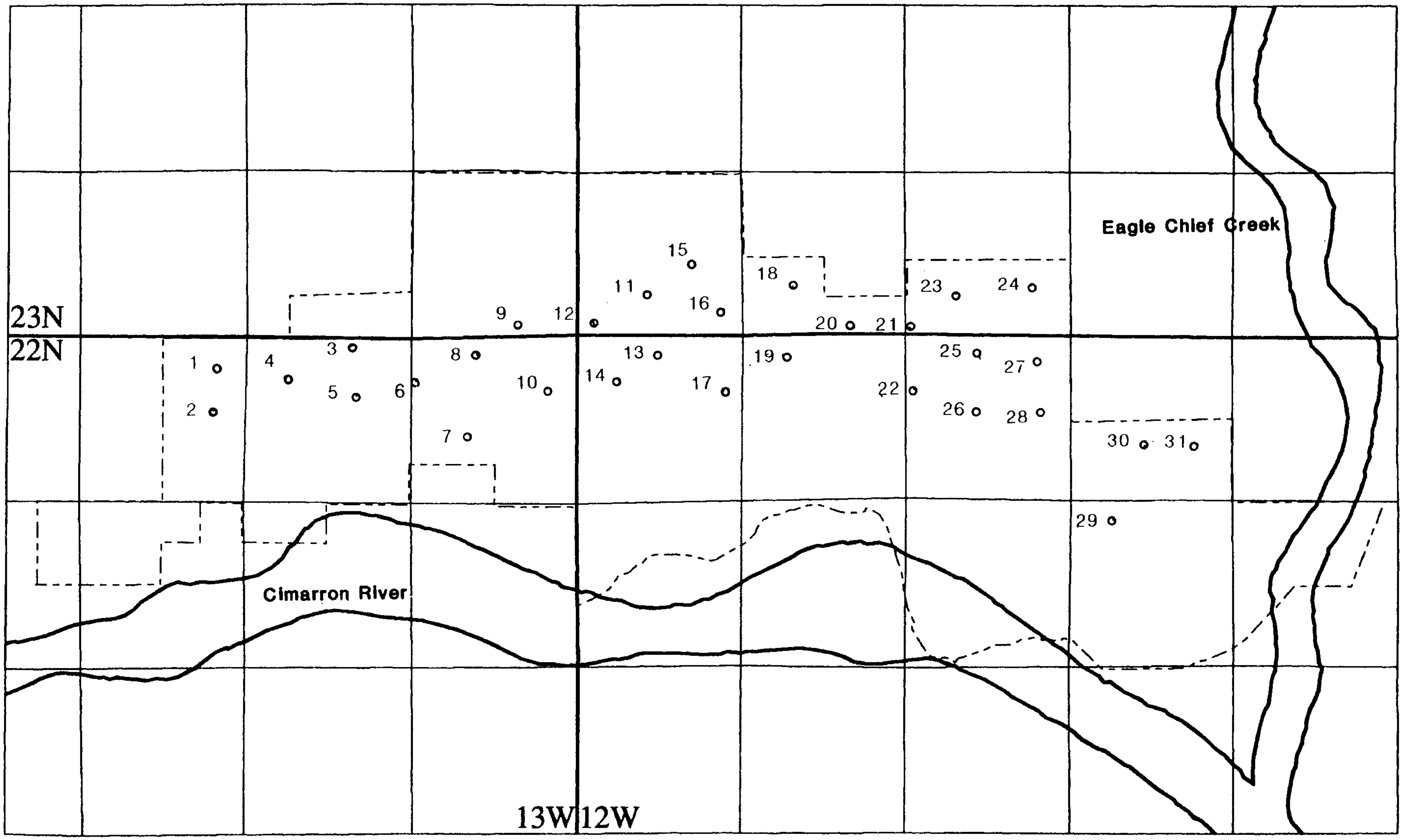


Figure 13. Locations of water wells sampled in the Cleo Springs well field during 1992 sampling program.

Table 1. Groundwater analyses from the Cleo Springs well field - 1991 sampling program.

[Source: Ca, Mg, Na, K, Cl, SO_4, and NO_3 were analyzed by the Oklahoma State University Agronomy Department. The trace elements Br, I, and Sr were analyzed by the U.S. Geological Survey's water-quality laboratory in Denver Colorado. All concentrations are dissolved. Specific conductance, dissolved oxygen, pH, temperature, and HCO_3 are field measurements. Hardness and TDS are calculated. --, no data].

Well#	Ca (meq/L)	Mg (meq/L)	Na (meq/L)	K (meq/L)	Cl (meq/L)	Cl (mg/L)	SO_4 (meq/L)	SO_4 (mg/L)	HCO_3 (meq/L)	NO_3 - N (mg/L)	TDS
1	7.5	2.5	3.8	0.05	2.6	91.1	3.6	171.1	6.2	4.0	910.0
2	5.1	1.5	1.5	0.04	1.1	38.0	1.5	70.1	5.3	0.0	590.0
3	4.9	1.6	1.4	0.04	1.1	38.0	1.2	58.0	4.8	2.0	544.0
4	4.9	1.6	1.4	0.04	1.1	38.0	1.1	54.0	4.8	2.0	538.0
5	5.0	2.3	2.6	0.04	2.2	77.0	2.0	97.1	5.3	5.0	688.0
6	4.3	1.5	1.7	0.03	1.7	61.0	1.3	61.0	4.6	10.0	547.0
7	5.3	1.9	1.3	0.05	1.1	40.0	1.8	86.1	5.2	5.0	605.0
8	5.4	2.0	2.2	0.02	2.7	95.0	1.6	78.0	5.0	7.0	664.0
9	9.5	2.8	1.9	0.04	10.6	374.0	1.0	46.0	3.3	3.0	890.0
10	4.7	1.5	2.3	0.03	2.7	94.0	1.0	47.0	4.6	6.0	591.0
11	3.1	1.0	1.1	0.03	0.5	18.0	1.1	53.0	2.9	4.0	350.0
12	2.9	0.8	0.8	0.03	0.3	12.0	0.9	41.0	3.1	4.0	328.0
13	3.1	1.1	1.1	0.03	1.3	45.0	0.8	37.0	3.1	3.0	372.0
14	3.7	1.2	1.9	0.04	2.1	76.0	0.8	38.0	3.6	4.0	465.0
15	3.0	1.1	1.1	0.02	0.7	25.0	0.7	33.0	3.4	4.0	368.0
16	2.8	0.9	0.8	0.03	0.4	14.0	0.6	28.0	3.1	4.0	319.0

Table 1. Groundwater analyses from the Cleo Springs well field - 1991 sampling program. (Continued)
[Source: Ca, Mg, Na, K, Cl, SO_4, and NO_3 were analyzed by the Oklahoma State University Agronomy Department. The trace elements Br, I, and Sr were analyzed by the U.S. Geological Survey's water-quality laboratory in Denver Colorado. All concentrations are dissolved. Specific conductance, dissolved oxygen, pH, temperature, and HCO_3 are field measurements. Hardness and TDS are calculated. --, no data].

Well#	Ca (meq/L)	Mg (meq/L)	Na (meq/L)	K (meq/L)	Cl (meq/L)	Cl (mg/L)	SO_4 (meq/L)	SO_4 (mg/L)	HCO_3 (meq/L)	NO_3 - N (mg/L)	TDS
17	3.4	1.1	0.8	0.03	0.7	25.0	0.5	25.0	4.1	2.0	400.0
18	5.0	1.7	1.9	0.02	1.8	64.0	1.7	80.0	4.9	7.0	609.0
19	3.1	1.0	0.6	0.02	0.4	16.0	0.5	24.0	3.5	3.0	341.0
20	4.6	1.5	1.6	0.07	1.3	45.0	1.4	69.0	4.7	5.0	553.0
21	4.3	1.6	2.2	0.03	1.6	57.0	1.4	69.0	4.9	6.0	581.0
22	3.0	1.4	1.9	0.03	1.6	58.0	1.1	51.0	4.5	3.0	508.0
23	5.3	2.8	5.8	0.13	3.6	128.0	3.4	164.1	7.0	5.0	999.0
24	2.7	4.0	14.6	0.02	4.2	147.2	5.9	284.4	11.6	2.0	1,582.0
25	5.8	2.5	3.4	0.09	3.2	112.1	2.9	140.1	5.9	2.0	839.0
26	5.4	1.6	1.6	0.05	1.4	51.0	2.0	100.0	4.8	0.0	613.0
27	6.7	4.7	8.5	0.04	9.4	332.0	6.4	307.4	7.1	--	1,462.0
28	10.2	3.6	5.0	0.07	6.0	212.2	5.4	260.2	6.9	0.0	1,260.0
29	6.7	2.3	3.2	0.07	2.7	96.0	3.5	170.1	5.6	0.0	846.0
30	4.8	2.1	3.5	0.04	3.4	121.0	2.8	133.1	5.2	3.0	775.0
31	3.0	1.5	2.1	0.03	1.2	43.0	1.3	64.0	4.6	4.0	519.0

Table 1. Groundwater analyses from the Cleo Springs well field - 1991 sampling program (Continued).

[Source: Ca, Mg, Na, K, Cl, SO_4, and NO_3 were analyzed by the Oklahoma State University Agronomy Department. The trace elements Br, I, and Sr were analyzed by the U.S. Geological Survey's water-quality laboratory in Denver Colorado. All concentrations are dissolved. Specific conductance, dissolved oxygen, pH, temperature, and HCO_3 are field measurements. Hardness and TDS are calculated; --, no data].

Well#	Br (mg/L)	I (mg/L)	Sr (mg/L)	Specific conductance (umhos)	Dissolved oxygen (mg/L)	pH	Temperature (°C)	Hardness as mg/L of $CaCO_3$
1	0.260	0.004	0.320	935	2.0	7.3	16.5	495.6
2	0.080	0.004	0.440	569	0.30	7.4	16.5	331.4
3	0.060	0.002	0.360	559	3.60	7.4	17.5	329.7
4	0.060	0.001	0.340	547	3.60	7.1	17.0	327.2
5	0.140	0.002	0.510	755	3.70	7.3	17.0	365.2
6	0.030	0.002	0.220	664	6.10	7.2	16.5	290.5
7	0.060	0.003	0.430	660	4.65	7.2	17.0	360.5
8	0.110	0.002	0.480	765	4.90	7.2	17.0	368.7
9	1.400	0.002	0.720	1395	3.80	7.3	16.5	617.6
10	0.190	0.002	0.330	693	5.80	7.3	16.5	309.0
11	0.041	0.002	0.290	394	5.90	7.4	17.0	204.3
12	0.041	0.002	0.190	356	6.65	7.4	17.0	189.1
13	0.041	0.002	0.240	404	7.00	7.5	17.0	208.4
14	0.100	0.002	0.260	545	6.70	7.4	17.0	245.0
15	0.041	0.001	0.220	386	6.70	7.3	17.0	205.9
16	0.041	0.002	0.170	345	5.80	7.7	16.5	187.7

Table 1. Groundwater analyses from the Cleo Springs well field - 1991 sampling program (Continued).

[Source: Ca, Mg, Na, K, Cl, SO_4, and NO_3 were analyzed by the Oklahoma State University Agronomy Department. The trace elements Br, I, and Sr were analyzed by the U.S. Geological Survey's water-quality laboratory in Denver Colorado. All concentrations are dissolved. Specific conductance, dissolved oxygen, pH, temperature, and HCO_3 are field measurements. Hardness and TDS are calculated; --, no data].

Well#	Br (mg/L)	I (mg/L)	Sr (mg/L)	Specific conductance (umhos)	Dissolved oxygen (mg/L)	pH	Temperature (°C)	Hardness as mg/L of $CaCO_3$
17	0.030	0.002	0.250	394	3.40	7.4	17.0	225.9
18	0.110	0.003	0.420	678	5.00	7.2	16.5	338.9
19	0.030	0.001	0.220	355	4.70	7.5	17.0	206.8
20	0.070	0.003	0.380	599	1.70	7.4	17.0	308.0
21	0.070	0.003	0.390	645	2.80	7.4	17.0	296.3
22	0.080	0.003	0.360	580	2.45	7.3	17.0	222.4
23	0.130	0.010	0.800	1,050	1.10	7.1	17.0	405.0
24	0.270	0.110	0.850	1,550	0.70	7.3	16.5	335.2
25	0.110	0.008	0.740	920	1.65	7.3	17.0	416.0
26	0.060	0.004	0.470	610	1.20	7.6	18.5	352.3
27	0.640	0.030	1.100	1,668	2.20	7.1	16.5	573.6
28	0.190	0.028	1.000	1,354	0.40	7.4	17.0	694.2
29	0.110	0.015	0.790	1,020	0.50	7.3	17.0	450.0
30	0.110	0.005	0.600	878	2.40	7.3	17.0	347.5
31	0.060	0.004	0.310	577	3.80	7.4	17.0	226.5

were measured in these samples. An additional endmember (FP-LM), from the USPCI Lone Mountain waste facility located approximately 16 miles west of the well field, was supplied by the Oklahoma Department of Environmental Quality. This data set consists of nine analyses taken over 3 years from three wells located upgradient from the waste facility. The water samples were taken from intervals screened in the Flowerpot at 150 feet or more below land surface. These water samples were analyzed for major ions only.

Shown on figure 14 are the sample locations for the Flowerpot. The endmembers are given on table 2.The analyses from which the endmembers were generated are given in Appendix B.

Oil and Gas Production

The oil and gas endmembers were generated from eighty-five analyses from Alfalfa, Major, and Woods Counties in Oklahoma (Appendix B). The analyses were collected in the late 1970's and early 1980's by Geological Information Systems in Norman, Oklahoma from various oil companies. The analyses were separated into groups, determined by age of formation from which the brine sample was taken, and the median ion concentrations were used to create three oil and gas endmembers; OG-P, Pennsylvanian; OG-M, Mississippian; and OG-OD, Ordovician-Devonian. The trace elements Br, I, and Sr were measured in 14 of the 85 analyses. The median ion concentrations from this group were used to make a fourth oil and gas endmember called OG-T, that is used for ionic ratios using trace elements. The endmembers are given on table 3.

Cimarron River

The water type of the Cimarron River is represented by two analyses, each an endmember. One analysis was retrieved from NWIS (CMRN-1) and the other is from the 1991 sampling program (CMRN-2). Figure 15 shows the sample locations. The endmembers are shown on table 4.

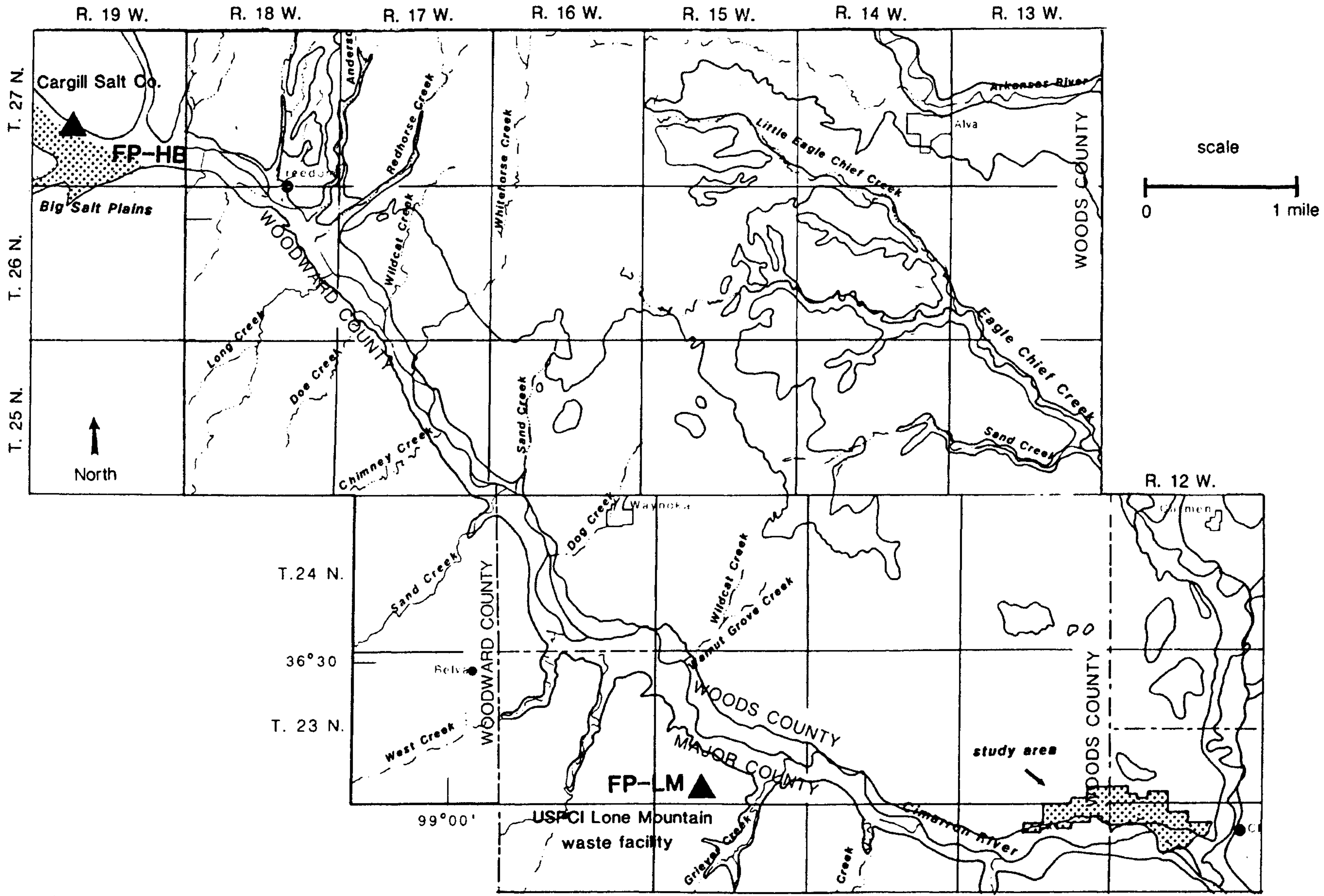


Figure 14. Sample locations for the Flowerpot Shale.

Table 2. Flowerpot Shale endmember analyses.

[Source: FP-HB, all major ions except HCO_3 were analyzed by the Oklahoma State University Agronomy Department; HCO_3 is a field measurement; Br, I, and Sr were analyzed by the U.S. Geological Survey's water-quality laboratory, Denver Colorado; TDS is calculated; all concentrations are dissolved; field parameters for FP-HB are shown in Appendix B. Source: FP-LM, Oklahoma State Department of Health. --, no data].

End-member	Ca^{2+} (meq/L)	Mg^{2+} (meq/L)	Na^+ (meq/L)	K^+ (meq/L)	Cl^- (meq/L)	Cl^- (mg/L)	SO_4^{2-} (meq/L)	SO_4^{2-} (mg/L)	HCO_3^- (meq/L)	Br^- (mg/L)	I^- (mg/L)	Sr (mg/L)
FP-HB	101.2	82.2	6,618.8	4.1	6,415.1	227,405	182.6	8,769	0.7	20.00	0.27	36.00
FP-LM	90.5	27.6	1,387.7	1.6	1,483.9	52,600	106.4	5,110	0.4	--	--	--

Table 3. Oil and gas endmember analyses.

[Source: Geological Information Systems, Norman Oklahoma; --, no data; HCO_3 concentrations were not available; analyses are shown in Appendix B].

End-member	Ca^{2+} (meq/L)	Mg^{2+} (meq/L)	Na^+ (meq/L)	Cl^- (meq/L)	Cl^- (mg/L)	SO_4^{2-} (meq/L)	SO_4^{2-} (mg/L)	Br^- (mg/L)	I^- (mg/L)	Sr (mg/L)
OG-P	610.4	157.2	2,958.0	3,359.3	119,080	5.3	255	--	--	--
OG-M	239.5	51.9	1,133.6	2,220.6	78,718	16.3	783	--	--	--
OG-OD	421.2	132.4	2,541.0	3,074.9	109,000	16.1	775	--	--	--
OG-T	464.4	110.9	2,270.0	3,001.2	106,387	11.7	561.0	533.00	157.00	445.00

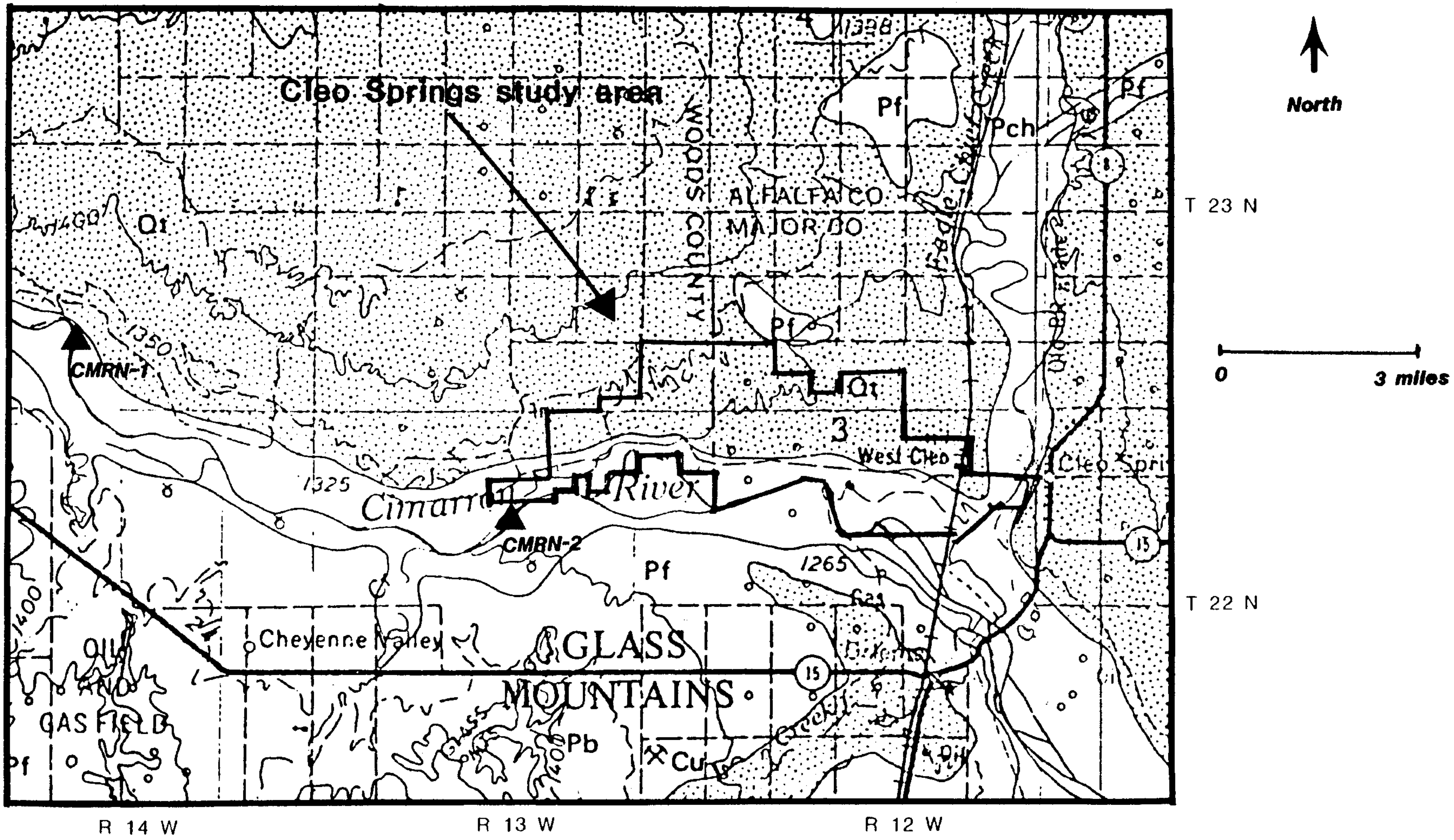


Figure 15. Sample locations for the Cimarron River.

Table 4. Cimarron River endmember analyses.

[Source: CMRN-1, U.S. Geological Survey, National Water Information Systems; CMRN-2, sampled in August, 1991. The major ions for CMRN-2, except HCO_3, were analyzed by the Oklahoma State University Agronomy Department. HCO_3 is a field measurement. Br, I, and Sr were analyzed by the U.S. Geological Survey's water-quality laboratory, Denver Colorado. TDS is calculated. All concentrations are dissolved. --, no data. Field parameters for CMRN-2 are shown in Appendix B].

End-member	Ca^{2+} (meq/L)	Mg^{2+} (meq/L)	Na^{+} (meq/L)	K^{+} (meq/L)	Cl^{-} (meq/L)	Cl^{-} (mg/L)	SO_4^{2-} (meq/L)	SO_4^{2-} (mg/L)	HCO_3^{-} (meq/L)	Br^{-} (mg/L)	I^{-} (mg/L)	Sr (mg/L)	TDS
CMRN-1	14.5	8.2	234.9	0.25	256.7	9,100	19.6	940	3.5	2.20	--	--	16,600
CMRN-2	12.6	5.6	158.8	0.24	157.1	5,568	17.0	815	3.3	0.99	0.03	3.20	10,562

CHAPTER IV

CLEO SPRINGS WELL FIELD: RESULTS

Increased salinization is indicated in the eastern and western parts of the well field by elevated concentrations of SO_4 and TDS. The central part of the well field produces water with the lowest TDS. In general, the groundwater is predominately fresh and calcium-bicarbonate type. The chemical characteristics are similar to water from a carbonate aquifer, as it is saturated with several carbonate minerals.

Extent of Salinization

The EPA (1992) and the OSDH (1992) have set standards regulating the SMCL for the constituents TDS, SO_4, and Cl and the MCL for nitrogen as NO_3 in drinking water. Shown on table 5 are the SMCL and MCL set for these constituents, and the number of samples from the well field that exceed them.

Table 5. Number of samples from the Cleo Springs well field exceeding the maximum concentration level (MCL) for nitrate (NO_3) as nitrogen and secondary maximum concentration levels (SMCL) for total dissolved solids (TDS), chloride (Cl), and sulfate SO_4 in drinking water. [Milligrams per liter (mg/L)].

Constituent	MCL (mg/L)	SMCL (mg/L)	Number of samples exceeding
TDS	--	500	23
Cl	--	250	2
SO_4	--	250	3
NO_3	10	--	1

Total dissolved solids range from 319 mg/L to 1,582 mg/L with a median value of 590 mg/L. Three samples were classified as brackish with TDS over 1,000 mg/L. Twenty-three of the 31 wells sampled exceeded the SMCL of 500 mg/L for TDS in drinking water. Shown in figure 16 is a

TDS concentration map of the well field. Contours show that the freshest water is located in the center of the well field in section 31 T. 23 N., R. 12 W. and sections 5 and 6, T. 22 N., R. 12 W. Total dissolved solids are highest in the northeast region of the well field.

Chloride concentrations range from 11 mg/L to 374 mg/L. Two samples exceeded the SMCL of 250 mg/L for Cl in drinking water; one is an anomalous concentration of 374 mg/L (CLEO-9) in section 36 T. 23 N., R. 13 W., as shown on the Cl concentration map in figure 17. Chloride concentrations are similar to TDS, as the lowest concentrations are in the central region of the well field and are highest in the northeast.

Sulfate concentrations range from 24 mg/L to 307 mg/L with three exceeding the SMCL of 250 mg/L set for SO_4 in drinking water. Figure 18 is a SO_4 concentration map of the well field. Similar to TDS and Cl, SO_4 concentrations are lowest in the center region of the field and are higher in the northeast.

Samples were analyzed for nitrogen in 30 of the 31 wells. Nitrogen is generally associated with waste products from septic tanks and animal feed lots, and agricultural activities where nitrogen-based fertilizer is used. Nitrogen also occurs naturally in soils from the decomposition of organic material, in some instances at concentrations high enough to cause significant groundwater contamination (Kreitler and Jones, 1975). In water used for drinking, nitrogen as NO_3 poses the greatest risk to bottle-fed infants, causing methemoglobinemia (blue baby syndrome) (National Academy of Science, 1977). As a result the EPA (1992) and the OSDH (1992) have set the MCL for nitrogen as NO_3 in drinking water at 10 mg/L. Figure 19 shows that concentrations of nitrogen as NO_3 range from 0 to 10 mg/L in the well field, with the only one sample (CLEO-6) exceeding the MCL. Cattle are in the well-field area and are probably the primary source of nitrogen in the groundwater. With only one household in the well-field area the likelihood of contamination from septic tank waste water is minimal. Agriculture is almost nonexistent, therefore applied fertilizers containing nitrogen are not a likely source of contamination.

The hardness of water is defined as the concentration of Ca and Mg expressed in mg/L equivalent $CaCO_3$. Water is considered soft if the concentration is less than 60 mg/L. Water with a concentration greater than 150 mg/L is considered very hard (Freeze and Cherry, 1979). The Cleo Springs waters are considered very hard, with concentrations ranging from 188 to 694 mg/L and a median hardness value of 323 mg/L.

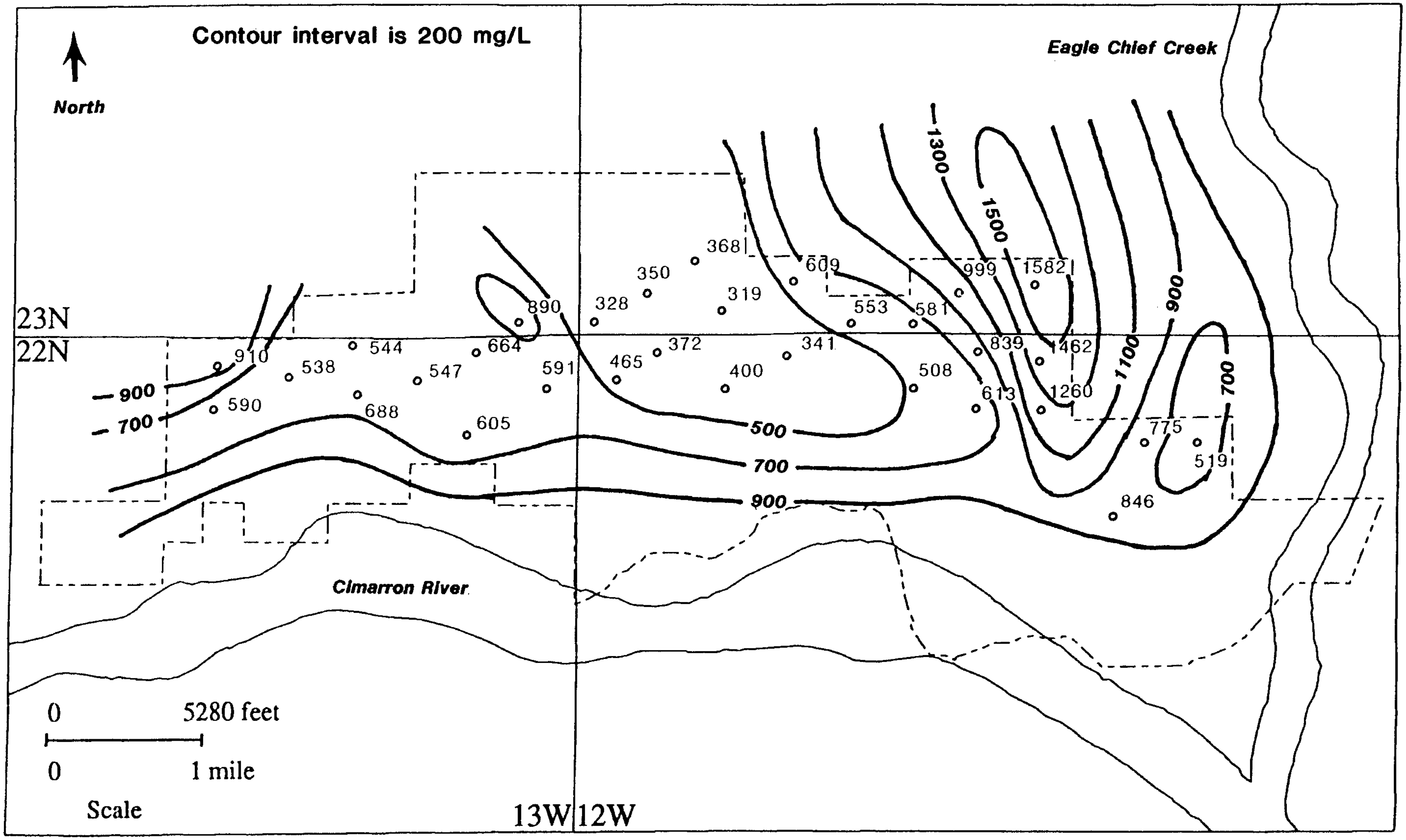


Figure 16. Total dissolved solids concentration map of the Cleo Springs well field from groundwater samples collected in August 1991.

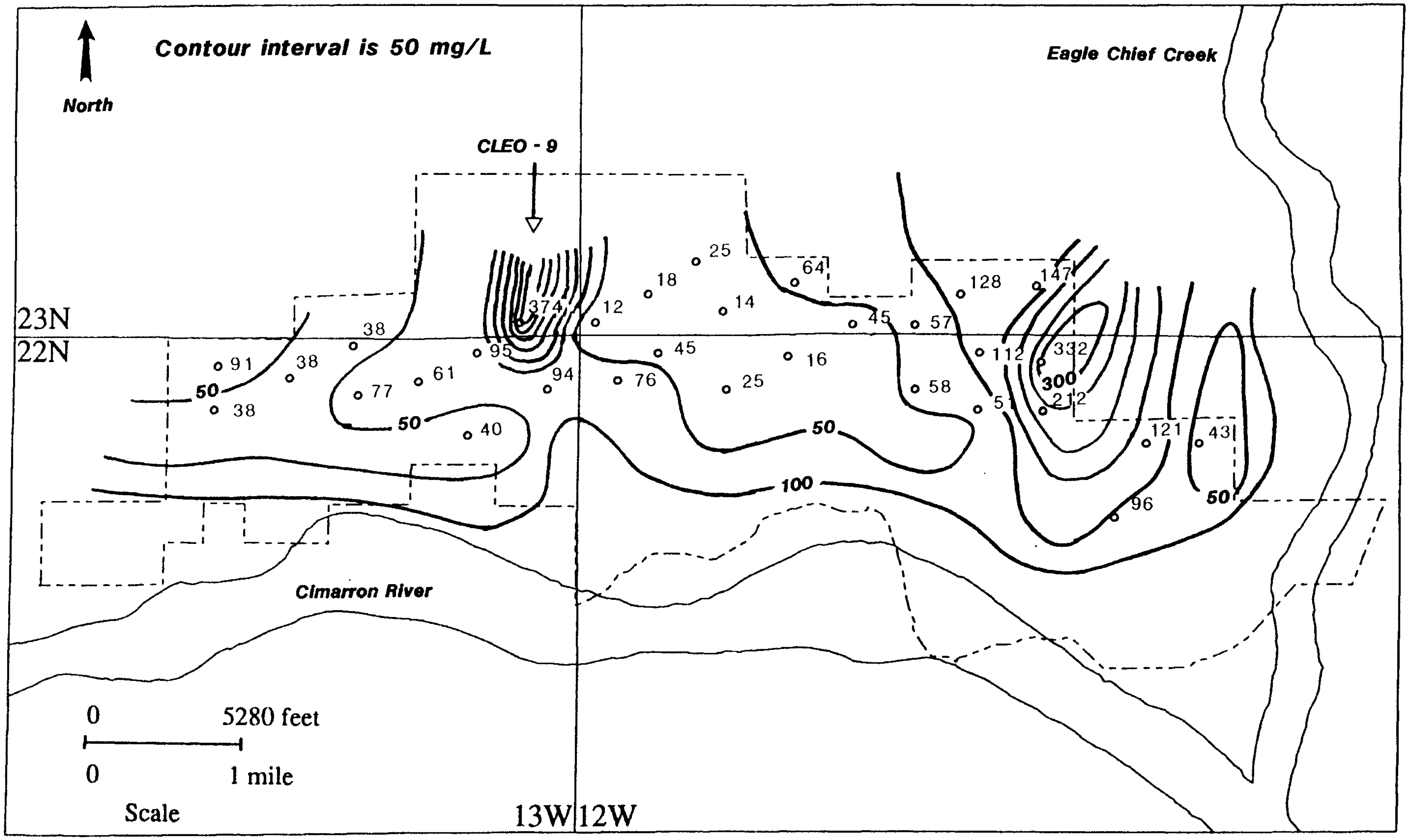


Figure 17. Chloride-concentration map of the Cleo Springs well field from groundwater samples collected in August 1991.

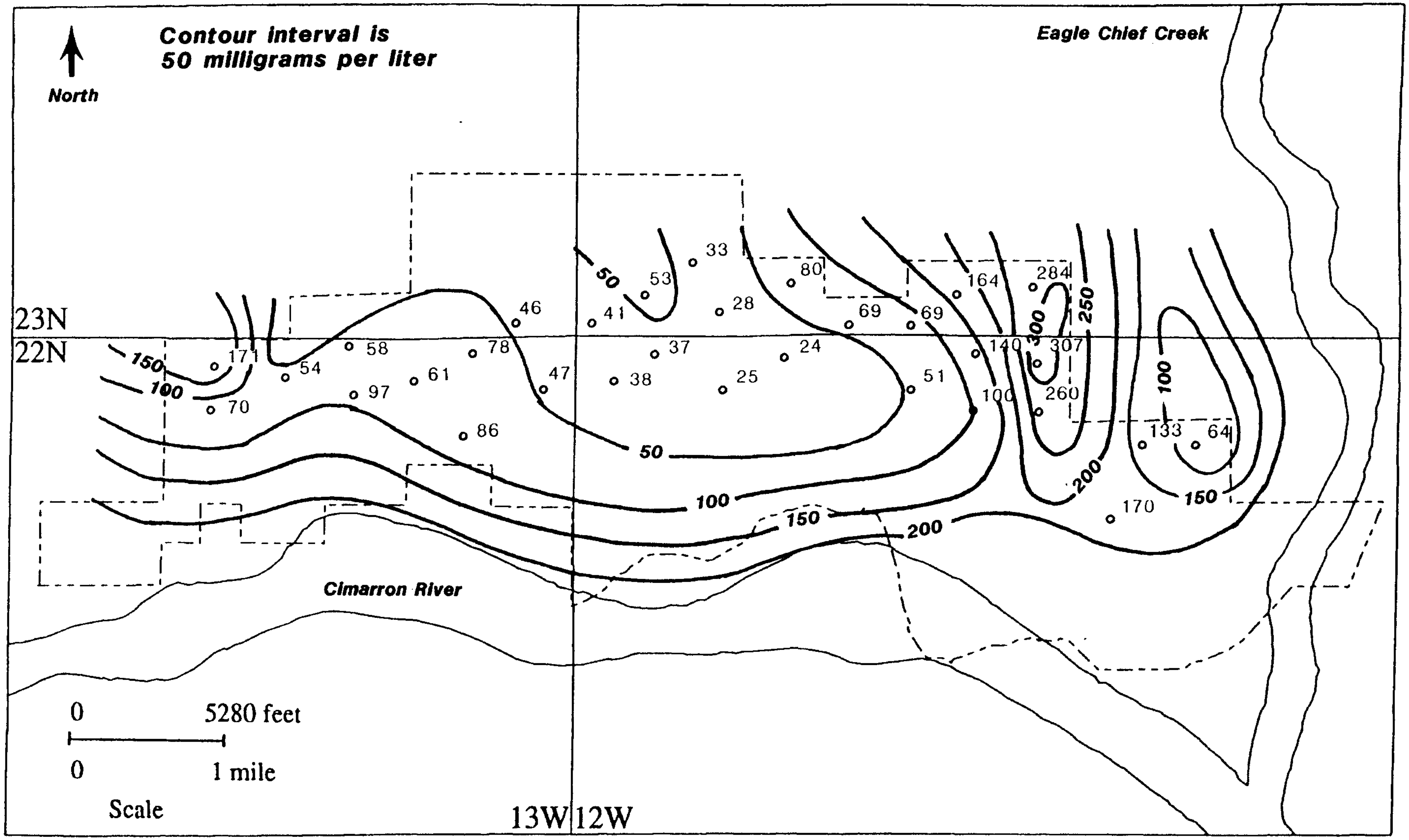


Figure 18. Sulfate-concentration map of the Cleo Springs well field from groundwater samples collected in August 1991.

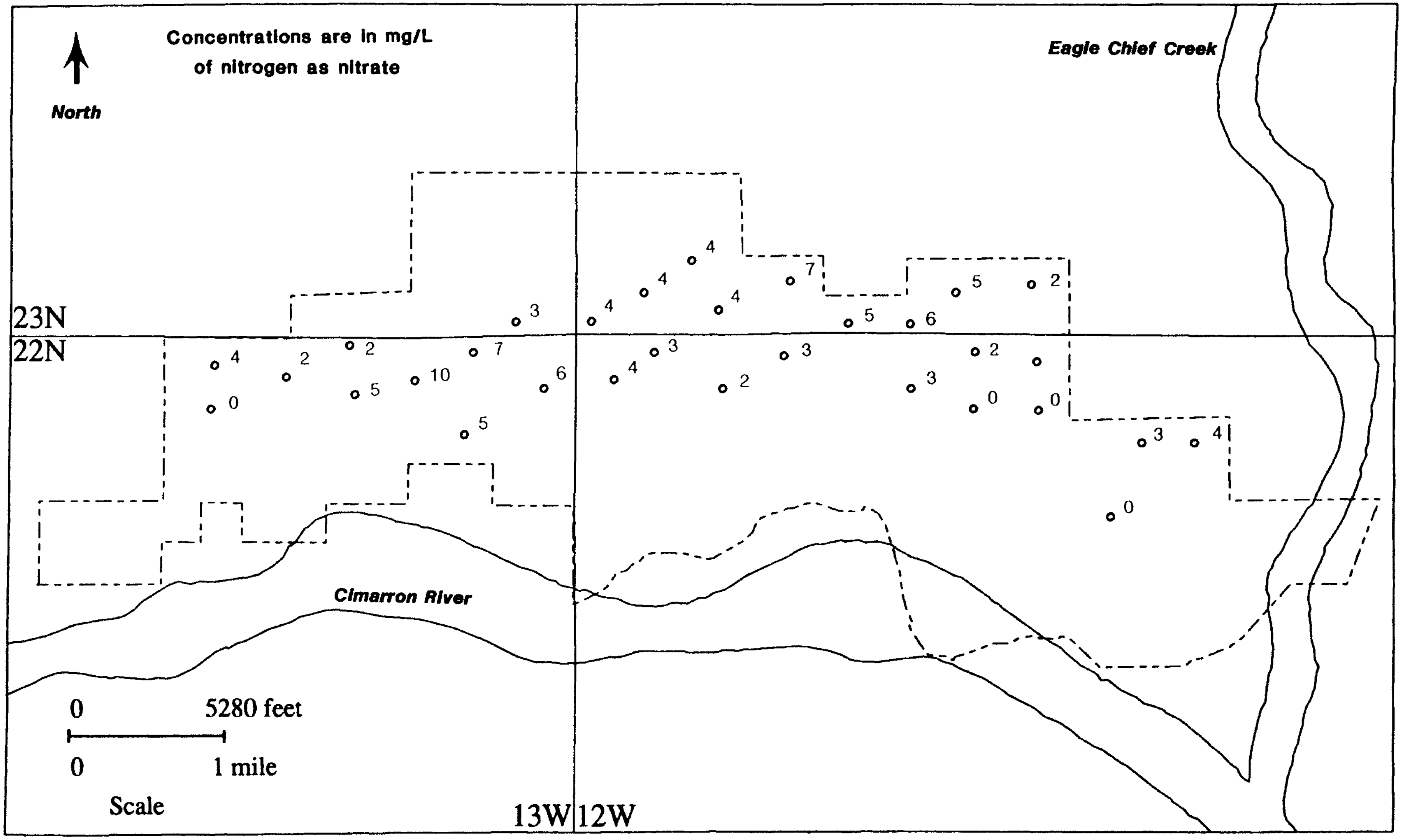


Figure 19. Nitrogen as nitrate concentration map of the Cleo Springs well field from groundwater samples collected in August 1991.

Water Chemistry

Three common graphing techniques were used to help determine water type, explain water chemistry or reveal mixing relationships that could be helpful in determining the source or sources responsible for salinization to the well field. The Stiff diagram is used for visual comparison of water types. The molar concentration of the major ions in a sample are plotted on four parallel horizontal axes and connected with a line creating a polygon distinctive for each water type. The Piper diagram is another convenient graphing technique; samples are plotted by the percentage of each major ion on triangular diagrams. Cations are plotted separately from anions. One application of the Piper diagram is its use in helping identify a sample that is a result of two water types mixing (two component mixing). If a line is drawn connecting two samples on a plot, each representing a distinct water type, a sample that is a mixture of the two will plot on the line, with the percentage of contribution proportional to the distance separating them. If the sample is a mixture of the two endmembers without the addition or removal of any ion, then the mixture will exhibit exactly the same proportions between the endmembers on both cation and anion triangles (Hounslow, 1989). For example, figure 20 shows two endmembers, calcium-sulfate type and sodium-chloride type and four potential mixtures (A, B, C, and D) plotted.

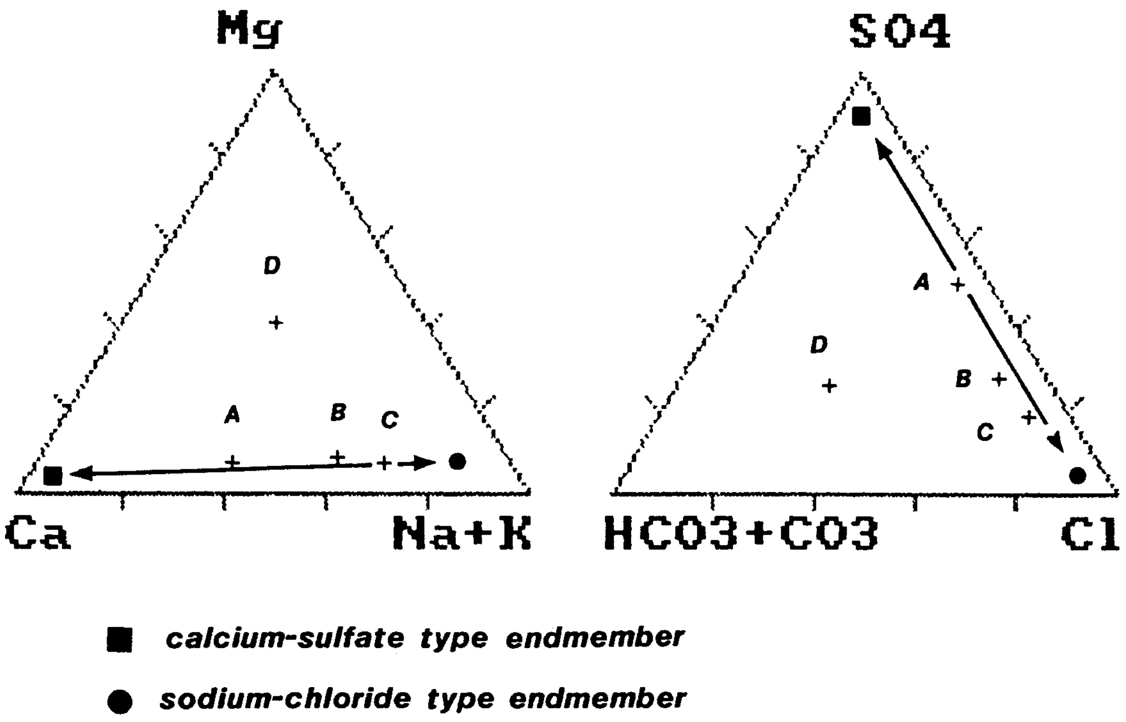


Figure 20. Example Piper diagram showing mixing relationship between two endmembers.

Samples A, B, and C plot on the line drawn between the two water types implying that these samples are mixtures of the two endmembers whereas, the position of D indicates it is not. The position of sample A on the line indicates that the calcium-sulfate endmember contributes more than 50 percent to the mixture, whereas the sodium-chloride endmember comprises the majority of samples B and C.

X-Y plots of ion concentrations and their ratios were also used; they are discussed in greater detail in a later section.

The general water types of the endmembers and well-field samples were determined by the dominant ions. For an anion or cation to be considered dominant it must have equaled or exceeded 50 percent of the total cations and anions per analysis. For the purpose of this report, the concentrations of the major ions are expressed in milliequivalents per liter (meq/L) on graphs. Concentrations of the trace elements, and major ions when used in combination with them on X-Y plots, are expressed in milligrams per liter (mg/L). To enable the reader to easily convert concentration units from mg/L to meq/L, or meq/L to mg/L, conversion factors are shown below.

Ion	To convert mg/L to meq/L multiply by:	To convert meq/L to mg/L multiply by:
Calcium (Ca)	.04990	20.04
Magnesium (Mg)	.08229	12.15
Sodium (Na)	.04350	22.99
Chloride (Cl)	.02821	35.45
Sulfate (SO_4)	.02082	48.03
Bicarbonate (HCO_3)	.01639	61.01

Water samples from the well field show that the waters are predominately fresh, calcium-bicarbonate type with the cation Ca > Na > Mg >> K and the anion HCO_3 > Cl and SO_4. In general, chemical characteristics of the groundwater are similar to water from a carbonate aquifer as the waters are saturated or close to saturation with respect to several carbonate minerals.The WATEQF computer program was used to calculate the saturation indices, a measure of the thermodynamic stability of a mineral relative to a solution. The calculated saturation indices show that of the 31 samples, 24 were saturated with respect to calcite, 5 were saturated with respect to aragonite, and 10 were saturated with respect to dolomite. This does not indicate that calcite, aragonite, and dolomite will precipitate, but that the minerals will not go into solution. All the samples were undersaturated in respect to halite and gypsum. Saturation indices are given in Appendix C.

It appears that a significant source of carbonate to the system and the main factor controlling its chemical equilibrium is the reaction of carbon dioxide (CO_2) with water. Precipitation percolating downward through the soil and alluvial sediments, reacts with CO_2 and forms carbonic acid (H_2CO_3). Carbon dioxide is in the atmosphere, but the major sources are in the soil, where CO_2 is generated by plant respiration and the decay of dead plant material (Hem, 1989). This reaction is shown as the equation below:

$$CO_2 + H_2O \text{ ----> } H_2CO_3.$$

Carbonic acid, as it buffers alkaline water, will disassociate producing HCO_3 and H in the reaction:

$$H_2CO_3 \text{----> } HCO_3^- + H^+,$$

H can then be consumed in the dissolution of calcite/aragonite (or dolomite) in the aquifer with the release of Ca (Mg) and HCO_3:

$$CaCO_3 + H^+ \text{ ----> } Ca^{2+} + HCO_3^-.$$

Calcite can also react with water producing Ca, HCO_3 and OH:

$$CaCO_3 + H_2O \text{ ----> } Ca^{2+} + HCO_3^- + OH^-.$$

The last two reactions are important processes in the alluvial aquifer and help explain the presence of Ca, Mg, and HCO_3 in the groundwater but do not account for the additional Na, Cl, and SO_4 ions. The presence of Na, Cl, and SO_4 indicate that all of the CLEO samples have been affected by salinization from an outside source.

The Major Source of Salinization

The Piper diagram suggests the underlying Flowerpot Shale is the major source of salinization to the Cleo Springs well field. The diagram indicates the formation water has higher proportions of SO_4 and Ca then the Flowerpot analyses used in the investigation. Geologic evidence shows the presence of gypsum is responsible for the change in water type.

As previously shown the Piper diagram is a useful tool in analyzing two component mixing relationships. Figure 21 is a Piper diagram showing the CLEO samples and the relative position of the two parent water types. The freshwater (FW) endmember, left of and nearest to CLEO-16, represents the uncontaminated formation water of the alluvial aquifer. The ionic proportions of the endmember responsible for the general increase in TDS can be approximated from the diagram by locating a point on the opposite end of the trend from FW on both triangles. It is hypothesized that these points represent the composition of the formation water from the underlying Flowerpot Shale in the well field. This new Flowerpot endmember is referred to as H-FP.

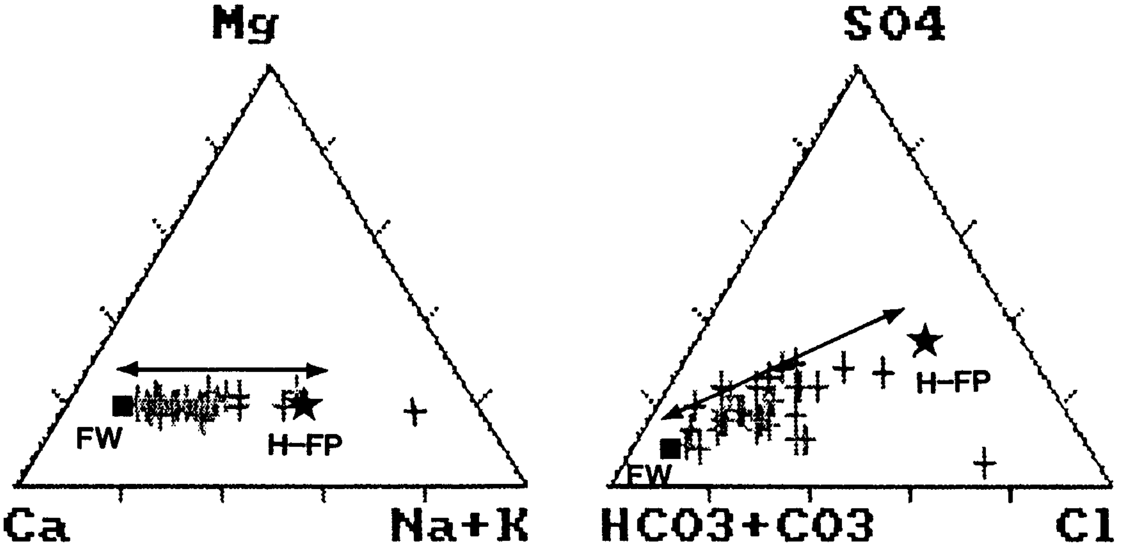


Figure 21. Approximate locations of the [FW] freshwater and [H-FP] hypothetical Flowerpot endmembers on the Piper diagram.

Measurements of specific conductance, reported by EEI (1982) and by the U.S. Geological Survey of groundwater samples from the Flowerpot, indicate the TDS of H-FP would be approximately 4500 mg/L. The composition of H-FP determined from its location on the Piper diagram at the given TDS, is shown on page 43

Ion	meq/L	mg/L
Ca	24.3	277
Mg	13.9	168
Na+K	31.3	952
HCO_3	13.9	842
SO_4	24.3	1160
Cl	31.3	1100

As shown on figure 22 the two Flowerpot analyses (FP-HB and FP-LM) are sodium-chloride type brines with Na and Cl constituting more than 95 percent of the ions in solution. In contrast, at the well field Ca and SO_4 are significant components of the formation water in addition to Na and Cl. The dissimilarity between the Flowerpot analyses used in this study (LM-FP and HB-FP) and H-FP determined from the Piper diagram, is a result of lithologic differences between the locations at which the samples were taken. Halite in the Salt Member of the Flowerpot, dominates the evaporite sequence at the locations where the LM-FP and HB-FP samples were taken. In contrast to the well field, where gypsum/anhydrite is dominant and halite is minor. This change in evaporite facies from halite to gypsum/anhydrite is suggested by the stratigraphic work of Jordan and Vosberg (1965) and is reported by EEI (1981).

The Piper diagrams in figure 22 also show that the Cimarron and oil and gas endmembers are not major sources of salinization to the well field. Both endmembers are sodium-chloride type waters and contain insufficient quantities of Ca, Mg, and SO_4 (with respect to Na and Cl) to be a component of the CLEO samples.

Several CLEO samples plot off the mixing line of H-FP and FW on the Piper diagram in figure 21. There are two general explanations for this circumstance; three component mixing and laboratory error during analysis. If a sample is a mixture of three components, not two, the sample will plot within a triangle created by the three endmembers. In freshwater, a small analytical error can have a significant affect on the major ion concentrations, causing the sample to plot off its true mixing line. Because an analytical error rarely affects more than one or two ions, X-Y plots of the major ions and certain trace elements can be helpful in determining if a third component is present

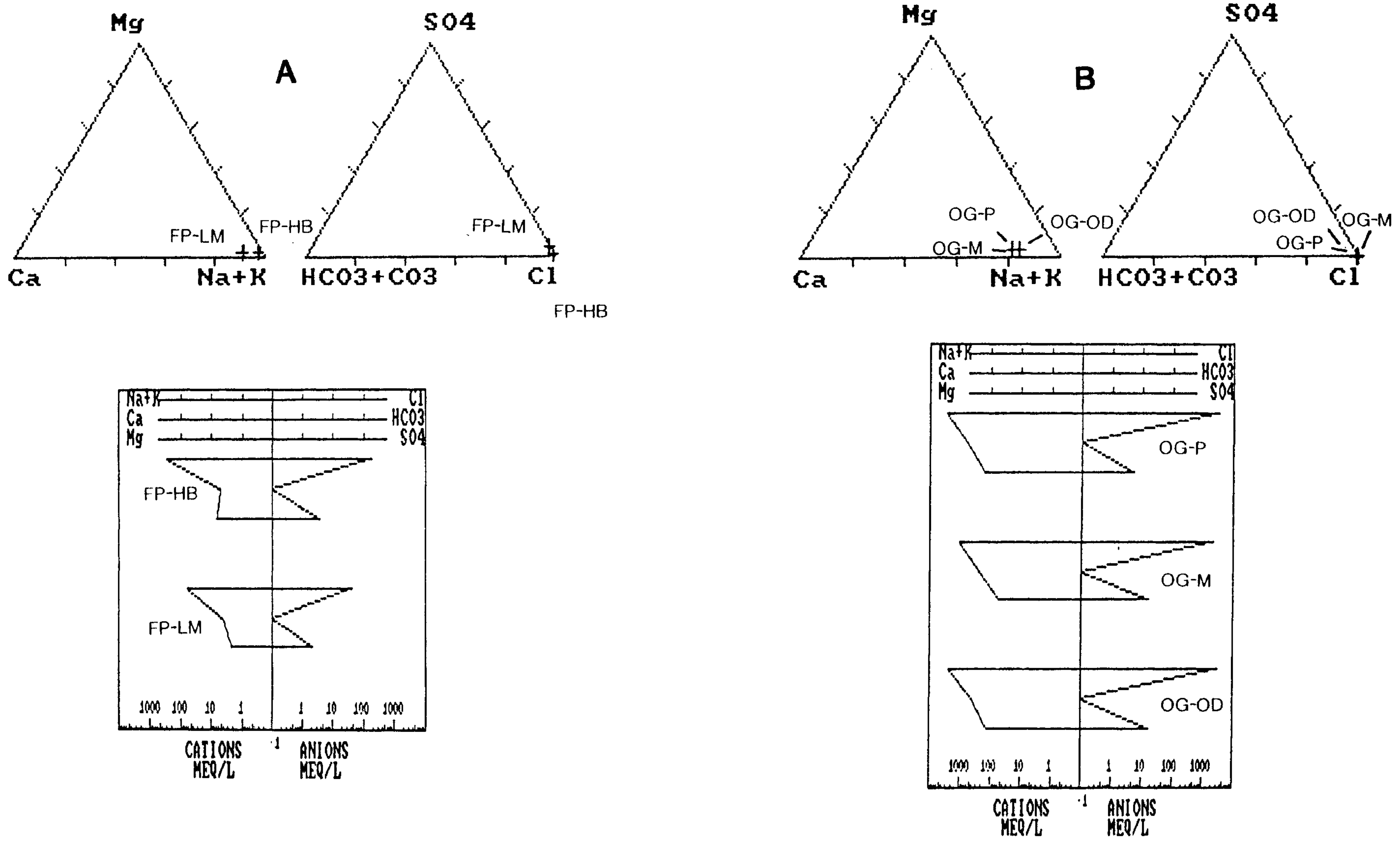


Figure 22. Piper and Stiff diagrams illustrating water types of the [A] Flowerpot Shale, [B] oil and gas, and [C] Cimarron River endmembers.

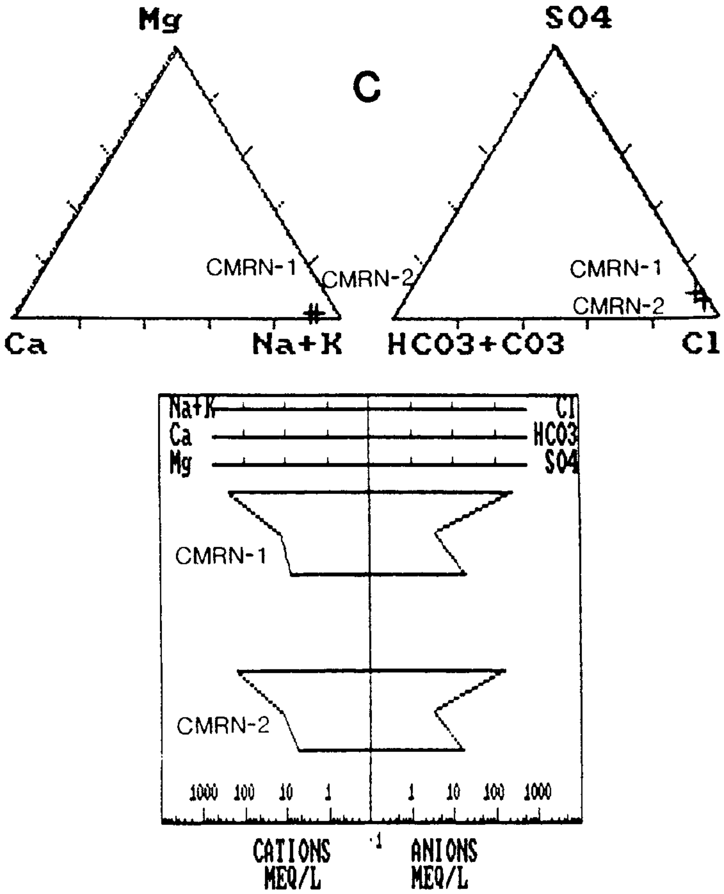


Figure 22. Piper and Stiff diagrams illustrating water types of the [**A**] Flowerpot Shale, [**B**] oil and gas, and [**C**] Cimarron River endmembers (-Continued).

and its source. The following chapter takes a closer look at the CLEO samples and the major and possible minor salinization sources by use of X-Y plots.

CHAPTER V

IONIC RELATIONSHIPS ON X-Y PLOTS

A series of X-Y plots illustrate and support the hypothesis that the major source of salinization to the well field is formation water from the underlying Flowerpot Shale. The plots help explain water chemistry and also indicate the possibility of a third component in several CLEO samples — oil and gas brine.

Graphic methods using ionic ratios have been studied and used extensively for delineating the source of Cl and other ions in groundwater (Novak and others, 1988; Richter and others, 1987). The premise for using ionic ratios in hydrogeochemical studies is that when mixing occurs between a brine and fresh water, all constituents are diluted equally and at the same rate, thus preserving their ionic proportions to each other. Certain geochemical mechanisms such as ion exchange, mineral dissolution and/or precipitation, can modify the proportions of most ions in groundwater after mixing. Ion- exchange reactions occur when cations in water are exchanged with cations on or within the crystal lattices of clays or other minerals the water passes over. As discussed by Freeze and Cherry (1979), the divalent cations normally have stronger adsorption affinity than the monovalent cations. The normal order of preference for some of the most common is:

$$Sr^{2+} > Ca^{2+} > Mg^{2+} > K^{+} > Na^{+}$$

A common ion- exchange process in fresh-water environments, referred to as "natural softening", replaces the Na ion within the clays with Ca. An indication of this process are samples showing an enrichment in Na with respect to Cl, resulting in a Na/Cl molar ratio that is greater than 1.0. Twenty-three of the Cleo Springs samples show some degree of ion exchange having occurred, with Na/Cl ratios greater than 1.0. In general, natural softening does not appear to have been an important geochemical process affecting the Cleo Springs samples. Calcium probably occupies all of the available exchange sites within the clays as a result of the saturated conditions with respect to calcite/aragonite and dolomite.

The direction of this reaction can be reversed in waters having high ionic strength where concentrations of Na far exceed those of Ca.

(2Na+ clay) + (Ca) <—> (Ca + clay) + (2Na)

reverse softening <—> natural softening

The reverse softening process occurs in deep-basin brines and results in an enrichment in Ca and a decrease in the Na ion. As a result deep-basin brines, and fresh water that has been contaminated by them, reflect characteristic Na/Cl ratios of less than 1.0 and may exhibit elevated Ca/Cl and Ca/SO_4 ratios.

Another important process that can modify ion proportions and mask mixing relationships, is the dissolution or precipitation of minerals after mixing. The saturation indices for the minerals calcite/aragonite and dolomite relative to the study-area samples, indicate their presence. Depending upon the state of equilibrium, their precipitation or dissolution can occur. This dynamic process has increased the proportion of Ca and Mg with respect to Cl, SO_4, Na, Br, I, and Sr in the well-field samples. As a result, ionic ratios using Ca and Mg do not reflect true mixing relationships but indicate geochemical processes that occurred after mixing, while ratios using the conservative ions Cl, SO_4, Br, and I more accurately portray mixing relationships.

The following X-Y plots use the major cations; Ca, Mg, and Na and the trace elements Br, I, and Sr plotted against, and in combination with, the major anions Cl and SO_4. Only those graphic relationships deemed useful are used in this report. Two factors hampering the use of X-Y plots in this investigation are; the low concentrations of Cl and TDS in the CLEO samples, and the lack of site specific water-quality data for the Flowerpot. Mixing relationships are best defined at high concentrations when ionic ratios are more discernible. As stated by Whittemore (1984) "ratios of major ions in waters containing less than several hundred mg/L Cl are often not sufficiently differentiable to identify salinity sources." The X-Y plots are very effective in showing a relation between the CLEO, Cimarron River, and the Flowerpot samples because of their common ion origin — dissolution of evaporites. This relationship is seen on all the plots as a linear trend between the three groups.

Sodium/Chloride Ratio

One of the most common ionic ratios used to distinguish brine sources has been Na/Cl. Dissolution of pure halite results in a Na/Cl molar ratio of 1.0, whereas, oil and gas brines generally have a Na/Cl molar ratio of less than 1.0. In Oklahoma, Leonard and Ward (1962) used it to distinguish oil and gas brine from salt spring brines emanating from the Flowerpot. They found the Na/Cl ratio of the salt springs to be greater than 0.92 and the average ratio for oil and gas brines to be 0.77. The OWRB (1975) in their brine source study near Cresent in western Oklahoma, found a Na/Cl ratio of 0.95 for salt-water springs and 0.57 for oil and gas brines in the area.

Figure 23 shows the Na/Cl ratio of the endmembers and CLEO samples at their respective Cl concentration. Ratios of the CLEO samples range from 3.53 to 0.18. Ratios of the Flowerpot endmembers FP-HB and FP-LM are 1.03 and 0.94 respectively, indicating that these brines were generated from the dissolution of halite. Ratios of the oil and gas endmembers OG-P, OG-M and OG-OD, are 0.88, 0.51, and 0.83, respectively, which are considerably greater than values reported in other studies of oil and gas brines from Oklahoma. The Cimarron endmembers CMRN-1 and CMRN-2 have ratios close to 1.0, indicating the halite deposits in northwestern Oklahoma are the primary influence on the River's water chemistry.

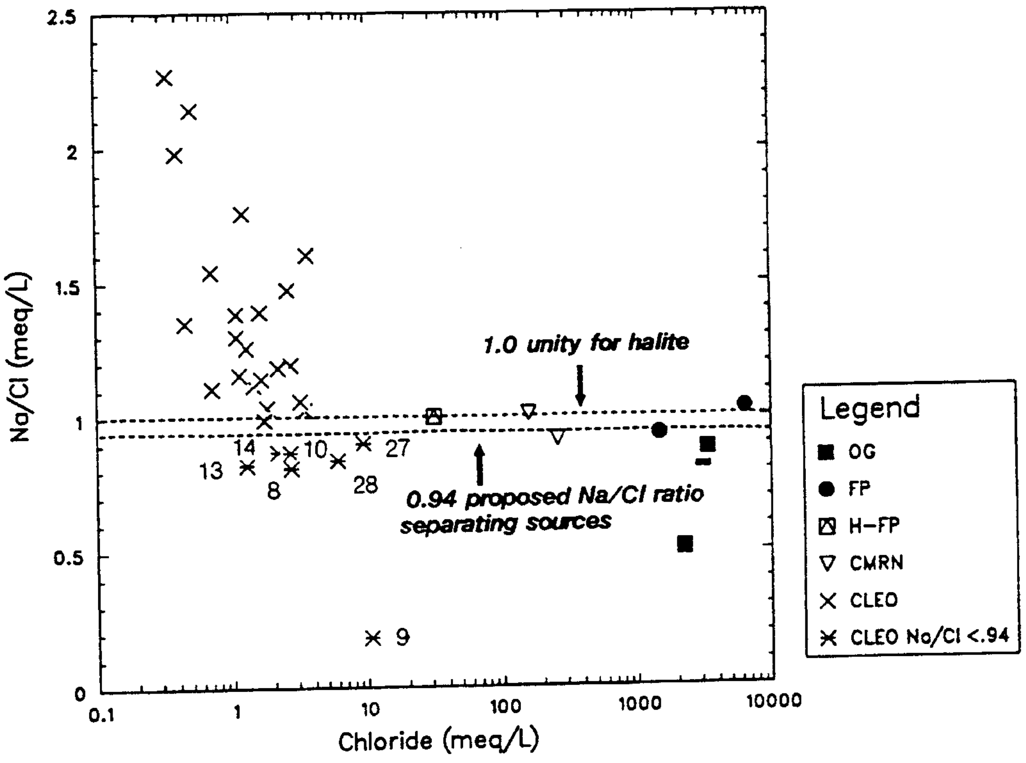


Figure 23. X-Y plot: Na/Cl versus Cl.

As 0.94 is the lowest evaporite Na/Cl ratio determined in this investigation, CLEO- 8, 9, 10, 13, 14, 27, and 28 having ratios less than 0.94, would be suspect of oil and gas brine contamination. The exceptionally low Na/Cl ratio exhibited by CLEO-9 (0.18) would first be questioned of analytical error since the lowest oil and gas Na/Cl ratio is 0.51. But, exceptionally low Na/Cl ratios have been documented at the advancing fronts of salt-water intrusions (Richter and Kreitler, 1991) and other ratios also suggest oil and gas brine contamination. Samples having Na/Cl ratios less than 0.94 are demarcated on future plots and as will be shown, indications of this third component are also seen in samples CLEO- 10, 14, 27, and 28, but only CLEO-9 consistently shows indications of oil and gas brine contamination.

Major Cations Versus Sulfate

Sulfate is a good indicator ion for the delineation of oil and gas brine contamination in fresh water. Reverse ion exchange and the reducing conditions present in deep-basin environments result in oil and gas brines exhibiting elevated Ca and decreased SO_4 concentrations. Shown on figure 24 and 25 are Ca plotted against SO_4 and Mg plotted against SO_4. Both plots illustrate the depletion of SO_4 in the oil and gas brines and their dissimilarity to the CLEO samples and other endmembers. The Ca/SO_4 ratio is normally close to unity (one) when dissolution of gypsum is the primary source of Ca and SO_4. This is evident in the Flowerpot and Cimarron endmember samples. Whereas, the Ca/SO_4 ratio is greater than 1.0 in CLEO samples because of Ca enrichment from the dissolution of calcite/aragonite and dolomite in the alluvial aquifer. It should be pointed out that CLEO-9 plots off the general trend created by the CLEO samples and the Cimarron and Flowerpot endmembers on both graphs.

Sulfate/Chloride Ratio

Of the all the major ions in natural waters SO_4 and Cl are least affected by alteration processes after mixing. Additionally, because SO_4/Cl ratios are distinctive for oil and gas and halite brines, it can be very useful in brine delineation studies. Whittemore (1984) and Richter and Kreitler (1987) both found the SO_4/Cl ratio higher in halite dissolution brines as compared to deep basin brine associated with oil and gas. As shown in figure 26, the oil and gas brines have higher SO_4/Cl ratios than the other endmembers and the CLEO samples. Again, CLEO-9 departs from the general trend.

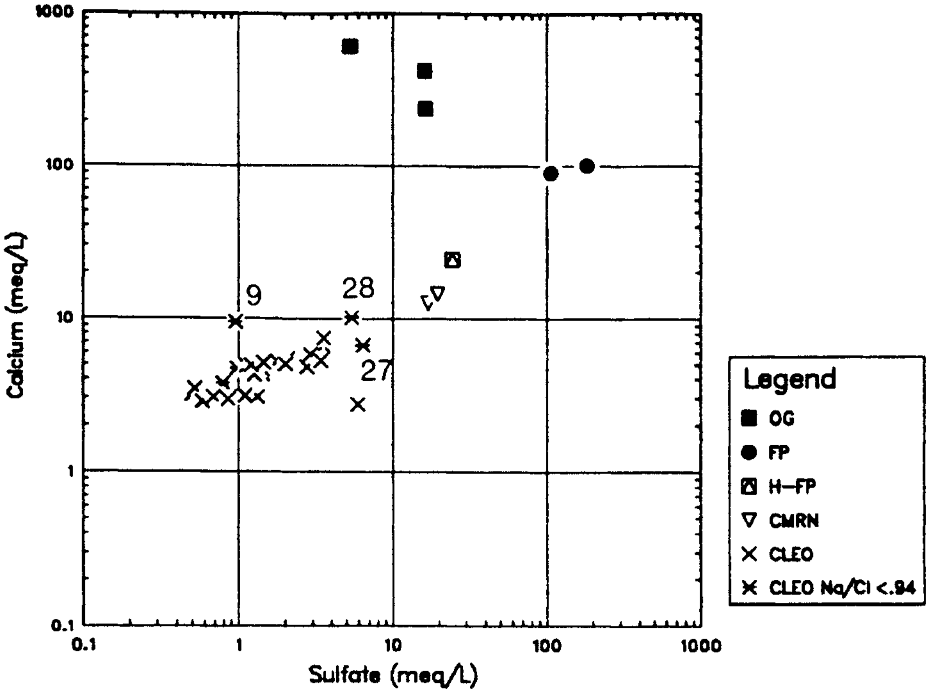


Figure 24. X-Y plot: Ca versus SO_4.

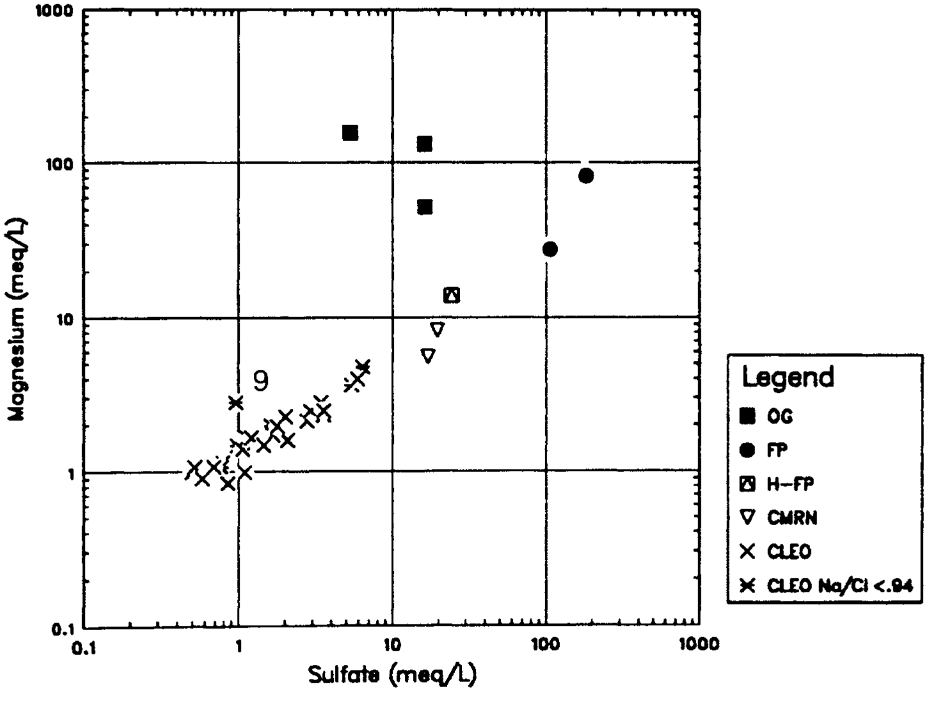


Figure 25. X-Y plot: Mg versus SO_4.

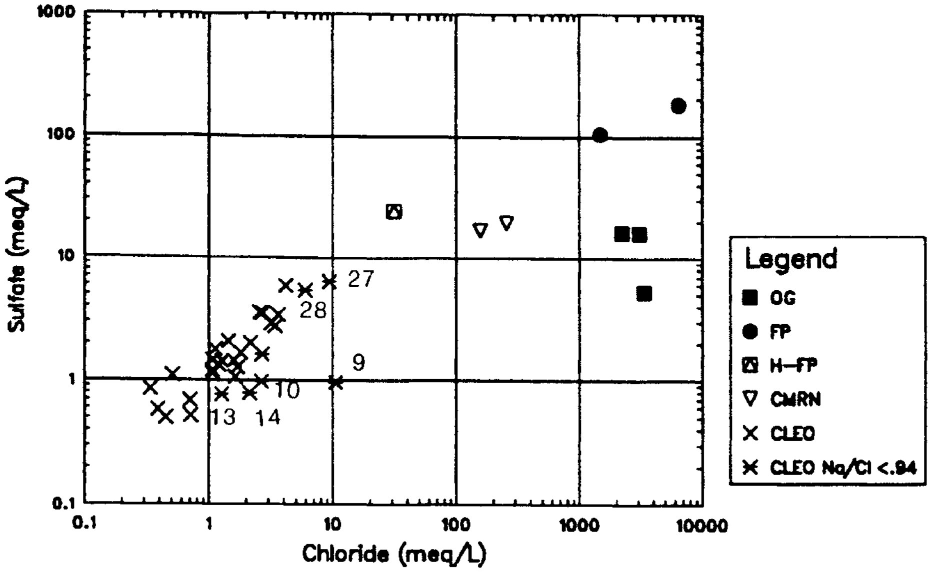


Figure 26. X-Y plot: SO_4 versus Cl.

Bromide Ratios

The trace element bromide is considered one of the most conservative ions in natural waters as it does not participate in ion-exchange processes and rarely forms minerals of its own. Both bromine and iodine are biophilic elements and show a close correlation with organic carbon in soil and in sediments (Fuge, 1974). In seawater it is removed during evaporation only when it substitutes for Cl in the crystal lattice of the evaporitic minerals halite, sylvite, and carnallite (Collins, 1975). As a result, Br concentrations with respect to Cl are relatively minor in evaporite dissolution brines in comparison to oil and gas brines, where they are generally enriched. Whittemore (1988) found that the large difference in ratios allow for the generation of site-specific mixing curves for local differentiation of brine sources. The lack of water-quality data for the Flowerpot from the well field area prevented the generation of these type curves using Br and the other trace elements I and Sr.

Concentrations of bromide and other trace elements generally occur at such small concentrations in natural waters that it is common to multiply ratios by 10,000. For the purpose of this report, all trace element ratios are expressed as x 10^4.

When Br/Cl x 10^4 ratios are plotted against Cl concentrations in figure 27 a linear trend is evident between the CLEO samples and the Cimarron and Flowerpot endmembers. This suggests that oil and gas brine is not the source of salinization to these samples. CLEO -9 and 27 plot off the major trend suggesting an oil and gas brine component in these samples. As with Br/Cl, the same type of relationship is seen when Br and SO_4 are combined in figure 28. Again CLEO - 9 deviates away from the general trend. Organic-rich sediments in the alluvial aquifer are probably responsible for elevated Br (with respect to Cl) concentration in CLEO samples.

Iodide Ratios

The trace element I is in the same group of elements as Br and is also considered conservative in its behavior in natural waters. Iodide is found in most nearshore ocean sediments in small concentrations (Collins, 1975) but its presence in evaporitic minerals, where it substitutes for Cl, is so minor as to be hardly measurable (Holser, 1979). Accordingly, evaporite dissolution brines and fresher water in contact with evaporites have very low concentrations of I. In contrast, I is present in most oil and gas brines and is found in exceptionally high concentrations in some Pennsylvanian-aged brines in western Oklahoma, where concentrations average around 300 parts per million (Cotton, 1978). Kansas brine studies by Whittemore and Pollock (1979) found that ratios of $I/Cl \times 10^4$ were typically less for halite brine in comparison to oil and gas brines.

As shown in figure 29, a linear trend is apparent when ratios of $I/Cl \times 10^4$ are plotted against corresponding Cl concentrations for the CLEO samples and Cimarron and Flowerpot endmembers. The position of the oil and gas endmember on the graph shows enrichment in I with respect to Cl, in contrast to the other analyses which show a decrease in the concentration of I with an increase in Cl. When $I/SO_4 \times 10^4$ ratios are plotted against corresponding SO_4 concentrations (fig. 30), the results are similar but more pronounced. The concentrations of I and SO_4 stay relatively constant as the SO_4 concentration increases. The anomalously high I concentration in CLEO - 24 is probably a result of analytical error, as this sample shows no other indications of oil and gas brine contamination on other X-Y plots. CLEO - 27 and 28 are found slightly off the general trend on both I plots, while CLEO - 9 unexpectedly is not.

Strontium Ratios

The trace element Sr forms celestite ($SrSO_4$) and strontianite ($SrCO_3$), both of which occur commonly in sediments (Collins, 1975). Strontium resembles Ca chemically and may replace it during the formation of both carbonate and sulfate evaporite minerals (Holser, 1979). The concentration of Sr in evaporite-dissolution brines is relatively minor compared to oil and gas brines

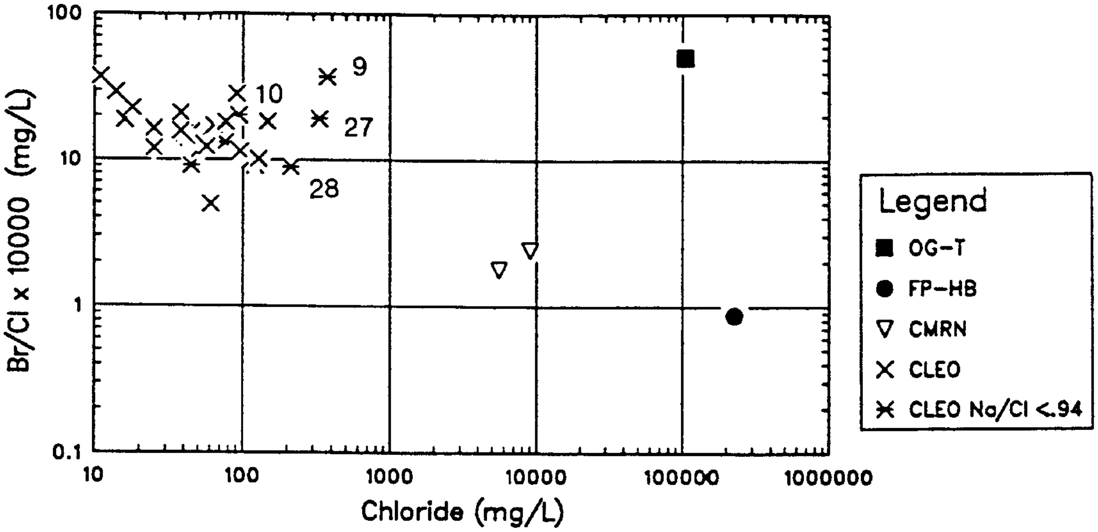


Figure 27. X-Y plot: Br/Cl versus Cl.

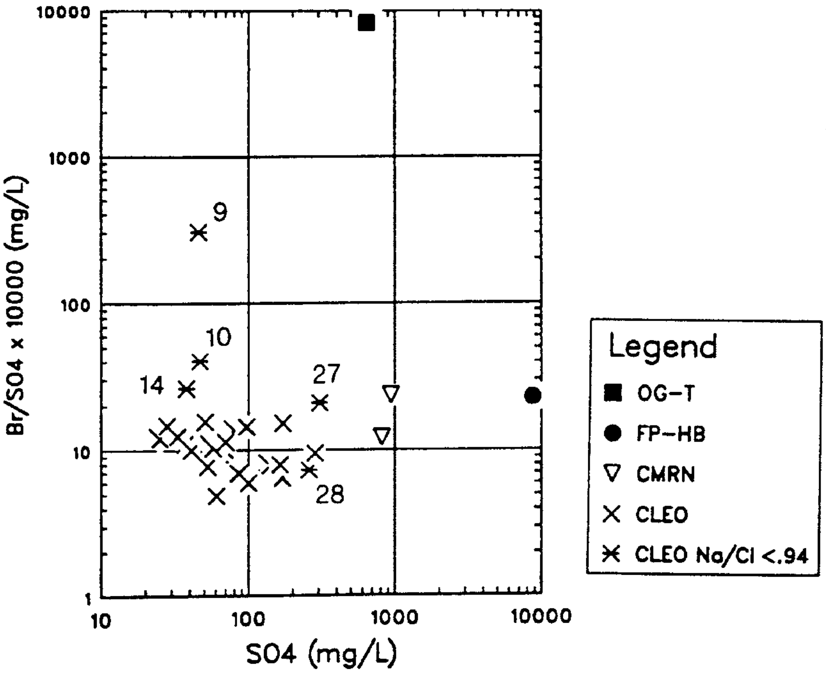


Figure 28. X-Y plot: Br/SO_4 versus SO_4.

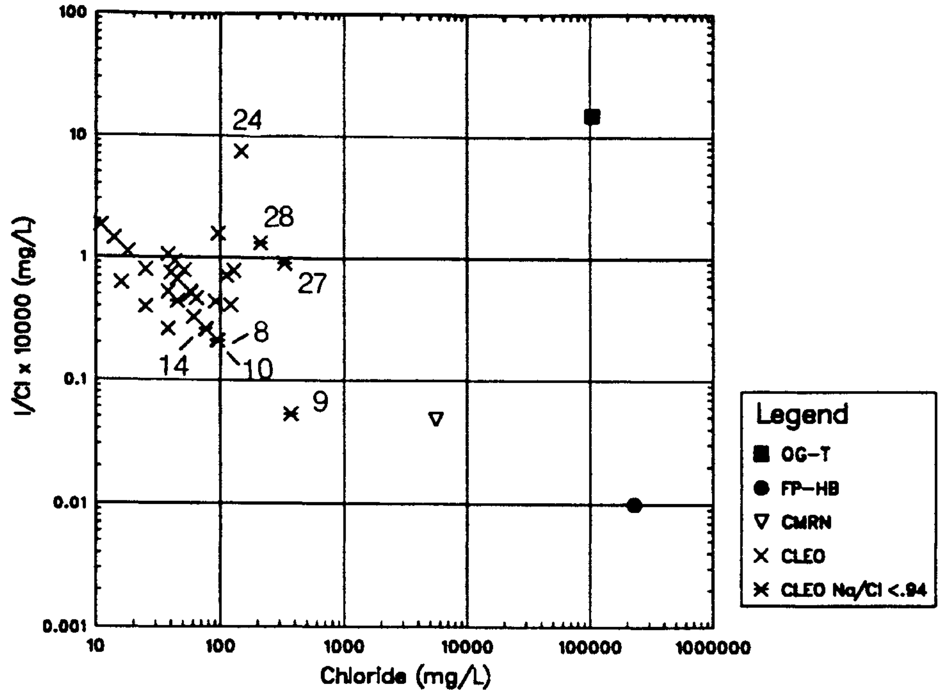


Figure 29. X-Y plot: I/Cl versus Cl.

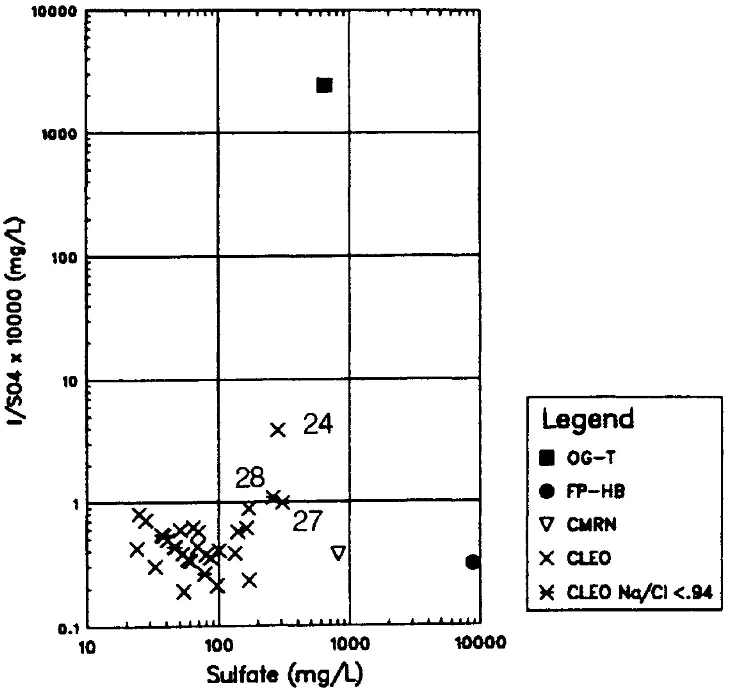


Figure 30. X-Y plot: I/SO_4 versus SO_4.

where it is found in concentrations up to 3,400 mg/L (Collins 1975). Because the concentration of Sr is easily affected by ion-exchange processes after mixing, it is not commonly used in brine-detection studies.

When ratios of Sr/Cl x 10^4 are plotted against corresponding Cl concentrations, a strong linear relationship is exhibited between the CLEO samples and the Cimarron and Flowerpot endmembers (fig. 31). The decrease in Sr as concentrations of Cl increase or as water type changes from calcium-bicarbonate to sodium-chloride, indicates the calcium-rich minerals, calcite/aragonite and gypsum are the source of Sr to the system.

A similar relationship is seen in figure 32 when Sr/SO_4 x10^4 are plotted against corresponding SO_4 concentrations. It should be noted that CLEO - 9 shows no indication of a third component on the Sr/Cl plot in contrast to the Sr/SO_4 plot. Even though Sr is not considered a reliable trace element for brine delineation studies, it appears that in this study when used in combination with Cl and SO_4, their relationship is helpful in showing that oil and gas brine is not a general source of salinization. Strontium is probably more reliable in this study, in comparison to other brine source studies, because of the large difference in Sr ratios between the Flowerpot and oil and gas endmembers.

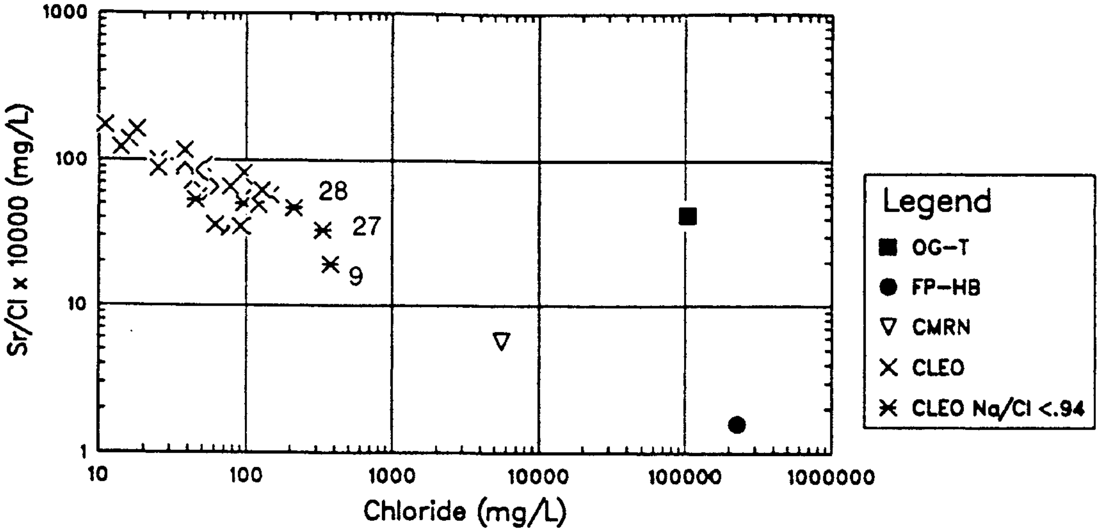


Figure 31. X-Y plot: Sr/Cl versus Cl.

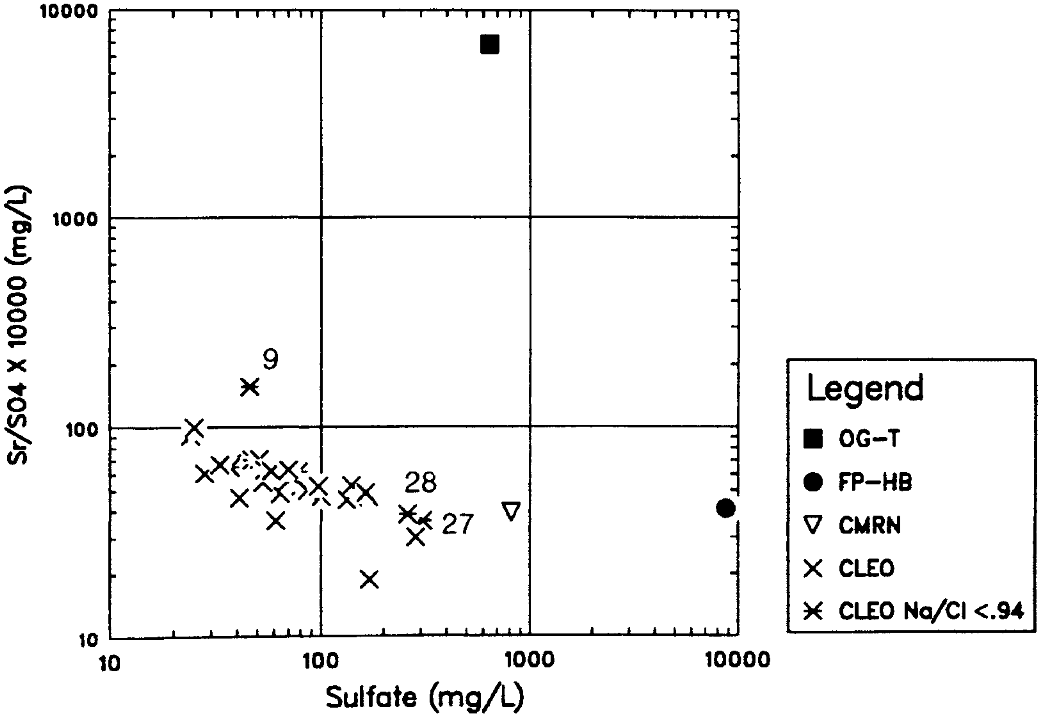


Figure 32. X-Y plot Sr/SO_4 versus SO_4.

CHAPTER VI

MIXING PROPORTIONS

To estimate the affect of salinization on the well field, the percentage of the H-FP and FW endmembers in each CLEO sample were calculated using the WATEVAL computer program (Hounslow and Goff, 1991). The mixing calculations performed by WATEVAL are based on the equation:

$$(V_1 * C_{H\text{-}FP}) + (V_2 * C_{FW}) = C_{mix}$$

where V = volume, C = ion concentration, and $V_1 + V_2 = 1$.

The sample CLEO-16 was used as the FW endmember because it appears to be the least affected by salinization. A stacked-bar graph illustrating the percentage of both endmembers comprising the CLEO samples, indicates the percentage of H-FP ranges from near 0 percent in CLEO -16 to a high of 26.4 percent in CLEO - 24 (fig. 33). As CLEO - 9 shows indications of a third mixing component on the ionic plots, mixing proportions for this sample and others that may be affected are misleading.

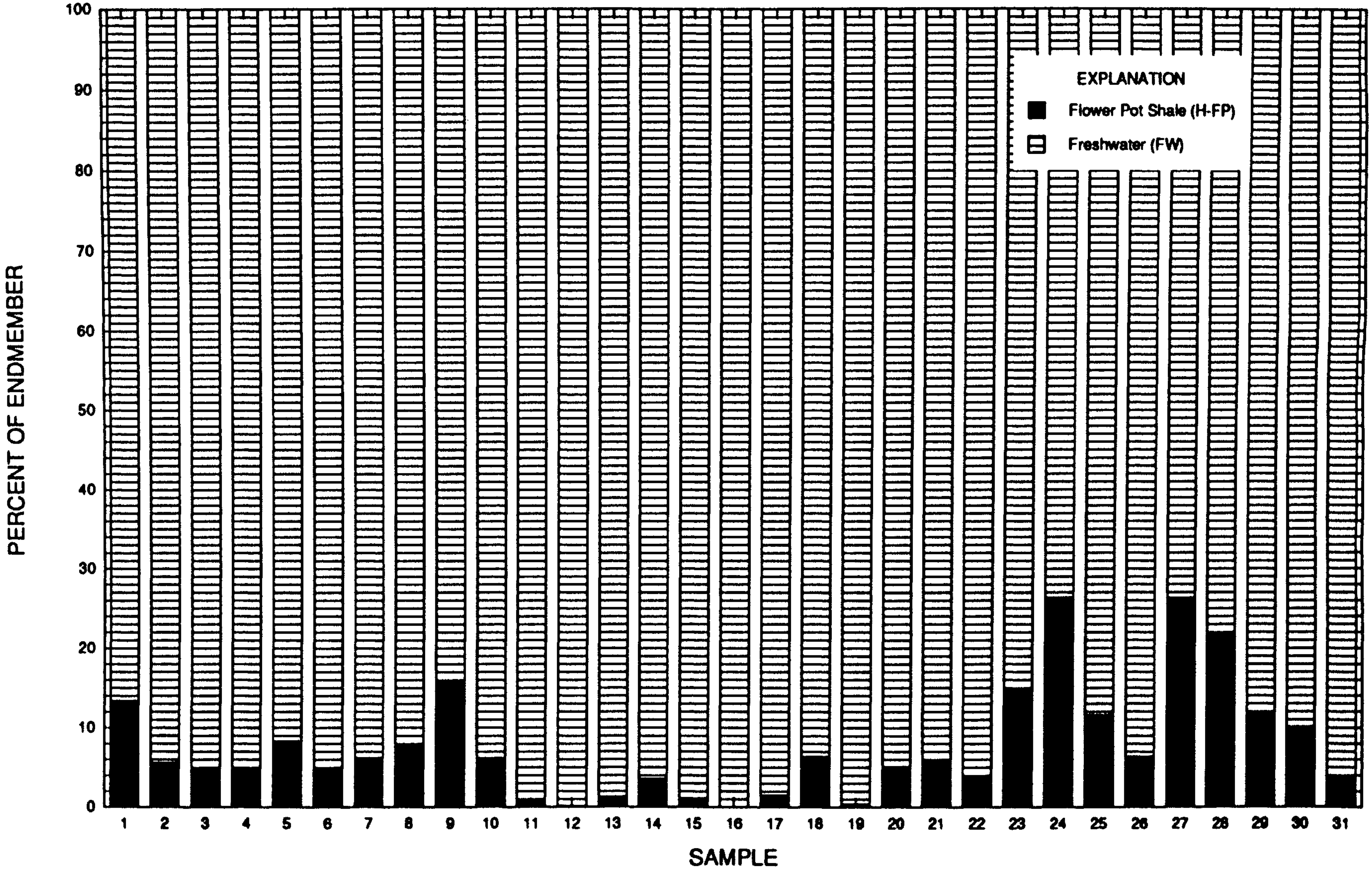


Figure 33. Stacked-bar chart showing percentage of freshwater and Flowerpot endmembers composing water samples collected from the Cleo Springs well field in August 1991.

CHAPTER VII

CONCLUSIONS

The Piper diagram and ionic plots indicate the general source of salinization to the well field is the underlying Flowerpot Shale. It is likely that CLEO - 9 has been affected by oil and gas brines, as this sample shows indications of three-component mixing on almost all X-Y plots. Whereas, there is not enough evidence to conclude oil and gas brine contamination in CLEO-10, 14, 27, and 28, as these samples plot off the general trend only on selected plots. The lack of water-quality data for the Flowerpot at the well field area and the low Cl concentrations make an exact determination difficult.

An increase in salinization is evident in the western and eastern parts of the well field. The TDS is considered high with respect to drinking-water standards; 23 of the 31 wells sampled exceeded the SMCL of 500 mg/L. Two samples exceeded the SMCL of 250 mg/L of Cl and 3 samples exceeded the SMCL of 250 mg/L of SO_4. The freshest water is located in the center of the well field. Only one sample exceeded the MCL for nitrogen as NO_3. Cattle are probably the primary source of nitrogen in the well field.

In areas where salinization has occurred, it appears that a difference in fluid potential has created an upward movement of brackish water from the Flowerpot through fractures and dissolution features. This mixing relationship between the fresh Ca-HCO_3 type water of the alluvial aquifer and formation water of Flowerpot is seen on the Piper diagram. The Flowerpot analyses used in this study do not appear to be representative of the Flowerpot in the well field. The halite units present in the deeper parts of the basin, where the samples were taken, are absent in the well field with gypsum/anhydrite being the dominant facies present. As a result, groundwater moving upward from the Flowerpot into the alluvial aquifer has higher concentrations of Ca and SO_4.

The principal source of recharge to the alluvial aquifer in the well field is precipitation and its reaction with carbon dioxide in the atmosphere and the soil, is the primary factor controlling the groundwater chemistry. The dominant cation Ca is derived from the dissolution of calcite/aragonite and dolomite in the aquifer, as is the dominant anion HCO_3. The underlying Flowerpot is also a significant source of Ca, Cl, and SO_4, in addition to the secondary ion Mg.

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APPENDIXES

APPENDIX A

SAMPLING METHODS AND MATERIALS

Sampling Methods and Materials

All water samples were analyzed for the major ions Ca, Mg, Na, K, Cl, SO_4, HCO_3, and the trace elements Br, I and Sr. The surface-water and study-area samples were also analyzed for nitrogen. The major ions and nitrogen were measured by the Oklahoma State University Agronomy Department. The trace elements Br, I, and Sr were measured by the U.S. Geological Survey's National Water-Quality Laboratory in Denver Colorado.

The Cleo Springs water-well field contains 31 water wells, all completed and screened in the alluvial deposits. Twenty-nine wells had been producing water for approximately a month at the time of sampling. Two of the wells had not been pumping, but were purged for 1 to 2 hours before sampling. The three wells at the Cargill Solar Salt Plant were active brine production wells at the time of sampling. All water samples were filtered using a 0.45 µm filter. A portable peristaltic pump was used when sampling surface waters and water samples from the three brine wells.

The field parameters specific conductance, pH, dissolved oxygen, and temperature were measured using a flow-through cell, before and after sampling. Bicarbonate concentrations were measured by alkalinity titrations performed within 12 hours of sampling. Sample bottles were filled and capped leaving the least amount of air space possible and were kept on ice until titration.

Water samples were collected in 250 ml polyethylene bottles. A separate bottle was used for the major cations and anions and for the trace elements. The anion bottles were acid rinsed prior to use. To prevent post-collection changes, nitric acid was added to the bromide-iodide sample and hydrochloric acid was added to the major anion sample. Water samples for the major cations and strontium were untreated. Nitrogen samples were stored in opaque bottles, preserved with hydrochloric acid, and were refrigerated before and after arrival at the lab.

APPENDIX B

ANALYSES FROM WHICH THE FLOWERPOT AND OIL AND GAS ENDMEMBERS WERE DETERMINED

APPENDIX B. Analyses from which the Flowerpot endmembers FP-LM and FP-HB were determined.

[Source: FP-LM, Oklahoma Department of Environmental Quality; FP-HB, sampled August, 1991, Ca, Mg, Na, K, Cl, and SO_4, were analyzed by the Oklahoma State University Agronomy Department. The trace elements Br, I, and Sr were analyzed by the U.S. Geological Survey's water-quality laboratory in Denver Colorado. Concentrations of Cargill samples are dissolved; pH, temperature, and HCO_3 are field measurements; --, no data]

Well location	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Cl (mg/L)	SO_4 (mg/L)	HCO_3 (mg/L)	pH	Tempera-ture (C)	Br (mg/L)	I (mg/L)	Sr (mg/L)
FP-LM												
MW #CH-D	1813	646	90,560	--	127,700	5350	--	--	--	--	--	--
MW #CH-D	1760	622	100,100	112	168,000	4345	90	--	--	--	--	--
MW #1-D	2000	84	27,600	52	48,100	4900	24	--	--	--	--	--
MW #1-D	1780	134	28,000	67	39,000	4300	22	--	--	--	--	--
MW #1-D	1810	224	26,500	61	43,000	5300	20	--	--	--	--	--
MW #1-D	1646	281	31,450	--	44,500	4470	--	--	--	--	--	--
MW #1-D	1820	372	33,600	60	58,150	5315	24	--	--	--	--	--
MW #1-D	1870	335	32,500	119	54,100	5110	29	--	--	--	--	--
MW #2-C	1880	452	31,900	--	52,600	5840	41	--	--	--	--	--
FP-HB												
Cargill #4 27N-19W-21	2013	1018	142,461	141	230,305	4476	32	6.9	21	21.00	0.27	37.00
Cargill #6 27N-19W-21	2029	999	153,425	181	227,434	8769	43	6.9	21	20.00	0.28	36.00
Cargill #11 27N-19W-21	2156	885	152,172	161	230,832	8771	41	6.9	21	17.00	0.27	33.00

APPENDIX B. Analyses from which the endmembers OG-M, OG-P, and OG-OD were determined [Data source: Geological Information Systems, Norman, Oklahoma; – no data]..

Period	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	Cl (mg/L)	SO_4 (mg/L)
Pennsylvanian					
27N-10W-30	13,000	2,030	69,900	136,000	240
27N-11W-25	4,500	644	20,300	42,900	1,100
27N-11W-28	12,920	1,968	56,600	124,060	255
27N-9W-13	16,000	2,210	67,700	139,000	200
27N-9W-14	15,300	2,030	66,800	136,000	184
27N-9W-14	15,800	2,150	68,000	139,000	200
28N-10W-23	13,300	3,050	69,600	133,000	110
28N-11W-26	11,200	2,700	68,800	132,400	328
27N-10W-30	13,654	2,284	75,862	147,600	240
27N-11W-23	12,310	1,910	70,861	136,200	500
27N-11W-26	10,400	2,800	56,200	116,600	720
27N-7W-6	12,614	1,942	56,416	114,660	355
27N-9W-16	12,232	1,774	67,326	129,888	960
NW Avard	6,007	1,344	28,169	58,472	416
23N-13W-32	8,700	1,446	48,028	93,517	132
26N-16W-1	11,296	1,701	61,128	119,080	358
26N-16W-1	12,001	1,256	61,127	118,890	163
26N-16W-1	4,531	792	30,244	56,562	244
26N-16W-1	13,004	1,090	58,575	116,472	157
26N-16W-2	11,800	1,960	58,700	117,000	150
22N-12W-15	4,597	682	42,600	69,398	1,209
22N-16W-36	520	107	9,823	15,500	450
28N-9W-13	16,880	787	81,400	170,445	1,070

APPENDIX B. Analyses from which the endmembers OG-M, OG-P, and OG-OD were determined [Data source: Geological Information Systems, Norman, Oklahoma; -- no data]. (Continued).

Period	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	Cl (mg/L)	SO_4 (mg/L)
Mississippian					
SW Ringwood	7,417	1,695	49,965	94,466	821
Ringwood	1,562	226	5,070	11,054	83
Ringwood	1,404	264	11,066	19,160	1,383
Ringwood	1,068	126	8,098	13,531	1,475
SW Ringwood	439	89	4,137	6,165	1,403
Ringwood	2,180	632	12,584	24,679	988
Ringwood	82	20	3,620	3,993	1,724
Ringwood	1,157	202	16,113	27,165	201
SW Ringwood	426	101	3,755	5,597	1,359
SW Ringwood	1,918	423	17,724	30,784	1,285
SW Ringwood	587	46	5,971	9,412	958
SW Ringwood	279	92	1,859	2,392	1,467
21N-10W-33	1,197	62	24,190	39,410	744
21N-10W-34	1,269	175	20,100	37,306	660
21N-11W-1	200	29	2,213	3,868	1
21N-11W-12	2,023	496	12,221	22,902	997
21N-11W-12	2,004	435	12,124	22,502	999
21N-11W-12	9,021	3,401	102,027	182,575	842
21N-11W-12	1,763	253	10,760	19,266	1,353
21N-11W-13	15,681	2,335	63,754	132,774	68
22N-11W-28	10,128	1,160	49,500	103,090	498
22N-11W-36	34,569	2,076	18,953	95,919	597
22N-11W-36	24,002	1,514	22,496	81,026	680
22N-12W-25	7,824	1,535	66,000	108,935	888
22N-12W-3	7,072	427	41,640	77,185	893
23N-9W-7	12,668	1,091	58,190	120,028	412
23N-10W-5	11,067	1,642	65,480	111,710	561

APPENDIX B. Analyses from which the endmembers OG-M, OG-P, and OG-OD were determined [Data source: Geological Information Systems, Norman, Oklahoma; – no data]. (Continued).

Period	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	Cl (mg/L)	SO_4 (mg/L)
23N-11W-36	11,507	3,932	38,700	103,840	560
23N-15W-28	3,520	830	27,930	51,00	1,500
23N-16W-36	128	57	13,291	19,172	1,828
24N-11W-32	6,590	2,085	47,000	99,895	196
24N-11W-33	8,486	2,474	54,860	114,665	–
26N-14W-11	4,600	580	46,625	80,250	1,825
26N-14W-11	5,000	630	50,681	87,232	1,984
26N-15W-8	7,736	1,279	43,538	85,230	378
26N-15W-8	8,534	1,411	48,724	94,026	417
27N-7W-3	13,264	1,820	68,468	132,990	450
28N-10W-19	12,500	4,320	71,500	145,000	58
28N-10W-19	12,600	4,220	67,700	139,000	125
28N-11W-33	14,000	2,800	68,800	136,500	455
Ordovician-Devonian					
20N-11W-30	7,120	1,320	47,212	90,800	960
21N-11-W	7,539	1,432	58,503	107,050	806
21N-11W	6,794	1,559	61,036	110,043	775
21N-11W	7,225	1,297	62,860	112,969	801
21N-11W-11	7,420	1,869	57,751	106,996	795
21N-11W-11	802	131	66,639	103,983	706
21N-11W-11	7,042	2,325	55,997	104,952	830
21N-11W-11	,8460	1,209	57,852	106,976	782
21N-11W-11	7,245	1,697	55,150	102,039	837
21N-11W-11	7,586	1,455	61,651	111,890	821
21N-11W-11	8,422	1,090	58,683	107,958	745
21N-11W-3	8,622	948	55,477	103,045	774
21N-14W-27	12,000	1,880	56,823	117,000	520

APPENDIX B. Analyses from which the endmembers OG-M, OG-P, and OG-OD were determined [Data source: Geological Information Systems, Norman, Oklahoma; -- no data]. (Continued).

Period	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	Cl (mg/L)	SO_4 (mg/L)
21N-14W-3	10,700	1,760	58,326	116,000	630
22N-14W-6	13,884	2,151	71,819	141,112	597
22N-16W-9	11,209	2,916	62,184	125,990	22
23N-14W-31	3,040	830	23,891	42,200	2,900
23N-14W-32	9,000	1,420	52,488	102,000	880
23N-15W	11,784	2,549	60,394	121,242	521
23N-15W	12,733	1,660	67,532	130,743	530
23N-15W	12,724	1,659	61,009	121,563	529
23N-15W	13,566	2,322	58,108	126,616	709

APPENDIX B. Analyses from which OG-T were determined [Data source: Geological Information Systems, Norman, Oklahoma; -- no data].

Location	Br (mg/L)	I (mg/L)	Sr (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	Cl (mg/L)	SO_4 (mg/L)
21N-10W-33	334	464	141	1,197	62	24,190	39,410	744
21N-10W-34	282	473	160	1,269	175	20,100	37,306	660
22N-11W-28	533	131	430	10,128	1,160	49,500	103,090	498
22N-12W-3	1,280	182	1,190	7,072	427	41,640	77,185	893
22N-12W-15	267	162	1,030	4,597	682	4,600	69,398	1,209
22N-12W-25	1,845	37	200	7,824	1,535	66,000	108,935	888
23N-9W-7	573	213	1,110	12,668	1,091	58,190	120,028	412
23N-10W-5	645	190	560	11,067	1,642	65,480	111,710	561
23N-11W-36	458	396	350	11,507	3,932	38,700	103,840	560
24N-11W-32	336	135	390	6,590	2,085	47,000	99,895	196
24N-11W-33	366	152	450	8,486	2,474	54,860	114,665	--
22N-16W-9	--	63	591	11,209	2916	62,184	125,990	22
27N-11W-28	617	66	520	12,920	1,968	56,600	124,060	255
28N-9W-13	626	32	440	16,880	787	81,400	170,445	1,070

APPENDIX C

SATURATION INDICIES FOR GROUNDWATER SAMPLES FROM THE CLEO SPRING WELL FIELD - 1991 SAMPLING PROGRAM

APPENDIX C. Saturation indices for groundwater samples from the Cleo Springs well field - 1991 sampling program .

Well	Aragonite	Calcite	Dolomite
1	0.05707	0.33506	0.18112
2	0.01592	0.29390	0.03450
3	0.05156	0.32633	0.17453
4	-0.33691	-0.06058	-0.60180
5	-0.10663	0.16971	-0.01201
6	-0.35579	-0.07781	-0.61447
7	-0.17259	0.10375	-0.22792
8	-0.20250	0.07383	-0.29417
9	-0.12045	0.15754	-0.22774
10	-0.18482	0.09316	-0.32830
11	-0.40423	-0.12789	-0.75779
12	-0.36491	-0.08857	-0.72905
13	-0.31798	-0.04164	-0.55215
14	-0.21437	0.06197	-0.39561
15	-0.48634	-0.21001	-0.88262
16	-0.16010	0.11788	-0.27647
17	-0.19441	0.08193	-0.35329
18	-0.24359	0.03439	-0.40822
19	-0.23251	0.04383	-0.42483
20	-0.09876	0.17758	-0.12494
21	-0.05998	0.21636	0.00300
22	-0.31476	-0.03842	-0.42198
23	-0.23151	0.04483	-0.18869
24	-0.21633	0.06165	0.28200
25	-0.07601	0.20032	0.02459
26	0.20672	0.47857	0.43588
27	-0.17936	0.09862	0.04612
28	0.25517	0.53151	0.61409

APPENDIX C. Saturation indices for groundwater samples from the Cleo Springs well field - 1991 sampling program (Continued).

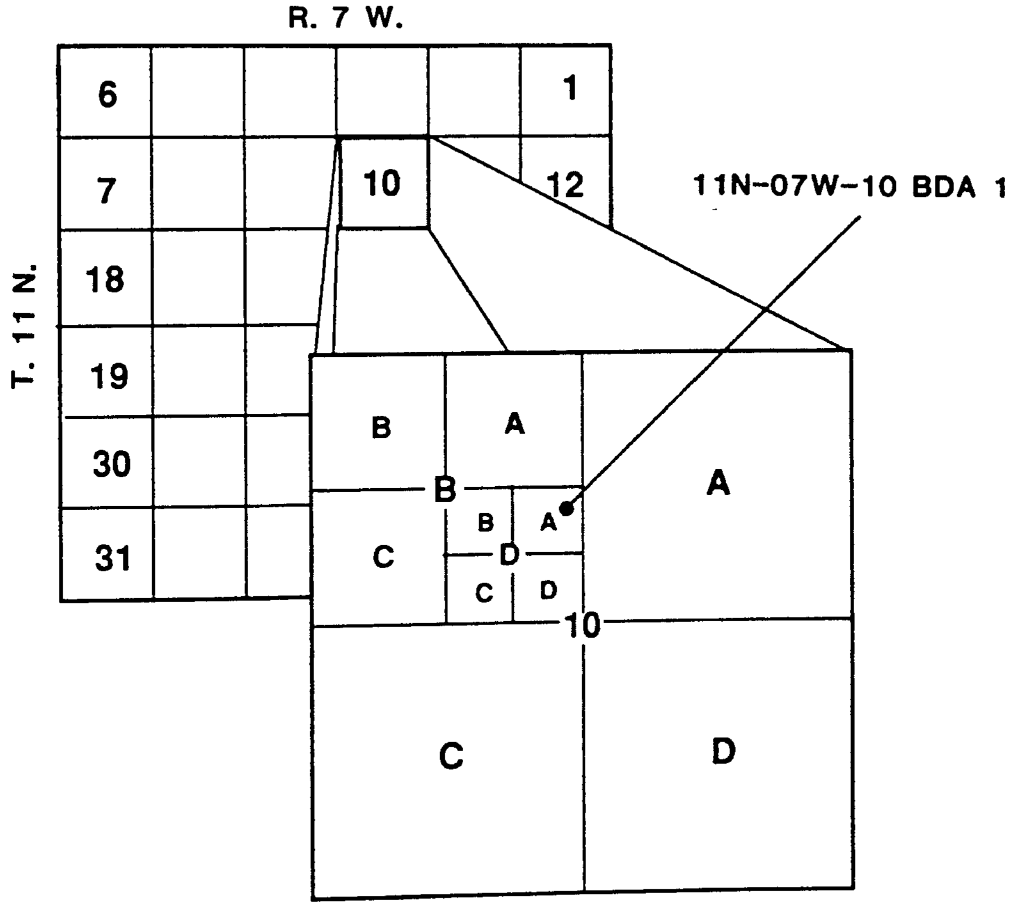
Well	Aragonite	Calcite	Dolomite
29	-0.01141	0.26493	0.06891
30	-0.14291	0.13343	-0.09330
31	-0.23377	0.04257	-0.23416

APPENDIX D

EXPLANATION OF SITE NUMBERING SYSTEM

Explanation of the Site-Numbering System

The standard method of describing a location by fractional section, section, township, and range is replaced in this report by the system illustrated in the diagram below. The location of a site indicated by the *x* normally would be described as NE 1/4, SE 1/4, NW 1/4, sec. 10, T. 11 N., R. 7 W. The method used in this report indicates quarter-section subdivisions of the section by letters, from largest to smallest. By this method the location of the site is 11N-7W-10 BDA 1. The final digit (1) is the sequential number of a well within the smallest fractional subdivision.



VITA

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