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1972 PROGRESS REPORT

PREDICTING NITROGEN TRANSFORMATIONS AND AMMONIA VOLITALIZATION IN WARM DESERT SOILS

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ABSTRACT

A digital computer model predicting the nitrogen and salt content of soil water draining from irrigated agricultural soils has been completed and verified (Dutt et al., 1972). To further test this model and extend its usefulness, continued laboratory, field and computer research has been conducted.

An attempt was made to apply the model to simulated nitrogen transformations, nitrogen movement and plant uptake of N in a warm desert soil under range grass. For the site selected, a soil moisture model predicting water movement in layered soils was required to describe the soil textural parameters important in the infiltration and storage of plant-available moisture. With the moisture flow data as input, the Biological-Chemical Program predicted NO_3-N concentrations in the surface 10 cm of soil within experimental error of field-obtained values in the top 15 cm for a simulation period of 45-130 days. Difficulty in the 0-45 day period and the predicted concentration in the 0-15 cm depth was due to that portion of the model which predicts the net mineralization-immobilization rate and the breakdown of organic residues. Once the indicated modifications are made to this subroutine, the model is expected to be applicable to warm desert range grass systems, and may be further verified on data which is now available.

A laboratory study was performed to acquire data necessary to develop a digital computer subroutine compatible with the overall model which would predict losses of ammonia by volatilization from desert soils. Preliminary work verified that the experimental procedure selected for the data collection is sufficiently accurate to provide basic information necessary to develop this subroutine.

INTRODUCTION

Over the past ten years, the chief investigator has been working on computer models of soil-water systems. The U.S. Bureau of Reclamation, under contract agreement, financed the development of a systems analysis model for predicting nitrogen in irrigation drainage water. 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. 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.

OBJECTIVE

The 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-plant systems, to a warm desert ecosystem. If the model fails to duplicate the field observations, those observations, and others which could be readily made at the site, could then be used to indicate what portions of the computer model should be modified to enable its use under these input conditions.

METHODS

The Site*

The site selected to test the computer simulation model previously described in the literature by the principal investigator and colleagues (Dutt,et al., 1972) was on the Page-Trowbridge Experimental Ranch 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 called the Page Ranch site, is located in the NE ¼ of SW ¼, Section 27, Township 9S, Range 14E at an elevation of approximately 3580 feet. This site was the location of a range fertilization study conducted by Bahe Billy in 1967 and 1968 under the direction of Dr. J. L. Stroehlein (Billy, 1970).

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* Material in this section was extracted from Billy, 1970.

The Soil*

The soil at the Page Ranch site is an 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.

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 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	August 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.

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.

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

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-N and available PO_4-P were determined on these soil and plant samples.

Computer Simulation

The Page Ranch range fertilization study summarized above offered a unique opportunity to test the applicability of the soil-water-plant systems analysis model. This model has previously been verified in certain agricultural applications and it was hypothesized that it could produce reasonably accurate simulation of this native grass environment. If the model failed to duplicate the determinations made during the range fertilization study, those determinations, and others which could be readily made on this site, could then be used to indicate what portions of the computer model should be modified to enable its use in the prediction of the soil-water-plant system in desert environments.

From the outset, it was recognized that because of the sandy loam A horizon overlying a slowly permeable B horizon in the Whitehouse soil (both of which are important in the storage of plant-available moisture) the moisture flow part of the model would not be applicable. This computer program was developed to predict the moisture regime independently of the chemical and biological changes in the system by modelling the unsteady, one-dimensional infiltration, redistribution, plant root extraction, and drainage of soil water in homogeneous, isotopic, nonhysteretic soils. Dr. R. J. Hanks made available a soil moisture model he had previously developed which is capable of predicting similar parameters in layered soils and also adapted laboratory data and data from the range grass study to meet the input requirements of his model. The model supplied by Dr. Hanks was then executed and its output (on magnetic tape) utilized as input data to the Biological-Chemical Model.

RESULTS AND DISCUSSION

Inputs

Input requirements of the computer model have been described by the principal investigator and colleagues (Dutt et al., 1972), and those which are required by the soil moisture model of Dr. Hanks are similar to those normally needed. In order to obtain input data which was not available from the dissertation of Billy or other literature, soil samples were taken at several depths at the Page Ranch site. At the location where these samples were taken, the A horizon, although quite close to sandy loam as reported by Billy, was actually loam in texture (see Table 1).

Table 1. Initial soil chemical analysis of Whitehouse loam from Page Ranch site

Depth cm	NH_4^+	NO_3^-	Ca^{++}	Mg^{++}	Na^{++}	HCO_3^-	$CO_3^=$	Cl^-	$SO_4^=$	C.E.C. meq/ 100 gm	Organic Matter µg/gm	C/N Ratio
	meq/l											
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

Mathematical functions or tables relating the pressure head (h) and unsaturated hydraulic conductivity (K) to volumetric moisture content (Θ) are necessary in that portion of the overall model which describes the infiltration, redistribution, evaporation, and root plant withdrawal of soil moisture under growing vegetation. To obtain these relationships retentivity measurements were performed in triplicate on disturbed or core samples (when possible) from 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 were obtained by interpolation of the experimental results of Table 2.

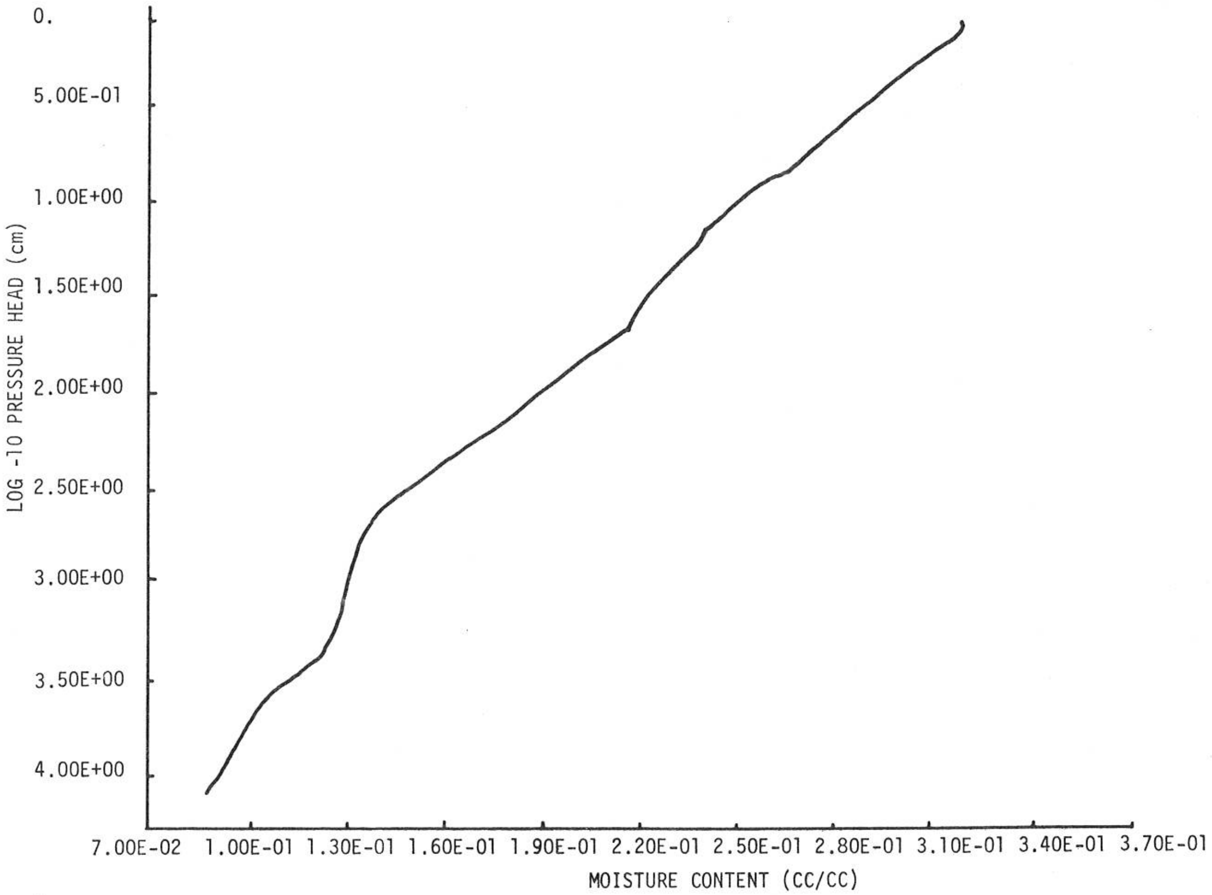

Figure 1. Whitehouse loam, 3.0-85 cm.

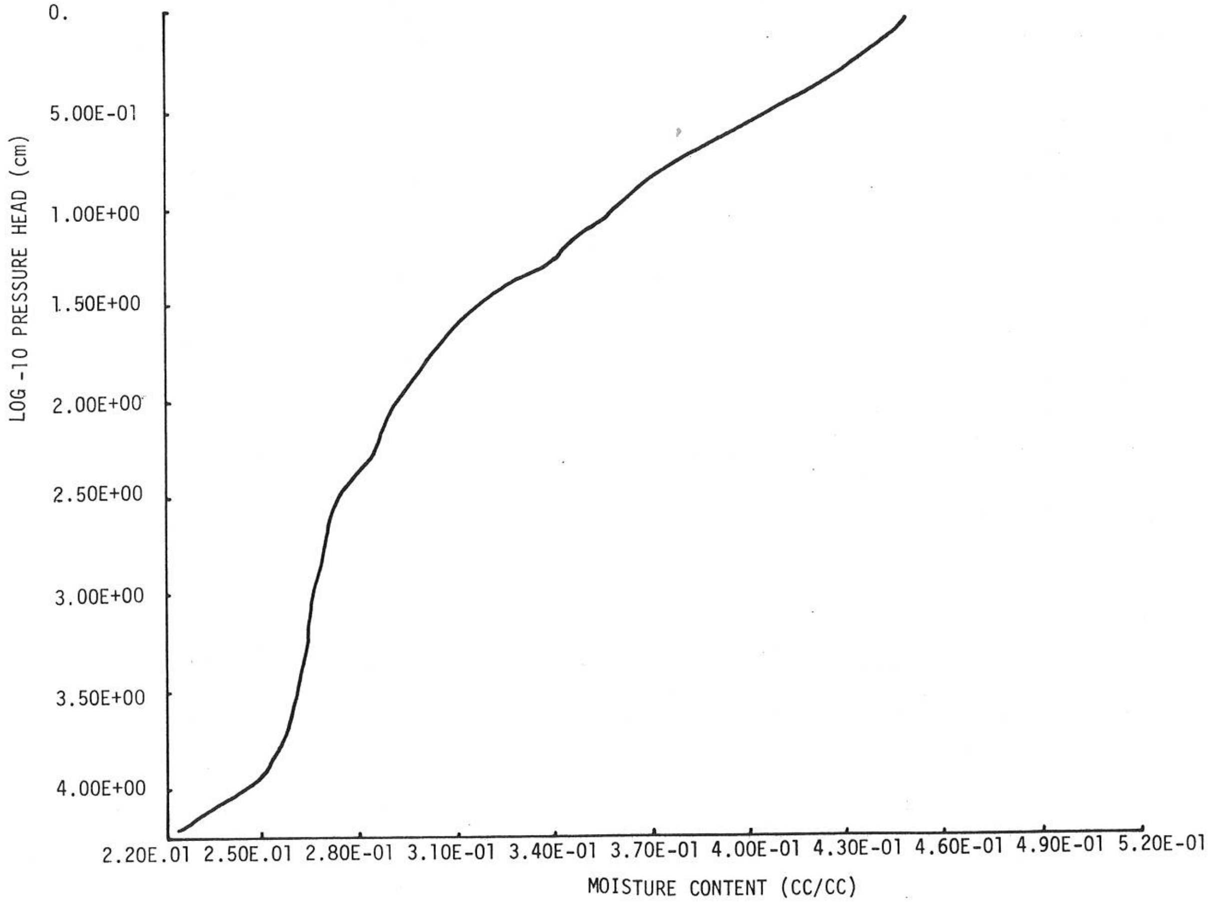

Figure 3. Whitehouse loam, 15.0-19.0 cm.

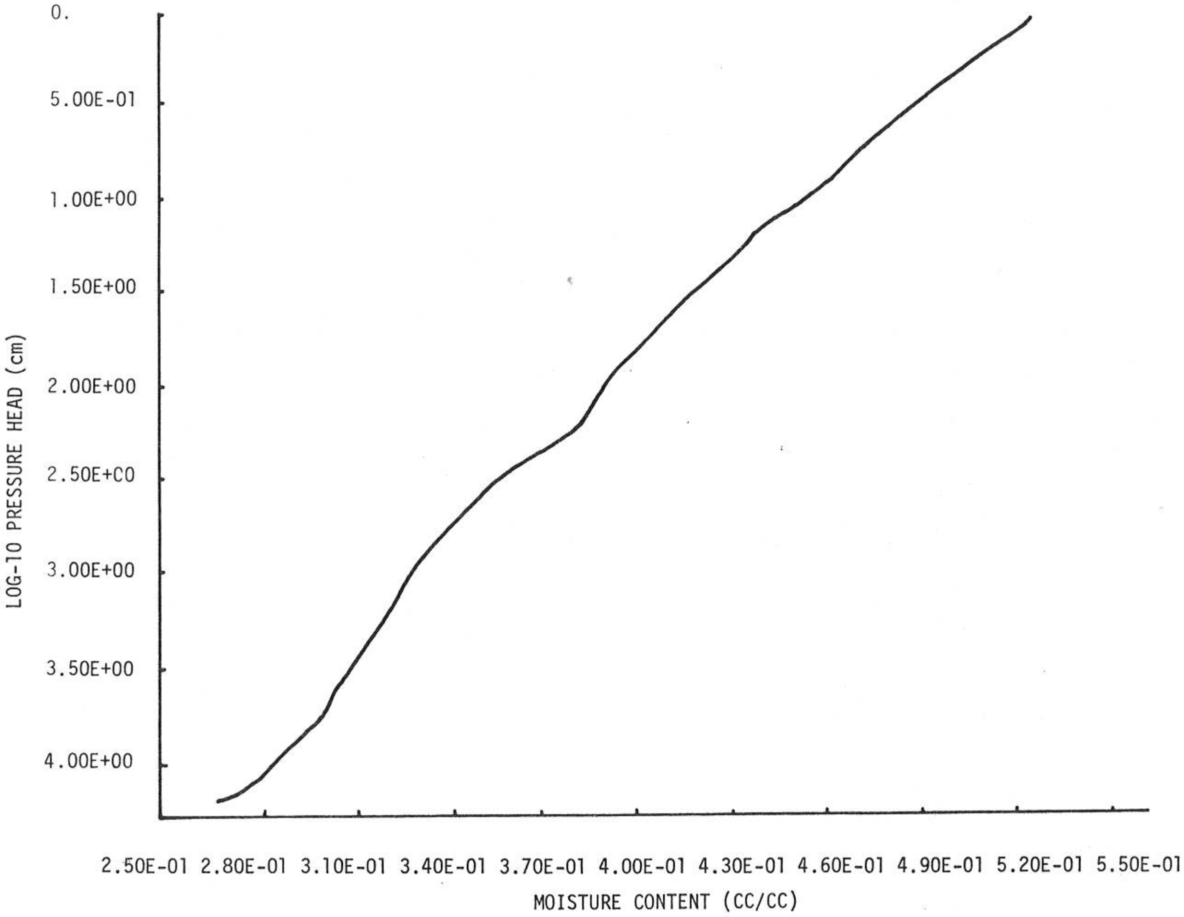

Figure 2. Whitehouse loam, 8.5-15.0 cm.

Table 2. Physical properties of Whitehouse loam from Page Ranch site

				Volumetric Moisture Contents (cm^3/cm^3)							
				Pressure (cm H_2O)							
Depth (cm)	Bulk Density (gm/cm^3)	$K_{Sat'd}$ (cm/min)	Sat'd	5.09×10^1	1.02×10^2	2.04×10^2	3.36×10^2	2.10×10^3	5.26×10^3	1.03×10^4	1.54×10^4
3.0-8.5	1.81	1.52×10^{-4}	.3194	.2099	.1724	.1527	.1409	.1218	.097	.0971	.0801
8.5-15	1.26	2.32×10^{-6}	.5242	.4057	.3880	.3711	.3509	--	.3005	.2822	.2580
15-19	1.45	2.37×10^{-5}	.4515	.3060	.2930	.2860	.2712	--	.2599	.2456	.2267

Laboratory measurements of the saturated hydraulic conductivities determined by the constant head method (Black, 1965) are also shown in Table 2 for each of the three depths. From this data and the modified Millington-Quirk equation (Stockton and Warrick, 1971), unsaturated hydraulic conductivity values were estimated for each of the three depths over the pressure range from 0-15 bars. These relationships are shown in Figures 4, 5 and 6.

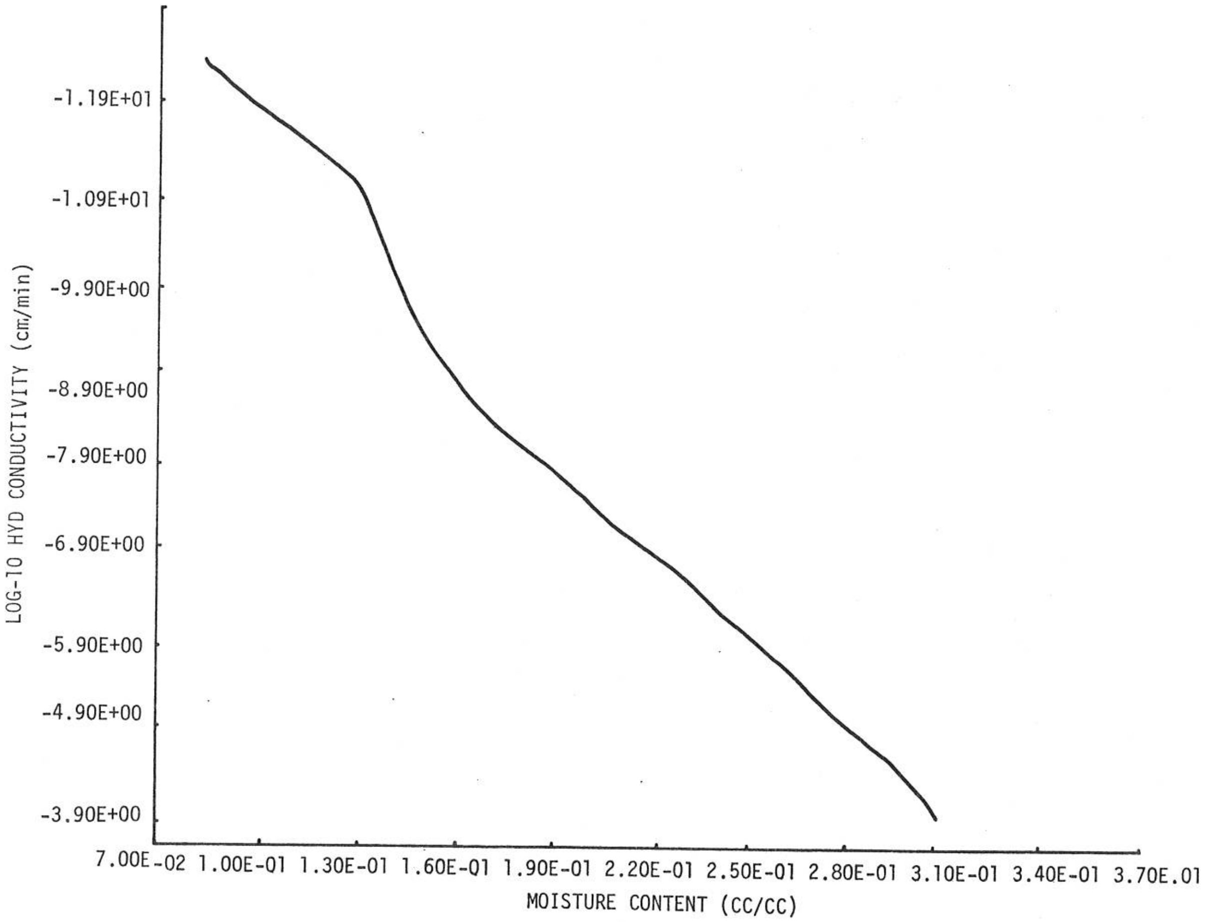

Figure 4. Whitehouse loam, 3.0-5 cm.

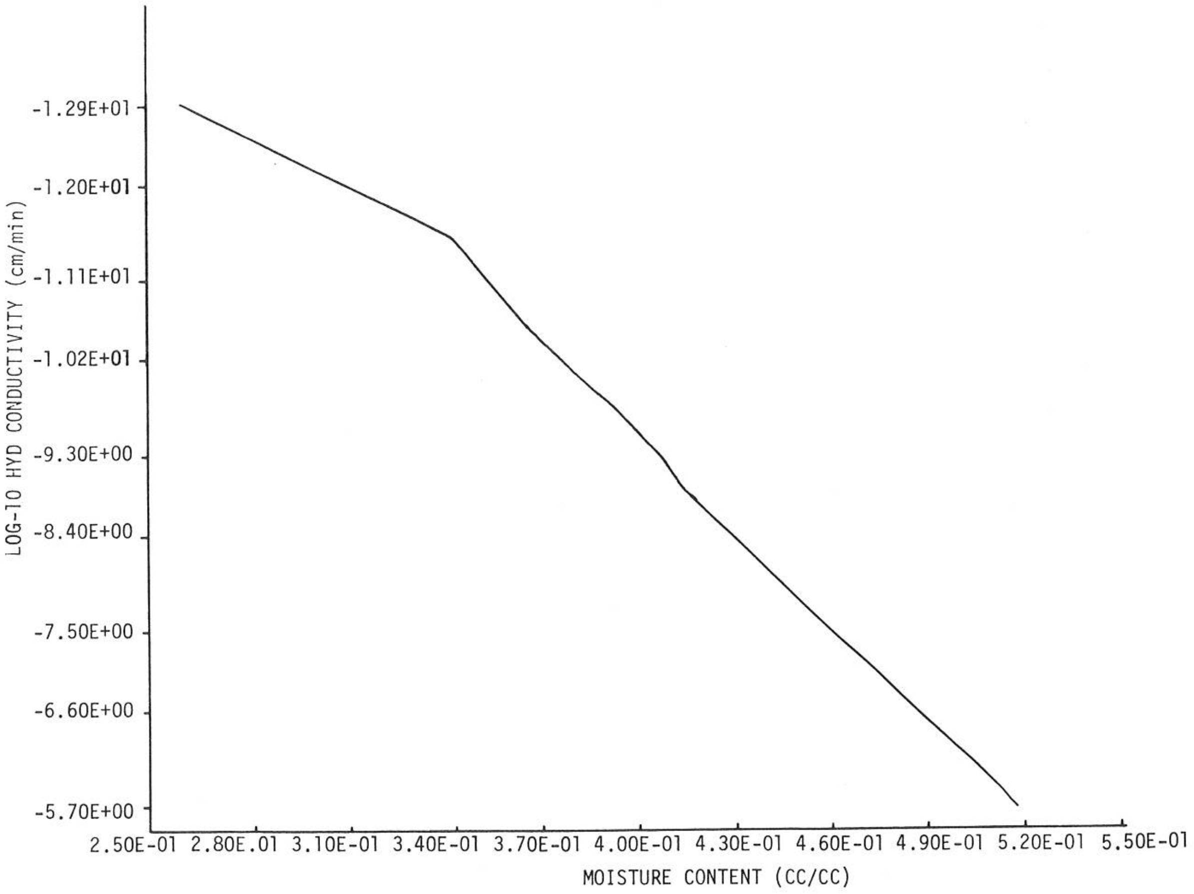

Figure 5. Whitehouse loam, 8.5-15.0 cm.

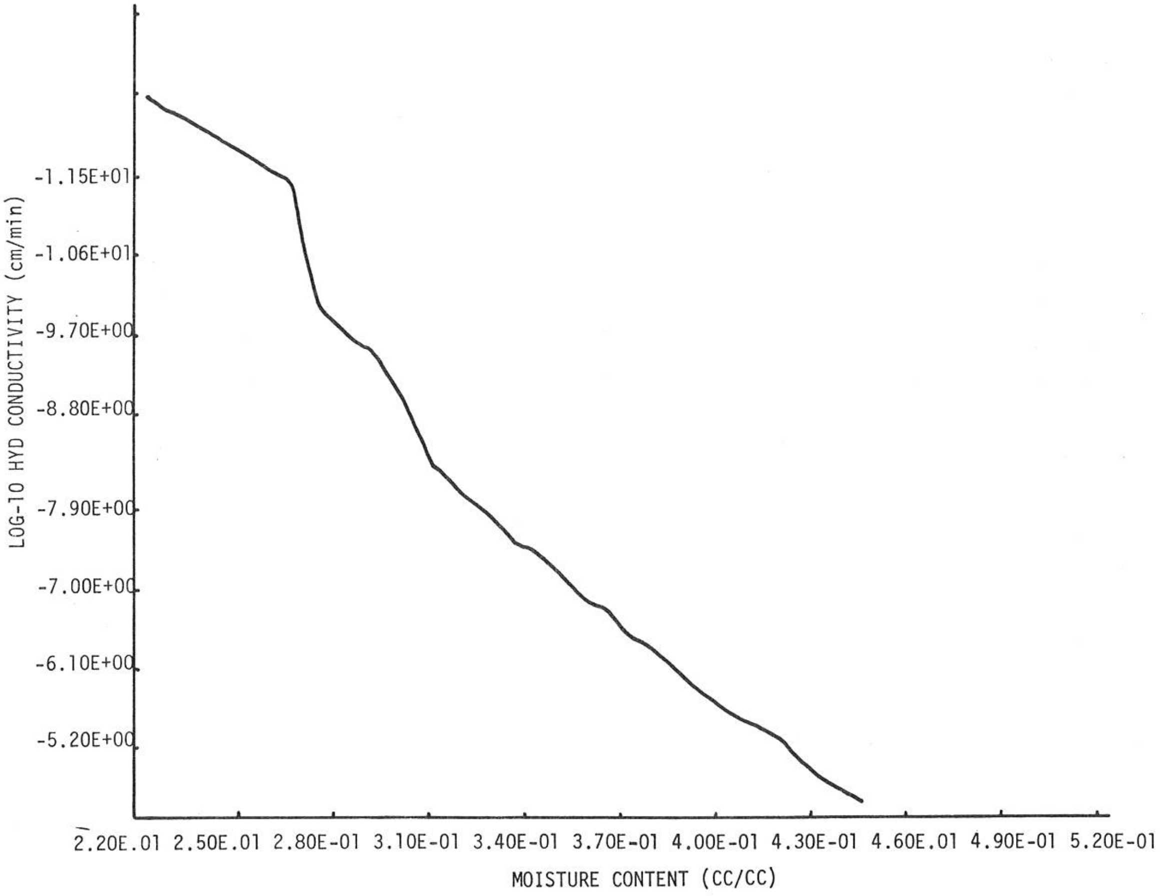

Figure 6. Whitehouse loam, 15.0-19.0 cm.

The maximum or "potential" 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 blue panicum grass at the University of Arizona Mesa Experimental Farm (Erie et al., 1968) were selected to approximate the "potential" rate of plant root extraction expected at the Page Ranch site (see Figure 7). Average effective root distribution for the composite native vegetation was approximated so that 0.75 of the extraction would occur in the top 30.5 cm of soil and 0.25 from 30.5-61 cm depth, as shown in Figure 7. Rainfall records for the period of June - October, 1967, were available and utilized, but no temperature data from the Page Ranch site were recorded. Instead, average monthly maximum and minimum temperatures from the Willow Springs Ranch, located approximately eight miles north of the Page Ranch site, were utilized.

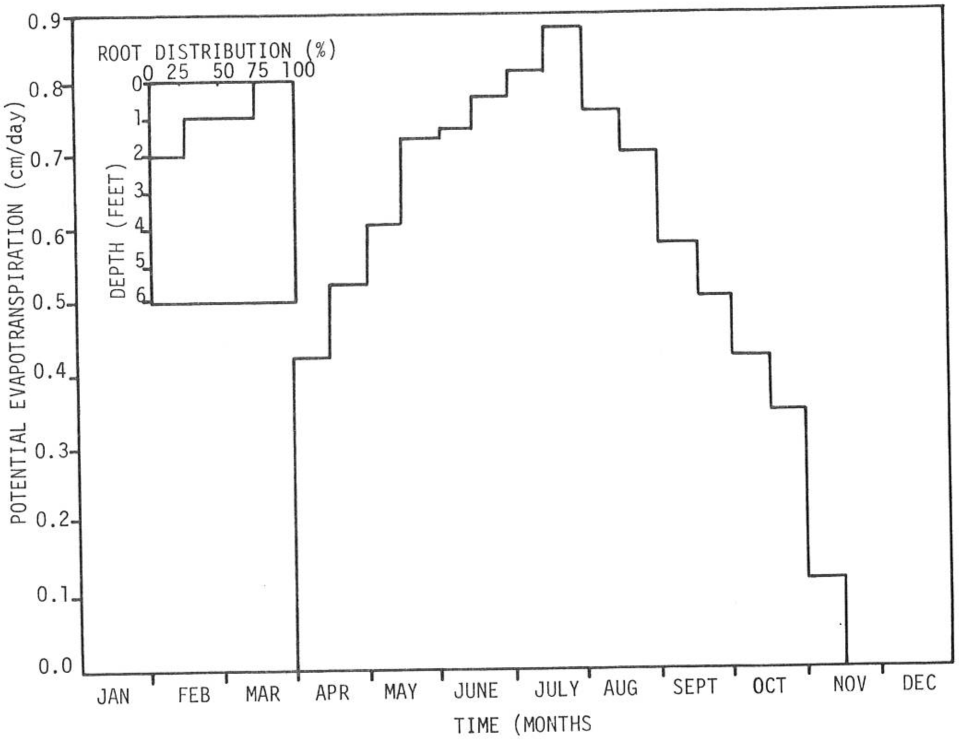

Figure 7. Field determinations of the evapotranspiration rate from blue panicum grass at The University of Arizona Mesa Experimental Farm (Erie et al., 1968) selected to approximate the maximum rates allowable at the Page Ranch site.

Assumptions

For the purpose of reducing computer execution time, the spatial unit for modelling purposes was considered to be a one cm^2 area of soil along a vertical flow line from the surface to a depth of 50 cm. Further, only one textural change, occurring at 16 cm, was considered. Four distinct horizons (each composed of several Δx segments) were visualized to represent the initial chemical composition of the profile. A zero flux boundary condition was assumed at 50 cm and a variable flux (for evaporation) or head (for infiltration) boundary assumed at the soil surface.

Due to the low hydraulic conductivity values of the soil, it was assumed that rainfall rate would exceed the infiltration rate of the soil, resulting in ponding of water at each rainfall. This assumption causes the precipitation from each rainfall to be highly dependent on the length of time the water is ponded on the soil surface, so that this length of time can be utilized to characterize each rainfall. The date, day number, length of time free water was available at the soil surface to infiltrate, and predicted infiltration values, are shown in Table 3.

Table 3. Day number, date, duration, and predicted infiltration of each rainfall from June 20, 1967 (DAY = 0) through October 27, 1967 (DAY = 130)

Rainfall		Duration* (day)	Infiltration (cm)
Date	Day No.		
6/20/67	0	1.00	3.67
7/3/67	13	0.12	0.46
7/10/67	20	0.02	0.09
7/12/67	22	0.22	1.18
7/22/67	32	0.07	0.37
8/5/67	46	0.62	3.16
8/7/67	48	0.10	0.51
8/14/67	55	0.43	2.26
8/17/67	58	0.30	1.52
8/18/67	59	0.01	0.05
8/19/67	60	0.23	1.17
8/29/67	70	0.55	2.79
9/6/67	78	0.10	0.50
9/13/67	85	0.10	0.49
9/25/67	97	0.30	1.49
10/12/67	114	0.80	3.62
		TOTAL =	23.33

* Length of time free water is assumed present at soil surface.

The extremely low saturated hydraulic conductivity values measured in the laboratory were judged not to represent those of the soil *in situ*, probably because of shrink-swell and cracking characteristics which can be readily observed. These measured conductivities are used as scaling factors in the Millington-Quirk procedure to predict the hydraulic conductivity at any moisture content, $K = f(\Theta)$. Lack of faith in the accuracy of the laboratory procedure made it necessary to increase the value of $K_{sat'd}$ by a factor of 60 in the upper modelling horizon, and 600 in the less permeable lower horizon to more accurately represent field observations of the moisture intake rate. Addition of $\log_{10}60$ to the vertical scale of Figure 4 and $\log_{10}600$ in Figure 5 yields the conductivity values used in the upper and lower modelling horizons, respectively. The pressure head-moisture content relationships shown in Figures 1 and 2 are unchanged.

Further, it may be noted that in the range fertilization study by Billy, the fertilizer was applied on June 5, but in the computer simulation day 0 corresponds to June 20. This difference is due to the fact that no precipitation occurred at the site during the period from June 5-20 and that the model is incapable of predicting fertilizer input at the soil surface without accompanying infiltration. Since fertilizer applied by the model at June 5 would not enter the soil profile until day 15 due to the absence of precipitation, the starting day number was made to correspond to the date of the first rainfall after the application.

Computer Simulation

The Moisture Flow Program was executed for a period of 130 days and its output written on magnetic tape. Following a tape-tape data "interfacing" program, which is necessary to modify data formats (Dutt et al., 1972), the predicted soil-water characteristics were utilized as input data to the Biological-Chemical Program and the latter executed for the same time period. Output from both submodels may then be used to characterize the conditions predicted for the Page Ranch site from June 20, 1967, to October 27, 1967.

Table 3 may be re-examined to observe the infiltration predicted to occur from each of the 16 rainfalls during the simulation period. Total infiltration predicted was 23.3 cm (9.12 in.) which compares favorably with the 26.3 cm (10.4 in.) of precipitation observed from June through October due to the permeable sandy loam or loam surface horizon.

The relationship between infiltration and evapotranspiration (moisture storage) is shown in Figure 8. Each of the peaks corresponds with a rainfall (increase in moisture storage in the profile). Portions of the graph with negative slopes are due to evapotranspiration loss of soil moisture (decrease in storage). The progressive decrease in negative slope between moisture applications is due mainly to drying of the A horizon, resulting in decreased evapotranspiration rates as moisture becomes

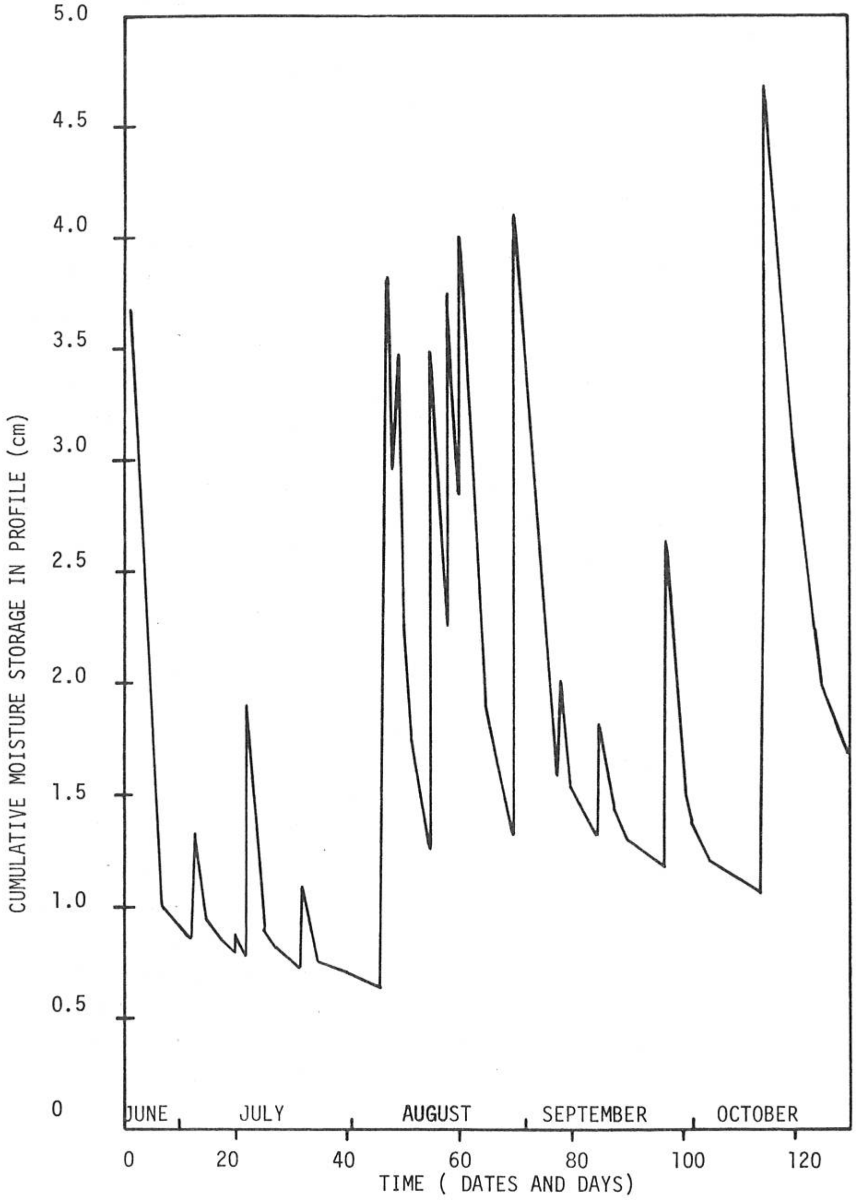

Figure 8. Cumulative moisture storage versus time in dates and days for the simulation period. Cumulative moisture storage = 0 at day 0 (June 20).

less available to plants in that zone. At all times following the first rainfall, total water in the Whitehouse profile exceeded that which it contained initially, although the surface frequently reached its air dry moisture content. This anticipated observation, caused by increased storage in the heavy B horizon, as shown in Figure 9, was responsible for the availability of some soil moisture to the vegetation throughout the 130-day period. Total evaporation from the soil surface was about 4.7 cm and total plant uptake was 16.9 cm of soil moisture.

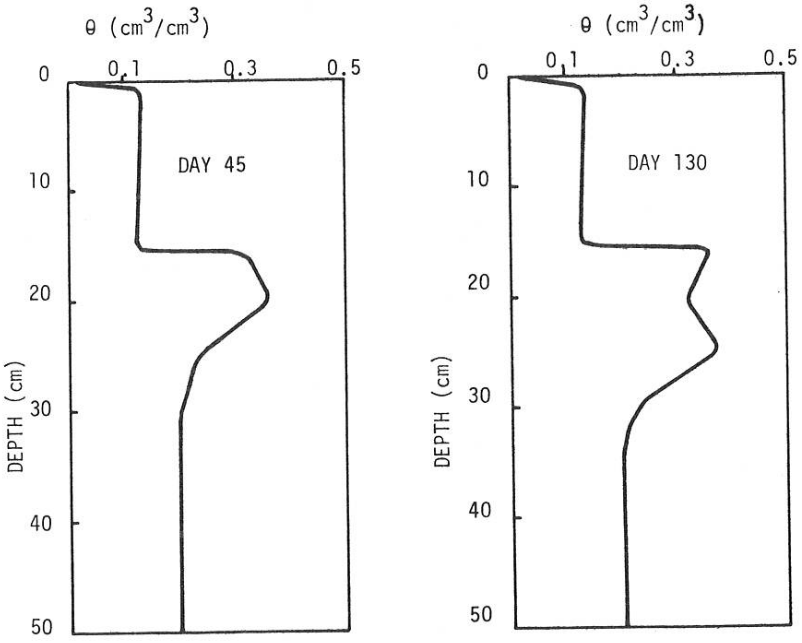

Figure 9. Moisture profiles in Whitehouse loam at day 45 and day 130 showing increased moisture in the heavy textured B horizon (16-50cm).

The effect of available soil water on the transpiration rate may be observed from Figure 10, in which cumulative moisture uptake is plotted for the 130-day period. The greatest transpiration rates (i.e., greatest slopes) occurred from August through October, in spite of the highest "potential" transpiration occurring in July (Figure 7), because of the increase in available soil water stored in the B horizon. It may be noted that although potential transpiration and rainfall were higher in July than in September (Figure 7, Table 3), the transpiration predicted in July was only 1/3 that for September (Figure 10). The total "potential" transpiration for the 130-day period was about 80 cm, while only about 20% was actually predicted to be available to the vegetation.

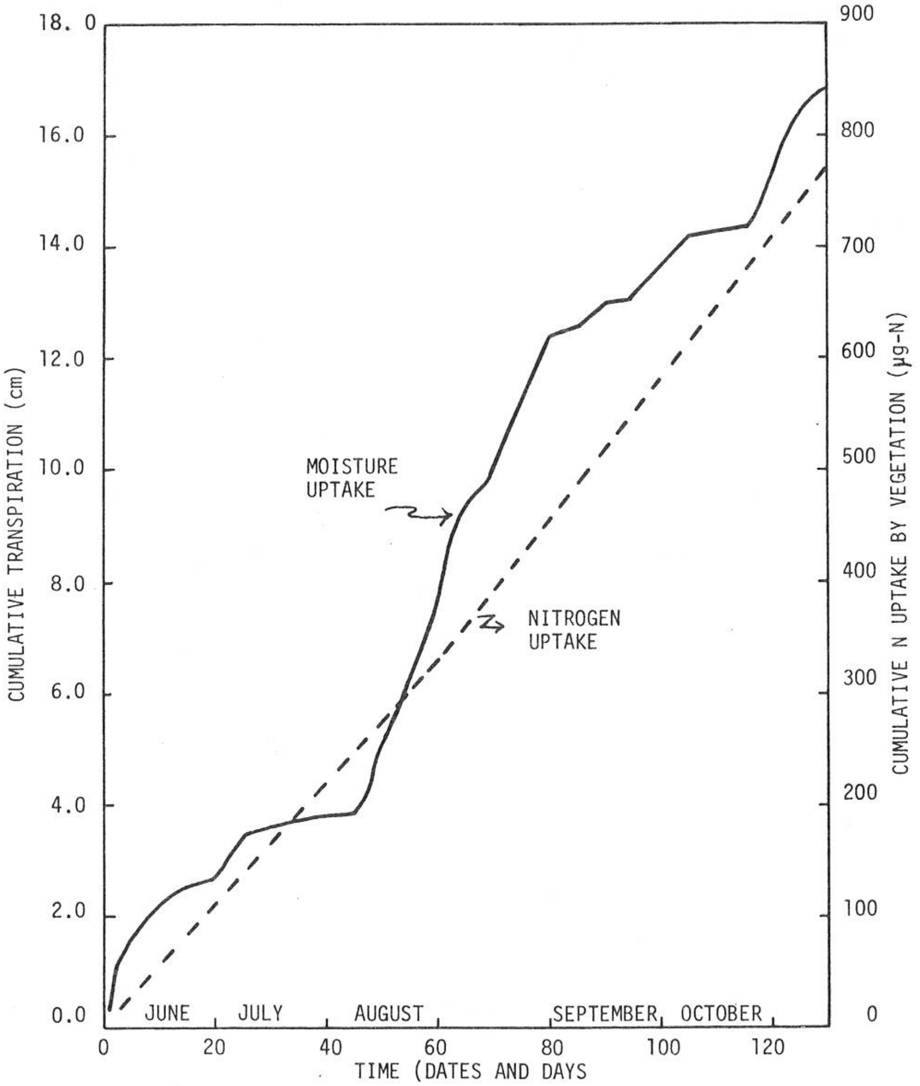

Figure 10. Cumulative transpiration (cm of H_2O) and cumulative nitrogen uptake (µg NO_3^--N) by the vegetation for the 130-day period of simulation. $r^2 = 0.966$.

Estimates of the nitrogen uptake rate by the growing vegetation were obtained from the plant-N analyses performed on August 19 and October 12 by Billy. These estimated rates were 6.07 μg NO_3-N/day from June 20 to August 19 (DAYS 0-60), and 7.03 μg NO_3-N/day from August 19 through October 27 (DAYS 60-130), and are linearly related to the predicted moisture uptake by the vegetation ($r^2 = 0.966$). The model predicted that with the input assumptions and data used in this simulation, the soil root zone contained sufficient NO_3-N to supply the plants throughout the 130-day period; i.e., all estimated NO_3^--N uptake (Figure 10) was actually withdrawn by the vegetation. Nitrogen concentration in the vegetation could not be compared with measurements made by Billy because the current model does not predict the mass of the vegetation.

Ultimate evaluation of the accuracy of the model is obtained by examining the soil NO_3^--N values predicted during the simulation with the field determinations by Bahe Billy from June through October. None of these determinations, including the initial NO_3^--N concentration, had been used in determining the modelling inputs or assumptions. The predicted values are compared to laboratory determinations made by Bahe Billy on core samples from the 0-15 cm depth in Figure 11. When interpreting these results, it should be recalled that the site used by Billy had a much deeper A horizon than the site on which the supplemental input data was determined five years later. For this reason the 0-10 and 0-15 cm depths were compared to the field observations made on 0-15 cm cores.

To explain the results of Figure 11, it was necessary to examine the detailed printed output from the computer simulation. In addition to the fertilizer application, on day 0 large amounts of organic matter were assumed to occur in the soil profile (particularly in the surface 1 cm of soil) to simulate the presence of fresh organic matter from decaying vegetation. The Biological-Chemical Program, developed primarily for agricultural applications, handled this organic matter in the same way it would a crop residue; i.e. rapid decomposition of residues with low C:N ratios which resulted in the mineralization of very large amounts of NH_4^+ and subsequently NO_3^-. The excessive amount of NO_3^- occurring in the profile from days 0-45 is from this source.

About day 45 the period of the highest rainfall began (see Figure 8), leaching the NO_3^- to below about 10 cm. The extent of this leaching accounts for the difference between the 0-15 cm predictions and the 0-10 cm predictions. This explanation is supported by the much greater decrease in NO_3^--N in the 0-10 cm zone than in the 0-15 cm zone following the rainfall on day 46 (see Figure 11).

It appears that after the extraneous NO_3^--N from organic matter decomposition was removed from the surface by leaching (as is the case with the 0-10 cm line), the model produced reliable predictions of the NO_3^--N concentration. From day 45 through 130, the modelling predictions were within the experimental error of the field determinations made by Billy.

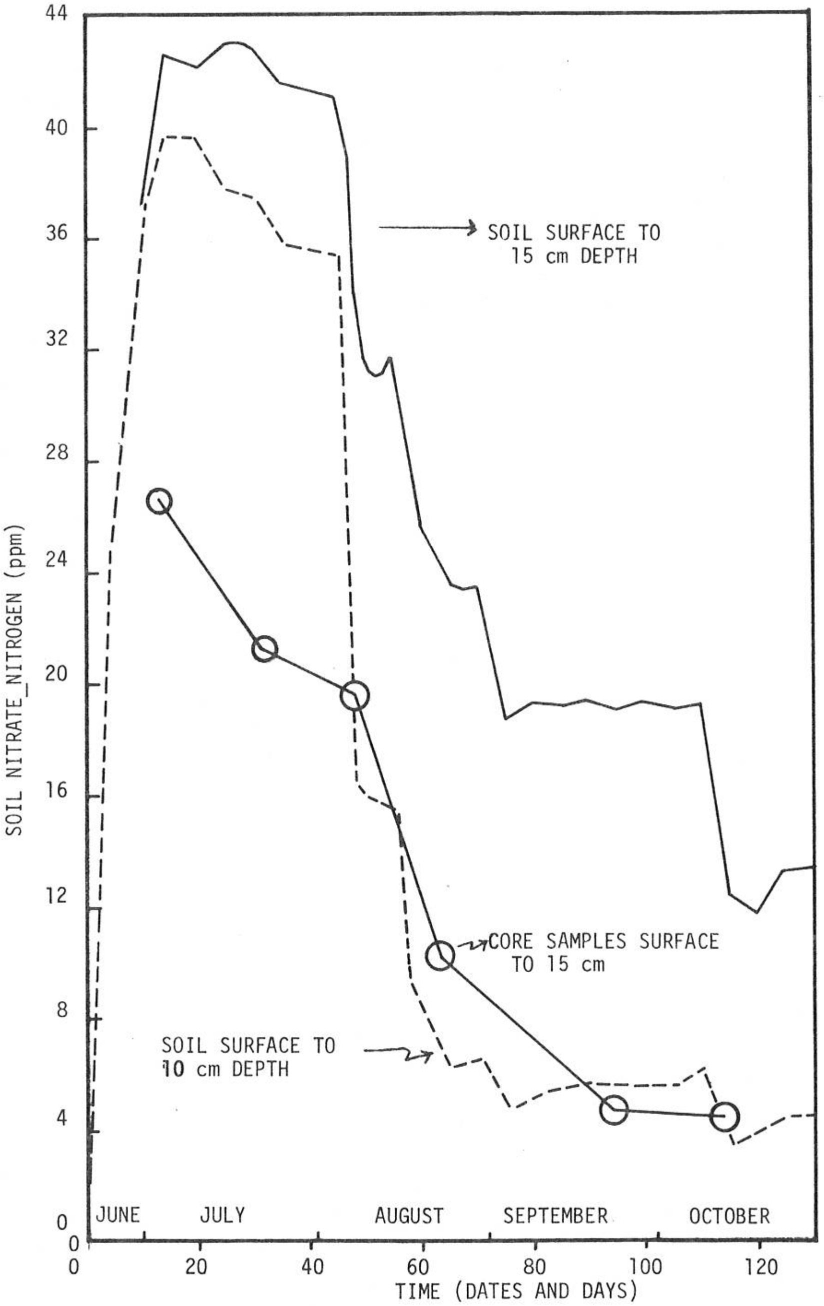

Figure 11. Measured and predicted soil nitrate concentrations (ppm) for the 130-day simulation period.

It is anticipated that with more time (and more precipitation), continued leaching of the 0-15 cm depth would decrease the NO_3^--N concentration there to a level only slightly greater than that in the 0-10 cm zone, since both zones are totally within the A horizon. Further, it should be recalled that the observed NO_3^--N concentrations are shown as linear between the arbitrary sampling dates for convenience of presentation only. Although this factor should be noted when graphically comparing actual (discrete) and predicted (continuous) data, it is unlikely that the actual concentration in the field ever reached those which were predicted on days 10-45 because of the explanation proposed above.

Probably the major modification needed to utilize this systems model to simulate warm desert soils is in the subroutine that predicts the mineralization-immobilization of soil nitrogen. The routine (as previously developed and used in this study) is principally concerned with predicting the influence of crop residues at varying C:N ratios on the system, and has been verified in certain agricultural applications (Dutt, et al., 1972). However, under native desert vegetation, where C:N ratios in the soil are commonly 8:1-10:1 (Fuller, pers. communication), the amount of plant residues returning to the soil is much lower than the return from crop residues on agricultural soils. It appears that in the systems analysis model of desert soils, proper maintenance of the "residual" soil organic fraction, although quite low in actual mass, would be best achieved if it was modelled separately from the more readily decomposed fresh organic residues. The observations from this simulation study suggest that the organic fraction should be considered in two pools: the first always present in some degree as the "residual" soil organic matter (C:N≈8:1-10:1), and the second the more readily decomposed organic fraction resulting from fresh plant material (C:N ratio of the residue). With modifications of this type, it is anticipated that the current systems analysis model, using the moisture flow model of Dr. Hanks in cases where homogeneity should not be assumed for the physical parameters affecting soil water, can yield accurate simulation of desert grass land.

An important, and frequently limiting, factor regarding the usefulness of any systems analysis model is the computer time required in the simulation. Since the time required for a model to execute a given problem depends on the type of computer system, compiler options, efficient use of peripheral devices and other factors, and algorithms for determining computer charges are so variable, the most useful standard is often the actual cost of executing a problem on one computer system. For the Page Ranch simulation study, the computer costs and a few important parameters of each submodel are listed in Table 4.

Table 4. Computer times and charges required for 130-day Page Ranch simulation study on Control Data Corporation 6400 computer system at University of Arizona Computer Center

Submodel	CPU Time (Sec) Compilation*	CPU Time (Sec) Execution	Submodel cost	Comments
Moisture Flow	12.6	72.5	$12.98	14 nodes, at Δt_{max} = 0.1 day.
Interface	3.7	18.4	4.92	Tape-tape data conversion and print.
Bio-Chemical	40.4	87.1	21.59	11 segments, Δt_{max} = 0.1 day.

* FTN compiler option.

EXPECTATIONS

The utilization of the soil moisture program written by Dr. Hanks increases the applicability of the model to systems in which the physical parameters affecting moisture redistribution cannot be considered homogeneous with depth. With the modifications which were made during this study, the program is completely compatible with the rest of the systems analysis model.

From this study, it appears that the model can be modified from a form designed for agricultural applications to a form which will yield accurate simulation of desert grassland systems. Major changes will be required in the subroutine which predicts the net mineralization-immobilization rates and the decomposition of organic residues. The organic nitrogen will be divided into two pools: one of which represents the residual soil organic nitrogen, and the other decomposing plant residues.

SUPPLEMENT

INTRODUCTION

Evaluation of nitrogen losses from desert soils via ammonia volatilization and the incorporation of a volatilization subroutine into the existing computer model is necessary to improve predictions of nitrogen behavior in warm desert soils. Desert soils which commonly exhibit properties of high temperature, high pH and low moisture content can display as a result of these properties a significant loss of nitrogen as ammonia.

OBJECTIVES

The specific objectives of this study are:

1. Experimentally determine the ammonia partial pressures above NH_4Cl solutions at various pH levels and compare experimental values to theoretically calculated values.
2. Determine the partial pressures of ammonia for complex systems containing other anions abundant in desert soils such as carbonates and sulfates. Subsequently, to illustrating that the ammonia partial pressures from chloride solutions agree with the theoretical values.
3. Evaluate experimentally the effect of clay minerals and desert soils of different physical and chemical properties on the partial pressure of ammonia.
4. Use the experimental results to incorporate the volatilization of ammonia nitrogen into a computer model compatible with the model previously developed (Dutt,et al., 1972).

METHODS

Ammonia partial pressures above solutions of NH_4Cl

As a test for the reliability of the experimental design and technique for the analysis of the ammonia volatilization from solutions and soil systems, the experimental partial pressures of ammonia over NH_4cl were compared with the theoretical values.

Gas ollection ystem

Gas samples above NH_4Cl solutions were collected by means of a mechanical press precalibrated to squeeze out 400 ml of gas above 500 ml solutions of 0-1M NH_4Cl in one liter polyethylene bottles. A similar press technique was utilized by Blanchor (1967) to study the ammonia partial pressures in soil inhibiting seed production. Tests run on the precalibrated press indicated that the volumes collected were within the accuracy of 400 ± 5 ml or within 0.125% error.

The ammonia gas was trapped by passing it through 8.0 ml of 0.1 N HCL as it was pressed from the polyethylene bottles. A dual trap system containing two solutions of 8.0 ml of 0-1N HCl indicated that all of the ammonia was collected in the first trap even at high pH values where the ammonia partial pressures were high.

Ammonia analysis

The trapped ammonia was determined colorimetrically via nesslerization in 0-1N HCl described by Yuen and Pollard (1952). The color was developed in a total volume of 10.0 ml with the addition of 1.0 ml of Nessler's reagent to the trapping solution.

Sample preparation

The ammonium chloride solutions were 0.1 M in 500 ml of deionized water. Various pH levels were obtained by the addition of standard NaOH. The standard NaOH was added to deionized H_2O to make a total volume of 500 ml. Subsequent to the addition of the NaOH, the NH_4Cl salt was added and the bottle immediately stoppered as a final step to prevent any loss of ammonia.

Equilibration of the samples was attained by shaking the samples mechanically for 2 hours at a room temperature of 25 ± 1 C. The samples were finally placed on a combined shaker and water bath set at 25 ± 0.5 C prior to analysis.

Calculations

The partial pressures were calculated using the ideal gas law

$$P_{NH_3} = n\ RT/V$$

where P_{NH_3} is the partial pressure of ammonia in mm Hg,, n is the number of moles of ammonia gas collected, R is the gas constant with a value of 62.4 liters mm Hg/mole degree, T is the temperature in degrees Kelvin and V is the volume in liters of the gas collected.

The number of moles (n) of ammonia was determined by nesslerization, the temperature (T) was maintained at 298 ± 0.5 K with a constant temperature water bath and room temperature of 25 ± 0.5 C, and the volume (V) of gas was determined by precalibration to be 0.390 liters or 400 ml of gas squeezed from the sample bottle minus 10 ml retained in the delivery tube leading from the sample bottle to the 0.1N HCl trap.

Ammonia partial pressures above other salt solutions and soil systems

According to the procedure outlined for NH_4Cl solutions, the partial pressures above ammonium sulfate solutions were determined at various pH levels.

Ammonium solutions containing other anions abundant in desert soils such as $CO_3^=$ will also be tested to determine any anion effect on the ammonia partial pressure prior to determining the effects of clay minerals and complete soil systems.

RESULTS AND DISCUSSION

The experimental and theoretical partial pressures above 0.1M NH_4Cl are illustrated in Table 5. The experimental and theoretical values agree well ($r^2 = 0.999$), verifying the reliability of the experimental technique in measuring partial pressures of more complex systems. A minimum of three experimental values were determined for each partial pressure. The average deviation of these values listed in the same table indicate the good precision obtained with our experimental design.

With solutions containing sulfate, the ammonia partial pressures were only slightly higher than the solutions containing chloride. Table 6 gives the experimental ammonia partial pressures above 0.1M $(NH_4)_2SO_4$ solutions. The average deviations are as low as previously obtained with the chloride solutions.

Table 5. Experimental and theoretical P_{NH_3} above 0.1M NH_4Cl at 25 C and at various pH and Na^+ levels

pH	Na^+ (moles/l)	P_{NH_3} (mm H_g) Theoretical	P_{NH_3} (mm H_g) Experimental*	Average Deviation
8.00	4.55×10^{-3}	.0613	.0555	± .0021
9.03	3.12×10^{-2}	.421	.385	± .0093
10.10	8.52×10^{-2}	1.15	.997	± .049

* Mean of 3 or 4 experimental values.

Table 6. Experimental P_{NH_3} above 0.1M $(NH_4)_2$ at 25 C and at various pH and Na^+ levels

pH	Na^+ (moles/l)	P_{NH_3} (mm H_g)*	Average Deviation
7.55	2.26×10^{-3}	.0307	± .0017
7.88	4.55×10^{-3}	.0564	± .0039
8.40	1.45×10^{-2}	.179	± .013
8.79	3.09×10^{-2}	.362	± .0076
9.13	5.90×10^{-2}	.712	± .011
9.65	1.13×10^{-1}	1.333	± .045

* Mean of 3 experimental values

EXPECTATIONS

The preliminary findings reported here verify the experimental methodology to be utilized throughout this investigation, with precision demonstrated by low experimental deviations and accuracy demonstrated by agreement with the theoretical values. The remaining objectives can now be approached with the confidence that the data so obtained will be sufficiently accurate to be the basis of the computer subroutine.

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