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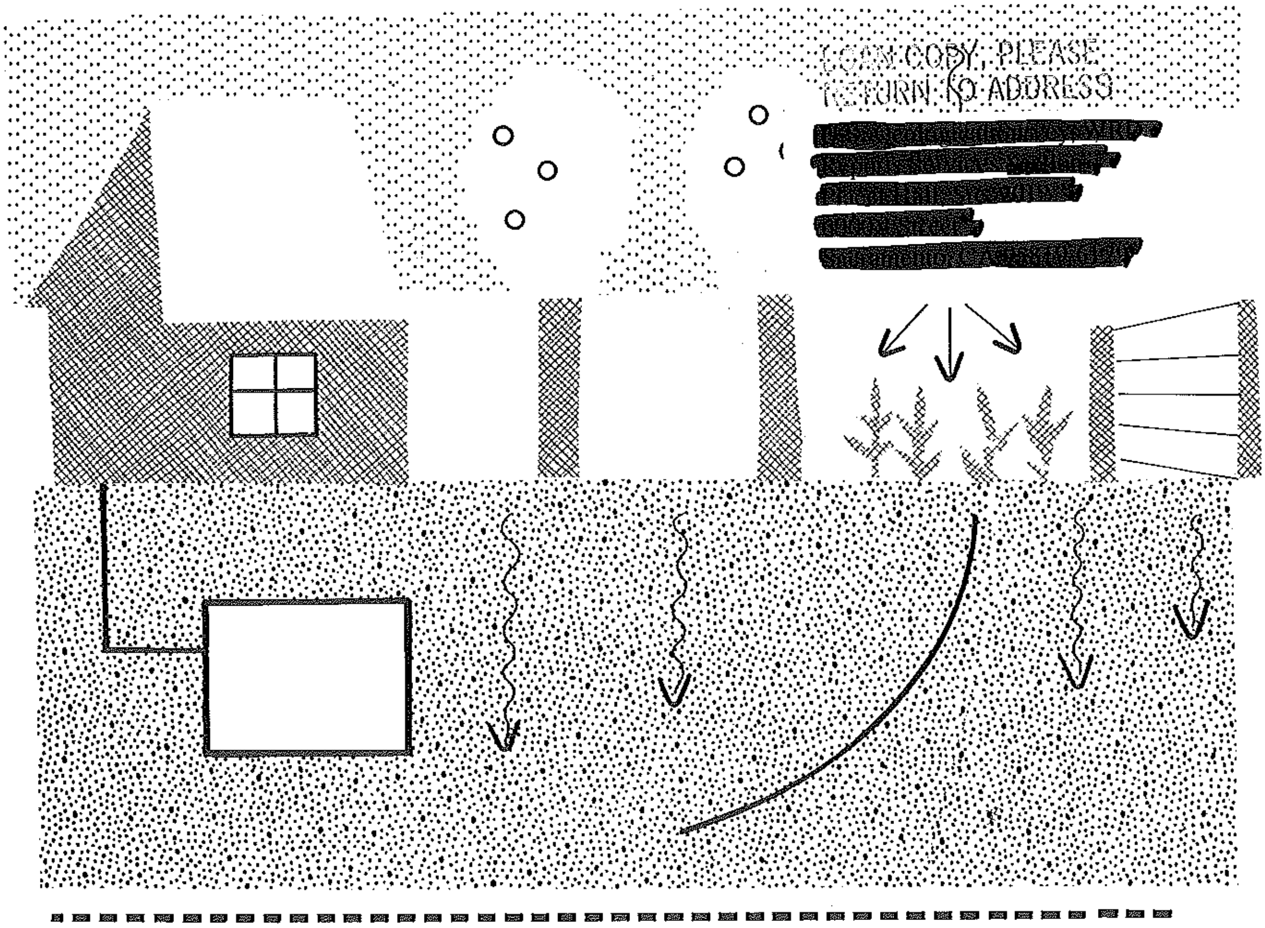
DISTRIBUTION OF NITRATE IN THE UNSATURATED ZONE HIGHLAND-EAST HIGHLANDS AREA SAN BERNARDINO COUNTY, CALIFORNIA

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

U.S. GEOLOGICAL SURVEY
Water-Resources Investigations 80-48



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In the vicinity of Highland-East Highlands, San Bernardino County, California, plans to recharge local aquifers with imported water would raise the water table and intercept nitrogen in the unsaturated zone. Samples from 13 test holes were analyzed to ascertain the distribution of nitrate and related inorganic nitrogen species and other parameters. Test holes were ranked according to maximum NO_3^--N in the top 10 feet, total NO_3^--N in the top 10 feet, and total NO_3^--N in the top 40 feet. In all three rankings, the top seven test holes were the same--five in or near past or present agricultural areas (primarily citrus groves), one in a feedlot, and one adjacent to an abandoned sewage-treatment plant. Two test holes in uninhabited areas ranked lowest. The control test hole ranked high in geometric mean ammonium nitrogen, suggesting that NH_4^+-N is present in freshly weathered granite. The geometric mean NH_4^+-N concentrations in six of eight test holes in citrus-related areas were significantly lower than in the control hole. High NO_3^--N concentrations tended to be found with high specific conductance and chloride concentrations. If recharge is carried out as planned, assuming complete mixing of the recharge water and interstitial pore water in the top 20 feet of the saturated zone, NO_3^--N concentrations in water at the top of the saturated zone may exceed 10 milligrams per liter in seven areas studied.

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By John M. Klein and Wesley L. Bradford

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UNITED STATES DEPARTMENT OF THE INTERIOR

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GEOLOGICAL SURVEY

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DISTRIBUTION OF NITRATE IN THE UNSATURATED ZONE,
HIGHLAND-EAST HIGHLANDS AREA, SAN BERNARDINO COUNTY, CALIFORNIA

By John M. Klein and Wesley L. Bradford

ABSTRACT

Nitrogen in the unsaturated soil zone in the Highland-East Highlands area of San Bernardino County, Calif., has been suspected as the source of nitrate in water from wells. Plans to recharge the local aquifers with imported surface water would raise the water table and intercept that nitrogen. This study was made to describe the distribution of inorganic nitrogen and other chemical constituents and nitrogen-using bacteria in the unsaturated zone, to relate nitrogen occurrences, in a general way, to present and historical land use, and to attempt to predict nitrogen concentrations in ground water after recharge.

Some generalized correlations between nitrogen occurrence and land use were observed. In 11 of 13 test holes, the maximum nitrate-nitrogen (NO_3^--N) concentrations occurred within 10 feet of the surface, suggesting that the major source of nitrogen is from the surface at these sites. Test holes were ranked according to maximum NO_3^--N in the top 10 feet, total NO_3^--N in the top 10 feet, and total NO_3^--N in the top 40 feet. In all three rankings, the top seven test holes were the same--five in or near present or historical agricultural areas (primarily citrus groves), one in a feedlot, and one adjacent to an abandoned sewage-treatment plant. Two test holes in historically uninhabited areas ranked lowest.

The control test hole in an uninhabited area ranked high in geometric mean of ammonium-nitrogen concentration (NH_4^+-N), suggesting that NH_4^+-N is present in freshly weathered granite. The geometric means of NH_4^+-N concentrations in six of eight citrus-related test holes were significantly lower than in the control hole, suggesting that irrigation in citrus groves may have created conditions favoring nitrification of the primary NH_4^+-N.

Rank correlation analyses between various measurements in test holes showed that high NO_3^--N concentrations tend to occur with high specific conductance and chloride concentrations in soil extracts.

If recharge is carried out as planned, assuming complete mixing of the recharge water and interstitial pore water in the top 20 feet of the saturated zone, NO_3^--N concentrations in water at the top of the saturated zone may exceed 10 milligrams per liter in seven areas studied. Concentrations could reach as high as 66 milligrams per liter in the worst case projected. The highest concentrations may be found in three areas that are now, or were recently, citrus groves.

INTRODUCTION

Statement of the Problem

From the late 1800's until about 1960, raising citrus fruit was a major enterprise in the Highland-East Highlands area, San Bernardino County, Calif. In recent years, urban and municipal development, generally at the expense of citrus groves, has resulted in changes in land use and local ground-water use. Since extensive urbanization began, numerous irrigation wells and municipal supply wells have yielded water with nitrate-nitrogen (NO_3^--N) concentrations greater than 10 mg/L, the limit in water for domestic use recommended by the National Academy of Sciences, National Academy of Engineering (1972) and the mandatory maximum contaminant level for public water supplies (U.S. Environmental Protection Agency, 1977).

Above-average precipitation in 1968 and 1969 resulted in above-average recharge through stream channels and a rise in the ground-water levels of as much as 100 ft in some areas. Accompanying this rise were large increases in dissolved NO_3^--N concentrations in water from some wells. Because NO_3^--N concentrations were much lower in stream water than in water from wells, and percolations from land surface could not have occurred in the time over which the increases in NO_3^--N were observed, it is probable that NO_3^--N in the pore water of the unsaturated zone had been intercepted by the rising water table and added to the water in wells. Imported water is artificially recharged at various locations and is a significant part of the water-management activities in the Highland-East Highlands area. If the unsaturated zone was the source of this new NO_3^--N, then water-quality degradation due to rising water levels could reduce the benefits derived from an increased supply. A definition of the areal and vertical distribution of NO_3^--N in the unsaturated zone is needed to evaluate the severity of the problem.

It is commonly believed that the major source of dissolved NO_3^--N in the ground water is nitrogen fertilizer, which has been added in excess of crop needs since 1900. In the early 1900's, farmers used large quantities of manure for fertilizer (P. F. Pratt, University of California, Riverside, oral commun., 1977). The nitrogen in the manure also may have been in excess of crop needs. Remnants of this excess nitrogen are probably still in the unsaturated zone. Other possible sources include liquid and solid wastes from domestic, industrial, and agricultural activities, native fossil nitrate in the soil and unsaturated zone, and high-nitrate underflow from adjacent ground-water basins.

The U.S. Geological Survey, in cooperation with the San Bernardino Valley Municipal Water District, began a two-phase study in 1976 to determine the severity of the ground-water nitrate problem. Phase 1 described the distribution of nitrate and fluoride in the saturated zone (Eccles and Klein, 1978). This report, summarizing phase 2, describes the distribution of nitrate in the unsaturated zone.

Objectives of the Study

The objectives of this study were to describe the distribution of NO_3^--N and other inorganic nitrogen species in the unsaturated zone of the Highland-East Highlands area and to examine relations between nitrogen content and other variables that may give insight on the sources and behavior of nitrogen in the unsaturated zone. No attempt was made to determine the rate of movement of NO_3^--N through the unsaturated zone or to quantify the contribution of NO_3^--N to the unsaturated zone from particular types of land use and land-management practices.

Previous Investigations

The earliest reports by Hall (1888) and Lippincott (1902a, 1902b) presented and discussed data on the use of surface water for irrigation in the upper Santa Ana River valley. Although Hall referred to early ground-water development, Lippincott presented the first inventory of wells. A study by Mendenhall (1905) resulted in a comprehensive analysis of the hydrology of the San Bernardino Valley. Subsequent reports by Eckis (1934) and Gleason (1947) further described ground-water movement, occurrence, and storage. Burnham and Dutcher (1960), Dutcher and Burnham (1960), and Dutcher and Garrett (1963) described the geology and hydrology of the water-bearing deposits. They delineated ground-water basins and subbasins defined by flow barriers and identified sources of recharge and discharge.

Chemical characteristics of the ground water were mentioned in a general way in several of the above reports; however, with the advent of an apparent nitrate-contamination problem, several specific reports were prepared. The Kearney Foundation of the University of California (1973) described areas of high concentrations of NO_3^--N in ground water in the upper Santa Ana River valley, identified the probable cause, and made recommendations to alleviate the problem. Eccles and Bradford (1977) and Eccles, Klein, and Hardt (1976) found dissolved NO_3^--N concentrations as high as 27 mg/L in the Redlands area nearby. The concentrations were observed to decrease with depth in the saturated zone. Concentrations of dissolved NO_3^--N in the ground water were found to be highest under land that has been and still may be primarily citrus groves. Eccles and Klein (1978) presented data and a summary of nitrate in the saturated zone of the Highland-East Highlands study area. Klein and Bradford (1979) described the distribution of nitrate and related nitrogen species in the unsaturated zone of the Redlands area.

Acknowledgments

The authors are grateful to numerous individuals and organizations who facilitated the data collection. The cooperator, the San Bernardino Valley Municipal Water District, provided laboratory space, staff, and equipment for assistance during drilling breakdown. Jack Littleton of Patton State Hospital provided necessary information and aid in selecting test-hole drill sites on State-owned land. Officials from the East Highlands Orange Co. allowed access to their land. Southern California Water Co. and East San Bernardino County Water District officials and personnel helped in site selection and manpower. Numerous other citizens allowed access to privately owned land.

DESCRIPTION OF THE STUDY AREA

Location

The Highland-East Highlands study area (fig. 1) is in the northern part of the upper Santa Ana River valley, east of San Bernardino, Calif. The boundaries of the triangular-shaped study area are formed to the northeast by the base of the San Bernardino Mountains, which coincides with the approximate trace of the San Andreas fault, to the south by the generally dry Santa Ana River, and to the west by Del Rosa Avenue.

Geohydrologic Environment

Dutcher and Garrett (1963) described three main geologic units in the upper Santa Ana River valley: consolidated bedrock (basement complex), alluvium, and river-channel deposits.

Consolidated bedrock deposits, which underlie the study area and form the surrounding mountains and hills, are composed primarily of metamorphic rocks of pre-Tertiary age and igneous rocks of Tertiary age.

Alluvium of Quaternary age comprises most of the unsaturated and saturated zones in the study area. According to Dutcher and Garrett (1963), the unconsolidated alluvial deposits include both a younger alluvium underlying the river-channel deposits and an older alluvium. These alluvial deposits are composed of boulders, gravel, sand, silt, and clay. In general the alluvium is coarser and more poorly sorted near the mountains and becomes better sorted with fewer boulders farther away from the mountains. The alluvial deposits are moderately permeable and, where saturated, yield water freely to properly constructed wells (Schaefer and Warner, 1975, p. 6).

River channel deposits of Holocene age occupy the main channel of the Santa Ana River and consist of silt, sand, and gravel with numerous boulders. These deposits are described by Schaefer and Warner (1975, p. 6) as highly permeable, allowing large seepage losses from the river to the underlying alluvial aquifer.

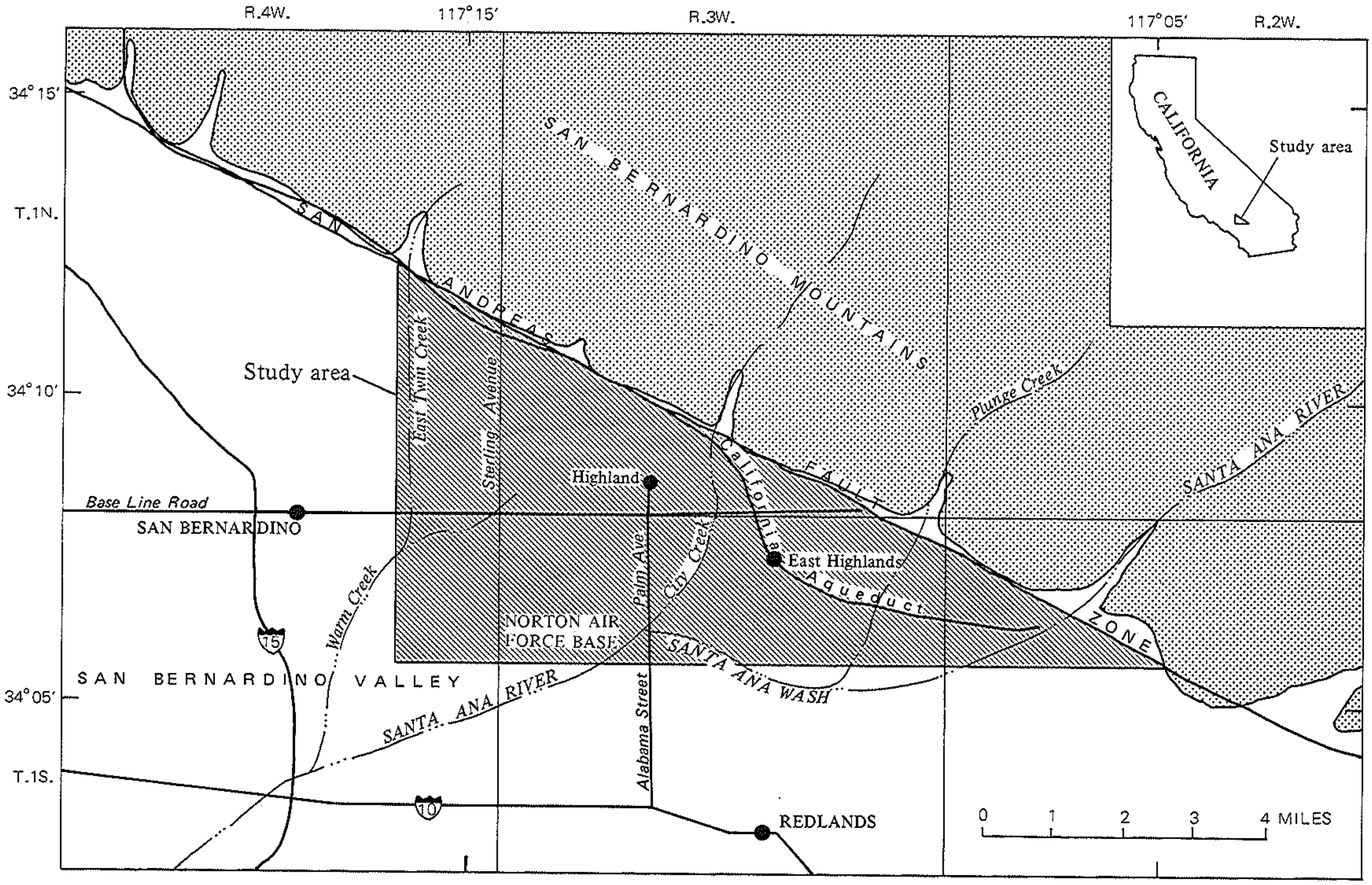


FIGURE 1.--Location of Highland-East Highlands study area.

In the eastern part of the study area the ground-water table slopes predominantly westward, parallel to the Santa Ana River channel. In the western part of the area, however, the slope is to the south.

Ground water is supplied by recharge from the following sources:

1. Natural flow in streams that traverse the area.
2. Artificial recharge in the Santa Ana River basin.
3. Percolation of precipitation.
4. Percolation of applied irrigation water.

The depth to the water table varies widely in the study area due to discontinuities in the local aquifers caused by widespread faulting. Depths to water range from about 30 to 700 ft. In the area where most of the test holes were drilled, depth to water was generally 130 to 200 ft.

NITROGEN IN THE ENVIRONMENT

Nitrogen, although present in the Earth's crust only in relatively small concentrations (0.005 percent by weight), is the most abundant gas in the atmosphere (75 percent by weight). Plant and animal life requires nitrogen for synthesis of tissue proteins and amino acids. Plants that fix atmospheric nitrogen in the synthesis of proteins and amino acids make that nitrogen available to animals in a usable form. The fixed nitrogen is also oxidized in soil to NO_3^-, in which form it is usable by other plants. Other organisms reduce NO_3^- to nitrogen gas that returns to the atmosphere, completing the cycle. The cycle most widely accepted (fig. 2) is a continuous biochemical process of converting organic nitrogen to inorganic forms, such as ammonium (NH_4^+), followed by oxidation to NO_3^- (nitrification), utilization of NH_4^+ and/or NO_3^- by plants and animals, and finally bacterial reduction of the oxidized nitrogen species to molecular nitrogen.

It is difficult to determine how long nitrogen has been in the soil because the ability of a nitrogen compound to exist under a specific set of conditions is a function of solubility, the degree to which it may be bound on soils, and the ease with which it is broken down by microorganisms. A given nitrogen atom may be cycled rapidly or may persist in the soil for years or centuries (Delwiche, 1977, p. 109).

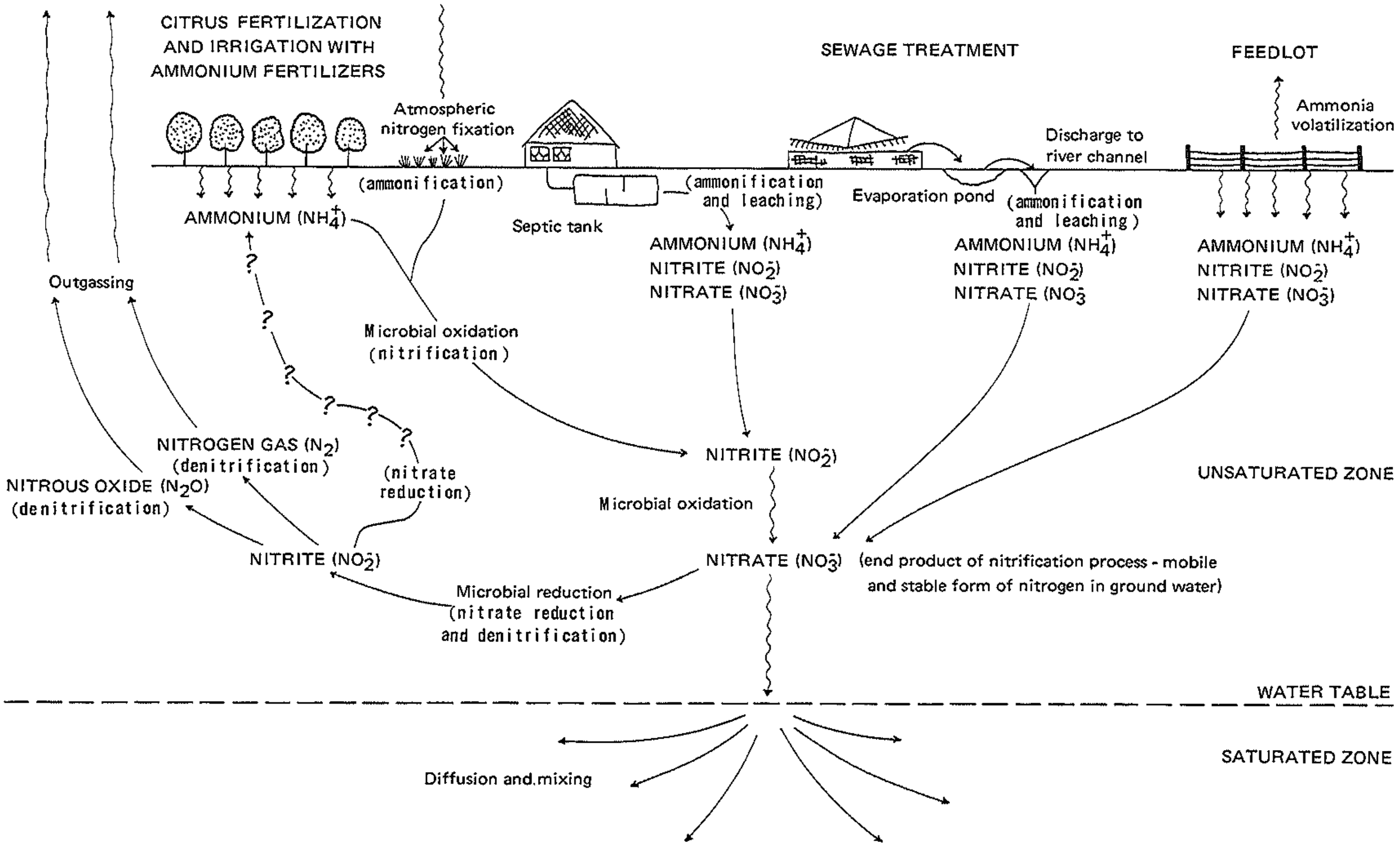


FIGURE 2.--Nitrogen cycle and prominent transformation processes in the study area.

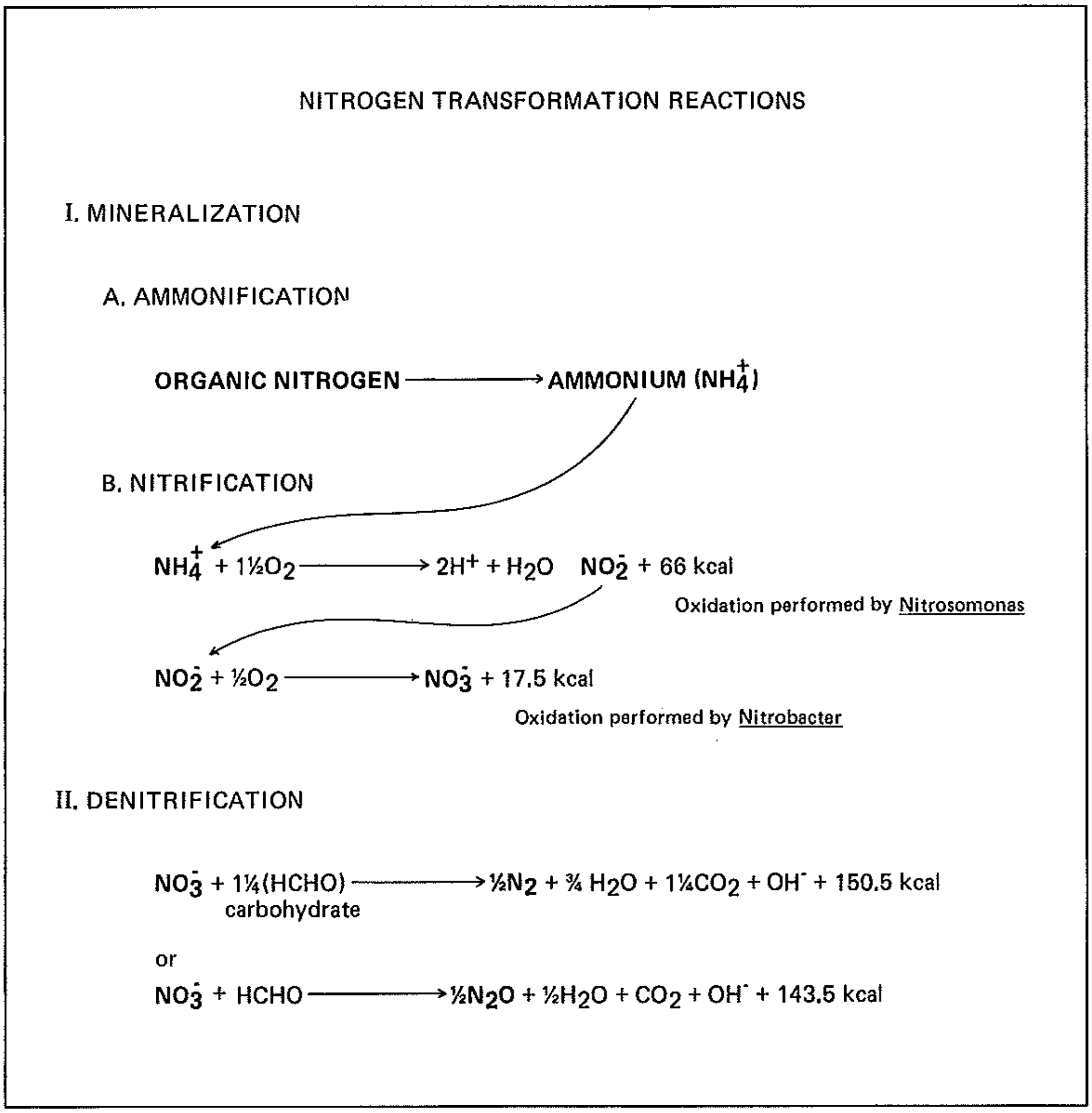
The process of converting organic nitrogen into inorganic forms (mineralization) involves two separate microbial conversions, ammonification and nitrification (fig. 3). Ammonification can be accomplished by both aerobic and anaerobic (exists in the absence of oxygen) bacteria; however, nitrification involves two species of aerobic bacteria. The end product of mineralization is NO_3^-, which is the most stable and most mobile of the nitrogen ions.

Both of the bacterial species (fig. 3) involved in nitrification--(Nitrosomonas and Nitrobacter)-- are special purpose, strictly aerobic, and autotrophic (utilize inorganic materials for food). They obtain energy from the oxidation of ammonia and nitrite and produce cellular carbon from the reduction of carbon dioxide (CO_2). In general, the second reaction, oxidizing NO_2^- to NO_3^-, closely follows the first and does not permit the accumulation of NO_2^-; therefore, NO_2^- is generally thought of as an unstable transition product in the nitrification process.

Denitrification reactions reduce NO_3^- to molecular nitrogen gas (N_2) or nitrous oxide (N_2O), generally not usable by animals or most plants. The bacteria responsible for the biological reduction are heterotrophic (obtain energy from breakdown of organic compounds in the soil) and anaerobic. Hence denitrification cannot proceed in the presence of significant oxygen or without a ready source of available carbon.

Nitrate reduction, the utilization by vegetation of nitrate as a nutrient source, transfers NO_3^- to cellular material (nitrate assimilation); but, unharvested vegetation remains in or on the soil as a potential nutrient source.

Environments generally considered most favorable for denitrification are soils with poor drainage, where the moisture level exceeds two-thirds of the water-holding capacity of the soil, or the micropores of well-drained soils that may be filled with water and have the necessary organics to supply carbon for the bacteria, according to Broadbent (1973) and Ardakani and others (1975). They found that added nitrate almost completely disappeared in the first 0.002 inch of well-drained but saturated soil. Similarly Willihan (1937), Bremner and Shaw (1958), Broadbent and Tusneem (1971), and Broadbent (1973) all attributed NO_3^- disappearance in submerged soils to denitrification, provided an energy source (carbon) was present.



NITROGEN TRANSFORMATION REACTIONS

I. MINERALIZATION

A. AMMONIFICATION

ORGANIC NITROGEN $\longrightarrow$ **AMMONIUM (NH_4^+)**

B. NITRIFICATION

$NH_4^+ + 1\frac{1}{2}O_2 \longrightarrow 2H^+ + H_2O \quad NO_2^- + 66$ kcal

Oxidation performed by *Nitrosomonas*

$NO_2^- + \frac{1}{2}O_2 \longrightarrow NO_3^- + 17.5$ kcal

Oxidation performed by *Nitrobacter*

II. DENITRIFICATION

$NO_3^- + 1\frac{1}{4}(HCHO) \longrightarrow \frac{1}{2}N_2 + \frac{3}{4}H_2O + 1\frac{1}{4}CO_2 + OH^- + 150.5$ kcal

carbohydrate

or

$NO_3^- + HCHO \longrightarrow \frac{1}{2}N_2O + \frac{1}{2}H_2O + CO_2 + OH^- + 143.5$ kcal

FIGURE 3.--Nitrogen transformation reactions.

Patrick and Wyatt (1964) noted the importance of cyclic submergence and drying that provides for cyclic nitrification (drying--aerobic) and then denitrification (submerged--anaerobic). The persistence of either aerobic or anaerobic conditions would allow for either continual formation of NO_3^- from available inorganic nitrogen or continual denitrification resulting in total consumption of available NO_3^-.

The rates of soil-nitrogen transformations are associated closely with chemical and physical properties of the soil. Dancer and others (1973) found a three- to five-fold increase in nitrification when soil pH increased from 4.7 to 6.5. Cornfield (1952) compared mineralization rates and found that NO_3^- accumulated in soils with pH values of 6.5 or higher, while NH_4^+ accumulated in more acid soils, indicating a lack of nitrifying bacteria in acidic environments. Morrill and Dawnson (1967) also noted NH_4^+ accumulations at soil pH values of 4.4.

METHODS OF DATA COLLECTION

Collection of Drill-Core Samples

Thirteen drill sites (fig. 4) were selected to represent a variety of land uses such as fertilized cropland, feedlot, urban areas, and vacant land within the inhabited areas (table 1). One site (20) served as the control site and provided data on NO_3^--N outside the inhabited area. Test hole 21, in an area of no known habitation or previous land use that would contribute nitrogen, nevertheless was not a control site due to numerous upgradient nitrogen sources.

Drilling was done with 5-foot sections of hollow-stem auger. At each sampling depth, relatively undisturbed samples were extracted without removing the auger from the hole. A special, cylindrical, 18-inch drive-core sampler, attached to a solid 1-inch rod, was lowered through the auger to the existing depth of the hole. The sampler was driven with a piston into the soil beyond the maximum depth penetrated by the auger. The sampler was then brought to the surface and the hole augered to the next sampling depth, where the sampling process was repeated.

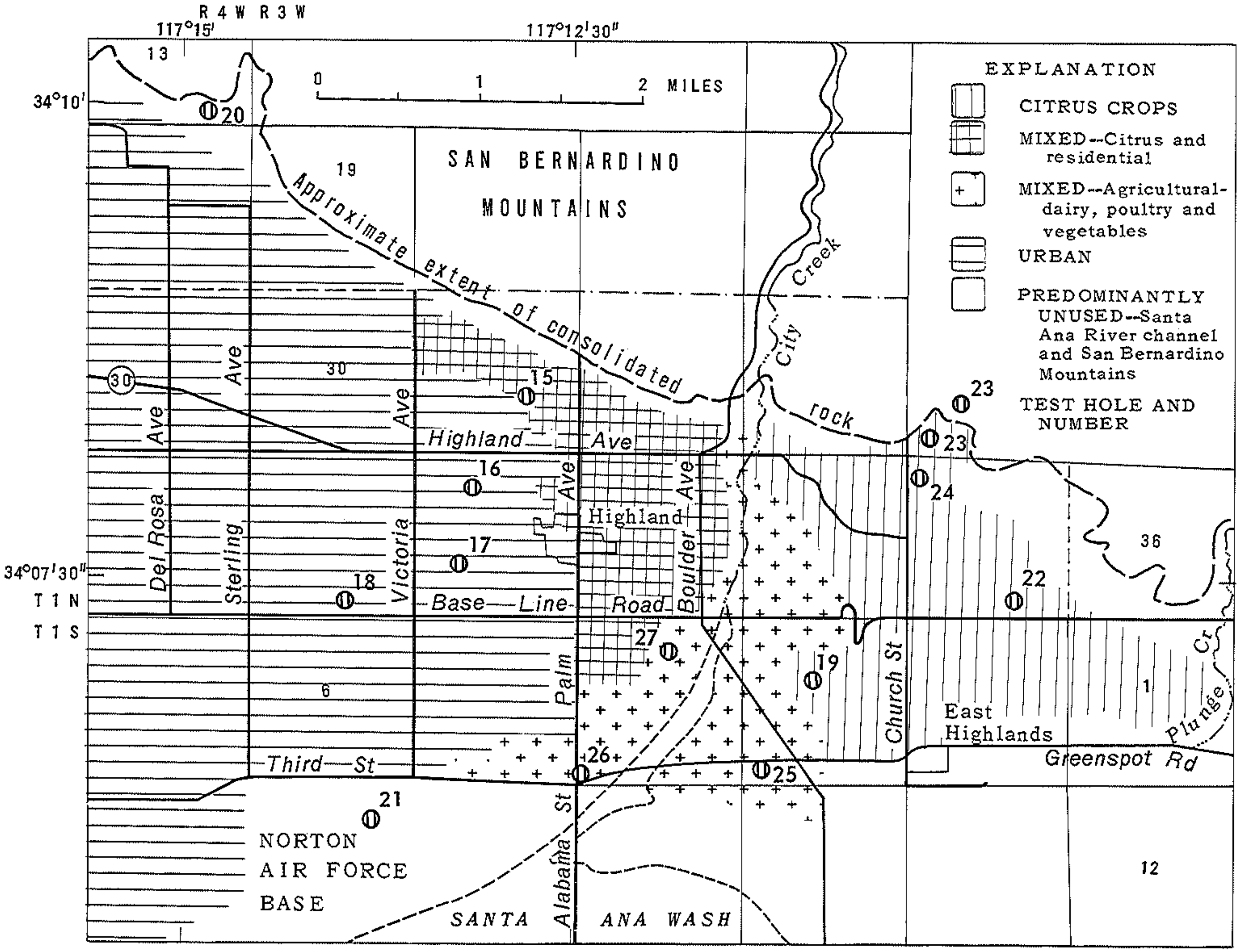


FIGURE 4.--Location of test holes and generalized land use as of 1976.

TABLE 1.--Test-hole numbers and predominant land use

[Land use classification: Ag, agriculture other than citrus; Cs, citrus grove; DyF, dairy feedlot; Mx, mixed urban and agriculture; Sew, sewage-treatment plant; Un, uninhabited; Ur, urban; VUr, vacant urban]

Test hole No.	Land use	Land use classification present/ historical	Comment
15	Vacant urban	VUr/Cs	Once a citrus grove--groves upgradient and adjacent
16	Vacant urban	VUr/Sew	Adjacent to abandoned sewage-treatment plant
17	Vacant urban	VUr/Cs	Once a citrus grove--grove now adjacent
18	Urban	Ur/Ur	Near a known fault and hot-water wells
19	Citrus grove	Cs/Cs	
20	Uninhabited area	Un/Un	Control test hole
21	Uninhabited area	Un/Un	On Norton Air Force Base. Historically uninhabited and unused
22	Citrus grove	Cs/Cs	High on alluvial fan
23	Citrus grove	Cs/Cs	High on alluvial fan
24	Citrus grove	Cs/Cs	High on alluvial fan
25	Dairy feedlot	DyF/DyF	Abandoned about 10 years ago. (Present feedlot about 100 ft from test hole.)
26	Mixed agriculture-urban	Mx/Ag	
27	Mixed agriculture-urban	Mx/Cs	Citrus grove adjacent, once a grove

Test holes were drilled to the top of the saturated zone except when obstructions were encountered. Augering was stopped when wet material, thought to be the top of the saturated zone, was reached.

The tip of the drive-core sampler was dipped into isopropyl alcohol and flamed until dry to insure sterilization prior to the collection of a sample for microbial analysis. When the drive core returned to the surface, about 20 g of sample was scraped from the tip of the sampler into a plastic bag and taken at once to the field laboratory for culture preparation.

At most drill sites a continous core sample was collected from the land surface to a depth of 5 ft; then cores were taken at 5-foot intervals to 50 ft. Below 50 ft, core samples were collected at 10-foot intervals to the bottom of the hole. At each sampling depth, the soil core sample was obtained in three continous 6-inch hollow tubes (2-inch ID) which fit into the cylindrical, 18-inch drive-core sampler. The middle 6-inch sample tube was immediately sealed to prevent loss of moisture. The material in the remaining two tubes was removed and individually placed in heavy-duty plastic sacks that were immediately sealed, labeled, and frozen as a precaution against microbial activity that could cause transformation of the nitrogen species.

Porosity and grain size were determined on the sealed middle 6-inch samples at the Geological Survey National Water Quality Laboratory in Arvada, Colo., by using standard soil classification and analysis procedures (Morris and Johnson, 1967). Only enough analyses were performed to determine porosity and grain size at depths where changes were apparent by visual inspection.

Field Tests for the Presence of Denitrifying Bacteria

Bacterial cultures were prepared in nutrient broth containing 0.1 percent (weight/weight) potassium nitrate (KNO_3) according to procedures specified by Garry G. Ehrlich (U.S. Geological Survey, Menlo Park, Calif., written commun. 1977). Ten grams of wet soil screened to pass a 10-mesh sieve (0.079-inch holes) was added to 95 mL of autoclaved de-ionized water and thoroughly mixed. Decimal dilutions of this sample were then made and used to inoculate the culture medium. After incubating for 7 days at 30°C, the culture medium was tested for NO_2^--N and NO_3^--N. The presence of NO_3^--N indicates the absence of both denitrifiers and nitrate reducers. The presence of NO_2^--N indicates the presence of nitrate reducers. The absence of NO_3^--N and NO_2^--N indicates the presence of both denitrifiers and nitrate reducers.

Chemical Analyses of Core Samples

Nitrogen forms (NH_4^+, NO_2^-, and NO_3^-) were extracted from core samples in de-ionized water. For each extraction, 20.0 g of wet sample was weighed and mixed in a 250-mL polycarbonate round-bottom centrifuge bottle with 100 mL of de-ionized water. The sample-extraction slurries were shaken for 1 hour on a wrist-action shaker and allowed to stand a few minutes to separate the coarse material. The bottle was then centrifuged for 15 minutes at 2,400 revolutions per minute, which, according to the equation for settling time (Whittig, 1965), is sufficient to settle clay particles with effective radii of less than 0.16 µm. The supernate solution was decanted from the centrifuge bottles into a 250-mL polyethylene sample bottle that had previously been rinsed with de-ionized water.

The pH and specific conductance were measured on the de-ionized water extracts, using an Orion[1] field pH meter and a Lab-Line[1] conductivity bridge; NO_3^--N concentration was determined by using an Orion NO_3^--sensitive electrode. The chloride concentrations were measured on an Aminco[1] automatic titrator.

The de-ionized water extracts were analyzed by the Geological Survey National Water Quality Laboratory in Arvada, Colo., for NO_3^--N, NO_2^--N and NH_4^+-N by methods described by the U.S. Environmental Protection Agency (1974).

The methods described by Bremner and Keeney (1965) and Bremner and Edwards (1965) were used to evaluate sample-extraction procedures and to routinely check reagent and de-ionized water nitrogen blanks at the field laboratory. All nitrogen forms were converted to ammonia gas (NH_3) in reactions with magnesium oxide (MgO), Devarda's alloy (50 percent copper, 45 percent aluminum, 5 percent zinc, all reagent grade and ground until 75 percent would pass through a 200-mesh screen), and steam distilled from the reaction vessel into an indicating boric acid solution in which it was captured as NH_4^+. The total NH_3 distilled was titrated with 0.005 normal sulfuric acid. Recoveries of 1 to 5 mg nitrogen additions to the reaction flasks ranged from 99.4 to 101.0 percent.

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[1] The use of brand names in this report is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.

The nitrogen blanks in de-ionized water were checked on several occasions during the period of field operations. Blanks were always below the limit of detection (0.035 mg/L). The blanks in de-ionized water were also checked at the National Water Quality Laboratory and found to be as follows: NO_2^--N <0.01 mg/L; NO_3^--N, 0.06 mg/L and NH_4^+-N, 0.04 mg/L. Blank corrections were applied to the extract concentration where appropriate, and corrected values were used in this report.

Replicate samples were processed and analyzed in the laboratory to define the variability in the methods used. Two sets of samples were analyzed 12 times each. Coefficients of variation on measurements and analyses were as follows: specific conductance, 5.4 percent; pH, 0.3 percent; and NO_3^--N, 8.5 percent.

The average coefficients of variation on determination of chloride in extracts of the blank, 1.0, and 2.0 mg/L levels were 4.4, 5.0, and 1.9 percent, respectively. The detection limit at the 95-percent confidence level above the blank averaged 0.51 mg/L, equivalent to 2.7 mg/kg dry weight of sample, based on a 5.0-percent moisture content.

Moisture Content

Moisture content was determined in the field laboratory by methods described by Gardner (1965). Twenty to forty grams of wet soil were weighed in a tared weighing dish on a Mettler top-loading balance, dried for 24 hours at 110°C, cooled and reweighed.

Percent moisture was calculated as:

$$\text{Percent moisture} = \frac{(\text{weight of wet soil and tare}) - (\text{weight of dry soil and tare})}{(\text{weight of dry soil and tare}) - (\text{tare})} \times 100$$

ANALYSIS AND INTERPRETATION OF CHEMICAL, BIOLOGICAL, AND PHYSICAL CHARACTERISTICS

The chemical and physical data from analyses of soil cores from each of the test holes are presented in figures 5 through 17.

All the soil-water nitrogen and chloride concentration data were calculated from de-ionized water-extract concentrations and expressed as milligrams of nitrogen per kilogram of dry soil.

The pH and specific-conductance values reported here were obtained directly on the extracts. The specific conductance of the extract is probably related to that of the soil water itself by the ratio of the extract-water volume to the soil-water volume. At the soil/water ratio of 1:5 used for extraction in this work, however, additional solids may be dissolved directly from the soil.

The pH values determined in a 1:5 soil/water ratio in the field laboratory are useful when compared between samples or between test holes. The pH increases with decreasing soil/water ratios (Peech, 1965), and at a 1:5 ratio may be more than 1 pH unit higher than in a saturated soil paste; however, in the previous investigation (Klein and Bradford, 1979), the extract pH for several soil/water ratios (1:1, 1:2.5, and 1:5) varied only from 8.7 to 9.2.

Nitrate

The predominant form of inorganic nitrogen in the unsaturated zone is NO_3^- (figs. 5-17). Near the surface and in very moist zones at depth, NH_4^+ and NO_2^- may exist but generally NO_3^- still predominates.

The maximum NO_3^--N concentrations occurred at or within 10 ft of the surface in 11 of the 13 test holes, suggesting that the major source of nitrogen at these sites is the surface. Test hole 20 (Un/Un, see table 1) contains only minor amounts of NO_3^--N with no observed peaks (fig. 10). Low surface concentrations were found in test holes 19 (Cs/Cs) and 21 (Un/Un) (figs. 9 and 11). A low surface concentration at test hole 21 (Un/Un) (fig. 11) was expected because there are no known man-related sources of nitrogen near the runways at Norton Air Force Base. The lack of a major peak in test hole 19 (Cs/Cs) (fig. 9) until 65 ft is puzzling since it was drilled in an established citrus grove and near an irrigation well which pumps water containing more than 20 mg/L NO_3^--N.

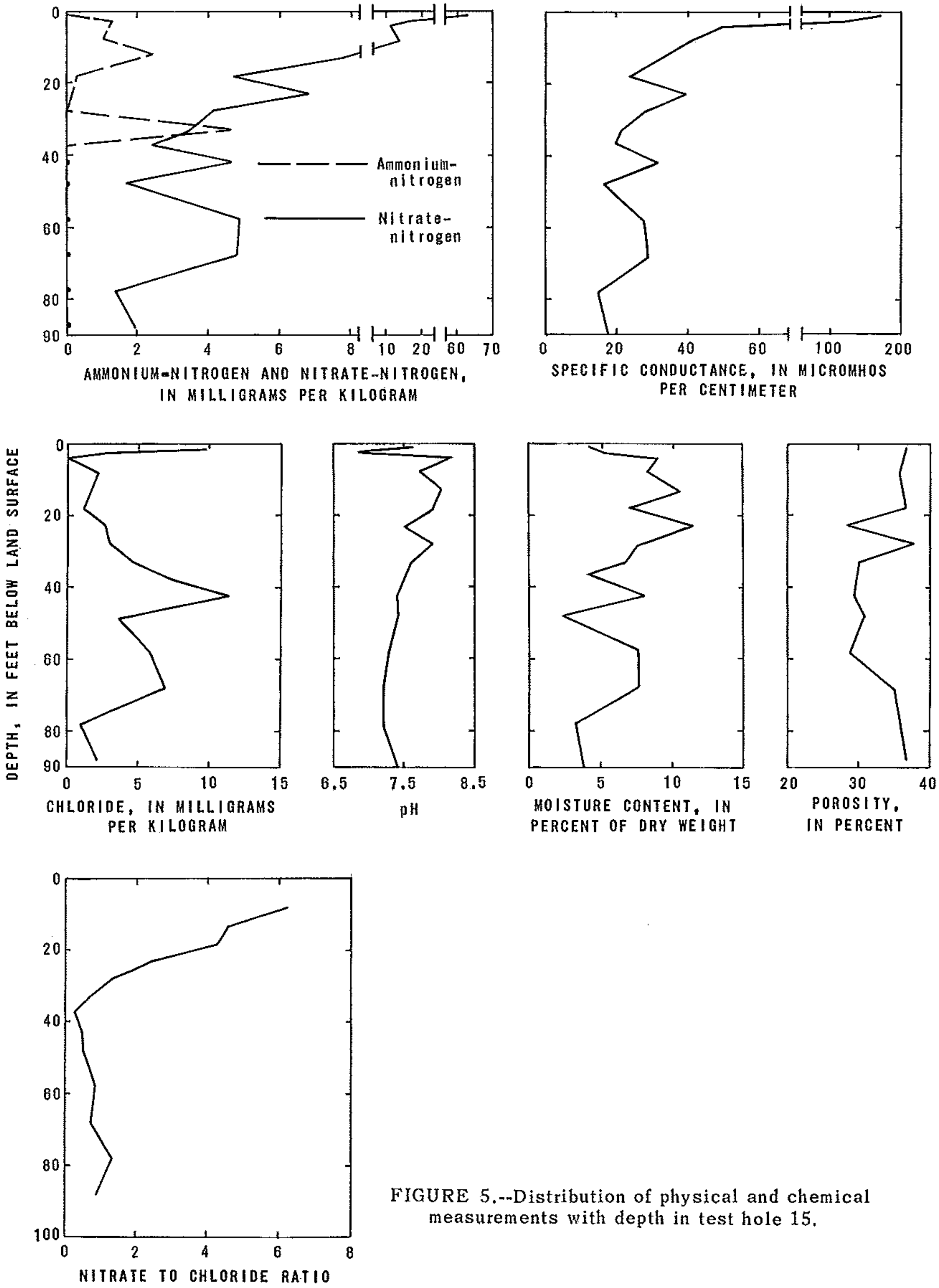

FIGURE 5.--Distribution of physical and chemical measurements with depth in test hole 15.

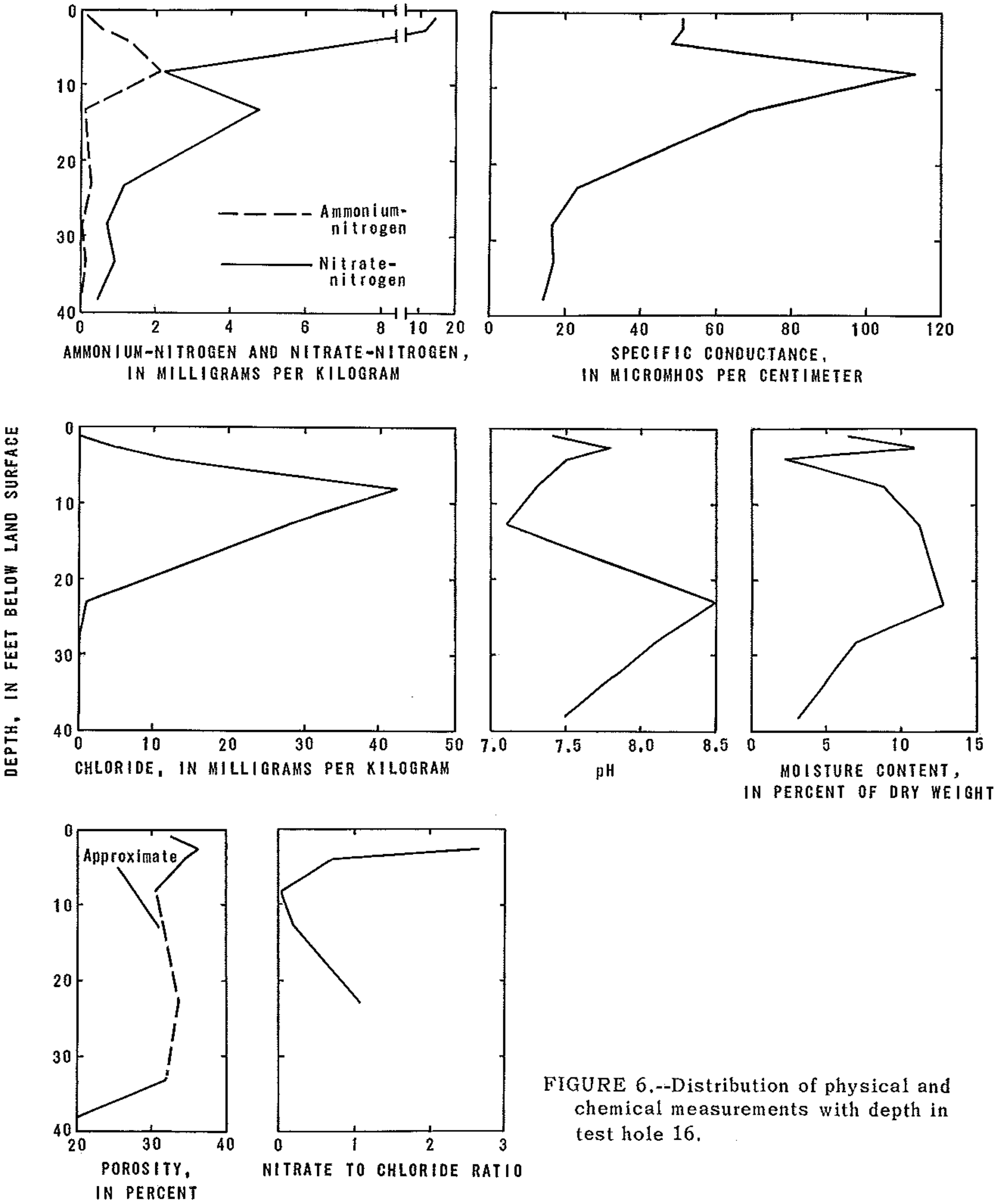

FIGURE 6.--Distribution of physical and chemical measurements with depth in test hole 16.

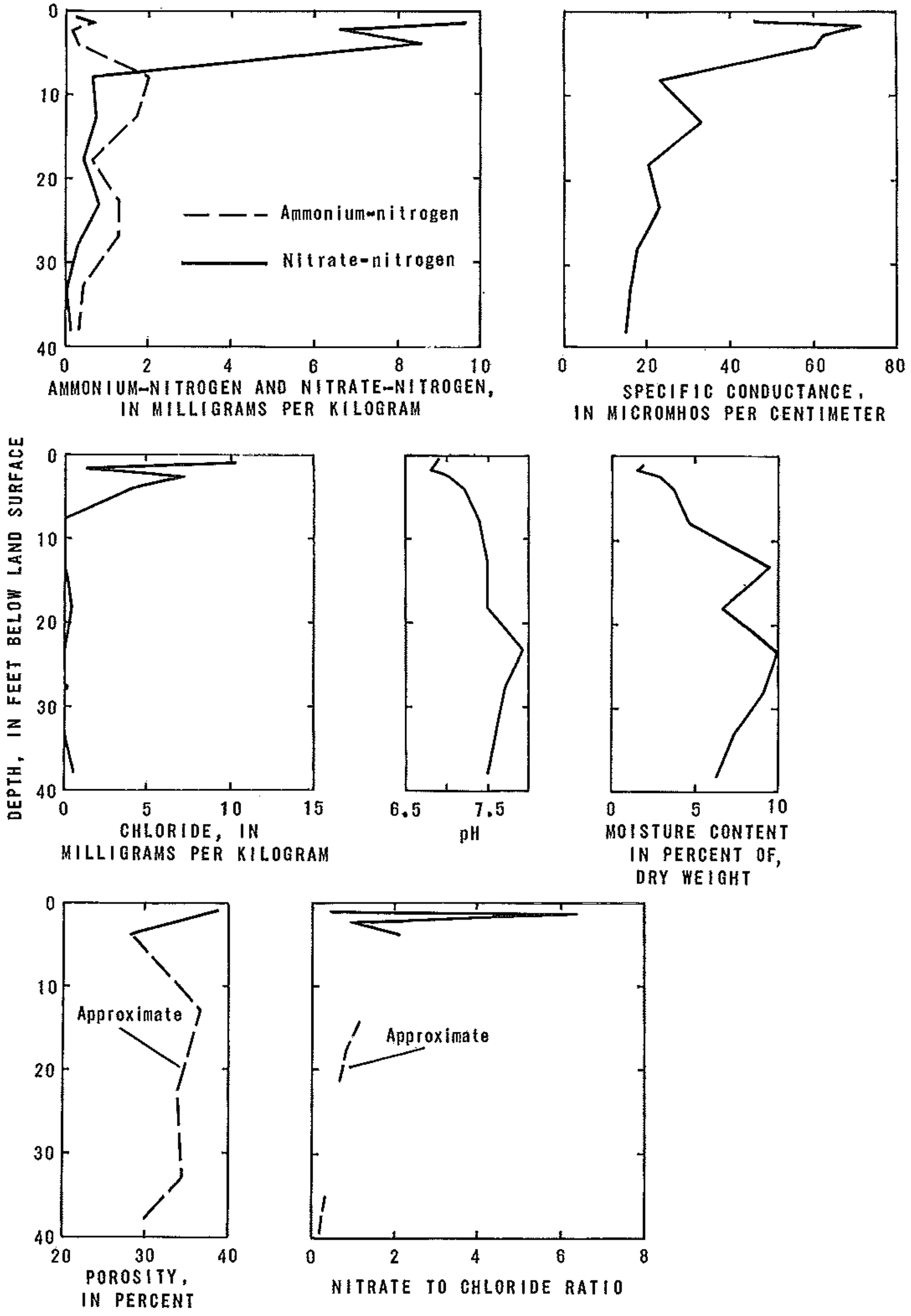

FIGURE 7.--Distribution of physical and chemical measurements with depth in test hole 17.

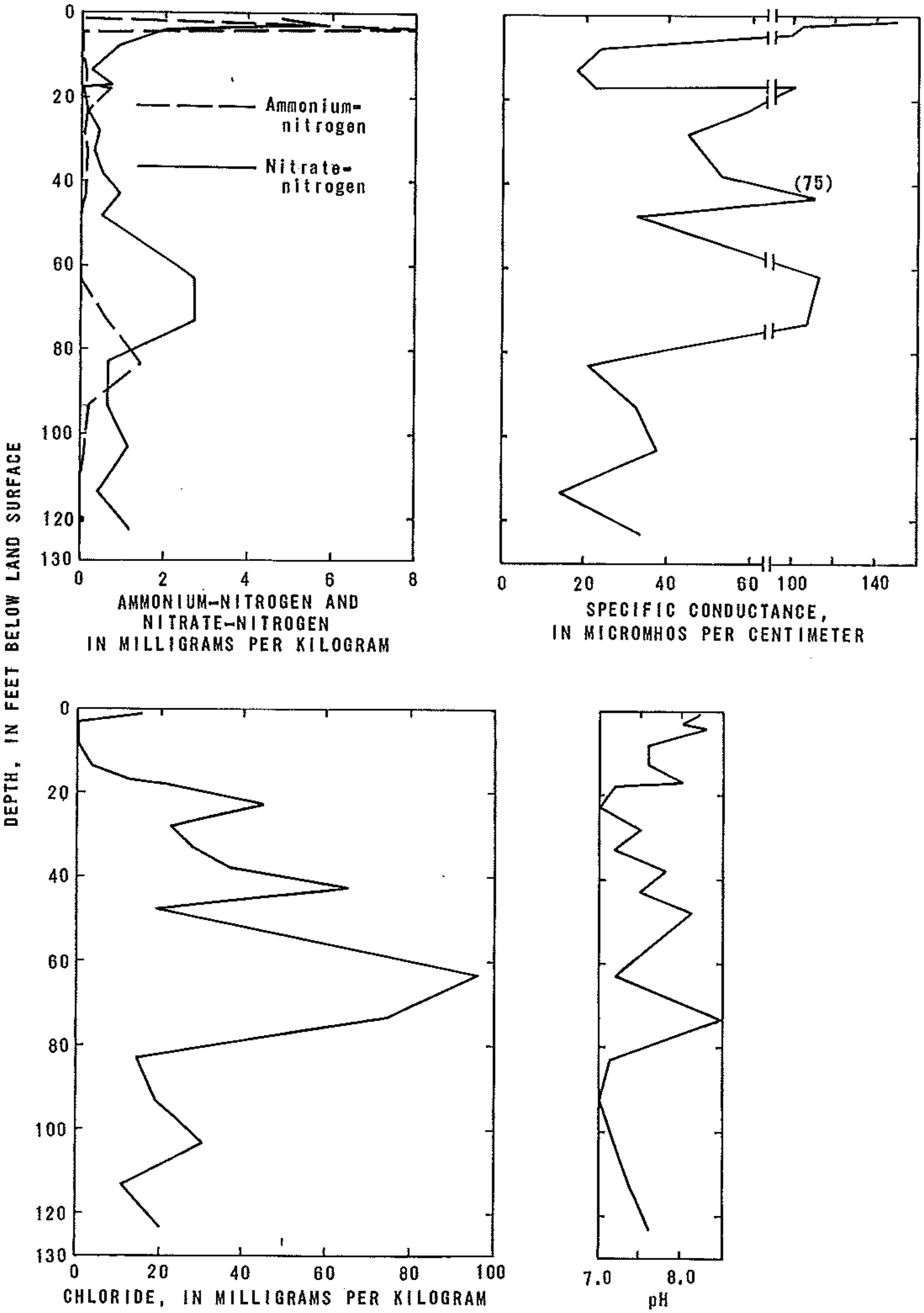

FIGURE 8.--Distribution of physical and chemical measurements with depth in test hole 18.

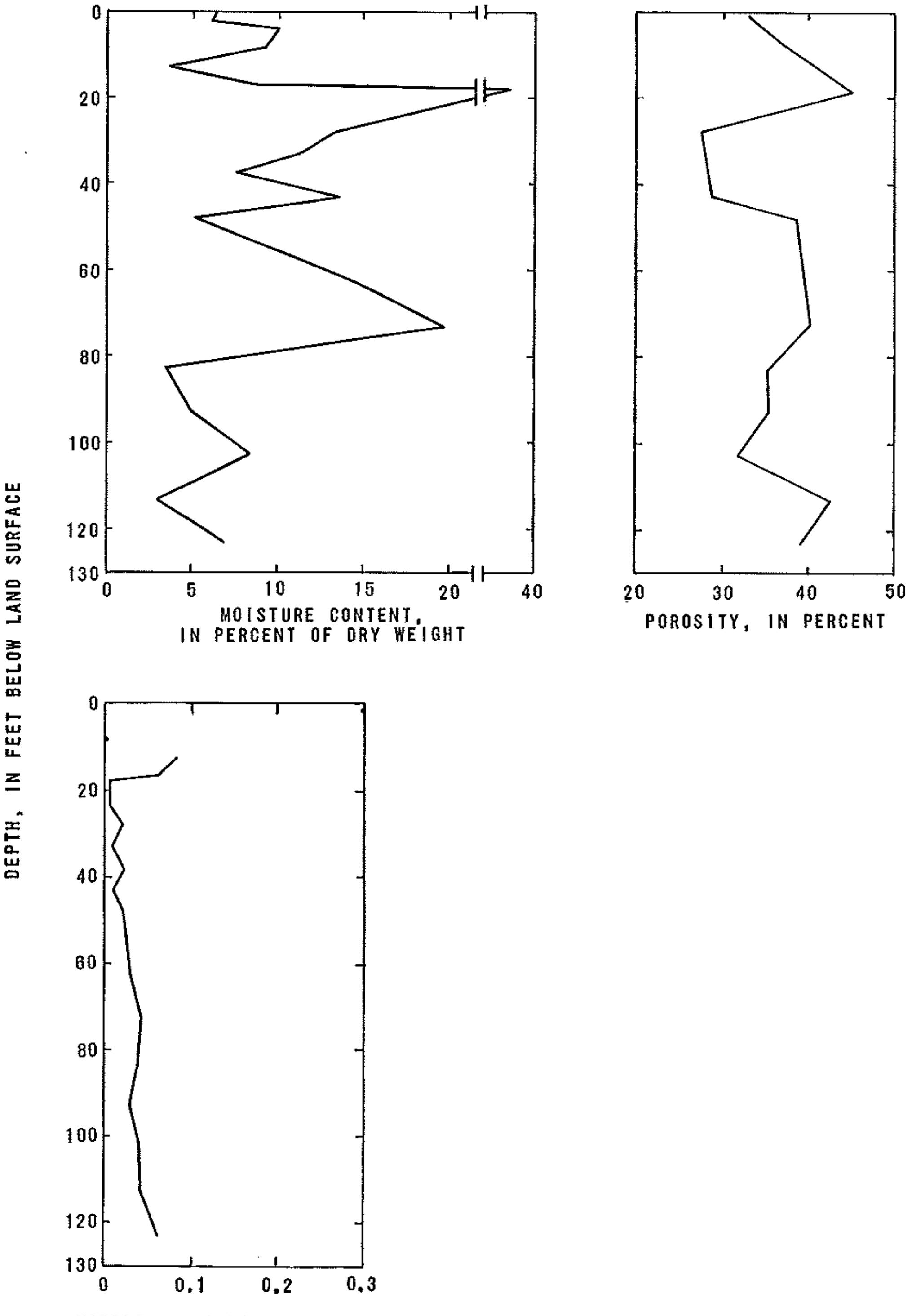

FIGURE 8.--Continued

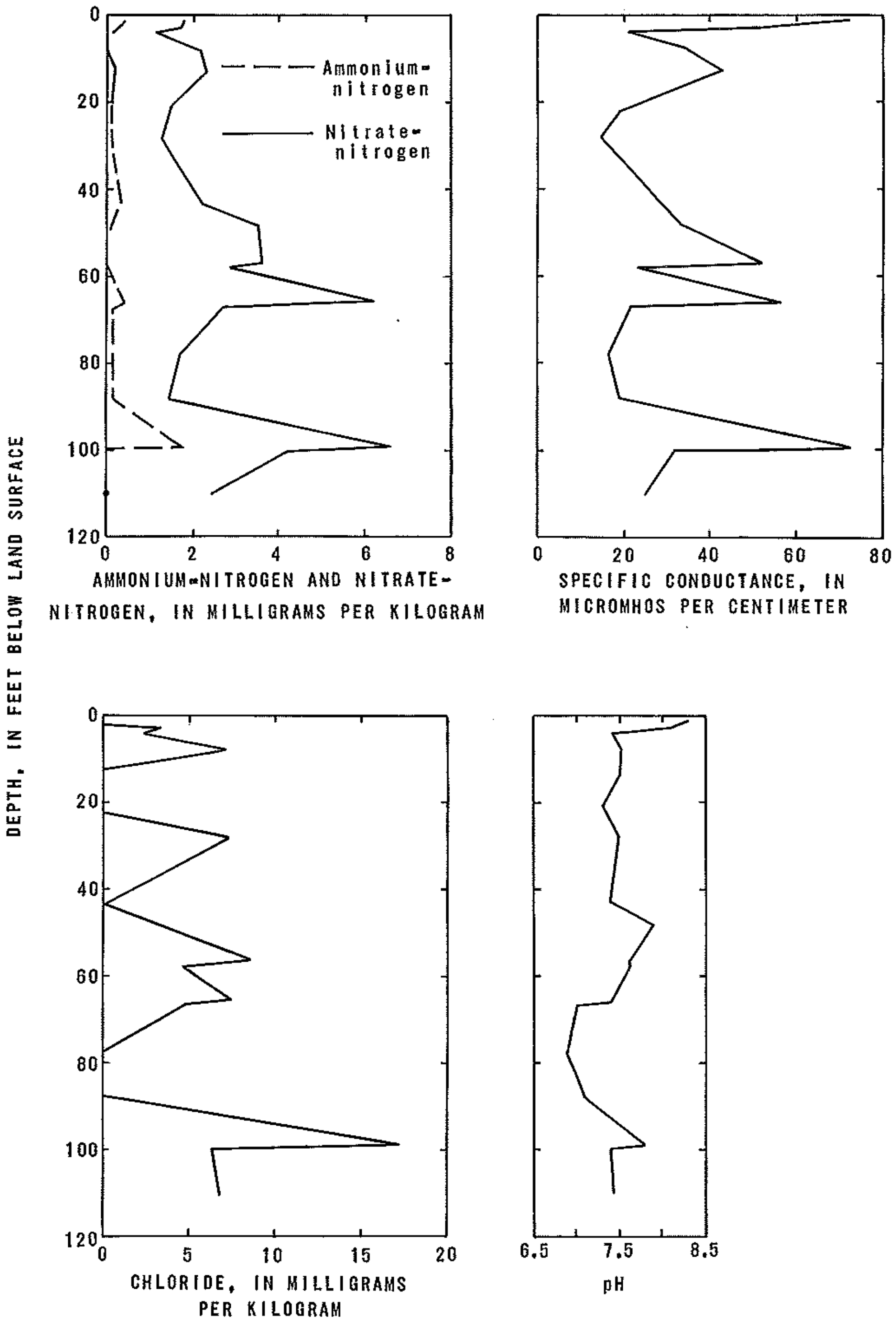

FIGURE 9.--Distribution of physical and chemical measurements with depth in test hole 19.

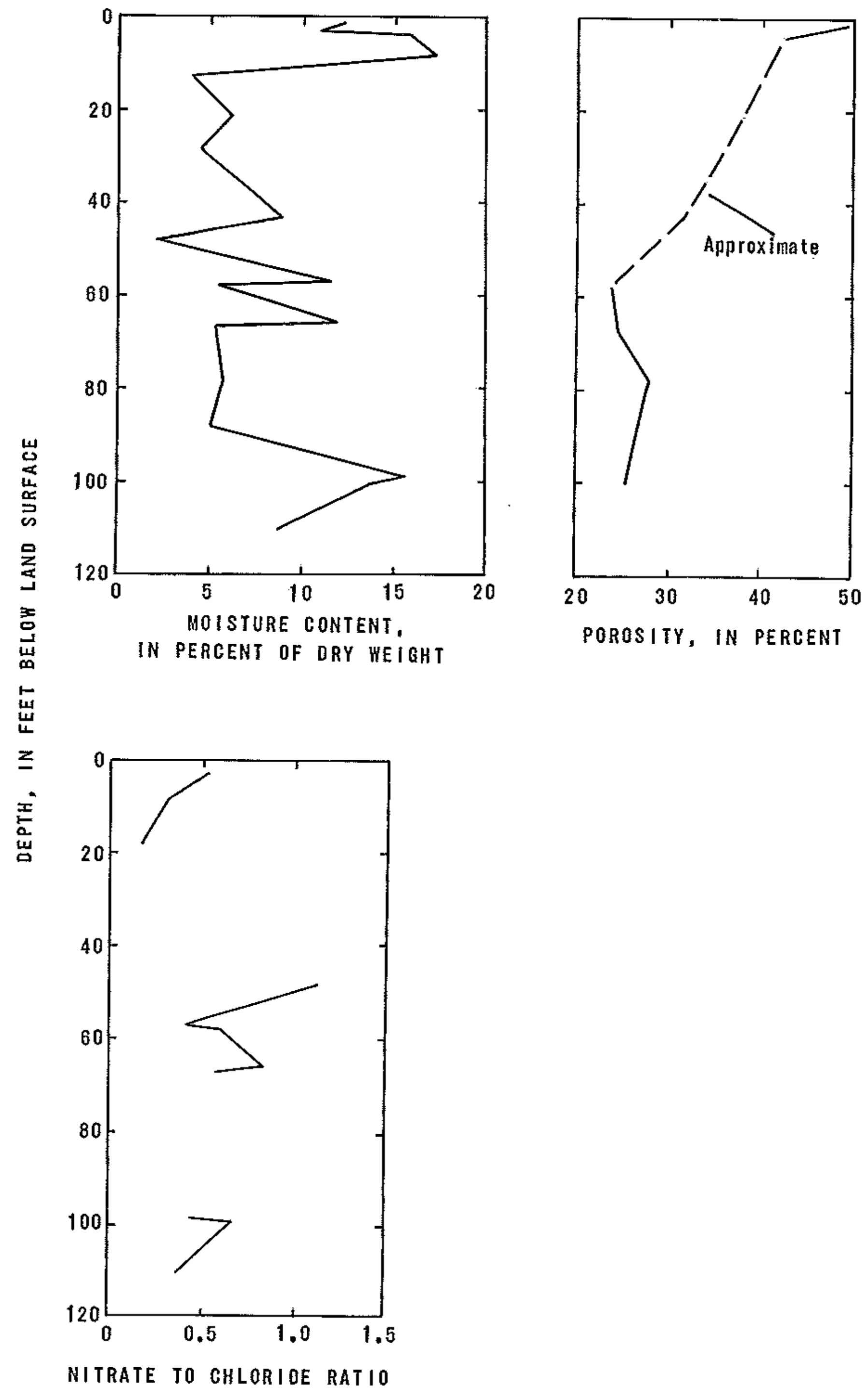

FIGURE 9.--Continued

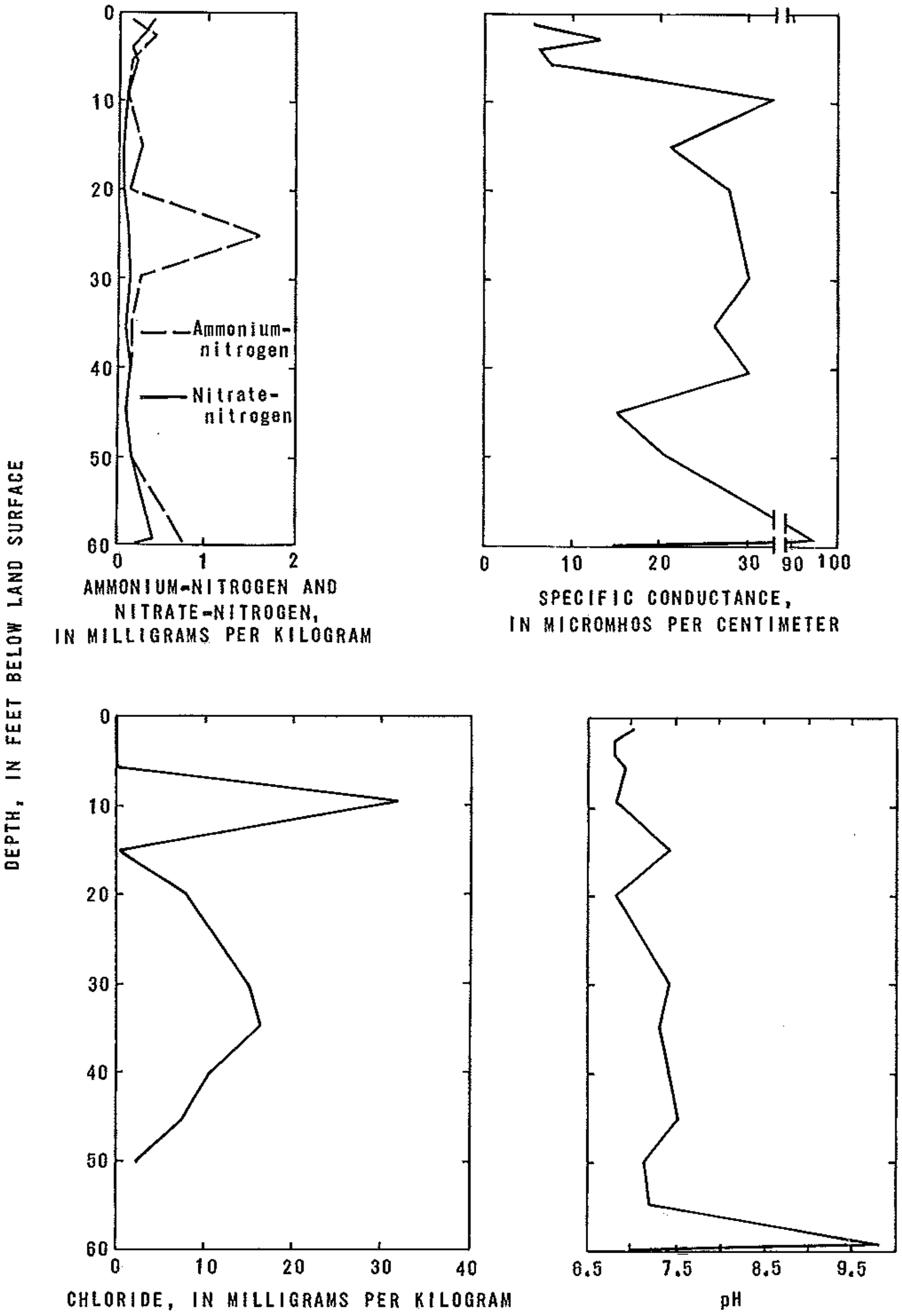

FIGURE 10.--Distribution of physical and chemical measurements with depth in test hole 20.

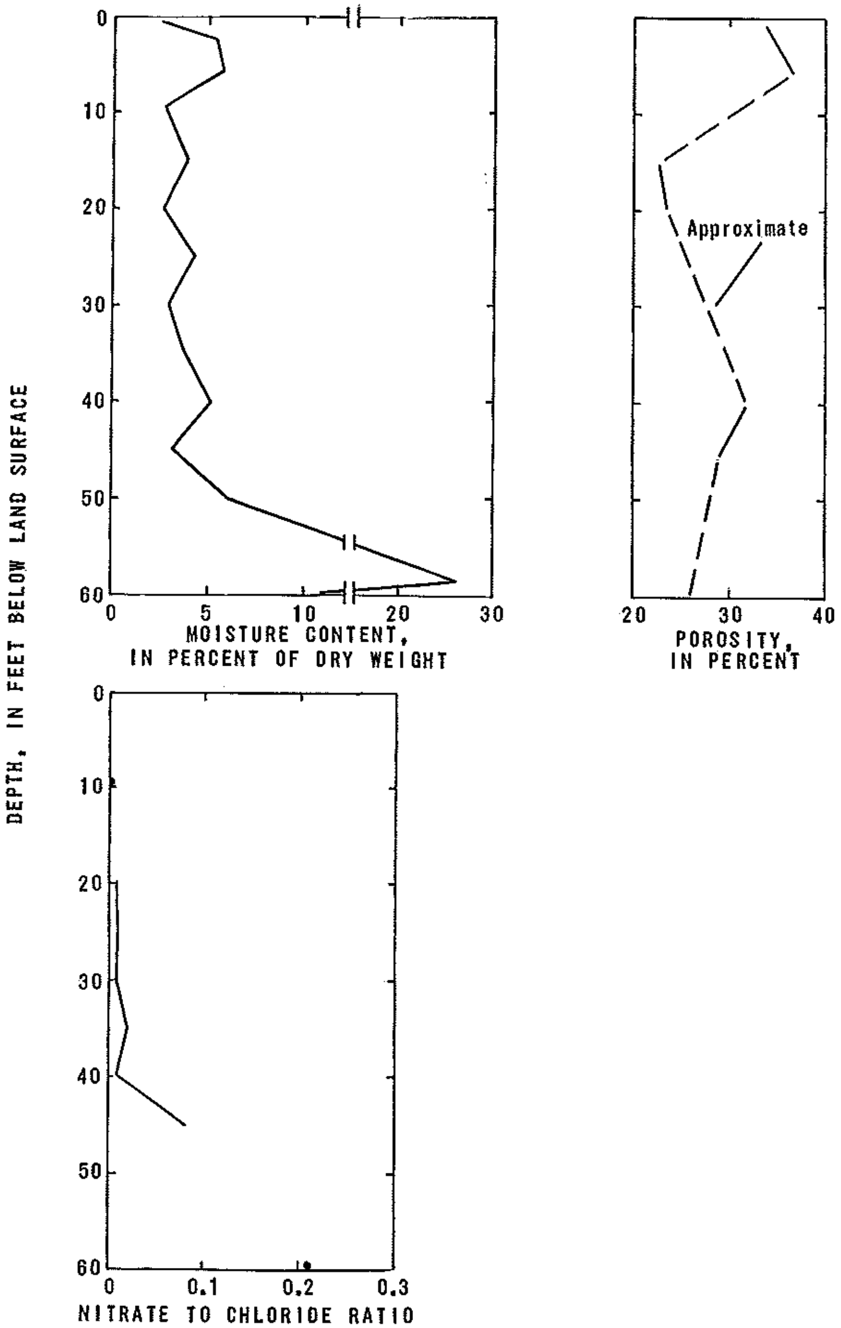

FIGURE 10.--Continued

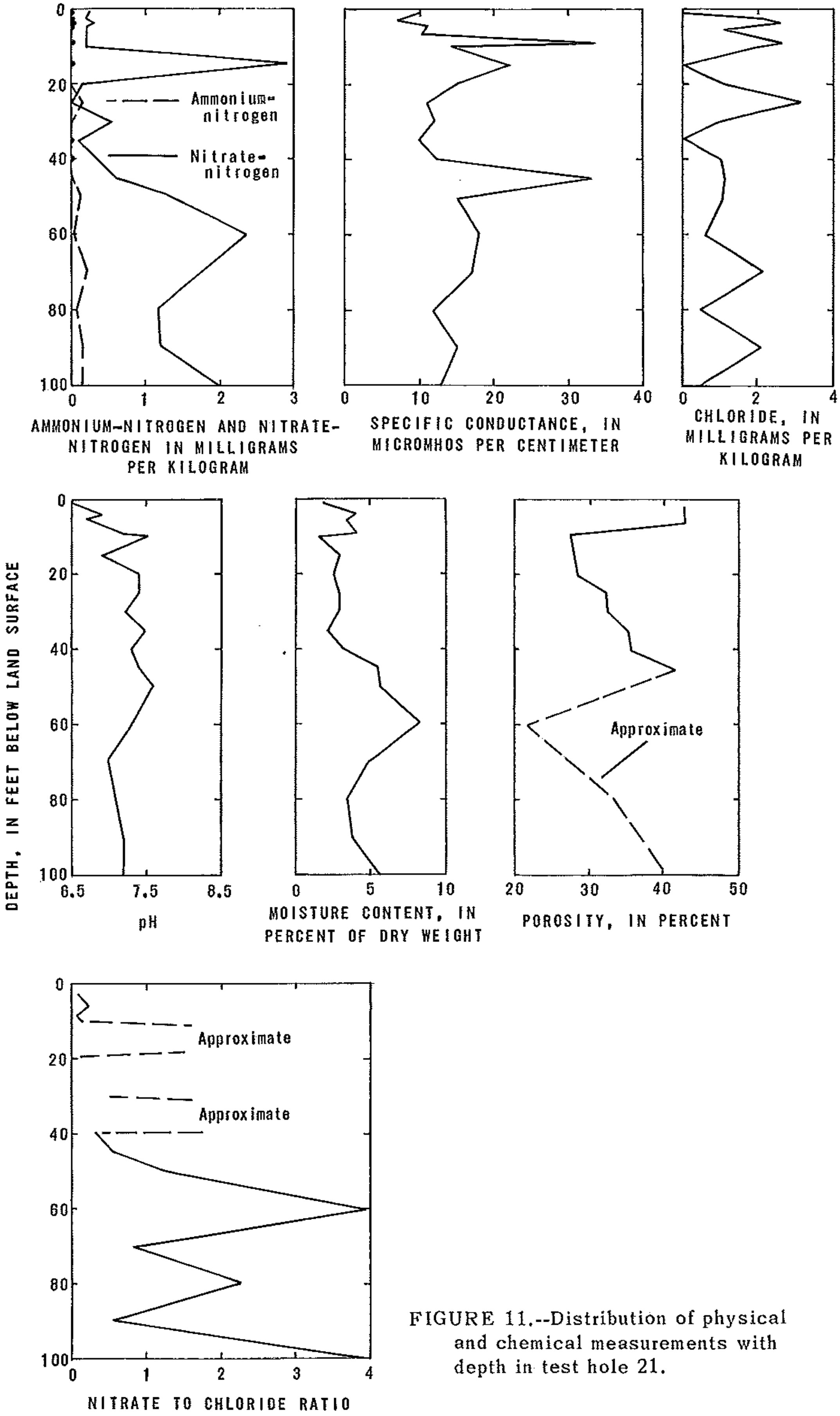

FIGURE 11.--Distribution of physical and chemical measurements with depth in test hole 21.

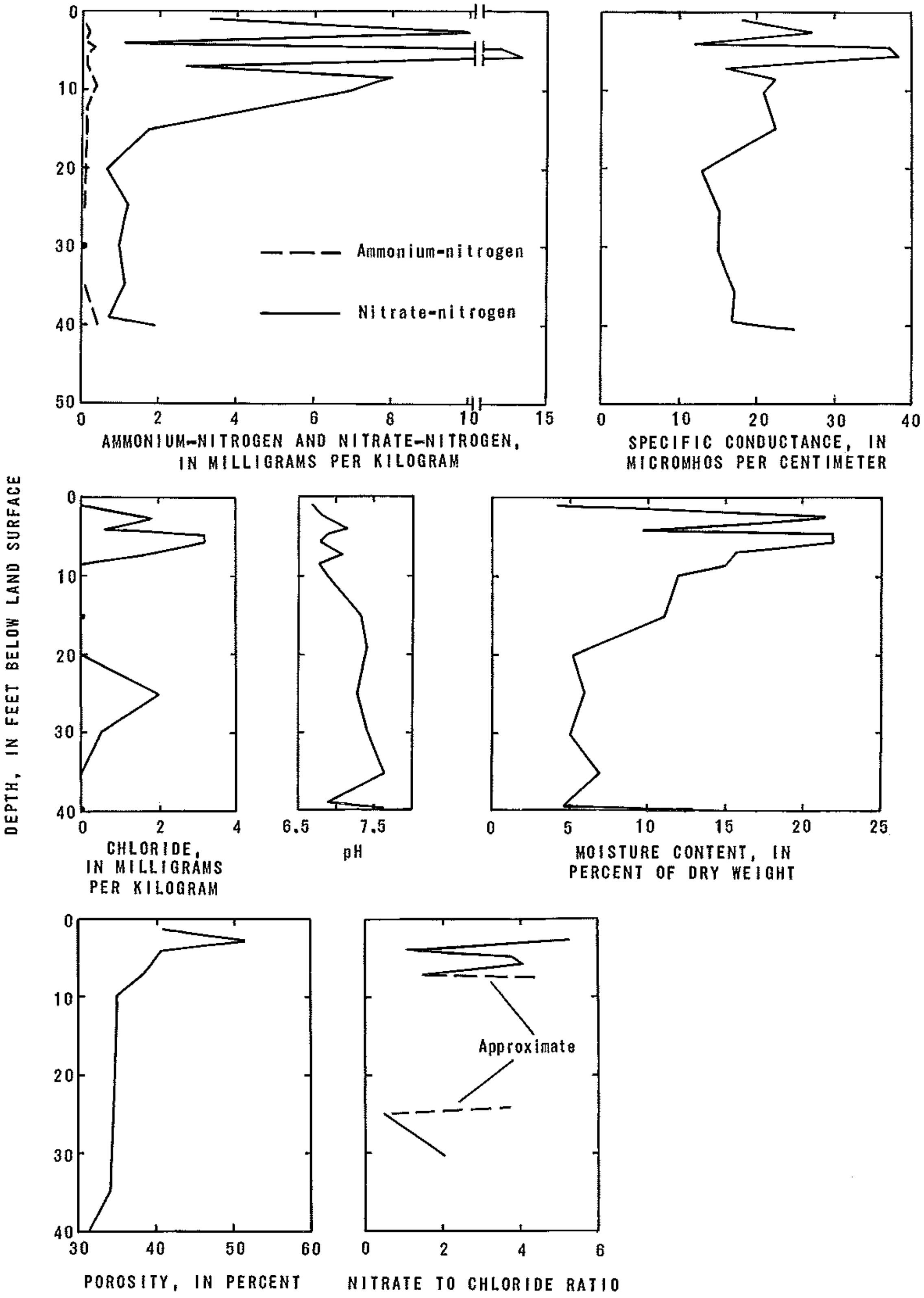

FIGURE 12.--Distribution of physical and chemical measurements with depth in test hole 22.

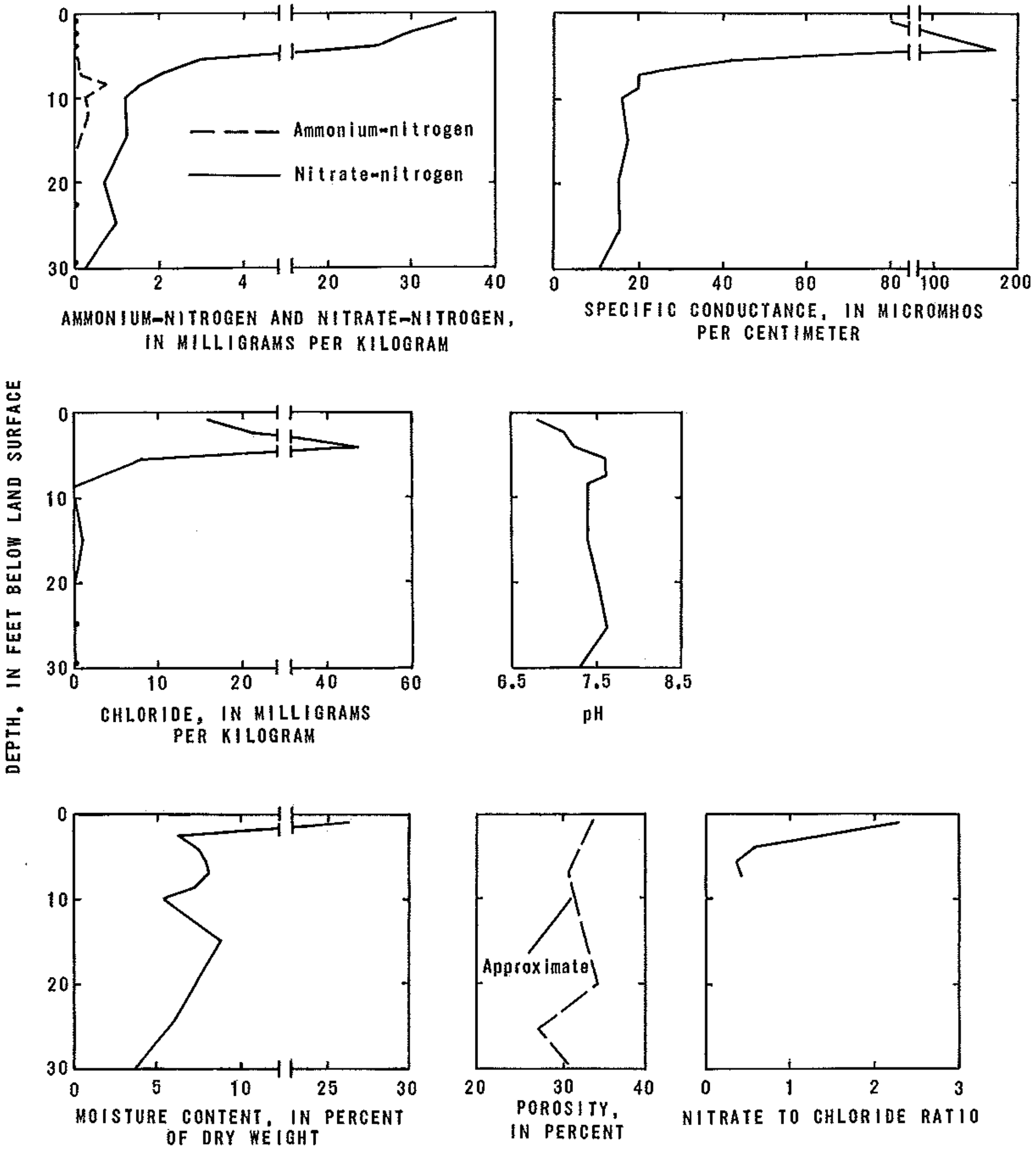

FIGURE 13.--Distribution of physical and chemical measurements with depth in test hole 23.

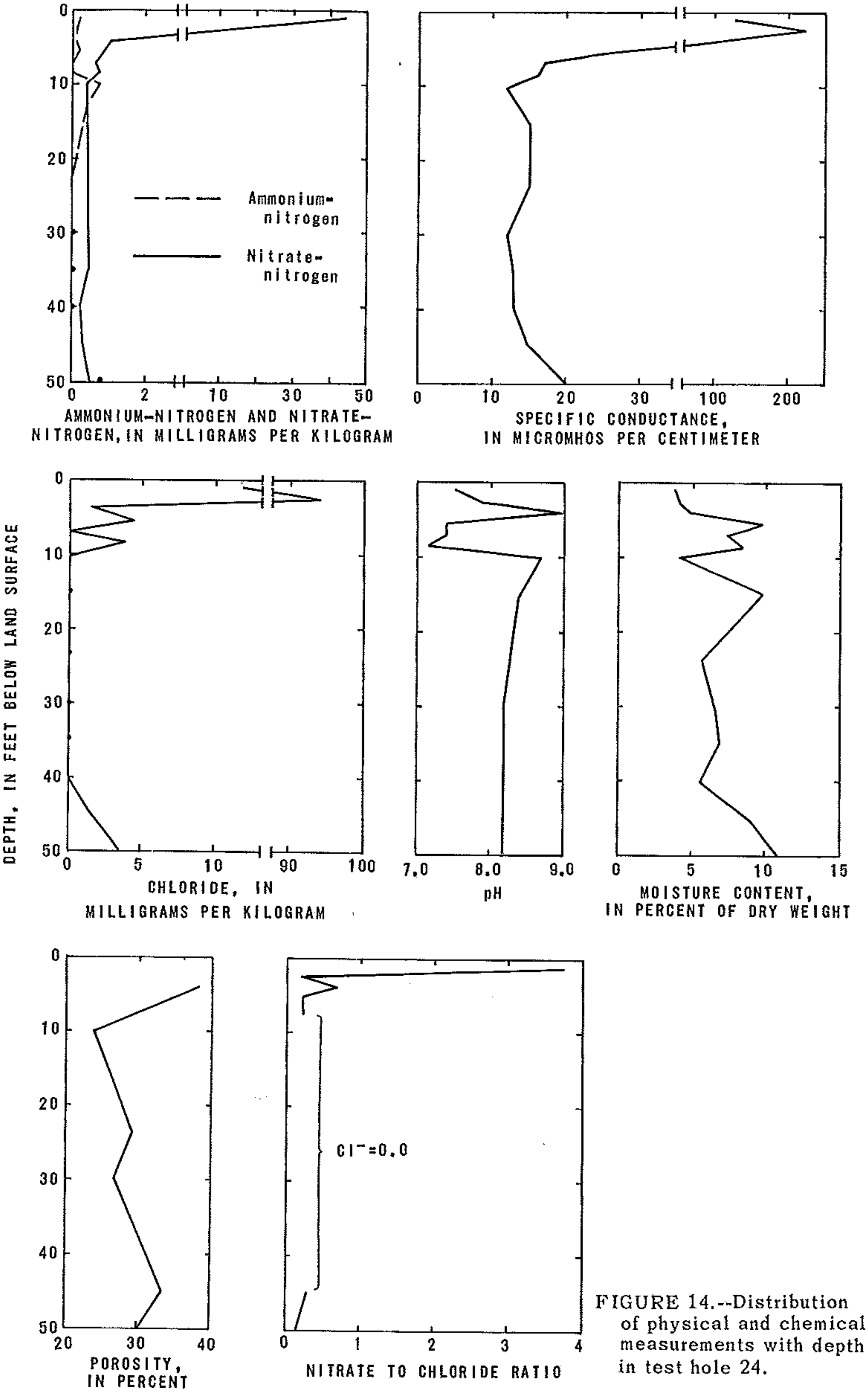

FIGURE 14.--Distribution of physical and chemical measurements with depth in test hole 24.

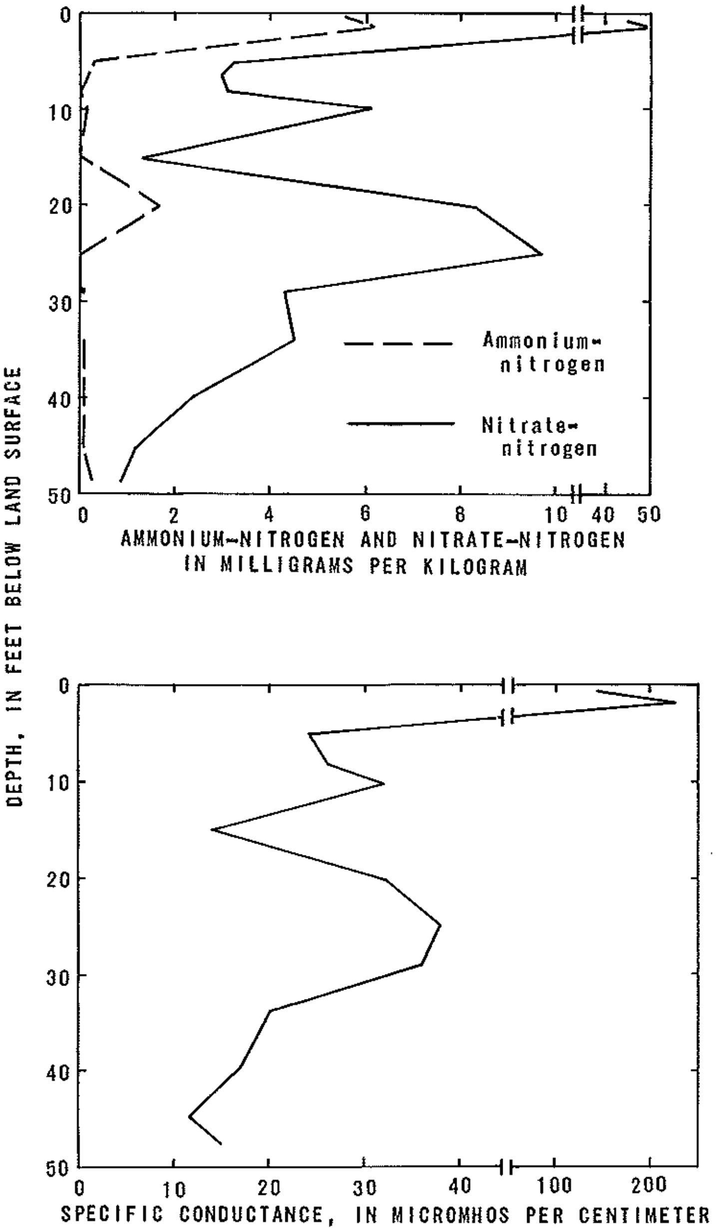

FIGURE 15.--Distribution of physical and chemical measurements with depth in test hole 25.

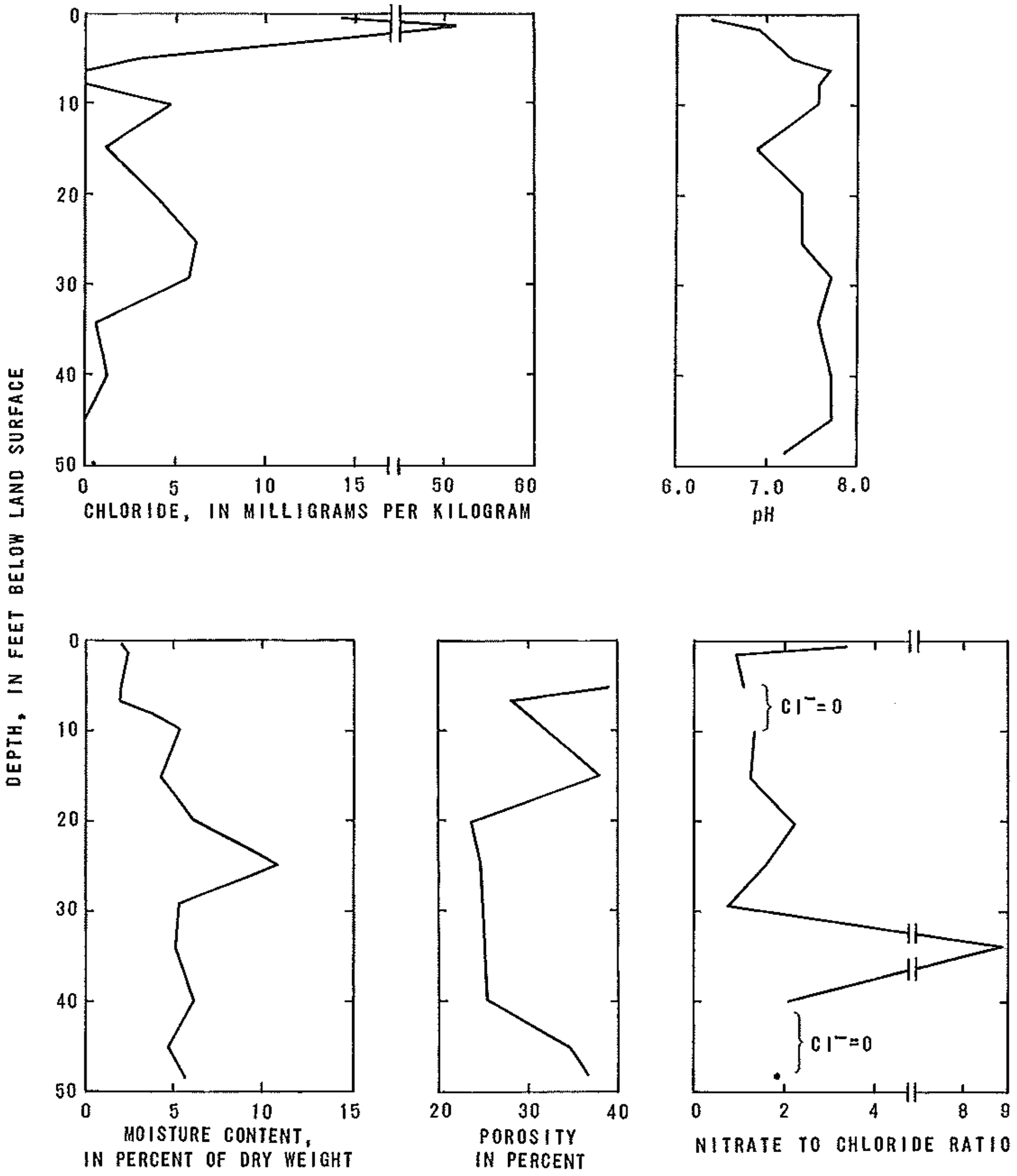

FIGURE 15.--Continued.

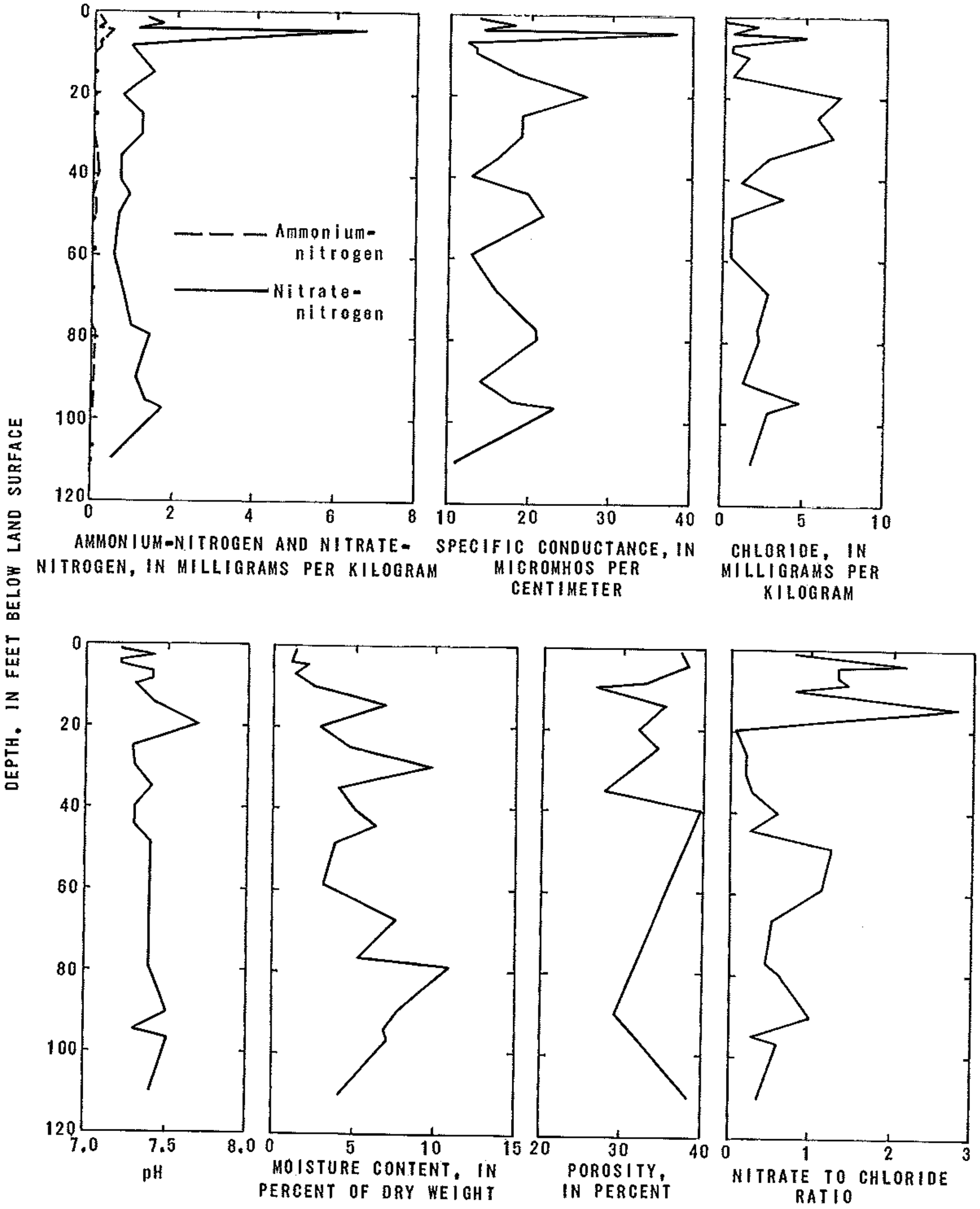

FIGURE 16.--Distribution of physical and chemical measurements with depth in test hole 26.

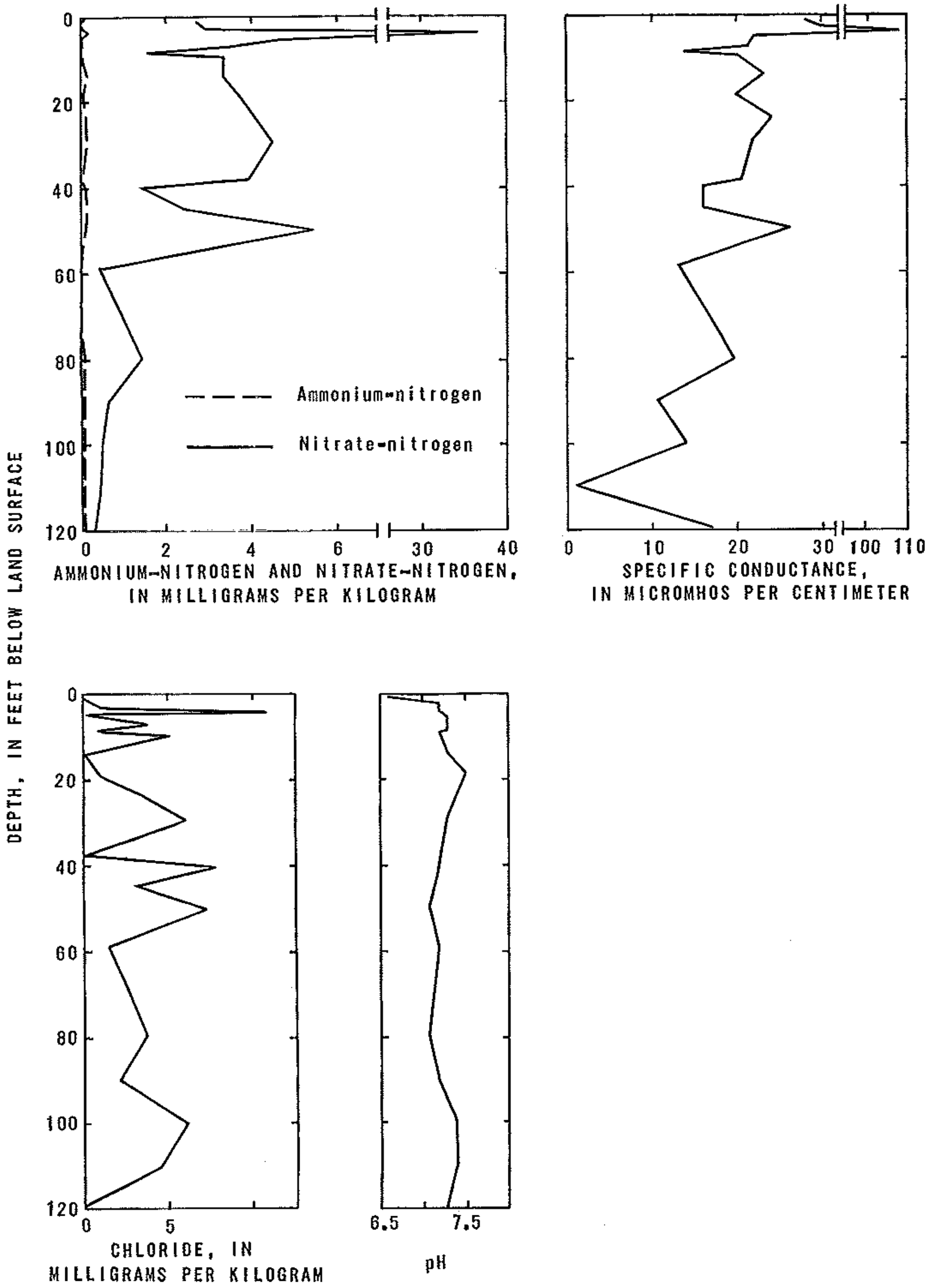

FIGURE 17.--Distribution of physical and chemical measurements with depth in test hole 27.

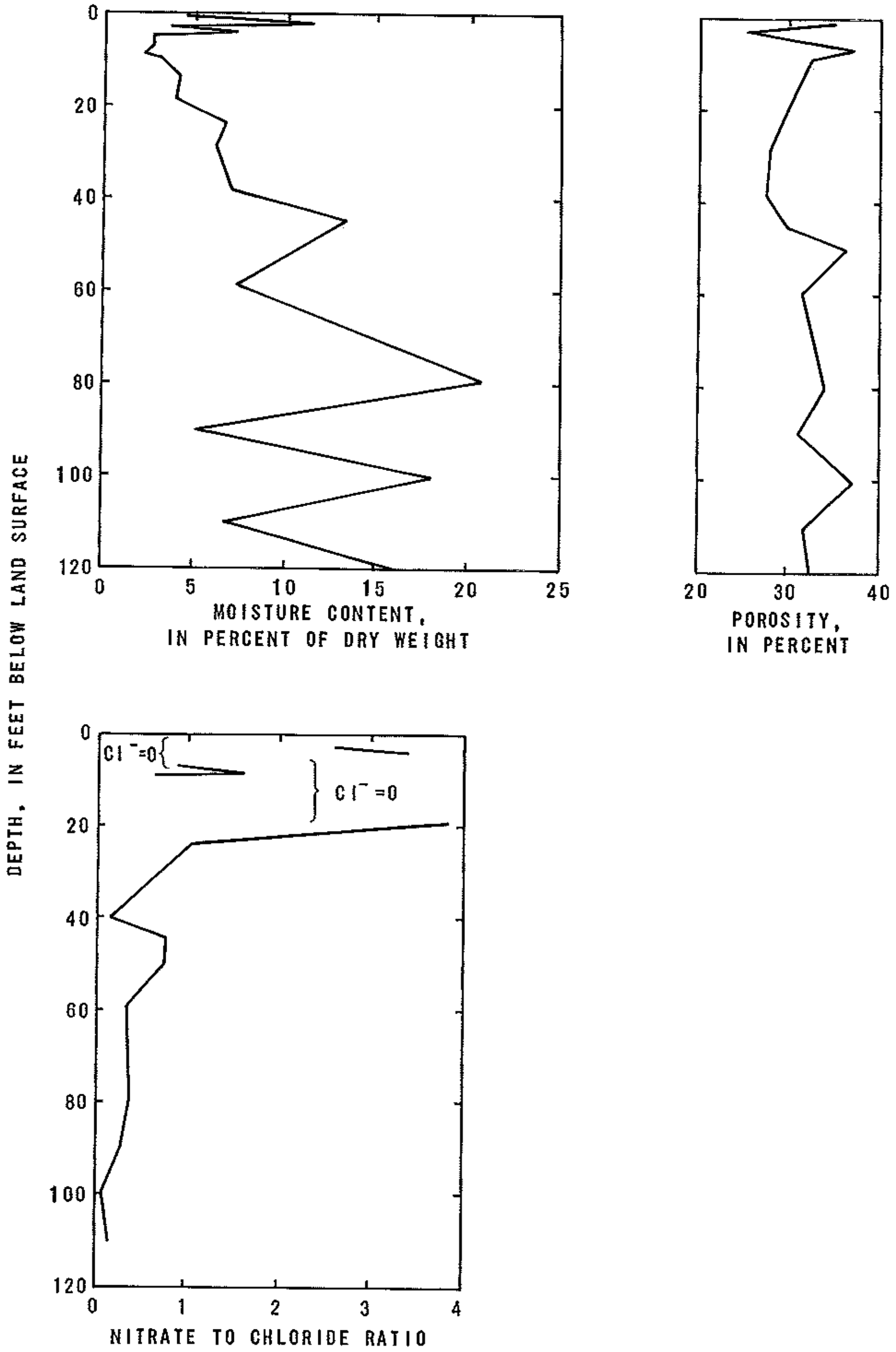

FIGURE 17.--Continued.

The maximum NO_3^--N concentrations and the total quantity of NO_3^--N (obtained by procedures described later in the text) found in the top 10 ft of each test hole are ranked for comparison in table 2.

The same seven test holes ranked highest in both columns. Of these, three are in citrus groves, two are in developed land covered with groves about 5 years ago, one is in an abandoned dairy feedlot (adjacent to an active feedlot), and one is near the abandoned sewage-treatment plant.

Of the six ranked lowest in both columns, two are in uninhabited areas and one each is in an urban area, a mixed agriculture-urban area, a former citrus grove, and an existing grove. Test holes 19 (Cs/Cs) and 26 (Mx/Ag) are ranked among the lowest but are near wells that yield water with NO_3^--N concentrations exceeding 20 mg/L, among the highest found in the study area. The contrast between relatively high NO_3^--N concentrations in the well water and relatively low NO_3^--N abundance in the unsaturated zone suggests that high NO_3^--N ground water may originate in upgradient citrus groves and that other chemical, biological, or physical features are controlling the downward movement of the nitrogen applied at the land surface at the drill site.

TABLE 2. - Ranking of maximum concentration and total NO_3^--N in top 10 feet of test holes

[Land use classification: Ag, agriculture other than citrus; Cs, citrus grove; DyF, dairy feedlot; Mx, mixed urban and agriculture; Sew, sewage treatment plant; Un, uninhabited; Ur, urban; VUr, vacant urban]

Rank	Test hole No.	Land use classification present/ historical	Maximum NO_3^--N (mg/kg)	Test hole No.	Land use classification present/ historical	Total NO_3^--N (mg)
1	15	VUr/Cs	63	23	Cs/Cs	149
2	25	DyF/DyF	50	15	VUr/Cs	145
3	24	Cs/Cs	44	25	DyF/DyF	131
4	27	Mx/Cs	36	24	Cs/Cs	104
5	23	Cs/Cs	35	16	VUr/Sew	72
6	16	VUr/Sew	14.5	22	Cs/Cs	64
7	22	Cs/Cs	13.1	27	Mx/Cs	64
8	17	VUr/Cs	9.7	17	VUr/Cs	46
9	26	Mx/Ag	6.7	18	Ur/Ur	24
10	18	Ur/Ur	5.9	26	Mx/Ag	19
11	19	Cs/Cs	2.2	19	Cs/Cs	17
12	20	Un/Un	.4	20	Un/Un	2.3
13	21	Un/Un	.3	21	Un/Un	2.3

To further compare the occurrence of NO_3^--N among the test holes, the total NO_3^--N in the top 40 ft (the minimum depth penetrated) is ranked in table 3. The seven test holes ranked highest in total NO_3^--N in the top 40 ft are the same seven that ranked highest in the analyses for the top 10 ft.

Test hole 27 (Mx/Cs), which ranked seventh in total NO_3^--N in the top 10 ft, ranks fourth in total NO_3^--N in the top 40 ft, suggesting that NO_3^--N has entered the deeper zones of this test hole to a greater extent than in the other test holes. This may be due to lateral migration from the nearby grove or the accumulation of remnant nitrogen added when the site was covered by a grove.

The foregoing analysis suggests a general correspondence among land uses expected to contribute nitrogen and the occurrence of NO_3^--N in the unsaturated zone (table 4).

The low ranking of test hole 19 plus the occurrence of peak NO_3^--N concentrations below 40 ft invites further discussion. The near-surface material is among the most porous found in this study (fig. 9), but the porosity decreases with depth to low values around 60 ft, where saturated conditions were observed concurrent with the higher NO_3^--N concentration. It is possible that the porous surface soil allows relatively rapid percolation of irrigation water to a depth where a layer of low-porosity material tends to retard its downward movement. (Dry clay was observed at 77 ft.) Hence, there is a buildup of moisture, a decreased porosity, and higher NO_3^--N values above the point where the downward movement slows. It is also possible that water containing NO_3^--N is moving laterally, just above the stratum with low porosity, into the vicinity of test hole 19 from numerous citrus groves upgradient. Upgradient sources could be a significant source of the high NO_3^--N in water from a nearby irrigation well if the clay observed at the 75- to 77-foot depths is extensive enough beneath the general area of test hole 19 to prevent the fertilizer NO_3^--N from the citrus grove from percolating to the zone of saturation.

TABLE 3. - Ranking of total NO_3^--N in top 40 feet of test holes

[Land use classification: Ag, agriculture other than citrus; Cs, citrus grove; DyF, dairy feedlot; Mx, mixed urban and agriculture; Sew, sewage treatment plant; Un, uninhabited; Ur, urban; VUr, vacant urban]

Rank	Test hole No.	Land use classification present/ historical	NO_3^--N in 40 feet of test hole (mg)
1	15	VUr/Cs	296
2	25	DyF/DyF	286
3	23	Cs/Cs	166
4	27	Mx/Cs	155
5	16	VUr/Sew	127
6	24	Cs/Cs	117
7	22	Cs/Cs	111
8	19	Cs/Cs	69
9	17	VUr/Cs	58
10	26	Mx/Ag	51
11	18	Ur/Ur	35
12	21	Un/Un	19
13	20	Un/Un	5

TABLE 4. - Summary of ranking analysis

Land use	Test hole No.	
	High ranked	Low ranked
Formerly grove	15	17
Active grove	22, 23, 24	19
Mixed citrus-urban	27	26
Dairy feedlot	25	--
Near sewage-treatment plant	16	--
Urban	--	18
Uninhabited	--	20, 21

The data are insufficient to determine the significance of differences between groups by common statistical tests. But the data set for test holes in areas that are now or have been citrus groves are numerous enough to establish measures of central tendency and dispersion. It is helpful to examine how data from the other test holes relate to data from this group of test holes (table 5). The data from citrus areas were log-normally distributed so that the central tendency of the data was best described by the geometric mean. The measure of NO_3^--N occurrence in test holes near the sewage-treatment plant, in the urban area, and in the dairy feedlot are all within the range of 1.96 standard deviations about the geometric mean of the measures from citrus holes, suggesting that NO_3^--N occurrence in these test holes (16, 18, and 25) is not distinguishable from that in test holes in citrus areas. Measures from test holes in uninhabited areas are clearly outside the range of 1.96 standard deviations.

TABLE 5. - Comparison of NO_3^--N occurrence among present and former citrus land use and other land uses

Land use (test hole No.)		Peak NO_3^--N in top 10 feet (mg/L)	Total NO_3^--N in top 10 feet (mg)	Total NO_3^--N in top 40 feet (mg)
Present and former citrus grove (15,17,19,22,23, 24,26,27)	(1)	17	59	110
	(2)	1.8-162	11-299	34-355
Near sewage-treatment plant (16)		14.5	72	127
Urban (18)		5.9	24	35
Uninhabited (20)		[3].4	[3]2.3	[3]5
Uninhabited (21)		[3].3	[3]2.3	[3]19
Dairy feedlot (25)		50	131	286

[1] The geometric mean is the antilogarithm of the mean of logarithmically transformed data.

[2] Range of ±1.96 standard deviations about the geometric mean: (95 percent of the values used to compute the mean are within 1.96 standard deviations about the mean).

[3] Value outside the range of 1.96 standard deviations about the geometric mean of present and former citrus grove group.

Ammonium

The concentrations of NH_4^+-N (obtained in the de-ionized water extract) are variable both within and among the test holes (figs. 5-17). Concentrations ranged from 0.00 to 8.15 mg/kg. The greatest variability with depth and the highest concentration were found in test holes 15, 16, 17, 18, and 25 in areas that were converted some time ago from citrus groves or have a long-term history of land use other than citrus groves. In contrast, test holes 19, 21, 22, 23, 24, 26, and 27 contain relatively low concentrations of NH_4^+-N that vary little with depth. Six of these test holes are currently in citrus groves or in land only recently developed for residential property from citrus groves.

Contrasts in NH_4^+-N concentrations among test holes are further demonstrated by ranking the geometric mean concentration for each test hole (table 6). The geometric mean is a better measure of central tendency of data from each test hole than is the arithmetic mean, because the frequency distribution of data is apparently log-normal. The six test holes ranked highest include the five mentioned above that showed the greatest variability in NH_4^+-N concentration with depth.

The control hole (20) is ranked second in this analysis, indicating that NH_4^+-N is available from the freshly weathered granitic material encountered at this site. But the concentrations are relatively constant with depth in this hole, suggesting that there are few natural processes in operation that cause the NH_4^+-N to move from one stratum to another (fig. 10).

The mean NH_4^+-N concentrations in test holes 19, 21, 22, 23, 24, 26, and 27 are all significantly lower than the mean in test hole 20, evidence that citrus-grove agriculture has created conditions favoring nitrification of NH_4^+ to NO_3^-. Apparently both the NH_4^+-N originally available in the weathered granites and that added as fertilizer were efficiently nitrified to NO_3^-. This apparent greater efficiency of nitrification in citrus grove-related test holes with respect to that in other test holes may be due to the predominance of moisture conditions favoring nitrification in irrigated soils (Patrick and Wyatt, 1964) (See also p. 10 and 12.)

TABLE 6. - Ranking of geometric mean NH_4^+-N concentration in test holes

[Land use classification: Ag, agriculture other than citrus; Cs, citrus grove; DyF, dairy feedlot; Mx, mixed urban and agriculture; Sew, sewage-treatment plant; Un, uninhabited; Ur, urban; VUr, vacant urban]

Rank	Test hole No.	Land use classification present/ historical	Geometric mean[1] (mg/kg)
1	17	VUr/Cs	0.60 a
2	20	Un/Un	.23 b
3	16	VUr/Sew	.22 a,b,c
4	25	DyF/DyF	.17 b,c
5	18	Ur/Ur	.125 b,c
6	15	VUr/Cs	.116 b,c
7	19	Cs/Cs	.110 c
8	24	Cs/Cs	.106 c,d
9	22	Cs/Cs	.082 c,d,e
10	23	Cs/Cs	.072 c,d,e
11	27	Mx/Cs	.052 e
12	21	Un/Un	.051 d,e
13	26	Mx/Ag	.051 d,e

[1] The geometric mean is the antilogarithm of the mean of logarithmically transformed data.

a,b,c,d,e Values subscripted by the same letter are not significantly different at the 95-percent confidence level. (Differences evaluated with a one-tailed Student-t test using the mean and standard deviation of log-transformed data. The Null Hypothesis is that the two means tested are equal. The alternative hypothesis is that one is larger than the other.)

Test holes 21, 26, and 27 were drilled in reworked alluvium of the Santa Ana River and contain the smallest NH_4^+-N concentrations. Reworking and flooding may have leached the original NH_4^+-N.

Test hole 17, also in an area once a citrus grove, does not fit the pattern of low geometric mean NH_4^+-N concentrations in citrus-related test holes. Insufficient information on such factors as fertilizer applications and irrigation history is available to support further discussion regarding this discrepancy.

Specific Conductance

The specific conductance of the de-ionized water extracts is related in a general manner to the NO_3^--N and chloride (Cl^-) concentrations in the soil (figs. 5 through 17). High or peak NO_3^--N concentrations are usually accompanied by peaks in specific conductance, indicating that NO_3^--N and other soluble solids tend to move together. Exceptions are noted in test hole 20, where NO_3^--N concentrations relatively consistent with depth contrast with varying specific-conductance values, and in test hole 21, where at 45 ft a peak in specific conductance does not coincide with a peak in the NO_3^--N distribution; rather, a NO_3^--N peak appears at 60 ft. Specific-conductance values from test holes in citrus areas are generally more variable with depth below 10 ft than those values from test holes in other areas.

Table 7 shows the highest specific conductance observed in extracts from the top 10 ft of the test holes, ranked from highest to lowest. Of the top six, four (15, 23, 24, and 25) are also ranked highest in occurrence of NO_3^--N in the top 10 ft (table 2). Four of the top six are in areas that are now or have been citrus groves, one is in the feedlot, and one (18) is close to a known fault, an area where hot-water wells are found.

Of the six test holes ranked lowest, four are in areas that are now or have been citrus groves and two are in uninhabited areas. The lowest near-surface specific-conductance values were from the test holes in the uninhabited areas.

TABLE 7. - Ranking of maximum specific conductance observed in extracts from top 10 feet of test holes

[Land use classification: Ag, agriculture other than citrus; Cs, citrus grove; DyF, dairy feedlot; Mx, mixed urban and agriculture; Sew, sewage-treatment plant; Un, uninhabited; Ur, urban; VUr, vacant urban]

Rank	Test hole No.	Land use classification present/ historical	Maximum specific conductance (μmho/cm)
1	15	VUr/Cs	170
2	18	Ur/Ur	151
3	25	DyF/DyF	145
4	24	Cs/Cs	120
5	23	Cs/Cs	80
6	19	Cs/Cs	72
7	16	VUr/Sew	51
8	17	VUr/Cs	46
9	27	Mx/Cs	28
10	22	Cs/Cs	18
11	26	Mx/Ag	14
12	21	Un/Un	10
13	20	Un/Un	5

To assist in further analysis, the mean specific conductances observed in extracts from below 10 ft are shown in table 8, ranked from highest to lowest. In this analysis, the specific conductances were normally distributed, so that an arithmetic mean was an appropriate measure of central tendency.

Of the six highest ranked test holes, only two are in areas that are now or were citrus groves. Three are near potential sources of dissolved solids--the abandoned treatment plant, a hot-water well area (18), and the abandoned feedlot. The control hole (20) is ranked sixth, suggesting that the freshly weathered granite contains considerable soluble solids. Indeed, perched ground water encountered just above bedrock in test hole 20 (fig. 10) had a specific conductance of 1,500 μmho/cm, evidence that natural dissolution processes can contribute appreciable dissolved-solids concentrations.

TABLE 8. - Ranking of mean specific conductance in extracts from below 10 feet in test holes

[Land use classification: Ag, agriculture other than citrus; Cs, citrus grove; DyF, dairy feedlot; Mx, mixed urban and agriculture; Sew, sewage-treatment plant; Un, uninhabited; Ur, urban; VUr, vacant urban]

Rank	Test hole No.	Land use classification present/ historical	Mean specific conductance[1] (μmho/cm)
1	18	Ur/Ur	51
2	19	Cs/Cs	33 a
3	16	VUr/Sew	[2]28 a
4	15	VUr/Cs	25 a,b
5	25	DyF/DyF	24 a,b
6	20	Un/Un	24 a,b
7	17	VUr/Cs	21 b,c
8	22	Cs/Cs	18 c,d
9	26	Mx/Ag	18 c,d
10	27	Mx/Cs	17 c,d,e
11	21	Un/Un	16 d,e
12	23	Cs/Cs	15 e
13	24	Cs/Cs	14 e

[1] a,b,c,d,e Values subscripted by the same letter are not significantly different at the 95-percent confidence level. (Differences evaluated with a one-tailed Student-t test. The Null Hypothesis is that the two means tested are equal. The alternative hypothesis is that one is larger than the other.)

[2] Value not significantly different from any lower values shown.

Of the seven test holes ranked lowest, six are in areas that are now or were citrus groves. Low specific conductances below 10 ft seem to be associated with greater applications of water. Among the lowest mean specific conductances observed below 10 ft were samples from test holes 22, 23, and 24 (table 8), located along the perimeter of the study area in material resembling the highly weathered and fractured granites in test hole 20 (Un/Un). The mean specific conductances below 10 ft in these three test holes were significantly lower than those in test hole 20, due probably to the regular application of irrigation water.

Chloride

The depth distributions of chloride concentrations are shown in figures 5 through 17; concentrations ranged from 0 to 96 mg/kg. The concentrations were below detection (about 2.7 mg/kg) in 55 of 204 analyses.

As discussed previously, a key feature of NO_3^--N distribution is the predominance of a concentration maximum in the top 10 ft of test hole; in contrast, the chloride concentration maximum occurred in the top 10 ft in only six (15, 17, 23, 24, 25, and 27) of the test holes. Of these six, all but one (25) are now, or were in the recent past, in citrus grove areas.

Peak chloride concentrations found in the top 10 ft of each test hole are shown in table 9, ranked highest to lowest. Of the seven ranked lowest, six are in areas that are now, or were recently, citrus groves, and one (21) is in the uninhabited area. The mean chloride concentrations below 10 ft are shown in table 10, ranked highest to lowest. Of the seven ranked lowest, six are in areas that are now, or were recently, citrus groves. All these had mean concentrations significantly lower than the control test hole (20). Test hole 18 (Ur/Ur), near hot-water wells, had a significantly higher mean chloride concentration than all the others.

TABLE 9. - Ranking of maximum chloride concentration in top 10 feet of test holes

[Land use classification: Ag, agriculture other than citrus; Cs, citrus grove; DyF, dairy feedlot; Mx, mixed urban and agriculture; Sew, sewage-treatment plant; Un, uninhabited; Ur, urban; VUr, vacant urban]

Rank	Test hole No.	Land use classification present/ historical	Maximum chloride concentration (mg/kg)
1	24	Cs/Cs	94
2	25	DyF/DyF	51
3	23	Cs/Cs	47
4	16	VUr/Sew	42
5	20	Un/Un	32
6	18	Ur/Ur	18
7	27	Mx/Cs	10.6
8	17	VUr/Cs	10.2
9	15	VUr/Cs	10.0
10	19	Cs/Cs	7.2
11	26	Mx/Ag	5.1
12	22	Cs/Cs	3.2
13	21	Un/Un	2.6

From this analysis, there appears to be a relation between irrigated citrus agriculture and low chloride concentrations in test holes. The lowest mean chloride values below 10 ft were observed in test holes 21, 22, 23, and 24. Holes 22, 23, and 24 are along the perimeter of the study area in material resembling the highly weathered and fractured granites encountered in the control hole (20). The significantly lower mean chloride concentrations in these test holes than in test hole 20 further suggest that regular application of irrigation water has leached away the chlorides in the source material. In test hole 21, the low chloride concentrations probably resulted from leaching as the soils were reworked and sorted in the process of transport to their present locations.

TABLE 10. - Ranking of mean chloride concentration below 10 feet in test holes

[Land use classification: Ag, agriculture other than citrus; Cs, citrus grove; DyF, dairy feedlot; Mx, mixed urban and agriculture; Sew, sewage-treatment plant; Un, uninhabited; Ur, urban; VUr, vacant urban]

Rank	Test hole No.	Land use classification present/ historical	Mean chloride concentrations[1] (mg/kg)
1	18	Ur/Ur	32
2	20	Un/Un	8.4 a
3	16	VUr/Sew	[2]5.7 a
4	19	Cs/Cs	4.7 a,b
5	15	VUr/Cs	4.3 a,b
6	27	Mx/Cs	3.4 b
7	26	Mx/Ag	2.8 b
8	25	DyF/DyF	2.6 b,c
9	21	Un/Un	1.2 c
10	24	Cs/Cs	.64 c,d
11	22	Cs/Cs	.36 d
12	17	VUr/Cs	.17 d
13	23	Cs/Cs	.10 d

[1] a,b,c,d Values subscripted by the same letter are not significantly different at the 95-percent confidence level. (Differences evaluated with a one-tailed Student-t test. The Null Hypothesis is that the two means tested are equal. The alternative hypothesis is that one is larger than the other).

[2] Value not significantly different from any lower values shown.

pH

The pH values measured in this study are generally one pH unit lower than those measured in the earlier study in nearby Redlands, Calif. (Klein and Bradford, 1979), and the profiles with depth are generally less variable. Values observed ranged from 6.4 in a near-surface sample in test hole 25 to 9.0 in a sample at a depth of 4 ft in test hole 24. A pH of 9.8 was observed in a zone of perched water at 59 ft in test hole 20, but it is not included in this analysis.

Generally, the pH was lowest at the surface, increased abruptly to a subsurface maximum in the zone between 20 and 40 ft, and decreased gradually with depth below 40 ft. This pattern is illustrated in table 11.

For comparison among test holes, the mean pH values are shown in table 12, ranked highest to lowest. No relation between mean pH and land use is apparent; however, several features are worth noting. The mean pH in test hole 24 is significantly higher than in four of the other six citrus-related test holes. The mean pH in test hole 20, the control, is significantly lower than in five of the seven citrus-related test holes. In the analyses of specific conductance and chloride data, test holes 20, 21, 22, 23, and 24 were discussed together because they all contained the same highly weathered and fractured granites. In the pH analysis, test holes 20, 21, 22, and 23 are among the five test holes ranked lowest, while test hole 24 is ranked highest. These discrepancies are unexplained.

TABLE 11. - Median pH in 10-foot increments with depth in all test holes

Depth increment (ft)	Median pH
0-9.9	7.24
10-19.9	7.48
20-29.9	7.48
30-39.9	7.58
40-49.9	7.42
>50	7.35

TABLE 12. - Ranking of mean pH in test holes

[Land use classification: Ag, agriculture other than citrus; Cs, citrus grove; DyF, dairy feedlot; Mx, mixed urban and agriculture; Sew, sewage-treatment plant; Un, uninhabited; Ur, urban; VUr, vacant urban]

Rank	Test hole No.	Land use classification present/ historical	pH[1]
1	24	Cs/Cs	7.84 a
2	16	VUr/Sew	7.68 a,b
3	18	Ur/Ur	7.60 a,c
4	15	VUr/Cs	7.54 a,c,d
5	19	Cs/Cs	7.51 a,c,d
6	26	Mx/Ag	7.37 b,d,e
7	25	DyF/DyF	[2]7.36 c,e
8	17	VUr/Cs	[2]7.36 c,e
9	23	Cs/Cs	7.35 c,e,f
10	27	Mx/Cs	7.25 f,g
11	21	Un/Un	7.16 f,g
12	22	Cs/Cs	7.11 g
13	20	Un/Un	7.10 g

[1] a,b,c,d,e,f,g Values subscripted by the same letter are not significantly different at the 95-percent confidence level. (Differences evaluated with a one-tailed Student-t test. The Null Hypothesis is that the two means tested are equal. The alternative hypothesis is that one is larger than the other).

[2] Value not significantly different from any lower values shown.

Denitrifying and Nitrate-Reducing Bacteria

The general pattern of occurrence of NO_3^--reducing bacteria in the test holes (fig. 18) is that the largest numbers of bacteria are in the near-surface material, followed by sharply decreasing numbers with depth. Several occurrences of large numbers at depth oppose this pattern, however, and test holes 18 (Ur/Ur) and 20 (Un/Un) contained uniformly small numbers of bacteria from the surface to the maximum depth sampled.

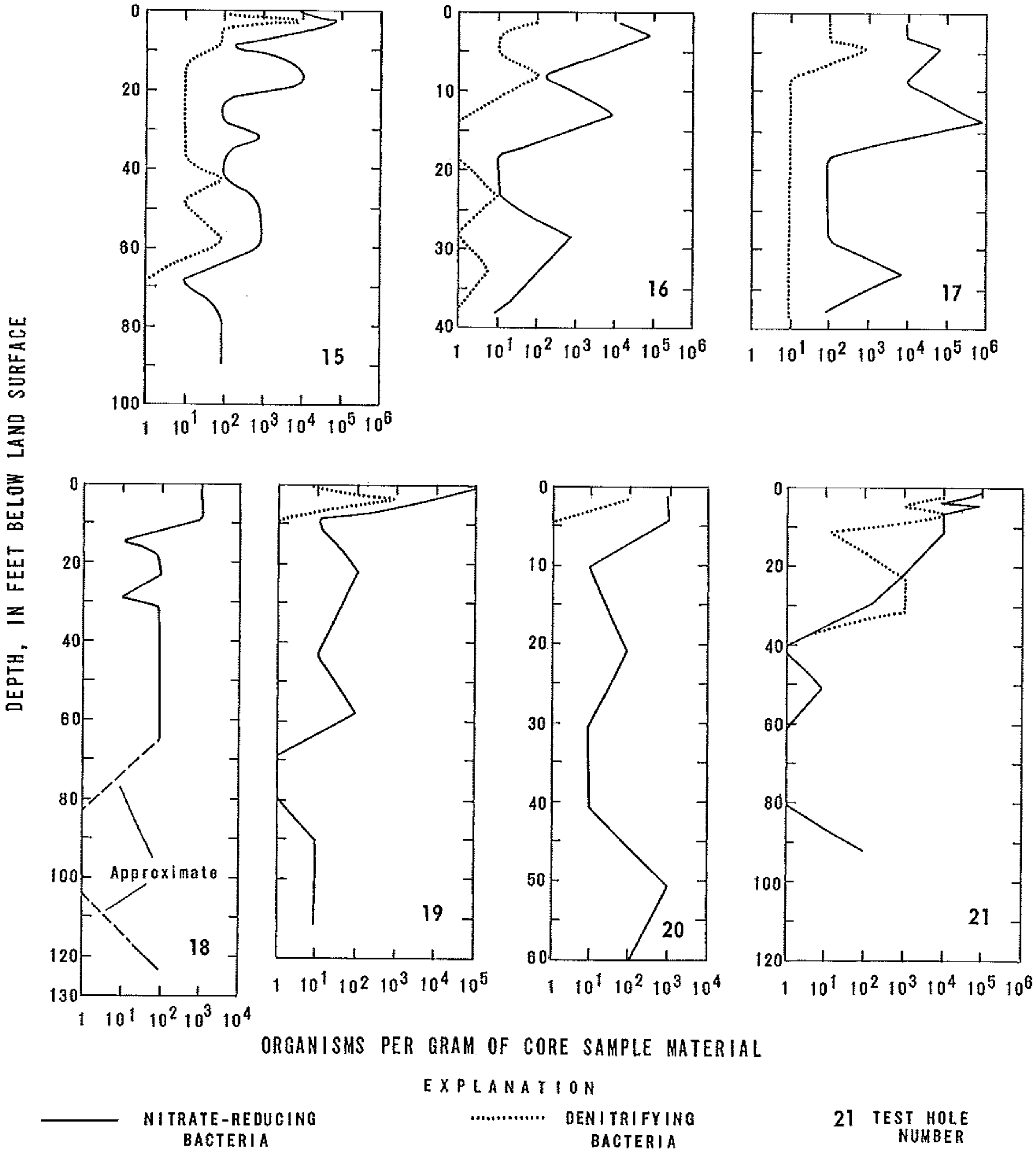

FIGURE 18.--Numbers of denitrifying and nitrate-reducing bacteria per gram of core sample material.

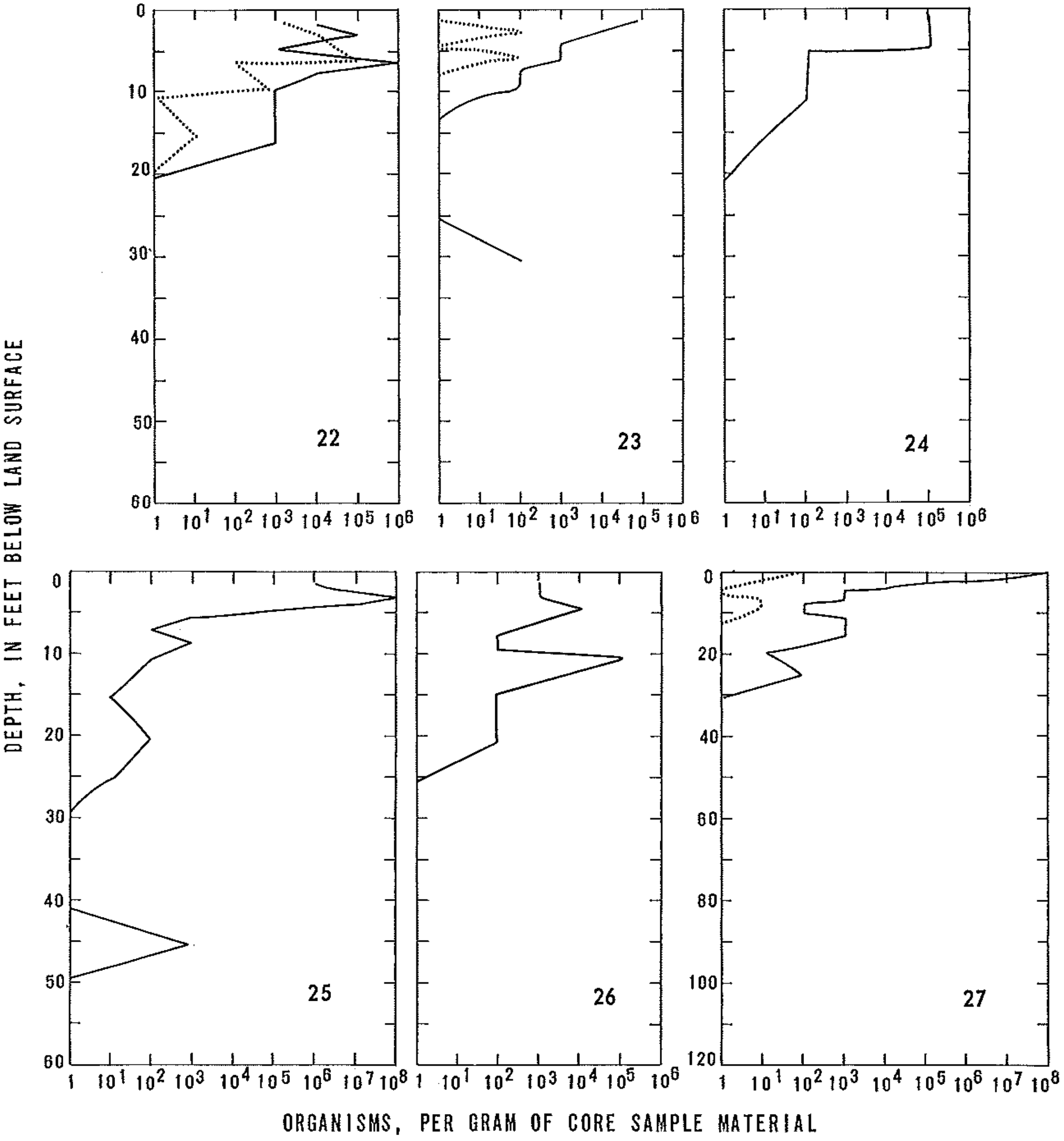

FIGURE 18.--Continued.

Maximum numbers of nitrate-reducing bacteria in the top 10 ft ranged from 10^8 to 10^5 organism/g, while between 10 and 20 ft they were fewer than 10^4 organism/g (except test hole 17, 10^6 organism/g at 13 ft). Below 20 ft, NO_3^--reducing bacteria are frequently undetectable and were fewer than 10^3 organism/g in all test holes. Denitrifying bacteria were found mostly in the upper 10 ft. Between 10 and 20 ft, counts were generally 10 organism/g or less except in test hole 21 (10^3 organism/g at 20 ft). Below 20 ft, denitrifiers were observed only in test holes 15, 16, 17, and 21.

For further analysis, the geometric mean of NO_3^--reducing bacteria in each test hole is shown in table 13 and ranked highest to lowest. Of the seven test holes ranked lowest, four are in areas that are now, or were until recently, citrus groves. In contrast, the three test holes ranked highest are also in citrus-related areas. The test holes that are in other than citrus-related areas are ranked in the middle. There does not appear to be any relation between citrus land uses and abundance of bacteria, either in the near-surface zone or in the top 40 ft. There may be a relation between bacteria abundance and lithology, however. Test holes 20, 22, 23, and 24, which rank low, are in highly weathered and fractured granitic material, somewhat different from the lithology of other holes.

The smallest numbers of NO_3^--reducing bacteria in near-surface samples inhabit areas that are not exposed to any sort of nitrogenous material--test holes 18 (Ur/Ur) and 20 (Un/Un). The bacteria are most numerous in areas presumably highest in nitrogenous material--test holes 25 (DyF/DyF) and 27 (Mx/Cs).

It is worth mentioning again the probable effect that large populations of bacteria may have on concentrations of NO_3^--N. Test hole 19, although in an area of intense, historical citrus cultivation, contained relatively low concentrations of NO_3^--N in the top 40 ft (table 3), perhaps because of the presence of large numbers of NO_3^--reducing bacteria (table 13). Concentrations of NO_3^--N were higher below 60 ft where there were either not any, or only small numbers of, NO_3^--reducing bacteria.

TABLE 13. - Ranking of geometric mean of nitrate-reducing bacteria in top 40 feet of test holes

[Land use classification: Ag, agriculture other than citrus; Cs, citrus grove; DyF, dairy feedlot; Mx, mixed urban and agriculture; Sew, sewage-treatment plant; Un, uninhabited; Ur, urban; VUr, vacant urban.

Notes: A, No denitrifying bacteria in the test hole; B, Denitrifying bacteria in upper 10 ft only; C, Appreciable numbers of denitrifying bacteria present; D, Nitrate-reducing bacteria found only above 30 ft]

Rank	Test hole No.	Land use classification present/ historical	Geometric mean (number/g)	Notes
1	17	VUr/Cs	1,780	C
2	19	Cs/Cs	830	B
3	15	VUr/Cs	790	C
4	21	Un/Un	630	C
5	16	VUr/Sew	230	C
6	18	Ur/Ur	120	A
7	27	Mx/Cs	105	B, D
8	25	DyF/DyF	52	A
9	20	Un/Un	43	B
10	22	Cs/Cs	42	C, D
11	26	Mx/Ag	34	A, D
12	24	Cs/Cs	13	A, D
13	23	Cs/Cs	10	B

Correlations Among Chemical and Biological Measurements

In the foregoing discussions, certain relations are apparent among the various chemical and biological measurements. To summarize these relations, the rankings assigned to the test holes according to nine sets of measurements in tables 2, 3, 6-10, 12, and 13, were tested for correlation by using the Spearman's Rho rank correlation test described by Conover (1971). The results are shown in table 14.

Significant correlations were observed between maximum NO_3^--N concentrations in the top 10 ft and the following: (1) Total NO_3^--N in the top 10 ft, (2) total NO_3^--N in the top 40 ft, (3) maximum specific conductance in the top 10 ft, and (4) maximum chloride in the top 10 ft. The first two correlations suggest that the peak NO_3^--N concentrations in the top 10 ft affect the totals found both in the top 10 ft and in the top 40 ft. The last two correlations show that NO_3^--N, chlorides, and other dissolved solids contributing to the specific conductance tend to occur together. This may be further interpreted to mean that the soluble solids tend to move together through the unsaturated zone.

Correlations are significant between total NO_3^--N in the top 10 ft and the following: (1) Total NO_3^--N in the top 40 ft, (2) maximum specific conductance in the top 10 ft, and (3) maximum chloride in the top 10 ft.

Total NO_3^--N in the top 40 ft is significantly correlated with peak specific conductance in the top 10 ft, further indicating that NO_3^--N and other soluble solids tend to occur together.

The geometric mean NH_4^+-N is significantly correlated with the mean specific conductance. This is due, in part, to the fact that low soluble NH_4^+-N and low specific conductances are both found in citrus-related areas.

Significant correlations that cannot be explained at this time are between the maximum specific conductance in the top 10 ft and the mean pH, and between the geometric mean of NO_3^--reducing bacteria in the top 40 ft and the mean specific conductance.

Mean specific conductance is significantly correlated with mean chloride concentration below 10 ft, indicating that chlorides are a principal component of the soluble solids contributing to the specific conductance.

TABLE 14. - Rank correlations among test holes

Parameter	Maximum NO_3^--N in top 10 feet	Total NO_3^--N in top 10 feet	Total NO_3^--N in top 40 feet	Geometric mean NH_4^+-N concentration	Maximum specific conductance in top 10 feet	Mean specific conductance below 10 feet	Maximum chloride concentration below 10 feet	Mean chloride concentration in top 10 feet	Mean pH	Geometric mean bacteria in top 40 feet
Maximum NO_3^--N in top 10 feet										
Total NO_3^--N in top 10 feet	*									
Total NO_3^--N in top 40 feet	*	*								
Geometric mean NH_4^+-N concentration										
Maximum specific conductance in top 10 feet	*	*	*							
Mean specific conductance below 10 feet				*						
Maximum chloride concentration in top 10 feet	*	*								
Mean chloride concentration below 10 feet						*				
Mean pH					*					
Geometric mean bacteria in top 40 feet						*				

*Asterisk means the Null Hypothesis is rejected at the 95-percent confidence level. (The Null Hypothesis is that the parameters are mutually independent. The alternative hypothesis is that larger values of one tend to be paired with larger values of the other.)

Moisture Content

Moisture content of soil depends on the amount of water available at the land surface from precipitation and irrigation and on the ability of the soil to percolate or retain this water. Although moisture content within the test holes varied from 1.1 percent in test hole 26 to 34.2 percent in test hole 18, 80 percent of the observed values were less than 10 percent (figs. 5-17). Forty-one percent of the values were between 5 and 9.9 percent, 39 percent of the values were between 0 to 4.9 percent, and those test holes with moisture content greater than 10 percent are in or near irrigated citrus groves or other sources of local recharge.

Figure 19 shows the frequency distribution of moisture content for each test hole, and table 15 shows the mean moisture content for each site, the standard deviation of these values, and the number of observations. Only test holes 18 and 22 had a mean moisture content greater than 10 percent. Test hole 22 is in an irrigated area; however, test hole 18 does not receive surface water from any known source except precipitation. All test holes in or near irrigated areas had mean moisture contents greater than 5 percent.

TABLE 15. - Statistics on moisture content of samples from test holes

[Land use classification: Ag, agriculture other than citrus; citrus grove; DyF, dairy feedlot; Mx, mixed urban and agriculture; Sew, sewage-treatment plant; Un, uninhabited; Ur, urban; VUr, vacant urban]

Test hole No.	Land use classification present/ historical	Mean moisture content (percentage of dry weight)	Standard deviation	Number of observations
15	VUr/Cs	6.6	2.6	16
16	VUr/Sew	7.6	3.6	9
17	VUr/Cs	5.8	3.1	11
18	Ur/Ur	10.4	7.3	20
19	Cs/Cs	9.2	4.6	18
20	Un/Un	4.8	2.3	14
21	Un/Un	3.8	1.6	19
22	Cs/Cs	11.5	6.4	15
23	Cs/Cs	8.5	6.1	11
24	Cs/Cs	7.0	2.4	14
25	DyF/DyF	4.7	2.3	14
26	Mx/Ag	4.7	2.8	23
27	Mx/Cs	7.8	5.4	21

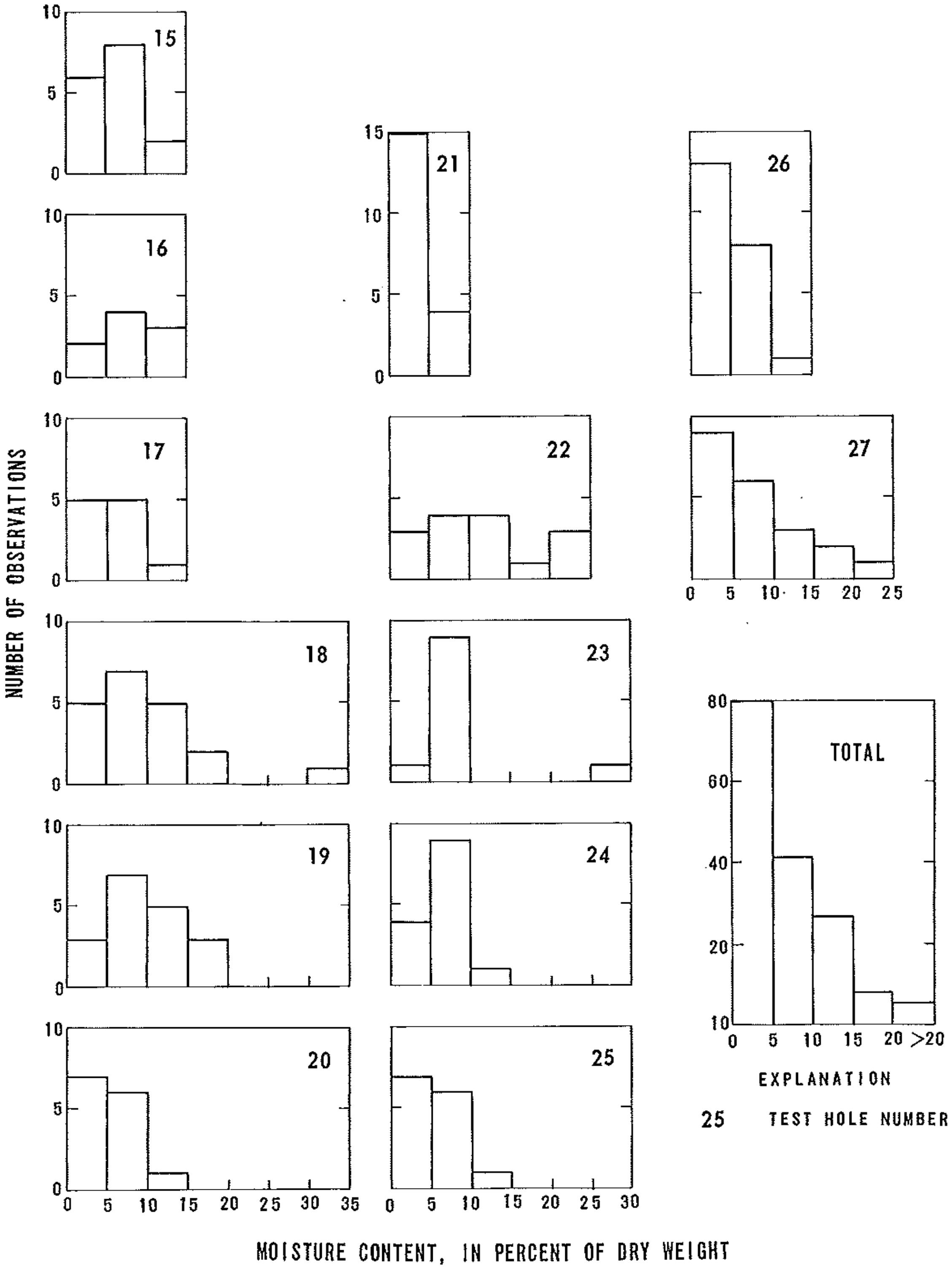

FIGURE 19.--Frequency distribution of moisture content in test holes.

Implementation of present plans to increase recharge to the local aquifers with imported water will raise the water table and may intercept NO_3^--N in the unsaturated zone. The data obtained in this study will now be used to assess the magnitude of potential increases in NO_3^--N concentrations in water from wells as recharge proceeds.

Under existing conditions, NO_3^--N is moving downward with the soil water through the unsaturated zone and will eventually reach the water table. The average velocity of the soil water that infiltrates beneath irrigated land is probably 3.5 to 4.0 ft/yr in the study area (Kearney Foundation of the University of California, 1973; Pratt and others, 1972). The transit rate is certainly slower in the unirrigated areas because less water is available annually to migrate downward to the water table. The data in table 16 show the cumulative mass of NO_3^--N in a 2-inch diameter core that is available to be dissolved by rising ground water. Test holes 20, 22, 23, and 24 are not shown because they are in areas that would be unaffected by rising ground water. Test holes 16 and 17, because they did not penetrate deep enough to provide data suitable for this analysis, are also not shown.

If the water table rises uniformly into the unsaturated zone so that little vertical mixing takes place, the pore water of the unsaturated zone (and the NO_3^--N dissolved therein) will be driven ahead of the saturated front, forming a layer of water with a high NO_3^--N concentration (Childs, 1969). The thickness of this high-NO_3^--N overriding layer will vary with the magnitude of the water-table rise and the initial moisture content of the unsaturated zone.

As a first approximation, an estimate of the thickness of this layer may be obtained by assuming an average porosity of 40 percent, an average moisture content of 10 percent, and an average dry weight of core of 0.99 kg/ft. In a 2-inch diameter core 1 ft in length (total volume, 618 mL), the total void space available is approximately 250 mL. Pore water of the core amounts to about 10 percent by weight (100 mL). The pore water is pushed upward as water rises into the 1 ft of core. Assuming the porosity to be 100-percent effective, this 100 mL of pore water then moves upward into the next 1-foot section and combines with the 100 mL of pore water in that section. Following this operation incrementally upward, a recharge rise in the water table of 3.2 ft would have an upper layer of pore water 1.2 ft thick.

Present models for the mixing of the intercepted NO_3^--N are considered by the authors to be inadequate to correctly simulate the concentration/depth profiles that might result from mixing of NO_3^--N intercepted in a one-time rise of the water table combined with normal seasonal water-level fluctuations. It is even more difficult to simulate the profiles that might result if the water-table altitude increases continuously over a period of years and normal seasonal fluctuations occur simultaneously.

Lacking the ability to predict NO_3^--N concentration/depth profiles accurately, it is useful to consider mechanisms that may aid in an approximation of the behavior of intercepted NO_3^--N under the conditions described above.

TABLE 16. - Cumulative mass of NO_3^--N, in milligrams, in 5-foot increments in each test hole (2-inch diameter) that would be intercepted by a rising water table

Depth below land surface (feet)	Test hole No.						
	15	18	19	21	25	26	27
30-35	189	101	234	127	94.0	81.6	139
35-40	172	100	226	127	72.3	77.0	117
40-45	159	97.0	216	126	56.5	71.5	100
45-50	139	93.0	204	124	47.8	67.8	91.1
50-55	127	90.1	188	119	42.8	64.3	72.3
55-60	112	84.9	171	111	39.1	61.3	52.5
60-65	88.7	76.3	155	101	36.0	58.4	45.7
65-70	64.6	64.4	131	89.6	33.0	52.9	42.2
70-75	41.4	51.5	113	80.2	30.0	49.4	37.6
75-80	25.2	38.5	102	72.3	27.0	45.2	32.1
80-85	16.8	29.7	93.4	65.9	24.0	39.9	25.5
85-90	8.9	25.7	85.6	60.2	21.0	33.7	19.3
90-95		22.6	77.5	54.4	18.0	28.1	15.1
95-100		19.3	60.5	47.6	15.0	22.3	12.1
100-105		15.0	32.7	38.8	12.0	15.0	9.6
105-110		10.0	14.2	29.1	9.0	9.3	7.1
110-115		6.1		19.4	6.0	5.6	4.5
115-120		3.6		9.7	3.0	2.8	2.0
120-125		--		--	--	--	--

If, as in the above example, the water table rises uniformly and no mixing due to water-table fluctuations occurs, the major mixing mechanism of the NO_3^--N ion will be molecular diffusion. As a first approximation, this layer of highly concentrated NO_3^--N water atop the dilute water rising from below can be treated as a planar source containing a mass of NO_3^--N. The resultant NO_3^--N concentration/depth profile due to diffusion is obtained from the one-dimensional diffusion equation (Crank, 1956) from a planar source,

$$C = \frac{M}{(\pi Dt)^{\frac{1}{2}}} e^{-x^2/4Dt}$$

where C is the resultant NO_3^--N concentration, in milligrams per liter; M is the mass of nitrogen, in micrograms, in a 1-cm^2 source; D is the diffusion coefficient, in centimeters squared per second; t is the time, in seconds, from the start of diffusive flux; and x is the distance from the top of the dilute recharge front, in centimeters, to the depth in question. π and e are constants. The best value of D (self-diffusion coefficient) available for the conditions presented is 1.9×10^5 cm^2/s, obtained in potassium nitrate solutions (Harned and Owen, 1958). Because this value of D is obtained in solutions unconstrained by a soil medium, it may be too high by as much as a factor of three. It is, however, adequate for this discussion.

Solution of the one-dimensional equation shows that diffusion from a planar source into a dilute recharge water would be a slow process. As an example, detectable increases ($\sim$2 mg/L) in NO_3^--N would not occur at a depth of 10 ft below the source within 10 years, nor 13 ft within 20 years, nor 20 ft within 50 years. This analysis illustrates the best case where intercepted NO_3^--N would apparently not cause degradation of the ground water below the layer of intercepted pore water. It is not a realistic case, however, and can be used only to illustrate the mechanisms involved.

A more realistic analysis must take into account the mixing caused by seasonal fluctuations in the water table. Seasonal fluctuations will vary greatly, both areally and temporally, due to differences in pumping and recharge. These water-table fluctuations will probably be the most important mixing mechanism, causing the intercepted nitrate to be mixed vertically much faster than if diffusion were the only process operating.

To estimate increases in NO_3^--N concentrations where mixing by water-table fluctuations is the dominant process, it is assumed that the intercepted NO_3^--N will mix within the saturated zone to a depth equal to the seasonal water-table fluctuations--about 20 ft.

Figure 20 shows the NO_3^--N concentration profiles that would probably be obtained in the top 20 ft of saturation in each test hole if the available NO_3^--N in the saturated zone were to mix with water initially free of NO_3^--N. The concentration profiles were obtained by dividing the mass of intercepted NO_3^--N, from table 16, by the volume of water in a 2-inch diameter core. The water volumes were obtained by multiplying the core volumes by the porosity. As an example, if in the vicinity of test hole 19 the water level were to rise from 110 to 80 ft, the resulting concentration of NO_3^--N in the top 20-foot layer would be approximately 31 mg/L as compared with 8.5 mg/L at 110 ft. An unusually large water-table rise to 50 ft below land surface could further increase the NO_3^--N to about 65 mg/L near test hole 19.

This analysis indicates that the greatest concentrations of NO_3^--N would be found beneath the areas that are now, or were recently, citrus groves (test holes 15, 19, and 27). For comparison, test holes 18 (Ur/Ur), 25 (DyF/DyF), and 26 (Mx/Ag) contain relatively minor amounts of NO_3^--N in the zone into which the water is expected to rise. Because test hole 21 (Un/Un) contains appreciable NO_3^--N below 40 ft, estimates of resultant NO_3^--N concentration due to recharge are surprisingly high.

The conceptual model presented herein will not be applicable unless the recharge occurs by a hydrologic process resulting in a vertical and uniform rise in the water table. Substantial lateral flow could accompany a rising water table, resulting in migration of the NO_3^--N downgradient to other parts of the aquifer. If this were to occur, a major effort to mathematically simulate the recharge process and its consequences would be necessary to determine NO_3^--N distributions.

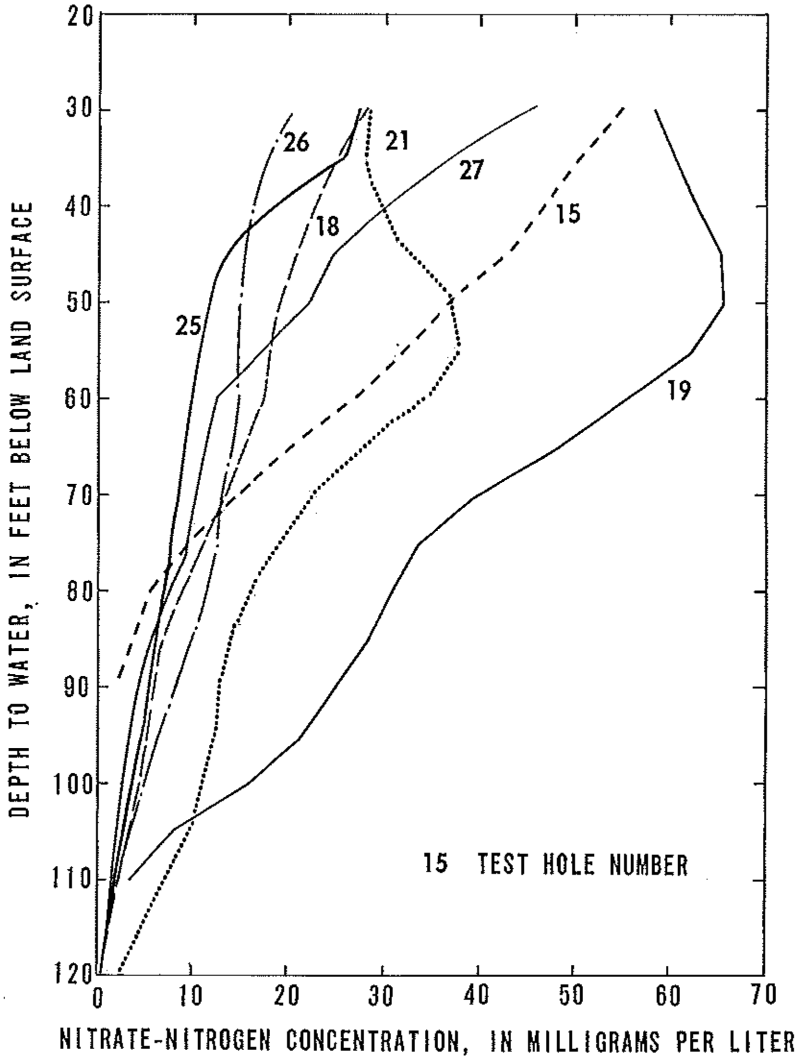

FIGURE 20.--Concentration of NO_3^--N dissolved at the top of the saturated zone in a recharged aquifer. Assumes that the NO_3^--N intercepted by the rising water table is mixed uniformly in the top 20 feet of water.

SUMMARY AND CONCLUSIONS

Thirteen test holes were drilled in the vicinity of Highland-East Highlands area, Calif., to ascertain the areal and vertical distribution of nitrate and related inorganic nitrogen species and other physical and chemical parameters in the unsaturated zone. A knowledge of nitrate distribution in the unsaturated zone is a prerequisite to effective water-quality management and an aid in evaluating various recharge alternatives.

The soil samples were analyzed for moisture content and leached with distilled water to determine extract pH, specific conductance, chloride, nitrate, nitrite, and ammonium.

Nitrate (NO_3^--N) was the predominant form of inorganic nitrogen in all the test holes; however, ammonium (NH_4^+-N) was occasionally quantitatively important. Nitrite (NO_2^--N) was not quantitatively important in any of the test holes.

The results are presented and analyzed, in part, by ranking the test holes according to 10 measures: (1) Maximum NO_3^--N concentration in the top 10 ft; (2) total NO_3^--N in the top 10 ft; (3) total NO_3^--N in the top 40 ft; (4) geometric mean of the NH_4^+-N concentration; (5) maximum specific conductance in extracts from the top 10 ft; (6) mean specific conductance of extracts; (7) maximum chloride concentration in the top 10 ft; (8) mean chloride concentration below 10 ft; (9) mean pH of extract; (10) geometric mean of denitrifying-bacteria counts.

The maximum NO_3^--N concentration occurred at or within 10 ft of the surface in 11 of the 13 test holes, indicating that the source of nitrogen in the subsurface is at land surface. The same seven test holes ranked highest in total NO_3^--N in the top 10 ft and total NO_3^--N in the top 40 ft. Of these, three (22, 23, and 24) are in citrus groves, two (15 and 27) are in land developed from citrus groves about 5 years ago, one (25) is in an abandoned dairy feedlot, and one (16) is near an abandoned sewage-treatment plant. The two test holes that ranked lowest (20 and 21) are in uninhabited areas.

Maximum NO_3^--N in the top 10 ft, total NO_3^--N in the top 10 ft, and total NO_3^--N in the top 40 ft in the test holes in uninhabited areas (20 and 21) were more than 1.96 standard deviations lower than the geometric means in test holes from areas that are now, or were recently, citrus groves. These analyses clearly established a relation between citrus agriculture and the presence of NO_3^--N above background levels in the unsaturated zone.

The analyses of NH_4^+-N in test holes show that a supply of NH_4^+-N is available from the freshly weathered granitic material, such as is present at the control site (20), or from the mineralization of organic nitrogen. Furthermore, the geometric mean NH_4^+-N concentrations in six of the eight citrus-related test holes were significantly lower than in the control hole, evidence that citrus cultivation had created conditions favoring nitrification of NH_4^+ to NO_3^-. Nitrification in these areas may have prevented accumulations of NH_4^+-N from applied fertilizers.

The distribution of maximum specific conductance in the top 10 ft, maximum chloride concentration in the top 10 ft, mean chloride concentration, and mean specific conductance suggested that high values of all four were associated with man-related or natural sources of soluble solids other than those related to citrus cultivation. In fact, of the six test holes ranked lowest in mean specific conductance, five are in areas that are now, or were, citrus groves. It was apparent that low mean specific-conductance values were associated with greater applications of water, either by natural flooding or by irrigation.

The largest numbers of NO_3^--reducing bacteria were observed in the near-surface soils, but the numbers decreased sharply with depth. Numbers in the top 10 ft reached maximums of 10^8 organism/g but were less than 10^3 organism/g in all holes below a depth of 20 ft. The largest numbers in near-surface samples occurred in areas thought to be high in organic nitrogenous material--hole 25 (DyF/DyF) and hole 27 (Mx/Cs).

To aid in evaluating recharge-management alternatives, two conceptual models of resultant NO_3^--N concentration in rising ground water were examined. One extreme assumes no mixing other than self-diffusion of the NO_3^- ion. Only after 50 years are significant concentrations of NO_3^--N added to a depth of 20 ft below a layer of high NO_3^--N pore water pushed upward by the rising water table. The other model assumes complete mixing of the recharge water and pore water in the top 20 ft of the saturated zone. The greatest concentrations of NO_3^--N that would be added to the 20-foot-thick layer would be at the top of the saturated zone in the vicinity of test holes 15, 18, 19, 21, 25, and 27. In the worst case, if the water table were to rise uniformly to 50 ft below land surface in the vicinity of test hole 19, a NO_3^--N concentration of about 65 mg/L would be found in the top 20 ft of the saturated zone.

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