

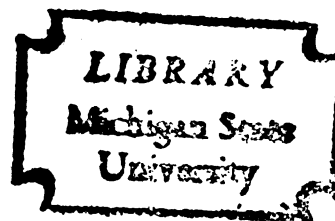
REMOVAL OF PHOSPHORUS AND NITROGEN FROM
WASTEWATER BY SPRAY IRRIGATION OF LAND

Dissertation for the Degree of Ph. D.

MICHIGAN STATE UNIVERSITY

DHANANJAI B. SHAH

1975



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thesis entitled

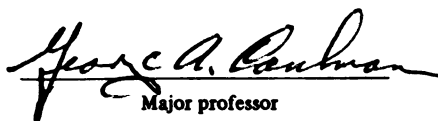
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presented by

Dhananjai Bhogilal Shah

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemical
Engineering


Major professor

Date September 11, 1975

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ABSTRACT

REMOVAL OF PHOSPHORUS AND NITROGEN FROM WASTEWATER BY SPRAY IRRIGATION OF LAND

By

Dhananjai B. Shah

Increased attention is being paid recently to the removal of phosphorus and nitrogen compounds from the wastewater along with organic carbon and biological oxygen demand because high concentrations of these compounds in our lakes and streams result in algal blooms and create serious other problems. One of the treatment methods being considered is spray irrigation of land. Phosphorus is removed by adsorption to the soils and nitrogen species are converted into atmospheric nitrogen via nitrification and denitrification reactions.

In order to design and manage a land treatment facility, mathematical models are needed that describe the movement of various phosphorus and nitrogen species in soil. This work addresses itself to studying the various reactions such as phosphorus adsorption, nitrification and denitrification and to developing mathematical models to predict their movements in soil. Results of these models are to be compared with experimental results to test the validity of the models.

The phosphorus model was derived by taking material balances on water and on phosphorus in the liquid and solid phase. Non-equilibrium conditions were assumed to prevail between phosphorus concentration in the liquid phase and on the soil. A mass transfer model was used to describe the rate of transfer of phosphorus from the liquid phase on to the solid phase. A Langmuir adsorption isotherm was used to describe the equilibrium relationship between the concentrations of phosphorus in the liquid and solid phases.

Solution of these equations for appropriate initial and boundary conditions showed that the water front moved much faster than the phosphorus front. This enabled the water transport equation to be dropped from the model equations and computations became less complex. Results of the simulation were compared with data from an existing spray irrigation site and they compared remarkably well with one another. These simulation studies showed that the soil system is very efficient in phosphorus removal.

Nitrification and denitrification are important microbiological reactions of nitrogen. Ammonium nitrogen gets converted to nitrate nitrogen by nitrifiers in the presence of dissolved oxygen. This nitrate nitrogen is then reduced by facultative anaerobes to atmospheric nitrogen in the presence of organic carbon. Kinetics of these reactions were investigated based on a Monod type expression involving two growth limiting substrates,

$$\mu = \mu_m \left(\frac{S_1}{K_{S_1} + S_1} \right) \left(\frac{S_2}{K_{S_2} + S_2} \right) .$$

The following table summarizes the various substrates considered in the two reactions.

	<u>S₁</u>	<u>S₂</u>
Nitrification :	Ammonium nitrogen	Dissolved oxygen
Denitrification :	Nitrate nitrogen	Organic carbon

Kinetic constants (μ_m , K_{S_1} , and K_{S_2}) were evaluated for the nitrification and denitrification reactions.

Past experimental work was used to determine the constants for the nitrification reaction. For the denitrification reaction, steady state experiments were performed in a stirred tank reactor under conditions such that only one substrate was growth limiting. Steady state values of the substrate in the reactor were determined at various dilution rates. These data were analyzed to obtain the kinetic and stoichiometric constants. From these constants, it was concluded that in the range of nitrate concentrations encountered in wastewater, the denitrification reaction can be considered a first order reaction. It was also found that three times as much organic carbon is required as nitrate nitrogen for complete nitrogen removal.

Using these kinetic expressions, material balance equations were written for ammonium nitrogen and nitrate nitrogen in the

liquid phase. Material balance equations were also written for all the gas phase components. These equations were solved to obtain some preliminary estimates of the extent of nitrogen removal. The simulation results compared very well with the experimental results. Even at very low flow rates, complete nitrogen removal was not accomplished.

The nitrogen removal ability of the soil was found to be of greater importance in selecting a land disposal site than the phosphorus removal capability. Because of great variability in physical, chemical and biological properties of soils, it was established that some preliminary experimental work would be absolutely essential before a successful land disposal site can be designed and operated. The transport models developed here can give some preliminary estimates on the quantity of phosphorus and nitrogen that can be removed by a spray irrigation site under a given operating policy.

REMOVAL OF PHOSPHORUS AND NITROGEN FROM WASTEWATER
BY SPRAY IRRIGATION OF LAND

By

Dhananjai B. Shah

A DISSERTATION

Submitted to
Michigan State University
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DOCTOR OF PHILOSOPHY

Department of Chemical Engineering

1975

To my parents

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CHAPTER I

INTRODUCTION

Phosphorus and Nitrogen as Pollutants in Wastewater

The removal of phosphorus and nitrogen compounds from wastewater is very important because these contaminants, present in high enough concentrations, in an aquatic environment, promote unwanted growth of algae and aquatic plants. The resulting blooms of blue-green algae lead to a higher biological oxygen demand and lower dissolved oxygen levels affecting fish population and would interfere with the recreational uses of water. Other problems associated with high algal growth in surface waters include production of objectionable taste and odors and increased chlorine demand. This necessitates the control of the discharge of these compounds into an aquatic environment. Nitrogen compounds of major importance in water are ammonia, nitrites and nitrates and those of phosphorus include organic phosphorus, inorganic polyphosphates and soluble ortho and metaphosphates.

Sources of phosphorus and nitrogen compounds in an aquatic ecosystem are both natural and man-made. Contributions from natural sources include runoff and rainfall. Man-made sources include municipal wastewater, industrial wastes, urban runoff and agricultural runoff from fertilized fields and livestock feedlots. Eliassen et al. (1969), Grundy (1971) and Ferguson (1968) have

tabulated the amounts of phosphorus and nitrogen entering the aquatic environment from each of these sources.

Detergents contain phosphates and they account for 30-40 percent of all phosphorus entering the aquatic environment. Industrial wastes contain high concentrations of phosphorus and nitrogen and these concentrations would vary depending on the type of waste. It has been estimated by Ferguson (1968) that of the total quantity of nitrogen contributed to an aquatic ecosystem, one-third can be attributed to municipal sewage effluents and one-half to the runoffs from beef feedlots. Most of the nitrogen in raw municipal sewage is in a form from which ammonia is easily derived.

One of the major difficulties in designing for the removal of nitrogen and phosphorus is a lack of reliable information on the critical concentrations of these compounds below which their adverse effects are minimized. Few attempts have been made to quantify limiting concentrations for both nitrogen and phosphorus. Sawyer (1947) and Benoit et al. (1947) concluded from their studies of some lakes that, if at the time of the spring season, the concentration of inorganic phosphorus exceeds 0.3 ppm, rapid algal growth would occur. On the other hand, some workers (Mackenthum 1962, Fitzgerald et al. 1965) have stated that of the two, nitrogen is the limiting nutrient and its control is more important. Besides playing a role in the algal bloom, high concentrations of nitrate nitrogen cause problems in industrial and domestic use of water. They are also believed to cause infant cyanosis. In view of these

reasons, the U.S. has adopted 10 ppm nitrate nitrogen or less as the standard for drinking water use.

Advanced Treatment Methods for Phosphorus and Nitrogen Removal

The conventional treatment processes are not capable of removing most of the phosphorus and nitrogen compounds found in wastewater to the required limits. This forces us to modify the existing processes. These advanced treatment methods fall into chemical, physico-chemical and biological classes. These methods are summarized, their main advantages enumerated, and the costs and efficiencies for phosphorus and nitrogen removal compared in Table 1.1. The conventional treatment plant (first line in Table 1.1) removes only 50 per cent and 30 per cent of the incoming nitrogen and phosphorus, respectively. A slight modification of the above process (third line) involving nitrification and denitrification can remove a high percentage of the incoming nitrogen. It is quite inexpensive and is compatible with phosphorus removal. Of the chemical methods listed in the table, only nitrogen removal by ammonia stripping is inexpensive.

Land Disposal of Effluent

All the methods in Table 1.1 are treatment methods, except waste disposal by spray irrigation of land. This is the only recycling method which purifies wastes from the treatment plants while it enriches the soil and recharges the groundwater. Land disposal is characterized by the application of sewage effluents

TABLE 1.1.--Methods of Phosphorus and Nitrogen Removal.*

Process	Type and Mechanism	Percent Removed	Cost \$/mil.gal.	Remarks
<u>Nitrogen Removal Processes</u>				
1. Conventional biological treatment	Biological $N, P \rightarrow \text{Cell Mass}$	30-50 N 10-30 P	30-100	Sludge disposal problem. P and N removal unsatisfactory.
2. Algae harvesting	Biological $N, P \rightarrow \text{Cell Mass}$	50-90	20-35	Final liquid and sludge to be disposed off. P and N removed simultaneously. Large land area needed. Requires favorable climate.
3. Aerobic nitrification followed by anaerobic denitrification	Biological $NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + H^+$ $NO_3^- \rightarrow N_2 + CO_2 + H_2O$	70-95	25-30	No ultimate waste disposal problem. Compatible with P removal. 100% removal not possible.
4. Ammonia stripping	Chemical $NH_4^+ \rightleftharpoons NH_3 + H^+$	80-98	9-25	No ultimate waste disposal problem. Problem of increasing NH_4^+ solubility with lower temperature. Air pollution problems. Scaling due to metal deposits.
5. Breakpoint chlorination	$NH_4^+ + Cl_2 \rightarrow NCl_3, NHCl_2, NH_2Cl$	Quite high	100-200	High increase in total dissolved solids. Nitrate may be a product of chlorination.
<u>Phosphorus and Nitrogen Removal Processes</u>				
1. Ion exchange	Chemical $NO_3^- + RCl \rightleftharpoons Cl^- + RNO_3$	Quite high	100-150	Both P and N can be removed. Problem of disposal of regeneration liquid. Pretreatment required to remove interfering ions.
2. Electro-chemical	Chemical Sewage + Seawater <u>Current</u> . Precipitation of P and N as Ca and Mg salts.	80-85		Liquid and solid disposal required.
3. Electro-dialysis	Chemical Separates the cationic and anionic components by using selective membranes.	30-50	100-250	Problems of chemical precipitation and membrane clogging. High degree of pretreatment necessary.
4. Reverse osmosis.	Physical Forced passage of water through membranes against osmotic pressure.	65-95	250-400	Problems of liquid disposal and membrane fouling.
5. Distillation	Physical Distill off water	90-98	Very expensive	Can obtain drinking water. Problem of liquid disposal.
6. Land application	Physico-chemical Chemical and biological filtering action to remove P and N.	60-90	75-150	High removal possible. Large land area needed. Advantage of recycling the nutrients. Management of the system very important.
<u>Phosphorus Removal Processes</u>				
1. Chemical precipitation	Chemical P precipitated by addition of alum, lime, etc.	Quite high	70-90	Liquid and sludge to be disposed off. Can be combined with conventional activated sludge process quite easily.
2. Adsorption	Physical P removed by adsorption.	90-98	40-70	High removal possible.

*Most of the information contained in this table was taken from Eliassen et al. (1969), Stensel (1971) and Sutton et al. (1975).

on forest or crop land in predetermined rates and amounts. It is based on the concept of "living filter"--letting nature recycle nutrients and water beneficially on land rather than detrimentally through the lakes and streams.

The concept of recycling is important because pollution can be viewed as a maldistribution of matter and energy among the three media of the earth: air, water and soil (Bohn and Cauthorn 1972). Nitrogen and phosphorus compounds cause algal blooms in lakes and streams, but in soil they are beneficial to plants. Hot water in a stream can cause thermal pollution but would increase plant growth when applied to soils. Sulfur dust is a pollutant in the atmosphere but can act as a nutrient for plant growth in soils. Hence, the problem of nitrogen and phosphorus pollution in an aquatic environment can be solved by putting effluent on land where these compounds are beneficial to plants and vegetation.

Phosphorus and Nitrogen Transformations

The ability of the soil to act as a filter is based on the many physical, chemical and biological reactions it can carry out. Chemical functions of the living filter during irrigation include ion-exchange, adsorption and precipitation, and chemical alteration. Phosphorus, which is generally present in the form of soluble orthophosphates, can undergo adsorption and precipitation by reaction with calcium, manganese, and iron as the effluent moves down the soil. Along with the phosphorus, some sulfate, boron and heavy metals are also removed from the wastewater by

adsorption. The adsorbed phosphorus on the soil can be removed by cropping the soil. The cleaner effluent, then, can recharge the groundwater. Soil has net cation exchange capacity and thus can also adsorb positively charged ions like ammonium.

As a biological filter, soil contains microbes. Soil microbes decompose and metabolize biodegradable organic materials to carbon dioxide and water. Nitrogen present in the form of ammonium gets converted via the nitrification reaction to nitrate nitrogen which subsequently is converted to gaseous nitrogen by the denitrification reaction. Both these reactions are micro-biological in nature. The nitrification reaction is carried out by the microbes which oxidize the ammonium nitrogen in the presence of oxygen to nitrate nitrogen. As the wastewater moves down the soil, concentrations of the ammonium nitrogen in the liquid phase and oxygen in the gas phase decrease. When oxygen concentration goes down sufficiently to form an anaerobic environment, some microbes utilize nitrate as an alternative electron acceptor in the presence of organic carbon as an energy source. This is termed the denitrification reaction. The top layers of the soil profile are usually the most active sites for biological and chemical filtration.

Objectives and Scope of Present Work

The soil treatment method can remove phosphorus and nitrogen consistently, only under proper management practices. Application rates of the wastewater should be such as to give

sufficient residence times in the soil for complete phosphorus adsorption and nitrogen transformations. High leaching of nitrate, phosphate and other ions is conceivable in intensively irrigated areas. To properly design and manage such systems, enough information is needed about the various chemical and biological reactions involved.

Phosphorus adsorption in different soils has been studied by a number of soil scientists and they have shown that the equilibrium relationship between the two phases can be described by the Langmuir isotherm. Adsorption in packed saturated columns has also been studied by chemical engineers, but in the soil treatment method, water flow through the soil is unsaturated. One of the objectives of the present research has been to study the kinetics of phosphorus adsorption and develop a mathematical model to simulate the phosphorus movement in soils. Results of this simulation are to be compared with the data from an operating land treatment facility.

Nitrification and denitrification have been studied by soil scientists in soil columns. As some nitrification and denitrification does occur in the conventional activated sludge plants, these reactions have also been studied by sanitary engineers, in stirred tank reactors. Until now, rates of these reactions have been determined as a function of one limiting substrate. For nitrification, this limiting substrate is assumed to be ammonium nitrogen and for denitrification it is assumed to be nitrate nitrogen. These rate expressions are valid when other

substrates needed for microbial growth are in excess. When they are not in excess, their concentrations also influence the reaction rates. The nitrification reaction requires ammonium nitrogen and dissolved oxygen, and organic carbon is required as an energy source to drive denitrification. If these substrates are also limiting, the reaction rates would be greatly affected. An attempt has been made in this work to modify the existing reaction rate expressions involving a single substrate to include the effect of other substrates, if they are not in excess. These modifications are to be made on the basis of past work and some present experimental work. Having identified the kinetics, mathematical models are to be developed to predict the movement of various nitrogen species and compare the simulated results with some experimental data from literature.

In short, objectives of the present work have been to (1) summarize the kinetics of (a) phosphorus adsorption, (b) nitrification reaction, and (c) denitrification reaction on the basis of past and present work; (2) develop mathematical models describing the movements and transformations of phosphorus and nitrogen; and (3) validate these models by comparing the predicted results with the experimental profiles.

It is obvious that the waste-processing capability as well as the design and management criteria for land disposal of wastewater will be strongly dependent upon the characteristics of the terrestrial ecosystem under consideration. Soil characterization will be an important factor in site selection and long-term

operation of the disposal site. The expression of these soil characteristics in modeling equations will be quite important in the design of land waste disposal systems. The increasing scarcity of land will dictate that disposal areas not become merely dumps but be wisely used to allow harvest and recycling of essential plant nutrients. Since the plants and vegetation can take up only a finite amount of phosphorus and nitrogen and soil can process only a fixed amount of phosphorus and nitrogen, this method cannot be used for the disposal of industrial wastes which contain high concentrations of these compounds.

The present work can give some indication as to how much of the incoming phosphorus and nitrogen, under a given operating and management practice, leaks into the ground water system. This can help define the upper limit on the application rate, beyond which chemical and biological filtering action is not fast enough to prevent the leakage of the nutrients into the lakes and streams. It can also help determine when the phosphorus adsorption capacity of soil may be exhausted. Double substrate limited kinetic expressions would also be helpful in designing reactors in the activated sludge process for nitrification and denitrification.

Organization of Information Provided in This Work

This work is mainly concerned with identifying the kinetics of phosphorus adsorption, nitrification and denitrification reactions and using this information to develop mathematical models to simulate the movements of phosphorus and nitrogen in soils spray irrigated

by wastewater. Chapters II and III deal with phosphorus transformations and its movement, whereas Chapters IV and V are concerned with the nitrogen transformations and modeling its movement.

Chapter II deals with the phosphorus chemistry. It identifies the forms of phosphorus and their fractions in wastewater, and adsorption and precipitation as the main phosphorus reactions when this wastewater is applied to the soil. It reviews the past work in the area of adsorption columns and discusses the phosphorus adsorption kinetics. In Chapter III, a mathematical model for the movement of phosphorus has been developed based on a series of assumptions and on the groundwork laid in Chapter II. The numerical method of solution of these equations is also given and the results of simulation are compared with the data taken from an operating land disposal facility. Chapter III also deals with the effect of various physical parameters on the phosphorus profiles in soils.

Chapter IV discusses the nitrogen transformations in soils with emphasis on the nitrification and denitrification reactions. Past work in the area of kinetics of these reactions has been summarized. The existing kinetic rate expressions based on a single limiting substrate have been modified to include the effect of a second limiting substrate. The constants involved in the nitrification rate expression have been evaluated by combining the data of various workers. The experimental work done to evaluate the denitrification rate expression has also been outlined in this chapter.

In Chapter V, a mathematical model has been proposed for the movement of nitrogen species in soils. It takes into account

the important nitrogen transformations and interactions between the solid, liquid, and gas phases. The numerical method used to solve these equations is outlined and the simulation results of the nitrogen movement in soils based on this model have been compared with some experimental data taken from the literature.

Chapter VI concludes this work by discussing the results and the pertinent points to be considered while selecting a spray irrigation site and management practice. Wherever possible, the points have been illustrated with example calculations. The appendices following the text contain such things as data used to construct figures in the text and complete descriptions of the computer programs used to determine the phosphorus and nitrogen movement in the soils.

CHAPTER II

BACKGROUND

Phosphorus Chemistry

Phosphorus, in the form of phosphate, occurs in all the known minerals as orthophosphate, represented as $(\text{PO}_4)^{-3}$. Apatites such as hydroxylapatite, $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$, and fluorapatite, $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$, are a major source of phosphorus in soils. Crystalline phosphate minerals in addition to apatites include $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (Brushite), $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ (Variscite) and $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ (Strengite). There are also some amorphous phosphates containing iron and aluminium and these, poorly soluble phosphates, may exhibit a wide range of composition when they appear.

Dissolved phosphorus may exist in aqueous solution as (1) orthophosphates (PO_4^{-3} , HPO_4^{-2} , $\text{H}_2\text{PO}_4^{-}$, H_3PO_4); (2) complex or inorganic condensed phosphates as pyrophosphate ($\text{P}_2\text{O}_7^{-4}$, $\text{HP}_2\text{O}_7^{-3}$, . . .), tripolyphosphate ($\text{P}_3\text{O}_{10}^{-5}$, $\text{HP}_3\text{O}_{10}^{-4}$, . . .) and trimetaphosphate ($\text{P}_3\text{O}_9^{-3}$, $\text{HP}_3\text{O}_9^{-2}$); (3) organic orthophosphates such as sugar phosphates, phospholipids, phosphoamides, etc.; and (4) organic condensed phosphates. Complex or the condensed phosphates are largely contributed by man's activities. They are man-made for use in detergents, water treatment, etc., and are discharged with domestic and industrial wastewaters. The condensed phosphates are unstable in water where they are hydrolyzed to the orthophosphate form. The

presence of phosphorus compounds in soils and water can be attributed to biological processes. But in domestic and industrial wastewater, organic phosphorus may not be present in high concentrations.

The total phosphorus in domestic wastewater effluent, not treated specifically for phosphorus removal, varies from 3 to 10 ppm. Seventy to ninety percent of the total phosphorus in the secondary sewage effluent is present as a soluble orthophosphate. The remainder consists of pyrophosphates, polyphosphates, inorganic condensed phosphates and organic phosphorus species. Table 2.1 summarizes the various forms of phosphorus and their concentrations encountered in water and in soils.

Phosphorus Precipitation in Soils

Various metal phosphates present in water can precipitate in the soil. The distribution of phosphates in solution is governed by the pH. Given the equilibrium constants for various phosphate acid-base reactions, it is possible to calculate the amount of phosphate in solution at a particular pH. If the solution contains phosphate in concentrations greater than this number, the excess amount will get precipitated. The calculation procedure for determining the solubility relationship is illustrated below.

The solubility products and the dissociation constants used in determining the pH-solubility relationship are summarized in Table 2.2.*

*Personal communication with Dr. B. G. Ellis, Professor of Soil and Crop Science, Michigan State University, 1973.

TABLE 2.1.--Forms of Phosphorus in Water and Soils.*

Dissolved Phosphorus Forms		Source	Composition of Wastewater (Total P=10 ppm)	Solid Phase Forms
Forms	Compounds or Species			
Orthophosphate	H_2PO_4^- , HPO_4^{2-} , PO_4^{3-} , FeHPO_4^+ , $\text{CaH}_2\text{PO}_4^+$	Hydrolysis of condensed phosphates	70-90%	Soil-Mineral Phases Hydroxylapatite Fluorapatite Variscite Strengite
Inorganic condensed phosphates:				
Pyrophosphate	$\text{H}_2\text{P}_2\text{O}_7^{2-}$, $\text{HP}_2\text{O}_7^{3-}$, $\text{P}_2\text{O}_7^{4-}$, $\text{CaP}_2\text{O}_7^{2-}$, $\text{MnP}_2\text{O}_7^{2-}$	Detergents, Biological processes	10-30%	Mixed phases, Solid solutions, Sorbed species 1. Clay phosphate kaolinite 2. Clay-organo-phosphate
Tripolyphosphate	$\text{H}_2\text{P}_3\text{O}_{10}^{3-}$, $\text{HP}_3\text{O}_{10}^{4-}$, $\text{P}_3\text{O}_{10}^{5-}$, $\text{CaP}_3\text{O}_{10}^{3-}$			
Trimetaphosphate	$\text{HP}_3\text{O}_9^{2-}$, $\text{P}_3\text{O}_9^{3-}$, $\text{CaP}_3\text{O}_9^{1-}$			
Organic orthophosphates	Sugar phosphates, phospholipids, phosphoamides, phosphoproteins	Biological processes	5-10%	Suspended organic phosphorus Bacterial cells

*Report of the Water Quality Division Committee on Nutrients in Water (1970).

TABLE 2.2.--Solubility Products and Dissociation Constants Used in Developing Figure 2.1.

Species	Formula	Solubility Expression	pK
Variscite	$\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$	$\text{pK} = \text{pAl} + \text{pPO}_4$	22.52
Dicalcium phosphate	CaHPO_4	$\text{pK} = \text{pCa} + \text{pHPO}_4$	6.66
Octacalcium phosphate	$\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 3\text{H}_2\text{O}$	$\text{pK} = 4\text{pCa} + \text{pH} + 3\text{pPO}_4$	46.91
Phosphoric acid	H_3PO_4	$\text{pK} = \text{pH} + \text{pH}_2\text{PO}_4 - \text{pH}_3\text{PO}_4$	2.12
Dihydrogen phosphate ion	H_2PO_4^-	$\text{pK} = \text{pH} + \text{pHPO}_4 - \text{pH}_2\text{PO}_4$	7.20
Monohydrogen phosphate ion	$\text{HPO}_4^{=}$	$\text{pK} = \text{pH} + \text{pPO}_4 - \text{pHPO}_4$	12.32

For dicalcium phosphate,

$$\text{pK} = 6.66 = \text{pCa} + \text{pHPO}_4 . \quad (2.1)$$

pHPO_4 can be replaced by an expression containing pH and pH_2PO_4 .

For H_2PO_4^- ,

$$\text{pK} = 7.2 = \text{pH} + \text{pHPO}_4 - \text{pH}_2\text{PO}_4 . \quad (2.2)$$

Substituting for pHPO_4 from (2.2) in (2.1), we get

$$6.66 = \text{pCa} + 7.2 - \text{pH} + \text{pH}_2\text{PO}_4 ,$$

i.e.,

$$\text{pH}_2\text{PO}_4 = \text{pH} - \text{pCa} - 0.54 . \quad (2.3)$$

Equation (2.3) defines the concentration of H_2PO_4^- in solution at a given pH and Ca^{+2} concentration. The total dissolved orthophosphate, P_T , would be given by

$$P_T = \text{H}_3\text{PO}_4 + \text{H}_2\text{PO}_4^- + \text{HPO}_4^{2-} + \text{PO}_4^{3-} .$$

Calculations based on the values given in Table 2.2 show that at pH 6-9, the predominant orthophosphate species are H_2PO_4^- and HPO_4^{2-} . In Equation (2.3), pH_2PO_4 can be substituted by an expression involving the total phosphorus as given below:

$$\text{total P} = P_T = \frac{[\text{H}_2\text{PO}_4^-]}{\gamma_1} + \frac{(\text{H}_2\text{PO}_4^-) 10^{-7.2}}{(\text{H}^+) \gamma_2} \quad (2.4)$$

where γ_1 and γ_2 are activity coefficients of H_2PO_4^- and HPO_4^{2-} , respectively. Equations (2.3) and (2.4) combine to give

$$P_T = f(\text{pCa}, \text{pH}) .$$

Similar equations can be derived for octacalcium phosphate and aluminium phosphate and these are plotted in Figure 2.1.

At low pH, phosphorus solubility is limited to low levels by the availability of Ca^{++} ions in soil. For pH values above 7.0, the solubility will be limited by the Ca^{++} ions. It is expected that dicalcium phosphate will form rapidly but it will limit the phosphorus in solution to only 4 ppm at pH 9 and 8 ppm at pH 7. Octacalcium phosphates are slower to form. They are formed in soils in a few weeks to several months. This is advantageous

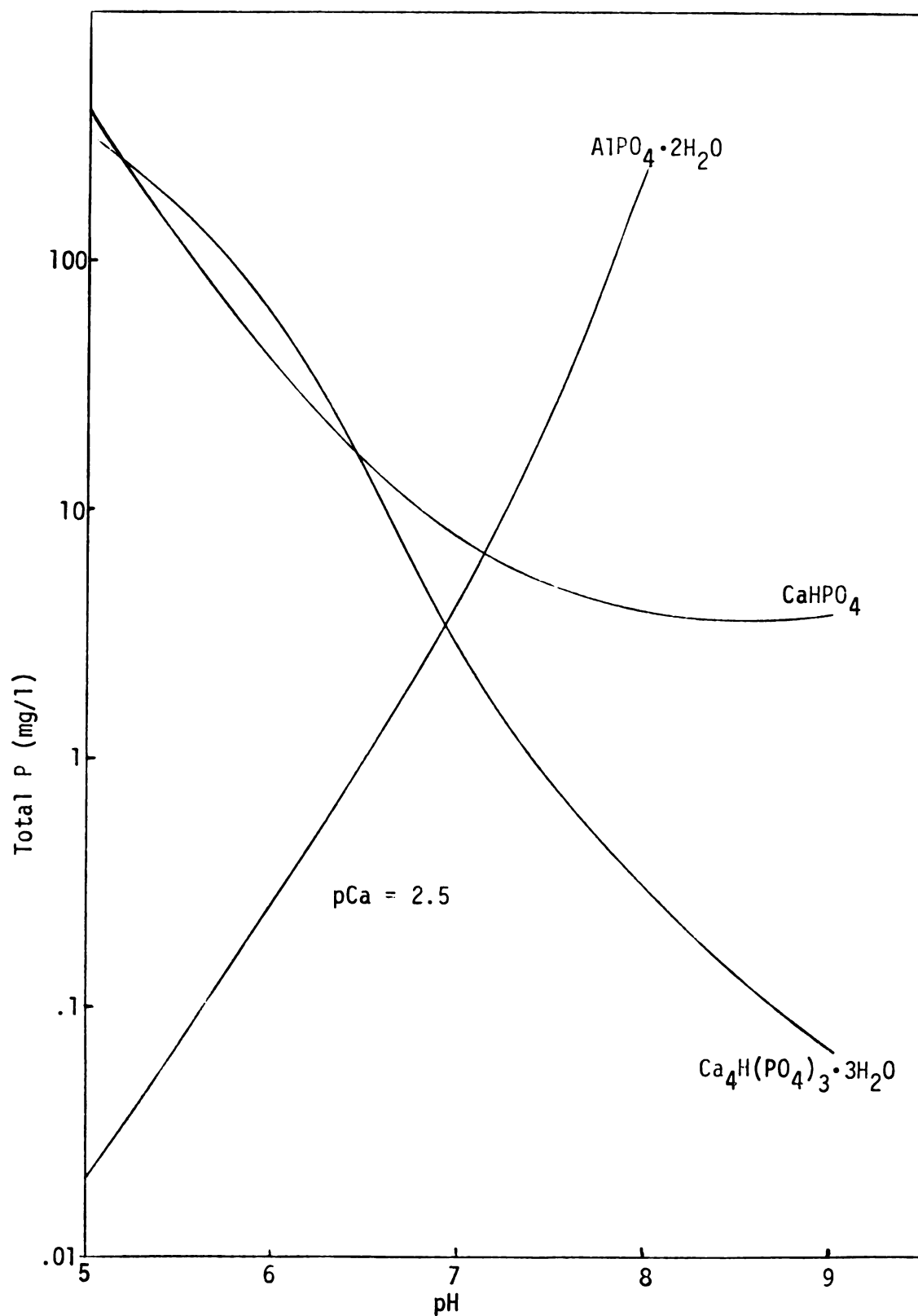


Figure 2.1.--Solubility of Various Phosphorus Compounds as a Function of pH [Al^{3+} Ions Availability Controlled by Dissociation of $\text{Al}(\text{OH})_3$].

because, if they are formed at all, they will limit the solubility of phosphates to levels between .3 ppm at pH 8 and 2.7 ppm at pH 7. Other calcium phosphates are much less soluble but they form so slowly that they are not expected to have any effect on the precipitation of phosphorus from wastewater. Thus, the pH of wastewater and the soil composition will determine the phosphorus solubility relationship in a land disposal system.

Phosphorus Adsorption in Soil

Dissolved phosphorus can also be adsorbed by the soils. Soils are made up of, among other things, clay minerals, kaolinites and montmorillonites. Phosphate ions are taken up by these clay minerals and activated alumina. Freshly precipitated ferric and aluminium hydroxides can also take up phosphates and polyphosphates. The reason for adsorption seems to be the presence of a strong force for chemical bonding between the phosphate groups and the metal ions on a solid lattice. The adsorption of phosphates on clay minerals involves at least two mechanisms: (1) chemical bonding of anions on the positively charged edges of the clays and (2) substitution of phosphates for silica in the clay structures.

Studying the phosphorus chemistry in detail allows us to conclude the following. (1) Most of the dissolved phosphorus is in the form of orthophosphates. Polyphosphates and condensed phosphates hydrolyze to the orthophosphates. (2) The incoming phosphorus can undergo two basic reactions:

- a. Precipitation--The solubility of various phosphates depends on the pH, the solubility products and the dissociation

constants of various phosphates. If the pH of the wastewater is 7.0 and soils contain enough calcium, dicalcium phosphate would limit the solubility of phosphorus at 10 ppm total phosphorus.

b. Adsorption--Dissolved phosphorus can be removed from the liquid phase by adsorption onto the clay minerals and ferric or aluminium hydroxides.

Phosphorus Adsorption Kinetics

Establishing the equilibrium distribution of the solute between the solid and the liquid phases and determining the rate of solute transfer from the liquid phase to the solid phase are two important steps in developing a mechanistic mathematical model to predict the phosphate movement in soils. Quite a few kinetic models have been used by different workers in their investigations and their equilibrium relations and rate expressions are summarized below.

Equilibrium Relationship

First order expression.--The simplest model is the first order reaction model. Kuo and Lotse (1973) have reviewed the phosphate kinetics literature and have listed a number of references which used first order kinetics to describe the phosphorus adsorption. This is an oversimplification of this phenomenon. According to this model, at equilibrium, the concentration of the solute in soils is proportional to the solute concentration in the liquid as given by

$$Y^* = \alpha X \quad (2.5)$$

where

X = solute concentration in the solid phase, and

Y^* = solute concentration in the liquid phase.

The superscript * indicates equilibrium conditions. Equation (2.5) does not take into account the fact that there are a fixed number of adsorption sites available on the solid surface. This limits the amount of solute that can be adsorbed by the solids whereas Equation (2.5) predicts no such limitation.

Nonlinear expression.--Two adsorption isotherms commonly used to describe the equilibrium relationship between the solute concentrations in the liquid and solid phases are the Freundlich and Langmuir isotherms. They are

$$\text{Freundlich isotherm: } X = KY^{\frac{1}{n}} \quad (2.6)$$

where K and n are constants, and

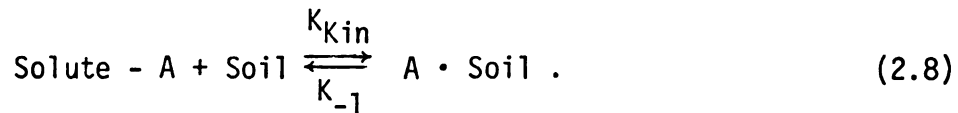
$$\text{Langmuir isotherm: } \frac{Y^*}{X} = \frac{1}{KQ} + \frac{Y}{Q} . \quad (2.7)$$

There have been many reports concerning the applicability of both these isotherms to adsorption in soils. The Freundlich isotherm is somewhat empirical in nature but the Langmuir isotherm can be theoretically derived considering both the adsorption and desorption reactions and that at equilibrium both are equal. K represents the ratio of rate constants for the adsorption and

desorption reactions. The Langmuir adsorption isotherm has been applied to phosphorus adsorption in soils by Fried and Shapiro (1956), Olsen and Watanabe (1957), and Ellis and Erickson (1969). In this work, the Langmuir isotherm will be used to describe the equilibrium relationship for the adsorption reaction.

Rate Expression for Adsorption

Bilinear adsorption kinetics.--The bilinear form of adsorption has been proposed by Hiester and Vermeulen (1952). It is quite a representative form of expression for the adsorption of phosphorus in soils. The adsorption reaction can be represented by



The rate of adsorption at the solid surface is

$$\begin{aligned} \frac{d}{dt} (A \cdot \text{Soil}) &= k_{\text{Kin}} (A) (\text{Soil}) - k_{-1} (A \cdot \text{Soil}) \\ &= k_{\text{Kin}} \left[(A) (\text{Soil}) - \frac{1}{k_{\text{ad}}} (A \cdot \text{Soil}) \right] . \quad (2.9) \end{aligned}$$

If Q represents the ultimate capacity of the soil in gm solute/gm soil and Q_{∞} the capacity of the adsorbent, that is reached when it is in equilibrium with the entering feed, then concentrations in Equation (2.9) become

$$\left. \begin{aligned} (A) &= Y = \text{solute concentration in liquid,} \\ (A \cdot \text{Soil}) &= X = \text{concentration of occupied sites,} \end{aligned} \right\} (2.10)$$

and $(\text{Soil}) = Q - X = \text{concentration of unoccupied sites.}$ }

Substituting (2.10) in (2.9) results in

$$\frac{dX}{dt} = K_{\text{Kin}} \left[Y(Q-X) - \frac{Y}{K_{\text{ad}}} \right] . \quad (2.11)$$

The above equation takes into account both the adsorption and desorption reactions. Gupta and Greenkorn (1973) used this kinetic expression and thought it to be the most representative of the physical situation.

Mass transfer kinetics.--This model assumes the rate of adsorption of the solute to be proportional to the driving force. The driving force is dependent on the deviation of the system from equilibrium. The model can be represented as

$$\text{Rate of adsorption} = K_0 a (Y - Y^*) . \quad (2.12)$$

Here,

$Y - Y^*$ = departure of the system from equilibrium,

Y^* = solute concentration in the liquid in equilibrium

with solute concentration in the solid phase,

mg/l, and

$K_0 a$ = constant of proportionality, i.e., volumetric mass transfer coefficient, day^{-1} .

Y^* will be given by one of the isotherms as a function of X . The basis for using Equation (2.12) for the phosphorus adsorption kinetics will be established later. Novak and Adriano (1975)

considered the various kinetic models and concluded that bilinear adsorption kinetics and mass transfer kinetics models adequately express the experimental data in conjunction with the equilibrium relationship given by the Langmuir isotherm.

Scope of Past Work

As established earlier, the important reactions of phosphorus in soils are the adsorption-desorption reactions of orthophosphates with the soils. Thus, developing a mathematical model for the phosphorus movement in soils is equivalent to describing the behavior of adsorption columns. One major difference between these columns and the soil adsorption system is the nature of liquid flow. In soil, under the conditions of low application rates, water flow is generally unsaturated. As the time passes, saturation (moisture content of soil) increases. This results in varying velocity of liquid as a function of depth. Most of the adsorption columns studied have been operated at saturated conditions (all the pore spaces occupied by water) and hence velocity in the column is assumed constant throughout.

The dynamic response of adsorption, ion exchange and chromatographic columns has been a topic of interest for a long time. If a material balance is made for the solute in a thin section ΔZ of a column, the various components that have to be considered are as follows:

rate of incoming solute across the surface at Z $VAY|_Z$,

rate of outgoing solute
across the surface at $Z + \Delta Z$ $VAY|_{Z + \Delta Z}$,

rate of adsorption of the
solute by the solid phase $A\Delta Z\rho_b \frac{\partial X}{\partial t}$, and

rate of accumulation of
the solute $\frac{\partial}{\partial t} (A\Delta ZY)$.

Putting all the components together and dividing by ΔZ gives

$$\frac{VAY|_Z - VAY|_{Z+\Delta Z}}{\Delta Z} - A\rho_b \frac{\partial X}{\partial t} = \frac{\partial}{\partial t} (AY) .$$

As $\Delta Z \rightarrow 0$, the above equation gives

$$-V \frac{\partial Y}{\partial Z} - \rho_b \frac{\partial X}{\partial t} = \frac{\partial Y}{\partial t} . \quad (2.13)$$

Here,

A = cross-sectional area, cm^2

V = superficial velocity of the liquid, cm/day

Y = concentration of the solute in the liquid phase, mg/l

X = solute concentration on the solid phase, mg/kg

t = time, day, and

ρ_b = bulk density of the soil.

The middle term in the above equation represents the rate of increase of the solute on the soils. Since this increase is accomplished only by adsorption, it represents the rate of transfer of the solute from the liquid phase onto the solid phase. The equilibrium relationship, $Y^* = f(X)$, along with Equation (2.13) and an expression for $\partial X/\partial t$, defines the system completely. Inherent

in the derivation of the above equations are the following assumptions:

1. Pore spaces are completely occupied by the liquid phase and hence the pore velocity is constant.
2. The percolating fluid displaces this liquid evenly so that the solute concentration is always uniform over any cross section.
3. Nature of the liquid flow is plug-flow and the effect of dispersion and diffusion is not considered.

Thomas (1948), using the above assumptions, proposed a model for the chromatographic columns. The velocity through the column was constant and the flow was saturated. For the equilibrium relationship $X = f(Y^*)$, he used first order and second order chemical reactions as kinetic models for adsorption and desorption. He also assumed that equilibrium between the two phases is established immediately and the mass transfer resistance is negligible. These assumptions result in

$$Y^* = \alpha X,$$

i.e.,

$$\frac{\partial X}{\partial t} = \frac{1}{\alpha} \frac{\partial Y^*}{\partial t} = \frac{1}{\alpha} \frac{\partial Y}{\partial t}. \quad (2.14)$$

Thomas solved his system of equations analytically to obtain the dynamic behavior of an adsorption column.

Hiester and Vermuelen (1952) studied the cation adsorption operation in resin beds. They used second order kinetics in the form of bilinear adsorption to define the rate of cation exchange. In this case, $\partial X/\partial t$ is given by Equation (2.11). They performed

the analysis in dimensionless variables to generalize the earlier results of Thomas. The model of Thomas and that of Hiester and Vermuelen did not consider the effect of dispersion in fluid flow.

Lapidus and Amundson (1952) studied the same problem but incorporated the longitudinal dispersion effect which modified Equation (2.13) as follows,

$$D \frac{\partial^2 Y}{\partial Z^2} - V \frac{\partial Y}{\partial Z} - \rho_b \frac{\partial X}{\partial t} = \frac{\partial Y}{\partial t} .$$

They used a linear adsorption isotherm and considered the cases of no mass transfer resistance and finite mass transfer resistance. For the latter case, they used

$$\rho_b \frac{\partial X}{\partial t} = K_o a (Y - Y^*) \quad \text{and} \quad Y^* = \alpha X . \quad (2.15)$$

The above cases were solved analytically by Lapidus and Amundson to obtain the dynamic response of an adsorption column.

Neilson and Biggar (1962) made a comparative study of theoretical transport models using a series of carefully conducted soil column experiments. They concluded that none of the models tested agreed quantitatively with experimental results but the approach of Lapidus and Amundson gave the best qualitative prediction.

Rhee and Amundson in a series of papers (1971, 1972) derived a model for the adsorption-desorption for saturated flow in columns. Their model consisted of the dispersion equation and the adsorption

rate expression (2.15) but used the nonlinear expression of Langmuir to describe the adsorption isotherm. They showed that under certain conditions (dependent mainly on the type of adsorption isotherm used), after some time of operation, the shape of the solute concentration profile in the solid phase becomes constant. This solute profile of constant pattern was termed as a shock layer. Once the shock layer is established, it moves down the column with a constant velocity which depends only on the adsorption isotherm and the initial and boundary conditions used. The various physical properties such as dispersion coefficient and mass transfer coefficient do affect the shape of the shock layer, but the velocity of the shock layer is not affected by these constants. They also considered the case of interphase equilibrium and showed that the same results are applicable in this case.

Lai and Jurinak (1972) studied the effect of the shape of the equilibrium curve on the concentration profile for a soil column cation adsorption problem. They used an equilibrium model and for the case of convex isotherms they presented data which bear out the shock layer theory of Rhee et al. (1971).

Cho et al. (1970) studied phosphorus movement in soil columns in which phosphorus adsorption was described as a first order chemical reaction. He demonstrated that the water movement was much faster than the phosphorus movement and that the phosphorus movement in soils was dependent on the rate of adsorption and the mode of application of phosphorus.

Present Work

All the above models consider constant pore velocity. This is not necessarily true in the case of a spray irrigation system. As the wastewater is sprayed on the soil, the moisture content in the soil increases. Development of the saturation profile depends on the physical properties of the soil such as hydraulic conductivity (ability of the soil to conduct water) and capillary potential gradient. This gives rise to a varying velocity of water in the soil. This feature has to be included in any attempt to model the phosphorus movement in soils. After sufficient time elapses, flow becomes steady and the model will reduce to the regular adsorption-desorption model. Present work will use the Langmuir adsorption isotherm to describe the equilibrium relationship between the two phases, and will assume no interphase equilibrium. External film diffusion controlling the adsorption process will be used as the basis for the development of the model.

CHAPTER III

MODELING OF PHOSPHORUS MOVEMENT IN SOIL

Physical Situation and Assumptions

The physical situation in a soil column is quite complex. In an unsaturated flow through the soil, three phases exist: (1) gas, (2) liquid, and (3) solid. The solid phase consists of particles and aggregates of particles. The pore spaces existing between the particles are termed micropores and those between the particles and the aggregates or between the aggregates are defined as macropores. Liquid, carrying the solute, moves down through the pore spaces. The solute, in order to get adsorbed at the solid surface, has to diffuse from the bulk of the liquid to the solid surface where it is adsorbed. Thus, there are three steps in series.

1. External diffusion: Diffusion of the solute from the bulk of fluid to the outer surface of the solid particle.
2. Internal diffusion: Diffusion of the solute through the pores of the particle to the point where adsorption occurs.
3. Adsorption: Adsorption of the solute on the solid phase.

The rate of adsorption will be controlled by the step that offers the greatest resistance to the transfer and hence the step that is the slowest. In this model, it will be assumed that the

combined resistance of the external and internal diffusion is much greater and, therefore, it is the rate controlling mechanism. In that case, the rate of phosphate adsorption-desorption is defined by

$$R = K_0 a (Y - Y^*)$$

where

$$Y^* = aX/(1 - bX) \quad (\text{from 2.7}).$$

This is called the mass transfer model. It assumes that diffusion limits the rate of transfer of phosphate between the solution and the solid surface. The solid surface contains the active sites for phosphate adsorption. The rate of adsorption is proportional to the driving force measured by the departure of the system from equilibrium, the overall mass transfer coefficient, and the solid-liquid interfacial area per unit bulk volume of the soil. The overall mass transfer coefficient incorporates both the micro-pore and macropore diffusional resistances.

The flow of water through the soil deviates considerably from plug flow. This phenomenon is due largely to the wide range of pore sizes which results because of the heterogeneity in the soil particle sizes and shapes. This fact can be accounted for by incorporating a dispersion coefficient in the flow equation. At low flow rates, its value approaches the diffusion coefficient but at high flow rates, the dispersion coefficient is much larger than the diffusion coefficient (Chung, 1967). Nielson and Biggar's

data (1962) at low flow rates indicate dispersion coefficients of the same order of magnitude as diffusion coefficients.

Based on the above discussion, the following assumptions are made in the development of the model for phosphorus adsorption in soil.

1. Flow is unidirectional with uniform cross-sectional area.
2. An effective axial dispersion coefficient represents the combined effect of both diffusion and dispersion.
3. Porosity of the soil is assumed constant.
4. The system is isothermal.

Water Transport

Phosphorus is carried through the soil by water. This necessitates describing the movement of water before one can accurately predict the phosphorus movement through the soil. In developing a model for the two phase water movement in the soil, Novak and Coulman (1972) have shown that a one phase water model is sufficient to describe the soil water movement in irrigated soil over a wide range of non-isothermal conditions. The single phase water movement will be used as a base component of the phosphorus model.

The velocity of a liquid in a porous medium like soil is directly proportional to the potential gradient as given by Darcy's law

$$V_{ES} = -K \frac{\partial \phi}{\partial Z} = -K \left(\frac{\partial \psi}{\partial Z} - 1 \right), \quad (3.1)$$

where

- V = pore velocity, cm/day,
 ϵ = porosity of the soil,
 K = hydraulic conductivity of the soil, cm/day,
 S = saturation, percent of void space occupied by water,
 ϕ = total potential, cm of water,
 ψ = capillary potential, cm of water, and
 Z = soil depth, cm.

Equation (3.1) can be rewritten as

$$V\epsilon S = -K \left(\frac{\partial \psi}{\partial S} \frac{\partial S}{\partial Z} - 1 \right) . \quad (3.2)$$

Both the hydraulic conductivity and the capillary potential are functions of soil moisture content or soil saturation, S .

Development of Model

Water Balance

Consider a thin section of soil of ΔZ thickness. The various components of the material balance equation are as follows:

- rate of incoming water across the surface at Z $V\epsilon SA|_Z$,
 rate of outgoing water across the surface at $Z + \Delta Z$ $V\epsilon SA|_{Z + \Delta Z}$, and
 rate of accumulation of water $\frac{\partial}{\partial t} (A\Delta Z\epsilon S)$.

Adding the various components of the material balance equation and dividing by ΔZ gives

$$\frac{V_{\epsilon S} A|_Z - V_{\epsilon S} A|_{Z + \Delta Z}}{\Delta Z} = \frac{\partial}{\partial t} (A_{\epsilon S}) .$$

Taking the limit as $\Delta Z \rightarrow 0$, gives

$$- \frac{\partial}{\partial Z} (V_{\epsilon S}) = \frac{\partial}{\partial t} (\epsilon S) \quad (3.3)$$

where $V_{\epsilon S}$ is given by Equation (3.2).

Phosphorus Balance

The various components of the material balance equation for phosphorus in liquid phase are given below:

rate of incoming phosphorus by diffusion and dispersion across the surface at Z	$-DA_{\epsilon S} \left. \frac{\partial Y}{\partial Z} \right _Z ,$
rate of incoming phosphorus by convection across the surface at Z	$V_{\epsilon S} A Y _Z ,$
rate of outgoing phosphorus by diffusion and dispersion across the surface at Z + ΔZ	$DA_{\epsilon S} \left. \frac{\partial Y}{\partial Z} \right _{Z + \Delta Z} ,$
rate of outgoing phosphorus by convection across the surface at Z + ΔZ	$V_{\epsilon S} A Y _{Z + \Delta Z} ,$
rate of adsorption of phosphorus	$K_0 a (Y - Y^*) A \Delta Z , \text{ and}$
rate of accumulation of phosphorus	$\frac{\partial}{\partial t} (Y A \Delta Z \epsilon S) .$

Adding up all the contributions and dividing by ΔZ , one gets

$$\frac{D\epsilon S \left. \frac{\partial Y}{\partial Z} \right|_{Z+\Delta Z} - D\epsilon S \left. \frac{\partial Y}{\partial Z} \right|_Z}{\Delta Z} + \frac{V\epsilon SY|_Z - V\epsilon SY|_{Z+\Delta Z}}{\Delta Z} - K_0 a(Y - Y^*)A = \frac{\partial}{\partial t} (Y\epsilon S) .$$

Taking the limit as $\Delta Z \rightarrow 0$, gives

$$D\epsilon \frac{\partial}{\partial Z} \left(S \frac{\partial Y}{\partial Z} \right) - \frac{\partial}{\partial Z} (V\epsilon SY) - K_0 a(Y - Y^*) = \frac{\partial}{\partial t} (Y\epsilon S) . \quad (3.4)$$

Phosphorus balance on the soils is quite simple since the rate of increase of the phosphorus concentration on soils is the same as the rate of transfer of the solute from the liquid phase, i.e.,

$$\rho_b \frac{\partial X}{\partial t} = K_0 a(Y - Y^*) . \quad (3.5)$$

Equations (3.1) through (3.5) along with the Langmuir adsorption isotherm completely define the system. This model can describe the phosphorus movement in soils at constant or varying velocity, at saturated or unsaturated conditions. When the flow is steady, the model reduces to Equations (3.4) and (3.5) which are of the same form as those of Rhee et al. (1972). However, there are some differences between the definition of the variables in the analogous equations. In the papers by Rhee et al. (1971, 1972), the pore velocity and time correspond to a saturated flow rate and actual time, respectively. In contrast, this model contains pore velocity

and time variables, which correspond to the irrigation rate and the cumulative irrigation time, respectively.

The mathematical form of the problem can be summarized as follows:

$$\left. \begin{aligned}
 \frac{\partial}{\partial t} (\epsilon S) &= - \frac{\partial}{\partial Z} (V \epsilon S) , \\
 V \epsilon S &= -K \left(\frac{\partial \psi}{\partial S} \frac{\partial S}{\partial Z} - 1 \right) , \\
 D \epsilon \frac{\partial}{\partial Z} \left(S \frac{\partial Y}{\partial Z} \right) - \frac{\partial}{\partial Z} (V \epsilon S Y) - K_0 a (Y - Y^*) &= \frac{\partial}{\partial t} (Y \epsilon S) , \\
 \rho_b \frac{\partial X}{\partial t} &= K_0 a (Y - Y^*) , \text{ and} \\
 Y^* &= \frac{aX}{1 - bX} .
 \end{aligned} \right\} \quad (3.6)$$

The initial and boundary conditions for solving Equations (3.6) are given below:

$$\left. \begin{aligned}
 S(Z,0) &= S_0 , \\
 Y(Z,0) &= Y_0 , \\
 X(Z,0) &= X_0 ,
 \end{aligned} \right\} \quad \text{initial conditions,} \quad (3.7)$$

and

$$\left. \begin{aligned}
 \text{at } Z &= 0, \\
 V(0,t) &= \text{application rate at the surface}
 \end{aligned} \right\}$$

$$\begin{aligned}
 &= -K \left[\frac{\partial \psi}{\partial S} \frac{\partial S}{\partial Z} - 1 \right] \Big|_{Z=0}, \\
 Y(0,t) &= Y_i, \quad \text{and} \\
 X(0,t) &= \frac{Y_i}{a + bY_i}, \\
 &\text{at } Z = L, \\
 \frac{\partial S}{\partial Z} &= 0, \quad \text{and} \quad \frac{\partial Y}{\partial Z} = 0.
 \end{aligned}
 \quad \left. \vphantom{\begin{aligned} &= -K \left[\frac{\partial \psi}{\partial S} \frac{\partial S}{\partial Z} - 1 \right] \Big|_{Z=0}, \\ Y(0,t) &= Y_i, \quad \text{and} \\ X(0,t) &= \frac{Y_i}{a + bY_i}, \\ &\text{at } Z = L, \\ \frac{\partial S}{\partial Z} &= 0, \quad \text{and} \quad \frac{\partial Y}{\partial Z} = 0. \end{aligned}} \right\} \begin{array}{l} \text{boundary} \\ \text{conditions} \end{array} \quad (3.8)$$

In the above equations, X_0 and Y_0 are in equilibrium and so are X_i and Y_i . The physical constants needed to solve the above equations are

- a. hydraulic conductivity of the soil as a function of saturation,
- b. capillary potential of the soil as a function of saturation,
- c. overall mass transfer coefficient for the system, and
- d. Langmuir isotherm constants.

To validate the above model, simulation results are to be compared with data obtained from an actual operating facility. Such a facility was constructed on the campus of Michigan State University and was called BLWRS (Barrierred Land Water Renovation System). A detailed discussion on BLWRS will be given in a later section.

Model Parameters

Mass Transfer Coefficient and Langmuir Adsorption Isotherm

To determine the mass transfer coefficient and the Langmuir adsorption isotherm for the BLWRS system, an experiment was carried out in the Crop and Soil Science Department, Michigan State University. The Langmuir isotherm coefficients were obtained for the BLWRS soil by the method of Olsen and Watanabe (1957). Five grams of soil was allowed to equilibrate with 40 ml of solution containing a known concentration of phosphorus. Equilibrium was assumed to have been reached in eight hours. At equilibrium, the phosphorus concentration in the liquid was determined and the concentration on the soil was calculated by the difference between the initial and the final concentrations in the liquid phase. This process was carried out for five different initial concentrations. During the isotherm determinations, the phosphorus concentrations in solution were also tracked as a function of time, until equilibrium had been attained. The data are given in Table 3.1.

The phosphorus concentration on the soil can be calculated by using

$$X = X_0 + \frac{V_L}{W_S} (Y_0 - Y) \quad (3.9)$$

where

X_0 = initial concentration on the soil,

V_L = volume of the liquid,

W_S = weight of the soil, and

Y_0 = initial phosphorus concentration in the liquid.

TABLE 3.1.--Equilibrium and Approach to Equilibrium Data for Liquid Concentration in Phosphorus Adsorption.

Time hrs	Run 1	Run 2	Run 3	Run 4	Run 5
0	2.9	5.55	8.67	11.60	13.57
0.5	1.08	3.09	5.81	7.98	9.69
1	1.07	2.92	5.15	7.46	10.00
2	0.45	1.98	4.77	6.16	8.67
4	0.47	1.76	3.94	5.73	7.73
8	0.38	1.56	2.62	4.70	6.21

The equilibrium relationship is expressed as $Y^*/X = 1/KQ + Y^*/Q$. A plot of Y^*/X versus Y^* will result in a straight line with slope and intercept equal to $1/Q$ and $1/KQ$, respectively. Such a plot is shown in Figure 3.1.

An ordinary differential equation for the phosphorus concentration in liquid phase was written and integrated to obtain the mass transfer coefficient (see Appendix A). The calculated value of K_0a was found to be 2.0 day^{-1} .

Hydraulic Conductivity

Hydraulic conductivity, as the name signifies, represents the ability of the soil to conduct water. For high saturations, the hydraulic conductivity is determined by steady flow experiments and Darcy's law. For lower saturations, it is determined from unsteady state flow experiments, and Darcy's equation and water balance equation. Experimental data on the hydraulic

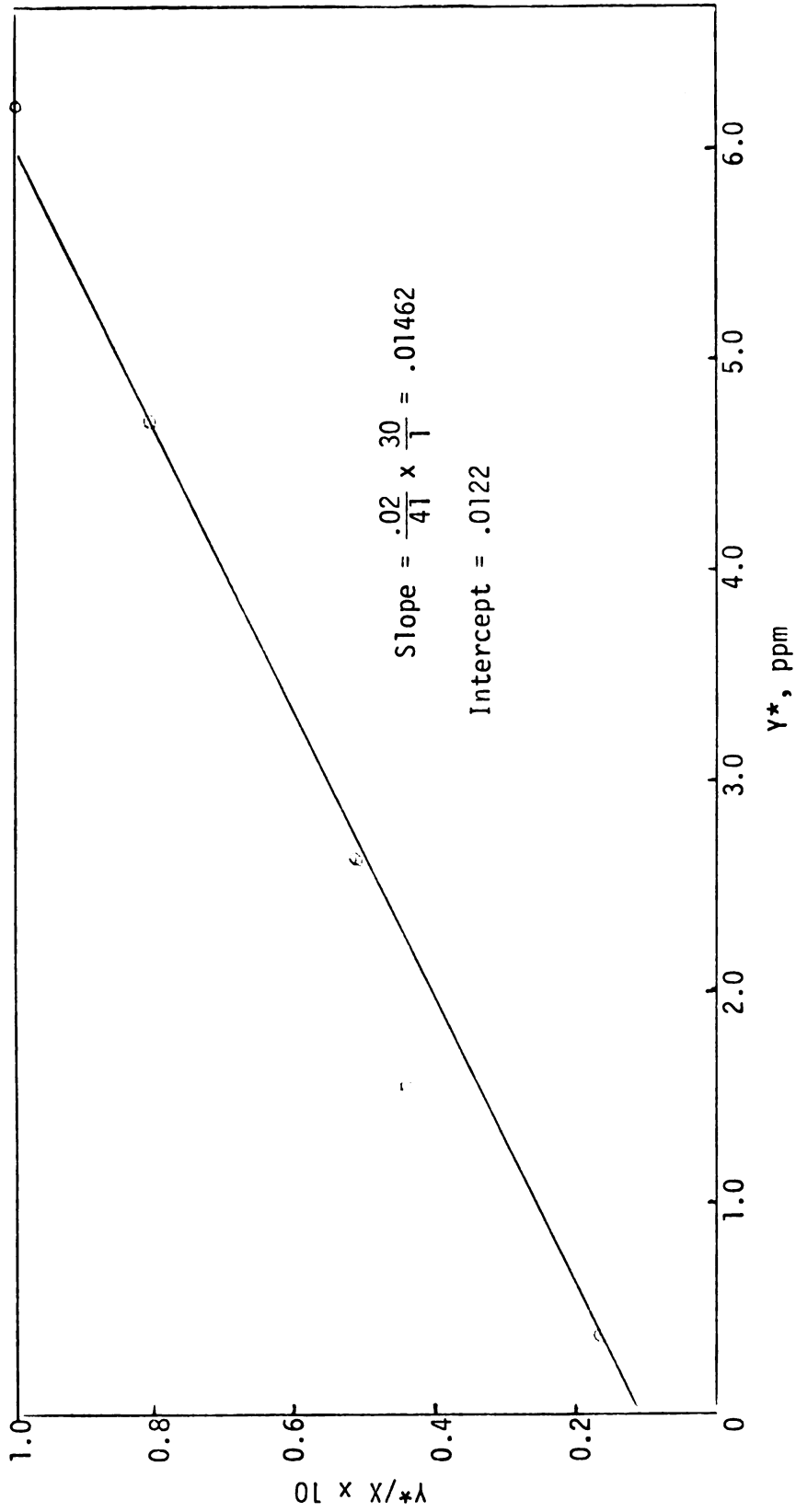


Figure 3.1.--Equilibrium Relationship Between Phosphorus in Liquid Phase and Phosphorus in Solid Phase as Given by Langmuir Equation.

conductivity on Uplands sand are given in Figure 3.2. The data points were curve fitted using a least squares technique to obtain an expression for hydraulic conductivity as a function of saturation.*

Capillary Potential

Figure 3.3 contains the capillary potential data on Uplands sand. Capillary potential is determined by manometer measurements at high saturations, but at low saturations, it is determined by vapor pressure measurements (Novak, 1972). The experimental data were curve fitted to obtain an expression for capillary potential as a function of saturation.* From this, a graph of $d\psi/dS$ versus saturation can be obtained as shown in Figure 3.4. Hydraulic conductivity and capillary potential data for the Spinks sandy soil which was used in the construction of BLWRS were not available, hence the data of Staple (1969) for Uplands sand were used.

Barrierred Land Water Renovation System (BLWRS)

A facility for spray irrigation of land using wastewater has been operated at Michigan State University. The soil system was modified to accomplish phosphorus and nitrogen removal within a short distance into the soil. The system is diagrammed in Figure 3.5. It has a mound of soil underlain by a barrier impervious to water. This has the result of creating aerobic and anaerobic environments in series. On the top of the mound, a thin band of limestone is placed to increase the calcium content of the

*Modified from Novak (1972).

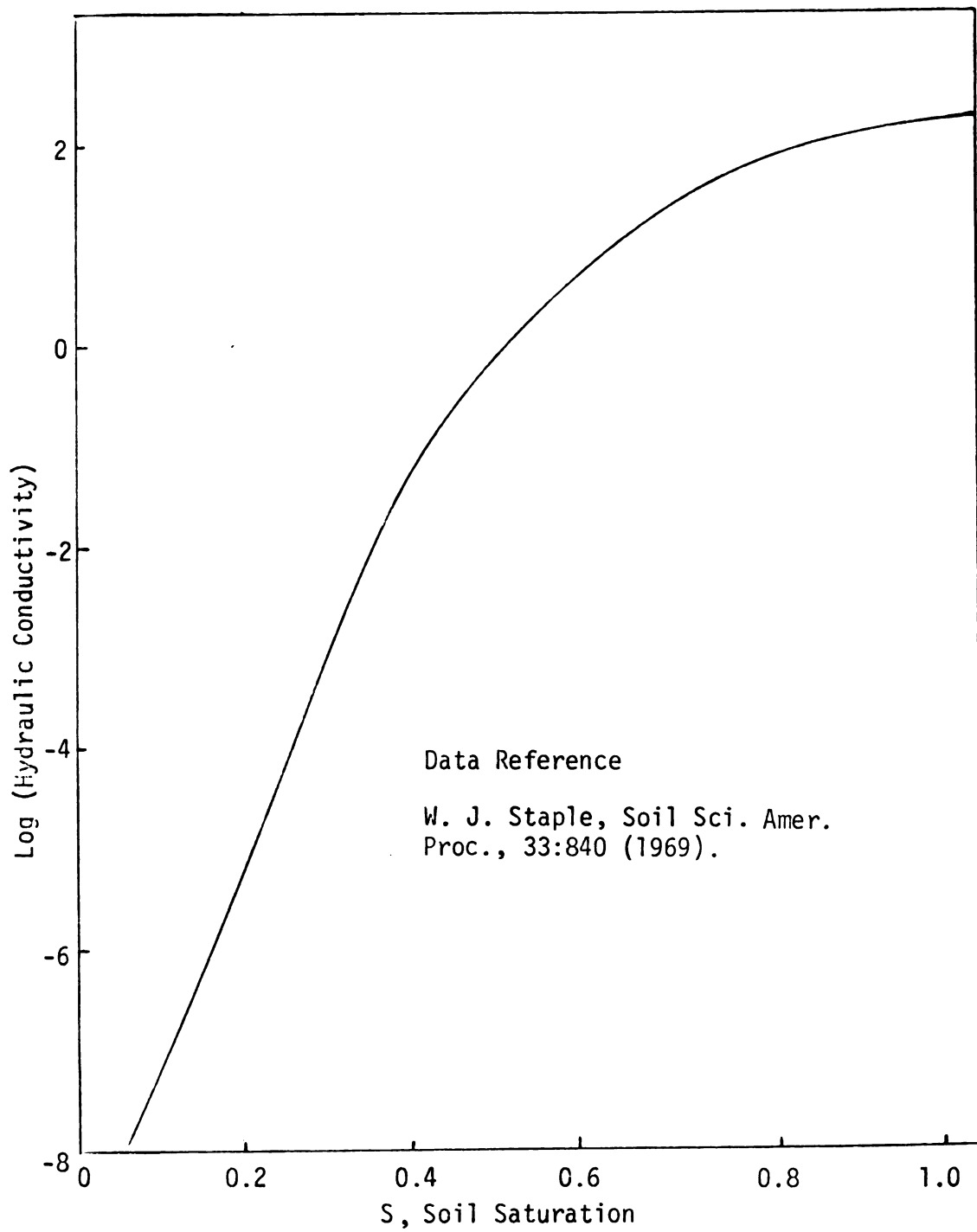


Figure 3.2.--Hydraulic Conductivity Versus Soil Saturation.

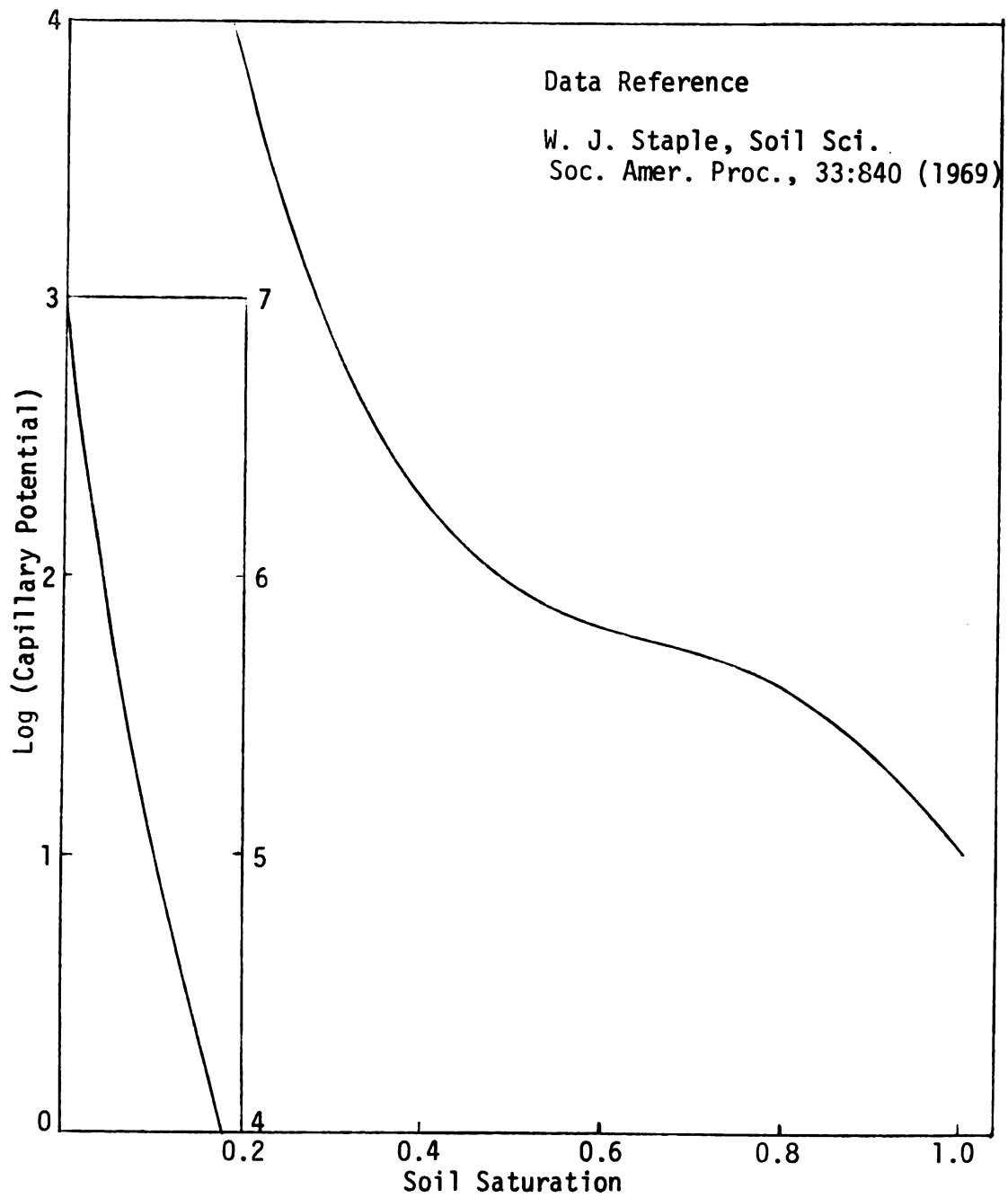


Figure 3.3.--Capillary Potential Versus Soil Saturation.

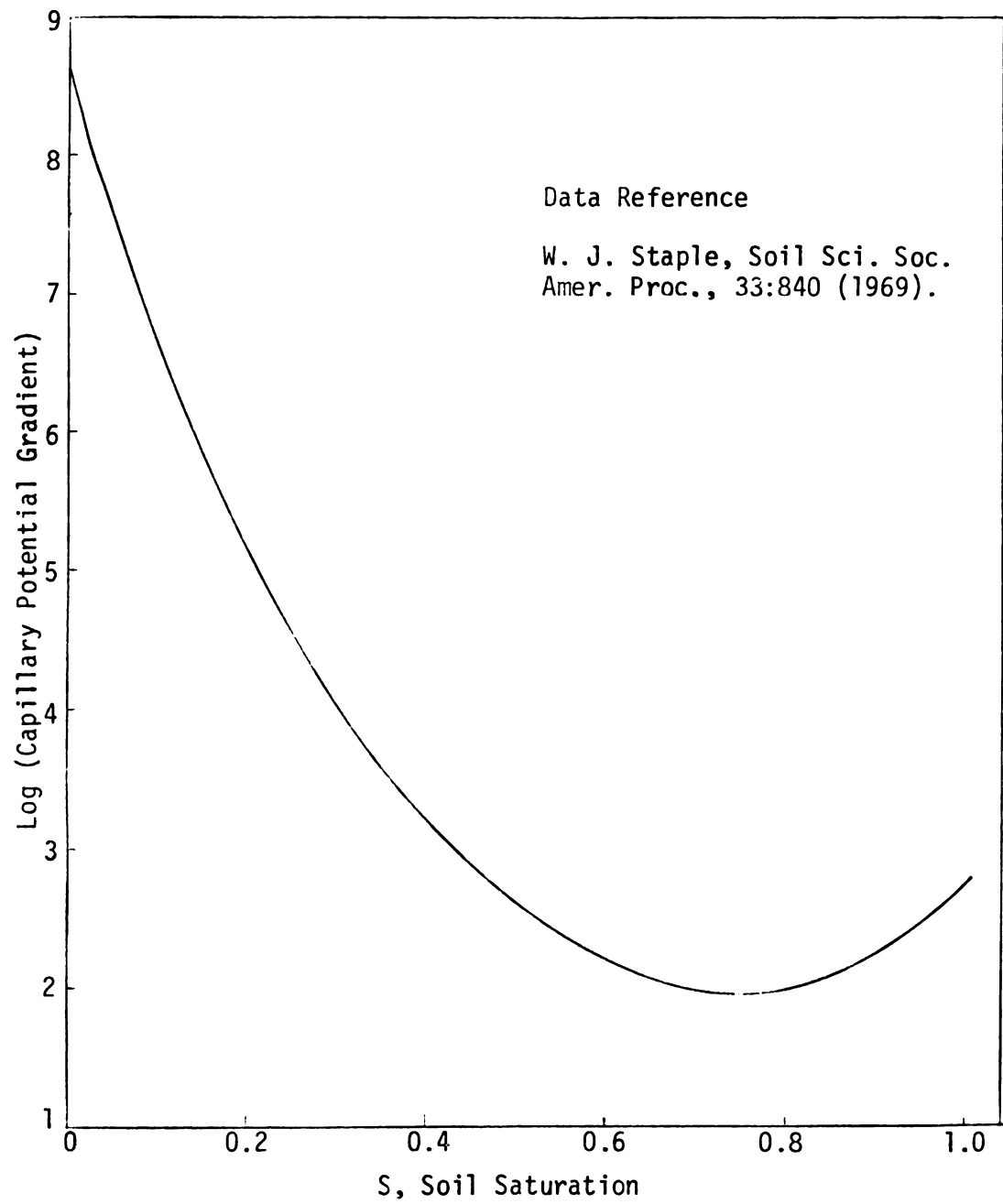


Figure 3.4.--Capillary Potential Gradient as a Function of Soil Saturation.

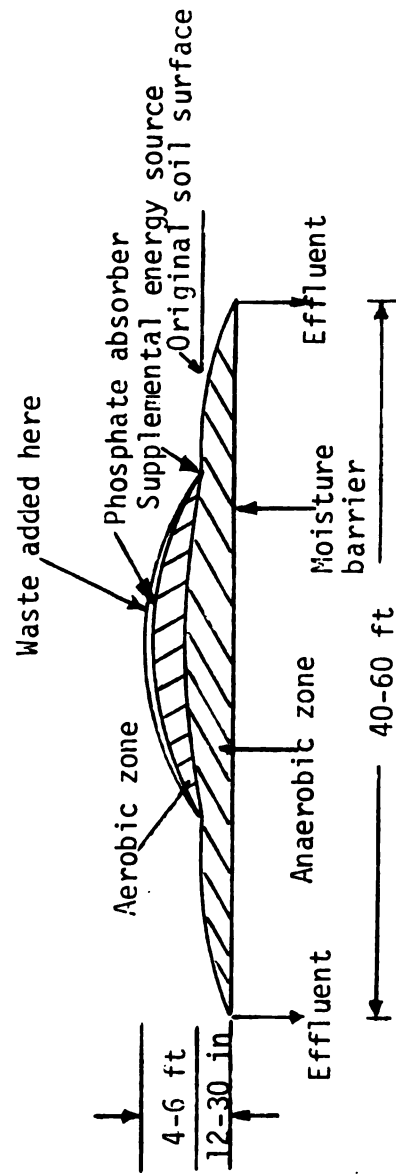


Figure 3.5.--Schematic Cross-Section of Barriered Land Water Renovation System (BLWRS).

soil. Phosphorus adsorption takes place in the upper part and nitrification and denitrification occur in the aerobic and anaerobic regions. BLWRS was constructed of Spinks loamy fine sandy soil. Data obtained from this system after 60 days of operation at an average application rate of 2.11 cm/day were used to validate the model developed here.

Anaerobic swine waste was spread on the BLWRS at an average rate of one inch per day. The application rate was reduced during rainy periods. The liquid wastes contained an average of 40 ppm of organic and inorganic phosphorus. Periodically, samples were taken at various depths and were analyzed for their phosphorus content. The detailed description of the system and the operating procedure can be found in Erickson et al. (1971).

When the liquid waste from the anaerobic holding pits was applied to the surface of the soil, the first reaction to be expected was precipitation of calcium phosphate. The existing soil pH after operation of the BLWRS for a short period of time was 7.0-7.2 and the calcium content of both the soil and waste material was sufficiently high to precipitate orthophosphate as calcium phosphate. As discussed in the phosphorus precipitation section, dicalcium phosphate forms rapidly under these conditions, but the other calcium phosphates form more slowly (a few weeks for octacalcium phosphate and several years for apatite). Since dicalcium phosphate limits the solubility of phosphorus, the phosphorus concentration in solution would be from 7-9 ppm total phosphorus in the pH range 7.0-7.2 (from Figure 2.1). As the precipitation

phenomenon was not considered in developing the model and approximately 80 percent of the phosphorus added to the BLWRS can be removed by this mechanism, it is very important to establish the phosphorus concentration in solution at the surface.

From the application rate, the total time of irrigation and the quantity of adsorbed phosphorus, the phosphorus input concentration to the adsorption zone was calculated by material balance. For the BLWRS, it turned out to be 9-10 ppm corresponding to the theoretical value for dicalcium phosphate solubility at pH 7.0. It was verified that precipitation had occurred, as the surface soil after several months of operation was found to contain 853 ppm total phosphorus as compared to 132 ppm for the soil at a 5 foot depth. Of the 853 ppm, only 67 ppm was in the adsorbed state. Thus, during continuous operation of the BLWRS, dicalcium phosphate controls the level of phosphorus in solution at 9 ppm. This did not preclude the formation of less soluble phosphates with time but suggested that they would not control the level of phosphorus in solution leaching into the adsorption zone.

Initial and Boundary Conditions

Based on the above discussion, the concentration of 10 ppm phosphorus in solution was used as a boundary condition. The phosphorus concentration from that point onwards was obtained by numerically solving Equations (3.6) under the following simulation conditions:

$$\left. \begin{aligned} S(Z,0) &= 0.1, \\ X(Z,0) &= 4 \text{ ppm}, \\ Y(Z,0) &= .06 \text{ ppm}, \end{aligned} \right\} \quad \begin{array}{ll} & \\ & (I.Cs) \end{array} \quad (3.10)$$

and

$$\left. \begin{aligned} S(0,t) &= 0.53, \\ X(0,t) &= 63.13, \\ Y(0,t) &= 10 \text{ ppm, and} \\ \frac{\partial S}{\partial Z} \Big|_L &= \frac{\partial Y}{\partial Z} \Big|_L = 0. \end{aligned} \right\} \quad \begin{array}{ll} & \\ & (B.Cs) \end{array} \quad (3.11)$$

Here, $X(Z,0)$ and $Y(Z,0)$ are in equilibrium and so are $X(0,t)$ and $Y(0,t)$. The values of the constants in the Langmuir isotherm equation are

$$a = .0122, \text{ and } b = .01462.$$

Method of Solution

Equations (3.6) cannot be solved analytically and hence a numerical solution was sought instead. The equations can be divided into two sections: (1) water transport equations and (2) phosphorus transport equations. These two sets of equations can be solved either separately or simultaneously. In the first method, the water transport equations can be solved first and the saturation profiles computed at different times are stored in the computer. The phosphorus profile can then be computed from the phosphorus equations and from the computed saturation profiles. The second method would involve solving, at every time interval,

the water transport and phosphorus balance equations in succession. The latter method was used in solving the above set of equations.

An implicit method was employed to compute the saturation and phosphorus profiles at the next time interval. All the first order and second order derivatives were approximated by finite difference equations at the next increment in time, resulting in a set of simultaneous equations. These equations were solved, to give the saturation profile and the phosphorus profiles in the liquid and solid phases. Both the water and phosphorus balance equations are nonlinear. In order to follow the above procedure, the equations have to be linearized. Approximate estimates of saturation and phosphorus profiles were made and an iterative procedure was established. Iterations were continued until the computed and estimated profiles converged to the same values.

A general FORTRAN program PMODEL was written to solve the above equations numerically to obtain the phosphorus profiles. The program is quite general in the sense that another soil system, having different Langmuir adsorption isotherm constants, and different physical constants, can be simulated quite easily by changing some parts of the subprograms. Also, by selecting the proper option, it can be made to simulate both the water and phosphorus movement or just the phosphorus movement (this statement will be elaborated later).

A complete description of the numerical method used to solve these equations, along with a listing of the FORTRAN program PMODEL and its associated subprograms, may be found in Appendix B.

The following steps illustrate the calculation procedure used to solve the equations numerically.

1. Input the properties of the soil system, the operating conditions, and the increment sizes of the length and time axes. The program establishes the initial conditions in the soil and the boundary condition at the surface.

2. Compute the saturation profile in the soil. This involves carrying out the following steps.

- a. Assume a saturation profile at the next time interval. This linearizes the equation and allows us to compute the hydraulic conductivities and the gradients of capillary potential at the next time interval.

- b. By using a second order finite difference approximation for the partial derivatives, an equation is written for each grid point resulting in a set of simultaneous linear equations.

- c. Solve these equations to obtain the saturation profile at the next time interval.

- d. Compare the calculated profile with the assumed profile. If they do not match, assume a new profile based on the average of the computed and assumed values at the previous iteration and go back to step b. If both the profiles match, go to step 3.

- e. Continue this procedure until convergence is obtained within the required limit of accuracy.

3. Calculate the phosphorus profile in the liquid and solid phases. This involves carrying out the following steps.

a. Assume a phosphorus profile in the soil at the next time interval based on the past available information. This has the effect of linearizing the equations. As the X-profile is known, Y^* is also known at the next time increment.

b. By using a second order finite difference approximation for all the partials, an equation for the phosphorus concentration in the solution can be written for each grid point resulting in a set of simultaneous linear equations.

c. Solve these equations to obtain the phosphorus concentrations in solution at each grid point at the next time increment.

d. From the Y profile, the X-profile, i.e., the profile of phosphorus concentrations in the soil, can be computed at each grid point (as Y^* at the next time increment is already known).

e. Compare the calculated and assumed X-profiles. If they are not converged to the same values within given limits, go back to step 3a. If they do, all the required information has been computed. Start the whole cycle again for computing the profiles at the next time increment.

4. All the variables are outputted at the beginning of each computation cycle.

Results and Discussion

Numerical Problems

As the equations in set (3.6) are nonlinear and quite complex, a numerical analysis of these equations was not possible. The final values of the time and depth increments had to be chosen after some trial and error procedure. In almost all cases, a time increment of 0.25 day and a depth increment of 0.5 cm or 1 cm were found quite adequate. A very small improvement in the values of the variables compared to the greatly increased computation time did not justify going to smaller increment values.

Another problem is the selection of the proper length of soil to simulate at a given time. The soil length should not be too large as this would increase the number of grid points to be used and hence the number of simultaneous equations to be solved. At the same time, it should be large enough so that the boundary condition $\partial Y/\partial Z = \partial S/\partial Z = 0$ at $Z = \infty$ can be applied realistically enough. In general, a 20 cm or a 40 cm zone was simulated at a time. This depth was sufficiently large so that the concentration values at the lowest point were not greatly different from the initial values. This ensured that the lower boundary condition was applied properly.

Surface Boundary Condition for Saturation

From Darcy's equation, one can see that when $\partial S/\partial Z = 0$, the saturation is constant and the velocity through the soil is equal to the hydraulic conductivity. The saturation at which the

hydraulic conductivity equals the surface application rate of 2.11 cm/day at BLWRS is 0.534512 (from Staple's data on hydraulic conductivity as a function of saturation). If the initial saturation is 0.1, then it would be expected that the soil saturation will increase from 0.1 to 0.534512 gradually.

There are two surface saturation conditions that can be used as one of the boundary conditions: constant surface saturation or constant velocity at the surface. Qualitative descriptions for both these situations are depicted in Figure 3.6 which shows the development of the saturation profile as a function of time. Figure 3.6a refers to a constant surface saturation, say, at 0.53. This assumes that as soon as the wastewater is sprayed on the land, surface saturation reaches 0.53. In this case, the surface velocity varies from a high value to the surface application rate as the time progresses. Figure 3.6b refers to the case where the surface velocity is constant but not the surface saturation. The surface saturation varies continuously such that it provides the proper saturation and capillary potential gradient to keep the surface application rate constant. The condition of constant surface velocity is more realistic than that of constant surface saturation. Simulation of water movement with constant surface velocity has been tried but without any success. Childs (1965) reports that mathematical analysis of this case is quite complex. In this work, the case was treated as if the surface saturation was maintained constant at 0.53.

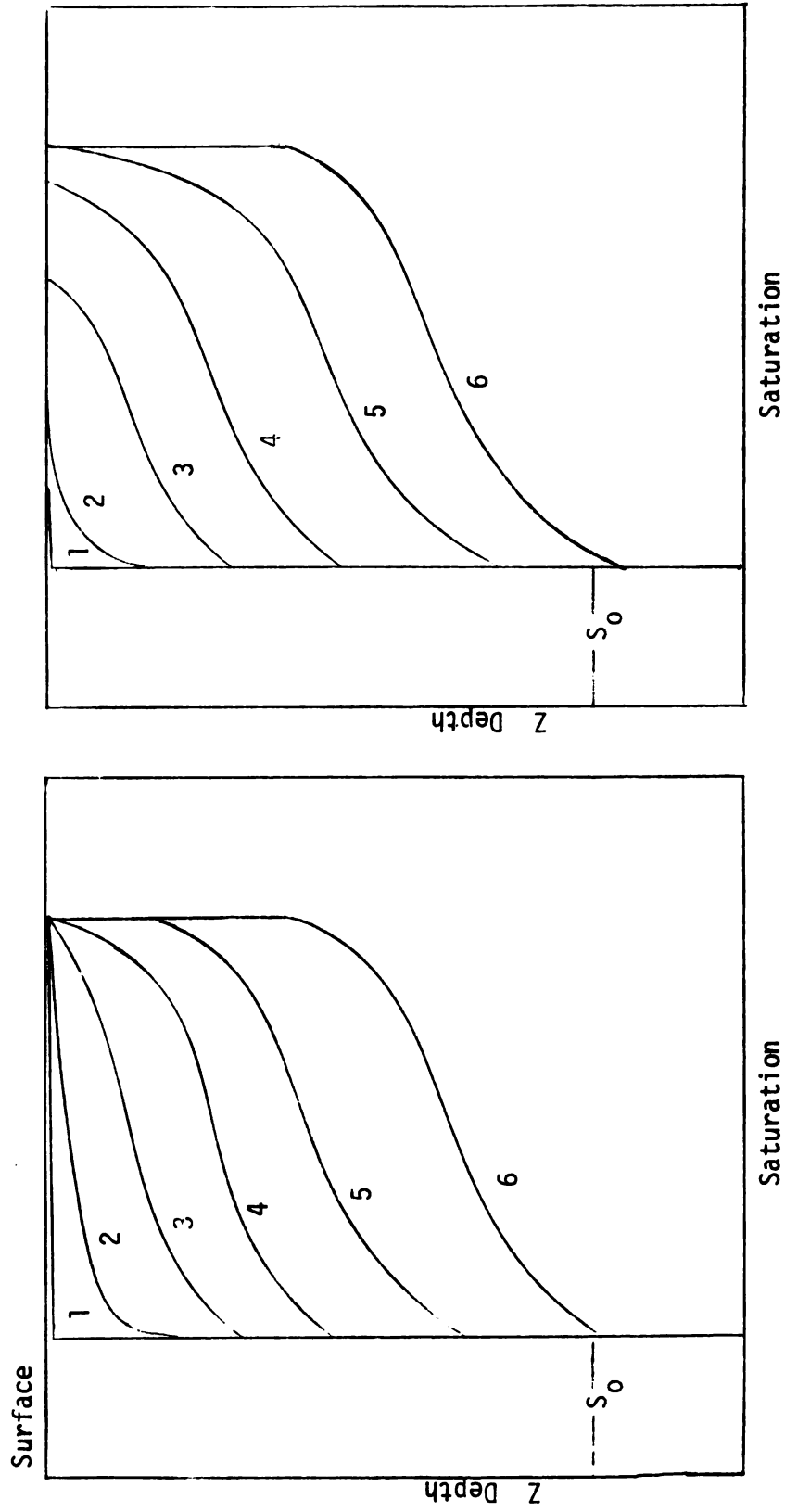


Figure 3.6a.---Development of Saturation Profile With Constant Surface Saturation.

Figure 3.6b.---Development of Saturation Profile With Constant Surface Velocity.

Water Transport

As the wastewater starts moving down the soil, the moisture content in the soil increases and so does the phosphorus concentration. If the experiment was being carried out in a soil column of finite length, one would expect that water would start filling the column and after some time, the column would be completely filled with water. Beyond this point, there would be no need to consider the water balance equation and the model reduces to the phosphorus balance equations. Similarly, in a soil system like the BLWRS (infinitely long), one would expect the water front to move much faster than the phosphorus profile. This was verified quite conclusively by some preliminary runs, and the results of one of these runs are shown in Figure 3.7 wherein the saturation and phosphorus profiles are plotted at different time intervals.

After operating the system for 1-3/4 days, the entire 20 cm of soil length considered shows moisture content at 0.5345. But the phosphorus concentrations in soil are affected only up to 5 cm. The advancing water front is so far ahead of the phosphorus front that, for all practical purposes, in the region of the phosphorus profile, the velocity of water is constant at 2.11 cm/day and the saturation at 0.534512. After 1-3/4 days, the water balance equation drops out and the simulation equations reduce to the phosphorus balance equations in the liquid and solid phases. Experimental evidence to support the fact that the water front moves much faster than the phosphorus front comes from Cho (1970). He found that in a soil column, the phosphorus movement is four to eight times slower

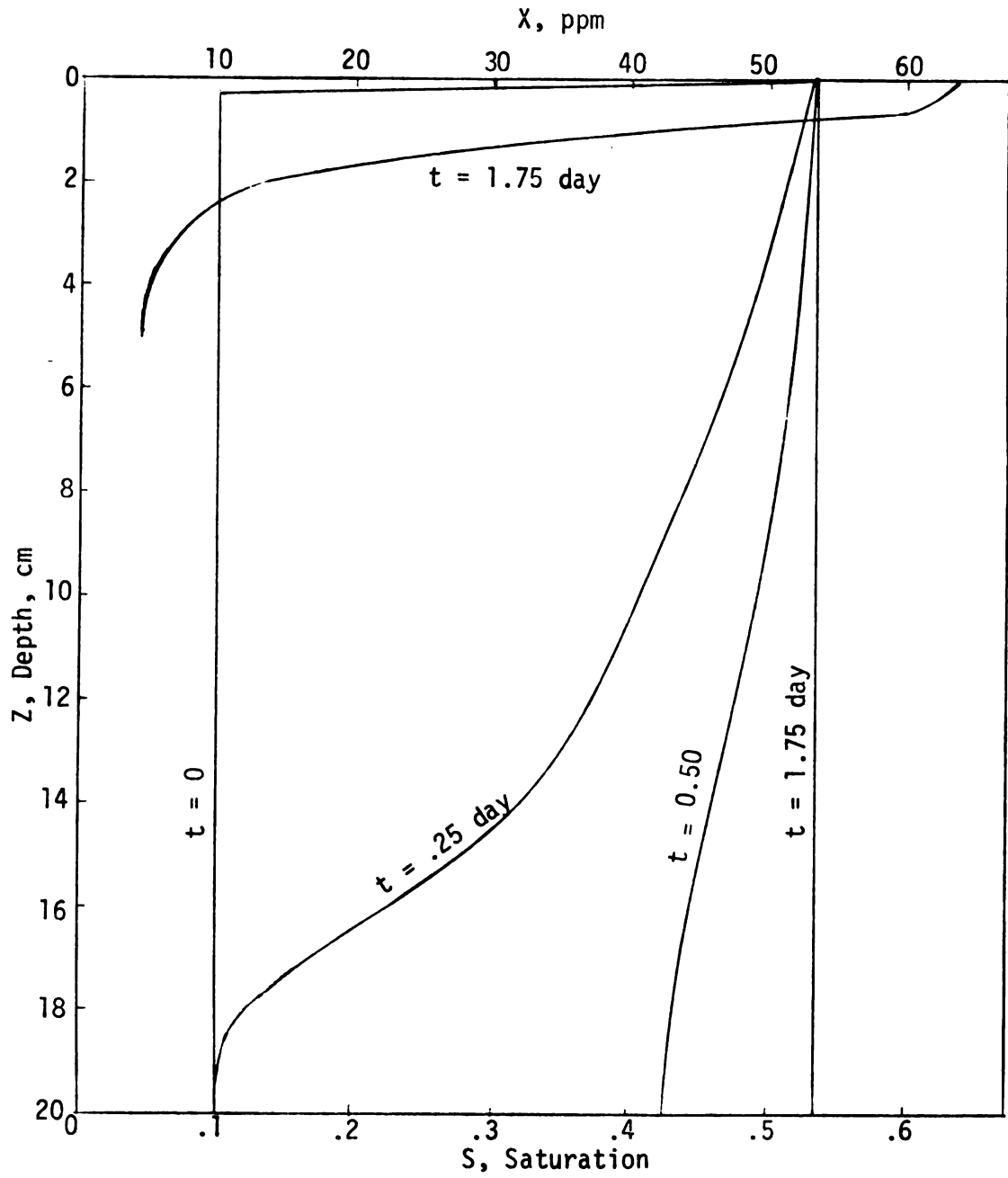


Figure 3.7.--Development of Saturation and Phosphorus Profile During Simulation.

than the water movement. This observation can be easily verified by a simple calculation. The water and phosphorus balances can be established after some application time, and the depths of the soil to which the water and phosphorus fronts have penetrated can be determined. This would show that the water front is way ahead of the phosphorus front. For the simulation of BLWRS system, only the phosphorus balance equations were solved.

Another interesting feature of Figure 3.7 is the extent of penetration of the water front in the soil after only six hours and the very small rate of penetrations thereafter. This is explained easily by the fact that, when a constant surface saturation of 0.53 is assumed, the instantaneous surface velocity is much higher than the actual 2.11 cm/day. The water profile thus penetrates much farther. After six hours, the saturation gradient is not so steep and the surface velocity is quite close to the actual application rate. This reduces the rate of the water front advance to reasonable values.

Phosphorus Transport

If moisture distribution is neglected for a continuous input of liquid wastes, the calculation procedure is significantly reduced as the numerical procedure outlined in the previous section is followed without step 2. The corresponding simulating equations are

$$D_e S \frac{\partial^2 Y}{\partial Z^2} - V_e S \frac{\partial Y}{\partial Z} - K_o a (Y - Y^*) = \frac{\partial \epsilon S Y}{\partial t} , \quad \left. \vphantom{\frac{\partial^2 Y}{\partial Z^2}} \right\}$$

$$\rho_b \frac{\partial X}{\partial t} = K_0 a (Y - Y^*) , \text{ and} \quad (3.12)$$

$$Y^* = \frac{aX}{1 - bX} .$$

The numerical solution of Equations (3.12) was obtained and the results are shown in Figure 3.8. The comparison of the BLWRS data with the simulation results shows remarkable agreement. Even though there are only three data points available at every three inch interval, they lie almost on the predicted curve. This is remarkable, considering the fact that the system simulated here is quite complex. The phosphorus profile has traveled about 12-13 cm in soil after wastewater has been applied for 60 days. The phosphorus concentration at 25 cm soil depth is around 4 ppm in soil and .06 ppm in solution, indicating almost no leakage from the soil system.

Rhee and Amundson (1972) have predicted that under the conditions of favorable equilibrium, the phosphorus profile would attain a constant shape which would move down through the soil. They termed this phosphorus profile of constant pattern a shock layer. They also showed that the shape of the shock layer is dependent on the physical constants such as the dispersion coefficient, the mass transfer coefficient, etc. In simulating the BLWRS system, a provision was made to move the coordinate axes down if the profile approached a constant shape. This occurs when the second point from the top surface reaches the maximum attainable concentration of 63.13 ppm. During the BLWRS simulation, it was

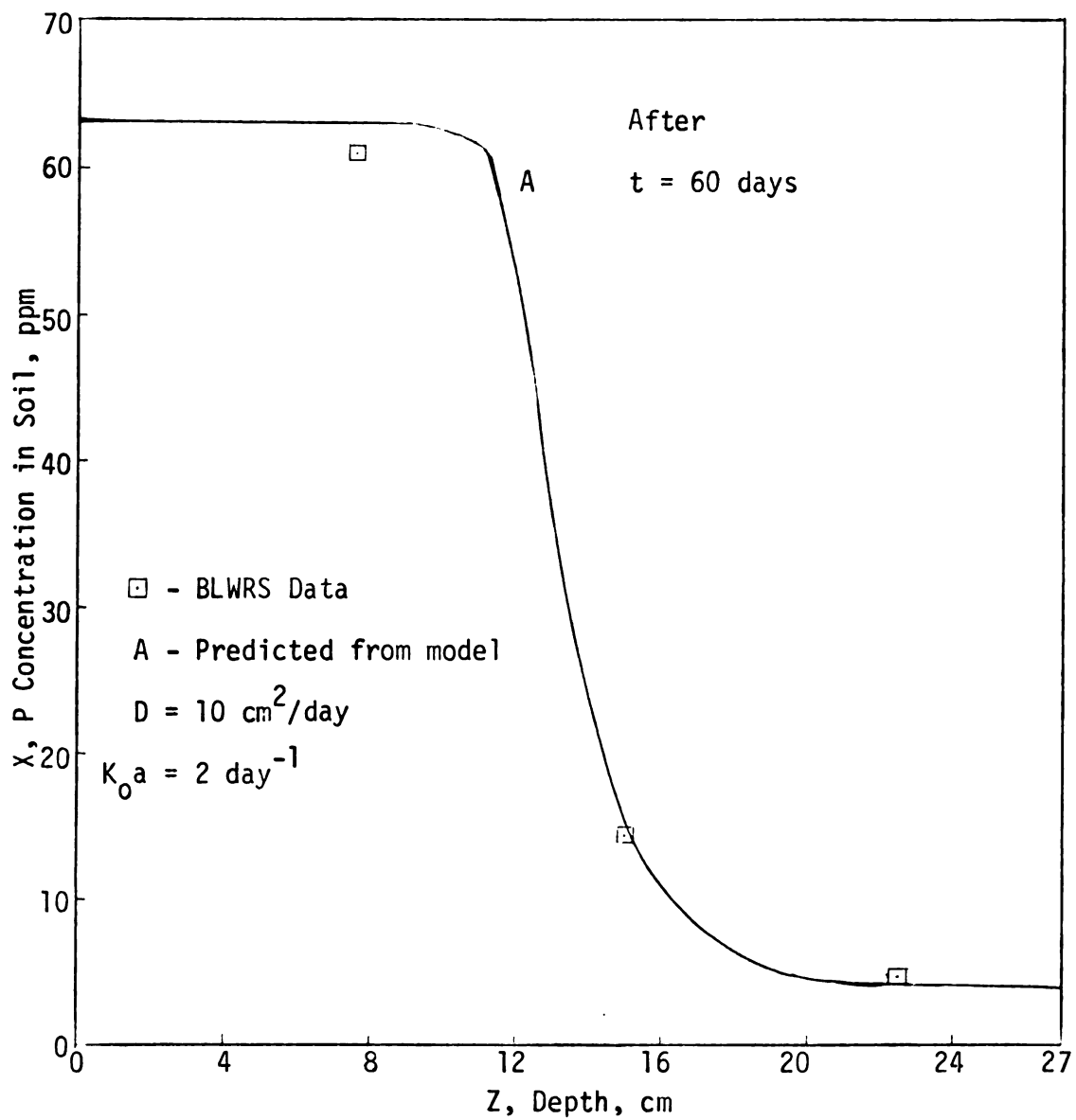


Figure 3.8.--Comparison of BLWRS Data With Predicted Results From the Model.

found that after nearly 60 days of operating time, the profile approached a constant pattern.

The effect of the mass transfer coefficient on the shape of the shock layer was investigated and the results are shown in Figure 3.9. It is seen that lower overall mass transfer coefficient results in wider shock layers. This can be easily explained by the fact that with higher mass transfer coefficients, phosphorus will be adsorbed much quicker before it can go too far. Thus, the resulting shock layer would be smaller, and vice versa.

The effect of the dispersion coefficient on the shock layer thickness is quite predictable. The dispersion coefficient represents some measure of deviation from the ideal plug flow. The greater the value of the dispersion coefficient, the greater is the deviation from the plug flow and this would give greater shock layer width. These arguments are shown to be correct by Figure 3.10. The shock layer width for the case of $D = 10 \text{ cm}^2/\text{day}$ is about 8 cm compared with 4 cm for the case of $D = 2 \text{ cm}^2/\text{day}$.

Figure 3.11 shows the location of the phosphorus profile in soil when the application rates are different. Because of a greater input rate of 4.22 cm/day, the phosphorus profile represented by the curve A is much farther in the soil than the curve B representing the application rate of 2.11 cm/day. The profiles plotted do not represent the shapes of the corresponding shock layers because the computations were not carried out for long enough times.

Soils, because of their different compositions and structures, may exhibit different values of the various physical constants.

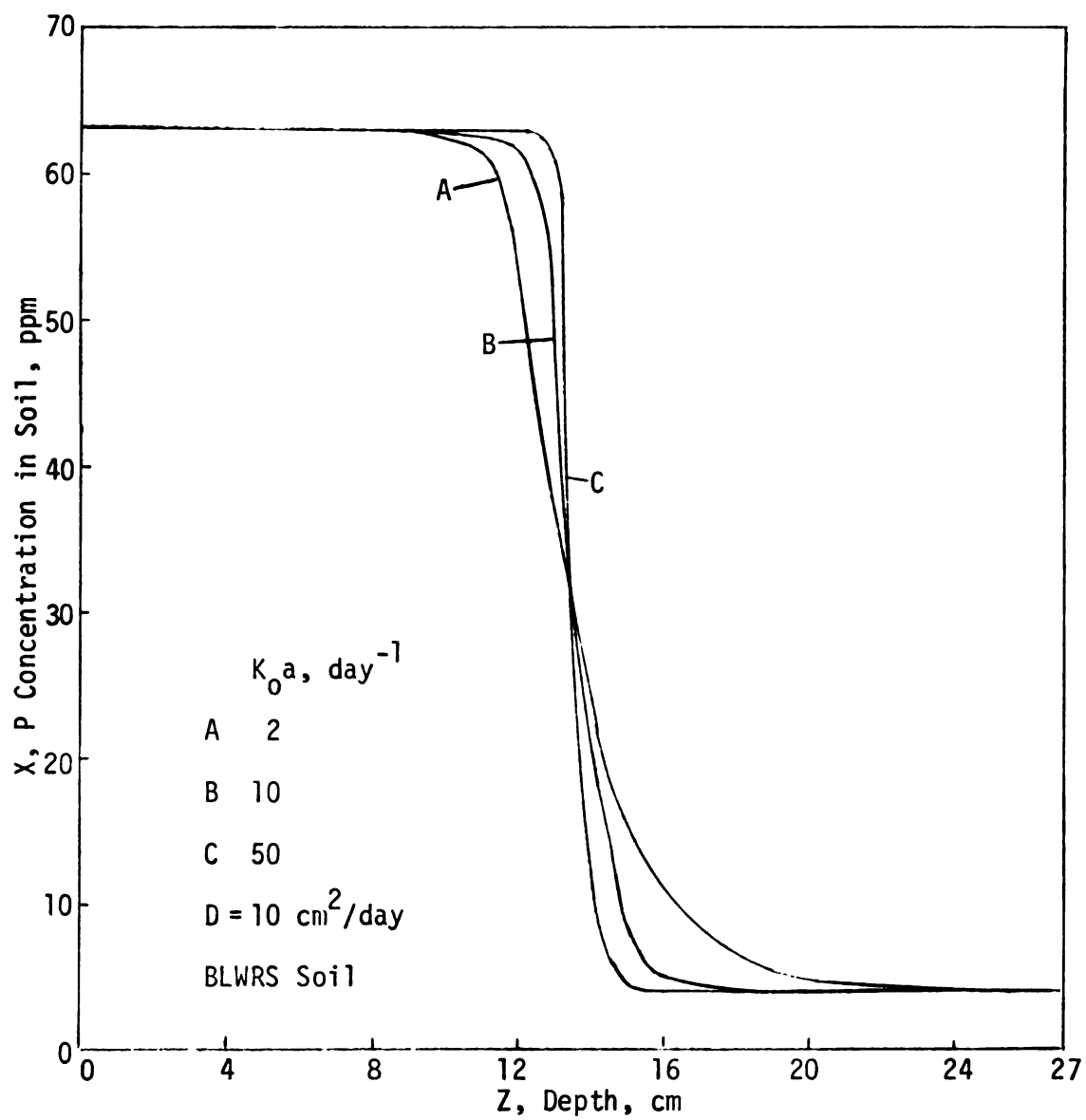


Figure 3.9.--Effect of Mass Transfer Coefficient on Shock Layer Shape.

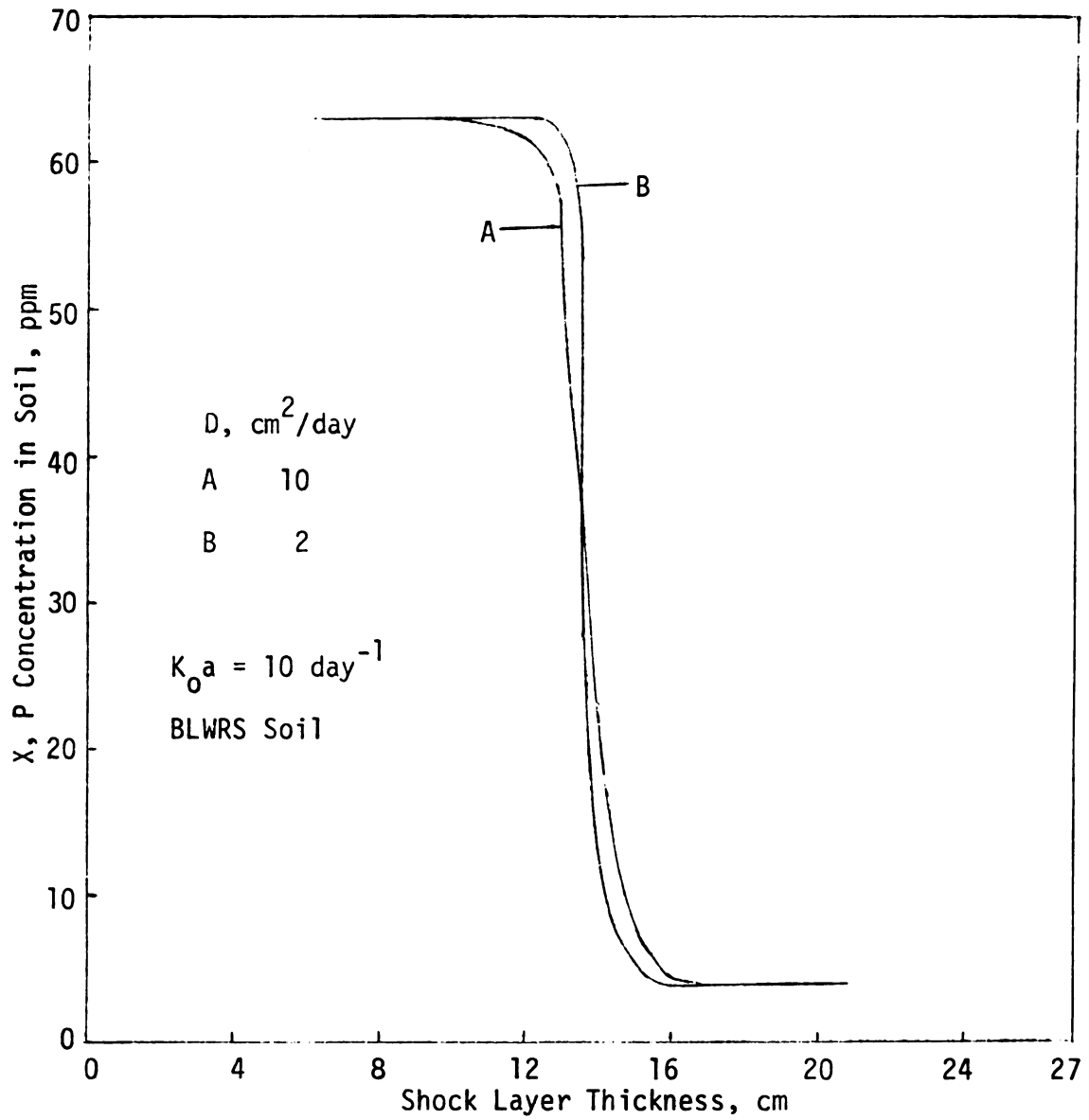


Figure 3.10.--Effect of Dispersion Coefficient on the Advancing Front Thickness.

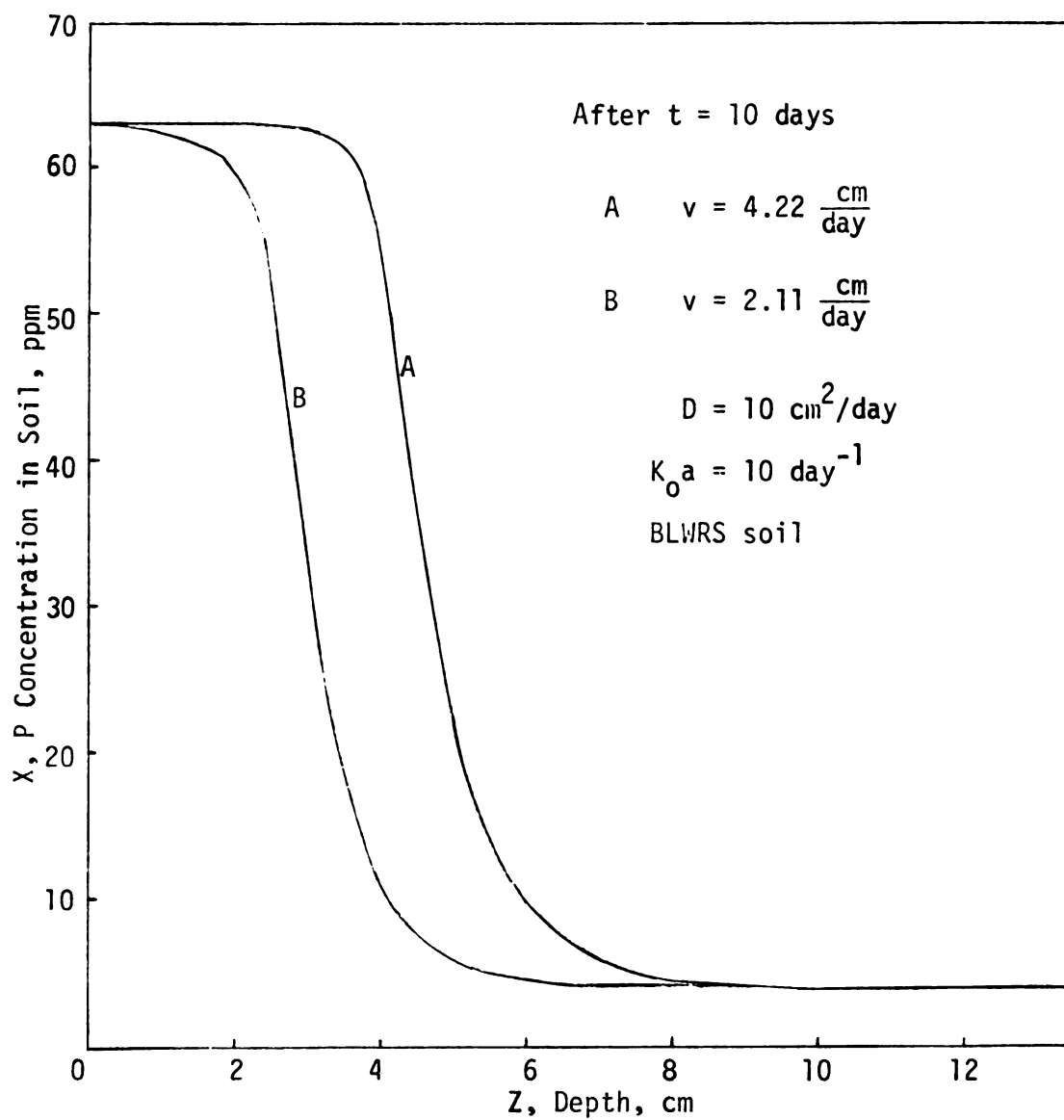


Figure 3.11.--Effect of Increasing Application Rate on the X-Profile.

For this reason, the above discussion on the effect of various factors on the shock layer shape has been included. For a detailed qualitative discussion on the effect of various parameters on the shock layer thickness, the reader is referred to Novak et al. (1975).

There are two important points that need to be considered. This model considered continuous application of wastewater on the land. This is not necessarily true. When the rains come, the application has to be stopped so as to prevent ponding on the soil. The rainwater percolates through the soil and some desorption of phosphorus is likely to occur from the solid phase to the liquid phase. This could lead to some oscillations in the phosphorus profiles in soil and in solution. This is just speculation and no experimental evidence has been found to support it. Further work in this area would definitely be helpful.

Although a soil system has been found to be very efficient in removing phosphorus from the wastewater, a way must be found to remove this phosphorus from the soil. Otherwise, soil becomes a dumping site for phosphorus and we have succeeded only in transferring the pollutant from the wastewater to the soil. The best way to remove this phosphorus is to crop the soil and let vegetation use this phosphorus as nutrient. This enables us to recycle the phosphorus rather than let it accumulate in the soil. Thus, a sound ecological land disposal system would be operated on a cyclic basis of spreading the wastewater and cropping the soil.

CHAPTER IV

NITROGEN TRANSFORMATIONS

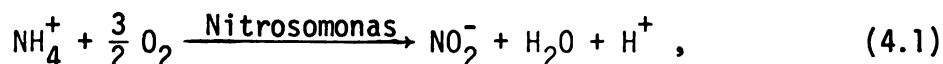
Background

Nitrogen exists in soils in both organic and inorganic forms. It undergoes a number of reactions. The main reactions of nitrogen are mineralization, nitrification, denitrification and immobilization. All of these reactions are microbial in nature. There have been a number of reviews on the nitrogen reactions in soils (Bartholomew and Clark 1965). A brief summary of the nitrogen transformation processes is given below.

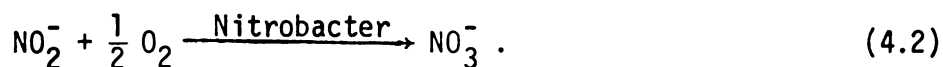
Mineralization is the process of converting organic nitrogen into the inorganic ammonium form whereas immobilization involves converting the inorganic nitrogen into the organic form by assimilation and incorporation into microbial cells. Both these reactions occur in opposite directions but which one will predominate depends on the availability of organic carbon (C) to organic nitrogen (N) ratio. If the ratio is high, immobilization proceeds faster and the reverse would be the case if the C:N ratio is low. If an equilibrium can be assumed between these two reactions in the soil, nitrification and denitrification become the predominant reactions of nitrogen.

Nitrification is a reaction wherein nitrogen in the form of ammonium is converted in the presence of dissolved oxygen to nitrate

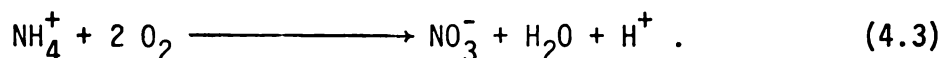
nitrogen. This process is carried out by chemoautotrophic bacteria. These bacteria obtain their energy requirement from oxidization of oxidizable compounds. Nitrification is believed to take place in two steps as given below:



and

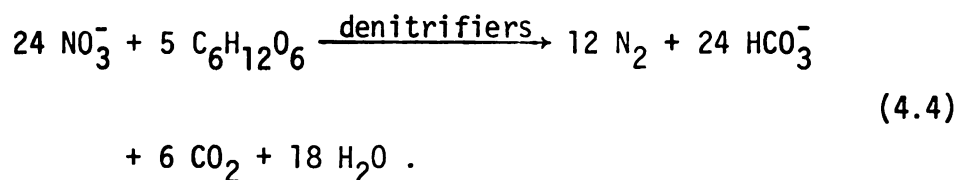


The overall reaction is

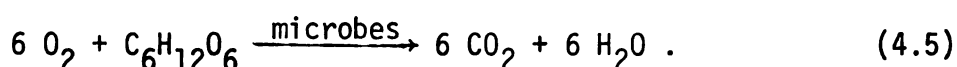


The second reaction is much faster than the first, therefore nitrite accumulation in the soil is negligible. Nitrosomonas and Nitrobacter are the species of microorganisms that carry out each reaction. They use carbon dioxide as the source for their carbon requirement.

The denitrification reaction involves the reduction of nitrate nitrogen to atmospheric nitrogen. This reaction is carried out by some facultative bacteria. In an anaerobic environment, these microbes use an alternative electron acceptor such as nitrate in the place of oxygen. If an energy source such as organic carbon is present, nitrate nitrogen is reduced to nitrogen gas. If glucose is that energy source, denitrification can be written as



In the presence of enough oxygen, the same reaction would proceed as



Under some conditions, it is possible to reduce nitrate to nitrogen chemically. However, Brezonik (1966) has shown that for significant chemical denitrification to occur, soil pH has to be very low.

The wastewater to be sprayed on the land disposal site generally contains nitrogen in the form of ammonium or in the form of proteins, amino acids and urea from which ammonia is easily derived. The main nitrogen component is thus ammonium and the important reactions to be considered are nitrification and denitrification. These two reactions have been studied by sanitary engineers and soil microbiologists. Recent interest by sanitary engineers is due to the fact that a modified activated sludge plant involving nitrification and denitrification has been suggested to remove nitrogen along with the biological oxygen demand. The interest of soil scientists in nitrogen transformations is understandable because these are the premier microbial reactions in the soil by which soil nitrogen is lost. Laboratory experiments by soil scientists have been done mainly in soil columns whereas

those by sanitary engineers have been carried out mostly in continuous stirred tank reactors. In this work, an attempt will be made to integrate the work done by sanitary engineers and soil scientists.

Reaction Kinetics

The nitrification and denitrification reactions are biochemical in nature. The biochemical pathway of each reaction consists of a number of steps in series. Each step is enzymatic in nature and is catalyzed by a very specific enzyme. Overall rate of the reaction is determined by the slowest step in the series.

The most widely accepted model of enzyme kinetics is that of Michaelis-Menten. They represented the reaction $S_1 \rightarrow P$ as



where

$E \equiv$ enzyme,

$S_1 \equiv$ substrate,

$P \equiv$ product, and

$E - S_1 \equiv$ enzyme-substrate complex.

The rate of product formation is given by

$$r = r_m \frac{S_1}{K_m + S_1} \quad (\text{Aiba et al. 1960}) \quad (4.7)$$

where

r = rate of product formation,

r_m = maximum rate of product formation at very high substrate concentration, and

K_m = substrate concentration at which $r = r_m/2$.

Here substrate S_1 is assumed to be the limiting substrate.

Since nitrification depends on the metabolism of a certain group of microorganisms, the rate of product formation would also depend on the growth rate of microbes and their numbers. Monod (1949), in his study of bacterial growth in a continuous culture, where there was one limiting substrate, found that his data behaved in a manner typified by the Michaelis-Menten equation and proposed the following equation

$$\mu = \mu_m \frac{S_1}{K_{S_1} + S_1} \quad (4.8)$$

where

μ_m = maximum growth rate when the substrate is present in excess, day^{-1} ,

μ = specific growth rate, day^{-1} , and

K_{S_1} = saturation constant; i.e., substrate concentration at which $\mu = \mu_m/2$.

Here

$$\mu = \frac{1}{X} \frac{dX}{dt}$$

where

X = concentration of microorganisms, mg/l .

Equation (4.8) incorporates both the first order and the zero order models. If $S_1 \gg K_{S1}$, then $\mu = \mu_m S_1/S_1 = \mu_m$, i.e., the growth rate is constant and is independent of the substrate concentration. If $K_{S1} \gg S_1$, then $\mu = \mu_m S_1/K_{S1}$ which indicates that the growth rate is directly proportional to the substrate concentration.

At steady state, in a continuous stirred tank reactor, the dilution rate equals the specific growth rate of the bacteria in the reactor (to be shown later). The chemostat can be operated at various dilution rates (residence times) and the effluent substrate concentration at each dilution rate can be determined. The results can be plotted in two ways as shown in Figure 4.1.

In Figure 4.1a, the dilution rate is plotted against the substrate concentration. From this graph, μ_m and K_{S1} can be calculated as the dilution rate at large S_1 values and the substrate concentration at growth rate equal to $\mu_m/2$, respectively. The bottom figure illustrates the "washout" phenomenon. If the reactor is operated at a dilution rate greater than the maximum specific growth rate, the microbes do not have enough time to grow in the reactor and are washed out. The substrate comes out at the initial concentration only. It can be shown that the Michaelis-Menten constant and the saturation constant are equal and that r_m and μ_m are related. If the yield coefficients for the microbial reactions are constant, then for a batch system, three differential equations can be written as

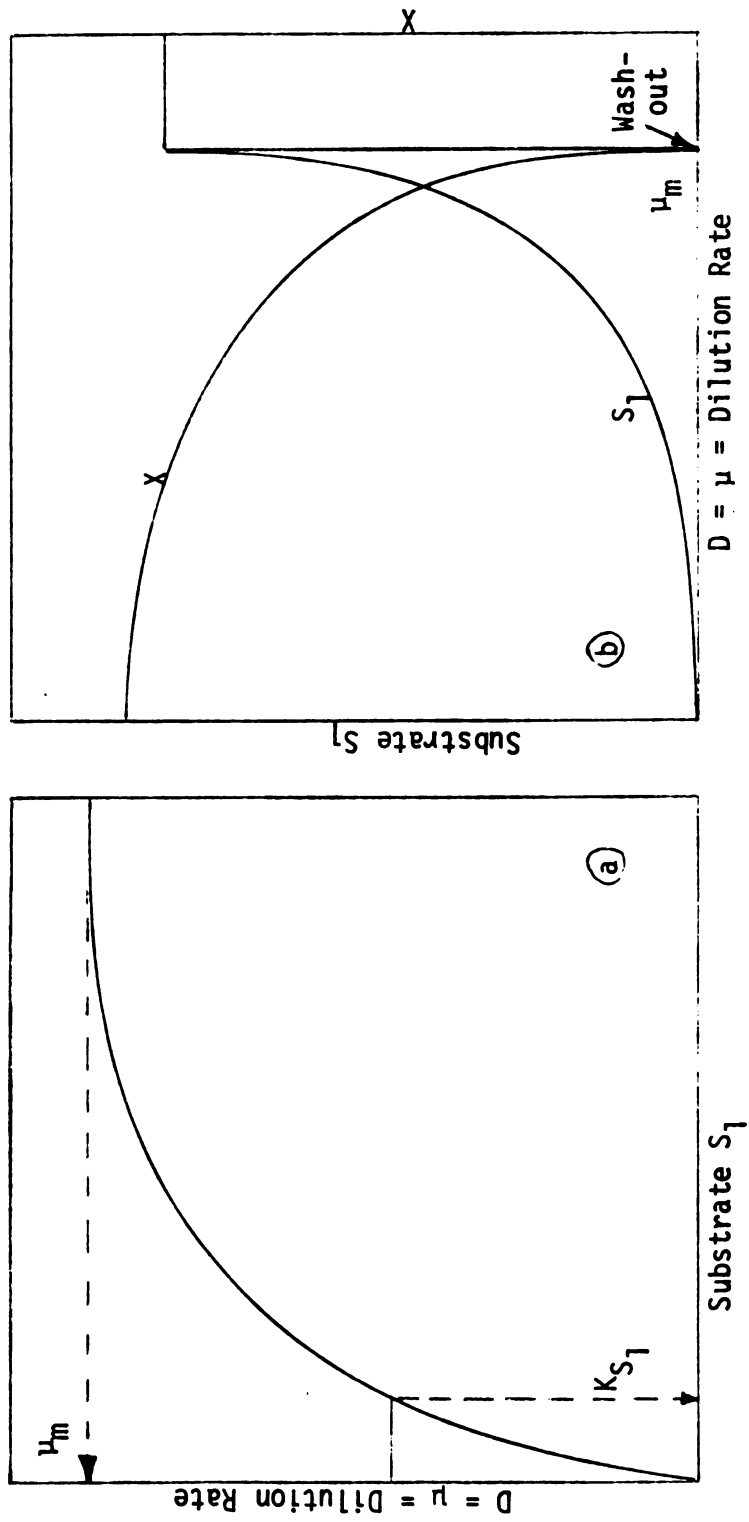


Figure 4.1.--Illustration of Monod Kinetics.

$$\frac{dX}{dt} = \mu X = \mu_m \left(\frac{S_1}{K_{S_1} + S_1} \right) X , \quad (4.9)$$

$$\frac{dS_1}{dt} = - \frac{\mu_m}{Y_1} \left(\frac{S_1}{K_{S_1} + S_1} \right) X = \text{rate of substrate consumption,} \quad (4.10)$$

and

$$\frac{dP}{dt} = \frac{\mu_m}{Y_2} \left(\frac{S_1}{K_{S_1} + S_1} \right) X = \text{rate of product formation.} \quad (4.11)$$

Comparing Equations (4.7) and (4.11) gives

$$r_m = \mu_m \frac{X}{Y} . \quad (4.12)$$

The maximum specific growth rate and the maximum rate of product formation are connected by the microbial concentration and the yield coefficient.

Most of the workers have assumed Equation (4.8) to describe the specific growth rate of microorganisms. This expression assumes that only one substrate is limiting. This is true when all the other substrates are in excess. Situations can arise when more than one substrate can become growth limiting. Under these conditions, the Monod expression has to be modified to include the effect of other substrates. A mechanism (given in Appendix C) has been proposed which is described by the following equation:

$$\mu = \mu_m \left(\frac{S_1}{K_{S_1} + S_1} \right) \left(\frac{S_2}{K_{S_2} + S_2} \right) . \quad (4.13)$$

Mahler and Cordes (1968) indicate other mechanisms which are prevalent in bisubstrate enzyme kinetics. Equation (4.13) very conveniently reduces to (4.8) if one of the substrates is in excess.

Most of the work on nitrification and denitrification has been done on the basis of single substrate growth limiting kinetics. In a soil column, the concentrations of ammonium nitrogen and oxygen decrease with length. At some point in the column, both these concentrations can be sufficiently low to be limiting. Thus, it is important to determine the growth rate expression as a function of two limiting substrates. The constants involved in Equation (4.13) will be evaluated from past work and, in the absence of any past appropriate work, experiments will be performed to calculate these constants.

Past Work

Nitrification

The substrates required for the nitrification reaction are ammonium nitrogen and dissolved oxygen. One would therefore expect the rate of the reaction to depend on the concentration of both these substrates.

At high concentrations of the substrates, the reaction rate is expected to be zero order. Nakos and Wolcott (1972) carried out the nitrification reaction batchwise at ammonium nitrogen concentrations of 400 ppm and higher. The ammonium nitrogen concentration decreased linearly with time indicating a zero order

reaction, but such high concentrations are not encountered in a land disposal system.

On the other hand, Wild et al. (1970), in a batch nitrification unit at ammonium concentrations of 30-40 mg/l, still found the reaction rate zero order. The unit was operated at very high microbial concentration and greater numbers of microbes could conceivably keep up the ammonium consumption.

Knowles et al. (1965) studied the growth rate of nitrifiers as a function of ammonium concentration as given by the Monod expression. Some of their results are tabulated below.

			Temperature °C		
			10	20	30
μ_m	<u>Nitrosomonas</u>	day ⁻¹	0.29	0.76	2.0
	<u>Nitrobacter</u>		0.59	1.0	1.9
K_{S_1}	<u>Nitrosomonas</u>	mg/l	0.22	0.73	2.4
	<u>Nitrobacter</u>		0.30	1.3	5.5

Downing et al. (1964) found the growth rate constant of Nitrosomonas double that of Nitrobacter. From the above values, it can be shown that the doubling time for nitrifiers is 10-20 hours compared to 2-3 hours for the activated sludge bacteria. This shows that for sufficient nitrification to occur, the detention time in the reactor has to be quite high. Many workers (Mulbarger 1971, Johnson and Schroepfer 1964) have proposed a separate nitrification unit from the carbon oxidation unit because of the slower

growing nitrifiers. The nitrification unit is followed by the denitrification unit. These workers have shown quite conclusively that such a system is very efficient in carbon and nitrogen removal.

The research efforts mentioned above did not consider the effect of dissolved oxygen on the rate of nitrification. Most of the work was done under the condition of a high degree of aeration. The dissolved oxygen concentration was quite high and it was not the limiting substrate. Wuhrmann (1963) showed that for good nitrification, the dissolved oxygen concentration must be greater than 1 mg/l. Amer and Bartholomew (1952) studied the effect of the oxygen concentration in soil air on nitrification. The graph of rate of reaction versus oxygen concentration is shown in Figure 4.2. This is described by the Monod expression and from the graph, one obtains

$$K_{S_1} = 0.8 \text{ mg/l} . \quad (4.14)$$

From the stoichiometric relation [Equation (4.1)], it can be easily seen that for every gm of ammonium nitrogen oxidized, 4.57 gms of oxygen are required. Wezernak and Gannon (1967) experimentally determined the net oxygen requirement to be 4.33 gms of oxygen per gm of ammonium nitrogen oxidized. Thus, if not available in sufficient quantities, oxygen can become limiting in the nitrification reaction.

Pruel and Schroepfer (1968) carried out nitrification in soil columns under saturated and unsaturated conditions. They

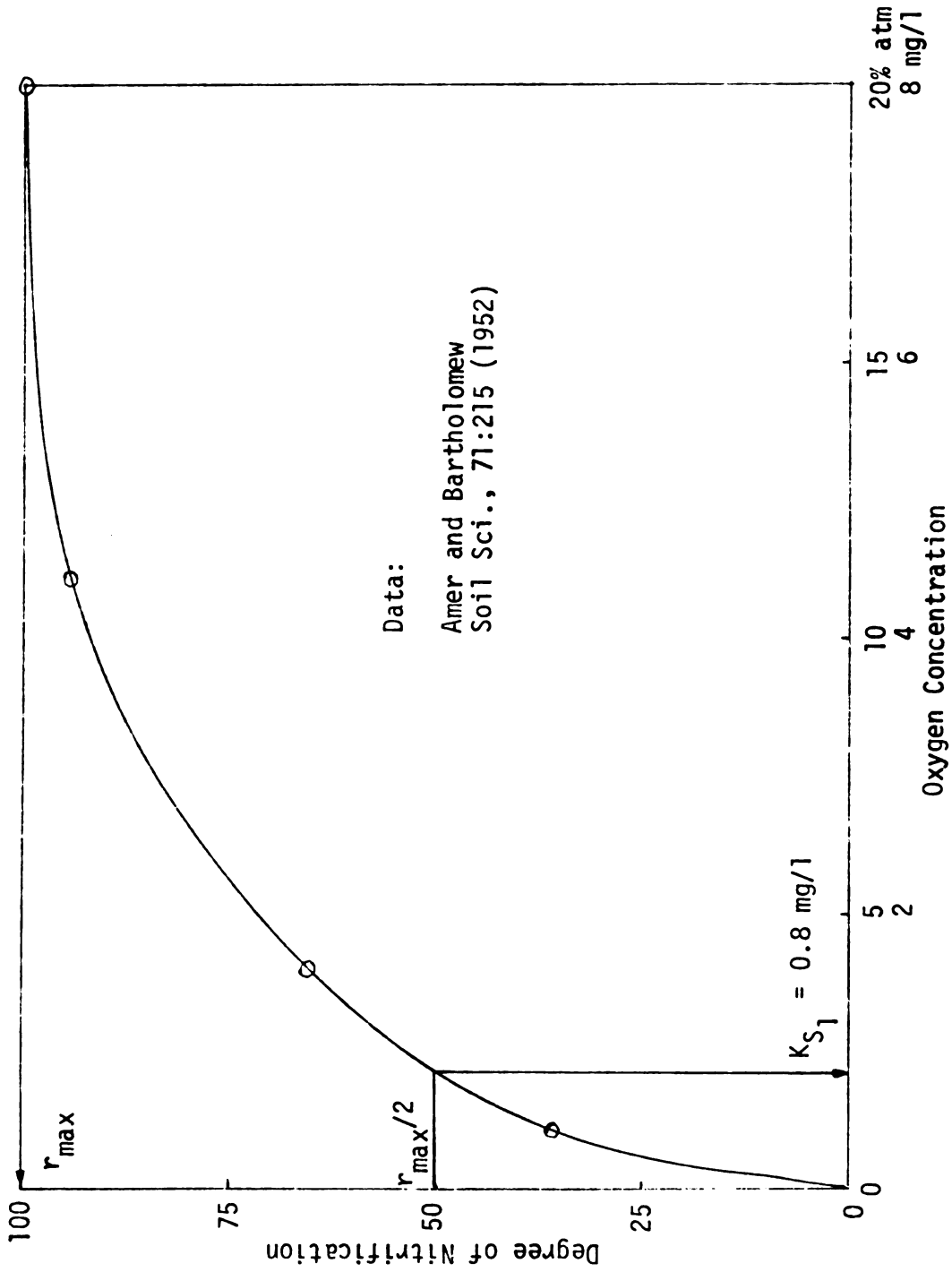


Figure 4.2.--Degree of Nitrification as a Function of Oxygen Concentration.

showed that under unsaturated conditions, nitrification was predominant and adsorption of ammonium was of little significance.

Starr (1973) studied nitrogen transformations in a soil column under continuous flow. He measured the concentration of ammonium ions as a function of the soil depth. From this, he computed the first and second derivatives and these he plotted against the ammonium concentration to obtain the first order reaction constant. The method is quite crude (and the author does not agree with the analysis of his data) but the data plotted in such a fashion do indicate that the reaction is a combination of zero order and first order reaction (Figure 4.3). The saturation constant and the maximum reaction rate are found to be 10-15 mg/l and $30 \mu\text{g}/\text{cm}^3/\text{day}$, respectively.

The effect of various other factors on nitrification has been studied quite extensively. Lower temperatures reduce the rate of nitrification. As nitrification is accompanied by an increase in the H^+ ions concentration, thus reducing the pH, the rate of the forward reaction can be increased by carrying out the reaction at higher pH. In fact, a pH of 8.5-9.0 has been found to be optimum.

From the above discussion, the approximate values of the various constants can be estimated as follows:

$$\mu_m = 2.5 \text{ day}^{-1},$$

$$K_{S1} = 5-15 \text{ mg/l (closer to 15 mg/l), and}$$

$$K_{S2} = 1-2 \text{ mg/l.}$$

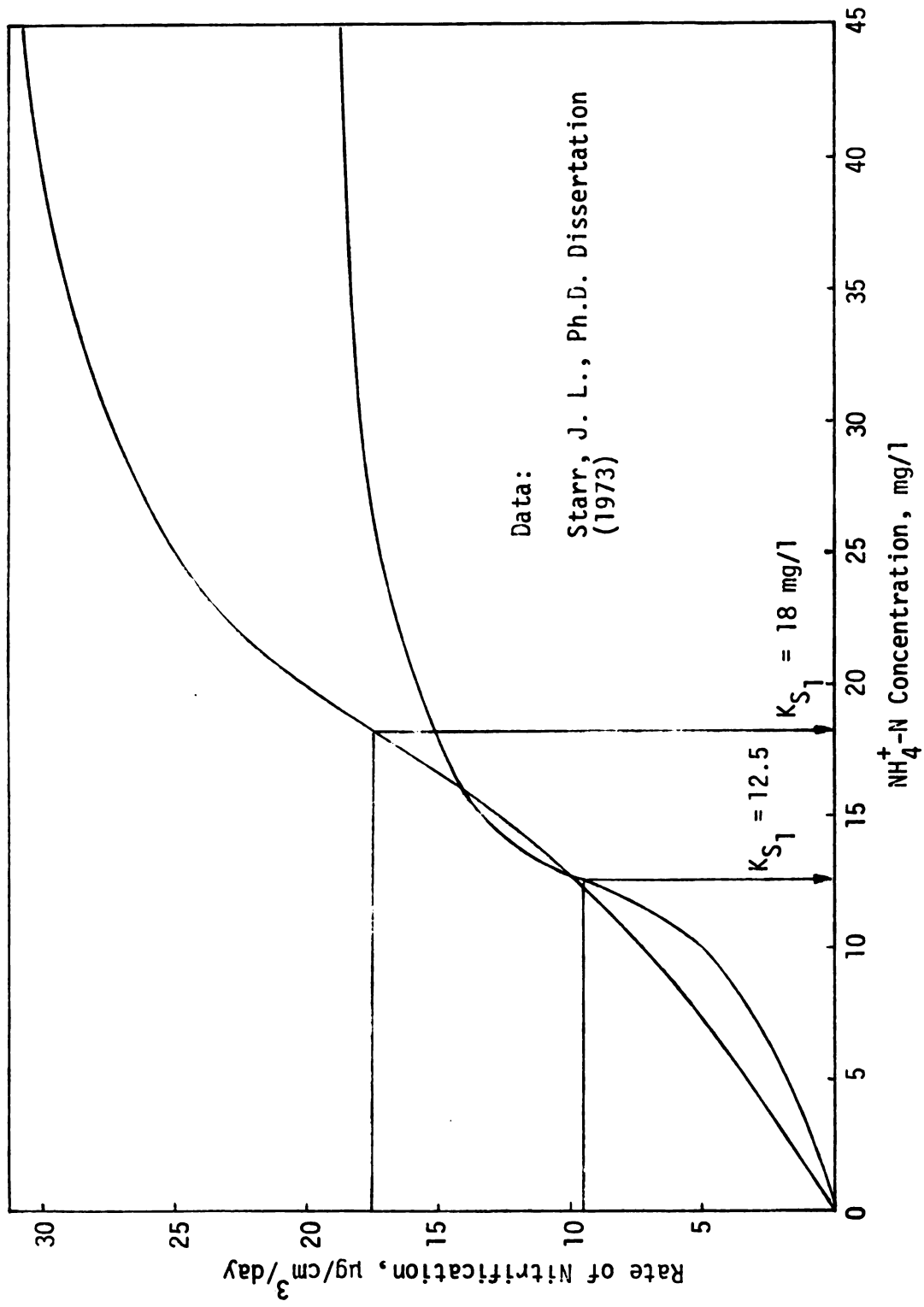


Figure 4.3.--Rate of Nitrification as a Function of Ammonium Nitrogen Concentration.

The growth rate expression for the nitrifiers is then

$$\mu = 2.5 \left(\frac{S_1}{15 + S_1} \right) \left(\frac{S_2}{0.8 + S_2} \right) . \quad (4.15)$$

Denitrification

Denitrification was observed and reported by soil scientists as it sometimes represented the chief route by which the nitrogen in soils could be lost. It was observed that it takes place in a highly organic environment such as manured soils and progresses slowly in well aerated soils.

Denitrification is brought about by facultative bacteria such as Pseudomonas, Achromobacter, Bacillus and Micrococcus.

There are two types of nitrate reduction that can occur:

1. Assimilatory denitrification--In this case, nitrate is reduced to ammonium which enters the pathway leading to the synthesis of protein. The reduction of nitrogen for incorporation into the cell material is called assimilatory denitrification.

2. Dissimilatory denitrification--Here, nitrate is used as an electron acceptor in the absence of oxygen and is reduced to nitrogen gases. This is the type of denitrification we are more interested in.

The rate of denitrification can be expected to be a function of the organic carbon concentration, the nitrate nitrogen concentration, the oxygen concentration and the physical factors such as pH and temperature.

The optimum pH for denitrification lies in the neutral region. The final products of denitrification depend on the pH. If the pH is below 6, a significant amount of N_2O is present but at pH 7, the N_2O is reduced to nitrogen and the predominant product is N_2 . Lower temperatures reduce the rate of the reaction and the optimum temperature for the reaction is around 30°C . Denitrification in soil and the effect of various parameters on it has been studied in detail by Wijler and Delwiche (1954) and Nommik (1956).

There have been conflicting reports whether complete absence of dissolved oxygen is required for denitrification to occur. A report of the Gulf Research Institute (1970) found that denitrification can occur even at dissolved oxygen levels of 4 ppm. On the other hand, Skerman and MacRae (1957) observed that even very low concentrations of dissolved oxygen (0.2-0.4 mg/l) inhibited the rate of denitrification. A number of workers have reported denitrification to occur even in aerobic conditions in the soil. This can be explained on the basis that an anaerobic microenvironment exists in spots where denitrification can take place. It has been established quite conclusively that if oxygen is present, it will be consumed much faster than nitrates (Strickland, 1931). Thus oxygen will be used first and nitrates will be used only after all of the oxygen has been consumed.

Denitrification has been accomplished in continuous stirred tank reactors as well as in packed columns. Amant and McCarty (1969) studied the effect of detention time and various types of packing materials on denitrification. Sand columns worked very

well initially but encountered clogging problems later. A detention time of 1 hour enabled 90 percent reduction of the incoming nitrate nitrogen. DuToit and Davies (1972) studied denitrification in both suspended growth and packed column units and found the packed units much more efficient in nitrogen removal than the suspended growth units. Residence times in the packed units ranged from 0.5 hour to 4 hours.

The quantity of nitrate nitrogen that can be removed in denitrification depends on the quantity of the available organic carbon in the system. Organic carbon acts as an electron donor for denitrification and energy derived by the oxidation of organic carbon is used for cell synthesis. The quantity of organic carbon that must be added to the system per unit of nitrogen removal must be known to effectively design the denitrification system. Once the organic carbon requirements are known, the necessary influent methanol or glucose concentration can be determined to remove a given quantity of nitrogen.

Sources of organic carbon can be methanol, glucose, acetic acid, etc. The rate of denitrification will depend on the ease with which these substrates can be degraded. Soils generally have a high fraction of organic carbon. Denitrification would take place even if no energy source is added to the soil. The organic substrates that are added to act as energy sources include glucose, methanol, lactic acid, etc. An equation has been developed to predict the quantity of the methanol required to reduce the nitrate, nitrite and dissolved oxygen (Amant and McCarty 1969):

$$C_{\text{methanol}} = 2.47 C_{\text{NO}_3^- - \text{N}} + 1.53 C_{\text{NO}_2^- - \text{N}} + 0.87 C_{\text{DO}} .$$

Sanitary engineers have studied the rate of denitrification and have generally assumed the rate to be a function of organic carbon concentration as defined by an equation of the Michaelis-Menten type. Johnson (1972) used the following equation for the rate of denitrification:

$$r = \frac{2.5 S_1}{K_{S_1} + S_1} \quad (4.16)$$

where

S_1 = limiting substrate concentration in mg/l of biological oxygen demand (BOD), and

K_{S_1} = 150 mg/l of BOD.

Translated into organic carbon, the value of the saturation constant could be in the range of 25-50 ppm organic carbon concentration. An exact value cannot be determined without knowing the actual composition of the substrate used.

Stensel (1971) carried out denitrification in suspended growth units and determined the constants which are given below:

$$\left. \begin{aligned} \mu_m &= 10 \text{ day}^{-1} , \\ K_{S_1} &= 50-75 \text{ mg/l chemical oxygen demand (COD),} \\ &\text{and} \\ \text{yield coefficient} &= 0.15 - 0.18. \end{aligned} \right\} \quad (4.17)$$

The experiments were performed under what Stensel thought were COD limiting conditions. Some of his experiments, though, were performed under conditions when both the COD and nitrate nitrogen could have been limiting.

Requa and Schroeder (1972) reported the rate of denitrification as a function of the nitrate nitrogen concentration with a very small value of the saturation constant. This essentially reduced the Michaelis-Menten expression to zero order form, with the rate being equal to about 5 mg nitrate nitrogen reduced/day/l. Starr (1973) studied nitrification and denitrification in a packed column and assumed first order kinetics for the denitrification reaction with the rate constant being equal to 0.08 day^{-1} . Soils generally contain a large amount of organic matter and the rate expression for the growth rate of microbes becomes zero order with respect to the organic carbon concentration. This explains why soil scientists always worked with nitrate nitrogen as the limiting substrate.

Both these microbiological reactions are multiple substrate limited but no attempt has been made to study the growth characteristics of the microbes as a function of these two substrates. For nitrification, a rate expression involving two substrates has been derived but a similar expression for denitrification cannot be derived. For this reason, experiments have been performed to estimate μ_m , K_{S1} , K_{S2} , Y_1 , and Y_2 . Here, Y_1 and Y_2 represent the yield coefficients with respect to substrates 1 and 2, respectively.

Experimental Method

Suspended Growth Units Vs. Packed Columns

Determining the kinetics of different reactions from field studies is very difficult. Micrometeorological conditions play a vital role in affecting microbial ecology by changing soil temperature and soil moisture. Field studies of nitrogen transformation processes are under conditions of constantly changing soil temperature and moisture. Under these conditions, all the microbial processes are occurring simultaneously and it is very difficult to differentiate between various processes because of complex interactions. Laboratory studies of these transformation processes make use of the ability to control conditions so as to be able to isolate a particular reaction and study its kinetics.

As the rate expressions to be estimated are to be used in simulating nitrogen movement in soils, the first temptation is to study the reaction in soil columns. The physical situation in both the cases is quite similar and the results obtained from soil column experiments will be applicable in designing a land disposal system. Soil column studies are analogous to actual field studies. Although soil conditions can be controlled in a laboratory soil column, it is still difficult to isolate the effect of a particular reaction. Starr (1973) studied the nitrogen transformations in an unsaturated soil column under continuous flow. He measured the concentrations of various nitrogen species such as nitrogen, ammonium, nitrate nitrogen, etc. Assuming double

substrate limited kinetics, one can write a series of nonlinear second order differential equations involving parameters for the denitrification reaction. Determining these constants then becomes a very lengthy parameter estimation problem (the equations necessary in the analysis of data will be derived in the chapter on nitrogen modeling). Derivation of the above equations does not even consider other nitrogen reactions. Thus, the soil column experiment itself is long (steady state conditions are achieved after operating the soil column continuously for three to four months) and analysis of the data is quite difficult.

Suspended growth units are continuous stirred tank reactors. They are very easy to use and amenable to easy mathematical analysis. Not much sophisticated equipment is required. In the light of the above discussion, continuous stirred tank reactors were used in this work to evaluate the constants in the rate expression.

Theory

The specific growth rate of microbes is defined as the rate of increase in cell mass per unit cell mass, i.e.,

$$\mu = \frac{1}{X} \frac{dX}{dt} . \quad (4.18)$$

Taking cell mass balance for a stirred tank reactor gives

$$\begin{aligned} & [\text{incoming rate}] - [\text{outgoing rate}] + [\text{rate of generation}] \\ & = [\text{rate of accumulation of cell mass}] . \end{aligned}$$

Substituting for the various terms gives

$$FX_i - FX + \mu XV = V \frac{dX}{dt} \quad (4.19)$$

where

F = flow rate, l/day,

X_i = microbial concentration in mg/l, and

V = reactor volume, l.

Dividing Equation (4.19) by V throughout gives

$$\frac{dX}{dt} = D (X_i - X) + \mu X \quad (4.20)$$

where

D = dilution rate, day^{-1} ,

= reciprocal of residence time.

Similar balance equations for substrates 1 and 2 can be written as

$$\frac{dS_1}{dt} = D (S_{1i} - S_1) - \frac{\mu X}{Y_1}, \quad (4.21)$$

and

$$\frac{dS_2}{dt} = D (S_{2i} - S_2) - \frac{\mu X}{Y_2} \quad (4.22)$$

where Y_1 and Y_2 are yield coefficients; i.e., they represent the units of cell mass produced per unit consumption of substrates.

If steady state conditions are allowed to be reached in the reactor, then

$$\frac{dX}{dt} = \frac{dS_1}{dt} = \frac{dS_2}{dt} = 0 .$$

Using the above relationship, Equations (4.20), (4.21), and (4.22) can be rewritten as

$$\left. \begin{aligned} D (X_i - X) + \mu &= 0 , \\ D (S_{1i} - S_1) - \mu X/Y_1 &= 0 , \\ \text{and} \\ D (S_{2i} - S_2) - \mu X/Y_2 &= 0 . \end{aligned} \right\} \quad (4.23)$$

If the incoming cell mass, X_i , is equal to zero, the first equation of (4.23) simplifies still further, i.e.,

$$D = \mu = \mu(S_1, S_2) .$$

At steady state conditions, if there is no cell mass entering with the feed stream, the dilution rate equals the specific growth rate of the bacteria. Thus, stirred tank reactors provide a very convenient way of measuring the specific growth rate of the microbes. The value of μ is given by

$$D = \mu = \mu_m \left(\frac{S_1}{K_{S_1} + S_1} \right) \left(\frac{S_2}{K_{S_2} + S_2} \right) . \quad (4.24)$$

Solving Equations (4.23) and (4.24) simultaneously, one obtains the substrate concentrations and the cell mass as follows:

$$\left. \begin{aligned} S_1 &= \frac{-\beta \pm \sqrt{\beta^2 - 4\alpha\gamma}}{2\alpha}, \\ X &= Y_1 (S_{1i} - S_1), \text{ and} \\ S_2 &= S_{2i} - X/Y_2 \end{aligned} \right\} \quad (4.25)$$

where

$$\alpha = \frac{D}{\mu_m} \frac{Y_2}{Y_1} - \frac{Y_2}{Y_1},$$

$$\beta = \frac{D}{\mu_m} (K_{S_1} + S_{1i} - \frac{Y_2}{Y_1} S_{2i} + \frac{Y_2}{Y_1} K_{S_2}) - S_{1i} + \frac{Y_2}{Y_1} S_{2i}, \text{ and}$$

$$\gamma = \frac{D}{\mu_m} K_{S_2} (K_{S_1} + S_{1i} - \frac{Y_2}{Y_1} S_{1i}).$$

The parameters to be estimated for the above kinetic model are

Kinetic parameters: μ_m , K_{S_1} , K_{S_2} , and

Stoichiometric parameters: Y_1 , Y_2 .

This can be accomplished by carrying out two different sets of experiments in continuous stirred tank reactors. In one set, the operating conditions can be maintained such that one of the substrates is present in excess and is not growth limiting. If S_2 is present in excess, Equation (4.24) reduces to

$$D = \mu_m \frac{S_1}{K_{S_1} + S_1}. \quad (4.26)$$

Starting with the same initial concentrations of S_1 and S_2 , one can operate a stirred tank reactor at different residence times, and determine the concentrations of the two substrates in the effluent. Thus, a functional relationship between D and S_1 is obtained in terms of a series of values of D and S_1 . Similarly, a second set of experiments can be carried out to obtain a relationship between D and S_2 under the conditions of excess S_1 .

Analysis of these data can be carried out in two ways. The data can be plotted either on a Monod plot or a Lineweaver-Burk plot. In the Monod plot, dilution rate is plotted against the effluent substrate concentration. The shape of the curve would be of the same nature as in Figure 4.1a. From this figure, an approximate value of μ_m is obtained as the maximum value of μ approached asymptotically at very high substrate concentrations. The value of K_{S1} is then obtained as the substrate concentration at which the growth rate equals $\mu_m/2$. The Monod plot is very easy to visualize and use, but it is very difficult to obtain an accurate estimate of the parameter values from it. If the experiments have not been carried out at a quite high substrate concentration, it is very difficult to establish accurately the values of μ_m and K_{S1} .

Another way of plotting the data is to transform them in such a way that when plotted they fall on a straight line. This is very easily done by transforming Equation (4.26) to

$$\frac{1}{D} = \frac{1}{\mu_m} + \frac{K_{S1}}{\mu_m} \frac{1}{S_1} . \quad (4.27)$$

A plot of $1/D$ against $1/S_1$ results in a straight line with slope equal to K_{S1}/μ_m and intercept equal to $1/\mu_m$. From these two values, a much better estimate of the parameters can be obtained. Both these methods will be used in interpreting the data obtained in this work.

Knowledge of the values of all the kinetic parameters would enable us to predict the effluent concentrations at any operating conditions and this feature would be very helpful in designing modified activated sludge plants to remove nitrogen.

The above model has been tested by growing denitrifiers in a continuous culture on a suitable medium. The required parameters were determined by carrying out sets of experiments under either carbon limiting conditions or nitrate nitrogen limiting conditions at various dilution rates.

Materials and Operating Procedures

Apparatus.--For the continuous feed experiments, a unit is required that will provide a completely mixed system and a completely air-free system. The experimental unit consisted of a feed unit, a gas purging unit, a reactor and an effluent collection system. A diagram of the experimental apparatus is shown in Figure 4.4.

Two different chemostats of two liters each were used for this study. The feed system consisted of a cassette tubing pump. The pumping action of the pump was peristaltic in nature. A certain feed rate was required to maintain a desired residence time. The

EXPERIMENTAL SETUP

1-Nitrogen Cylinder

2-Nutrient Storage Tank
Jacketed with Ice to
Maintain Low Temperature

4-Magnetic Stirrer

5-Anaerobic Continuous
Stirred Tank Reactor

6-Effluent Storage
Vessel

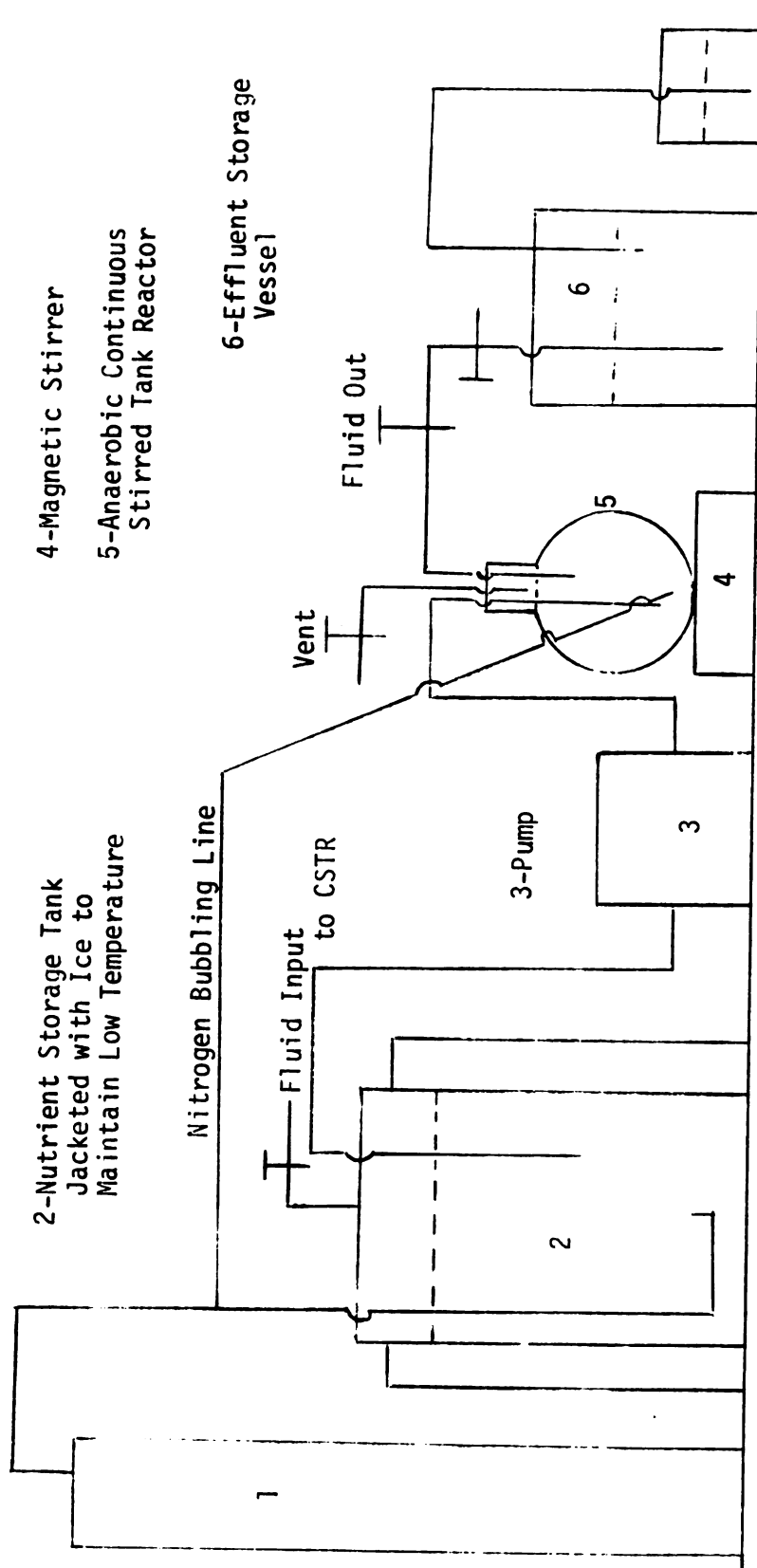


Figure 4.4.--Experimental Setup for the Study of Denitrification Reaction.

feed rate was determined by measuring the change in volume in the effluent collector per unit of time. Before the experiment was started, the flow rate was measured and was checked against the rate of increase of effluent and the rate of decrease of feed solution. The pumping action on the fluid is created by the squeezing action on the tubing. After a while, the tube became harder and the flow rate through the system decreased. This necessitated increasing the pump speed to compensate for the increased resistance on the tubing.

The volume of the feed tank was 18 liters. The feed tank was kept at 0°C by surrounding it with ice which was changed every 12 hours. The ice container was surrounded by a layer of insulating material to decrease the ice melting rate. This precaution was taken to prevent microbial growth in the feed solution itself. Two feed tanks were alternatively used. Every two days the feed tank was replaced by another with freshly prepared feed solution. The feed bottles were washed with a cleansing agent and rinsed with tap water prior to preparing each new feed solution.

The feed tank and the reactors were connected to a nitrogen cylinder containing technically pure nitrogen. Periodically, nitrogen was purged through the system (feed tank and reactor) for 45 minutes to 1 hour to ensure completely anaerobic conditions. Variable speed laboratory magnetic mixers were placed beneath each reactor. Teflon-coated magnetic stirrers 3/8" x 1" were used to mix the reactor contents.

Medium.--The nutrient solution was prepared from analytical grade chemicals. Glucose was used to provide organic carbon as an energy source. Potassium nitrate was used as a nitrogen source. These chemicals were dissolved in tap water along with appropriate quantities of potassium hydrogen phosphate (KH_2PO_4), ferric chloride, magnesium sulfate and calcium chloride to provide essential nutrients for growth. Tap water was expected to provide trace elements in sufficient concentrations so as not to be growth limiting. Table 4.1 contains the recipe used in preparing the nutrient solution for the nitrate nitrogen limiting case and the organic carbon limiting case.

TABLE 4.1.--Growth Media Used in Experimental Studies.

Component	N Limiting and C in Excess, mg/l	C Limiting and N in Excess, mg/l
$\text{NO}_3 - \text{N}$	100	250
$\text{C}_6\text{H}_{12}\text{O}_6 - \text{C}$	1,000	100
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	25	25
KH_2PO_4	100	100
FeCl_3	5	5
CaCl_2	25	25

Inoculum.--Soil extract was used as an inoculum for the denitrifiers. Soil from the site of the engineering building, Michigan State University, was contacted with tap water and allowed to stand for a few days. It was filtered, and the filter bed of soil was washed with water a few times. The filtrate was then used as an inoculum for the experiments.

Operation.--The reactors were properly cleaned with a cleansing agent and rinsed with tap water. They were sterilized by autoclaving at 120°C for one hour. These were then filled with the nutrient medium and inoculated. The chemostats were purged with nitrogen gas for about an hour to drive out the oxygen and ensure complete anaerobic conditions. The microbes were grown batchwise until a good sized population was obtained. Before the system was made continuous, the feed tank solution was also purged with nitrogen so that it would not contain any dissolved oxygen.

The system was then made continuous and, at this time, it was assumed that the denitrifying microorganisms were in active growth condition. Sampling was started after five residence times had elapsed. Experiments were continued until the effluent substrates and microbial concentrations stabilized. In general, the system was kept running for 10-15 residence times or 20-25 days, whichever was higher.

Sampling.--Samples were taken from the reactors every 12 hours. At the time of sampling, stirring was stopped and one of

the necks on the reactors was opened up. A sample of approximately 60 ml volume was pipetted into a sampling bottle. The bottle was closed immediately and refrigerated at 5°C so that no further microbial growth could occur. This sampling procedure did not take more than 2 to 3 minutes. The chemostats were closed immediately thereafter, and they, along with the feed tank, were purged with nitrogen for an hour. The system was then started again. The samples were analyzed later but were never kept waiting for more than 7 days. All the samples were analyzed for suspended solids, nitrate nitrogen, glucose carbon, and some were also analyzed for pH, dissolved oxygen and chemical oxygen demand.

Microbial growth on walls.--In the development of equations for a continuous stirred tank reactor carrying out a biological reaction, it was assumed that all of the substrate utilization and cell growth occurs in a completely mixed phase. If microbial growth occurs on the walls of the reactor, these cells utilize some substrate from the solution. To prevent or to reduce this substrate utilization by the microbes attached to the reactor, the walls of the reactor were scraped with a rod. The scraping was carried out every time a sample was taken from the reactor (every 12 hours) and was accomplished within 5 minutes. Care was also taken to prevent microbial growth in the feed lines.

Analytical Techniques

Suspended solids.--Two different methods were tried to measure the microbial concentration of the sample. One of the

methods used was filtration through a glass fiber filter as described in Standard Methods (1965). The glass fiber filter used was a Whatman filter paper with a diameter of 5 cm. The recommended volume of the sample to be used is 14 cm^3 per unit cm^2 area of filter paper. This required a sample size of 280 cc just for determining suspended solids. This represented rather a large percent of reactor volume and withdrawing such a large volume could conceivably introduce some fluctuations in steady state conditions.

The second method consisted of taking 10 ml of filtered and unfiltered samples and evaporating both these in an oven at 120°C for 24 hours. Dissolved solids were left behind in the tray which contained the filtered sample whereas the tray which had the unfiltered sample contained dissolved solids and microbial cell mass. The difference between these two weights represented the cell mass in 10 ml of sample. The second method was more regularly used but the value obtained by this method was checked against the value obtained by filtration. Average deviation of 7-10 percent was encountered.

Nitrate nitrogen.--Nitrate nitrogen was determined with an ion specific electrode from Orion Research. The concentration was indicated in terms of a millivoltmeter reading. The equipment was calibrated against standard nitrate nitrogen solutions. A typical calibration curve is shown in Figure 4.5. The readings were reproducible within 0.5-1.0 millivolts. A small dish of 2 ml capacity

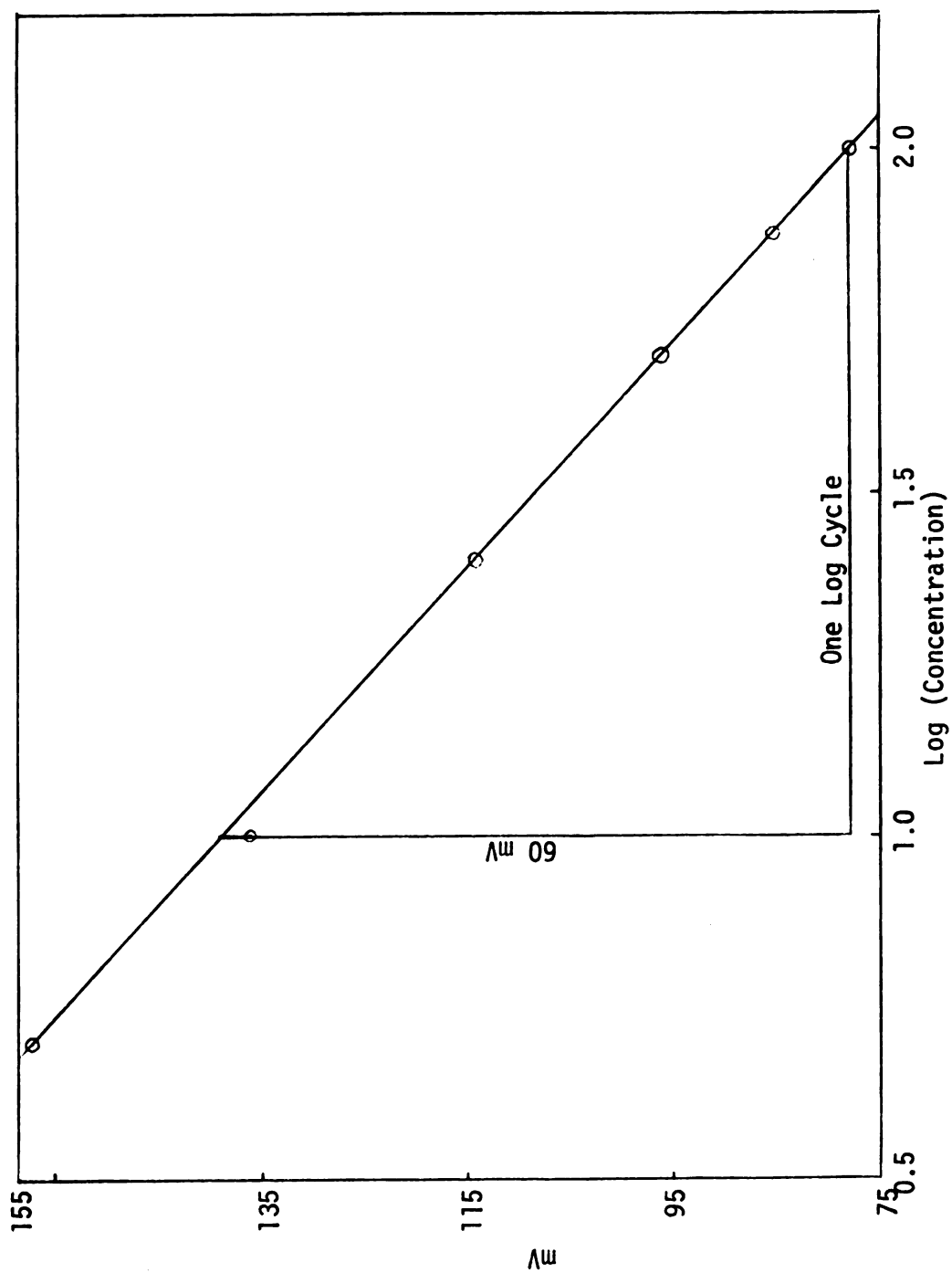


Figure 4.5.--A Typical Calibration Curve for Determining Nitrate Nitrogen.

was used as a sample dish. If the sample was suspected of having a nitrate nitrogen concentration greater than 100 ppm, it was diluted so as to bring the concentration in the 20-100 ppm range. A quick way of checking whether the calibration curve is right is to see if for every log cycle on concentration, the millivolt reading changes by 59 mV. In Figure 4.5, the millivolt change is 60 so the calibration curve was checked.

Glucose carbon.--The glucose concentration in a sample was determined using Nelson's method (1957). The samples were centrifuged before being analyzed. Addition of Nelson's reagents A and B to the sample resulted in the formation of a color, the intensity of which was translated into a transmittance reading on a Bausch and Lomb Spectronic 20 spectrophotometer. With the help of a calibration curve, this reading was converted into concentration. A typical calibration curve is shown in Figure 4.6. The samples were analyzed in duplicate to check for reproducibility. Along with the unknown samples, four standards were also analyzed. The concentrations of the standards obtained from the analysis gave an indication of the reliability of the analysis.

Chemical oxygen demand (COD).--Occasionally, COD was determined to obtain some measure of the amount of carbon present in organic compounds other than glucose. The method used is called "Rapid COD" determination.* Regular COD determination by

*State of Michigan Laboratory Manual for Wastewater Analyses 1974.

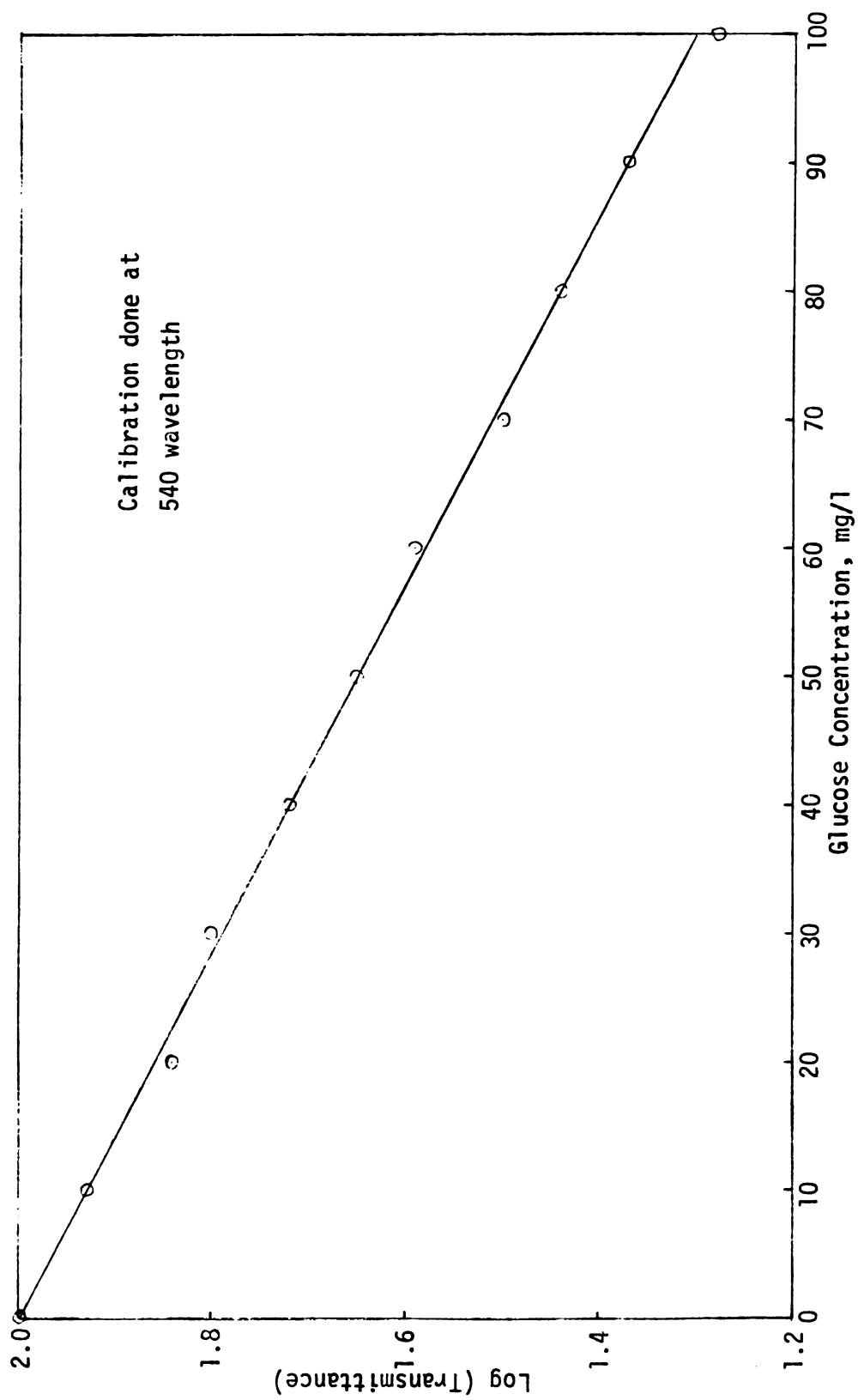


Figure 4.6.--A Typical Calibration Curve for Determining Glucose Concentration.

dichromate reflux method was not used because of the quite lengthy and time consuming procedure. A carbon analyzer was due to arrive when this work was near completion. It would have been a very convenient instrument to determine the carbon concentration. A "Rapid COD" test was carried out whenever steady state conditions were thought to have been achieved.

Dissolved oxygen.--Dissolved oxygen concentrations of the samples were frequently determined to check for the anaerobic conditions in the reactor. A Yellowsprings Instrument Co., Ltd., polarographic probe was used to measure the dissolved oxygen concentration.

pH.--The pH in the reactor was monitored quite frequently. It was maintained near the neutral range. A double junction electrode of Orion Research was used to measure the pH of the reactor solution.

Experimental Results and Discussion

Two different sets of experiments were performed under conditions when (a) the glucose concentration is in excess and only nitrate nitrogen is the limiting substrate, and (b) the nitrate nitrogen is in excess and the glucose concentration is limiting.

Runs were made at different residence times and the effluent substrate concentration S_1 was determined at steady state conditions. Equation (4.26) was plotted appropriately in terms of

D and S_1 to obtain the parameters μ_m and K_{S_1} . Next, a set of experiments was carried out at conditions in which S_1 was in excess and S_2 was limiting. From these observations, μ_m and K_{S_2} were to be estimated. Y_1 and Y_2 were to be determined from the relationships between the amounts of solids produced and the amounts of substrates utilized.

The two liter laboratory scale denitrification reactors were operated for about 12 months. When steady state conditions were thought to exist, the samples were analyzed in detail. The reactors at steady state were operated for 2 to 3 days and the average values of the data at steady state are reported in Appendix D.

Excess Concentrations

The most important aspect is the choosing of proper initial concentrations for the nitrate nitrogen and glucose substrates. The glucose concentration should be such that not only should it be in excess at the start of the experiments but also at the steady state conditions. This has been very vividly illustrated by Bader et al. (1975). It is possible to supply glucose concentration in such a way that it would be in excess at the beginning but towards the end of the reaction it also could become rate limiting.

In Figures 4.7a and 4.7b are plotted contour lines of constant μ on S_1 - S_2 axes. As S_1 and S_2 increase, μ also increases. Drawing Figure 4.7 presupposes the knowledge of the nature of μ as a function of S_1 and S_2 . The shape of the contour lines in Figure

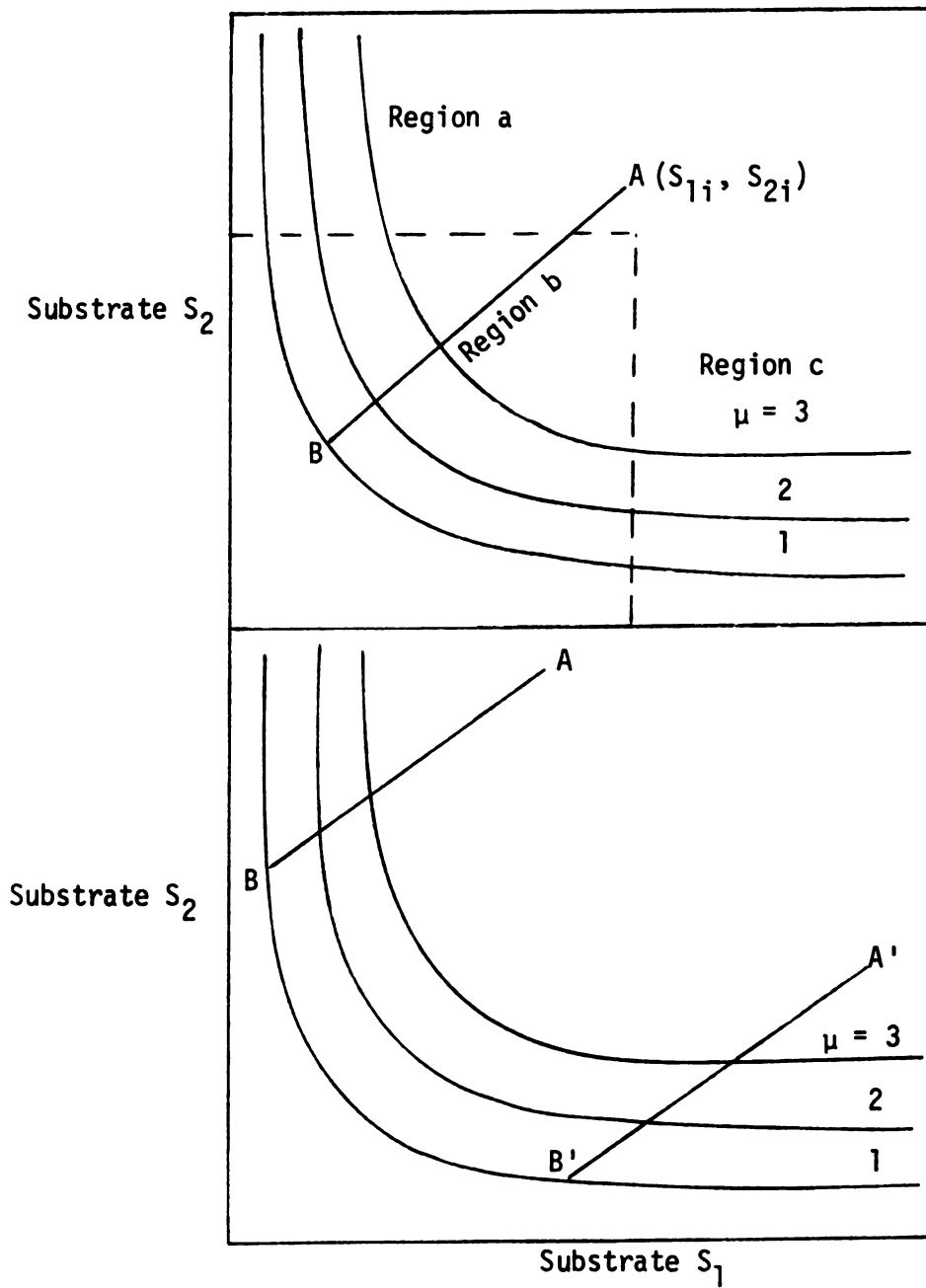


Figure 4.7.--Plot of Bader et al. (1975) to Illustrate How to Take Proper Excess Concentration.

4.7 corresponds to the type of Equation (4.24). The plot can be divided into three regions: (a) a region of excess S_2 , (b) a transition region where both S_1 and S_2 are growth limiting, and (c) a region of excess S_1 . An operating line on this diagram can be drawn quite easily. Since the feed substrate concentrations are known (S_{1i} , S_{2i}), point A is immediately defined. The slope of the line is represented by the ratio of yield coefficients because $Y_1 (S_{1i} - S_1) = Y_2 (S_{2i} - S_2)$. The exit concentrations S_1 and S_2 are obtained from point B which represents the point of intersection of the operating line with the contour curve given by $\mu = D$.

If the line AB traverses through the two regions a and b or b and c, it indicates that the substrate that was in excess to begin with, also becomes growth limiting at the steady state conditions. If, however, the substrates are provided as shown in Figure 4.6b, then substrate 1 or 2 remains in excess throughout the course of the reaction.

From the past work in denitrification, it was concluded that, at the most, three parts of carbon are required per every part of nitrogen reduced. The input nitrate nitrogen concentration was decided at 100 ppm. If all of the nitrate nitrogen is reduced, the amount of organic carbon required would be, at the maximum, 300 ppm. Taking this into account, it was decided to keep the incoming glucose concentration at 1000 ppm. Even with the loss of 300 ppm organic carbon, 700 ppm would still be left in the solution and this would ensure the operation of the denitrification

reactors at excess organic carbon. Some exploratory experiments would have been unavoidable if information about the approximate value of Y_1/Y_2 were not available.

Choice of Inoculum

This method of determining kinetic constants for a multiple substrate model has been applied successfully by Sinclair and Ryder (1975) for a pure culture. In the present experiments, a heterogeneous population obtained from soil extract was used. For a pure culture, there would be very few problems as there are no interacting and competing species as is the case of a mixed culture.

One of the problems of growing mixed culture in a chemostat is the selection of different species at different dilution rates. At very low dilution rates, the residence time is sufficiently large for almost all species to grow. As the dilution rate is increased, the microbes which require larger residence time for their growth are washed out. At each dilution rate, thus, a different kind of population prevails. This has been proved quite conclusively by Chiu et al. (1972). They used samples from reactor contents that were operated at different dilution rates and grew them batchwise. Different samples had different growth rates indicating different types of microbial population at different dilution rates. This could lead to some discrepancies in data.

In spite of the disadvantages listed above, a heterogeneous population was used in this work for two reasons. Firstly, the

denitrifying organisms are facultative organisms. If oxygen is available, they use it as an electron acceptor but in the absence of oxygen, they use nitrate as an electron acceptor. Thus, denitrifiers are different classes of organisms which change their habits depending on their environment. "Pure culture" is somewhat of a misnomer in the case of denitrifiers. Secondly, in an activated sludge plant or a land disposal system, there is a very remote possibility of a pure culture being maintained. Since the results of the experiments are to be used in the design of a land disposal system or a tertiary treatment plant, an inoculum from soil extract was thought to be appropriate.

Choice of Carbon Source

Some discussion is also merited on the choice of glucose as the source of organic carbon. Glucose is a very common carbon source for a very large number of microbes. Moreover, the inoculum used was mixed culture so there would exist possibilities for other microbes to grow on glucose in an anaerobic environment. Lactic acid bacteria can anaerobically convert glucose into lactic acid. Glucose depletion, therefore, is not only due to denitrifiers but also due to some other bacteria. Methanol, on the other hand, is quite specific and not many microorganisms can use it anaerobically. Methanol consumption would be, thus, a better indicator of the growth of the denitrifiers than the glucose utilization. On the other hand, glucose is more representative of the dissolved organic matter in wastewater.

Moreover, determining the methanol concentration in solution would be difficult. One can use COD as a measure of the methanol present but COD determinations are quite lengthy, whereas the glucose concentrations can be determined by a comparatively easy and more accurate method. Glucose was therefore used as the carbon source with certain precautions. If any suspicions arose about the type of population present in the reactor, the experiment was started again with a fresh soil extract inoculum.

Nitrate Nitrogen Limiting System

Table 4.2 shows the average steady state data obtained from the chemostats. The daily data taken near the steady state are given in Appendix D. These data will be analyzed with the help of a Monod plot and a Lineweaver-Burk plot. Figures 4.8 and 4.9 show the results of the Monod plot and the Lineweaver-Burk plot, respectively.

Figure 4.9 shows that the first four points lie on a straight line but the next three points do not. The point representing the experiment N-6 does not even fall into a pattern and thus is obviously in error. Instead of a straight line passing through the points, a smooth curve may be made to pass through these points.

The Monod plot, too, shows that at high residence times, the experimental points fall below the theoretical curve. These discrepancies in the Monod and Lineweaver-Burk plots can be explained either by considering a different kinetic model or by accounting for experimental errors.

TABLE 4.2.--Average Steady State Data for Nitrogen Limiting System.

Experiment Number	Residence Time Days	Concentration, mg/l					Suspended Solids mg/l	Dissolved Oxygen mg/l	pH
		Incoming		Outgoing		NO ₃ ⁻ -N			
		Glucose-C	NO ₃ ⁻ -N	Glucose-C	NO ₃ ⁻ -N				
N-1	0.3103		97.72	925	79.43		9.2	0.4	7.3
N-2	0.3464		95.49	850	56.15		27.3	0.5	7.1
N-3	0.4464		97.7	800	37.8		40.3	0.2	7.5
N-4	0.769		95.5	750	23.2		47.5	0.1	7.3
N-5	1.075		102.3	713	20.1		50.7	0.3	7.5
N-6	2.00		97.8	625	22.3		75.9	0.2	7.1
N-7	2.777		100.0	375	9.8		150.7	0.3	6.8

Average = 1000

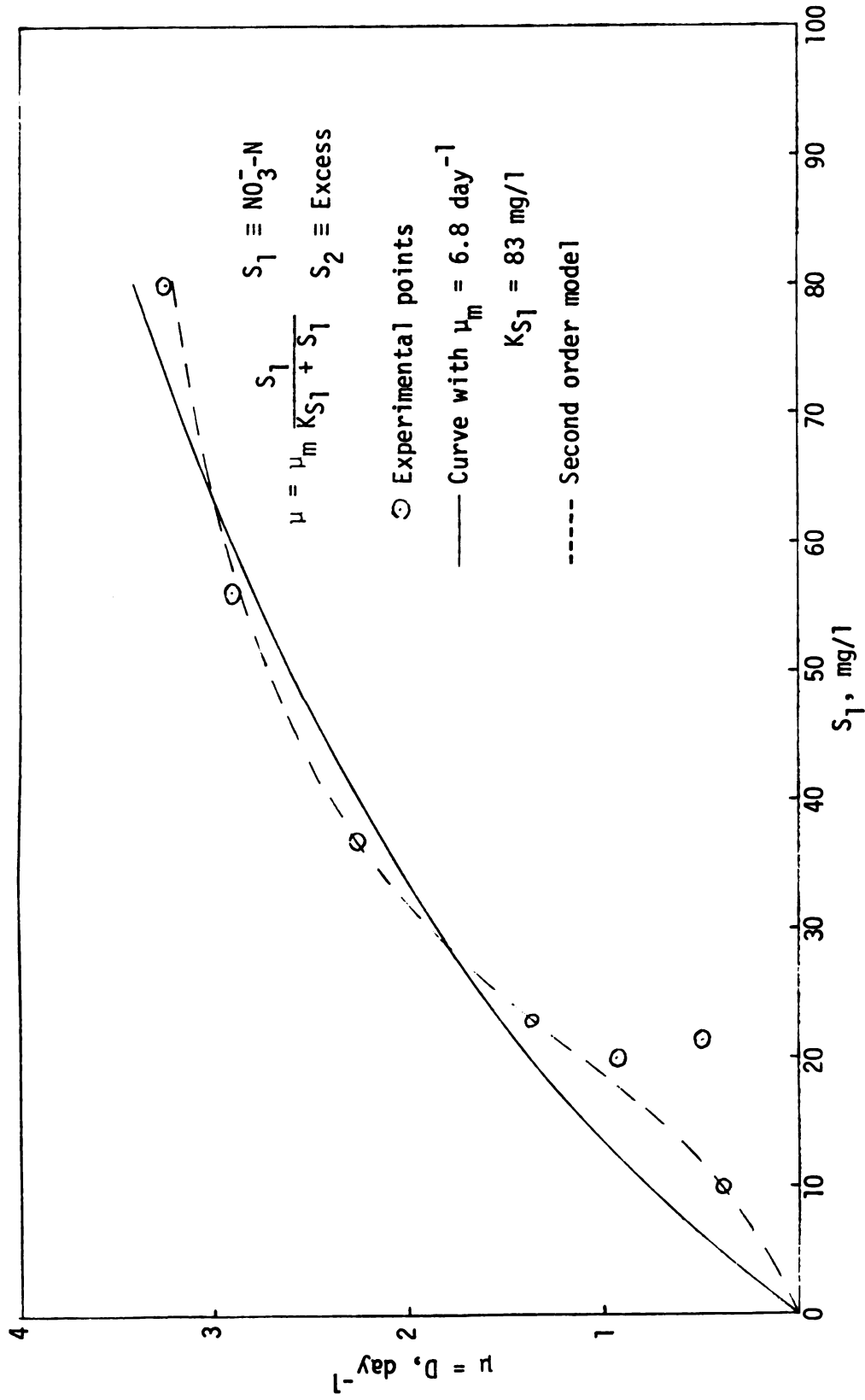


Figure 4.8.---Plot of Dilution Rate Against Substrate Concentration.

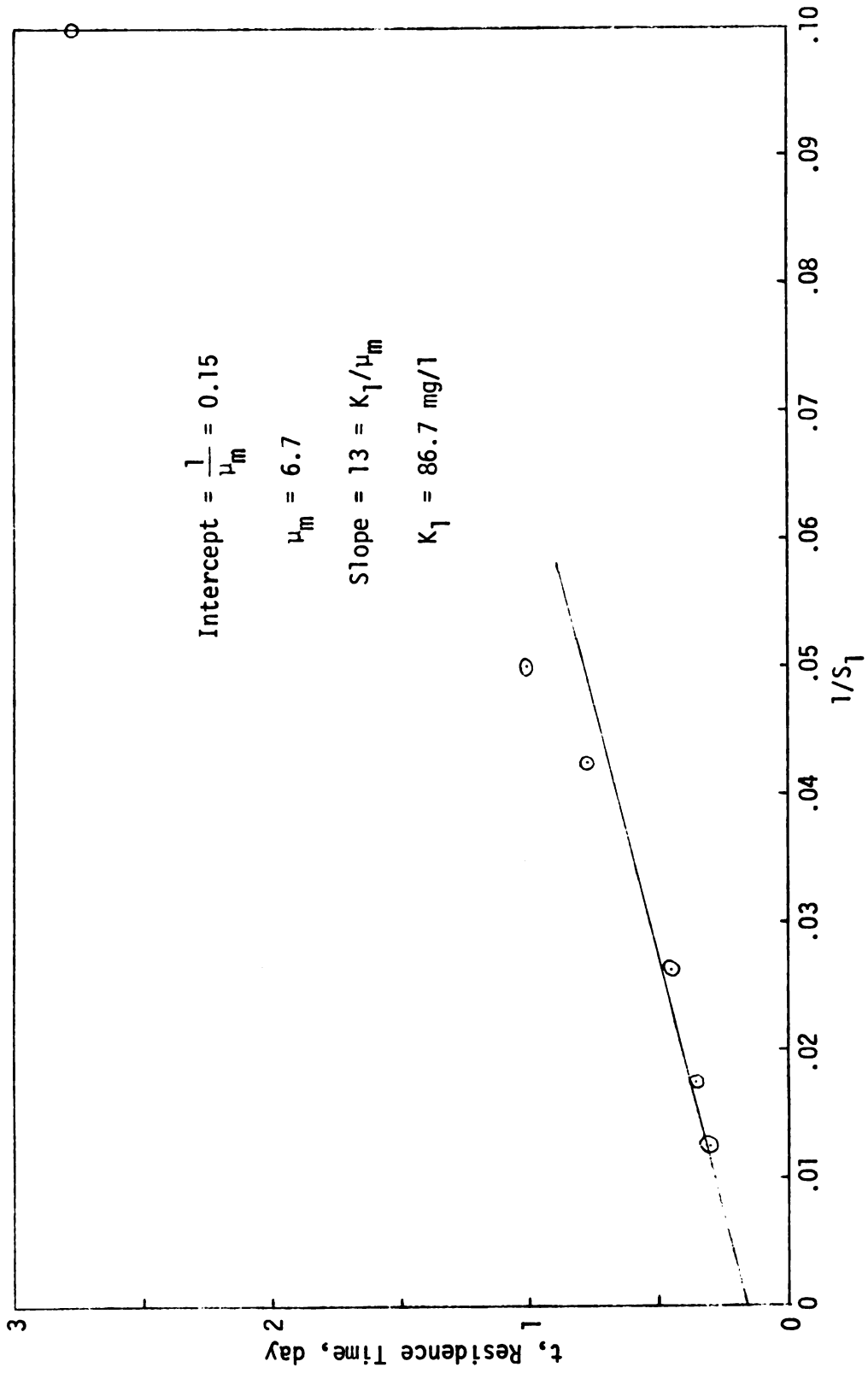


Figure 4.9.--Lineweaver-Burk Plot for Nitrogen Limiting Case.

If a smooth curve is made to pass through the experimental points, an S-shaped curve results. This type of curve is not predicted by a Monod growth model. To account for these deviations at low dilution rates, a different model was considered,

$$D = \mu_m \frac{S_1^2}{K_{S_1}^2 + S_1^2} \quad (4.28)$$

Physically, this model predicts a somewhat smaller growth rate up to a certain threshold concentration of the limiting substrate due to the squared dependence of the growth rate on the limiting substrate concentration at low values of S_1 . This helps in accounting for the deviations of the experimental data at low growth rates. Beyond this substrate concentration, the model behaves in a manner similar to the Monod model. With $\mu_m = 3.7 \text{ day}^{-1}$ and $K_{S_1} = 30 \text{ mg/l}$, a smooth curve may be drawn that passes through most of the experimental points. A Lineweaver-Burk plot of this model does smooth out most of the variations encountered in Figure 4.9 (Figure 4.10). This indicates that this model is capable of fitting the experimental data. However, an expression of the type of Equation (4.28) could not be justified on a sound theoretical basis as in the case of Equation (4.26). Based on this discussion, the possibility of a different kinetic model controlling the reaction was discounted.

For some reason, the nitrate nitrogen was not reduced to the fullest extent at very high residence times. Earlier, the possibility of selecting a different species at different dilution

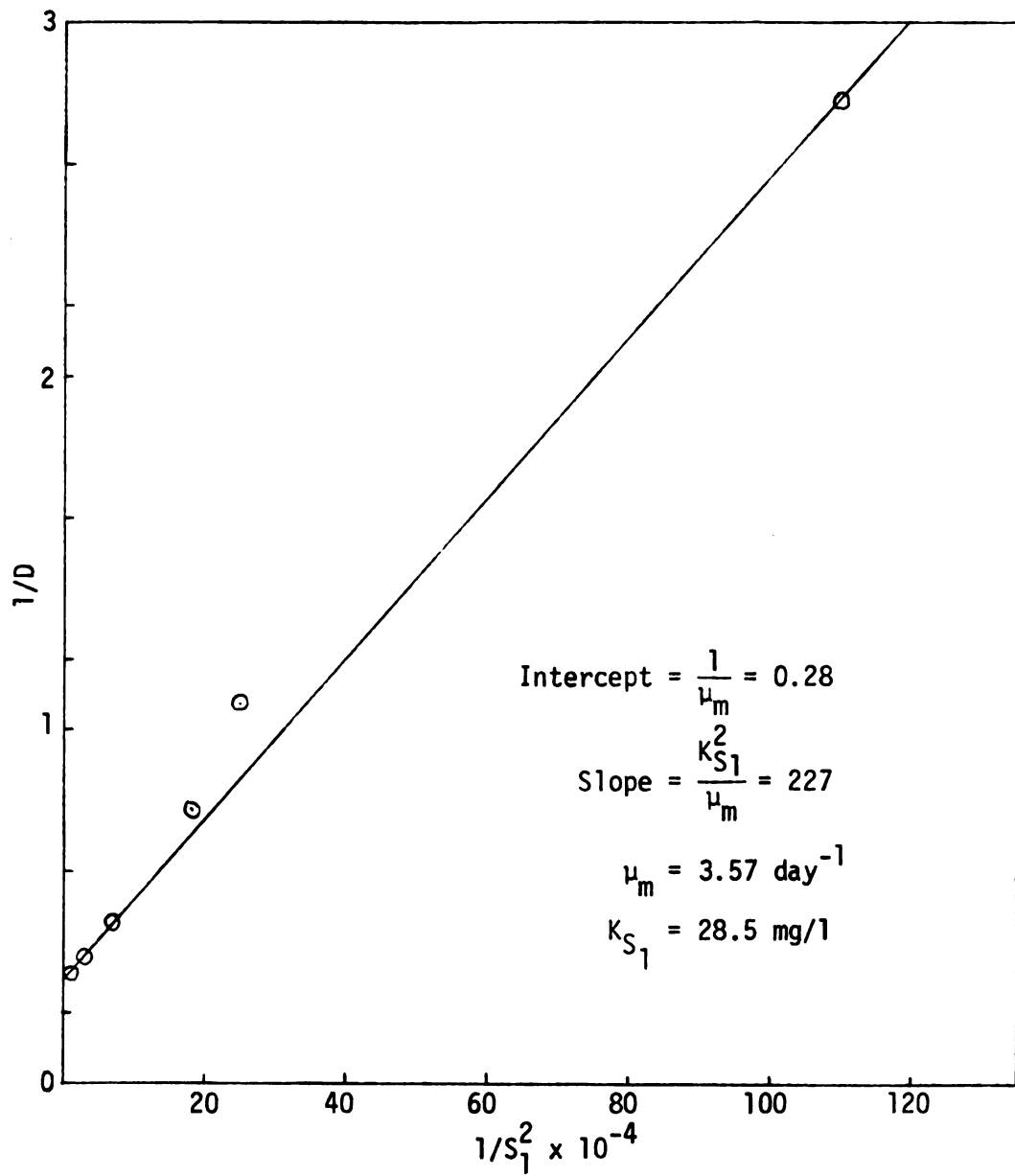


Figure 4.10.--Lineweaver-Burk Plot for the Second Order Model for Nitrate Nitrogen Limiting Case.

rates was considered for a continuous stirred tank reactor containing heterogeneous population. This incomplete reduction occurs at very high residence times which would be expected to give ample time for the growth of many organism species. It was felt very strongly that some other species could have been growing along with the denitrifiers at these high residence times. The complex interactions between the various species could have been the cause of this incomplete reduction of the nitrate. Another source of error could have been due to the problem associated with maintaining low flow rates. Since Equation (4.26) is theoretically sound, it was concluded that the experimental errors were the prime reasons for the discrepancies in the data.

Because of the incomplete reduction of nitrate nitrogen, the points representing the experiments N-5 and N-7 do not lie on the straight line. A straight line was made to pass through the first four points giving $\mu_m = 6.7 \text{ day}^{-1}$ and $K_{S1} = 88 \text{ mg/l}$. The same four points were curve fitted to a Monod curve and the required parameters were estimated to be $\mu_m = 6.8 \text{ day}^{-1}$ and $K_{S1} = 83 \text{ mg/l}$. These two sets of values are quite close to one another.

From Equation (4.23), one obtains,

$$X = Y_1 (S_{1i} - S_1) = Y_2 (S_{2i} - S_2) .$$

When the microbial cell mass is plotted against the substrate used, the slopes of the lines would give the yield factors. The lines are plotted in Figure 4.11. From the graph, $Y_1 = 0.6363$ and $Y_2 = 0.1875$.

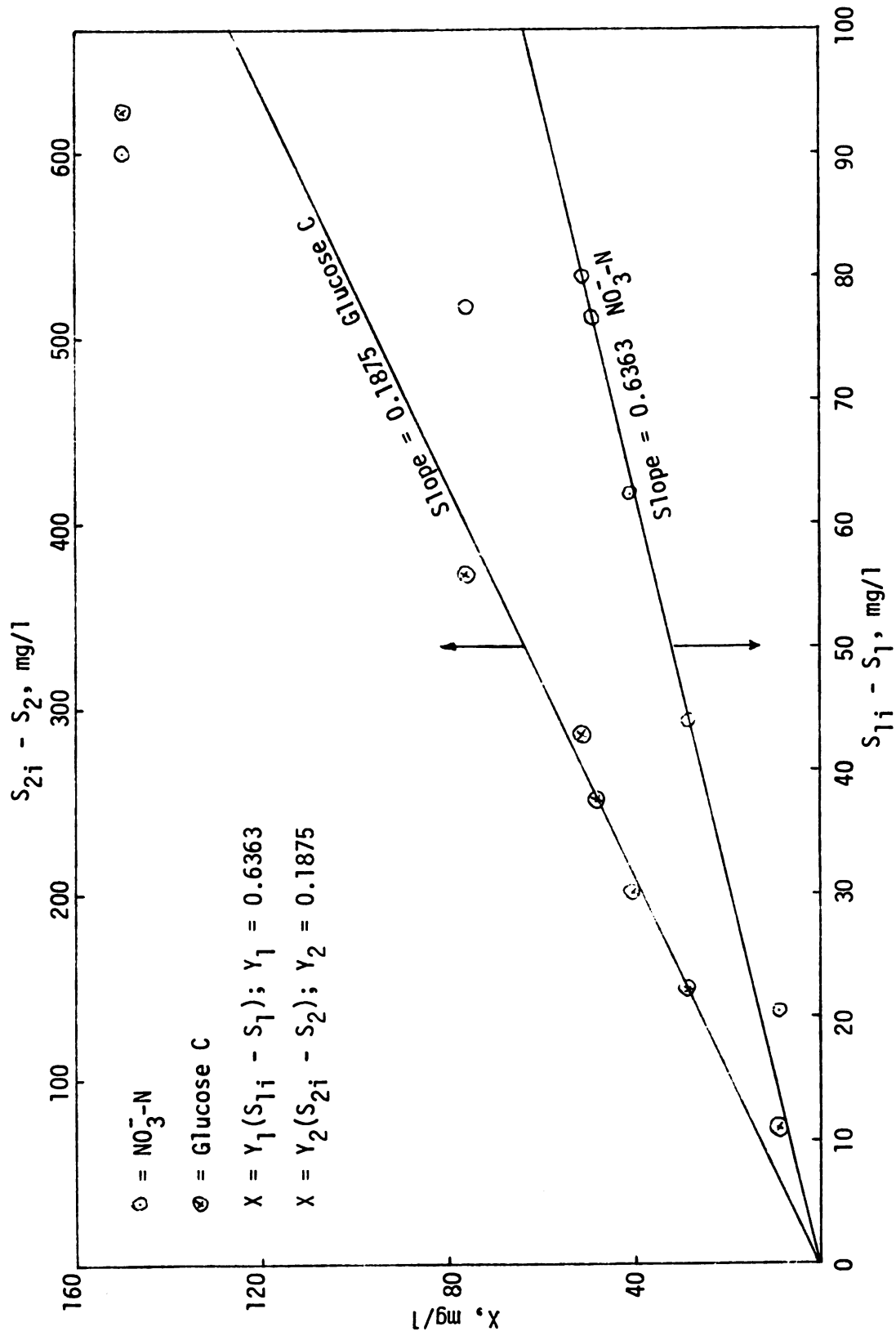


Figure 4.11.--Plot of Microbial Concentration Against Substrate Utilized.

The point representing experiment N-7 is way up the nitrate nitrogen line indicating a very high yield factor, but the same experiment gives very reasonable approximation for the glucose line.

This indicates that the microbes produced do utilize glucose as an energy source but do not reduce the nitrate. Therefore, there is a strong possibility of two different populations being present together for the experiment N-7 and some new species invading the reactor contents at high residence times.

Glucose Carbon Limiting System

Table 4.3 contains the average steady state data obtained from the chemostats. The raw data are given in Appendix D.

The nitrate nitrogen concentration chosen for this set of experiments was 250 ppm. The glucose carbon concentration was 100 ppm. For complete glucose oxidation, 50 ppm of nitrate nitrogen may be used. That would still leave about 200 ppm of nitrate nitrogen in the solution and the factor $\frac{200}{200 + 80} = 0.7$ is fairly close to 1. This will ensure an excess of nitrate nitrogen in the reactor solution.

A quick look at the table shows that for residence times greater than 1 day, complete glucose removal takes place. The variations in the influent concentration are due to changing of the feed solution every two days. These data are subjected to the same analysis as the data in Table 4.2.

The Monod plot for the system is shown in Figure 4.12. Because of the absence of glucose in the effluent in experiments

TABLE 4.3.--Average Steady State Data for Carbon Limiting System.

Experiment Number	Residence Time Days	Concentration, mg/l					Suspended Solids mg/l	Dissolved Oxygen mg/l	pH
		Incoming		Outgoing					
		Glucose-C	NO ₃ ⁻ -N	Glucose-C	NO ₃ ⁻ -N				
C-1	0.2917	100	250	82	233.8	7.7	0.3	7.8	
C-2	0.4861	100	250	21	218.3	27.3	0.2	8.2	
C-3	0.9722	100	250	5	213.3	32.2	0.4	8.5	
C-4	1.2153	100	250	--	208.4	39.3	0.3	7.7	
C-5	1.6204	100	250	--	203.7	42.7	0.2	7.5	
C-6	1.9445	100	250	--	195.5	35.0	0.2	7.9	
C-7	2.6515	100	250	--	198.2	40.7	0.1	8.0	

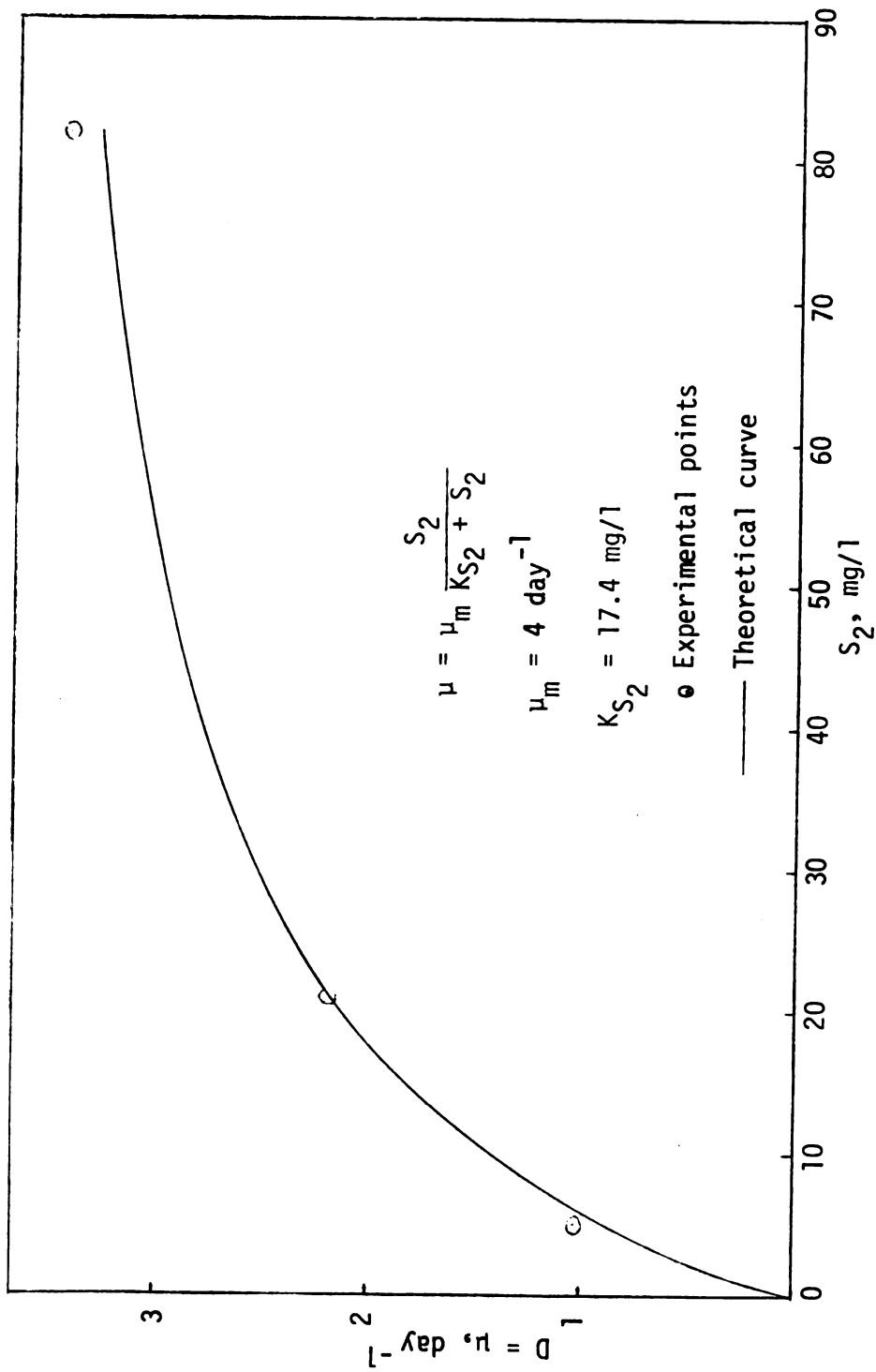


Figure 4.12.--Monod Plot for Carbon Limiting Case.

C-4 through C-7, these four points lie on the Y-axis. A smooth curve can be passed through the remaining three points as shown in the figure. The Lineweaver-Burk plot for the same data is shown in Figure 4.13. Only three points are available. The straight line through these points gives $\mu_m = 4.0 \text{ day}^{-1}$ and $K_{S_2} = 17.4 \text{ mg/l}$. Using these parameters, a curve may be drawn on the Monod plot. The three experimental points on the Monod plot lie near the theoretical curve indicating that both these plots give consistent results.

To determine the yield coefficient for the two substrates, the cell mass obtained is plotted against the respective substrates utilized. The results are shown in Figure 4.14. The values of Y_1 and Y_2 obtained from the slopes of the lines are 0.857 and 0.375, respectively.

Parameter Values

Table 4.4 summarizes the values of the various parameters evaluated in this work.

μ_m .--The values of μ_m obtained from the Lineweaver-Burk plots are more representative than those obtained from the Monod plots. In the carbon limiting system, it was assumed that the factor $\frac{S_1}{K_{S_1} + S_1}$ equaled unity, but it was approximately $\frac{200}{200 + 80} = 0.7$. From the value of μ_m calculated, correction can be applied to it as follows:

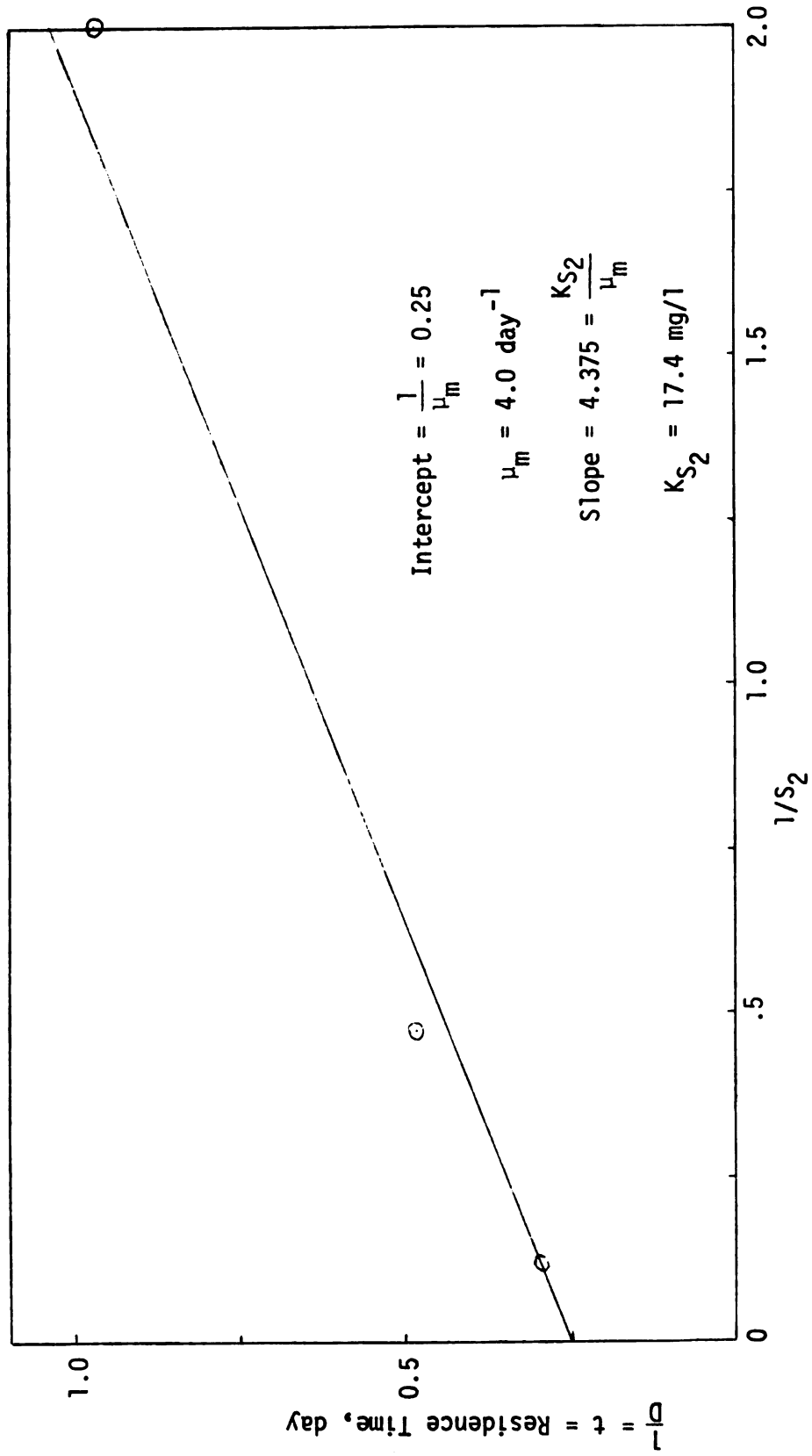


Figure 4.13.--Lineweaver-Burk Plot for Carbon Limiting Case.

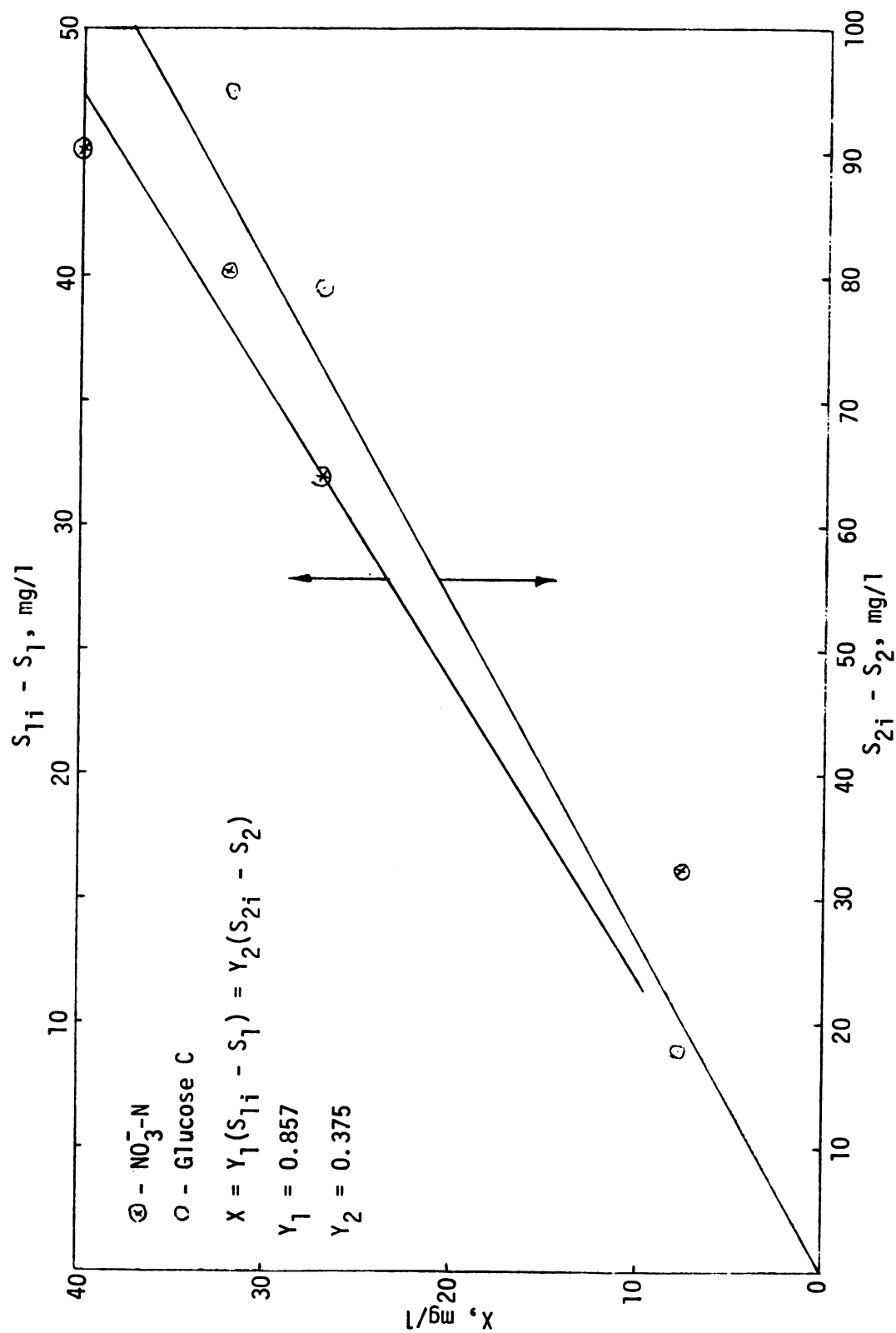


Figure 4.14.--Microbial Concentration Against Substrate Utilized.

TABLE 4.4.--Parameter Values Obtained from Experimental Work.

Type	Parameter Symbol	Obtained from System			
		Nitrogen Limiting		Glucose-C Limiting	
		Monod Plot	Lineweaver- Burk Plot	Monod Plot	Lineweaver- Burk Plot
Kinetic	μ_m day ⁻¹	6.8	6.67	5.7	5.7
	K_{S1} mg/l	83	88	--	--
	K_{S2} mg/l	--	--	16	17.4
Obtained from Cell Mass Plot					
Stoichiometric	Y_1 mg cell produced /mg	0.6363		0.857	
	Y_2 substrate used	0.1875		0.375	

$$\text{apparent } \mu_m = \mu'_m = \mu_m (0.7) = 4.0,$$

$$\text{i.e., } \mu_m = 5.7 \text{ day}^{-1}.$$

This value is smaller than the one obtained from the Lineweaver-Burk plot for the nitrogen limiting system. The value of μ_m chosen is 6.8 day^{-1} because of the greater accuracy of the nitrogen limiting experiments.

K_{S1}.--Two different values, 83 mg/l and 88 mg/l are obtained from the Monod and Lineweaver-Burk plots, respectively. The value of 83 mg/l will be chosen as the more representative one.

K_{S2}.--The two values obtained from the two plots are quite close to one another. The value of 17.4 mg/l will be chosen for K_{S2}.

Y₁.--The values of Y₁ obtained from the nitrogen limiting system and the carbon limiting system are 0.6363 and 0.857, respectively. Since the analysis of the limiting substrate is more accurate than that of the excess substrate, more weight will be assigned to the first value. The value of Y₁ chosen is, therefore, 0.7.

Y₂.--Similarly, the value obtained from the carbon limiting system is considered more accurate and the value of Y₂ is chosen as 0.333.

The results of the experiments can be summarized as follows:

$$\mu_m = 6.8 \text{ day}^{-1},$$

$$K_{S_1} = 83.0 \text{ mg/l},$$

$$K_{S_2} = 17.4 \text{ mg/l},$$

$$Y_1 = 0.7, \text{ and}$$

$$Y_2 = 0.333.$$

Comparison of Parameter Values With Those Obtained From Past Work

Hadjipetrou (1965) determined yield coefficient for an anaerobic system with nitrates and glucose as the source of carbon. His yield was 0.65 mg cells/gm organic carbon, twice as high as the value obtained in this work. This could be due to the fact that he was working with a pure culture of Aerobacter Aerogenes, whereas a heterogeneous population was used in this work. Stensel's work with the denitrification in a chemostat gave him a value of $Y_2 = 0.18 \text{ mg cell/mg COD} = 0.48 \text{ mg cell/mg organic carbon}$.

Chang and Morris (1962), from the studies of the utilization of nitrate by Micrococcus Denitrificans in an anaerobic system, found the maximum growth rate of 6.3 day^{-1} , a value close to 6.8 day^{-1} obtained in this work. This also compared well with the values $3\text{-}6 \text{ day}^{-1}$ reported by Stensel (1971).

Stensel also reported the values of K_{S_2} in the range of 40-75 mg/l of COD, i.e., 15-28 mg/l of organic carbon. This compares well with the value of 17.4 mg/l estimated in this work. All of the work cited above has assumed carbon as the only limiting substrate.

Moore and Schroeder (1971) worked with a nitrogen limiting kinetic model and found the value of μ_m 3-7 day⁻¹, the same as the one obtained from carbon limiting systems, but their value of K_{S_1} was 0.8 mg/l, much lower than 83 mg/l estimated in this work.

The best way to validate the double substrate model would be to carry out the reaction when both the substrates are limiting and see how well the experimental outcome and the prediction based on the model would match. This approach presents a problem in the case of a chemostat. The main difficulty arises in choosing the operating conditions such that the concentrations of the substrates in the reactor are limiting.

An alternative would be to carry out the reaction batchwise and keep track of the substrates' concentrations and the cell mass as a function of time. Model equations can be written for the three variables, S_1 , S_2 , and X , and they can be integrated to give the three profiles as functions of time. Comparison between the experimental and the predicted profiles would give some measure of the validity of the model.

Stensel (1971) carried out a number of batch experiments. His results have been compared with the predicted profiles. The following three differential equations completely define a batch system:

$$S_1 : \frac{dS_1}{dt} = - \frac{\mu_m}{Y_1} \left(\frac{S_1}{K_{S_1} + S_1} \right) \left(\frac{S_2}{K_{S_2} + S_2} \right) X ,$$

$$S_2 : \frac{dS_2}{dt} = - \frac{\mu_m}{Y_2} \left(\frac{S_1}{K_{S_1} + S_1} \right) \left(\frac{S_2}{K_{S_2} + S_2} \right) X , \text{ and}$$

$$X : \frac{dX}{dt} = \mu_m \left(\frac{S_1}{K_{S_1} + S_1} \right) \left(\frac{S_2}{K_{S_2} + S_2} \right) X .$$

Stensel used COD as a measure of carbon; therefore, the values of Y_2 and K_{S_2} obtained in this work have been changed from the basis of organic carbon to COD. The results for the various data are shown in Figures 4.15 through 4.19. Although the data set B-3 does not fit the model equations well at all, the fit with the data sets B-5, B-6, B-2, and B-7 is remarkable, considering the heterogeneous populations involved, degree of accuracy of the analytical techniques, and completely independent sets of experiments.

The usefulness of the double substrate model has been illustrated in the form of example problems for a continuous stirred tank system (Shah et al. 1975). Activated sludge processes are carried out generally in chemostats. This model enables one to determine the effluent concentration of both the substrates at any given operating conditions. The effect of substrate concentrations on the rate of reaction is accounted for, regardless of whether the substrate is in excess or in limiting supplies. The application of this equation to the design of a land disposal system will be discussed in the next chapter.

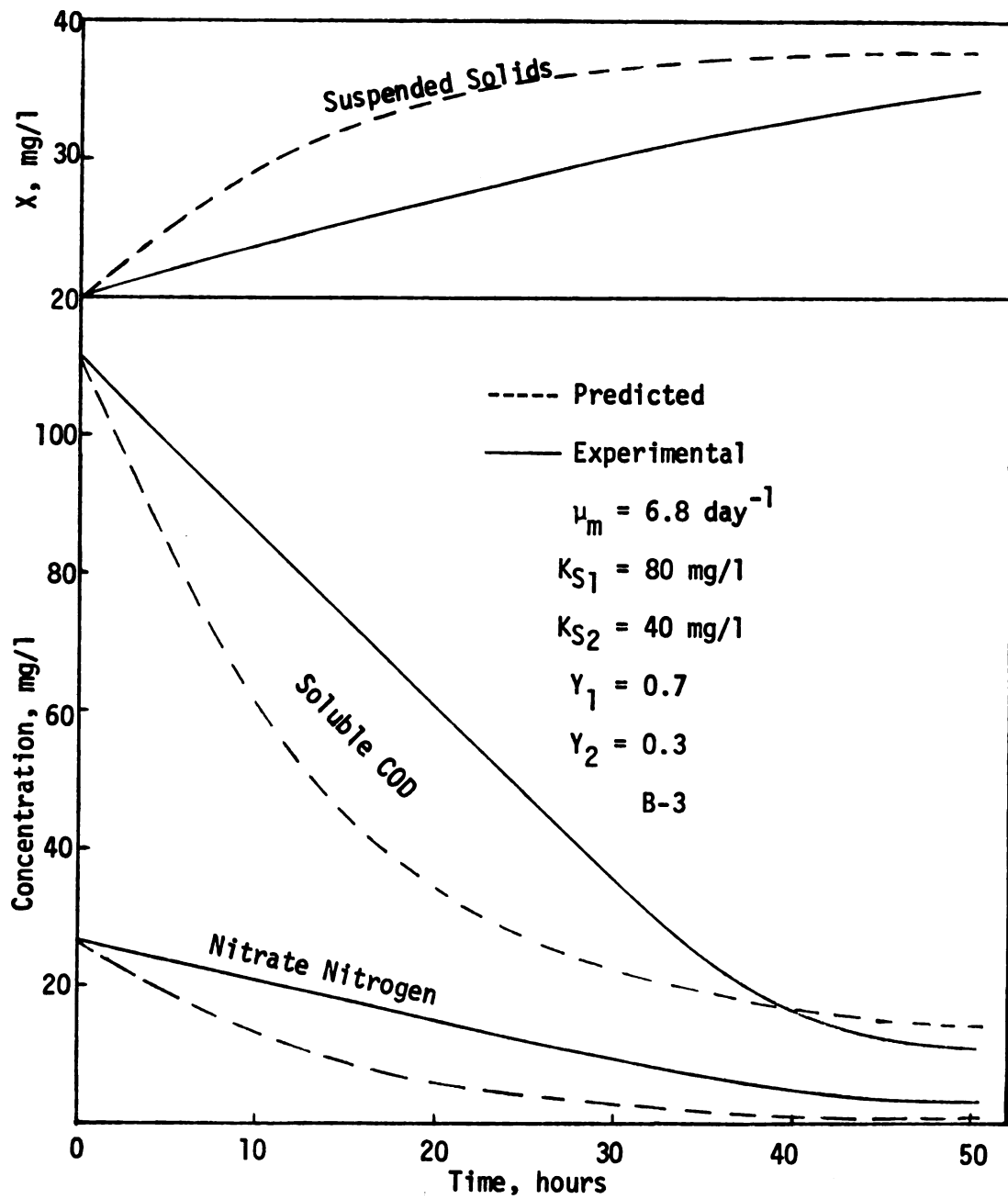


Figure 4.15.--Prediction of Stensel's Batch Data B-3 Using Parameters Obtained from This Work.

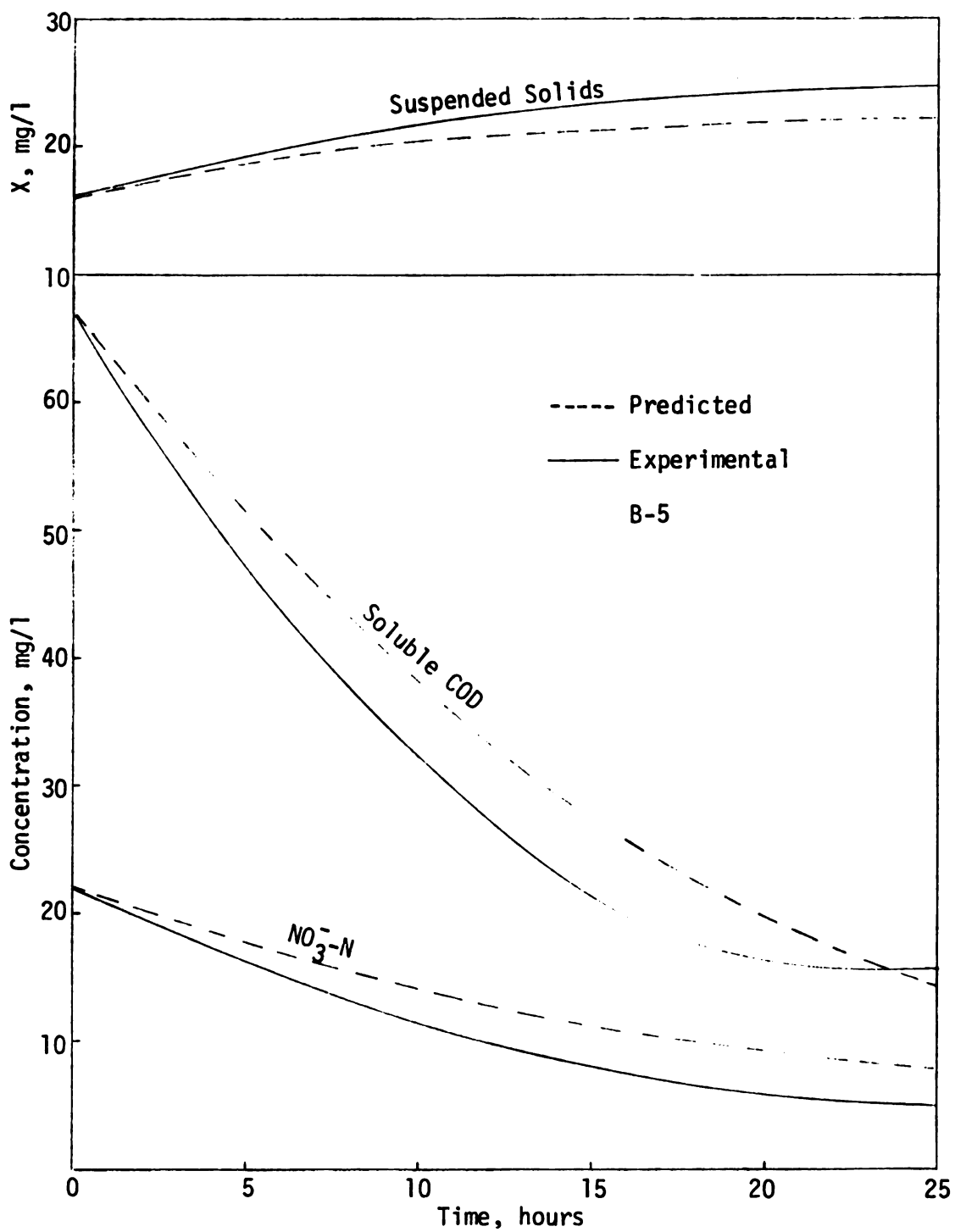


Figure 4.16.--Prediction of Stensel's Batch Data B-5 Using Parameters Obtained from This Work.

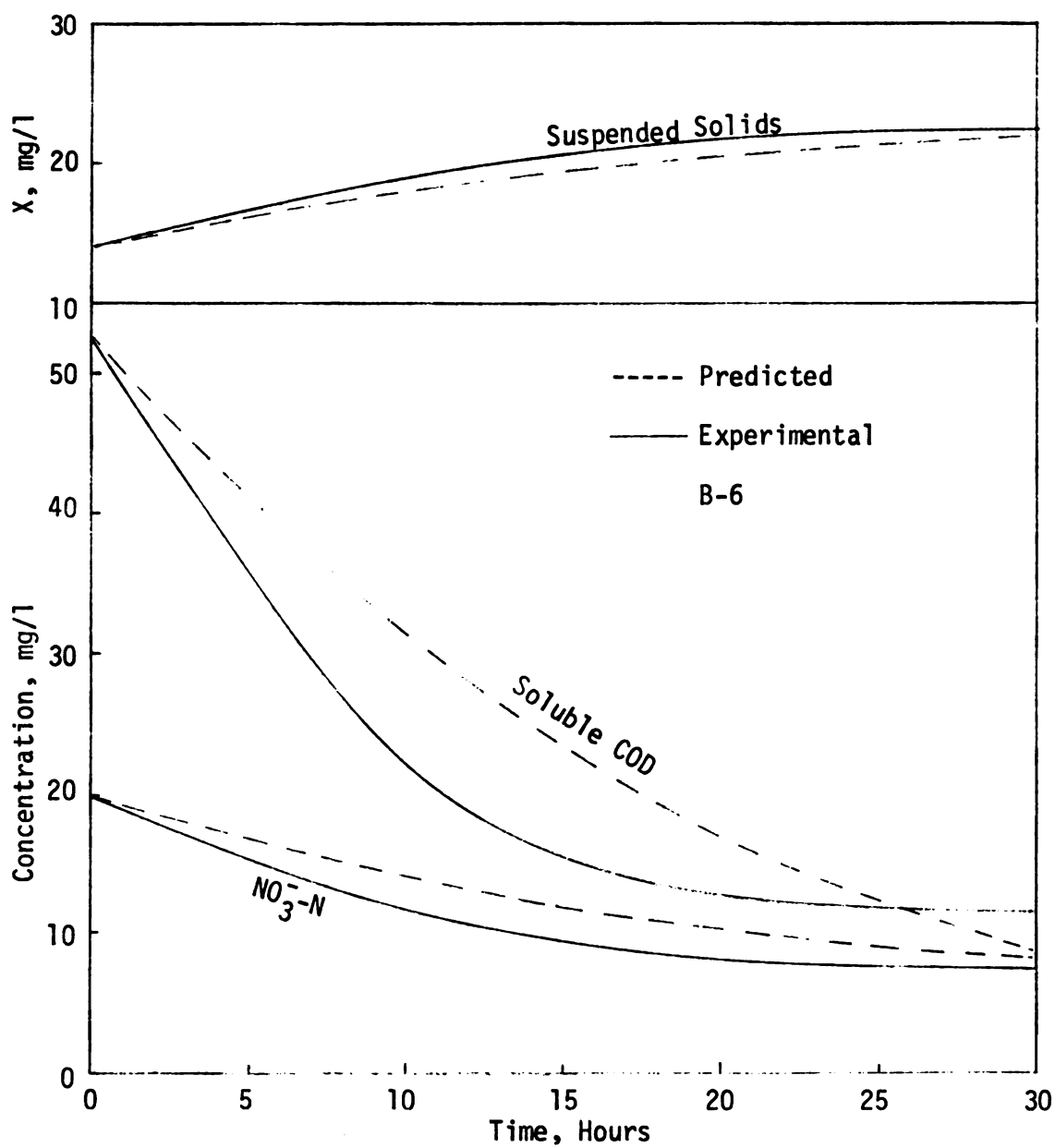


Figure 4.17.--Prediction of Stensel's Batch Data B-6 Using Parameters Obtained from This Work.

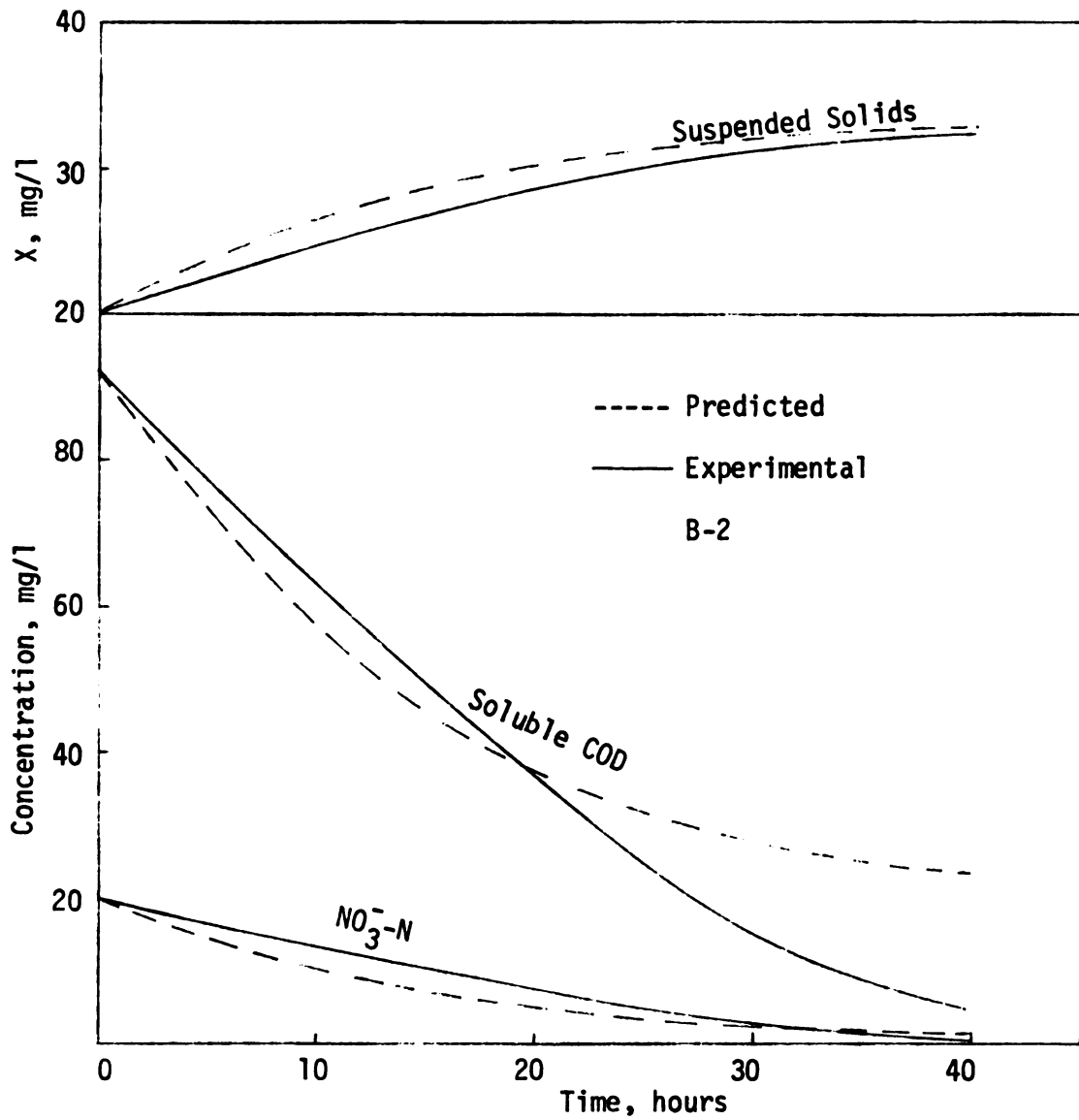


Figure 4.18.--Prediction of Stensel's Batch Data B-2 Using Parameters Obtained from This Work.

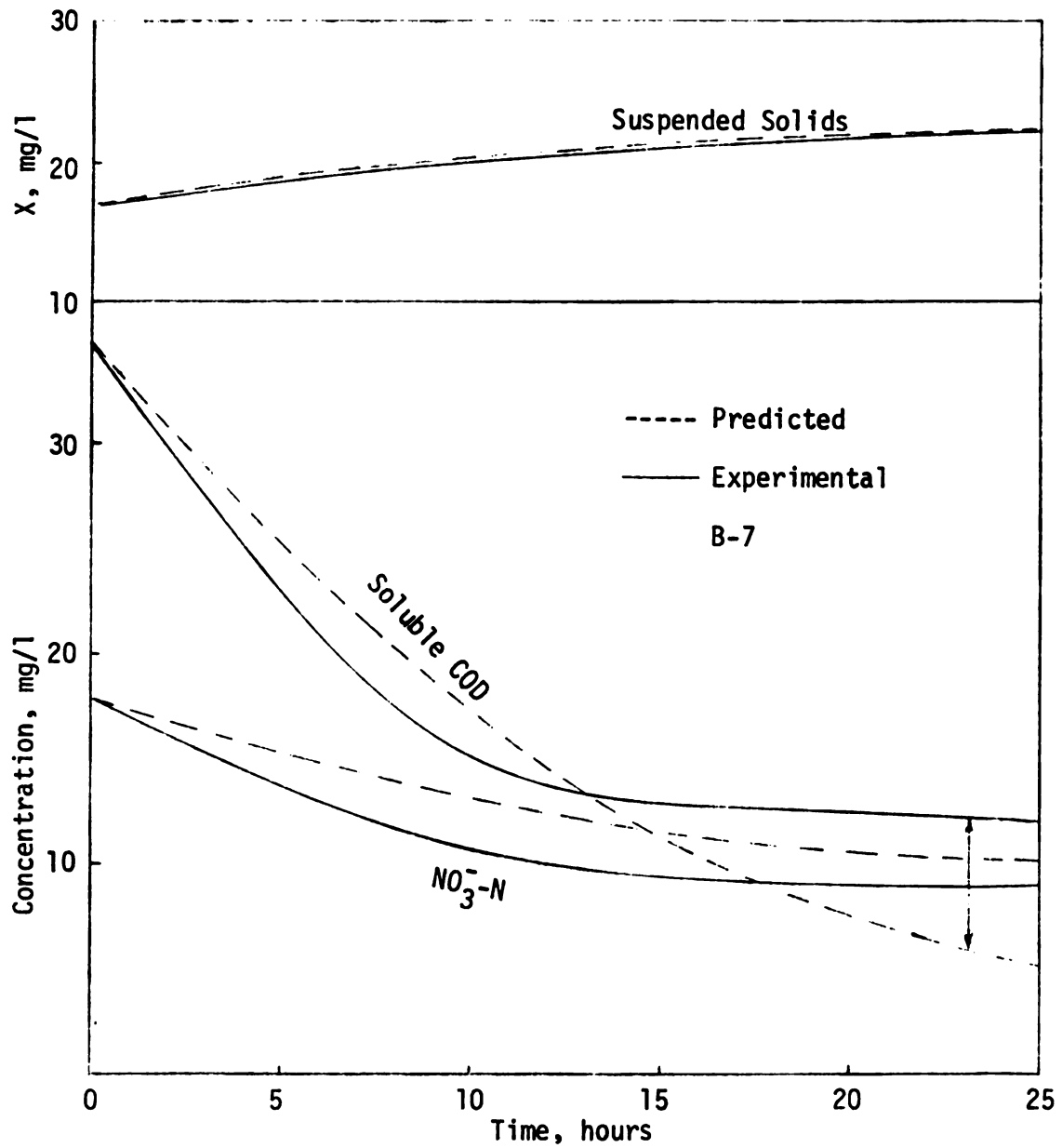


Figure 4.19.--Prediction of Stensel's Batch Data B-7 Using Parameters Obtained from This Work.

CHAPTER V

MODELING OF NITROGEN MOVEMENT IN SOILS

Wastewater contains nitrogen mainly in the form of ammonium nitrogen and nitrate nitrogen. Proteins, amino acids and urea also occur in abundance but ammonia is readily derived from them. If the wastewater is subjected to primary treatment, most of the nitrogen from proteins, amino acids and urea is converted to the ammonium nitrogen form. If the wastewater effluent is from an activated sludge plant, some ammonium nitrogen could also be converted to nitrate nitrogen.

The nitrogen in the wastewater, when applied to the land disposal system, gets converted from ammonium nitrogen to atmospheric nitrogen via the nitrification and denitrification reactions. An efficient spray irrigation site would maximize the removal of nitrogen with minimum leakage into the groundwater system. In order to properly design and manage a wastewater land treatment facility, quantitative understanding of the movements of various nitrogen species involved in the nitrogen transformations is required. This chapter presents an attempt to develop a mathematical model to describe the nitrogen movement in the soil.

Literature Survey and Physical Situation

Modeling efforts of the past can be divided into two classes: (1) empirical and (2) mechanistic. Duffy and Franklin (1972) took the first approach and developed a rate expression for nitrification by curve-fitting the data. This rate expression can predict the effect of various factors such as pH, dissolved oxygen concentration, ammonium concentration, etc., on the rate of nitrification but has no theoretical basis. Beek and Frissel (1971), using a semi-empirical approach, developed a very detailed model to describe the behavior of nitrogen in the soil. They considered decomposition of organic material, mineralization, nitrification and the physical processes of the movement of water, heat, and salt but considered no denitrification in the system.

Several attempts have been made to develop mathematical models to describe the concentration profiles of ammonium and nitrate nitrogen on a theoretical basis. McLaren (1969, 1970) developed a mathematical model to describe the steady state and unsteady state concentration profiles of ammonium, nitrite, and nitrate nitrogen in the absence of ionic dispersion and ion-exchange reaction involving the adsorption of ammonium by the soil. He assumed first order reaction kinetics for both the nitrification and denitrification reactions. Cho (1971) also assumed first order kinetics for these reactions, but he accounted for dispersion and ammonium disappearance due to ion exchange. He derived a set of second order linear partial differential equations and solved them analytically to obtain the steady state and unsteady state

concentration profiles of ammonium, nitrite and nitrate. Since nitrification and denitrification require quite opposite environmental conditions, mainly oxygen rich versus oxygen deficient, it is hard to visualize that both the reactions can be carried out in the same equipment. Starr (1973) showed experimentally that using a soil column, it is possible to carry out both the nitrification and denitrification reactions simultaneously. He measured concentration profiles of the liquid phase and the gas phase species.

The physical situation in a soil column is quite complex. In an unsaturated flow through the soil, three phases exist: (1) gas, (2) liquid, and (3) solid (see Figure 5.1). The solid phase consists of particles and aggregates of these particles. The voids within the aggregates are called micropores and those between the particles and/or the aggregates are called macropores. Even if the soil is oxygen rich, it is quite possible to have anaerobic spots or regions, as in micropores, in the soil column. Microbes are attached to these soil particles and aggregates. As the wastewater moves down, the ammonium concentration and the dissolved oxygen concentration decrease due to the nitrification reaction. If the gas phase and the liquid phase are in equilibrium, some oxygen is transferred from the gas phase to the liquid phase, and thus, oxygen concentration in the gas phase decreases. In the lower part of the soil column where oxygen concentration is sufficiently low, denitrification begins to dominate. Even in the upper part of the column, some denitrification does take place in the

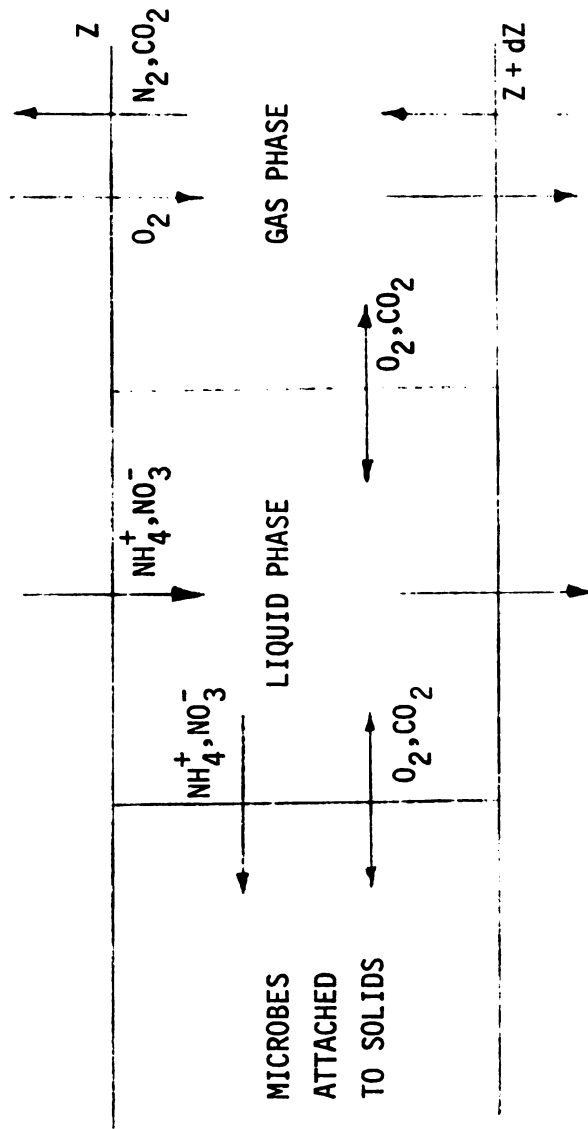


Figure 5.1.--Solid-Liquid-Gas Phase Interrelationship.

oxygen deficient micropores. The nitrogen and carbon dioxide evolved during denitrification move upwards. All three phases are involved in mass transfer and are thus interrelated.

Modeling efforts so far have been restricted to ammonium and nitrate nitrogen, i.e., liquid phase species without regard to the interactions between the gas phase and the liquid phase. Both the nitrification and denitrification rate constants are affected by the oxygen concentration. If the oxygen concentration falls below a critical level, the nitrification reaction is severely affected and the denitrification does not start until the oxygen concentration falls below a certain level. Modeling of the nitrogen movement will have to take into account compositions of both the liquid and gas phases.

Method of Attack

This complex situation can be modeled only with some simplifying assumptions. The line of attack to be used is to make as many reasonable assumptions as required to make the system simple enough for mathematical treatment. This model is then made more and more complex by relaxing, one by one, the assumptions made in the simple model. The concentration profiles obtained from various stages of the model are compared with one another and with the experimental data. From this, the effect of making an assumption or relaxing one, on the concentration profiles of various species, becomes apparent. This approach enables us to determine how complex or how simple a system can be made and still model it reasonably well to represent the experimental data.

The model will have to be validated by simulating some experimental conditions and by comparing the predicted profiles with the experimental profiles. The data from BLWRS (Erickson et al. 1971) cannot be used for validation because, by placing an impermeable layer at the bottom, the system was artificially made anaerobic and such a thing will not occur in most natural systems. Starr (1973) performed his experiments in a soil column under unsaturated flow conditions. His data will be used to validate the model developed here.

Assumptions

Following are the basic assumptions made to simplify the physical situation to begin with.

1. Steady state conditions exist in the soil column. This is true when the system has been operating for some time.
2. Adsorption of ammonium by the soil is negligible.
3. Mass transfer of a component, say, oxygen, from the gas phase to the liquid phase and the loss of dissolved oxygen in nitrification are steps in series. At steady state, they have to be equal. It is assumed that mass transfer is much faster than the reaction rate term and hence reaction kinetics is the rate controlling step.
4. The rate of substrate consumption and the rate of product formation are related to stoichiometric coefficients. This is not exactly true because of the enzymatic nature of the reactions involved. In the absence of any data on product yield coefficients, this assumption is quite necessary.

5. Organic carbon required for the denitrification reaction is present in excess, in the form of glucose. The denitrification rate thus does not depend on the organic carbon concentration. This assumption is quite necessary because Starr in his work did not measure the organic carbon concentration and hence there is no way of accounting for the effect of organic carbon on the rate of denitrification.

6. The only sink for oxygen is assumed to be due to nitrification. Oxygen consumption due to respiration is neglected. Carbon dioxide and nitrogen are produced because of denitrification.

Model

Liquid Phase

Based on the above assumptions, we can write second order differential equations for ammonium and nitrate nitrogen concentrations in the liquid phase as follows:

$$\left. \begin{aligned} \text{NH}_4^+-\text{N} : D_1 \frac{d^2 C_1}{dz^2} - V \frac{dC_1}{dz} - R_1(C_1, C_3) &= 0, \\ \text{NO}_3^--\text{N} : D_2 \frac{d^2 C_2}{dz^2} - V \frac{dC_2}{dz} + R_1(C_1, C_3) - R_2(C_2, C_3) &= 0 \end{aligned} \right\} \quad (5.1)$$

where

D = dispersion coefficient, cm^2/day ,

C = concentration in the liquid phase, $\mu\text{moles}/\text{cm}^3$,

Z = soil depth, cm ,

R_1 = rate of nitrification, $\mu\text{moles/cm}^3/\text{day}$, and

R_2 = rate of denitrification, $\mu\text{moles/cm}^3/\text{day}$.

The above equations state that at steady state, dispersive and convective influx balance the rate of production or the rate of consumption term. Here, subscripts 1, 2, and 3 refer to ammonium nitrogen, nitrate nitrogen, and oxygen species.

Gas Phase

Changes in the fluxes of oxygen, nitrogen and carbon dioxide are governed by the rate of consumption or formation and are given by

$$\left. \begin{aligned} \text{O}_2 : \epsilon(1 - S) \frac{dN_3}{dz} + \alpha_1 R_1(C_1, C_3)\epsilon S &= 0, \\ \text{N}_2 : \epsilon(1 - S) \frac{dN_4}{dz} + \alpha_2 R_2(C_2, C_3)\epsilon S &= 0, \text{ and} \\ \text{CO}_2 : \epsilon(1 - S) \frac{dN_5}{dz} + \alpha_3 R_2(C_2, C_3)\epsilon S &= 0, \end{aligned} \right\} \quad (5.2)$$

where

ϵ = soil porosity,

S = moisture content in terms of the fraction of pore space occupied by water,

N = flux of a component, $\mu\text{mole/cm}^2/\text{day}$, and

α_i = stoichiometric coefficient.

Here, $\alpha_1 = -2$, $\alpha_2 = 1/2$, and $\alpha_3 = 1/4$ from Equations (4.3) and (4.4). The fluxes obtained from the set (5.2) are converted into the concentrations by using

$$N_i = D_{im} \frac{dC_i}{dZ} + X_i (N_3 + N_4 + N_5), \quad i = 3, 4, 5 \quad (5.3)$$

where

D_{im} = diffusivity of a component i into a mixture,
cm²/day, and

X_i = mole fraction of a component.

The set of Equations (5.1) and (5.2) are subject to the boundary conditions,

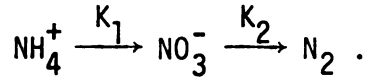
$$\begin{aligned} &\text{at } Z = 0, \text{ all } C\text{'s are known, and} \\ &\text{at } Z = \infty, dC_i/dZ = 0, \text{ and } N_i = 0. \end{aligned} \quad (A)$$

The first term in Equation (5.3) represents the diffusive flux and the second term the convective flux.

Solution of the sets of Equations (5.1), (5.2), and (5.3) would describe completely the concentration profiles for all the species in the soil column. These equations are solved for different cases and the results are produced below.

Case 1.--Assume that both the nitrification and denitrification reactions are first order with respect to ammonium, nitrogen, and nitrate nitrogen concentrations, respectively. In reality, the rate term is similar to the Michaelis-Menten type which incorporates

both the zero order and the first order rate regimes. These reactions are considered to occur in series as typified by



Under these conditions,

$$R_1 = K_1 C_1 \quad \text{and} \quad R_2 = K_2 C_2 . \quad (5.4)$$

Combining Equations (5.1) with (5.4) results in the formation of two linear second order differential equations with the specified boundary conditions. Analytical solution of these equations results in

$$\left. \begin{aligned} C_1 &= C_{10} e^{\beta_1 Z}, \text{ and} \\ C_2 &= \frac{C_{10} K_1}{K_1 - K_2} \left[e^{\beta_2 Z} - e^{\beta_1 Z} \right] \end{aligned} \right\} \quad (5.5)$$

where

$$\beta_1 = \frac{V}{2D_1} - \left(\frac{V^2 + 4D_1 K_1}{4D_1^2} \right)^{1/2}, \text{ and}$$

$$\beta_2 = \frac{V}{2D_2} - \left(\frac{V^2 + 4D_2 K_2}{4D_2^2} \right)^{1/2} .$$

Substituting Equation (5.5) in the set of differential equations (5.2), we can solve for the fluxes as functions of soil depth, as given below:

$$\left. \begin{aligned}
 N_3 &= - \frac{2SC_{10}K_1}{(1-S)\beta_1} e^{\beta_1 Z}, \\
 N_4 &= \frac{SC_{10}K_1K_2}{2(1-S)(K_1-K_2)} \left[\frac{e^{\beta_2 Z}}{\beta_2} - \frac{e^{\beta_1 Z}}{\beta_1} \right], \text{ and} \\
 N_5 &= \frac{SC_{10}K_1K_2}{4(1-S)(K_1-K_2)} \left[\frac{e^{\beta_2 Z}}{\beta_2} - \frac{e^{\beta_1 Z}}{\beta_1} \right] = \frac{1}{2} N_4.
 \end{aligned} \right\} \quad (5.6)$$

Sets (5.5) and (5.6) define the concentrations of ammonium nitrogen, nitrate nitrogen and the fluxes of oxygen, nitrogen and carbon dioxide. These fluxes have to be converted to concentrations by using Equation (5.3).

Case 1A.--In a soil column, there is a counter-current diffusion of oxygen in a mixture of nitrogen and carbon dioxide. If we assume that the downward flux of oxygen is balanced by the combined upward flux of nitrogen and carbon dioxide, the second term in Equations (5.3) drops out and the flux is made up of only a diffusive term. The convective flux term is also negligible for a component present in small amounts. This assumption is not quite true. At the top of the column, the flux of oxygen would more than counter-balance the fluxes of nitrogen and carbon dioxide, while at the bottom the reverse would be true. Assuming no dependence of diffusion coefficients on concentration, the concentration profiles of oxygen, nitrogen, and carbon dioxide can be derived

quite easily. Substituting $N_i = -D_i \frac{dC_i}{dz}$ in Equations (5.6) and solving for C's gives us

$$\left. \begin{aligned} C_3 &= C_{30} + \frac{2SC_{10}K_1}{(1-S)D_3\beta_1^2} [e^{\beta_1 Z} - 1], \\ C_4 &= C_{40} + \frac{SC_{10}K_1K_2}{2(1-S)D_4(K_1-K_2)} \left[\frac{1}{\beta_2^2} - \frac{1}{\beta_1^2} - \frac{e^{\beta_2 Z}}{\beta_2^2} + \frac{e^{\beta_1 Z}}{\beta_1^2} \right], \text{ and} \\ C_5 &= C_{50} + \frac{SC_{10}K_1K_2}{4(1-S)D_5(K_1-K_2)} \left[\frac{1}{\beta_2^2} - \frac{1}{\beta_1^2} - \frac{e^{\beta_2 Z}}{\beta_2^2} + \frac{e^{\beta_1 Z}}{\beta_1^2} \right]. \end{aligned} \right\} \quad (5.7)$$

Equations (5.7) give the concentration profiles and hence the mole fractions of oxygen, nitrogen and carbon dioxide in the soil column.

Case 1B.--We relax some of the assumptions made in Case 1A. As explained in the above case, the convective flux is not zero, but has finite value, i.e., $N_3 + N_4 + N_5 \neq 0$. Moreover, the diffusion coefficient is a function of the concentrations of the species. The set of Equations (5.3) cannot be solved analytically now. These equations are solved numerically, with the diffusion coefficient of a component in mixture calculated by the following equation as given by Bird et al. (1960),

$$D_{im} = \frac{N_i - X_i \sum_{j=3}^5 N_j}{\sum_{j=3}^5 \frac{1}{D_{ij}} (X_j N_i - X_i N_j)}, \quad i = 3, 4, 5. \quad (5.8)$$

The gas profiles can also be calculated directly from the fluxes with the help of the Stefan-Maxwell equations,

$$\frac{dC_i}{dz} = \sum_{j=3}^5 \frac{1}{D_{ij}} (X_i N_j - X_j N_i) , \quad i = 3, 4, 5, \quad (5.9)$$

where D_{ij} 's are the binary diffusivities. The Stefan-Maxwell equations allow us to calculate the concentration profiles without calculating D_{im} .

Case 2.--In Case 1, first order kinetic rate expressions were used to describe the two reactions. The enzymatic reactions can be both first order and zero order depending on the substrate concentration. They are better described by the Michaelis-Menten rate expressions, which incorporate both zero order and first order rate extremes. Hence,

$$R_1 = \frac{K_1 C_1}{K_{C_1} + C_1} \quad \text{and} \quad R_2 = \frac{K_2 C_2}{K_{C_2} + C_2} . \quad (5.10)$$

The set of Equations (5.1) and (5.10) combine to give second order nonlinear differential equations with (A) as the boundary conditions. To solve (5.1), we will have to employ some trial and error procedure.

Until now, the sets of Equations (5.1), (5.2), and (5.3) were independent of one another. The next two cases will interconnect these three sets of equations simultaneously.

Case 3.--An assumption required in this case is that the rates of reactions are first order, but denitrification does not begin until the concentration of oxygen drops below a certain level, say, 5 percent. This is more realistic since denitrification is essentially an anaerobic reaction. Therefore,

$$R_2 = K_2 C_2, \quad K_2 = 0 \quad \text{if } X_3 \geq .05.$$

With this assumption, the calculating procedure becomes more complex, since the region from which denitrification begins is not known. All the three sets of equations will have to be solved simultaneously with iterations on the oxygen profile.

Case 4.--Instead of first order reaction kinetics, a Michaelis-Menten rate expression is used to describe the nitrification and denitrification reactions, with the added restriction that denitrification would not proceed if the oxygen concentration is above 5 or 10 percent.

This is the most cumbersome case of the four cases considered. The calculating procedure involves outer loop iterations with respect to the oxygen profile. Within each of these iterations, there are smaller iterations involved for determining the ammonium nitrogen and nitrate nitrogen profiles.

Method of Solution

The method of solution is quite simple for Case 1A (completely analytical) and becomes progressively more complex for

Cases 2, 3, and 4. Analytical solution for the other cases was not possible and hence a numerical solution was sought.

Equations (5.1) along with the boundary conditions (A) represent a boundary value problem with second order linear or nonlinear differential equation as the case may be. The numerical approach chosen was to solve the second order differential equation in an implicit way. The differential equation is written in the form of a finite difference equation for each grid point resulting in a set of simultaneous equations. These simultaneous equations were solved by using the scientific subroutine ONEDIAG. Equations (5.2) and (5.3) were integrated using Milne's integration technique.

To obtain the numerical solution to all the cases, a general FORTRAN program GASTRAN aided by the subroutine ONEDIAG was written. The program was written so that all the input variables are read from data cards. Depending on the value of the option parameters, it would execute any of the above mentioned cases.

A complex listing of the finite difference formulae used to approximate the various derivatives and a complete listing of the FORTRAN program and the subprograms can be found in Appendix E. The following is a brief outline of the calculation procedure used in each of the cases.

1. Input the operating conditions and proper values of the option parameters.
2. Divide the soil column length into grid points spaced at every 2 cm. Using smaller sized grid points gave essentially no improvement in the solutions.

3. Case 1A

Solve Equations (5.1), (5.2), and (5.3) analytically to obtain the liquid phase and the gas phase concentrations.

Case 1B

- a. Solve Equations (5.1) and (5.2) analytically to obtain the liquid phase concentrations and the fluxes of the gas components.
- b. Solve Equations (5.9) numerically (because of the nonlinear nature of the equations) by Milne's integration method to obtain the gas phase composition.

Case 2

- a. Since the reaction rate terms assumed in this case are of Michaelis-Menten type, the resulting Equations (5.1) are nonlinear. To linearize these, assume the profile in question, ammonium nitrogen or nitrate nitrogen.
- b. Convert the differential equations into finite difference equations written for each point in the grid and form a diagonal matrix.
- c. Solve the simultaneous linear equations to get the computed profile. If the computed and the assumed profiles do not match, assume a new profile and start all over again.
- d. Numerically integrate Equations (5.2) to obtain fluxes of the gas components.
- e. Solve Equations (5.9) for the gas phase composition.

Case 3

- a. Assume an oxygen profile in the soil. This defines the regions of (1) nitrification alone, and (2) nitrification and denitrification.
- b. Solve Equations (5.1) analytically. The differential equation for nitrate nitrogen is split into two equations applicable in the two regions, i.e.,

$$D_2 \frac{d^2 C_2}{dz^2} - V \frac{dC_2}{dz} + K_1 C_1 - K_2 C_2 = 0, \text{ with}$$

$$K_2 = 0 \quad \text{up to} \quad Z = Z_0 \quad (X_3 \geq .05).$$

- c. Calculate the fluxes from Equations (5.2) by solving them analytically.
- d. Obtain the concentration profiles from Equations (5.9) by numerical integration.
- e. Compare the calculated and the assumed oxygen profiles and if they do not compare well, assume a different oxygen profile and go back to step (b).

Case 4

- a. Assume an oxygen profile to start with. This would define the regions of (1) no denitrification, and of (2) denitrification, depending on where the cut-off point of 5 percent or 10 percent oxygen concentration falls.
- b. Determine the ammonium nitrogen concentration profile using a trial and error procedure as outlined in Case 2.
- c. Determine the nitrate nitrogen concentration profile using the iterative technique, taking care to use the right type of equation for each of the two regions.
- d. Calculate the fluxes of the gas phase components from Equations (5.2) by numerical integration.
- e. Using these fluxes, the concentration profiles of the gas components are calculated from Equations (5.9). The oxygen profile assumed in step (1) is compared with the oxygen profile calculated. If they do not match within given accuracy, assume a new profile and go back to step (3). Five times as many calculations are required in this case as in Case 3.

The program was executed on a Control Data Corporation 6500 digital computer and required only a few seconds of central processor time.

Results and Discussion

The concentration profiles obtained from the computations in the four cases outlined above are to be compared with the experimental results of Starr. The physical parameters chosen are such as to duplicate the physical situation of Starr's column. The kinetic parameters used in the simulation were obtained from other independent sources. The constants for the denitrification reaction were taken from this work. The kinetic constants for the nitrification reaction were computed from various sources as shown in Chapter IV. The first order rate constants were taken from Starr's work, so it would come as no surprise if the first order rate model fits Starr's data quite well. The simulation results of the different models will demonstrate the effect of different assumptions. The values used in the simulation study are tabulated below.

First Order Reaction Constants:

$$K_1 = 0.8 \text{ day}^{-1}, \text{ and } K_2 = 0.08 \text{ day}^{-1}.$$

These values were obtained from Starr's data. These constants were not available from other sources and could not be computed from other kinetic constants.

Michaelis-Menten Constants:

$$K_1 = 2 \text{ } \mu\text{moles/cm}^3/\text{day}, \text{ } K_{S1} = 1 \text{ } \mu\text{mole/cm}^3,$$

$$K_2 = 1 \text{ } \mu\text{mole/cm}^3/\text{day}, \text{ and } K_{S2} = 6 \text{ } \mu\text{moles/cm}^3.$$

The values of K_1 and K_{S1} were obtained by reinterpretation of Starr's results. From Figure 4.1, the maximum rate of nitrification varies between 16-30 $\mu\text{g}/\text{cm}^3/\text{day}$. This translates into 1-2 $\mu\text{moles}/\text{cm}^3/\text{day}$. From the same figure, $K_{S1} = 15 \text{ mg/l} = 1 \mu\text{mole}/\text{cm}^3$. The value of K_{S2} was taken to be 6 $\mu\text{moles}/\text{cm}^3$ based on the present work. The values of K_1 and K_2 can also be estimated from Equation (4.12),

$$K_i = \frac{\mu_{m_i} X_i}{Y_i},$$

if the maximum specific growth rate, the yield coefficient and the microbial concentration are known. Starr, in his experiments, did not measure the microbial cell mass as a function of soil depth. Hence, accurate estimates of the constants K_1 and K_2 were not available. Estimates of diffusivities of various components in the liquid and gas phases were obtained on the basis of some experiments carried out by Starr. The same values can be obtained by using theoretical equations.

Physical Constants:

$$\begin{aligned} \epsilon &= 0.4, \quad X = 0.85, \quad L = 100 \text{ cm}, \\ D_1 &= D_2 = 3 \text{ cm}^2/\text{day}, \\ D_3 &= 250 \text{ cm}^2/\text{day}, \quad D_4 = D_5 = 150 \text{ cm}^2/\text{day}, \quad \text{and} \\ V &= 6 \text{ cm}/\text{day}. \end{aligned}$$

These constants were obtained on the basis of the physical condition existing in the soil column operated by Starr.

Surface Concentrations:

$$\begin{aligned}
 C_{10} &= 3.57 \text{ } \mu\text{moles/cm}^3 \\
 C_{20} &= 0.00 \\
 C_{30} &= 9.33 \text{ } \mu\text{moles/cm}^3 \\
 C_{40} &= 35.155 \text{ } \mu\text{moles/cm}^3 \\
 C_{50} &= 0.013355 \text{ } \mu\text{moles/cm}^3.
 \end{aligned}$$

Surface concentrations of the various gases were taken based on their atmospheric concentrations.

Experimental data were available for ammonium nitrogen, nitrate nitrogen, oxygen, nitrogen and carbon dioxide concentrations. The simulated results are shown with the related experimental data in Figures 5.2 through 5.5. It is significant to note that the models differ very little in the form of the response. The profiles differ very little in the shape. The deviations could probably be removed by minor adjustments in the parameters.

Scientifically, it would seem that the more detailed a mathematical model is, the more precise its results will be. Consequently, one would surmise that a model which neglects as many mechanisms as number 1 does, would be the least acceptable. In contrast, an engineer would like the simplest model consistent with the accuracy and reproducibility of the data.

The experimental measurements of ammonium and nitrate nitrogen are well predicted by the simplest model (refer to Figure 5.2) which considers the first order kinetic models. The simulation and experimental results will match because the kinetic parameters were

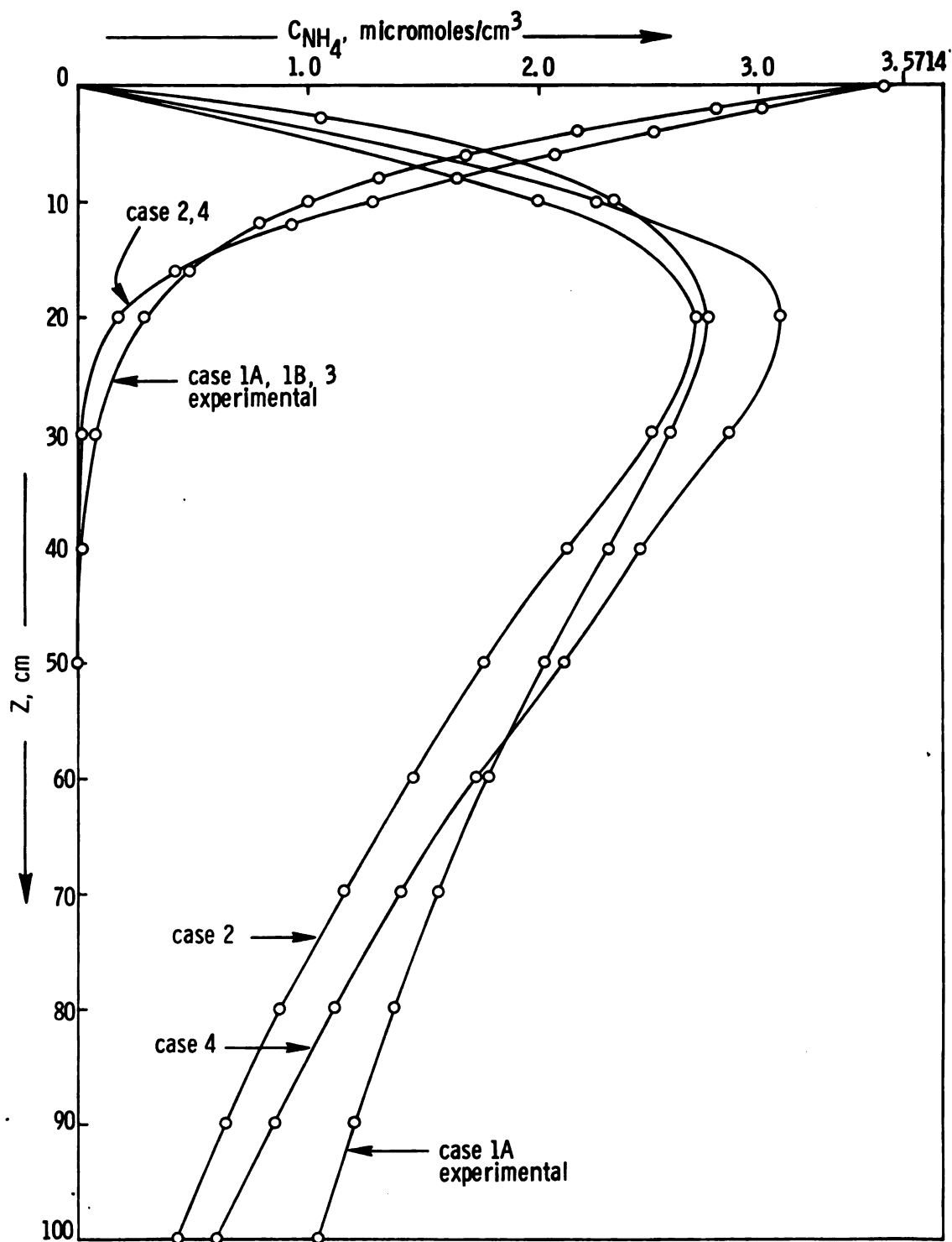


Figure 5.2.--Concentration Profiles of Ammonium Nitrogen and Nitrate Nitrogen in Liquid Phase.

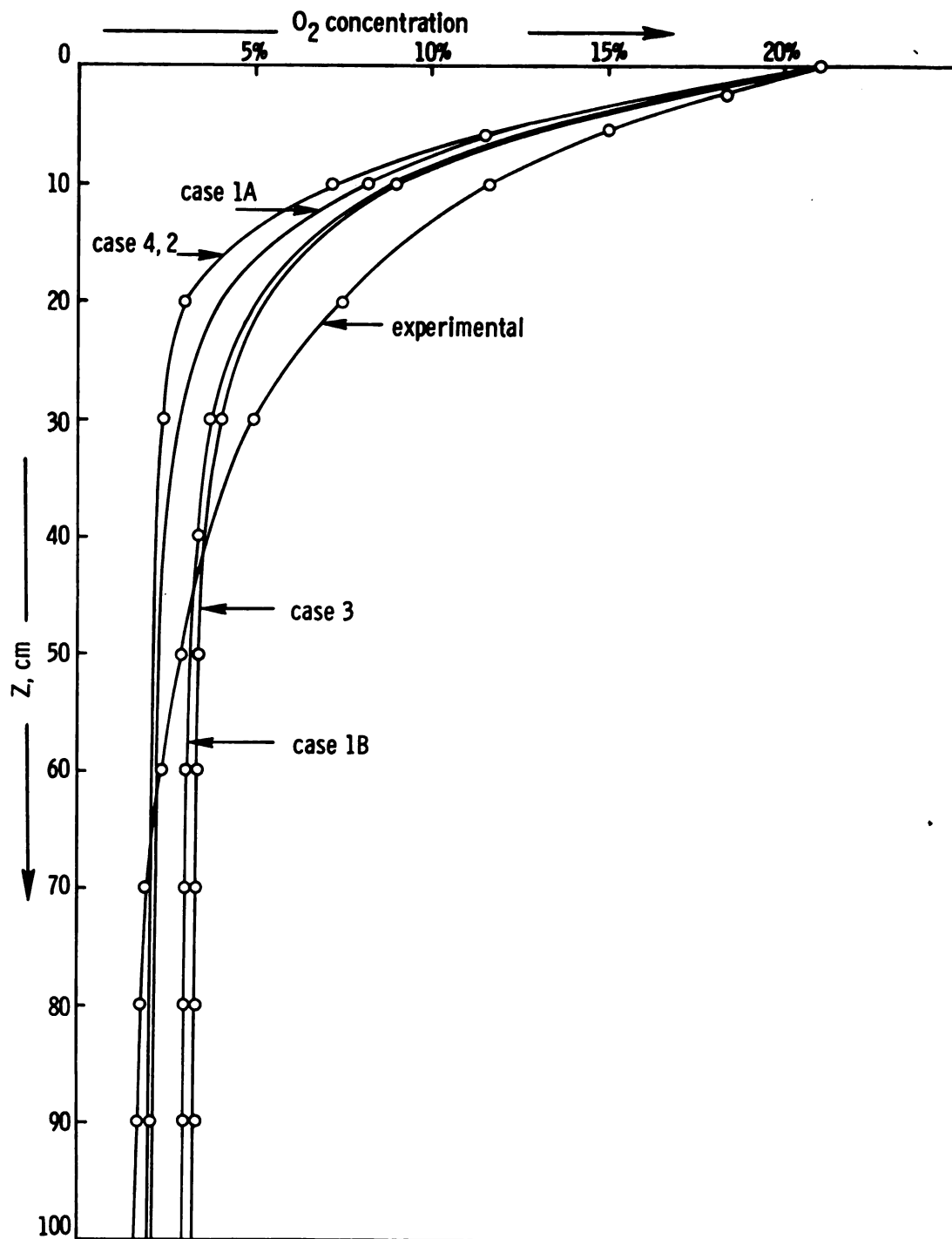


Figure 5.3.--Concentration Profiles of Oxygen in Gas Phase.

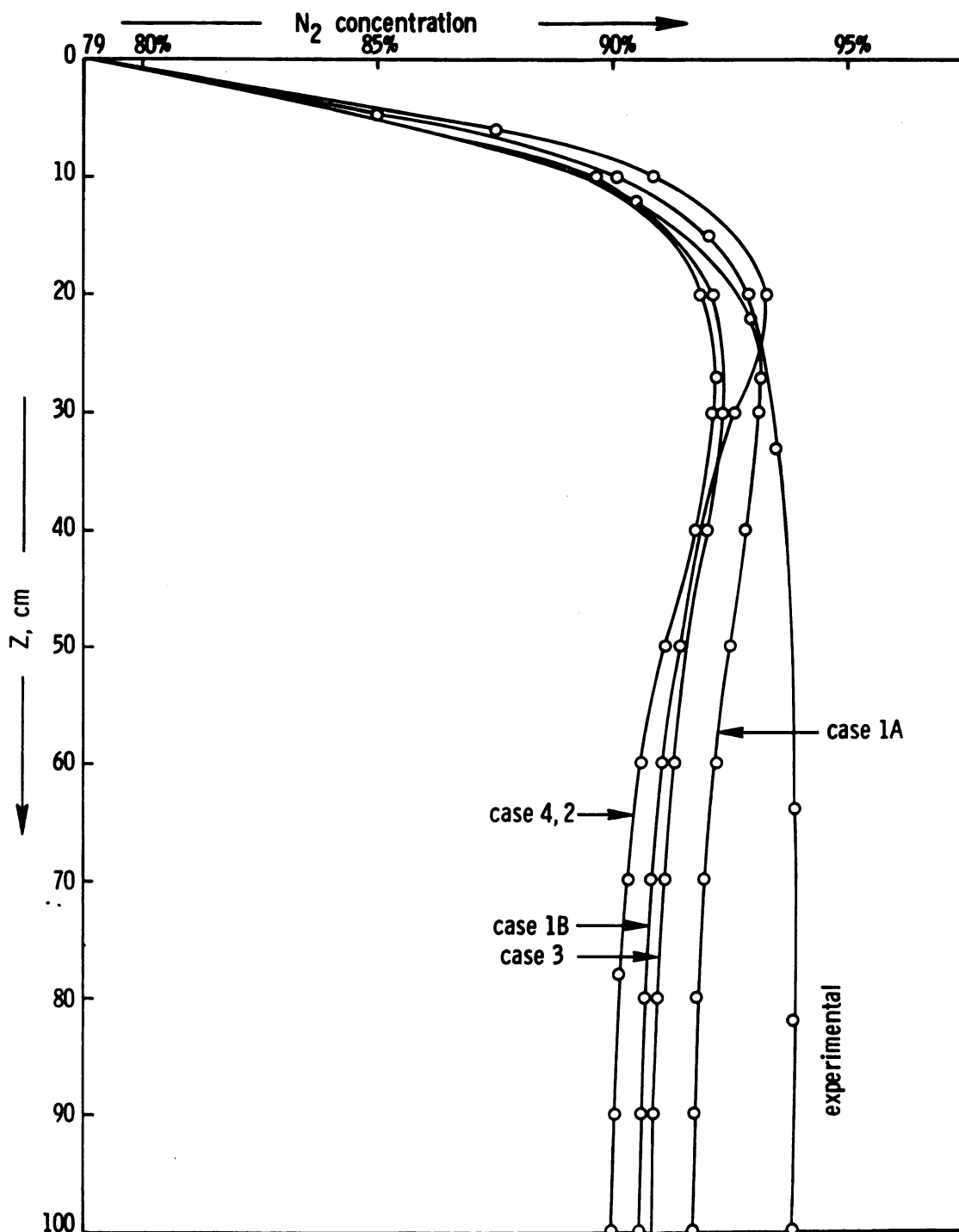


Figure 5.4.--Concentration Profiles of Nitrogen in Gas Phase.

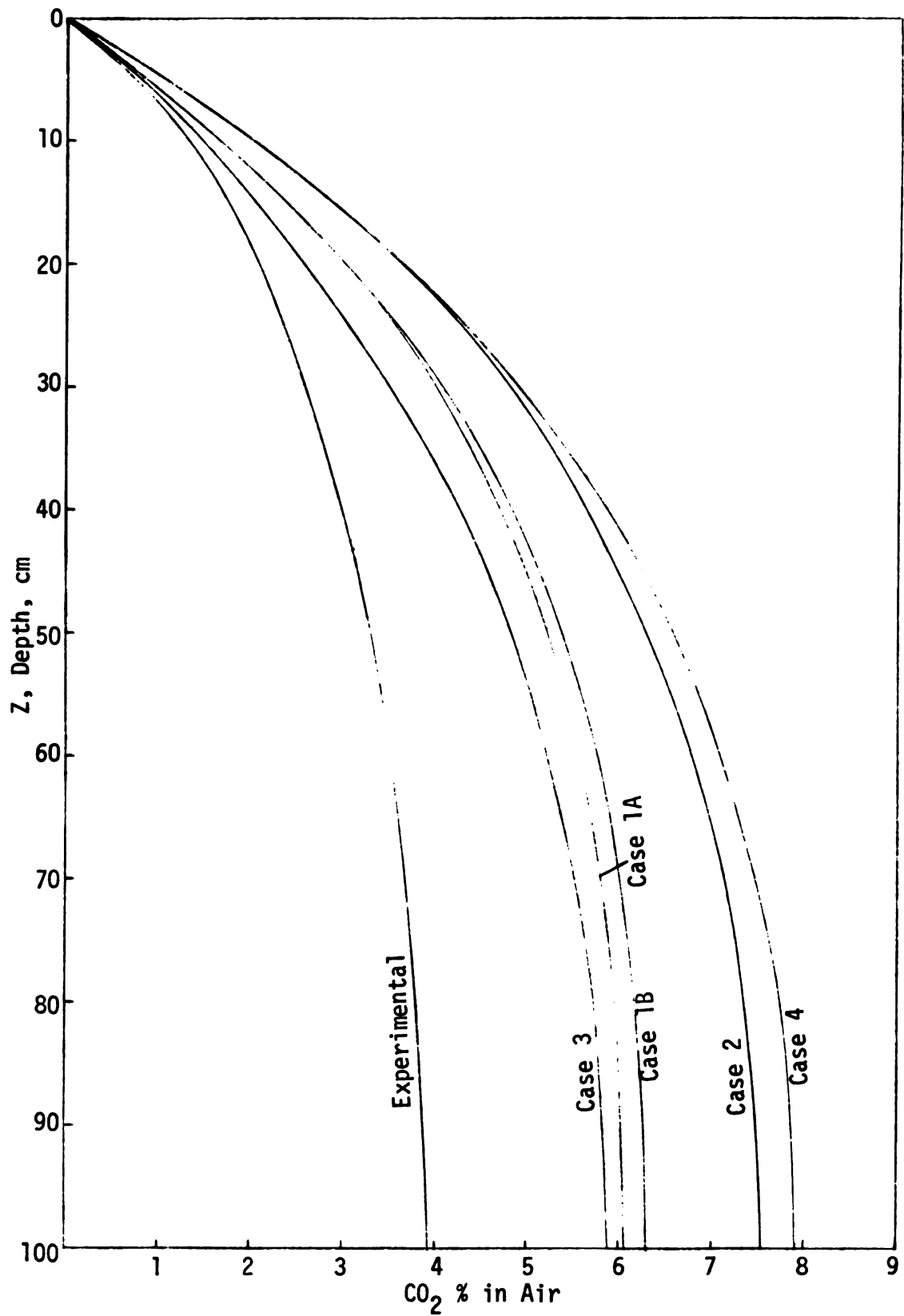


Figure 5.5.--Concentration Profiles of Carbon Dioxide in Gas Phase.

obtained by Starr from the analysis of his liquid phase profiles. Thus, validity of the models can be established only by comparing the gas phase profiles and not by comparing the ammonium and nitrate nitrogen profiles. The liquid phase profiles have also been predicted reasonably well by the other models. The various assumptions made in the different models do not affect the ammonium nitrogen profile and hence there are only two curves for it, i.e., for the first order kinetic model and the Michaelis-Menten model. All the nitrate nitrogen profiles peak at the same point but the maximum value in Case 4 is greater than that for Case 2. This is understandable as Case 4 makes the assumption of no denitrification for soil layers having oxygen concentrations greater than 5 percent.

The gas phase profiles of oxygen, nitrogen and carbon dioxide have been plotted in Figures 5.3, 5.4, and 5.5, respectively. All the models predict a much greater oxygen consumption rate than is shown by the experimental data. This could be remedied by using a double substrate kinetic model containing dissolved oxygen as one of the substrates. The rate of nitrification will then decrease with decreasing oxygen concentration. Such a decrease in the oxygen consumption rate would tend to improve the oxygen profile prediction.

Significant error appears for all the models in reproducing the nitrogen and carbon dioxide experimental results. The carbon dioxide profiles have the same general form and may simply reflect inaccuracies in data. This does not appear to be the case with nitrogen. The experimental data are in the form of a smooth, monotonically increasing function, while each of the models generates

a function which peaks. The peak can be justified since the oxygen profile drops rapidly at the surface whereas the carbon dioxide is not generated until deeper in the soil. Near the surface, nitrogen increases rapidly, whereas in the deeper regions, carbon dioxide increases rapidly. This would make the nitrogen concentration go down a little from the maximum value. It is thus tempting to suggest that better data are needed. However, the quality of the set of data more realistically indicates that we are missing some mechanism. One would hope, however, that a significant lowering of the carbon dioxide concentration profile would essentially eliminate the nitrogen deviation. This is numerically true, and hopefully a basic rationale for it can be found. Changing the N_2/CO_2 ratio predicted by Equation (4.4) from 2/1 to 4/1 improved the response form.

In calculating the profiles, Stefan-Maxwell equations were generally used to calculate the gas phase compositions. This bypassed the necessity of computing the diffusivity of each species at every point in the column. Just for curiosity, the same problem was solved by using Equations (5.3) and (5.8) and diffusivity values were printed for each point in the soil column. The diffusivity values of oxygen and carbon dioxide were consistent but in a small region near the nitrogen peak, a region existed where the nitrogen diffusivity was negative. This implied that nitrogen moved in the opposite direction of the concentration gradient. This is a strange phenomenon and can be explained as follows.

At every point in the system,

$$X_3 + X_4 + X_5 = 1 ,$$

or

$$\frac{dX_3}{dZ} + \frac{dX_4}{dZ} + \frac{dX_5}{dZ} = 0 .$$

From Bird et al. (1960), a similar equation holds for the diffusive fluxes of all components, i.e.,

$$J_3 + J_4 + J_5 = 0 \quad (5.12)$$

where

$$J_i = -D_{im} \frac{dC_i}{dZ} . \quad (5.13)$$

At the point where nitrogen passes through the maximum, the gradient is zero, i.e.,

$$\frac{dX_4}{dZ} = 0 .$$

If by some way, J_4 , calculated from the formula

$$J_4 = N_4 - X_4(N_3 + N_4 + N_5) ,$$

does not become zero at the same point but becomes zero at a different point, then in the region between these two points the signs of J_4 and dX_4/dZ are the same. For this case, Equation (5.13) indicates a negative diffusivity. This is clearly illustrated by Figures 5.6 and 5.7. Such a phenomenon can only occur in a multicomponent counter-current diffusion system.

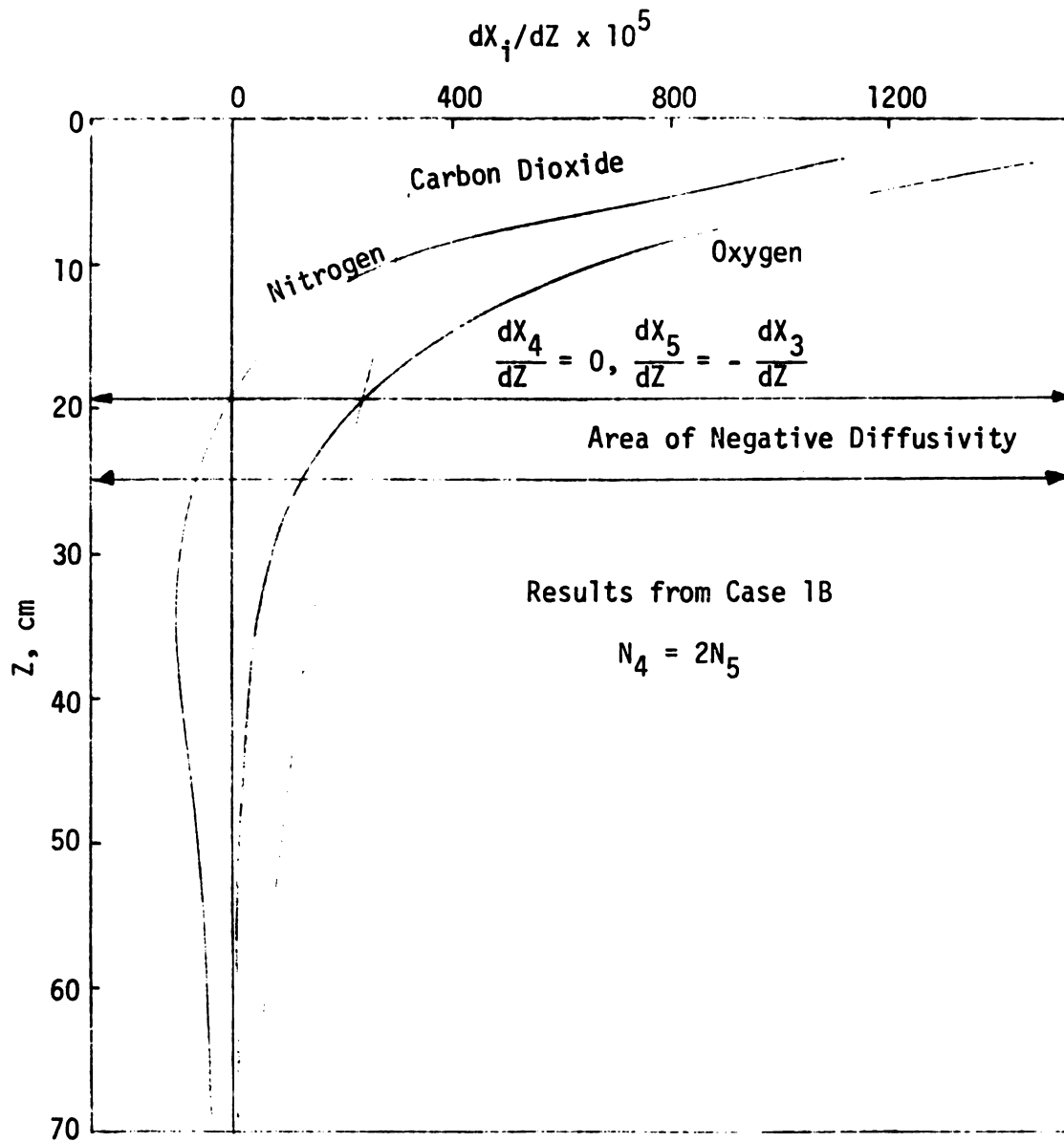


Figure 5.6.--Gradients of Various Components in Gas Phase Against Soil Depth.

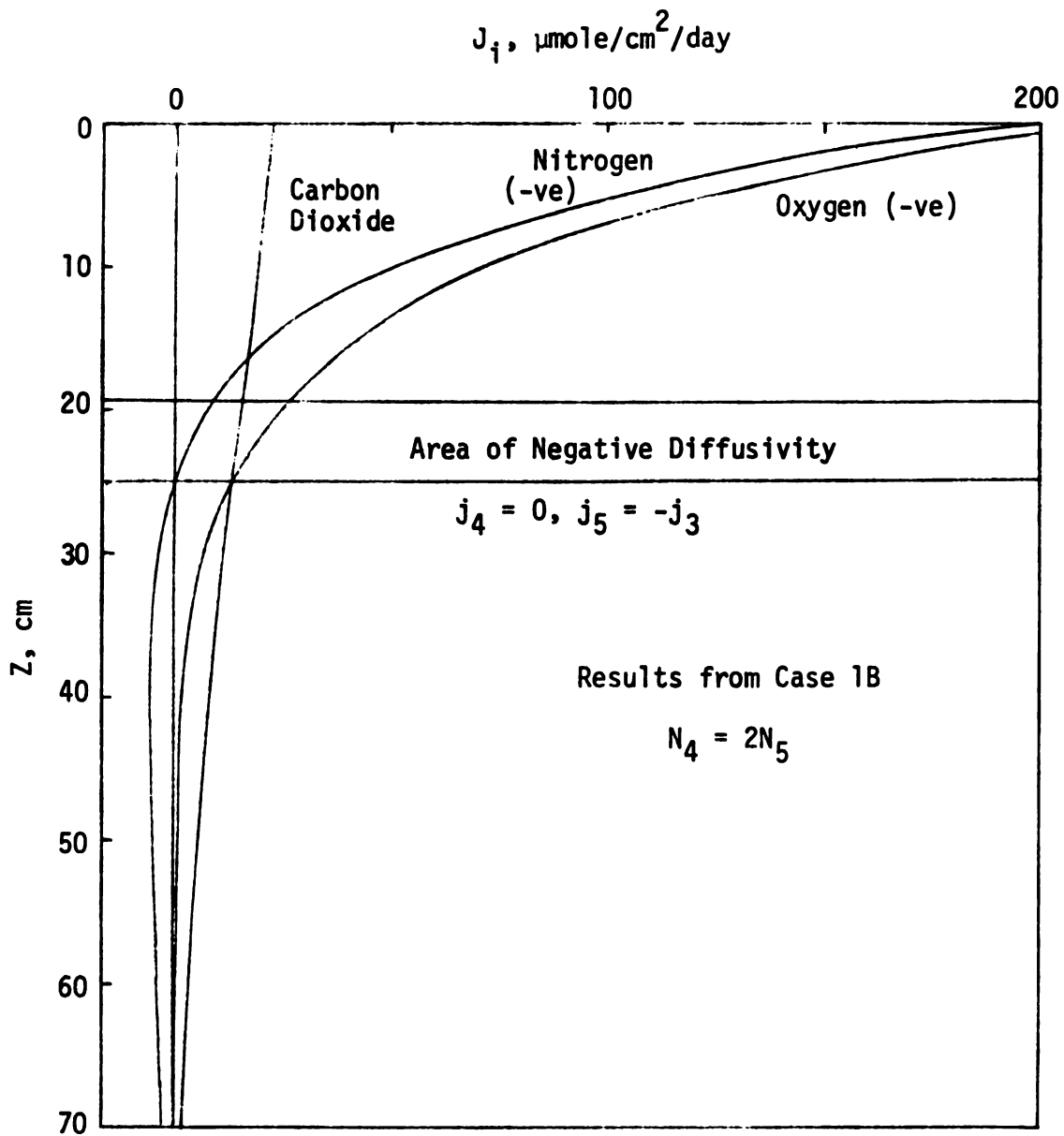


Figure 5.7.--Diffusive Fluxes of Components in Gas Phase Against Depth.

Some of the assumptions made in the development of the above model can also be relaxed quite easily. The above model can be modified to calculate time dependent profiles. The solution of the unsteady state problem is lengthy and would be of only academic interest as there is no way to validate the unsteady state model.

One of the assumptions made was that no loss of ammonium occurs due to adsorption by the soils. This, in fact, is not true and the ammonium differential equation can be modified to account for ammonium adsorption by the soil as follows:

$$\text{NH}_4^+-\text{N} : \frac{\partial C_1}{\partial t} = \frac{D}{1+R} \frac{\partial^2 C_1}{\partial Z^2} - \frac{V}{1+R} \frac{\partial C_1}{\partial Z} - \frac{R_1(C_1, C_3)}{1+R}, \quad (5.14)$$

where R represents the ratio of adsorbed ions to solution ions. In deriving Equation (5.14), equilibrium condition was assumed between the adsorbed ion concentration and the solution concentration. At steady state, $\partial C_1 / \partial t = 0$, i.e.,

$$\frac{D}{1+R} \frac{d^2 C_1}{dZ^2} - \frac{V}{1+R} \frac{dC_1}{dZ} - \frac{R_1}{1+R} = 0$$

or

$$D \frac{d^2 C_1}{dZ^2} - V \frac{dC_1}{dZ} - R_1 = 0.$$

At steady state, thus, the same concentration profile is obtained whether ammonium adsorption is accounted for or not. Physically,

this makes sense because once the capacity of the soil is exhausted, no more adsorption is likely to take place.

It was not the purpose of this work to curve fit the data. The purpose was to see how a simplistic model, developed on a theoretical basis, would do for a very complex system. It has been demonstrated that a very simple model is quite satisfactory for simulation of nitrogen movement in the soil. This does not imply that the simplest model is an accurate reflection of the system. Conditions could conceivably be generated which would be best described by a more complex case. It is, however, a valid tool for the situation studied. Development of a detailed model would generally be expected to be quite helpful in designing a land disposal system. Reliable field data for an operating system are needed to validate such models before they can be properly used. Beek and Frissel (1971) had the same problem. Their detailed model could not be verified because of nonavailability of field data. Such models, though, could point to the directions in which new experiments are to be carried out to increase the knowledge about a given system.

CHAPTER VI

CONCLUSIONS

The primary objective of this work was to study the feasibility of using land as a waste disposal site to remove the nutrients, mainly phosphorus and nitrogen. Phosphorus is removed by adsorption to the soils and nitrogen by the reactions nitrification and denitrification. Rate expressions for these reactions were derived and mathematical models for the movement of phosphorus and nitrogen species into the soil were formulated. On the basis of the above work, the following conclusions may be made.

Phosphorus Removal

With respect to phosphorus removal from the wastewater, the BLWRS system was found to be very efficient. It removed nearly 95-99 percent of the incoming phosphorus. Simulation results obtained by solving the model equations were very good for the BLWRS system and they fell directly on the experimental data points. This proves that a land disposal system can be very efficient in phosphorus removal. The entire system is also amenable to mathematical treatment. But after operating the disposal site for a few months, the soil system has to be regenerated in the same way as a packed adsorption column needs to be regenerated. Otherwise, the phosphorus front keeps moving down and, at some point, the soil will

be completely saturated with phosphorus. The regeneration can be done by operating the land system in cycles of applying wastewater and cropping. The crops can use the adsorbed phosphorus as a nutrient. With the help of proper management practice, it is possible to use a land disposal system for complete phosphorus removal.

Nitrogen Removal

To estimate the removal of nitrogen from the wastewater by the soil system, it is important to determine the rate expressions for the reactions nitrification and denitrification. Double substrate kinetic models were proposed for the nitrification and denitrification reactions and it was shown that such models can describe the microbial reactions at conditions when two substrates simultaneously affect the growth of microorganisms. The kinetic and stoichiometric parameters involved in such a model were estimated from experimental works of past and present.

Nitrifiers were found to be slower growing than the activated sludge bacteria. This would require a separate nitrification stage, if the traditional activated sludge plants were to be modified for a greater nitrogen removal. From the values of the parameters for the denitrification reaction, it can be concluded that in the range of the nitrate nitrogen concentrations encountered in wastewater (20-30 ppm), the reaction is a first order reaction. For complete nitrogen removal, nearly three times as much organic carbon has to be provided. These double substrate

kinetic expressions would be very useful in designing the modified activated sludge plants to accomplish the nitrogen removal as well as the biological oxygen demand removal.

Solving the equations formulated to describe the movement of nitrogen species shows that even at the very low application rate of 2 cm/day, the exit nitrate nitrogen concentration is 11 ppm. This shows that the land disposal system may not be able to accomplish complete nitrogen removal. The success of the entire method will depend upon the development of good nitrifying and denitrifying populations. If enough denitrifiers are not available, most of the nitrate nitrogen will leak through the system unaffected and whatever removal of nitrogen occurs would be due to the physical adsorption of ammonium nitrogen by the soil. When the land disposal system is started, considerable leakage of nitrogen can be expected initially because of the absence of adequate numbers of microbes. Once the populations are established, nitrogen leakage will decrease. The nitrogen removal ability of the soil is thus more important in designing a land disposal system than its phosphorus adsorption capacity.

It is important to remember that different soils exhibit different properties and thus different reaction rates for phosphorus adsorption, nitrification and denitrification. Before any land disposal system can be designed, some preliminary experiments in the laboratory need to be carried out to determine the appropriate rate constants. A preliminary estimate of the performance

of a land disposal system can be obtained by using the FORTRAN programs PMODEL and GASTRAN. It is hoped that this work may represent a step forward in understanding the nitrification and denitrification reactions and, thus, help enable one to design a land disposal site for phosphorus and nitrogen removal with a good deal of theoretical basis.

NOMENCLATURE

Sometimes the same symbol is used to represent more than one quantity to maintain the established nomenclature in the literature.

a	Solid-liquid interfacial area, cm^2/cm^3
A	Cross-sectional area, cm^2
a, b	Langmuir adsorption isotherm constants
b	Maximum concentration of phosphorus that soil can attain, ppm
C	Concentration, mg/l in liquid phase, $\mu\text{moles}/\text{cm}^3$ in gas phase
D	Axial dispersion coefficient in phosphorus work, cm^2/day
D	Dilution rate in Chapter IV, day^{-1}
D	Diffusivity of various species in gas phase, cm^2/day
F	Feed rate in the reactor, l/day
J	Diffusive flux of a component in a gas phase, $\mu\text{mole}/\text{cm}^2/\text{day}$
K	Hydraulic conductivity of the soil, cm/day
K	Constant in Equation (2.7), ratio of rate constants of adsorption and desorption
K_o	Overall volumetric mass transfer coefficient, cm/day
K_{Kin}	Rate of forward reaction (2.8)
K_{-1}	Rate of backward reaction (2.8)
K^{ad}	Equilibrium rate constant for reaction (2.8)

K_m	Substrate concentration at which rate of reaction is half the maximum, mg/l
K_{S_1}, K_{S_2}	Saturation constants, substrate concentrations at which growth rate of microbes is half the maximum, mg/l
L	Length of soil column, cm
n	Constant in nonlinear adsorption isotherm
N	Flux of a component in gas phase, $\mu\text{moles}/\text{cm}^2/\text{day}$
p_A	Negative of the logarithm of concentration of species A
p_K	Negative of the logarithm of the dissociation constant
P_T	Total phosphorus concentration in liquid, mg/l
Q	Ultimate concentration of phosphorus that is reached in soil, mg/kg
r	Rate of reaction, mg/l/day
R	Rate of mass transfer, mg/l/day
R	Ratio of adsorbed ions to ions in solution
R_1, R_2	Rate expression for nitrification or denitrification
S	Saturation, fraction of pore space occupied by water
S_1, S_2	Substrate concentration, mg/l
t	Time, day
v	Rate of product formation in Appendix C
V	Pore velocity, cm/day
V	Reactor volume, l
W_S	Weight of soil, gm
X	Concentration of phosphorus on soil, mg/kg or ppm
X	Concentration of suspended solids, mg/l or ppm
X	Mole fraction of a component in gas phase

Y	Phosphorus concentration in liquid, mg/l or ppm
Y^*	Equilibrium concentration, mg/l or ppm
Y_1, Y_2	Yield coefficients with respect to substrates S_1 and S_2
Z	Soil depth, cm

Greek Symbols

α	Constant, or stoichiometric coefficient
β	Constant
γ	Constant
γ	Activity coefficient
δ	Constant
μ	Specific growth rate of microbes, day^{-1}
ρ	Density, gm/cm^3
ψ	Capillary potential, cm
ϕ	Total potential, cm
ϵ	Porosity of soil, cm^3/cm^3

Subscripts

1	Ammonium nitrogen, liquid phase
2	Nitrate nitrogen, liquid phase
3	Oxygen, gas phase
4	Nitrogen, gas phase
5	Carbon dioxide, gas phase
b	Bulk
i	Denotes position along distance axis
i	Input condition
i	Any one of above components

j	Denotes position along time axis
m	Maximum
0	Initial condition or a boundary condition
ij	Binary property, e.g., diffusivity
im	Property involving mixture, e.g., diffusivity of i into a mixture

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APPENDICES

APPENDIX A

DETERMINATION OF MASS TRANSFER COEFFICIENT

FOR PHOSPHORUS ADSORPTION FROM

BATCH EXPERIMENTS

APPENDIX A

DETERMINATION OF MASS TRANSFER COEFFICIENT FOR PHOSPHORUS ADSORPTION FROM BATCH EXPERIMENTS

Experiments were carried out batchwise to calculate the mass transfer coefficient and the Langmuir isotherm constants. Five grams of BLWRS soil was contacted with 40 ml of liquid solution containing a known concentration of phosphorus. The concentration of phosphorus in solution was determined at regular time intervals. The equilibrium was assumed to have been reached at 8 hours. This experiment was carried out for 5 different initial phosphorus concentrations in solution. The experimental data are summarized in Table 3.2.

For a batch system, one can write,

$$- \frac{dY}{dt} = K_o a (Y - Y^*) . \quad (A.1)$$

The various terms have been defined previously in Chapter III. The above equation is true because the rate at which the liquid phase loses phosphorus is the same as the rate of phosphorus transfer to the solid phase. Y^* is related to X by the Langmuir adsorption isotherm, i.e.,

$$Y^* = \frac{aX}{1 + bX} . \quad (A.2)$$

The constants a and b were determined as described in Chapter III.

Substituting (A.2) in (A.1) gives

$$- \frac{dY}{dt} = K_o a \left(Y - \frac{aX}{1 - bX} \right),$$

or

$$- \frac{dY}{dt} = K_o a \left(\frac{Y - bXY - aX}{1 - bX} \right). \quad (A.3)$$

To replace X in terms of Y , a simple mass balance equation is written based on the fact that phosphorus lost by the liquid phase goes on to the solid phase,

$$X = X_o + \frac{V_L}{W_S} (Y_o - Y) \quad (A.4)$$

where X_o and Y_o are the initial concentrations of phosphorus in the solid and liquid phases, respectively, and V_L and W_S are the volume of solution and the weight of soil, respectively. Substituting (A.4) in (A.3) and simplifying gives

$$- \frac{dY}{dt} = K_o a \left(\frac{8bY^2 + \beta Y - \gamma}{8bY + \alpha} \right) \quad (A.5)$$

where

$$\alpha = 1 - 3b - 8bY_o,$$

$$\beta = 1 - 3b - 8bY_o + 8a = \alpha + 8a, \text{ and}$$

$$\gamma = 3a + 8aY_o.$$

Separating the variables, Equation (A.5) gives

$$\int_0^Y \frac{(8bY + \alpha) dY}{(8bY^2 + \beta Y + \gamma)} = -K_0 a \int_0^t dt .$$

The integral can be evaluated quite easily and the final form is given by

$$\begin{aligned} \frac{1}{2} \ln \left(\frac{8bY^2 + \beta Y - \gamma}{8bY_0^2 + \beta Y_0 - \gamma} \right) + \frac{\alpha - \beta/2}{16b\delta} \ln \left(\left[\frac{Y + \beta/16b - \delta}{Y + \beta/16b + \delta} \right] \left[\frac{Y_0 + \beta/16b + \delta}{Y_0 + \beta/16b - \delta} \right] \right) \\ = -K_0 a t , \end{aligned}$$

where

$$\delta = (\beta^2/256b^2 + \gamma/8b)^{1/2} .$$

A plot of the left hand side against time should result in a straight line with slope equal to $K_0 a$. A small computer program was written to accomplish this and the results are shown in Figure A.1. The points do lie on a straight line but the lines do not pass through the origin as Equation (A.6) indicates. This probably could be due to some inaccuracies in data or due to the variability of the mass transfer coefficient with the change in concentration in the liquid phase. All four lines for the four different experimental runs are parallel and the average slope is 3.0. The value of the mass transfer coefficient used in simulation was 2.0 day^{-1} .

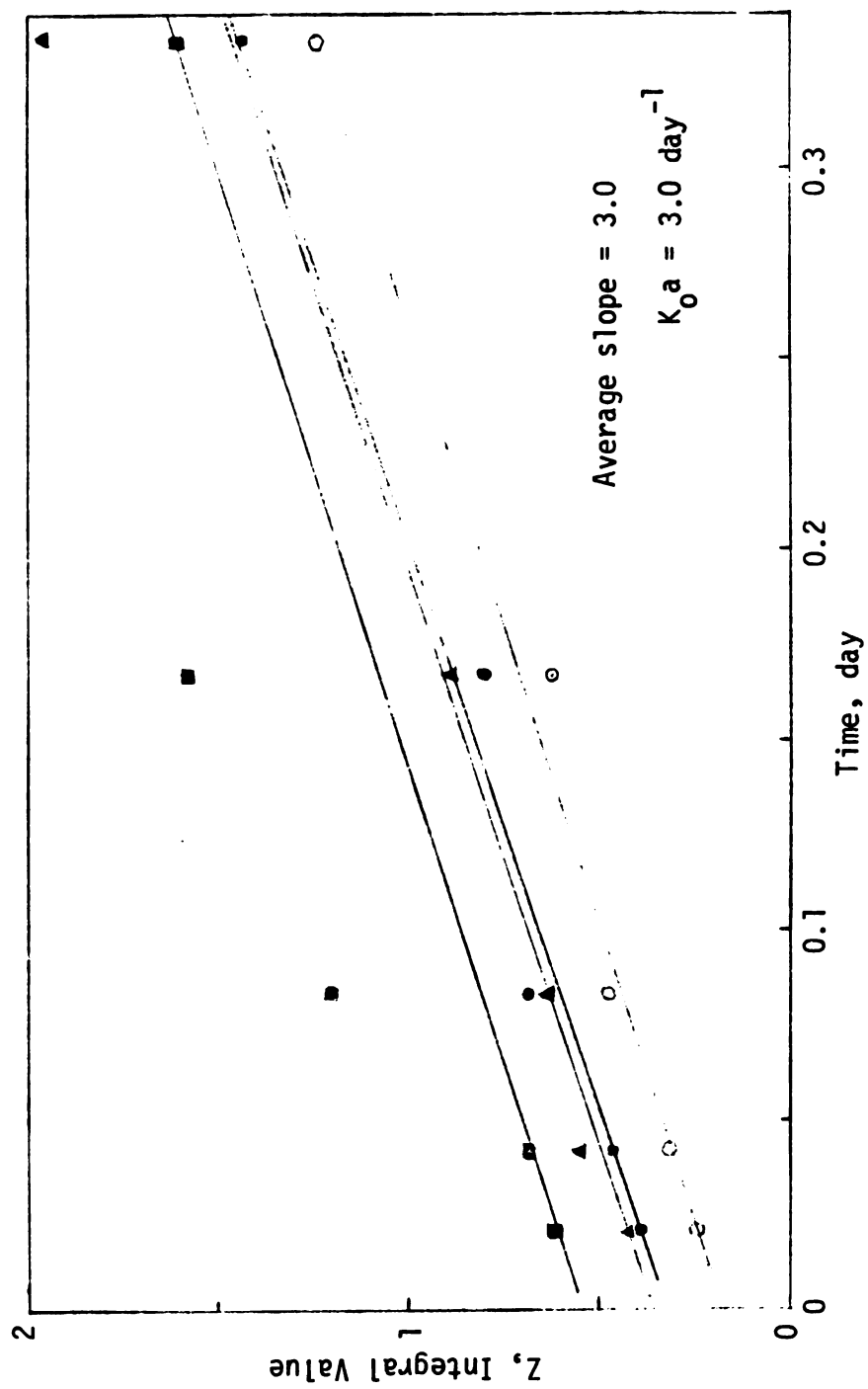


Figure A.1.--Determination of Mass Transfer Coefficient for Phosphorus Adsorption.

APPENDIX B

NUMERICAL METHOD AND FORTRAN PROGRAM
USED FOR SIMULATING PHOSPHORUS
MOVEMENT IN SOIL

APPENDIX B

NUMERICAL METHOD AND FORTRAN PROGRAM USED FOR SIMULATING PHOSPHORUS MOVEMENT IN SOIL

As established in Chapter III, the following equations define the phosphorus movement in soil.

1. The Continuity Equation for Water:

$$\frac{\partial(\epsilon S)}{\partial t} = - \frac{\partial}{\partial Z} (V\epsilon S)$$

where

$$V\epsilon S = -K \left(\frac{\partial \psi}{\partial S} \frac{\partial S}{\partial Z} - 1 \right) .$$

The boundary conditions to be used are

$$S = 0.53 \text{ at } Z = 0, \text{ and } \partial S / \partial Z = 0 \text{ at } Z = L.$$

When Darcy's equation is substituted in the continuity equation, the following equation results,

$$\frac{\partial(\epsilon S)}{\partial t} = KA \frac{\partial^2 S}{\partial Z^2} + K \frac{\partial S}{\partial Z} \frac{\partial A}{\partial Z} + (A \frac{\partial S}{\partial Z} - 1) \frac{\partial K}{\partial Z} \quad (B.1)$$

where

$$A = \partial \psi / \partial S.$$

2. The Continuity Equation for Phosphorus in the Liquid

Phase:

$$D_e \frac{\partial}{\partial Z} S \frac{\partial Y}{\partial Z} - \frac{\partial}{\partial Z} (V_e S Y) - K_0 a (Y - Y^*) = \frac{\partial \epsilon S Y}{\partial Z},$$

with the boundary conditions

$$Y = 10 \text{ ppm at } Z = 0, \text{ and}$$

$$\partial Y / \partial Z = 0 \text{ at } Z = L.$$

The above equation, on simplification, gives

$$\begin{aligned} \frac{\partial Y \epsilon S}{\partial t} = & D_e S \frac{\partial^2 Y}{\partial Z^2} + \left[D_e \frac{\partial S}{\partial Z} + K \left(A \frac{\partial S}{\partial Z} - 1 \right) \right] \frac{\partial Y}{\partial Z} \\ & + Y \left[K A \frac{\partial^2 S}{\partial Z^2} + K \frac{\partial S}{\partial Z} \frac{\partial A}{\partial Z} + \left(A \frac{\partial S}{\partial Z} - 1 \right) \frac{\partial K}{\partial Z} \right] \\ & - K_0 a (Y - Y^*). \end{aligned} \quad (B.2)$$

The soil length of 20 cm or 40 cm was divided into $N = 40$ intervals of 0.5 cm or 1 cm. The finite difference equations for the first order and second order partials used are given below:

$$\left. \begin{aligned} \frac{\partial f}{\partial Z} \Big|_{i,j+1} &= \frac{f_{i+1,j+1} - f_{i-1,j+1}}{2\Delta Z}, \\ \frac{\partial^2 f}{\partial Z^2} \Big|_{i,j+1} &= \frac{f_{i+1,j+1} - 2f_{i,j+1} + f_{i-1,j+1}}{\Delta Z^2}, \\ \text{and} \\ \frac{\partial f}{\partial t} \Big|_{i,j+1} &= \frac{f_{i,j+1} - f_{i,j}}{\Delta t}. \end{aligned} \right\} \quad (B.3)$$

Here, the subscript i refers to the location of a point in the Z direction and j refers to a particular time interval. Equations (B.1) and (B.2) were solved in an implicit way, hence the expansions of the derivatives were written at a future time increment. Equations (B.1) and (B.2) were approximated with the help of the finite difference approximations (B.3) at each grid point in the system, resulting in a simultaneous set of equations.

Due to the nonlinear nature of the partial differential equations, the values of S and X had to be estimated at the next time increment. This was accomplished with the help of Taylor's series,

$$S_{j+1} = S_j + \left. \frac{\partial S}{\partial t} \right|_j \Delta t, \text{ and}$$

$$X_{j+1} = X_j + \left. \frac{\partial X}{\partial t} \right|_j \Delta t.$$

Here, the time derivative of the function was approximated as

$$\left. \frac{\partial f}{\partial t} \right|_j = (\frac{1}{3} f_{j+1} + \frac{1}{2} f_j - f_{j-1} + \frac{1}{6} f_{j-2}) / \Delta t.$$

Substituting the above equations in the Taylor's series gives the expressions for the estimation of S_{j+1} and X_{j+1} ,

$$S_{j+1} = 2.25 S_j + 1.5 S_{j-1} + 0.25 S_{j-2}, \text{ and}$$

$$X_{j+1} = 2.25 X_j + 1.5 X_{j-1} + 0.25 X_{j-2}.$$

With these estimates, the set of simultaneous nonlinear equations can be turned into a set of simultaneous linear equations. These equations were solved using the scientific subroutine ONEDIAG to obtain S and X at $j+1$ time interval. Iterations were continued until the estimates matched with the computed values. The saturation value at which the hydraulic conductivity equals the application rate was found by using the subroutine CONVERG.

To obtain the phosphorus profile as a function of depth and time, a FORTRAN program PMODEL was written and executed on Control Data Corporation 6500. Table B.1 contains the list of the subroutines used in PMODEL and their functions. The main program was mainly used to command the subroutines. The computing options and the data required for using the program are listed in Table B.2. A sample output and a complete listing of the program are included in the following pages.

TABLE B.1.--Structure of PMODEL Program.

Program	Functions
PMODEL	To read in data, establish initial conditions, and command other subroutines in a way so as to achieve desired results.
SATURN	To calculate saturation profile at the next time interval.
HYCON	To calculate hydraulic conductivity if saturation profile is given.
DCAPP	To calculate derivative of capillary potential at a given saturation.
EQUIL	To calculate Y^* given the X-profile using an equilibrium relationship.
PCONCN	To evaluate phosphorus concentration profile in liquid as well as in solid phase.
OUTPUT	To output the complete information at a particular time interval.
ONEDIAG [†]	To solve the set of simultaneous linear equations.
CONVERG [†]	To find the root of a given equation (two initial estimates on either side of zero are needed).

[†]S. R. Auvil, "A General Analysis of Gas Centrifugation with Emphasis on the Countercurrent Production Centrifuge," Ph.D. dissertation, Michigan State University, 1974.

TABLE B.2.--Data Required by the FORTRAN Program PMODEL.

Parameter	Description	Units
YIN	Input phosphorus concentration in liquid phase	ppm
VS	Surface application rate	cm/day
XI	Initial phosphorus concentration on soil	ppm
SI	Initial saturation in soil	--
EPS	Porosity of soil	--
BD	Bulk density of soil	gm/cm ³
TC	Mass transfer coefficient	day ⁻¹
ACC	Required limit on convergence	--
This completes the first data card. Format 8F10.0.		
D	Dispersion coefficient of phosphorus in solution	cm ² /day
AC, BC	Langmuir adsorption isotherm constants	--
DZ	Depth increment used in numerical evaluation	cm
DT	Time increment used in numerical solution	day
N	Number of depth increments	--
ITOTAL	Total simulation time intervals	--
IFREQ	Output to be printed every so many time intervals	--
IOPT	Option parameter = 1; both P and S profiles are computed, = 0; assumes constant saturation and only phosphorus profile is computed	--
MAX	Maximum number of iterations allowed	

This completes the second data card. Format 5F10.0, 5I5.

```

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3  PMODEL
4  PMODEL
5  PMODEL
6  PMODEL
7  PMODEL
8  PMODEL
9  PMODEL
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35 PMODEL
36 PMODEL

PROGRAM PMODEL( INPUT, OUTPUT )
COMMON YIN, VS, XI, YI, SI, EPS, BD, TC, O, AC, BC, DZ, DT, NP1,
1 ITOTAL, IFREQ, FAC, S1, S3, S4, S5, S6, S7, S8, ICHECK, ICOUNT
COMMON YSTAR(201), Y(4,201), A(201), S(4,201), K(201), X(4,201)
COMMON ACC, SFINALS, MAX, C4, XMAX, S9
REAL K

C----- TO READ IN INPUT -----
C
C
      READ 5, YIN, VS, XI, ST, EPS, BD, TC, ACC
      READ 10, O, AC, BC, DZ, DT, N, ITOTAL, IFREQ, IOPT, MAX
      5 FORMAT( 8F10.0 )
      10 FORMAT( 5F10.0, 5I5 )
      INUMBER = ITOTAL / IFREQ $ NP1 = N + 1
      YI = AC * XI / ( 1.0 - BC * XI ) $ ICHECK = 0
      XMAX = YIN / ( AC + BC * YIN ) $ FAC = 1.0
      S1 = 0.25 / EPS / DZ / D7 $ S4 = 1.0 / EPS / DZ / CZ
      S5 = 0.5 / DZ $ S3 = 0.5 / EPS / DZ
      C4 = 1.0 - EPS $ S9 = S4 * EPS

C----- TO PRINT OUT THE HEADING -----
C
      CALL OUTPUT( 0 )
C
C----- TO ESTABLISH INITIAL CONDITIONS IN THE SOIL -----
C
      DO 15 I = 1, NP1
        X(1,I) = X(2,I) = X(3,I) = X(4,I) = XI
        S(1,I) = S(2,I) = S(3,I) = S(4,I) = SI
        YSTAR(I) = Y(1,I) = Y(2,I) = Y(3,I) = Y(4,I) = YI
      15 CONTINUE
C
C----- TO ESTABLISH BOUNDARY CONDITIONS AT THE SURFACE -----
C
      Y(1,1) = Y(2,1) = Y(3,1) = Y(4,1) = YIN

```

```

C----- X(1,1) = X(2,1) = X(3,1) = X(4,1) = XMAX PMODEL 37
C----- TO ESTABLISH SATURATION AT THE SURFACE AFTER LONG TIMES ----- PMODEL 38
C----- PMODEL 39
C----- PMODEL 40
C----- PMODEL 41
C----- PMODEL 42
C----- PMODEL 43
C----- PMODEL 44
C----- PMODEL 45
C----- PMODEL 46
C----- PMODEL 47
C----- PMODEL 48
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C----- PMODEL 54
C----- PMODEL 55
C----- PMODEL 56
C----- PMODEL 57
C----- PMODEL 58
C----- PMODEL 59
C----- PMODEL 60
C----- PMODEL 61
C----- PMODEL 62

      S(4,1) = 0.05 $ S2 = 0.95 $ IND = 1
23 CALL HYCON(1)
      ZERO = VS - K(1) $ XG = S(4,1)
      CALL CONVERG( XG, ZERO, S2, IND, 0 ) $ S(4,1) = XG
      IF ( IND ) 21, 22, 23
21 STOP1
22 IF ( IOPT .NE. J ) GO TO 24
DO 16 I = 2, NP1
      S(1,I) = S(2,I) = S(3,I) = S(4,I) = S(4,1)
16 CONTINUE
24 SFINALS = S(4,1)
      S(1,1) = S(2,1) = S(3,1) = S(4,1)
      S7 = EPS * SFINALS / DT
      S6 = 0 * EPS * SFINALS / DT / DZ $ S8 = VS / 2.0 / DZ
      ICOUNT = 0 $ CALL OUTPUT( 1 )

C----- TO START COMPUTING .....
C-----
C----- DO 35 I = 1, INUMBER
C----- DO 40 J = 1, IFREQ
C----- ICOUNT = ICOUNT + 1
C----- IF ( ICOUNT .GT. 7 ) IOPT = 0
C----- TO CALCULATE SATURATION PROFILE -----
C-----
C----- CALL SATURN( IOPT )
C-----
C----- TO CALCULATE PHOSPHORUS CONCENTRATIONS IN LIQUID AND SOLID
C----- PHASES -----
C-----

```

C	CALL PCONCN(IOPT)	PMODEL	63
	40 CONTINUE	PMODEL	64
C	----- TO OUTPUT THE RESULTS AFTER IFREQ TIME INTERVALS -----	PMODEL	65
C	CALL OUTPUT(1)	PMODEL	66
	35 CONTINUE	PMODEL	67
C	----- TO INTEGRATE THE AREA UNDER THE CURVES OF Y AND X AND PRINT	PMODEL	68
C	THE RESULTS OUT -----	PMODEL	69
C	CALL OUTPUT(2)	PMODEL	70
C	END	PMODEL	71
		PMODEL	72
		PMODEL	73
		PMODEL	74

2	SUBROUTINE EQUIL	EQUIL
3	COMMON YIN, VS, XI, VI, SI, EPS, BD, IC, D, AC, BC, DZ, OT, NP1,	EQUIL
4	1 ITOTAL, IFREQ, FAC, S1, S3, S4, S5, S6, S7, S8, ICHECK, ICOUNT	EQUIL
5	COMMON YSTAR(201), Y(4,201), A(201), S(4,201), K(201), X(4,201)	EQUIL
6	COMMON ACC, SFINALS, MAX, C4, XMAX, S9	EQUIL
7	REAL K	EQUIL
8		EQUIL
9	C----- TO CALCULATE YSTAR FROM X FROM LANGMUIR ADSORPTION ISOTHERM	EQUIL
10	C	EQUIL
11	DO 10 I = 1, NP1	EQUIL
12	10 YSTAR(I) = AC * X(4,I) / (1.0 - BC * X(4,I))	EQUIL
13	RETURN	EQUIL
14	END	EQUIL

```

SUBROUTINE OUTPUT( NPRINT )
COMMON YIN, VS, XI, YI, SI, EPS, BD, TC, D, AC, BC, DZ, DT, NP1,
1 ITOTAL, IFREQ, FAC, S1, S3, S4, S5, S6, S7, S8, ICHECK, ICOUNT
COMMON YSTAR(201), Y(4,201), A(201), S(4,201), K(201), X(4,201)
COMMON ACC, SFINALS, MAX, C4, XMAX, S9
REAL K
IF ( NPRINT .GT. 0 ) GO TO 5
C----- TO OUTPUT THE HEADING -----
C
PRINT 10
10 FORMAT( *1*, //, 43X, *SIMULATION OF PHOSPHORUS MOVEMENT IN A SOIL
1 COLUMN*, //, 43X, *-----* )
2----*, /// )
PRINT 15
15 FORMAT( //, 56X, *DATA INPUT TO THE SYSTEM*, /, 56X, *-----*
1-----* )
PRINT 20, YIN, VS, YI, XI, SI
20 FORMAT( ///, 20X, *A. OPERATING CHARACTERISTICS OF THE SYSTEM*,
1//, 25X, *1. INPUT CONCENTRATION OF PHOSPHORUS IN LIQUID PHASE =
2 *, F7.3, 5X, *PPM*, //, 25X, *2. RATE OF PRECIPITATION AT THE SUR
3FACE = *, F7.3, 5X, *CM / DAY*, //, 25X, *3. INITIAL PHOSPHORUS
4CONCENTRATION IN LIQUID PHASE = *, E14.7, 5X, *PPM*, //, 25X, *4
5. INITIAL PHOSPHORUS CONCENTRATION IN SOIL = *, E14.7, 5X, *PPM*
6, //, 25X, *5. INITIAL MOISTURE CONTENT OF THE SOIL = *, E14.7,
75X, *CC WATER / CC VOIDS* )
PRINT 25, EPS, BD, TC, D
25 FORMAT( ///, 20X, *B. PHYSICAL CHARACTERISTICS OF THE SOIL SYSTEM
1*, //, 25X, *1. POROSITY OF THE SOIL = *, F7.3, 5X, *CC VOIDS /
2CC SOIL*, //, 25X, *2. BULK DENSITY OF THE SOIL = *, F7.3, 5X,
3*GM / CM3*, //, 25X, *3. MASS TRANSFER COEFFICIENT FOR THE SOIL SY
4STEM = *, F7.3, 5X, * / DAY*, //, 25X, *4. DISPERSION COEFFICIENT
5 FOR PHOSPHORUS = *, F7.3, 5X, *CM2 / DAY * )
XMAX1 = 1.0 / BC $ PRINT 30, AC, BC, XMAX1, XMAX

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67      YD = Y(4,I) / YIN      $      YSTARD = YSTAR(I) / VIN      OUTPUT
68      55 PRINT 60, I, DEPTH, X(4,I), XD, Y(4,I), YD, YSTAR(I), YSTARD, S(4,  OUTPUT
69      1I)  OUTPUT
70      60 FORMAT( 3X, I2, 2X, *,*, 1X, F5.2, 7( 4X, E13.6 ) )  OUTPUT
71      PRINT 65, ICHECK  OUTPUT
72      65 FORMAT( //, 30X, *SATURATION FRONT HAS MOVED*, I5, 5X, *SPACE INC  OUTPUT
73      1REMENTS* )  OUTPUT
74      PRINT 70  OUTPUT
75      70 FORMAT( /, *-----  OUTPUT
76      1-----* )  OUTPUT
77      2-----* )  OUTPUT
78      RETURN  OUTPUT
79      75 T = FLOAT( ICOUNT ) * JT  OUTPUT
80      C----- TO OUTPUT THE MATERIAL BALANCE .....  COREC8
81      C  TIN = VS * T * VIN      $      DTP = 0.0  COREC8
82      TP = FLOAT( ICHECK ) * DZ * C4 * 80 * ( XMAX - XI )  COREC8
83      PRINT 95  OUTPUT
84      95 FORMAT( *1* )  OUTPUT
85      DO 80 I = 1, N  OUTPUT
86      80 DTP = DTP + ( X(4,I) + X(4,I+1) ) / 2.0 - XI  OUTPUT
87      DTP = DTP * ( 1.0 - EPS ) * 80 * DZ  OUTPUT
88      TP = TP + DTP  OUTPUT
89      TLP = FLOAT( ICHECK ) * DZ * EPS * SFINALS * ( YIN - YI )  OUTPUT
90      DTLP = 0.0  OUTPUT
91      DO 85 I = 1, N  OUTPUT
92      85 DTLP = DTLP + ( Y(4,I) + Y(4,I+1) - 2.0 * YI ) / 2.0  OUTPUT
93      TLP = TLP + DTLP * SFINALS * EPS * DZ  OUTPUT
94      TAC = TP + TLP  OUTPUT
95      PRINT 90, TIN, TP, TLP, TAC  OUTPUT
96      90 FORMAT( //, 30X, *TOTAL PHOSPHORUS DUMPEC OVER 1 CM2 AREA = *,  OUTPUT
97      1 E20.10, /, 30X, *TOTAL PHOSPHORUS ADSORBED BY THE SOIL = *, E2  OUTPUT
98      20.10, /, 30X, *TOTAL PHOSPHORUS IN LIQUID PHASE = *, E20.10, /,  OUTPUT

```

330X, *TOTAL PHOSPHORUS ACCOUNTED FOR = *, E20.10)
RETURN
END

OUTPUT 98
OUTPUT 99
OUTPUT 100

```

SUBROUTINE SATURN( IOPT )
COMMON YIN, VS, XI, YI, SI, EPS, BD, IC, D, AC, BC, DZ, DT, NP1,
1 ITOTAL, IFREQ, FAC, S1, S3, S4, S5, S6, S7, S8, ICHECK, ICOUNT
COMMON YSTAR(201), Y(4,201), A(201), S(4,201), K(201), X(4,201)
COMMON ACC, SFINALS, MAX, C4, XMAX, S9
DIMENSION Z(201,4), ANS(201)
REAL X
ITER = 0 $ N = NP1 - 1
IF ( IOPT .EQ. 0 ) RETURN

C----- TO CALCULATE THE SATURATION PROFILE .....
C
C----- TO ASSUME NEW PROFILE .....
C
      IF ( ICOUNT .LT. 4 ) GO TO 10
      DO 15 I = 2, NP1
        15 S(4,I) = 2.25 * S(3,I) - 1.5 * S(2,I) + 0.25 * S(1,I)

C----- TO COMPUTE HYDRAULIC CONDUCTIVITY AND POTENTIAL DERIVATIVE--
C
      10 CALL HYCON( NP1 )
      CALL DCAPP( NP1 )

C----- TO GENERATE COEFFICIENT MATRIX -----
C
      Z(1,1) = 0.0
      Z(1,2) = - 1.0 / FAC / DT - 2.0 * K(2) * A(2) * S4
      Z(1,3) = K(2) * A(2) * S4 + K(2) * S3 * ( A(3) - A(1) ) * S5 +
      1A(2) * ( K(3) - K(1) ) * S1
      ANS(1) = - S(3,2) / FAC / DT + ( K(3) - K(1) ) * S3 - S(3,1) *
      1( K(2) * A(2) * S4 - K(2) * ( A(3) - A(1) ) * S1 - A(2) * ( K(3) -
      2 K(1) ) * S1 )
      DO 35 I = 3, N
        C1 = A(I+1) - A(I-1) $ C2 = K(I+1) - K(I-1)

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C3 = K(I) * A(I)
Z(I-1,1) = C3 * S4 - K(I) * C1 * S1 - A(I) * C2 * S1
Z(I-1,2) = - 1.0 / FAC / DT - 2.0 * C3 * S4
Z(I-1,3) = C3 * S4 + K(I) * C1 * S1 + A(I) * C2 * S1
ANS(I-1) = - S(3,I) / FAC / DT + C2 * S3
35 CONTINUE
Z(N,3) = 0.0 * Z(N,1) = 2.0 * K(NP1) * A(NP1) * S4
Z(N,2) = - 1.0 / FAC / DT - 2.0 * K(NP1) * A(NP1) * S4
ANS(N) = - S(3,NP1) / FAC / DT
C----- TO SOLVE THESE LINEAR EQUATIONS SIMULTANEOUSLY -----
C
C CALL CNEDIAG(Z, ANS, 1, N, 1, DETERM, 201, 4, 1)
C----- TO COMPARE THE CALCULATED AND ASSUMED PROFILES -----
C
C DO 40 I = 2, NP1
C   DIFF = ABS( S(4,I) - ANS(I-1) )
C   IF ( DIFF .GT. ACC ) GO TO 55
C 40 CONTINUE
C----- THE CONVERGENCE IS REACHED -----
C
C DO 45 I = 2, NP1
C   S(4,I) = ANS(I-1)
C 45 TO 50
C----- TO ASSUME NEW VALUES OF SATURATIONS -----
C
C 55 ITER = ITER + 1
C   IF ( ITER .GT. MAX ) GO TO 60
C   DO 65 I = 2, NP1
C     S(4,I) = ( S(4,I) + ANS(I-1) ) / 2.0
C 65 TO 10

```

```

C----- TO STOP IF ITERATIONS EXCEED THE LIMIT SET BY MAX .....
C
    60 DO 75 I = 2 , NP1
        DIFF = ABS( S(4,I) - ANS(I-1) )
    75 PRINT 80, S(4,I), ANS(I-1), DIFF
    80 FORMAT( 3( 15X, E20.7 ) )
        STOP4
    50 CONTINUE
        RETURN
        END

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2      SUBROUTINE PCONCN( IOPT )
3      COMMON YIN, VS, XI, YI, SI, EPS, BD, TC, D, AC, BC, DZ, DT, NP1,
4      1 ITOTAL, IFREQ, FAC, S1, S3, S4, S5, S6, S7, S8, ICHECK, ICOUNT
5      COMMON YSTAR(201), Y(4,201), A(201), S(4,201), K(201), X(4,201)
6      COMMON ACC, SFINALS, MAX, C4, XMAX, S9
7      DIMENSION Z(201,3), ZDUM(201,4), ANS(201), XDUM(201)
8      REAL K
9
10     C----- TO CALCULATE PHOSPHORUS CONCENTRATIONS IN LIQUID AND SOLID
11     C PHASES-----
12     C----- TO ASSUME SOLID CONCENTRATION PROFILE -----
13     C
14     IF ( ICOUNT .LT. 4 ) GO TO 90
15     DO 95 I = 2, NP1
16     95 X(4,I) = 2.25 * X(3,I) - 1.5 * X(2,I) + 0.25 * X(1,I)
17     DO 3 I = 1, NP1
18     3 XDUM(I) = X(4,I)
19     CALL EQUIL $ Z(1,1) = 0.0 $ N = NP1 - 1
20     ITER = 0
21     IF ( IOPT .EQ. 0 ) GO TO 100
22     CALL HYCON( NP1 ) $ CALL DCAPP( NP1 )
23
24     C----- TO ESTABLISH COEFFICIENT MATRIX -----
25     C IF IOPT EQUALS ZERO, ONLY + PROFILE IS COMPUTED
26     C IF IOPT EQUALS 1, COMBINED WATER AND P PROFILES ARE COMPUTE
27     C
28     Z(1,2) = K(2) * A(2) * ( S(4,3) - 2.0 * S(4,2) + S(4,1) ) * S4 +
29     1 K(2) * ( S(4,3) - S(4,1) ) * ( A(3) - A(1) ) * S1 + ( A(2) * ( S(
30     24,3) - S(4,1) ) * S5 - 1.0 ) * ( K(3) - K(1) ) * S3 - TC / EPS -
31     3S(4,2) / FAC / DT - 2.0 * S(4,2) * D * S9
32     Z(1,3) = K(2) * ( A(2) * ( S(4,3) - S(4,1) ) * S5 - 1.0 ) * S3
33     1 + D * S(4,2) * S4 + D * ( S(4,3) - S(4,1) ) * S9 / 4.0
34     DO 10 I = 3, N
35     C1 = K(I+1) - K(I-1) $ C2 = A(I+1) - A(I-1)

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```

34      C3 = S(4,I+1) - S(4,I-1)
35      Z(I-1,1) = 0 * S(4,I) * S9 - K(I) * ( A(I) * C3 * S5 - 1.0 ) * S3
36      1 - 0 * ( S(4,I+1) - S(4,I-1) ) * S9 / 4.0
37      Z(I-1,2) = - S(4,I) / FAC / DT - 2.0 * S(4,I) * D * S9 + K(I) * A
38      1(I) * ( S(4,I+1) - 2.0 * S(4,I) + S(4,I-1) ) * S4 + K(I) * C2 *
39      2C3 * S1 + ( A(I) * C3 * S5 - 1.0 ) * C1 * S3 - TC / EPS
40      Z(I-1,3) = 0 * S(4,I) * S9 + K(I) * ( A(I) * C3 * S5 - 1.0 ) *
41      3 S3 + 0 * ( S(4,I+1) - S(4,I-1) ) * S9 / 4.0
42      10 CONTINUE
43      Z(N,3) = 0.0 $      Z(N,1) = 2.0 * D * S(4,NP1) * S9
44      Z(N,2) = - S(4,NP1) / FAC / DT - 2.0 * S(4,NP1) * D * S9 + K(NP1)
45      1 * A(NP1) * ( S(4,N) - S(4,NP1) ) * 2.0 * S4 - TC * 1.0 / EPS
46      GO TO 60
47      100 DO 105 I = 1, N
48      Z(I,1) = S6 + S8 $      Z(I,3) = S6 - S8
49      105 Z(I,2) = - 2.0 * S6 - TC - S7 / FAC
50      Z(1,1) = 0.0 $      Z(N,3) = 0.0 $      Z(N,1) = 2.0 * S6
51      60 DO 15 I = 1, N
52      DO 15 J = 1, 3
53      15 ZDUM(I,J) = Z(I,J)
54      IF ( IOPT .EQ. 0 )      GO TO 110
55      ANS(1) = - S(3,2) * Y(3,2) / FAC / DT - TC / EPS * YSTAR(2) - Y(
56      14,1) * ( 0 * S(4,1) * S9 - K(2) * ( A(2) * ( S(4,3) - S(4,1) ) * S
57      25 - 1.0 ) * S3 - D * ( S(4,3) - S(4,1) ) * S9 / 4.0 )
58      DO 20 I = 3, NP1
59      20 ANS(I-1) = - TC * YSTAR(I) / EPS - Y(3,I) * S(3,I) / FAC / DT
60      GO TO 115
61      110 DO 120 I = 1, N
62      120 ANS(I) = - TC * YSTAR(I+1) - S7 / FAC * Y(3,I+1)
63      ANS(1) = ANS(1) - Y(3,1) * ( S6 + S8 )
64      C----- TO SOLVE THE LINEAR EQUATIONS SIMULTANEOUSLY -----
65      C
66      115 CALL ONEDIAG( ZDUM, ANS, 1,N,1, DETERM, 201, 4, 1 )
67      C

```



```

C----- TO CALCULATE XS BASED ON THE CALCULATED VALUES OF YS -----
C
C
C      DO 25 I = 2 , NP1
C      25 X(4,I) = X(3,I) + DT * ( ANS(I-1) - YSTAR(I) ) / BD * TC
C
C----- TO CHECK FOR CONVERGENCE -----
C
C      DO 30 I = 2 , NP1
C      DIFF = ABS( X(4,I) - XDUM(I) )
C      IF ( DIFF .GT. ACC ) GO TO 35
C      30 CONTINUE
C
C----- CONVERGENCE REACHED .....
C
C      DO 40 I = 2 , NP1
C      Y(4,I) = ANS(I-1)
C      40 XDUM(I) = X(4,I)
C      GO TO 45
C
C----- ASSUME NEW X PROFILE .....
C
C      35 ITER = ITER + 1
C      IF ( ITER .GT. MAX ) GO TO 50
C      DO 55 I = 2 , NP1
C      X(4,I) = ( X(4,I) + XDUM(I) ) / 2.0
C      55 XDUM(I) = X(4,I)
C      CALL EQUIL $ GO TO 60
C
C----- STOP IF ITERATIONS EXCEED THE LIMIT SET BY MAX .....
C
C      50 DO 65 I = 2 , NP1
C      DIFF = ABS( X(4,I) - XDUM(I) )
C      65 PRINT 70, X(4,I), XDUM(I), DIFF
C      70 FORMAT( 3 ( 15X, E20.7 ) )

```



```

1 SUBROUTINE HYCON( NUMBER )
2   COMMON YIN, VS, XI, YI, SI, EPS, BD, TC, D, AC, BC, DZ, DT, NP1,
3   1 ITOTAL, IFREQ, FAC, S1, S3, S4, S5, S6, S7, S8, ICHECK, ICOUNT
4   COMMON YSTAR(201), Y(4,201), A(201), S(4,201), K(201), X(4,201)
5   COMMON ACC, SFINALS, MAX, C4, XMAX, S9
6   REAL K
7
8   C----- TO CALCULATE HYDRAULIC CONDUCTIVITY FROM SATURATION
9   C----- DATA FROM STAPLE SOIL SC. PROC. 33, 840, 1969 CURVEFIT -----
10
11   DO 10 I = 1, NUMBER
12     IF ( S(4,I) - 0.410 ) 5, 15, 15
13     5 K(I) = EXP( 44.2 * S(4,I) - 20.2 )
14     GO TO 10
15   IF ( S(4,I) - 0.96 ) 20, 20, 25
16   20 K(I) = EXP( - 17.1845 + 46.3447 * S(4,I) - 23.9431 * S(4,I) **2 )
17   GO TO 10
18   IF ( S(4,I) .LT. 1.00001 ) GO TO 30
19   S(4,I) = 1.0
20   30 K(I) = 188.75522
21   10 CONTINUE
22   RETURN
23   END
24

```

```

SUBROUTINE DCAPP( NUMBER )
COMMON YIN, VS, XI, YI, SI, EPS, BD, TC, D, AC, BC, DZ, DT, NP1,
1 ITOTAL, IFREQ, FAC, S1, S3, S4, S5, S6, S7, S8, ICHECK, ICOUNT
COMMON YSTAR(201), Y(4,201), A(201), S(4,201), K(201), X(4,201)
COMMON ACC, SFINALS, MAX, C4, XMAX, S9
REAL K
C----- TO CALCULATE DERIVATIVE OF CAPILLARY POTENTIAL FROM SATURA-
C          TION DATA FROM STAPLE -----
C
DO 10 I = 1, NUMBER
IF ( S(4,I) - 0.98 ) 5, 5, 15
5 A(I) = - EXP( 16.1309 - 50.6683 * S(4,I) + 72.862 * S(4,I) * S(4,I) + S(4,
1I) - 36.0635 * S(4,I) * S(4,I) * S(4,I) ) * ( - 50.6683 + 145.724
2 * S(4,I) - 108.1905 * S(4,I) * S(4,I) )
GO TO 10
15 IF ( S(4,I) .LT. 1.000001 ) GO TO 20
S(4,I) = 1.0
20 A(I) = 615.2176
10 CONTINUE
RETURN
END

```

DCAPP
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```

SUBROUTINE CONVERG( X, ZERO, XGUESS, INDEX, NOPT )
C
C ..... THIS CONVERGING SUBROUTINE REQUIRES THAT THE ZERO POINT
C OF THE FUNCTION BE BRACKETED --- ONCE THIS IS ACCOMPLISHED
C THEN A POLYNOMIAL OF DEGREE TWO IS USED TO
C INTERPOLATE TO THE ZERO POINT --- IF THIS CAN NOT BE
C DONE THEN A LINEAR INTERPOLATION IS USED --- IF THE ZERO
C IS INCREASING IN MAGNITUDE THEN THE NEW GUESS AT THE
C ARGUMENT IS SIMPLY 1/4 TH THE SEPARATION FROM THE
C SINGLY REPRESENTED SIDE .....
C
      DATA CLIMIT/ 1.0E-12 /
      XKEEP = X $ ZERO = ZERO
      IF( ZERO ) 240, 10, 240
C
C ..... CHECK TO SEE WHICH MODE CONVERG IS IN .....
C       INDEX = 1 --- CONVERG IS BEING INITIALIZED
C       INDEX = 123456 --- TEST TO SEE IF THE ZERO IS BRACKETED
C       INDEX = 654321 --- CONVERGING ON THE ZERO VALUE
C       INDEX = ANYTHING ELSE TERMINATES THE PROGRAM .....
C
      240 IF( INDEX - 654321 ) 1, 2, 60
      1 IF( INDEX - 123456 ) 3, 4, 60
      3 IF( INDEX - 1 ) 60, 5, 60
C
C ..... INITIALIZING MODF .....
C
      5 ITER = 1 $ XZERO = ZERO
      IF( NOPT .EQ. 1 ) PRINT 100, ITER, X, ZERO
      100 FORMAT( //, 54X, *CONVERGING SUBROUTINE OUTPUT*, //, 43X,
      1 *ITERATION*, 9X, *VARIABLE*, 14X, *ZERO*, //, 43X, I6, 3X,
      2 2E20.8 )
      INDEX = 123456
      CALL SWITCH( XPOS, ZEROPOS, XNEG, ZERONEG, XKEEP, ZERO )

```

```

36 CONVERG
37 CONVERG
38 CONVERG
39 CONVERG
40 CONVERG
41 CONVERG
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43 CONVERG
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66 CONVERG
67 CONVERG
68 CONVERG
69 CONVERG

X = XGUESS      $      KOPT = 1      $      GO TO 50

..... MODE TO CHECK IF THE ZERO IS BRACKETED .....

4 IF( NOPT .EQ. 1 ) PRINT 110, ITER, X, ZERO
110 FORMAT( 43X, I6, 3X, 2E20.8 )
IF( ZERO / XZERO .GT. 0.0 ) GO TO 45
XDIV = 10.0      $      DIVISCR = XDIV
INDEX = 654321
CALL CHECK( ISIT, XS, XPOS, ZEROPOS, XNEG, ZERONEG, XKEEP, ZEROT )
IF( ISIT ) 223, 224, 223

223 CALL SWITCH( XPOS, ZEROPOS, XNEG, ZERONEG, XKEEP, ZEROT )
X = XS      $      GO TO 50

224 KOPT = 0
CALL SWITCH( XPOS, ZEROPOS, XNEG, ZERONEG, XKEEP, ZEROT )
BX = ( ZEROPOS + ZERONEG ) / DIVISCR
GO TO 322

..... CONVERGING MODE .....

2 IF( NOPT .EQ. 1 ) PRINT 110, ITER, X, ZERO
CALL CHECK( ISIT, XS, XPOS, ZEROPOS, XNEG, ZERONEG, XKEEP, ZEROT )
IF( ISIT .EQ. 0 ) GO TO 220
CALL SWITCH( XPOS, ZEROPOS, XNEG, ZERONEG, XKEEP, ZEROT )
X = XS      $      GO TO 50

..... TO GET A NOTION AS TO HOW WELL THE FUNCTION IS BEING
REPRESENTED INTERPOLATE TO TO THE SUM OF THE NEW ZERO AND
AN OLD ZERO OF OPPOSITE SIGN DIVIDED BY A NUMBER LARGER
THAN 10 --- THIS ALSO KEEPS THE BRACKET WIDTH DECREASING .

220 IF( KOPT .EQ. 1 ) GO TO 801
A = BX / ZERO
IF( A .GT. 0.1 .AND. A .LT. 10.0 ) DIVISOR = DIVISOR*XDIV

```

```

      IF( A.GT. 0.5 .AND. A.LT. 2.0 ) DIVISOR = DIVISOR*XDIV
      GO TO 802
      801 KOPT = 0
      802 IF( ZERO ) 800, 10, 810
      800 BX = ( ZERO + ZEROPOS ) / DIVISOR
      FIRSTP = ( ZERO - ZEROPOS ) / ( X - XPOS )
      IF( ZERO.GT. ZERONEG ) GO TO 850
      KOPT = 1 $ XDUM = X/4.0 + XPOS * 3.0/4.0
      CALL SWITCH( XPOS, ZEROPOS, XNEG, ZERONEG, XKEEP, ZEROT )
      X = XDUM $ GO TO 320
      810 BX = ( ZERO + ZERONEG ) / DIVISOR
      FIRSTP = ( ZERO - ZERONEG ) / ( X - XNEG )
      IF( ZEROPOS.GT. ZERO ) GO TO 850
      KOPT = 1 $ XDUM = X/4.0 + XNEG * 3.0/4.0
      CALL SWITCH( XPOS, ZEROPOS, XNEG, ZERONEG, XKEEP, ZEROT )
      X = XDUM $ GO TO 320
      ..... ESTABLISH THE FIRST AND SECOND DERIVATIVES .....
      850 A = XNEG-X $ B = XPOS-X
      DET = ( B*A*A - A*B*B ) / 2.0
      ..... IF THE DETERMINANT IS ZERO REVERT TO LINEAR INTERPOLATION ..
      IF( DET.EQ. 0.0 ) GO TO 840
      FIRST = ( (ZEROPOS-ZERO)*A - (ZERONEG-ZERO)*B ) / DET / 2.0
      SECOND = ( B*(ZERONEG-ZERO) - A*(ZEROPOS-ZERO) ) / DET
      IF( ABS(FIRST).GT. 10.0*ABS(FIRSTP) ) GO TO 840
      ..... COMPUTE THE NEW X ES .....
      A = FIRST*FIRST + 4.0*SECOND*( BX-ZERO )
      IF( A.LE. 0.0 .OR. SECOND.EQ. 0.0 ) GO TO 840
      IF( ABS( FIRST*FIRST/A-1.0 ) .LE. 1.0E-05 ) GO TO 840

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104 CONVERG
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136 CONVERG
137 CONVERG

X1 = X + ( -FIRST - SQRT(A) ) / SECOND / 2.0
X2 = X + ( -FIRST + SQRT(A) ) / SECOND / 2.0
CALL SWITCH( XPOS, ZEROPOS, XNEG, ZERONEG, XKEEP, ZERO )
..... CHECK TO SEE IF EITHER ONE OF THE XES LIE IN THE RANGE .....
      A = ( ABS(XPOS-X1) + ABS(XNEG-X1) ) / ABS( XPOS-XNEG )
      IF( ABS( A-1.0 ) - 1.0E-07 ) 920, 920, 910
920 X = X1 $ GO TO 320
910 A = ( ABS(XPOS-X2) + ABS(XNEG-X2) ) / ABS( XPOS-XNEG )
      IF( ABS( A-1.0 ) - 1.0E-07 ) 930, 930, 322
930 X = X2 $ GO TO 320
..... LINEAR INTERPOLATION EQUATION .....
840 CALL SWITCH( XPOS, ZEROPOS, XNEG, ZERONEG, XKEEP, ZERO )
322 X = ( BX - ZERONEG ) / ( ZEROPOS - ZERONEG )
      X = XNEG * ( 1.0 - X ) + XPOS * X
..... THE TEST OF CONVERGENCE IS PRINCIPALLY MADE ON THE BASIS OF
      DEGREE OF CHANGE OF THE VALUE OF X .....
320 IF( X ) 300, 310, 300
310 TESTX = ABS( XKEEP - X ) $ GO TO 40
300 TESTX = ABS( ( XKEEP - X ) / X )
40 IF( TESTX - CLIMIT ) 10, 10, 50
50 ITER = ITER + 1 $ RETURN
..... OUTPUT IF INDEX IS NOT INITIALIZED PROPERLY .....
60 PRINT 61 $ STOP
61 FORMAT( '1+', ///, 5X, 'THE VALUE OF INDEX WAS EITHER NOT INITIA
1LIZED WITH 1 OR, WAS ALTERED DURING THE CONVERGENCES --- CALCULA
2TIONS ARE TERMINATED' )

```



```

C      ..... DID NOT BRACKET THE ZERC .....
C
C      45 INDEX = - 1000      $      RETURN
C
C      ..... CONVERGENCE .....
C
C      10 IF( NOPT .EQ. 1 )      PRINT 11, X
C      11 FORMAT( 36X, *CONVERGED VALUE =*, E18.8, // )
C      INDEX = 0      $      RETURN
C      END
CONVERG 138
CONVERG 139
CONVERG 140
CONVERG 141
CONVERG 142
CONVERG 143
CONVERG 144
CONVERG 145
CONVERG 146
CONVERG 147
CONVERG 148

```

```

C
C
C
C
SUBROUTINE SWITCH( XPOS, ZEROPOS, XNEG, ZERONEG, X, ZERO )
C
C      ..... THIS SUBROUTINE SIMPLY UPDATES THE CLOSENESS TO THE
C      ZERO POINT .....
C
      IF( ZERO ) 1, 2, 3
1 XNEG = X      $      ZERONEG = ZERO
  RETURN
3 XPOS = X      $      ZEROPOS = ZERO
2 RETURN
  END
CONVERG 149
CONVERG 150
CONVERG 151
CONVERG 152
CONVERG 153
CONVERG 154
CONVERG 155
CONVERG 156
CONVERG 157
CONVERG 158
CONVERG 159

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```

SUBROUTINE CHECK( ISIT,X,XPOS,ZEROPOS,XNEG,ZERONEG,XKEEP,ZEROT )
..... THIS SUBROUTINE USES A GEOMETERIC MEAN TO REDUCE THE
      RATIO OF THE XES THAT BRACKET THE ZERO POINT TO LESS
      THAN FIVE AND GREATER THAN 0.2 .....
      IF( ZEROT ) 30, 5, 40
      30 A = XKEEP $ 8 = XPOS $ C = ZEROT $ D = ZEROPOS
      GO TO 50
      40 A = XNEG $ B = XKEEP $ C = ZERONEG $ D = ZEROT
      50 IF( B ) 1, 2, 1
      2 IF( A ) 4, 5, 6
      4 IF( A + 10.0 ) 7, 5, 5
      7 X = - SQRT( - A ) $ GO TO 20
      6 IF( A - 10.0 ) 5, 5, 8
      8 X = SQRT( A ) $ GO TO 20
      1 IF( A ) 10, 11, 10
      11 IF( B ) 12, 5, 13
      12 IF( B + 10.0 ) 14, 5, 5
      14 X = - SQRT( - B ) $ GO TO 20
      13 IF( B - 10.0 ) 5, 5, 15
      15 X = SQRT( B ) $ GO TO 20
      10 X = A / B
      IF( X ) 16, 5, 17
      17 IF( X .LT. 5.0 .AND. X .GT. 0.2 ) GO TO 5
      X = SQRT( A * B )
      IF( B .LT. 0.0 ) X = - X
      GO TO 20
      16 X = 0.0
      20 XNEG = A $ XPOS = B $ ZERONEG = C $ ZEROPOS = D
      ISIT = 1 $ RETURN
      5 ISIT = 0 $ RETURN
      END

```

C
C
C
C
C

CONVERG 160
CONVERG 161
CONVERG 162
CONVERG 163
CONVERG 164
CONVERG 165
CONVERG 166
CONVERG 167
CONVERG 168
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CONVERG 183
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CONVERG 185
CONVERG 186
CONVERG 187
CONVERG 188
CONVERG 189
CONVERG 190
CONVERG 191
CONVERG 192

```

SUBROUTINE ONEDIAG( COEFF, ANS, IM, IEQ, MSETS, DETERM, MD, KD, ND )
..... THIS SUBROUTINE SOLVES SIMULTANEOUS EQUATIONS WHICH HAVE
      A DIAGONAL COEFFICIENT MATRIX .....
      DIMENSION COEFF(MD,KD), ANS(MD,ND)
      DOUBLE PRECISION DUM, DUMMY, BD(50), E(10)
      ..... CHECK DIMENSIONS .....
      IF( IEQ .LE. MD ) GO TO 1
      PRINT 2, IEQ, MD
      2 FORMAT( '1*, 20X, I5, * EQUATIONS ARE SPECIFIED, BUT ONLY*, I5,
1* ARE PROVIDED FOR IN THE DIMENSION STATEMENT* )
      ..... IF MSETS = 0 ONLY THE DETERMINANT IS WANTED
      MSETS = 1-10 = THE SETS OF EQUALITIES ANYTHING
      ELSE TERMINATES THE PROGRAM .....
      1 IF( MSETS .LE. ND ) GO TO 3
      PRINT 4, MSETS, ND
      4 FORMAT( '1*, 10X, I5, * SETS OF EQUALITIES ARE SPECIFIED, BUT ONL
1*, I5, * ARE PROVIDED FOR IN THE DIMENSION STATEMENT* )
      3 IF( MSETS .GE. 0 .AND. MSETS .LE. 10 ) GO TO 5
      PRINT 7, MSETS
      7 FORMAT( '1*, 20X, *MSETS CAN BE 0 THRU 10, YOU SPECIFIED*, I5 )
      5 IF( KD .GE. IM+IM+2 ) GO TO 8
      PRINT 6, IM, KD
      6 FORMAT( '1*, 20X, *YOU SPECIFIED A MAXIMUM OF*, I20, *MINOR DIAGO
1NALS*, //, 20X, *HOWEVER, KD IS ONLY*, I20 )
      ..... BEGIN SOLUTION .....

```

[illegible]

```

990 DO 910 J = 1, L
910 BD(J) = DBLE( COEFF(I,J) )
    IF( MSETS .EQ. 0 ) GO TO 925
    DO 915 J = 1, MSETS
      915 E(J) = DBLE( ANS(I,J) )
      925 DO 920 J = 1, IM
        C
        ..... CHECK FOR NON ZERO ENTRIES BEFORE THE DIAGONAL .....
        IF( BD(J) ) 926, 920, 926
          926 M = I - IMID + J $ JJ = J
          IF( M .LE. 0 ) GO TO 9000
            C
            ..... SUBTRACT DUM TIMES ROW M TO REDUCE AN ELEMENT TO ZERO .....
            DUM = BD(J) / DBLE( COEFF(M,IMID) )
            DO 930 LL = IMIDP1, L
              JJ = JJ + 1
              930 BD(JJ) = BD(JJ) - DUM * DBLE( COEFF(M,LL) )
              IF( MSETS .EQ. 0 ) GO TO 935
              DO 940 LL = 1, MSETS
                940 E(LL) = E(LL) - DUM * DBLE( ANS(M,LL) )
                935 COEFF(I,J) = 0.0
                920 CONTINUE
                  C
                  ..... GIVE THE DOUBLE PRECISION UPPER TRIANGULATED ROW BACK
                    TO COEFF .....
                    DO 950 J = IMID, L
                      950 COEFF(I,J) = SNGL( BD(J) )
                      IF( MSETS .EQ. 0 ) GO TO 955
                      DO 960 J = 1, MSETS
                        960 ANS(I,J) = SNGL( E(J) )
                          C

```

```

C          ..... CHECK IF A RELATIVELY SMALL NUMBER IS LEFT ON THE DIAGONAL .
C
C          955 SUM = SUM + ABS( COEFF(I,IMID) )
C              IF( ABS( COEFF(I,IMID) ) / SUM * FLOAT( I ) .GT. 1.0E-08 )
C                  1 GO TO 900
C
C          ..... IF ISIT IS ONE IT MEANS THAT A ROW HAS ALREADY BEEN
C              SWITCHED AND THE SUBROUTINE CAN NOT CONTINUE .....
C
C              IF( ISIT .EQ. 1 ) GO TO 9200
C              IF( I .NE. IEQ ) GO TO 9410
C              IF( MSETS .NE. 0 ) GO TO 9400
C              GO TO 900
C
C          ..... SWITCH THE BAD ROW WITH THE ONE FOLLOWING IT .....
C
C          9410 ISIT = 1 $ II = I + 1 $ DETERM = -DETERM
C              DO 970 J = 1, K
C                  X = COEFF(I,J+1) $ COEFF(I,J+1) = COEFF(II,J)
C              970 COEFF(II,J) = X
C                  IF( MSETS .EQ. 0 ) GO TO 990
C              DO 980 J = 1, MSETS
C                  X = ANS(I,J) $ ANS(I,J) = ANS(II,J)
C              980 ANS(II,J) = X
C
C          ..... GO BACK AND REUPPER TRIANGULATE ROW I .....
C
C              GO TO 990
C          900 DETERM = DETERM * COEFF(I,IMID)
C
C          ..... IF MSETS IS ZERO ONLY THE DETERMINANT IS WANTED .....
C
C              IF( MSETS .EQ. 0 ) RETURN
C
C
C          104 ONEDIAG
C          105 ONEDIAG
C          106 ONEDIAG
C          107 ONEDIAG
C          108 ONEDIAG
C          109 ONEDIAG
C          110 ONEDIAG
C          111 ONEDIAG
C          112 ONEDIAG
C          113 ONEDIAG
C          114 ONEDIAG
C          115 ONEDIAG
C          116 ONEDIAG
C          117 ONEDIAG
C          118 ONEDIAG
C          119 ONEDIAG
C          120 ONEDIAG
C          121 ONEDIAG
C          122 ONEDIAG
C          123 ONEDIAG
C          124 ONEDIAG
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C          127 ONEDIAG
C          128 ONEDIAG
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C          130 ONEDIAG
C          131 ONEDIAG
C          132 ONEDIAG
C          133 ONEDIAG
C          134 ONEDIAG
C          135 ONEDIAG
C          136 ONEDIAG
C          137 ONEDIAG

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```

C      BEGIN THE BACK SUBSTITUTION .....
C
      MIEQ = IEQ - 1
      DO 1000 J = 1, MSETS
        1000 ANS(IEQ,J) = SNGL( E(J) / RD(IMID) )
C
C      ..... CALCULATIONS ARE DONE IN DOUBLE PRECISION .....
C
      DO 1100 IY = 1, MIEQ
        I = IEQ - IY
        IF( IY - IMID ) 1200, 1200, 1300
        1200 IC = IMID + IY
        1300 DO 1350 LL = 1, MSETS
          1350 E(LL) = DBLE( ANS(I,LL) )
          DO 1400 JJ = IMIDP1, IC
            LL = I + JJ - IMID $ DUMMY = DBLE( COEFF(I,JJ) )
            DO 1400 KK = 1, MSETS
              1400 E(KK) = E(KK) - DUMMY * DBLE( ANS(LL,KK) )
C
C      ..... GIVE DOUBLE PRECISION ANSWERS TO ANS .....
C
      DO 1500 JJ = 1, MSETS
        1500 ANS(I,JJ) = SNGL( E(JJ) / DBLE( COEFF(I,IMID) ) )
        1100 CONTINUE
        RETURN
C
C      ..... OUTPUT IN THE CASE OF TROUBLE .....
C
      9000 PRINT 9001 $ CALL MMTOUT( COEFF, IEQ, 1, K, MD, KD )
      9001 FORMAT( *1*, 20X, *THE FIRST IM EQUATIONS HAVE ENTRIES WHICH ARE
        1 INCONSISTANT WITH THE DIAGONAL FORM* )
        STOP
      9200 PRINT 9201, I $ CALL MMTOUT( COEFF, IEQ, 1, K, MD, KD )
      9201 FORMAT( *1*, 20X, *A VERY SMALL NUMBER WAS ENCOUNTERED ON THE OIA

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138 ONEDIAG
 139 ONEDIAG
 140 ONEDIAG
 141 ONEDIAG
 142 ONEDIAG
 143 ONEDIAG
 144 ONEDIAG
 145 ONEDIAG
 146 ONEDIAG
 147 ONEDIAG
 148 ONEDIAG
 149 ONEDIAG
 150 ONEDIAG
 151 ONEDIAG
 152 ONEDIAG
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 163 ONEDIAG
 164 ONEDIAG
 165 ONEDIAG
 166 ONEDIAG
 167 ONEDIAG
 168 ONEDIAG
 169 ONEDIAG
 170 ONEDIAG
 171 ONEDIAG


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1GONAL AFTER UPPER TRIANGULATING*, //, 20X, *ROW*, IS, * AND THE ONEDIAG 172
2FOLLOWING ROW OFFERS NO HELP --- THE EQUATIONS NEED BETTER ORDERIN ONEDIAG 173
3G OR THEY ARE DEPENDENT* ) ONEDIAG 174
STOP ONEDIAG 175
9400 PRINT 9401 $ CALL MMTOUT( COEFF, IEQ, 1, K, MD, KD ) ONEDIAG 176
9401 FORMAT( *1*, 20X, *A VERY SMALL NUMBER WAS ENCOUNTERED ON THE DIAG ONEDIAG 177
1GONAL OF THE LAST EQUATION*, //, 20X, *BACK SUBSTITUTION WILL NOT B ONEDIAG 178
2E MADE --- THE FIRST MATRIX IS COEFF AND THE SECOND IS ANS* ) ONEDIAG 179
CALL MMTOUT( ANS, IEQ, 1, MSETS, MD, ND ) $ STOP ONEDIAG 180
END ONEDIAG 181

```

```

SUBROUTINE HMTOUT( A, N, MS, M, MD, ND )
DIMENSION A(MD,ND)
C
C ..... THIS SUBROUTINE SIMPLY PRINTS OUT ANY MATRIX IN A
C          STANDARD FORM .....
C
      MSTART = MS
      $
      40 IF( MSTOP .GT. M ) MSTOP = M
      PRINT 10, N, MSTART, MSTOP
      10 FORMAT( //, 31X, '... OUTPUT FOR ROWS 1 THROUGH', I4, ' ... A
      1ND COLUMNS', I4, ' THROUGH', I4, ' ...', / )
      DO 20 I = 1, N
      20 PRINT 30, ( A(I,J), J = MSTART, MSTOP )
      30 FORMAT( 20X, 5E20.9 )
      IF( MSTOP .EQ. M ) RETURN
      MSTART = MSTOP + 1
      MSTOP = MSTOP + 5
      GO TO 40
      END

```

ONEDIAG 182
 ONEDIAG 183
 ONEDIAG 184
 ONEDIAG 185
 ONEDIAG 186
 ONEDIAG 187
 ONEDIAG 188
 ONEDIAG 189
 ONEDIAG 190
 ONEDIAG 191
 ONEDIAG 192
 ONEDIAG 193
 ONEDIAG 194
 ONEDIAG 195
 ONEDIAG 196
 ONEDIAG 197
 ONEDIAG 198
 ONEDIAG 199

SIMULATION OF PHOSPHORUS MOVEMENT IN A SOIL COLUMN

DATA INPUT TO THE SYSTEM

A. OPERATING CHARACTERISTICS OF THE SYSTEM

1. INPUT CONCENTRATION OF PHOSPHORUS IN LIQUID PHASE = 10.000 PPM
2. RATE OF PRECIPITATION AT THE SURFACE = 2.110 CM / DAY
3. INITIAL PHOSPHORUS CONCENTRATION IN LIQUID PHASE = .5183108E-01 PPM
4. INITIAL PHOSPHORUS CONCENTRATION IN SOIL = .4000000E+01 PPM
5. INITIAL MOISTURE CONTENT OF THE SOIL = .1000000E+00 CC WATER / CC VOIDS

B. PHYSICAL CHARACTERISTICS OF THE SOIL SYSTEM

1. POROSITY OF THE SOIL = .400 CC VOIDS / CC SOIL
2. BULK DENSITY OF THE SOIL = 1.650 GM / CM3
3. MASS TRANSFER COEFFICIENT FOR THE SOIL SYSTEM = 10.000 / DAY
4. DISPERSION COEFFICIENT FOR PHOSPHORUS = 10.000 CM2 / DAY

C. LANGMUIR EQUILIBRIUM ISOTHERM CONSTANTS IN $Y = AX / (1 - BX)$

- A = .1220000E-01 AND B = .1462000E-01
1. MAXIMUM CONCENTRATION OF PHOSPHORUS THAT CAN BE ATTAINED BY THE SOIL = .6839945E+02 PPM
 2. MAXIMUM P CONCENTRATION IN SOIL IN EQUILIBRIUM WITH THE INPUT P CONC = .6313131E+02 PPM

D. VALUES OF PARAMETERS USED IN THE NUMERICAL SOLUTION

1. TOTAL DEPTH OF SOIL SIMULATED AT A TIME = 20.000 CM
2. NUMBER OF GRID POINTS USED = 41
3. DEPTH INCREMENT USED IN THE SOLUTION = .500CM
4. TIME INCREMENT USED = .2500000E+00 DAY
5. TOTAL TIME OF SIMULATION = 5.000 DAYS
6. OUTPUT PRINTED EVERY 1 TIME INTERVALS

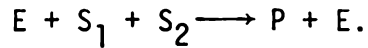
APPENDIX C

PATHWAY FOR AN ENZYMATIC REACTION $S_1 + S_2 + E \rightarrow E + P$
LEADING TO AN EXPRESSION FOR DOUBLE
SUBSTRATE KINETICS

APPENDIX C

PATHWAY FOR AN ENZYMATIC REACTION $S_1 + S_2 + E \rightarrow E + P$ LEADING TO AN EXPRESSION FOR DOUBLE SUBSTRATE KINETICS

Consider the following enzymatic reaction:

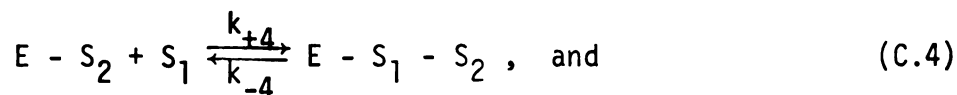
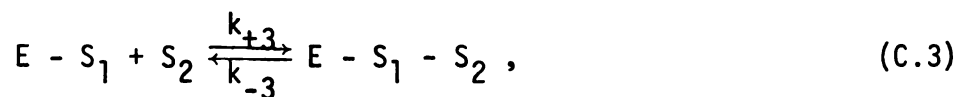


Here, S_1 and S_2 represent the two substrates, and E and P, the enzyme and the product, respectively. For nitrification and denitrification, they represent the following.

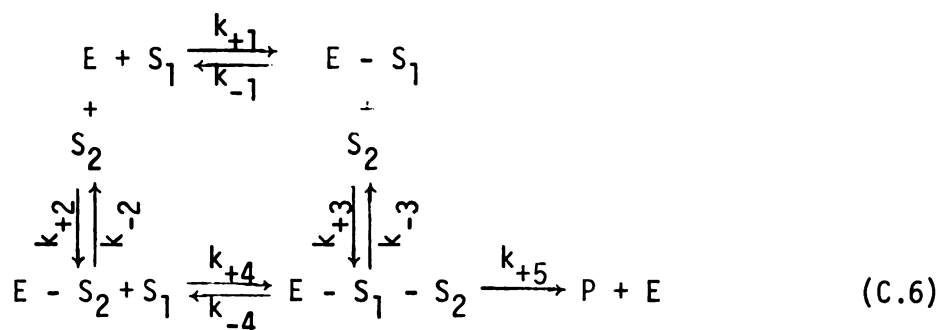
	<u>Nitrification</u>	<u>Denitrification</u>
S_1	Ammonium Nitrogen	Nitrate Nitrogen
S_2	Dissolved Oxygen	Organic Carbon
P	Nitrate Nitrogen	Nitrogen, Carbon Dioxide, etc.

Postulate the following sequence of enzyme reactions:





The above sequence of reactions can be very handily represented as



where

$E - S_1$ = enzyme substrate 1 complex,

$E - S_2$ = enzyme substrate 2 complex,

$E - S_1 - S_2$ = enzyme substrate 1 and substrate 2 complex,

k_{+i} = forward reaction rate constants, and

k_{-i} = reverse reaction rate constants.

The mechanism postulated is that the enzyme combines with the substrates 1 and 2 to form $E - S_1$ and $E - S_2$ complexes. These complexes then combine with the other substrate to form $E - S_1 - S_2$

complex which dissociates to give back the enzyme and the product.

Let, at the equilibrium conditions,

b = concentration of total enzyme,

S_1 = concentration of substrate 1,

S_2 = concentration of substrate 2,

c = concentration of complex $E - S_1$,

d = concentration of complex $E - S_2$, and

e = concentration of complex $E - S_1 - S_2$.

The concentration of free enzyme E is, then, represented as $b - c - d - e$. Let K_1 , K_2 , K_3 , and K_4 represent the equilibrium constants for the reactions (C.1), (C.2), (C.3), and (C.4), i.e.,

$$K_1 = \frac{k_{-1}}{k_{+1}}, \quad K_2 = \frac{k_{-2}}{k_{+2}}, \quad K_3 = \frac{k_{-3}}{k_{+3}}, \quad \text{and} \quad K_4 = \frac{k_{-4}}{k_{+4}}.$$

These, when written in terms of the concentrations of various species, become

$$\left. \begin{aligned} K_1 &= \frac{S_1 (b - c - d - e)}{c}, \\ K_2 &= \frac{S_2 (b - c - d - e)}{d}, \\ K_3 &= \frac{cS_2}{e}, \quad \text{and} \quad K_4 = \frac{dS_1}{e}. \end{aligned} \right\} \quad (C.7)$$

If we further assume that $K_1 = K_4$ and $K_2 = K_3$, it means that neither substrate 1 nor substrate 2 affects the affinity of

the enzyme for the other substrate, i.e., the affinity of the enzyme for a substrate is unaffected by the presence of other enzyme substrate complexes. Let

$$K_1 = K_4 = K_1 \quad \text{and} \quad K_2 = K_3 = K_2.$$

From (C.7),

$$c = \frac{K_2 e}{S_2} \quad \text{and} \quad d = \frac{K_1 e}{S_1}. \quad (\text{C.8})$$

Substituting (C.8) in equation for K_1 in (C.7) and computing for e , one gets

$$e = \frac{b S_1 S_2}{(K_1 + S_1) (K_2 + S_2)}. \quad (\text{C.9})$$

Rate of product formation, v , is $k_{+5}e$, i.e.,

$$v = \frac{k_{+5} b S_1 S_2}{(K_1 + S_1) (K_2 + S_2)}.$$

If the maximum rate of product formation is denoted by V , then

$$V = k_{+5}b, \text{ i.e.,}$$

$$v = V \left(\frac{S_1}{K_1 + S_1} \right) \left(\frac{S_2}{K_2 + S_2} \right). \quad (\text{C.10})$$

Equation (C.10) represents the double substrate limited kinetic model that is used in this work.

APPENDIX D

CONTINUOUS FEED EXPERIMENTS,
STEADY STATE DATA

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TABLE D.1.--Daily Steady State Data for Experiment N-1.
 Dilution factor for glucose analysis = 25.
 Dilution factor for nitrate nitrogen analysis = 1.

Feed Rate ml/min	Feed Concentration mg/l		Sample Analysis				X mg/l
			Nitrate Nitrogen		Glucose Carbon		
	NO ₃ ⁻ -N	Glucose C	Sample S ₁		Sample S ₂		
			Actual	Actual	Actual	Actual	
4.7	97.7	1080	66.8	66.8	32	800	40
4.63	95.5	1010	79.4	79.4	36	900	30
4.59	100.0	1000	77.6	77.6	37	925	15
4.67	98.85	1000	81.3	81.3	36.6	915	20
4.61	97.7	1010	75.8	75.8	38	950	15
4.73	100.0	965	77.6	77.6	37.6	940	25
4.78	95.5	975	79.4	79.4	37	925	15
<u>Average</u>							
4.7	97.7	1010	79.4				925

Dissolved oxygen of final reactor solution = 0.4 mg/l.
 Cell mass obtained by filtration = 9.2 mg/l.

TABLE D.2.--Daily Steady State Data for Experiment N-2.
 Dilution factor for glucose analysis = 25.
 Dilution factor for nitrate nitrogen analysis = 1.

Feed Rate ml/min	Feed Concentration mg/l		Sample Analysis				X mg/l
			Nitrate Nitrogen		Glucose Carbon		
	NO ₃ ⁻ -N	Glucose C	Sample S ₁	Actual	Sample S ₂	Actual	
4.2	102.3	1030	38.0	38.0	30	750	45
4.23	95.5	1030	53.7	53.7	33	635	25
4.27	97.7	1030	51.3	51.3	34	850	50
4.21	100.0	1030	57.5	57.5	35	885	40
4.30	97.7	985	60.3	60.3	31	775	30
4.25	98.9	985	56.7	56.7	33	845	25
4.17	100.0	985	59.3	59.3	35	885	35
4.21	97.7	985	55.9	55.9	34	845	25
<u>Average</u>							
	100	1000	56.15			850	

Dissolved oxygen of final reactor solution = 0.5 mg/l.
 Cell mass obtained by filtration = 27.3 mg/l.

TABLE D.3.--Daily Steady State Data for Experiment N-3.
 Dilution factor for glucose analysis = 25.
 Dilution factor for nitrate nitrogen analysis = 1.

Feed Rate ml/min	Feed Concentration mg/l		Sample Analysis				X mg/l
			Nitrate Nitrogen		Glucose Carbon		
	NO ₃ ⁻ -N	Glucose C	Sample S ₁	Actual	Sample S ₂	Actual	
3.27	95.5	1050	50.1	50.1	26	650	130
3.33	97.7	1050	33.5	33.5	28.2	705	100
3.4	102.3	1050	38.0	38.0	32.6	815	70
3.35	98.8	1025	43.65	43.65	32.8	820	50
3.29	95.5	1025	30.9	30.9	32.0	800	55
3.26	100.0	1025	36.3	36.3	32.6	815	40
3.17	97.7	1025	37.7	37.7	32.2	815	50
3.24	100.0	1025	38.0	38.0	32.0	800	55
Average			37.8		800		

Dissolved oxygen in final reactor solution = 0.2 mg/l.
 Cell mass obtained by filtration = 40.3 mg/l.

TABLE D.4.--Daily Steady State Data for Experiment N-4.
 Dilution factor for glucose analysis = 25.
 Dilution factor for nitrate nitrogen analysis = 1.

Feed Rate ml/min	Feed Concentration mg/l		Sample Analysis				X mg/l
			Nitrate Nitrogen		Glucose Carbon		
	NO ₃ ⁻ -N	Glucose C	Sample S ₁	Actual	Sample S ₂	Actual	
2.0	97.7	1025	42.66	42.66	26	650	80
1.95	98.8	1025	27.7	27.7	29	725	60
1.97	100.0	1025	24.8	24.8	30.2	755	75
1.83	100.0	1025	24.0	24.0	29.4	735	55
1.87	100.0	985	24.54	24.54	29.8	745	50
1.89	95.5	985	21.54	21.54	29	725	60
1.87	98.8	985	23.71	23.71	29.8	745	55
1.87	97.7	985	22.39	22.39	30.2	755	65
<u>Average</u>			23.2		7.50		
1.89							

Dissolved oxygen in final reactor solution = 0.1 mg/l.
 Cell mass obtained by filtration = 50.7 mg/l.

TABLE D.5.--Daily Steady State Data for Experiment N-5.
 Dilution factor for glucose analysis = 25.
 Dilution factor for nitrate nitrogen analysis = 1.

Feed Rate ml/min	Feed Concentration mg/l		Sample Analysis				X mg/l
	NO ₃ ⁻ -N	Glucose C	Nitrate Nitrogen		Glucose Carbon		
			Sample S ₁	Actual	Sample S ₂	Actual	
1.35	97.7	1025	27.7	27.7	26.0	650	75
1.30	95.5	1000	20.9	20.9	25.0	625	65
1.33	100	965	21.6	21.6	28.0	700	60
1.36	102.5	975	22.4	22.4	29.0	725	65
1.35	100	1010	21.4	21.4	29.8	745	70
1.37	97.7	1000	20.4	20.4	29.0	725	60
1.35	98.8	1025	19.5	19.5	28.5	713	65
1.36	97.7	1000	20.2	20.2	28.5	713	60
<u>Average</u>							
1.355	100	1000	20.1	20.1		713	

Dissolved oxygen in final reactor solution = 0.3 mg/l.
 Cell mass obtained by filtration = 50.7 mg/l.

TABLE D.6.--Daily Steady State Data for Experiment N-6.
 Dilution factor for glucose analysis = 25.
 Dilution factor for nitrate nitrogen analysis = 1.

Feed Rate ml/min	Feed Concentration mg/l		Sample Analysis				X mg/l
			Nitrate Nitrogen		Glucose Carbon		
	NO ₃ ⁻ -N	Glucose C	Sample S ₁	Actual	Sample S ₂	Actual	
0.72	97.7	1080	24.4	24.4	24	600	120
0.73	98.8	1025	17.8	17.8	26	650	100
0.77	98.8	1000	19.7	19.7	25	725	80
0.69	100.0	985	25.4	25.4	23	575	85
0.71	102.5	1025	23.7	23.7	24	600	75
0.67	95.5	1000	16.2	16.2	24.6	615	85
0.73	97.7	985	24.6	24.6	24.8	620	90
0.73	95.5	965	26.9	26.9	25	625	85
<u>Average</u>							
0.73	100.0	1000.0	22.3			625	

Dissolved oxygen in final reactor solution = 0.2 mg/l.
 Cell mass obtained by filtration = 75.9 mg/l.

TABLE D.7.--Daily Steady State Data for Experiment N-7.
 Dilution factor for glucose analysis = 25.
 Dilution factor for nitrate nitrogen analysis = 1.

Feed Rate ml/min	Feed Concentration mg/l		Sample Analysis				X mg/l
			Nitrate Nitrogen		Glucose Carbon		
	NO ₃ ⁻ -N	Glucose C	Sample S ₁	Actual	Sample S ₂	Actual	
0.51	97.7	1010	12.3	12.3	12	300	200
0.49	95.5	985	11.7	11.7	13	325	175
0.45	95.5	965	10.7	10.7	14	350	190
0.53	102.5	1025	7.3	7.3	13	325	195
0.51	100.0	1000	9.9	9.9	15	375	225
0.53	102.5	965	8.7	8.7	16	400	215
0.53	95.5	985	9.8	9.8	15	375	200
0.53	97.7	1000	9.9	9.9	14.6	365	185
<u>Average</u>							
0.525			9.8			375	

Dissolved oxygen in final reactor solution = 0.3 mg/l.
 Cell mass obtained by filtration = 150.7 mg/l.

TABLE D.8.--Daily Steady State Data for Experiment C-1.
 Dilution factor for glucose analysis = 4.
 Dilution factor for nitrate nitrogen analysis = 5.

Feed Rate ml/min	Feed Concentration mg/l		Sample Analysis				X mg/l
	NO ₃ ⁻ -N	Glucose C	Nitrate Nitrogen		Glucose Carbon		
			Sample S ₁	Actual	Sample S ₂	Actual	
5.0	244.8	101.6	46.77	233.8	19.0	76.0	20.0
4.97	244.8	100	47.86	239.3	19.4	77.6	15
4.93	242	98.4	48.97	244.8	18.8	75.2	15
5.07	256.4	98.4	48.4	242	20	80.0	10
5.0	256.4	100	47.31	236.6	20.5	82.0	25
4.94	259.4	101.6	45.70	228.5	20.8	83.2	15
4.97	259.4	103.2	46.24	231.2	20.52	82.08	15
5.03	259.4	103.2	46.77	233.8	21.0	84.0	20
<u>Average</u>							
5.00	250.0	100.0	233.8		82		

Dissolved oxygen in final reactor solution = 0.3 mg/l.
 Cell mass obtained by filtration = 7.7 mg/l.

TABLE D.9.--Daily Steady State Data for Experiment C-2.
 Dilution factor for glucose analysis = 1.
 Dilution factor for nitrate nitrogen analysis = 5.

Feed Rate ml/min	Feed Concentration mg/l		Sample Analysis				X mg/l
	NO ₃ ⁻ -N	Glucose C	Nitrate Nitrogen		Glucose Carbon		
			Sample S ₁	Actual	Sample S ₂	Actual	
3.0	244.8	100.0	42.16	210.8	16.8	16.8	55
3.05	242.0	98.4	43.67	218.3	19.0	19.0	50
2.97	256.4	98.4	45.19	225.9	21.0	21.0	55
2.95	259.4	103.2	43.15	215.8	22.0	22.0	45
2.99	256.4	101.6	45.70	228.5	23.0	23.0	40
3.03	244.8	98.4	44.67	223.3	20.2	20.2	30
3.11	256.4	100	43.7	218.3	21.2	21.2	40
3.02	250.0	100	43.7	218.3	21.0	21.0	45
<u>Average</u>							
3.00	250.0	100		218.3	21.0		21.0

Dissolved oxygen in final reactor solution = 0.2 mg/l.
 Cell mass obtained by filtration = 27.3 mg/l.

TABLE D.10.--Daily Steady State Data for Experiment C-3.
 Dilution factor for glucose analysis = 1.
 Dilution factor for nitrate nitrogen analysis = 5.

Feed Rate ml/min	Feed Concentration mg/l		Sample Analysis				X mg/l
	NO ₃ ⁻ -N	Glucose C	Nitrate Nitrogen		Glucose Carbon		
			Sample S ₁	Actual	Sample S ₂	Actual	
1.47	256.4	100	35.5	177.5	2.2	2.2	55
1.49	256.4	98.4	38.9	194.5	5.0	5.0	50
1.53	250.00	98.4	42.65	213.3	4.6	4.6	45
1.45	244.8	103.6	42.7	213.5	4.8	4.8	45
1.51	244.8	101.6	42.7	219.5	5.2	5.2	50
1.57	259.4	98.4	43.2	216.0	4.8	4.8	40
1.55	256.4	100.0	42.7	213.5	4.8	4.8	45
<u>Average</u>							
1.5	250.0	100.0	42.7	213.3	5.0	5.0	

Dissolved oxygen in final reactor solution = 0.4 mg/l.
 Cell mass obtained by filtration = 32.2 mg/l.

TABLE D.11.--Daily Steady State Data for Experiment C-4.

Dilution factor for glucose analysis = 1.

Dilution factor for nitrate nitrogen analysis = 5.

Feed Rate ml/min	Feed Concentration mg/l		Sample Analysis				X mg/l
			Nitrate Nitrogen		Glucose Carbon		
	NO ₃ ⁻ -N	Glucose C	Sample S ₁	Actual	Sample S ₂	Actual	
1.17	244.8	100.0	39.41	199.00	--	--	75
1.15	244.8	98.4	41.69	208.4	--	--	80
1.23	256.4	95.5	42.17	210.8	--	--	65
1.23	256.4	95.5	40.74	203.7	--	--	55
1.20	259.4	100.0	41.20	206.0	--	--	60
1.20	256.4	105.5	43.65	218.25	--	--	65
1.22	250.0	103.6	42.75	213.7	--	--	40
1.21	250.0	100.0	41.70	208.4	--	--	55
<u>Average</u>							
1.2	250.0	100.0	208.4				

Dissolved oxygen in final reactor solution = 0.3 mg/l.

Cell mass obtained by filtration = 39.3 mg/l.

TABLE D.12.--Daily Steady State Data for Experiment C-5.
 Dilution factor for glucose analysis = 1.
 Dilution factor for nitrate nitrogen analysis = 5.

Feed Rate ml/min	Feed Concentration mg/l		Sample Analysis				X mg/l
	NO ₃ ⁻ -N	Glucose C	Nitrate Nitrogen		Glucose Carbon		
			Sample S ₁	Actual	Sample S ₂	Actual	
0.87	250	98.4	40.74	203.7	--	--	75
0.84	250	98.4	40.74	203.7	--	--	80
0.95	256.4	100.0	41.69	208.4	--	--	85
0.93	250.0	100.0	42.17	210.8	--	--	70
0.93	259.4	98.4	41.21	206	--	--	65
0.91	244.8	95.5	41.21	206	--	--	50
0.90	244.8	95.5	40.74	203.7	--	--	55
0.89	250.0	100.0	40.74	203.7	--	--	70
<u>Average</u>							
0.90	250.0	100.0					

Dissolved oxygen in final reactor solution = 0.2 mg/l.
 Cell mass obtained by filtration = 42.7 mg/l.

TABLE D.13.--Daily Steady State Data for Experiment C-6.
 Dilution factor for glucose analysis = 1.
 Dilution factor for nitrate nitrogen analysis = 5.

Feed Rate ml/min	Feed Concentration mg/l		Sample Analysis				X mg/l
	NO ₃ ⁻ -N	Glucose C	Nitrate Nitrogen		Glucose Carbon		
			Sample S ₁	Actual	Sample S ₂	Actual	
0.78	256.4	100.0	38.9	194.5	--	--	85
0.75	250	98.4	38.46	192.3	--	--	90
0.72	250	98.4	39.36	196.77	--	--	70
0.80	244.8	100.0	39.81	199.05	--	--	50
0.77	244.8	98.4	38.9	194.52	--	--	55
0.75	250	95.5	39.9	194.52	--	--	60
0.75	250	100.0	39.36	196.77	--	--	70
<u>Average</u>							
.75	250	100.0	195.5				

Disolved oxygen in final reactor solution = 0.2 mg/l.
 Cell mass obtained by filtration = 35.0 mg/l.

TABLE D.14.--Daily Steady State Data for Experiment C-7.

Dilution factor for glucose analysis = 1.

Dilution factor for nitrate nitrogen analysis = 5.

Feed Rate	Feed Concentration mg/l		Sample Analysis				X mg/l
			Nitrate Nitrogen		Glucose Carbon		
	NO ₃ ⁻ -N	Glucose C	Sample S ₁	Actual	Sample S ₂	Actual	
ml/min							
0.53	250	100	39.8	199	--	--	55
0.50	250	100	40.27	201.4	--	--	75
0.54	250	100	39.36	196.8	--	--	85
0.55	250	100	40.70	203.7	--	--	65
0.55	250	100	40.27	201.4	--	--	45
0.53	250	100	38.9	194.5	--	--	50
0.55	250	100	38.0	190.1	--	--	55
<u>Average</u>							
0.55	250	100	198.2				

Dissolved oxygen in final reactor solution = 0.1 mg/l.
 Cell mass obtained by filtration = 40.7 mg/l.

APPENDIX E

NUMERICAL METHOD AND FORTRAN PROGRAM
USED FOR SIMULATING NITROGEN
MOVEMENT IN SOIL

APPENDIX E

NUMERICAL METHOD AND FORTRAN PROGRAM USED FOR SIMULATING NITROGEN MOVEMENT IN SOIL

As established in Chapter V, the mathematical form of the problem can be summarized as follows.

Liquid Phase:

$$\text{NH}_4^+-\text{N} : D_1 \frac{d^2 C_1}{dz^2} - V \frac{dC_1}{dz} - R_1(C_1, C_3) = 0 , \text{ and}$$

$$\text{NO}_3^--\text{N} : D_2 \frac{d^2 C_2}{dz^2} - V \frac{dC_2}{dz} + R_1(C_1, C_3) - R_2(C_2, C_3) = 0 .$$

Gas Phase:

$$\text{O}_2 : \epsilon(1 - S) \frac{dN_3}{dz} + \alpha_1 R_1 \epsilon S = 0 ,$$

$$\text{N}_2 : \epsilon(1 - S) \frac{dN_4}{dz} + \alpha_2 R_2 \epsilon S = 0 ,$$

$$\text{CO}_2 : \epsilon(1 - S) \frac{dN_5}{dz} + \alpha_3 R_2 \epsilon S = 0 , \text{ and}$$

$$\frac{dC_i}{dz} = \sum_{j=3}^5 \frac{1}{D_{ij}} (X_i N_j - X_j N_i) .$$

The above equations are subject to the following boundary conditions:

at $Z = 0$, all C_i 's are known, and

$$\text{at } Z = L, \quad \frac{dC_1}{dZ} = \frac{dC_2}{dZ} = N_3 = N_4 = N_5 = 0.$$

When the rate expressions are assumed to be first order, the liquid phase equations are analytically solvable. But when the rate expressions are assumed to be of the Michaelis-Menten type, the equations become nonlinear and cannot be solved analytically. Hence, they have to be solved numerically. Because of the nonlinear nature of the equations, the values of the concentrations of ammonium or nitrate nitrogen have to be assumed first. The concentration profiles obtained by the analytical solution of the equations for the first order reaction case were used as a starting point.

The soil column length of 100 cm was divided into $N = 50$ intervals of 2 cm each. The approximations used for the second order and the first order derivatives are given below:

$$\left. \frac{d^2C}{dZ^2} \right|_i = \frac{C_{i+1} - 2C_i + C_{i-1}}{\Delta Z^2}, \quad \text{and}$$

$$\left. \frac{dC}{dZ} \right|_i = \frac{C_{i+1} - C_{i-1}}{2\Delta Z}.$$

Here, the subscripts represent the location of the point. These approximations were written for each point in the grid, resulting in a set of simultaneous equations. These equations were solved using a subprogram ONEDIAG. In applying the boundary condition $dC/dZ = 0$ at $Z = L$, the function $C = C(Z)$ was assumed to be continuous beyond the point $Z = L$ (subscript $N+1$). By the method of images, $C(N)$ was assumed equal to $C(N + 2)$. Iterations on ammonium and nitrate nitrogen profiles were continued until convergence within the desired degree was attained.

Equations for fluxes and concentrations of the gas components are first order equations. The flux equations were easily integrated by using Milne's integration scheme. To solve the equation of the type

$$\frac{dY}{dX} = f(X) ,$$

Milne's relationship was used:

$$Y_{i+1} = Y_{i-1} + \frac{\Delta Z}{3} (f_{i+1} + 4f_i + f_{i-1}) .$$

The equations involving the concentrations of gas components were integrated using Hamming's fourth order integration formulae.

In Cases 3 and 4, it is necessary to distinguish the regions of nitrification and denitrification. Once these regions are defined, the calculation procedure becomes the same as in Case 1. To define these regions, the oxygen profile needs to be assumed. The solution thus involves the procedures of Cases 1 and 2

overlapped with the oxygen profile iterations. The oxygen profile calculated analytically for the first order kinetic model case was assumed for Cases 3 and 4 to begin with. Table E.1 summarizes the calculation procedure for all the four cases.

The numerical solution of the above set of equations was found using the FORTRAN program GASTRAN along with its five subprograms. Table E.2 contains a list of the subroutines used and their functions. The main program was used to command the various subroutines. The computing options and the data required for solving the equations along with the proper units are listed in Table E.3. Included in the following pages are a sample output and a complete listing of the entire program. Many comment cards are included which make the program self-explanatory.

TABLE E.1.--Summary of Solution Methods for the Cases Considered.

Model Number	Kinetic Type	Mechanism Included	Solution Method			
			Liquid Phase	Gas Phase		Concentrations
				Fluxes		
			Eqs. (5.1)	Eqs. (5.2)	Eqs. (5.3)	Eqs. (5.9)
1A	First order reactions	Simplest	Analytical	Analytical	Analytical	--
1B	First order reactions	Convective flux exists	Analytical	Analytical	--	Numerical
2	Michaelis-Menten reaction	Convective flux	Numerical	Numerical	--	Numerical
3	First order reaction	Convective flux and $X_{O_2} \geq 5\%$ inhibits denitrification	Analytical	Analytical Iterations of O_2 profile	--	Numerical
4	Michaelis-Menten reaction	Convective flux and $X_{O_2} \geq 5\%$ inhibits denitrification	Numerical	Numerical Iterations of O_2 profile	--	Numerical

TABLE E.2.--Structure of Program GASTRAN.

Program	Functions
GASTRAN	To read in data, establish initial conditions, and command other subroutines to accomplish calculations for the desired case.
CONCLIQ	To calculate liquid phase concentrations of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$.
FLUXES	To evaluate the fluxes of gas components from liquid phase concentrations.
CONCGAS	To evaluate gas phase concentrations based on the fluxes.
OUTPUT	To print out the input information, the concentration profiles in liquid phase, and other information.
ONEDIAG	To solve simultaneous linear equations to obtain liquid phase concentration profiles.

TABLE E.3.--Data Required by the FORTRAN Program GASTRAN.

Parameter	Description	Unit
EPS	Porosity of soil	--
S	Saturation of soil	--
ALFA	Respiration rate of microbes	$\mu\text{mole O}_2/\text{cc soil/day}$
BD	Bulk density of soil	gm/cc
CNHI	Input NH_4^+ -N concentration	$\mu\text{mole/cc}$
V	Pore velocity of liquid	cm/day
DNH	NH_4^+ -N diffusivity in liquid	cm^2/day
DNO	NO_3^- -N diffusivity in liquid	cm^2/day
This completes the first data card. Format 8F10.0.		
D(1)	Diffusivity of O_2 - N_2 pair	cm^2/day
D(2)	Diffusivity of O_2 - CO_2 pair	cm^2/day
D(3)	Diffusivity of N_2 - CO_2 pair	cm^2/day
RK1	Rate constate for nitrification	day ⁻¹ , or $\mu\text{mole/cc/day}$
RK2	Rate constant for denitrification	day ⁻¹ , or $\mu\text{mole/cc/day}$
DZ	Space increment	cm
ACC	Convergence limit desired	--
CNOI	Input NO_3^- -N concentration	$\mu\text{mole/cc}$
This completes the second data card. Format 8F10.0.		
IA	Option = 1; both reactions first order	--
	Option = 2; both reactions Michaelis-Menten type	--
IB	Option = 0; no dependence of denitrification on oxygen	--
	Option = 1; dependence of denitrification on oxygen	--
IC	Useless parameter	--
N	Number of Z intervals	--
MAX	Maximum number of iterations allowed	--
KM1	Saturation constant for nitrification	$\mu\text{mole/cc}$
KM2	Saturation constant for denitrification	$\mu\text{mole/cc}$
XMIN	Denitrification occurs below this oxygen concentration	--
This completes the third data card. Format 5I5, 3F10.0.		

```

2      PROGRAM GASTRAN( INPUT, OUTPUT )
3
4      C----- THIS IS A CONTROL SUBROUTINE COMMANDING THE OTHER SUBROUTINE
5      C          IN SUCH A WAY SO AS TO ACCOMPLISH A GIVEN OBJECTIVE ....
6      C
7      COMMON F(3,201), X(3,201), D(3), CA(201), CB(201), C(3,201)
8      COMMON DNH, DNO, CNHI, V, ALFA, EPS, S, BO, RK1, RK2, TL, NP1, DZ,
9      1 MAX, ACC, CNOI, KM1, KM2, XMIN
10     DIMENSION XDUM(201)
11     REAL KM1, KM2
12
13     C----- TO READ IN INPUT -----
14     C
15     READ 5, EPS, S, ALFA, BO, CNHI, V, DNH, DNO
16     READ 5, D(1), D(2), D(3), RK1, RK2, DZ, ACC, CNOI
17     READ 10, IA, IB, IC, N, MAX, KM1, KM2, XMIN
18     5 FORMAT( 8F10.0 )
19     10 FORMAT( 5I5, 3F10.0 )
20     NP1 = N + 1 $      TL = FLOAT( N ) * DZ
21     CALL OUTPUT ( 0, IA, IB )
22     CNHI = CNHI / 17.0
23
24     C----- TO CALCULATE OXYGEN PROFILE ....
25     C
26     CALL CONCLIQ ( IA, 0, NP1 )
27     CALL FLUXES ( IA, 0, NP1 )
28     CALL CONCGAS
29     IF ( IB .EQ. 0 ) GO TO 50
30
31     C----- X CONTAINS APPROXIMATE OXYGEN PROFILE ....
32     C
33     ITER = 0
34     DO 20 I = 1, NP1
35     20 XDUM(I) = X(1,I)
36     40 NPOINT = 0

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DO 23 I = 1, NP1
  IF ( X(1,I) .LE. XMIN ) GO TO 45
  23 NPOINT = NPOINT + 1
  PRINT 55
  55 FORMAT( *1*, ///, 20X, *OXYGEN CONCENTRATION DOES NOT GO BELOW XMI
    1N IN ONE METER DEPTH OF SOIL. INCREASE XMIN AND RERUN.* )
  PRINT 53, ( X(1,I), I = 1, NPOINT )
  53 FORMAT( 8( 2X, E14.7 ) )
  XMIN = XMIN + 0.05 $ GO TO 40
  40 XMIN = XMIN + 0.05 $ GO TO 40

C----- NPOINT CONTAINS THE NUMBER OF POINTS WHICH SHOW HIGHER OXYGEN
C----- CONCENTRATIONS THAN XMIN .....
C----- TO CALCULATE LIQUID CONCENTRATIONS -----
C-----
C 45 CALL CONCLIQ( IA, IB, NPOINT )
C----- TO CALCULATE FLUXES OF THE GASES -----
C-----
C CALL FLUXES ( IA, IB, NPOINT )
C----- TO CALCULATE GAS CONCENTRATIONS -----
C-----
C CALL CONCGAS
C----- TO COMPARE CALCULATED AND ASSUMED OXYGEN PROFILE .....
C-----
C DO 15 I = 1, NP1
C DIFF = ARS( XDUM(I) - X(1,I) )
C IF ( DIFF .GT. ACC ) GO TO 25
C 15 CONTINUE
C----- PRINT OUT ANSWERS -----

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C
C
C----- REQUIRED DEGREE OF CONVERGENCE HAS BEEN ATTAINED .....
C
      50 CALL OUTPUT( 1, IA, IB )
        CALL OUTPUT( 2, IA, IB )
        GO TO 30
C
C----- TO ASSUME NEW OXYGEN PROFILE .....
C
      25 ITER = ITER + 1
        IF ( ITER .LT. MAX ) GO TO 60
        DO 65 I = 1, NP1
          DIFF = ABS( X(1,I) - XNUM(I) )
        65 PRINT 70, X(1,I), XNUM(I), DIFF
        70 FORMAT ( 3 ( 20X, E15.7 ) )
        STOP5
        60 DO 35 I = 1, NP1
          X(1,I) = ( X(1,I) + XNUM(I) ) / 2.0
          35 XNUM(I) = X(1,I)
          GO TO 40
        30 CONTINUE
        IF ( IB .EQ. 1 ) GO TO 80
        PRINT 75, ITER, NPOINT
        75 FORMAT( ///, 28X, *NUMBER OF ITERATIONS REQUIRED FOR OXYGEN PROFIL
          15 CONVERGENCE = *, I5, ///, 28X, *NUMBER OF POINTS HAVING HIGHER C
          20 CONCENTRATIONS OF OXYGEN THAN XMIN = *, I5 )
        80 CONTINUE
          END

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GASTRAN 71
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1 SUBROUTINE CONCLIQ( IA, IB, NPOINT )
2
3 C----- THIS SUBROUTINE CALCULATES LIQUID PHASE CONCENTRATIONS .....
4 C
5 COMMON F(3,201), X(3,201), D(3), CA(201), CB(201), CG(3,201)
6 COMMON DNH, DNO, CNHI, V, ALFA, EPS, S, BD, RK1, RK2, TL, NP1, DZ,
7 1 MAX, ACC, CNOI, KM1, KM2, XMIN
8 DIMENSION C(201,4), ANS(201)
9 REAL KM1, KM2
10 NM1 = NP1 - 2 $ N = NP1 - 1
11
12 C----- ASSUME FIRST ORDER REACTIONS -----
13 C
14 IF ( IA .EQ. 1 ) GO TO 5
15 C1 = RK1 $ C2 = RK2 $ RK1 = 0.8 $ RK2=0.08
16 5 IF ( IB .EQ. 0 ) GO TO 7
17 BETAI = ( V - SQRT( V * V + 4.0 * DNH * RK1 ) ) / 2.0 / DNH
18 RETA2 = 0.0
19 DO 6 I = 1, NPOINT
20 CA(I) = CNHI * EXP( BETAI * DZ * FLOAT( I - 1 ) )
21 CB(I) = CNHI * ( 1.0 - EXP( BETAI * DZ * FLOAT( I - 1 ) ) )
22 6 CONTINUE
23 IDUM = NPOINT + 1 $ GO TO 8
24 7 IDUM = 1
25 BETAI = ( V - SQRT( V * V + 4.0 * DNH * RK1 ) ) / 2.0 / DNH
26 BETA2 = ( V - SQRT( V * V + 4.0 * DNO * RK2 ) ) / 2.0 / DNO
27
28 C----- TO CALCULATE THE PROFILES FROM ANALYTICAL EXPRESSIONS .....
29 C
30 DO 9 I = IDUM, NP1
31 CA(I) = CNHI * EXP( BETAI * DZ * FLOAT( I - 1 ) )
32 CB(I) = CNHI * RK1 / ( RK1 - RK2 ) * ( EXP( BETAI * DZ * FLCAI
33 1 ( I - 1 ) ) - EXP( BETAI * DZ * FLOAT( I - 1 ) ) )
34 9 CONTINUE
35

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36      IF ( IA .EQ. 1 )      RETURN
37
38      C----- ASSUMING MICHELIS MFWTEN RATE EXPRESSIONS -----
39
40      C----- TO ESTABLISH THE COEFFICIENTS -----
41
42      RK1 = C1 $ RK2 = C2
43      CON1 = 1.0 / DZ / DZ $ CON2 = 1.0 / 2.0 / DZ
44      C3 = 2.0 * DNH * CON1 $ ITER = 0
45      C1 = - RK1 / ( KM1 + CA(2) ) - C3
46      C2 = DNH * CON1 - V * CON2
47      C4 = DNH * CON1 + V * CON2
48
49      35 C(1,1) = 0.0
50      C(1,2) = C1 $ C(1,3) = C2 $ C(N,1) = C3
51      C(N,3) = 0.0
52      DO 1A I = 2 , NM1
53          C(I,1) = C4 $ C(I,3) = C2
54          C(I,2) = - RK1 / ( KM1 + CA(I+1) ) - C3
55          18 ANS(I) = 0.0
56          ANS(1) = - C4 * CNHI $ ANS(N) = 0.0
57          C(N,2) = - C3 - RK1 / ( KM1 + CA(NP1) )
58
59      C----- TO SOLVE THE LINEAR EQUATIONS SIMULTANEOUSLY -----
60
61      CALL ONEDIAG( C, ANS, 1, N, 1, DETERM, 201, 4, 1 )
62
63      C----- TO COMPARE THE CALCULATED AND ASSUMED PROFILES.....
64
65      DO 20 I = 2 , NP1
66          DIFF = ABS( CA(I) - ANS( I-1 ) )
67          IF ( DIFF .GT. ACC ) GO TO 25
68      20 CONTINUE
69      DO 40 I = 2 , NP1

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70 CONCLIQ
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103 CONCLIQ

40 CA(I) = ANS(I-1)
   GO TO 45
25 ITER = ITER + 1
   IF ( ITER .GT. MAX ) GO TO 50
   DO 30 I = 2 , NP1
30 CA(I) = ( CA(I) + ANS( I - 1 ) ) / 2.0
   GO TO 35
50 DO 55 I = 2 , NP1
55 DIFF = ABS( CA(I) - ANS( I-1 ) )
60 PRINT 60, CA(I), ANS(I-1), DIFF
   FORMAT( 3 ( 15X, E20.7 ) )
   STOP1

C----- AMMONIUM CONCENTRATIONS ARE ESTABLISHED. SIMILARLY OBTAIN
C NITRATE CONCENTRATIONS -----
C
45 C1 = 2.0 * DNO * CON1
   C2 = DNO * CON1 - V * CON2 $ ITER = 0
   C4 = DNO * CON1 + V * CON2
   C5 = RK1 / ( KM1 + CA(2) ) * CA(2)
   C6 = RK1 * CA(NP1) / ( KM1 + CA(NP1) )

C----- TO ESTABLISH COEFFICIENT MATRIX .....
C
95 C(1,1) = 0.0
   C(1,3) = C2
   IF ( IB .EQ. 0 ) GO TO 96
   C3 = - C1 $ C(1,2) = C3 $ NPOINT = NPOINT - 1
   DO 97 I = 2 , NPOINT
   C(I,1) = C4 $ C(I,3) = C2 $ C(I,2) = - C1
97 ANS(I) = - RK1 * CA(I+1) / ( KM1 + CA(I+1) )
   NPOINT = NPOINT + 1 $ IDUM = NPOINT
96 IDUM = 2
   C3 = - RK2 / ( KM2 + CB(2) ) - C1 $ C(1,2) = C3

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98 DO 99 I = IDUM , NM1
   C(I,1) = C4 $ C(I,3) = C2
   C(I,2) = - RK2 / ( KM2 + CB(I+1) ) - C1
99 ANS(I) = - RK1 * CA(I+1) / ( KM1 + CA(I+1) )
   C(N,2) = - C1 - RK2 / ( KM2 + CB(NP1) )
   C(N,1) = C1 $ C(N,3) = 0.0
   ANS(1) = - C4 * CNOI - C5 $ ANS(N) = - C6
C----- TO SOLVE THESE EQUATIONS SIMULTANEOUSLY .....
C
C      CALL ONEDIAG( C, ANS, 1, N, 1, DETERM, 201, 4, 1 )
C----- TO COMPARE CALCULATED AND ASSUMED PROFILES .....
C
DO 75 I = 2 , NP1
  DIFF = ABS( CB(I) - ANS(I-1) )
  IF ( DIFF .GT. ACC ) GO TO 80
75 CONTINUE
DO 85 I = 2 , NP1
  CB(I) = ANS(I-1)
  RETURN
80 ITER = ITER + 1
  IF ( ITER .GT. MAX ) GO TO 105
DO 90 I = 2 , NP1
  CB(I) = ( CB(I) + ANS( I - 1 ) ) / 2.0
  GO TO 95
105 DO 100 I = 2 , NP1
  DIFF = ABS( CB(I) - ANS(I-1) )
100 PRINT 60, CB(I), ANS(I-1), DIFF
  STOP2
  ENO

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CONCLIQ 105
CONCLIQ 106
CONCLIQ 107
CONCLIQ 108
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CONCLIQ 134

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```

SUBROUTINE FLUXES( IA, I3, NPOINT )
COMMON F(3,201), X(3,201), O(3), CA(201), C8(201), C(3,201)
COMMON DNH, DNO, CNHI, V, ALFA, EPS, S, BD, RK1, RK2, TL, NP1, DZ,
1 MAX, ACC, GNOI, KM1, KM2, XMIN
REAL KM1, KM2
IF ( IA .EQ. 2 ) GO TO 25

C----- TO CALCULATE THE FLUXES ANALYTICALLY -----
C
F(1,NP1) = F(2,NP1) = F(3,NP1) = 0.0
BETA1 = V / 2.0 / DNH - SQRT( ( V*V + 4.0 * DNH * RK1 ) / 4.0 /
1DNH / DNH )
BETA2 = V / 2.0 / DNO - SQRT( ( V*V + 4.0 * DNO * RK2 ) / 4.0 /
1 DNO / DNO )
C0 = 1.0 - S $ C1 = 2.0 * RK1 * S / C0 / BETA1 * CNHI
C2 = ALFA * BD / EPS / C0
C3 = 0.5 * RK1 * RK2 * S * CNHI / C0 / ( RK1 - RK2 )
C4 = 0.25 * C3
C5 = EXP( BETA1 * TL ) / BETA1 - EXP( BETA2 * TL ) / BETA2
Z = TL - DZ $ N = NP1 - 1 $ IDUM = N
IF ( IB .EQ. 1 ) IDUM = N - NPOINT
DO 12 I = 1, IDUM
J = N - I + 1
C6 = EXP( BETA2 * Z ) / BETA2 - EXP( BETA1 * Z ) / BETA1
C7 = C2 * ( Z - 0.8 * Z ** 1.25 / TL ** 0.25 - 0.2 * TL )
F(1,J) = - C1 * ( EXP( BETA1 * Z ) - EXP( BETA1 * TL ) ) - C7
F(2,J) = C3 * ( C6 + C5 )
F(3,J) = C4 * ( C6 + C5 ) + C7
12 Z = Z - DZ
IF ( IB .EQ. 0 ) RETURN
IDUM = IDUM + 1 $ BETA2 = 0.0 $ C3 = C4 = 0.
C5 = EXP( BETA1 * TL ) / BETA1
DO 13 I = IDUM, N
J = NP1 - I

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 3 FLUXES
 4 FLUXES
 5 FLUXES
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 34 FLUXES
 35 FLUXES

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36      C6 = - EXP( BETA1 * Z ) / 95TA1      FLUXES
37      C7 = C2 * ( Z - 0.8 * Z ** 1.25 / TL ** 0.25 - 0.2 * TL )      FLUXES
38      F(1,J) = - C1 * ( EXP( BETA1 * Z ) - EXP( BETA1 * TL ) ) - C7      FLUXES
39      F(2,J) = C3 * ( C6 + C5 )      FLUXES
40      F(3,J) = C4 * ( C6 + C5 ) + C7      FLUXES
41      13 Z = Z - DZ      FLUXES
42      RETURN      FLUXES
43      C----- TO CALCULATE FLUXES NUMERICALLY USING MILNES METHOD ----- FLUXES
44      C      25 CONTINUE      FLUXES
45      N = NP1 - 1      $      F(1,NP1) = F(2,NP1) = F(3,NP1) = 0.0      FLUXES
46      C----- TO GET STARTING THREE POINTS USING MODIFIED EULERS METHOD -- FLUXES
47      C      CON1 = 2.0 * RK1 * S / ( 1.0 - S )      FLUXES
48      CON2 = 0.5 * RK2 * S / ( 1.0 - S )      $      CON3 = DZ / 3.0      FLUXES
49      DO 30 I = 1, 2      FLUXES
50      J = NP1 - I      $      JP = J + 1      FLUXES
51      F(1,J) = F(1,JP) - DZ / 2.0 * ( - CON1 * CA(JP) / ( KM1 + CA(JP)      FLUXES
52      1 ) - CON1 * CA(J) / ( KM1 + CA(J) ) )      FLUXES
53      SLPM = DZ / 2.0 * ( CON2 * CB(JP) / ( KM2 + CB(JP) ) + CON2 * CB      FLUXES
54      1(J) / ( KM2 + CB(J) ) )      FLUXES
55      F(2,J) = F(2,JP) - SLPM      $      F(3,J) = F(3,JP) - SLPM * 0.25      FLUXES
56      30 CONTINUE      FLUXES
57      C----- START REGULAR MILNES METHOD ----- FLUXES
58      C      NM2 = N - 2      $      IDUM = NM2      FLUXES
59      IF ( I8 .EQ. 1 )      IDUM = NM2 - NPOINT      FLUXES
60      DO 36 I = 1, IDUM      FLUXES
61      J = NM2 - I + 1      $      JP2 = J + 2      $      JP = J + 1      FLUXES
62      F(1,J) = F(1,JP2) - CON3 * ( - CON1 ) * ( CA(JP2) / ( KM1 + CA(J      FLUXES
63      1P2) ) + 4.0 * CA(JP) / ( KM1 + CA(JP) ) + CA(J) / ( KM1 + CA(J) ) )      FLUXES
64      36 CONTINUE      FLUXES
65      C----- TO CALCULATE FLUXES NUMERICALLY USING MILNES METHOD ----- FLUXES
66      C      25 CONTINUE      FLUXES
67      N = NP1 - 1      $      F(1,NP1) = F(2,NP1) = F(3,NP1) = 0.0      FLUXES
68      C----- TO GET STARTING THREE POINTS USING MODIFIED EULERS METHOD -- FLUXES
69      C      CON1 = 2.0 * RK1 * S / ( 1.0 - S )      FLUXES
70      CON2 = 0.5 * RK2 * S / ( 1.0 - S )      $      CON3 = DZ / 3.0      FLUXES
71      DO 30 I = 1, 2      FLUXES
72      J = NP1 - I      $      JP = J + 1      FLUXES
73      F(1,J) = F(1,JP) - DZ / 2.0 * ( - CON1 * CA(JP) / ( KM1 + CA(JP)      FLUXES
74      1 ) - CON1 * CA(J) / ( KM1 + CA(J) ) )      FLUXES
75      SLPM = DZ / 2.0 * ( CON2 * CB(JP) / ( KM2 + CB(JP) ) + CON2 * CB      FLUXES
76      1(J) / ( KM2 + CB(J) ) )      FLUXES
77      F(2,J) = F(2,JP) - SLPM      $      F(3,J) = F(3,JP) - SLPM * 0.25      FLUXES
78      30 CONTINUE      FLUXES
79      C----- START REGULAR MILNES METHOD ----- FLUXES
80      C      NM2 = N - 2      $      IDUM = NM2      FLUXES
81      IF ( I8 .EQ. 1 )      IDUM = NM2 - NPOINT      FLUXES
82      DO 36 I = 1, IDUM      FLUXES
83      J = NM2 - I + 1      $      JP2 = J + 2      $      JP = J + 1      FLUXES
84      F(1,J) = F(1,JP2) - CON3 * ( - CON1 ) * ( CA(JP2) / ( KM1 + CA(J      FLUXES
85      1P2) ) + 4.0 * CA(JP) / ( KM1 + CA(JP) ) + CA(J) / ( KM1 + CA(J) ) )      FLUXES

```

```

      SLPM = CON2 * ( CB(JP2) / ( KM2 + CB(JP2) ) + 4.0 * CB(JP) / ( K
70  FLUXES
71  FLUXES
72  FLUXES
73  FLUXES
74  FLUXES
75  FLUXES
76  FLUXES
77  FLUXES
78  FLUXES
79  FLUXES
80  FLUXES
81  FLUXES
82  FLUXES
83  FLUXES
84  FLUXES

      1M2 + CB(JP) ) + CB(J) / ( KM2 + CB(J) ) ,
      F(2,J) = F(2,JP2) - CON3 * SLPM
      F(3,J) = F(3,JP2) - CON3 * SLPM / 4.0
36 CONTINUE
      IF ( I8 .EQ. 0 ) RETURN
      IDUM = IDUM + 1 $ CON2 = 0.0
      DO 37 I = IDUM , NM2
         J = NM2 - I + 1 $ JP2 = J + 2 $ JP = J + 1
         F(1,J) = F(1,JP2) - CON3 * ( - CON1 ) * ( CA(JP2) / ( KM1 + CA(J
         1P2) ) + 4.0 * CA(JP) / ( KM1 + CA(JP) ) + CA(J) / ( KM1 + CA(J) ) )
         F(2,J) = F(2,J+1) $ F(3,J) = F(3,J+1)
37 CONTINUE
      RETURN
      END

```

```

2          SUBROUTINE CONCGAS
3          COMMON F(3,201), X(3,201), D(3), CA(201), CB(201), C(3,201)
4          COMMON DNH, DNO, CNHI, V, ALFA, EPS, S, BD, RK1, RK2, TL, NP1, DZ,
5          1 MAX, ACC, CNOI, KM1, KM2, XMIN
6          REAL KM1, KM2
7          DIMENSION SDUM(6), SLOP(3,201), XDUM(3), COUM(6), ERROR(3)
8          IF ( IB .EQ. 1 ) GO TO 70
9
10         C----- SOLVE CONCENTRATION EQUATIONS SIMULTANEOUSLY -----
11         C
12         C(1,1) = 0.2097 * 44.5      $      C(2,1) = 0.79 * 44.5
13         C(3,1) = 0.0003 * 44.5      $      CON4 = 4.0 / 3.0
14         SUM = C(1,1) + C(2,1) + C(3,1)      $      X(1,1) = C(1,1) / SUM
15         X(2,1) = C(2,1) / SUM      $      X(3,1) = C(3,1) / SUM
16         CON3 = DZ / 3.0
17         CON1 = 112.0 / 121.0      $      CON2 = 1.0 - CON1
18
19         C----- USE FOURTH ORDER HAMMINGS METHOD -----
20         C----- USE MODIFIED EULERS METHOD TO GET STARTING POINTS -----
21         C
22         DO 20 J = 1, 3
23             XDUM(J) = X(J,1)
24             DO 30 II = 2, 4
25                 I = II - 1
26                 SDUM(1) = 1.0 / D(1) * ( XDUM(1) * F(2,I) - XDUM(2) * F(1,I) ) +
27                 1 1.0 / D(2) * ( XDUM(1) * F(3,I) - XDUM(3) * F(1,I) )
28                 SDUM(2) = 1.0 / D(1) * ( XDUM(2) * F(1,I) - XDUM(1) * F(2,I) ) +
29                 1 1.0 / D(3) * ( XDUM(2) * F(3,I) - XDUM(3) * F(2,I) )
30                 SDUM(3) = 1.0 / D(2) * ( XDUM(3) * F(1,I) - XDUM(1) * F(3,I) ) +
31                 1 1.0 / D(3) * ( XDUM(3) * F(2,I) - XDUM(2) * F(3,I) )
32             DO 25 J = 1, 3
33                 XDUM(J) = C(J,I) + SDUM(J) * DZ
34             SUM = COUM(1) + COUM(2) + COUM(3)
35             XDUM(1) = COUM(1) / SUM      $      XDUM(2) = COUM(2) / SUM

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36 XDUM(3) = CDUM(3) / SUM CONCGAS
37 I = I + 1 CONCGAS
38 SDUM(4) = 1.0 / D(1) * ( XDUM(1) * F(2,I) - XDUM(2) * F(1,I) ) + CONCGAS
39 1 1.0 / D(2) * ( XDUM(1) * F(3,I) - XDUM(3) * F(1,I) ) CONCGAS
40 SDUM(5) = 1.0 / D(1) * ( XDUM(2) * F(1,I) - XDUM(1) * F(2,I) ) + CONCGAS
41 1 1.0 / D(3) * ( XDUM(2) * F(3,I) - XDUM(3) * F(2,I) ) CONCGAS
42 SDUM(6) = 1.0 / D(2) * ( XDUM(3) * F(1,I) - XDUM(1) * F(3,I) ) + CONCGAS
43 1 1.0 / D(3) * ( XDUM(3) * F(2,I) - XDUM(2) * F(3,I) ) CONCGAS
44 DO 35 J = 1, 3 CONCGAS
45 35 C(J,I) = C(J,I-1) + DZ / 2.0 * ( SDUM(J) + SDUM(J+3) ) CONCGAS
46 SUM = C(1,I) + C(2,I) + C(3,I) CONCGAS
47 XDUM(1) = C(1,I) / SUM $ XDUM(2) = C(2,I) / SUM CONCGAS
48 XDUM(3) = C(3,I) / SUM CONCGAS
49 SLOP(1,I) = 1.0 / D(1) * ( XDUM(1) * F(2,I) - XDUM(2) * F(1,I) ) CONCGAS
50 1 + 1.0 / D(2) * ( XDUM(1) * F(3,I) - XDUM(3) * F(1,I) ) CONCGAS
51 SLOP(2,I) = 1.0 / D(1) * ( XDUM(2) * F(1,I) - XDUM(1) * F(2,I) ) CONCGAS
52 1 + 1.0 / D(3) * ( XDUM(2) * F(3,I) - XDUM(3) * F(2,I) ) CONCGAS
53 SLOP(3,I) = 1.0 / D(2) * ( XDUM(3) * F(1,I) - XDUM(1) * F(3,I) ) CONCGAS
54 1 + 1.0 / D(3) * ( XDUM(3) * F(2,I) - XDUM(2) * F(3,I) ) CONCGAS
55 DO 40 J = 1, 3 CONCGAS
56 40 X(J,I) = XDUM(J) CONCGAS
57 30 CONTINUE CONCGAS
58 DO 45 I = 5, NP1 CONCGAS
59 DO 50 J = 1, 3 CONCGAS
60 CDUM(J) = C(J,I-4) + CON4 * CZ * ( 2.0 * SLOP(J,I-1) - SLOP(J,I-12) + 2.0 * SLOP(J,I-3) ) CONCGAS
61 IF ( I.EQ. 5 ) GO TO 75 CONCGAS
62 DO 80 J = 1, 3 CONCGAS
63 CDUM(J+3) = CDUM(J) + CON1 * ERROR(J) CONCGAS
64 SUM = CDUM(4) + CDUM(5) + CDUM(6) CONCGAS
65 GO TO 76 CONCGAS
66 75 SUM = CDUM(1) + CDUM(2) + CDUM(3) CONCGAS
67 76 CONTINUE CONCGAS
68 XDUM(1) = CDUM(1) / SUM $ XDUM(2) = CDUM(2) / SUM CONCGAS
69

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```

XOUM(3) = COUM(3) / SUM
SDUM(1) = 1.0 / D(1) * ( XCOUM(1) * F(2,I) - XOUM(2) * F(1,I) ) +
1 1.0 / D(2) * ( XOUM(1) * F(3,I) - XOUM(3) * F(1,I) )
SDUM(2) = 1.0 / D(1) * ( XOUM(2) * F(1,I) - XOUM(1) * F(2,I) ) +
1 1.0 / D(3) * ( XOUM(2) * F(3,I) - XOUM(3) * F(2,I) )
SDUM(3) = 1.0 / D(2) * ( XCOUM(3) * F(1,I) - XOUM(1) * F(3,I) ) +
1 1.0 / D(3) * ( XOUM(3) * F(2,I) - XOUM(2) * F(3,I) )
DO 55 J = 1, 3
55 C(J,I) = 1.125 * C(J,I-1) - 0.125 * C(J,I-3) + 0.375 * DZ * ( SD
1UM(J) + 2.0 * SLOP(J,I-1) - SLOP(J,I-2) )
DO 90 J = 1, 3
ERROR(J) = ( C(J,I) - COUM(J) )
90 C(J,I) = C(J,I) - ERROR(J) * CON2
SUM = C(1,I) + C(2,I) + C(3,I)
XOUM(1) = C(1,I) / SUM
XOUM(3) = C(3,I) / SUM
SLOP(1,I) = 1.0 / D(1) * ( XOUM(1) * F(2,I) - XOUM(2) * F(1,I) )
1 + 1.0 / D(2) * ( XOUM(1) * F(3,I) - XOUM(3) * F(1,I) )
SLOP(2,I) = 1.0 / D(1) * ( XOUM(2) * F(1,I) - XOUM(1) * F(2,I) )
1 + 1.0 / D(3) * ( XOUM(2) * F(3,I) - XOUM(3) * F(2,I) )
SLOP(3,I) = 1.0 / D(2) * ( XOUM(3) * F(1,I) - XOUM(1) * F(3,I) )
1 + 1.0 / D(3) * ( XOUM(3) * F(2,I) - XOUM(2) * F(3,I) )
DO 60 J = 1, 3
60 X(J,I) = XOUM(J)
45 CONTINUE
70 CONTINUE
RETURN
END

```

```

SUBROUTINE OUTPUT( NPRINT, IA, IB )
COMMON F(3,201), X(3,201), D(3), CA(201), CB(201), C(3,201)
COMMON ONH, DNO, CNHI, V, ALFA, EPS, S, BD, RK1, RK2, TL, NP1, DZ,
1 MAX, ACC, CNOI, KM1, KM2, XMIN
2 DIMENSION DIFF(3,201)
3 REAL KM1, KM2
4
5
6
7
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C----- OUTPUT SUBROUTINE -----
C----- TO OUTPUT THE HEADING -----
C

```

IF ( NPRINT .GT. 0 ) GO TO 100
PRINT 5
5 FORMAT( *1, //, 35X, *DETERMINATION OF SOIL AIR COMPOSITION USIN
16 EQUATION OF CONTINUITY*, /, 35X, *-----* )
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PRINT 10
10 FORMAT(//, 56X, *DATA INPUT TO THE SYSTEM*, /, 56X, *-----*)
1

```

PRINT 15, CNHI, V, ALFA
15 FORMAT( ///, 20X, *A. OPERATING CHARACTERISTICS OF THE SYSTEM*,
1//, 25X, *1. INPUT CONCENTRATION OF THE AMMONIA SOLUTION = *, F7
2.3, 5X, *PPM*, //, 25X, *2. RATE OF PRECIPITATION AT THE SURFACE
3= *, F7.3, 5X, *CM / DAY*, //, 25X, *3. MAXIMUM RATE OF RESPIRATI
4ON AT THE SURFACE = *, F7.3, 5X, *MICRO-MOLES / GM SOIL / DAY* )
PRINT 20, EPS, S, 90
20 FORMAT( ///, 20X, *B. PHYSICAL CHARACTERISTICS OF THE SOIL SYSTEM
1*, //, 25X, *1. POROSITY OF SOIL = *, F7.3, 5X, *CC VOIDS / CC S
2OIL*, //, 25X, *2. MOISTURE CONTENT OF THE SOIL = *, F7.3, 5X, *
3PERCENT VOIDS OCCUPIED BY WATER*, //, 25X, *3. BULK DENSITY OF THE
4 SOIL = *, F7.3, 5X, *GM / CC SOIL* )
IF ( IA .EQ. 2 ) GO TO 27
PRINT 25, RK1, RK2
25 FORMAT( ///, 20X, *C. BIOLOGICAL REACTION RATE CONSTANTS*, //, 25
1X, *1. RATE OF NITRIFICATION ( FIRST ORDER WRT NH4 ) = *, F7.3,

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25X, *1 / DAY*, //, 25X, *2. RATE OF DENITRIFICATION( FIRST ORDER W
3RT NO3 ) = *, F7.3, 5X, *1 / DAY* )
GO TO 29
27 PRINT 28, RK1, RK2, KM1, KM2
28 FORMAT( ///, 20X, *C. BIOLOGICAL REACTION RATE CONSTANTS ( REACTI
IONS ARE ASSUMED TO BE OF MICHELIS MENTEN TYPE ) *, //, 25X, *1. MA
2XIMUM RATE OF NITRIFICATION = *, F10.4, 5X, * MICROMOLES / DAY *,
3 //, 25X, *2. MAXIMUM RATE OF DENITRIFICATION = *, F10.4, 5X, *
4MICROMOLES / DAY *, //, 25X, *3. MICHELIS-MENTEN CONSTANT FOR NITR
IFICATION REACTION = *, F10.4, 5X, * MICROMOLES / CM3 *, //, 25X
6, *4. MICHELIS-MENTEN CONSTANT FOR DENITRIFICATION REACTION = *,
7 F10.4, 5X, * MICROMOLES / CM3 * )
29 IF ( IB .EQ. 0 ) GO TO 78
PRINT 79, XMIN
79 FORMAT( ///, 28X, *DENITRIFICATION IS ASSUMED TO TAKE PLACE ONLY
1IF OXYGEN CONC IS LESS THAN*, F10.5 )
78 PRINT 30, ONH, ONO,D(1), D(2), D(3)
30 FORMAT( ///, 20X, *0. DIFFUSIVITIES OF DIFFERENT SPECIES*, //, 25
1X, *1. DIFFUSIVITY OF NH4 IN LIQUID SOLUTION = *, F5.2, 5X, 11HCM
2**2 / DAY, //, 25X, *2. DIFFUSIVITY OF NO3 IN LIQUID SOLUTION =
3*, F7.3, 5X, 11HCM**2 / DAY, //, 25X, *3. DIFFUSIVITY OF OXYGEN IN
4 NITROGEN = *, F7.2, 5X, 11HCM**2 / DAY, //, 25X, *4. DIFFUSIVI
5TY OF OXYGEN IN CARBON DIOX = *, F7.2, 5X, 11HCM**2 / DAY, //, 2
65X, *5. DIFFUSIVITY OF CO2 IN NITROGEN = *, F7.2, 5X, 11HCM**2
7 / DAY )
PRINT 35, TL, NP1, JZ
35 FORMAT( ///, 20X, *E. VALUES OF PARAMETERS USED IN NUMERICAL SOLU
TION*, //, 25X, *1. TOTAL DEPTH OF SOIL TO BE SIMULATED = *, F7.
22, 5X, *CMS*, //, 25X, *2. NUMBER OF GRID POINTS USED = *, I4, /
3/, 25X, *3. DEPTH INCREMENT USED IN NUMERICAL SOLUTION = *, F6.2
4, 5X, *CM* )
RETURN
100 IF ( NPRINT .GT. 1 ) GO TO 55

```

```

C----- TO OUTPUT LIQUID CONCENTRATIONS AND GASEOUS FLUXES -----
C
    PRINT 40 $ Z = 0.0
    40 FORMAT( *1*, ///, 10X, *Z*, 13X, *CNH4*, 17X, *CN03*, 16X, *FLUXA
      1*, 16X, *FLUXB*, 16X, *FLUXC*, //, 8X, *(CM)*, 16X, *MICROMOLES /
      2CM3*, 34X, *MICROMOLES / CM2 / DAY*, //, 15X, *.....
      3.....
      4.....*, /, 15X, **, /, 15X, **, )
      00 45 I = 1, NP1
      PRINT 50, Z, CA(I), C3(I), F(1,I), F(2,I), F(3,I)
      50 FORMAT( 7X, F6.2, 2X, **, 2X, 5( E16.8, 5X ) ,
      45 Z = Z + DZ
      RETURN
C
C----- TO PRINT CONCENTRATIONS AND MOLE FRACTIONS -----
C
    55 PRINT 60
    60 FORMAT( *1*, ///, 5X, *Z*, 12X, *CA*, 16X, *CB*, 16X, *CC*, 16X,
      1*CT*, 16X, *XA*, 16X, *XB*, 16X, *XC*, //, 29X, *MICROMOLE / CM3*,
      2 57X, *MOLE FRACTION*, //, 10X, *.....
      3.....
      4.....*, /, 10X, **, )
      Z = 0.0
      00 65 I = 1, NP1
      SUM = C(1,I) + C(2,I) + C(3,I)
      PRINT 70, Z, C(1,I), C(2,I), C(3,I), SUM, X(1,I), X(2,I), X(3,I)
      70 FORMAT( 2X, F6.2, 2X, **, 1X, E14.7, 6( 4X, E14.7 ) ,
      65 Z = Z + DZ
C
C----- TO CALCULATE DIFFUSIVITIES, DIFFUSIVE AND CONVECTIVE FLUXES
C      AND GRADIENTS OF VARIOUS SPECIES AND PRINT THEM OUT ....
C
      N = NP1 - 1
      00 199 I = 1, N

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100 OUTPUT
101 OUTPUT
102 OUTPUT
103 OUTPUT

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104  C1 = 1.0 / D(1) * ( X(2,I) * F(1,I) - X(1,I) * F(2,I) ) OUTPUT
105  C2 = 1.0 / D(2) * ( X(3,I) * F(1,I) - X(1,I) * F(3,I) ) OUTPUT
106  C3 = 1.0 / D(3) * ( X(3,I) * F(2,I) - X(2,I) * F(3,I) ) OUTPUT
107  SUM = F(1,I) + F(2,I) + F(3,I) OUTPUT
108  DIFF(1,I) = ( F(1,I) - X(1,I) * SUM ) / ( C1 + C2 ) OUTPUT
109  DIFF(2,I) = ( F(2,I) - X(2,I) * SUM ) / ( C3 - C1 ) OUTPUT
110  DIFF(3,I) = ( F(3,I) - X(3,I) * SUM ) / ( -C3 - C2 ) OUTPUT
111  Z = 0.0 $ PRINT 97 OUTPUT
112  97 FORMAT( *1*, ///, 5X, *Z*, 11X, *D02-M*, 13X, *DN2-M*, 13X, *CCO OUTPUT
113  12M*, 15X, *JA*, 14X, 6HXA*SUM, 14X, *JC*, 14X, 6HXC*SUM, //, 3X, *( OUTPUT
114  2CM)*, 26X, 11HCM**2 / DAY, 45X, 23HMICROMOLF / CM**2 / DAY, /// ) OUTPUT
115  C0 98 I = 1, N OUTPUT
116  SUM = F(1,I) + F(2,I) + F(3,I) $ C1 = X(1,I) * SUM OUTPUT
117  C2 = X(3,I) * SUM $ C3 = F(1,I) - C1 OUTPUT
118  C4 = F(3,I) - C2 OUTPUT
119  PRINT 77, Z, DIFF(1,I), DIFF(2,I), DIFF(3,I), C3, C1, C4, C2 OUTPUT
120  Z = Z + DZ OUTPUT
121  77 FORMAT( 2X, F6.2, 7(4X, E14.7) ) OUTPUT
122  PRINT 99 OUTPUT
123  99 FORMAT( *1*, ///, 5X, *Z*, 13X, *JC*, 16X, 6HXA*SUM, 16X, *SUM*, 1 OUTPUT
124  15X, *DXA/DZ*, 14X, *DXB/DZ*, 14X, *DXC/DZ*, /// ) OUTPUT
125  Z = 0.0 $ NM1 = N01 - 2 $ CON = 1.0 / 60.0 OUTPUT
126  C0 96 I = 1, NP1 OUTPUT
127  SUM = F(1,I) + F(2,I) + F(3,I) OUTPUT
128  C1 = X(2,I) * SUM $ C2 = F(2,I) - C1 OUTPUT
129  IF ( I .LE. 3 .OR. I .GE. NM1 ) GO TO 95 OUTPUT
130  K = I - 1 $ K1 = I - 2 $ K2 = I - 3 OUTPUT
131  J = I + 1 $ J1 = I + 2 $ J2 = I + 3 OUTPUT
132  C3 = - CON * X(1,K2) + 0.15 * X(1,K1) - 0.75 * X(1,K) + 0.75 * X OUTPUT
133  1(1,J) - 0.15 * X(1,J1) + CON * X(1,J2) OUTPUT
134  C4 = - CON * X(2,K2) + 0.15 * X(2,K1) - 0.75 * X(2,K) + 0.75 * X OUTPUT
135  1(2,J) - 0.15 * X(2,J1) + CON * X(2,J2) OUTPUT
136  C5 = - CON * X(3,K2) + 0.15 * X(3,K1) - 0.75 * X(3,K) + 0.75 * X OUTPUT
137  1(3,J) - 0.15 * X(3,J1) + CON * X(3,J2) OUTPUT

```

```
PRINT 94, Z, C2, C1, SUM, C3, C4, C5
94 FORMAT( 2X, F6.2, 6( 5X, E15.7) )
GO TO 96
95 PRINT 93, Z, C2, C1, SUM
93 FORMAT( 2X, F6.2, 3( 5X, E15.7) )
96 Z = Z + 0Z
RETURN
END
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 DETERMINATION OF SOIL AIR COMPOSITION USING EQUATION OF CONTINUITY

 DATA INPUT TO THE SYSTEM

A. OPERATING CHARACTERISTICS OF THE SYSTEM

1. INPUT CONCENTRATION OF THE AMMONIA SOLUTION = 60.714 PPM
2. RATE OF PRECIPITATION AT THE SURFACE = 6.000 CM / DAY
3. MAXIMUM RATE OF RESPIRATION AT THE SURFACE = .000 MICRO-MOLES / GM SOIL / DAY

H. PHYSICAL CHARACTERISTICS OF THE SOIL SYSTEM

1. POROSITY OF SOIL = .400 CC VOIDS / CC SOIL
2. MOISTURE CONTENT OF THE SOIL = .850 PERCENT VOIDS OCCUPIED BY WATER
3. BULK DENSITY OF THE SOIL = 1.650 GM / CC SOIL

C. BIOLOGICAL REACTION RATE CONSTANTS (REACTIONS ARE ASSUMED TO BE OF MICHELIS MENTEN TYPE)

1. MAXIMUM RATE OF NITRIFICATION = 2.0000 MICROMOLES / DAY
2. MAXIMUM RATE OF DENITRIFICATION = 1.0000 MICROMOLES / DAY
3. MICHELIS-MENTEN CONSTANT FOR NITRIFICATION REACTION = 1.00n0 MICROMOLES / CM3
4. MICHELIS-MENTEN CONSTANT FOR DENITRIFICATION REACTION = 4.0000 MICROMOLES / CM3

DENITRIFICATION IS ASSUMED TO TAKE PLACE ONLY IF OXYGEN CONC IS LESS THAN .05000

D. DIFFUSIVITIES OF DIFFERENT SPECIES

1. DIFFUSIVITY OF NH4 IN LIQUID SOLUTION = 3.00 CM**2 / DAY
2. DIFFUSIVITY OF NO3 IN LIQUID SOLUTION = 3.000 CM**2 / DAY
3. DIFFUSIVITY OF OXYGEN IN NITROGEN = 250.00 CM**2 / DAY
4. DIFFUSIVITY OF OXYGEN IN CARBON DIOX = 150.00 CM**2 / DAY
5. DIFFUSIVITY OF CO2 IN NITROGEN = 150.00 CM**2 / DAY

E. VALUES OF PARAMETERS USED IN NUMERICAL SOLUTION

1. TOTAL DEPTH OF SOIL TO BE SIMULATED = 100.00 CMS
2. NUMBER OF GRID POINTS USED = 51
3. DEPTH INCREMENT USED IN NUMERICAL SOLUTION = 2.00 CM

λ (Å)	CNH4	MICROMULES / CM3	CNU3	FLUXA	MICROMULES / CM2 / DAY	FLUXB	FLUXC
2.00	35114294E+01	0	50609764E+00	24892096E+03	54898112E+01	3724528E+02	3724528E+02
4.00	305373269E+01	0	59147554E+00	18085966E+03	54898112E+01	3724528E+02	3724528E+02
6.00	20789811E+01	0	14781739E+01	14926208E+03	54898112E+01	3724528E+02	3724528E+02
8.00	165343344E+01	0	10797176E+01	11979113E+03	54898112E+01	3724528E+02	3724528E+02
10.00	135883929E+00	0	26298803E+01	9298565E+02	54898112E+01	3724528E+02	3724528E+02
12.00	934422697E+00	0	2772973E+01	4935717E+02	54898112E+01	3724528E+02	3724528E+02
14.00	65545531E+00	0	2772973E+01	3351487E+02	54898112E+01	3724528E+02	3724528E+02
16.00	43618497E+00	0	28518051E+01	2173683E+02	50190918E+01	5255821E+01	5255821E+01
18.00	27832390E+00	0	2870237E+01	1355544E+02	47831448E+01	45783144E+01	45783144E+01
20.00	1712467E+00	0	2838518E+01	8203024E+01	45292760E+01	43198452E+01	43198452E+01
22.00	10290065E+00	0	2770127E+01	26778843E+01	40198452E+01	3876512E+01	3876512E+01
24.00	60390219E+01	0	26778843E+01	28414008E+01	43198452E+01	3663751E+01	3663751E+01
26.00	35149764E+01	0	2458807E+01	1646917E+01	3876512E+01	3258354E+01	3258354E+01
28.00	21100131E+01	0	2333217E+01	9497402E+00	3663751E+01	3065998E+01	3065998E+01
30.00	17100131E+01	0	22250650E+01	5460581E+00	3258354E+01	2808008E+01	2808008E+01
32.00	17100131E+01	0	22250650E+01	31341259E+00	3065998E+01	2701454E+01	2701454E+01
34.00	38555087E+02	0	2114648E+01	17970405E+00	2808008E+01	2529285E+01	2529285E+01
36.00	38555087E+02	0	2004024E+01	10297736E+00	2701454E+01	2205446E+01	2205446E+01
38.00	12662082E+03	0	1896736E+01	5899187E+00	2529285E+01	1909329E+01	1909329E+01
40.00	12662082E+03	0	17930936E+01	10297736E+00	2205446E+01	1771162E+01	1771162E+01
42.00	23737245E+03	0	15973160E+01	1934945E+00	2054462E+01	1639035E+01	1639035E+01
44.00	17637448E+03	0	1505288E+01	1108041E+00	1909329E+01	1513644E+01	1513644E+01
46.00	77992259E+04	0	1417159E+01	6344940E+00	1771162E+01	1394033E+01	1394033E+01
48.00	44863259E+04	0	1332927E+01	3332070E+00	1639035E+01	1280873E+01	1280873E+01
50.00	25574464E+04	0	1252515E+01	2080403E+00	1513644E+01	1171187E+01	1171187E+01
52.00	1464403E+04	0	1175813E+01	1912466E+00	1394033E+01	1071625E+01	1071625E+01
54.00	8351908E+05	0	1102929E+01	6821092E+00	1280873E+01	9751905E+01	9751905E+01
56.00	48013654E+05	0	1033041E+01	3905749E+00	1171187E+01	8845202E+01	8845202E+01
58.00	27493227E+05	0	9678089E+00	2284520E+00	1071625E+01	7986033E+01	7986033E+01
60.00	15742627E+05	0	905493E+00	1280873E+00	9751905E+01	7180667E+01	7180667E+01
62.00	90140150E+06	0	8464263E+00	7332348E+00	8845202E+01	647277E+01	647277E+01
64.00	51614199E+06	0	7906347E+00	4198349E+00	7986033E+01	5706991E+01	5706991E+01
66.00	29522749E+06	0	7374646E+00	2403844E+00	7180667E+01	5036677E+01	5036677E+01
68.00	16922749E+06	0	6883040E+00	1376290E+00	647277E+01	4408183E+01	4408183E+01
70.00	96839545E+07	0	6483040E+00	7874344E+00	5706991E+01	3817307E+01	3817307E+01
72.00	55744611E+07	0	5975380E+00	4510218E+00	5036677E+01	3255821E+01	3255821E+01
74.00	3770451E+07	0	5562275E+00	2581263E+00	4408183E+01	2701454E+01	2701454E+01
76.00	18191738E+07	0	5174356E+00	1476539E+00	3817307E+01	2255821E+01	2255821E+01
78.00	10416576E+08	0	4810730E+00	8481794E+00	3255821E+01	1809329E+01	1809329E+01
80.00	59645243E+08	0	4470194E+00	4818877E+00	2701454E+01	1403263E+01	1403263E+01
82.00	34155584E+08	0	4151555E+00	2746423E+00	2255821E+01	1020459E+01	1020459E+01
84.00	1955584E+08	0	3853761E+00	1557712E+00	1809329E+01	7986033E+01	7986033E+01
86.00	11174740E+08	0	3575460E+00	8790826E+00	1403263E+01	647277E+01	647277E+01
88.00	64118097E+09	0	3312304E+00	4847368E+00	1020459E+01	5036677E+01	5036677E+01
90.00	36712626E+09	0	3072636E+00	2688380E+00	7986033E+01	4408183E+01	4408183E+01
92.00	21080702E+09	0	2827043E+00	1378999E+00	647277E+01	3817307E+01	3817307E+01
94.00	12003936E+09	0	2627043E+00	6611513E+00	5036677E+01	3255821E+01	3255821E+01
96.00	70677380E+10	0	2480469E+00	2288600E+00	4408183E+01	2701454E+01	2701454E+01
98.00	30290306E+10	0	2141669E+00	0	3817307E+01	2255821E+01	2255821E+01
100.00		0		0	3255821E+01	1809329E+01	1809329E+01

Z (CH)	DUZ-M	UN2-M UM*2 / DAY	U0U2M	JA	XA*SUM MICROMULE / UM*2 / DAY	JC	XC*SUM
00	2476905E+03	2594403E+03	1500000E+03	2111124E+01	3780856E+02	1377802E+02	5408950E+01
200	2470027E+03	2604497E+03	1500000E+03	1854911E+03	2523120E+02	1433019E+02	5444255E+00
400	2458017E+03	2630427E+03	1500000E+03	1903149E+03	1581751E+02	1476087E+02	5452632E+01
600	2445801E+03	2640175E+03	1500000E+03	11519430E+03	4590135E+01	1463057E+02	5453184E+00
800	2435562E+03	2649672E+03	1500000E+03	91219000E+02	1727567E+01	1426072E+02	5459190E+00
1000	2433941E+03	2652664E+03	1500000E+03	6924336E+02	3727627E+01	1426072E+02	5459190E+00
1200	2431730E+03	2654771E+03	1500000E+03	5045495E+02	8712037E+00	1414171E+02	5462379E+00
1400	2429490E+03	2656102E+03	1500000E+03	3457005E+02	1120437E+00	1204371E+02	5463726E+01
1600	2427315E+03	2657672E+03	1500000E+03	2148026E+02	1312679E+01	1007721E+02	5467229E+01
1800	2425125E+03	2659472E+03	1500000E+03	1480265E+02	1324914E+01	953549E+01	5469623E+01
2000	2423029E+03	2661497E+03	1500000E+03	6082480E+01	1226660E+01	8788439E+01	5471335E+01
2200	2421027E+03	2663751E+03	1500000E+03	4002604E+01	1161204E+01	7884398E+01	5473501E+01
2400	2419147E+03	2666174E+03	1500000E+03	2743327E+01	1094404E+01	7066212E+01	5475497E+01
2600	2417382E+03	2668790E+03	1500000E+03	1973977E+01	1028317E+01	6296716E+01	5477497E+01
2800	2415731E+03	2671545E+03	1500000E+03	1510849E+01	9640313E+00	5496716E+01	5479497E+01
3000	2414192E+03	2674422E+03	1500000E+03	1022621E+01	9020319E+00	5432490E+01	5481497E+01
3200	2412767E+03	2677422E+03	1500000E+03	8917057E+00	8429169E+00	5428739E+01	5483497E+01
3400	2411452E+03	2680542E+03	1500000E+03	7917055E+00	7867349E+00	5428739E+01	5485497E+01
3600	2410247E+03	2683782E+03	1500000E+03	7152346E+00	7327399E+00	5428739E+01	5487497E+01
3800	2409154E+03	2687142E+03	1500000E+03	6584400E+00	6816566E+00	5428739E+01	5489497E+01
4000	2408171E+03	2690622E+03	1500000E+03	5984400E+00	633352E+00	5428739E+01	5491497E+01
4200	2407307E+03	2694222E+03	1500000E+03	5506703E+00	5933254E+00	5428739E+01	5493497E+01
4400	2406562E+03	2697942E+03	1500000E+03	4664273E+00	543319E+00	5428739E+01	5495497E+01
4600	2405927E+03	2701782E+03	1500000E+03	4294273E+00	4647608E+00	5428739E+01	5497497E+01
4800	2405402E+03	2705742E+03	1500000E+03	3942780E+00	4294273E+00	5428739E+01	5499497E+01
5000	2404987E+03	2709822E+03	1500000E+03	3612342E+00	3938665E+00	5428739E+01	5501497E+01
5200	2404682E+03	2714022E+03	1500000E+03	331907E+00	3614242E+00	5428739E+01	5503497E+01
5400	2404387E+03	2718342E+03	1500000E+03	302251E+00	3309671E+00	5428739E+01	5505497E+01
5600	2404102E+03	2722782E+03	1500000E+03	275227E+00	3021772E+00	5428739E+01	5507497E+01
5800	2403827E+03	2727342E+03	1500000E+03	2497705E+00	275227E+00	5428739E+01	5509497E+01
6000	2403562E+03	2732022E+03	1500000E+03	226888E+00	2497705E+00	5428739E+01	5511497E+01
6200	2403307E+03	2736822E+03	1500000E+03	2038833E+00	226888E+00	5428739E+01	5513497E+01
6400	2403062E+03	2741742E+03	1500000E+03	1827849E+00	2038833E+00	5428739E+01	5515497E+01
6600	2402827E+03	2746782E+03	1500000E+03	1631093E+00	1827771E+00	5428739E+01	5517497E+01
6800	2402602E+03	2751942E+03	1500000E+03	1479338E+00	1631093E+00	5428739E+01	5519497E+01
7000	2402387E+03	2757222E+03	1500000E+03	127611E+00	1479338E+00	5428739E+01	5521497E+01
7200	2402182E+03	2762622E+03	1500000E+03	1115332E+00	1275566E+00	5428739E+01	5523497E+01
7400	2401987E+03	2768142E+03	1500000E+03	962493E+00	1115332E+00	5428739E+01	5525497E+01
7600	2401802E+03	2773782E+03	1500000E+03	825604E+00	962493E+00	5428739E+01	5527497E+01
7800	2401627E+03	2779542E+03	1500000E+03	692758E+00	825604E+00	5428739E+01	5529497E+01
8000	2401462E+03	2785422E+03	1500000E+03	572560E+00	692758E+00	5428739E+01	5531497E+01
8200	2401307E+03	2791422E+03	1500000E+03	458452E+00	572560E+00	5428739E+01	5533497E+01
8400	2401162E+03	2797542E+03	1500000E+03	353554E+00	458452E+00	5428739E+01	5535497E+01
8600	2401027E+03	2803782E+03	1500000E+03	260908E+00	353554E+00	5428739E+01	5537497E+01
8800	2400902E+03	2810142E+03	1500000E+03	1827849E+00	260908E+00	5428739E+01	5539497E+01
9000	2400787E+03	2816622E+03	1500000E+03	1631093E+00	226888E+00	5428739E+01	5541497E+01
9200	2400682E+03	2823222E+03	1500000E+03	1479338E+00	2038833E+00	5428739E+01	5543497E+01
9400	2400587E+03	2830042E+03	1500000E+03	127611E+00	1827771E+00	5428739E+01	5545497E+01
9600	2400502E+03	2837082E+03	1500000E+03	1115332E+00	1631093E+00	5428739E+01	5547497E+01
9800	2400427E+03	2844342E+03	1500000E+03	962493E+00	1479338E+00	5428739E+01	5549497E+01
10000	2400362E+03	2851822E+03	1500000E+03	825604E+00	1275566E+00	5428739E+01	5551497E+01
10200	2400307E+03	2859422E+03	1500000E+03	692758E+00	1115332E+00	5428739E+01	5553497E+01
10400	2400262E+03	2867142E+03	1500000E+03	572560E+00	962493E+00	5428739E+01	5555497E+01
10600	2400227E+03	2875082E+03	1500000E+03	458452E+00	825604E+00	5428739E+01	5557497E+01
10800	2400192E+03	2883242E+03	1500000E+03	353554E+00	692758E+00	5428739E+01	5559497E+01
11000	2400167E+03	2891522E+03	1500000E+03	260908E+00	572560E+00	5428739E+01	5561497E+01
11200	2400142E+03	2900022E+03	1500000E+03	1827849E+00	458452E+00	5428739E+01	5563497E+01
11400	2400127E+03	2908742E+03	1500000E+03	1631093E+00	353554E+00	5428739E+01	5565497E+01
11600	2400112E+03	2917682E+03	1500000E+03	1479338E+00	260908E+00	5428739E+01	5567497E+01
11800	2400097E+03	2926842E+03	1500000E+03	127611E+00	226888E+00	5428739E+01	5569497E+01
12000	2400082E+03	2936222E+03	1500000E+03	1115332E+00	2038833E+00	5428739E+01	5571497E+01
12200	2400067E+03	2945822E+03	1500000E+03	962493E+00	1827771E+00	5428739E+01	5573497E+01
12400	2400052E+03	2955642E+03	1500000E+03	825604E+00	1631093E+00	5428739E+01	5575497E+01
12600	2400037E+03	2965682E+03	1500000E+03	692758E+00	1479338E+00	5428739E+01	5577497E+01
12800	2400022E+03	2975942E+03	1500000E+03	572560E+00	1275566E+00	5428739E+01	5579497E+01
13000	2400007E+03	2986422E+03	1500000E+03	458452E+00	1115332E+00	5428739E+01	5581497E+01
13200	2400002E+03	2997122E+03	1500000E+03	353554E+00	962493E+00	5428739E+01	5583497E+01
13400	2400002E+03	3008042E+03	1500000E+03	260908E+00	825604E+00	5428739E+01	5585497E+01
13600	2400002E+03	3019182E+03	1500000E+03	1827849E+00	692758E+00	5428739E+01	5587497E+01
13800	2400002E+03	3030542E+03	1500000E+03	1631093E+00	572560E+00	5428739E+01	5589497E+01
14000	2400002E+03	3042122E+03	1500000E+03	1479338E+00	458452E+00	5428739E+01	5591497E+01
14200	2400002E+03	3053922E+03	1500000E+03	127611E+00	353554E+00	5428739E+01	5593497E+01
14400	2400002E+03	3065942E+03	1500000E+03	1115332E+00	260908E+00	5428739E+01	5595497E+01
14600	2400002E+03	3078182E+03	1500000E+03	962493E+00	226888E+00	5428739E+01	5597497E+01
14800	2400002E+03	3090642E+03	1500000E+03	825604E+00	2038833E+00	5428739E+01	5599497E+01
15000	2400002E+03	3103322E+03	1500000E+03	692758E+00	1827771E+00	5428739E+01	5601497E+01
15200	2400002E+03	3116222E+03	1500000E+03	572560E+00	1631093E+00	5428739E+01	5603497E+01
15400	2400002E+03	3129342E+03	1500000E+03	458452E+00	1479338E+00	5428739E+01	5605497E+01
15600	2400002E+03	3142682E+03	1500000E+03	353554E+00	1275566E+00	5428739E+01	5607497E+01
15800	2400002E+03	3156242E+03	1500000E+03	260908E+00	1115332E+00	5428739E+01	5609497E+01
16000	2400002E+03	3170022E+03	1500000E+03	1827849E+00	962493E+00	5428739E+01	5611497E+01
16200	2400002E+03	3184022E+03	1500000E+03	1631093E+00	825604E+00	5428739E+01	5613497E+01
16400	2400002E+03	3198242E+03	1500000E+03	1479338E+00	692758E+00	5428739E+01	5615497E+01
16600	2400002E+03	3212682E+03	1500000E+03	127611E+00	572560E+00	5428739E+01	5617497E+01
16800	2400002E+03	3227342E+03	1500000E+03	1115332E+00	458452E+00	5428739E+01	5619497E+01
17000	2400002E+03	3242222E+03	1500000E+03	962493E+00	353554E+00	5428739E+01	5621497E+01
17200	2400002E+03	3257322E+03	1500000E+03	825604E+00	260908E+00	5428739E+01	5623497E+01
17400	2400002E+03	3272642E+03	1500000E+03	692758E+00	226888E+00	5428739E+01	5625497E+01
17600	2400002E+03	3288182E+03	1500000E+03	572560E+00	2038833E+00	5428739E+01	5627497E+01
17800	2400002E+03	3303942E+03	1500000E+03	458452E+00	1827771E+00	5428739E+01	5629497E+01
18000	2400002E+03	3319922E+03	1500000E+03	353554E+00	1631093E+00	5428739E+01	5631497E+01
18200	2400002E+03	3336122E+03	1500000E+03	260908E+00	1479338E+00	5428739E+01	5633497E+01
18400	2400002E+03	3352542E+03	1500000E+03	1827849E+00	1275566E+00	5428739E+01	5635497E+01
18600	2400002E+03	3369182E+03	1500000E+03	1631093E+00	1115332E+00	5428739E+01	5637497E+01
18800	2400002E+03	3386042E+03	1500000E+03	1479338E+00	962493E+00	5428739E+01	5639497E+01
19000	2400002E+03	3403122E+03	1500000E+03	127611E+00	825604E+00	5428739E+01	5641497E+01
19200	2400002E+03	3420422E+03	1500000E+03	1115332E+00	692758E+00	5428739E+01	5643497E+01
19400	2400002E+03	3437942E+03	1500000E+				

