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MODELLING SULPHATE DYNAMICS IN SOILS –

THE EFFECT OF ION-PAIR ADSORPTION

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MODELLING SULPHATE DYNAMICS IN SOILS –

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ABSTRACT

Sulphur is an important nutrient to plants, and reports of its deficiency have been increasing worldwide. Sulphur starvation causes losses in both yield and quality, and it reduces nitrogen use efficiency of plants. As the timing for fertilisation can be decisive for avoiding deleterious effects, improvements in the description of the sulphur balance in fields are a valuable contribution for assisting fertiliser management. Sulphate is the most important inorganic form of sulphur in soils. Being the mobile form, sulphate is readily available for plants, and also prone to be leached. Therefore the description of the movement of sulphate is the key component of the sulphur balance.

Leaching of sulphate from the soil can be significantly delayed by its adsorption onto the soil particles. Soil type and pH are the main factors defining the sulphate adsorption capacity; although the presence of other ions in the soil solution can have a considerable effect. It has been reported that in some soils, typically volcanic and tropical soils with variable-charge characteristics, the co-presence of sulphate and calcium can substantially enhance their retention via ion-pair adsorption (IPA).

To determine the influence of cations on the movement of sulphate, series of batch and miscible displacement experiments were conducted using two New Zealand soils, of contrasting ion adsorption capacities: the Taupo sandy and Egmont loam soils. These experiments demonstrated the occurrence of cooperative adsorption of sulphate and calcium in the Egmont soil, but not in the Taupo soil. Batch experiments were conducted to examine the IPA adsorption process in the Egmont soil in more detail.

Based on the analyses of the results from these two series of experiments, plus the review of published data, three different mathematical

approaches for evaluating the amount of solute adsorbed as ion-pairs are proposed. A computer program was built for solving an adsorption model using these three approaches, and was used to compare the model's predictions and the observed adsorption data. An extension of this program, coupling the adsorption model with a solute transport description, was used to simulate the movement of sulphate and calcium. Comparisons between the data from the miscible displacements and the results from this model are used to demonstrate the applicability of the proposed IPA description for modelling the transport of these ions in the soil.

Finally, results from a pot trial with Egmont soil are used to examine the relevance of IPA for the movement of sulphate under non-equilibrium conditions, and with active plant growth. Although the results from this experiment regarding IPA were statistically non-significant, some insights could be obtained and are discussed. More studies involving IPA under non-equilibrium experiments are needed for a better understanding of the relevance of IPA in field conditions.

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LIST OF SYMBOLS AND ABBREVIATIONS

Roman letters

Symbol	Description	Unit
a	Constant used for computing the value of D	-
b	The slope of the linear relationship between S_1 and S_2	-
C	Concentration of a solute dissolved in the soil solution	[mol m ⁻³]
\hat{C}	The value of C predicted by the model	[mol m ⁻³]
D	Hydrodynamic dispersion coefficient for solute movement	[m ² s ⁻¹]
D_o	Diffusion coefficient of a solute in water	[m ² s ⁻¹]
D_w	Water diffusivity	[m ² s ⁻¹]
h	Hydraulic head	[m]
i	An integer used as index to indicate the ion species	-
j	An integer used as a counter	-
K_w	Soil hydraulic conductivity	[m s ⁻¹]
K_s	Saturated soil hydraulic conductivity	[m s ⁻¹]
k_{cb}	Crop coefficient for evapotranspiration	-
k_b	Constant for ion-pair equilibrium in saline solutions	[mol]
k_d	The distribution factor	[L kg ⁻¹]
k_F	Parameter of the Freundlich isotherm equation	[L kg ⁻¹]
k_s	IPA equilibrium factor for PGA approach	[mol kg ⁻¹]
k_c	IPA equilibrium factor for SGA1 approach	[mol L ⁻¹]
k_r	IPA equilibrium factor for SGA2 approach	[L kg ⁻¹]

M_L	Maximum adsorption capacity, from Langmuir equation	[mol kg ⁻¹]
m_{soil}	Dry mass of soil	[kg]
N	Exponent of the Freundlich isotherm equation	-
n_D	The total number of elements in a data set	-
n_P	The number of parameters	-
O	A value from an observed data set	-
P	A value from an predicted data set	-
p	Representation of a generic model's parameter	-
Q	The solute concentration in the soil (volume basis)	[mol m ⁻³]
Q_S	The solute concentration in the soil (mass basis)	[mol kg ⁻¹]
Q_A	Amount of solute added to the soil in the MD experiments	[mol]
Q_F	Solute amount in the soil after the MD experiments	[mol]
Q_I	Solute amount in the soil before the MD experiments	[mol]
Q_L	Amount of solute leached during the MD experiment	[mol]
Q_{Sol}	A given amount of solute	[mol]
q_s	Solute flux density in the soil	[mol m ⁻² s ⁻¹]
q_w	Water flux density in the soil	[m s ⁻¹]
R	Retardation factor for the solute movement in the soil	-
R^2	Pearson correlation coefficient	-
S	Concentration of a solute adsorbed onto the soil particles	[mol kg ⁻¹]
\hat{S}	The value of S predicted by the model	[mol kg ⁻¹]
S_{IP}	Concentration of a solute adsorbed due to IPA	[mol kg ⁻¹]
S_s	Single species adsorption concentration	[mol kg ⁻¹]

S_{s0}	The intercept of the linear relationship between S_1 and S_2 , representing the adsorption of an ion without the presence of its counter ion.	[mol kg ⁻¹]
t	Temporal ordinate	[s]
v	Water velocity in the soil	[m s ⁻¹]
V_w	Volume of water or solution	[L]
y	The calibration function or a value of that function	[mol L ⁻¹]
\bar{y}	The average of several realisations of y	[mol L ⁻¹]
z	Spatial ordinate, commonly vertical (depth)	[m]

Greek letters

Symbol	Description	Unit
β	Mass balance estimator	[%]
δ	A sink-source term	[mm s ⁻¹]
ϕ	Parameter of the Langmuir equation	-
Φ	The objective function	-
Φ_C	The objective function comparing values of C	-
Φ_S	The objective function comparing values of S	-
ϑ	Specific water volume or water-to-soil ratio	[L kg ⁻¹]
φ	The weighting factor in the objective function	-
λ	Soil dispersivity	[m]
μ	A generic measurement of a measuring device or procedure	-
θ	Volumetric soil water content	[m ³ m ⁻³]
ρ	Soil bulk density	[kg m ⁻³]

σ_m^2	Variance of the measuring procedure	-
σ_{μ}^2	Variance of the measurements of a measuring device	-
σ_o^2	The variance of the observed data	-
σ_p^2	The variance of a parameter estimate	-
σ_r^2	Variance of the experimental replications	-
τ	Tortuosity coefficient	-
ψ	Soil water potential	[Pa]

Additional symbols

Symbol	Description	Unit
\mathcal{D}	The χ^2 probability density function.	-
\mathcal{P}_{Adeq}	The probability of the model adequacy	-
\mathcal{P}_{Conf}	The probability for the confidence interval of a parameter estimate	-

Abbreviations:

AEC	Anion exchange capacity
BTC	Breakthrough curve
CDE	Convection-dispersion equation
CEC	Cation exchange capacity
CH	Treatment using CaSO ₄ and high irrigation rate
CL	Treatment using CaSO ₄ and low irrigation rate
FDM	Finite-difference model
IPA	Ion-pair adsorption

KH	Treatment using K_2SO_4 and high irrigation rate
KL	Treatment using K_2SO_4 and low irrigation rate
MD	Miscible displacement
NH	Treatment using no fertiliser and high irrigation rate
NL	Treatment using no fertiliser and low irrigation rate
OM	Organic matter
PV	Pore volume = number of WFPV leached through a soil column
PGA	Particle governed approach for describing IPA
SGA1	Linear solution governed approach for describing IPA
SGA2	Radical solution governed approach for describing IPA
RMSE	Root mean squared error
WFPV	Water filled pore volume
