Utah State University

DigitalCommons@USU

Memorandum

US/IBP Desert Biome Digital Collection

1972

# Predicting Nitrogen Transformations and osmotic Potentials in Warm Desert Soils

G. R. Dutt

J. Hanks

# RESEARCH MEMORANDUM

RM 72-39

# PREDICTING NITROGEN TRANSFORMATIONS AND OSMOTIC POTENTIALS IN WARM DESERT SOILS

G. R. Dutt with J. Hanks

DESERT BIOME
U.S. INTERNATIONAL BIOLOGICAL PROGRAM

ABSTRACT

A digital computer model predicting the nitrogen and salt content of drainage water from irrigation agriculture has been completed and verified. A complete description of the model including theoretical considerations, user's manual and complete computer listings may be found in Dutt et al. (in press).

An attempt was made to apply this model to simulate nitrogen transformations, nitrogen movement and plant intake of N in a warm desert soil under range grass. However, the moisture movement portion of the model proved to be inadequate for the two-layered case encountered in the field. Dr. John Hanks of Utah State University has agreed to make the moisture movement simulation using a two-layered unsaturated moisture movement model. The nitrogen transformation and plant uptake portion of the run will be completed at the University of Arizona using unsaturated flow data supplied by Dr. Hanks.

An incubation study is in progress to assess the application of the nitrification portion of the model to soils under conditions of low moisture content and high temperature and, to some extent, pH < 7. These conditions, with the exception of acid pH, often are characteristic of warm desert soils. Preliminary data indicate that, in the above soils, nitrification of applied $NH_4^+$-N (e.g. 100 ppm $NH_4^+$-N) may exhibit nitrification rates which are at least an order of magnitude less than those predicted by the present model designed for alkaline soil conditions.

In addition, the data from the incubation study will be used to develop a more sophisticated rate subroutine for nitrification in soils. This new subroutine will be based on transition state theory, and principles of statistical thermodynamics. The model will include hydrogen ion activity as a variable as well as $NH_4^+$ and $O_2$ activities. The applicability of the existing model to alkaline, well-buffered warm desert soils is still under investigation at this writing.

The results of the field simulation run and the incubation data should allow further evaluations of the model with respect to application to a desert biome model.

# INTRODUCTION

Over the past ten years, the chief investigator has been working on computer models of soil-water systems. During the last three years the U.S. Bureau of Reclamation has been financing, under contract agreement, the development of a system analysis model for predicting nitrogen in irrigation drainage water. The development has been directed by the chief investigator. This model has been verified for some agricultural soils and predicted values compare favorably with verification data tested to date. The model, in fact, is a systems analysis model considering the dynamic soil water system and may be directly applicable to a desert biome model in its present form under certain conditions. However, under high temperatures, low moisture contents, and occasional low pH found in many desert soils, it is possible that the moisture movement subroutine will not correctly predict the concentrations and distribution of nitrogenous compounds. It would seem that the current model needs to be evaluated and possibly modified if it is to be used as a subroutine in a desert biome model.

# OBJECTIVES

The overall objective of this study is to evaluate the applicability of the current version of a digital computer model predicting the transformation and movement of nitrogenous compounds in soil-water systems to a desert biome model.

The specific objectives attempted during 1971 were as follows:

1. Evaluate the overall model with respect to nitrogen transformation and movement in a soil located in a typical warm desert ecosystem (Page Ranch Simulation Study).
2. Evaluate the predictive capabilities of the nitrogen transformation subroutine with respect to high temperatures, low moistures and low pH. (The experimental portion of this objective was carried out in the laboratory).
3. Begin development of a more sophisticated rate relationship for nitrification. The equations developed are to be based on transition state theory and basic principles of statistical thermodynamics.

# METHODS

## Page Ranch Simulation Study

*The Site** The site selected to test the current model was on the Page-Trowbridge Experimental Range located 28 miles due north of Tucson, Arizona. The range belongs to the University of Arizona and is fenced, so that the vegetation has not been disturbed by livestock for several years.

This location, hereafter referred to as the Page Ranch site, is located in the NE1/4 of SW1/4, Section 27, Township 9S, Range 14E. At an elevation of approximately 3680 feet, this site was the location of a range fertilization study conducted in 1967 and 1968 under the direction of Dr. J. L. Stroehlein (Billy, 1970).

*The Soil**. The soil is a Ustollic Haplargid, fine, mixed, thermic, Whitehouse sandy loam. It has an unusually deep, permeable A1 horizon overlying a very deep, slowly permeable, heavy textured, prismatic B horizon. The grass root zone extends well down to approximately 24 inches and from there down the roots are few and fine in size. The soil is slightly acidic (pH 6.5) at the surface and increases with depth to approximately 8.2 at 3 feet. Calcium carbonate nodules are observed at 24 inches and below. The site is on a 1% slope with a westerly aspect.

---

* Material in these sections was extracted from Billy, 1970.

*Vegetation**. The plots selected for the 1967-1968 experiment were located among invading mesquite with Lehmann's lovegrass as the dominant grass. Mixed within were scattered plants of Boer lovegrass. The three dominant spring annuals were six weeks fescue, filesee, and Indianwheat. Undesirable vegetation included barrel cactus, burroweed and other minor weeds.

*Experimental Procedure**. In the spring of 1967, 35 plots, each 20' x 30', were selected and staked. Thirty of these plots were then selected randomly and preclipped two inches above the ground between May 31 and June 5 and the loose plant materials removed. The five remaining plots were used to estimate the effect of clipping on grass growth.

Seven treatments were assigned to the 35 plots as follows:

| Treatment | Date of fertilizer application |
|---|---|
| 1 | June 5, 1967 |
| 2 | July 3, 1967 |
| 3 | July 13, 1967 |
| 4 | July 22, 1967 |
| 5 | Aug. 7, 1967 |
| 6 | Check (unfertilized) |
| 7 | July 12, 1967 (not pre-clipped) |

The fertilizer material applied in all cases was granulated ammonium nitrate-phosphate (30-10-0) applied at 50 lb/acre. This rate of N had been previously shown to give maximum yield return of forage production on soil and vegetation similar to those at the Page Ranch site (Billy, 1970).

The plots were harvested on August 19, 1967, September 13, 1967, and October 12, 1967, and moisture determination, dry weight of tops and seeds, and chemical analyses performed on the harvested vegetation on each date. Additionally, in 1968 the spring annuals were harvested. A final harvest occurred on October 16, 1968, and the vegetation was analyzed in the same manner.

Sampling of individual plants (10 plants/plot) in each of the 35 plots occurred prior to each fertilizer application, and soil samples (5 cores/plot) were taken five times throughout the growing season in 1967. Plant N and P and soil $NO_3$-nitrogen and available $PO_4$-phosphorus were determined on these soil and plant samples.

*Reaction Mechanism.* A theoretical reaction mechanism for nitrification was established to include the reactants ($NH_4^+$ and $O_2$) and a critical intermediate activated complex, such as $NH_2$-OH or HO-N=N-OH. The design of the activated complex must, by necessity, be kept relatively simple to allow generation of a partition function, q, describing its motions. The assumption may be made that contributions to the partition function made by any missing part(s) of the activated complex are negligible or constant.

As an illustration of the complexity attained by partition functions, even for relatively uncomplicated molecules such as $O_2$, the partition function $q_{O_2}$ for oxygen (less any electronic contributions) may be written as follows (Hill, 1960):

$$q_{O_2} = V(2\pi mkT/h^2)^{3/2} \cdot T/\sigma\theta_r \cdot e^{-\theta_v/2T}/(1-e^{-\theta_v/T}), \quad [1]$$

*Material in these sections was extracted from Billy, 1970.

where:

- V is volume,
- $m$ is mass,
- k is Boltzmann's constant,
- T is temperature (°K),
- h is Planck's constant,
- $\sigma$ is the symmetry number,
- $\theta_r$ is the rotational temperature for $O_2$, and
- $\theta_v$ is the vibrational temperature for $O_2$.

Polyatomic molecules rapidly become unworkable with respect to establishment of a partition function for the entire molecule as the number of atoms and side chains increases.

*Reaction Rate.* Two basic assumptions from transition state theory were applied to allow derivation of a function for the rate constant. First, the assumption was made that chemical equilibrium exists between the reactants and the activated complex (plus any intermediates formed with the complex). Second, it was assumed that the energy of activation associated with the activated complex represents the highest energy barrier between reactants and products (i.e., between $NH_4^+$ and $O_2$, and $NO_3^-$). With the above assumptions and an application of statistical thermodynamics, it may be shown (Hill, 1960) that for a reaction of the type aA + bB = c (ACTIVATED COMPLEX) - PRODUCTS,

$$K = kT/h \frac{(q^*/v)\ e^{-\Delta\mu/kT}}{(q_A/v)\ (q_B/v)} , \qquad [2]$$

where:

- K is the rate constant,
- k is Boltzmann's constant,
- T is temperature (°K),
- h is Planck's constant,
- $\Delta\mu$ is the energy of activation,
- q is the partition function for reactant A,
- $q_B$ is the partition function for reactant B,
- q*is the partition function for the activated complex with one degree of freedom removed for the reaction pathway, and
- v is volume.

Also, the rate of reaction may be expressed as follows:

$$R = K a_A a_B \qquad [3]$$

where:

- R is the rate of reaction,
- K is the rate constant,
- $a_A$ is the activity of reactant A, and
- $a_B$ is the activity of reactant B.

The activation energy for the reaction is computed by solving equation [3] for $\Delta\mu$ using experimental data for reaction rates and concentrations. If the assumption is made that $\Delta\mu$ is independent of temperature over the temperature range existing in soil systems, identical values should be obtained for $\Delta\mu$ regardless of the data used in their determination. This criterion is being used as one means of testing the validity of the model.

In order to apply equation [3], activities must be determined for the reactants. Application of Debye-Huckel theory allows computation of activities of charged species (e.g., $NH_4^+$) in the soil solution. Activities of uncharged species (e.g., $O_2$) may be computed by application of the following relationship (Garrels et al., 1965):

$$\ln\gamma = K_m\mu \qquad [4]$$

where:

$\gamma$ is the activity coefficient,
$K_m$ is the salting coefficient, and
$\mu$ is the ionic strength of the soil solution.

*Experimental.* Nitrification rate data were obtained for two warm desert soils incubated at 15, 25, and 35°C and at moisture tensions of 0.3, 5 and 15 bars. Each soil was treated with 500 ppm $NH_4^+$-N added in the form of $NH_4Cl$, and preincubated for 3 weeks at 0.3 bars and 25°C. This procedure was done to insure that a maximal population of nitrifying organisms was established before collection of rate data began. At the end of three weeks, the soils were incubated at the above-mentioned temperatures and moistures, with duplicate samples being removed at two-week intervals. The samples were analyzed for $NH_4^+$-N and $NO_3^-$-N by extraction with $CO_2$-free water (1:6) followed by steam distillation with MgO and Devarda's alloy. Also, the pH values of the extracts were determined at this time. The exchangeable $NH_4^+$-N in each sample was computed using a computer subroutine of Dutt (Dutt et al., in press).

## FINDINGS & DISCUSSION

### Page Ranch Simulation Study

Input requirements of the previously developed model have been described by the principal investigator and colleagues (Dutt et al., in press). In order to obtain input data which was not available from the dissertation of Billy (1970), soil samples were taken at three depths from the Page Ranch site. The results of the chemical and physical analyses performed on these samples are shown in Tables 1 and 2.

Mathematical expressions relating the soil moisture diffusivity (D) and pressure head (h) to volumetric moisture content ($\theta$) are necessary in that portion of the model which describes the infiltration redistribution and plant withdrawal of soil water under growing vegetation. To obtain these relationships, retentivity measurements were performed in triplicate on core and disturbed samples taken from the three depths according to methods described in the literature (Black, 1965). The relationships shown in Figures 1, 2, and 3 between pressure head and moisture content, ignoring hysteresis, were obtained by interpolation of the experimental determinations in Table 2. Laboratory measurements of the saturated hydraulic conductivities determined by the constand head method (Black, 1965) are also shown in Table 2 for each of the three depths.

Table 1. Initial Soil Chemical Analysis of Whitehouse loam from Page Ranch Site.

| Depth | $NH_4^+$ | $NO_3^-$ | $Ca^{++}$ | $Mg^{++}$ | $Na^{++}$ | $HCO_3^-$ | $CO_3^=$ | $Cl^-$ | $SO_4^=$ | C.E.C. | Organic Matter | C/N Ratio |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CM | | | | meq/l | | | | | | meq/100 gm | ug/gm | |
| 0-7.62 | 0.00 | 0.113 | 2.40 | 1.00 | 0.390 | 3.60 | 0.00 | 5.64 | 5.83 | 6.45 | $1.53 \cdot 10^4$ | 13.6 |
| 7.62-21.6 | 0.00 | 0.129 | 3.80 | 1.40 | 1.52 | 4.80 | 0.00 | 8.46 | 4.17 | 7.74 | $1.07 \cdot 10^4$ | 13.0 |
| 21.6-38.1 | 0.833 | 0.0968 | 2.20 | 3.60 | 4.61 | 5.60 | 0.00 | 8.46 | 5.83 | 31.5 | $1.52 \cdot 10^4$ | 9.68 |
| 38.1-48.3 | 0.00 | 0.121 | 2.20 | 1.00 | 5.70 | 6.80 | 0.00 | 8.46 | 5.83 | 21.1 | $7.77 \cdot 10^3$ | 8.86 |
| 48.3-78.7 | 0.00 | 0.121 | 2.80 | 1.40 | 8.91 | 3.40 | 0.00 | 14.0 | 8.33 | 18.1 | $4.49 \cdot 10^3$ | 8.57 |
| 78.7-107 | 0.00 | 0.113 | 4.20 | 2.80 | 16.7 | 3.80 | 0.00 | 16.9 | 10.8 | 16.5 | $3.50 \cdot 10^3$ | 10.0 |
| 107-112 | 0.00 | 0.121 | 3.40 | 1.80 | 16.4 | 4.80 | 0.00 | 14.1 | 12.5 | 13.2 | $3.75 \cdot 10^3$ | 15.0 |
| 112-122 | 0.00 | 0.113 | 2.40 | 0.40 | 12.6 | 4.80 | 0.00 | 11.3 | 9.16 | 9.36 | $2.51 \cdot 10^3$ | 15.9 |

Table 2. Physical Properties of Whitehouse loam from Page Ranch Site.

| Depth | Bulk Density | K Sat'd | Volumetric Moisture Contents ($cm^3/cm^3$) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Pressure (cm $H_2O$) | | | | | | | |
| (cm) | ($gm/cm^3$) | (cm/min) | Sat'd Paste | $5.09 \times 10^1$ | $1.02 \times 10^2$ | $2.04 \times 10^2$ | $3.36 \times 10^2$ | $2.10 \times 10^3$ | $5.26 \times 10^3$ | $1.03 \times 10^4$ | $1.54 \times 10^4$ |
| 3.0-8.5 | 1.81 | $1.52 \times 10^{-4}$ | .3194 | .2099 | .1724 | .1527 | .1409 | .1218 | .0971 | .0971 | .0801 |
| 8.5-15 | 1.26 | $2.32 \times 10^{-6}$ | .5242 | .4057 | .3880 | .3711 | .3509 | --- | .3005 | .2822 | .2580 |
| 15-19 | 1.45 | $2.37 \times 10^{-5}$ | .4515 | .3060 | .2930 | .2860 | .2712 | --- | .2599 | .2456 | .2267 |

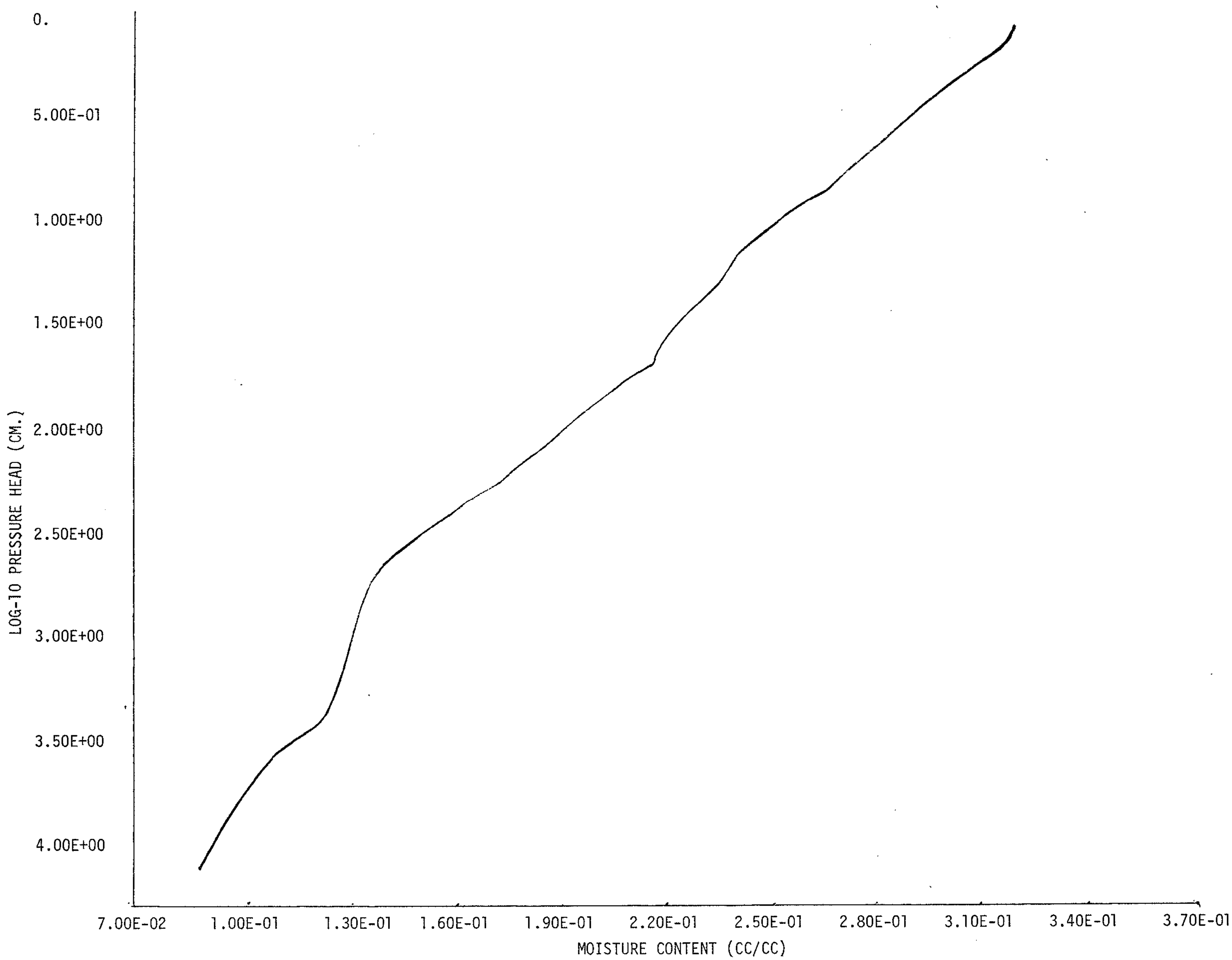


Figure 1. Whitehouse loam, 3.0-8.5 CM.

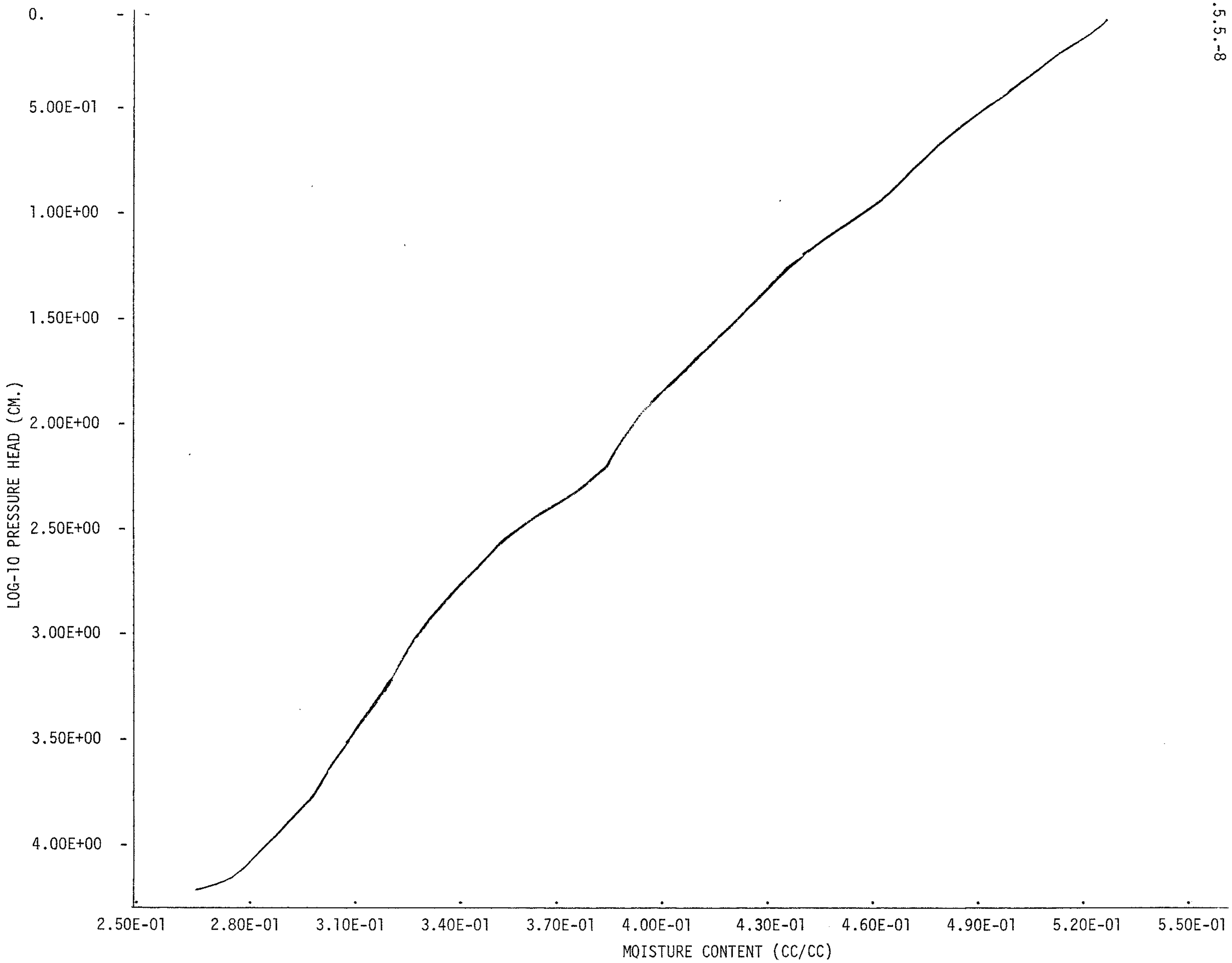


Figure 2. Whitehouse loam, 8.5-15.0 CM.

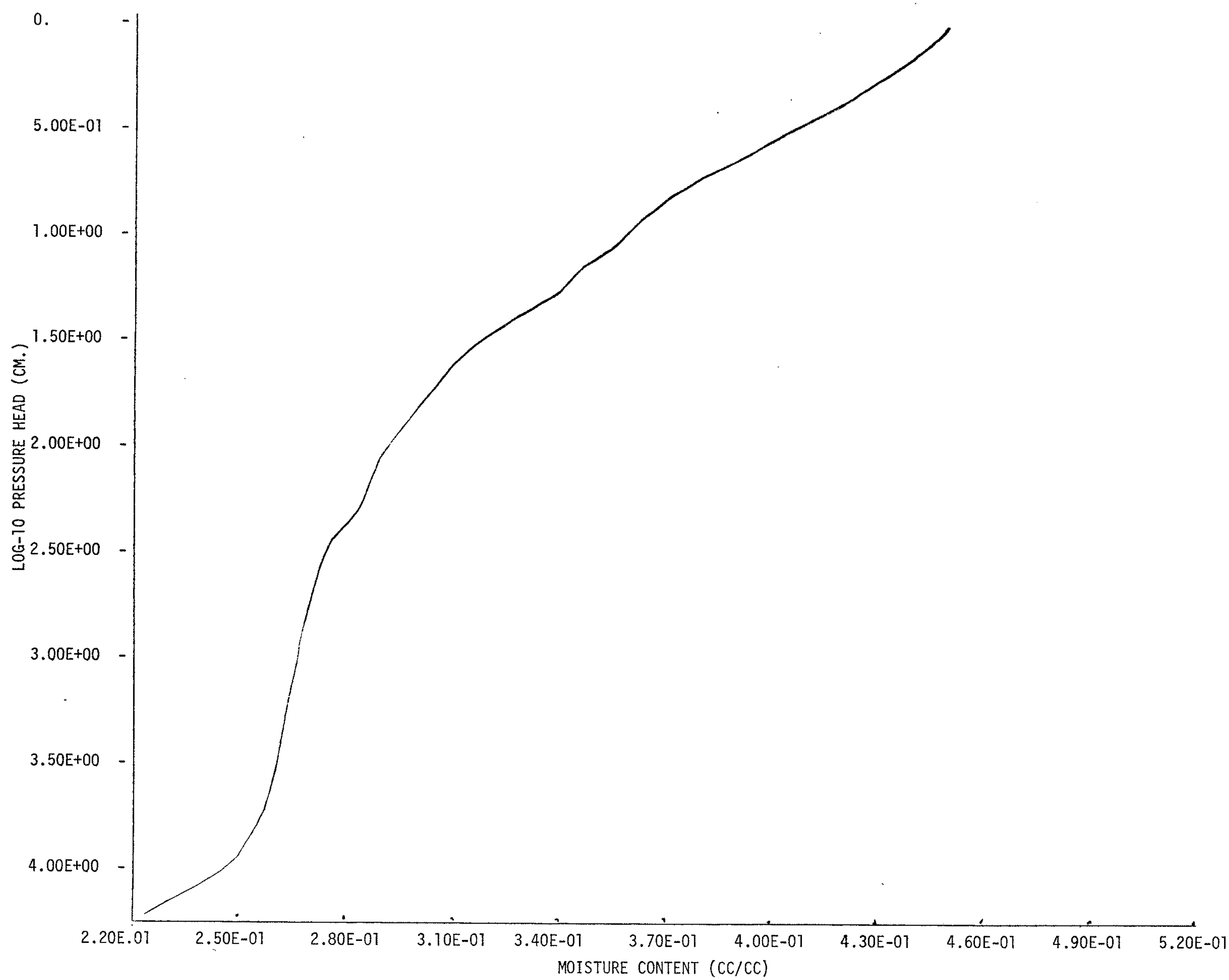


Figure 3. Whitehouse loam, 15.0-19.0 CM.

From the above data and the modified Millington-Quirk equation presented by Stockton and Warrick (1971), unsaturated hydraulic conductivity values were estimated for each of the three depths over the pressure range from 0 to 15 bars. These relationships are shown in Figures 4, 5, and 6.

The rates of soil moisture removal over the growing season by the roots of growing vegetation and evaporation from the soil surface are other inputs that are required to predict the moisture regime under field conditions. Field determinations of the evapotranspiration rate from Boer lovegrass at the University of Arizona Mesa Experimental Farm (Erie et al., 1968) were selected to approximate the rates expected at the Page Ranch site (see Figure 7). Average effective root distribution for the composite native vegetation was approximated from the literature (Erie et al., 1968) with 0.75 of the extraction occurring in the top 12 inches of soil and 0.25 from 12-24 inch depth, as shown in Figure 7. Rainfall records for the period of June-October 1967 are shown in Table 3, but no temperature data from the Page Ranch site was available; instead, average monthly maximum and minimum temperatures from the Willow Springs Ranch, located approximately eight miles north of the Page Ranch site, will be utilized.

Table 3. Rainfall dates, Julian dates and amounts from June 20 to October 12, 1967, at Page Ranch Site.

| Date | Day Number | Amount (cm) |
|---|---|---|
| 6/20 | 171 | 5.80 |
| 7/3 | 184 | 0.61 |
| 7/10 | 191 | 0.15 |
| 7/12 | 193 | 1.12 |
| 7/22 | 203 | 0.38 |
| 8/5 | 217 | 3.17 |
| 8/7 | 219 | 0.51 |
| 8/14 | 226 | 2.16 |
| 8/17 | 229 | 1.52 |
| 8/18 | 230 | 0.05 |
| 8/19 | 231 | 1.17 |
| 8/29 | 241 | 2.79 |
| 9/6 | 249 | 0.51 |
| 9/13 | 256 | 0.51 |
| 9/25 | 268 | 1.52 |
| 10/12 | 285 | 3.94 |

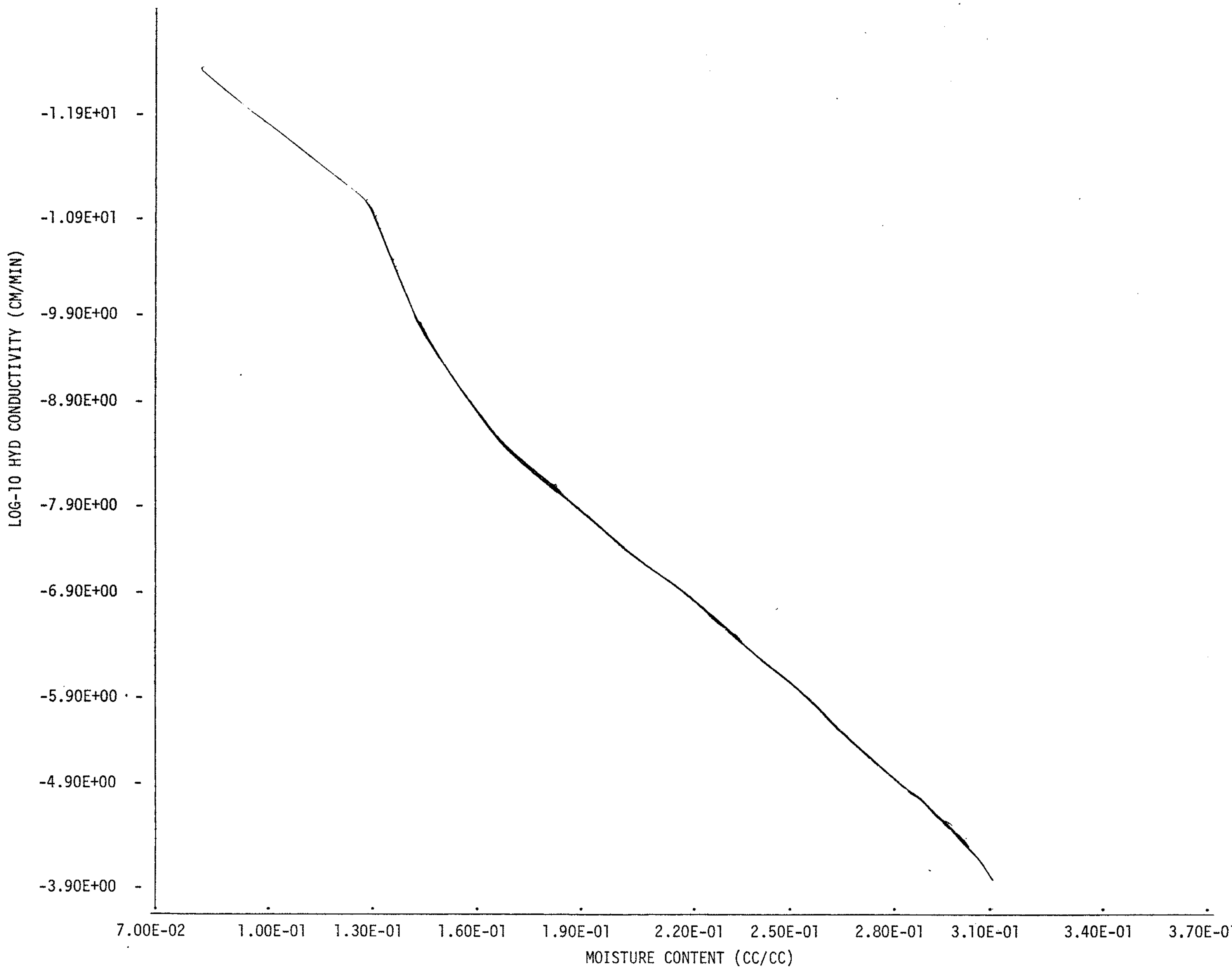


Figure 4. Whitehouse loam, 3.0-8.5 CM.

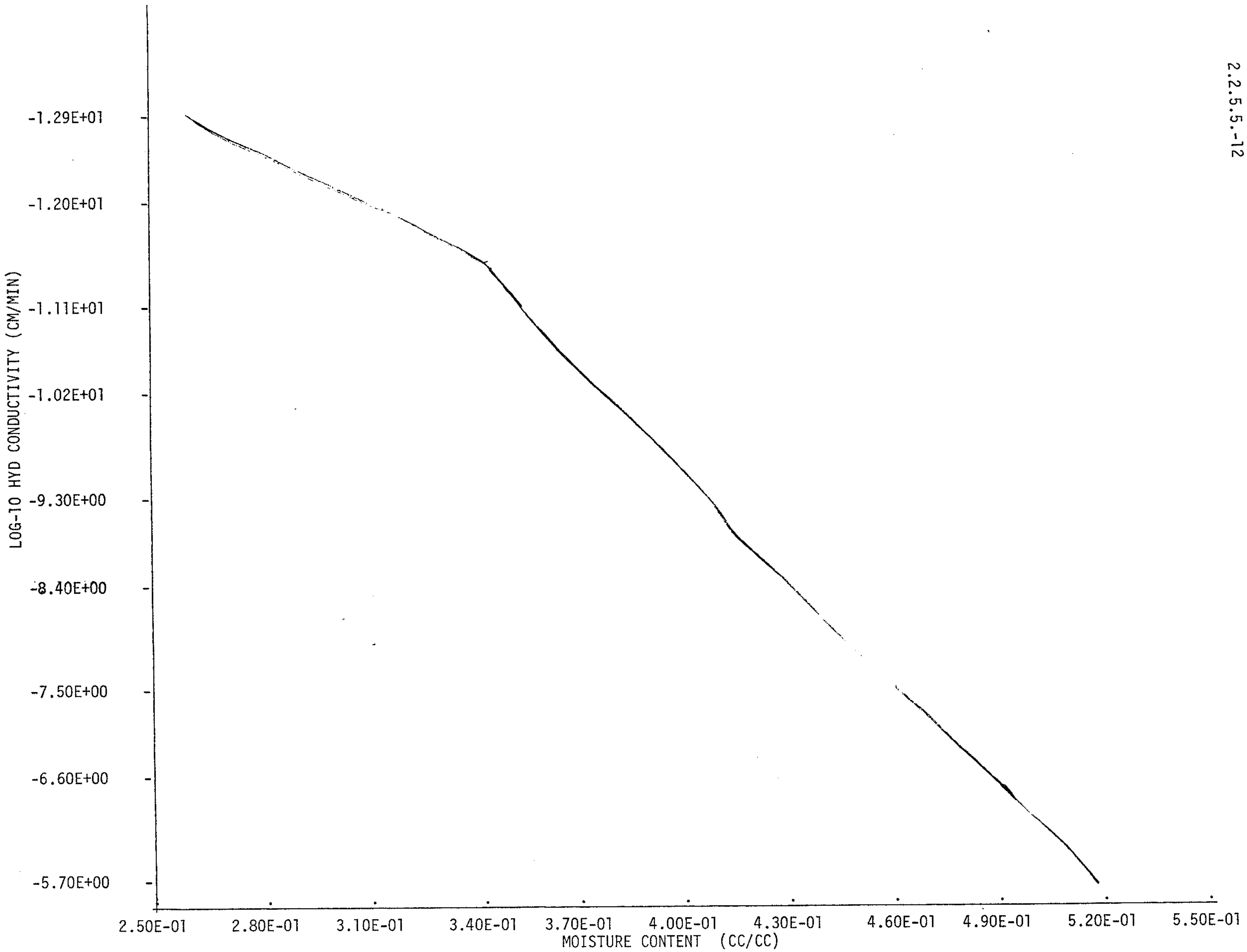


Figure 5. Whitehouse loam, 8.5-15.0 CM.

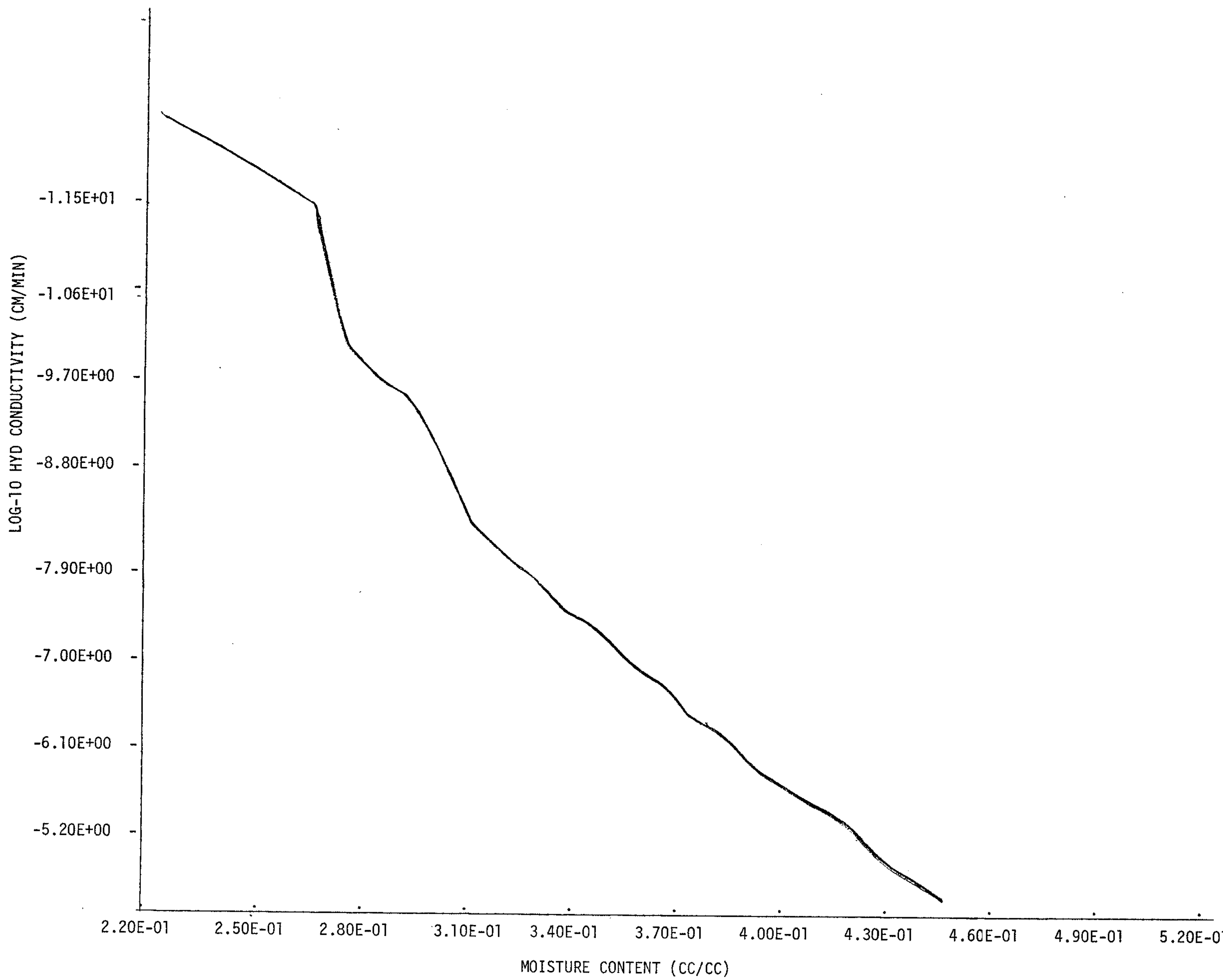


Figure 6. Whitehouse loam, 15.0-19-0 CM.

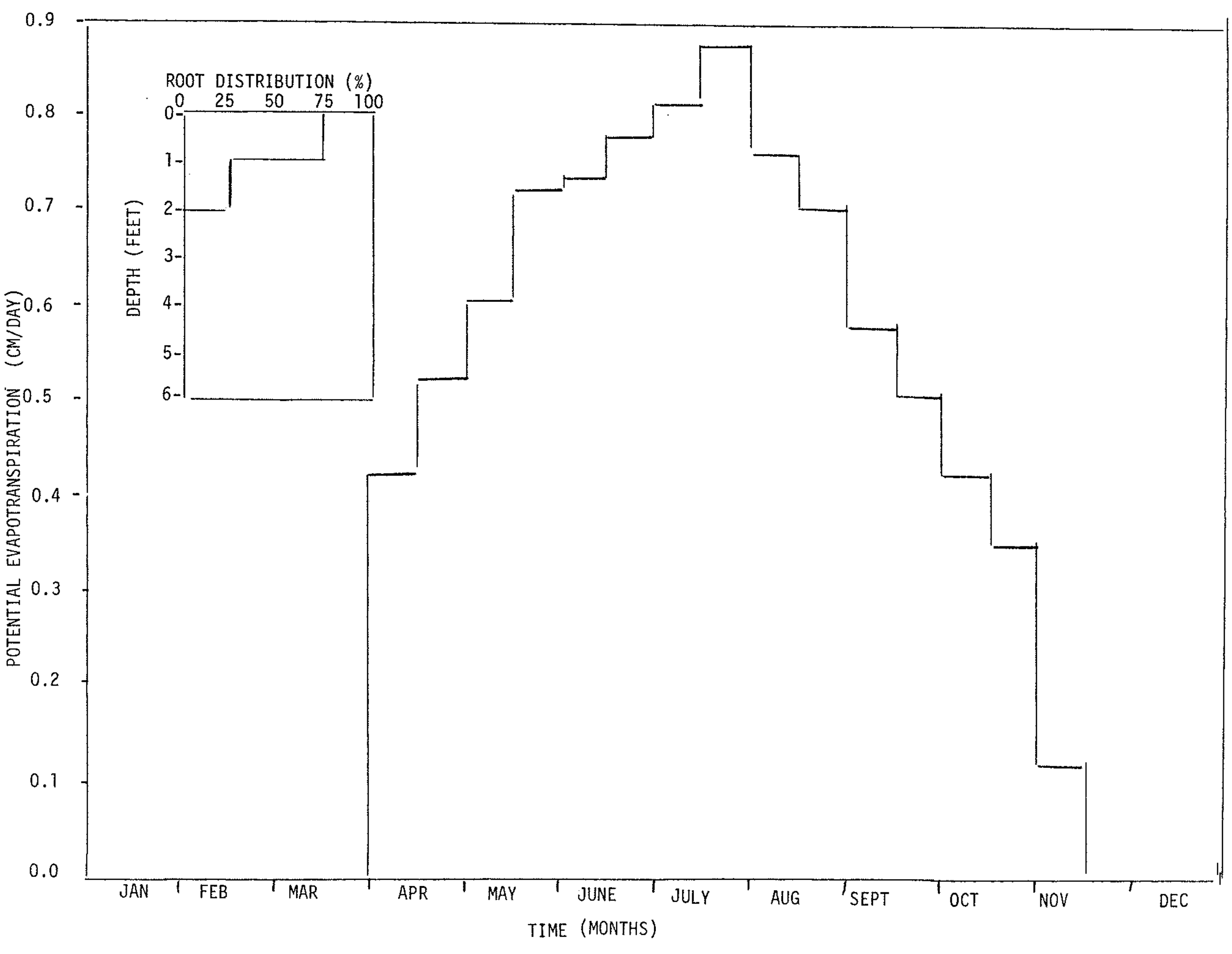


Figure 7. Field determinations of the evapotranspiration rate from Boer lovegrass at the University of Arizona Mesa Experimental farm (Erie et al., 1968), selected to approximate rates expected at the Page Ranch site.

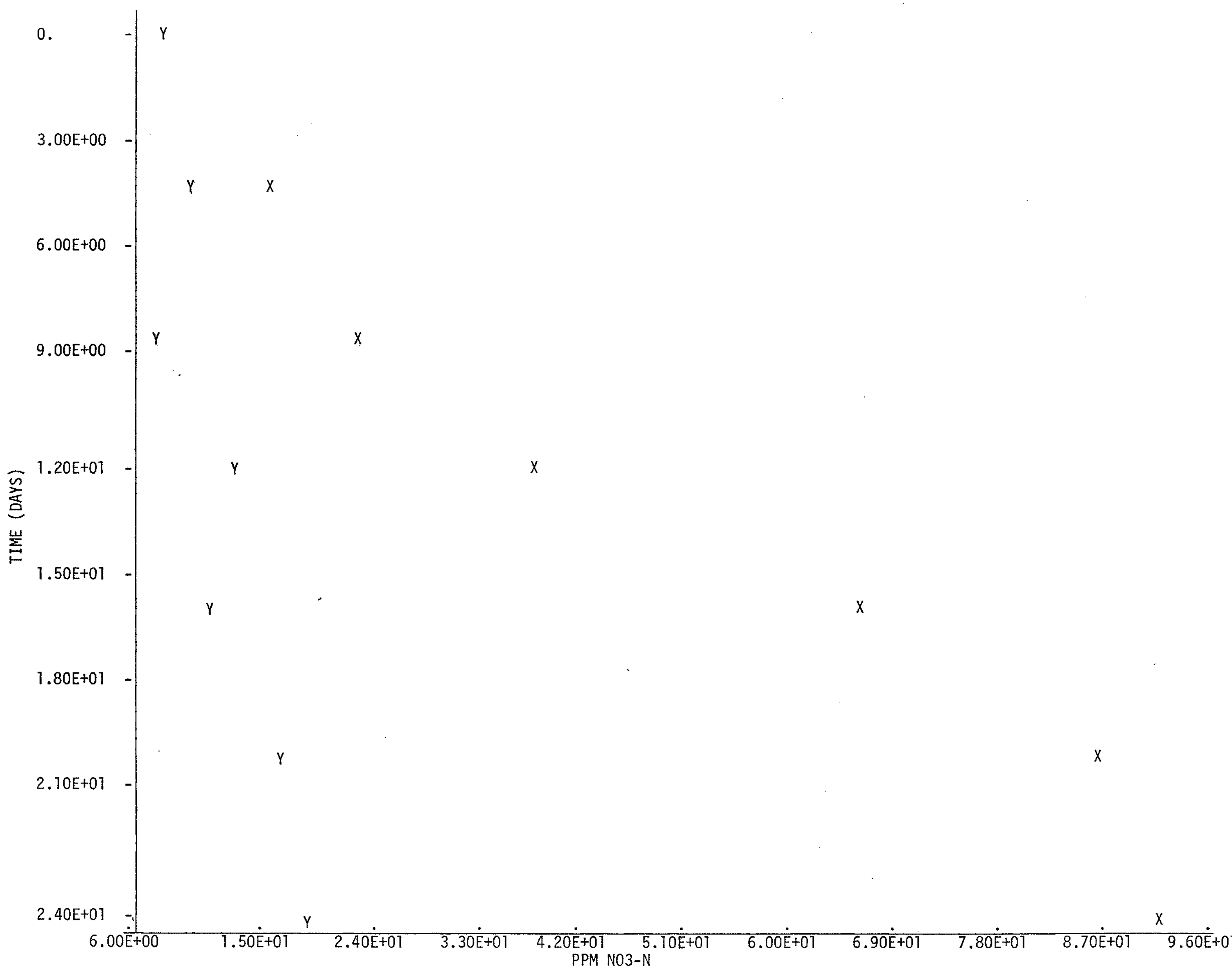


Figure 8. Time vs. PPM NO3-N (X=SOIL 1, Y=SOIL 2)

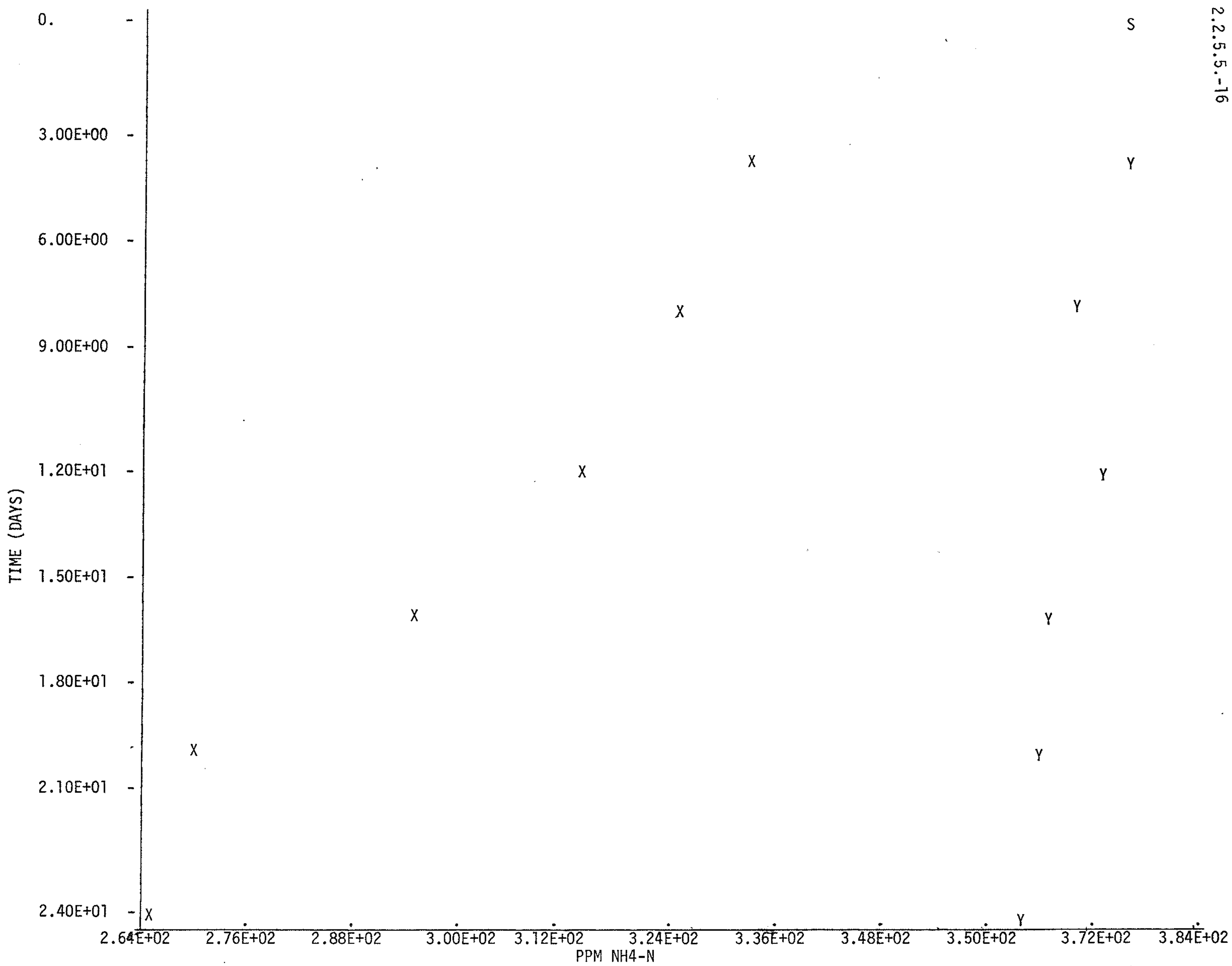


Figure 9. TIME VS. PPM NH4-N (X=SOIL 1, Y=SOIL 2).

The portion of the model which predicts the moisture regime independently of chemical and biological changes in the system was designed to predict the one-dimensional, unsteady, infiltration, redistribution, plant root extraction, and drainage of soil water in homogeneous, isotropic, isothermal, non-hysteretic soils from the surface to an unfluctuating water table. Although this model was developed with additional capabilities which make it useful for certain other unsaturated moisture flow problems (Dutt et al., in press), these capabilities have not been tested and verified. Difficulty was encountered with the accuracy of the finite difference approximation to the moisture flow equation, sink term included, during periods when infiltration would be predicted to occur for periods more than 12 hours. The reasons for this behavior can only be hypothesized at this time; i.e., inaccuracy caused by extremely low-valued diffusivity and conductivity relationships, large moisture extraction (sink) term, and wide range in moisture contents between adjacent nodes due to the above factors which could no longer be self-correcting by the variable $\Delta t$ mechanism.

During the period when this problem was being studied, Dr. R.J. Hanks suggested using a similar model that he had previously developed which could simulate a two-layered soil. Because of the distinct layering of the soil at the Page Ranch site and the problems encountered by using the homogeneous model, it was decided that Dr. Hanks would utilize his model with the same inputs to simulate the moisture regime data. The nitrogen transformation and plant uptake portion of the model will be completed at the University of Arizona when the unsaturated moisture flow data are received from Dr. Hanks.

Figures 8 and 9 contain plots of $NO_3^-$-N and $NH_4^+$-N versus time for soil samples taken from two warm desert soils, fertilized with 400 ppm $NH_4^+$-N, and incubated at 25°C and 0.3 bar moisture tension. Note the difference in nitrification rates for the two soils. The initial pH of soil 1 was 7.3, while soil 2 showed a pH of 6.6. At the end of 24 days of incubation, soil 1 had a pH of 6.7 and soil 2, 6.6. The inference may be made that pH is a factor involved in the rate differences obtained. The rates for both soils at the end of 24 days are at least an order of magnitude lower than those observed in some alkaline agricultural soils (Broadbent et al., 1957).

# EXPECTATIONS

The evaluation of the computer model regarding application to a desert biome model will be completed. A more sophisticated subroutine predicting nitrification rates will be completed and added to the model. Moisture movement data supplied by Dr. John Hanks will be used together with data included in this report to complete the Page Ranch Simulation study.

# LITERATURE CITED

Billy, Bahe. 1970. The effects of rates and dates of application of commercial fertilizers on four rangeland sites. Ph.D. Dissertation, University of Arizona, Tucson.

Black, Ca. A. (Ed.). 1965. Methods of Soil Analysis; Part 1, Physical and Mineralogical Properties, Including Statistics of Measurement and Sampling, Agronomy No. 9, Amer. Soc. of Agron., Madison.

Broadbent, F.E., Tyler, K.B., and Hill, G.M. 1957. Nitrification of ammoniacal fertilizer in some California soils, Hilgardia, Vol. 27(9):247-267.

Dutt, G.R., Shaffer, M.J. and Moore, W.J. Computer simulation model of dynamic bio-physicochemical processes in soils, Arizona Agr. Expt. Sta. Technical Bulletin No. 196, (in press).

Erie, L.J., French, O.F., and Harris, K. 1968. Consumptive use of water by crops in Arizona, Arizona Agr. Expt. Sta. Technical Bulletin No. 168.

Garrels, R.M. and Christ, C.L. 1965. Solutions, Minerals, and Equilibria, 1st ed., New York, Harper and Rowe.

Hill, T.L. 1960. An Introduction to Statistical Thermodynamics, 1st ed., New York, Addison-Wesley Publishing Company, Inc.

Stockton, J.G., and Warrick, A.W. 1971. "Spatial variability of unsaturated hydraulic conductivity", Soil Sci. Soc. Amer. Proc., Vol. 35:847-848.