FATE AND TRANSPORT OF AGRICULTURAL CHEMICALS IN A SANDY AQUIFER NEAR PERKINS, OKLAHOMA

By

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University of Udaipur
1980

Master of Science in Geology
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CHAPTER I

INTRODUCTION

The potential for groundwater contamination with excessive usage of fertlizers and pesticides has increased the necessity to explore and gain knowledge about chemical transport by subsurface water movement. Leaching of agricultural chemicals along with soil-water infiltration and deep percolation in many of the cropped watersheds in Oklahoma and other states in the Southern Plains of the United States is of great concern.

Pesticide persistence and mobility in soils and groundwater has traditionally been evaluated by conducting laboratory and/or field experiments over an appropriate range of environmental conditions. These data are very site specific and are valid for certain pesticides tested at that site. In order to evaluate the persistence and mobility of a chosen pesticide or a number of different pesticides under varying environmental conditions, a large quantity of field and/or lab experiments must be conducted. Evaluation of agricultural chemicals based on field and lab experimentation is very expensive and time consuming.

An alternative approach is computer simulation. Within the last decade, some attempts have been made to use models for predicting chemical behavior and movement in unsaturated and saturated zones. The most significant problem with the modeling of chemicals in the subsurface is the unknown transformation processes that may be taking place as nutrients, pesticides and other constituents move through the unsaturated zone to the saturated zone. The success of model predictions depends on the accuracy and availability of data regarding these natural processes which control the solute movement in unsaturated and saturated groundwater zones. The entire mechanism of solute movement through the unsaturated and the saturated zone is a dynamic process which depends upon a large number of soil chemical and environment-related factors. Most hydrogeological studies related to ground water pollution have been targeted toward either unsaturated zone studies or saturated zone studies; however, these two areas can not be looked upon separately when attempting to address a groundwater contamination problem with more success and control.

The parameters which are required for computer simulation include unsaturated and saturated hydraulic properties, pesticide-soil interaction properties, and dispersivity and persistivity in groundwater and boundary conditions. Many of these parameters are not typically characterized for a specific site.

A field monitoring strategy is proposed in order to utilize various techniques in gathering information regarding field processes affecting the fate of agricultural chemicals in unsaturated and saturated zones. The information obtained will be utilized to evaluate the extent of groundwater contamination, resulting from the application of agricultural chemicals, in the alluvial and terrace aquifer at Perkins. The findings of this research would be applicable to the major alluvial and terrace aquifers in Oklahoma, and other midwestern states in the U.S.

Objectives

The primary objective of this study is to evaluate the relation of groundwater quality and agricultural practices; more specifically, to identify and characterize the input parameters required for simulating the fate and transport of nitrate-N and selected pesticides through the unsaturated and saturated zones. Specific objectives are as follows:

1) Establish a ground water monitoring network at the Perkins Site.
2) Characterize the site geology.

3) Define the hydrogeological framework of the Perkins Terrace aquifer.
4) Characterize the hydraulics of the unsaturated zone at the Perkins site.
5) Determine the effects of agricultural practices on groundwater quality.
6) Establish leaching and movement of non-organic chemicals, primarily Nitrate-N and Chloride, in the unsaturated and saturated zones at the Perkins site.
7) Utilize the field data for simulating pesticide and nitrate-n transport in the unsaturated and saturated zones.
8) Conduct field calibration and verification of the Pesticide Root Zone Model (PRZM) and KONIKOW models.
9) Infer, from the findings of this study, whether pesticide and fertilizer usage poses a potential threat of groundwater contamination at the Perkins site.
10) Make recommendations for further monitoring of pesticides in the unsaturated and saturated zones.

Location

The site selected for field-testing this strategy is the Oklahoma State University Agronomy Research Station at Perkins, Oklahoma. The study area is located approximately 8 miles south of Stillwater, near the intersection of State Highways 177 and 33 (Figure 1).

Methods of Investigation

The methods utilized to accomplish the objectives set in this study were conducted in three phases. A simplified expert system approach is applied, where an extensive data base of model parameters is created. An expert system consists of a data base and a knowledge base. The knowledge base is developed by acquiring human expertise in the form of rules, typically many hundred of them together make up the computers "knowledge base". The expert system together with an "inference engine" perform as a program that works out the logical sequences of all rules taken together. Some rules are unequivocal, in the form for example: IF this AND that THEN some results. Others are vague and involve probabilities: IF (to some degree) this AND (to some degree) that, THEN (to some degree) result. It is here that the ability to deal with lore rather than facts come in most strongly. The program works through the rules, asks for appropriate information, and then arrives to conclusions (Gevarter, 1985). Expert systems that have been constructed so far, advise on diverse areas such as

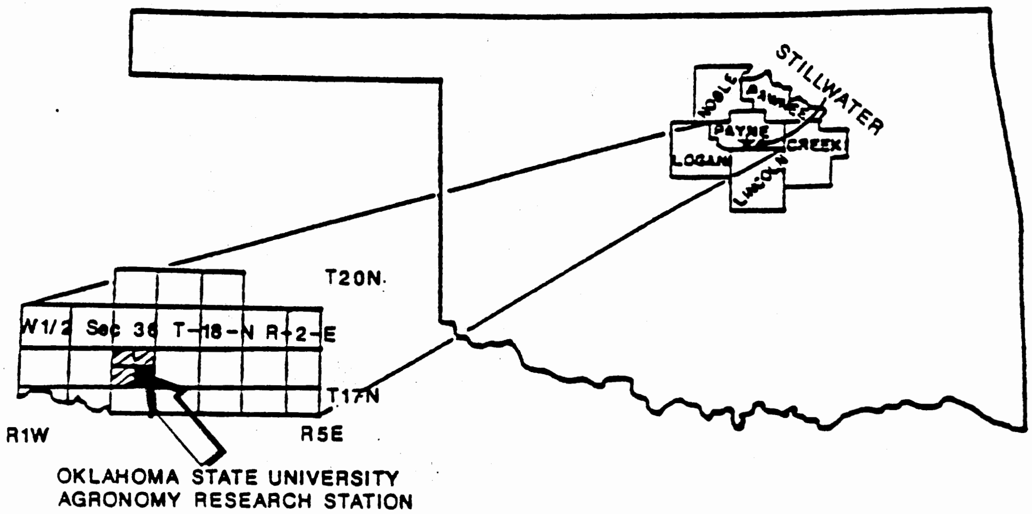


Figure 1. Site Location Map

the diagnosis of diseases, mineral exploration, and recently the expert systems have began to represent areas like seismic analysis, hazardous management and environmental management (Charniak and McDermott, 1986). It was not the intention in this research to develop a computer based expert system, however a database has been acquired which later on can be used to develop an advanced expert system. The basic structure of the simplified expert system is shown in Figure 2. The structure is organized in separate modules. The module definitions and methods used to acquire data for the modules are described in the following chapters:

MODULE	CHAPTER
A	I, II, and III, Appendix A, and B
B	VI, Appendix D
C	V, VI, Appendix E
D	VI, Appendix E and F
E	VII, Appendix G, H and I
F	VII, VIII

The data base generated was utilized for performing model simulation for predicting fate and transport of agricultural chemicals in the subsurface.

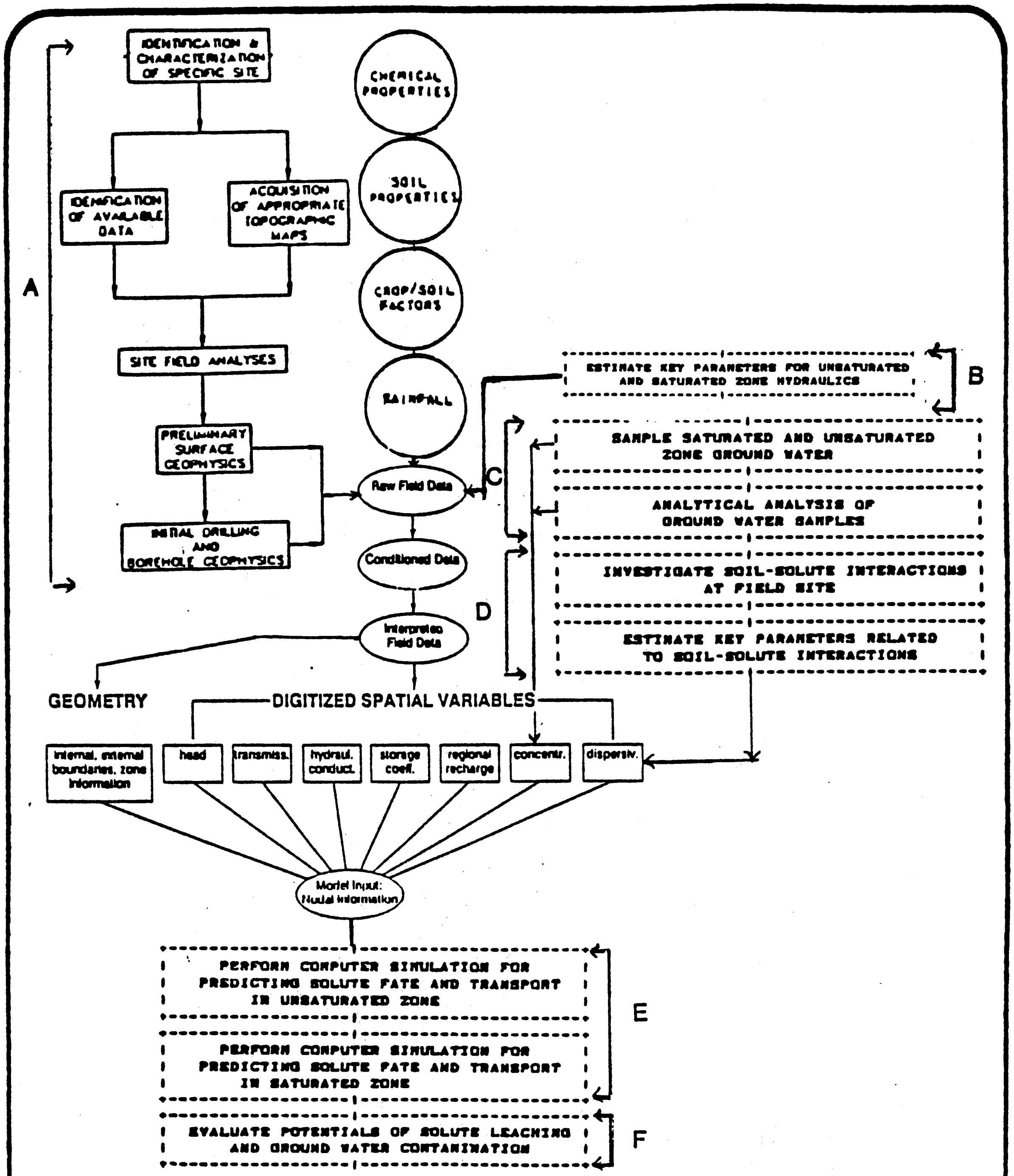


Figure 2. Flow Chart for Simplified Expert System

CHAPTER II

LITERATURE REVIEW

Continued demand for water supplies in the Southwest, including Oklahoma, has intensified the necessity to gain information regarding the effect of agricultural practices. Agricultural applications of fertilizers and pesticides are being increasingly recognized as a significant sources of groundwater pollution. Within the last decade there have been numerous publications related to nitrate and pesticide contamination of groundwater, and this chapter summarizes pertinent literature concerning agricultural impacts on groundwater quality, groundwater sampling, temporal and spatial variations in groundwater quality, transport, fate, and mathematical modeling of agricultural chemicals in the unsaturated and saturated zones.

Groundwater Quality

The U.S. Environmental protection agency (U.S. EPA) has estimated that roughly 50 percent of the Nation's water pollution can be attributed to non-point sources (U.S. EPA, 1984). The large increase in the use of agricultural chemicals and the extensive use of irrigation in past years has made groundwater quality concerns a major issue in the 1980's; as a result, efforts to control non-point source pollution have become a major priority. Nitrates and pesticides are the two major categories of agricultural contaminants of groundwater (Kovan, 1988). Recent studies have shown that agricultural activities are the largest source of increased nitrate levels in groundwater. Current research (Staver, Magette, & Brinsfield, 1987; Angle, Gross, & McIntosh, 1988; Kent, Dwivedi, & Naney, 1987; Naney, Smith, Berg, & Kent, 1987; Kent, & Dwivedi, 1988) suggests that farm chemicals which are highly mobile in water, such as nitrate, may impact ground water even when used according to recommended guidelines.

Natural soil nitrogen, rare geologic nitrogen deposits, manures, sewage and precipitation all contribute nitrogen to groundwater, however numerous studies on various scales, from controlled plot studies to basinwide inventories have shown that nitrate concentrations in groundwater can be directly related to agricultural land use (Hallberg, 1986; Keeney, 1986; Adelman, 1985; Blodgett, 1986). In particular many of these studies show a direct relationship between nitrate leaching to groundwater and nitrogen fertilization rates and/or fertlization history

(Adelman, 1986; Baker, 1985; Hallberg, 1985; Hill, 1982). The greatest nitrate problem arises with the heavy fertilization commonly practised throughout the rain-fed Corn belt, and in irrigated agriculture in the western and southeastern U.S. The five major corn-producing states (Iowa, Illinois, Indiana, Minnesota, and Ohio) have 57% of the total U.S. harvested corn area and use 26% of the fertilizer nitrogen (Harget and Berry, 1983). Data obtained from various field investigations in these states indicate concentrations of nitrate-nitrogen in the tile drainage ranged from 10 ppm to 81 ppm (C.A.S.T., 1985). Extensive summarization of literature related to agricultural contamination of groundwater has been conducted by Canter, 1987; Halberg, 1986; Baker, 1984; Connely, 1984; Barles, 1987; Nielsen, 1987; Halberg, 1987; and Dobkowski, 1987.

Compared with nitrogen, pesticide losses in groundwater and surface waters are quite low, usually less than 5 percent (Baker, 1985; Hallberg, 1986). The potential health effects from low concentrations of pesticides generally occurring in groundwater are unclear, both public and private water supply wells have been closed in several states. Routine monitoring of groundwater across the nation has resulted in detection of as many as 25 pesticides (Holden, 1986). The Environmental Protection Agency (Cohen and others, 1984) has listed 12 pesticides that have been detected in drinking water wells from the limited monitoring that has been done. Occurrence of potentially toxic chemicals in groundwater, even in low concentrations, is of real concern because of potential for long-term and widespread exposure to the public (Hallberg, 1986). A preliminary exploratory study on the extent of groundwater contamination from agricultural use, involving monitoring groundwater from major alluvial and terrace aquifers in Oklahoma has recently been conducted. The study reported no detection of any pesticides in the sampled groundwater and concluded that pesticides, when properly used, do not pose a threat to Oklahoma groundwater (Marak, 1986).

Cyclic Fluctuations in Groundwater Quality

Most previous research and work efforts related to groundwater pollution investigations have relied on the data obtained from scant and irregular sampling periods. Past researchers have based their predictions about the temporal and spatial migration of contaminants on such data, assuming that the natural groundwater quality is nearly constant at any particular site and therefore, does not change rapidly. Pettyjohn (1976) reported that the chemical quality of groundwater can change significantly and rather rapidly, perhaps by as much as an order of magnitude within a few hours or days. A concept of cyclic fluctuations and their mechanisms was discussed by Pettyjohn in his study of causes and effects of cyclic changes in groundwater quality (Pettyjohn, 1982). Concentrations of many water-soluble substances are stored in the vadose zone, and during each recharge event the macropores and fractures can serve as highly permeable connecting routes between the land surface and the water table (Anderson, 1977; Robert and others, 1986; Smettem, 1986; Hillel, 1987).

Transport and Fate of Agricultural Chemicals

Solutes move in the unsaturated zone along with infiltrating water and in response to concentration gradients. Simultaneously, the solutes react among themselves and interact with the solid matrix of the unsaturated zone. Hillel, (1980) reported that these interactions are strongly influenced by soil ph, temperature, oxidation-reduction potential, composition and concentration of the solutes in solution. The key physical factors which govern inorganic solute movement in the unsaturated zone are: 1) convection; 2) diffusion; and 3) hydrodynamic dispersion. During transport in the unsaturated zone, specific pollutants in solution may flow at a rate which is less than equal, equal to, or greater than the water flow rate. Wilson (1983) states that conservative ions, such as chloride and nitrate, move at essentially the same rate as water; in contrast, the mobility of heavy metals and organics is restricted because of a number of attenuating factors. Wilson also researched different attenuation mechanisms and summarized the primary mechanisms responsible for attenuating pollutants in the unsaturated zone. These mechanisms are as follows:

Physiochemical processes such as:

1) Physical/chemical reactions
2) Biological processes

The physical/chemical reactions include adsorption, volatilization, chemical degradation or decay and hydrolysis. The biological attenuation involves microbiological breakdown of organic chemicals. Research relevant to the problem of organic chemicals transported through soil may be broadly divided into two categories: 1) studies characterizing pesticide adsorption processes and 11) studies modeling the convective, dispersive and adsorptive transport of pesticides through soils (Elabhad, 1987). The published literature on adsorption of organic chemicals is quite voluminous and has been summarized by Bailey and White, 1972; Green, 1974; Weed and Weber, 1974; Hamaker and Thompson, 1972; Rao and Davidson, 1980; Calvet, 1980; Kenaga and Goring, 1980; Karickhoff, 1981; Mingelgrin and Gerstl, 1983. Much of the available information relevant to adsorption mechanisms in soils is empirical, and largely controlled by the diverse and heterogeneous nature of soil properties at different sites. The lab determinations and results often do not correlate with the actual solute movement profiles in the field, because of differences in scale and boundary conditions. Results from different field studies have indicated that large spatial variability exists in the solute movement characteristics of the unsaturated zone (Van De Pol and others, 1977; Jury and others, 1986; White, 1986; Richter and Jury, 1986; Starr and others, 1986). A debate continues concerning the mechanisms of soil-moisture movement through the unsaturated zone. Several mechanisms have been postulated to be responsible for the movement of water in the unsaturated zone. These mechanisms include: piston or wetting-front flow and macropore or fracture-flow mechanisms (Robert and others, 1986; Smettem, 1986; and Moore, 1986).

Current views of infiltration of water into soils are based on nearly complete displacement of soil water by incoming water (Piston flow). In general rapid flow (macropore flow) in soils and its effect on water and solute displacement have not been considered very important by the majority of researchers (Hillel, 1987).

Lawer and others (1882) concluded that water moved through preferential paths, only slightly interacting with surrounding soil in his study of solution samples from field tile drain. Thomas and others (1978) investigating earlier work involving solute movement, concluded that water added to a soil does not stay in surface soil, but will move as much as 20 times deeper than calculated from piston like flow. Utilizing the above mentioned theory ground water recharge will become much sooner than expected. McMahon and Thomas (1974), Bouma and Anderson (1977), and Thomas (1979), theorized that some solutes moved through the large pores, by-passing much of the water already within the peds. More recently a large number of investigations have been conducted relevant to macropore flow in soils. Smettem and Collis-George (1979) in their study of the influence of cylindrical macropores on steady-state infiltration in a soil under pasture indicates that steady-state infiltration was controlled primarily by the size and number of macropores within an infiltrometer ring. Robert and others (1986), Smettem (1986), Moore and others (1986) reports macroporosity was a significant factor in controlling the hydraulic conductivity of the unsaturated soils and supported the theory of water and solutes moving along preferential paths. Beven and Germann (1982) reviewed the significance of large continuous openings (macropores) on water flow in soils. The research indicates that the presence of macropores may lead to spatial concentrations of water flow through unsaturated soil that will not be described well by a Darcy approach to flow through porous media. This has important implications for the rapid movement of solutes through soils. Hillel (1987) in his review of unsteady flow in layered soils states that transient and random (preferential) paths associated with unsaturated flow are likely to occur in layered soils. The wetting front, instead of advancing continuously in a piston flow manner from one soil layer to the next, may begin to propagate downwards along vertically continuous macropores or preferential paths. However Hillel adds that no systematic empirical data, or a proven comprehensive theoretical framework, exists by which to assess where, when, and according to what pattern, such phenomena are likely to occur.

Modeling

During the past few years, a great deal of effort has been directed towards the understanding and quantification of physical and chemical processes which affect the transport of contaminants in the subsurface (Abriola, 1987). Investigators have established through the laboratory and field observations that prediction of fate and transport of contaminants in the subsurface is a much more complex subject than heretofore imagined (Abriola, 1987).

Successful application of computer models for predicting the environmental fate of chemicals in unsaturated and saturated zones, requires the collection of a wide variety of extensive field data (Carsel and others, 1985). Wagner and others (1984) evaluated four computer models for simulating solute transport in unsaturated soils, and concluded that the application of any of these models in a predictive mode requires detailed sets of data characterizing physical and chemical soil properties, solute dispersion and decay rates, and values for the boundary conditions (Figures 4 and 5). Kent and others, (1986) reported the necessity of field controlled parameters for accurately predicting solute fate in groundwater systems when modeling solute transport through groundwater. Jury and others, (1985) in their research for application of two unsaturated models to actual field conditions, signifies the importance of extensive field data required for calibration and validation of solute transport models.

CHAPTER III

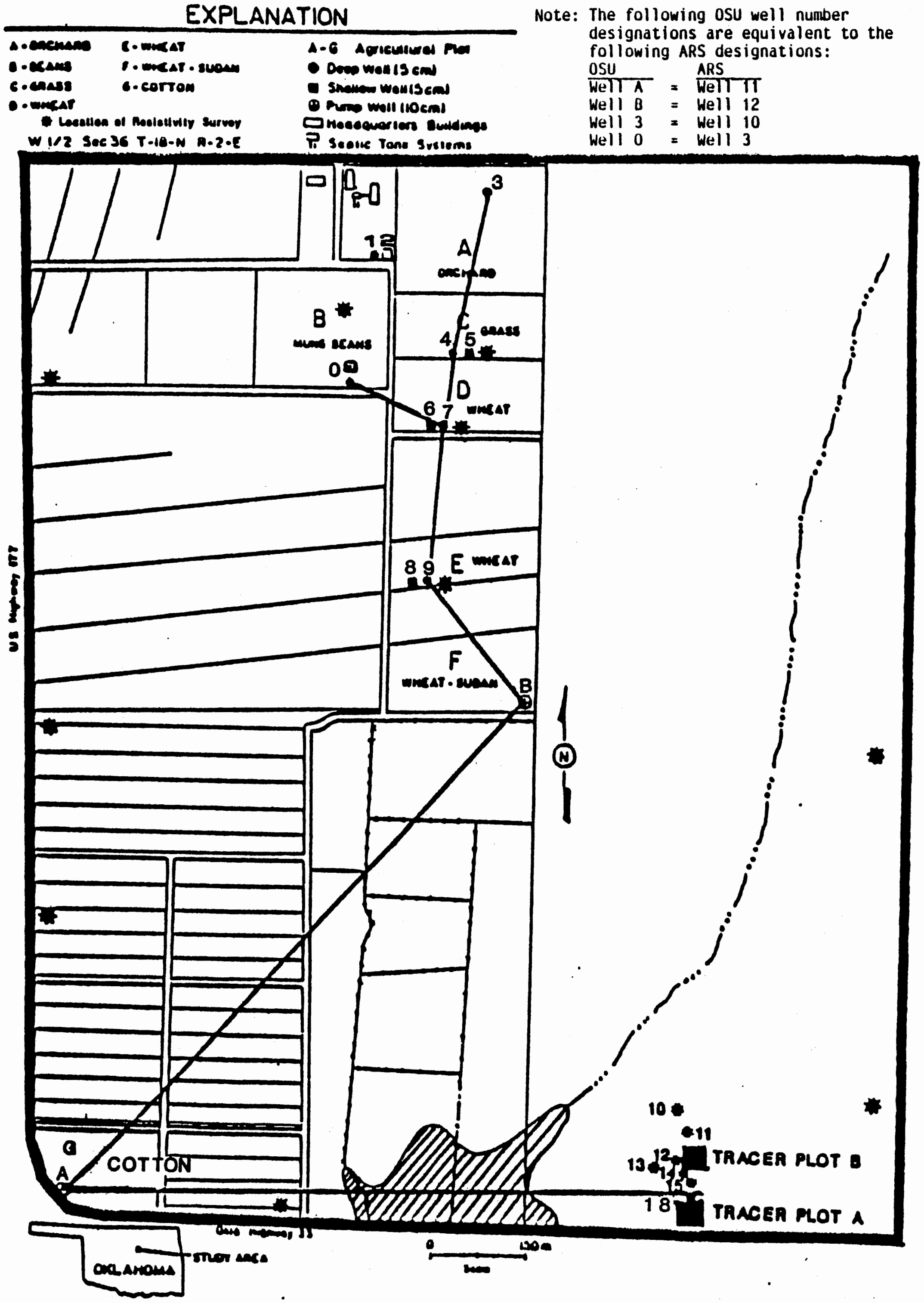
GEOLOGY AND SOILS

Physiography

The study area lies in a transitional zone between the Central Redbed Plains and the Northern Limestone Cuesta Plains (Curtis and Ham 1957). Most of the surrounding countryside has been used for farming and cattle ranching. The topographic expression consists of rounded hills and gentle valleys. The study area lies in the Cimarron River drainage basin of the Arkansas River. The Cimarron River is 1 1/4 miles south of the site and flows towards the southeast. The mean temperature of the area is 59^{0}F (28^{0}C); the average annual rainfall is approximately 35 inches (87cm); (Shelton, Ross, Garden and Franks 1985).

Geologic Framework

The interpretation of the local geologic framework was aided by data obtained through the drilling of 20 monitoring wells in the study area (Figure 3). Depths of the wells ranged from 21 to 58 feet. Eleven wells



Note: The following OSU well number designations are equivalent to the following ARS designations:

OSU		ARS
Well A	=	Well 11
Well B	=	Well 12
Well 3	=	Well 10
Well 0	=	Well 3

Figure 3. Location of Groundwater Monitoring Wells at Agronomy Research Station

penetrated bedrock. Drillers logs are included in Appendix B, along with the gamma ray correlation.

Bedrock Geology

The bedrock geology in the study area is dominated by interbedded sandstones, siltstones, and shales belonging to the Wellington formation of Permian age, the lowest unit of the Cimarron Series. The Wellington Formation is comprised of lenticular sandstones, shales, and thin carbonate beds (Shelton. 1985).

Only the upper few feet of bedrock were penetrated during the drilling. The well cuttings obtained from the bedrock consisted of red-brown to gray shale and orange-brown fine grained, sandstones with interbedded limestones. From a regional perspective, the area lies on the Central Oklahoma Stable Platform. The bedrock has been warped by Permian orogenic activity. No faults have been recognized locally (Bingham 1975).

Quaternary System

The surficial geology of the study area is dominated by alluvial terrace deposits formed by the Cimmaron River. These deposits act as a principal aquifer in the area and are commonly referred to as the Perkins Terrace Aquifer. The Perkins Terrace Aquifer is an unconsolidated terrace deposit of Quaternary age, consisting primarily of fine to medium grained sand with occasional thin discontinuous silt and clay layers throughout. The terrace deposits are overlying the Permian bed rock, which consists of red shales and sandstones (Blair, 1975). These sediments, except the eolian silt, occur as mappable units in the flood plain and terraces of the Cimarron River and along major creeks (Figure 4).

Sample cuttings from drilling consist primarily of fine-grained red, orange, and tan silty sands. These fine-grained units are often separated by yellow, tan, and gray silty clay lenses. Two stratigraphic cross sections, Figures 5 and 6 and 7, were plotted utilizing the sample cutting data and geophysical (gamma ray) data. There is a general increase in grain size in the stratigraphic section from fine-grained material in the top to coarse-grained sediments in the bottom of the section, this trend is indicative of fluvial sedimentation. This is clearly shown by sample cuttings from monitoring wells 11 and 12. In general, the geophysical logs and the sample cuttings indicate the presence of isolated and discontinuous clay lenses throughout the study area. As typical of terrace deposits, the thickness of the unconsolidated section at the Perkins site is topographically controlled. The saturated thickness for the Perkins Terrace aquifer is

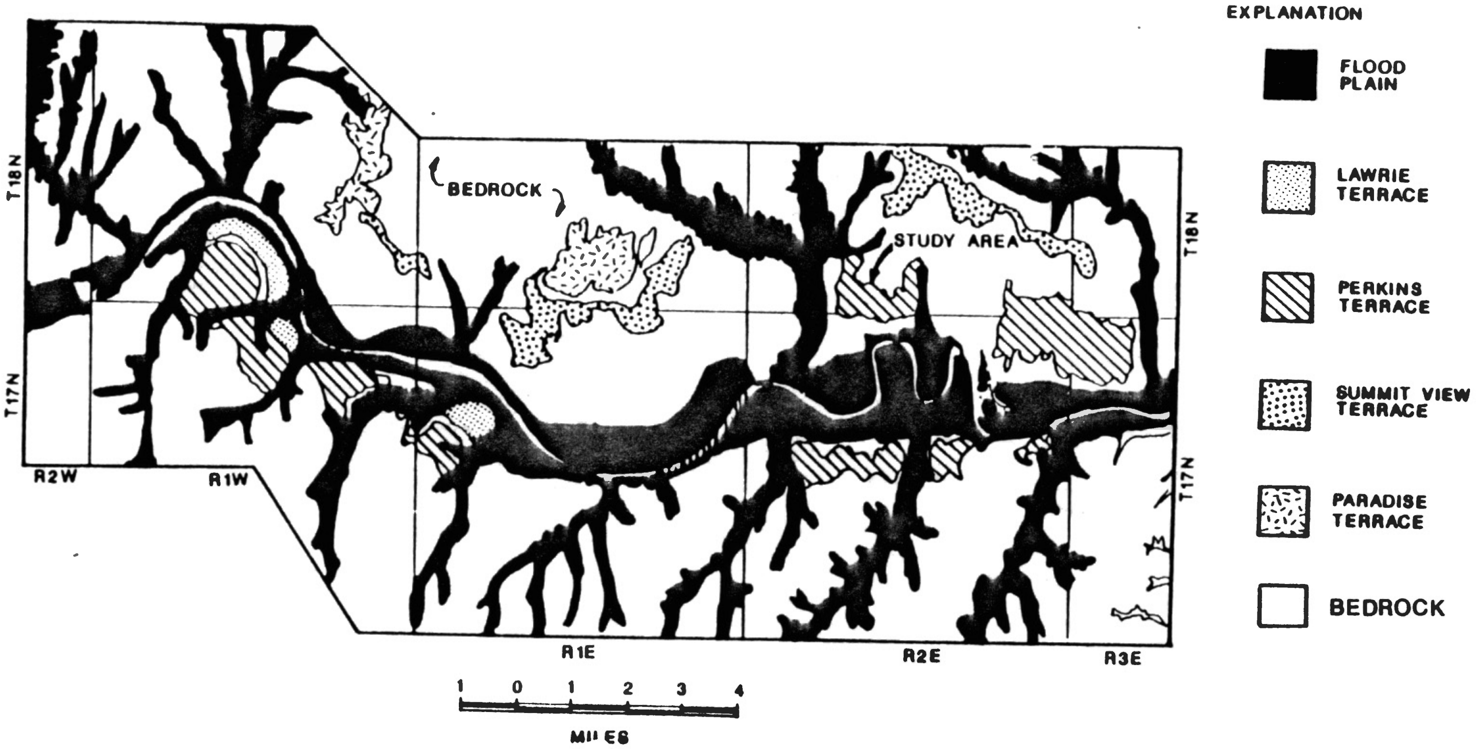


Figure 4. Alluvial Surface Map of the Cimarron Valley from Interstate 35 to Perkins, North-Central Oklahoma (After Blair, 1975)

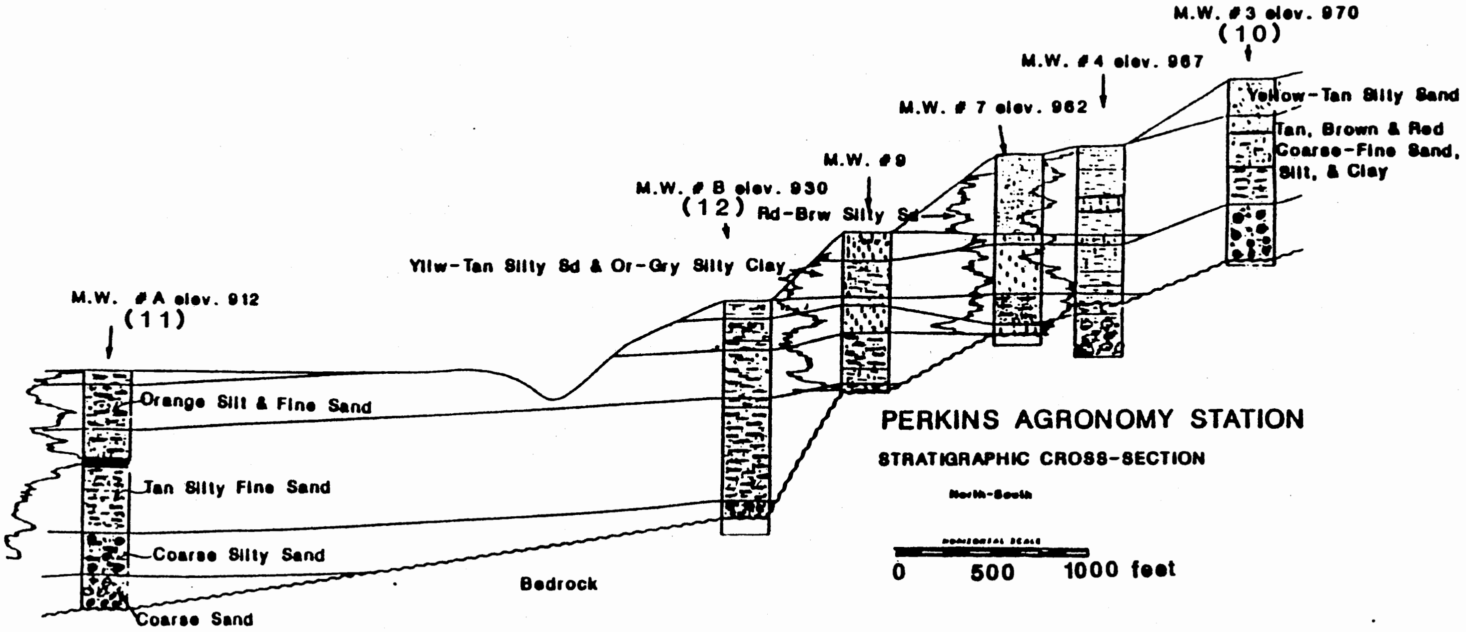


Figure 5. North-South Stratigraphic Cross-Section

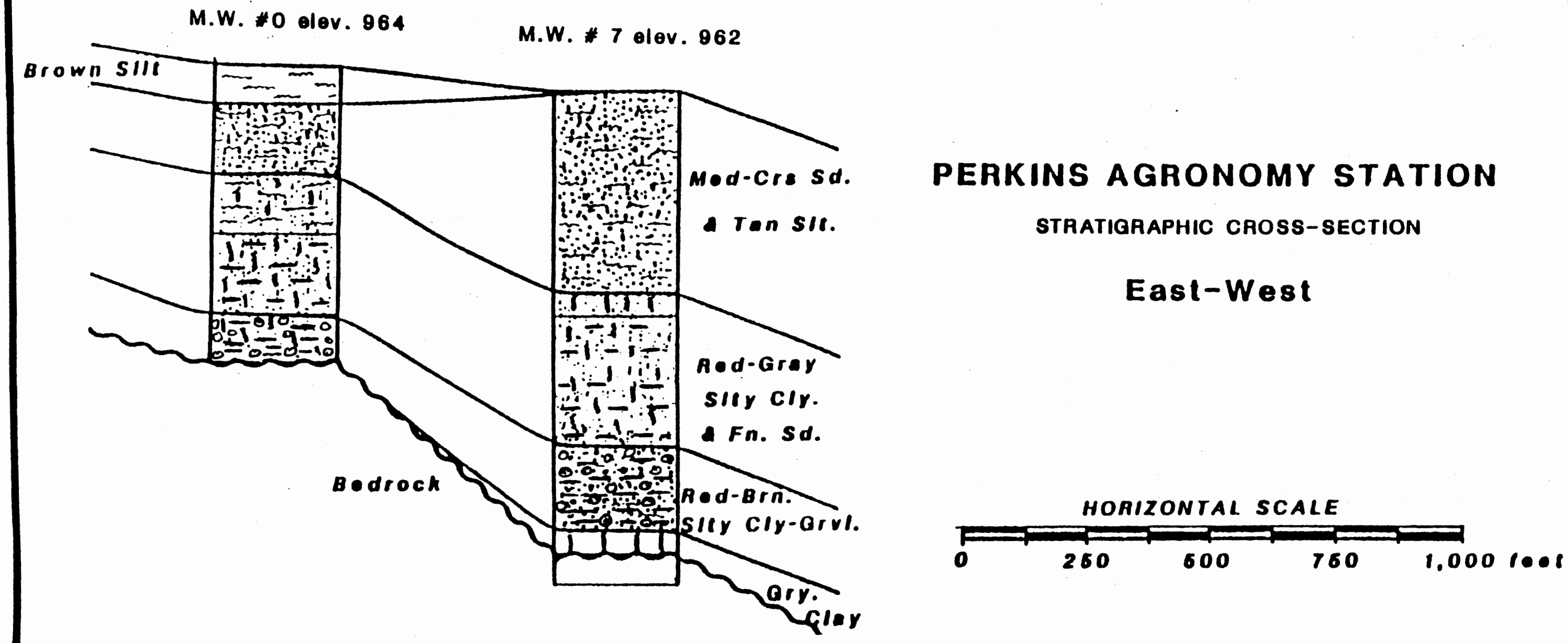


Figure 6. East-West Stratigraphic Cross-Section

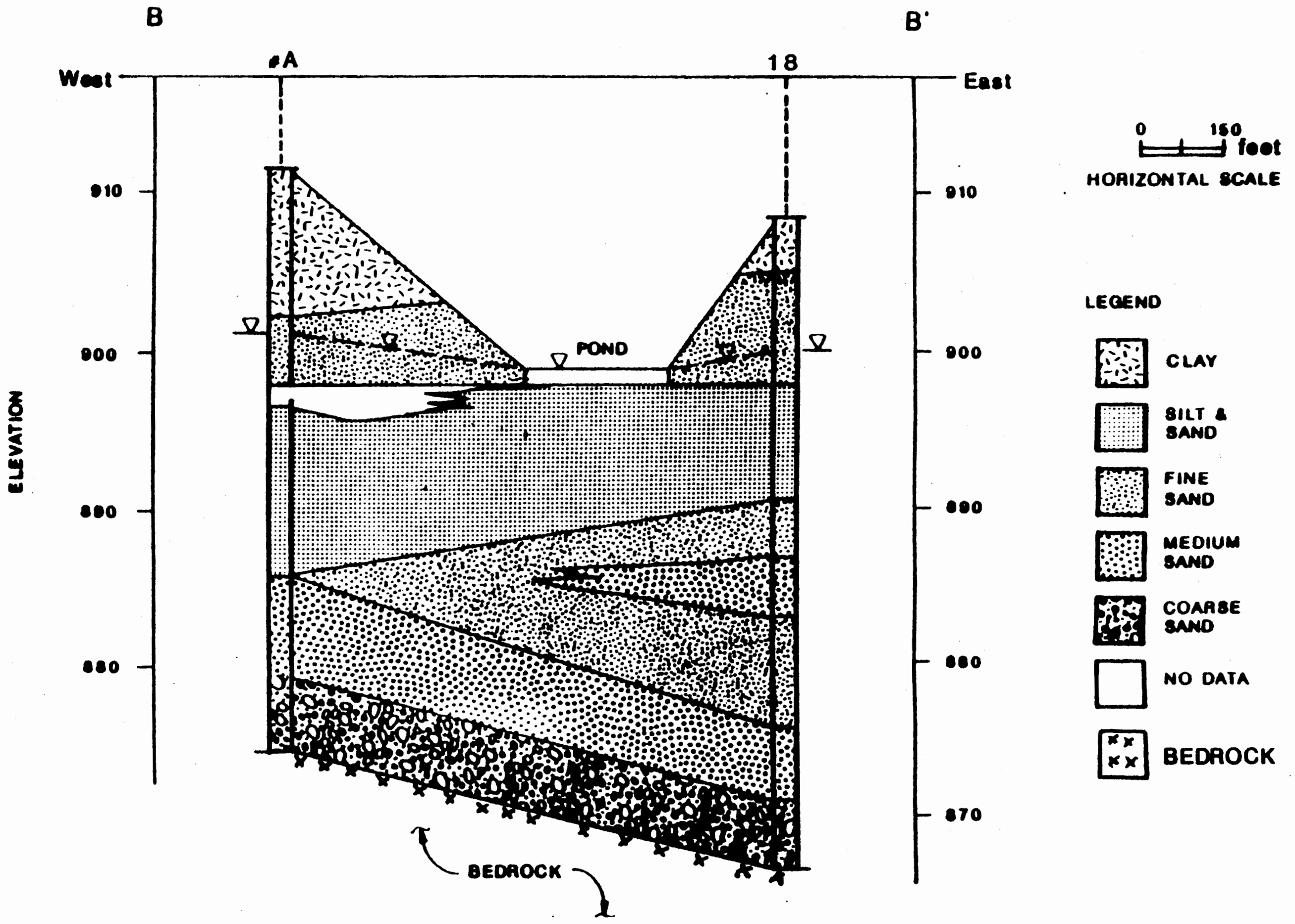


Figure 7. East-West (B-B') Stratigraphic Cross-Section

plotted in Figure 8 and is outlined in Table I. The overall thickness increases consistently south towards the Cimarron River.

Soils

The geologic framework of the area exerts a strong influence on soil development. Soils of terrace deposits are cultivated where the surface is flat and is not subject to rapid erosion. Terrace soils in the study area are representative of the Dougherty, Teller, Reincach, and Eufaula Series (Shelton, 1985). The two soils which cover approximately 80 percent of the study area belong to the Teller and Konawa soil groups. A map of typical pattern of soils and underlying material in the Teller-Konawa unit and other soil information is included in Appendix C.

Teller Soil

Teller soils occur on ridgetops and side slopes. These soils are deep, nearly level to gently sloping, and well-drained. Typically, the surface layer is reddish brown loam. The subsoil consists of reddish brown loam, yellowish red clay loam, and red fine sandy loam. These soils are well suited for raising small grains, sorghums, cotton, legumes and grasses (Henley and others, 1987).

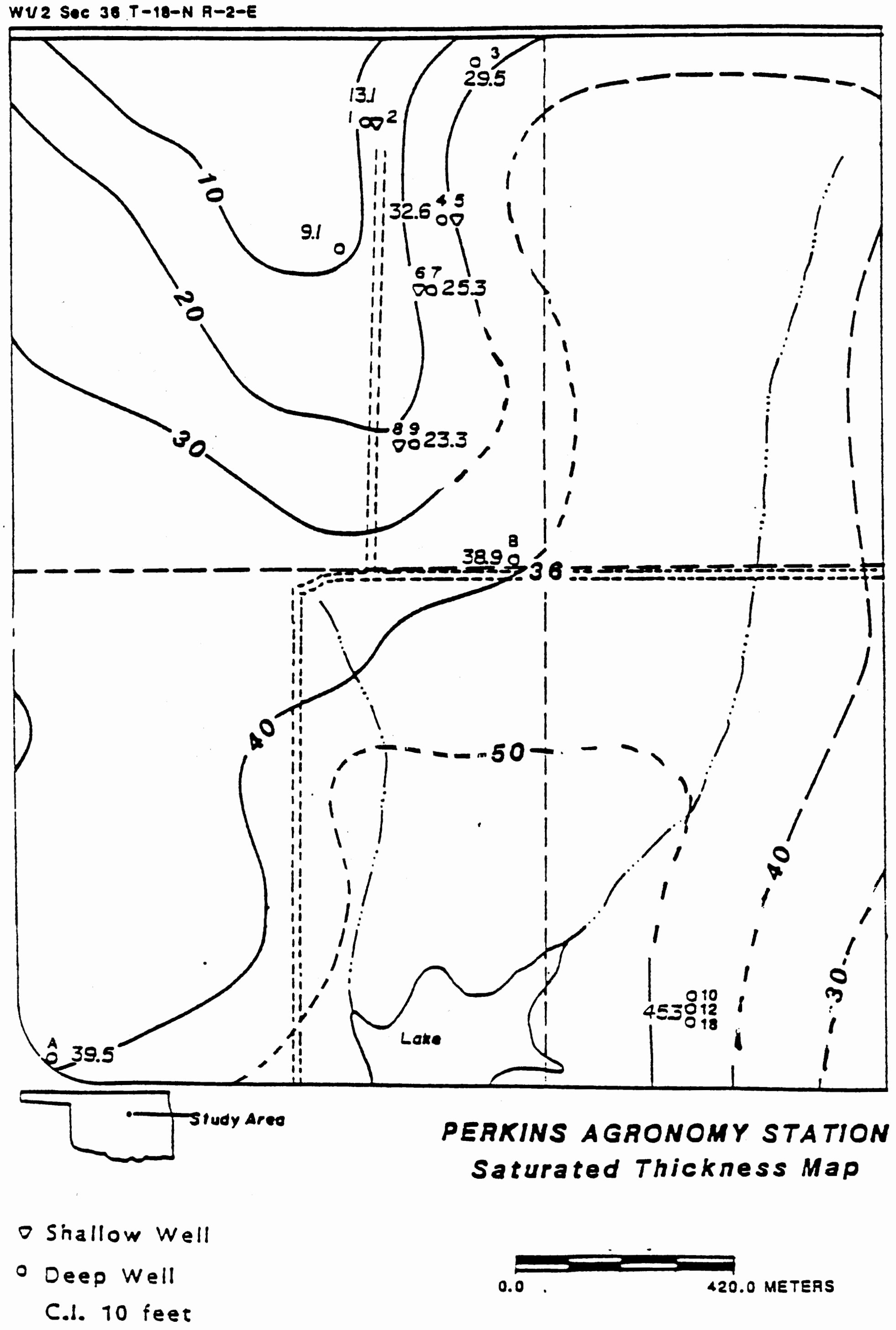


Figure 8. Saturated Thickness Map of Perkins Terrace Aquifer

TABLE I

SUMMARY OF WATER-TABLE ELEVATIONS, BEDROCK ELEVATIONS, AND SATURATED THICKNESS

Well	Elev. of TOC (ft)	Stick Up (ft)	Land Surface Elev. (ft)	Depth to Water (ft)	Elev. of Water Table (ft)	Depth to Bedlock (ft)	Elev. of Bedlock (ft)	Sat Thick (ft)
1	974	1.42	972.58	16.91	957.09	30	942.58	14.51
2	974	1.38	972.62	17.05	956.95	—	—	—
3	974	1.5	962.50	15.91	948.09	25	937.50	10.59
4	967	1.46	965.54	14.34	952.66	46.5	919.04	33.62
5	967	1.39	965.61	15.12	951.88	—	—	—
6	962	1.2	960.80	13.55	948.45	—	—	—
7	962	1.2	960.80	13.69	948.31	39	921.80	26.51
8	945	1.4	943.60	12.31	932.69	—	—	—
9	945	1.27	943.73	11.73	933.27	35	908.73	24.54
10	979	1.4	977.60	10.43	968.57	39	938.60	29.97
11	912	1.29	11.47	910.71	900.53	51	859.71	40.82
12	930	1.55	928.45	12.03	917.97	51	877.45	40.52
E-P	909	0.0	909.00	12.67	896.33	57	852.00	44.33

Bedrock elevation = elevation T.O.C. - height of casing above pad - depth to bedrock

Potentiometric surface = elevation T.O.C. - depth to water from T.O.C.

Saturated Thickness = depth to bedrock + height of casing above pad - depth to water from T.O.C.

Transmissivity = K * B, where K = 364 gpd/ft*ft

Surface elevation = elevation T.O.C. - height of casing above pad

Konawa Soil

Konawa soils also occur on ridgetops and side slopes. These soils are deep, very gently sloping to sloping, and well-drained. Typically, the surface layer consists of brown and light reddish-brown, fine, sandy loam. The subsoil contains red, sandy, clay loam and red, fine, sandy loam (Henley and others, 1987).

Detailed profiles describing different horizons in the Teller and Konawa soils and graph analysis showing the percent of clay, organic matter, and cation exchange capacity for the Teller and Konawa soils are included in Appendix C.

CHAPTER IV

HYDROGEOLOGICAL FRAMEWORK

Groundwater wells in the study area provide water for rural homes, for municipal use in small communities, and for farming. The area most favorable for ground water development lies along the flood plain and terrace deposits of the Cimarron River (Bingham, 1980). The average saturated thickness of the Perkins Terrace Deposit ranges from 25 to 55 feet (7 to 18 m). The average yield is about 20 to 60 gpm, although yields of 100 gpm are possible where wells penetrate local lenses of gravel at the base (Shelton 1985). The total annual precipitation is 32 inches (88 cm) or 70 percent, and usually falls between the months of April and September (Shelton, 1985).

Water Levels

Historical water levels have been described by Bingham, (1980) in the reconnaissance of water resources of the Enid Quadrangle, north-central Oklahoma (U.S.G.S., 1980). Water level fluctuations are created by variations in precipitation, evapotranspiration and by intermittent pumping of water from nearby wells. Groundwater level measurements were recorded for the monitoring wells installed at the Perkins site during the period between January, 1986 and June, 1988. The potentiometric surface map containing groundwater flow paths is represented in Figure 9. Precipitation and evaporation data is shown in Figure 10. A composite plot containing hydrographs for all monitoring wells at the test site is included as Figure 11. This plot provides information about the spatial variability in recharge response time across the site. The hydrographs correlate quite well with the frequency and magnitude of precipitation. The correlation of precipitation and hydrograph response indicates a lag of 20 to 30 days between the maximum water level increase and the time of precipitation. The precipitation data is plotted as monthly cumulative precipitation at the end of each representative month. The short-term (bi-weekly) data shows an instantaneous response of the water table to precipitation, which is indicated by the increase and decrease of water inorganics in the ground water as a response to precipitation. Gillham (1987) also indicates that an instantaneous response of the water table to rainfall will occur if the capillary fringe extends to the land surface. The composite hydrograph plotted for data collected from January, 1987 to June, 1988 shows a general

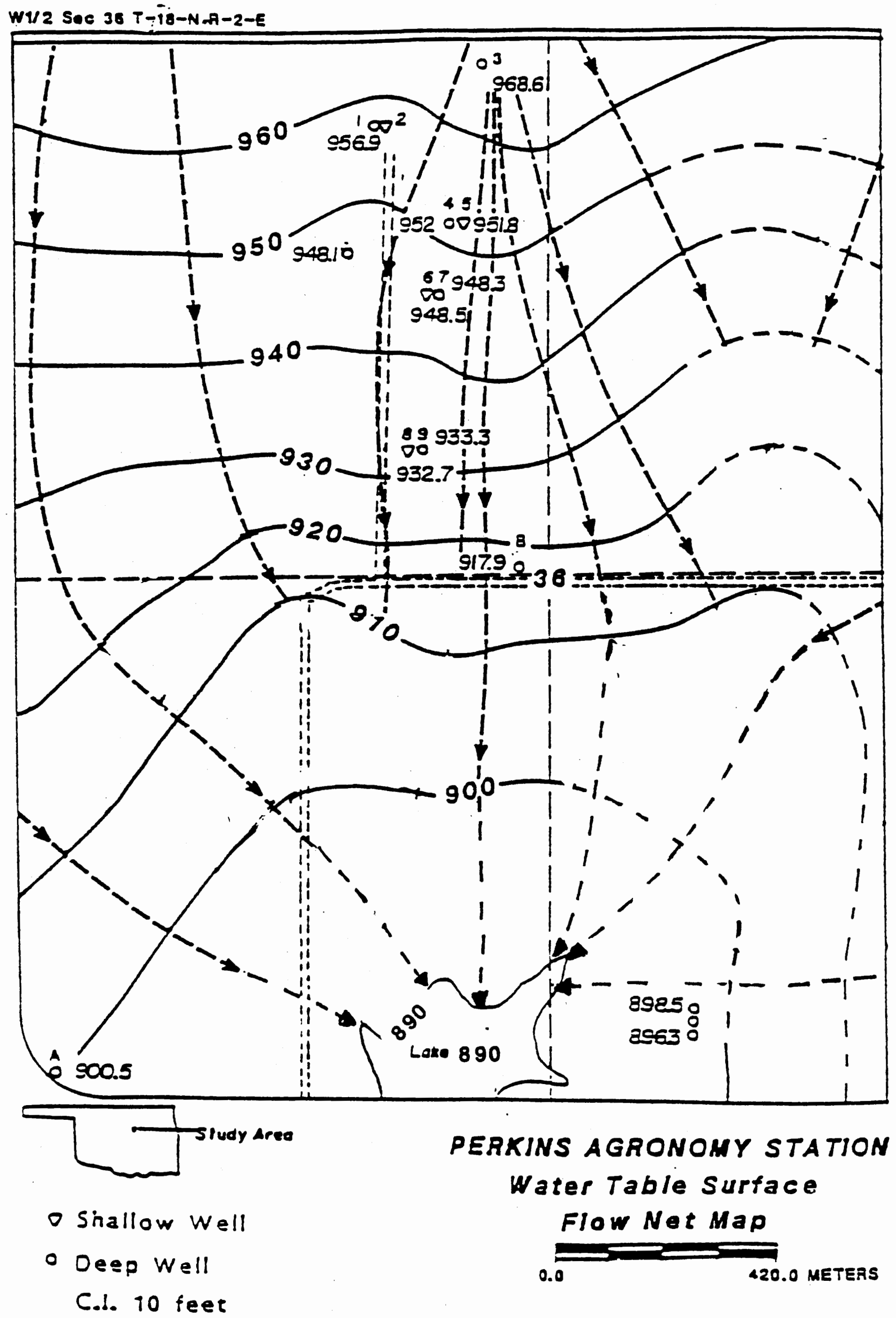


Figure 9. Potentiometric Surface Map of Perkins Terrace Aquifer

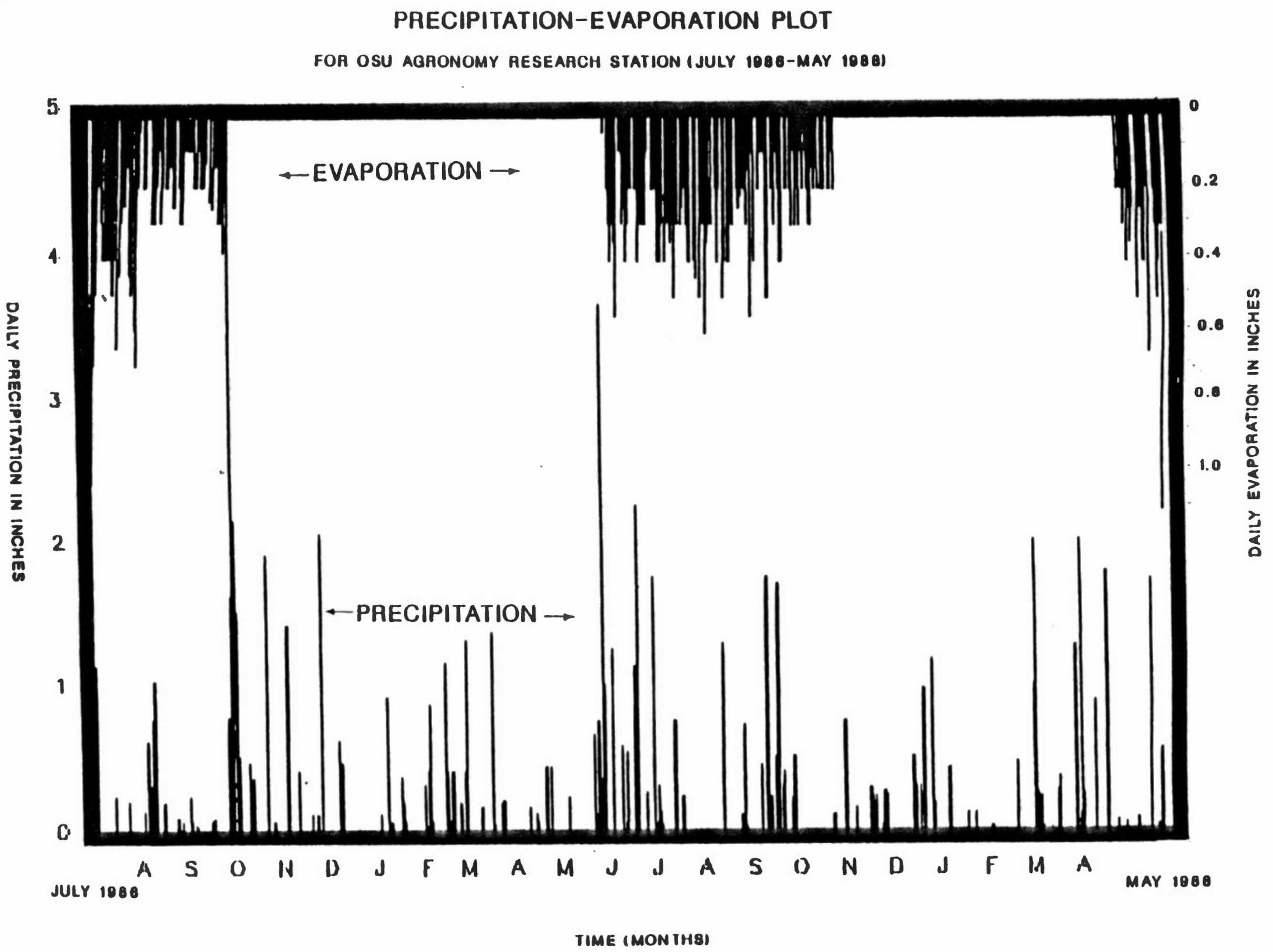


Figure 10. Precipitation-Evaporation Plot for Agronomy Research Station

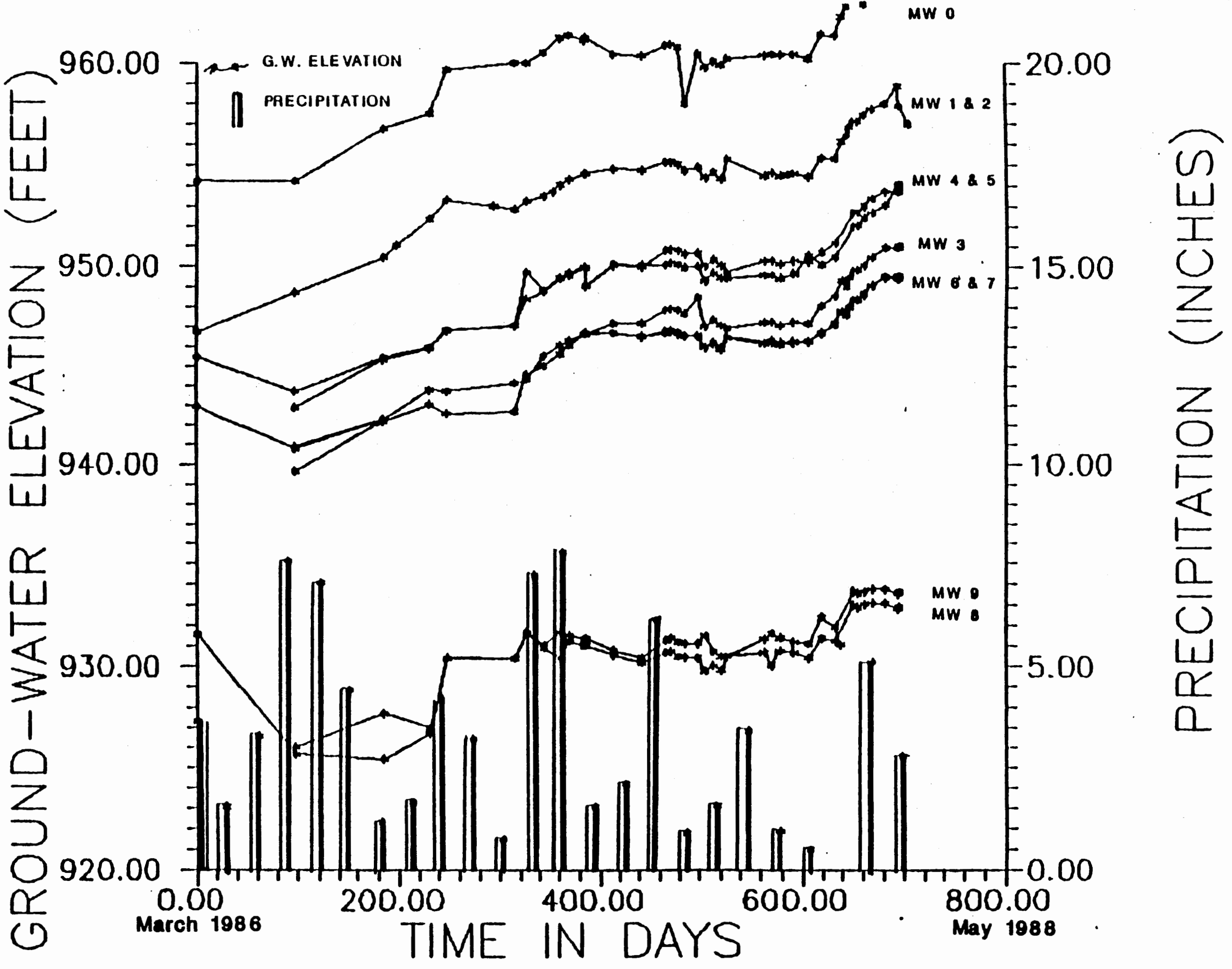


Figure 11. Composite Hydrographs for Groundwater Monitoring Wells at Agronomy Research Station

increase in water levels in all monitoring wells ranging from 3 to 5 feet (1 to 1.5 m).

Slug tests were conducted repetitively on an individual well at intervals of 3 to 4 weeks. Slug tests were also performed by the evacuation of different volumes of slug at each different test site. Slug test results for all tests are included in Table II. The results indicate a greater degree of variation in the hydraulic conductivities obtained from slug tests performed on different monitoring wells. A general trend of an increasing K with an increasing frequency of slug tests is noted. The increased trend may result from removal of finer sediments around the screen during each slug test. This brings forth the question: "How representative are estimates ?" from slug test technique. The recovery time resulting from a slug test is a factor of aquifer storitivity, aquifer transmissivity, gravel pack storage and transmissivity, and finally, the open surface area of the well screen. Each time the slug test was performed by the evacuation of a certain volume of water, the well was further developed and the hydraulic conductivity was increased to a degree. It is hard to stipulate exactly how many times a well should be developed in order to obtain true aquifer representative values. The average hydraulic conductivity values obtained for slug tests range from 68 gpd/ft^2 to 323 gpd/ft^2.

TABLE II

SLUG TEST RESULTS

DATE	MW 0	MW 1	MW 3	MW 4	MW 5	MW 6	MW 7	MW 9
7/87	25	31	25	32	10	200	40	310
10/87	27	84	27	33	13	160	44	403
12/87	•	•	•	•	•	•	44	404
01/88	•	300	•	53	•	•	57	201
01/88	•	315	•	269	•	•	62	404
01/88	•	•	•	440	•	•	62	1262
02/88	•	300	•	620	•	•	67	1345
02/88	•	340	•	505	•	•	67	1615

Note: • = no data, and MW = Monitoring Well.

In general, hydraulic conductivities obtained from slug tests in this study are an order of magnitude less than those obtained through aquifer pump tests; the only exception being well # 9, where a value of K of 323 gpd/ft^2 was obtained. It appears that this well has been developed, by repeated bailing, to a stage at which its K values can be considered representative of the aquifer. The majority of the results obtained show a higher degree of variability (Figure 12). This variability can be attributed to both spatial heterogeneity of the aquifer and the degree of individual well development.

Analysis of Aquifer Pump Test Data

The primary goal in most aquifer tests is to determine the transmissivity, hydraulic conductivity, and storativity of the aquifer within the tested areas. Pumping tests conducted at the Perkins site provided in situ values for these parameters. The data acquired during the pumping tests were analyzed using the Cooper-Jacob (1946) non-equilibrium equation, the Prickett (1965) equation, and the Theis non-equilibrium equation. Results obtained from different aquifer pump test are included in Table III. The calculated hydraulic conductivities range from 204 gpd/ft^2 to 738 gpd/ft^2. The analysis of data using the Cooper-Jacob equation produced an average transmissivity value of

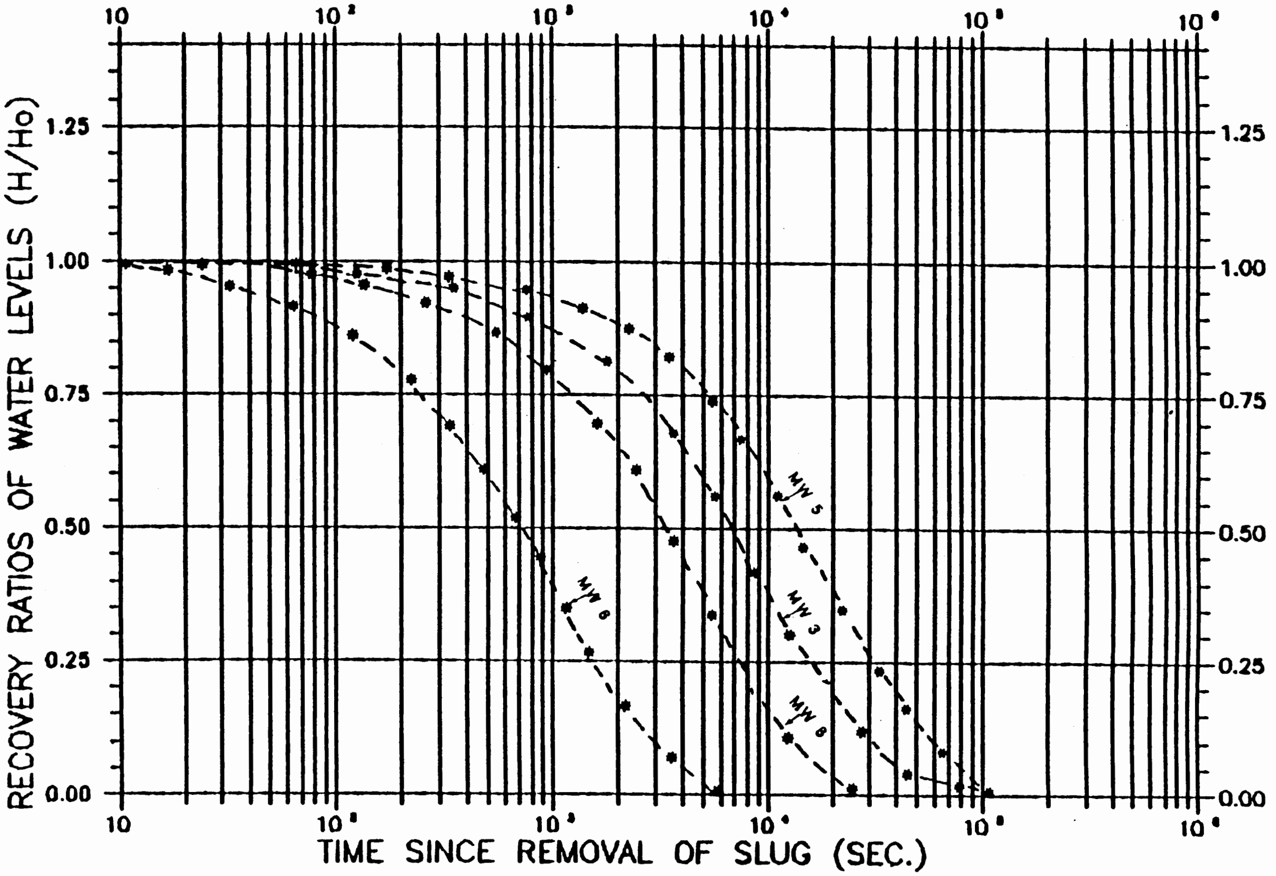


Figure 12. Slug Test Curves for Groundwater Monitoring Wells at Agronomy Research Station

TABLE III

SUMMARY OF AQUIFER COEFFICIENTS

WELL #	MW 15	MW 14	MW 12	MW 11	MW 10
Distance from Pumping well MW 18 (feet)	7.65	12.65	20.4	39.5	80.6
<u>Cooper-Jacob</u>					
Transmissivity (gpd/ft)	17296	13360*	16062*	16615*	23748*
Hydraulic conductivity (gpd/ft**)	432	334*	401*	415*	593*
Storativity	0.018	0.110*	0.007*	0.019*	0.002*
<u>Prickett</u>					
Transmissivity (gpd/ft)	--	11532*	15915*	12458*	12048*
Hydraulic Conductivity (gpd/ft**)	--	288*	397*	311*	301*
Storativity	--	0.240*	0.320*	0.110	0.300*
<u>Theis</u>					
Transmissivity (gpd/ft)	--	1.900*	8175*	21705*	29545*
Hydraulic Conductivity (gpd/ft**)	--	272*	204*	542*	738*
Storativity	--	0.030*	0.06*	0.006*	--

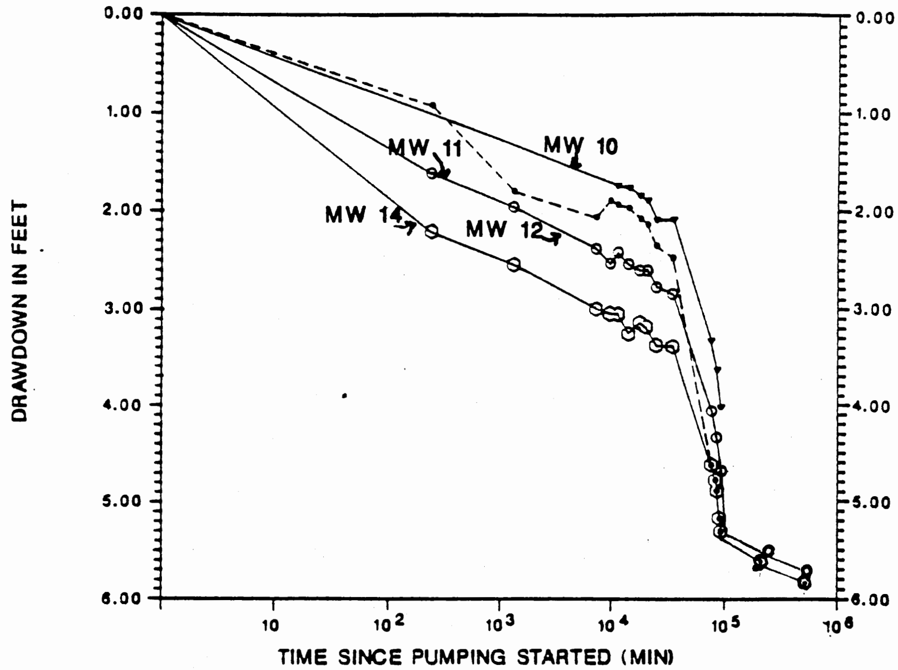
Note : * next to values are average values of pump test performed in 1985, 1987, and 1988.

MW = Monitoring Well

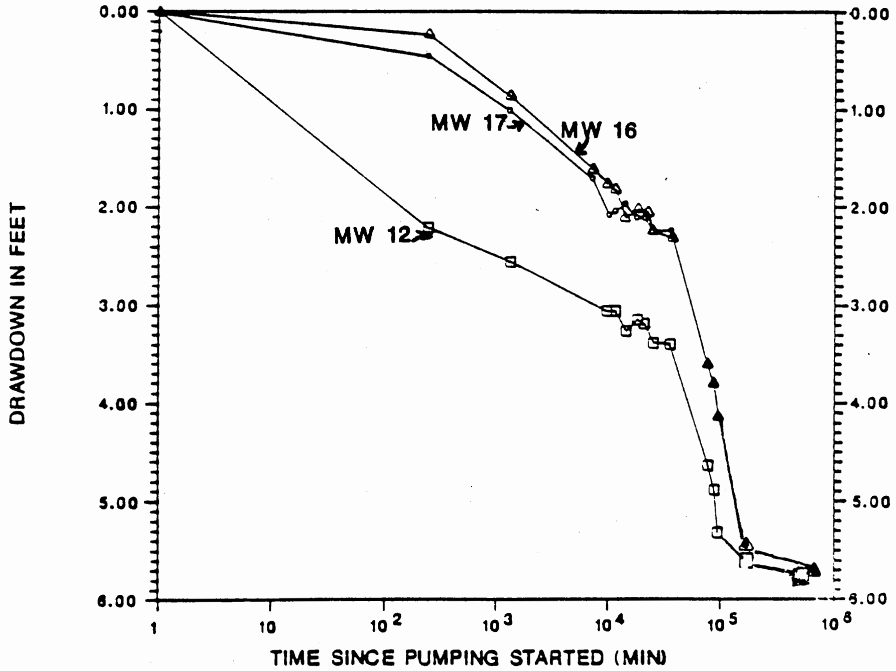
17,416 gpd/ft. The Prickett method generated an average transmissivity value of 12,988 gpd/ft. Average values of 15,331 gpd/ft for transmissivity were obtained using the Theis non-equlibrium equation. Estimated aquifer coefficient values for various observation wells obtained using the Cooper-Jacob and Theis methods differ greatly with increased distance between the observation well and the pumping well, however, wells 11, 12, and 14 appear to provide consistent aquifer parameter values. The Theis estimation is less applicable because it assumes confined conditions and aquifer homogeneity.

In general, the best estimates of the aquifer coefficients are obtained using the Prickett method. The Prickett plot method considers the non-steady state and non-equilibrium conditions inherent in the water table aquifer and is not significantly influenced by the varying distance of observation wells from the pumping wells. Therefore, this method is ideally suited for the Perkins test data.

A plot of time versus drawdown data was created for shallow observation wells 16 (21 feet depth), 17 (35 feet depth), 15, 14, 12, 11, and 10 (Figure 13). Observation wells 15 and 14 contain three screens at depths of 11-21, 25-35, and 40-50 foot intervals. The drawdown curves for wells 12, 11, and 10 have a similar slope; however,



DISTANCE VS DRAWDOWN CURVES FO DEEP WELL 14 WITH THREE SCREENS AND DEEP SINGLE SCREENED WELLS 12, 11 AND 10



DRAWDOWN RESPONSE CURVES FOR SHALLOW MW #16 (SCREEN-11-21FT) MIDDLE MW #17 SCREEN 21-31FT) AND DEEP MW #12 (SCREEN 40-51FT)

Figure 13. Time Versus Drawdown Curves Groundwater Monitoring Wells at Agronomy Research Station

drawdown in each well decreases with increasing distance. Wells 15 and 16 have a lesser drawdown and are more rapidly influenced by surface recharge. The drawdown values obtained in wells 16 and 17 were the least even though they are closest to the pumping well, which strongly indicates perched water table conditions because of the confining clay layer, separating shallow and deep portions of the aquifer. The presence of clay lens is also indicated by the gamma-ray logs.

Vadose Zone Hydraulics

Volumetric soil moisture measurements were made between March and June, 1988, using a neutron moderation technique (Appendix A). Soil moisture determinations were made at 0.5 foot (0.15 m) intervals to a depth of 7 feet (2.1m) below land surface. Soil water contents measured at test plot-A and test plot-B range from 0.16 to 0.38 cm^3 water / cm^3 soil, respectively. Soil moisture content readings were taken at test plot B before ponding the plot and after ponding the plot with 3 inches (7.5 cm) of water. The curves plotted for test plot B, Figure 14, indicate the same general trend with the exception of the upper 30 cm of soil where a change of 15 to 25 percent in volumetric water content is noted. The rapid change in the soil moisture at the surface is largely due to evaporation and drying of the

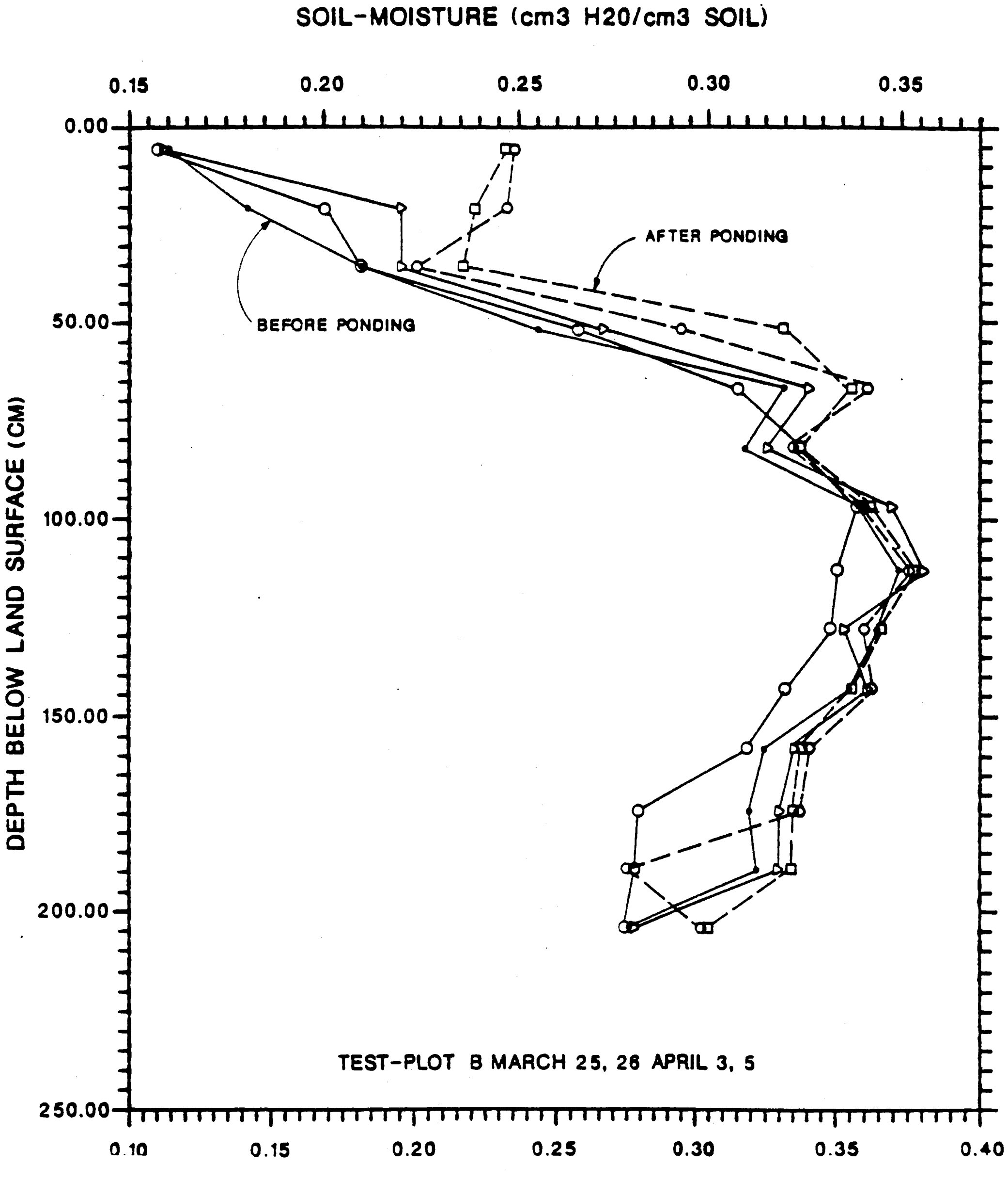


Figure 14. Soil Moisture Profiles at Test-Plot B

soil. Soil moisture content increases by approximately 5 percent in the rest of the profile as a result of infiltration. Similar readings were recorded for plot A and were plotted in Figure 15. The profile of soil moisture contents with depth show a greater variability than those measured at test plot B. This could be attributed to the difference in soil compaction surrounding the aluminum access tubes. The profiles obtained from the two test plots correlate very well, indicating the presence of similar soil profiles at the two sites (Figure 16). This is to be expected because the two plots are separated by only a short distance of 20 feet (6 m). The only variation in correlation is in the upper 20 cm of soil, where the readings for soil moisture content are significantly higher at test plot A than at test plot B. This can be easily explained since the upper 10 to 20 cm of soil was removed while designing test plot A and around 20 to 25 cm of surface soil was removed from test plot B. In general, a comparison of profiles measured between March and June, 1988 does not vary significantly except in the upper 30 to 40 cm of soil.

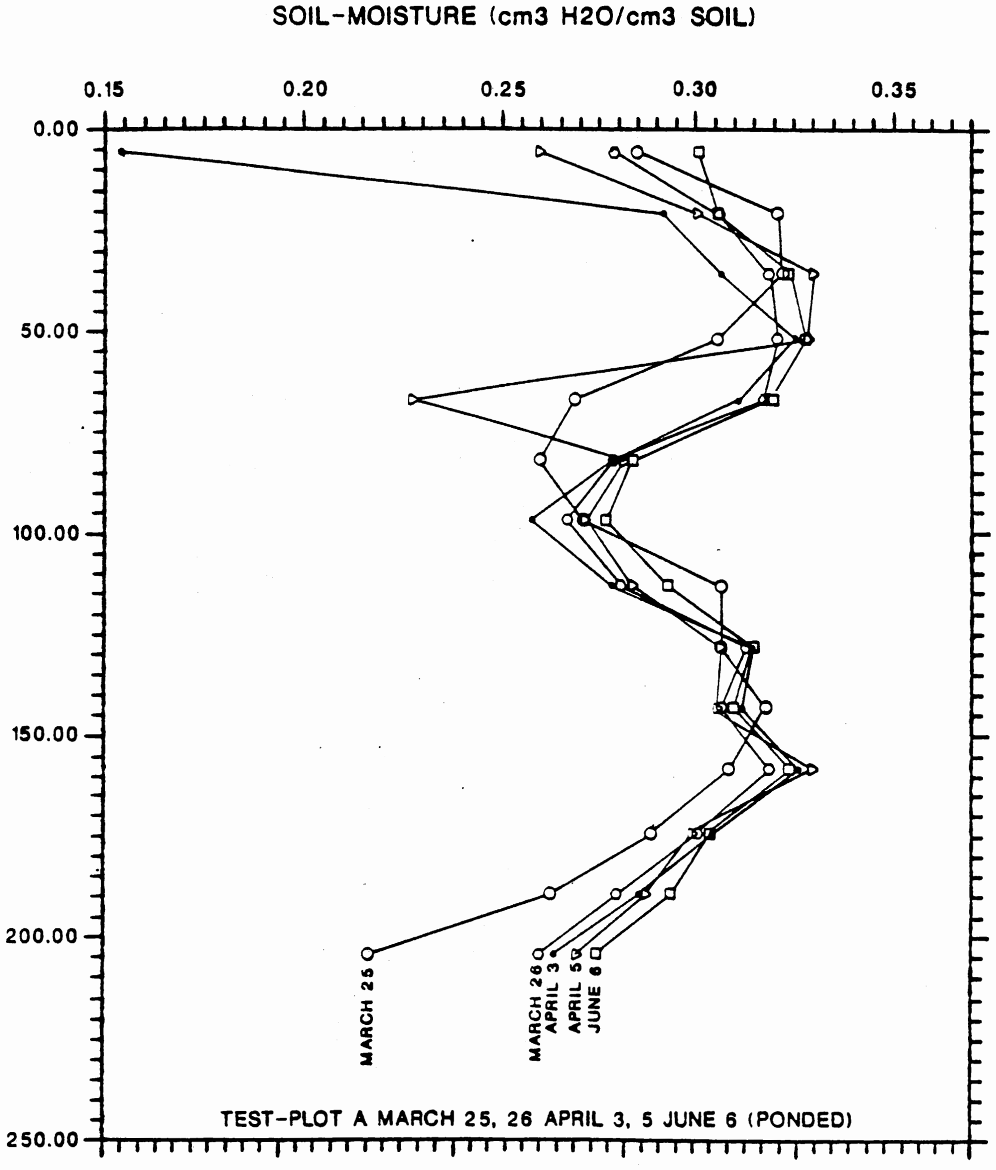


Figure 1 5 Soil Moisture Profiles at Test-Plot A

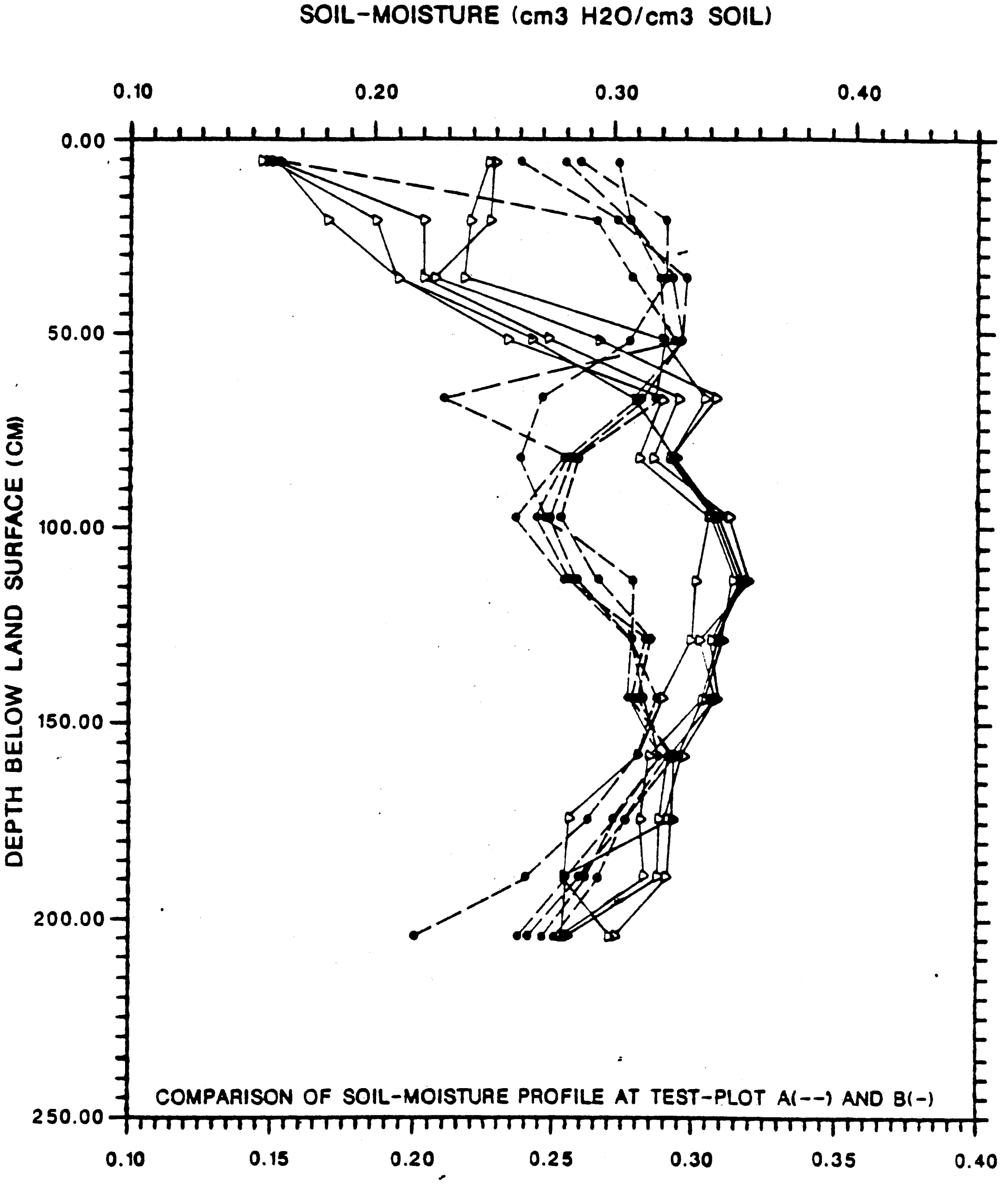


Figure 16. Comparison of Soil Moisture Profiles Obtained from Test-plots A and B

CHAPTER V

GROUNDWATER QUALITY

Introduction

In order to determine the impact of agricultural activities on groundwater quality at the Perkins research site, basic data needed to be gathered concerning groundwater quality variations over time (seasons and weeks) and space (location and vertical distribution). Quality variations, in turn would be correlated with groundwater hydraulics (direction and rate), potential nitrate source, recharge events, and topography.

Groundwater Monitoring of Inorganic Chemicals

A network of monitoring wells installed in the early stages of this research was utilized to acquire groundwater quality data. The monitoring wells were completed at different depths for monitoring the shallow and deep levels of saturated thickness of the Perkins Terrace Aquifer. Sample cutting data and gamma ray data indicate the presences of a semi-confining, thin, red silty clay layer present at a depth of approximately 24 to 26 feet (7 to

8m). Wells completed below this layer were sealed with bentonite clay-cement slurry in the annulus to restrict the leakage of water from above the semi-confining layer. The location of the monitoring wells is shown in Figure 3. As with designing and installing the monitoring well network, monitoring protocol for the test site was developed in consideration of the project objectives. The study concentrated on determining: 1) the long-term or seasonal variation in ground water quality over time by sampling all the monitoring wells on a quarterly basis for a period of three years. and 2) the short-term or weekly variation in groundwater quality over a period of 8 months, to correlate with individual recharge events.

Groundwater sampling procedures utilized in this study were developed using the "Handbook for Sampling and Sample Preservation of Water and Waste Water" (EPA-600/4-82-029). Groundwater samples were collected using a teflon point sampler, and samples were preserved until the time of lab analysis. The ph and specific conductance of all water samples were recorded in the field. Sample bottles were prepared by washing with distilled water before each sampling period. Four to five bailer volumes of water were evacuated before sampling to ensure that representative samples of the groundwater were obtained.

Overall Groundwater Quality

Groundwater quality has been observed at the Perkins site in 11 wells near 7 agricultural plots which are planted with wheat, cotton, beans, and orchard. The plots range in area from approximately 0.4 to 5.7 ha in area. Groundwater samples collected between March, 1986 and June, 1988 were analyzed for nine chemical parameters. Plots showing the distribution of cations and anions measured in groundwater samples over time in individual monitoring wells are shown in Appendix E. Total Concentration of cations and anions is greater at shallow depths than at deeper depths in monitoring well nests (well no's 4, 5, 8, and 9) ; however, the total concentrations are greater at deeper depths than shallow depths in monitoring well nests containing well no's 8 and 9. In most monitoring wells, concentrations seem to decrease in a downslope direction. The highest concentrations are present in monitoring wells 4 and 5, located near the minimum tillage wheat plot. A trend of increasing concentrations is noted from March, 1986 to January, 1987 and then decreasing with time in monitoring wells 1, 3, 4, 7, and 8. Of the nine measured chemical parameters, all are below National drinking water standards except nitrates which range from 5 to 150 mg/1.

Long-term Groundwater Quality Data (1986 to 1988)

Nitrates

Concentrations of nitrate-nitrogen in the groundwater samples measured at the Perkins site between March, 1986 and June, 1988 ranged from 5 to 150 mg/l. Fertilizer-N was applied to different agricultural plots at rates of 80 to 90 kg per hectare. Nitrate-n concentrations increased with depth in well no's 6, 7, 8, and 9; however, nitrate concentrations decreased with depth in well no's 4 and 5. Measured nitrate concentrations in all monitoring wells increased consistently from March, 1986 to June, 1988. The highest nitrate concentrations were observed in monitoring wells 1 and 2, and 4 and 5. The high nitrate-n concentrations in monitoring wells 1 and 2 result from proximity of an old septic tank, where as monitoring wells 4 and 5 having high nitrate-n concentrations are near conservative tillage wheat plot. The lowest nitrate-n values were obtained in monitoring well A, which is an upgradient well that provides background water quality information. A comparison of nitrate-n concentrations versus time and water levels shows a good correlation (Figures 17, 18 and 19). Groundwater levels at the Perkins site have increased consistently since 1985. The increase in nitrate-n concentrations at Perkins is more directly

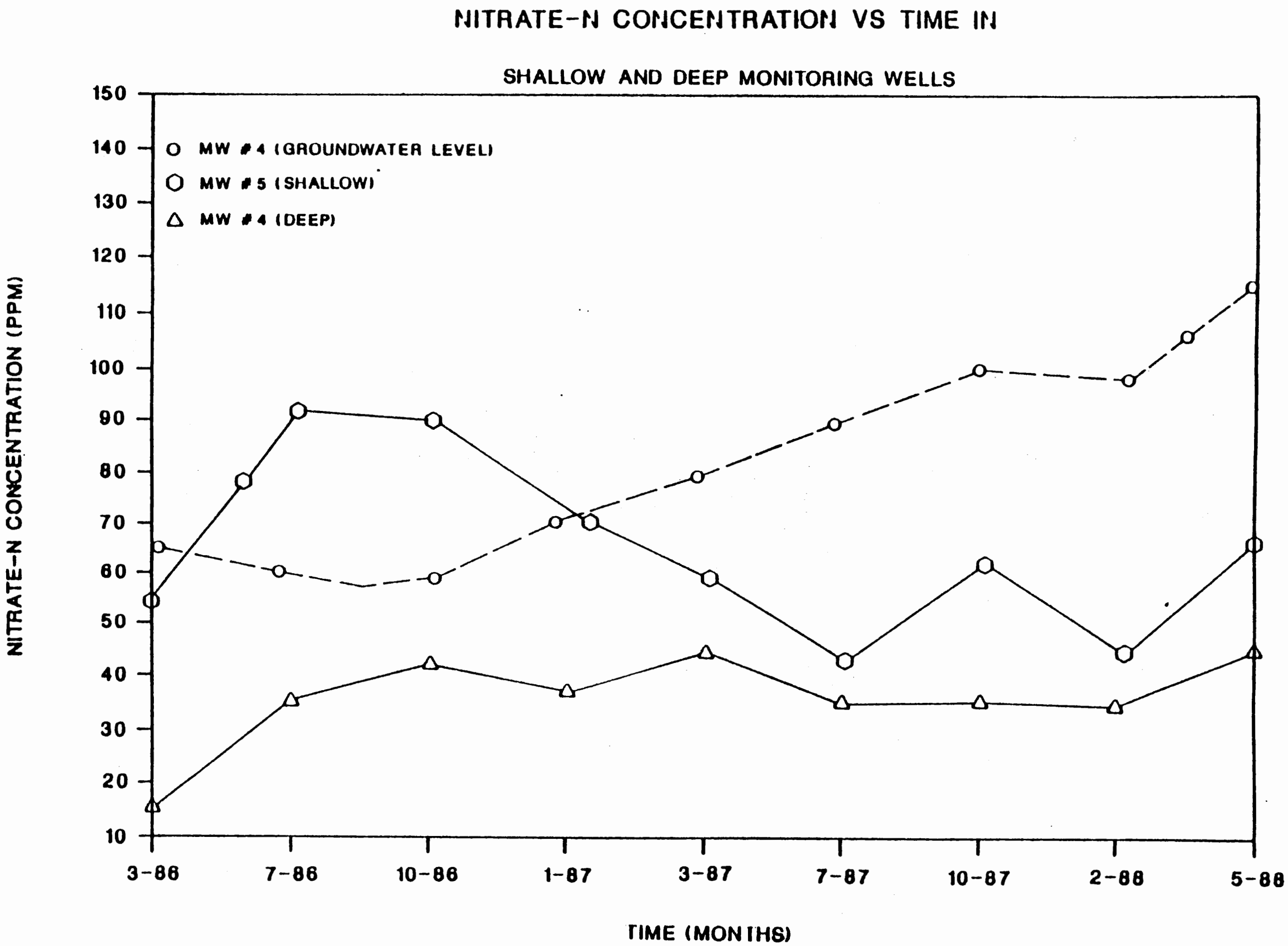


Figure 17. Nitrate-n Concentration Versus Time in Monitoring Wells 4 and 5

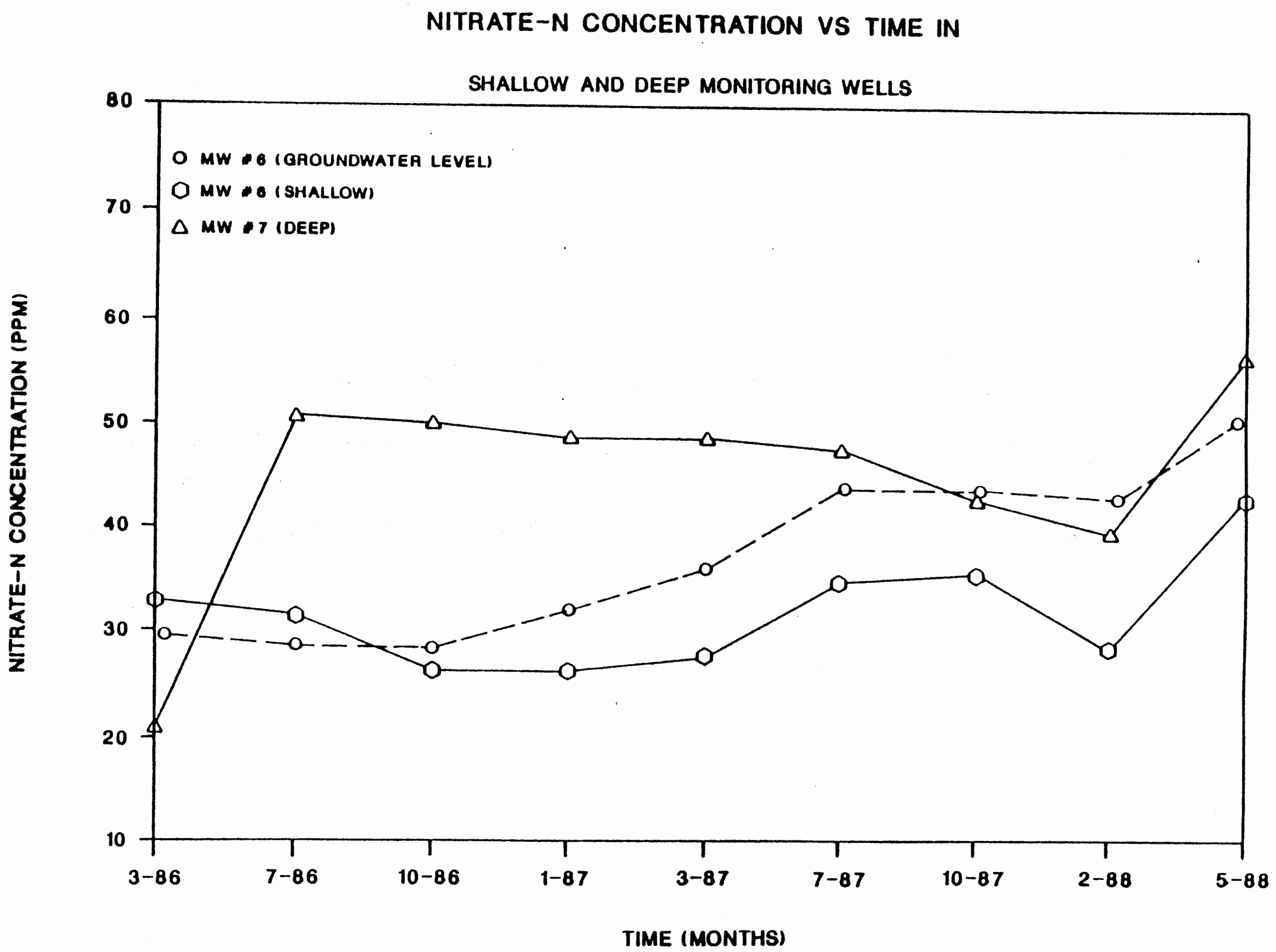


Figure 18 Nitrate-n Concentration Versus Time in Monitoring Wells 6 and 7.

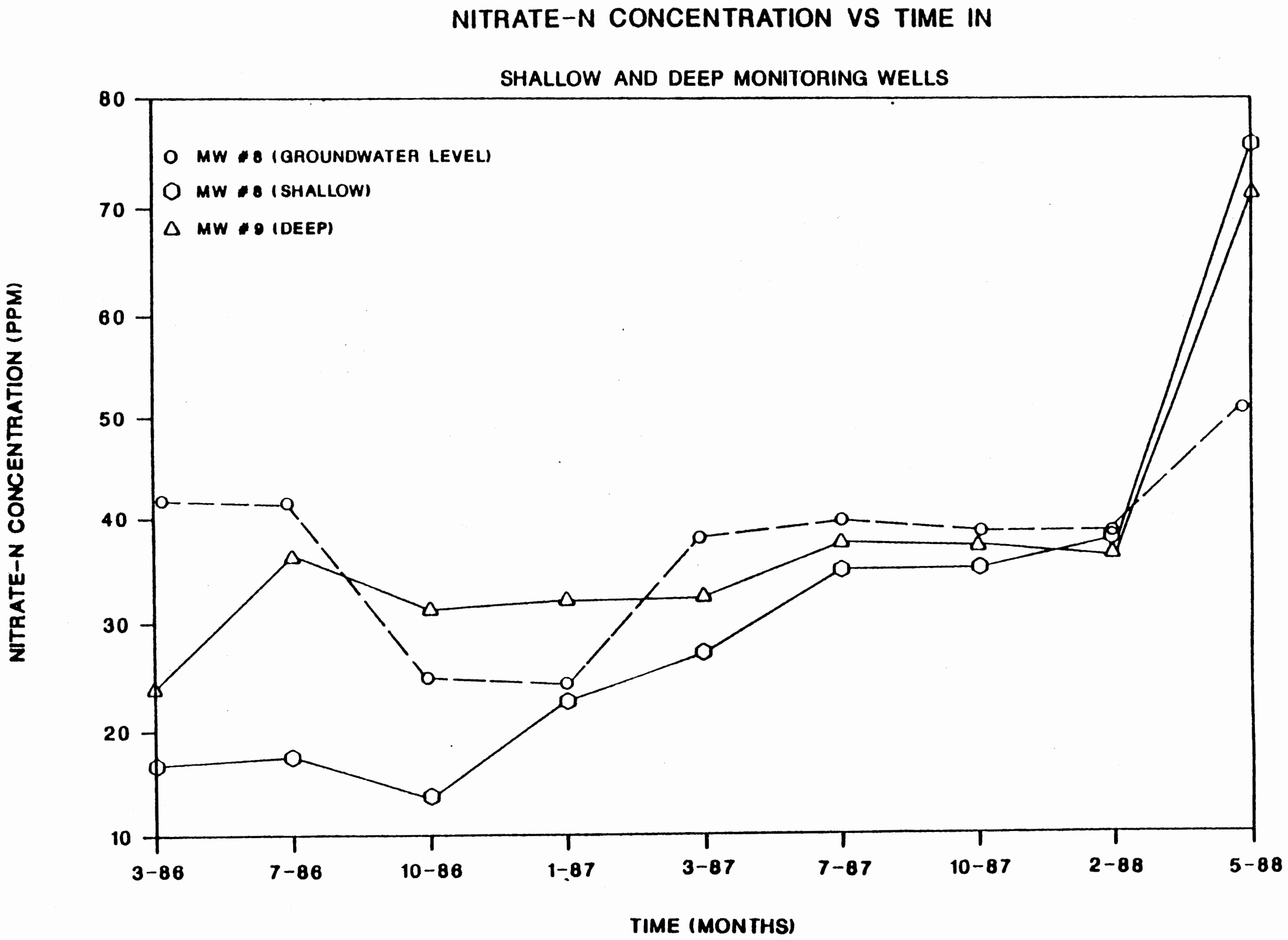


Figure 19. Nitrate Concentration Versus Time in Monitoring Wells 8 and 9

associated with recharge of water through fertilized plots planted with wheat than any other factor. The groundwater containing high nitrate-n concentrations, supplied from the water supply well at Agronomy Research Station will provide an average of about 50 percent of the amount of nitrate-n required by some crops.

Sulfates

Sulfate concentrations ranging from 10 to 100 mg/1 in groundwater samples were noted. Sulfates increased with depth in monitoring well no's 6, 7, 8, and 9 while they decreased with depth in nests 4 and 5. A trend of decreasing sulfate concentrations with time has been observed in all monitoring wells. A comparison of sulfate concentrations versus time with groundwater levels indicates an inverse relationship between the two (Appendix E). Sulfate concentrations have decreased since 1986, whereas, the groundwater levels have been increasing. Concentrations for other parameters including chloride, sodium, calcium, have also been consistently decreasing since the first sampling date in 1986 (Appendix E). The decrease in the concentrations of ions other than nitrate can be explained as a result of increasing recharge and ground water levels and thus dilution of concentrations over time. Unlike most other elements in groundwater, nitrate is not derived from the minerals in rocks that form the groundwater reservoir; instead, nitrates enter groundwater either as a part of the Earth's nitrogen cycle (Dirscoll, 1986) or as supplied by nitrogen fertilizers. Thus, with each recharge event, nitrates are leached into groundwater and thereby increase the concentrations in the groundwater with time at the Perkins site.

Short-term Groundwater Quality Data (7 - 1987 to 4 - 1988)

Traditionally, the assessment and characterization of groundwater quality is based on either seasonal or quarterly groundwater monitoring. Currently, legislation addressing environmental protection issues does not require more than four sampling periods in a year. The focus of this section of the research is to evaluate the validity of characterizing groundwater quality based on as few as four sampling periods a year. An attempt to characterize short-term variations of the fluctuations in groundwater quality was made at the Perkins site. Groundwater samples were taken once every week between July, 1987 and April, 1988 and were analyzed for nitrate-n and chlorides. The main intent of this portion of research was to establish the relationship between individual precipitation events, recharge, and groundwater quality and to confirm the need for the development of a groundwater monitoring protocol that can adequately define the temporal and spatial migration of contaminants. The data were interpreted to obtain the response time of the groundwater table to a rainfall event and the travel time of a contaminant from the surface to the groundwater table.

Groundwater levels, superimposed with daily precipitation, were plotted for each of the monitoring wells for the period of July, 1987 through April, 1988. These plots provide a comparison of the frequency of rainfall and water table response as a function of time. The hydrographs correlate very well with the frequency of daily precipitation, especially when the hydrographs are shifted ten to fifteen days. There seems to be very little difference between the response time of shallow and deep monitoring wells. A clay layer is present at depths of 10 to 15 feet in all monitoring wells, it acts as a semi-confining layer, not completely impeding the flow of infiltrating water from the saturated interval above to one and below the clay layer. This phenomena suggests the presence of macropores and possible fractures which act as pathways for water infiltration. This concept disproves the traditional and popular concept of water traveling in a "piston movement" or "wetting-front fashion." This concept may prove to be valid in the early phase of a recharge event, where water percolates as wetting front and also through the macropores; however, once the water content of the soil reaches its maximum level, breakthrough occurs and complete water movement through macropores results. A lag time of about fifteen days is noted from July, 1987 through October, 1987, however the lag time between the precipitation event and water table change ranges from a few hours to few days between December, 1987 and March, 1988 (Figures 20, 21, 22, and 23).

Concentration profiles of nitrates measured during the same time period were compared with the water table elevations (Figures 20, 21, 22, and 23). In most of the monitoring wells, concentrations are found to be slightly higher in the deeper wells, indicating that, upon the arrival of contaminant with the infiltrating water at the water table, rapid vertical mixing occurs throughout the entire aquifer. The differences in the concentrations in the shallow and deep portions of the aquifer can be attributed to the varying transmissivity values and also the dilution effect. The greatest variability in the concentrations present in monitoring wells 4 and 5; is probably caused by the differing recharge rates of the shallow and deep portions of the aquifer. A comparison of the hydrographs of the shallow (MW 5) and deep (MW 4) wells also shows the greatest variance, possibly influenced by impact of land use.

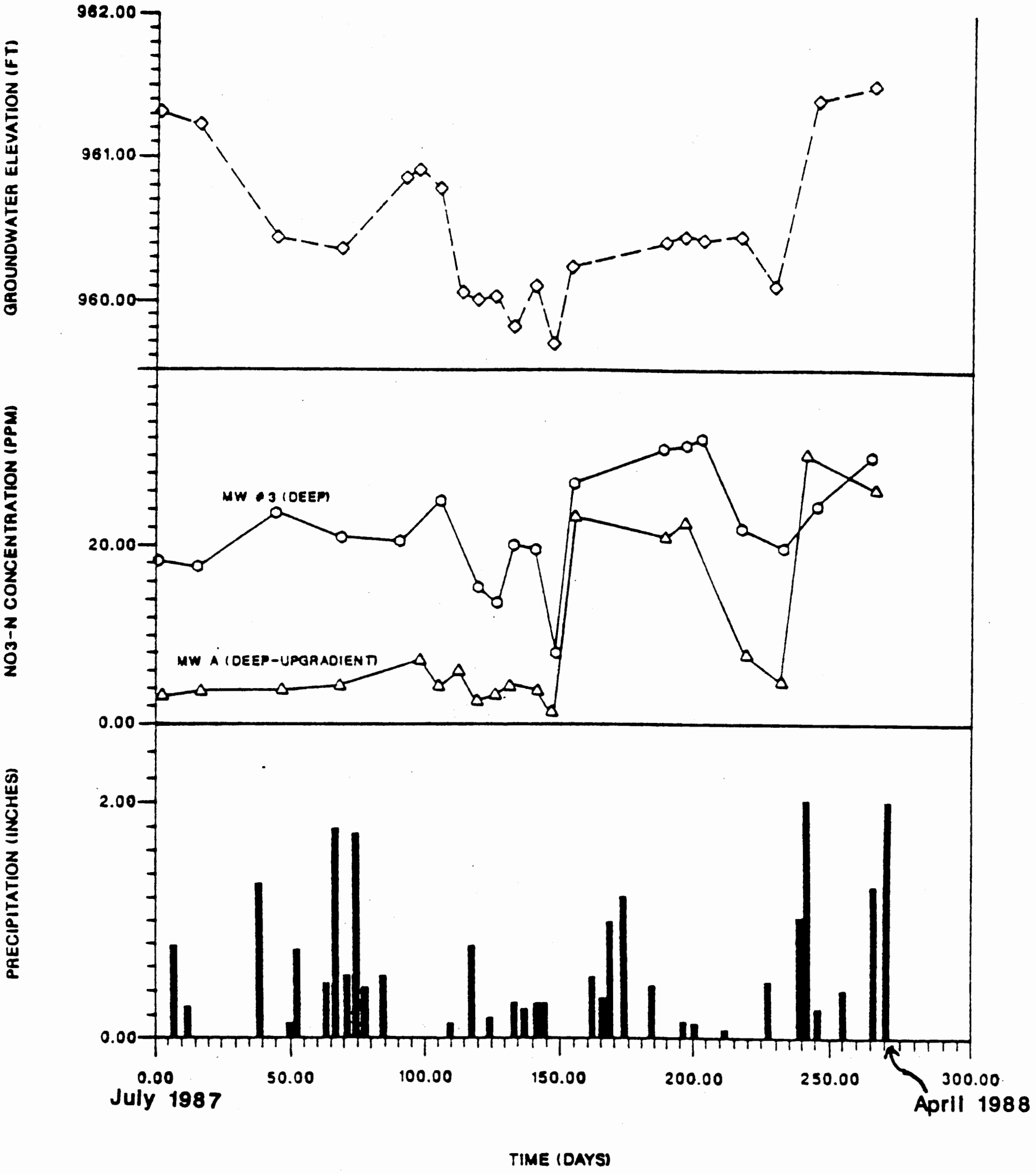


Figure 20. Relationship Between Biweekly Nitrate-n, Groundwater Levels and Precipitation (MW 3 & MW A)

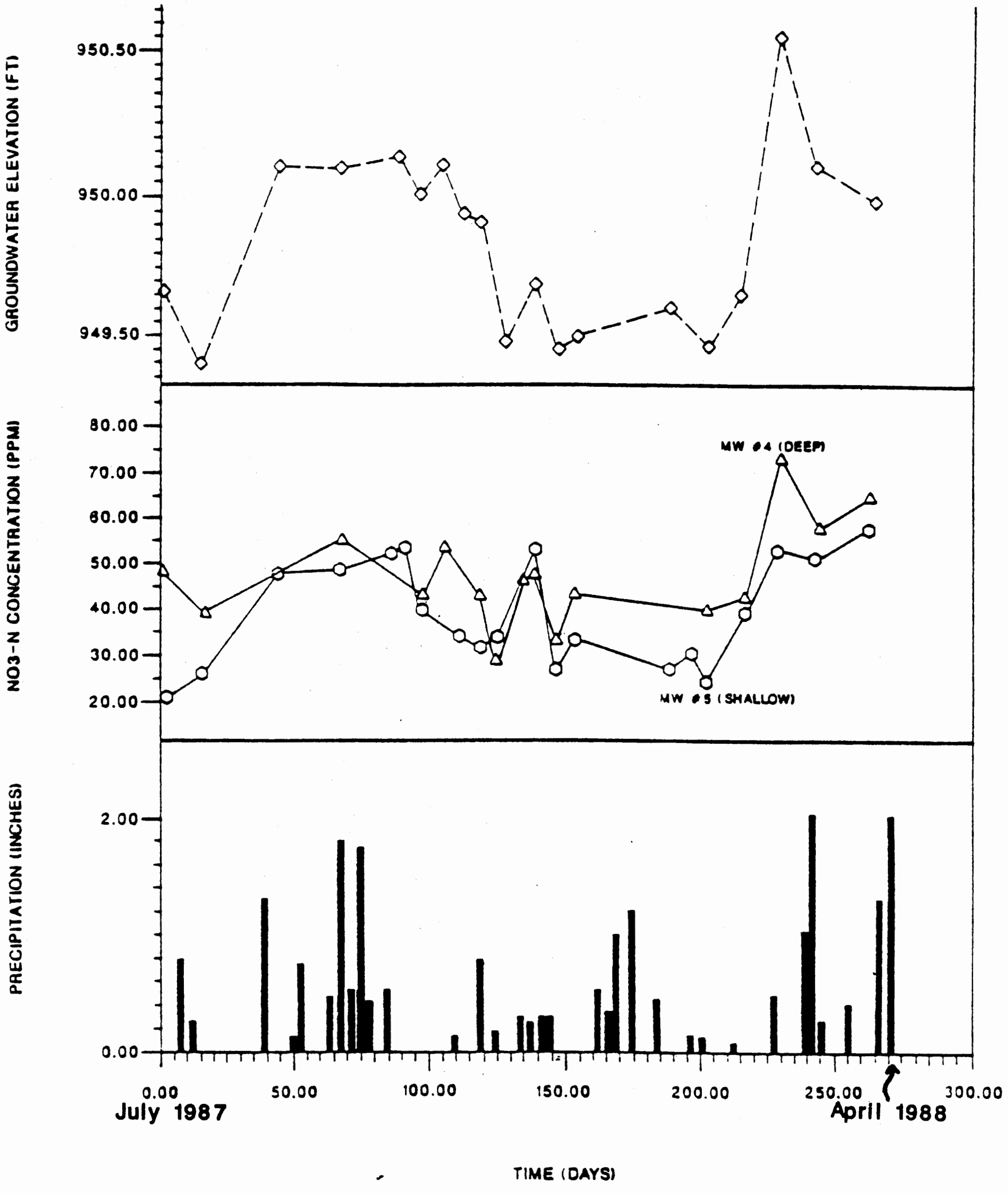


Figure 21. Relationship Between Biweekly Nitrate-n, Groundwater Levels and Precipitation (MW 4 & MW 5)

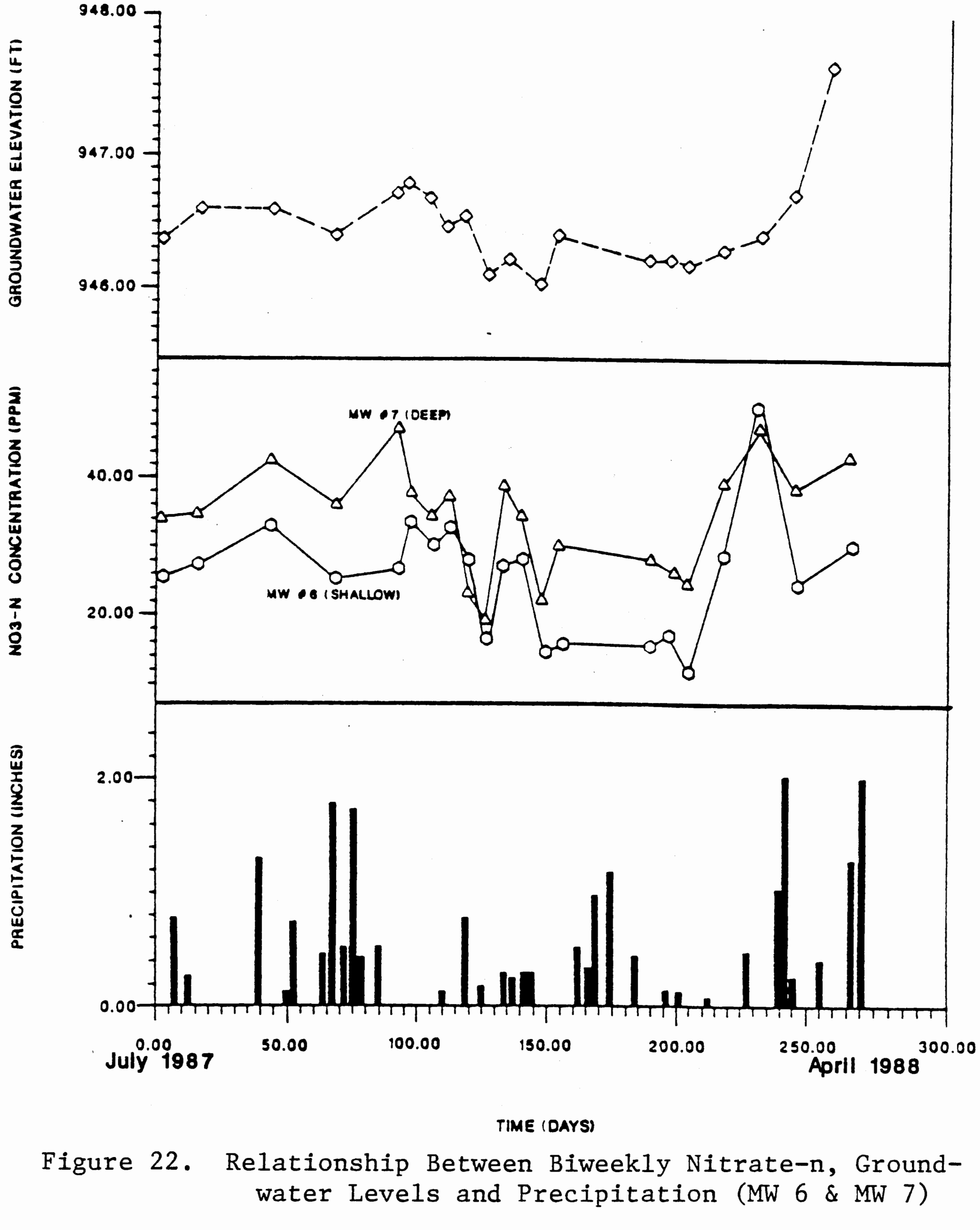


Figure 22. Relationship Between Biweekly Nitrate-n, Groundwater Levels and Precipitation (MW 6 & MW 7)

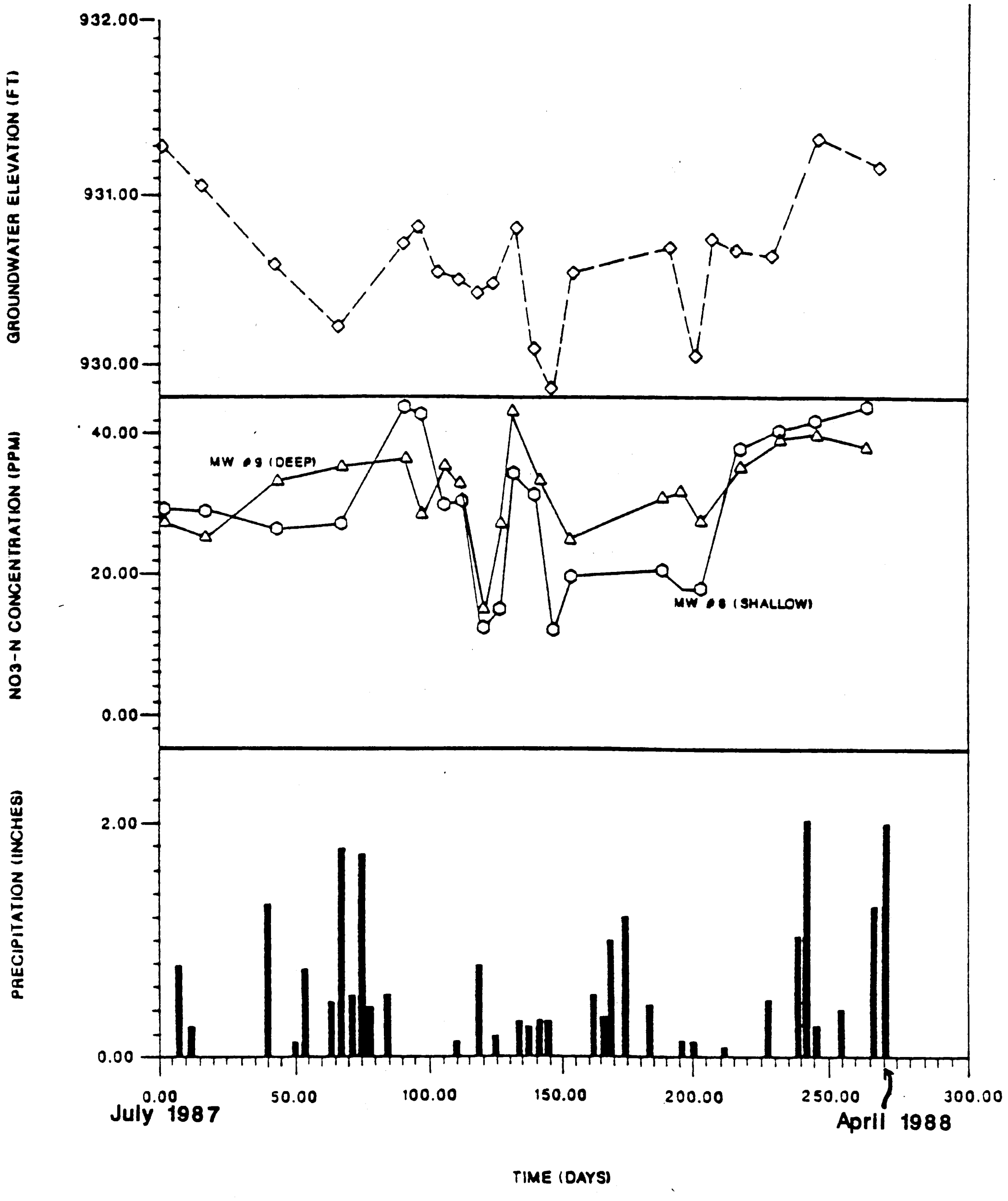


Figure 23. Relationship Between Biweekly Nitrate-n, Groundwater Levels and Precipitation (MW 8 & MW 9)

The analysis of short-term data (July, 1987 to April, 1988) gathered at the Perkins site provide information about the loading rates and travel times of nitrates to the groundwater table from the surface. The study strongly emphasizes that the overall water quality characterization of a site, in either point or nonpoint source pollution, based on investigations implementing few sampling periods over a period of only a few years can be extremely misleading and erroneous; especially when one decides to interpret trends of water quality based on such data. In this study, long-term (Quarterly sampling) water quality data (1986 to 1988) was analyzed and, as a result, emerging trends such as the increase of nitrate-n values with time have been interpreted. Although this type of data is useful to a certain extent in evaluating overall water quality, caution should be taken in the judgement process. Considerably different values of nitrates could have been obtained if the sampling schedule had been different; primarily controlled by the time lapse between sampling periods and precipitation events.

Groundwater Monitoring of Organics

Organic solutes in groundwater have been identified primarily through discovery in water-supply wells (U.S. Environmental Protection agency, 1977). The potential for pesticide residue being transported to groundwater is dependent upon physical, chemical, and biological processes in the soil and meterological factors. If pesticide residues reach groundwater, they will be transformed and transported at rates related to chemical formulation and hydrogeological properties of the aquifer. The residual at the point of removal is largely dependent, therefore, upon groundwater velocity, pesticide transformation rate, initial concentration underneath the source area, and location with respect to the source area (Carsel, et al., 1988).

A variety of organic chemicals are used at the Perkins site, as pest and herb control measures. Prior to collecting groundwater samples, three to four bore-volumes of water were withdrawn from the monitoring wells using a teflon bailer. This was done to ensure the collection of a representative groundwater sample. A stainless steel point sampler tied with nylon rope was used to collect groundwater samples. The water samples were collected in 4 liter amber-colored glass bottles, to prevent the degradation of organic chemicals which had previously been rinsed with methylene chloride. The glass bottles were then capped with foil-lined lids and placed in a refrigerator until they could be analyzed for the presence of pesticides. A preliminary analysis of groundwater samples was conducted in September, 1986 and, at that time, no pesticides were detected. A detailed analysis of water samples for pesticides Carbaryl and Diuron was conducted in June, 1987. A method for determining Carbaryl and 1-Napthol residue in water and a standard method of analyzing wastewater for Methomyl, Linuron, and Diuron was utilized. No residues of either pesticide were recovered in the water samples. The reported detection limits of Carbaryl and Diuron are 0.01 ppm and 0.3 ppm, respectively.

An exploratory study of the extent of groundwater contamination from the agricultural use of selected pesticides in Oklahoma has been conducted by the Oklahoma State Department of Agriculture. A total of 67 groundwater wells located in alluvial and terrace soils in Oklahoma were sampled. No pesticide residues were recovered in any of the well samples collected for this study.

CHAPTER VI

IN SITU TRACER TEST

Tracer Transport in Unsaturated Zone

An unsaturated zone monitoring program consists of a set of techniques for characterizing the physical parameters, mainly storage and hydraulic conductivity, and chemical parameters, including solute movement in the unsaturated zone. Two test plots were designed at the Perkins site to obtain these parameters in the field. The soils present at the two plots belong to the Konawa-Daugherty soil series. The acquisition of the physical parameters of the unsaturated zone at the Perkins site has been discussed in an earlier section entitled "Unsaturated Zone Hydraulics." The primary intent of this section is to characterize the movement of solutes in the unsaturated zone, its interaction with the soil matrix, and finally, to obtain the travel times to the groundwater table, and the chemical concentrations reaching the saturated zone.

The parameters defining the solute movement in the unsaturated zone are acquired by obtaining the physical and chemical properties of the unsaturated zone, including: clay content, specific surface, organic matter, and cation exchange capacity. For organic solutes, parameters such as water solubility, volatility, octanol water partition coefficients, and decay rates are defined. Field plot studies were conducted to determine pollutant mobility under simulated and actual field conditions. A technique for continuous non-destructive sampling of soil moisture was utilized to define solute movement under field conditions (Hillel, 1980).

On February 20, 1988, three sets of initial samples were collected from the lysimeters. It was observed that lysimeters # 1 and # 12 ceased to operate; no obvious reason was noted. Soil moisture samples were analyzed for the presence of nitrates, chloride and zinc, and very low concentration values were obtained for these elements (Table IV).

Soil Water Sampling

Simulations of chemical transport in the unsaturated zone for worst-case conditions were conducted at the test plots. This was achieved by keeping the soil saturated to its near maximum water content, thus maximizing the unsaturated hydraulic conductivity. On march 6, 1988, one thousand grams of ammonium-nitrate fertilizer, containing 34 percent total nitrogen was applied to plots A and B

TABLE IV

BACKGROUND SOIL MOISTURE CONCENTRATION FOR CL, NO3, SO4, AND ZN

February 20, 1988

Lysimeter No.	Depth (FEET)	CL (PPM)	NO3 (PPM)	SO4 (PPM)	ZN (PPM)
L-1	1.0	7.2	0.1	65.1	0.1
L-14	1.0	3.2	0.1	76.4	0.5
L-6	2.0	5.3	0.1	47.0	0.1
L-8	2.2	1.9	1.1	31.2	0.3
L-13	2.2	3.5	0.7	10.7	0.5
L-3	4.0	2.1	0.2	19.4	0.3
L-11	4.0	4.2	0.1	8.4	0.1
L-7	5.0	3.3	0.1	4.0	0.1
L-2	7.0	3.6	0.1	17.6	0.2

respectively. The same day, 500 grams of potassium-sulfate was applied to the larger plot, B. On march 16, 1988 five hundred grams of zinc-chloride was applied to plot B. On April 20, 1988, a second loading of ammonium-nitrate, three thousand grams, and one thousand grams was applied to plots B and A respectively.

Soil water samples were taken twice every week between March 5, 1988 and July 15, 1988. Electrical conductivity and ph readings were noted in the field and the samples were later analyzed for nitrate-n, chloride, sulfate, potassium, and zinc. The concentration values for all lysimeter data were plotted as a function of time (Figure 24). The resulting graphs clearly show the variability of solute movement within each of the field plots as well as the variability between plot A and plot B (Figures 25 and 26). The first arrival time of the tracer at all lysimeters installed at depths varying from 1 to 9 feet (0.3 to 2.7 m) ranged from two to four days. The concentrations in the soil water obtained from all the lysimeters during the first three days of tracer experiment changed from 0.5 mg/l to around 3 mg/l. This was to be expected because the water was ponded and the soil profile fully saturated before commencing the tracer test. The maximum arrival time for all lysimeters however was determined to be between 25 and 30 days and was more a

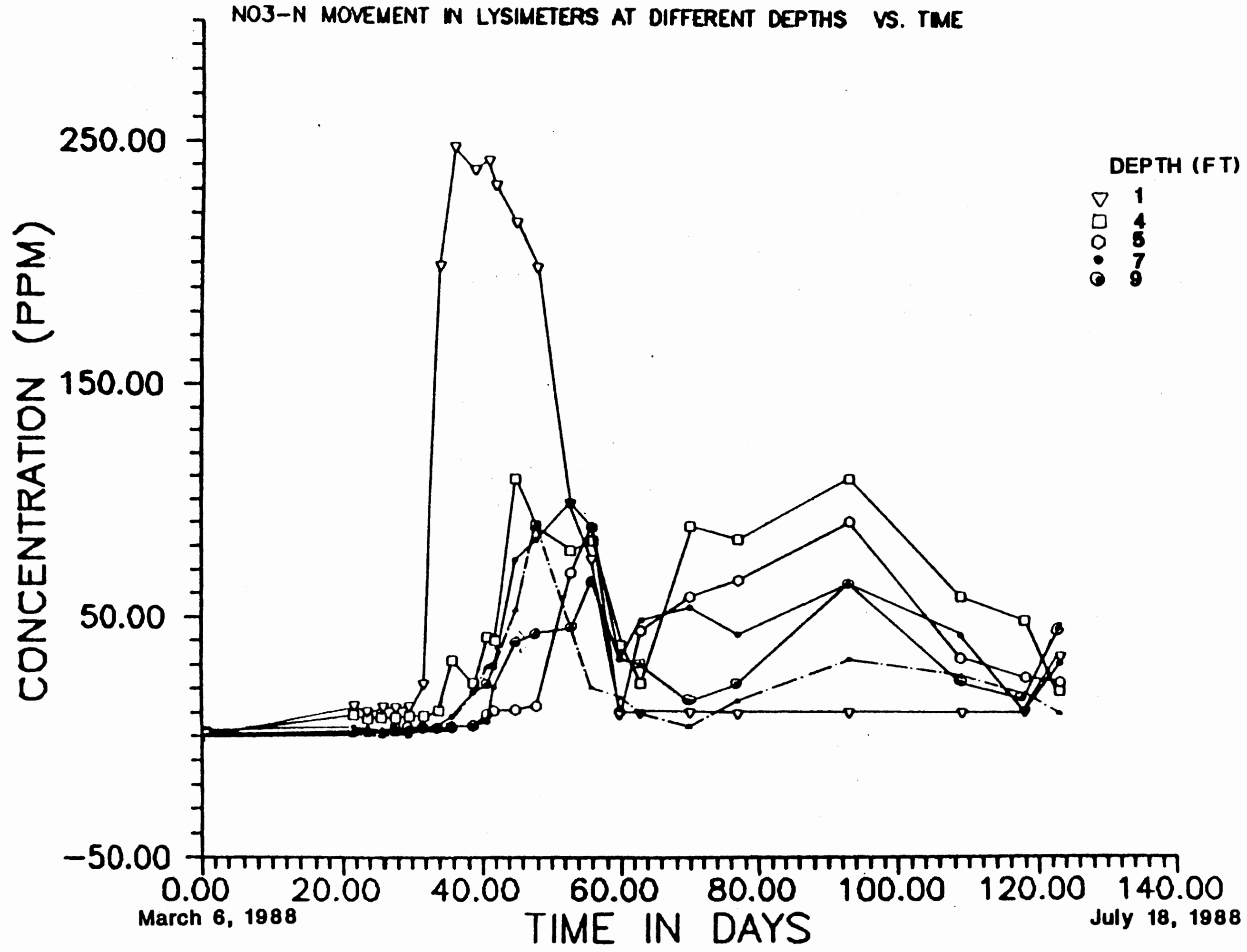


Figure 24. Nitrate-n Concentrations at Different Depths in Subsurface with Time at Test-Plot B

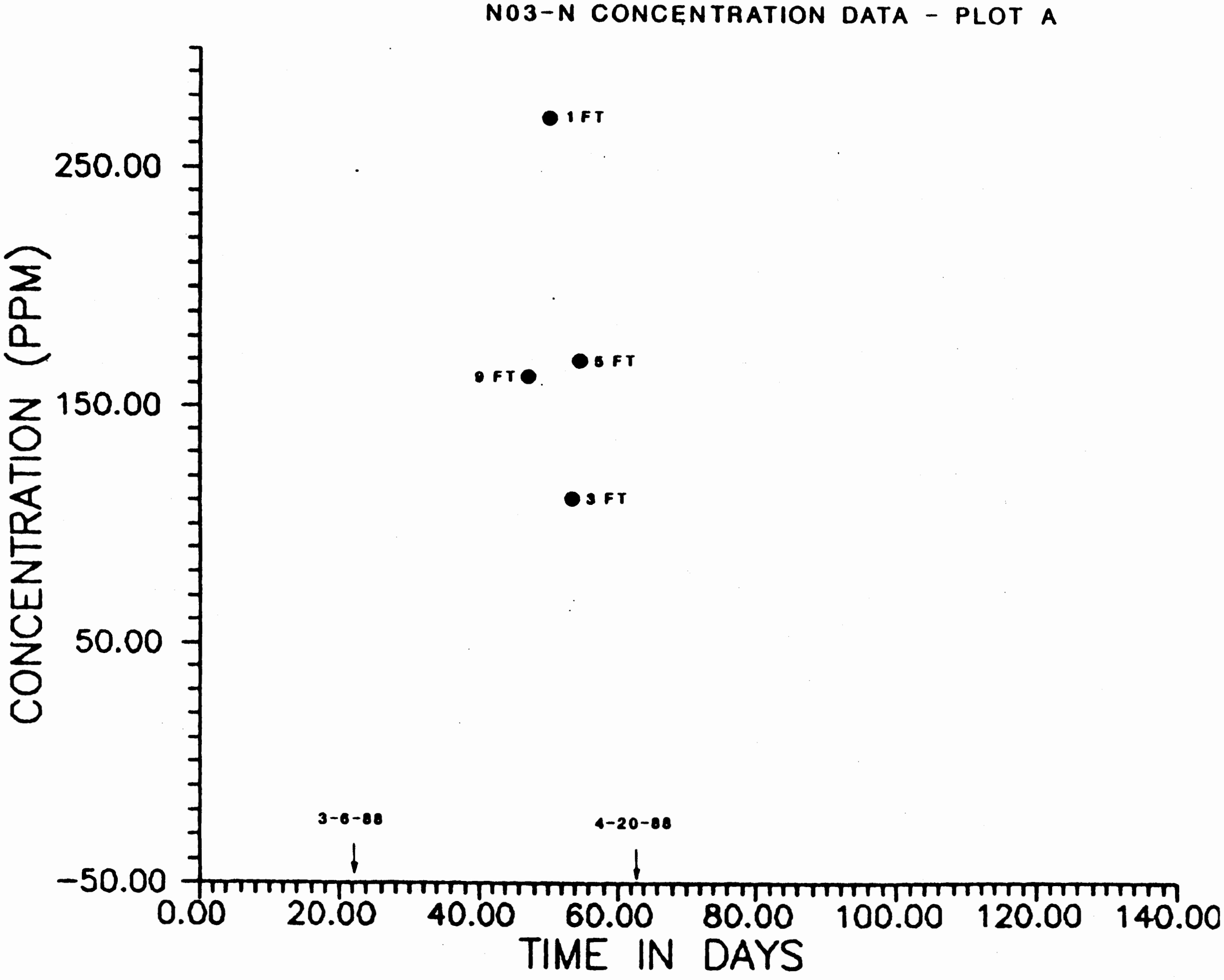


Figure 25. Peak Nitrate-n Concentrations in Different Lysimeter Depths at Test-Plot A

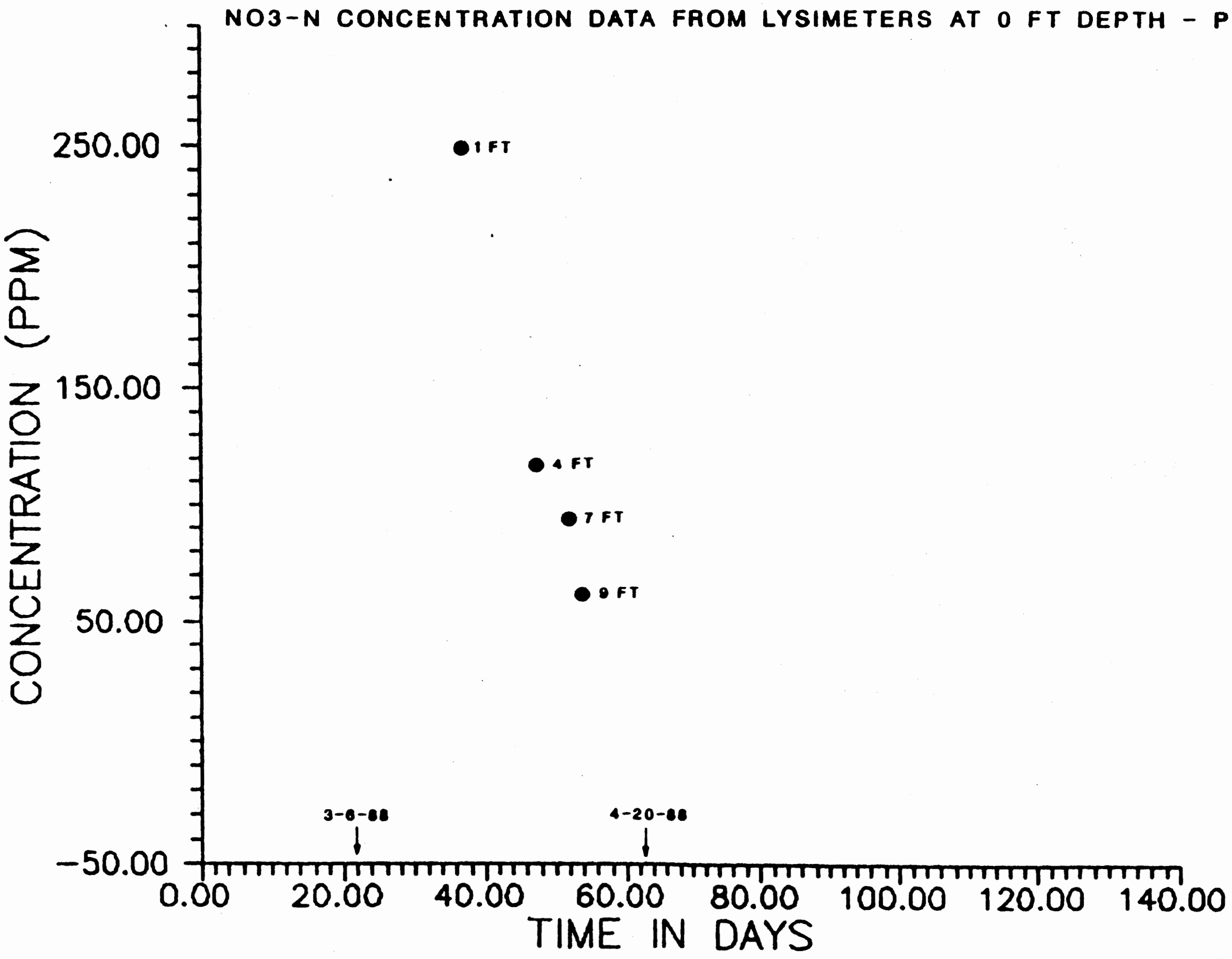
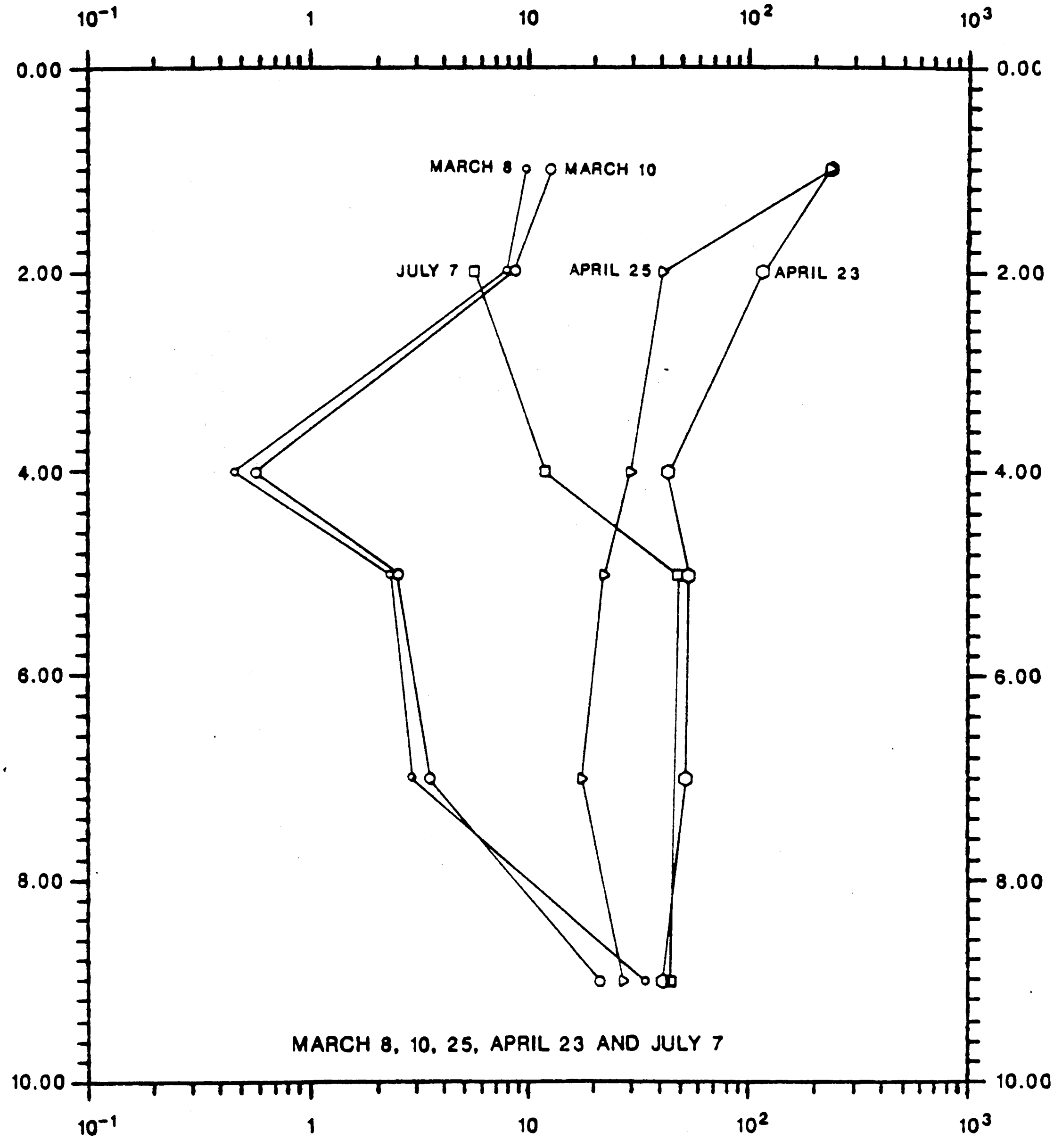


Figure 26. Peak Nitrate-n Concentrations in Different Lysimeter Depths at Test Plot B

function of depth. Since the time of fertilizer application to the surface, concentrations of nitrate gradually increased from a median background value of 0.1 to around 5 mg/l over a time span of ten days in all lysimeters. A greater increase in the nitrate concentrations occurred after ten days and the concentration maxima are reached in approximately thirty to thirty-five days. After one week of ammonium fertilizer application, relatively immobile ammonia is transformed to nitrates thus increasing the concentrations in soil water; therefore, nitrification is a possible source of increasing nitrate-n concentration in soil water and groundwater. Some fixation of ammonia occurred initially; however, nitrification acts as a major sink for ammonia in the unsaturated zone after the fixation capacity of the clays is exceeded (Keeney, 1984). No vegetation was present at the surface, thus removal of nitrogen by plant uptake can be eliminated. Infiltrating water provided dissolved oxygen for the nitrification of ammonia at relatively deeper depths, which may be an important factor in the transport of nitrates during excessive rainfall periods.

The arrival time of the maximum concentration of the nitrate-n pulse at a depth of nine feet was determined to be around thirty days. A comparison of soil water nitrate in the vertical soil profile is shown in Figure 27.



NO3-N IN SOIL-WATER FROM LYSIMETERS INSTALLED
AT TEST PLOT B FROM MARCH 3 TO JULY 7

Figure 27. Nitrate-n Concentrations in Soil-Water at Test-Plot B

Profiles of chloride concentration versus time and depth is shown in Figure 28. Channeling or macropore effects were obvious in lysimeter # 8 because of high amounts of nitrate observed only a few hours after starting the test.

A second loading of three thousand grams of ammonium-nitrate was applied on April 16, 1988. The results obtained are quite similar to those obtained with the smaller loading, however a wider pulse width was observed for the heavier load. This indicates that the maximum concentration leaching into the ground-water table has a longer duration and remains constant for a longer period of time. Comparison of nitrate-n concentrations obtained from lysimeters installed at one depth but at different locations, does indicate some variability in the concentration levels (Figures 29, and 30). The nitrate-n spike occurs at a depth of 9 ft earlier than the occurrence of a spike at 5 ft, this suggests that the contaminant pulse is nonuniform as it moves down through the soil profile, and is possibly influenced by the macropores. Interpretation of sulfate data was a difficult task because of the comparably high background levels in the soil water. The analysis of data accumulated for zinc indicates little or no movement of zinc below twelve inches (30 cm). This can be attributed to the significant attenuation of zinc through the absorption process. This indicates that zinc

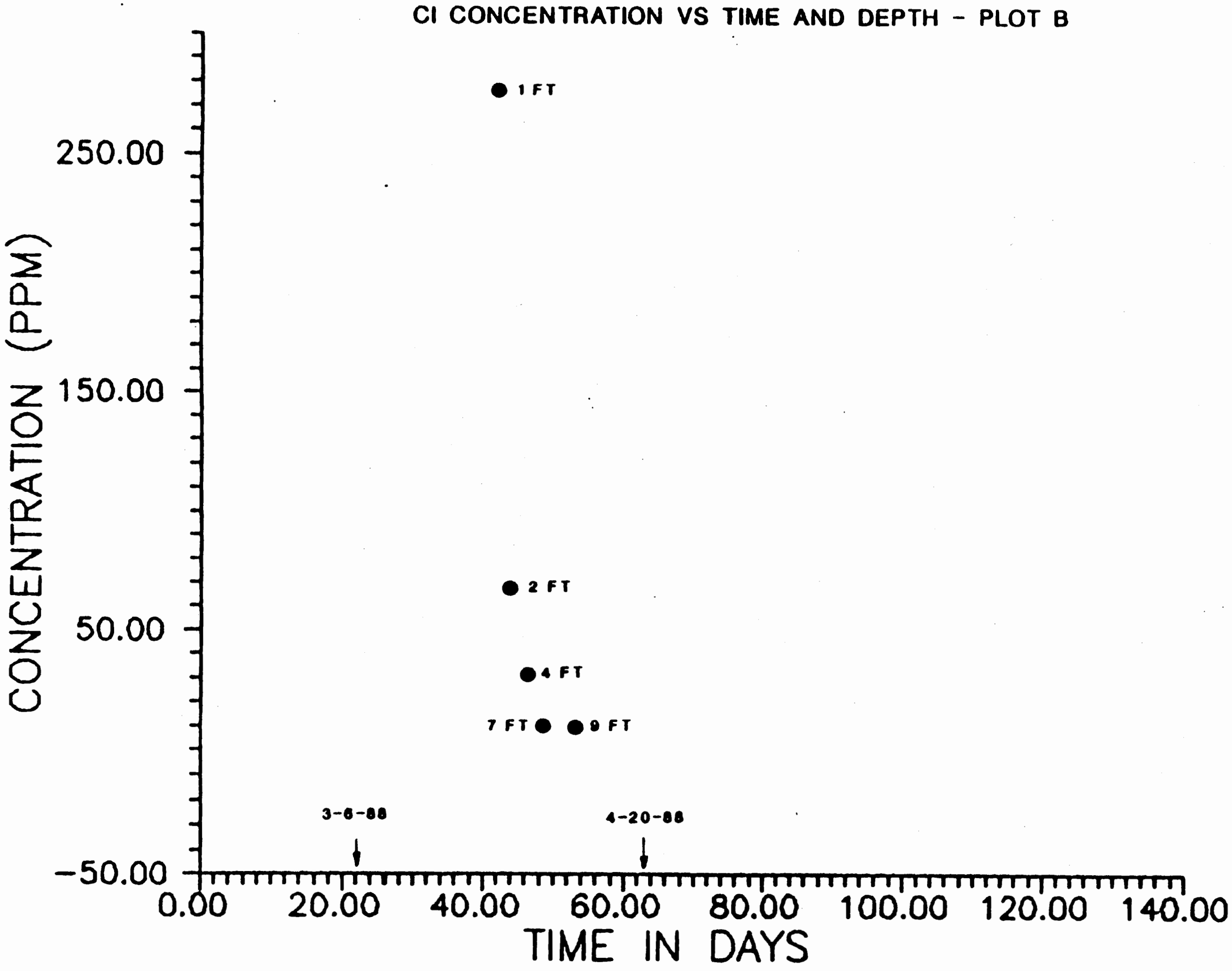


Figure 28. Chloride Concentrations at Different Lysimeter Depth with Time at Test-Plot B

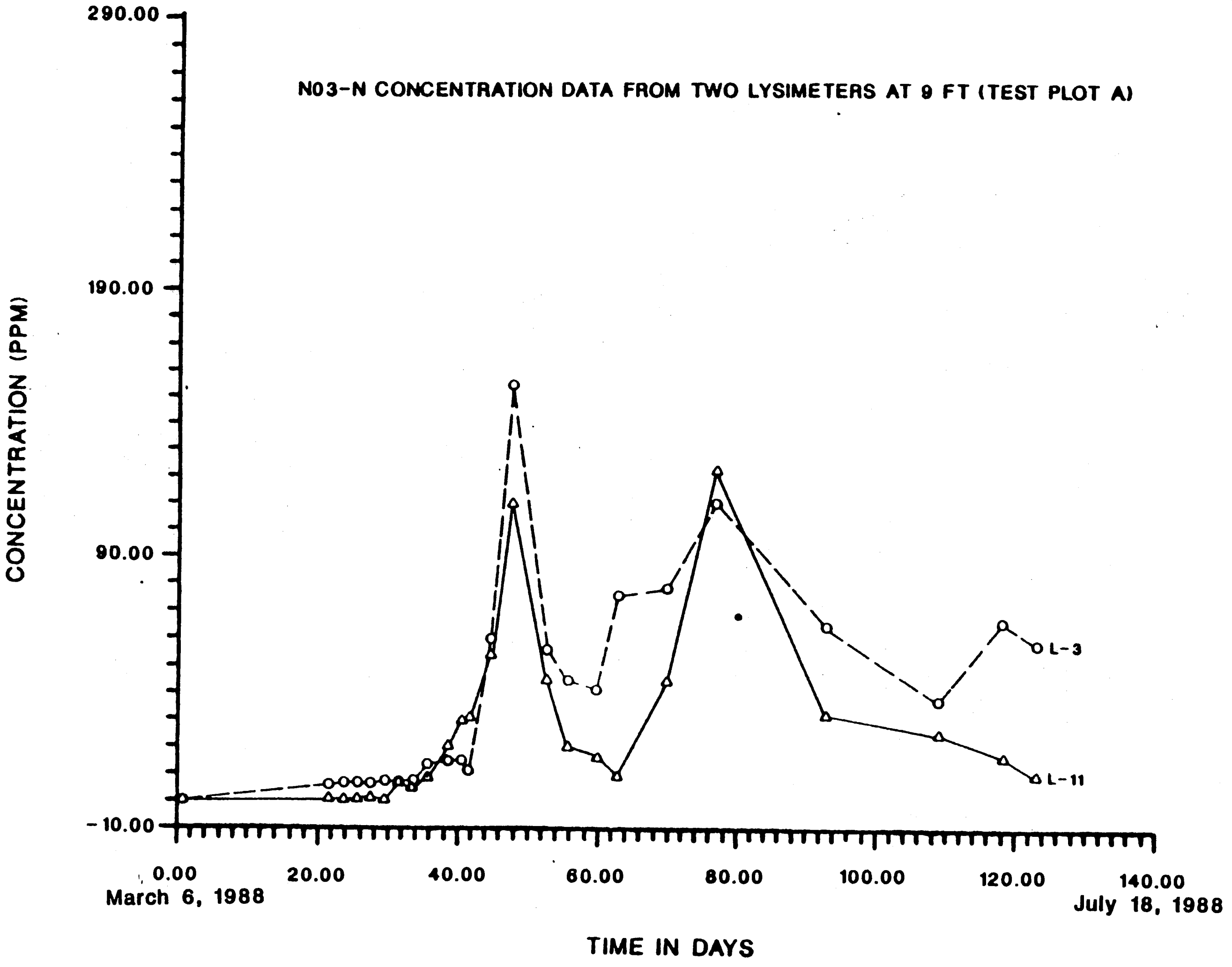


Figure 29. Nitrate-n Concentrations from Two Lysimeters at Depths of 9 Feet (Test-Plot A)

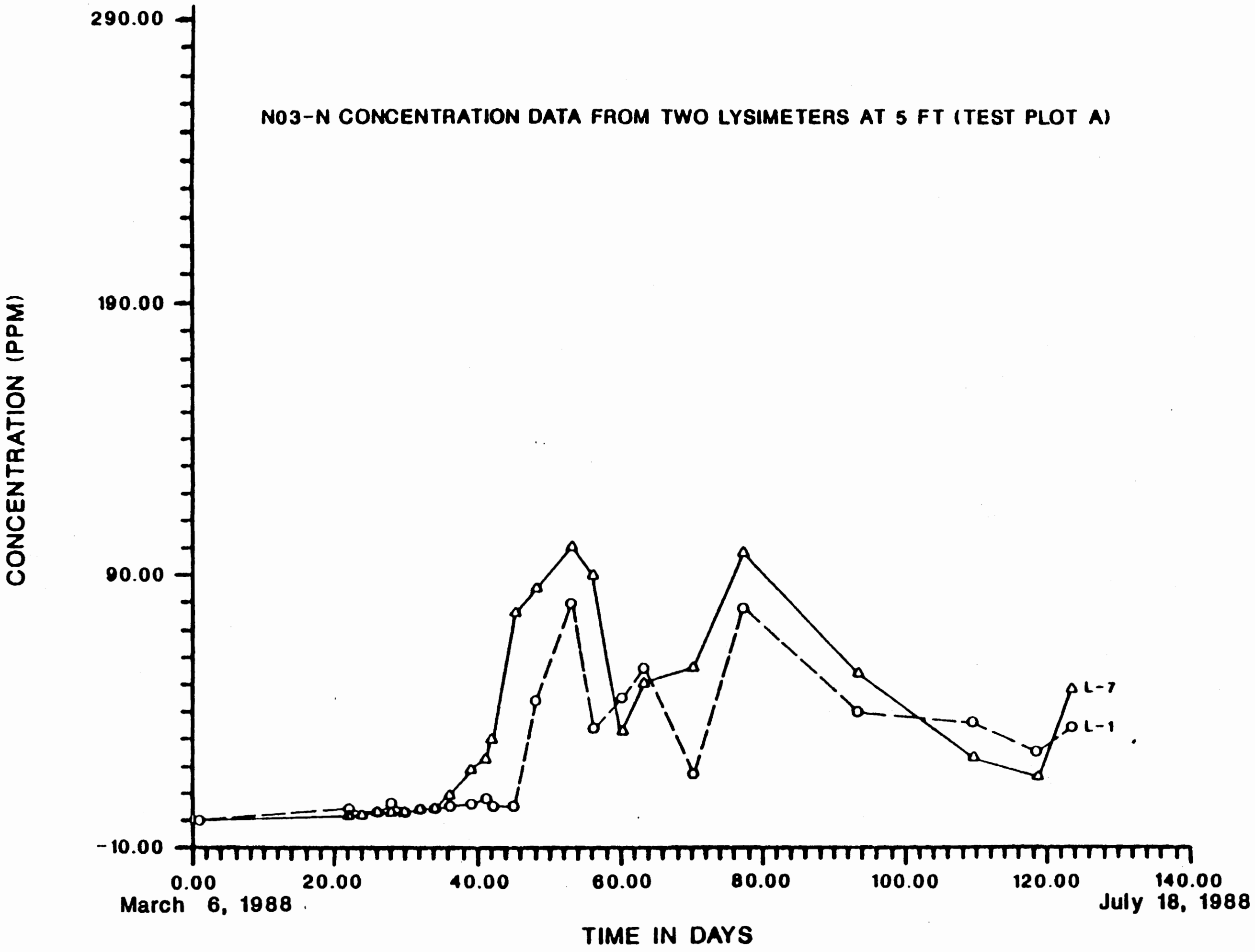


Figure 30. Nitrate-n Concentration from Two Lysimeters at Depths of 5 feet (Test-Plot A)

forms slowly soluble precipitates when combined with carbonate, sulfide, silicate, and phosphate ions, and is strongly sorbed on the exchange complex of soil.

Soil Sampling

Core samples were taken to a depth of nine feet (2.7 m), at six inch (0.15 m) intervals, by a truck-mounted soil probe. A 2 1/2 inch O.D. split-spoon type core barrel was used to obtain continuous core samples. Nitrate-n was extracted from the soil core using a calcium-chloride solution, and determined by ion chromatography. Variations in nitrate-n concentrations occurring at the same soil depth at different times were plotted in Figures 31 and 32. These profiles correlate well with the nitrate-n concentration profiles of the soil water. The highest concentrations in both soil (15 to 55 mg/l) and soil water (40 to 280 mg/l) were acquired in the upper two feet (0.6m) of the unsaturated zone. The nitrate concentration values measured in the upper 2 - 9 feet (0.6 to 2.7 m) of the unsaturated zone ranged from 0.1 to 22 mg/l. Concentrations at all depths increased and decreased at about the same rate, with a very short lag time of only a few hours to one day. Because the soil-sample data was taken irregularly (a total of only six sampling periods), it is difficult to substantiate the above theory. Soil water data which was

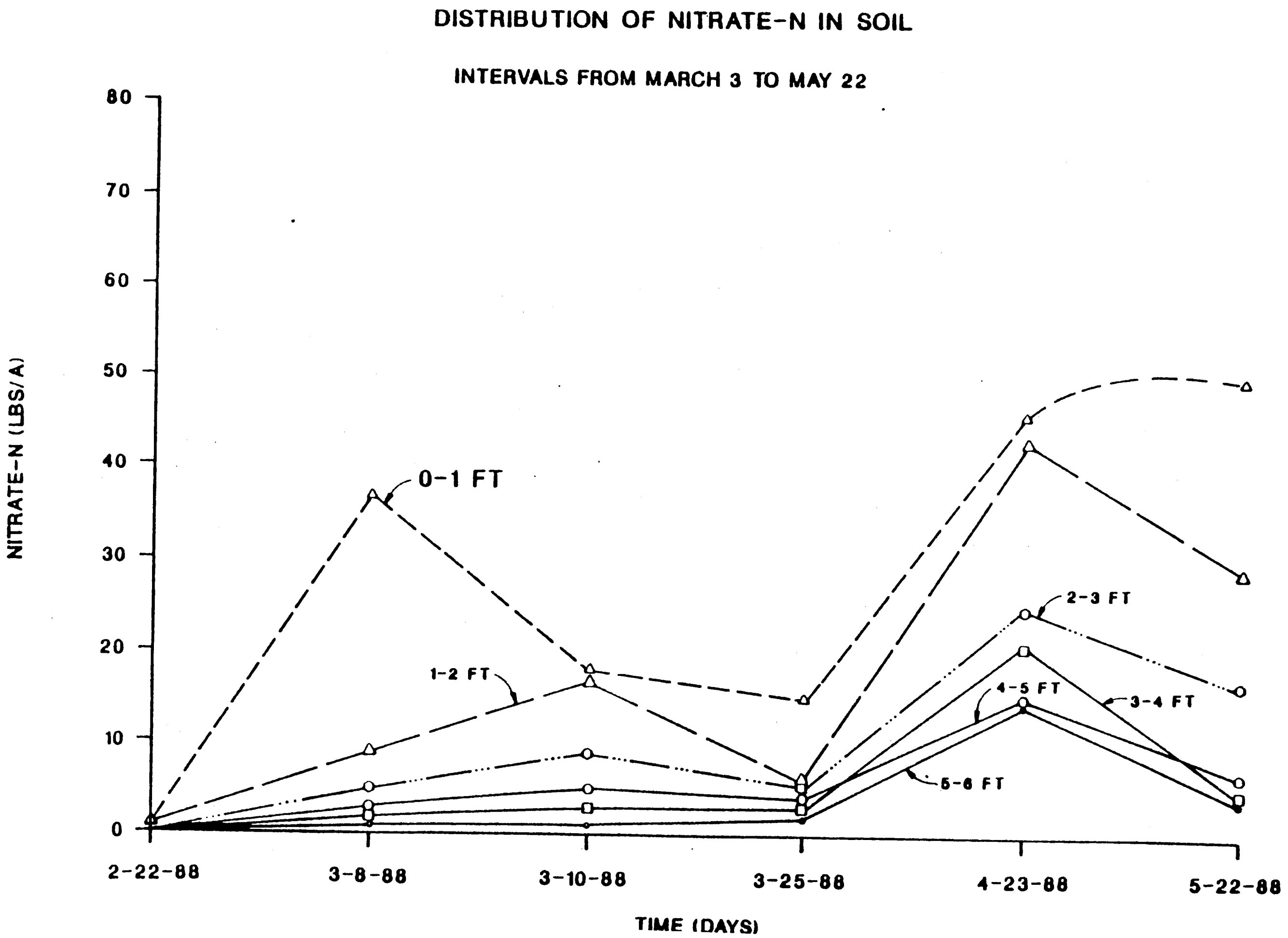


Figure 31. Variation of Nitrate-n Concentration in Soil with Time at Test-Plot A

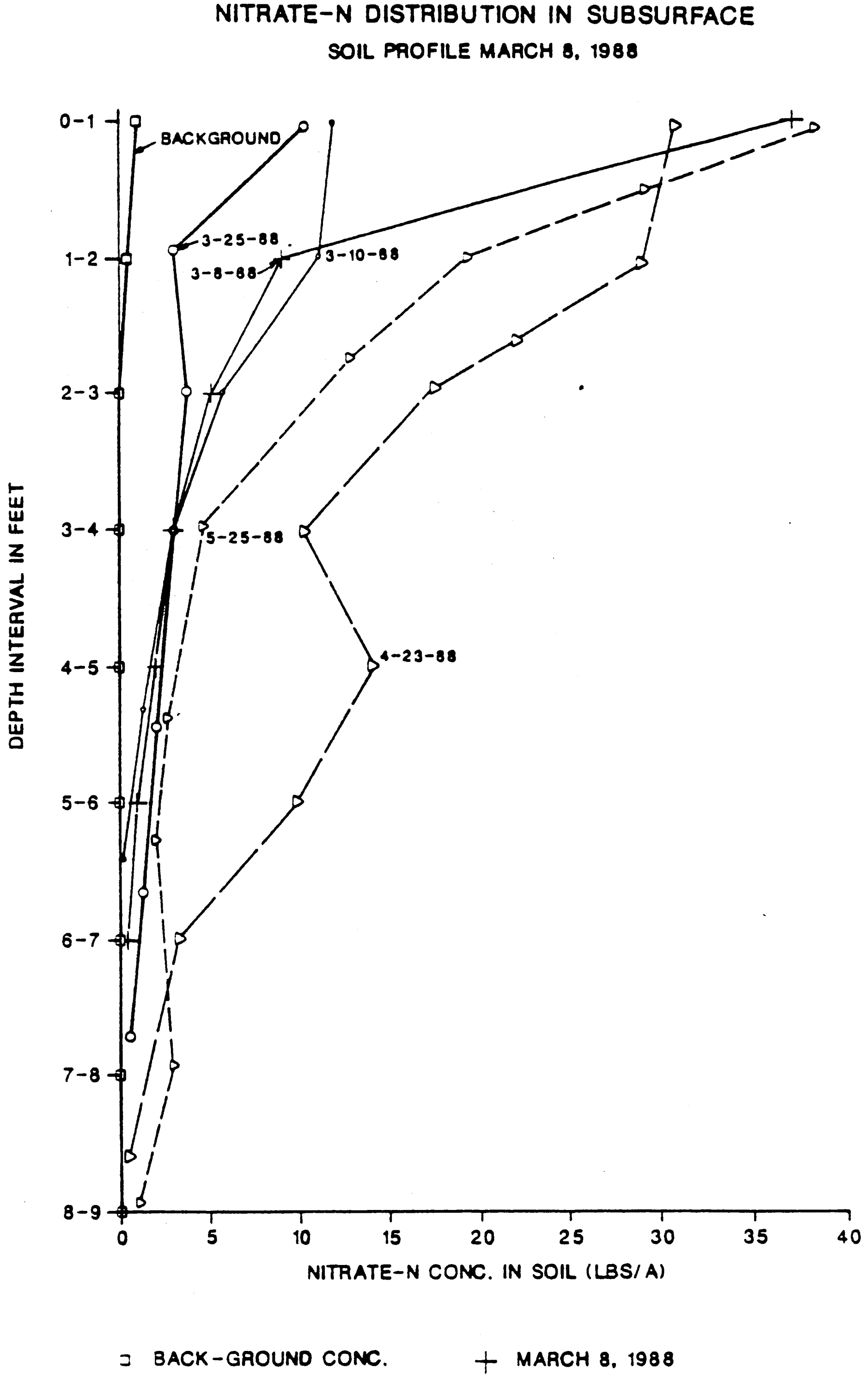
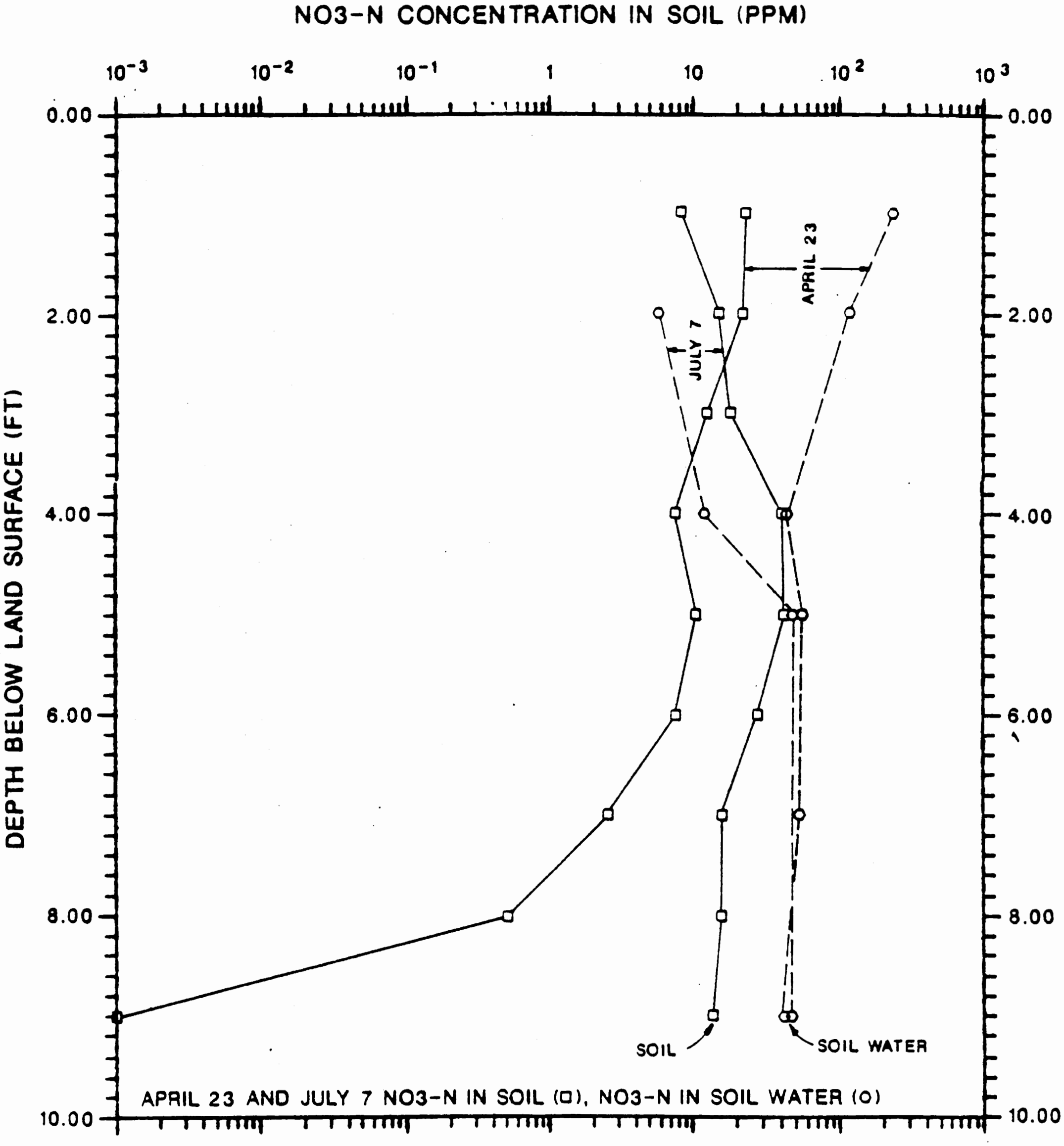


Figure 32. Nitrate-n Distribution in Subsurface Profile at Test-Plot A

recorded at intervals of two to three days seems to indicate this.

Plots of nitrate-n concentrations at varying depths in the vertical soil profile at a given time were constructed. These graphs indicate a linear decrease of nitrate-n with time after application of fertilizer at the surface. Figures 33 and 34 are comparisons of nitrate concentrations retained in the soil and dissolved in the soil water at different times. Spatial variability of the nitrate-n movement data in the unsaturated zone was analyzed by comparing soil data collected from test plot A against data obtained at test plot B. Data for soil moisture, conductivity, nitrate-n, and ammonia-n were plotted in a vertical soil profile. A comparison of Figures 35 and 36 indicates similar leaching patterns in the unsaturated zone at the two plots. The only variation occurred in the top twelve inches (30 cm) of the soil, which, as previously discussed, has different water-holding capacities in the two plots. Interestingly, an inverse relationship between ammonia-n and nitrate-n was observed; at various depths in the unsaturated zone, high ammonia-n concentrations were found to be associated with low nitrate-n concentrations. This strongly supports the idea that ammonium nitrification was a major source of nitrate-n in the unsaturated zone at the test site when ammonium nitrate fertilizer was applied.



COMPARISON OF NO3-N IN RETAINED IN SOIL AND
NO3-N ON SOIL WATER WITH DEPTH AT TEST PLOT B

Figure 33. Nitrate-n in Soil and Soil water (Test-Plot B)

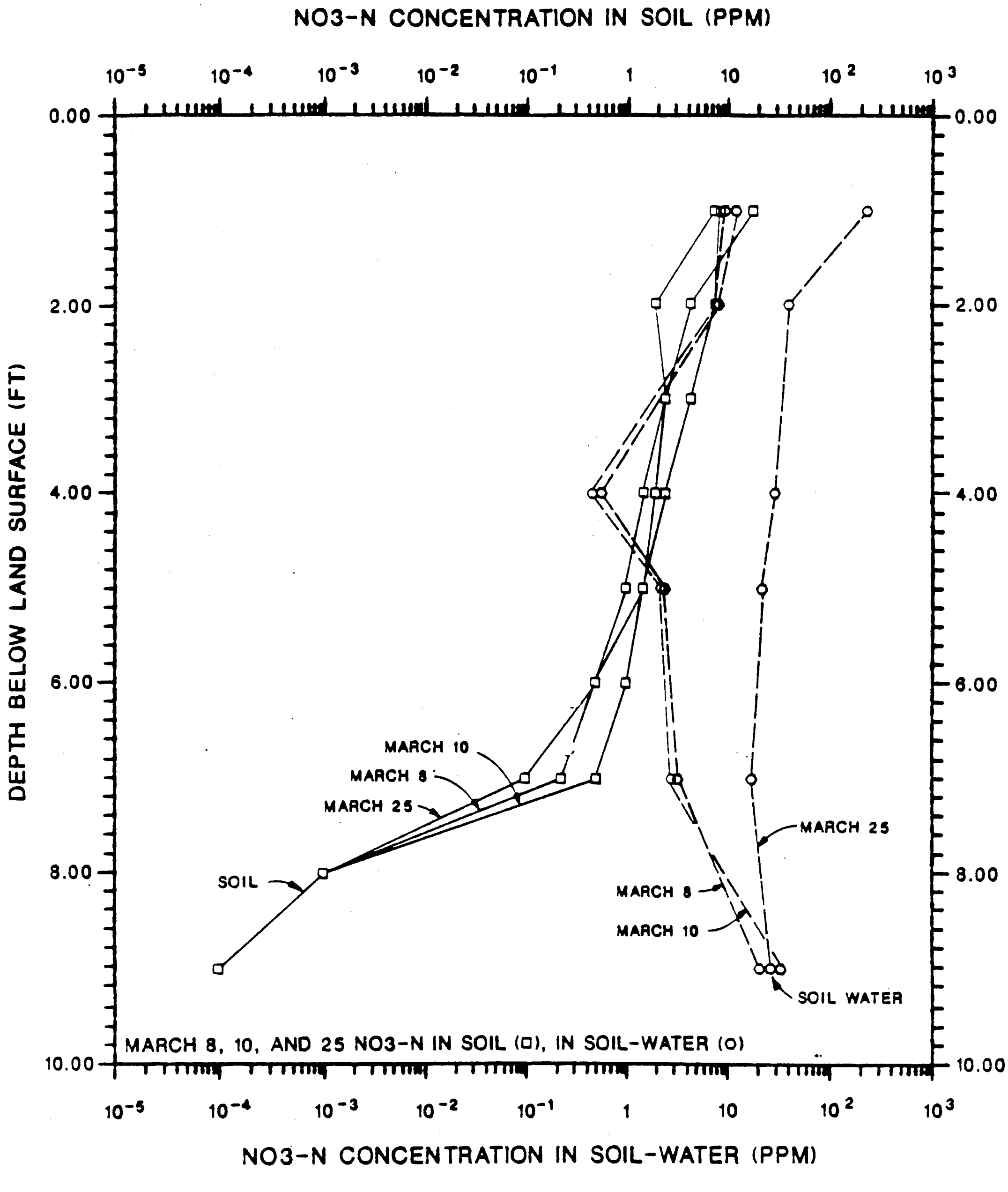
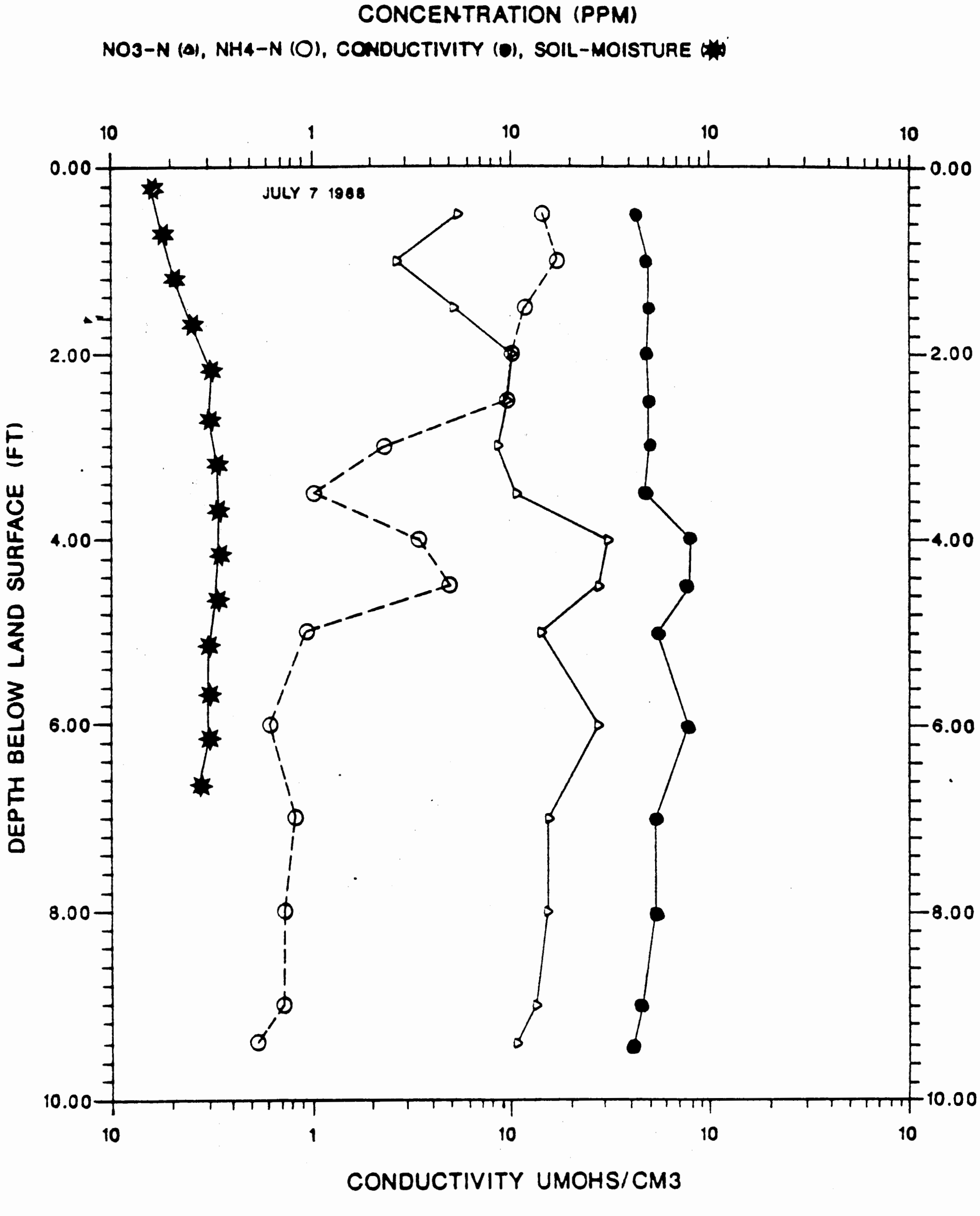
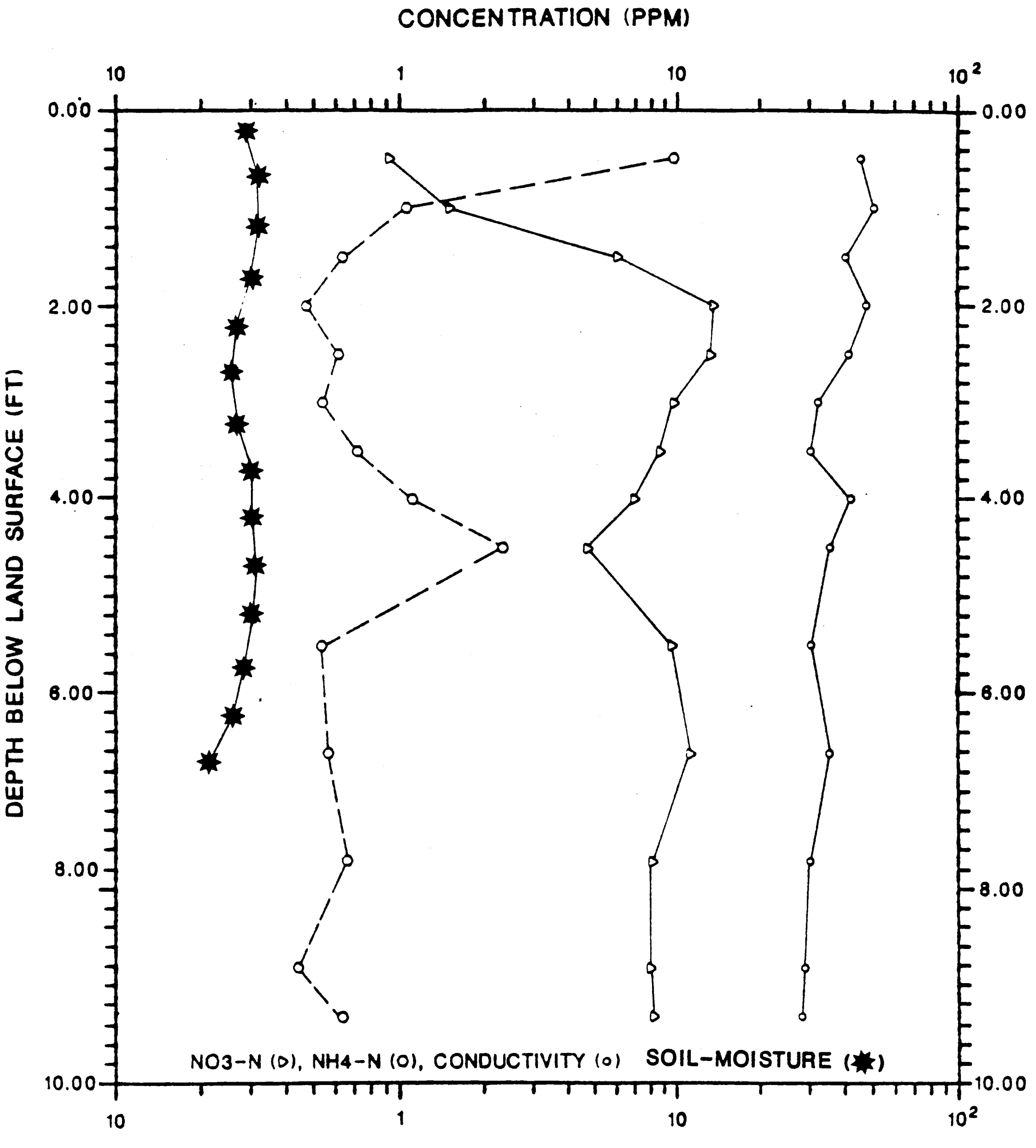


Figure 34. Nitrate-n in Soil and Soil Water Between March 8 and March 25 (Test-Plot B)



COMPARISON OF NO3-N, NH4-N CONCENTRATION, CONDUCTIVITY AND SOIL MOISTURE VALUES AT DIFFERENT DEPTH (TEST PLOT A)

Figure 35. Nitrate-n and Ammonia-n in Soil (Test -Plot B)



COMPARISON OF NO3-N, NH4-N CONCENTRATION AND CONDUCTIVITY VALUES WITH DEPTH AT TEST PLOT B

Figure 36. Nitrate-n and Ammonia-n in Soil (Test Plot-A)

Saturated Zone Monitoring at Test Plots A and B

A groundwater monitoring well network was established to monitor the leaching of the solutes from test plots A and B (Figure 37). The saturated zone monitoring system was designed specifically to monitor the lateral as well as the vertical variation of leached solutes. The groundwater quality data collected indicate an increase in nitrate and chloride concentrations approximately one week after application of the contaminant pulse; however, maximum concentrations were not recorded until approximately thirty days after the initial fertilizer application. The maximum nitrate concentrations in monitoring well # 13, which is installed at a depth of fourteen feet from the surface, were recorded twenty-seven days after the initial fertilizer application (Figure 38). This well is located 6 feet (1.8 m) away from test plot B. Overall, the greatest concentration values occurred in the deeper monitoring well, # 12. Similar results were obtained from the nested monitoring wells, # 16, # 17, and # 18, located near test plot A (Figure 39).

Tracer Transport in Saturated Zone

The use of tracers in hydrogeology gained popularity in the early 1960's for characterizing groundwater in Karst terrains. Use of the tracer has been reported by Davis, (1985) as early as 1869 when dyes and salts were used to

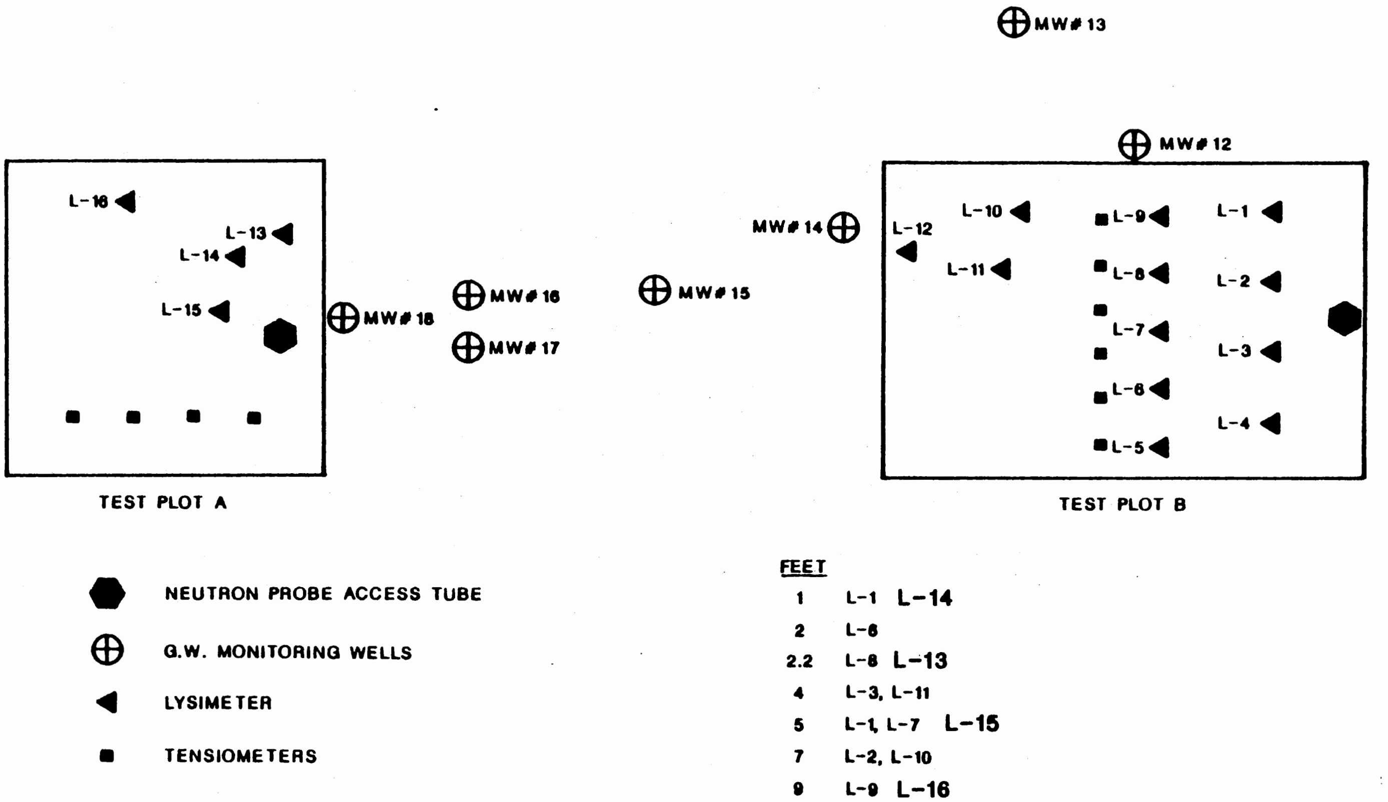


Figure 37. Plan Map of Saturated and Unsaturated Monitoring Instrumetation near Test Plots A and B

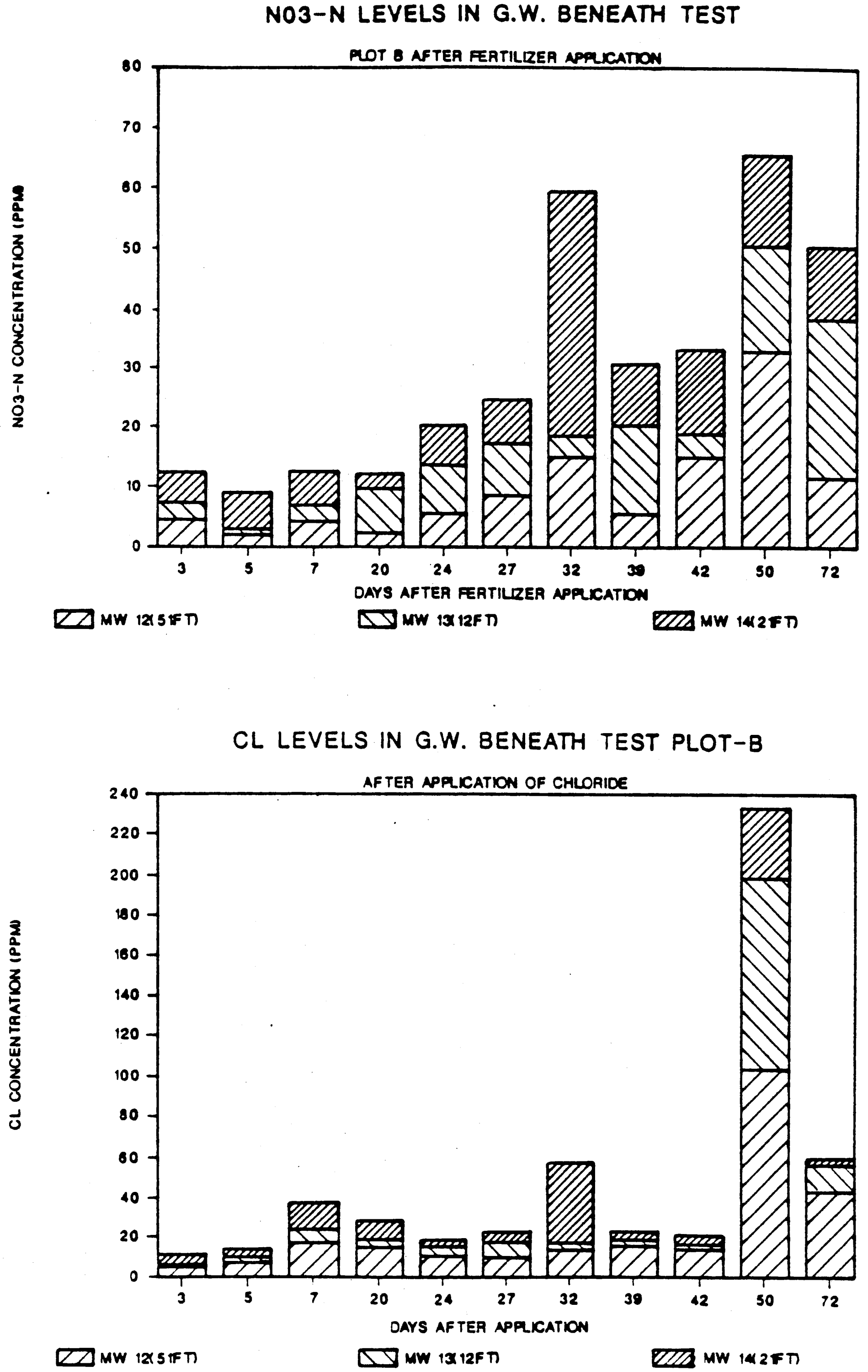


Figure 38. Nitrate-n Levels Beneath Test-Plot B

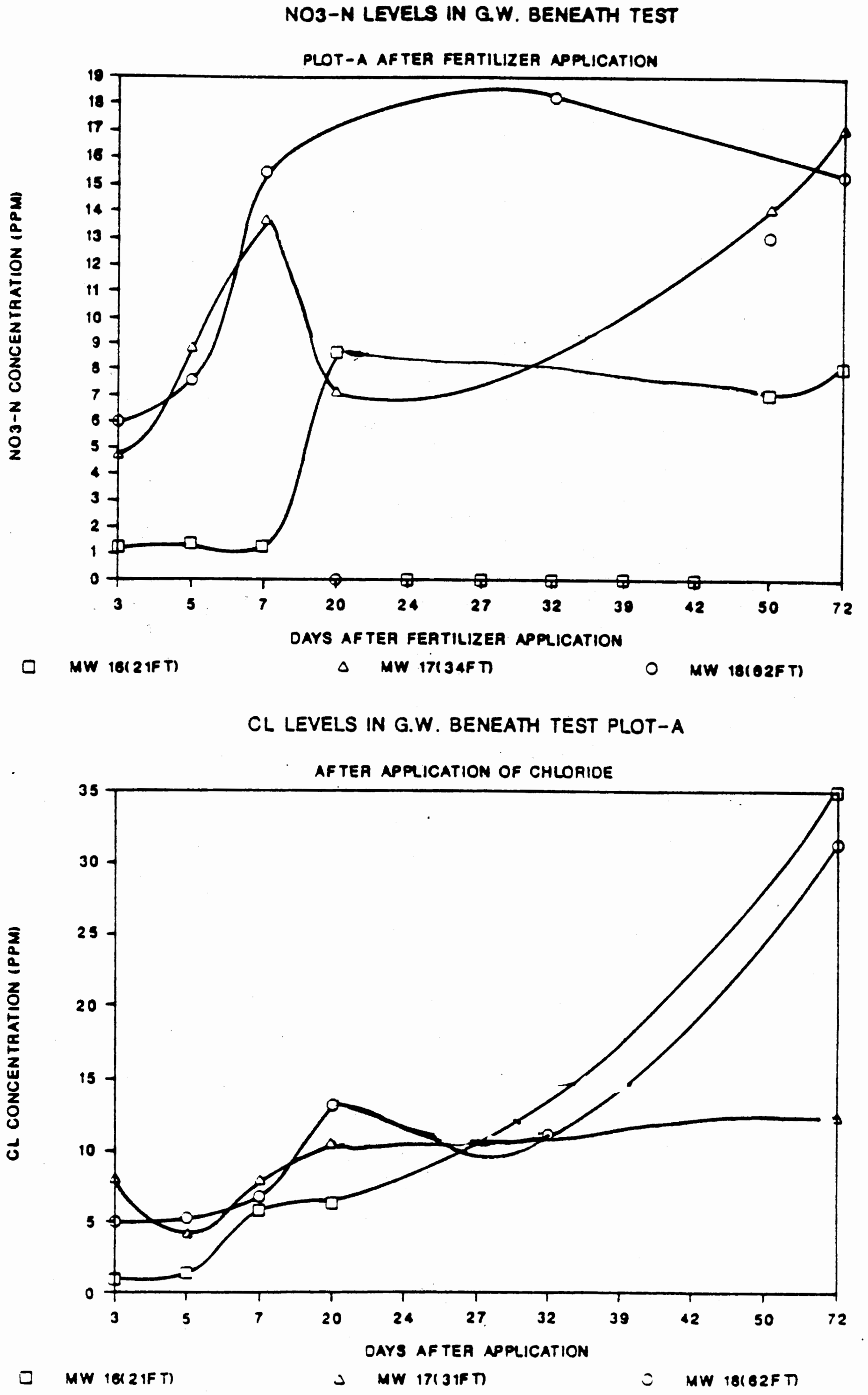
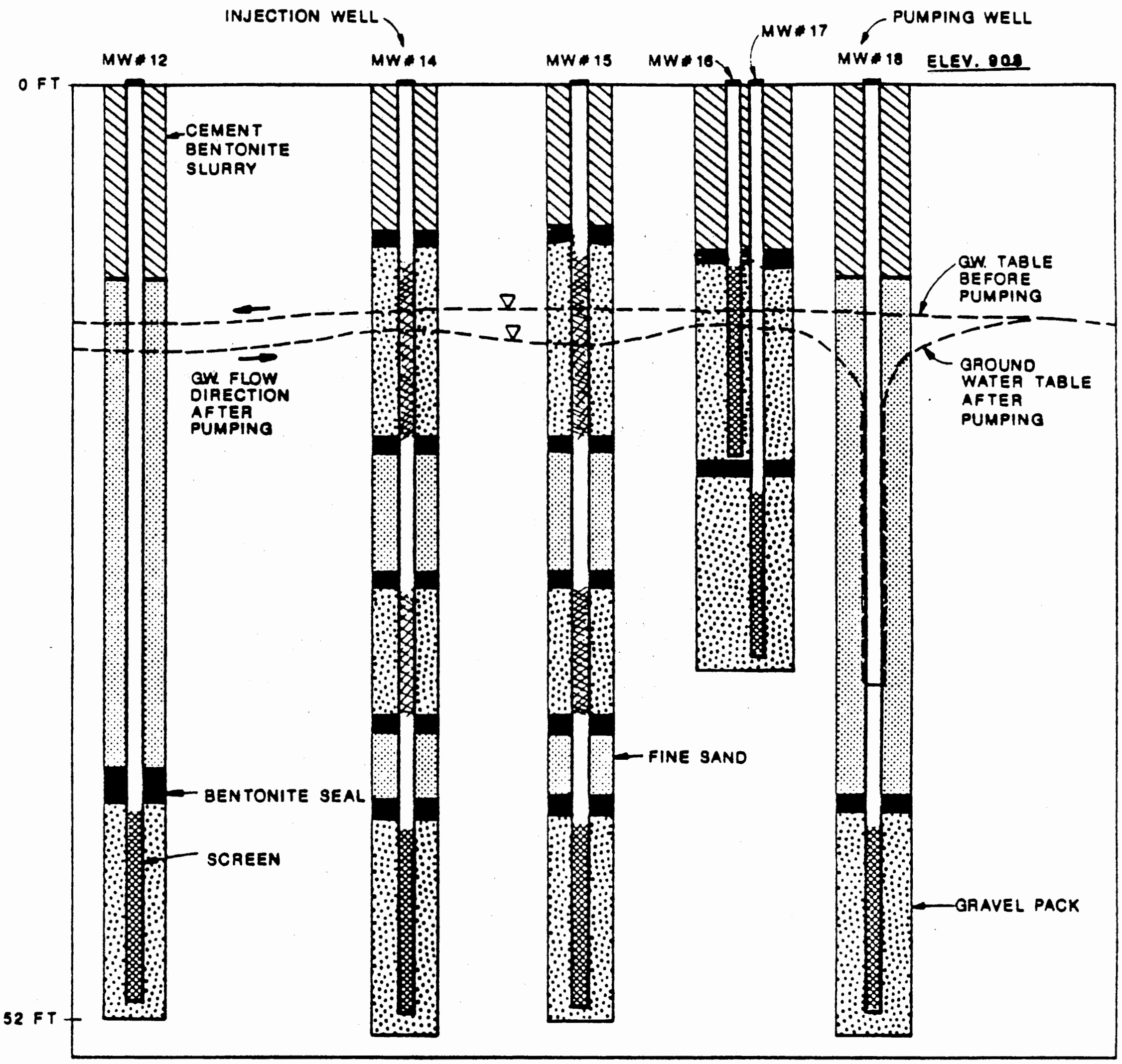


Figure 39. Nitrate-n Levels Beneath Test-Plot A

find hydraulic connections in karst areas. Tracer application in hydrogeology has become more modern and advanced since that time. Most of the current tracer studies have been concerned with solute movement in groundwater, and primarily with the characterization of the aquifer parameters which would affect the fate and transport of solutes in groundwater (Guven, 1986; Keely, 1986; Davis, 1985; and Molz, 1983).

Design of groundwater monitoring wells used for tracer testing with groundwater levels prior to tracer testing are shown in Figure 40. The direction of groundwater flow is from the pump well toward the injection well at a gradient of 0.4 ft/ft (12 cm/cm). The pumping of well 18 was initiated on May 12, 1988; the average discharge rate was 57 gpm. For the next few days, water levels were recorded until a near steady state in the drawdown values was achieved. The pumping of well 18 caused a reversal in the groundwater flow direction and an induced gradient of 0.6 ft/ft (18 cm/cm) was established.

A slug-release contaminant source was used rather than the most commonly used continuous contaminant source, because most of the contaminants in the actual field setting do not arrive at groundwater table in a continues pattern. Fifteen gallons of solution containing 3 kg of ammonium-nitrate, ten gallons of solution containing 2.1 kg of potassium-sulfate, and five gallons of solution



SCALE:
HORIZONTAL: NOT TO SCALE

Figure 40. Cross-section of Groundwater Monitoring Wells Used for Aquifer Tracer Testing

containing 2.2 kg of sodium-chloride were injected into well 14 at a rate of one gallon per minute. A surger was constantly utilized in order to assure adequate mixing of the contaminant inside the well. Three point source bailers constructed of teflon were used to sample injection well 14, observation well 15, and an observation well nest (wells 16 and 17). Samples were taken at discrete intervals and were later analyzed for the tracers. Normalized nitrate concentrations, C/Co, were plotted for the observed data in the injection and observation wells (Figures 41 and 42). The observed concentration in the observation well at any given time is represented by C; Co is the initial concentration in the source well at time zero. The nitrate breakthrough curves obtained for different depths indicate dispersion in combination with advection to be the main physical process responsible for nitrate transport. In a typical advection (velocity) dominated concentration distribution, a sharp concentration front with concentrations throughout the plume equal to the input concentration is expected (Mok, 1986). The incorporation of dispersive effects would however dilute the plume by dispersion dominated by gaussian distribution. There appears to be some degree of sorption of nitrates into the aquifer matrix at the shallow interval. The highest nitrate concentrations were obtained in the deeper interval and the lowest values were noted in the shallow

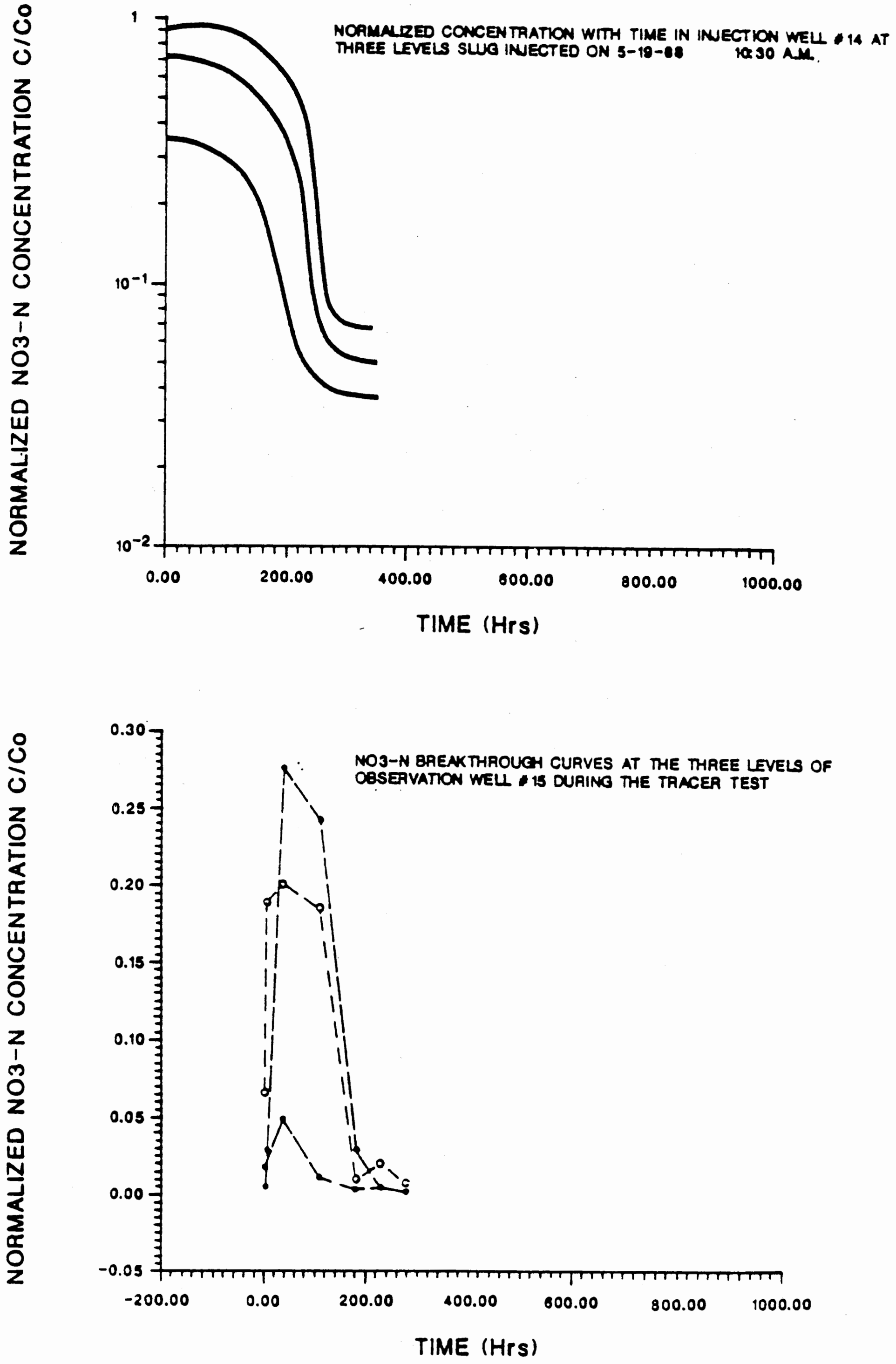
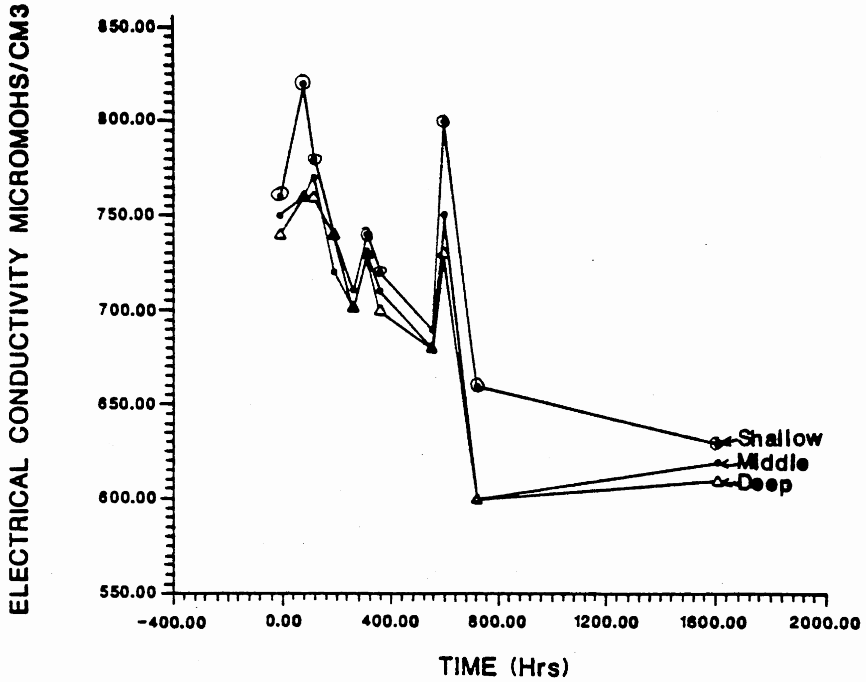
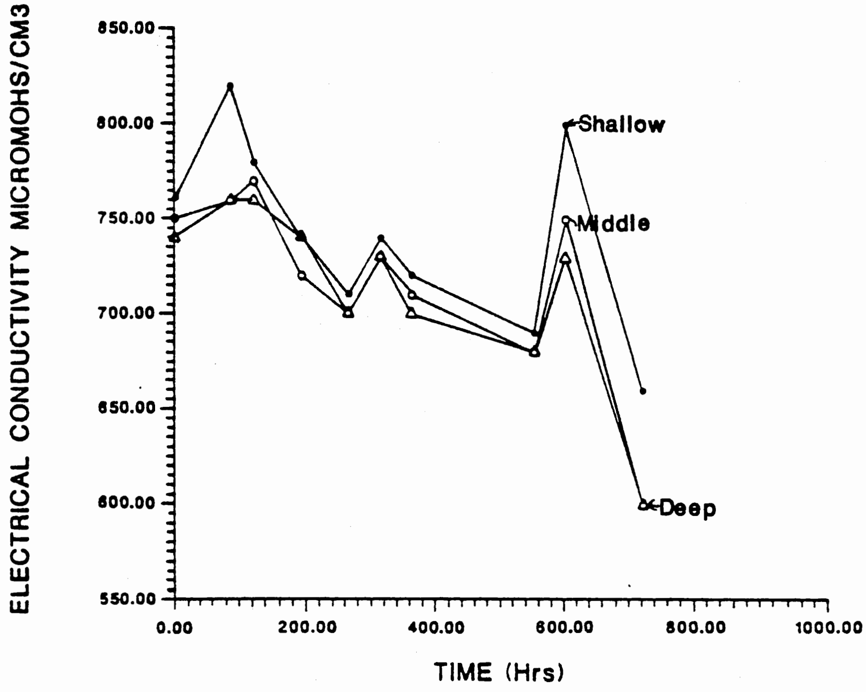


Figure 41. Normalized Nitrate-n Breakthrough Curves for Injection Well 14 and observation Well 15



CONDUCTIVITY WITH TIME AFTER INJECTION OF CHEMICAL SLUG IN WELL 14 AT THREE LEVELS



CONDUCTIVITY WITH TIME AFTER INJECTION OF CHEMICAL SLUG IN WELL 15 AT THREE LEVELS

Figure 42. Electrical Conductivity Variations with Time injection and Observation Wells 14 and 15

interval of observation well 15. This probably results from the density-controlled distribution of nitrate concentration in the injection well. The first arrival time of the nitrate slug occurred after approximately six hours. Nitrate concentration values at different distances and at the three depth intervals in the aquifer are included in Appendix F. A significant decrease occurs in the nitrate concentration pulse with increased distance from the pumping well; reduction from 2000 mg/l to 20 mg/l over a distance of eight feet (2.4) is noted.

Based on the arrival time of the nitrate pulse, an expression for hydraulic conductivity is determined using a modified form of Darcy's equation. Darcy's equation, $Q = -KA\, dh/dl$, states that for a simplified hydrologic system volume of water flowing per unit of time (Q) through a given cross-sectional area (A), is directly proportional to the hydraulic gradient (dh/dl) and the hydraulic conductivity (K) (Davis, 1985). When water flows through a porous media, the discharge is a product of the velocity (v), cross-sectional area (A), and the porosity (n) of the porous media:

$$Q = vnA \tag{1}$$

The term v in equation (1) can be replaced by dl/dt where dt is the length of time taken by the average water particle to move through a distance (dl) (Davis, 1985).

Darcy's equation can be combined with equation (1) and written as:

$$K = n(dl)^2/tdh$$

This equation can be used to estimate the hydraulic conductivity of the aquifer. An arrival time of the nitrate pulse five feet (3.2 m) away from the source well was determined to be six to seven hours. Using the arrival time of seven hours, an aquifer porosity of 30 percent, and a head difference of 0.6 ft/ft (18 cm/cm), a hydraulic conductivity of 320 gpd/ft^2 was determined. When an arrival time of six hours was used, a value of 374 gpd/ft^2 was obtained.

CHAPTER VII

MODELING OF INORGANIC AND ORGANIC AGRICULTURAL CHEMICALS

Characterization of contaminant transport in the unsaturated and saturated zones, risk assessment, and problems relating to waste disposal are increasingly being approached through the use of computer models (Abriola, 1987). Evaluation of each of these subjects to obtain possible hydrological, soil, chemical, and meteorological conditions based on field experimentation is very time consuming, expensive, and site specific.

The success of model prediction depends upon the accuracy and availability of data regarding the natural processes which control solute movement in the unsaturated and saturated zones. In order to apply a model to a particular situation, specification of the physical, chemical, and hydrological parameters pertaining to the particular system being addressed is required. Parameters identified and determined during various phases of this research are shown in the flow chart (Figure 2). When using a mathematical model, the user inputs all the necessary information (geometry, physical properties, initial and boundary conditions) into the model and a computer is employed to rapidly solve the resulting equations which generate the model output (Molz, 1985). Three mathematical models have been developed to simulate (1) the vertical movement of solutes in the unsaturated zone and (2) the lateral and vertical movement of solutes in the saturated zone.

All models describing the fate and transport of agricultural chemicals, primarily pesticides, are based on the principles of the conservation of mass (Carsel, 1985; Abriola, 1987). Two computer models, PRZM (Carsel et al., 1984) and CMIS (Nofziger et al., 1985) describing solute transport in the unsaturated zone and a third computer model, KONIKOW (Kent et al., 1986), describing solute transport in groundwater are utilized for predicting the fate of agricultural chemicals in the subsurface at the Oklahoma State University Agronomy Research Station test site. The three models utilized in this study are of varying degrees of simplification in both the general theory and the numerical methods used to solve the resulting set of non-linear partial differential equations.

Unsaturated Zone Modeling of Tracer Test

Various models exist for estimating the movement and degradation of pesticide residues in the unsaturated zone (Jones, 1983). Two models, Chemical Movement in Soils

(CMIS) developed at the University of Florida and Pesticide Root Zone Model (PRZM) developed by the U.S. Environmental Protection Agency (EPA) are used in this study.

CMIS Model

The CMIS, model is the simplest of the three models and estimates the location of the leading edge of a non-polar organic chemical as it moves downwards through the soil (Nofziger, 1985). The software for this model is based on the water and solute transport principles presented by Rao and others, (1976). Input requirements and output forms for this program are included in Appendix H. Simulations for 2,4-Dichlorophenoxy acetic acid (2,4-D) Malathion, Diuron, Aldicarb, and Lindane were executed for the Teller soils. The results indicate the movement of 2,4-D, Aldicarb, and Lindane below the root zone, however there is no evidence of chemical leaching into saturated zone. The validity of these results is highly questionable because the simulated results do not correlate well with the field leaching patterns of the nitrate tracers described herein. This model assumes that piston flow is the primary mechanism for water movement through the soils, and does not consider the the influence of preferential flow through macropores on chemical transport.

Pesticide Root Zone Model (PRZM)

PRZM, Pesticide Root Zone Model was developed by the U.S. Environmental Agency and has been adequately tested and verified by field data. PRZM was developed to aid in the exposure assessments of potentially toxic pesticides in groundwater. This is a dynamic, compartmental model for simulating the movement of pesticides in unsaturated systems within and below the root zone. Time-varying transport, including advection and dispersion, is represented in the model program. PRZM has two major components: 1) hydrology and 2) chemical transport (Figures 43 and 44). The following discussion is based on the user's manual for PRZM model developed by USEPA, (Carsel, 1984). The hydrology component for calculating runoff and erosion is based on the SCS curve number and soil loss equation. Evaporation is estimated from pan evaporation data. Water movement is simulated by the use of generalized soil terms including field capacity, wilting point, and saturation. To produce soil water and solid phase concentrations, the chemical transport model calculates pesticide evapotranspiration by plants, surface runoff, erosion, decay, vertical movement, dispersion, and retardation. A finite difference numerical solution, using a backwards difference implicit scheme, is employed (Carsel and others, 1984).

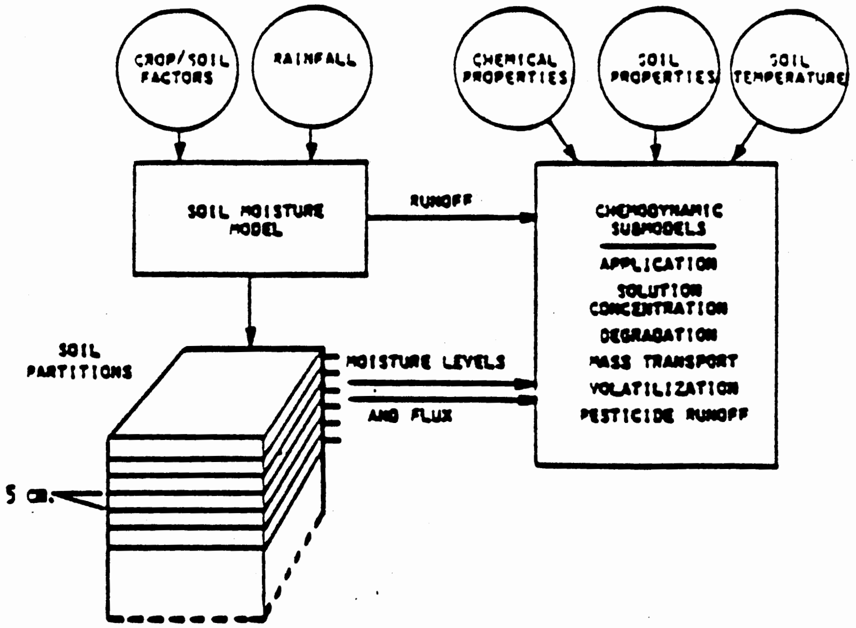


Figure 43. Typical Soil Pesticide Model Organization (After Voss, 1984)

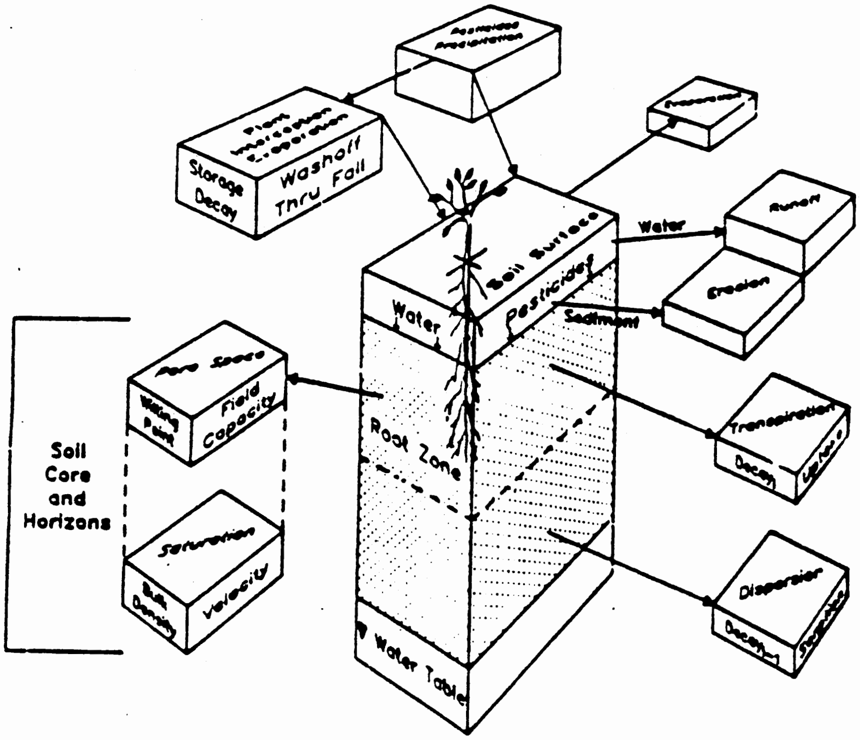


Figure 44. Schematic of Processes Influencing Fate and Transport of Chemicals in Unsaturated Zone (After Carsel, 1985)

Results

The PRZM model was calibrated for nitrate using field leaching and tracer data. The model was used to simulate the fate and transport of Carbaryl, Carbofuran, Trifluralin, Malathion, Atrazine, Diuron, and 2,4-D. Two soils belonging to the Konawa and Teller soil groups were selected. The simulations were executed for a wheat crop over a duration of two years, 1986 and 1987. Results obtained using Teller soils indicate leaching of Diuron, Atrazine, and 2,4-D to a depth of ten feet (3 m). The groundwater table at the site varies from ten to fourteen feet 3 to 4.3 m). All concentrations leached were, however, below present detectable limits. The leached concentrations ranged from 0.2 E-08 for 2,4-D to 0.18 E-15 mg/l for Diuron. The simulated results obtained for Konawa soils indicate that pesticide usage on this soil poses some potentials of groundwater contamination. All pesticides leached to a depth of ten feet (3 m), with the exceptions of Trifluralin, Malathion, and Carbaryl. No signs of leaching were indicated for Malathion below the first few inches of soil; whereas, Trifluralin leached to a depth of twelve inches and Carbaryl leached to depths of approximately four feet. The greatest leaching potential 0.13 E-6 mg/l, existed for 2,4-D.

Saturated Zone Modeling

A modified two-dimensional areal solute-transport model originally developed and documented by Konikow and Bredehoeft (1978) is utilized at the Perkins site. Modifications by Kent and others, (1985) include an option to solve the groundwater flow equation using the Strongly Implicit Procedure (SIP), rather than the Alternating-Directional Implicit Procedure ADIP). For this study SIP was utilized, which converges in about one-half the iterations required for the ADIP procedure. Therefore, SIP results in a saving of considerable computer time.

Model Application of KONIKOW

The Perkins Terrace aquifer supplies water to the local farming community. The groundwater at the Oklahoma State University Agronomy Research Station is primarily used for irrigation purposes. The Konikow Model has been applied in the past primarily to point source contaminant transport in groundwater. An effort was made in this research to apply the Konikow Model to a non-point source contamination scenario.

A very simplistic approach was taken, and point source values were assigned to the nodes in the grid matrix which was constructed for the area. The grid consists of 14 rows and 6 columns (Figure 45). Each grid block represents an area of 1296 m^2. Figure 46 shows the location of different

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1NODE IDENTIFICATION MAP
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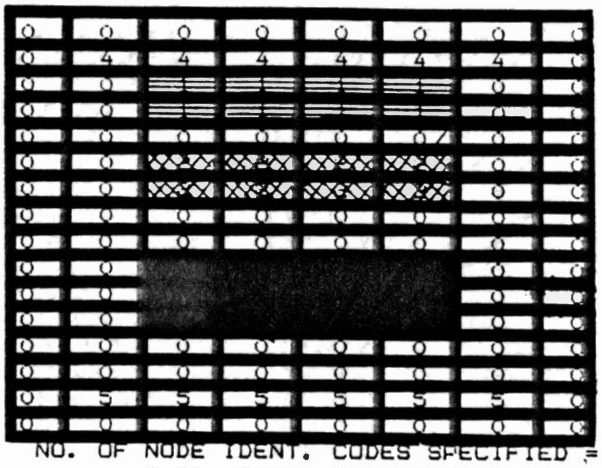

```
0      NO. OF NODE IDENT. CODES SPECIFIED =   5
0           THE FOLLOWING ASSIGNMENTS HAVE BEEN MADE:
     CODE NO.        LEAKANCE       SOURCE CONC.      RECHARGE
0        1          2.000E-05       5.000E+01
0        2          2.000E-05       5.000E+01
0        3          2.000E-05       5.000E+01
0        4          2.000E-05        .000E+00
                                                    -3.500E-06
0        5          2.000E-05        .000E+00
                                                     3.500E-06
```

▤ **Orchard**

▨ **Grass**

■ **Wheat**

Figure 45. Node Identification and Grid Location map for KONIKOW Model

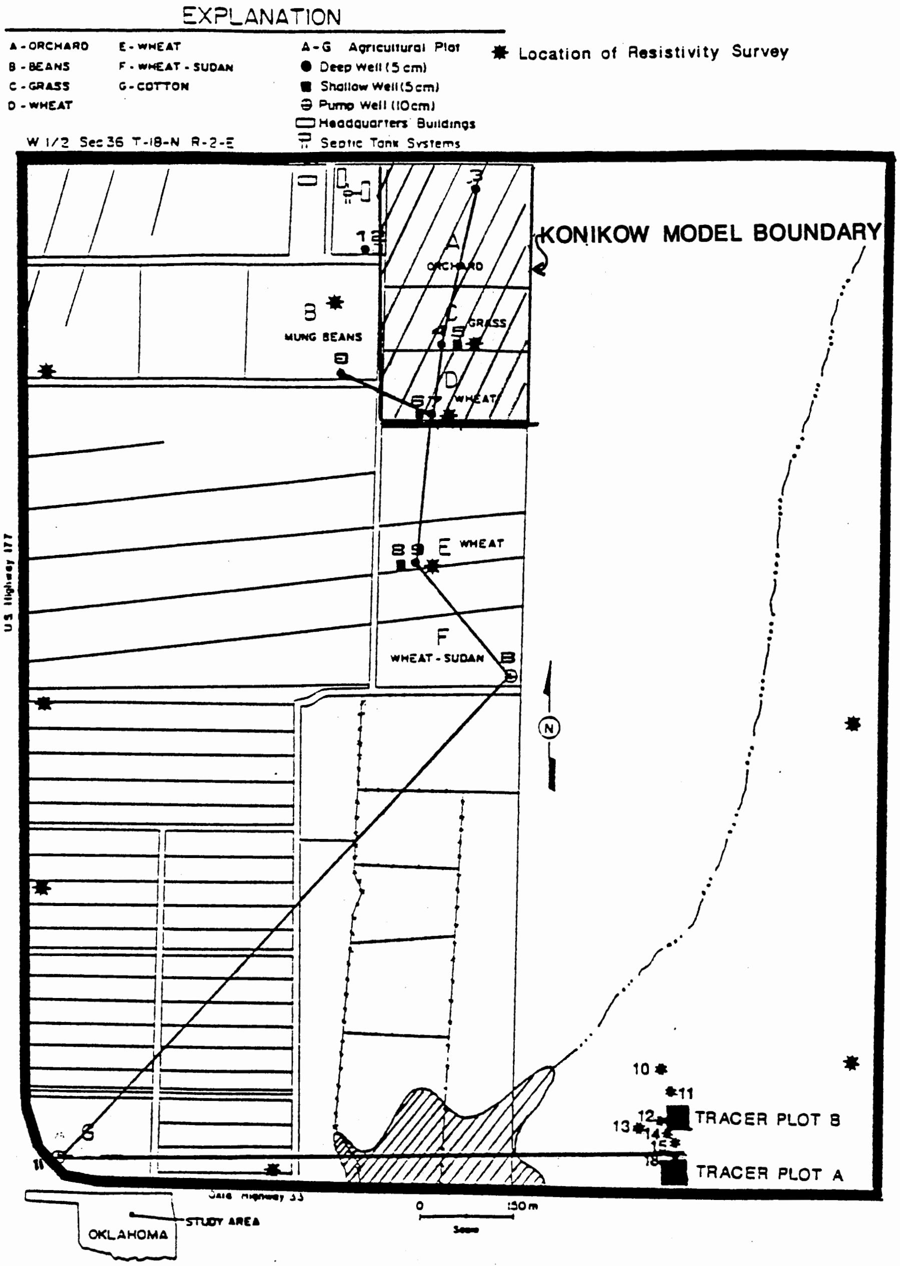

Figure 46. Location of Modeled Area

agricultural plots, observation wells, and nodes used as source points. Each input to the node is considered to be the average value over the entire block. Input parameters such as transmissivity, porosity, storage coefficient, saturated thickness, water table elevation, and recharge were entered in the model as matrices. Two different scenarios, the first (A) for low hydraulic conductivity and low storage coefficient and the second (B) for high hydraulic conductivity and high storage coefficient were used.

Before the Konikow Model was used for solute transport it was calibrated for ground-water hydraulics, using the water level data obtained between 1986 and 1987. After calibration, the model was used to simulate the lateral solute transport of nitrate in groundwater. The loading rates of nitrate to the groundwater table were obtained from the PRZM output data as well as from the water quality data. The model runs were made assuming that the application rate of fertilizer and areal distribution remain constant.

Results

The Konikow Model was run for the two scenarios, previously described in the section entitled Model Application, for a duration of three years. A constant source concentration of 50 mg/l was injected at each node representing the agricultural plots. The results of Scenarios A and B showing the concen-tration distribution are included in Appendix I. The simulated concentrations observed in the downgradient observation wells correlate well with the actual concentrations noted in the field, thus verifying the field calibration of the KONIKOW model. The concentrations range from 40 to 46 mg/l in the upper portion of the grid area and between 12 and 25 mg/l in the lower portion of the area. No significant difference between the concentration plots obtained for the two scenarios were observed. This indicates that the increase of 50 gpd/ft^2 in the hydraulic conductivity value did not significantly alter the concentrations of nitrate obtained by using the initial hydraulic conductivity value of 350 gpd/ft^2.

CHAPTER VIII

RESULTS AND CONCLUSIONS

Site Characterization

An attempt has been made to characterize agricultural impacts on groundwater quality and to acquire input parameters required for the simulation of the fate and transport of chemicals in the unsaturated and saturated zones of alluvial and terrace aquifers. Parameters acquired in this study include unsaturated and saturated zone hydraulic properties, physical and chemical properties of the unsaturated zone, and chemical-soil interaction properties and boundary conditions.

The site geology was characterized based on the drilling, surface, and borehole geophysical data. The Perkins Terrace aquifer is an unconsolidated terrace deposit of Quaternary age, consisting primarily of fine to medium-grained sand with occasional thin discontinuous silt and clay layers throughout. There is a general increase in grain size in the stratigraphic cross-section from finer materials in the top layers to coarser-grained sediments in the bottom layers of the section.

The soils belonging to the Konawa and Teller soil groups were selected for use in computer simulation and field testing of chemicals. Parameters for soil hydraulic conductivity, bulk density, percent sand, percent silt, percent clay, and percent organic matter at different depths were either collected in the field or obtained from previous investigations. A neutron moderation method was used to obtain soil moisture profiles in the Konawa soils during the unsaturated zone tracer test.

Water levels for all monitoring wells were recorded between Spring, 1986 and Summer, 1988 and were used to plot hydrographs and a potentiometric map. The data indicates a lag of 20 to 30 days from the time of precipitation to the maximum groundwater level increase and the time of precipitation. A point-measure field test in the form of a slug test was applied and hydraulic conductivity values for all monitoring wells were obtained. The average hydraulic conductivity values acquired range from 68 gpd/ft^2 to 323 gpd/ft^2. The variability was more a function of well development rather than spatial heterogeneity. In general, slug test values were an order of magnitude lesser than the aquifer pump test results. The best estimated hydraulic conductivity value of 324 gpd/ft^2 was obtained using the Prickett Method. Other methods provided values which compared well with the Prickett method.

Groundwater Quality

An overall water quality for the nutrients and common chemical ions at the site was established using both long-term (quarterly) and short-term (bi-weekly) data. The long-term data indicates a strong correlation between water quality fluctuations and recharge. All parameters, other than those for nitrate, decrease with an increasing recharge; however, nitrates increase with an increase in recharge, which indicates that either fertilizer is leached into the groundwater or nitrification occurs in the unsaturated zone. Nitrate concentrations ranging between 5 and 150 mg/l have been observed in different monitoring wells. Groundwater samples were analyzed for Diuron and Carbaryl pesticides, however, none were recovered.

The analysis of the collected short-term data at the Perkins site provided information about the loading rates and the travel time of nitrates to the groundwater from the surface; however, the travel times obtained vary depending upon the initial soil moisture condition. In general, a travel time of 15 to 30 days is noted during the dry season; whereas, a travel time of only a few hours to few days was observed during the winter season. The results obtained from the short-term data (March 1987 to July 1988) strongly emphasize that the overall water quality assessment, based on a few samples collected over a period of a few years (2 to 3 years), can be extremely misleading and erroneous. A considerably different interpretation can be made concerning groundwater quality, depending upon the sampling frequency and spacing. Other findings in recent years suggest that in shallow, unconfined aquifers with rapid horizontal flow conditions, frequent sample collection with economic feasibility is necessary to ensure adequate characterization of groundwater quality (McKenna and others, 1988, Gibb and others, 1981).

Tracer Test

Two test plots were designed at the Perkins site to characterize solute movement in the unsaturated zone, both spatially and temporally. The typical site instrumentation consisted of soil moisture monitoring and sampling devices including tensiometers, moisture access tubes, and vacuum lysimeters installed at varying depths between the surface and the top of the groundwater table.

Field tracer studies were conducted at these plots simulating worst case conditions where the unsaturated hydraulic conductivity is at its maximum and nearly approaches the saturated hydraulic conductivity. Tracers in the form of ammonium-nitrate, potassium-sulfate, and zinc-chloride were applied to the plots which were ponded with water. Soil samples were collected using a splitspoon sampler and soil-water samples were obtained periodically using the lysimeters. The results indicated the arrival time of the nitrate pulse at a depth of nine feet (2.7 m) below the ground surface after the tracer fertilizer application to be approximately 30 days. Nitrification of ammonia appears to interfere with the tracer application as additional nitrate-n was introduced to the system.

Approximately ten days after the application of the fertilizer tracer, a break-through in solute movement occurred. The concentration of nitrate-n gradually increases from 0.1 mg/l to 5 mg/l in ten days; significantly higher values were noted in all lysimeters after the break-through. A comparison of the results from test plots A and B indicates some spatial variability, but this does not seem to be significant.

The primary mechanisms of solute transport are macropore, fracture, and fissure flow. All data collected in this study strongly contradicts the field applicability of piston flow theory, however macropore flow theory better explained the analysis of field data. A number of researchers in recent years have also supported the macropore flow theory over piston flow theory (Robert et al., 1986; Smettem, 1986; Moore et al., 1986; Hillel, 1987). Channeling effects were quite obvious in two of the lysimeters, 1-8 and 1-11, and may have influenced soil-water sampling to a small degree in another lysimeter. Preferential flow or channeling through the unsaturated zone obviously occurred because the discharged water from the pumping well virtually disappeared in the ground and reappeared 200 feet (60 m) downslope as a local spring, moving along existing root cavities.

Soil samples analyzed for nitrates in test plots A and B show leaching to the top of the water table 5 days after fertilizer application. The concentrations in the later periodic soil samples show decreasing nitrate-n values. This is highly indicative of macropore flow or rapid solute movement through the unsaturated zone. A comparison of soil chemical data from the two plots shows little spatial variability and similar leaching patterns. Nitrate concentrations in the groundwater below the test plots increase approximately one week after the application of the tracer; however, maximum concentrations are not observed until thirty days after tracer application.

The loading rates, approximately 30 mg/l, and travel times compare well with the short-term and long-term water quality data. Saturated zone tracer results provide a hydraulic conductivity value of 320 gpd/ft^2, and a travel time of 6 to 7 hours at a distance of 5 feet from the source. The depth specific sampling data do not indicate significant variations in travel time, although a slightly higher velocity is observed in the deeper portions of the aquifer. Dilution, rather than dispersion, is the main mechanism controlling solute concentration distribution in the saturated zone.

Agricultural Transport Modeling

The data collected during the different phases of the study were used as input parameters in the unsaturated zone (CMIS, PRZM) and saturated zone (KONIKOW) models. Results of the CMIS Model do not correlate with the field data. This can be attributed primarily to the fact that the model is based on the piston flow theory.

The Pesticide Root Zone Model (PRZM) was calibrated using the field data and simulations were conducted for seven different pesticides. The results indicate that the potential for leaching into the groundwater exists for the following pesticides: Carbofuran, Atrazine, Diuron, and 2,4-D; however, the concentrations leached are well below the analytical detectable limits. Malathion shows no indication of movement; Trifluralin leached to a depth of twelve inches; and Carbaryl leached to depth of four feet. Results from another study (Marak, 1986) conducted by the Agricultural Research Service in conjunction with the Oklahoma Department of Agriculture concerning pesticides in groundwater in alluvial and terrace aquifers in Oklahoma did not recover any pesticides in the groundwater samples. It can therefore be said, that although the potential of pesticide leaching into the groundwater table is a strong possibility, the concentrations recorded to date are well below the detectable limits.

The results of the saturated zone flow model, Konikow, characterize the lateral transport of nitrates in groundwater below the field plots. The concentrations obtained from simulation compare well with the field-observed data. Two different scenarios using K-min (300 gpd/ft^2) and K-max (350 gpd/ft^2) were simulated; however, the simulated results do not show significant variability.

Recommendations

Results obtained from this study produced ideas which require additional research in order to be developed accurately. Further research would expand the understanding of solute transport in the unsaturated zone at the Perkins site. Recommendations for future research are as follows:

1. Perform tracer tests using different inorganic tracer loading rates, vegetation, and initial soil moisture conditions at the test plots.
2. Conduct tracer tests under constant source loading conditions in order to enable the plotting of break-through curves in the unsaturated zone.
3. Conduct a constant source tracer test in the saturated zone. In this study, a slug type source was used.
4. Conduct a tracer test using 2,4-D, Lindane, and Atrazine pesticides in the unsaturated zone and

obtain field leaching characterization.

5. Utilize cartridge absorption sampling techniques in the field. The utilization of this method would save time, lower costs, and better preserve the organics in samples.
6. Perform simulations using the PRZM for other soils at the Perkins site for different pesticides and then compare the leaching potentials of these soils.

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APPENDICES

APPENDIX A

METHODS OF SITE INVESTIGATION

METHODS OF SITE INVESTIGATION

The methods utilized to accomplish the objectives of this study were conducted in different phases and tasks. A simplified expert system approach is utilized, where an extensive database of model parameters is generated. The database created is applied for simulating various scenarios of chemical transport at the Perkins Site. The various tasks performed to create this database are as follows:

Site Characterization

Exploratory Drilling

The initial step in the research was to establish a groundwater monitoring network at the Perkins site in cooperation with the Agricultural Research Service (USDA). Fifteen monitoring wells, 2 inches in diameter, and three production wells, 4 inches in diameter, were drilled and completed. Schematic of a typical monitoring well design utilized at the Perkins site is shown in Figure 47. Sample cuttings were obtained at the time of the drilling and were later analyzed and interpreted for characterization of the

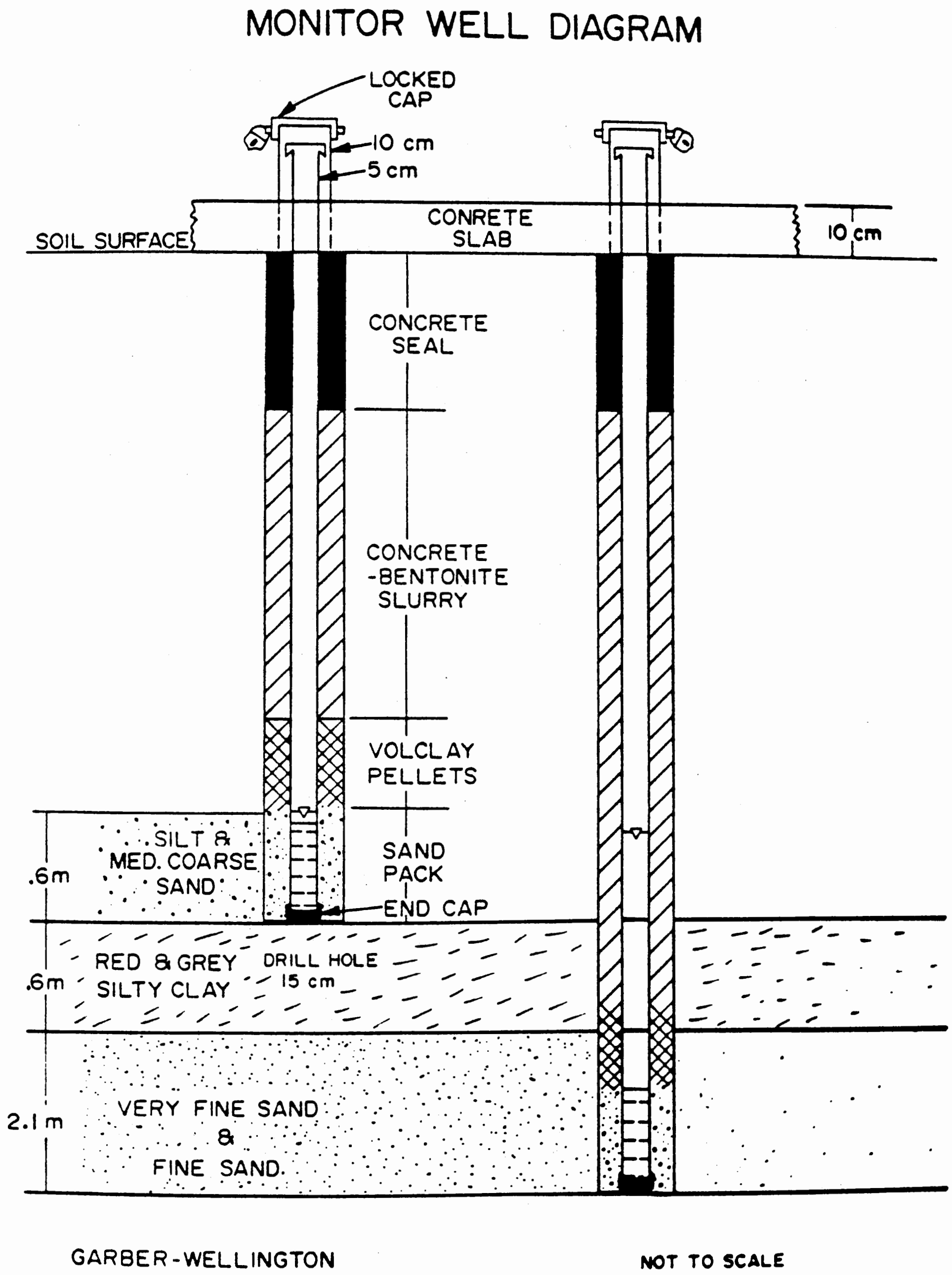


Figure 47. Typical Design for Groundwater Monitoring Well

site geology. The monitoring well network consists of four nests of two wells installed at depths of 25 feet (7.6 m) and 45 feet (13.7 m). Five additionall wells were installed for performing aquifer pump tests and tracer studies.

Surficial Geophysics

A direct current (DC) earth resistivity survey was conducted in the early stages of the research. The survey was conducted on ten stations as shown on Figure 3. Earth resistivity techniques incorporate the introduction of an electrical potential into the ground surface via a pair of electrodes and the measurement of the decrease in potential over an interval using another pair of electrodes which are connected to a current measuring device. The Wenner configuration (Zohdy et al., 1974), was the primary configuration in this study, and the drillers logs of nearby monitoring wells were used for control. The resistivity data was interpreted in order to obtain the depth to bedrock values and thus the saturated thickness at those points.

Borehole Geophysics

All of the groundwater monitoring wells were geophysically logged using gamma ray, resistivity, and self-potential tools. These logs were used to interpret subsurface stratigraphy across the site. The best interpretation of lithology was made from the natural gamma ray tool. The natural gamma ray signatures on the geophysical logs correlate well over short distances; however, correlation across the site is not very clear. This is due to the presence of isolated and discontinuous clay lenses. The logs, however, did clearly indicate cleaner sands at the bottom of the section and siltier sands above a clay lense, which creates two hydrogeologic zones within the terrace deposits.

GROUNDWATER HYDRAULICS

Estimation of Aquifer Coefficients

Several techniques exist for estimating the aquifer parameters using transmissivity, hydraulic conductivity, storitivity, porosity and specific yield. The values obtained from lab testing, aquifer pump testing and tracer testing are not always comparable. The techniques can be primarily categorized into point measure estimates and regional field estimates.

Point Measure Estimates

Point measure estimates are comprised of laboratory techniques, such as permeameter testing. The aquifer coefficients obtained from the use of these techniques are a gross approximation and are not necessarily representative of the true aquifer coefficients, because the point measure estimates are obtained from lab testing of disturbed aquifer sediments. Grain-size analyses were performed on drill cutting samples with the aid of a visual accumulation tube. The purpose of analyzing the drill cuttings was to establish a graphical relationship between in situ permeability, median grain size, and particle sorting. Permeameter tests were performed in the laboratory on sediment core samples to obtain permeabilities for the sediment type. A laboratory permeability of 733 gpd/ft^2 was determined using a reverse falling head permeameter and a value of 293 gpd/ft^2 was determined using a constant head permeameter. A porosity value of 34 percent and a specific yield value of 20 percent was obtained.

Slug Test Analysis

A number of point-measure field tests were described in the literature, however, the most widely used test was introduced by Cooper, Bredehoeft, and Papadopulos, (1967). This particular technique provides an estimate of hydraulic conductivity based on the response of a well to the sudden removal of a slug of water (Canter, 1987). This method is the fastest and most economic way of estimating hydraulic conductivity in the field. The obvious advantage of this technique is that it is a single well test and therefore a separate observation well is not required.

Slug tests were performed on all monitoring wells installed at the Perkins site. The following equation was utilized to determine hydraulic conductivity:

$$T = 1.0xrc^2/t \qquad (1)$$

Where:

T = transmissivity, gpd/ft (m^3/d)

rc = the effective radius, ft (m)

t = match point time, since removal of slug, sec

Using T the hydraulic conductivity (k) is computed as:

$$K = T/b$$

Where:

K = hydraulic conductivity, gpd/ft^2 (cm/sec)

b = aquifer saturated thickness , ft (m)

Aquifer Testing

The Perkins Terrace Aquifer is an partially confined or water table aquifer. The pumping of a well located in an unconfined aquifer extracts water primarily through two mechanisms: 1) specific yield (Sy) and 2) gravity drainage. A number of flow equations have been derived for solving radial flow in compressible unconfined aquifers under various hydrologic conditions (Fetter, 1988; Molz, 1986). These techniques can be classified as time-drawdown and distance-drawdown techniques. The data obtained from the aquifer pump tests were analyzed using the equations derived by Theis, Cooper-Jacob and Prickett (Driscoll, 1986).

Pumping Test Design

Adequate design and execution of a pumping test involves considerable planning and detail. Eight wells were drilled and installed at the Perkins test site for the purpose of performing aquifer pump testing. A four inch diameter well, MW 18, (drilled to bed rock) was installed and used as the main pumping well. Seven observation wells were drilled and installed at varying distances from the pumping well (Figure 37). All wells were developed by surging and bailing before a pump test was initiated. Controlled aquifer pumping tests were conducted at the test site between April, 1985 and May, 1988. The tests were conducted for different periods ranging from a 12-hour, short-term test to a long-term, 66-day test.

Vadose Zone Hydraulics

The geologic profile which extends from the ground surface to the top of the water table, the principal water bearing formation, is called vadose zone (Everett, 1984). The terms "unsaturated zone" and "zone of aeration" are often used synonymously.

The driving energy for water movement in saturated soils is positive potential gradient. However, in unsaturated soils, water movement is subjected to a negative suction or potential, and the movement of water is from areas of lower suction to areas of higher suction.

Unsaturated hydraulic conductivity, $k(0)$ is a major factor in a soil's ability to transmit water. Hydraulic properties of soil are of considerable importance when considering solute movement in the vadose zone.

Application of the theories of soil physics, upon which most of the numerical models are based, for the prediction of the actual processes in the field depends upon knowledge of the pertinent hydraulic characteristics of soil, including functional relation of hydraulic conductivity and matric suction to soil wetness as well as spatial and temporal variation of these in the often heterogeneous field conditions (Hillel 1980). The amount of soil water retained at low suction (0 to 1 bar) is dependent on capillarity and pore-size distribution. Water retention at high matric suction is primarily affected by soil texture.

Measurements of various soil-water properties for the Teller soil series at the Perkins site have been made in situ by Keisling, 1974. Keisling determined unsaturated hydraulic conductivity and its spatial variability at the Perkins site. The procedure used by Davidson and others, (1969) to evaluate soil hydraulic properties was used in that study. The procedure consisted of measuring soil moisture content and soil matric suction under conditions of drainage. From these measurements, it is possible to obtain instantaneous values of potential gradients and fluxes operating within the drainage profile, and hence to also obtain hydraulic conductivity values (Hillel 1980). A plot of distribution of unsaturated hydraulic conductivity in the soil profile with depth is shown in Figure 48. Unsaturated hydraulic conductivity is primarily a function of soil moisture content. The rate of infiltration depends upon the antecedent moisture content and the soil type, which control the moisture holding capacity.

Soil Moisture Profiles

The movement and distribution of water in the soil profile after precipitation or irrigation depends upon numerous factors which include the presence of impeding layers in the top soil, surface slope, soil texture, soil structure and the initial soil moisture content. Once infiltration has occurred, initial soil moisture content, soil texture, and soil structure govern the distribution of water fluxes in the soil profile.

Soil moisture and soil tension profiles with depth were recorded by Keisling, (1974) for the Teller soils at the Perkins site. Generally, higher moisture contents were associated with clay soil than with silty or sandy soil.

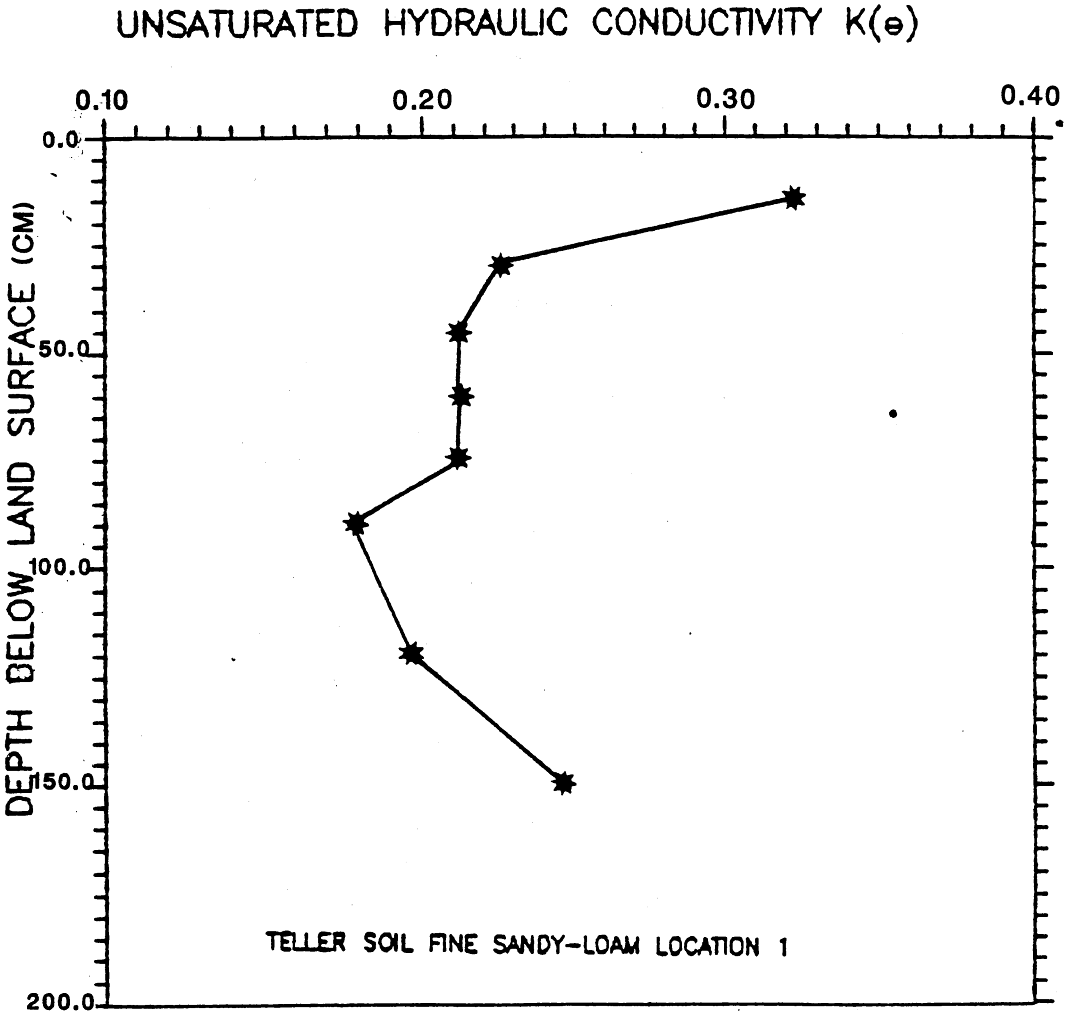


Figure 48. Unsaturated Hydraulic Conductivity Profile for Teller Soils (After Keisiling, 1974)

The Konawa soil series is present at the two test plots where tracer and nitrate-n leaching studies were conducted.

Methodology

Soil physical properties for the Konawa soils were characterized by measuring soil moisture profiles at the test site. A number of techniques have been developed for monitoring water content in the vadose zone; however, a neutron moderation method was utilized in the field. This particular method depends upon the interaction of neutrons with matter: scattering and capturing (Everett, 1984). This method has gained wide acceptance as an efficient and reliable technique for monitoring soil moisture in the field (Hillel, 1980). Its principal advantages over gravimetric methods are its speed and the ability to make repeated nondestructive measurements. In operation, a source of fast neutrons is lowered into the soil through a casing. The fast-energy neutrons are bombarded on the surrounding soil. The energy of these fast neutrons is lowered, as a result of collision with the nuclei of soil matter. Collision with hydrogen nuclei causes greater energy loss, and higher energy loss ia a measure of increased moisture content of the soil.

This method was used to acquire moisture data for a range of soil depths under field conditions which required the installation of aluminium access tubes. Two tubes, having an outside diameter of 5 cm each, were installed to a depth of 274 cm at test plots A and B. Aluminum was chosen for the access tube material because of its small cross-sectional area for intercepting neutrons. The soil moisture probe (Troxler model 3330) consists of a 10 mci Americium-241, Beryllium source, which yields 25000 neutrons per second (Troxler Manual 1983), a slow neutron detector, and a ratemeter to monitor the flux of neutrons scattered by the soil matter nuclei. Slow neutrons are counted by a ratemeter and are converted to volumetric water content by the following equation:

$$OV = A + (B \times R)$$

where:

OV = volumetric water content (cm^3 water / cm^3 soil)

R = field measured count divided by the standard count

A = -0.0087

B = 0.5424

A and B are calibration constants determined in the laboratory for each probe (Ross, 1988).

Unsaturated Zone Tracer Testing - Methodology

The field arrangement for monitoring the unsaturated zone consisted of two test plots, plot A with an area of 96 ft^2 and plot B with an area of 64 ft^2 (Figure 37). Unsaturated zone thickness at the two plots ranges from ten to thirteen feet. A large number of unsaturated zone sampling techniques are available, and can be classified as solid sampling and solution sampling (Wilson, 1983). Both techniques are utilized at the test plots to monitor solute movement with time in the unsaturated zone. Pore water in the unsaturated zone is held under capillary tension and will not freely move into a borehole unless a gradient is induced. A vacuum lysimeter system, which allows the extraction of soil moisture samples at tensions greater than the soil tension, is utilized. The basic design of a suction sampler, otherwise known as a vacuum lysimeter, consists of a porous ceramic cup cemented to a plastic pipe in such a way as to create an air and water-tight seal. Lysimeters were also constructed with all glass materials, and therefore, the application of any adhesive or glue was eliminated; these lysimeters were used to monitor organic solutes in the field test plots. Figure 49 shows in detail the basic components and construction of the vacuum lysimeters used in the field test plots. When placed in the soil, the pores in the cups become an extension of the pore space of the soil. Consequently, the water content of the soil and the cup becomes equilibrated at the existing soil water pressure.

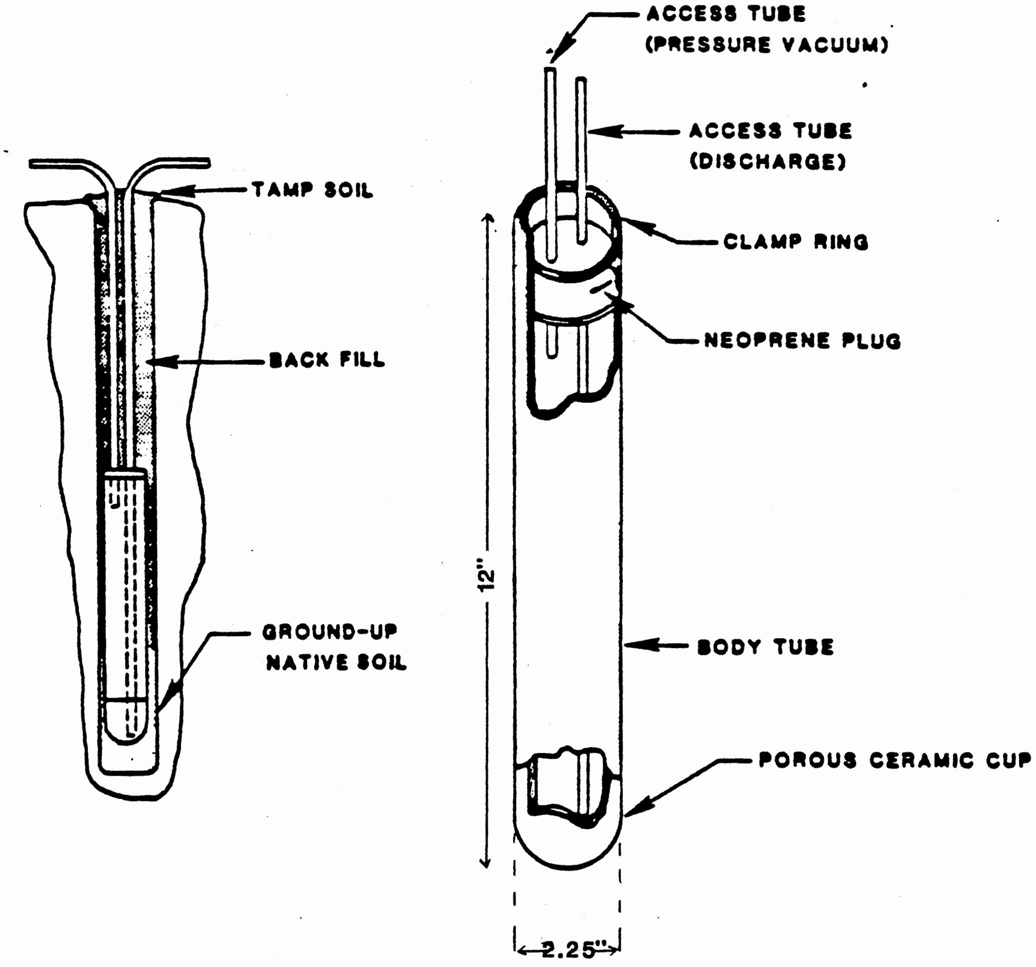


Figure 49. Typical Design of Vacuum Lysimeter

By applying a vacuum to the interior of the cup such that the pressure is slightly less inside the cups than in the soil solution, flow into the cup was induced (Evrett, 1984). The sample was pumped to the surface and analyzed for solute concentrations. The cups were rinsed with dilute hydrochloric acid and distilled water to removed dissolved ions present in the cup. Concerns about the validity and representativeness of the soil water samples and cup-solute interaction using the vacuum lysimeters have been raised in the past; however, these tools appear to be the best available for sampling the unsaturated zone at the present time (Evrett, 1984).

The installation of the previously described monitoring equipment was initiated after test plots A and B were constructed. Ten to fifteen centimeters of top soil were removed from each of the two test plots and eight inch ceramic tiles were placed at the edges of the plots. Boreholes four inches in diameter were installed using a hand auger. Neutron access tubes, tensiometers, and lysimeters were installed in the augered holes at several depths. A schematic of the unsaturated and saturated zone monitoring system at test plot B is shown in Figure 50. A slurry of native soil was poured into the holes to ensure contact with the surrounding soil. Water was poured on top of the slurry in order to compact it. When this water had

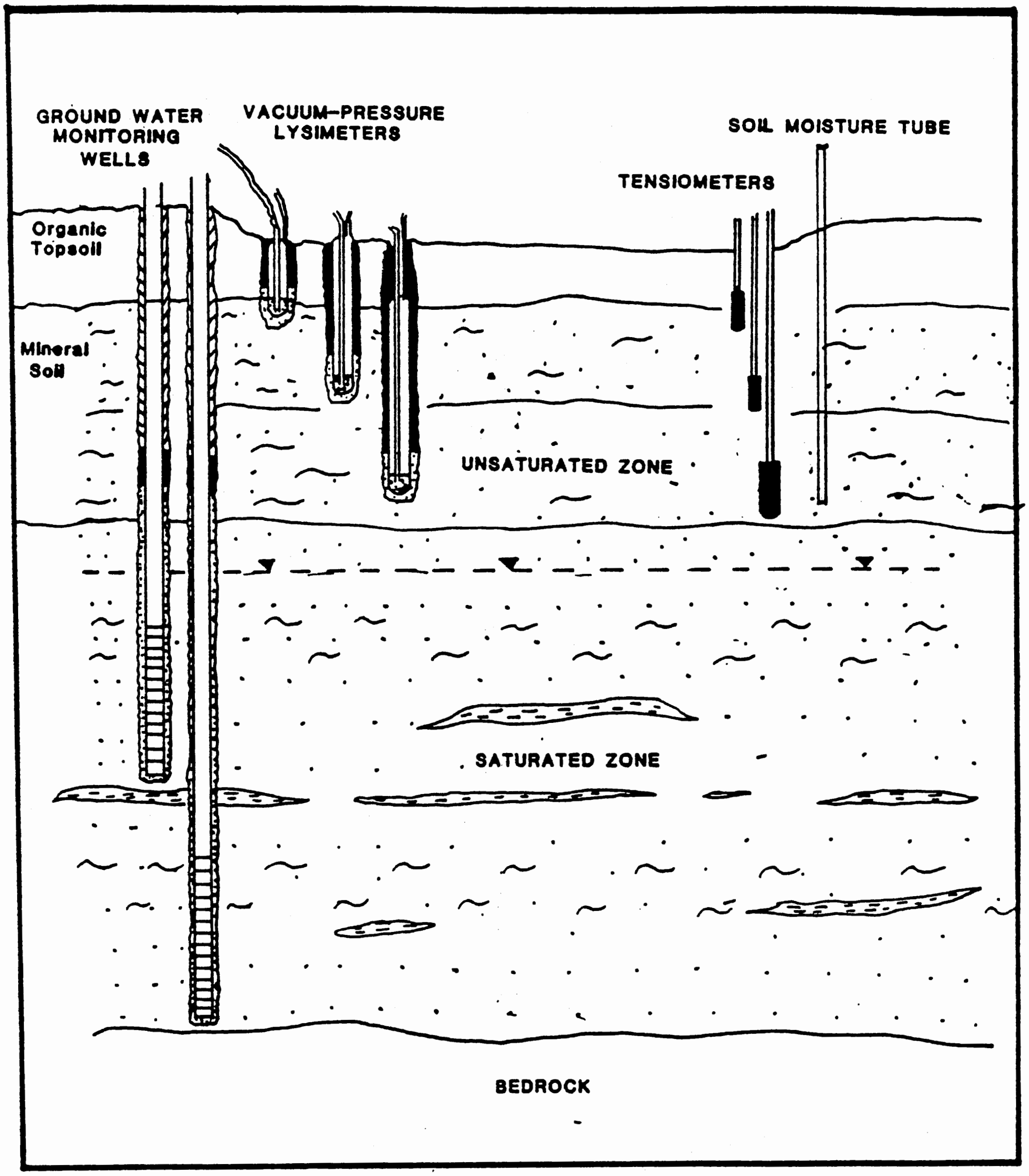


Figure 50. Schematic of Unsaturated and Saturated Zone Monitoring System

drained, additional slurry was poured down the hole and the process was repeated. This was done in order to minimize channeling effects. A total of sixteen lysimeters were installed to obtain soil water samples from depths of 1, 2, 4, 5 , 7, and 9 feet. The lysimeter designations and their respective depths are shown in Figure 37.

Saturated Zone Tracer Testing

In hydrogeology, a tracer when used is a material, carried by groundwater, which will provide information concerning the direction of water movement and velocity. Information gathered by a tracer test can also aid in the determination of hydraulic conductivity, porosity, dispersivity, and chemical distribution coefficients (Davis, 1985). Tracer tests are also utilized for the analysis and prediction of solute transport in the saturated zone.

The main intent of this section is primarily to characterize the movement of nitrate and chloride in groundwater and to obtain aquifer parameters such as travel time of a contaminant, change in initial concentration with time and distance from a source because of dispersivity, advection and dilution of a contaminant. The information gained from tracer test data collection will also be used to verify results of hydraulic conductivity obtained from aquifer pump test data.

Two four-inch and six two-inch O.D. groundwater wells were installed at the Perkins site to perform tracer tests. The four-inch O.D. well MW 18 was used as a discharging pump well and the other four-inch O.D. well, MW 14, was used as a source injection well. Source injection well MW 14 was screened at shallow, middle, and deeper portions of the forty foot saturated Perkins Terrace Aquifer. An observation well, MW 15, with three screens at the same intervals as well as MW 14 was installed five feet from the source injection well. The screen intervals in these two wells were isolated and separated by using a seal which consisted of bentonite pellets. A nest of two wells, MW 16 and MW 17, was installed at shallow and middle levels of the aquifer near the pump well. All wells were logged using a borehole gamma ray geophysical method and an interpreted stratigraphic cross-section was plotted (Figure 51). Analysis of the stratigraphic cross-section indicates near homogeneity in the aquifer; all the identified lithologic units located in the subsurface were traceable from one well to another.

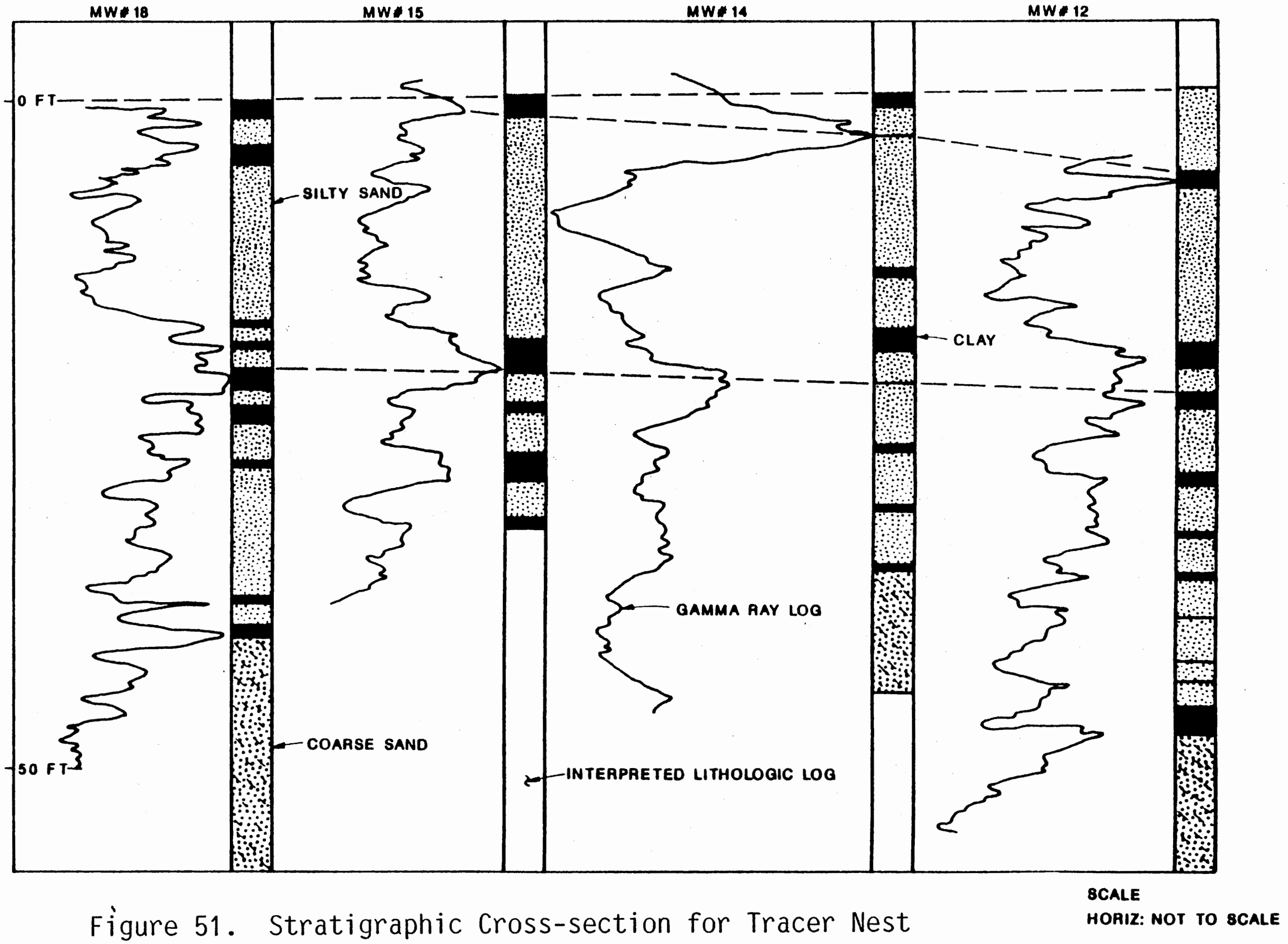


Figure 51. Stratigraphic Cross-section for Tracer Nest

APPENDIX B

GEOPHYSICAL AND DRILLERS LOGS

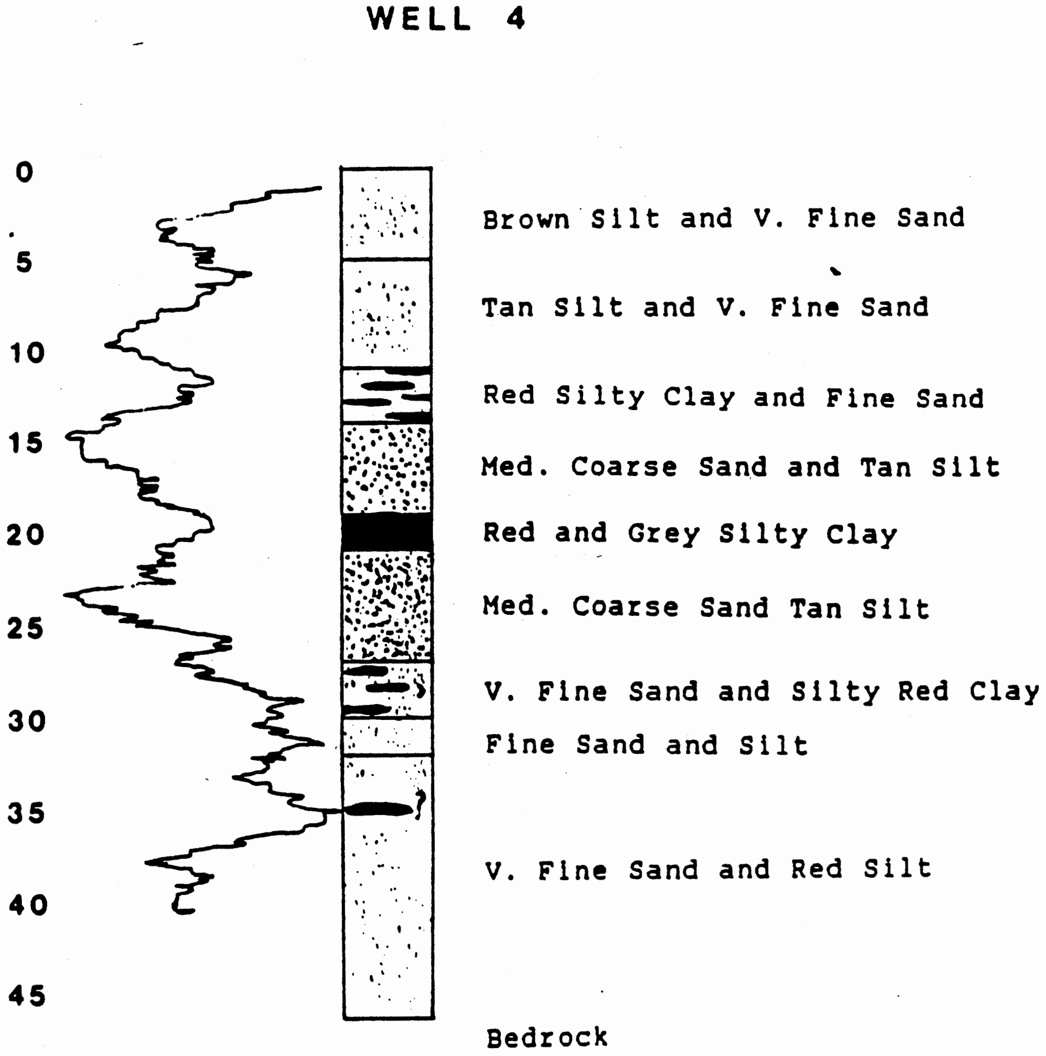


Figure 52. Geophysics and Drillers Log for MW 4

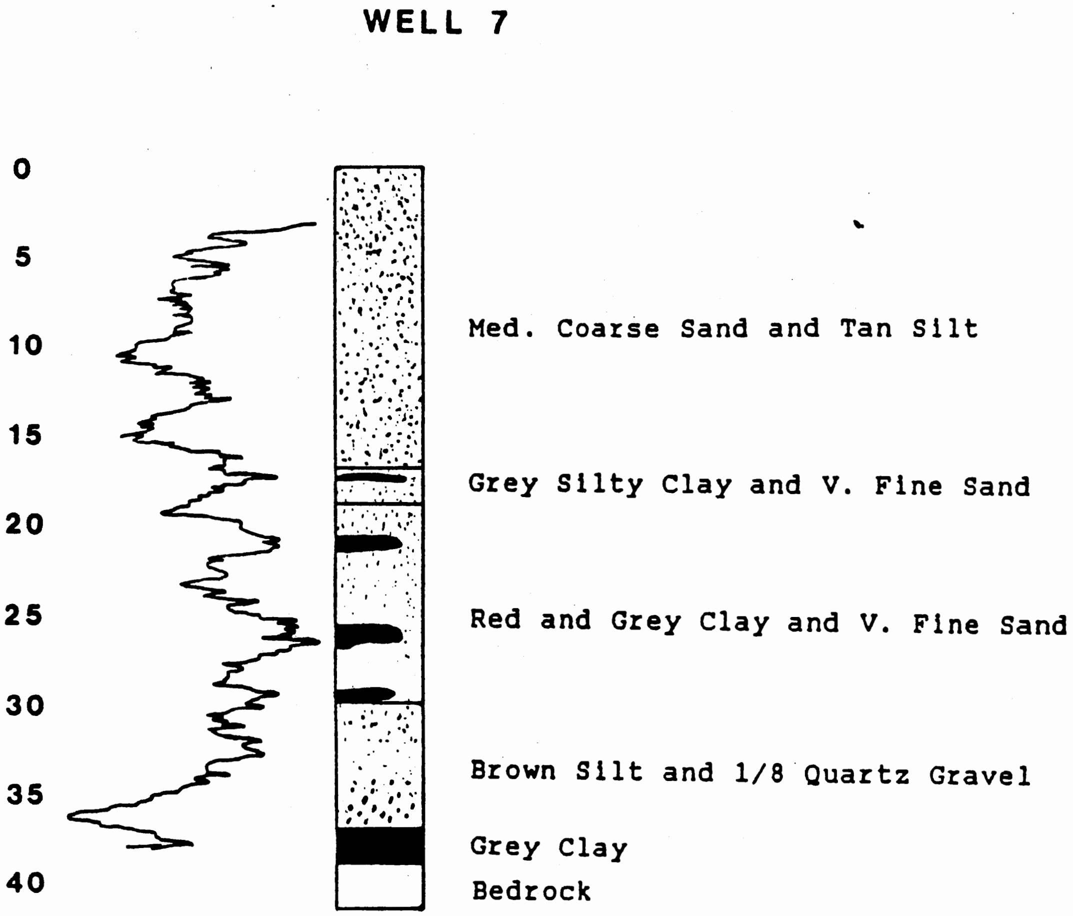


Figure 53. Geophysical and Drillers Log for MW 7

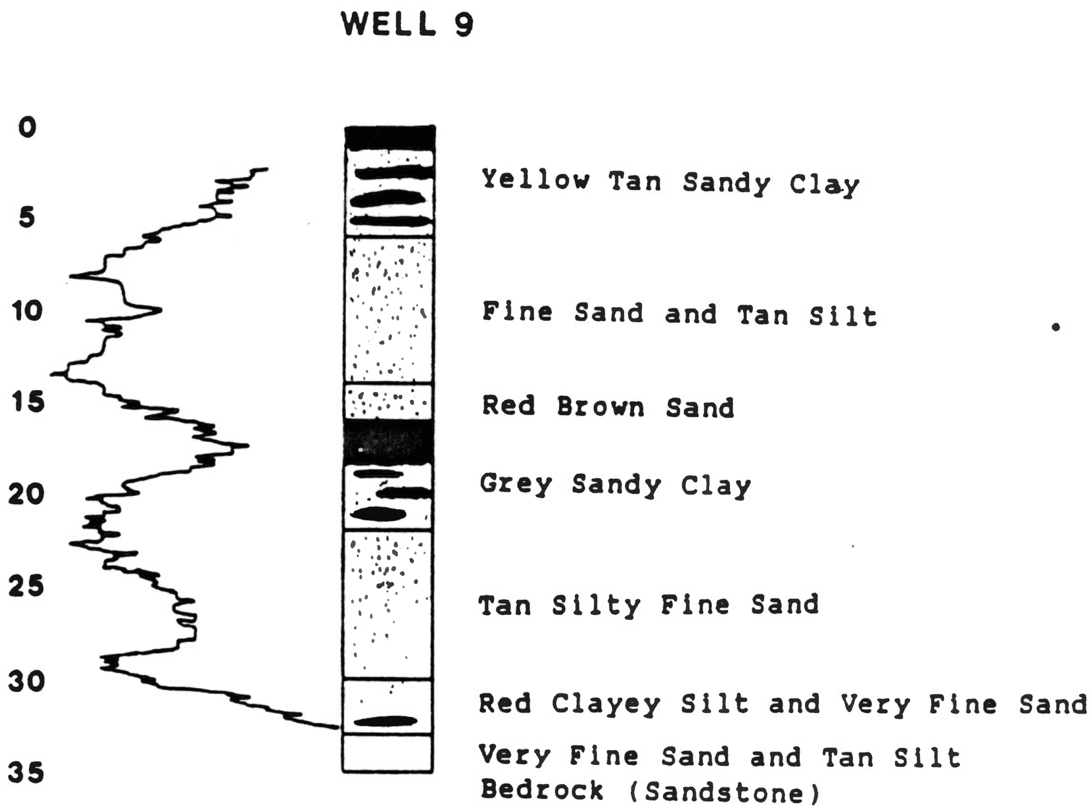


Figure 54. Geophysical and Drillers Log for MW 9

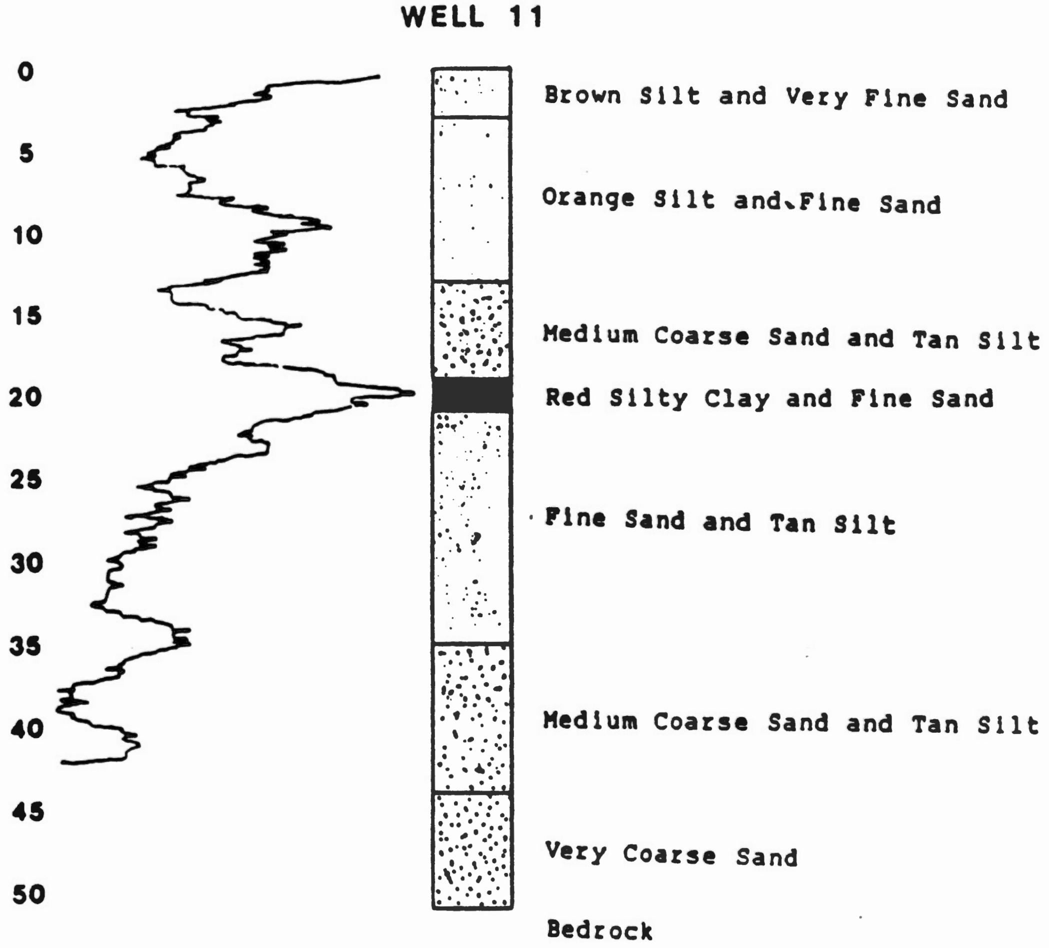


Figure 55. Geophysical and Drillers Log for MW 11

APPENDIX C

SOIL DATA USED IN PRZM MODEL

Teller Loam - 0 to 1 Percent Slopes.

Horizon	Depth (Inches)	Description
Ap	0-7	Dark brown (10YR 3/3) moist, loam, moderate medium granular structure; very friable when moist; abrupt boundary.
A1	7-13	Dark brown (7.5YR 3/2) moist, loam, weak medium subangular blocky structure; friable when moist; gradual boundary.
B1	13-18	Dark brown (10YR 3/3) moist, loam, moderate medium subangular blocky structure; friable when moist; gradual boundary.
B21t	18-26	Dark yellowish brown (10YR 4/4) moist loam, strong medium subangular blocky structure; firm when moist; gradual boundary.
B22t	26-35	Brown (7.5YR 4/4) moist, sandy clay loam, strong. medium subangular blocky structure; firm when moist; gradual boundary.
B3	35-43	Brown (10YR 4/3) moist, sandy loam, weak medium subangular blocky structure; friable when moist; gradual boundary.
C1	43-50	Yellowish brown (10YR 5/4) moist, sandy loam, structureless, single grain; friable when moist; diffuse boundary.
C2	50-55	Yellowish brown (10YR 5/4) moist, sandy loam, old alluvium.

Figure 56. Soil Description for Teller Loam, 0 to 1 Percent Slopes (After Ford and Others)

Konawa Fine Sandy Loam - 3 to 5 Percent Slopes, Eroded

Horizon	Depth (Inches)	Description
B22t	23-32	Red (2.5YR 4/6) moist, sandy clay loam compound weak coarse prismatic and weak medium subangular blocky; friable; common fine roots; diffuse smooth boundary.
B31	32-40	Dark reddish brown (2.5YR 4/6) moist, loamy sand with common coarse distinct light brown (7.5YR 5/4) mottles; weak coarse prismatic and weak medium subangular blocky; friable; few fine roots; diffuse smooth boundary.
B32	40-56	Red (2.5YR 4/6) moist fine sandy loam with common coarse distinct light brown (7.5YR 5/4) mottles; friable; diffuse smooth boundary.
C	56+	Mixed red (2.5YR 4/6) moist, and brown (7.5YR 5/4) moist, loamy sand, old alluvium.
Ap	0-7	Dark brown (7.5YR 3/2) moist, fine sandy loam, with few distinct red (2.5YR 4/6) mottles; weak medium subangular blocky and weak medium granular; very friable; many fine roots; many worm casts; abrupt smooth boundary.
B21t	7-23	Red (2.5YR 4/6) moist, fine sandy loam, moderate coarse prismatic; firm; many fine roots; common worm casts; moderate continuous clay films; gradual smooth boundary.

Figure 57. Soil Decription for Konawa Fine Sandy Loam 3 to 5 percent (After Ford and Others, 1976)

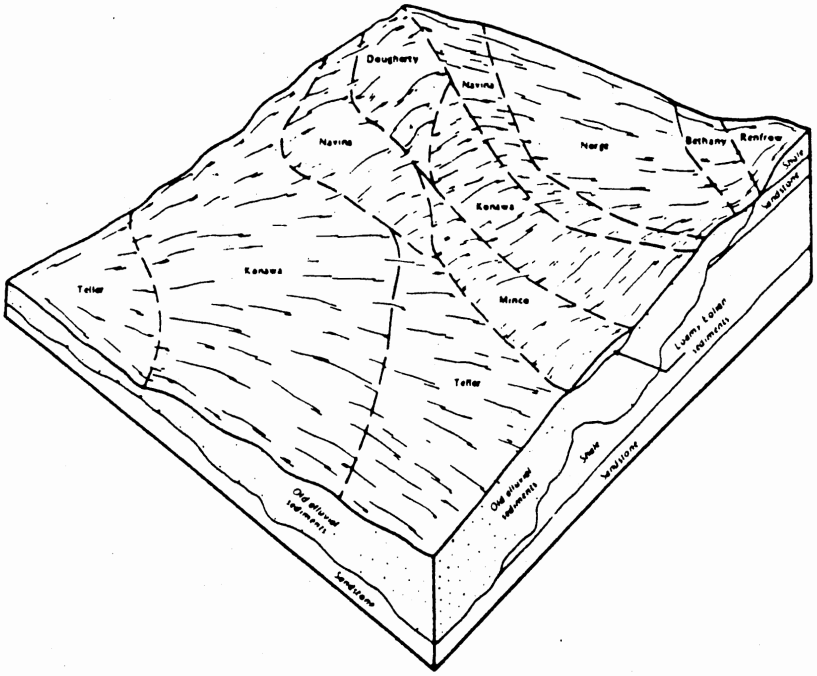


Figure 5.—Typical pattern of soils and underlying material in the Norge-Teller-Konawa map unit.

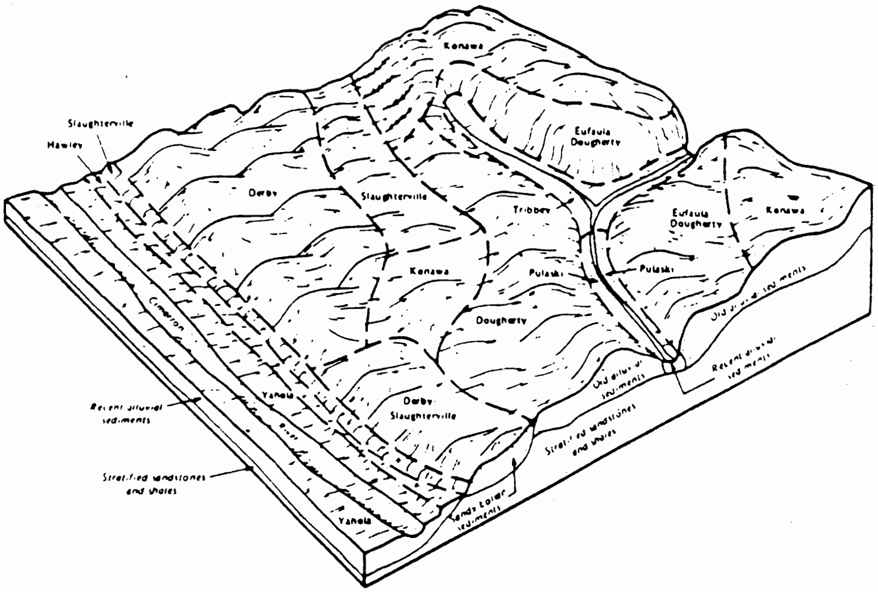


Figure 6.—Typical pattern of soils and underlying material in the Konawa-Dougherty-Derby map unit.

Figure 58. Typical Patterns of Soils in the Norge-Teller-Konawa and Konawa-Daugh erty-Derby map unit Map Unit (After Henley and others, 1985)

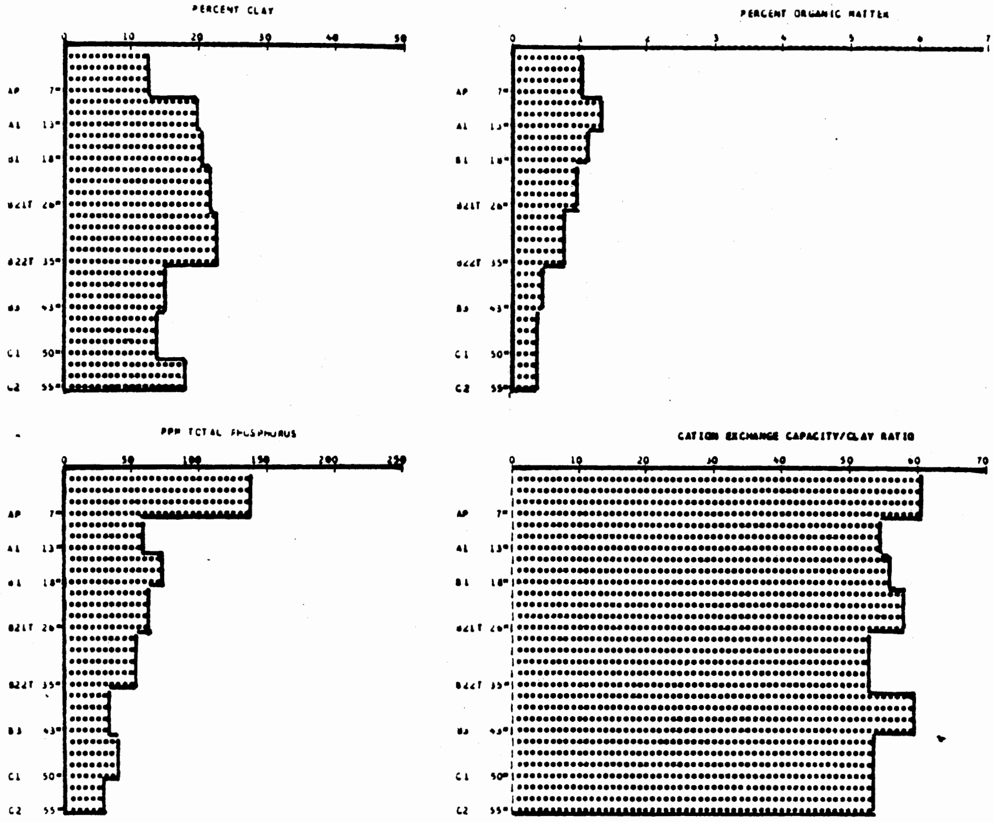


Figure 59. Graph Analysis of Teller Loam, 0 yo 1 Percent Slopes (After Ford and Others, 1976)

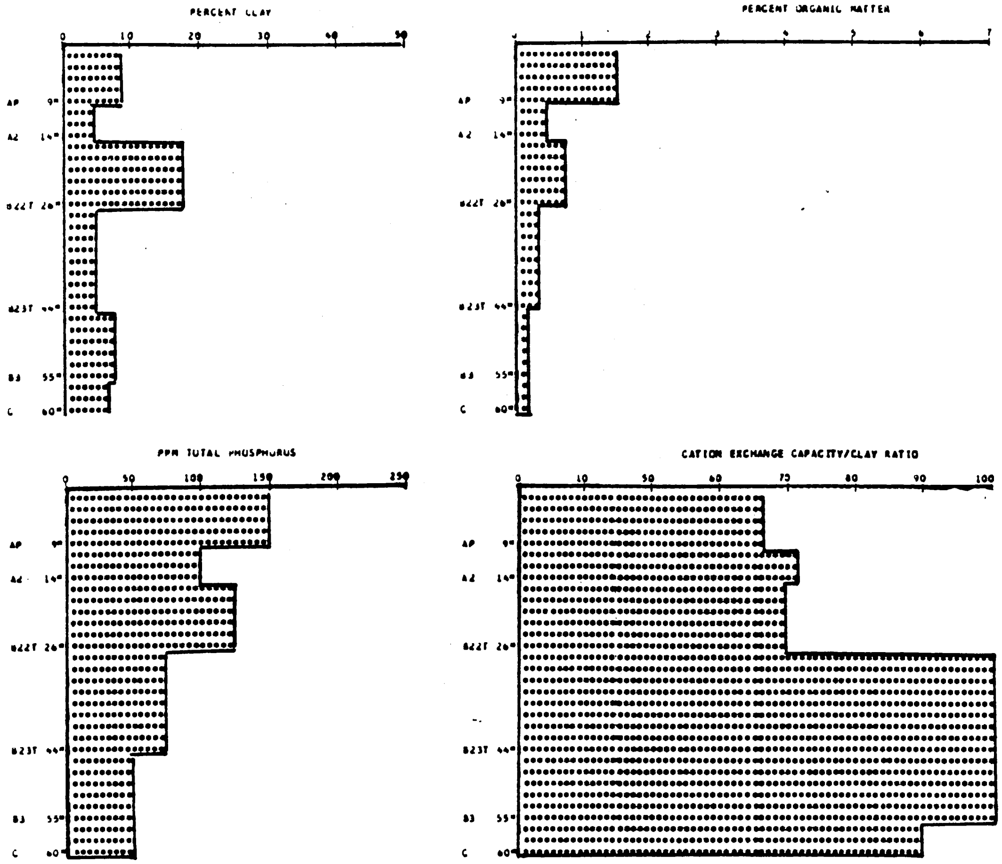


Figure 60. Graph Analysis of Konawa Sandy Loam, 3 to 5 Percent Slopes (After Ford and Others, 1976)

APPENDIX D

GROUNDWATER HYDRAULICS DATA

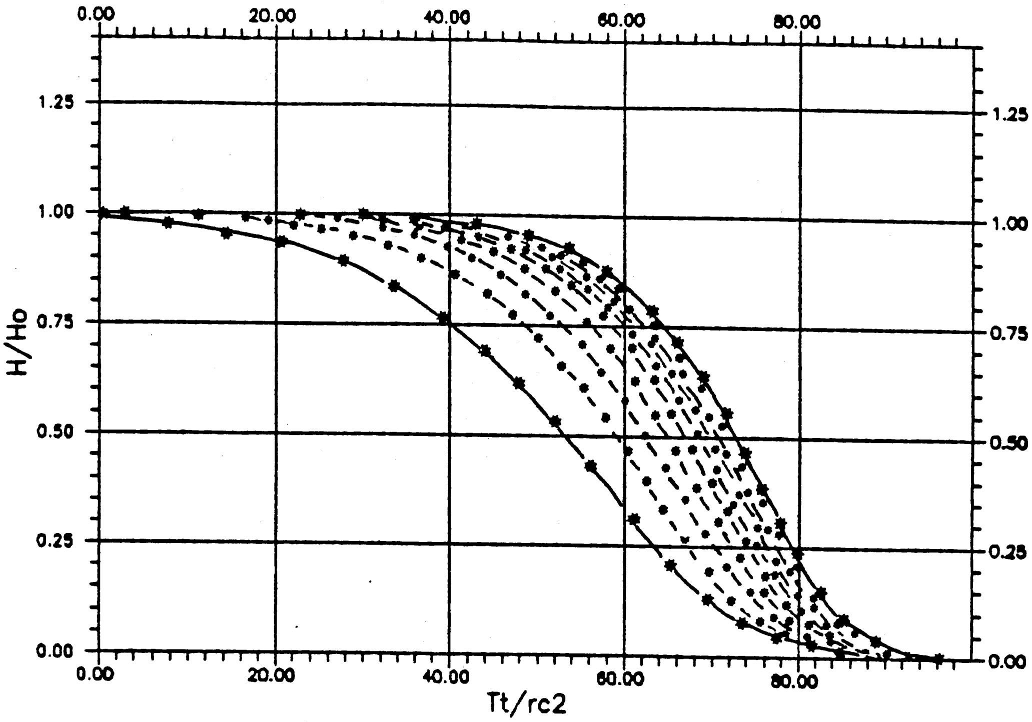


Figure 61. Type Curve for Slug Test Data (After Papadopolus and others, 1973)

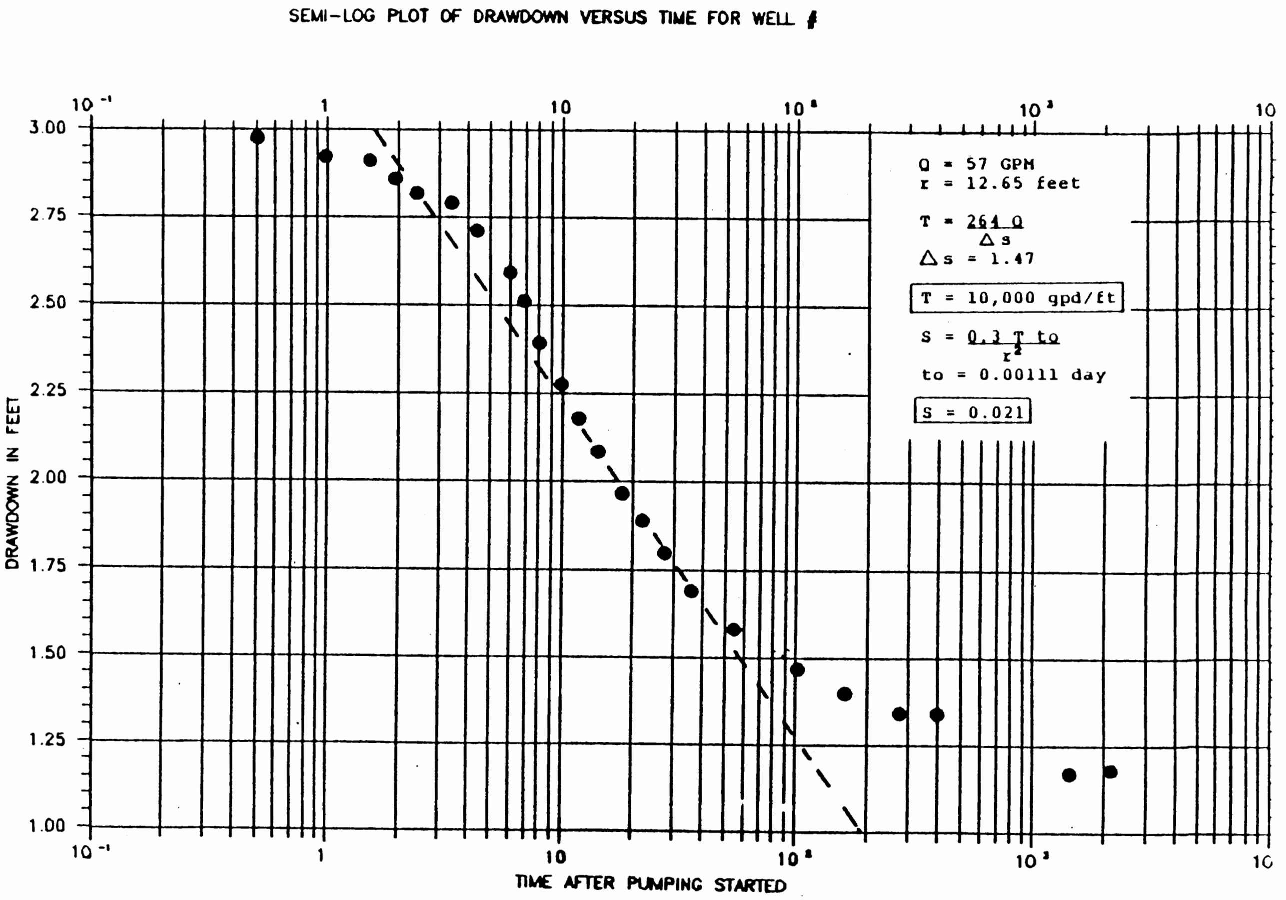
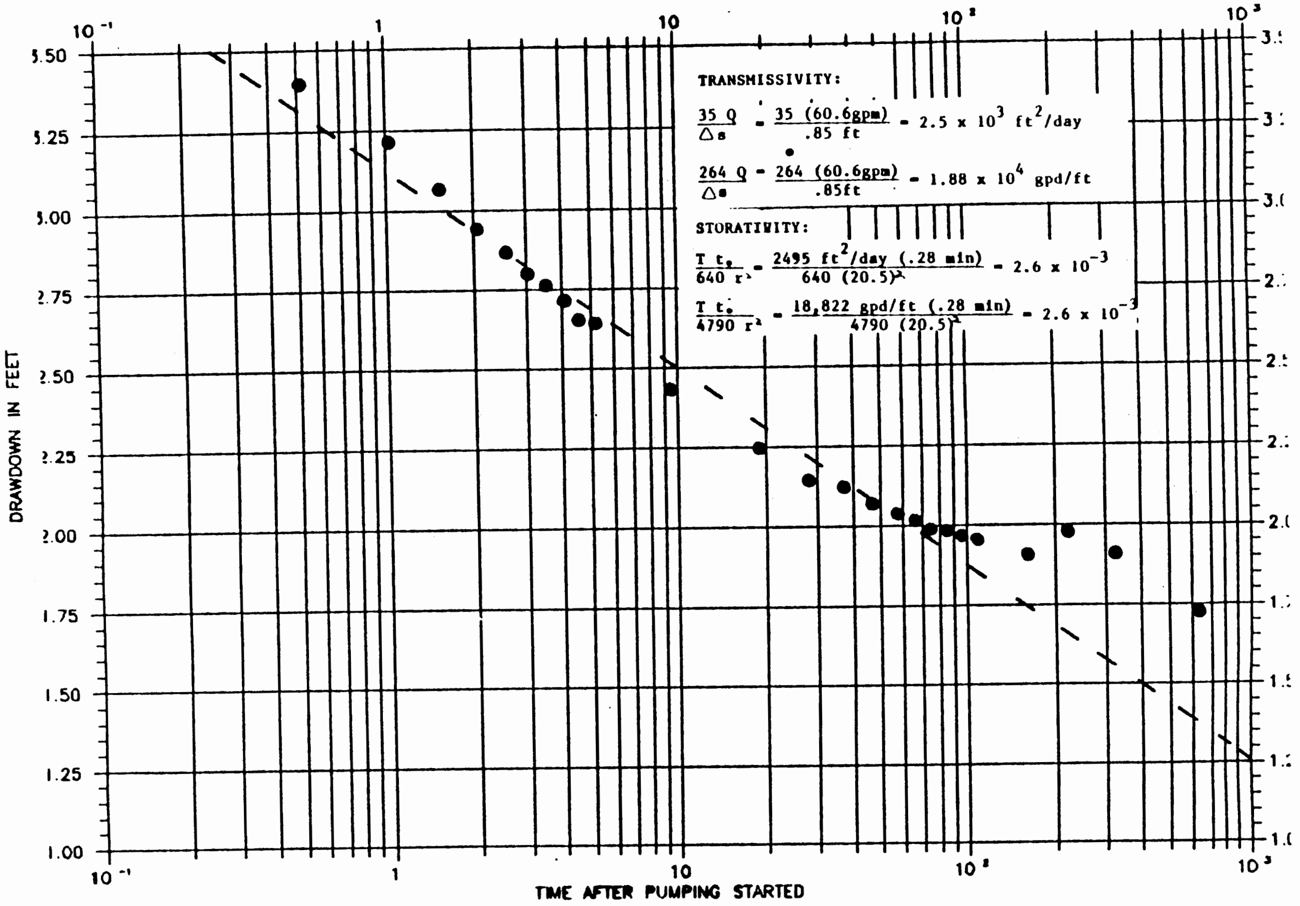


Figure 62. Semi-Log Plot of Drawdown VS. Time for MW 14



TRANSMISSIVITY:

$$\frac{35\ Q}{\Delta s} = \frac{35\ (60.6\text{gpm})}{.85\ \text{ft}} = 2.5 \times 10^{3}\ \text{ft}^{2}/\text{day}$$

$$\frac{264\ Q}{\Delta s} = \frac{264\ (60.6\text{gpm})}{.85\text{ft}} = 1.88 \times 10^{4}\ \text{gpd/ft}$$

STORATIVITY:

$$\frac{T\ t_o}{640\ r^2} = \frac{2495\ \text{ft}^2/\text{day}\ (.28\ \text{min})}{640\ (20.5)^2} = 2.6 \times 10^{-3}$$

$$\frac{T\ t_o}{4790\ r^2} = \frac{18{,}822\ \text{gpd/ft}\ (.28\ \text{min})}{4790\ (20.5)^2} = 2.6 \times 10^{-3}$$

Figure 63. Semi-Log Plot of Drawdown VS. for MW 12

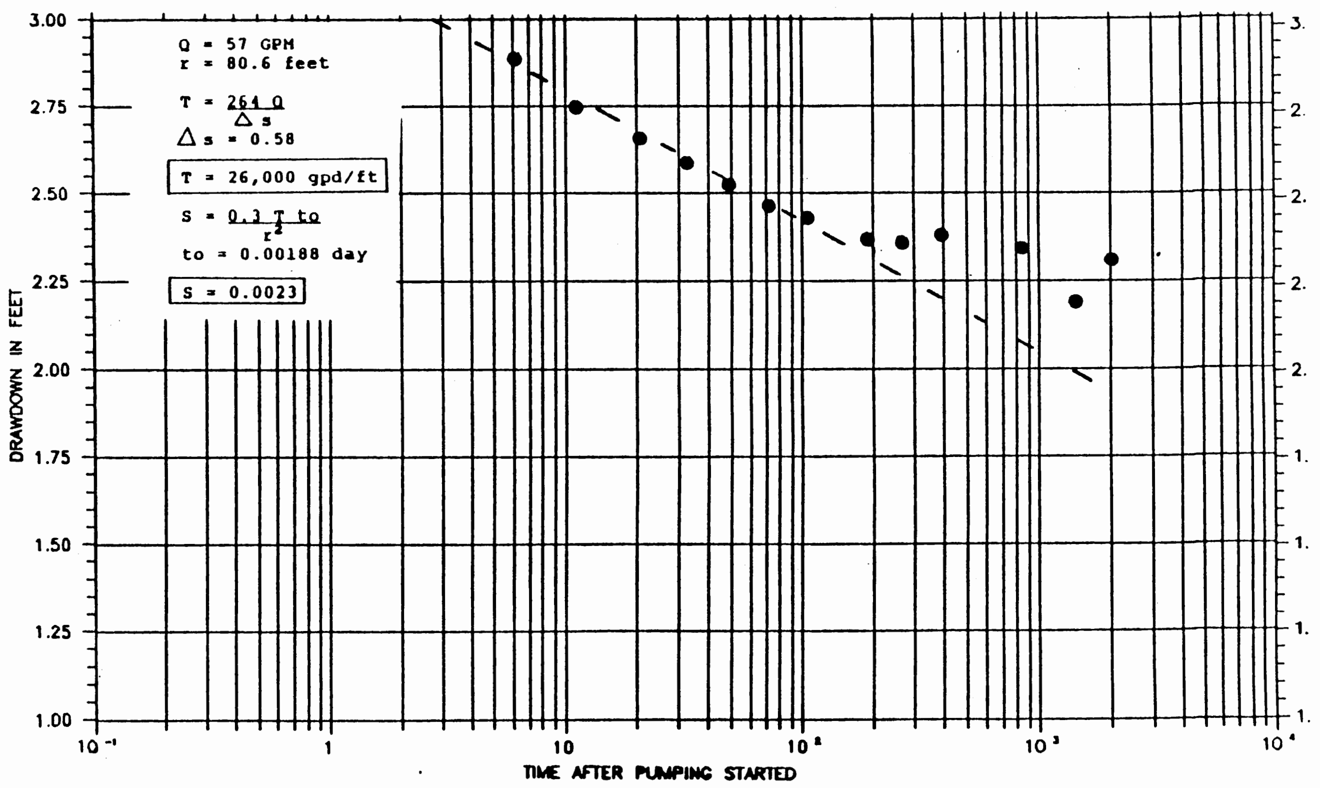
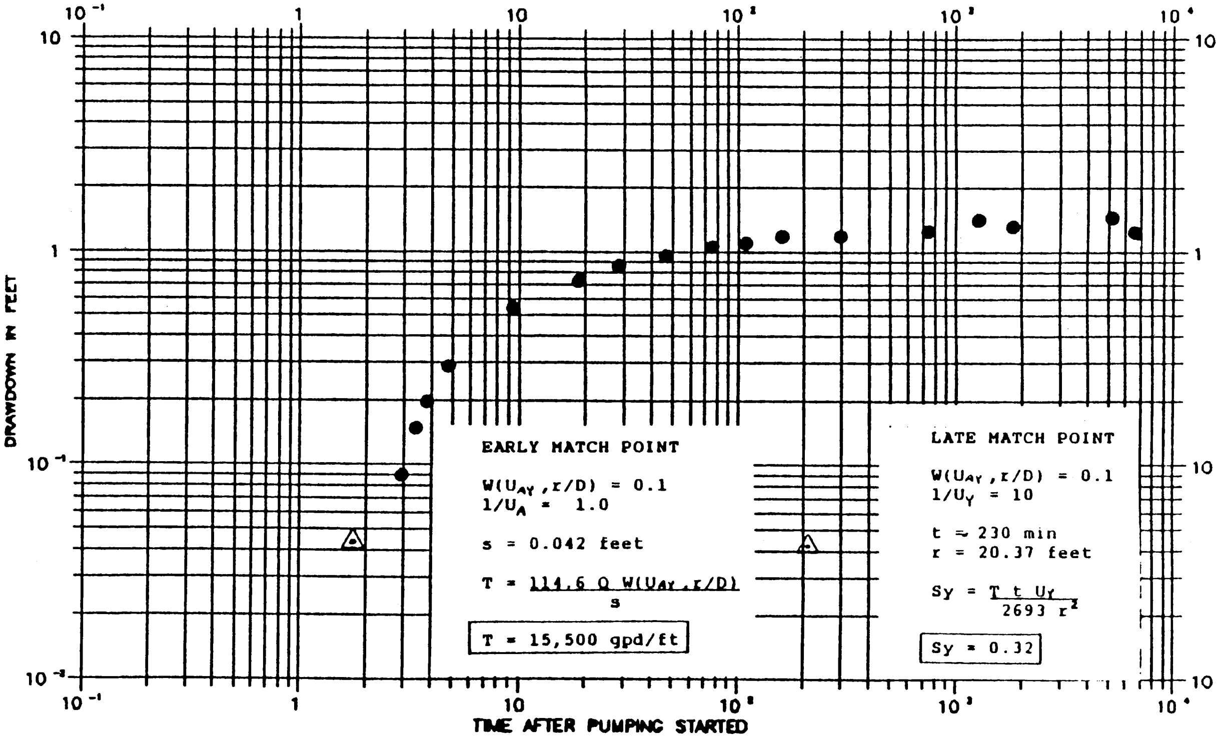


Figure 64. Semi-Log Plot of Drawdown VS. time for MW 11



EARLY MATCH POINT

$W(U_{AY}, r/D) = 0.1$
$1/U_A = 1.0$

$s = 0.042$ feet

$T = \frac{114.6\ Q\ W(U_{AY}, r/D)}{s}$

$\boxed{T = 15{,}500 \text{ gpd/ft}}$

LATE MATCH POINT

$W(U_{AY}, r/D) = 0.1$
$1/U_Y = 10$

$t \approx 230$ min
$r = 20.37$ feet

$Sy = \frac{T\ t\ U_Y}{2693\ r^2}$

$\boxed{Sy = 0.32}$

Figure 65. Log-Log Plot of Drawdown VS. Time for MW 12

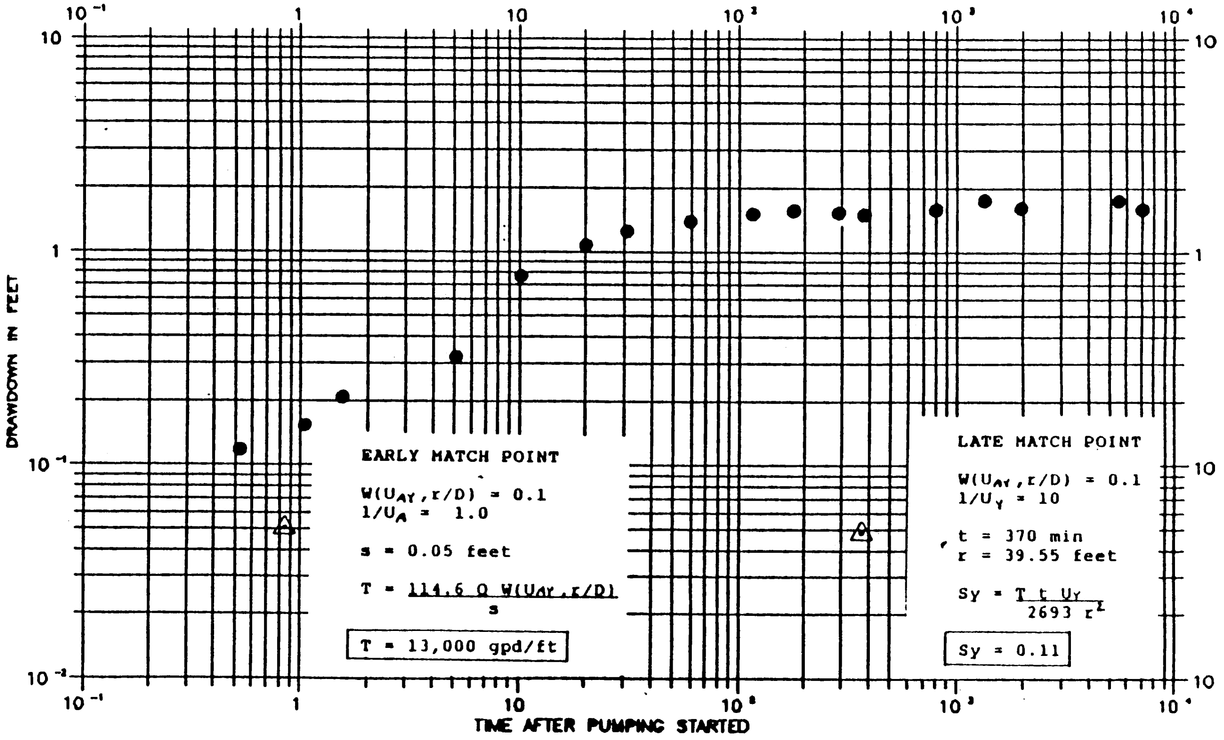


Figure 66. Log-Log Plot of Drawdown VS. Time for MW 11

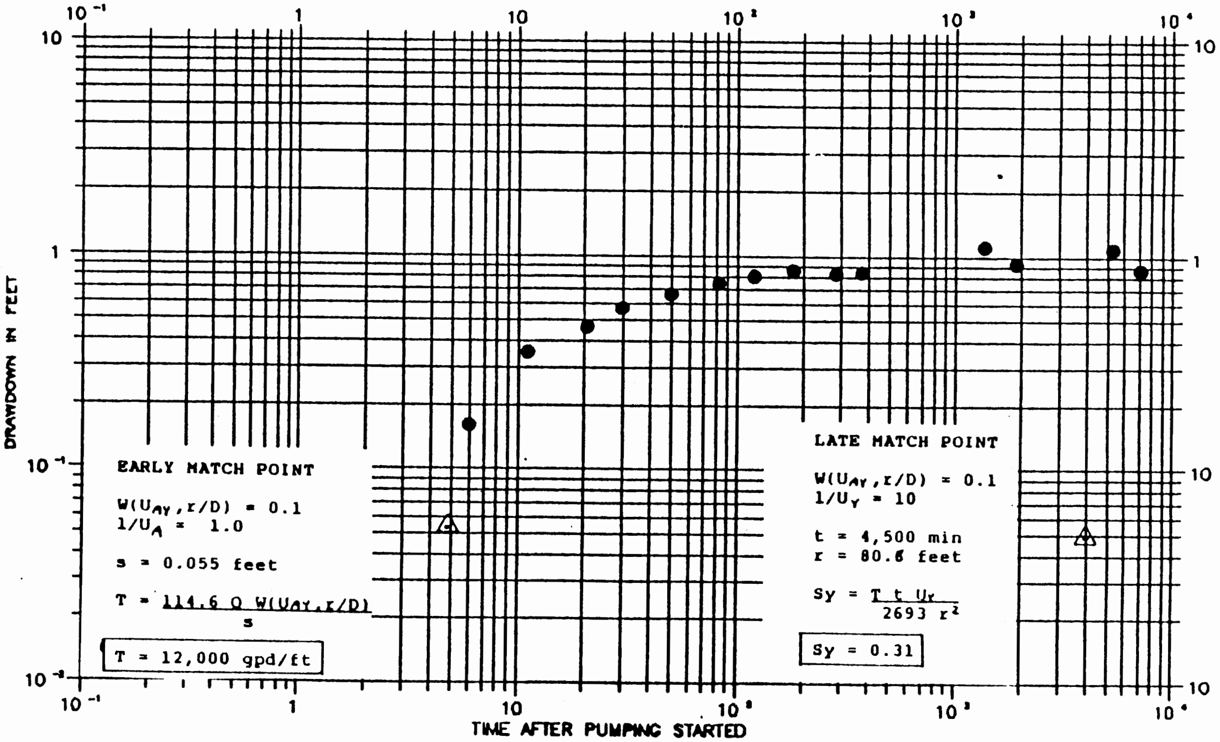


Figure 67. Log-Log Plot of Drawdown VS. Time for MW 10

APPENDIX E

WATER QUALITY DATA

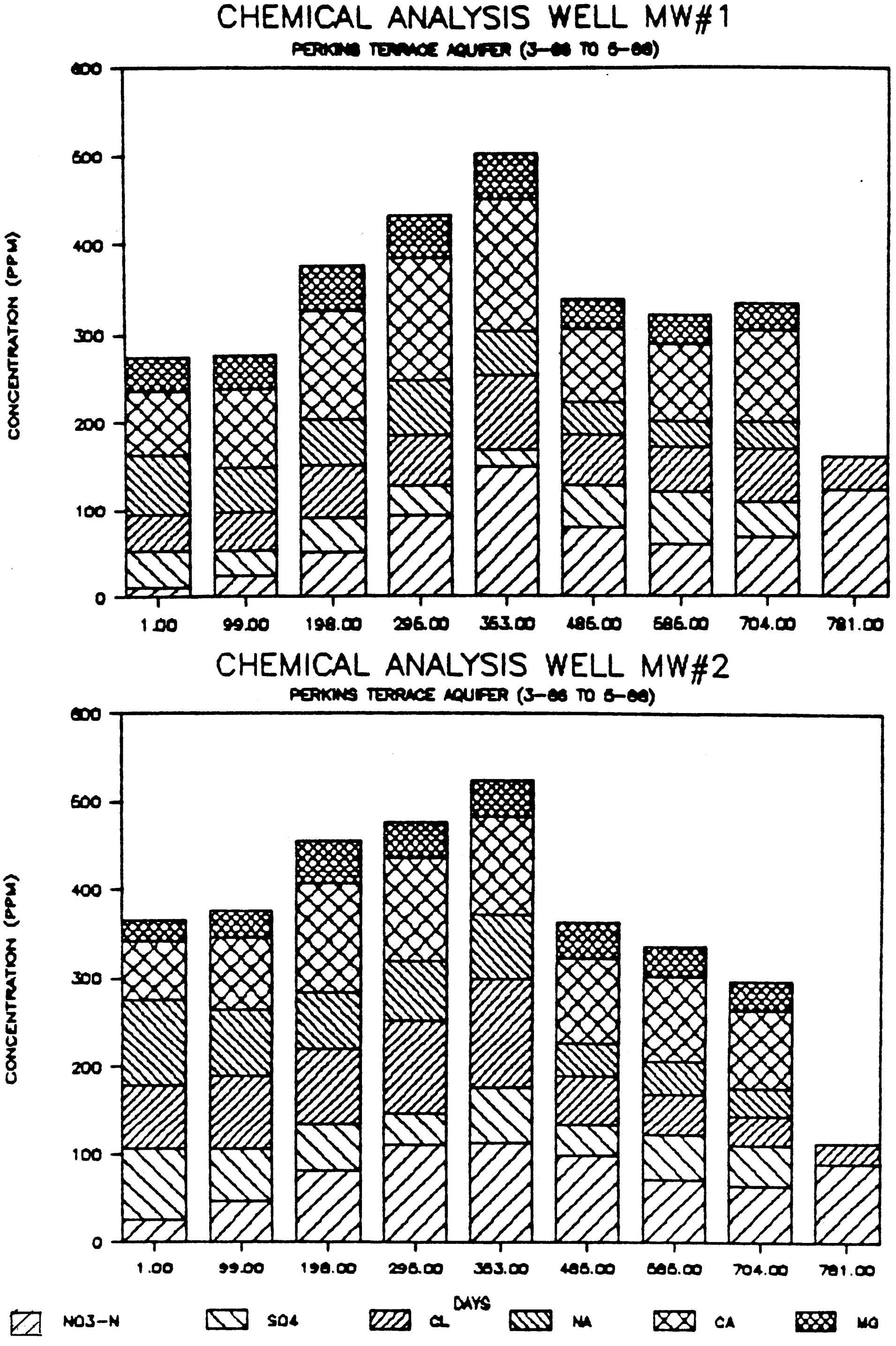


Figure 68. Inorganic Chemical Analysis for MW 1 and MW 2

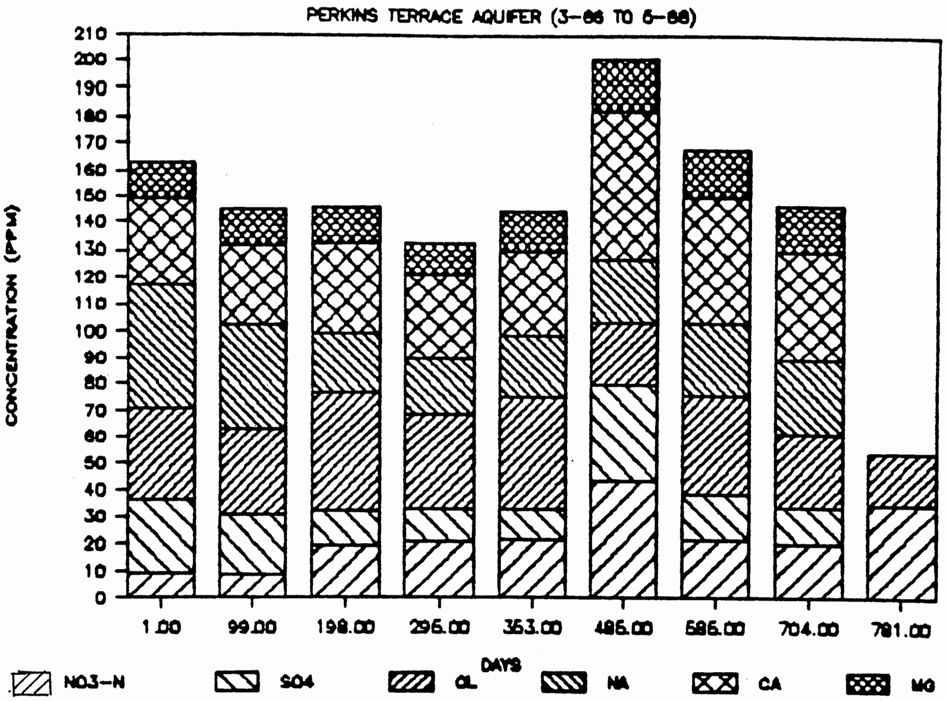


Figure 69. Inorganic Chemical Anlysis for MW 3

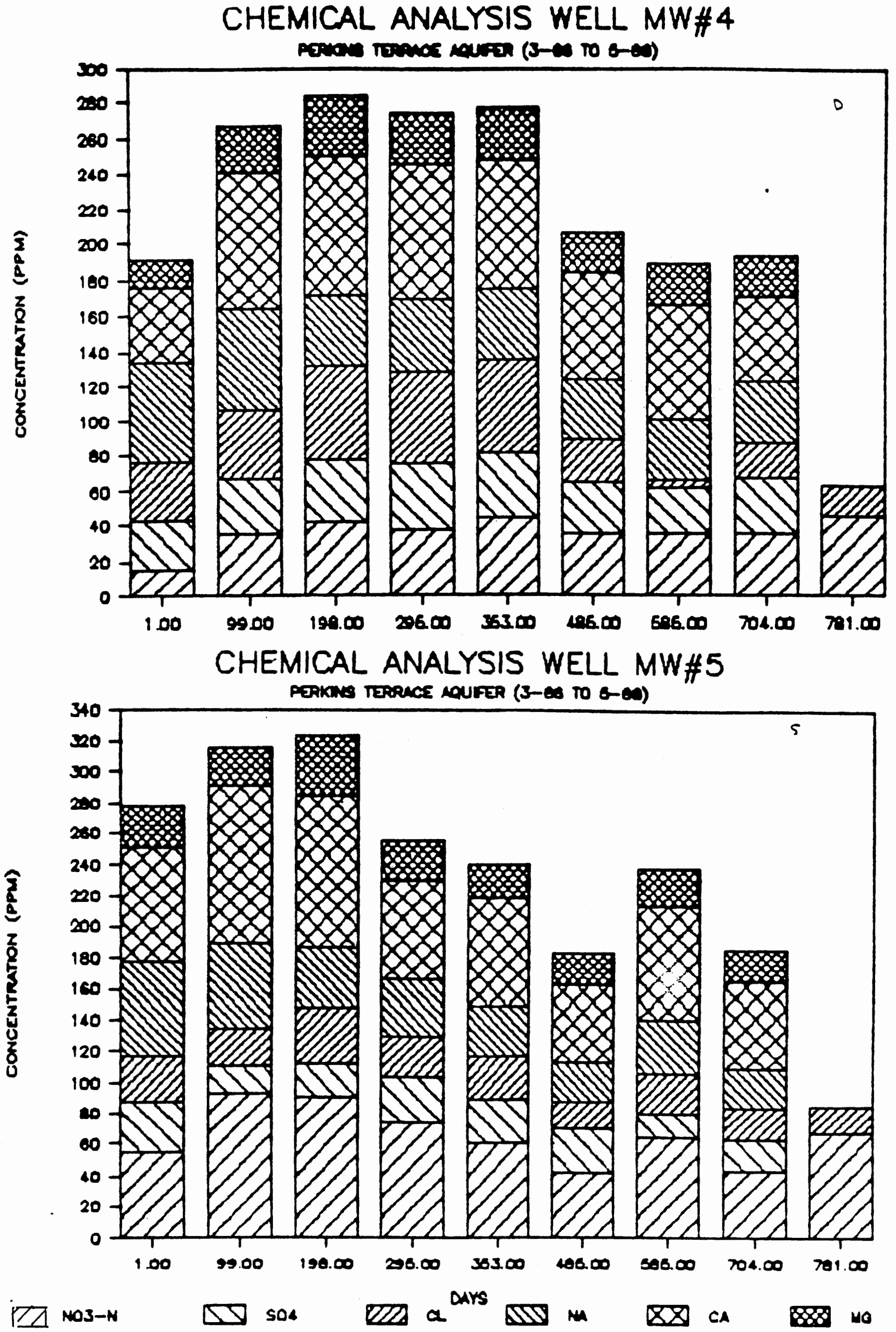


Figure 70. Inorganic Chemical Analysis for MW 4 and MW 5

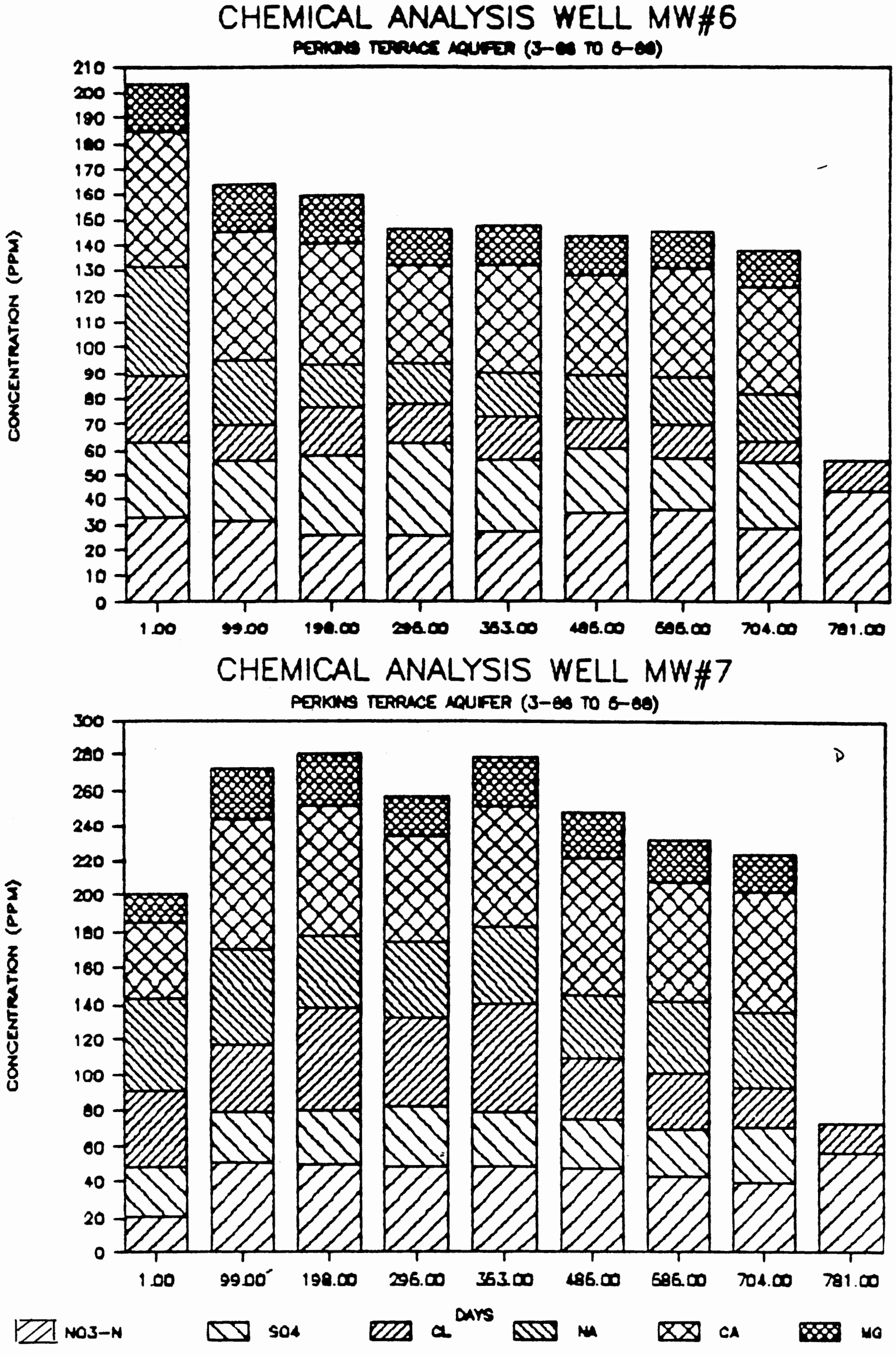


Figure 71. Inorganic Chemical Analysis for MW 6 and MW 7

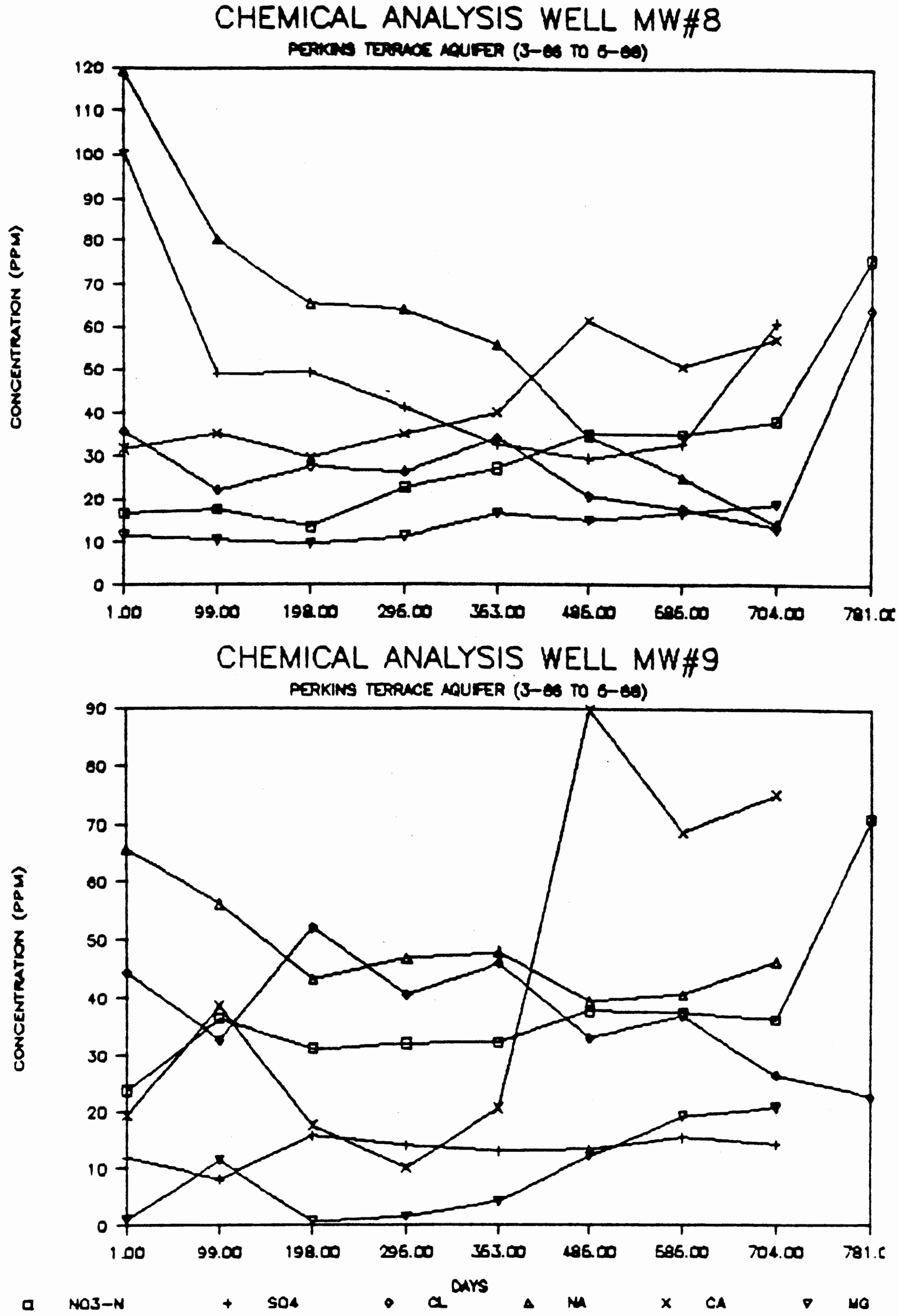


Figure 72. Inorganic Chemical Analysis for MW 8 and MW 9

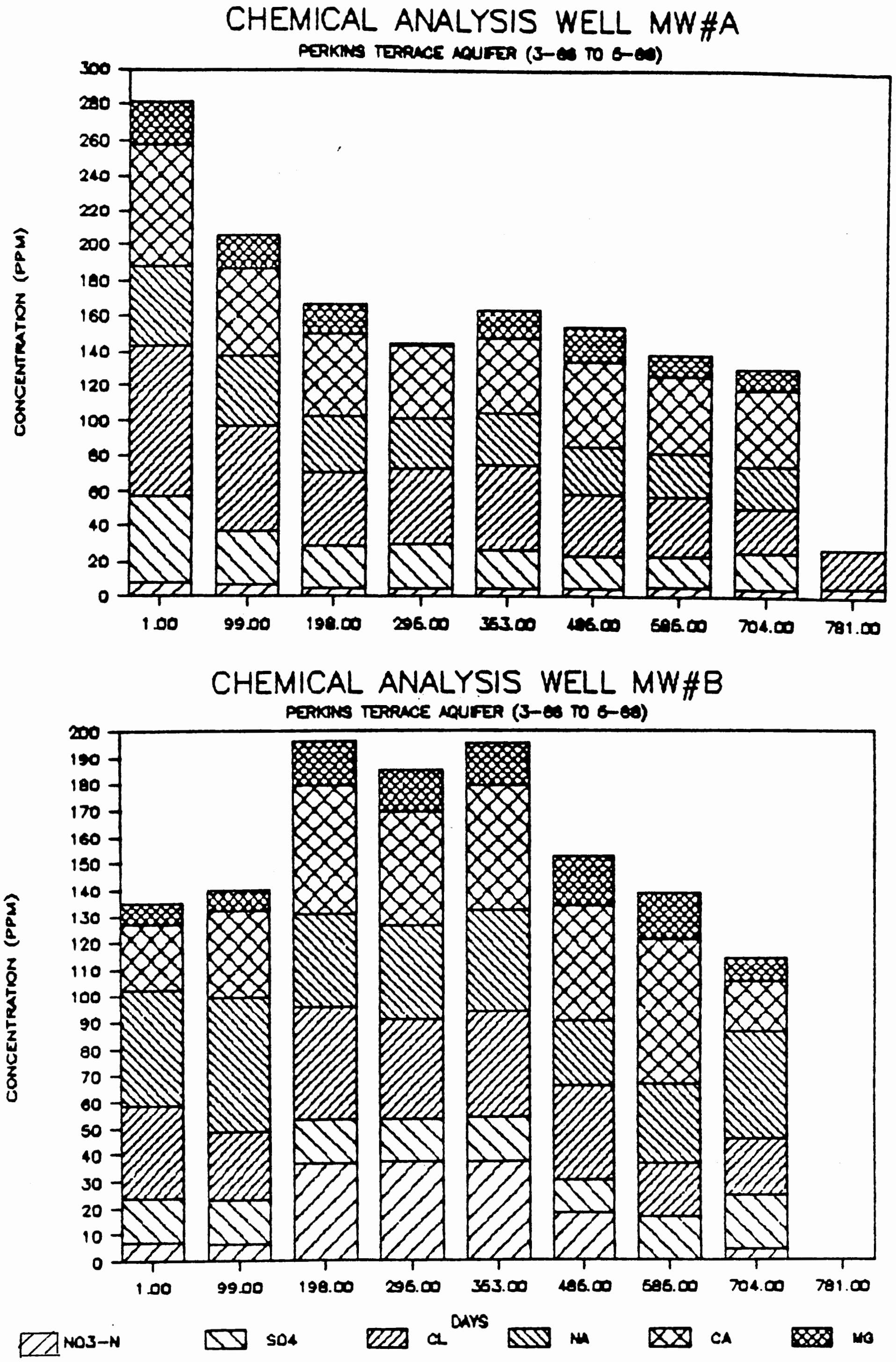


Figure 73. Inorganic chemical Analysis for MW A and MW B

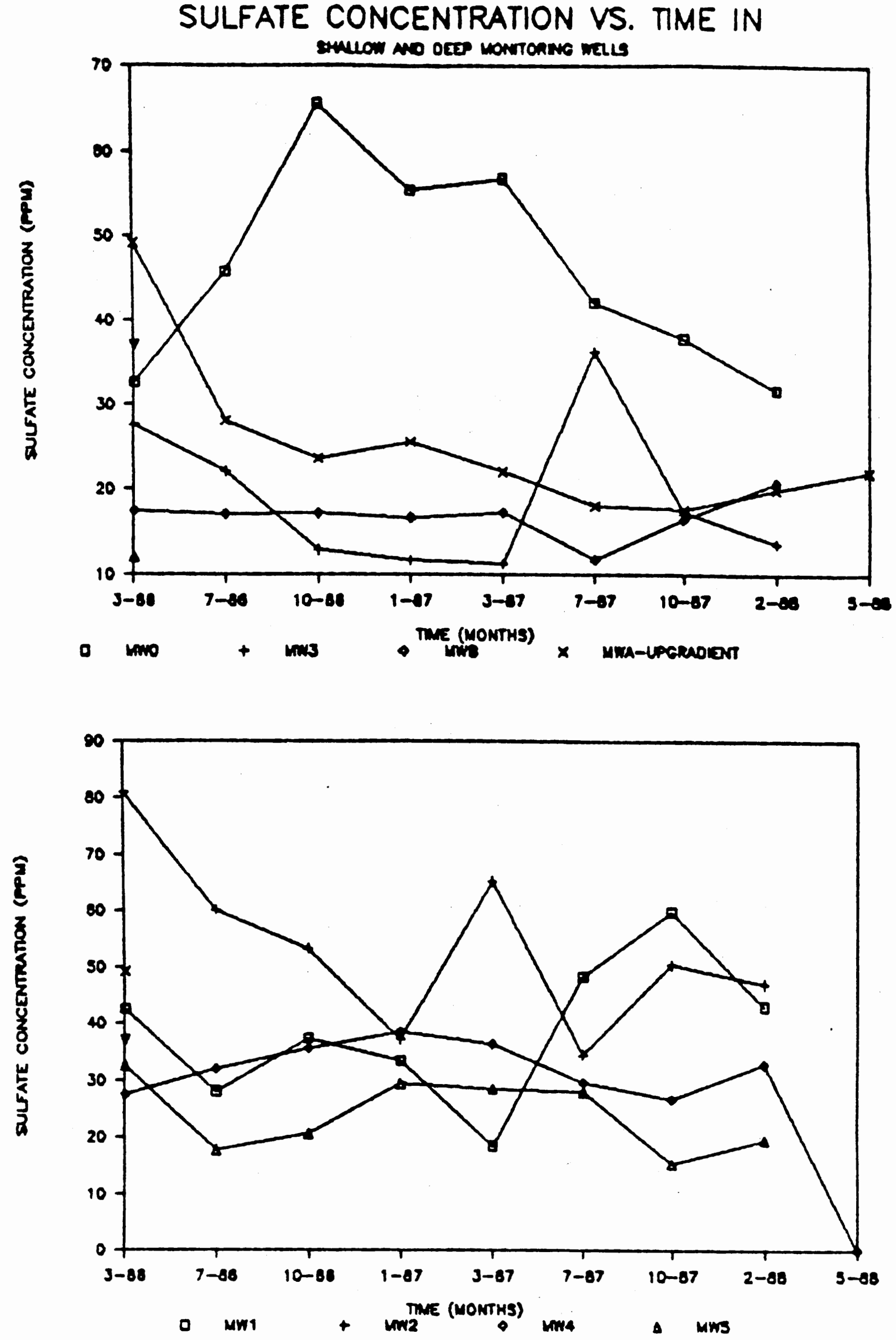
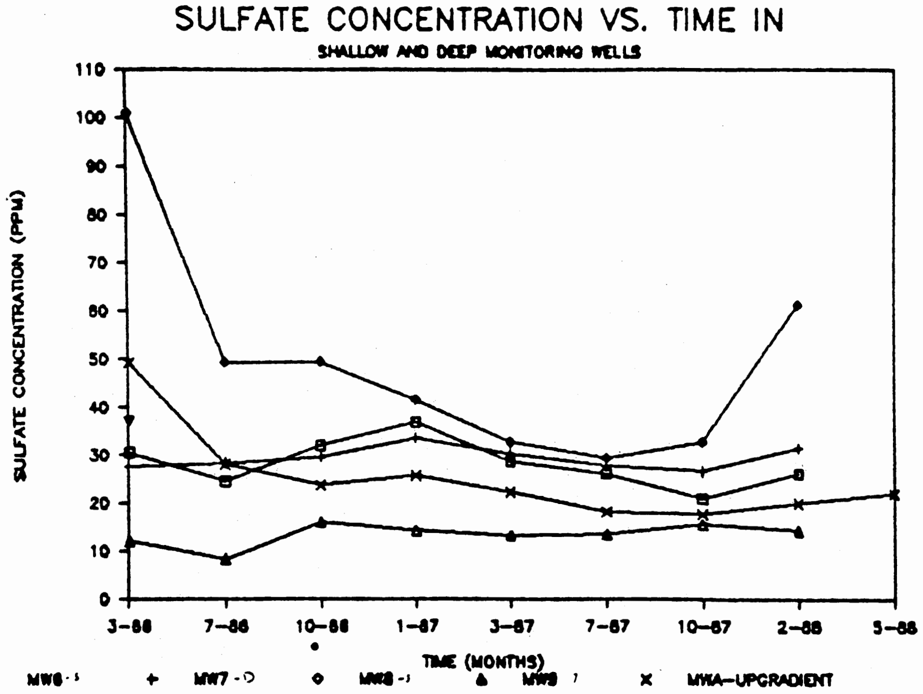


Figure 74. Sulfate Concentration VS. Time in Shallow and Deep Monitoring Wells - A



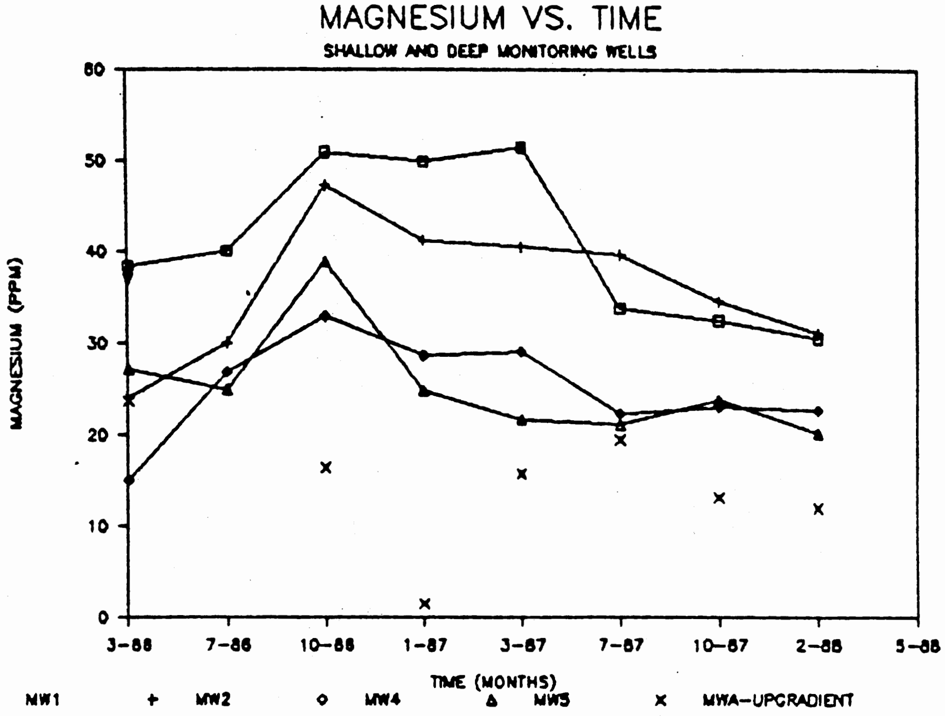


Figure 75. Sulfate Concentration VS. time in Shallow and Deep Monitoring Wells - B

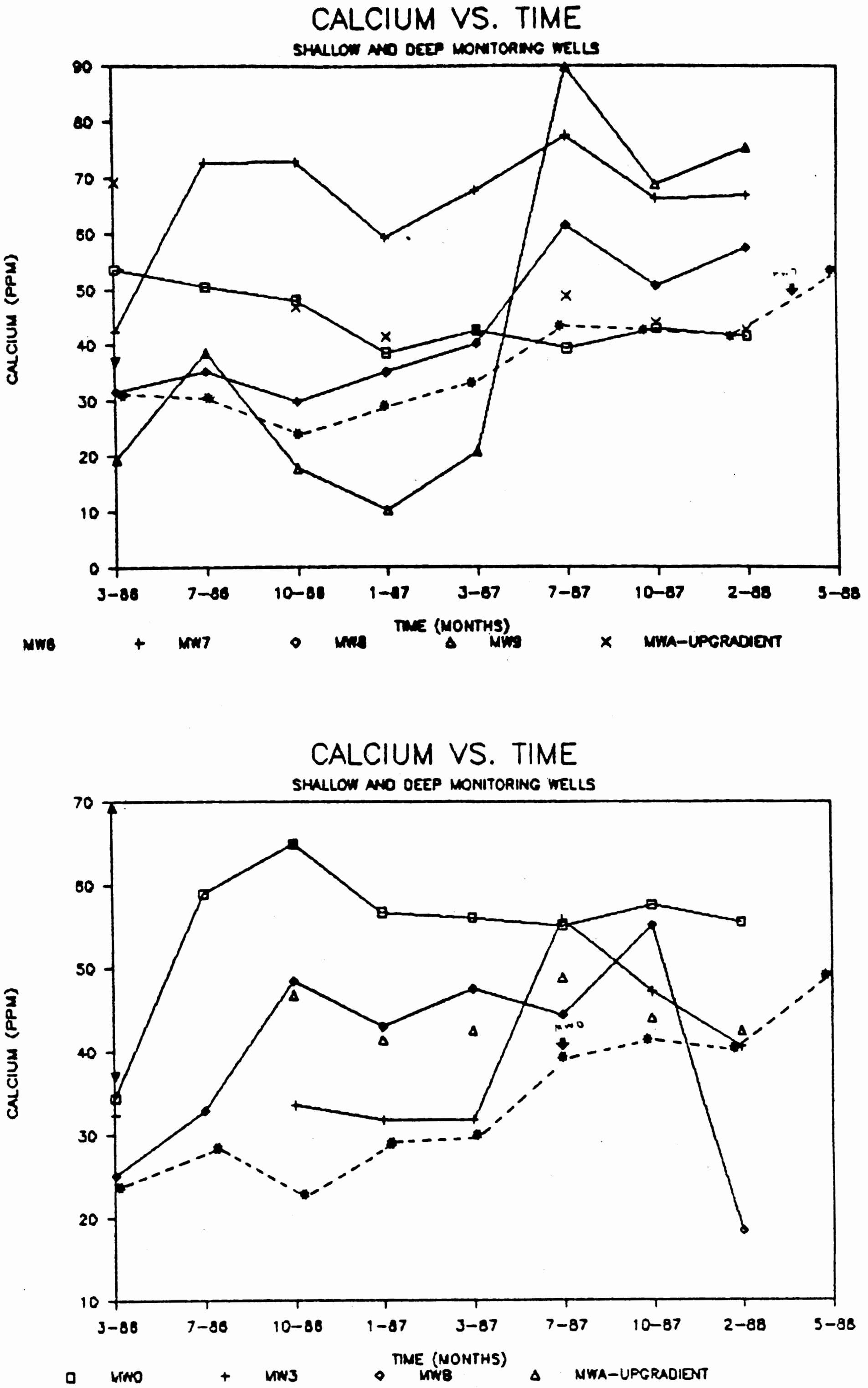


Figure 76. Calcium Concentrations VS. Time in Shallow and Deep Monitoring Wells

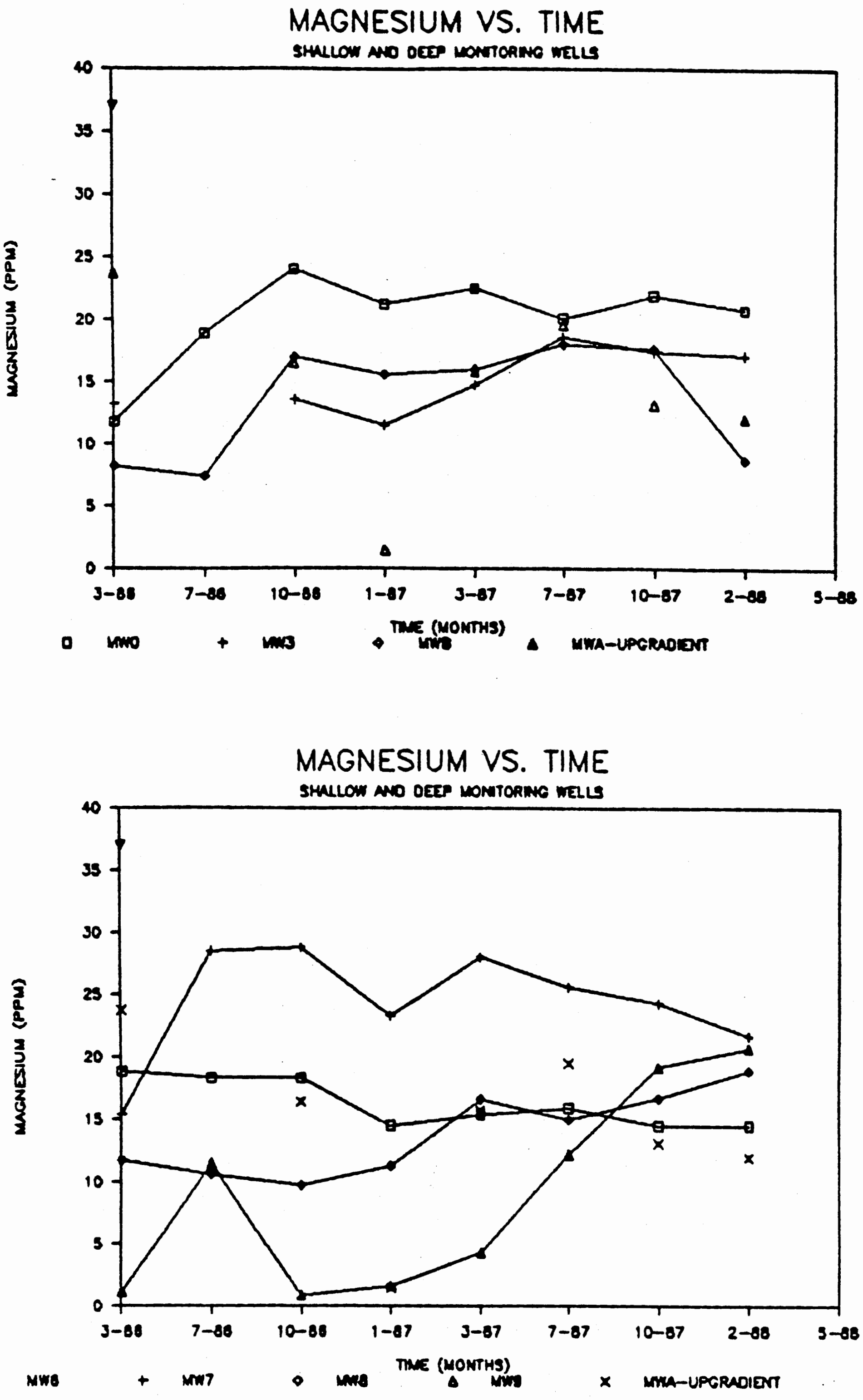
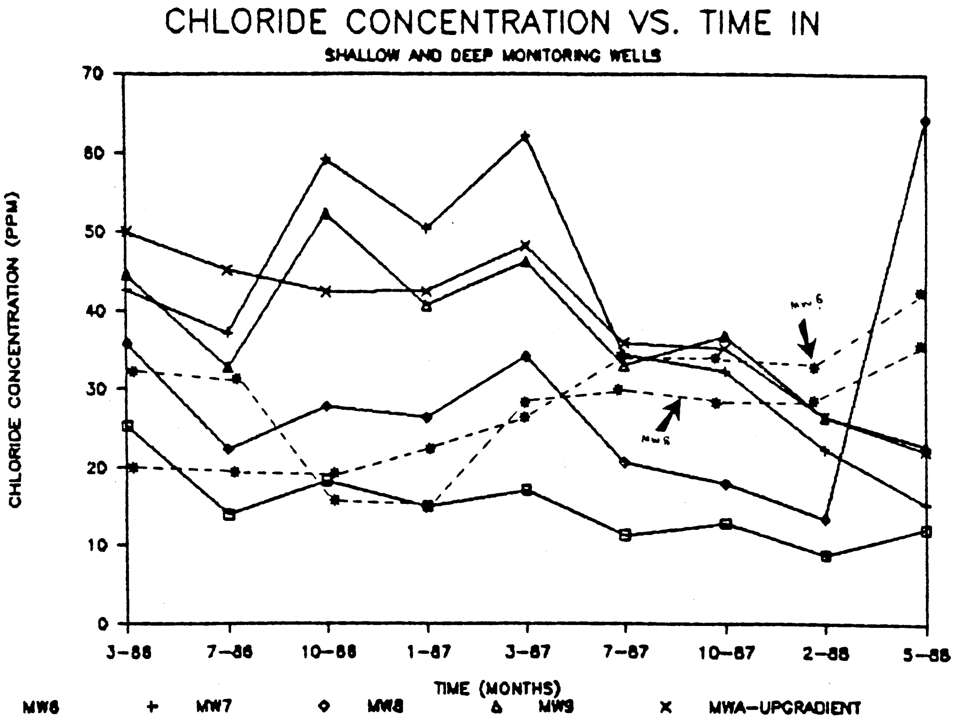


Figure 77. Magnesium Concentrations VS. Time in Shallow and Deep Monitoring Wells



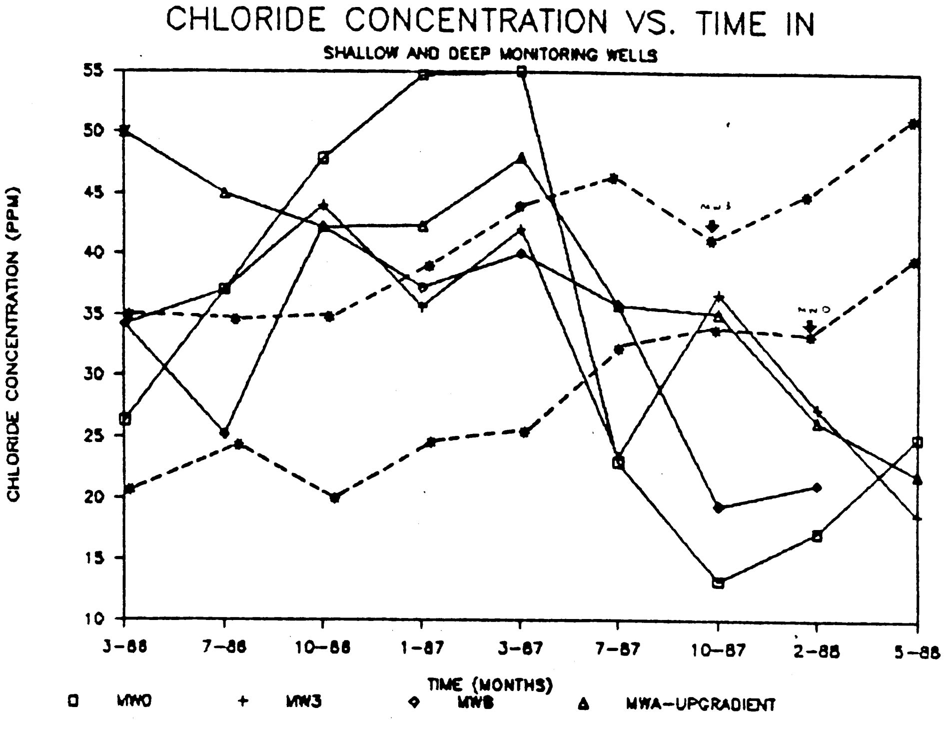


Figure 78. Chloride Concentrations VS. Time in Shallow and Deep Monitoring Wells

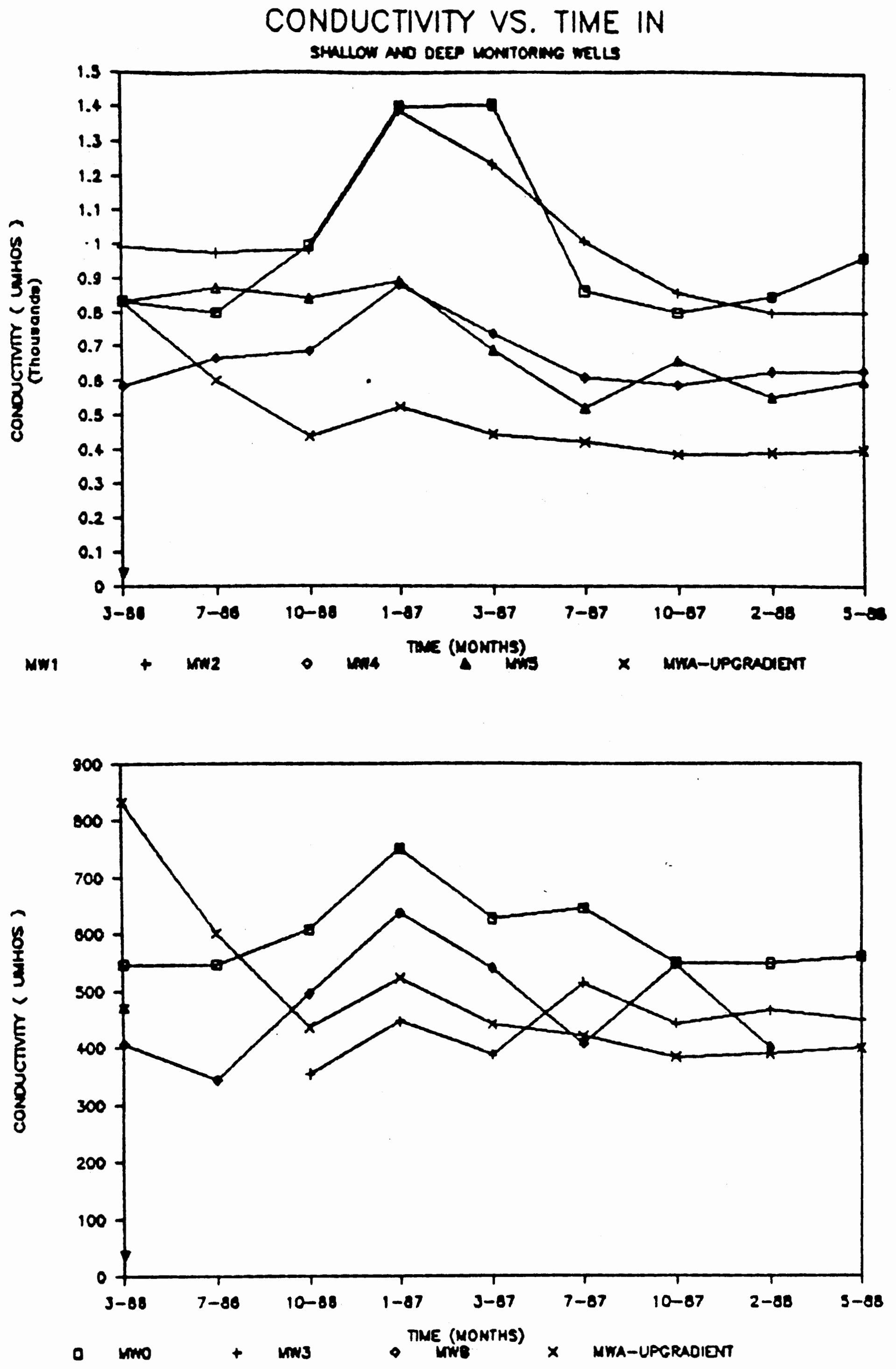


Figure 79. Conductivity VS. Time in Shallow and Deep Monitoring Wells - A

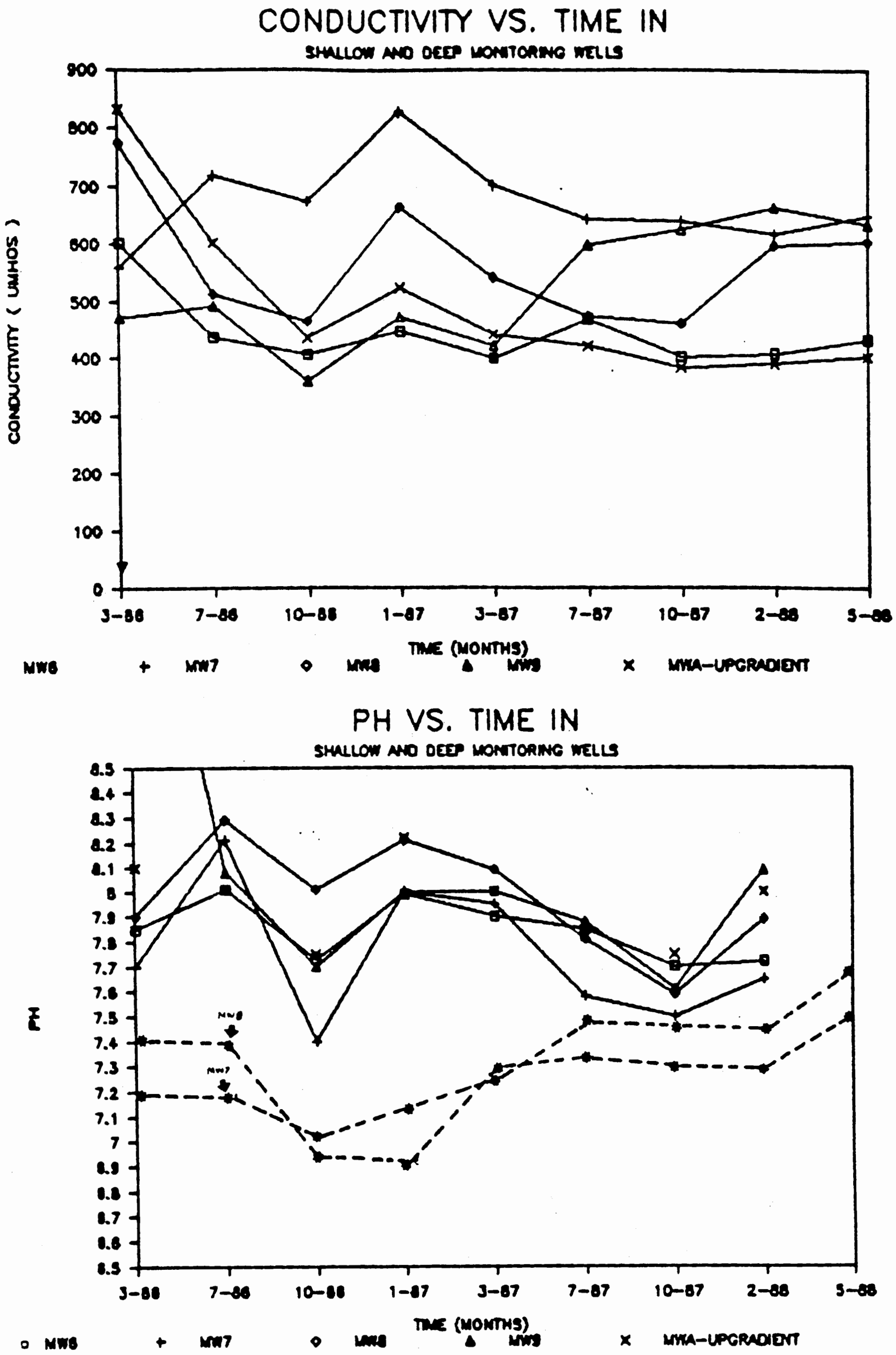


Figure 80. Conductivity VS. Time in Shallow and Deep Monitoring Wells - B

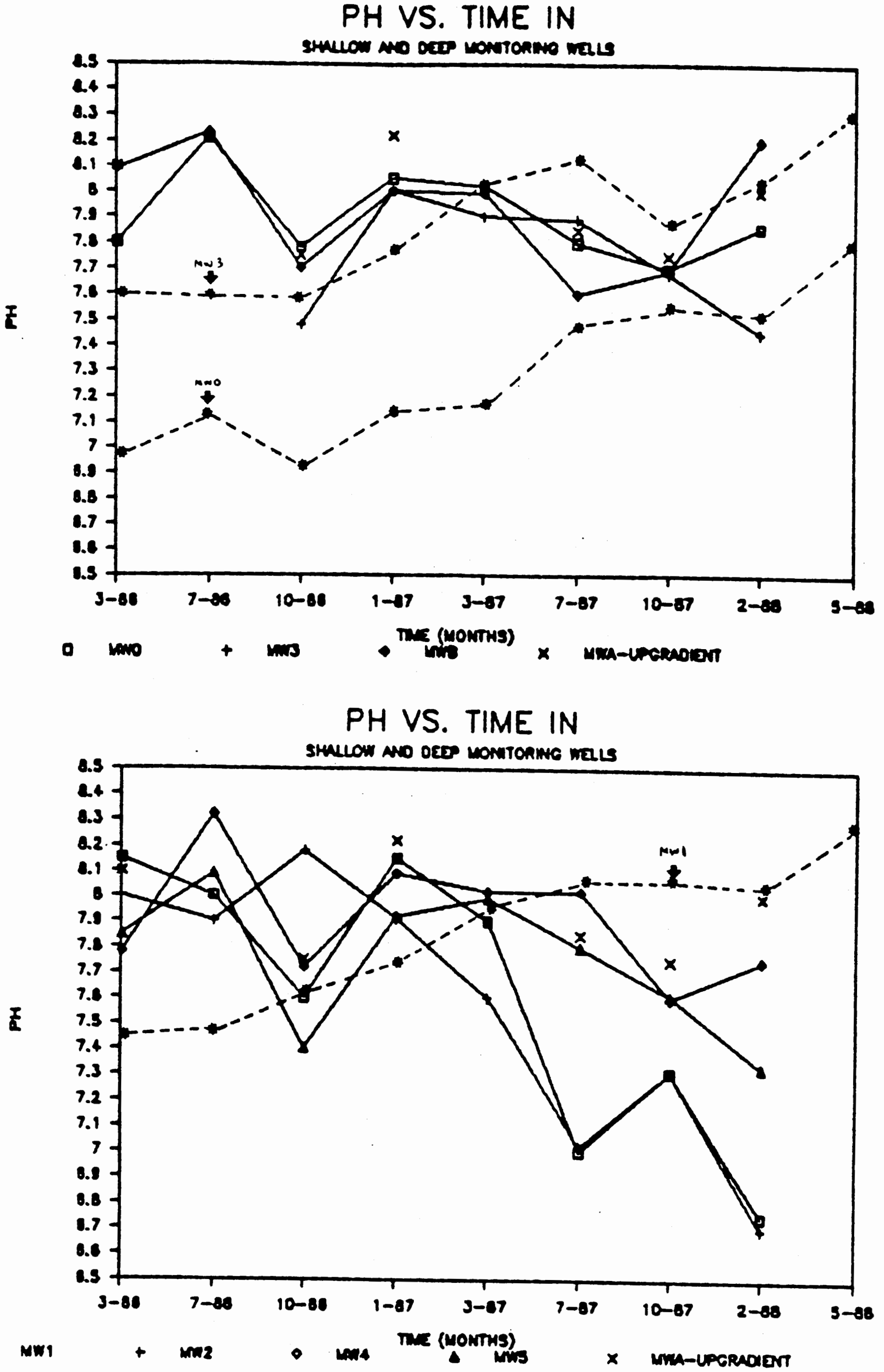
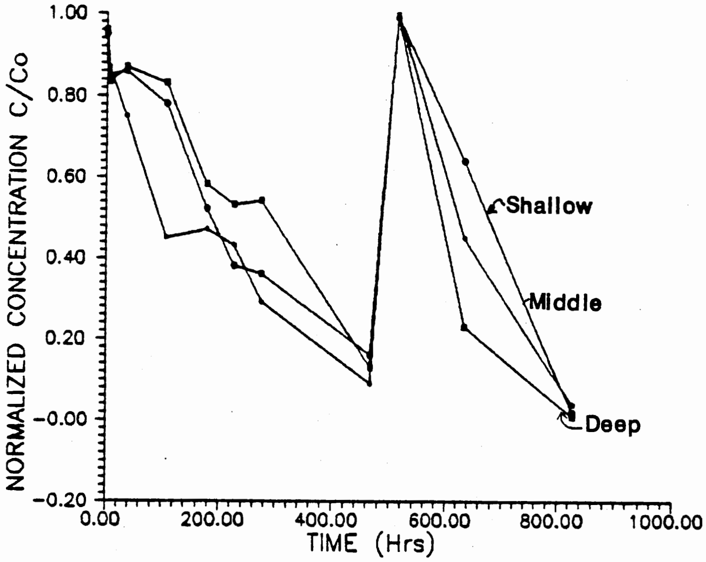


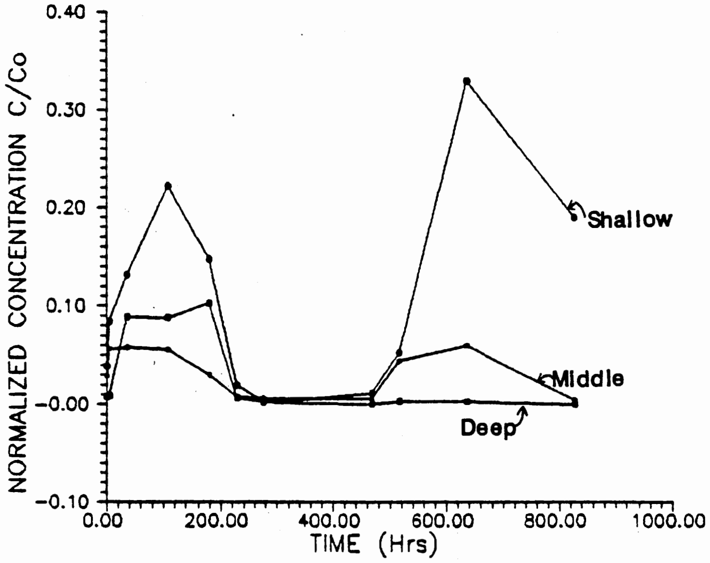
Figure 81. Ph VS. Time in Shallow and Deep Monitoring Wells

APPENDIX F

SATURATED ZONE TRACER TEST DATA

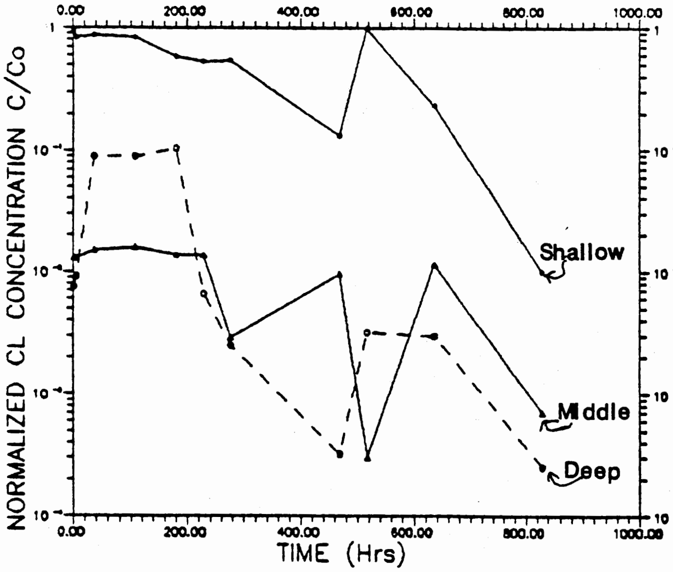


NORMALIZED CL CONCENTRATION WITH TIME IN INJECTION WELL 14 AT SHALLOW MIDDLE AND DEEP LEVEL

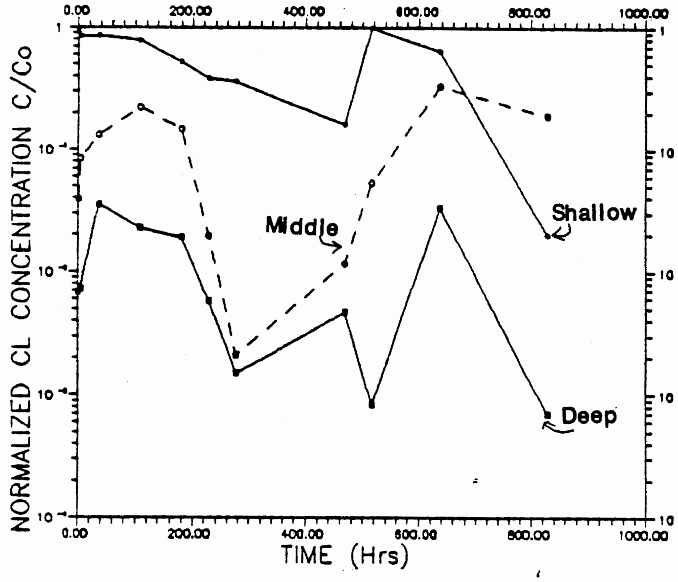


NORMALIZED CL CONCENTRATION WITH TIME IN NEAR OBSERVATION WELL 15 AT SHALLOW, MIDDLE AND DEEP LEVEL

Figure 82. Normalized Chloride Concentrations in MW 14 and MW 15



NORMALIZED CL CONCENTRATION WITH TIME IN INJECTION WELL 14 (DEEP LEVEL)
NEAR OBSERVATION WELL 15 (DEEP LEVEL) AND FAR OBSERVATION WELL 17 (DEEP)

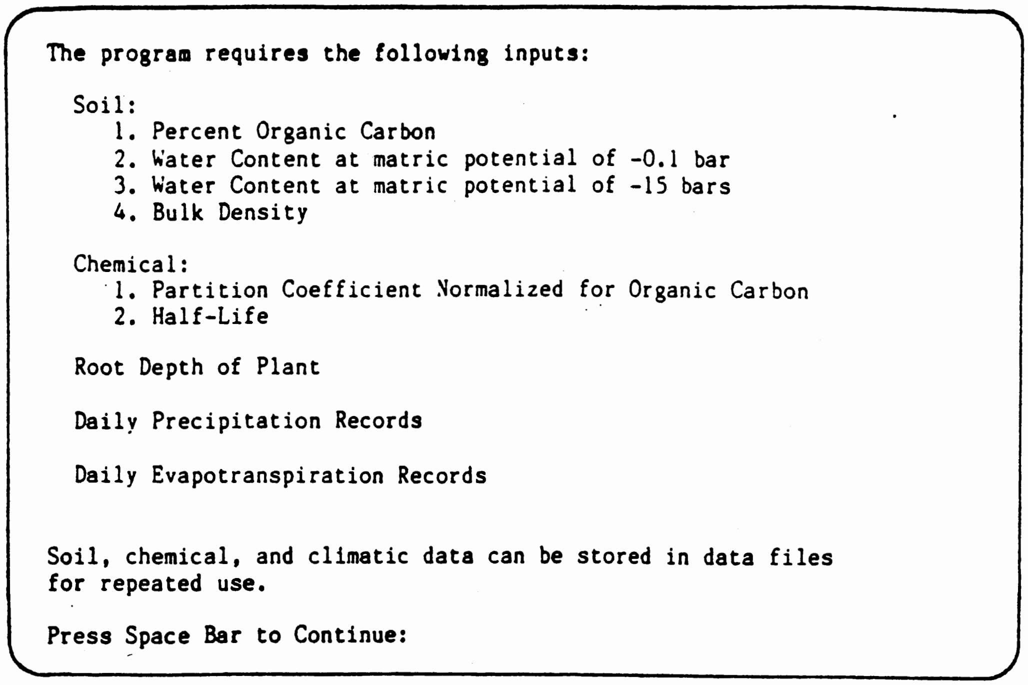


NORMALIZED CL CONCENTRATION WITH TIME IN INJECTION WELL 14 (MIDDLE LEVEL)
NEAR OBSERVATION WELL 15 (MIDDLE LEVEL) AND FAR OBSERVATION WELL 17 (MIDDLE)

Figure 83. Normalized Concentrations in MW 14, MW 15 and MW 17

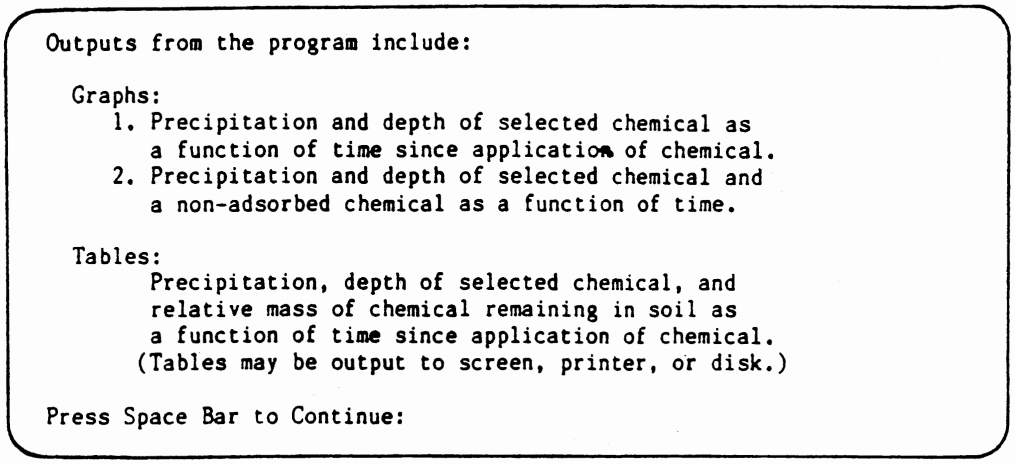
APPENDIX G

CMIS MODEL RESULTS



```
The program requires the following inputs:

  Soil:
     1. Percent Organic Carbon
     2. Water Content at matric potential of -0.1 bar
     3. Water Content at matric potential of -15 bars
     4. Bulk Density

  Chemical:
     1. Partition Coefficient Normalized for Organic Carbon
     2. Half-Life

  Root Depth of Plant

  Daily Precipitation Records

  Daily Evapotranspiration Records


Soil, chemical, and climatic data can be stored in data files
for repeated use.

Press Space Bar to Continue:
```

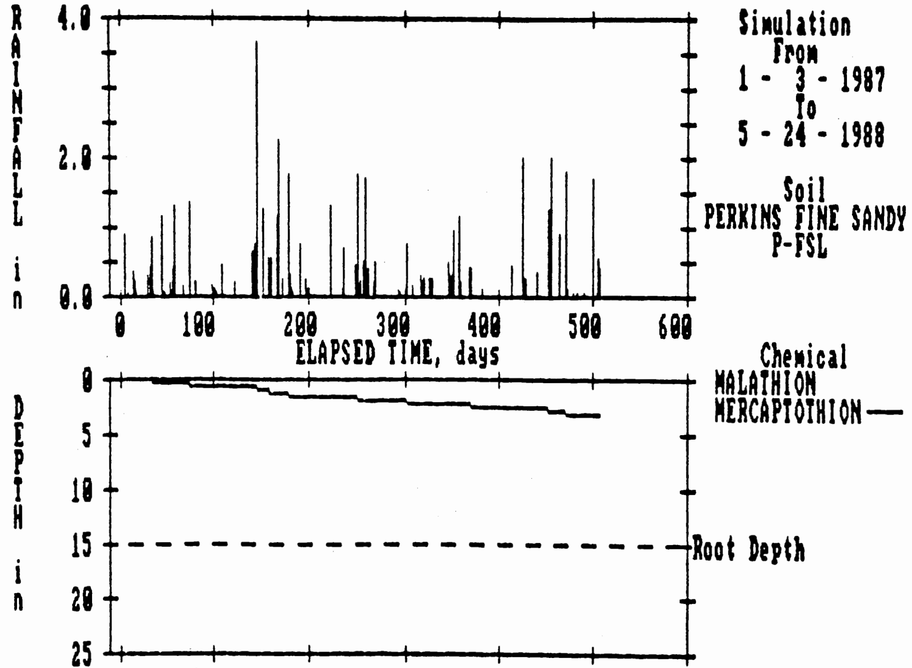
Screen 2. Required inputs for the model.



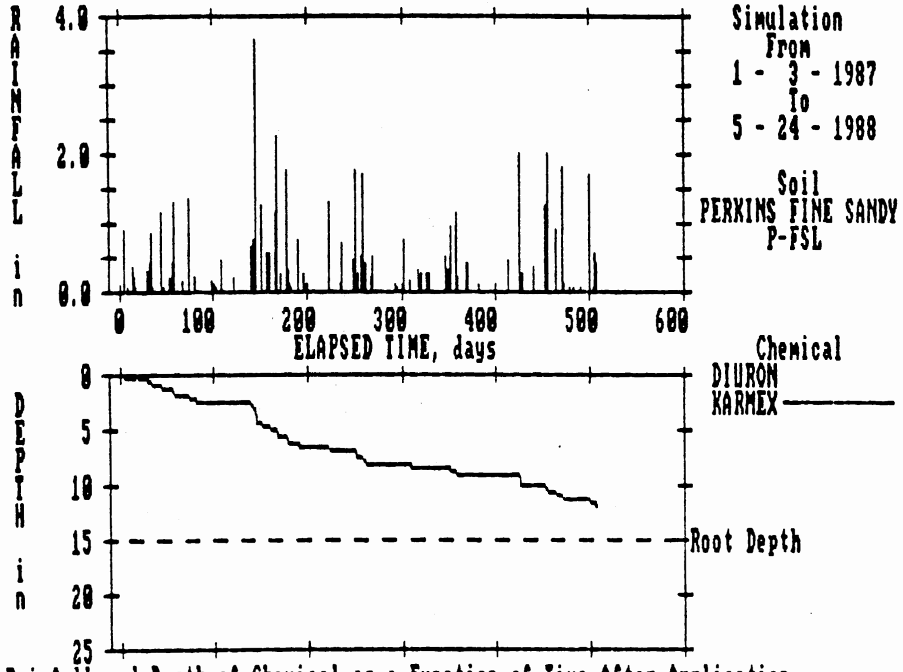
```
Outputs from the program include:

  Graphs:
     1. Precipitation and depth of selected chemical as
        a function of time since application of chemical.
     2. Precipitation and depth of selected chemical and
        a non-adsorbed chemical as a function of time.

  Tables:
        Precipitation, depth of selected chemical, and
        relative mass of chemical remaining in soil as
        a function of time since application of chemical.
       (Tables may be output to screen, printer, or disk.)

Press Space Bar to Continue:
```

Screen 3. Types of output available from the model.

Figure 84. Typical Input Requirements and Output Format for CMIS Model (After Nofziger, 1985)

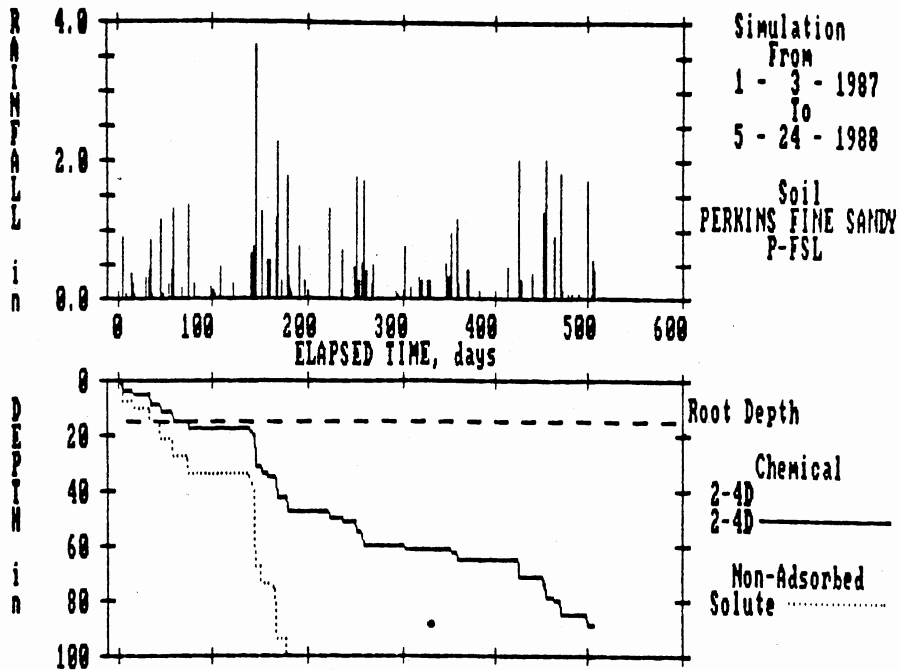


Rainfall and Depth of Chemical as a Function of Time After Application.

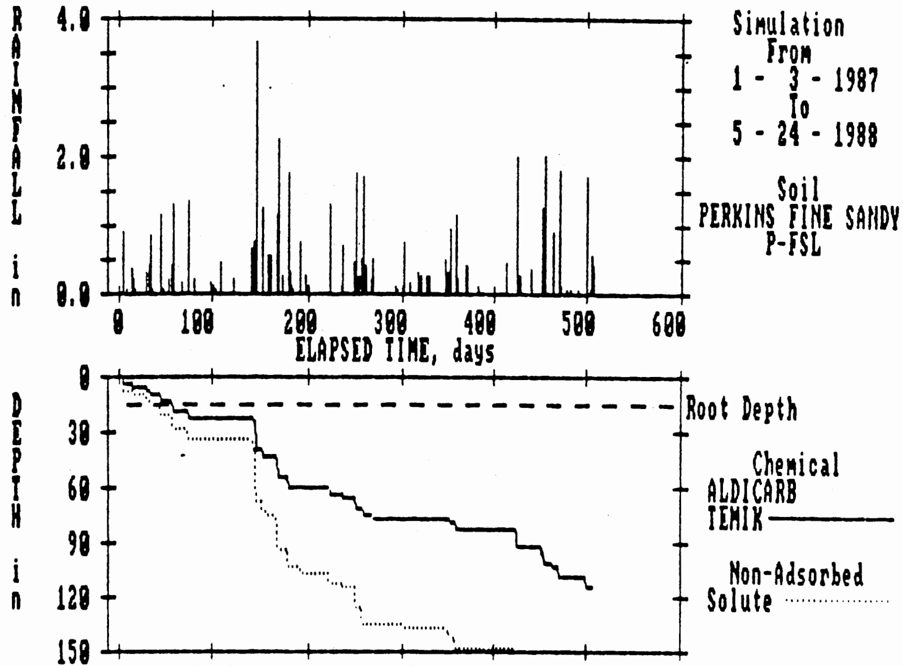


Rainfall and Depth of Chemical as a Function of Time After Application.

Figure 85. Plots for Leaching of Malathion and Diuron as a Function of Rainfall and Time



Rainfall and Depth of Chemical as a Function of Time After Application.



Rainfall and Depth of Chemical as a Function of Time After Application.

Figure 86. Plots for Leaching of 2,4-D and Aldicarb as a Function of Rainfall and Time

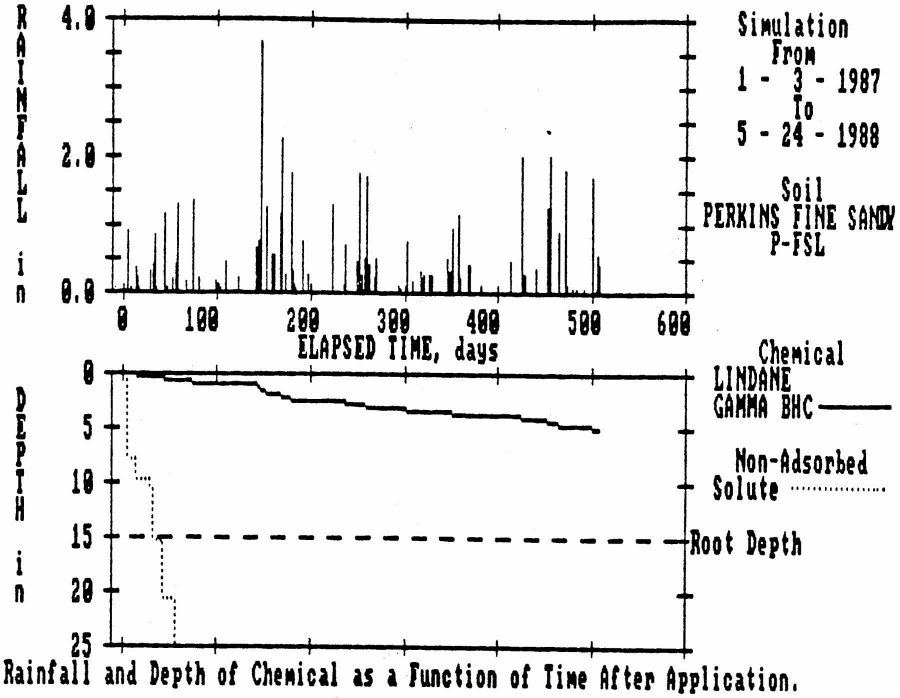


Figure 87. Plot for Leaching of Lindane as a Function of Rainfall and Time

APPENDIX H

PRZM MODEL DATA AND RESULTS

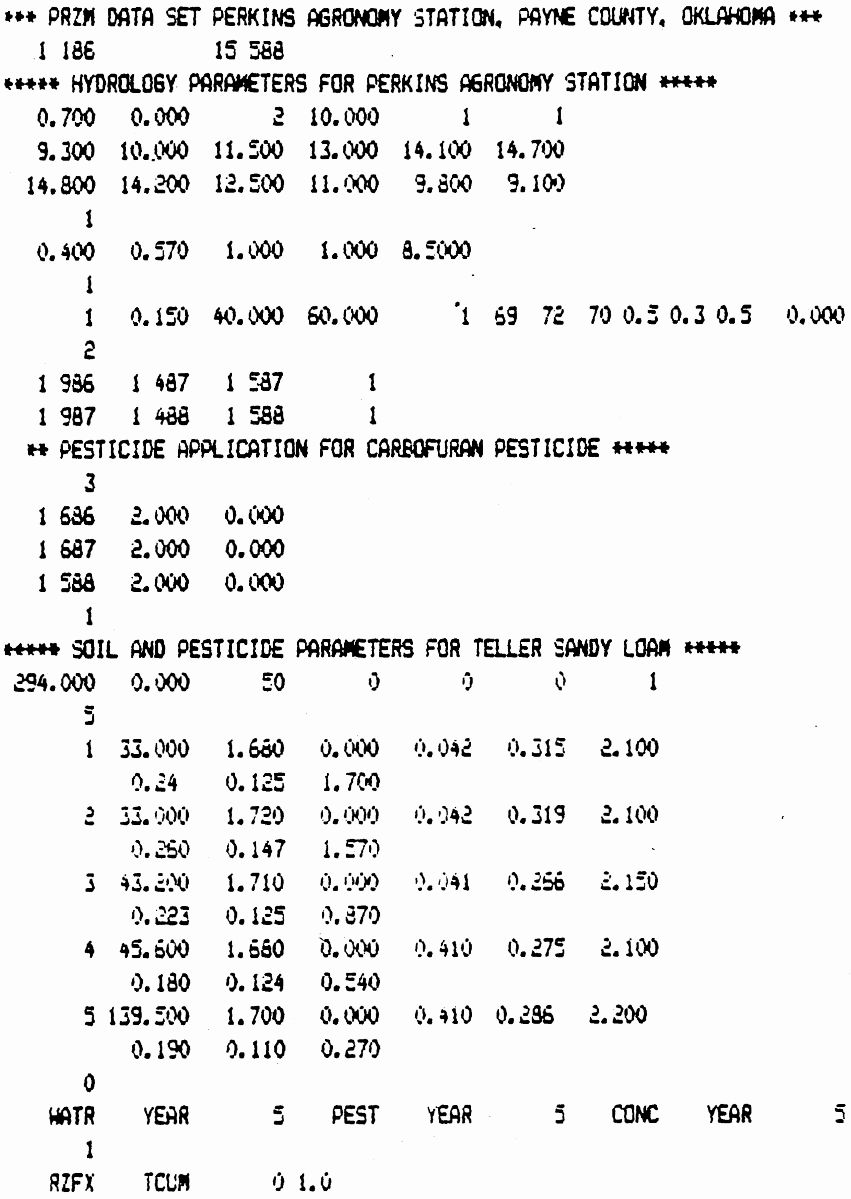
TABLE V

RETARDATION FACTOR FOR SIMULATED PESTICIDES

HORIZON	DEPTH (inches)	CARBARYL	2, 4-D	DIURON	MALATHION	ATRAZINE	TREFLAN	CARBOFURON
1	0-9	1.87	0.18	3.34	6.52	1.45	291.2	2.31
2	9-14	0.62	0.06	1.11	2.17	0.48	97.1	0.77
3	14-44	0.26	0.026	0.47	0.93	0.20	41.6	0.33
4	44-60	0.09	0.009	0.16	0.31	0.07	13.8	0.11
5	60-115	0.07	0.007	0.12	0.23	0.05	10.4	0.08

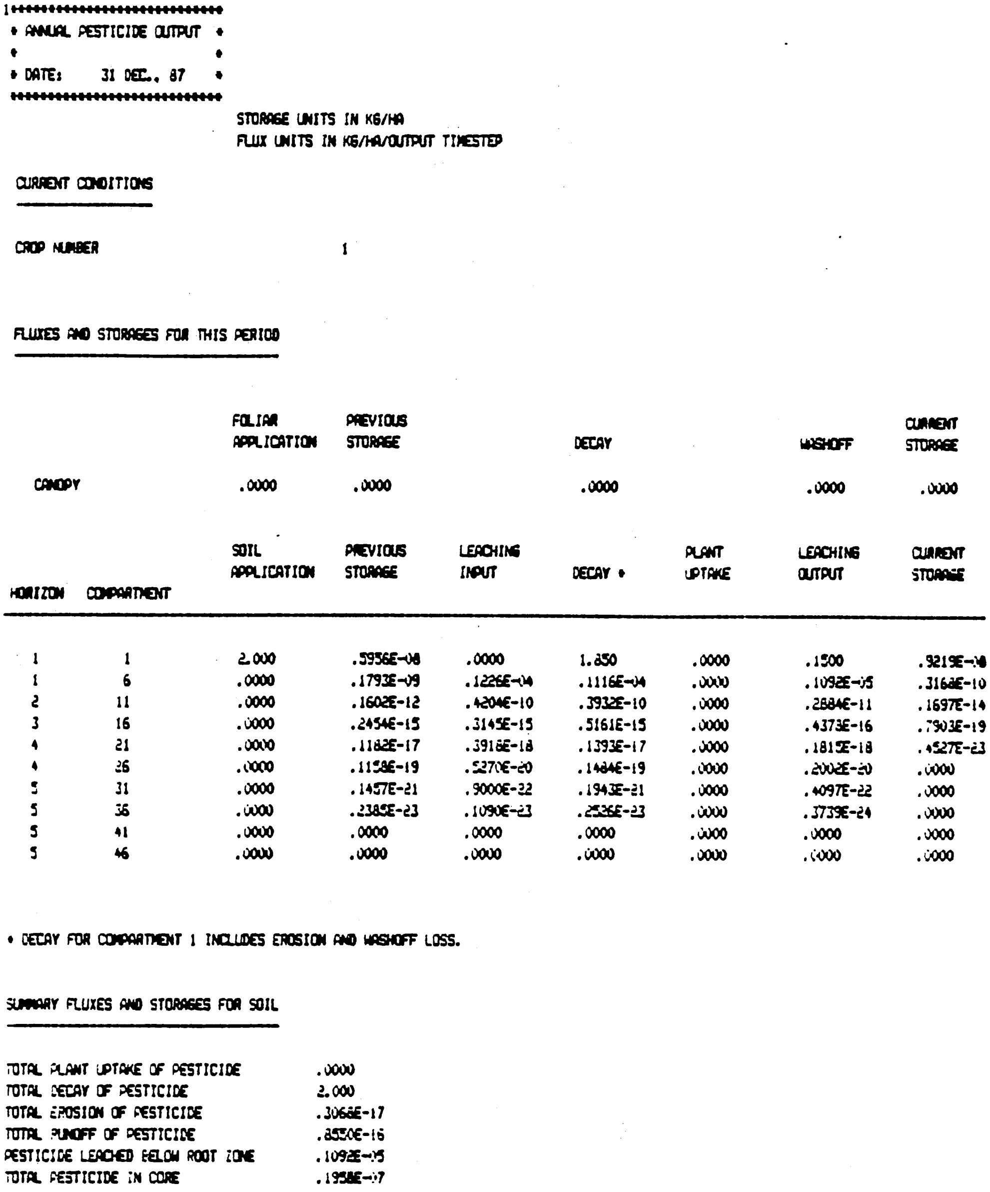
Note : Koc (organic carbon distribution coefficient) and
Kow (octanol-water distribution coefficient) are obtained from Kenaga, 1980.

$$Kd = \frac{Koc\ (\text{percent organic carbon})}{100}$$



```
*** PRZM DATA SET PERKINS AGRONOMY STATION, PAYNE COUNTY, OKLAHOMA ***
   1 186          15 588
***** HYDROLOGY PARAMETERS FOR PERKINS AGRONOMY STATION *****
   0.700   0.000       2  10.000       1       1
   9.300  10.000  11.500  13.000  14.100  14.700
  14.800  14.200  12.500  11.000   9.800   9.100
       1
   0.400   0.570   1.000   1.000  8.5000
       1
       1   0.150  40.000  60.000       1  69  72  70 0.5 0.3 0.5   0.000
       2
   1 986   1 487   1 587       1
   1 987   1 488   1 588       1
  ** PESTICIDE APPLICATION FOR CARBOFURAN PESTICIDE *****
       3
   1 686   2.000   0.000
   1 687   2.000   0.000
   1 588   2.000   0.000
       1
***** SOIL AND PESTICIDE PARAMETERS FOR TELLER SANDY LOAM *****
 294.000   0.000      50       0       0       0       1
       5
       1  33.000   1.680   0.000   0.042   0.315   2.100
            0.24   0.125   1.700
       2  33.000   1.720   0.000   0.042   0.319   2.100
           0.260   0.147   1.570
       3  43.200   1.710   0.000   0.041   0.256   2.150
           0.223   0.125   0.870
       4  45.600   1.680   0.000   0.410   0.275   2.100
           0.180   0.124   0.540
       5 139.500   1.700   0.000   0.410  0.286   2.200
           0.190   0.110   0.270
       0
    WATR    YEAR       5    PEST    YEAR       5    CONC    YEAR       5
       1
    RZFX    TCUM       0 1.0
```

Figure 88. Typical Input Data Set for PRZM Model



```
1***************************
* ANNUAL PESTICIDE OUTPUT  *
*                          *
* DATE:     31 DEC., 87    *
****************************
                             STORAGE UNITS IN KG/HA
                             FLUX UNITS IN KG/HA/OUTPUT TIMESTEP

CURRENT CONDITIONS
__________________

CROP NUMBER                             1


FLUXES AND STORAGES FOR THIS PERIOD
___________________________________


                             FOLIAR      PREVIOUS                                                     CURRENT
                             APPLICATION STORAGE                 DECAY                     WASHOFF    STORAGE

  CANOPY                     .0000       .0000                   .0000                     .0000      .0000


                             SOIL        PREVIOUS    LEACHING                  PLANT       LEACHING   CURRENT
                             APPLICATION STORAGE     INPUT       DECAY *       UPTAKE      OUTPUT     STORAGE
HORIZON   COMPARTMENT
_____________________________________________________________________________________________________________

   1          1              2.000       .5956E-08   .0000       1.850         .0000       .1500      .9219E-08
   1          6              .0000       .1793E-09   .1226E-04   .1116E-04     .0000       .1092E-05  .3168E-10
   2         11              .0000       .1602E-12   .4204E-10   .3932E-10     .0000       .2884E-11  .1697E-14
   3         16              .0000       .2454E-15   .3145E-15   .5161E-15     .0000       .4373E-16  .7903E-19
   4         21              .0000       .1182E-17   .3918E-18   .1393E-17     .0000       .1815E-18  .4527E-23
   4         26              .0000       .1158E-19   .5270E-20   .1484E-19     .0000       .2002E-20  .0000
   5         31              .0000       .1457E-21   .9000E-22   .1943E-21     .0000       .4097E-22  .0000
   5         36              .0000       .2385E-23   .1090E-23   .2536E-23     .0000       .3739E-24  .0000
   5         41              .0000       .0000       .0000       .0000         .0000       .0000      .0000
   5         46              .0000       .0000       .0000       .0000         .0000       .0000      .0000


* DECAY FOR COMPARTMENT 1 INCLUDES EROSION AND WASHOFF LOSS.


SUMMARY FLUXES AND STORAGES FOR SOIL
____________________________________


TOTAL PLANT UPTAKE OF PESTICIDE          .0000
TOTAL DECAY OF PESTICIDE                 2.000
TOTAL EROSION OF PESTICIDE               .3066E-17
TOTAL RUNOFF OF PESTICIDE                .8550E-16
PESTICIDE LEACHED BELOW ROOT ZONE        .1092E-05
TOTAL PESTICIDE IN CORE                  .1958E-07
```

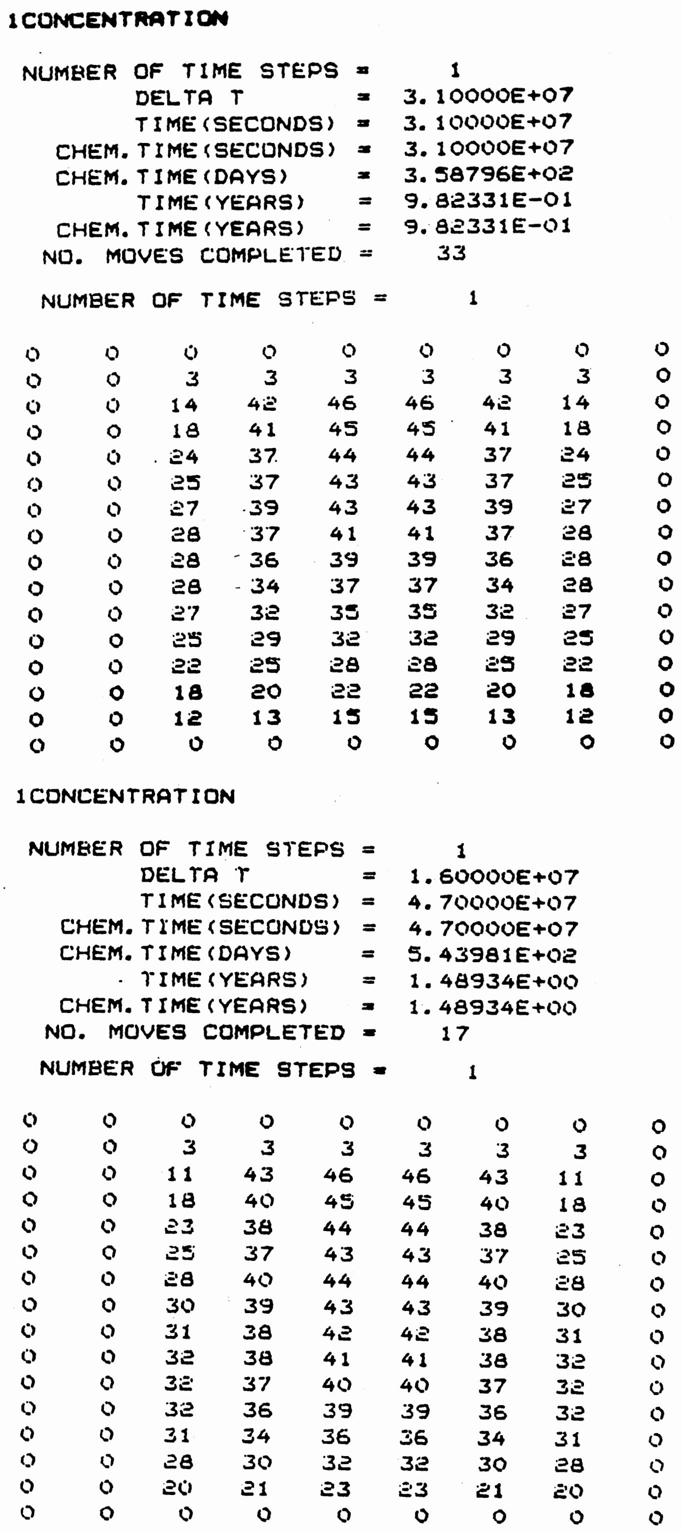
Figure 89. Typical Output Results from PRZM Model

APPENDIX I

KONIKOW MODEL DATA AND RESULTS

```
NUMBER OF TIME STEPS =        1
       DELTA T         =  3.10000E+07
       TIME(SECONDS)   =  3.10000E+07
  CHEM.TIME(SECONDS)   =  3.10000E+07
  CHEM.TIME(DAYS)      =  3.58796E+02
       TIME(YEARS)     =  9.82331E-01
  CHEM.TIME(YEARS)     =  9.82331E-01
 NO. MOVES COMPLETED   =     29
 NUMBER OF TIME STEPS  =      1

 0    0    0    0    0    0    0    0    0
 0    0    3    2    3    3    2    3    0
 0    0   14   42   46   46   42   14    0
 0    0   18   41   45   45   41   18    0
 0    0   23   37   44   44   37   23    0
 0    0   24   36   43   43   36   24    0
 0    0   26   38   42   42   38   26    0
 0    0   27   36   40   40   36   27    0
 0    0   27   34   38   38   34   27    0
 0    0   26   32   35   35   32   26    0
 0    0   24   29   32   32   29   24    0
 0    0   22   26   29   29   26   22    0
 0    0   18   21   24   24   21   18    0
 0    0   14   17   18   18   17   14    0
 0    0    8    9   11   11    9    8    0
 0    0    0    0    0    0    0    0    0

1CONCENTRATION

 NUMBER OF TIME STEPS =      1
        DELTA T        =  3.10000E+07
        TIME(SECONDS)  =  7.80000E+07
   CHEM.TIME(SECONDS)  =  7.80000E+07
   CHEM.TIME(DAYS)     =  9.02778E+02
        TIME(YEARS)    =  2.47167E+00
   CHEM.TIME(YEARS)    =  2.47167E+00
 NO. MOVES COMPLETED   =     29
 NUMBER OF TIME STEPS  =      1

 0    0    0    0    0    0    0    0    0
 0    0    3    2    3    3    2    3    0
 0    0   14   42   46   46   42   14    0
 0    0   18   41   45   45   41   18    0
 0    0   24   38   44   44   38   24    0
 0    0   25   37   43   43   37   25    0
 0    0   28   40   44   44   40   28    0
 0    0   30   39   43   43   39   30    0
 0    0   32   39   42   42   39   32    0
 0    0   33   38   42   42   38   33    0
 0    0   33   38   41   41   38   33    0
 0    0   33   37   40   40   37   33    0
 0    0   32   36   38   38   36   32    0
 0    0   29   31   33   33   31   29    0
 0    0   19   20   22   22   20   19    0
 0    0    0    0    0    0    0    0    0
```

figure 90. Konikow Results for Scenario 1



```
1CONCENTRATION

 NUMBER OF TIME STEPS =        1
          DELTA T      =  3.10000E+07
          TIME(SECONDS) = 3.10000E+07
    CHEM.TIME(SECONDS) =  3.10000E+07
    CHEM.TIME(DAYS)    =  3.58796E+02
          TIME(YEARS)  =  9.82331E-01
    CHEM.TIME(YEARS)   =  9.82331E-01
  NO. MOVES COMPLETED =     33

  NUMBER OF TIME STEPS =        1

 0     0     0     0     0     0     0     0     0
 0     0     3     3     3     3     3     3     0
 0     0    14    42    46    46    42    14     0
 0     0    18    41    45    45    41    18     0
 0     0    24    37    44    44    37    24     0
 0     0    25    37    43    43    37    25     0
 0     0    27    39    43    43    39    27     0
 0     0    28    37    41    41    37    28     0
 0     0    28    36    39    39    36    28     0
 0     0    28    34    37    37    34    28     0
 0     0    27    32    35    35    32    27     0
 0     0    25    29    32    32    29    25     0
 0     0    22    25    28    28    25    22     0
 0     0    18    20    22    22    20    18     0
 0     0    12    13    15    15    13    12     0
 0     0     0     0     0     0     0     0     0

1CONCENTRATION

 NUMBER OF TIME STEPS =        1
          DELTA T      =  1.60000E+07
          TIME(SECONDS) = 4.70000E+07
    CHEM.TIME(SECONDS) =  4.70000E+07
    CHEM.TIME(DAYS)    =  5.43981E+02
          TIME(YEARS)  =  1.48934E+00
    CHEM.TIME(YEARS)   =  1.48934E+00
  NO. MOVES COMPLETED =     17

  NUMBER OF TIME STEPS =        1

 0     0     0     0     0     0     0     0     0
 0     0     3     3     3     3     3     3     0
 0     0    11    43    46    46    43    11     0
 0     0    18    40    45    45    40    18     0
 0     0    23    38    44    44    38    23     0
 0     0    25    37    43    43    37    25     0
 0     0    28    40    44    44    40    28     0
 0     0    30    39    43    43    39    30     0
 0     0    31    38    42    42    38    31     0
 0     0    32    38    41    41    38    32     0
 0     0    32    37    40    40    37    32     0
 0     0    32    36    39    39    36    32     0
 0     0    31    34    36    36    34    31     0
 0     0    28    30    32    32    30    28     0
 0     0    20    21    23    23    21    20     0
 0     0     0     0     0     0     0     0     0
```

Figure 91. Konikow Results for Scenario 2

2

VITA

Rajeev L. Dwivedi

Candidate for the Degree of

Doctor of Philosophy

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