HYDROGEOCHEMISTRY AND SOURCES OF CHLORIDE AND SULFATE IN THE VERDIGRIS RIVER BASIN IN OKLAHOMA

By

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CHAPTER I

INTRODUCTION

Statement of Problem

Contamination of natural waters by man's activities is receiving increased awareness by the general public. Excessive concentrations of sulfate and chloride have been known to occur in the Verdigris River Basin in Oklahoma and possible sources of such excessive concentrations may be from oil field brines (Marcher and Bingham, 1971) and coal strip-mining (Bingham and Bergman, 1980). Petroleum production and coal mining are important industries in the state and knowledge of their effects on water quality should enhance delineation of possible problem areas, and aid in identifying contamination of natural waters on a regional scale.

Study Area

The Verdigris River Basin is located in northeastern Oklahoma and south-central Kansas (figure 1). This study is restricted to the Oklahoma portion of the Verdigris River Basin (hereafter referred to as Verdigris Basin). Streams and associated tributaries in the basin that were

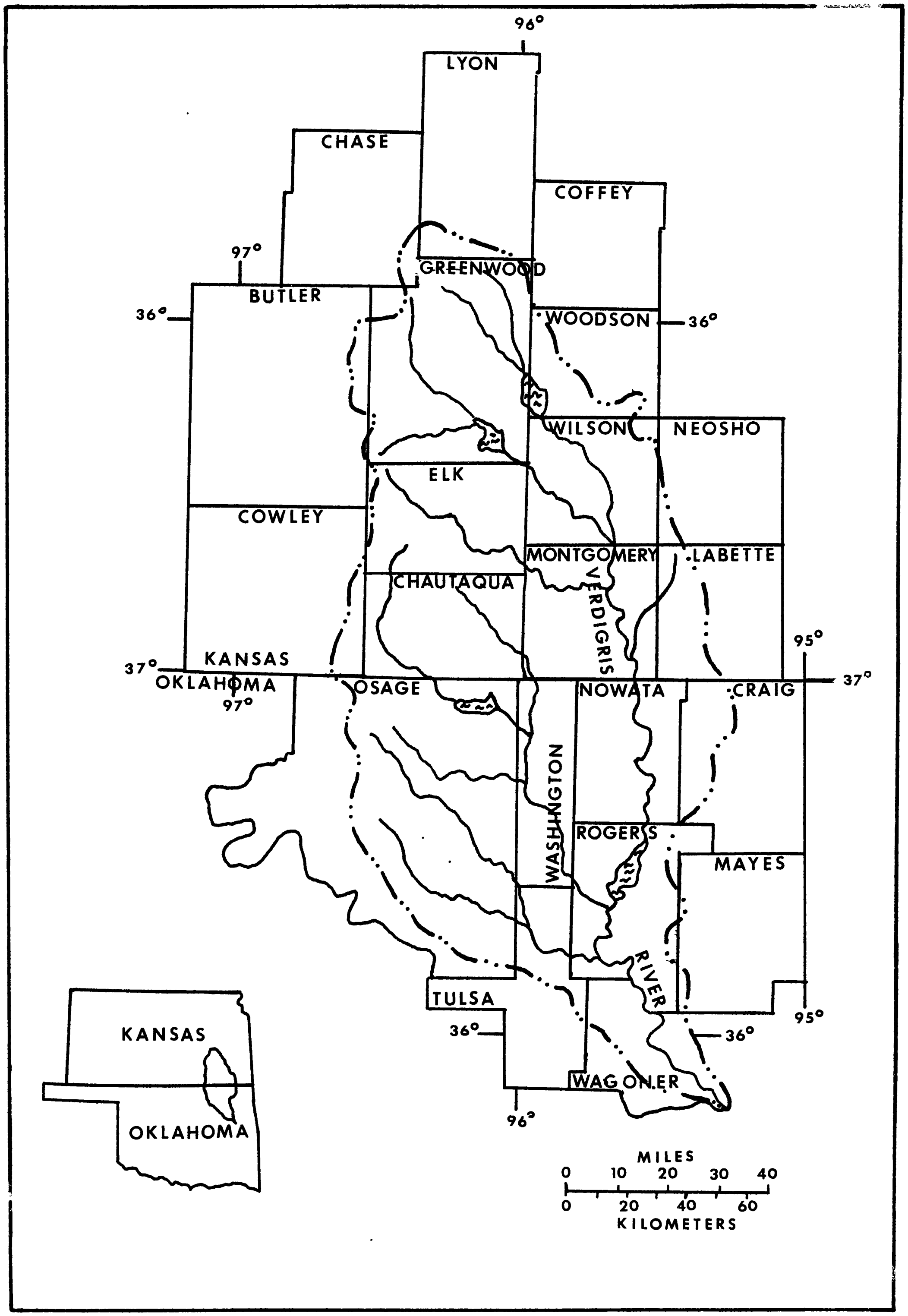


Figure 1. Location of the Verdigris River Basin in Kansas and Oklahoma (after Fader and Morton, 1975)

studied include are the following streams and associated tributaries: Hominy, Delaware, Dog, Fourmile, Lightning, Panther, Plumb, Spencer, and Blue Creeks (figure 2). Selection of these areas was based on results of sulfate and chloride analyses of samples, collected by the author, from major tributaries to the Verdigris River during a period of low flow on October 11, 1984.

Objectives and Scope

The following objectives are necessary to delineate sources of sulfate and chloride contamination, and identify the geochemical reactions responsible for the composition of "background" and "contaminated" ground-water.

1) Sample major tributaries throughout the Verdigris Basin and analyze for sulfate and chloride to select for further study tributaries that contain anomalous concentrations,
2) Delineate probable sources of the contamination, show where mixing occurs in tributary reaches, and identify streams where contamination does not occur,
3) Determine the dilution effect of surface runoff on the concentrations of Cl- and SO4=,
4) Determine geochemical reactions that influence the input of sulfate and chloride from source areas, and
5) Evaluate the influence of man's activities, especially coal strip-mining and petroleum exploration, on the composition of ground water.

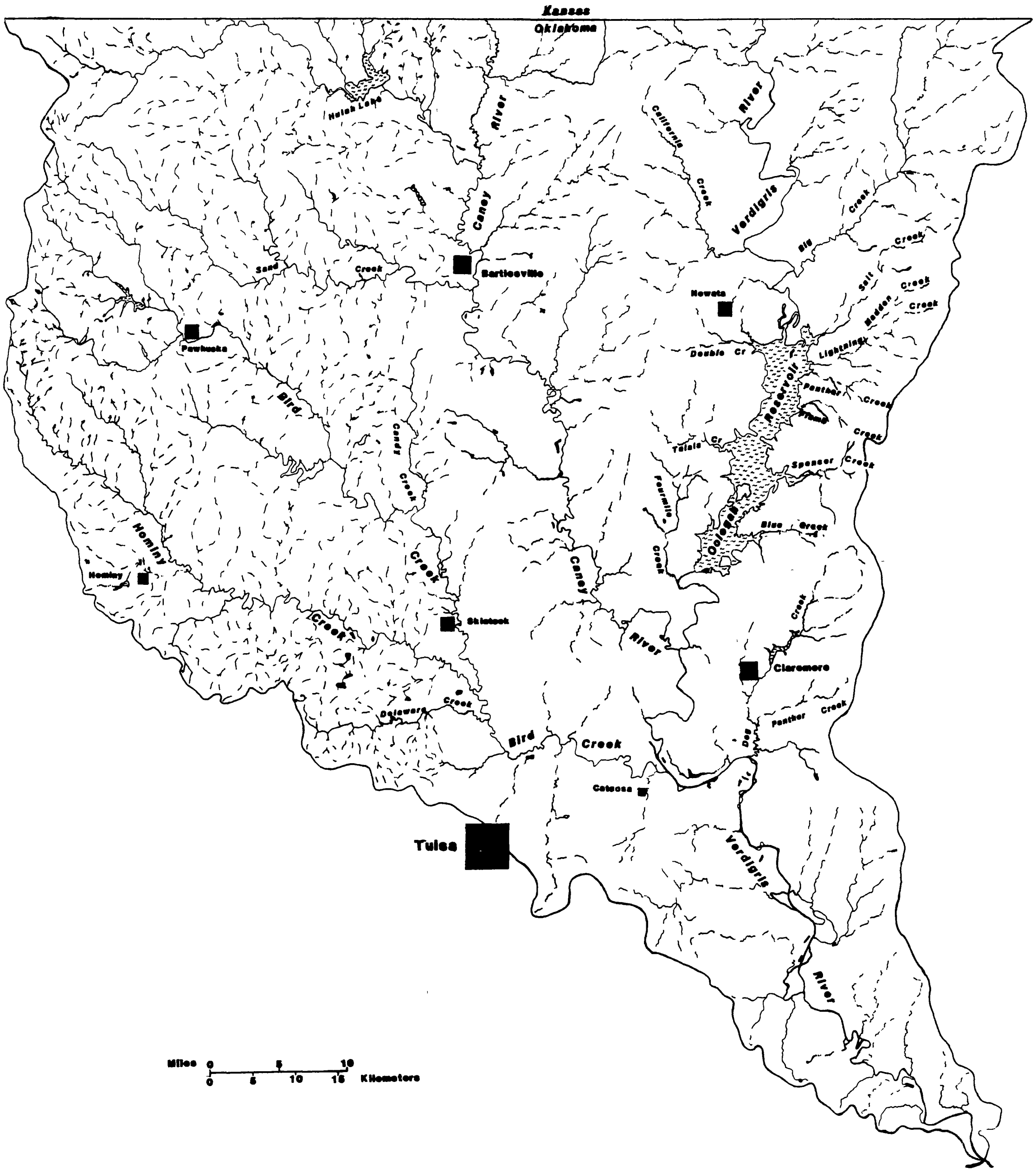


Figure 2. Location of Verdigris River Basin in Oklahoma

Contamination by organic compounds, determining the influence of microbial activities, and determining loading rates are beyond the scope of this study.

It is hoped that knowledge gained from this study may be applied to other areas in Oklahoma that may be receiving contaminants associated with similar activities of man.

Methodology

Water samples were collected from streams, on seven occasions in October, November, and December 1984, during periods of ground-water runoff.

Parameters measured at each stream were temperature, pH, and specific conductance. Samples were collected in acid-washed, polyethylene bottles and placed immediatedly on ice. At the end of the day, sample containers were refrigerated, at four degrees centigrade, until analysed.

Analysis of chloride was by titration with mercuric nitrate, method 325.3, and sulfate was done by turbometric sulfate using method 375.4 (U. S. Environmental Protection Agency, 1983). Precision testing was accomplished by randomly selecting one-third of the samples for analyses and determining the percent error between duplicates.

Results of chloride and sulfate determinations were interpreted using cumulative probability distributions (Sinclair, 1981). This method involves 1) grouping, for example chloride analyses, into numerical order and then into classes, 2) determining the cumulative percent for the midpoint of each class, 3) plotting cumulative percent (x-axis) versus concentration (y-axis), 4) drawing a smooth curve through the data points, 5) partitioning the resulting cumulative probability curve into contributing populations, (sources) and 6) verifying selection of the number of sources and percentage of each by calculating "check points" (indicated by triangles) which should fall essentially on the original curve.

Once the populations have been correctly partitioned, then the mean and standard deviations can be read directly from the probability axis. Further, the significance of each source and their statistical parameters may be evaluated by comparison of the analyses with respect to locations along streams, rock lithology and man's activities. Sample locations that reflect anomalous values can be evaluated as a first priority. Coding of the chemical analyses, at each sampling location, using threshold limits estimated at 2 and 98 cumulative percent, aids in distinquishing sources. Further, concentration limits for each source may be based on statistical parameters. Therefore, the natural variation of background and the variation of concentration of the contaminants can be determined on a statistical basis.

CHAPTER II

GEOLOGY

Introduction

The Verdigris River Basin is located in the northern shelf geologic province of northeast Oklahoma.
The altitude ranges from a maximum of 1279 feet, 13 miles northwest of Pawhuska, to 540 feet near the confluence of Bird Creek with the Verdigris River.

Previous Studies

Geological mapping was done in the 1950's for the purposes of describing the stratigraphy, lithology and paleontology of the rock units that are present at the surface. Several carbonates were analyzed for their insoluble residue content.

Friedman (1974) described the stratigraphic occurrence, sulfur content, and commercial coal mining activities in the Oolagah Reservoir area. Further, Friedman (1982) delineated coal mining areas that were mined, and coal beds that are potentially strippable to depths up to 100 feet.

Alteration of opaque minerals in the Vanoss Formation was studied by Steffans (1980), in Seminole, Pontotoc and Murray Counties. Opaque minerals are replaced by iron hydroxides: goethite, limonite and lepidocrocite. Hematite commonly occurs as martite in red mudrocks. A significant amount of the total opaque fractions, especially that found in gray mudrocks and associated sandstones is represented by authigenic ilmenite, replacement pyrite and psuedomorphs after pyrite.

Sedimentary rocks of Pennsylvanian Age underlie unconsolidated sediments of Quaternary Age associated with rivers and major tributaries throughout the Verdigris Basin. Progressively older Pennsylvanian rocks are exposed at the surface with decreasing altitude from west to east across the basin. These strata are mostly sandstone and shale with lesser limestone and dolomite.

Homoclines, composed of more resistant sandstones and carbonates, are separated by less steep slopes comprised of shales and/or friable sandstones. Rock units strike generally from the north to northeast and dip gently, about 40 feet per mile, to the west and northwest (Marcher and Bingham, 1971).

Faults, both normal and reverse, are present throughout the Verdigris Basin. En echelon faults occur in abundance in Osage County. They are mainly normal faults that trend northeast or northwest and are two to three miles long. Fault displacement is usually less than 100 feet, commonly about 50 feet. Displacement decreases with depth and probably does not extend below Pennsylvanian Rocks (Levorson, 1928).

Hominy Creek Basin

Lithologic units that are exposed at the surface in the Hominy Creek Basin are shown in figure 3.

Alluvium and Terrace Deposits

Quaternary alluvium and locally exposed terrace deposits are present immediately adjacent to major streams and tributaries. Constituents are unconsolidated gravel, sand, silt and clay present as distinct, heterogeneous, commonly discontinuous beds of variable thickness.

Vanoss Group

The Vanoss Group, in the eastern portion of the study area, is comprised of alternating layers of limestone and shale. Thin coal seams may occur locally. The Vanoss Group occurs in the easternmost portion of Hominy Creek Basin.

Ada Group

The Ada Group, which immediately underlies the Vanoss Group, is composed predominantly of shale with numerous fine-grained sandstones and limestones. It crops out just west of the Vanoss Group.

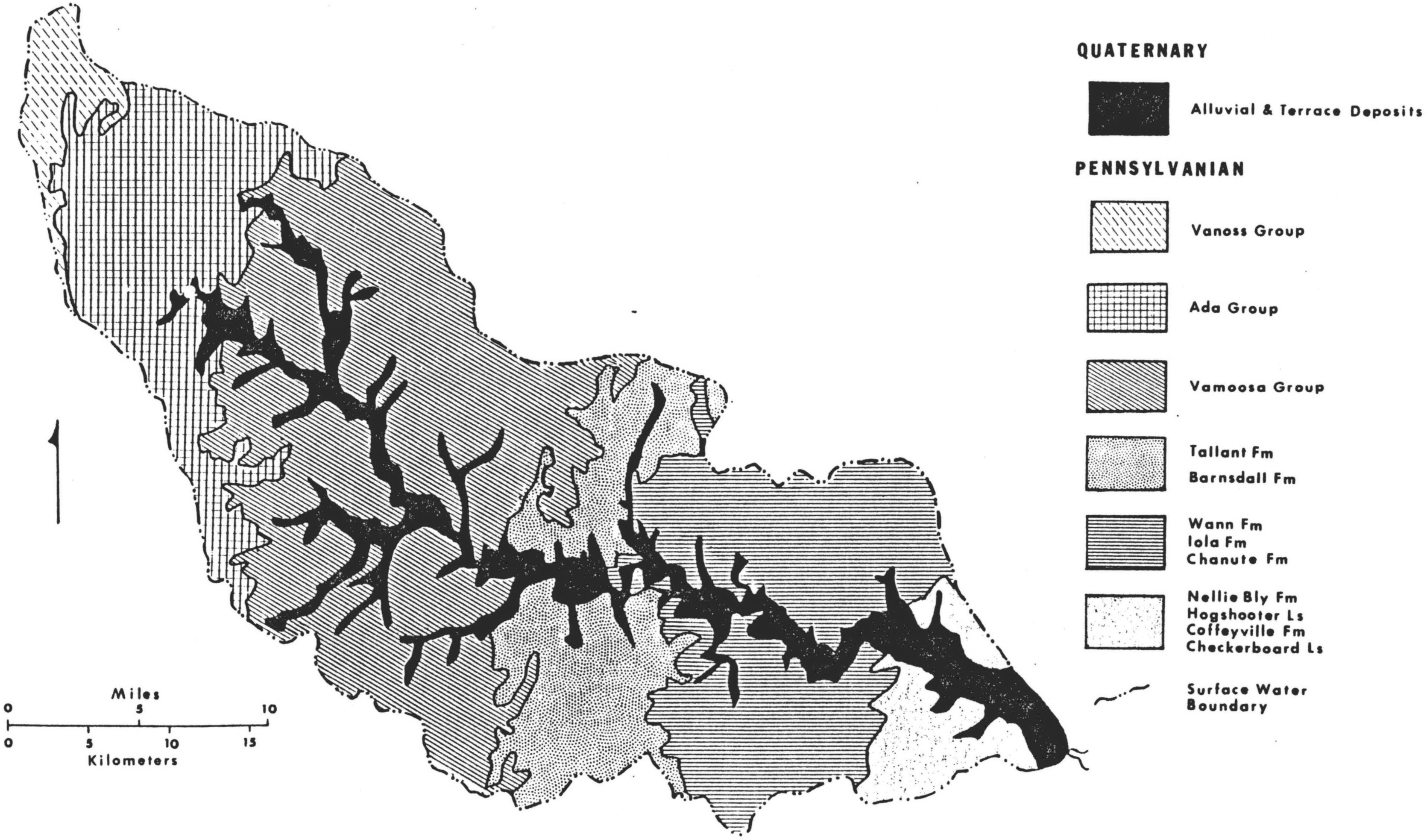


Figure 3. Rock Units that Crop Out in Hominy Creek Basin

Vamoosa Formation

The Vamoosa Formation occurs at the surface in the central portion of Hominy Creek Basin. It is comprised of alternating beds of fine- to coarse-grained sandstone, shale and thin limestone.

Tallant and Barnsdall Formations

Immediately underlying the Vamoosa Formation are the Tallant and Barnsdall Formations. They are lithologically similar but are separated by a thick shale unit at the top of the Barnsdall. The Tallant is composed of fine- to medium-grained sandstone with interbedded shale, whereas the Barnsdall is comprised of primarily fine- to medium-grained sandstone beneath a thick shale unit.

Wann Formation, Iola Limestone and Chanute Formation

The Wann Formation and Iola Limestone, grouped with the Chanute Formation, underlie the Barnsdall Formation. The Wann Formation consists of fine- to medium-grained sandstone and shale with numerous thin beds of fossiliferous limestone. The underlying Iola Limestone consists mainly of limestone, calcareous sandstone and shale. The Chanute Formation consists of predominately fine-grained, micaceous sandstone and coarse-grained, cross-bedded sandstone separated by shale. Thin coal seams occur locally.

Nellie Bly and Hogshooter Formations

The Nellie Bly Formation consists of predominately shale with several beds of fine- to medium-grained sandstone. The underlying Hogshooter Limestone consists wholly of massive crinoidal limestone.

Coffeyville and Checkerboard Formations

The Coffeyville Formation, underlying the Hogshooter, is comprised of predominately shale with interbeds of fine- to medium-grained sandstone. Thin coal seams occur locally. Beneath the Coffeyville is the Checkerboard Limestone. It is composed of variably-crystalline limestone.

Oolagah Reservoir Area

Lithologic units that crop out in the Oologah Reservoir Area are shown on figure 4.

Alluvium and Terrace Deposits

Alluvium and terrace deposits, Quaternary in age, are adjacent to major streams and tributaries, overlying Pennsylvanian strata. Their lithologic composition has been previously described.

Coffeyville, Checkerboard, and Seminole Formations

The Coffeyville and Checkerboard Formations occur

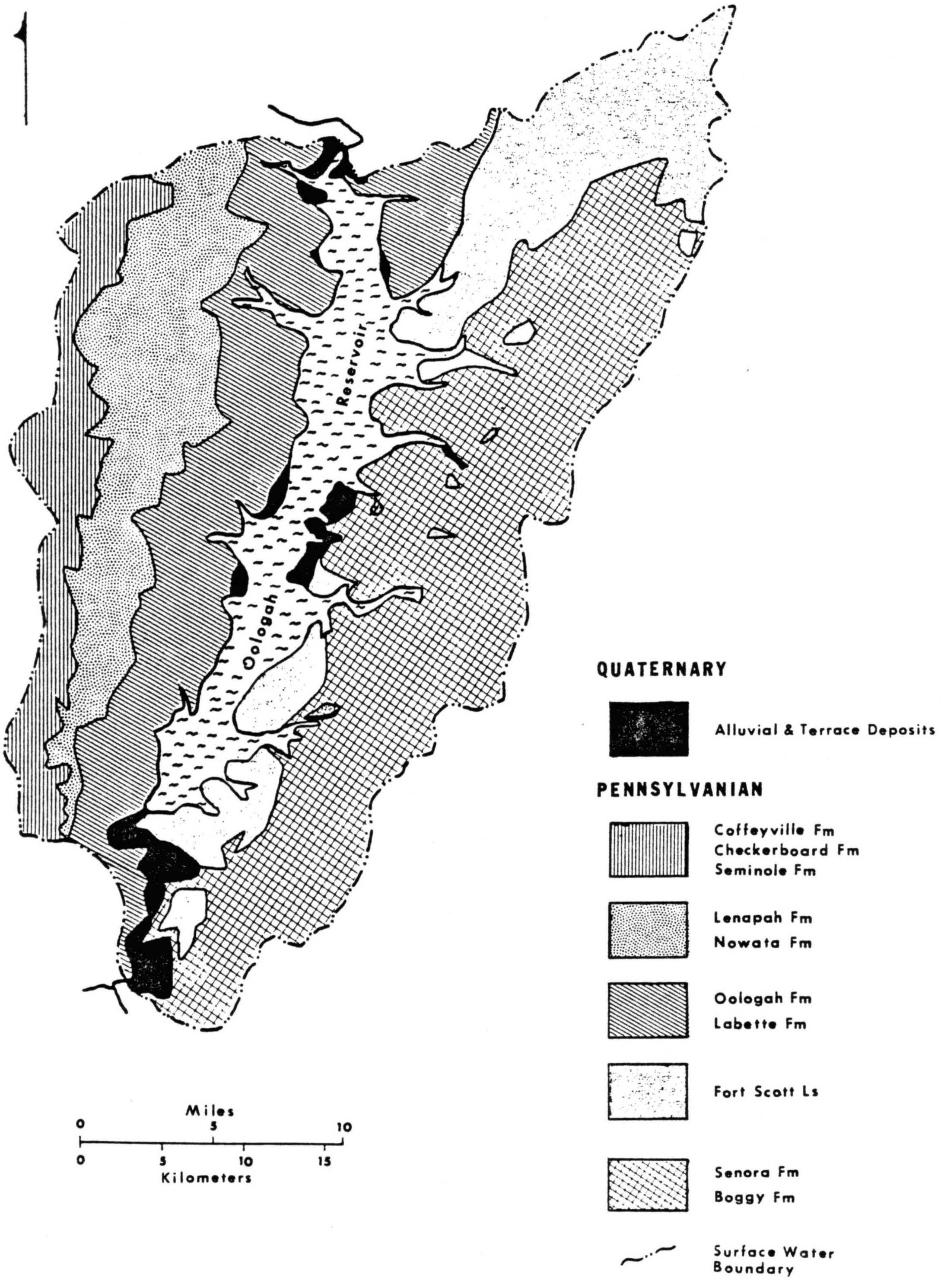


Figure 4. Rock Units that Crop Out in the Oologah Reservoir Area

near the western border of the study area. Lithology and ground-water quality has been described in the previous section. Underlying the Checkerboard Formation is the Seminole Formation which contains sandstone, shale and thin coal seams.

Lenapah and Nowata Formations

The Lenapah Formation underlies the Seminole Formation. It consists of limestone and shale. The Nowata Formation contains shale and minor sandstone and limestone. It occurs stratigraphically between the Lenapah and underlying Oologah Formation.

Oologah and Labette Formations

The Oologah Formation primarily consists of thin-bedded limestone with minor shale. Rock units that are grouped here and crop out in western Rogers County include the Altamont Pawnee, and Bandera Formations. Limestone with minor shale comprise the Altamont and Pawnee Formations, while the Bandera Formation is composed of shale and thin sandstone. Underlying the Oologah Formation is the Labette Formation. It consists of shale and thin sandstone and limestone.

Fort Scott Limestone

The Fort Scott Limestone, which underlies the Labette Formation, is comprised of limestone and shale. It overlies the Senora Formation.

Senora and Boggy Formations

The Senora Formation contains primarily shale and thin lenticular sandstone with minor limestone and coal. The Chelsea Sandstone Member occurs near the Senora base in Rogers, Craig and Mayes Counties. The Boggy Formation occurs immediately below the Senora Formation and crops out near the east boundary of the study area. It is comprised of shale, sandstone and coal. The Bluejacket Sandstone Member is located near the base of this rock unit.

Occurrence of Coal

In the Oologah Reservoir Area six important coal seams occur (figure 5). Each of these are commercially mined currently or have been in the past. The type of coal is high sulfur bituminous and can be high in volatility (Friedman, 1974). Each coal bed is presented below in stratigraphic order, from top to bottom.

Dawson Coal

The Dawson Coal occurs near the base of the Seminole Formation, just west of Fourmile Creek, being exposed in abandoned mines. Thickness varies from 1.5 to 2.8 feet. Sulfur content ranges from 3.4 to 4.8 percent.

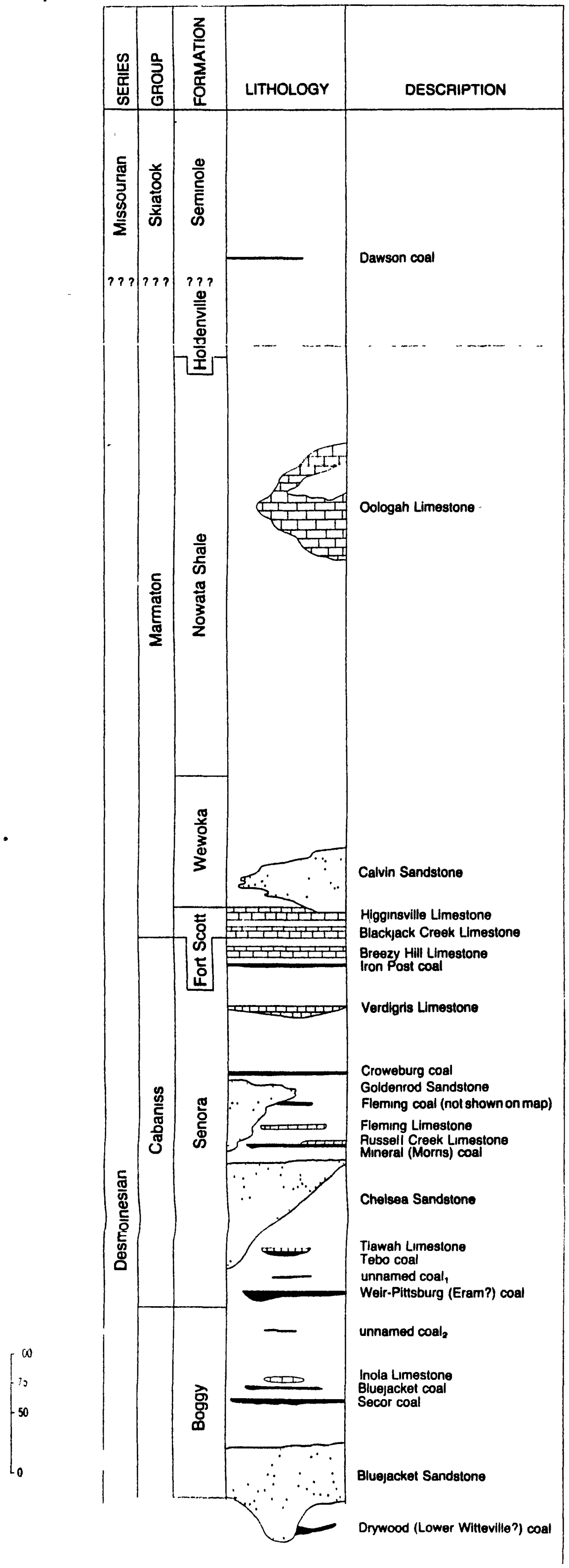


Figure 5. Stratigaphic Position of Coal Seams (from Friedman, 1984)

Iron Post Coal

The Iron Post Coal occurs near the top of the Senora Formation. It is from 1.0 to 1.4 feet thick and is overlain by 30 to 45 feet of overburden. The overburden consists (in descending order) of dense limestone, dark-gray shale, dense, massive limestone, and dark gray shale with pyrite. Sulfur content of the coal varies from 3.5 to 5.0 percent.

Croweburg Coal

The Croweburg coal occurs as a bed from 1.0 to 3.4 feet thick in the upper middle Senora Formation. Sulfur content varies from 0.4 to 3.5 percent, and is less than 1.0 percent at exposures in strip pits in Wagoner and Rogers Counties. Overburden is from 40 to 75 feet thick, and consists of (in descending order) a shale and thin limestone unit, thick gray shale, and thin black shale.

Mineral Coal

The Mineral coal is from 1 to 2 feet thick and occurs in the lower-middle Senora Formation. Sulfur content ranges from 3.5 to 4.7 percent, and averages 4.5 percent.

Weir-Pittsburg Coal

The Weir-Pittsburg coal occurs near the base of the Senora Formation. Sulfur content varies from 4.5 to 5.4 percent, averaging 4.8 percent. Thickness datum is not available (Friedman, 1974).

CHAPTER III

HYDROGEOLOGY

Previous Studies

Most of the hydrogeological studies of the Verdigris basin contain compilations of existing information by the U. S. Geological Survey and cooperating agencies. Information collected by these agencies consists of precipitation hydrographs, stream discharge hydrographs, ground-water level measurements, and chemical analyses of ground- and surface waters (Marcher and Bingham, 1971; and Bingham and Bergman, 1980).

Fader and Morton (1975) described the occurrence, uses, and general water quality of ground water using existing analyses of the streams in the Verdigris Basin in Oklahoma and Kansas.

Geohydrology and general water quality of the Vamoosa-Ada aquifer, located in the western one-third of the Verdigris Basin, was done by D'Lugosz and others (in press). They reported the analyses of major ions and bromide from selected wells and streams. Bromide analyses, however, were not done on all the samples.

Tanaka (1972) studied the geohydrology of the lower

Verdigris River between Catoosa and Muskogee, Oklahoma. Aquifer tests were conducted, monitoring wells were constructed, core samples were analyzed, and the composition of ground water determined throughout the study area. No studies have been done of the Verdigris Basin relating the natural ground-water composition, mineralogy or geochemistry of the sources of the contamination.

Hydrologic Cycle

The climate of the Veridgris Basin is continental, subhumid. Average annual precipitation ranges from 36 to 41 inches, from west to east, respectively, across the Basin; mean daily temperature in January varies from 30 to 32 degrees F. from north to south, and in July is about 80 degrees F. across the Verdigris Basin (Pettyjohn and others, 1983). The climate data are based on a 10 year period, 1970 to 1979.

Precipitation is the primary source of recharge to aquifers in the Verdigris Basin. The effective regional ground water recharge rate, during the period 1970 to 1979, ranges from 2 inches in the western third to about 5 inches in the eastern third of the Verdigris Basin (Pettyjohn and others, 1983).

Average annual runoff is about 10 inches immediately north of the confluence of Bird Creek and Verdigris River, increasing northwestward to about 5 inches near the headwaters of Caney River, Sand, Bird, and Hominy Creeks

(Pettyjohn and others, 1983).

Perennial streams, or those in which ground-water flow is supplied throughout the year, are located in major alluvial valleys include the Verdigris and Caney Rivers; and the Sand, Bird, Hominy, Big, and Dog Creeks. Tributaries to the perennial streams are intermittent. The smallest streams are generally ephemeral and here stream flow is limited to surface runoff.

Evapotranspiration depletes soil moisture significantly during the summer and early fall, and lowers the water table if it is near land surface. Average annual evapotranspiration, during the period 1970 to 1979, was about 30 inches throughout most of the study area, although it increased to 32 inches in western Nowata and Rogers Counties (Pettyjohn and others, 1983).

Alluvial and Terrace Aquifers

Alluvial aquifers provide generally good (less than 500 mg/l total dissolved solids) to fair (500-1000 mg/l T.D.S.), although it is often hard (121-180 mg/l as CaCO3) (Tanaka, 1972; Fader and Morton, 1975).

Water type in the lower Verdigris alluvium and terrace deposits (between Catoosa and Muskogee) is generally calcium-magnesium-bicarbonate (Tanaka, 1972). It is suitable for irrigation and livestock uses and potentially for domestic use after purification and/or softening. Maximum values of sulfate and chloride that occur can represent local or temporary conditions. Ground water may be contaminated by seepage from underlying rocks, or as a result of man's activities.

The ground-water table occurs in the lower Verdigris alluvium lies 17 to 33 feet below the land surface and saturated thickness varies from 0 to 47 feet (Tanaka, 1972). Water-level fluctuations vary from 1 to 5 feet throughout the year due to seasonal changes in recharge and discharge. Long-term fluctuations of as much as 10 feet occurred over an 8 year period (Tanaka, 1972). The occurrence of ground water in alluvium associated with perennial streams is probably similar to that observed by Tanaka (1972).

In the lower Verdigris River alluvium, three aquifer tests were conducted (Tanaka, 1972) over a 72 hour period, which indicated a transmissivity of 1400 to 12,000 gallons per day per foot, and a storativity of 0.026 to 0.030. The saturated thickness of the alluvium where these aquifer test were done ranged from 12 to 19 feet. Therefore, the hydraulic conductivity ranged from 115 to 800 gallons per day per square foot. Yields in most areas underlain by alluvium were 1 to 10 gallons per minute, increasing to 30 gallons per minute in areas where the proportion of gravel to fine particles increases (Tanaka, 1972). Coarse sand and gravel, near the base of the alluvium, as much as 20 feet thick and averages about 5 feet in thickness (Tanaka, 1972).

Alluvium associated with the ephemeral and intermittent tributaries is, in general, commonly finegrained and of low transmissivity.

Vamoosa-Ada Aquifer

The Vamoosa-Ada aquifer is consists of the Ada Group which is underlain by and in hydrologic connection with the Vamoosa Formation. The Vanoss Group, which overlies the Ada forming an aquitard, confines the Vamoosa-Ada aquifer where it occurs.

The Vamoosa-Ada aquifer is the only major non-alluvial aquifer in the Verdigris Basin. It is located near the headwaters of Hominy and Bird Creeks, and Caney River. The Vamoosa Formation contains generally less then 500 mg/l dissolved solids, whereas the Ada Group generally contains 500 to 1000 mg/l of dissolved solids (D'Lugosz and others, 1985). Locally dissolved solids may deviate from these values.

Transmissivity, based on aquifer tests in the confined portion of the Vamoosa-Ada aquifer, range from 70 to 3660 gallons per day per foot, decreasing to the north with decreasing saturated thickness (D'Lugosz and others, 1985). Storativity values vary from 0.0001 to 0.003, averaging 0.002 for the confined portion. Hydraulic conductivity for all aquifer tests was 15 to 30 gallons per day per foot square. Specific yield is determined to be 0.12 (D'Lugosz and others, 1985).

Sodium bicarbonate or sodium calcium bicarbonate type ground water represents 75 percent. The remaining 25 percent is represented by sodium sulfate, calcium sulfate, sodium chloride or intermediate types, based on 55 chemical analyses (D'Lugosz and others, 1985).

Calcium and magnesium decrease with depth, while sodium, bicarbonate, sulfate, and dissolved solids increase with depth. Chloride is nearly constant with depth and concentrations exceeding 250 mg/l represent 10 percent of 83 samples (D'Lugosz and others, 1985).

Contamination of ground water by brines has occurred in some areas of the Vamoosa-Ada aquifer; however, bromide data from brines and ground water is not available,hence the relation between Br in fresh water and brines cannot be determined (D'Lugosz and others, 1985). Trace element concentrations do not exceed the 1976 U.S. Environmental Protection Agency's mandatory limit for municipal supplies (D'Lugosz and others, 1985).

Pennsylvanian Rocks

The quality of ground water from Pennsylvanian rocks, other than the Vamoosa Formation is generally good at shallow depths, however, as well depths increase, the water contains higher dissolved solids (Fader and Morton, 1975).

Forty-eight chemical analyses of water from

Pennsylvanian sandstone, shale and limestone and Upper Mississippian shale and limestone, from the Tulsa Quadrangle were summarized by Marcher and Bingham (1971). Total dissolved solids of more than 500 mg/l were contained in 62 percent of the samples. Twenty-seven percent of the samples contained more than 250 mg/l sulfate and the maximum analyzed was 2090 mg/l. Twenty percent of the samples contained more than 250 mg/l chloride, and the maximum analyzed was 1520 mg/l. Hard (121-180 mg/l as CaCO3) or very hard (more than 180 mg/l as CaCO3) water was present in 72 percent of the samples. Nitrate was more than 45 mg/l in three samples.

Forty-two chemical analyses from water in Pennsylvanian Rocks other than the Vamoosa Formation, in the Enid Quadrangle, were summarized by Bingham and Bergman (1980). The total dissolved solids content (residue on evaporation at 180 degrees C.) was over 636 mg/l in 50 percent of the samples. Twenty-five percent of the samples contained more than 200 mg/l chloride and/or 150 mg/l sulfate. The maximum concentration analyzed was 618 mg/l chloride and 2740 mg/l sulfate. More than 50 percent of the samples contained very hard water. Nitrate concentrations exceeded 20 mg/l in twenty percent of the samples.

Storativity is more then 0.001 for unconfined, near surface conditions. For confined conditions it probably ranges from 0.0001 to 0.000001. Transmissivity is believed to be less then 20,200 gallons per day per square foot (Fader and Morton, 1975). Yield of good quality water from shallow wells near the surface is less then 10 gallons per minute (Fader and Morton, 1975).

CHAPTER IV

HYDROGEOCHEMISTRY

Introduction

Chemical composition of natural waters not influenced by activities of man is influenced by climate, geology, biology, and time. Climate factors are temperature and precipitation. Mineralogy, porosity and permeability are the important geological factors. Microbial activities influence the chemical composition primarily by acting as catalysts in promoting the rate of reaction of certain equilibria, or by enriching or depleting certain ions or gases. Time is a very important factor. In near surface systems, the residence time of water in contact with minerals, amorphous oxides-hydroxides and organic matter is relatively short. Equilibrium of certain solids may not be attained. Hence, certain reactions can not reach equilibrium before surface or ground-water runoff reaches a point of discharge, because of reduced distance along flow lines. The thermodynamic approach may lead to a better understanding of natural water chemistry by establishing limits for which certain phases and species can exist under equilibrium conditions.

The chemical composition of natural waters reflects the mineralogical composition of the sediments and rocks the water passes through. Solutes input from precipitation are usually insignificant compared to their concentrations in ground water. However, precipitation and its composition are both variable in space and time.

Gases that react with moisture in the atmosphere are generally more soluble that those that do not react, and are least abundant. Abundant atmospheric gases include oxygen, and dioxides of carbon, nitrogen and sulfur. Junge and Werby (1958) observed trends in the chloride and sulfate content of rain relative to distance from the ocean. They found that the average chloride concentration in rainfall increases from a few tenths of a milligram per liter inland to several milligrams per liter toward an ocean. Sulfate concentations, on the other hand decreases as one approaches the ocean, increasing inland to between 1 and 3 mg/l. However, sulfate concentrations inland may locally exceed 10 mg/l in industrialized areas. These levels may or may not be significant when compared to concentrations observed in some ground-waters.

Surface runoff is in contact with the soil and upper unsaturated zones for a limited duration. Suspended silts and clays, organic matter and clay-organic complexes are carried with the water with solutes. The time it takes for surface runoff to reach a nearby stream or lake depends on precipitation intensity, duration, and aerial extent; relief and topography; permeability of materials the water passes through; and the relationship of soil moisture to field capacity.

In the saturated zone, ground-water is in contact with geologic materials and equilibrium may be attained for certain phases. Chemical composition is also influenced by mineral properties such as crystal structure, crystalline form, purity, and most important, solubility. With increased depth in a ground-water system: temperature increases, mineral-water contact time increases, flow paths increase, and as expected the dissolved solid content also increases. The effect of temperature is not important except at several thousand feet in depth (depending on the geothermal gradient) where higher temperature leads to increasing solubilities and dissolution rates of most inorganic substances.

Phenomena which influence the chemical composition of ground and surface waters include the following: membrane effects of shale, adsorption/desorption, and reactions of solution/precipitation, reduction/oxidation and ion exchange.

Shales act as semipermeable membranes where they separate waters of significantly different chemical compositions. Water molecules, but not large ions pass through the shale. This is osmosis. Some shales may allow only certain ions of smaller ionic radii to pass through. This effect is known to occur because of the difference in potential between sandstones and shales as indicated by the spontaneous potential curve.

Adsorption is simply the attraction of molecules or ions to the surface of a solid. It results from an affinity of the solute for the solid, or lack of affinity of the solute for the solvent (Weber, 1972). An affinity of the solute occurs as a result of exchange adsorption, physical adsorption, or chemisorption (Hounslow, 1983). These occur at the liquid-solid interface. Lack of affinity of the solute for the solvent simply occurs as a result of low solubility of the solute. With exchange adsorption, electrical charges at the surface of the solid attract oppositely charged ions from solution to the surface. Ions with higher charge and smaller radius are more strongly adsorbed. Hydrated radii must also be considered (Hounslow, 1983). Chemisorption is bonding that occurs at specific sites on the adsorbent surface. Physical adsorption results from van der Waals forces which results from fluctuations in electron distributions producing instantaneous dipoles (Hounslow, 1983). Adsorption/desorption reactions are reversible. Water molecules do not participate in these reactions except to form hydrated sheaths around charged ions.

Sulfate ions in natural waters are weakly adsorbed because of low charge densities and large ionic radii. Chloride has a lower electron charge and smaller ionic radii then sulfate. However, the ionic radius of chloride is considerably larger then other common ions in ground water (Hem, 1970). Thus chloride is not involved in adsorption or ion exchange reactions, is not a nutrient for bacteria and is therefore an excellent tracer for determining ground-water movement.

Ion exchange is the replacement of adsorbed ions by ions in solution. It occurs usually as a result of local unsaturation of chemical bonds within the mineral structure (Hem, 1970). Ion exchange approximately obeys the law of mass action. Sulfate and chloride anions are not attracted to clay minerals.

Solution and precipitation reactions are those which obey the law of mass action. Reversible reactions are those in which solution or precipitation can occur except at equilibrium where neither occurs. Common minerals which participate in reversible reactions include calcite, dolomite, anhydrite, gypsum and halite. However, a solution may be supersaturated with respect to a phase and precipitation not occur because of a lack of activation energy. Ion pairs or complexes may also interfere with the equilibrium by reducing the concentration of ions in the reaction. These effects can be compensated by using activity coefficients.

Irreversible reactions involve solution of a solid which results in a change in the chemical compostion and structure of the phase undergoing dissolution. Weathering of certain silicate minerals to clay minerals occurs by acid hydrolysis. Examples include chemical weathering of plagioclase to montmorillonite or kaolinite, and potassium feldspar to kaolinite. Ions are put into solution as a result of these reactions: calcium and sodium in the former, potassium in the latter.

The solubility product is an equilibrium expression for a solution of a certain compound. Instead of using the concentration of a mineral of concern, activity or the effective concentration is used. Activities take into account the effects of neutral ion pairs, or complexes containing a common ion. Ion activities and concentrations are essentially the same in dilute, natural waters where concentrations are below about 1000 mg/l total dissolved solids (Hem, 1970). The effects of ion pairs and complexes may be considered at higher ionic strengths.

Oxidation and reduction reactions involve a change in oxidation state of ions. Elements involved in redox reactions which occur under natural near surface and surface conditions include sulfur, iron and manganese. If bacteria are present and metabolically active, redox reactions are catalyzed as a result of their activities. Bacteria derive energy through release of electrons from these elements and increase the rate of reaction. If metabolically active bacteria are not present the rate of reaction is slow. Nutrients which may limit the activity of subsurface bacteria are organic carbon, oxygen, and perhaps the presence of some dissolved inorganic element which is necessary for metabolism.

Geochemistry of Sulfur

Under oxidizing conditions, sulfur found in natural waters is usually combined with oxygen as the sulfate anion. The valency of sulfur in sulfate is positive six. In reducing conditions the form of sulfur is sulfide and it is usually combined with hydrogen as dissolved hydrogen sulfide, or HS-. The valency of sulfur in sulfide is negative two.

Sulfur occurs as gaseous oxides or as a constituent in sulfide minerals. Pyrite (FeS2) is abundant under reducing conditions with available ferrous iron. In the presence of oxygen it is rapidly oxidized. It may also occur as a yellow amorphous coating of elemental sulfur. It is commonly associated with organic matter which probably serves as the principle source of sulfur and a possible source of iron. Other common sulfide minerals simply involve combination of sulfur at lower oxidation states with certain heavy metals depending on availability of the metal and the occurrence of reducing conditions.

Sulfate is the predominate ion containing sulfur (under oxidizing conditions). Common minerals which contain sulfate include gypsum (or anhydrite), and less common are insoluble barium and strontium sulfates.

Sodium sulfate is thought to have precipitated in some sediments deposited in former restricted marine basins in arid or semiarid climates.

Chemical reactions involving solution or precipitation of sulfur involve saturation or undersaturation with respect to gypsum.

Reactions involving sulfur oxidation or reduction may proceed and form more rapidly at slow rates or at faster rates when by bacteria. Nonequilibrium forms of sulfur may remain for long periods of time because of the slow kinetics of the chemical reaction (Hem, 1970).

Sulfur species present in reducing environments are also pH dependent. Hydrogen sulfide exists primarily below neutral pH, and dissolved HS- predominates above pH 7.0. In uncommonly high alkaline waters, sulfur may be present with a valency of minus two. Waters in contact with sulfide minerals, in reducing environments, usually contain usually contain H2S or HS- depending on the hydrogen activity.

Hydrogen sulfide gas can be detected in water with only a few tenths of a milligram per liter by a distinctive "rotten egg" odor. Sulfides are usually present in low concentrations in natural waters because precipitation usually takes place within short distances from sources (Hem, 1970).

Bisulfate ion (HSO4-) constitutes a considerable part of the total sulfate concentration below pH 3.9. Further, it predominates below pH 1.9. Exact calculation of bisulfate may be done if the following variables are available: pH, ionic strength, and total sulfate concentration. Hem (1970) stressed that total sulfate may be difficult to determine because of interference by ion pairs, possibly sulfates of sodium or calcium. As the sulfate concentration increases, so does the amount of sulfate locked up in ion pairs. Divalent and trivalent cations form strong complexes with sulfate (Hem, 1970). The influence of ion pairs may be predicted through thermodynamic data.

Sodium chloride brines affect the solubility of calcium sulfate. The effect is through ionic strength and the presence of ion pairs. The influence of insoluble barium or strontium sulfates which remove sulfate from solution usually is unimportant. Low sulfate concentrations in aquifers may result from bacterial reduction of sulfate in anaerobic zones.

Petroleum associated with brines contains several hundred milligrams per liter dissolved hydrogen sulfide (Hem, 1970). Bacterial reduction of sulfate requires the presence of organic matter which is supplied by hydrocarbons. Methane produced by the respiration of active anaerobic bacteria, using carbon dioxide as a source of carbon, is stable within the stability field of reduced sulfur species (Hem, 1970).

Sulfate is transported to surface water bodies by surface and ground-water runoff. Removal rate usually lags behind the rate at which sulfate is produced in near-surface aquifers. Solutes are removed as rapidly as they are formed; Concentrations are diluted by infiltrating rainwater.

In coal mining areas where large amounts of rocks and sediments containing commonly pyrite are exposed to rapid oxidation. Weathering of pyrite is shown by the following equilibrium (redox) reaction:

$$FeS_2 + H_2O + 3.5(O_2) \Leftrightarrow Fe{+}{+} + 2H{+} + SO_4{=}$$

$$+$$

$$0.5(O_2) + 2H_2O \Leftrightarrow Fe(OH)_3 + 2H{+}.$$

Products generated under oxidizing conditions are hydrogen ions, sulfate and ferrous ions. If there is more dissolved oxygen present in the water then ferrous iron will oxidize and precipitate as ferric hydroxide and more Large amounts of sulfate may be mobilized by infiltrating rainwater and discharged to a nearby stream, pond or lake. If carbonates are present, the pH may be buffered to the usual range in natural water, 6 to 8. Hydrogen sulfide gas becomes oxidized to sulfur dioxide and further to sulfur dioxide in the atmosphere.

Geochemistry of Chloride

Chloride is the most abundant halogen in natural waters and is present as the chloride (Cl-) ion. All oxidized forms of chlorine are unstable in aqueous solution under conditions commonly encountered in natural waters (Hem, 1970).

Chloride anions are least abundant among major ions comprising common rock types. In igneous minerals, chloride is found in sodalite and rarely apatite. Major sources of natural chloride are from dissolution of halite present in large quantities in evaporite mineral deposits; connate water trapped in marine sediments during deposition; and atmospheric precipitation especially in the vicinity of an ocean.

Membrane effects of shales must be considered. Because the ionic radius of chloride is large it is usually not transmitted through relatively impermeable shales. However, sodium and chloride ions may remain concentrated in shale by removal of water from the shale through the process of osmosis. Calcium cations are exchanged for sodium cations at exchange sites on clay minerals because calcium is divalent whereas sodium is monovalent.

Chloride ions are relatively unreactive and mobile in natural waters. They do not participate in redox reactions, are not adsorbed significantly on mineral surfaces, do not form important complexes, do not form salts of low solubility, and are not involved in important biochemical reactions (Hem, 1970).

Natural waters saturated with respect to halite would contain about 121,000 mg/l sodium and 189,000 mg/l chloride (Hem, 1970). A ground water with a dissolved solid content this high would be called a brine.

Chemical Equilibrium Model

A chemical equilibrium (mass-balance) model WATEQF (Plummer et al, 1976) was used with the Debye-Huckle equation to suggest processes and origins of the ground-water composition. The saturation index, SI = log (ion activity product/equilibrium product), indicates waters at equilibrium (SI = 0), undersaturation (SI = -1), or oversaturation (SI = +1) with respect to mineral or amorphous phases. Molal concentration ratios, calculated by the model can also be used to suggest possible origins of dissolved constituents.

Chemical Analyses

Two chemical analyses of ground-water were selected to investigate the origin of dissolved constituents in the Vamossa-Ada aquifer in Hominy Creek Basin (table 1). Estimation of pH was done by taking the average of chemical analyses (WATSTORE) that occurred within the Hominy Creek Basin (Vamoosa-Ada aquifer) and at similar depths for the two selected analyses. Both analyses, with a cation-anion balance were less than three percent, were obtained within one day of each other (4-3 and 4-4-75). They were collected and analyzed by the U.S. Geological Survey (WATSTORE). Chemical analyses of runoff from

TABLE I

CHEMICAL COMPOSITION OF GROUND WATER FROM THE VAMOOSA-ADA AQUIFER

Well No.	Ca	Mg	Na	K	Cl	SO4	HCO3	Br	Fe
			(milligrams/liter)						
1	220	57	140	2.3	570	120	176	3.3	0.04
2	87	60	77	3.3	110	190	205	0.6	-
			(total millimoles)						
1	5.49	2.35	6.10	0.06	16.10	1.25	2.89	0.04	-
2	1.91	2.22	3.33	0.08	3.10	1.57	3.18	0.04	-

Well No.	T.(C.)	pH	total ionic sum (milligrams/liter)	Mg/Ca (moles)	$I \times 10^{-3}$
1	11	7.9	1410	0.43	29.22
2	17	8.0	733	1.16	16.34

streams were not used as input to the model because it was considered likely that mineral and amorphous phases would be undersaturated.

Location of well 1 is at the headwaters of a tributary of Nicicola Creek (figure 6). Chloride and sulfate are 570 mg/l and 120 mg/l, respectively. The well is 350 feet deep; water-level was at 85 feet below land surface when analysed (Havens, 1978).

Well 2 is located within the surface drainage of Sand Creek. Chemical analysis showed 110 mg/l chloride and 190 mg/l sulfate. Total depth of the well is 187 feet; depth to water was 96 feet when analyzed (Havens, 1978).

Mineral Equilibria

Mineral phases that are saturated in ground water from well 1 are aragonite, calcite, dolomite, and magnesite. Ground water in well one is oversaturated with respect to iron oxides and hydroxides: magnetite, hematite, goethite, maghemite, and amorphous ferric hydroxide. Common minerals that are undersaturated are halite, gypsum and anhydrite. Goethite, limonite, lepidocrocite are known to occur in the Vanoss Group (Steffans, 1980), which overlies the Vamoosa-Ada Aquifer.

Ground water from well two is saturated with respect to aragonite, calcite, and magnesite and oversaturated with respect to dolomite. Undersaturation occurs with

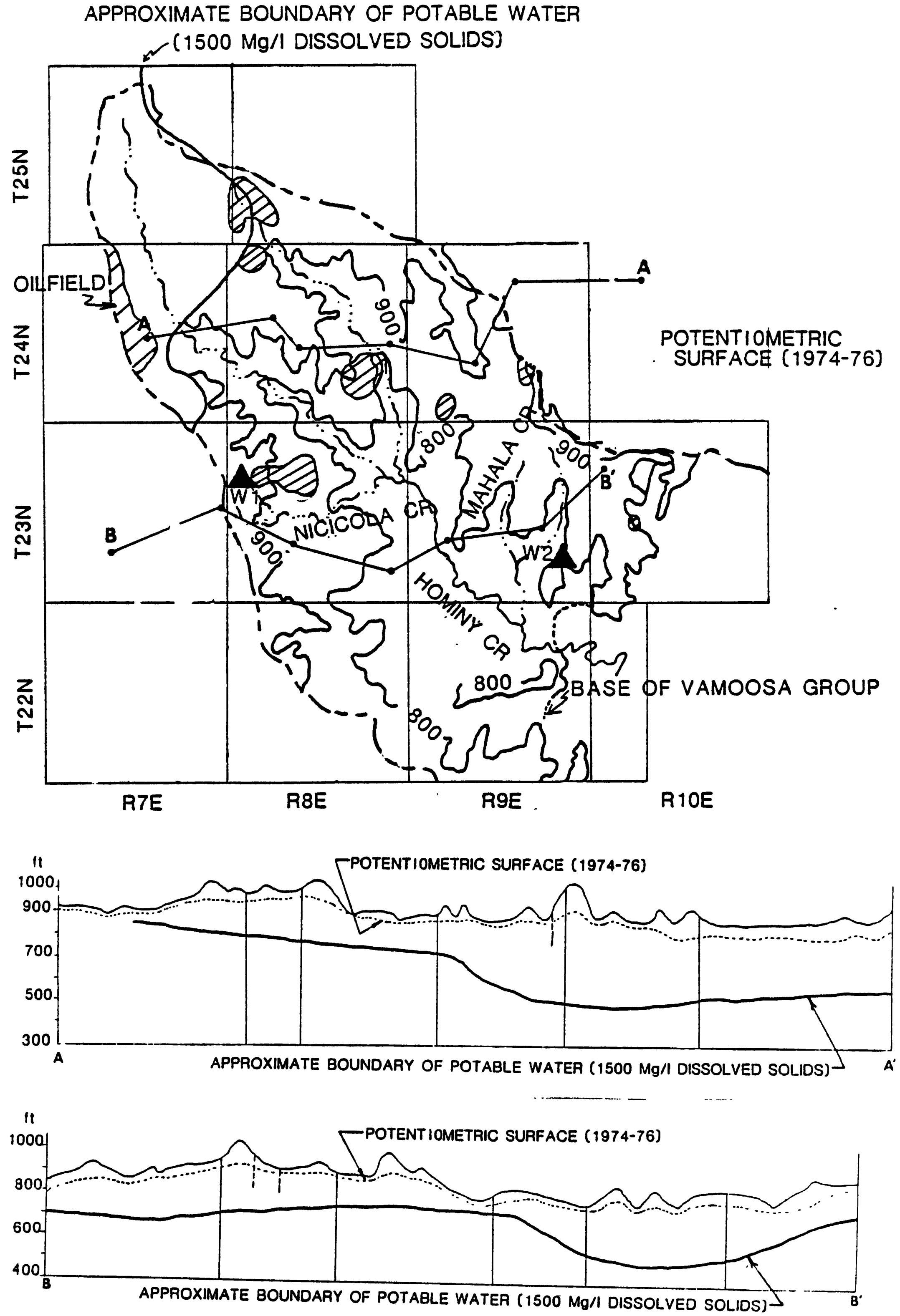


Figure 6. Potentiometric Surface and Aquifer Cross Sections of the Vamoosa-Ada Aquifer in Hominy Creek Basin

respect to the same minerals listed for well one. Chemical analysis of iron was not done for well two. Limestone is known to occur in the Vamoosa-Ada aquifer and the overlying Vanoss Group (Bingham and Bergman, 1980).

Comparison of Mineral Equilibria

Ground water from well one is contaminated with Cl- as a result of mixing of ground water with oil field brines. Concentrations of sodium (140 mg/l) and calcium (220 mg/l) in well one are high relative to well two (77 mg/l Na+; 87 mg/l Ca++). Halite, anhydrite (or gypsum) are not known to occur in rocks, in the study area, which are all Pennsylvanian in age.

Ground water from the Vamoosa-Ada aquifer is saturated with respect to calcite at both wells. With respect to dolomite ground water is saturated at well one, and oversaturated at well two.

Comparison of the Mg/Ca molar ratios shows an increase from well one (0.43) to well two (1.16), as a result of additional available Ca++ at well one. The Mg/Ca ratio may decrease because magnesium decreases, or calcium increases as a result of solution of calcium carbonate. The Mg/Ca ratio may increase because magnesium increases, or 2) calcium decreases by precipitation of calcium carbonate.

The source of calcium at well 1 is inferred to be oil field brine mixing with ground water in the Vamoosa-

Ada aquifer.

A possible mechanism that can account for the relatively low Mg/Ca molar ratio is reverse softening. Concentration (molar) of chloride is in excess of sodium and the difference is approximated by the additional calcium. This probably results from exchange of sodium ions in sodium-chloride brines for calcium ions at exchange sites on clay minerals (particularly montmorillonite) which depletes the solution in sodium and enriches it with calcium. Chemical analyses of sodium-chloride brines (Petroleum Data Systems) from oil wells within Hominy Creek Basin contain molar concentrations of calcium approximately equal to the molar concentration difference of chloride minus sodium, suggesting that reverse softening of the brine took place in the reservoir before sampling.

CHAPTER V

ACTIVITIES OF MAN

Introduction

Man's activities can influence the chemical composition of natural waters. Stream basins containing Hominy, Delaware, Fourmile, and Dog Creeks and streams that discharge into Oologah Reservoir from the east side will be discussed. These stream basins are selected because of the possible impact of coal mining and oil field activities.

Oil Field Activities

Introduction

The first oil well in Oklahoma was drilled in 1882 near an oil-seep along Spencer Creek in the Oologah Reservoir Area. Oil was first located at a depth of 36 feet; however, more oil was produced from a second well that was drilled to a depth of 86 feet (Ver Wiebe, 1957). Many of the earliest wells were drilled on the basis of occurrence of oil seeps. small domes and anticlines were used to located hydrocarbon production wells in Osage County during 1896-1906 (Ver Wiebe, 1957). The South

Burbank pool in Osage County, discovered in 1920, is an exception, however, in that it is independent of structure and is believed to be an offshore bar complex (Ver Wiebe, 1957). The most prolific zones that produced oil are the Burbank and Bartlesville of the Pennsylvanian System. En echelon faults appear to be of minor importance in determining the occurrence of oil where they occur in Pennsylvanian strata (Ver Wiebe, 1957).

Source of Information

The Oklahoma Corporation Commission, Resource Conservation Division, contains records of brine disposal wells, and secondary recovery wells which are available in notebooks for inspection. Data supplied by the OCC, are the following: well location, date of permit, depth of production and formation from which production occurs. Well fields that were delineated on figures were those 1) indicated on the Tulsa and Enid topographic (1:250,000 series) base maps, and well fields that were observed in the vicinity of streams that were sampled. Information was also made available by the Osage Indian Agency which has juristiction of oil field activities in Osage County.

Sulfur Content of Crude Oil

Sulfur analyses were done by Carrales and others (1975) on crude oil from fields in the Verdigris River Basin (Oklahoma) that produced more that 5000 barrels of oil in 1971. The sulfur content ranged from 0.12-0.29 weight percent. These are paraffinic (light) oils which, in general, contain essentially C- and H-compounds, other elements are minor (Collins, 1971).

Oil and Gas Fields

Oil and gas fields that occur throughout study areas are shown on figure 7.

Hominy Creek and Delaware Creek Basins

Production Zones

Production of hydrocarbons has occurred from certain zones at certain depths, and the information in this section is based on a geologic column for T.22N-23N, R.10-12E (BIA, 1985).

Pennsylvanian units from which there has been production are the Upper and Lower Cleveland Sand, Big Lime, Oswego Limestone, Red Fork, Bartlesville, and Burgess Sands. They are presented below in descending stratigraphic order.

Buzzard Formation produces oil and occurs above the Dewey Limestone about 600-800 feet below the surface and is 600 feet thick.

Upper Cleveland Sand and Lower Cleveland Sand occur in the Checkerboard Formation. Depth of the Coffeyville and Checkerboard Formations in townships 22N-23N and ranges 10-12E is 1150-1625 feet. Wells which have

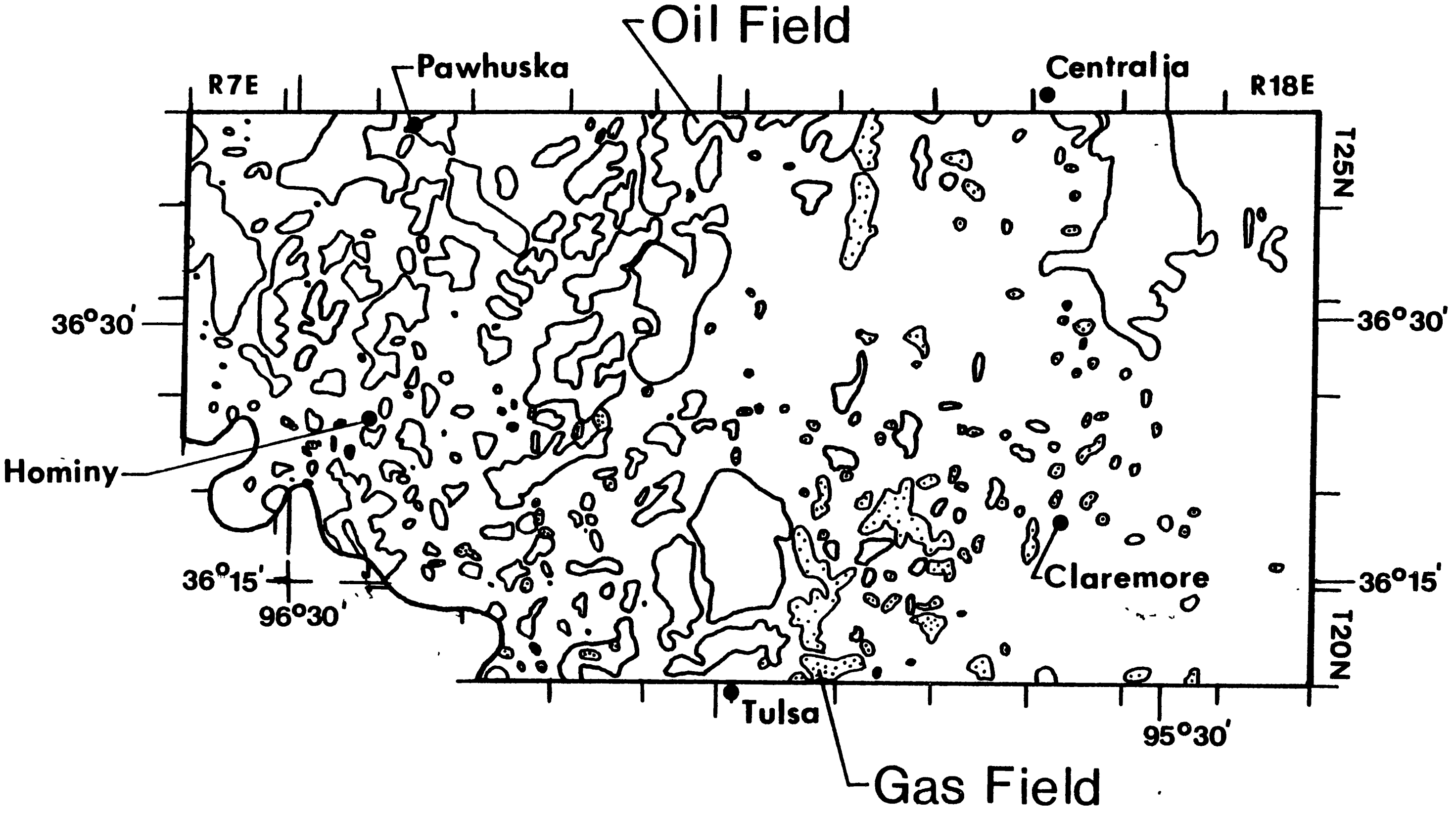


Figure 7. Oil and Gas Fields in the Verdigris River Basin

obtained oil from these units are concentrated in T.22N-R.10E, in south portions of sections 27-29, and north portions of sections 32-36.

Big Lime occurs in the Oologah Limestone, 1700-1850 feet below the surface.

Oswego Limestone occurs in the Fort Scott Limestone, 1900-2000 feet below the surface. Cherokee Shale occurs below Fort Scott Limestone, 2000-2450 feet below the surface and production was from three units: Red Fork Sand, Bartlesville Sand, and Burgess Sand. Wells that have produced from the Bartlesville Sand occur T.23N, R.10-12E.

Oil-field Brines

Sodium-chloride brines from oil wells located in Hominy Creek Basin ranged from approximately 82,000 to 138,000 mg/l chloride and from 0 to 150 mg/l sulfate, based on thirteen chemical analyses of oil-field brines Chemical analyses of brines is from Petroleum Data Systems.

Oil-field brines are injected into production zones as a means of secondary oil recovery. Most of the oil production in Osage County is currently by injection of brines (BIA, 1985).

Oologah Reservoir Area

Production of oil or gas has occurred in certain

Creek Basins in the Oologah Reservoir Area and in isolated areas of Dog Creek Basin based on indication by topographic maps and by observation during sample collection.

Panther Creek Basin

Oil wells were located in portions of the following areas: 1) T.25N, R.17E, sections 27, 28, 33, 34, and 36; and 2) T.24N, R.17E., sections 2 and 11. Wells used for secondary recovery (OCC, 1985) showed zones that receive injected fluids: 1) wells located in section 11 are perforated between depths 240-532 ft in the Bartlesville Sand, 2) a well located in section 2 is perforated at about 1325 ft in the Bartlesville, and 3) the Bartlesville Sand receives injected fluids between depths of 320-500 ft in T.25N, R.17E., sections 27, 28, 33, 34, and 36.

Spencer Creek Basin

Oil wells that are included in T.23N, R.17E, section 5 receive injected fluids between 350-400 ft in the Bartlesville Sand. Oil wells also occur in T.24N, R.17E, sections 21, 22, 27, and 29 as follows: Three wells used for secondary recovery were indicated in sections 21 at 440 ft, and in sections 22, at depths of 300-350 ft. They were all injecting into the Bartlesville Sand.

Sources of Pollution

Contamination of natural waters by oil field activities leakage occurs as follows (Collins, 1971; EPA, 1977): 1) from unlined pits or abandoned wells not designed to handle the induced injection pressures, 2) by direct discharge to streams, 3) by water flooding operations, 4) by vertical leakage through improperly plugged production wells, 5) by discharge from shallow wells directly into an aquifer, and 6) through contamination related to drilling activities by drilling fluids or additives.

Pipelines can leak brine by rupture (88% of all cases) by equipment failure or defective pipe seams; through external deterioration of pipeline casing; because of internal corrosion or improper operation by carrier personnel (EPA, 1977).

Contaminants Associated with Brines

The predominant contaminant is sodium chloride with calcium and magnesium sulfates and heavy metals are of lesser importance. Toxic elements include barium, lead, lithium, strontium, boron, bromine and iodine (EPA, 1977). Collins (1971) lists many organic compounds that may occur in drilling muds or fluids. Many organic compounds are toxic (Pettyjohn and Hounslow, 1983) in trace quantities and may impart undesirable odor and taste. If organic gases accumulate a fire or explosion can develop.

Acids that are used to improve permeability of reservoir rocks include sulfuric, hydrochloric, nitric, hydrofluoric, formic, and acetic. The last three, in order of increasing importance, are the most abundantly used for oil and gas well treatment (Collins, 1971).

Metals that are found in economic quantities in some brines include the following: Calcium, magnesium, potassium, bromine, iodide, boron, and lithium (Collins, 1971). The concentrations of metals depends mainly on the source rock, from which brine and oil are being produced.

Detection of Contaminants

Chloride contamination of water in Alum Creek Basin, central Ohio was done by a stream survey (Pettyjohn, 1975). Uncontaminated samples (36) from tributaries ranged 5-23 mg/l Cl- and averaged 13 mg/l. It was assumed that, based on these data any surface water sample beyond 25 mg/l was contaminated with Cl-. Streams were sampled on 5 occasions: November 12, 26; December 3, 22, 1972; and January 6, 1973. Contaminated water ranged 26-28000 mg/l Cl-. Samples collected from brine pits ranged 3,360-56,672 mg/l Cl-. All samples were diluted by an unknown factor by rainfall that occurred during the sampling period by extremely wet weather during sampling.

The sources of Cl- contamination were from seepage of oil-field brines into the tributaries or mainstem of Alum Creek, and by discharge of contaminated ground water into the streams.

In earlier studies in Ohio by Shaw (1966) and Boster (1967) (Pettyjohn, 1975) of ground water in oil-fields near the headwaters of Alum Creek. Concentration ranges of Cl-, based on 536 wells and test holes, were as follows: less than 25 mg/l (49%), 25-100 mg/l (46%), 100-250 (3.5%), and 250-3360 mg/l (1%).

Cyclic fluctuations of Cl- were documented (Pettyjohn, 1982) from monitoring of wells on the floodplain of the Olentangy River, west of Alum Creek. He showed that the unsaturated zone can store large quantities of soluble salts that can be introduced intermittantly for many years into a shallow aquifer. The main mechanisms leading to cyclic flutuations proposed by Pettyjohn were: 1) the vadose zone may contain water soluble substances in considerable volumes; and 2) fractures and macropores are the most important paths by which contaminants move from the vadose to the saturated zones.

Coal Field Activities

Sources of Information

Strip mining of commercially available coal is permitted under the jurisdiction of the Oklahoma Department of Mines. A list of active permits were provide by the ODM, which included the location and the maximum number of acres permitted to be mined. This is not an indication, however, that active mining has taken place. The Oklahoma Conservation Commission administers the Abandoned Mine Land Reclamation Program through local Conservation Districts. Inventory of abandoned lands took place during 1979-80.

Information made available were as follows: 1) copies of topographic quadrangles delineating areas of active mining, reclamation projects, partially and totally reclaimed land, abandoned strip mines, and problem areas currently under evaluation, 2) data sheets that are part of the National Inventory of Abandoned Mine Lands and list specific information about each problem area. Observations of mining and reclamation activities were also made and incorporated on copies of topographic maps. Photorevised topographic maps were also used. Fields that were strip-mined were delineated by Friedman (1982) on a map and this was used as a base map and modified using current photorevised topographic maps and information provided by the OCC (1985). Data given in this section is based on the information above.

Oologah Reservoir Area

Introduction

Creek basins in the Oologah Reservoir area, contained the following: 1) abandoned coal strip mines, 2) partially reclaimed coal mining areas, and 3) reclaimed coal mining areas. Problem areas are those of abandoned coal strip

1970: Spoils were reshaped, however, highwalls and pits were left.

Surface mining occurred at PA-11 in 1975 and all the spoil piles were reclaimed. Three strip-pits account for 27 acres and water is contained in the pits. Coal mining occurred in PA-12 in 1972-73. Spoils encompass 372 acres. Some gullies have formed on partially reclaimed spoils. Strip-pits represent about 75 acres in total. Strip-pits are about 40 ft deep and contained 7-15 ft of water.

Two large spoil areas encompass about 1140 acres at PA-13. Surface mining was done in 1972. Peaks were removed and pushed down the flanks of the spoil piles. Five strip-pits encompass 60 acres and are essentially continuous. Depth of the pits is generally about 35-40 ft. Trash was disposed in the pits.

Blue Creek Basin

Tributaries of Blue Creek show one problem area (figure 11). Problem area PA-14 was surface mined in 1960-62. Spoil piles are about 168 acres. Strip-pits encompass about 25 acres.

Dog Creek Basin

Six problem areas were identified (OCC, 1985) in Dog Creek Basin (figure 12). Surface mining occurred in 1956 at PA-15. Spoil piles are 30-35 ft high, 75-100 ft wide and encompass 380 acres. Strip pits are 35-60 ft deep and

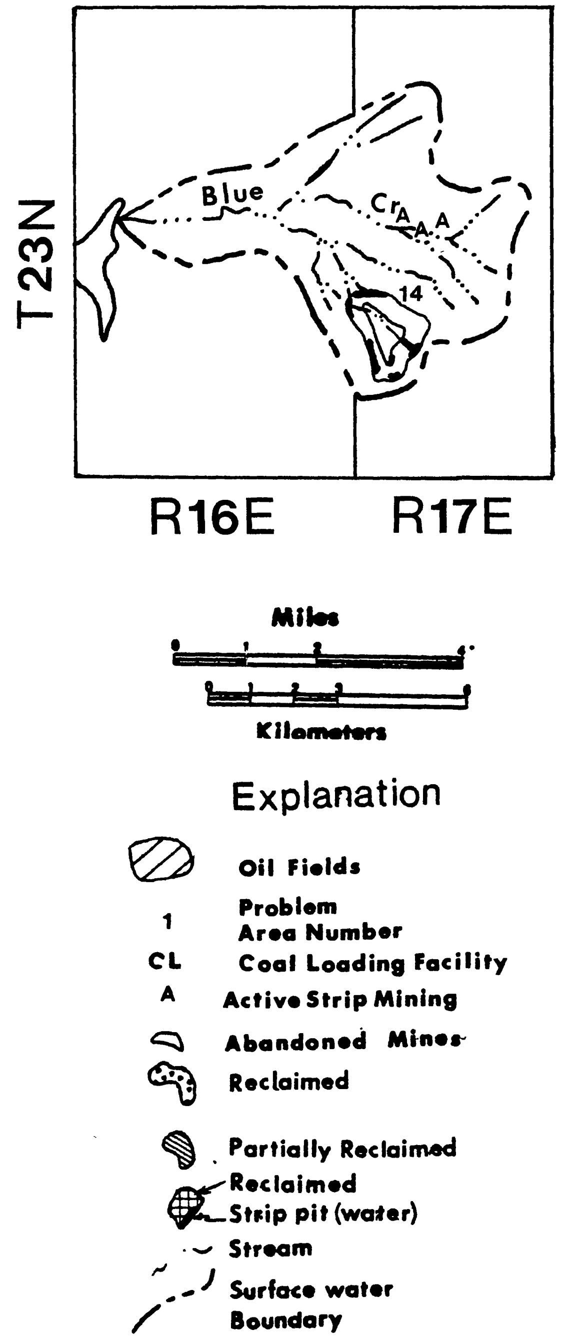


Figure 11. Coal Field Activities in Blue Creek Basin

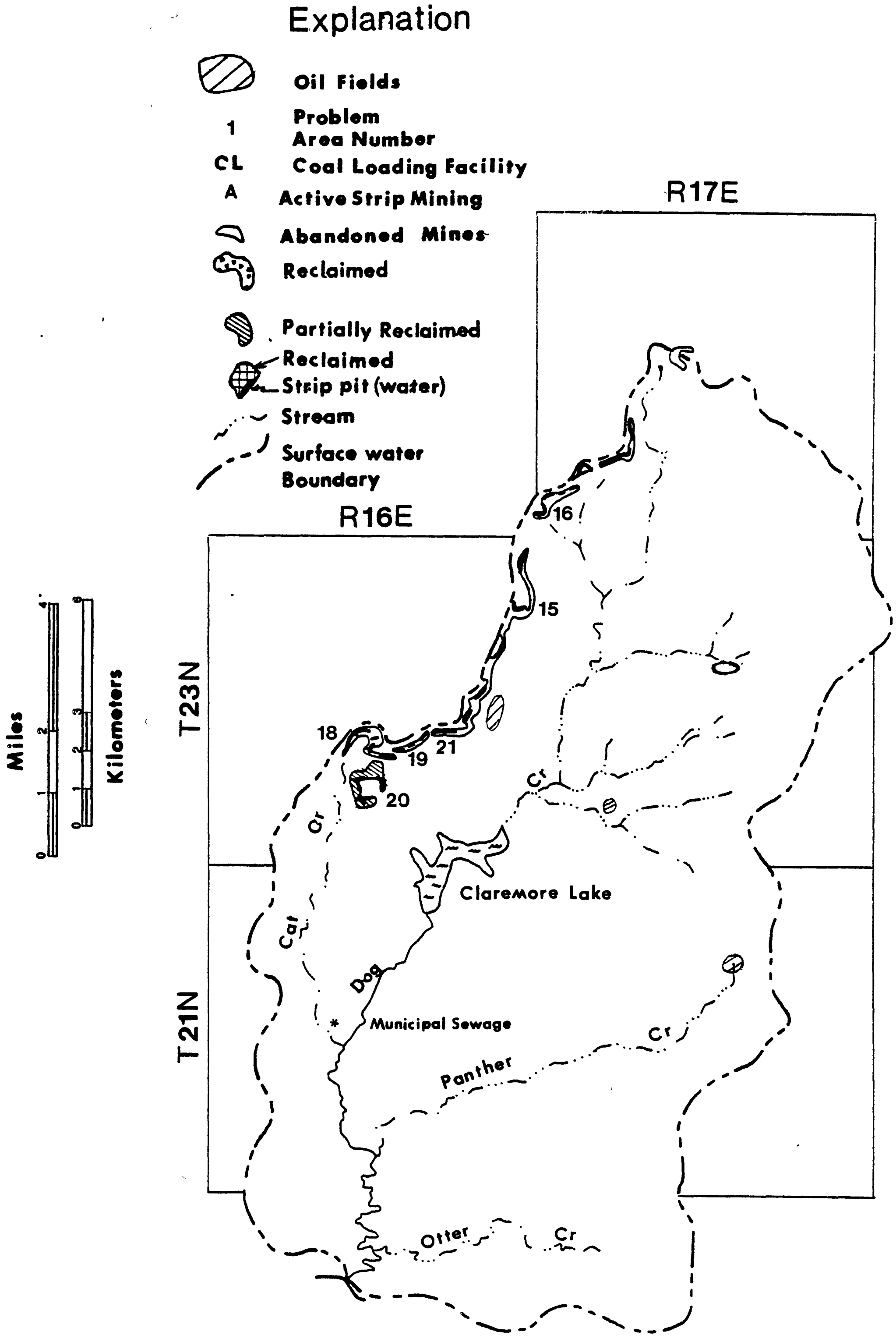


Figure 12. Oil fields and Coal Field Activities in Dog Creek Basin

contained trash. Runoff from a trash dump flows into pits which contain water.

Surface mining occurred in PA-16 during 1960-63. Tailing piles encompass 116 acres. Strip pits encompass 60 acres. Drainage from PA-16 is received by a tributary of Dog Creek.

Three problem areas (PA-18, 19, 20) are located at the headwaters of Cat Creek, a tributary of Dog Creek. Surface mining occurred at all three and only in 1951. Strip pits are 30-65 ft deep and mine spoils are at least 20-30 ft high and 75-100 ft wide at the base. Most spoil piles have steep that have been eroded in places and angular boulders from the overburden are commonly exposed.

Portions of PA-20 became a municipal landfill. Progression of the landfill was to the west into a pit containing water. Runoff discharges to Cat Creek.

In PA-21, coal was removed by strip-mining methods during 1951-52. Spoil piles are 57 acres in total. Spoils have been eroding since mining began. Two pits encompass 16 acres.

Effects and Detection of Contamination

Seepage from ponded waste is the most common mechanism for contamination, (EPA, 1977). Contamination can also occur from outflow from abandoned pits, which also may be a source of aquifer recharge. Percolation of rain or melt waters through mine tailings dissolves water soluble compounds present in the tailings. Test borings also provide conduits for contaminant waters to reach aquifers.

Reclamation of open pits by backfilling and grading do not prevent contamination (EPA, 1977) because the fill tends to be permeable and rainfall can infiltrate through waste material and become contaminated. Acid mine drainage can result in coal mining areas where pits are unlined, and the acid runoff is not buffered by bases present in the surrounding geologic materials.

Acid mine drainage in an abandoned coal strip mine in eastern Ohio (Pettyjohn, 1975) is characterized by low pH, and high concentrations of sulfate, hardness, iron, low bicarbonate and dissolved solids. Other pits were used to store municipal, industrial (including pickling liquors) and domestic wastes.

An example of possible recharge of wells from spoil banks in south-central Ohio is given by Studlick (1978). Strip mining occurred 1949-1966. Acid mine drainage from a nearby (50 ft) spoil pile infiltrated the water table and discharged into a 19 ft deep partially cased well. A hand dug well. Effects of acid-mine drainage from coal mining in Tom's Run drainage basin in northwestern Pennsylvania is described by Emrich and Merritt, (1968). Abandoned oil and gas wells provide hydrologic connection between the aquifers, allowing acid mine drainage to be transmitted to the aquifers. Drainage from coal mines at the headwaters of Tom's Run moves through wells downward to lower units, then move laterially and discharge from abandoned oil and gas wells or flowing iron-rich springs.

CHAPTER VI

VERDIGRIS RIVER BASIN AND HOMINY CREEK BASIN

Verdigris River Basin

Introduction

Major tributaries above the Verdigris River near Oologah were sampled during low flows on October 11, and streams in Hominy Creek Basin were selected for further sampling on October 19 because three locations at Hominy Creek contained more then 300 mg/l chloride, exceeding the 250 mg/l concentration limit for public drinking water recommended by the U.S. Environmental Protection Agency.

On November 4, 8, and 11, streams in Hominy Creek and Delaware Creek Basins were sampled further to locate sources of Cl- contamination and examine the dilution effects of rainfall on chloride and sulfate concentrations.

Rainfall

Chemistry of Rainfall

The National Atmospheric Deposition Program, organized in 1978, monitors stations surrounding the Verdigris Basin (NADP, 1985). The stations are located as follows: 1) Salt Plains National Wildlife Refuge, 2) Salt Plains Apiaries, Criner, Oklahoma, 3) Fayetteville, Arkansas, and 4) Farington Fish Hatchery, Kansas. The most recent rainfall chemistry isopleth map is that for 1982. The 1982 precipitation-weighted mean at Fayetteville is 0.15 mg/l chloride and 1.2 mg/l sulfate (figure 13).

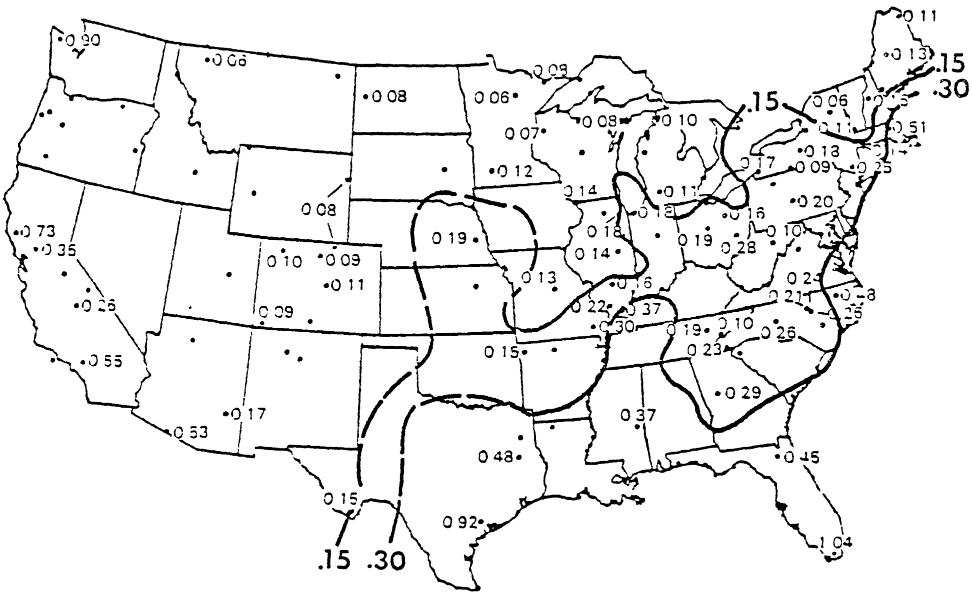
Precipitation chemistry from Salt Plains Apiaries, collected from rainfall that also occurred in the Verdigris Basin, during October through November showed that chloride and sulfate concentrations were both less than 1 mg/l (Fredrickson, 1985).

Rainfall

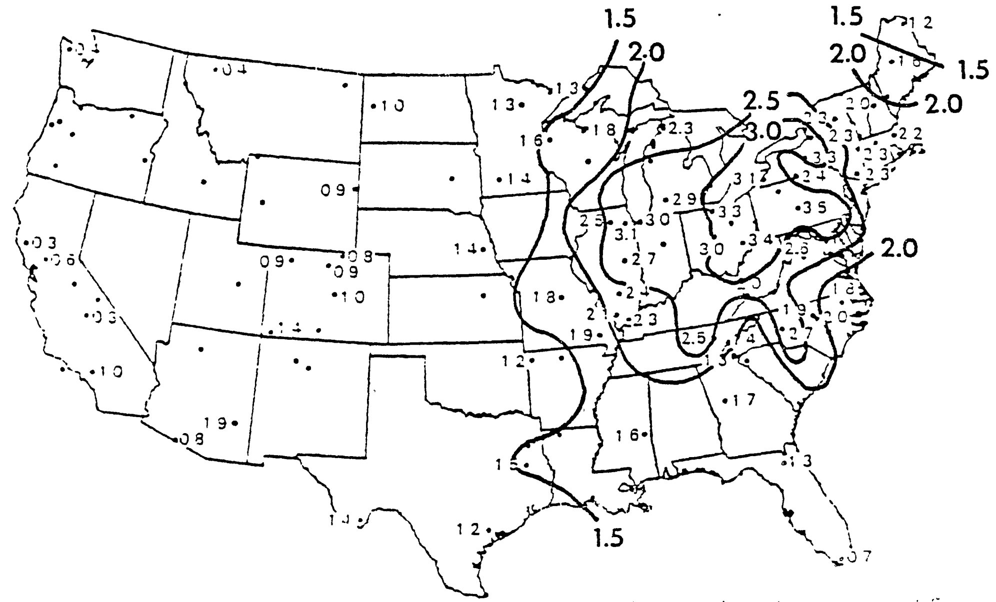
Rainfall is monitored at Hominy. Prior to sampling on October 11, during October, a total of 0.09 inches occurred at Tulsa (NOAA, 1984). Rainfall occurred between sampling on October 11 and 19 at Hominy (0.48 inches), which is the only station monitored by NOAA at Hominy Creek Basin.

Probability Graphs

Fifty-one chemical analyses of Cl- and SO4= were respectively plotted individually into cumulative frequency curves. Distinct populations were partitioned



1982 annual weighted mean chloride ion concentrations (mg/L).



1982 annual weighted mean sulfate ion concentrations (mg/L).

Figure 13. Precipitation-Weighted Mean of Chloride and Sulfate for 1982 (NADP, 1985)

from the curve and check points calculated based on the method of Sinclair (1981). Check points essentially fall on the curve, therefore, the populations that were partitioned are plausible. Thresholds were estimated at 2 and 98 percent, which effectively limit concentrations for each population.

Partitioning of the Cl- cumulative frequency curve is successful with two populations, A (29%) and B (71%) (figure 14). Attempts to partition the curve into three populations A:B:C (29:61:10) and (29:31:40); or four populations (29:31:30:10) did not allow better agreement of checkpoints with the cumulative frequency curve

The SO4= cumulative frequency curve is successfully partitioned into two populations, A (17%) and B (83%) at the major inflection point at 17 cumulative percent (figure 15).

Veridgris River Basin

Sources of Chloride

Anomalous Cl- concentrations (850-2200) mg/l, based on threshold limits, do not occur in any of the streams sampled in the Verdigris Basin on October 11 (figure 16), however, chloride anomalies do occur at four locations in Hominy Creek Basin on October 19 and are discussed in the next section titled "Hominy Creek Basin".

Chloride contaminated ground-water runoff occur in Verdigris Basin streams sampled that contain (160-850)

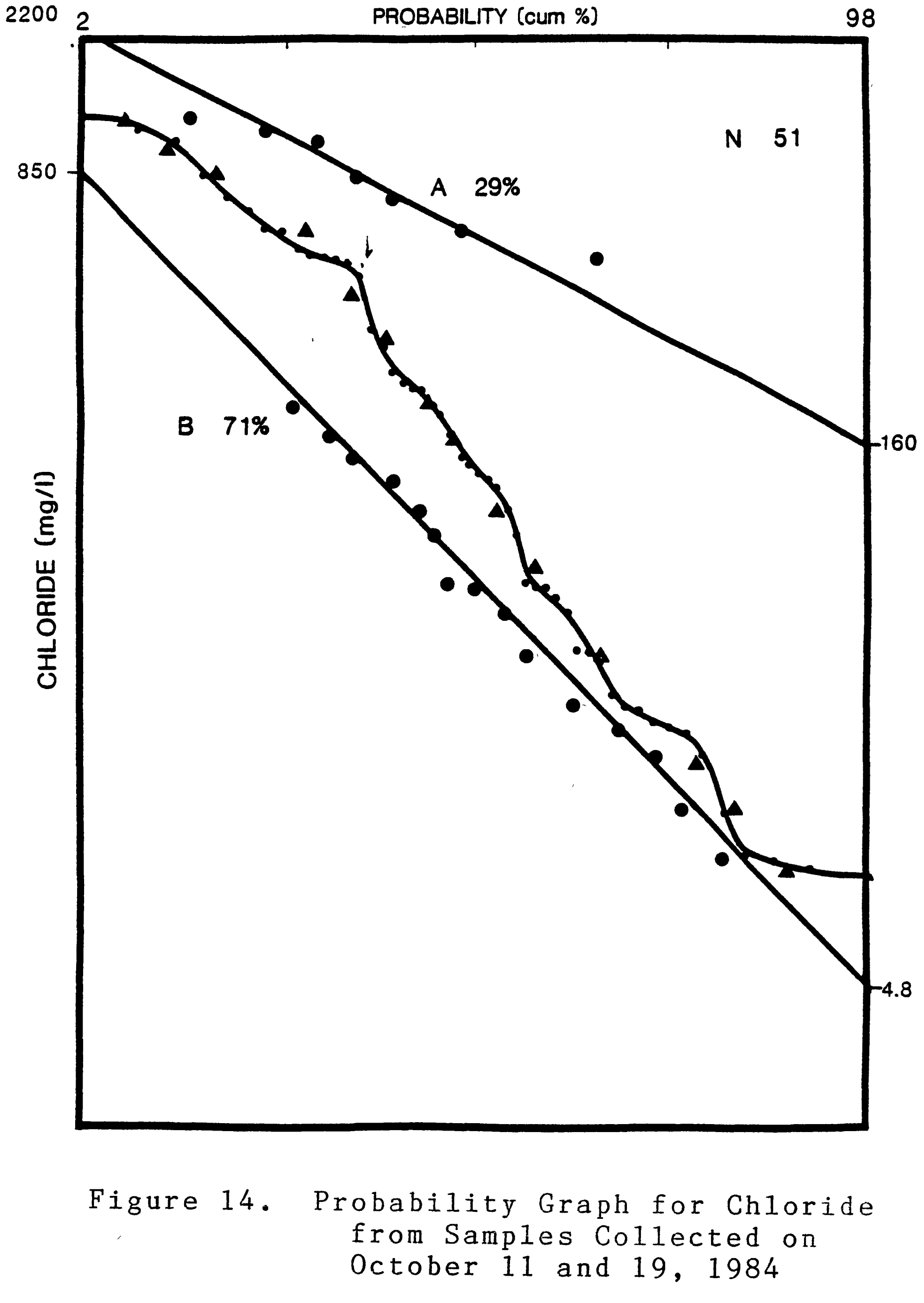


Figure 14. Probability Graph for Chloride from Samples Collected on October 11 and 19, 1984

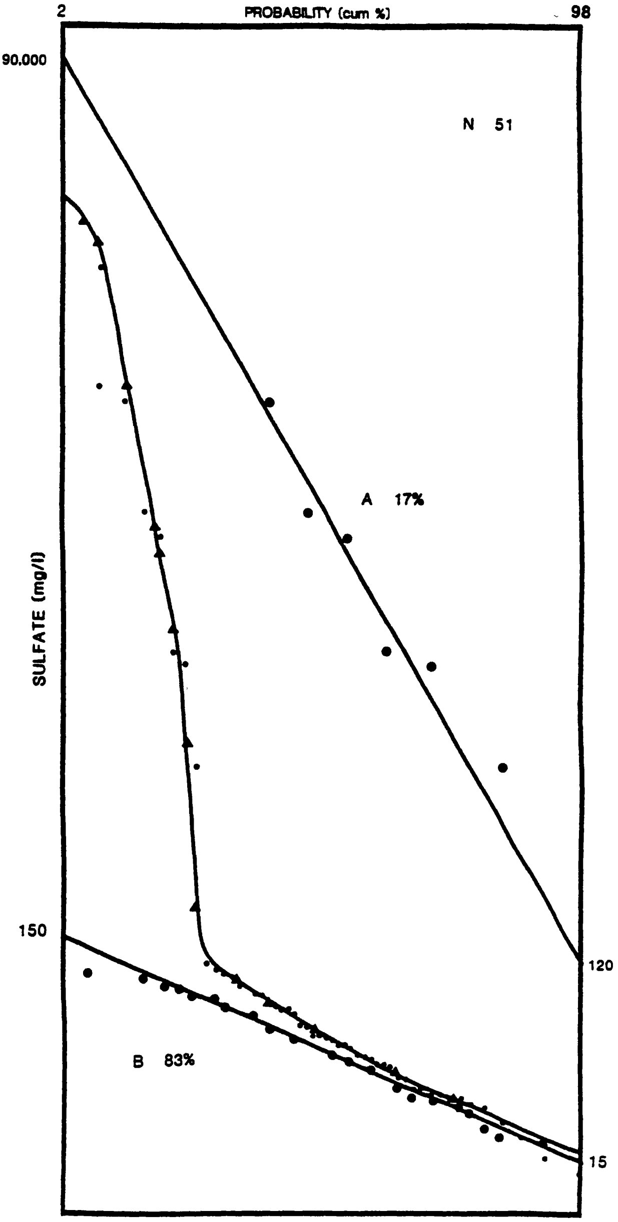
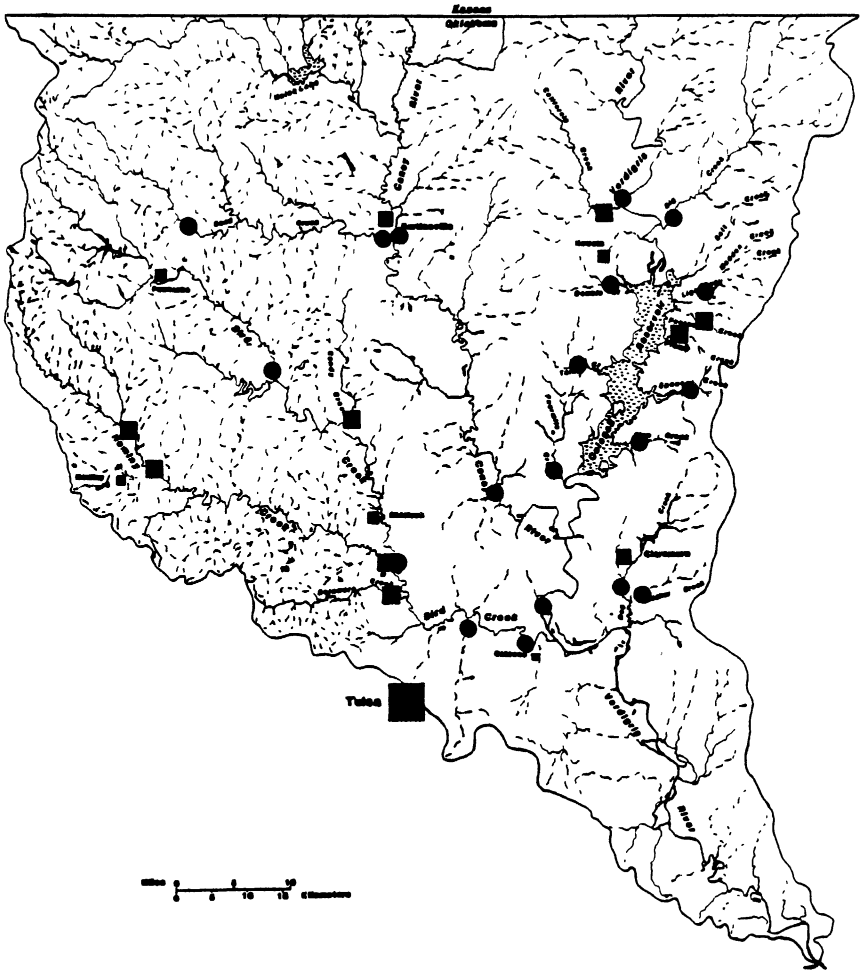
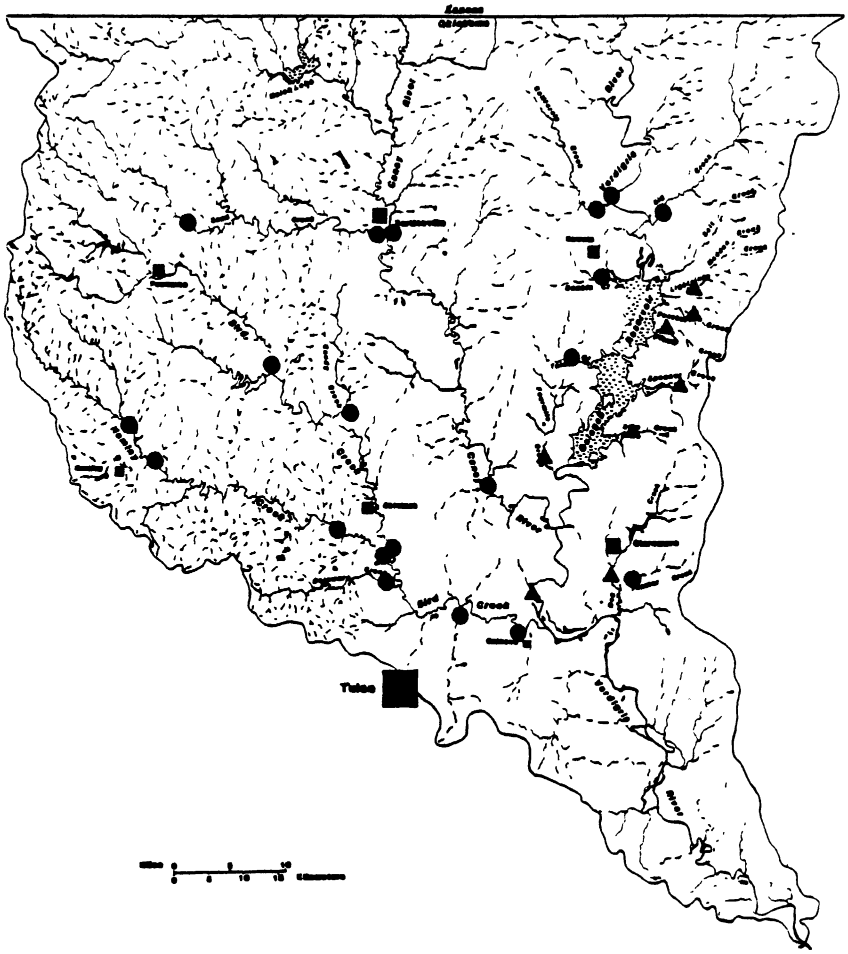


Figure 15. Probability Graph for Sulfate from Samples Collected on October 11 and 19, 1984



SYMBOL	ESTIMATED THRESHOLD LIMITS
▲	850 - 2200
■	160 - 850
●	4.8 - 160

Figure 16. Chloride Concentrations in Streams Sampled on October 11, 1984



SYMBOL	ESTIMATED THRESHOLD LIMITS
▲	150 - 190,000
—	120 - 150
●	15 - 120

Figure 17. Sulfate Concentrations in Streams Sampled on October 11, 1984

mg/l based on threshold limits of combined populations A and B.

Chloride concentrations from 4.8-160 mg/l, based on on threshold limits, may represent mixing of uncontaminated ground-water runoff and contaminated ground-water runoff in the remaining streams sampled in the Verdigris Basin and Hominy Creek Basin.

Sources of Sulfate

Anomalous (150-190,000) mg/l S04=, based on partitioning of population A, occur in eight streams sampled in the Verdigris Basin (figure 17). Coal strip mining and reclamation activities are currently or have been conducted in the past in each of these stream basins. Five of the streams discharge into Oologah Reservoir. Fourmile Creek discharges into the Verdigris River downstream from Oologah Reservoir. Dog Creek discharges into the Verdigris River from the east. Verdigris River also contained anomalous concentrations of sulfate below the confluences with Fourmile and Bird Creeks.

Natural variation (15-120) mg/l S04=, based on threshold limits of population B, occur in the remaining streams sampled in the Verdigris Basin. Coal strip mining has not been conducted in any of the remaining streams.

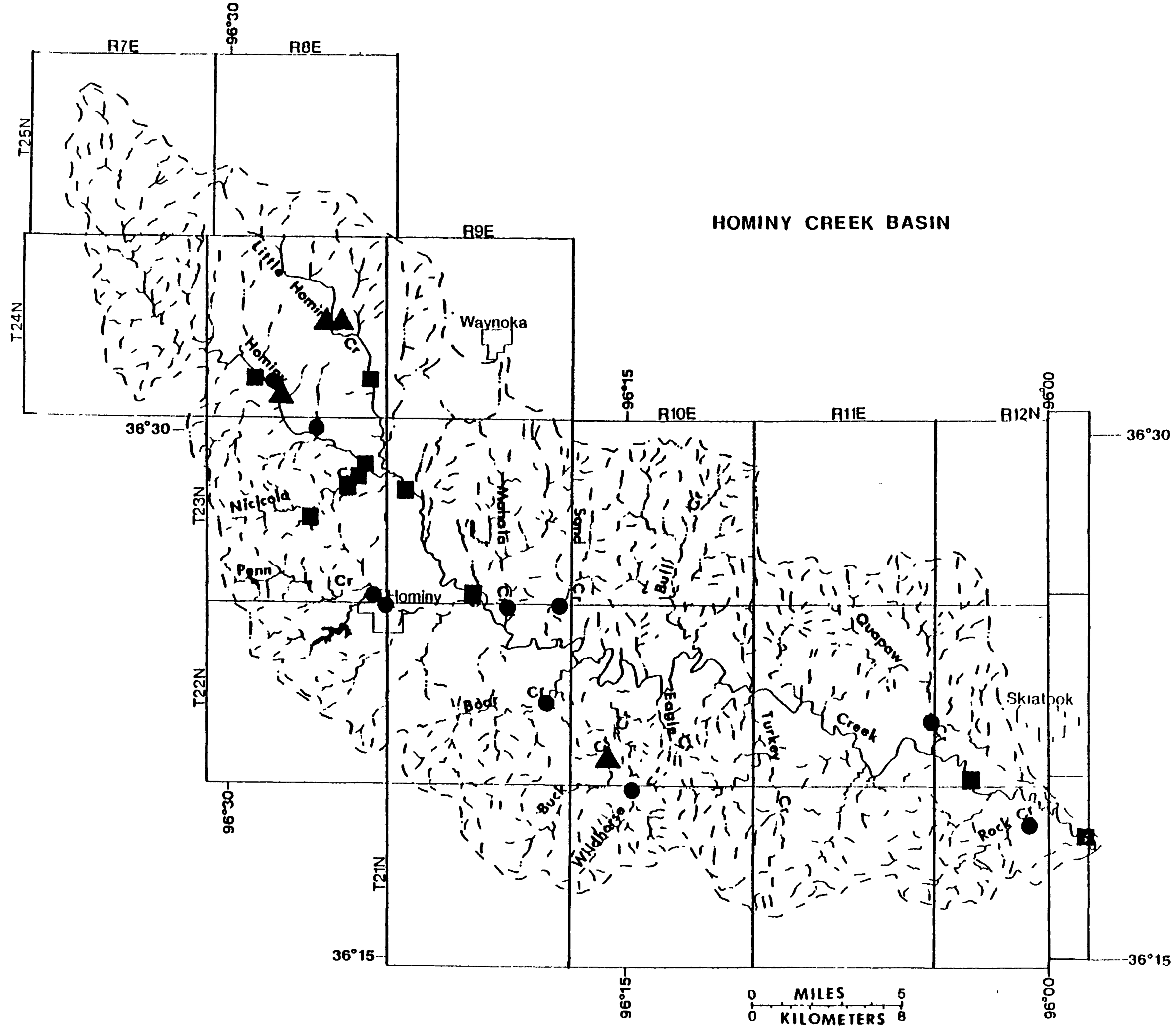


Figure 18. Chloride Concentrations at Locations Sampled on October 19, 1984

Sources of Chloride

Streams that show anomalous (850-2200 mg/l) Cl- were from Little Hominy, Hominy, Buck, and Nicicola Creeks (figure 18). Oil wells were estimated to occur within a few hundred feet of each of the sampling locations on the basis of observation on October 19.

Mixing of anomalous Cl- and contaminated ground-water runoff (160-850 mg/l) occur downstream from source areas in Little Hominy and Hominy Creeks. Mixing of anomalous Cl- and ground-water runoff occurs at three locations along Nicicola Creek.

Other tributaries that were not sampled on October 19 may also contribute anomalous Cl- to the mainstem of Hominy Creek. Therefore, further sampling was undertaken in Hominy Creek Basin on November 4, 8, and 11, to further located sources of chloride contamination and is discussed in the next section titled: "Hominy Creek Basin".

Sources of Sulfate

Sulfate concentrations in streams on October 11 in Hominy Creek Basin were 15-120 mg/l and is natural variation in sulfate, based on threshold limits.

Chloride and Sulfate

Anomalous concentrations of Cl- and SO4= did not occur in the same streams except for Panther and Plume Creeks in the Oologah Reservoir Area. Further sampling of streams in the Oologah Reservoir Area and Dog Creek Basin is discussed in the next chapter.

Hominy Creek Basin

Introduction

Samples were collected from streams in Hominy Creek Basin on November 4, 8, and 11 to further delineate source areas of contamination.

Rainfall at Hominy

Rainfall records of the town of Hominy show that 4.18 inches of rain fell between October 20 to November 1. Sampling began 3 days after rainfall ended. However, no rainfall occurred at Hominy during or between sampling (NOAA, 1984).

Control Stations

Comparison of Cl- concentrations from samples obtained on October 19 and November 4 indicated that Cl- concentrations were diluted, and to as much as a magnitude in Hominy Creek above the confluence with Bird Creek (figure 19).

Chloride concentrations at selected control sites obtained on November 4, 8 and 11 are compared.
Chloride concentrations were similar at 3 of 4 sites:
1) near the mouth of Hominy Creek, 2) Hominy Creek just below the confluence of Little Hominy and Nicicola Creeks, and
3) at Nicicola Creek.

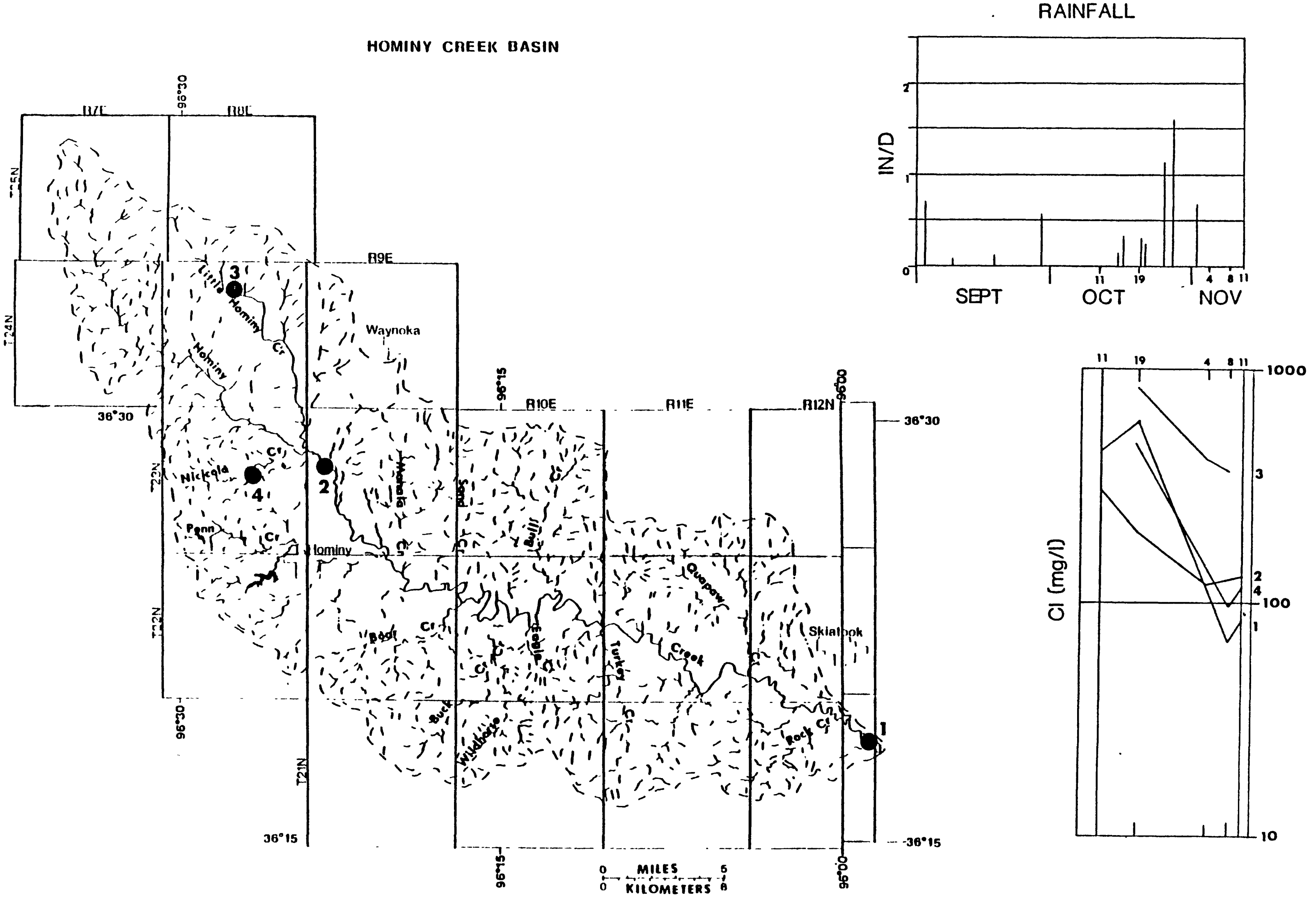


Figure 19. Dilution Effects of Rainfall on Chloride Concentrations in Hominy Creek Basin

Chloride Probability Graphs

Sixty-two chemical analyses of Cl- and SO4= were plotted individually to form probability graphs. The probability graph for chloride (figure 20) is done with the best agreement of checkpoints with the cumulative distribution curve with three populations: A:B:C (33:52:15).

Sources of Chloride

Sixteen streams sampled were contaminated (120-1500 mg/l) Cl- based on threshold limits (figure 21). Twelve streams contained contaminated ground-water runoff, three streams contained contaminated ponded surface runoff, and the remaining stream contained contaminated stagnant groundwater (table 2). All observations were obtained from streams except for one sample from ponded water in an oil-field four miles west of Hominy. All 16 locations are contaminated by oil-field brine and occur above the Vamoosa-Ada aquifer, except for Eagle Creek. Sources of Cl- contamination in ponded or stagnant surface runoff may be from solution of salts from the unsaturated zone or ground surface.

Sources of Cl- contamination are in central segments of the following streams (figure 21): 1) Hominy Creek above the confluence of Little Hominy and Hominy Creeks, and 2) Little Hominy Creek. Tributaries which show local Cl- contamination are 1) a tributary of Hominy Creek, just north of Nicicola Creek, located in an oil field; and 2)

TABLE II

STREAM OBSERVATIONS AND CHLORIDE CONCENTRATIONS

P	N	Chloride (mg/1)	Ponded	Stagnant	Flowing
A	16	120 - 1500	3	1	12
A+B	26	30 - 120	2	7	17
B	09	13 -30	2	3	4
C	11	1.5 - 13	6	5	0

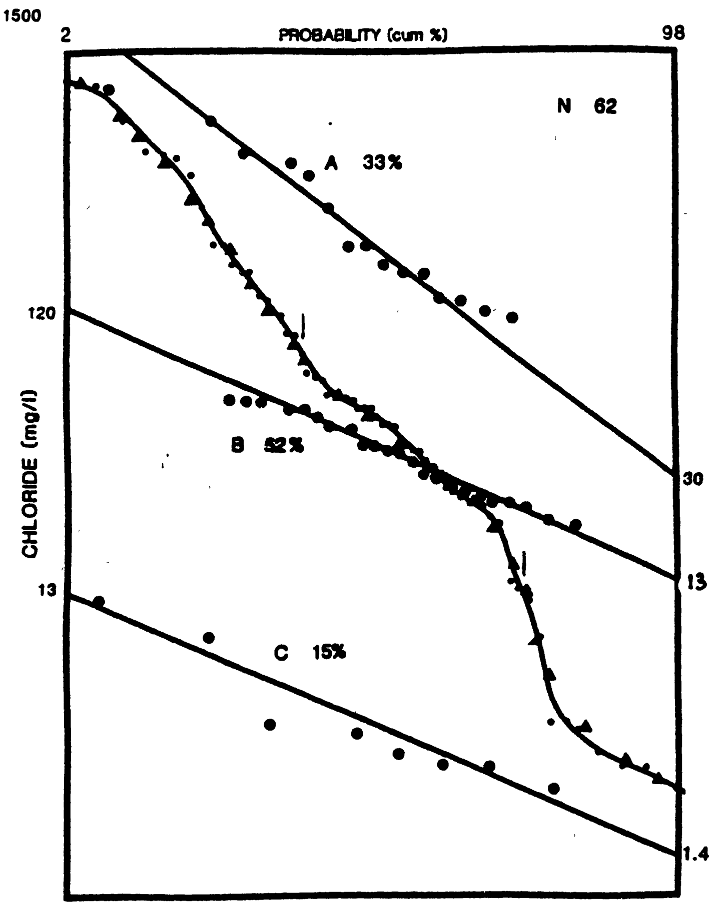


Figure 20. Probability Graph for Chloride Analyses From Samples Collected on November 4, 8 and 11, 1984

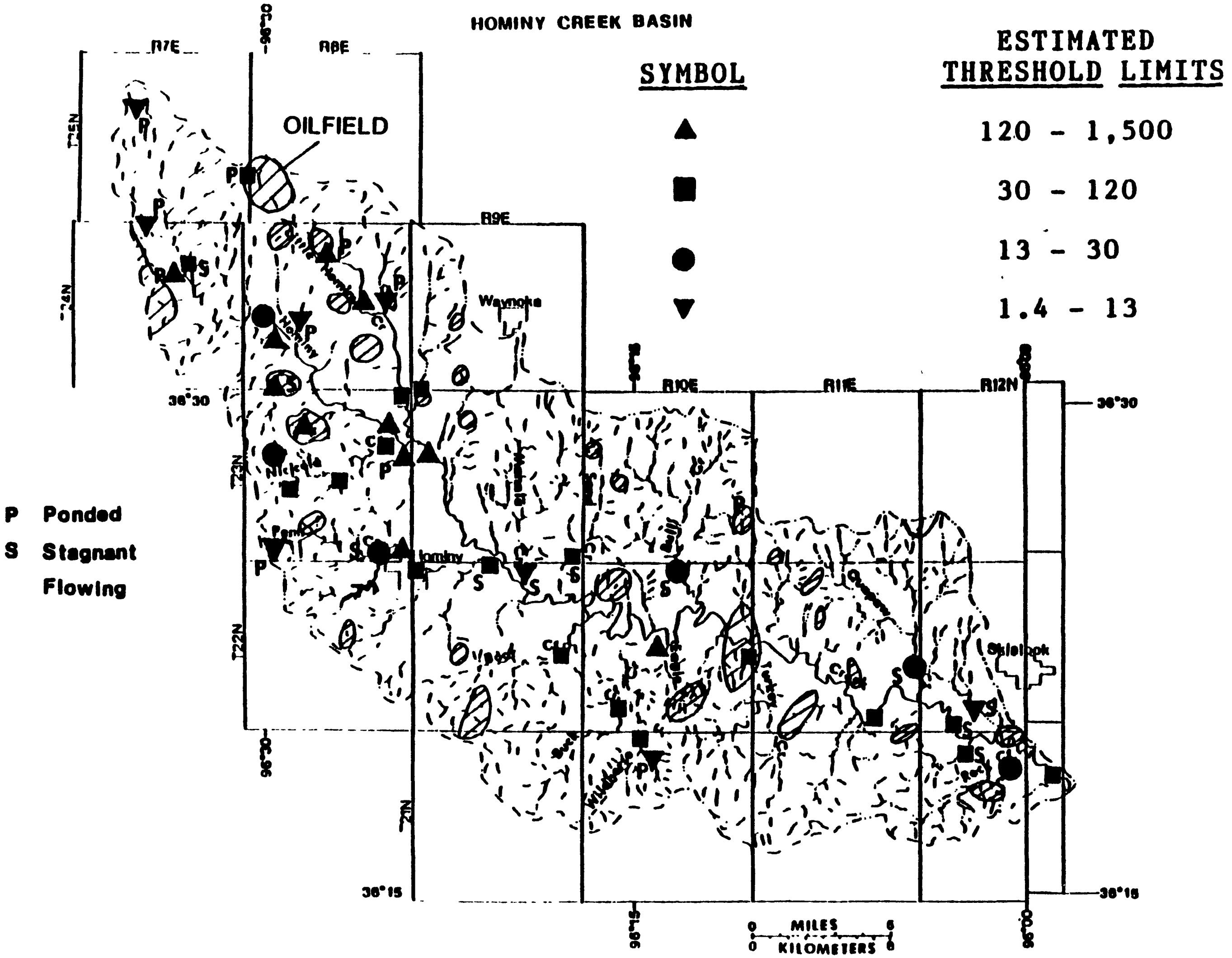


Figure 21. Chloride Concentrations at Locations in Hominy Creek Basin

a tributary to Hominy Creek, just east of Wildhorse Creek, downstream from oil tanks. Also, surface water sampled from a ditch in an oilfield west of Hominy contained 280 mg/l Cl-. This area up-gradient from the confluence of Hominy and Little Hominy Creeks.

Mixing of Cl- contaminated waters and uncontaminated waters (30-120 mg/l), based on threshold limits of combined populations A and B, occurs at 26 locations. Ground water runoff represents 65%; streams with stagnant waters are 27%, and 8% sampled contained ponded water. All streams containing (30-120 mg/l) Cl- are downstream from oil fields.

Waters that are essentially uncontaminated with respect to Cl- (13-30 mg/l), based on threshold limits occur at nine locations. Ground-water runoff were sampled from three streams, stagnant waters were sampled from three streams, ponded waters were sampled from two streams, and a flowing spring discharging from the Vamoosa-Ada aquifer, contained 24 mg/l Cl-.

Surface runoff containing 1.4-13 mg/l Cl-, based on threshold limits of population C, occur in 11 streams. No samples collected represented ground water runoff. Waters that were sampled were ponded in six streams, and stagnant in five streams. Rainfall contains probably less than 1 mg/l (Frederickson, 1985; NADP,1985) which supports the concentration limits for surface runoff in streams sampled in Hominy Creek and Delaware Creek basins on November 4, 8, and 11, 1984.

Sulfate Probability Graphs

Sixty-two chemical analyses were assigned individual frequencies and summed to form a cumulative probability curve (figure 22). Partitioning of two populations, A (12%) and B (88%) were done based on the major inflection point at 12 percent.

Sources of Sulfate

Anomalous (140-8000 mg/l) SO4=, based on threshold limits, occurs at six stream locations (figure 23). Each stream receives drainage from the Vanoss Group, which contains coal seams. Coal commonly contains pyrite, and oxidation of pyrite by oxygenated waters may account for the SO4= anomalies observed.

Anomalous SO4= concentrationsSulfate anomalies occur in 1) two tributaries near the headwaters of Hominy Creek, 2) a tributary near the of upper Hominy Creek, 2) headwaters of Nicicola Creek, 3) upper Penn Creek, and 4) Mahala Creek.

Sulfate concentrations in upper Hominy Creek are 2400 mg/l near the headwaters, and 700 mg/l in a tributary about four miles south. These samples were obtained from ponded water in the stream on November 8 suggesting that this was surface runoff.

Sources of SO4= are oxidation of pyrite containing soils, shales and/or coal seams in the Vanoss Group (Bingham and Bergman, 1980) which underlies these streams.

Mixing of anomalous SO4= and naturally occurring

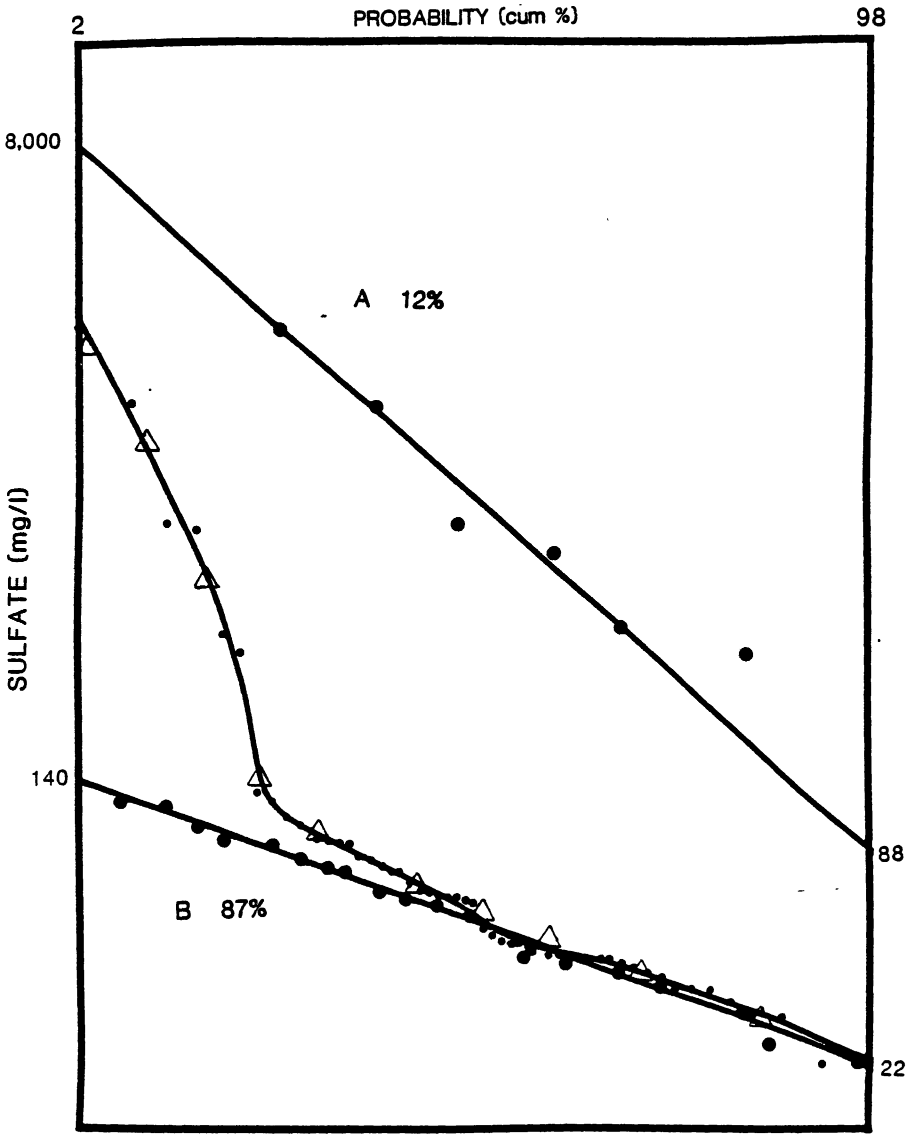


Figure 22. Probability Graph for Sulfate Analyses from samples Collected on November 4, 8 and 11, 1984

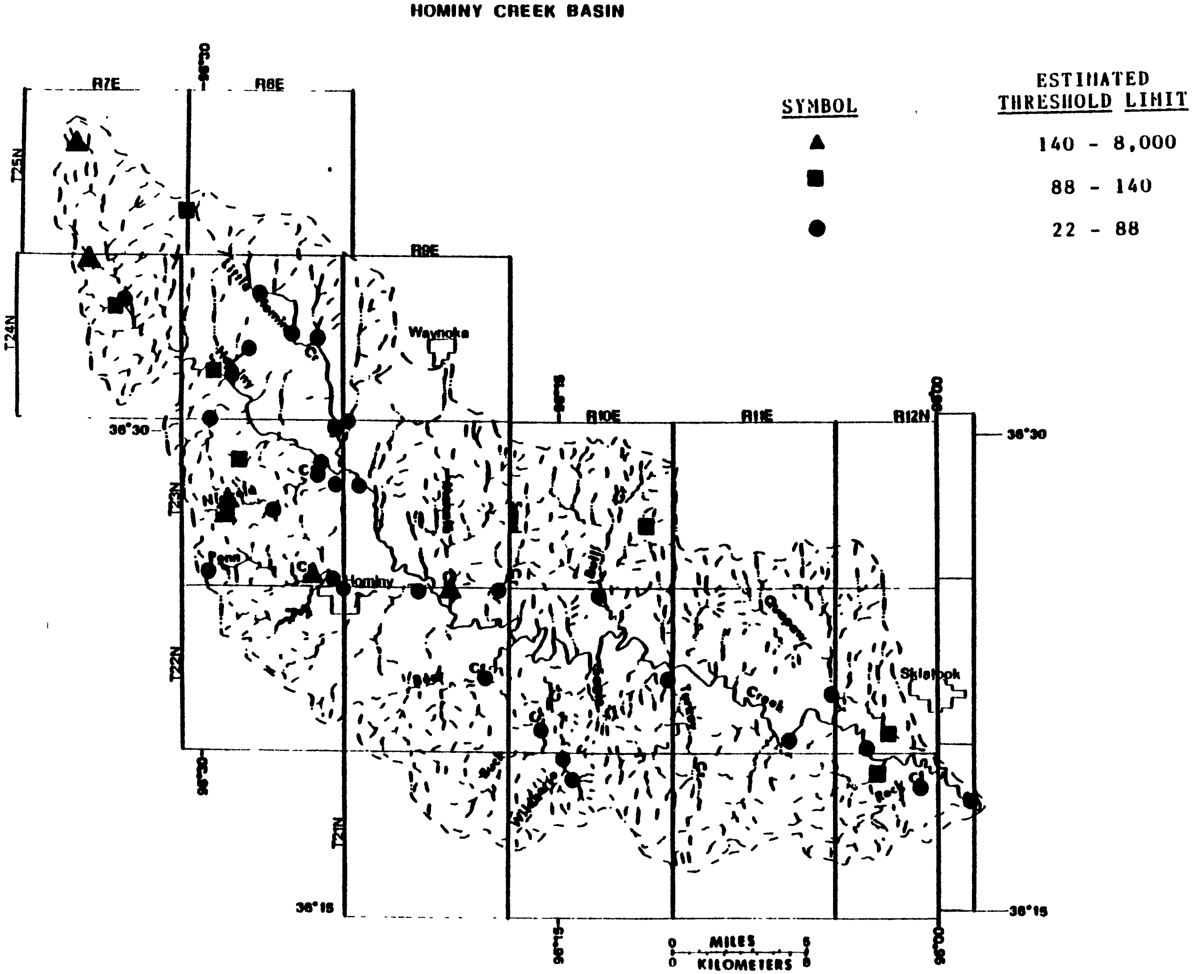


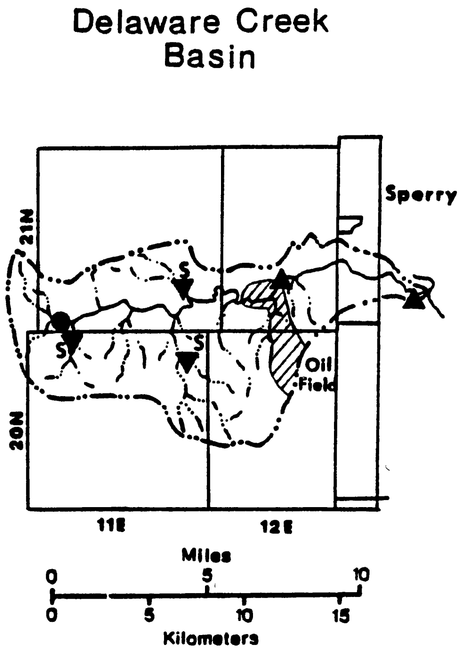
Figure 23. Sulfate Concentrations at Locations Sampled in Hominy Creek Basin

$SO_4^=$ (88-140 mg/l), based on threshold limits of combined populations A and B, were observed at seven streams. Four observations contain drainage from the Vanoss Group in lower reaches of streams and may represent dilution of anomalous $SO_4^=$ in the streams. Two tributaries of lower Hominy Creek receive drainage from the Coffeyville Formation, and the remaining stream, a tributary of Bull Creek receives drainage from the Chanute Formation. Coal seams occur in all three rock units units (Bingham and Bergman, 1980).

Variablility in background concentrations of sulfate (22-88 mg/l) are based on threshold limits at 98% (population A) and 2% (population B). Sulfate which occurs (22-88 mg/l) represents 74% of the $SO_4^=$ analyses from Hominy Creek and Delaware Creek Basins.

Delaware Creek Basin

Streams in Delaware Creek Basin were sampled at one time on November 11 to further delineate source areas of Cl^- pollution. A sampled obtained previously on October 11 showed 588 mg/l Cl^-. The sample was obtained from stagnant water near the mouth of the stream. Tributaries upstream were dry or contained puddles; therefore, they were not sampled at that time. Delaware Creek was flowing throughout its length on November 11. Tributaries sampled on the same



SYMBOL	ESTIMATED THRESHOLD LIMITS
▲	120 - 1,500
■	30 - 120
●	13 - 30
▼	1.4 - 13

P **Ponded**
S **Stagnant**
Flowing

Figure 24. Chloride Concentrations in Streams in Delaware Creek Basin

Ground-water in Hominy and Delaware Creek Basins

Chemical analyses of ground-water in the Verdigris River Basin in Oklahoma were provided by the U.S. Geological Survey in Oklahoma City, current to February 8, 1985. Selection of analyses was done from a single data-set National Uranium Evaluation (NURE). Analyses of SO4= were listed, however, a default value was consistantly indicated for Cl- suggesting Cl- analyses were not done. Therefore, Cl- was calculated by subtracting the anion sum from the cation sum and multiplying the difference (in milliequivalents) by the atomic weight of Cl. It is assumed that the water analyzed was electrically neutral and that chemical analyses were of adequate precision. to construct probability graphs.

Chloride Probability Graph

Forty chemical analyses from within Hominy Creek and Delaware Creek Basin were selected for construction of probability graphs of chloride and sulfate. Each observation was given an equal frequency and summed to form a cumulative distribution curve. Each curve is approximated by a single lognormal population (figure 25). Statistical parameters, antilogs of the mean, mean plus one standard deviation, and mean minus one standard deviation are (50,140,19).

Sulfate Probability Graph

Forty chemcial analyses of sulfate were assigned equal frequencies, summed, and were plotted to form a

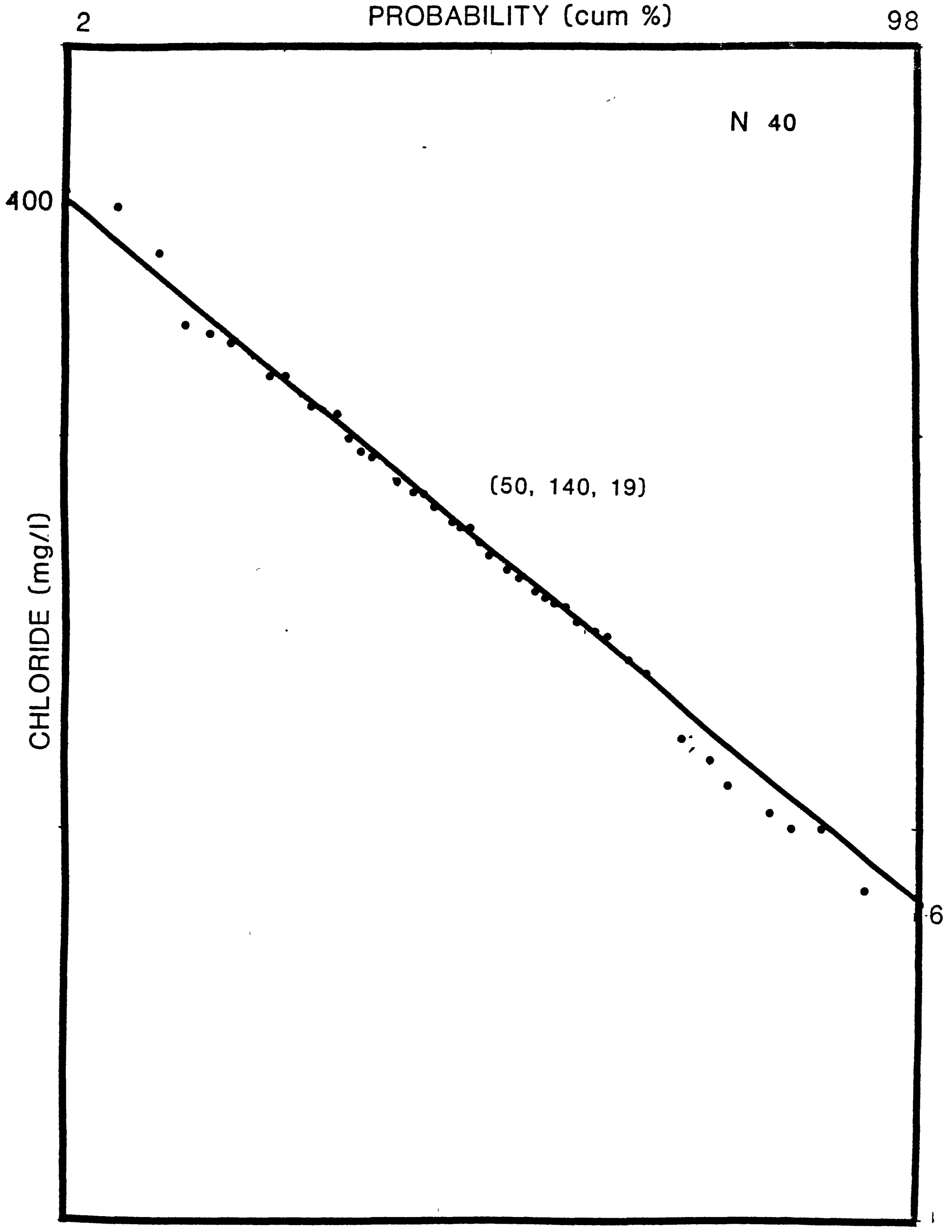


Figure 25. Probability Graph of Chloride Analyses of Ground Water in Hominy and Delaware Creek Basins

cumulative distribution curve (figure 26). Statistical parameters for the resulting single lognormal population are (50,160,15).

Hominy Creek Basin Stream Survey

A survey of streams in Osage County was conducted in July 5-17, 1981 (EPA, 1985). Chloride was determined at streams by titration with mercuric nitrate and accuracy was estimated to be within 5 mg/l (EPA, 1985). Chloride analyses were selected during the period from July 5-15, 1981, in which no rain occurred in Osage County (EPA, 1985).

Probability Graph

Forty-six Cl- determinations were used to construct a cumulative probability curve (figure 27). Individual observations were plotted directly. Partitioning of the curve into 2 populations A (20%) and B (80%) is done based on a major inflection point in the curve at 20 cumulative percent. Check-points fell on the original curve, therefore these populations are plausible.

Sources of Chloride

Anomalous (2500-28,000 mg/l) Cl-, based on threshold limits, occur at five stream locations (figure 28). Four of the observations were done within a 660 foot reach of

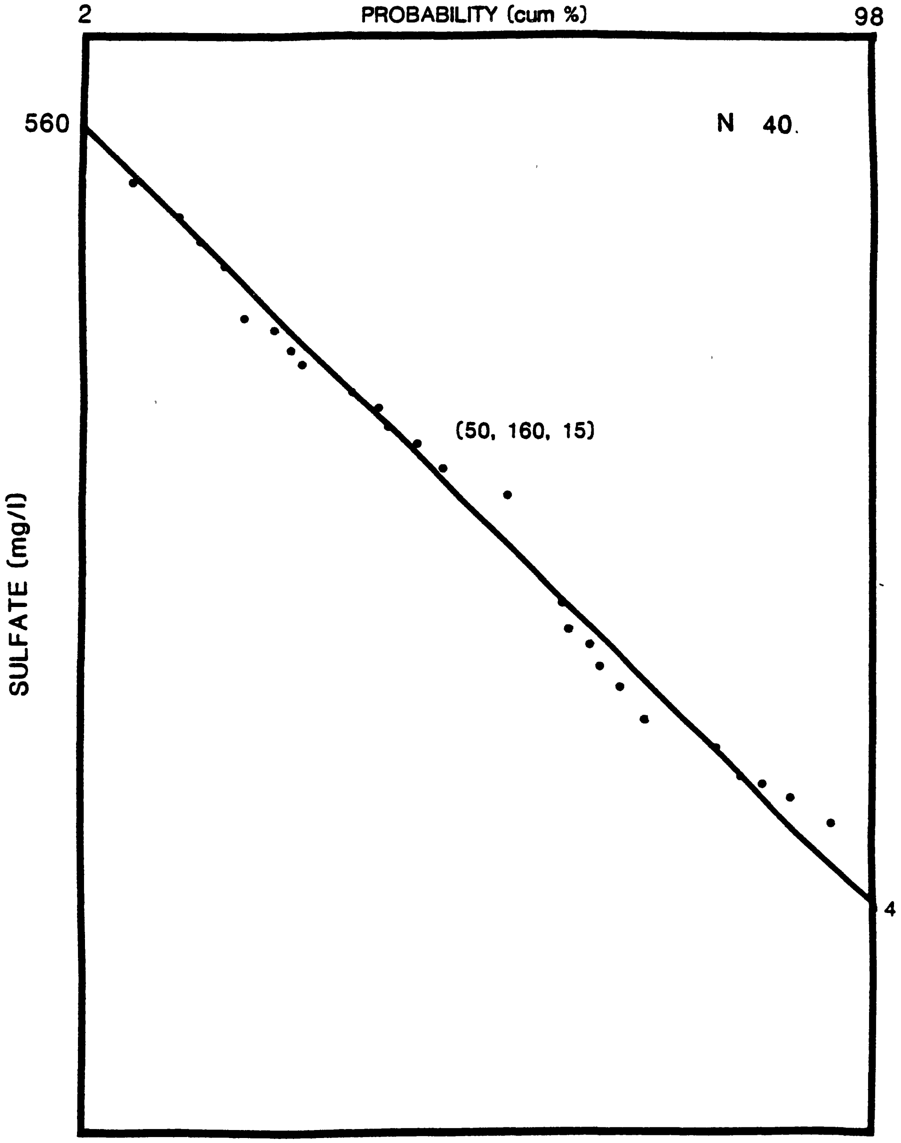


Figure 26. Probability Graph of Sulfate Analyses of Ground Water in Hominy and Delaware Creek Basins

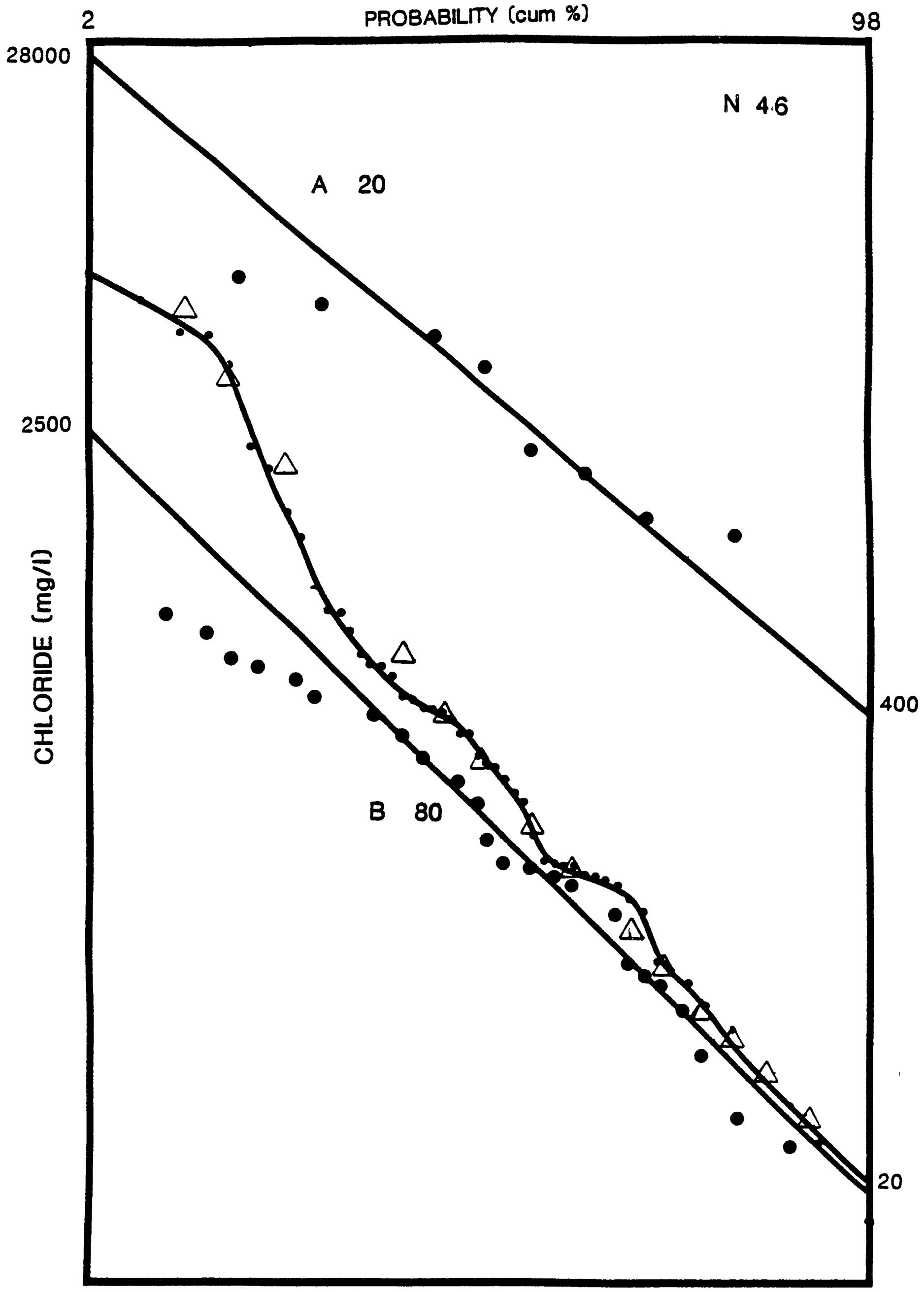


Figure 27. Probability Graph of Chloride in Streams in Hominy Creek Basin during July 5-15, 1981

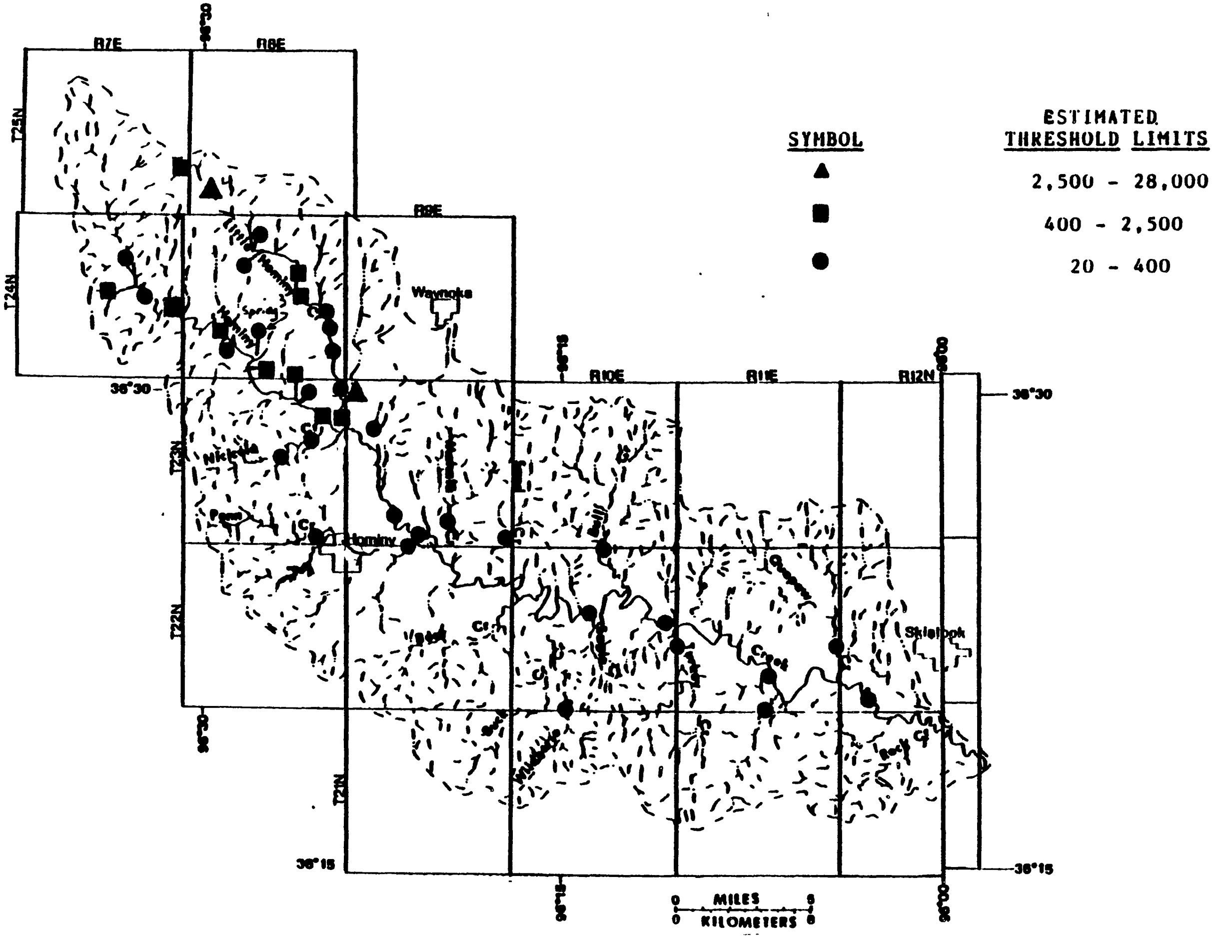


Figure 28. Chloride Concentrations in Streams in Hominy Creek Basin during July 5-15, 1981

Little Hominy Creek. Locations sampled were a seep, a spring above the seep, and two sites in Little Hominy Creek. The remaining Cl- anomaly occurred at a tributary of lower Little Hominy Creek which contained 6650 mg/l Cl-. All chloride anomalies here occur in water associated with the Vamoosa-Ada aquifer. Concentrations of anomalous chloride are higher compared to chloride anomalies from streams in Hominy Creek on October 19, and November 4, 8, and 11, 1984, because of the dilution effects of rainfall that occurred during the fall in Hominy Creek Basin.

Mixing of populations A and B (400-2500 mg/l) Cl-, based on threshold limits, occur at 12 locations along Little Hominy Creek and upper Hominy Creek. All observations represent Cl- contaminated ground-water runoff from the Vamoosa-Ada aquifer.

Twenty-eight stream locations contained from 20-400 mg/l Cl- based on threshold limits of population A and B at 98 and 2 cumulative percents, respectively. Dilution of Cl- anomalies occurs downstream at 6 locations in Hominy Creek. Ten observations that occur in Hominy Creek indicate mixing of uncontaminated and Cl- contaminated ground-water runoff.

Two samples from along Penn Creek decreased from 135 mg/l to 75 mg/l Cl- downstream which indicated dilution in the stream. Two samples from Nicicola Creek, in contrast, showed increasing concentrations from 280 to

350 mg/l of chloride downstream suggesting a source of oil-field brine between locations. The remaining 7 tributaries of Hominy Creek that were sampled also indicated mixing, from 20-400 mg/l Cl-, of anomalous sources (that probably occur upstream) and background chloride concentrations downstream. Last, a spring of the Vamoosa-Ada aquifer contained 30 mg/l Cl- and was probably not contaminated by oil-field brine.

CHAPTER VII

OOLOGAH RESERVOIR AREA AND DOG CREEK BASIN

Rainfall

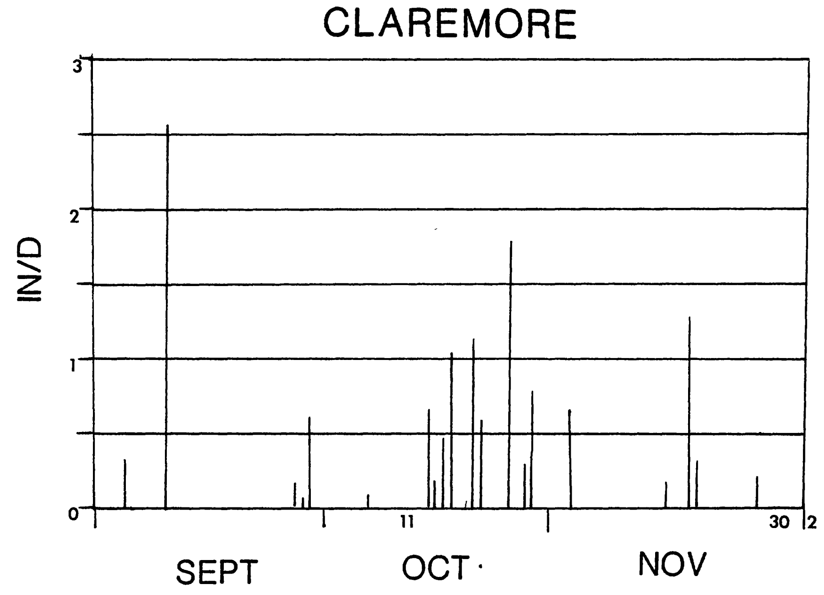
Rainfall that occurred after initial sampling of Creeks on October 11, and three days before sampling on November 30, totalled 10.4 inches at Claremore, and 9.3 inches at Nowata (figure 29). No rainfall occurred during sampling on November 30 and December 2 (NOAA, 1984).

Control Stations

Concentrations of chloride and sulfate sampled at streams on October 11 and November 30 (or December 2) showed the following (table 3): 1) Cl- decreased generally by a factor of two, 2) SO4= increased by a factor of about two at Blue and Panther Creeks, 3) SO4= decreased by a factor of three to four in Lightning Creek, and 4) in Plumb Creek, SO4= concentrations were about the same by comparison of the two sampling times.

Chloride Probability Graphs

Individual frequencies were assigned to each concentration and summed to form a cumulative frequency



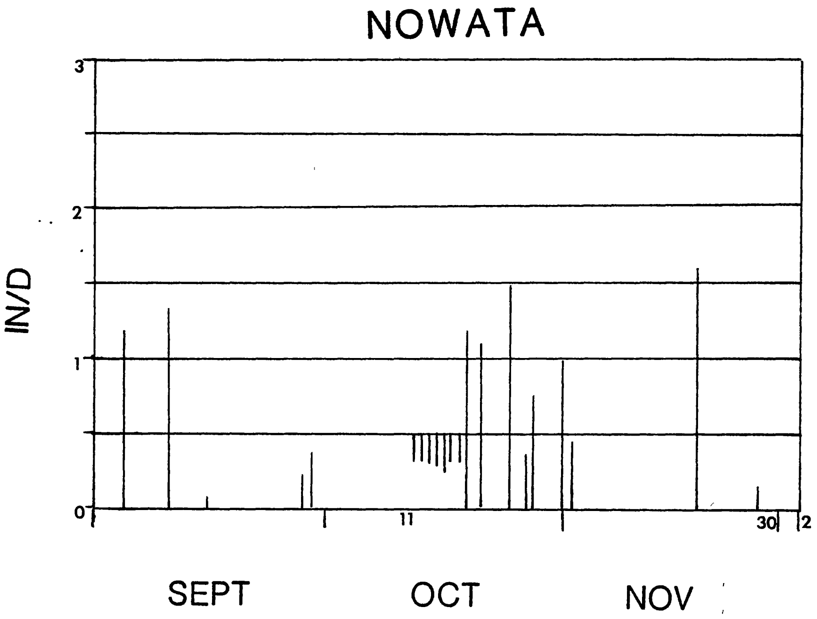


Figure 29. Rainfall at Claremore and Nowata during the fall of 1984

TABLE III

CHLORIDE AND SULFATE IN STREAMS IN THE OOLOGAH RESERVOIR AREA

Stream	Date	Sample	(milligrams/liter) Chloride	Sulfate *
Blue Creek	10/11	A6	15	26,800
	11/30	F10	6.8	43,600
Spencer Creek	10/11	A7	57	43,600
	12/2	G7	13	10,400
Plume Creek	10/11	A8	668	9,200
	12/2	G13	336	7,400
Panther Creek	10/11	A9	218	7,200
	12/2	G16	14	13,200
Lightning Creek	10/11	A10	24	190,000
	12/2	G21	14	50,900

* Rounded to nearest one-hundred.

curve (figure 30). Check-points fall on the original curve based on partitioning the cumulative probablity curve into two populations, A (20%) and B (80%), at the major inflection point located at 20%. Partitioning the curve into three populations (20:50:30) was unreliable because check-points did not coincide with the curve.

Oologah Reservoir Area

Sources of Chloride

Ground-water runoff contaminated with Cl- (40-520 mg/l) is based on threshold limits of populations A and B at two cumulative percent (figure 31). Five stream locations were contaminated. Four of the streams were flowing, and Fourmile Creek contained stagnant water. Ground-water runoff containing from 40-520 mg/l Cl- was sampled at the four streams in: 1) lower Plume Creek, 2) a tributary of lower Plume Creek, 3) a tributary to lower Panther Creek, and 4) lower Spencer Creek. The first three all occur in a major oil-field. Salts were observed on the surface of the ground beside a pond located beside the location sampled in a Tributary of lower Plume Creek. Therefore, a possible source of contamination is by solution of salts in the unsaturated zone at this location. A possible source of anomalous (70 mg/l) Cl- at lower Fourmile Creek on December 2 may be from leaking brine disposal wells.

Waters that were sampled containing from 11-40 mg/l Cl-, based on threshold limits of population B at two cumulative

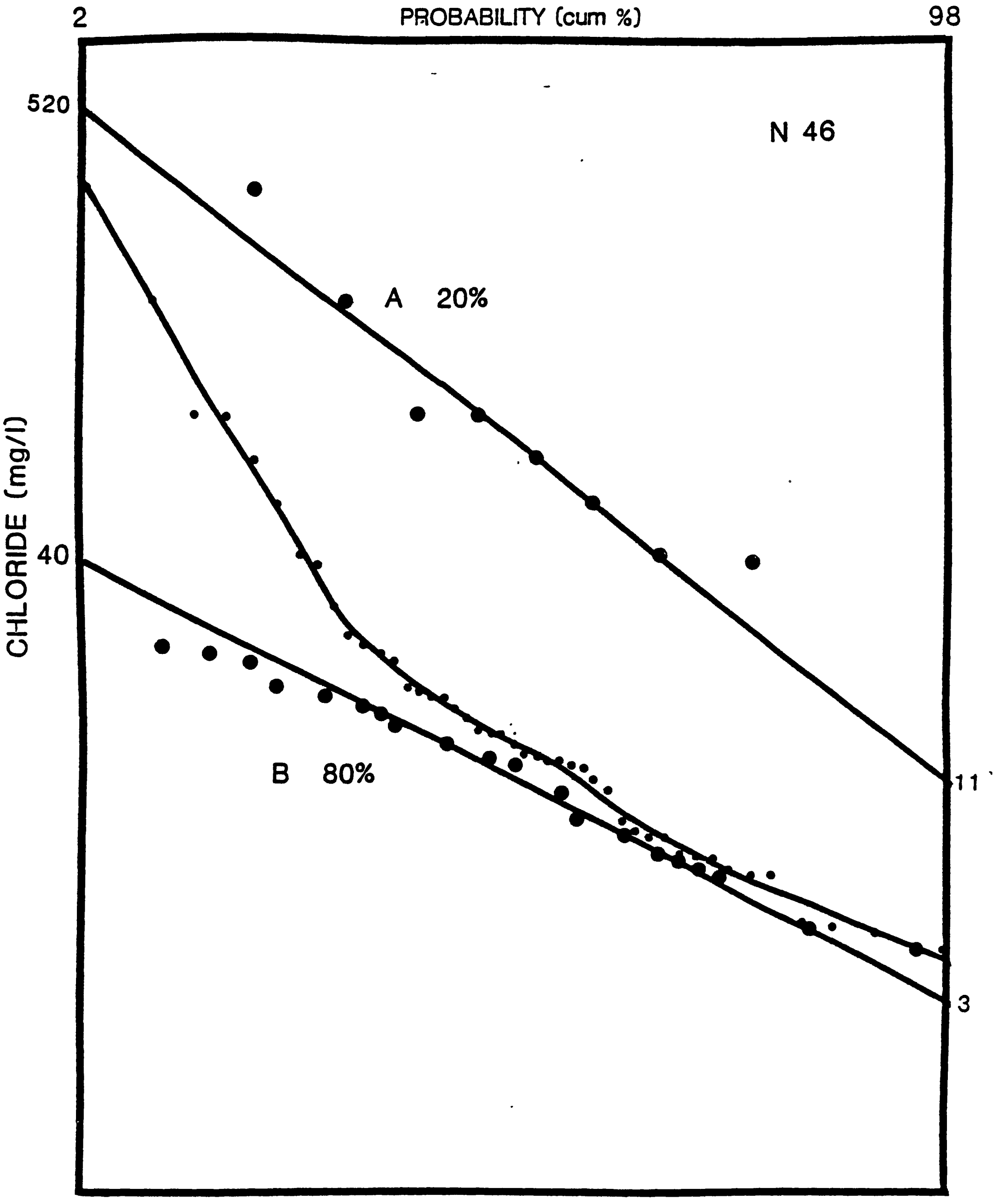
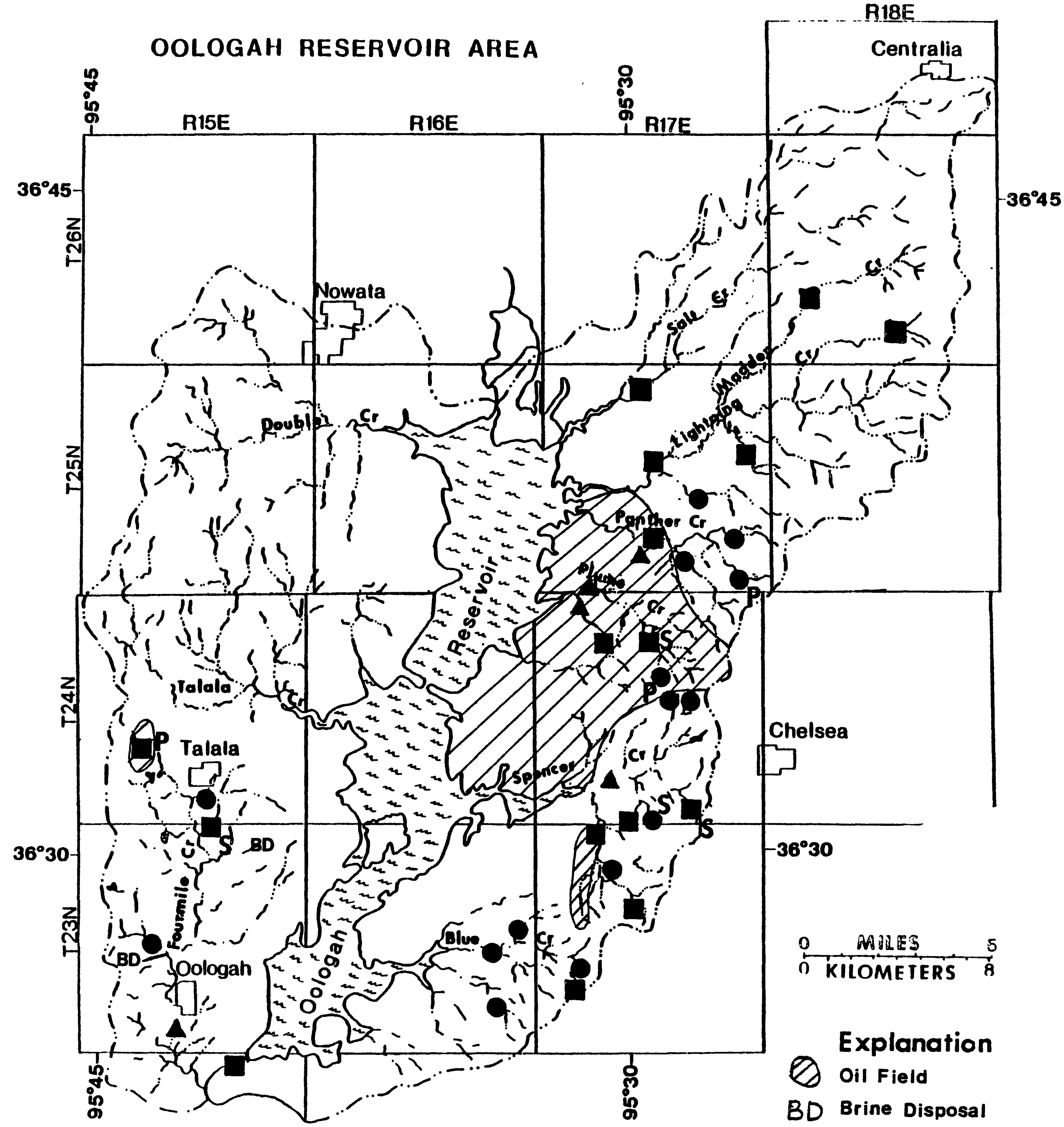


Figure 30. Probability Graph of Chloride Analyses From Streams sampled on November 30, and December 2, 1984



SYMBOLS	ESTIMATED THRESHOLD LIMITS
▲	40 - 520
■	11 - 40
●	3 - 11

Figure 31. Chloride Concentrations in streams in the Oologah Reservoir Area

percent and population A at 98 percent. Twenty-one streams sampled are represented: Ground-water runoff was sampled from 17 streams that were flowing; stagnant water, was sampled from 3 streams, and surface water was sampled from a stream at the headwaters of Fourmile Creek in an oil field. Waters containing from 12-40 mg/1 Cl- may represent mixing of brines with background concentrations. Brine disposal and secondary recovery wells are located throughout the Oologah Reservoir Area (based on records at the Oklahoma Corporation Commission) and brine has been injected at shallow depths from 240-532 feet based on records that were made available at the Oklahoma Corporation Commission. Injection of fluids may overpressurize the formation and artifically induce upward migration of brines through the fractured rocks in the area, and mix with fresh ground water.

Ground-water runoff in Spencer Creek, containing 54 mg/1 Cl- (November 30) and 57 mg/1 Cl- (December 2), is contaminated by brines. Brine injection or disposal wells that are located in section 27 T.24N, R.17E are a possible source of Cl- contamination in lower Spencer Creek.

Waters uncontaminated with respect to Cl- (3-12 mg/1) represent background variation. in chloride. Ground-water runoff was sampled from 14 streams that were flowing at the time of sampling. Water was also sampled from two streams with stagnant ground water, and a sample of ground water from an abandoned strip pit contained 4.6 mg/1 Cl-. Anomalous and background concentrations are diluted by rainfall that occurred during the fall. Ground-water runoff that contains 3-12 mg/l is discharged to streams by abandoned strip pits located above streams that were sampled in the Oologah Reservoir Area.

Dog Creek Basin

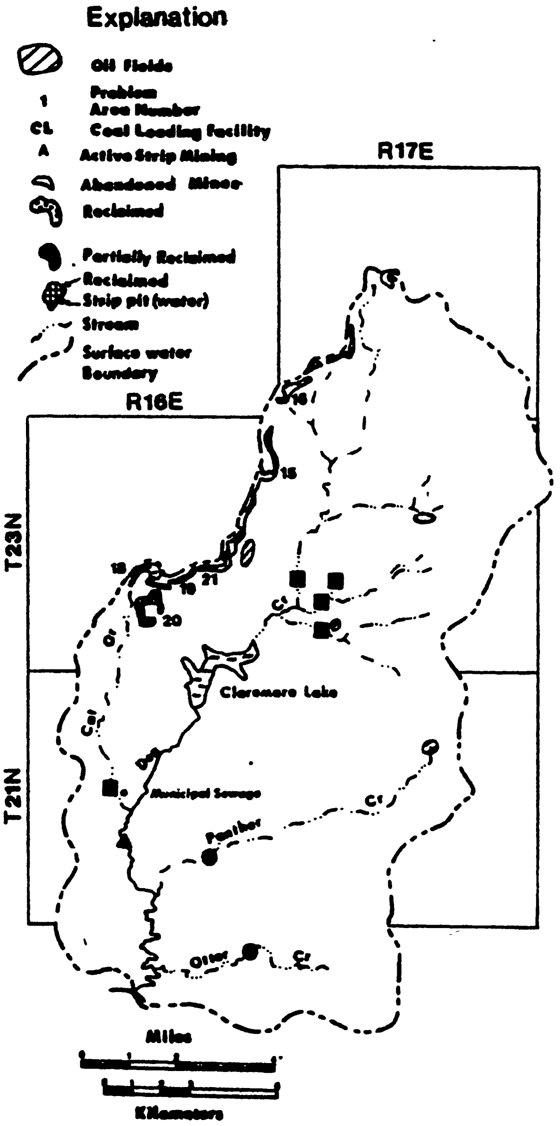
Stream Observations

Streams in Dog Creek basin were sampled at one time on November 30. Prior sampling on October 11 below the confluence of Cat and Dog Creeks showed anomalous 2100 mg/l S04=. All streams that were sampled on November 30 were flowing; therefore, ground-water runoff was sampled.

Sources of Chloride

Anomalous Cl- concentrations occur near the mouth of Dog Creek (figure 32). Chloride contamination occurs in Dog Creek below the confluence of Cat and Dog Creeks. A municipal sewage treatment facility discharges treated effluent into Cat Creek downstream from the sampling location. Oil wells are not indicated on topographic maps between sampling locations. A possible source of Cl- contamination in lower Dog Creek is from the municipal sewage treatment facility.

Another local source of Cl-contamination is above site F-8, where oil wells were observed. Dilution of higher Cl- concentrations occurs in the stream by mixing with ground-



SYMBOL	ESTIMATED THRESHOLD LIMITS
▲	40 - 520
■	12 - 40
●	3 - 12

Figure 32. Chloride Concentrations in Streams in Dog Creek Basin

water runoff containing background concentrations (3-12 mg/l Cl-), based on theshold limits of populations A and B. Anomalous Cl- values are not associated with anomalous SO4= values in the main stem of Dog Creek. Source of Cl-pollution is not the town of Claremore because of lower Cl- concentrations in Cat Creek.

Possible Sources of Cl- Contamination

Possible sources of Cl- pollution are by leakage from: 1) production wells, 2) brine disposal or secondary recovery wells, and/or 3) improperly abandoned petroleum wells. Another related source of Cl- may be from dissolution of salts in the vadose zone associated with evaporation pits that were constructed without effective liners during drilling of exploration wells (lower Plume Creek). Chloride contamination may also result from secondary oil recovery by overpressuring the formations, which are relatively shallow, generally 240-500 ft in depth, and are probably hydrologically connected to the surface via fractures.

Rocks in the Oologah Reservoir Area and Dog Creek Basin, predominately limestones and shales, represent fractured media that controls the movement of waters through the ground-water system. Although contamination by oil-field brines through leaking oil-wells or possibly fractures may account, in part, for contamination of Cl-; input of Cl- from garbage illegally dumped into abandoned strip pits; direct discharge of effluent from municipal treatment plants; and leakage of sewage from domestic septic systems are also contributors to Cl- and SO4= contamination.

Sulfate Probability Graphs

The SO4= analyses were plotted a cumulative probability curve (figure 33). Three major inflection points occur in the curve at cumulative percentages of 20, 50, and 82. Sulfate analyses were partitioned into four populations, verified with check points, and thresholds were estimated at 2 and 98 cumulative percents. The populations are A (20%), B (30%), C (32%), and D (18%). Partitioning of populations using concentrations from a smooth curve provided additional data points, after partitioning, which complemented previous partitioned points from the original concentrations plotted. These additional points helped to define populations C and D. A previous attempt at partitioning the curve into four populations (26:21:40:13) did not allow check points to fall on the original curve below 500 mg/l SO4=.

Dog Creek Basin

Sources of Sulfate

Sulfate concentrations were 469 mg/l near the mouth of Dog Creek (figure 34). Cat Creek is located immediately upstream contained approximately 450 mg/l SO4=. Sulfate contamination occurs in Cat Creek. Coal strip mining was done in 1951-52 at the headwaters of Cat Creek. Pits were left abandoned and have partially filled with water. One of

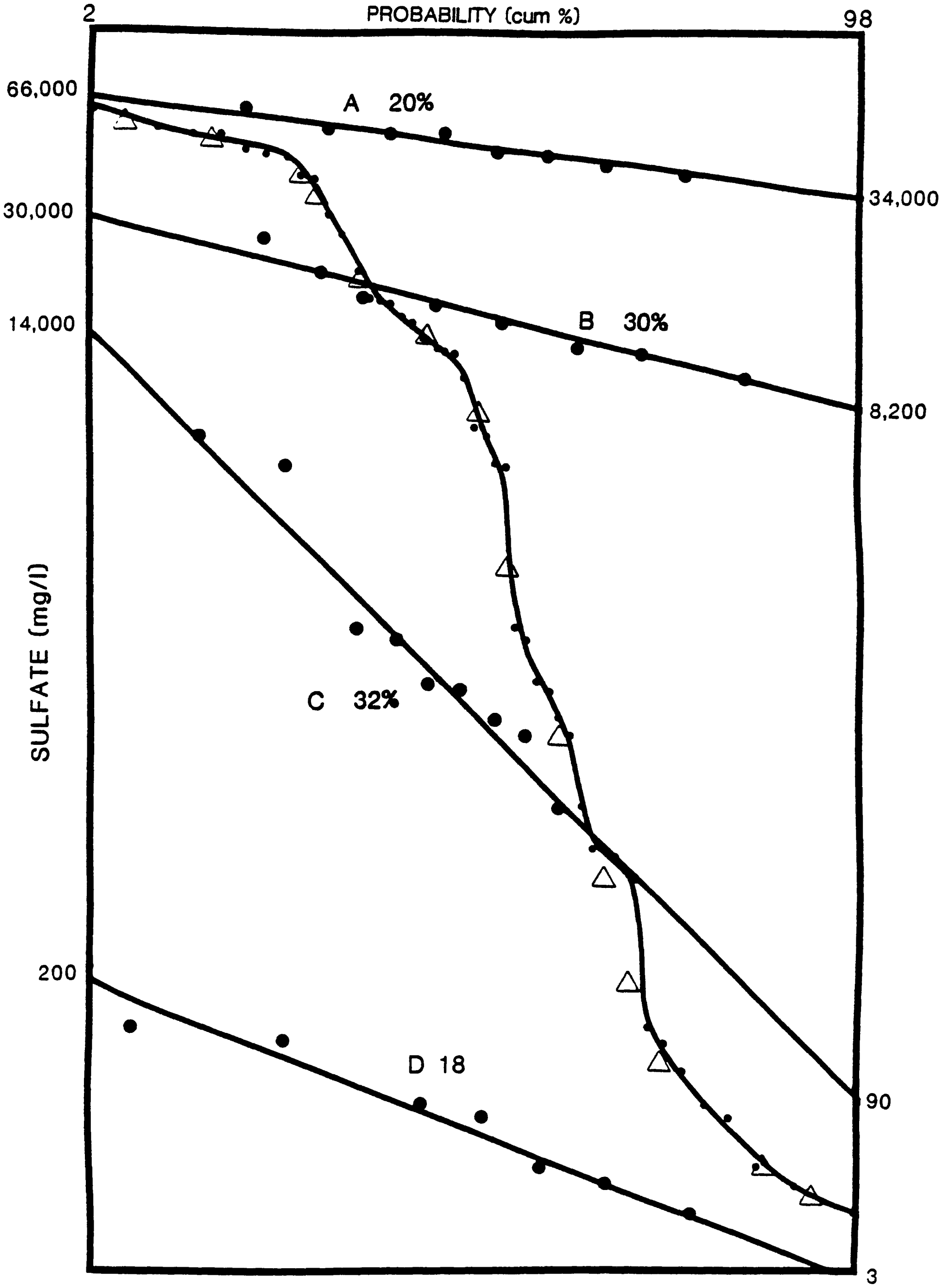
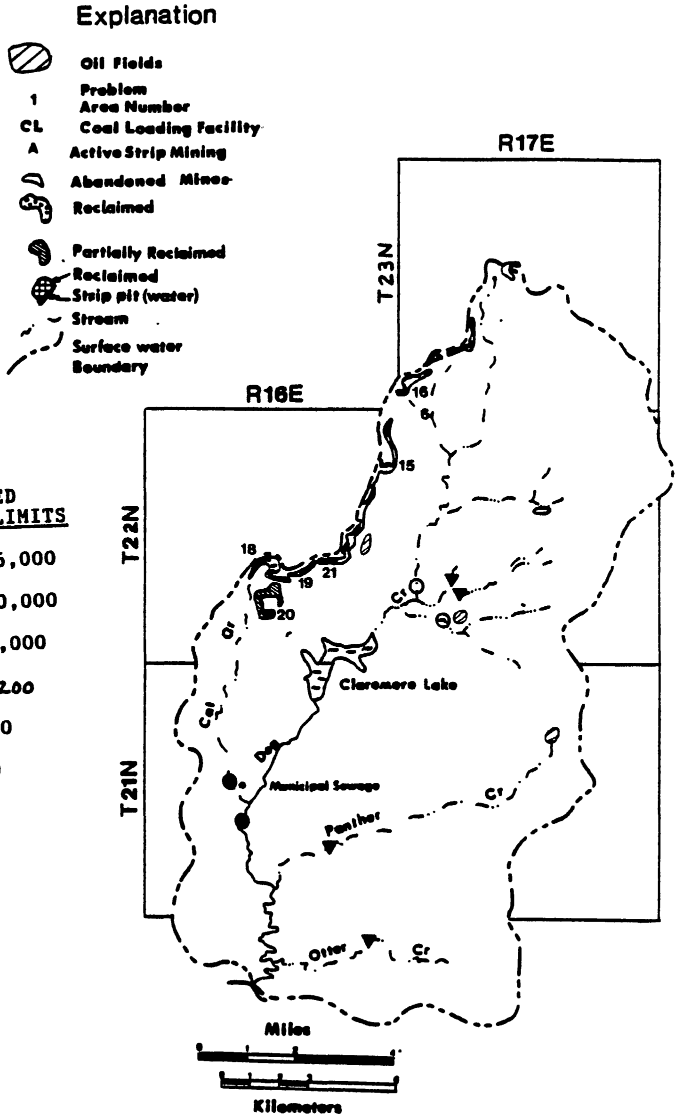


Figure 33. Probability Graph of Sulfate Analyses from Samples Collected on November 30, and December 2, 1984



SYMBOL	ESTIMATED THRESHOLD LIMITS
▲	34,000 - 66,000
■	14,000 - 30,000
□	8,200 - 14,000
●	200 - 8,200
○	90 - 200
▼	3 - 90

Figure 34. Sulfate Concentrations in streams in Dog Creek Basin

the pits was also used as a municipal landfill.

Mixing of anomalous concentrations of SO4= from abandoned strip pits and background concentrations of SO4= in ground-water runoff occurs in upper Dog Creek at a location with 148 mg/l SO4=, based on threshold limits of combined waters C and D. Anomalous concentrations of SO4= were probably diluted by mixing with background concentrations of ground-water runoff downstream in Dog Creek.

An "west-flowing" tributary of upper Dog Creek contained 111 mg/l SO4= and also indicated mixing of anomalous and background concentrations of ground-water runoff. The source of the anomaly is inferred to be coal seams that are located within the drainage basin of this tributary.

The remaining streams, in Dog Creek Basin, sampled on November 30 contained background concentrations (3-90 mg/l SO4=), based on threshold limits at 2 and 98 cumulative percent.

Oologah Reservoir Area

Sources of Sulfate

Anomalous (34,000-66,000 mg/l) SO4= were sampled from ground-water runoff in five streams, and a tributary of Spencer Creek (F14) on November 30 and December 2 (figure 35). Three streams in Lightning Creek Basin also contained anomalous (34,000-66,000 mg/l) SO4=.

Active strip mining occurred in 1976 and approximately

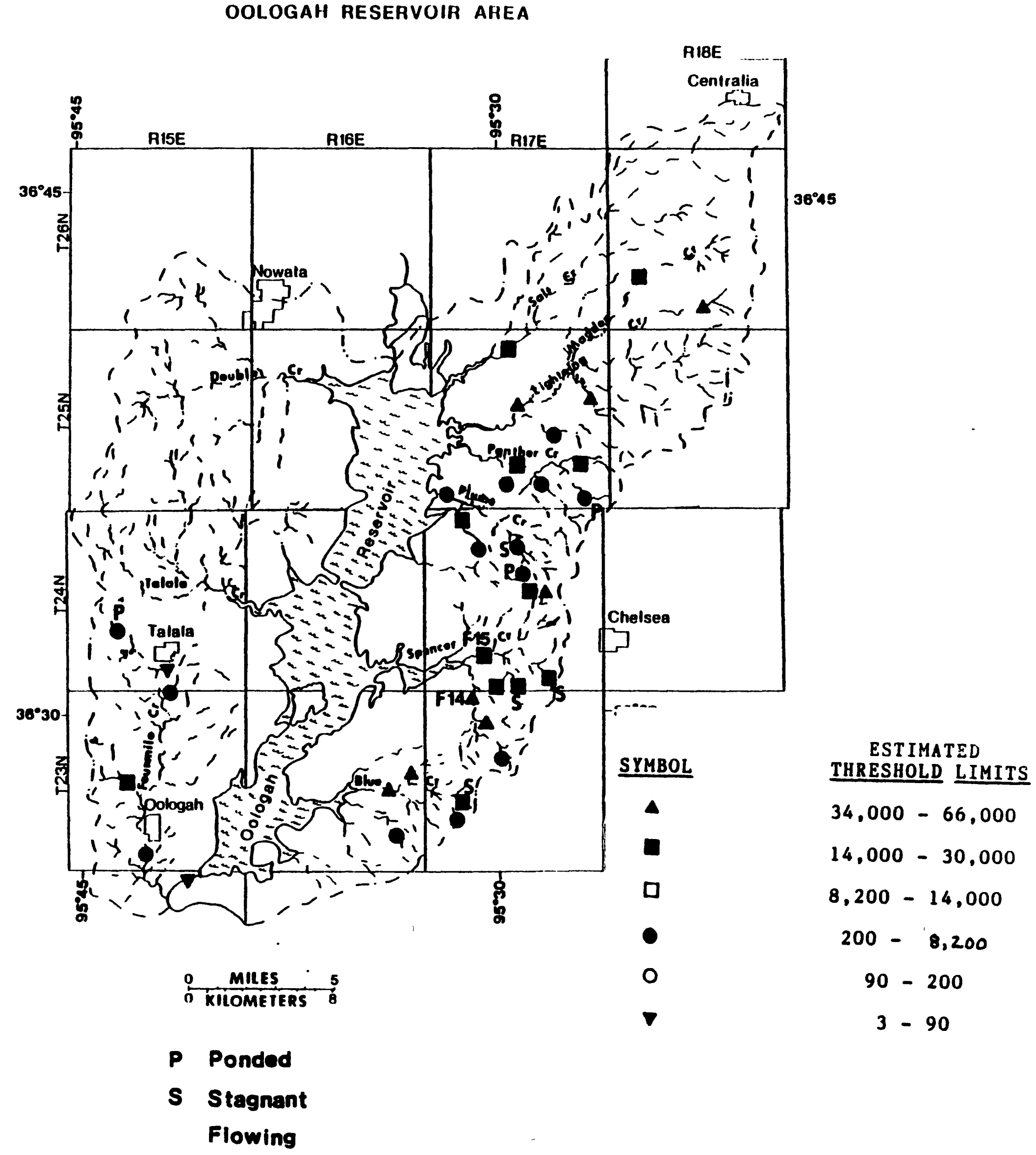


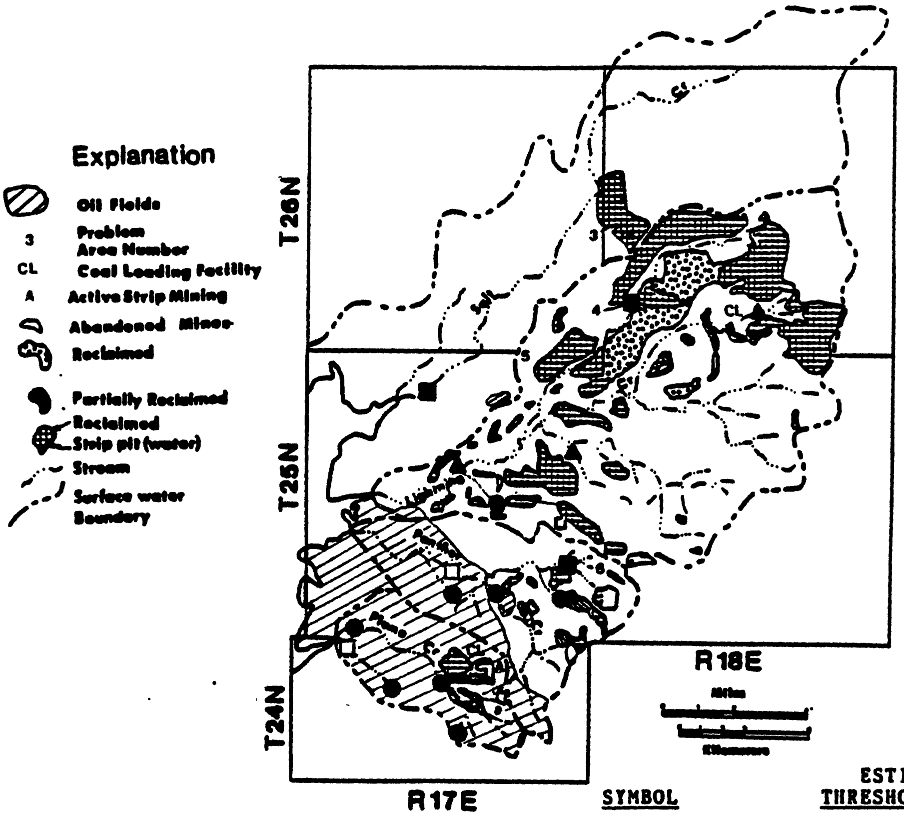
Figure 35. Sulfate Concentrations in streams in the Oologah Reservoir Area

1500 acres was disturbed near Madden Creek (figure 36). Coal loading facilities ar located near the headwaters of Lightning Creek. Madden Creek and the other tributaries contribute to the anomalous S04= observed downstream in Lightning Creek.

A tributary of Spencer Creek (figure 37) contributes anomalous (44,475 mg/1) S04= to Spencer Creek and concentrations were diluted downstream to 37,853 mg/1 in lower Spencer Creek. This location was used also for control: On November 30 it contained 38,904 mg/1 S04=, and on December 2 it contained 37,853 mg/1 S04=. Anomalous 50,575 mg/1 S04= was also observed at the headwaters of a tributary of Spencer Creek on December 2. and the source was an abandoned strip pit that discharges ground water to the tributary.

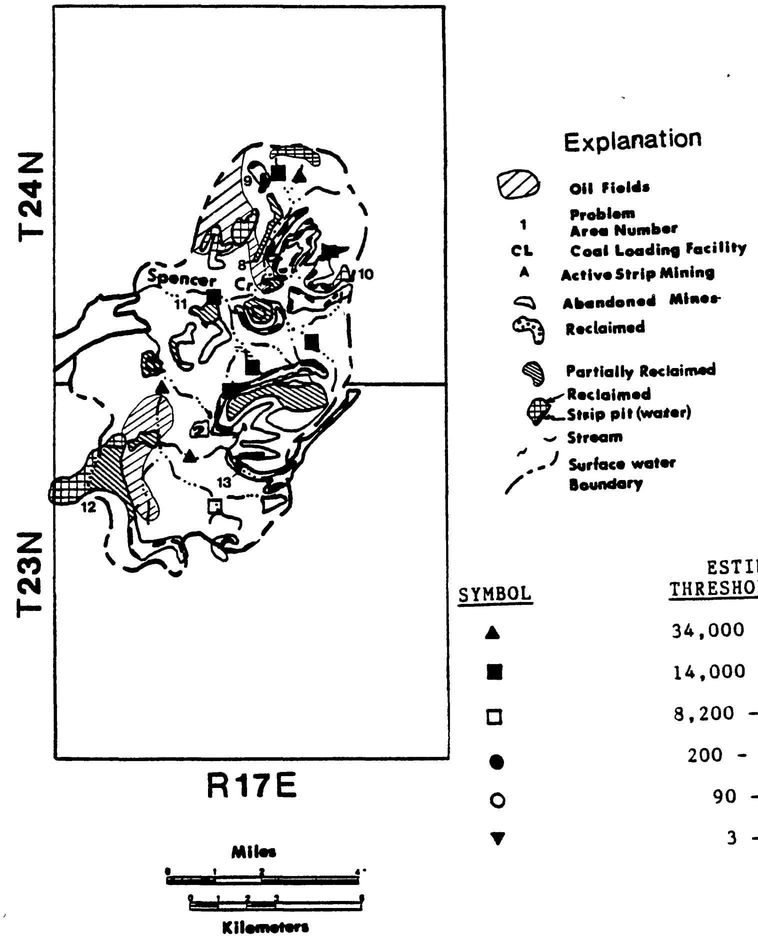
Source of anomalous (53,206 mg/1) S04= in a tributary of Blue Creek was ground-water runoff from areas that were probably strip mined (figure 38). Downstream a location sampled in middle Blue Creek contained 43,650 mg/1 S04= on the same day. Upstream from active coal mining, a stream which receives drainage from undisturbed coal fields contained 383 mg/1 S04=. Another stream sampled upstream from active coal mining during fall 1984, contained 20,878 mg/1 S04=. It was sampled adjacent to and upstream of a partially reclaimed coal field.

Anomalous (14,000-30,000 mg/1) S04= is based on threshold limits of populations B and C at two cumulative



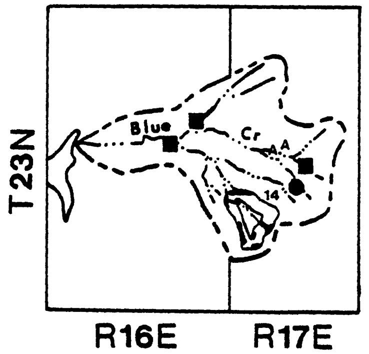
SYMBOL	ESTIMATED THRESHOLD LIMITS
▲	34,000 - 66,000
■	14,000 - 30,000
□	8,200 - 14,000
●	200 - 8,200
○	90 - 200
▼	3 - 90

Figure 36. Sulfate Concentrations in streams in Lightning, Panther and Plume Creek Basins



SYMBOL	ESTIMATED THRESHOLD LIMITS
▲	34,000 - 66,000
■	14,000 - 30,000
□	8,200 - 14,000
●	200 - 8,200
○	90 - 200
▼	3 - 90

Figure 37. Sulfate Concentrations in streams in Spencer Creek Basin



SYMBOL	ESTIMATED THRESHOLD LIMITS
▲	34,000 - 66,000
■	14,000 - 30,000
□	8,200 - 14,000
●	200 - 8,200
○	90 - 200
▼	3 - 90

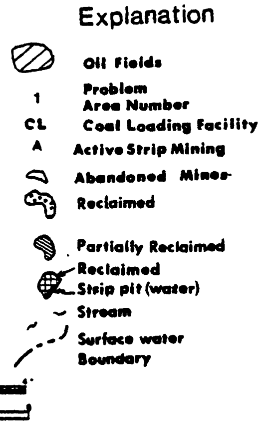


Figure 38. Sulfate Concentrations in streams in Blue Creek Basin

percent. Eight locations occur in the Oologah Reservoir Area. Seven of the eight observations occur near the headwaters of tributaries of Creeks where ground water was discharged from abandoned pits. Flowing water was sampled at five streams; the remaining three were stagnant and located at the headwaters of tributaries of Spencer and Blue Creeks.

Mixing of anomalous (8200-14,000 mg/1) S04=, based on threshold limits of combined S04= populations B and C, occur in four streams in the Oologah Reservoir Area. A control station, located at middle Spencer Creek, was sampled on November 30 (12,600 mg/1 S04=) and on December 2 (10,350 mg/1 S04=). All four streams were flowing at the time of sampling and are located in the lower reaches of Creeks or tributaries.

Anomalous (200-8200 mg/1) S04=, based on threshold limits, occurs at 15 locations. Seven of the locations occur near the headwaters of Creeks in the Oologah Reservoir Area. Four locations occur in the lower reaches of tributaries of major Creeks in both the Oologah Reservoir Area and Dog Creek Basin. Ten of the 15 observations were from flowing stream; three were from stagnant waters; and the remaining two were from waters ponded in stream. The stagnant and ponded waters were sampled from streams near or at the headwaters of tributaries.

Mixing of anomalous S04= and waters with background concentrations from (90-200 mg/1) S04=, based on threshold limits, occur at 3 locations. Two of the observations were from flowing streams, in Dog Creek Basin, above Lake Claremore (figure 39). The third sample was obtained from the headwaters of a tributary of Blue Creek and contained 134 mg/l SO4=, and is located below partially reclaimed coal strip mines.

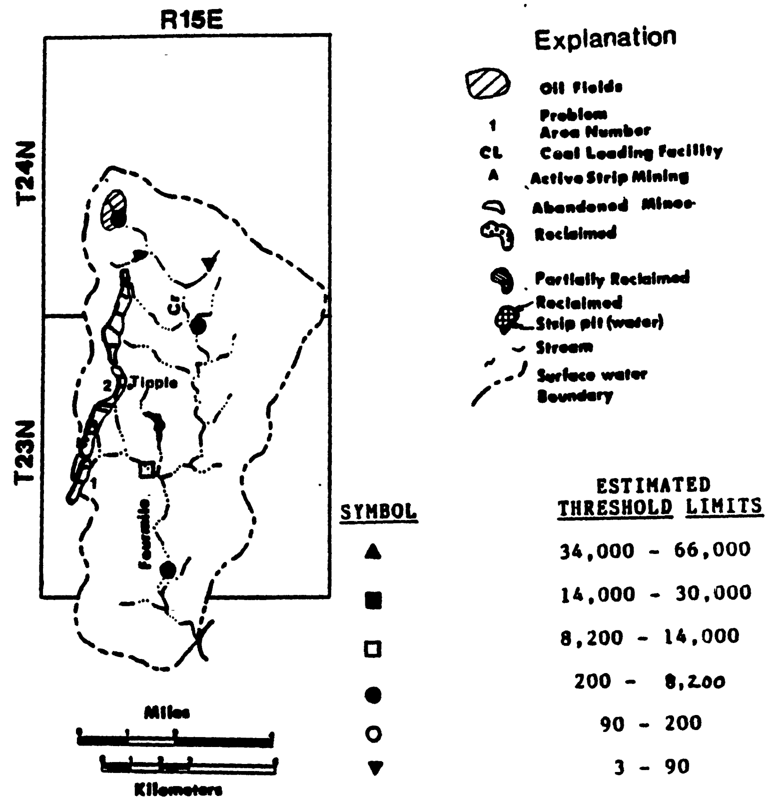
Background variation from (3-90 mg/l) SO4=, based on threshold limits, occur in ground-water runoff sampled on November 30 and December 2 from 6 flowing streams.
Four of the streams are tributaries of Dog Creek, surface runoff was sampled from the headwaters of Fourmile Creek, and last, runoff discharged from Oologah Reservoir contained 61 mg/l SO4=.

Ground water

Chemical analyses of Cl- and SO4=, from the Oologah Reservoir Area and Dog Creek Basin from the U. S. Geological Survey were selected and used to construct probability graphs.

Chloride Probability Graph

Partitioning of the Cl- cumulative probability curve into three populations A:B:C (15:25:60) was done after summing and plotting frequencies for each observation (figure 40).



SYMBOL	ESTIMATED THRESHOLD LIMITS
▲	34,000 - 66,000
■	14,000 - 30,000
□	8,200 - 14,000
●	200 - 8,200
○	90 - 200
▼	3 - 90

Figure 39. Sulfate Concentrations in at streams in Fourmile Creek Basin

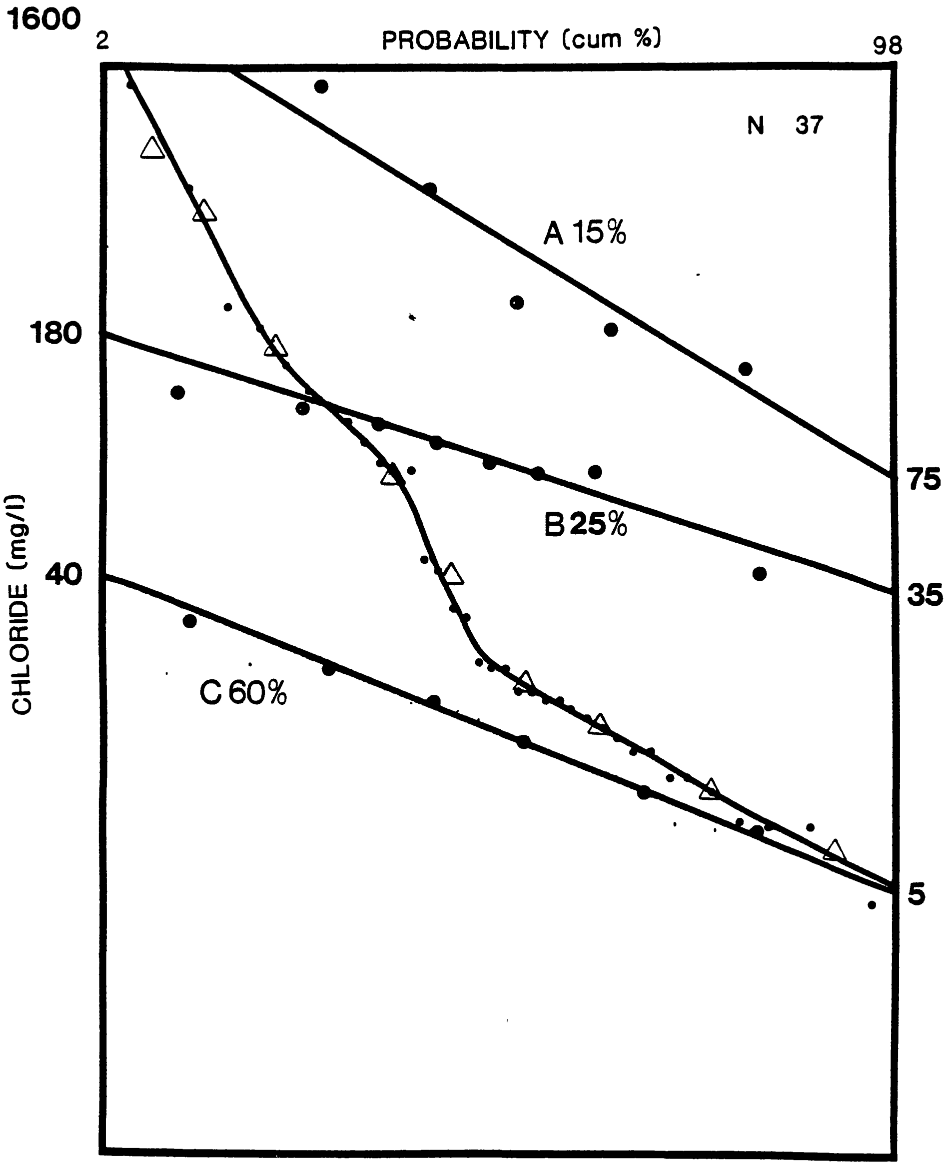


Figure 40. Probability Graph of Chloride Analyses from Ground Water in Oologah Reservoir Area and Dog Creek Basin

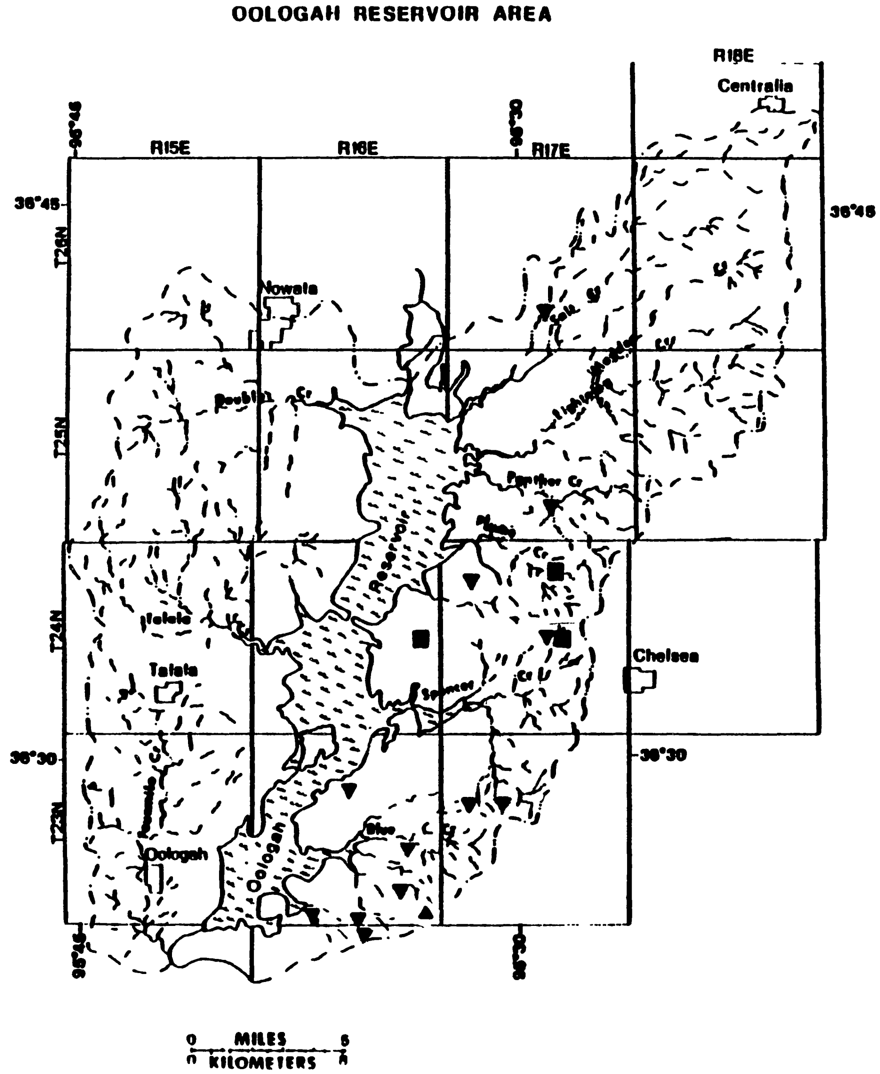
Sources of Chloride

Anomalous (180-1600 mg/l) Cl-, based on threshold limits, occur in four wells located in Blue Creek Basin (figure 41), Dog Creek Basin (figure 42) and in Sweetwater Creek Basin (located between both basins). Anomalous chloride is inferred to be associated with oil field activities.

Mixing of anomalous Cl- and Cl- contaminated ground water from 75-180 mg/l Cl- is based on threshold limits of combined populations A and B, are represented by eight samples as follows: One sample from a well near Plume Creek. Two samples from wells located in an oil field between Spencer and Plume Creeks. Three samples from wells located in Dog Creek Basin, and the two remaining samples that contained from 75-180 mg/l Cl- are located in Sweetwater Creek Basin.

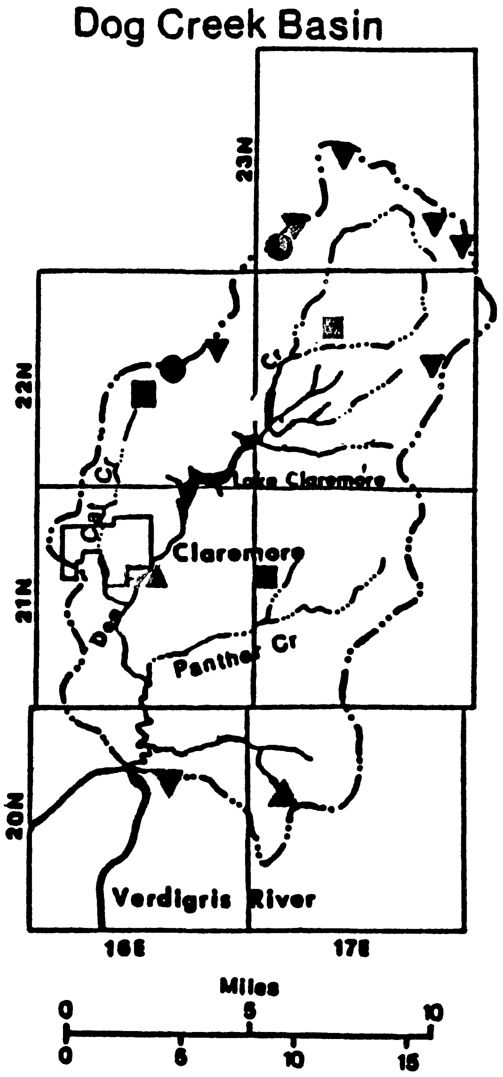
Contaminated ground water from 35-75 mg/l Cl-, based on threshold limits, occurs at two locations downgradient from abandoned water filled pits in Dog Creek Basin and may result from leakage of oil-field brines into the pits.

Background variation of chloride, from 5-35 mg/l, is based on threshold limits of Cl- population C. The twenty-three observations are located in areas near oil- and coal fields, or areas isolated from oil-field or coal-field activities.



SYMBOL	ESTIMATED THRESHOLD LIMITS
▲	180 - 1,600
■	75 - 180
●	35 - 75
▼	5 - 35

Figure 41. Chloride Concentrations in the Oologah Reservoir Area



SYMBOL	ESTIMATED THRESHOLD LIMITS
▲	180 - 1,600
■	75 - 180
●	35 - 75
▼	5 - 35

Figure 42. Chloride Concentrations in Ground Water in Dog Creek Basin

Sulfate Probabilty Graph

Individual S04= concentrations were cumulated, each with equal frequencies (figure 43). A single lognormal population approximates the data points. Statistical parameters (antilogs) are as follows : mean (50 mg/l), mean plus one standard deviation (300 mg/l), and mean minus one standard deviation (9 mg/l).

Geochemical Origins of Anomalous Sulfate

Oxidation of pyrite, catalyzed by bacteria, may account for the observed anomalous sulfate concentrations.

Possible sources are the older water filled pits that have undergone extensive evaporation. Another possibility for concentrating sulfate in the waste piles is as follows: Rainfall, which contains dissolved oxygen, infiltrates into the piles and, after initial dilution of sulfate, pyrite (or other sulfide bearing compounds) are oxidized and sulfate is added to infiltration waters in the unsaturated zone, flows rapidly downward through permeable spoils, recharges the fractured ground water system, and discharged into an adjacent abandoned pit or stream.

Groundwater may also contain anomalous sulfate concentrations resulting from probably oxidation of pyrite that probably occurs in coal and associated rocks in areas that have not been disturbed by coal strip mining.

Anomalous sulfate concentrations that were observed to increase between sampling on October 11, and November 30 (or December 2) are inferred to result from ground-

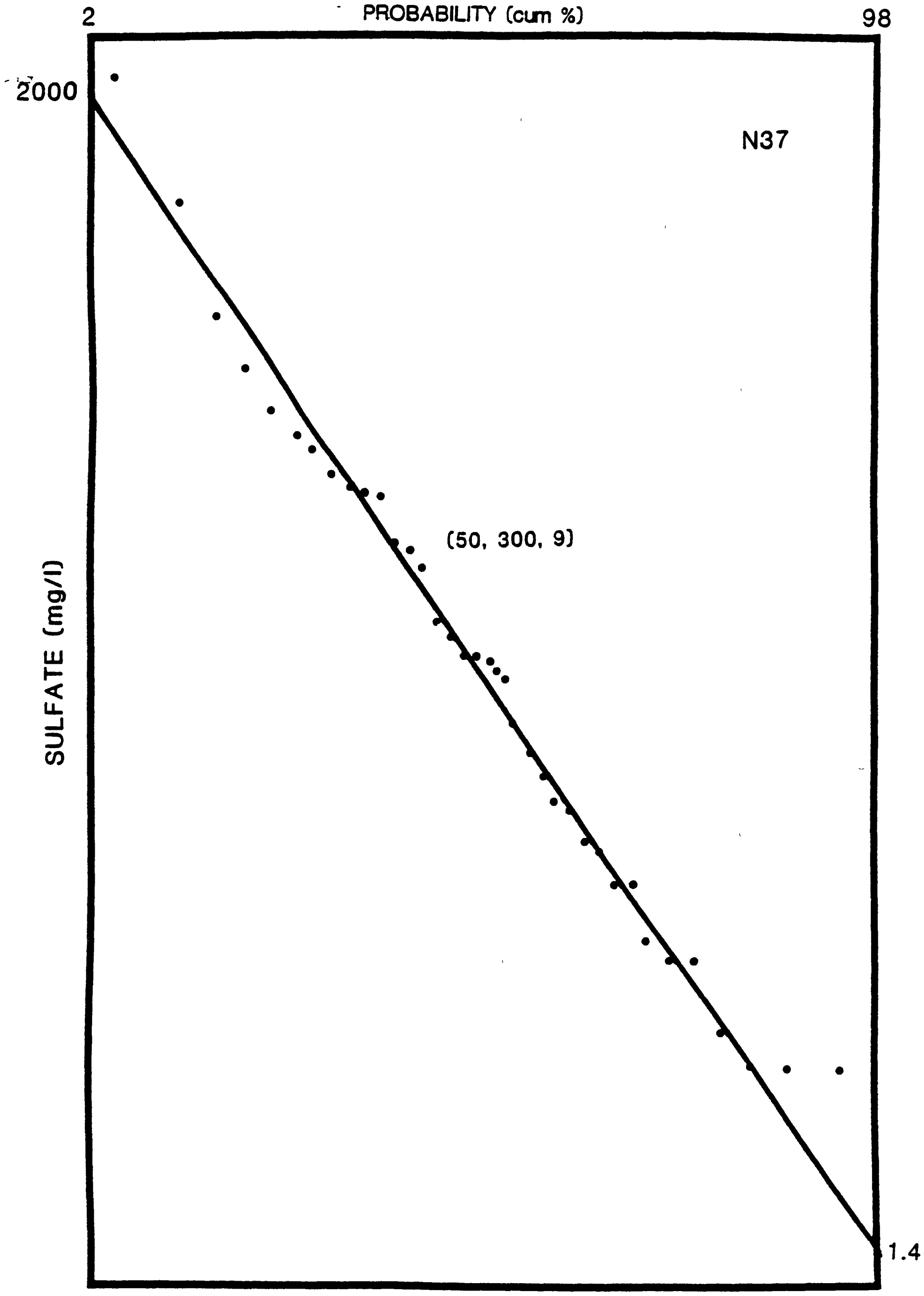


Figure 43. Probability Graph of Sulfate Analyses From Ground Water in the Oologah Reservoir Area and Dog Creek Basin

water runoff from spoil piles, and decreased sulfate concentrations that occur in streams probably result of dilution by rainfall that recharged the ground-water system between sampling on October 11, and November 30, 1984.

Acid mine drainage is not a problem in the study area, as indicated by variation in pH between 6 and 9 and probably results from buffering of the hydrogen ion concentration with calcium supplied by solution of calcium carbonate present in limestone in the Oologah Reservoir Area and Dog Creek Basin.

Comparison of Probability Graphs

Comparison of sources of waters may be done by using the mean (indicated by the solid circle) and the mean +/- 1 standard deviation, represented by the length of each bar (figure 44). All sources (populations) of chloride and sulfate are approximated by lognormal distributions and 67% of the analyses which comprise each population are contained within 2 standard deviations.

Anomalous chloride sources are a result of leakage of oil field brine from producing oil wells, abandoned wells, wells used for secondary oil recovery and brine injection, and solution of salts from abandoned evaporation ponds. The highest concentrations of chloride were observed in streams in Hominy Creek Basin during

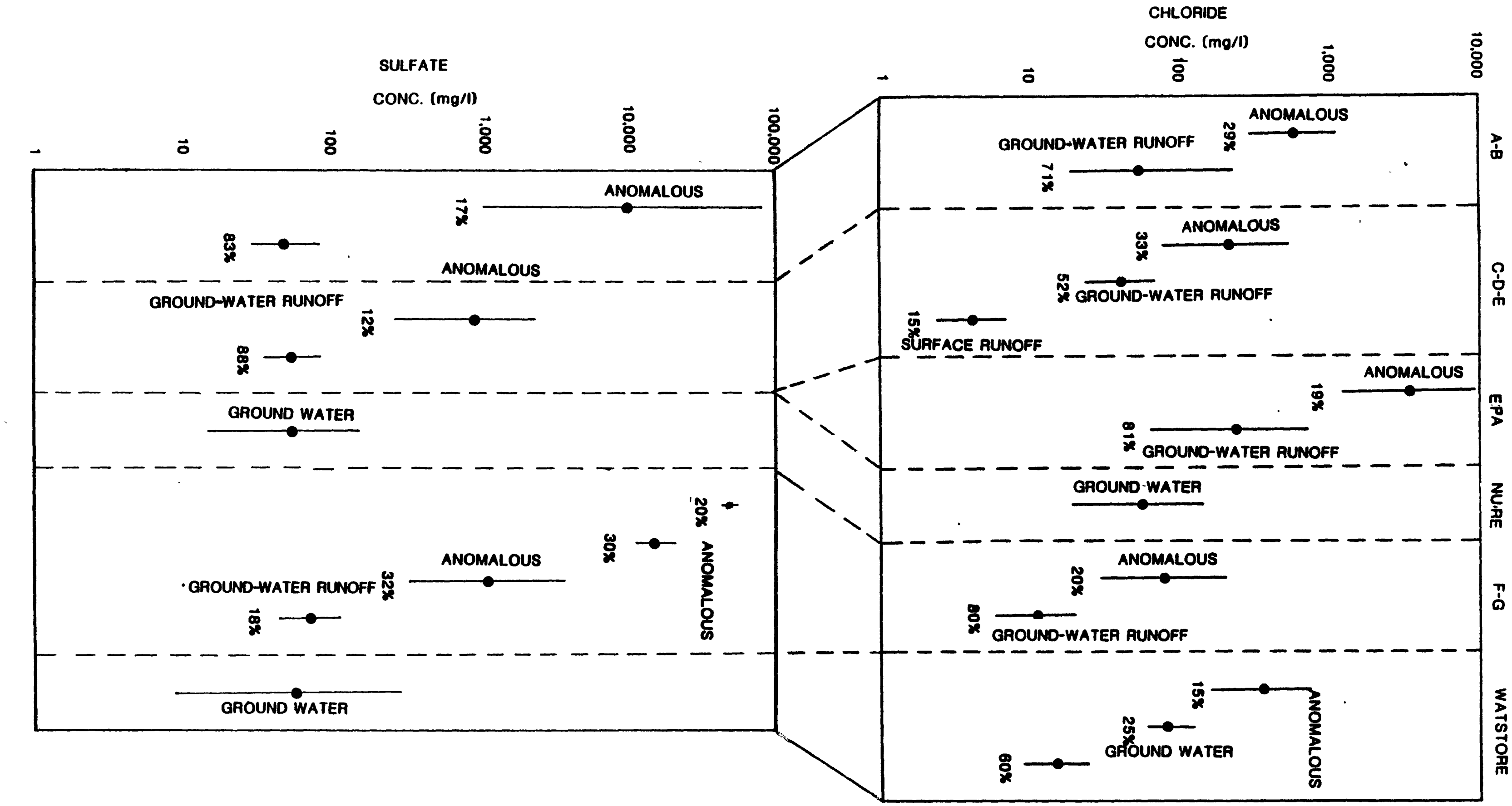


Figure 44. Sources and Concentration Limits for Chloride and Sulfate Based on the Mean +/- 1 Standard Deviation Plotted as the Length of Each Bar

baseflow conditions in July 1981 (EPA). Dilution of chloride anomalies is indicated by the mean and 2 standard deviations: decreased chloride concentrations as a result of recharge of water table aquifers during the fall of 1984 before samples were obtained in Hominy Creek Basin on October 11 and 19 (A-B), and further dilution by recharge between sampling on October 19 and November 4, 8, and 11, 1984 (C-D-E). Indeed water level rose in intermittent Delaware Creek, where ponded water was observed on October 11; On November 11, Delaware Creek was flowing at locations that contained ponded water one month before. Surface runoff containing the lowest variation in chloride concentration occurred in streams containing ponded or stagnant waters. Further, rainfall contains probably less than 1 mg/l Cl- (NADP, 1985; Fredrickson, 1985). Comparison of chloride from ground water (NURE, WATSTORE) with that of ground water runoff in all areas under study indicated that dilution by rainfall did not significantly effect the mean and standard deviations of background variation of chloride.

Anomalous sulfate variation based on samples collected in streams in the Oologah Reservoir Area (A-B) compared with samples collected on November 30 (and December 2, 1984) indicated that the standard deviations of anomalous sources overlapped. Anomalous sulfate sources in the Oologah Reservoir Area and Dog Creek Basin (F-G) occur in groundwater runoff from streams that are in near 1) active coal strip mines, 2) abandoned coal strip mines, and 3) in partially or totally reclaimed coal strip mines. Sulfate anomalies in Hominy Creek Basin (C-D-E) occurred in streams that receive runoff from rock units that contain coal seams that have not been commercially mined. Natural variation in background sulfate concentrations, by comparison of means and standard deviations indicates that rainfall did not dilute sulfate contained in ground water runoff compared to concentrations in ground water (NURE, WATSTORE) in all areas that were studied.

CHAPTER VIII

SUMMARY AND CONCLUSIONS

Summary

1. Excessive concentrations of Cl- and SO4= are known to occur in the Verdigris River Basin in Oklahoma. Sources of excessive Cl- are related to contamination by oil field brines or other activities of man. Sources of excessive SO4= are associated to contamination of water in contact with coal beds, waste piles or abandoned pits associated with coal mining areas. Pollution by oil field brines was identified in Caney River and its tributaries above the confluence with Double Creek near Ramona, and the Verdigris River above Oologah Reservoir. Sulfate pollution was suggested for some small streams, associated with coal mining waste piles in the upper reaches of the Verdigris River. Contamination of ground water was identified to occur in coal field areas, such as Rogers, Nowata, and Craig Counties.

2. Concentration limits, established by the U.S. Environmental Protection Agency are 250 mg/l for either SO4= or Cl-. These are recommended mainly to provide acceptable taste and esthetic characteristics.

Hydrologic Cycle

Precipitation provide essentially all of ground-water recharge. The following statistics are based on stream flow data from the U.S. Geological Survey during the period 1970-79.

1. Average annual precipitation ranges 36-41 inches, wer to east, across the Verdigris River Basin.
2. Effective ground-water recharge rate varies 2-5 inches, west to east over the Verdigris Basin.
3. Average annual evapotranspiration is about 30 inches throughout the Verdigris Basin, increasing to 32 inches in western Nowata and Rogers Counties.
4. Average annual runoff is 10 inches near the confluence of Bird Creek and Verdigris River, decreasing to hte northwest to about 5 inches near the western drainage divide of the Verdigris River Basin.

Alluvial and Terrace Aquifers

1. Quaternary sediments consisting of hetereogeneous arranged gravel- to clay-sized particles occur beneath floodplains that consist of predominately silt and clay. Thickness usually range up to 80 ft. Yields are moderate to large. Ground-water composition is wdely variable and generally hard. Concentrations of Cl- and SO4= may loccally exceed 250 mg/l.
2. Quaternary alluvial and terrace deposits associated with

the Lower Veridgris Rover, vary in thickness 56-101 ft. Course sands and gravels, up to 20 ft thick and averaging about 5 ft, occur near the alluvium-rock contact. Depth to water ranges from 17-33 ft. Water level fluctuates 1-5 ft due to seasonal chages in discharge and recharge, increasing up to 10 ft over an 8 year period.

3. Transmissivity ranges 1400-12,000 gpd/ft. Storativity varies 0.026-0.03. Saturated thickness varies 12-19 ft where three aquifer tests were done for 72 hours.
4. Well yields range generally 1-10 gpm, increasing to 30 gpm in areas underlain by thicker saturated coarse sands and gravels.
5. Water-type is predominately Ca-Mg-HCO3. Maximum concentrations of Cl- and SO4= were associated with seepage from Pennsylvanian strata or activities of man.

Vamoosa-Ada Aquifer

1. The Vamoosa-Ada aquifer consists of the Ada Group underlain by and in hydrologic connection with the Vamoosa Formation. The western boundary of the confined Vamoosa-Ada aquifer is defined by the occurrence of 1500 mg/1 dissolved solids. Highest yields are in Creek County where some sandstone beds are coarse-grained.

2. The Vanoss Group consists of mostly interstratified limestones and shales approaching 500 ft thick. It confines the Vammoosa-Ada aquifer to the west where it directly overlies it.

3. The Ada Group consist of predominately shale with numerous fine-grained sandstone and limestone. Total thickness is about 400 ft. The Vamoosa Formation consist of fine- to coarse sandstones with interbedded shales. Total thickness is about 630 ft.

4. Water type is 75 percent sodium bicarbonate or calcium bicarbonate. The ramaining 25 percent consists of Na-SO4, Ca-SO4; and Na-Cl types. Trends are as follows: Decreasing with depth are Ca and Mg; Increasing with depth are Na, HCO3, SO4= and total dissolved solids; Chloride is constant with depth, and 10% exceed 250 mg/l. Ground-water contamination by brines has occurred in some areas.

Pennsylvanian Rocks

1. The Vamoosa-Ada aquifer is underlain also by Pennsylvanian strata, in descending stratigraphic order as follows: Tallant, Barnsdall, Wann, Iola, Chanute, Nellie Bly, Hogshooter, Coffeyville and Checkerboard Formations.

2. Pennsylvanian rock units that crop out in the Oologah Reservoir area include the following in descending stratigraphic order: Coffeyville, Checkerboard, Seminole, Lenapah, Nowata, Oologah, Labette, Fort Scott, Senora and Boggy Formations.

3. Strippable coal beds (5) occur near the Seminole base and Secor Formations. Coal is bituminous with sulfur contents ranging from 0.4 to 5 percent, and of variable volitility.

Thicknesses vary between about 1.0 to 3.4 ft.

4. Carbonates, and resistant sandstones crop out as homoclines facing the east, separated by less resistant shales and sandstones. Regional strike varies to the north, from north to northeast and dip is about 40 ft/mi to the west to northwest.

5. Domes, basins, and plunging anticlines and synclines occur as isolated folds.

6. En echelon faults occur in abundance in Osage County as predominately normal faults that trend northeast or northwest. Lengths are between 2 adn 3 miles. Displacement is usually less then 100 ft, commonly 50 ft. Displacement decreases with depth.

Conclusions

Verdigris River and Hominy Creek Basins

1. Anomalous (850-2200 mg/l) Cl- occur at four stream locations in Hominy Creek Basin based on threshold limits of Cl-population A from samples obtained on October 11 and 19, 1984.

2. Chloride contaminated ground-water (160-850 mg/l), based on threshold limits of combined Cl- populations A and B, occurred in several streams in the Verdigris Basin on October 11, and 19. Ground-water runoff contaminated with Cl- include Delaware, Hominy, Candy, California, Panther, and Plume Creeks.

3. Ground-water runoff containing (4.8-160 mg/l) Cl-, based on threshold limits of Cl- population B, occur in other

streams sampled throughout the Verdigris River Basin in Oklahoma on October 11 and 19, 1984.

4. Anomalous (780-190,000 mg/l) SO4=, based on analyses that occur within the threshold limits of SO4= population A, occur in stream basins that contain active coal strip mining, partially or totally reclaimed strip mining lands, and/or abandoned strip-mines. Anomalous SO4= occurred in the following streams at sampling locations on October 11, 1984: Lightning, Panther, Plume, Spencer, Blue, Fourmile, and Dog Creeks. The Verdigris River, below Fourmile Creek also contained anomalous SO4= in ground-water runoff on the same day.

5. Background variation of SO4= (15-120 mg/l) represents 43 analyses of ground-water runoff from streams throughout the Verdigris River and Hominy Creek Basins on October 11, and 19, 1984, based on thresholds of population B.

6. Anomalous concentrations of Cl- and SO4= contamination occur in Panther and Plume Creeks based on threshold limits of (1) combined Cl-populations A and B, and (2) SO4= population A.

Hominy Creek and Delaware Creek Basins

7. Further sampling of streams occurred on November 4, 8, and 11, 1984, during a period when no rainfall occurred at Hominy.

8. Anomalous (120-1500 mg/l) Cl-, based on threshold limits of Cl- population A, occur in 15 streams where

ground-water runoff is from the Vamoosa-Ada aquifer, and Eagle Creek, which discharges into Hominy Creek.

9. Oil-field brines range 81,780-137,700 mg/l Cl-, and 0-150 mg/l SO4= in Hominy Creek and Delaware Creek Basins. Oil production is primarily by secondary oil recovery and injection of oil-field brines. Zones which produce hydrocarbons occur between 1650 and 2450 feet below the surface in fractured Pennsylvanian Rocks.

10. A ground-water equilibrium model indicates that ground water from the Vamoosa-Ada aquifer containing 570 mg/l Cl- and 120 mg/l SO4= is oversaturated with respect to iron oxides and hydroxides; in equilibrium with calcite, dolomite, and magnesite; and undersaturated with respect to common evaporite minerals including halite, anhydrite or gypsum. Reverse softening of sodium chloride brines prior to mixing with Vamoosa-Ada ground water can account for enrichment of calcium for the relatively low Mg/Ca ratio.

11. Mixing of anomalous and background concentrations (30-120 mg/l), based on threshold limits of combined populations A and B, occurs at 26 locations.

12. Background variation of ground-water runoff (13-30 mg/l) Cl-, based on threshold limits, occur at nine locations: three streams containing ground-water runoff; stagnant ground water at three streams and ponded surface water at two streams. Ground water from a Vamoosa-Ada spring contained 24 mg/l Cl-.

12. Surface runoff (1.4-13 mg/l) Cl- is based on threshold

limits of population C. In support, five of the streams contained ponded surface runoff and the remaining six were contained stagnant waters.

13. Source of anomalous 206 mg/l Cl- on November 11 in ground-water runoff in Delaware Creek is related to leakage of oil field brines from an oilfield upstream. Ground-water runoff in Delaware Creek on the same day showed uncontaminated ground-water runoff. Dilution of contaminated ground-water runoff occurred in Delaware Creek on November 11th downstream above the confluence with Bird Creek: Chloride was 167 mg/l from ground-water runoff. On October 11, in comparison, this site contained ponded water that showed 588 mg/l Cl-.

14. Chloride analyses done at streams in Hominy Creek Basin in July, 1981, during a period of low flow (EPA,1985) shows the following: Anomalous (2500-28000 mg/l) Cl- at five locations; Chloride contamination (400-2500 mg/l) Cl- at 17 streams that discharge groundwater runoff from the Vamoosa-Ada aquifer; and streams with 20-400 mg/l Cl-, based on threshold limits, suggest mixing of uncontaminated and contaminated ground water-runoff, during low flows.

15. Ground water in Hominy Creek and Delaware Creek Basins range 19-140 mg/l Cl- based on the mean +/- one standard deviation.

16. Anomalous (318-2462 mg/l) SO4=, based on analyses which occur within the threshold limits of SO4= population A, occur in 6 streams in Hominy Creek Basin sampled on November 4, 8,

and 11, 1984. Streams with anomalous SO4= are as follows: (1) Headwaters of Hominy Creek, (2) tributary to Hominy Creek about 4 miles south of (1), (3) two tributaries near the headwaters of Nicicola Creek, (4) Mahala Creek, and (5) middle Penn Creek above the town of Hominy.

17. Source of anomalous SO4= is probably oxidation of pyrite associated with coal seams of the Vanoss Group which occurs within the surface drainage of these streams.

18. Ground-water containing 110 mg/l Cl- and 190 mg/l SO4= is oversaturated with respect to dolomite; in equilibrium with calcite, magnesite, aragonite; and undersaturated with respect to halite, anhydrite and calcite, based on results from a chemical equlibrium model.

19. Mixing of anomalous SO4= and natural concentrations of sulfate in ground-water runoff occurs in the range 88-140 mg/l based on threshold limits of combined SO4= populations A and B. Streams in which samples show SO4= mixing are as follows: (1) headwaters of an unnamed tributary of Bull Creek, associated with mixing of contaminated Cl- and surface runoff in water ponded in the stream, (2) two unnamed tributaries to lower Hominy Creek in Range 12E, which contained apparantly nonflowing water within the stream on November 11.

20. Natural variation of SO4= (22-88 mg/l), occurs in all other streams sampled in Hominy and Delaware Creek Basins on November 4, 8, and 11, 1984, based on threshold limits of SO4= population B.

21. Ground water in Hominy and Delaware Creek Basins contain between 15-160 mg/l SO4= based on the mean +/- one standard deviation.

Oologah Reservoir Area and Dog Creek Basin

1. Chloride contamination (40-520 mg/l), based on threshold limits, occurred in ground-water runoff from four flowing streams, and stagnant ground water in lower Fourmile Creek.
2. Anomalous (120-1500 mg/l Cl-), based on threshold limits occurred in oil fields and indicates contamination by oil field brines. Contaminated ground water (30-120 mg/l Cl-) is based on threshold limits of population B and occurred in or near oil fields.
3. Oil-field brines are injected into the Bartlesville Formation at depths ranging from 240-500 ft below land surface for secondary oil recovery or brine disposal.
4. Mixing of contaminated and uncontaminated ground-water runoff (12-40 mg/l) is based on threshold limits of combined Cl- populations A and B, and occurs in 21 streams. Ground-water runoff was sampled from 17 streams. Ground water was sampled from 3 streams that contained stagnant water and a location that contained ponded surface water.
5. Ground water from four wells in the Oologah Reservoir Area and Dog Creek Basin contained anomalous (180-1600) mg/l Cl-, based on threshold limits. Mixing of contaminated ground water (75-180 mg/l Cl-), is based on threshold limits of combined populations A and B, and occurred at eight

locations. Contaminated ground water (35-75 mg/l Cl-) and background variation (5-35 mg/l Cl-) is based on threshold limits.

6. Uncontaminated waters (3-12 mg/l) Cl- occurs in 17 streams sampled on November 30, and December 2, based on threshold limits. Of these streams, 14 contained flowing ground-water runoff; three contained ground water stagnant in each stream; and ponded surface water was also in this range.

7. Streams in Dog Creek Basin were sampled on November 30, 1984, and all were flowing at that time. Chloride contaminated ground-water runoff, based on threshold limits, occurs in Dog Creek below the confluence with Cat Creek. Source of Cl- contamination is inferred to be direct discharge of treated municipal effluent from facilities located between sampling locations at Cat and Dog Creeks.

8. Anomalous sources of sulfate, occurred in samples from streams in Dog Creek Basin and the Oologah Reservoir Area on November 30, and December 2, based on threshold limits: A (34,000-66,000 mg/l), B (14,000-30,000), combined B+C (8,200-14,000), and C (90-8,200).

9. Natural variation of SO4= (3-90 mg/l), based on threshold limits occured at seven locations.

10. Sulfate in ground water, from the same areas, shows one lognormal population with a range of 9-300 mg/l, based on the mean +/- one standard deviation.

11. Sulfate anomalies in streams in the Oologah Reservoir Area and Dog Creek Basin are the effects of coal strip

mining, and coal reclamation activities.

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APPENDIX

Field Parameters and Chemical Determinations

Sample	Temp(°C) (°C)	pH	S.C.	Chloride #1	Chloride D	Sulfate #1	Sulfate D
2	22	7.6	230	10.65		47.62	
3	20	7.5	690	52.34		2092.56	
4	22	8.2	450	39.86		781.89	
5	23	7.7	1000	130.54		2383.82	
6	22.5	7.75	1500	14.61		26816.7	
7	23	8.1	1800	56.60		30700.2	
8	23	7.9	3100	668.23		9228.42	
9	21	8.0	1800	218.18		7189.61	
10	20	7.6	3600	23.74		191,150	188,820
13	22.5	8.2	460	28.91	28.91	34.48	27.56
14	21	8.7	490	40.17	41.08	85.97	84.52
15	20	8.0	1300	241.91	242.22	80.63	84.52
16	24	9.0	350	20.99	21.60	67.04	78.69
17	21	7.6	420	7.61	8.52	88.4	93.26
18	--	7.9	760	125.06	126.89	58.79	52.96
20	--	7.7	800	139.37	140.58	41.31	45.68
21	--	7.7	660	84.90		84.03	
24	21	7.4	640	63.60	62.99	99.57	
25	19	8.0	440	27.69		93.26	
26	17	7.1	2100	587.90		24.32	
27	18.5	8.2	540	61.16		47.14	
28	18	7.5	1800	442.75		50.05	
29	19	7.2	2000	508.78		70.44	
30	17	6.9	1200	310.68	311.60	52.48	
31	17.5	7.5	1400	284.21		33.55	
32	19	7.6	370	31.34		34.03	
34	--	7.9	330	10.04		17.04	

A-Series Samples Collected 10-11-84

T - Temperature C - Centigrade D - Duplicate
S.C. - Specific Conductance (μMHOS/cm)

Field Parameters and Chemical Determinations

Sample	Temp(°C) (°C)	pH	S.C.	Chloride #1	Chloride D	Sulfate #1	Sulfate D
4	13	6.6	200	25.56		61.81	
5	17	7.6	2600	1138.47	1136.23	7.37	7.64
6	14	7.8	810	180.81	185.80	53.89	
7	14	7.2	530	122.33		45.48	
8	17	8.4	1300	485.06	511.82	31.13	30.63
9	14	8.0	570	154.62	163.71	51.42	52.90
10	15	7.4	2900	1231.78		21.23	
11	15	8.1	480	38.03		114.77	
12	19	8.2	240	11.00		73.19	
14	15	7.7	840	115.02		108.33	
15	15	8.0	430	99.20		14.30	
16	17	7.6	270	25.26		56.86	
18	16	7.8	520	61.10		36.57	
19	15	7.9	760	224.45		57.36	
20	19	7.4	2200	850.42		100.91	
21	15	7.7	1300	491.74		27.66	
22	15	8.1	1300	483.82	481.32	28.16	29.64
23	14	7.7	120	9.74		42.51	
24	15	8.2	840	1067.39		32.12	
25	14	8.1	920	216.97	216.05	63.30	62.80
26	15	8.0	1800	715.13		32.12	
28	15	6.8	1600	606.64	584.82	37.56	38.06
29	16	7.8	1400	528.25		75.67	
30	15	7.5	1100	197.18	192.92	42.01	43.50

B-Series Samples Collected 10-19-84

T - Temperature C - Centigrade D - Duplicate
S.C. - Specific Conductance (μMHOS/cm)

Field Parameters and Chemical Determinations

Sample	Temp(°C) (°C)	pH	S.C.	Chloride #1	Chloride D	Sulfate #1	Sulfate D
1	14	7.1	5050	585.75		127.65	
2	13	7.6	1100	97.19		46.73	
3	14	7.5	310	13.13		94.84	
4	13	7.6	130	21.01		23.40	
5	16	8.0	210	28.52		49.65	
6	17	8.2	250	33.40		318.14	
7	13	7.8	300	35.27		40.90	
8	15	7.7	2200	744.85	805.53	95.57	
9	14	8.0	670	133.96		45.27	
10	14	7.9	220	2.88		68.83	
11	15	7.7	2300	792.50	800.01	93.39	
12	14	7.6	600	24.39		63.50	
13	13	7.3	1200	436.78	421.47	43.82	44.54
14	13	7.8	310	11.26		40.90	43.09
15	13	7.6	260	59.85	57.36	75.89	80.26
16	--	7.6	680	164.35	194.53	75.89	76.62
17	--	7.6	370	37.90	38.66	64.96	67.87
20	14	7.2	1600	427.02	413.89	66.41	66.41
26	16	7.6	3000	52.91	62.35	46.00	
30	--	7.8	600	120.45		62.04	67.87

C-Series Samples Collected 11-4-84

T - Temperature

C - Centigrade

D - Duplicate

S.C. - Specific Conductance (μMHOS/cm)

<u>Field Parameters and Chemical Determinations</u>

Sample	Temp(°C) (°C)	pH	S.C.	Chloride #1	Chloride D	Sulfate #1	Sulfate D
1	15	7.4	270	3.19		694.47	
2	14	7.2	160	4.13		2462.22	
3	15	7.6	310	49.88		105.05	
4	15.5	7.6	720	366.60		48.92	
5	19.5	8.3	470	53.62		1514.56	
6	19	8.4	230	26.27		54.02	
7	17	8.1	110	1.75		26.32	
8	18	7.5	200	24.77		366.44	
9	19	7.6	400	98.31		44.55	
10	19	8.0	620	205.75		72.97	
11	19	7.8	420	54.03		48.19	
12	19	8.4	820	280.56		46.00	
13	17	7.9	520	58.91		86.83	81.72
14	21	7.7	130	12.38		712.70	
15	17	7.2	210	46.53	47.66	43.82	45.27
16	17	7.9	250	30.39	31.14	51.83	52.56
17	21	8.0	370	72.80	72.05	118.17	121.82
18	17	7.6	280	21.39	22.51	86.10	84.64
19	20	7.4	120	2.88	2.88	93.39	
20	19	7.1	220	39.78	39.40	75.16	85.37
21	21	7.5	380	39.02	40.15	121.09	
22	18	7.7	200	25.14		67.14	68.60
23	17	7.2	330	67.92		23.40	
24	18	7.8	380	69.42	68.29	48.92	48.92

D-Series Samples Collected on 11-8-84 T - Temperature C - Centigrade D - Duplicate
S.C. - Specific Conductance (μ MHOS/cm)

Field Parameters and Chemical Determinations

Sample	Temp(°C) (°C)	pH	S.C.	Chloride		Sulfate	
				#1	D	#1	D
1	10	6.4	140	4.13		35.24	38.14
2	10	7.0	200	27.39		64.32	
3	10	7.2	180	8.26		45.42	45.42
4	11	7.2	80	2.38		30.15	33.78
5	11	6.7	700	206.01			
6	10.5	7.1	580	167.36			
7	11.5	7.1	430	84.05			
8	14	7.2	370	60.04		45.42	
9	12	7.4	250	54.41		40.33	
10	14	6.8	1200	444.66			
11	12	8.0	140	3.85		22.88	
12	13	8.5	200	37.90		34.51	
13	12	8.2	240	46.15	47.66	36.69	
14	12	7.5	280	45.03	46.15	38.14	
15	12	7.3	590	128.33	130.96		
16	10	8.0	490	112.20	113.32		
17	11	7.8	700	175.24	177.49		
18	10.5	7.8	340	59.66	60.79		

E-Series Samples Collected 11-11-84

T - Temperature C - Centigrade D - Duplicate
S.C. Specific Conductance (μ MHOS/cm)

Field Parameters and Chemical Determinations

Sample	Temp(°C)	pH	S.C.	Chloride		Sulfate	
	(°C)			#1	D	#1	D
1	9.5	7.0	620	90.03		468.99	
2	9.0	7.2	430	18.24		454.12	
3	9.5	7.5	120	6.26		43.65	
4	8.5	6.8	140	6.53		90.48	
5	9.0	6.9	200	15.63		147.73	
6	10	7.0	140	11.73		42.90	
7	9	7.2	170	12.16		111.30	
8	8	7.2	200	38.22		52.57	
9	16	8.2	390	4.49		134.34	
10	11	8.1	2100	6.80		43649	
11	9.5	8.0	2500	6.12	6.39	52001.	54410
12	11	7.9	710	21.28	22.15	373.8	391.7
13	10.5	7.3	590	8.57	8.57	20135	21622
14	10.5	7.2	2000	13.90	12.59	39,958	37850
15	10.5	8.0	1300	53.85	54.72	12,632	
16	10.5	8.2	1200	6.94	7.21	16,033	17847

F-Series Samples Collected 11-30-84

T - Temperature   C - Centigrade   D - Duplicate
S.C. - Specific Conductance (μ MHOS/cm)

Field Parameters and Chemical Determinations

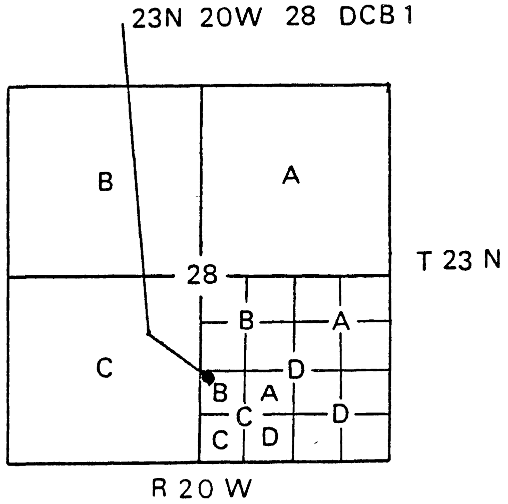
Sample	Temp(°C) (°C)	pH	S.C.	Chloride #1	Chloride D	Sulfate #1	Sulfate D
1	7.5	6.7	1000	23.88		15,126.4	
2	6.0	7.0	1100	8.69	7.48	17,393.9	
3	8.0	7.4	1100	12.59		14,899.7	
4	8.0	7.6	2200	8.25	7.35	44,473.9	
5	7.5	7.9	620	17.80		1,109.77	
6	9.0	7.6	1800	12.16		35,441.3	40,265.2
7	7.5	7.8	1500	12.59		10,364.8	
8	8.0	8.0	2400	7.75		50,574.6	
9	8.0	7.8	1300	22.58		5,808.23	
10	11	7.3	840	4.63		5,851.42	
11	9.5	7.2	960	25.19		1,857.56	
12	8.0	7.0	1200	174.57		12,155.9	
13	8.0	7.8	1500	336.32	335.11	6,840.62	8,003.22
14	9.0	7.6	680	86.85	90.76	1,014.32	978.44
15	8.0	7.9	1200	10.27	10.15	6,902.65	7,340.42
16	8.0	8.0	1400	14.43	14.68	13,031.4	13,469
17	8.0	7.7	2000	6.94	7.07	30,964.5	28,639.3
18	8.0	7.8	530	3.40	3.54	2,001.09	2,001.09
19	6.0	8.0	1100	4.76		1,330.22	
20	8.0	7.6	2000	12.16	11.73	45,787.6	46,368.9
21	7.5	7.8	2600	14.33		50,932.1	
22	7.0	8.1	1800	39.95	39.95	17,304	
23	7.0	7.7	1600	17.80	17.55	26,604.7	
24	7.5	7.8	2400	16.50		58,412.6	61,886
25	5.5	8.2	580	29.53		476.08	
26	7.5	7.4	500	18.67		634.83	
27	7.0	7.8	520	4.08		83.14	
28	8.5	7.4	880	10.86		12,166.8	
29	8.0	7.4	660	69.91		1,401.98	
30	9.0	6.6	250	14.33	14.33	60.67	59.23

G-Series Samples Collected 12-2-84 T-Temperature C-Centigrade D-Duplicate S.C. Specific Conductance (μMHOS/cm)

Explanation of Sampling Locations

The system used to specify sampling locations that I used in the Appendix is that used by the U.S. Geological Survey and replaces the standard legal system. A location given by the legal system, in the example below, as NW1/4 SW1/4 SE1/4 sec. 28, T.23 N., R.20 W. can be replaced by the USGS method as 23N-20W-28DCB1 which is in reverse order of the legal method, letters replace the fractional subdivisions, and numbers after the last letter distinguish locations within the smallest subdivision. . Locations that were plotted on figures in this study were identified using the USGS method.

The latitude-longitude system was used for locating wells that were unnecessary to be plotted on figures in this thesis. A location indicated by the latitude-longitude system, for example, 36 13 44/96 14 42 refers to 36 degrees, 13 minutes, 44 seconds latitude and 96 degrees, 14 minutes, 42 seconds longitude. Latitude and longitude are designated on topographic maps.



Sampling Locations and Stream Observations.

Sample Number	USGS Location	S.O.	Sample Number	USGS Location	S.O.
A2	21N-16E-26BCD	-	A3	21N-16E-21CCC	S
A4	20N-15E-05ABB	F	A5	23N-15E-33ACB	-
A6	23N-16E-24BCB	-	A7	24N-17E-28CCB	-
A8	25N-17E-32CCB	P	A9	25N-17E-27BCC	-
A10	25N-17E-15BCC	-	A13	26N-17E-07DBB	SR
A14	26N-16E-05ADD	SR	A15	26N-16E-07DAA	F
A16	25N-16E-07ADD	SR	A17	24N-16E-14BCA	S
A18	22N-14E-10CCC	F	A20	26N-12E-24DCB	F
A21	26N-13E-19ACC	F	A24	20N-15E-19BBB	F
A25	20N-14E-07AAA	F	A26	21N-12E-25ADA	S
A27	21N-13E-07DDC	F	A28	21N-12E-12DDD	F
A29	23N-09E-33DCC	F	A30	23N-08E-18ABC	F
A31	23N-12E-08DBA	-	A32	24N-11E-17BCC	F
A34	26N-09E-11DCD	-	B4	21N-12E-09ADA	S
B5	21N-12E-08BBA	POND	B6	22N-12E-31DAA	S
B7	22N-11E-24ADC	S	B8	23N-08E-12CDA	F
B9	22N-10E-32DDD	S	B10	22N-10E-29CCD	S
B11	22N-09E-13CDC	S	B12	22N-09E-08DBB	POND
B14	22N-09E-06BBB	S	B15	23N-09E-36ADD	F
B16	23N-09E-34ADD	S	B18	23N-08E-36DBD	S
B19	24N-08E-36BAA	F	B20	24N-08E-14CAB	F
B21	23N-08E-12DCB	F	B22	23N-08E-13BBB	F
B23	23N-08E-03ADB	P	B24	24N-08E-33DCA	F
B25	24N-08E-32AAB	F	B26	23N-08E-15DCD	F
B28	21N-12E-12DDD	F	B29	23N-09E-33DCC	F
B30	23N-08E-18ABC	F	C1	24N-07E-10DDA	P
C2	24N-07E-10DDB	S	C3	25N-08E-30CBA	P
C4	23N-08E-32BCB	P	C5	23N-08E-20AAD1	F
C6	23N-08E-20AAD2	F	C7	23N-08E-35DAA	S
C8	23N-08E-09BBD	F	C9	23N-08E-05BCB	S
C10	24N-08E-29ADB	P	C11	24N-08E-29BDD	F
C12	24N-08E-21ABC	SPRING	C13	24N-08E-09ADA	F
C14	24N-08E-24BBB	P	C15	24N-09E-31CCC	F
C16	23N-08E-36DBD	F	C17	22N-09E-06BBB	F
C20	24N-08E-14CAB	F	C26	23N-08E-15DCD	F
C30	23N-08E-18ABC	F	D1	24N-07E-04CAB	P
D2	25N-07E-08DDA	P	D3	25N-08E-30CBA	P
D4	24N-08E-09ADA	P	D5	23N-08E-20AAD1	F
D6	23N-08E-20AAD2	F	D7	23N-08E-32BCB	P
D8	23N-08E-35DAA	S	D9	23N-08E-12CDA	F
D10	23N-08E-12DCB	F	D11	23N-08E-01DAB	F
D12	23N-08E-13AAD	DITCH	D13	23N-09E-33CDC	S
D14	23N-09E-34ADD	S	D15	23N-09E-36ADD	S
D16	22N-10E-03BAB	S	D17	23N-10E-24CBA	P
D18	22N-11E-24ADC	S	D19	22N-12E-33DDA	S
D20	22N-12E-31DAA	S	D21	21N-12E-08BBA	S
D22	21N-12E-09ADA	S	D23	21N-12E-12DDD	F

Sample Number	USGS Location	S.O.	Sample Number	USGS Location	S.O.
D24	23N-08E-15DCD	F	E1	21N-11E-33ADA	S
E2	21N-11E-33DAA	F	E3	21N-11E-26ACD	S
E4	20N-11E-12BBA	S	E5	21N-12E-29AAA	F
E6	21N-12E-25ADA	F	E7	21N-12E-12DDD	F
E8	22N-11E-26DAB	F	E9	22N-11E-30BBA	F
E10	22N-10E-21ABD	F	E11	21N-10E-04BBB	P
E12	22N-10E-32DDD	F	E13	22N-10E-29CCD	F
E14	22N-09E-13CDC	F	E15	23N-08E-18ABC	F
E16	22N-08E-12CDA	F	E17	23N-08E-12DCB	F
E18	23N-08E-01DAB	F	F1	21N-16E-21CCC	F
F2	21N-16E-17DDD	F	F3	21N-16E-26BCD	F
F4	20N-17E-01ACC	F	F5	22N-17E-19CDC	F
F6	22N-17E-20CCD	F	F7	22N-17E-31AAB	F
F8	22N-17E-30ADA	F	F9	23N-16E-25CCC	F
F10	23N-16E-24BCB	F	F11	23N-16E-13CDD	F
F12	23N-17E-29BBB	F	F13	23N-17E-20CBB	S
F14	23N-17E-05ABA	F	F15	24N-17E-28CCB	F
F16	24N-17E-15DCD	F	G1	24N-17E-34ADB	S
G2	24N-17E-34CCB	S	G3	24N-17E-33DAD	PIT
G4	23N-17E-09BBB	F	G5	23N-17E-16ABB	F
G6	23N-17E-05ABA	F	G7	24N-17E-28CCB	F
G8	24N-17E-15DDD	F	G9	24N-17E-10BBB	S
G10	24N-17E-10CCD	P	G11	24N-17E-08AAA	P
G12	24N-17E-05BBC	F	G13	25N-17E-32CCB	F
G14	25N-17E-33ABA	F	G15	25N-17E-34BAB	F
G16	25N-17E-27BCC	F	G17	25N-17E-25BCC	F
G18	25N-17E-36BCB	P	G19	25N-17E-23BCC	F
G20	25N-17E-13BAB	F	G21	25N-17E-15BCC	F
G22	25N-17E-03BCB	F	G23	26N-18E-34BBC	F
G24	26N-18E-30CDD	F	G25	24N-15E-20DCC	P
G26	24N-15E-34CDD	S	G27	24N-15E-27CDC	F
G28	23N-15E-20AAA	F	G29	23N-15E-33ACB	S
G30	22N-15E-02BBD	F			

* All locations sampled are streams unless otherwise indicated. S.O. Stream Observations (P Ponded Water, S Stagnant Water, F Flowing Water or Ground Water Runoff, SR Stagnant Water influenced by Oologah Reservoir). The letters A, B, C, etc, designated for each sample number refer to dates sampled as follows: A-Series (October 11, 1984), B-series (October 19, 1984), C-Series (November 4, 1984), D-Series (November 8, 1984), E-Series (November 11, 1984), F-Series (November 30, 1984) and G-Series (December 2, 1984).

Specific Conductance and Chloride Analyses
from streams in Hominy Creek Basin during
July 5-15, 1981 (EPA, 1985).

Sample Number	USGS Location	Date of Collection	Specific Conductance (μmhos/cm)	Cl- (mg/l)
J45	22N-10E-13DAB	07/09/81	950	180
J46	22N-10E-16AAD	07/09/81	780	140
E10	22N-10E-24DAA	07/10/81	650	140
E9	22N-10E-32DDD	07/10/81	590	80
J43	22N-11E-24DAB	07/09/81	460	45
J44	22N-11E-27CDB	07/09/81	800	152
E11	22N-11E-34CCA	07/10/81	350	25
J42	22N-12E-32CBB	07/09/81	720	130
G5	23N-08E-02CAD	07/10/81	2928	770
G4	23N-08E-02CDD	07/10/81	129	15
I42	23N-08E-06DAD	07/09/81	19200	6650
G3	23N-08E-12DCB	07/10/81	1410	400
G2	23N-08E-14AAA	07/10/81	1400	350
G1	23N-08E-15DCA	07/10/81	1280	280
I41	23N-08E-36CBB	07/09/81	600	135
G11	23N-09E-07DDA	07/11/81	500	5
G15	23N-09E-32AAD	07/11/81	1450	380
G12	23N-09E-33CCC	07/11/81	590	75
G13	23N-09E-33DDB	07/11/81	1500	350
G14	23N-09E-34ADC	07/11/81	310	30
G16	23N-09E-36ADC	07/11/81	580	120
G17	23N-10E-34CCC	07/11/81	790	150
D6	23N-08E-01DAB	07/15/81	800	155
D5	23N-08E-12DAA	07/15/81	2400	760
G33	24N-07E-10DDA	07/13/81	438	60
G31	24N-07E-14CDD	07/13/81	950	225
G32	24N-07E-15DCA	07/13/81	8000	2200
D13	24N-07E-25AAD	07/15/81	2700	880
G8	24N-08E-09ADA	07/10/81	1280	150
G9	24N-08E-14CAB	07/10/81	1720	410
G10	24N-08E-24DCB	07/10/81	1300	260
G6	24N-08E-29ABD	07/10/81	940	70
G7	24N-08E-29BDD	07/10/81	4200	1275
F1	24N-08E-33AAB	07/09/81	420	30
I44	24N-08E-33DBD	07/09/81	2600	675
D12	24N-08E-09AAC	07/15/81	1200	290
D11	24N-08E-14BBA	07/15/81	1738	540
D10	24N-08E-14CAB	07/15/81	1705	560
D9	24N-08E-23DAB	07/15/81	1450	440
D8	24N-08E-24DCB	07/15/81	1150	300
D7	24N-08E-36ABB	07/15/81	920	240
G35	25N-07E-25AAD	07/13/81	2700	1410
G34	25N-08E-31ABA1	07/13/81	8000	4620
D14	25N-08E-31ABA1	07/15/81	16000	5600
D15	25N-08E-31ABA2	07/15/81	13000	3750
G34A	25N-08E-31ABA2	07/13/81	8000	4560

Field Parameters, Chloride (Cl-) and Sulfate (SO4=) from Ground Water* in Hominy Creek and Delaware Creek Basins.

					Cl-	SO4=	
Latitude/Longitude	D.	T.	pH	S.C.	(mg/l)		Rock Unit
36 13 44/96 14 42	30.5	21.0	7.00	690	173	28	Wann
36 15 54/96 06 54	24.4	19.5	7.00	770	118	232	Nellie Bly
36 17 13/96 03 58	6.1	19.5	7.00	230	9.8	24	Nellie Bly
36 17 13/96 26 31	39.6	25.0	5.80	710	61	21	Vanoss
36 17 28/96 29 38	30.5	20.0	6.50	810	72	16	Vanoss
36 19 16/96 26 17	146.3	26.0	7.60	2780	71	106	Vanoss
36 19 52/96 15 29	137.2	31.5	7.40	1190	61	30	Barnsdall
36 20 17/96 29 42	106.7	26.5	6.80	1150	34	88	Vanoss
36 20 24/96 24 58	338.3	24.0	8.50	1440	16	6.4	Vanoss
36 20 28/96 13 55	143.3	23.0	6.90	1030	31	104	Barnsdall
36 20 53/96 06 40	9.1	20.5	7.40	180	53	7	Nellie Bly
36 22 05/96 12 43	36.6	21.5	7.20	460	13	11	Barnsdall
36 22 44/96 25 34	76.2	21.0	8.5	1550	38	100	Barnsdall
36 22 55/96 23 20	91.4	19.0	6.90	700	72	12	Tallant
36 23 20/96 02 20	6.1	24.0	6.70	840	85	30	Chanute
36 23 20/96 19 52	45.7	23.5	7.00	2021	39	270	Tallant
36 24 14/96 26 42	91.4	20.0	7.00	840	47	123	Barnsdall
36 25 05/96 21 22	36.6	18.0	6.20	570	59	77	Tallant
36 25 16/96 01 26	6.1	20.5	6.80	1080	50	152	Chanute
36 26 10/96 06 14	91.4	28.5	7.20	770	19	58	Wann
36 26 17/96 12 40	228.6	29.0	7.70	970	12	54	Barnsdall
36 26 31/96 09 32	152.4	36.5	7.90	2220	141	22	Barnsdall
36 27 18/96 21 11	152.4	25.5	8.30	3590	426	19	Tallant
36 27 40/96 23 17	3.0	24.0	7.00	980	66	104	Tallant
36 27 50/96 03 32	3.0	27.5	6.90	2020	27	323	Wann
36 28 08/96 26 24	12.2	19.5	5.40	2450	291	414	Tallant
36 29 17/96 06 50	73.2	27.5	6.90	1730	123	51	Chanute
36 30 18/96 21 22	76.2	25.5	7.40	630	52	29	Barnsdall
36 30 29/96 27 14	30.5	18.0	7.00	670	42	99	Barnsdall
36 30 47/96 23 17	91.4	24.0	8.70	690	46	66	Barnsdall
36 31 19/96 13 44	15.2	17.5	6.70	340	99	7	Vamossa
36 31 55/96 17 02	30.5	24.0	7.20	890	59	72	Barnsdall
36 32 20/96 22 59	137.2	23.0	8.90	670	43	53	Barnsdall
36 33 14/96 25 52	182.9	24.0	8.10	1650	192	68	Barnsdall
36 33 58/96 06 32	45.7	24.0	7.20	1430	159	73	Barnsdall
36 35 31/96 16 48	121.9	24.5	7.50	1370	119	100	Barnsdall
36 35 60/96 01 12	30.5	27.5	6.80	6350	32	168	Tallant
36 37 48/96 08 28	45.7	20.5	5.80	260	38	7	Vamoosa
36 38 35/96 22 48	6.1	21.5	6.80	570	15	29	Ada
36 38 60/96 20 53	24.4	19.0	5.40	220	17	30	Vamossa

* Source: National Uranium Evaluation (NURE) (Provided by USGS). Samples were collected from June 19-July 14, 1978.
D. Depth to top of sample interval (feet).
T. Temperature (Centigrade).
S.C. Specific Conductance (µmhos/cm).

Field Parameters and Chemical Analyses of Brines from Oil Wells Located within Hominy Creek Basin.

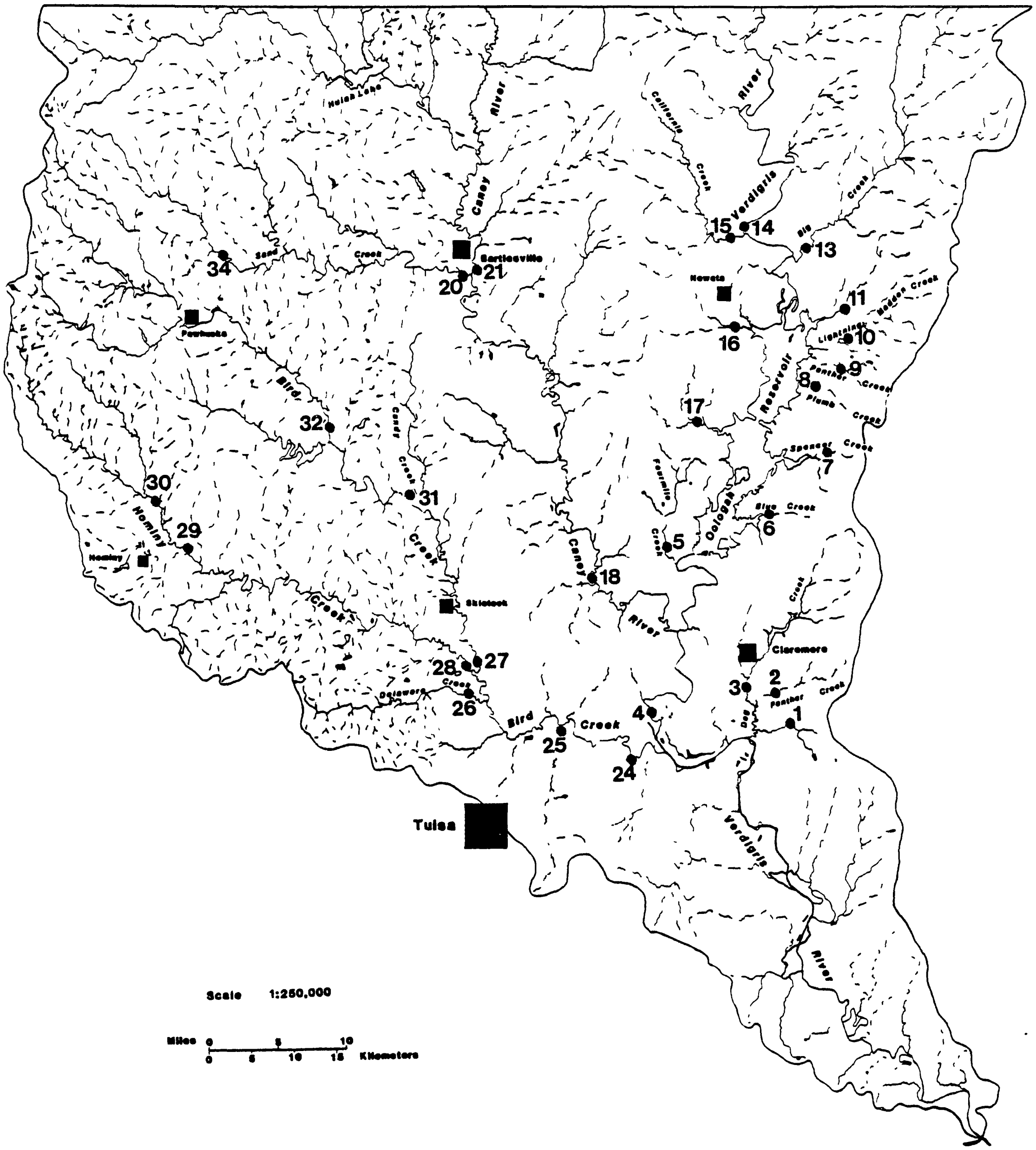
Latitude/Longitude	Date of Collection	D.	T.	pH	Ca++	Mg++	Na+	HCO3-	Cl-	SO4=	Rock Unit
						(milligrams/liter)					
36 21 54/96 11 11	01/07/53	1730	25	-	8805	2545	48600	384	97640	0	CHRK
36 27 19/96 07 42	04/07/54	1670	25	-	8740	2448	47320	77	95530	0	CHRK
36 27 19/96 07 42	04/07/54	1920	25	-	11100	2275	52390	170	106900	54	CHAT
36 29 56/96 15 13	04/07/54	2120	25	-	17140	2735	64470	77	137700	62	CHRK
36 30 48/96 28 06	02/19/53	2270	25	-	14700	2524	58460	55	123400	-	CHRK
36 30 48/96 28 06	02/19/53	1950	25	-	7602	2638	39420	166	81780	109	FRSC
36 31 05/96 23 28	05/07/79	2208	-	6.20	8630	2069	41840	63	85750	-	FRSC
36 31 56/96 24 36	05/29/67	2407	-	5.30	11680	1824	58809	149	117000	-	CHRK
36 32 31/96 25 01	08/21/79	2503	-	4.90	12840	2647	55430	33	116100	-	CHRK
36 32 34/96 25 03	05/29/67	2160	-	6.80	11600	1200	68000	196	129900	-	CHAT
36 33 24/96 24 53	04/29/54	2230	25	-	9830	1008	53690	63	103100	32	CHRK
36 36 01/96 25 54	04/08/54	2480	25	-	14630	2666	58500	72	123800	150	CHAT
36 36 53/96 28 03	04/29/54	2490	25	-	14310	2648	61200	76	127400	98	CHAT

D. Depth to top of sample interval (feet). T. Temperature (Centigrade)
CHRK Pennsylvanian Checkerboard Formation.
CHAT Mississippi Chat (Limestone).
FRSC Pennsylvanian Fort Scott Formation.

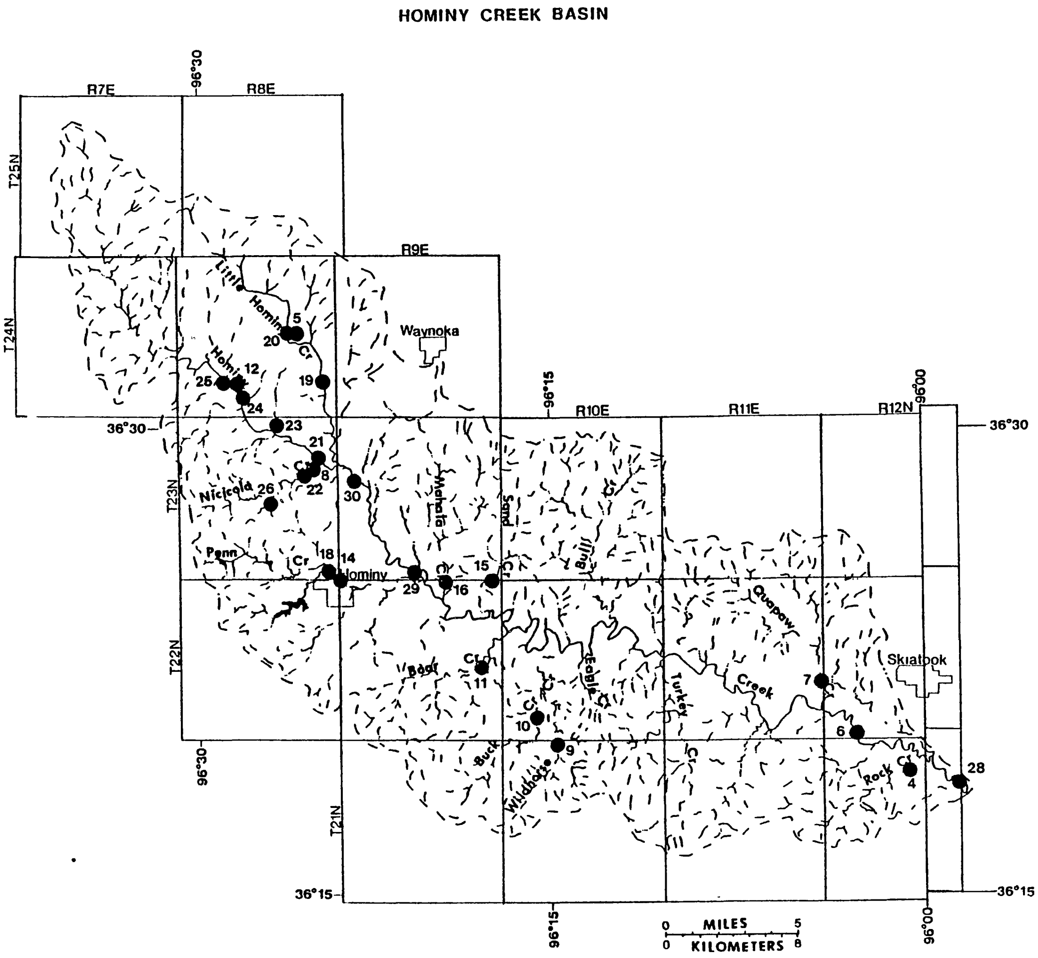
Field Parameters, Chloride (Cl-) and Sulfate (SO4=) from Ground Water* in the Oologah Reservoir Area and Dog Creek Basin.

Well	USGS	Date of					Cl-	SO4=
ID.	Location	Collection	D.	T.	pH	S.C.	(mg/l)	
16B	20N-16E-10DCD	06/23/77	-	18.0	7.50	565	17	9
16A	20N-17E-18AAB	06/23/77	-	15.5	7.60	2200	463	30
26A	21N-16E-15BCC	06/21/77	-	17.0	8.00	1380	219	17
26B	21N-17E-18BBB	06/22/77	-	17.5	9.00	830	92	22
48A	22N-16E-03ABD	07/02/80	36.0	19.0	6.90	740	11	230
#44A	22N-16E-10AAB	07/02/80	72.0	19.0	8.00	1500	81	26
#43C	22N-16E-11DCD	06/16/77	-	17.0	6.90	2190	18	1003
#43D	22N-16E-11DCD	07/02/80	-	29.0	7.80	980	13	48
#43E	22N-16E-11DCC	06/16/77	-	21.0	8.30	930	30	56
43B	22N-16E-14AAA	07/01/80	50.0	18.0	6.90	770	14	270
40B	22N-16E-15ACD	07/01/80	46.5	18.0	8.40	1200	44	350
#43A	22N-16E-16ADD	07/02/80	51.5	18.5	6.90	950	150	70
#40D	22N-16E-16ADD	07/01/80	55.0	18.5	8.20	1380	890	8
#40A	22N-16E-20CCC	06/16/77	-	17.0	7.00	680	18	99
38A	22N-16E-22BBB	07/01/80	105.0	18.5	4.50	1340	77	2300
43F	22N-17E-09CBD	06/16/77	-	18.0	7.80	920	128	1
40C	22N-17E-14ADD	06/16/77	-	19.0	6.30	165	22	13
59B	23N-16E-10CCB	06/15/77	-	23.0	7.50	350	23	41
53C	23N-16E-24CBC	07/15/80	30.0	19.9	7.00	881	4.9	180
51B	23N-16E-26DDC	07/15/80	29.0	22.8	7.20	625	19	63
48D	23N-16E-32DAD	06/16/77	-	24.0	7.10	870	22	113
48B	23N-16E-34CCD	07/14/80	31.0	25.7	6.90	610	11	110
48C	23N-16E-36DCA	07/14/80	102.0	22.3	7.30	1600	190	210
59A	23N-17E-08DDD	06/15/77	-	15.0	5.60	-	16	13
57A	23N-17E-16DBC	07/15/80	63.0	24.0	7.20	686	8.3	54
58A	23N-17E-18ADA	07/15/80	287.0	23.2	7.30	602	19	36
52A	23N-17E-26DAD	07/16/80	65.5	24.6	6.20	272	15	8
52B	23N-17E-29BCC	07/16/80	51.0	18.7	5.20	595	32	160
51A	23N-17E-30DDD	06/15/77	-	22.0	6.20	-	41	499
49A	23N-17E-36ADD	06/16/77	-	20.0	6.90	920	13	165
73A	24N-16E-24BAA	06/17/77	-	15.0	7.20	780	77	16
76A	24N-17E-03DCD	06/14/77	-	17.0	8.50	830	106	5.0
74A	24N-17E-08BCB	07/24/80	11.0	25.8	8.00	25	1.2	21
72A	24N-17E-22ABA	06/15/77	-	17.0	7.70	550	8.0	4.0
72B	24N-17E-22ABA	06/15/77	-	18.0	7.40	810	117	4.0
89C	25N-17E-34ABA	06/14/77	-	14.0	7.00	770	8.0	155
95B	26N-17E-34BBB	06/14/77	-	17.5	7.40	640	10	56

* Data source: WATSTORE. # Samples from wells located in Sweetwater Creek Basin (included to increase the number of elements for statistical evaluation using probability graphs). Samples of water are from the following rock units: Boggy Formation (52A, 52B), Blue Jacket Sandstone Member of the Boggy Formation (16A, 26B), Fort Scott Limestone (48D, 59B, 95B) and the remaining samples are from the Senora Formation. D. Total Depth of well (feet). T. Temperature (Centigrade). S.C. Specific Conductance (µmhos/cm).

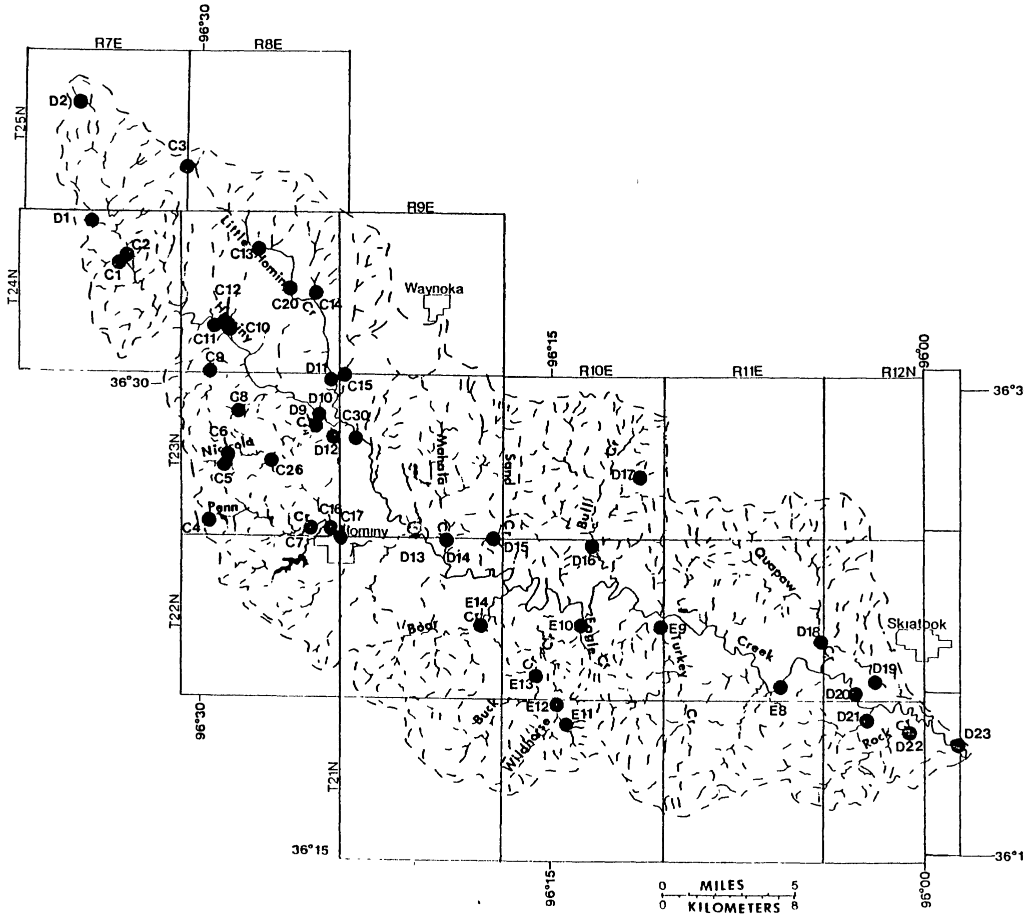


Location of water samples (A-Series) collected on October 11, 1984.



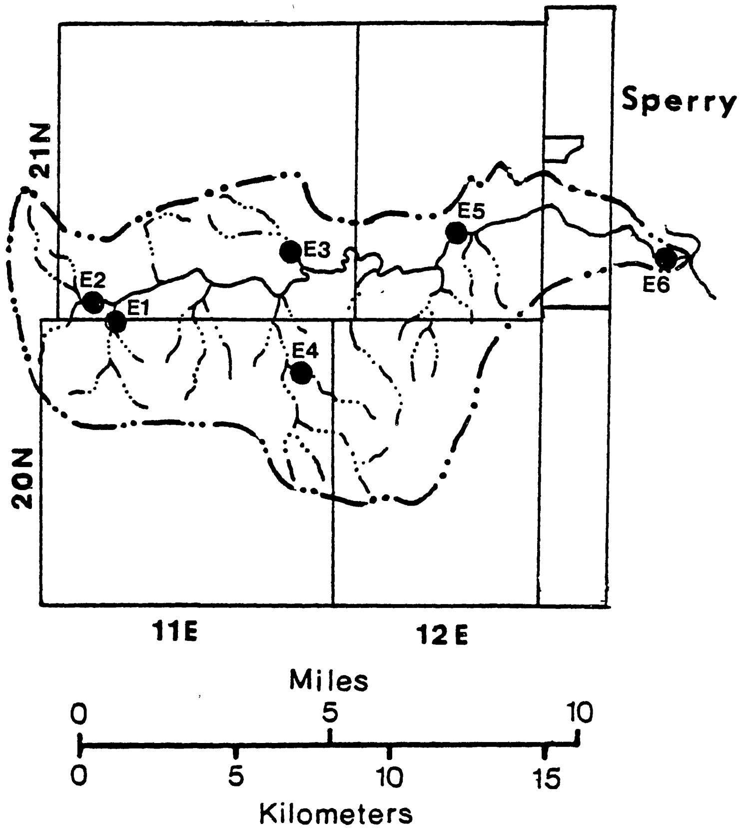
Location of water samples (B-Series) collected on October 19, 1984.

HOMINY CREEK BASIN



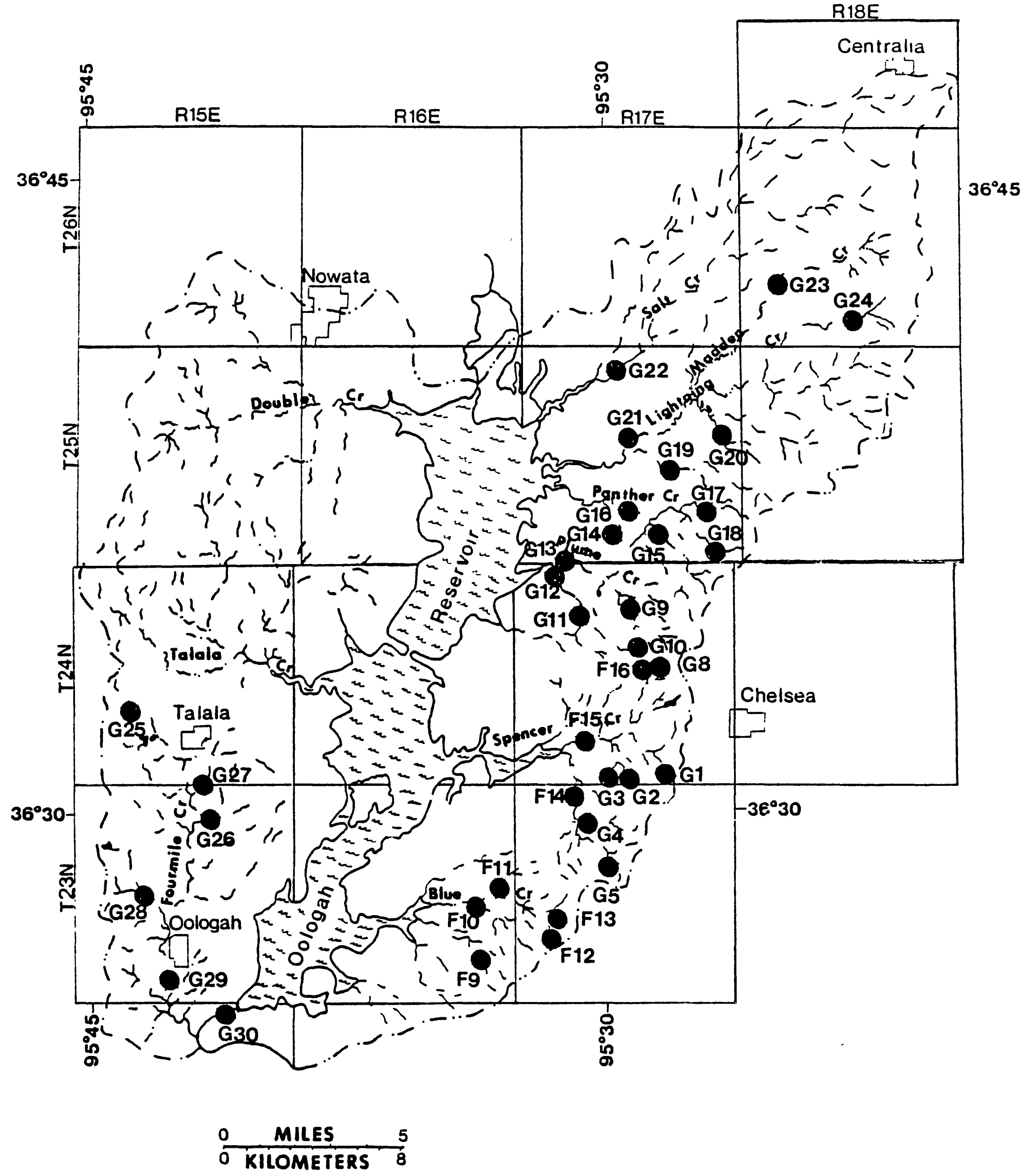
Location of water samples collected on November 4 (C-Series), November 8 (D-Series), and November 11 (E-Series), 1984.

Delaware Creek Basin

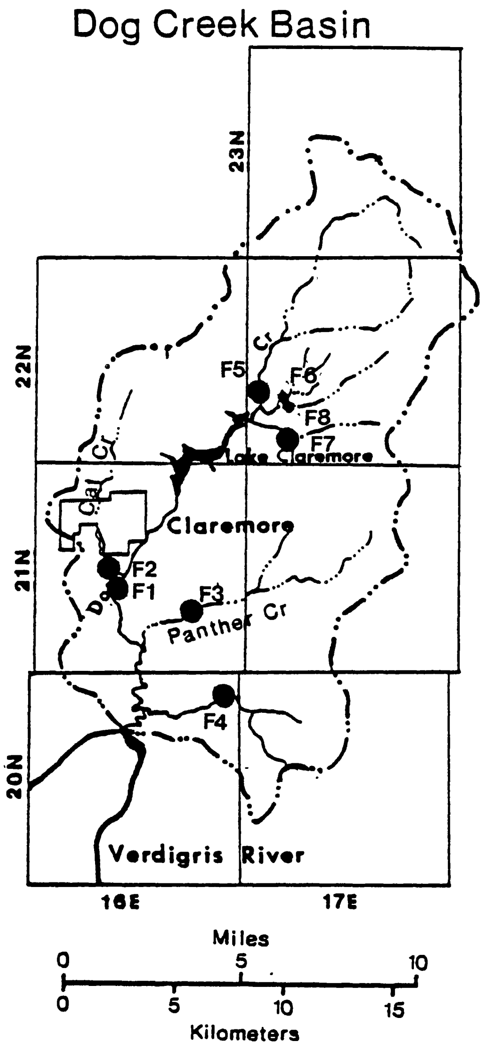


Location of water samples collected in Delaware Creek Basin on November 11, 1984.

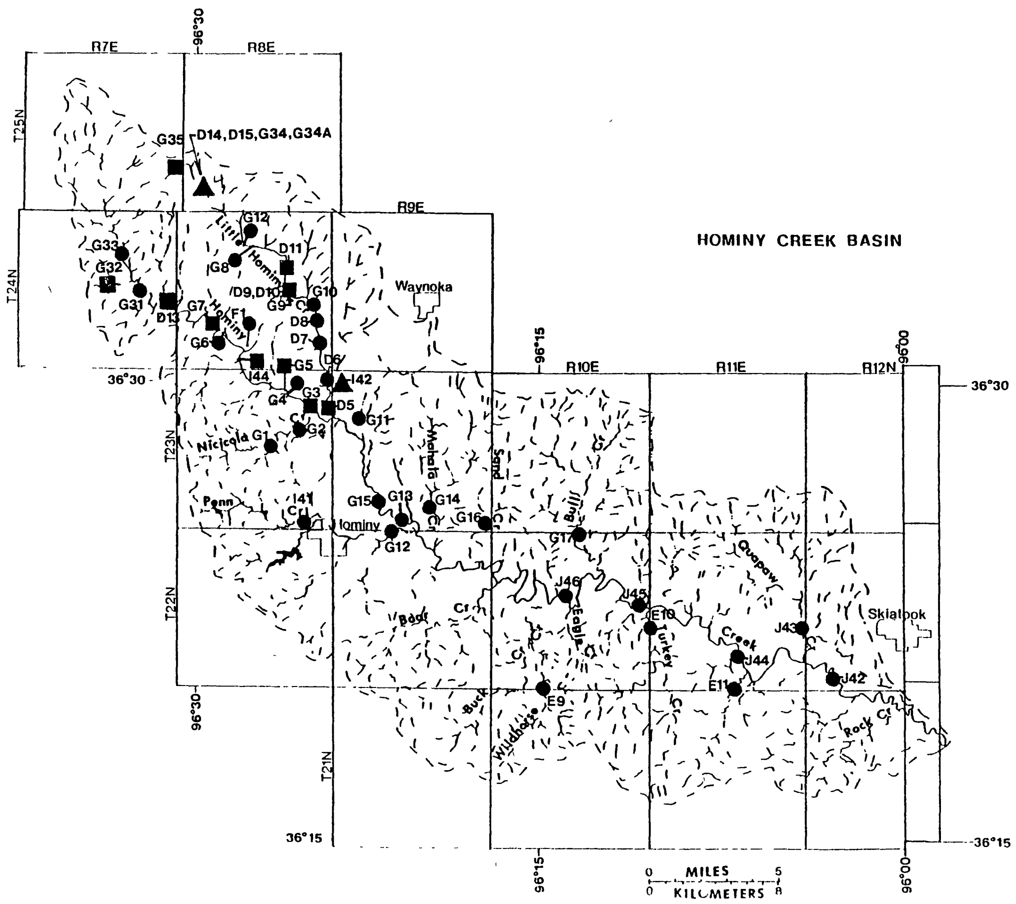
OOLOGAH RESERVOIR AREA



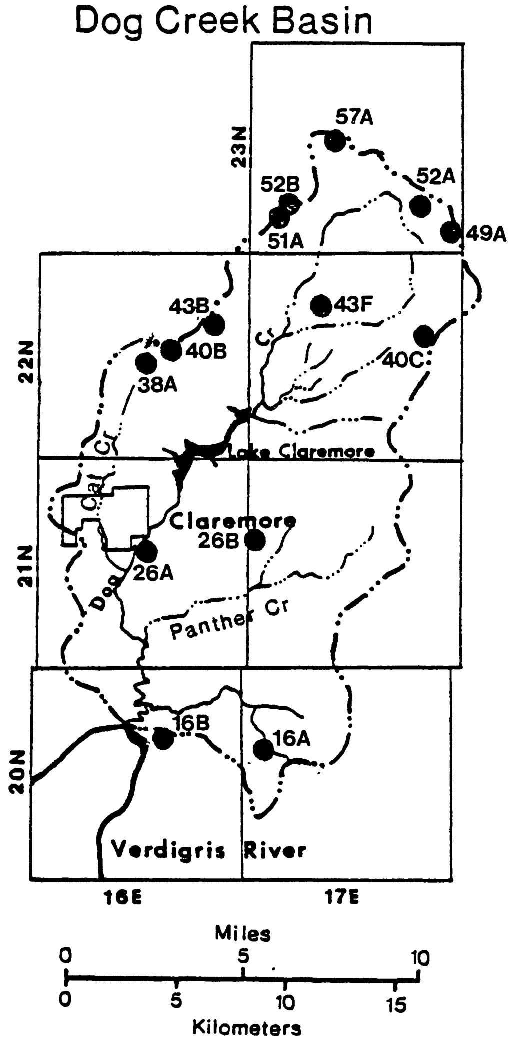
Location of water samples collected on November 30 (F-Series), and December 2 (G-Series), 1984.



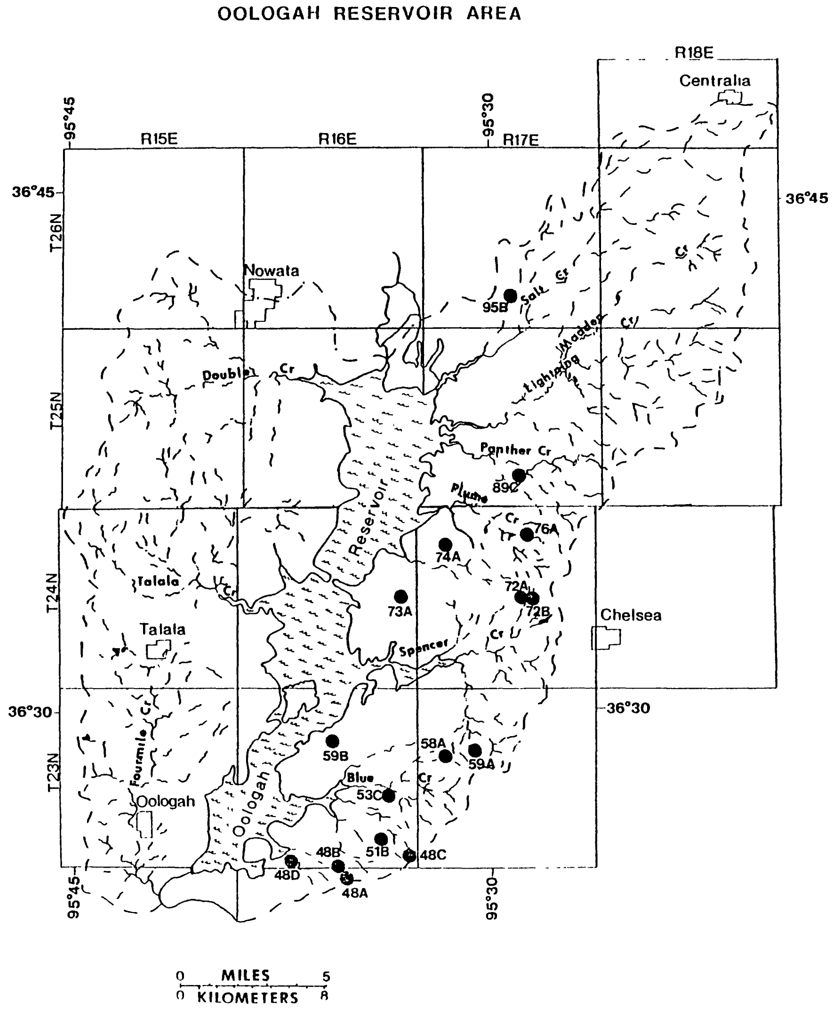
Location of water
samples collected
in Dog Creek Basin
on November 30, 1984.



Location of selected water samples collected during July 5-15, 1981 in Hominy Creek Basin (EPA, 1985).



Location of water samples from wells (USGS, 1985).



Location of water samples from wells (USGS, 1985).

VITA

Charles Dana Race

Candidate for the Degree of

Master of Science

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