THE EFFECT OF SUBSOIL STRUCTURE ON THE

MOVEMENT OF TWO NON-VOLATILE

ORGANIC POLLUTANTS

By

LAWRENCE JOHN HENDERSON

Bachelor of Science
Brigham Young University
Provo, Utah
1977

Master of Science
Oklahoma State University
Stillwater, Oklahoma
1980

Submitted to the Faculty of the Graduate College
of the Oklahoma State University
in partial fulfillment of the requirements
for the Degree of
DOCTOR OF PHILOSOPHY
May, 1983

THE EFFECT OF SUBSOIL STRUCTURE ON THE

MOVEMENT OF TWO NON-VOLATILE

ORGANIC POLLUTANTS

Thesis Approved:

_____
Thesis Adviser

_____

_____
Laval M. Verhalen

_____
Ardhesh K. Tyagi

_____
Dean of the Graduate College

ACKNOWLEDGMENTS

I would like to express my appreciation to the Agronomy Department at Oklahoma State University for the facilities and equipment used in this study and for the graduate research assistantship that enabled me to continue my schooling. I am also thankful to the Agronomy faculty for the ideas and information they taught me and for their help and encouragement in my studies.

I am especially grateful to my major adviser, Lawrence G. Morrill, for his valuable guidance during this study and for his continual friendship during my stay here at Oklahoma State University. My special thanks goes to Lester W. Reed for leaving his door open for my numerous questions over the years. I would also like to express my thanks to Laval M. Verhalen and Avdhesh K. Tyagi for their help and advice during many of the decision-making periods of my thesis work and for serving on my committee. I appreciate the help of R. Dwaine Gelnar of the Soil Conservation Service for his assistance in soil location.

I would be ungrateful if thanks was not expressed to John C. Osborne of the OSU Physical Plant Services Department for his expert mechanical abilities in keeping the coring machine in good running order. I am thankful to the many friends I have made over the years among my fellow graduate students. I am thankful to my close friend, Terry A. Tindall, for his help and companionship over the years and to Edward Hanlon for his friendship and expert advice.

Without the continual belief and support of my parents,

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

Water movement in the soil zone of saturation has been exten-
sively investigated and has resulted in a number of useful mathemati-
cal models describing the system. This is true to a lesser extent for
the unsaturated zone. However, there is little known with regard to
solute movement, particularly in the unsaturated subsoil (below plow
depth). The interactions between solutes and reactive surfaces of
structured soils are not well understood and require intensive research
for satisfactory description and explanation.

The soil can be imagined as an enormous liquid chromatograph with
many complex and diverse stationary phases and with great variability
in pore size distribution and solvent flow. While it is difficult to
quantify the movement of the numerous solutes in the soil environment,
it may be possible to define general parameters of solute movement as
well as quantify specific classes of potential pollutants. One of the
subsoil characteristics that may have a significant effect on the rate
of solute movement and variations in distribution is the soil
structure.

The primary purpose of this study was to determine the influence
of subsoil macrostructure on the movement of nitrobenzene (NB) and
trichlorobenzene (TCB) in the soil profile. A secondary purpose was to

investigate the spatial distribution of the pollutant as a means of describing the pathway of the solute movement through structured soils.

CHAPTER II

REVIEW OF LITERATURE

Introduction

Geraghty and Miller (1978) estimated that more than 100 billion gallons of industrial effluents enter groundwater systems annually. They indicated that landfills can be a major source for this type of contamination because of the leachates generated by water percolating through the landfills (such as leachates being largely mineralized). However, septic tanks and cesspools rank highest in total volume of waste water discharged directly to groundwater. Disposal of brine from oil and gas production remains an important source of groundwater contamination. Surface and underground mining and slurry lagoons also make significant contributions to groundwater contamination. Animal feedlots contaminate groundwater through runoff, through infiltration from the lot, and from the waste products disposed of on land surfaces. The principle contaminants from all sources are chlorides, nitrates, hydrocarbons, and heavy metals (Corr and Cole, 1977).

Otis et al. (1978) stated that an "ideal" soil adsorption system should adsorb all the effluents generated. However, a good adsorption system should provide a high level of treatment before the effluent reaches the groundwater and should have a long useful life. To meet those goals, proper site selection is necessary. Factors to be considered in site selection include the hydraulic conductivity of the

3

soil, distance to bedrock, the landscape position, slope, proximity to surface wells, road cuts, and buildings. Adsorption of waste effluent in a soil drainage system demands that soil pores remain open. If the pores are sealed by compaction, smearing, or puddling, which generally occurs in soils with a clay content of 25% or more, the system may be rendered unless as an infiltration bed. Through careful planning and construction techniques these above problems can be minimized.

A wide range of results have been observed where sewage sludge has been applied to various soils. Baumann and Bram (1977) indicated that when high rates of nitrates (NO^-_3), potassium (K^+), and sodium (Na^+) are added with the sewage water, the soil, at first, exhibits a cleansing action by adsorption. After large applications, however, there is a sharp decrease in the ability of the soil to cleanse effluents, resulting in an increase of both NO^-_3 and K^+ concentrations in the seepage water.

Huser (1977) found that seepage tests provided reliable indications of the potential for contamination of the groundwater with specific elements. The best example he found was Na^+. Digested sewage sludge with four to eight percent organic matter (OM) was applied to a 60 year old spruce forest on a loam soil. The pH of the humus layer increased from 4.2 to 6.2 in the test plots. Huser (1977) theorized that the NO^-_3, calcium (Ca), Na^+, and chloride (Cl^-) content was increased in the groundwater from the additions of the sewage sludge.

Hoeks (1977) determined that pollutant mobility through soils is dependent on a variety of processes which include cation exchange, chemical solubility equilibria, and biochemical interactions. Cation exchange processes are important for inorganic cations including heavy

metals. Phosphates, carbonates, and sulfates of iron (Fe), aluminum (Al), Ca, magnesium (Mg), and heavy metals are involved in chemical processes. Biochemical processes are important when considering organic substances and nitrogen compounds. Hoeks (1976) also mentioned that the effect of leachate from waste disposal sites on groundwater quality is highly dependent on geohydrological conditions. Conditions are more favorable when transport of leachate to the aquifer is slow, giving ample opportunity for biological decomposition, adsorption, and precipitation of contaminants. Young and Clark (1978) showed that even after chemical dumping or mining activities are terminated, water quality can continue to be adversely affected for many years. This is due, in part, to the continued movement of organic and inorganic contaminants in percolating water.

Solute Movement in Structured Soils

Lawes et al. (1882), analyzing solutions collected from field tile drains, found that a large part of added water moves rapidly through open channels (macropores) and interacts only slightly with the water held by the soil mass. They also found that subsequent drainage was more representative of the 'existing' water in the soil matrix. They stated that in a heavy soil direct channel-drainage will, in most cases, precede general drainage; . . . this will especially be the case if the rain fell rapidly and water accumulated on the surface.

Whipkey (1967) recognized the importance of waste movement through macropores in forest soils during heavy rains which he termed "subsurface storm flow." Aley (1977) estimated that water entering soil macropores without visible opening contributed five times as much to

groundwater recharge and stream flow as movement of water through micropores. Thomas et al. (1978) stated it does not appear to be a requirement that the macropores extend to the soil surface for 'flow down' to occur. An example they noted was when soils were plowed the macropores were disturbed in the upper 15 cm of the profile; yet, deep flow still occurs, though to a lesser extent than in an undisturbed soil.

Thomas and Phillips (1979) reasoned that a given rainfall or irrigation does not completely wet (saturate) the root zone before moving deeper in the soil. They found labeled water 80 cm below the surface shortly after application and before the water content of the root zone was raised to field capacity.

Thomas et al. (1978) used simple ion-exchange chromatographic theory to explain earlier work and concluded:

1. Water added to a soil does not stay in the surface soil, but will move as much as 20 times deeper than calculated for water moving in a piston-like fashion (piston flow).

2. Salts in the soil surface will not be moved to the expected water depth at time t, assuming piston flow (X_t), but will be distributed rather evenly through the soil to great depths.

3. Because of 2 above, there will not be a large surge of NO_3^-, pesticide, or other solutes at the time X_t arrives at the water table.

4. Because of 1 above, groundwater recharge will begin much sooner than expected, even when there is a soil water deficit.

5. The term "field capacity" is not well related to water

   flow because significant partial displacement flow can

   occur at water contents below field capacity.

The conclusions of Thomas et al. (1978) are in partial disagreement with the conclusions of Biggar and Nielson (1962) who stated that small differences in velocity among pores, even under nearly ideal conditions, tend to spread the solute like a normal probability density function with the mean concentration at the depth of the added water penetration. They stated that most packed columns with small aggregates show this type of behavior.

In a theoretical approach, Passioura (1971) stated that because soil grains are three to four times that for pores and since diffusion coefficients in macropores are probably 2 to 10 times that within the aggregates, the characteristic time for diffusion in macropores should be 20 to 150 times less than within the aggregates. Thus any concentration gradients in the macropores should be trivial compared to those in the aggregates. He concludes that when one solution displaces another from a saturated aggregated medium, viscous flow takes place effectively only in the voids between the aggregates and, consequently, movement of solutes within the aggregates occurs only by diffusion.

Most of the column-soil work until the 1970's was done with packed, or disturbed, columns. Although they gave important information with respect to textural and general parameters for water movement and a few solutes, little applicable field data was available. During the 1970's a number of column experiments were conducted regarding the soil as a structural unit.

Rao et al. (1976) evaluated a capillary bundle model for

describing solute dispersion in aggregated soils because of the lack of information on the "true" pore geometry of intact soils. They recommended a model which utilized an average pore-velocity and an appropriate dispersion coefficient for describing solute transport in soil columns. They, however, realized little success in their attempt. DeJong (1978) studied the movement of ions from sewage effluent in disturbed and undisturbed 20 cm columns. He found no difference between the type of columns and attributed the lack of difference to the poor structure of the soils investigated.

McMahon and Thomas (1974) used three soils of different structures to measure Cl^- and tritiated water movement through disturbed and undisturbed columns. In all cases the Cl^- and tritiated water moved much faster in the undisturbed columns. They believed, as others discussed earlier, that some solutes moved through the large pores, by-passing some of the water within the peds.

Cassel et al. (1974), in an experiment similar to that of McMahon and Thomas (1974) with the exception that NO_3^- was used instead of labeled water, found that disturbing a soil decreased bulk density and increased mean water content by increasing the total porosity. They stated that the undisturbed columns required less water to displace the solutes than the packed columns because the undisturbed columns retained less applied water at a given soil water tension. Cassel et al. (1974) concluded that, based on disturbed column studies, thoughtful consideration should be made before extrapolating fertilizer and pesticide movement rates to field conditions.

Tyler and Thomas (1981) studied the movement of Cl^- under unsaturated conditions on three undisturbed columns ranging from well

structured to unstructured (massive), with water being added at a rate
just under the infiltration capacity. They observed that the Cl^- moved
more rapidly through the well-structured soil even though it had a
higher clay content.

Anderson and Bouma (1977a) used undisturbed soils with different
structures, but nearly identical textures. They found that differences
in dispersion of Cl^- were due to soil structural effects. Because they
did not use disturbed columns of the same soils for comparison, it is
difficult to determine whether the observed differences in dispersion
coefficients were effected by other soil physical or chemical
characteristics.

In a second paper, Anderson and Bouma (1977b) studied the same
soils under unsaturated conditions. Again, they concluded that differ-
ences in dispersion coefficients were due to characteristic flow pat-
terns within the soils, a result of structural variation.

Most work on solute movement has been done on non-reactive ions
such as Cl^- and NO_3^-. Kanchanasut et al. (1978), though, used both
nonreactive Cl^- and highly reactive phosphates (PO_4) to monitor prefer-
ential solute movement through saturated undisturbed and disturbed soil
columns. They found a relative concentration (RC) of 0.5 Cl^- and PO_4
reached the bottom of their 50 mm packed columns in 8 minutes and 7
hours, respectively, while less than 1 minute was required for both to
reach the same RC in the undisturbed columns.

Dekkers and Barbera (1977) investigated the effect of aggregate
size on leaching of metribuzin in soil columns. They used a retarda-
tion factor to express the difference between the percolating water and
the solute movement.

$$R_{ac} = d_l/d_s$$

d_l = depth of penetrating liquid
d_s = depth of the peak solute concentration

$$R_{eq} = 1+(P_{s/l})b/w$$

$P_{s/l}$ = partition coefficient
b = bulk density
w = volumetric water content

They stated that $R_{eq} = R_{ac}$ if equilibrium between solute adsorption and desorption is maintained. They showed that R_{eq} overestimated solute movement because equilibrium was not attained, aggregate size being a significant factor. They concluded that "the kinetic effects induced by structure are more important for herbicide transport than the adsorption capacity."

Increased concern for groundwater and stream contamination, with a continued interest in the accumulation of fertilizer salts, pesticides, and feedlot wastes in soils, are some of the major reasons for such an active interest in the movement of solutes through the soil. In the last 10 years, considerable research has been reported regarding pollutants and their impact on the soil environment.

Organics in Soils

Wilson et al. (1981) studied the movement and fate of selected organic compounds in soils including trichloro-(TCB) and nitrobenzene (NB). Packed 1.4 m columns of sandy soil (92 to 87% sand) were leached with 14 cm solution/day, this being less than the saturated hydraulic conductivity, for a period of 45 days. Most of the compounds used moved readily through the profile. The movement of TCB was significantly retarded though NB moved readily.

Rogers et al. (1980) investigated the adsorption and desorption of

benzene in two soils and a montmorillonitic clay. One gram soil and
0.5 g clay samples were used with a mixing ratio of 1:25 (adsorbant:
solution) and 1:50 for soil and clay, respectively. The solution con-
centrations were 10, 100 and 1000 ppb of C^{14} labeled benzene; and
analyses were conducted by scintillation. They found that clay adsorp-
tion of benzene did not increase after a 16 hour equilibrium. This was
also reported by Morrill et al. (1981) for other organic pollutants.
Soil adsorption of the benzene, however, continued to increase for many
hours (Rogers et al. 1980). They speculated that degradation products
were being adsorbed on the soil and was being interpreted as benzene by
their analytical procedure. They summarized their study stating that
adsorption is not the major effect of soil on benzenes but rather that
soil is a medium for degradation.

Rao and Davidson (1979) investigated the sorption of 2,4-D,
Atrizine, Terbacil and methyl parathion on three soils. They found
that if a compound was strongly adsorbed by one soil it was also
strongly adsorbed by other soils.

Chiou et al. (1979) found that soil-water distribution coeffi-
cients (sorption coefficient) appeared to be inversely proportional to
the corresponding water solubility of the compound. They believed that
"uptake" of organics by soils is due to partioning in soil OM and clays
but that OM is a more important factor! The importance of OM is sup-
ported by Hamaker and Thompson (1972). The work of Haque and Freed
(1974) agrees with Choiu et al. but further states that sorption of
organics on solid surfaces is a function of solubility, molecular
weight, functional groups, charge distribution and polarity, and
molecular configuration.

Mosier et al. (1972) investigated the movement of water soluble organic substances under and near feedlots. They failed to reveal water soluble organics unique to feedlots in the groundwater. They did, however, find free phenolics in the manure and in the upper few cm of the soil. Low-mole-weight organics were encountered in the groundwater samples examined. They concluded that there was no uniform or continuing movement of organic materials from the feedlots through the soil profile.

Polychlorinated biphenys (PCBs) have been found in raw sewage and sludge with significant uptake of PCBs by crops seen measured (Lawrence and Tosine, 1977). Kunte (1977) evaluated native concentrations of polycyclic aromatic hydrocarbon in German soils. Kunte found the sum of the six organics investigated ranged between 50 and 500 µg/kg soil and reasoned that higher concentrations of PCBs in soils would be due to pollution from various sources.

CHAPTER III

METHODS AND MATERIALS

Undisturbed Columns

Four Payne County, Oklahoma, soils were selected for study with
the assistance of the Soil Conservation Service. Selections were made
on the basis of differing soil structure (i.e., blocky, subangular
blocky, granular, and prismatic) with similarity of the soils in
other characteristics (Table I). The soils were used to assess the
effect of soil macrostructure on the movement and distribution of
nitrobenzene (NB) and trichlorobenzene (TCB) in subsoils. Four un-
disturbed 10 cm x 1 m soil cores (SC) were taken at each site
(Figure 1) with a soil coring machine developed by Utah State
Technical Services (Kelley et al. 1947).

Each SC was enclosed in two 10 cm ID plexiglass tube halves and
placed in a transportation crate to maintain the structural integrity
of the columns. The SC were transferred to the lab and painted with
molten microcrystalline wax over the soil column rounded surface. The
tube half was replaced, the SC was rotated one-half turn, and the other
half of the SC was coated with microcrystalline wax in the same fash-
ion. Perforated 12 x 12 cm plexiglass plates were covered with nylon
window screen and secured to the bottom of the prepared soil columns
with wax. Strapping tape was placed around the SC to add radial sup-
port. The columns were mounted with the perforated plexiglass square

13

TABLE I

CHEMICAL AND PHYSICAL CHARACTERISTICS OF SELECTED SOILS

Treatment	pH	CEC	OM	Bd	Pores	Sand	Silt	Clay	Description
		meq/100g	—%—	g/cm^3	—%—	—%—	—%—	—%—	
Blocky I, P	6.50	17.4	0.838	1.37	48.1	62	5	33	Cumulic Haplustoll fine-loamy, mixed, thermic
Blocky I, U	-	-	-	1.60	39.6	-	-	-	
Blocky II, P	6.70	22.78	1.378	1.37	48.1	62.5	12.5	25	Pachic Arigiustoll fine-loamy, mixed, thermic
Blocky II, U	-	-	-	1.39	47.5	-	-	-	
Granular, P	6.15	15.5	1.058	1.37	48.1	65.5	9.5	25	Cumulic Haplustoll fine-loamy, mixed, thermic
Granular, U	-	-	-	1.56	41.1	-	-	-	
Prismatic, P	6.80	20.1	1.105	1.37	48.1	57.5	6.5	35	Cumulic Haplustoll fine-loamy, mixed, thermic
Prismatic, U	-	-	-	1.38	47.9	-	-	-	

P = Packed
U = Undisturbed
CEC = Cation exchange capacity
OM = Organic matter
Bd = Bulk density

1 - Blocky I

2 - Blocky II

3 - Granular

4 - Prismatic
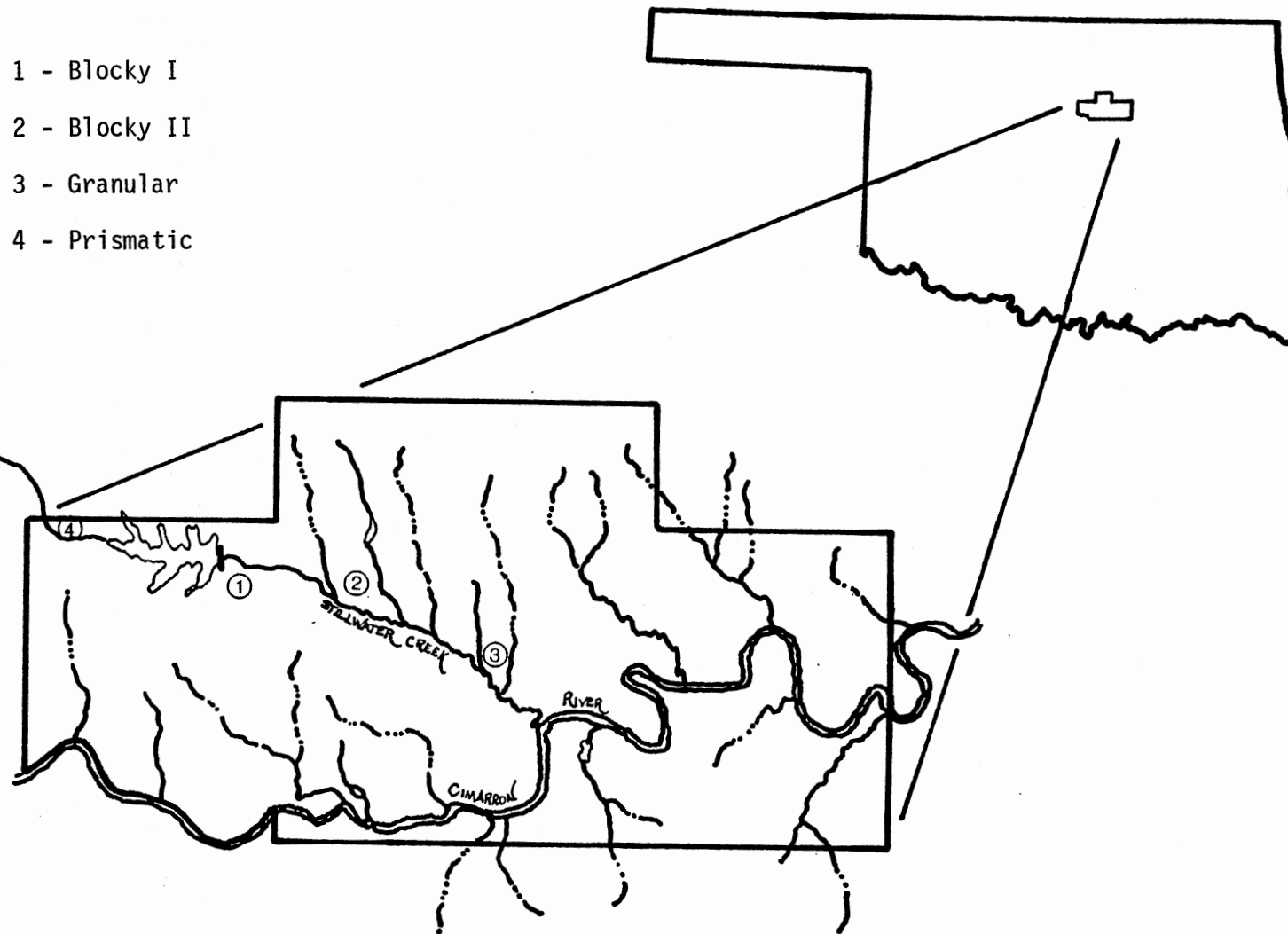
Figure 1. Soil Sampling Locations within Payne County, Oklahoma.

over a plastic funnel for weight support and drainage. The circum-
ference of the upper end of the SC was sealed to the tube so that the
infiltrating solution would not move along the soil core-plexiglass
interface. The plexiglass columns were held rigidly on a flex-frame
in a constant temperature laboratory (approximately $21^{o}C$). The columns
were kept moist by daily watering until the experiment was begun.

Packed Columns

Realizing that several soil characteristics, in addition to struc-
ture, might contribute to differences in solute movement, a method was
sought to eliminate structural effects. This was approached by using
packed columns (PC). The PC were prepared with soil collected from the
same depth ranges represented in the corresponding undisturbed SC. The
collected soil materials were oven dried, ground, and passed through a
20-mesh sieve. Plexiglass tubes (10 cm x 120 cm) were split longitu-
dinally and the inside of each tube half was coated with a thin layer
of microcrystalline wax. The seams were fitted together and glued with
a silicone sealant and taped with strapping tape to add radial
strength. The bottom of the tubes were fit with nylon window screen
and a plexiglass sieve as previously described. The soil was packed
into the tubes at a rate of 500 grams per 4.6 cm depth. This packing
procedure (a modification of the ASTM method) provided an average bulk
density of 1.37 g/cm^3. The PC were then placed in the constant
temperature lab as described for the SC.

All SC and PC columns were topped with a 5 cm layer of acid-washed
flint shot sand and saturated with distilled-deionized water. After
saturation, 0.8 cm holes were drilled with a masonry bit 4 cm into the

column at 8, 16, 32, 48, 64, and 80 cm from the upper soil surface so that the holes were in spirial pattern. Ceramic cups were fitted into the prepared holes and used for solution extraction. The ceramic cups (1 cm x 1.5 cm) were fitted previously (epoxied) to 3 mm spaghetti tubing and were used for solution sample conveyance into 16 ml screw-cap vials. The 3 mm tubing was attached to a two hole '00' rubber stopper with the second hole being attached to a vacuum manifold (Figure 2).

Solution Application and Extraction Procedure

The NB and TCB containing solution was added to the top of each column at a rate of 10 ml every 8 hours. This rate was selected because it was less than the infiltration capacity for all columns. A 35 ug NB/ml and 29 ug TCB/ml stock solution was prepared by placing the pollutant in approximately 400 ml of methanol then increasing the solution to a volume of 18 liters with distilled-deionized water.

The sample vials were removed from the columns when they contained over 6 ml of extractant (approximately 1 week sampling periods). As the sample vials were removed, they were covered with aluminum foil and sealed. The sampling process continued for 10 weeks.

The solution samples were prepared for GC analysis by placing a 2 ml aliquot into a 16 ml screw-cap vial with septum with 2 ml of distilled-deionized water. Two ml of hexane were then added to the vial to provide an immiscible solvent phase extractant for NB and TCB. With the vials capped, the internal standard (ISTD) chloroform was added to the hexane phase and weighed to four decimal places.
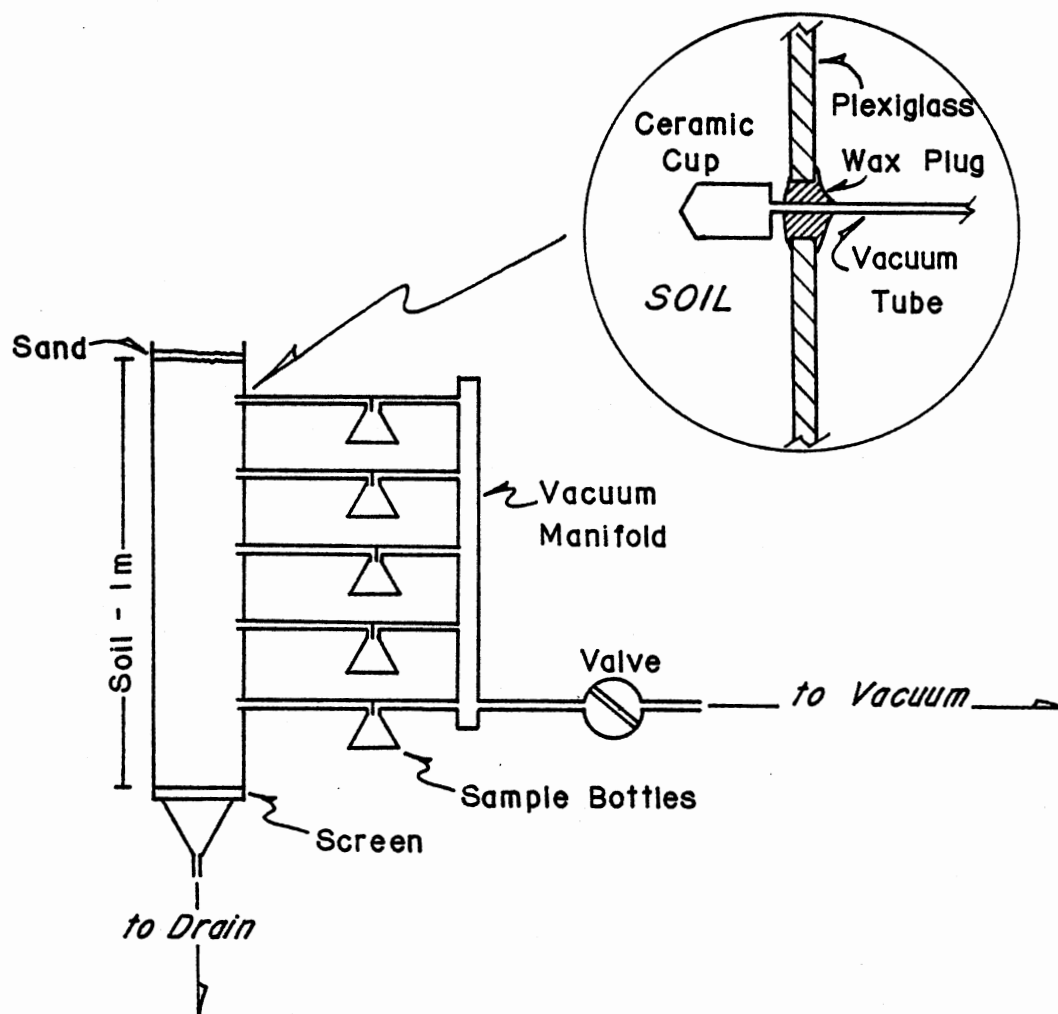
Figure 2.   Schematic of Laboratory Design for Soltuion Application
            and Withdrawal.

(The operating parameters for the internal standard method for NB with chloroform are contained in Appendix A). After mixing, a measured amount of the hexane phase was injected with µl syringes into a Hewlett-Packard Gas Chromatograph Model 5830A (GC) equipped with an electron-capture detector (ECD).

Time periods (weeks) were converted into number of soil pore volume equivalents by dividing the total volume of solution applied by the volume of pores for a given column depth. One "pore volume" refers to the quantity of solution equivalent to the total pore space contained in a given soil volume calculated from the bulk densities of the individual columns. By statistical necessity, time was used in the analyses of variance because the pore volume source of variation was not consistent from soil to soil. Pore volume was used graphically to base the different soils on a numerically equivalent axis. While this is important when comparing different depths of the same soil, the differences in pore volume were small when equivalent depths of different soils were compared.

Soil Sample Study Procedure

After a 10 week solution sampling period, the columns were removed from the racks and opened lengthwise. Soil samples were then taken at 1 cm intervals to a depth of 10 cm, 2 cm intervals to 32 cm, 4 cm intervals to 64 cm and 8 cm intervals to the 88 cm depth. Ped surface scraping samples were taken from the SC of the Blocky I, Blocky II and Prismatic soils. Ped scrapings were not taken for the granular SC because of the small size of its peds. Matrix or bulk samples were taken from all soils. The samples were frozen until analysis was

performed.

The soils were analyzed for NB and TCB using the following procedure: approximately 2 g soil were placed into a preweighed 16 ml screw-cap-septum vial and 4 ml of distilled-deionized water added. Two ml of hexane was added as an immiscible solvent phase extractant and the vial sealed with a septum. The samples were shaken with a vortex mixer until the soil was visibly mixed (approximately 3 minutes) and allowed to stand for 1 hour. Amounts of NB and TCB were determined by the GC methods described above. After the analysis was completed, the vials were uncapped and placed in an oven ($125^{o}C$) dry overnight and the soil weight determined.

Soil depths were converted into soil mass by multiplying the depth of soil sampled by 78.54 cm^{2} (column area), particle density, and the solid fraction of the given soil. The term "soil mass" refers to the weight of soil contained at specified depths.

Sorption Study Procedure

An NB sorption isotherm study was run for the soils studied. The TCB data were not included because of large determination errors due to its low solubility and high soil affinity.

Five g of each soil were weighed and placed into five 40 ml centrifuge tubes with 25 ml distilled-deionized water. The tubes were fitted with septa caps and placed on an Eberbach horizontal shaker for 15 minutes of every hour for 16 hours. The tubes were removed, and one of six treatments was made (0.25, 0.50, 1.0, 2.0, 4.0, and 8.0 ppm NB) by addition of μl volumes of stock solutions weighed to four decimal places. The tubes were returned to the shaker for 16 hours as

described above. At the end of the equilibrium period, 0.1 ml of 1 N CaCl$_2$ was added to each tube to floculate the clay. Samples were cen-trifuged at 1000 rpm for 20 minutes. Solution sample extraction and GC analysis were carried out as before with the exception that the highest concentration of NB in distilled-deionized water was used as a standard to make adjustments for the extraction efficiency of NB in hexane.

CHAPTER IV

RESULTS AND DISCUSSION

NB Isotherm Sorption Study

Regression parameters for the equation initial NB concentration equals equilibrium NB concentration are given for each soil in Table II. In the context of this experiment, the slope values (b_1) are indicative of the strength of soil adsorption of NB. A lower b_1 indicates the stronger affinity for NB. In all soils the regression models were highly significant (0.05 probability level) with correlation coefficients greater than 0.9.

Figure 3 depicts the confidence intervals of the b_1 values for the four soils. Note that the granular soil had the lowest b_1 and that the granular and prismatic soils had significantly lower values than the blocky II soil. When looking at b_1 values only, the order of increasing value is Granular, Prismatic, Blocky I and Blocky II. This is also the order of decreasing affinity of the respective soils for NB. This would suggest that, with all other variables being equal, NB solution concentrations, extracted from the soil, would be dependent on the sorption characteristics of the soil as well as the amount of NB that had reached that same point in the soil. Therefore, direct comparisons of extracted solutions between structural types should not be made without first comparing columns where structural effects have been removed.

TABLE II

REGRESSION STATISTICS FOR NB
SORPTION ISOTHERM

Soil	Equation 1/	R^2	CV 2/
Blocky I	Y = -0.16 + 0.724X	0.93	41.6
Blocky II	Y = -0.02 + 0.755X	0.98	18.6
Granular	Y = 0.14 + 0.585X	0.97	19.4
Prismatic	Y = -0.03 + 0.597X	0.93	38.5

1/ Y = initial concentration; X = final concentration.
2/ Coefficient of variation.
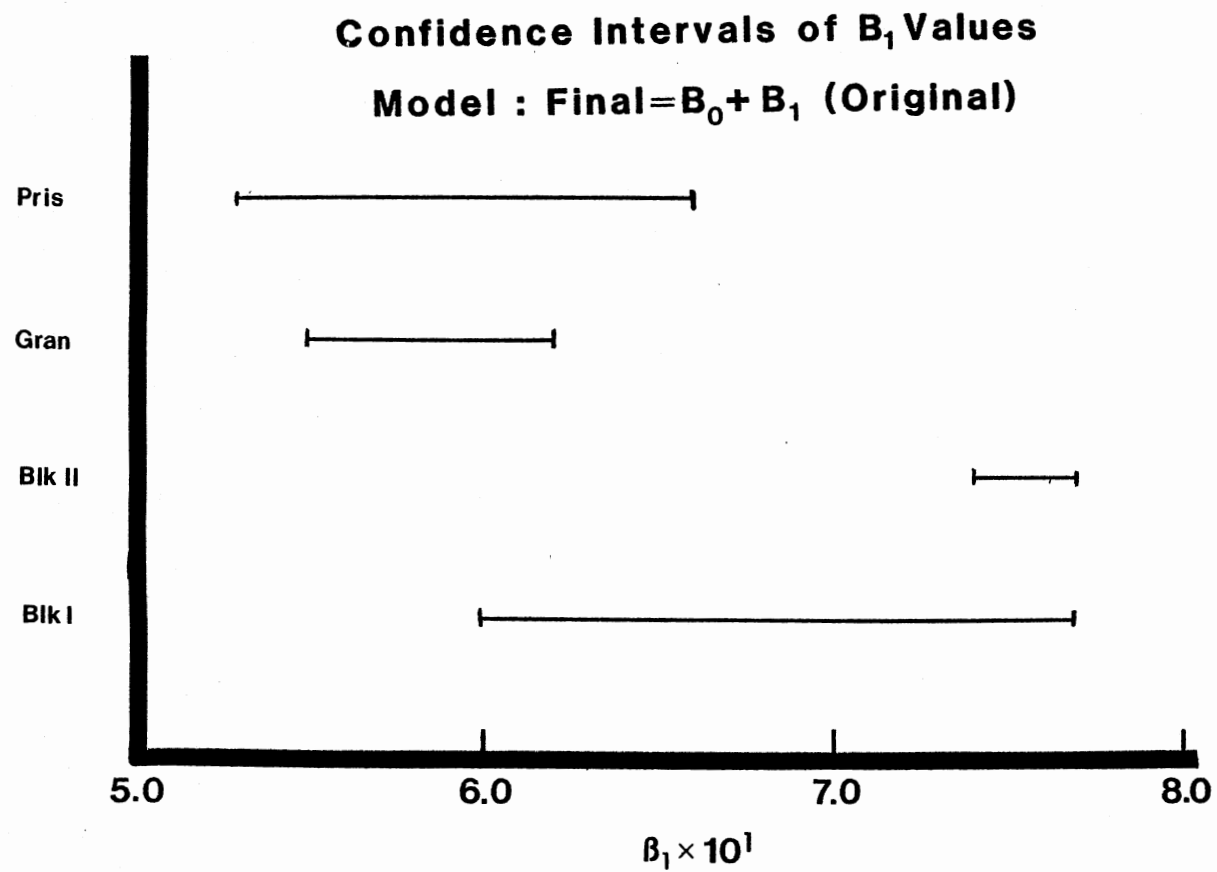
Figure 3. Confidence Intervals of B_1 Values for NB Sorption Isotherm.

Wilson et al. (1981) determined that TCB movement was retarded by the soil four times as much as NB. It would be expected that the order of TCB-soil affinity would be similar to NB (Rao and Davidson, 1979; Chiou et al. 1979). When column soil samples were extracted with water and hexane the granular soil showed the lowest TCB concentrations for all soils followed by the prismatic soil. This follows the NB sorption work discussed above. Column soil sampling will be discussed in a later section.

Solution Study

The determined concentrations of NB are listed by time for eight treatments and three depths in Tables III, IV, and V. The number of pore volumes of solution which passed a given depth after 10 weeks are given in Table IX, Appendix B. The values can be used to calculate the actual pore volumes for the individual treatments at any given time (weeks). Nitrobenzene was measured down to the 4th depth (48 cm) for the blocky II packed soil after 5 weeks, but NB was not observed below the 4th level for any soil. TCB was not detected in any of the per-coalating soil solution samples, presumably due to the low water solubility and/or the strong soil adsorption of TCB.

It should be noted that there were large variabilities in the NB concentrations between replicates. Brunauer (1965) attributed this type of variation to the complex nature of soil surfaces. However, from this study, there has been no consistant explanation. It should be also noted that the mean NB concentration decreases drastically after the 5th week in all soils. The cause is likely microbial degradation of NB. Wilson et al. (1981) found NB microbial decomposition

TABLE III

MEAN NB CONCENTRATION OF TREATMENTS AT RESPECTIVE WEEKS FOR DEPTH 1

Trt	| Time (Weeks)* 1	2	3	4	5	6	7	8	9
Blocky I, P	0.000	0.000	0.056	0.052	0.051	0.049	0.000	0.000	0.000
Blocky I, U	0.005	0.046	0.092	0.136	0.036	0.010	0.000	0.000	0.000
Blocky II, P	0.168	0.496	1.084	2.252	1.129	0.721	1.363	1.655	1.318
Blocky II, U	0.302	0.623	0.707	1.486	1.198	0.932	0.686	0.866	0.425
Granular, P	0.019	0.344	0.184	0.316	0.175	0.213	0.394	0.227	0.117
Granular, U	0.000	0.045	0.050	0.055	0.000	0.185	0.000	0.000	0.000
Prismatic, P	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Prismatic, U	0.111	0.227	0.166	0.660	0.766	0.678	0.309	0.024	0.000

*The pore volumes can be calculated by multiplying this value by the appropriate value found
 in Appendix B divided by 9.
P = Packed
U = Undisturbed

TABLE IV

MEAN NB CONCENTRATION OF TREATMENTS AT RESPECTIVE WEEKS FOR DEPTH 2

| Trt | Time (Weeks)* | | | | | | | | |
	1	2	3	4	5	6	7	8	9
Blocky I, P	0.000	0.000	0.000	0.000	0.003	0.023	0.038	0.009	0.017
Blocky I, U	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Blocky II, P	0.000	0.000	0.056	0.198	0.149	0.226	0.412	0.223	0.071
Blocky II, U	0.017	0.099	0.187	0.443	0.635	0.431	0.572	0.580	0.581
Granular, P	0.000	0.002	0.038	0.098	0.094	0.111	0.082	0.112	0.072
Granular, U	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Prismatic, P	0.005	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Prismatic, U	0.000	0.004	0.010	0.055	0.128	0.219	0.374	0.185	0.057

*The pore volumes can be calculated by multiplying this value by the appropriate value found
 in Appendix B divided by 9.
P = Packed
U = Undisturbed

TABLE V

MEAN NB CONCENTRATION OF TREATMENTS AT RESPECTIVE WEEKS FOR DEPTH 3

Trt	Time (Weeks)*								
	1	2	3	4	5	6	7	8	9
Blocky I, P	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Blocky I, U	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Blocky II, P	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.002
Blocky II, U	0.000	0.002	0.000	0.015	0.000	0.066	0.050	0.051	0.053
Granular, P	0.000	0.000	0.000	0.000	0.000	0.003	0.000	0.000	0.000
Granular, U	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Prismatic, P	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Prismatic, U	0.000	0.000	0.000	0.000	0.000	0.015	0.002	0.003	0.003

*The pore volumes can be calculated by multiplying this value by the appropriate value found
 in Appendix B divided by 9.
P = Packed
U = Undisturbed

after 3 weeks during a column study when the initial NB concentration was greater than 0.9 ppm. The work of Rogers et al. (1980) would support the possible microbial decomposition of NB as well.

Figures 4 through 7 depict the mean concentration of the NB vs. soil pore volume. Figures 8 through 10 are overlays for NB vs. pore volumes for depths 1 through 3 over treatments. At depth 1 (8 cm), treatments 2 and 6 (blocky II packed and undisturbed, respectively) exhibit the highest concentration of NB at any pore volume. It should be noted that the bulk density of treatment 2 is slightly less than treatment 6 (1.39 vs. 1.37). The importance of the bulk density difference is in relation to total porosity, namely, higher bulk densities give lower total porosity. With this in mind it is proposed that the difference between the curves is due to structural effects. However, there appears to be little difference between treatments 2 and 6 and the reasons or causes have not been determined. At the two lower depths the difference is much more obvious, higher concentrations in the solutions extracted from the undisturbed columns (Figures 9 and 10).

The blocky I and prismatic soils are the most highly structured soils in this study and the difference between treatments 1 and 5, and 4 and 8 show, that the undisturbed soils (treatments 5 and 8) had the highest average NB concentration. This indicates that NB moves down the soil mass more rapidly through the macropores in highly structured soils. This effect was most evident in the case of the prismatic soil where the bulk density of the undisturbed columns and packed columns are nearly the same (1.38 vs. 1.37 g/cm^3, respectively), yet the undisturbed columns show a higher NB concentration at all points. Therefore, the major difference may be in the relative proportion and
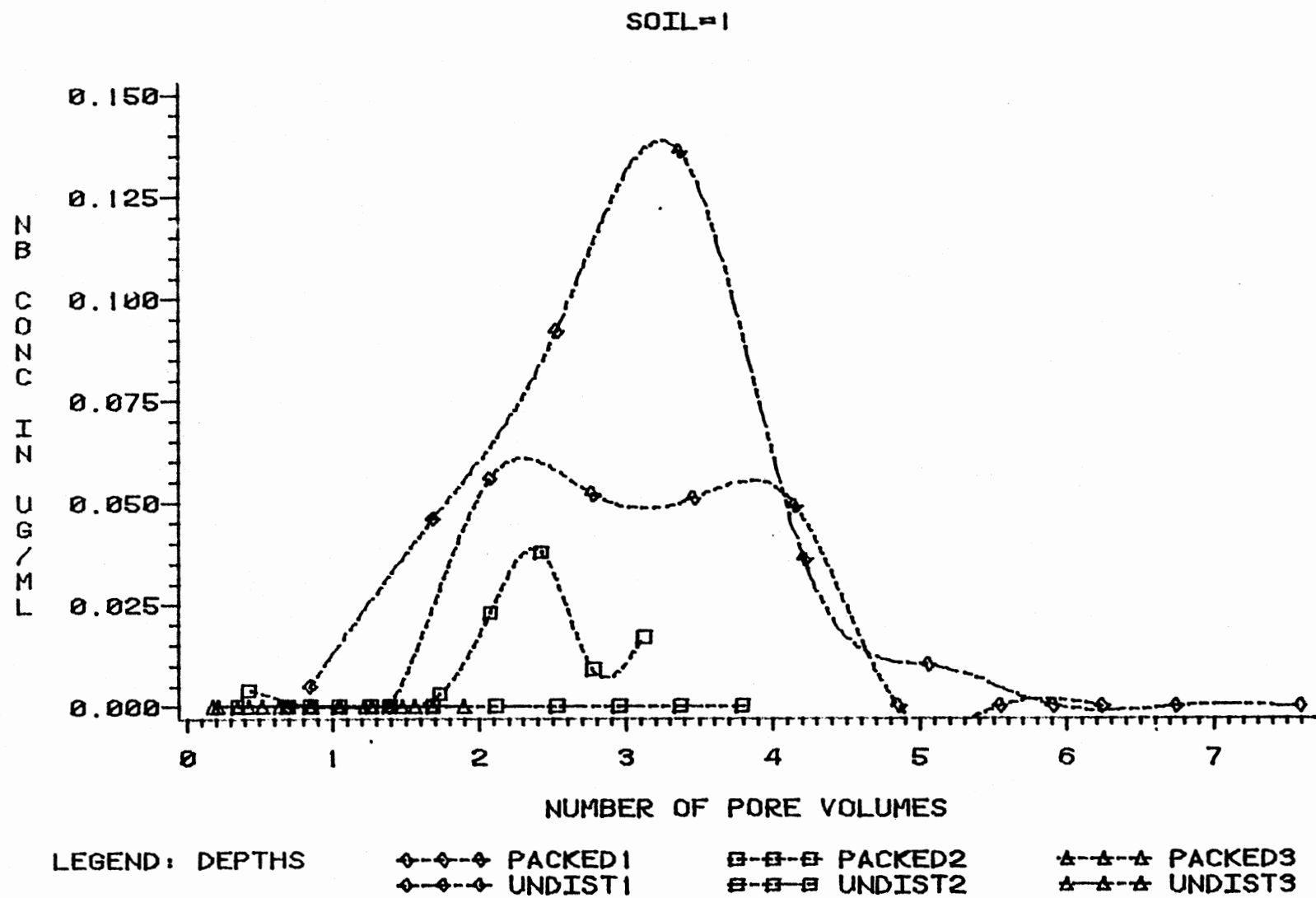
Figure 4. Mean NB vs. Pore Volume Curves for Blocky I Soil at Various Depths (Both Undisturbed and Packed Columns).
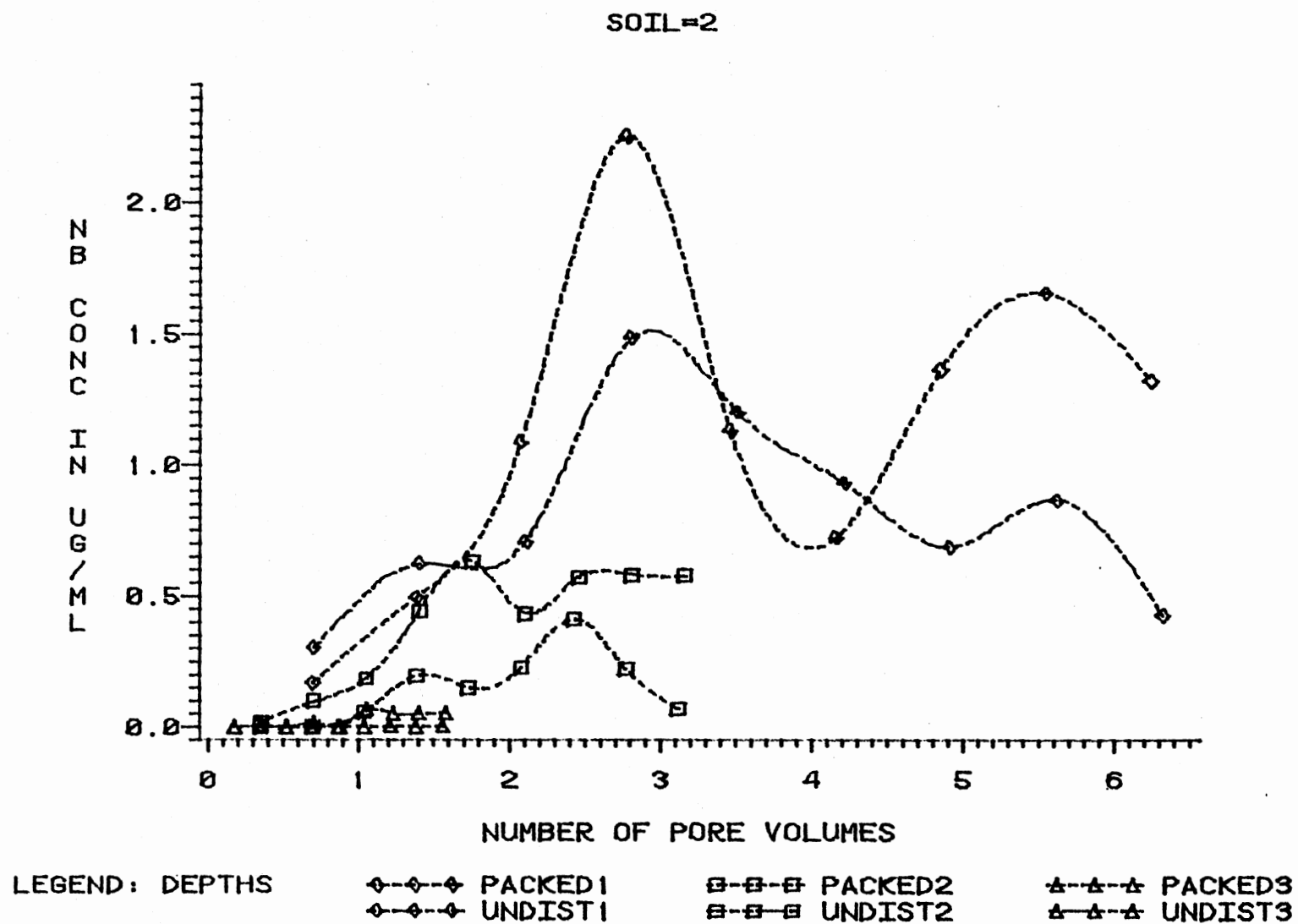
Figure 5. Mean NB vs. Pore Volume Curves for Blocky II Soil at Various Depths (Both Undisturbed and Packed Columns).
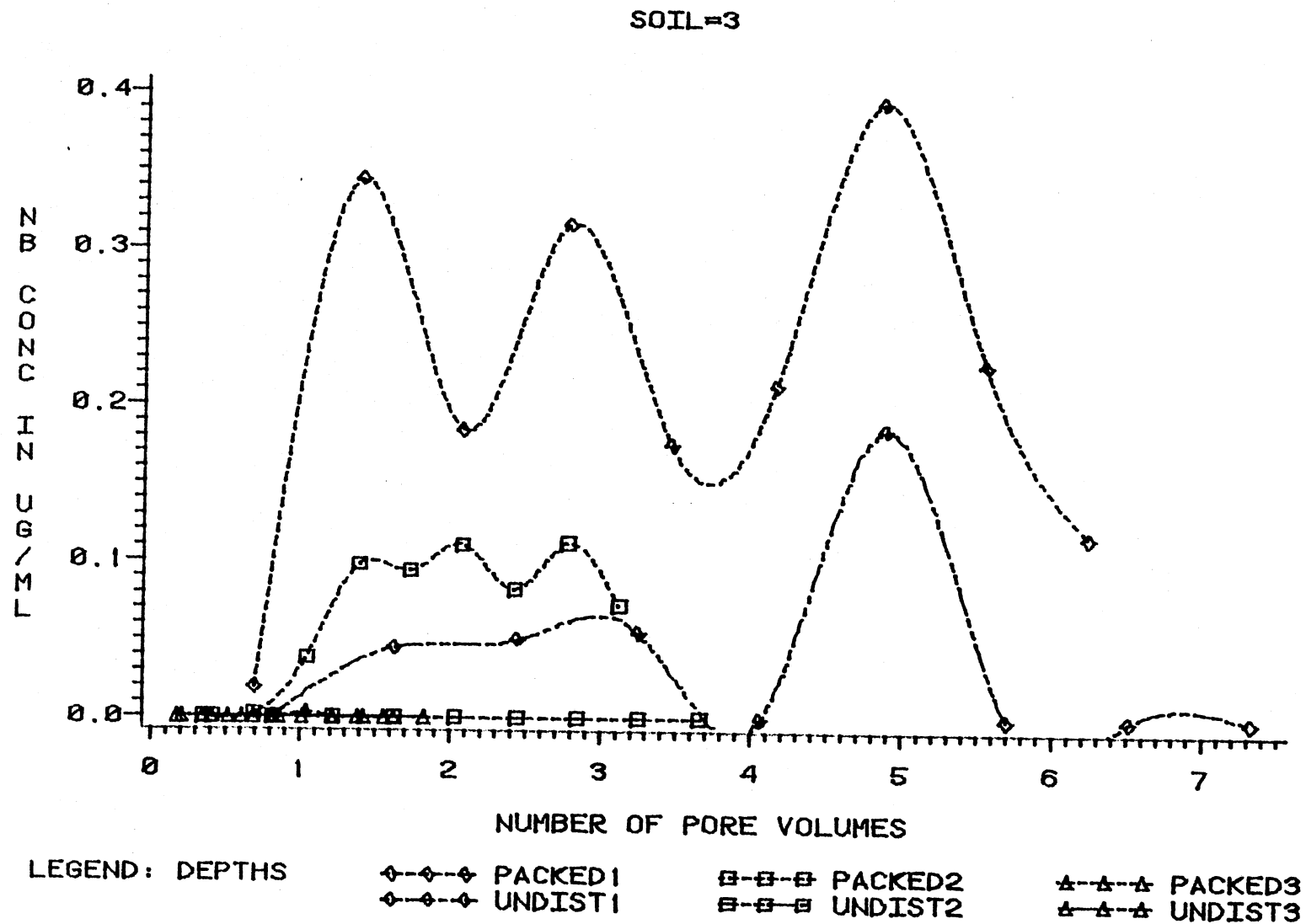
Figure 6. Mean NB vs. Pore Volumn Curves for Granular Soil at Various Depths (Both Undisturbed and Packed Columns).
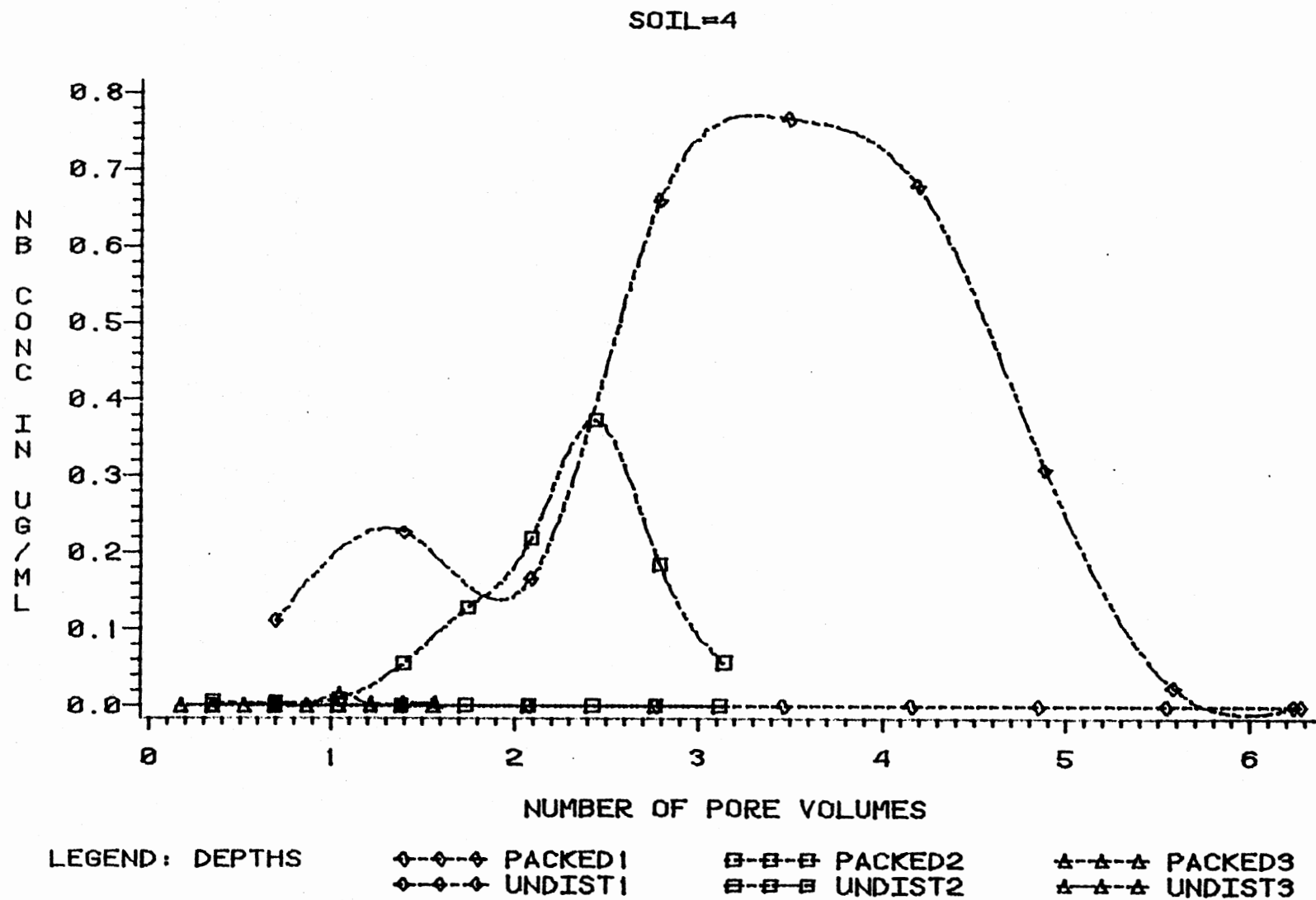
Figure 7. Mean NB vs. Pore Volume Curves for Prismatic Soil at Various Depths (Both Undisturbed and Packed Columns).
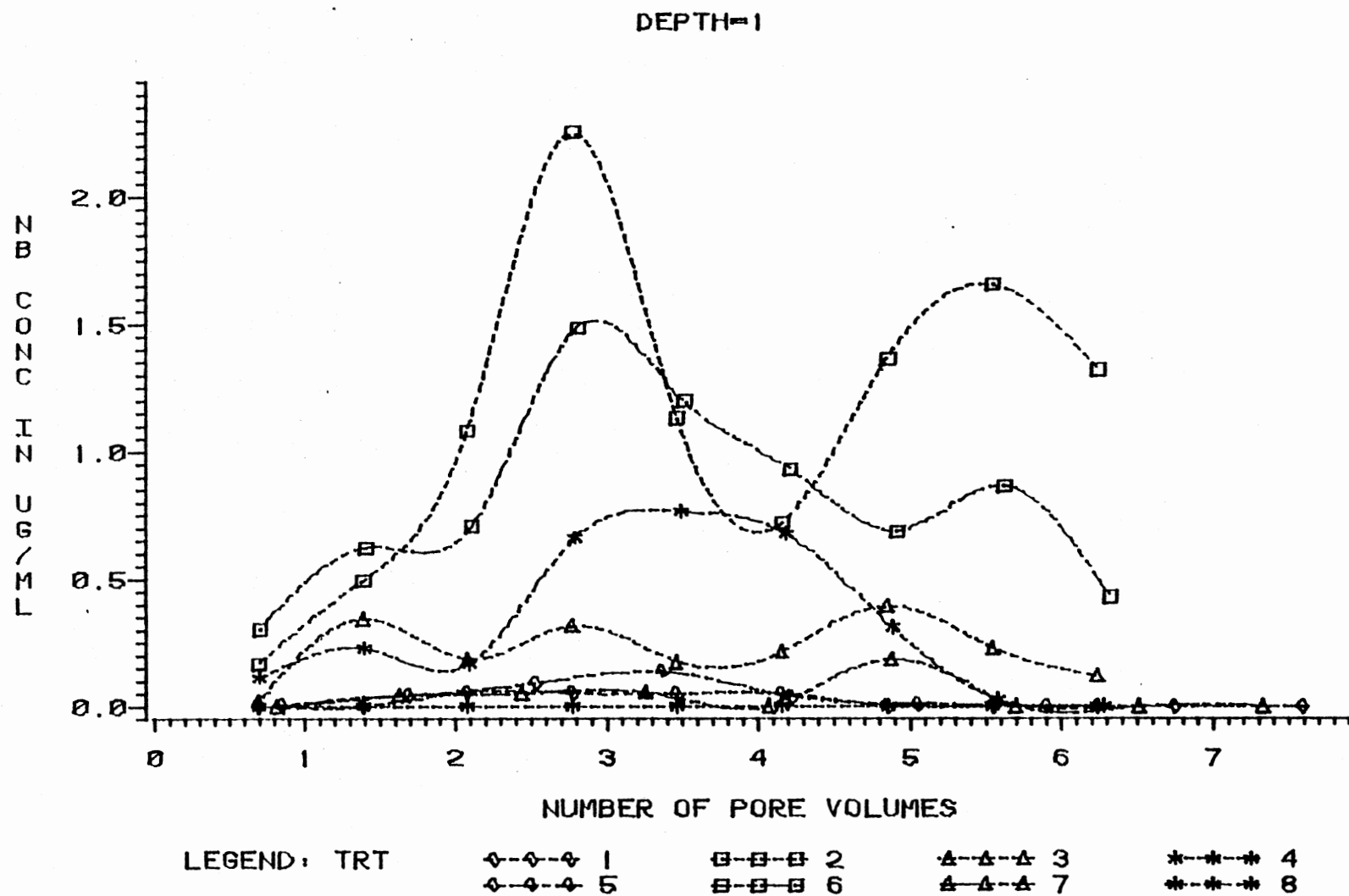
Figure 8. Mean NB vs. Pore Volume Curves at Depth 1 (8 cm) for all Treatments.
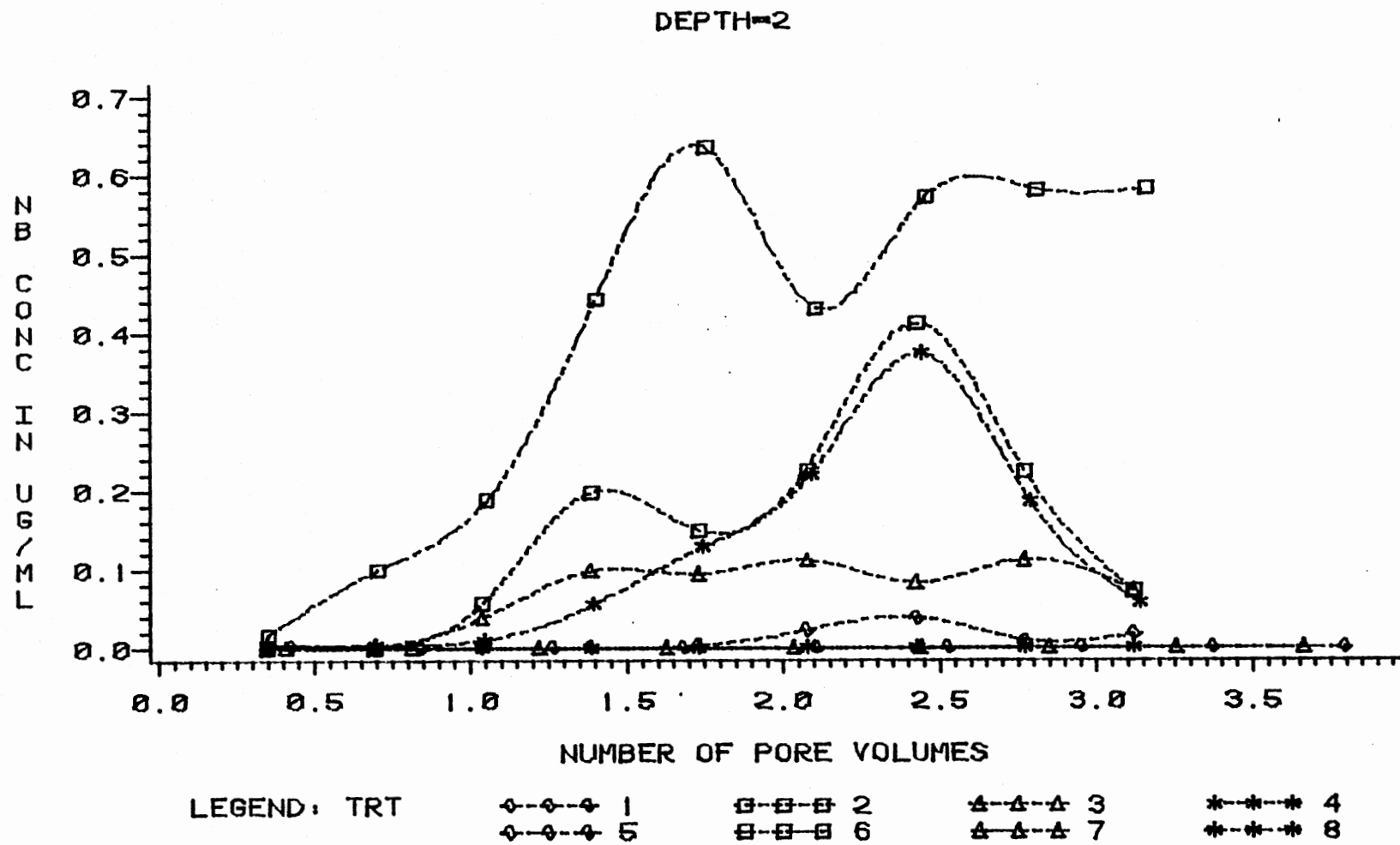
DEPTH=2

Figure 9.   Mean NB vs. Pore Volume Curves at Depth 2 (16 cm) for all Treatments.

DEPTH=3

NB CONC IN UG/ML

NUMBER OF PORE VOLUMES

LEGEND: TRT   ◇--◇--◇ 1   ▣-▣-▣ 2   ▵--▵--▵ 3   *--*--* 4
               ◇--◇--◇ 5   ▣-▣-▣ 6   ▵--▵--▵ 7   *--*--* 8
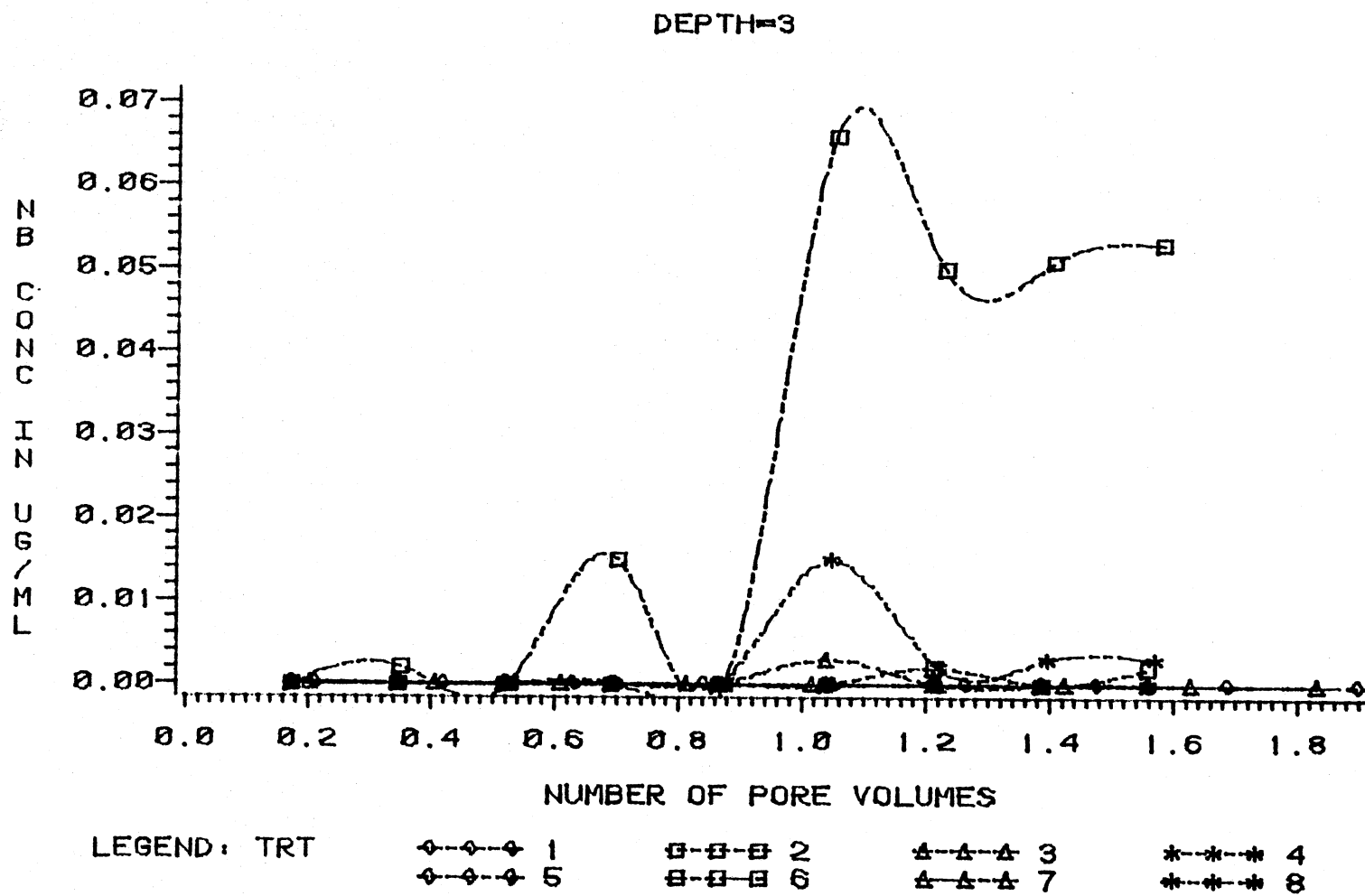
Figure 10.   Mean NB vs. Pore Volume Curves at Depth 3 (32 cm) for all treatments.

distribution of micro- and macropores, a result of structure. With long vertical macropores, a characteristic of the prismatic structure, the pollutant may move down the column and bypass much of the soil mass and, therefore, be observed at higher concentrations at lower depths than if the solution passed through a larger portion of the soil mass. The same reasoning holds for the blocky I structure, though to a lesser extent, where there is a greater disparity between bulk densities.

The granular soil is the least structured soil studied and is, therefore, more like its packed counterpart than the other soils in this experiment. The packed columns had higher mean NB solution levels than the undisturbed columns. Because of the lower expression of structure and higher bulk density (lower total porosity), this appears to be a consistent trend with the observations for the other soils. With a higher density of soil particles and extremely limited longitudinal macropores, the undisturbed columns would be expected to yield soil extracts of lower concentrations.

The same general observations appear to hold for the second and third depths especially for the blocky II soil where the undisturbed solution samples are much higher in NB than the packed columns.

Although analysis of variance generally shows differences between soil types (Table VI), it seldom detected differences within a soil for undisturbed vs. packed columns. When looking at differences between column types for individual soils, an analysis of variance shows statistical differences in the prismatic and granular soils but not for the blocky I and blocky II soils. Variation in replicates of the blocky I soil masks the statistical difference between the

TABLE VI

SIGNIFICANCE TABLE FOR NB = SOIL (S)
COLUMN TYPE (CT) S X CT††

Source of Variation	Time in Weeks								
	2	3	4	5	6	7	8	9	10
A. Depth 1									
Soil (S)	*	*	†	*	*	*	*	*	*
Column Type (CT)									
SxCT									
B. Depth 2									
Soil (S)		*	*	*	*	*	*	*	*
Column Type (CT)		*			*				
SxCT		*	*		*				*
C. Depth 3									
Soil (S)				*		*	*	*	*
Column Type (CT)				*		*	*	*	*
SxCT				*		*	*	*	*

*.05α   †† See Table X in Appendix B.
†.10α

concentration vs. time curves for the packed (treatment 1) and undisturbed (treatment 5) columns. However, it is still believed that NB was preferentially moved within the column as shown by the mean curves (Figure 3). Failure to see statistical differences may be due to too few replicates and possible methodology impairments.

For all soils the classification variable "depth" was significantly different at the .05 level, however, the prismatic and granular soils exhibited significant column type x depth interaction. The column type x depth interaction may not be important when considering that the structure may have some effect on the accumulation of NB at various points down the column and give rise to the spiking seen instead of uniform concentration curves.

When considering the length of time, from time of application to first detection of NB at the various depths, averaged over replication, NB was observed first at depth 1 in treatments 8, 6 and 2. At the 3rd depth the NB of treatment 6 was detected first followed by treatments 8 and 2. Treatment 3 was the only other treatment where NB was observed at depth 3. However, the occurrence of NB in treatment 3 was in a single column observation while in treatments 2, 6 and 8 multiple observations were made. It is noteworthy that for all treatments NB was first observed at the third depth in the undisturbed columns (treatments 6 and 8).

Soil Sample Study

The concentrations of TCB and NB matrix samples are listed by soil depth for all treatments in Tables VII and VIII. Concentrations for NB were lower than for TCB, a postulated result of NB decomposition via a microbial population while, on the other hand, TCB is very slowly

TABLE VII

MEAN TCB CONCENTRATION EXTRACTED FROM
SOIL SAMPLES AT GIVEN DEPTHS*

Treatment	Depth in Cm																	
	1	2	3	4	5	6	7	8	9	10	12	14	16	18	20	22	24	26
Blocky I Packed	0.561	0.831	0.568	0.417	0.147	0.062	0.049	0.044	0.021	0.012	0.001	0.016	0.004	0.005	0.002	0.003	0.000	0.000
Blocky I Undisturbed	0.590	0.553	0.491	0.464	0.345	0.178	0.199	0.145	0.087	0.057	0.028	0.018	0.003	0.000	0.002	0.001	0.002	0.002
Blocky II Packed	0.158	0.422	0.480	0.392	0.326	0.339	0.308	0.384	0.199	0.177	0.108	0.086	0.039	0.025	0.008	0.005	0.003	0.003
Blocky II Undisturbed	0.847	0.406	0.564	0.634	0.396	0.346	0.273	0.378	0.349	0.307	0.215	0.227	0.062	0.082	0.042	0.012	0.008	0.005
Granular Packed	0.192	0.466	0.559	0.406	0.097	0.264	0.161	0.036	0.051	0.018	0.014	0.013	0.003	0.003	0.002	0.004	0.004	0.001
Granular Undisturbed	0.105	0.125	0.123	0.077	0.074	0.041	0.024	0.015	0.024	0.033	0.026	0.011	0.027	0.010	0.012	0.000	0.016	0.003
Prismatic Packed	0.716	0.591	0.352	0.091	0.052	0.027	0.022	0.052	0.019	0.031	0.022	0.002	0.014	0.011	0.033	0.004	0.003	0.004
Prismatic Undisturbed	0.286	0.368	0.354	0.223	0.228	0.227	0.282	0.423	0.153	0.179	0.084	0.071	0.037	0.025	0.006	0.010	0.007	0.018

*Parts per million

TABLE VIII

MEAN NB CONCENTRATION EXTRACTED FROM
SOIL SAMPLES AT GIVEN DEPTHS†

	Depth in Cm																	
Treatment	1	2	3	4	5	6	7	8	9	10	12	14	16	18	20	22	24	26
Blocky I Packed	0.250	0.180	0.124	0.049	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Blocky I Undisturbed	0.029	0.050	0.017	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Blocky II Packed	0.310	0.528	0.518	0.738	0.719	0.713	0.889	0.537	0.534	0.200	0.088	0.091	0.028	0.000	0.000	0.000	0.000	0.000
Blocky II Undisturbed	0.187	0.177	0.149	0.217	0.192	0.160	0.173	0.226	0.194	0.178	0.083	0.091	0.033	0.040	0.023	0.005	0.002	0.001
Granular Packed	0.052	0.047	0.048	0.031	0.022	0.061	0.024	0.006	0.023	0.009	0.028	0.015	TR*	0.001	0.000	0.000	0.000	0.000
Granular Undisturbed	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Prismatic Packed	0.048	0.005	0.002	0.001	TR	TR	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Prismatic Undisturbed	0.051	0.024	0.016	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.017	0.019	0.022	0.014	0.008	0.018

*TR – Trace Amounts
†Parts per million

biodegraded in soils (Marinucci and Bartha, 1979). Figures 11 through 14 depict the mean TCB concentrations vs. soil mass for all soils while Figure 15 contains the same information for structured soils only. There was no statistical difference found between matrix and ped scraping samples for structured soils.

The work of Wilson et al. (1981) has shown that TCB is sorbed more strongly on the soil than NB. As presented earlier in this study, NB is sorbed in decreasing strength; granular > prismatic > blocky I > blocky II. It is reasonable to consider that TCB would be sorbed in similar order and that desorption would occur in reverse order (Rao and Davidson, 1979). Note in Figure 15, TCB values are lowest for treatment 7 (granular undisturbed). When this is compared to treatment 8 (prismatic undisturbed), which has a slightly higher b_1 sorption value, it appears that more TCB was accumulating in the prismatic soil because more TCB passed a given depth. The trend supports the notion that TCB was transmitted deeper in the prismatic soil than in the granular soil, i.e., more TCB detected indicates more rapid transmission of TCB. Statistical evaluation does not confirm this observation.

Comparison of the undisturbed columns with their packed counterpart by analysis of variance show statistical differences (0.05 level) only within the granular soil for TCB. In this case the packed columns show the highest concentrations at any given point. This follows the same pattern found in the solution study for NB. Statistical differences were not seen for the other soils, however, the highest average TCB concentration was measured in the prismatic and blocky II undisturbed soils at the 26 cm depth.

Analysis of variance data for NB vs. depth shows significant

SOIL=1

Figure 11. Mean TCB vs. Soil Mass Curves for Blocky I Soil (Packed (1) and Undisturbed (2) Columns).
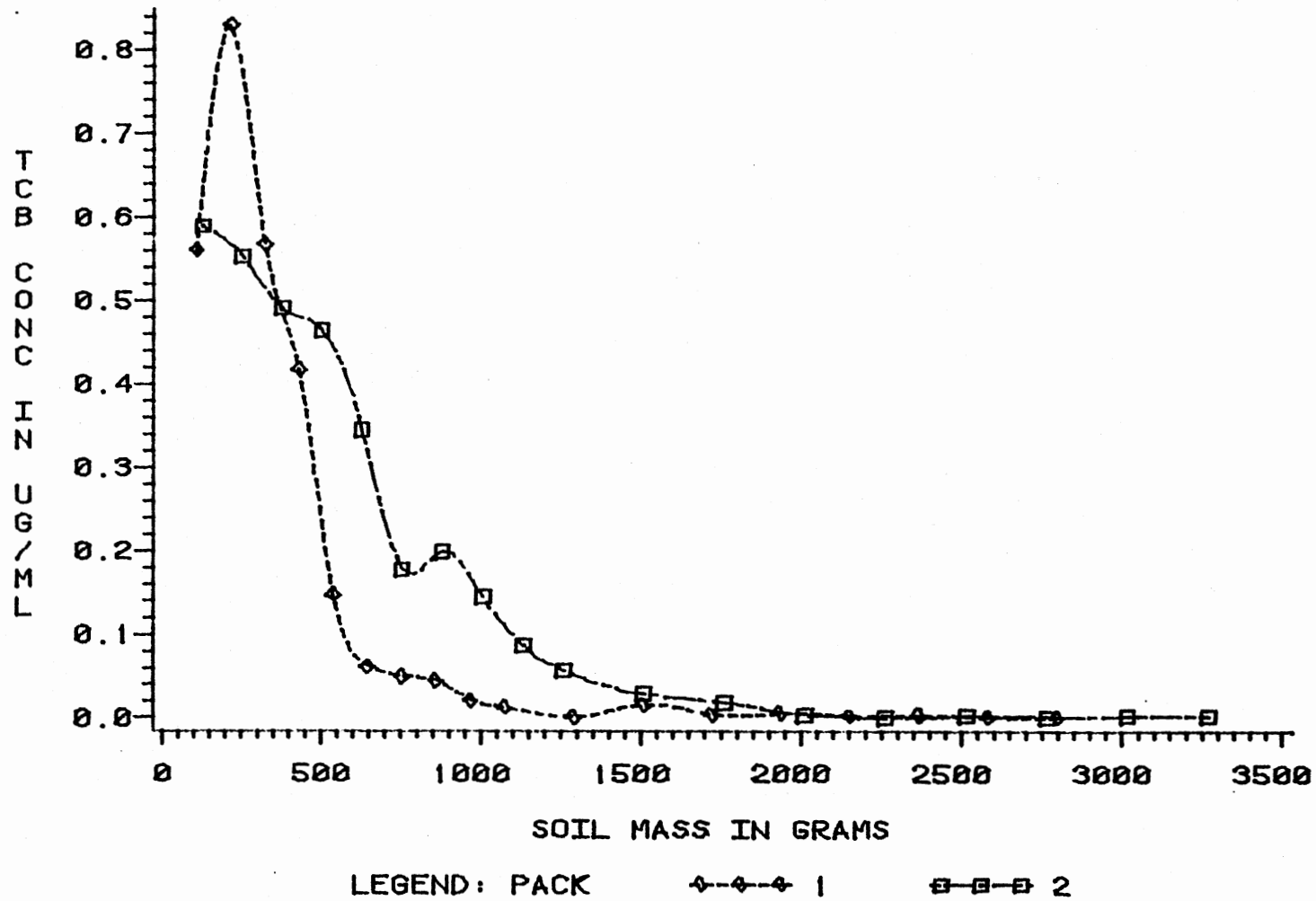
SOIL=2
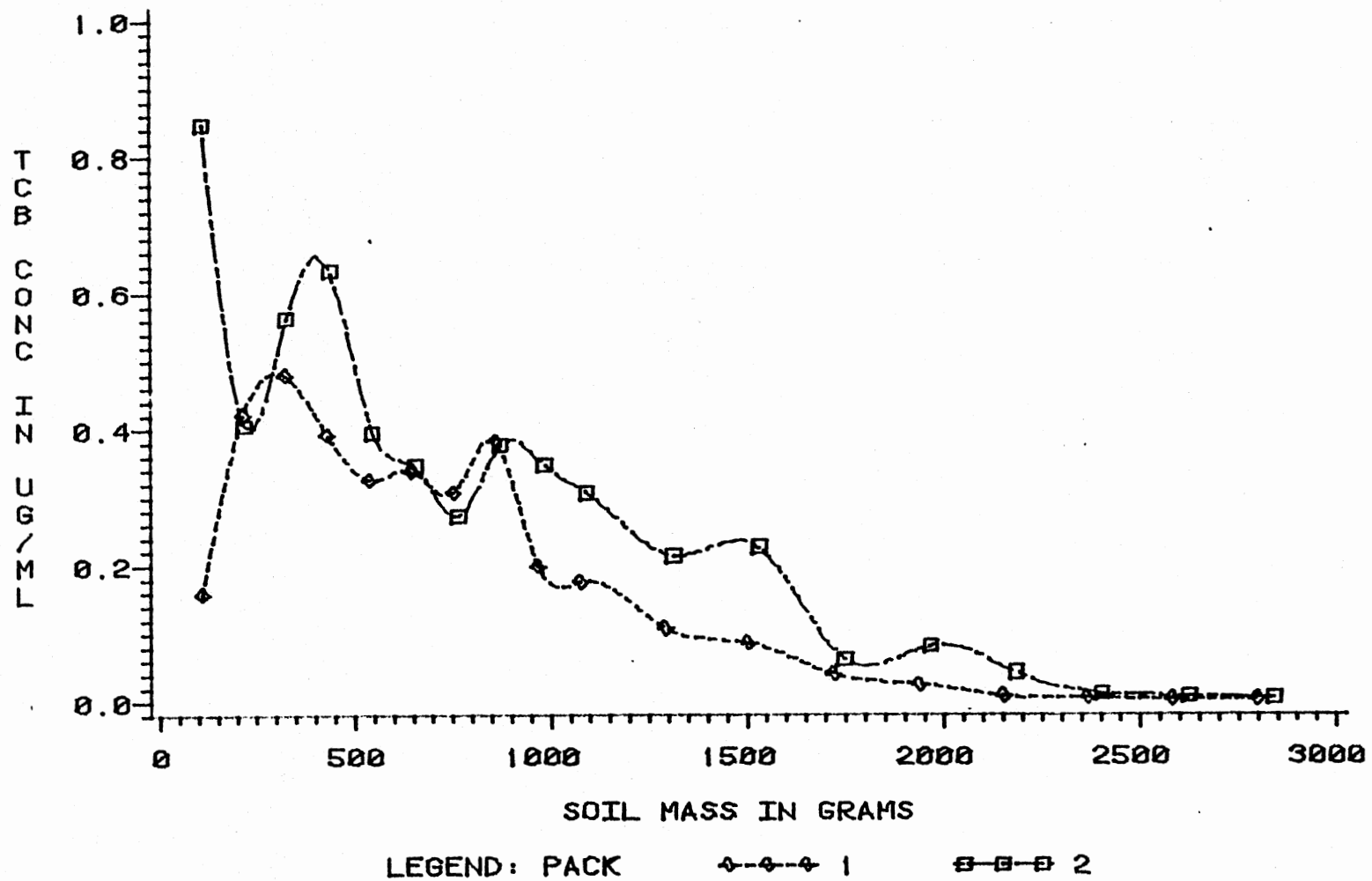

Figure 12. Mean TCB vs. Soil Mass Curves for Blocky II Soil (Packed (1) and Undisturbed (2) Columns).

SOIL-3

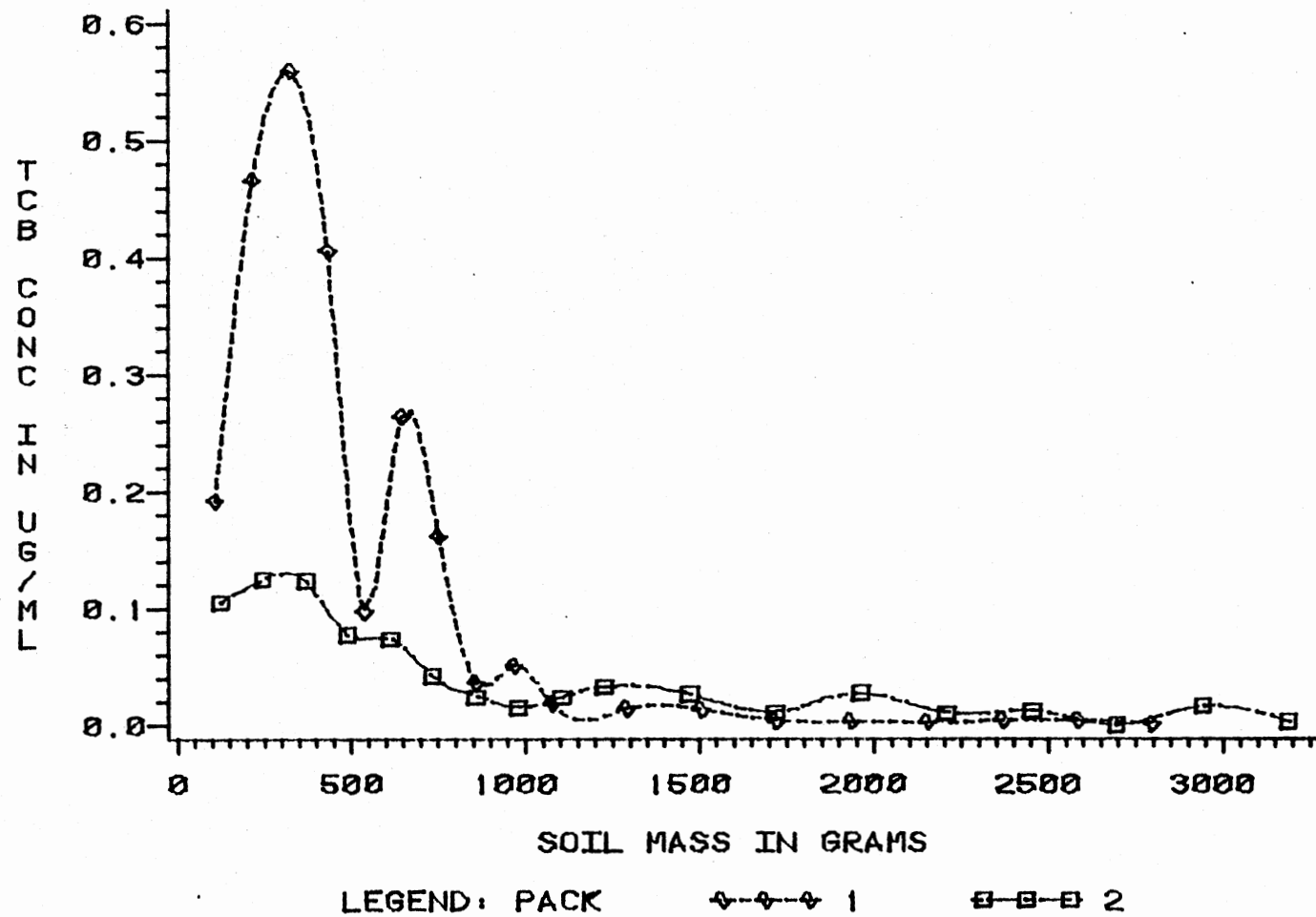
Figure 13.   Mean TCB vs. Soil Mass Curves for Granular Soil (Packed (1) and Undisturbed (2) Columns).
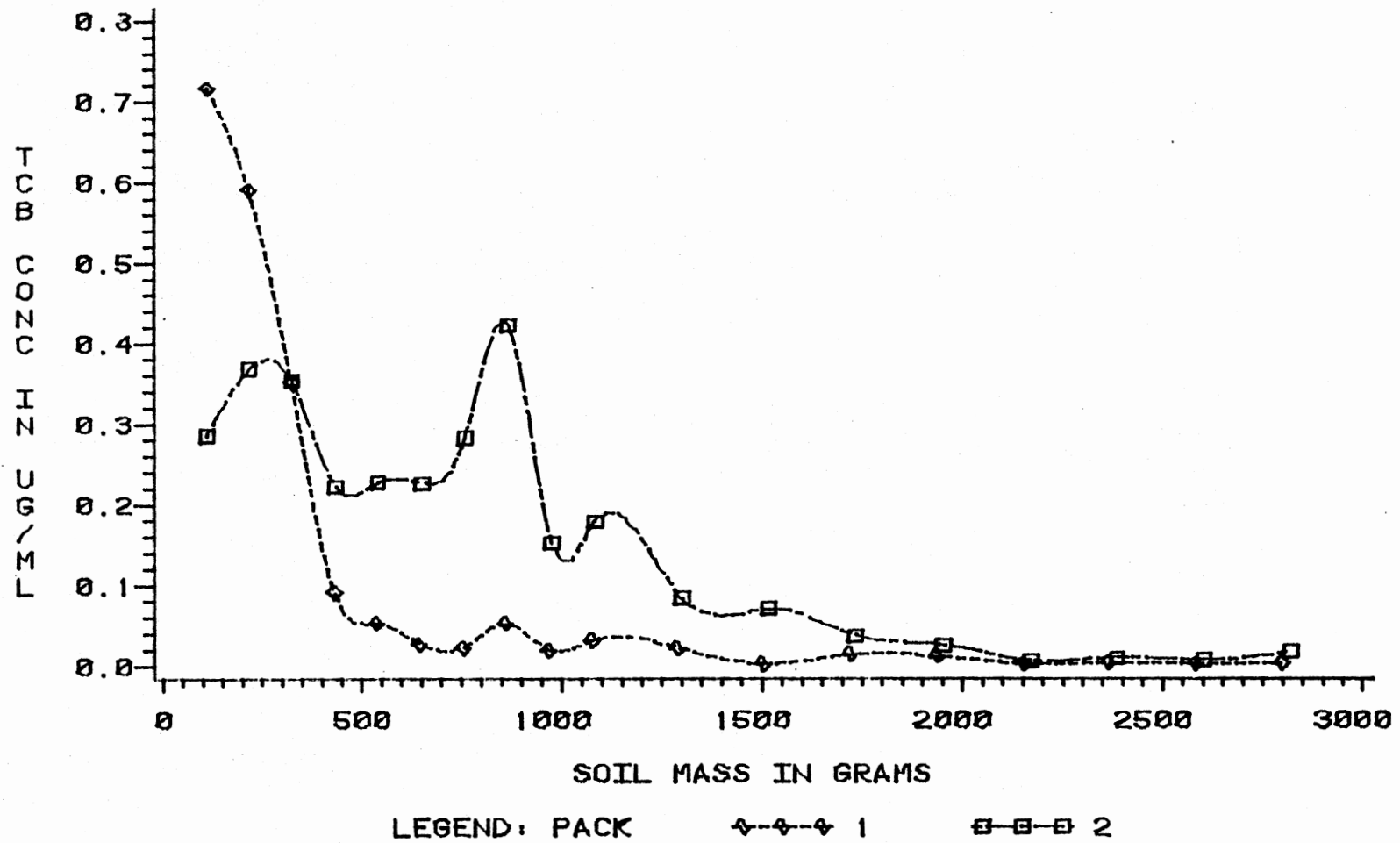
Figure 14. Mean TCB vs. Soil Mass Curves for Prismatic Soil (Packed (1) and Undisturbed (2) Columns).
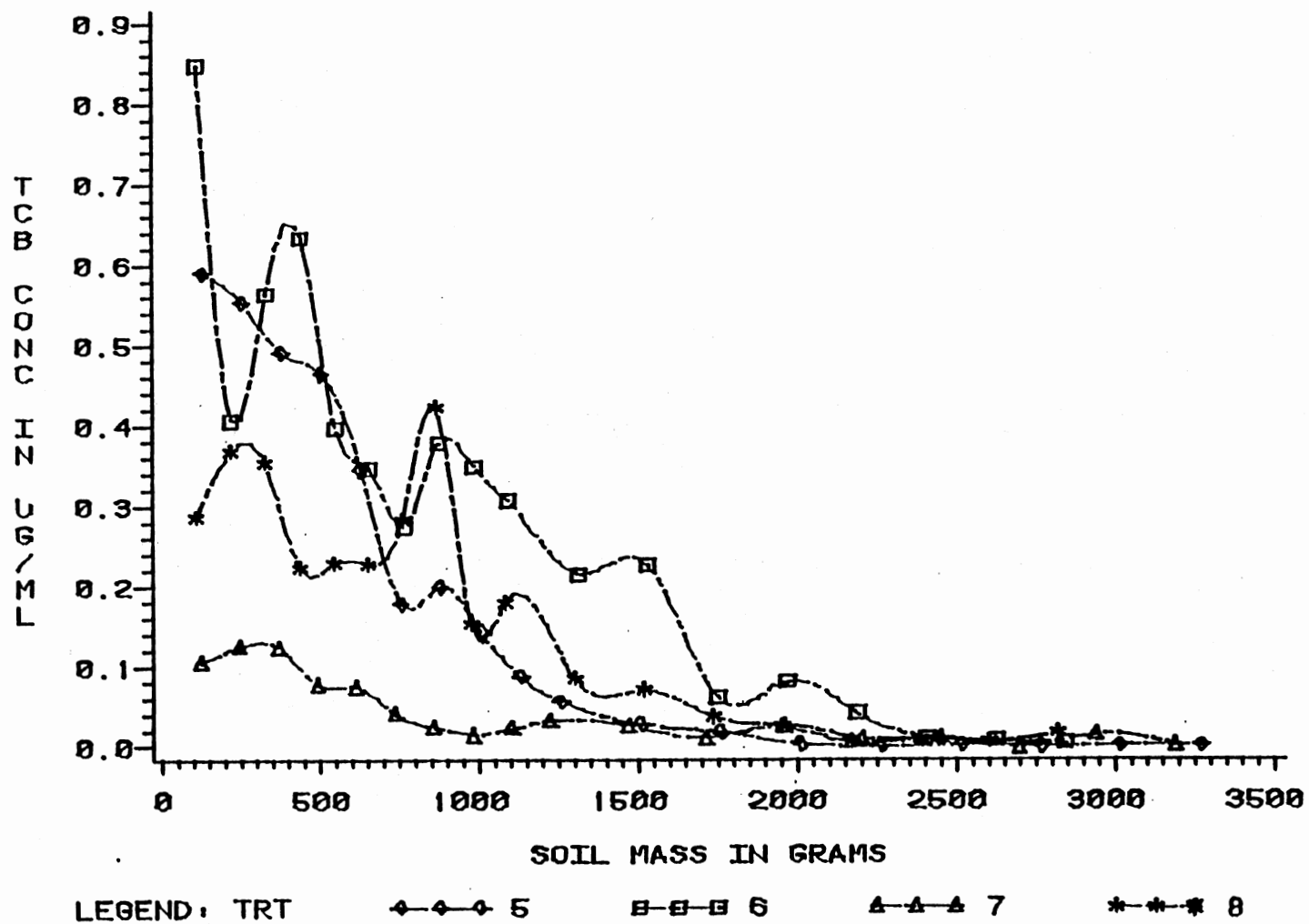
Figure 15. Mean TCB vs. Soil Mass Curves for Undisturbed Treatments.

differences (0.05 level) between depths for all soils except the granular soil. The reason for the lack of significance for the granular soil is not known at this time. When comparing column types within soil type, analysis of variance indicates no difference due to column type for NB. When all soils are compared there is a significant difference between soils, ignoring column type. Figure 16 and 17 show that extraction of NB from the soil was higher for the blocky II soil than for the other soils. This is believed to be due to the low affinity the blocky II soil has for NB as indicated by the sorption isotherms. It is interesting to note that NB was detected at the 26 cm depth for both prismatic and blocky II undisturbed soils. This is the same general pattern as seen for the TCB discussed above.

Figure 16.   Mean NB vs. Soil Mass Curves for Packed Treatments.

PACK=2
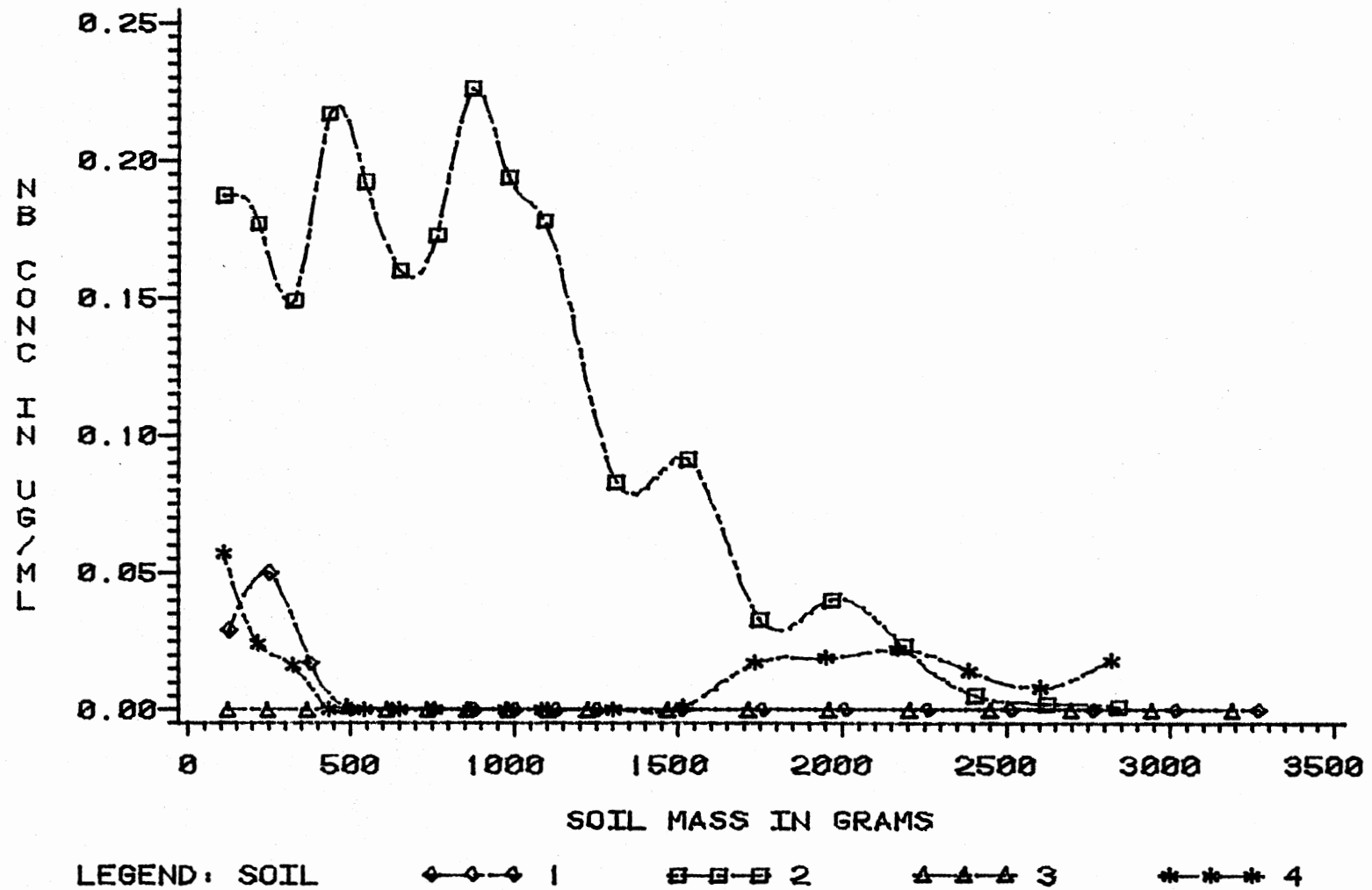
Figure 17.   Mean NB vs. Soil Mass Curves for Undisturbed Treatments.

CHAPTER V

SUMMARY AND CONCLUSIONS
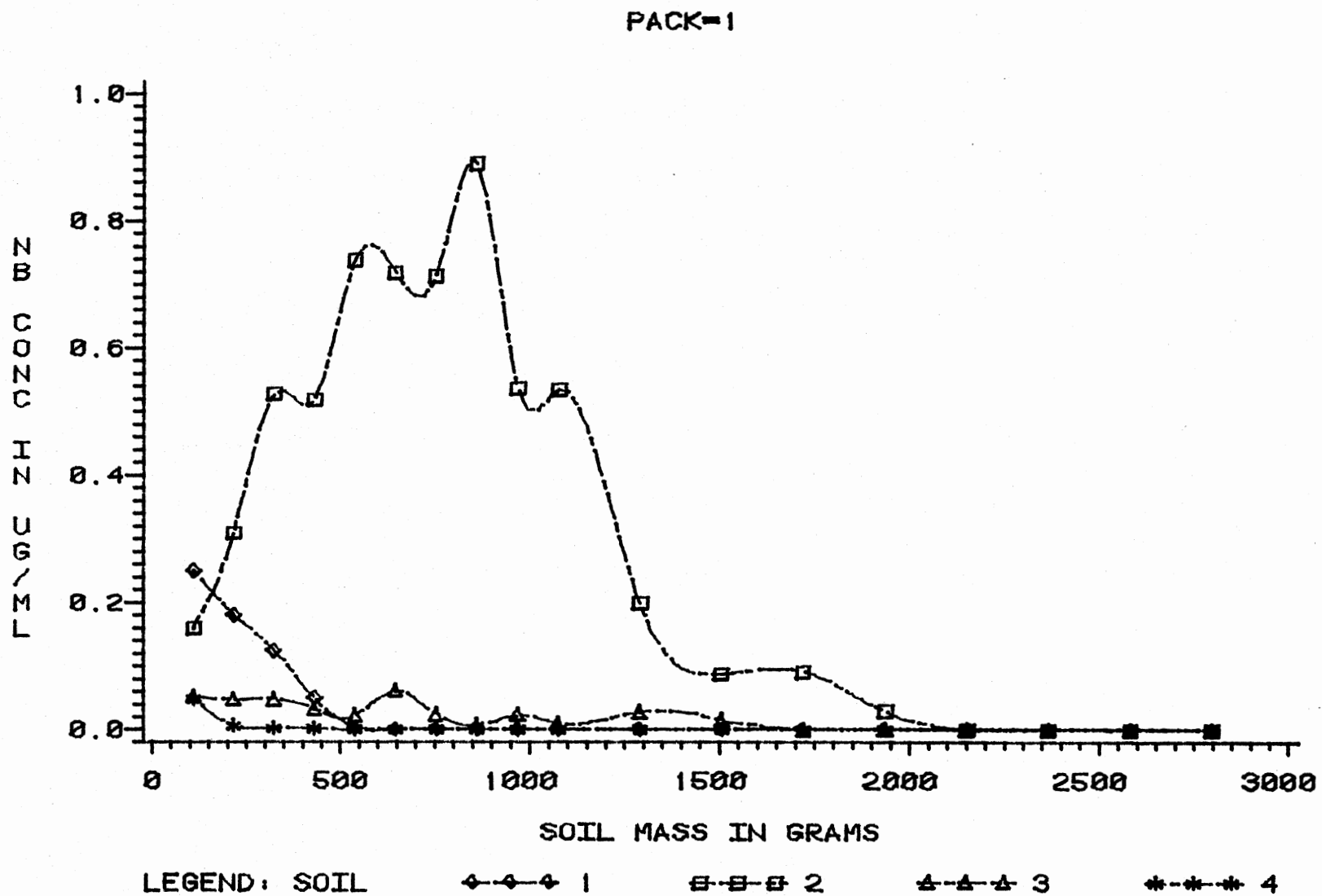
Results of the solution and soil sampling studies lead to the following summary statements and conclusions:

1. The soil solution sampling study provided more information than the soil sampling study concerning the movement of NB through the soils. The TCB was not detected in the solution samples, apparently, because of its low water solubility and high soil adsorption.

2. When individual soil column types are compared, the prismatic soil showed the greatest effect of soil structure on the movement of NB. No NB was observed in extracted solutions from the packed prismatic columns at any depth while it was detected in the undisturbed columns at depth 3 (32 cm) after 6 weeks.

3. The blocky II soil solution had the highest NB concentrations at any depth and time. This is thought to be a result of the lower sorption characteristic of the blocky II soil. Lower sorption strengths were demonstrated by adsorption isotherm data for the blocky II soil.

4. The soil sampling portion of this study was less definitive than the solution extraction study, though it supports the conclusions reached from the solution study. The NB

was found on soil samples taken at the 26 cm depth for prismatic and blocky II undisturbed columns. The TCB was found in the highest concentrations in the same soils.

5. There were no detected differences between matrix and ped surface samples for NB and TCB in this investigation. However, it is possible that an improved surface and matrix sampling technique may improve differentiation such that differences might be found.

6. A soil with a well defined structure tends to allow movement of pollutants more rapidly than soils with shorter vertical ped axises. Movement down ped faces appears to play a greater role in solute transport than movement through micropores.

7. In weakly structured soils, or soils with small structural units, sorption and bulk density appear to be major factors in determining solute transport rates. These measurements relate to a greater soil matrix exposure to applied pollutants. Movement rates of the pollutants are slower where there is greater soil exposure for sorption.

8. From this experiment it appears that soil structure and sorption characteristics play a vital role in the movement of NB and TCB through a soil profile and that structural characteristics should not be ignored when considering field application of organic pollutants. The differences are great enough to justify more extensive evaluation in field experiments.

9. Based on the results of this study, long-term field experiments (greater than 2 years) are expected to demonstrate greater soil penetration of pollutants in blocky II and prismatic soils and a significantly reduced penetration in a granular soil with otherwise similar characteristics.

10. Extrapolation of the limited data indicates that after a 10 year period, a well structured soil would allow pollutant penetration up to 2.5 times greater depth than expected for a massive or poorly structured soil, with all other factors being equal. Wherever or whenever soil selection permits the use of comparable soils differing in structure for waste organic disposal, poorly structured or massive soils may provide more and/or larger protection from groundwater pollution. In some cases there may be economic justification for soil disturbance to increase the soil's capacity to retain pollutants or to disturb and compact soils to measurably reduce pollutant movement downward from periodic as well as permanent impoundments.

LITERATURE CITED

1. Aley, Thomas. 1977. A model for relating land use and ground-
    water quality in Southern Missouri. pp. 232-332. In R. R.
    Dilamarter and S. C. Csallany (ed.) Hydraulic problems in
    Karst regions. Western Kentucky Univ., Bowling Green, Ky.

2. Anderson, J. L., and J. Bouma. 1977a. Water and chloride move-
    ment through pedal soils: I. Saturation flow. Soil Sci.
    Soc. Am. J. 41:413-418.

3. _____, and _____. 1977b. Water and chloride movement through
    pedal soils: II. Unsaturated flow. Soil Sci. Soc. Am. J.
    41:419-423.

4. Baumann, H., and A. Bram. 1977. Investigations on the possible
    contamination of groundwater as a result of sewage water
    treatment of the land within the sewage water association of
    Braunschweig. Zeitschrift fur Kulturtechnic und
    Flurbereinigung 18(4):200-212.

5. Biggar, J. W., and D. R. Nielson. 1962. Miscible displacement:
    II. Behavior of tracers. Soil Sci. Soc. Am. Proc. 26:
    125-132.

6. Brunauer, B. 1965. Surface of solids. Pure Appl. Chem.
    10:293-307.

7. Cassel, D. K., T. H. Krueger, F. W. Schroer, and E. B. Norum.
    1974. Solute movement through disturbed and undisturbed soil
    cores. Soil Sci. Soc. Am. Proc. 38:727-732.

8. Chiou, C. T., L. J. Peters, and V. H. Freed. 1979. A physical
    concept of soil-water equilibria for nonionic organic com-
    pounds. Science 206:831-832.

9. Corr, S. H., and C. J. Cole. 1977. Land disposal of waste acti-
    vated sludge. New England Water Pollution Control Associa-
    tion. 11:101-113.

10. DeJong, E. 1978. The movement of sewage effluent through soil
    columns: the major ions (Na, Ca, Cl and SO_4). J. Environ.
    Qual. 7:133-136.

11. Dekkers, W. H., and F. Barbera. 1977. Effect of aggregate size
    on leaching of herbicide in soil columns. Weed Res.
    17:315-319.

12. Geraghty, J. J., and D. W. Miller. 1978. Status of groundwater contamination in the U. S. Am. Water Works Assoc. J. 70: 162-167.

13. Hamaker, J. W., and J. M. Thompson. 1972. In C. A. I. Goring and J. W. Hamaker (ed.) Organic chemicals in the soil environment. Vol. 1 pp. 49-143. Marcel Dekker, Inc., New York.

14. Haque,R.,and V. Freed. 1974. Behavior of pesticides in the environment -- environmental chemodynamics. Res. Rev. 52: 89-116.

15. Hoeks, J. 1976. Pollution of soil and groundwater from land disposal of solid wastes. Inst. for Land and Water Manage., Tech. Bull. No. 96.

16. _____. 1977. Mobility of pollutants in soil and groundwater near disposal sites. Inst. for Land and Water Manage. IAHS Publ. 123:38-388. Postbut 35, Wageningen, Netherlands.

17. Huser, R., 1977. The application of sewage sludge in forests. Forstnissenschaftliches Centralblatt 96:238-245.

18. Kanchanasut, P., D. R. Scotter, and R. W. Tillman. 1978. Preferential solute movement through larger soil voids II: Experiments with saturated soil. Aust. J. Soil Res. 16:269-276.

19. Kelley, O. J., J. A. Hardman, and D. S. Jennings. 1947. Soil-sampling machine for obtaining two-, three-, and four-inch diameter cores of undisturbed soil to a depth of six feet. Soil Sci. Soc. Am. Proc. 11:85-87.

20. Kunte, H. 1977. Polycyclic aromatic hydrocarbons in agricultural soil (Possible consequences from the agricultural use of composted sewage sludge). Zentralbl. Bakkteriol. Parasitenkol. Infektionskr. Hyg. 1 Abt. 164:469-475.

21. Lawes, J. B., J. H. Gilbert, and R. Warington. 1882. On the amount and composition of the rain and drainage waters collected at Rothamstead. William Clowes and Sons, LTD. London.

22. Lawrence, J., and H. M. Tosine. 1977. Polychlorinated biphenyl concentrations in sewage and sludges of some waste treatment plants in southern Ontario. Bull. Environ. Contam. Toxicol. 17:49-56.

23. Marinucci. A. C., and R. Bartha. 1979. Biodegration of 1, 2, 3- and 1, 2, 4-trichlorobenzene in soil and in liquid enrichment culture. Appl. Environ. Microbiol. 38:811-817.

24. McMahon, M. A., and G. W. Thomas. 1974. Chlroide and tritiated water flow in disturbed and undisturbed soil cores. Soil Sci. Soc. Am. J. 38:727-732.

25. Morrill, L. G., B. Mihalium, and S. Maudiun. 1981. Bio-organic indicators of ground-water pollution: Organic compound sorption of soils and soil components. Submitted to R. S. Kerr Environ. Lab., Ada, Ok. O.S.U. Dept. of Agronomy (unpublished report).

26. Mosier, A. R., K. Haider, and F. E. Clark. 1972. Water soluble organic substances leachable from feedlot manure. J. Environ. Qual. 1:320-323.

27. Otis, R. J., G. D. Plews, and D. H. Patterson. 1978. Design of conventional soil absorption trenches and beds. Third Annual Illinois Private Sewage Disposal Symposium. Champaign, Ill.

28. Passioura, J. B. 1971. Hydrodynamic dispersion in aggregated media: I. Theory. Soil Sic. 111:339-344.

29. Rao, P. S. C., and J. M Davidson. 1979. Adsorption and movement of selected pesticides at high concentration in soils. Water Res. 13:375-380.

30. _____, R. E. Green, L. R. Ahuja, and J. M. Davidson. 1976. Evaluation of a capillary bundle model for describing solute dispersion in aggregated soils. Soil Sci. Soc. Am. J. 40: 815-820.

31. Rogers, R. D., J. C. McFarland, and A. J. Cross. 1980. Adsorption and desorption in two soils and montmorillonite. Environ. Sci. Technol. 14:457-460.

32. Thomas, G. W. and R. E. Phillips. 1979. Consequences of water movement in macropores. J. Environ. Qual. 8:149-152.

33. _____, _____, and V. L. Quisenberry. 1978. Characterization of water displacement in soils using simple chromatographic theory. J. Soil Sci. 29:32-37.

34. Tyler, D. D., and G. W. Thomas. 1981. Chloride movement in undisturbed soil columns. Soil Sci. Soc. Am. J. 45:459-461.

35. Whipkey, R. Z. 1967. Theory and mechanics of subsurface storm-flow. pp. 255-260. In W. E. Sopper and H. W. Lull (ed.) Int. Symp. on For. Hydrol., Natl. Sci. Found., Pennsylvania State Univ., University Park, Pa.

36. Wilson, J. T., C. G. Enfield, W. J. Dunlap, R. L. Cosby, D. A. Foster, and L. B. Baskin. 1981. Transport and fate of selected organic pollutants in a sandy soil. J. Environ. Qual. 10:501-506.

37. Young, D. W., and R. B. Clark. 1978. The effects on water quality by mining activity in the Miami, Arizona region. Hydrology and Water Resources in Ariz. and the Southwest Amer. Water Resources Assoc., (Hydrology Sect.), Flagstaff, Ariz.

APPENDIXES

APPENDIX A

OPERATING PARAMETERS FOR HEWLETT-PACKARD

GAS CHROMATOGRAPH 5830A

OPERATING PARAMETERS FOR HEWLETT-PACKARD

GAS CHROMATOGRAPH 5830A

Column Temperature:	120°C
Run Time:	5.5 min
Injector Temperature:	250°C
ECD Temperature:	240°C
Chart Speed:	1.50 cm/min
Attenuation 2():	8
Slope Sensitivity:	0.00
Area Reject:	1
Gas Flow:	40 ml/min

Time Programing:

Slope Sensitivity: 0.50   Time: 2.0 min

Carrier Gas: Argon/Methane   5/95

Column Material: 6 ft 4mm ID 6 mm OD
3% SE-30 + 4% QF-1 on
Chromosorb 750 100/120

APPENDIX B

TABLES

TABLE IX

PORE VOLUMES AT SPECIFIC DEPTHS
AFTER THE TENTH WEEK

TRT	Depth in cm		
	1	2	3
* 1-4	6.24	3.12	1.56
5	7.59	3.80	1.90
6	6.32	3.16	1.58
7	7.33	3.66	1.83
8	6.28	3.14	1.57

*Treatments 1 through 4 were packed the same density.

TABLE X

SUM OF SQUARES VALUES FOR COMPARING SOILS AND COLUMN TYPES AT GIVEN TIMES AND DEPTHS FOR NB SOLUTION STUDY

Source of Variation	df	Weeks After First Application								
		2	3	4	5	6	7	8	9	10
A. Depth 1										
Soil (S)	3	0.228	1.074	3.000	13.187	5.023	2.804	4.171	7.051	3.433
Column Type (CT)	1	0.024	0.033	0.025	0.038	0.204	0.135	0.216	0.303	0.327
SxCT	3	0.028	0.159	0.262	1.526	0.850	0.608	0.852	0.701	0.886
Error/df	-	0.228/20	0.616/14	6.157/18	8.630/17	5.685/19	3.106/19	5.351/17	9.131/20	5.442/20
B. Depth 2										
Soil (S)	3	-‡	0.013	0.083	0.544	0.757	0.522	0.855	0.652	0.511
Column Type (CT)	1	-	0.005	0.004	0.010	0.146	0.012	0.036	0.035	0.047
SxCT	3	-	0.014	0.028	0.092	0.373	0.110	0.195	0.186	0.282
Error/df	-	-	0.011/23	0.058/22	0.246/21	0.669/23	0.351/19	0.572/18	0.583/18	0.449/20
C. Depth 3										
Soil (S)	3	-‡	-	-	0.032*	-	0.004	0.003	0.129*	0.155*
Column Type (CT)	1	-	-	-	0.011*	-	0.002	0.001	0.074*	0.078*
SxCT	3	-	-	-	0.032*	-	0.005	0.003	0.267*	0.271*
Error/df	-	-	-	-	0.045/23*	-	0.003/20	0.004/22	0.012/21*	0.016/21*

‡NB was not detected for most data points.
*Value times 1×10^{-2}.

2

VITA

Lawrence John Henderson

Candidate for the Degree of

Doctor of Philosophy

Thesis: THE EFFECT OF SUBSOIL STRUCTURE ON THE MOVEMENT OF TWO NON-
VOLATILE ORGANIC POLLUTANTS

Major Field: Soil Science

Biographical:

Personal Data: Born in Oceanside, California, August 10, 1952,
the son of Mr. and Mrs. Andrew C. Henderson; married June 16,
1973 to Margaret Jean Irwin. Father of four children, Karen
Michelle, Jeffery Young, Emily Dawn, and Jordan Andrew.

Education: Graduated from Lakeland High School, Rathdrum, Idaho
in June, 1970; received the Bachelor of Science degree in
Agronomy from Brigham Young University, Provo, Utah in
August, 1977; received the Master of Science degree from
Oklahoma State University, Stillwater, Oklahoma in August,
1980; and completed requirements for the Doctor of Philosophy
degree from Oklahoma State University in May, 1983.

Professional Experience: Served a four year tour of duty for the
U.S. Navy from 1970-1974; research and teaching assistant at
Brigham Young University from 1975-1977; and research assis-
tant at Oklahoma State University from 1977-1982.