

Modelling the Transport of SO_4^{2-} Ions in Acid Sulphate Soils

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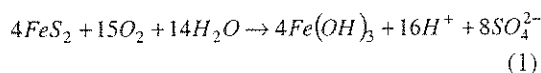
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Abstract: Modelling solute transport in acid sulphate soils is crucial to identifying their long-term hazards to the environment. The modelling work requires the knowledge of solute transport parameters, which are specific to any soil-solute system. In addition, the model requires site-specific calibration to ensure reliable results. In this work, the relevant solute transport parameters were estimated from the inverse solution of the convection-dispersion equation and a solute breakthrough curve obtained from a laboratory leaching column experiment. HYDRUS-2D was used to model water and solute transport under variably saturated conditions. Field drainage data obtained from a controlled irrigation trial and inverse modelling techniques were coupled to calibrate the model. Incorporating physical non-equilibrium into the solute transport model produced the best match to the cumulative SO_4 -ions measured in the field. This is in agreement with the findings obtained from the laboratory leaching column experiment.

Keywords: Inverse modelling, Solute transport, Drainage, Acid sulphate soils, Breakthrough curve

1. INTRODUCTION

Acid sulphate (AS) soils have formed within the past 10,000 years (the Holocene epoch), after the last major sea level rise. When the sea level rose and inundated land, sulphates in the seawater mixed with land sediments containing iron oxides and organic matter. The resulting chemical reactions produced large quantities of iron sulphides in the waterlogged sediments, the most common form being pyrite (FeS_2). When iron sulphides are exposed to oxygen, they oxidise to produce sulphuric acid. The overall oxidation equation is written as:



AS soils are considered to be a global environmental hazard. Along the 6500-km coastline of Queensland alone, there are an estimated 2.3 million hectares of AS soils [Powell and Ahern, 2000]. Acid sulphate soils have environmental impacts such as fish disease and death. They adversely impact estuarine waters and result in high toxicity due to a combination of an extremely low pH (below 4) and an elevated concentration of metals such as aluminium, iron, and manganese [Sammot et al., 1996]. The released aluminium and iron react with the

receiving water and produce further acidity. Based on an experimental study in South-East Queensland, Australia, Cook et al. [2000a] have shown that most of the acidity produced during a drainage event was attributable to the released Fe^{2+} and Al^{3+} ions. Acidic waters destroy food resources, displace biota to other areas, precipitate iron, and smother vegetation [Powell and Ahern, 2000]. Economic impacts include: poor plant productivity, corrosion to concrete and steel structures, and clogging of aquifers and waterways.

The pattern in which ions are leached from AS soils is greatly relevant to their management. The leaching process is most frequently described by assuming that water entering any layer of soil displaces water already in that layer and that solutes initially present near the soil surface are moved downward as a 'band' or a 'concentration bulge' that is moved progressively deeper with each additional amount of water passing through the soil [Priebe and Blackmer, 1989]. However, preferential flow may bypass many of the smaller pores without displacing their contents thus resulting in a delayed movement of the concentration bulge. Depending on whether the solutes are present in the macro- or in the micro-pores, preferential flow may lead to earlier or

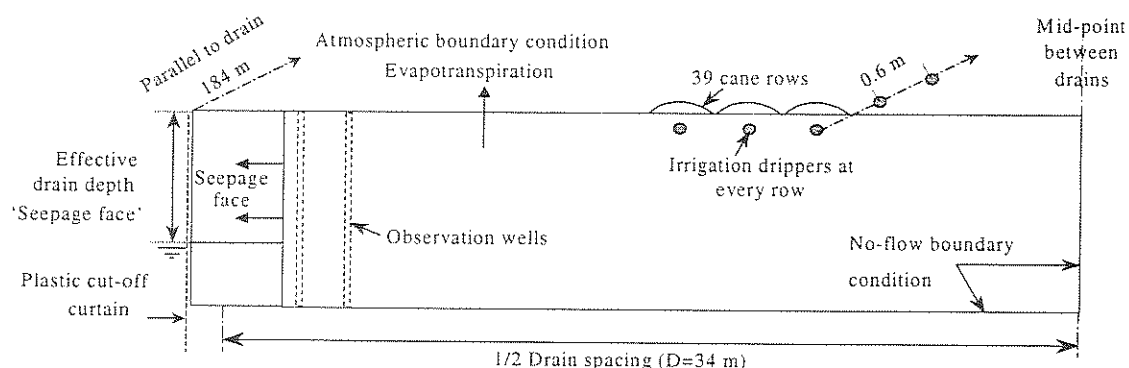


Figure 1. Schematic showing field set-up and model boundary conditions.

later arrival of solutes, respectively (Snow et al., 1994). The pore structure of the soil plays an important role, whereby most of the mass transport occurs through the continuous pore system, that is, through mobile phase. However, solutes have to diffuse from the discontinuous pore system (the immobile phase) to the mobile system in order to be transported.

Numerical modelling is a useful tool that can be adopted to predict solute fluxes from AS soils, and hence assess the hazards posed by these soils. Solute transport parameters, which are unique for every soil-solute system, are a vital input for numerical models. The hydraulic conductivity function of the soil is a vital input for models that simulate unsaturated water flow. The saturated hydraulic conductivity, which is used to calibrate this hydraulic conductivity function, is recognised as one of the most variable soil physical properties. Laboratory measurements suffer a scale problem whereby a small sample may not represent field conditions. Daniel [1984] observed many cases where the actual permeability of clay liners used to retain water were 10 to 1000 greater than that designed for. The interaction of permeant with the soil fabric further adds to the variability of the hydraulic conductivity. Chemical reactions that take place as a result of permeation with acid-base solutions reactions alter the hydraulic conductivity of the soil. Rassam and Cook [2001a] have reported a three-fold increase in conductivity during flow of de-ionised water containing a bromide tracer through an AS soil sample.

In this work, a field trial conducted to investigate the environmental hazards of AS soils, is described. An experimental solute break through curve (BTC) for SO_4 ions was estimated from a leaching column experiment conducted on an

undisturbed AS soil sample obtained from the experimental site. The inverse analytical solution of the convection-dispersion equation was adopted to evaluate the transport parameters for sulphate ions. To match the observed field drainage data, an inverse modelling approach was adopted to optimise the hydraulic conductivity of the soil. The optimised input parameters were used to model the transport of SO_4 ions on a field scale. The predicted cumulative SO_4 ion export via the drainage water was compared with the field observations.

2. EXPERIMENTAL WORK

2.1 Description of Fieldwork

A field study was conducted to investigate the environmental impacts of AS soils [Rassam et al., 2001; Cook et al., 2000b]. The experimental site is situated in Pimpama, a flat coastal plain in southeast Queensland, which is planted to sugar cane.

The soil at this site is an Ultisol [Soil Survey Staff, 1996] with a total oxidisable sulphur of 0.1%S in the 0 to 0.6 m and 1.2%S in the next 0.6 m of soil (D. Smith *pers. comm.*). The bulk density and porosity of the soil were measured to be 1200 kg/m^3 and 0.6, respectively.

The experimental irrigated site area is 1.04 ha. It has been drained for the last ten years. Figure 1 illustrates the experimental set-up described herein. The drains were spaced at 68 m (half spacing $D=34 \text{ m}$) and were 184 m long. The depth of the drain was about 1 m and the water table level is set at 0.43 m below the soil surface. Observation wells which were perforated to within 0.3 m from the soil surface, were installed to monitor water table

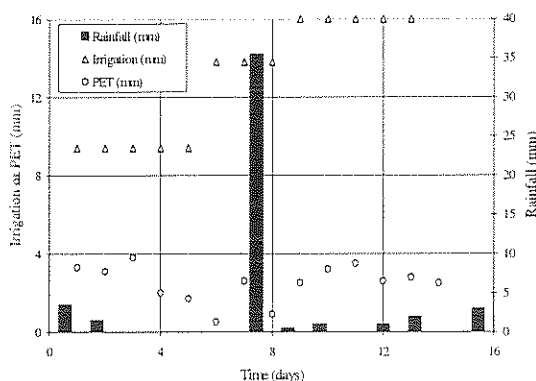


Figure 2. Irrigation, rainfall, and PET data.

fluctuations and were later utilised to monitor water quality. The irrigation drippers were designed to supply a maximum rate of 1.3 L/hr (approximately 24 mm/day). The irrigation drippers were spaced as shown in Figure 1.

The drainage water that flows into the ditch drain is subsequently transported through the tile drain to a concrete sump via a riser, which controls the minimum watertable level. The collected water is pumped from the concrete sump through a flow meter, which measures its volume. The cumulative water volume was recorded every 10 minutes, thus allowing the average discharge rate for that time period to be calculated. During a drainage event, water was automatically sampled at pre-set volume intervals of 1000 L, 3000 L, and 6000 L. Sampling continues to the end of drainage at the latter rate. Al ion concentration was quantified using inductively coupled plasma atomic emission spectroscopy (ICPAES) following the Standard Methods for the Examination of Water and Wastewater [1995].

An irrigation event was conducted during the period between 30/10/2000 and 8/11/2000. The recorded amounts of irrigation, PET, and rainfall during that period are shown in Figure 2.

The field hydraulic conductivity was measured using the auger-hole method [Youngs, 1991].

$$K = \frac{4.17}{(10 + h_i/R)(2 - h_t/h_i)} \frac{R}{h_t} \frac{dh_t}{dt} \quad (2)$$

where K is the hydraulic conductivity (m/s), h_i is the initial height of the water table measured relative to the base of the dip-well, R is the radius of the dip-well, h_t is the water table height at any time t , measured relative to the initial water table level. The estimated hydraulic conductivity is listed in Table 1.

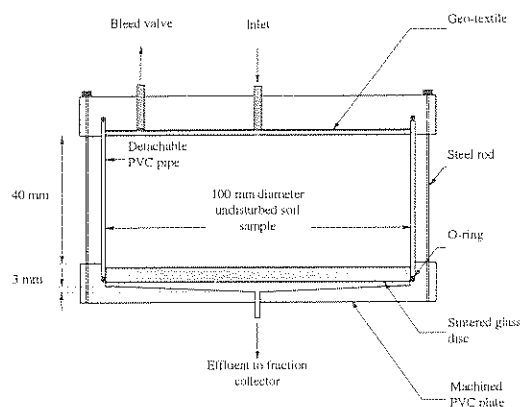


Figure 3. Flow cell.

2.2 Description of Laboratory Work

Undisturbed soil cores were obtained from the two experimental sites following the procedure described by Cook et al. [1993].

The undisturbed soil sample was then placed on the cell base shown in Figure 3. The permeating fluid was supplied at a constant head with the aid of a 2 L Marriot bottle. Permeation with deionised water was then initiated and the effluent was collected at prescribed time intervals with the aid of an automated fraction collector. Sulphate ion concentration was measured with the aid of a Merck Nova-60 Spectroquant using the relevant cell test-kit supplied by the same manufacturer.

A constant-head permeability test was conducted in the flow cell shown in Figure 3 using undisturbed, cracked and intact samples obtained from the experimental site; results are shown in Table 1.

3. NUMERICAL MODELLING

3.1 Field-scale Modelling

The finite element model HYDRUS2D [Simunek et al., 1999] was used to calculate the sulphate transport in an acid sulphate soil. The domain, initial conditions and boundary conditions are shown in Figure 1. The initial watertable height was taken as that of observation wells at the site prior to irrigation. The soil hydraulic properties were obtained from inverse modelling to fit the drainage volume data. The initial SO_4 concentration in the soil pore water (resident concentration) was measured by sampling water from the observation wells prior to the irrigation event; it amounted to 2.6 kg/m^3 . The solute transport parameters were obtained from analysing the breakthrough curves as described in the following section.

Table 1. Estimates of hydraulic conductivity.

	Hydraulic conductivity m/s
Field auger hole method	1.5×10^{-8}
Intact lab sample	1.4×10^{-9}
Cracked lab sample	2.5×10^{-8}
Inverse modelling	2.3×10^{-6}

3.2 Laboratory-scale Modelling

Solute transport through a one-dimensional column may be described by the well-known convection-dispersion equation (CDE):

$$R_d \frac{\partial C_r}{\partial t} = D \frac{\partial^2 C_r}{\partial x^2} - v \frac{\partial C_r}{\partial x} \quad (3)$$

where C_r is the volume-averaged solute concentration within the soil pore water usually known as the resident concentration ($M/L^3_{\text{pore-water}}$), D is the hydrodynamic dispersion coefficient that lumps the additive effects of mechanical dispersion and effective diffusion (L^2/T), v is the average pore-water velocity equal to the fluid flux (q) given by Darcy's law divided by the volumetric water content (L/T), and x is the distance in the direction of transport (note that M , L , and T refer to mass, length, and time units, respectively). The retardation factor R_d is a dimensionless factor that relates to the adsorption capacity of the soil for a specific solute species. The solution of Equation (3), subject to a flux boundary condition, is given by van Genuchten and Alves [1982].

When there is physical equilibrium, all the pores in the soil structure actively participate in fluid transport, i.e., effective porosity is equal to total porosity. However, under physical non-equilibrium conditions, a dual-porosity concept is used where the medium is discretised into two regions; a mobile water region (θ_m) where convective/dispersive transport dominates, and an immobile region ($\theta - \theta_m$) where water is stagnant and solute transport between the two regions is strictly diffusive. Two terms, namely, β and ω are introduced to define mass transport from the immobile to the mobile phases. The former, is a partitioning factor that relates to the mobile water fraction θ_m/θ and the fraction of adsorption sites that are assumed to be in equilibrium with the mobile liquid region. The latter, is a mass transfer coefficient defining the rate of solute exchange between the mobile and immobile regions. A detailed description of the physical non-equilibrium model is found in van Genuchten and Wagenet [1989].

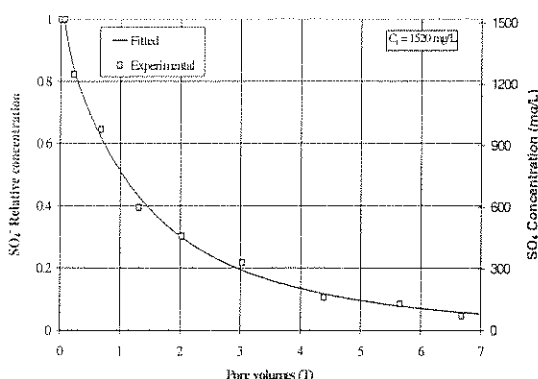


Figure 4. Experimental and fitted BTC for SO_4 .

The software package "STANMOD" [Simunek et al., 1999] was adopted to provide the analytical solutions for the governing differential equations. It uses the CXTFIT code of Toride et al. [1995] for estimating solute transport parameters using a non-linear least-squares parameter optimisation method.

4. RESULTS AND DISCUSSION

4.1 Laboratory Work

Rassam and Cook [2001b] estimated the transport parameters for chloride, aluminium, and bromide ions by analysing BTC obtained from undisturbed AS soil samples. They verified the presence of physical non-equilibrium in those soils. The effluent obtained from the same leaching experiments were analysed for sulphate ions, and is shown in Figure 4. The parameters listed in Table 2 as 'not optimised' were obtained from Rassam and Cook [2001b], and were used as known input parameters in the current analysis. The pore water velocity and the mobile water content are physical properties relevant to both solutes. However, the dispersion coefficient may be different for the two solutes. Toride et al. [1995] have suggested that D might be assumed to remain constant for two BTC's obtained from the same soil sample. Reducing the number of optimised parameters avoids non-uniqueness of solution, a problem that has been highlighted by Rassam and Cook [2001b].

The optimised parameters that include the

Table 2. Transport parameters for SO_4 ions.

Not optimised	v (cm/day)	D (cm^2/day)	θ_m/θ
	1.33	3.32	0.692
Optimised	R_d	β	ω
	1.88	0.368	2.27

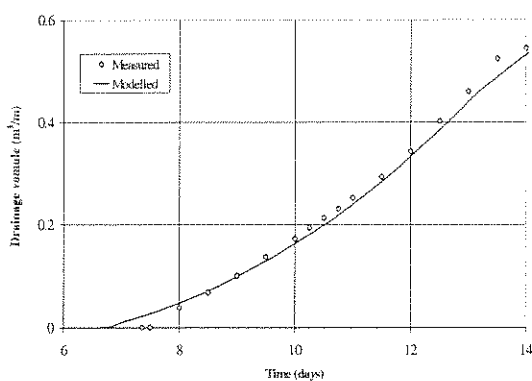


Figure 5. Observed and modelled drainage.

retardation factor R_d , the partitioning coefficient β , and the mass transfer coefficient ω are listed in Table 2. The resulting good fit to the experimental BTC is shown in Figure 4.

4.2 Field Work

The hydraulic conductivity of the soil has a major and direct impact on solute export from draining soils. Table 1 shows that the field measurement of the hydraulic conductivity was one order of magnitude higher than that of the intact lab sample. The field estimate was closer to the conductivity of the cracked lab sample. However, it was two orders of magnitude lower than the measured seepage flux during the irrigation trial, which amounted to about 2.5×10^{-6} m/s. These contradicting figures warrant extreme care in choosing the right value for modelling purposes.

Inverse modelling of the drainage data provides a realistic estimate for the hydraulic conductivity on a large field scale. The estimated hydraulic conductivity listed in Table 1 was close to the measured seepage flux. Figure 5 shows the resulting fit to the field drainage data. The results demonstrate the extent of presence of preferential paths, which dominate the field-scale hydraulic conductivity. Preferential paths have an impact on solute transport in low-conductivity AS soils [Rassam and Cook, 2001a]. Although field measurements of hydraulic conductivity are considered to be more reliable than laboratory measurements, extreme care must be taken when up-scaling to a much larger field area.

The field-scale modelling of cumulative SO_4 ion export is shown in Figure 6. It shows that excluding physical non-equilibrium greatly overestimates the cumulative mass. Passive and reactive transport, result in very close estimates for

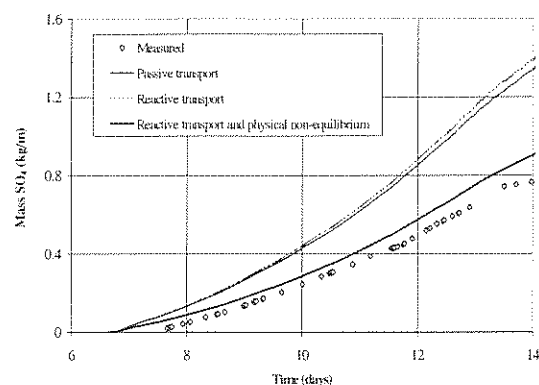


Figure 6. Predicted and modelled SO_4 loads.

the cumulative mass. Adopting the physical non-equilibrium model resulted in predictions of cumulative SO_4 ions, which were closest to those observed in the field. Results shown in Figure 6 verify the presence of an immobile water phase, whose presence was observed in the leaching column experiments.

5. CONCLUSIONS

Numerical modelling of coupled water and solute transport require proper parameterisation in order to obtain reliable results that match field observation. In this work, experimental breakthrough curves (BTC) for sulphate ions were obtained from a leaching column experiment conducted on undisturbed acid sulphate soil samples. Inverse solution of the convection-dispersion equation for solute transport has verified the suitability of a physical non-equilibrium, reactive transport model to fit the experimental BTC. The estimated solute transport parameters included the retardation factor, the fraction of adsorption sites in contact with the mobile phase, and the mass transfer coefficient between the mobile and immobile phases.

Results of the field-scale inverse modelling have shown that the hydraulic conductivity was two orders of magnitude higher than the field measurement using the auger hole method. Adopting the physical non-equilibrium model resulted in predictions of cumulative SO_4 ions, which were closest to those observed in the field. This confirmed the presence of physical non-equilibrium, which was observed in the laboratory columns.

6. ACKNOWLEDGEMENTS

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7. REFERENCES

- American Public Health Association, American Water Works Association, and Water Environment Federation, *Standard Methods for the Examination of Water and Wastewater*, (Editorial board A.D. Eaton, L.S. Clescera, and A.E. Greenberg). Publisher, American Public Health Association, Washington, 1995.
- Cook, F.J., G.P. Lilley, and R.A. Nunns, Unsaturated hydraulic conductivity and sorptivity: Laboratory measurement, in *Soil Sampling and Methods of Analysis*, Ed. Carter, M.R., Canadian Society of Soil Science, Lewis Publishers, Boca Raton, Florida, pp. 615-624, 1993.
- Cook, F.J., W. Hicks, E.A. Gardner, G.D. Carlin, and D.W. Froggatt, Export of acidity in drainage water from acid sulphate soils, *Marine Pollution Bulletin*, 41:319-326, 2000a.
- Cook, F.J., D.W. Rassam, G.D. Carlin, and E.A. Gardner, Acid Flow from Acid Sulphate Soils: Measurement and Modelling of Flow into Drains, in *Sustainable Environment Solutions for Industry and Government*, 3rd Queensland Environmental Conference, The Institute of Engineers, Australia, 2000b.
- Daniel, D.E., Predicting hydraulic conductivity of clay liners, *Journal of Geotechnical Engineering*, 110(2), pp. 285-300, 1984.
- Powell, B., and C.R. Ahern, Nature, origin, and distribution of acid sulphate soils: issues for Queensland, Proceedings of workshop on Acid Sulphate soils: Environmental Issues, Assessment and Management (Ahern et al. editors), pp 1.1-1.12, 2000.
- Priebe, D.L., and A.M. Blackmer, Preferential movement of oxygen-18-labeled water and nitrogen-15-labeled urea through macropores in a nicollet soil, *Journal of Environmental Quality*, 18: 66-72, 1989.
- Rassam, D.W., and F.J. Cook, Interaction of hydraulic conductivity, solute transport, and preferential paths on field and laboratory scales, Submitted to the *Canadian Geotechnical Journal*, 2001a.
- Rassam, D.W., and F.J. Cook, Solute transport parameters from experimental solute breakthrough curves, Submitted to the *Canadian Geotechnical Journal*, 2001b.
- Rassam, D.W., F.J. Cook, and E.A. Gardner, Field and laboratory studies of acid sulphate soils, *Journal of Irrigation and Drainage Engineering, ASCE*, In Press, 2001.
- Sammut, J., R.B. Callinan, and G.C. Fraser, An overview of the ecological impacts of acid sulphate soils in Australia, Proceedings of 12th National Conference of Acid Sulphate soils, Coffs Harbour, 5-6 September 1996, Smith and Associates and ASSMAC, Australia, pp 140-145, 1996.
- Simunek, J., M. Senja, and M. Th. van Genuchten, HYDRUS-2D, V2 software package for simulating water flow and solute transport in two-dimensional variably saturated media. U.S. Salinity Laboratory, Agricultural Research Service, U.S. Dept. Agriculture, Riverside, California, 1999.
- Simunek, J., M. Th. van Genuchten, M. Senja, N. Toride, and F.J. Leij, STANMOD, V2 Computer software for evaluating solute transport in two porous media using analytical solutions of convection-dispersion equation, U.S. Salinity Laboratory, Agricultural Research Service, U.S. Dept. Agriculture, Riverside, California, 1999.
- Snow, V.O., B.E. Clothier, D.R. Scotter, and R.E. White, Solute transport in a layered field soil: Experiments and modelling using the convection-dispersion approach, *Journal of Contaminant Hydrology*, 16: 339-358, 1994.
- Soil Survey Staff, *Keys to Soil Taxonomy*, 7th edition, US Department of Agriculture, Soil Conservation Services, USA, 1996.
- Toride, N., F.J. Leij, and M. Th. van Genuchten, The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments, V 2.1. U.S. Salinity Laboratory, Agricultural Research Service, U.S. Dept. Agriculture, Riverside, California, 1995.
- van Genuchten, M. Th., and W.J. Alves, Analytical solutions of the one-dimensional convective-dispersive solute transport equation, Tech. Bull. 1661, U.S. Dept. Agri., 1982.
- van Genuchten, M. Th., and R.J. Wagenet, Two-site/two-region models for pesticide transport and degradation: Theoretical development and analytical solutions, *Soil Science Society of America Journal*, 53: 1303-1310, 1989.
- Youngs, E.G. Hydraulic conductivity of saturated soils, in *Soil Analysis Physical Methods*, Smith and Mullins eds, pp 161-207, 1991.