Inverse modelling for predicting both water and nitrate movement in a structured-clay soil (Red Ferrosol)

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Soil physical parameter calculation by inverse modelling provides an indirect way of estimating the unsaturated hydraulic properties of soils. However many measurements are needed to provide sufficient data to determine unknown parameters. The objective of this research was to assess the use of unsaturated water flow and solute transport experiments, in horizontal packed soil columns, to estimate the parameters that govern water flow and solute transport. The derived parameters are then used to predict water infiltration and solute migration in a repacked soil wedge. Horizontal columns packed with Red Ferrosol were used in a nitrate diffusion experiment to estimate either three or six parameters of the van Genuchten–Mualem equation while keeping residual and saturated water content, and saturated hydraulic conductivity fixed to independently measured values. These parameters were calculated using the inverse optimisation routines in Hydrus 1D. Nitrate concentrations measured along the horizontal soil columns were used to independently determine the Langmuir adsorption isotherm. The soil hydraulic properties described by the van Genuchten–Mualem equation, and the NO\textsubscript{3}– adsorption isotherm, were then used to predict water and NO\textsubscript{3}– distributions from a point-source in two 3D flow scenarios. The use of horizontal columns of repacked soil and inverse modelling to quantify the soil water retention curve was found to be a simple and effective method for determining soil hydraulic properties of Red Ferrosols. These generated parameters supported subsequent testing of interactive flow and reactive transport processes under dynamic flow conditions.
Inverse modelling for predicting both water and nitrate movement in a structured-clay soil (Red Ferrosol)

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Abstract

Soil physical parameter calculation by inverse modelling provides an indirect way of estimating the unsaturated hydraulic properties of soils. However, many measurements are needed to provide sufficient data to determine unknown parameters. The objective of this research was to assess the use of unsaturated water flow and solute transport experiments, in horizontal packed soil columns, to estimate the parameters that govern water flow and solute transport. The derived parameters are then used to predict water infiltration and solute migration in a repacked soil wedge. Horizontal columns packed with Red Ferrosol were used in a nitrate diffusion experiment to estimate either three or six parameters of the van Genuchten-Mualem equation while keeping residual and saturated water content, and saturated hydraulic conductivity fixed to independently measured values. These parameters were calculated using the inverse optimisation routines in Hydrus 1D. Nitrate concentrations measured along the horizontal soil columns were used to independently determine the Langmuir adsorption isotherm. The soil hydraulic properties described by the van Genuchten–Mualem equation, and the NO$_3^-$ adsorption isotherm, were then used to predict water and NO$_3^-$ distributions from a point-source in two 3D flow scenarios. The use of horizontal columns of repacked soil and inverse modelling to quantify the soil water retention curve was found to be a simple and effective method for determining soil hydraulic properties of Red Ferrosols. These generated parameters supported subsequent testing of interactive flow and reactive transport processes under dynamic flow conditions.

Additional Keywords: Hydrus-1D, Hydrus-2D, Pedotransfer functions, rosetta, water flow
Introduction

Simulation models are useful for examining water and solute movement in soil profiles, such as when improving water and nutrient use efficiency or designing fertigation systems (Cote et al. 2003; Skaggs et al. 2004; Siyal and Skaggs 2009). There are a number of soil water models, such as LeachM (Wagenet and Hutson 1989), Wet-Up (Cook et al. 2003), Hydrus 1D (Šimůnek et al. 2008), Hydrus 2D/3D (Šimůnek et al. 2006), and numerical procedures described by Wu and Chieng (1995a; 1995b) which are all capable of describing water flow, and in some cases solute transport, in one, two, or three dimensions. In this study, we selected the suite of Hydrus models, because they can simulate solute flow under both 1D and 3D conditions. The van Genuchten-Mualem water content, capillary pressure and hydraulic conductivity models were used to predict water flow (Šimůnek et al. 2006), but physically realistic parameters are needed for the intended application if accurate predictions are to be made.

Inverse optimisation techniques have become increasingly popular for parameter estimation and many soil models now have user-friendly optimisation tools built in (Hopmans et al. 2002; Vrugt and Bouten 2002; Wohling et al. 2008; Kandelous et al. 2011). The method involves multiple calculations in which parameters are adjusted, using a method such as the Levenberg–Marquardt or Bayesian procedure, until predictions agree sufficiently well with the measured data (Šimůnek et al. 2006). This has advantages over other techniques for estimating hydraulic parameters, such as pedotransfer functions, because the optimised parameters are estimated directly from measured data for a particular soil hydrological problem of interest. Care however must be taken when using this method to ensure parameters are physically realistic and representative of the spatial scale of interest (Hopmans et al. 2002; Vrugt and Bouten 2002; Mallants et al. 2007; Wohling et al. 2008).
Šimůnek et al. (2000) used inverse optimisation to estimate soil hydraulic parameters from water content data measured in horizontal absorption columns. Similarly, inverse optimisation has been used in Hydrus to predict water flow from water potential and cumulative outflow data (Van Dam et al. 1994; Hopmans et al. 2002; Arbat et al. 2008). Kandelous and Šimůnek, (2010a,b) and Kandelous et al. (2011) used inverse optimisation to estimate soil hydraulic parameters to predict water distribution from a point source, including sub-surface irrigation, in the field. Mallant et al. (2007) used Hydrus 2D and cumulative infiltration data from a deep borehole infiltration test in clayey gravel and carbonated loess soil to estimate field-scale soil hydraulic properties.

Despite the increasing popularity of inverse optimisation, there are few published examples in which parameters derived from unsaturated flow absorption columns have been tested in 3D flow scenarios. Obtaining parameters for a specific flow scenario does not guarantee they will be suitable for extrapolation outside the measured data set to which they were fitted (Sonnleitner et al. 2003). Vrugt and Bouten (2002) and Wohling et al. (2008) recommend the use of the Metropolis algorithm to determine parameter uncertainty, given measurement errors and the models inability to perfectly represent the system. However, if the derived parameters can be shown to be capable of approximating the observed water content distribution under contrasting conditions, it is likely they are physically realistic for the conditions being investigated. To this end, Sonnleitner et al. (2003) and Kandelous et al. (2011) used inverse parameter estimation to improve simulations of water content data under different flow scenarios. Minimising the number of optimised parameters, increases the likelihood that the parameters are physically realistic (Hopmans et al. 2002).

Although several numerical models, including Hydrus (Hanson et al. 2006), have looked at reactive solute transport (Molinero et al. 2008; Kuntz and Grathwohl, 2009; Nakagawa et al. 2009).
Phillips (2006) used Hydrus and some unpublished data to predict the transport of $K^+$ in unsaturated repacked horizontal columns of reactive soil similar to the one used in this study. In field-scale simulations using Hydrus 1D, Persicani (1995) and Moradi et al. (2005) had limited success in simulating reactive metal movement over extended time-scales. However, Rassam and Cook (2002) were able to use modelling of solute fluxes in soils to explain results from the field and laboratory measurements of Rassam et al. (2002). Recently, Ramoss et al. (2011 and 2012) provide examples where Hydrus was successfully used to predict water and solute movement under saline conditions. Validation of the reactive solute module in Hydrus has received considerable attention; however a continued effort is needed to demonstrate its ability to properly investigate soil hydrological processes and reactive transport.

In this paper we use inverse parameter estimation to determine soil hydraulic properties from measured water content profiles in horizontal soil columns (1D transport), and apply the parameters to predicting water flow from a point source into a wedge of soil. We also investigated $NO_3^-$ transport, using an adsorption isotherm determined in the horizontal soil columns that were subsequently used in Hydrus 2D/3D to predict $NO_3^-$ distributions in the soil wedge under two different irrigation scenarios.
Materials and Methods

Experiments used surface soil (0 – 15 cm) of a free-draining, well-structured Red, Mesotrophic, Humose, Ferrosol (Isbell 1996). Soil was collected from Moina in northwest Tasmania, Australia (41° 29’ 28.80” S and 14° 60’ 34.70” E) from a site under long-term pasture. Samples of soil were air-dried at 40°C, sieved to retain the <2 mm fraction and stored for later use. Chemical and physical properties are presented in Table 1.

Soil pH and EC were measured on 1:5 soil to water extracts (Rayment and Higginson, 1992). Solution concentrations were measured from soil samples wet to a water content of 0.55 g_w g^{-1} soil. The solution was extracted by centrifuging samples with 10 cm^3 of 1,1,2-trichloro-1,2,2-trifluoroethane (TFE) as described by Phillips and Bond (1989). Exchangeable cations were determined by extraction with 1M NH_4Cl after the water-soluble ions had been extracted. Organic carbon was analysed using the Walkley and Black (1934) method. Particle size analysis (USDA; Gee and Bauder 1986) was undertaken by pipette method after pretreatment to remove both organic carbon and iron oxides using hydrogen peroxide and sodium dithionate respectively (McKenzie et al. 2002). Semi-quantative mineralogy was determined using x-ray diffraction on the pretreated clay fraction from the particle size analysis.

Horizontal Solute Absorption

Absorption of a NO_3^- solution by the soil was measured in horizontal columns between 17 and 50 cm in length depending on absorption periods. The air dry soil was moistened before packing into the columns. Columns were packed (using a drop hammer) with relatively dry soil (water content 0.15 g g^{-1}) in 2–3 g increments to achieve a bulk density of close to 1.03 g cm^{-3}, which is similar to that measured in the field. Using a Marriotte bottle, a 110 µmol cm^{-3} NO_3^- solution was applied to the inlet of the soil column at zero suction. The outlet of the column remained open, tamped...
with cotton wool to hold the soil in place. Flow was stopped at set times and the column divided into sections that ranged from 1 to 2.5 cm. Short sections were placed near the wetting front to provide an accurate measure of the solute and water contents in this area. The soil sections were transferred to tubes and weighed to determine moist weight.

Two types of column experiments were conducted, and are referred to as Set A and Set B. Each individual experiment in both Set A and Set B used a freshly prepared soil column. Set A consisted of five experiments with infiltration times of 26, 30, 43, 47 and 70 minutes. In these experiments, water-soluble $\text{NO}_3^-$ versus distance in the column was determined by adding deionised water to each column section to make a soil-to-water ratio of 1:5.5 (SD±0.4). The soil plus water was weighed. Samples were shaken for 4 hours in an end-over-end shaker, centrifuged at 9800 m s$^{-2}$ for 10 minutes, and the supernatant decanted and weighed. The soil remaining in the tubes was also weighed.

Set B involved four columns with absorption times for two of 80 min and 320 min for the others. Duplicate columns in this series were either i) extracted as in Set A or ii) the soil solution was extracted using the TFE method described by Phillips and Bond (1989). The adsorbed $\text{NO}_3^-$ was extracted by adding a volume of 2M KCl to form a 1:5.5 (SD±0.5) soil:solution ratio (Rayment and Higginson, 1992).

The tubes were reweighed and shaken for 1 h to extract adsorbed $\text{NO}_3^-$. The soil plus 2M KCl samples were centrifuged at 9800 m s$^{-2}$ for 10 min, and the supernatant decanted in pre-weighed falcon tubes and weighed. The soil remaining in the tubes was washed twice by shaking for 30 min in 20 cm$^3$ deionised water to remove residual salts. The tubes were centrifuged at 9800 m s$^{-2}$ for 10 min and the wash solution discarded. The washed soil was oven-dried at 105°C and weighed.
to give the oven-dry mass of soil in each section. Water and KCl extracts were analysed for NO$_3^-$-N on an Alpkem autoanalyser (Alpkem 1992).

**Point-source solute infiltration**

Perspex wedges were constructed with the same dimensions described by Li *et al.* (2003) and packed with dry soil (water content of 0.2 g g$^{-1}$) to a bulk density of 0.95 g cm$^{-3}$. All solutions were applied to the 15º corner of the wedge at a depth of 5 cm (Fig. 1) with a peristaltic pump set to deliver solution at 50 cm$^3$ h$^{-1}$, equivalent to a dripper output of 1200 cm$^3$ h$^{-1}$ in a 360º flow environment.

Figure 2 shows the two irrigation scenarios applied to the wedge experiments. Both treatments were irrigated for 0.5 h (equivalent to 25 cm$^3$ of solution) with the NO$_3^-$ solution applied to the horizontal columns, i.e. 110 µmol$_c$ NO$_3^-$ cm$^{-3}$. This was immediately followed by a 1.5 h application of solute free water (75 cm$^3$). The soil was either i) sampled immediately after the water application (Scenario A) or ii) allowed to rest for 16 h before irrigating again with water for 6 h (300 cm$^3$) prior to sampling (Scenario B). That is, a total of 375 cm$^3$ of water was applied to the wedge in Scenario B with samples being taken 24 hours after initial application of the solute.

A single replicate was used for Scenario A and Scenario B was duplicated.

Soil was sampled using the method described by Li *et al.* (2003). Briefly, a 5 cm grid was placed over the column and a soil core (2 cm internal diameter) taken from the centre of each grid. Additional soil samples were taken at the edge of the wetting front. The soil from the core was sub-sampled to determine gravimetric water content and total NO$_3^-$ concentration (solution and adsorbed). Wet soil was extracted with 2M KCl (1:10 soil : KCl ratio) and analysed on an Alpkem autoanalyser (Rayment and Higginson 1992). Calculations of total NO$_3^-$ partitioned into the
solution and the amount of adsorbed NO$_3^-$ were done using the adsorption isotherm determined from the horizontal column data (described below).

**Nitrate Adsorption Isotherm**

Partitioning of NO$_3^-$ between the adsorbed and solution phases, over the range of soil solution concentrations in the columns, was measured by displacing the soil solution with TFE (Philips and Bond 1989). The Langmuir equation (equation 1) was then fitted to the data to describe the NO$_3^-$ adsorption isotherm.

\[
C_a = \frac{C_{\text{max}} \phi C_w}{1 + \phi C_w},
\]

where $C_a$ is the concentration of adsorbed solute (µmol·g$^{-1}$), $C_w$ is the concentration of solute in the soil solution (µmol·cm$^{-3}$), $C_{\text{max}}$ is the maximum amount of solute that can be adsorbed by the soil (g·cm$^{-3}$), and $\phi$ determines the magnitude of the initial slope of the isotherm (Sposito, 1989). $C_{\text{max}}$ and $\phi$ were determined using the Gauss–Newton non-linear curve model in the statistical program SAS (version 9.1). $C_{\text{max}}$ and $\phi$ were determined to be 23.17 (95% confidence interval (CI) ±3.43) and 0.00766 (95% CI ±0.00194) respectively.

**Hydrus Flow Equations**

Water flow is described by the Richards Equation modified to describe horizontal flow in one dimension with no loss of water due to evaporation of root uptake (Simunek et al. 2008):

\[
\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left( K \frac{\partial \psi}{\partial x} \right),
\]

where $\theta$ is the volumetric water content (cm$^3$·cm$^{-3}$), $t$ is time (min), $x$ is the horizontal distance (cm), $\psi$ is the water tension (cm) and $K$ is the hydraulic conductivity (cm·min$^{-1}$) given by:
where $K_r$ is the relative hydraulic conductivity (no unit) and $K_{sat}$ is the saturated hydraulic conductivity (cm min$^{-1}$; Simunek et al. 2008).

The modified form of the Richards equation that describes water movement in two dimensions assuming no loss of water through root uptake or evaporation can be written (Simunek et al. 2006):

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x_i} \left[ K \left( K_{ij}^A \frac{\partial \psi}{\partial x_j} + K_{iz}^A \right) \right]$$

where $x_i$ ($i=1,2$) are the spatial coordinates (cm), and $K_{ij}^A$ and $K_{iz}^A$ are components of a dimensionless anisotropy tensor $K^d$. Assuming flow is isotropic (that is, $K$ is equal in horizontal and vertical directions) the diagonal entries of $K_{ij}^A$ equal one and the off-diagonal entries equal zero (Simunek et al. 2006).

In the two dimensional flow scenario $K$ is given by:

$$K(\psi, x) = K_{sat}(x, z)K_r(h, x, z).$$

If the modified form of the Richards equation is applied to planar flow in a vertical cross section, $x_1=x$ is the horizontal coordinate and $x_2=z$ is the vertical coordinate. This equation can also describe axi-symmetric flow when $x_1=x$ represents a radial coordinate (Gardenas et al. 2005). The transcripts $i$ and $j$ denote either the $x$ or $z$ coordinate.

To solve the Richards equation, Hydrus implements the soil hydraulic functions of the van Genuchten-Mualem to describe unsaturated hydraulic conductivity in terms of soil water retention parameters (Simunek et al. 2006). Water retention is described by Simunek et al. 2006 as:
\[ \theta(\psi) = \begin{cases} 
\frac{\theta_s - \theta_r}{1 + |\alpha\psi|^n} & \psi < 0 \\
\theta_s & \psi \geq 0 
\end{cases} \]

and unsaturated conductivity is written (Simunek et al. 2006):

\[ K(\psi) = K_s S_e \left[ 1 - (1 - S_e^{1/n})^m \right]^2 \quad \psi < 0 \]

where:

\[ m = 1 - 1/n, \quad n > 1 \]

and:

\[ S_e = \frac{\theta_s - \theta_r}{\theta_s - \theta_r} \]

In the above equations \( \theta_r \) is the residual water content (cm\(^3\) cm\(^{-3}\)), \( \theta_s \) is the saturated water content (cm\(^3\) cm\(^{-3}\)), \( \alpha \) (cm\(^{-1}\)), \( n \) (no unit) and \( l \) (no unit) are curve fitting parameters for the hydraulic conductivity function and \( S_e \) is the effective water content (cm\(^3\) cm\(^{-3}\)).

When the van Genuchten-Mualem model is used to solve Richards equation in Hydrus there are six soil hydraulic parameters required (\( \theta_r, \theta_s, \alpha, n, l \) and \( K_{sat} \)).

The Langmuir equation was used to predict the reactive solute transport. In Hydrus, desorption of a non-transforming solute is described by the generalised non-linear equation (Šimůnek et al. 2006):

\[ C_a = \frac{k_a C_{aw}}{1 + \phi C_{aw}} \]

and:

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\[
\frac{\partial C_a}{\partial t} = \frac{k_s \omega C_w^{\alpha-1}}{(1 + \phi C_w^{\alpha})^2} \frac{\partial C_w}{\partial t} + \frac{C_w^{\alpha}}{1 + \phi C_w^{\alpha}} \frac{\partial k_s}{\partial t} - \frac{k_s C_w^{2\alpha}}{(1 + \phi C_w^{\alpha})^2} \frac{\partial \phi}{\partial t} \\
+ \frac{k_s C_w^{\alpha} \ln C_w}{(1 + \phi C_w^{\alpha})^2} \frac{\partial \omega}{\partial t},
\]

where \(k_s\) (cm\(^3\) g\(^{-1}\)), \(\omega\) (dimensionless), and \(\phi\) (cm\(^3\) g\(^{-1}\)) are constants. In the case of the Langmuir equation, \(k_s = C_{\text{max}} \phi\) (where \(C_{\text{max}}\) and \(\phi\) are the Langmuir equation constants from equation 1) and \(\omega = 1\).

**Estimation of Flow Equations Parameters**

Soil hydraulic parameters for the van Genuchten equation were determined using the inverse optimisation procedure in Hydrus 1D (Šimůnek et al. 2008). Water profile data from the soil columns in Set A were used, after removing obvious outliers in the data that were determined to be due to soil loss during column sampling (Hopmans et al. 2002). The initial water content was set to 0.15 (cm\(^3\) cm\(^{-3}\)), the measured water content of the repacked columns, for all optimisations. Free water absorption was simulated by applying constant water content boundary condition of 0.64 (cm\(^3\) cm\(^{-3}\)) to the opening of the column. The lower boundary condition was set to free drainage. The maximum number of iterations was set to 50 and 86 water content points across 5 time steps were used in the inverse scenario from the Set A column experiments. Weighting of inverse data was by standard deviation and an equal weighting was applied to all the water content values. Residual soil water content \((\theta_r)\), \(\theta_s\), and \(K_{\text{sat}}\) were set or optimised depending on the optimisation scenario (\textit{Fit All} is the term applied when all parameters were optimised and \textit{Set Measured} is used when \(\theta_r\), \(\theta_s\) and \(K_{\text{sat}}\) were set to independently measured values). The remaining empirical parameters, \(\alpha\), \(n\), and \(l\) were fitted by running the inverse parameter estimation option in Hydrus 1D. The initial values of \(\alpha\), \(n\), and \(l\) were based on the default values given for the Loam soil in Hydrus 1D (\(\alpha=1.56\), \(n=0.173\), and \(l=0.5\)).
Initial estimates for $\theta_r$ and $\theta_s$ were 0.05 and 0.58 (cm$^3$ cm$^{-3}$) and $K_{sat}$ was set to 0.10 cm min$^{-1}$. Saturated soil water content ($\theta_s$) and $K_{sat}$ values were independently measured in falling head $K_{sat}$ experiments (Reynolds et al. 2002). A column of water (4.2 cm in diameter and 12 cm high) was applied to wet repacked soil core packed to a bulk density of 1.0 with air dry soil sieved to <2 mm. The soil cores were 2 cm high and had an internal diameter the same as the water column sitting above it. Triplicate measurements of conductivity were recorded on four separate cores. Residual soil water content ($\theta_r$) was estimated based on the air-dry soil water content.

The Rosetta pedotransfer function model (Schaap et al. 2001) was used to estimate soil hydraulic properties as a comparison against the inverse modelling method. The soil particle size measurements (Table 1) and bulk density (1.03 g cm$^{-3}$) were used to estimate soil hydraulic parameters. In a second prediction, moisture retention at -33 and -1500 kPa (0.34 and 0.22 cm$^3$ cm$^{-3}$, respectively) were also included as inputs into Rosetta. The water content at -33 kPa was determined on a suction table apparatus and -1500 kPa were determined using pressure plate apparatus (Cresswell 2002).

**Modelling Water and Solute Absorption in Soil Wedges**

Hydrus 2D/3D was used to model water distribution in the horizontal column experiments based on the same initial and boundary conditions used in Hydrus 1D during inverse optimisation. Horizontal flow in Hydrus 2D/3D was simulated by setting the geometry to a 2D horizontal plane. The geometry of the flow domain was set to a column 2 cm in diameter and 50 cm long. Soil hydraulic parameters having the lowest values for the objective function were used to simulate water absorption. Nitrate absorption was predicted by applying a third-type (Cauchy) solute boundary at the inlet of the column ($x=0$ cm) at a constant concentration of 110 µmol NO$_3^-$ cm$^{-3}$. Bulk density was set to the measured value of 1.03 g cm$^{-3}$, longitudinal and transverse
dispersivities were set to 0.3 and 0.03 cm, respectively (Ajdary et al. 2007), and the diffusion coefficient was neglected as it was considered negligible relative to the dispersion (Hanson et al. 2006; Ajdary et al. 2007). Parameters for the Langmuir equation (equation 1) to describe NO$_3^-$ adsorption were determined from the data measured in column Set B.

**Modelling Water and Solute in Horizontal Columns**

To simulate water and NO$_3^-$ distribution in the wedge experiments, a 40 × 40 cm flow domain was created in a 2D axi-symmetrical vertical flow geometry. The infiltration point at 5 cm depth was represented by a semicircle with 3 cm radius. The flux from the source was 10.61 cm h$^{-1}$ (equation 4), equivalent to a dripper output of 1200 cm$^3$ h$^{-1}$.

$$\sigma = \frac{Q}{4 \pi r^2},$$  \hspace{1cm}  \text{(4)}

where $\sigma$ is the flux from the surface of the source (cm h$^{-1}$), $Q$ is the total volumetric flux (cm$^3$ h$^{-1}$), and $r$ is the radius of the spherical source (cm).

The finite element mesh of the flow domain, which determines the level of model resolution in the calculations, was set to 0.5 cm in both $z$ and $h$ directions. No flux was allowed through the column boundaries. The infiltration source was set as a variable flux boundary so that water and solute applications could be controlled according to the two irrigation scenarios described for the wedge columns (Fig. 2). Nitrate absorption was predicted in the same way as for the horizontal columns. The time-variable boundary condition was used to apply the solute (110 µmol$_e$ NO$_3^-$ cm$^{-3}$) only for the first 0.5 h of water application to the column.

**Statistical Analysis**

The root mean square error (RMSE) was calculated as the error between the measured and simulated water content and NO$_3^-$ concentrations. Comparisons of the RMSE values with
predictions from different parameter sets allowed those that produced the lowest errors to be identified. Comparisons of simulated RMSE values with those calculated from measured data allowed the significance of the model error to be assessed in relation to measurement error. This method has been commonly used to measure the quality of model predictions in previous studies (Skaggs et al. 2004; Ajdary et al. 2007; Arbat et al. 2008; Patel and Rajput 2008). Part of the inverse modelling in Hydrus 1D allows calculation of a correlation matrix that specifies the correlation between the fitted coefficients and statistical information about the fitted parameters.

Results

Parameter determination and model validation in horizontal columns

Values for soil hydraulic parameters estimated from column Set A are presented in Table 2. The two inverse scenarios produced slightly differing values, with the Fit All parameters having a lower value for the objective function $\Phi$ than the Set Measured suggesting that the former gave a slightly closer fit between the predicted and measured soil water profiles. The 95% confidence intervals for the optimised values for $\alpha$, $n$, and $l$ where smaller compared to the values when all parameters were optimised. The parameters in the Fit All scenario had higher uncertainty and greater correlation between fitted parameters compared to the Set Measured parameters (Table 2 and 3).

The correlation matrix shows there were three high values in the Fit All parameter function compared to one in the Set Measured results; $\alpha$ and $n$ being highly correlated (Table 3, bold entries). High correlation values (magnitude $> 0.9$) indicate parameter non-uniqueness and a correspondingly high uncertainty (Hopmans et al. 2002; Šimůnek and van Genuchten, 1996). The optimised value of $\theta_r$ was 0.112 and the 95% confidence interval that ranged from -0.135 to 0.359, which includes the measured value (0.054 ± 0.003). Saturated water content ($\theta_s$) was 0.56 (0.553 to 0.567) and was significantly different from the independently measured values (0.58 ± 0.04;
Table 2). The measured $K_{sat}$ (0.104 ± 0.0299) fall within the 95% confidence interval (0.054 to 0.176; mean best fit value of 0.115) of the optimised value.

The two parameter sets were tested against independently measured data from the horizontal columns (Column data Set B) and the point-source wedge experiments. Predicted water distributions and measured water content in the horizontal columns from column Set B are shown in Figure 3A. We have plotted $\theta$ and NO$_3^-$ profiles against the Boltzmann variable $X$ (distance/$\sqrt{\text{time}}$; cm s$^{-1/2}$; Smiles et al. 1978; Philips and Bond 1989). Both parameter sets showed similarly good correspondence to the measured data (continuous and dotted lines), which is confirmed by the RMSE and $R^2$ values (Table 4). Accurate predictions of $\theta$ profiles after absorbing water for 80 and 320 minutes are not surprising given that data from Set A (27 to 70 minutes) are not statistically different from Set B when normalised against the Boltzmann variable. The results however do show that under the unsaturated absorption scenario, predictions made for longer times (80 and 320 minutes) are still accurate when the predictions are extended beyond the range of optimised data. The consistency between predictions based on short time $\theta$ and NO$_3^-$ data (Set A) and longer time $\theta$ and NO$_3^-$ data (Set B) further demonstrate the experiments had a good degree of repeatability and produced consistent data across a range of time scales.

In comparison, predicted water content using soil hydraulic parameters determined by Rosetta are shown in Fig. 4. These data show the piston front to be significantly behind the measured data (combined data from column Set A and B) especially when the water content at -33 and -1500 kPa are included in the model. Removal of the iron oxides (FeO) before determining the sand, silt and clay content did not improve the predictions of water retention parameters or saturated hydraulic conductivity. Deriving the water retention parameters and saturated hydraulic conductivity with Rosetta, values that use pedotransfer functions to predict the Van Genuchten parameters, produced
significant inaccuracies in the predictions (see Fig 4). In these experiments they are certainly less accurate than parameters derive from inverse modelling (Fig. 3).

The predicted NO$_3^-$ distribution is shown in Fig. 3B. The measured and predicted NO$_3^-$ distributions were compared from both Set A (27-70 minutes) and Set B (80 and 320 minutes) because the NO$_3^-$ distribution was not used in the inverse optimisation. The good prediction of NO$_3^-$ distribution by the two parameter sets, when the Langmuir isotherm parameters were included in the simulations, is confirmed by the $R^2$ and RMSE values (Table 4). Due to the inaccuracy of water content prediction using Rosetta, no NO$_3^-$ data are presented.

**Model validation using 3D wedge infiltration**

The predicted distributions of water and NO$_3^-$ throughout the soil wedge after the two irrigation scenarios are shown in Fig. 5. This figure also shows the positions of horizontal and vertical transects presented in Figs. 6 and 7. These figures show the agreement between the measured and predicted water and NO$_3^-$ profiles in the wedge. Comparisons of the RMSE and $R^2$ calculations indicated that both the *Fit All* and *Set Measured* parameter sets predicted very similar distributions, although the *Fit All* parameters produced slightly better predictions of NO$_3^-$ distribution in the longer irrigation scenario. The measured RMSE, calculated from columns where duplicate measurements were taken at identical times and locations, were similar to the RMSE of the predicted values (Table 5). This indicates that the errors between the measured and predicted values were very similar to the errors of replicate measurements at identical points and times in the wedge experiments. The predictions achieved using the two parameter sets were therefore considered to be suitable to estimate water and NO$_3^-$ distribution in the point-source flow scenario of the wedge column. The “*Set Measured*” parameters are preferred because there is less auto correlation between the fitted parameters ($\alpha$, $n$, $l$).
Discussion

Inverse optimisation using Hydrus-1D can be used to effectively estimate soil hydraulic properties from simple 1D flow experiments. The flow parameters derived from 1D columns were suitable for describing flow under more complex 3D flow scenarios. These results show that the use of absorption columns offers an alternative to pedotransfer function methods and has the advantage that the parameters are determined using data from the actual soil type under consideration.

Comparisons of optimised parameters with independently measured data in the horizontal column showed that the fitted parameters were able to accurately predict water distribution in these flow scenarios. Further, water distribution could be accurately predicted for absorption periods four times longer than the data used in the inverse optimisation. This provides preliminary evidence that the parameters can predict water distribution outside the range of fitted values. However, this result is not surprising because the measured water content profiles coalesce to a single curve when presented against the Boltzmann variable $X$ (cm s^{-1/2}). Further evidence for this was provided by testing the parameters in the alternative point-source 3D flow scenario. The results presented in this paper demonstrate there is scope to use soil hydraulic parameters obtained from simple horizontal absorption experiments to accurately estimate water flow under more complex 3D conditions in uniform re-pack soil conditions (isotropic).

The inverse optimisations in this study produced two parameter sets that were capable of providing good predictions of water flow in the two flow scenarios. Hopmans (2002) suggests that if various parameter sets produce similar model outcomes, the soil hydraulic parameters may be unidentifiable and the inverse optimisation may be ill-posed. However, our data (Table 2) shows that the values identified in the two scenarios are within the 95% confidence interval estimates of the predictions; the difference between the parameter sets are therefore not significant.
the number of parameters optimised in the inverse procedure reduced the uncertainty of the fitted
parameters without significantly affecting the accuracy of model predictions. Further, the *Fit All*
scenario gave high correlations of three parameters in comparison to the one high value for the *Set
Measured* scenario (Table 3). Limiting the number of parameters in the inverse scenario was
shown to be advantageous because parameter variation was reduced. These findings are consistent
with the recommendations of Hopmans *et al.* (2002) but contrast with the study of Sonnleitner *et
al.* (2003). The latter work indicated that maximising the number of variables in the inverse
optimisation increased the ability of parameters to describe water flow in alternative scenarios.

In our wedge study, only minor differences were observed between predictions when the number
of optimised parameters was reduced. Furthermore, reducing the number of parameters in the
inverse optimisation was advantageous because parameter uncertainty was reduced (Table 2). Our
results show that, where practical, there is benefit in conducting additional measurements to
estimate $\theta_s$ and $K_{sat}$, which are two of the most sensitive parameters of the model (Arbat *et al.*
2008). The benefits of using measured parameters, in combination with inverse modelling of water
content data, has also been demonstrated by Kandelous *et al.* (2011). In these columns, hydraulic
conductivity is not independently measured; rather sorptivity is measured and the hydraulic
conductivity must be inferred with a model.

Including solute reaction parameters enables the Hydrus model to accurately predict reactive solute
distribution in the soil. The retardation in the $NO_3^-$ relative to the inflowing water indicates that
the solute was adsorbed by the soil. Sorption of $NO_3^-$ was included in Hydrus by using the
Langmuir equation to approximate the partitioning of $NO_3^-$ between the soil solution and the
adsorbed phases. The Langmuir equation has been used previously to describe solute adsorption
in soil (Katou *et al.* 1996; Qafoku *et al.* 2000; Phillips 2006).
The distribution of solutes adsorbed to soil during water flow has been simulated under point-source infiltration in previous studies using Hydrus 2D/3D (Hanson et al. 2006). However, validation under these flow scenarios has received little attention. Ben-Gal and Dudley (2003) observed that predictions of reactive P transport from a drip irrigation system showed a similar distribution to measured data, but they did not make any statistical comparisons. Reactive solute transport was previously validated under other flow scenarios (Persicani 1995; Moradi et al. 2005).

Our results validate the inclusion of the Langmuir equation in Hydrus for the prediction of reactive solute movement for 1D and 3D flow conditions. Furthermore, the results show that reactive solute parameters determined from relatively simple 1D adsorption columns can be used to accurately predict solute distribution under 3D conditions.

Other studies that have used Hydrus to predict water movement through soils have utilised pedotransfer functions (PTF) to estimate soil hydraulic parameters (Espino et al. 1995; Skaggs et al. 2004; Li et al. 2005; Phillips 2006; Siyal and Skaggs 2009). The suitability of parameters predicted by PTFs relies on the amount of data collected from soils with similar particle size distribution, bulk density, and water-holding capacity. We investigated use of the Rosetta model (Schaap et al. 2001) to obtain parameters for the same Red Ferrosol used here, but it provided less accurate estimates of water distribution in comparison to parameters determined from inverse modelling (Fig. 4). The high value of the pore connectivity parameter, l (Table 2), that resulted from inverse optimisation is in contrast to the value of 0.5 used on the Rosetta model (Cook and Cresswell, 2007)). This difference may explain the limitations of Rosetta to accurately predict water flow in the repacked columns in these particular experiments.

This finding contrasts with those of Kandelous and Šimůnek (2010a) where parameters estimated from Rosetta produced acceptable predictions of water movement in laboratory studies. The
differing results in our study may be in part due to the limited data for Australian Red Ferrosols available in the Rosetta soil database. In general, this paper confirms that inverse optimisation is advantageous provided enough data has been collected over a sufficient range of water contents (Šimůnek et al. 2000; Sonnleitner et al. 2003). The use of inverse optimisation applied to horizontal infiltration columns provides a simple technique to accurately determine reaction parameters.

If parameters determined from inverse optimisation are to successfully describe water flow in alternative scenarios the soil properties must be the same. This was achieved in our laboratory because careful packing was possible in both the horizontal columns and soil wedges. For a field scenario, a similar method of predicting water and solute flow would need laboratory experiments on undisturbed cores. Similarly, Kandelous and Šimůnek (2010a) found that parameters suitable for describing water movement in packed laboratory columns were not capable of describing water distribution in an undisturbed field soil.

**Conclusion**

Inverse modelling procedures in Hydrus confirm that soil hydraulic parameters can be reliably obtained from simple 1D diffusive water uptake soil column studies. The derived parameters are capable of accurately describing diffusive water movement over extended times and in alternative dynamic flow scenarios to those in which they were fitted. These results demonstrate that simple water uptake column experiments can be used to provide suitable flow conditions for accurate determination of reaction parameters under dynamic flow conditions. Reducing the number of parameters in the optimisation procedures by imposing independently measured values for $\theta_s$, $\theta_r$ and $K_{sat}$ decreased parameter uncertainty (or increased parameter uniqueness) without significantly impacting the accuracy of model predictions. These results show there is merit in pursuing this
method in more complex scenarios since it may provide a simpler and cheaper way of determining hydraulic parameters in field conditions.

Solution NO$_3^-$ and adsorbed NO$_3^-$ concentrations collected from a combined water uptake-NO$_3^-$ tracer test provided the data to fit the reaction parameters for the Langmuir isotherm, which in turn were included in the Hydrus model to predict reactive solute transport. We have demonstrated the ability of HYDRUS to integrate unsaturated flow processes and independently determined reactive transport processes based on independent experiments involving the complex interplay of dynamic flow and reactive transport.

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Table 1 (on next page)

Soil chemical and physical properties for the surface soil (0–15 cm depth).
Table 1. Soil chemical and physical properties for the surface soil (0–15 cm depth).

|                              | pH  | EC (mS cm⁻¹) | Soil solution cations (µmol cm⁻³ soil solution) | Soil solution anions (µmol cm⁻³ soil solution) | Exchangeable cations (µmol g⁻¹ soil) | Organic carbon (%) | Particle size distribution (%) | OC removed | OC and iron oxides removed |
|------------------------------|-----|--------------|-------------------------------------------------|------------------------------------------------|--------------------------------------|--------------------|-------------------------------|-------------|-----------------------------|
|                              | 5.8 | 0.10         | Ca 19.96 Mg 11.04 Na 18.32 NH₄-N 13.33           | NO₃-N 45.84 Cl 15.07 PO₄-P 0.52 SO₄-S 2.90   | Ca 827.46 K 114.17 Mg 83.34 Na 0     | 4.73               | sand 15–25 silt 10–15 clay 8  | 80          | 45                          |
|                              |     |              |                                                 |                                                |                                      |                    |                               |             |                             |
|                              |     |              |                                                 |                                                |                                      |                    |                               |             |                             |
|                              |     |              |                                                 |                                                |                                      |                    |                               |             |                             |
|                              |     |              |                                                 |                                                |                                      |                    |                               |             |                             |
| Clay mineralogy (%)          |     |              | Quartz Kaolinite, organic Garnet, Gibbsite Epidote Smectite, Rutile, Amphibole | 25–35 15–25 10–15 5–10 2–5 <5               |                                      |                    |                               |             |                             |
Table 2 (on next page)

Parameter estimation results for the *Fit All* and *Set Measured* parameter sets.
Table 2. Parameter estimation results for the *Fit All* and *Set Measured* parameter sets.

| Inverse scenario | $\theta_r$ (cm$^3$ cm$^{-3}$) | $\theta_s$ (cm$^3$ cm$^{-3}$) | $\alpha$ (cm$^3$) | $n$ | $K_{sat}$ (LT$^{-1}$) | $l$ (LT$^{-1}$) | $\Phi$ |
|------------------|-------------------------------|-------------------------------|-------------------|-----|----------------------|-----------------|-------|
| **Fit All**      | 0.112 (0.247)                 | 0.560 (0.007)                 | 0.036 (0.006)     | 2.030 (0.684) | 0.115 (0.061)       | 3.847 (5.442)   | 0.014 |
| **Set Measured** | 0.054 (0.003*)                | 0.580 (0.04*)                 | 0.038 (0.005)     | 2.335 (0.279) | 0.104 (0.029*)      | 3.175 (0.578)   | 0.020 |

Values in parentheses show the 95% confidence intervals of the estimated parameters. $\Phi$ indicates the value of the objective function.

*Independently measured*
Table 3 (on next page)

Correlation matrix of the inverse function.
Table 3. Correlation matrix of the inverse function.

|       | $\theta_r$ | $\theta_s$ | $\alpha$ | $n$   | $K_{\text{sat}}$ | $l$  |
|-------|------------|------------|----------|-------|------------------|-----|
| $\theta_r$ | 1.000      |            |          |       |                  |     |
| $\theta_s$ | 0.016      | 1.000      |          |       |                  |     |
| $\alpha$  | 0.977      | -0.046     | 1.000    |       |                  |     |
| $n$      | 0.656      | -0.243     | 0.561    | 1.000 |                  |     |
| $K_{\text{sat}}$ | -0.753     | 0.118      | -0.649   | -0.976| 1.000            |     |
| $l$      | -0.975     | -0.149     | -0.941   | -0.605| 0.737            | 1.000|

|       | $\alpha$ | $n$   | $l$  |
|-------|----------|-------|-----|
| $\alpha$ | 1.000    |       |     |
| $n$    | 0.937    | 1.000 |     |
| $l$    | -0.283   | 0.063 | 1.000|
Table 4 (on next page)

Root mean square error (RMSE) of water and NO$_3^-$ profiles determined using the *Fit All* and *Set Measured* parameters in comparison to the measured data in the horizontal column experiments presented in Fig 3.
Table 4. Root mean square error (RMSE) of water and NO$_3^-$ profiles determined using the *Fit All* and *Set Measured* parameters in comparison to the measured data in the horizontal column experiments presented in Fig 3.

| Inverse scenario | \( \theta_c \) (cm$^3$ cm$^{-3}$) | NO$_3^-$ (µmol cm$^{-3}$ soln) | RMSE | \( R^2 \) | RMSE | \( R^2 \) |
|------------------|---------------------------------|---------------------------------|------|---------|------|---------|
| *Fit All*        | 0.04                            | 7.50                            | 0.04 | 0.89    | 7.50 | 0.97    |
| *Set Measured*   | 0.05                            | 7.96                            | 0.05 | 0.91    | 7.96 | 0.97    |
| Measured†        | 0.04                            | 6.19                            | 0.04 | 6.19    |      |         |

† “Measured” indicates the variation in the measured data calculated from the second set of horizontal soil columns where two NO$_3^-$ and water measurements were made at identical points and times.
Table 5 (on next page)

Root mean square error (RMSE) of the fit of the two parameter sets used to predict water and NO$_3^-$ distribution in the wedge experiments.
**Table 5:** Root mean square error (RMSE) of the fit of the two parameter sets used to predict water and NO$_3^-$ distribution in the wedge experiments.

| Parameters | Irrigation treatment | $\theta_i$ (cm$^3$ cm$^{-3}$) | NO$_3^-$ (µmol cm$^{-3}$ solution) | RMSE | $R^2$ | RMSE | $R^2$ |
|------------|----------------------|--------------------------------|------------------------------------|------|------|------|------|
| Fit All    | Scenario A           | 0.04                           | 2.40                               | 0.94 | 0.95 | 2.40 | 0.95 |
|            | Scenario B           | 0.03                           | 3.05                               | 0.97 | 0.81 | 3.05 | 0.81 |
| Set Measured | Scenario A       | 0.04                           | 2.16                               | 0.96 | 0.95 | 2.16 | 0.95 |
|            | Scenario B           | 0.02                           | 3.43                               | 0.98 | 0.76 | 3.43 | 0.76 |
| Measured† |                      | 0.03                           |                                    |      |      | 2.64 |      |

† “Measured” RMSE values indicate the variation in the measured data calculated from the wedge experiments from Irrigation Scenario B columns where two NO$_3^-$ and water measurements were made at identical points in the wedges.
**Figure 1** (on next page)

Geometry of the wedge apparatus.
Figure 2 (on next page)

Schematic of the two irrigation scenarios (A and B) applied to the wedge columns.
Figure 3 (on next page)

(A) Fits of the *Fit All* (solid line) and *Set Measured* (dotted line) parameters to the measured water profile data (squares) from column Set B not included in the inverse optimisation. (B) Fits for soil solution NO$_3^-$.
Figure 4 (on next page)

Predicted volumetric water content using Rosetta derived soil hydraulic parameters and measured water profile data (squares) against the Boltzmann variable (X).

The *solid* line represents derived parameters using particle size data measured after removal of iron oxides and no water content data; the *dash* line represents parameters predicted using particle size without removing iron oxides and without water content data; the *dash-dot-dash* line refers to parameter predicted using particle size without removing iron oxides and with soil water content at -33 and -1500 kPa; the *dash-dot-dot-dash* line refers to parameters predicted using particle size after removing iron oxides and with soil water content at -33 and -1500 kPa.
Figure 5 (on next page)

Estimation of water and NO$_3^-$ in the wedge experiment scenario using the *Set Measured* parameters.

A and C show water content (cm$^3$ cm$^{-3}$) and NO$_3^-$ (μmol cm$^{-3}$), respectively, for irrigation scenario A (2 h experiment, Fig. 2). B and D show water content (cm$^3$ cm$^{-3}$) and NO$_3^-$ (μmol cm$^{-3}$), respectively, for irrigation scenario B (24 h experiment, Fig. 2). Horizontal and vertical transects and their symbols correspond to the water and solute profile plots in Figs 6 and 7.
Figure 6 (on next page)

Horizontal (A, B, E, F) and vertical transects (C, D, G, H) of water content (cm³ cm⁻³) in the wedge columns. The symbols indicate measured data (squares represent replicate one and triangles replicate two). Solid lines repre
A

Depth = 2.5 cm

B

Depth = 12.5 cm

C

Horiz Dist = 2.5 cm

D

Horiz Dist = 7.5 cm

E

Depth = 2.5 cm

F

Depth = 17.5 cm

G

Horiz Dist = 2.5 cm

H

Horiz Dist = 17.5 cm
Figure 7 (on next page)

Horizontal (A, B, E, F) and vertical (C, D, G, H) transects of soil solution NO$_3^-$ concentration (μmol$_c$cm$^{-3}$) in the wedge columns.

Symbols indicate measured data (squares represent replicate one and triangles replicate two). Solid lines represent simulations using the *Fit All* parameters and dotted lines simulations using the *Set Measured* parameters. The NO$_3^-$ reaction parameters were included in all simulations. Key to panels and transects same as for Fig. 5. The profiles were taken at same times as snapshots shown in Fig. 5.
