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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 (S<sup>0</sup>), were applied to two of the paddocks, while the third served as a control. The amount of KCl applied was 200 kg ha<sup>-1</sup> yr<sup>-1</sup>, while sulphur was applied at 50 kg S ha<sup>-1</sup> in 1988 and 30 kg S ha<sup>-1</sup> 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<sup>-1</sup> yr<sup>-1</sup>.

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<sup>-1</sup> were measured from the SSP and S<sup>0</sup> fertilized paddocks, respectively, in 1988, and 9.4 and 3.5 kg S ha<sup>-1</sup> 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 S<sup>0</sup> 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 S<sup>0</sup>. The reduced leaching of S when applied as S<sup>0</sup> resulted from the slow oxidation of S<sup>0</sup> to sulphate-S.

Relatively little nitrate-N was leached, the amount ranging from 11 to 17 kg N ha<sup>-1</sup> yr<sup>-1</sup>. Losses of potassium were less than 10 kg K ha<sup>-1</sup> yr<sup>-1</sup>, 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<sup>-1</sup> yr<sup>-1</sup>. The amount of magnesium leached was between 9 and 15 kg ha<sup>-1</sup> yr<sup>-1</sup>. A considerable quantity of sodium was

leached, around 58 kg ha<sup>-1</sup> in 1988, and 31 kg Na ha<sup>-1</sup> 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 [ $M L^{-2} T^{-1}$ ]
- $F_\theta$  = 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  $S^\circ$  particle at time  $t$  [L]  
 $r_o$  = initial radius of  $S^\circ$  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  
 $S_\theta$  = 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

$\alpha$	= a dimensionless empirical constant in the Priestley-Taylor equation (Ch 2) = rate coefficient for solute diffusion between phases [ $T^{-1}$ ] (Ch 5)
$\beta$	= horizontal dispersivity [L]
$\gamma$	= psychrometric constant [ $M L^{-3}$ per degree temperature change]
$\theta$	= volumetric water content [ $L^3 L^{-3}$ ]
$\rho$	= bulk density of soil [ $M L^{-3}$ ]
$\rho_s$	= specific gravity of elemental S [ $M L^{-3}$ ]
$\mu$	= mean of $\ln x$ (Ch 4) = mean of the log-normal pdf for travel pathway lengths of a non-reactive solute (Ch 6)
$\mu_{ad}$	= mean of the log-normal pdf for travel pathway lengths of a reactive (adsorbed) solute
$\sigma$	= standard deviation of $\ln x$ (Ch 4) = standard deviation of the log-normal pdf for travel path lengths (Ch 6)

$\psi_m$  = 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  $j^{\text{th}}$  class of  $S^{\circ}$  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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