HYDROGEOLOGY, DIGITAL SOLUTE-TRANSPORT
SIMULATION OF NITRATE AND
GEOCHEMISTRY OF FLUORIDE
IN GROUND WATERS OF
COMANCHE COUNTY
OKLAHOMA

BY

DAVID BISHOP BACK

Bachelor of Science

College of William and Mary

Williamsburg, Virginia

1980

Submitted to the Factulty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
MASTER OF SCIENCE
December, 1985

HYDROGEOLOGY, DIGITAL SOLUTE-TRANSPORT SIMULATION OF NITRATE AND GEOCHEMISTRY OF FLUORIDE IN GROUND WATERS OF COMANCHE COUNTY OKLAHOMA

Thesis Approved:

A. Hounslow
Thesis Adviser

Douglas C. Kent

Wayne A. Pettyjohn

Norman N. Durham
Dean of the Graduate College

PREFACE

The author wishes to thank Dr. Arthur W. Hounslow, his thesis adviser, for his valuable assistance and guidance during this and previous studies. Special appreciation is extended to Dr. Douglas C. Kent, whose knowledge of computer modeling proved invaluable. Gratitude is also extended to Dr. Wayne A. Pettyjohn who provided many of the hydrological "concepts" needed to properly evaluate the collected data. Recognition is also extended to Benjamin B. Greeley whose joint effort in the data collection, interpretation, and computer modeling was greatly appreciated. Appreciation is further extended to Dr. Al-Shaieb whose help interpreting the geology of the study area was deeply appreciated. Gratitude is extended to the Oklahoma Water Resources Board (OWRB) for providing pertinent data and funds for the project which was arranged through the Oklahoma State university and Dr. Hounslow, who was the principal investigator for this project. Special thanks is given to my father and the U.S. Geological Survey for help with data interpretation and analysis. Recognition is also extended to Lorraine Lemaster and Chi-Chung Chang for their technical assistance with the solute-transport model. Further appreciation is extended to Talya Henderson and Chi-Chung

Chang for their help in getting the manuscript into final form.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Figure Page

CHAPTER I

ABSTRACT

The hydrogeology and ground-water geochemistry of the Post Oak aquifer (Permian) Comanche County, Oklahoma was studied in order to evaluate the availability and chemical quality of water from this aquifer.

The Post Oak aquifer, one of the major water producing units in the area, unconformably overlies the Arbuckle Formation and consists primarily of medium- to coarse-grained quartz sand. Laterally discontinuous Permian channel deposits are interbedded with silts and clays. The Post Oak aquifer in this area attains a thickness of 2,500 feet and transmissivities range from 9,629 to 600,000 gal/day/ft.

Fluoride, nitrate and dissolved solids are major water-quality problems in the area. Presently, fluoride levels are high in the west-central part of the county, and decrease near Lawton, high Nitrates define local problem areas southeast of Lawton.

A geochemical evaluation of Post Oak waters revealed that high levels of fluoride are a result of cation-exchange reactions which rename Ca from solution, initiate calcite dissolution, increasing pH levels and enabling fluoride to

be desorbed from clays.

Nitrogen contamination has been reported to be a major water-quality problem in the area. A modified two-dimensional area solute-transport model of the Post Oak aquifer was constructed for the southern half of Comanche County to determine the movement, occurrence and future concentrations of nitrogen derived from fertilizer.

The model predicts background concentrations that generally match observed field data. It becomes apparent that directly south of the Wichitas nitrogen values, are genrally relatively low. This could be expected because very little land is cultivated in this area. The rocks consist of very coarse gravels with high fracture permeability resulting in a steep water-table gradient and therefore, nitrogen that is applied to the system it quickly flushed down gradient to discharge points.

The nitrogen mounds (8 mg/l NO_3-N), that have formed northeast of Chatanooga, are underlying areas of intense agriculture and gentle water-table gradient.

It is important, however, to realize that high nitrogen concentrations may be indicative of other, far more harmful constituents, the most deadly of which are pesticides. It is reasonable to assume that pesticides applied with the fertilizer, migrate under similar physical parameters governing nitrogen migration. Thus, there may be a direct relationship between levels of nitrogen and pesticides.

Although the movement of pesticides in the soil may be retarded because of adsorption on soil organic matter or clay minerals, some may not be. Also the presence of fissures or macropores in the soil may, in fact, preclude adsorption of even those pesticides that may suffer retardation under homogeneous conditions.

The presence of extremely high nitrogen in some areas may also be the result of poor well placement or casing which allows the ingress of human or animal waste into the drinking water supply. Again even if the nitrogen is considered harmless the associated microorganisms may not be.

In summary, although nitrogen contamination in Comanche County may not be a major pollution problem, it can be a indicator of more serious pollution; namely, pesticides and/or pathogenic microorganisms.

CHAPTER II

BACKGROUND

Introduction

Lawton, the largest city in Comanche County has an adequate, good quality, source of surface water for its drinking water supply. In contrast, the smaller communities in the remainder of the country rely on ground water of marginal quality as the source of their drinking water. The chemical constituents that are a problem in these rural areas are nitrate, fluoride and a high total dissolved solids content.

Nitrogen contamination has been a water-quality problem within Comanche County since people began applying nitrogen-based fertilizer to fields. Nitrogen concentrations in the Post Oak aquifer and recent alluvium may exceed 40 mg/l as N within the county .

Most of the farming in the area is dry-land and very little irrigation water is applied. Lawton's water requirements are satisfied by Lake Elsworth and Lake Latonka. Therefore, ground-water use is confined to small, localized areas. In the absence of large pumping centers, nitrogen migration within the saturated zone is controlled by the regional water-table gradient.

Nitrogen concentrations are seasonally variable and depend largely upon the quantity of rainfall available as recharge to the aquifer. Major sources of nitrate include inorganic fertilizers, naturally occurring organic matter and sewage. The greatest source of nitrates in southwestern Oklahoma are fertilizers and sewage. Nitrate is a health hazard to pregnant women and infants less than six months old because it leads to metahemoglobinemia or "blue babies".

The major focus of this study was to develop information on the hydrogeology and ground-water geochemistry particularly fluoride, of the Post Oak Conglomerate and to apply a two-dimensional areal solute-transport model which will aid in predicting future movement, concentrations and distributions of nitrate within Comanche County.

Study Area

The field area lies within the gently rolling portion of the southern great plains of southwestern Oklahoma (Figure 1). The area covers nearly 1000 square miles. The northern portion of the county includes the Wichita Mountains which rise to a maximum 2,479 feet at Mt. Pinchot and are composed of a series of Cambrian to possibly Proterozoic igneous rocks. The remaining area consist of south-easternly dipping beds underlain by weakly consolidated, clays, shales, and sandstones.

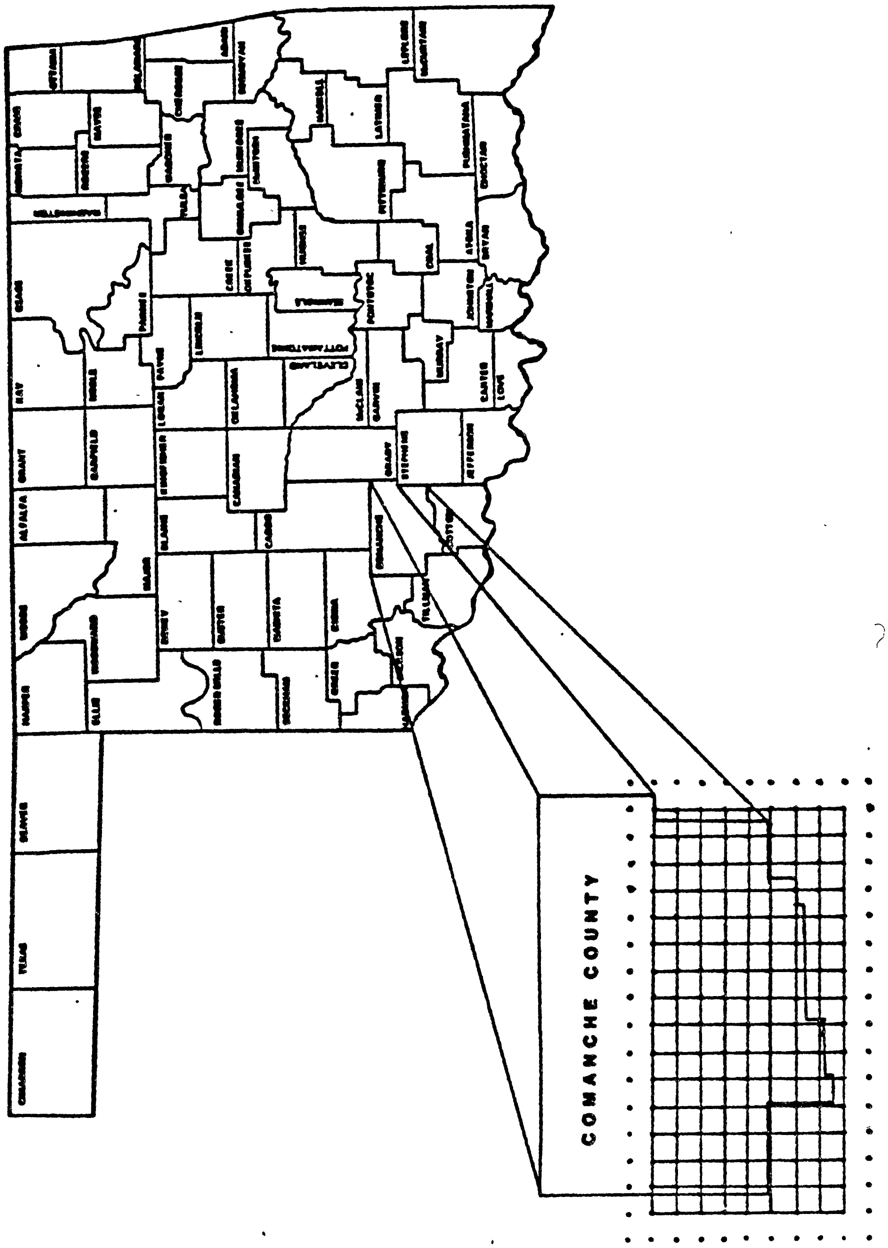


Figure 1. Location of Study Area

The area chosen to apply a finite-difference solute-transport model encompasses the southern half of Comanche County (Figure 1) and incorporates 945 square miles. This area is particularly well suited for application of the model because natural flow barriers (Wichita Mts.) are easily adapted into the initial no flow boundaries of the model.

The major aquifer in the area consist of the alluvial flood plain deposits in combination with the Post Oak Conglomerate. In the tributary streams the alluvium is generally thin and fine grained. The surface area of the aquifer is approximately 500 square miles (Figure 2). While the vertical thickness is highly variable ranging from 20 to 2700 feet.

Previous Work

Our geological knowledge of the Wichita Mountains - Arbuckle Mountains basement is due largely to Ham et. al. (1964); Powell et. al. (1980) revised the basement lithostratigraphy and discussed uncertainties in the ages and correlations; while Myers et. al. (1981) examined the geochemistry of the Wichita Granite group. Numerous people have made significant contributions to our understanding of the geology in the study area, the list is far too extensive to continue here, for a more detailed outline of the geological history see Gilbert and Donovan (1982).

The hydrogeology of Comanche County was investigated by

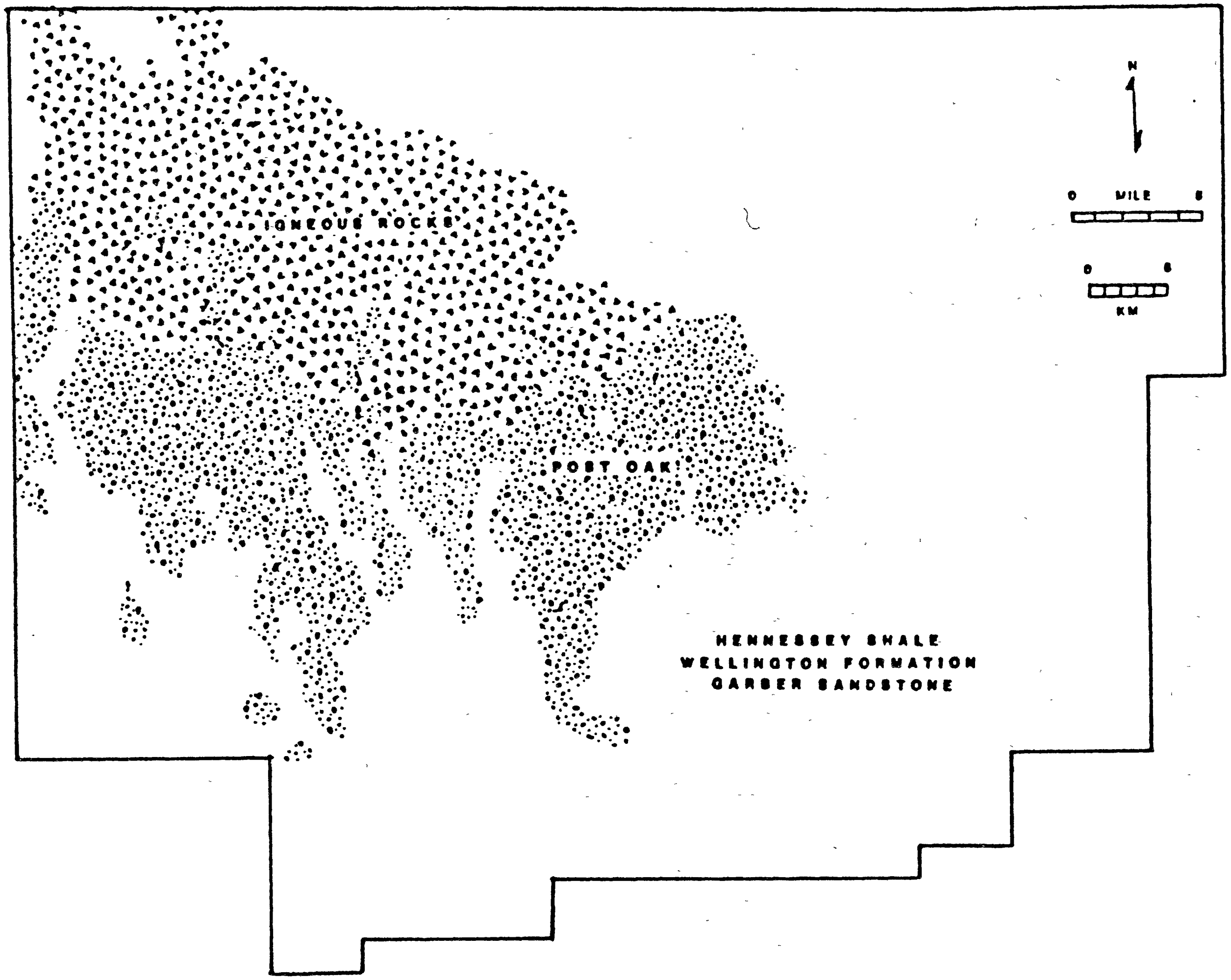


Figure 2. Aeral Geology of Comanche County

Havens (1977) whose report is formatted as a hydrologic atlas and includes a general description of the physiography, hydrogeology and water quality in Comanche County. The report includes plates with locations, depths and owners of water wells.

Al-Shaieb and others (1980) performed a number of petrographic and geochemical studies in the Wichita Mountains region and have critically evaluated high fluoride concentrations in the area, which are discussed in the geochemical section of this report.

A reconnaissance study of the water resources of Comanche County was carried out by Stone (1981) who briefly describes the availability and quality of water in the area, and discusses the geology and potential yields of aquifers.

The two-dimensional areal solute-transport model, applied in this study, was orginally developed and documented by Konikow and Bredehoeft (1978). Tracy (1982) incorporated radioactive decay and equilibrium adsorption mechanisms for the U.S. Nuclear Regulatory Commission. Kent et. al. (1985) made several modifications, one of which, is an option to solve the ground-water flow equation using the Strongly Implicit Procedure (SIP), rather than the Alternating-Direction Implicit Procedure (ADIP). The major advantage is that SIP converges in about half of the iterations as the ADIP procedure and for this reason, saves considerably on computer time.

LeMaster (1985) modified the existing program to enable the incorporation of 105 injection wells necessary to accomodate the non-point source addition of nitrogen.

CHAPTER III

NITROGEN

The Nitrogen Cycle

Nitrogen, an important component of proteins, is an indispensable element for the growth of micro-organisms, plants and animals. Nearly 98 percent of the Earth's total nitrogen is trapped in rocks, while almost 79 percent of the planets atmosphere is composed of elemental dinitrogen (Winneberger, 1982).

Fixation and Retention (nitrogen --> ammonia)

Despite a seemingly endless supply of nitrogen, living systems require ammonia to satisfy their nutritional requirements. Ammonia is a form of nitrogen that has been chemically reduced by micro-organisms (bacteria) that are capable of transforming atmospheric nitrogen gas into ammonia that may then be utilized by plants and animals (Payne, 1981). The bacteria use a variety of enzymes to catalyse this transformation (Nielsen and McDonald, 1978).

Ammonia is the only product generated by normal nitrogen fixation, in this form nitrogen may be reabsorbed and reassimilated many times in the nitrogen clycle (Payne, 1981).

Nitrification (ammonia --> nitrite --> nitrate)

Nitrification is the oxidation of ammonia to nitrite and finally nitrate which is carried out predominantly by autotrophs under aerobic conditions (Payne, 1981). If ammonia is oxidized to nitrite and nitrate the possibility exist for nitrogen loss from the cycle. However, many macrophytes can reduce nitrate to nitrite and ammonia which may be reincorporated into plant components during biosynthesis (Postgate, 1982).

Denitrification (nitrate --> nitrite --> nitrous oxide --> nitrogen)

Biological denitrification completes the nitrogen cycle and is accomplished by bacteria which reduce nitrates or nitrites to gaseous forms of nitrogen, such as nitrous oxide and molecular nitrogen (Aldrich, 1980).

Denitrification is a respiratory process, whereby nitrate may be utilized by aerobic bacteria as the terminal electron acceptor in the absence of oxygen (Aldrich, 1980). Denitrifying bacteria differ from the facultative anaerobic bacteria, whichcan reduce nitrate to nitrite but nofurther, inthattheycannot grow fermentativelybyusing organic compounds as electron acceptors (Winneberger,1982).

The rate of denitrification is affected by many physicochemical factors such as oxygen availability, moisture content, temperature, soil pH, and access to electron donors (Payne, 1981).

Sources of Nitrogen in Oklahoma

Major industrial centers of Oklahoma are sporatically spaced throughout the state so contamination by municipal sewage will be variable. There are approximately 40 major feedlots in Oklahoma so livestock waste probably is not a major regional contributor to high nitrate levels in Oklahoma streams and this Nitrogen-based fertilizer is the most likely source of high levels of nitrate often present in many of the surface and ground-water supplies in the state.

Aldrich (1980) makes two generalizations concerning nitrate concentrations in midwestern streams in which urban effects are minimal:

1. Nitrates are highest during the spring--March to June, this is due to the surface runoff caused by high rainfall in combination with few crops to extract nitrate out of the soil. During the summer there is relatively little discharge of water because evaporation from the soil and transpiration usually equal or exceed rainfall.
2. Nitrate concentrations tend to increase with increasing amounts of flow up to a point as a result of flushing action. Beyond some flow rate, probably characteristic of each stream and depending upon time of year, the dilution effect of additional water more than offsets the flushing

effect. The significance of time of year is that heavy rainfall on soil that is frozen or already fully saturated can only run off the surface with no opportunity to flush out nitrates. Nitrate concentration would be expected to be above average in a year in which total precipitation was above average and was well distributed throughout the year.

There are several modifying factors to the two generalizations. Nitrate levels in streams would expected to be high: (a) when fall, winter, and spring precipitation is high; (b) following a fall in which the amount of nitrate in the soil was unusually high; (c) following a dry year in which crop removal was low; (d) after a warm fall which maximized the growth of microorganisms that decay residues and convert the resulting ammonia to nitrate; (e) from the fields with drainage tiles because the pathways from the point of nitrogen application to receiving waters are more direct.

Pollution Potential

As previously discussed the behavior of nitrate and ammonium ions indicate that only the nitrate ion is susceptible to being leached into ground water or surface water through base flow and tile drainage. There are relatively minor differences amoung the various nitrogen fertilizers in the potential for adding nitrates in the manner just mentioned under practical field conditions. It is, of course, possible to apply the various fertilizers in ways that would cause substantial differences in their pollution potential. For example, the nitrate form if applied early in the fall on a field where an annual crop was to be planted the following year might lead to a substantial amount of leaching well in advance of the time of planting the crop (Aldrich,1980). Nitrate fertilizer could also be applied in the fall or even very early spring on extremely sandy soils with a great potential for leaching (Aldrich, 1980). In general, farmers are aware of these limitations and they adapt their practices accordingly.

Nitrates in Water

The behavior and movement of nitrates is based chiefly upon general theory of water movement and the hydrogeology of the area. As nitrate moves through the soil it displaces the interstitial water and inhibits diffusion. When nitrate reaches the water table, it seemingly travels as a semi-discrete pulse rather than a diluted mass. This is why there is extreme varibility in nitrate samples from adjoining areas at different periods of time (Aldrich, 1980).

Nitrogen in Groundwater

Denitrification is probably the only natural mechanism for removing excess nitrates in ground water. The state of our knowledge concerning nitrogen in ground water is as follows (Aldrich, 1980):

Most of the nitrogen in ground water is present as nitrate having been oxidized from nitrite while being transported downward by percolating water. An exception occurs under old manure-storage areas where the ammonium-holding capacity of clay and humus in the upper layers is exceeded and hence ammonium moves downward.

Nitrate is transported coincident with the permeating ground water. The penetration depth of the nitrate will be influenced by the water-holding capacity of the soil, while the total amount of nitrogen as nitrate will determine the size of the migrating plume.

When percolating nitrates reach the water table, it might be expected that the concentration would decline because of dilution. It is observed, however, that a front of high nitrate water will move in the direction of flow as a pulse or bulge.

The flow path of ground water will be down gradient within a geographic region. In the vicinity of a well, the natural flow direction may be upset as a result of water withdrawal from the well.

Rates of flow vary tremendously. In limestone regions, percolating water may enter caverns and flow uninhibited for miles. This explains the pollution of some water sources that appear to be a safe distance from feedlots etc. In many soils there are sand or gravel lenses through which water may travel several feet per day. But in very dense compact subsoils movement may be as slow as one foot per year (Freeze and Cherry, 1979).

There are conflicting data in the literature concerning the movement of nitrogen. In studies (Aldrich, 1980) where heavy application of fertilizer occurred over several years, the nitrate front continued to move down to the deepest zone sampled. On the other hand, Jones (1951) found little or no nitrates at a depth of 16 feet even, though nitrates were relatively high at lesser depths.

Nitrogen fertilizer applied to fields is dissolved during the first few minutes of rain, and carried beneath the surface. By the time the rainfall is sufficient to cause surface runoff, the soluble nitrogen has already infiltrated the soil and is thus positionally unavailable for transport.

Denitrification of nitrate in ground water occurs very slowly and in many places appears to be non-existant (Focht, 1978) because even though the prerequisite of low oxygen supply for denitrification is satisfied there is little if any energy source, that is, food for the denitrifying organisms. In general, knowledge is meager about transport and behavior of nitrate after it has progressed below the soil zone affected by humus and plant roots.

Nitrate in Surface Water

In the Central United States nitrate concentrations are highest in the Spring and lowest in the mid- to late Summer (Delwiche, 1981).

The watershed concentration of nitrate depends primarily upon three factors (1) the supply of nitrate available (fertilizer, industry, feedlots). (2) the degree of movement, contingent upon rainfall (3) and extent to which nitrate is removed, by plants and denitrification (Aldrich, 1980).

Roughly 90 percent of all fertilizer nitrogen is applied in the ammonium form (Aldrich, 1980), which electrically bonds to clay particles and humus, and will not leach through or wash off the soil surface. However, if rainfall is heavy enough to cause soil erosion, ammonium will then be displaced with the soil. Therefore, nearly all nitrogen from cultivated fields entering lakes, streams, and rivers moves through the soil rather than across the surface (Nielson and McDonald, 1978).

In essence, nitrogen transformations in surface waters are similar to those in soils. Losses by volatilization following denitrification are comparable, although nitrogen in well oxygenated surface water will denitrify at a slower pace.

Health Implications

The maximum nitrogen concentration for public drinking water is 10 milligrams per liter of nitrate as nitrogen or 1 mg/l of nitrite as nitrogen or 10 mg/l total nitrate and nitrite nitrogen (Aldrich, 1980). In the absence of pollution from high nitrogen sources ie., feedlots, agriculture, and industry, nitrite concentrations are ordinarily very low. Consequently, 10 mg/l nitrogen is, in effect, a nitrate standard.

The nitrogen standard, established in 1962, was decided upon because there were no reports of infant deaths on account of methemoglobinemia in the United States at levels below 10 mg/l. It was also a standard that could be met by most municipal water supplies (Luhrs, 1973).

California operates under a standard of 20 mg/l nitrate nitrogen, double the suggested maximum. Californians adopted the higher limit because many of their public water supplies exceed 10 mg/l nitrate nitrogen and there are no adequate alternative water sources with lower nitrate concentrations. Nitrate removal was deemed cost prohibitive (Luhrs, 1973). Interestingly, California has had no more cases of methemoglobinemia per capita than any other state (Aldrich, 1980). The last infant death reported in the United States, attributed to methemoglobinemia was in 1949 (Shearer, et. al. 1972). Public health officials have recognized that high concentrations of nitrate in well water may be indicative of surface contamination as a consequence of improper well construction, and illness may be linked to harmful bacteria as well as nitrate (Luhrs, 1973). Obviously, the daily intake of nitrate will vary with the quantity of water consumed. In warmer climates, even if nitrate concentrations are very low, injestion of substantial amounts of nitrate is possible.

Nitrogen as nitrate poses little danger to humans or animals. However, a health threat does exist when nitrate is chemically reduced to nitrite by bacteria in the digestive tracts of human infants or animals. This transformation depends upon bacteria that are highly sensitive to acidity and flourish only near a neutral pH (Focht, 1978).

Nitrite toxicity results from the ability of nitrite to change ferrous iron which is capable of transporting and releasing oxygen, to ferric iron which is an ineffective oxygen supplier (Postgate, 1982). A shortage of oxygen in a living system results in cyanosis (methemoglobinemia). Therefore, nitrogen problems arise when nitrate is converted to nitrite. Health complications which result from injestion of large doses of nitrate are generally restricted to babies under six months of age (Shearer, 1972). Infants are more susceptible to nitrate poisoning because of the relatively low acidity of their stomach fluids. Complicating matters is the ease at which infants hemoglobin is converted to oxygen deficent methemoglobin (Metcalf, 1961).

Livestock Health

The detrimental effect of nitrogen to livestock is largely dependent upon the animals digestive system. Swine have a highly acidic stomach which successfully inhibits nitrate reducing bacteria (Aldrich, 1980). Ruminant types of livestock ie., cattle, goats, sheep, and related wild animals consume mainly roughage and are equiped with a rumen, which is similar to a second stomach inhabited by specialized bacteria responsible for the digestion of the injested fibrous material. The rumen is only slightly acidic and nitrate reducing bacteria are ubiquitous. However, under the strong reducing conditions nitrate is completely converted ammonia which is harmlessly eliminated (Aldrich, 1980).

CHAPTER IV

GEOLOGY

The Permian conglomerates unique to the Wichita Mountains area were informally designated by Chase (1954) to be the Post Oak Conglomerate (Collins, 1985). Chase and Miser (1954), on the Geologic Map of Oklahoma, mapped Permian sediments exposed around the eastern segment of the Wichita Mountains as the Wichita Formation, which is equivalent to the Wellington Formation, the Garber Sandstone (both Leonardian) and the upper part of the Pontotoc Group (Wolfcampian) (Al-Shaieb et. al., 1980). It is impossible to distinguish these units in southwestern Oklahoma, thus necessitating their inclusion under one formational name (Al-Shaieb, 1977). Pennsylvanian-Permian stratigraphy in Oklahoma is being re-evaluated by the Oklahoma Geological Survey in cooperation with the United States Geological Survey. For example, in the Hydrologic Atlas of the Lawton Quadrangle, (Havens, 1977) equates the Post Oak with the Hennessey Shale, which lies above the Garber Sandstone (Figure 3). Because such questions do not directly relate to the present work, the older system suggested by Chase (1954) will be followed. Stratigraphic nomenclature and

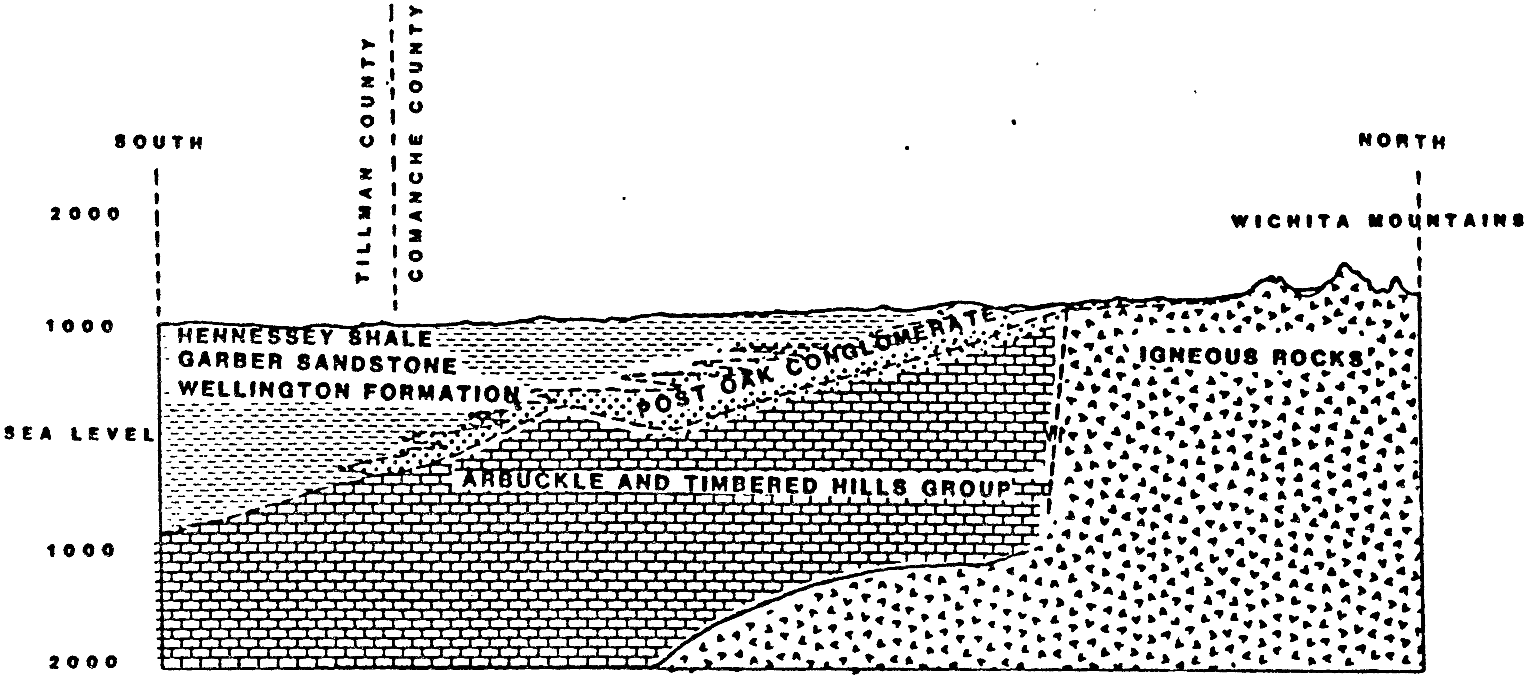


Figure 3. Stratigraphic cross-section of Comanche County (After Havens, 1977)

classification within the study area is described in some detail by Shelton and Al-Shaieb (1976).

Igneous Rocks

The Wichita Mountains are a group of three "en echelon" granite ridges trending approximately N.70W. and cover an area of 1500 square miles. The three predominate varieties of igneous rocks composing the core of the Wichita Mountains are gabbro, granite, and rhyolite, all of which are Cambrian in age (Stone, 1977). During early Cambrian time gabbro covered much of southern Oklahoma. Rhyolite was later extruded over the gabbro floor, followed by granite which intruded a zone of weakness between the gabbro and rhyolite (Stone, 1977).

Wichita Granite Group. The Wichita Granites were formed approximately 525 million years ago (middle Cambrian), and are characterized by mineralogic homogeneity; are leuocratic, with microperthite, quartz and albite-oligoclase being the dominant primary minerals, while biotite, hornblende, and magnetite are the most prominant ferromagnesium minerals (Al-Shaieb et.al, 1980). Several varieties of granite crop out in the Wichita Mountains. Merritt (1967) determined the relative ages and standardized the following terminology: Mount Scott Granite (oldest), Headquarters Micro-granite, Reformatory Granite, Lugert Granite, and the Quanah Granite (youngest).

Quanah Granite. The Quanah Granite crops out along the southeastern margin of the Wichita Mountains. Both the Quanah and the Lugart granites intrude the Mount Scott

Granite (Al-Shaieb et. al., 1977). Al-Shaieb and others (1979) performed a petrographic study of the Quanah Granite and observed that the petrology is somewhat variable, largely because the Quanah Granite consist of several different intrusions. They described it as generally coarse-grained with hypidiomorphic granular texture, and microperthite as the dominant mineral, followed by quartz. Riebeckite and aegirine both occur as constituent minerals in small but significant amounts. Riebeckite also is present in miarolitic cavities. Titaniferous magnetite, horneblende, and zircon are minor constituents, and traces of fluorite, apatite, and monazite are present.

Riebeckite-Aegirine Granite Dikes and Pegmatites. Riebeckite-Aegirine dikes are located in the western portion of the Wichita Mountains and cut both the Reformatory and Lugart Granites and range from 1 to 16 inches in width, dip 25-40 N and may be traced for distances of half a mile or more (Al-Shaieb et. al., 1977). Merritt (1967) describes the rock as fine grained and aplitic with constituents that average 1 mm. in diameter. He states that riebeckite and aegirine appear to be the primary magmatic minerals in these dikes although in the miarolitic cavities of the Lugart and Reformatory granites, where riebeckite occasionally occurs, it is a hydrothermal mineral. In addition, riebeckite is present in small amounts in a few granite outcrops of the area and in these it replaces hornblende or other minerals and is secondary. In some places the aegirine is partly altered to riebeckite. The dikes are believed to be cogenetic with the peralkaline Quana Granite and represent the latest phase of silicic igneous activity in this area (Al-Shaieb et. al., 1977).

Post Oak Conglomerate

The Permian conglomerate which crops out in the eastern part of the Wichita Mountains of southwestern Oklahoma, was first described by Taft (1904) as "Red-beds" conglomerate, and was thought by him that they were deposited contemporaneously with the "Red-bed" shales of Permian age as a near-shore facies equivalent. Hoffman (1930) described this conglomerate as Pleistocene gravels and correlated them to the gravels of similar age in old stream channels north of Frederick, Oklahoma. Merritt et. al.,(1964) published a lithofacies map of the Post Oak Conglomerate which surrounds a part of the gabbro-anorthosite hills in the north-central part of the Wichita Mountains. They named the conglomerate the Tepee Creek Formation. Mayes (1947) after studying stratigraphic relationships concluded that the conglomerate was early Permian in age. Chase (1954) outlined four distinct lithologic facies of the Post Oak Conglomerate. These conglomerate facies are granite boulder conglomerate, rhyolite porphyry conglomerate, limestone conglomerate, and granite-gabbro conglomerate with zeolite-opal cement.

Sedimentology. The following is a summary from Al-Shaieb (1977). The Post Oak occurs as massive beds of conglomerates and flanks the granite and rhyolite hills of the Wichita Mountains. This nonconformity is irregular and depicts relief locally and in the limestone hills to the north.

Sedimentary structures are scarce in the massively bedded conglomerates, however previously formed channels in the conglomerate may sometimes be found locally. Clasts are commonly 15 to 45 cm. in length. Limestone and rhyolite clasts are angular or subangular. However, many granite clasts are well rounded it is believed that this is due to in situ weathering and not transport. Coarse-grained sand occurs as a matrix between boulders in the granite and rhyolite conglomerates, but not in the limestone conglomerates and also as irregular lenses having medium sized trough cross-bedding. Changes in grain size are often abrubt both vertically and laterally. Sandstones and mudstones have been deposited farther from the Wichita source area, therefore the average grain size decreases away from the mountains. The coarser lithologies are developed as laterally discontinuous channel deposits that have pronounced erosional bases. Often, these deposits are no more than 2 meters thick and 10 to 30 meters wide. They commonly contain basal channel-lag deposits of both exotic and intraformational clast and are futher characterized by medium-sized trough cross-bedding, and cut-and-fill structures.

Petrology and Diagenesis. The granite conglomerate is poorly exposed on the north flank of the Wichitas. The Post

Oak is more extensively weathered south of the Wichitas, where many facies changes occur (Al-Shaieb et. al., 1980). This boulder conglomerate weathers to boulder beds composed of unconsolidated well rounded boulders surrounded by yellow to browish clay, and are well cemented with calcite and limonite and the intersticies are filled with arkose and clay (Chase,1954). The dominant clay minerals are sodium montmorillite, illite, kaolinite and mixed-layer clays (Kwang, 1977). The conglomerate rests unconformably upon granite and grades in short distances southward from a boulder facies into a gravel facies containing an increasing number of arkose lenses. Six to eight miles south of the mountains the conglomerate has changed to a coarse cross-bedded arkosic sandstone with some zones grading into red Permian shale, while laterally grading into the limestone conglomerate eastward along the mountains (Chase, 1954). Al-Shaieb and others (1980) made a sedimentologic-petrographic study of sandstones of the Post Oak Conglomerate in the Wichita Mountains area, the following is a summary. The Post Oak sandstones are texturally immature feldspathic litharenites and lithic arkoses, whose detrital sand-sized grains are predominantly quartz (13-63%), feldspar (2-38%), and rock fragments (2-53%). Microperthite is the most common feldspar, and small amounts of plagioclase were present in several samples. Riebeckite is absent within the Post Oak sediments.

Although amphiboles are present in variable amounts within the Wichita granites, they appear to be absent within the Post Oak. Detrital magnetite and ilmenite are fairly common, but they are generally altered to hematite, limonite, and leucoxene. Detrital brown biotite, which is less common, shows variable degrees of oxidation to iron oxide.

The Post Oak sandstones have been cemented by at least two cementation stages consisting of carbonate, iron oxide, barite (locally), and two or more generations of authigenic clay. Sequential evidence of these stages was based primarily on microtextural (fabric) relationships, the sequence of cements was clay (commonly kaolinite), iron oxide, and carbonate before iron-rich illite and minor mixed-layer smectite-illite.

Depositional Environments. Al-Shaieb et. al., (1977) showed that the sedimentary structures, paleocurrents, and texture, indicate that the Post Oak was deposited by small, probably ephemeral streams, that eroded and drained the Wichita Mountains. Also that adjacent to the mountains, deposition occurred on alluvial fans, while several kilometers from the mountains, small braided streams flowed across alluvial plains which, together with the fans, formed a piedmont plain. Small local granite hills disrupt the otherwise south- flowing drainage pattern. Local anomalies in the overall south-flowing drainage pattern represent diversion of streams around isolated granite hills. Desiccation cracks and calcretes further indicate episodic sedimentation (Al-Shaieb et. al. 1980).

Arbuckle Group

The Arbuckle Group is not surficially exposed south of the Wichita Mountains in Comanche County. However, in the northeast corner of Comanche County, within the Slick Hills, the carbonate rocks of the Arbuckle Group are well exposed. The Arbuckle Group is divided into the following formations; Fort Sill (Cambrian), Signal Mountain, Butterly, McKenzie Hill, Cool Creek, Kindblade, and West Spring Creek (Ordovician). The Fort Sill Formation is further divided into three members. The uppermost member, a massive limestone, may be used as a reliable marker bed due to the easily weathered units above and below it (McDaniel, 1959).

CHAPTER V

HYDROGEOLOGY

The climate of Comanche County is outlined by Mobley et al. (1967), and consist of a dry, subhumid, continental climate. Rainfall is heaviest in spring. Summers are hot and generally dry, winters are mild, although severe cold spells sometimes occur. The rainfall is often of high intensity but because of strong winds, high temperatures, and the high rate of evaporation little water moves through the soils, except for the more permeable sandy ones. Leaching is therefore minimal and the presence of a lime zone in many soils indicates the average depth to which water infiltrates.

Climate is directly or indirectly the cause of many variations in plant and animal life and thus affects the changes in soils that are brought about by biologic factors.

Comanche County has nine soil associations, encompassing 86.4 percent of the county. For full descriptions and areal extent see Mobley et. al. (1967).

Ground Water

The hydraulic characteristics of an aquifer describe its ability to store and transmit water and can be described in terms of storage coefficient and transmissivity. The specific capacity of a well is a measure of the ability of a well to yield water with respect to drawdown and can be used to approximate transmissivity (Walton, 1970). The most significant determinant of these analytical properties is whether the aquifer is confined, semi-confined or unconfined. On the other hand, properties such as, porosity, permeability, and the degree of homogenity are determined largely by the depositional environment and diagenesis.

Post Oak Aquifer

The Post Oak Aquifer is used as a source of fresh water for irrigation and supply for the rural water districts in Comanche County. It is most productive as a water source in the ancient Permian stream channels deposited during the Wichita uplift. The facies consist primarily of coarse sands and gravels that exhibit high permeability (Figure, 4). Separating the paleo-stream channels the sediments are fine grained sands decreasing in size away from the mountains.

The ground-water gradient in the study area trends southeast, roughly following the topography. In general, recharge areas are topographically high and discharge areas are topographically low. Directly south of the Wichitas the ground-water gradient is relatively steep ranging from 5 ft/mi to 8 ft/mi. Further south the gradient levels off to approximately 1 ft/mi.

Major pumping areas are non-existant in the country, although localized pumping takes place near Lawton,

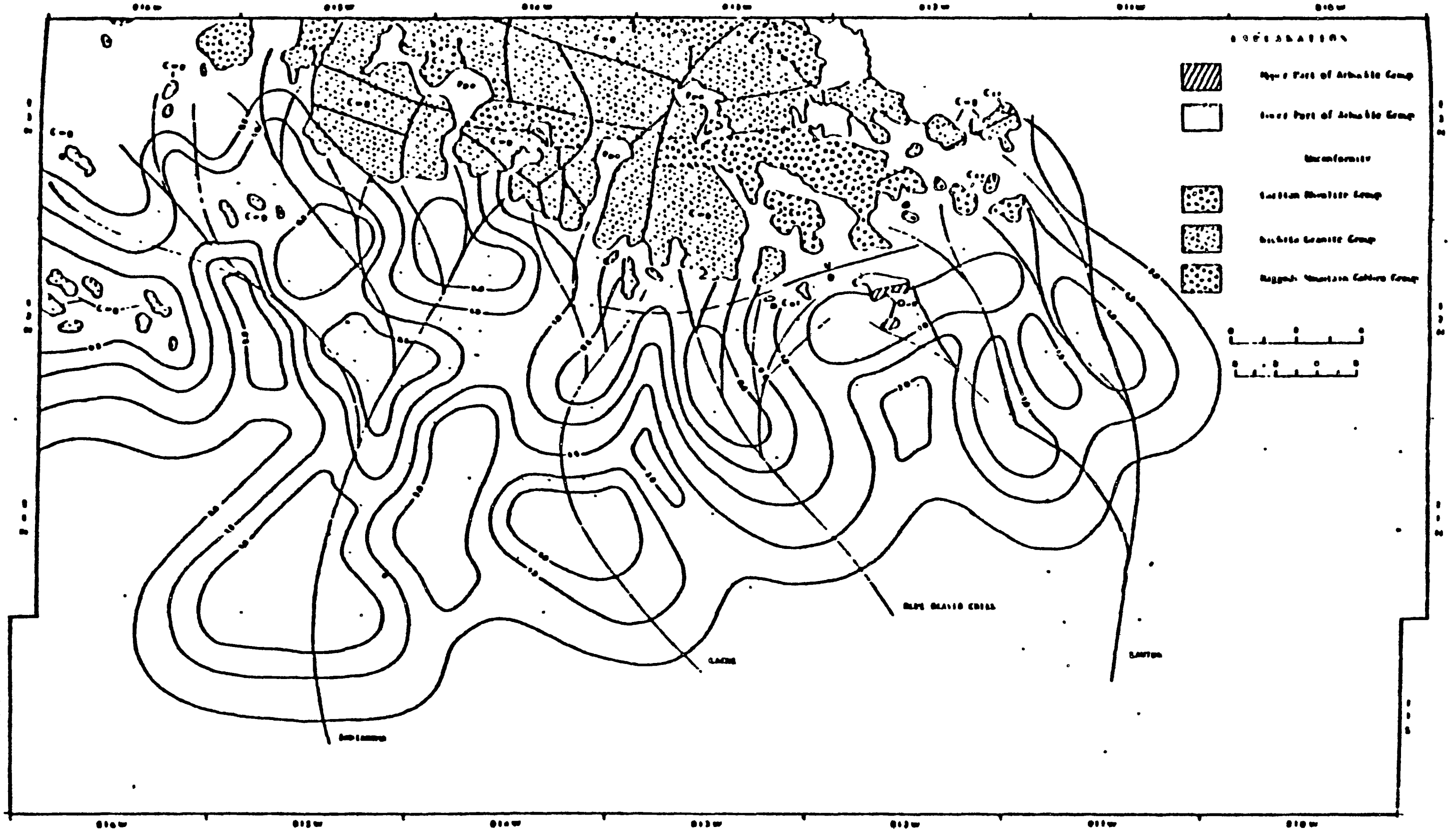


Figure 4. Proposed Paleo-stream Channels and Sediment phi size of Post Oak Conglomerate (After Stone, 1977)

Indiahoma, Cache, Geronimo and Chatenooga, generally for irrigation and to supply the local rural water districts.

There is a general trend of transmissivity increase to the southeast which coincides with increasing thickness of the formation and decreasing grain size. For a more detailed development of the hydrogeology see Appendix 1.

Lower Confining Beds. There is little information available on the hydraulic properties of the rocks that directly underlie the aquifer. The underlying rocks for the most part consist of limestones that are probably fractured, thus enabling water from the Post Oak to leak downward where the hydrostatic pressure allows. The absence of upward leakage was confirmed with carbon isotope data (isotope section).

Arbuckle Aquifer

The Arbuckle aquifer is not extensively used as a water source within Comanche County as most of the farming is dry-land and little irrigation is required. The Arbuckle is often present several thousand feet below land surface and the water quality and yields from it are often better than that of the shallower Post Oak Conglomerate.

Very little data has been collected on the hydrologic properties of the Arbuckle aquifer within Comanche County. However, Fairchild and Davis (1983) have done extensive work with the hydraulics of the Arbuckle-Simpson Group to the southeast in the eastern part of the Arbuckle Mountains.

The Arbuckle is semi-confined with the upper confining beds located at the base of the Post Oak. These confining beds are discontinuous layers of low permeability shales and silts. The hydraulic gradient is controlled by the Wichita Mountains, which due to the increased hydrostatic pressure with increasing distance from the mountains, elevates the potentiometric surface.

CHAPTER VI

ISOTOPES

Isotopes of both hydrogen and oxygen in water are fractionated by evaporation and precipitation in the hydrologic cycle and by chemical reactions with rocks. Ground water in virtually all systems originates as precipitation. Thus, the spatial and temporal variations in isotopic content of precipitation can be used to investigate ground-water recharge (Coplan, 1984).

Carbon isotopes are fractionated by several natural processes, including photosynthesis and isotope exchange reactions among carbon compounds (Faure, 1977). These processes may be indicative of the orgin of carbonate and bicarbonate ions which in turn aid in delineating the system.

Oxygen and Hydrogen Isotopes

Hydrogen and oxygen are stable isotopes and are both closely associated with the water molecule. Therefore, their isotopic ratios will be discussed together. Numerous factors control the isotopic content of precipitation. However, only the few that are likely to effect a relatively small geographical area (Comanche County) are discussed.

Increasing altitude will decrease the abundance of ^{18}O

and deuterium (D) depleting the heavy isotopes on the windward side of a mountain but not on the lee side (Coplan, 1984). This phenomenon is supported by the isotope data measured within the study area (Figs. 5 and 6). The degree of fractionation is dependent upon local topography and climate, typical gradients for ^{18}O are -0.15 to -0.5 o/oo per 100 m and for D are -1.5 to -4 o/oo per 100 m (Coplan, 1984). If rain evaporates as it falls the altitude effect will be enhanced.

Seasonal variation can play a significant role in isotopic fractionation. Winter precipitation is depleted in D and ^{18}O relative to summer rains. The amount of rain will also effect the D and ^{18}O content. The greater the rainfall, the more depleted the D and ^{18}O values (Coplan, 1984). Evaporation increases the D and ^{18}O content of precipitation derived from small rainfall events more than large storms. This effect does not occur for snow (Coplan, 1984).

The relationship between D and ^{18}O in meteoric water is represented by the equation 1:

$$D = \Delta\ ^{18}O + d \qquad (1)$$

where d is the deuterium excess parameter (Coplan, 1984). Craig (1961) found that the global mean value of d for fresh water sources is 10. The value of d may be used to isotopically identify the source and time of recharge. For instance, during Pleistocene glaciation, cooler and more humid conditions were often characterized by a lower deuterium excess (Coplan, 1984).

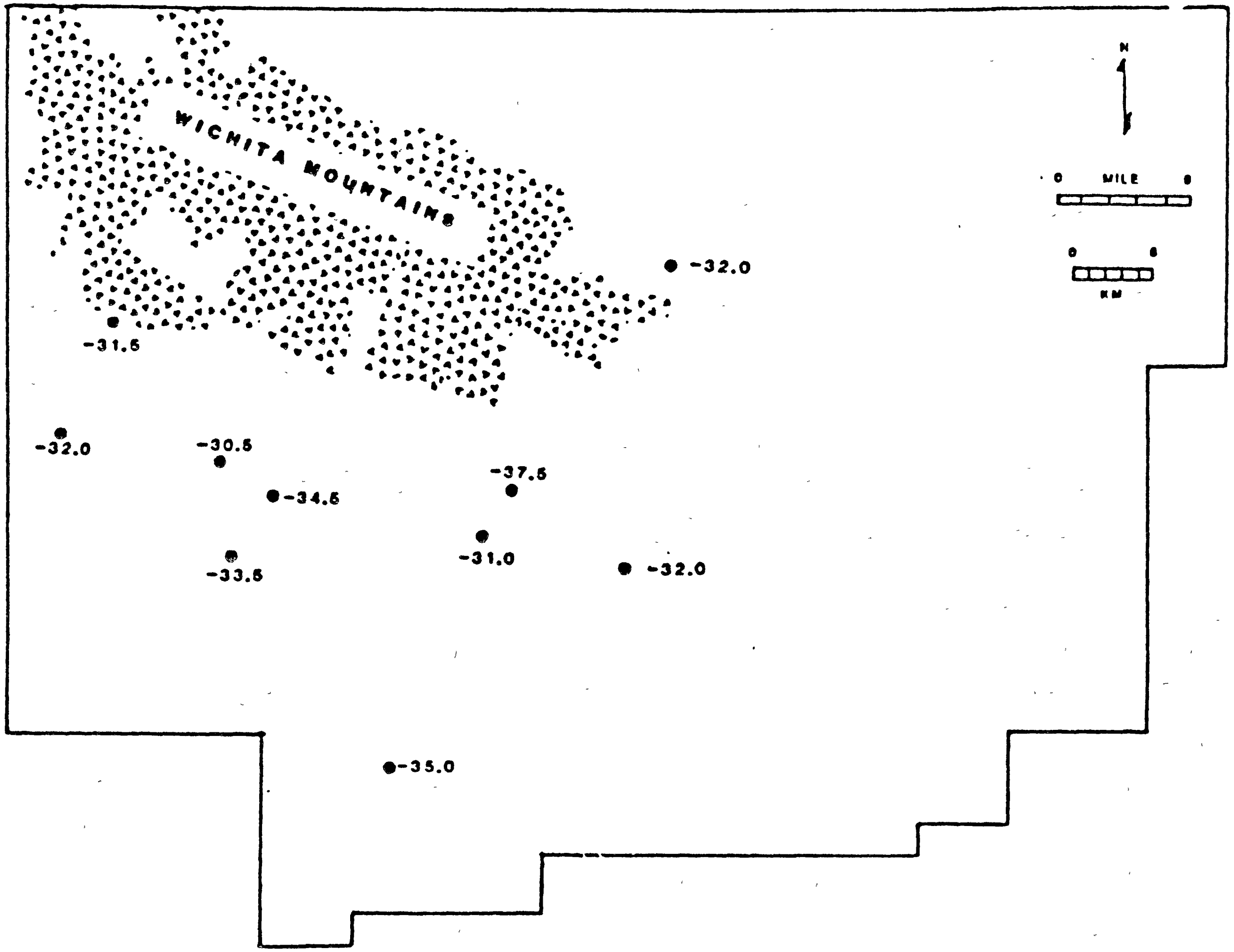


Figure 5. Areal Distribution of Deuterium in Comanche County

Oxygen and hydrogen isotopes were measured from ten samples taken within the study area Table 1. A graph of D vs ^{18}O (Figure 7) shows that most of the sample points plot near the world meteoric water line first identified by Craig (1961). This supports the premise that the Post Oak aquifer is fed entirely, or almost entirely, by meteoric water derived from "modern rainfall". There is an interesting trend in the isotopic compositions, from east west the water becomes more depleted in heavy isotopes of hydrogen and oxygen (Figs. 5 and 6). This is interpreted to be a function of the rainfall pattern where the west side of the Wichitas is influenced by isotopically depleted rainfall from prevailing nortwesterly storms. Using these values to intrepret the local rainfall pattern it appears that the Post Oak is recharged over much of the area by water precipitated in the Wichitas.

Carbon Isotopes

Carbon in ground water is derived primarily from the following components of the carbon cycle: carbonate sediments, soil humus, and decay of land-plant biomass (Coplan, 1984). The isotopic composition of calcium carbonate precipitated from aqueous solutions is controlled by several factors, including pH temperature, carbon species present and their origin (Faure, 1977).

The ^{13}C values of carbonate rocks of marine origin of Cambrian to Tertiary age are virtually constant and have values close to zero on the PDB (Belemnitella Americana, Peedee Formation, Cretaceous, South Carolina) scale (Faure,

TABLE I

ISOTOPE DATA COLLECTED IN COMANCHE COUNTY

Sample Number	Location	DELTA C-13 in permil rel PDB	DELTA O-18 in permil rel. V-snow	DELTA D in permil rel V-snow
L-1	T3NR12W SEC 14	-8.45	-5.00	-32.0
L-2	T3NR15W SEC 7	-8.65	-5.25	-31.5
L-3	T1SR13W SEC 12	-16.55	-4.85	-35.0
L-4	T1NR14W SEC 5	-13.95	-5.55	-33.5
L-5	T2NR14W SEC 19	-9.25	-5.20	-30.5
L-6	T2NR14W SEC 20	-10.60	-5.00	-34.5
L-7	T2NR13W SEC 23	-10.25	-5.60	-37.5
L-8	T2NR12W SEC 17	-8.65	-6.20	-32.0
L-9	T2NR1W SEC 28	-13.60	-4.90	-32.0
L-10	T2NR13W SEC 27	-10.15	-5.05	-31.0

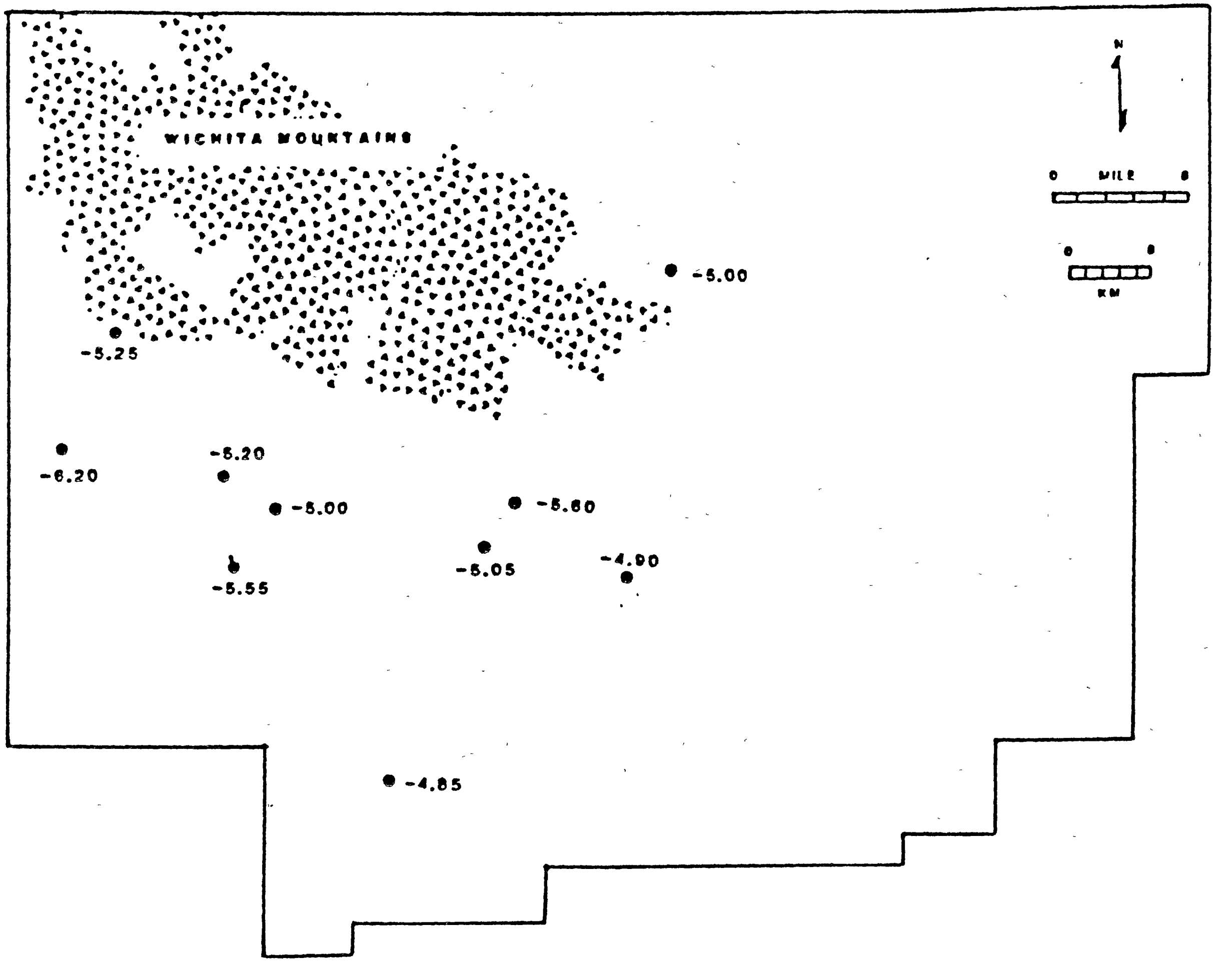


Figure 6. Areal Distribution of ^{18}O in Comanche County

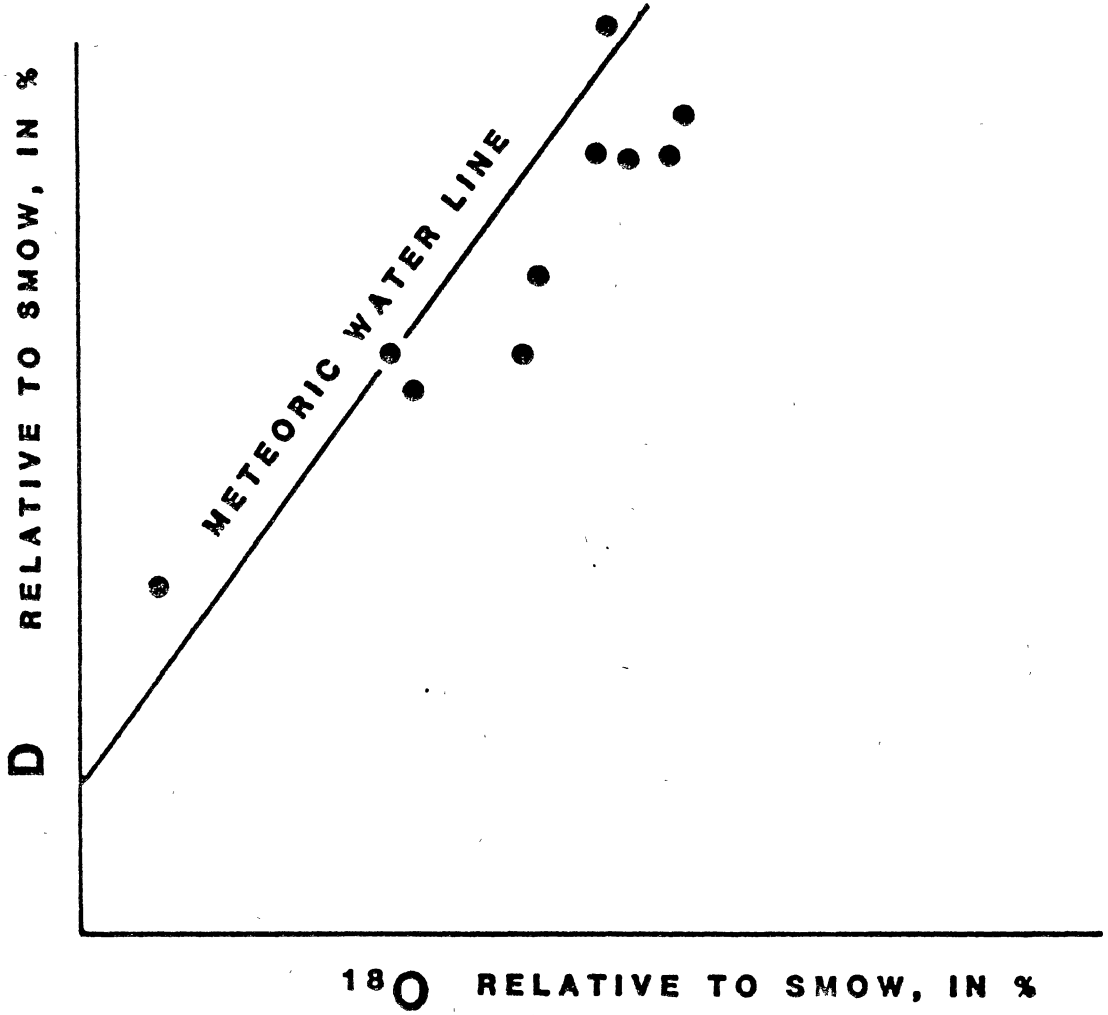


Figure 7. Relationship of ^{18}O to Deuterium in Comanche County

1977). On the other hand, freshwater carbonates are enriched in ^{12} C compared to marine carbonates and have more variable ^{13}C values (Faure, 1977). The relative enrichment in ^{12} C and greater variability of the ^{13}C values of the fresh water carbonates is attributable primarily to the presence of CO_2 gas derived by the oxidation of plant debris in soils and by plant respiration (Faure, 1977).

The chemical speciation of dissolved inorganic carbon is pH dependent. Bicarbonate (HCO_3) is dominant for pH values between 6.4 and 10.3. Carbonic acid (H_2CO_3) prevails below 6.4, and carbonate (CO_3) is dominant above 10.3 (Freeze and Cherry, 1979). The equilibrium isotopic fractionation between some carbon species is relatively large (10 o/oo) (Coplan, 1984). As a consequence, the total dissolved inorganic carbon in the ground-water sample, which is the parameter measured in the laboratory, is a function not only of the isotopic compositions of the individual species, but also of the pH of the sample (Coplan, 1984). Thus, calculation of the ^{13}C of gaseous CO_2 in carbon isotopic equilibrium with ground water requires knowledge of both pH and ^{13}C of total dissolved inorganic carbon.

The chemical reaction that describes the primary process for producing dissolved carbon in ground water is

$$CO_2 + CaCO_3 + H_2O \dashrightarrow Ca^{2+} + 2HCO_3$$

Most frequently, CO_2 is derived from root respiration or decomposition of soil organic matter, and is seldom atmospheric CO_2 (Coplan, 1984). The CO_2 reacts with carbonate sediments to produce dissolved calcium bicarbonate. Note that the bicarbonate contains carbon from two different sources, so that the ^{13}C and ^{14}C content of the bicarbonate depends upon the ^{13}C and ^{14}C content of reactants (Coplan, 1984).

Within Comanche County &^{13}C species range from -8.45 o/oo near the recharge area (Wichita Mountains) to -16.55 o/oo downgradient (Table 1). The progressive depletion in ^{13}C implies that very little water from the isotopically light marine derived limestones of the underlying Arbuckle is leaking upward into the Post Oak and that the bicarbonate is derived from fresh-water sources (Figure 8).

CHAPTER VII

SAMPLING PROCEDURES

Sampling procedures outlined by the U.S Geological Survey (1982) were followed to obtain ground-water samples from the study area during July 1984. Sampling locations were selected with the project objectives in mind (Table, 1).

(1) Determine the geochemical parameters govering the driving reactions, and to assess the state of the aqueous system, with respect to the geologic framework of mineral components with which it is in contact.

(2) Obtain pertinent data to use in the solute-transport model

(3) Collect isotopic data to delineate flow system.

Water samples were collected from wells that were fully cased, when possible, and screened at varing depths within the Post Oak Aquifer (Table 2). Before taking a water sample the wells were pumped until temperature and pH became constant. Conductivity measurements were made with a YSI model 32 conductivity meter. The pH meter was calibrated with standardized 7.0 buffer solution in the field prior to each determination.

Additional samples were preserved in the field, also following recomendations described by the previously mentioned Survey publication. Samples collected for 13 carbon isotope determinations were preserved by adding $SrCl_2$ and KOH to the water samples while the deterium and oxygen needed no preservation.

TABLE II

WATER ANALYSES COLLECTED FROM COMANCHE COUNTY

Constituents(mg/l)	CO_3	HCO_3	SO_4	Cl	F	NO_3	Ca	Mg	Na	K	Sr	SiO_2	TDS
Sample No.													
L-1	0	377	225	32	.7	7.0	104	16	115	3.5	.4	14	536
L-2	0	284	33	22	.4	7.7	83	7.0	38	.5	3	4.0	201
L-3	0	86	17	11	.3	.2	30	2.2	8.5	.7	.2	7.6	501
L-4	0	640	290	279	24	.9	3.0	.9	583	3.7	.3	7.8	1340
L-5	0	340	77	59	.6	82	99	28	58	1.1	.6	11.0	510
L-6	0	264	43	87	4.3	.3	6.7	1.8	166	1.4	.1	7.2	536
L-7	0	374	38	84	35	.2	1.5	.2	269	.4	.0	11.0	636
L-8	0	353	74	58	.5	91	82	27	85	1.6	.6	12.0	536
L-9	0	130	23	14	.4	37	31	7.8	31	1.6	.3	12.0	201
L-10	4	559	64	192	12	.6	20	7.0	343	1.8	.4	5.8	2010

* water samples collected during June 1985 and analyzed by the U.S.G.S.

CHAPTER VIII

GEOCHEMISTRY

The chemical quality of ground water is an important factor in water-supply planning. For an aquifer to be a reliable water source, not only must predictable quantities of water be available, but the water must also be of predictable and satisfactory chemical quality. The following discussion will outline the chemical processes that determine the water composition of the Post Oak aquifer.

In Comanche County, the ground waters have high concentrations of nitrate and fluoride. Calcium and magnesium are also dominant ions in some ground waters within the county (Figure, 9). Of more importance are a group of sodium and potassium rich waters that have fluoride concentrations which range from 4 to 35 mg/l, these waters greatly exceed the EPA recomended limit of 2.7 mg/l F^- (temperature dependent) for this geographical area and are accompanied by a high total dissolved solids content. Health risk at these elevated concentrations are numerous, including dental fluorosis (tooth mottling) and deterioration of the skeletal structure. Yiamouyiannis (1985) throughly discusses the detrimental effects from high

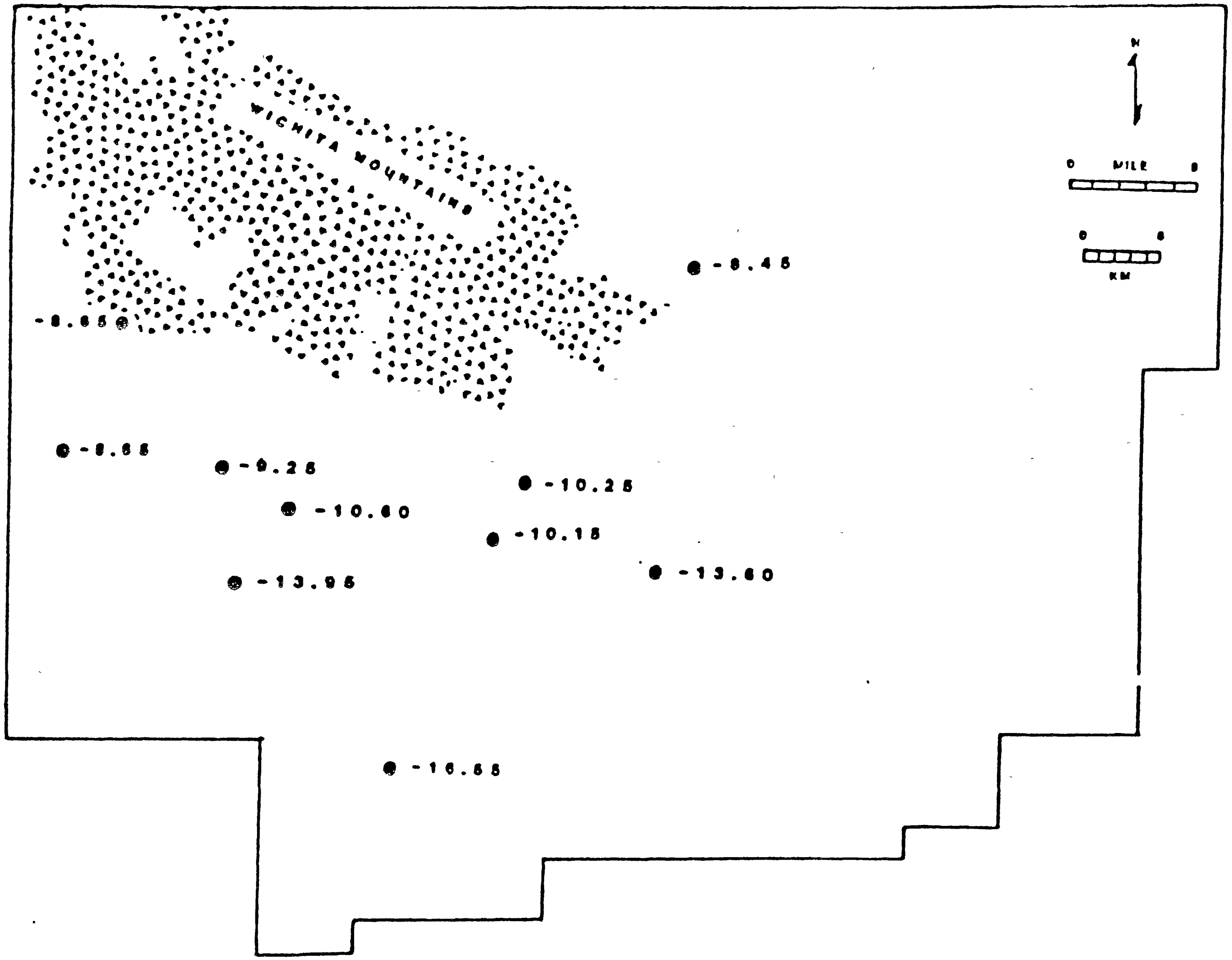


Figure 8. Areal Distribution of ^{13}C in Comanche County

levels of fluoride.

Fluoride

Fluoride in Comanche County originates from the dissolution of riebeckite, a fluoride-bearing amphibole contained in the Quanah granite of the Wichita Mountains. Green and Al-Shaieb (1981) analyzed Post Oak rock samples for fluoride to determine the areal extent of fluoride source rocks (Figure, 10). The greatest concentrations within the rocks are found on the south side of the Wichita Mountains near the Tillman County line, while levels taper off near Lawton.

On the other hand, fluoride concentrations in waters, directly south of the Wichitas are less than 1 mg/l, whereas futher south, away from the source, concentrations increase to 35 mg/l fluoride (Figure, 11). Presently there is a chemical zone approximately 12 miles south of the Wichitas within which the waters have the greatest concentrations of fluoride (Figure 12). This enrichment of fluoride may be understood through an evaluation of the hydrology and geochemistry of the system.

During the uplift and erosion of the Wichitas and subsequent deposition of the Post Oak fluvial deposits, riebeckite present in the rocks was weathered and released fluoride which was then absorbed on the kaolinite and any amorphous clays formed in the weathering process. Appreciable amounts of sodium were leached from the sodic feldspars contained within the Quana granite and absorbed on

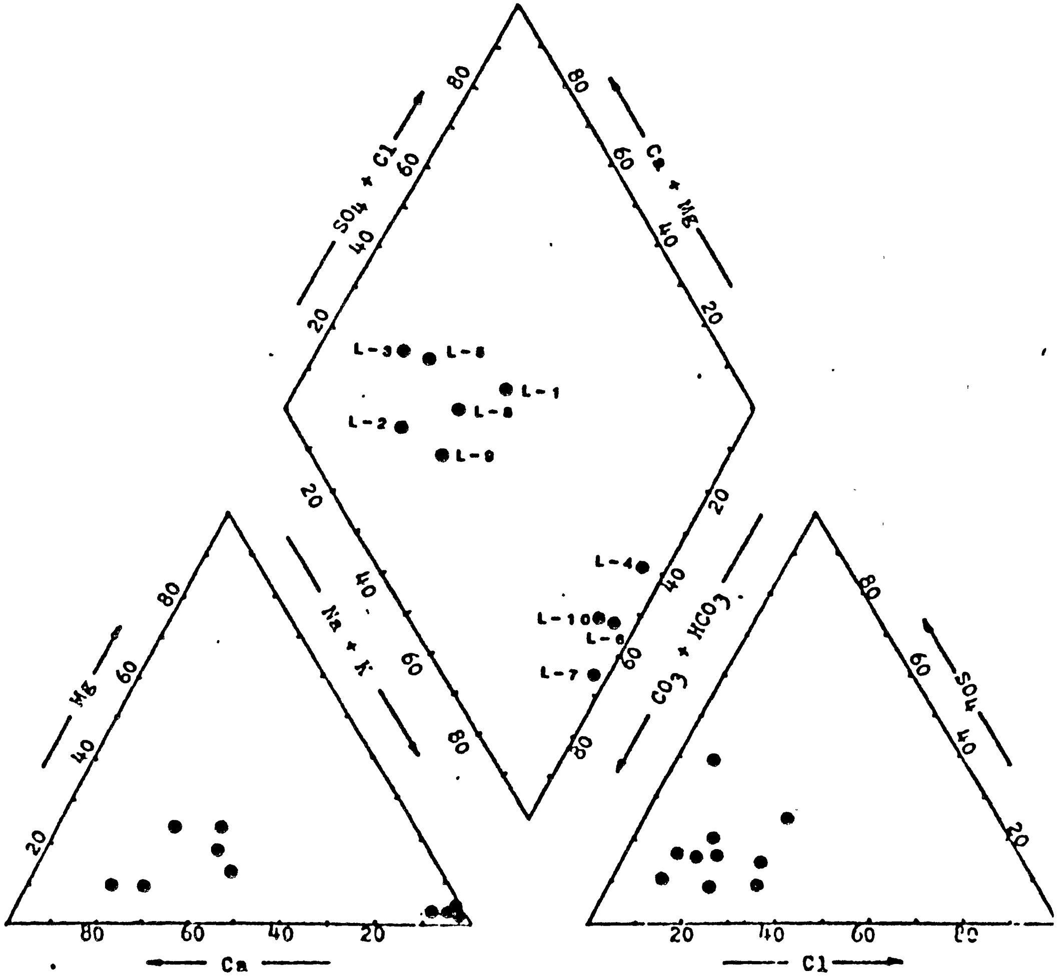


Figure 9. Piper Diagram of Post Oak Waters (After Freeze and Cherry, 1979)

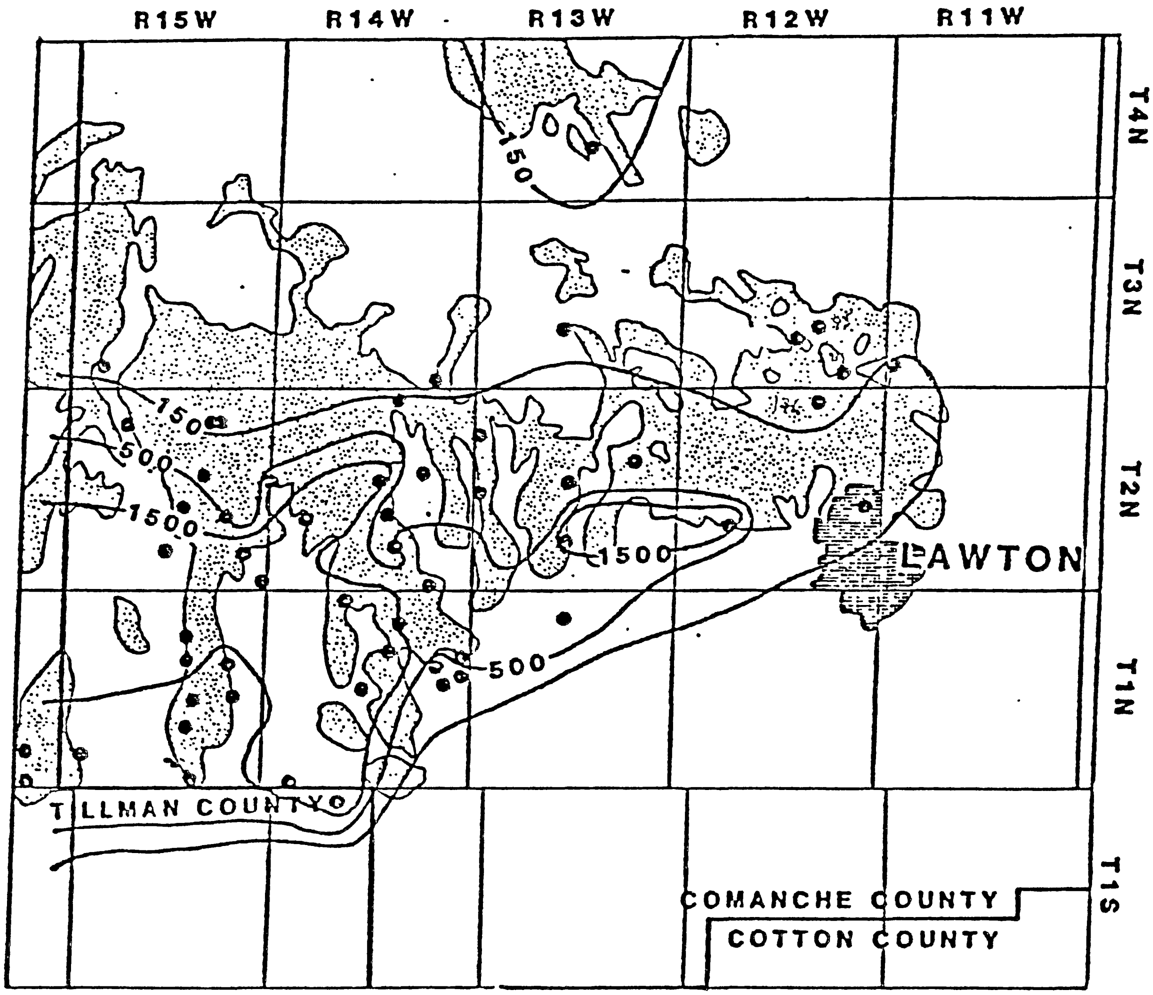


Figure 10. Distribution of fluoride in the Post Oak Formation. Stippled area represents the extent of Post Oak outcrop, solid dots indicate the location of analyzed samples. Concentrations are continued in parts per million. (From Green and Al-Shaieb, 1981)

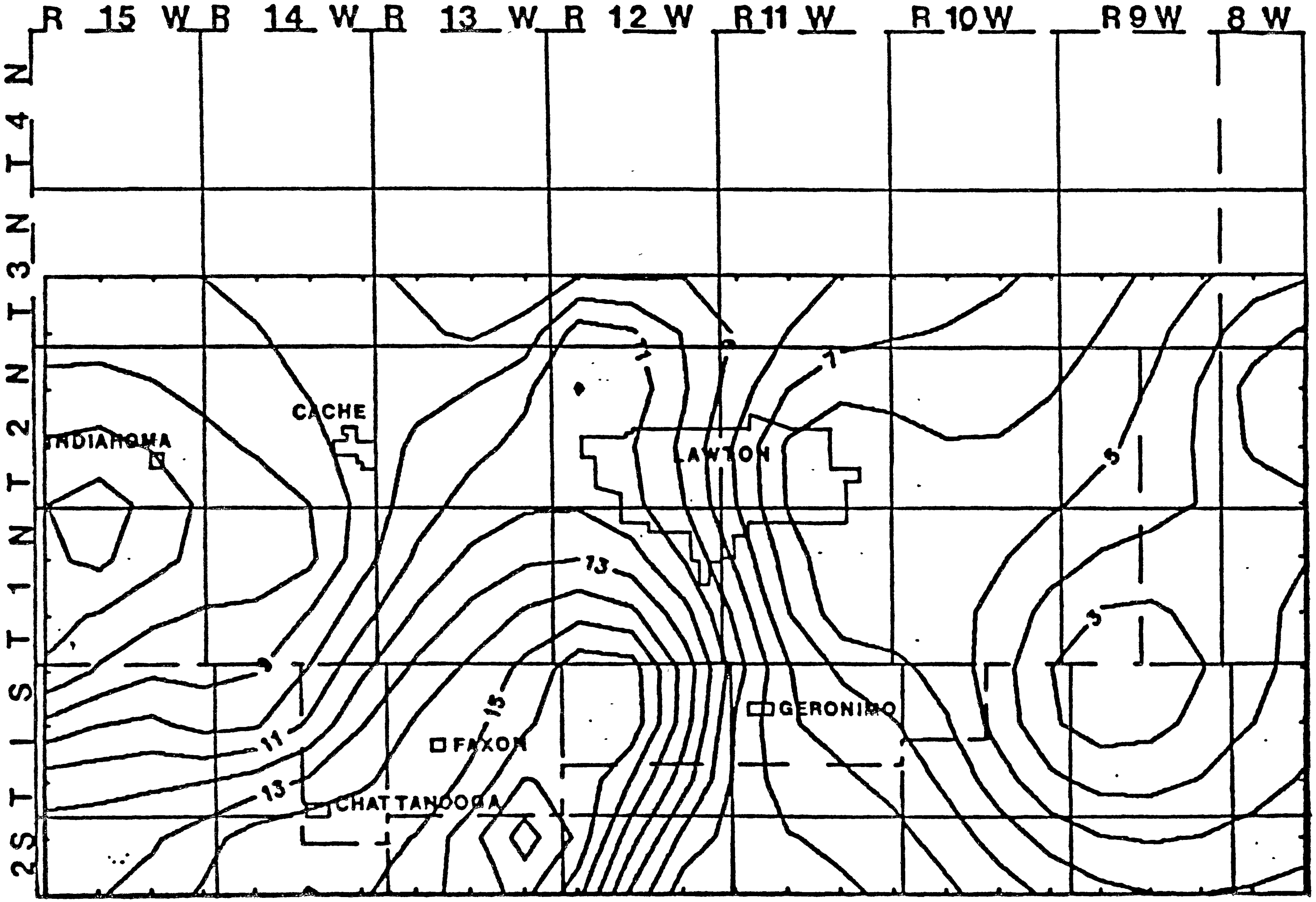


Figure 11. Distribution of Fluoride in the Post Oak Waters

the montmorillinite present in the Post Oak. Both clays being fine grained were deposited in greater quantities furthest from the source.

Subsequently the Raggady Mountain gabbros, high in calcium plagiclase, were weathered and released large quantities of calcium which led to the precipitation of calcite cement in the deposited Post Oak.

The distribution of clay minerals within the Post Oak have never been mapped. The grain size of the Post decreases away from the Wichitas (Figure, 4).

Chemical Reactions

Several important reactions will be discussed that will lead to an explanation of why fluoride is high in these waters.

Bicarbonate. Calcium from the dissolution of calcite cement is replacing sodium attached to the montmorillonitic clays on account of the greater charge and smaller ionic radius (Figure, 13). The preferential replacement of sodium by calcium creates a solution undersaturated with respect to calcite. This disequilibria is satisfied by the dissolution of calcite cement, following the equation:

$$CaCO_3 + H_2O + CO_2 \text{ ---> } 2HCO_3^- + Ca^{2+}$$

The carbon dioxide is derived from the atmosphere, and the overall result is an approximate pH value of 8.4 (Garrels and Christ, 1967).

WATEQ, a thermodynamic-geochemical-reaction model

(Plummer et.al., 1976) was applied to determine in what waters calcite dissolution was occurring and to define the geochemical boundaries. Generally, calcite has a tendency to dissolve from the northernmost boundary, of the chemically active zone, southward (Figure, 14).

Calcium-Sodium Ratio. In further evaluation of the previous senerio, it appears that the geochemical transition zone is slowly migrating south away from the mountains, roughly following the hydrologic flow paths. At a rate dependent upon the available supply of calcium ions to drive the reactions.

North of this reaction zone calcium has already flushed the sodium from the clays, enabling the ground water to become saturated with respect to calcite, thus limiting calcite dissolution. This is reflected by the lower pH of these waters. Below the transition zone, a chemically inactive system would be expected, contingent upon the scarcity of calcium ions required to drive the ion-exchange reactions and initiate calcite dissolution.

Discussion

The following text will trace the methods and conclusions from previous studies on fluoride adsorption mechanisms in the lab and field.

In an attempt to quantitatively desorb phosphate from kaolinite using ammonium fluoride Dickerman and Bray (1941) found that 100 g. of kaolinite could adsorb up to 41 meq

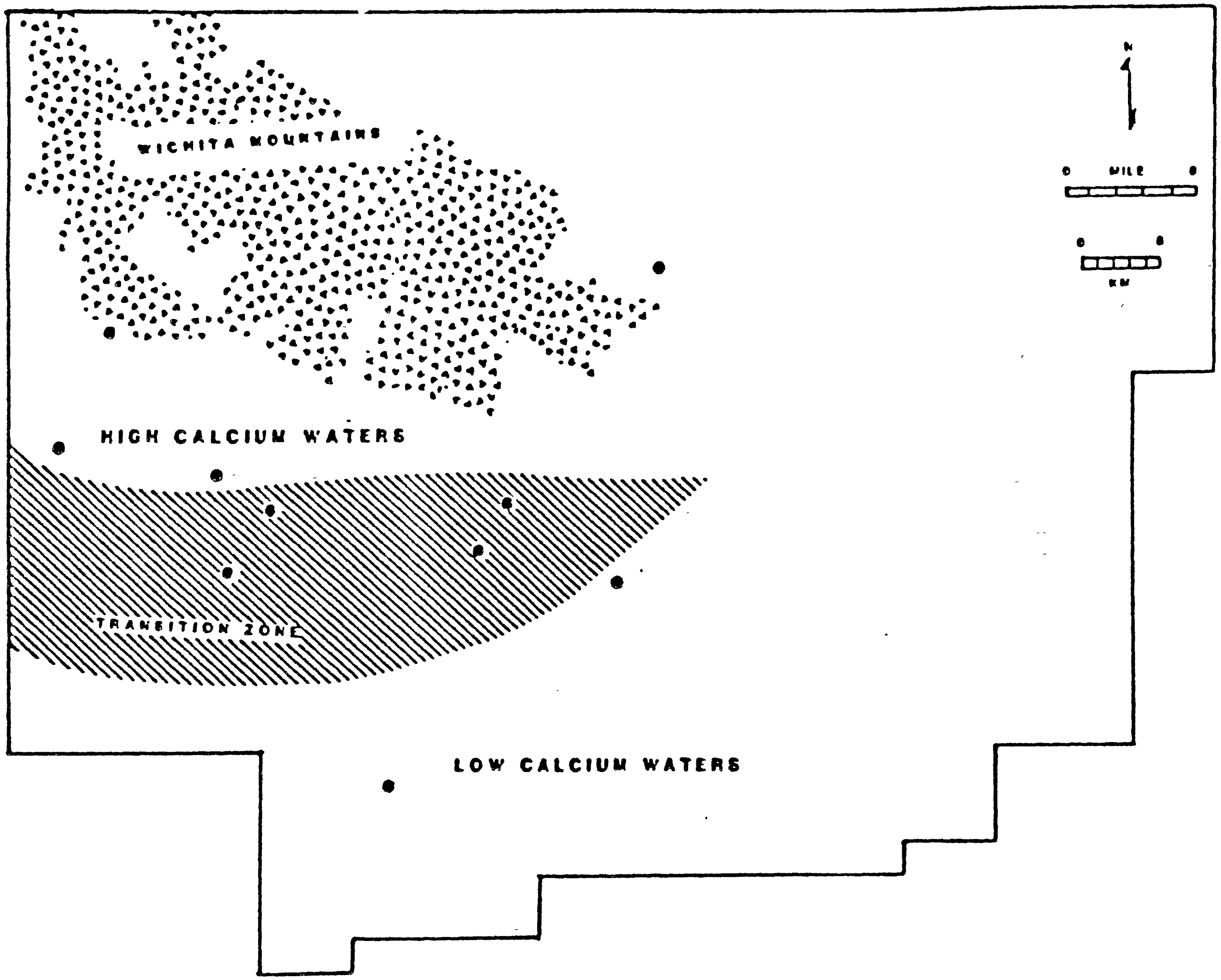


Figure 12. Geochemical Transition Zone in Comanche County

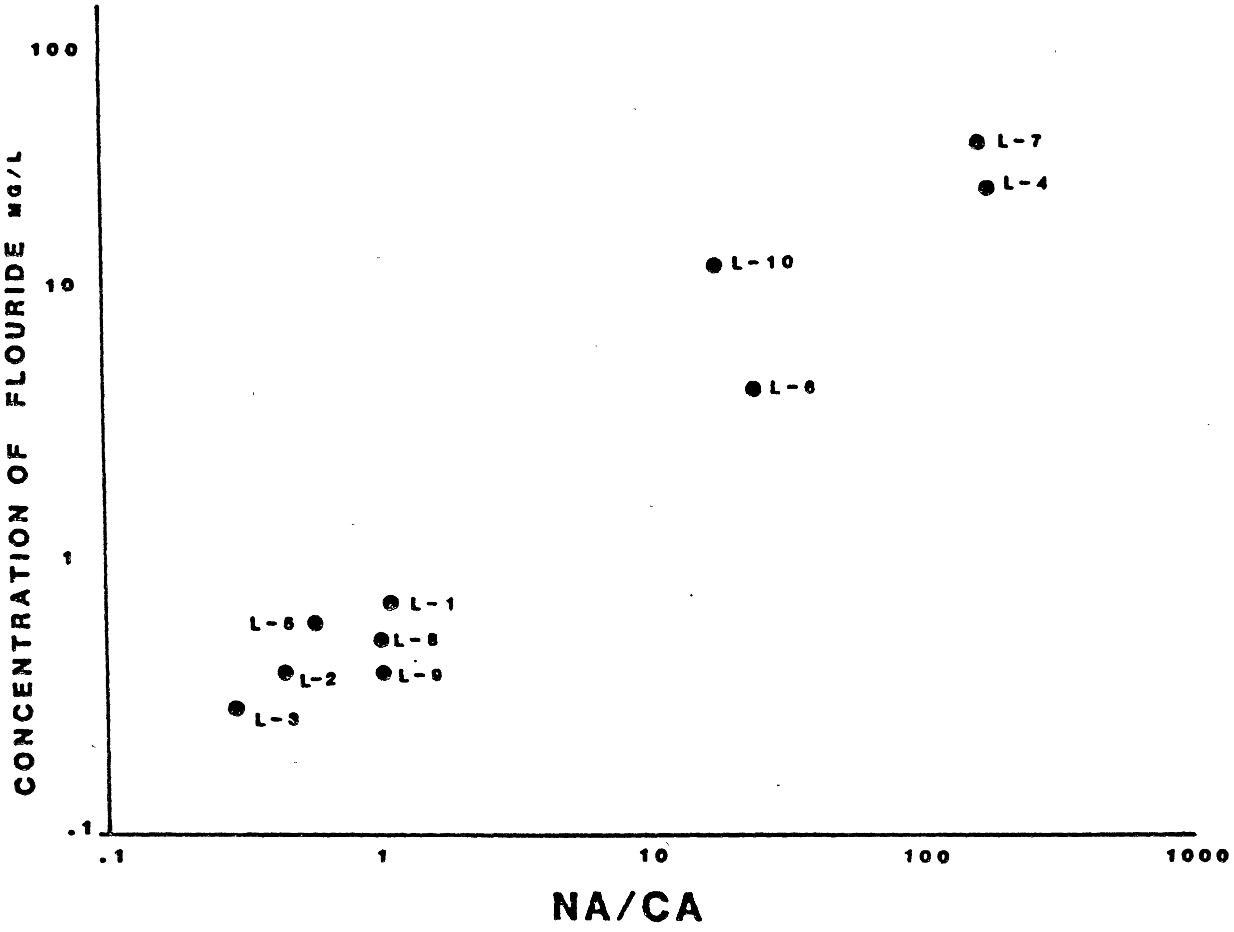


Figure 13. Sodium-calcium Ratio Relative to Fluoride

fluoride at a pH of 7.

Romo (1954) investigating the replacement of phosphate by fluoride on kaolinite by infrared spectroscopy and x-ray diffractometry concluded that fluoride displaced the lattice hydroxyls from the kaolinite.

Romo and Roy (1956) discuss, but do not resolve, the problem of the two types of hydroxyl groups: those on the outer edges of the octahedral layers, and those inside the lattice that are less accessible.

Bower and Hatcher (1967) studied the reactions of low concentrations of fluoride with soils and minerals, with the aim of removing excess fluoride from waters by adsorption on soils. They found that goethite, bentonite and vermiculite adsorbed only traces of fluoride, whereas gibbsite, kaolinite and halloysite adsorbed fluoride in a manner predictable by the Langmuir isotherm equation. They also found that alkali soils had low fluoride adsorption capacities.

Larsen and Widdowson (1971) showed experimentally that pH had a major effect in soil fluoride adsorption. They found adsorption to be greatest at pH 6, and decreased rapidly on either side. At pH's of 4 and 7.5 very little adsorption occurs.

Perrott et al (1976) again using strong fluoride solutions found that amorphous clay minerals such as allophane adsorbed much more fluoride than did the crystalline varieties, based on the amount of hydroxyl ions released.

Omueti and Jones (1977) found that the adsorption of fluoride by soils followed the Langmuir Isotherm below 20 mg/l F-, although deviations from this occurred at concentrations above this. They also found that on liming the soil to above pH 7 caused a dramatic reduction of F- adsorbed by the soil.

A reconnaissance study of the water resources of Comanche County was carried out by Stone (1981) who briefly described the availability and quality of water in the area and discussed the geology and potential yields of aquifers. He surveyed the various sources of potable water for the Comanche county area of southwestern Oklahoma not served by the Lawton surface water distribution system and from the data available he found that all ground water was high in TDS, that the alluvial ground water was high in nitrate and the Post Oak water high in fluoride. The fluoride content of the Post Oak water varied over the aquifer, so he suggested that a further examination of it may find local areas with acceptably low fluoride. It was implied in the report that the Arbuckle was recharged via the Post Oak, thus explaining the high fluoride content of the Arbuckle, that is from 5-17 mg/l F^-. He suggested a more intensive investigation of the fluoride distribution and its geochemistry. He also suggested that a study of the fertilizer practices may possibly suggest ways to minimize the nitrate pollution of the ground water.

Green and Al-Shaieb (1981) in an effort to find the source of the high fluoride ground water in Comanche county analyzed a variety of rocks in the area and confirmed that the fluoride occurs in the Post Oak conglomerates and sandstones. They proposed that the fluoride from the weathered riebeckite containing granites was adsorbed by clay minerals and released to bicarbonate ground waters at a later time by exchange with hydroxyl ions produced by the dissolution of calcite and feldspars. Further concentration increases was postulated to be the result of membrane effects caused by the intertonguing shale. The analytical data from the rocks showed that fluoride increased in a general way from the Wichitas towards the south, namely from 138 to 5622 ppm F^-.

Present Study.

Many investigations (Larsen & Widdowson, 1971 and Omueti & Jones, 1977) have shown the fluoride absorption on kaolinite and amorphous clays is extremely pH dependent. If the pH is above or below an approximate pH range of 5-7 very little absorption takes place (Figure 15). It is suggested, therefore, that the release is strictly a desorption phenomenon and that fluoride concentrations increase with pH, as a consequence of calcite dissolution. In support of this hypothesis several lines of evidence are presented.

Within the geochemical transition zone pH increases proportionally to fluoride concentrations (Figure, 16). Results from WATEQ program indicate that calcite dissolution is probable. Therefore, the mechanism that

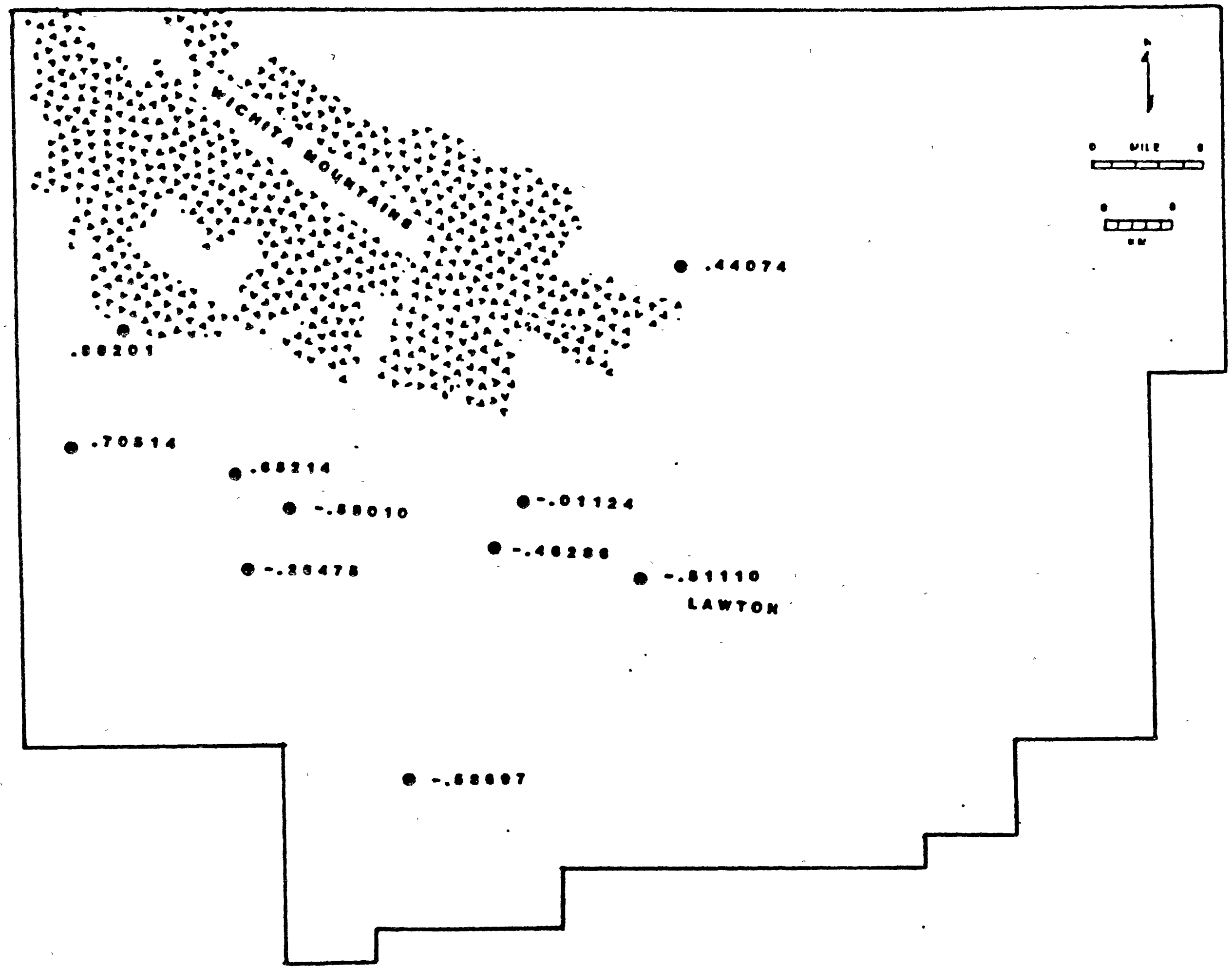


Figure 14. Saturation Index of calcite (negative values undersaturated with respect to calcium)

ultimately raises the pH is closely associated with high fluoride values.

The dissolution of carbonate cement produces bicarbonate ions, therefore where calcium carbonate is dissolving there should be and is, a large concentration of bicarbonate (Figure, 17).

High levels of fluoride are associated with high concentrations of sodium and low levels of calcium. Conversely, high levels of calcium occur in waters with low levels of sodium and fluoride (Figure, 13). This relationship is dependent upon the availability of clay in the area, with which cation-exchange reactions can occur. This relationship is not tied directly to high fluoride concentrations. However, it is a good indication that clay is present to host the desorption reactions.

The total dissolved solids content increases with fluoride Table 2, and further suggest that large amounts of clay are present.

Within the transition zone there are channel deposits of coarse sand in which there is little clay. Without the clays cation-exchange and desorption reactions will not occur and very little fluoride will be released to the water. Therefore, this transition zone is bisected by areas from which potable water could be obtained.

CHAPTER IX

DIGITAL SOLUTE-TRANSPORT MODEL OF THE POST OAK AQUIFER

The following discussion will focus on the theoretical development of the model, the method employed for calculating the amount of nitrogen introduced to the aquifer and the solute-transport simulations of future nitrogen movement. A more detailed description of the flow hydraulics is developed in Appendix 1.

Theoretical Development

For this project, a modified two-dimensional areal solute-transport model originally developed and documented by Konikow and Bredehoeft (1978) was used. Modifications by Kent et. al. (1985) include an option to solve the groundwater flow equation using the Strongly Implicit Procedure (SIP), rather than the Alternating-Direction Implicit Procedure (ADIP). For this study SIP was utilized, which converges in about half the iterations as the ADIP procedure and therefore, saves considerably on computer time.

Konikow and Bredehoeft (1978) in the following discussion outline the capabilities, limitations and assumptions inherent within their model.

The model calculates transient changes in the

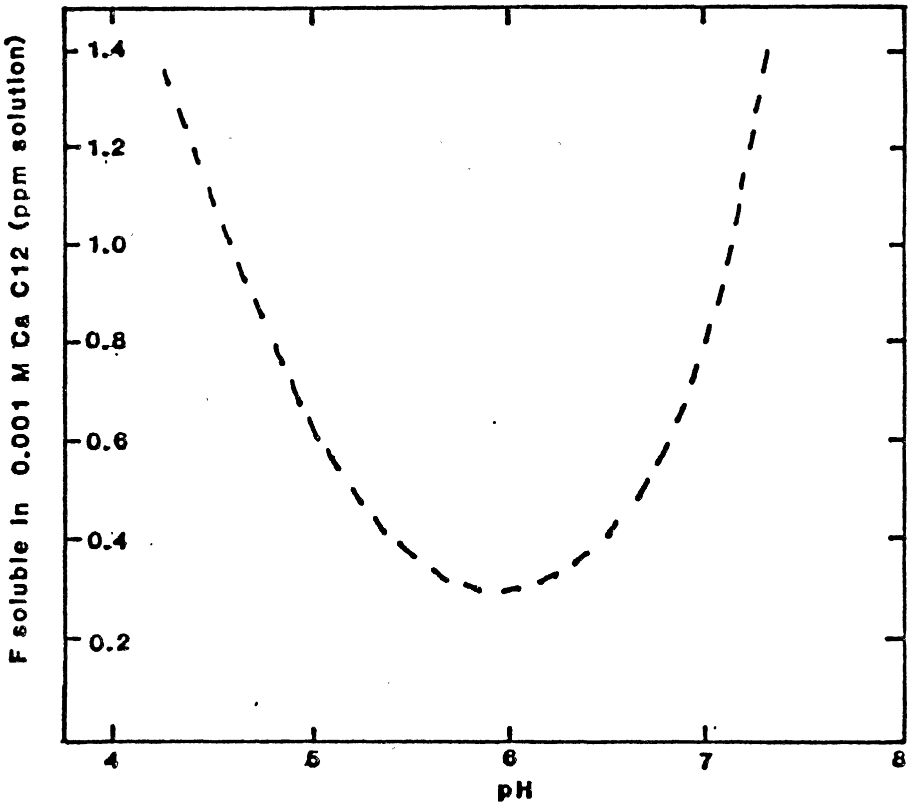


Figure 15. The Relationship between Soil pH and Soil Fluoride. (After Larsen and Widdowson, 1971)

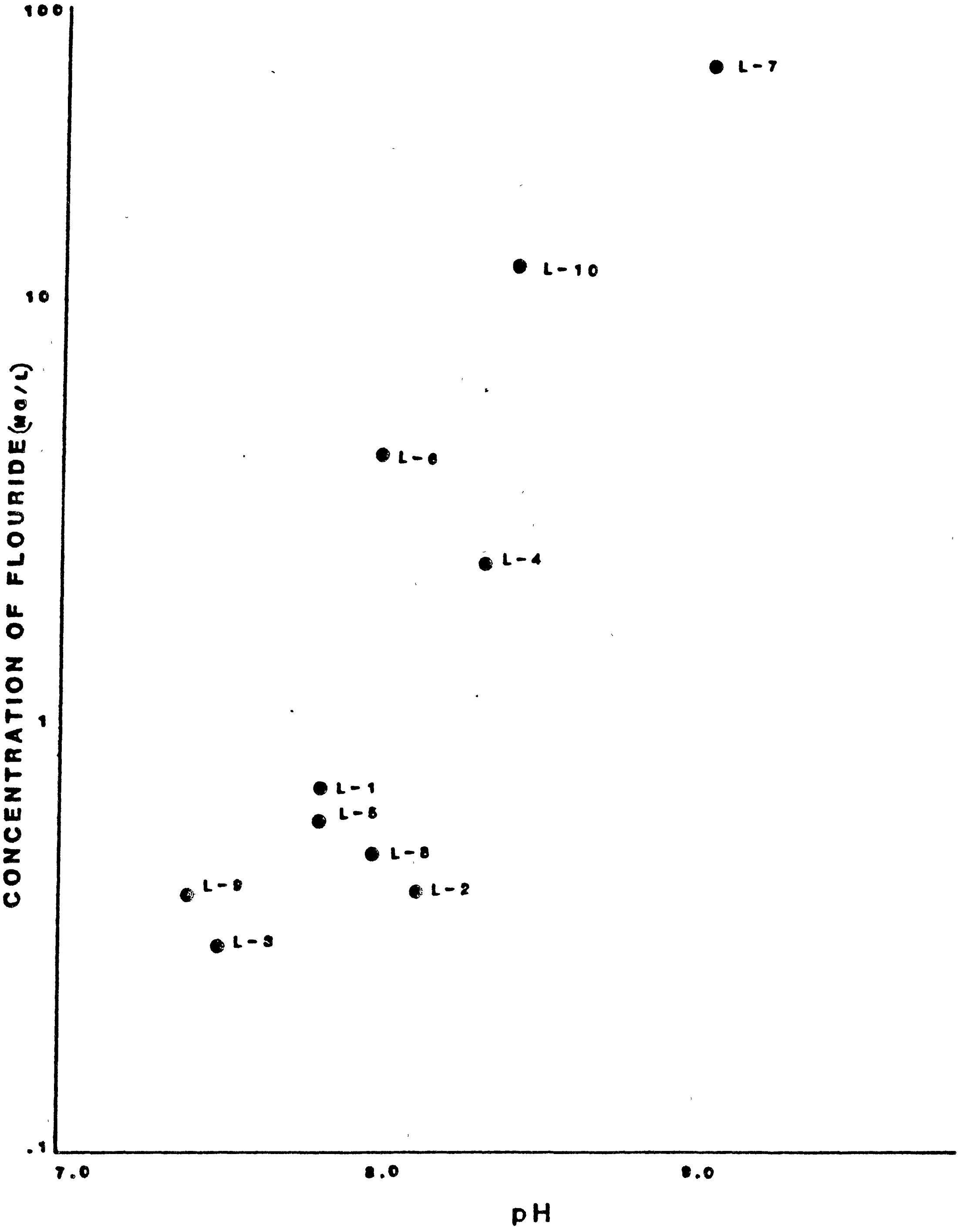


Figure 16. The Relationship between Fluoride Concentrations and pH

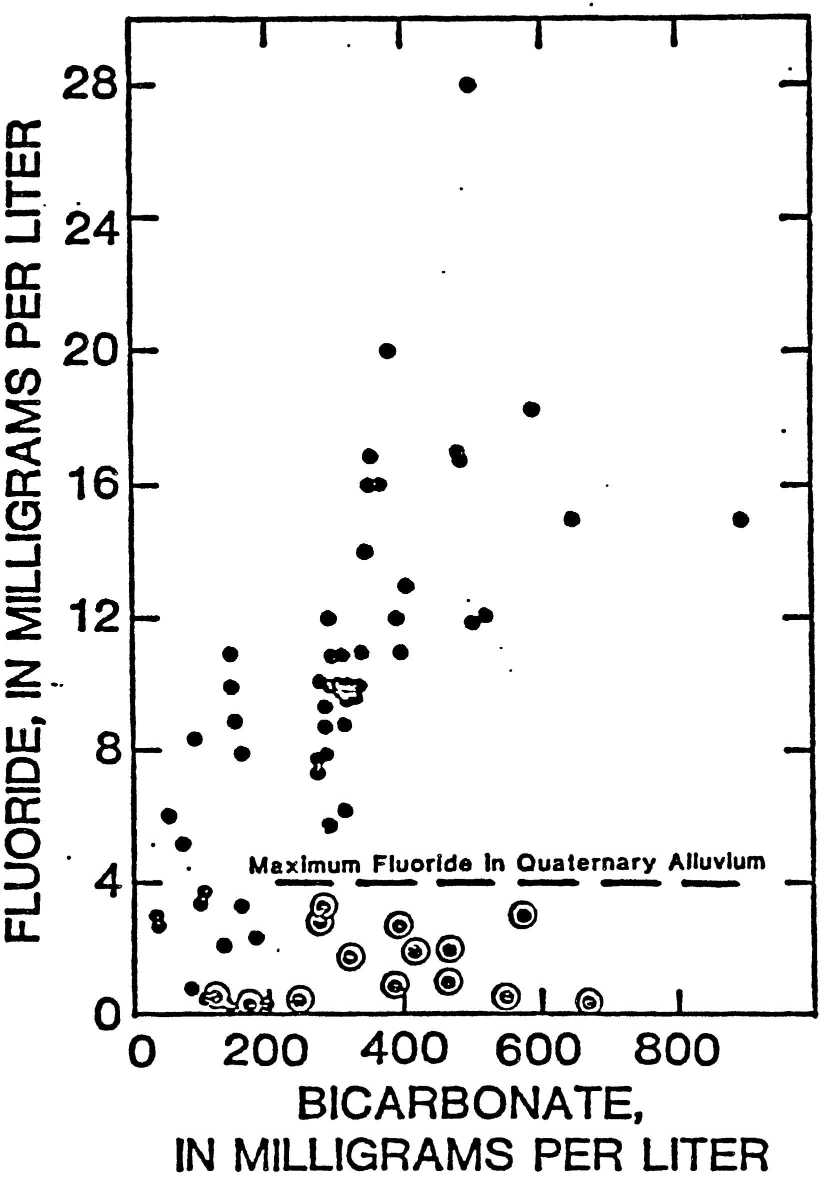


Figure 17. Relation of fluoride and bicarbinate in ground water drawn from the Post Oak and Arbuckle aquifers (solid dots) and from alluvium (circled dots). (From Green and Al-Shaieb, 1978)

concentration of a nonreactive solute in flowing ground water. The computer program solves two simultaneous partial differential equations. One equation is the ground-water flow equation, which describes the head distribution of the aquifer. The second is the solute-transport equation, which describes the chemical concentration of the system. By coupling the flow equation with the solute-transport equation, the model can be applied to both steady-state and transient flow problems.

This simulation model will compute the concentration of a dissolved chemical species in an aquifer at any specified place and time. The four factors that will affect the chemical concentration within a dynamic ground-water system are; (1) convective transport, in which dissolved chemicals are moving with the flowing ground water; (2) hydrodynamic dispersion, in which molecular and ionic diffusion enable particles to diverge from the dominant flow direction; (3) fluid sources, where water of differing compositions are mixed; (4) reactions, in which dissolved chemical species may be added or removed from the system. This particular model assumes that no reactions occur affecting the concentration and that gradients of fluid density, viscosity, and temperature do not affect the velocity distribution. The solute-transport model is contingent upon the following assumptions.

(1) Darcy's law is valid and hydraulic-head gradient are the only significant driving mechanism for fluid and solute flow.

(2) The porosity and hydraulic conductivity of the aquifer are constant with time, and porosity is uniform in space.

(3) Gradients of fluid density, viscosity, and temperature do not affect the velocity distribution.

(4) No chemical reactions occur that affect the concentrations of the solute, the fluid properties, or the aquifer properties.

(5) Ionic and molecular diffusion are negligible contributers to the total dispersive flux.

(6) Vertical variations in head and concentration are negligible.

(7) The aquifer is homogeneous and isotropic with respect to the coefficients of longitudinal and transverse dispersivity.

The accuracy with which a natural aquifer system can be simulated depends in large part on how well these assumptions are met. Most aquifer systems are much too complex for such simplifications to be valid. However, if the assumptions are met within acceptable limits, then the simulation can be useful if interpreted carefully.

Description of the Model

Before constructing a digital solute-transport model it is important to clearly define what questions need to be answered. These questions will determine the grid design, boundary conditions, and time steps that are initally used.

The Post Oak aquifer presently supplies water to local farming communities and to the Comanche County rural water program. Nitrogen in the Post Oak is largely derived from the application of nitrogen based fertilizer by farmers. Because it is difficult to delineate descrete plumes from non-point sources of contamination, the model will simply predict nitrogen concentrations if application rates and areal distribution are **kept constant.** From the standpoint of planning future utilization of the Post Oak aquifer, the most important questions about these contamination problems are:

(1) What are the geological and hydrologic conditions that have led to the contamination?

(2) What will the future concentration of nitrogen be?

(3) Is the contamination affected by pumping centers, for example, Lawton or Indiahoma?

(4) What actions may be taken to reduce the present contamination problem?

(5) How should local water supplies be developed to minimize health risk?

Conceptual Model

A digital solute-transport model is a mathematical representation of an aquifer system. It is constructed by (1) quantifying the physical and chemical characteristics of the system, and (2) translating these characteristics into a form that can be manipulated by a computer. Because of the complexity of natural aquifer systems, digital models must be constructed from idealized and simplified representations of the actual systems that are called conceptual models. Figure 3 shows schematically the conceptual model used to construct the digital model of the Post Oak Aquifer.

Matrix Design

To determine the optimum scale several factors must be considered. First, the scale must be large enough to incorporate regional hydrologic influences outside of the immediate area. Second, the scale must be small enough to give adequate definition to the boundaries of the contamination. Designing the model at a scale compatible with these conflicting needs will result in several limitations. Which will be discussed as they arise during model construction.

The model grid, time steps, and boundary conditions selected were designed to describe at a relatively large scale the movement and concentration fluctuations of nitrogen.

Several important factors were taken into consideration in determining the matrix design. The size of the area to be modeled in conjunction with the inherent limitations of accuracy and computer cost suggested that the most appropriate grid size should be 9 rows and 17 columns (Figure 18). Each grid block represents an area of 9 square miles. This scale will easily incorporate the available data from the field and literature.

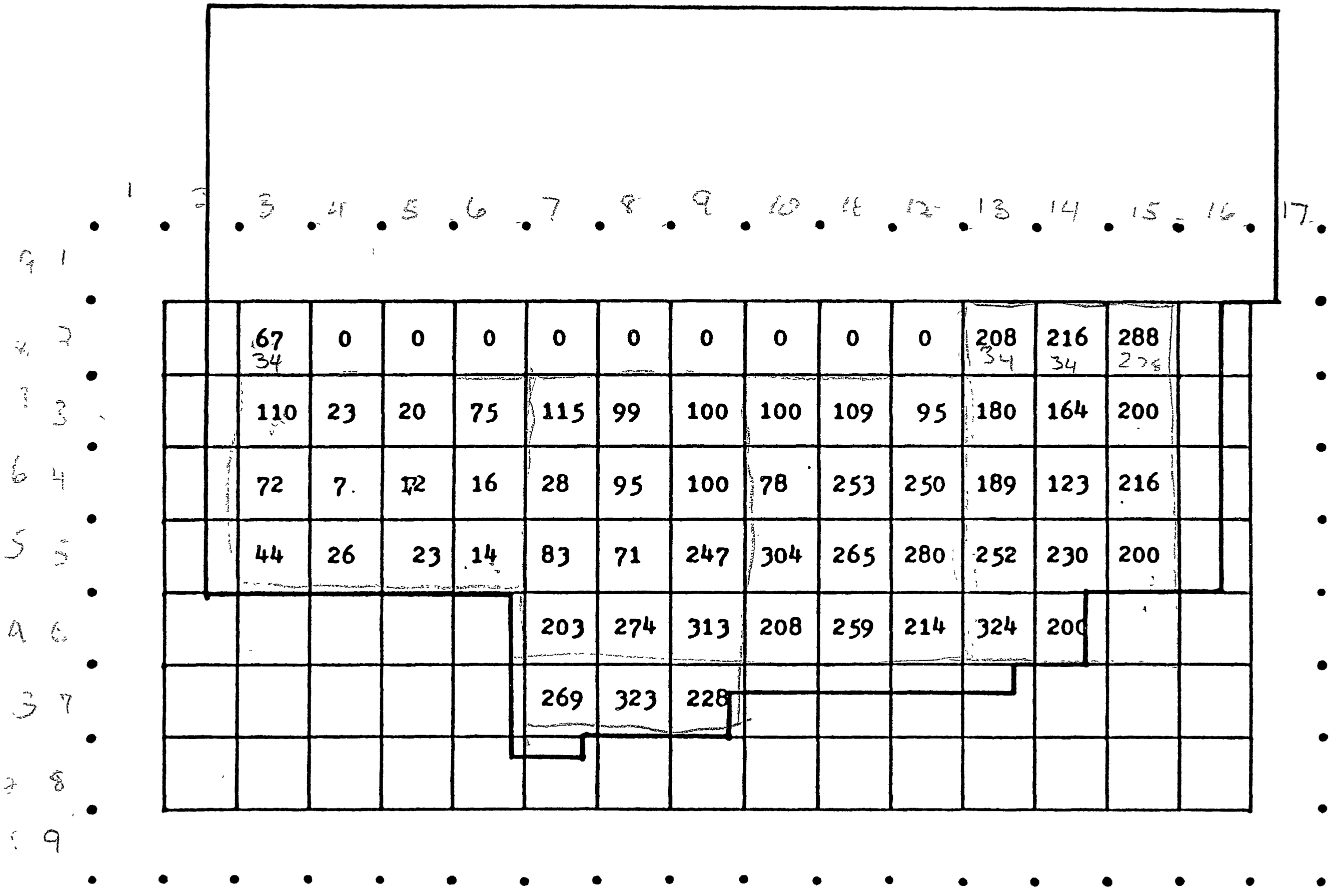
By convention, the point at the center of each block is called the node. The nodes are labeled in the same manner as an x-y coordinate system. Each input to the node ie. permeability, aquifer thickness etc., is considered to be the average value over the entire block. Similarly, each output value (hydraulic head, nitrogen concentration) is also an average for that block.

Model Boundaries

The area and boundaries of the aquifer were taken from geologic maps of the region and the Hydrologic Atlas for the Lawton Quadrangle (Havens, 1977).

The Post Oak aquifer is a massive conglomerate deposited during the Permian by ephemeral streams. It is unconfined and is underlain by the Arbuckle Formation composed of marine carbonates, capped by a leaky confining bed under artesian head in the southern half of the modeled area. However, for modeling purposes it was assumed that all vertical flow was downward, through the Post Oak and into the Arbuckle.

Southward, towards Cotton County the Post Oak is overlain by undifferentiated Hennessey Shale, Garber and Wellington Formations. No attempt was made to hydrogeologically separate them. Therefore, saturated thickness calculated for nodes containing all four formations will be considerably greater than if the Post



	67 34	0	0	0	0	0	0	0	0	0	208 34	216 34	288 278	
	110	23	20	75	115	99	100	100	109	95	180	164	200	
	72	7.	12	16	28	95	100	78	253	250	189	123	216	
	44	26	23	14	83	71	247	304	265	280	252	230	200	
					203	274	313	208	259	214	324	200		
					269	323	228							

Figure 18. Areal Distribution of Cultivated Land
1 unit = 17 square acres within nodal area

Oak had been modeled alone. This assumption is justified on the basis that the primary interest is in the hydrogeological properties of the rocks themselves and not arbitrary formational boundaries.

The Post Oak aquifer has one natural boundary (the Wichita Mountains in the north) that was used in the modeling process. This boundary was modeled as a no-flow boundary and correctly assumes that the aquifer begins at this border and that the hydraulic head may change with time. The remaining boundaries were also assumed to be no-flow boundaries to accomodate the change in head during low recharge and increased pumping. The upper boundary which coincides with land surface was modeled as a transient boundary. The lower boundary, which consist of the Arbuckle formation (marine carbonates) was modeled as a leakage boundary. This intrepretation was based upon isotopic ^{13}C data that which indicated that little, if any, of the water in the Post Oak is derived from marine limestones. This lower boundary was considered the base of the saturated thickness incorporated into the model.

Determination of Nitrogen Input

Comanche County is largely an agricultural area with very few cities and no large commerical feedlots. Therefore, the nitrogen accumulation in ground water will be controlled by three major processes. (1) Nitrogen input from the soil zone to the unsaturated zone. (2) Nitrogen movement and modification within the unsaturated zone and

(3) Nitrogen movement and modification within the saturated zone.

The quantity of nitrogen leached from the soil is dependent upon a large number of factors including crop type, antecedent cropping, fertilizer applications, soil type, soil environment and climate. The complex nature of the relationship between the factors controlling nitrogen losses from the soil zone together with the limited available field data make it next to impossible to construct a detailed regional model to describe leaching losses from the soil.

The major nitrogen input to the aquifer is derived from nitrogen-based fertilizer applied to agricultural land. Although urban waste and sewage effluents may be important local sources of pollution, their contribution of nitrogen contamination to the Post Oak were neglected.

Almost 25 percent of the modeled area is, at present, used as agricultural land. Non-agricultural land use is mainly urban development, mountains, and woodland.

Oklahoma Agricultural Statistics (Anon. 1982) provide an annual census of agricultural land use (Table 3) and was utilized in conjunction with the Oklahoma Fertilizer Statistics (Table 4) (Anon. 1984) to provide information about land use changes and to assess the regional nitrogen input to the aquifer. A limitation on the Oklahoma Agricultural Statistics is that they only provide a summary of how many total acres were under cultivation in the

TABLE III

AVERAGE CULTIVATED ACREAGE 1970 - 1980: COMANCHE COUNTY

100,100	Wheat
56,500	Hay
7,800	Cotton
3,700	Oats
2,200	Sorgum
600	Peanut
600	Barley
171,500	Total Acres

TABLE IV

YEARLY FERTILIZER APPLICATION: COMANCHE COUNTY

1970 - 71	5131
1971 - 72	4125
1972 - 73	5570
1973 - 74	7732
1974 - 75	5865
1975 - 76	10,469
1976 - 77	9975
1977 - 78	9026
1978 - 79	8487
1979 - 80	8260
1980 - 81	7777
1981 - 82	6112
1982 - 83	7091
1983 - 84	7870

Total = 103490

Avg = 7392 Tons/yr

county per year and do not provide data on actual crop-type distribution.

Similarly, the information obtained on fertilizer use from data provided by the Department of Agriculture, has limitations in that only yearly sum totals of fertilizer application are supplied and not the actual areal distribution, there may be variations in fertilizer applications between fields that may not always be explained in terms of soil type, rainfall and antecedent cropping history. The implication of this variation is that while the data may be suitable for the calculation of the regional nitrogen load, care should be exercised in assessing nitrogen inputs to the smaller nodal areas. Trends in fertilizer application over the last 15 years have remained fairly constant. In this study a number of assumptions were made involving probable leaching rates and nitrogen concentrations reaching the water table. The methodology adopted is described as follows:

(1) The average number of acres under cultivation in Comanche County during 1970-1980 was obtained from Oklahoma Agricultural Statistics (171,500 acres).

(2) Aerial photographs were used to map the areas of cultivation in the modeled area (Figure, 18).

(3) The average yearly fertilizer application for the entire county was then calculated using data obtained from the Department of Agriculture (7392 tons/yr).

(4) The percent of the cultivated area within the

county, incorporated into the modeled area was determined to be 85.67 percent.

(5) The percent of fertilizer applied in the modeled area vs. the entire county, was calculated by assuming even distribution of fertilizer over all cultivated acreage and multiplying the percent (85.67) of cultivated acreage in the modeled area by the average amount of fertilizer applied during 1970-1984. The result is the average amount of fertilizer applied within the modeled area (6333 tons/yr).

(6) The cultivated area within each nodal area determined by aerial photographs was converted to a percent of the total cultivated area within the model (Table, 5).

(7) By assuming the percent of the area under cultivation, within the model, is equal to the same percent of fertilizer applied within the modeled area, the load of fertilizer applied to each indivudal node could be calculated (Table, 5).

(8) Since not all of the fertilizer applied was nitrogen based, a conservative estimate of 50 percent of the applied fertilizer was assumed to be nitrogen as N. Therefore, the value obtained in step number 7 was divided in half (Table, 5).

(9) Payne (1981) estimated that between 40-60 percent

TABLE V

CALCULATIONS FOR DETERMINATION OF NITROGEN INPUT TO THE POST OAK

NODE	Unit Area Fertilized	Cultivated Area covered (percent)	Fertilizer Consumed (tons/yr)	50% N- (X.5)	Reacharge Mul. Factor	Load Reaching Water Table (Tons)	mg/l-N Injected into Aquifer
1	67	.008	51	25.5	.52	13.26	33.8
11	208	.025	158	79.0	.48	37.2	33.8
12	216	.026	165	82.5	.44	36.3	277.7
13	288	.035	222	111.0	.44	48.84	373.6
14	110	.013	82	41.0	.46	18.86	96.2
15	23	.003	19	9.5	.52	4.94	12.6
16	20	.002	13	6.5	.5	3.25	9.9
17	75	.009	57	28.5	.52	14.82	37.8
18	115	.014	89	44.5	.58	25.81	43.9
19	99	.012	76	38.0	.52	19.76	50.4
20	100	.012	76	38.0	.54	20.52	44.9
22	109	.013	82	41.0	.54	22.14	48.4
23	95	.011	70	35.0	.46	16.1	82.1
24	180	.022	139	69.5	.44	30.58	233.9
25	164	.02	127	63.5	.44	27.94	213.7
26	200	.024	152	76.0	.44	33.44	255.9
27	72	.009	57	28.5	.5	14.25	43.6
28	7	.0008	5	2.5	.44	1.1	8.4
29	12	.001	6	3.0	.46	1.38	7.0
30	16	.002	13	6.5	.5	3.25	9.9
31	28	.003	19	9.5	.56	5.32	10.2
32	95	.011	70	35.0	.5	17.5	53.5
33	100	.012	76	38.0	.52	19.76	50.4
34	78	.009	57	28.5	.5	14.25	43.6
35	253	.03	190	95.0	.52	49.4	126.0
36	250	.029	184	92.0	44	40.48	309.7
37	189	.022	139	69.5	.44	30.58	233.9
38	123	.014	89	44.5	.42	18.69	286.2
39	216	.025	158	79.0	.42	33.18	508.0
40	44	.005	32	16.0	.44	7.04	53.9
41	26	.003	19	9.5	.46	4.37	22.3
42	23	.003	19	9.5	.46	4.37	22.3
43	14	.002	13	6.5	.5	3.25	9.9
44	83	.01	63	31.5	.46	14.49	73.9
45	71	.008	51	25.5	.48	12.24	46.8
46	247	.03	190	95.0	.42	39.90	611.0
47	304	.37	234	117.0	.44	51.96	393.9
48	265	.032	203	101.5	.44	44.66	341.7
49	280	.034	215	107.5	.44	47.3	361.9
50	252	.031	196	98.0	.44	43.12	329.9
51	230	.028	177	88.5	.44	38.94	297.9
54	324	.039	247	123.5	.42	51.87	794.3
55	203	.025	158	79.0	.42	33.18	508.1
56	274	.033	209	104.5	.44	45.98	351.8
57	313	.038	241	120.5	.46	55.43	282.8
58	208	.025	158	79.0	.44	34.76	266.0
59	259	.032	203	101.5	.44	44.66	341.5
60	214	.026	165	82.5	.42	34.65	530.6
63	303	.037	234	117.0	.44	51.48	196.9
64	269	.033	209	104.5	.44	45.98	175.8
65	323	.039	247	123.5	.46	56.81	289.8
66	228	.028	177	88.5	.42	37.17	569

of the applied nitrogen was leached to the water table. Assuming these figures are tied to recharge, which is indirectly related to grain size, Figure 19 was used to assign a recharge multiplication factor and determine what percent of the applied nitrogen actually would infiltrate to the water table (Table, 5).

(10) Finally, the number obtained in step 9 (tons) was converted to mg/l in order to input the data into the model (Table, 5). The calculation is given in equation 2.

$$\text{mg/l} = (\text{Load (tons)})/(.00027 * \text{number of days (365)} * \text{CFS (cubic/ft/sec recharge)}) \qquad (2)$$

After the concentration (mg/l) of nitrogen was calculated, 105 injection wells were incorporated into the model (LeMaster,1985). Movement and retention of nitrogen through the unsaturated zone was ignored. Thus, the input to the saturated zone was calculated as the sum component of nitrogen transmitted rapidly through the unsaturated zone via fissures.

There is much debate as to whether fissure flow or intergranular flow is the predominant mechanism of water and nitrogen movement in the unsaturated zone. In forecasting nitrogen concentrations for this model, the worst case situation has been considered and a fissure flow mechanism assumed. This assumption will minimize the retention time and storage capacity of the unsaturated zone, sometimes approaching 70 feet in the modeled area.

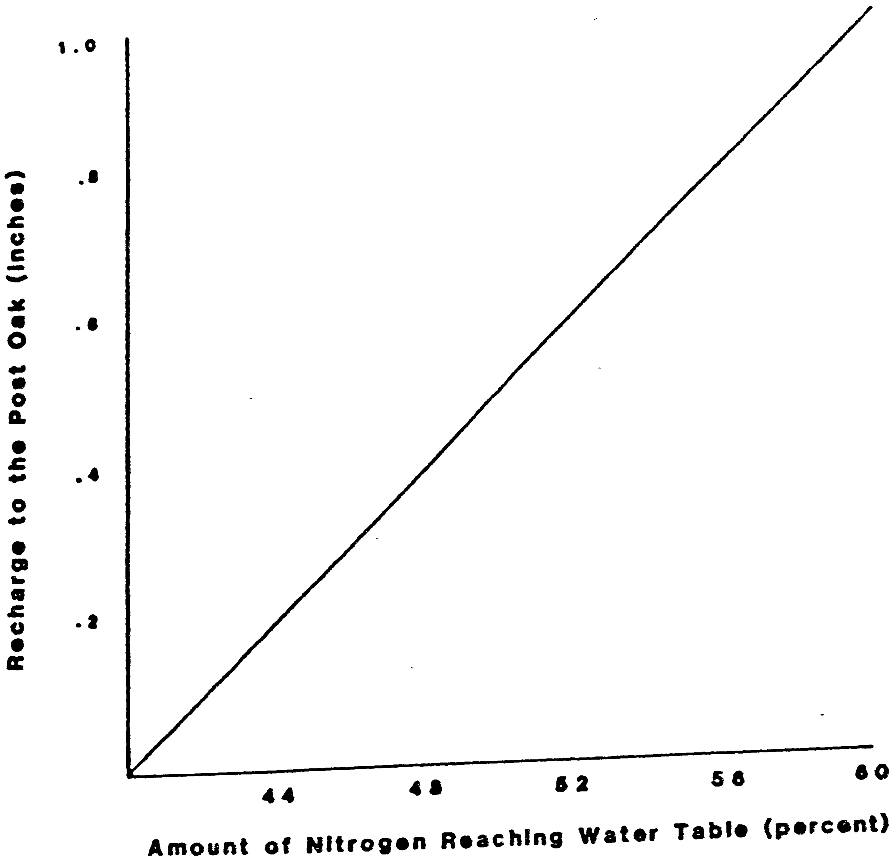


Figure 19. Relationship of Recharge to the Volume of Nitrogen Reaching the Water Table

Solute-Transport Calibration

Before a model can be used to estimate the future behavior of an aquifer system, the model's ability to reproduce historical behavior must be verified. Although the best available information is used in model construction, these parameters frequently have to be adjusted before the model accurately reproduces historical behavior. This process of adjusting parameters is termed "calibration". Calibrating a digital solute-transport model must be accomplished in two distinct steps. First, the ground-water flow portion of the model must be calibrated using historical pumpage and water levels Appendix 1. When this phase of calibration is complete, the solute-transport portion of the model may be calibrated using available historical water-quality data.

The exact procedures followed during model calibration are largely determined by the kinds of available historical data. Historical nitrogen concentrations may be of little help in determining the the true concentrations of nitrogen at the time the water samples were obtained because of possible improper well construction which enables nitrogen solutes to flow directly down the wells eliminating the normal filtration effect of the aquifer (Figure 20). Therefore, an alternate method for calibration was required to lessen the importance of historical water-quality data.

It is assumed within the solute-transport model that nitrogen mixes throughout the entire saturated thickness of the cell. Normally such a model would be ideal because of the diffuse nature of the nitrogen input to the aquifer. However, on account of the large variation in saturated thickness over the modeled area (15 feet - 2718 feet) this assumption created large dilution errors (Figs. 21-27) which were corrected by adjusting the mixing zone of nitrogen to approximately 100 feet below the water-table surface.

This was accomplished by converting the concentration (mg/l) of nitrogen within each node to milligrams of solute (Table, 6). A new concentration was then calculated assuming that the saturated thickness was only 100 feet (Table, 6). When the initial saturated thickness was less than 100 feet the value calculated by the model was taken directly from the output (Figs. 28-34).

The aim of the investigation was to simulate long-term trends of nitrogen concentrations in ground water and the model results were therefore considered to be satisfactory. Calculated trends for areas with a thin unsaturated zone, probably had better simulation results than otherwise obtained, on account of the large storage capacity of the unsaturated zone.

Historical records indicate that the natural background nitrogen concentrations are 0.2 mg/l NO3-N, and this value was assumed to be the initial background concentration throughout the grid matrix.

No attempt was made to measure the dispersion coefficient for nitrogen in the Post Oak aquifer. Values of this parameter were assumed fairly high (ratio of T-YY to T-

XX = 1.0) on account of the diffuse nature in which the nitrogen was injected into the aquifer (105 wells).

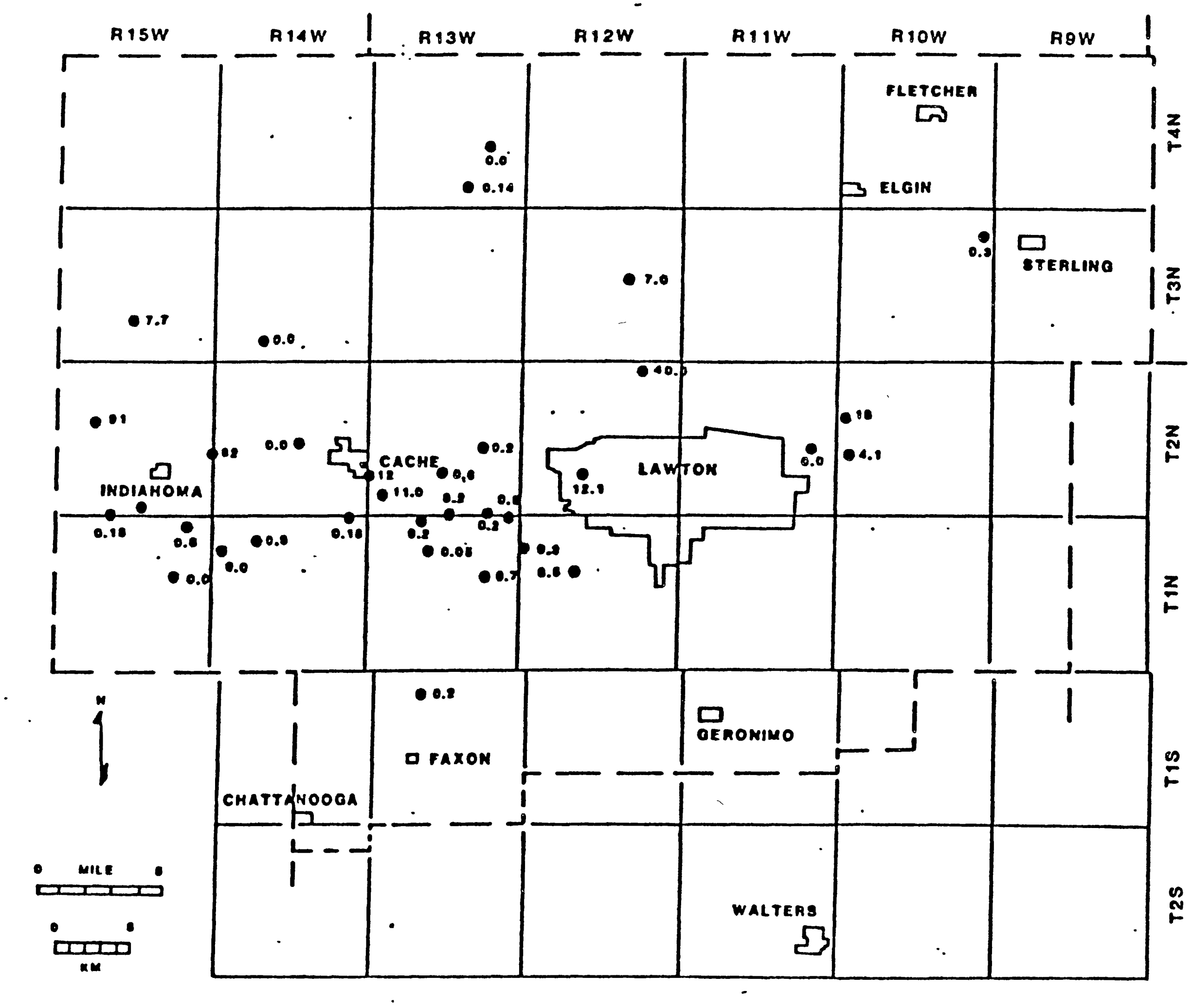


Figure 20. Areal Distribution of NO_3-N Concentrations 1971-1984

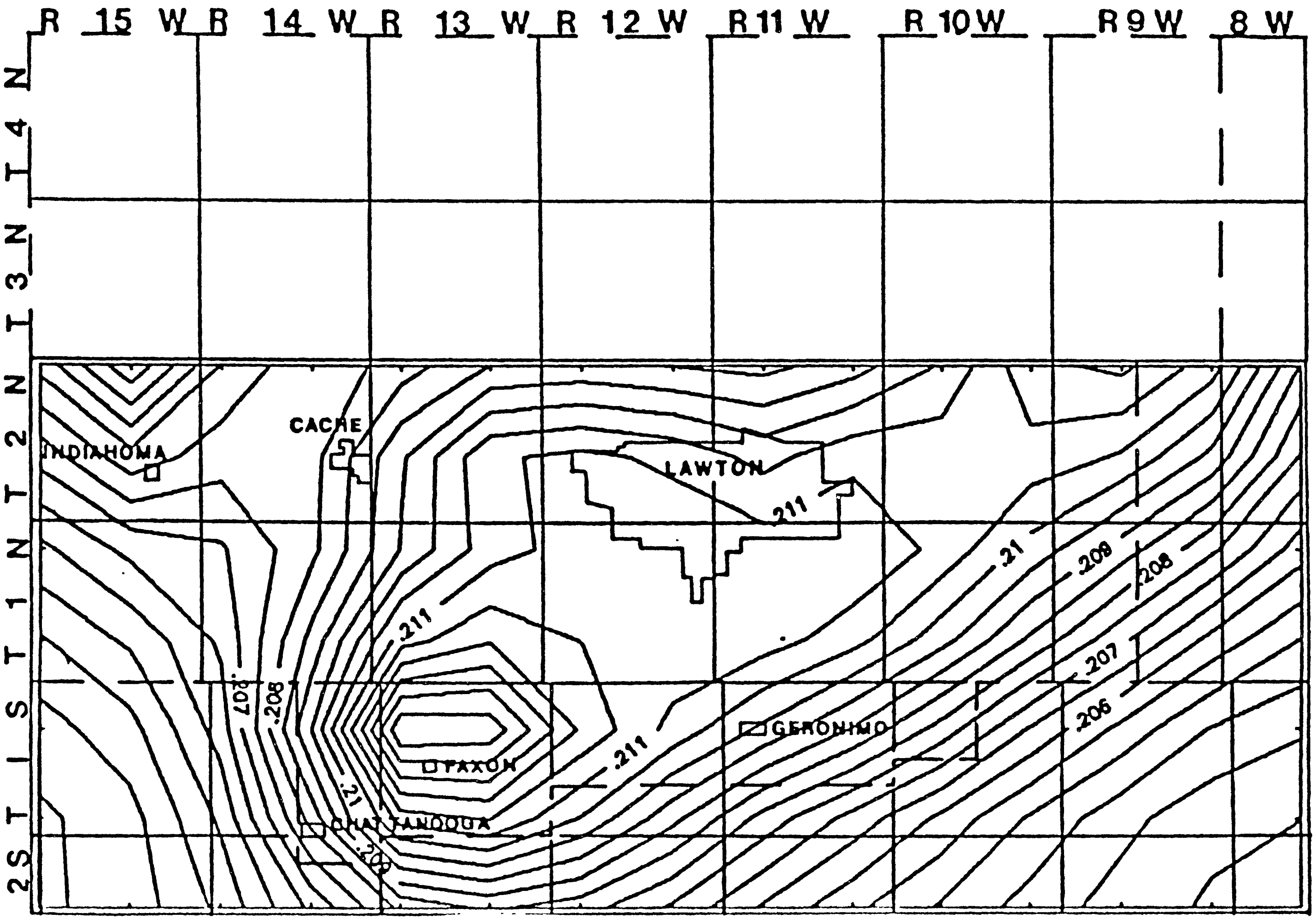


Figure 21. NO_3-N(mg/l): Pumping Period 1 (concentrations calculated using entire saturated thickness)

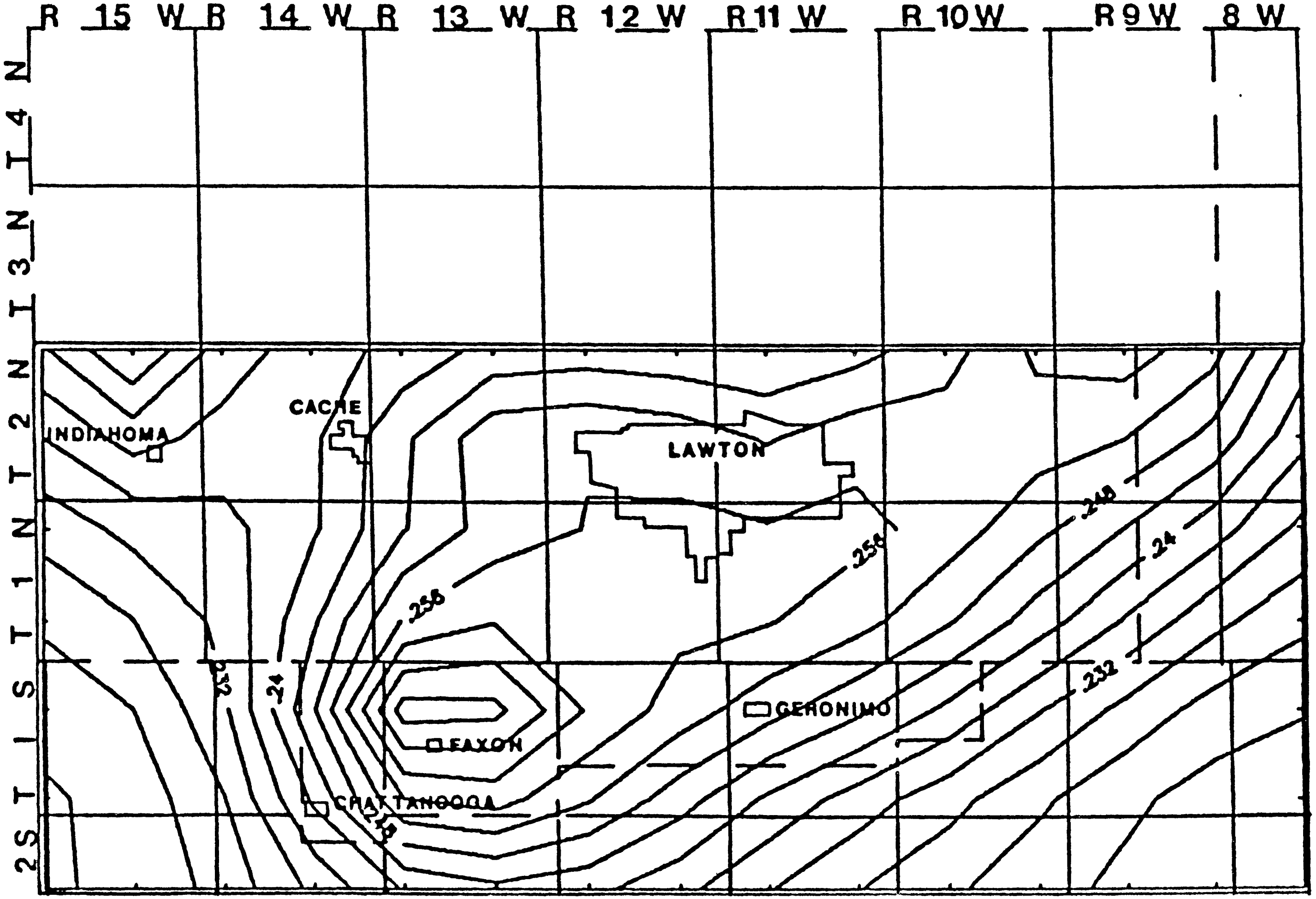


Figure 22. NO_3-N (mg/l): Pumping Period 5 (concentrations calculated using entire saturated thickenss)

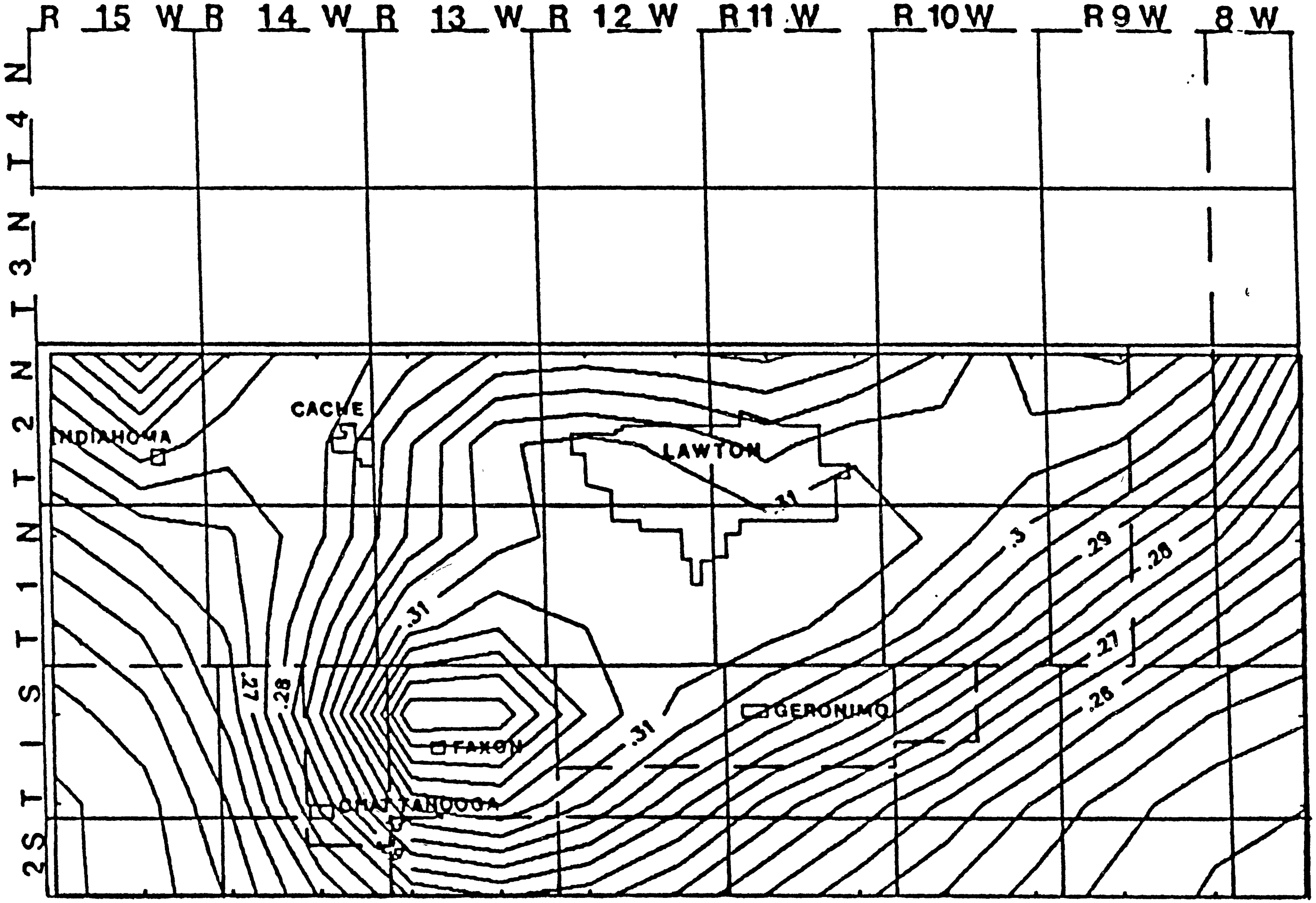


Figure 23. NO_3-N (mg/l): Pumping Period 10 (concentrations calculated using entire saturated thickness)

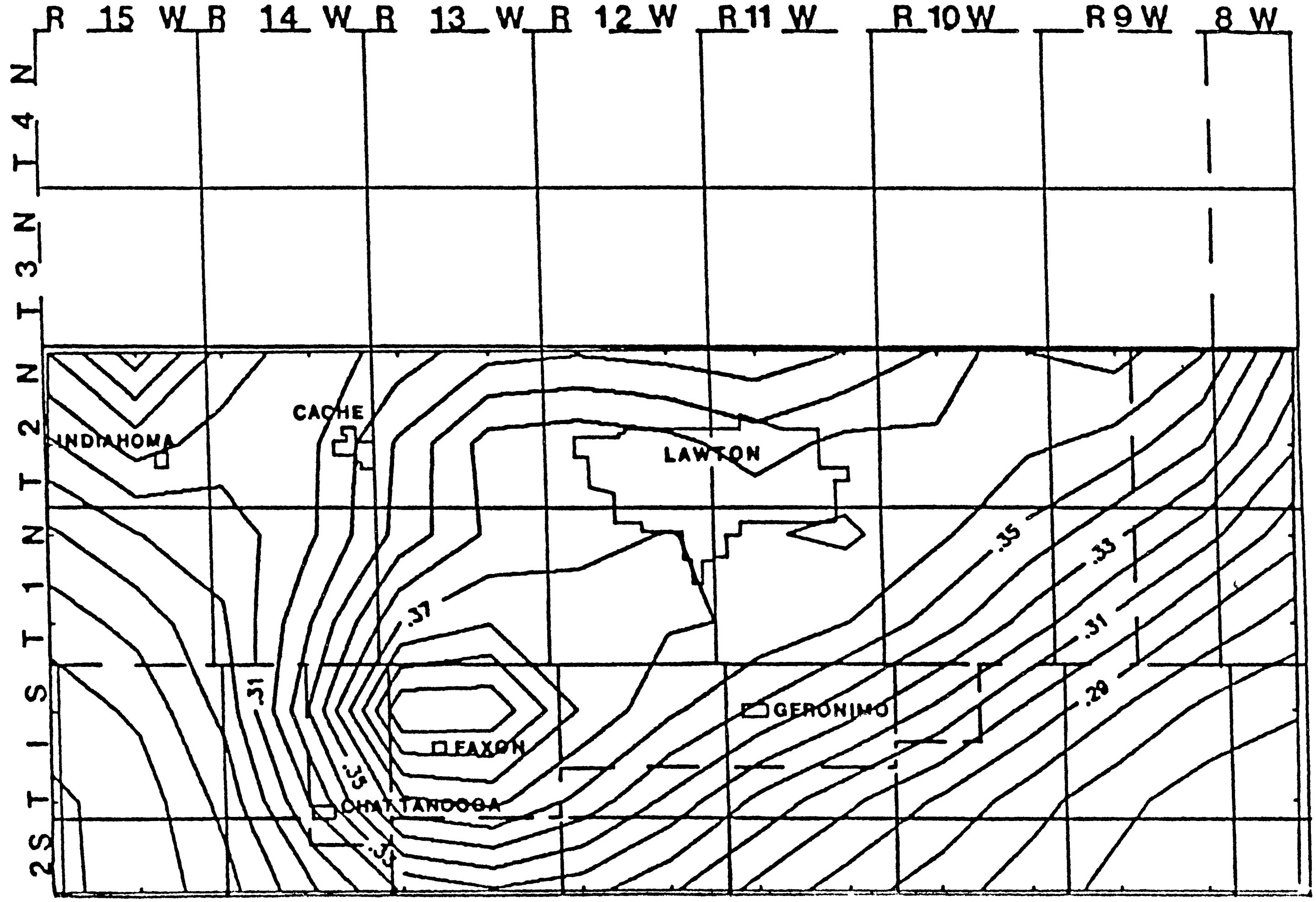


Figure 24. NO$_3$-N (mg/l): Pumping Period 15 (concentrations calculated using entire saturated thickness)

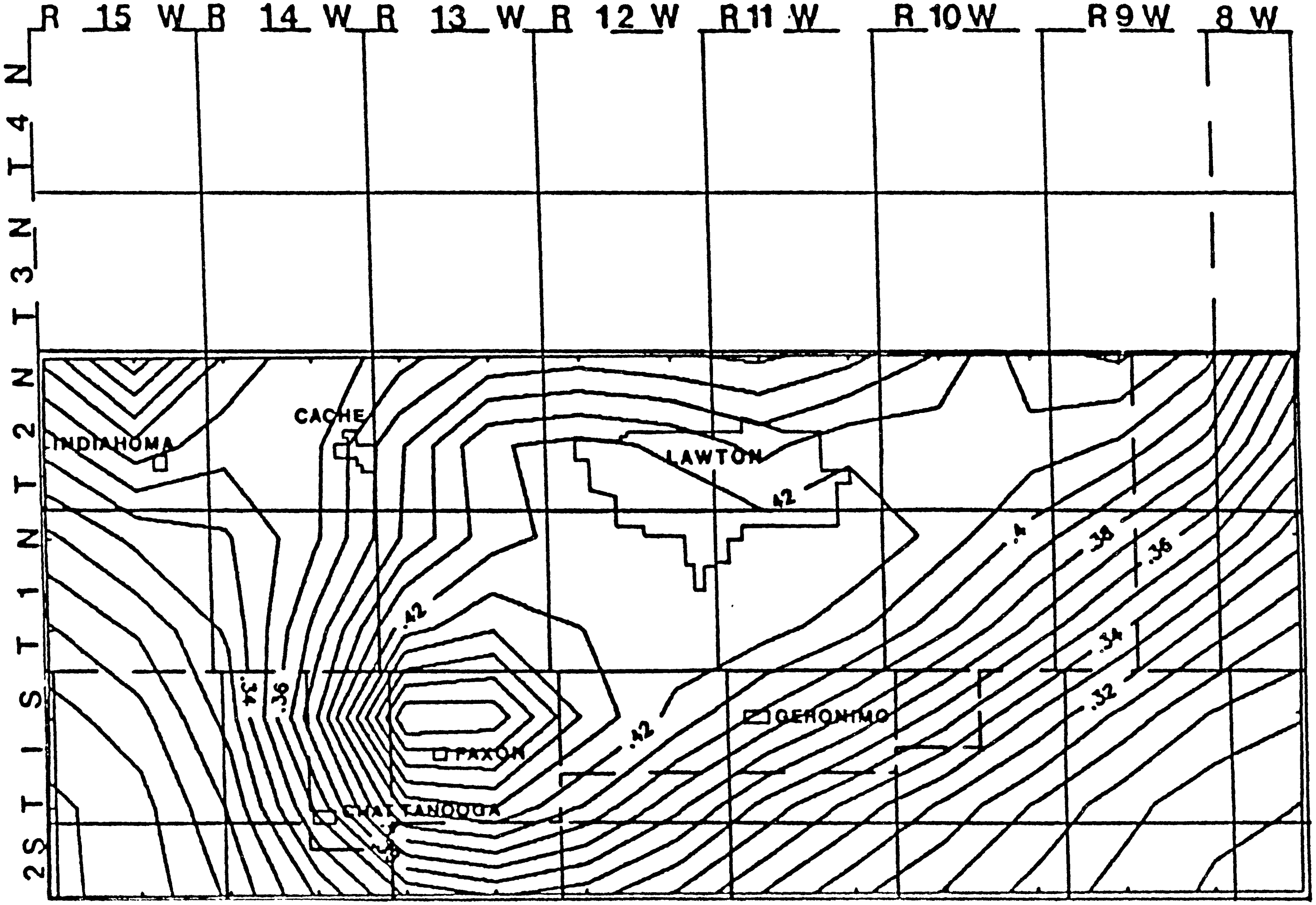


Figure 25. NO_3-N (mg/l): Pumping Period 20 (concentrations calculated using entire saturated thickness)

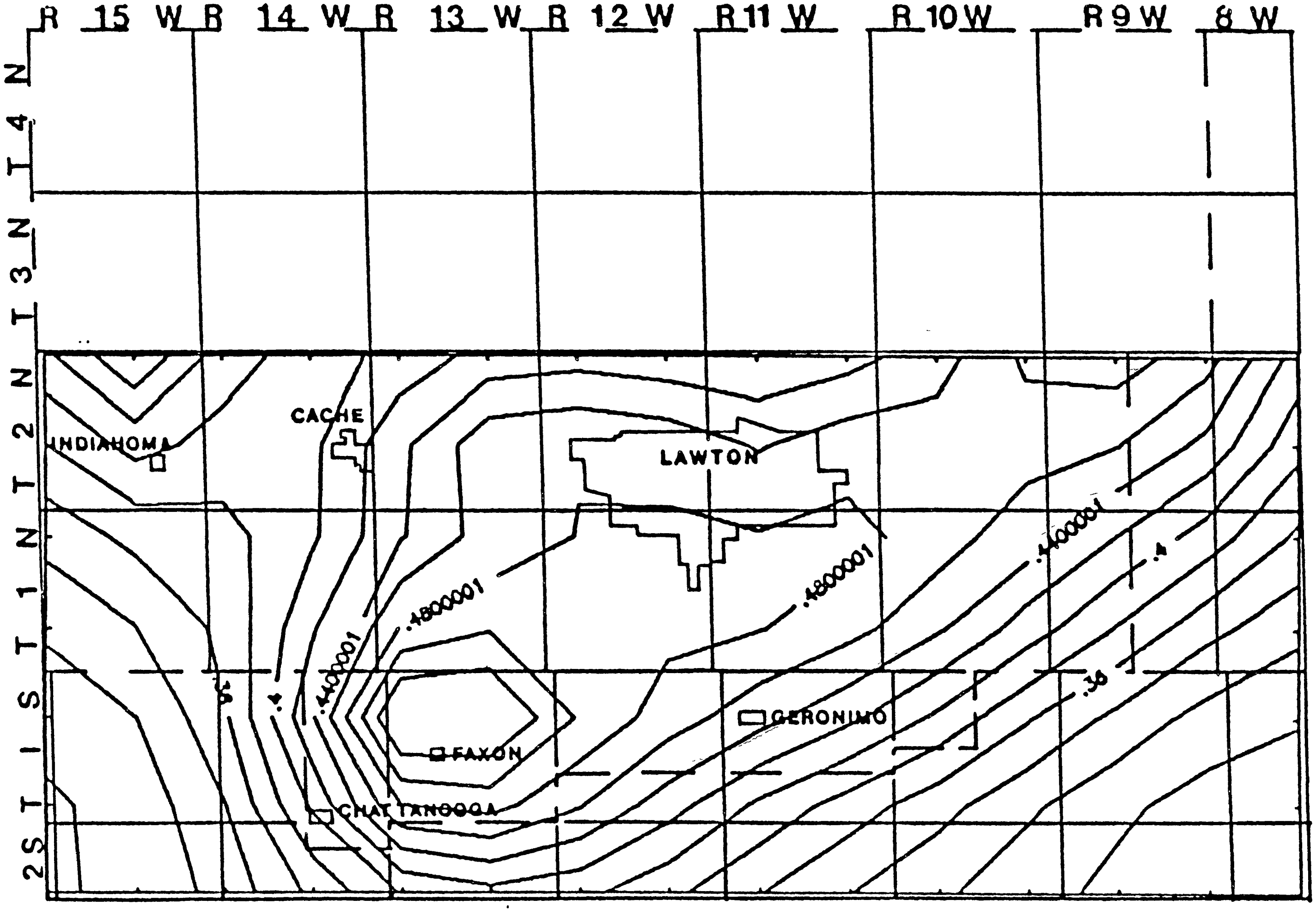


Figure 26. NO_3-N (mg/l): Pumping Period 25 (concentrations calculated using entire saturated thickness)

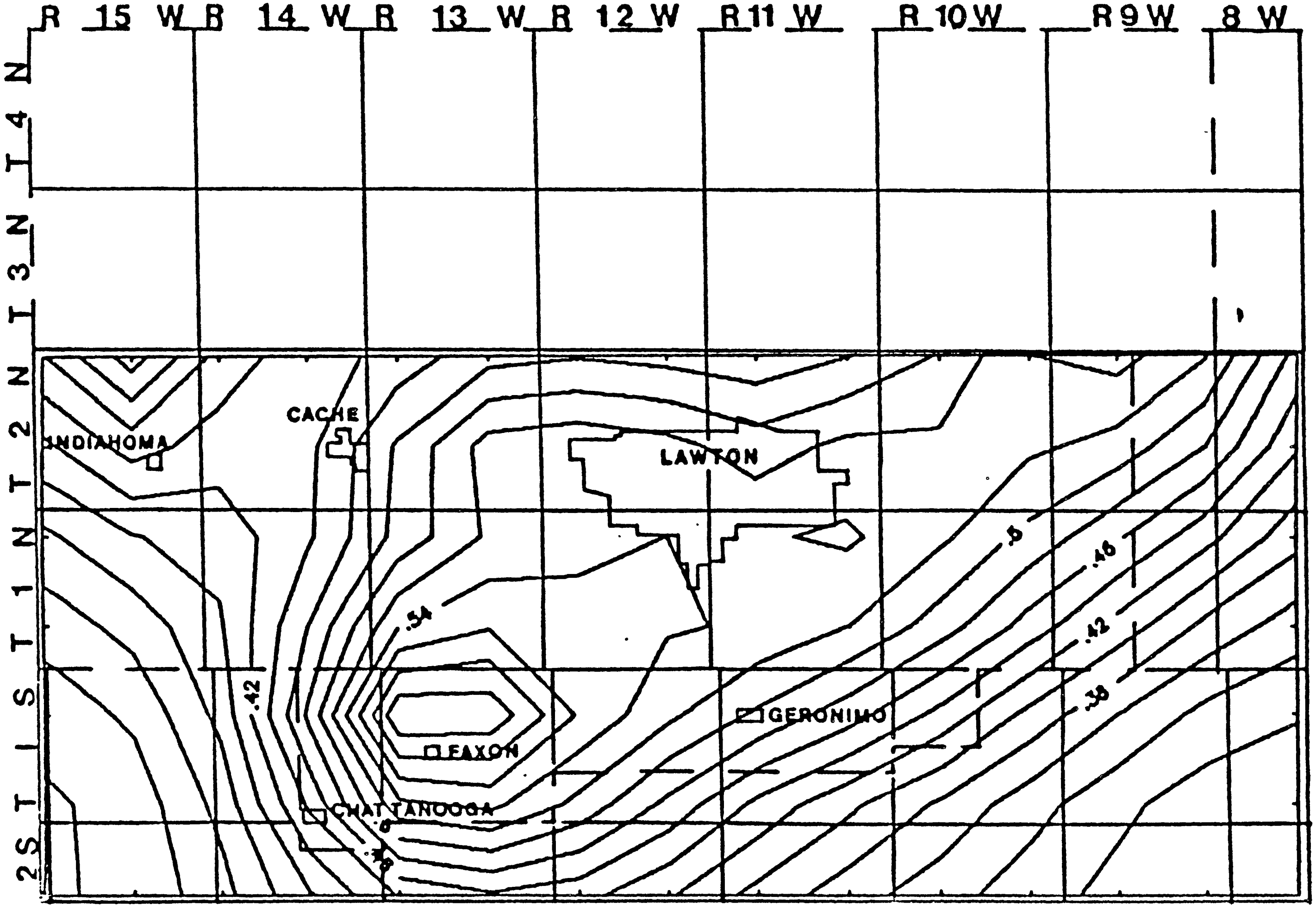


Figure 27. NO_3-N (mg/l): Pumping Period 30 (concentrations calculated using entire saturated thickness)

TABLE VI

EXAMPLES OF NITROGEN CONCENTRATIN (NO_3-N) CORRECTIONS TO REDUCE DILUTION ERRORS INHERENT WITHIN THE MODEL (TAKEN FROM TIME STEP 1).

Node	Vol. of Water per node X10^9 ft^3	Model Calculation of of Model Conc. (mg/l)	Milligrams of Solute per Model Volume	Vol. of Water Per Node/x10^{11} (adjusted to saturated thickness =100ft)	Adjusted Conc. mg/l Assuming (saturated thickness =100ft)
1	8.15	.2508	5.78	1.78	.3253
2	7.52	.1998	4.20	1.78	.2392
3	6.27	.1996	3.5	1.78	.1192
*4	3.13	.1995	----	----	.1995
*5	1.26	.1967	----	----	.1967
*6	1.26	.1967	----	----	.1967
*7	.95	.1965	----	----	.1965
*8	4.5	.1993	----	----	.1993
9	5.9	.1995	3.3	1.78	.1995
10	23.1	.1999	13.0	1.78	.7355

*No modifications to concentrations were required, saturated thickness was less than 100 ft.

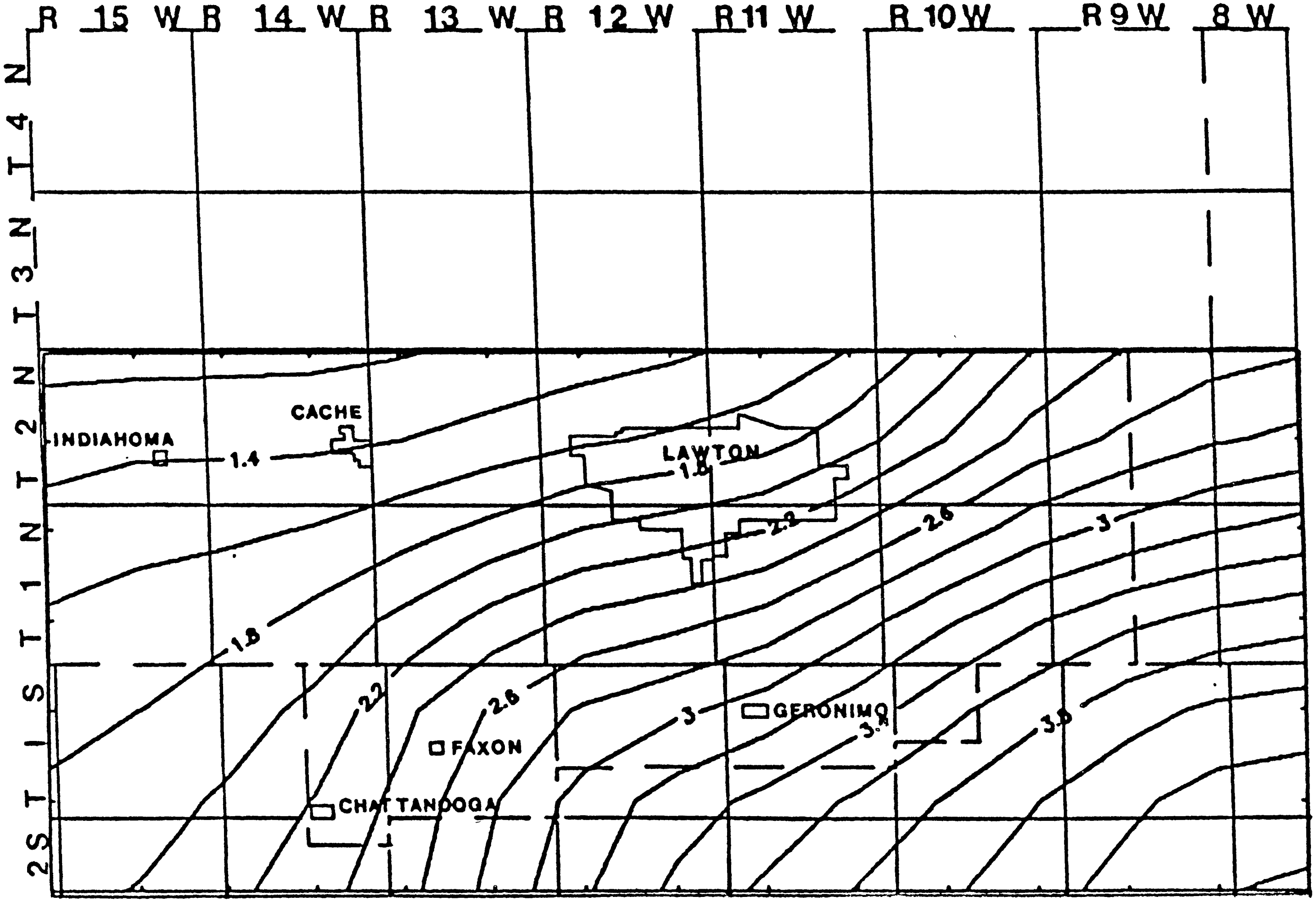


Figure 28. NO_3-N (mg/l): Pumping Period 1 (concentrations calculated using modified saturated thickness)

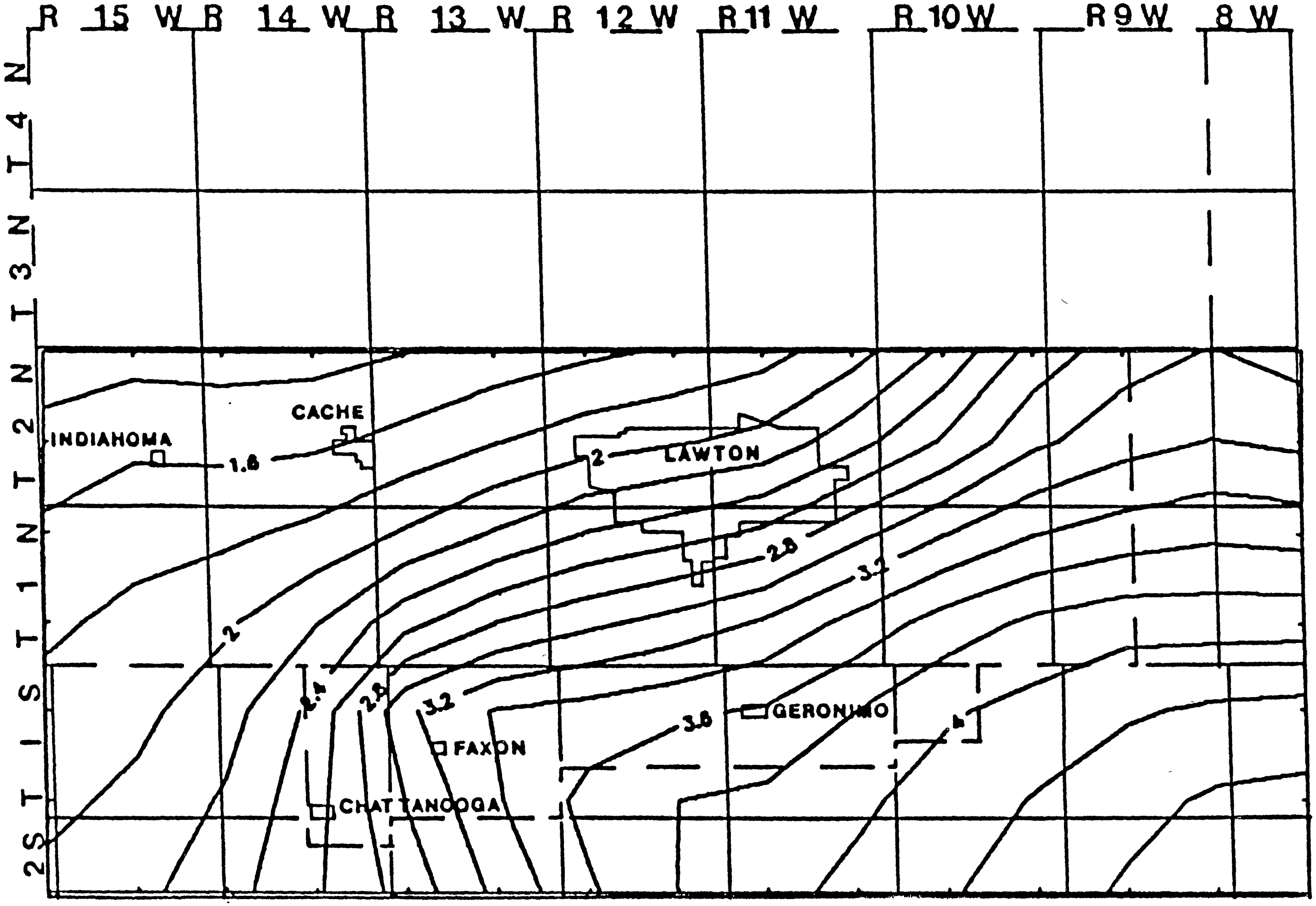


Figure 29. NO$_3$-N (mg/l): Pumping Period 5 (concentrations calculated using modified saturated thickness)

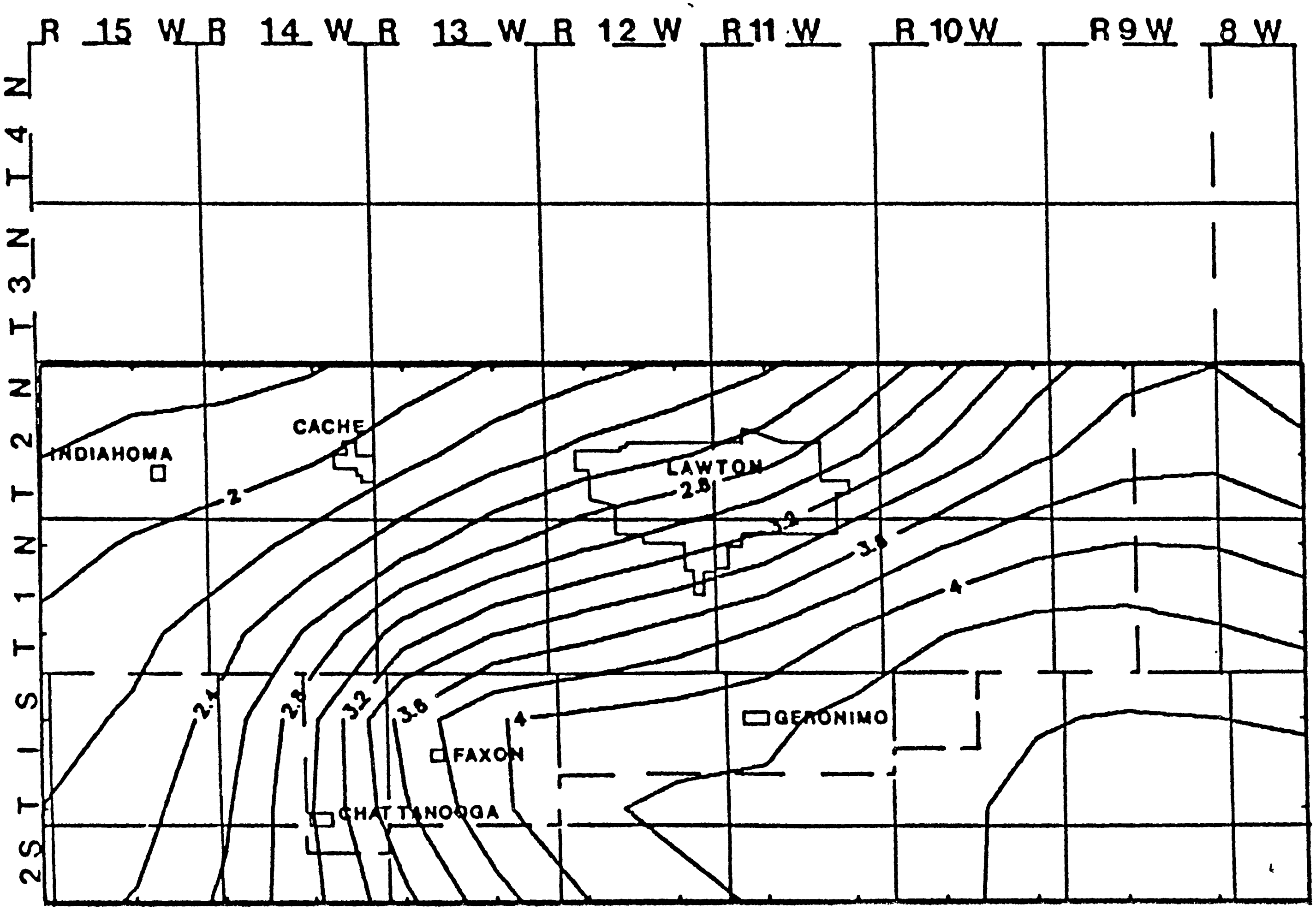


Figure 30. NO_3-N (mg/l): Pumping Period 10 (concentrations calculated using modified saturated thickness)

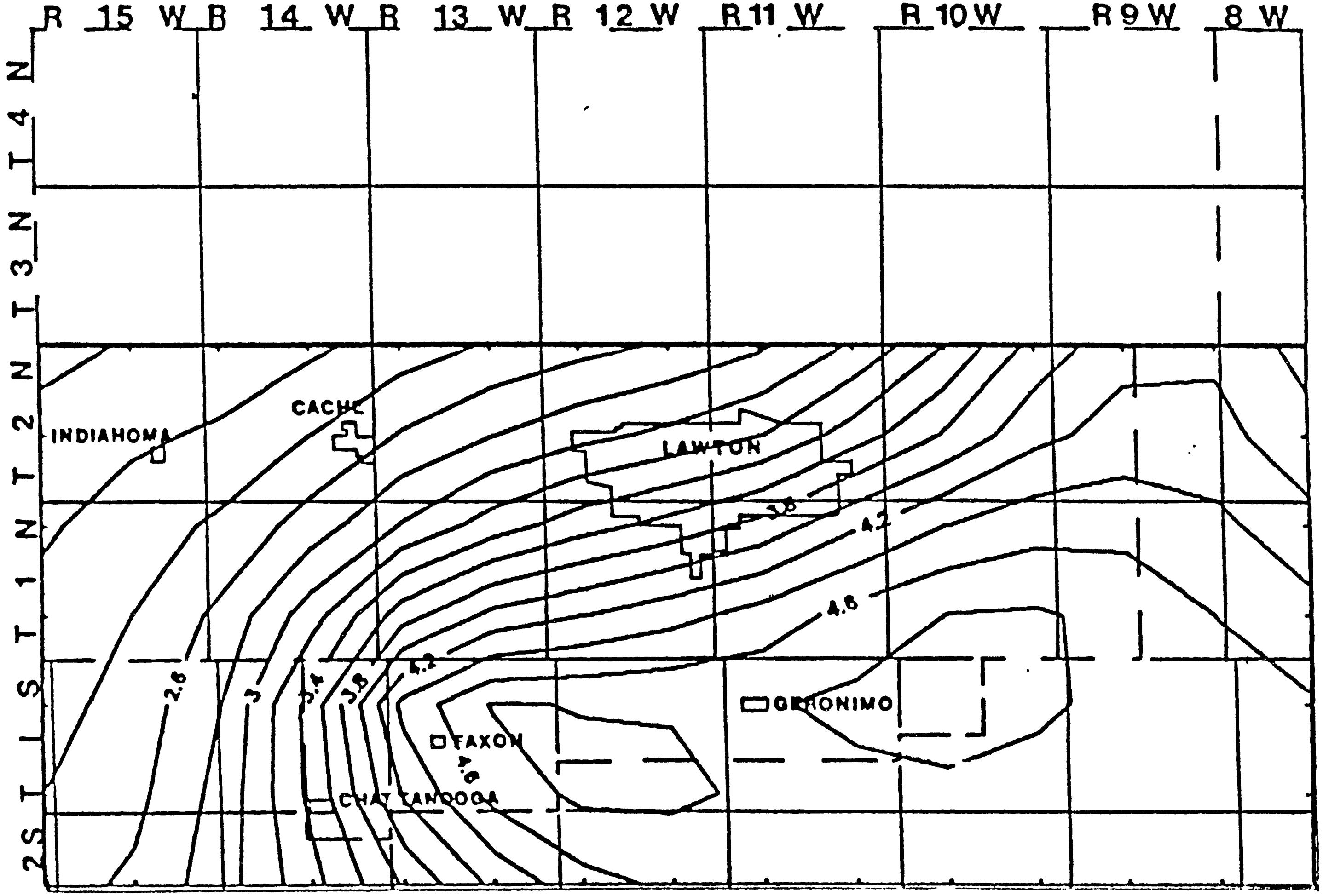


Figure 31. NO_3-N (mg/l): Pumping Period 15 (concentrations calculated using modified saturated thickness)

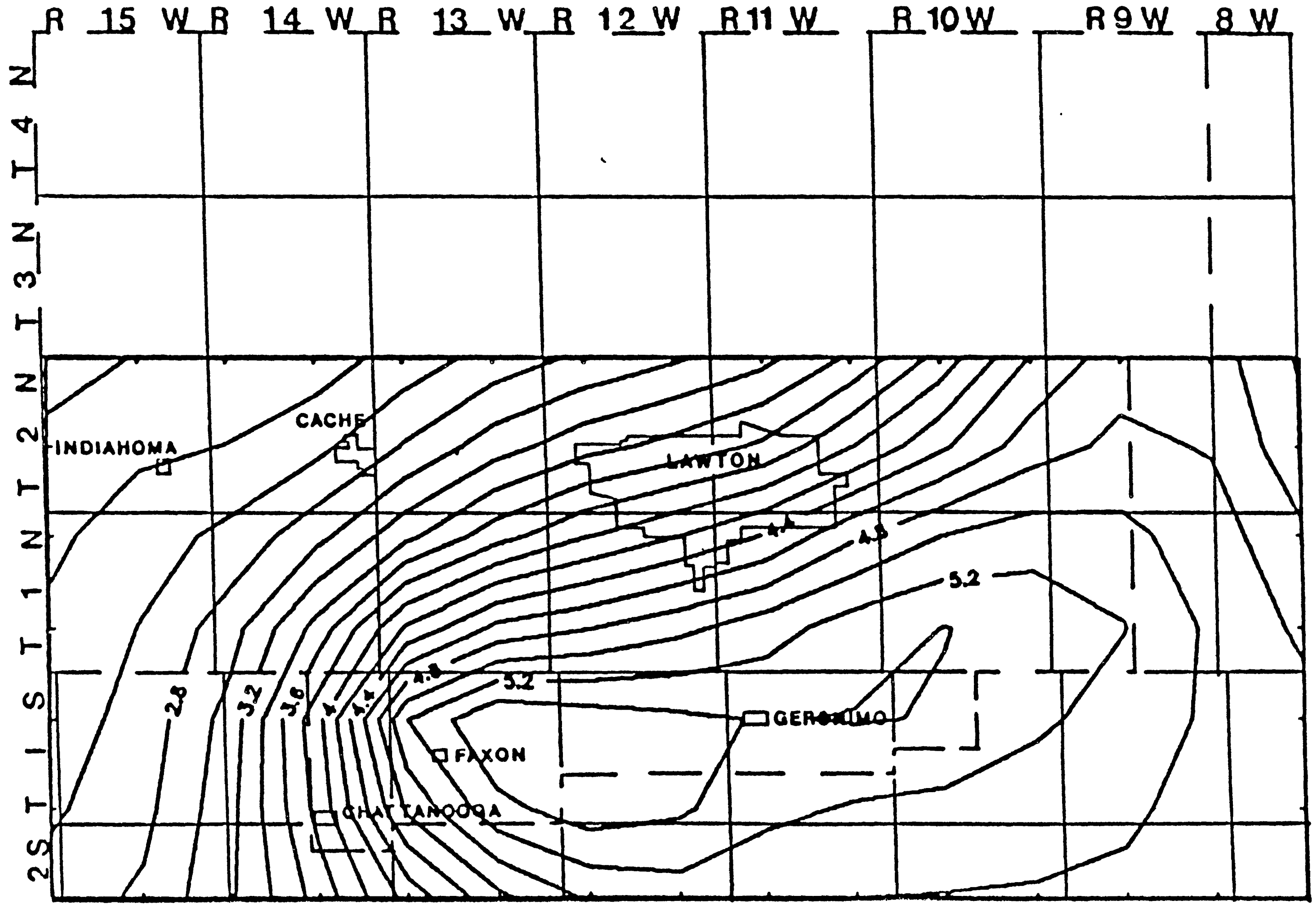


Figure 32. NO_3-N (mg/l): Pumping Period 20 (concentrations calculated using modified saturated thickness)

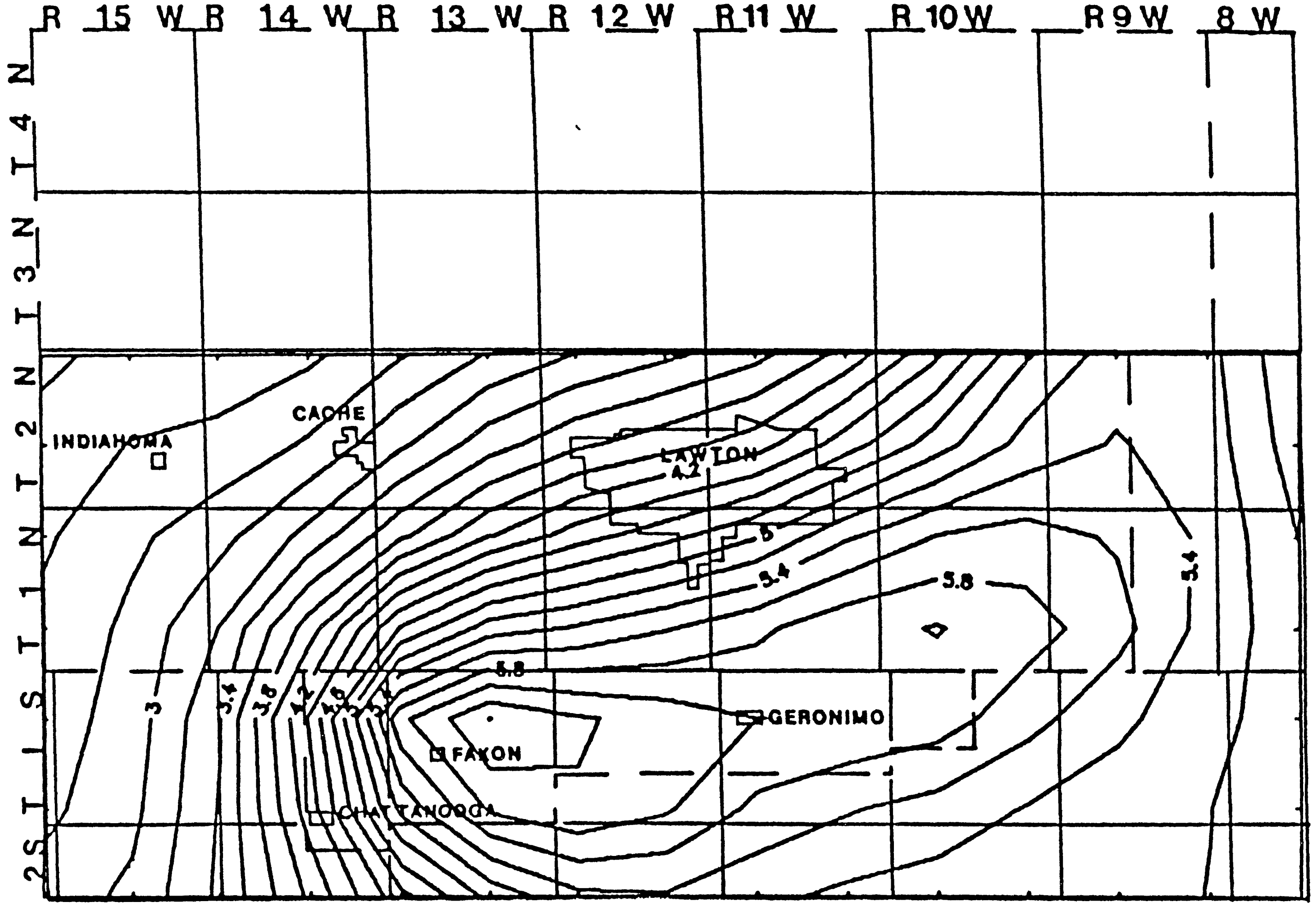


Figure 33. NO$_3$-N (mg/l): Pumping Period 25 (concentrations calculated using modified saturated thickness)

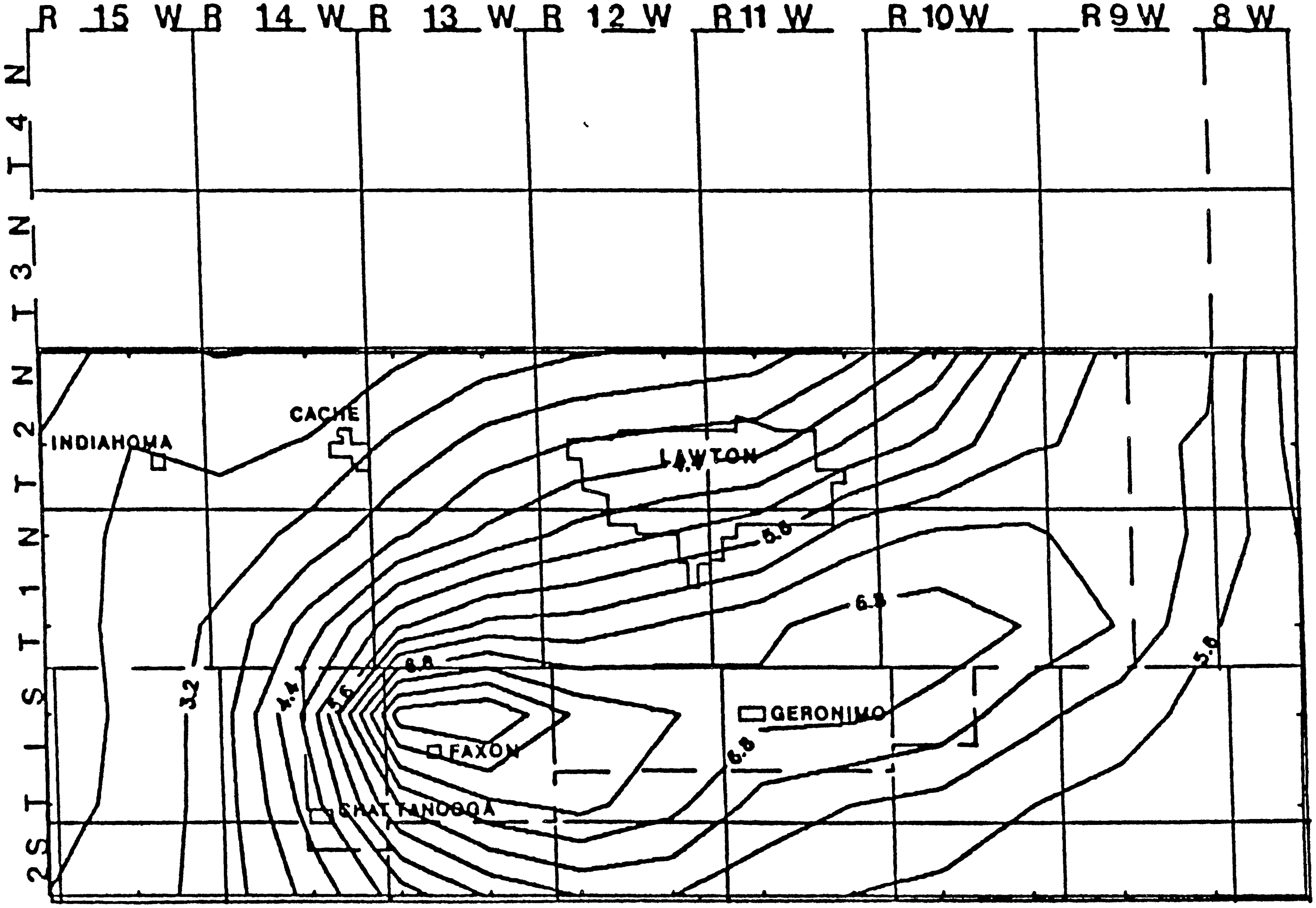


Figure 34. NO_3-N (Mg/l): Pumping Period 30 (concentrations calculated using modified saturated thickness)

CHAPTER X

SIMULATIONS OF FUTURE NITROGEN MOVEMENT AND CONCENTRATION

After calibration, the solute-transport model was used to simulate the future movement and concentrations of nitrogen. It should be emphasized at this point that the results of these simulations are subject to varying degrees of uncertainties. These uncertainties arise from the assumption inherent in the modeling process, simplifications made in conceptualizing the natural system, and limited data available for model calibration. Thus, the simulations of future behavior should be regarded as estimates only.

The solute-transport simulation consisted of 30 time steps, each lasting one year. The results, corrected for dilution errors, from the 30 year simulation are shown in Figures 28-34. Unadjusted results assuming a mixing zone is entire sat thickness are shown in Figure 21-27.

Several important factors that will affect the accuracy of the model predictions are discussed below.

Recharge. Where high values of recharge were assumed, greater loads of nitrogen were input to the aquifer (Figure, 19), because the degree of movement through the unsaturated zone is largely dependent upon the volume of recharge. The errors in correlating recharge values to nitrogen infiltration include the amount and type of vegetation, antecedent soil-moisture, soil type, and rainfall. During the sensitivity analysis it was found that varying amounts of recharge had very little effect on the final head distribution. Therefore, errors in recharge estimates will produce errors in the calculated input of nitrogen to the aquifer, rather than head-distribution.

Permeability. In a natural system, coarse-grained rocks with a high permeability would be more likely to allow nitrogen to flush through to the water table. Figure 19 which correlates recharge to the volume of nitrogen reaching the unsaturated zone, aided in determining nitrogen input. Note, that recharge was previously tied directly to permeability (Appendix 1).

Thickness of the Unsaturated Zone. Kreitler (1975) demonstrated the large storage capabilities of the unsaturated zone. This will most affect the model in the north, towards the Wichitas, on account of the thick unsaturated zone. In this region the model predictions of nitrogen concentrations will be too high as nitrogen storage in the unsaturated zone has been ignored.

Well Construction. Many of the wells in Comanche County are used soley for irrigation purposes. Other wells have been abandoned or are used for watering livestock. These wells, in general, have not been properly maintained and/or constructed and create a conduit for runoff rich in nitrogen to pass directly to the aquifer. The model ignores extraneously high values of nitrogen probably indicative of this problem. Therefore, the model results are a regional average under natural geologic conditions.

Point Sources of Nitrogen. Comanche County has no major commercialized feed lots. Other patch sources of nitrogen are scattered (i.e. municipal sewage, small feed lots etc.). However, these relatively insignificant sources of nitrogen within Comanche County are difficult to quantify for model input, and were ignored.

Application Rate and Extent of Fertilization. The amount of fertilizer applied within Comanche County annually was available through the Department of Agriculture. Because records on the aerial extent were not kept an even distribution of fertilizer over the cultivated area was assumed, even though this created errors in assigning input values of nitrogen to the model.

Water-Table Gradient. The steepness of the water-table gradient will determine the rate at which nitrogen is transported through the saturated zone. The water-table gradient was determined and calibrated in the flow portion of the model see (Appendix 1).

Nitrogen simulation periods correspond to pumping periods. However, pumping periods for the flow portion of the model have a closer correlation to actual years i.e. pumping period two is equivalent to 1972. On account of the poor water-quality records for nitrogen and the crude solute-transport calibration techniques previously described the relationship between nitrogen simulation periods and actual years is present only as a trend rather than a specified time interval.

Pumping periods one through thirty (Figures 28-34) exemplify several of the hydrogeological relationships previously discussed concerning the movement and accumulation of nitrogen.

Pumping periods one and five (Figures, 28 and 29) depict an early trend for the greatest accumulation of nitrogen to occur in the southeastern part of the county. This is dependent gentle water-table gradient and a large amount of cultivated land and fertilizer applicated. Factors prevalent in this region that would normally reduce the volume of nitrogen accumulation are low recharge, and fine sediment size.

Pumping periods ten through thirty (Figs. 30-34) illustrate the ability of the unsaturated zone to store large quantities of nitrogen and show the formation of nitrogen mounds under areas of intensive agriculture combined with a gentle water-table gradient.

The model predicts background concentrations that generally match observed field data. However, the model prediction that concentrations of nitrogen near Indiahoma should approach 2 mg/l-N does not correlate well with existing field data. This area generally has much lower background concentrations, approximately 0.2 mg/l-N. This discrepancy can be explained by recognizing that the thickest unsaturated zone occurs within this region. Therefore, under the natural geologic conditions present, this thick unsaturated zone will store nitrogen that normally would have migrated to the water table.

It becomes apparent that directly south of the Wichitas nitrogen values, for the most part, are relatively low. This should be expected for a number of reasons; namely very little land is cultivated in this area, the rocks consist of very coarse gravels with fracture permeability and there is a steep water-table gradient. Therefore, nitrogen that is applied to the system is quickly flushed down gradient to discharge points.

The formation of nitrogen mounds (8 mg/l NO_3-N), northeast of Chatanooga, are underlying areas of intense agriculture and gentle water-table gradient.

It is important, however, to realize that high nitrogen concentrations may be indicative of other, far more harmful constituents, the most deadly of which are pesticides. It is reasonable to assume that pesticides applied with the fertilizer, migrate under similar physical parameters governing nitrogen migration. Thus, there may be a direct relationship between levels of nitrogen and pesticides.

Although the movement of pesticides in the soil may be retarded because of adsorption on soil organic matter or clay minerals, some may not be. Also the presence of fissures or macropores in the soil may, in fact, preclude adsorption of even those pesticides that may suffer retardation under homogeneous conditions.

The presence of extremely high nitrogen in some areas may also be the result of poor well placement or casing which allows the ingress of human or animal waste into the drinking water supply. Again even if the nitrogen is considered harmless the associated microorganisms may not be.

In summary, although nitrogen contamination in Comanche County may not be a major pollution problem, it can be indicator of more serious pollution; namely, pesticides and/or microorganisms.

CHAPTER XI

SUMMARY AND CONCLUSIONS

A detailed study of the water chemistry and quality of the Post Oak Conglomerate, was performed in Comanche County.

The Post Oak Formation is a massive conglomerate with few sedimentary structures deposited by small probably ephemeral streams that eroded and drained the Wichita Mountains during Permian time. Channel deposits within the conglomerate may be found locally. These paleo-channels are an important conduit for the transport of fluoride derived from igneous source rocks in the Wichitas.

The Arbuckle Group which underlies the Post Oak, is poorly exposed within the study area, and consist of seven formations composed predominantly of carbonate rocks. The environment of deposition for the majority of the seven formations making up the Arbuckle Group is shallow marine. The Arbuckle is semi-confined with the upper confing beds located at the base of the Post Oak.

The Post Oak conglomerate is the surficial aquifer in the study area. Values for hydrogeologic parameters were collected from the field and determined from published material. The chemical quality of the ground water derived from the Post Oak was evaluated to determine the source, occurrence, and distribution of fluoride. It was concluded that the fluoride originated in the Wichitas from the dissolution of riebeckite (sodium amphibole). The fluoride rich waters are prevalent in a wide belt, begining approximately 12 miles south of the Wichitas and trending east- west, in the east the belt originates at the Tillman County line and tends to vanish in the west near Lawton.

This belt is a chemically active zone where cation exchange replaces sodium with calcium on the surfaces of montmorellonitic clays. This exchange depletes the water with respect to calcite and therefore initiates calcite dissolution. This dissolution of calcite raises the pH of the ground water allowing desorption from the kaolinitic clay surfaces to occur, thus producing high fluoride waters.

North of this reactive zone the sodium ions have already been flushed from the clay surfaces by calcium ions and therefore the mechanism (calcite dissolution) by which the pH is raised is absent. South of this transition zone very little field data were obtainable, however, it is likely that the clays are still rich in sodium and fluoride and not enough calcium has been introduced into the system to initiate ion exchange.

In developing the local water supplies it is important to realize that these reactions are dependent upon the availability of clay to host the ion-exchange. Where an ample supply of both types of clays are absent the reactions cannot occur and fluoride levels in the water will be low. It was mentioned previously that the Post Oak was deposited by ephemermal streams during Permian time, these paleo-stream channels would be ideal sources from which to develop water supplies. The advantages would be high yields due to the coarser grain size and low concentrations of fluoride and other dissolved solids.

Nitrogen contamination a second major water-quality problem in the area was also investigated. A modified two-dimensional area solute-transport model of the Post Oak aquifer was constructed for the southern half of Comanche County to determine the movement, occurrence and future concentrations of nitrogen assumed to be derived primarily from fertilizer.

The model predicts background concentrations that generally match observed field data except that nitrogen concentrations near Indiahoma predicted to be 2 mg/l-N do not correlate well with existing field data. This area has an order of magnitude lower background concentration, (approximately 0.2 mg/l-N) which can be explained by recognizing that the thickest unsaturated zone occurs within this region, and which will store nitrogen that normally would have migrated to the water table.

It becomes apparent that directly south of the Wichitas nitrogen values are usually relatively low. This should be expected for a number of reasons; namely very little land is cultivated in this area, the rocks consist of very coarse gravels with fracture permeability and there is a steep water-table gradient. Therefore, nitrogen that is applied to the system is quickly flushed down gradient to discharge points.

The formation of nitrogen mounds (8 mg/l NO_3-N), northeast of Chatanooga, are underlying areas of intense agriculture and gentle water-table gradient.

It is important, however, to realize that high nitrogen concentrations may be indicative of other, far more harmful constituents, the most deadly of which are pesticides. It is reasonable to assume that pesticides applied with the fertilizer, migrate under similar physical parameters governing nitrogen migration. Thus, there may be a direct relationship between levels of nitrogen and pesticides.

Although the movement of pesticides in the soil may be retarded because of adsorption on soil organic matter or clay minerals, some may not be. Also the presence of fissures or macropores in the soil may, in fact, preclude adsorption of even those pesticides that may suffer retardation under homogeneous conditions.

The presence of extremely high nitrogen in some areas may also be the result of poor well placement or casing which allows the ingress of human or animal waste into the drinking water supply. Again even if the nitrogen is considered harmless the associated microorganisms may not be.

In summary, although nitrogen contamination in Comanche County may not be a major pollution problem, it can be indicator of more serious pollution; namely, pesticides and/or microorganisms.

REFERENCES CITED

Anon., Oklahoma Agricultural Statistics,, 1982, Oklahoma Department of Agriculture.

Anon., Tonnage Distribution of Fertilizer in Oklahoma Counties by Grades and Materials 1970-1984.

Aldrich, S.A., 1980, Nitrogen in Relation to Food, Environment, and Energy: Special Publication 61 Agricultural Experiment Station College of Agriculture University of Illinois at Urbana-Champaign, 452 p.

Al-Shaieb, Z., 1977, Evaluation of Uranium Potential in Selected Pennsylvanian and Permian Units and Igneous Rocks in Southeastern and Southern Oklahoma: U.S. Department of Energy Open-File Report GJBX-35 (78), 248 p.

Al-Shaieb, Z., Hanson, R.E., Donovan, R. N., and Shelton, J. W., 1979, Petrology and Diagenesis of Sandstones in the Post Oak Formation (permian), Southwestern Oklahoma. Journal of Sedimentary Petrology, v. 50, p. 43-50.

Al-Shaieb, Z., Thomas, R. G., and G. Stewart, 1980, Uranium Resources Evaluation, Lawton Quadrangle, Oklahoma and Texas: U.S. Department, Open-File report GJQ-017, 82 p.

Bower, C.A., and Hatcher, J.T., 1967, Adsorption of Flouride by Soils and Minerals: Soil Science, v. 103, p. 141-154.

Chase, G.W., 1954, Geological Notes on Permian Conglomerate Around the Wichita Mountains, Oklahoma, American Association of Petroleum Geologists Bulletin, v. 38, p. 2028-2035.

Collins, K.H., 1985, Depositional and Diagenetic History of the Permian Rocks in the Meers Valley, Southwestern, Oklahoma M.S. 1985 O.S.U.

Coplan, T.B., 1984, Environmental Isotopes in Ground Water Studies Chapter 33 in Ground Water Handbook (eds. S.C. Csallary and R.A. Kanivetsky) New York McGraw Hill 365 p.

Craig, H., 1961, Standard for Reporting Concentrations of Deuterium and Oxygen-18 in Natural Water: Science, v. 133, p. 1833-1834.

Delwiche, C.C., 1981, *The Nitrogen Cycle and Nitrous Oxide* (ed. Delwiche in Denitrification, Nitrification, and Atmospreric Nitrous Oxide, Nw York, John Wiley and Sons, 286 p.

Dickman, S.R. and Bray, R.H., 1941, Replacement of Adsorbed Phosphate from Kaolinite by Fluoride. Journal of Soil Science Vol. 52, p. 263-273.

Fairchild, R.V., R.L. Hanson, and R.E. Davis, 1982, Hydrology of the Arbuckle Mountain Area: U.S.G.S. Open-file Report 82-775, 153 p.

Faure, G., 1977, *Principles of Isotope Geology*: New York, John Wiley and Sons, 464 p.

Focht, D.D., 1974, The Effect of Temperature pH, and Aeration on the Production of Nitrous Oxide and Gaseous nitrogen-a Zero-Order Kinetic Model. Soil Science 118: 173-179.

Focht, D.D., 1978, *Methods for Analysis of Denitrification in Soils*. In D.R. Nielson and J.G. MacDonald (eds.), Nitrogen in the Environment, vol. 2, Soil-Plant-Nitrogen Relationships. Academic Press, New York, p. 433-490.

Freeze, R. A., and J.A. Cherry, 1979, *Ground Water: Englewood Cliffs, N.J.*: Prentice-Hall, 604 p.

Garrels. R.M. and Christ, C.L., 1965, *Solution, Minerals, and Equilibria*. Freeman, Cooper and Company, San Francisco. p. 450.

Gilbert, C. M. and T.N. Donovan (editors) 1982, Geology of the Eastern Wichita Mountains Southwestern Oklahoma, Guidebook 21, The University of Oklahoma Norman printing services.

Green, N.L., and Al-Shaieb, Z., 1981, Source of High-Flouride Ground Water West-Central Comanche, Oklahoma, Water Research Institute Oklahoma State University.

Ham, W.E., Denison R.E., Merritt, C.A., 1964, Basement Rocks and Structural Evolution of Southern Oklahoma. Oklahoma Geological Survey Bulletin 95, 302 p.

Havens, J.S., 1975, Reconnaissance of Ground Water in the Vicinity of the Wichita Mountains, Southwestern Oklahoma: U.S. Geological Survey, Open-File Report, 22 p.

Havens, J.S., 1977, Reconnaissance of the Water Resources of the Lawton Quadrangle, Southwestern Oklahoma: Oklahoma Geological Survey Hydrologic Atlas HB-6 (prepared in cooperation with the U.s. Geological Survey). 4 sheets.

Hoffman, M.G., 1930, Geology and Petrology of the Wichita Mountains, Oklahoma Geological Survey Bulletin, 52, 83p.

Jones, E.J., 1951, Loss of Elemental Nitrogen from Soils Under Anaerobic Conditions. soil Sci. 71: 193-196.

Kent, D.C., et al., 1985, Modifications to the U.S.G.S. Solute Transport Model: U.S. Environmental Protection Agency Cooperative Agreement No. CR811142-01-0.

Kent, D.C. et., al., 1985, Interative Preprocessor Program for the U.S.G.S Konikow Solute Transport Model, U.S. Environmental Protection Agency Cooperative Agreement No. CR811141-01-0.

Kent, D.C., and Greeley, B.B., 1985, Assessment of Ground-Water Availability for Communities and Rural Water Districts in Comanche County, Southwestern Oklahoma. A final Report to Oklahoma Water Resources Board.

Konikow, L.F., and Bredehoeft, J.D., 1978, Computer Model of Two-Dimensional Solute Transport and Disperison in Ground Water; Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 7, Chapter C_2. 90 p.

Kreitler, C.W., 1975, Determining the Source of Nitrate in Ground Water by Nitrogen Isotope Studies. Bureau of Economic Geology. The University of Texas at Austin.

Kwang, J.A., 1977, Petrography and Geochemistry of Lower Permian Cornstones in Southwestern Oklahoma M.S. Thesis Oklahoma State University.

Larsen, S. and Widdowson, A.E., 1971, Soil Fluoride. Journal of Soil Science, Vol. 22, No. 2, p. 210-221.

LeMaster, L., 1985, Personal Communication

Luhrs, C.E., 1973, Nitrogenous Compounds in the Environement: Human Health, U.S. EPA-SAB-73-001: 159-173.

Mayes, J.M., 1947, A Further Study of the Tepee Creek Formation, Wichita Mountains, Oklahoma M.S. thesis, University of Oklahoma.

McDaneil, G.A., 1959, Isopachous and Paleo-Geologic Studies of Southwest Oklahoma: Shale Shaker, V. 10, No. 3, Nov. 1959 pp. 4-27.

Merrit, C.A., 1967, Mt Scott Granite: In Stone G.T. (ed.), The Structure and Igneous Rocks of the Wichita Mountains, Oklahoma: Geol. Soc. America, South Central Sec., 1st Ann. Mtg., Field Trip Guide Book, p. 22-25.

Merritt, C.A., and Ham, W.E., 1941, Precambrian Zeolite-Opal Sediments in the Wichita Mountains, Oklahoma: Bull. of Am. Assoc. Petro. Geol., Vol. 25, pp. 287-299.

Metcalf, W.K., 1961, A Biochemical Change in Blood in Pregnancy and Malignant Disease, Physics in Medicine and Biology 5: 259-269 p.

Mobley, H.L., Brinlee R.C., 1967, Soil Survey of Comanche County, Oklahoma. U.S. Governmnet Printing Office 58 p.

Nielson, Donald R., MacDonald, J.G., 1978, Nitrogen in the Environment, Volume 2, New York, Academic Press, 528 p.

Omveti, J.A., and Jones, R.L., 1977, Fluoride Adsorption by Illinois Soils. Journal of Soil Science, Vol. 28 p. 564-572.

Payne, W.J., 1981, Denitrification: New York, John Wiley and Sons, Inc., 214 p.

Perrott, K.W., Smith B.F., and Inkson, R.H., 1976, The Reaction of Flouride with Soils and Soil Minerals. Journal of Soil Science, Vol. 27, p. 58-67.

Pettyjohn, W.A., White, H.O., Dunn S.A., 1982, Water Atlas of Oklahoma. University Center for Water Research.

Plummer, L.N., Parkhurst, D.L., and Thorstenson, D.C., 1983, Development of Reaction Models for Ground-Water Systems: Geochemisty et Cosmochimica Acta, v. 77, p. 665-686.

Plummer, L.N., Jones B.F., and Truesdell, A.H., 1976, Wate QF-A Fortran IV Version of Water, A Computer Program for Calculating Chemical Equilibrium of Natural Waters: U.S. Geological Survey Water Resources Investigations 76-13, 63 p.

Postgate, J.R., 1982, The Fundamentals of Nitrogen Fixation: Cambridge, Cambridge University Press, 252 p.

Powell, B.N., Golbert, M.C., and Fisher, J.F., 1980, Lithostratigraphic Classification of Basement Rocks of the Wichita Province, Oklahoma. Geological society of

America Bulletin, v. 91, p. 509-514.

Romo, L.A., 1954 Role of Lattice Hydroxyls of Kaolinite in Phosphate Fixation and Their Replacement by Fluoride. Journal of Colloid Chemistry Vol. 9 p. 385-392.

Romo, L.A., and Roy, R., 1957, Studies of the Substitution of OH-By F-in Various Hydroxylic Minerals American Mineralogist, Vol. 42, p. 165-177.

Shearer, L.A., J.R. Goldsmith, C. Young, O.A. Kearns, and B.R. Tamplin, 1972, Methemoglobin Levels in Infants in an Area With High Nitrate Water Supply, American Journal of Public Health 62: 1174-1180.

Shelton, J.W., and Al-Shaieb, Z., 1976, Summary of the Stratigraphy and Mineralogy of Pennsylvanian and Permian Rocks of Oklahoma in Relation to Uranium-Resource Potential: Department of Geology, Oklahoma State University, Stillwater, Okla., 156 p.

Stone, J.E., 1981, Sources of Municipal and Rural Water Supplies in the Comanche County Area, Southwestern Oklahoma, 1981, Final Report to Oklahoma Water Resources Board, Oklahoma State University.

Stone, W.B., 1977, Mineralogic and Textural Dispersal Patterns within the Permian Post Oak Formation of Southwestern Oklahoma. Unpub. M.S. Thesis Oklahoma University.

Taff, J. A., 1904, Preliminary Report on the Geology of the Arbuckle and Wichita Mountains in Indian Territory and Oklahoma: U.S.G.s. Prof. Paper 31, pp. 51-97.

Tracy, J.V., 1982, User Guide and Documentatation for Adsorption and Decay Modifications to the U.S.G.S. Solute Transport Model: U.S. Nuclear Regulatory Commission, Office of Nuclear Material Safety and Standards, Division of Waste Management, NUREGICR-2052 90p.

U. S. Geological Survey, 1977, National Handbook of Recommended Methods for Water-Data Acquisition, Chapter 5, Chemical and Physical Quality of Water and Sediment: U.S. Geological Survey, Office of Water-Data Coordination, 196 p.

Walton, W.C., 1970, Ground Water Resource Evaluation: New York, McGraw-Hill, 664 p.

Winneberger, J.H., 1982, Nitrogen, Public Health, and the Environment: Michigan, Ann Arbor Science, 77 p.

Yiamouyiannis, J., 1985, Flouride the Aging Factor: Ohio, Health Action Press, 210 p.

APPENDIX

FLOW HYDRAULICS OF MASS-TRANSPORT MODEL

Model Imput Values

Land. The surface elevation of each node was determined by superimposing the node grid onto topographic maps and estimating the average elevation over the nodal area.

Bottom Elevation. Many of the geologic logs for wells in the study area recorded the depth at which the Arbuckle Group was encountered. Havens (1977) published a map contoured on top of the Arbuckle (base of the Post Oak) these data used in conjunction with several electric logs from the area made possible the assignment of values to the bottom matrix (Figure 35).

Recharge. Values for recharge were estimated by using Oklahoma's Water Atlas (Pettyjohn et.al., 1982) to obtain a rough range of values (Figure 36). These numbers were further refined by relating the amount of recharge to the intrinsic permeability of the rocks (Figure 37). Errors are generally encountered when estimating recharge, which is highly variable and dependent upon rainfall duration, intensity and antecedent soil moisture.

Effective Porosity. The most representative effective porosity of the Post Oak was estimated based upon average grain size (Figure 4). A value of 25 percent was assigned.

Storage Coefficient. The storage coefficient of an aquifer is defined as the volume of water released from a unit surface area of aquifer per unit drop in head (Lohman and others, 1972) and is a dimensionless quantity. It is

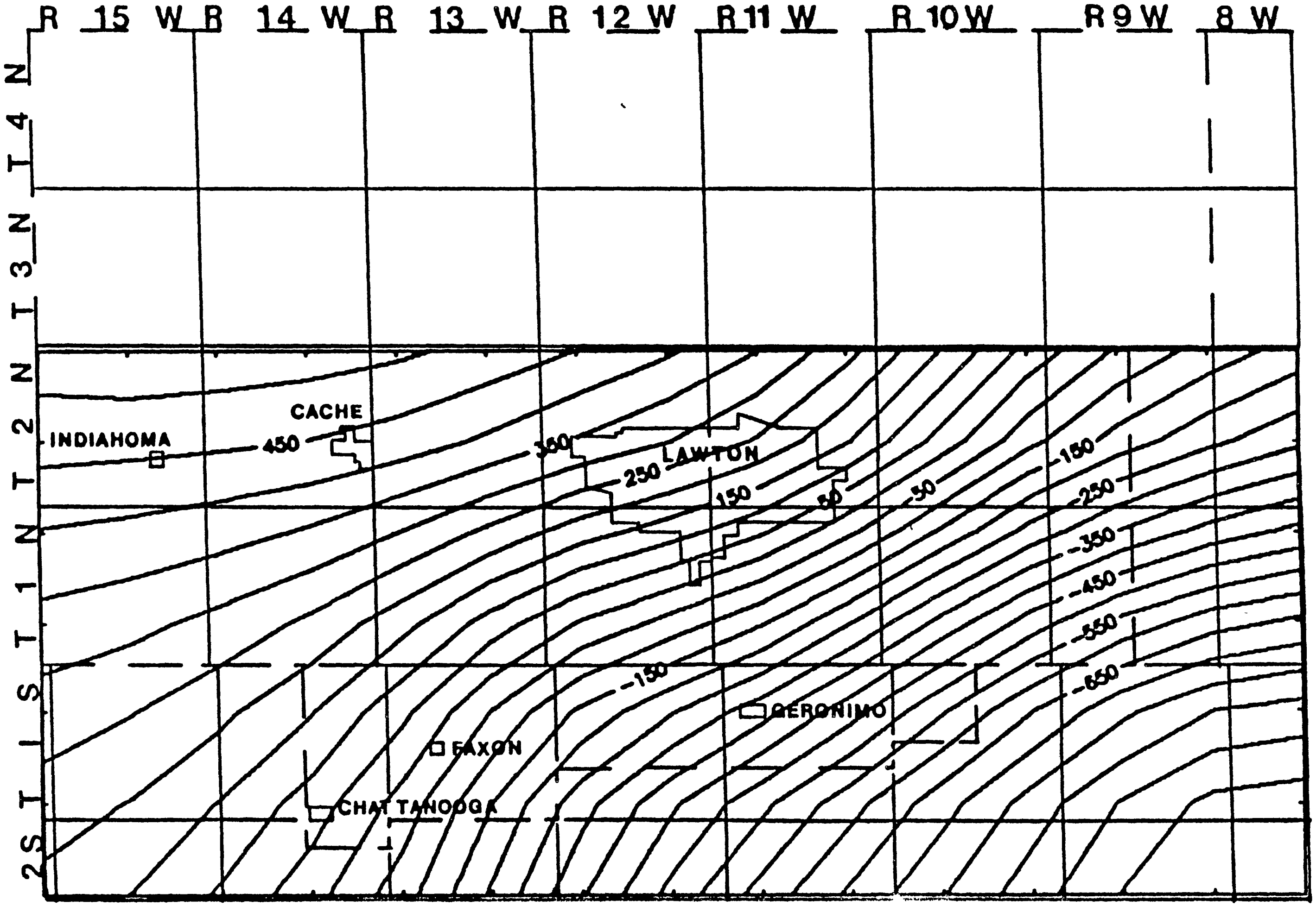


Figure 35. Bottom Elevation of Post Oak

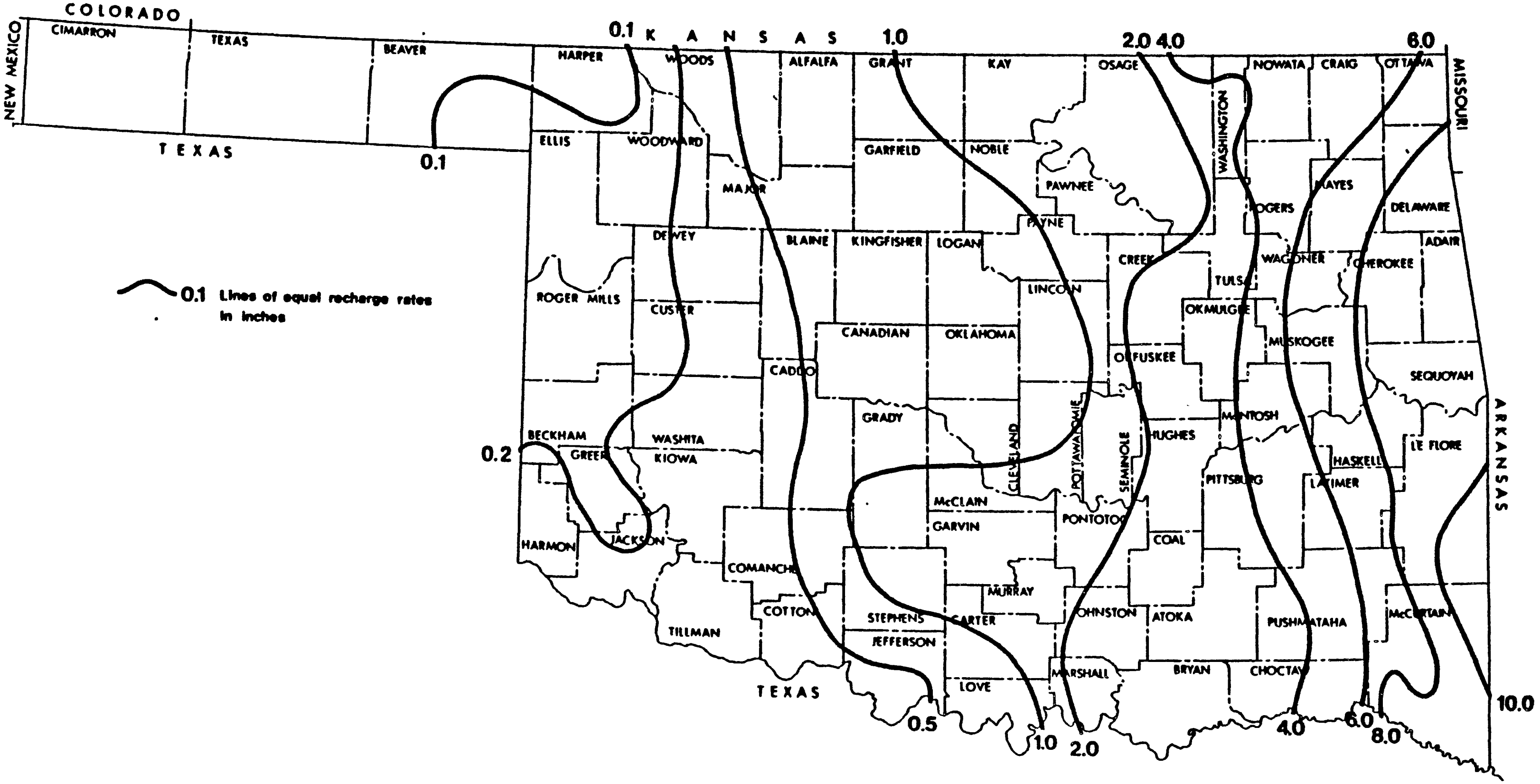
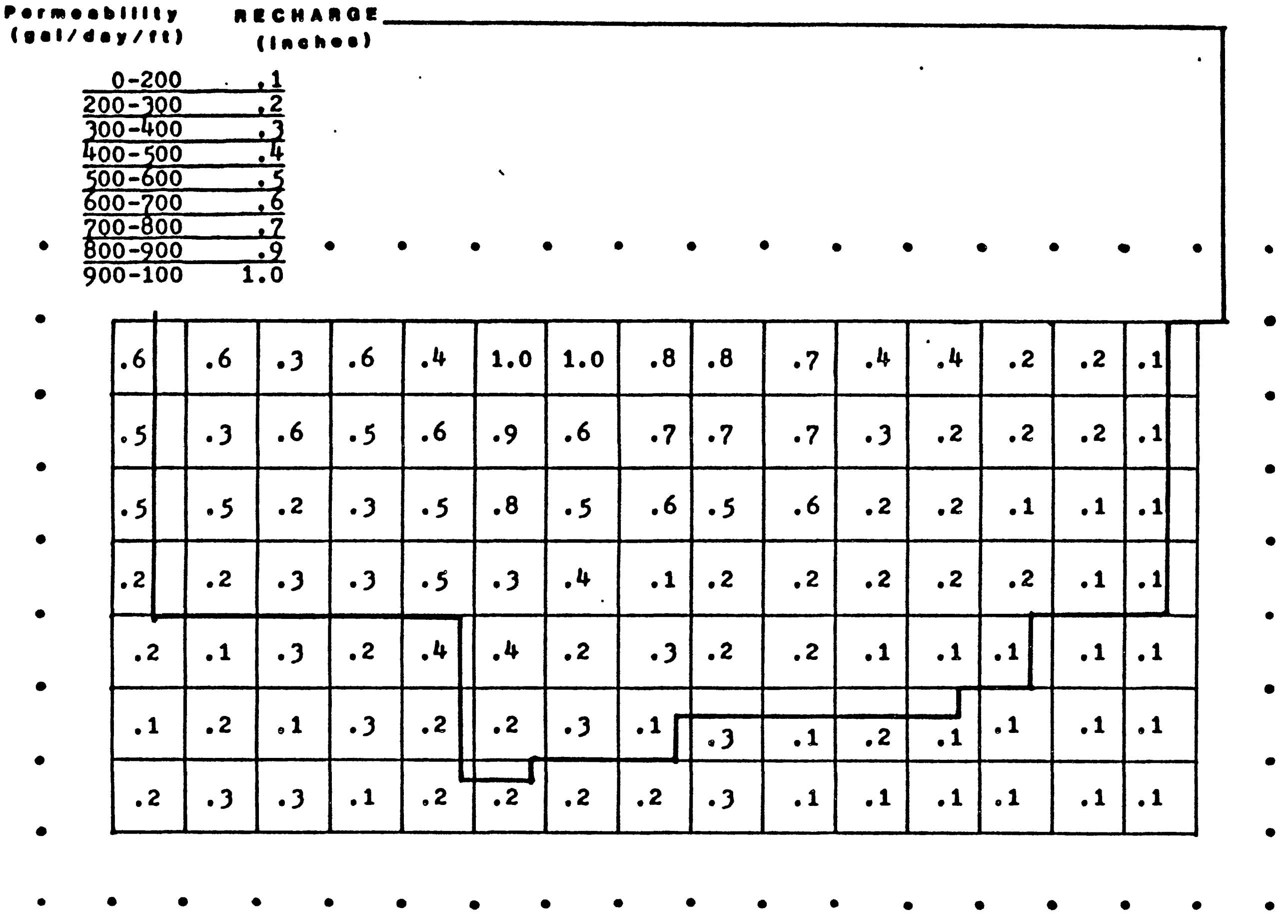


Figure 36. Effective Regional Ground-Water Recharge Rates (In Inches) (Period 1970-79) (After Pettyjohn et.al., 1982)



Permeability (gal/day/ft)	RECHARGE (inches)
0-200	.1
200-300	.2
300-400	.3
400-500	.4
500-600	.5
600-700	.6
700-800	.7
800-900	.9
900-100	1.0

.6	.6	.3	.6	.4	1.0	1.0	.8	.8	.7	.4	.4	.2	.2	.1
.5	.3	.6	.5	.6	.9	.6	.7	.7	.7	.3	.2	.2	.2	.1
.5	.5	.2	.3	.5	.8	.5	.6	.5	.6	.2	.2	.1	.1	.1
.2	.2	.3	.3	.5	.3	.4	.1	.2	.2	.2	.2	.2	.1	.1
.2	.1	.3	.2	.4	.4	.2	.3	.2	.2	.1	.1	.1	.1	.1
.1	.2	.1	.3	.2	.2	.3	.1	.3	.1	.2	.1	.1	.1	.1
.2	.3	.3	.1	.2	.2	.2	.2	.3	.1	.1	.1	.1	.1	.1

Figure 37. Recharge to the Post Oak

calculated by the ratio of recharge to rise of the groundwater level. In unconfined aquifers, water derived from storage comes from the actual draining of the pores. The storage coefficient of an aquifer is usually determined by analysis of pumping-test data using the Theis equation (Lohman and others, 1972). Unconfined aquifers have a range in storativity values .02-.3 (Walton, 1970). The upper bound .3 was assigned on account of the satisfactory results during calibration.

Historical Water-Table. Water-level values obtained from well logs and Haven's Water Atlas (1977) were measured over a reasonably short time interval during 1971 and were used to re-create the historical water-table needed for calibration purposes (Figure 38).

Present Water-Table. The 1984 water-table was constructed from depth to water table measurements (Table 7) and electrical resistivity surveys completed as part of this study (Figure 39).

Permeability. Commonly, permeability and storage coefficient values for an aquifer are determined by running aquifer test. Generally, a well is pumped for a specified time interval at a constant rate, observed changes in nearby monitoring wells are recorded and interpreted using several available techniques (Lohman, 1972).

Aquifer test on the Post Oak in the study area were not available. Therefore, determination of permeability was made with information contained in driller's logs and mean grain size analyses (Stone, 1977). Two methods were used.

TABLE VII

WELLS IN POST OAK AND ALLUVIUM

Location	Well Depth	Ele. Static W-L (MSL)	Ele. Well
*3N-15W-17 SW NW NW NW	20.75'	1454	1468
*3N-15W-31 SE NE SE SE	17.25	1389	1410
*2N-15W-16 SE SW SW SW	19.5	1345	1360
* -17 NW NE NE	25.7	1338	1360
* -22 SW SW SW SE	13	1311	1320
* -24 SW NE SE NE	16	1283	1295
* -24 SW NE SE NE	29	1282	1295
* -27 NE NW NW	32.9	1297	1320
* -34 NE NE SE	35.5	1259	1280
* 2N-14-19 SW SW SW SW	37.7	1265	1290
* -19 W/2 SW SW SW	33	1271	1290
-20 SE SW NE NE	240	1339	1350
-25 NW SE SW SW	15-18	1217	1220
* -26 SE SW SE SE	25	1199	1210
-27 NW SW SE SE	150	1294	1310
-27 SE SW SE SE	350		1310
* -30 E/2 NW NE NW	36	1257	1280
* -30 NW NE NE NW	21.8	1257	1257
-33 SE SE SW SE	21	1226	1240
-36 SE SE SE SE	16	1168	1180
2N-13W-23 NW NE NE NE	750	1164	1253
-27 NW NE NE NW	250	1164	1302
-31 S/2 SW SE SE	300	1190	1220
-33 E/2 NE NE SE	200	1260	1220
1N-15W-3 SE NE NE NE	187	1260	1320
* -11 E/2 E/2 NE SE	40.5	1212	1230
-22 NE NE NE NW	23R	1231	1250
1N-14W-1 5/2 NW	22.5	1181	1200
-5 NE NE NE SE	280-320		1270
-15 SE NW SW SW	220	1157	1195
-15 NE SW SW SW	19.5	1183	1195
-16 NW SE SW SW	143	1176	1195
-16 NW SE SW SW	23.6	1176	1195
-16 N/2 SW SE	17.7	1166	1175
-20 SE SE NE SE	22.1	1190	1205
-20 SE SE NE SE	40.1	1168	1205
-21 NW NW SW SW	65	1160	1220
-21 SW NW SW SW	360		1225
-22 NE NE SE SE	180	1140	1200
* -32 SE NE NE NE	13.5	1155	1165
1N-13W-4 NE SE NW NE	135	1155	1191
-6 S/2 NW NE NE	285-90	1169	1220
-14 SE SW SW	38	1186	1200
* -33 SE	PIT	1128	1130
3N-10W-4 SE SW SW	30	1242	1250
-28 NW NW NW	50	1148	1160
3N-9W-5 SW NW SW	45	1271	1280
-29 NW SW SW	30	1188	1200
2N-12W-10 S/2 S/2	20	1087	1100
2N-11W-27 SW SE SE	40	1151	1165
2N-10W-16 SW SW SW	60	1184	1200
-36 S/2	25	1147	1160
2N-9W-33 SW SE SE	130	1090	1150
1N-12W-15 SE SE SE	43	1056	1070
-30 NE NE NE NE	37	1035	1150
1N-11W-13 SW SW SW	38	1106	1120
* -28	60	1032	1045
* -36 SE SW SW	35	1034	1050
1N-10W-10 SW SW SW SW	50	1098	1110
-36 E/2 SW	30	1066	1080
1N-9W-20 SE SE SE SE	45	1037	1050
1S-14W-25 N/2 N/2	40	1102	1115
*1S-13W-17 E/2 E/2	PIT	1088	1100
-25 SW SW SW SW	55	1067	1083
1S-12W-4 SW NW NW NW	60	1125	1140
* -17 SW SW SW SW	60	1035	1048
1S-11W-21 SW SW SW SW	30	1047	1059
* -35 W/2 W/2	PIT	988	1000
*1S-10W-9 SW SW SW SW	32	1051	1065

*ALLUVIAL WELLS

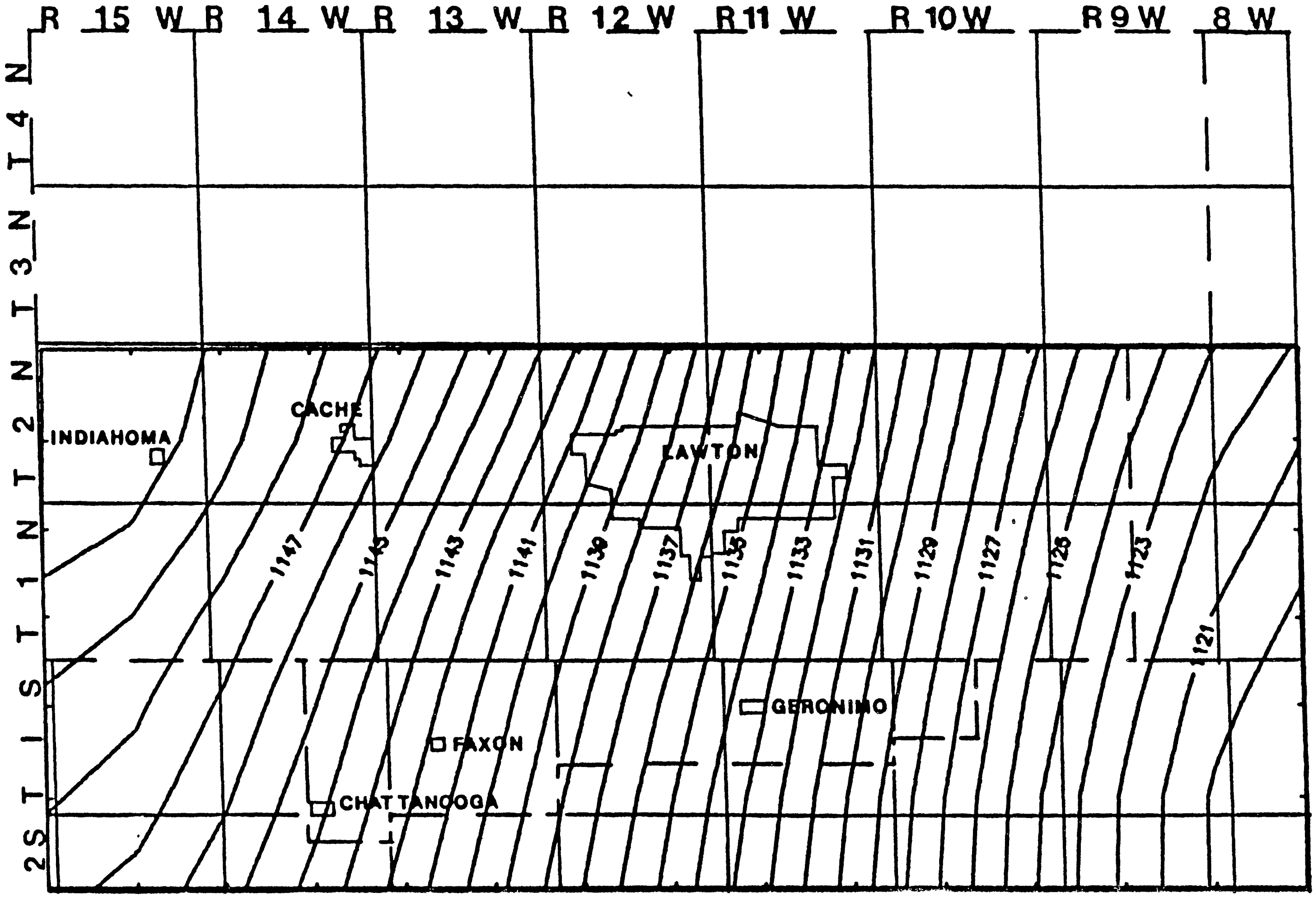


Figure 38. Water-Table Elevation 1971

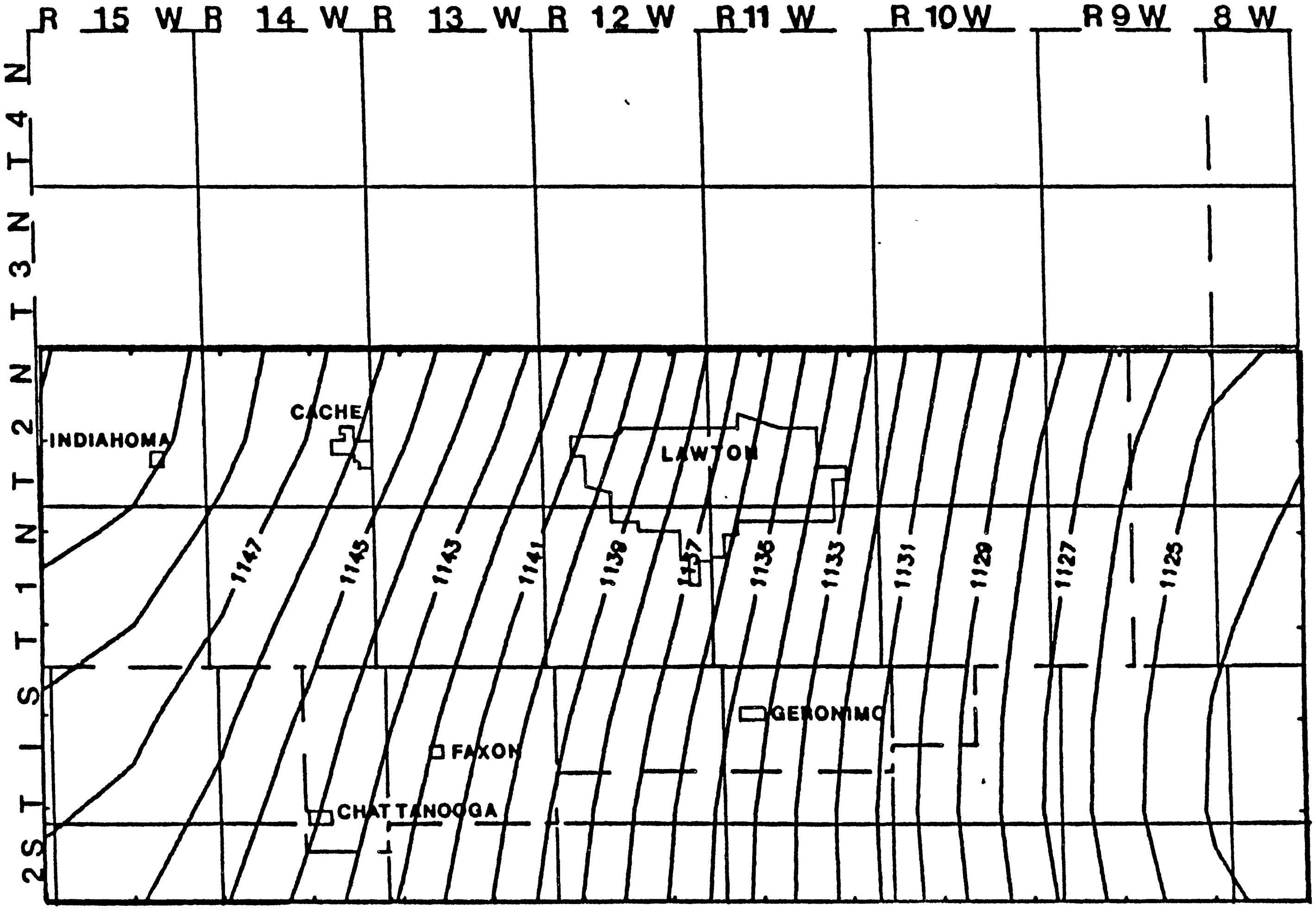


Figure 39. Water-Table Elevation 1984

An equation from Walton (1970) relates specific capacity of an aquifer to transmissivity. Transmissivity divided by saturated thickness equals permeability. Another method developed by Kent et. al. (1973) ties mean grain size of the aquifer material to permeability.

Permeability From Specific Capacity. Equation (3) presented by Walton to find transmissivity from specific capacity is:

$$Q/s = T/[264 \log (T_t/2693 r_w{}^2 s) - 65.5] \qquad (3)$$

where

$\frac{Q}{S}$ = specific capacity in gpm/ft drawdown
Q = discharge in gpm
s = drawndown in feet
T = coefficient of transmissivity in gpd/ft
S = storage coefficient, fraction
r_w = nominal radius of well, in feet
t = time after pumping started, in minutes

Specific capacity data were taken from drillers' log (Tables 8 and 9). A graphical method (Walton, 1970) was used to solve equation (3) and is shown in Figure 40.

Equation (3) assumes one hundred percent well efficiency. Well completion methods and pumping rates for wells in the Post Oak suggest that 60 percent would be a reasonable estimate of average well efficiency. Therefore transmissivity values found in equation (3) were divided by 0.60.

Permeability From Mean Grain Size. Stone (1977) completed a mean grain size analysis of sediments deposited within the Post Oak (Figure 4). The mean grain size of each node was determined by superimposing the node grid on top of

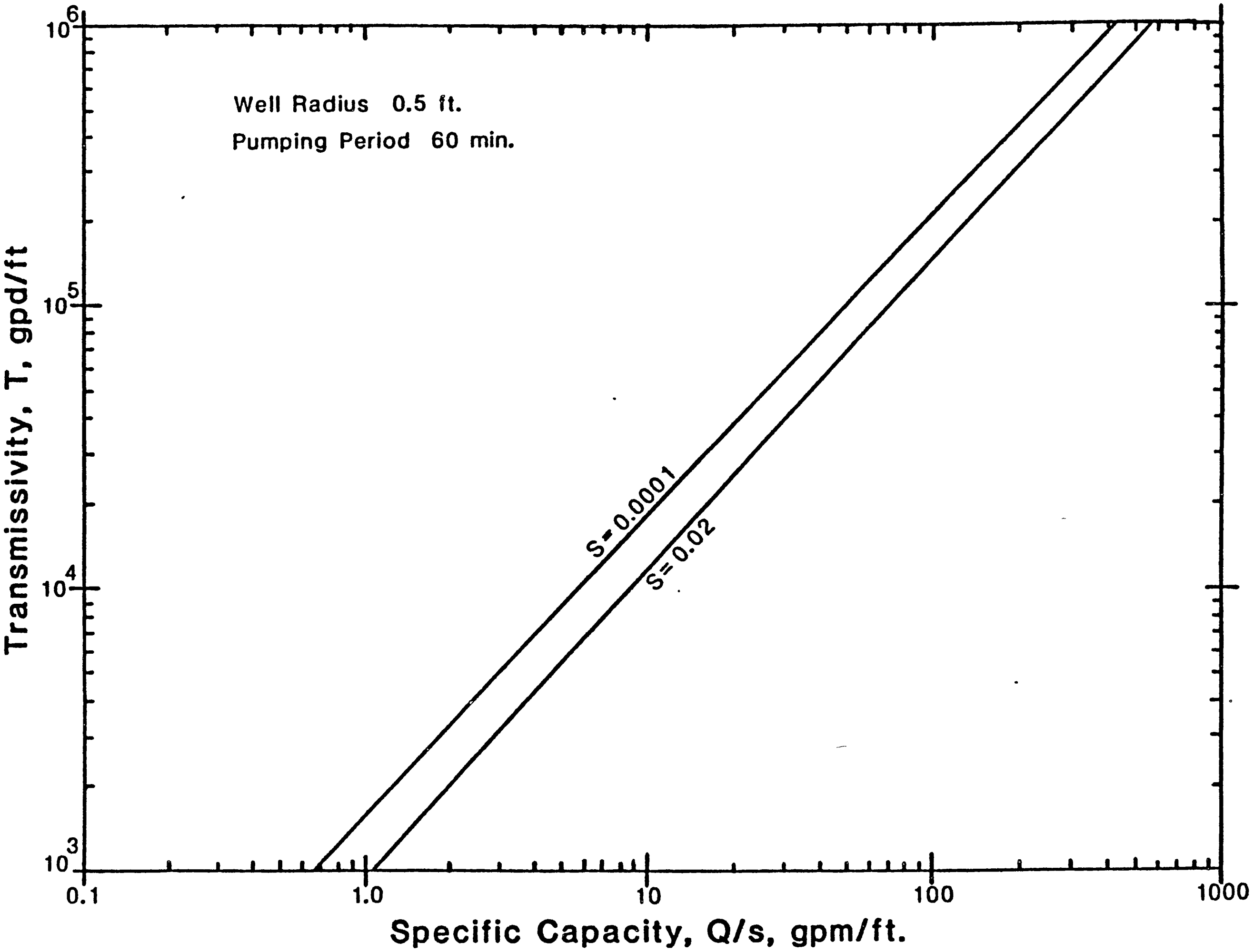


Figure 40. Relationship of Transmissivity to Specific Capacity

TABLE VIII

LOCATIONS OF WATER WELLS IN ALLUVIUM AND POST OAK

Location of Water Wells in Alluvium

Code	Location
Q1	3N-16W-29 BA
Q2	3N-11W-5B E/2
Q3	3N-11W-5B W/2
Q4	3N-11W-5 BAC
Q5	2N-15W-34 DAA
Q6	2N-14W-23 CCB
Q7	2N-14W-23 CCD
Q8	1N-11W-32 ADAA
Q9	1S-11W-9 DBAD 1
Q10	1S-11W-9 DABB 2
Q11	25-12W-8 DDDD
Q12	25-12W-18 AAA
Q13	25-12W-28 AAA

Location of Water Wells in Post Oak

Code	Location
P1	2N-15W-24 DDD
P2	2N-14W-21 BBD
P3	2N-14W-24 Cache
P4	2N-14W-24 Cache
P5	2N-14W-35 CCD
P6	2N-14W-36 ACA
P7	2N-14W-36 ACC
P8	2N-9W-21 DAB
P9	1N-14W-20 DAA
P10	1S-14W-2 BD
P11	1S-14W-12 B
P12	1S-14W-12 B
P13	1S-13W-18
P14	1S-13W-19
P15	2S-12W-17 BBB
P16	2S-12W-17 BBB
P17	2S-12W-21 BBBB

TABLE IX

DRILLER'S LOGS FOR WELLS IN ALLUVIUM AND POST OAK

Location	Total Depth (ft) (1)	Well Radius (ft)	Depth to Static Water Level (ft) (2)	Test Yield (gpm) (3)	Test Pumping Duration (hrs) (4)	Test Pumping Drawdown (ft) (5)	Specific Capacity (gpm/ft) of drawdown (3)-(5)	Transmissivity from Specific Capacity (gpd/ft)	Transmissivity from Specific Capacity SC*1.66 (gpd/ft)	Permeability from Specific Capacity (gpd/ft²)	Permeability from Specific Capacity SC*1.66 (gpd/ft²)
ALLUVIUM											
Q1	35	0.5	26	302	100	30	10	17563	30151	1176	2010
Q2	46		7.5	156		23	6.5				
Q3	33		5.5	60		11	5.5				
Q4	45	1.6	8	900	36	18	46.4	71853	123921	1963	3349
Q5	33.5	0.21	15.2	12.5	1	0					
Q6	29	0.21	12	6	1	0					
Q7	28.5	0.21	15.5	20	2	0					
Q8	18	0.5		50	24	0					
Q9	60	0.09	28.7	60	24	8.15	7.36	14668	25020	468	806
Q10	50	0.08	31	55	5	12.7	4.33	7597	12512	259	445
Q11	65	0.33	26	103.2	23	6	17.5	30530	52288	783	1343
Q12	53	0.45	32.6	540	24	41.4	5.2	8916	15407	480	791
Q13	21	0.5	6	273	0.17	14.3	19.3	19758	34556	1369	2050

Location	Total Depth (ft)	Well Radius (ft)	Depth to Static Water Level(ft)	Test Yield (gpm)	Test Pumping Duration (hrs)	Test Pumping Drawdown (ft)	Specific Capacity (gpm/ft of drawdown)	Transmissivity from Specific Capacity (gpd/ft)	Transmissivity from Specific Capacity SC*1.66 (gpd/ft)	Permeability from Specific Capacity (gpd/ft²)	Permeability from Specific Capacity SC*1.66 (gpd/ft²)
Post Oak Aquifer											
P1	35	0.21	22	7	1	0					
P2	230	0.19	90	9.3	48	230					
P3	21.3	0.31	12.5	14.3	1	0					
P4	26	0.21	9.8	15	1	0					
P5	35.5	0.21	2	8.5	1	0					
P6	200	0.19	70	3	1	150					
P7	25.5	0.21	9.8	20	1	0					
P8	350	0.19	83	4	0.5	180					
P9	39	0.31	35.5	3	1	0					
P10	42	0.75		165	14	25	5.23	6984	12234		
P11	44	0.33	20	850	10	17	47.1	76544	23177	3189	5491
P12	42	0.5	14	500	10	15	33.3	57912	82566	1823	3321
P13	32	0.5	15	350	32	8	43.8	33375	12637	4314	7430
P14	30	0.25	9	200	72	13	33.9	22326	43766	1319	2084
P15	30	0.33	23	340	3	22	15.4	20930	31419	557	1457
P16	46	0.45	32	38	1	26	7.83	2263	4806	55.3	174
P17	48	0.33	21.5	202	24	11	18.4	32309	55465	1219	2092

the contoured mean-grain-size map and estimating the average value over the nodal area (Figure 37). The mean grain size was then related to permeability using a graphical technique developed by Kent et. al. (1973) (Figure 41). The calculated permeability and transmissivity are shown in Figures 42 and 43.

Sensitivity Analysis

Prior to calibrating the flow portion of the model, a series of simulations were made to determine the model's sensitivity to various hydrologic parameters. This analysis was made in order to facilitate the calibration process and to gain a better understanding of the hydrologic system.

The results from the sensitivity analysis indicate that the system is most sensitive to water-table gradient, aquifer storativity and transmissivity, while porosity and recharge have lessening effects upon the water-table surface.

Flow Calibration

In Comanche County very little water level or pumpage data were recorded prior to the year 1970. However, Havens collected a series of water levels in 1971 from wells screened in the Post Oak from which a water-table surface could be constructed. Hydrographs were not available for the desired time interval used in calibration. However, sporatic water level measurements were taken from various wells penetrating the Post Oak during this time interval and

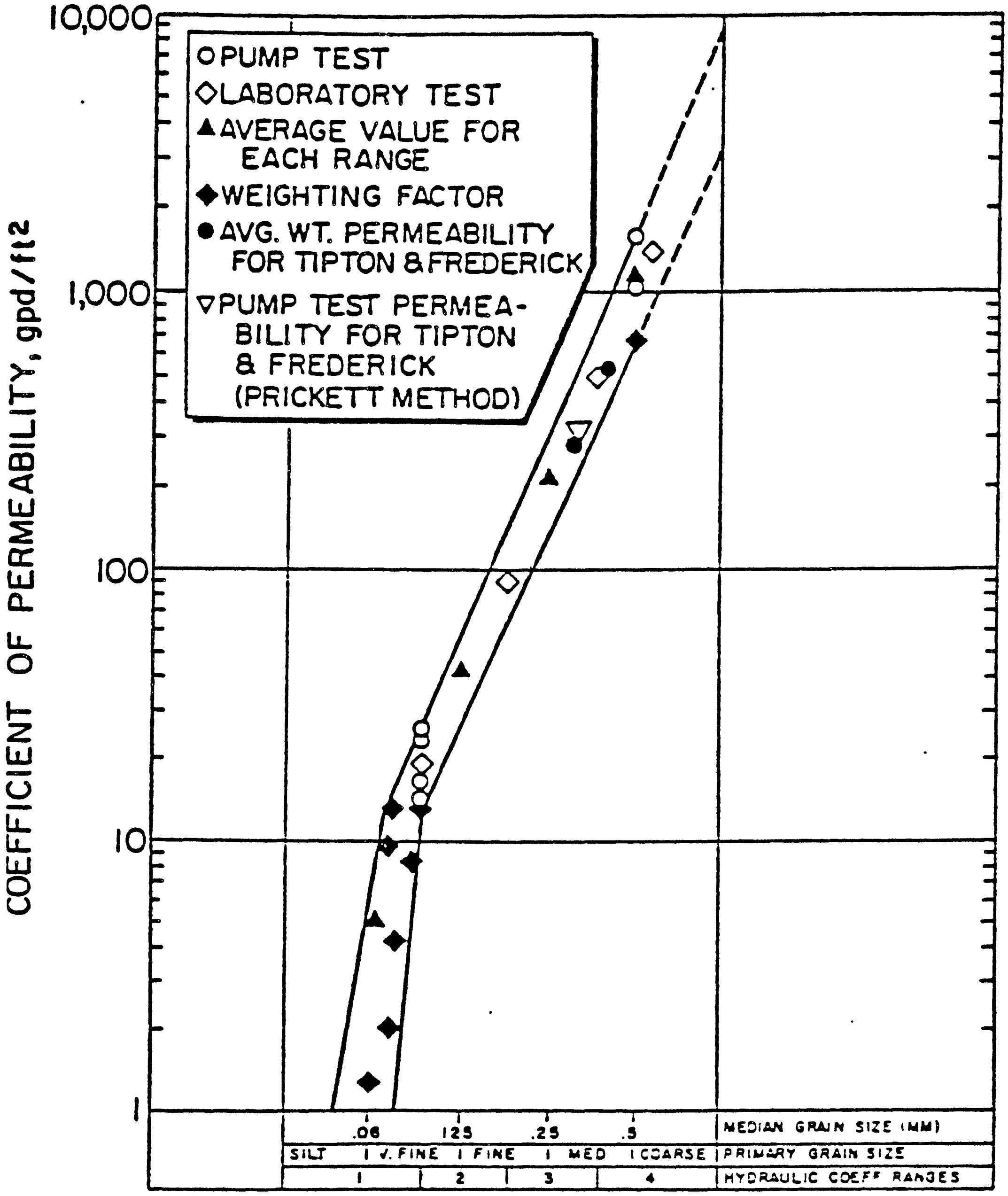


Figure 41. Coefficient of Permeability vs. Grain Size Envelope (After Kent et. al., 1973)

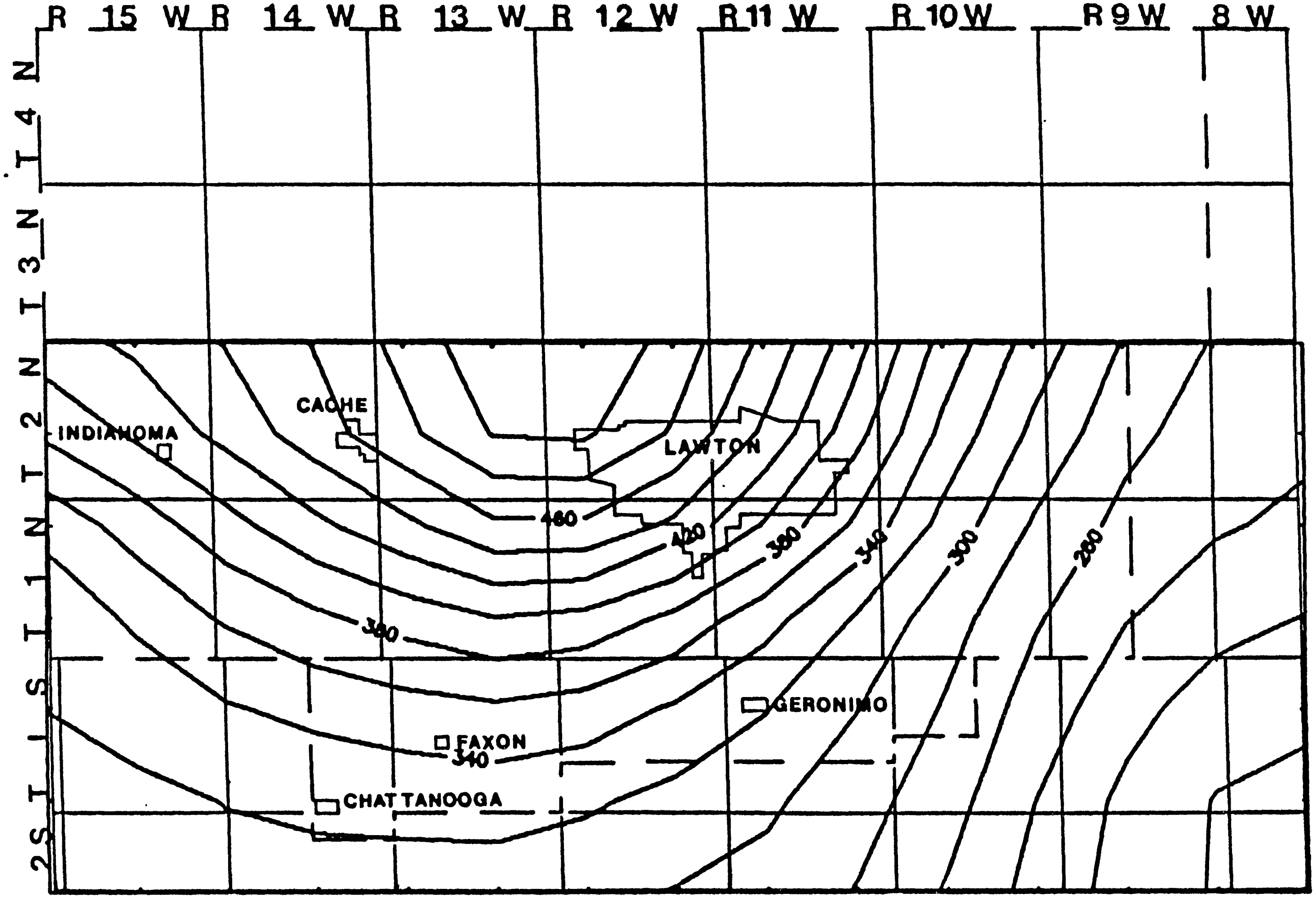


Figure 42. Permeability of Post Oak (gpd/ft 2)

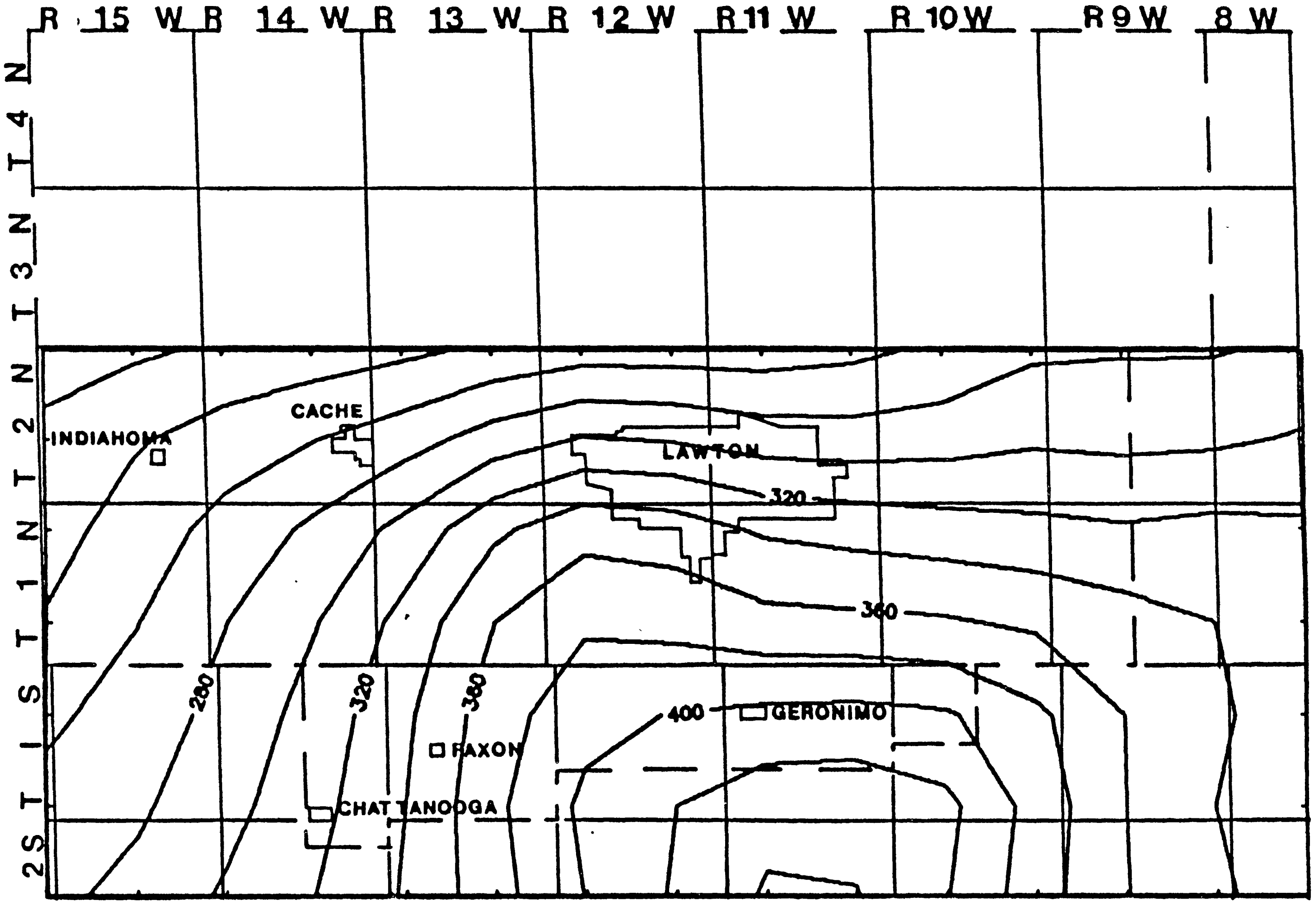


Figure 43. Transmissivity (x10 3 gpd/ft) 1984

were incorporated into the calibration effort. In addition, the 1984 water level of the Post Oak was measured as part of this study.

It was judged that the 1970-71 water levels, and the measured 1984 water-table surface were the best available data for calibrating the ground-water flow portion of the model.

In order to simulate the pumping history of the Post Oak aquifer, the simulation period (1970-1984) was divided into 14 discrete pumping periods. The year 1970 was chosen to start the simulation period because this is the most distant year that both water-level data and nitrogen application rates are readily available. The pumping periods were chosen to coincide with the yearly influx of nitrogen. Because transient flow, rather than steady-state, was assumed a fewer number of pumping periods are required to accurately simulate the natural system.

The sensitivity analysis indicated that the ground-water flow portion of the model is most sensitive to potentiometric gradient, transmissivity and aquifer storativity. However, because the Post Oak aquifer transmissivity is fairly well documented, that parameter was not varied during calibration. The storativity of the Post Oak aquifer, which is much more uncertain, was varied on a trial-and-error basis in order to calibrate the model. The water-table gradient was varied by raising or lowering the entire saturated thickness over a particular node. This was the most powerful tool for calibration, with a poor data base for the true elevation for the base of the aquifer and the surface elevation averaged over 9 square miles the adjustments made for calibration purposes were justified. The ground-water flow portion of the model was considered calibrated when the configurations of the 1971 and 1984 water-table surfaces were reproduced, and water-level measurements taken throughout this time period matched the simulated water levels within a 5-ft. margin of error.

VITA

David Bishop Back

Candidate for the Degree of

Master of Science

Thesis: HYDROGEOLOGY, DIGITAL SOLUTE-TRANSPORT SIMULATION OF NITRATE AND GEOCHEMISTRY OF FLUORIDE IN GROUND WATERS OF COMANCHE COUNTY, OKLAHOMA

Major Field: Geology

Biographical:

Personal Data: Born in Alexandria, Virginia, March 30, 1958, the son of Dr. and Mrs. William T. Back.

Education: Graduated from Washington and Lee High School, Arlington, Virginia, in June 1976; received Bachelor of Science degree from the College of William and Mary, Williamsburg, Virginia, with a major in geology; completed requirements for the Master of Science degree at Oklahoma State University, Stillwater, Oklahoma, in December 1985.