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**MEASUREMENT AND MODELLING OF CHLORIDE AND SULPHATE
LEACHING FROM A MOLE-DRAINED SOIL**

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

Lee Kheng Heng

1991

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ABSTRACT

A study of the leaching of sulphate, chloride, nitrate and the associated cations was carried out over two winter periods on three mole-drained paddocks on a yellow-grey earth (Tokomaru silt loam). The paddocks were occasionally grazed by sheep. At the beginning of each drainage season potassium chloride (KCl) and sulphur fertilizer, as either single superphosphate (SSP) or elemental sulphur (S⁰), were applied to two of the paddocks, while the third served as a control. The amount of KCl applied was 200 kg ha⁻¹ yr⁻¹, while sulphur was applied at 50 kg S ha⁻¹ in 1988 and 30 kg S ha⁻¹ 1989. Drain flow from the fertilized paddocks was measured with V-notch weirs, and sampled using proportional samplers.

Large differences in the total drainage flow were measured in the two years, with values of approximately 280 mm in 1988 and 110 mm in 1989. Significant amounts of the chloride added through both fertilizer and rainfall were leached, amounting to approximately 105 kg Cl ha⁻¹ yr⁻¹.

The leaching of sulphate-S depended on the form of S fertilizer applied, the quantity of drainage, and the rate of mineralization. Leaching losses of 17 and 3.4 kg S ha⁻¹ were measured from the SSP and S⁰ fertilized paddocks, respectively, in 1988, and 9.4 and 3.5 kg S ha⁻¹ in 1989. The study showed that applying SSP just before the drainage season increased leaching losses of sulphate-S substantially. Although the particle sizes of S⁰ used in both years were much bigger than those specified by the Ministry of Agriculture and Fisheries of New Zealand, there appeared to be no difference in the yield response to S applied either as SSP or as S⁰. The reduced leaching of S when applied as S⁰ resulted from the slow oxidation of S⁰ to sulphate-S.

Relatively little nitrate-N was leached, the amount ranging from 11 to 17 kg N ha⁻¹ yr⁻¹. Losses of potassium were less than 10 kg K ha⁻¹ yr⁻¹, despite the large quantity applied as KCl fertilizer immediately before winter. However a large amount of calcium was leached, between 31 and 52 kg ha⁻¹ yr⁻¹. The amount of magnesium leached was between 9 and 15 kg ha⁻¹ yr⁻¹. A considerable quantity of sodium was

leached, around 58 kg ha⁻¹ in 1988, and 31 kg Na ha⁻¹ in 1989, roughly equal to the input in rainfall.

Good mass balances were obtained for both chloride and sulphate. The measured moles of negative and positive charge from cations and anions in the leachate were also almost equal.

Three models were developed for the leaching of chloride and sulphate-S. An approach dividing the soil water into mobile-immobile phases, and using a fairly detailed soil water flow model was developed. The model was able to simulate the concentration of chloride in the drainage closely, even just after the application of chloride fertilizer, and during highly preferential flow conditions induced by heavy rain.

A transfer function model, assuming a log-normal probability density function (pdf) of solute travel pathway lengths, was able to simulate the leaching of chloride reasonably well in 1988. The prediction was less satisfactory in 1989 and during highly preferential flow. By adapting the pdf for chloride to sulphate and by taking adsorption of sulphate into account, the model could predict the sulphate concentration in the drainage quite successfully.

A simpler model, using the idea that the two-dimensional flow geometry to the mole drain implies that the drainage concentration approximately equals the average soil solution concentration, was also developed. Despite its simplicity it was able to simulate the leaching of chloride and sulphate as well as the transfer function model.

Irrespective of the model being used, the net mineralization rate of soil organic sulphur emerged as an important factor in predicting the leaching of sulphate.

ACKNOWLEDGEMENTS

My gratitude and appreciation to the following people for their contributions toward the completion of this thesis:

Prof. R.E. White, my chief supervisor and head of the department, for his encouragement and guidance towards this project, his readiness to listen and explain despite his busy schedule.

Dr. D.R. Scotter, whom I learned much about soil physics, modelling, and the "principles and integrity" towards science, for all the good and bad moments we gave to each other.

Dr. N.S. Bolan, for his help in the chemical aspect of the thesis, his friendship, advice and lots of Indian foods.

Dr. Mike Hedley, Dr. S.K. Sagar, Mr. Russ Tillman and Mr. Sathien Phimsarn, for valuable discussions and friendships.

Mr. G.N. Magesan, for the 1990 data, and Mr. I. Furkert, for helping in the field.

Mrs Ann Rouse, the department secretary, for her valuable help and friendship.

Other members of the department, especially Miss K. Hodgson, Mr. M. Bretherton and Mr. Aravind for their friendship, coffee and biscuits we shared together that made this place pleasant for study.

Ravensdown Fertiliser Cooperative Ltd., for their financial support.

Pastors and friends at the Palmerston North Central Baptist Church, especially those in the International Students Fellowship, in particular Mr. & Mrs Vincent and Heather Norrish, Mr. & Mrs Jones, Mr. & Mrs Crawford and Jo-ann for their care, concern and hospitality.

Wayne, Nuchanat, Joshy and Ranee Scott, for accepting me as part of the family and the much needed Thai food.

My family whom I am so proud to belong to. My parents, for their love and support. My brothers and sister, and all their families, for their continual care and protection all these years.

Finally, to the one who inspired King Solomon to write the beautiful book of *Ecclesiastes*.

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LIST OF SYMBOLS

Roman letters

- a = an empirical constant related to the Freundlich type adsorption isotherm
- A = Inorganic animal returns [$M L^{-2}$]
- A_s = area of soil under consideration [L^2]
- b = an empirical constant related to the Freundlich type adsorption isotherm
- C = solution concentration [$M L^{-3}$]
- C_d = solution concentration at the drain [$M L^{-3}$]
- C_i = initial solute concentration [$M L^{-3}$]
- C_s = source/sink concentration [$M L^{-3}$]
- D = drain flow rate per unit soil area [$L T^{-1}$] (Ch 5 and 7)
= cumulative drain flow per unit soil area [L] (Ch 6)
- D_c = drainage coefficient of the mole-pipe drainage system [$L T^{-1}$]
- D_h = dispersion coefficient [$L^2 T^{-1}$]
- D_t = drainage at time t [L]
- e = slope of soil water characteristic [L^{-1}]
- E_t = evaporation rate [$L T^{-1}$]
- f = soil porosity [$L^3 L^{-3}$]
- f_j = fraction of elemental S in class j
- F = sulphate-S input rate from superphosphate [$M L^{-2} T^{-1}$]
- F_θ = fractional moisture content relative to "field capacity"
- $g(D-D')$ = probability density function of apparent drainage pathway lengths [L^{-1}]
- $g(t-t'|t')$ = probability density function of solute lifetimes [T^{-1}]

- $g(t-t')$ = probability density function of solute travel times [T^{-1}]
- G = sulphate-S input rate from the oxidation of S^0 [$M L^{-2} T^{-1}$]
- H_w = hydraulic head over the crest of weir [L]
- j = horizontal solute flux density [$M L^{-2} T^{-1}$]
- j_{ab} = vertical solute flux density between layers [$M L^{-2} T^{-1}$]
- j_d = vertical solute flux density at z_d [$M L^{-2} T^{-1}$]
- k = a proportionality related to the oxidation of elemental S [$M L^{-2}$]
- k_1 = first order immobilization rate constant [T^{-1}]
- k_2 = first order mineralization rate constant [T^{-1}]
- k_3 = proportionality constant related to atmospheric sulphur input [$M L^{-3}$]
- k_4 = proportionality constant related to plant sulphur uptake [$M L^{-3}$]
- k_{ad} = an empirical constant related to sulphate adsorption [$L^3 M^{-1}$]
- K = saturated hydraulic conductivity [$L T^{-1}$]
- K_w = a constant relating to the weir flow rate calculation
- L = the latent heat of vaporization [$M L^{-1} T^{-2}$] (Ch 2)
= rate of solute leached per unit soil area [$M L^{-2} T^{-1}$] (Ch 5 and 7)
- m = number of notional horizontal compartments in the model (Ch 5)
- M = solute present in unit soil volume [$M L^{-3}$] (Ch 5)
= solute present under unit soil area to depth z_d [$M L^{-2}$] (Ch 6 and 7)
- M_o = mass of solute applied at $D = 0$ [$M L^{-2}$]
- M_t = mass of solute mineralized at time t [$M L^{-2}$]
- n = number of particle classes of elemental sulphur
- N = an operationally-defined readily mineralizable soil organic sulphur pool [$M L^{-2}$]
- N_o = N at the start of each drainage season [$M L^{-2}$]
- P = pressure potential in head units [L]

- q = average water flux density [$L T^{-1}$]
 q_d = vertical water flux density at depth z_d [$L T^{-1}$]
 q_w = flow rate measured over the V-notch weir [$L^3 T^{-1}$]
 Q = horizontal flow rate per unit length of plane [$L^2 T^{-1}$] (Ch 5)
 = mass rate of solute entrance or exit from soil [$M T^{-1}$] (Ch 6)
 r = radius of S° particle at time t [L]
 r_o = initial radius of S° particle [L]
 R = rainfall intensity [$L T^{-1}$]
 R_n = net radiation [$M T^{-3}$]
 R_o = surface runoff per unit length of plane [$L^2 T^{-1}$]
 R_{rc} = retardation coefficient
 s = rate of change of saturation vapour density with temperature
 [$M L^{-3}$ per degree temperature change] (Ch 2)
 = standard deviation of x (Ch 4)
 S = source/sink term [$M L^{-3} T^{-1}$] (Ch 5)
 = source/sink term [$M L^{-2} T^{-1}$] (Ch 6 and 7)
 S_{ad} = mass of sulphur adsorbed per unit mass of dry soil [$M M^{-1}$]
 S_t = temperature reduction factor for oxidation of elemental S
 S_θ = moisture reduction factor for oxidation of elemental S
 t = time [T]
 T = depth to water table [L]
 T_s = soil temperature at 300 mm depth ($^\circ C$)
 v = average pore water velocity [$L T^{-1}$]
 v_{ad} = average pore water velocity of an adsorbed solute [$L T^{-1}$]
 W = equivalent depth of water stored above drain depth [L]
 W_c = average of W_d and W_o [L]
 W_d = W when T is at z_d [L]

W_o	= W when T is at surface [L]
x	= value from an individual soil sample (Ch 4) = horizontal distance from mid-mole plane [L] (Ch 5) = distance in x direction [L] (Ch 6)
\bar{x}	= mean of x (Ch 4)
x_d	= x at the mole [L] (Ch 5)
X	= amount of S^o remaining after time t [$M L^{-2}$]
X_o	= amount of S^o applied [$M L^{-2}$]
X_w	= a variable defined in Equation (7.1) [L]
z	= depth from soil surface [L]
z_a	= depth of notional top layer [L]
z_d	= depth of topsoil or depth to mole [L]

Greek letters

α	= a dimensionless empirical constant in the Priestley-Taylor equation (Ch 2) = rate coefficient for solute diffusion between phases [T^{-1}] (Ch 5)
β	= horizontal dispersivity [L]
γ	= psychrometric constant [$M L^{-3}$ per degree temperature change]
θ	= volumetric water content [$L^3 L^{-3}$]
ρ	= bulk density of soil [$M L^{-3}$]
ρ_s	= specific gravity of elemental S [$M L^{-3}$]
μ	= mean of $\ln x$ (Ch 4) = mean of the log-normal pdf for travel pathway lengths of a non-reactive solute (Ch 6)
μ_{ad}	= mean of the log-normal pdf for travel pathway lengths of a reactive (adsorbed) solute
σ	= standard deviation of $\ln x$ (Ch 4) = standard deviation of the log-normal pdf for travel path lengths (Ch 6)

ψ_m = matric potential dividing the mobile and immobile water [L]

Subscripts

a = denotes upper notional soil layer or horizontal flux density from it

b = denotes lower notional soil layer or horizontal flux density from it

i = denotes immobile soil solution phase

m = denotes mobile soil solution phase

j = denotes j^{th} class of S° particles

n = denotes the value of the variable on a certain day

ent = denotes entrance surface of a soil volume

ex = denotes exit surface of a soil volume

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CHAPTER 1

INTRODUCTION AND REVIEW OF LITERATURE

1.1 INTRODUCTION

The increasing demand for high productivity farming systems has resulted in greater usage of fertilizers, herbicides and insecticides. Once they have moved below the plant root zone, the fertilizers applied are unavailable for plant uptake. Such losses of plant nutrients are expensive to replace and cause pollution of surface and groundwater. Field-scale studies of leaching are needed in order to more fully understand the factors and mechanisms causing these losses. Studies of leaching so far have generally focused on nitrate, pesticides, herbicides, and heavy metals, because of their environmental impact. Sulphur (S), a major plant nutrient, has not received much attention, despite the fact that substantial leaching of sulphate has been reported both in New Zealand (Walker, 1957; Gregg and Goh, 1978; Smith *et al.*, 1983; McLay, 1989; Saggar *et al.*, 1990) and in overseas studies (Chao *et al.*, 1962a; Korentajer *et al.*, 1983).

Leaching is normally the major mechanism by which sulphate is lost from the soil system in New Zealand. This has led several researchers (Till, 1980; Nguyen *et al.*, 1983; Tillman, 1983; Sinclair *et al.*, 1985) to suggest that a major emphasis on sulphur research should be to improve our understanding of the leaching process, as knowledge of the mechanisms involved in the leaching process and its interaction with other soil processes would help in developing strategies to reduce losses and maximise the efficiency of sulphur use in agriculture. This is important because New Zealand imports approximately \$40 million worth of sulphur each year (Saggar and Hedley, 1989). Such information may also be useful in places where there is increasing evidence of soil sulphur deficiencies as a consequence of reduced atmospheric input from industrial pollution (Morris *et al.*, 1984; Syers *et al.*, 1987). Under these conditions plants have to rely more on soil S, and such information may help to reduce further losses through leaching from this pool.

Sulphur has been generously added to soil in New Zealand in the past, as a result of the application of single superphosphate (SSP) as a source of phosphorus (P) to pasture. However, with the recent marked increase in the cost of manufacturing and transporting SSP, the current trend in New Zealand is towards using higher analysis phosphate fertilizers such as reactive phosphate rocks (RPRs) and partially acidulated phosphate rocks (PAPRs) so that the cost of phosphorus (P) application to many remote hill country areas can be reduced (Sinclair and Dyson, 1988). To provide the sulphur needed, elemental sulphur (S^0) rather than SSP is normally used along with the high analysis P fertilizers. This is due to the high S content (90-100% S) of S^0 ; also sulphur in the S^0 form is easier to store and transport than the bulkier sulphate form. The main difference between SSP and S^0 in terms of plant availability is that sulphate-S in the former is readily soluble, is available to the plant immediately, but is also very susceptible to leaching. In contrast, S^0 is insoluble and needs to be oxidised before sulphate is released, and therefore is less prone to leaching.

While a widely claimed advantage of S^0 over SSP as a source of S is that it maintains yield while reducing leaching losses, this claim has not been experimentally verified. Long-term field studies undertaken to compare the effectiveness of S^0 with SSP (e.g. Boswell, 1987; Swanney *et al.*, 1988; Smith and McDougall, 1988) have mostly concentrated on the differences in dry matter production and plant S uptake, without explicitly considering the leaching losses. A comparison between the effectiveness of these two sources of sulphur fertilizer (SSP and S^0) under field conditions is therefore needed, and was carried out in the work reported here by monitoring the dry matter production, plant S uptake, soil sulphate level and leaching losses.

In order to understand the leaching of sulphate which is subject to biological transformations and adsorption, it is useful to have an independent measure of how the soil water is moving. Chloride (Cl) has often been used as a tracer for this movement (Dyer, 1965; Anderson and Bouma, 1977; Addiscott *et al.*, 1978). This is because it is a very mobile solute, does not undergo biological or chemical transformations and is not adsorbed (Tisdale *et al.*, 1985). Chloride can be

excluded from the surfaces of negatively charged soil particles, and as a result the rate at which it travels downward through the soil can be increased relative to the water itself. This can be demonstrated by comparing the movement of chloride and tritium ^3H (McMahon and Thomas, 1974; Bond *et al.*, 1982; White *et al.*, 1984). However, significant anion exclusion only occurs in soil with a high cation exchange capacity (CEC) and large particle surface area. The relatively low CEC of the soil used in this study, Tokomaru silt loam soil (approximately 220 mmol kg^{-1} or 22 meq/100 g , Williams, 1988), meant that anion exclusion was not a major problem. Chloride was therefore used as a tracer. However, because it is generally present in soil, rainfall and irrigation water, the amount added must be large enough to mask that derived from other sources.

Although there are many models for predicting the movement of solutes, few if any have proved satisfactory for field soils, particularly those under grazed pasture. No models for sulphate leaching have been developed for artificially drained soils. In New Zealand a sulphate leaching index (SLI) (Sinclair, 1982) was developed to measure the susceptibility of the soil to lose sulphate by leaching. The SLI is determined by 3 parameters: the sulphate retention of the topsoil, the annual rainfall and irrigation input, and the drainage status of the soil. The index is useful on a long term basis, however the accuracy with which it can predict sulphate leaching on a seasonal basis is questionable. This is partly because the estimated leaching loss is based on total rainfall while often it is the timing and nature of individual rainfall events relative to evaporation that determines the amount of leaching. One of the aims of this study was to explore various approaches to modelling the leaching of sulphate, a reactive solute, and chloride, a non-reactive solute. Modelling of chloride was seen as a stepping stone to sulphate modelling.

Scotter *et al.* (1990) developed a model to predict the movement of soil water to mole-drains. As the hydrology of the soil was simulated quite successfully in this model, it is extended to include solute and used to predict the concentration of chloride in drainage water in Chapter 5. However this solute model requires relatively detailed soil physical properties. For a reactive solute such as sulphate, it was found that the leaching process was governed more by biological and chemical

processes than the physical properties of the soil, hence the detailed leaching model was not extended to sulphur. In Chapter 6 a totally different approach to modelling the leaching of both chloride and sulphate is described. It is an approach using the transfer function model (TFM) of Jury (1982) and Jury *et al.* (1986). The transfer function model requires the determination of a probability density function (pdf) of solute travel times (or pathways) between the input and output surfaces of the soil. If this pdf of travel times or pathways can be assumed to conform to a simple function such as a log-normal distribution, then the moments of that distribution are the essential parameters of the model.

In Chapter 7, a "well mixed" model is described. In comparison to the two previously mentioned models in Chapters 5 and 6, the "well mixed" model is a significant simplification. The model is based on the theory of Raats (1978) for water and solute movement through soil to a drain. Under certain conditions, the concentration of solute in the drainage is the average soil solution concentration, that is the system behaves as if the soil solution were "well mixed".

Most reported leaching experiments have focused on one or two ions, without considering the accompanying cations and anions. Hogg and Cooper (1964) reported that the addition of superphosphate to KCl markedly increased the amount of potassium leached in a laboratory study. Cronan *et al.* (1977) and Singh *et al.* (1980) observed that when a soil is subject to inputs of sulphuric acid from acid precipitation, the movement of sulphate may affect leaching losses of nutrient cations. Similar effects could occur in farming situations. For example, Steele *et al.* (1984) showed that increased leaching losses of nitrate (resulting from nitrogen application) resulted in increased losses of calcium, magnesium, sodium and potassium, but that the leaching of sulphate was reduced. These results have important implications for nutrient availability. As a complete study on the major nutrient losses from mole drains has not been carried out in New Zealand, it was also the purpose of the study described here to investigate the leaching losses of the major anion and cation nutrients from a mole-drained soil.

1.2 LITERATURE REVIEW

Although the leaching of both anions and cations is investigated in this study, the main aim was to compare the leaching losses from the two forms of sulphur fertilizer (SSP and S^o) currently used in New Zealand, and to develop a model to predict these losses. So this literature review will concentrate mainly on sulphur.

Sulphur occurs in both organic and inorganic forms in the soil. Although the proportion of each form varies with soil type, depth, and the management system, in most well-drained soils in humid-temperate regions, the amount of inorganic sulphur comprises less than 10% of the total sulphur present (Ensminger, 1954; Freney, 1961; Metson, 1969), with the rest in the organic form in the topsoil (Tisdale *et al.*, 1985; Syers *et al.*, 1987). The quantity of organic S in a soil depends on the amount of organic matter and the level of S inputs. In well-drained and aerated soils, inorganic sulphur normally exists as sulphate. This sulphate can be either in solution or weakly adsorbed by the soil solids. Although the proportion of inorganic sulphur is small in comparison to the organic component, it is this sulphate that plants utilize. Organic sulphur has to be mineralized to sulphate before it becomes available to plants.

The major sources of sulphate available to plants in a farming environment such as New Zealand are fertilizers, mineralization of organic sulphur, return in animal waste products, and to a lesser extent, inputs from rainfall and the atmosphere (dry deposition), and irrigation water. The amount of this plant available sulphate is affected by the climatic conditions, the soil and plant type, and by management practices. These factors also influence the rate and amount of sulphur likely to be leached.

1.2.1 Factors Affecting the Plant Availability and Leaching Loss of Sulphur

1.2.1.1 *Climate*

Climate affects leaching through rainfall and evaporation. The amount of sulphate leached is generally approximately proportional to the quantity of drainage (Jones *et al.*, 1968; Smith *et al.*, 1983). In New Zealand, leaching occurs mostly in winter when evaporation is lowest. Considerable quantities of sulphate can be lost then. Using ^{35}S labelled gypsum, Gregg and Goh (1978) observed a significant proportion of the 45 kg S ha^{-1} fertilizer added had moved below 600 mm depth in the winter 48 days after its application. Smith *et al.* (1983) reported a similar finding, that between 25-33% of the 45 kg ha^{-1} of the sulphate-S fertilizer they applied was leached in 165 mm of winter drainage. Leaching can also be high in spring when warmer temperatures occur. When combined with wet soil conditions, this can result in substantial mineralization of organic S to sulphate-S, and hence substantial leaching, as observed by Jones and Woodmanse (1979) and Steele *et al.* (1984).

1.2.1.2 *Soil texture and structure*

Higher leaching loss generally occurs from coarser textured soils. In a laboratory study, Chao *et al.* (1962a) found sandy soils more prone to leaching than finer textured soil. Gregg and Goh (1978) also found more sulphate leaching occurred from a sandy loam than a heavy silt loam. This is partly because the field capacity is smaller in sandy soils. For a given water application rate (q), the lower volumetric water content (θ) of sandy soil will increase the percolating velocity (v), through the relationship $v = q/\theta$, hence the rate of leaching of the applied S is faster. The lower available water holding capacity of sandy soils also means less recharge is needed in autumn before drainage occurs.

The effect of texture tends to be modified by soil structure through the existence of macropores such as cracks, and worm and roots channels. Macropores can provide the major flow paths for water and solute under certain conditions in either very wet

or dry soil. As a result, drainage from field soils can begin long before the soil reaches field capacity (Jarvis and Leeds-Harrison, 1987a,b), and deeper penetration and earlier appearance of solute in drainage than expected may also occur, as shown by the work of McKell and Williams (1960), Quisenberry and Phillips (1976), Wild and Babiker (1976), and Smettem *et al.* (1983). Scotter and Kanchanasut (1981) observed that when preferential flow occurs, even a strongly adsorbed solute such as phosphate applied to the surface can arrive at a tile drain as fast as a non-adsorbed solute such as chloride.

1.2.1.3 *Fertilizers*

The type and form of S fertilizer used, and the rate of application have a major influence on the leaching losses. For each fertilizer type, finer particles are more susceptible to leaching than coarser materials because the bigger surface area means a quicker dissolution or transformation to sulphate in solution (Korentajer *et al.*, 1983). The amount of fertilizer leached is also dependent on the rate of fertilizer applied. Both McKell and Williams (1960) and Nguyen *et al.* (1983) reported increased leaching of sulphate with increasing amounts of fertilizer input. The timing of fertilizer application is another major factor affecting the amount leached. More leaching tends to occur when fertilizer is applied just before the winter drainage season (Kissel *et al.*, 1973; Gregg and Goh, 1978; Smith *et al.*, 1983).

Elemental sulphur is insoluble in water and requires biological oxidation to be converted to soluble sulphate. Because the rate of oxidation is relatively slow, it is less susceptible to leaching. However, this particular characteristic also means that it is not suitable for situations where an immediate source of plant-available sulphur is required. Elemental S also has the potential of increasing the acidity, and hence lowering the pH of the soil, due to the production of sulphuric acid during oxidation (Li and Caldwell, 1966). This may affect its adsorption on subsequent leaching, especially in variable charge soils. The factors influencing the rate of oxidation of elemental sulphur will be discussed later.

1.2.1.4

Net mineralization

Mineralization is the conversion of organic S into inorganic sulphate, while immobilization is the reverse process. Both processes occur simultaneously in the soil as a result of biological activity. Hence they are regulated by factors which influence the growth of microorganisms, such as soil moisture, temperature, pH, nutrient supply and organic matter. Mineralization has been found to increase with increasing content of organic matter, especially in soils with low C:S ratios (ratio less than 200) (Harward *et al.*, 1962; Nelson, 1964). Chaudhry and Cornfield (1967) found that mineralization increases with temperature from 20 to 40° C. In a laboratory study, Williams (1967) observed that mineralization of S declined at moisture contents above and below "field capacity", while Chaudhry and Cornfield (1967) reported that maximum mineralization occurred at 60% "field capacity". These studies were carried out in the laboratory with other interacting factors such as temperature kept constant, therefore direct extrapolation to field situations may be misleading. Other factors which affect mineralization include air-drying and repeated drying and wetting of soil (Barrow, 1961; Williams, 1967; Kowalenko and Lowe, 1975; Biederbeck, 1978). The presence of growing plants also increases the mineralization of organic sulphur in the field (Sorn-srivichai, 1980). This is probably due to greater biological activity and substantial removal of mineralized sulphate (Tsuji and Goh, 1979). The addition of lime has also been observed to increase mineralization (Williams, 1967; Sorn-srivichai, 1980), due probably to bacteria growing better in a more favourable pH environment, sulphate released from soil organic matter by chemical hydrolysis, and adsorbed sulphate released from soil exchange sites because of an increase in pH. Sorn-srivichai (1980) studied the mineralization of S using Tokomaru silt loam topsoil. She found that the amount mineralised varied considerably. For 6 "field pot" samples the values ranged from 11 to 23 kg S ha⁻¹ during a 13 week study, and were highly correlated with the total S content. This implies that the organic S in soils, as indicated by the total S value, may be a useful indicator of the extent of mineralisation of S within a soil type.

Immobilization of inorganic sulphate tends to take place in soils with high C:S ratio (>400) (Barrow, 1960). Significant amounts of fertilizer sulphate have been reported to be immobilized by micro-organisms in both field and laboratory incubation studies (Freney *et al.*, 1971, 1975; Goh and Gregg, 1982; Ghani *et al.*, 1988; McLay, 1989). Values as high as 50% of the added sulphate-S being immobilized within a short time have been reported. This process is normally very rapid initially, and slows down with time. Because the balance between mineralization and immobilization is so dynamic, and the governing factors interact with each other, inconsistency within and between data sets is often observed; consequently a generalized pattern of immobilization and mineralization cannot be described, making it difficult to model. Ellert and Bettany (1988) presented several kinetic models which have been developed for describing mineralization. These models ranged from a simple first order model to complicated models attempting to account for the sudden flushes, or initial lags in mineralization which have sometimes been observed. In the more complicated models, substrates are assumed to consist of different pools which mineralize at different rates, depending on variables such as substrate concentration, catalytic activity of the biomass, or the mineralization capacity of the microbial community.

1.2.1.5 *Adsorption*

The amount of sulphate adsorbed varies according to the adsorption capacity of the soil, and affects the amount of sulphate leached. Increasing adsorption normally results in less sulphate leaching, as shown by the work of Hogg (1965), and Gregg and Goh (1978, 1979). Adsorption of S is observed to be reversible and concentration dependent (Chao *et al.*, 1962b; Chang and Thomas, 1963; Marsh *et al.*, 1987), which means that when the solution sulphate concentration is low, desorption can occur to supply the sulphate needed for plant growth. Adsorption is affected by various soil properties which include: clay and phosphate content, pH and exchangeable cations (Ensminger, 1954; Kamprath *et al.*, 1956; Chao *et al.*, 1962b; Chang and Thomas, 1963; Williams, 1974; Metson and Blackmore, 1978; Bolan *et al.*, 1986). Generally adsorption increases with soil depth (Williams, 1974) due to the presence of higher concentrations of sesquioxides, allophane, and

kaolinite type clay minerals, and a low base saturation in the subsoil. The lower sulphate retention in the topsoil is normally due to the higher number of immobile phosphate ions competing for adsorption sites (McLaren and Cameron, 1990). The low adsorption of most New Zealand topsoils is probably due to the accumulation of P added through long-term application of SSP. For variably charged soils, adsorption tends to increase with decreasing pH (Marsh *et al.*, 1987; Bolan *et al.*, 1988) due to an increase in positive sites for anion adsorption as pH decreases. Marsh *et al.* (1987) showed that the adsorption of Tokomaru silt loam dropped to nil as the pH increased to 5.8. Consequently enhanced leaching of sulphate out of the root zone is possible from soils of low adsorption capacity which have recently been limed (Kamprath *et al.*, 1956; Bolan *et al.*, 1988).

The adsorption capacity is generally expressed in terms of an adsorption isotherm, which is normally measured using a laboratory batch method. A small quantity of air-dried soil is shaken in an extractant with a known range of sulphate concentrations, and the change in concentration in the extractant measured. Column studies by Schweich and Sardin (1981), and Hodges and Johnson (1987) showed that the batch method may not simulate field situations accurately, because during shaking, breakdown of soil aggregates can occur. Also the soil to solution ratio is not the same as in the field. The concentrations and composition of the solution also change during the equilibration period, depending on whether a background electrolyte has been used (Kanchanasut, 1980; Bond and Phillips, 1990). Alternative ways of obtaining adsorption isotherms using leaching columns are available (Bond and Phillips, 1990). So far, a field-determined sulphate adsorption isotherm has never been obtained. In this thesis, a field-measured adsorption isotherm which overcomes some of the above limitations is described.

1.2.1.6

Plant uptake, animal return and removal

Plants require S to synthesize protein, and as much as 90% of the total S in plants may be present as protein-S (McLaren and Cameron, 1990). The concentration of S in pasture is between 0.25 and 0.32% (During, 1984); this however depends on the plant parts, age and the interaction with the N supply to the plant. The amount of S

uptake by pasture ranges between 10 and 50 kg S ha⁻¹ yr⁻¹, depending on the level of dry matter production.

Animal return is a major contribution to the sulphur cycle of New Zealand pastures (Saggar *et al.*, 1990). Generally, over a long period, animals retain between 10-15% of the S ingested in plant materials and the rest is returned to the soil through urine and faeces (Till, 1980). For sheep, the ratio of S in urine and faeces is approximately 60:40 (Wilkinson and Lowrey, 1973). Most of the S present in urine is in the water soluble sulphate form while that in faeces is mostly insoluble. The latter goes into the organic pool and therefore is not immediately available to the plant. The distribution of urine and faeces over pasture is dependent upon factors such as stocking rate, grazing pattern, type of animal, topography and the amount and frequency of excretion. The distribution tends to be very non-uniform, with large amounts concentrating on small flat areas. Considerable transfer of nutrients from one part of a paddock to another can therefore occur. Because of its high concentration and soluble form, sulphur in urine is susceptible to leaching (Hogg, 1981; Sinclair, 1983). The extent of leaching loss depends on the climate and the soil properties.

1.2.1.7 Wet deposition and atmospheric sulphur

Sulphur present in the atmosphere may reach the soil through wet (in rainfall) or dry deposition (as SO₂ gas, and deposits of aerosols and dust particles containing ammonium sulphate, for example). The amount received depends on the closeness to industry and the sea coast. In New Zealand, Walker and Gregg (1975) found that the sulphate S concentration in rainfall in Canterbury decreased with increasing distance from the sea, with about 4 kg S ha⁻¹ yr⁻¹ deposited for distances less than 20 km from the sea, and much less for greater distance. Ledgard and Upsdell (1991) found little annual variability in the S deposited in rainfall at 4 sites in the North Island of New Zealand, with values ranging between 0.5 and 15 kg ha⁻¹ yr⁻¹, with the highest values near the coast. Smith *et al.* (1983) measured approximately 5 kg ha⁻¹ yr⁻¹ of sulphate-S deposited from rain in the Manawatu, while Blake more (1973) reported a mean figure of 7.7 kg S ha⁻¹ yr⁻¹ at Taita, near Wellington. The

amount of S deposited through dry deposition in New Zealand is expected to be little. The S model developed by MAF takes atmospheric input into account, by allowing an addition of 2 kg S ha⁻¹ for distances less than 20 km from sea shore. Leaching of atmospheric S is expected to be less than urinary S because the inputs are generally quite low in intensity, and more of it is intercepted and taken up directly by plants.

1.2.1.8 *Runoff*

Very few studies have been undertaken to look into the amount of sulphur in surface runoff in New Zealand. However it could be expected to depend on the soil, the slope, vegetation cover, management practice and local climate (Till, 1975). Smith *et al.* (1983) measured the sulphate loss via runoff and observed that the amount lost was minimal from drained gently sloping soil (6°), but when fertilizer was applied to undrained soil immediately before the drainage season, 8% of the total 45 kg S ha⁻¹ was lost through runoff. In general, subsurface drainage tends to reduce losses in runoff but increases leaching losses.

1.2.2 Factors Affecting the Oxidation of Elemental Sulphur

Various factors associated with soil, climate and fertilizer affect the oxidation of elemental sulphur. Some of these factors are briefly discussed below.

1.2.2.1 *Particle size*

The most important factor affecting the oxidation of elemental sulphur is its particle size. Both glasshouse and field studies have shown that the oxidation rate increases as the particle diameter decreases (Jansen and Bettany, 1987b; McCaskill and Blair, 1989; Chatupote, 1990). In New Zealand the particles have to be < 0.15 mm in the cooler temperature zones and < 0.25 mm in warmer temperature zones in order for the particles to be effective within a year, according to the classification given by the Ministry of Agriculture and Fisheries of New Zealand (Sinclair *et al.*, 1985;

Fig. 1.1). Boswell and Swanney (1988) and Chatupote (1990) showed that particles larger than 0.5 mm generally cannot oxidise rapidly enough to meet plant requirements during the year of application. However finely-ground particles pose an explosive fire hazard when used on their own for aerial topdressing (Rothbaum *et al.*, 1983). Elemental sulphur is observed to be most effective when applied in early spring, and when mixed into the soil, as that stimulates its oxidation. The oxidation rate also increases with increasing pH, therefore it tends to be stimulated by liming (Nor and Tabatabai, 1977).

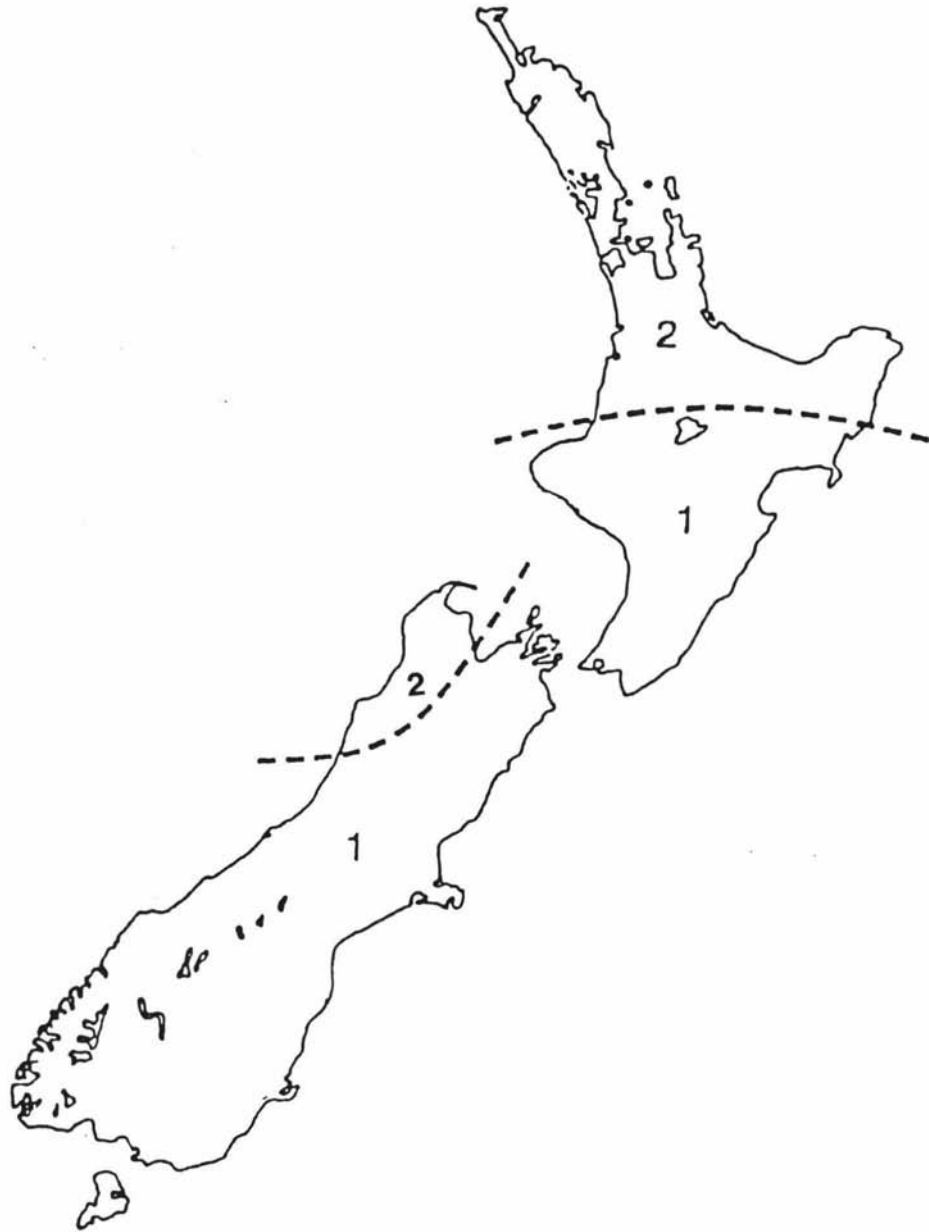
1.2.2.2 *Soil temperature*

The oxidation of elemental sulphur is dependent on soil temperature because of the temperature effect on microbial activity. Oxidation is found to be very slow at low temperatures (below 10°C) but increases rapidly with increasing temperature to a maximum at 40°C (Li and Caldwell, 1966; Weir, 1975; Nor and Tabatabai, 1977). The importance of both temperature and moisture for the oxidation of S⁰ can be seen from Fig. 1.1, where the effectiveness of different S⁰ particle sizes was classified according to climatic zones within the country. Both Shedley (1982) and Janzen and Bettany (1987a) examined the effect of temperature on S⁰ oxidation in detail. From the results obtained by Shedley (1982), Chatupote (1990) developed an equation relating the rate of oxidation of S⁰ to temperature to account for below optimal temperature conditions in the field.

1.2.2.3 *Soil moisture*

The oxidation of elemental sulphur proceeds most rapidly at a soil moisture content at or near "field capacity" and tends to decrease at either very high or very low moisture contents (Moser and Olson, 1953; Kittams and Attoe, 1965). This is probably due to the reduction in soil aeration near saturation, and insufficient water for transporting nutrients to the microbes at lower water contents (Jensen and Bettany, 1987a). McCaskill and Blair (1989) derived a relationship to account for below optimal moisture conditions from the data of Moser and Olson (1953). This relationship was used by Chatupote (1990) to model the oxidation of S⁰ under field

Fig. 1.1 Map of New Zealand showing broad climate zones affecting recommended fertilizer S^o particle size ranges (after Sinclair *et al.*, 1985)



Recommended elemental S^o particle size ranges (μm)

Annual Application	Biennial Application
Region 1 < 150 μm	< 250 μm (50% < 150 μm)
Region 2 < 250 μm	< 500 μm (50% < 250 μm)

conditions.

1.2.2.4 *Microbial population*

Both the type and number of microorganisms affect oxidation. The autotrophs of genus *Thiobacillus* (*T. thioparus*, *T. neapolitanus* and *T. denitrificans*) are important S-oxidising microorganisms. These organisms oxidise S^o at soil pH 4 to 7.

Heterotrophs (fungi and actinomycetes) have also been identified as possessing the ability to oxidize S^o, and as the number of heterotrophs is more than autotrophs in most soils, they could play an important role in the oxidation. However these groups tend to be more sensitive to pH changes than the thiobacilli species (Wainwright, 1984).

1.2.3 **Measurement of Elemental Sulphur Oxidation**

The rate and extent of sulphur oxidation has been found from the changes in soil sulphate (Li and Caldwell, 1966; Jansen and Bettany, 1987b) and the decrease in soil pH (Li and Caldwell, 1966). The first method was found to work only in laboratory incubation studies in the absence of plants. In pot or field studies, plant uptake, immobilization and mineralization of organic sulphur makes quantitative measurement of the total sulphate released difficult. The decrease in pH as S^o oxidised is due to the production of sulphuric acid according to the equation



Equation (1.1) implies that approximately 3 kg of pure limestone is needed to neutralize the acid produced by 1 kg of S^o. Decreases in pH were observed in soils of low pH buffering capacities at high levels of S^o application (Li and Caldwell, 1966; Rajan and Edge, 1980; Lee *et al.*, 1987). However at normal application rates (about 50 kg S ha⁻¹), the decrease in pH is often too small to be detected in the field, as the sulphate produced may be immobilized by soil microorganisms which results in the consumption of protons. Thus the second method is also not feasible.

Although direct measurement of the residual S° concentration with time is in principle the most accurate way of assessing the oxidation rate (Chatupote, 1990), this method is laborious and most often unreliable in the field. Barrow (1968), Watkinson *et al.* (1987) and Lee *et al.* (1987) all observed very large field sampling errors, with the variability increasing with particle size of S° . These errors are largely associated with the small number of particles applied per unit area, and the difficulty of applying S° uniformly. Although this error can be reduced by taking more soil cores, sub-sampling errors still exist (Barrow, 1970) due to the difficulty of uniformly mixing particles of S° throughout a large bulk of soil. Lee *et al.* (1987) used three particle size ranges (<0.15 mm, 0.15-0.25 mm, and 0.5-1.0 mm) but did not report the results of soil analyses for the coarse size fraction, presumably due to extreme spatial variability.

The rate of oxidation of S° can be estimated using a predictive model. Several models of S° oxidation exist (McCaskill and Blair, 1989; Watkinson, 1989), but they have not been validated experimentally. Using the McCaskill and Blair approach, Chatupote (1990) successfully predicted the oxidation rates of various S° particle sizes under field conditions in the Tokomaru silt loam. McCaskill and Blair (1989) assumed that the S° particles are spherical in shape, and the oxidation rate is proportional to their surface area, i.e. the rate of change in the radius of all particles is constant. The model of Chatupote (1990) is used in this thesis to predict the amount of S° oxidised. A complete presentation of the model is given in Chapter 4.

1.2.4 Methods for Measuring Leaching in the Field

Various methods have been employed to measure leaching losses from soils. These include: soil sampling, lysimeters, suction cups, monitoring of mole-pipe drainage, catchment studies and groundwater sampling (Wild and Cameron, 1980; White, 1988). Often more than one method is used. Each of these will be discussed briefly here.

1.2.4.1 *Soil sampling*

Soil sampling is the most commonly used method for studying leaching losses. When large numbers of soil samples are taken, the changes in profile distribution of sulphate can be monitored with time. Then if other inputs and outputs are known, leaching losses may be estimated using a mass balance approach. May *et al.* (1968), During and Cooper (1974) and Gregg and Goh (1978) are some of those who used this method to study sulphate leaching. The large number of samples required to be representative of an area, to overcome the problem of spatial variability, and the difficulty to accurately quantify all the inputs and outputs make this method undesirable. The method is also laborious, time-consuming and destructive in nature.

1.2.4.2 *Suction cups*

Suction cups when connected to a vacuum provide a simple way of collecting *in situ* soil solution samples. They are economical, easy to use and can extract solution samples at a particular depth repeatedly without disturbing the profile or the rooting system. The solute flux can then be estimated as the product of the water flux and the soil solution concentration. However, care must be taken when the data collected are interpreted, because the sampling procedure and the exchange properties of the ceramics have been observed to give ion screening, or release or adsorption of solute on the cup walls, as described in the reviews of Litaor (1988) and Grossmann and Udluft (1991). The ambiguity as to whether the cups sample the resident or flux concentrations, or some mixture of the two, (Parker and van Genuchten, 1984) also makes interpretation difficult. Steele *et al.* (1984) estimated the leaching of soil sulphate beyond the root zone using this technique, and found that application of nitrogen fertilizer on intensively grazed pasture reduced the amount leached from 25.1 kg S ha⁻¹ to 13.3 kg S ha⁻¹.

1.2.4.3 *Mole-pipe drainage*

Tile drains are commonly installed in agricultural fields as a land improvement practice in areas with shallow groundwater or seasonally perched water tables. Leaching losses are normally calculated from the flow rate measured using a small V-notch weir or H-flume, and the sampled drainage concentration. Studies have shown that intermittently sampled pipe drains may not provide a good estimate of nutrient losses (Kolenbrander, 1969; Cooke and Williams, 1970) because the concentration can vary considerably with flow rate (Wild and Cameron, 1980; White, 1988). Also not all the excess water may leave the soil via the drains, and so leaching losses may be underestimated. However, when these two shortcomings are overcome by collecting samples proportional to flow rate (Hood, 1976; Haigh and White, 1986) and by having a large number of closely-spaced mole drains over an impermeable subsoil, it is an excellent way of monitoring leaching losses. This is because the spatial variability in solution concentration over a relatively large area is integrated in the drainage. The mole-pipe drainage method was used for measuring leaching losses in this study. The availability of the mole-tile drainage system and the flow measuring and sampling equipment at the experimental site allowed leaching to be conveniently monitored. Several workers have used tile drains to characterize subsurface water quality and quantity, including Baker *et al.* (1975), Smith *et al.* (1983), White (1987) and Richard and Steenhuis (1988).

1.2.4.4 *Lysimeters*

Tanner (1967) defined a lysimeter as a device in which a volume of soil, which may be planted to vegetation, is located in a container to isolate it hydrologically from the surrounding soil. This method is commonly used in water movement and nutrient leaching studies because it allows a precise measurement and easy management of inputs and outputs of solute and water. However, the method often suffers from edge flow between the soil and its container (Till and McCabe, 1976; Wild and Cameron, 1980). Lysimeters also usually cannot apply the same matric potential at the base of the core as would apply in undisturbed soil in the field. The problem of edge flow has been overcome by injecting microcrystalline wax or

petroleum jelly between the soil and the lysimeter wall (Cameron *et al.*, 1990). Using large lysimeters treated in this way, McLay *et al.* (1988) monitored the leaching of native sulphate compared to applied sulphate.

1.2.4.5 *Catchment monitoring*

The catchment method can provide useful data on a large scale if losses due to leaching and surface runoff can be distinguished (McColl *et al.*, 1975; Christophersen and Wright, 1981; White *et al.*, 1983). The amount and type of solute leached from the catchment are influenced by the land use and management practices, such as the crop grown and tillage methods.

1.2.5 **Effects of Mole-Drainage on Water and Solute Movement**

Artificial-drainage is a common land-improvement practice for agricultural management. It is used extensively in seasonally, or perennially, wet soils. It has been estimated that approximately 42% of the arable land in New Zealand has a wetness limitation and requires drainage of some kind (Horne, 1985). A common form of artificial drainage used in New Zealand is mole-drainage. A mole drain is a channel formed below the land surface by a circular, torpedo-shaped plug. The mole drain is normally 75 mm in diameter, pulled at a spacing of 2 m, at a depth of 400 to 500 mm below the soil surface.

Moling has been observed to increase the effective conductivity of heavy-textured, undrained soils (Rycroft, 1972; Horne, 1985). That increase enables rapid removal of excess water, and hence decreases the amount of surface runoff and helps in lowering of the water table (Bowler, 1980). As a result, pugging of soil surfaces by animals can be reduced and a greater utilization of pasture can be achieved during winter. Moling also increases the number and continuity of macropores and therefore alters the flow paths of the water, due to the fissures caused by the mole plough blade. Because of that, the principle flow pathways in the subsoil tend to occur directly above the moles (Bowler, 1980; Leeds-Harrison *et al.*, 1982; Goss *et*

al., 1983). Because these cracks tend to close when the soil is wet but reopen when the soil begins to dry, faster and more preferential flow in late autumn compared to late winter may occur (Scotter and Kanchanasut, 1981). Molding also increases the leaching losses. Losses of nutrients and chemicals have been shown to increase with artificial drainage (Baker *et al.*, 1975; Smith *et al.*, 1983).

1.2.6 Fundamental Principles of Modelling

As a significant part of this thesis is devoted to modelling leaching losses, a discussion of the principles of modelling is needed before the various approaches are described.

Models can either be a set of equations or a physical system. Hillel (1977) defined a model as a simplified version or description of reality. A model makes the situation easier to define and manage, by considering only the most important aspects and ignoring all the less important detail. Although this is the strength of a model, i.e. making a complicated situation simple, it is also its weakness in that all the less important contributing factors are ignored.

A model allows interpolation and extrapolation of a limited set of data so that the amount of repetitive, laborious and time-consuming experimentation can be reduced. It can also help to identify the gaps in our knowledge. Although models are useful, they are considered complimentary to experimentation, and are not meant to take its place. A model cannot be developed or verified without a good data set. Often much effort is spent in developing a model, while less effort is put into conducting appropriate experiments to parameterize and test the model.

Solute movement models can be classified as either deterministic or stochastic (Addiscott and Wagenet, 1985). Deterministic models assume that the system operates such that the occurrence of a given set of events leads to a uniquely-definable outcome, which can be described mathematically. Stochastic models assume the outcome of any one realization of a process is uncertain but if enough sample realizations are observed the probability density function inherent in the

process can be defined. However, such a simple classification is becoming less useful in recent years, as there is an increasing overlapping of these two different classifications. For example, studies by Dagan and Bresler (1979), Bresler and Dagan (1979), Amoozegar-Fard *et al.* (1982) and Gelhar and Axness (1983) of groundwater solute transport have all introduced a randomness function into the pore water velocity and apparent diffusion coefficient in the convective-dispersive equation, making their models both deterministic and stochastic.

Models can also be distinguished on the basis of whether they are developed primarily for research purposes or as guides to agricultural management. The first type of model tends to be more mechanistic and is mainly for helping to understand how the processes underlying the system interact. Examples of models in this category are those of van Genuchten and Wierenga (1976) and Dagan and Bresler (1979). The second type of model is more "functional", in that the treatment of soil water and solute flow is simplified enough for them to be used for practical management decision. The input information and computer expertise requirement for their use is also less demanding. The models of Burns (1974) and Addiscott (1977) are two examples of models that are functional in nature. Both mechanistic and functional models are developed in this thesis.

1.2.7 Soil Water and Solute Transport Models

1.2.7.1 Soil water models

Various soil water models are available. Some of them have been specifically developed for flow to drains. One of these is called "SWATRE", originally developed by Feddes *et al.* (1978) and extended by Belmans *et al.* (1983). Another is "DRAINMOD", developed by Skaggs (1982). Although these models were quite successful, they were developed mainly for pipe drainage systems and therefore are not suitable in a mole drain situation. This is because pipes are generally laid at a greater depth (between 1-2 m) than mole drains which are located at approximately 0.5 m depth. In a pipe system, the water table seldom rises to the surface, as it does very frequently in a mole drain system. Also the models calculate the

horizontal flow to the drains in a very simplified way using the ellipse equation. They assume drain flow lowers the water table by a constant amount between the drains and that the shape of the water table is constant. At high flows in a mole drain system, the water table between the drains is partly at the surface and partly below it, and the above models cannot account for this. Finally, the extensive information on the soil hydraulic properties required to run the models is not always available.

In view of the above limitations, Scotter and Horne (1984) developed a model which allows transient mole-drain flow, surface runoff and water table depth to be computed. The model was able to predict the water table levels and the number of unsafe grazing days successfully. However, because of a lack of flow data, comparison of measured and predicted flow was not made. Such a comparison was made by Scotter *et al.* (1990). The model is extended in Chapter 5 to describe non-reactive solute movement so that the solute concentration in the drainage can be predicted.

1.2.7.2 *Solute transport models*

Numerous solute transport models have been developed in the past. They were generally developed to assist in providing more accurate nutrient budgets and in improving the understanding of nutrient cycling. This would allow better prediction of the effects of the soil on plant nutrition, help in the design of management schemes that minimise fertilizer losses and keep concentrations of certain solutes, such as nitrate, within acceptable water quality standards. Solute models are also developed for better understanding of the movement of pesticides, microorganisms and other toxic compounds such as heavy metals and radioactive materials, as this is essential for predicting their impact on the environment. A knowledge of solute transport in soil is also important in reclaiming salt-affected soils and in devising management practices for irrigated cropland to prevent salt accumulation in soils.

Most solute transport models are based on the convective-dispersive equation (CDE) which assumes the transport to be due to convective transport of a solute and

hydrodynamic dispersion in response to a concentration gradient. For steady, one-dimensional liquid flow in a uniform soil, the CDE for a non-reactive solute can be written as

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial z^2} - \frac{q}{\theta} \frac{\partial C}{\partial z} \quad (1.2)$$

where C is the solution concentration [$M L^{-3}$], t is time [T], z is depth [L], D_h [$L^2 T^{-1}$] is the dispersion coefficient which includes the effects of diffusion and mechanical dispersion, q is the water flux density [$L T^{-1}$] and θ is the volumetric water content [$L^3 L^{-3}$]. The ratio $q/\theta = v$ is the average pore water velocity defined earlier. This equation works well in laboratory columns of repacked soil where the medium is homogenous and flow is uniform (Gardner, 1965; Biggar and Nielsen, 1967). However, in undisturbed cores and in the field where the soil is neither isotropic nor uniform, significant deviation between theory and experimental observations usually results. Severely skewed breakthrough curves often result from soil core miscible displacement experiments (Passioura, 1971; van Genuchten and Wierenga, 1976). Solute appears earlier than expected in the effluent, and there is also a long "tail" before full breakthrough when the input and output concentrations are equal. In the field macropore flow often leads to an asymmetric leaching pattern (Quisenberry and Phillips, 1976; Wild and Babiker, 1976; Scotter and Kanchanasut, 1981). These observations have been explained by the existence of a wide range of pore sizes. As a result, a wide range of pore water velocities occurs, rather than the average value assumed in Equation (1.2).

Several models have been proposed to take account of the large variations in flow velocity referred to above. One of these is the bi-modal or mobile-immobile model of Coats and Smith (1964) and van Genuchten and Wierenga (1976). In the mobile-immobile model, flow is assumed to occur in a mobile phase (in larger pores) where solutes are transported by convection and hydrodynamic dispersion. The effectively immobile phase consists of fluid in smaller pores. Solute are transferred between the mobile and immobile phases by molecular diffusion at a rate proportional to the concentration gradient between the two. Given the assumption

that only a certain fraction of the soil water is mobile, the predicted velocity in the mobile phase can be several times greater than the average velocity. This can explain the early appearance of surface-applied solutes. 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. Thus this type of model can simulate the observed behaviour described in the preceding paragraph.

A disadvantage of the mobile-immobile model is that it requires the soil water to be arbitrarily divided into mobile-immobile phases. There is no agreement on the matric potential which should be used as the dividing potential, e.g. -200 kPa by Addiscott (1977) and -8 kPa by Nkedi-Kizza *et al.* (1982). However the concept seems to be applicable in mole-drained soil because of the preferential nature of soil water flow there. In a mole-drained soil, water tends to move slowly through the subsoil to the moles at low flows, yet to largely by-pass this subsoil at higher flows. At even higher flows, flow will be mostly over the soil surface, then directly down the cracks initially induced by moling above the moles. The first model developed in this thesis simulates the leaching losses of chloride by coupling the mobile-immobile water concept with the theory of water flow to a mole drain.

Another approach which has generated considerable interest is the transfer function model (TFM) of Jury (1982) and Jury *et al.* (1982, 1986). The transfer function model usually involves measuring the frequency distribution of solute travel times from the surface to a reference depth, through a probability density function (pdf).

For a non-reactive solute, often the rate of solute mass output through a defined exit Q_{ex} can be related to the rate of mass input through a defined entrance surface Q_{ent} by the equation

$$Q_{ex}(t) = \int_0^t g(t-t'|t) Q_{ent}(t') dt' \quad (1.3)$$

where Q_{ex} and Q_{ent} are $[M T^{-1}]$ the respective mass rates of solute output from and input into a soil system. Both Q_{ex} and Q_{ent} represent all modes of entrance into or exit from the soil volume. $g(t-t'|t')$ $[T^{-1}]$ is the probability density function or transfer function of solute lifetimes. If the lifetime pdf is independent of the input time t' , $g(t-t'|t')$ then becomes $g(t-t')$. Equation (1.3) can then be solved for $g(t-t')$ if the rates of solute mass input and output for the soil volume as a function of time are known. 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 drainage rather than time is more appropriate (Jury, 1982; White *et al.*, 1984). The theory of the TFM is discussed in greater detail in Chapter 6.

The TFM has been applied satisfactorily to both laboratory and field experiments (Jury *et al.*, 1982; White, 1987; White *et al.*, 1986; Utermann *et al.*, 1990) to predict the movement of Br, Cl, NO₃, ³HOH and pesticides. White (1985a, 1989) showed that the pdf of an externally applied solute was able to predict the concentration of indigenous nitrate and of applied bacteria in the effluent from undisturbed cores. It is the aim here to use the transfer function approach to predict leaching losses from a mole-drained soil. Attempts to include source/sink terms in the transfer function model will be described.

1.2.8 Summary

Relatively little research has been carried out on the leaching of sulphate under field conditions. Studies so far have generally been done under laboratory conditions or using small lysimeters. As losses of this nutrient are becoming more expensive to replace, it is important that leaching studies under field conditions are carried out so that the mechanisms involved can be better understood. No mechanistic models have been published for sulphate leaching. Two different approaches to modelling sulphate leaching are developed in this thesis.

CHAPTER 2

MATERIALS AND METHODS

2.1 INTRODUCTION

A two-year field experiment was carried out in 1988 and 1989 to measure the leaching of sulphate-S and other major plant nutrients from a mole-drained pasture soil. Sulphate leaching data were also collected in 1990.

2.2 FIELD PREPARATION AND METHODS

2.2.1 Soil Properties, Site Description and Instrumentation

The field experiment was carried out at the Massey University No. 4 Dairy Farm. The site had not had any recent fertilizer application, had been under perennial ryegrass (*Lolium perenne*) and white clover (*Trifolium repens*) pasture for several years, and been periodically grazed by sheep. The soil was a Tokomaru silt loam, classified as a Typic Fragiaqualf (Anon, 1974), and a Yellow Grey Earth (New Zealand Soil Bureau, 1968). It has an organic carbon content of approximately 5%, a cation exchange capacity of 220 mmol kg⁻¹ (Williams, 1988) and a low sulphate retention capacity (Metson, 1969; Bolan *et al.*, 1986).

The morphological properties of the soil described by Pollock (1975) show that the soil consists of 0.3 m of relatively well structured silt loam A horizon, a compact clay loam B horizon to 0.7 m, and a very compact silt loam fragipan below that. The compact nature of the B horizon was also observed experimentally by Scotter *et al.* (1979a). The existence of the fragipan impedes the movement of percolating water, and as a result a perched watertable normally occurs during winter and spring, causing waterlogging. To alleviate the waterlogging problems, mole-drains, which are a relatively inexpensive form of drainage particularly suited to fine-textured soils with an impermeable subsoil, were installed in these paddocks and the surrounding areas in 1975. The paddocks were remoled in spring of 1986. The moles which were 75 mm in diameter (Horne, 1985), were pulled at a depth of

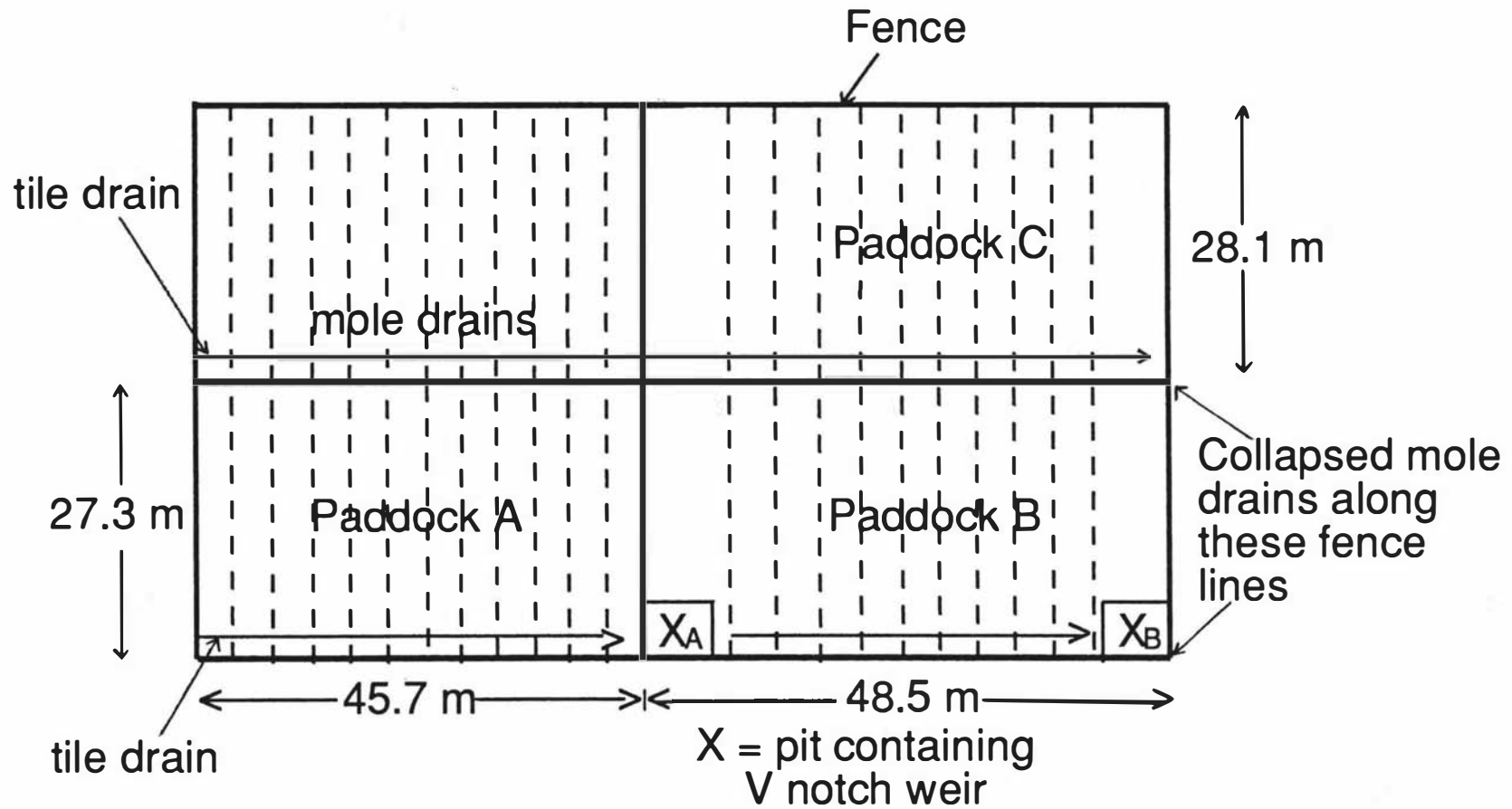
approximately 0.45 m, at a spacing of 2 m on a gradient of 1%. Flow from the mole drains was intercepted by 100 mm diameter tile drains laid perpendicular to the moles, at 40 m spacing, at a depth of approximately 0.75 m, with a minimum grade of 0.4%. Backfill above the tile-drains was the topsoil removed during trenching, which ensured that the low permeability of the subsoil did not affect flow from the moles to the tile drains.

The experimental site consisted of three small adjacent paddocks, each with a drained area of approximately 1250 m², at the site described by Turner *et al.* (1976). The dimensions and lay-out of the paddocks are shown in Fig. 2.1. The moles were collapsed along the paddock boundaries, allowing flow from each paddock to be isolated and collected individually. The drainage from the two treatment paddocks (designated A and B) was piped to two 30° V-notch weirs installed in the pits (pits A and B respectively), allowing flow rates to be continuously monitored. The weir in pit A monitored flow from paddock A to which single superphosphate (SSP) was applied, whereas that in pit B monitored flow from paddock B which was fertilized with elemental sulphur (S⁰). Drainage from an adjacent control paddock (paddock C) drained directly into a nearby dam. No pit, weir and flow recording equipment were available to monitor flow from the C paddock. The flow rate through the weir, which is a function of the height of the water passing through the V-notch, was sensed by a pressure transducer, placed at the bottom of the weir and connected to a flow meter. The flow meter (ISCO Inc, Model 2310) was calibrated to convert water level into the corresponding flow rate. The flow meter displayed flow rates and total flow at the time of observation. To record the flow, a plotter (ISCO Inc, Model 2310) was used.

Manually measured flow rates from the V-notch weirs over a range of flow rate were compared with the recorded flow rates before commencement of the experiment. The recorded flow rates of the weirs were automatically calculated using the equation

$$Q_w = K_w H_w^{2.5} \quad (2.1)$$

Fig. 2.1 Dimensions and lay-out of the drained paddocks



where q_w [$L^3 T^{-1}$] is flow rate, H_w [L] is head over the crest of the weir, and K_w is a constant determined by the angle of the V-notch and the units of measurement. For the present 30° V-notch weir set-up, a value of 1.17×10^{-5} was obtained for K_w from a least-squares fit, as shown in Fig. 2.2 and using the units given there. The above K_w value agrees with that given in the Stevens Water Resources Data Book (Anon, 1978). Because of the non-linear $q_w(H_w)$ relationship, it is very important that the flowmeter be properly "zeroed" with the zero reference level in the weir. Failure to do so can result in a flow rate error whose magnitude becomes very large at high water levels.

Drainage samples were collected for analysis using an automatic water sampler (ISCO Inc, Model 2900). As intermittent sampling during drainflow has been found to be unsatisfactory in monitoring drainage concentration in the past (Kolenbrander, 1969; Cooke and Williams, 1970), samples were collected at a frequency which varied with the flow rate (Martin and White, 1982). A 100 ml sample of drainage was collected into one of the twenty-four 500 ml polyethylene bottles for every 600 litres (equivalent to 0.48 mm) of drainage. Sampling at this frequency allowed enough flow and concentration data to be collected during an average drain flow event, and allowed both the total quantity of solute leached and the solute mass flux to be calculated. Figs. 2.3, 2.4 and 2.5 show the V-notch weir, the flow meter and the automatic water sampler. Drainage events were monitored over the drainage season of winter and spring of 1988 and 1989. Rainfall was measured 50 m from the paddocks using both a continuous recording raingauge and a 250 mm diameter Marquis manual raingauge. The hourly rainfall intensity data from the continuous recording raingauge were used as an input into the leaching model in Chapter 5, while the daily rainfall data from the Marquis raingauge were used in the transfer function and the "well mixed" models. Sunshine hour and air temperature data were obtained from the Department of Scientific and Industrial Research (DSIR), approximately 1 km away, and were used to obtain the evaporation estimates used in all models.

Fig. 2.2 Calibration curve for flow meters in paddocks A and B

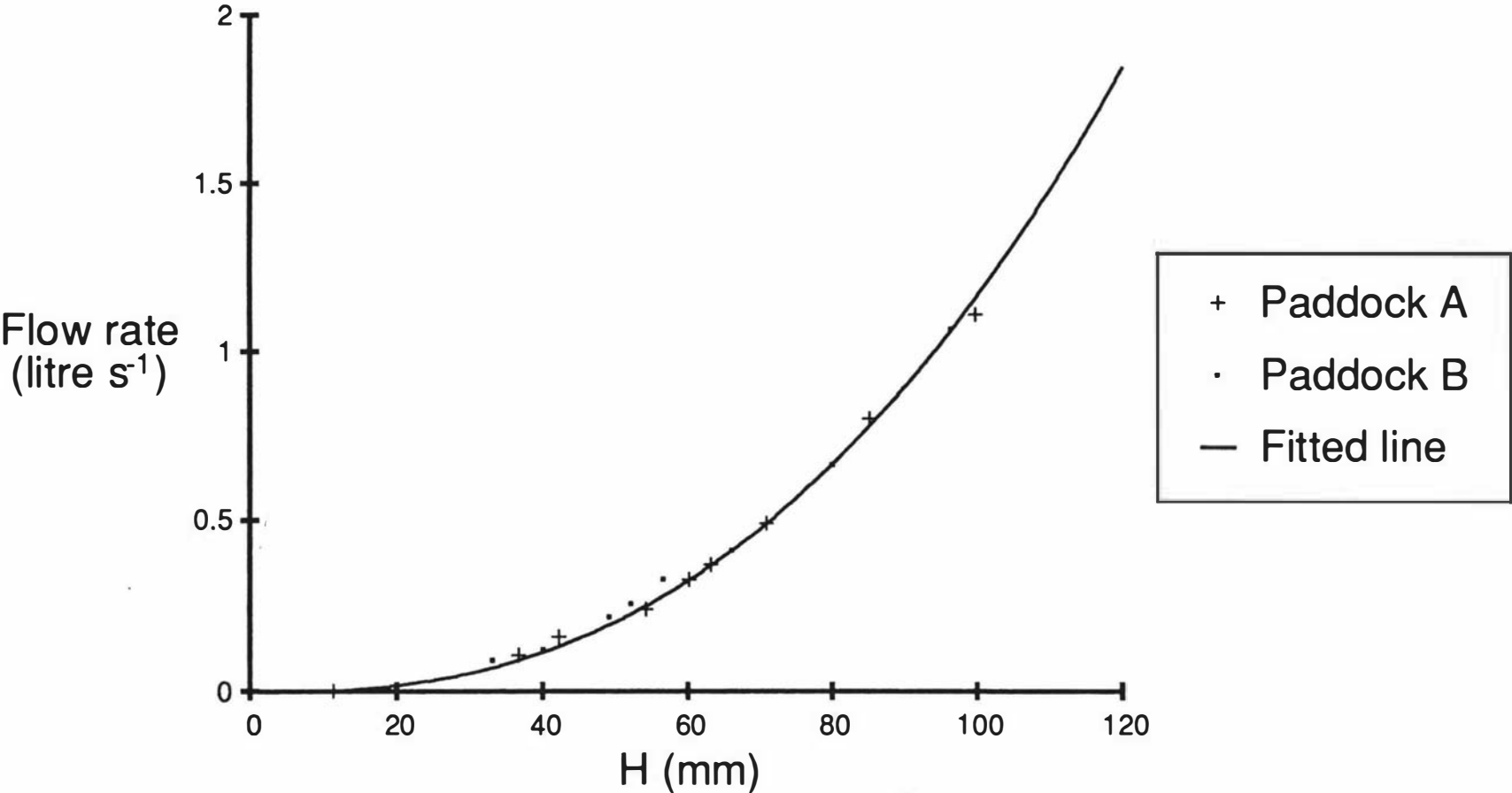




Fig. 2.3 V-notch weir for monitoring the flow rates

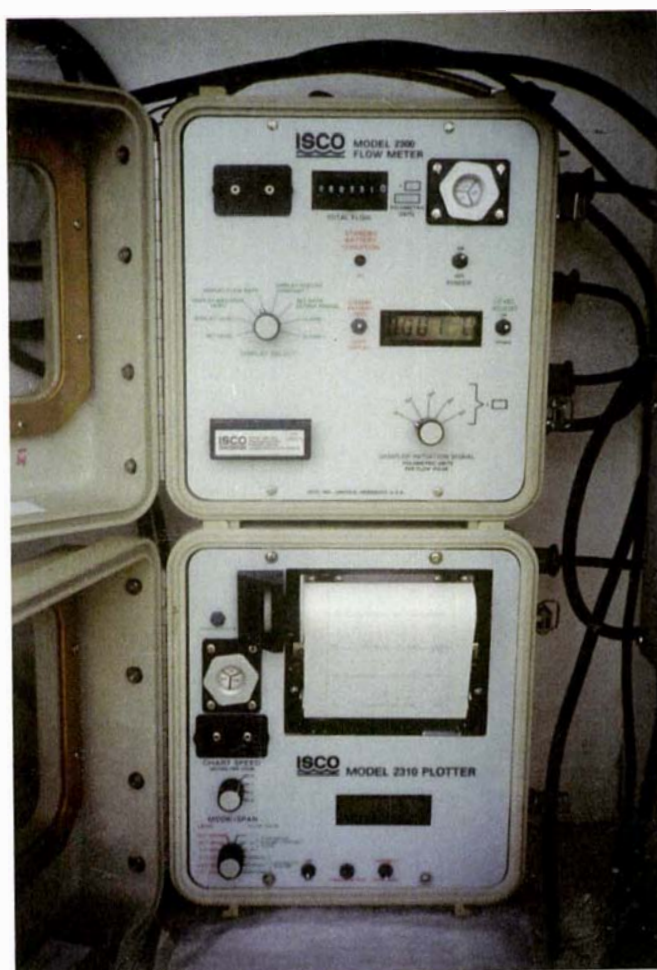


Fig. 2.4 The ISCO flow meter and plotter used



. 2.5 The automatic water sampler used for collecting drainage samples for analysis

2.2.2 Fertilizer Application

One of the claimed advantages of elemental S (S^0) over single superphosphate (SSP) as a source of sulphur is that it not only maintains yields but also reduces leaching losses. To compare the effectiveness of these two forms of sulphur in reducing leaching losses, sulphur fertilizer as readily soluble sulphate (SSP) and as insoluble S^0 were applied to paddocks A and B, respectively. The amount of sulphur required was based on the sulphate status before fertilizer application, calculated according to the procedure developed by the Ministry of Agriculture and Fisheries (MAF) (Sinclair and Saunders, 1984). The detailed calculation is given in Appendix A. Based on this, a rate equivalent to 50 kg S ha^{-1} was hand-applied on the 16 June 1988. To obtain more even spreading, each paddock was sub-divided into 15 small plots and the appropriate amount of each fertilizer was applied individually on each of these sub-plots. Triple superphosphate (TSP) was applied to the S^0 paddock, to give the same quantity of P as that provided by SSP. Potassium chloride (KCl) at a rate of $200 \text{ kg KCl ha}^{-1}$ was also applied to both paddocks, to supply potassium, and to provide chloride, which served as a tracer for the movement of water. Both sulphur and KCl fertilizers were reapplied on 31 May, 1989, at the same rate of KCl but with only 30 kg S ha^{-1} . No fertilizer was applied in 1990. Urea at a rate of 50 kg N ha^{-1} was applied to all three paddocks on 7 September, 1989 as a part of another experiment in which leaching of N was monitored.

2.2.3 Soil Sampling

Soil sampling was carried out for sulphate-S and chloride analysis from paddocks A, B and C on the dates shown in Table 2.1. Twelve samples per paddock were taken to mole-drain depth (450 mm). Each sample consisted of two 50 mm diameter cores bulked together. Soil samples were divided into 50 mm segments for the top 150 mm and into 150 mm segments below that depth, except for the sampling on 13/6/88 which was divided into 75 mm segments for the top 150 mm. Field moist soil was used for all chemical analyses. The chloride and sulphate contents of the soil were measured using the methods described in Section 2.3. The soil water content was measured gravimetrically on a sub-sample of each soil sample.

2.2.4 Suction Cup Solution Sampling

Porous ceramic suction cup samplers (22 mm in outside diameter, 80 mm long) were installed into the paddocks in August 1988. The samplers were presoaked with deionised water before insertion at approximately 200-250 mm and approximately 500 mm (below mole-drain) depths. A total of 10 samplers were installed at the shallower depth and 5 at the deeper depth in each paddock. The samplers were put under vacuum with a hand-operated pump the day after all major rainfall events, and samples were collected the following day using a neoprene tubing attached to a syringe. The extracted solution was analyzed for sulphate-S as described in Section 2.3.

2.2.5 Grazing

The paddocks were not grazed for most of the 1988 drainage season. Regular grazing at intervals of 6 to 8 weeks was carried out after October 1988 and continued through 1989. The grazing dates and duration, as well as the stocking rates are given in Table 2.1.

2.2.6 Bulk Density Measurements

Bulk density for the top 150 mm, at 50 mm depth intervals, was determined using the technique described by Loveday (1974). Three cores, 50 mm long and 50 mm in diameter, were taken from paddock C for each sampling depth in the winter of 1988. The same bulk density values were assumed for paddocks A and B. Below 150 mm the values for the site reported by Scotter *et al.* (1979a) were used.

2.2.7 Herbage Sampling

Herbage was sampled on the dates indicated in Table 2.1. Four 0.25 m² quadrats were cut randomly from each paddock at each sampling. The herbage was dried at 60° until constant weight was obtained. It was then weighed for dry matter production and then finely ground, and the chloride and sulphur levels measured

using the methods described in Section 2.3.

2.2.8 Rainfall Chloride and Sulphate Measurements

Chloride and sulphate in rainfall were measured by analyzing rain collected through a glass funnel in a large conical flask. Samples represented rain water collected from individual rain events or from several events occurring over a short period of time. The rain water was filtered through Whatman No. 41 filter paper and stored at 4°C until analyzed.

2.2.9 Adsorption Isotherms

A laboratory batch method was used to obtain sulphate adsorption data for the 0-50, 50-300 and 300-450 mm depths of the Tokomaru silt loam. Five grams of < 2 mm sieved, air-dried soil from the above three depths were shaken in an end-over-end shaker for 40 hours with a 40 ml solution containing varying amounts of SO₄-S (0, 1, 2, 4, 6, 8, 10 g S m⁻³) in 5 mM KCl (a concentration near to the ionic strength of Tokomaru silt loam soil solution at field capacity, Bramley, 1989). The solution was then centrifuged and filtered through Whatman No. 41 filter paper. The amount adsorbed was estimated from the difference between the amount of SO₄-S added and that remaining in solution (Bolan *et al.*, 1986). Sulphate extractable in 0.01 M Ca(H₂PO₄)₂ extractable sulphate (solution plus adsorbed S) was also determined for each depth, using the method given in Section 2.3.

A field sulphate adsorption isotherm was also calculated from the soil sulphate-S and solution sulphate-S data obtained from the suction cups.

Table 2.1 **Dates of soil sampling, herbage cuts and grazing**

Soil Sampling	Herbage Cut	Start of Grazing	Number of Grazing Days	Stocking Rate (sheep per paddock)
13/06/88	15/06/88	23/04/88	3	40
04/08/88	--	--	--	--
14/10/88	14/10/88	14/10/88	6	18
--	16/12/88	16/12/88	3	56
--	02/02/89	03/02/89	5	48
--	--	29/03/89	2	56
12/05/89	14/05/89	08/05/89	3	40
05/08/89	02/08/89	11/08/89	5	24
--	06/09/89	--	--	--
--	13/10/89	20/10/89	10	32
08/11/89	--	--	--	--
--	--	20/12/89	8	50
--	02/03/89	--	--	--
05/04/90	--	--	--	--
--	20/04/89	--	--	--
--	--	02/05/90	7	40
--	29/06/90	--	--	--
--	--	10/07/90	5	21
--	--	25/08/90	2	52
--	28/08/90	--	--	--
04/10/90	04/10/90	--	--	--
--	--	10/10/90	8	46

2.3 CHEMICAL ANALYSES

All chemical analyses were done in duplicate, or in triplicate in the case of marked variation in the duplicates, and the two closest values taken.

2.3.1 Drainage

2.3.1.1 *pH*

The pH of the drainage water was measured using a glass electrode (PHM 82 Standard pH Meter).

2.3.1.2 *Chloride*

The chloride concentration was analyzed colorimetrically with a Flow Injection Analyzer (Tecator) using an automated version of a mercuric thiocyanate-ferric nitrate procedure (Florence and Farrar, 1971). The reaction of chloride with mercuric thiocyanate releases thiocyanate ions which react with ferric iron to give a red-coloured ferric-thiocyanate complex, the intensity of which was measured at a wavelength of 463 nm.

2.3.1.3 *Sulphate-S*

The sulphate concentration of the drainage water was determined by reducing it to hydrogen sulphide at 120°C with a strong reducing mixture of hydriodic acid, hypophosphoric acid and formic acid, using a modification of the Johnson and Nishita (1952) method (CSIRO Division of Forest Research, Method No. PS17), on an autoanalyzer (Technicon, Series II).

2.3.1.4 *Nitrate-N*

The nitrate ($\text{NO}_3\text{-N}$) concentration in the drainage samples was analyzed by reducing the nitrate to nitrite using hydrazine sulphate followed by complex formation with sulphanilamide (Griess-Ilvsvay reaction) and colour development. This was then

measured on a Technicon autoanalyzer (Series II) following the method of Kamphake *et al.* (1978).

2.3.1.5 *Cations*

The drainage water was also analyzed for cations. The concentration of calcium (Ca) and magnesium (Mg) in the drainage was determined using absorption spectroscopy (422.7 nm for Ca and 285.2 nm for Mg). Potassium (K) and sodium (Na) were determined using emission spectroscopy (766.5 nm and 589 nm respectively) on an atomic absorption spectrophotometer. Strontium chloride ($7500 \text{ g m}^{-3} \text{ Sr}$) and caesium chloride ($25000 \text{ g m}^{-3} \text{ Cs}$) were added to the solutions as a releasing agent and an ionisation suppressant, respectively.

2.3.2 **Rainfall**

2.3.2.1 *Chloride*

The filtered rain water was concentrated by evaporating the sample slowly on a hot plate at 60°C . The chloride content was measured using the mercury thiocyanate method described above.

2.3.2.2 *Sulphate-S*

The sulphate content in the concentrated rainfall water was measured by the modified Johnson and Nishita method.

2.3.3 **Soil**

2.3.3.1 *Chloride*

Soil chloride was determined on a moist soil sample equivalent to 10 g of air-dried soil. It was extracted with a 0.01 M KNO_3 solution at a 1:2 soil:solution ratio. The samples were shaken for 30 min. on an end-over-end shaker, centrifuged and filtered, and chloride determined in the filtrate using the mercury thiocyanate method described above.

2.3.3.2 *Calcium phosphate extractable sulphate-S*

Soil sulphate was measured using the method developed by the Ministry of Agriculture and Fisheries (MAF) of New Zealand (Sinclair and Saunders, 1984). Moist soil, equivalent to 5 g air-dried soil, was extracted with 0.01 M $\text{Ca}(\text{H}_2\text{PO}_4)_2$ solution at a 1:5 soil:solution ratio for 30 min. on an end-over-end shaker. The suspensions were centrifuged, filtered, and an aliquot analyzed using the modified Johnson and Nishita method. The results were expressed in g S m^{-3} soil.

2.3.3.3 *Total sulphur*

The total sulphur in the soil was measured on soil taken prior to fertilizer application by ashing it at 550°C for 3 h with a sodium bicarbonate/silver oxide mixture (Steinberg *et al.*, 1962). The total sulphur in the digest was then measured using the modified Johnson and Nishita method.

2.3.3.4 *Phosphate*

To formulate the fertilizer requirement, the plant available phosphorus content of soil (Olsen *et al.*, 1954) was measured using the soil collected early in 1988. This was done by extracting 1 g of air-dried soil with 20 ml of 0.5 M NaHCO_3 solution on an end-over-end shaker for 30 min. The solution was then centrifuged, filtered, and the phosphorus determined by ^{the} Murphy and Riley (1962) method.

2.3.4 **Herbage**

2.3.4.1 *Chloride*

Herbage chloride was determined using a similar procedure to that for water-soluble carbon, as described by White and Ayoub (1983). A 0.2 g ground sample was extracted by simmering (90°C) with 60 ml of deionised water on a hot plate for 2 hours with constant stirring. The mixture was then filtered and made up to volume, and analyzed for chloride on the Flow Injection Analyzer using the mercuric thiocyanate method.

2.3.4.2 *Total sulphur*

The total sulphur in herbage was extracted from a 0.02 g finely ground (<1.5 mm) oven dry sample by the alkali sodium hypobromide method (Tabatabai and Chae, 1982). The S concentrations were analyzed using the modified Johnson and Nishita method described above.

2.3.5 **Fertilizers**

2.3.5.1 *Total sulphur*

The sulphur content of single superphosphate (SSP) was measured prior to its application, by ashing it with a sodium bicarbonate/silver oxide mixture (Steinberg *et al.*, 1962) as described above.

2.3.5.2 *Phosphorus*

The phosphorus content of SSP and triple superphosphate (TSP) was measured following a tri-acid digestion procedure (O'Connor and Syers, 1975) by the vanadomolybdate method.

2.3.5.3 *Elemental sulphur*

Elemental S in the moist soil was extracted using a 1:5 soil:acetone ratio for 16 h on an end-over-end shaker, according to the method of Nguyen (1988) and Chatupote (1990). The S⁰ concentration in the extract was measured using the modified Johnson and Nishita procedure. The weight of soil used was equivalent to 5 g air-dried soil for samples collected on 23 June 1988. However due to variability in the results, soil equivalent to 20 g dry soil was used in the subsequent two samplings.

2.4 EVAPORATION CALCULATION

The daily potential or reference crop evaporation rate, E_t [$L T^{-1}$] was estimated from the mean air temperature, and sunshine hours, using the Priestley-Taylor (1972) equation

$$E_t = \alpha \frac{s}{s+\gamma} R_n / L. \quad (2.2)$$

Here α is a dimensionless empirical constant taken as 1.26, R_n is the net radiation [$M T^{-3}$], s is the rate of change of the saturation vapour density with temperature ($kg m^{-3} K^{-1}$), γ the psychrometric constant ($kg m^{-3} K^{-1}$) and L is the latent heat of vaporization [$M L^{-1} T^{-2}$]. The value of $s/(s+\gamma)$ depends on temperature, and was found from the average daily air temperature. R_n was calculated from sunshine hours as described by Scotter *et al.* (1979b).

CHAPTER 3

METEOROLOGICAL DATA, DRAINAGE AND LEACHING RESULTS

3.1 INTRODUCTION

The field experimental results are given in Chapters 3 and 4. In Chapter 3, the meteorological data and drainage and leaching results are presented, while results for the soil and pasture dry matter, and chloride and sulphur uptake and mass balances are given in Chapter 4.

3.2 METEOROLOGICAL DATA

The rainfall and evaporation data are presented because they determined the quantity of drainage available for solute leaching. The monthly rainfall in Palmerston North for 1988 and 1989, together with the long term average (obtained from the New Zealand Meteorological Service), are shown in Fig. 3.1. There was a total of 509 mm rainfall during the drainage period of 1988. The drainage period is calculated from the day fertilizers were applied until drainage finally stopped, normally in October. For the same period in 1989 the rainfall was 343 mm, and below average for the months of July, August and September. The 163 mm of rainfall recorded in July 1988, with over 90 mm during one weekend, was one of the highest in Palmerston North. The intense storm event in July 1988, and the long dry spell in the middle of winter of 1989 with very little rainfall, had significant consequences for the leaching.

The monthly potential evaporation for 1988 and 1989 is shown in Fig. 3.2. Totals of 151 and 237 mm of evaporation were calculated for the drainage periods of 1988 and 1989 respectively, with higher evaporation for the longer but drier drainage season of 1989. The months of May, June and July generally have low evaporation, with averages of 30 mm or less, giving an average daily evaporation of less than 1 mm. In summer, evaporation can be as high as 4-6 mm d⁻¹. Such high evaporation rates, coupled with low rainfall, can cause a severe soil water deficit

Fig.3.1 Rainfall distribution for Palmerston North

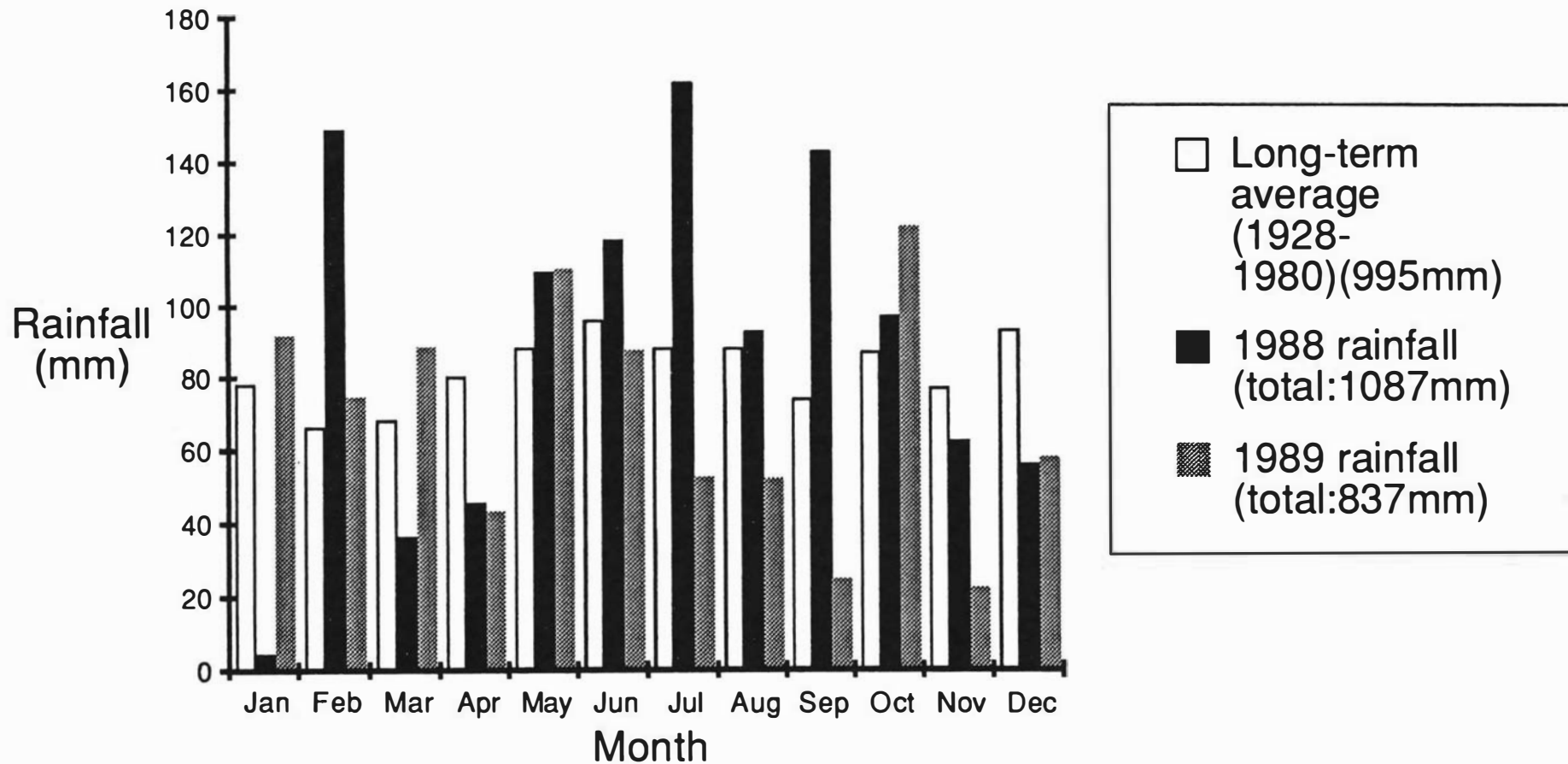
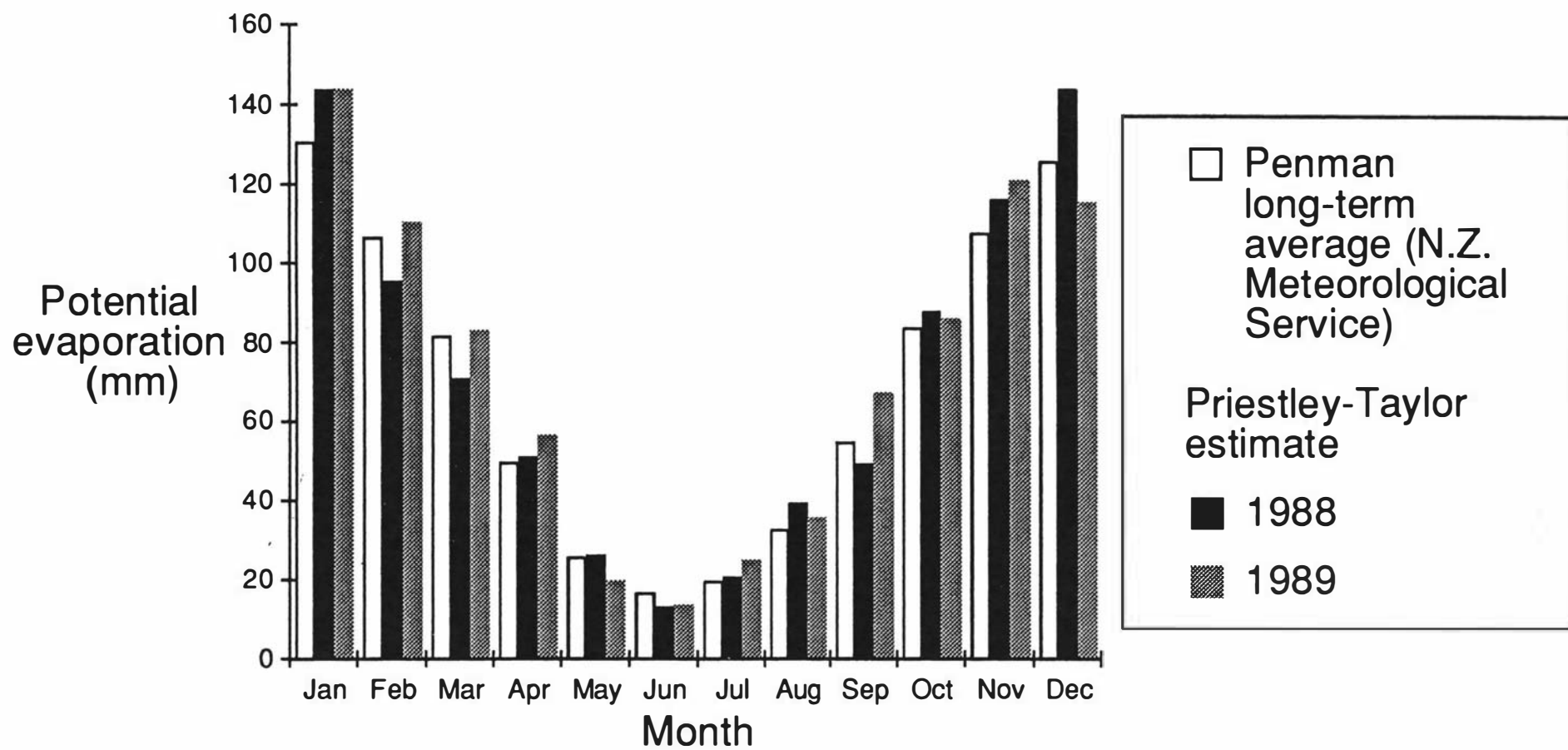


Fig. 3.2 Potential evaporation distribution for Palmerston North



(SWD), and thus limit pasture and crop growth. A SWD of more than 220 mm has been observed in late summer by Scotter *et al.* (1979b). On the other hand, the low evaporation and high rainfall during winter and early spring season lead to a surplus of water which, for a soil with poor internal drainage, may cause waterlogging and surface runoff. However, in a freely drained soil, or one with subsurface artificial drainage, surplus water is removed, along with the dissolved solutes.

3.3 DRAINAGE

3.3.1 Individual Drain Flow Events

The individual drain flows were recorded as hydrographs. The hydrographs for some of the rainfall events in 1988 are shown in Figs. 3.3, 3.4 and 3.5. Almost identical hydrographs in terms of flow rate and response time were observed for paddocks A and B for most events, indicating the similarity in their hydrological characteristics, except toward the end of 1989 when there was less drain flow from paddock B. This was possibly due to a drift in the electronics of the flow meter which necessitated frequent resetting of the zero level, and may have led to disagreement between the final cumulative drainage for the two paddocks for that year.

The rainfall intensities for the above three rainfall events have been superimposed on the hydrographs to show the effects of rainfall intensity and duration on drain flow rates. Of note are the high maximum drain flow rates, and the rapid response of the drain flow to changes in rainfall intensity, particularly when there had been rain a few hours earlier. The rainfall event on June 29, 1988 (Fig. 3.3) was rather long and moderate in intensity, with many small intermittent sub-events, giving a total of 34.1 mm rain, and 18.4 and 18.1 mm drainage for paddocks A and B, respectively. Reid and Parkinson (1984) observed that the first fall of rain of a multiple storm often acts to fill the storage capacity in the soil, and so even though the subsequent rainfall intensity is smaller, the corresponding peak flow can be significantly larger.

Fig. 3.3 Rainfall intensity and drain flow for paddocks A and B for the event of 29/6/88

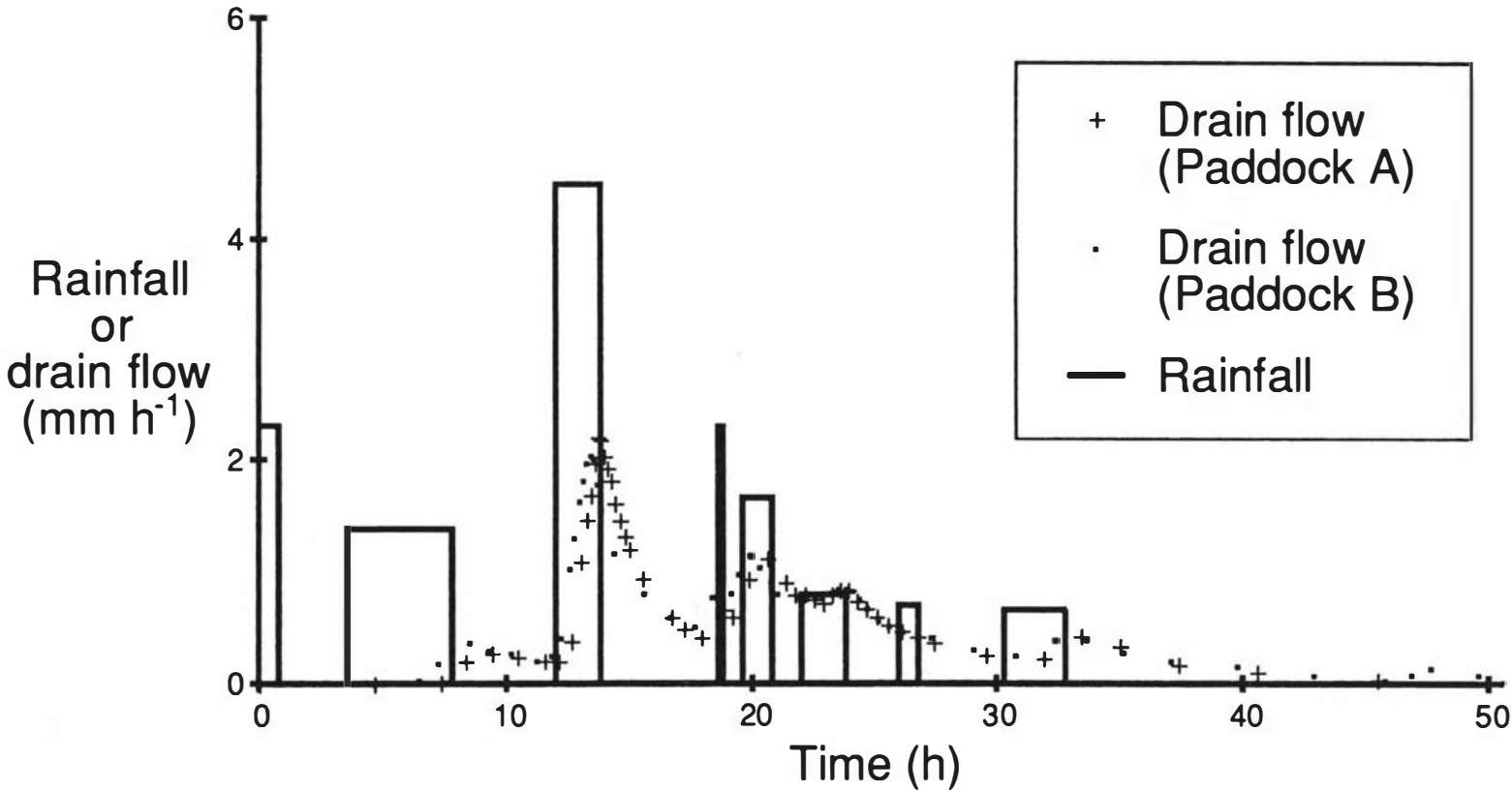


Fig. 3.4 Rainfall intensity and drain flow for paddock B for the event of 25/7/88

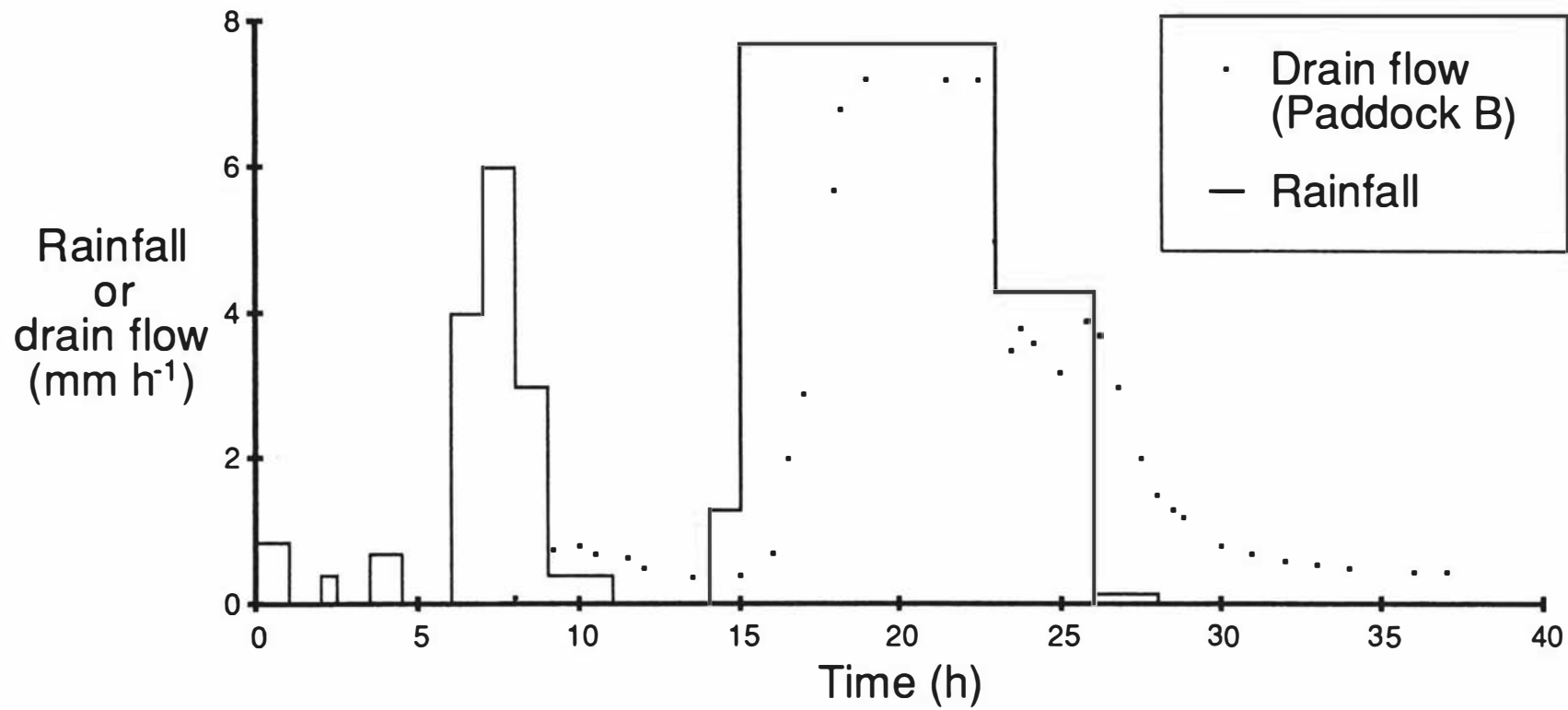
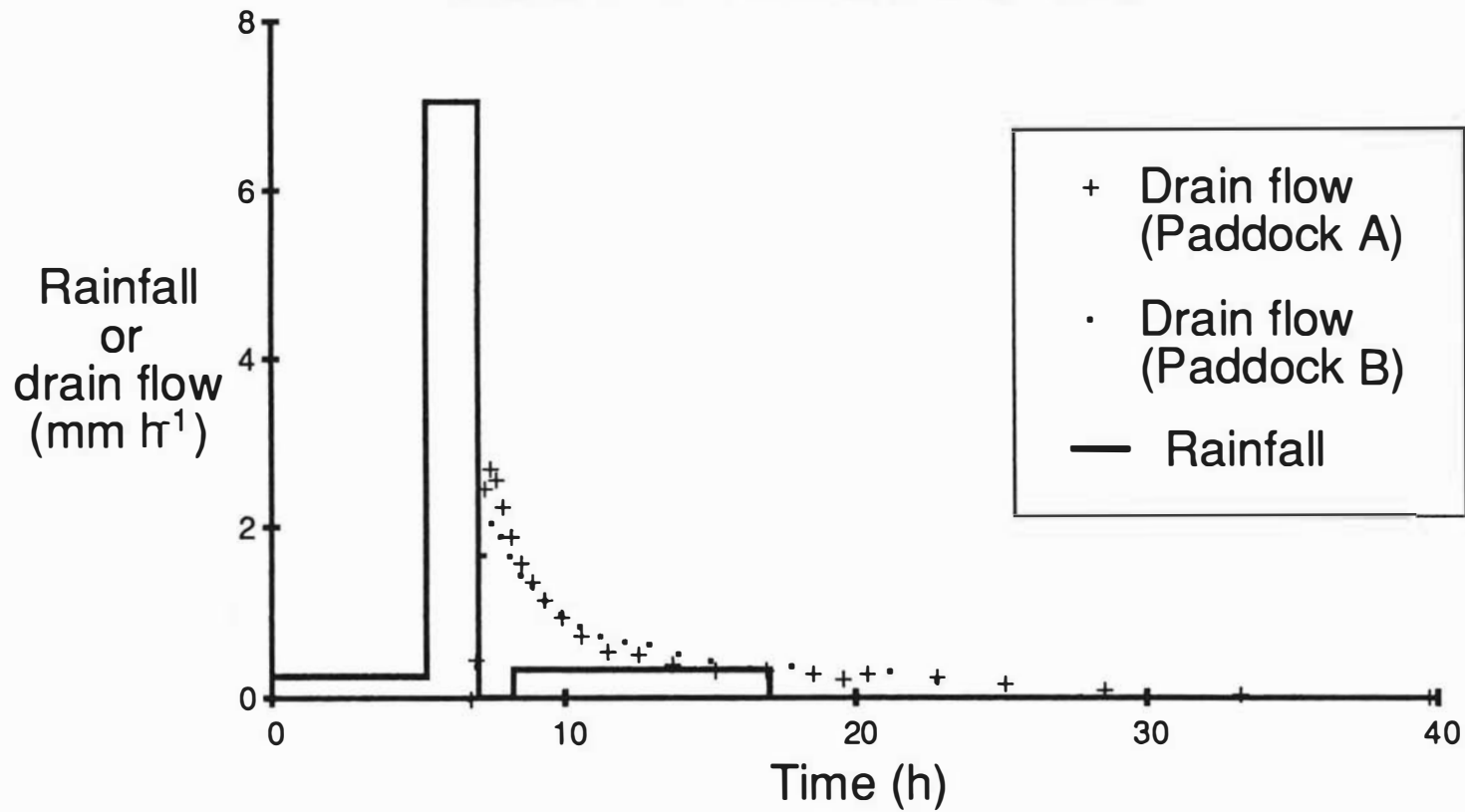


Fig. 3.5 Rainfall intensity and drain flow for paddocks A and B for the event of 6/10/88



The rainfall on July 24, 1988 (Fig. 3.4) was unusually large and heavy, with an intensity of 7.7 mm h^{-1} lasting for almost 6 hours. The long-lasting high rainfall intensity in this event was the only event for the two years which resulted in a quasi-steady state being reached in the drain flow, with a flow rate of 7.2 mm h^{-1} lasting for 3 hours. The total drainage from paddocks A and B for this event was 117.4 and 71.3 mm respectively. The 117.4 mm drainage was more than the total rainfall of 91.3 mm, apparently because of surface run-on from an adjacent area. Hence flow data for paddock A is not shown. The results of this particular drain flow event show that the mole and tile drainage system has an unusually high drainage coefficient, to be able to produce this high flow rate. The drainage coefficient is usually defined as the depth of water, in mm, which can be removed in a day (Bowler, 1980). Calculation using Manning's equation indicates that the system had a drainage coefficient of at least 270 mm d^{-1} , compared to the more typical value of 10 mm d^{-1} for mole-drained pasture (Bowler, 1980). The vast difference between the two drainage coefficients has important consequences for the efficiency and cost of installing the drainage system. It results from the small area drained by the tile drain in each paddock.

The October 6 1988 rain event (Fig. 3.5) was short but rather intense, with 17.8 mm of rainfall, giving 11.7 and 10.3 mm of drainage from paddocks A and B. In all three hydrographs shown, a quick response to changes in rainfall intensity at peak flow rates was observed, with the flow rate declining almost instantly when rain stopped. This quick response is one of the characteristic features of a successful mole drainage system (Jarvis and Leeds-Harrison, 1987b). It is due both to the closeness of moles to the surface, and to the cracks and fissures caused by the mole-plough blade. Without these cracks and fissures, water flow is slower and recession periods are longer. Bowler (1980) gave a list of factors which can influence drain flow rates. They are: (a) distance between drains, (b) pipe spacing, (c) backfill, (d) depth of drains, (e) nature and permeability of the soil, (f) antecedent moisture content and rainfall intensity, (g) slope of land, and (h) vegetation. For a particular type of soil and mole system, the initial response time depends mainly upon the antecedent moisture content and the intensity of rainfall, as observed by Baker *et al.* (1975), Reid and Parkinson (1984), and Horne and

McAuliffe (1988).

Flow tended to continue for 20 to 40 hours after rainfall ceased in most cases. The recession limbs of the hydrograph are primarily a function of the water table height, the drain spacing, and the characteristics of the soil. For our particular drainage system, the limbs reflect the low conductivity of the subsoil, and therefore the slow rate of lowering the water table and removal of excess water.

3.3.2 Cumulative Drainage

The cumulative drainage from paddocks A and B in 1988 was 304 and 257 mm respectively (Fig. 3.6). The two drainage values agreed well throughout the season, except on day 40 after fertilizer application, when the 90 mm storm event referred to above occurred and paddock A gave 46 mm more drainage than paddock B. When this extra drainage was discounted, the total seasonal measured drainage values agreed well.

For 1989 (Fig. 3.7), the measured quantities of drainage from both paddocks A and B agree well in the early part of the season, but deviate later, with more drainage being collected from paddock A (118 mm) than from paddock B (100 mm).

3.4 DRAINAGE SOLUTE CONCENTRATIONS

3.4.1 pH of Drainage

In both seasons the pH of the drainage water was determined because it could affect the charge balance of soil cations and anions. pH can affect the biological and chemical properties of the soil. The availability of plant nutrients, the adsorption capacity of sulphate (Curtin and Syers, 1990), the short-term nitrification activity of a soil (Bramley and White, 1990) and the potential toxicity of certain ions all depend on the pH of the soil, which can be inferred from its value in the drainage. The pH of the drainage is shown in Figs. 3.8a and 3.8b. Little difference was observed between the two paddocks and between the two years, the pH being

Fig. 3.6 Cumulative drainage for 1988

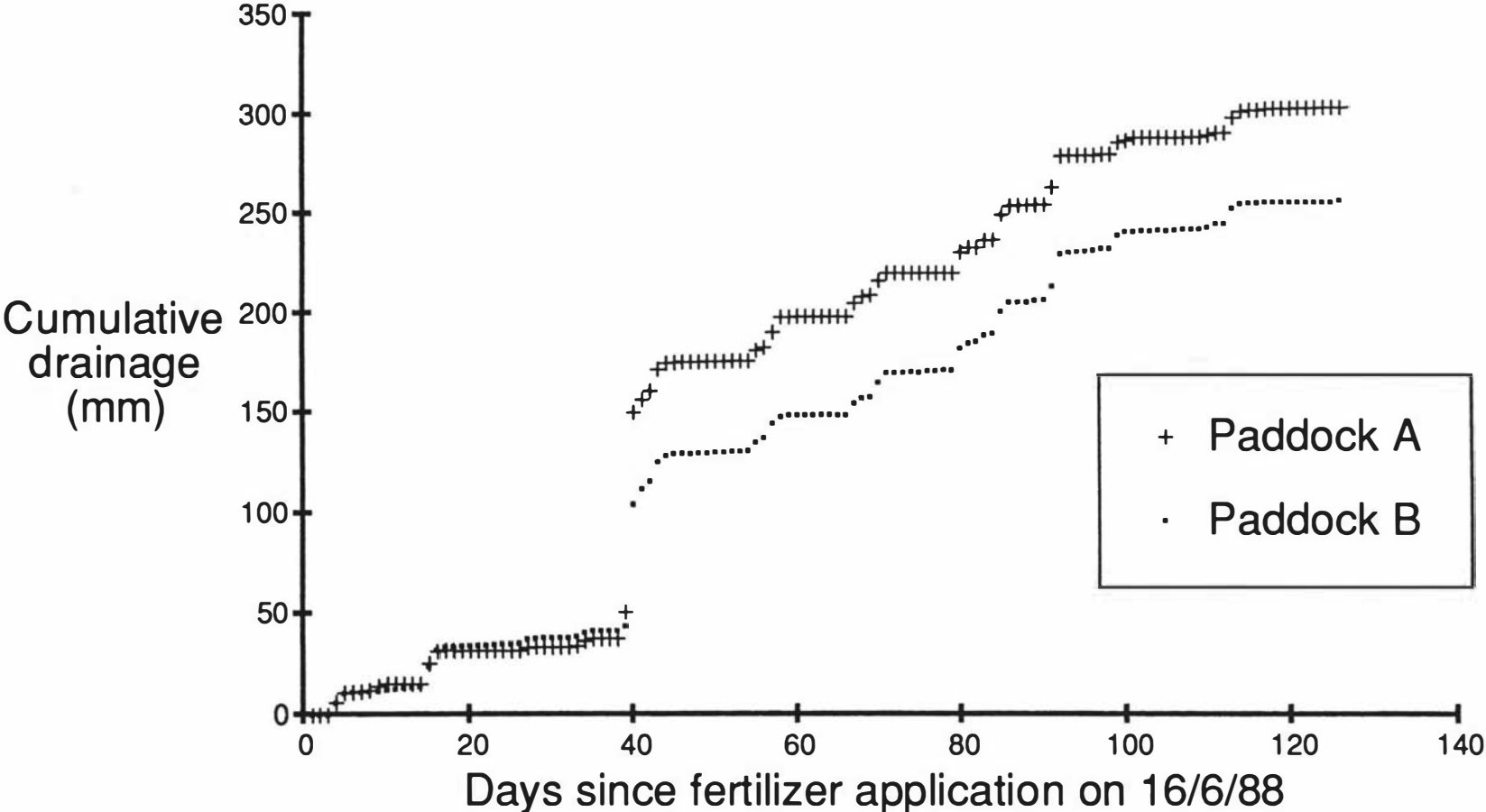


Fig. 3.7 Cumulative drainage for 1989

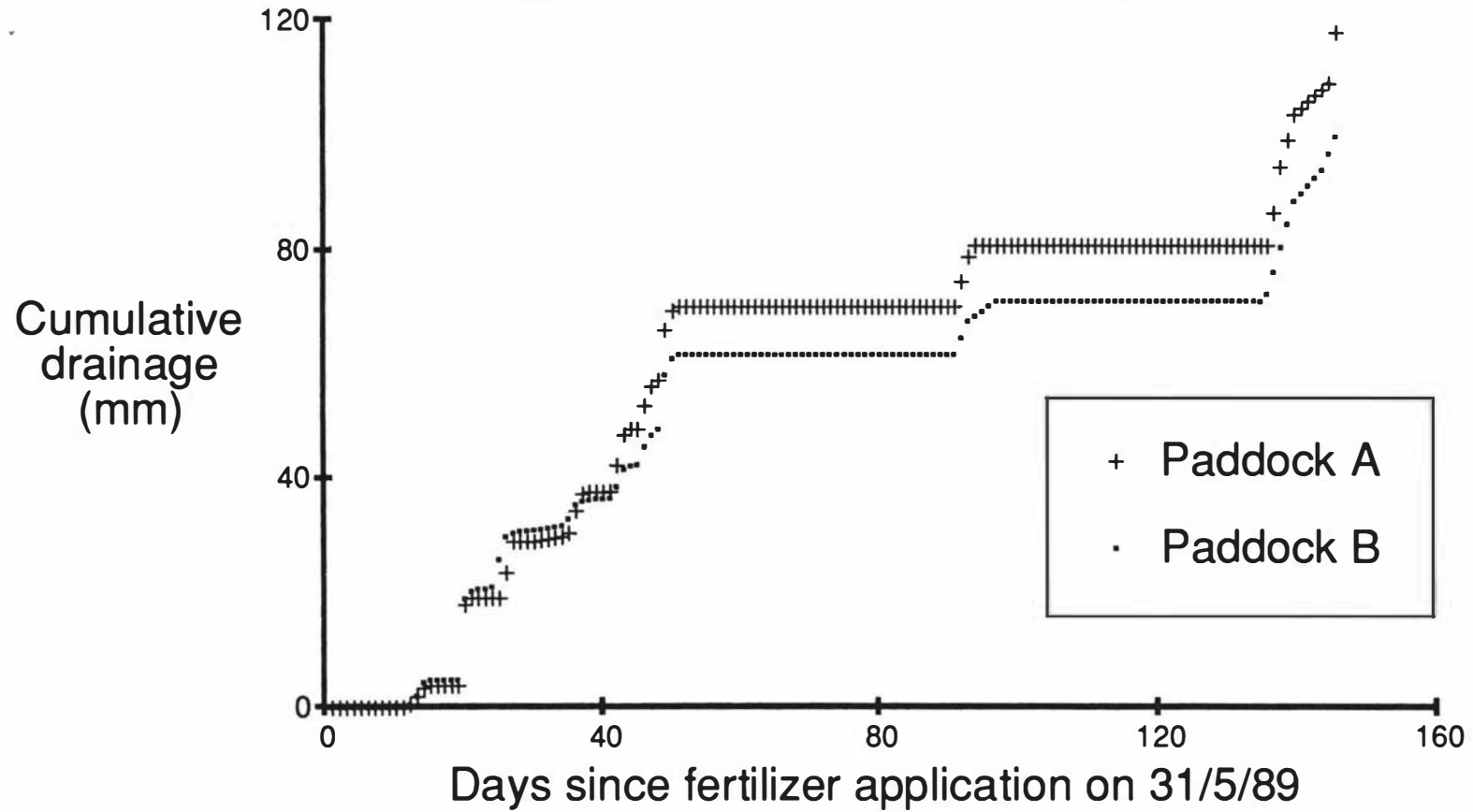
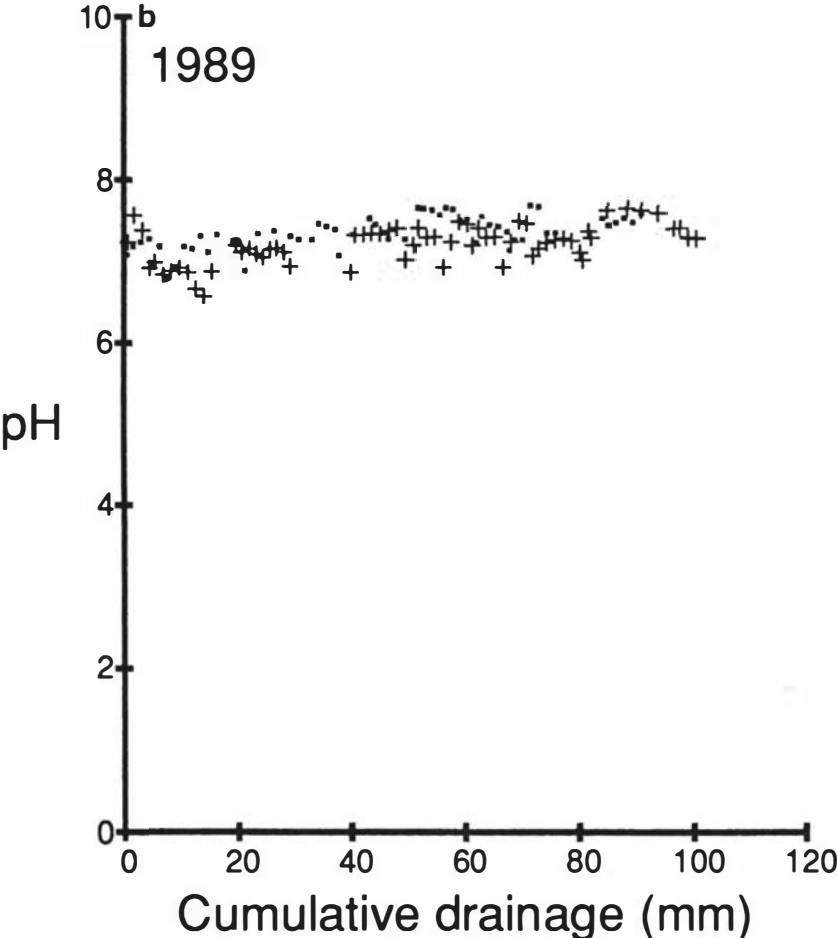
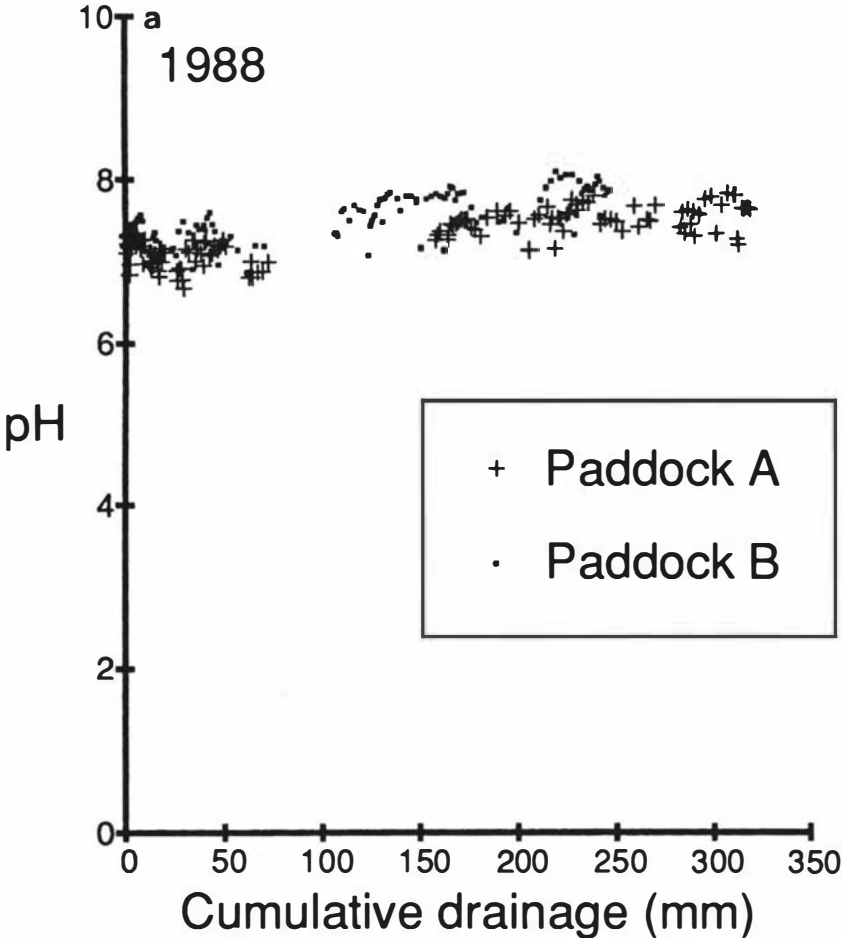


Fig. 3.8 pH of the drainage water in paddocks A and B for 1988 and 1989



around 7. This is higher than the soil pH reported for Tokomaru silt loam by Williams (1988) of 6.4 (using a 1:2.5 soil:water ratio) and between 5.2 to 6.2 by Bramley (1989). The higher pH in the drainage may be due to its lower ionic strength compared to that of the soil solution.

3.4.2 Chloride Concentration

3.4.2.1 *Individual drain flow events*

The chloride concentration during some individual drain flows is shown in Figs. 3.9 and 3.10. Also shown are the hydrographs, to indicate the effect of flow rate on chloride concentration. In the 29/6/88 early-season event (Fig. 3.9), the chloride concentration increased with drain flow early in the event, then stayed high even though flow rate decreased. The increase in chloride concentration at high flow rates observed at the beginning of the drainage season could be due to the rapid transfer of fertilizer Cl to the drain through preferential flow paths. That is, Cl concentration increases with increasing flow rate due to preferential flow of the recently applied KCl. However, as the season progressed, a strong inverse concentration-flow relationship was observed, as shown in the October 6 flow event (Fig. 3.10). This trend was also reported by Richard and Steenhuis (1988) in their study of chloride leaching into drains. The reason for the inverse relationship is probably because as time proceeds, diffusion of the applied KCl into the soil matrix occurs and so preferential water flow from the soil surface is inefficient at leaching it.

3.4.2.2 *Seasonal hydrographs*

The seasonal trend in drainage chloride concentration for 1988 is shown in Fig. 3.11. Both paddocks started with an initial chloride concentration of approximately 60 g m^{-3} , which increased to approximately 80 g m^{-3} in the first 50 mm of drainage, indicating the rapid dissolution of fertilizer KCl and the preferential movement of Cl to the drains. The concentration of chloride decreased to about 20 g m^{-3} over the next 50 mm of cumulative drainage. This corresponded to the intense storm event of 24 July. Under such a situation, most flow will be through cracks induced

Fig. 3.9 Concentration of chloride (+ and .) and flow rate (solid line) during the 29/6/88 flow event

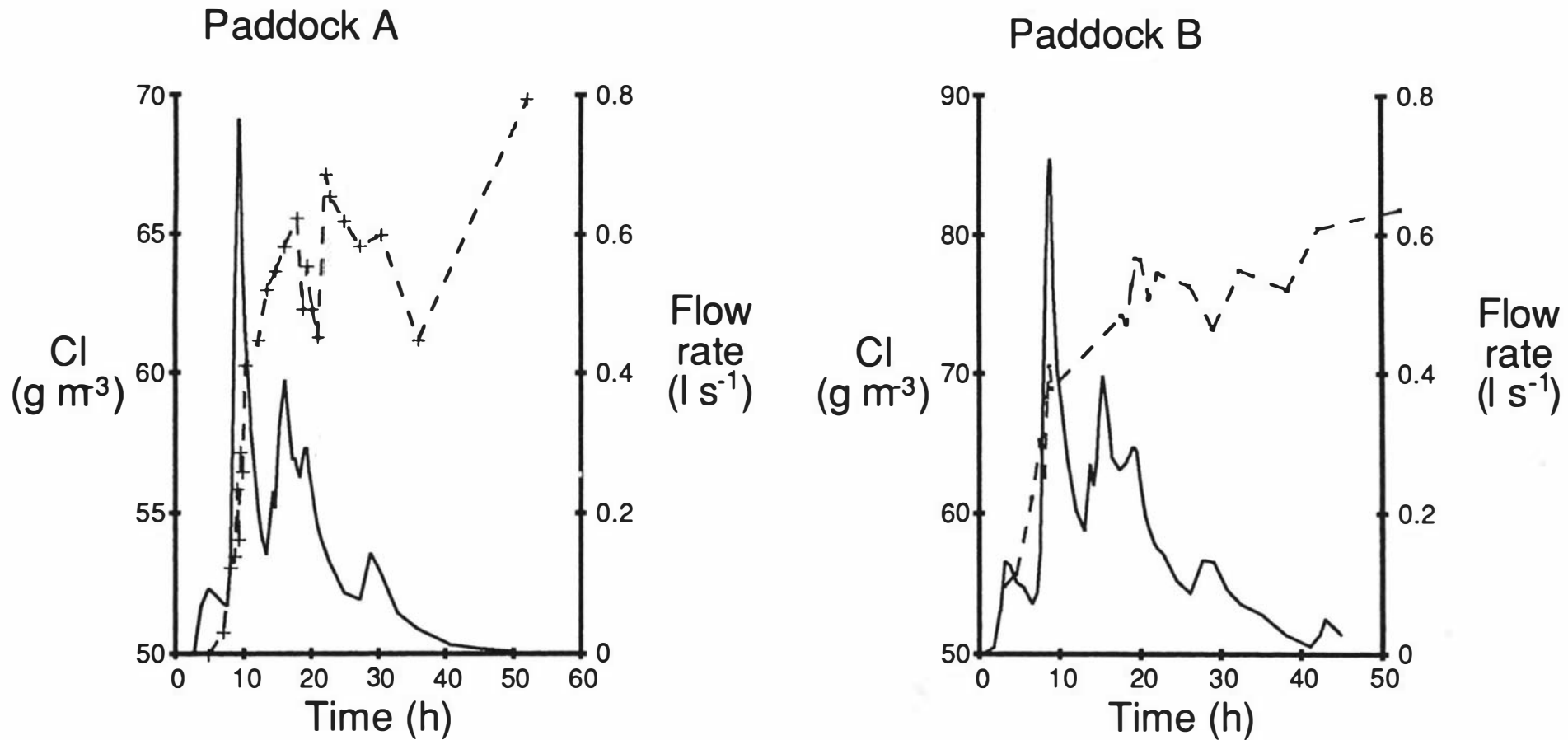


Fig. 3.10 Concentration of chloride (+ and .) and flow rate (solid line) during the 6/10/88 flow event

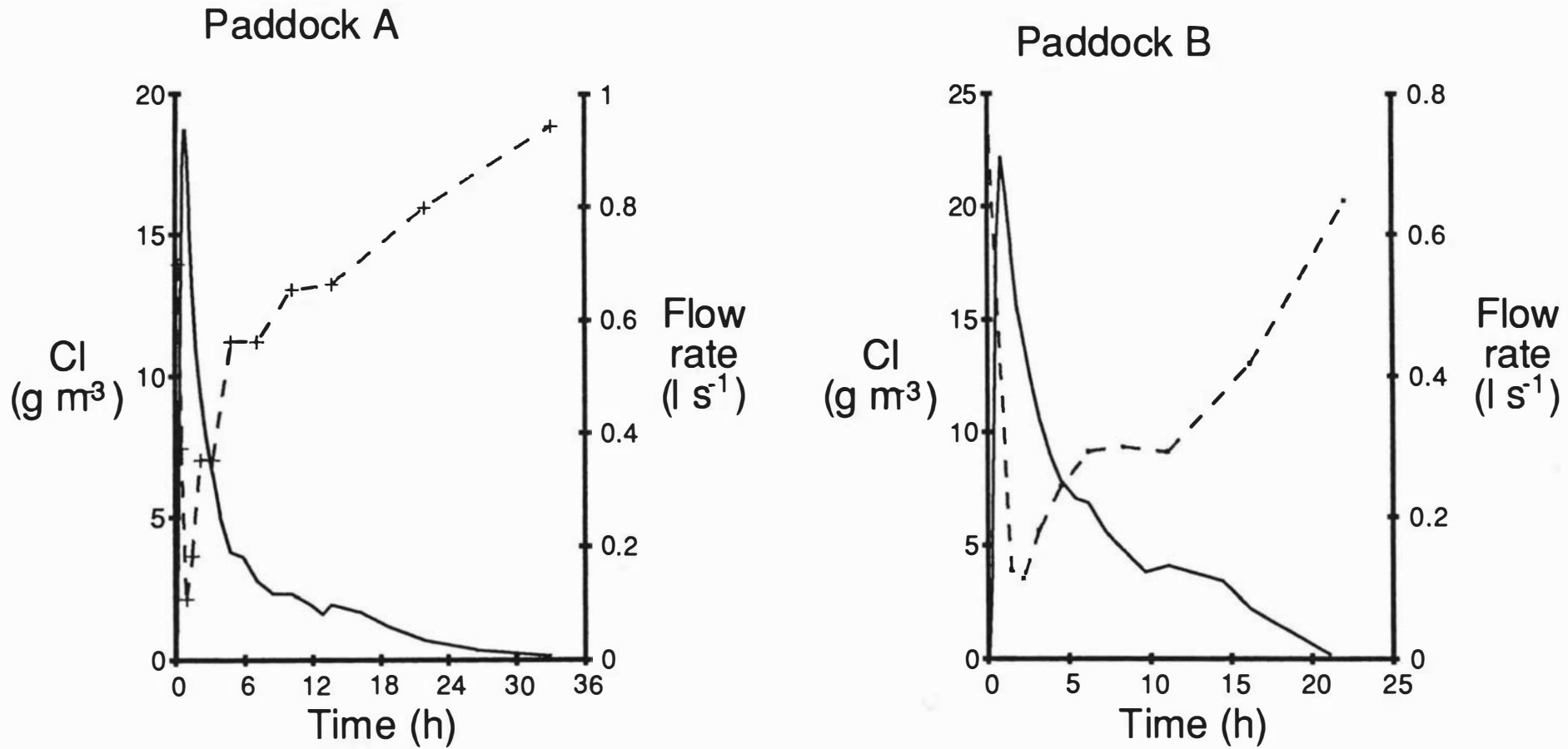
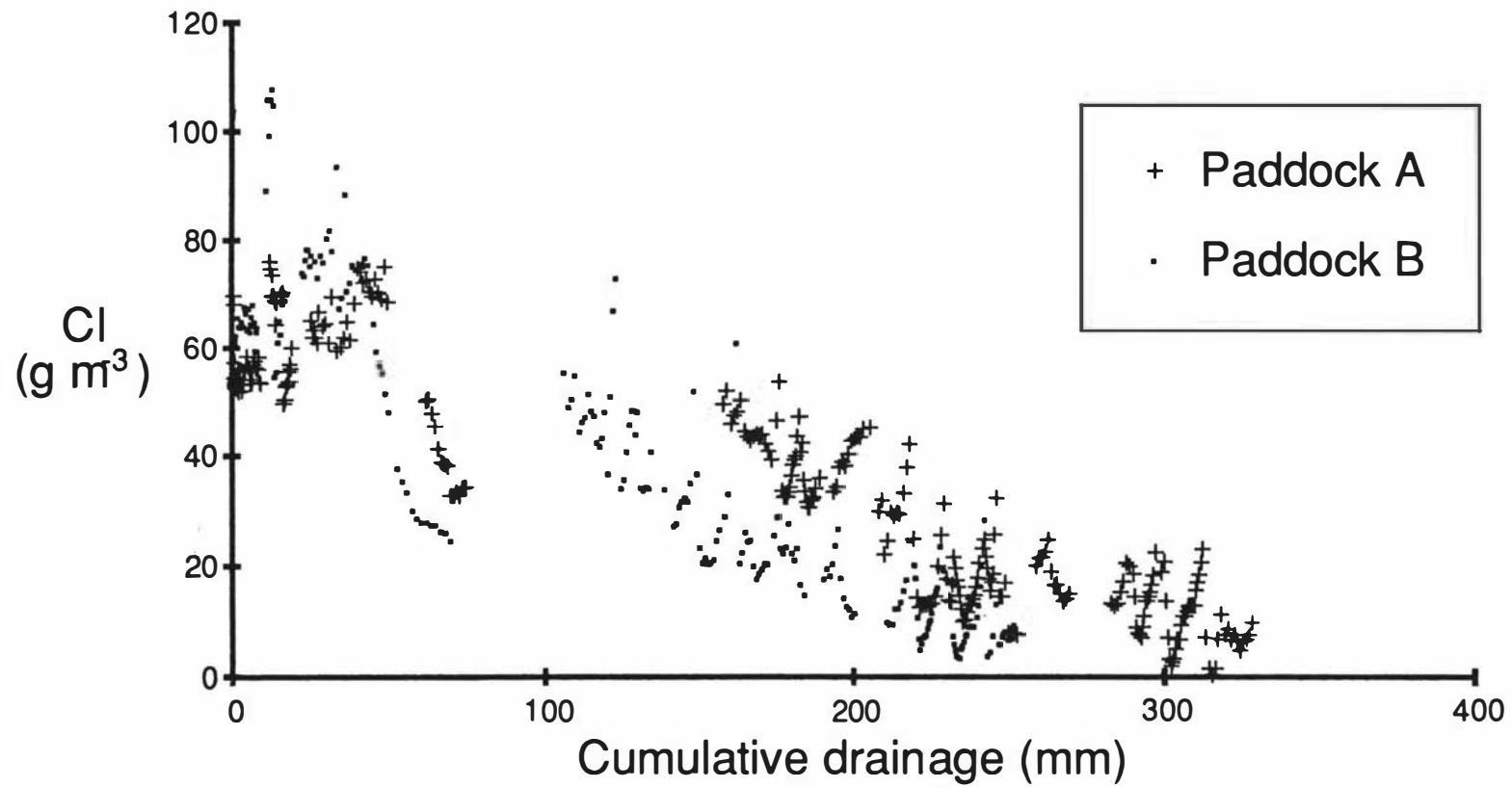


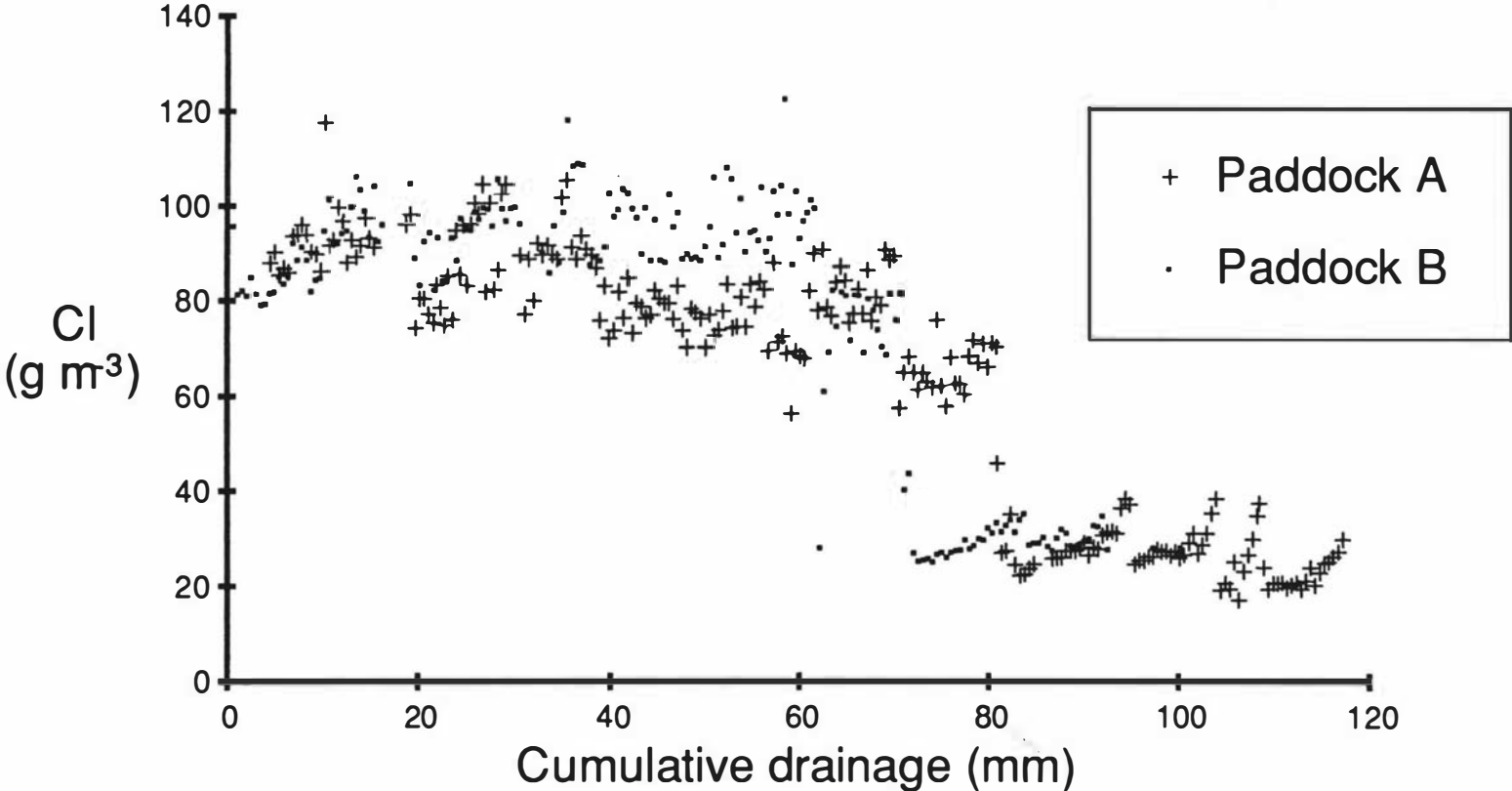
Fig. 3.11 Chloride concentration in the 1988 field drainage



through moling, resulting in preferential flow and dilution of drainage water (Thomas and Phillips, 1979; White, 1985b). Thus even though the quantity of drainage was large, the amount of chloride leached was relatively small during that event. The concentration of chloride increased again after the storm event but only to 50 g m^{-3} ; it then decreased gradually with further drainage to about 10 g m^{-3} by the end of the drainage season. There is a gap due to missing data between the 80 and 110 mm cumulative drainage. The total amount of chloride leached in 1988 was 118 and 93 kg ha^{-1} for paddocks A and B respectively (Table 3.1).

Higher chloride concentrations of around 90 g m^{-3} were observed early in the 1989 drainage season compared to 1988 (Fig. 3.12). The relatively high and stable drainage chloride concentration was probably due partly to the high soil chloride level at the beginning of the season which resulted from the fresh KCl application, and to the atmospheric input during summer when there was no drainage. It was also partly due to the different flow mechanisms involved in 1989 because of the lower rainfall intensities and more intermittent rainfall, which have been shown by Talsma (1967), Oster *et al.* (1972) and Kanchanasut *et al.* (1978) to be more effective at leaching solutes than heavy, continuous rainfall. Drainage chloride concentration dropped after about 70-80 mm of drainage which corresponded to the end of a relatively dry and mild period. Herbage growth and plant uptake of chloride were probably stimulated during this period. The increased growth may also have been due to urea applied to both paddocks A and B in early September. Hence when the soil rewetted again, a much lower chloride concentration was observed in the drainage. The total chloride leached during 1989 was 76 and 72 kg Cl ha^{-1} for paddocks A and B respectively (Table 3.1). It is interesting to see that although the quantity of drainage in 1989 was less than half that in 1988, the amount of chloride leached was only 25% less, with most of the chloride leached in the early part of the drainage season in both years. The values for the two years were comparable to the leaching losses measured by Steele *et al.* (1984) in their lysimeters studies. The above results suggested that the timing of KCl application relative to the occurrence of drainage, and the intensity and frequency of rainfall events are important factors in the leaching of chloride.

Fig. 3.12 Chloride concentration in the 1989 field drainage



3.4.3 Sulphate-S Concentration

3.4.3.1 Individual drain flow events

The concentration of $\text{SO}_4\text{-S}$ during the rainfall events of 29/6/88 and 6/10/88 is shown in Figs. 3.13 and 3.14. Contrary to the chloride results, there was little change in concentration of $\text{SO}_4\text{-S}$ at different flow rates for both paddocks during both events. This result is interesting and is probably due to the sulphate adsorption buffering capacity of the soil. Bolan *et al.* (1986) showed that the adsorption process was reversible, and adsorbed sulphate is in rapid equilibrium with the soil solution (Kamprath *et al.*, 1956).

Table 3.1 Losses of nutrients (kg ha^{-1}) in drainage from the Tokomaru silt loam

Element	1988		1989	
	Paddock A	Paddock B	Paddock A	Paddock B
Chlorine	117.8	92.8	76.3	71.9
Sulphur	17.0	3.4	9.4	3.5
Nitrogen	12.6	8.6	19.1	14.9
Calcium	52.4	35.2	40.8	30.7
Potassium	10.8	5.7	7.1	3.3
Magnesium	15.0	10.8	11.3	9.1
Sodium	64.5	50.8	31.9	31.1

Fig. 3.13 Concentration of sulphate-S (+ and .) and drain flow rate (solid line) during the 29/6/88 flow event

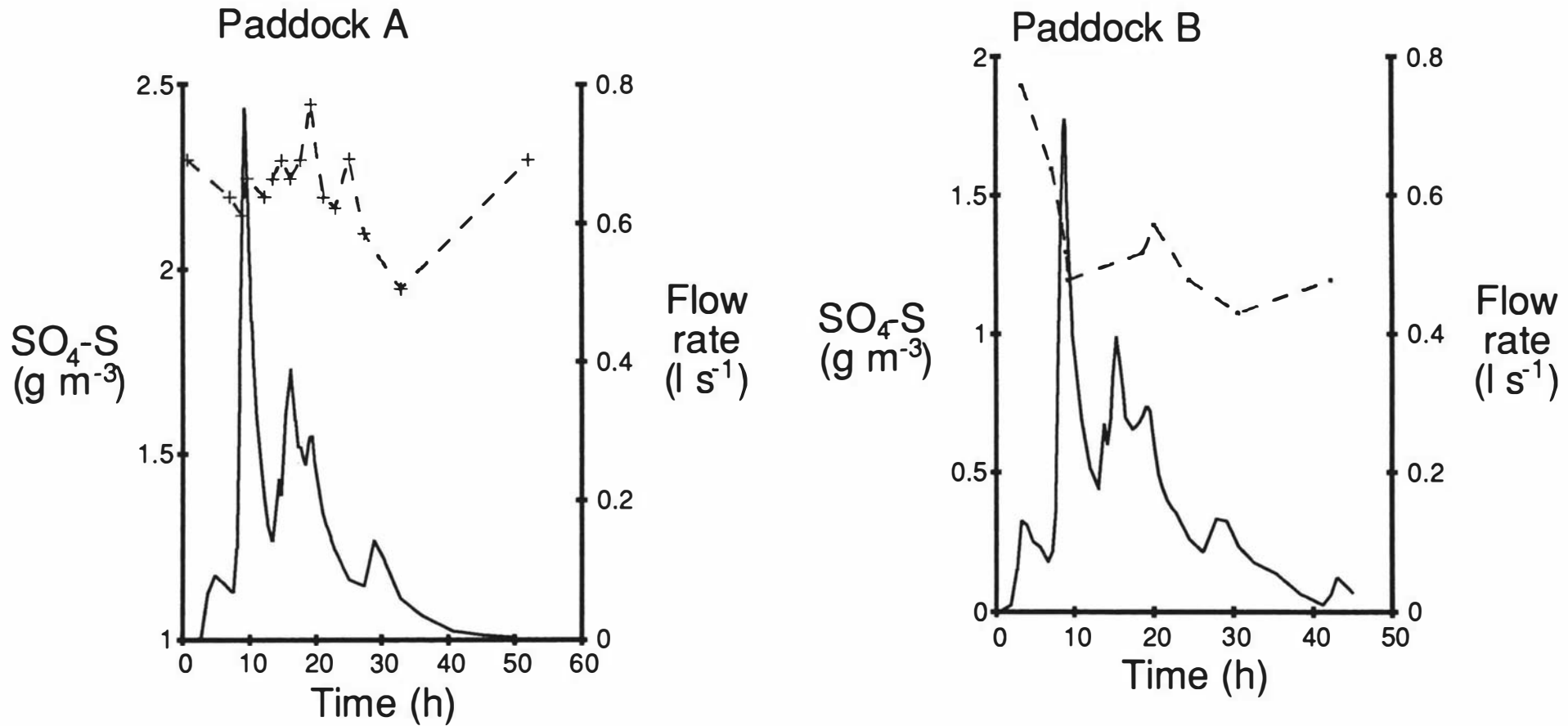
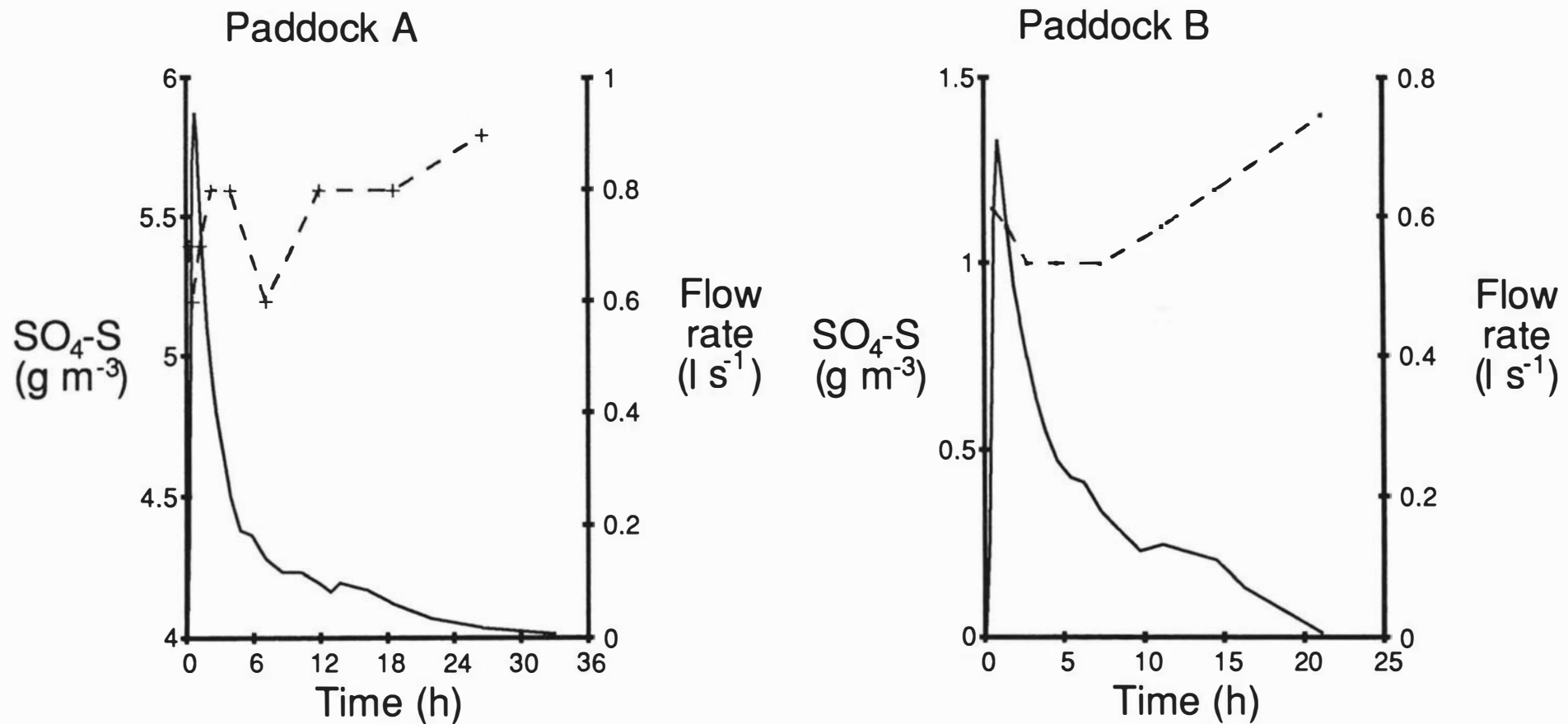


Fig. 3.14 Concentration of sulphate-S (+ and .) and drain flow rate (solid line) during the 6/10/88 flow event



3.4.3.2 *Seasonal hydrographs*

The seasonal drainage sulphate concentrations for both paddocks A and B for 1988, 1989 and 1990 are given in Figs. 3.15, 3.16 and 3.17 respectively. In 1988, both paddocks began the drainage season with a similar $\text{SO}_4\text{-S}$ concentration of 2 g m^{-3} . However after 50 mm of drainage, $\text{SO}_4\text{-S}$ concentrations in paddock A showed a 3 fold increase to 6 g S m^{-3} , and remained roughly constant at this level until the end of the season. In contrast, the sulphate concentration from paddock B was steady at $1\text{-}2 \text{ g m}^{-3}$, except for occasional higher values. The rapid increase in the $\text{SO}_4\text{-S}$ concentration in paddock A suggests that the sulphate applied in SSP was readily leached, as observed in the field studies of Gregg and Goh (1978) and Smith *et al.* (1983). Rapid leaching of sulphate to depth through macropores after 150 mm of irrigation was also observed by McLay (1989) in his lysimeter leaching study. The steady seasonal $\text{SO}_4\text{-S}$ concentration was very similar to that in individual rain events. While the buffering effect of adsorption/desorption was suggested to explain the short-term steady concentration, transformations to and from organic forms could also be involved in stabilizing the concentration on a seasonal basis.

The low drainage concentration in paddock B suggests that the application of S° with the particle size range used in 1988 resulted in little leaching of sulphate. The S° particle size distributions given in Table 3.2 show that in the 1988 application, 73% of the particles were larger than $500 \mu\text{m}$, while 50% were in this size range in 1989. This is much bigger than the size recommended by MAF in New Zealand (Sinclair *et al.*, 1985; Edmeades *et al.*, 1990). According to the recommendation, the particles should be 100% $< 250 \mu\text{m}$ and 50% $< 150 \mu\text{m}$ for it to be effective during the year of application for the cool temperate zone. The relatively big S° particles applied in 1988 and 1989 probably meant that the rate of oxidation was slow and therefore explains the small amount of sulphate leached in 1988. The total $\text{SO}_4\text{-S}$ leached for the drainage season of 1988 was 17.0 kg ha^{-1} for paddock A and 3.4 kg ha^{-1} for paddock B (Table 3.1). Thus, assuming the S° had no effect on leaching loss of $\text{SO}_4\text{-S}$, the application of 50 kg ha^{-1} of sulphur as SSP in early winter caused a five fold increase in leaching. Smith *et al.* (1983) also observed increased leaching when SSP was applied, with 7.5 kg ha^{-1} of S lost in tile drainage.

Fig. 3.15 Sulphate-S concentration in the 1988 field drainage

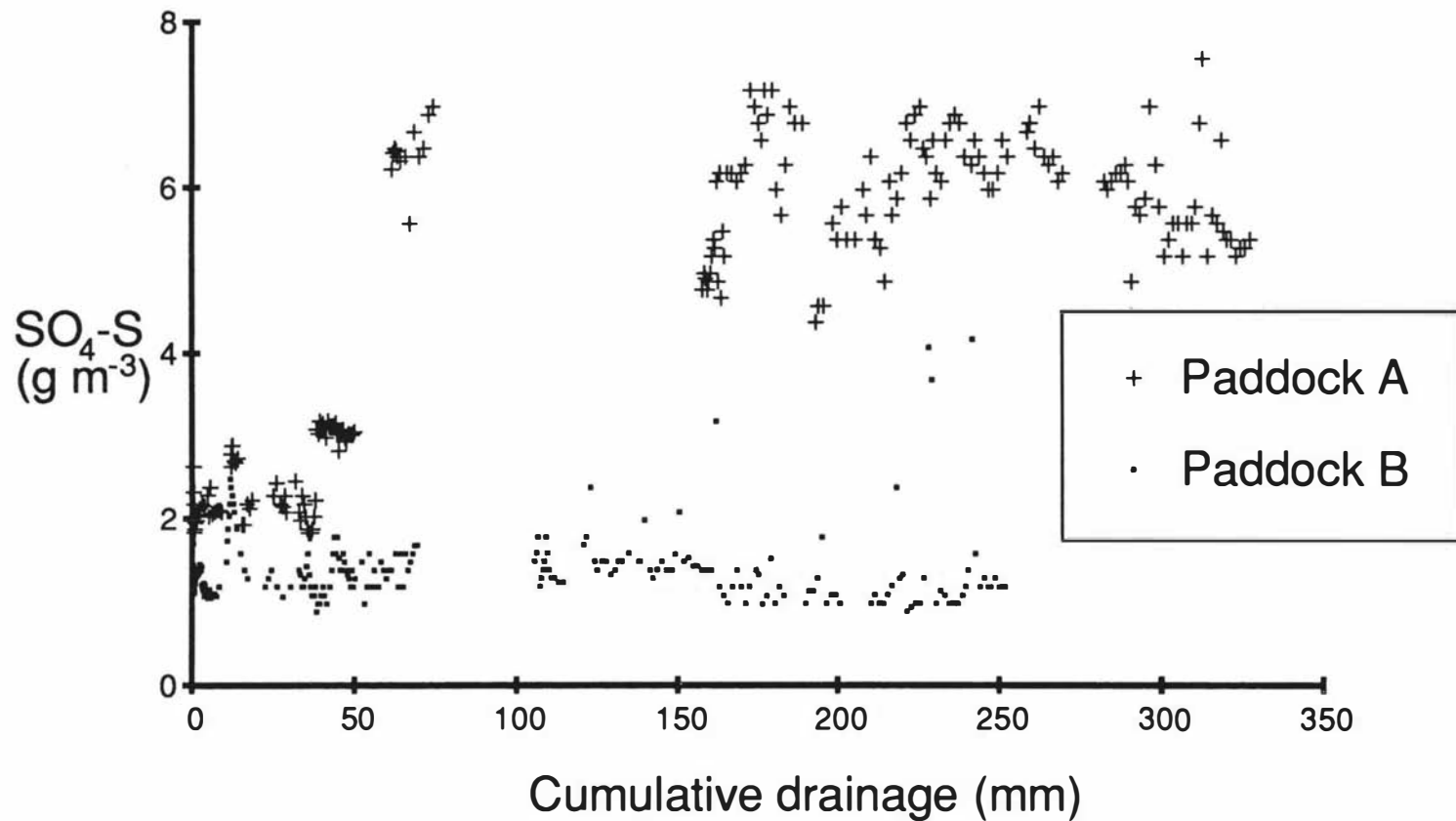


Fig. 3.16 Sulphate-S concentration in the 1989 field drainage

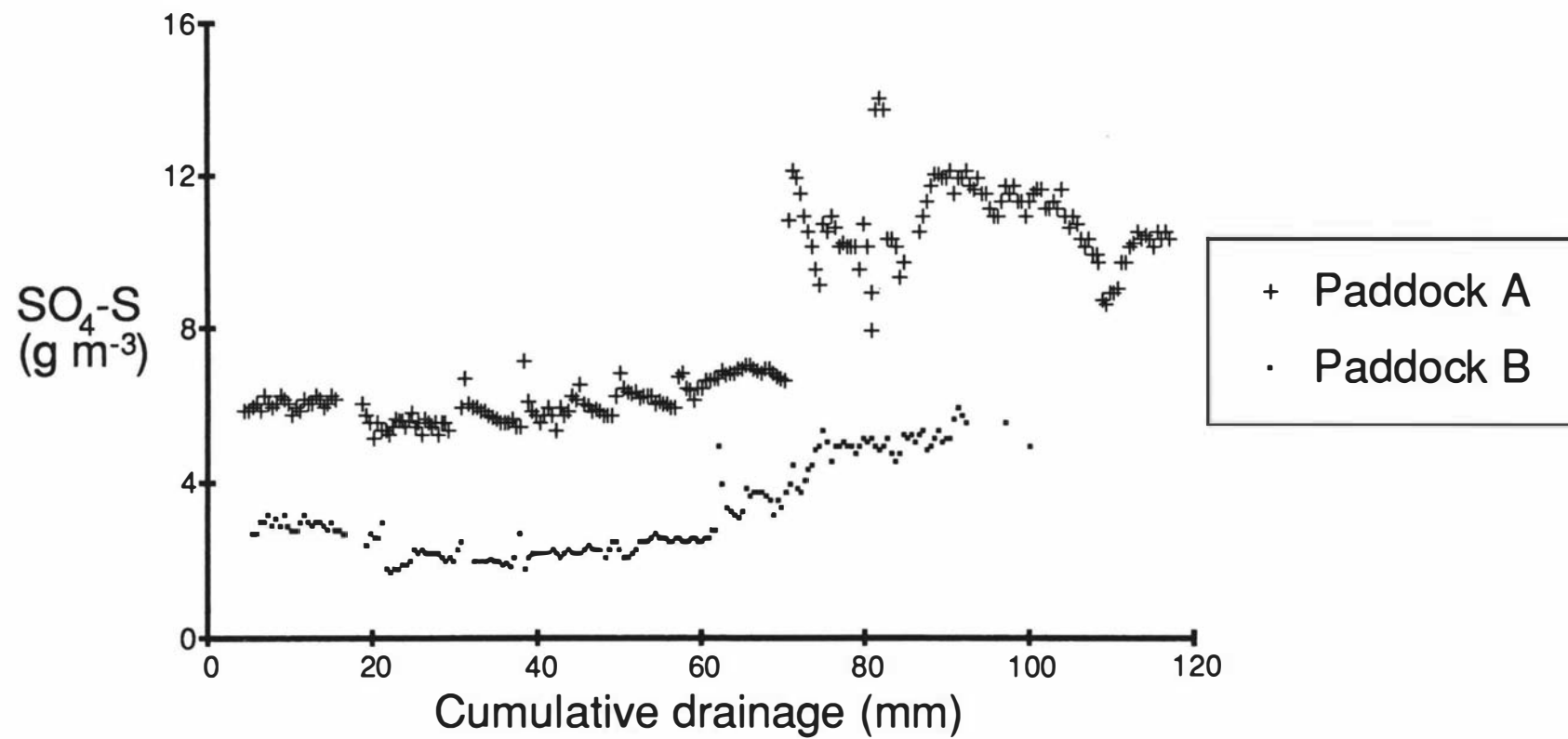


Fig. 3.17 Sulphate-S concentration in the 1990 field drainage

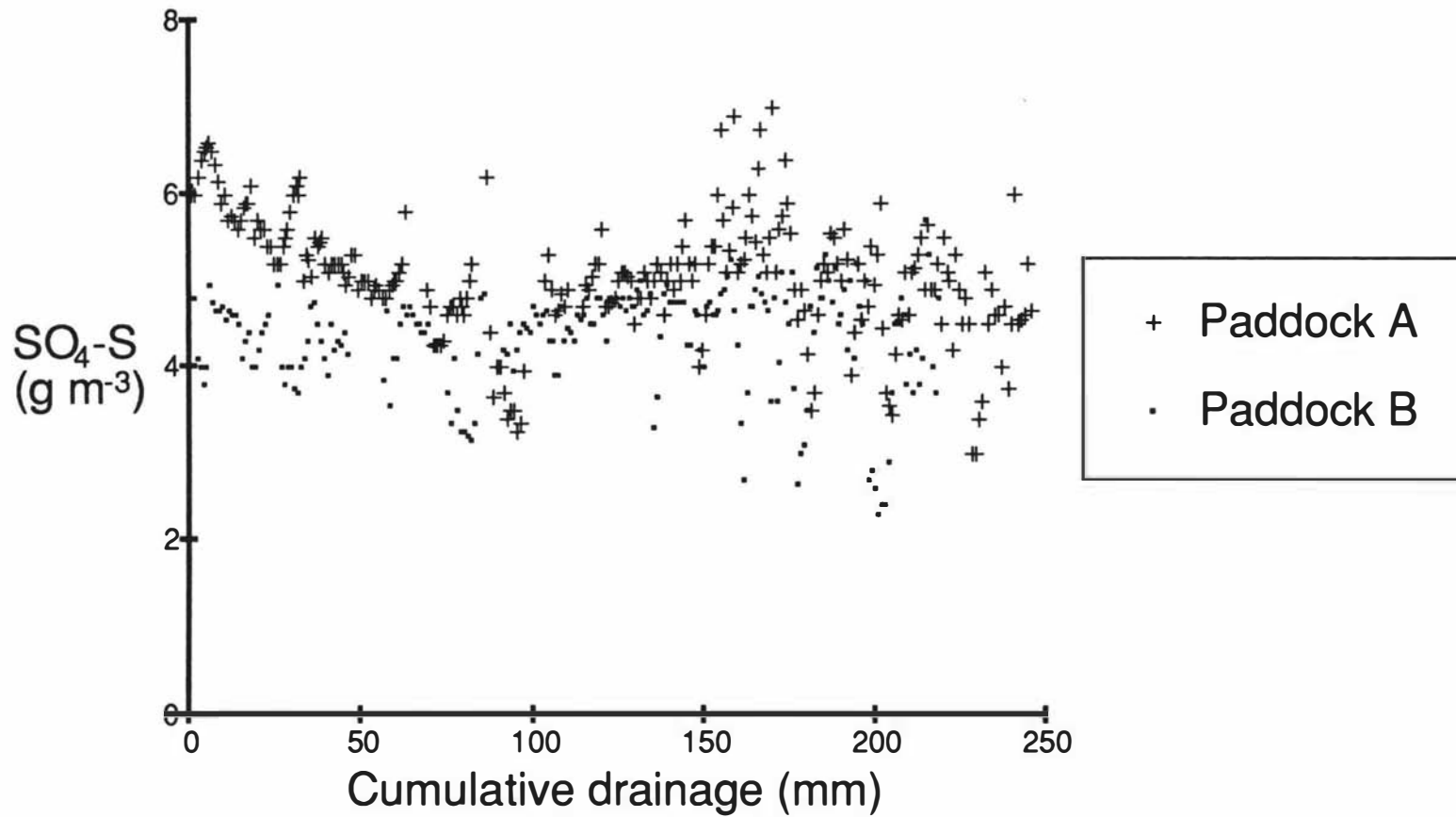


Table 3.2 Particle size distribution of elemental sulphur applied

Particle size (mm)	Percentage by mass	
	1988	1989
<0.075	4.4	7.9
0.075-0.15	4.5	8.0
0.15-0.25	5.3	9.5
0.25-0.5	12.5	24.9
0.5-1.0	19.8	19.5
1.0-1.4	39.0	30.2
1.4-2.0	14.5	0.0

The 30 kg S ha⁻¹ applied at the beginning of the drainage season of 1989 did not result in a further increase in sulphate concentration in paddock A (Fig. 3.16), but probably helped to maintain the concentration at 6 g m⁻³ throughout the first half of the season. The concentration in the S^o paddock drainage was around 3 g m⁻³. However the concentrations increased to about 13 and 6 g m⁻³ respectively after the prolonged dry and mild period between August and October of that year. This increase can probably be attributed to the higher than normal daytime soil temperatures, together with wetting and drying cycles which increased both net mineralization and S^o oxidation rates. The effect of moisture fluctuations on mineralization has been investigated in pot trials by Freney *et al.* (1975). Their results suggest that when drastic changes in soil moisture conditions occur, a flush of S mineralization can be produced. Also higher leaching losses during spring due to warmer temperatures were observed by Jones and Woodmanse (1979) and Steele *et al.* (1984). The total amount of sulphate leached during the drainage season of 1989 was 9.4 kg S ha⁻¹ from paddock A, and 3.5 kg S ha⁻¹ from paddock B (Table 3.1).

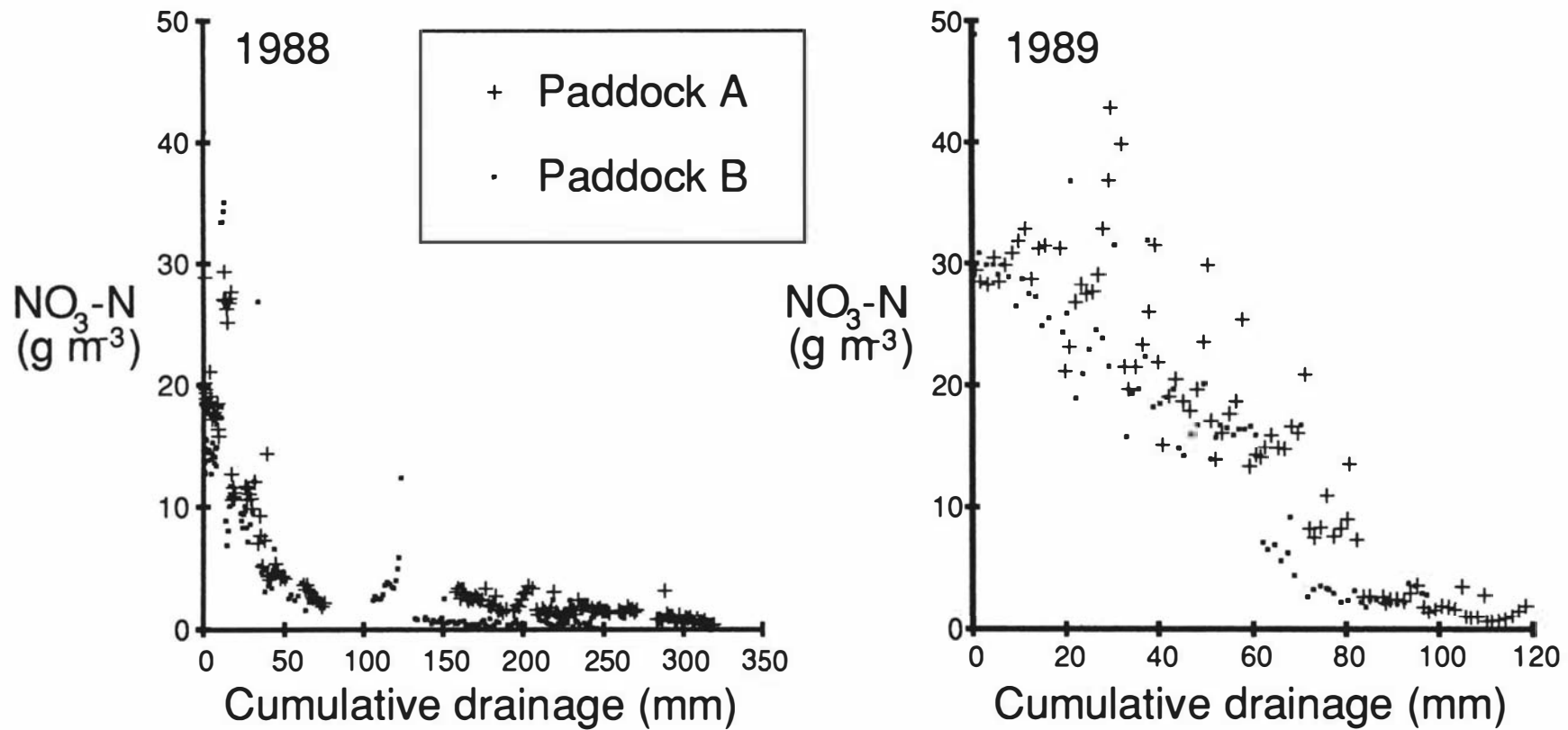
No additional S fertilizer was applied in 1990. Thus most of the sulphate in the 1990 drainage must have come from mineralization of organic sulphur and oxidation of residual sulphur from the previous two years' applications. A slightly higher $\text{SO}_4\text{-S}$ concentration was observed in paddock A drainage (around 6 g m^{-3}) than B (5 g m^{-3}) in the first 50 mm of drainage. However the difference became less with increasing drainage. The concentration in both paddocks tended to increase after 100 mm drainage, probably due to mineralization and some contribution from oxidation of S^0 in paddock B. The total amounts of $\text{SO}_4\text{-S}$ leached in 1990 were 12.3 and 9.5 kg S ha^{-1} from paddocks A and B respectively.

From the above results, it can be seen that the form of sulphur applied, and the rates of mineralization and immobilization are important factors affecting the rate of sulphate leaching. As the sulphate concentration in the drainage was relatively constant over most of the drainage season, the amount of S leached was approximately proportional to the amount of drainage. The results also indicate that application of a soluble form of sulphur near the start of the drainage season is not recommended.

3.4.4 Nitrate Concentration

The nitrate concentrations in the drainage during 1988 and 1989 are given in Fig. 3.18. Generally, the concentration was highest in the first drainage event after the summer-autumn season and declined rapidly with further drainage. This pattern of leaching was also observed by Turner *et al.* (1976) and Haigh and White (1986). White *et al.* (1983) attributed the high autumn concentrations to be due to a flush of mineralization of soil organic N, especially in the top 200 mm, as the soil rewetted. Interestingly only in the first 50 to 80 mm of drainage did the nitrate concentration exceed the World Health Organization (WHO) guideline for potable water of 10 g N m^{-3} . This suggests that a substantial improvement in water quality could be achieved by temporary storage or treatment of just the early drainage water. Similar to the Cl leaching pattern, a decrease in nitrate concentration was also observed during the intense rainfall event. The possible explanation for this low concentration was that most of the nitrate was held within the soil aggregates, and

Fig. 3.18 Nitrate-N concentration in the field drainage of 1988 and 1989



was not accessible for leaching when bypass flow occurred (Cunningham and Cooke, 1958; Wild, 1972; Thomas and Phillips, 1979).

The nitrate level in 1989 was generally higher than that in 1988, especially in the first 70 mm of drainage. Since no nitrogen was added to the paddocks until late 1989, the higher concentration in early 1989 could be due to more efficient leaching (i.e. less preferential flow) under the drier soil conditions prevailing during 1989 compared to 1988. During the dry period between August to mid-September in 1989, urea was applied at 50 kg N ha⁻¹ to all three paddocks A, B and C as part of another experiment and grazing also took place in August. However the addition of nitrogen from these two sources did not result in a measurable increase in concentration either in the first drainage event following the dry mid-winter period, or in the subsequent events. This was different from the increased nitrate concentration in tile drainage reported by Sharpley and Syers (1979) after the application of urea (60 kg N ha⁻¹) to dairy-cattle grazed paddocks in July. The extra nitrogen added may have been taken up by the pasture, as indicated from the large increase in the pasture growth rate (result presented in Chapter 4) following urea application. Other possible processes which could account for nitrogen losses are NH₃ volatilization, denitrification and immobilization. Some volatilization could have taken place, because the process tends to increase with temperature and in soils of high moisture that are allowed to dry. Such conditions prevailed after urea application. Little denitrification would be expected to occur as the soil was not saturated or waterlogged. These processes were not measured in this experiment. Losses in drainage as ammonium were also not measured, because studies by Turner *et al.* (1979) and Sharpley and Syers (1981) showed little NH₄ was lost in drainage water. Measurement of ammonium in the tile drainage made by G.N.Magesan (pers. comm.) after urea application in September 1989 confirmed this.

The amounts of nitrogen leached during the two winter periods were 12.6 and 8.6 kg N ha⁻¹ in 1988 and 19.1 and 14.9 kg ha⁻¹ in 1989, for paddocks A and B respectively (Table 3.1). More nitrogen was leached in 1989 compared to 1988, although there was less drainage in that year. In both years, most of the nitrogen

was lost in the first 50 to 80 mm of drainage, hence the total drainage is of little relevance to the amount of nitrogen leached. The amounts leached were also very much less than those found by Steele *et al.* (1984) for intensive dairy cattle-grazed pasture and Haigh and White (1986) for both cattle and sheep-grazed pasture. Differences in the grazing animal could be one of the reasons for the large difference between the amount leached in the Steele *et al.* (1984) study and the present study, because of the larger volume of urine excreted per urination by cattle (1600 ml), compared to sheep (150 ml) (Doak, 1952). Ryden *et al.* (1984) argued that 'hot spots' resulting from urination by grazing animals were the major cause of nitrogen leaching losses. Although enhanced leaching following grazing by sheep has also been observed (Turner *et al.*, 1979; Field *et al.*, 1985), it is likely to be less pronounced than that following grazing by cattle.

3.4.5 Cation Concentrations

3.4.5.1 Calcium

The concentrations of calcium (Ca) in the drainage for 1988 and 1989 are presented in Figs 3.19 and 3.20. The calcium concentration was high at the start of 1988 (around 40 g m⁻³) but dropped off steadily with increasing drainage, to less than 20 g m⁻³ by the end of the drainage season, resulting in total leaching losses of 35 and 52 kg ha⁻¹ (Table 3.1). In 1989, the Ca concentration remained steady above 40 g m⁻³ during the first stage of the leaching period but dropped off rapidly to about 10 g m⁻³ after the dry period at 70 mm. It is interesting that the application of urea which generated NO₃⁻ did not increase the loss of Ca and other cations when drainage resumed that year. The total Ca leached in 1989 was 41 and 31 kg ha⁻¹ for paddocks A and B respectively. The large losses of Ca can be attributed to its application and to calcium being the dominant cation present on the exchange sites in Tokomaru silt loam (Pollock, 1975; During, 1984).

3.4.5.2 Potassium

The concentration of potassium (K) in the drainage was low in both years, despite the high rate of potassium fertilizer applied (Figs. 3.19 and 3.20). The

Fig. 3.19 Concentration of cations (Ca, K, Mg & Na) in the 1988 field drainage

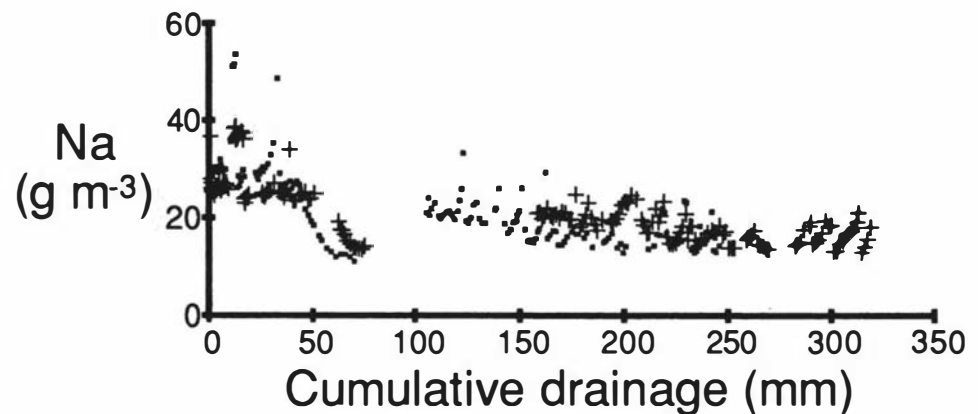
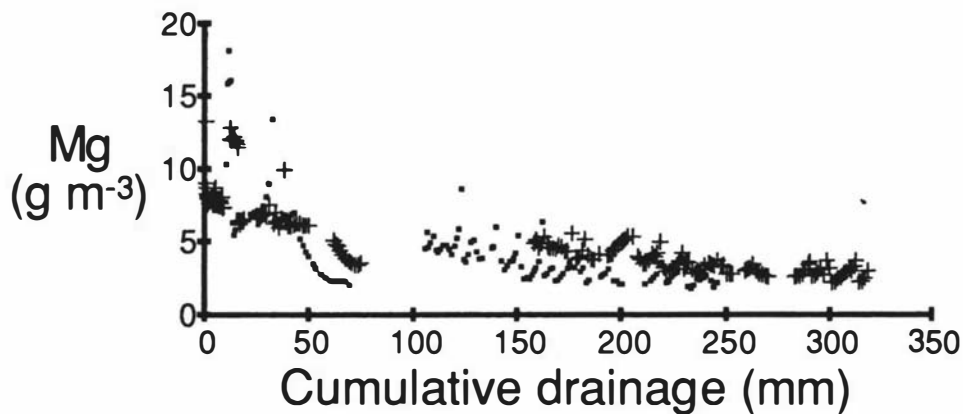
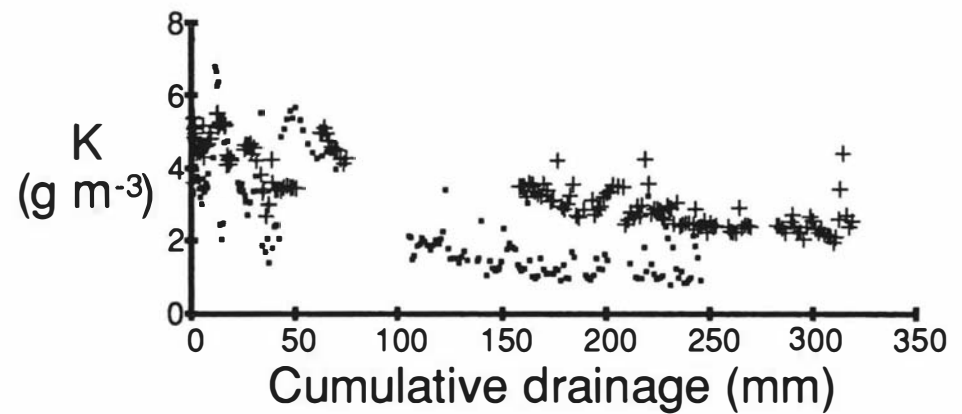
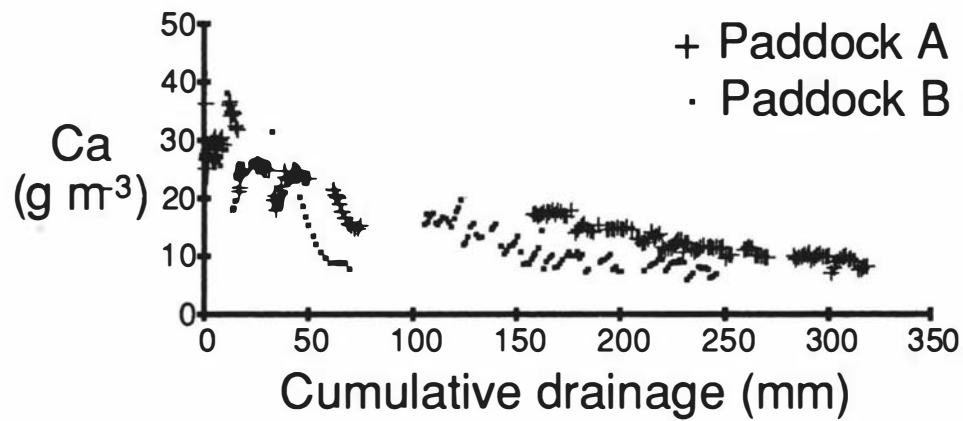
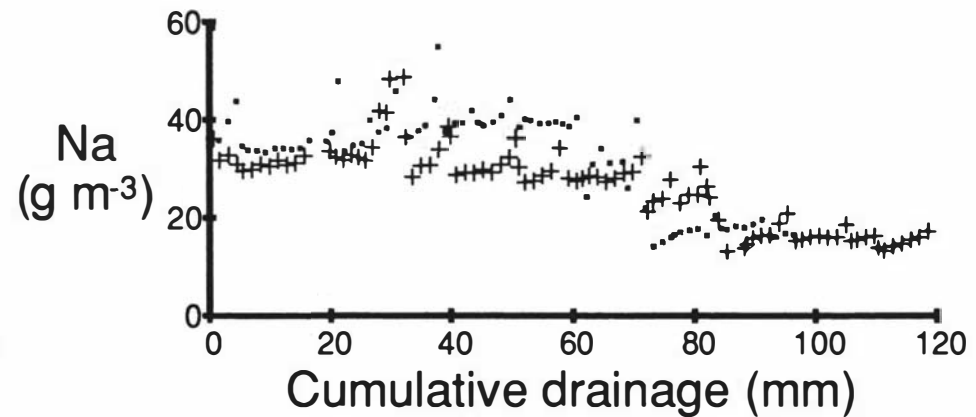
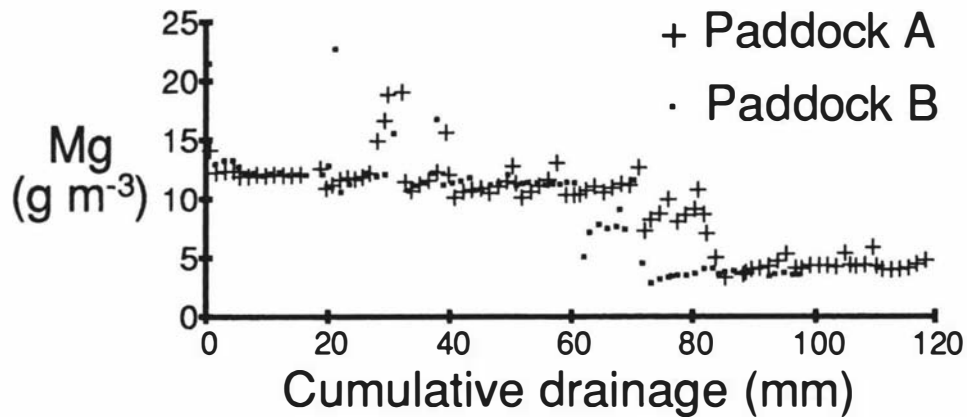
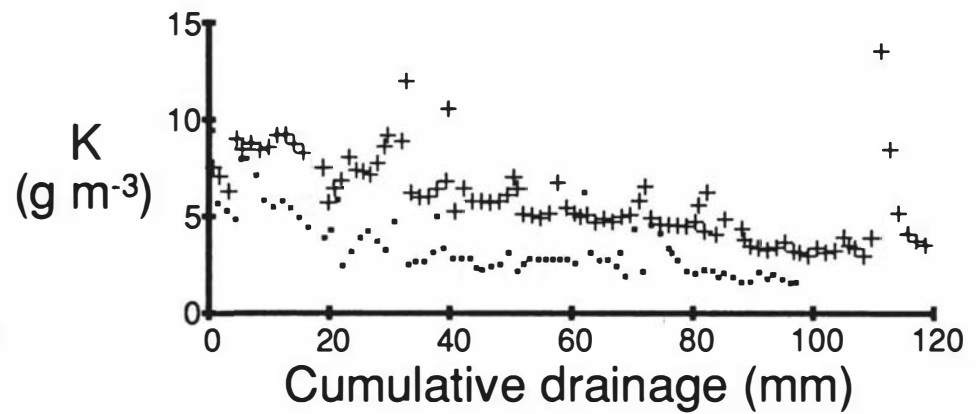
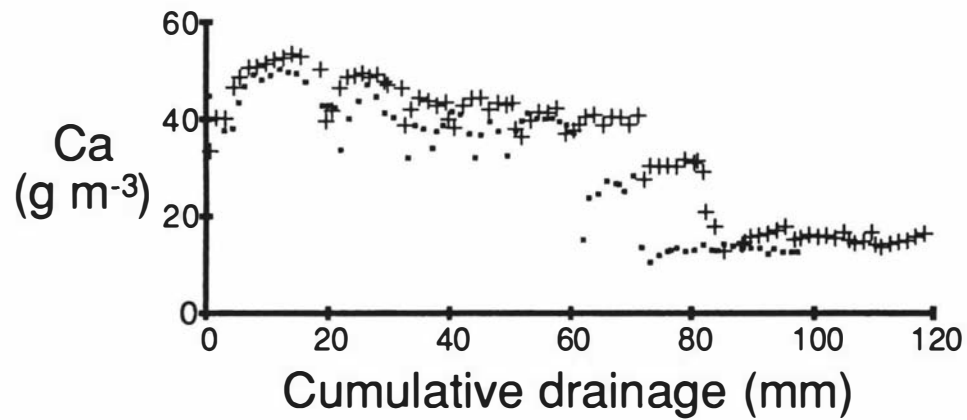


Fig. 3.20 Concentration of cations (Ca, K, Mg & Na) in the 1989 field drainage



concentration varied between 1 and approximately 12 g m⁻³. In general, the amount leached is small compared to that taken up by plants (During, 1984). Although Hogg (1981) and Williams *et al.* (1990) observed that preferential K leaching can occur from cattle urine patches, only small amounts of K loss through leaching were observed here. The low and stable potassium concentration can be attributed to the presence of mixed layer clay minerals in this soil, which help to hold it on the exchange sites and hence retard movement down the profile. The amount of K leached was between 3 to 11 kg ha⁻¹ (Table 3.1). This is similar to that found by Smith *et al.* (1984) and Steele *et al.* (1984) for New Zealand pasture soils, and by Bolton *et al.* (1970) and Burke *et al.* (1974) in overseas studies.

3.4.5.3 *Magnesium*

The magnesium (Mg) concentrations in the drainage water are also shown in Figs. 3.19 and 3.20. Although magnesium was not applied, significant amounts were detected in both years' drainage. In general the concentration profiles followed the same trends as those of calcium, but were somewhat lower. Losses were between 9 and 15 kg ha⁻¹ yr⁻¹. As magnesium losses of this magnitude can lead to low Mg concentration in pasture, magnesium may need to be added to feed in early spring for treatment of hypomagnesaemia, which generally occurs then.

3.4.5.4 *Sodium*

The high sodium level in the drainage compared to most other cations (Figs. 3.19 and 3.20) is worth noting. The concentrations were much higher than those reported by Steele *et al.* (1984). This is probably due to the high salt input through rainfall, as discussed in Chapter 4. The amount lost was approximately 64 kg ha⁻¹ in 1988 and 31 kg ha⁻¹ in 1989 (Table 3.1). It is reasonable to assume a quasi-steady state for sodium in the soil with leaching losses in approximate balance with the atmospheric input from rainfall and dry deposition. It can therefore be inferred that the higher Cl concentration over Na in the drainage was attributed to the KCl application. When that was assumed, about 45% and 57% of the Cl leached in 1988 and 1989 respectively came from fertilizer KCl. The low levels of sodium

adsorbed on the exchange sites of unimproved Tokomaru silt loam (Pollock, 1975) would reflect the relatively weak adsorption of this cation, in accordance with the lyotropic series (Bohn *et al.*, 1979).

3.5 CHARGE BALANCE

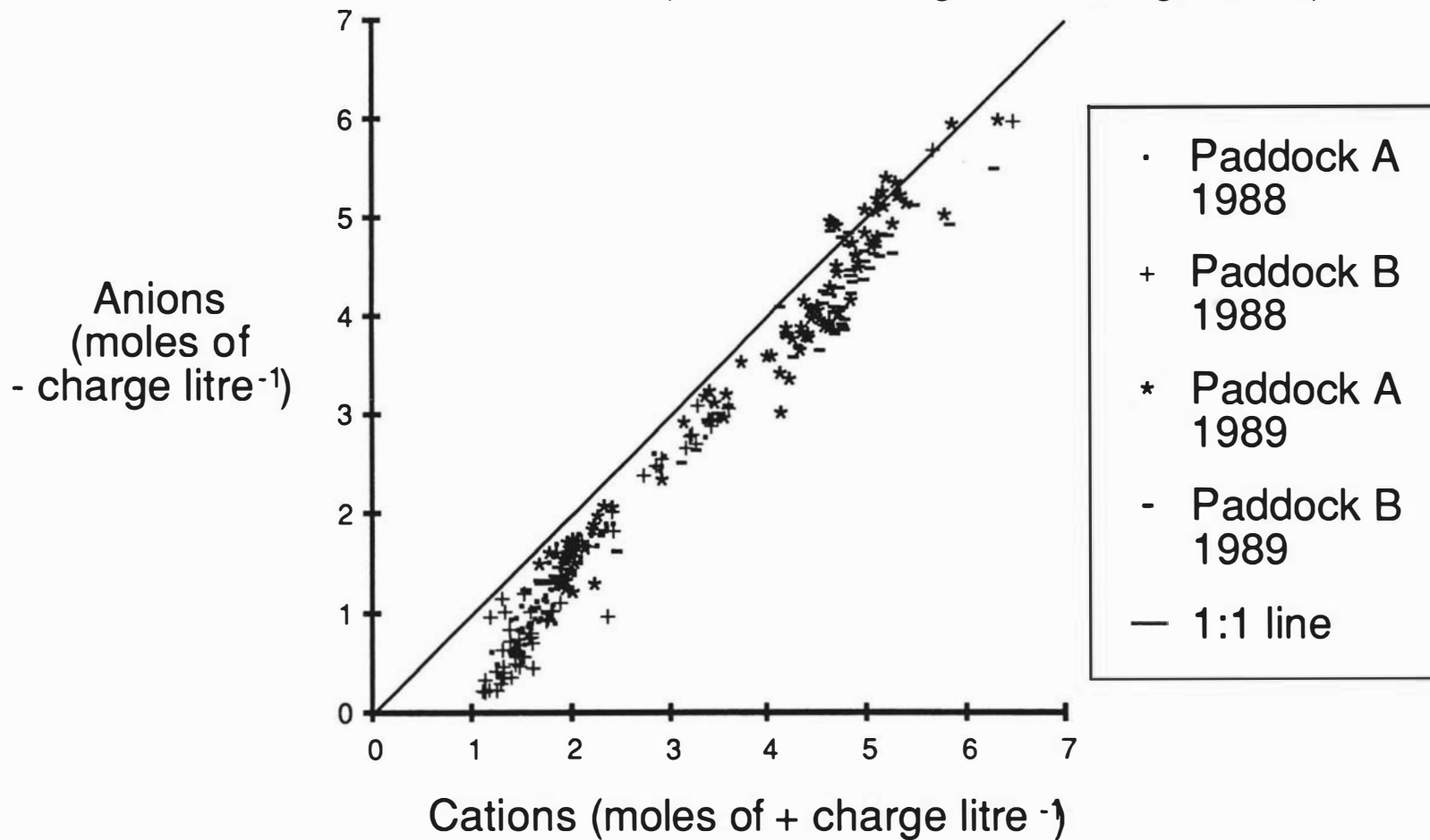
The moles of charge from the three main anions ($\text{SO}_4\text{-S}$, Cl, $\text{NO}_3\text{-N}$) in each drainage sample are plotted against the total moles of cation charge in Fig. 3.21. Phosphate was not measured because studies have shown that its concentration in drainage water is negligible relative to other anions (Turner *et al.*, 1976; Sharpley *et al.*, 1977; Steele *et al.*, 1984). The data show that there was a near balance of positive and negative charges, with only slightly more cations than anions at all concentrations. A contribution from bicarbonate may be the possible reason for the discrepancy, as pH was found to be between 6.5 and 7.5 in the drainage throughout the two drainage seasons.

3.6 SUMMARY AND CONCLUSIONS

The above results show that chloride was the dominant anion in the drainage, with losses totalling approximately $100 \text{ kg ha}^{-1} \text{ yr}^{-1}$. The large losses of Cl through leaching were due to KCl fertilizer application, and the high Cl input from wet and dry deposition from the atmosphere. The rate of leaching depended on the intensity of rainfall, as with high drain flows the chloride concentration decreased.

For sulphate, a biologically and chemically active solute, the instantaneous, reversible nature of the adsorption capacity of the soil apparently helped to buffer the sulphate concentration in the drainage, hence the amount leached was approximately proportional to the amount of drainage. The leaching pattern is also affected by the rate of mineralization of organic sulphur, and the form of sulphur applied. Application of coarse elemental sulphur instead of superphosphate on average reduced leaching losses from approximately 13 to $3 \text{ kg S ha}^{-1} \text{ yr}^{-1}$. The

Fig. 3.21 Correlation between sum of anions (moles of charge of Cl, SO₄, NO₃) and sum of cations (moles of charge of Ca, Mg, K, Na)



results also show that application of SSP in late autumn or early winter resulted in a large proportion of it being leached, hence such practice is not recommended. In situations where sulphur is needed, pure elemental sulphur or a mixture of S⁰ with reactive phosphate rock or partially acidulated phosphate rocks should be considered as alternatives.

The amount of nitrogen lost was less than 20 kg N ha⁻¹ yr⁻¹, so relatively little was lost through leaching. This could have been due to the relatively small inputs to the system from fertilizer and grazing animals. Although as much as 150 to 200 kg ha⁻¹ of nitrogen can be fixed symbiotically, a significant amount of N is also being taken up by pasture.

Leaching of potassium was minimal, even when it was applied in relatively large quantities just before the drainage season. Losses totalled less than 11 kg ha⁻¹ yr⁻¹. Relatively large amounts of sodium were leached, with amounts up to 65 kg ha⁻¹ yr⁻¹. As no sodium was added, this reflects the significance of Na contributed through wet and dry deposits from the atmosphere. Substantial amounts of calcium and magnesium were also leached, the losses amounting to approximately 40 and 10 kg ha⁻¹ yr⁻¹ respectively. These losses should be taken into account when fertilizers and food additive recommendations are being made.

Close agreement between the anion and cation moles of charge in the drainage samples was obtained, even though the contribution from bicarbonate ions was not measured.

CHAPTER 4
SOIL AND PASTURE MEASUREMENTS AND ELEMENT MASS
BALANCES

4.1 SOIL DATA

4.1.1 Bulk Density

Bulk density data are given in Table 4.1. Data for depths greater than 150 mm are from Scotter *et al.* (1979a). The bulk density in Tokomaru silt loam topsoil is approximately 1 Mg m⁻³, but it increases markedly with depth.

Table 4.1 Bulk density of the Tokomaru silt loam (means and standard errors)

Depth (mm)	Bulk Density (Mg m ⁻³)
0 - 50	0.99 ± 0.12
50 - 100	1.18 ± 0.03
100 - 150	1.25 ± 0.03
150- 300	1.35
300 - 450	1.57
450 - 600	1.62

4.1.2 Soil Moisture

The mean volumetric water contents measured at the various soil samplings during 1988 and 1989 are given in Figs. 4.1 and 4.2. They were calculated from the measured gravimetric water contents and the bulk density values given above. The soil moisture contents at each sampling were comparable for paddocks A, B and C

Fig. 4.1 Volumetric water content profiles in 1988 for paddocks A (+), B (.) and C (*)

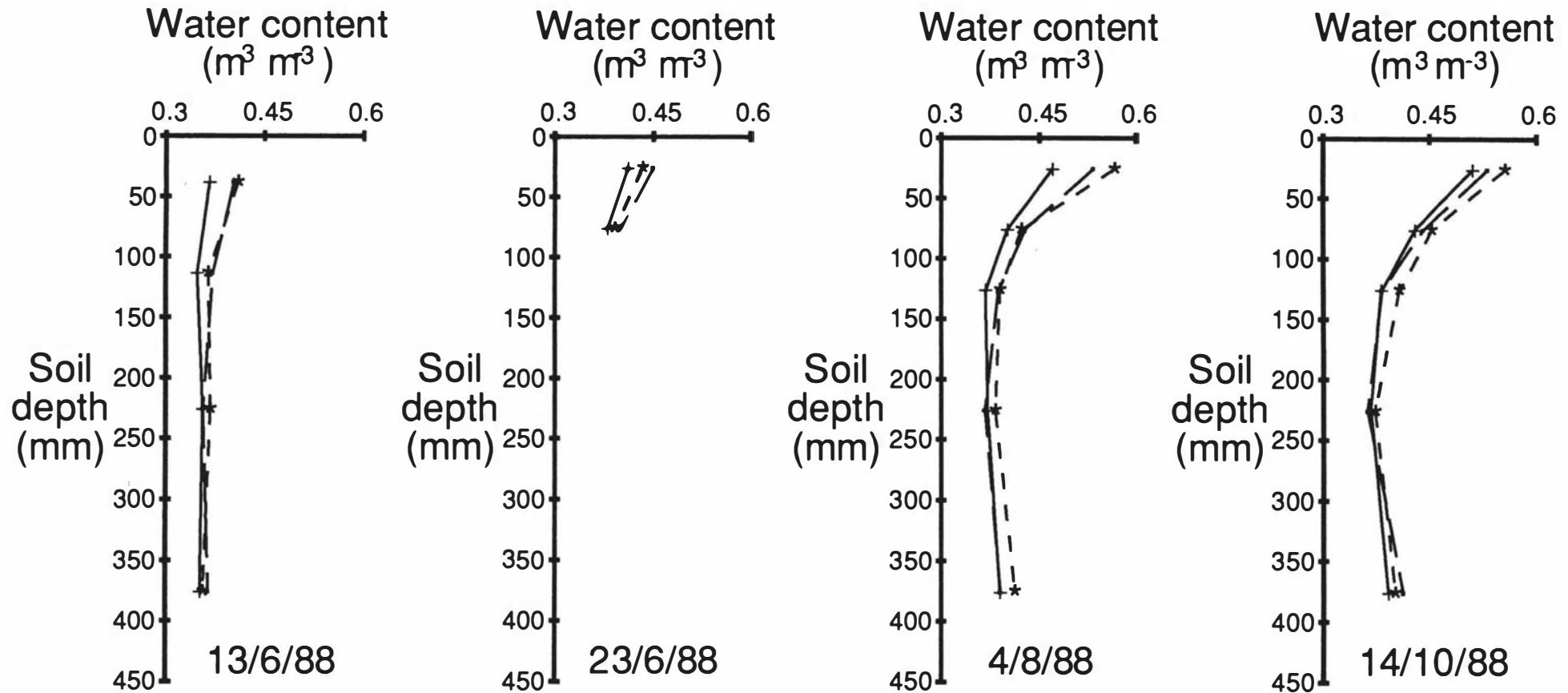
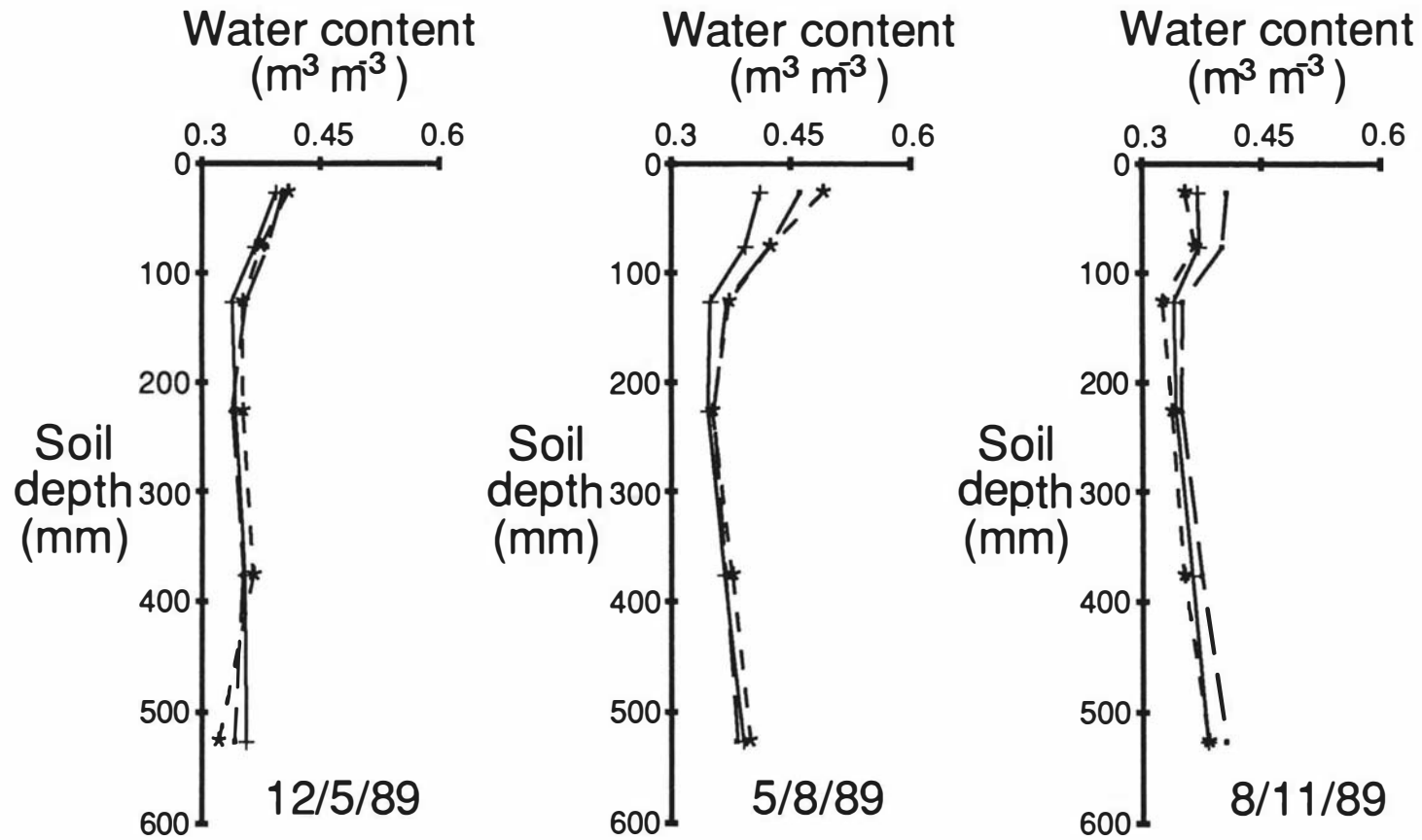


Fig. 4.2 Volumetric water content profiles in 1989 for paddocks A (+), B (.) and C (*)



throughout the experimental period. In general, moisture contents before fertilizer application was less than those later in the year, and the soil was drier in 1989 than in 1988.

4.1.3 Soil Chloride

Soil chloride concentration data are given in Figs. 4.3 and 4.4 for 1988 and 1989 respectively. The data were tested for normality using a fractile diagram (Warrick and Nielsen, 1980). Whenever a log-normal distribution was observed, the data were transformed and statistical analyses performed on the transformed data. The best estimate of the arithmetic mean was then calculated as

$$\bar{x} = \exp(\mu + \sigma^2/2) \quad (4.1)$$

where μ = mean of the $\ln x$ (x is a single measurement) and σ^2 = variance of $\ln x$ values (White *et al.*, 1987). The variance s^2 of the estimated mean was found from the following equation (Parkin *et al.*, 1988)

$$s^2 = \bar{x}^2 [\exp(\sigma^2) - 1] . \quad - \text{wrong} \quad (4.2)$$

The paddocks exhibited very similar initial soil chloride concentrations, with a higher solution concentration in the top 100 mm, and a relatively uniform concentration in the lower layers. For soil taken on 23/6/88, a week after 95.3 kg Cl ha⁻¹ was applied, the concentration rose to around 150 g m⁻³ in the top 50 mm layer in both paddocks A and B. The concentration at 50-100 mm depth in these two paddocks was also higher than paddock C. Soil below 100 mm was not taken at this sampling. During the week between fertilizer application and soil sampling 24 mm of rain fell. A mass balance calculation showed that most of the applied chloride remained in the top 100 mm in the first week, indicating little downward movement of chloride beyond 100 mm depth, despite the rainfall.

A total of 202 mm of rainfall fell between 23/6/88 and the next sampling on 4/8/88. This caused a large quantity of drainage, which resulted in considerable movement

Fig. 4.3 The distribution of chloride in the soil profiles of paddocks A (+), B (.) and C (*) in 1988

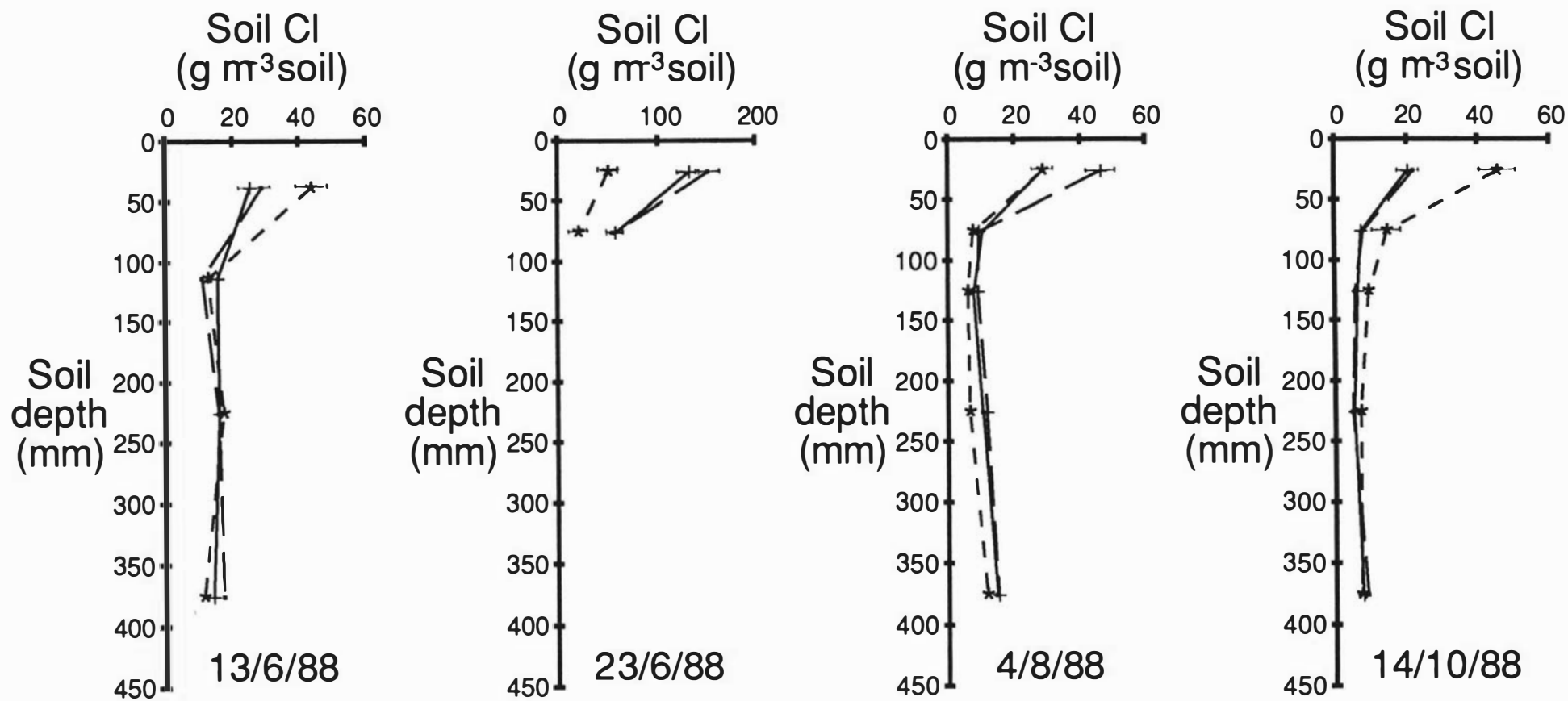
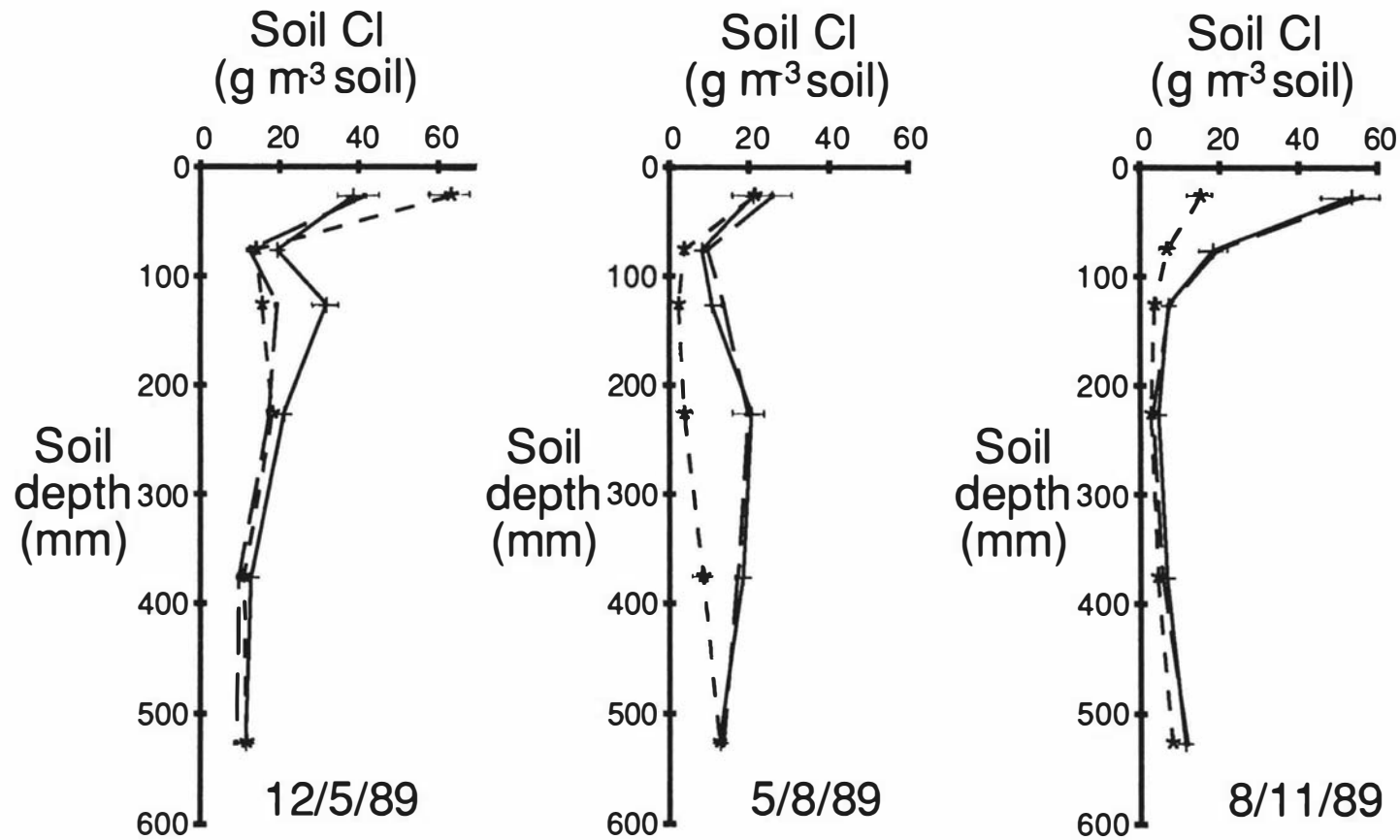


Fig. 4.4 The distribution of chloride in the soil profiles of paddocks A (+), B (.) and C (*) in 1989



and leaching of soil chloride. The amount of chloride remaining in the soil during this and the following sampling taken on 14/10/88 was close to the level prior to its application. These low soil chloride concentrations were also reflected in the low drainage chloride concentration towards the end of the drainage season. It is interesting to observe that even towards the end of the season, higher chloride levels were found in the topsoil.

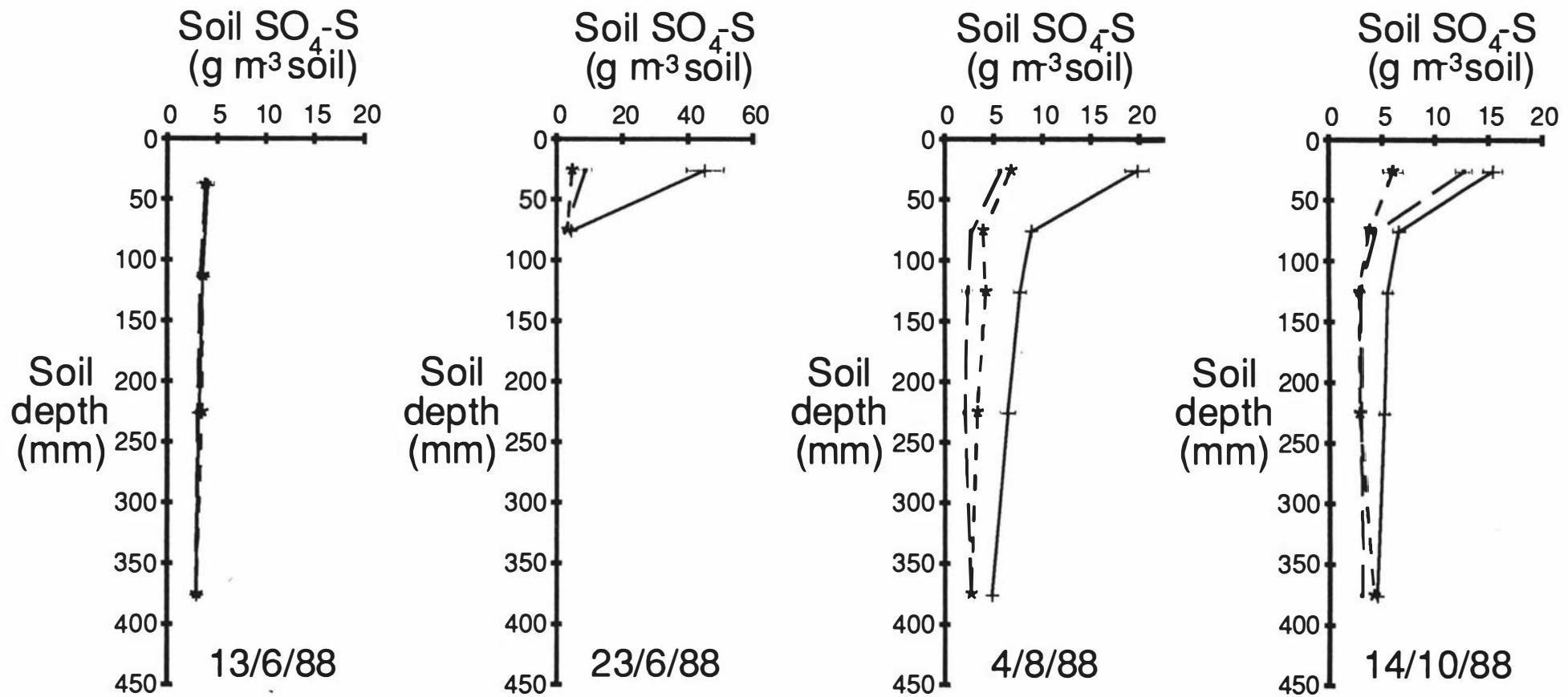
The initial chloride distribution in the soil profile in 1989 (Fig. 4.4) was quite different from that at the end of the previous drainage season. The chloride profiles on 12/5/89 showed generally higher soil solution chloride levels than the last sampling in 1988, although no Cl fertilizer was applied over the summer and early autumn period. Urine patches from sheep could be part of the cause of the increase, however the most likely reason was the atmospheric input of Cl. The increase at the lower depths was probably because of upward movement from greater depths induced by water extraction by plant roots.

Only approximately 70 mm of drainage occurred between the first two soil samplings in 1989, which was less than half the quantity in 1988. As a result, considerable chloride remained in the soil in paddocks A and B at the 5/8/89 sampling, especially at 150-300 mm depth. Such a build-up was not observed at this time in 1988, suggesting a difference in flow patterns. For the sampling on 8/11/89, it is interesting to see that although there was only another 30 mm of drainage after the previous sampling, the soil chloride below 100 mm depth was depleted to the level in paddock C. The uniform depletion to mole depth suggests that soil water and nutrient extraction can occur to a considerable depth.

4.1.4 Soil Sulphate

The concentration of 0.01 M $\text{Ca}(\text{H}_2\text{PO}_4)_2$ extractable soil sulphate in the soil in 1988 is shown in Fig. 4.5. A relatively uniform distribution, with concentrations around 3.5 g S m^{-3} soil, was observed for all three paddocks before fertilizer was applied. This amount was considered low according to the MAF soil S test classification. Fig. 4.5 also shows no differences in soil sulphate between the three paddocks on

Fig. 4.5 The distribution of sulphate-S in the soil profiles of paddocks A (+), B (.) and C (*) in 1988



13/6/88. The above finding agreed with the low level of drainage sulphate-S for both paddocks at the start of the season. Application of 50 kg ha⁻¹ of sulphur fertilizer in the SSP form increased the concentration to more than 45 g S m⁻³ soil in the top 50 mm of paddock A when the soil was sampled 7 days after application. However, there was no observable increase at 50-100 mm depth, suggesting little sulphate had moved below 50 mm. Assuming the level of SO₄-S in the lower depths was the same as before, and from the difference in the soil sulphate-S in the top 50 mm, it can be shown that 30 kg ha⁻¹ of the sulphate-S in the soil was not accounted for. Although interception of SSP on grass leaves and stems and incomplete dissolution of SSP granules could account for some of this, the apparent loss was probably mainly due to rapid immobilization of the applied sulphate, as observed by Till and May (1971), Chaudhry and Cornfield (1967), Gregg and Goh (1978) and Ghani *et al.* (1988) in both field and laboratory incubation studies.

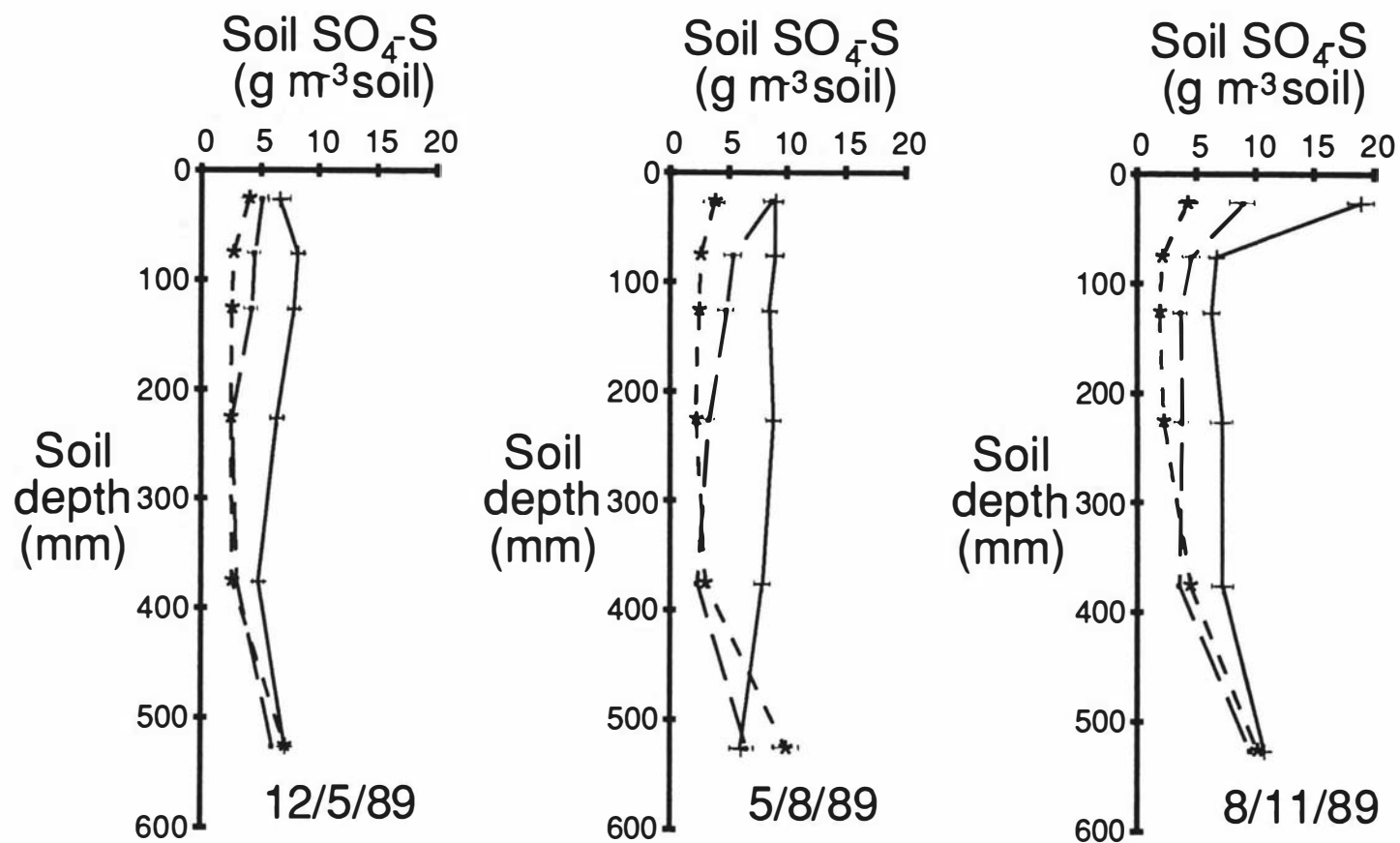
Much higher soil sulphate levels were observed throughout the profile in paddock A (SSP treatment) than paddocks B (S^o treatment) and C (control) at the 4/8/88 sampling, although by this time most of the applied chloride had been leached. This was probably due to the faster rate of dissolution of KCl compared to SSP and the faster movement of chloride compared to sulphate. With increasing drainage, less sulphate was measured in paddock A as the 14/10/88 data show.

The amount of soil SO₄-S in paddocks B and C was comparable

in 1988, except at the 14/10/88 sampling when a higher level was observed in the top 50 mm in paddock B. This was probably due to oxidation of S^o. The relatively low level in paddock B during the drainage season of 1988 suggested that little oxidation of S^o occurred. The fairly constant level of sulphate in paddock C indicates that mineralization of organic S was able to replace the sulphur that was lost through leaching and plant uptake.

Prior to fertilizer application in 1989, higher levels of soil sulphate were observed in paddock A than in the other two paddocks (Fig. 4.6). This was probably because of residual sulphate from the previous year's fertilizer application. However, the amount in the top 50 mm at the 12/5/89 sampling was very much less than at the

Fig. 4.6 The distribution of sulphate-S in the soil profiles of paddocks A (+), B (.) and C (*) in 1989



14/10/88 sampling. As minimal leaching occurred during summer, this suggests that considerably more S uptake than mineralization occurred during this period. At the 5/8/89 sampling, a considerably higher sulphate concentration was observed in the top 150 mm in paddock B but not in C, again presumably due to the oxidation of S°. This difference was also evident in the 8/11/89 sampling.

Soil measurements were made on two occasions in 1990 (Fig. 4.7). The sampling before drainage started showed a substantially higher sulphate concentration in the top 50 mm in paddock B than in paddocks A and C, probably because of additional oxidation of S°. However, the total amount of sulphate in the soil was still higher in paddock A at that sampling, and this was reflected in the higher initial concentration in the drainage in that year. The soil sampling at the end of the drainage season (4/10/90) showed little difference in sulphate level between the two fertilized paddocks; however this level was still much higher than that in paddock C.

4.1.5 Oxidation of Elemental Sulphur

The particle size distribution of the S° used in 1988 and 1989 was given in Table 3.2. The amount of S° remaining in the soil was analyzed in the top 100 mm soil samples collected in 1988. The results presented in Fig. 4.8 show mean S recoveries with systematic errors and large standard errors, with recovery around 70% for the first sampling taken on 23/6/88. The recovery decreased to around 45% 120 days after fertilizer application, but the error remained large. Difficulties in obtaining high recoveries, due to spatial variability, were also encountered by Watkinson *et al.* (1987) and Lee *et al.* (1988) in their field S° oxidation studies, especially for the big particle sizes (1-2 mm). They found that the errors tended to increase as particle size increased because as the particle size increases, the number of particles per unit area of soil surface decreases. In such situations, Lee *et al.* (1988) suggested more cores should be used for bulking to give more soil for analysis. Although this step was taken by increasing the amount of soil four times from 5 g to 20 g for extraction in the 4/8/88 sampling, it did not improve the recovery, with the standard error still large. Lee *et al.* (1988) used three particle

Fig. 4.7 The distribution of sulphate-S in the soil profiles of paddocks A (+), B (.) and C (*) in 1990

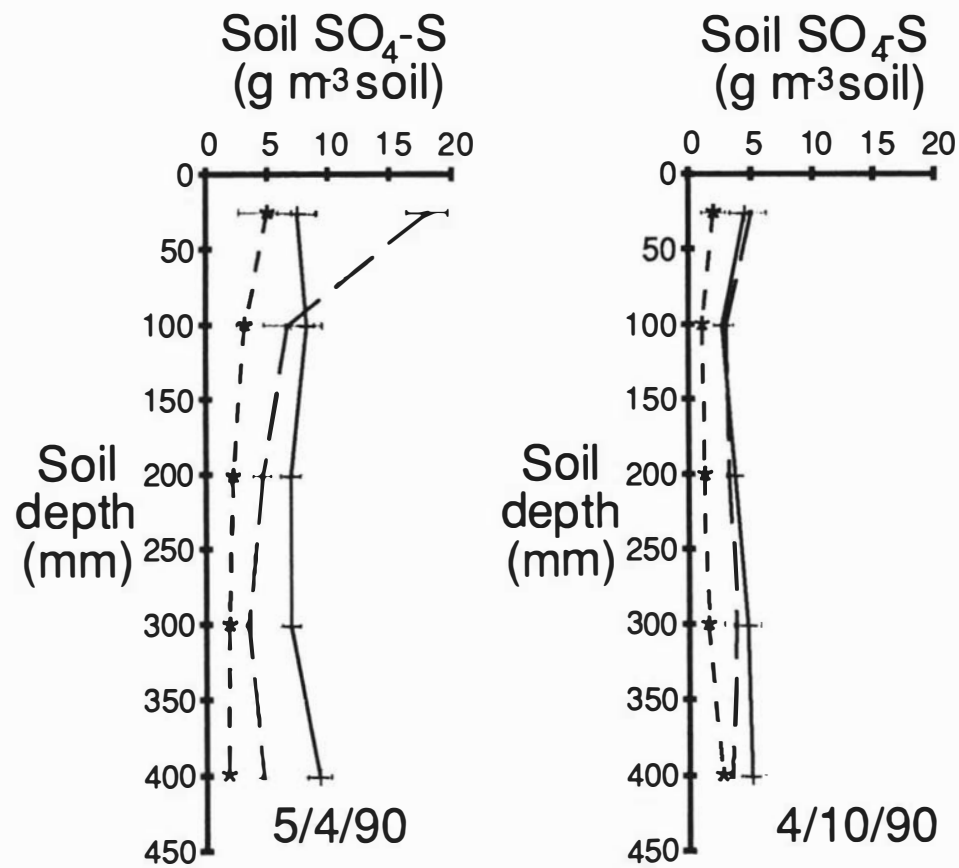
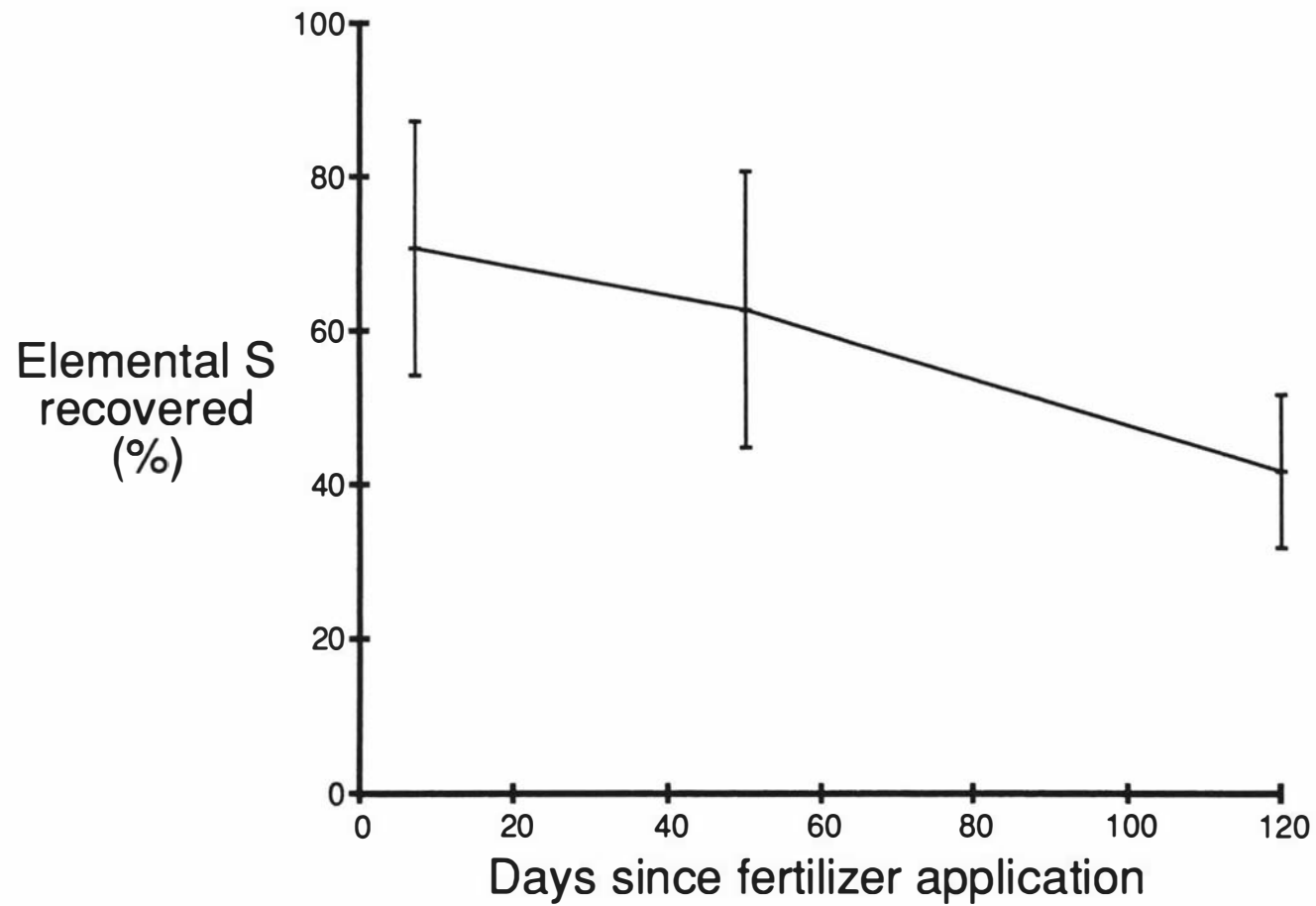


Fig. 4.8 The percentage of elemental S recovered at various sampling times in 1988



size ranges (<0.15 mm, 0.15-0.25 mm and 0.5-1.0 mm) but did not show the results for the coarsest size particles, presumably due to excessive variability.

Because of these problems, the amount of S^o remaining in the soil was not measured in 1989. Rather, the oxidation of S^o was predicted using the method of Chatupote (1990), which was a modification of the McCaskill and Blair (1989) approach.

In the model of Chatupote (1990) particles are assumed to be spherical in shape and the rate of oxidation to be proportional to surface area, i.e.

$$\frac{d}{dt} \left(\frac{4}{3} \pi r^3 \rho_s \right) = k 4 \pi r^2 \quad (4.3)$$

where r is particle radius [L], ρ_s is the specific gravity of the S^o particles [$M L^{-3}$], and k is a proportionality constant [$M L^{-2} T^{-1}$]. From Equation (4.3) it follows by differentiation that

$$\frac{dr}{dt} = k / \rho_s. \quad (4.4)$$

Equation (4.4) above shows that the rate of change in the radius is constant.

Assuming that the particles initially had radius r_o [L], and were applied at a rate of X_o [$M L^{-2}$], then the amount remaining after time t is

$$X = X_o (r/r_o)^3. \quad (4.5)$$

Differentiating Equation (4.5) with respect to time, and using the chain rule gives

$$\frac{dX}{dt} = 3X_o \frac{r^2}{r_o^3} \frac{dr}{dt}. \quad (4.6)$$

Equation (4.6) can be modified to take account of particles consisting of a range of sizes, and for sub-optimal temperature and moisture effects, to become

$$\frac{dX}{dt} = 3 X_o S_t S_m \frac{dr_j}{dt} \sum_{j=0}^n \frac{r_j^2 f_j}{r_{o,j}^3} \quad (4.7)$$

where S_t and S_m are factors ≤ 1 accounting for the reduction from the optimum oxidation rate due to temperature and moisture, n is the number of particle classes, f_j is the fraction of X_o in class j and $r_{o,j}$ the average initial radius of the j^{th} class. An optimum value of $0.087 \mu\text{m d}^{-1}$ for dr/dt was obtained by Chatupote (1990) from his glasshouse study.

The temperature reduction factor, S_t was calculated from the empirical relationship

$$S_t = 1 - 0.027 (25 - T_s) \quad (4.8)$$

where T_s is the mean daily soil temperature at 300 mm depth ($^{\circ}\text{C}$). The temperature at 300 mm depth was used rather than at shallower depths because soil temperature measurement was only taken at 0900 h each day. As the diurnal fluctuation in soil temperature at the 300 mm depth is very much less than that at 100 and 200 mm, it is therefore more representative of the daily average soil temperature near the soil surface. The constant 25 is the optimum oxidation temperature ($^{\circ}\text{C}$) from the glasshouse experiments of Chatupote (1990).

The reduction due to moisture depletion was based on the following relationship from McCaskill and Blair (1989)

$$S_m = -0.386 + 2.37 F_{\theta} - 0.945 F_{\theta}^2 \quad (4.9)$$

where F_{θ} is the fractional moisture content relative to "field capacity", the latter being taken as equal to $0.5 \text{ m}^3 \text{ m}^{-3}$. Assuming only the top 20 mm of soil affects the oxidation rate, because most of the applied S° remained in that soil layer, a daily soil water balance was carried out to estimate the soil water storage in that layer. Chatupote (1990) assumed that the percentage of total evaporation from the top 20 mm of soil was proportional to the fraction of the pasture root system present in that

zone. A value of 0.21 was used based on the measurement of Williams (1988). The soil water balance in the top 20 mm for day n was then calculated as

$$W_n = W_{n-1} + (R - 0.21 E_t) \Delta t \quad \text{writing} \quad (4.10)$$

where W is the equivalent depth of water in the layer [L] (W is between 0 and 10 mm), R is rainfall intensity [$L T^{-1}$], E_t is the rate of evaporation [$L T^{-1}$], calculated using the approach given in Chapter 2, and Δt is one day. Any excess of soil water content above "field capacity" in the top 20 mm layer was considered to be lost immediately as drainage. The above relation also implies that oxygen was never limiting.

Figs. 4.9 and 4.10 show the predicted oxidation rates for S^0 over the experimental period in 1988, 1989 and 1990. Using this approach cumulative totals of 4.6, 17.6 and 28.0 kg S ha⁻¹ were predicted to have been oxidized by the end of the 1988, 1989 and 1990 drainage seasons respectively. Values for 1989 and 1990 are the result of simultaneous oxidation of both the 1988 and 1989 applications. The simulated results show that less than 10% of the sulphur applied was oxidised in 1988, which was the likely reason for the low drainage sulphate concentration from paddock B in that year. The model predicted that by the end of 1990 only 35% of the 80 kg ha⁻¹ of elemental sulphur applied had been oxidised. As a significant number of assumptions have been made in the model, the above predicted values can only be treated as approximate.

4.1.6 Sulphate Adsorption Isotherm

Both the field and laboratory determined isotherms are given in Fig. 4.11. The field isotherm was obtained from the soil sulphate-S extracted using 0.01 M Ca(H₂PO₄)₂ and solution sulphate-S from the suction cups. It is assumed that the Ca(H₂PO₄)₂ extractable sulphate consists of both adsorbed and solution sulphate, and that the suction cup measurements are representative of the soil solution. The suction cup sulphate at 200 mm depth for the three paddocks was therefore correlated with the soil sulphate at that depth for various sampling times in 1988

Fig. 4.9 Predicted oxidation of elemental S applied in 1988

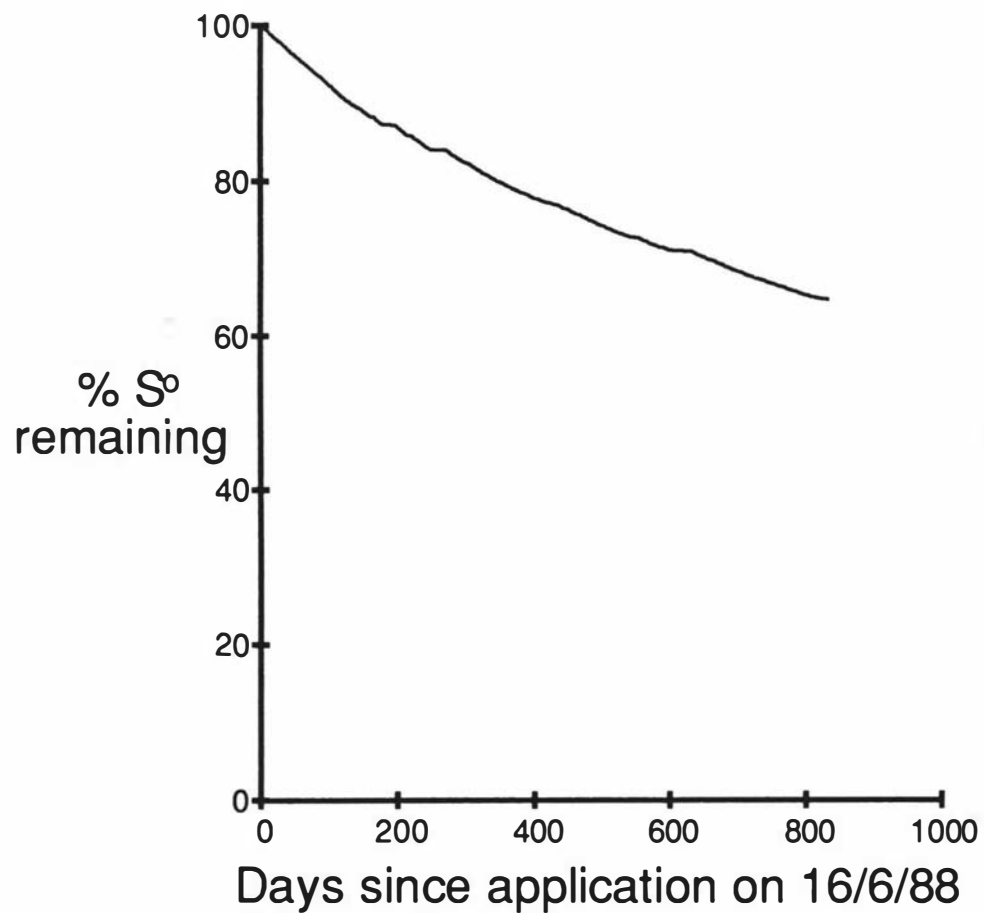


Fig. 4.10 Predicted oxidation of elemental S applied in 1989

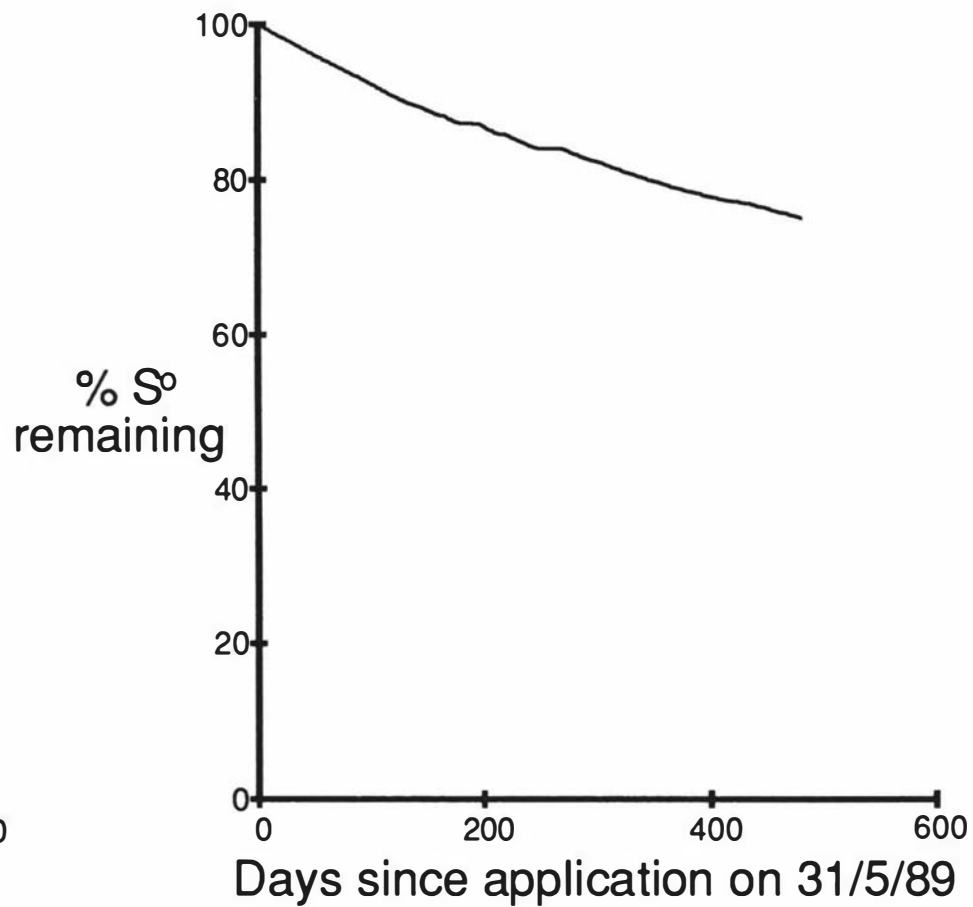
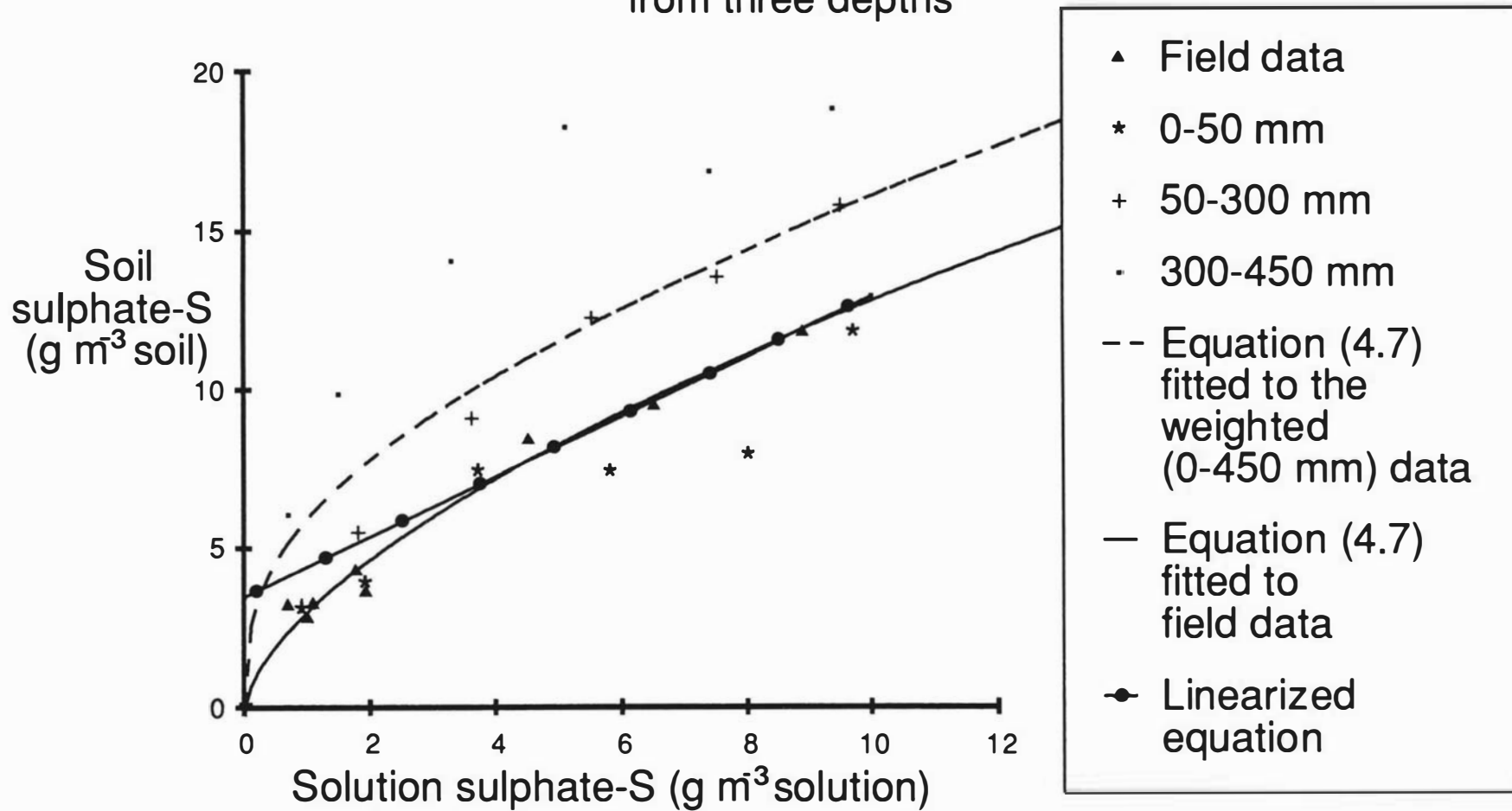


Fig. 4.11 Measured and predicted sulphate-S adsorption data obtained using field suction cups and batch method determinations on soil samples from three depths



and 1989. Each suction cup concentration in Fig. 4.11 represents the average of 10 measurements, and for the soil samples, it was the average of 9 or 15 soil samples from each paddock taken at the time when the suction cup measurements were made. An equation of the Freundlich type was used to relate the two concentrations, given as

$$M = aC^b \quad (4.11)$$

where M is the average soil concentration obtained from the $\text{Ca}(\text{H}_2\text{PO}_4)_2$ extractable sulphate, in units of g S m^{-3} soil, C is the average solution concentration (g S m^{-3} solution), and a and b are empirical constants. M consists of both the solution and adsorbed sulphate. The fitted equation is given in Table 4.2.

Table 4.2 Freundlich type equation fitted to the laboratory and field measured isotherms (units are given in Fig. 4.11.)

Isotherms	Fitted equation
Laboratory batch method:	
0-50 mm depth	$M = 2.87 C^{0.397}$
50-300 mm depth	$M = 3.78 C^{0.382}$
300-450 mm depth	$M = 5.63 C^{0.284}$
Weighted average (0-450 mm depth)	$M = 5.57 C^{0.465}$
Field method:	$M = 3.03 C^{0.627}$

The laboratory batch method adsorption isotherms for the three depths (0-50 mm, 50-300 mm and 300-450 mm) show a gradual increase in adsorption with depth, with adsorption nearly 2-3 times greater at the lowest depth compared to the topsoil (Fig. 4.11). Again Equation (4.11) was fitted to the data, assuming a moisture

content, θ , of $0.5 \text{ m}^3 \text{ m}^{-3}$ for all depths and bulk densities ρ of 0.99 Mg m^{-3} for 0-50 mm depth, 1.2 Mg m^{-3} between 50-300 mm, and 1.45 Mg m^{-3} between 300-450 mm. The resulting equations are also given in Table 4.2. An average isotherm for the 0-450 mm depth, weighted according to the depth of soil in each layer is also given. Comparison of the field and laboratory-determined isotherms shows that the field isotherm was closer to the 0-50 mm depth isotherm, rather than the weighted isotherm. Hence the sulphate adsorption measured can vary depending on the method of determination. Fig. 4.11 also shows a linear isotherm for the field data between solution concentrations of 2 and 10 g S m^{-3} . This was used in the transfer function model of sulphate leaching discussed in Chapter 6.

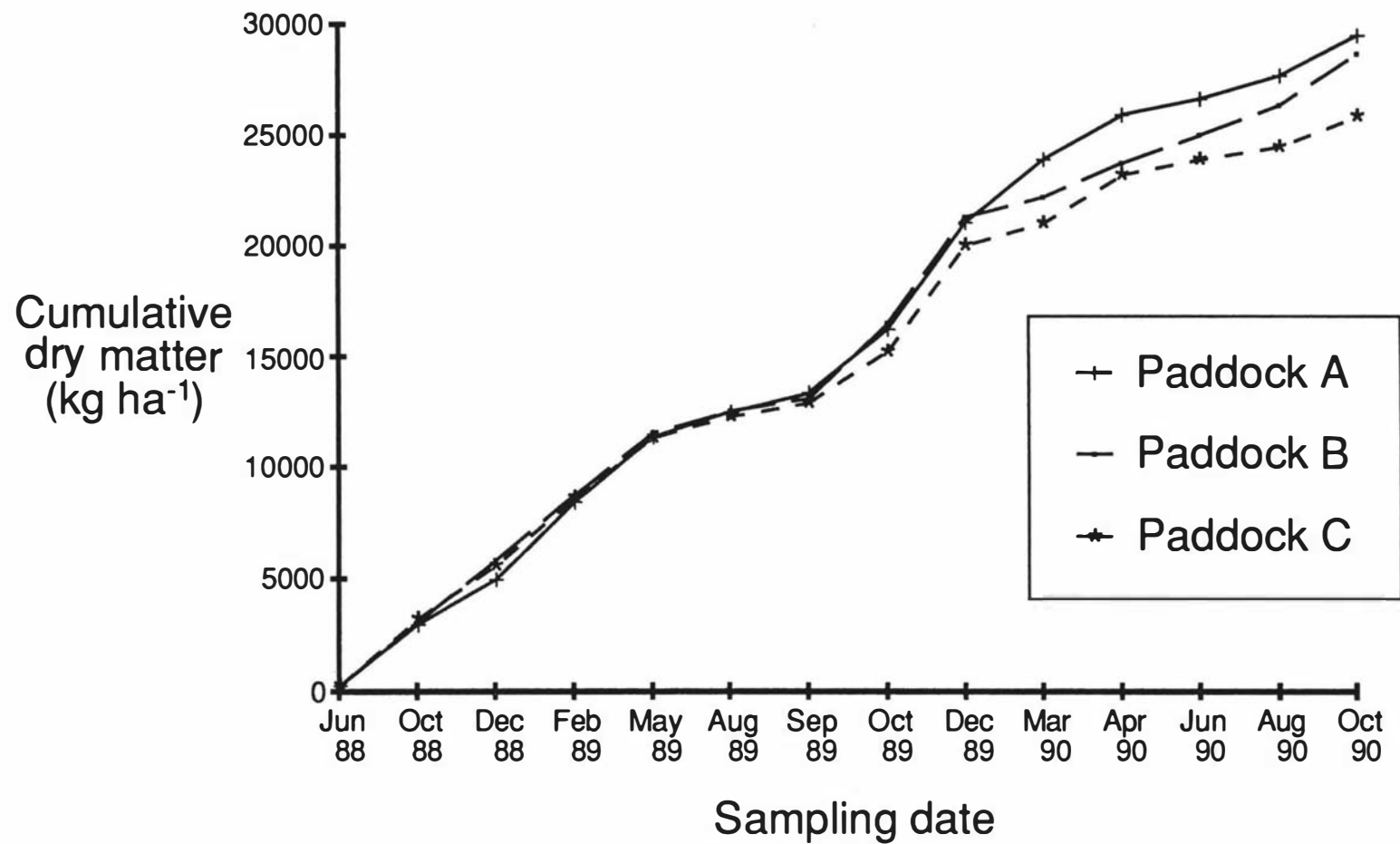
4.2 DRY MATTER PRODUCTION AND PLANT UPTAKE

4.2.1 Dry Matter Production

The cumulative dry matter production for the three paddocks is shown in Fig. 4.12. Little difference in dry matter production was observed between paddocks A and B, which had S fertilizer applied, and paddock C, the control. The results show that the pasture was not responding to fertilizer S application, despite the low initial soil sulphate concentration. A lack of correlation between pasture response and $\text{Ca}(\text{H}_2\text{PO}_4)_2$ extractable soil S test was also reported by Spencer and Glendenning (1980), Rayment (1983) and Saunders *et al.* (1987). Indications that soil testing is not a useful means of assessing the S status for grazed pasture have led a few workers to consider an alternative method of assessing S status (Hoque *et al.*, 1987; Saunders *et al.*, 1988). No response of dry matter to S application in pot trials using Tokomaru silt loam was also reported by Muller and McSweeney (1977).

The annual dry matter production for the three paddocks was about $12\,000 \text{ kg ha}^{-1}$, which is the average pasture production in the Manawatu region and in New Zealand (Smith, 1979; During, 1984; Sorn-srivichai, 1980). In all three paddocks, the fastest growth period tends to be between late spring and early summer when the weather is warm and moisture is not limiting. When these conditions occur in winter or early spring, such as in August-October 1989, rapid plant growth can also

Fig. 4.12 Cumulative dry matter production for 1988-1990



occur then. Growth was slow between February and May when moisture deficits occurred.

4.2.2 Chloride Uptake

A considerable amount of Cl was taken up by the herbage during 1988 and 1989. At the start of the experiment, the chloride content in the herbage was similar for all three paddocks, with a concentration of approximately 1.5%. This value is comparable to values reported by Goh *et al.* (1979) from their glasshouse perennial ryegrass N and S treatment studies. The herbage concentration increased after KCl application to around 2% for paddocks A and B, while values in paddock C remained between 1 and 1.5%.

The amount of uptake was calculated from the dry matter production and herbage concentration. The cumulative chloride uptake as a function of time is given in Table 4.3. A total of approximately 60 kg ha⁻¹ of chloride was estimated to have been taken up by the herbage in paddocks A and B during the drainage season of 1988. The amount was even higher in 1989. On the other hand, about 50 kg ha⁻¹ of Cl was taken up by herbage in paddock C in each drainage season.

Table 4.3 Cumulative chloride uptake (kg ha^{-1}) in herbage as a function of time

Period	Paddock A	Paddock B	Paddock C
Jun 88 - Oct 88	57.6	63.5	49.3
Jun 88 - Dec 88	89.5	111.9	84.1
Jun 88 - Feb 89	144.8	161.5	129.6
Jun 88 - May 89	195.9	210.9	166.8
Jun 88 - Aug 89	213.2	224.3	177.4
Jun 88 - Sep 89	225.7	232.0	185.5
Jun 88 - Oct 89	272.6	291.2	215.8

4.2.3 Sulphate Uptake

There was an apparent difference in the S concentration in the herbage, and hence the amount of plant S uptake between the paddocks (Figs. 4.13 and 4.14). The three paddocks started with almost the same plant S content of 0.22% before S fertilizer was applied in 1988, which was slightly below the critical level of 0.24% for pasture (McNaught and Chrisstoffels, 1961). The concentration increased rapidly to approximately 0.35% S for herbage in paddock A by October 1988 and remained relatively constant at that level, except at the December 1989 sampling. A slower increase in herbage S level was observed in paddock B over the same period of time, with the concentration there approaching that in paddock A by May 1989. The rapid increase in herbage S concentration in paddock A in 1988, with concentrations much higher than those in the other two paddocks, indicates "luxury uptake" following the application of SSP fertilizer. Luxury uptake of sulphur is commonly observed (O'Connor and Vartha, 1969; Spencer *et al.*, 1977). The higher S content in S° herbage samples compared to those from paddock C suggests that there was some contribution of sulphate from the oxidation of S°. A drop in S

Fig. 4.13 Concentration of sulphur in herbage for 1988-1990

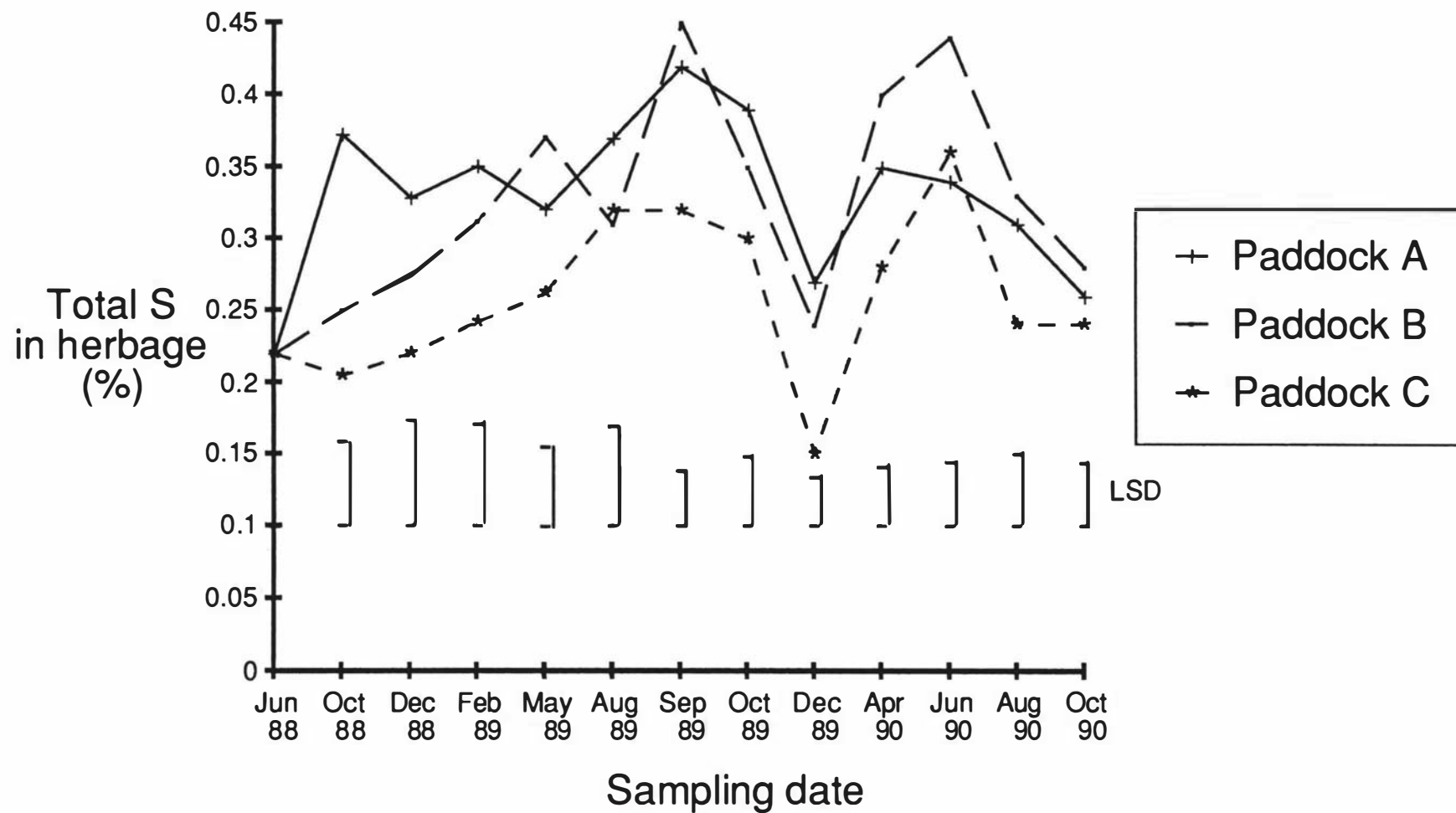
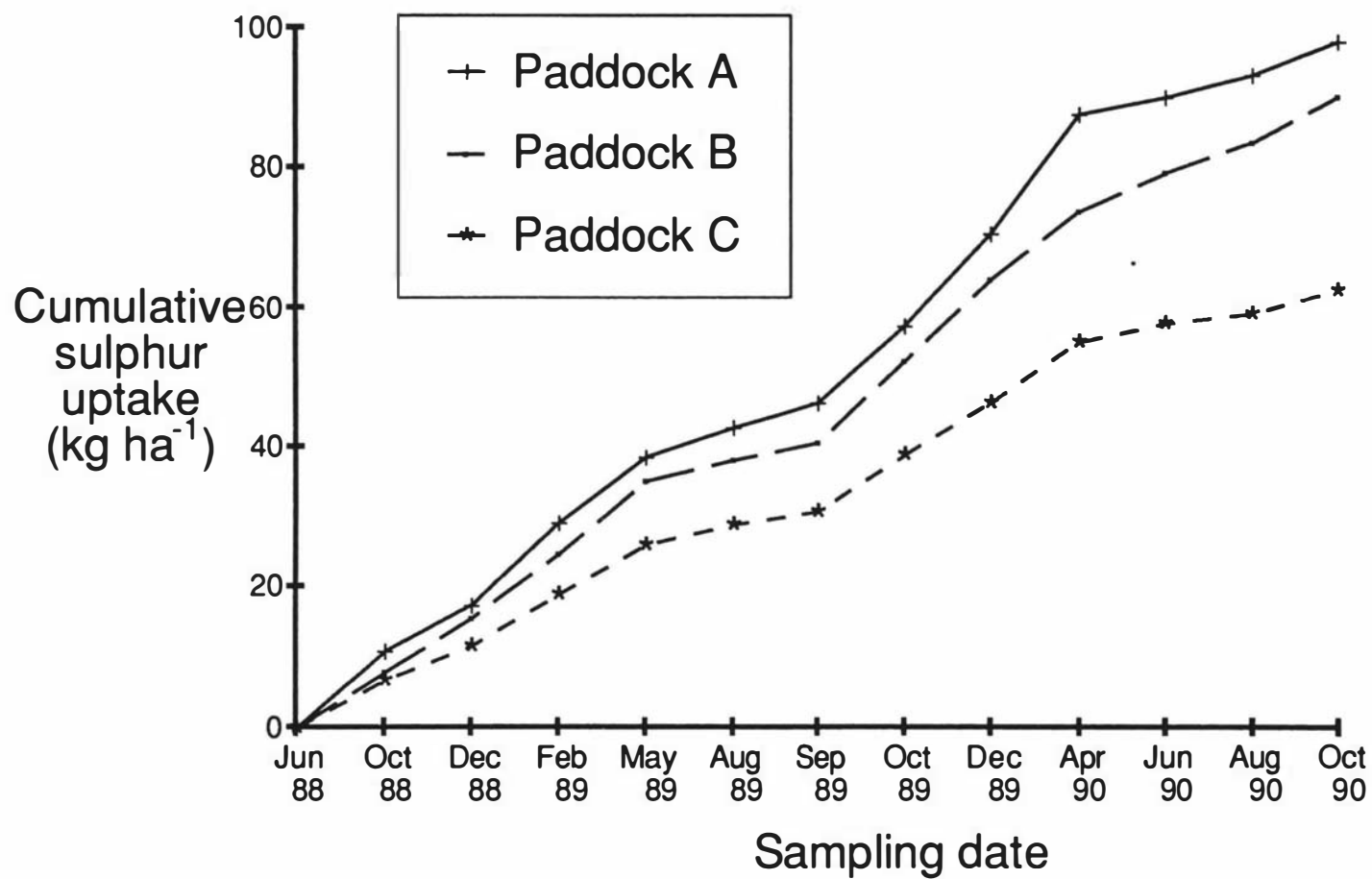


Fig. 4.14 Cumulative plant sulphur uptake for 1988-1990



content was observed in the three paddocks towards the end of 1989, after the rapid growth in September-October, which probably depleted much of the available soil S.

The cumulative S uptake for paddocks A, B and C with time is given in Fig. 4.14. In general, higher uptake occurred in paddock A compared to paddocks B and C. Approximately 10 kg S ha⁻¹ was taken up by pasture from paddock A at the end of the drainage season in 1988, however, this value is not significantly different from those from paddocks B and C. A total of 38, 35 and 26 kg ha⁻¹ of S had been taken up by the herbage in paddocks A, B and C respectively a year after the experiment started in June 1988. No significant difference was observed between the two fertilized paddocks, a significant difference in plant S uptake was only observed in the control paddock C compared to the two fertilized paddocks. By the end of the drainage season in 1990, a total of 98 kg S ha⁻¹ had been taken up from paddock A, while for the same period, the amount taken up from paddocks B and C was 90 and 63 kg ha⁻¹ respectively. The 27 kg S ha⁻¹ extra plant S uptake from paddock B compared to C was probably obtained from the oxidation of S⁰.

4.3 RAINFALL CHLORIDE AND SULPHATE

Rainfall chloride and sulphate were measured on several occasions during the drainage seasons of 1988 and 1989. Rain water from individual rainfall events was bulked, the average of three bulked samples giving 4.0 ± 0.1 g Cl m⁻³ and 0.5 ± 0.05 g S m⁻³ for chloride and sulphate respectively. This implies a total of 20.4 kg ha⁻¹ Cl for the drainage season of 1988 and an average of 40 kg ha⁻¹ yr⁻¹; assuming an average annual rainfall of 1000 mm. At Taita, near Wellington in New Zealand, Blakemore (1973) recorded an average of 113 kg Cl ha⁻¹ yr⁻¹ between 1963-1971, which is more than twice the amount recorded in this experiment. However, as Taita is only 12 km from the sea, a higher value is expected there. Although the rainfall sulphate level may seem low, its contribution can be significant. With an average annual rainfall of 1000 mm in Palmerston North, it amounts to 5 kg S ha⁻¹ yr⁻¹. The rainfall sulphate data are comparable to those given by Smith *et al.* (1983) of 5.5 kg S ha⁻¹ yr⁻¹ in the Manawatu region of New Zealand. Both McLaren and

Cameron (1990) and Ledgard and Upsdell (1991) gave rainfall S values for other parts of New Zealand. Rainfall S could be an important source of S for grazed pasture in regions near the coast where leaching losses are not significant. Using the rainfall concentration given above, estimates were made of the S contribution from rainfall in 1990. The value is given in the mass balance table presented below.

4.4 ANIMAL RETURNS

The amount of chloride and sulphur deposited through animal excreta was not measured in this experiment. However it was estimated from published data, assuming pasture utilization was 70% (Sinclair *et al.*, 1985) and an accumulation of 15% of ingested element in animal product (Sinclair *et al.*, 1985). As there was no contribution from dung, the amount of chloride deposited through urine was then 0.7×0.85 of the total chloride uptake for the period between grazings.

A similar approach was used to calculate the amount of sulphur returned from animals. However, because both dung and urine contain sulphur, in a 40:60 ratio (Wilkinson and Lowrey, 1973), with sulphur in dung in an organic form which is not readily available, the contribution of animal S was assumed to be only from urine. The amount deposited was estimated as $0.7 \times 0.85 \times 0.6$ which is 0.36 of the total S uptake for the period between grazings.

4.5 MASS BALANCES

4.5.1 Chloride Mass Balance

Table 4.4 gives the chloride mass balances for the drainage season of 1988. Good balance was observed, implying all the major inputs and outputs were reasonably accurately measured or estimated, unless compensating errors occurred. Leaching was the greatest loss in 1988.

The chloride mass balance for the drainage period in 1989 is given in Table 4.5. The magnitudes of leaching and plant uptake were similar in 1989. In this year, because of grazing, animal return contributed towards the balance. A less complete recovery is observed, with values between 81 % and 87% respectively. The reason for this is not known, it may be due to the effect of grazing, or other cumulative errors.

Table 4.4 Mass balance of chloride for 1988, in kg Cl ha⁻¹

Paddock A	Input	Output	Paddock B	Input	Output
Herbage:	3.8	57.6	Herbage:	2.9	63.6
Soil:	98.9	45.1	Soil:	104.8	48.5
Fertilizer:	95.3	0.0	Fertilizer:	95.3	0.0
Leachate:	0.0	117.8	Leachate:	0.0	92.8
Rainfall:	20.4	0.0	Rainfall:	20.4	0.0
Animal:	0.0	0.0	Animal:	0.0	0.0
Total:	218.4	220.5	Total:	223.4	204.9
Recovery:	101.0%		Recovery:	91.7%	

Table 4.5 Mass balance of chloride for 1989, in kg Cl ha⁻¹

Paddock A	Input	Output	Paddock B	Input	Output
Herbage:	0.0	76.7	Herbage:	0.0	77.3
Soil:	148.4	91.4	Soil:	118.3	88.3
Fertilizer:	95.3	0.0	Fertilizer:	95.3	0.0
Leachate:	0.0	76.3	Leachate:	0.0	71.9
Rainfall:	13.7	0.0	Rainfall:	13.7	0.0
Animal:	46.0	0.0	Animal:	43.3	0.0
Total:	303.4	244.4	Total:	273.7	237.5
Recovery:	81%		Recovery:	87%	

4.5.2 Sulphur Mass Balance

The mass balances for sulphur are given in Tables 4.6, 4.7 and 4.8 for 1988, 1989 and 1990 respectively. Note net mineralization over each drainage season has been ignored. A relatively good recovery was observed each year. For all three drainage seasons and in particularly the first one, leaching was the largest loss in paddock A. However, this component was relatively small in paddock B, where herbage uptake accounted for most of the loss. The results confirm that applying SSP before the drainage season increases the leaching losses of sulphate, and that leaching losses can be reduced by using the less soluble elemental S form of S fertilizer.

Table 4.6 Mass balance of sulphate-S for 1988, in kg S ha⁻¹

Paddock A	Input	Output	Paddock B	Input	Output
Herbage:	0.8	11.3	Herbage:	0.6	7.9
Soil: SO ₄ -S	19.0	34.9	Soil: SO ₄ -S	19.0	23.2
: S°	0	0	: S°	0	45.4
Fertilizer:	50.0	0.0	Fertilizer:	50.0	0.0
Leachate:	0.0	17.0	Leachate:	0.0	3.4
Rainfall:	2.5	0.0	Rainfall:	2.5	0.0
Animal:	0.0	0.0	Animal:	0.0	0.0
Total:	72.3	63.2	Total:	72.1	79.9
Recovery:	87%		Recovery:	111%	

Table 4.7 Mass balance of sulphate-S for 1989, in kg S ha⁻¹

Paddock A	Input	Output	Paddock B	Input	Output
Herbage:	0.0	17.6	Herbage:	0.0	16.2
Soil: SO ₄ -S	36.4	48.2	Soil: SO ₄ -S	20.2	25.0
: S°	0.0	0.0	: S°	42.2	62.4
Fertilizer:	30	0.0	Fertilizer:	30.0	0.0
Leachate:	0.0	9.4	Leachate:	0.0	3.5
Rainfall:	1.7	0.0	Rainfall:	1.7	0.0
Animal:	6.3	0.0	Animal:	5.8	0.0
Total:	74.4	75.2	Total:	99.9	107.1
Recovery:	101%		Recovery:	107%	

Table 4.8 Mass balance of sulphate-S for 1990, in kg S ha⁻¹

Paddock A	Input	Output	Paddock B	Input	Output
Herbage:	0.0	10.4	Herbage:	0.0	16.3
Soil: SO ₄ -S	45.2	24.5	Soil: SO ₄ -S	34.8	20.5
: S°	0.0	0.0	: S°	57.4	52.0
Fertilizer:	0.0	0.0	Fertilizer:	0.0	0.0
Leachate:	0.0	12.3	Leachate:	0.0	9.5
Rainfall:	2.1	0.0	Rainfall:	2.1	0.0
Animal:	2.0	0.0	Animal:	3.0	0.0
Total:	49.3	47.2	Total:	97.3	98.3
Recovery:	96%		Recovery:	101%	

4.6 SUMMARY AND CONCLUSIONS

A high level of chloride was found in the soil at the start of each drainage season. This was apparently due to atmospheric deposition over summer when there was little drainage. An average of 4 g Cl m^{-3} was measured for rainfall chloride. A high concentration of plant chloride was also measured, indicating a significant amount of uptake over each drainage season.

A low soil sulphate-S level was measured in all three paddocks at the start of the study in 1988; although there was no pasture growth response to the addition of sulphur fertilizer, irrespective of the form of fertilizer applied. The concentration of S in the herbage was generally higher in paddock A than in paddock B, although the difference was not statistically significant. However over the whole study period significantly less S plant uptake was observed in the control paddock C compared to the fertilized paddocks A and B.

Measurement of the oxidation of S^0 by soil sampling was attempted during the 1988 drainage season. Only 70% of the S^0 applied was recovered 7 days after its application, and only 45% after 120 days. A large systematic error and spatial variance was associated with each sampling. The soil measurements referred to above imply the oxidation of 25% of the amount applied (i.e. $12.5 \text{ kg S ha}^{-1}$) between days 7 and 120 after S^0 application in 1988. As there was some doubt as to the reliability of these measurements, an alternative way of estimating the oxidation of S^0 was adopted, using a previously calibrated model. The model predicted that only 4.6 kg S ha^{-1} had been oxidized by the end of the 1988 drainage season, which is only a one-third the amount estimated from the soil S^0 oxidation measurements. Although both methods of estimating involve errors, the consistently low sulphate concentration in paddock B throughout the drainage season seems to suggest the estimation using the S^0 model is more accurate.

The difference in plant S uptake between paddocks B and C can also be used to give an indication of the amount of S^0 oxidized over an extended period. If it can be assumed that factors such as net mineralization, leaching losses and changes in soil

sulphate levels in these two paddocks are the same, the higher plant S uptake in paddock B compared to paddock C can then be assumed to be due to the oxidation of S^0 . A total of 33 kg S ha^{-1} difference in plant S uptake for paddocks B and C was observed over the three year study, while the oxidation prediction from the S^0 model was 28 kg ha^{-1} .

Adsorption isotherms, determined using the laboratory batch method, and in the field from suction cup and soil measurements, were found. The two methods gave different isotherms, indicating care must be taken if laboratory-determined isotherms are used to predict leaching in a field study.

Good balances were obtained for chloride and sulphate for 1988, 1989 and 1990.

CHAPTER 5

MODELLING THE LEACHING OF CHLORIDE TO A MOLE DRAIN USING A MECHANISTIC MODEL

5.1 INTRODUCTION

Studies have shown that when water and solute move through structured and heterogeneous field soils, they often involve flow processes that are not described by the convective-dispersion equation. This is particularly so when a soil is mole drained, as the cracks induced during moling often provide major pathways for water and solute. Also the flow is two-dimensional, and depending on whether the incoming water is infiltrating directly above a drain or midway between two moles, different flow patterns will pertain.

A promising approach to handling preferential flow is the bimodal (or mobile-immobile water) approach where soil water and solute are partitioned between micropores and macropores. Although solute models based on the bimodal assumption have been developed (van Genuchten and Wierenga, 1976; Addiscott, 1977), they are one-dimensional in nature and are not suitable for mole-drained systems.

Here a mechanistic solute model aimed at improving understanding of the underlying solute transport mechanisms is given. It is developed from the soil water model of Scotter *et al.* (1990), which is given as Appendix B of this thesis, and incorporates the bimodal assumption mentioned above. The model predictions are compared with the chloride leaching data given in Chapter 3.

5.2 THEORY

5.2.1 Basic Equations

The model for soil water flow to a mole drain assumes instantaneous hydraulic equilibrium in the soil above the water table and Dupuit-Forchheimer (DF) lateral

flow towards the drain in the soil below the water table. The horizontal flow through the soil towards the drain per unit length of plane parallel to the drain, Q [$L^2 T^{-1}$], is

$$Q = -(z_d - T)K dT/dx \quad (5.1)$$

where T is the depth to the water table [L], z_d is the topsoil depth [L], K is the saturated hydraulic conductivity [$L T^{-1}$] and x is horizontal distance from the mid-drain plane. All depths are measured positively downwards. A simplification of the model of Scotter *et al.* (1990) is made by assuming that flow only takes place in the topsoil. This simplification is possible because the saturated hydraulic conductivity of the topsoil is much higher than that of the subsoil (Scotter *et al.*, 1979a). In view of this, the contribution of flow to the drain from the subsoil can be ignored.

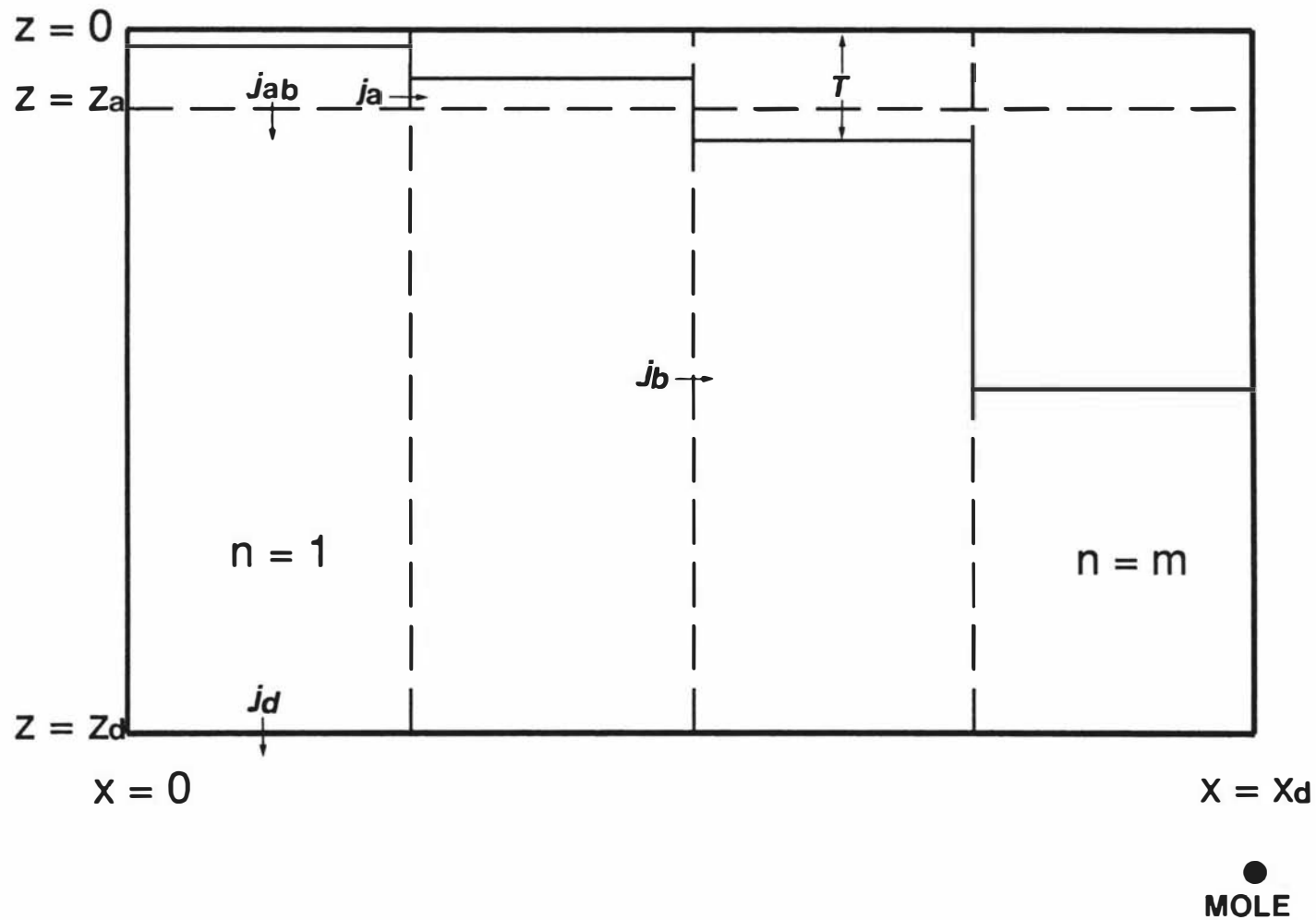
Within the topsoil, the profile is divided into two notional layers. Layer a is a thin layer from the surface to depth z_a , to take account of the vertical non-uniformity in solute distribution due to fertilizer application, and layer b extends from z_a to z_d , the boundary between the topsoil and subsoil. The soil is also divided into several notional vertical planes, giving a number of compartments (m) as shown in Fig. 5.1. The soil water, and so solute, in any compartment are assumed to be present in both mobile (denoted by subscript m) and immobile (subscript i) phases, with diffusion tending to equalize the concentration in the two phases. Water in pores still filled at a matric potential of $-\psi_m$ is defined as being effectively immobile.

As only the total horizontal movement was described in Scotter *et al.* (1990), additional equations were needed to describe the vertical water movement in order to model solute transport.

Assuming q_a is the horizontal water flux density in layer a [$L T^{-1}$]. Then

$$q_a = Q(z_a - T)/[z_a(z_d - T)]; \quad T < z_a \quad (5.2)$$

Fig. 5.1 Schematic diagram of chloride leaching model. The symbols are defined in the text



$$q_a = 0; \quad T \geq z_a \quad (5.3)$$

Given Q and q_a , the value of q_b can be found, as

$$q_b = (Q - z_a q_a) / (z_d - z_a). \quad (5.4)$$

Note q_a and q_b are averages over the whole layer, regardless of T .

Assuming a linear and non-hysteretic water characteristic for matric potentials between 0 and -500 mm, and hydraulic potential equilibrium in the soil above the water table, the volumetric water content (θ) [$L^3 L^{-3}$] below the water table is then equal to the porosity (f), and that above the water table is given by

$$\theta = f + e(z - T) \quad (5.5)$$

where e is the assumed constant slope of the retentivity curve [L^{-1}] and z is depth [L]. Integration gives W , the equivalent depth of water in the soil to depth z_d , as

$$W = fz_d - eT^2/2. \quad (5.6)$$

The change in W with time can be found from the equation of conservation of mass

$$\frac{\partial W}{\partial t} = R - E_t - q_d - \frac{\partial Q}{\partial x} - \frac{\partial R_o}{\partial x} \quad (5.7)$$

where R is the rainfall intensity, E_t is the evaporation rate, q_d is the deep percolation rate below z_d , all with dimensions [$L T^{-1}$], and R_o is the surface runoff per unit length of plane [$L^2 T^{-1}$]. Details as to how R_o is determined, and how it interacts with the drainage coefficient D_c are given in Appendix B. Solving Equations (5.1), (5.6) and (5.7) simultaneously allows Q (as a function of time) to be found.

The equivalent depth of water stored in layer a (W_a) (which is the sum of mobile and immobile water) is a function of water table depth. If the water table is above z_a the layer is essentially saturated and

$$W_a = fz_a. \quad (5.8)$$

If the water table is below z_a , and assuming the water content at $z_a/2$ represents the average water content in the layer, then

$$W_a = z_a[e(z_a/2 - T) + f]. \quad (5.9)$$

The total water in layer b (W_b) is then $W - W_a$. W can be found using Equation (5.6).

The immobile water is assumed to be constant with depth and time. For layer a ,

$$W_{i,a} = z_a(f + e\psi_m), \quad (5.10)$$

and layer b ,

$$W_{i,b} = (z_d - z_a)(f + e\psi_m) \quad (5.11)$$

where ψ_m is the matric potential dividing the mobile and immobile water. The mobile water in each layer was then found as the difference between the total and immobile water.

The remaining unknown water flow is the vertical water flux density from layer a to b ($q_{a,b}$), with dimensions $[L T^{-1}]$. Conservation of mass gives this as

$$q_{a,b} = (z_d - z_a)\partial q_y/\partial x + q_d + \partial W_y/\partial t. \quad (5.12)$$

With the water fluxes described, equations for the solute fluxes can be developed. The concentration of solute in the soil solution in each phase in each layer was calculated from the amount of solute present. For non-reactive solutes

$$C = M/\theta \quad (5.13)$$

where C is the soil solution concentration [$M L^{-3}$], and M is the amount of solute present in unit soil volume [$M L^{-3}$]. θ is given by

$$\theta = W/z . \quad (5.14)$$

Subscripts a or b and i or m added to C , M , W , θ and z in Equations (5.14) and (5.15) indicate the phase and layer involved.

Next the continuity equations for the solute are given. For solute in the mobile phase of layer a

$$\partial M_{m,a}/\partial t = S_{m,a} - \partial j_a/\partial x - j_{a,b}/z_a - \alpha \theta_{i,a}(C_{m,a} - C_{i,a}), \quad (5.15)$$

where j_a is the horizontal solute flux density [$M L^{-2} T^{-1}$], $j_{a,b}$ is the vertical solute flux density between layers [$M L^{-2} T^{-1}$], α is a rate constant for diffusion between mobile and immobile phases [T^{-1}], and S is a source/sink term [$M L^{-3} T^{-1}$] which can be used to describe processes such as mineralization, immobilization, and plant uptake, as well as accounting for additions from rainfall, animal wastes and fertilizer. As convection and dispersion are the assumed solute transport processes

$$j_a = C_{m,a} q_a - \beta q_a dC_{m,a}/dx \quad (5.16)$$

where β is a constant called the dispersivity [L]. As the dispersion coefficient D_h is given by (van Genuchten and Wierenga, 1986)

$$D_h = \beta v \quad (5.17)$$

and $v = q/\theta$,

$$\beta q = \theta D_h. \quad (5.18)$$

An analogous equation applies in layer b .

For solute in the immobile phase of layer a

$$dM_{i,a}/dt = S_{i,a} + \alpha \theta_i (C_{m,a} - C_{i,a}) \quad (5.19)$$

again with an analogous equation applying in layer b . For mobile solute in layer b

$$\partial M_{m,b}/\partial t = S_{m,b} - \partial j_b/\partial x + (j_{a,b} - j_d)/(z_d - z_a) - \alpha \theta_i (C_{m,b} - C_{i,b}) \quad (5.20)$$

where j_d is the vertical flux density out of layer b . Values of $j_{a,b}$ and j_d are assumed equal to the product of the solute concentration in the mobile phase of the layer above and the water flux density through the surface of interest. Lastly, the solute concentration of the water entering the mole drain C_d is found as

$$C_d = (j_a z_a + j_b z_b)/Q \quad (5.21)$$

where Q , j_a and j_b are evaluated at $x = x_d$.

5.2.2 Numerical Solution

A simple finite difference approach to the solution of the above set of equations was used. The compiled BASIC program was an extension of that used by Scotter *et al.* (1990). The time step used was 0.1 h; running the programme with a smaller time step confirmed its numerical stability. The only aspect that needs discussion here is how hydrodynamic dispersion was treated. The horizontal solute flux density out of

a compartment was calculated as the product of the mobile phase solute concentration in the compartment and the water flux density out of it. "Numerical dispersion" results from this approach because the concentration in the compartment rather than the concentration at the exit surface is used. If the time steps are small relative to the compartment width (Δx) divided by the water flux density, calculating the solute flux density in this way is equivalent to using Equation (5.16) with a β value of $\Delta x/2$ (Campbell, 1985). A similar argument applies to the vertical solute flux densities, but because there were only two layers, vertical solute movement is only crudely described.

The outputs from the model were cumulative drainage [L], solute concentration in the drainage [$M L^{-3}$], and total solute leached and solute remaining in the soil, both expressed in [$M L^{-2}$].

5.3 PARAMETERIZATION

5.3.1 z_a , z_d , f , e and ψ_m

The value of z_a was set at 50 mm, and z_d 300 mm. Following Scotter *et al.* (1990), values of $f = 0.526$, $e = 2.16 \times 10^{-4} \text{ mm}^{-1}$ were chosen. The matric potential dividing the mobile and immobile water (ψ_m) was taken as -500 mm. At this potential, pores with effective diameter greater than 0.06 mm are drained. This pore size is also often taken as the size of the smallest macropores (White, 1985b).

5.3.2 K , m , β , α and D_c

(Scotter *et al.* 1990).

The hydraulic conductivity K was taken as 372 mm d^{-1} . The distance between the mid-mole and the mole was divided into four compartments, giving $\Delta x = 250 \text{ mm}$. This gave β a value of 125 mm. The value of α was arbitrarily taken as 0.05 h^{-1} . This is within the range of values used by other workers for both undisturbed soil cores and field studies (Smettem, 1984; Barraclough, 1989; Scotter and Tillman, 1991). The drainage coefficient, D_c , of the present drainage system was calculated using Manning's equation to be equal to 270 mm d^{-1} . The unusually high drainage

coefficient means that there was negligible surface runoff. Deep percolation was also assumed negligible, due to the dense impermeable fragipan in Tokomaru silt loam.

5.3.3 Initial Values

The soil water and chloride contents for the top 300 mm measured the day before potassium chloride application were used as the initial values for W and M .

5.3.4 Source-Sink Term, S

5.3.4.1 Fertilizer chloride

The fertilizer chloride used in the model was that applied at the start of each drainage season, i.e. 95 kg Cl ha^{-1} .

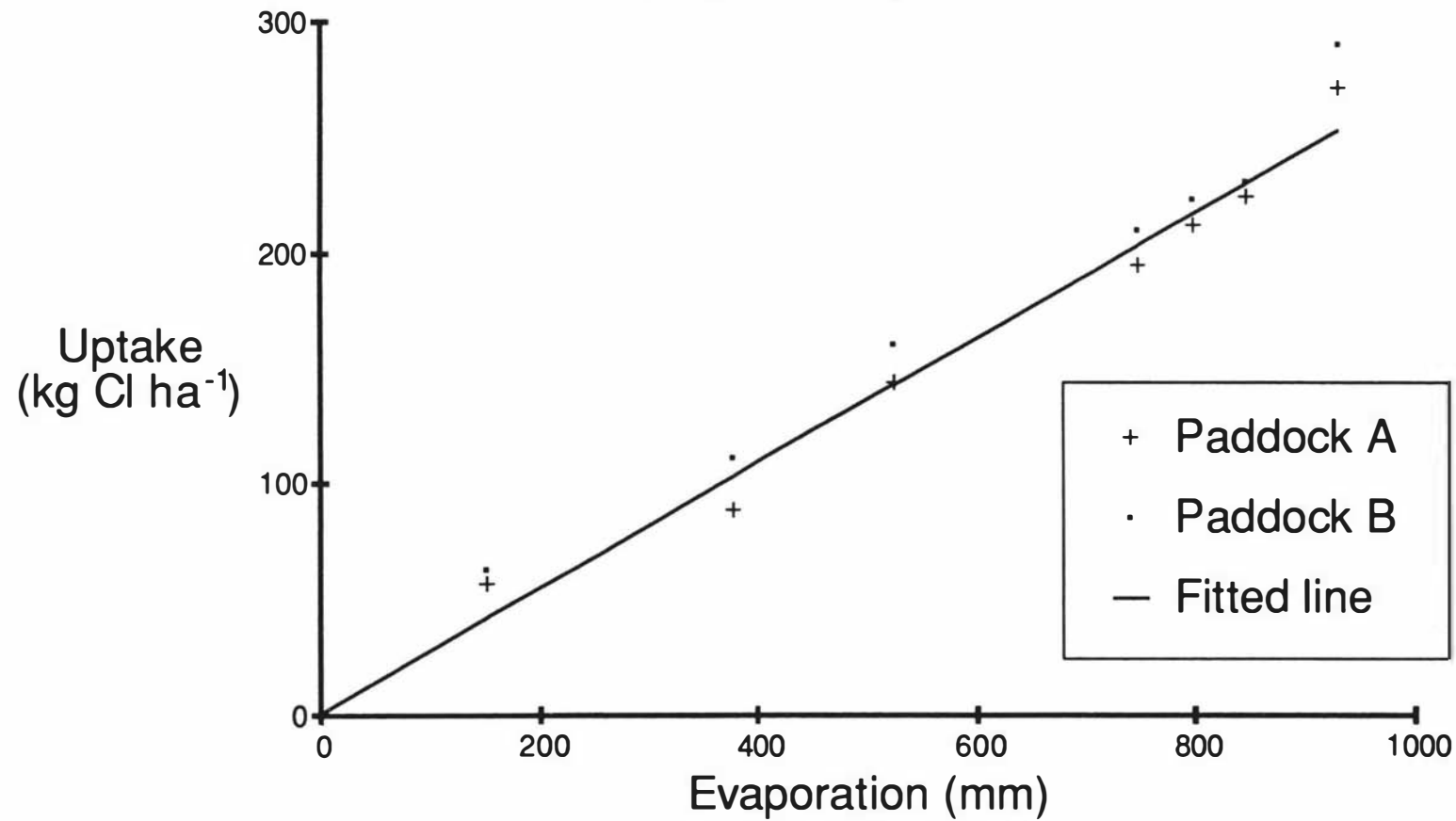
5.3.4.2 Herbage uptake

The amount of chloride taken up by herbage was assumed proportional to the rate of transpiration. The measured cumulative chloride uptake is plotted as a function of the estimated cumulative evaporation from June 1988 to October 1989 in Fig. 5.2. Except for the last measurement, the points fall close to a straight line with slope of $0.27 \text{ kg Cl ha}^{-1}$ per mm of evaporation. This value was used in the model. The product of this slope and the daily evaporation rate gave the estimated plant uptake component of S . Herbage uptake from the soil was assumed to be uniform with depth down to z_d .

5.3.4.3 Rainfall input

The product of the 4 g m^{-3} rainfall chloride concentration (given in Chapter 4) and the rainfall intensity was assumed to be the rainfall input. As no independent measurement was made of dry deposition, all atmospheric input for chloride in the model was considered to be through rainfall.

Fig. 5.2 Measured chloride uptake by pasture as a function of estimated cumulative evaporation. The line is a linear regression fitted by least squares



5.3.4.4 *Animal return*

Animal return was ignored in the model, as no grazing took place during the drainage period in 1988, and only two grazings in 1989, both after most of the drainage for that year had occurred.

5.4 RESULTS AND DISCUSSION

5.4.1 Cumulative Drainage

The predicted and measured cumulative drainage for the two years as a function of time is shown in Figs. 5.3 and 5.4. The predicted drain flow was 338 mm in 1988, 20% higher than the average of the measured values for the two paddocks (Table 5.1). The discrepancy between the measured and predicted drainage in that year was probably due in part to deep percolation below mole-drain depth. Although the subsoil is very impermeable and swells when wet, the associated swelling takes place slowly, during which time water and solute movement into the subsoil may take place (Scotter *et al.*, 1979a). Solute (sulphate) bypassing the drains in water seeping below the mole drains in Tokomaru silt loam soil has been observed by Smith (1979). Local variability, errors in the measurement of rainfall, and the estimation of evaporation are other possible causes for the discrepancy. For each parameter measured, error can be as high as 5 to 10% (Scotter *et al.*, 1979b), and the effects can be cumulative. A 5% systematic error is equivalent to 38 mm of rainfall, or 12 mm of evaporation for the 1988 winter period. This could lead to an error of 50 mm in the prediction of cumulative drainage.

The predicted drainage for 1989 was 104 mm (Fig. 5.4), 4% less than the average measured drainage (Table 5.1). Although this amount was within the range of the two measured values, short term prediction was not good, with over-prediction in the earlier part of the season and under-prediction during and after the dry period in August-September. The over-prediction in the earlier season which was also observed in 1988 could be due to deep percolation, while under-prediction later in the season was most likely due to over-estimation of evaporation in the dry August-

Fig. 5.3 Measured and predicted cumulative drainage as a function of time after fertilizer application on 16/6/88.

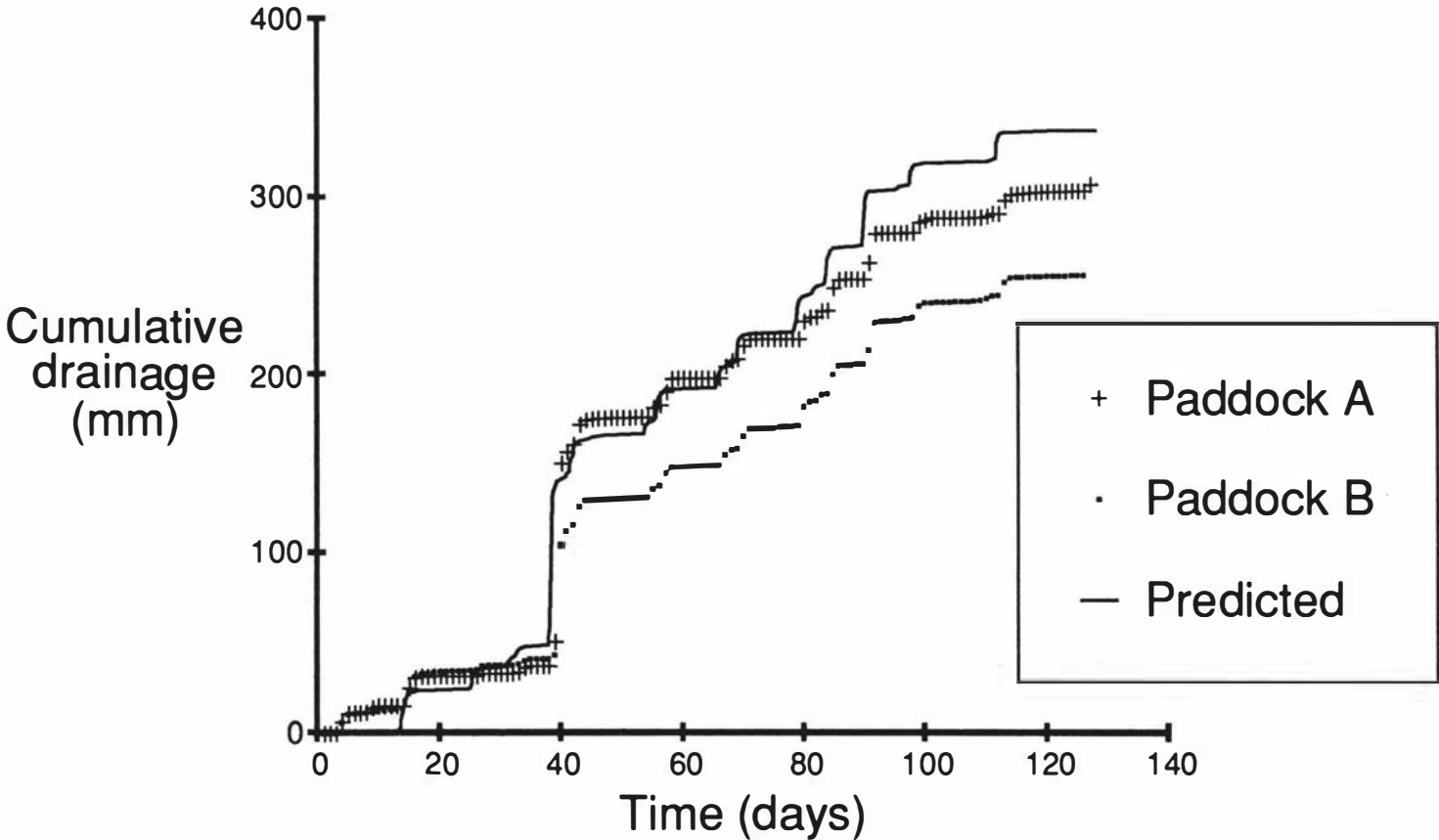
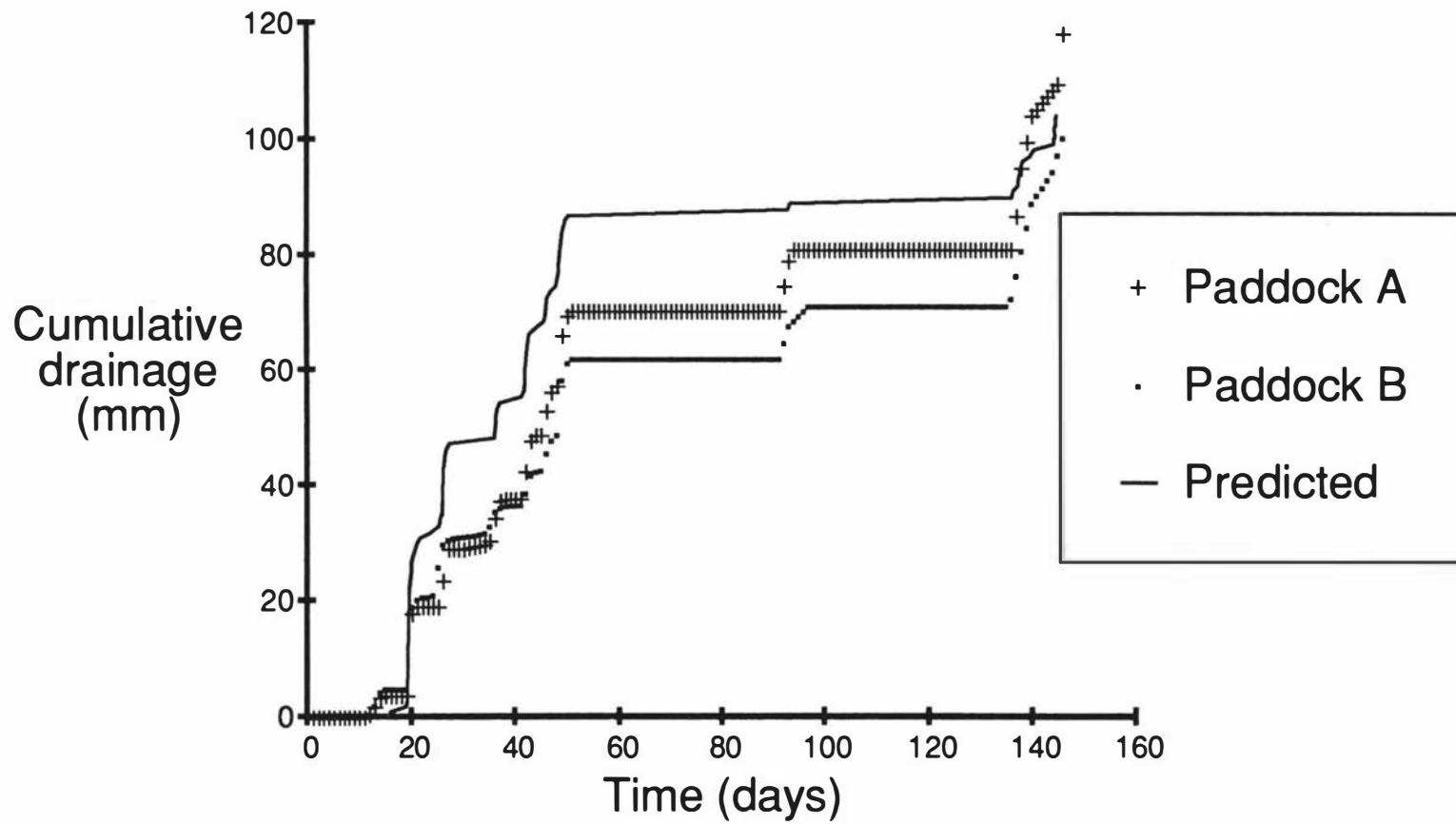


Fig. 5.4 Measured and predicted cumulative drainage as a function of time after fertilizer application on 31/5/89



September period, when the ground cover was incomplete after grazing and the soil surface became dry. In such a situation, the potential evaporation calculation using the Priestley and Taylor (1972) equation may not be appropriate and the proportion of plant cover needs to be taken into consideration (Johns and Lazenby, 1973). Kanemasu *et al.* (1978) presented an approach which can be used to account for the effect of partial cover on evaporation loss. Another possibility could be due to rainfall moving preferentially through cracks or channels after the dry period (Thomas and Phillips, 1979; White, 1985b). A calculation of the soil water balance indicates a deficit of 45 mm was attained by the end of the dry period. However, drainage before the soil rewetted to "field capacity" was observed which indicated preferential flow. Preferential flow through cracks and channels to moles has been observed by Scotter (1978) in Tokomaru silt loam, and by McGowan and Williams (1980) and Reid and Parkinson (1984) in overseas soils.

Table 5.1 Comparison between measured and predicted drainage

Year	Measured (mm)		Predicted (mm)	
	Paddock A	Paddock B	$D_c = 270 \text{ mm d}^{-1}$	$D_c = 10 \text{ mm d}^{-1}$
1988	304	257	338	222
1989	118	100	104	93

5.4.2 Drainage Chloride Concentration

The predicted and measured chloride concentrations in the drainage are shown in Figs. 5.5 and 5.6 for 1988 and 1989 respectively. In 1988 the predicted leaching loss was 123 kg ha⁻¹ compared to measured losses of 118 and 93 kg ha⁻¹ for paddocks A and B respectively. Good agreement between predicted and measured total chloride in paddock A was observed. The lower leaching in paddock B was due to the difference in drainage. In 1989 the predicted loss was 73 kg ha⁻¹, which was also in good agreement with the measured values for the two paddocks of 76

Fig. 5.5 Measured and predicted drainage chloride concentration in 1988. The solid line is the prediction with $D_c = 270 \text{ mm d}^{-1}$; the dotted line is the prediction with $D_c = 10 \text{ mm d}^{-1}$

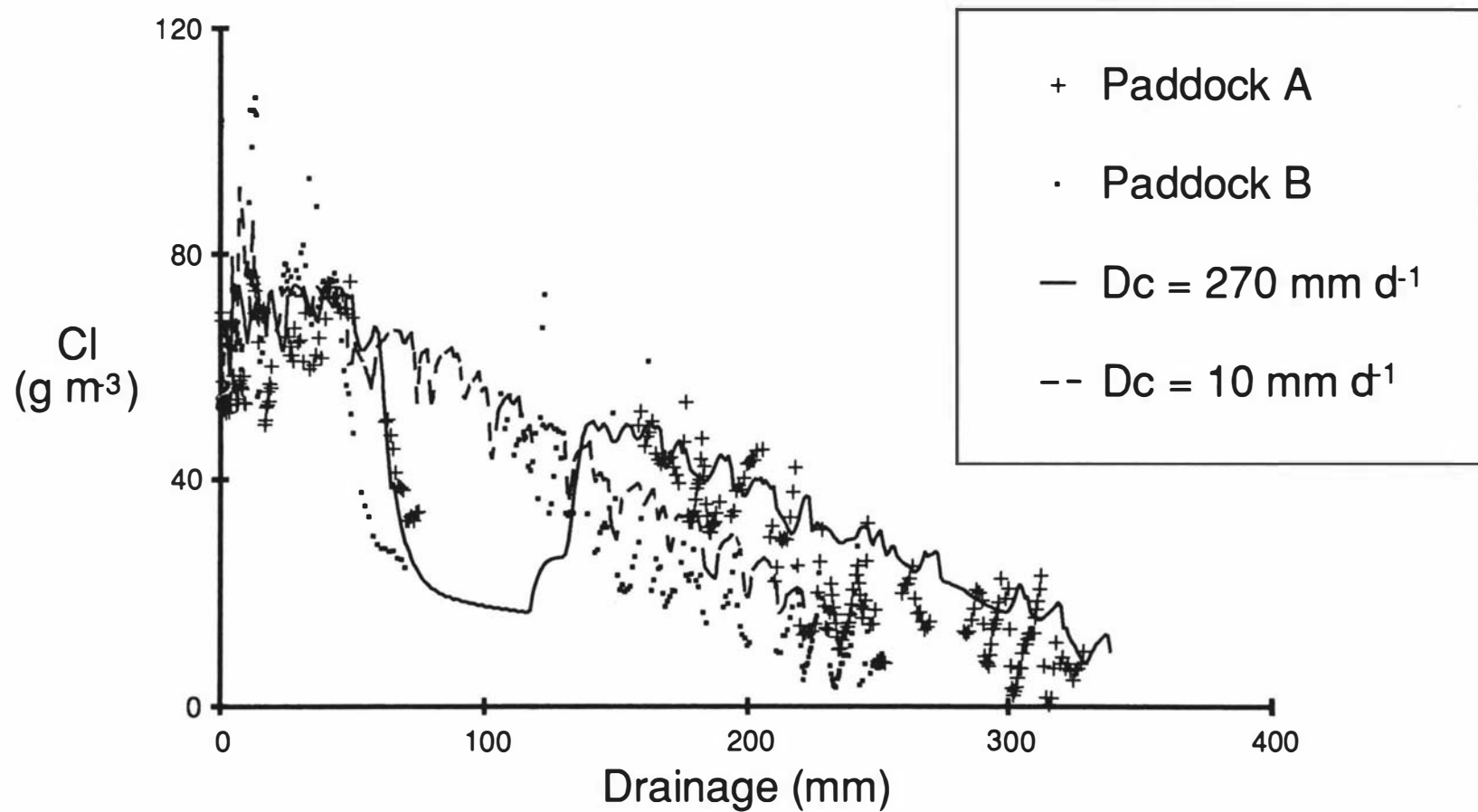
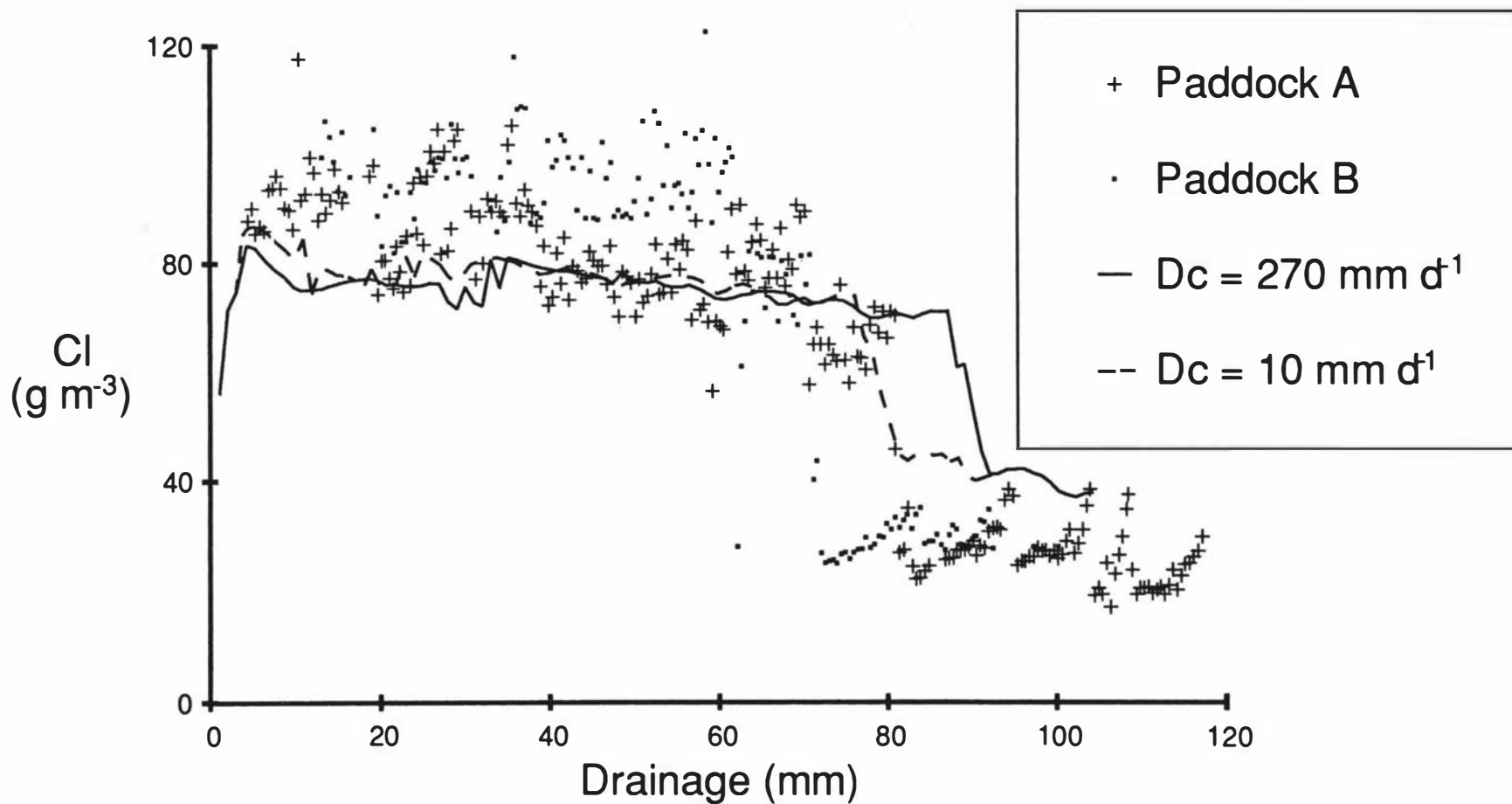


Fig. 5.6 Measured and predicted drainage chloride concentration in 1989. The solid line is the prediction with $D_c = 270 \text{ mm d}^{-1}$; the dotted line is the prediction with $D_c = 10 \text{ mm d}^{-1}$



and 72 kg ha^{-1} . Considering the standard error of $\pm 12 \text{ kg ha}^{-1}$ in the initial soil chloride measurements, which corresponds to an uncertainty of $\pm 6 \text{ g m}^{-3}$ in the soil solution concentration, the above predictions are good.

The behaviour on the day with almost 100 mm of rain in July 1988 is interesting. Both the measured and modelled concentrations dropped from approximately 70 to 20 g m^{-3} during that flow event (Fig. 5.5). The sudden drop in concentration predicted was due to the perched water table rising to the surface during the prolonged and intense rain. During such a situation, the water table will be at the surface over most of the soil, resulting in surface ponding. Because there is no slope on the water table, according to Dupuit-Forchheimer theory there is no driving force for lateral flow through the soil. The water then only infiltrates into the soil immediately above the moles. Under these conditions most of the soil is bypassed, diluting the chloride concentration in the drainage. The water table dropped after the flood and flow returned to normal, hence an increase in the predicted chloride concentration is obtained in subsequent drainage. A comparison of the predicted and measured amounts of chloride remaining in the soil, and leached from the soil at various times, is given in Tables 5.2 and 5.3. Table 5.2 shows that the predicted soil chloride tends to over estimate that measured, especially in the August samplings of both years.

The effect of the prolonged dry period during the 1989 winter is also of interest (Fig. 5.6). Because plant uptake of chloride continued over this period, when the soil rewetted it had a lower chloride content, and so the first drainage event after the dry period had a much lower chloride concentration. Thus the dry period appears in both the measured and modelled data in Fig. 5.6 as a sudden drop in chloride concentration.

Table 5.2 Comparison between measured and predicted chloride remaining in the soil

Date	Measured (kg ha ⁻¹)		Predicted (kg ha ⁻¹)	
	Paddock A	Paddock B	$D_c = 270 \text{ mm d}^{-1}$	$D_c = 10 \text{ mm d}^{-1}$
16/6/88	65.7	64.0	64.9*	64.9*
5/8/88	45.4	57.0	84.0	96.8
14/10/88	28.0	28.0	18.7	30.5
31/5/89	92.5	74.2	83.4*	83.4*
5/8/89	62.7	66.0	104	110
8/11/89	50	49.1	61.6	67.4

* Initial value chosen to agree with measured value

Table 5.3 Comparison between measured and predicted chloride leached for 1988 and 1989

Period	Measured (kg Cl ha ⁻¹)		Predicted (kg ha ⁻¹)	
	Paddock A	Paddock B	$D_c = 270 \text{ mm d}^{-1}$	$D_c = 10 \text{ mm d}^{-1}$
16/6/88-5/8/88	87.2	65.5	75.0	61.5
16/6/88-14/10/88	117.8	92.8	122.7	111.0
31/5/89-5/8/89	58.0	60.5	66	59.3
31/5/89-8/11/89	76.3	71.9	73.4	67.5

5.4.3 Sensitivity Analysis

Fig. 5.7 shows the effects of changing α on the predictions of drainage chloride concentration. Halving α to 0.025 h^{-1} decreased the predicted chloride concentration during the flood, but otherwise the effect was small. Conversely, doubling α increased the predicted concentration during the intense rain. This is because when α is doubled, the rate of solute exchange between mobile and immobile phases increases, reducing the effect of preferential flow. At small α , and with rapid flow, there is little interaction between solute in the mobile and immobile phases.

Varying the number of compartments, m , from 4 to 2 or 8 had minimal effect on most of the model output, except during the intense flow event when a lower chloride concentration was predicted (Fig. 5.8). Although varying the number of compartments did change the horizontal dispersivity, the changes in predicted concentration during the intense flow event were not because of this. They were due to the flow from the surface passing through a larger or smaller soil volume nearest to the drain.

The effect of changing z_a was also tested by changing it from 50 to 150 mm. The effect was found to be small as shown in Fig. 5.9, suggesting that the choice of value for this parameter is not critical to the output of the model.

An important determinant of the amount of leaching under farm conditions will be the amount of surface runoff relative to drain flow. In the situation simulated above, the drainage coefficient of the drains was unusually high, so that they could handle all surplus water. A typical drainage coefficient is 10 mm d^{-1} rather than the 270 mm d^{-1} found above. With the lower value, surface runoff may occur. Using a value of 10 mm d^{-1} , the model was again run for the 1988 drainage season. The results, given in Figs. 5.5, 5.6 and Tables 5.1 and 5.3 show that there would be 34% less drain flow, but only 10% less chloride leached in 1988, and 10% less drain flow and 8% less chloride leached in 1989. Surface runoff appears to affect the total drain flow more than the total amount of leaching, because it occurs mainly

Fig. 5.7 The effect of changing alpha on predicted chloride concentration in 1988 drainage

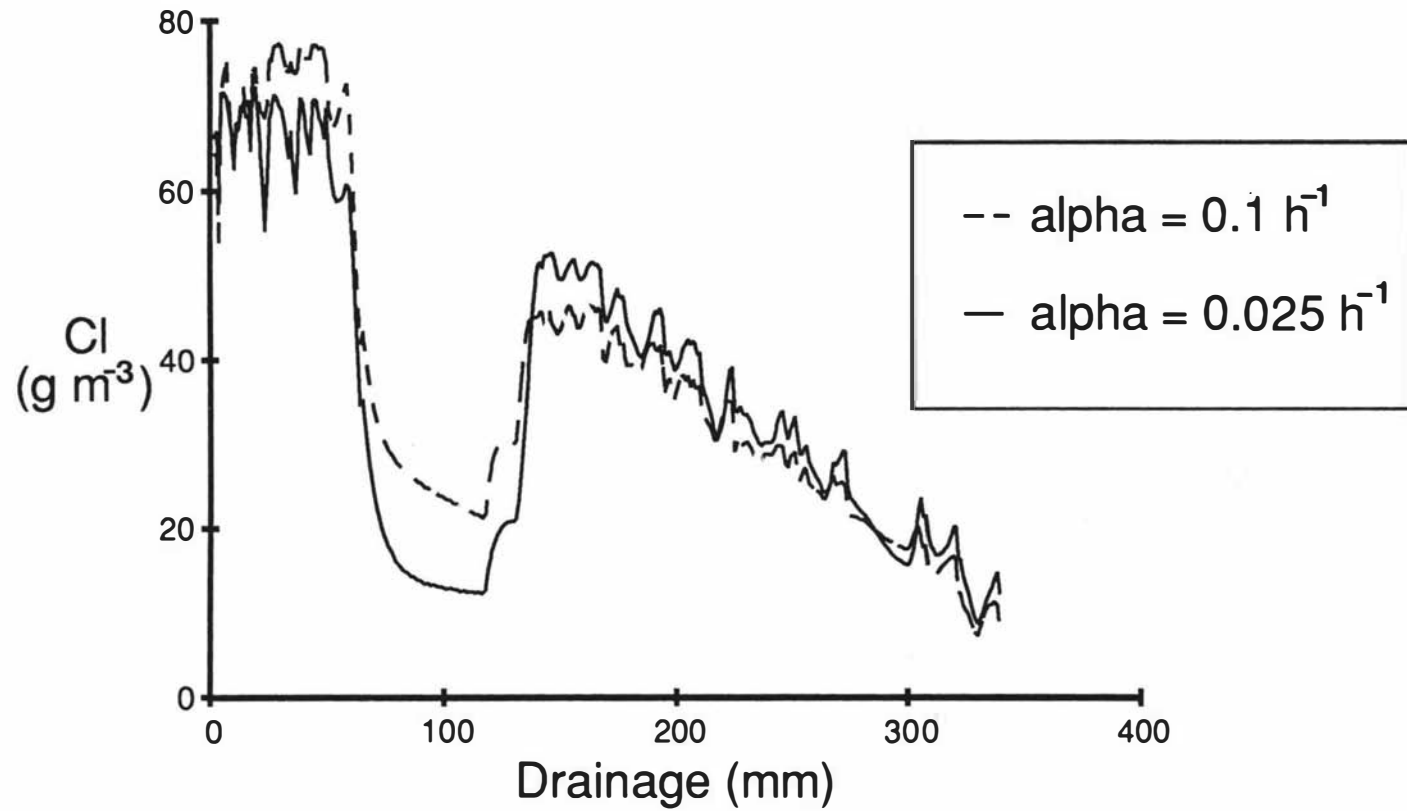


Fig. 5.8 The effect of changing the number of compartments (m) on predicted chloride concentration in 1988 drainage

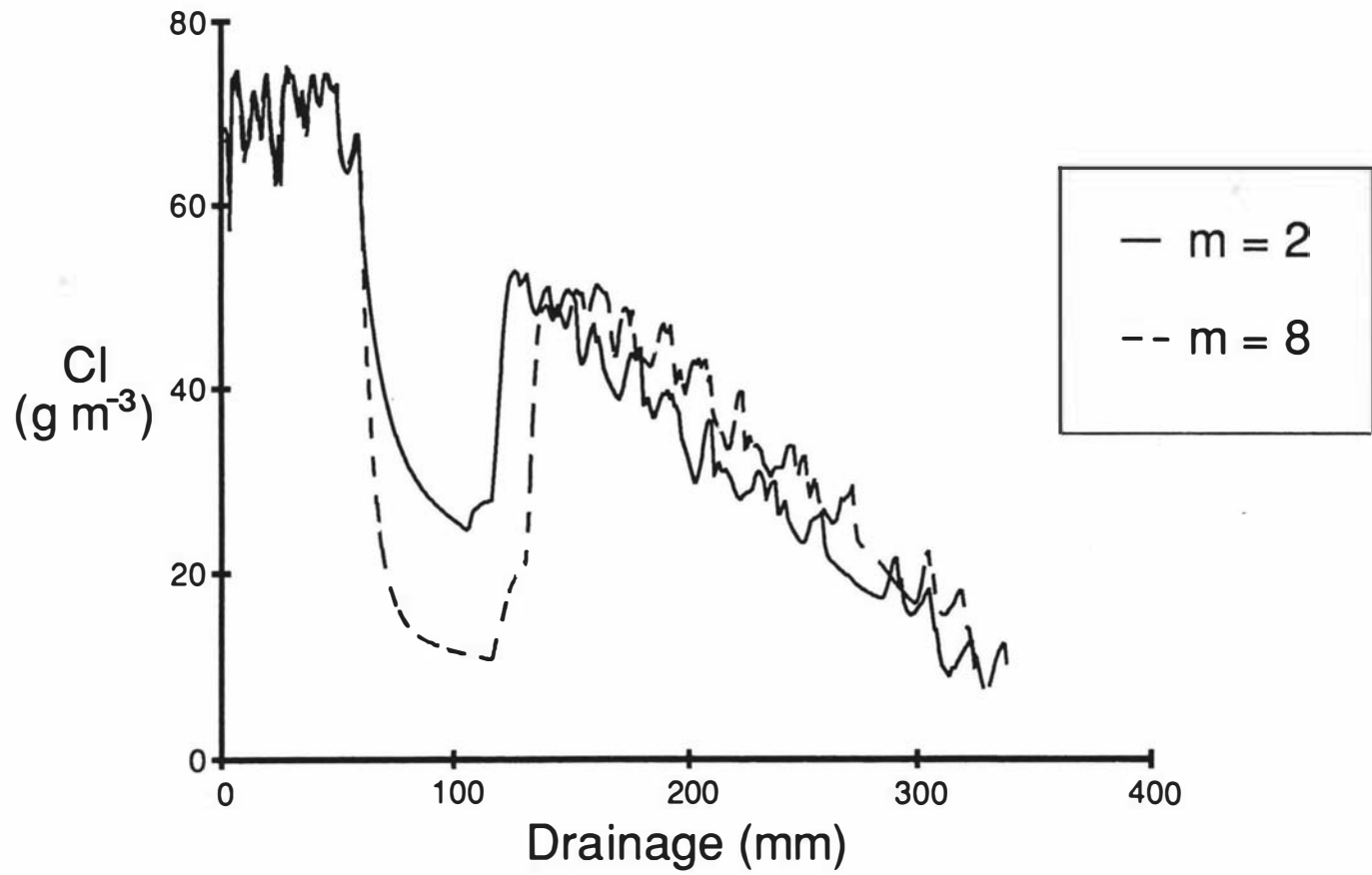
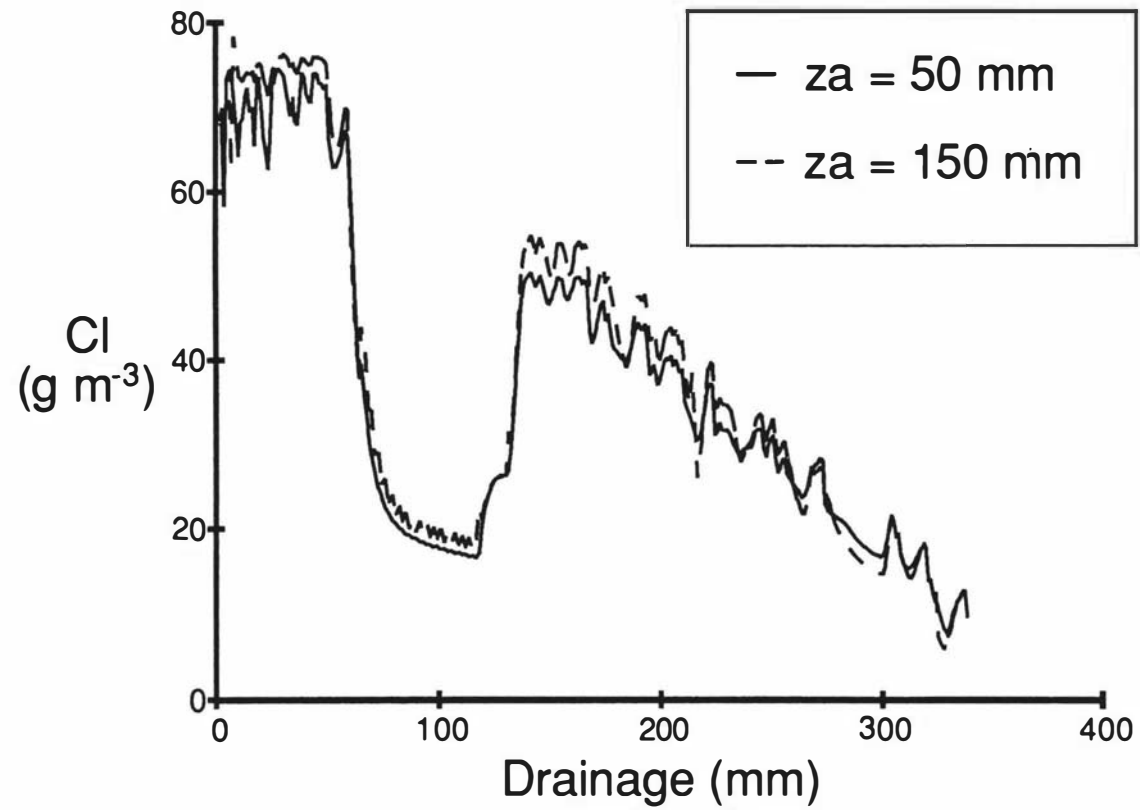


Fig. 5.9 The effect of changing z_a on predicted chloride concentration in 1988 drainage



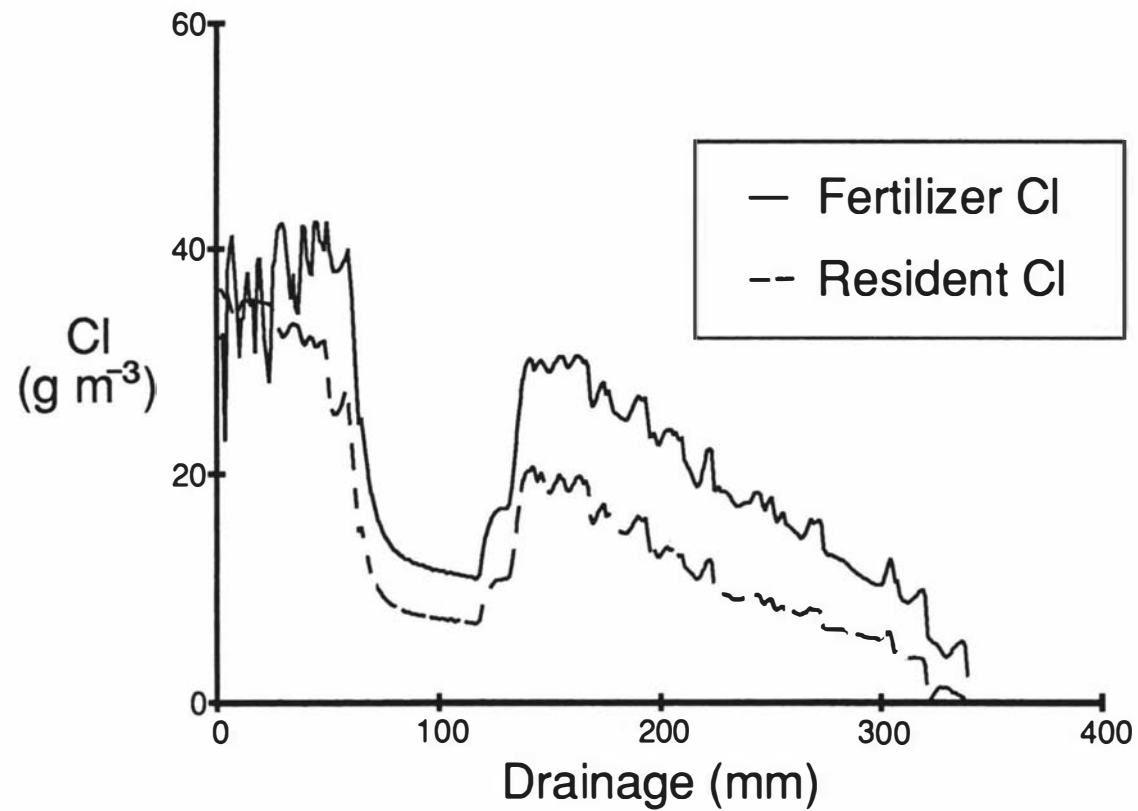
during the intense and prolonged rainfall. Under those conditions, the bypass flow features predict lower solute concentrations in the drainage.

The model was also used to simulate leaching when the fertilizer pulse was the only solute present in the soil, and also when resident chloride was the only solute present. Such simulations were carried out for 1988, and are given in Fig. 5.10. The amount of chloride leached from the 95 kg ha⁻¹ of fertilizer applied was 71 kg ha⁻¹ while the amount leached from the 65 kg ha⁻¹ of resident chloride was 48 kg Cl ha⁻¹. Though more was leached from the fertilizer chloride, the proportion from each pool leached was similar.

5.5 SUMMARY AND CONCLUSIONS

A physically based mechanistic model was developed to predict the leaching of chloride from a mole drained soil. Despite the complexity of the system and the simplifying assumptions of the model, the concentration of chloride in the drainage was predicted quite well over a two-year period. The model was able to simulate the concentrations just after fertilizer was applied, during preferential flow induced by prolonged heavy rain event, and after an extended dry period. The model can also be used to predict the effects of different drainage coefficients on the leaching of chloride.

Fig. 5.10 Predicting the leaching of fertilizer and resident chloride for 1988 rainfall data



CHAPTER 6

MODELLING THE LEACHING OF CHLORIDE AND SULPHATE USING A TRANSFER FUNCTION MODEL

6.1 INTRODUCTION

A model which was able to simulate preferential flow of water and chloride to a mole drain under field conditions was presented in Chapter 5. Here a transfer function model (TFM) which also has the potential to predict field solute movement is described, and used to predict the chloride and sulphate leaching losses measured in the field experiment.

Application of transfer function theory to soils originated from the work of Raats (1978), who derived equations on soil water and solute travel times. Further development by Jury (1982) and Jury *et al.* (1986) has led to its successful description of solute flow in both laboratory cores and field plot experiments (White *et al.*, 1984; White, 1985a; Dyson and White, 1987; Jury *et al.*, 1982; Butters *et al.*, 1989). It has been used to predict the movement of externally applied bromide, chloride, nitrate, ^3HOH and bacteria.

The TFM has been applied to artificially drained soils to evaluate the leaching of chloride and nitrate (White, 1987), and pesticide migration (Utermann *et al.*, 1990). White (1987) computed the probability density function (pdf) of solute travel times during individual drain events to estimate the leaching of chloride and nitrate. Using such an approach to obtain a pdf of the system is inappropriate because soil water and solute transport are not just due to the parcels of water/solute entering the surface during that event. Utermann *et al.* (1990) partitioned the soil into unsaturated and saturated zones above and below the water table, using different pdfs to account for preferential and non-preferential flow. Flow in the saturated zone was described by a gamma or a factorial function, and that in the unsaturated zone by either a unimodal, Gaussian-like pdf or a bimodal pdf, to account for preferential flow. The model was able to explain the preferential leaching of pesticides in drain outflow.

White (1985a, 1989) showed that the transport parameters of the probability density function of travel times derived from the movement of an externally applied solute (Cl) were able to predict the movement of indigenous soil nitrate and surface applied bacteria (*Escherichia coli*) through soil cores.

It was the purpose of the work described in this chapter to investigate to what extent the transport parameters determined for one solute (chloride) in one year can be used to predict the leaching of another solute (sulphate) in another year. In summary, are the TFM transport parameters essentially a characteristic of a given soil type, relatively stationary in time, and relevant to the transport of all solutes ?

In most work on transfer function modelling, with the exception of that of Utermann *et al.* (1990) (who assumed linear equilibrium adsorption and first order decay), sink and source terms such as plant uptake, and biological transformations such as decay, mineralization and immobilization, have been neglected. This was reasonable in those particular studies, either because the solutes used were non-reactive, or the experiments were carried out over relatively short periods of time, and/or on bare soil in which plant uptake did not occur. Thus, another aim of this chapter was to assess the ability of the TFM to predict the leaching of chloride (Cl) and sulphate from a mole-drained pasture soil over a winter season by incorporating all the major source/sink terms.

6.2 THEORY

6.2.1 Solute Travel Times and Pathway Lengths

The general form of the TFM is

$$Q_{ex}(t) = \int_0^t g(t-t'|t') Q_{ent}(t') dt' \quad (6.1)$$

where Q_{ex} and Q_{ent} [$M T^{-1}$] are the respective mass rates of solute output from, and input into, a defined soil volume, at time t and t' [T] respectively. $g(t-t'|t')$ [T^{-1}] is

the conditional probability density function (pdf) of solute lifetimes. As mentioned in Chapter 1 the pdf above can be reduced to $g(t-t')$, the pdf of solute travel times if the pdf is independent of the input time t' .

Equation (6.1) can be expressed in terms of the input and output solution concentrations, C [$M L^{-3}$], rather than Q if we note that

$$Q = C A_s \frac{dD}{dt} \quad (6.2)$$

where A_s is the area of soil under consideration [L^2], and D is the cumulative drainage per unit soil area [L]. Substitution of Equation (6.2) into (6.1) gives (Jury, 1983)

$$C_{ex}(D) = \int_0^D g(D-D') C_{ent}(D') dD'. \quad (6.3)$$

When the water input is non-steady and intermittent, Equation (6.3) is a more appropriate form of the TFM than Equation (6.1) (Jury, 1982; White *et al.*, 1984). Note that $g(D)$ has dimensions [L^{-1}], and may be thought of as the probability density function of drainage pathway lengths. It therefore depends on the distribution of travel distances and velocities for water flow from the entrance to the exit surfaces.

6.2.2 Step Change and Pulse Inputs

Solution of (6.3) for a non-reactive solute source given a steady concentration, C_s , in the input, such as in rain water, and no sinks, is

$$C_{ex} = C_{ent} = C_s. \quad (6.4)$$

For a Dirac delta solute input, which is a sudden input at a certain instant of time, such as an application of readily soluble fertilizer,

$$C_{ex} = M_o g(D) \quad (6.5)$$

where M_o [$M L^{-2}$] is the input applied at $D = 0$.

For vertical flow of ponded water through soil, water travel times have often been found to be log-normally distributed (Biggar and Nielsen, 1976; Van de Pol *et al.*, 1977; Jury *et al.*, 1976, 1982). The ability of the log-normal equation to predict the water distribution during unsteady flow through undisturbed, structured clay soil was tested by White (1985c). The equation was found to fit the data well for moist or prewetted cores but was inadequate for very dry soil. The two dimensional, rainfall-induced flow to mole drains will be different from one-dimensional ponded flow or from flow in soil cores. Nevertheless, it will be assumed here that $g(D)$ is also log-normally distributed, as the analytical solutions for the TFM with this pdf are readily available. The log-normal pdf equation is

$$g(D) = \frac{\exp\{-[\ln(D) - \mu]^2 / 2\sigma^2\}}{\sqrt{2\pi}\sigma D} \quad (6.6)$$

where μ and σ are the mean and standard deviation of the log-normal distribution.

The boundary condition relevant to the flushing of uniformly-distributed resident solute with concentration, C_i out of the soil by water that does not contain any solute is a step down in C_{ent} from C_i to 0 at $D = 0$. The analytical solution to Equation (6.3), assuming a log-normal pdf and this boundary condition is (White and Magesan, 1991)

$$C_{ex}(D) = \frac{C_i}{2} \{1 - \text{erf}[\frac{\ln(D) - \mu}{\sqrt{2}\sigma}]\}. \quad (6.7)$$

6.2.3 Source-Sink Term, S

As the TFM equation is linear, solutions for different boundary conditions may be superimposed. The general solution for a situation with a steady input from rainfall, plus a Dirac delta input from fertilizer, and with leaching of resident solute is then

$$C_{ex}(D) = M_o g(D) + \frac{C_i}{2} \{1 - \text{erf} [\frac{\ln(D) - \mu}{\sqrt{2}\sigma}]\} + C_s. \quad (6.8)$$

If other possible source/sink terms such as net mineralization and plant uptake are assumed to be linear functions of drainage, they can also be included in C_s .

In situations where a second Dirac delta input (M_t) is added to the system, such as when a flush of mineralization occurs during a dry period at drainage D_t , for $D > D_t$

$$C_{ex}(D) = M_o g(D) + M_t g(D - D_t) + \frac{C_i}{2} \{1 - \text{erf} [\frac{\ln(D) - \mu}{\sqrt{2}\sigma}]\} + C_s. \quad (6.9)$$

Rapid immobilization of an applied solute before significant drainage occurs may be taken into account by reducing the size of the initial Dirac delta pulse, M_o .

6.2.4 Adsorption/Desorption

For a solute that undergoes adsorption, a different approach is needed. The concept of adsorption is different from the source/sink terms described above. Rather it can be visualized as a slowing down of the movement of a reactive solute, or the retardation of its travel time, due to a greater capacitance in the soil. This assumption ignores the effect of preferential flow, as work by Kanchanasut (1980) for example showed that during such flow, even a very strongly adsorbed solute such as phosphate may end up in the drain soon after its application. A similar observation was reported by Jury *et al.* (1986) who found that part of the applied napropamide, a sorbing chemical, moved to a greater depth than that predicted if it

had undergone equilibrium adsorption. This shows that the effects of adsorption may be reduced under preferential flow conditions. In the simple approach adopted here, the effects of preferential flow are ignored however.

Assuming adsorption to be instantaneous and reversible, and the isotherm linear, then it may be described by the equation

$$S_{ad} = k_{ad}C \quad (6.10)$$

where S_{ad} is the mass adsorbed per unit mass of dry soil [$M M^{-1}$], and k_{ad} is an empirical constant related to adsorption, with dimensions [$L^3 M^{-1}$]. Defining M as the total mass of solute present in the soil per unit surface area to the drainable depth z_d , we have

$$M = (\theta C + \rho S_{ad}) z_d \quad (6.11)$$

where θ is volumetric water content [$L^3 L^{-3}$], ρ is the bulk density [$M L^{-3}$], and z_d is the soil depth considered [L]. Substitution of Equation (6.10) into (6.11) gives

$$M = (\theta C + \rho k_{ad}C) z_d \quad (6.12)$$

Differentiating with respect to C gives

$$\frac{d(M/z_d)}{dC} = \theta(1 + R_{rc}) \quad (6.13)$$

where $R_{rc} = \rho k_{ad}/\theta$, and is called the retardation coefficient. When the adsorption isotherm is expressed in the form given in Fig. 4.11, $\theta(1 + R_{rc})$ is the slope of the linearized isotherm. Note M/z_d is the amount of sorbed plus solution solute present in unit soil volume.

Assuming a log-normal distribution of solute pathway lengths, the μ of an adsorbed solute, μ_{ad} , can be related to the μ of a non-adsorbed solute using the retardation

coefficient. For a solute subject to convection in the x direction, conservation of mass gives

$$\frac{\partial (M/z_d)}{\partial t} = -q \frac{\partial C}{\partial x} \quad (6.14)$$

where q is the Darcy water flux density [$L T^{-1}$]. As the average pore water velocity $v = q/\theta$

$$\frac{\partial (M/z_d)}{\partial t} = -v\theta \frac{\partial C}{\partial x}. \quad (6.15)$$

Use of the chain rule and substitution of Equation (6.13) into (6.15) gives

$$\frac{\partial C}{\partial t} = -\frac{v}{(1+R_{rc})} \frac{\partial C}{\partial x}. \quad (6.16)$$

If the system can be visualized as consisting of various flow tubes of different pathway lengths, each with different flow velocities, Equation (6.16) implies that the velocity of the concentration front in each of these flow tubes during adsorption is retarded by the factor $1/(1 + R_{rc})$ relative to the velocity with no adsorption, i.e.

$$v_{ad} = \frac{v}{(1+R_{rc})} \quad (6.17)$$

where v_{ad} is the apparent solute velocity of an adsorbed solute. The cumulative drainage required to move a solute a distance x is inversely related to the pore water velocity. Equation (6.17) implies that the amount of drainage needed to move solute through a particular flow pathway from the soil surface to a mole drain increases by $(1 + R_{rc})$ for an adsorbed solute relative to a non-reactive solute. Given that $\exp(\mu)$ is the median drainage pathway length for a non-reactive solute,

$$\exp(\mu_{ad}) = \exp(\mu) (1+R_{rc}) \quad (6.18)$$

and

$$\mu_{ad} = \mu + \ln(1 + R_{rc}) . \quad (6.19)$$

Equation (6.19) assumes R_{rc} is not spatially variable so that $\sigma_{ad} = \sigma$. Dyson *et al.* (1990) give equations for situations when $\ln(D)$ and $\ln(R_{rc})$ are jointly continuously log-normally distributed, but this possibility is not explored here.

The model uses predicted (as in Chapter 5) rather than measured drainage in the simulation.

6.3 PARAMETERIZATION

6.3.1 Initial Values

The soil chloride measurements made just before fertilizer application in each year, averaged over paddocks A and B, were used to calculate the initial average values of the soil solution concentration (C_i). The amount applied, 95 kg Cl ha⁻¹, at the start of each drainage season was M_o for the initial Dirac delta input. Although the drain depth is 450 mm, the much lower saturated conductivity in the subsoil (between 300-450 mm depth) compared to the topsoil meant that the contribution from the subsoil to drain flow was small. Hence z_d was taken as 300 mm, as assumed in Chapter 5, where the initial soil solution concentration was calculated.

Two separate models are needed for sulphate-S, to take account of the two forms of S fertilizer used in the experiment. For sulphur applied in SSP form, nearly 30 kg of the 50 kg S ha⁻¹ applied in 1988 could not be accounted for a week after application. It was assumed this amount was rapidly immobilized, so M_o for the Dirac delta input was taken as 20 kg S ha⁻¹. The amount rapidly immobilized in 1989 was assumed to be the same proportion as in 1988, i.e. 60% of 30 kg S ha⁻¹, giving M_o of 12 kg S ha⁻¹ for 1989. M_o was put at zero for 1990 in the SSP paddock. $M_o = 0$ was also assumed in the S^o paddock in all three years because of the slow release of sulphate from S^o. Instead oxidation of S^o to sulphate was

incorporated into the source-sink term as described below.

6.3.2 Source-sink Term, S

6.3.2.1 *Rainfall input*

The amounts of rainfall Cl and sulphur calculated for 1988 (Chapter 4), assuming constant concentrations of 4 g Cl m^{-3} and 0.5 g S m^{-3} respectively, were plotted as a function of drainage (Fig. 6.1a). The results show that the relationship between rainfall solute input and drainage was relatively linear as would be expected. A C_s of 6.0 g Cl m^{-3} was obtained by dividing the total rainfall Cl by the predicted cumulative drainage.

A total of 2.5 kg S ha^{-1} of rainfall S was estimated to have been deposited during the drainage season in 1988 (Fig. 6.1b). This gives a C_s of 0.74 g S m^{-3} for rainfall S.

6.3.2.2 *Herbage uptake*

In Chapter 6 it was shown that herbage uptake of chloride was proportional to estimated evaporation. Here Cl uptake was re-expressed as a function of drainage for 1988, as shown in Fig. 6.2a. A very non-linear relationship was observed. Therefore assuming a linear relationship for the whole drainage period can only be a rough approximation, as over-estimation and under-estimation will occur at various times. Because of this non-linearity, and in order to preserve mass balance, C_s for herbage Cl was based on the average total uptake for both paddocks divided by the cumulative predicted drainage, giving a value of $-13.3 \text{ g Cl m}^{-3}$.

A non-linear relationship between uptake and drainage was also observed for sulphur, as shown in Fig. 6.2b for 1988, but again a linear relationship was assumed as an approximation. C_s for 1988 herbage sulphur uptake was equal to -3.11 and -2.16 g S m^{-3} for paddocks A and B respectively.

Fig. 6.1 Estimated rainfall chloride and sulphate-S as a function of estimated drainage in 1988

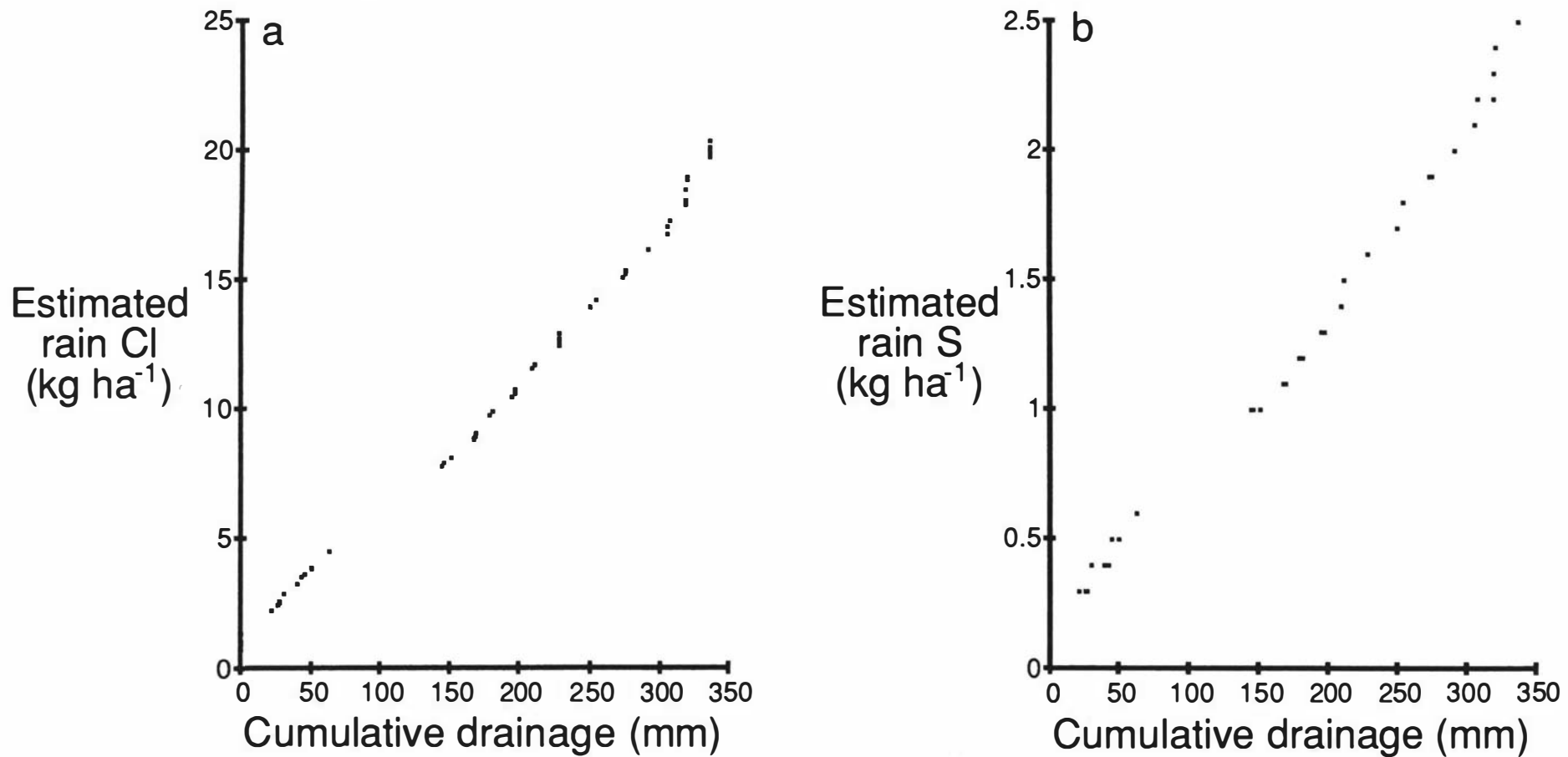
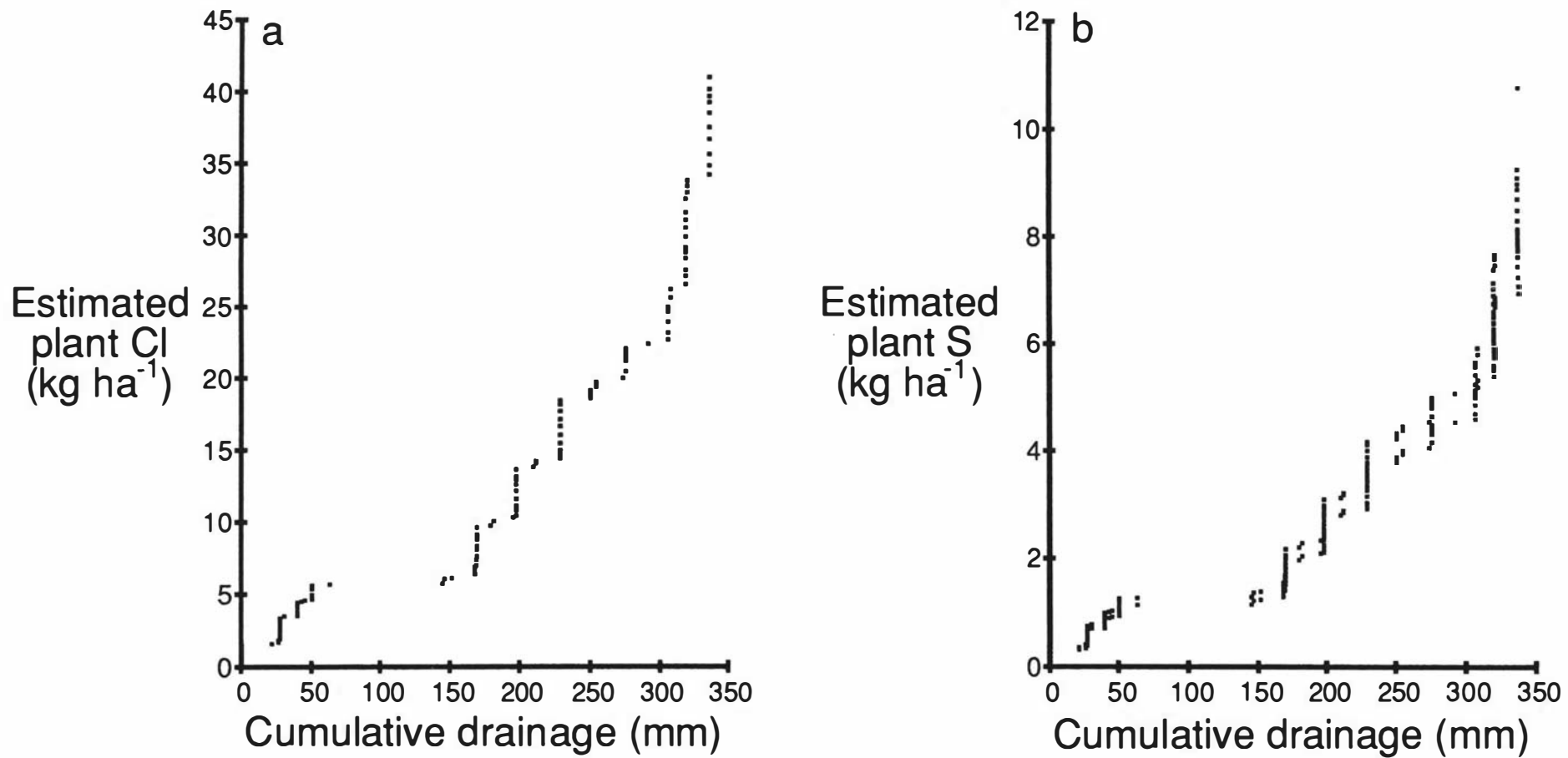


Fig. 6.2 Estimated plant chloride and sulphate-S as a function of estimated drainage in 1988



6.3.2.3 *Mineralization/immobilization of organic sulphur*

The long term average mineralization rate of soil sulphate was estimated by balancing the various sulphate-S components going into and out of the soil in the top 300 mm between 23/6/88 and 14/10/88, an approach similar to that of Macduff and White (1984). From the balance, it was estimated that the amount mineralized was 16.8 and 11.1 kg S ha⁻¹ for paddocks A and B, giving C_s of 5.0 and 3.3 g S m⁻³ respectively for 1988. These values were also assumed to apply during 1989.

6.3.2.4 *Oxidation of S⁰*

The generation of sulphate through oxidation of S⁰ was a slow process over the drainage season, hence the oxidation was treated as a source term entering the system at a rate proportional to drainage. The prediction using the model of Chatupote (1990) gave 4.6 kg S ha⁻¹ of S⁰ being oxidised during the 1988 season, with a predicted drainage of 338 mm. Based on this, a value of 1.36 g S m⁻³ was obtained for C_s for S⁰ oxidation.

Animal returns were ignored in the model, as no grazing occurred over the 1988 drainage season, and the two grazings in 1989 were near the end of the drainage season.

6.3.3 **Retardation Coefficient, R_{rc}**

The retardation coefficient for sulphate, R_{rc} , was obtained from the field determined adsorption isotherm presented in Chapter 4. This isotherm was linearized for soil solution concentrations between 2 and 10 g S m⁻³, as shown in Fig. 4.11, giving R_{rc} a value of 1.6 which was used in the model. This value of R_{rc} was obtained by assuming $\theta = 0.5$ m³ m⁻³, a reasonable assumption because the field was normally near "field capacity" when suction cups samples were taken, and when drainage occurred.

6.3.4 Net C_s for Chloride and Sulphate-S

Net C_s values for Cl and S can be obtained by summing the individual C_s values for the above source/sink terms. The net C_s for Cl was found to be equal to -7.3 g Cl m^{-3} . Having a negative net C_s value means that if drainage were to continue long enough, a negative concentration would be predicted. However, provided the effect of C_s is small relative to M_o and C_i , assuming a negative C_s seems a reasonable way to take account of a small net sink term distributed throughout the drainage season.

For sulphur the net C_s was calculated as 2.6 g S m^{-3} for paddock A and 3.2 g S m^{-3} for paddock B. However the effect of adsorption needs to be taken into account, so the C_s for sulphate needs to be divided by $(1+R_{rc})$ or 2.6. Thus, the final C_s for sulphate in paddock A is 1.0 and 1.2 g S m^{-3} for paddock A and B respectively.

6.4 RESULTS AND DISCUSSION

6.4.1 Drainage Chloride Concentration

The simulated drainage chloride concentrations for 1988 and 1989 are given as solid lines in Figs. 6.3 and 6.4. The predictions were based on a trial and error approach to choose the combination of μ and σ which gave the best fit to the 1988 chloride data. This procedure gave $\mu = 4.8$ and $\sigma = 0.8$.

A good fit was observed between measured and predicted drainage concentration in 1988, except between 50-100 mm cumulative drainage, that is during the intense rain event when preferential flow caused a sharp decrease in chloride concentration. Presumably during such an event a different set of flow pathways occurred, which could not be taken account of by the transfer function model with its constant μ and σ . Despite this discrepancy, good agreement between predicted and measured total amounts of leaching was observed (Table 6.1). Also shown in Fig. 6.3 are the two components (the Dirac delta input and the step-down in concentration) that are represented in Equation (6.8). These two components (Equations (6.5) and (6.7)) and the net C_s added together (Equation (6.8)) gave the predicted drain chloride

Fig. 6.3 Measured and predicted drainage chloride concentration in 1988 using a transfer function model, assuming fertilizer chloride as a Dirac delta pulse, and resident soil chloride uniformly distributed in the profile

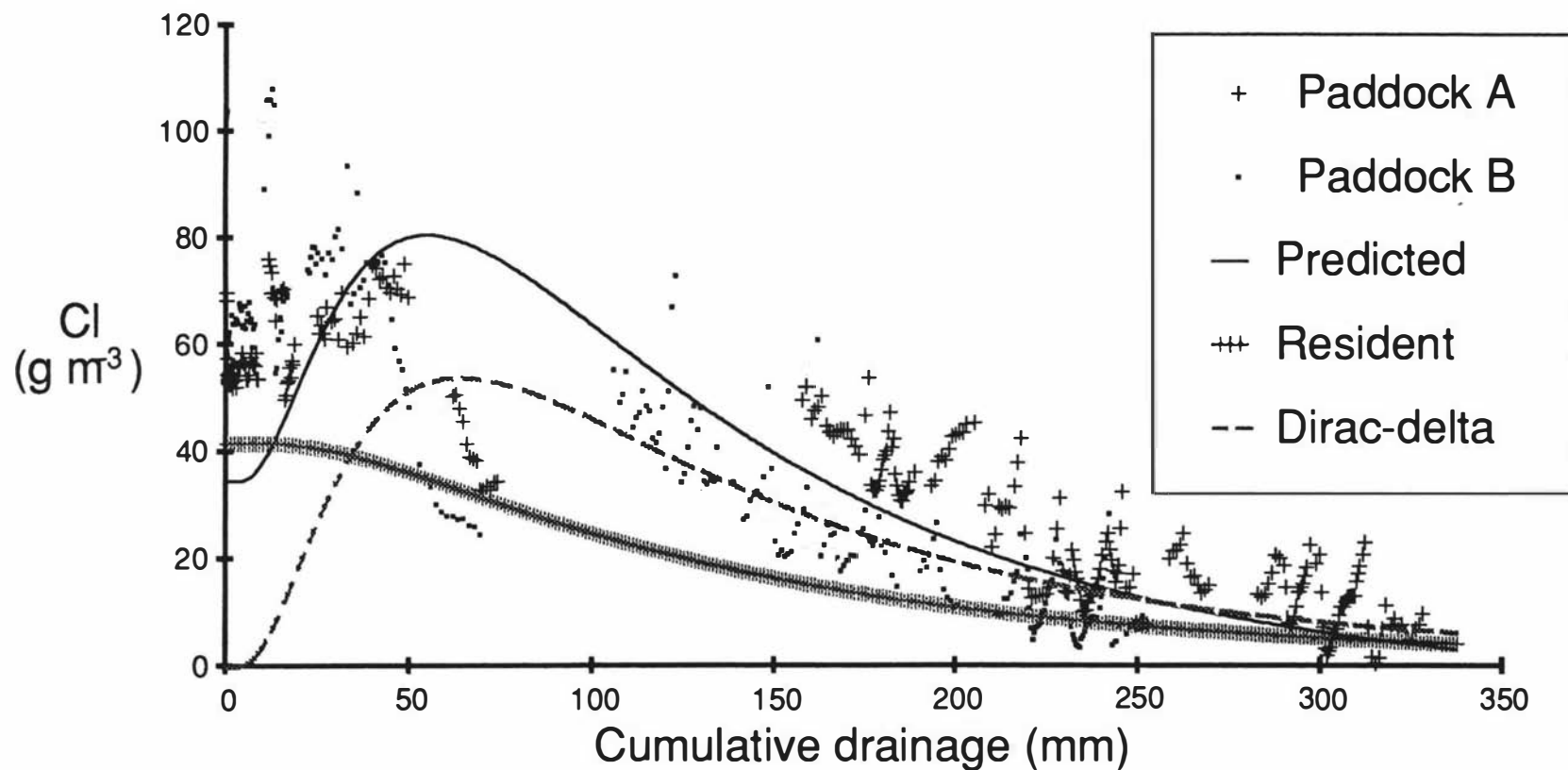
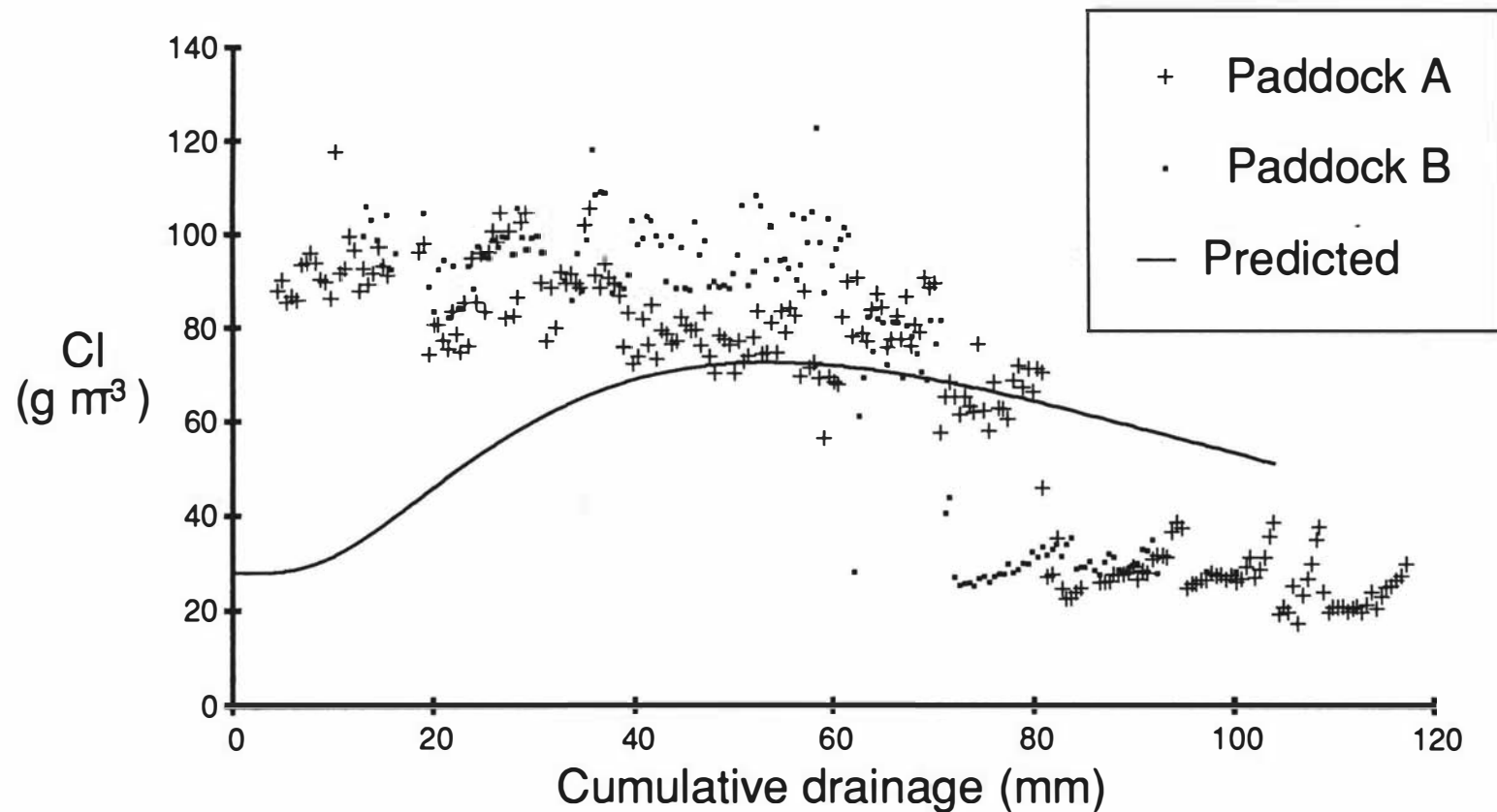


Fig. 6.4 Measured and predicted drainage chloride concentration in 1989 using a transfer function model, assuming fertilizer chloride as a Dirac delta pulse, and resident soil chloride uniformly distributed in the profile



concentration.

Using the same μ and σ as for 1988, a simulation of drainage Cl concentration was carried out for 1989. Although the cumulative drainage for 1989 was only a third of that in 1988, a similar amount of chloride uptake was observed for both years. Hence using the C_s for the plant uptake in 1988 would inevitably lead to an under-prediction of the total Cl uptake for that year. Thus to account for uptake in 1989, C_s for 1989 was taken as the cumulative Cl uptake for 1988 but divided by the cumulative predicted drainage in 1989. The same μ and σ as for 1988 were then used.

Under-prediction of drain chloride at the start of the drainage season, and over prediction after approximately 70 mm cumulative drainage occurred (Fig. 6.4). Spatial variability errors in soil sampling could be one of the causes for the under prediction at the start of the season, giving an estimate of C_i that is too low. However, other possible reasons were probably either because the pdf was not log-normal, or that the transport parameters were non-stationary, or both. Further work is needed to clarify the discrepancy. The over-prediction towards the end of the season was probably because of increased plant growth and greater uptake of chloride than the model accounted for. This would decrease the total mass of chloride in the soil. However, using the simple analytical approach above, this effect cannot be taken into account. The cumulative amounts of chloride leached for 1989 are given in Table 6.1, from which it is seen that predicted and measured amounts leached were in reasonable agreement.

Table 6.1 Comparison between measured and predicted chloride leached in 1988 and 1989

	Chloride leached (kg Cl ha ⁻¹)		
Year	Measured		Predicted
	Paddock A	Paddock B	
1988	118	93	123
1989	76	72	61

6.4.2 Drainage Sulphate-S Concentration

Assuming μ of 4.8 for chloride and accounting for adsorption as described earlier gives μ_{ad} of 5.75 for sulphate, with σ still equal to 0.8. These values were used to predict the drainage sulphate-S concentrations shown in Fig. 6.5. The model predicted the concentration in paddock A well in 1988, but slightly over-predicted that of paddock B. Sulphate concentration in paddock C, which was not measured because the paddock was not instrumented, was also predicted using the model. A slightly lower concentration than in paddock B was predicted in 1988. The total amounts of S leached from the three paddocks are given in Table 6.2. The over-estimation of leaching from paddock B was probably in part due to the over-estimation of the total drainage.

The simulated results for 1989 are shown in Fig. 6.6. The prediction from the model for paddock A was reasonable for the first 70 mm of drainage, however under-prediction was observed after that. A higher concentration of sulphate was predicted in the first 70 mm of drainage than the measured concentration in paddock B. Fig. 6.6 shows that adding an additional Dirac-delta pulse of 20 kg S ha⁻¹ did little to improve the prediction after 70 mm drainage. This was probably because there was only 30 mm extra drainage after the pulse of mineralization. This amount is small in comparison to the overall range of drainage flow pathlengths used to

Fig. 6.5 Measured and predicted drainage sulphate-S concentration in 1988 using a transfer function model

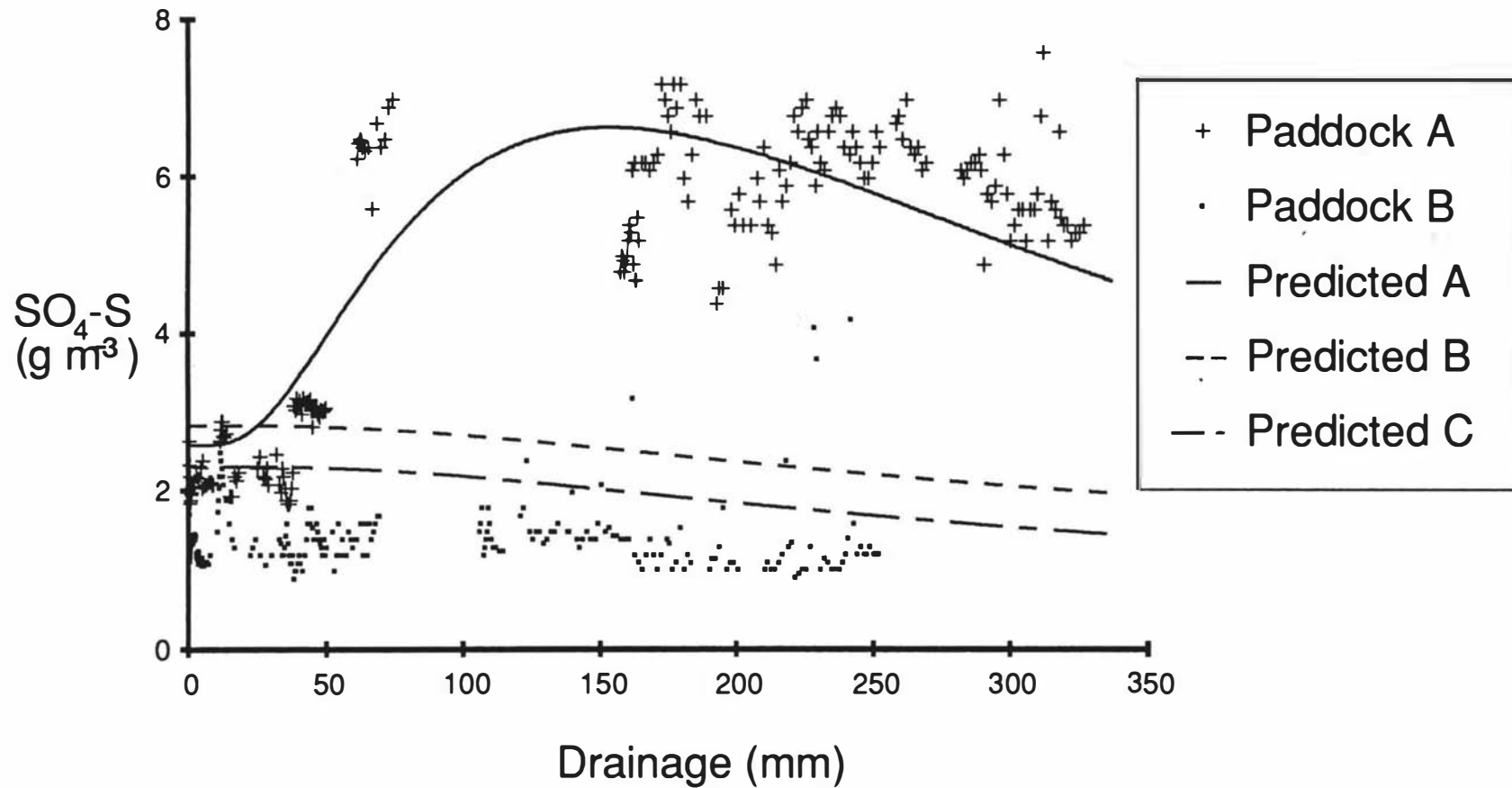
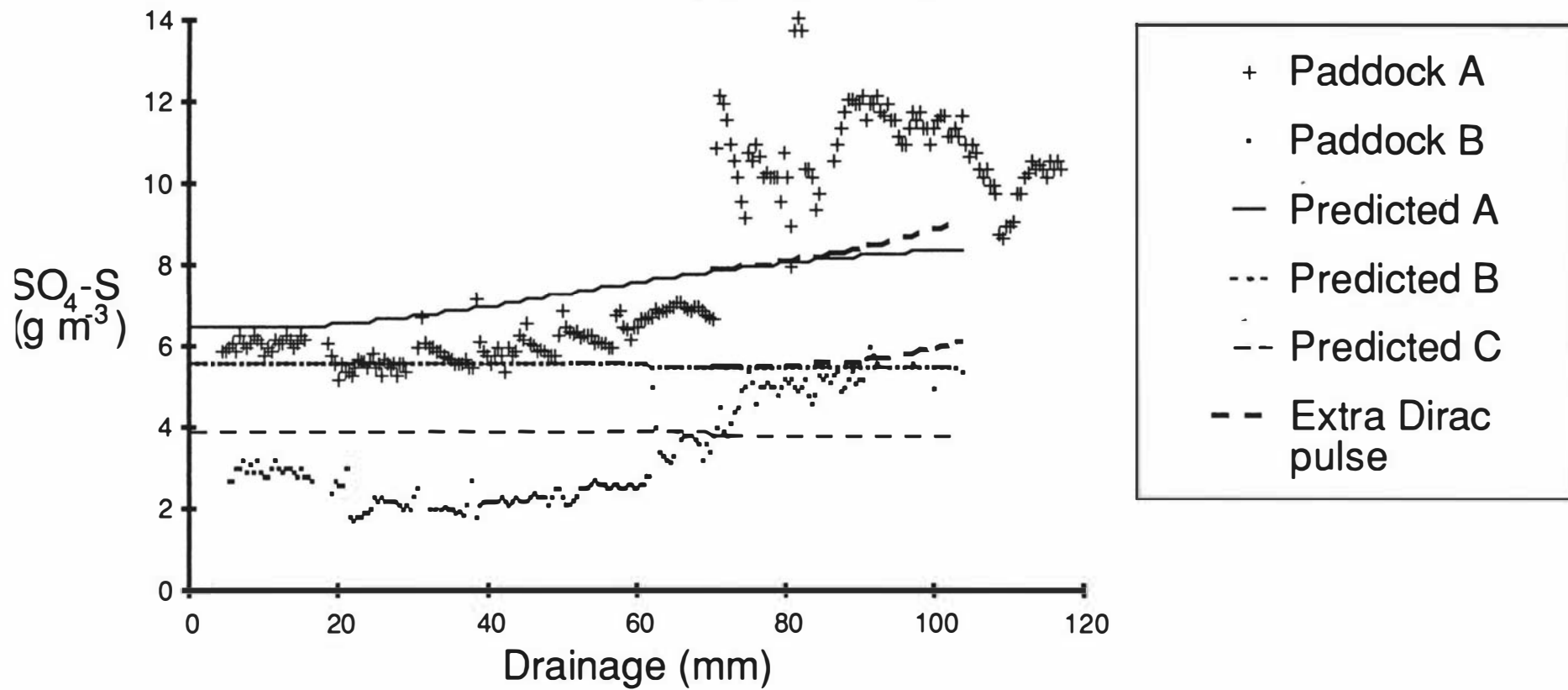


Fig. 6.6 Measured and predicted drainage sulphate-S concentration in 1989 using a transfer function model



parameterize the log-normal pdf. The result shows that not only is the rate and amount of mineralization difficult to predict, but it is also difficult to find the form of pdf that best describes the observed behaviour. A prediction of paddock C drainage concentration was also made. The difference between the predicted concentration of sulphate-S in paddock B and C was larger in 1989 than in 1988, due to the longer period available for the oxidation of S^0 .

Table 6.2 Comparison between measured and predicted sulphate-S leached in 1988, 1989 and 1990

Year	Sulphate-sulphur leached (kg S ha ⁻¹)				
	Measured		Predicted		
	Paddock A	Paddock B	Paddock A	Paddock B	Paddock C
1988	17.0	3.4	18.3	8.4	6.6
1989	9.4	3.5	7.8	5.8	4.1
1990	12.3	9.5	11	11.8	10.0

The predicted drainage sulphate concentrations for the 1990 season are shown in Fig. 6.7. Quite good agreement between the predicted and measured values was observed for the two fertilized paddocks. The difference in predicted sulphate level between paddocks A, B and C continued in the third season of the experiment.

6.4.3 Sensitivity Analysis

Fig. 6.8 shows the effect of changing the value of the sulphate adsorption coefficient on the drainage sulphate data. When $R_{rc} = 0$, i.e. when there was no adsorption, then $\mu_{ad} = \mu$ of Cl. The simulated concentration shows a pronounced peak in the SO_4 -S concentration which did not appear in the data. A total of 24 kg ha⁻¹ of S was predicted to be leached. The result illustrates that without adsorption sulphate can be leached as quickly as chloride. On the other hand, doubling R_{rc}

Fig. 6.7 Measured and predicted drainage sulphate-S concentration in 1990 using a transfer function model, assuming resident soil sulphate-S uniformly distributed in the profile

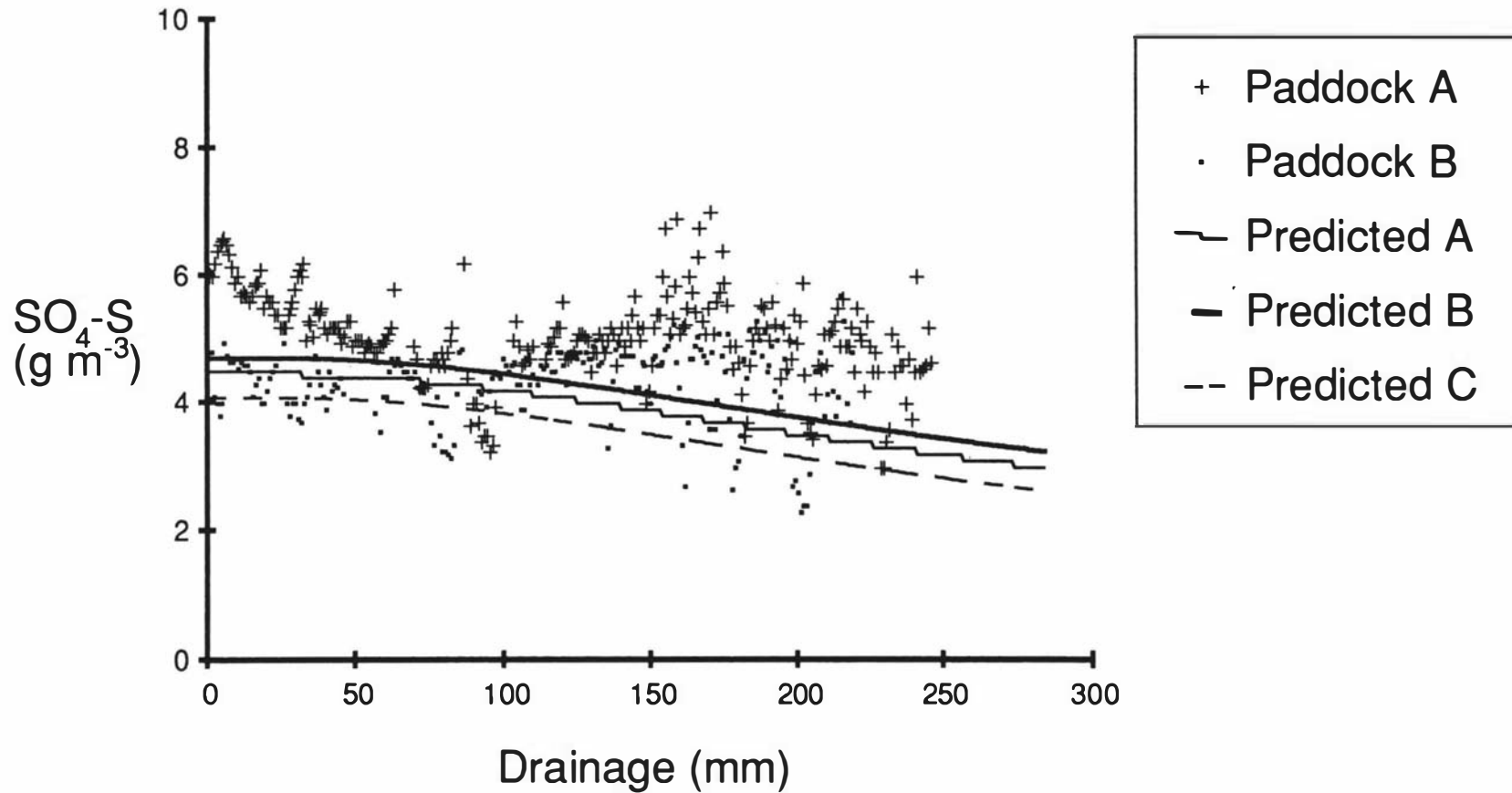


Fig. 6.8 The effect of changing the value of adsorption coefficient on the predicted drainage sulphate-S concentration in 1988 for paddock A

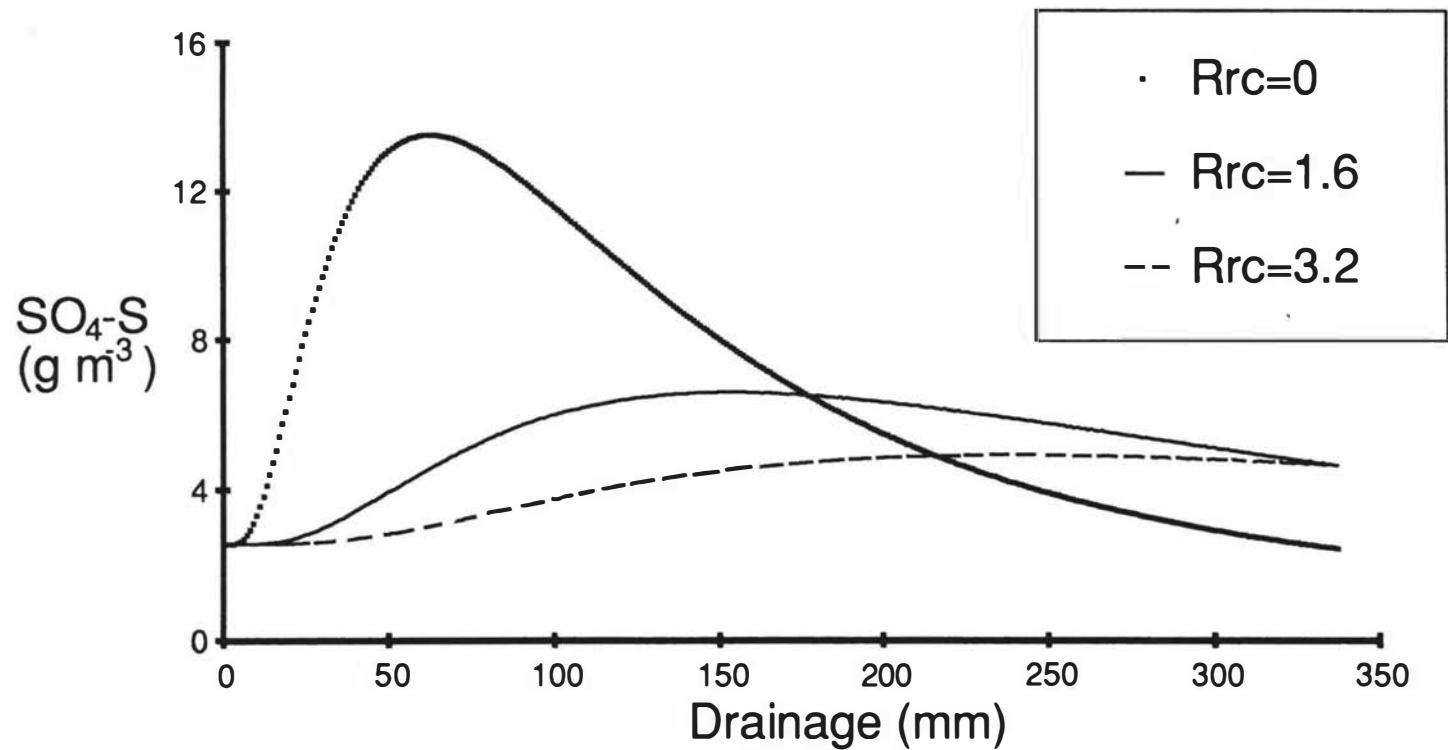
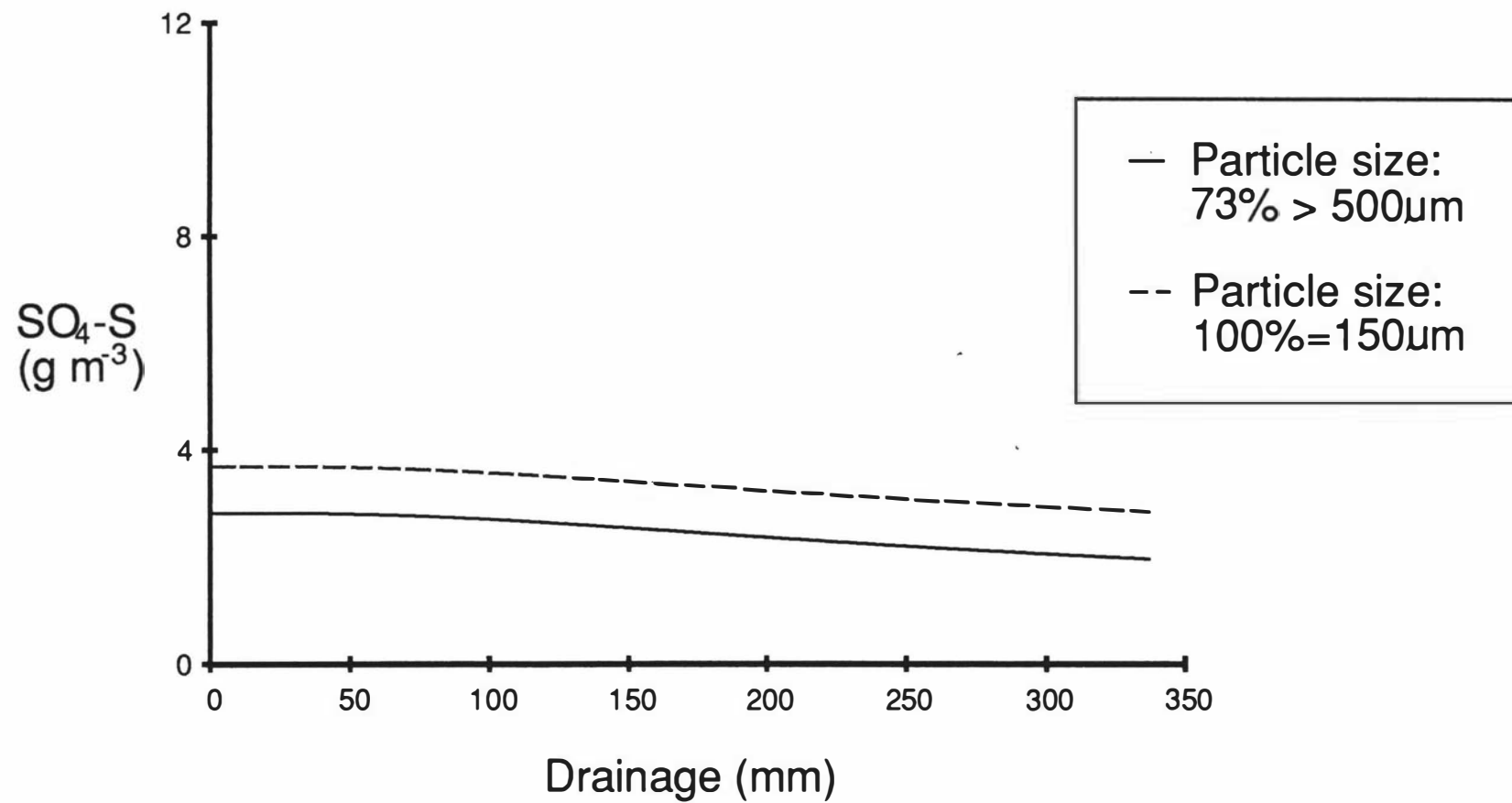


Fig. 6.9 The effect of using different particle sizes of elemental S on the predicted drainage sulphate-S concentration in 1988 for paddock B



flattens the peak and markedly reduces the predicted sulphate concentration, showing how adsorption retards leaching losses. The predicted amount leached when $R_{rc} = 3.2$ was 14 kg S ha^{-1} .

The particle size analysis showed that the S° particles applied in 1988 and 1989 were bigger than is specified by the MAF model. The effect of applying a finer particle size of elemental S on leaching of $\text{SO}_4\text{-S}$ was therefore interesting to simulate. Assuming the particles were all $150 \mu\text{m}$ in diameter, a total of $12.3 \text{ kg S ha}^{-1}$ instead of 4.6 kg ha^{-1} was predicted to have oxidised during the winter season of 1988. Fig. 6.9 shows the effect of using smaller particles on the leaching of sulphate-S from paddock B. An increase in concentration is predicted, and using a $150 \mu\text{m}$ S° particle size resulted in a prediction of 11 kg ha^{-1} of S being leached, compared to 8.4 kg ha^{-1} for the larger particle size material.

6.5 SUMMARY AND CONCLUSIONS

The ability of the transfer function model to predict the leaching of both a non-reactive solute (Cl) and an adsorbed solute ($\text{SO}_4\text{-S}$) through a mole drained soil under natural rainfall was tested. Mixed success was obtained. The results show that the transport parameters of the assumed log-normal pdf (μ and σ) could be extrapolated from one solute to another with suitable adjustment for retardation, but the extrapolation of the values found from one year to another year was less satisfactory. Also certain source/sink terms such as plant uptake were actually very non-linear with drainage. Using a constant C_s to account for their effects resulted in poor prediction of drainage solute concentrations, especially in 1989 for chloride. Comparison of predicted and measured values for sulphate suggested that the ability to describe biological and chemical transformations is as important as modelling the transport process itself. Prediction would be improved if the biological processes such as the rates of mineralization and immobilization could be more accurately described. Nevertheless, the model was able to show the effect of applying fertilizer in different forms, and the effect of some of the key processes, such as adsorption, on the rate of leaching.

CHAPTER 7
MODELLING THE LEACHING OF CHLORIDE AND SULPHATE USING A
"WELL MIXED" MODEL

7.1 INTRODUCTION

Two rather different approaches of modelling chloride were presented in Chapters 5 and 6. Although both models predicted reasonably well the leaching losses, they either required relatively detailed rainfall data, and soil hydraulic properties, or transport parameters which needed calibration using a whole season's leaching data. This information may at times be difficult to obtain. The results in Chapter 6 also suggested that accurate modelling of the leaching of a reactive solute such as sulphate relies on the ability to predict accurately its rate of mineralization. A simple model suitable for management purposes, which takes the above factors into account, is presented here.

Raats (1978, 1980) showed that for steady flow to a drain, with spatially uniform water input at the soil surface, and vertically uniform horizontal flow towards the drain, the solute concentration in the drain flow was the same as the average soil solution concentration in the soil below the water table. That is, the system behaves as if it is "well mixed". While the assumption of horizontally uniform flow to the drain will not be met exactly in any field drainage system, it may be true enough for the "apparently well mixed" assumption to be useful, particularly for mole drain systems where the drains are shallow, the soil below them impermeable, and the water table often near the surface during drainage events. The above reasoning provides the rationale for the development of a "well mixed" model. The model is simpler than the previous two, as it requires only daily rainfall and evaporation data, the drainage coefficient of the mole-drain system, and the soil macroporosity as inputs.

7.2 THEORY

The water sub-model uses a daily time step, and is similar to that described by Scotter *et al.* (1979b). The required inputs are measured daily rainfall (R) and estimated evaporation (E_e) rates [$L T^{-1}$]. Deep percolation is assumed to be negligible. Let D be the drainage rate and R_o the surface runoff rate per unit surface area [$L T^{-1}$], and let W [L] be the equivalent depth of water in the soil to depth z_d . As in Chapter 5, z_d can be either the depth to the mole drains, or if there is an impermeable subsoil at a shallower depth than the drains, then z_d is the depth of permeable topsoil. Let W_o be the value of W when the water table is at the surface, and W_d the value when the water table is at depth, z_d . Values for W_o and W_d can be found from Equation (5.6) in Chapter 5. Given an impermeable subsoil, W_d was then the effective "field capacity" of the drained soil. Let W_n and W_{n-1} denote the value of W at the end of day n , and day $n-1$ respectively. Let D_c be the drainage coefficient [$L T^{-1}$] of the drainage system, defined as the maximum drainage water that the mole-pipe system can deliver in a day. The rates of drainage, D , and surface runoff, R_o , occurring on a given day may then be calculated from the following soil water balance equations. Let

$$X_w = W_{n-1} + (R - E_e) \Delta t \quad (7.1)$$

where Δt is 1 day.

If $X_w \leq W_d$ then

$$\begin{aligned} D &= 0; \\ R_o &= 0; \\ W_n &= X_w. \end{aligned} \quad (7.2)$$

If $W_d < X_w \leq W_d + D_c$ then

$$\begin{aligned} D &= X_w - W_d; \\ R_o &= 0; \\ W_n &= W_d. \end{aligned} \quad (7.3)$$

If $W_d + D_c < X_w \leq W_o + D_c$ then

$$\begin{aligned} D &= D_c; \\ R_o &= 0; \\ W_n &= X_w - D_c. \end{aligned} \quad (7.4)$$

If $X_w > W_o + D_c$ then

$$\begin{aligned} D &= D_c; \\ R_o &= X_w - D_c - W_o; \\ W_n &= W_o. \end{aligned} \quad (7.5)$$

Assuming M_n to be the average amount of solute present under unit soil area to depth z_d at the end of day n [$M L^{-2}$], conservation of mass gives the value of M_n as

$$M_n = M_{n-1} + (S_n - L_n) \Delta t \quad (7.6)$$

where S_n is a source/sink term, and L_n is the rate of solute loss from unit volume of soil in drainage, both with dimensions [$M L^{-2} T^{-1}$].

Included in S_n are inputs from fertilizer (in the case of sulphur, it can be sulphate from SSP or S^o), atmospheric inputs, mineralization and immobilization of organic sulphur and output due to plant uptake. With N [$M L^{-2}$] an operationally-defined readily-mineralizable organic sulphur pool, mineralization and immobilization were both assumed to follow first order kinetics, with rate constants k_1 and k_2 [T^{-1}] respectively. Note that this is a different approach to that used to estimate mineralization in Chapter 6. The atmospheric sulphur input was assumed proportional to the rainfall intensity, with k_3 [$M L^{-3}$], being the proportionality constant. Plant uptake was assumed proportional to the evaporation rate, with k_4 [$M L^{-3}$] being the proportionality constant. Thus

$$S_n = k_1 N_{n-1} - k_2 M_{n-1} + k_3 R_n - k_4 E_{t,n} + F_n + G_n \quad (7.7)$$

where F and G are sulphate-sulphur inputs from superphosphate and elemental sulphur respectively. All terms are input rates per unit soil area to depth z_d , with dimensions $[M L^{-2} T^{-1}]$. The mass balance for readily-mineralizable organic sulphur is then

$$N_n = N_{n-1} + (k_2 M_n - k_1 N_{n-1}) \Delta t. \quad (7.8)$$

The sulphate-S in superphosphate was assumed to be readily soluble in wet soil, so F was added to M on the day of application. However G , the rate of oxidation of elemental sulphur, is slow because it depends on the activity of the microorganisms. The oxidation of elemental sulphur was calculated as described in Chapter 4.

It remains to estimate C from M . Let W_c be the average of W_o and W_d . Then if W is reasonably constant during drain flow (i.e. W_o and W_c are not too different), the concentration of a non-reactive solute in the drainage water, C_d $[M L^{-3}]$, can be obtained as

$$C_d = M_n / W_c. \quad (7.9)$$

The value of M can change significantly during a day of high rainfall, and so it cannot be assumed constant over that time period. As the effect of S_n on M over a day is small, and W is reasonably constant, then to a good approximation

$$dM/dt = -MD/W_c. \quad (7.10)$$

Integrating Equation (7.10) and substituting the result into (7.6) gives

$$L_n \Delta t = M_{n-1} - M_n = M_{n-1} [1 - \exp(-D_n \Delta t / W_c)] \quad (7.11)$$

where D_n is the average drainage flow rate per unit area during day n .

For a solute that undergoes adsorption, an adsorption isotherm is needed to estimate C from M . Using a Freundlich type isotherm as in Chapter 6, we have

$$C_d = \left(\frac{M_n}{a z_d} \right)^{(1/b)} \quad (7.12)$$

where a and b are constants. The isotherm in Equation (7.12) relates the sum of solution and adsorbed sulphate to solution sulphate. The amount of leaching L_n in one day was estimated as

$$L_n = C_{n-1} D_n \quad (7.13)$$

where C_{n-1} is the average soil solution concentration on day $n-1$. The approach used in Equation (7.11) is not necessary for an adsorbed solute because C changes much more slowly than for a non-adsorbed solute such as chloride.

7.3 PARAMETERIZATION

7.3.1 Initial Values

As in Chapters 5 and 6, z_d was taken as 300 mm. The measured amount of soil chloride and phosphate extractable sulphate-S [$M \text{ L}^{-2}$] in the top 300 mm at the start of each drainage season was used to initialize M .

Due to the high drainage coefficient of the mole-pipe system, surface runoff was zero. W_c was calculated to be 153 mm.

7.3.2 Source-Sink Term, S

7.3.2.1 Fertilizer input

Fertilizer input was taken as 95 kg ha^{-1} for chloride. For sulphate in paddock A, F was the amount of sulphate in the SSP applied, as given in Chapter 2. For paddock B, the input of sulphate from S° oxidation was calculated as described in Chapter 4.

7.3.2.2 k_1, k_2, k_3 and k_4

To describe mineralization/immobilization during each drainage season, values for k_1, k_2 , and N_o i.e N at the start of each drainage season, were needed. They were estimated using soil sulphate data for the 1988 drainage season. The value of M in paddock B remained at approximately 12.5 kg S ha⁻¹ soil throughout the 120 days, while in paddock A there was approximately 25 kg S ha⁻¹ soil present as sulphate for most of the time. About 30 kg S ha⁻¹ of sulphate from the 50 kg S ha⁻¹ applied as SSP was apparently immobilized within 7 days of application. Assuming this went into N , and that for the rest of the time N and M were in approximate equilibrium, it follows that in paddock B

$$k_1 N_o - 12.5 k_2 = 0, \quad (7.14)$$

and in paddock A

$$k_1 (N_o + 30) - 25 k_2 = 0. \quad (7.15)$$

Simultaneous solution of these two equations gave N_o as 30 kg ha⁻¹ and $k_2 = 2.4 k_1$. Given immobilization of 30 kg ha⁻¹ was the dominant process in paddock A during the 7 days after fertilizer application, then $(M + N)$ will be the sum of 50 kg ha⁻¹ from SSP applied, 12.5 kg ha⁻¹ from the soil SO₄-S and 30 kg ha⁻¹ from N_o , giving a value of 92.5 kg ha⁻¹ and

$$dM/dt = k_1 (92.5 - M) - k_2 M \quad (7.16)$$

i.e.

$$dM/dt = -3.4 k_1 (M - 27.2). \quad (7.17)$$

Given N_o before SSP addition was 30 kg S ha⁻¹, M immediately after fertilizer addition would be 12.5 + 50 = 62.5 kg S ha⁻¹. Immobilization of 30 kg ha⁻¹ would drop M to 32.5 kg ha⁻¹ after 7 days. Integration of Equation (7.17) with these limits

gives

$$\int_{62.5}^{32.8} \frac{dM}{M - 27.2} = -3.4 k_1 \int_0^7 dt, \quad (7.18)$$

and evaluation of this integral gives $k_1 = 0.08 \text{ d}^{-1}$, and so $k_2 = 0.192 \text{ d}^{-1}$.

The constant k_3 was the average concentration of chloride or sulphate in the rainfall, the values of 4 g Cl m^{-3} and 0.5 g S m^{-3} respectively being used. The linear relationship between the cumulative plant chloride uptake and the cumulative evaporation (Fig. 5.2) discussed in Chapter 5 gave k_4 as 27.1 g Cl m^{-3} for chloride. Fig. 7.1 shows that a linear relationship between total S uptake and cumulative evaporation can also be assumed for sulphur, giving k_4 values of 6.12, 5.49 and 3.88 g S m^{-3} for paddocks A, B and C respectively.

The amount returned through animals was ignored in both the chloride and sulphur models for the reason given in previous chapters.

7.4 RESULTS AND DISCUSSION

7.4.1 Cumulative Drainage

The measured and predicted cumulative drainage as a function of time from this model is shown in Figs. 7.2 and 7.3 for 1988 and 1989 respectively. The prediction from the mechanistic model (Chapter 5) is also shown. The closeness of the two predicted lines shows that both the mechanistic and "well mixed" models essentially gave the same amount of drainage.

7.4.2 Drainage Chloride Concentration

The predicted drainage chloride concentrations are shown in Figs. 7.4 and 7.5. Despite the simplicity of the "well mixed" model, its predictions do not differ greatly from the previous two models (the mechanistic and TFM). Only early in

Fig. 7.1 Measured cumulative sulphur uptake as a function of estimated cumulative evaporation. The lines are linear regressions fitted by least squares

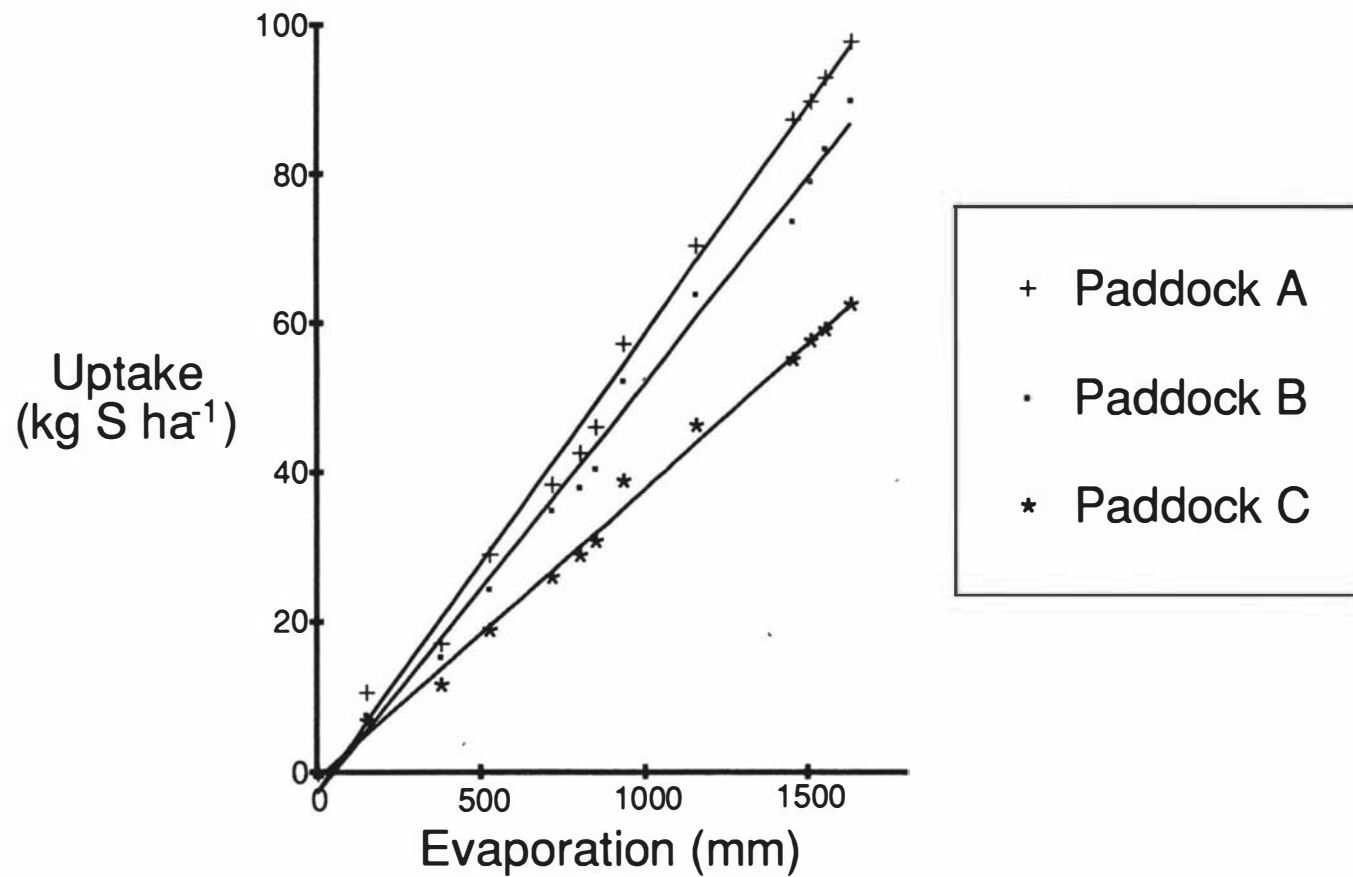


Fig. 7.2 Measured and predicted cumulative drainage as a function of time using a "well mixed" model after fertilizer application on 16/6/88

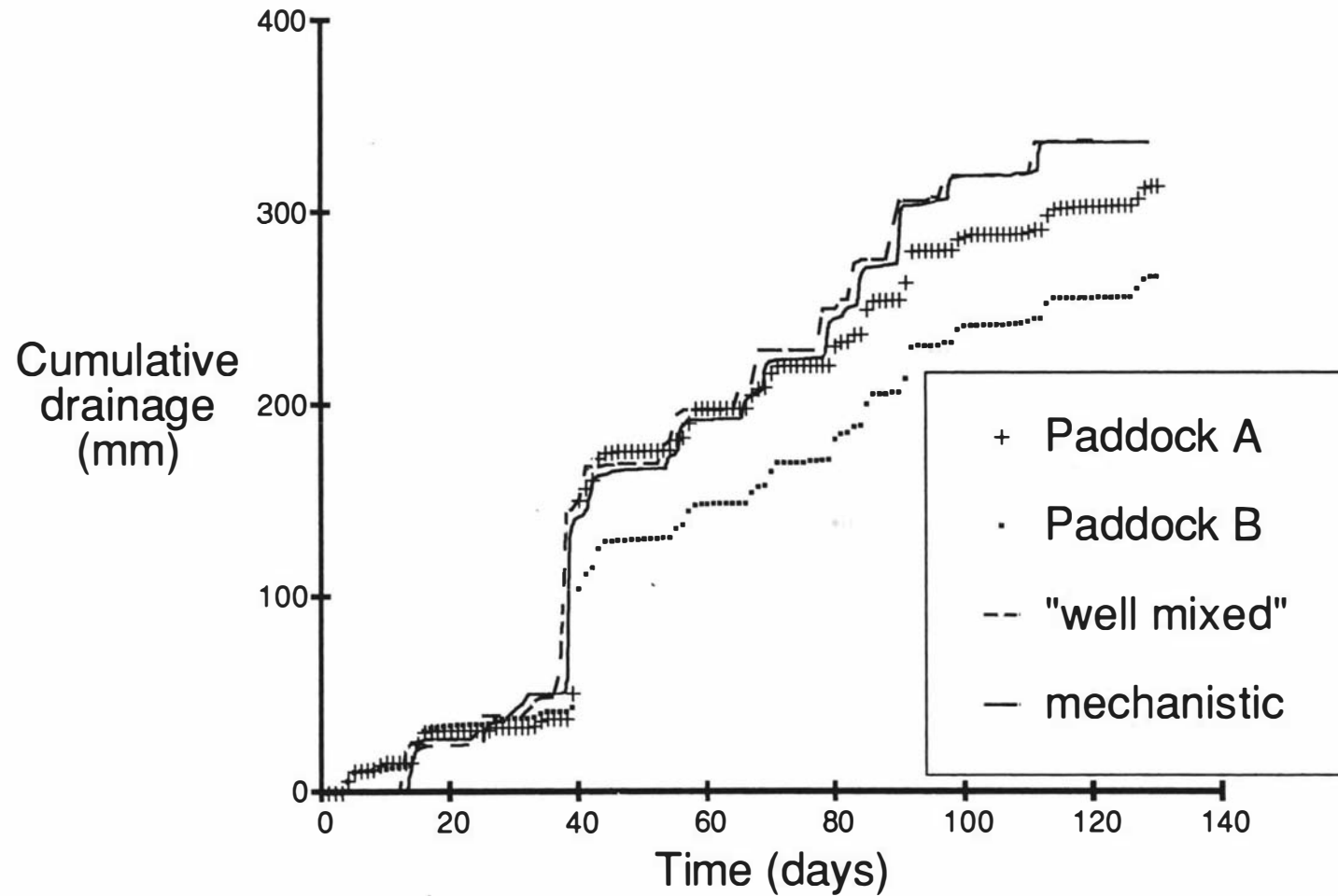


Fig. 7.3 Measured and predicted cumulative drainage as a function of time after fertilizer application on 31/5/89

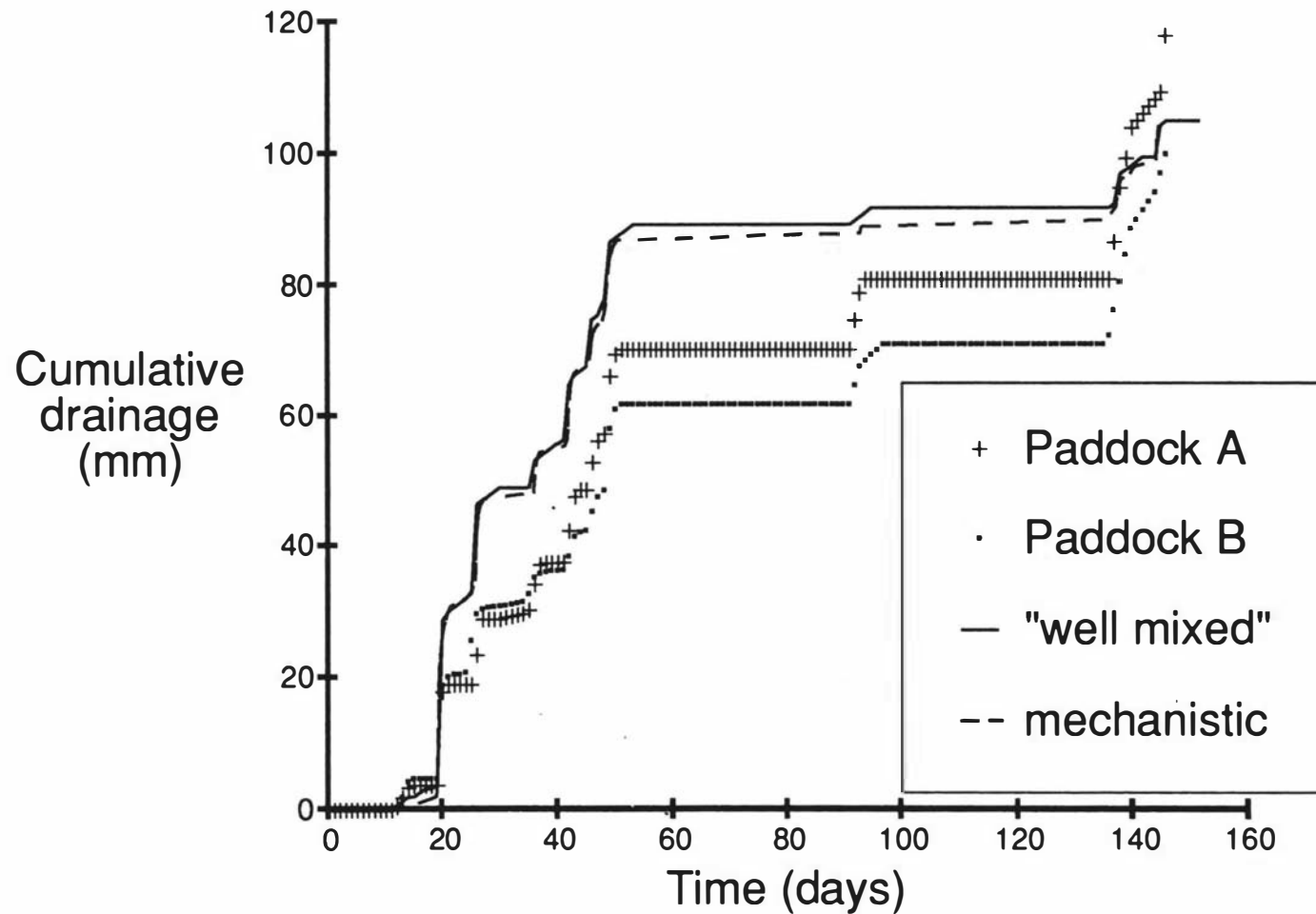


Fig. 7.4 Measured and predicted drainage chloride concentration in 1988 using a "well mixed" model. The solid line is prediction with $D_c = 270 \text{ mm d}^{-1}$; the dotted line is prediction with $D_c = 10 \text{ mm d}^{-1}$

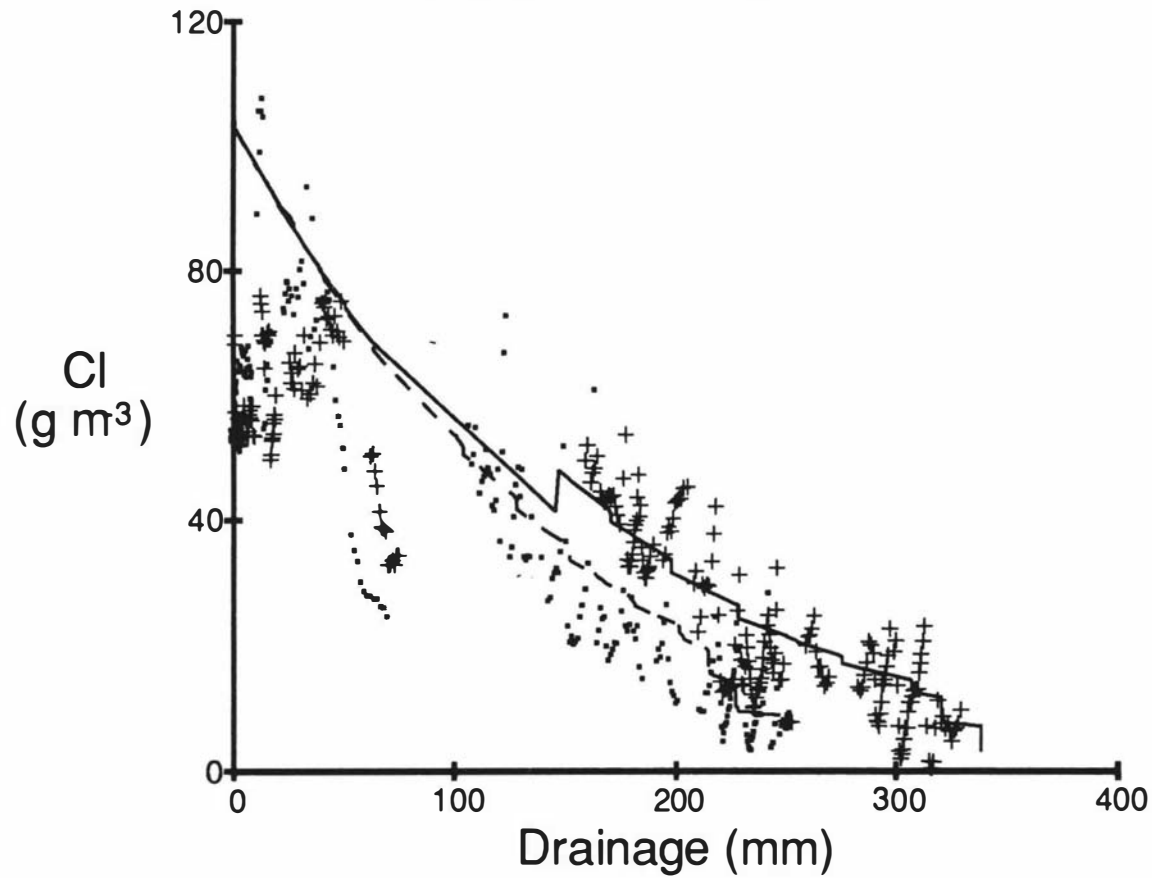
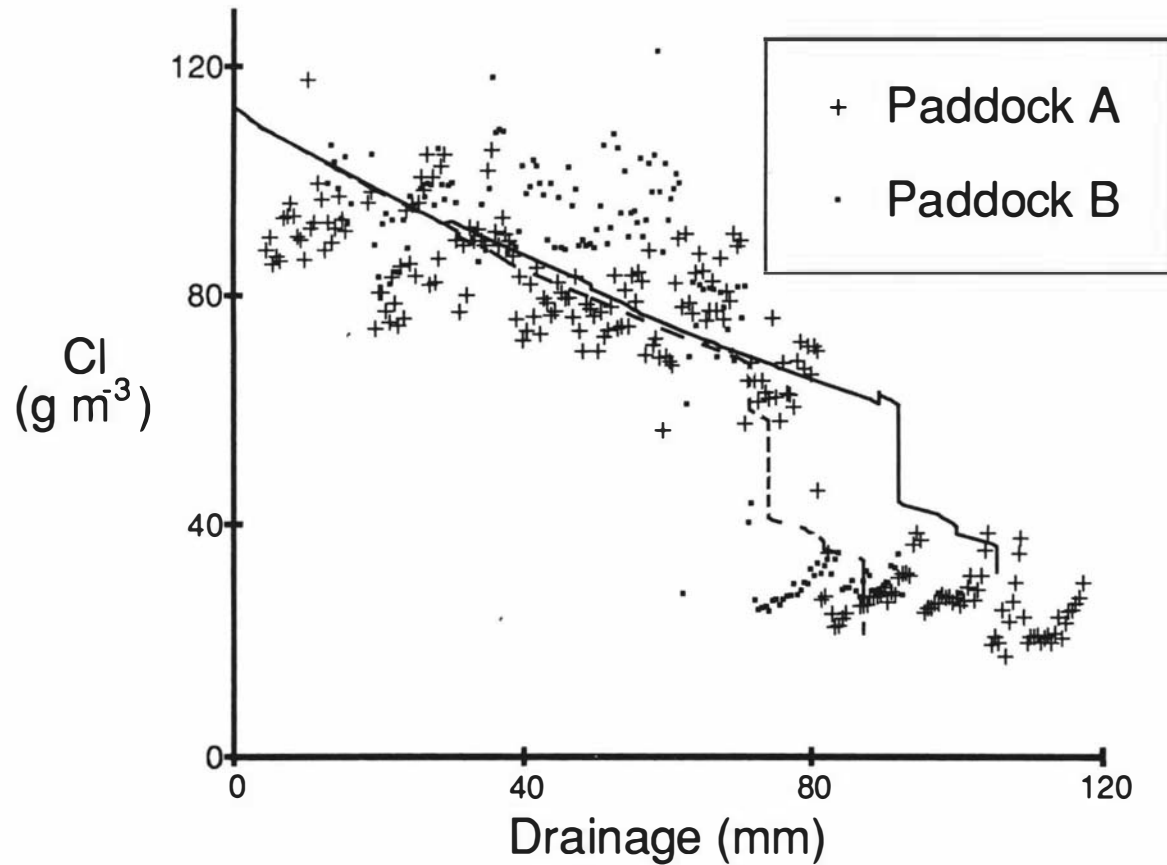


Fig. 7.5 Measured and predicted drainage chloride concentration in 1989 using a "well mixed" model. The solid line is prediction with $D_c = 270 \text{ mm d}^{-1}$; the dotted line is prediction with $D_c = 10 \text{ mm d}^{-1}$



1988, and during the intense rain event of 1988 does the mechanistic model of Chapter 5 match the measured drainage concentrations better than this much simpler model. The early-season discrepancy was again probably caused by the high chloride concentration in the surface soil initially, as this soil is usually not part of the "apparently well mixed" system below the water table. The discrepancy during the intense rain event was due to the inability of the model to describe bypass flow. Despite these discrepancies, the predicted amounts of chloride leached in 1988 and 1989 were 132 and 81 kg ha⁻¹ respectively. These values are slightly higher than the amounts predicted by the previous two models. The total measured and predicted amounts leached are given in Table 7.1.

The effect of changing the drainage coefficient to 10 mm d⁻¹ was also tested and the results are shown in Figs. 7.4 and 7.5. The predicted amounts of chloride leached are given in Table 7.1. Changing the drainage coefficient to 10 mm d⁻¹ reduced the predicted total drainage by 33%, and the amount of Cl leached by 13% in 1988. For 1989 the corresponding predicted drops were 17% and 15%.

Table 7.1 Comparison between measured and predicted drainage and chloride leached in 1988 and 1989

Year	Measured				Predicted			
	Drainage (mm)		Cl leached (kg ha ⁻¹)		Drainage (mm)		Cl leached (kg ha ⁻¹)	
Year	Paddocks		Paddocks		$D_c=270$ mm d ⁻¹	$D_c=10$ mm d ⁻¹	$D_c=270$ mm d ⁻¹	$D_c=10$ mm d ⁻¹
	A	B	A	B				
1988	304	257	118	93	337	227	132	115
1989	118	100	76	72	105	87	81	69

7.4.3 Drainage Sulphate-S Concentration

The predicted sulphate concentrations in the drainage from paddocks A and B are shown in Fig. 7.6. The model was able to simulate reasonably well the drainage concentration from paddock B in 1988, and for both paddocks in 1990. Less satisfactory agreement between measured and predicted drainage concentrations was observed for paddock A in 1988 and for both paddocks in 1989. The poor agreement at the beginning of the season of 1988 and 1989 for paddock A was probably due to the assumption that the concentration in the drainage equals the average soil solution concentration. This assumption implies that all the SSP fertilizer was completely dissolved by the time of the first drainage event following application, which was probably not true. The reason for the poor prediction in the latter part of 1989 was probably similar to that given in earlier chapters, that the drier and warmer winter resulted in much more mineralization than was predicted. This would result in an increase in sulphate concentration in the soil, and also in the drainage. As the rate of mineralization and immobilization depends on both biological and environmental factors, which interact with each other in a complicated way, it is difficult to describe the process accurately using simple first-order kinetics with constant rate coefficients. The measured and predicted amounts of sulphate-S leached are given in Table 7.2.

By way of illustration, it could be assumed that the extra 20 kg S ha⁻¹ pulse of net mineralization used in Chapter 6 applied here also to paddocks A and B. However achieving a net increase of 20 kg S ha⁻¹ in this model would require a much higher M value being used in the second term of Equation (7.7). Using an iterative approach, the value of M was determined as 60 kg S ha⁻¹. The result of including the extra mineralization is also shown in Fig. 7.6. An increase in sulphate-S concentration is observed in both paddocks, but the synchronization with the measured values was not good.

Fig. 7.6 Measured sulphate-S concentration as a function of cumulative drainage in 1988, 1989 and 1990. Predicted lines are: paddock A (solid), paddock B (long dashed) and paddock C (short dashed). An extra pulse is also included for paddocks A and B in 1989

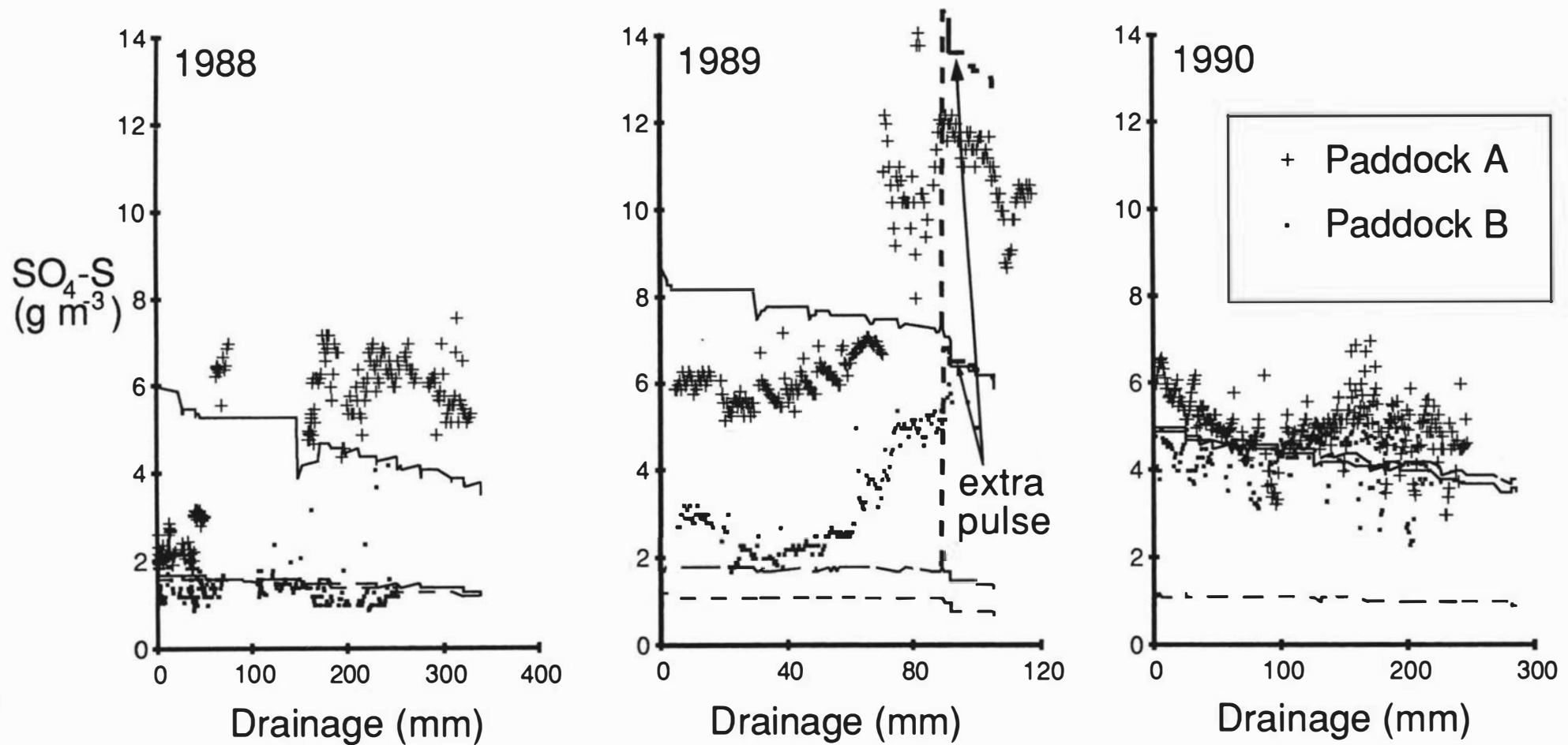


Table 7.2 Comparison between measured and predicted sulphate-S leached in 1988, 1989 and 1990

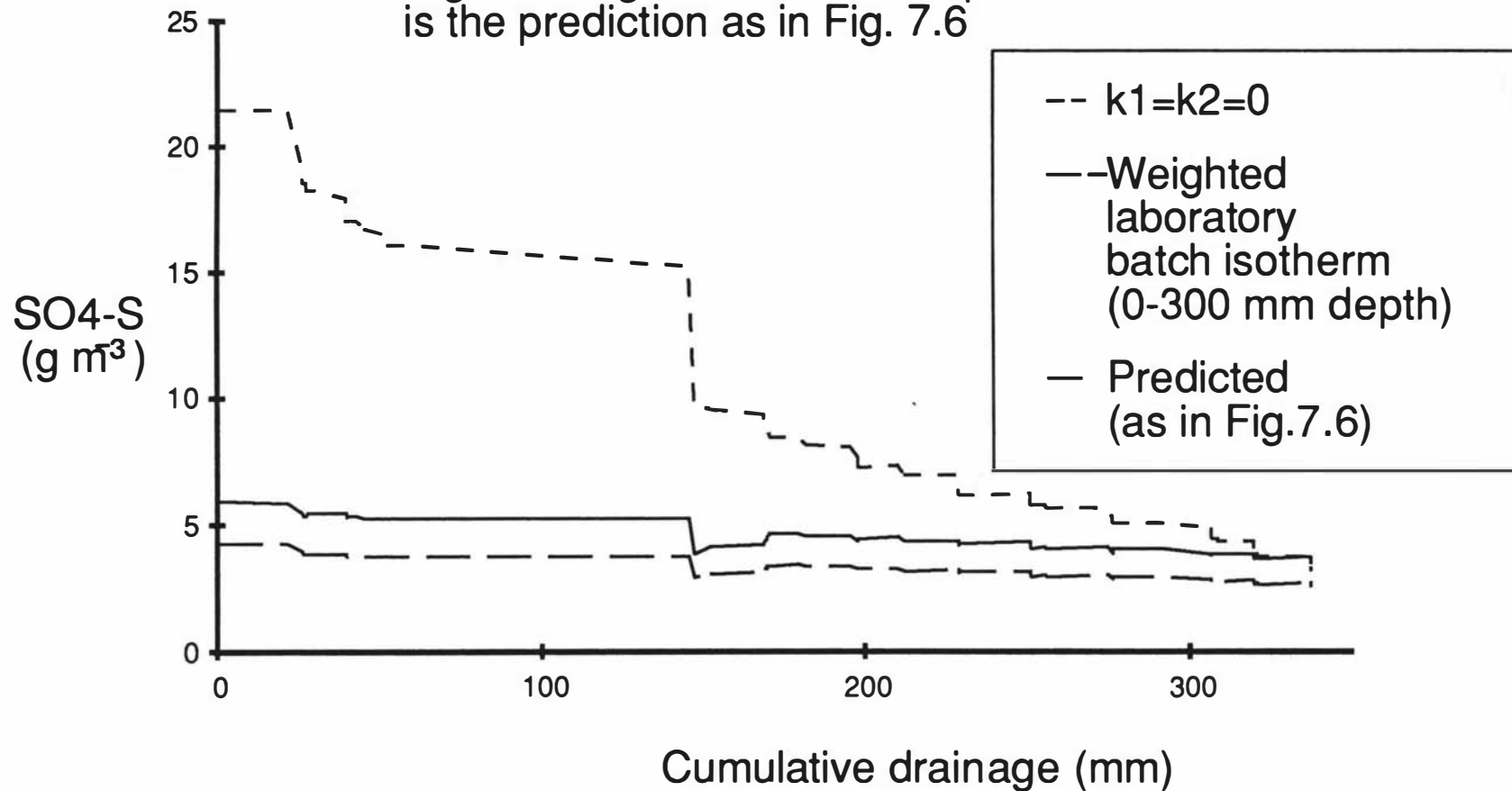
Year	Measured (kg S ha ⁻¹)		Predicted (kg S ha ⁻¹)		
	Paddock A	Paddock B	Paddock A	Paddock B	Paddock C
1988	17.0	3.4	16.0	5.2	4.9
1989	9.4	3.5	8.0	1.8	1.2
1990	12.3	9.5	12.0	12.4	3.0

Prediction of the leaching losses from paddock C was also made, as it can give an indication of the amount of sulphate-S leached in paddocks A and B that was not derived from the applied S fertilizers. The results for paddock C for the three years are shown as dotted lines in Fig. 7.6. As in Chapter 6, the drainage sulphate concentration in paddock C was predicted to be quite similar to that of paddock B in 1988. The difference in the predicted drainage concentration between paddocks B and C was larger in 1989, and this difference became very marked in 1990. Losses from paddock C in 1990 were much lower than from the two previously fertilized paddocks A and B, despite no fertilizer being added in 1990. Table 7.2 shows that the predicted amount of SO₄-S leached for paddock C in 1988 is 5 kg S ha⁻¹. In that year, the predicted sulphate-S loss from paddocks B and A were 5.2 and 16 kg S ha⁻¹ respectively. This implies that approximately 70% of the total amount of sulphate leached in paddock A in 1988 came from the SSP fertilizer.

7.4.4 Sensitivity Analysis

The model can also be used to illustrate the effect of mineralization and immobilization on drainage sulphate concentrations. Using paddock A input data for 1988, but assuming no transformations between organic and inorganic fractions (i.e. putting $k_1 = k_2 = 0$), the predicted outcome is shown as the dotted line in Fig. 7.7. A much higher drainage concentration is predicted, with a total of 37 kg ha⁻¹ of sulphur leached, equivalent to 73 % of the amount applied. This result has important implications for soils having little organic activity, and hence potential for

Fig. 7.7 The effect of changing parameters on the predicted drainage sulphate-S concentration in 1988. The short dashed line is for $k_1=k_2=0$. The long dashed line shows the effect of using the weighted batch adsorption isotherm, the solid line is the prediction as in Fig. 7.6



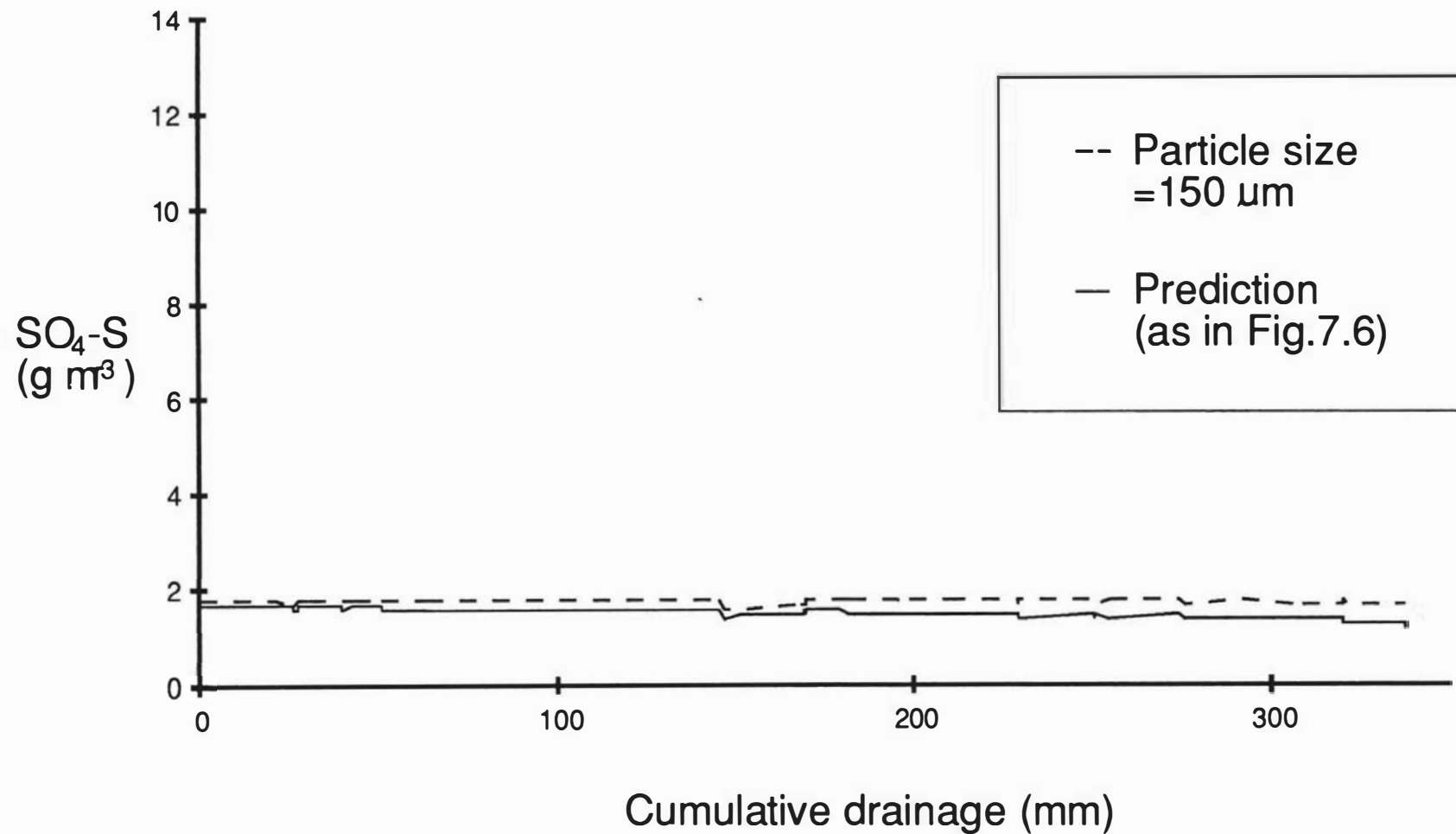
sulphate immobilization, indicating that substantial leaching can occur if a soluble form of sulphur fertilizer is applied at the wrong time.

The effect of adsorption was also tested. Gregg and Goh (1978), Bolan *et al.* (1986) and Mclay (1989) all showed that leaching losses were less from soils with high adsorption capacities. In the model, an adsorption isotherm derived from the suction cup data was used. However obtaining such data is very time consuming. Laboratory data obtained using the batch equilibration method are more readily obtained. The predicted concentration for paddock A using the laboratory determined sulphate adsorption isotherm, averaged over the top 300 mm depth, is shown as the dashed line in Fig. 7.7. Only a slightly lower drainage concentration was predicted. This implies that an isotherm determined in the laboratory may sometimes be accurate enough for use in modelling sulphate leaching from field soils.

The effect of applying a smaller elemental sulphur particle size was also modelled. Assuming the particles were all 150 μm in diameter, the model was run for the 1988 drainage season, and the result is shown in Fig. 7.8. Only a slight increase in the sulphate concentration in the drainage is predicted. The increase was predicted to be more in Chapter 6, where the buffering effect of immobilization/mineralization was ignored.

In New Zealand, the susceptibility of a soil to lose sulphate through leaching is often estimated by the sulphate leaching index (SLI) developed by MAF. On a scale of 0 to 6, the SLI is interpreted as no leaching for SLI of 0, 1, 2. On the other hand, complete winter leaching and severe summer leaching is expected to happen for an SLI of 6. For a mole-drained Tokomaru silt loam, which is a yellow-grey earth occurring in regions which have an annual rainfall of 750-1500 mm, an SLI of 5 is obtained. Under this category, complete winter leaching and some summer leaching is expected. It is suggested that the leaching from mainly urine patches for animals grazing at 18 stock units ha^{-1} is approximately 4, 9, 14 and 17 kg S ha^{-1} for soils with SLI's of 3, 4, 5 and 6 (Sinclair, 1982). Since a stock unit is defined as an animal consuming 550 kg $\text{ha}^{-1} \text{yr}^{-1}$ of dry matter, and

Fig. 7.8 The effect of using different elemental S particle size on the predicted drainage sulphate-S concentration in 1988.



assuming the concentration of S in the dry matter is approximately 0.3%, and that only the urine contribution is immediately available for leaching, then it can be shown that 18 stock units would give an excretal input of approximately 17 kg S ha⁻¹. When this amount is assumed about 23%, 53%, 82% and 100% of the 17 kg S ha⁻¹ applied will be leached from soils with SLI's of 3, 4, 5 and 6 respectively. The prediction of 70% of the sulphate in SSP being leached in this work is not far from the 82% predicted from the SLI for a yellow-grey earth. However, in the case where there was no addition of S, such as in 1990, the SLI would predict similar amounts of leaching for paddocks A and C; but the modelled and measured values for S leached from paddock C were much lower than from A.

7.5

SUMMARY AND CONCLUSIONS

A simple, "well mixed" model was developed to describe chloride and sulphate leaching. The model was able to predict the different amounts of leaching following the application of chloride fertilizer and different forms of sulphur fertilizers, except during the highly preferential flow conditions and at the start of 1988 and 1989. The results seem to suggest that the "well mixed" assumption will be met less satisfactorily if the amount applied is very much higher than the amount of resident solute. However, the model is much easier to use than the previous two models presented in Chapters 5 and 6, and needs less detailed soil and weather data. The modest information requirement of the model implies that it can be adapted to other situations, given appropriate adjustment of the parameters. It can also be used to predict the rate of leaching when the hydrology, chemistry or biology of the soil-plant system changes, and thus enhance the value of the limited number of field experiments it is possible to conduct. The results show that when modelling leaching losses of a biologically and chemically active solute, it is vital that the biological and chemical processes are adequately described. The dominance of these processes in determining leaching losses means that the use of more sophisticated models of the leaching process itself, such as the previous two approaches, does not significantly improve the predictions of leaching losses. The simple leaching model presented here seems quite adequate.

The prediction of the initial average soil solution concentration when KCl and SSP are applied could be improved if an equation describing the dissolution and mixing of the fertilizer with the soil was introduced. As the over-prediction in initial solution was not as bad in the case of chloride, perhaps different rates of dissolution for the SSP granules and the KCl crystals are needed. Further improvement could be made if a temperature-dependent first order rate equation was used for net mineralization/immobilization of sulphate.

CHAPTER 8

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

8.1 INTRODUCTION

The general significance and practical implications of the leaching results, together with the soil and plant uptake data presented in the previous chapters, are discussed in this chapter. The different modelling approaches used in this study are compared. Finally suggestions for future work are given.

8.2 LEACHING RESULTS AND THEIR PRACTICAL IMPLICATIONS

The field leaching experiment showed the importance of the interactions between physical, chemical and biological processes in determining the leaching losses of individual ions. For chloride, which is a mobile and non-reactive solute, factors such as the rate of fertilizer applied, its addition from the atmosphere and the intensity of rainfall influence the leaching pattern. The large amount of chloride being leached results in a corresponding loss of cations, which accompany chloride in order to maintain the charge balance.

For a biologically and chemically active ion such as sulphate, the rate of leaching is also affected by the rate of mineralization, adsorption and the form of sulphur applied. Warmer temperatures than usual in winter would encourage mineralization of organic sulphur which in turn results in an increased leaching of sulphate-S. As expected the application of elemental S (S^0) rather than single superphosphate (SSP) reduced the amount of sulphate-S leached significantly in both drainage seasons. This confirms that applying sulphate fertilizer in the soluble SSP form in late autumn to soils of low sulphate adsorption, such as the Tokomaru silt loam, is not desirable, as much of it will end up being leached. Because of this, an alternative to SSP as sulphur fertilizer has to be considered. In many situations where sulphur is needed, the slowly oxidising, insoluble S^0 is preferred. S^0 can be formulated in

different particle sizes to suit the requirements. In most farms in New Zealand, both phosphorus (P) and sulphur are needed to improve pasture growth. In that case, a mixture of S^o with high analysis sulphate-free P fertilizers, such as reactive phosphate rock, and partially acidulated phosphate rocks should be considered. The low plant sulphur content generally observed at the end of each spring and summer indicates that if S fertilizer were to be applied as SSP, it should be after the winter season, as it is not so susceptible to leaching then.

Good mass balances (between 90-110%) were obtained for both sulphate and chloride, implying all the major inputs, outputs and storage change were reasonably accurately measured or estimated.

Comparatively little nitrate was lost in the drainage water in both years, probably because little nitrogen was added to the system in winter. Only the initial autumn drainage had a high nitrate concentration, which was above the level specified by the World Health Organization for potable water. A significant improvement in the drainage water quality could be made by storing or treating this early drainage water.

A substantial amount of calcium was leached. It was the dominant cation in the drainage. On the other hand, the leaching of potassium was minimal, even though a relatively large amount was applied at the start of both drainage seasons. Most of the potassium applied was apparently retained preferentially on the exchange sites of the vermiculite clay present in the soil. Significant amounts of magnesium and sodium were leached, although they were not applied in fertilizer. The loss of magnesium is important because it is a vital nutrient for the ruminant animal. Such losses mean that it has to be taken into consideration when fertilizers and food additive recommendations are made. The large losses of sodium reflect the significant contribution through wet and dry deposition from the atmosphere.

Good agreement between the anion and cation charges in the drainage was obtained. The pH of the drainage was near 7 throughout the two seasons. There was no evidence for the acidification of the soil due to excessive Ca leaching.

8.3 SOIL AND PLANT UPTAKE DATA AND THEIR SIGNIFICANCE

Both field and laboratory-batch methods of obtaining the sulphate adsorption isotherm were used. The two methods of determining sulphate adsorption gave different isotherms, suggesting that care must be taken if laboratory-determined isotherms are used to predict field leaching behaviour.

The significant chloride uptake during the experiment is worth noting. It indicates that the presence of the plant helps to reduce leaching losses, and that much higher leaching of chloride and other ions would be expected from fallow soil. This also suggests that in the absence of large amounts of nitrogen input through N fixation and fertilizer use, chloride is the dominant anion in the drainage water.

There was no response in pasture production to the addition of S fertilizer, despite the low initial soil sulphate-S value. This result is in agreement with previous findings by Hoque *et al.* (1987) and Saunders *et al.* (1988) that the phosphate extractable sulphate-S method of measuring soil sulphate status is not a good way of assessing the S status for grazed pasture. Alternative methods should be sought.

8.4 A COMPARISON OF THE MODELLING APPROACHES USED

Three models were developed to predict the leaching of chloride and sulphate to the mole drains. The models differ markedly in terms of complexity and philosophy. The first model, given in Chapter 5, was developed from the soil water flow model of Scotter *et al.* (1990). The model divides the soil between the mid-mole plane and the mole drain into several notional compartments, assuming convection and mechanical dispersion to be the mechanisms for solute movement between compartments. Solute is also assumed to be present in both mobile and immobile soil water phases, with diffusion occurring between the two phases. The model was able to simulate the concentration of chloride immediately after fertilizer

application, and the observed drop in chloride concentration during bypass flow induced by intense rainfall. However, because of its complexity, and the detailed rainfall and soil hydraulic property data required to run the model, it cannot be easily adapted for management purposes.

The second model developed was very different in approach. A transfer function model (TFM) was used to predict the leaching of both chloride and sulphate-S to the drain. The TFM required measurement of the probability density function (pdf) of the apparent solute travel pathway lengths. A log-normal pdf of pathway lengths was assumed. The mean (μ) and standard deviation (σ) of the log normal pdf could be extrapolated from a non-reactive solute to a reactive one. However extrapolation from one year to another was not as good. Nevertheless, the model was an improvement over the previously used transfer function models in that it allows source/sink terms to be added in a simple way. The model was also able to demonstrate the effect of different types of sulphur fertilizer on sulphate-S leaching losses, and to illustrate the importance of adsorption on the rate of leaching.

The last model developed was the "well mixed" model. The rationale for this model came from the finding of Raats (1978) that for steady flow to a drain, with spatially uniform water input at the soil surface, and vertically uniform horizontal flow towards the drain, the solute concentration in the drain flow was the same as the average soil solution concentration. The model simulated the seasonal drain chloride concentration well, but like the TFM model, it could not predict the observed drop in concentration during highly preferential flow. The model also predicted the general seasonal trend in the leaching of sulphate-S reasonably well, except at the start of the drainage season when SSP was applied, and during increased mineralization of organic S. In comparison to the previous two models, this model is a much simpler model in terms of the input information required and running of the model, and is therefore more likely to be used for management purposes.

8.5 SUGGESTIONS FOR FUTURE WORK

Key information lacking in this work was accurate data on mineralization of organic sulphur, immobilization of applied S fertilizer, and the oxidation of S^0 . Also unknown was exactly how these processes were affected by temperature and moisture. In the third model, simple first order kinetic equations were used to describe these processes, ignoring the effect of variations in moisture and temperature. As the rate of mineralization of sulphur tends to depend on the nitrogen status of the soil (Sakadevan, pers. comm.), perhaps using nitrogen as a determining factor should be taken into account. These considerations highlight the complexity of the processes involved. It is very clear that a better way of describing the net mineralization rate is needed to accurately model the leaching losses of sulphate under field situations.

For the transfer function model, the present method of treating plant uptake and oxidation of S^0 as linear functions of drainage is not accurate enough, and an alternative approach is needed. Also whether the assumption of a log-normal pdf is justified may need further investigation.

For the "well mixed" model, a much higher initial sulphate concentration than the measured concentration in the drainage was predicted by the model. This was due to the assumption that the concentration in the drainage equals the average soil solution concentration at all times. This assumption implies that all the applied SSP fertilizer completely dissolved immediately after its application; but in many instances, the applied fertilizer is delayed in entering the soil solution by being caught in the grass sward, or by slow dissolution. Both assumptions need verification or modification. The high initial concentration prediction could be avoided if a method could be found to describe the gradual entrance of fertilizer into the soil solution. The time lag between dissolution and reaching the drain can be better understood by following the movement of a non-reactive tracer pulse, such as bromide or tritium, introduced into the soil.

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APPENDIX A

AMOUNTS OF SULPHUR FERTILIZER REQUIRED BASED ON THE MAF MODEL

In New Zealand, the sulphur maintenance requirements of the pasture on a given soil can be estimated from the S model developed by the Ministry of Agriculture and Fisheries (MAF) (Sinclair and Saunders, 1984). The amount required is that needed to replace losses of S in animal products, excreta transfer, leaching and immobilisation, less inputs from the atmosphere and irrigation water. The essential information needed for the S model are values of stocking rate (SU ha^{-1}), the sulphate leaching index (SLI), the pasture development index (PDI), and soil sulphate level which is generally taken as that from soil samples collected between 0-75 mm depth.

In the present study, the soil collected before fertilizer application in 1988 had the following values:

Calcium phosphate extractable sulphate: $5 \mu\text{g g}^{-1}$.

Sodium bicarbonate phosphorus (Olsen P): $14 \mu\text{g g}^{-1}$.

Thus according to the MAF sulphur model, the maintenance requirements were:

Sulphur: 36 kg ha^{-1} .

Phosphorus: 24 kg ha^{-1} .

However for intensive production system, a soil test of $10 \mu\text{g S g}^{-1}$ and $20 \mu\text{g P g}^{-1}$ is needed (Sinclair and Saunders, 1984). To achieve that level, amounts of S and P more than the maintenance requirements are required. In view of these, applications of 50 kg S ha^{-1} and 36 kg P ha^{-1} were decided on. As the S and P content of SSP was found to be 12% and 8.5% respectively, supplying 50 kg S ha^{-1} in SSP form would also give 35 kg ha^{-1} of P.

The same quantities of P and S were applied to paddock B as elemental S and triple superphosphate (TSP) fertilizer, which had a P content of 18%.