

December 1972

WRRRI Report No. 018

SOIL AND WATER MANAGEMENT FOR SALINITY CONTROL

Technical Completion Report
Project No. 14-01-0001-1973
14-31-0001-3148 and
14-31-0001-3376

July 1968 - August 1972

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The work upon which this report is based was supported by funds provided by the United States Department of the Interior, Office of Water Resources Research as authorized under the Water Resources Research Act of 1964.

ABSTRACT

Heavy applications of irrigation water for the purposes of removing accumulated salts or preventing excessive increases of salts in soils constitutes an inefficient use of irrigation water. It also contributes to salt pollution of ground water supplies. Use of many smaller applications of water and unsaturated flow conditions has been shown to be more efficient for removing salts from the root zone of crops. This study investigated movement of salts and pesticides in lysimeters under unsaturated soil water conditions. Computer models, using S/360 CSMP, were developed for predicting the movement of water, of nitrates and chlorides, and of pesticides.

Adequate predictions were made of the infiltration, redistribution, and drainage of water from uniform and layered lysimeter columns. Accounting for hysteresis in the hydraulic properties of the soil improved the predictions of water content distributions and drainage rates. Without accounting for hysteresis, the use of drying curves was preferred for predicting redistribution and drainage in soil after irrigation. Changes in the composition of drainage water from the lysimeters repeatedly irrigated with a prepared saline water were slow for certain ions (Na^+ , PO_4^-) and fast for others (Cl^- , NO_3^- , SO_4^{--} , Ca^{++}). Negative adsorption was the main reason chloride and nitrate ions moved faster than the irrigation water. Phosphorus movement was very restricted due to precipitation and adsorption. Pesticide movement was restricted by adsorption on the soil complex. The adsorption-desorption process was found to be subject to hysteresis. Degradation rates of 2,4,5-T were relatively high. No 2,4,5-T was detected in the drainage water from the columns.

The movement of nitrates or chlorides in the lysimeter columns was adequately predicted from knowledge of the dispersion coefficients and the anion exclusion volume. Prediction of picloram movement seemed satisfactory when equilibrium conditions were assumed. The use of rate equation did little to improve the prediction of picloram movement. At high flow velocities the prediction of salt and pesticide movement in soil is complicated by anion exclusion, dead pores, dispersion, and diffusion into aggregates. A physical model to account for all these phenomena is not yet available.

Key words: salt movement, water movement, hysteresis, pesticides, nitrate movement, anion exclusion, dispersion phosphorus, S/360 CSMP

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INTRODUCTION

The conventional method for controlling soil salinity in irrigated areas is to leach soils by applying more water than is actually needed for producing a crop. This method represents a costly use of water and a source of pollution to both ground and surface water supplies. Recent investigations (Miller, et. al., 1965) indicated that the use of smaller applications of water increased the efficiency of salt removal from the root zone; the use of smaller quantities of water for leaching would also have the advantages of saving irrigation water and reducing problems of ground water pollution.

Since soils have a large buffering capacity, it takes a long time before changes in irrigation regimes or management can be measured by their effect on the quality of the drainage water. Consequently, for predictive purposes, it is essential to have models which make possible the determination of the effects of irrigation management procedures on salinity levels in the soil profiles and the composition of the drainage water. Such models are also needed for predicting the transfer times of nitrates, phosphates, and pesticides from the time of application to their arrival at the ground water table.

The objective of this project was to determine, through the construction of a model, water and salt movement under unsaturated soil water conditions. This information would permit maintenance of a desired salinity level in soils and the reduction of pollution of ground water supplies.

An important part of model development is testing it with data. This study presents, in addition to computer models for predicting the simultaneous movement of water and nitrates or pesticides, a large amount of data on movement of salts and pesticides through soil columns. In addition to data on total salts, data are presented on the movement of individual anions and cations since both the concentration and the ratio of the various ions in the drainage water need to be known for predictive purposes. These data provide much needed information on the behavior of these various ions during movement through a soil profile, and allow extensive testing of existing and future models on salt movement in a calcareous soil.

EXPERIMENTAL PROCEDURES

In order to determine water and salt movement under unsaturated soil water conditions, a number of column studies were initiated. Two types of soil columns were used for this study. Large lysimeter-type columns were set up to study the movement of the anions and cations commonly found in irrigation water and to follow the downward movement of 2,4,5-T added to the irrigation water. Smaller laboratory-type columns were used for studying the effects of the calcium/magnesium ratio on the solubility of calcium carbonate, for studies of the movement of individual ions such as chlorides or nitrates, and for determining the dispersion coefficients of the soil at different flow velocities. The studies are hereafter designated lysimeter studies and laboratory studies, respectively.

A. Lysimeter studies

1. Construction of the columns

A lysimeter installation consisting of four large soil columns, each 75 cm in diameter and 150 cm high, was built. The columns were made of Techite, a composite structure of fiberglass, polyester resin and sand. Techite has a high mechanical strength and is lightweight compared with concrete or steel. It is also an inert material and can easily be drilled or glued. These properties make it an excellent material for building soil columns of the size used in this experiment. The columns were placed in a greenhouse which had an air temperature between 20° and 30° C.

Two columns were filled with air-dried Glendale silty clay loam passed through a 6 mm sieve. Two additional columns were filled with 90 cm of Glendale silty clay loam on top of 60 cm of river sand. The sand had been air-dried and passed through a 1 mm sieve. The first two columns represented a uniform soil profile while the last two columns represented a layered soil, in this case a clay loam on top of sand, which is very common in the Mesilla Valley of New Mexico. The particle size distributions of the two soils used in the experiment are presented in Table 1.

Table 1. Particle size distributions of Glendale clay loam and river sand.

Soil	Textural Fractions		
	Sand (> 50 μ)	Silt (2-50 μ)	Clay (< 2 μ)
		<u>Percentage</u>	
Glendale clay loam	38.8	29.8	31.4
River sand	95.6	2.4	2.0

After the columns were packed, average bulk density was 1.26 gr/cm^3 for the Glendale clay loam and 1.62 gr/cm^3 for the sand. Porous filter candles, 25 cm long and 5 cm O.D., were installed at the bottom of the columns to remove drainage water. A constant suction of 140 cm water was maintained on these filter candles during the course of the experiment. The drainage water was collected in large bottles and measured volumetrically. Samples were taken from this drainage water for laboratory analysis.

Tensiometers were installed through the sides of the columns, three at each depth, at 20, 40, 60, 80, 100, and 120 cm below the soil surface. The tensiometers were installed at an angle of 15° and positioned such that the tips of the tensiometer cups were at the center of the columns. Additional tensiometers were installed, one at each depth, at 10, 30, 50, 70, 90, 110, 130, and 140 cm below the soil surface. Suction cups for removal of the soil solution for chemical analysis were installed at 5, 15, 25, 35, 50, 75, 100, and 125 cm below the soil surface. Samples of the soil solution were removed by application of a constant suction of about 30 cm mercury. Neutron access tubes were installed in one column with uniform soil and in one column with layered soil. The soil in the columns was wetted by addition of 11 liters of tap water to the surface of the columns at one or two day intervals. Evaporation from the columns was minimized by a cover of polyethylene plastic on the soil surface. The slow wetting of the columns was considered necessary to prevent excessive expansion of the soil within the columns upon wetting. No appreciable change was found in the level of the surface soil within the columns after the soil was completely wetted.

2. Determination of hydraulic properties of the soils

a. Soil-water characteristic curve

Soil-water characteristic curves for the soils in the experiment were determined on disturbed soil samples, and from tensiometer and water content data directly from the columns. In the dry range, water content-tension relationships were determined on disturbed samples with pressure plate apparatus (Black, 1964). In the wet range, the relationship between soil-water tension and water content was obtained from simultaneous determinations of the soil-water tensions with tensiometers and water contents with the neutron meter. The relationship was also determined with a modification of the hanging water columns method on disturbed soil in the laboratory.

Figure 1 shows the water release curve for the Glendale clay loam in column IV, and Figure 2 shows the water content-tension relationship for the sand in column III. Each figure shows two curves, one for drying and one for wetting of the soil in the columns. The curves are drawn to envelop the experimentally determined data points. The data show that there is considerable hysteresis in the water content-tension relationship for both the clay loam and the sand. The effects of hysteresis on infiltration and redistribution of water in the large lysimeter columns were

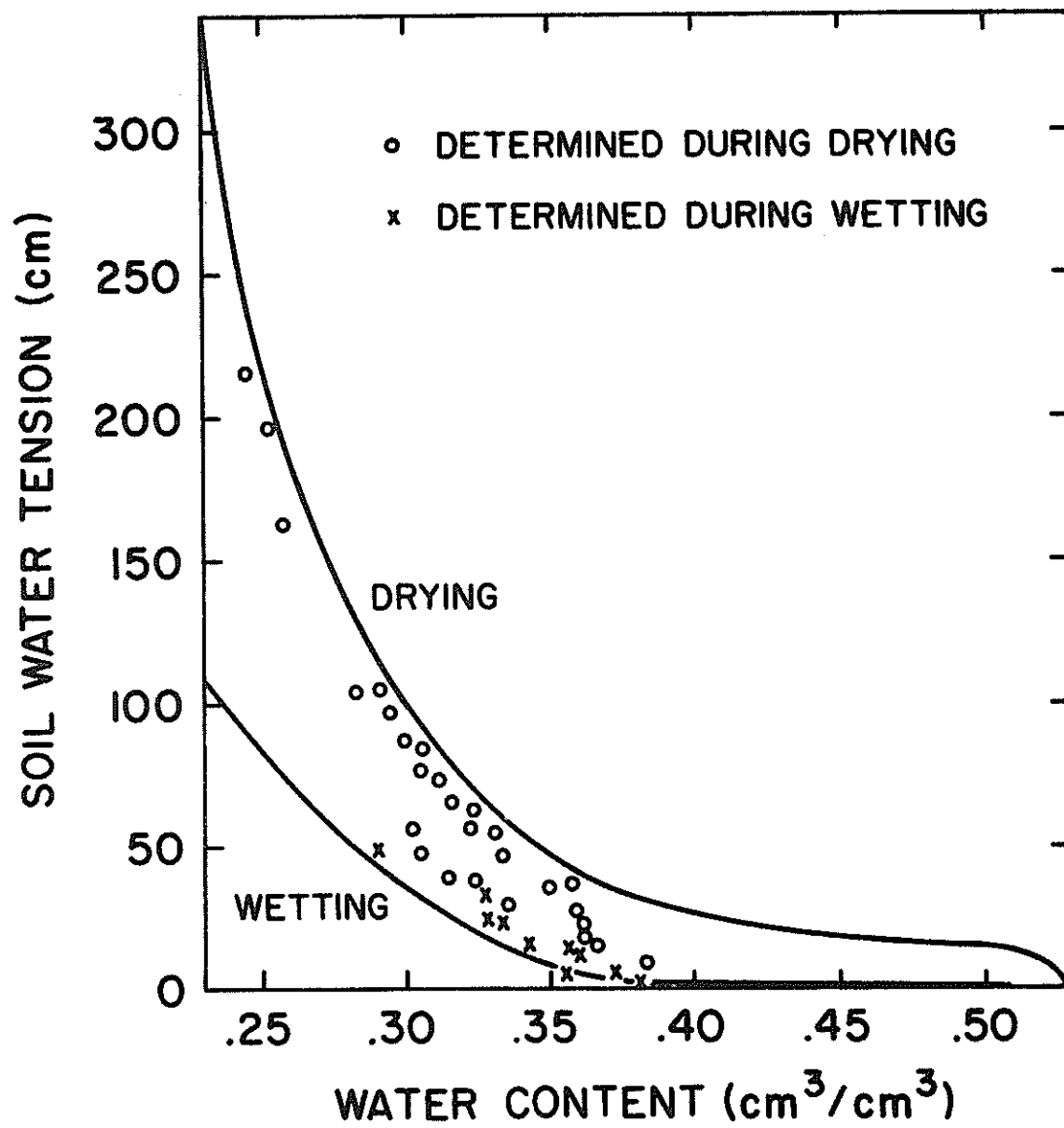


Figure 1. Soil water tension - water content relationships of Glendale clay loam in column IV.

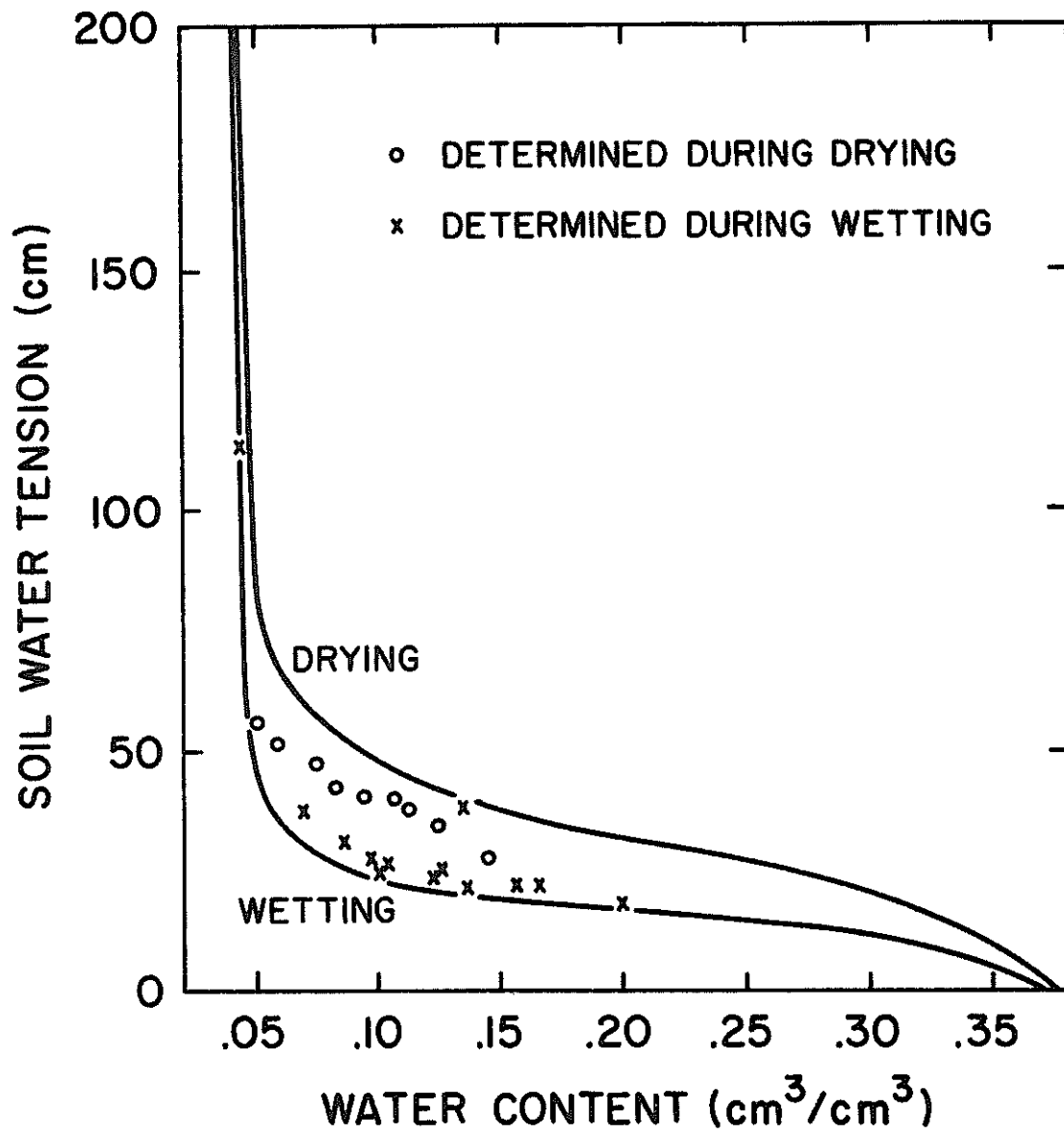


Figure 2. Soil water tension - water content relationships of the sand in column III.

studied with the help of a computer model. The results are presented on pages 21 to 27.

b. Hydraulic conductivity - water content relationship

The relationship between hydraulic conductivity and water content was partially determined by establishing steady state flow conditions within the lysimeter columns. Steady state flow conditions were established with the use of adjustable constant flow pumps (models RRP1G50 and RRP1G400 from Fluid Metering, Inc.). Water was applied at 12 points equally spaced over the surface of each column. Initially low flow rates were used. After establishing steady state conditions, indicated by a constant rate of outflow from the columns, neutron meter readings were recorded for the entire columns. The inflow rate was then increased and after a constant flux was established, neutron meter readings were obtained. This procedure was repeated until a maximum flux was established. Thereafter, the rate of inflow was decreased stepwise, and after equilibrium was established, neutron meter readings were obtained. The above procedure provided hydraulic conductivity values during both wetting and drying of the soil. The water content at each flux was determined with the neutron meter. At fluxes less than .2 cm/day, hydraulic conductivity values, as a function of the water content, were obtained following the method described by Nielsen et al. (1964) and van Bavel et al. (1968). The saturated hydraulic conductivity was assumed to be equal to the infiltration rate measured at the end of irrigation with 10 cm of water (Philip, 1969). Hydraulic conductivity values between saturated hydraulic conductivity and the highest value obtained with the steady state procedure were determined by interpolation.

Figures 3 and 4 present hydraulic conductivity data for the clay loam and the sand, respectively. The hydraulic conductivity values of the Glendale clay loam were higher during wetting than during drying (Figure 3), while the reverse was the case for the sand (Figure 4). This phenomenon had been observed in the literature also (Staple, 1966; Naar et al. 1962). No explanation is as yet available to fully account for this behavior.

3. Irrigation treatments

The columns were irrigated at 3 to 8 week intervals with an amount of water corresponding to a height of 10 cm, a normal irrigation practice. Instantaneous flooding was approximated by emptying a large container of prepared irrigation water over the column. Sprinkler irrigation was simulated by applying the water at a rate of about 6 mm/hour with a constant flow pump at 12 points equally spaced over the surface of the columns. The quality of the irrigation waters, prepared to simulate local conditions, is presented in Table 2.

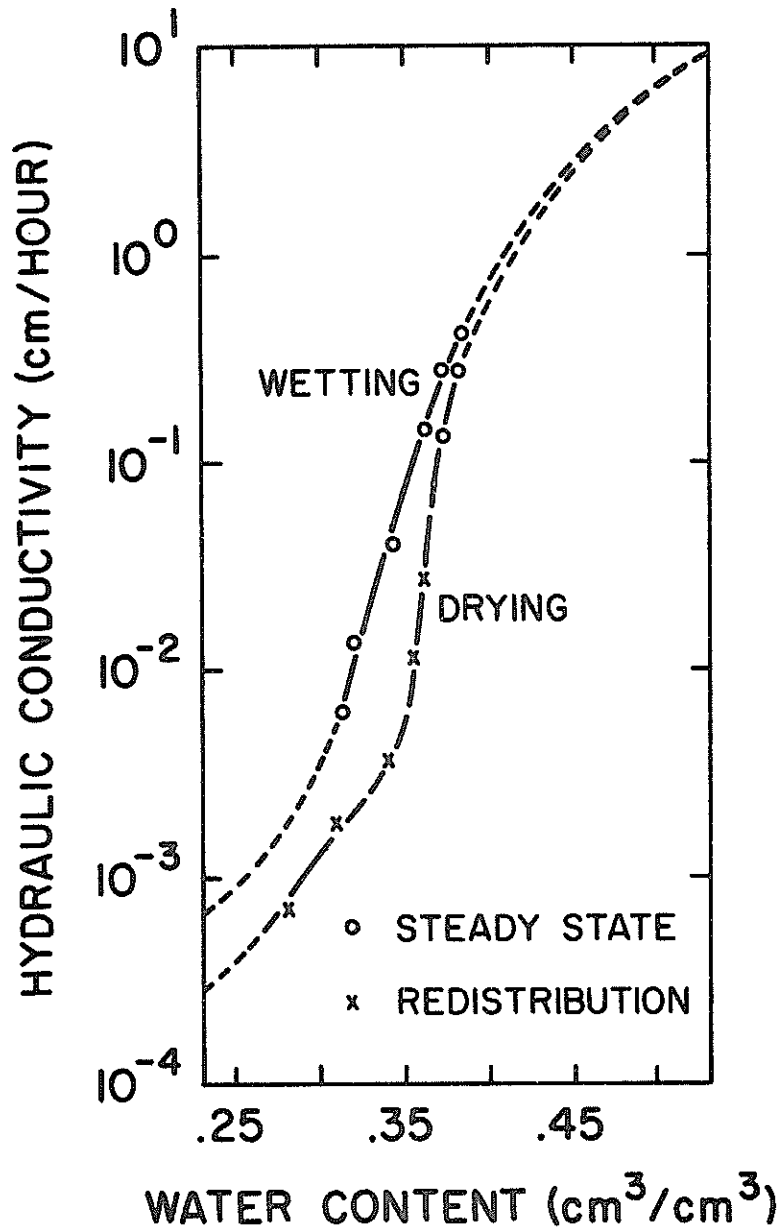


Figure 3. Hydraulic conductivity-water content relationships of Glen-dale clay loam in column IV. The dashed lines are extrapolated from the best fitting lines through the data points.

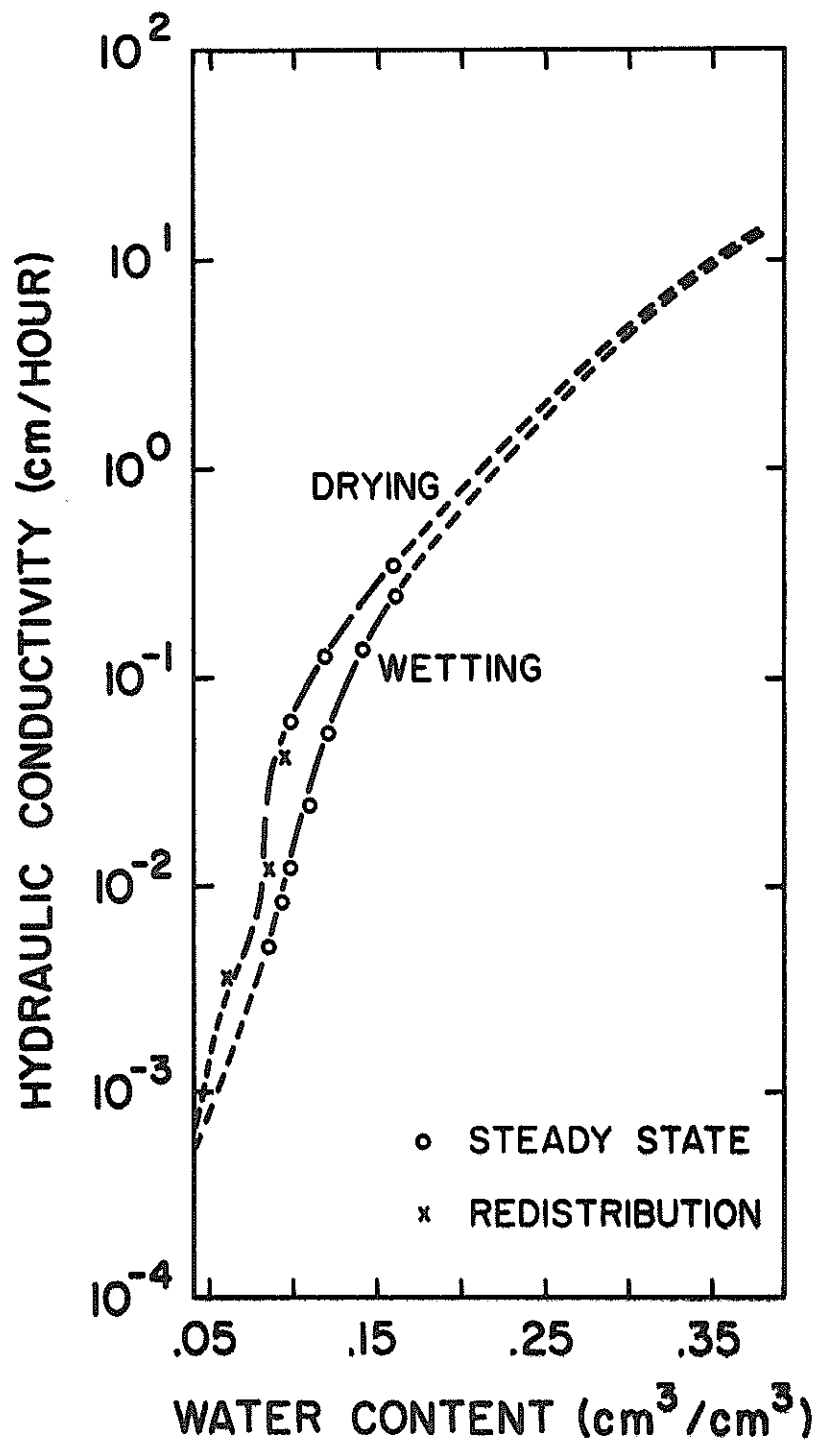


Figure 4. Hydraulic conductivity-water content relationships of the sand in column III. The dashed lines are extrapolated from the best fitting lines through the data points.

Table 2. Quality of irrigation water used (meq/l)

Period	Cations	Ca	Mg	Na	K	SO ₄	Cl	CO ₃	HCO ₃
6/1/69-9/9/69	6	2.8	0.9	1.9	0.4	1.3	1.4	-	3.3
9/9/69-2/12/70	32	15	3	11	3	9	18	-	5
2/12/70-4/14/72	32	15	3	11	3	11	21	-	-

During a number of irrigation treatments, the chlorides in the prepared irrigation water were replaced by an equal amount of nitrates in order to study the movement of chlorides and nitrates separately.

Herbicide was applied in three subsequent irrigations with 10 cm water each. The herbicide-irrigation water had the same composition as that used to equilibrate the columns except that either 40 or 80 ppm unformulated 2,4,5-T was also dissolved in the water.

Both columns were irrigated for the first time with irrigation water containing 80 ppm 2,4,5-T.

During the second irrigation with herbicide solution, column I received irrigation water containing 40 ppm 2,4,5-T, and column II received water containing 80 ppm 2,4,5-T. Samples of the soil solutions from both columns were collected 3, 48, 52, and 58 days after irrigation.

The total elapsed time between the first and second irrigations with herbicide was 8.25 months. Although no herbicide was applied during this period, a total of six 10 cm irrigations with a similar irrigation water, minus the herbicide, was applied.

During the third irrigation with herbicide both columns received solutions containing 80 ppm 2,4,5-T. Soil solution samples were collected 4, 13, 27, and 43 days after the irrigation.

During irrigation, the infiltration rate was measured with a pointed ruler; the column edge was used as a reference point. Tensiometer and neutron meter readings were recorded during the infiltration and redistribution processes to follow changes in soil water tension and water content in the entire columns. Drainage water volume was measured periodically after irrigation; thus, values for cumulative drainage and drainage rate as a function of time were obtained.

4. Methods of analysis used

During the course of the experiment, efforts were made to continuously improve the procedures for the analyses of the samples collected from the columns. One such improvement was the acquisition of an atomic absorption spectrophotometer for the determination of metal ions in the soil extracts. The instrument, a Perkin-Elmer model no. 403, was obtained during the second year of study. Considerable time was also spent on development of a gas chromatography method for determining 2,4,5-T in the soil extracts collected from the columns. The rather time-consuming gas chromatography method was chosen for analyses because a simpler spectrophotometric procedure failed to yield the required accuracy, and the use of radioactive labeled 2,4,5-T was not feasible in the greenhouse.

An improved method was also developed for determining the sulfate concentration in soil solutions. The method consists of precipitation of sulfate with an excess amount of barium chloride, centrifugation, and determination of the barium remaining in solution by atomic absorption. From the original barium concentration and the amount of barium remaining in solution after precipitation of sulfates, the sulfate concentration can be calculated.

Frequent checks of the analytical procedures were made by analyzing test samples having known amounts of cations and anions, provided by the Quality Control Laboratory of the Federal Water Pollution Control Administration.

A detailed description of the various analytical procedures used during the experiment is presented in Appendix I.

B. Laboratory studies

1. Solubility of calcium carbonate as affected by the calcium-magnesium ratio in the irrigation water

Glendale clay loam contains a relatively large amount of calcium carbonate, as do many other soils in arid and semiarid regions. Inasmuch as models to predict solution of calcium carbonate during leaching are rather inadequate at present, a separate experiment was undertaken to measure the solution of calcium carbonate under continuous irrigation with waters of different quality.

Six columns, 7.62 cm in diameter and 60 cm long, were filled with air-dried Glendale silty clay loam which had been passed through a 6 mm screen. The bulk density of the soil in the columns was 1.26 gr/cm³. A constant suction of 125 cm water was provided at the bottom of the columns. Solutions were added to the columns at a constant rate with a syringe pump designed in cooperation with the Physical Science Laboratory and the Department of Electrical Engineering at New Mexico State University (Wierenga et al. 1973). A constant flux of 4 cm/day was maintained in the

columns. After thoroughly leaching the columns with deionized water, the columns were leached with irrigation water containing calcium and magnesium chlorides in a 5:1 ratio and 0, 7.5, or 15 meq/l of sodium chloride. Throughout the experiment, samples were taken from the effluent for chemical analysis. After the effluent solution had reached equilibrium, a new solution was introduced with calcium and magnesium chlorides in a 2:1 ratio maintaining the same flux. Upon equilibration (after about 8 months), a third solution was introduced with calcium and magnesium chlorides in a 1:2 ratio. Table 3 presents the compositions of the irrigation solutions used during this experiment.

Table 3. Composition of irrigation solutions used during leaching of laboratory columns

Period	Column No.	Ca	Mg	Na	Cl	Cations	Ca/Mg
10/5/70-	1,2	25.0	5.0	0	30	30	5:1
5/6/71	3,4	18.75	3.75	7.5	30	30	5:1
	5,6	12.5	2.5	15.0	30	30	5:1
5/6/71-	1,2	20.0	10.0	0	30	30	2:1
6/7/72	3,4	15.0	7.5	7.5	30	30	2:1
	5,6	10.0	5.0	15.0	30	30	2:1
6/7/72	1,2	10.0	20.0	0	30	30	1:2
Present	3,4	7.5	15.0	7.5	30	30	1:2
	5,6	5.0	10.0	15.0	30	30	1:2

At regular time intervals samples were taken from the effluent solutions for chemical analysis.

2. Movement of chlorides

In order to predict nitrate or chloride movement through soils, it is necessary to know the dispersion coefficients for the soil over a range of soil water fluxes. Three leucite cylinders, 30 cm long and 5 cm in diameter, were filled with Glendale silty clay loam to a bulk density of 1.26. The soil had been air dried and passed through a 6 mm sieve. A constant suction was maintained at the bottom of the columns to provide unsaturated soil-water conditions over the length of the columns. Samples were collected in a time controlled fraction collector set for 6 ml effluent samples. A modified Orion syringe pump was used to deliver the leaching solutions to each of three soil columns at a constant rate. A diagram of the experimental set up is presented in Figure 5.

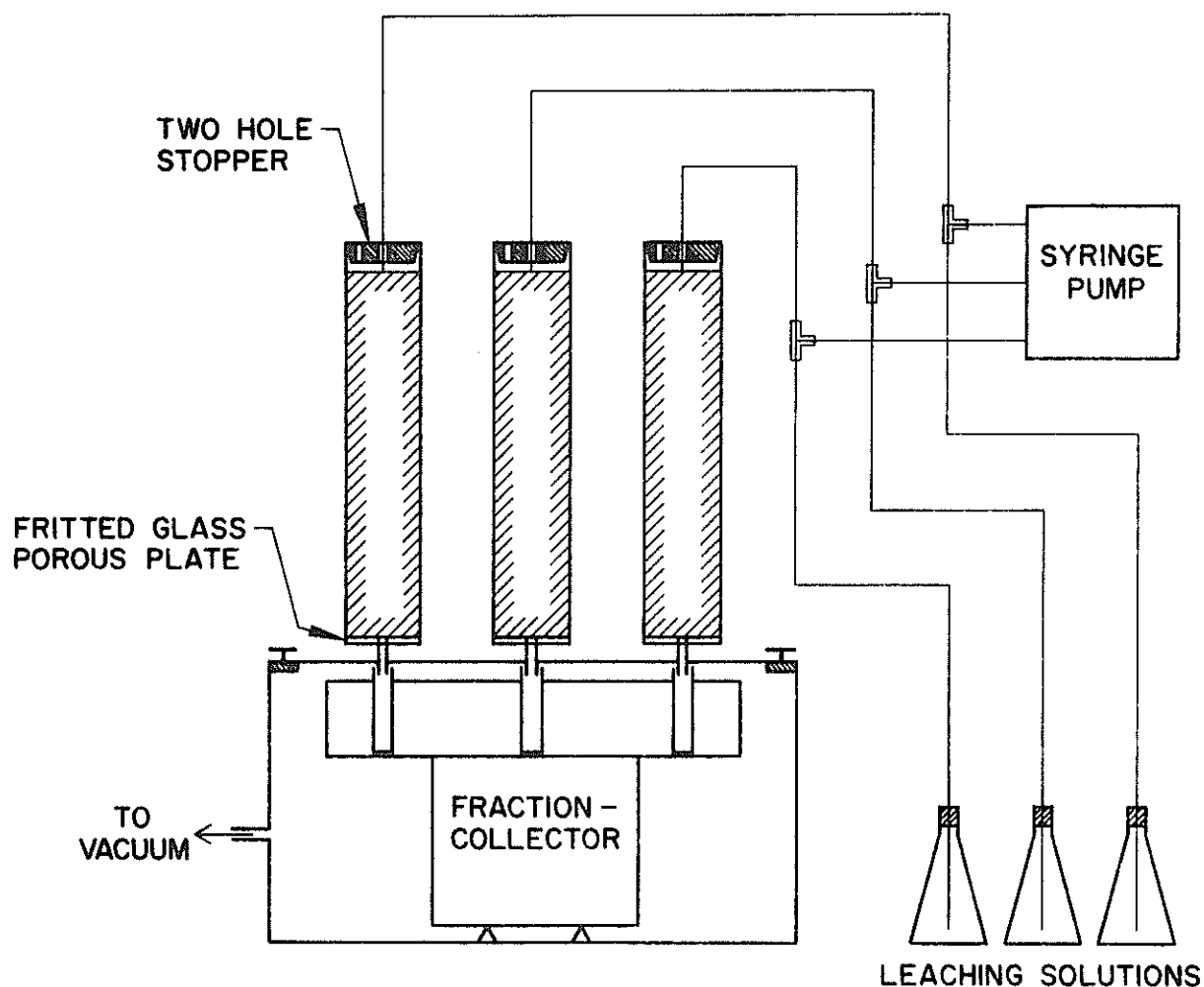


Figure 5. Schematic diagram of experimental set up during movement of chlorides through soil columns.

The columns were first leached with $\text{Ca}(\text{NO}_3)_2$ solutions at concentrations of 1, 2, 3.5 or 5, 10, and 20 meq/l. After steady state conditions had been established and no more chloride was found in the effluent, the $\text{Ca}(\text{NO}_3)_2$ solutions were replaced by CaCl_2 solutions of the same concentration. The effluent solution was collected and analyzed for chloride content. The relative concentration (C/C_0) was calculated from the chloride concentration in the effluent (C) and the initial concentration (C_0) of the leaching solution at the inflow location. From the relative concentration (C/C_0) and the pore volumes of effluent, the dispersion coefficient was calculated. The number of pore volumes displaced through the soil (V/V_0) was calculated by dividing the volume of effluent (V) by the volumetric water capacity (V_0) of the soil.

DESCRIPTION OF COMPUTER MODELS

For predictive purposes it is essential to have models which make it possible to extrapolate the results of experiments, which have been done under given conditions, to situations where the conditions are different. In salt management studies, computer modeling of the movement of salt and water in soil is particularly important because soils have a large buffering capacity; as a result it takes a long time before the effects of irrigation management practices (e.g. on the quality of the drainage water) can be measured. With a model the data from a relatively short term experiment, e.g., several months, may be extrapolated to the real situation for a period of several years.

Another reason for developing computer models is that they allow a sensitivity analysis of some of the parameters used in the models. An example of this follows below, where the effects of hysteresis on soil-water movement is studied by comparing water content distributions in the lysimeters computed with and without hysteresis.

In this study models were developed for predicting water movement in soil, for predicting water and salt movement, and for predicting pesticide movement.

A. Water movement

The general flow equation for vertical water movement in soil profiles is:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial Z} \left(K(\theta) \frac{\partial \psi}{\partial Z} \right) + \frac{\partial K(\theta)}{\partial Z} \quad [1]$$

where θ is the water content (cm^3/cm^3), t is time (days), Z is depth below the soil surface (cm), $K(\theta)$ is the hydraulic conductivity (cm/day), and ψ is the soil water potential (cm).

In order to solve equation [1], the relationships between ψ and θ , and $K(\theta)$ and θ must be known. These relationships are complicated, however, by hysteresis. An example of hysteresis in the relationship between soil water tension (ψ) and water content (θ) is illustrated in Figure 6. Values of ψ in Figure 6 at a particular value of θ are influenced by the history of wetting and drying of the soil. By wetting the completely dry soil to saturation, the main wetting curve, W, originates. The main drying curve, D, occurs when the reverse process takes place. Curves W and D form the main hysteresis loop. Between the main wetting and drying curve a family of scanning curves exists, illustrated with the dashed lines in Figure 6.

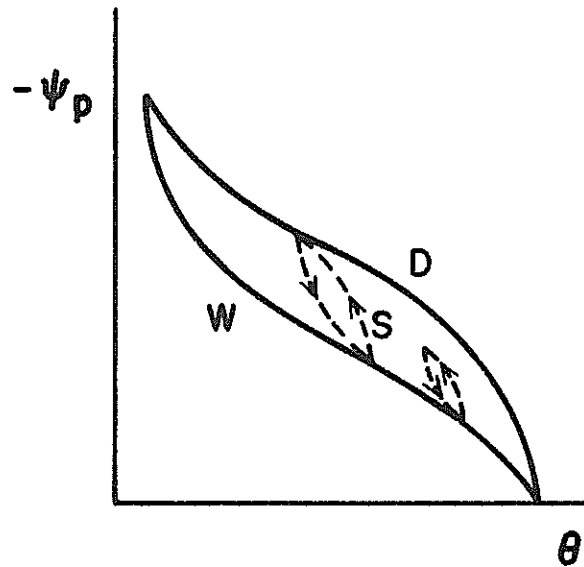


Figure 6. Soil water tension (ψ)-water content (θ) relationships during drying and wetting. D represents the main drying curve, W the main wetting curve. The dashed loops are scanning curves (S).

The shape of a scanning curve is dependent on the transition point; i.e., the water content from which the soil starts to rewet or redry. During infiltration and redistribution of water in the soil, wetting and drying occur simultaneously at different parts of the profile. Thus at different depths, different scanning curves have to be used for the relationships between ψ and θ , and between K and θ .

The solution of equation [1] is complicated further by the upper boundary condition. During irrigation, water is ponded on the soil surface. The head of this ponded water decreases with time as water moves into the soil until all the water has disappeared from the soil surface.

A third complicating factor is that most natural soils are layered. This means that different relationships between ψ and θ , and between $K(\theta)$ and θ , have to be used for each distinct soil layer.

An analytical solution of equation [1] with the above conditions is not available. For this reason a numerical method was used. This method is similar in many respects to the one used by Wierenga and de Wit (1970) for simulating heat transfer in soils. The soil is divided into a number of layers which may vary in thickness but which are considered homogeneous with respect to physical and chemical properties. However, individual layers may vary in these properties as is normally the case in natural soils. Just as in the heat transfer model (Wierenga and de Wit, 1970), a number of variables are calculated in the INITIAL part of the computer program (e.g. layer thickness, diffusion distances). The initial water content and salt content profiles are also defined. In the DYNAMIC part of the model, the hydraulic conductivity and the soil-water pressure head of each layer are calculated from its water content.

From the pressure gradients between adjacent layers and from values of the hydraulic conductivity, the flux into each layer is calculated. Calling the rate of water movement into layer I $FLOWIN(I)$, and that moving into layer I+1 $FLOWIN(I+1)$, the net change in water content in layer I is $FLOWIN(I) - FLOWIN(I+1)$. The water content at time $t + \Delta t$ is obtained by integrating this net change in water content with respect to time, and adding the resulting amount of water to the water present in the layer at time t . A diagram of the layers, and the main CSMP statements describing this process, is given in Figure 7.

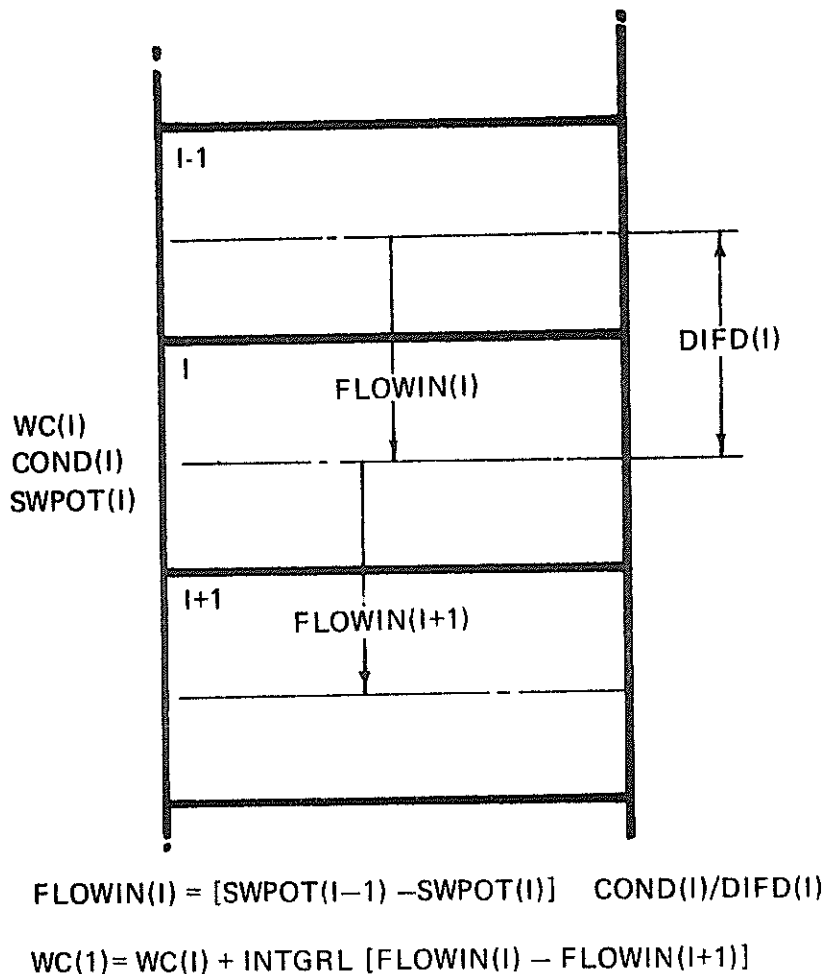


Figure 7. Diagram of layers and the main CSMP statements describing water movement in soil.

Hydraulic conductivity values were obtained by taking the average of the hydraulic conductivity values for each two successive layers, a procedure which is, according to Van Keulen and Van Beek (1971), equivalent to several others tested by them. In the computer model, hysteresis was taken into account. The program was designed such that the scanning curves caused by wetting converged to the main wetting curve, and the scanning curves caused by drying converged to the main drying curve. The procedure is explained in detail by Dane (1972), and will not be repeated here.

B. Water and salt movement

An equation describing the simultaneous movement of water and salt in a one dimensional soil profile is:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} D(v) \frac{\partial C}{\partial x} - v_o \frac{\partial C}{\partial x} \quad [2]$$

where C is the total concentration of salt in the soil water, t is the time, x the distance along the sample, and v_o the pore water velocity. D is the apparent diffusion coefficient; it includes the effects of molecular diffusion, and dispersion caused by variations in pore water velocity within the sample. Its value is dependent upon the flow velocity within the sample (13).

The pore water velocity v_o is equal to the bulk flow velocity V divided by the volumetric water content θ . The value of V can be obtained from:

$$V = -K(\theta) \frac{\partial H}{\partial z} \quad [3]$$

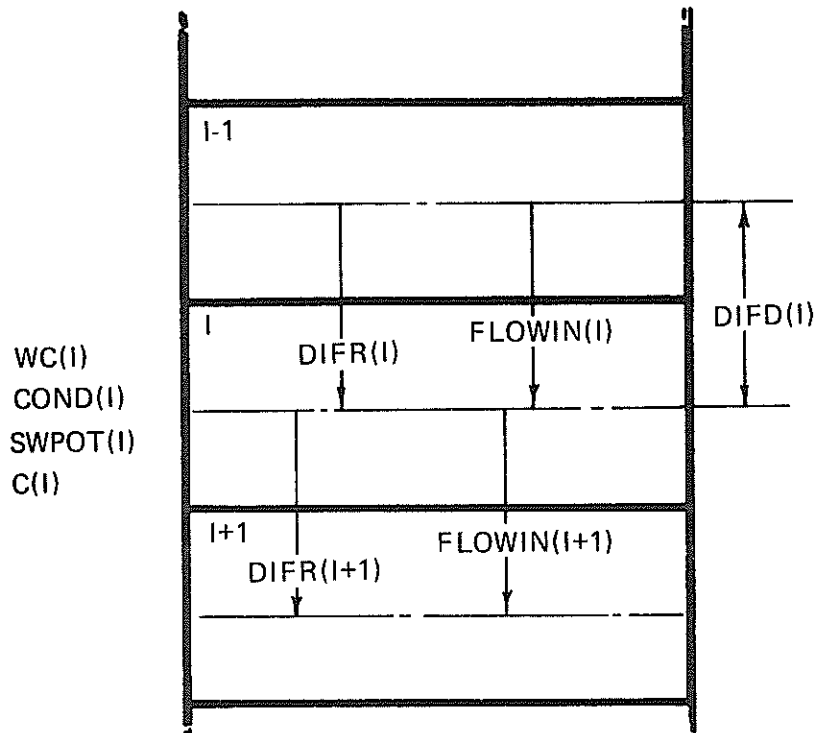
and is subject to:

$$\frac{\partial \theta}{\partial t} = - \frac{\partial V}{\partial z} \quad [4]$$

where θ is the soil water content, $K(\theta)$ is the hydraulic conductivity of the soil, and H is the soil-water pressure head.

The solution of equations [2], [3], and [4] is obtained by dividing the soil profile into a number of layers as was done for the water movement model discussed above. The chief mechanisms of salt movement are mass movement with the water, and diffusion resulting from concentration gradients between successive layers.

Dispersion due to nonuniform flow velocities within the soil is introduced by the dispersion coefficient D (See Figure 8).



$$\text{FLOWIN}(I) = [\text{SWPOT}(I-1) - \text{SWPOT}(I)] * \text{COND}(I) / \text{DIFD}(I)$$

$$\text{DIFR}(I) = D * [\text{C}(I-1) - \text{C}(I)] / \text{DIFD}(I)$$

$$\text{WC}(I) = \text{WC}(I) + \text{INTGRL}[\text{FLOWIN}(I) - \text{FLOWIN}(I+1)]$$

$$\text{C}(I) = \text{C}(I) + \text{INTGRL}[\text{FLOWIN}(I) * \text{C}(I-1) - \text{FLOWIN}(I+1) * \text{C}(I) + \text{DIFR}(I) - \text{DIFR}(I+1)]$$

Figure 8. Diagram of layers and the main CSMP statements for simultaneous movement of salt and water.

From the initial salt distribution within the soil, the salt concentration of each layer is known. The rate of salt diffusion into layer I is:

$$\text{DIFR}(I) = D * [C(I-1)-C(I)]/\text{DIFD}(I) \quad [5]$$

where D is a dispersion factor dependent on the bulk flow rate, C(I) is the concentration of layer (I), and DIFD(I) is the diffusion distance between layers I and I+1.

The salt transfer by mass movement into layer I is FLOWIN(I) times C(I-1), assuming downward flow. The net rate of transfer into layer I is:

$$\begin{aligned} \text{INFLOW}(I) = & \text{FLOWIN}(I) * C(I-1) - \text{FLOWIN}(I+1) * C(I) \\ & + \text{DIFR}(I) - \text{DIFR}(I+1). \end{aligned} \quad [6]$$

Integrating the net rate of transfer with respect to time and adding the resulting amount of salt to the amount of salt present in the layer at time t gives the salt concentration at time t + Δt. Figure 8 presents a simplified example of this salt and water movement model.

C. Pesticide movement

A general equation for the movement of an adsorbing chemical through soil is:

$$\frac{\partial S}{\partial t} + \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v_o \frac{\partial C}{\partial x} \quad [7]$$

where C is the concentration of the chemical in solution ($\mu\text{g}/\text{cm}^3$), S the amount adsorbed per gram of soil ($\mu\text{g}/\text{g}$), D the dispersion coefficient (cm^2/day), v_o the average pore water velocity (cm/day), ρ the bulk density (g/cm^3), θ the volumetric water content (cm^3/cm^3), x the distance in the direction of flow (cm), and t the time (days).

At high soil-water flow velocities, it is necessary to consider the rate of adsorption and desorption $\left(\frac{\partial S}{\partial t}\right)$.

A non-linear adsorption rate equation in which the energies of activation change with surface coverage during adsorption is (Lindstrom and Boersma, 1971):

$$\frac{\partial S}{\partial t} = k_2 \exp(bS) \left[\frac{k_1}{k_2} \exp(-2bS) C - S \right] \quad [8]$$

where k_1 and k_2 are the forward and backward kinetic rate coefficients ($1/\text{day}$), and b is similar to the surface stress coefficient ($\text{g}/\mu\text{g}$) described by Fave and Eyring (1956).

A second rate equation that has been used in the literature (Oddson et al. 1970) is:

$$\frac{\partial S}{\partial t} = \alpha (KC^N - S) \quad [9]$$

where α is a rate coefficient, N a coefficient usually assumed to be unity, and K the partition coefficient equivalent to k_1/k_2 in equation [8]. Equation [9] states that the rate of adsorption is proportional to the amount of adsorbing chemical left in solution.

Under equilibrium adsorption conditions, the adsorption relation is given by the Freundlich equation:

$$S = KC^N \quad [10]$$

Differentiation of equation [10] with respect to time gives:

$$\frac{\partial S}{\partial t} = K N C^{N-1} \frac{\partial C}{\partial t} \quad [11]$$

In many cases the adsorption-desorption reaction is non-reversible, and therefore the values of the parameters K and N depend on the direction of the reaction; i.e. whether $\partial S/\partial t$ is positive or negative. A combination of equations [8], [9], or [11] with the general transport equation [7] yields equations for the transport of adsorbing chemicals through soil. The complexity of these equations is such, however, that computer solutions are the only ones available.

As was the case with water and salt movement, the soil profile is again divided into layers. The flow of herbicide (HFLW) into and out of each layer per unit of time and unit surface area is calculated by means of the average pore water velocity (V_o), the water content (θ), the dispersion coefficient (D), and the herbicide concentration in each compartment at time t :

$$HFLW_i = [D *(C_{i-1} - C_i) + V_o * C_{i-1}] * \theta \quad [12]$$

where i is the index for depth ($i = 1, 2, \dots, n$). The net flux of herbicide into each compartment is:

$$NHFLW_i = HFLW_i - HFLW_{i+1} - ADSR_i * VOLL$$

$ADSR_i$ is the adsorption rate calculated at time t ($\mu\text{g}/\text{cm}^3/\text{day}$).
 $VOLL_i$ is the volume of each layer and is equal to $\Delta x \text{ AREA}$.

The net flow of herbicide per unit of time into each layer (NHFLW) causes a change in the amount of herbicide in each layer, $\Delta AMHLT_i$, where AMHLT is the amount of herbicide in each layer. The amount of herbicide at time $t + \Delta t$ in layer i is:

$$AMHLT_{t+\Delta t}^i = AMHLT_t^i + NHFLW_i * \Delta t \quad [13]$$

The adsorption rate is given by:

$$ADSR_i = RHO * \frac{\partial S}{\partial t}, \text{ where } \frac{\partial S}{\partial t} \text{ is given by equation [8], [9], or [11].}$$

A diagram of the computer program is presented in Figure 9. The amount of herbicide adsorbed in every layer is:

$$AMADS_{t+\Delta t}^i = AMADS_t^i + ADSR_i * VOLL * \Delta t.$$

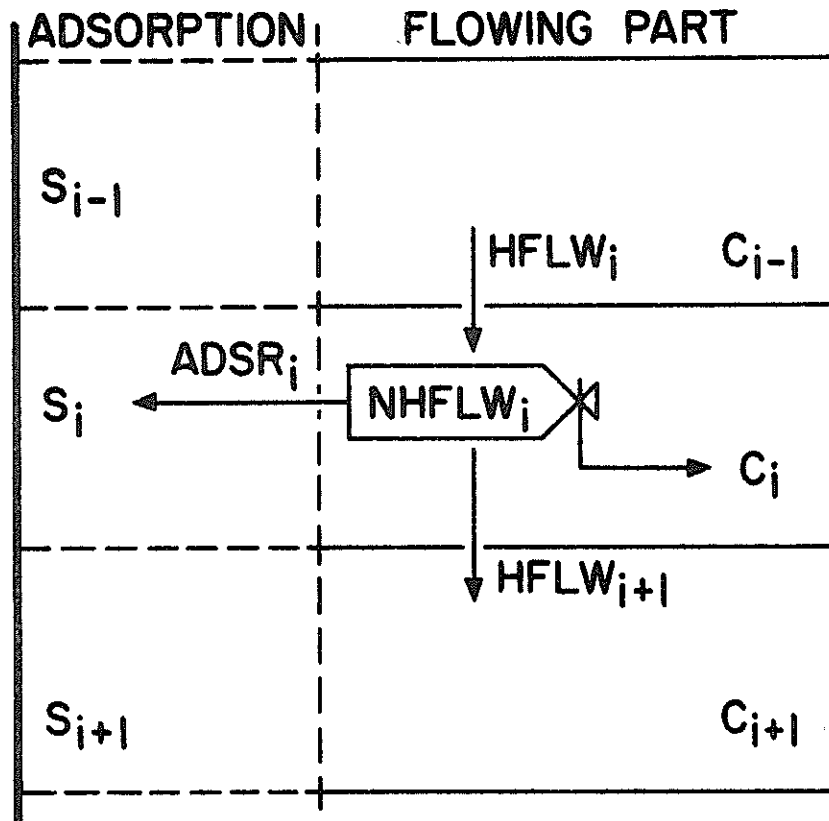


Figure 9. Diagram of CSMP model for pesticide movement in soil.

RESULTS AND DISCUSSION

A. Water movement

Observed and calculated water content distributions for uniform soil are presented in Figure 10. Water contents are given at 1.1 and 10.1 hours after irrigation with 10 cm water. Figure 11 shows observed and calculated water content distributions at 1, 4, and 44 days after irrigation. The calculations were based on hydraulic properties of the soil as determined during redistribution of the soil water, without taking into account hysteresis. Observed and computed water content distributions at 24 hours after irrigation of a layered soil column are presented in Figure 12. The water content distribution at 26 days after irrigation for this column is presented in Figure 13. Calculations were based on hydraulic properties of the layered soil determined during wetting and during drying, thus accounting for hysteresis. The dashed lines in Figures 12 and 13 are based on hydraulic properties determined during drying of the soil (curve D in Figure 6), and the dash-dotted lines on hydraulic properties determined during wetting of the soil (curve W in Figure 6). The solid lines were calculated from scanning curves (S curves) between the D curve and the W curve.

The results in Figures 10-13 show agreement between observed and calculated water contents in the two soil profiles. Calculation of the water contents, using hydraulic properties of the soil determined during wetting, appears to be the least satisfactory method. Calculations made for the uniform soil with hysteresis taken into account indicate that water content profiles during redistribution and drainage can be predicted using the main drying or the scanning curves.

In Figures 14 and 15, the measured and computed cumulative drainage is presented for uniform and layered soil, respectively. The data show that the use of the hydraulic properties of the soil determined during wetting resulted in overestimation of the amount of water drained from the columns, particularly for the uniform soil. Use of the hydraulic properties of the soil established during drying resulted in underestimation of the amount of water drained from the lysimeter columns. Calculations based on hysteresis in the soil-water properties gave good agreement for the uniform soil, but slightly low predictions for the layered soil profile.

The results show that with knowledge of the hydraulic properties of the soil, good estimates can be made of the soil-water content at various times after irrigation and the amount of water lost by percolation to the subsoil. Taking into account hysteresis in the hydraulic properties of the soil seems to improve the predictions of water-content

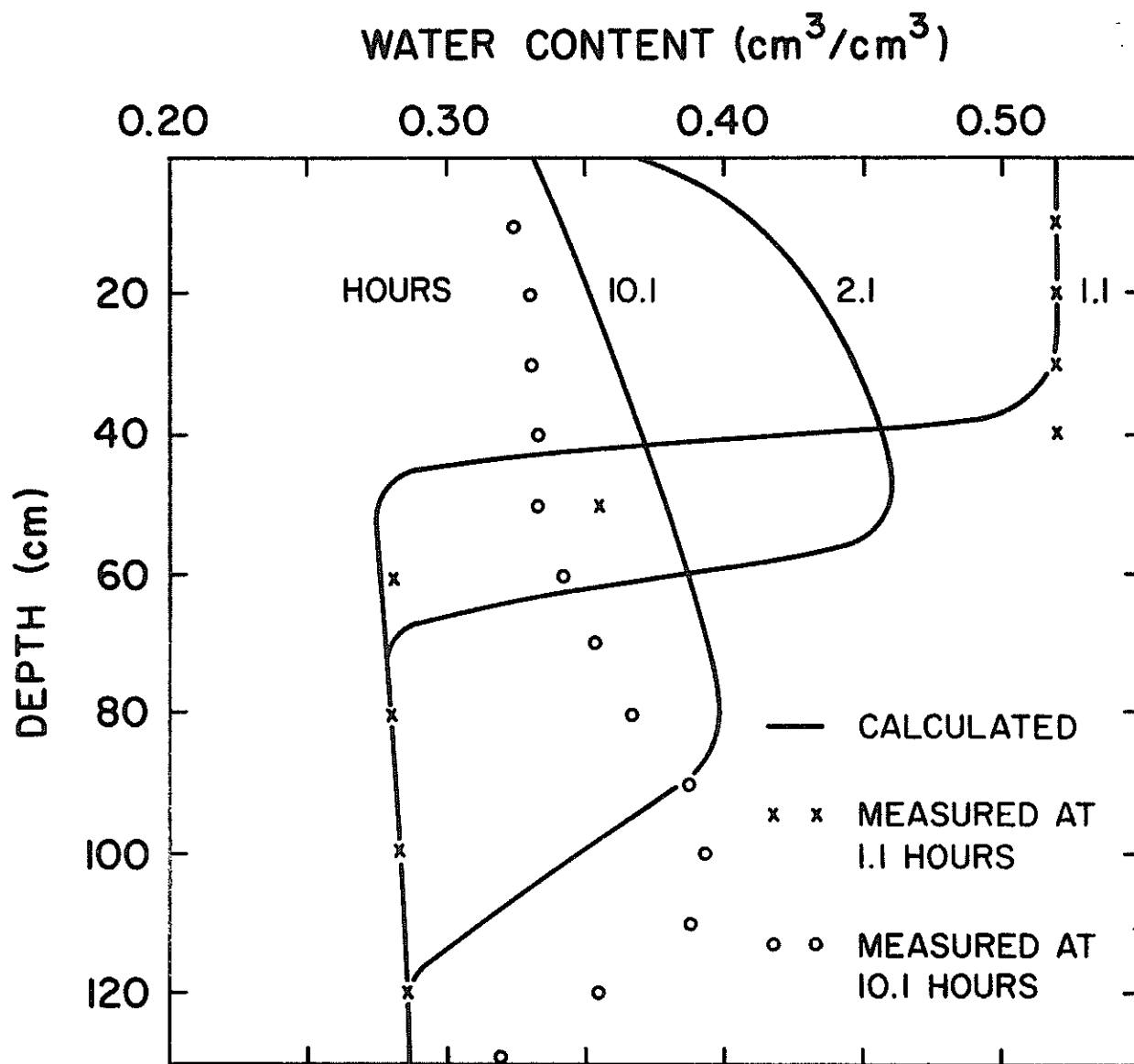


Figure 10. Observed and calculated water content distributions at 1.1 and 10.1 hours after irrigation of column II.

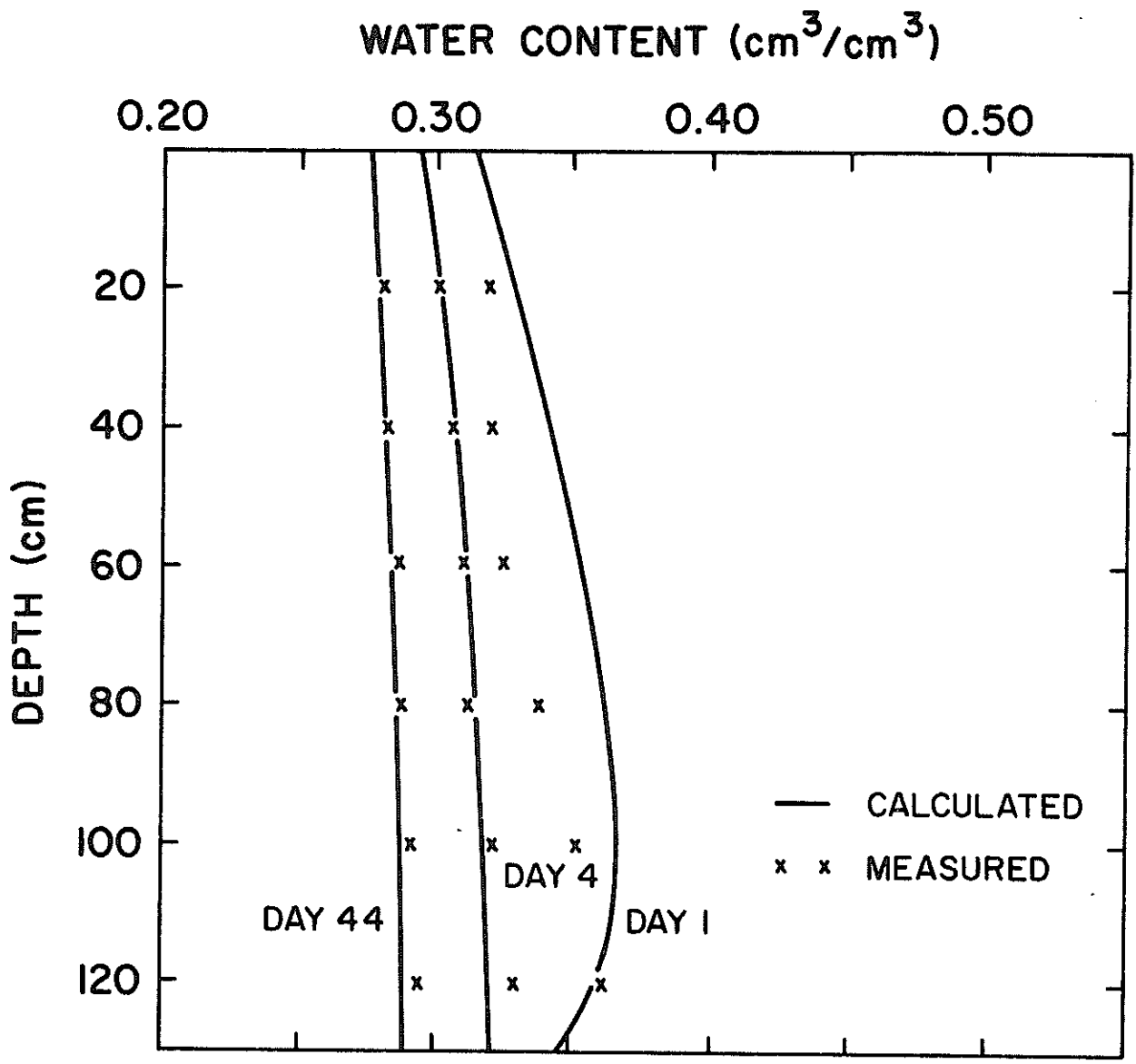


Figure 11. Observed and calculated water content distributions at 1, 4 and 44 days after irrigation of column II

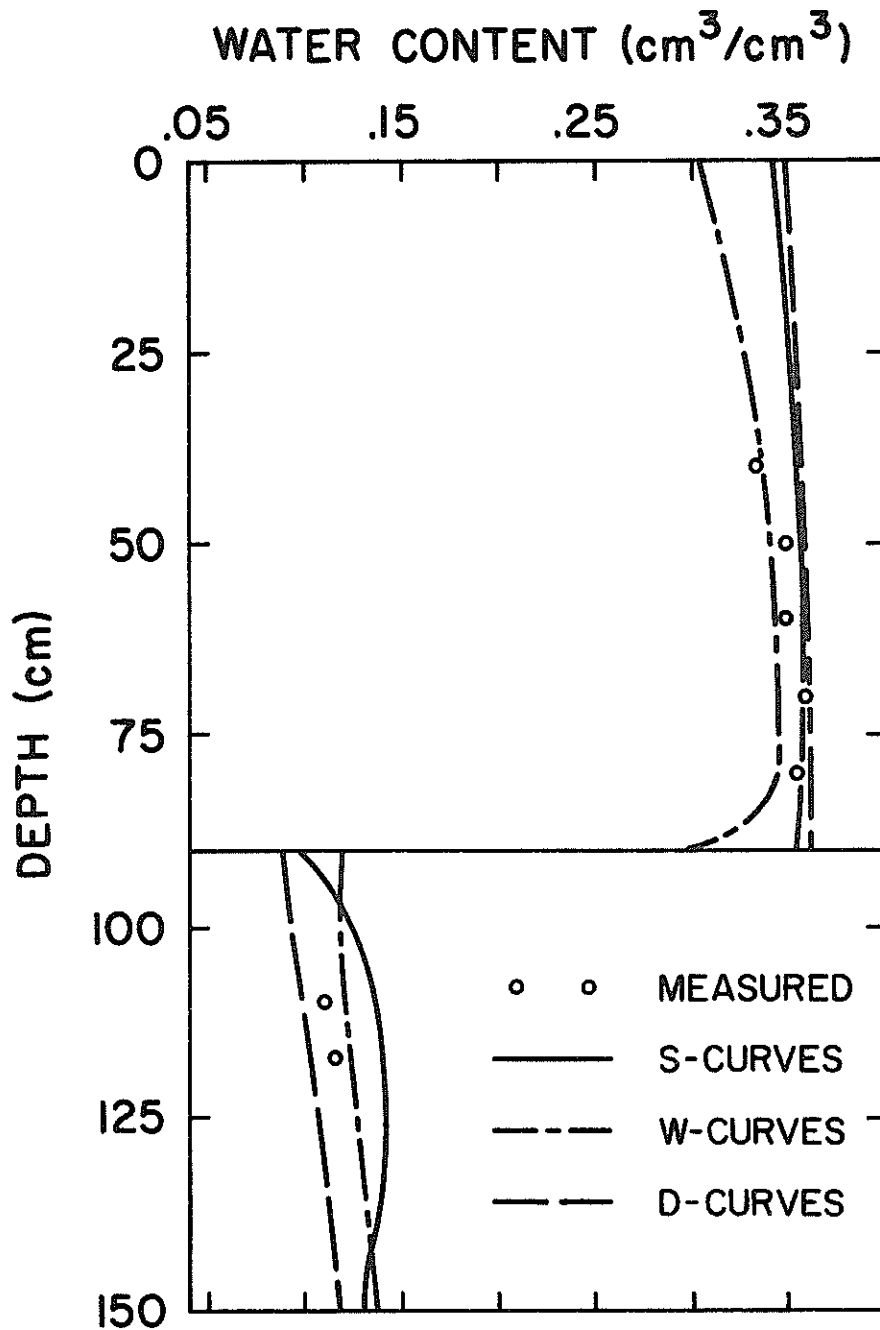


Figure 12. Measured and computed water content profiles 24 hours after irrigation of column III.

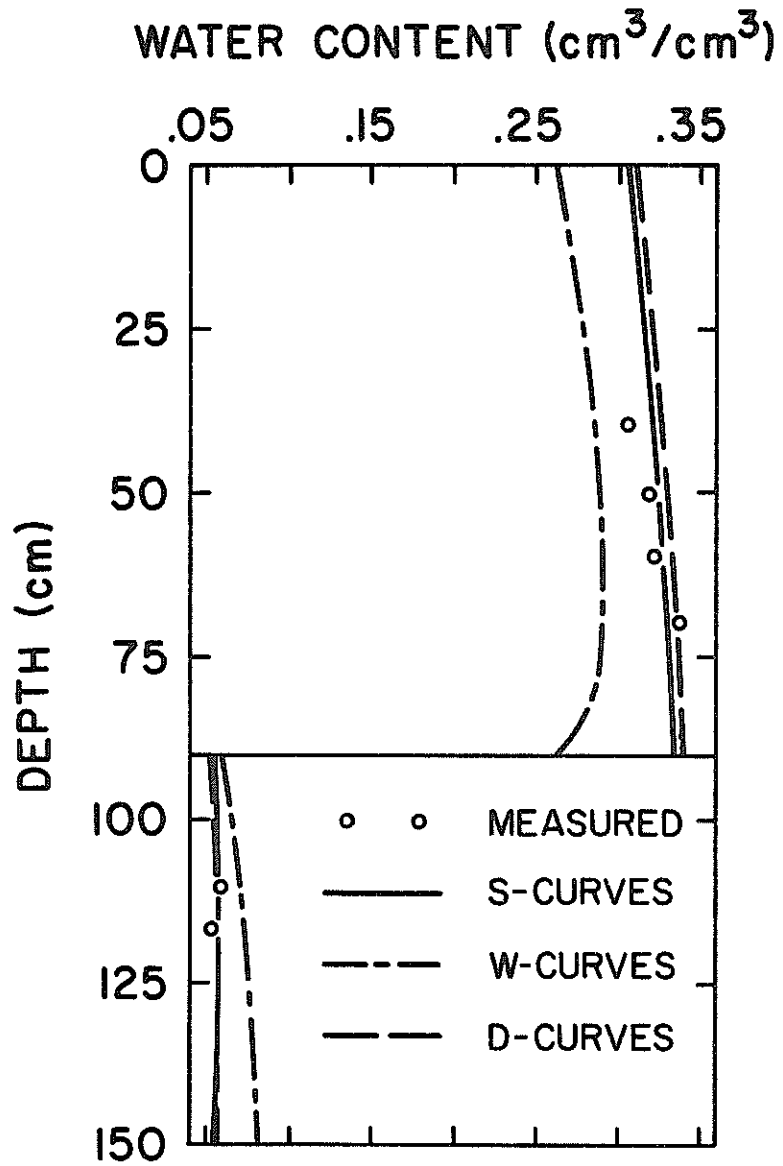


Figure 13. Measured and computed water content profiles 26 days after irrigation of column III.

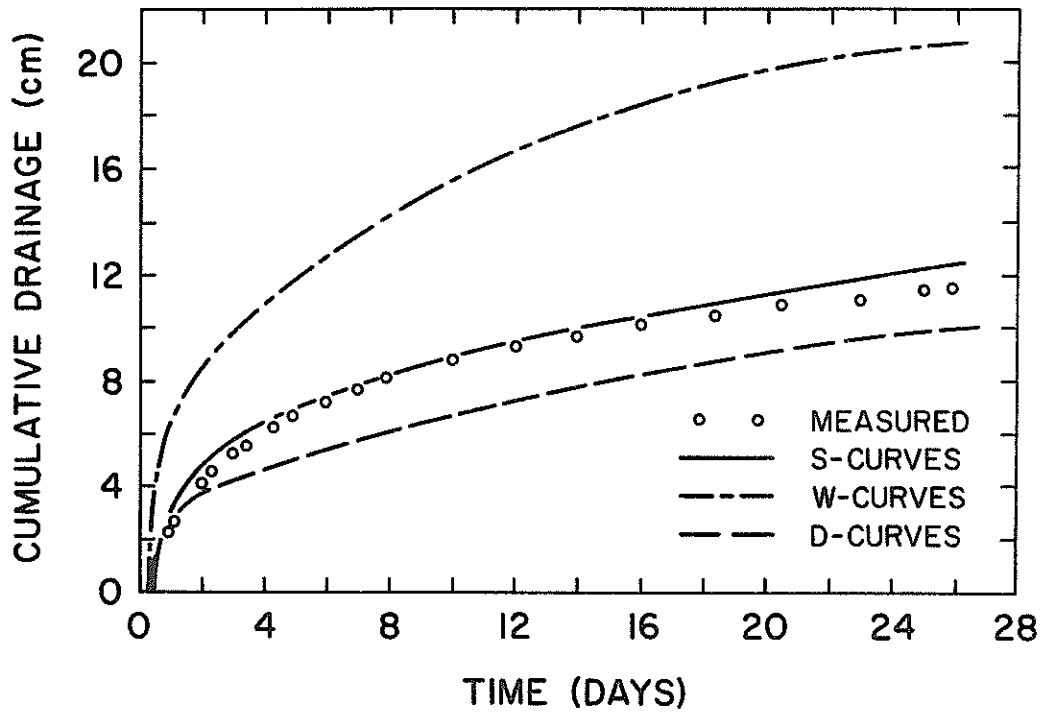


Figure 14. Measured and computed cumulative drainage from uniform soil column (column IV).

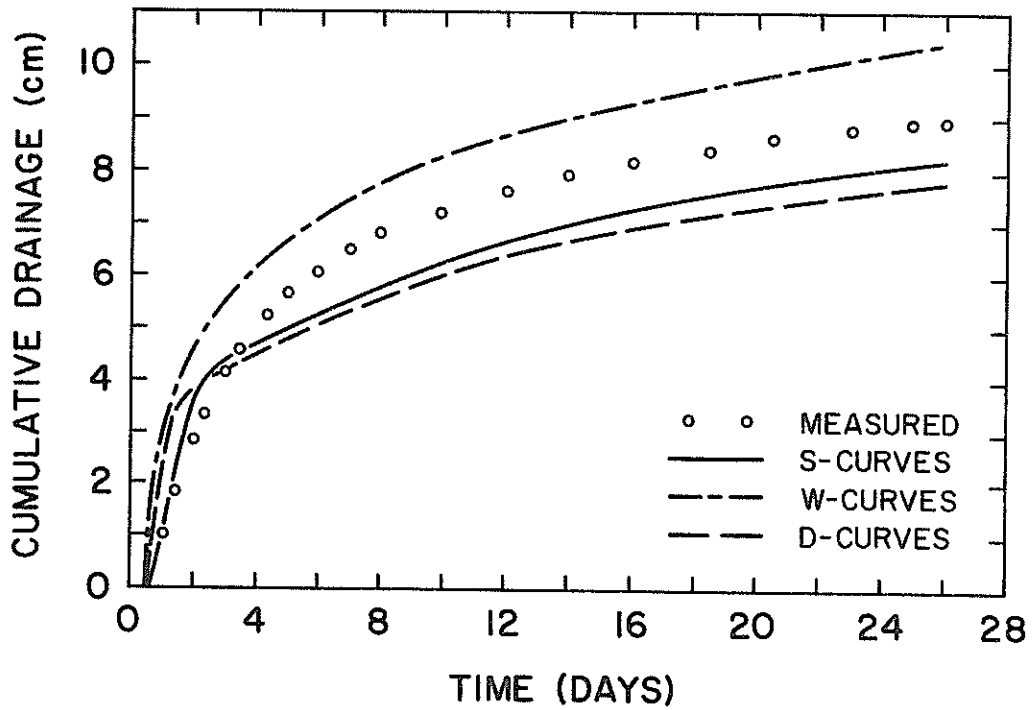


Figure 15. Measured and computed cumulative drainage from layered soil column (column III).

distribution and drainage rates. If no hysteresis data are available, use of the hydraulic properties determined during drying is preferable for prediction of redistribution and drainage in a soil after irrigation.

B. Salt movement

The salt distribution in columns I and II was determined during repeated irrigations with prepared irrigation water having an ionic composition as reported in Table 2. After each irrigation, samples of the soil solution were removed from the soil by applying a suction of about 500 cm of water for about one day. The results of the analyses of the samples taken after 2, 6, and 18 surface irrigations in column II (uniform soil) are presented in Figures 16-20. Except for the first irrigation during which 5 cm water was applied, all irrigations were with 45.6 liters of solution equivalent to 10 cm water.

Figure 16 shows the calcium distribution in the soil after 2, 6, and 18 irrigations with water containing 15 meq/l of calcium. It shows that introducing saline water rapidly increased the calcium concentration in the soil solution to about 20 meq/l of calcium. Upon further leaching of the soil, the calcium concentration in the soil solution gradually decreased to that of the applied irrigation water. The concentration of the magnesium in the soil solution (Figure 17) also rapidly increased to a maximum of about 6 meq/l and then started to decrease. The initial increase in Ca and Mg in the soil solution above the concentration of the irrigation water is apparently due to exchange of calcium and magnesium on the adsorption complex of the soil by sodium. Compared to calcium and magnesium, the sodium concentration of the subsoil in column II increased relatively slowly (Figure 18). Even after 18 irrigations (equivalent to about 3 pore volumes of water) the sodium concentration in the drainage water remained essentially constant. A large fraction of the added sodium exchanged for calcium and magnesium on the adsorption complex, while the remaining sodium stayed in soil solution.

The distribution of potassium ions after 2, 6, and 18 irrigations with water containing 3 meq/l of potassium is presented in Figure 17. It is clear from this figure that potassium does not move very readily in this soil. It appears that most of the potassium is strongly adsorbed, since changes in the amount of soluble potassium below 25 cm are very small. The concentration of potassium below 25 cm at first increased after irrigation with the prepared irrigation water, and then started to decrease upon further leaching. This behavior is similar to that for the other cations. By increasing the calcium, magnesium, and sodium concentration in the soil solution, potassium ions on the adsorption complex are replaced by calcium and sodium ions, thus increasing the amount of soluble potassium. Continued leaching of the soil reduces the amount of soluble potassium after this initial increase. Ganje and Page (1972) also noted an initial increase in potassium when leaching

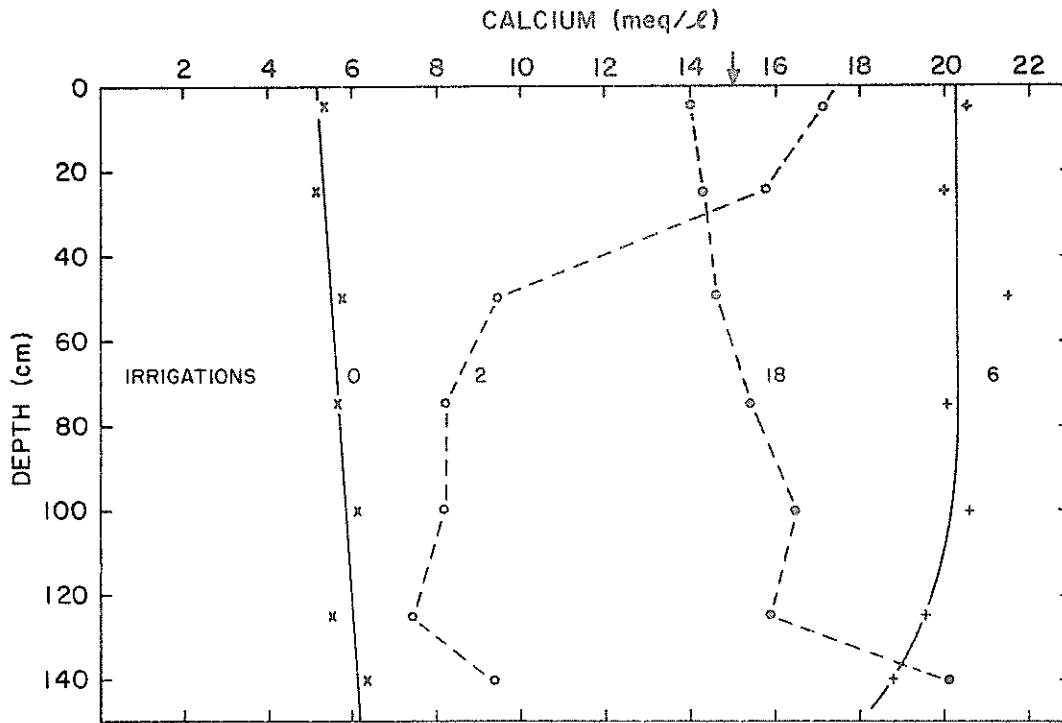


Figure 16. Calcium distribution in Column II before and after 2, 6, and 18 irrigations with water containing 15 meq/l of calcium.

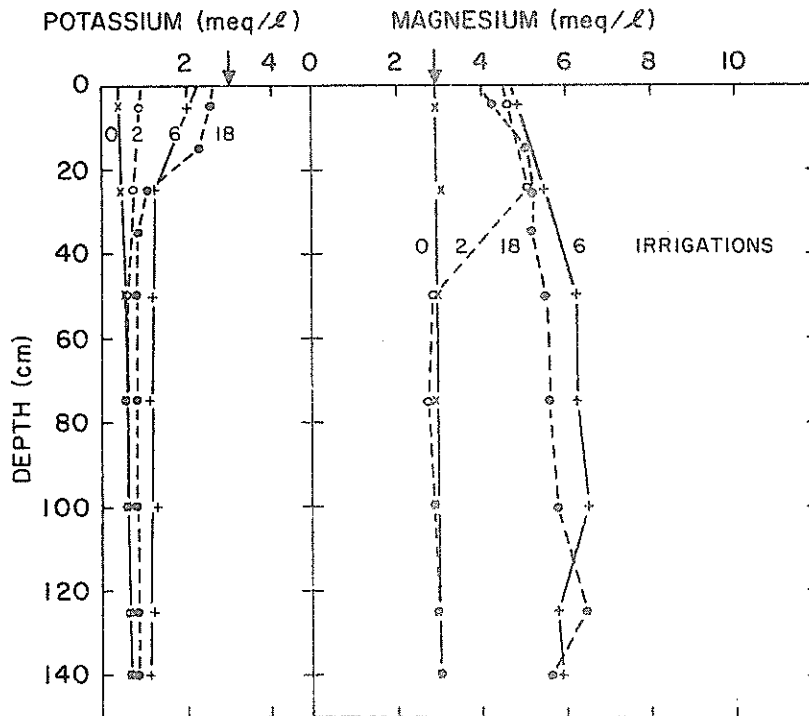


Figure 17. Magnesium and potassium distribution in column II before and after 2, 6, and 18 irrigations with water containing 3 meq/l magnesium and 3 meq/l of potassium.

soil columns with waters of different chemical composition, and a successive decrease. For two of their soils, they found that essentially all of the applied potassium remained close to the surface with very little loss by leaching. In one of the soils, however, potassium ions moved rapidly.

The chloride distribution before and after 2 and 6 irrigations is presented in Figure 19. A comparison of Figure 19 with Figures 16, 17, and 18 shows that chloride ions move very readily through this soil. After irrigation with 55 cm water or 250 liters, which is slightly less than one pore volume, the chloride concentration of the drainage water approximated the chloride concentration of the irrigation water. The chloride concentration after 18 irrigations is not presented since the irrigation water used between the 10th and 16th irrigations did not contain chloride, and as such these data are not comparable.

Figure 20 presents the sulfate distribution after 2, 6, and 18 irrigations. Sulfate moves considerably slower than chloride, probably due to precipitation of calcium or magnesium sulfate.

The bicarbonate concentration of the soil solution decreased considerably during leaching of the soil profile as evidenced in Figure 20. However, after 6 irrigations, observed changes in the bicarbonate distribution were small. The large initial decrease in bicarbonate concentration is probably due to precipitation of calcium or magnesium carbonate.

The phosphorus distributions in columns I and II following irrigation with water containing 190 ppm phosphorus are presented in Figures 21 and 22. In no case did soluble P exceed 1.0 ppm in any of the soil solution samples analyzed. There was a tendency for the soluble P concentration to remain relatively high (0.80 ppm) immediately following irrigation on column I at the shallow depths (Figure 21). Approximately one week after irrigation, however, soluble P at all depths in both columns was less than 0.1 ppm. Lack of equilibrium conditions immediately following irrigation may have been the cause of the temporarily high soluble P levels observed in column I. Results from subsequent irrigations (data not presented) also indicated initially high soluble P, but in no case were the high P levels noted below 15 cm. Insufficient volumes (due to the low moisture status of the soil) of samples taken some time after irrigation resulted in limited analysis of shallow samples. However, the data obtained indicated that once equilibrium was established, soluble P levels returned to their initially low values of <0.1 ppm in both columns after all three irrigations. The reasons for the restricted phosphorus movement in this soil are precipitation and adsorption. In Table 4 and Figure 23, the results of a phosphorus samples adsorption experiment for this soil are presented. In the adsorption study five gram samples of the soil were shaken with 100 ml of P solutions of various concentrations for 24 hours. Following equilibration, the soil suspensions were filtered to obtain a clear filtrate. The equilibrium P concentration was determined and the amount of adsorbed P obtained by difference.

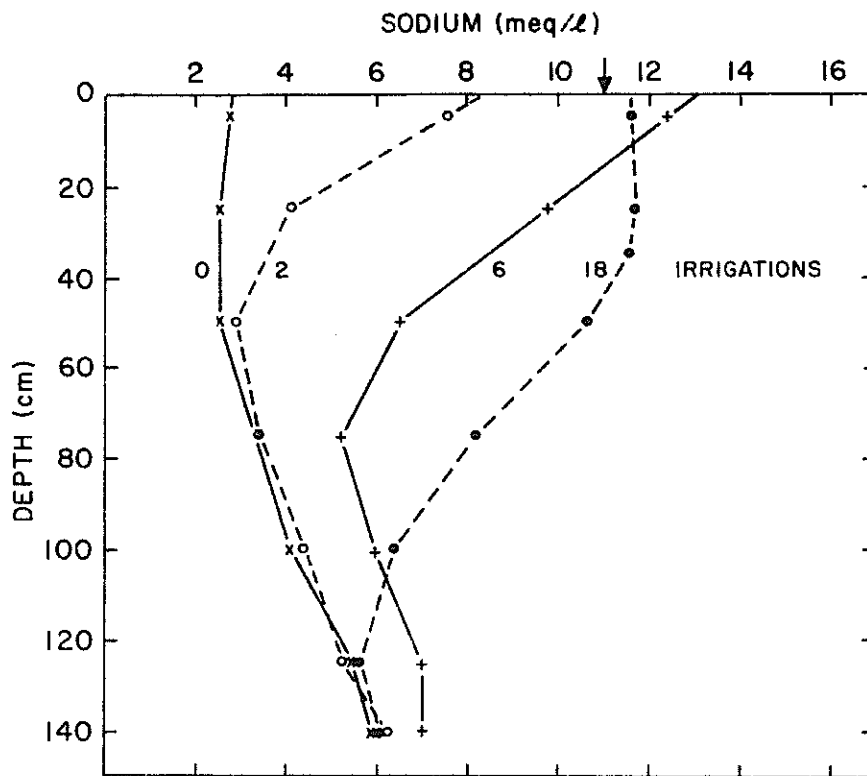


Figure 18. Sodium distribution in column II before and after 2 and 6 irrigations with water containing 2 meq/l of sodium.

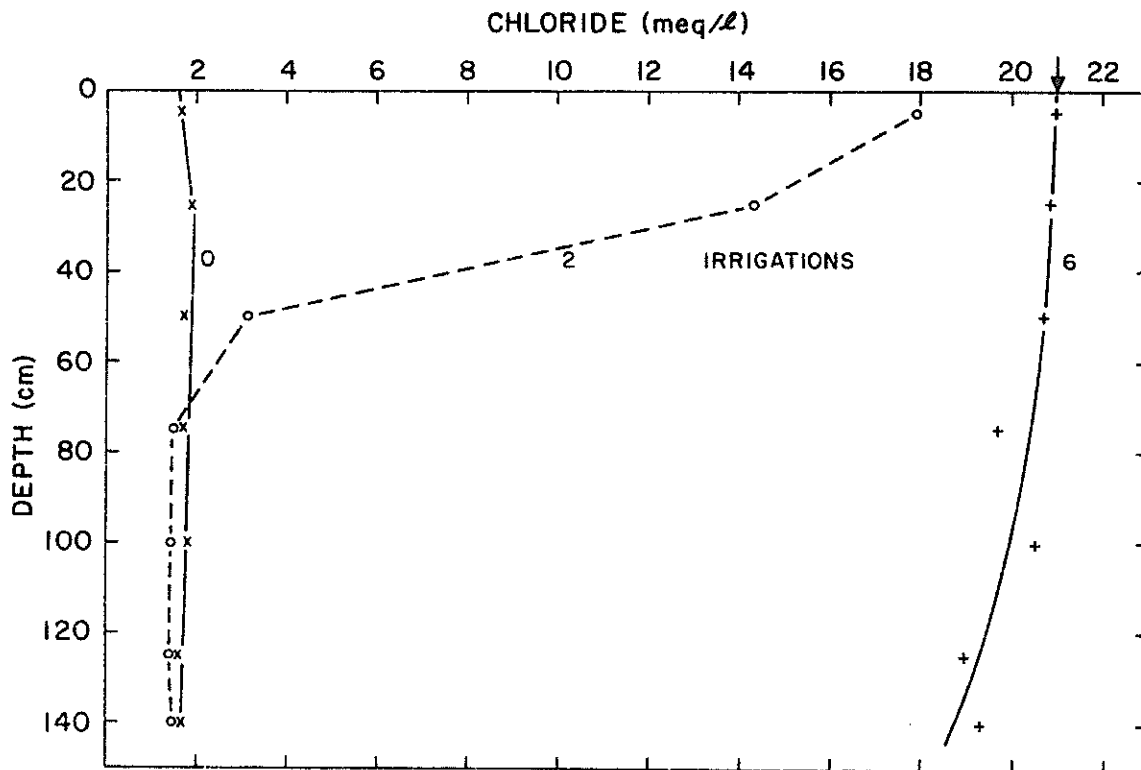


Figure 19. Chloride distribution in column II before and after 2 and 6 irrigations with water containing 2 meq/l of chloride.

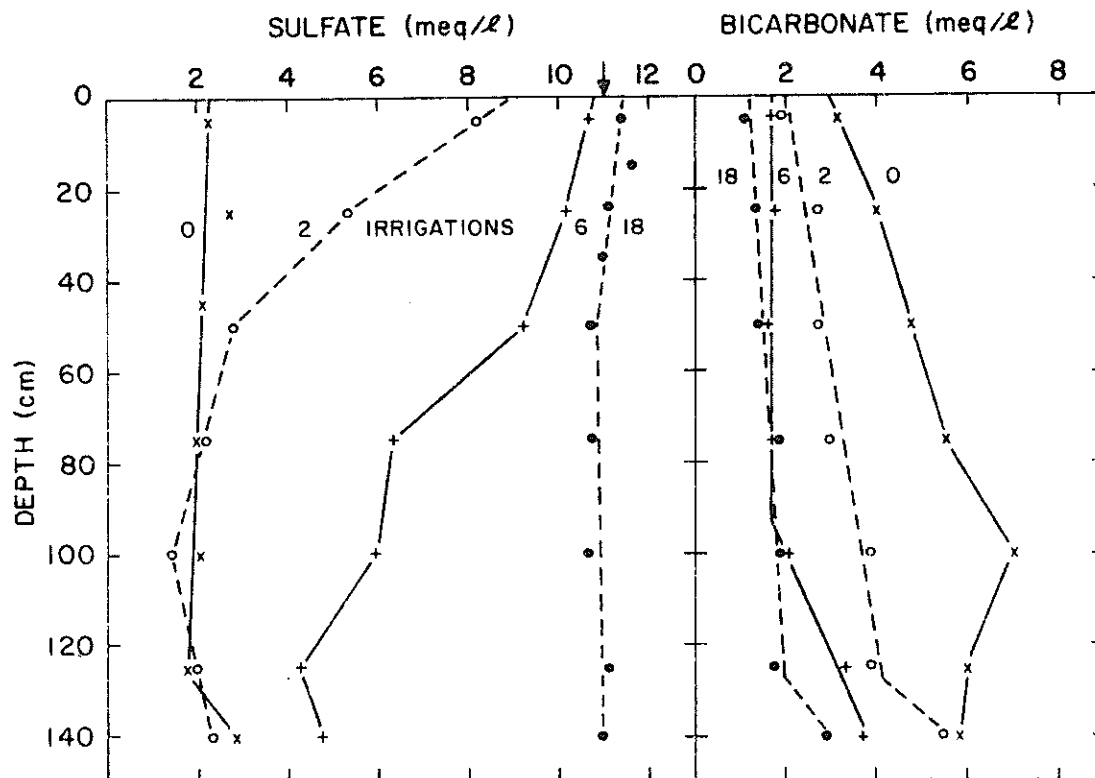


Figure 20. Sulfate and bicarbonate distribution in column II before and after 2, 6, and 18 irrigations with water containing 11 and 0 meq/l of sulfate and bicarbonate.

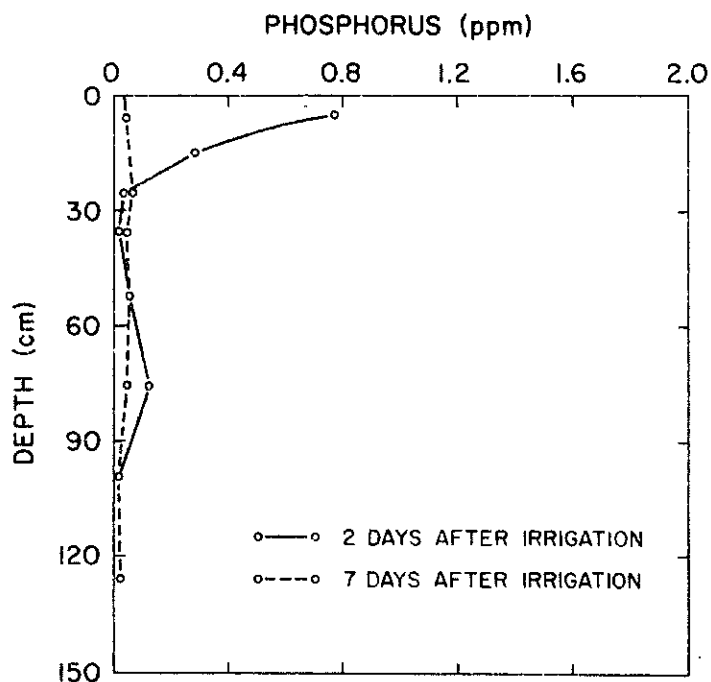


Figure 21. Phosphorus distribution in column I following irrigation with water containing 190 ppm phosphorus.

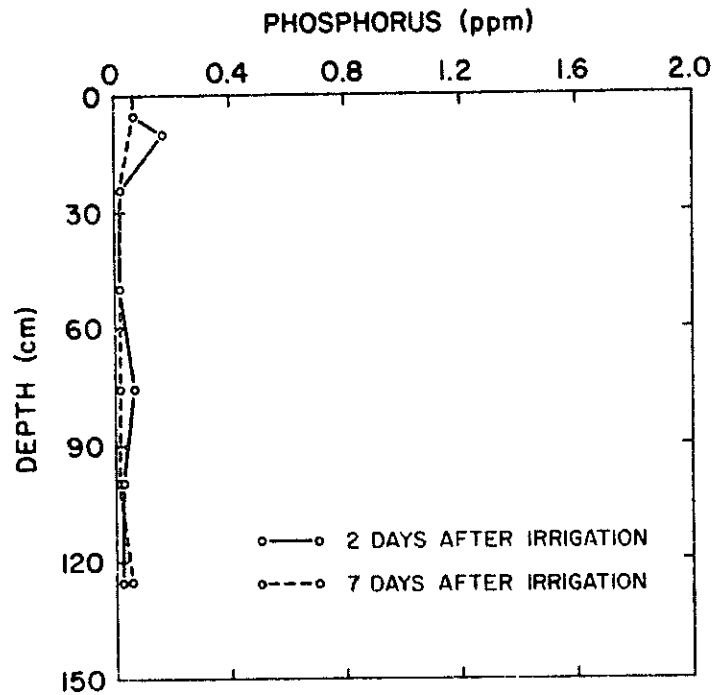


Figure 22. Phosphorus distribution in column II following an irrigation with 190 ppm phosphorus.

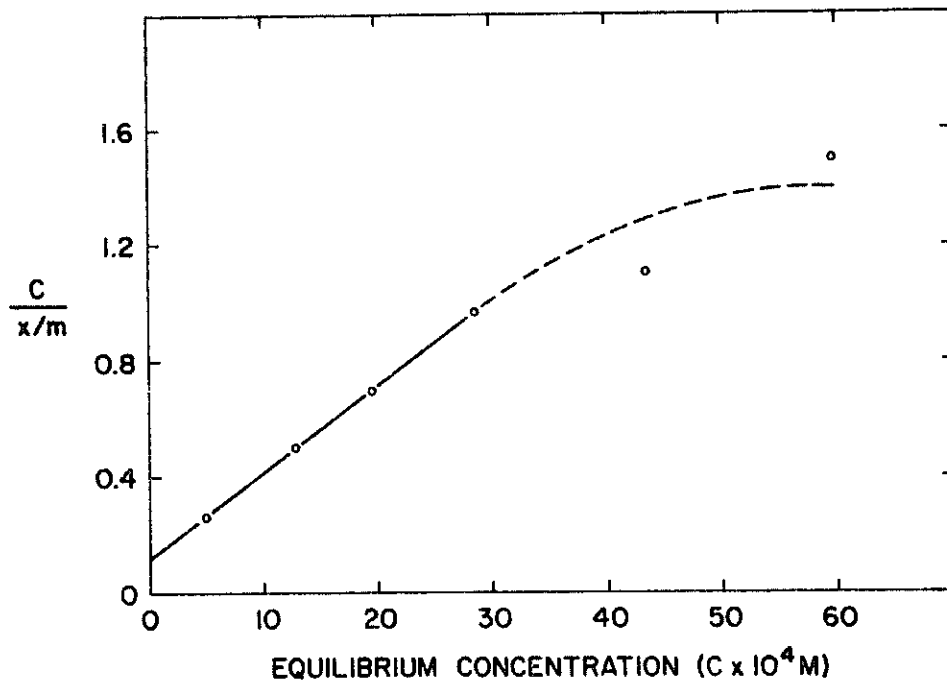


Figure 23. Phosphorus adsorption data for the Glendale soil according to the Langmuir isotherm.

Table 4. Data* for the P adsorption isotherm for the Glendale soil

<u>Initial Solution Concentration</u> ppm	<u>Equilibrium Solution Concentration (C)</u> ppm	<u>P adsorbed per 100g soil (x/m)</u> mg/100g	<u>C</u> x/m
204	185.0	38.0	1.5
157	133.9	36.5	1.1
102.5	88.0	29.0	0.97
73.3	60.0	27.0	0.71
50.0	39.4	21.3	0.50
25.0	15.5	19.0	0.26

* Each data point is the average of two replications.

The data in Table 4 were plotted according to the Langmuir isotherm so that the adsorptive maximum of the soil could be calculated. (The slope of the linear portion of the Langmuir isotherm is equal to the reciprocal of the adsorptive maximum.) The adsorptive maximum for the Glendale soil was calculated to be 333.3 $\mu\text{g/g}$ soil. On the basis of the adsorptive maximum of this soil, it was calculated that all of the soluble P added in each irrigation could be adsorbed on just 57 lbs of soil. Thus, adsorption alone could result in P movement being restricted to only 7.6 cm in the 150 cm lysimeters. Adsorptive sites, however, could become saturated in time so that P movement must be restricted by other reactions as well. These other reactions are most likely precipitation reactions resulting in the formation of insoluble calcium phosphates. The initial pH of our irrigation water was 4.75. Upon reaction with the calcareous Glendale soil, the pH likely increased to the soil pH of 7.9 and thereby removed most of the soluble P by precipitation.

C. Prediction of water and salt movement

Results of the column experiments set up in the laboratory to determine dispersion coefficients at different unsaturated water fluxes are presented in Figures 24 and 25. In these figures the ratio of the chloride concentration in the drainage water to the chloride concentration of the leaching solution is plotted versus the volume of effluent. Similar breakthrough curves were obtained for nitrate ions displacing chloride ions. The solid lines through the data points in Figures 24 and 25 were calculated using the computer model presented in section III b, and layer

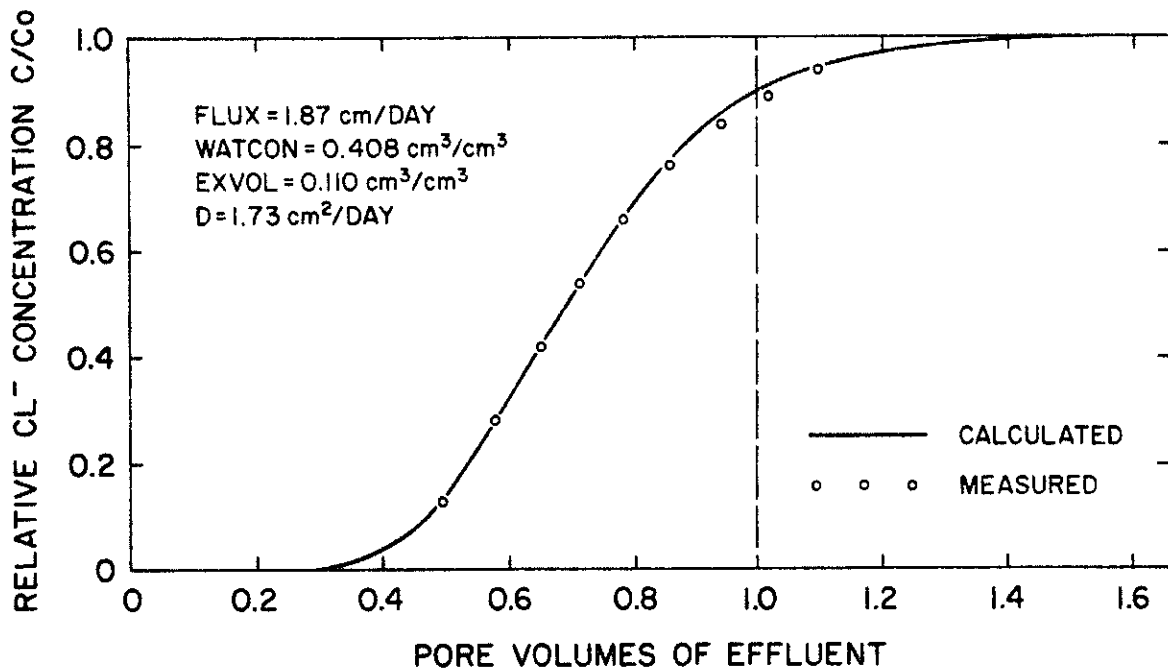


Figure 24. Relative concentration of chloride versus pore volumes of effluent for Glendale clay loam.

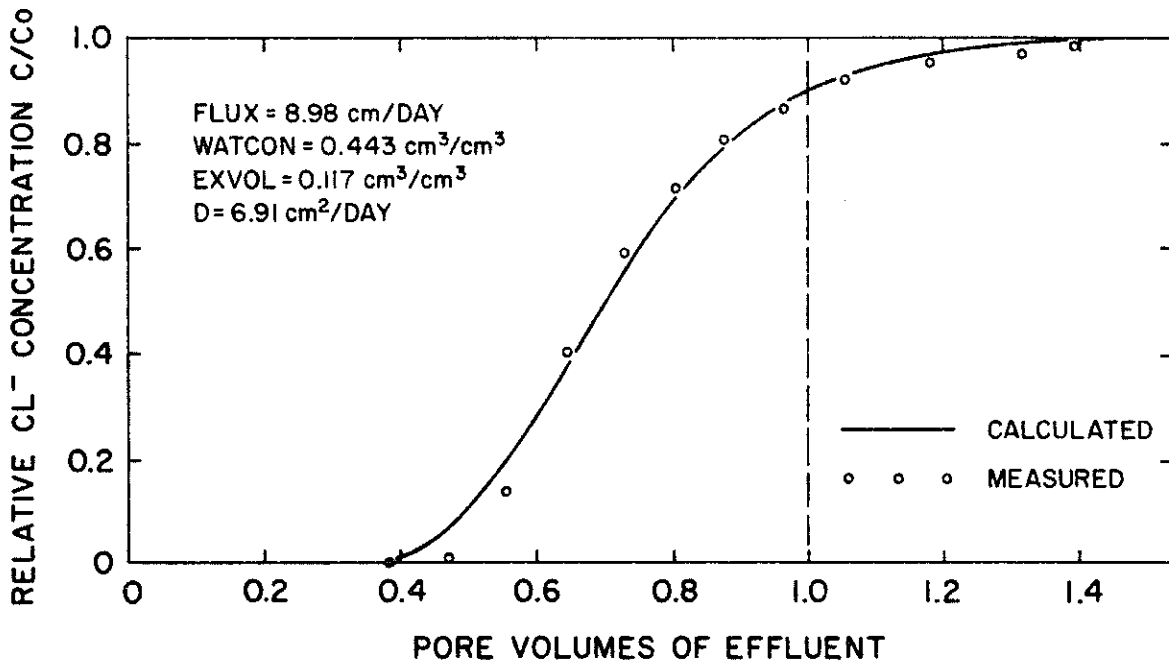


Figure 25. Relative concentration of chloride versus pore volumes of effluent for Glendale clay loam.

dispersion coefficients of 1.73 and 6.91 cm²/day, respectively. The vertical dotted lines in these figures indicate one pore volume: i.e. the total amount of water present in the columns during the displacement experiments. If the chloride or nitrate ions had behaved as perfectly noninteracting ions, the breakthrough curves would cross the vertical dotted lines close to C/Co = 0.5. However, in this soil, the breakthrough curves were displaced to the left, and the chloride ions appeared much earlier in the drainage effluent than would have been the case with noninteracting ions. This more rapid movement of chloride and nitrate through the soil is caused by negative adsorption and by the non-uniform velocity distribution of the water in the soil. The negatively charged ions are repelled by the negatively charged clay surfaces which results in a nitrate free volume around these clay particles. In very fine pores, where opposing walls are close together, the concentration of chloride ions would therefore be very low. In addition, the velocity of water in the fine pores is much slower than in the larger pores. Consequently the soil solution containing chlorides would move very slowly into and out of these pores. This latter effect is called here the "dead pore effect." At low fluxes, equilibrium is established over most of the soil during displacement, and the dead pore effect is small. At high soil-water fluxes the dead pore effect is relatively large and its contribution to the early appearance of chloride in the drainage water is significant.

In the computer model the results of negative adsorption and the dead pore effect are lumped together under exclusion volume (EXVOL in cm³/cm³). The exclusion volume in the model is given as a function of the chloride or nitrate concentration in the soil profile through the use of a non-linear function generator. This results in a continuous updating of the exclusion volume in the calculations as the chloride or nitrate front moves down the soil profile.

Figure 26 shows observed and computed chloride distributions in a lysimeter column at 2.5, 6.5, and 8.5 days after the start of continuous irrigation with water containing 22.4 meq/l chloride ions. The value of 3.6 cm²/day was obtained from the column experiments in the laboratory. From the data in Figures 24 and 25 it can be seen that the dispersion coefficient increased with increasing soil-water flux. By plotting the dispersion coefficient versus soil-water flux, a straight line through zero was obtained. From this straight line relationship a dispersion coefficient of 4.8 cm²/day was found at a flux of 3.6 cm/day as was used in the lysimeter column (Figure 26). A dispersion coefficient of 4.8 cm²/day with 1 cm layers is equivalent to a dispersion coefficient of 3.6 cm²/day with 2 cm layers, which were used in the calculations for Figure 26. Thus the dispersion coefficient of the lysimeter column could be estimated from dispersion coefficients determined in the laboratory. It therefore appears that the dispersion characteristics of the soil in the large lysimeters were similar to the dispersion characteristics of the soil in the small laboratory columns.

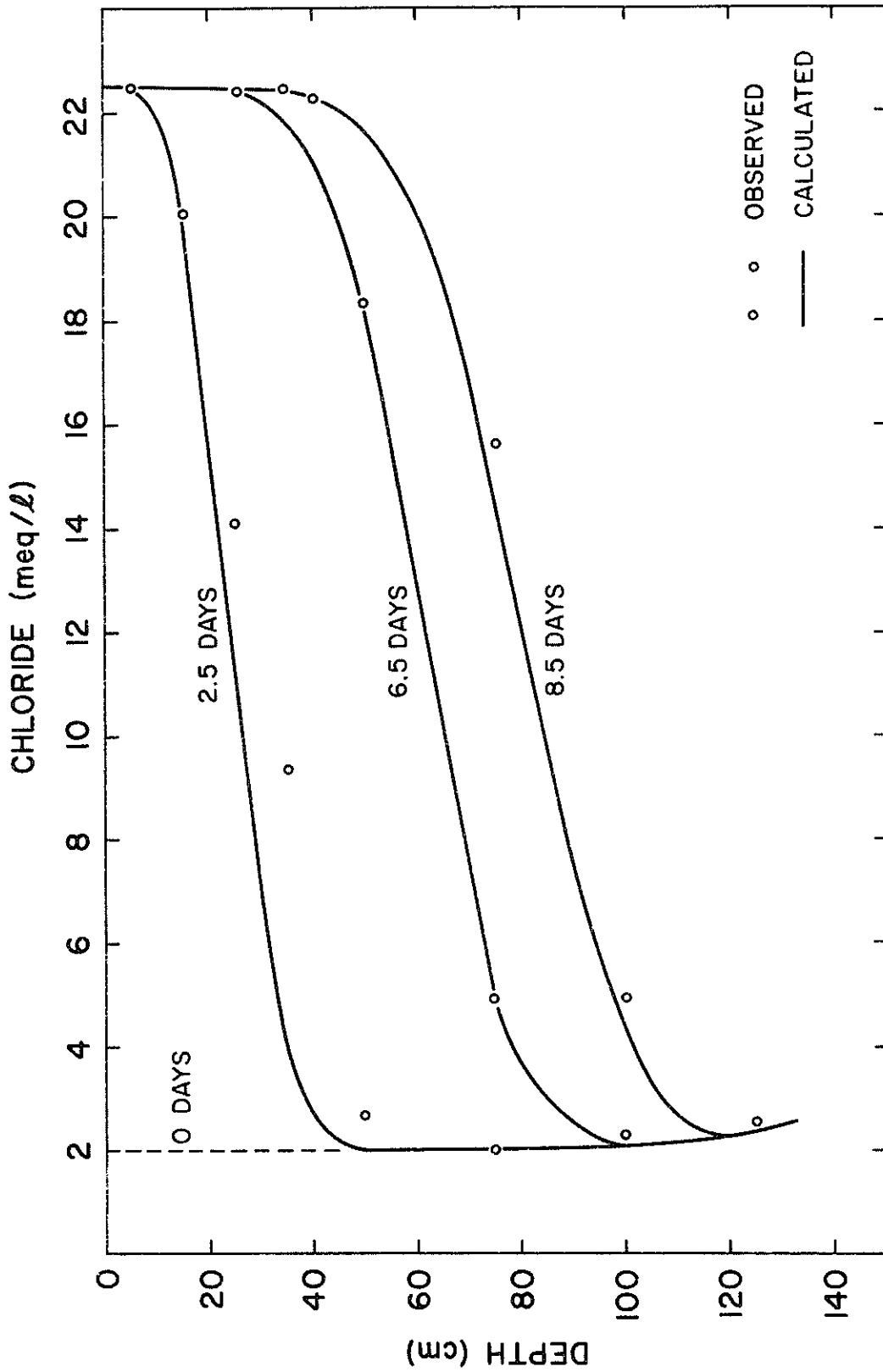


Figure 26. Observed and calculated chloride distributions in column II during leaching at steady state flow.

The discrepancy between observed and computed chloride distributions at 2.5 days after irrigation may be due to the method of removing samples from the soil column. Because of the relatively low hydraulic conductivity of the soil around the extraction cups in the soil, suction had to be applied for a period of up to 12 hours. When the salt front reaches a particular extraction cup, the soil solution is rapidly changing. As a result the solution which is collected over a 12 hour period, especially when the concentration is rapidly increasing, may not have the same concentration as the soil solution calculated at a specific point in time.

D. Pesticide movement

The distributions of 2,4,5-T following the second herbicide irrigation of columns I and II are given in Tables 5 and 6, respectively. Soil solution samples taken just prior to irrigation contained no measurable quantities of the herbicide which indicated that no herbicide remained from the first application made 8.25 months earlier. Unpublished data indicate that the six irrigations with non-herbicide irrigation water between the first and second herbicide irrigations would have been sufficient to leach the herbicide into samples collected from the bottom of the columns.

No herbicide was detected below the 35 cm depth in either column (Tables 5 and 6). Unpublished data for this soil indicate that a 10 cm irrigation transports non-interacting ions such as Cl⁻ to about the 50 cm depth. Hence, no herbicide would be expected below the 50 cm depth.

There was little difference in the herbicide distribution patterns in either column after 3 days. Forty-eight days after irrigation, however, the column irrigated with 40 ppm 2,4,5-T (column I) contained less than 1 ppm 2,4,5-T at the 5 and 15 cm depths, and no detectable herbicide at greater depths (Table 5). Column II, irrigated with 80 ppm 2,4,5-T, contained measurable quantities of herbicide even at the 35 cm depth after 48 days. The difference in herbicide distributions between columns was likely a result of the higher concentration of herbicide added to column II, and the difference persisted to the last sampling 58 days after irrigation.

Unpublished data from this laboratory indicate that adsorption reactions are complete after about 3-6 hours with this soil. The first sampling taken 3 days after irrigation therefore is indicative of equilibrium conditions with respect to adsorption. Also, the rate of downward movement of the water becomes very slow three days after irrigation. Therefore, a decrease in herbicide concentration at any particular depth following the 3 day sampling was attributed to herbicide degradation rather than to adsorption or downward movement of the herbicide. After 58 days, no 2,4,5-T was detected in column I and only small (3 ppm or less) amounts remained in column II. As solution 2,4,5-T is degraded and thereby removed from solution, adsorbed

Table 5. The concentration (ppm) of 2,4,5-T in column 1 following the second irrigation with 2,4,5-T (40 ppm).

Depth (cm)	Time after irrigation (days)			
	3	48	52	58
5	16	<1*	<1*	N
15	14	<1*	<1*	N
25	4	N	N	N
35	<1*	N	N	N
50	N	N	N	N
75	N	N	N	N
100	N	N	N	N
125	N	N	N	N
150 (bottom)	N	N	N	N

* Herbicide detected, but exact concentration not determined
(see text)

N No herbicide detected

Table 6. The concentration (ppm) of 2,4,5-T in column 2 following the second irrigation with 2,4,5-T (80 ppm).

Depth (cm)	Time after irrigation (days)			
	3	48	52	58
5	17	11	8	3
15	13	5	5	2
25	10	<1*	<1*	<1*
35	6	<1*	N	N
50	N	N	N	N
75	N	N	N	N
100	N	N	N	N
125	N	N	N	N
150 (bottom)	N	N	N	N

* Herbicide detected, but exact concentration not determined
(see text)

N No herbicide detected

2,4,5-T would be released in accordance with adsorption-desorption reactions and would be subjected to degradation as well. Hence, assuming equilibrium conditions, the very low solution 2,4,5-T concentrations present 58 days after irrigation are also indicative of very low adsorbed 2,4,5-T concentrations.

The distribution of solution 2,4,5-T in columns I and II following the third irrigation with 80 ppm 2,4,5-T is given in Tables 7 and 8, respectively. A total of 85 days separated the second and third irrigations and no herbicide was detected in samples taken just prior to the third irrigation.

The distribution pattern was similar in both columns although solution concentrations of 2,4,5-T were higher in column I than in column II 4 days after irrigation with the herbicide. Degradation was fairly rapid in both columns and was essentially complete 43 days after irrigation. Even 13 days after irrigation only low levels of 2,4,5-T (2 and 4 ppm for columns I and II, respectively) were found in solution.

Data from column II following both the second and third herbicide irrigations (Tables 6 and 8) are directly comparable since 80 ppm of 2,4,5-T was added in each irrigation. The data for the first sampling following irrigation (3 days after the second herbicide irrigation, and 4 days after the third herbicide irrigation) were similar at all depths. However, the data for longer time intervals (48 days after the second irrigation, and 43 days after the third irrigation) were quite different. Degradation was more rapid following the third herbicide irrigation presumably because of the presence of a larger microbial population capable of degrading 2,4,5-T that was induced by the herbicide in the second irrigation. The well documented "time-lag" necessary for microbial buildup was evidently greatly shortened after the third herbicide irrigation.

Data for the second irrigation were felt to represent what could be expected when 2,4,5-T is added to a soil not previously treated with the herbicide. Biological detoxification of the 80 ppm solution was complete in about 85 days. Herbicide was added in the first irrigation, but the 8.25 month interval between the first and second irrigations was probably sufficient to greatly reduce the effect of any microbial population that developed during the first herbicide treatment. Apparently, herbicide applied only once yearly would degrade at the same rate as the initial application of 2,4,5-T.

Data for the third irrigation were thought to represent what could be expected when 2,4,5-T is applied repeatedly to a soil at relatively short intervals. Biological detoxification of the 80 ppm solution was essentially complete in about 45 days. The rapid degradation observed in this instance would likely protect groundwater supplies against 2,4,5-T pollution.

Table 7. The concentration of 2,4,5-T (ppm) in column I following the third irrigation with 2,4,5-T (80 ppm).

Depth (cm)	Time after irrigation (days)			
	4	13	27	43
5	30	2	1	<1*
15	15	<1*	N	N
25	6	<1*	N	N
35	<1*	N	N	N
50	N	N	N	N
75	N	N	N	N
100	N	N	N	N
125	N	N	N	N
150 (bottom)	N	N	N	N

* Herbicide detected, but exact concentration not determined
(see text)

N No herbicide detected

Table 8. The concentration of 2,4,5-T (ppm) in column II following the third irrigation with 2,4,5-T (80 ppm)

Depth (cm)	Time after irrigation (days)			
	4	13	27	43
5	20	4	2	<1*
15	7	1	N	N
25	5	N	N	N
35	3	N	N	N
50	<1*	N	N	N
75	N	N	N	N
100	N	N	N	N
125	N	N	N	N
150 (bottom)	N	N	N	N

* Herbicide detected, but exact concentration not determined
(see text)

N No herbicide detected

The degradation rates observed herein are probably the maximum rates that could be expected due to the highly favorable environmental conditions in the lysimeters. The concentration of 2,4,5-T applied, however, was unrealistically high (equivalent to about 64 kg/ha) as compared to the normal agricultural application rates (about 1-2 kg/ha). Therefore, proper application of 2,4,5-T at normal application rates should not constitute a pollution hazard.

Figure 26 shows the adsorption and desorption isotherms for 4-amino-3,5,6-trichloropicolinic acid (picloram). The data in Figures 26 and 27 were made available by Dr. J. M. Davidson, Department of Agronomy, Oklahoma State University, for the purpose of testing the computer models developed in this project. The calculated lines are based on the Freundlich equation (equation [10]) and on the non-linear adsorption equation derived from equation [8], respectively. Both type of equations seem to fit the data reasonably well.

The hysteresis between adsorption and desorption is evident, which indicates that adsorption and desorption are non-reversible processes. Unpublished data from this laboratory and others also show hysteresis in the adsorption-desorption process of many pesticides. The effects of hysteresis on the displacement of picloram is shown in Figure 27. The symbols are data points. The solid line was calculated with the computer model based on equations [7] and [10], and with hysteresis in the adsorption-desorption process. The dashed line was calculated with the computer model using equations [7] and [10], but without hysteresis in the adsorption-desorption process. The presence of hysteresis causes the peak concentration to be considerably lower; it also results in considerable tailing of the effluent curve.

The calculated effluent curves in Figure 27 are based on equilibrium conditions in the soil column during displacement. When the soil water flux was considerably higher than in Figure 27, the difference between observed and computed curves was much greater. At high soil water fluxes, true equilibrium conditions do not exist. The use of the rate equations (equation [8] and [9]) in the computer model gave some improvement over the use of the equilibrium solution, but no equation was entirely satisfactory for describing pesticide movement through soil.

At high pore-water velocities, the flow of water with its solute through the relatively large pores is enhanced. Hence a change in the pore-water velocity distribution occurs. This creates a relatively mobile part, where the water moves with a velocity higher than the average, and a relatively immobile part of the soil-water system. This immobile part may include excess dead end pores, the interior of aggregates, and some very slow-moving small pore channels. The bulk of the chemical moves through the mobile part, while the presence of solute in the immobile part is highly dependent upon molecular diffusion, convection, and consecutive adsorption. During the displacement a quantity of solute will be shunted

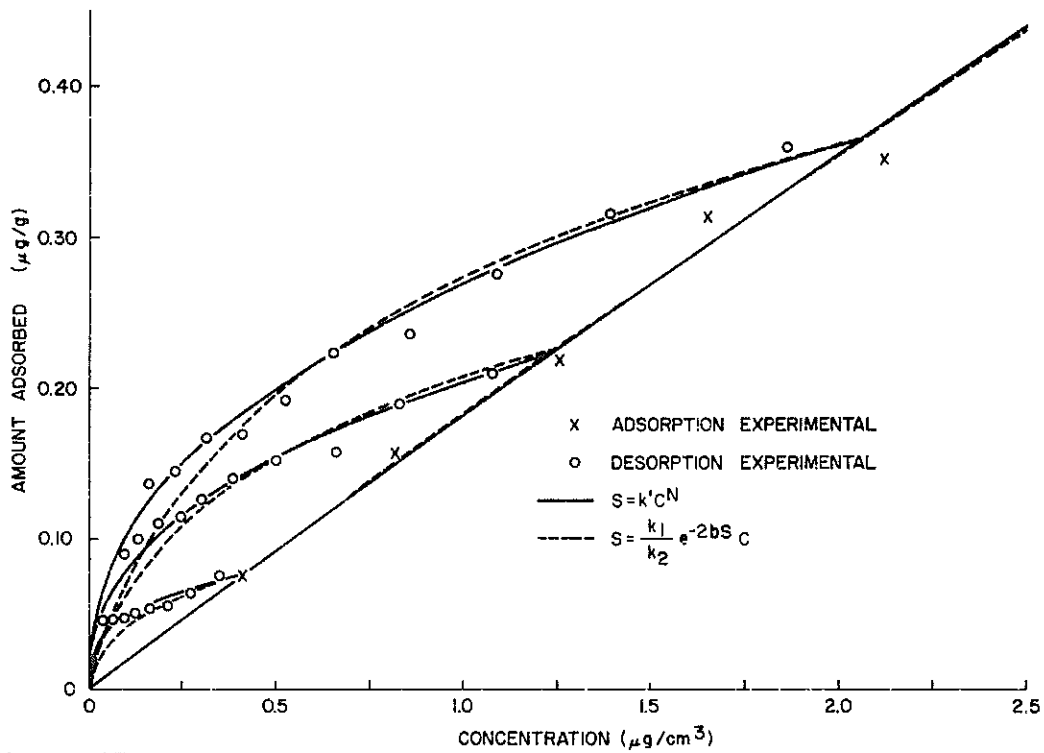


Figure 27. Adsorption and desorption isotherms for picloram in Norge loam.

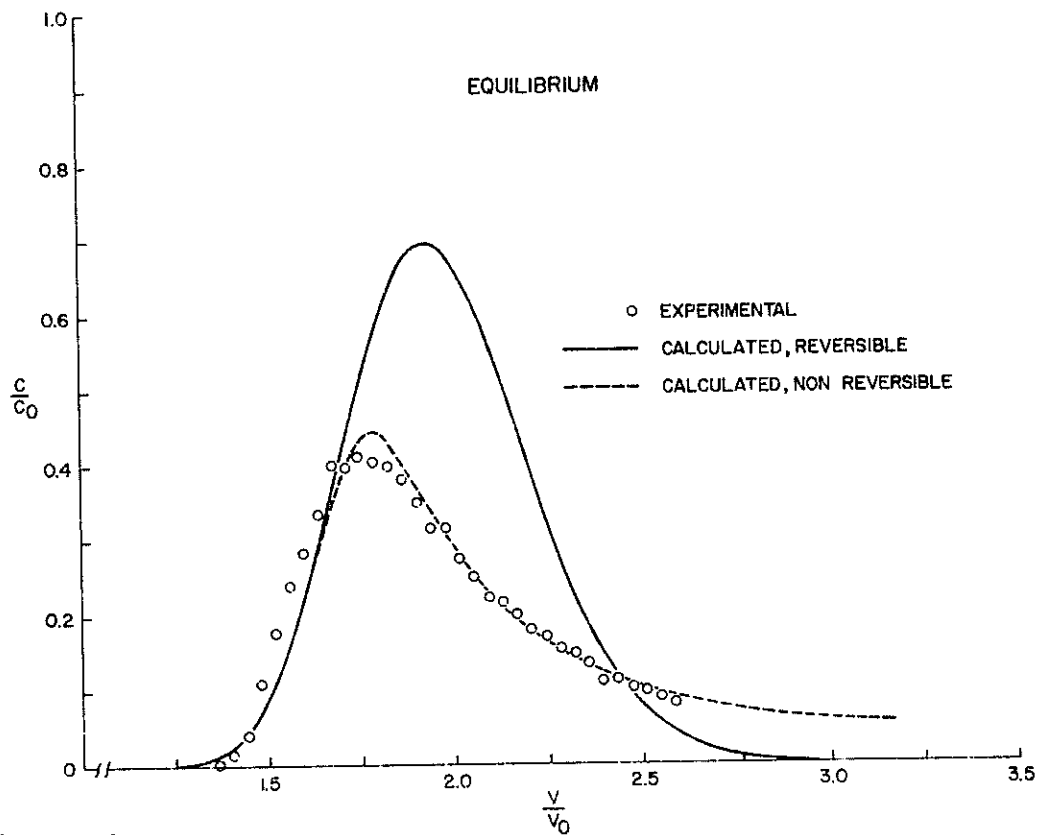


Figure 28. Observed and computed effluent curves for picloram movement through Norge loam.

into this immobile part. The release during the trailing period of the displacement period may be much slower than its capture. The continuous desorption of the chemical from this immobile part may act as a source for a relatively long time period. No adequate model is as yet available to describe the above phenomena.

At low soil water velocities the use of an equilibrium equation, or of the two rate equations (equations [8] and [9]), is satisfactory for predicting movement of pesticides through soil.

At high velocities dispersion, anion exclusion, dead pores, and diffusion into aggregates apparently become important. The result is that agreement between observed and computed breakthrough curves is poor, since a physical model to account for all these phenomena is not yet available.

E. Calcium and magnesium equilibria

In Figures 29 to 34, the calcium, magnesium, and sodium concentrations in the drainage water from six 60-cm long soil columns were plotted versus pore volumes of effluent. The water content of the soil in the columns during leaching was below saturation and estimated at $0.48 \text{ cm}^3/\text{cm}^3$. This means that one pore volume of effluent was equal to 1300 ml. The average flux of water through the columns was 3.75 cm/day for the duration of the experiment: i.e. for more than two years. Columns 1 and 2, 3 and 4, and 5 and 6 behaved identically. Therefore, only the results of columns 1, 4, and 5 were plotted.

Prior to introduction of the first leaching solution (Ca:Mg = 5:1; see Table 3) all columns were leached with deionized water. Equilibrium, as indicated by a constant effluent composition, was attained after leaching with 10 pore volumes of deionized water. Leaching was continued, however, until a total of 18 pore volumes of deionized water was applied.

Introduction of the first irrigation solution in columns 1 and 2 (Ca/Mg = 5, and zero sodium) resulted in a relatively rapid increase in the effluent concentrations of calcium and magnesium due to the addition of these salts (Figure 29). Approximate equilibrium was attained after about 20 pore volumes had passed through the columns. Solution concentrations of Na first increased due to replacement of exchangeable Na by Ca and Mg, and then decreased as Na was leached from the columns.

Figure 30 shows the changes in effluent concentration upon leaching column 4 with calcium and magnesium in a 5:1 ratio, and 7.5 meq/l Na. Solution Ca increased fairly rapidly to a maximum value of 24 meq/l and then approached an apparent equilibrium value of 19.89 meq/l (see Table 8). Solution Mg also showed the initial increase in concentration followed by a slower decrease to an average equilibrium value of 3.81 meq/l. While

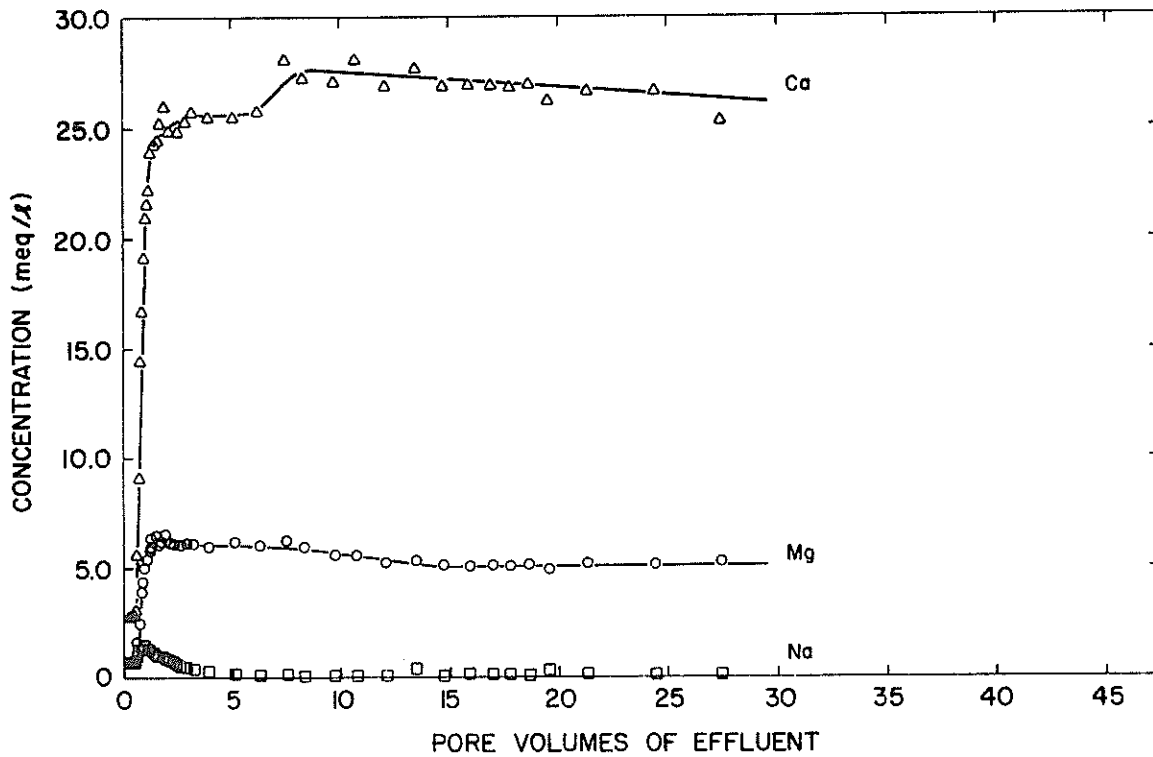


Figure 29. Calcium, magnesium, and sodium concentrations versus pore volumes of effluent upon leaching with a solution having Ca/Mg=5, and 0 Na.

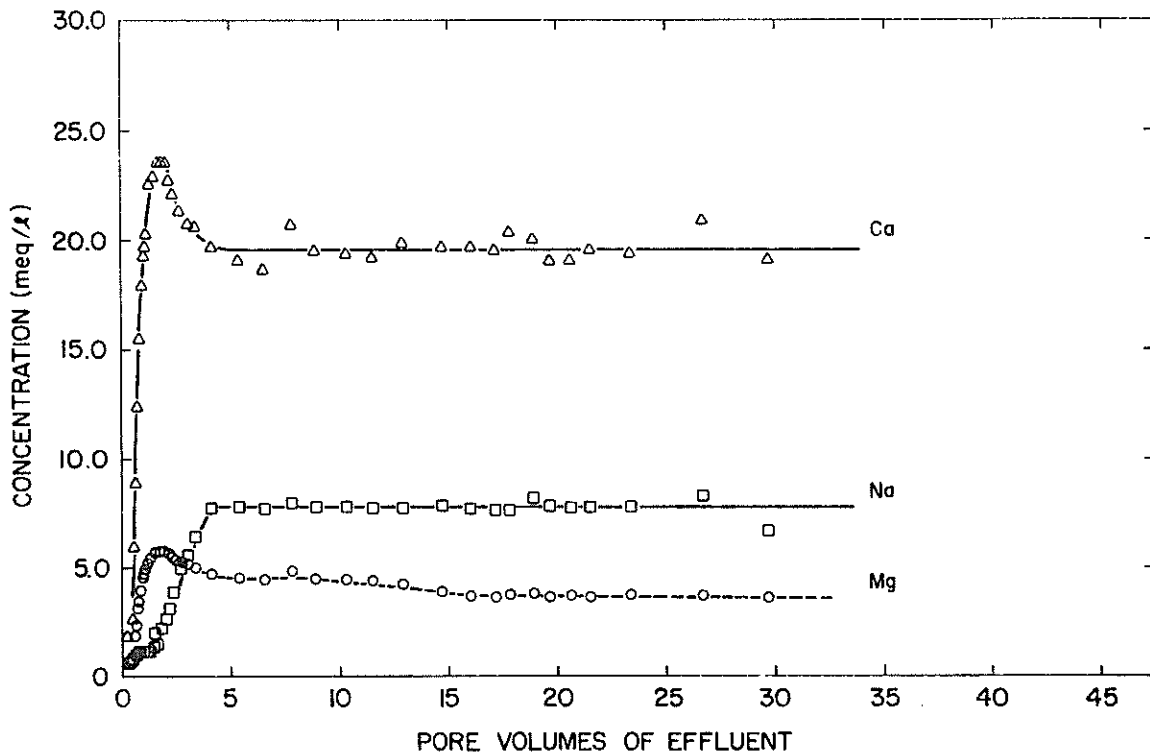


Figure 30. Calcium, magnesium, and sodium concentrations versus pore volumes of effluent upon leaching with a solution having Ca/Mg=5, and 7.5 meq/l Na.

Mg and Ca were increasing initially, solution Na did not change much, indicating that Na was replacing exchangeable Ca and Mg rather than increasing in solution. The increases in Ca and Mg concentration above the concentrations of these ions in the leaching solution represented exchangeable Ca and Mg brought into solution by Na. Equilibrium was attained with respect to all three cations after about 16 pore volumes of solution had leached through the columns.

Figure 31 shows the changes in effluent concentration upon leaching column 4 with calcium and magnesium in a 5:1 ratio, and 7.5 meq/l Na. Solution Ca increased fairly rapidly to a maximum value of 24 meq/l and then approached an apparent equilibrium value of 19.89 meq/l (see Table 8). Solution Mg also showed the initial increase in concentration followed by a slower decrease to an average equilibrium value of 3.81 meq/l. While Mg and Ca were increasing initially, solution Na did not change much, indicating that Na was replacing exchangeable Ca and Mg rather than increasing in solution. The increases in Ca and Mg concentration above the concentrations of these ions in the leaching solution represented exchangeable Ca and Mg brought into solution by Na. Equilibrium was attained with respect to all three cations after about 16 pore volumes of solution had leached through the columns.

Figure 31 shows the changes in effluent concentration upon leaching column 5 with calcium and magnesium in a 5:1 ratio, and 15 meq/l Na. The larger percentage of Na in the leaching solution used for column 5, as opposed to those used for columns 1 and 4, caused greater adsorption of Na on the exchange complex and displacement of Ca and Mg into solution. Equilibrium was again attained after about 16 pore volumes of solution had leached through the columns.

The data in Figures 32, 33, and 34 show the effects of reducing the Ca/Mg ratio from 5:1 to 2:1. The amount of sodium in the leaching solutions remained the same. Reducing the Ca/Mg ratio in the leaching solutions from 5:1 to 2:1 resulted in similar reductions in these ratios in the effluent solutions after extensive leaching. The rate with which the 2:1 ratios were attained in the effluent solutions depended on the concentrations of Ca, Mg, and Na. In column 1 the Mg concentration started to increase after 11 pore volumes had been leached through. In column 4 it took about 14 pore volumes, and in column 5 about 25 pore volumes of leaching solution before the Mg concentration in the effluent solution started to increase. A new apparent equilibrium was obtained after about 27 pore volumes (or 770 surface centimeters) of solution were added in column 1, while column 5 had not yet reached equilibrium after 48 pore volumes were added (Figure 32).

These data show that changes in the composition of drainage water upon using a different irrigation water can be very slow, especially in arid areas and for calcareous soils. Assume, e.g., irrigation with 4 feet of water during a normal irrigation season with 50% application efficiency on a soil with 60 cm Glendale clay loam on top of a sand. With a percolation loss of 60 cm per year, it would then, according to the above data,

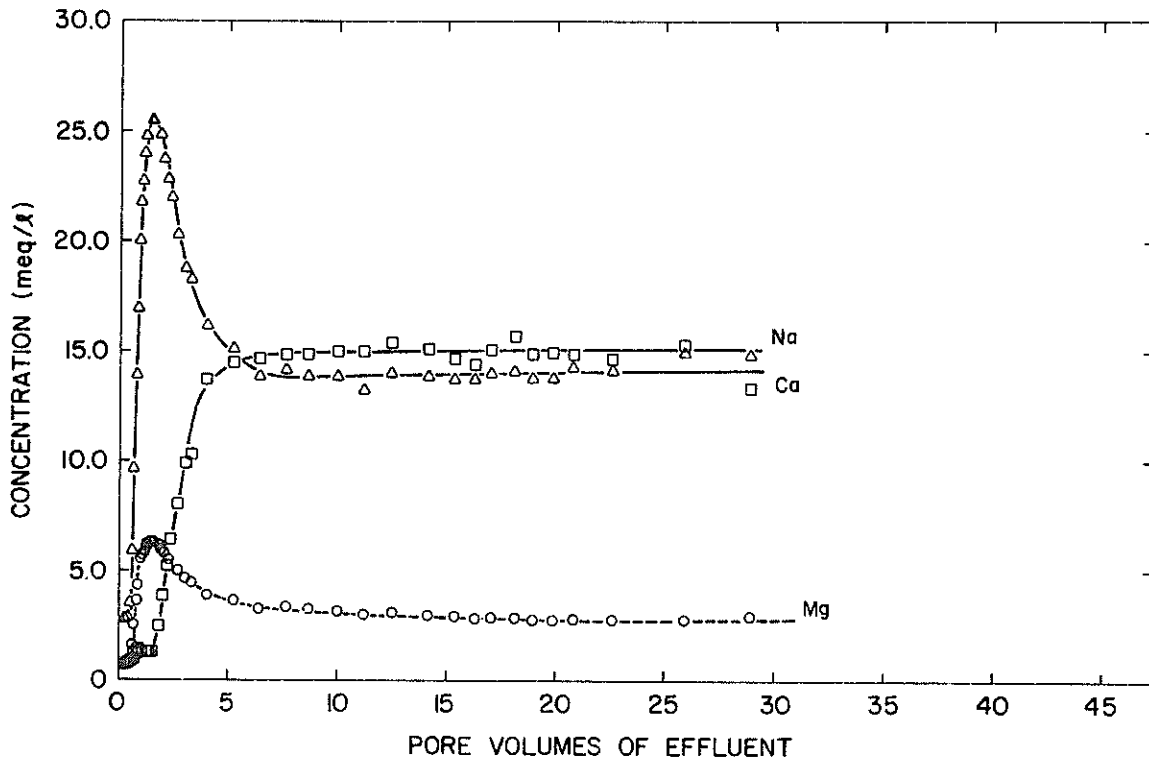


Figure 31. Calcium, magnesium, and sodium concentrations versus pore volumes of effluent upon leaching with a solution having Ca/Mg=5, and 15 meq/l Na.

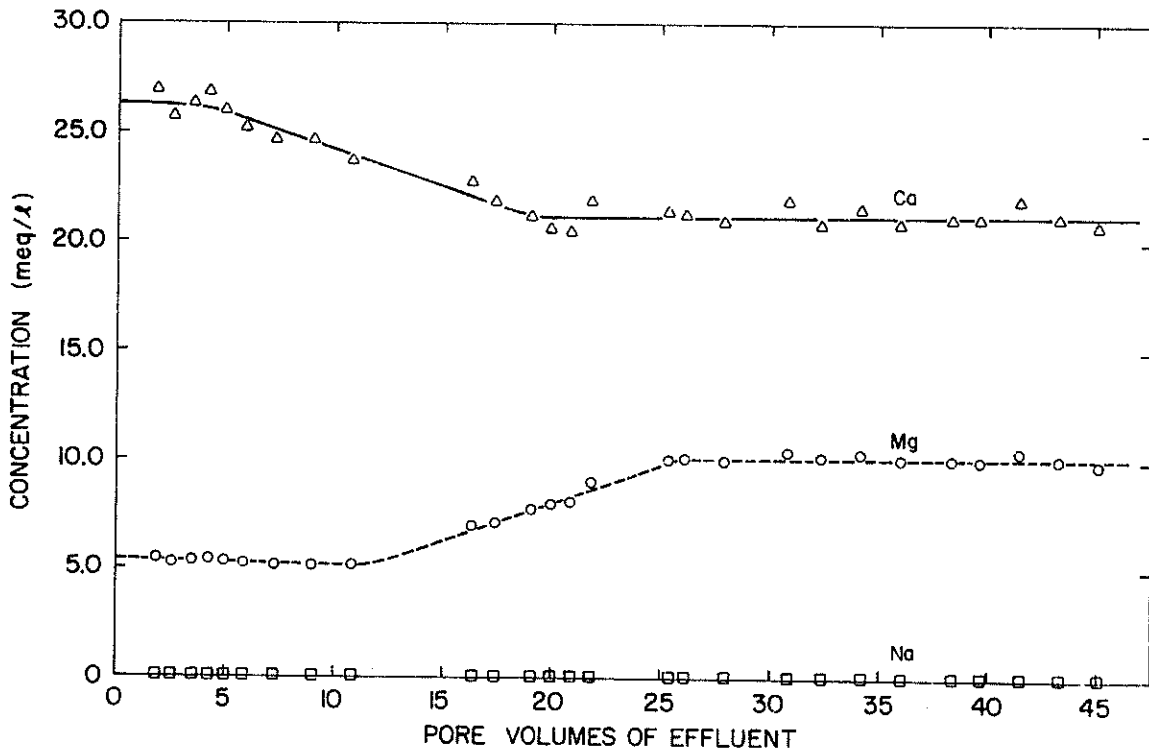


Figure 32. Calcium, magnesium, and sodium concentrations versus pore volumes of effluent upon leaching with a solution having Ca/Mg=2, and 0 Na.

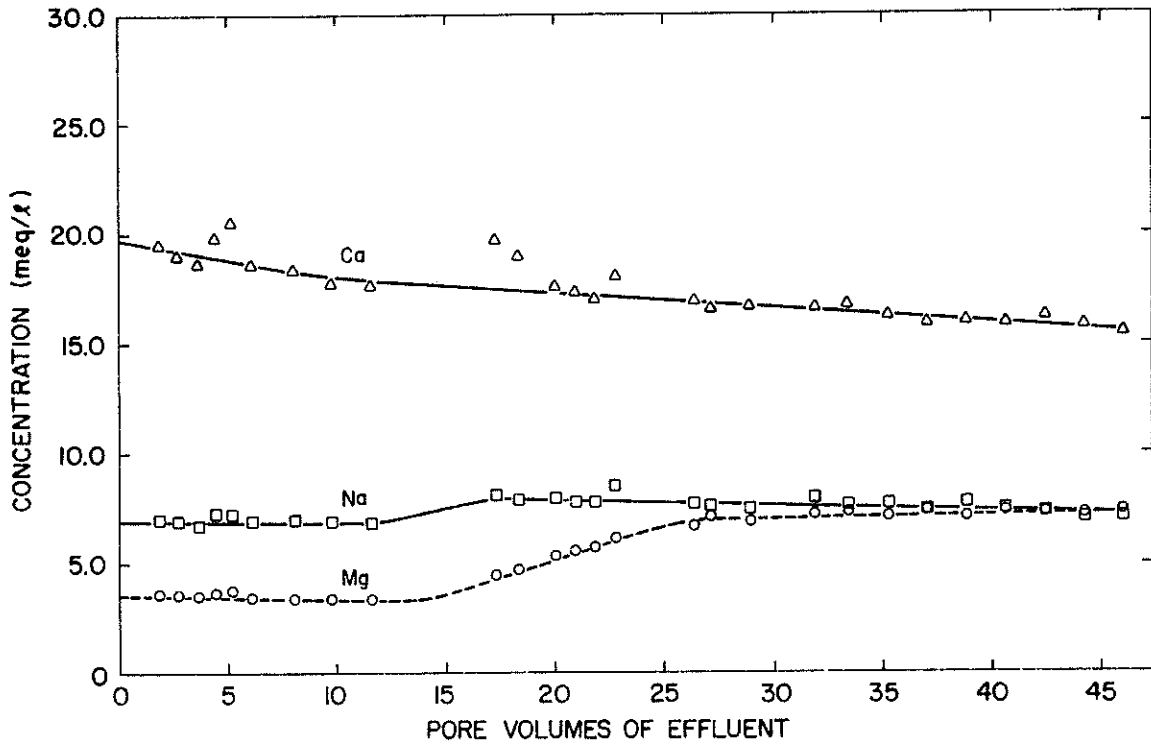


Figure 33. Calcium, magnesium, and sodium concentrations versus pore volumes of effluent upon leaching with a solution having Ca/Mg=2, and 7.5 meq/l Na.

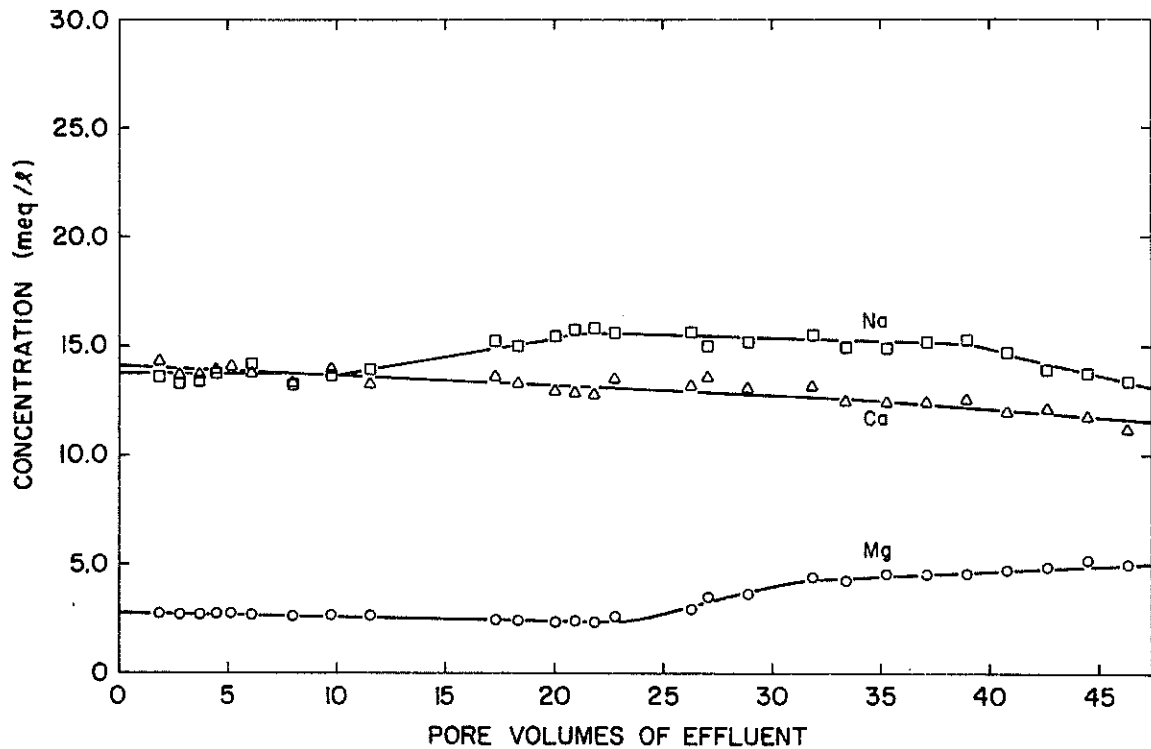


Figure 34. Calcium, magnesium, and sodium concentrations versus pore volumes of effluent upon leaching with a solution having Ca/Mg=2, and 15 meq/l Na.

take at least $770/60 = 12.8$ years after introduction of a new irrigation water before a new equilibrium in the Ca/Mg ratio of the drainage water is established. Under ordinary irrigation conditions with sodium present and a deeper soil profile, it would take much longer than 12.8 years.

Data in Figures 29 to 34 are summarized in Table 9, together with more complete data on pH, EC, anion concentrations, and on the actual composition of the irrigation waters used during the experiment.

The data presented are averages from six samples taken near the end of each leaching period. The differences between the irrigation waters and the drainage waters are also given. The data show that the sums of anions and cations for the drainage water are always larger than for the irrigation water. The increases vary from 1 to 2.4 meq/l or 3 to 7.5%, with an average increase of 1.62 meq/l or 5%. The 5% increase in salt concentration is mainly due to increases in calcium and bicarbonate from solution of calcium carbonate. Although the experiment has been run continuously for two years, there is no indication that the solution of calcium carbonate is decreasing. The amount of calcium carbonate present in the soil is large enough to sustain leaching of calcium carbonate at this rate for a long time to come.

In contrast, the concentration of potassium in the drainage water shows a slow but continuous decrease. For columns 5 and 6 the average potassium concentration in the drainage water decreased from .61 meq/l at the end of the first leaching period to .23 meq/l at the end of the second leaching period.

Table 9. Electrical conductivity (mmhos/cm), pH and anion and cation concentrations (meq/l) of irrigation, and drainage waters of soil columns at or near equilibrium. The data are averages of 6 samples taken near the end of each leaching period.

Averages of columns 1 and 2											
EC	pH	Ca	Mg	Na	K	Cl	HCO ₃	Cations	Anions	SAR	
Ca/Mg = 5											
Dr. W.	3.47	7.57	26.52	5.09	.06	.45	30.03	1.99	32.13	31.94	.01
Irr. W.	3.33	5.96	25.16	4.90	.02	.0	30.22	.09	30.09	30.32	0
Dr. W. - Irr. W.	.14	1.61	1.36	.19	.04	.45	-.19	1.90	2.04	1.62	.01
Ca/Mg = 2											
Dr. W.	3.30	7.55	21.09	9.95	.04	.17	28.59	1.70	31.26	30.29	.01
Irr. W.	3.20	7.61	19.92	10.06	.02	.0	28.67	.23	30.01	28.90	0
Dr. W. - Irr. W.	.10	-.06	1.17	-.11	.02	.17	-.08	1.47	1.25	1.39	.01
Averages of columns 3 and 4											
Ca/Mg = 5											
Dr. W.	3.52	7.69	19.89	3.81	7.68	.58	29.91	1.85	31.95	31.76	2.23
Irr. W.	3.34	5.88	18.65	3.65	7.76	.0	29.62	.09	30.06	29.71	2.32
Dr. W. - Irr. W.	.18	1.81	1.24	.16	-.08	.58	.29	1.76	1.89	2.05	-.09
Ca/Mg = 2											
Dr. W.	3.32	7.07	15.75	7.29	7.31	.21	28.76	1.23	30.55	30.00	2.15
Irr. W.	3.25	6.87	15.05	7.57	7.38	.0	28.80	.18	30.05	28.98	2.19
Dr. W. - Irr. W.	.07	.20	.70	-.28	-.07	.21	-.04	1.05	.50	1.02	-.04
Averages of columns 5 and 6											
Ca/Mg = 5											
Dr. W.	3.55	7.70	14.24	2.67	14.67	.61	29.72	2.44	32.18	32.16	5.04
Irr. W.	3.35	5.94	12.43	2.44	14.97	.0	29.75	.07	29.85	29.82	5.45
Dr. W. - Irr. W.	.20	1.76	1.81	.23	-.30	.61	-.03	2.37	2.33	2.34	-.41
Ca/Mg = 2											
Dr. W.	3.39	7.16	11.73	4.72	14.46	.23	28.86	1.71	31.14	30.58	5.04
Irr. W.	3.28	6.41	10.03	4.97	14.93	.0	28.55	.17	29.93	28.72	5.45
Dr. W. - Irr. W.	.11	.75	1.70	-.25	-.47	.23	.31	1.54	1.21	1.86	-.41

SUMMARY

A study was made of the movement and distribution of water, salts, and herbicides in soil columns. The results of the study indicate that the response of soil to changes in irrigation water quality and irrigation management procedures is very slow due to the large buffering capacity of soils. The response time depends on the soil type, the depth of soil profile considered, the amount of irrigation water applied, and the type of salt or chemical considered. For example, the sodium concentration in the drainage water from lysimeters 1.5 m deep started to change only after more than 180 cm of relatively high sodium water, equivalent to more than 3 pore volumes, had been passed through the soil. In another study, soil columns 60 cm deep were thoroughly leached with a solution containing calcium and magnesium chloride in a 5 to 1 ratio. Upon reducing the calcium/magnesium ratio in the irrigation water to 2, it took from 11 to 27 pore volumes (= 313 to 770 cm of water) of leaching solution before the calcium/magnesium ratio in the drainage water started to decrease. The amount of pore volumes required before changes in the drainage water were found depended on the amount of sodium in the leaching solution.

The rate at which individual ions and chemicals move through soil varies greatly and depends on the physical-chemical processes involved. For example, in the soil tested there was very little downward movement of phosphate applied with the irrigation water due to adsorption and precipitation. The phosphorus concentration below 30 cm was always very low, indicating that there is almost no chance for phosphates to leach down to the subsoil and groundwater table.

The movement of potassium was equally restricted due to adsorption on clay. All of the applied potassium remained close to the soil surface with very little loss by leaching.

Chloride and nitrate ions moved very readily through this soil. Negative adsorption of the ions by the clay particles resulted in chloride and nitrates moving ahead of the water front. These data show that nitrates are easily leached out of the surface soil. As a consequence, irrigation should be managed so that very little leaching occurs after the fertilizer has been applied in the spring and when nitrates are most needed by the plants. Nitrogen transformations in the soil were not studied, and therefore no conclusions can be made whether, and in how much time, surface applied nitrates travel to the groundwater under given irrigation management procedures.

The movement of herbicides was restricted by soil adsorption. Adsorption was intimately associated with the organic fraction of the soil; hence,

herbicides are expected to move with the water in the subsoil where the organic matter content is low. Herbicide downward movement was restricted by microbial degradation. In the columns, biological detoxification of an application of 80 ppm 2,4,5-T with 10 cm irrigation water was essentially complete in 45 days. Although the rates of degradation were relatively high in the columns due to the highly favorable conditions, the normal application of 2,4,5-T in agriculture (about 1-2 hg/ha as against 64 hg/ha in the columns) is much lower. Therefore, proper application of 2,4,5-T at normal application rates should not constitute a pollution hazard.

This study also showed that even after extensive leaching, in the absence of evaporation from the soil surface, the concentration of salts in the drainage water was higher than the total salt concentration of the irrigation water. The increase in salt concentration was about 5 percent, and was mainly due to increases in calcium and bicarbonate from solution of calcium carbonate. Many arid soils are calcareous and, therefore, could release more salts to the soil solution than are added with the irrigation water. The traditional leaching equation based on maintaining a salt balance would not be valid for these conditions since the amount of salt dissolved from soil minerals is usually considered negligible.

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Four graduate students participated in various aspects of the study and received training in the techniques involved. Three of these have completed the requirements for the M.S. degree, while the fourth student is working toward his Ph.D. degree in the Agronomy Department on a subject

which is a continuation of part of this research project. Of the three students who completed their M.S. degree, two are working toward a Ph.D. degree at other universities. One graduate student is employed by the California State Department of Water Resources as a Land and Water Use Analyst in an area closely related to this project. Five undergraduate students were employed during various phases of the project. Three of these were trained extensively in the analysis of soil solution samples for anions and cations and in numerous other phases of the project. One undergraduate chemistry student did most of the pesticide analysis by gas chromatography.

During the second project year an atomic absorption spectrophotometer was purchased with funds from this project. This was the first such unit on campus. The equipment has been used extensively for teaching and research on the campus, specifically by the departments of chemistry, biology, and sanitary engineering, in addition to its use by the Department of Agronomy in its Soil Chemistry classes.

During the period of this project one senior course was developed by Dr. P. J. Wierenga in soil-water relations, and one senior course by Dr. G. A. O'Connor in saline and sodic soils.

APPENDIX

A. Analytical procedures

pH: Measurements of pH were made with a Beckman Expandomatic pH-meter, and an Orion model 701 digital pH-meter.

Electrical Conductivity: The electrical conductivity was measured with a Solu Bridge RD 15 and the more sensitive Barnstead model PM-70CB conductivity bridge.

Nitrate: Nitrate concentrations were determined by the Orion model 92-07 nitrate selective electrode in combination with the Beckman Expandomatic pH-meter and the Orion digital pH-meter. Concentrations were obtained through a standard curve relating millivolt readings and nitrate concentrations of standard solutions. When NO_3 concentrations were below the sensitivity of the NO_3 electrode, a steam distillation procedure was used. Nitrate was converted to NH_3 using MgO and collected in a boric acid indicator which was then back titrated with standard acid.

Chloride: Concentrations were determined by titration with silver ions. The titrations were automated by a Buchler-Cotlove chloridometer, an instrument similar to the one described by Cotlove et. al. 1958.

Carbonate and bicarbonate were determined by titration with 0.01 N sulfuric acid in the presence of phenolphthalein and methyl orange (U. S. Salinity Laboratory Staff, 1954).

Sulfate: During the first project year, sulfate was determined by precipitation as calcium sulfate in the presence of acetone, centrifugation, and titration of the calcium with versenate. After the purchase of the atomic absorption spectrophotometer, the sulfate concentration was determined by precipitation with barium chloride, and by determination of the excess barium in the supernatant solution with flame emission using a nitrous oxide-acetylene flame. This method was found to give satisfactory results in this laboratory. It is a modification of the procedure published by Borden and McCormick, 1970 and by Galindo et. al. 1969.

Phosphate was determined by a method described by Murphy and Riley (1962) in which the blue color of a heteropoly molybophoric acid is determined with a spectrophotometer. The method was very sensitive and phosphorous concentrations as low as 0.1 ppm were easily determined.

Sodium and potassium concentrations were determined by flame emission on the Perkin-Elmer model no. 403 Atomic Absorption Spectrophotometer. Depending on the concentration of the extract, ten- or hundred-fold dilutions were made in order to be in the optimum range.

Calcium and magnesium were determined by atomic absorption following the general procedures described in Analytical Methods for Atomic Absorption Spectroscopy (1968). 1500 ppm strontium chloride was added to the solutions to prevent interferences.

2,4,5-T: All samples of the soil solutions were analyzed for 2,4,5-T using a Varian Aerograph Pestilyzer equipped with an electron capture detector containing tritium as the ionization source. A coiled glass column (150 x 0.32 cm) packed with 5% Dow 11 on 60/80 Chromosorb W was used. Purified nitrogen was used as the carrier gas at a flow rate of 50 ml/min. The column, injector, and detector temperatures were 180°C, 182°C, and 188°C, respectively.

The herbicide was extracted from acidified aqueous samples by shaking with two equal volume portions of ethyl ether in a separatory funnel. The ether extracts were combined and evaporated to dryness on a hot plate. The herbicide was then esterified with 5 ml of boron-trifluoride-methanol solution containing 0.125g BF₃/ml methanol, and finally dissolved in 10 ml of hexane. One µl of the hexane solution was injected into the chromatograph, and the herbicide content was determined by comparing the peak height produced by the sample to the peak height produced by known concentrations of the herbicide.