

MOVEMENT PATTERN OF NO_3^- -N THROUGH A SOIL COLUMN
UNDER STEADY STATE CONDITION

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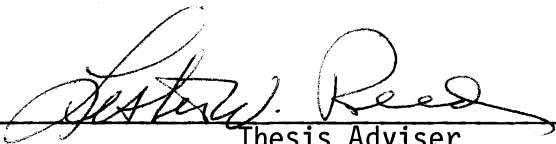
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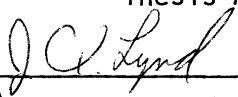
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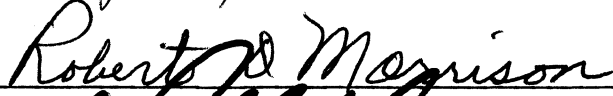
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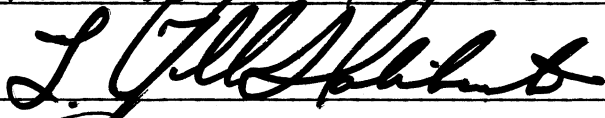
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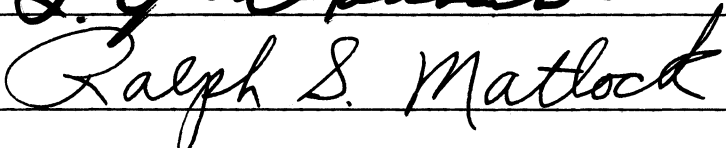


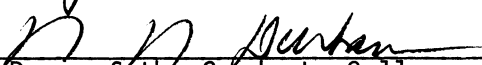
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CHAPTER I

INTRODUCTION

Nitrogen is applied to the soil in large quantities than any other plant nutrient, and is one of the key elements needed for high productivity of agricultural crops. This element exists in many chemical or molecular combinations; it is indispensable for sustaining life, but is harmful to human and animal health when found in drinking water as NO_3^- in excess of 45 PPM.

Until recently the main reason for measuring the concentration of nitrate (NO_3^-) in the water in the soil material below the effective rooting depth of crop plants was to evaluate the loss of NO_3^- to the crop and estimate the loss of production or a need for more fertilizer N to adjust for the losses. In the last few years, with a tremendous increase in the concern for NO_3^- in surface and ground waters, the emphasis has changed to the study of NO_3^- leaching because of the potential pollution of waters.

Current literature contains data which shows that some ground water aquifers in many states are contaminated with NO_3^- (e.g., California, Missouri, and Colorado) while high NO_3^- concentrations were reported in some wells of Iowa, Wisconsin, Oklahoma, and Minnesota over two decades ago. Thus, it seems that this problem has existed for quite some time, but has only received national attention within the last decade.

A survey report published in 1950 by the Oklahoma Water Quality Section of the Water Resources Board showed that many of the ground and surface water supplies of Oklahoma were heavily contaminated with N (5 to 160 PPM NO_3^-). During that time the use of N fertilizers amounted to less than 5,000 tons per year for the entire state. Thus, it may be safe to conclude that the ultimate source of high NO_3^- levels in these waters was not due to fertilizer N but derived from other sources, since some of the areas located close to wells heavily contaminated with NO_3^- have yet to be fertilized. It should also be noted that since 1950, the quantity of fertilizer N added to some Oklahoma soils has increased to approximately 170,000 tons. Therefore, it is important to evaluate the potential of fertilizer N as a pollutant of Oklahoma water supplies in these areas.

As our agro-industrial civilization becomes more and more complex, the rate at which NO_3^- enters public water supplies could possibly be accelerated. Management of this complex system and control of NO_3^- concentrations in ground and surface waters will therefore require an integration of research efforts.

The primary objective of this study was to determine the pattern of NO_3^- movement in the soil profile which are eventually found in water supplies.

CHAPTER II

LITERATURE REVIEW

Nitrogen as the inert gas N_2 constitutes nearly 80 percent of the volume of the earth's atmosphere. Nitrogen is continuously cycled through the environment from the atmosphere to growing plants and back to nitrogen gas. The principal species are presented in the classical nitrogen cycle as shown below (Figure 1).

Fixtion of nitrogen to produce organic nitrogen is carried out by specialized bacteria, algae and a few higher plants. When these organisms decompose, much of the organic nitrogen is converted to ammonia. A small fraction, however, is converted to relatively stable humus nitrogen in the soil.

Ammonia is nitrified or converted to nitrates by two specialized groups of bacteria. Nitrosomonas oxidizes ammonia to nitrite and Nitrobacter oxidizes nitrite to nitrate. Oxygen is required as well as CO_2 for bacterial growth but dissolved organic matter has little or no influence. Nitrates can be reduced by many bacteria that use the oxygen for metabolism. Nitrites are the first product but they are usually rapidly reduced to nitrogen gas by further bacterial action. Nitrates can also be utilized as a source of nitrogen by most growing plants.

The nitrogen content of natural unpolluted waters is normally less than one milligram per liter, and during the growing season soluble nitrogen compounds are virtually completely depleted by growing plants

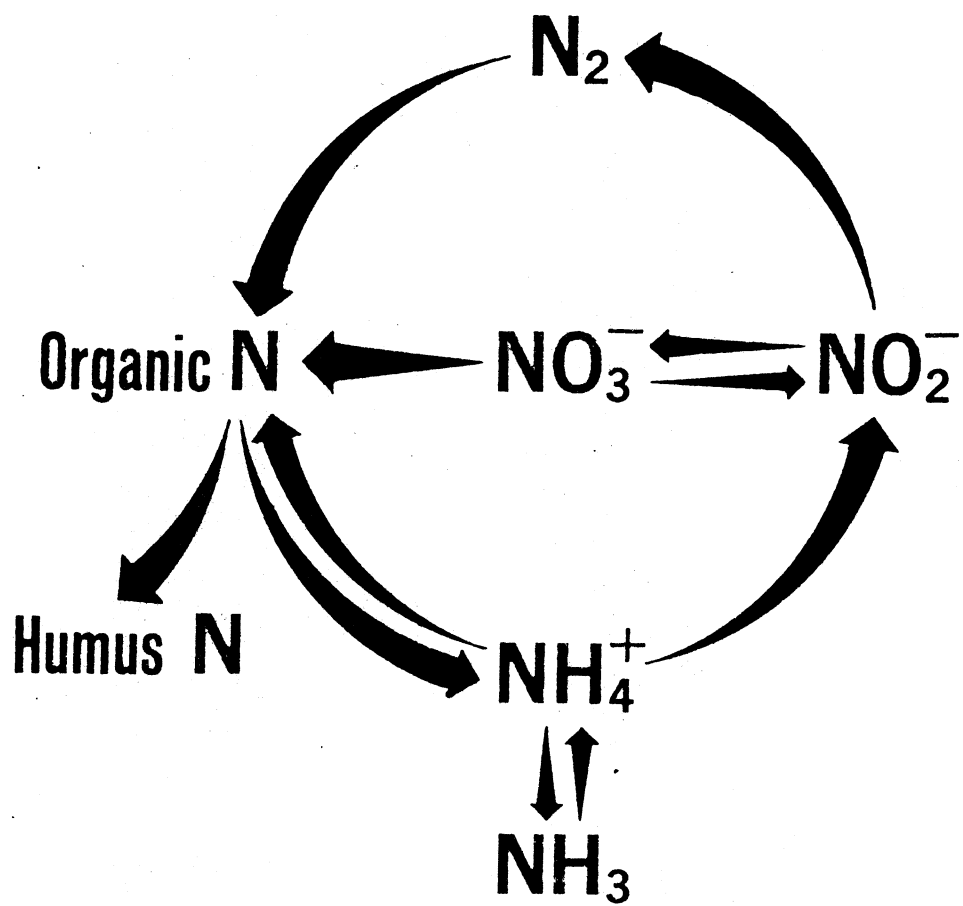


Figure 1. Classical Nitrogen Cycle

and algae (5). The presence of nitrogen compounds, particularly nitrate, has therefore been taken as an indication of pollution for many years.

The sources of NO_3^- found in public water supplies have been attributed to: (1) fertilizers, (2) reclaimed waste water used for irrigation, (3) leaching waste from sewage disposal areas, (4) subsequent leaching and deposition of NO_3^- due to bacterial oxidation of plant nutrients, (5) animal waste from feed lots, and (6) runoff from agricultural and nonagricultural land. Other potentially dangerous sources of NO_3^- have been pointed out by Goldberg (22).

Katta (26) showed that the NO_3^- concentration in some Oklahoma soils fertilized with 67 Kg N/ha averaged 10 PPM NO_3^- from the surface down to the perched-water table and increased to higher values in the free or drainage water. Hassan (23) found that excessively high fertilization rates (1790 Kg N/ha) resulted in the accumulation of 400 PPM NO_3^- at a six-foot depth under bermuda grass. High NO_3^- levels were also noted at a six-foot depth below heavily fertilized (670 Kg N/ha) Georgian soil by ✓ Boswell and Anderson (10). Some of the soils used in their experiments were left fallow and some cropped. The level of NO_3^- found at six-foot depth as a result of this treatment varied by only about 20 PPM with the highest amount existing under fallowed soils. Stewart et al. (44) reported that the repeated application of fertilizer N can lead to a build-up of NO_3^- in soils, particularly those with medium heavy textures. Their data showed that after a seven-year annual application of fertilizer at a rate of 200 lbs N/acre to continuous corn, a high of 875 lbs/acre of NO_3^- -N was found in the 0 to 8 foot depth of clay pan soil, up to 700 lbs N/acre in a silty soil, and up to 375 lbs N/acre in a silt loam. MacGregor et al. (30) recently published results of 15-year fertilization

studies of continuous corn on Forman clay loam in West Central Minnesota showing maximum corn yields sustained by applying N in quantities equivalent to that removed in the grain, with little increase in soil $\text{NO}_3\text{-N}$ when optimum fertilizer -N was applied. In contrast, Nelson and MacGregor (32) reported an analysis of results from a similar long-term continuous corn study on tile drained Webster loam on the southwest experiment station near Lamberton, Minnesota, which showed that 70 percent more N was applied to obtain maximum grain yields than was removed in corn grain. Evidently significant quantities of fertilizer -N were either immobilized by incorporation into organic matter, or were lost by leaching, tile drainage, or denitrification, since there was no significant net increase in soil $\text{NO}_3\text{-N}$. In a subsequent study, Gast et al. (21) reported the same results for Webster loam soil with maximum $\text{NO}_3\text{-N}$ accumulation accounted for less than half of the fertilizer -N added but unrecovered in the corn grain. In comparison with Cl^- accumulation in the same soil profiles and by assumption that Cl^- and NO_3^- move with water at about the same rate, Gast and coworkers concluded that downward leaching losses are apparently minimal, leaving denitrification and/or incorporation into organic matter as the mechanisms largely responsible for disappearance of the unused fertilizer -N.

✓ Sommerfeldt and Smith (42) studied the movement of nitrate nitrogen in dryland soils under native grass of southern Alberta, and reported that it took six to eight years after N was applied at the rate of up to 976 Kg/ha to reach a depth of 180 cm. Under seeded grasses, there was no evidence of $\text{NO}_3\text{-N}$ accumulation two years after single application of N at rates up to 944 Kg/ha. However, after repeated annual applications of N that totaled up to 3776 Kg/ha over a four-year period, $\text{NO}_3\text{-N}$

accumulations were found at depths of 90 to 120 cm.

Nitrate is the form of N that is most mobile and is of greatest concern from the standpoint of leaching losses and movement into water supplies. Leaching of nitrates constitutes one of the main channels of outgo of nitrogen from soils. The movement of the nitrate is closely related to the movement of the soil water. The amounts of nitrogen lost will depend on a large number of variables. Among the more important of these variables are:

1. Form and amount of soluble and unadsorbed nitrogen present or added;
2. Amount and time of rainfall;
3. Infiltration and percolation rates which are markedly affected by soil composition, texture, structure, depth of profile, and surface treatment;
4. Water-holding capacity of the soil and its moisture content throughout the profile at the time a rain occurs;
5. Presence or absence of a crop and its growth characteristics;
6. Evapotranspiration;
7. Rate of removal of the nitrogen by the crop; and
8. Extent to which there is an upward movement of nitrogen in the soil during periods of drought (2).

✓ Wetselaar (50) has shown that the nitrate movement is not due to a complete displacement of the soil solution by the rainwater, but there occurs a gradual dilution out of the top soil. As more and more water enters the soil, the nitrate level in the top soil may approach zero but increases markedly at levels of 1, 2, 3 or more feet. Under the conditions of Wetselaar's experiments on a fallow clay loam where 23.7

in. of rain fell during a six-month period, the mean movement of the nitrate ion was 1.075 in. for each inch of rainfall. There was a positive correlation of 0.946 between mean movement and rainfall.

✓Bates and Tisdale (7) conducted a laboratory experiment in which the movement of nitrate nitrogen through columns of coarse textured soil materials was studied. Their results indicate that 3.29 cm of water added to so-called large pore space aggregate leached 63.2 percent of nitrogen and 34.1 percent in smaller soil aggregate. They found that the mean movement of nitrates was related to pore space distribution of the soil when this pore space distribution was expressed as a porosity index.

The pattern of downward movement of nitrate in soil of different textures and structures differs markedly. ✓Shaw (40) states that there is little difference in the amount of rain required to remove nitrate from surface layers of light or heavy soils, but heavy and continuous rain is required to remove nitrate completely from either type of soil. In a laboratory experiment, ✓Wallace and Smith (48) observed that when nitrate was added to the surface of a two foot column of loam soil at field capacity, approximately 10 in. of water was required to leach 50 percent of the added nitrogen from the column, and 16 in. to remove 98 percent of the nitrogen. ✓Boswell and Anderson (10) reported a marked retardation of nitrogen movement on two widely differing Georgian bare soils. Their data showed that after five weeks and two inches of rainfall on a Marlboro loamy sand, almost all of the applied N was found in 0-3 and 3-6 in. layers. After 20 weeks and 27 inches of rainfall on sandy clay loam, and 17 weeks and 10.3 inches of rainfall on the loamy sand, almost all of the applied N was still found in the top 2 to 3 ft

of both soils. In a recent study by Endelman et al. (19) conducted in Wisconsin in 150 cm depth lysimeters containing Plainfield loamy sand, they showed that the movement of $\text{NO}_3\text{-N}$ was 15 to 20 cm/day under 2.5 cm water application. The authors concluded that additional rainfall of 7.5 to 10 cm, or irrigation, or both can rapidly move $\text{NO}_3\text{-N}$ beyond the rooting depth of 45 to 60 cm.

The interest in pollution control has resulted in a rapid expansion of studies to characterize and control the movement and accumulation of nitrogen in the soil. Corey et al. (15) studied the effect of water flow velocity and water content of the soil column on nitrate movement. They reported that the amount of nitrate immobilized by microbial activity is related to the velocity of flow. At a velocity of 1.32 cm/hr no added nitrate was immobilized, but at 0.11 cm/hr 21 percent of the added nitrate was immobilized. Also, loss of added nitrate was lower when the soil solution was flowing than when the soil solution was stationary. Under unsaturated flow conditions a net gain of 5 percent more nitrate was observed. In a recent study by Balasubramanian et al. (6) they reported that the mobility of applied fertilizer N in the aggregated Molokai silty clay soil was low relative to that of water. Nitrate retention was further enhanced when applied fertilizer was equilibrated (nitrate application followed by a one-week equilibration time before the first leaching) with the soil before irrigation. The authors stated that "equilibration prior to irrigation apparently allows bulk flow and diffusion of nitrate into aggregate micropores where the solute is less susceptible to transport in macropore water. This temporary detention of fertilizer nitrate in aggregate micropores may significantly reduce the possibilities of ground water contamination by nitrate."

To characterize N transformations in a soil system Lance and Whisler (28) studied the nitrogen balance in soil columns and reported that in short, frequent cycles of flooding soil columns (2 days flooded and 5 days dry) with secondary sewage effluent caused no net removal of N but transformed almost all of the N to nitrate. The net N removal during longer cycles (9 to 23 days flooded and 5 days dry) was 30 percent. Flooding periods longer than 9 days did not consistently increase net N removal, and N removal ceased after 80 days of continuous flooding. Lance and Whisler stated that much of the net N removal was attributed to denitrification, with N leaving the columns as dissolved N_2 during the flooding period and by diffusion during the dry period.

One of the sources of NO_3 that is found in public water supplies is land disposal of liquid sewage sludge. The pattern of sludge application can be adjusted to supply adequate N for maximum crop production but prevents excessive applications which would lead to NO_3 -N pollution of ground water. King (27) stated that incorporation of the sludge with the soil resulted in a greater accumulation of NO_3 -N and lower gaseous losses than when the sludge was left on the surface. Therefore, when the primary purpose of land application is for maximum N utilization by crops, sludge should be incorporated when feasible.

Since dissolved nitrates move with the water, there may occur a considerable upward movement of any such nitrogen present during long periods of drought. In practice this reverse movement is usually limited to the upper 12 to 18 in. of soil (49).

One of the more important developments is the emphasis that has been put on precipitation-evapotranspiration data (2). If during a period of a few days evapotranspiration exceeds precipitation, obviously

there can be no leaching if soil moisture was not above field capacity initially. When precipitation exceeds evapotranspiration, leaching can occur after the soil has reached field capacity. Such studies show that during the period of about May to October there is little likelihood of loss of nitrates from regions where the annual rainfall is below 50 in. unless the soil is very sandy or the rainfall is unusually heavy during short periods. In the winter months, however, much movement of water through the soil profile may be expected unless the soil is frozen. These studies emphasize how essential it is to avoid the accumulation of nitrates in soils during the late summer and fall months except of course where rainfall is so low that leaching is not of common occurrence.

A great deal of information is available on nitrogen behavior in soil and the NO_3 leaching from the plant-soil system in relation to climate and the nature of the soil and crop. Thomas (47) and Stewart (43) have reviewed some of the more important factors. In both of these reviews, the authors strongly emphasized the importance of the rainfall or quantity of drainage water as a factor in leaching of NO_3 .

The downward movement of water, other than that in capillary pores of the soil, is rather rapid through the macropore systems of medium-textured soils. The larger the volume of this system, the more readily the water will move. The presence of a crop, however, tends to reduce this movement because of evapotranspiration. The crop, therefore, greatly minimizes leaching losses of nitrogen both directly, by assimilation, and indirectly, by reducing the amount of leachate.

✓ Morgan et al. (31) and Allison (1) studied the effect of cropping systems, using 28-in. lysimeters filled with Merrimac sandy loam and

receiving 200 lbs of Calurea nitrogen annually for ten years. The percentages of the added plus that released from the soil that were collected in the leachates were: fallow 83, tobacco 42, tobacco and oat cover crop 23, and grass sod 14. Most of the loss from the grass sod apparently occurred before the sod was well established.

An 11-year experiment, conducted by Karraker et al. (25) in Kentucky in 26-inch deep lysimeters containing Maury silt loam that received no fertilizer nitrogen, shows the importance of continuous plant cover. The average annual nitrogen contents of the leachate in pounds per acre from the various cropping treatments were: uncropped 74, Korean lespedeza 58, Korean lespedeza plus bluegrass 20, Korean lespedeza and rye cover crop 15, alfalfa 9, alfalfa plus bluegrass 2, and bluegrass alone 5.

Allison et al. (3) reported experiments conducted in South Carolina in lysimeters 5 feet wide and 30 inches deep containing Lakeland sand. Those that were fertilized annually for five years with a mixture of animal manure and commercial nitrogen at the rate of 131 pounds of nitrogen per acre lost only 3 percent of this in the leachates where the cropping system was Millet and small grain cover. The leaching losses from this coarse sand were larger for most other treatments.

Rural runoff of agricultural land has been described as a major source of nitrate contamination of water supplies. Approximately 742 million hectares of rural land in the United States produce runoff, and it has been estimated that from 750,000 tons of N from rural agricultural land and from 200,000 to 950,000 tons of N from nonagricultural land is deposited into public water supplies annually. Agricultural drainage waters contain N concentrations ranging from 1 to 60 PPM, mostly in NO_3

form (22). The nitrate -N losses in runoff from a natural "1000-acre lysimeter," located on granitic soils over granite or gabbro near Riverside, California, were investigated by Davis et al. (16) and compared with the 135 pounds of N as urea per acre applied annually in split applications to the citrus grove. The loss in 1966 and 1967, respectively, were 57 and 72 pounds per acre, amounting to 42 and 53 percent of the N applied. NO_3 -N concentrations of the drainage were generally above 10 PPM. Both the amount of N and irrigation applied were excessive according to Davis and coworkers. In a subsequent paper, Bingham et al. (9) gave additional data for 1968 and 1969. Nitrogen losses in runoff and percolate for 1967 were 45.6 pounds per acre, for 1968 were 55.1 pounds, and for 1969 were 69.6 pounds. They stated that nitrogen in drainage averages about 45 percent of the nitrogen applied. Average NO_3 concentration of percolate for any two-month period in the three years ranged from 37 to 81 PPM.

Doneen (18) measured the nitrate in the tile effluents from three irrigated fields in the San Joaquin Valley and compared the results with the nitrate in the saturation extracts of two adjacent virgin land sites that had never been irrigated. One field had grown cotton, rice, barley, and lettuce in the 1962-1966 period. The average annual application of N fertilizer was 167 pounds per acre. The irrigation water contained 1.7 PPM of nitrate -N. Water applied ranged from 7.4 to 12.1 feet per year. The NO_3 -N in the tile effluent averaged 44.5 PPM, which was two to four times the concentration of the saturation extract of the profile samples. Another field had been cropped to tomatoes, cotton, wheat, safflower, barley, and lettuce. Annual application of fertilizer N had been about 100 L.b.S/acre. Water application ranged from 2.5 to 6.1

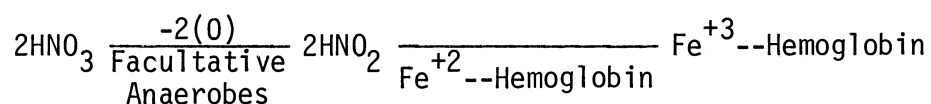
feet per year and contained 2.1 PPM of $\text{NO}_3\text{-N}$. The average $\text{NO}_3\text{-N}$ concentration of the drainage water was 23 PPM.

Timmons et al. (46) conducted a definitive study on the loss of crop nutrients through runoff of some Minnesota soils. Their results indicated that 29 Kg N/ha was lost in 1966, with a high of 9.65 cm of runoff, and 101 Kg N/ha was lost in 1967, with a high of 11.8 cm of runoff. The majority of the N lost in this experiment was in the NO_3 form. Similar studies by Schuman et al. (40) on nitrogen losses from surface runoff from four field-size watersheds in southwestern Iowa, during 1969, 1970, and 1971, in which a contour-planted corn watershed was N-fertilized at the rate of 168 Kg/ha. They reported that 5.36 Kg N/ha was lost during 1969, with a high of 5.97 cm of runoff, 26.06 Kg N/ha was lost during 1970, with a high of 4.55 cm of runoff, and 43.75 Kg N/ha was lost in 1971, with a high of 9.75 cm of runoff. Nitrogen losses associated with sediment in the runoff accounted for 92 percent of the total loss for the three-year period. The three-year average annual solution N losses were low, only amounting to 1.89 Kg N/ha mostly in NO_3 form. The authors strongly emphasized the importance of erosion control practices as a first step in eliminating N as a pollutant in surface runoff.

One way to control the erosion is by tillage methods. The effect of fine tillage methods (coultter-plant; till-plant; chisel-plant; disk and coultter-plant; and conventional-plant) on the N composition in runoff water and runoff sediment from corn plots was studied by Römken et al. (39) on Bedford silt loam soil by applying simulated rainstorms. They reported that coultter and chisel systems controlled soil loss, but runoff water contained high levels of soluble N. Conventional tillage,

with fertilizer plowed under, had the highest losses of soil and water but small loss of soluble N. However, high percentages of the total N removed by runoff was a component of the sediment from all treatments.

The most alarming problem with high NO_3^- levels in ground water aquifers is the possible deleterious effects on human and animal health. Nitrate toxicity can result in abortions, lowered productivity and other problems in animals. With humans, only infants under six months of age (apparently not on solid food) suffer lethal effects (52). Burden (13) reported that NO_3^- toxicity is a result of microbial reduction of NO_3^- to NO_2^- in the lower intestine of human adults and in the stomach of human infants (pH above 5.0) suffering from achlorhydria.



Nitrates are absorbed directly into the bloodstream from the stomach where it reacts with ferric iron in hemoglobin to yield ferrous iron hemoglobin (methemoglobin), which cannot support oxygen transport. For cattle, the lethal rate for potassium nitrate is 1 gm/Kg, and for rabbits and pigs, 90 mg/Kg. The United States National Research Council (1963) recommends that any water containing over 10 PPM of NO_3^- -N is unfit for consumption by infants. The United States Public Health Service (1962) recommends that drinking water containing more than 45 PPM NO_3^- is unfit for human consumption. High NO_3^- levels in irrigation water can be detrimental to agriculture. The quality and yield of crops such as grapes and sugar beets can be reduced if excessive amounts of N are applied at the wrong time (45). Industrial processes may also be adversely influenced by high N concentration in water.

From a review of the literature, it seems that very little has been done to locate the source of NO_3^- contamination of water supplies in Oklahoma. Therefore, the objective of this study was to determine the accumulation and flow pattern of NO_3^- through soil columns which were heavily fertilized with nitrogen.

CHAPTER III

MATERIAL AND METHODS

The soil used in this study was Teller sandy loam from the Perkins Experimental Station at Perkins, Oklahoma (see Appendix for detailed soil description). The soil samples used in this study were from an area where nitrate-type fertilizers have been used for long periods of time.

The distribution of nitrates in the soil was studied by taking samples from the surface down to the depth of 152 cm. All soil samples were placed in plastic (polyethylene) bags and removed to the agronomy farm at Stillwater, Oklahoma. The samples were air dried and then ground to pass a 5 mm mesh sieve.

Twelve soil columns constructed of polyvinyl carbonate (20.3 cm-I.D., 183 cm in length) were carefully packed; in the inverse order the sample was removed from the field to a height of 152 cm. The soil was removed from the earth and packed in the soil column so that it would represent a homogenous soil profile.

Mercury-regulated tensiometers and suction cups were inserted at 30 cm intervals throughout each column. The tensiometers measure soil-water tensions at each depth and provide data necessary to calculate the rate of water movement between successive depths within the soil profile. Periodic eight-water sampling of the soil-water as it moves through the soil profile is achieved by pulling a small vacuum across the inserted

suction cups. A schematic representation of the soil column is shown in Figure 2.

The experiment was also utilized to monitor and establish the movement characteristics of various solutes and particulate matter in soil-water (e.g., Ca^{++} , Mg^{++} , K^+ , and Na^+).

After each soil column was carefully packed, they were eluted with tap water (nutrient concentrations of .4 PPM $\text{NO}_3\text{-N}$, 21 PPM Na^+ , 4 PPM K^+ , 40 PPM Ca^{++} , and 11 PPM Mg^{++}) to remove native NO_3 and allowed to settle to give a bulk density comparable to the field condition. A siphon apparatus was used to maintain a constant 10 cm water head above the surface soil level. Consequently, after two months, the amount of water moving through the column was established to be constant at a rate of .05 cm/hr. Subsequently, a column was amended with 620 Kg of N/ha as $\text{Ca}(\text{NO}_3)_2$ dissolved in 100 ml of water. This solution was then added to the existing 10 cm water head (approximately 3294 cm^3) and allowed to move through the soil profile under normal gravitational forces.

Water samples were collected at 30, 60, 90, and 120 cm depths within the soil profile via the inserted suction cups and also at the outflow until the bulk of the added nitrogen had moved through the column. The elapsed time was approximately $3\frac{1}{2}$ months. The NO_3^- content of each sample was determined via a specific ion electrode. Prior to NO_3^- analysis, all samples were treated with phenyl mercuric acetate to retard microbial growth.

The content of NH_4 and $\text{NO}_2\text{-N}$ in the water extract was determined by Micro-Kjeldahl technique and Modified Griess-Llosvay Method (11).

Analysis of the Mg^{++} , Ca^{++} , K^+ , and Na^+ in water extract were determined with an atomic absorption spectrophotometer (38).

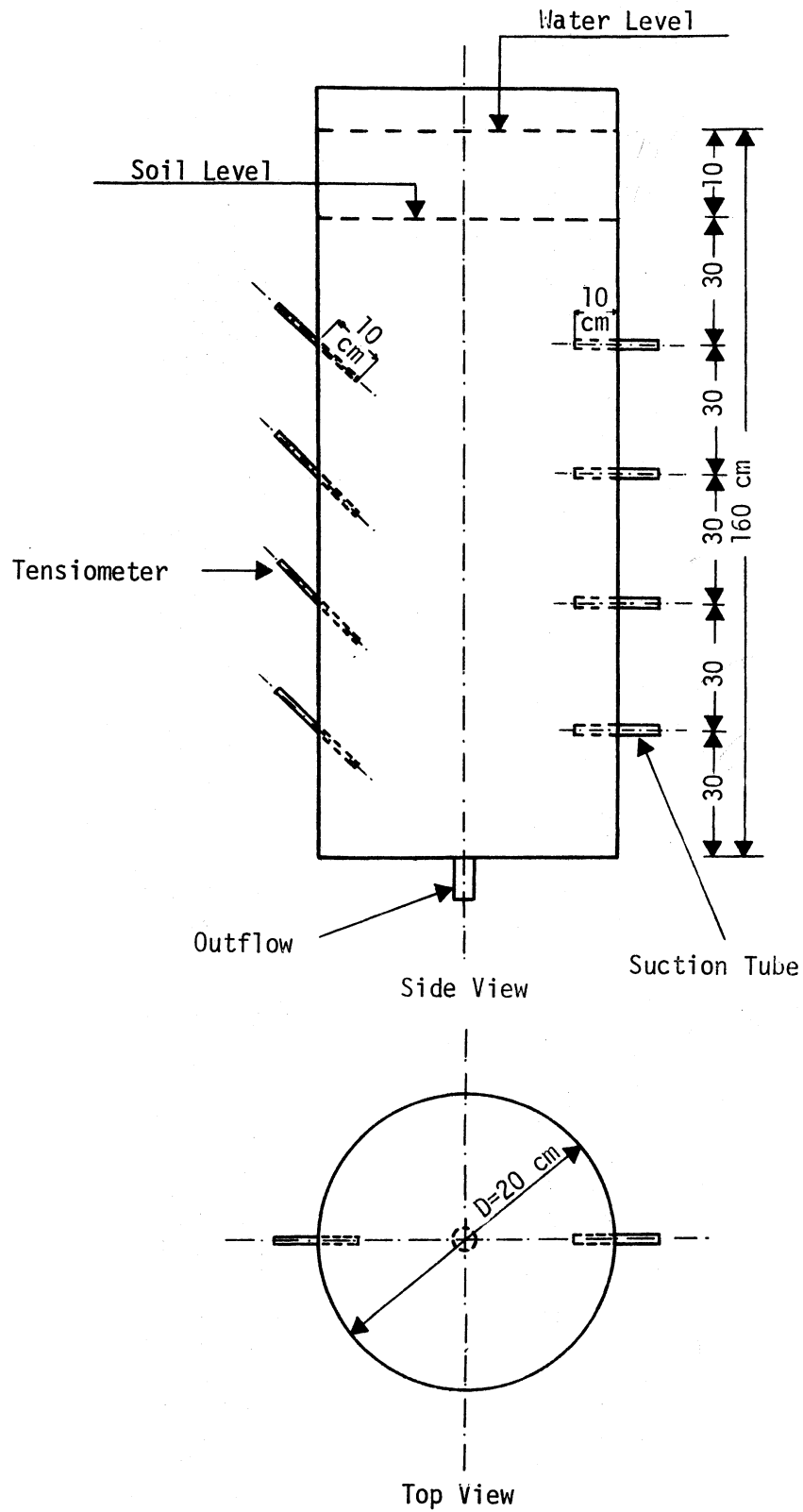


Figure 2. Diagrams of the Experimental Soil Column

Laboratory Analyses

Physical Analyses

Soil samples were air dried under laboratory conditions and processed sufficiently to pass through a 2 mm screen. Percents of sand, silt and clay were determined using the method outlined by Day (17). The soil-water characteristics for bulk density was determined for each soil depth increment using the undisturbed soil cores.

Chemical Analyses

Chemical analyses were conducted using the methods outlined below, which are employed by the Oklahoma State University Soil Chemistry Laboratory.

Soil reaction was measured by mixing a 1:1 paste of soil and distilled water and a 1:1 paste of soil and 1.0 N potassium chloride. The pH was then measured using a glass-electrode pH meter.

The extractable cations were determined using soil extracts obtained by washing the soil samples with ammonium acetate (38). Na^+ , K^+ , Mg^{++} , and Ca^{++} were estimated using atomic absorption and plotting the results against a standard curve.

The total potassium, sodium, calcium, and magnesium were determined using soil extracts obtained by digestion with hydrofluoric and perchloric acids (37). Total Na^+ , K^+ , Mg^{++} , and Ca^{++} were estimated using atomic absorption and plotting the results against a standard curve.

Extractable hydrogen was calculated by leaching the soil with barium chloride TEA solution and titrating the extract to a pink end-point using 0.25 N hydrochloric acid (35).

The cation exchange capacities were determined by washing the soil four times with 1N Ca Cl_2 . The excess salt was removed by washing the soils four times with deionized water and one time with 95% ethanol until the excess Ca Cl_2 was removed, as indicated by a negative Ag NO_3 test for Cl in the last of the washings. Finally, the Ca was replaced by means of four washings with 1N Na Cl_2 . The extract solution was then brought to the volume with distilled water and the Ca content was measured by versene titration to ice blue end-point, according to Jackson (24).

CHAPTER IV

RESULTS AND DISCUSSION

The data for textural components, bulk densities, and pore space of Teller fine sandy loam profile are summarized in Table I. The clay content of the soil profile ranged from 6% at the soil surface to more than 20% at greater depths. The percent sand ranged from 64% at the soil surface to 84% at the 150 cm depth. The soil bulk density was 1.602 g/cm^3 with slightly greater values occurring at the 150 cm depth. Percent pore space was 40.04% with slightly higher values in high clay horizon. This soil is heterogeneous, vertically and horizontally, with respect to its physical properties.

The chemical analyses of Teller fine sandy loam profile is presented in Table II. Initial soil $\text{NO}_3\text{-N}$ concentration ranged from 8.8 PPM at the soil surface to >1 PPM at greater depths. Initial soil pH was 6.2 in 1:1 paste of soil and distilled water and 5.65 in 1:1 paste of soil and in potassium chloride. The cation exchange capacities ranged from 4.50 m.e./100g in the surface to 9.79 m.e./100g at the 60 cm depth and decreases to 4.15 m.e./100g at the 150 cm depth. The exchangeable H^+ , Ca^{++} and Mg^{++} dominated the exchange complex.

The Distribution pattern of $\text{NO}_3\text{-N}$ in the 30 cm depth of the treated column is presented in Table III and Figure 3. Nitrate-nitrogen concentration peaked to 639 PPM within 9.3 days and gradually decreased with increasing time. At this depth $\text{NO}_3\text{-N}$ exhibited a more rapid rise and

TABLE I
 PHYSICAL ANALYSES OF A TELLER FINE SANDY LOAM PROFILE
 (AGRONOMY EXPERIMENT STATION, PERKINS, OKLAHOMA)

Depth cm	Sand ^{***} %	Silt %	Clay ^{***} %	Texture	Bulk Density* g/C _c	Pore Space** %
15	64	30	6	SL	--	--
30	62	30	8	SL	1.575	39.88
45	60	26	14	SL	--	--
60	66	14	20	SCL	1.6060	40.95
75	58	22	20	SCL	--	--
90	64	16	20	SCL	1.5959	41.32
105	68	12	20	SCL	--	--
120	70	12	10	SL	1.612	39.16
135	84	8	8	LS	--	--
150	84	8	8	LS	1.620	38.87

* ρ_B Bulk Density = $\frac{M_s}{V_t}$, where M_s = soil mass; V_t = total volume.

** % Pore Space = $(1 - \frac{\rho_B}{\rho_p}) \times 100$.

*** ρ_p were assumed to be 2.65 and 2.72 for sand and clay, respectively.

TABLE II
 CHEMICAL ANALYSES OF A TELLER FINE SANDY LOAM PROFILE
 (AGRONOMY EXPERIMENT STATION, PERKINS, OKLAHOMA)

Depth cm	pH 1:1		C.E.C.	Exchangeable Cation, MeQ/100g					PPM NO ₃ -N
	H ₂ O	K _{Cl}		H ⁺	Ca ⁺⁺	Mg ⁺⁺	K ⁺	Na ⁺	
15	6.0	5.9	4.50	1.25	1.11	.58	.32	.08	8.80
30	6.0	5.7	5.05	1.50	1.03 ⁻	.57	.24	.11	5.00
45	6.4	6.1	7.01	2.25	1.96	1.65	.69	.09	2.40
60	6.3	6.0	9.79	4.25	2.66	2.96	.95	.15	1.65
75	6.4	6.1	9.37	4.00	2.57	2.55	.95	.11	1.65
90	6.3	5.4	9.28	2.75	2.70	2.80	.91	.11	1.70
105	6.1	5.5	9.20	3.00	2.50	2.92	.90	.11	1.65
120	5.9	5.0	6.66	3.00	1.36	1.81	.18	.09	1.15
135	6.25	5.7	4.16	.50	1.20	1.60	.17	.11	1.35
150	6.3	5.1	4.15	.50	.78	1.07	.13	.09	>1

TABLE III
 DISTRIBUTION PATTERN OF NO₃-N CONCENTRATION AND
 SOLUTION pH IN 30 CM DEPTH OF TELLER SANDY
 LOAM PROFILE AS A FUNCTION OF TIME

Time Days	ml of Sample Collected	NO ₃ -N Conc. PPM	NO ₃ -N Conc. γ	pH
1	25	1.10	27.50	8.03
2	25	1.55	38.75	8.29
3	25	1.40	35.00	8.16
4	25	1.40	35.00	7.67
5	25	12.40	310.00	8.07
6	25	80.00	2000.00	8.05
7	25	312.00	7800.00	7.69
8	25	549.00	13725.00	7.24
9	25	624.00	15600.00	7.23
10	25	507.00	12675.00	7.23
11	25	444.00	11100.00	7.78
12	25	366.00	9150.00	7.79
13	25	312.00	7800.00	7.48
14	25	264.00	6600.00	7.11
15	25	192.00	4800.00	7.67
16	25	138.00	3450.00	7.38
17	25	102.00	2550.00	7.80
18	25	78.00	1950.00	7.87
19	25	41.75	1043.75	7.95
20	25	24.00	600.00	7.91
21	25	11.10	277.50	7.72
22	25	3.30	82.50	8.19
23	25	1.60	40.00	7.71
24	25	1.00	25.00	8.25
25	25	1.05	26.25	8.21
30	25	1.15	28.75	8.01
35	25	1.05	26.25	7.66
40	25	1.05	26.25	7.85

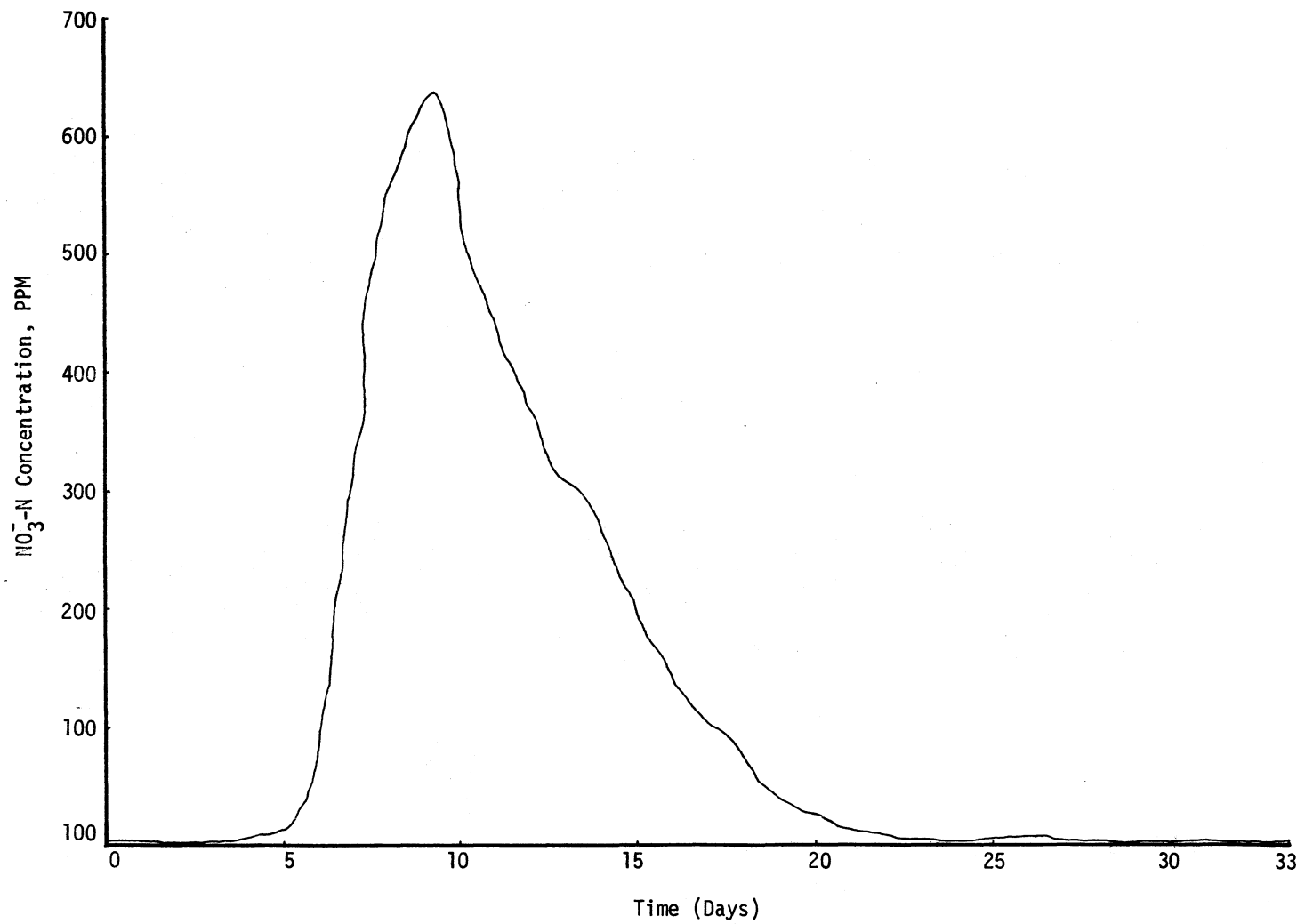


Figure 3. Distribution Pattern of $\text{NO}_3\text{-N}$ Concentration in the 30 cm Depth of the Soil Column as a Function of Time

subsequent decline than at greater depths in the soil column.

When one fluid displaces another, a mixing takes place between the two fluids which depends on the properties of the fluids and the material in which the fluids are contained. The processes which contribute to mixing in a porous material are basically two. The first is the variation in the pore velocity of the solution as it moves through the column. Since there is a distribution of pore sizes and shapes, there is also a distribution of velocities, which have both magnitude and direction. The second process is that of diffusion. This process, a result of random motion of the ions or molecules, occurs preferentially in one direction or another depending on the activity gradients which provide the driving force. These activity gradients depend in part on the variations in the pore velocity which is governed by the nature of the porous material (33). The progress of these two processes occurring simultaneously during displacement suggests the superposition of one upon the other to obtain a total impression of the mixing which occurs (8). Therefore, due to large pore distribution in the soil above the 30 cm depth, there will be less contact between the pores resulting in a continuous macropore system in which mixing becomes less complete.

Under a 10 cm constant water head, the average velocity of NO_3^- -N at the 30 cm depth was .1339 cm/hr. The average velocity of NO_3^- -N was determined by measuring the distance the nitrates traveled over a measured time. The total time required to move the added NO_3^- -N past the 30 cm depth was 40 days.

The effluent pH as a function of time is also presented in Table III. There is no significant change in concentration of Ph effluent in the 30 cm depth. However, the pH values in the effluent were higher

than the soil pH (Table II). The ions Ca^{++} , Mg^{++} , K^+ , and Na^+ leached from the soil column were probably responsible for the relatively high effluent pH. Also, under reducing conditions the pH of soils has been shown to increase when an acid soil was submerged (36).

The distribution pattern of NO_3^- -N in the 60 cm depth of the soil column is presented in Table IV and Figure 4. NO_3^- -N concentration peaked to 460 PPM within 16.3 days and gradually decreased with increasing time. Because of the larger number of small pores occurring at the 60 cm depth, the soil acts as "sink" for NO_3^- ions and a greater volume of water must pass through the soil in the higher clay horizon to reduce the NO_3^- ion to a low concentration. Therefore, mixing becomes more complete.

Under a 10 cm constant water head, the average velocity of NO_3^- -N at the 60 cm depth was .2083 cm/hr. The average velocity for nitrates was determined by measuring the distance the nitrates moved over a measured time. This higher velocity rate is due to small particle sizes present in the soil at the 60 cm depth. Since nitrate-nitrogen moves through the pore spaces of the soil in the water solution, the velocity of the NO_3^- -N depends directly on the soil particle size.

The pH of the effluent as a function of time is also shown in Table IV. There was no significant relation between NO_3^- -N concentration and effluent pH. Total time required to move all applied NO_3^- -N past the 60 cm depth was 40 days.

The distribution pattern of NO_3^- -N passing the 90 cm depth of the soil column is shown in Table V and Figure 5. Nitrate-nitrogen concentration peaked to 420 PPM within 20.6 days and gradually decreased with increasing time. This sandy clay loam region of the soil profile also

TABLE IV
 DISTRIBUTION PATTERN OF NO₃-N CONCENTRATION AND
 SOLUTION pH IN 60 CM DEPTH OF TELLER SANDY
 LOAM PROFILE AS A FUNCTION OF TIME

Time Days	MI of Sample Collected	NO ₃ -N Conc. PPM	NO ₃ -N Conc. γ	pH
1	5	1.50	7.50	8.31
2	5	2.00	10.00	8.38
3	5	1.95	9.75	8.32
4	5	1.70	8.50	8.46
5	5	2.00	10.00	8.02
6	5	1.88	9.40	8.42
7	5	1.75	8.75	8.47
8	5	2.55	12.75	8.38
9	5	19.90	99.50	8.29
10	5	75.60	378.00	8.02
11	5	132.00	660.00	7.92
12	5	205.00	1025.00	8.14
13	5	285.00	1425.00	8.29
14	5	416.00	2080.00	7.30
15	5	452.00	2260.00	7.74
16	5	416.00	2080.00	7.88
17	5	436.00	2180.00	7.76
18	5	414.00	2070.00	8.02
19	5	385.00	1926.00	8.01
20	5	225.00	1125.00	7.80
21	5	227.50	1137.50	8.05
22	5	182.00	910.00	8.26
23	5	125.00	623.00	8.34
24	5	105.00	525.00	8.30
25	5	70.80	354.00	8.50
30	5	15.50	77.50	8.24
35	5	5.00	25.00	8.43
40	5	4.20	21.00	8.22

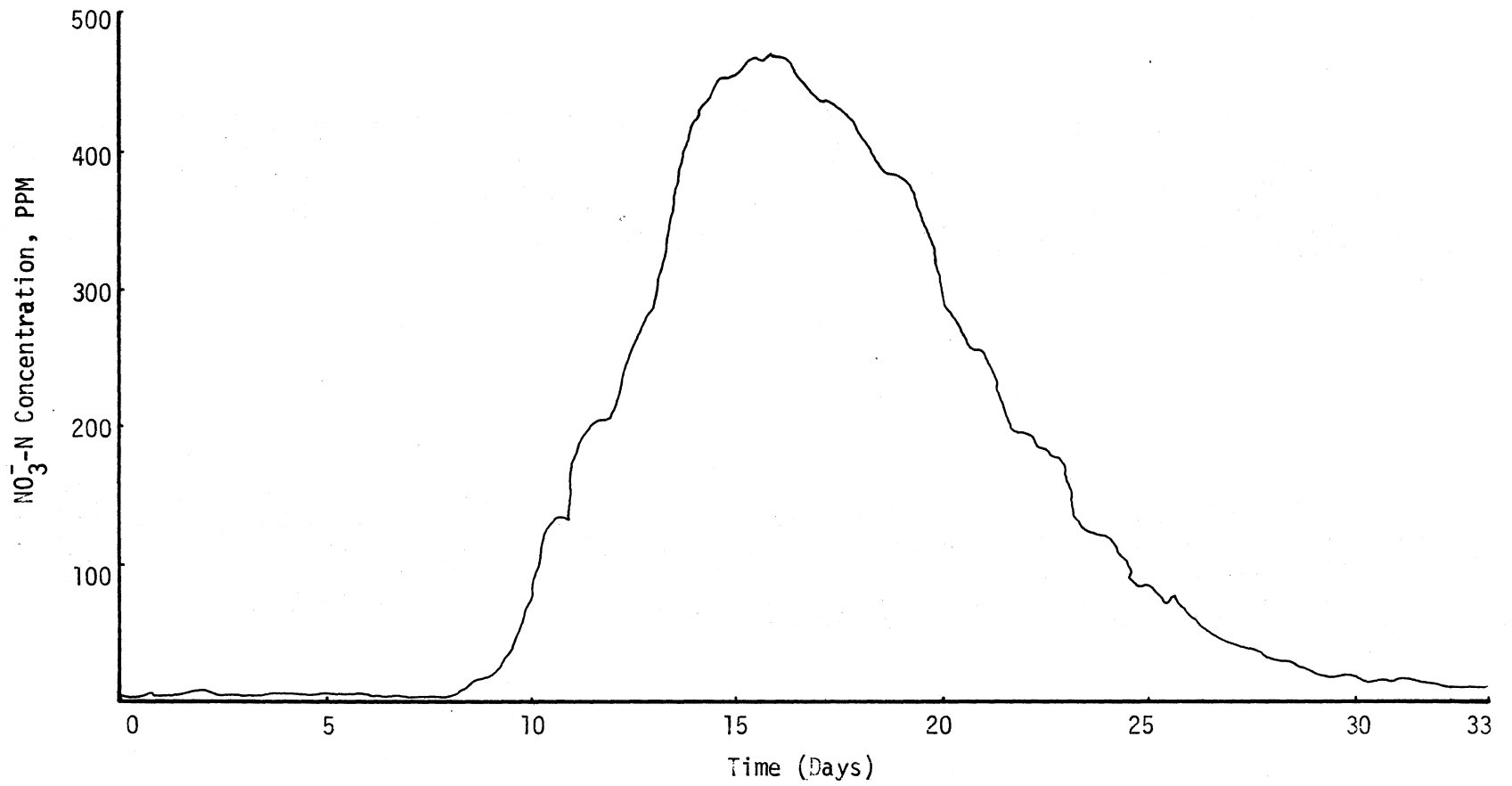


Figure 4. Distribution Pattern of NO_3^- -N Concentration in the 60 cm Depth of the Soil Column as a Function of Time

TABLE V
 DISTRIBUTION PATTERN OF NO₃-N CONCENTRATION AND
 SOLUTION pH IN 90 CM DEPTH OF TELLER SANDY
 LOAM PROFILE AS A FUNCTION OF TIME

Time Days	MI of Sample Collected	NO ₃ -N Conc. PPM	NO ₃ -N Conc. γ	pH
1	10	2.60	26.00	7.80
2	10	1.80	18.00	8.07
3	10	1.85	18.50	8.17
4	10	1.55	15.50	7.96
5	10	1.45	14.50	8.31
6	10	1.50	15.00	8.30
7	10	1.72	17.20	8.04
8	10	1.72	17.20	8.05
9	10	1.30	13.00	8.14
10	10	2.40	24.00	8.17
11	10	4.65	46.50	8.04
12	10	17.50	175.00	8.21
13	10	43.00	430.00	7.99
14	10	72.50	725.00	8.07
15	10	126.00	1560.00	7.35
16	10	210.00	2100.00	7.40
17	10	306.80	3068.00	7.23
18	10	340.00	3400.00	7.13
19	10	410.00	4100.00	6.97
20	10	400.00	4000.00	6.85
21	10	395.50	3955.00	7.07
22	10	339.50	3395.00	7.07
23	10	287.00	2870.00	7.10
24	10	258.00	2580.00	7.15
25	10	195.00	1950.00	7.30
30	10	16.00	160.00	7.50
35	10	6.30	63.00	7.65
40	10	3.90	39.00	7.67

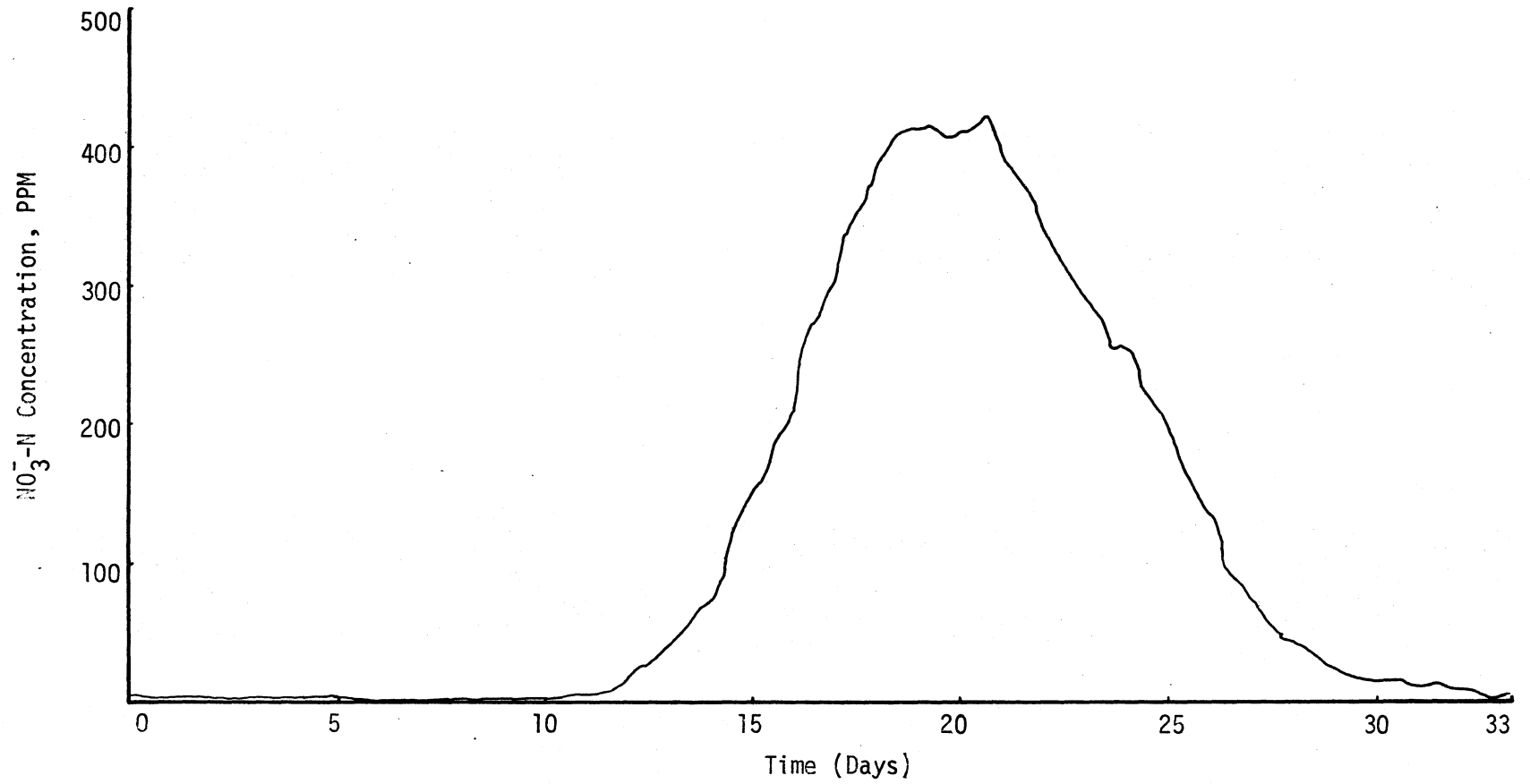


Figure 5. Distribution Pattern of NO_3^- -N Concentration in the 90 cm Depth of the Soil Column as a Function of Time

tended to exhibit a substantial decrease in vertical velocity of the NO_3^- -N ion which is probably due to a larger percentage of clay present at the 90 cm depth. Thus, more complete NO_3^- -N distribution occurs.

Under 10 cm constant water head, the average velocity of NO_3^- -N was determined by measuring the distance the nitrates traveled over a measured time. The movement of NO_3^- -N through the 90 cm depth of the soil column was .3125 cm/hr. There was no significant change found in effluent pH (Table V). The total time required to move the applied NO_3^- -N past the 90 cm depth was 40 days.

The distribution pattern of NO_3^- -N in the 120 cm depth of the soil column is presented in Table VI and Figure 6. NO_3^- -N concentration peaked to 360 PPM within 25.3 days and gradually decreased with increasing time. Because of the higher percentage of sand in this horizon at the 120 cm depth, mixing becomes less complete than in the higher clay horizons and flow is dominated more by the larger pores between aggregates. Levin (29) reports that aggregation and rate of leaching do not greatly affect the depth of maximum concentration of NO_3^- -N under saturation condition but does influence the distribution about that depth.

Under a 10 cm constant water head, the average velocity of NO_3^- -N at the 120 cm depth of the soil column was .2085 cm/hr. The average velocity for nitrates was determined by the distance the nitrates moved over a measured time. There was early relatively high concentration of NO_3^- -N in the leachate at the 120 cm depth of the soil column (Table VI). This is believed to be due to mineralization of native soil humus and not from the $\text{Ca}(\text{NO}_3)_2$ initially added. There was no significant change found in pH of the effluent (Table VI). The total time required to move NO_3^- -N past the 120 cm depth of the soil column was 50 days.

TABLE VI
 DISTRIBUTION PATTERN OF NO₃-N CONCENTRATION AND
 SOLUTION pH IN 120 CM DEPTH OF TELLER SANDY
 LOAM PROFILE AS A FUNCTION OF TIME

Time Days	MI of Sample Collected	NO ₃ -N Conc. PPM	NO ₃ -N Conc. γ	pH
1	30	20.00	600.00	7.27
2	30	13.20	396.00	7.57
3	30	8.90	267.00	7.42
4	30	6.00	180.00	7.52
5	30	3.40	102.00	7.67
6	30	2.25	675.00	7.94
7	30	1.90	57.00	7.52
8	30	1.98	59.40	7.49
9	30	1.90	57.00	7.37
10	30	1.50	45.00	7.66
11	30	1.55	46.50	7.35
12	30	1.85	55.50	7.22
13	30	1.70	51.00	7.09
14	30	2.50	75.00	7.07
15	30	4.20	126.00	7.04
16	30	11.20	336.00	7.07
17	30	20.00	600.00	6.88
20	30	84.00	2520.00	6.89
21	30	140.40	4212.00	7.01
22	30	216.00	6480.00	7.06
23	30	264.00	7920.00	7.15
24	30	304.00	9120.00	7.34
25	30	361.00	10830.00	7.27
26	30	320.00	9600.00	7.22
27	30	312.00	9360.00	7.13
30	30	180.00	6400.00	7.30
35	30	37.00	1110.00	7.28
40	30	8.30	249.00	7.74
45	30	5.70	171.00	7.80

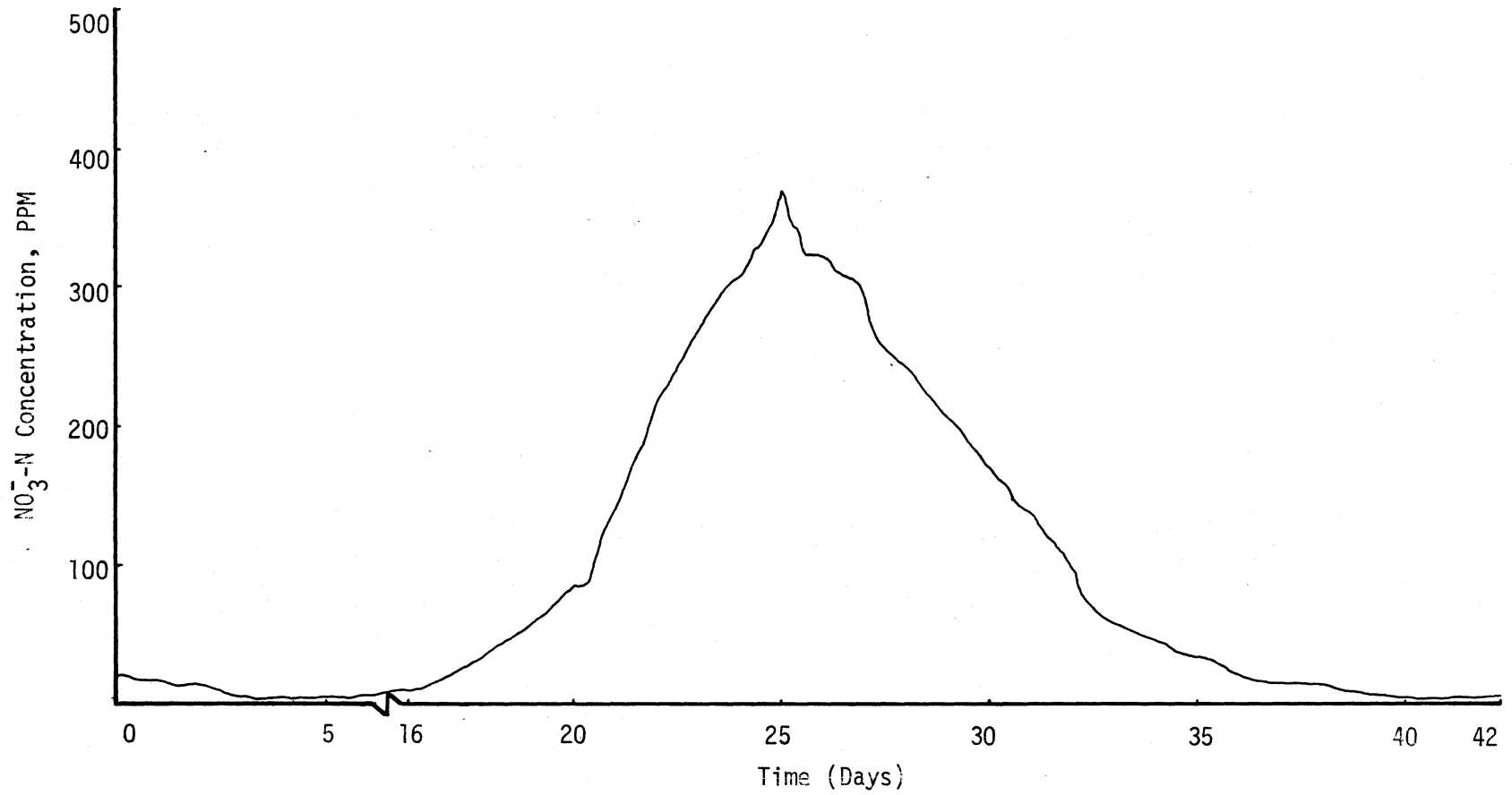


Figure 6. Distribution Pattern of NO_3^- -N Concentration in the 120 cm Depth of the Soil Column as a Function of Time

The distribution pattern of NO_3^- -N at the 150 cm depth of the soil column (outflow) is presented in Table VII and Figure 7. NO_3^- -N concentration peaked to 336 PPM within 33 days and gradually decreased with increasing time. The distribution pattern of NO_3^- -N through the 150 cm depth of the soil column is believed to be less complete. Because at the outflow water was drained via a 5/8 in. tube to the open atmosphere and resulted in air entrapment, an unsaturated condition was created. Desaturation eliminates the larger flow-paths and increases the proportion of water which does not readily move within the soil. The proportion of film water is significantly increased and the ion distribution within the various sized pores is modified according to changes in film thickness and pore saturation (8). The average velocity of NO_3^- -N in the outflow was .163 cm/hr. This slightly lower value of the average velocity is associated with the unsaturated condition created at the outflow and higher percentage of coarse sand present in the 150 cm horizon of the soil column. Consequently, mixing becomes less complete and is dominated more by the larger pores between soil particles.

A noticeable decrease in flow rate after 40 days (Table VII) was due to packing of the soil column. One inch of settling of the soil column had occurred during the study, resulting in compaction of the soil column, therefore reducing the flow rate. However, a siphon apparatus was regulated to maintain a constant 10 cm water head above the soil level. This settling effect is believed to have little effect, if any, for the flow regions of the upper layer, since after 40 days the bulk of NO_3^- -N had already passed through the 120 cm depth of the soil column. There was a relatively high detention of NO_3^- -N in the leachate at the beginning of the experiment as shown in Table VII and Figure 7.

TABLE VII

DISTRIBUTION PATTERN OF NO₃-N CONCENTRATION AND SOLUTION pH IN 150 CM DEPTH (OUTFLOW) OF TELLER SANDY LOAM PROFILE AS A FUNCTION OF TIME

Time Days	MI of Sample Collected	NO ₃ -N Conc. PPM	NO ₃ -N Conc. γ	pH
1	416	30.96	12,879.36	7.95
2	418	32.00	13,376.00	7.61
3	414	31.00	12,834.00	7.95
4	416	29.00	12,064.00	7.90
5	426	26.20	11,161.00	7.60
10	416	9.66	4,018.56	7.79
15	420	2.36	991.20	7.84
20	420	3.50	1,470.00	7.34
25	416	43.00	17,888.00	7.83
30	416	202.00	84,032.00	6.95
31	416	241.00	100,256.00	6.74
32	412	321.66	132,523.92	6.81
33	408	324.33	132,326.64	6.73
34	384	330.00	126,720.00	6.71
35	362	328.00	118,736.00	6.63
36	356	310.00	110,360.00	6.60
37	354	280.00	99,120.00	6.57
38	318	220.00	69,960.00	6.57
39	318	195.83	62,273.94	6.76
40	316	168.33	53,192.28	6.75
41	280	124.13	34,756.40	6.70
42	275	94.66	26,031.50	6.94
43	250	82.33	20,582.50	7.16
44	262	66.00	17,292.00	7.25
45	214	56.83	12,161.62	7.21
50	200	16.50	3,300.00	7.40
55	190	5.30	1,007.00	7.45
60	192	1.60	307.20	7.43

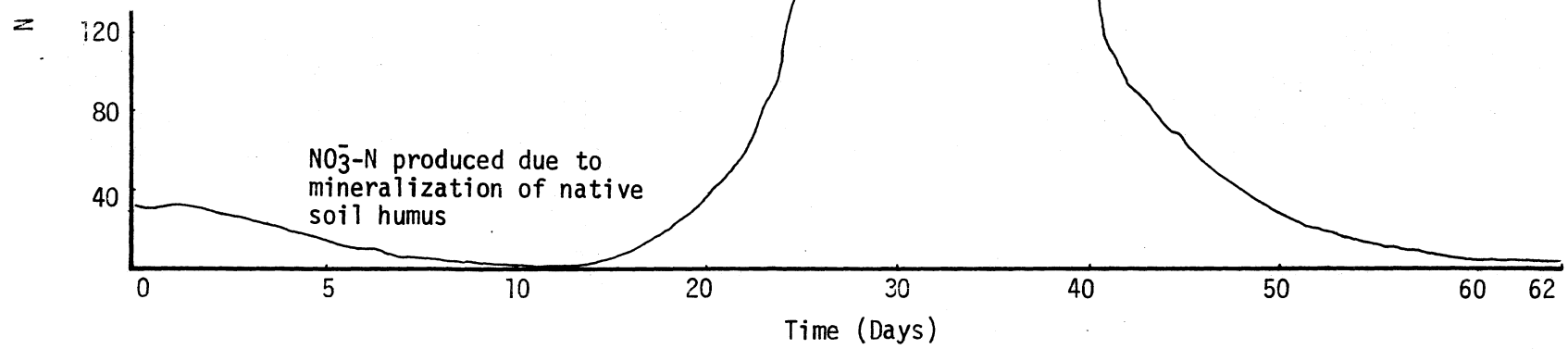


Figure 7. Distribution Pattern of $\text{NO}_3\text{-N}$ Concentration in the 150 cm Depth of the Soil Column as a Function of Time

This relatively high concentration of NO_3^- -N in the early stages of the study is believed to be due to mineralization of native soil humus. The total time required to move NO_3^- -N completely past the 150 cm depth of the soil column was 62 days.

An overall examination of NO_3^- -N concentration in the soil solution, extracted at each 30 cm depth to the 120 cm depth of the soil column, is plotted versus time in Figure 8. Zero time corresponds to the time when $\text{Ca}(\text{NO}_3)_2$ was first applied to the constant 10 cm water head. A maximum concentration of 639 PPM was reached at the 30 cm depth after 9.3 days of continuous leaching with the 10 cm water head. Relative maximum concentration values were reached at the 60, 90 and 120 cm depths at 16.3, 20.6 and 25.3 days, respectively. These relative maximum values never exceeded 464 PPM and decreased with increasing depth. The total time required to complete the leaching phase of this experiment was 62 days.

Higher concentration of NO_3^- -N and faster movement of NO_3^- -N past the 30 cm depth as compared to the deeper sampling depths is undoubtedly related to the water content distribution and flow velocity occurring during leaching, as shown by the shapes of these curves (Figure 8), and as determined by the velocity distribution data (Table IX). Because the total number of contacts between soil particles in the 30 cm depth of the soil column decreases with increasing soil particle size, the proportion of the total flow through the pores between the soil particles will decrease with increasing particle size. Thus, as the particle size increases, mixing becomes less complete and the effluent concentration is dominated by flow through the large soil pores.

Relative lower maximum concentration and therefore dilution of the NO_3^- -N in the 60 and 90 cm depths of the sandy clay loam are also related

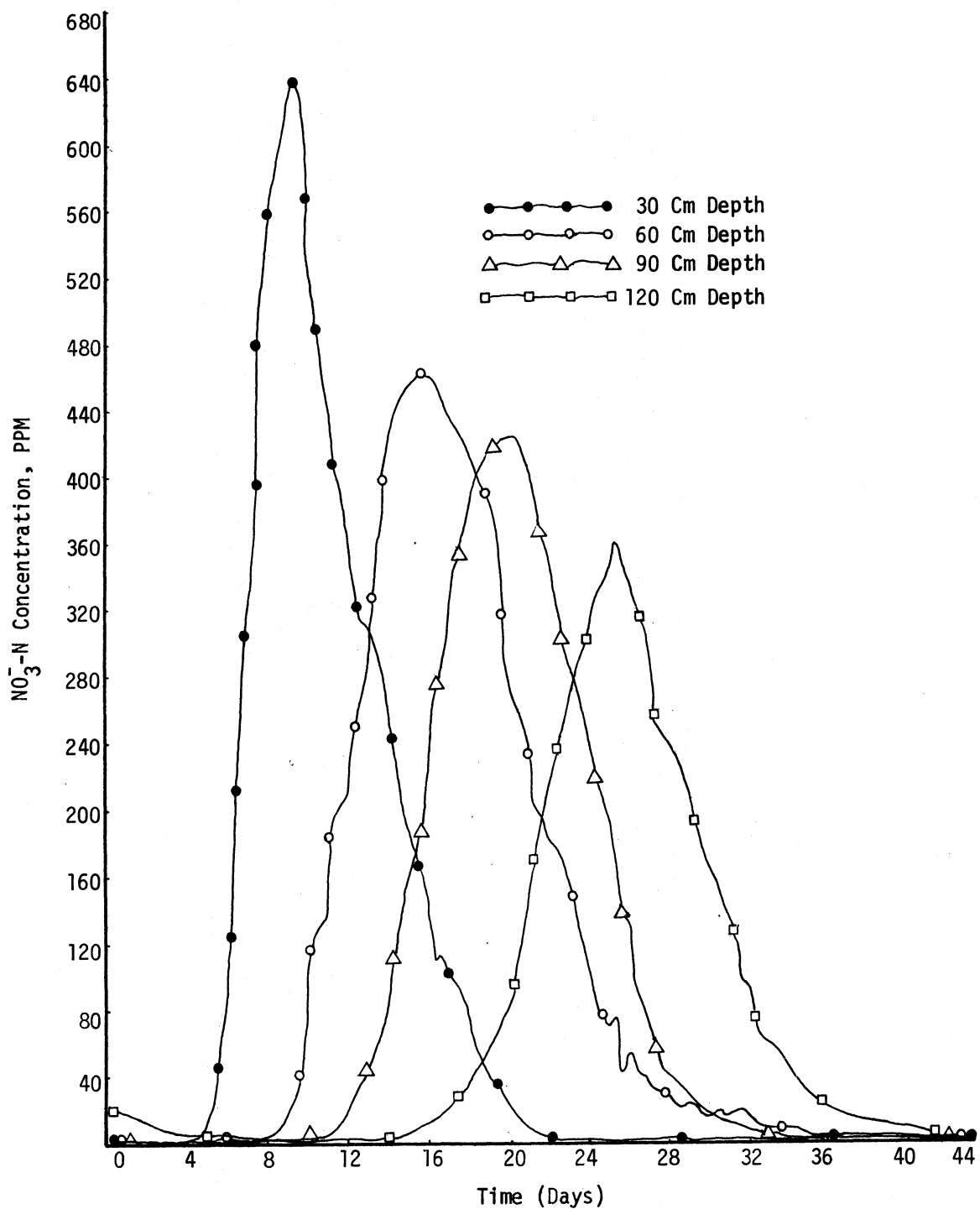


Figure 8. Distribution Pattern of NO_3^- -N Concentration in the 30, 60, 90, and 120 cm Depths of the Soil Column as a Function of Time

to the water content and flow velocity distribution. The shapes of the curves (Table VII) and the concentration distribution of NO_3^- -N in these depths tend to demonstrate the dilution of NO_3^- -N which is associated with a larger number of slower conducting pores as compared to the more coarse textured horizons. Therefore, because of the important difference in pore structure and consequently flow velocity distribution, the larger number of slowly conducting pores act as "sink" for NO_3^- -N ion and a greater volume of water must pass through the soil to reduce the NO_3^- -N ion to a lower concentration; therefore, more complete mixing occurs.

The shape of the curves (Figure 8) and concentration distribution of NO_3^- -N in the 120 cm depth of the soil column tend to demonstrate less complete mixing. The average flow velocity was apparently changed due to a larger number of smaller soil particles in the 60 and 90 cm depths of the soil column. This minimized both water and NO_3^- -N movements and tended to cause nonuniformity of ion distribution at the 120 cm depth. Similar results have been reported by other workers (14, 20).

Since $\text{Ca}(\text{NO}_3)_2$ was used as a carrier in this study, an attempt was made to determine the movement of the Ca^{++} ion with respect to NO_3^- -N ion within a given treatment.

Cations are probably not good indicators of a fluid movement pattern because of the cation exchange reactions that occur in soils. However, when the soil column was saturated with tap water (Ca^{++} concentration of 40 PPM) for two months, it appears the column was fully saturated with the Ca^{++} ion and any exchange involving the Ca^{++} ion was negligible. Therefore, the movement pattern of the Ca^{++} ion tends to be similar to the movement pattern of NO_3^- -N. Consequently, the Ca^{++}

ion could be used as a tracer of NO_3^- -N ion in this study and the Ca^{++} also provides information on N losses through denitrification.

An overall examination of Ca^{++} concentration in the soil effluent is presented in Table VIII and is plotted versus time in Figures 9 and 10. Zero time corresponds to the time when $\text{Ca}(\text{NO}_3)_2$ was first applied to the constant 10 cm water head. A maximum concentration of 587 PPM was reached at the 30 cm depth after 9 days of continuous leaching. Relative maximum concentration values were reached at the 60, 90, 120, and 150 cm depth at 15.3, 19.3, 25.3, and 32.6 days, respectively. These relative maximum values of the Ca^{++} ion never exceeded 488 PPM and decreased with increasing depth. The total time required to complete the leaching phase of the experiment was 62 days.

The average velocities of NO_3^- -N and Ca^{++} were found to be about equal at the 30 cm depth of the soil column, which indicates that both of these ions moved at the same rates in the 30 cm depth of the soil column (Table IX). Both relative NO_3^- -N and Ca^{++} concentration reached their maximum at about the same time at the 30 cm depth. The average velocity of Ca^{++} as compared with the NO_3^- -N in the 60 cm depth of the soil column was slightly slower. However, both relative NO_3^- -N and Ca^{++} concentrations reached their maximum at identical times. At the 90 cm depth of the soil column both average velocity and relative concentrations of NO_3^- -N and Ca^{++} reached their maximum at identical times. For all practical purposes, this equal rate movement of NO_3^- -N and Ca^{++} in the 90 cm depth of the soil column tends to indicate that there is little, if any, exchange reactions of Ca^{++} with the exchangeable ions already in the soil, considering no denitrification, since NO_3^- -N adsorption from the water medium by the soil clay is not of major importance.

TABLE VIII
 DISTRIBUTION PATTERN OF Ca^{++} CONCENTRATION IN 30, 60, 90,
 120, AND 150 CM DEPTH OF TELLER SANDY LOAM PROFILE
 AS A FUNCTION OF TIME

Time Days	30 Cm PPM	60 Cm PPM	90 Cm PPM	120 Cm PPM	150 Cm PPM
1	26.61	22.36	28.28	16.76	39.51
2	32.81	20.81	26.75	20.22	35.54
3	28.65	23.63	25.24	21.10	40.01
4	31.75	24.23	28.83	23.33	34.56
5	43.48	29.32	25.74	20.66	30.72
6	85.64	39.75	30.24	25.14	30.72
7	335.53	29.84	26.24	20.66	24.23
8	394.74	22.36	24.26	23.78	26.97
9	587.83	65.27	24.75	25.14	20.22
10	435.57	110.81	29.84	25.59	19.78
11	385.78	167.31	33.04	23.78	19.34
12	365.93	232.20	22.32	23.28	13.81
13	320.81	320.00	48.14	21.84	17.61
14	342.01	400.25	80.92	22.32	19.34
15	252.67	488.99	156.58	18.91	22.43
16	200.18	475.20	226.02	20.22	18.04
17	146.84	450.50	305.00	25.59	21.10
18	107.34	436.08	407.16	36.90	23.33
19	93.97	314.25	394.65	60.84	21.10
20	74.60	257.65	410.00	96.42	27.90
21	57.78	246.87	376.70	151.13	32.63
22	38.29	165.26	345.16	241.14	30.24
23	36.06	116.21	258.70	260.16	35.05
24	37.17	96.42	223.26	325.47	40.52
25	34.42	73.03	174.21	378.38	61.40
30	38.86	23.76	37.47	214.00	250.02
35	38.86	36.62	24.26	41.50	289.98
40	39.43	30.71	22.80	24.26	162.91

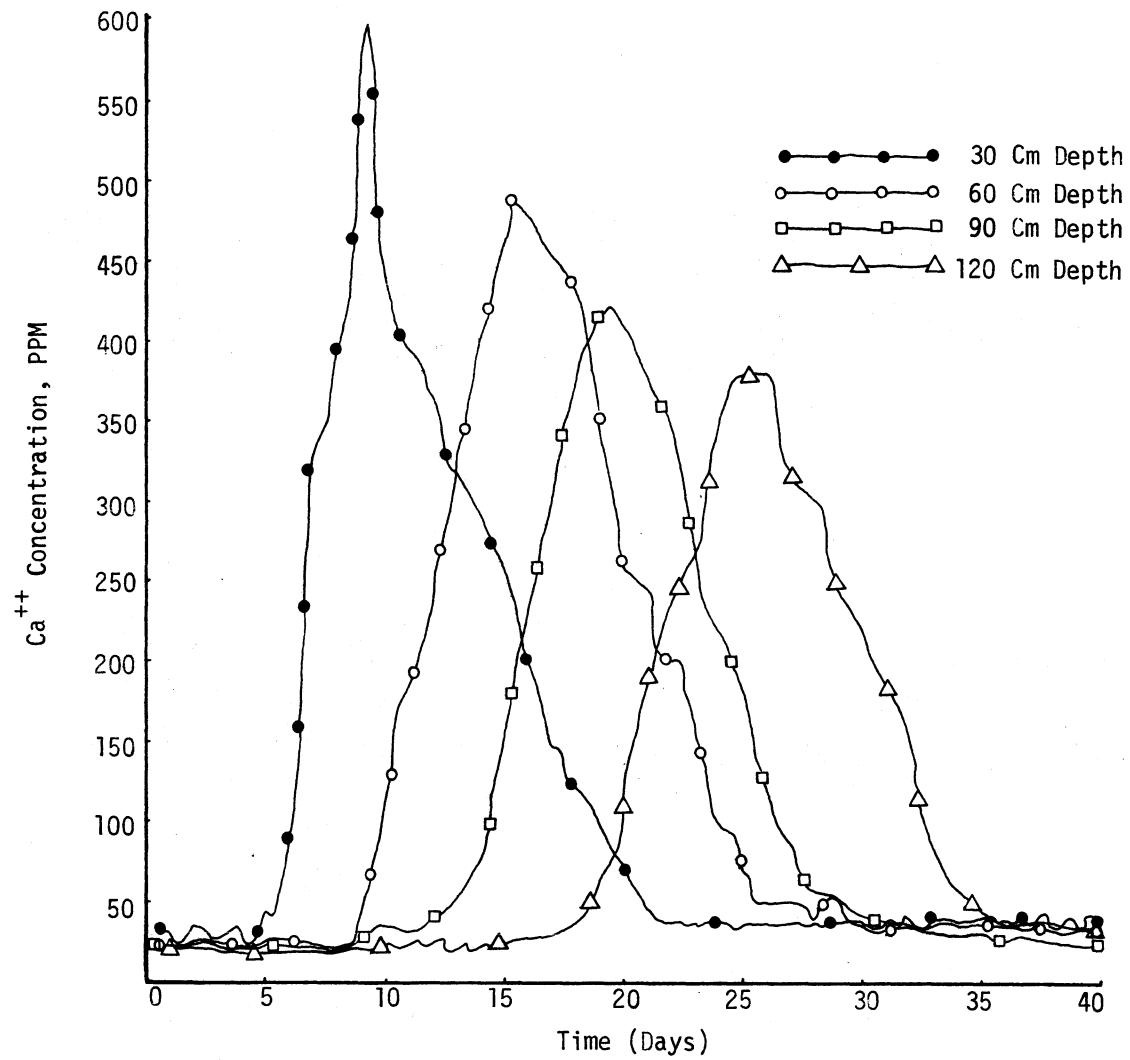


Figure 9. Distribution Pattern of Ca⁺⁺ Concentration in the 30, 60, 90, and 120 cm Depths of the Soil Column as a Function of Time

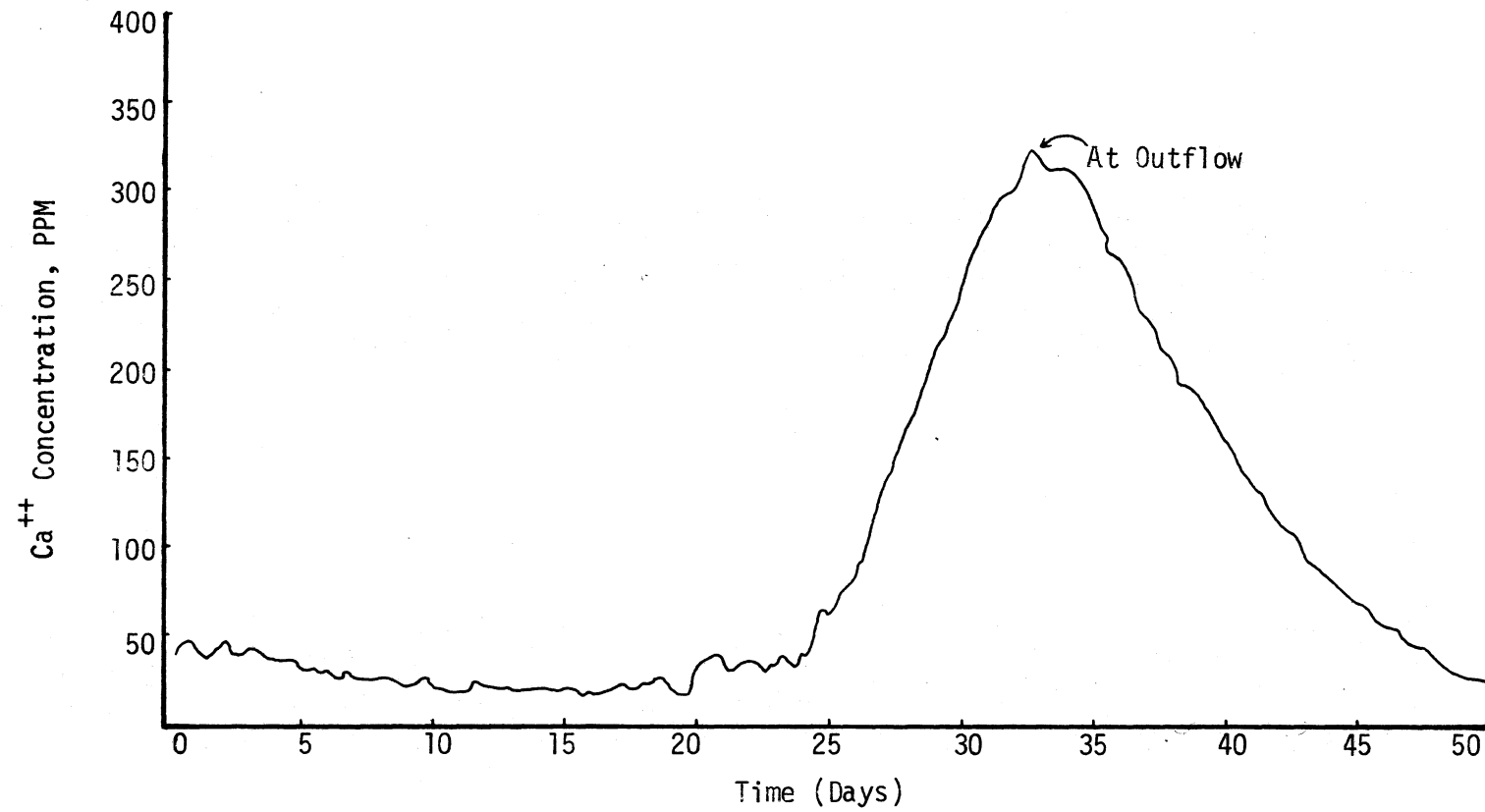


Figure 10. Distribution Pattern of Ca⁺⁺ Concentration in the 150 cm Depth of the Soil Column as a Function of Time

TABLE IX
VALUES COMPARING THE AVERAGE VELOCITY FOR $\text{NO}_3\text{-N}$ AND Ca^{++}
APPLIED AS $\text{Ca}(\text{NO}_3)_2$ IN THE SOIL COLUMN
AS A FUNCTION OF DEPTH

Depth Cm	Average Velocity of $\text{NO}_3\text{-N}$ Cm/Hr	Average Velocity of Ca^{++} Cm/Hr
30	.1339	.1388
60	.2083	.1973
90	.3125	.3125
120	.2085	.2083
150	.1704	.1704

Higher velocities of NO_3^- -N and Ca^{++} in the 60 and 90 cm depth of the soil column is associated with a larger number of small soil particles and a greater volume of water must pass through the soil to reduce the ions to a lower concentration (Table IX). At greater depths in the soil column the average velocity of NO_3^- -N ion and Ca^{++} ion was found to be equal, and both relative NO_3^- -N and Ca^{++} concentrations reached their maximum at about the same time.

Denitrification is one of the major mechanisms by which nitrogen is lost from a flooded soil. In an attempt to explain this loss, some factors should be discussed. As long as oxygen is present in the soil, other oxidized components of the soil are relatively safe from biological and chemical reduction. After oxygen has disappeared from a water saturated soil, the need for electron acceptors by facultative anaerobic and true anaerobic organisms results in the reduction of easily oxidized compounds. Nitrate can be used by the microorganisms as an electron acceptor and reduced to N_2 or N_2O . Nitrate is reduced at fairly high redox potentials, approximately +340 millivolts at pH 5.1 and +225 millivolts at pH 7 (34). Whisler et al. (51) reported that when a soil column was flooded with sewage water, the redox probes which were placed at a 2 cm depth, dropped from 600 to 400 MV within two days and from 400 to 225 MV within six days. At deeper depths in the soil column the drop in redox potential was not as rapid. Losses of NO_3^- -N under saturated field conditions have been reported by other investigators (12, 53). With all this in mind, an attempt was made to determine denitrification rates by ascertaining the NO_2^- -N content and NH_4^- -N concentration in the soil solution. The results are not presented in this report because of the extremely low concentrations found for both NO_2^- -N and

$\text{NH}_4\text{-N}$. The concentration values that were found for both $\text{NO}_2\text{-N}$ and $\text{NH}_4\text{-N}$ ranged from 0 to .05 PPM, and most of the effluent samples had a zero PPM concentration. Therefore, when the anaerobic volume in the soil column was periodically increased by constant saturation, denitrification may have been somewhat limited by low nitrate-nitrogen concentration resulting from excessive leaching.

Total recovery of $\text{NO}_3\text{-N}$ in each depth of the soil column was obtained by integrating the area under the curve (Figure 8) as follows:

$$\frac{\text{Area under the curve}}{\text{Total time}} \times \text{total flow} = \gamma,$$

where

Area under the curve = PPM/time;

Total flow = total volume passing through each depth;

Total time = total time required to pass through each depth.

The total amount of nitrate-nitrogen present in each depth was then obtained by subtracting the total amount from the background levels of $\text{NO}_3\text{-N}$ in the tap water. The nitrate-nitrogen found in each depth minus added nitrate-nitrogen was then expressed as a percentage of the total recovery and is presented in Table X.

Table X shows a high recovery of $\text{NO}_3\text{-N}$ in the soil solution. The quantity of $\text{NO}_3\text{-N}$ detected in the effluent at termination of the study was greater than that initially added. This is believed to be due to mineralization of native soil humus. The higher recovery in the 60 cm depth of the soil column is also believed to be due to release of organic N upon the addition of $\text{NO}_3\text{-N}$. This high recovery of $\text{NO}_3\text{-N}$ apparently is associated with rapid velocities which would not permit microorganisms to use $\text{NO}_3\text{-N}$ moving through the soil. Therefore, the

TABLE X
VALUES COMPARING PERCENT RECOVERY OF NO₃-N AND Ca⁺⁺
APPLIED AS Ca(NO₃)₂ IN THE SOIL COLUMN
AS A FUNCTION OF DEPTH

Depth Cm	Percent Recovery of NO ₃ -N	Percent Recovery of Ca ⁺⁺
30	96.40	79.72
60	111.38	83.21
90	98.40	77.97
120	97.10	79.02
150	117.88	88.11

amount of nitrate-nitrogen immobilized and denitrified by microbial activity is related to the velocity of flow (15).

The total recovery of Ca^{++} ion was calculated in the same manner as $\text{NO}_3\text{-N}$. The lower recovery of the Ca^{++} ion compares with $\text{NO}_3\text{-N}$ and it is believed the Ca^{++} ion would undergo exchange reactions with the exchangeable ions already in the soil. However, the low recovery of Ca^{++} ion may be due to experimental error rather than exchange reactions of the Ca^{++} ion with other exchangeable ions. In the various depths of the soil column, both average velocities and relative concentrations of $\text{NO}_3\text{-N}$ and Ca^{++} ions reached their maximum at about the same times. Also, chemical analyses of the soil column at termination of the study shows a small decrease in exchange Ca^{++} ions as compared to that found initially in the soil (Table XI). Therefore, it is safe to assume that these lower recovery values of Ca^{++} compared to those of $\text{NO}_3\text{-N}$ is a result of experimental error rather than exchange reactions of the Ca^{++} ion with other exchangeable ions.

An attempt was made to determine the movement pattern of the cations Mg^{++} , K^+ and Na^+ in the soil solution, extracted at the 30, 60, 90, 120, and 150 cm depths. The following data sets forth the movement patterns of the cations in the soil column:

1. Movement pattern of Mg^{++} . An examination of Mg^{++} concentration in the soil effluent is presented in Table XII and is plotted versus time in Figures 11 and 12. A relative maximum concentration of 210 PPM was reached at the 30 cm depth after 9 days of leaching. Subsequent maximum concentration values were reached at the 60, 90, 120, and 150 cm depths at 16, 19.3, 26.3 and 31 days with relative maximum concentrations of 210, 218, 220, and 218 PPM, respectively.

TABLE XI
CHEMICAL ANALYSIS OF THE SOIL BEFORE AND AFTER EXPERIMENT

Depth Cm	<u>Before</u> Exchangeable Cation, MeQ/100g								<u>After</u> Exchangeable Cation, MeQ/100g							
	pH	C.E.C.	H ⁺	Ca ⁺⁺	Mg ⁺	K ⁺	Na ⁺	PPM NO ₃ -N	pH	C.E.C.	H ⁺	Ca ⁺⁺	Mg ⁺⁺	K ⁺	Na ⁺	PPM NO ₃ -N
30	6.0	5.05	1.50	1.03	.57	.24	.11	5.00	5.8	3.82	1.95	1.47	.12	.19	.09	3.50
60	6.3	9.79	4.25	2.66	2.96	.95	.15	1.65	6.7	7.74	2.42	2.12	.78	.72	.09	.10
90	6.3	9.28	2.75	2.70	2.80	.91	.11	1.70	6.8	9.83	3.11	2.32	1.32	.75	.13	.05
120	5.9	6.66	3.00	1.36	1.81	.18	.09	1.15	6.8	4.60	1.84	1.15	.45	.22	.04	.05
150	6.3	4.15	.50	.78	1.07	.13	.09	>1	6.85	2.96	1.27	.87	.45	.18	.09	.05

TABLE XII
 DISTRIBUTION PATTERN OF Mg^{++} CONCENTRATION IN 30, 60, 90,
 120, AND 150 CM DEPTH OF TELLER SANDY LOAM PROFILE
 AS A FUNCTION OF TIME

Time Days	30 Cm PPM	60 Cm PPM	90 Cm PPM	120 Cm PPM	150 Cm PPM
1	8.41	11.23	19.05	11.09	48.08
2	9.69	10.52	16.63	18.24	41.08
3	10.86	16.63	18.32	18.49	45.13
4	11.02	15.25	15.74	17.03	42.20
5	14.61	12.12	16.06	16.63	44.57
6	35.89	13.05	16.23	19.93	34.80
7	140.99	12.75	16.55	18.97	33.84
8	194.09	10.00	17.20	20.90	31.21
9	210.43	16.87	17.76	22.18	28.40
10	194.09	64.06	18.16	22.10	28.98
11	194.98	117.93	21.62	20.50	28.65
12	172.65	126.05	22.42	20.09	30.08
13	156.35	150.85	29.32	17.60	27.90
14	106.21	170.25	48.08	14.85	25.70
15	84.00	190.35	105.20	17.28	25.14
16	60.00	210.00	164.30	17.76	25.22
17	42.00	208.00	206.70	20.25	24.18
18	29.22	210.00	206.70	30.43	25.54
19	24.35	205.25	218.11	45.70	25.54
20	18.85	118.00	215.20	47.77	25.62
21	15.75	110.25	209.49	106.59	27.66
22	11.85	94.00	203.01	201.20	30.26
23	11.00	72.00	188.93	206.70	35.09
24	10.00	66.00	160.63	206.70	44.16
25	10.25	46.00	130.07	206.70	63.35
30	9.75	30.00	37.23	159.20	206.70
35	10.25	22.00	16.55	58.42	213.28
40	10.25	13.50	11.17	20.14	154.95

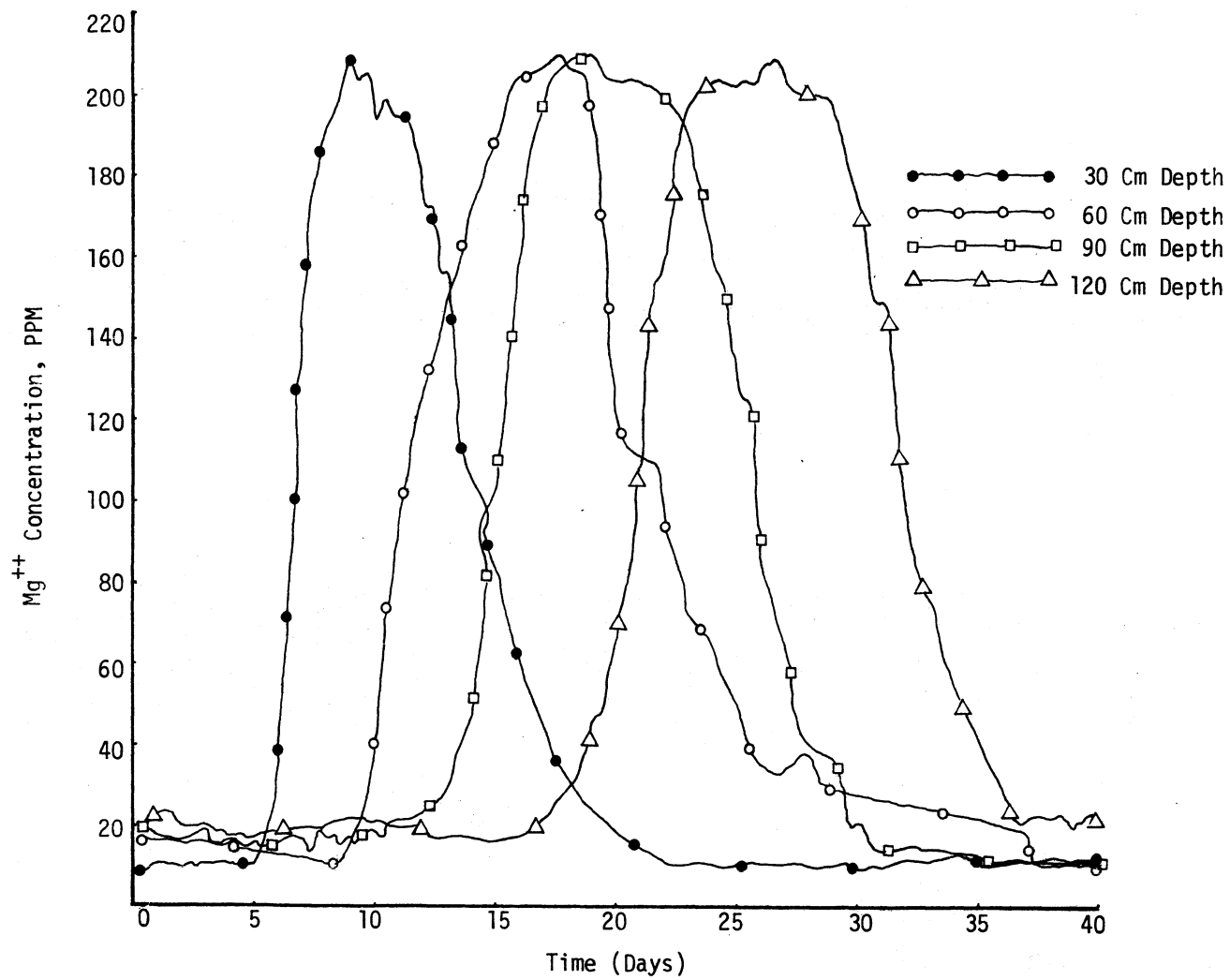


Figure 11. Movement Pattern of Mg⁺⁺ Concentration in the 30, 60, 90, and 120 cm Depths of the Soil Column as a Function of Time

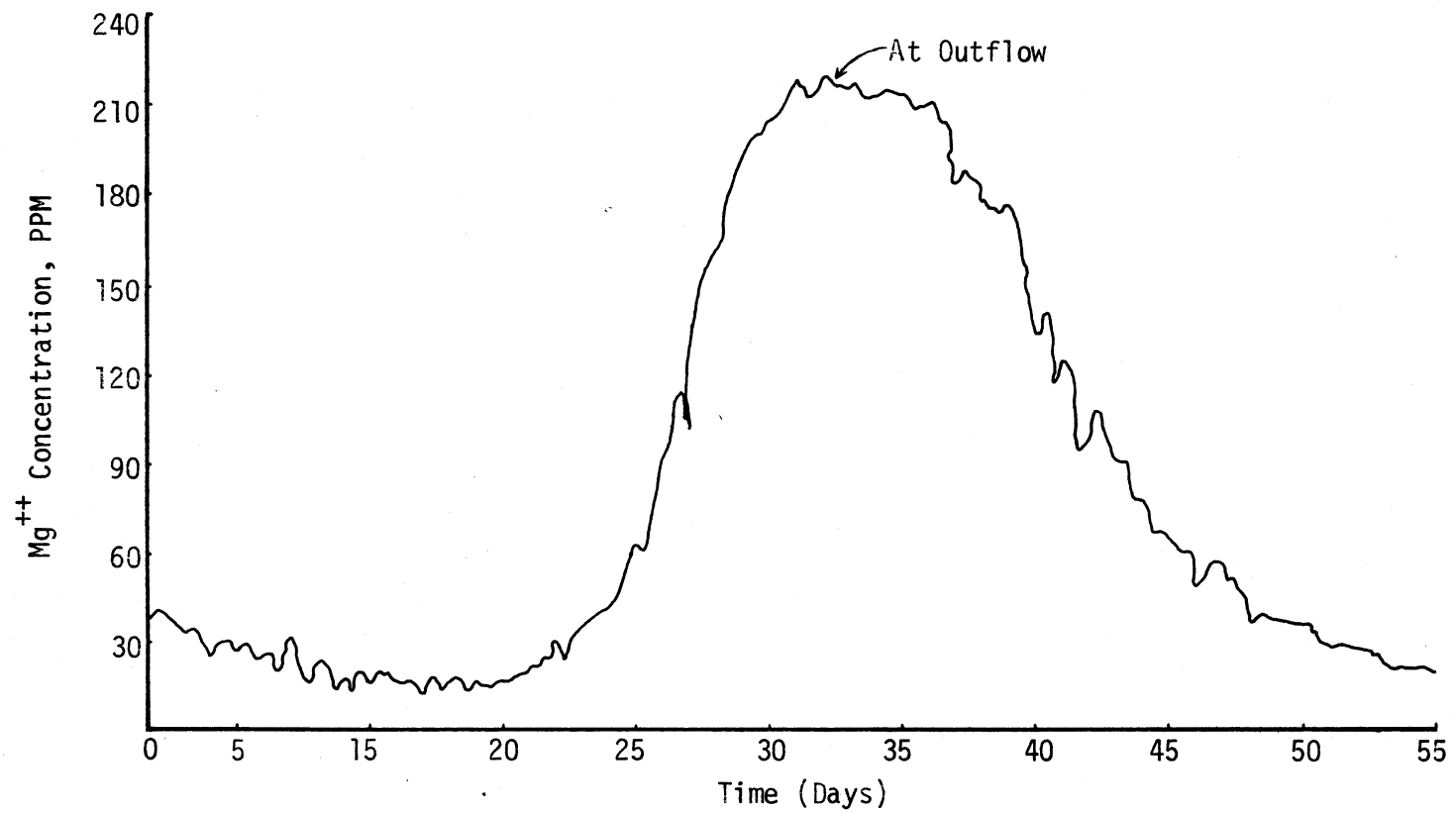


Figure 12. Movement Pattern of Mg⁺⁺ Concentration in the 150 cm Depth of the Soil Column as a Function of Time

The Mg^{++} ion in the effluent can come from two sources, namely exchangeable and tap water (Mg^{++} concentration of 11 PPM). However, the amount of tap water Mg^{++} was probably not high enough to overshadow the exchange reactions. It is interesting to note that Mg^{++} has a similar movement pattern to Ca^{++} and NO_3^- -N. The average velocities and relative concentration of Mg^{++} in the various depths of the soil column reached their maximum at about the same time as NO_3^- -N and Ca^{++} . The average velocities of Mg^{++} ion were .1338, .1785, .3750, .1785, and .2659 cm/hr for depths of 30, 60, 90, 120, and 150 cm, respectively. Distribution of exchangeable ions in the soil column and in the effluent is not, however, entirely statistical. Each ion has its characteristic affinity for each type of soil colloid and these attractions probably have a major influence. The early arrival of Mg^{++} in the effluent could be attributed to the differences in dispersion-exchange interactions that occur at the different velocities within the soil column.

2. Movement pattern of K^+ . An examination of K^+ concentration in the soil effluent is presented in Table XIII and is plotted versus time in Figure 13. The movement pattern of K^+ could not be fully explained since both exchange K^+ in the soil and concentration K^+ in the tap water (4 PPM K^+) were too low to determine the sources of K^+ as found in the soil effluent. However, relative maximum concentration as a function of time in the various depths of the soil column was probably due to the exchange of K^+ (K^+ release from both exchangeable and nonexchangeable form) by H^+ . The various maxima, in the 60 and 90 cm depths of the soil column were probably due to the exchange of K^+ by NH_4^+ and exchange of K^+ by H^+ .

TABLE XIII
 DISTRIBUTION PATTERN OF K^+ CONCENTRATION IN 30, 60, 90,
 120, AND 150 CM DEPTH OF TELLER SANDY LOAM PROFILE
 AS A FUNCTION OF TIME

Time Days	30 Cm PPM	60 Cm PPM	90 Cm PPM	120 Cm PPM	150 Cm PPM
1	13.0	18.0	29.5	16.0	2.05
2	14.0	29.0	32.0	18.5	2.75
3	14.0	30.0	33.5	14.5	2.00
4	15.0	32.0	33.0	11.0	2.00
5	16.0	26.5	31.0	11.0	2.00
6	24.5	29.0	34.0	12.5	2.00
7	49.0	27.0	34.0	12.5	2.00
8	68.0	30.5	34.0	11.5	2.00
9	72.5	32.0	34.0	11.5	3.25
10	75.0	44.0	34.5	11.5	2.05
11	70.0	59.5	39.0	10.5	3.25
12	64.5	70.5	42.5	12.5	2.05
13	60.0	95.0	48.5	12.5	2.00
14	69.0	136.0	65.0	15.0	2.00
15	61.0	142.0	81.0	8.5	1.75
16	54.0	159.0	100.0	10.5	2.00
17	48.0	156.0	146.0	10.0	2.05
18	40.0	154.0	186.0	11.5	2.50
19	38.0	154.0	148.0	11.5	1.75
20	35.0	116.0	148.0	14.0	1.75
21	30.5	124.0	146.0	20.5	2.05
22	17.5	72.5	138.0	25.0	2.00
23	17.0	64.0	120.5	25.5	2.05
24	17.5	54.0	121.0	25.5	2.75
25	17.5	54.5	100.0	25.0	3.00
30	21.5	58.0	61.0	18.0	5.95
35	20.0	56.0	45.0	10.0	6.10
40	19.5	48.0	44.0	8.0	3.95

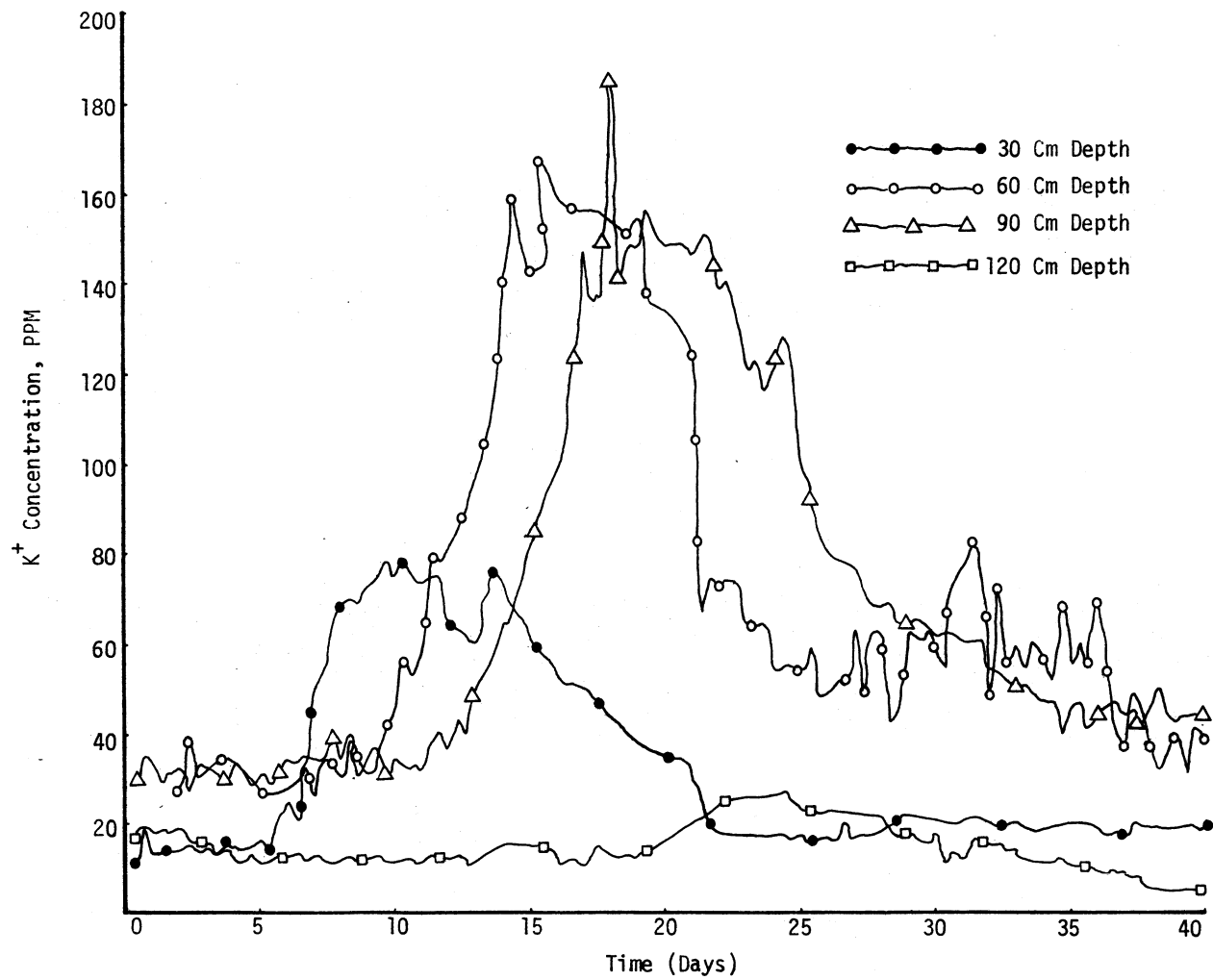


Figure 13. Movement Pattern of K^+ Concentration in the 30, 60, 90, and 120 cm Depths of the Soil Column as a Function of Time

3. Movement pattern of Na^+ . An examination of Na^+ concentration in the soil effluent is presented in Table XIV and is plotted versus time in Figure 14. A relative maximum concentration of 102 PPM was reached at the 30 cm depth after 8 days of continuous leaching. Subsequent maximum concentration values were reached at the 60, 90 and 120 cm depths at 17.3, 21.6 and 32 days. The Na^+ in the soil effluent can come from two sources: exchangeable and added tap water (21 PPM Na^+).

The relative affinities of the various cations for most soils and soil material are $\text{Ca}^{++} > \text{Mg}^{++} > \text{K}^+ = \text{NH}_4^+ > \text{Na}^+$. Thus, exchangeable Na^+ is quite readily displaced by Ca^{++} and Mg^{++} . Consequently, Na^+ tends to move farther and more readily in leachate and drainage waters.

TABLE XIV
 DISTRIBUTION PATTERN OF Na⁺ CONCENTRATION IN 30, 60, 90,
 120, AND 150 CM DEPTH OF TELLER SANDY LOAM PROFILE
 AS A FUNCTION OF TIME

Time Days	30 Cm PPM	60 Cm PPM	90 Cm PPM	120 Cm PPM	150 Cm PPM
1	23.70	25.97	27.45	12.05	10.85
2	17.32	28.32	15.95	5.69	9.42
3	17.21	20.96	15.95	13.14	9.56
4	23.71	34.05	34.33	19.54	8.74
5	32.66	46.91	26.08	17.76	8.28
6	38.05	51.48	29.56	20.31	8.21
7	79.27	49.25	21.28	21.70	7.88
8	99.15	47.00	32.08	18.68	6.88
9	96.55	45.14	23.65	23.03	7.63
10	67.21	53.95	35.88	18.59	6.39
11	31.57	29.77	21.83	7.56	7.31
12	22.50	36.07	21.15	8.33	6.04
13	18.17	70.05	23.19	7.62	6.21
14	17.64	80.00	14.95	8.27	6.94
15	15.14	80.50	17.76	6.69	7.19
16	15.14	78.65	25.47	6.63	6.75
17	12.63	72.14	30.34	5.98	6.88
18	11.59	82.53	43.21	9.82	6.63
19	11.10	81.73	43.29	9.42	6.69
20	10.80	66.00	56.08	13.50	6.04
21	10.76	50.25	52.42	15.03	7.06
22	11.24	51.07	66.03	19.63	7.37
23	12.30	34.30	60.95	25.80	7.95
24	12.77	37.92	58.37	31.35	9.28
25	11.63	30.18	42.86	28.74	10.56
30	16.64	35.50	28.53	24.55	19.44
35	24.91	31.51	24.22	17.83	21.80
40	28.74	32.81	19.92	11.05	16.50

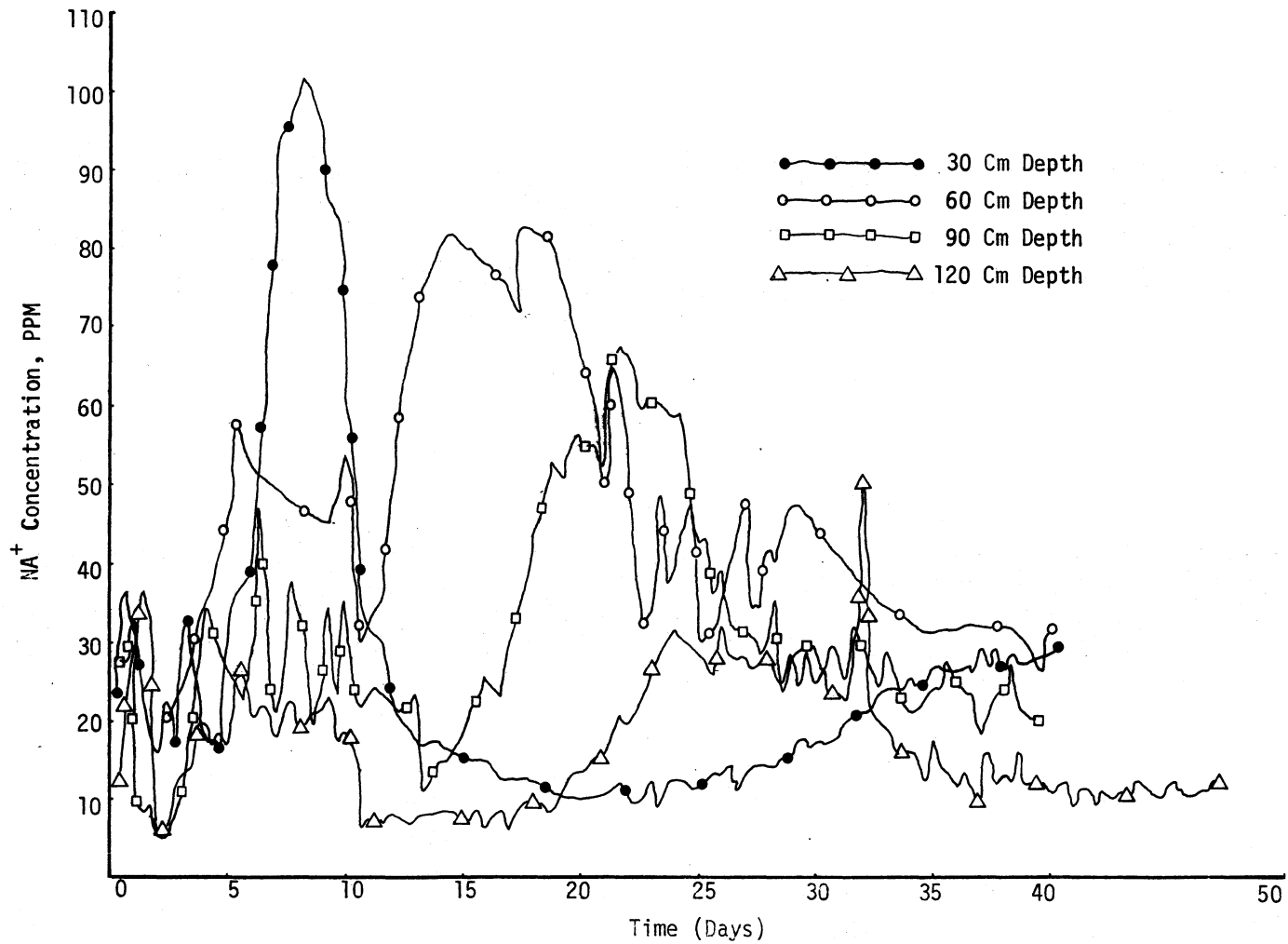


Figure 14. Movement Pattern of Na⁺ Concentration in the 30, 60, 90, and 120 cm Depths of the Soil Column as a Function of Time

CHAPTER V

SUMMARY AND CONCLUSIONS

The objective of this study was to determine the distribution pattern of $\text{NO}_3\text{-N}$ in a soil column under steady state conditions. The soil used in this study was Teller fine sandy loam and the fertilizer used was $\text{Ca}(\text{NO}_3)_2$ equivalent to an application of 620 Kg of N/ha, dissolved in 100 ml of H_2O and added uniformly to a 10 cm constant water head.

The distribution pattern of $\text{NO}_3\text{-N}$ in the soil solution, extracted at 30, 60, 90, 120, and 150 cm depths in the soil column were found to move with the average velocity rates of .1339, .2083, .3125, .2085, and .1630 cm/hr, respectively, under a 10 cm constant water head.

$\text{NO}_3\text{-N}$ distribution in the 30 cm depths of the soil column was found to exhibit a more rapid rise and subsequent decline than at the greater depths of the soil column probably due to coarse textured soil present in the 30 cm depth. Therefore, as the soil particle size increases, mixing becomes less complete and the effluent concentration is dominated by flow through the large pores. Distribution of $\text{NO}_3\text{-N}$ in the 60 and 90 cm sandy clay loam depths of the soil column were found to exhibit a greater dilution of $\text{NO}_3\text{-N}$, which is associated with a larger number of slowly conducting pores that act as "sink" for $\text{NO}_3\text{-N}$. Consequently, a ~~///~~ greater volume of water must pass through to reduce the $\text{NO}_3\text{-N}$ ion to a lower concentration with more complete mixing. $\text{NO}_3\text{-N}$ distribution in the 120 and 150 cm depths of the soil column was less complete because

of the presence of larger soil particles at these depths. Also, the relations obtained from this investigation were that NO_3^- -N concentration below the soil profile in a free drainage is lower when water movement through the profile is restricted at some point within the profile.

The total quantity of NO_3^- -N in the effluent at termination of the study was greater than that initially added in the soil solution. This is believed to be due to mineralization of native soil humus. Total recoveries of NO_3^- -N in each depth of the soil column was quite high, which indicates under constant saturation, denitrification has been limited by low NO_3^- -N concentration resulting from excessive leaching.

When the soil column was saturated with tap water (40 PPM Ca^{++}) for two months, it appeared that the column was fully saturated with Ca^{++} ion and since $\text{Ca}(\text{NO}_3)_2$ was used as a carrier, an attempt was made to determine the movement pattern of Ca^{++} ion with respect to NO_3^- -N ion within a given treatment. Ca^{++} ion was found to move with equal rates of NO_3^- -N. Both relative Ca^{++} and NO_3^- -N concentration reached their maximum at about the same times at the various depths of the soil column.

Movement patterns of Mg^{++} , K^+ and Na^+ were also studied and results indicated that Mg^{++} , K^+ and Na^+ in the soil effluent can come from two sources, namely exchangeable and added in the tap water.

In conclusion, the rate of N used in this study was much higher than the rate used in agriculture in Oklahoma; also, excessive amounts of water were applied to cause NO_3^- -N leaching. However, from the results of this study, it appears that leaching is a major mechanism responsible for disappearance of unused fertilizer N when fertilizer is applied to a field and denitrification may be somewhat limited due to

low NO_3^- -N concentration resulting from excessive leaching. The NO_3^- -N concentrations found in deep soil columns were profoundly influenced by the characteristics of the soil profile. Profile characteristics, such as high clay layers and textural discontinuities, influence nitrate concentrations through their effect on nitrification, denitrification, and leaching. The results obtained from this study indicate that profile characteristics should be considered when selecting soils to receive high nitrogen inputs both with and without irrigation. With properly designed and managed irrigation systems, little or no movement of nitrates outside the root zone should occur.

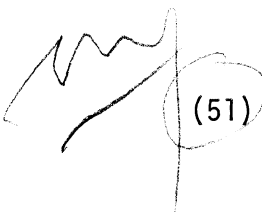
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APPENDIX

DESCRIPTION OF SOIL PROFILE

The profile was sampled approximately 1765 feet east and 2350 feet north of the southwest corner of Sec. 36, T18N, R2E, Payne County, Oklahoma.

Teller fine sandy loam, 1-3% slopes.

<u>Horizon</u>	<u>Depth (in.)</u>	<u>Description</u>
A _p	0-10	Grayish brown (10 yr 5/2 dry) fine sandy loam, medium granular structure; very friable; pH 6.0; abrupt smooth boundary.
A ₁	10-18	Strong brown (7.5 yr 5/6 dry) fine sandy loam, strong granular structure; friable; pH 6.4; gradual smooth boundary
B ₁	18-24	Yellowish red (5 yr 5/6 dry) light sandy clay loam; weak medium subangular blocky structure; friable; ph 6.4; gradual smooth boundary.
B _{21t}	24-36	Strong brown (7.5 yr 5/8 dry) sandy clay loam; moderate medium subangular blocky structure; slightly firm; pH 6.3; gradual smooth boundary.
B _{22t}	36-42	Strong brown (7.5 yr 5/8 dry) sandy clay loam; moderate medium subangular blocky structure; slightly firm; pH 6.1; gradual smooth boundary.
B ₃	42-50	Strong brown (7.5 yr 5/8 dry) sandy loam; strong granular structure; friable; pH 5.9; gradual smooth boundary.
C	50-60	Reddish yellow (7.5 yr 6/8 dry) loamy sand; massive; friable; pH 6.3; gradual smooth boundary.

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