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**SOLUTE MOVEMENT ASSOCIATED WITH
INTERMITTENT SOIL WATER FLOW**

A thesis presented in partial fulfilment of the requirements for the degree of Doctor
of Philosophy in Soil Science at Massey University

RUSSELL WOODFORD TILLMAN

1991

Soil Science

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ABSTRACT

The movement of nutrients within the root zone of orchard crops is important in determining both fruit yield and quality. Currently much of the research on solute movement in field soils concerns movement of chemicals to ground water. Little attention has been paid to smaller scale movement. In this study the movement of solutes in response to intermittent soil water flow was investigated in columns of repacked silt loam in the laboratory and in a similar soil in the field.

In the laboratory study a 5mm pulse of a solution of potassium bromide and urea in tritiated water was applied to columns of repacked soil, left for three or ten days, and then leached with 30 mm of distilled water. Twelve days after the solute pulse was applied, the distributions of water, tritiated water, applied and resident nutrients and pH were measured.

The bulk of the bromide and tritiated water was moved to between 50 and 150 mm depth in both water treatments. As the nitrogen applied in urea was mainly in the form of ammonium after three days, the water applied then caused little movement of nitrogen. But the water applied after 10 days caused the nitrogen, now in the form of nitrate, to move in a similar fashion to the bromide.

The soil solution anion concentration determined the amount of cations leached. Calcium and magnesium were the dominant cations accompanying the nitrate and bromide downwards. The added potassium remained near the soil surface.

Given the soil hydraulic properties, the behaviour of water and solutes could be simulated by coupling the water flow equations with the convection-dispersion equation, and by using solute dispersion, diffusion and adsorption parameters derived from the literature. The model assumed the Gapon relationship for cation exchange, and that hydrogen ion production during nitrification reduced the effective cation exchange capacity. It was able to simulate closely the experimental data.

Two field experiments were conducted. The first involved application of a 5 mm pulse of potassium bromide solution followed by 50 mm of water to pasture plots of contrasting initial water content. Twenty-four hours later core samples of soil were collected and the distribution of water and bromide measured. Bromide applied to initially dry soil was much more resistant to leaching than bromide applied to moist soil.

The second experiment lasted 12 days and was essentially an analogue of the laboratory experiment. The final nutrient distributions however differed considerably from those obtained in the laboratory, due to non-uniform flow in the structured field soil.

Coupling a mobile-immobile variant of the convection-dispersion model with a description of the water flow provided a mechanistic model. When combined with the submodels developed in the laboratory study describing nutrient interactions and transformations, this model successfully described the solute movement under the four different field regimes of water and solute application. Evaporation and plant uptake, and diffusion between mobile and immobile phases emerged as key processes affecting nutrient movement. It is suggested some control over nutrient movement is possible by varying the relative timing of water and fertiliser applications.

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LIST OF SYMBOLS

ARABIC

a	empirical coefficient [m]
b	empirical coefficient [dimensionless]
C	soil solution concentration [mol m ⁻³ solution]
C_{ent}	soil solution concentration at input surface [mol m ⁻³ solution]
C_{ex}	soil solution concentration at exit surface [mol m ⁻³ solution]
c	empirical constant [m s ⁻¹]
d	empirical constant [dimensionless]
D	molecular diffusion coefficient [m ² s ⁻¹]
D_o	molecular diffusion coefficient in pure solution
E	dispersion coefficient [m ² s ⁻¹]
f	probability density function [m ⁻¹] (Chapter 1)
f	porosity [m ³ m ⁻³] (Chapters 2 & 4)
I	cumulative drainage [m]
j	solute flux density [mol m ⁻² s ⁻¹]
K	hydraulic conductivity [m s ⁻¹]
K_d	distribution coefficient [m ³ kg ⁻¹]
k_a	rate constant for ammonia nitrification [s ⁻¹]
k_G	selectivity coefficient in Gapon equation [(mol m ⁻³) ^{1/2}]
k_u	rate constant for urea hydrolysis [s ⁻¹]
M	adsorbed plus solution solute concentration [mol m ⁻³ soil]
P	cation exchange capacity [mol charge m ⁻³ soil]
p	number of compartments in model
q	Darcy flux density of water [m s ⁻¹]
R	retardation factor [dimensionless]
S	sink for root water uptake [m ³ water m ⁻³ soil s ⁻¹]
t	time [s]
v	average velocity in soil [m s ⁻¹]
X	amount of cation charge balanced [mol m ⁻³ soil]
Y	adsorbed solute concentration [mol kg ⁻¹]
z	depth [m]

GREEK SYMBOLS

ϵ	empirical constant [dimensionless] (Chapter 2)
α	$M_k + M_a + M_s$ [mol m ⁻³ soil] (Chapter 3)
α	rate coefficient for mobile-immobile exchange [s ⁻¹] (Chapters 1,4 & 5)
β	$M_c + M_g$ [mol m ⁻³ soil]
γ	$(\alpha + 2\beta - P)/\Theta$ [mol m ⁻³ sol] (Chapter 3)
γ	empirical constant [m ⁻¹] (Chapter 4)
Θ	$\theta - \theta_x$
θ	soil water content [m ³ m ⁻³]
θ_c	water content dividing mobile and immobile water
θ_k	water content used in describing $K(\theta)$ in Chapter 2
θ_x	water content of double-layer
λ	dispersivity [m]
μ	mean
ρ_b	bulk density [kg m ⁻³]
σ	standard deviation
ψ	matric potential [m]

COMMON SUBSCRIPTS

a	ammonium
B	bivalent cations
c	calcium
g	magnesium
i	chemical species of interest (Chapters 2 and 3)
i	immobile phase (Chapters 1,4 and 5)
k	potassium
M	monovalent cations
m	mobile phase
n	nitrate or compartment number
s	sodium
u	urea

CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

THE PURPOSE OF THE STUDY

The aim of the study described here was to use modelling and experimentation to gain a better understanding of the movement and distribution of nutrients in soil, under conditions which are relevant to orchard crops. The concern with nutrient behaviour in orchard soils was prompted by a number of factors.

Kiwifruit has lost its status as a novelty fruit and this, together with increasing production in other countries, will mean that prices remain depressed in the foreseeable future. To remain viable therefore, growers have to maximise fruit quality and pack-out rate.

Furthermore there is a growing incidence of storage disorders in kiwifruit and other crops that appear related to vine nutrition and orchard management. It seems likely that these can be partly attributed to nutritional problems, which can arise when orchards are established on soils never before used for horticulture. Here there is no bank of past practical experience to draw on. There is also evidence that some of these problems can be attributed to ill-considered fertiliser and irrigation practices.

Also the introduction of new crops, such as nashi, has caused many difficulties when the traditional cultural practices in the country of origin prove unsuitable in the New Zealand environment.

As well it is now being realised increasingly that nutrients and other agricultural chemicals leaching from intensive horticultural systems can decrease the quality of ground and surface waters.

Thus it is clear that the nutritional management of orchard crops is much more complicated than is the case for pasture or broad-scale cropping. Consequently additional factors must be considered.

Plant roots, especially those of young plants, may not be evenly distributed through the soil, but may be concentrated in the herbicide strips. If so, it is here that the bulk of fertiliser and irrigation water is, or should be applied.

Confounding the issue is that there is a pronounced seasonality of demand for nutrients. This may preclude the use of a simple balance model for fertiliser application, whereby nutrients lost in production are replaced by a single annual application. This is likely to be more significant for vines such as kiwifruit which have little internal storage of nutrients as compared to larger plants such as apple trees.

Orchard plants are usually deep-rooting. This can be an advantage initially as the large soil volume explored can usually supply all the nutrients required. However once a nutrient imbalance does arise, it can require very high rates of application to overcome the problem throughout the entire root zone. An example of this is the exceedingly high rates of potassium which have been found necessary to overcome deficiencies in kiwifruit.

In New Zealand therefore the combination of spatially- and temporally-variable rates of fertiliser and irrigation water, supplemented by substantial but irregular rainfall, means that an understanding of water and nutrient movement through soils is a critical prerequisite for the successful management of orchard nutrition.

When considering the most appropriate form of model for nutrient movement relevant for orchard soils, the following factors need to be taken into account.

- The application of both water and nutrients is transient and spatially variable, thereby inducing large spatial and temporal variability in soil water and solute content.

- There is considerable time between applications to allow for redistribution of both water and nutrients.
- The majority of nutrients will be involved in strong chemical interactions with the surfaces of soil particles, and a number may be consumed or even released by a host of microbiological processes.
- Biological processes and fertiliser additions will alter the chemical environment (e.g. pH) within the soil, which in turn will affect the behaviour of other nutrients.
- Plant uptake of both water and nutrients will be a significant factor affecting their distribution.

As a consequence, regardless of the final form of the model of solute movement chosen to be appropriate for orchard soils, it will be necessary to take into account at least the first-order physical, chemical and biological processes affecting the major plant nutrients within the root zone.

REVIEW OF SOLUTE MOVEMENT IN SOIL

Introduction

Before outlining the structure of the study, it is pertinent to present an overview of the approaches that other workers have adopted to describe solute movement in soils.

Although scientists have developed a good qualitative understanding of the various physical, chemical and biological processes to which solutes in the soil are subject, attempts to integrate this information to provide quantitative descriptions of the movement of nutrients in field soils have often been unsatisfactory. This review discusses some of the reasons for these difficulties, and describes some of the

approaches used to explain the movement and subsequent distribution of nutrients in soils.

Water moves in soil in response to a potential gradient (e.g. Jury *et al.*, 1991). For water in the unsaturated zone of the earth's crust, the major contributors to these potential gradients are gravity (gravitational potential), the interaction of water with the soil surfaces (matric potential or soil water pressure potential) and the osmotic potential created by various solutes. While the potential gradient imposed by gravity is constant, the matric potential is a function of soil water content. These two potentials dominate.

The flow of water along these potential gradients occurs through soil pores, and the rate of flow is strongly dependent on the size and geometry of these pores. The other major factor governing the rate of flow along a given potential gradient is the water content of the soil, as this determines which of the pores are water-filled, and so conductive. For a given potential gradient the amount of flow through a water-filled pore varies as the fourth power of the radius. This very strong dependence upon the size of the pore means for structured soils at or close to saturation, total flow can be dominated by the movement through a small number of relatively large pores (Scotter and Kanchanasut, 1981). This phenomenon can lead to large quantities of water by-passing most of the soil, and is termed "preferential flow".

The large pores which are responsible for preferential flow are however the first to drain and become air-filled as the soil desaturates. Thus preferential flow is most apparent in situations where either the soil profile is saturated, or the rate of application of water to the soil surface exceeds the infiltrability, thereby causing ponding of free water.

The movement of chemicals dissolved in the soil water is the result of the convective mass flow of water, plus molecular diffusion in response to a concentration gradient within the water, and of the interaction between these two processes. Also, most nutrients of interest can either react chemically with one or more soil constituents, or are generated or consumed by soil organisms. Such chemical and biological processes must also be taken into account when considering solute movement.

When solutes are convected through soil in moving water, the initially-sharp solute front is gradually smeared or spreads out. This spreading of the solute front is termed dispersion, and is the result of molecular diffusion, and of hydrodynamic dispersion due to variations in pore size and tortuosity of flow path which result in a range of pore water velocities. Biggar and Nielsen (1967) provide an excellent description of the various physical processes operating during solute transport.

The Convection-Dispersion Equation

Classically the most common approach to describing hydrodynamic dispersion is to treat it mathematically as enhanced diffusion. Then the movement of a non-reactive solute during steady liquid flow can be described by (Nielsen and Biggar, 1962)

$$\frac{\partial C}{\partial t} = E \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} , \quad (1.1)$$

where C is the soil solution concentration of solute [mol m^{-3}], t is time [s], z is depth [m], and E is the dispersion coefficient [$\text{m}^2 \text{s}^{-1}$] which is dependent on the soil, the solute and the liquid flow rate. The average velocity of water through the soil v [m s^{-1}] is

$$v = \frac{q}{\theta} , \quad (1.2)$$

where q is the water flux density [m s^{-1}] and θ is the volumetric water content [$\text{m}^3 \text{m}^{-3}$]. Equation (1.1) is commonly referred to as the convection-dispersion equation (CDE), and equations of this type, when solved for the initial and boundary conditions describing the application of a short "pulse" of solute under steady-state flow conditions, depict a pulse moving down at velocity v and becoming more spread out and less peaked with time.

The CDE has been found to give a good description of the observed movement of non-interactive solutes through columns of repacked soils, as well as in some field situations (e.g. Gardner, 1965). A considerable body of literature now exists to provide solutions for a number of different initial and boundary conditions (e.g. Bresler and Hanks, 1969; van Genuchten and Cleary, 1979; van Genuchten and Alves, 1982), and also to offer insights into the nature of the dispersion coefficient (e.g. Warrick *et al.*, 1971, 1972; Smiles *et al.*, 1978, 1981; Bond, 1986).

The dispersion coefficient (E) in equation (1.1) accounts for both diffusion and hydrodynamic dispersion. The extent of hydrodynamic dispersion is approximately linearly-dependent on flow velocity, and at most flow rates in short-term experiments on coarse-textured soils is more important than diffusion (Fig 1.1) (Olsen and Kemper, 1968; Nye and Tinker, 1977; Campbell, 1985). In long-term experiments however, where inputs of water are intermittent, the intervening role of molecular diffusion becomes more important.

Although the CDE has been successful in describing outflow concentrations in miscible displacement experiments in uniform porous media, this does not necessarily provide any validation of the assumptions inherent in the mathematical model, as E cannot be determined independently. It must be deduced empirically for the soil and solute, by conducting similar experiments to that being modelled. This limitation has been highlighted recently in a review by Jury (1988), and an accompanying commentary by Knight (1988). Jury (1988) cites evidence, reviewed by Gelhar *et al.* (1985), which demonstrates that E is often not constant but can vary with z . Jury (1988) points out that such a dependence can be predicted by analogous theoretical considerations of solute transport through a capillary tube (Taylor, 1953). These considerations suggested that if the lateral variations in concentration within the tube, caused by variations in velocity, can be smoothed out by transverse mixing or diffusion during the time of residence between the point of entry and the point of observation, then E will be relatively constant and the CDE will be valid for the area-averaged concentration. If however the velocity is such that there is insufficient time for complete transverse mixing, then E will be expected to scale with z .

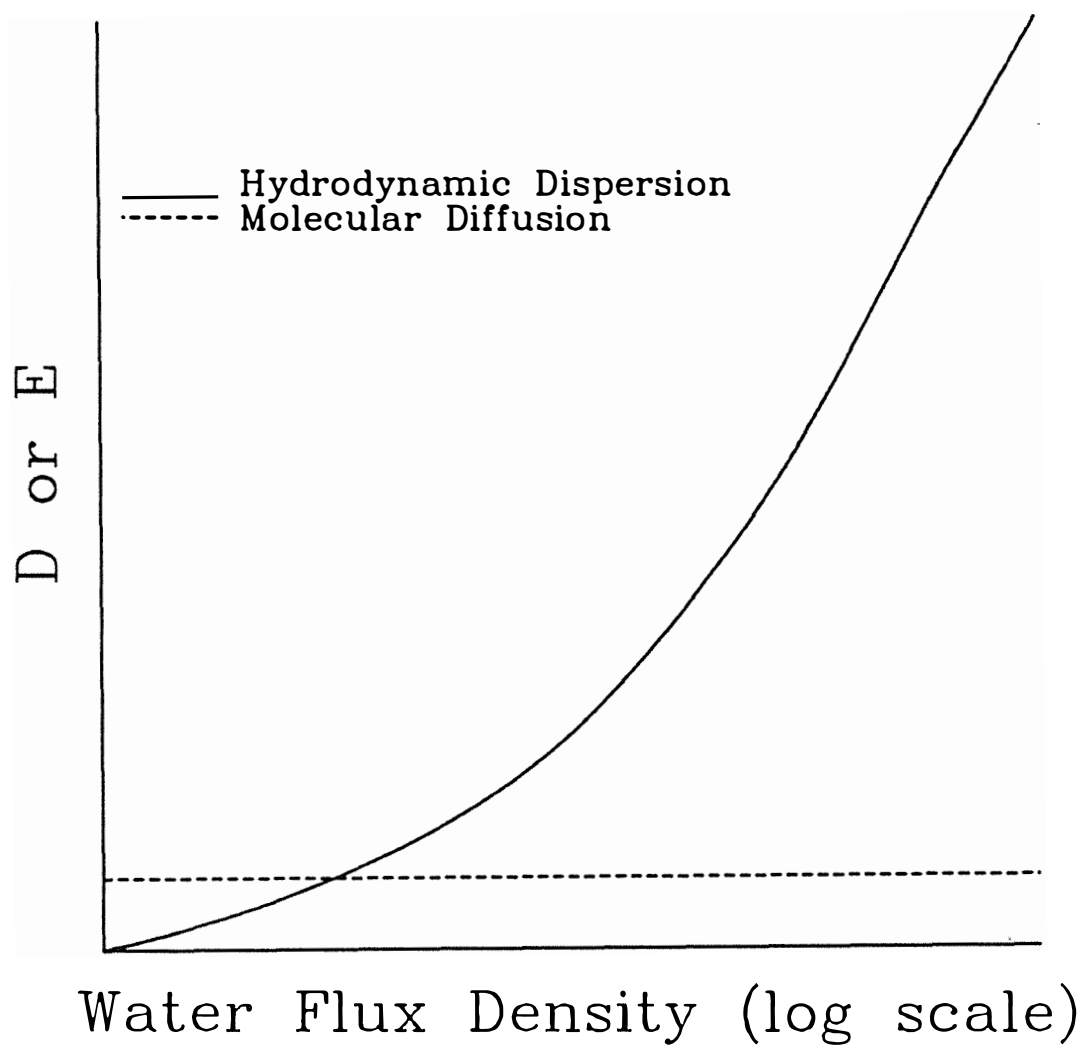


Fig. 1.1. Comparison of molecular diffusion and hydrodynamic dispersion as a function of flow velocity (from Campbell, 1985; after Olsen and Kemper, 1968)

Jury (1988) contends that the significance of the dependence of E on z in the CDE has been underestimated because the bulk of experimental evidence, which the CDE has been used to describe, comprises breakthrough curves in soil columns of a constant length. He then points out that "any experiment which maintains a fixed distance between the inlet and outlet ends of a solute transport column study and does not monitor the solute concentration except at the outlet end cannot detect a scale effect in E ". Jury (1988) also provides an additional warning to those wishing to use compliance with experimental data as confirmation of a particular physical mechanism. He demonstrates that several other two-parameter models, derived using quite different physical assumptions to the CDE, can fit a typical data set equally well.

Attempts to apply the CDE to solute movement in structured field soils have produced generally-disappointing results. This has been ascribed eloquently, if somewhat pessimistically, by White and Heng (1990) to the existence in field soils of "an essentially chaotic system: rainfall inputs that are episodic and variable in intensity, flow conditions ranging from transient to steady-state, complex and heterogeneous conducting pathways for water, and solutes that are reactive, biologically labile and can vary in concentration both spatially and temporally within the soil volume".

Many studies, both in the field (e.g. Nielsen *et al.*, (1973); Biggar and Nielsen, (1976); Quisenberry and Phillips, 1976) and in "undisturbed" soil columns in the laboratory (e.g. van Genuchten and Wierenga, 1976) have produced highly-skewed breakthrough curves, or final nutrient distributions, with a significant although highly-variable proportion of the solute moving more quickly than would be predicted by convection-dispersion theory.

This can occur because of preferential movement through a relatively small number of large pores, resulting in a non-symmetrical distribution of velocity about the mean. The effect can be more pronounced in "undisturbed" soil columns than in the field because some of the macropores which are continuous through the length of the column may terminate at a greater depth in the field soil. The existence of such "dead ends" reduces the incidence of preferential flow.

The relatively rapid flow rate through these large pores results in estimates of E apparently increasing with depth, for the reasons discussed earlier.

Adsorption and Solute Movement

The CDE has been modified to describe the movement of solutes which interact with the soil surfaces, or are produced or consumed within the transport column. Jury *et al.* (1991) review the theory for a number of scenarios, including that of an inert, sorbing solute, for which

$$\frac{\partial C}{\partial t} + \frac{\rho_b}{\theta} \frac{\partial Y}{\partial t} = E \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} \quad (1.3)$$

and ρ_b is the bulk density of the soil [kg m^{-3}] and Y is the adsorbed solute concentration [$\text{mol solute kg}^{-1} \text{ soil}$]. In order to solve equation (1.3) a relationship must be developed between the adsorbed concentration Y and the dissolved concentration C . This relationship at equilibrium is called an isotherm. In the special case where the isotherm is linear

$$Y = K_d C \quad (1.4)$$

where K_d , the slope of the isotherm, is called the distribution coefficient. If it is assumed that adsorption/desorption is linear and instantaneous then equation (1.3) reduces to

$$R \frac{\partial C}{\partial t} = E \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} \quad (1.5)$$

where

$$R = 1 + \rho_b \frac{K_d}{\theta} , \quad (1.6)$$

and R is the retardation factor. In this case the effect of the adsorption is to hold back, or retard the rate of solute movement by the factor R . It also acts to reduce the spreading by this factor.

In reality isotherms are seldom linear, and more complex equations such as Freundlich or Langmuir isotherms better describe the relationship between the relative surface and solution concentrations. Whereas this poses no additional conceptual difficulties, it does complicate the mathematics to the extent that analytical solution is seldom possible, and a numerical approach must be adopted.

Cation exchange is a type of adsorption of particular relevance to this study. In this process the relationship between the concentrations of an ion in solution and on the soil surface is also affected by the concentration of competing ions, which may have greater or lesser affinities for the exchange complex. The phenomenon of cation exchange has been much studied, although the early literature is complicated by the existence of two conventions ("Vanselow" and "Gapon") for describing the cation exchange processes. More recently theoretical description of cation exchange has been clarified by Sposito (1977, 1981).

Several workers, including Robbins *et al.* (1980) and Bond and Phillips (1990a and b), have incorporated cation exchange theory in salt transport models and the whole subject has been reviewed recently by Selim *et al.* (1990).

When considering cation exchange between two competing ions, the relative affinity of the two ions for the soil surfaces is described by a selectivity coefficient, written k_G in the present study. Early workers (Rubin and James, 1973; Robbins *et al.* 1980;

Valocchi *et al.*, 1981; Mansell *et al.* 1986) assumed that such a selectivity coefficient was constant for a given pair of ions, regardless of the relative exchange saturation of each ion. As Selim *et al.* (1990) and Mansell *et al.* (1988) point out however, the bulk of the isotherm data in the literature (Sposito, 1981; Jardine and Sparks, 1984; Parker and Jardine, 1986) can better be described by allowing the selectivity coefficient to vary with the relative fractions of the cations on the exchange surfaces. In recent work therefore Mansell *et al.* (1988) have introduced the concept of variable selectivity coefficients for exchangeable cations into solute transport models.

It should be noted however that much of the work investigating the application of cation exchange theory to solute transport models has been prompted by a concern over the rehabilitation of saline soils. Consequently, most experiments have involved treatments which produce a considerable change in the balance of cations on the exchanger, and hence there is the need to account for apparent changes in selectivity coefficients. In New Zealand's agricultural and horticultural soils the exchange complexes are normally dominated by calcium and magnesium and this cannot be greatly altered, even at high rates of fertiliser addition. Thus in modelling the movement of cations in New Zealand orchard soils, it is unlikely to be necessary to allow for variable selectivity coefficients as suggested by Mansell *et al.* (1988).

An interesting example of an interaction between a solute and the soil surface which expedites rather than retards movement, is that of anion exclusion. As Bond and Phillips (1990a) explain, this results from the repulsion of anions from the predominantly negatively-charged soil surfaces. This creates a volume of water adjacent to the surface from which anions are effectively excluded. The phenomenon has received considerable attention in the literature on solute transport, as it can affect the anions of chloride and bromide which are commonly used as "non-reactive" tracers. Bond and Phillips (1990a) in their introduction give a list of workers who have investigated the effect of anion exclusion on solute movement.

Other Solute Transport Models

The failure of the CDE to explain solute movement in field soils has been given as a justification for the development of less-deterministic approaches to modelling solute transport (e.g. Jury, 1982; White and Heng, 1990). It should be noted however that many of the earlier field experiments conducted to test the applicability of the convection-dispersion model (e.g. Nielsen *et al.* 1973; Biggar and Nielsen, 1976) were designed to satisfy the initial and boundary conditions for which analytical solutions existed. Thus they often involved pulse or step inputs of non-reactive solutes, under steady flow conditions, with application rates which were often high enough to cause ponding. It is under these conditions that preferential flow is most important, and the CDE most inappropriate.

Faced with the difficulties described above in applying the CDE to field soils, researchers have proffered a wide range of models of solute movement. These have been discussed in some detail in the excellent review by Addiscott and Wagenet (1985), and only a limited discussion need be given here.

A popular approach has been to divide the soil water into notionally "mobile" and effectively "immobile" phases (e.g. van Genuchten and Wierenga, 1976; Addiscott, 1977; Barraclough, 1989a; Addiscott and Whitmore, 1991). As Heng (1991) describes, water flow is thus assumed to occur in the mobile phase (associated with larger pores) in which solutes are transported by convection, hydrodynamic dispersion and diffusion. The effectively immobile phase consists of liquid in smaller pores in which diffusion is usually considered to be the dominant mechanism of solute transport. Solutes can be transferred between the mobile and immobile phases by diffusion. Given that only a certain fraction of the water is mobile, the predicted velocity in the mobile phase can be several times greater than the average velocity. This can then account for the oft-observed early appearance at depth of surface-applied solute. Also, because solutes are assumed to diffuse only slowly between the two phases, large volumes of fluid can move through the soil before complete equilibration of the incoming solution

with the fluid in the immobile phase is predicted. This results in a long tail on the predicted breakthrough curve, in correspondence with common observation.

It is interesting to note that the concept of mobile and immobile water is not the sole preserve of those studying water and solute movement in the field, or in cores of structured soil in the laboratory. Bond and Wierenga (1990) demonstrated the existence of an immobile phase during steady, miscible displacement experiments in repacked unsaturated soil. Their work is discussed more fully in the introduction to Chapter 4.

Heng (1991) comments that a disadvantage of the mobile-immobile model is that the soil water needs to be divided into mobile and immobile phases, and notes that there is no consensus on the matric potential which should be used to divide the two phases. Widely varying potentials of -200 kPa (Addiscott, 1977) and -8 Kpa (Nkedi-Kizza *et al.*, 1982) are cited.

The need to divide into mobile and immobile water should not however be seen as a weakness of the approach. Although there is obviously a continuum rather than a discontinuity of mobility in the soil water, the strongly non-linear dependence of hydraulic conductivity on water content (e.g. Jury *et al.*, 1991) means that there will be relatively "mobile" and "immobile" water at whatever water content currently exists in the soil. Given therefore that the concept of mobile and immobile water is merely an artifice to allow better description of experimental observations, it is entirely consistent that it should be allocated a value appropriate to the experimental system being studied. This would be expected to vary considerably between a saturated, steady-state, miscible displacement experiment, and a long-term experiment on the same soil, involving intermittent soil water flow and unsaturated conditions. The challenge is to devise rapid and independent means of assessing the most appropriate division of mobile and immobile water. The direct measurement approach of Clothier *et al.* (1992) using a disc permeameter (Perroux and White, 1988) shows considerable promise in this regard.

Another feature of the dual mobility approach is the description of movement between the mobile and immobile phases. This is given by

$$\frac{\partial C_i}{\partial t} = \alpha (C_m - C_i) \quad (1.7)$$

where the subscripts i and m refer to immobile and mobile phases respectively and α is the rate coefficient for exchange between the mobile and immobile phases [s^{-1}]. Van Genuchten and Wierenga (1977) described the flow of tritiated water through repacked columns using a mobile/immobile approach and observed that α was not constant but decreased with flow velocity. Subsequently Rao *et al.* (1980a) in a theoretical consideration of the flow of non-adsorbed solutes through porous spherical aggregates, demonstrated that α depended on a number of physical characteristics, such as the radius of the spheres, and also that it decreased with increasing time of diffusion. During miscible displacement, the time available for diffusion between mobile and immobile water is inversely related to pore water velocity. Thus α was expected to decrease with decreasing pore water velocity as observed by van Genuchten and Wierenga (1977). Despite this time-dependence of α Rao *et al.* (1980b) achieved a satisfactory description of experimental data by using a single "time-averaged" value for α . They then commented that simple models such as equation (1.7) with a single value of α , which do not require an explicit geometrical description of the system, were likely to be of most practical use in describing solute movement in well-structured field soils.

Selim *et al.* (1990) describe the application of cation exchange theory to mobile-immobile models and they note that both Schulin *et al.* (1989) and Mansell *et al.* (1988) reported improved predictions using the dual-mobility approach. An interesting issue relating to this mobility partitioning is the way in which the total soil cation exchange capacity should be allocated to each of the two phases. This issue is addressed in Chapter 5.

As Addiscott and Wagenet (1985) point out, there are many models describing solute movement. Indeed they lament that the literature is dominated by the construction of new models almost to the total exclusion of any validation or investigation of existing

models using independent data. The studies of Cameron and Wild (1982) and Barraclough *et al.* (1983) were acknowledged as exceptions to this general trend. It is beyond the scope of this review to provide an exhaustive listing of the various models. In addition to Addiscott and Wagenet (1985), Jarvis *et al.* (1991a) have given a useful summary of the more significant advances in the development of models of solute movement in field soils. A brief summary of their findings follows.

Quasi-deterministic models can be grouped according to a number of criteria. One such criterion is the manner in which they calculate water movement (Jarvis *et al.*, 1991a). Using this criterion the models of Burns (1974, 1975, 1976), Addiscott (1977), Barraclough (1989a and b) and Addiscott and Whitmore (1991) can be grouped together as using capacitance to describe the movement of water, rather than Richards' equation. In all of these studies, except for those of Burns, the soil water is divided into mobile and immobile phases. Despite the simplicity of his models, Burns (1974) obtained good agreement with observed values on a sandy loam, although it is acknowledged in the discussion that agreement may not be so good in strongly-structured soils. This difficulty of accounting for the movement of mobile anions in structured soils was again encountered in later models (Burns, 1975, 1976). It is interesting to note that the model of Burns (1975, 1976) has been used in a recent study by Rose (1991).

The model of Rose *et al.* (1982) combines the capacitance approach with an approximate solution of the CDE to describe dispersion. Cameron and Wild (1982) compared the performance of the models of Burns (1974), Addiscott (1977) and Rose *et al.* (1982) and concluded that although the model of Rose *et al.* (1982) was the most successful, there was still room for improvement in all three.

More mechanistic descriptions of water flow have been used by van Genuchten and Wierenga (1976), Skopp *et al.* (1981) and Jarvis *et al.* (1991a and b), who all couple use of the CDE with the concept of mobile and immobile water, albeit with different degrees of complexity. Hatano and Sakumo (1991a and b) have even used a 3-region model comprising the mobile phase, immobile phase and mixing phase to describe the movement of labelled water, plus anions and cations in repacked columns.

Faced with the apparent inability of the convection-dispersion approach to describe field-scale transport, a number of workers have introduced stochastic variation into one or more of the parameters in the CDE (e.g. Dagan and Bresler, 1979; Bresler and Dagan, 1983; Jaynes *et al.*, 1988). These and other similar approaches have been described in detail by Butters and Jury (1989) and will not be further discussed here.

A stochastic extension in the modelling of solute transport is provided in the log-normal transfer function model (CLT) which has been developed by a number of workers in recent years (e.g. Jury, 1982; Jury *et al.* 1982, 1986; White, 1987, 1989). As Heng (1991) explains, the CLT usually involves measuring the frequency distribution of travel times of solute convected from the surface to some reference depth, and describing it using a probability density function (pdf).

In the most-useful form of the CLT the concentration at the exit surface (C_{ex}) is given by (Jury *et al.*, 1991) as

$$C_{ex}(I) = \int_0^I f(I') C_{ent}(I - I') dI' \quad (1.8)$$

where C_{ent} [mol m⁻³] is the solute concentration at the input surface, I is the cumulative net water input or drainage [m], and $f(I)$ [m⁻¹] is a probability density function or transfer function given by

$$f(I) = \left[\frac{1}{(2\pi)^{1/2} \sigma I} \right] \exp \left[-\frac{(\ln I - \mu)^2}{2\sigma^2} \right]. \quad (1.9)$$

In this equation μ is the mean and σ the standard deviation of the log-transformed distribution. An equation similar to (1.8) can be written with time rather than I as the independent variable. But for water input that is non-steady and intermittent in nature,

such as rainfall over a season, a pdf which is a function of cumulative net input rather than time is more appropriate (Jury, 1982; White *et al.*, 1984).

A log-normal distribution is commonly assumed for the pdf because it has often been observed that during vertical flow of ponded water through soil, travel times are log-normally distributed (Biggar and Nielsen, 1976; Van de Pol *et al.*, 1977; Jury *et al.*, 1976, 1982).

Note that the CLT makes quite different assumptions about the nature of the dispersion process to the CDE. It implies that the water and solute flow down an infinite number of independent but fixed flow tubes at varying speeds. This means that the effective dispersivity increases linearly with depth, whereas the CDE implies it is constant with depth, as already pointed out.

Heng (1991) has recently derived a number of equations to incorporate in the CLT the existence of sources and/or sinks of solute near the soil surface, and the processes of adsorption/desorption in the soil.

In his original paper Jury (1982) commented that the transfer function model was a device already used in other fields such as electrical engineering and hydrology to characterise systems whose internal mechanisms are either unknown or unknowable. Its introduction into the area of solute movement has sparked an entertaining debate between "determinists" and "pragmatists" (e.g. Jury, 1988; Knight, 1988; Towner, 1989; White and Heng, 1990). It has also generated a very substantial literature in a short time. More recently the distinctions between the two approaches have become blurred, with the physical implications of equations such as the CLT being discussed. Indeed it has been pointed out that the CDE can be seen as just one particular type of transfer function (Jury and Roth, 1990).

Much of the experimental work used to assess the usefulness of the CLT approach has been summarised in recent articles by Butters *et al.* (1990) and White and Heng (1990). In a major study in California, Butters *et al.* (1989) and Butters and Jury (1989) compared the performance of a CDE and a CLT in predicting the movement of a

bromide pulse to considerable depth, under near steady-state conditions. When both models were parameterised at 300 mm depth the stochastic transfer function CLT model consistently out-performed the CDE in predicting the shape of the solute pulse at greater depth. In particular, the CDE did not predict the rapid movement of a portion of the solute far in advance of the main pulse.

In such situations the CLT would appear to offer advantages, particularly where it is desired to estimate when the first traces of a potential pollutant are likely to reach the ground water. Butters *et al.* (1990) have cautioned however that vertical heterogeneities in soil can change the observed dispersion of the solute pulse. They suggested the use of a semi-empirical approach for adjusting the CLT model parameters in vertically-heterogeneous soil. Very recently Ellsworth *et al.* (1991) and Ellsworth and Jury (1991) adopted a different approach to deal with the effects of vertical changes in soil texture on solute movement. They used a transformed advection-dispersion equation to derive constant field-averaged coefficients, which enabled a reasonable description of solute transport in a major field experiment on a vertically-heterogeneous soil.

Conclusion

It is apparent from the foregoing review that no single approach to the modelling of solute movement is likely to be appropriate in all situations. Thus in large-scale situations, involving pulse inputs of solutes, under water flow conditions which approach steady-state on some occasions, the CLT approach appears to have advantages. This is particularly the case where there is major interest in the position of the leading edge of the solute.

In contrast, in situations where solutes are already well-distributed through the soil, where inputs of water and solutes are transient, where there is considerable time for redistribution, and where the major concern is the distribution of the bulk of the solute rather than the position of the leading edge, the spatial variation in v may have little influence on the distribution of sorbed and non-sorbed nutrients behind the wet front. In such cases more deterministic approaches may be preferable.

What is apparent from the work of Heng (1991) and White and Magesan (1991) is that the adoption of a stochastic approach does not obviate the need for a thorough understanding of the processes affecting the concentration in solution of reactive solutes, or of those solutes for which biological sources or sinks exist within the soil.

THE STRUCTURE OF THE STUDY

The first major objective of the study was the construction and testing of a model to simulate the movement of a range of nutrients in repacked, laboratory columns. Chapters 2 and 3 address this objective. As discussed above, the CDE has been usually found to describe adequately solute movement in repacked columns, so it was used here. A more complex form of the equation than (1.5) was needed however in order to account for transient water flow, plus transformations of soil nitrogen, and cation exchange.

The experimental procedure used involved the transient input and redistribution of water and nutrients over a time-span long enough to allow microbial transformations of nitrogen with their attendant effects on soil pH and charge characteristics. It was felt that this may be of particular importance to nutrient movement under the trickle emitters that might be used for fertigation (Haynes and Swift, 1987).

The reason for using repacked soil columns in the laboratory was to have a system in which the movement of water was well understood, so that the data obtained could be used to study interactions between water movement and the adsorption and transformation of solutes.

As the initial intention in modelling the movement of water was to provide accurate information to assist in the development of the chemical sub-models, estimates of some physical parameters, in particular the relationship between hydraulic conductivity and water content, were obtained by fitting the model to the data, rather than by independent assessment. This prompted an attempt to make independent measurements of the relationship between water content and hydraulic conductivity, so that the water movement could be investigated more rigorously. Approaches used included those of

Bruce and Klute (1956) and White and Perroux (1987). But in all cases consistent measurement was thwarted by an unexplained variability in the results. It eventually transpired that the variability was caused by a time-dependent development of water-repellency in the soil. This was investigated further, and the resulting publication is included as Appendix 1.

Once it was demonstrated that the chemical and biological sub-models adequately described the transformations and movement of nutrients in the repacked columns, two further experiments were conducted in the field. These experiments, and the modelling of the data obtained, are described in Chapters 4 and 5. Given the variable water contents and flow rates experienced in the root zone, the modelling approach offering the most promise was a mobile-immobile version of the CDE.

The first of the two experiments was designed to provide information on the movement of water and a non-reactive solute, so as to enable the parameterisation of the mobile-immobile model. The second field experiment was essentially an analogue of the experiment conducted earlier in the laboratory. The major emphasis in this second experiment was to see if coupling of the water movement sub-model with the chemical and biological sub-models developed in the earlier laboratory experiment could describe the movement of reactive nutrients in the field.

In Chapter 6 the findings of the previous chapters are assessed and summarised. Some comments are made there on the relative importance of different processes in determining nutrient movement on a spatial and temporal scale of relevance to orchard soils.

CHAPTER 2

MOVEMENT OF NON-REACTIVE SOLUTES ASSOCIATED WITH INTERMITTENT SOIL WATER FLOW IN REPACKED SOIL

INTRODUCTION

Solute movement during steady soil water flow is a much-studied phenomenon. However solute movement during unsteady intermittent flow has received less attention, despite being the norm in the field. During constant flux absorption into relatively dry sand, Smiles *et al.* (1981) found that the invading solution effectively pushed the resident solution ahead of it, with no evidence of immobile water. Bond *et al.* (1982) and Bond (1987) found the same behaviour for tritiated water moving into a repacked clay soil, but found chloride moved ahead of the tritiated water due to anion exclusion.

In the field both fertilizer and water are usually applied infrequently, with considerable time between applications. Preferential flow down larger pores, chemical and biological reactions of nutrients, water and nutrient extraction by roots, and interactions between these processes, may further complicate the situation. It is difficult to study all these processes simultaneously, and to take account of field variability. While we concede any comprehensive study must end up in the field, a good understanding of the various processes occurring, and of as many interactions as possible, is needed when one ventures outdoors. Laboratory studies have a place in obtaining that understanding. This chapter and the following chapter discuss the behaviour of tritiated water, and bromide, potassium and urea when they are applied to repacked soil, left for several days, and then leached further down into the soil. The movement of tritiated water and bromide are the subject of this chapter while the fate of various cations and nitrogen are discussed in Chapter 3.

THEORY

A description of water flow is necessary to describe solute flow. As only one-dimensional vertical flow is considered, Darcy's equation is

$$q = K(\theta)\left[1 - \frac{d\psi}{dz}\right] \quad (2.1)$$

where q is the water flux density with units (m s^{-1}), K is the hydraulic conductivity (m s^{-1}), θ is the soil water content ($\text{m}^3 \text{m}^{-3}$), ψ is the matric potential (m) and z is depth. Conservation of water volume requires

$$\frac{\partial \theta}{\partial t} = - \frac{\partial q}{\partial z} \quad (2.2)$$

where t is time. The $\psi(\theta)$ relationship assumed was (Campbell, 1985)

$$\psi = a \left(\frac{f}{\theta} \right)^b \quad (2.3)$$

where f is the porosity and a and b are empirical constants. For reasons given later, the $K(\theta)$ relationship assumed was

$$K = c_1 \exp(d_1 \theta) \quad \text{for } \theta < \theta_k \quad (2.4a)$$

$$K = c_2 \exp(d_2 \theta) \quad \text{for } \theta \geq \theta_k \quad (2.4b)$$

where θ_k is a particular water content.

Given no chemical or biological transformations, conservation of solute mass implies

$$\frac{\partial M_i}{\partial t} = -\frac{\partial j_i}{\partial z} \quad (2.5)$$

where M_i is the amount of solute present in unit soil volume (mol m^{-3}), j is the solute flux density ($\text{mol m}^{-2} \text{s}^{-1}$), and the subscript i identifies the chemical species of interest. Solute movement is considered induced by the transport mechanisms of convection, hydrodynamic dispersion and molecular diffusion. Following Wagenet (1983)

$$j_i = qC_i - (\lambda|q| + \theta D) \frac{dC_i}{dz} \quad (2.6)$$

where C is the soil solution concentration (mol m^{-3}), λ is the dispersivity (m), and D is the molecular diffusion coefficient in the soil ($\text{m}^2 \text{s}^{-1}$) and

$$\theta = \theta - \theta_x \quad (2.7)$$

Here θ_x represents the water from which the chemical species of interest is effectively excluded due to double layer effects (Smiles and Gardiner 1982). The $D(\theta)$ relationship assumed was (Papendick and Campbell, 1981)

$$D = \epsilon \theta^2 D_o \quad (2.8)$$

where D_o is the molecular diffusion coefficient in pure solution, and ϵ is an empirical constant. Finally, C and M are related by

$$C = \frac{M}{\theta} . \quad (2.9)$$

As simultaneous non-linear partial differential equations with complex boundary conditions are involved, only numerical solution of the above set of equations is possible. An explicit finite-difference approach was used, similar to that described by de Wit and van Keulen (1975), but using a microcomputer and compiled BASIC. A comparison of numerical and analytical solutions for constant flux, and a comparison of the de Wit and van Keulen (1975) and Campbell (1985) numerical procedures for describing convection, confirmed that numerical dispersion was not affecting the results.

MATERIALS AND METHODS

The soil used was the topsoil of Manawatu silt loam (a Dystric Fluventic Eutrochrept). It was passed through a 2 mm sieve and then packed into hollow acrylic columns with an internal diameter of 43 mm, at a bulk density of 1.17 Mg m^{-3} , and at a volumetric water content of 0.145. The columns consisted of 10 mm and 20 mm thick rings taped together. This allowed rapid sectioning of the soil at the end of the experiment. During the experiment the columns were wrapped in aluminium foil and polythene film to minimize evaporation, and kept in an inside room subject to little temperature fluctuation. Draining retentivity data for the soil were obtained using Haines' and pressure-plate apparatus.

Two treatments were imposed on the soil-filled columns, each with four replicates. Both treatments initially received 5 mm of solution containing 670 MBq m⁻³ of tritiated water, 51 mol m⁻³ potassium bromide and 72 mol m⁻³ urea. The treatment that is subsequently referred to as the "early-water" treatment had 30 mm of distilled water applied to each column three days later. The "late-water" treatment had 30 mm of water applied ten days after the initial 5 mm of solution. The solution and water were applied with peristaltic pumps. Discs of filter paper on the soil surface spread the applied liquid over the soil and prevented soil structure damage. An application rate of 10 mm h⁻¹ was used for the initial 5 mm of solution and for the water in the early-water treatment. However when water was applied at this rate to the late-water columns, incipient ponding was noticed, so the rate was reduced to between 5 and 7 mm h⁻¹. No ponding occurred at this lower application rate. As described in Appendix 1, the reason for this behaviour was a tendency towards water repellency in this soil. While this tendency was reduced by sieving, it slowly returned with incubation at room temperature.

All eight columns were sectioned twelve days after the original solution application. Soil water content was determined gravimetrically on a sample of soil from each column section, and a variety of chemical analyses were conducted on other soil samples. A filtered water extract was obtained for tritiated water and bromide analyses, which were carried out using a scintillation counter and specific ion electrode respectively.

EXPERIMENTAL RESULTS AND DISCUSSION

The measured retentivity data are shown in Fig. 2.1. The soil water content profiles measured at the end of the experiment are shown in Fig. 2.2. The relatively small standard deviations at each depth shows close agreement between replicate columns. The soil water content was affected by the applied water to 210 mm depth in the early-water treatment. The late-water treatment, with less time for redistribution, was affected to only 170 mm depth, but remained wetter above that depth and with a sharper wetting front than the early water treatment. The average calculated recoveries

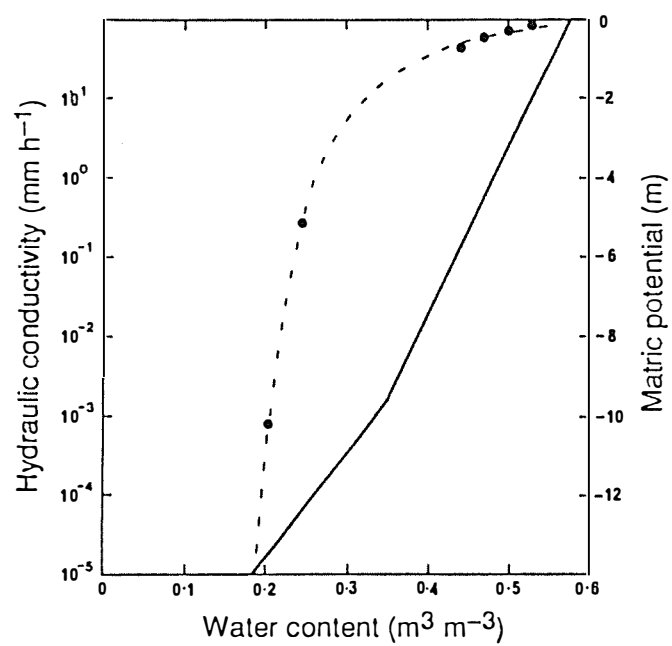


Fig. 2.1. Measured draining retentivity data (o), and assumed retentivity (_ _ _) and hydraulic conductivity (_____) relationships for the soil.

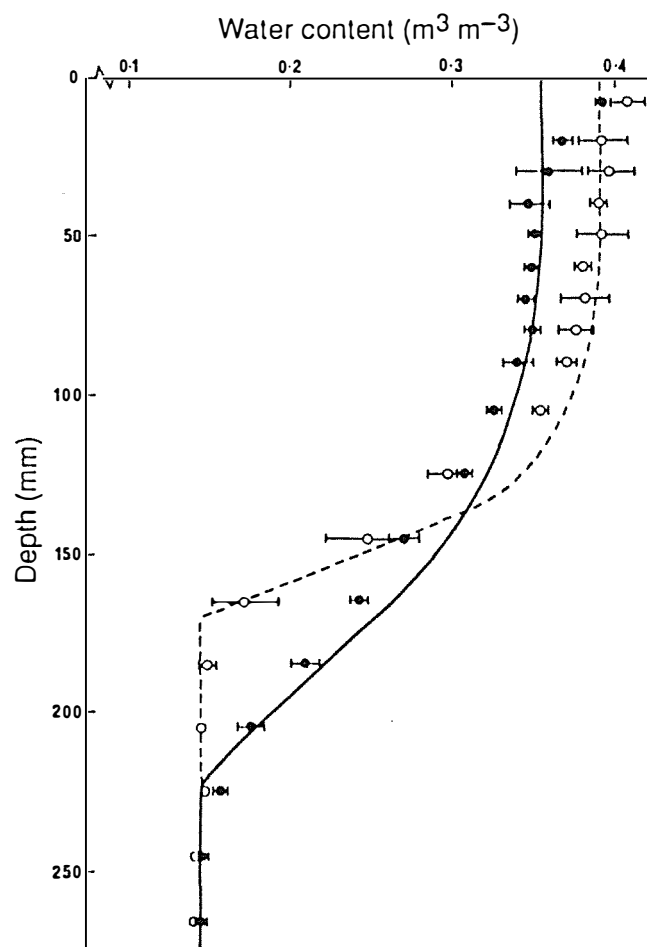


Fig. 2.2. Measured average soil water contents for early-water (●) and late-water (○) treatments and their standard deviations. Also shown are the simulated profiles for the early-water (——) and late-water (_ _) treatments

of the 35 mm of applied solution and water were 96% and 95% for the early- and late-water treatments respectively, indicating little evaporative loss during the experiment.

The measured tritiated-water profiles are shown in Fig. 2.3. To allow comparison with the bromide data to be presented below, tritiated water concentrations have been expressed as the percentage present in unit soil depth of the total amount of tritiated water recovered from the columns for that treatment. For the early- and late-water treatments, 88% and 86% of the applied tritiated water was recovered from the soil. The most likely reason for these relatively low recoveries was a failure to fully take account of quenching by the soil extracts in the scintillation cocktails; this would not affect the normalized results. Again the low standard deviations show the close agreement between the four replicate columns.

Bell-shaped curves with peaks at approximately 90 mm depth were found for both treatments. But the peak was much sharper for the late- than early-water treatment. As the water flow regimes, and so hydrodynamic dispersion, were quite similar, molecular diffusion is the probable main reason for the difference between treatments. Diffusion in dry soil is much slower than diffusion in moist soil. Equation (2.8) indicates ΘD_i at $\theta = 0.36$, a typical water content behind the wetting front, is 15 times the value of ΘD_i at $\theta = 0.145$, the water content ahead of the wetting front. Thus significant tritiated-water diffusion would only occur after the 30 mm of water had been applied. The early-water treatment allowed nine days for diffusion after the water application, while the late-water treatment only allowed two days. The asymmetry of the early-water data can also be attributed to the tritiated water diffusing more readily back up into the moister soil above the peak than down into the drier soil below it.

The bromide data are shown in Fig. 2.4. These have been normalized in the same manner as described above for the tritiated-water data. Recoveries were 94% and 90% of the bromide applied for the early and late water treatments respectively. The standard errors shown for the bromide data in Fig. 2.4 are higher than those for tritiated water in Fig. 2.3. This probably reflects the lower precision of the specific ion electrode relative to the scintillation counter. The curves for tritiated water and bromide show the same features, but the bromide early water peak is lower down the

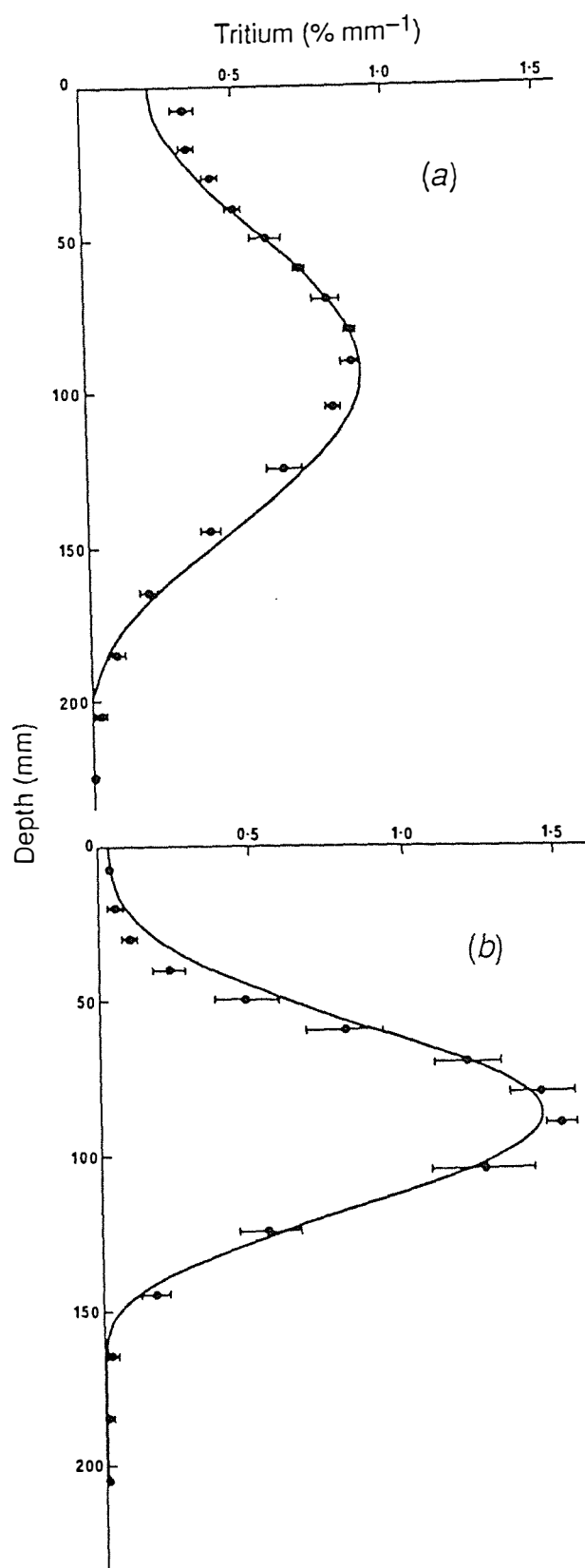


Fig. 2.3. Measured (●) and simulated (—) tritiated water content profiles for (a) the early-water treatment, and (b) the late-water treatment. Means and standard deviations are shown for the measured values

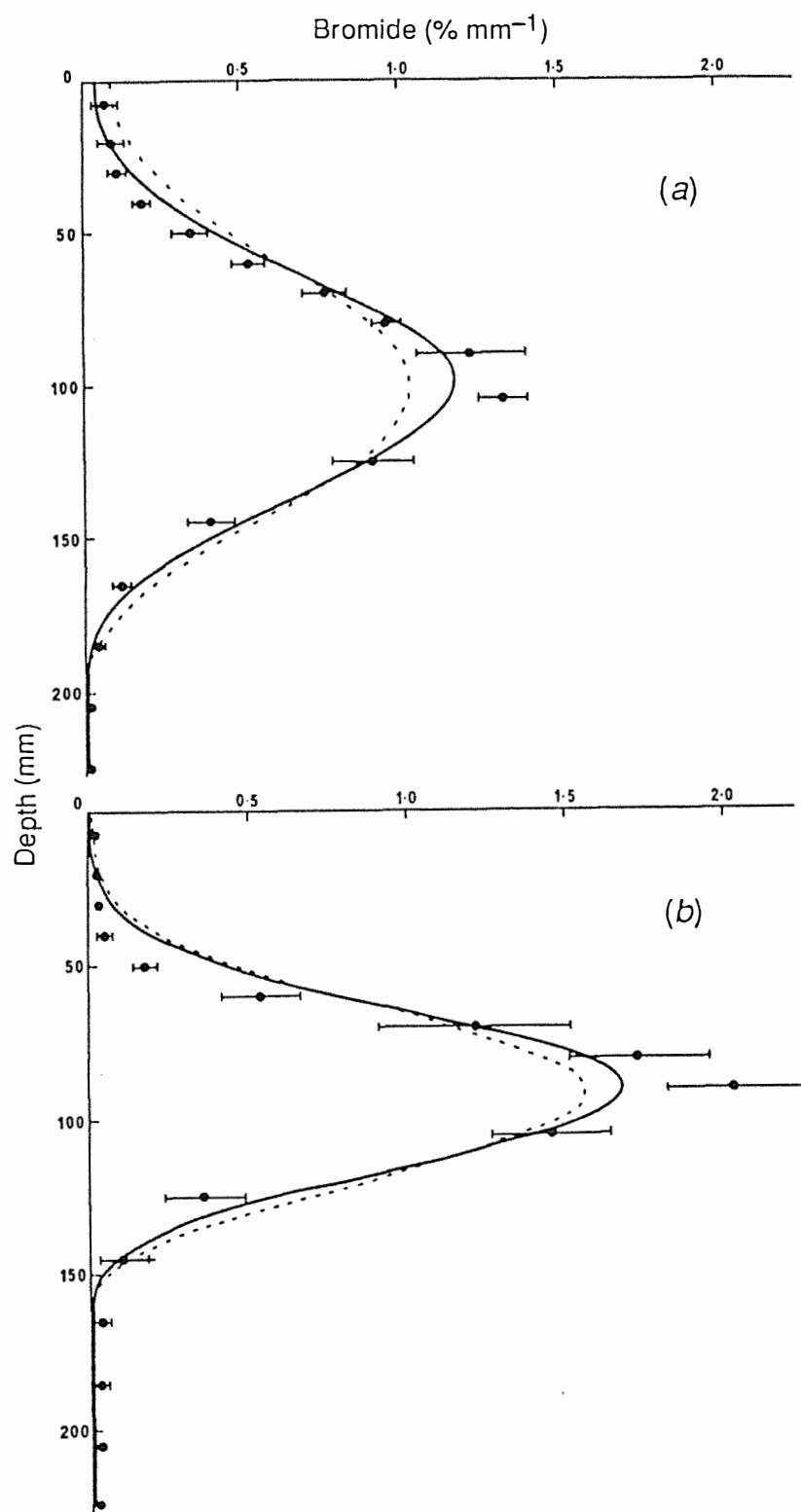


Fig. 2.4. Measured (●) and simulated (—— and) bromide content profiles for (a) the early-water treatment, and (b) the late-water treatment. Means and standard deviations are shown for the measured values. The difference between the two simulations is explained in the text

profile, occurring at 105 mm rather than 90 mm depth. Also the bromide peaks are much higher than the corresponding tritiated-water peaks. These differences are discussed further in the next section.

SIMULATION RESULTS AND DISCUSSION

Before the equations given above can be solved, the parameters in them must be evaluated. A least squares fit of equation (2.3) to the retentivity data in Fig. 2.1 gave values of -265 mm for a and 3.6 for b and the line shown in Fig. 2.1. If redistribution is to be realistically simulated, values for $K(\theta)$ at the relevant water contents must be correct (Scotter *et al.*, 1988). Thus the constants in equation (2.4) were evaluated by running the model and choosing values that gave approximately the measured final water content profiles. To obtain the observed treatment difference in water contents behind the wet front, and the observed wet front shapes, it was found necessary to use different values for c and d (subscripted 1 and 2) for water contents above and below $\theta_k = 0.35$. Trial and error gave values of $c_1 = 1.25 \times 10^{-14} \text{ m s}^{-1}$, $d_1 = 30$, $c_2 = 2.24 \times 10^{-17} \text{ m s}^{-1}$, $d_2 = 48.1$, and the curve shown in Fig. 2.1. The simulated water content profiles for the given boundary and initial conditions are shown in Fig. 2.2.

Given water flow had been adequately simulated, it was of interest to see if values for the remaining four parameters, λ , ϵ , θ_x and D_o , could be estimated from the literature, and used to realistically simulate tritiated water movement. We expected tritiated water to be fully miscible with the resident water, and so made $\theta_x = 0$. Bond (1987) quotes a tritiated water value for D_o at 293 K of $2.14 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. Papendick and Campbell (1981) and Campbell (1985) suggest ϵ equals approximately 2.8. The remaining parameter, the dispersivity λ , was the hardest to estimate accurately. Wagenet (1983) suggests that it ranges from 2 mm to 20 mm or more. As the soil used was fine-textured, with all but the smallest aggregates destroyed during sieving, a value of 2 mm was chosen.

The tritiated water profiles simulated assuming the above parameter values are shown in Fig. 2.3. The simulated concentrations are mostly less than one standard deviation

away from the measured mean values, suggesting the theory and parameter values given do reasonably well simulate the system studied experimentally.

To extend the simulation to bromide, new values for θ_x and D_o must be found. From the depths of the centres of mass of tritiated water and bromide in Figs. 2.3 and 2.4, θ_x was calculated to be 0.03. This indicates anion exclusion is a relatively unimportant phenomenon in this soil, and contrasts with the value of 0.11 Bond (1987) found in a clay soil. A value of $1.7 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for D_o for dilute potassium bromide at 293 K was estimated from Robinson and Stokes (1959). Use of these parameter values in the simulation produced the dotted curves shown in Fig. 2.4. Agreement between simulated and measured values was not nearly as good as it was for tritiated water. The simulated curves show flatter bromide peaks than the data, particularly for the early-water treatment. As the hydrodynamic dispersion term should be similar for tritiated water and bromide, it seemed that the molecular diffusion coefficient for the bromide in the soil had been over-estimated.

Analyses for the cation distribution in the soil columns (results of which are presented in the next chapter) suggested a reason why the diffusion of bromide was slower than simulated. While potassium bromide was applied to the soil, most of the applied potassium remained in the top 25 mm of soil, and the dominant cation convected down with the bromide was calcium. Thus it was mainly diffusion of calcium and bromide ions that spread out the convected peak during the several days after the 30 mm of water was applied. D_o for dilute calcium bromide at 293 K was estimated to be $1.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ from data in Robinson and Stokes (1959), 35% lower than the value for potassium bromide. The bromide concentration profiles simulated using this lower D_o are shown as the solid lines in Fig. 2.4. They agree better with the data, and are mostly within one standard deviation of the measured mean values. Even better agreement between the data and the simulations could have been obtained by optimizing ϵ and perhaps λ , but that was not the aim of this study. However it does appear, particularly from Fig. 2.4, that the dispersivity was less than the 2 mm assumed.

CONCLUSIONS

Tritiated water and bromide applied to soil generally behaved as expected during and after unsteady water flow into a fairly dry repacked fine sandy loam. There was only slight evidence of anion exclusion during flow. Tritiated water spread out more than bromide, due to its higher molecular diffusion coefficient.

The behaviour of tritiated water and bromide could be simulated reasonably well by coupling the water flow equations with the convection-dispersion equation, and using parameter values obtained from the literature. A significant assumption affecting the simulation was which cation was mostly convected with, and so diffused with, the bromide. Exchange of the applied potassium with calcium ions occurred in the surface soil. Thus use of the diffusion coefficient for calcium bromide rather than potassium bromide in the simulation resulted in a better description of the observed bromide profiles in the soil.

The movement of water, of an exotic water isotope, and of a non-reactive exotic anion have been analyzed with some success. With this background, the next chapter examines the movement of cations, and the transformation and movement of the nitrogen in the applied urea.

CHAPTER 3

MOVEMENT OF REACTIVE SOLUTES ASSOCIATED WITH INTERMITTENT SOIL WATER FLOW IN REPACKED SOIL

INTRODUCTION

In Chapter 2 the transient movement of water, tritiated water and bromide into columns of repacked silt loam was described. This chapter describes the movement in the same columns of nitrogen (applied as urea) and of cations. The effect on nitrogen movement of the timing of water application, relative to the extent of conversion of urea-nitrogen, firstly to ammonium and then nitrate, is discussed. Also examined are the effects of these nitrogen transformations on the movement of applied potassium and the other cations present in the soil.

The interaction of the physical, chemical and biological factors implicit in the study described above does not seem to have been studied before, even in repacked soil. Wagenet *et al.* (1977), Selim and Iskandar (1981), and Iskandar and Selim (1981) have studied, both experimentally and theoretically, the transformations of urea and ammonium under unsaturated steady-flow conditions. These and other studies (e.g. Scotter *et al.*, 1984) suggest that the amount of leaching is affected by the timing of irrigation, or of wetting by rainfall, relative to the progress of hydrolysis and nitrification.

Robbins *et al.* (1980) included cation exchange in a solute transport model, which reasonably successfully simulated some field data. They assumed a constant cation exchange capacity. However in many soils this will change when hydrogen ions are produced or consumed, as occurs during the transformation of urea-nitrogen to nitrate. This may affect the cation concentration in solution. For example, Fox (1980) quotes data showing substantially less potassium leached in a Dystrandept following liming. Thus it seems such interactions may be significant.

This study is not intended to produce new information on nitrogen transformations in soils, or on the chemical relationships governing cation exchange. Rather, the study examines the extent to which existing information on these chemical and biological processes can be used to explain the movement of anions and cations during intermittent flow in columns of repacked soil; a system in which the movement of water is relatively well understood. Once this has been achieved, it should assist in understanding the movement of solutes in structured field soils (Chapters 4 and 5), in which the movement of water is more complex.

THEORY

Most of the equations in Chapter 2 are also applicable to the movement of cations, urea and nitrate. However equations (2.5) and (2.9) need modification to account for nitrogen transformations and cation exchange.

Both the hydrolysis of urea to ammonium, and the nitrification of ammonium to nitrate are treated as first order reactions, following for example Wagenet *et al.* (1977). Thus

$$\frac{\partial M_u}{\partial t} = -\frac{\partial j_u}{\partial z} - k_u M_u, \quad (3.1)$$

where the subscript u refers to urea and k_u is the rate constant for urea hydrolysis (s^{-1}). Other symbols are defined in Chapter 2 and in the List of Symbols. For ammonium, identified by the subscript a ,

$$\frac{\partial M_a}{\partial t} = -\frac{\partial j_a}{\partial z} + k_u M_u - k_a M_a \quad (3.2)$$

where k_a is the rate 'constant' for nitrification. Similarly for nitrate, denoted by the subscript n ,

$$\frac{\partial M_n}{\partial t} = -\frac{\partial j_n}{\partial z} + k_a M_a . \quad (3.3)$$

Net mineralization and denitrification were assumed to be negligible during the experiment. The validity of this assumption will be discussed later.

Also required are the relationships between M_i , the total amount of a chemical species i present in unit volume of soil (both in solution and on exchange sites), and C_i , the concentration of that species in the soil solution. Only cation adsorption was considered, and instantaneous exchange was assumed. Cation exchange was simplified by assuming a binary system of monovalent and bivalent cations, i.e. there was no distinction made between the individual monovalent cations (K^+ and Na^+) or between the individual bivalent cations (Ca^{2+} and Mg^{2+}). The proportions of individual monovalent cations present in solution were then assumed to be equal to the amount of that cation present relative to the total presence of monovalent cations. The solution concentration of individual bivalent cations was similarly estimated. The relative concentration in the soil solution of monovalent and bivalent cations was found using the Gapon equation, which for such systems can be written as (Robbins *et al.*, 1980)

$$\frac{C_M}{C_B^{1/2}} = k_G \frac{X_M}{X_B} \quad (3.4)$$

where X is the amount of charge balanced by either monovalent (subscript M) or bivalent (subscript B) cations, C is their concentration in the soil solution, and k_G is a selectivity coefficient with units $(\text{mol m}^{-3})^{1/2}$.

We assume

$$C_M = C_k + C_s + C_a \quad (3.5)$$

and

$$C_B = C_c + C_g \quad (3.6)$$

where the subscripts k , s , a , c and g refer to potassium, sodium, ammonium, calcium and magnesium respectively. These were considered the only important cations. Also, if we define the variables α , β and γ by

$$\alpha = M_k + M_a + M_s \quad (3.7)$$

$$\beta = M_c + M_g \quad (3.8)$$

and

$$\gamma = \frac{(\alpha + 2\beta - P)}{\theta} \quad (3.9)$$

where P is the cation exchange capacity (expressed as mol m⁻³ of soil) then it follows that

$$X_M = \alpha - \theta C_M \quad (3.10)$$

$$X_B = 2(\beta - \theta C_B) \quad (3.11)$$

and

$$C_M = \gamma - 2C_B . \quad (3.12)$$

Substitution of equations (3.10), (3.11) and (3.12) into (3.4) and simplification yields

$$4\theta C_B^2 - 2k_G \theta C_B^{3/2} - 2(\gamma\theta + 2\beta)C_B + k_G(\theta\gamma - \alpha)C_B^{1/2} + 2\beta\gamma = 0. \quad (3.13)$$

Equation (3.13) can be readily solved for C_B using the Newton-Raphson technique, Equation (3.12) then yields C_M , and given the assumptions concerning individual cations stated above,

$$C_a = M_a \frac{C_M}{M_M} \quad (3.14)$$

$$C_k = M_k \frac{C_M}{M_M} \quad (3.15)$$

$$C_c = M_c \frac{C_B}{M_B} \quad (3.16)$$

$$C_g = M_g \frac{C_B}{M_B} . \quad (3.17)$$

The remaining issue to be addressed is the effect of the hydrogen ion consumption or production resulting from the hydrolysis of urea and nitrification of the resulting ammonium to nitrate. The pH data presented later indicate that changes in solution concentration accounted for only a negligible fraction of these hydrogen ions. So it was assumed that the effect of hydrogen ion consumption or production was to raise or lower the effective cation exchange capacity. This behaviour would result if the soil had variable charge characteristics, or if hydrogen ions were preferably absorbed over other cations. Thus

$$\frac{dP}{dt} = k_u M_u - 2k_a M_a . \quad (3.18)$$

The explicit finite difference approach referred to in Chapter 2 was modified to include the above equations. Values for M_i as a function of depth and time for the various chemical species of interest were then found using this approach.

MATERIALS AND METHODS

Details of the experiment conducted are given in Chapter 2, so only the chemical analyses need be described here. Soil pH was measured in both distilled water and calcium chloride (10 mol m^{-3}). Nitrate- and ammonium-nitrogen contents were measured on potassium chloride (2 kmol m^{-3}) extracts of moist soil obtained immediately after the columns were sectioned. The moist-soil:extractant ratio was 1:20 and the extraction time was 30 minutes. Exchangeable cation concentrations in the soil were measured by making two sequential 30-minute extractions with ammonium acetate (1 kmol m^{-3} , pH 7). The soil:extractant ratio in each extraction was 1:25. The extracts were combined prior to measuring the concentration of calcium, magnesium and potassium using atomic absorption.

EXPERIMENTAL RESULTS AND DISCUSSION

The pH profiles measured are shown in Fig. 3.1. There is a marked decrease in pH in the top 40 mm of soil resulting from the net production of hydrogen ions following urea hydrolysis and nitrification of ammonium ions. When the pH is measured in distilled water the pH is lower in the top 40 mm of the early-water treatment than in the late-water treatment. This is reversed between 70 and 90 mm with the late-water treatment having the lower pH. At first glance this would seem to indicate the leaching of hydrogen ions in the late-water treatment. In this treatment the leaching took place after the bulk of the added nitrogen had been nitrified, with the accompanying generation of acidity.

The pH profiles measured in calcium chloride are however, virtually identical for the two treatments, and there is little evidence of a drop in pH below approximately 40 mm. This suggests that little leaching of hydrogen ions occurs, and the differences between treatments, in pH measured in water, are the result of differences in soluble salt concentration. These arise because the early-water leaching took place while the applied nitrogen was predominantly in the ammonium form. This is relatively immobile in soils. Subsequent to the leaching the ammonium was largely nitrified, but

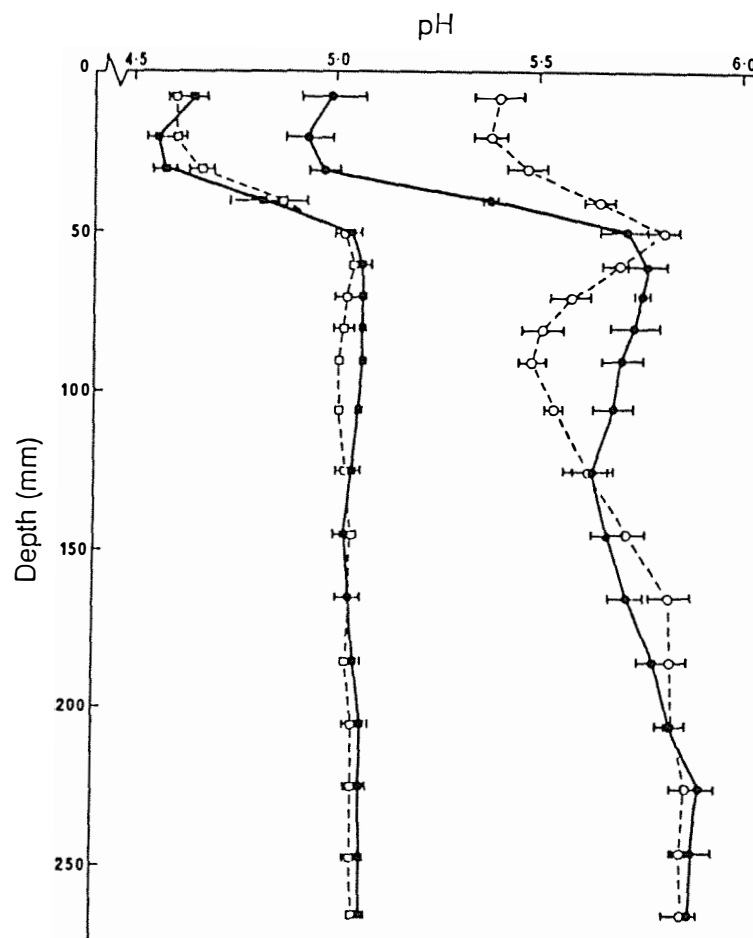


Fig. 3.1. Measured pH profiles in water (●,○) and calcium chloride (■,□) for early- (——) and late- (----) water treatments and their standard deviations

the resulting nitrate remained in a narrow band near the top of the column. This resulted in a high concentration of soluble salts which reduced the apparent pH when measured in water.

In contrast, the late-water leaching occurred after most of the added nitrogen had been converted to nitrate. This moved readily down the column, together with accompanying cations and formed a zone of high salt concentration (and apparently low pH) from 70 to 90 mm.

The measured ammonium profiles are shown in Fig. 3.2. More ammonium remained in the late-water than the early-water columns. This is presumably due to increasing inhibition of nitrification as the pH decreased. This effect would have been more marked in the late-water treatment as the ammonium band would have been much narrower. Even in the late-water columns however, only 22% of the applied nitrogen remained as ammonium. In all columns most of the ammonium was found in the top 50 mm of soil.

The measured nitrate profiles are shown in Fig. 3.3. Although the total amount of nitrate present in the early- and late-water columns was similar, delaying the application of the 30 mm of leaching water by 7 days had a marked effect on the nitrate distribution. In the early-water columns most of the nitrate was in the top 50 mm, where it apparently came from ammonium immune to leaching but later nitrified. In the late-water columns there was much less nitrate in the top 50 mm of soil, but a sharp peak at 90 mm depth, about the same depth that tritium and bromide peaks were observed (Chapter 2). This suggests it had been leached in a similar fashion.

The recovery of applied nitrogen was calculated as follows. First, the amount of 'native' ammonium plus nitrate in the columns was calculated from the M_n and M_a values at depth where no water content change was observed. This value was then subtracted from the total measured amount of ammonium plus nitrate in the columns. The answer was expressed as a percentage of the amount of nitrogen applied as urea. Recoveries of 123% and 108% were estimated for the early- and late-water columns respectively, indicating that wetting and incubating the soil might have induced some

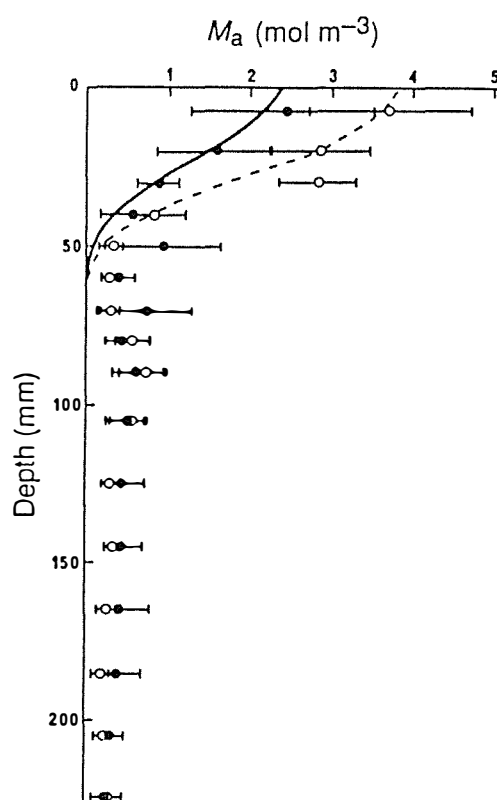


Fig. 3.2. Measured ammonium concentration profiles for early- (●) and late- (○) water treatments and their standard deviations. Also shown are the simulated profiles for early- (——) and late- (---) water treatments

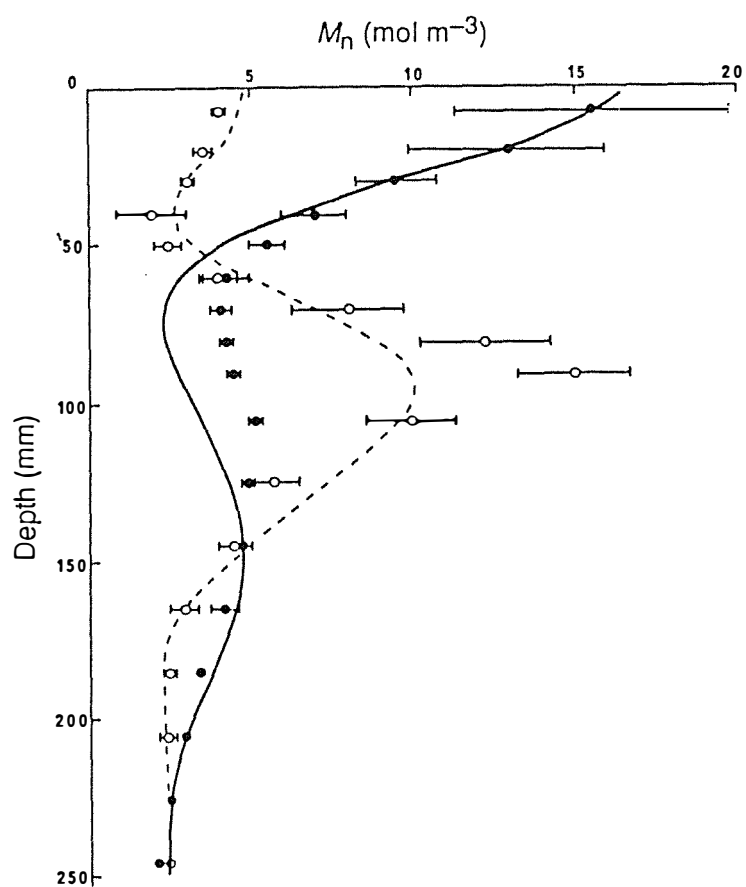


Fig. 3.3. Measured nitrate concentration profiles for early- (●) and late- (○) water treatments and their standard deviations. Also shown are the simulated profiles for early- (——) and late- (---) water treatments

net mineralization. As might be expected, more occurred in the early-water columns which were wet for longer. This will be discussed further below.

Fig. 3.4 shows the measured potassium profiles. The percentage recoveries of applied potassium, calculated in a manner similar to that described above for nitrogen, were 110% and 108% respectively for the early- and late-water treatments. The curves for both treatments are quite similar. Increases in the concentration of potassium over native levels were mainly in the top 25 mm of soil, but there was also some extra potassium found between 60 mm and 140 mm depth, particularly in the late-water columns.

In Figs. 3.5 and 3.6 the measured calcium and magnesium profiles are shown. The curves for these two cations are similar in shape, and show similar differences between the two treatments. For both cations there is a depletion in the top 40 mm of soil, but an increase in concentration between 70 and 130 mm depth. These concentration changes are much more marked in the late-water than early-water columns.

By comparing Figs. 3.5 and 3.6 with Figs. 3.2, 3.3, 3.4 and 2.4, it can be seen that calcium and magnesium were the dominant cations moving down with the nitrate and bromide. The depletion of these cations from the exchange sites in the top 40 mm of soil was apparently brought about by an increase in potassium adsorption, and a decrease in the cation exchange capacity due to the more acid environment. The concentration peak at 90 mm depth in the late-water treatment mirrors a similar nitrate concentration peak at that depth (Fig. 3.3).

The measured sodium profiles are not shown, as values were low relative to the other cations (less than 3 mole m^{-3}). However depletion of sodium in the top 50 mm of soil to less than half its value lower down in the columns was observed.

SIMULATION RESULTS AND DISCUSSION

Firstly we describe how the parameters appearing in the Theory section, but not discussed in Chapter 2, were evaluated. The initial values assumed for M_i , the amount

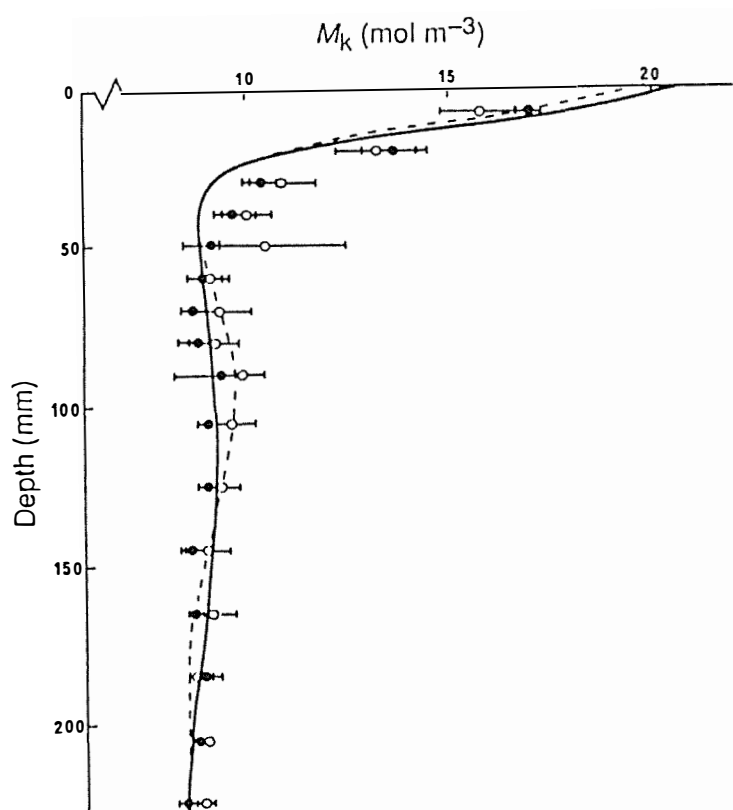


Fig. 3.4. Measured potassium concentration profiles for early- (●) and late- (○) water treatments and their standard deviations. Also shown are the simulated profiles for early- (——) and late- (---) water treatments

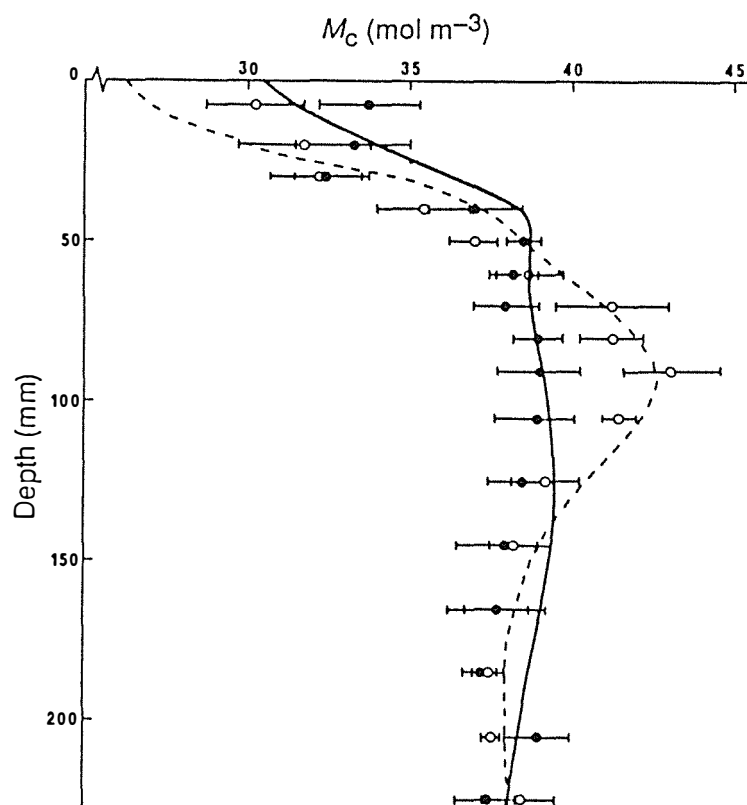


Fig. 3.5. Measured calcium concentration profiles for early- (●) and late- (○) water treatments and their standard deviations. Also shown are the simulated profiles for early- (——) and late- (---) water treatments

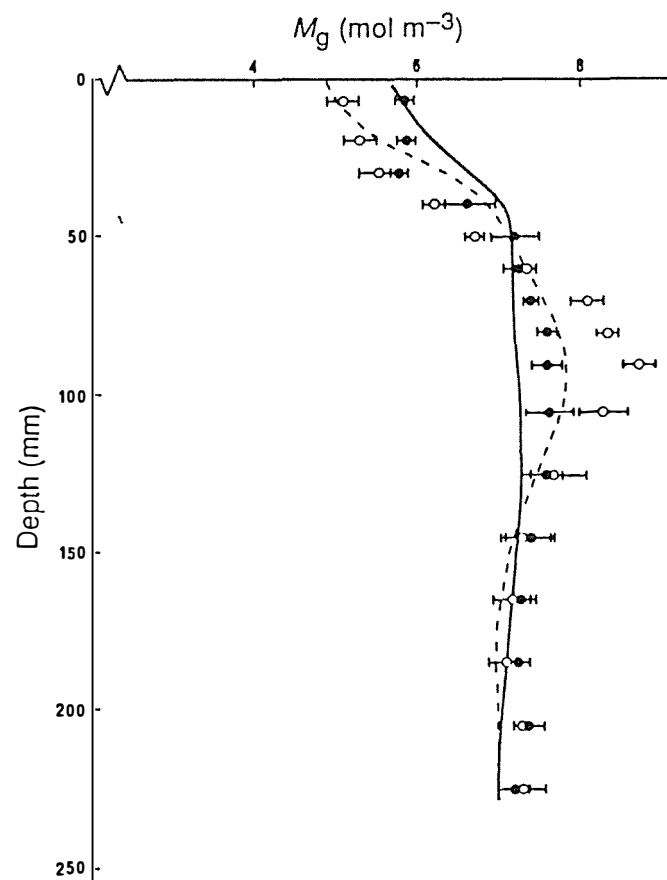


Fig. 3.6. Measured magnesium concentration profiles for early- (●) and late- (○) water treatments and their standard deviations. Also shown are the simulated profiles for early- (——) and late- (---) water treatments

of a particular chemical species in unit soil volume, were the amounts measured beyond the wetting fronts, as shown in Figs. 3.2 to 3.6. The initial value for γ , the charge on the cations present in unit volume of soil solution, was assumed equal to the concentration of nitrate initially present in the soil solution (M_n/Θ), as nitrate was the dominant anion in the soil solution. The initial cation exchange capacity value assumed was 97.5 mol m^{-3} , the difference between the total initial positive charge per unit soil volume due to the measured amounts of calcium, magnesium, potassium and sodium, less $\Theta\gamma$.

Published data suggest the urea would have been rapidly hydrolysed. At 20°C Kumar and Wagenet (1984) measured k_u values of 0.12 h^{-1} and 0.44 h^{-1} for two different soils. A value of 0.2 h^{-1} was assumed, implying that 99% of the applied urea would have been hydrolysed within 24 hours. As leaching was not commenced for at least 72 hours after urea application, the value assumed is not critical. Any value greater than 0.06 h^{-1} will ensure that the urea hydrolyses by the time of water application.

The nitrification 'constant' (k_a) would be expected to depend on a number of variables, such as soil water content, pH, and time for the population of nitrifying bacteria to build up (Bosatta *et al.*, 1981). As this was a study in solute movement rather than nitrification, k_a values were chosen which gave the measured amounts of ammonium remaining in the columns. This was determined at both the time of leaching and at the end of the experiment. The amount of nitrification at the time of leaching was estimated from the increase in nitrate content below 50 mm depth at the end of the experiment, less the 'native' nitrate leached from above 50 mm. That is, it was assumed the 30 mm of water leached all the nitrate, but none of the ammonium, below 50 mm depth. Then k_a was calculated as

$$k_a = \frac{\ln(M_{a,1}/M_{a,2})}{(t_2 - t_1)} \quad (3.19)$$

where $M_{a,1}$ and $M_{a,2}$ were the amounts of ammonium present at times t_1 and t_2 respectively. The values computed this way were 0.001 h^{-1} for the first three days for both treatments, and 0.011 h^{-1} for the early water treatment after this time. For the late-water treatment a value of 0.005 h^{-1} was found for times greater than three days but less than ten days (when water was applied), after which k_a is 0.021 h^{-1} . Similar values were found by Iskandar and Selim (1981).

The diffusion coefficients in pure solution (D_0) estimated from Robinson and Stokes (1959) were $1.4 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for monovalent cations and $1.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for bivalent cations. The bivalent cation value was also used for nitrate, as Figs. 3.5 and 3.6 show calcium and magnesium were the dominant accompanying cations.

The remaining parameter needed was k_G , the partition coefficient in equation (3.4). The value found for potassium and calcium exchange by Robbins *et al.* (1980) was used, $0.36 (\text{mol litre}^{-1})^{1/2}$, or $11.4 (\text{mol m}^{-3})^{1/2}$ in the units used here.

Simulated ammonium concentration profiles are shown in Fig. 3.2, and are quite close to the measured values in the top 50 mm. Below that depth the simulation predicts no ammonium. Low but measurable concentrations were however found there. This ammonium probably resulted largely from net mineralization during the experiment.

The simulated nitrate profiles are shown in Fig. 3.3. Again they agree well with the measured values in the top 50 mm, but below that depth they are lower than the measured values. Mineralization is the probable cause of this discrepancy also. For the late-water treatment the measured concentration peak at 90 mm depth is much sharper than the simulated peak. This suggests that much of the mineralization had occurred during the first 10 days, in the narrow band of soil moistened by the initial 5 mm of solution, and this band had then been moved down by the 30 mm of water. Another probable reason for the simulated peak being less sharp than the measured one is an over-estimation of the dispersivity, as discussed in Chapter 2.

In the early-water treatment, the envelope between the measured and simulated nitrate profiles is much more spread out than in the late-water treatment. Presumably this is

because after three days there was a much larger depth of moist soil. Despite the discrepancies discussed above, the simulated and measured profiles have very similar shapes for both the early and late treatments. Note that for the late-water treatment the "snow-plough effect" (Starr and Parlange, 1979) on the native nitrate has caused the simulated leached concentration peak to occur at 150 mm depth, rather than the 90 mm found for tritium and bromide in Chapter 2.

The simulated potassium profiles shown in Fig. 3.4 are similar in shape to the profiles obtained from the measured values. Although the measured treatment differences are small, the simulated profiles show similar consistent differences between the two treatments, with more downward potassium movement in the late-water treatment. However the main result is that the simple cation exchange model successfully simulated the retention of nearly all of the applied potassium in the top 25 mm of soil.

Fig. 3.5 shows the simulated calcium profiles, and they agree closely with the measured profiles, the simulated values falling within one standard deviation of the measured values in nearly all cases. The difference between treatments is clear in both the simulated and measured data. The simulated magnesium profiles in Fig. 3.6 reflect similar differences between treatments, but do not agree as well with the measured values. This is probably due to the assumption that the ratio of solution concentrations for magnesium and calcium equalled M_g/M_c being incorrect.

The data that we have not simulated are the pH data in Fig. 3.1. The simulation assumed that changes in the solution concentration accounted for only a negligible fraction of the hydrogen ions consumed or produced during the various transformations of added nitrogen. In terms of the effect of hydrogen ions on the movement of other cations, this is a good assumption. However, the small fraction of the hydrogen ions involved that did stay in solution significantly reduced the pH, measured in both water and calcium chloride. Predicting the magnitude of this drop would be very difficult, as it would need a very accurate description of the hydrogen ion chemistry in a very complex system.

It was interesting to see the local temporal changes in cation exchange capacity simulated. For example, for the early water treatment during the first three days the cation exchange capacity in the top 4 mm of soil was predicted to increase from the initial value of 97.5 mol m^{-3} to 138 mol m^{-3} . It was then predicted to decrease to 81 mol m^{-3} by the end of the 12 day experiment. On the other hand, below 50 mm depth the simulated cation exchange capacity remained constant, as no hydrolysis or nitrification occurred there.

CONCLUSIONS

The strong interactions between the physical, chemical and biological processes occurring in soils have been demonstrated in a number of ways. Firstly, the dynamic nature of many soil processes means their timing relative to each other can determine the outcome. This was shown by varying the timing of irrigation or rainfall relative to the application and nitrification of applied urea. The result was a large difference in the amount of nitrate leached down the profile.

Secondly, it has been shown that water movement is a necessary, but not a sufficient condition for cation movement. The addition or production of an accompanying anion is also needed. Thus for a given water addition, nitrification substantially increased the amount of calcium and magnesium leached down the profile.

Thirdly, it was shown that the cation applied as a salt to the soil surface may not be the one moving down through the soil with the anion applied. Following the surface application of potassium bromide, it was mainly calcium rather than potassium that was leached down through the soil with the bromide.

All of the above interactions could have been qualitatively predicted from current understanding of soil processes. But the simulation has been able to go further and describe them quantitatively, largely using parameter values taken from the literature. A limitation of the experiments is that they were conducted under controlled conditions, using repacked soil, and without evaporation and plants present. Quantitative description in the field is more difficult, but is attempted in the next two chapters. However the results presented in this chapter suggest there is considerable scope for the integration of mechanistic descriptions of basic physical, chemical and biological soil

processes. This could lead to a better understanding of how they interact to give different distributions of nutrients in the soil, and to improved management strategies for water and fertilizer application.

CHAPTER 4

MOVEMENT OF A NON-REACTIVE SOLUTE DURING INTERMITTENT WATER FLOW IN A FIELD SOIL

INTRODUCTION

Fertilizer that is applied to the soil surface in either liquid or solid form is carried into the soil by subsequent intermittent rainfall or irrigation. The distribution of fertilizer in the root zone affects its availability to plants and its susceptibility to leaching. If the processes involved are understood, management options can be devised which optimize nutrient uptake and minimize leaching. The initial soil water content and the timing of the fertilizer and water application are factors that can affect solute movement. This chapter investigates these factors for a non-reactive solute which behaves similarly to nitrate from fertilizer.

Solute movement through structured soils has been studied extensively in recent years. It is often observed that preferential flow through biologically-induced macropores, and the presence of relatively immobile water in smaller pores, leads to very non-uniform solute movement (White, 1985).

Evidence for apparently immobile water has also been obtained in columns of a repacked sandy soil in the laboratory. Bond and Wierenga (1990) list several workers, including themselves, who have demonstrated the existence of an immobile phase during steady unsaturated miscible displacement experiments. But, in contrast, other workers (Smiles and Philip, 1978; Smiles *et al.*, 1981; Bond *et al.*, 1982; Bond, 1986) have found no evidence of immobile water during unsteady, unsaturated miscible displacement experiments in repacked soil. They found that the invading solution appeared to push the resident solution ahead of it.

Bond and Wierenga (1990) explained these apparently contradictory results by suggesting that during wetting "the inflowing water was drawn into nearly all the pores

by capillarity. The solute was therefore carried into most of the wetted pore space by advection." However, even in repacked soil columns, "once the soil had reached a steady water content, water flow would have been biased towards the larger pores and sequences of pores offering the minimum resistance to flow."

The experiments described here look at the movement of a non-reactive solute associated with different antecedent water contents and irrigation timings in a field soil. The associated analysis looks at the relevance to the data obtained of the ideas in the preceding paragraph. Some consequences of the results for irrigation and fertilizer management are discussed.

THEORY

To describe solute flow, the macroscopic water flow must first be described. It is then assumed that the soil water can be operationally divided into water in which solute is potentially mobile, and water in which it is immobile. Solute movement in the mobile phase is described by the convection-dispersion equation. During wetting solute is convected into the immobile phase. But otherwise solute transport between the phases is only by molecular diffusion, and so to a first approximation linearly related to the soil solution concentration difference between the phases. Note that the mobile and immobile phases are defined in terms of solute rather than water movement. Solute in stationary water will be mobile if it can diffuse fast enough into adjacent moving water to be apparently convected with it.

As Wagenet (1983) pointed out, application of the approach described above "is not limited to strongly aggregated media, as almost any soil can be envisioned to consist of relatively mobile and immobile pore water phases." However such theory has so far been tested mainly under steady-flow conditions in laboratory columns, and has not been applied in the field under transient flow conditions (Wagenet, 1983; Addiscott and Wagenet, 1985). This is done here, but it requires numerical solution of the relevant equations, due to the complex boundary conditions.

As only one-dimensional vertical flow is considered, Darcy's equation can again be used to describe the water flow as

$$q = K \left(1 - \frac{d\psi}{dz} \right) . \quad (4.1)$$

Conservation of water requires that

$$\frac{\partial \theta}{\partial t} = - \frac{\partial q}{\partial z} - S \quad (4.2)$$

where S is a sink term accounting for root uptake and evaporation (s^{-1}). S is assumed to be of the form (Raats, 1974)

$$S = T \gamma \exp(-\gamma z) \quad (4.3)$$

where T is the evaporation rate ($m \ s^{-1}$) and γ is an empirical constant with units (m^{-1}). The $\psi(\theta)$ relationship is again assumed to take the form (Campbell, 1985)

$$\psi = a \left(\frac{f}{\theta} \right)^b . \quad (4.4)$$

The $K(\theta)$ relationship assumed is

$$K = \begin{cases} c \left(\frac{\theta}{f} \right)^d & \text{for } \theta > \theta_c \\ 0 & \text{for } \theta \leq \theta_c \end{cases} \quad (4.5)$$

where c and d are empirical constants and θ_c is the water content dividing the mobile and immobile phases.

While all solute is subject to molecular diffusion, only solute in the mobile phase is subject to convection and hydrodynamic dispersion. Often when hydrodynamic dispersion occurs, molecular diffusion is ignored. But when intermittent leaching events are separated by several days of relative quiescence, molecular diffusion can be a significant transport mechanism, as was shown in Chapter 2 . Thus it is included here. So in the mobile phase

$$j_m = q C_m - \lambda |q| \frac{dC_m}{dz} - \theta_m D \frac{dC}{dz} \quad (4.6)$$

where j is the solute flux density ($\text{mol m}^{-2} \text{s}^{-1}$), C is the soil solution concentration of the chemical species of interest (mol m^{-3}), and λ is the dispersivity (m) (Elrick and Clothier, 1990). The subscript m refers to the value of the parameter in the mobile phase. Lastly D is the molecular diffusion coefficient of solute in the soil ($\text{m}^2 \text{s}^{-1}$), assumed to be (Papendick and Campbell, 1981)

$$D = 3.5 \theta^2 D_o \quad (4.7)$$

where D_o is the diffusion coefficient in bulk solution.

C is found as M/θ where M is the total amount of solute present in unit soil volume (mol m^{-3}). Analogous equations give C_m and C_i as M_m/θ_m and M_i/θ_i respectively, where the subscript i denotes the value of the variable in the immobile phase. There

$$j_i = -\theta_i D \frac{dC}{dz} . \quad (4.8)$$

Conservation of solute mass, and the assumed link between mobile and immobile phases, gives

$$\frac{\partial M_m}{\partial t} = -\frac{\partial j_m}{\partial z} - \alpha \theta_i (C_m - C_i) \quad (4.9)$$

where α is the rate coefficient for exchange between the mobile and immobile phases (s^{-1}). Similarly

$$\frac{\partial M_i}{\partial t} = -\frac{\partial j_i}{\partial z} + \alpha \theta_i (C_m - C_i) . \quad (4.10)$$

Note that $\theta_m = \theta - \theta_c$ and $\theta_i = \theta_c$ if $\theta \geq \theta_c$, otherwise $\theta_m = 0$ and $\theta_i = \theta$.

The above equations were solved numerically, using an explicit forward finite-difference approach and a microcomputer running a compiled BASIC. The soil profile was divided into p compartments each Δz thick. During each time step Δt long, water and solute moved between compartments. Also solute moved between mobile and immobile phases in each compartment. Both these processes occurred at rates determined by the values of the parameters at the start of the time step. Thus from

equation (4.1), q_n , the water flux density between compartments $n-1$ and n , was found as

$$q_n = \left(\frac{(\psi_{n-1} - \psi_n + \Delta z)}{\Delta z} \right) \left(\frac{(K_{n-1} + K_n)}{2} \right) \quad (4.11)$$

where the subscript indicates the compartment for which the parameter was evaluated. The imposed surface boundary condition gave q_1 . At the bottom of the profile gravity drainage was assumed so q_{p+1} equalled K_p . The mobile-phase solute flux density into compartment n was found from equation (4.6) as

$$j_{m,n} = q_n C_{m,n-1} - \theta_m D_n \frac{(C_n - C_{n-1})}{\Delta z} \quad (4.12)$$

and a similar finite difference equation was derived from equation (4.8). Note that when the water flux was upwards and q_n negative, $C_{m,n-1}$ was replaced by $C_{m,n}$ in equation (4.12). Note also that equation (4.12) did not apply if $\theta < \theta_c$ in a compartment. Then the incoming convected solute went with the water into the immobile phase until that phase was full of water.

Hydrodynamic dispersion was not explicitly accounted for in equation (4.12). However as the solute concentration in the compartment rather than at the exit surface was used in the convection term, "numerical dispersion" resulted. Given $\Delta t \ll \Delta z/q$, the effect was to induce dispersion equivalent to that described by equation (4.6) with $\lambda = \Delta z/2$ (Campbell, 1985).

Once the various fluxes for each compartment and phase had been found for a certain time step, the new water and solute contents at the end of the time step could be found. For water in compartment n , from equation (4.2)

$$\theta_{t+\Delta t} = \theta_t + \left[\frac{(q_n - q_{n+1})}{\Delta z} - S \right] \Delta t. \quad (4.13)$$

The new concentration of mobile phase solute in compartment n followed from equation (4.9) as

$$M_{m,t+\Delta t} = M_{m,t} + \left[\frac{(j_{m,n} - j_{m,n+1})}{\Delta z} - \alpha \theta_m (C_{m,n} - C_{i,m}) \right] \Delta t \quad (4.14)$$

and an analogous equation for the immobile phase followed from equation (4.10). How the parameters in the above equations were evaluated is discussed later in the chapter.

Some comment on the simplifications involved in the above theory needs to be made. Spatial variability in both the water and solute fluxes is ignored. Studies of leaching under ponded boundary conditions (Biggar and Nielsen, 1976) show huge variability. But with unsaturated flow under conditions of a spatially uniform flux at the surface, such as under rainfall or sprinkler irrigation, one would expect the variability to be much less. The rate of exchange between the notional mobile and immobile phases will be highly variable in space and time, so use of a constant α in equations (4.9) and (4.10) described the exchange in only a crude way, as discussed in Chapter 1. Also, we would expect plant water extraction, and so γ , to vary with the soil water content distribution, and with plant growth, which will affect the ratio of surface evaporation to transpiration and root uptake. Further one would expect θ_c to vary with soil depth, due to changes in soil structure, texture and biopore density. For all these reasons, one would expect the above theory to give only a first-order approximation of solute flow in field soils. But a big advantage is that the model's mechanistic basis allows extrapolation to other boundary conditions, and extension to reactive solutes.

MATERIALS AND METHODS

The experimental site near Massey University was an area of Manawatu silt loam (a Dystric Fluventic Eutrochrept) under pasture, predominantly ryegrass/white clover. Prior to each experiment the pasture was cut very close to the surface with a rotary mower. The open nature of the sward remaining meant that approximately 50% of the soil surface was bare. A pit at either end of the site was dug, and cores taken for bulk density and soil water retentivity measurements. Two experiments were conducted, one in December 1988 and the other in January 1989. In the first experiment six adjacent square plots, each 0.5 m² in area, were pegged out. The area around the plots was used as a control. Two treatments were applied, each to three randomly selected plots. The first treatment involved the application of 5 mm (2.5 litres) of 77 mol m⁻³ potassium bromide solution over about a 6 minute period with a garden sprayer. This was followed immediately by the spray application of 50 mm of water, applied in 5 mm pulses (again with an application rate of approximately 50 mm h⁻¹) every 30 minutes. The second treatment was the same as the first. But prior to the application of the potassium bromide 20 mm of water was sprayed onto the soil surface, again in 5 mm pulses. Only small isolated areas of ponding for very short periods were observed at these application rates. The unsaturated flow which prevailed was probably similar to that occurring under sprinkler irrigation or rainfall.

Twenty-four hours after the bromide and water had been applied, nine soil cores, 25 mm in diameter and 500 mm deep, were extracted from each plot. Another nine cores were extracted from the surrounding control area. The top 200 mm of each core was divided into 25 mm long segments, and the remainder into 50 mm long segments. The nine samples from each depth from each of two replicate plots for each treatment were bulked. The nine cores from the third replicate plot for each treatment, and from the control area, were analyzed separately, to give an indication of variability within the plots.

Soil water content was measured gravimetrically on a subsample from each core. The independently measured bulk density values were used to calculate volumetric water

contents. The rest of each soil sample was air-dried, and for the bulked samples a 4 g subsample was shaken with 20 ml of distilled water on an end-over-end shaker for 30 minutes, and the mixture then centrifuged and filtered. For the smaller non-bulked soil samples, 2 g of soil was shaken with 15 ml of water. Aliquots (5 ml) of the filtrate were mixed with 10 ml of 150 mol m^{-3} of sodium nitrate solution to equalize the ionic strength, and the bromide concentration measured with a specific ion electrode. These data were used to calculate the amount of bromide per unit soil volume.

The second experiment involved 10 similar 0.5 m^2 plots. On 4 January 1989, 5 mm of solution containing 154 mol m^{-3} of potassium bromide and 71.4 mol m^{-3} of urea was applied to each plot. On 6 January 30 mm of distilled water was applied to five of the plots, which we will refer to as the "early water" treatment. On 14 January, 30 mm of water was applied to the remaining five "late water" plots. Water and the bromide/urea solution were applied using a sprayer in 5 mm pulses as described above for the first experiment. The experiment ended on 16 January (12 days after the bromide had been applied) when nine 500 mm deep soil cores were taken from each of three plots from each treatment, and also from the control area surrounding the plots. Also during the experiment, two cores were taken from each of the other four plots, and from the control area, every two days from 4 to 16 January. The top 300 mm of each core was cut into 25 mm long segments and the remainder into 50 mm segments, and the segments from each depth bulked for each plot. Soil water and bromide content were measured, as described for the first experiment.

Rainfall was measured daily at the site, and sunshine hours and air temperatures were measured at a site less than 1 km away.

EXPERIMENTAL RESULTS AND DISCUSSION

For the first experiment, the water contents measured one day after irrigation are shown in Fig. 4.1. The profile for the control area was assumed to represent the water content in the plots just prior to treatment on the preceding day. From the 500 mm depth of soil sampled, 74% and 68% of the applied water was recovered from the first and second treatments respectively. Presumably water movement below 500 mm depth

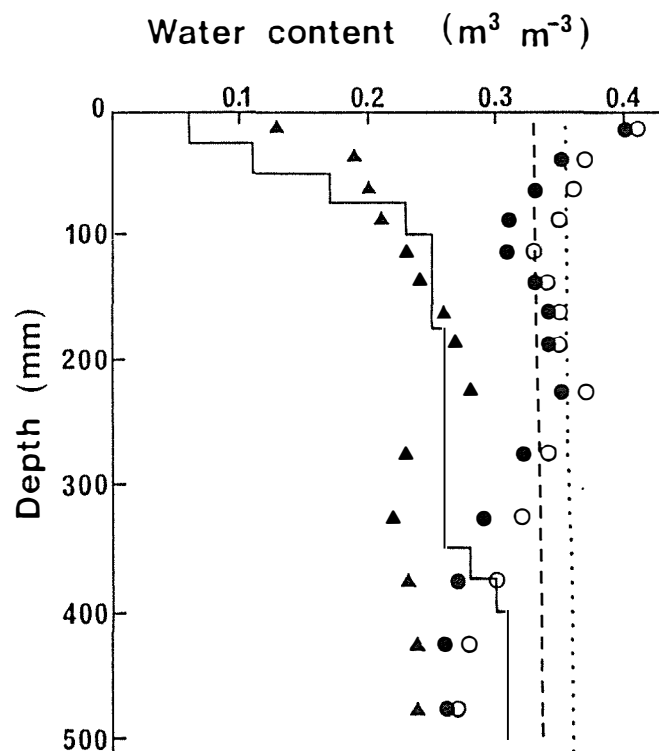


Fig. 4.1. Measured (symbols) and simulated (lines) water content profiles for the first experiment. The control is ▲ and the solid line, the first treatment is ● and the dashed line, and the second treatment is ○ and the dotted line.

was the main reason for the less than 100% recovery, with more movement from the second treatment, to which 20 mm more water had been applied.

The bromide concentrations per unit soil volume obtained from the nine individually-analyzed cores for one replicate for each treatment are shown in Fig. 4.2. There is considerable variability, but nevertheless the contrast between the data for the two treatments is clear. The mean bromide distributions for the three replicate plots for each treatment are shown in Fig. 4.3. The average recovery of bromide was 112% and 101% for treatment 1 and 2 respectively. Given the difficulty of uniformly applying the bromide, and the within-plot variability evident in Fig. 4.2, these values seem reasonable.

The data in Fig. 4.3 show clearly that the application of 20 mm of water prior to the bromide had a marked effect on the ability of the 50 mm of water applied after the bromide to move it further into the profile. The most likely explanation for the difference relates to the presence of relatively mobile and immobile water. In the first treatment, the 5 mm of bromide solution was applied to quite dry soil, with a volumetric water content of only 0.13 in the top 25 mm (Fig. 4.1). Thus the capillarity of the dry soil would pull the bromide solution into the smaller pores within the aggregates in the topsoil. During subsequent irrigation of the wetter soil, flow would have been mostly through the larger pores, largely bypassing the smaller pores containing the bromide, making it relatively immune to leaching.

However in the second treatment, the 20 mm of water applied before the 5 mm of bromide solution would have filled the smaller pores. So the bromide tended to remain in the larger pores, where it was much more prone to leaching by the subsequent 50 mm of water applied. The shape of the concentration profiles in Fig. 4.3 will be discussed further later in the chapter.

For the second experiment, the water applications, measured rainfall, and Priestley-Taylor evaporation estimates, calculated from the sunshine hour and temperature data as described by Scotter *et al.* (1979), are summarized in Table 4.1. The water content profiles measured during the experiment are shown in Fig. 4.4. In

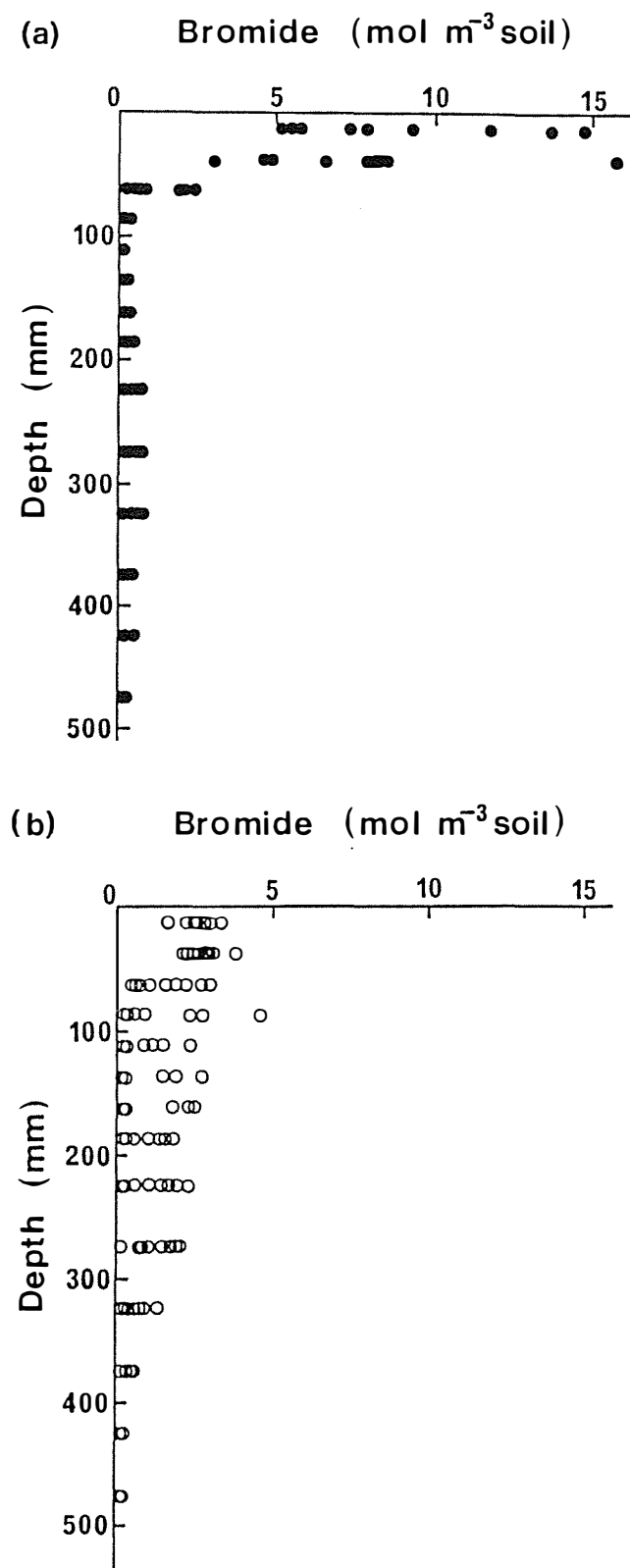


Fig. 4.2. Bromide concentration profiles for the nine individual cores from a replicate plot for the first experiment. (a) First treatment: 5 mm KBr solution then 50 mm water. (b) Second treatment: 20 mm water, then 5 mm KBr solution, then 50 mm water.

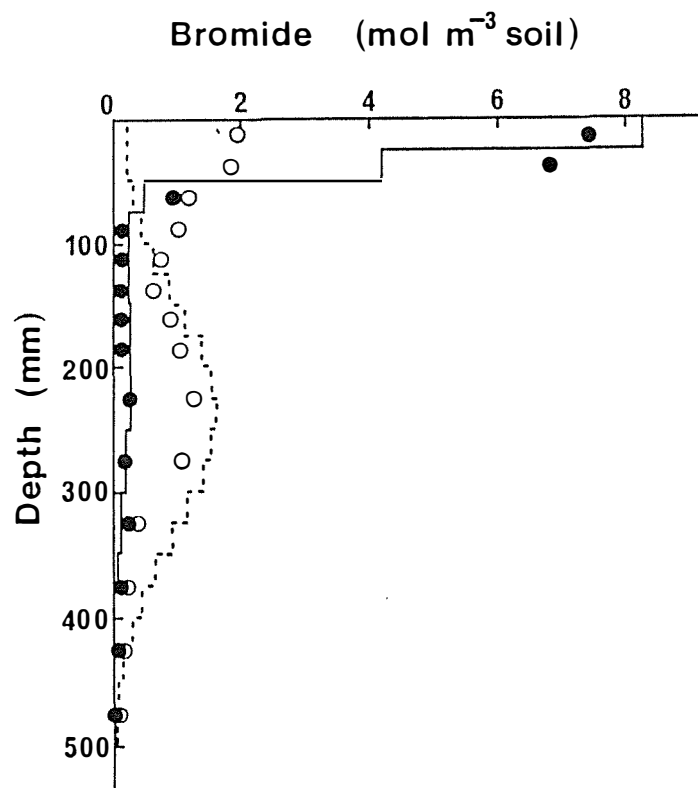


Fig. 4.3. Measured (symbols) and simulated (lines) bromide concentration profiles for the first experiment. The first treatment is ● and the solid line, and the second treatment is ○ and the dashed line.

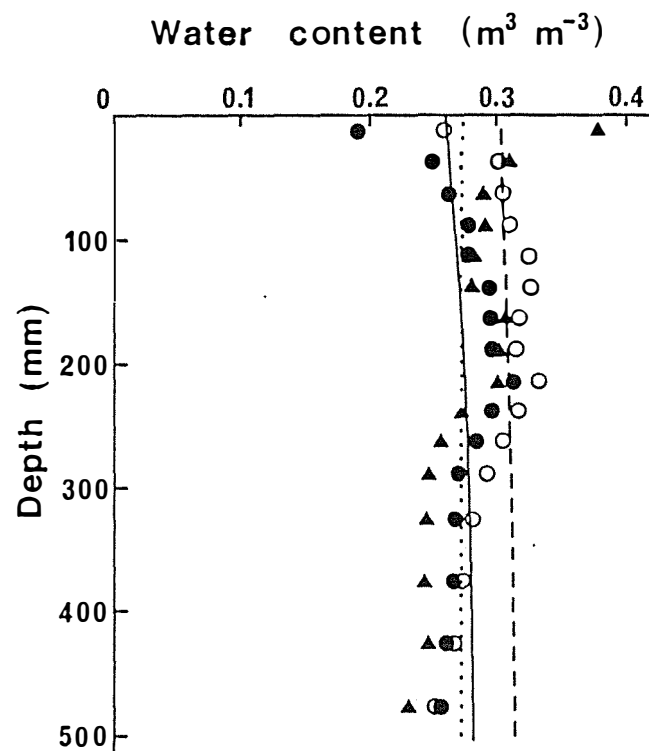


Fig. 4.4. Measured (symbols) and simulated (lines) water content profiles for the second experiment. The profile at the start of the experiment is ▲ and the dotted line. Profiles at the end of the experiment are ● and the solid line for the early-water treatment, and ○ and the dashed line for the late-water treatment

Table 4.1. Daily rainfall, irrigation, and estimated evapotranspiration during the second experiment. EW and LW denote early and late water treatments respectively, I denotes irrigation, and R rainfall.

Day	Irrigation or Rain (mm)	Evaporation (mm)
1	5.0 (I)	3.9
2	0	6.1
3	30.0 (EW - I)	6.0
4	0	2.1
5	0	2.6
6	8.7 (R)	2.2
7	22.6 (R)	5.4
8	0.1 (R)	5.0
9	0	4.8
10	1.2 (R)	4.4
11	30.0 (LW - I)	4.3
12	0	5.5
Total	67.6	52.3

contrast to the first experiment, rainfall prior to the commencement of the second experiment resulted in the top 25 mm of soil being quite wet at the start of the experiment, having a volumetric water content of 0.38. Despite the application of 67.6 mm of irrigation and rainfall during the 12 day duration of the experiment, the measured water content profiles changed relatively little, with 1 mm less water stored in the early water plots on 16 January than in the control area on 4 January, and 10 mm more water in the late water plots. The daily evaporation estimates (Table 4.1) for the 12 days totalled 52.3 mm, so the calculated surplus is 15.3 mm. Thus some water movement below 500 mm probably occurred, at least in the early water plots.

Only the bromide data from the second experiment are presented here; the potassium and nitrate data are presented in Chapter 5. The concentration profiles measured at the end of the second experiment are shown in Fig. 4.5. Recovery of the applied bromide was 83% and 82% for the early water and late water treatments respectively. The lower bromide recovery for this experiment could be due in part to plant uptake of bromide over the 12 days. The soil bromide data for the two treatments are very similar. The highest bromide concentrations were in the top 25 mm of soil. Below 50 mm depth the bromide concentration was much lower, but there was significant movement to below 300 mm depth and some bromide was leached below 450 mm depth.

Of note is the quite different bromide distribution found in the second experiment (Fig. 4.5) to that found in the second treatment of the first experiment (Fig. 4.3). Both involved the application of 5 mm of bromide solution to moist soil and its subsequent leaching with similar amounts of water. But there were two important differences. First in the first experiment the leaching was immediate, while in the second experiment it did not commence until either two or five days after the bromide application. This delay would have allowed the diffusion of some bromide from the mobile to immobile phases, making it less prone to leaching. Secondly, while only about 3 mm of evapotranspiration occurred over the one day duration of the first experiment, about 50 mm occurred during the 12 day duration of the second experiment. Most of this would have been lost as evaporation from the soil surface or plant uptake from the topsoil, inducing convective movement of water and bromide

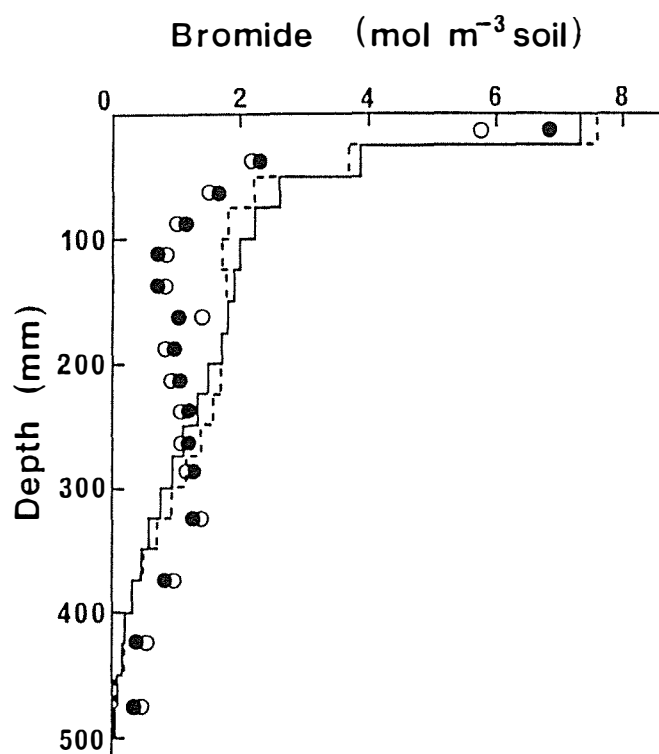


Fig.4.5. Measured (symbols) and simulated (lines) bromide concentration profiles for the second experiment. The early-water treatment is ● and the solid line, and the late-water treatment is ○ and the dashed line

back up towards the surface. The data from the monitoring samples taken during the 12 days, although very variable, suggest both the above mechanisms were significant. Their relative importance will be discussed in the next section.

SIMULATION RESULTS AND DISCUSSION

Before the theory outlined above can be used, values for the various parameters have to be found. No data for the relative amounts of evaporation and transpiration, and the depth distribution of root uptake were available. It was arbitrarily assumed that 80% of the evapotranspiration resulted from water taken from the top 100 mm of soil. Integration of equation (4.3) then gives γ as 0.0161 mm^{-1} . The bulk density data indicate a porosity value of 0.5 was reasonable for the whole profile. The measured soil water retentivity data were quite uniform with depth, and when fitted to equation (4.4) gave $a = -128 \text{ mm}$ and $b = 7.5$. If redistribution is to be realistically simulated, values for $K(\theta)$ at the relevant water contents must be correct, and extrapolation from measured values in wetter soil can lead to large errors (Scotter *et al.*, 1988). The constants in equation (4.5) were evaluated by simulating water flow as described, and choosing values that gave approximately the measured final soil water content profiles for the four quite different boundary conditions imposed in the two experiments. Values of 60 mm h^{-1} for c and 15 for d were selected. The initial water content profile assumed for the first experiment was selected so that the simulated soil water content change at each depth over the twenty-four hours equalled the measured change. The simulated soil water content profiles at the beginning and end of the two experiments are shown in Figs. 4.1 and 4.4. They are reasonably close to the measured profiles.

The water content dividing the mobile and immobile phases, θ_c , was selected so that the 5 mm of bromide solution applied to the first treatment of the first experiment just filled the immobile phase in the top 50 mm of soil. The value used was 0.18. D_o was taken as $3.6 \text{ mm}^2 \text{ h}^{-1}$, the value for calcium bromide, as in Chapter 3 it was shown that in this soil (and probably most other soils) the bromide carried with it predominantly native calcium rather than the applied potassium. As 20 compartments were used in the simulation, $\Delta z = 25 \text{ mm}$, so as explained above, numerical dispersion meant in effect λ was 12.5 mm. After a little experimentation with different values, an α value

of 0.028 h^{-1} was chosen. Stability criteria necessitated a relatively small time step when water fluxes were large, while at other times larger steps could be used. So values for Δt ranged from .005 to 0.05 h.

The simulated bromide concentrations per unit soil volume ($M = M_i + M_m$) for the four different sets of boundary conditions are shown in Figs. 4.3 and 4.5. The agreement between experiment and simulation is good for the first treatment in Fig. 4.3, but only fair for the second treatment. More bromide remained in the top 100 mm of soil than theory predicts. A plausible reason for this relates to the somewhat water repellent behaviour of this soil (Appendix 1). While water appears to infiltrate "normally", it goes in much more slowly than is predicted from the infiltration of ethanol. Thus water, and the solute it carries, may only gradually move into the smaller pores in the topsoil. So even though 20 mm of water had been applied immediately beforehand, some of the applied bromide in the second treatment may have moved with the water into the smaller topsoil pores. Once there it would be relatively immune to leaching.

For the second experiment, Fig. 4.5 shows the agreement between the measured and simulated bromide profiles is only reasonable. In this case the bromide moved somewhat further into the soil than the simulation predicted. Both the data and the simulation show it made little difference whether the 30 mm irrigation was applied on the third day or the tenth day of the 12 day experiment. It seems a couple of days delay is long enough for a substantial fraction of the applied bromide to diffuse into the immobile phase .

It was suggested above that both bromide diffusing into the immobile phase and being relatively immune to leaching there, and evapotranspiration inducing upwards convection of bromide, were responsible for the high bromide concentration in the surface soil shown in Fig. 4.5. Simulation allows the influence of these two processes to be separated. Fig. 4.6 shows three simulations of the final bromide concentration profile for the early water treatment of the second experiment. The solid line is redrawn from Fig. 4.5. It was computed assuming evaporation extracted soil water according to equation (4.3), with 80% of the water being taken from the top 100 mm.

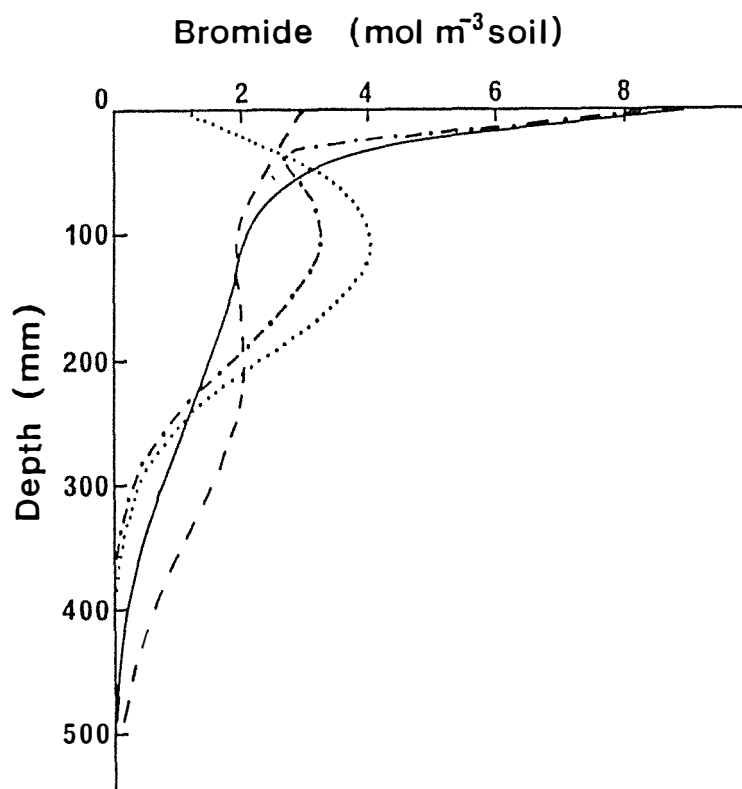


Fig. 4.6. Simulated bromide concentration profiles for the second experiment with early water. The solid line is redrawn from Fig. 4.5. The dashed line is as for the solid line, but with uniform water extraction with depth. The dotted line is as for the solid line, but with no immobile water. The dotted and dashed line is as for the solid line, but with all the water loss from the soil surface and no immobile water

The dashed line assumed the evaporated water was extracted uniformly from the 500 mm depth of soil sampled. While the highest concentration is still at the surface, the concentration there is much lower, and there is a secondary peak further down the profile. A secondary peak also appeared in the experimental data (Fig. 4.5). Another simulation, not shown in Fig. 4.6, assuming all the water was evaporated from the soil surface, predicted a bromide concentration of 12.4 mol m^{-3} of soil in the top 25 mm, approximately twice the measured value. These results suggest that the water extraction pattern strongly affected the bromide distribution.

The dotted line in Fig. 4.6 was simulated assuming the equation (4.3) extraction pattern with 80% of the water coming from the top 100 mm, but with θ_c equal to 0.001 rather than 0.18. That is, in effect assuming all the water is mobile, so the standard convection-dispersion equation applies. The common bell-shaped distribution is predicted, with little bromide near the soil surface or below 250 mm and a pronounced peak at 100 mm depth. Although alteration of the dispersivity (λ) would sharpen or flatten the bell-shaped peak, it would not greatly change its position. The dotted and dashed line in Fig. 4.6 was simulated by assuming all the evaporated water was lost from the soil surface, and with no immobile water. Although this simulation predicts a pronounced secondary peak at 100 mm depth which was not present in the experimental data, it is interesting to note that the final concentration in the top 50 mm of soil can be simulated quite closely using classical miscible displacement theory, without the need to invoke mobile and immobile water phases. The same cannot be said for the data in Fig. 4.3 however.

Fig. 4.6 illustrates the danger pointed out by Jury and Ghodrati (1989) of constructing models with several parameters that cannot be independently measured or estimated (e.g. γ , θ_c , λ and α in this study) and must be assigned arbitrary values. Nevertheless, as solute movement with four quite different water flow boundary conditions was reasonably well simulated, it appears probable that the model provides a reasonably realistic description of the main processes and interactions leading to the data shown in Figs. 4.3 and 4.5.

CONCLUSIONS

The results discussed above have some obvious practical implications. For example, a slug of liquid nitrogen fertilizer applied to a relatively dry topsoil will be much less prone to subsequent leaching than if applied to wet soil. Alternatively, if the slug is applied to wet soil, delaying irrigation for several days will also markedly reduce leaching. On the other hand, if it is desired to get a non-sorbed fertilizer down into the subsoil as quickly as possible, it should be applied to moist soil and followed immediately by irrigation.

Less directly, the results also imply that intermittent leaching will be more effective than continual leaching in removing excess salt from the soil, provided the same amount of drainage from the soil profile results, as Biggar and Nielsen (1967) suggest.

Coupling a mobile-immobile variant of the convection-dispersion equation with a description of transient water flow and extraction, provided a mechanistic model describing the main features of non-reactive solute movement under four different water application regimes. In such a model the dispersivity (λ) may be less significant than the parameters describing the relationship between the mobile and immobile phases (θ_c and α) and the distribution of water extraction with depth (γ).

CHAPTER 5

THE MOVEMENT OF POTASSIUM AND NITRATE DURING INTERMITTENT WATER FLOW IN A FIELD SOIL

INTRODUCTION

The movement, in response to intermittent water flow, of various forms of nitrogen and the major exchangeable cations was investigated in repacked soil columns in the laboratory and reported in Chapters 2 and 3. In this system, where the flow of water was well understood, it proved possible to construct a model based on convection-dispersion theory combined with simple descriptions of nutrient reactions and transformations. This model described quite closely the final distribution of nutrients in treatments which varied markedly in the relative scheduling of fertiliser and irrigation applications.

Since this experiment was conducted under controlled conditions, using repacked soil, without evaporation and plant uptake it was surmised that quantitative description in the field would be more difficult.

In Chapter 4 two field experiments were described, one of which was an analogue of the experiment conducted earlier in the laboratory. The patterns of both water and bromide movement obtained in the field were very different from those in the laboratory. Convection-dispersion theory could only describe the results if the soil water was divided into a notionally mobile and effectively immobile phase.

This chapter now presents data on the movement of nitrate-nitrogen and potassium in the field experiments described in Chapter 4. Particular attention is focused on the extent to which, given an adequate description of water movement in field soil, the chemical relationships developed earlier can be used to describe the movement of reactive nutrients such as nitrogen and potassium.

THEORY

The theory used to describe water flow and the movement of non-reactive solutes in a field soil has been described in Chapter 4. To recapitulate briefly, the macroscopic water flow within the soil profile is described by Richards' equation with allowance for loss of water by root uptake and evaporation.

Once the movement of water has been described, it is assumed that the soil water can be divided into water in which solute is potentially mobile and water in which it is relatively immobile. Vertical movement of non-reactive solutes in the mobile phase is described by the convection-dispersion equation. During wetting of soil with an initially low water content, solute is convected directly into the immobile phase. Otherwise solute transport between the mobile and immobile phases is only by molecular diffusion.

So in the mobile phase for a non-reactive solute

$$j_m = q C_m - \lambda |q| \frac{dC_m}{dz} - \theta_m D \frac{dC}{dz} \quad (5.1)$$

where j is the solute flux density ($\text{mol m}^{-2} \text{s}^{-1}$), q is the Darcy flux density (m s^{-1}), C is the soil solution concentration of the chemical species of interest (mol m^{-3}), λ is the dispersivity (m) (Elrick and Clothier, 1990), θ is the water content ($\text{m}^3 \text{m}^{-3}$) and z is depth (m). The subscript m refers to the mobile phase. Lastly D is the molecular diffusion coefficient of solute in the soil ($\text{m}^2 \text{s}^{-1}$), assumed to be of the form (Papendick and Campbell, 1981; see also Chapter 2)

$$D = 3.5 \theta^2 D_0 \quad (5.2)$$

where D_0 is the diffusion coefficient of the chemical species in bulk solution.

The concentration, C , is found as M/θ where M is the total amount of solute present in unit soil volume (mol m^{-3}). Analogous equations give C_m and C_i as M_m/θ_m and M_i/θ_i respectively, where the subscript i refers to the immobile phase. There

$$j_i = -\theta_i D \frac{dC}{dz} . \quad (5.3)$$

Conservation of solute mass, and the assumed link between mobile and immobile phases, gives

$$\frac{\partial M_m}{\partial t} = -\frac{\partial j_m}{\partial z} - \alpha \theta_i (C_m - C_i) \quad (5.4)$$

where α is the rate coefficient for exchange between the mobile and immobile phases (h^{-1}). Similarly for the immobile phase

$$\frac{\partial M_i}{\partial t} = -\frac{\partial j_i}{\partial z} + \alpha \theta_i (C_m - C_i) . \quad (5.5)$$

Note that $\theta_m = \theta - \theta_c$ and $\theta_i = \theta_c$ if $\theta \geq \theta_c$, where θ_c is the water content dividing the mobile and immobile phases. Otherwise if $\theta < \theta_c$ then $\theta_m = 0$ and $\theta_i = \theta$.

In both of the experiments reported here, bromide was added to the soil as potassium bromide. In the second experiment nitrogen as urea was also applied. While the theory outlined above is adequate to describe the distribution and movement of bromide, the chemical and biological transformations of soil nitrogen, and the interactions of cations such as potassium, ammonium and calcium with soil surfaces, introduce additional

complications. The approach described in Chapter 3, which was developed to describe the movement of cations and nitrogen in repacked soil columns, was applied here.

Urea applied to soil is hydrolysed to ammonium, which in turn is nitrified to nitrate. Both the initial hydrolysis and subsequent nitrification are treated as first order reactions, following for example Wagenet *et al.* (1977). Thus

$$\frac{\partial M_{u,m}}{\partial t} = -\frac{\partial j_{u,m}}{\partial z} - k_u M_{u,m} - \alpha \theta_i (C_{u,m} - C_{u,i}) \quad (5.6)$$

where the subscript u refers to urea and k_u is the rate constant for urea hydrolysis (h^{-1}). Similarly in the immobile phase

$$\frac{\partial M_{u,i}}{\partial t} = -\frac{\partial j_{u,i}}{\partial z} - k_u M_{u,i} + \alpha \theta_i (C_{u,m} - C_{u,i}) . \quad (5.7)$$

For ammonium, identified by the subscript a

$$\frac{\partial M_{a,m}}{\partial t} = -\frac{\partial j_{a,m}}{\partial z} + k_u M_{u,m} - k_a M_{a,m} - \alpha \theta_i (C_{a,m} - C_{a,i}) \quad (5.8)$$

and

$$\frac{\partial M_{a,i}}{\partial t} = -\frac{\partial j_{a,i}}{\partial z} + k_u M_{u,i} - k_a M_{a,i} + \alpha \theta_i (C_{a,m} - C_{a,i}) \quad (5.9)$$

where k_a is the rate constant for the first order reaction assumed to apply to nitrification. For nitrate, denoted by the subscript n , it follows that

$$\frac{\partial M_{n,m}}{\partial t} = -\frac{\partial j_{n,m}}{\partial z} + k_a M_{a,m} - \alpha \theta_i (C_{a,m} - C_{a,i}) \quad (5.10)$$

and

$$\frac{\partial M_{n,i}}{\partial t} = -\frac{\partial j_{n,i}}{\partial z} + k_a M_{a,i} + \alpha \theta_i (C_{a,m} - C_{a,i}) . \quad (5.11)$$

Plant uptake, denitrification, and net mineralisation were assumed to be negligible during the experiment. These assumptions will be discussed later.

For reactive solutes such as the exchangeable cations of ammonium, potassium, calcium and magnesium, relationships are required between the total amount of a chemical species in either the mobile or immobile phase present in unit volume of soil, and the concentration of that species in the soil solution.

Cation exchange was considered to occur instantaneously, and assumptions were made concerning the distribution of the soil cation exchange capacity between the mobile and immobile phases. These assumptions are discussed in more detail later. Cation exchange was simplified by assuming a binary system of monovalent and bivalent cations. There was no distinction made between the individual monovalent cations (K^+ , NH_4^+ and Na^+) or between the individual bivalent cations (Ca^{2+} and Mg^{2+}) in terms of the soil's affinity for them. The proportions of individual monovalent cations present in solution were then assumed to be equal to the amount of that cation present relative to the total presence of monovalent cations. The solution concentration of individual bivalent cations was similarly estimated.

For both mobile and immobile phases the relative concentration in the soil solution of monovalent and bivalent cations was found using the Gapon equation (Robbins *et al.*, 1980). For the mobile phase this can be written as

$$\frac{C_{M,m}}{(C_{B,m})^{\frac{1}{2}}} = k_G \frac{X_{M,m}}{X_{B,m}} \quad (5.12)$$

where $X_{M,m}$ and $X_{B,m}$ are the amounts of charge balanced by monovalent and bivalent cations respectively, C is their concentration in the mobile phase of the soil solution, and k_G is a selectivity coefficient with units $(\text{mol m}^{-3})^{1/2}$. An analogous equation can be written for the immobile phase.

The procedure used for calculating the relative amounts of each cation in solution, and on the exchange surfaces has been described in detail in Chapter 3 and is not repeated here, except for a comment on the estimation of the cation exchange capacity (CEC). This was initially assumed to be equal to the sum of exchangeable cations originally in the soil, less an amount of charge equivalent to the amount of chloride and nitrate initially present. It was assumed that these anions would not be adsorbed and would therefore all be in the soil solution. Their charge would be balanced by cations in the soil solution with an equivalent quantity of positive charge.

Hydrogen ions are consumed during the hydrolysis of urea and produced during the nitrification of the resulting ammonium. As was the case of the experiment described in Chapter 3, measured pH changes could account for only a negligible fraction of the hydrogen ions either consumed or produced. Most of the hydrogen ions must therefore have been either released from or adsorbed onto the soil surface, effectively changing the CEC. Thus for the mobile phase

$$\frac{dP_m}{dt} = k_u M_{u,m} - 2k_a M_{a,m} \quad (5.13)$$

where P_m is the cation exchange capacity available to the mobile phase expressed as mol m⁻³ of soil. A similar equation can be written for the cation exchange capacity in the immobile phase.

The above simultaneous equations were all solved numerically, using an explicit forward finite-difference scheme on a microcomputer running compiled BASIC. The procedure is an extension of that detailed in Chapter 4 to describe the movement of water and a non-reactive solute such as bromide. Briefly, the soil profile was divided into p compartments, each Δz thick. During each time step Δt long, water and solute moved between compartments. Also solute moved between mobile and immobile phases in each compartment. Both these processes occurred at rates determined by the values of the parameters at the start of the time step. Thus from Darcy's equation

$$q = K(1 - \frac{d\psi}{dz}) \quad (5.14)$$

where K is the hydraulic conductivity (m s⁻¹) and ψ is the matric potential (m). The water flux density between compartments $n-1$ and n , was found from the finite formulation as

$$q_n = \frac{(\psi_{n-1} - \psi_n + \Delta z)}{\Delta z} \frac{(K_{n-1} + K_n)}{2} \quad (5.15)$$

where the subscript indicates the compartment for which the parameter was evaluated. The imposed surface boundary condition is simply q_1 . At the bottom of the profile,

gravity drainage was set equal to K_p . The flux density of the mobile-phase solute across the boundary between compartments $n-1$ and n was found from equation (5.1) as

$$j_{m,n} = q_n C_{m,n-1} - \theta_m D_n \frac{(C_n - C_{n-1})}{\Delta z} . \quad (5.16)$$

A similar finite-difference equation was derived from equation (5.3) for the immobile-phase solute flux density from compartment $n-1$ into compartment n . Note that when the water flux was upwards and q_n negative, $C_{m,n-1}$ was replaced by $C_{m,n}$ in equation (5.16). Note also that equation (5.16) did not apply if $\theta < \theta_c$ in a compartment. Then the incoming convected solute went with the water into the immobile phase until that phase was full of water.

Once the various fluxes for each compartment and phase had been found for a certain time step, the new water and solute contents at the end of the time step could be found. For water in compartment n

$$\theta_{t+\Delta t} = \theta_t + \left[\frac{(q_n - q_{n+1})}{\Delta z} - S \right] \Delta t \quad (5.17)$$

where S is the sink term accounting for root uptake and evaporation (s^{-1}) as described in Chapter 4.

For solutes such as bromide, potassium and calcium, for which the total quantity of solute in a compartment is not changed by chemical or biological transformation, the new quantity of mobile-phase solute in compartment n followed from equation (5.4) as

$$M_{m,t+\Delta t} = M_{m,t} + \left[\frac{(j_{m,n} - j_{m,n+1})}{\Delta z} - \alpha \theta_m (C_{m,n} - C_{i,m}) \right] \Delta t \quad (5.18)$$

and an analogous equation for the immobile phase follows from equation (5.5).

For solutes such as urea, ammonium and nitrate, the change in the total quantity of mobile- or immobile-phase solute in a compartment during a time step depends not only on flux into and out of the compartment, and movement between phases, but also on removal and/or addition by chemical or biological processes. Thus for ammonium from equation (5.8)

$$M_{a,m,t+\Delta t} = M_{a,m,t} + \left[\frac{(j_{a,m,n} - j_{a,m,n+1})}{\Delta z} + k_u M_{u,m} - k_a M_{a,m} - \alpha \theta_i (C_{a,m} - C_{a,i}) \right] \Delta t. \quad (5.19)$$

Similar equations for mobile-phase urea and nitrate follow from equations (5.6) and (5.10) respectively, and for immobile phase urea, ammonium and nitrate from equations (5.7), (5.9) and (5.11) respectively.

Once the quantities of monovalent and divalent cations in each compartment at the end of a time step had been established, the distribution of the various cations between the solution and the exchange complex was calculated using the procedure described in Chapter 3. The new solution concentrations thus calculated for ammonium, potassium, calcium and magnesium were then used when calculating nutrient fluxes in the next time step.

A discussion of some of the simplifications involved in the above theory appeared in Chapter 3.

MATERIALS AND METHODS

Details of the experiment conducted are given in Chapter 4. Briefly, the experimental site was an area of Manawatu silt loam (a Dystric Fluventic Eutrochrept) under pasture. Prior to each experiment the pasture was cut very close to the surface with a rotary mower. Two experiments were conducted, one in December 1988 and the other in January 1989. In the first experiment, six adjacent square plots each 0.5 m^2 in area, were pegged out. The area round the plots was used as a control. Two treatments were applied, each to three randomly-selected plots. The first treatment involved the application of 5 mm (2.5 litres) of 77 mol m^{-3} potassium bromide solution over about a 6 minute period with a garden sprayer. This was followed immediately by the spray application of 50 mm of water, applied in 5 mm pulses (again with an application rate of approximately 50 mm h^{-1}) every 30 minutes. The second treatment was the same as the first, except that immediately prior to the application of the potassium bromide 20 mm of water was sprayed onto the soil surface, again in 5 mm pulses every 30 minutes.

Twenty-four hours after the potassium bromide and water had been applied, the plots and control area were soil sampled to a depth of 500 mm. The detailed procedures for soil sampling and determination of volumetric water contents are described in Chapter 4. Soil samples were also analysed for exchangeable potassium, calcium and magnesium using the procedures described in Chapter 3.

As described in the preceding chapter, the second experiment involved 20 similar 0.5 m^2 adjacent plots. On 4 January 1989, 5 mm of solution containing 154 mol m^{-3} of potassium bromide and 71.4 mol m^{-3} of urea was applied to ten of the plots and 5 mm of distilled water was applied to the remaining 10 plots. On 6 January 30 mm of distilled water was applied to five of the plots which had received the potassium bromide/urea solution and five of the plots which had received only distilled water. These plots will again be referred to as "early water plots". On 14 January, 30 mm of water was applied to the remaining ten "late water" plots. Water and the potassium bromide/urea solution were applied using a sprayer in 5 mm pulses, as described for the first experiment.

The purpose of the ten "irrigated", but not "fertilised" plots was to provide a more realistic control against which the movement of applied nutrients could be measured. For nutrients such as nitrogen, the changes in water regime brought about by irrigation are likely to affect mineralisation/immobilisation reactions within the soil and thus the quantity of nitrate present. This would confound an assessment of nutrient movement if the surrounding un-irrigated area was used as a control.

The experiment ended on 16 January (12 days after the potassium bromide and urea had been applied). At that time three of the plots from each treatment and also the control area surrounding the plots were sampled as described in Chapter 4. The resulting soil samples were analysed for volumetric water content and bromide as described in Chapter 2, and also for nitrate-nitrogen and exchangeable potassium, calcium and magnesium, as described in Chapter 3.

Also during the second experiment, the remaining two replicate plots in each treatment, and the un-irrigated area surrounding the plots, were sampled in a less-intensive manner every two days from 4 to 16 January and the samples analysed as described earlier.

Rainfall was measured at the site, and sunshine hours and air temperature were measured at a site less than 1 km away.

EXPERIMENTAL RESULTS AND DISCUSSION

The final distributions of water and bromide in the two experiments have been given in Chapter 4.

The final potassium concentrations per unit soil volume for the control and two treatments in experiment one are shown in Fig 5.1. There was a large quantity of "native" soil potassium present and there was considerable variability associated with its measurement. However despite this variability, in the top 25 mm of soil there were significant differences in potassium concentration between the two treatments, and between both treatments and the surrounding control area. Below this depth no differences were apparent.

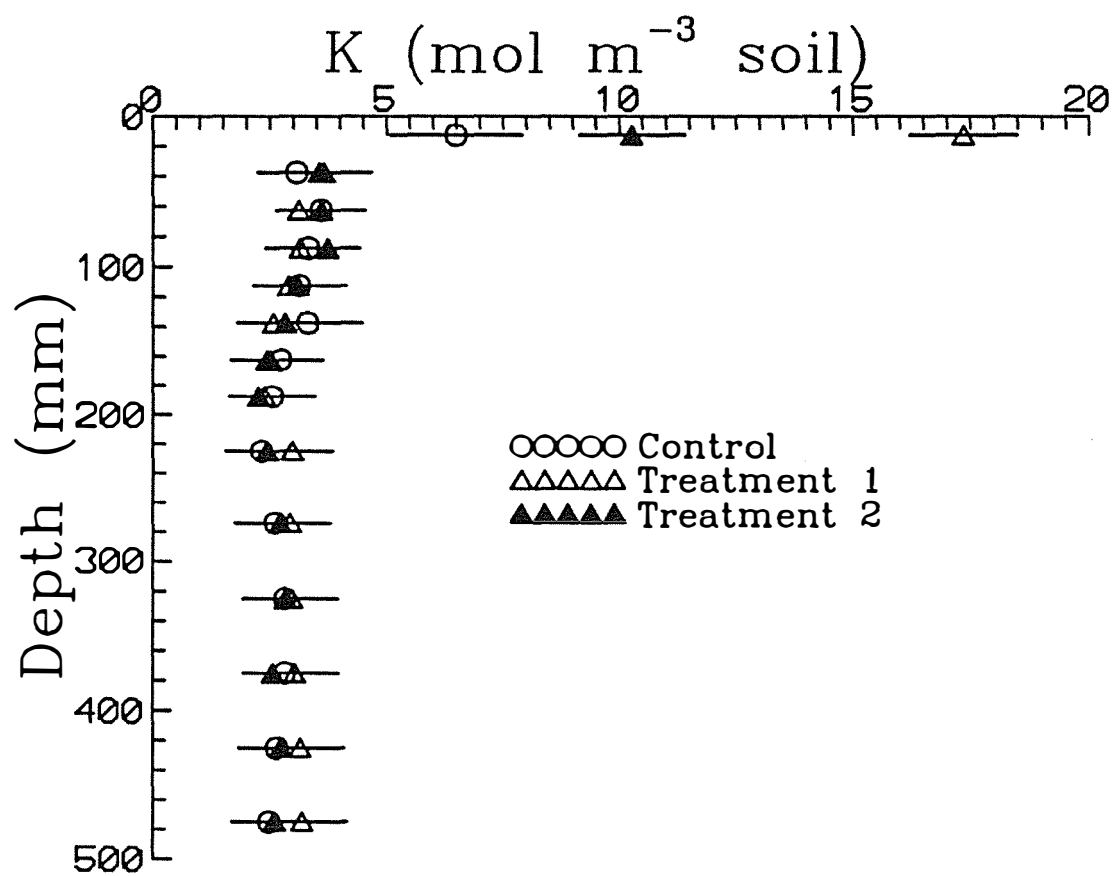


Fig. 5.1. Potassium distribution at the completion of the first experiment. Bars indicate standard errors of the mean

In the first treatment 71% of the added potassium was recovered in the top 25 mm with a further 3% in the next 25mm. This compares with recoveries of bromide of 48% and 44% in the 0-25 mm and 25-50 mm layers respectively (Chapter 4). This retention of bromide near the top of the soil profile, was perhaps surprising, given the amount of water applied after the potassium bromide. It was explained however in Chapter (4) by the observation that in this first treatment the potassium bromide solution was applied to quite dry soil. Thus the capillarity of the dry soil pulled the potassium bromide solution into a wide range of pores within the aggregates in the top soil. With subsequent irrigation of the now-wetted soil, flow would have been mostly through the larger pores, largely bypassing the smaller pores containing the potassium bromide, apparently making it relatively immune to leaching. The movement of potassium would be expected to be even more limited, given the possibility of cation exchange. This was observed (Fig. 5.1).

In treatment one the recovery of added potassium throughout the profile to 500 mm was 93%. The corresponding recovery of bromide was 112%. This lower recovery of potassium was a common feature of both experiments and is discussed in more detail below.

In treatment two significantly less potassium was retained in the top 25 mm than in treatment one (Fig. 5.1). Twenty-five percent of the added potassium was recovered in the top 25mm with a further 4% in the 25-50 mm layer. The corresponding recoveries of bromide were given in Chapter 4 as 13% and 12%. The greater movement of bromide out of the top soil in treatment two was attributed to the initial application of 20 mm of water. This would have filled the smaller pores before the 5 mm of potassium bromide solution was applied. The bromide therefore tended to remain in the larger pores, where it was much more prone to leaching by the subsequent 50 mm of water applied.

Given the behaviour of bromide, the extent to which this preferential flow through the larger pores would also influence the movement of an adsorbed ion such as potassium was of considerable interest. The low recovery of potassium in the top 25 mm suggests that some accelerated leaching of potassium had taken place, although not to the same

extent as bromide. Unfortunately it is not possible to be certain of the movement of potassium as no fertiliser potassium could be detected at depth. The total recovery of fertiliser potassium to 500 mm was only 27%. To some extent this inability to recover fertiliser potassium at depth can be attributed to the large and variable supply of native soil potassium. In simulation studies reported later, the predicted levels of potassium below the top layer were so close to the original levels of native potassium that no statistically significant differences could have been expected at depth. The fact however that potassium recoveries were consistently low suggests that there was incomplete extraction of added potassium. Either the extraction procedure was not sufficiently rigorous or else there had been some fixation into non-exchangeable forms. Despite these reservations, the data provide strong evidence of some preferential movement of potassium even though it is a reactive solute.

The distribution of potassium in the control and fertilised plots at the completion of experiment two is presented in Fig. 5.2. There were no significant differences between the pair of control treatments or the pair of fertilised treatments, although there was a clear effect of fertiliser in the top 25 mm. The final distribution of bromide was also very similar between the two fertiliser treatments (Fig. 4.5). Because of the similarities within the control and fertilised treatments, the data for the early- and late-water treatments were grouped when averaging the recoveries in an attempt to reduce variability.

Approximately 32% of the added potassium was recovered in the top 25 mm with a further 8% in the 25-50 mm layer. The corresponding recoveries of bromide from these depths were 9% and 2% respectively. Thus although at the end of twelve days the distributions of potassium and bromide were similar, in that the highest concentrations of applied nutrients were found in the top 25 mm of soil, more bromide than potassium had been leached downwards. Once again in this experiment the overall recovery of potassium to 500 mm was very low (43%) compared to bromide (83%). The retention of potassium near the soil surface is similar to that shown in Fig. 3.4 for the analogous experiment conducted on repacked soil columns.

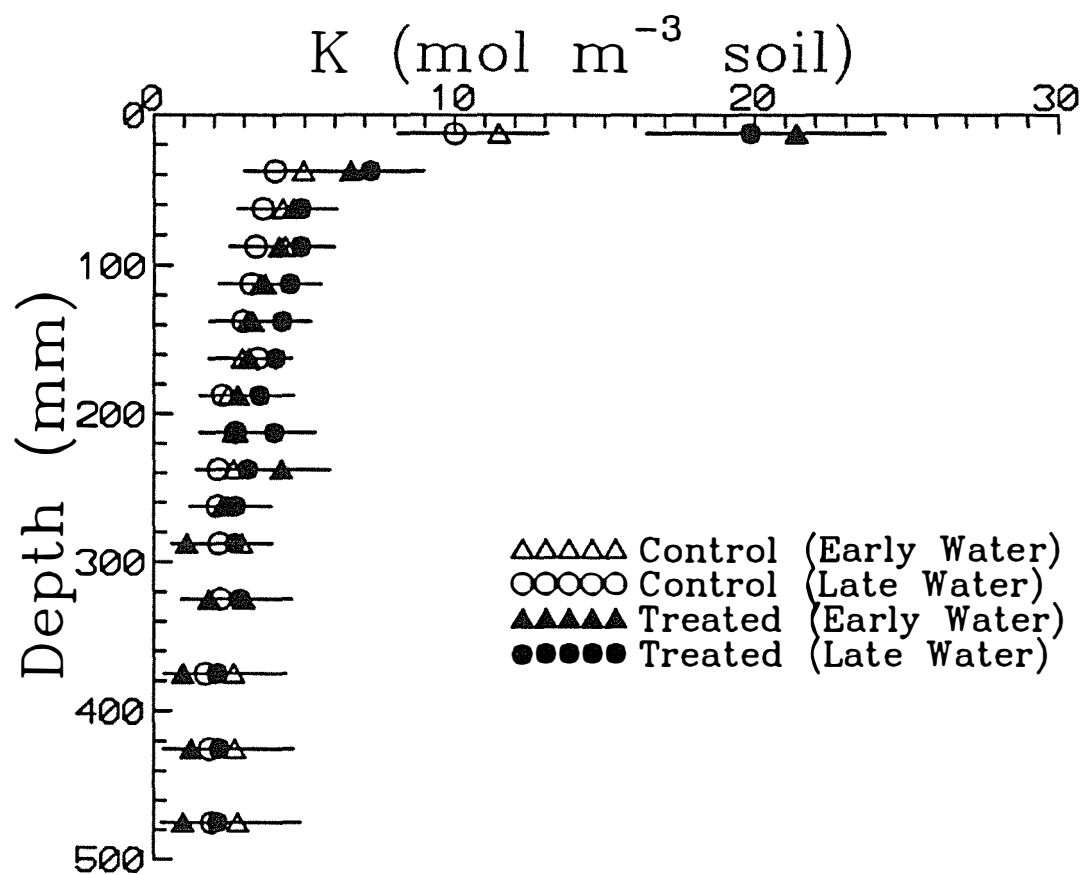


Fig. 5.2. Potassium distribution at the completion of the second experiment. Bars indicate the standard errors of the means

The final distributions of nitrate-nitrogen in the control and fertilised plots in experiment two are presented in Fig. 5.3. The nitrate-nitrogen distribution at the commencement of the trial was also measured, but as it was virtually identical to the final distribution in the two control plots it has not been included in Fig 5.3. After twelve days there was a very similar distribution of nitrate-nitrogen in the two fertilised treatments. The highest concentration of both total and also fertiliser nitrogen was still in the top 25 mm, but there had been considerable movement to at least 350 mm. The similarity in distribution of nitrate-nitrogen between the two fertilised treatments in this field study contrasts greatly with the disparate nitrate-nitrogen distributions observed in the analogous laboratory experiment described in Chapter 3. Reasons for this are discussed below.

The recovery of added nitrogen as nitrate-nitrogen was 77% for the early-water treatment and 56% for the late water treatment.

In both experiments exchangeable calcium and magnesium levels were assessed, but the large background soil levels and variability masked any differences between control and treated plots, so the data are not presented. This result also contrasts with the findings of Chapter 3, in which the use of columns of repacked, sieved soil reduced variability and enabled considerable downward movement of calcium and magnesium to be observed in response to additions of potassium and nitrogen fertilisers.

SIMULATION RESULTS AND DISCUSSION

In the laboratory, in columns of repacked soil, where the movement of water is well understood, it is possible to simulate quite accurately the movement of soil and fertiliser nitrogen and exchangeable cations in response to intermittent water flow (Chapters 2 and 3). This close agreement with experimental results was achieved assuming simple first-order kinetics for nitrogen transformations and the Gapon equation for cation exchange. Values from the literature were chosen for the selectivity coefficients.

In the model described above the "chemical" component is virtually identical to that developed in Chapter 3. It is the purpose now to investigate whether this simple

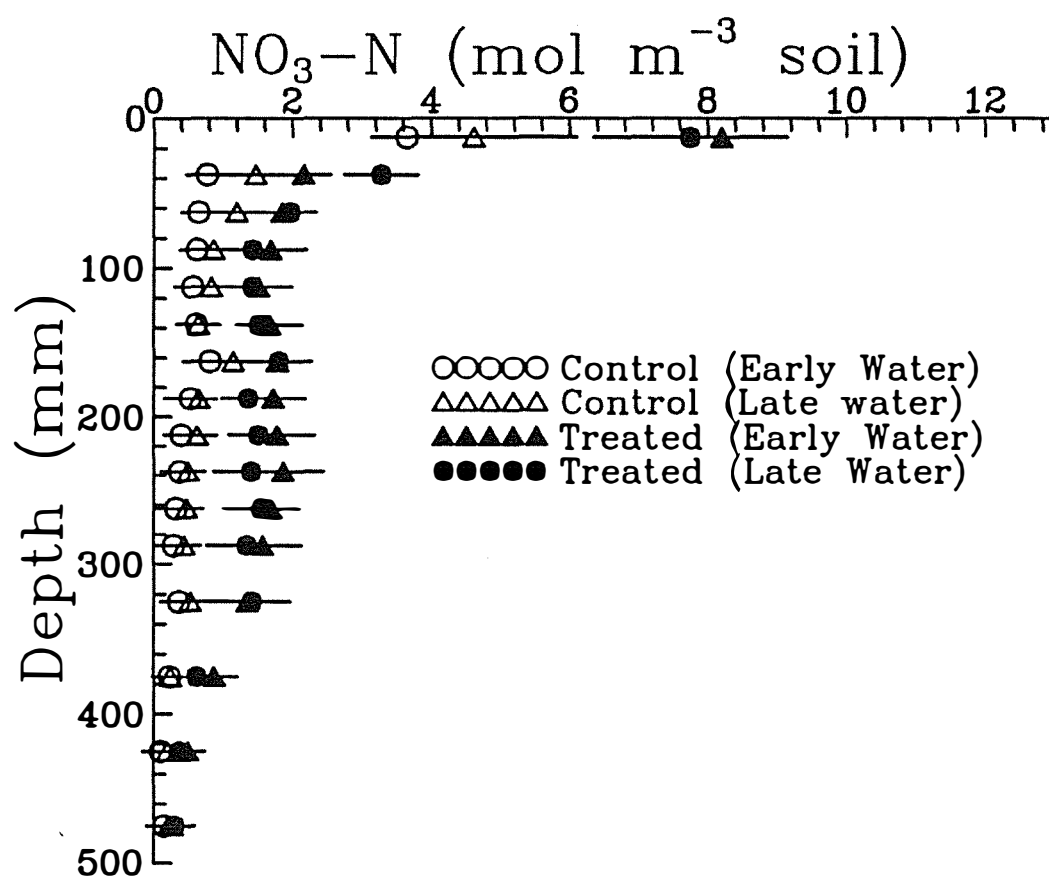


Fig. 5.3. Nitrate-nitrogen distribution at the completion of the second experiment. Bars indicate the standard errors of the means

chemical model is adequate to describe nutrient movement in field soils, where the movement of water is considerably more heterogeneous. The rate constants describing nitrogen transformations, plus the diffusion coefficients of the various ions in pure solutions, as well as the partition coefficients for cation exchange are all identical to those used in Chapter 3.

The model used to describe water movement, as described in Chapter 4, set the water content dividing the mobile and immobile phases (θ_c) at 0.18. For the divalent cations of calcium and magnesium and the monovalent anions, bromide and nitrate, D_o was set at $3.6 \text{ mm}^2 \text{ h}^{-1}$, the value for calcium bromide. This was because the exchange complex is so dominated by calcium and magnesium, the bromide and nitrate carried with them predominantly native calcium rather than the applied potassium. The D_o for potassium was $4.6 \text{ mm}^2 \text{ h}^{-1}$.

The derivations of the rate constants for hydrolysis of urea (k_u) and nitrification of ammonium (k_a) needed for modelling the second experiment are described in Chapter 2. The value used in the second experiment for k_u was 0.2 h^{-1} . The value for k_a was 0.001 h^{-1} for the first three days for both treatments, and 0.011 h^{-1} for the early-water treatment after this time. For the late-water treatment, a value of 0.005 h^{-1} was used for times greater than 3 days but less than 10 days (when water was applied) after which k_a was 0.021 h^{-1} .

The value of k_G , the partition coefficient in equation (5.12), was taken as $11.4 (\text{mol m}^{-3})^{1/2}$ from Robbins *et al.* (1980).

The remaining consideration was the division of the total cation exchange capacity between the mobile and immobile phases. In reality both phases will have a cation exchange capacity, although it might be expected that the very much smaller pore size, and hence larger surface area, associated with the immobile phase would lead to it being associated with the bulk of the cation exchange capacity. Two contrasting partitions of cation exchange capacity were used. In the first, all the cation exchange capacity was assigned to the immobile phase, meaning that all cations in the mobile phase remained in solution. But these could diffuse into the immobile phase and there

be adsorbed. In the second scenario, the cation exchange capacity was allocated to each phase in the proportion to their contribution to the porosity. Given θ_c is 0.18, then the ratio of cation exchange capacity in the immobile and mobile phases was 0.18 : 0.32. The real situation would lie somewhere between these two extremes.

The simulated potassium distributions for treatments 1 and 2 in the first experiment are presented in Figs 5.4 and 5.5 respectively. In treatment 1, in which the potassium bromide was applied to initially-dry soil, it made little difference whether potassium in the mobile phase was assumed to be able to exchange with the soil surface or not. Both models gave a reasonable description of the actual potassium distribution (Fig. 5.4).

Under the conditions prevailing in treatment 2, when potassium was applied to already wet soil, it makes a considerable difference whether or not cation exchange is assumed to take place in the mobile phase (Fig. 5.5). For no exchange there, considerable movement of potassium to depth is predicted. If exchange in the mobile phase is allowed then the predicted distribution differs only slightly from that observed in treatment 1 except right near the surface. Unfortunately it was in this treatment that the recovery of added potassium was very low and thus the experimental data must be viewed cautiously. Nevertheless it would appear that under the conditions of this experiment there was some deeper movement of potassium as a consequence of bypassing at least some part of the cation exchange capacity.

For the application rates of water used in these studies, only small isolated areas of surface ponding were observed, and then for very short periods. The resulting flow was therefore essentially unsaturated and would not have been via the very largest of the soil pores. The apparent preferential movement of a strongly reactive ion such as potassium under these conditions is therefore interesting.

The simulated final distributions of potassium in the two fertilised treatments in experiment 2 are presented in Figs 5.6 and 5.7. When it is assumed that cation exchange can take place in both mobile and immobile phases there is little difference between the early- and late-water treatments (Fig. 5.6). In both cases the actual levels of potassium found in the top soil were less than predicted but the low recovery of

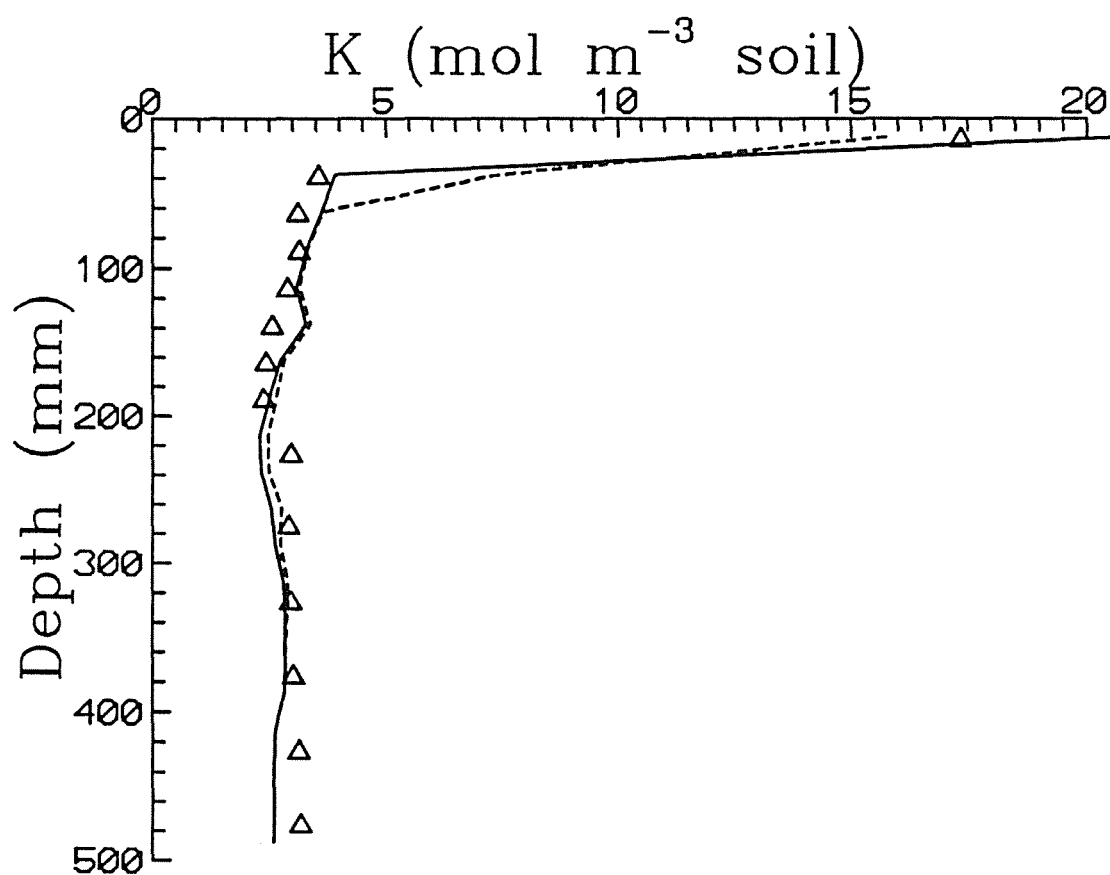


Fig. 5.4. Measured (symbols) and simulated (lines) potassium distributions for treatment 1 in the first experiment. The solid line is when cation exchange capacity is assumed to be distributed between immobile and mobile phases. The dotted line is when all cation exchange capacity is assumed to be solely in the immobile phase

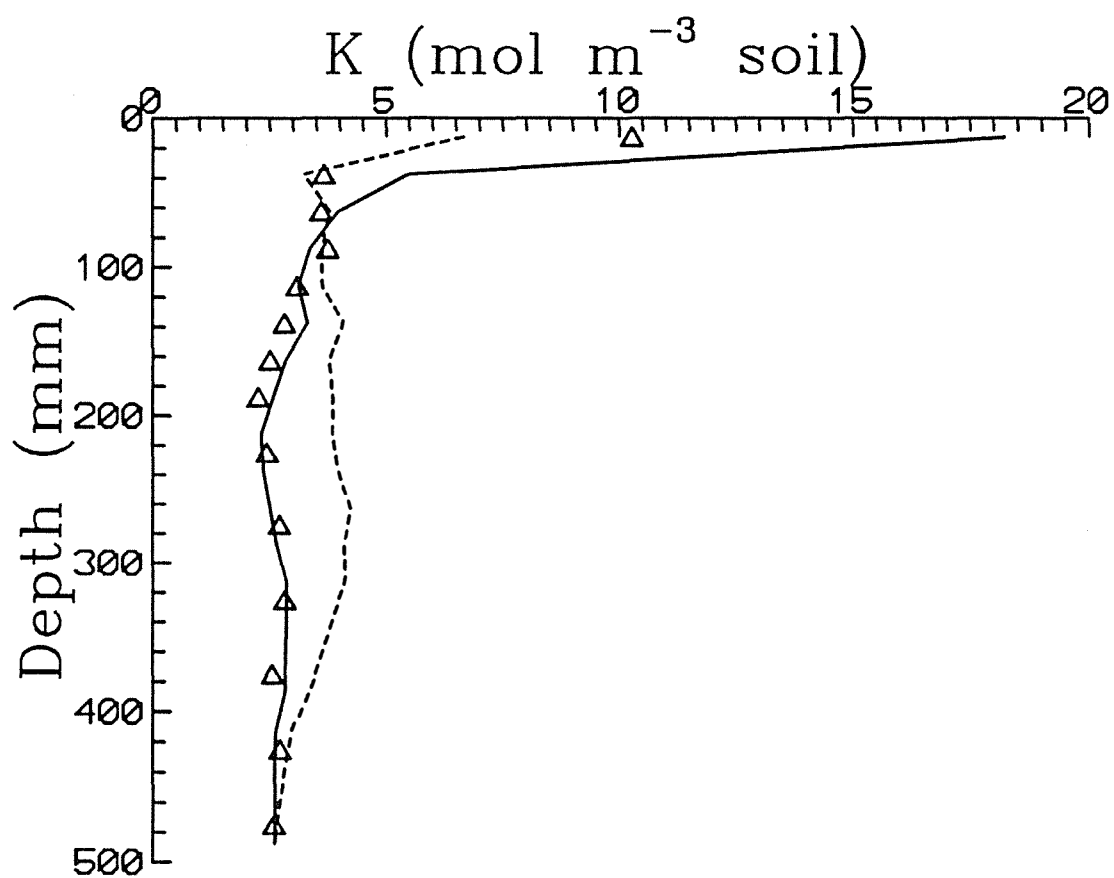


Fig. 5.5. Measured (symbols) and simulated (lines) potassium distributions for treatment 2 in the first experiment. The solid line is when cation exchange capacity is assumed to be distributed between immobile and mobile phases. The dotted line is when cation exchange capacity is assumed to be solely in the immobile phase

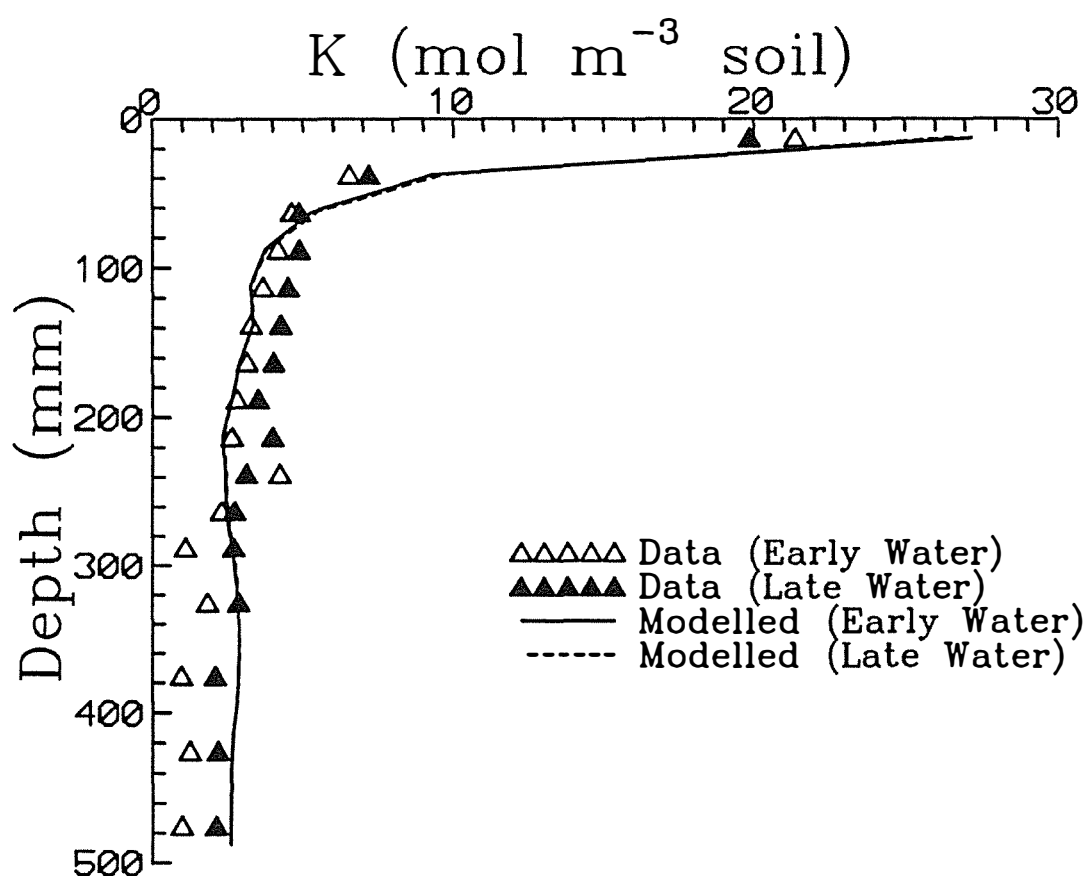


Fig. 5.6. Measured (symbols) and simulated (lines) potassium distributions in the second experiment, assuming cation exchange capacity is distributed between mobile and immobile phases

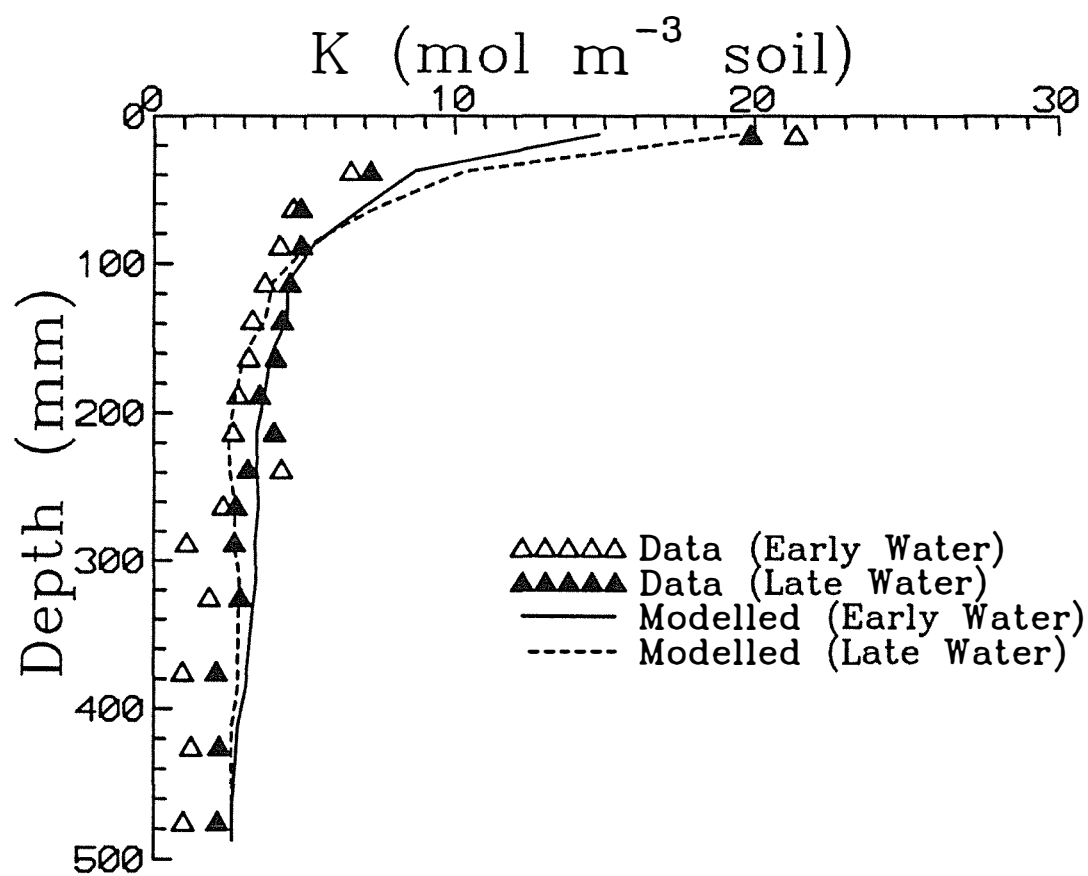


Fig. 5.7. Measured (symbols) and simulated (lines) potassium distributions in the second experiment, assuming cation exchange capacity is solely in the immobile phase

added potassium prevents this being interpreted as evidence of preferential downward movement.

If it is assumed that there is no cation exchange capacity associated with the mobile phase, then considerably more downward movement of potassium is predicted, and there is more of a difference between the treatments (Fig. 5.7). The movement is predicted to be less in the late-water treatment. In the ten days between the application of potassium bromide and irrigation more of the applied potassium would have diffused from the mobile to the immobile phase where it was relatively immune to subsequent leaching.

The nitrate-nitrogen distribution in the un-irrigated "control" area surrounding the plots was measured at the beginning and end of the trial. These data are presented in Fig. 5.8, along with the simulated final distribution obtained using the initial nitrate concentrations and the appropriate inputs of rainfall and evaporation. There was little change in the distribution of nitrate in this control area during the trial. The simulated final distribution agreed closely with the observed values.

The lack of change in nitrate-nitrogen distribution on the unirrigated control area during the trial provides some support for the omission of processes such as plant uptake, mineralisation and denitrification from this short term model. Assuming a uniform annual plant uptake of soil nitrogen of 300 kg ha^{-1} , the uptake over the 12 days of the trial would have been approximately 70 mmole m^{-2} . This compares with an initial soil nitrate-nitrogen level of 395 mmole m^{-2} to a depth of 500 mm and a fertiliser addition of 714 mmole m^{-2} .

This uptake would not occur uniformly throughout the top 500 mm of soil but would be concentrated near the surface. If the plant uptake of nitrogen followed the assumed pattern of water uptake, with 80% coming from the top 100 mm (Chapter 4), then 56 mmole would be taken up from a soil pool (to 100 mm) of 194 mmole on the unfertilised areas. If this was the only process occurring it may have had a measurable effect. Plant uptake is balanced however by mineralisation of organic nitrogen which, although difficult to measure, is similarly distributed throughout the soil profile and has

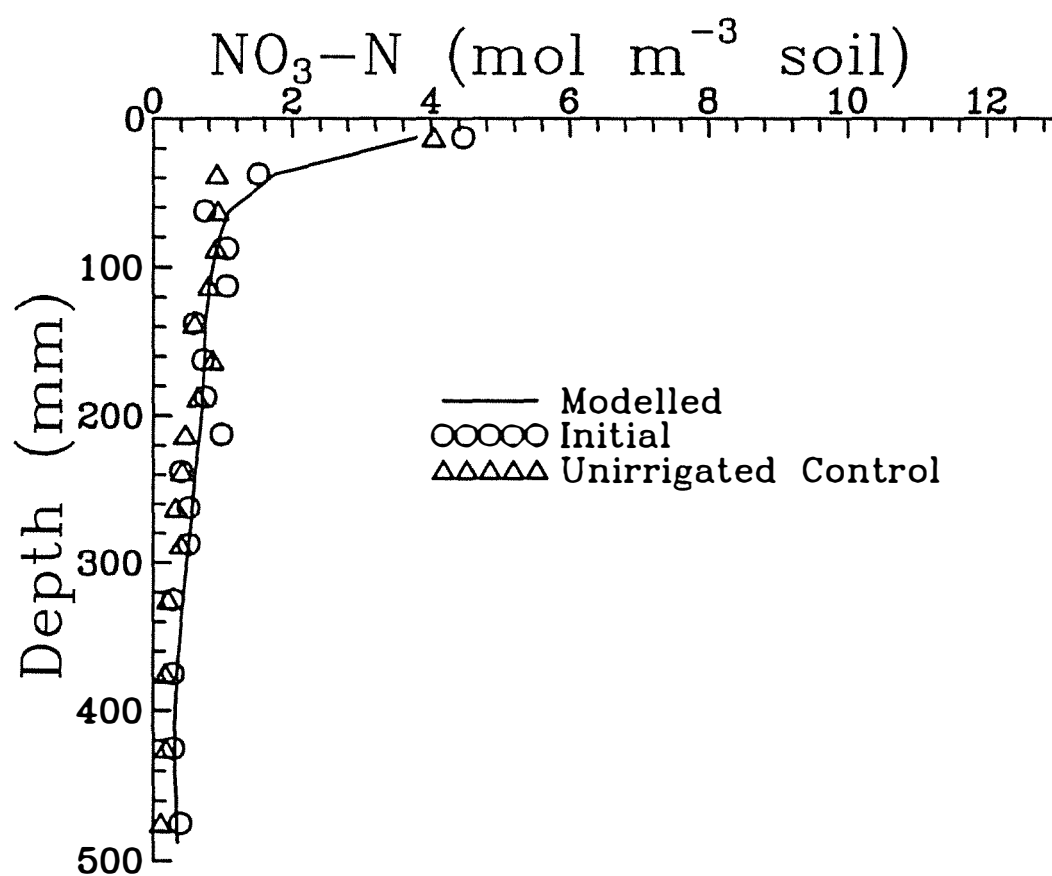


Fig. 5.8. Measured (symbols) and simulated (line) nitrate-nitrogen distributions in the unirrigated control area in the second experiment. The initial distribution is ○ and the final distribution is Δ

a similar magnitude to plant uptake when averaged over a year. Over the time scale of this experiment therefore the net effect of plant uptake and mineralisation is likely to be small.

The agreement between simulated and observed distributions of nitrate- nitrogen was not as good for the irrigated control plots (Fig. 5.9). In both cases the extent of nitrate movement downwards from the topsoil was overestimated. In contrast the model over-estimated the amount of nitrate- nitrogen in the top layer in the fertilised plots (Figs 5.10 and 5.11). This probably resulted from an over-estimation of the rate of nitrification as the recoveries of applied urea-nitrogen as nitrate-nitrogen (77% and 56% for early- and late-water treatments) were less than those predicted by the model (91% and 86% respectively).

Despite the discrepancies described above, the model was able to predict the general shape of the final nitrogen distribution in both the fertilised treatments. This was despite the markedly-different final distribution of nitrate-nitrogen in the late-water treatment in this experiment (Fig. 5.11), compared to the analogous treatment in a repacked soil column in the laboratory (Fig 3.3). In the latter case there was considerable movement of nitrate-nitrogen in response to the application of water 10 days after fertiliser application. The fact that this movement does not occur in the field suggests that most of the irrigation water is passing through the major pores and bypassing the nitrate-nitrogen held in the bulk of the soil matrix. This highlights the fact that in modelling short-term nutrient movement in field soils the difficulties in describing the physical movement of water are likely to outweigh the difficulties associated with describing the chemical and biological processes affecting the nutrient.

This is illustrated further in Figs. 5.12 and 5.13 in which the final nitrate-nitrogen distributions for the early- and late-water treatments are simulated assuming firstly that θ_c is 0.18, and secondly that θ_c is 0.001. In the latter case there is negligible immobile water. The absence of immobile water makes little difference in the early-water treatment, because at the time of the irrigation most of the nitrogen is in the ammonium form. In the late-water case however the assumption that there is no immobile water

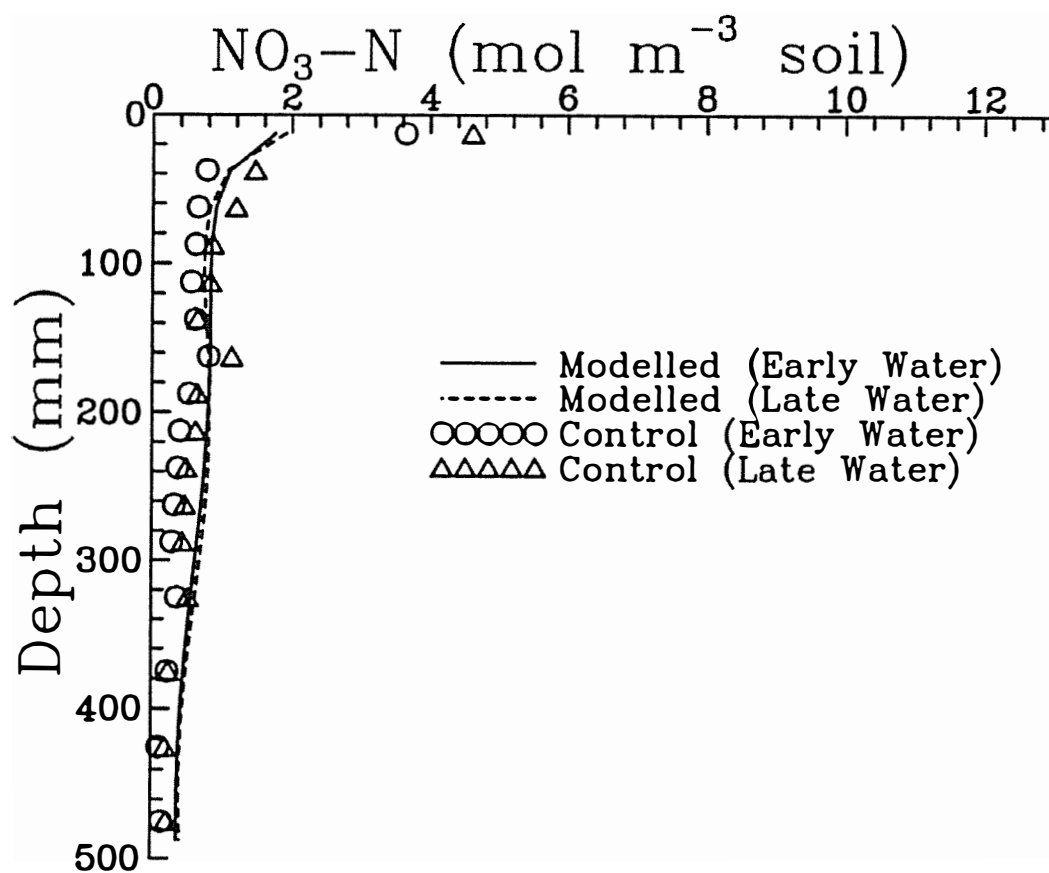


Fig. 5.9. Measured (symbols) and simulated (lines) final nitrate-nitrogen distributions in the irrigated control plots in treatment 2 of the second experiment

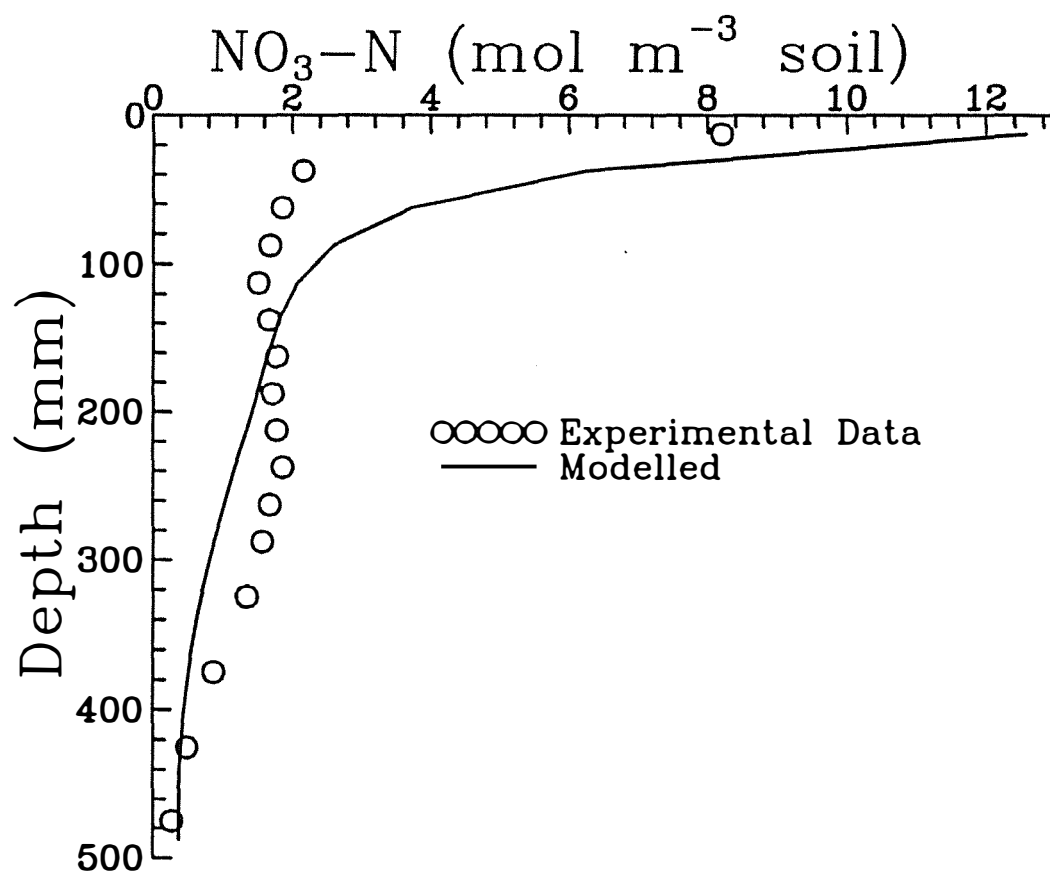


Fig. 5.10. Measured (symbols) and simulated (line) final nitrate-nitrogen distributions in the fertilised early-water treatment in the second experiment

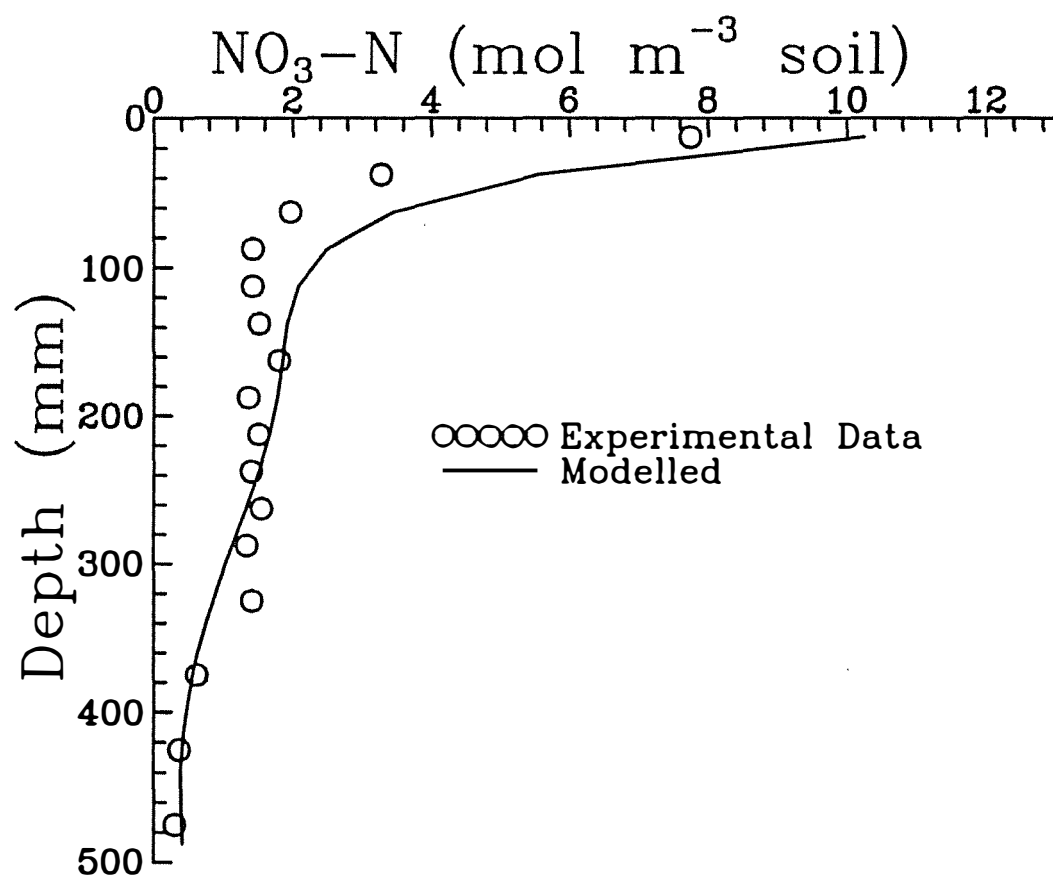


Fig. 5.11. Measured (symbols) and simulated (line) final nitrate-nitrogen distributions in the fertilised late-water treatment in the second experiment

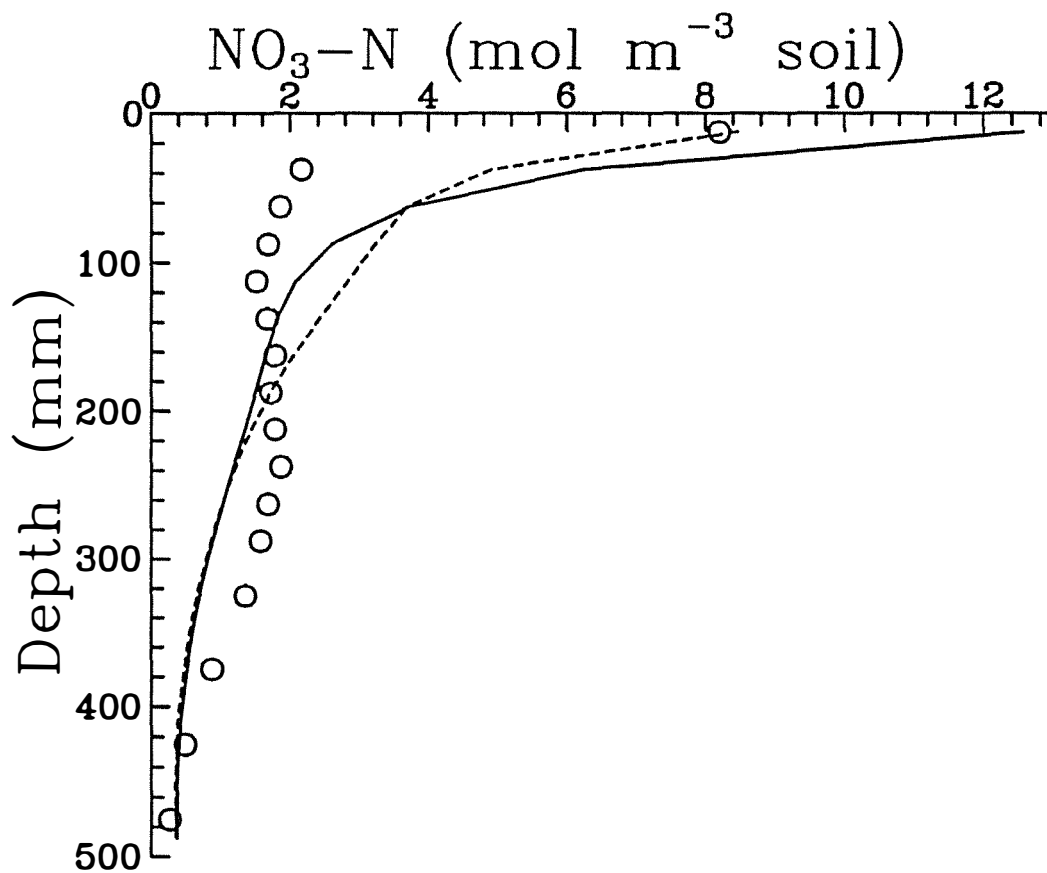


Fig. 5.12. Measured (symbols) and simulated (lines) final nitrate-nitrogen distributions in the fertilised early-water treatment in the second experiment. The solid line is when θ_c is set at 0.18. The dotted line is when θ_c is set at 0.001

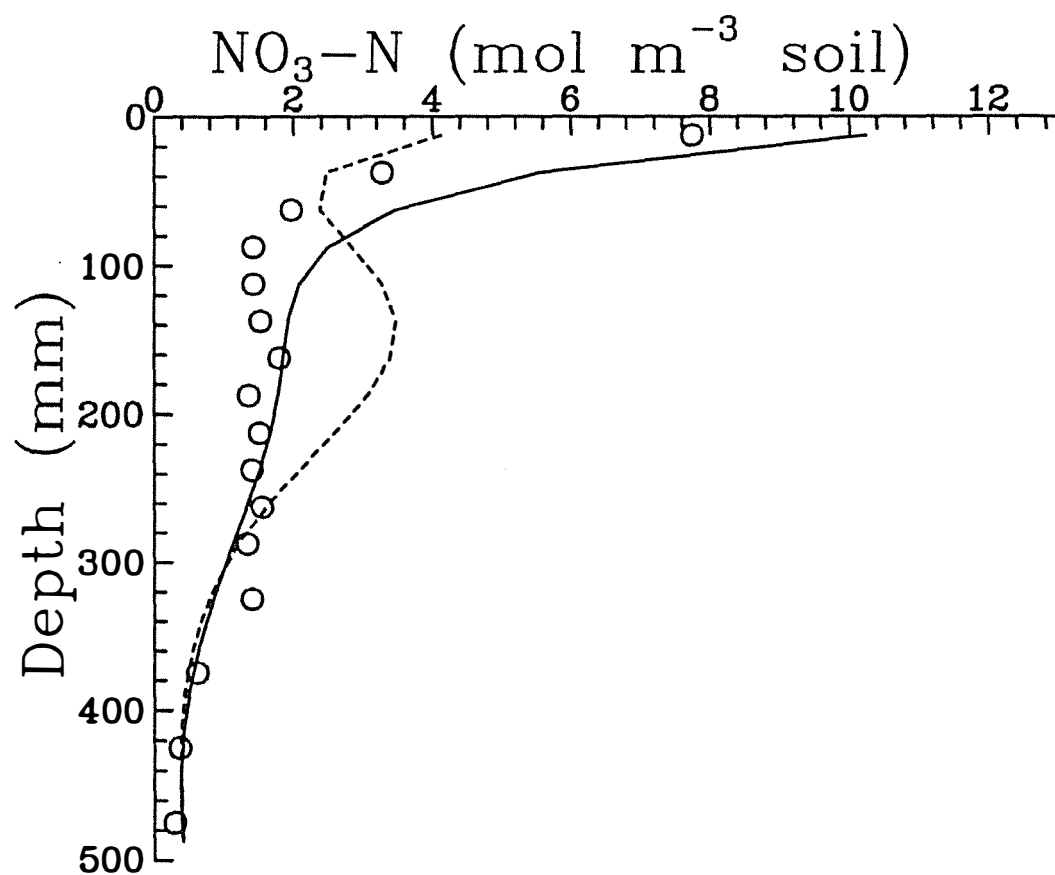


Fig. 5.13. Measured (symbols) and simulated (lines) final nitrate-nitrogen distributions in the fertilised late-water treatment in the second experiment. The solid line is when θ_c is set at 0.18. The dotted line is when θ_c is set at 0.001

leads to a final simulated description that differs considerably from the experimental data, with much greater leaching of nitrate from the topsoil.

CONCLUSIONS

The preferential movement of water down larger pores causes greater movement of the nutrients dissolved in the irrigation water than would be predicted by standard miscible displacement theory. This is illustrated by potassium in this study. Although the low recoveries of potassium in these experiments cast some doubt on its final distribution, there is good evidence, particularly in treatment 2 in the first experiment, for accelerated movement out of the top 25 mm of even this reactive solute.

For this to have occurred the preferential flow must not only bypass a fraction of the soil water but also carry the potassium past part of the soil's cation exchange capacity. This could occur in two ways. Firstly the travel times in these large soil pores may be short compared to the times required for lateral mixing within the pore and for the chemical reaction of cation exchange to reach equilibrium. The second possibility is that because of their large size, the conducting pores have a small surface area, and hence ions there are accessible to fewer cation exchange sites. Thus although cation exchange can take place during movement through the pore, the available exchange capacity is soon saturated with potassium, and so has little effect on movement.

Preferential movement of water also has the effect of reducing the leaching of nutrients already resident in the soil, and this was well evidenced by nitrate-nitrogen in the second experiment. The final distribution of nitrate was not greatly affected by the timing of water application, and in both irrigation treatments was similar to the final distribution of bromide. This was despite the fact that the nitrogen was originally applied as urea and then had to undergo hydrolysis and nitrification. This would suggest that, except perhaps where urea is applied to already wet soil and followed immediately by large quantities of water, the estimation of rate constants for urea hydrolysis and nitrification are not particularly critical when simulating nitrate movement.

It would appear that on this soil the movement of both reactive and non-reactive solutes, over the soil depths and time spans that are relevant to orchard crops, can be successfully described using a modelling approach which utilises the concept of mobile and immobile soil water, coupled with a relatively simple description of the soil chemistry.

CHAPTER 6

CONCLUSIONS AND DIRECTIONS FOR FUTURE WORK

INTRODUCTION

This study has used a combination of modelling and experimentation to gain a better understanding of the movement and distribution of nutrients in soils on a spatial and temporal scale relevant to orchard crops. In this final chapter the conclusions from the work described in Chapters 2 to 5 will be summarised, and some of the implications of the findings discussed in terms of the overall aim given above.

Particular emphasis will here be placed on:

- Identifying the critical physical, chemical and biological processes that influence nutrient movement.
- Assessing which of these processes are site specific, and those which can be adequately described just using information already available in the literature, or obtained in the laboratory.
- Suggesting convenient methods of characterising those important site-specific processes.

LABORATORY EXPERIMENT

Via laboratory experimentation it was demonstrated in Chapter 2 that, given the soil hydraulic properties then we could simulate in columns of repacked, unsaturated soil, the behaviour of water, tritiated water and bromide. The water flow equation was coupled with the convection-dispersion equation of solute transport.

The similar locations of the peaks of tritiated water and bromide within the soil profile suggested that in this soil there was little anion exclusion. The much flatter, asymmetric shape of the pulse for tritiated water, compared to that of bromide, did however point to the importance of diffusion as a dispersion process, as distinct from hydrodynamic dispersion, when the water flow is intermittent and spread over a period of several days.

In this case, for the tritiated water, the effect of this diffusion was to produce a pronounced asymmetry in the shape of the solute pulse in one of the treatments. This resulted from more rapid diffusion of the solute pulse in one direction than the other. Diffusion was very much slower in the drier soil ahead of the main solute pulse, than it was at the trailing edge of the pulse. This asymmetric diffusion acted to slow the downward movement of the solute peak during intermittent water flow. Furthermore it produced a "tailing" effect similar to that often attributed to the effect of mobile and immobile phases within the soil water. The effect can be explained satisfactorily by the strong dependence of the molecular diffusion coefficient in soil on the water content.

Simulation of the movement of bromide highlighted the necessity of identifying which cation was mostly convected with, and hence can diffuse with the bromide. Although the bromide was added as potassium bromide, the cation exchange complex within the soil was dominated by calcium. It was this ion which mainly accompanied the bromide once it was in the soil. The respective molecular diffusion coefficients values for dilute potassium bromide and calcium bromide solutions were estimated from the data of Robinson and Stokes (1959) to be $1.7 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and $1.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. In well-replicated experiments on repacked soil, where there is considerable time for diffusion, the effect of this difference can become readily discernable.

The movement of applied nitrogen and potassium through the same repacked columns is described in Chapter 3. Earlier incubation studies on this soil (S.N. Smith pers. comm.) had indicated that at moderate rates of nitrogen addition, urea hydrolysis occurred within 24 hours and nitrification was substantially complete within 10 days.

These observations led to the experimental design used which enabled demonstration of the importance of the timing of water movement, relative to the hydrolysis of urea and the nitrification of the resulting ammonium. These determine the final distribution of nitrate. Similar results have been presented by other workers (e.g. Wagenet *et al.* (1977); Iskander and Selim (1981); Scotter *et al.* (1984).

In simulating the nitrogen transformations in Chapter 3, first-order kinetics were assumed for hydrolysis and nitrification. It was anticipated however that nitrification would be hindered initially by a low population of nitrifying organisms, and also by low soil moisture. The rate "constants" were therefore modified with time to produce similar rates of nitrification to those inferred from the observations of nitrate movement in the laboratory study. A similar approach of varying the rate "constant" for nitrification with time and soil moisture was reported by Selim and Iskander (1981). This enabled a close fit with the experimental data obtained in the laboratory, although it did result in an over-estimation of nitrification in the field. A single rate constant of 0.006 h^{-1} , corresponding to a half life of approximately 5 days, would have been consistent with the observations of S.N. Smith (pers. comm.) and would have allowed a reasonable description of both laboratory and field data.

In contrast with most of the bromide, and a considerable proportion of the nitrate in the late-water treatment, which were leached to approximately 100 mm, nearly all the potassium remained in the top 25mm. This was due to cation exchange and could be simulated quite closely using the Gapon equation and a partition coefficient (k_G) between mono- and divalent cations derived from the literature (Robbins *et al.*, 1980). The soil exchange surfaces are initially dominated by calcium, and the amounts of potassium added in a single fertiliser application are small relative to the amounts of calcium initially present. Variations in k_G have little effect on the qualitative observation that most of the potassium remains near the soil surface. It is therefore not necessary to incorporate the concept of variable partition coefficients, as described recently by Mansell *et al.* (1988) and Selim *et al.* (1990).

It was interesting to note that the amount of cation leaching was dictated by the availability of an accompanying anion. Thus after nitrification of the ammonium to

nitrate in the late-water treatment, the leaching of calcium and magnesium was considerably enhanced. In the model this is simulated by assuming that the hydrogen ions produced during nitrification are preferentially adsorbed on the exchange surface. This then effectively decreases the cation exchange capacity. Inspection of the pH data suggested that this was a reasonable assumption as there was little evidence for the leaching of hydrogen ions. This adjustment of the cation exchange capacity is a necessary refinement if it is desired to obtain a precise estimate of cation leaching in response to nitrogen fertiliser addition in repacked columns. It may also be important in the field, particularly when simulating conditions underneath a drip emitter that might be used for "fertigation".

FIELD EXPERIMENTS

Bromide movement in the two field experiments was described by coupling a mobile-immobile variant of the convection-dispersion model with a description of the transient water flow and root water extraction. In such a model, assumptions were made as to the immobile water content (θ_c), the rate constant for diffusion between mobile and immobile water (α), and the distribution of root water extraction with depth. None of these parameters could be determined independently. They were therefore assigned values which appeared reasonable. In such cases caution must be exercised when interpreting agreement as being evidence for the operation of a particular mechanism (Jury and Ghodrati, 1989). Given this reservation, the fact that the model provided adequate descriptions of solute movement under four widely-different water flow conditions suggests that it may provide a realistic representation of the main processes and interactions occurring in the field.

In treatment 1 in the first field experiment, bromide added in solution to initially dry soil was very resistant to subsequent leaching. It remained almost entirely in the top 50 mm of soil. The water content dividing the mobile and immobile phases, θ_c , was therefore selected so that this 5 mm of bromide solution just filled the immobile phase in the top 50 mm of soil. The value of 0.18 thus obtained compares well with an estimate of θ_c of 0.21 on the same soil made by Clothier *et al.* (1992) using a disc permeameter, and also with estimates ranging from 0.1 to 0.2 calculated by Snow *et*

al. (1991) in a series of long-term experiments on a similar soil adjacent to the site used for these experiments.

Of particular interest is the value assigned to α . Evidence from both experiments suggested that the movement of solute from the immobile to the mobile phase was slow. This would explain the observed resistance to leaching of bromide in treatment 1 in the first experiment, and in both treatments in the second experiment. Simulation confirmed that the model was reasonably sensitive to the value assigned to α .

Equation (4.9) gives the rate of solute diffusion between mobile and immobile phases as $\alpha\theta_i(C_m - C_i)$. When $\theta_i = \theta_c = 0.18$ and with $\alpha = 0.028 \text{ h}^{-1}$ then the effective first-order rate constant was 0.005 h^{-1} . So during simulated leaching events with most of the flow occurring in a few hours, only a small fraction of the solute contained in the immobile phase could diffuse into the mobile phase. Conversely it would take many days for solute originally in the mobile phase to diffuse into the immobile phase. This second implication appears to be at variance with the experimental observations in the early-water treatment of the second experiment. Both the actual and simulated final distributions of bromide suggested that a substantial proportion of added bromide diffused into the immobile phase prior to the application of irrigation water just 48 hours after the initial application of bromide. But the simulated time course of the bromide concentration in the topmost layer of the soil provided interesting insights into a possible mechanism for the behaviour described above.

In the simulation, evaporation and the uptake of water by plants acted to reduce the amount of mobile water in the topsoil, increasing the bromide concentration in the mobile water that remained. This increased the concentration gradient between the two phases and thus the rate of diffusion between the two domains. The overall effect was to predict transfer of over 70% of the bromide in the topmost layer of soil into the immobile phase within 48 hours.

The same mechanism probably operates in the field. This would imply that solutes in soils which had undergone drying cycles between water applications would be more resistant to leaching, than if the soil remained wet between leaching events.

Sensitivity analyses on the model reported in Chapter 4 highlighted the importance of the distribution of evaporation and root water uptake to the final simulated distribution of bromide. A simulation of the bromide content in the top layer of soil during the second experiment (Fig 6.1) demonstrates how loss of water from the surface layers can result in convection of solute back towards the soil surface between rainfall or irrigation events.

Sub-models of nitrogen transformations and cation exchange, developed for the laboratory experiment, enabled a reasonable description of the final distributions of these nutrients in the field. Nonetheless the rate of nitrification appeared to be overestimated, particularly in the early-water treatment. Steele *et al.* (1980) have identified considerable variations in nitrification rates in soils under pasture in New Zealand. Similar information is also required on nitrification rates in orchard soils. Assuming however that nitrification is reasonably rapid, being of the order of weeks rather than months, then the exact rate will not be critical to nitrate movement, at least in response to regular but intermittent water inputs over a growing season. This occurs because the rate of diffusion between mobile and immobile phases is of a similar magnitude to the rate of nitrification. Thus there is unlikely to be a large build up of nitrate in the mobile phase where it would be susceptible to leaching by a single large rainfall or irrigation event. However nitrate added directly to the soil as a fertiliser is likely to be very susceptible to leaching in the first few days after application.

The study of potassium movement in the field experiments was inconclusive, largely because of sampling and analytical problems. Nevertheless there was evidence of preferential movement of potassium in treatment two of the first experiment, when potassium in solution was applied to an already-wet soil and followed immediately by irrigation. This is in accord with other reports of preferential movement of reactive solutes in field soils and undisturbed cores (e.g. Kanchanasut *et al.* 1978; Williams *et al.* 1990a and b). Preferential movement of potassium implies that the cation exchange process has not prevented leaching. Most workers when simulating this process have assumed that the non-equilibrium results from the requirement for solute to diffuse from the mobile to the immobile phase, rather than the chemical kinetics of the exchange process (Selim *et al.* 1990).

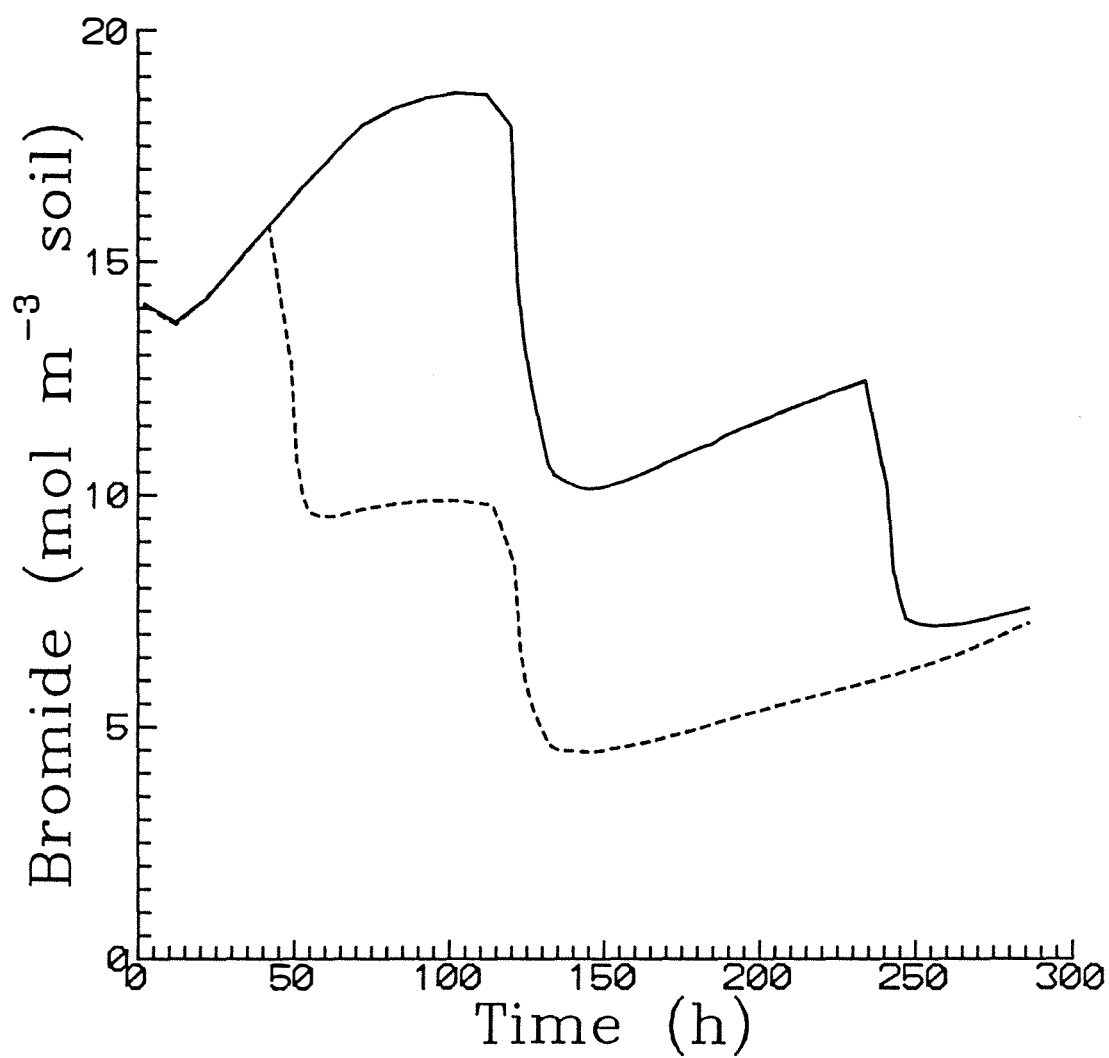


Fig. 6.1. Simulated bromide concentration in the top 25mm of soil in the second field experiment. The dotted line is the early-water treatment and the solid line is the late-water treatment

Simulations of this type require an allocation of exchange sites between mobile and immobile phases. Although this allocation has been discussed by a number of workers (e.g. van Genuchten and Wierenga, 1976; Mansell *et al.*, 1986; Selim *et al.*, 1990) few studies have considered the case of cation movement in structured field soils. van Genuchten *et al.*, (1977) simulated the movement of 2,4,5-T through columns of repacked soil. They calculated that although the immobile water only accounted for between 6 and 20% of the total volumetric water content, the immobile phase contained about 60% of the adsorption sites. This would result from the smaller pore size and larger surface area, associated with the immobile water.

Similar data are required on the division of cation exchange sites between mobile and immobile phases in field soils, as the simulation studies reported in Chapter 5 indicated that the model was sensitive to this allocation. For example, it is observed that once potassium deficiency has developed in some deep-rooted perennial crops such as kiwifruit, very large applications of potassium fertiliser are required to overcome the deficiency. These applications are very much larger than the expected annual uptake by the crop. In some instances they are suspected to cause other nutritional problems such as chloride toxicity when potassium chloride is the fertiliser used. One explanation of why such high application rates of potassium are required is that on soils with high cation exchange capacities that are calcium-dominated, applied potassium will remain in the very top layer of the soil rather than be more evenly distributed throughout the root zone. Any manipulation of fertiliser and irrigation strategies which could improve, even slightly, the redistribution of applied potassium may therefore have considerable benefits.

The spatial variability of native nitrate and potassium in field soils means that simple models of the chemical and biological transformations affecting nutrients applied as fertiliser are likely to produce adequate descriptions of nutrient movement, at least over the time scales involved in these experiments.

Over longer time scales factors such as plant uptake and the rate of mineralisation of organic nitrogen would become more critical in determining the overall loss of nutrients from the soil.

CONCLUSIONS AND FUTURE WORK

Rainfall and irrigation, root activity and distribution, soil properties, and fertiliser applications all interact in determining nutrient availability in the root zone. A failure to take all these factors into account when designing field trials, can limit the extent to which the results can be extended to other soils or to other seasons. The recent controversies in the kiwifruit industry concerning alleged chloride toxicity and the effect of nitrogen nutrition on fruit storage quality have been notable for apparently contradictory trial results. Many of these contradictions arose from inadequate trial design and could have been resolved, given a better understanding of the movement and transformations of nutrients in the root zone. This study makes a contribution to that understanding.

Contrasting patterns of solute movement were observed in two analogous experiments. One was conducted on columns of repacked soil in the laboratory, whereas the second was for undisturbed soil in the field. Simulation studies suggested that similar sub-models of the chemical and microbiological processes affecting the solutes could be used in both experiments. The chemical and biological parameters required were not particularly site-specific and could be obtained from extant values. Possible exceptions to this are the rate constant for nitrification, for which more information on orchard soils is required, and also the division of cation exchange sites between mobile and immobile phases. In the latter case, studies similar to the second treatment of the first field experiment, in which both reactive (potassium) and non-reactive (bromide) solutes underwent preferential flow, should provide information on potassium movement. It is however necessary that the high background variability of soil potassium be overcome. The replacement of potassium as a tracer by a non-resident chemical such as rubidium may assist in this regard.

In contrast, the "physics" of the system appears to be site specific. A model employing the concept of mobile and immobile water was able to describe the solute movement, but required the arbitrary assignment of a number of parameters. Experimental techniques need to be developed to allow evaluation of the immobile water content (θ_c) and the rate constant for transfer between mobile and immobile phases (α) from

experiments independent of situations being simulated. The approach of Clothier *et al.* (1992) using a disc permeameter appears to show promise as a means for assessing θ_c .

Assessments of α may be more difficult, but experiments with "undisturbed" cores or disc permeameters may be useful. A possible technique would involve initially leaching a soil with a solution containing a tracer and then allowing different periods for equilibration between the mobile and immobile phases, prior to leaching with tracer-free water.

A final area needing more investigation relates to the pattern of root water extraction. This needs to be monitored for a range of crops and environmental conditions, as simulation studies suggest that it is influential in determining the distribution of nutrients within the root zone during a growing season.

This study demonstrates that the distribution of nutrients in orchard soils can be influenced to a considerable extent by the relative timing of fertiliser addition and soil wetting. Rapid leaching of nitrogen applied as urea is likely only if the urea is applied to an already wet soil and is followed immediately by substantial rainfall or irrigation. This could occur under fertigation. After 12-24 hours the urea has hydrolysed to ammonium which is then retained on the cation exchange sites. After nitrification to nitrate the nitrogen is located substantially in the immobile phase, particularly if there is drying of the topsoil. The nitrate is then largely protected against leaching, although it will gradually move downward in response to intermittent water application, particularly if the soil remains constantly wet.

Cation exchange causes most of the applied potassium to remain in the topsoil. This can be a disadvantage when fertilising deep-rooting orchard crops. Potassium penetration into the soil can be enhanced by application in irrigation water to already wet soil, and followed immediately by application of further irrigation water.

REFERENCES

- Addiscott, T.M. 1977. A simple computer model for leaching in structured soils. *Journal of Soil Science* **28**: 554-563.
- Addiscott, T.M. and Wagenet, R.J. 1985. Concepts of solute leaching in soils: a review of modelling approaches. *Journal of Soil Science* **36**: 411-424.
- Addiscott, T.M. and Whitmore, A.P. 1991. Simulation of solute leaching in soils of differing permeabilities. *Soil Use and Management* **7**: 94-102.
- Barracough, D. 1989a. A usable mechanistic model of nitrate leaching. I. The model. *Journal of Soil Science* **40**: 543-554.
- Barracough, D. 1989b. A usable mechanistic model of nitrate leaching. II. Application. *Journal of Soil Science* **40**: 555-562.
- Barracough, D., Hyden, M.J. and Davies, G.P. 1983. Fate of fertiliser nitrogen applied to grassland. I. Field leaching results. *Journal of Soil Science* **34**: 483-497.
- Biggar, J.W. and Nielsen, D.R. 1967. Miscible displacement and leaching phenomena. Chapter 14 in: R.M. Hagen *et al.* (Editors), *Irrigation of Agricultural Lands*. American Society of Agronomy, Madison, WI, pp. 254-274.
- Biggar, J.W. and Nielsen, D.R. 1976. Spatial variability of the leaching characteristics of a field soil. *Water Resources Research* **12**: 78-94.
- Bond, W.J. 1986. Velocity-dependent hydrodynamic dispersion during unsteady, unsaturated soil water flow: experiments. *Water Resources Research* **22**: 1881-1889.
- Bond, W.J. 1987. Solute transport during unsteady, unsaturated soil water flow: The pulse input. *Australian Journal of Soil Research* **25**: 223-41.
- Bond, W.J., Gardiner, B.N. and Smiles, D.E. 1982. Constant-flux absorption of a tritiated calcium chloride solution by a clay soil with anion exclusion. *Soil Science Society of America Journal* **46**: 1133-1137.
- Bond, W.J. and Phillips, I.R. 1990a. Ion transport during unsteady water flow in an unsaturated clay soil. *Soil Science Society of America Journal* **54**: 636-645.

- Bond, W.J. and Phillips, I.R. 1990b. Approximate solutions for cation transport during unsteady unsaturated soil water flow. *Water Resources Research* **26**: 2195-2205.
- Bond, W.J. and Wierenga, P.J. 1990. Immobile water during solute transport in unsaturated sand columns. *Water Resources Research* **26**: 2475-2481.
- Bosatta, E., Iskander, I.K., Juma, N.G., Kruh, G., Reuss, J.O., Tangi, K.K. and van Veen, J.A. 1981. Soil microbiology. In 'Simulation of Nitrogen Behaviour in Soil-Plant Systems (Editors M. J. Frissel and J. A. van Veen) pp. 38-44. (PUDOC: Wageningen.)
- Bresler, E. and Dagan G. 1983. Unsaturated flow in spatially variable fields. 2. Application of water flow models to various fields. *Water Resources Research* **19**: 421-428.
- Bresler, E. and Hanks, R.J. 1969. Numerical methods for estimating simultaneous flow of water and salt in unsaturated soil. *Soil Science Society of America Proceedings* **33**: 827-832.
- Bruce, R.R. and Klute, A. 1956. The measurement of soil moisture diffusivity. *Soil Science Society of America Proceedings* **20**: 18-21.
- Burns, I.G. 1974. A model for predicting the redistribution of salts applied to fallow soils after excess rainfall and evaporation. *Journal of Soil Science* **25**: 165-178.
- Burns, I.G. 1975. An equation to predict the leaching of surface applied nitrate. *Journal of Agricultural Science, Cambridge* **85**: 443-454.
- Burns, I.G. 1976. Equations to predict the leaching of nitrate uniformly incorporated to a known depth or uniformly distributed throughout a soil profile. *Journal of Agricultural Science, Cambridge* **86**: 305-313.
- Butters, G.L., Ellsworth, T.R. and Jury, W.A. 1990. One and three-dimensional evaluation of solute macrodispersion in an unsaturated sandy soil. In "Field-scale Water and Solute Flow in Soils", (Editors K. Roth, H Flühler, W.A. Jury and J.C. Parker) Birkhauser Verlag, Basel, pp. 41-53.
- Butters, G.L. and Jury, W.A. 1989. Field scale transport of bromide in an unsaturated soil 2. Dispersion modeling. *Water Resources Research* **25**: 1583-1589.
- Butters, G.L., Jury, W.A. and Ernst, F.F. 1989. Field scale solute transport in an unsaturated soil. 1. Experimental methodology and results. *Water Resources Research* **25**: 1575-1581.

- Cameron, K.C. and Wild, A. 1982. Prediction of solute leaching under field conditions: an appraisal of three methods. *Journal of Soil Science* **33**: 659-669.
- Campbell, G.S. 1985. Soil Physics with BASIC: Transport Models for Soil-Plant Systems. Elsevier, Amsterdam, 150 pp.
- Clothier, B.E., Kirkham, M.B. and McLean, J.E. 1992. *In situ* measurement of the effective transport volume for solute moving through soil. *Soil Science Society of America Journal* **55**: (In press).
- Dagan, G. and Bresler, E. 1979. Solute dispersion in unsaturated heterogenous soil at field scale. I. Theory. *Soil Science Society of America Journal* **43**: 461-467.
- de Wit, C.T. and van Keulen, H. (1975). 'Simulation of Transport Processes in Soils.' (PUDOC: Wageningen.)
- Ellsworth, T.R. and Jury, W.A. 1991. A three-dimensional field study of solute transport through unsaturated, layered, porous media 2. Characterization of vertical dispersion. *Water Resources Research* **27**: 967-981.
- Ellsworth, T.R., Jury, W.A., Ernst, F.F. and Shouse, P.J. 1991. A three-dimensional field study of solute transport through unsaturated, layered, porous media 1. Methodology, mass recovery, and mean transport. *Water Resources Research* **27**: 951-965.
- Elrick, D.R. and Clothier, B.E. 1990. Solute transport and leaching. Chapter 5 in: (Editors B.A. Stewart and D.R. Nielsen). Irrigation of Agricultural Crops. American Society of Agronomy, Madison, WI. pp. 93-126.
- Fox, R.L. 1980. Soils with variable charge: Agronomic and fertility aspects. In 'Soils with Variable Charge' (Editor B. K. G. Theng) pp. 195-224. N. Z. Society of Soil Science: Wellington.
- Gardner, W.R. 1965. Movement of nitrogen in soils. In "Soil Nitrogen" (Editors Bartholomew, W.V. and Clark, F.E.) Agronomy 10, American Society of Agronomy, Madison, WI. pp. 550-572.
- Gelhar, L.W., Matuloglou, A., Welly, C. and Rehfeldt, K.R. 1985. A review of field scale physical solute transport processes in saturated and unsaturated porous media. EPRI Topical Report EA-4190, Electric Power Research Institute.
- Hatano, R. and Sakuma, T. 1991a. A plate model for solute transport through aggregated soil columns. I. Theoretical description. *Geoderma* **50**: 13-23.

- Hatano, R. and Sakuma, T. 1991b. A plate model for solute transport through aggregated soil columns. II. Experimental results and application of the model. *Geoderma* **50**: 25-36.
- Haynes, R.J. and Swift, R.S. 1987. Effect of trickle fertigation with three forms of nitrogen on soil pH, levels of extractable nutrients below the emitter and plant growth. *Plant and Soil* **102**: 211-221.
- Heng, L.K. 1991. Measurement and modelling of chloride and sulphate leaching from a mole-drained soil. Unpublished Ph.D. thesis, Massey University, Palmerston North, N.Z.
- Iskandar, I.K. and Selim, H.M. 1981. Modeling nitrogen transport and transformations in soils: 2. Validation. *Soil Science* **131**: 303-12.
- Jardine, P.M. and Sparks, D.L. 1984. Potassium-calcium exchange in a multi-reactive soil system, I. Kinetics. *Soil Science Society of America Proceedings* **48**: 39-45.
- Jarvis, N.J., Jansson, P.E., Dik, P.E. and Messing, I. 1991a. Modelling water and solute movement in macroporous soil. I. Model description and sensitivity analysis. *Journal of Soil Science* **42**: 59-70.
- Jarvis, N.J., Bergstrom, L. and Dik, P.E. 1991b. Modelling water and solute transport in macroporous soil. II. Chloride breakthrough under non-steady flow. *Journal of Soil Science* **42**: 71-81.
- Jaynes, D.B, Rice, R.C. and Bowman, R.S. 1988. Independent calibration of a deterministic-stochastic model for field-scale solute transport: Results from two field experiments. Proceedings of the International Conference and Workshop on the Validation of Flow and Transport Models for the Unsaturated Zone. New Mexico State University, Ruidoso, N.M.
- Jury, W.A. 1982. Simulation of solute transport using a transfer function model. *Water Resources Research* **18**: 363-368.
- Jury, W.A. 1988. Solute transport and dispersion. In "Flow and Transport in the Natural Environment" (Editors W.L. Steffen and O.T. Denmead) Springer-Verlag, Berlin. pp. 1-16.
- Jury, W.A., Gardner, W.R. and Gardner, W.H. 1991. "Soil Physics" 5th Edition. John Wiley and Sons Inc. New York, pp. 328.

- Jury, W.A., Gardner, W.R., Saffigna, P.G. and Tanner, C.B. 1976. Model for predicting movement of nitrate and water through a loamy sand. *Soil Science* **122**: 36-43.
- Jury, W.A. and Ghodrati, M. 1989. Overview of organic chemical environmental fate and transport modelling approaches. Chapter 11 in: B.L. Sawhney and K. Brown (Editors), *Reactions and Movement of Organic Chemicals in Soils*. Soil Science Society of America, WI, pp. 271-304.
- Jury, W.A. and Roth, K. 1990. "Transfer Functions and Solute Movement Through Soil: Theory and Applications." Birkhauser, Verlag, Berlin. pp. 226.
- Jury, W.A., Sposito, G. and White, R.E. 1986. A transfer function model of solute transport through soil. 1. Fundamental concepts. *Water Resources Research* **22**: 243-247.
- Jury, W.A., Stolzy, L.H. and Shouse, P. 1982. A field test of the transfer function model for predicting solute transport. *Water Resources Research* **18**: 369-375.
- Kanchanasut, P., Scotter, D.R. and Tillman, R.W. 1978. Preferential solute movement through larger soil voids. II Experiments with saturated soil. *Australian Journal of Soil Research* **16**: 269-276.
- Knight, J.H. 1988. Transport and Dispersion: Commentary. In "Flow and Transport in the Natural Environment: Advances and Applications." (Editors W.L. Steffen and O.T. Denmead) Springer-Verlag, Berlin. pp. 17-29.
- Kumar, V. and Wagenet, R.J. 1984. Urease activity and kinetics of urea transformation in soils. *Soil Science* **137**: 263-9.
- Mansell, R.S., Bloom, S.A., Selim, H.M. and Rhue, R.D. 1986. Multi-species cation leaching during continuous displacement of electrolyte solutions through soil columns. *Geoderma* **38**: 61-75.
- Mansell, R.S., Bloom, S.A., Selim, H.M. and Rhue, R.D. 1988. Simulated transport of multiple cations in soil using variable selectivity coefficients. *Soil Science Society of America Journal* **52**: 1533-1540.
- Nielsen, D.R. and Biggar, J.W. 1962. Miscible displacement. III. Theoretical considerations. *Soil Science Society of America Proceedings* **26**: 216-221.
- Nielsen, D.R., Biggar, J.W. and Erh, K.T. 1973. Spatial variability of field-measured properties. *Hilgardia* **42**: 215-260.

- Nkedi-Kizza, P., Rao, P.S.C., Jessup, R.E. and Davidson, J.M. 1982. Ion exchange and diffusive mass transfer during miscible displacement through an aggregated Oxisol. *Soil Science Society of America Journal* **46**: 471-476.
- Nye, P.H. and Tinker, P.B. 1977. "Solute Movement in the Soil-Root System." Blackwell, Oxford. pp.342.
- Olsen, S.R. and Kemper, W.D. 1968. Movement of nutrients to plant roots. *Advances in Agronomy* **30**: 91-151.
- Papendick, R.I. and Campbell, G.S. 1981. Theory and measurement of water potential. Chapter 1 in: J.F. Parr *et al.* (Editors), Water Potential Relations in Soil Microbiology. Soil Science Society of America, Madison, WI, pp. 1-22.
- Parker, J.C. and Jardine, P.M. 1986. Effect of heterogeneous adsorption behaviour on ion transport. *Water Resources Research* **22**: 1334-1340.
- Perroux, K.M. and White, I. 1988. Designs for disc permeameters. *Soil Science Society of America Journal* **52**: 1205-1215.
- Quisenberry, V.L. and Phillips, R.E. 1976. Percolation of surface-applied water in the field. *Soil Science Society of America Journal* **40** : 484-489.
- Raats, P.A.C., 1974. Steady flows of water and salt in uniform soil profiles with plant roots. *Soil Science Society of America Proceedings* **38**: 717-722.
- Rao, P.S.C., Jessup, R.E., Rolston, D.E., Davidson, J.M. and Kilcrease, D.P. 1980a. Experimental and mathematical description of nonadsorbed solute transfer by diffusion in spherical aggregates. *Soil Science Society of America Journal* **44**: 684-688
- Rao, P.S.C., Rolston, D.E., Jessup, R.E. and Davidson, J.M. 1980b. Solute transport in aggregated porous media: theoretical and experimental evaluation. *Soil Science Society of America Journal* **44**: 1139-1146.
- Robbins, C.W., Jurinak, J.J. and Wagenet, R.J. 1980. Calculating cation exchange in a soil transport model. *Soil Science Society of America Journal* **44**: 1195-1200.
- Robinson, R.A. and Stokes, R.H. 1959. 'Electrolyte Solutions' (2nd edition) (Butterworths: London.)
- Rose, C.W., Chichester, F.W., Williams, J.R. and Ritchie, J.T. 1982. Application of an approximate analytic method of computing solute profiles with dispersion in soils. *Journal of Environmental Quality* **11**: 151-155.

- Rose, D.A. 1991. The variability of winter drainage in England and Wales. *Soil Use and Management* **7**: 115-122.
- Rubin, J. and James, R.V. 1973. Dispersion-affected transport of reacting solutes in saturated porous media: Galerkin method applied to equilibrium controlled exchange in unidirectional steady water flow. *Water Resources Research* **9**: 1332-1356.
- Schulin, R.A., Papritz, H., Flühler, H. and Selim, H.M. 1989. Calcium and magnesium transport in aggregated soils at variable ionic strength. *Geoderma* **38**: 311-322.
- Scotter, D.R., Clothier, B.E. and Sauer, T.J. 1988. A critical assessment of the role of measured hydraulic properties in the simulation of absorption, infiltration and redistribution of soil water. *Agricultural Water Management* **15**: 73-86.
- Scotter, D.R., Clothier, B.E. and Turner, M.A. 1979. The soil water balance in a Fragiaqualf and its effect on pasture growth in central New Zealand. *Australian Journal of Soil Research* **17**: 455-465.
- Scotter, D.R. and Kanchanasut, P. 1981. Anion movement in a soil under pasture. *Australian Journal of Soil Research* **19**: 299-307.
- Scotter, D.R., Mohammed, I.H. and Gregg, P.E.H. 1984. The short-term fate of urea applied to barley in a humid climate. II. A simple model. *Australian Journal of Soil Research* **22**: 181-90.
- Selim H.M. and Iskandar, I.K. 1981. Modeling nitrogen transport and transformations in soils. 1. Theoretical considerations. *Soil Science* **131**: 233-41.
- Selim, H.M., Mansell, R.S., Gaston, L.A., Flühler, H. and Schulin, R. 1990. Prediction of cation exchange in soils using cation exchange reactions. In "Field-Scale Water and Solute Flux in Soils." (Editors K.Roth, H. Flühler, W.A. Jury and J.C. Parker.) Birkhauser Verlag, Basel. pp. 223-238.
- Skopp, J., Gardner, W.R. and Tyler, E.J. 1981. Solute movement in structured soils: two-region model with interaction. *Soil Science Society of America Journal* **45**: 837-842.
- Smiles, D.E. and Gardiner, B.N. 1982. Hydrodynamic dispersion during unsteady, unsaturated water flow in a clay soil. *Soil Science Society of America Journal* **46**: 9-14.

- Smiles, D.E., Perroux, K.M., Zegelin, S.J. and Raats, P.A.C. 1981. Hydrodynamic dispersion during constant rate absorption of water by soil. *Soil Science Society of America Journal* **45**: 453-458.
- Smiles, D.E. and Philip, J.R. 1978. Solute transport during absorption of water by soil: laboratory studies and their physical significance. *Soil Science Society of America Journal* **42**: 537-544.
- Smiles, D.E., Philip, J.R., Knight, J.H. and Elrick, D.E. 1978. Hydrodynamic dispersion during absorption of water by soil. *Soil Science Society of America Journal* **42**: 229-234.
- Snow, V.O., Austin, P.C. and Clothier, B.E. 1991. Modelling the leaching of a non-reactive solute through a layered soil using ARMA and aggregated mixing zone models. in *Proceedings of IVth International Symposium on Transport Phenomena, Heat and Mass Transfer.*, July 14-19, 1991, University of New South Wales, Sydney, Australia. (in press)
- Sposito, G. 1977. The Gapon and Vanselow selectivity coefficients. *Soil Science Society of America Journal* **41**: 1205-1206.
- Sposito, G. 1981. "The Thermodynamics of Soil Solution." Oxford University Press, New York.
- Starr, J.L. and Parlange, J.Y. (1979). Dispersion in soil columns: The snow plow effect. *Soil Science Society of America Journal* **43**: 448-50.
- Steele, K.W., Wilson, A.T. and Saunders, W.M.H. 1980. Nitrification activity in New Zealand grassland soils. *New Zealand Journal of Agricultural Research* **23**: 249-256.
- Taylor, G.I. 1953. The dispersion of matter in solvent flowing slowly through a tube. *Proceedings of the Royal Society, Series A* **219**: 189-203.
- Towner, G.D. 1989. The application of classical transport theory to water movement in soil: development and deficiencies. *Journal of Soil Science* **40**: 251-260.
- Valocchi, A.J., Street, R.L. and Roberts, P.V. 1981. Transport of ion-exchange solutes in groundwater: chromatographic theory and field simulations. *Water Resources Research* **17**: 1517-1527.
- van de Pol, R.M., Wierenga, P.J. and Nielsen, D.R. 1977. Solute movement in a field soil. *Soil Science Society of America Journal* **41**: 10-13.

- van Genuchten, M.Th. and Alves, W.J. 1982. Analytical solutions of the one-dimensional convective-dispersive solute transport equation. United States Department of Agriculture Technical Bulletin Number 1661, pp. 151.
- van Genuchten, M.Th. and Cleary, R.W. 1979. Movement of solutes in soil: computer-simulated and laboratory results. In "Soil Chemistry: B. Physico-Chemical Models." (Editor G.H. Bolt) Elsevier, Amsterdam. pp. 349.
- van Genuchten, M.Th. and Wierenga, P.J. 1976. Mass transfer studies in sorbing porous media I. Analytical solutions. *Soil Science Society of America Journal* **40**: 473-480.
- van Genuchten, M.Th. and Wierenga, P.J. 1977. Mass transfer studies in sorbing porous media: II. Experimental evaluation with tritium ($^3\text{H}_2\text{O}$). *Soil Science Society of America Journal* **41**: 272-278.
- van Genuchten, M.Th., Wierenga, P.J. and O'Connor, G.A. 1977. Mass transfer studies in sorbing porous media: III. Experimental evaluation with 2,4,5-T. *Soil Science Society of America Journal* **41**: 278-285.
- Wagenet, R.J. 1983. Principles of salt movement in soils. Chapter 9 in: D.W. Nelson *et al.* (Editors), Chemical Mobility and Reactivity in Soil Systems. Soil Science Society of America, Madison, WI, pp. 123-140.
- Wagenet, R.J., Biggar, J.W. and Nielsen, D.R. 1977. Tracing the transformations of urea fertilizer during leaching. *Soil Science Society of America Journal* **41**: 896-902.
- Warrick, A.W., Biggar, J.W. and Nielsen, D.R. 1971. Simultaneous solute and water transfer for an unsaturated soil. *Water Resources Research* **7**: 1216-1225.
- Warrick, A.W., Kichen, J.H. and Thames, J.L. 1972. Solutions for miscible displacement of soil water with time-dependent velocity and dispersion coefficients. *Soil Science Society of America Proceedings* **36**: 863-867.
- White, I. and Perroux, K.M. 1987. Use of sorptivity to determine field soil hydraulic properties. *Soil Science Society of America Journal* **51**: 1093-1101.
- White, R.E. 1985. The influence of macropores on the transport of dissolved and suspended matter through soil. *Advances in Soil Science* **3**: 95-120.
- White, R.E. 1987. A transfer function model for the prediction of nitrate leaching under field conditions. *Journal of Hydrology* **92**: 207-222.

- White, R.E. 1989. Predictions of nitrate leaching from a structured clay soil using transfer functions derived from externally applied or indigenous solute fluxes. *Journal of Hydrology* **107**: 31-42.
- White, R.E. and Heng, L.K. 1990. The effect of field scale variability in water flow and indigenous solute concentration on transfer function modelling of solute leaching. In "Field-Scale Water and Solute Flux in Soils." (Editors K. Roth, H. Flühler, W.A. Jury, and J.C. Parker) Birkhauser, Verlag, Basel. pp. 65-78.
- White, R.E. and Magesan, G.N. 1991. A stochastic-empirical approach to modelling nitrate leaching. *Soil Use and Management* **7**: 85-94.
- White, R.E., Thomas, G.W. and Smith, M.S. 1984. Modelling water flow through undisturbed soil cores using a transfer function model derived from $^3\text{H}\text{OH}$ and Cl transport. *Journal of Soil Science* **35**: 159-168.
- Williams, P.H., Gregg, P.E.H. and Hedley, M.J. 1990a. Use of potassium bromide solutions to simulate dairy cow urine flow and retention in pasture soils. *New Zealand Journal of Agricultural Research* **33**: 489-495.
- Williams, P.H., Hedley, M.J. and Gregg, P.E.H. 1990b. The effect of preferential flow of dairy cow urine and simulated rainfall on movement of potassium through undisturbed soil cores. *Australian Journal of Soil Research* **28**: 857-868.

APPENDIX 1

Water-repellency and its Measurement by using Intrinsic Sorptivity

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