THE MOVEMENT OF SALTS THROUGH SOIL

AS AFFECTED BY SUBSOIL STRUCTURE

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friend, but like a brother. The time we have spent together on this project, and others, will always be remembered with a smile.

My final thoughts of appreciation and love are to my wife, Camille and to our sons Christopher and Casey. There is no one more willing than Camille to give and to serve others. Her love, understanding, patience, prodding, and prayers allowed us to reach this important goal in our lives.

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CHAPTER I

INTRODUCTION

Technology and industrial capacity continue to expand. Associated with this development are vast quantities of generated wastes. These wastes frequently contain various industrial and agricultural pollutants and are placing a serious burden on society and on maintenance of the environment in which we live. A primary method of disposal for pollutants has been to place them on or incorporate them into soils. Danger of environmental contamination, particularly of groundwater, from this type of waste application can be related to a number of soil factors. One of the lesser studied variables is the effect of subsoil structural characteristics on pollutant movement. Evaluating the relationship between soil physical properties vs. the rate of pollutant movement with percolating water is required before reasonably accurate predictions for waste disposal can be made relative to subsoil structure. This procedure would be true regarding any model constructed for predictive purposes.

Soils constitute natural and, often, convenient depositories for various waste materials. A knowledge of water-pollutant movement relationships in various soils would be desirable. When placed on or in the soil, the pollutants may decompose or undergo transformation. Organic components are decomposed to their metabolities, i.e., carbon dioxide, water, or more persistent residual organic materials. Soluble inorganic

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constituents may be leached through the soil profile by percolating water. Inorganic constituents with low water solubility tend to accumulate in the soil and become a part of the soil matrix. Two important environmental questions asked by scientists are, "Will the inorganic constituents that remain accumulate in sufficient quantities to present future hazards to man as he uses these soils?" and "Will the soluble inorganic ions or salts leach through the soil profile in quantities high enough to contaminate the groundwater?" It is the second question to which this research is addressed.

Rubidium chloride (RbCl) was the inorganic salt utilized to investigate pollutant mobility vs. soil structure in this study. Rubidium (Rb^+) was selected because of its chemical similarities with potassium (K^+), it is not found in these soils, it is non-hazardous, and its easily determined in the laboratory. Inferences can be extended relative to K^+, and probably to other cations, by Rb^+ and K^+ interactions with soil structure.

CHAPTER II

REVIEW OF LITERATURE

Impact of Industrial and Agricultural Pollutants

on the Soil Environment

Concern for groundwater and stream contamination, with a growing

interest in the accumulation of fertilizer salts, pesticides, and feed-

lot wastes in soils, are reasons for a strong interest in solute move-

ment through soils. Soils comprise an involved physical and chemical

complex consisting of numerous primary and secondary minerals in various

stages of development or degradation. The clay fractions contain nega-

tively charged colloids capable of absorbing and exchanging cations.

Because of the amorphous nature and lack of knowledge of many of the

solid phases that form in soil, many scientists consider the chemical

reactions in soils solely as adsorption of the added constituents onto

soil surfaces. With time, added wastes or pollutants are broken down

and the soluble constituents become part of the soil solution. The re-

leased ions can exchange with other ions associated with the soil

exchange sites. When the concentration levels of ions in solution

exceed the solubility of ions from solid phase compounds and minerals,

they will precipitate. When the soil solution concentration is reduced

below equilibrium concentrations, such minerals or precipitates will

dissolve to establish an equilibrium concentration in the soil solution.

Ions in the soil solution can be removed by plants or leached from the

soil by water moving through the soil profile.

Hoeks (1977) stated that pollutant mobility through soils is largely dependent on a variety of processes which include cation exchange, chemical solubility, and biochemical reactions. Cation exchange processes are important for inorganic cations including heavy metals. Phosphates, carbonates, and sulfates of iron (Fe), aluminum (Al), calcium (Ca), and magnesium (Mg), are involved in chemical processes. Biochemical processes are important when considering nitrogen compounds and organic substances. Hoeks (1976) reported the effect of leachate from waste disposal sites on groundwater quality is largely dependent on geohydrological conditions. Biological decomposition, adsorption, and precipitation of contaminants are more favorable when transport of leachate through the aquifer to groundwater is slow. Young and Clark (1978) showed that even after chemical dumping or mining activity is terminated, water quality can continue to be adversely affected for many years. This contamination is due in part, to the continuous leaching of organic and inorganic contaminants. Baumann and Bram (1977) indicated that when high rates of nitrates (NO_3), K^+, and sodium (Na^+) are added with sewage effluents, the soil at first exhibits a cleansing ability tying up these elements by its cation exchange capacity. After large applications, however, there is a sharp decrease in the soils retention capacity resulting in increases of Na^+ and K^+ in the leachate water.

Baumann and Bram (1977) reported seepage tests were found to provide reliable indications of the degree of contamination in ground water with specific elements used. Similar results were obtained when pollutants were applied to forest soils (Huser, 1977). Digested sewage sludge with four to eight percent dry matter 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) also stated that NO_3, Ca^{++}, Na^+, and chloride (Cl^-) content increased in the groundwater from additions of sewage sludge. The NO_3 content of the leachate exceeded the limits set by the Environmental Protection Agency (EPA) for several subsequent months.

Hazardous wastes fall into one of five categories: 1) toxic, 2) flammable, 3) radioactive, 4) explosive, and 5) biologically hazardous (Morrison and Ross 1978). The most probable disposal method available for each of these wastes was tabulated by the Soil Conservation Service (S.C.S.) in 1978. The only disposal methods conducive to monitoring the hazardous wastes are lagooning, sanitary landfills, and chemical landfills. The prescribed disposal methods are to provide effective monitoring conditions for the gradual degradation of groundwater resources. The S.C.S. went on to say, the most frequent failure in the disposal programs is the lack of information on the sites' hydrogeologic characteristics, including pollutant movement through the soil profile into the groundwater recharge system.

A good soil absorption system should absorb all the contaminants generated. The soil absorption system should also provide a high level of treatment before any effluent reaches the groundwater, and should have a long useful life. To meet these criteria proper site selection is necessary. Factors to be considered in soil site selection include the hydraulic conductivity, distance to bedrock, bedrock characteristics, landscape position, slope, and proximity to surface wells, road cuts, buildings, and other factors adversely affected by drainage from the disposal site Otis et al. (1978).

Ideally, a soil should be able to convert a pollutant to a non-pollutant at a rate equal to or greater than the rate at which it is added to the soil. As previously mentioned, there are several soil characteristics which affect the pollution abatement potential. Septic tank installation or ponding of pollutants is not recommended on soils subject to flooding (S.C.S. 1978). Where soil is shallow to bedrock or for cemented ponds, the volume of adsorption is reduced, the only alternative is to increase the size of the adsorption field. A high water table reduces the open pore space of the soil, thus reducing exposure to cation exchange sites and increasing the groundwater pollution potential. The soil permeability indicates the potential for air and water movement. If movement is slow, a larger adsorption field may be required. If movement is rapid, the possibility of groundwater contamination is increased. Where soil is sloping, there is a danger of uneven distribution of the pollutant and the possibility of the pollutant coming to the surface. Coarse fragments in soils decrease the overall adsorption volume per unit area. Subsidence can also be a severe problem (Andrews, 1978; Mellen, 1978). It was also stated by Mellen (1978) that the maximum seasonal elevation of the groundwater table should be at least two feet below the bottom of a dump site.

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 of groundwater contamination because of the leachates generated by water percolating through the landfills. Septic tanks and cesspools rank highest in total volume of waste water discharged directly into groundwater. Animal feedlots contaminate groundwater through runoff and infiltration from

the lot itself, runoff and infiltration from the waste products disposed of on land surfaces, and seepage from waste collection lagoons. The principle contaminants from feedlot sources are Cl^-, NO_3, hydrocarbons, and heavy metals (Corr and Cole, 1977).

Lakshman (1979) described several examples of faulty municipal waste disposal practices, and groundwater contamination sources. Some of these sources included saltwater intrusions, insecticide, herbicide, fertilizer, and thermal pollution. Leachates have been characterized by high concentrations of dissolved organic and inorganic substances, and sometimes microbial pollutants. The primary concern in pollution control has not been locating the source of pollution, but the relatively difficult task of eliminating pollution. Pollution cleanup is very costly and often very time consuming.

Solute Movement in Structured Soils

In analyzing solutions collected from field tile drains Lawes et al. (1882), found that a large part of the added water moves rapidly through the open channels and interacts only slightly with water in the surrounding soil. They also showed that subsequent drainage was more representative of the 'existing' water in the soil matrix. They explained that in a clayey soil direct channel-drainage will, in most cases, precede general drainage. This will especially be the case if rain fall is rapid and water accumulates on the soil surface.

Aley (1977) estimated that water entering soil macropores without visible openings contributes five times as much to groundwater recharge and stream flow as movement through micropores. Thomas et al. (1978) stated that it did not appear to be a requirement for macropores to

extend to the soil surface for channel-flow to occur. An example they noted was plowed soils, with the macropores disturbed in the upper 15 cm of the profile, yet deep flow through the macropores still occured.

Thomas and Phillips (1979) reasoned that a given rainfall or irrigation will not completely wet the root zone without moving deeper in the soil. They found labeled water 80 cm below the surface, shortly after application, but before the water content of the root zone was raised to "field capacity."

Thomas et al. (1978) investigating earlier work involving solute movement, concluded that water added to a soil does not stay in the surface soil, but will move as much as 20 times deeper than calculated for piston like flow. Salts in the soil surface will not be moved by water to the expected water depth, but will be distributed rather evenly through the soil to lower depths. They went on to say that because of salt movement in this manner, there will not be a large surge of NO_3, pesticide, or other solutes at the time the primary water front arrives at the water table. Utilizing the above mentioned theory groundwater recharge will begin much sooner than expected, even when there is a soil water deficit. Thomas et al. (1977) furthur concluded that "field capacity" is not well related to water flow because significant partial displacement flow can occur at water contents below "field capacity."

This is in partial disagreement to the work of Biggar and Nielson (1962) who stated that small differences in velocity among pores, even under nearly ideal conditions, tend to spread the salt band so that it is distributed like a normal probability density function with the mean concentration at the depth of the added water penitration. They stated that most packed columns with small aggregates show this type of

behavior.

In contrast Passioura (1971) showed that because soil grains are three to four times the size of soil pores, and since the diffusion co-efficient in macropores is probably 2 to 10 times that in the aggregates, the characteristic time for diffusion in macropores should be 20 to 150 times faster than within the aggregates. Thus, any concentration gradients in the macropores should be trivial compared to those in the aggregates. He concluded that when one solution displaces another from a saturated aggregated medium, viscous flow takes place effectively only in the voids between the aggregates. Consequently movement of solutes within the aggregates occurs only by diffusion. Similar work was also done by Dekkers and Barbara (1977), Scotter (1978), and Tsuju et al. (1978).

McMahon and Thomas (1974) used three soils of different structure 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 compared to the packed columns. They theorized, as others discussed earlier, that some solutes moved through the large pores, by-passing much of the water already within the peds. Bouma and Anderson (1977) realized similar results from their work.

Cassel et al. (1974) found that disturbing a soil decreased bulk density and increased water holding capacity by increasing total porosity. They concluded the undisturbed columns, at a given soil moisture tension, required less water to displace solutes than constructed columns because the undisturbed columns retained less water at a given soil-water pressure. They added that thoughtful consideration should be made before extrapolating fertilizer and pesticide movement rates, based on

disturbed column studies, especially if the soils' bulk densities differed.

The movement of Cl^- under unsaturated conditions in three undisturbed columns ranging from well structured to unstructured was studied by Tyler and Thomas (1981). Water was added at a rate just under the infiltration rate. They observed that the Cl^- moved more rapidly through the well structured soil even though it had a higher clay content. Anderson and Bouma (1973) used undisturbed soils with different structures, but nearly identical textures. They stated that differences in dispersion of Cl^- were due to structural effects. However, because they did not compare constructed and undisturbed columns of the same soil for direct comparisons, it is difficult to determine if the observed differences in dispersion coefficients are confounded with other physical or chemical properties. Anderson and Bouma (1977) studied similar soils under unsaturated conditions and found differences between constructed and undisturbed soils in reference to water movement. Again, they attributed differences in dispersion coefficients to soil structural effects. They stated the differences were due to characteristic flow patterns within the soils, a result of structural variation.

Most work on solute movement has been done with non-reactive ions such as Cl^- and NO_3 (Kanchanasut et al. 1978). Bouma and Wosten (1976) used both nonreactive Cl^- and highly reactive phosphate (PO_4) to monitor preferential solute movement through saturated undisturbed and constructed soil columns. They found a relative concentration (RC) of 0.5 Cl^- and PO_4 reached the bottom of the 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 for the undisturbed columns.

In a column study by Doner et al. (1982) utilizing geothermal brine water with heavy metals of lead (Pb), zinc (Zn), copper (Cu), and cadmium (Cd) showed all soils adsorbed some Pb and Zn, but after passing through a 10 pore volume of solution the cation adsorption became negligible. They theorized that a combination of mass action and Cl^- complexation caused the high mobility of the cations in solution. Wolf et al. (1977) showed adsorption of similar cations is affected by the speciation of elements in soil solution, pH, and composition of the soil solution, as well as by the clay and organic matter content of soils (McLaren et al. 1981). In general, the increased mobility of elements in soils from sludges was summarized by Gerritse et al. (1982). They indicated ion mobility was due to a combination of complexation by dissolved organic compounds, high background concentrations, and high ionic strengths of the soil solutions. However, the relative effects of these factors will vary strongly among different elements.

The benefits of waste application to land have been demonstrated, but the benefits will be more than offset by the accumulation of toxic elements in the soil, if land disposal is not carefully controlled (Thabaraj 1978). Present practices of land application of pollutants are leading to the accumulation of a number of trace elements in the soil (Chang et al. 1981). Sewage sludge is very commonly applied as a fertilizer to arable lands. Cities, because of their high population concentrations and industries, produce comparatively large quantities of sludge. These sludges contain most of the potentially hazardous elements as reported by Haque and Subramanian (1982) and Leeper (1978).

One important source of contamination to farm land is from chemical fertilizers. Pleysier and Juo (1981) reported chemical fertilizer salts

normally contain heavy metals as impurities. When the fertilizers are applied to the land, the metals mix with the soil and cause contamination of the land. Sometimes, fertilizers are supplemented with salts of micronutrients. Salts of the micronutrients are never assimilated completely and accumulate in soils. An aspect of micronutrient fertilization is the presence of unwanted metals as impurities. For example, Pb is almost always present in copper sulfate, copper carbonate, zinc sulfate, and manganese sulfate and is consequently added to soil inadvertently (Lisk 1972). Manure, used as a fertilizer often contains pollutants that can cause serious soil contamination. This type of soil contamination with metals indicates, that even in the absence of industries, soils may still be contaminated with undesirable ions, as reported by Baker and Chesnin (1975) and Mosier et al. (1978).

Rubidium Utilization in Soils Research

Rubidium has been used in soils research because of its similarity to K^+ and the absence of Rb^+ in most natural soil environments. LeRoux and Coleman (1963) used Rb^+ in a column study investigating the sorption-desorption characteristics of clay and silt size materials. Rubidium was shown to have some irreversable sorption properties producing corresponding reductions in cation exchange capacity (CEC) for silt and coarse clays. The CEC reduction was negligible for fine clays. Rubidium and K^+ responded similarly in exchange processes for vermiculite, hydrobiotite and similar type clays. It was concluded by LeRoux and Coleman (1963) that the reaction of Rb^+ maybe a convenient guide for determining K^+ fertilizer reactions and plant requirements. Deist and Talibudeen (1967) (Table I) showed the activity coefficients of K^+ and

TABLE I

STANDARD FREE ENERGIES OF EXCHANGE FOR
K-NA, K-RB, AND K-CA ON SELECTED SOILS[†]

Soil Series	ΔG_o values for the reaction		
	NaE → KE	RbE → KE	CaE → KE
Tedburn	−927	+447	−1370
Bovey Basin	−888	+377	−1245
Cegin	−966	+435	−1050
Windsor	−1015	+555	−1550
Dunkeswick	−1083	+667	−1315
Sherborne	−−	−−	−2280
Long Load	−−	+474	−2120
Denchworth	−−	−−	−1770
Harwell	−−	+565	−3420
Newchurch	−−	+515	−1900

[†]Deist and Talibudeen (1967).

Rb^+ did not change appreciably from the standard state value of unity as the K^+/Rb^+ ratio on the soil changed. Both ions cause the interlayer spaces of illitic clays to collapse. In replacing K^+ with Rb^+ it was shown that there is little or no alteration in the interlayer distance of these type clays. Deist and Talibudeen (1967) went on to state that because of similarity K^+ and Rb^+ in many physical and chemical properties, they will be evenly distributed in the clay systems of the soil. It is because of K^+-Rb^+ similarities that Rb^+ was used as a quantitating-evaluating system in the reported research.

Fried et al. (1959) suggested that K^+ and Rb^+ are taken up by plants in a constant ratio. As the rate of applied Rb^+ increased the percent of the added Rb^+ fixed decreased markedly accompanied by an increase in the percent of added Rb^+ taken up by plants. High rates of applied K^+ had only a slight effect on Rb^+ uptake in plants. Evans and Barber (1964) worked with Rb^{86} and found that the more strongly the Rb^{86} was adsorbed by the soils the slower its rate of diffusion. In leached soils that were dried after labeling, diffusion was correlated with the ammount of Rb^{86} fixed against that extracted by ammonium acetate (NH_4OAc). In leached soils that were kept moist after labeling, diffusion was closely related to clay content and exchange capacity. In dilute kaolinite systems, diffusion was related to the amount of Rb^{86} in solution (Phillips and Brown 1965).

CHAPTER III

MATERIALS AND METHODS

Four soil sites were chosen in central Payne County, Oklahoma, with
help from the S.C.S. (Figure 1). The soil sites represented four sub-
surface soil structural types (i.e., prismatic, granular, angular
blocky, and subangular blocky). The soils chosen were similar in tex-
ture and other physical and chemical properties, including mixed clay
mineralogy throughout the soil depth sampled (Table II). Undisturbed
soil cores and soil from appropriate depths for packing the constructed
columns, were obtained from each site.

Preparation of Undisturbed Soil Columns

Four undisturbed soil samples were obtained at each site with a
soil coring machine produced by Utah Technical Services (Kelley et al.
1947). The coring machine takes an undisturbed soil core with a diam-
eter of approximately 10 cm and a length of up to 250 cm. Samples were
taken at each site by first removing the surface epipedon. This allowed
sampling of the subsurface structure with a minimum interference from
the tilled surface. After sample removal at each site, the soil cores
were placed on split plexiglas support tubes. A microcrystalline wax,
prepared by Petrolite Corporation, was melted and applied to one half of
the sample with a brush. The wax provided stability in transporting the
cores from the field to the laboratory with minimum disturbance and

1 = ANGULAR BLOCKY
2 = SUBANGULAR BLOCKY
3 = GRANULAR
4 = PRISMATIC
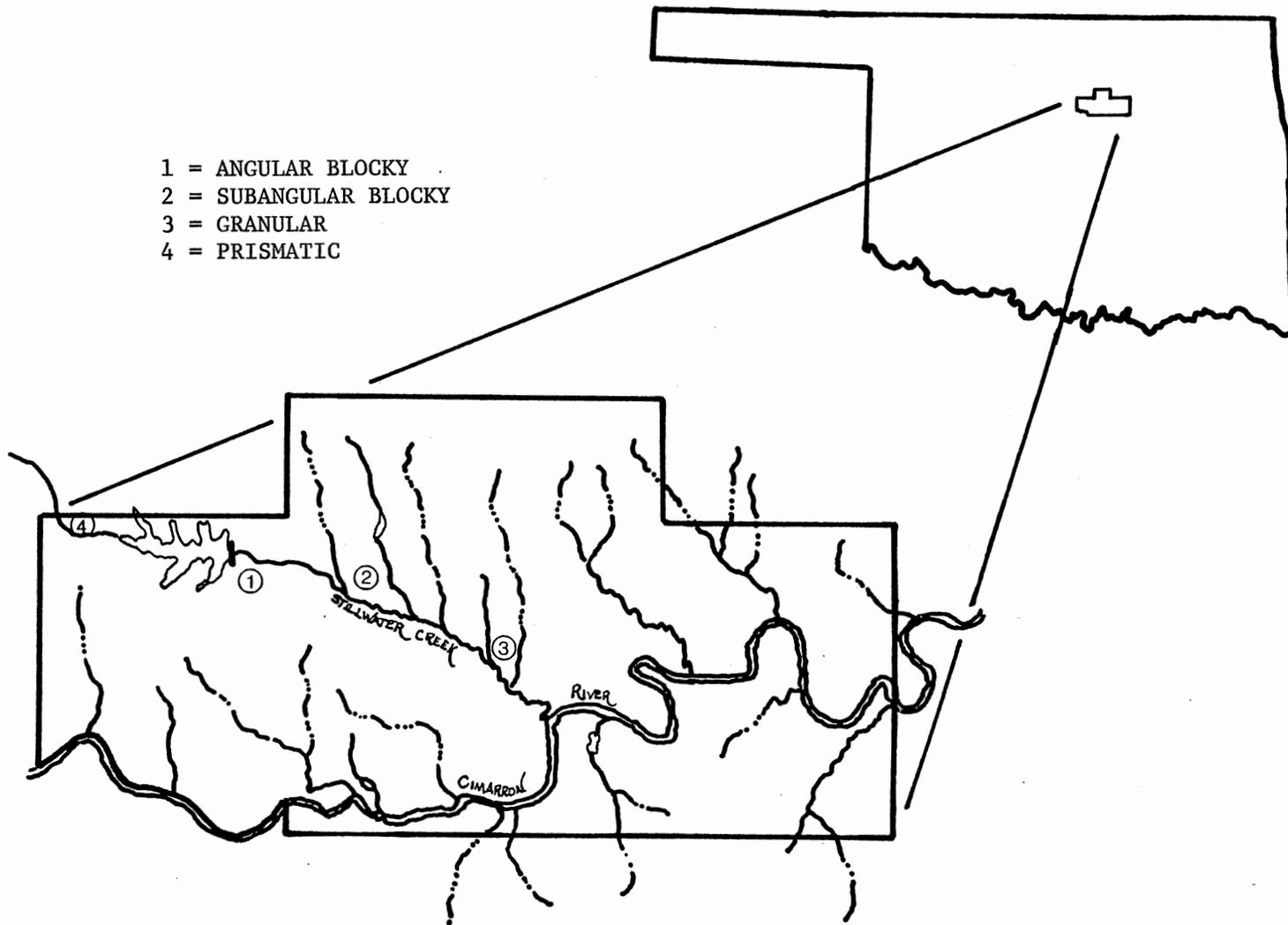
Figure 1. Sampling Locations Within Payne County, Oklahoma.

TABLE II

CHEMICAL AND PHYSICAL CHARACTERISTICS OF SELECTED SOILS

Treatment	pH	CEC	OM	BD	Pores	Sand	Silt	Clay	Taxonomic Description
		meq/100g	—%—	g/cm^3			%		
Angular Blocky, P	6.50	17.4	0.838	1.37	48.1	62	5	33	Cumulic Haplustoll fine-loamy, mixed, thermic
Angular Blocky, U	-	-	-	1.60	39.6	0	0	0	
Subangular Blocky, P	6.70	22.78	1.378	1.37	48.1	62.5	12.5	25	Pachic Argiustoll fine-loamy, mixed, thermic
Subangular Blocky, 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	-	-	-	

CEC = Cation Exchange Capactiy, OM = Organic Matter, and BD = Bulk Density.
P = Constructed and U = Undisturbed.

moisture loss. After waxing, the other half of the plexiglas tube was placed over the soil core. The cores were then carried in a specially constructed, shock-resistant transportation rack (developed by Oklahoma State University) for additional stability in transport.

The soil cores were brought into the laboratory where the unwaxed side of the core was also covered with wax. The waxing added more stability to the soil cores and prevented solution movement along the column-tube interface. When the waxing was completed, the plexiglas joints were sealed with wax. The bottoms of the columns were supported by placing a fine vinal screen over a perforated plexiglas plate. The columns were then mounted on plastic funnels and secured to a support frame in a controlled temperature room ($21^{o}C$). Five cm of acid washed quartz sand was placed on top of the soil to act as an interface between applied solute and soil. The soils were then brought to a near saturated state with deionized water and checked for continuity. The columns were taped in three places with strapping tape to secure the columns and help prevent any disturbance. A small bead of wax was placed around the upper edge of the wax-plexiglas interface to prevent water movement down this interface. A Brewer Automatic Pipetting Machine was utilized to apply the solute to the column surface at a uniform rate. Solute was applied at a rate of 10 ml per 8-hour period. It contained 100 ppm Rb^{+} for 6 weeks and 1000 ppm for an additional 4 weeks. The 8 hour time interval was chosen as the shortest time span in which all soils could infiltrate the amount of solute applied without ponding on the column surface.

Methods of Constructed Column Preparation

Constructed soil columns were made by using soil material from the same depths corresponding to the undisturbed soil columns. Soil for the columns of each sampling site was oven dried, ground, and sieved through a 2 mm screen. Soil columns were then made by packing 500 g of soil into plexiglas tubes at increments of 4.5 cm to a total depth of 1 meter. The plexiglas tubes utilized had the same demensions as the undisturbed columns. The constructed soils had an average bulk density of 1.37 g/cm^3. Four constructed soil columns were made for each site. These columns were mounted and sealed in a similar manner as were the undisturbed soil columns. The soil columns were arranged in a completely randomized experimental design. One of the undisturbed granular soil columns broke during preparation and was therefore, not evaluated.

Soil Solution Extraction

After saturation, 1.2 cm holes were made in the soil columns by drilling through the plexiglas and 4 cm into the soil column with a masonry bit at 8, 16, 32, 48, 64, and 80 cm depths down the columns in a spiral pattern. The holes were tightly fitted with 1 cm diameter by 1.5 cm porous ceramic cups. The cups were attached with 3 mm spaghetti tubing for sample convayance to 16 ml screw cap vials (Figure 2). The holes, after insertion of the cups, were sealed with wax. The 3 mm tubing was attached through one hole of a 2-hole rubber stopper. A second 3 mm section of tubing was inserted into the other hole of the stopper and attached to a vacuum manifold. The stopper was then used to seal the vials creating a sampling system. Because of differences in conveyance of solute, the collecting vials were removed when
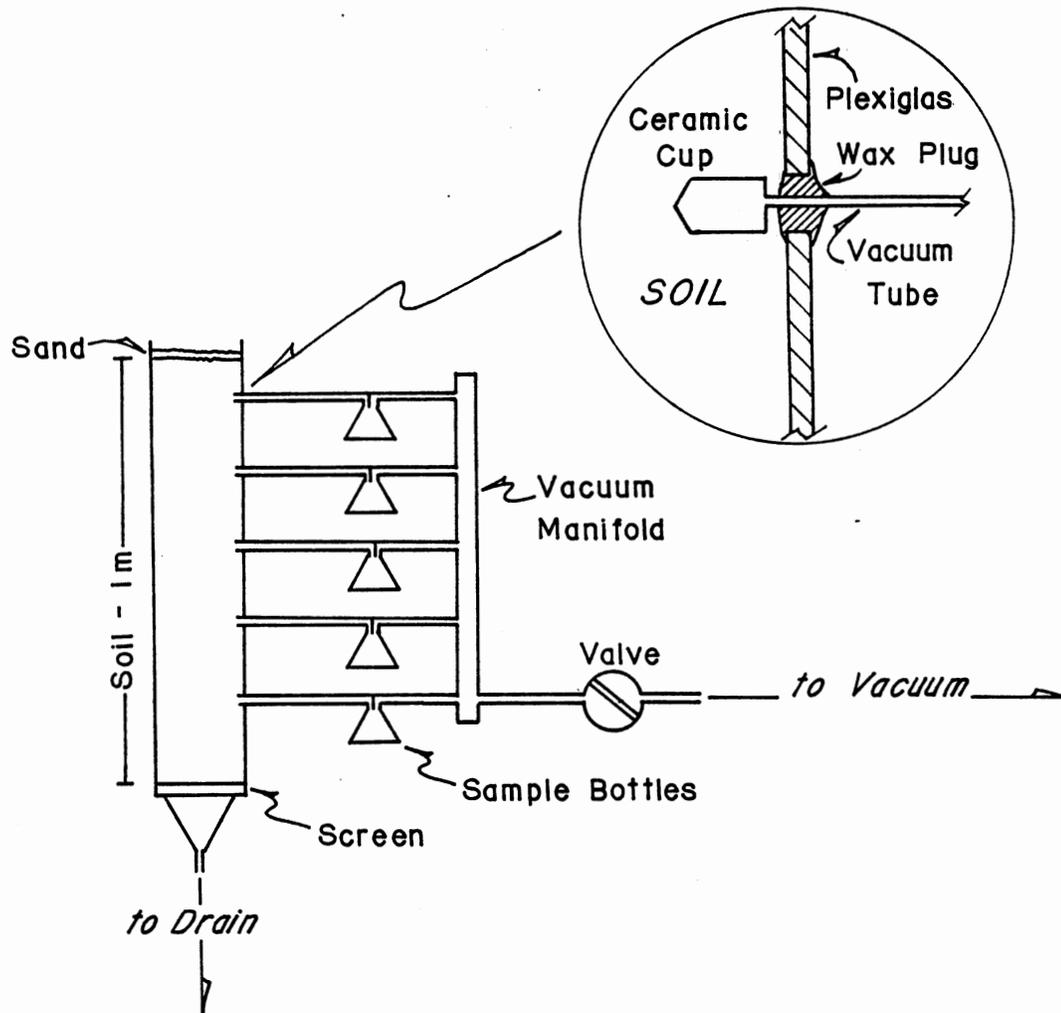
Figure 2. Schematic of Laboratory Design for Solution Application
and Withdrawal.

approximately 10 ml of sample were collected in the vials or at the end
of a 1-week period. The vials were detached from the column sampling
system, covered with aluminum foil, sealed, and left at room temperature
for analysis of Rb^+ content on the Perkin Elmer Model 2370 atomic
absorption spectrophotometer (AA).

Rubidium Exchange Determination Procedure

A 5 g sample of each structural type of soil used in this study
(viz., angular blocky, subangular blocky, granular, and prismatic) was
weighed into a 40 ml polyethelene centrifuge tube. A 25 ml volume of
Rb^+ solution at concentrations of 0, 25, 50, 75, 100, 200, and 400 g/ml
were added to 28 tubes (four soils and seven treatments). The treated
samples were shaken on a horizontal shaker set on high for 10 hours. At
the end of the equilibrium period, the samples were centrifuged at
15,000 rpm for 15 minutes. A 2 ml aliquot of supernatant solution was
removed and diluted with 2 ml of a 3000 g/ml solution of KCl. The
diluted sample was placed in a 16 ml screw cap vial and analyzed for Rb^+
by AA.

Soil Analyses for Rb^+ Movement

After a 10-week solution sampling period, the columns were allowed
to stand for 1 week to allow drainage of excess water from the column.
The plexiglas covers were removed from the soil columns and the columns
opened lengthwise. Soil samples were taken at 1 cm depth intervals for
the first 10 cm and every 2 cm thereafter from the center of the column
for analysis of Rb(+) content. The samples taken from the undisturbed
columns were of two types. One sample was taken from the ped faces, the

other sample was from within the ped (matrix). All samples were placed in screw cap sampling vials and frozen until analyses.

Approximately 2 g samples were taken from the soil sampling vials and placed in 25 ml vials with 20 ml of 1 N ammonium acetate in preparation for analysis. The soil-acetate vials were shaken horizontally for 10 hours to allow Rb^+ soil-solution equilibrium. The vials were removed from the shaker and allowed to settle overnight. A 2 ml aliquot of the supernatant was diluted with 2 ml of 3000 g/ml KCl in preparation for Rb^+ analysis by AA.

Soil depths were converted into soil mass equivalents by multiplying the depth of soil sampled by column area (78.54 cm^3), particle density, (2.65) and the solid fraction of the given soil, or bulk density. The "soil mass" value is used so all soils can be compared on an equivalent Rb^+-soil bases.

CHAPTER IV

RESULTS AND DISCUSSION

Solution Extractions

Sample solutions were extracted from all columns over a 10 week period. The Rb^+ content of the solution samples did not reflect high concentrations of Rb^+ movement through the columns. It was found that a high concentration of Rb^+ was in the upper 1 through 4 cm of soil. Rubidium was detected in solution for two undisturbed soil structural types, i.e., prismatic and angular blocky, and a constructed column of granular soil at the 8 cm depth. Solution concentrations of Rb^+ for the granular and prismatic soil were 0.4 µg/g soil and for the angular blocky soil 0.8 µg/g. Longer periods of application, higher solution concentration, more sensitive analytical instrumentation, with additional replications may have yielded more definitive Rb^+ movement information by soil solution extraction and analysis.

Soil Extraction Information

Ped surface and matrix samples were analyzed for Rb^+ separately. Separation of surface vs. matrix samples for the granular structure was not attempted because the peds were too small to make a reasonably reproducible separation. Peds were not present in the constructed columns.

Results of solute movement measurements for the constructed vs.

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undisturbed soil columns are presented graphically in Figures 3 through 7. The Rb^+ values for the undisturbed columns are the ped matrix soil sample means.

Comparisons of undisturbed matrix Rb^+ levels with constructed soil content demonstrates that the soil mass in undisturbed soils is not at equilibrium with Rb^+. These graphs indicate Rb^+ in undisturbed soils reacted with less soil mass at a given depth and moved down the ped faces prior to Rb^+-soil equilibrium. This difference is interpreted as an effect of soil structure since all other characteristics of the soil columns are essentially the same.

The analysis of variance comparing undisturbed and constructed columns (see Table III) indicates Rb^+ movement between the column types as being highly significant. Rubidium movement through unidsturbed soil columns compared to constructed soil columns was significantly greater indicating that soil structure can play an important role in salt movement through the soil profile. This movement for other solutes has been attributed to macropores and vertical axes associated with the strong structural components of undisturbed soils (Thomas et al. 1978). It appears that Rb^+ in solution moves down vertical macropores prior to saturation of the soil matrix as indicated by the increased concentrations of Rb^+ in the ped surface compared to the ped matrix in undisturbed soil columns. Movement of Rb^+ solution through the soil mass of the constructed soil columns was slower because movement occurred only after the soil mass was brought to near Rb^+-soil equilibrium. Rubidium movement through undisturbed soil columns is show in Figure 7. The interaction between constructed-undisturbed soil columns vs. depth was significant (Table III). This may not be important when considering
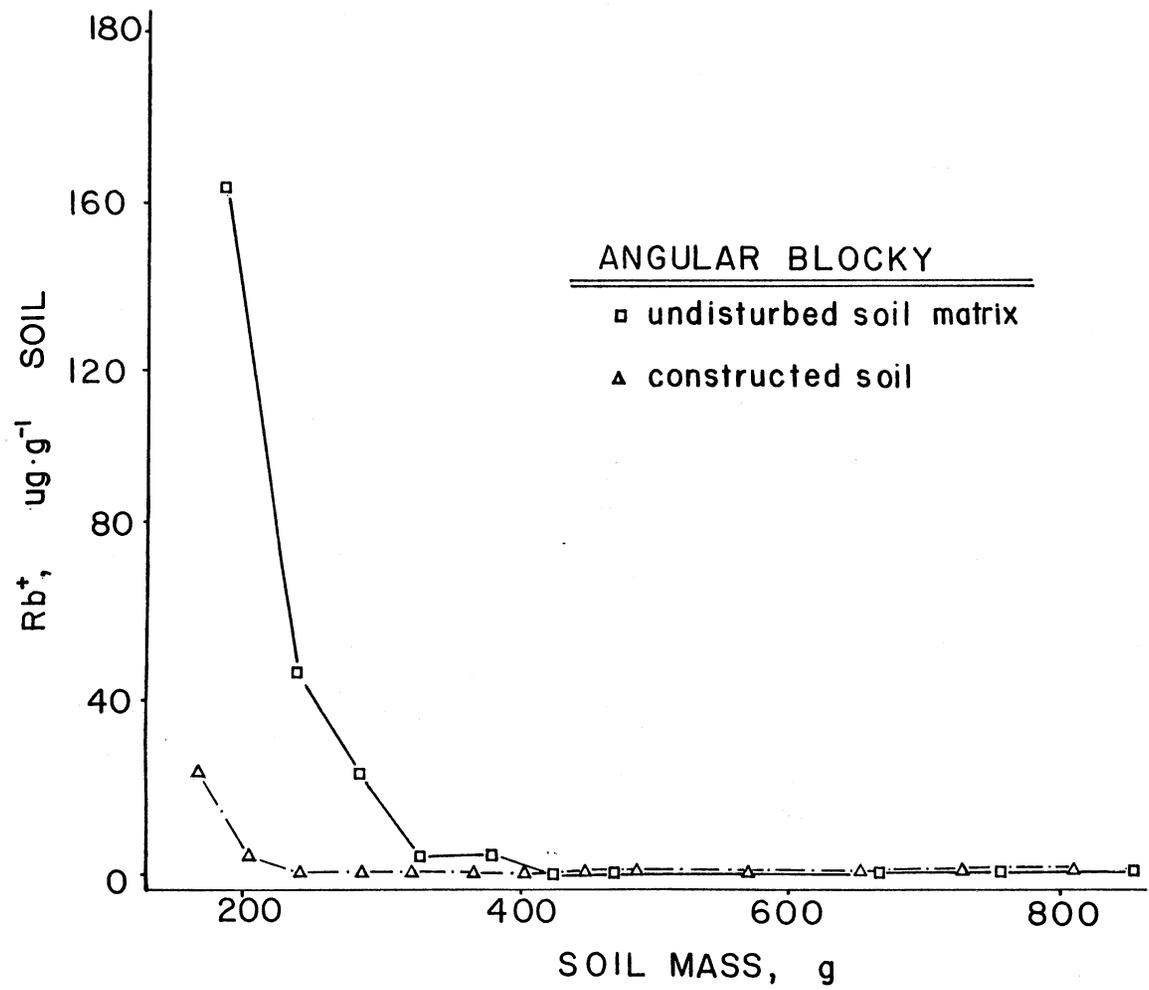
Figure 3. Rb+ Movement in Angular Blocky Soil Comparing Constructed and Undisturbed Columns at Various Depths from 4 cm.
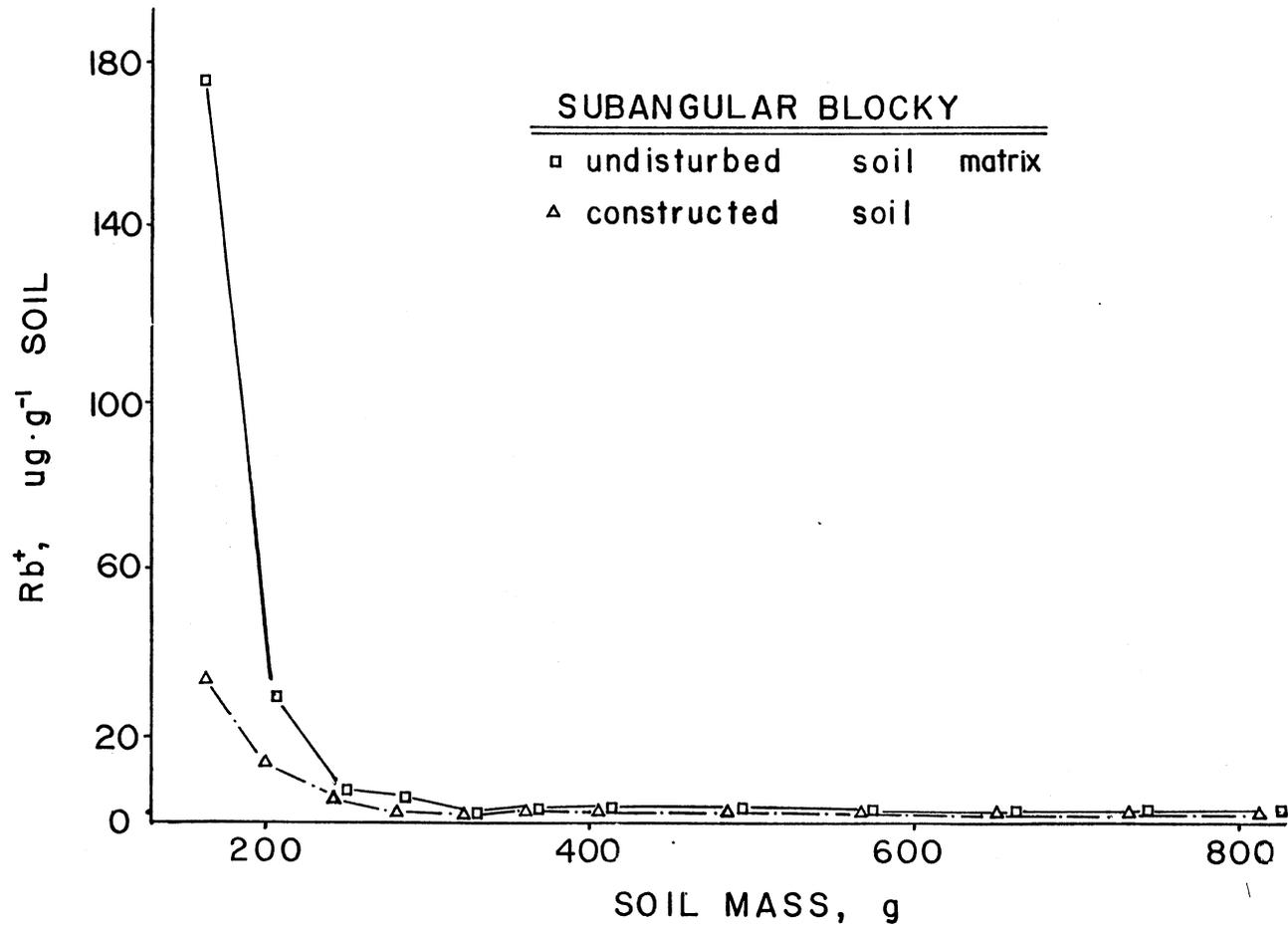
Figure 4. Rb$^+$ Movement in Subangular Blocky Soil Comparing Constructed and Undisturbed Columns at Various Depths from 4 cm.
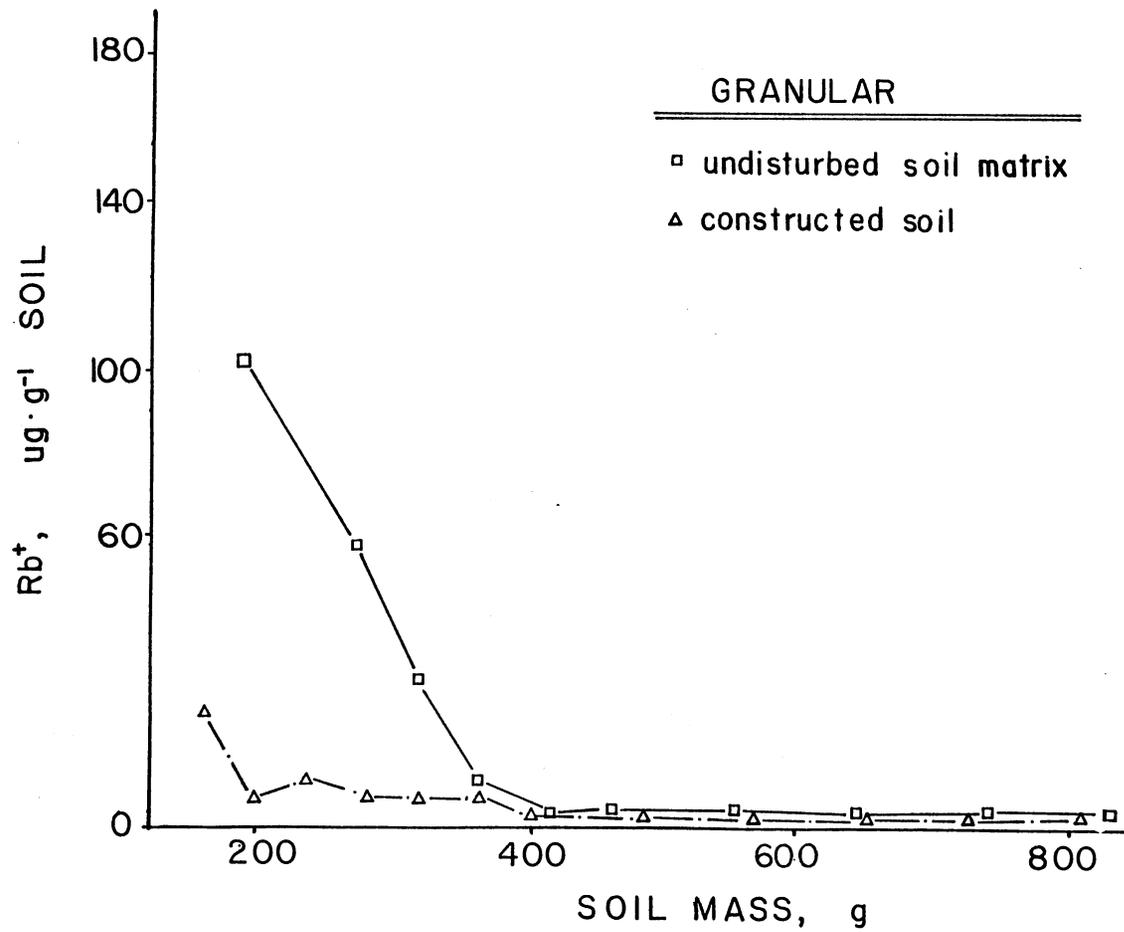
Figure 5. Rb^{+} Movement in Granular Soil Comparing Constructed and
Undisturbed Columns at Various Depths from 4 cm.
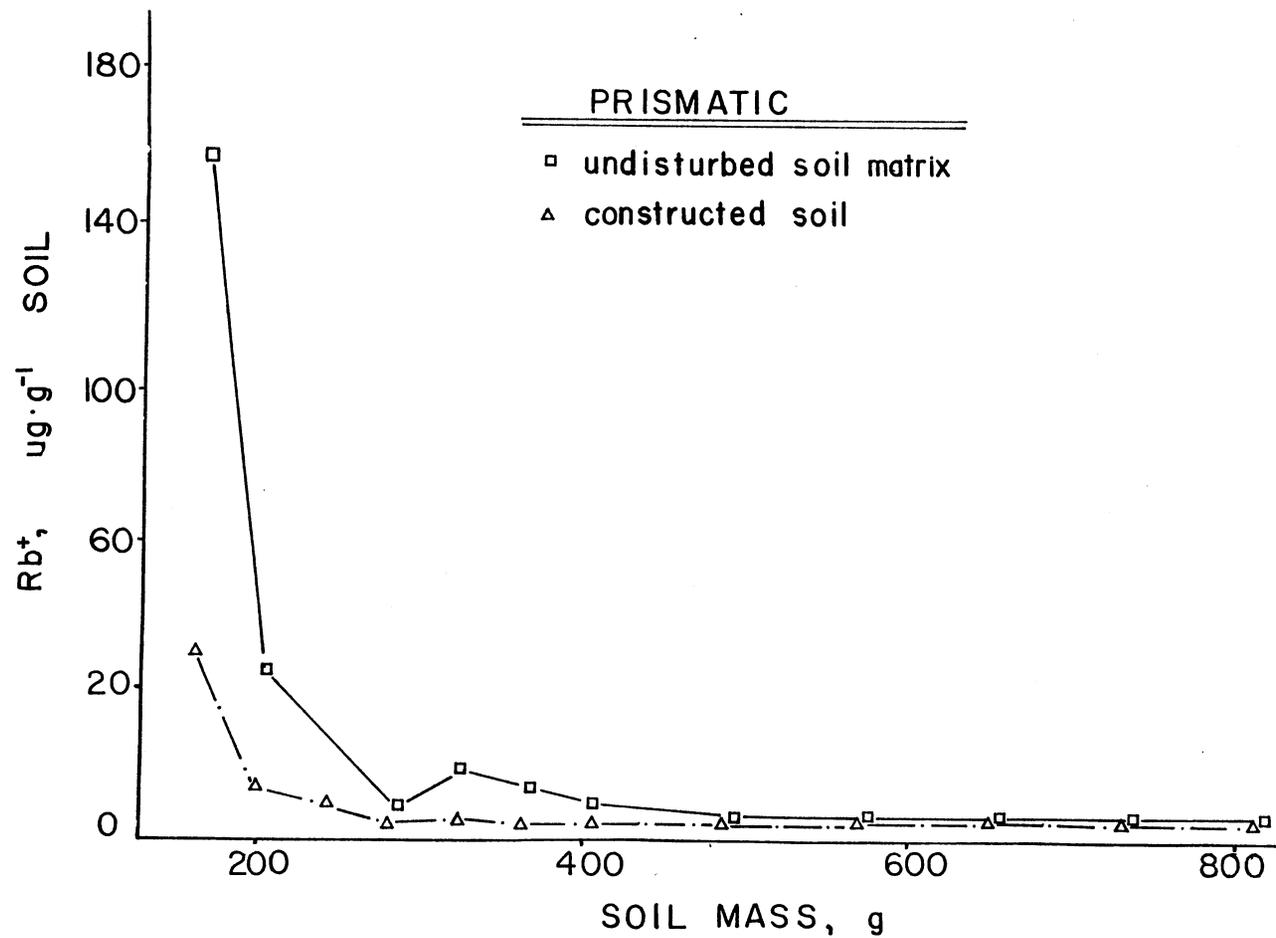
Figure 6. Rb^{+} Movement in Prismatic Soil Comparing Constructed and Undisturbed
Columns at Various Depths from 4 cm.
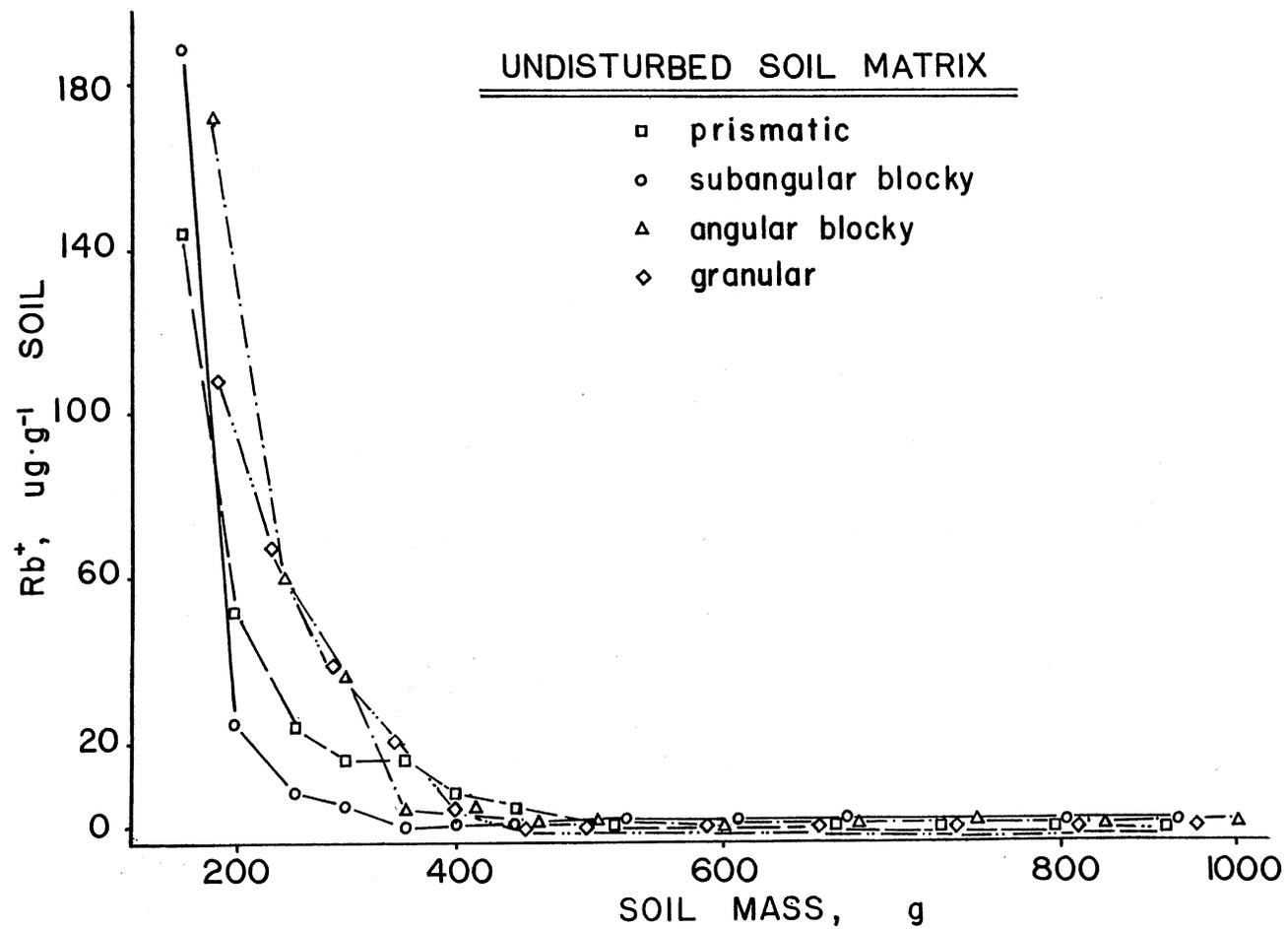
Figure 7. Rb$^+$ Movement Comparing Undisturbed Soil Columns for Four Subsoil Structures at Various Depths from 4 cm.

TABLE III

ANALYSIS OF VARIANCE FOR CONSTRUCTED
VS. UNDISTURBED SOIL COLUMNS

Source	df	Mean Square	F
Total	402	1784.45	
Soil	3	225.92	0.11
Pack‡	1	18828.85	9.58**
Soil*Pack	3	356.71	0.18
Error (A)	2	1965.78	
Depth	13	14567.44	11.82**
Soil*Depth	36	384.56	0.31
Pack*Depth	12	85001.26	6.90**
Soil*Pack*Depth	36	2019.13	0.16
Error (B)	275	1232.93	

**Significant at the 0.01 probability level.

‡Pack = Constructed vs. undisturbed soil columns.

that structure does have some effect on the accumulation of Rb^+ at various points down the column.

Differences between the four soil structures over depths were also significant (Table IV). The upper portion of all columns are apparently heavily saturated with Rb^+ (Table V); therefore, the differences in solute movement rates can most easily be observed as the lower extensions of the columns are examined. Rubidium movement data between undisturbed vs. constructed columns shows the least differences in depths of penetration for the subangular blocky and granular soils with the greatest differences between the prismatic and angular blocky soils. The two soils with the weakest structure (subangular blocky and granular) allowed Rb^+ movement through 12 cm of soil and the angular blocky, 16 cm soil (Table V). The prismatic soil, with the most pronounced structural expression, had detectable Rb^+ after the solution had passed through 20 cm of soil (Table VI). The vertical extension of the soil structural unit for the prismatic soil is thought to be the major factor for the differences found.

Undisturbed Soil-Matrix vs. Surface Samples

Figures 8 through 12 compare Rb^+ movement through undisturbed soil columns. The soils sampled were angular blocky, subangular blocky, and prismatic. Soil samples examined were from both ped surfaces and from within the ped (matrix). The granular soil did not have sufficient surface area along the ped faces to sample reproducibly and, therefore, was not included. The Rb^+ movement by soil structures, compared on an individual basis were again, statistically different. Graphical representation of the differences in Rb^+ movement by structures is presented

TABLE IV

ANALYSIS OF VARIANCE FOR MAXIMUM PENETRATION OF
RUBIDIUM IN UNDISTURBED SOIL COLUMNS

Source	df	Mean Square	F
Total	14		
Treatment (T)[‡]	3	24.67	3.02[†]
Error (R/T)	11	8.18	

[†]Significant at the 0.10 probability level.

[‡]Angular blocky, subangular blocky, granular, and
prismatic soil structures.

TABLE V

RB$^+$ CONCENTRATION MEANS AT DIFFERENT DEPTHS COMPARING
CONSTRUCTED VS. UNDISTURBED (PED MATRIX) COLUMNS

Treatment	Depth (cm)														
	2	3	4	5	6	7	8	9	10	12	14	16	18	20	22
A. Blocky[‡] Constructed	514.12	62.83	23.79	5.27	1.23	0.75	0.43	0.25	0.18	0	0	0	0	0	0
A. Blocky Matrix	677.22	427.27	164.53	48.98	23.76	3.16	2.94	1.49	0.35	0.49	0.22	0.22	0	0	0
S. Blocky[†] Constructed	609.88	214.23	30.77	11.21	4.91	0.54	0.72	0.72	0.53	0.09	0	0	0	0	0
S. Blocky Matrix	751.58	333.35	176.66	26.88	4.40	5.66	0.98	0.56	0.26	0.23	0	0	0	0	0
Granular Constructed	434.16	363.05	14.17	3.23	4.48	3.38	2.65	1.64	0.90	1.02	0	0	0	0	0
Granular Undisturbed	462.52	321.98	109.10	69.09	40.24	19.54	4.94	0.78	1.10	0.80	0	0	0	0	0
Prismatic Constructed	507.91	336.09	26.03	5.02	2.99	0.63	0.30	0.18	0	0	0	0	0	0	0
Prismatic Matrix	594.36	502.35	113.75	21.51	3.27	3.31	6.28	4.01	1.95	0.59	0.23	0	0	0	0

[‡] A. Blocky = Angular Blocky;   [†] S. Blocky = Subangular Blocky.

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TABLE VI

RB^+ CONCENTRATION MEANS AT DIFFERENT DEPTHS COMPARING MATRIX VS. PED SURFACE SAMPLES

Treatment	Depth (cm)														
	2	3	4	5	6	7	8	9	10	12	14	16	18	20	22
A.Blocky[‡] Matrix	677.22	427.27	164.53	48.98	23.76	3.16	2.94	1.49	0.35	0.49	0.22	0.22	0	0	0
A.Blocky Surface	576.49	354.47	180.30	70.80	52.18	7.82	1.65	0.81	0.52	0.37	0.11	0.33	0	0	0
S.Blocky[†] Matrix	751.58	333.35	176.66	26.88	4.40	5.66	0.98	0.56	0.26	0.23	0	0	0	0	0
S.Blocky Surface	686.87	514.49	200.72	20.33	11.49	4.63	1.43	0.86	0.84	0.13	0	0	0	0	0
Prismatic Matrix	594.36	502.35	113.75	21.51	3.27	3.31	6.28	4.01	1.95	0.59	0.23	0	0	0	0
Prismatic Surface	497.89	428.96	177.37	85.56	46.83	27.23	27.49	14.19	2.44	2.38	0.53	0.21	0.24	0.23	0

[‡] A. Blocky = Angular Blocky; [†]S. Blocky = Subangular Blocky.
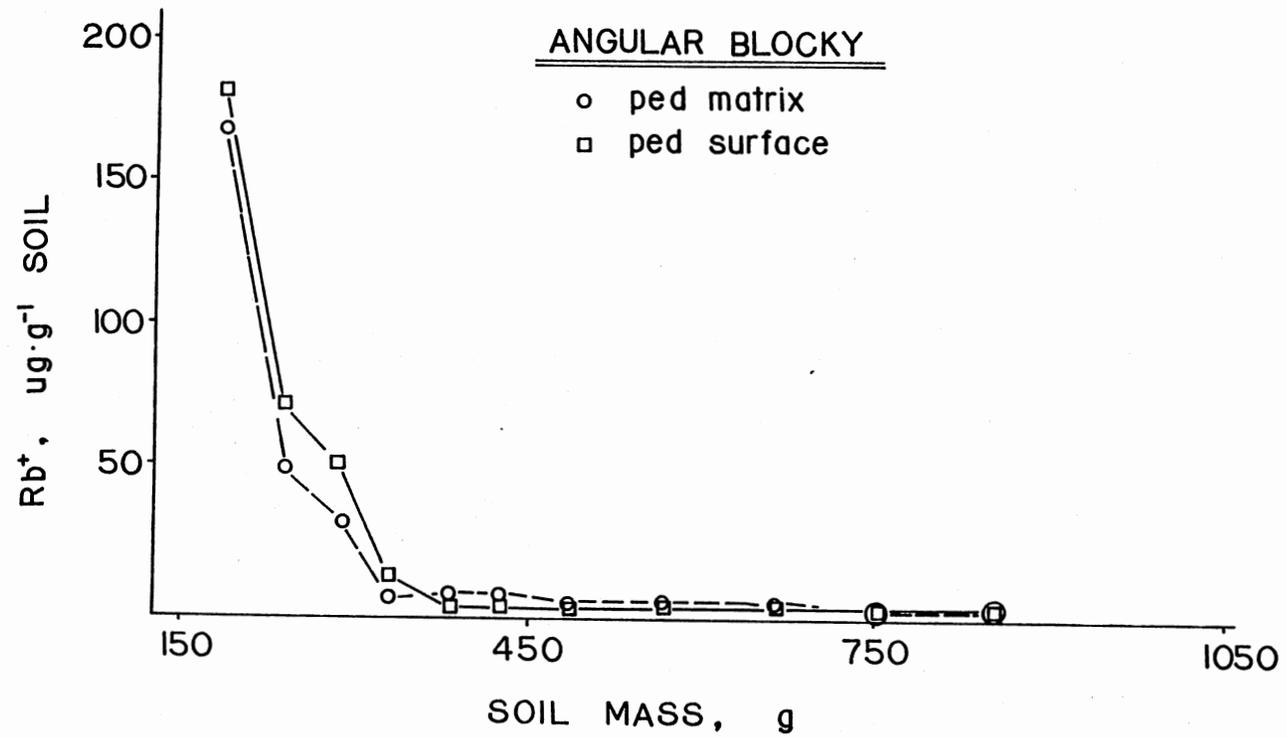
Figure 8. Rb^{+} Movement in Angular Blocky Soil Comparing Matrix and Ped Surface Samples at Various Depths from 4 cm.
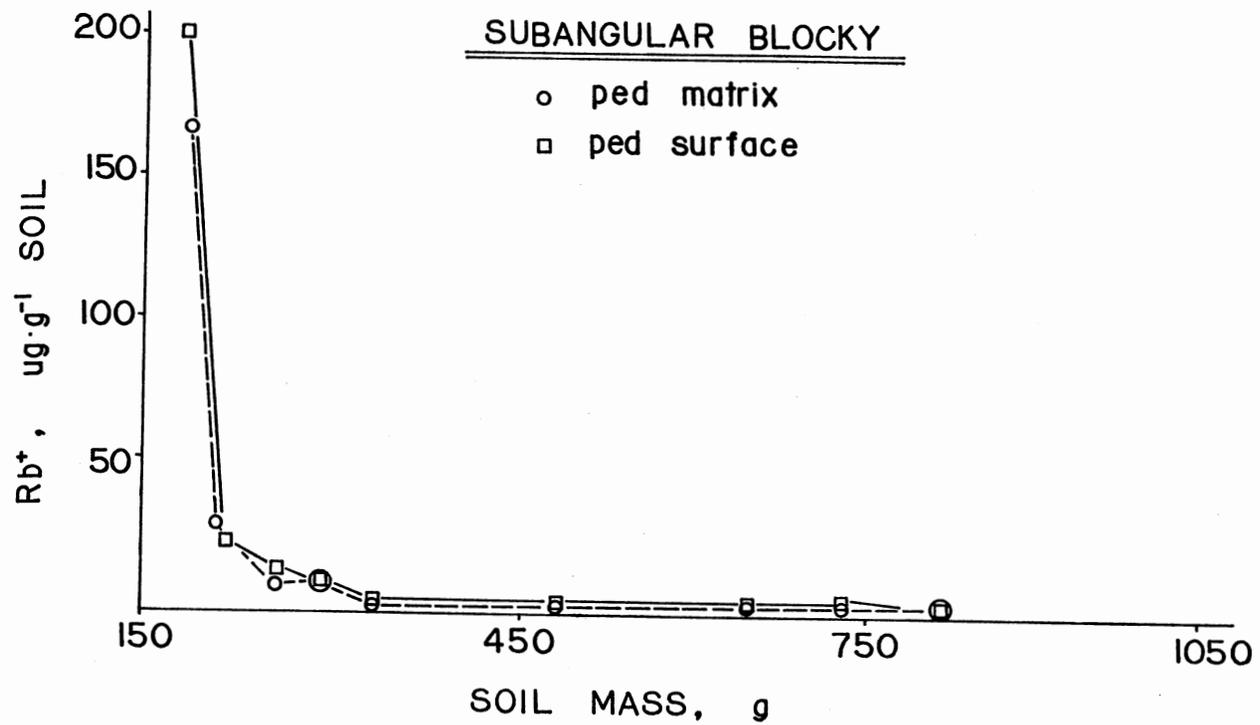
Figure 9. Rb$^+$ Movement in Subangular Blocky Soil Comparing Ped Matrix and Ped Surface Samples at Various Depths from 4 cm.
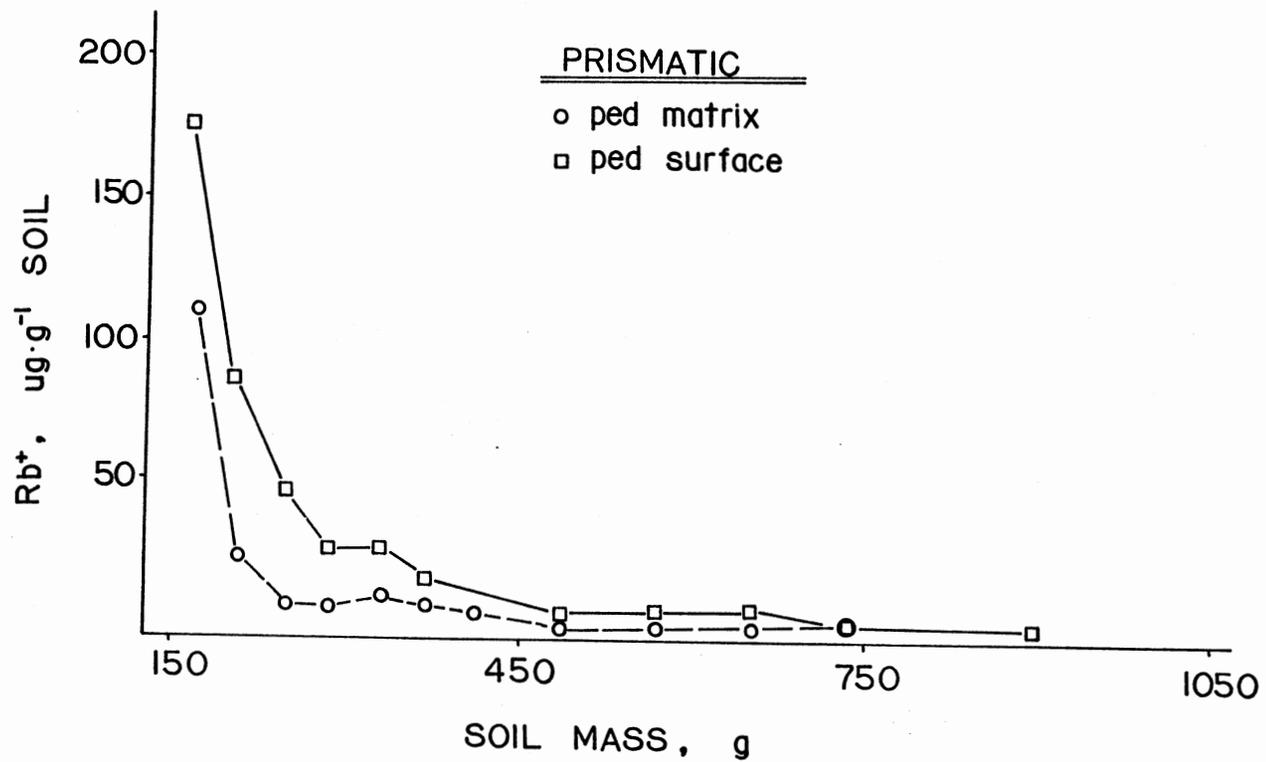
Figure 10. Rb^{+} Movement in Prismatic Soil Comparing Ped Matrix and Ped Surface
Samples at Various Depths from 4 cm.
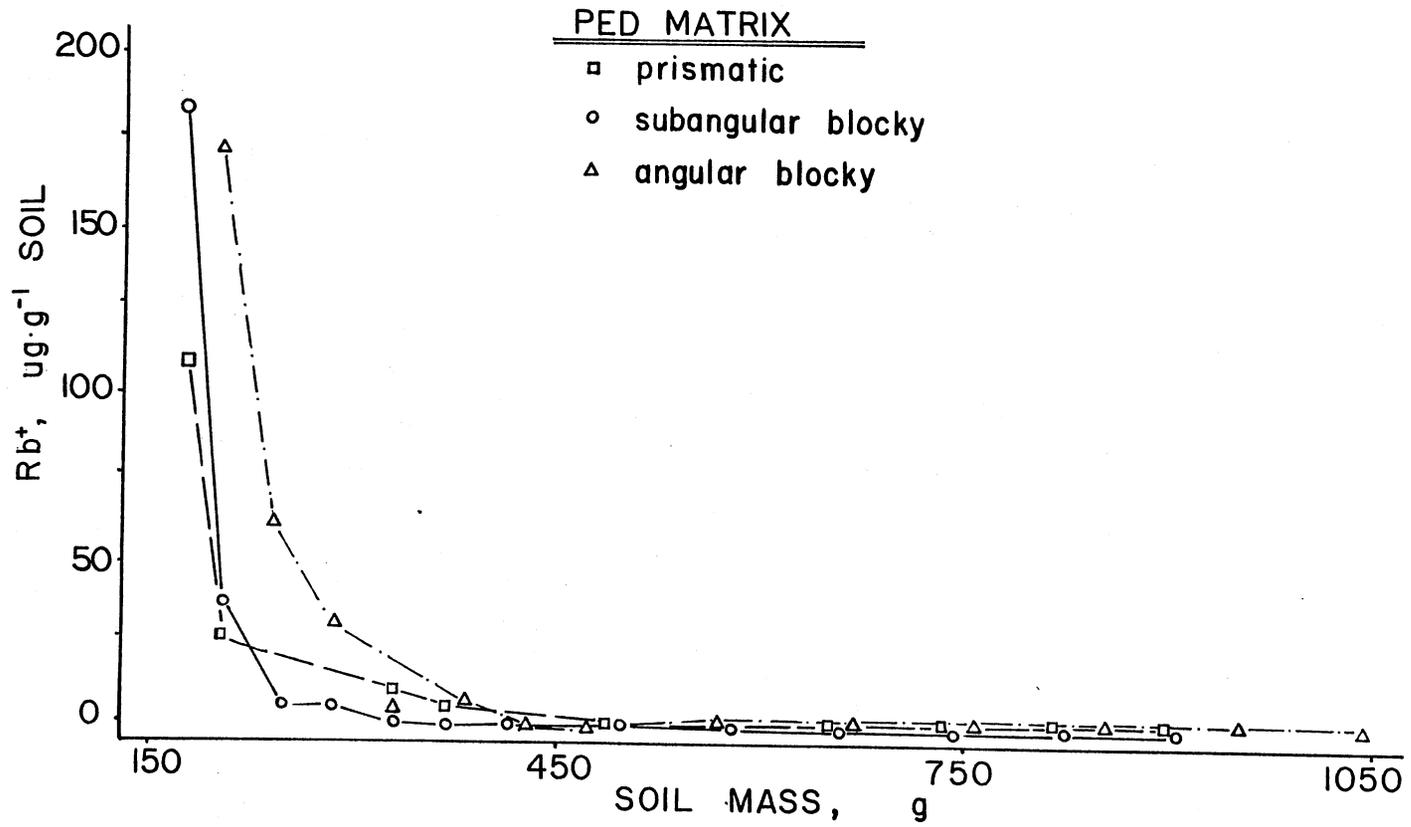
Figure 11. Rb$^+$ Movement in Structured Soils Sampled Within the Ped Matrix at Various Depths from 4 cm.
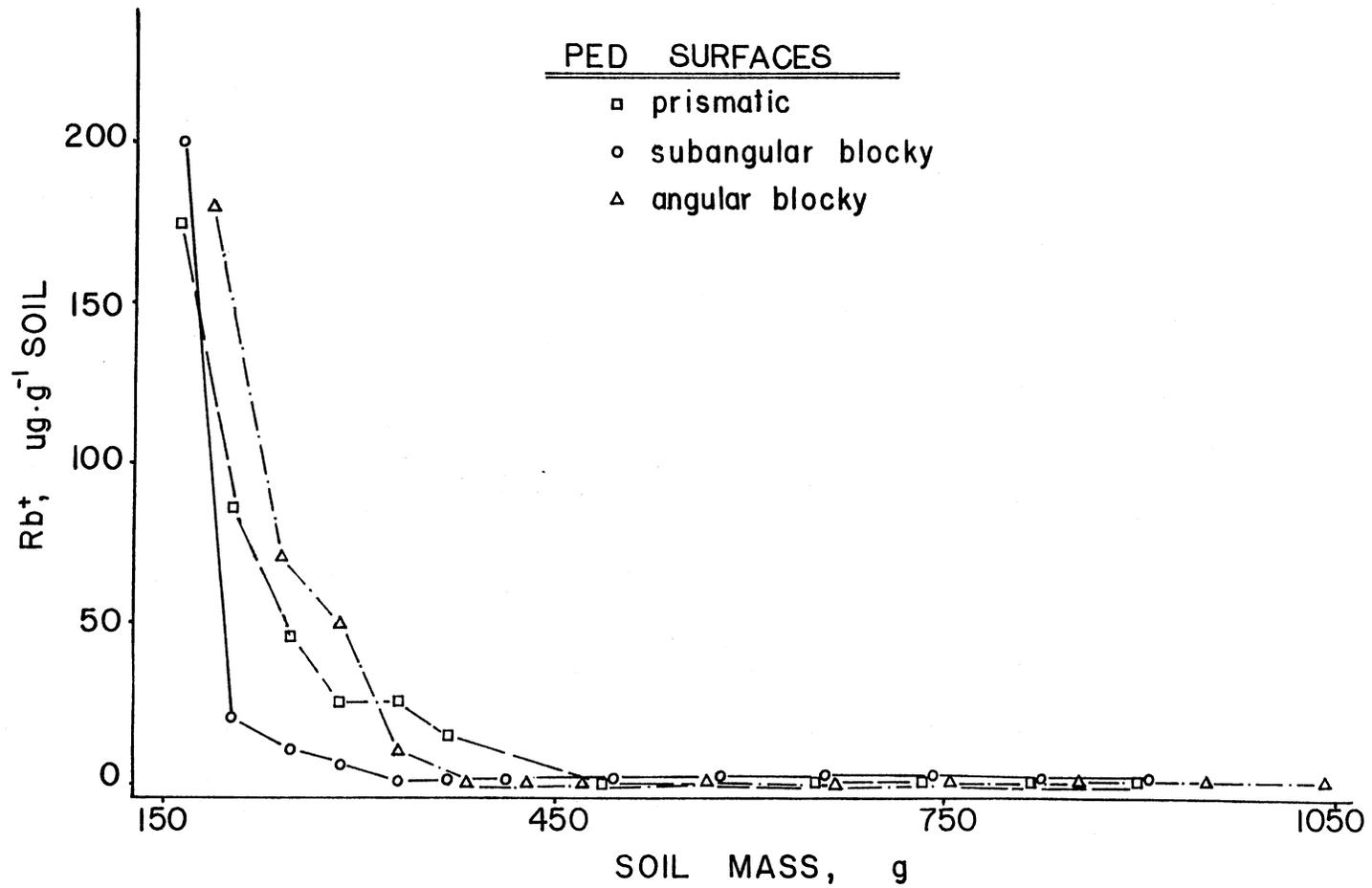
Figure 12. Rb$^+$ Movement in Structured Soils Sampled Along Ped Surfaces at Various
Depths from 4 cm.

in Figures 11 and 12 by plotting matrix and surface sample means respectively. As noted earlier the prismatic soil had solute moving through more soil mass to a greater soil depth (20 cm) than the angular blocky soil (16 cm) and subangular blocky soil (12 cm).

Thus, the more pronounced the structural features (i.e., prismatic, angular blocky, and subangular blocky), the greater the Rb^+ movement (Table VII). Indeed, there is a highly significant difference between the Rb^+ concentrations in the matrix and the surface samples (Table VIII). Surface samples taken from vertical ped faces exhibited higher Rb^+ concentrations than soil matrix samples when averaged over all replications. The statistical significance between matrix and ped surface Rb^+ content is in agreement with the findings of other workers (Anderson and Bouma, 1977; McMahon and Thomas, 1974). They postulated that some solutes moved through the soil macropores, bypassing water and other solutes already within the ped matrix. The effects of structural units on solute movement is shown by this research with a reactive cation as well as data sets of other researchers. The more distinct the structural units, the greater the change (increase) insolute movement.

TABLE VII

RB^{+} CONCENTRATION MEANS AT DIFFERENT DEPTHS COMPARING
CONSTRUCTED VS. UNDISTURBED (PED SURFACE) COLUMNS

Treatment	Depth (cm)														
	2	3	4	5	6	7	8	9	10	12	14	16	18	20	22
A.Blocky[‡] Constructed	514.12	62.83	23.79	5.27	1.23	0.75	0.43	0.25	0.18	0	0	0	0	0	0
A.Blocky Surface	576.49	354.47	180.30	70.80	52.18	7.82	1.65	0.81	0.52	0.37	0.11	0.33	0	0	0
S.Blocky[†] Constructed	609.88	214.23	30.77	11.21	4.91	0.54	0.72	0.53	0.09	0	0	0	0	0	0
S.Blocky Surface	686.87	514.49	200.72	20.33	11.49	4.63	1.43	0.86	0.84	0.13	0	0	0	0	0
Prismatic Constructed	507.91	336.09	26.03	5.02	2.99	0.63	0.30	0.18	0	0	0	0	0	0	0
Prismatic Surface	497.89	428.96	177.37	85.56	46.83	27.23	27.49	14.19	2.44	2.38	0.53	0.21	0.24	0.23	0

[‡]A. Blocky = Angular Blocky; [†]S. Blocky = Subangular Blocky.

TABLE VIII

ANALYSIS OF VARIANCE FOR MATRIX
VS. PED SURFACE SAMPLES

Source	df	Mean Square	F
Total	309	4748.68	
Treatment (T)	2	542.54	0.06
Error (A)	9	8913.61	
MORS‡	1	5370.99	11.30**
T*MORS	2	1753.24	3.69*
Error (B)	9	475.27	
Depth	12	5528.70	15.72**
T*Depth	24	761.28	0.23
MORS*Depth	12	914.32	0.28
T*MORS*Depth	24	290.20	0.09
Error (C)	214	3537.45	

†, ** Significant at the 0.10 and 0.01 probability levels,
respectively.

‡ Matrix or Surface Samples

CHAPTER V

SUMMARY AND CONCLUSIONS

The summary and conclusions for this research are presented as
follows:

1. Cations, with relatively high soil exchange capacity

    interactions, are conducted through undisturbed soils at

    a faster rate than through constructed columns of the

    same soil.

2. Prismatic and angular blocky structured soils allowed

    Rb^+ movement to greater depths than did weakly struc-

    tured or massive soils of similar texture and mineralogy.

    Prismatic and angular blocky soil peds (structured

    units) have more distinct and longer vertical ped sur-

    faces. It is reasoned, that solute movement rates in

    soil are directly related, to that structure, other

    factors remaining constant. Gravitational forces appar-

    ently move water through the associated structural

    macropores before the ped interiors are saturated.

3. Undisturbed column data exhibit the effect of soil

    characteristics other than texture and mineralogy on

    water and solute movement in soils, while constructed

    columns do not. Whenever column studies are used in

    lieu of field experiments, use of undisturbed columns

are recommended.

4. Calculations of Rb^+ movement rates in prismatic soils compared to subangular blocky soils indicate a 25% higher rate for the prismatic soils, approximately. Whenever soil selection for disposal is based on structure, poorly or unstructured soils provide the greatest protection against groundwater pollution.

5. In some cases, an economic advantage, to increase soil retention of pollutants and/or to reduce their movement rate through the soil, could be obtained by breaking down the peds of structured soils for intermittent or permanent impoundment of wastes.

6. More definitive information from undisturbed soil column studies of solute movement in soils may be obtained using a longer solute application period, improvements in solute application control, increased replication, and more sensitive analytical instrumentation.

7. Confirmation of the laboratory results in field studies is desirable. If differences in detail are obtained via field studies, a model may be constructed that will show that undisturbed cores can be used in lieu of more expensive field work with satisfactory precision.

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$\mathcal{V}$

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