

Single and Double Porosity Modeling of Solute Transport in Intact Soil Columns – Effects of Texture, Slurry Placement, and Intermittent Irrigation

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Abstract

We investigated using single and double porosity models implemented in HYDRUS-1D numerical code, solute transport and solute mass exchange between pore water regions in intact soil columns (20 cm diameter, 20 cm high) under variably-saturated flow conditions during injection and surface application of dairy slurry manure in three soil textures, and during continuous and intermittent irrigation. All models tested were able to describe breakthrough curves of nonreactive slurry components (Br tracer applied to slurry) and a tritium tracer applied with irrigation water for all experimental conditions. Simulation of intermittent irrigation with HYDRUS software was limited by the option of a fixed bottom seepage face value, which could not be changed in time according to experimental conditions. The problem was provisionally fixed by restarting the program with the modified bottom conditions at experimentally defined times using the calculated final distribution of state variables as new initial conditions. Both single and double porosity water flow and mobile-immobile solute transport models predicted decreased solute mass exchange when injecting slurry into the soil profile compared with surface application in a loam, but not in the more coarse-textured soils. These results suggest protection of slurry compounds when placed inside the soil matrix in finer-textured soils compared with placement of slurry at the soil surface. Introducing rainfall interruptions (and variably-saturated flow) led to higher leaching of injected slurry compounds compared with steady flow conditions. These results were explained by increased mass exchange from immobile to mobile pore water regions during interruptions. The model based analysis suggests considering more natural boundary conditions when trying to obtain improved understanding of nutrient leaching after slurry application.

1. Introduction

Leaching of plant nutrients from agricultural fields is causing eutrophication problems of surface waters worldwide. Nutrient losses especially occur from fields subjected to land application of animal manure in areas of high livestock production (Coelho et al., 2007; Kronvang et al., 2009). In order to minimize leaching of agricultural chemicals to the subsurface and aquatic environments, the effects of different soil management strategies are being evaluated (e.g., Maguire et al., 2011).

Injection of animal slurry into arable topsoil was proposed as an alternative to surface application to reduce ammonia gas emissions (Webb et al., 2010). Injection of dairy slurry has additionally been shown to reduce leaching of slurry components (Glæsner et al., 2011a,b) in loamy soils when compared with surface application; the effect was less obvious for the sandy soils. Early tracer appearance in the loam indicated the effects of preferential flow (e.g., Flühler et al., 1996; Gerke, 2006) and physical non-equilibrium solute transport (e.g., van Genuchten and Dalton, 1986). Physical non-equilibrium in the loamy soil could be explained by the existence of a two-domain pore system (van Genuchten and Wierenga, 1976) characterized by a mobile and an immobile (aggregate or less mobile soil matrix) pore water region.

Solute transport in column experiments has often been studied assuming steady-flow conditions (de Jonge et al., 2004; Glæsner et al., 2011a), thereby simplifying model analysis by neglecting soil hydraulic properties. Under steady flow conditions, breakthrough curves (BTCs) of percolation experiments can be analyzed with analytical solutions of the convection-dispersion equation (CDE); for instance, with the program CXTFIT (Toride et al., 1995). Transfer of steady flow laboratory column experimental data to field conditions however, can be criticized because the steady flow assumption rarely occurs. It is more realistic to have rain infiltration periods followed by dry periods, generating variably-saturated flow of water and locally varying pore water velocities (Wehrer and Totsche, 2003). While diffusion-limited solute mass transfer can already occur under steady-flow conditions, an additional mass exchange by transfer of water between the mobile and immobile pore regions has to be considered for intermittent flow conditions with physical non-equilibrium (e.g., Gerke, 2006; Jarvis, 2007).

This study aims at identifying the possible role of mass exchange between mobile and immobile pore regions during different slurry placements (surface application and injection) and irrigation regimes (steady-flow and intermittent irrigation). Based on the description of a set of soil column percolation experiments, the aim is achieved by a stepwise increase in model complexity using an analytical CDE model and numerical single and double porosity models. The analysis required i) choosing the most appropriate flow and transport model types, ii) determining parameters for each model type (again from simple to more complex), iii) identifying limitations given by experimental data at certain modeling steps, and iv) defining particular initial conditions and treatment of the boundary conditions for the injection case. The final aim was to couple experimental results with detailed understanding of the underlying mechanisms of leaching losses of slurry compounds.

2. Experimental Design and Modeling Approach

2.1. Experimental Design

Although experimental conditions are thoroughly described in the papers of Glæsner et al. (2011a,c), a short description is given here. Intact soil columns (20 cm diameter, 20 cm height) were excavated from the plough layer of an agricultural field in Denmark with a natural gradient of clay content; loamy sand, sandy loam, and loam. The effects of no slurry application, surface application of slurry, and injection of slurry were all studied (Glæsner et al., 2011a). The finer-textured loamy soil with injected slurry was furthermore studied during continuous irrigation and

intermittent irrigation at a rate of 2 mm h^{-1} (Glæsner et al., 2011c). The experiments were carried out in triplicate.

All intact soil columns, excavated at field capacity, were initially saturated and subsequently drained on tension tables to -100 cm . The columns were then transferred to an irrigation/leaching setup; irrigation was initiated, and a suction of -5 cm was applied at the lower boundary after $2.5 - 12.5 \text{ h}$ irrigation to ensure unsaturated conditions. Experiments were carried out for approximately 5 days, and during intermittent irrigation, suction was increased to -20 cm during irrigation interruptions.

Dairy slurry manure was initially homogenized and spiked with KBr (2.69 g L^{-1}), and then applied to the soil columns 52–53 h prior to initiation of the leaching experiment at an amount corresponding to 25 t ha^{-1} . Slurry was either evenly distributed at the soil surface or injected in a 1 cm wide and 10 cm long band, placed 5 cm from the edge of the cylinder and 8 cm below the soil surface. The columns received a pulse of $2.5 \text{ mm } ^3\text{H}_2\text{O}$ after steady outflow was reached.

2.2. Modeling Approach

For simulating tracer movement ($^3\text{H}_2\text{O}$), we used the equilibrium (EQ) and non-equilibrium (NEQ) convection-dispersion equations (CDE); model parameters were fitted using the CXTFIT program (Toride et al., 1995) as implemented in STANMOD software (Šimůnek et al., 2008).

For simulating solute transport under steady-state (continuous irrigation) and variably-saturated flow conditions (intermittent irrigation), we used: i) the single porosity model for uniform equilibrium-type flow and solute transport (SP-EQM), in which the volumetric water content, θ ($\text{cm}^3 \text{ cm}^{-3}$), the solute concentration, c (g L^{-1}), and the solute mass, $c\theta$, are defined for a single porosity soil, ii) the combination of equilibrium water flow (EQ water) with mobile-immobile solute transport (SP-MIM solute), and iii) the double porosity model for non-equilibrium mobile-immobile type water flow and solute transport (DP-MIM) (cf., Šimůnek and van Genuchten, 2008). These models were numerically solved as implemented in the HYDRUS-1D program (Šimůnek et al., 2008).

The double porosity and MIM approaches partition the bulk soil into fractions for mobile and immobile pore-water regions for the volumetric water content, θ , and the solute mass as $\theta = \theta_{im} + \theta_m$ and $c\theta = c_{im}\theta_{im} + c_m\theta_m$, respectively. Equations and parameters used in this paper are as in Toride et al. (1995) and Šimůnek et al. (2008).

2.2.1. Stepwise Parameter Estimation

The parameter estimation was carried out stepwise as illustrated in Figure 1. The $^3\text{H}_2\text{O}$ -BTCs were first analyzed with CXTFIT. The EQM model was used to fit an initial value of D to the $^3\text{H}_2\text{O}$ -BTCs for all columns, assuming a retardation factor of $R = 1$. These initial D values were used in the NEQM to further optimize the values of D , β , and ω to obtain λ , as well as θ_{im} , and α_s to be used in HYDRUS. The best fit was based on the lowest possible MSE (mean square error), low correlation between parameters, and low 95% confidence intervals as calculated in CXTFIT.

The β parameter (mobile water fraction) was used in the DP-MIM transport simulation (see below).

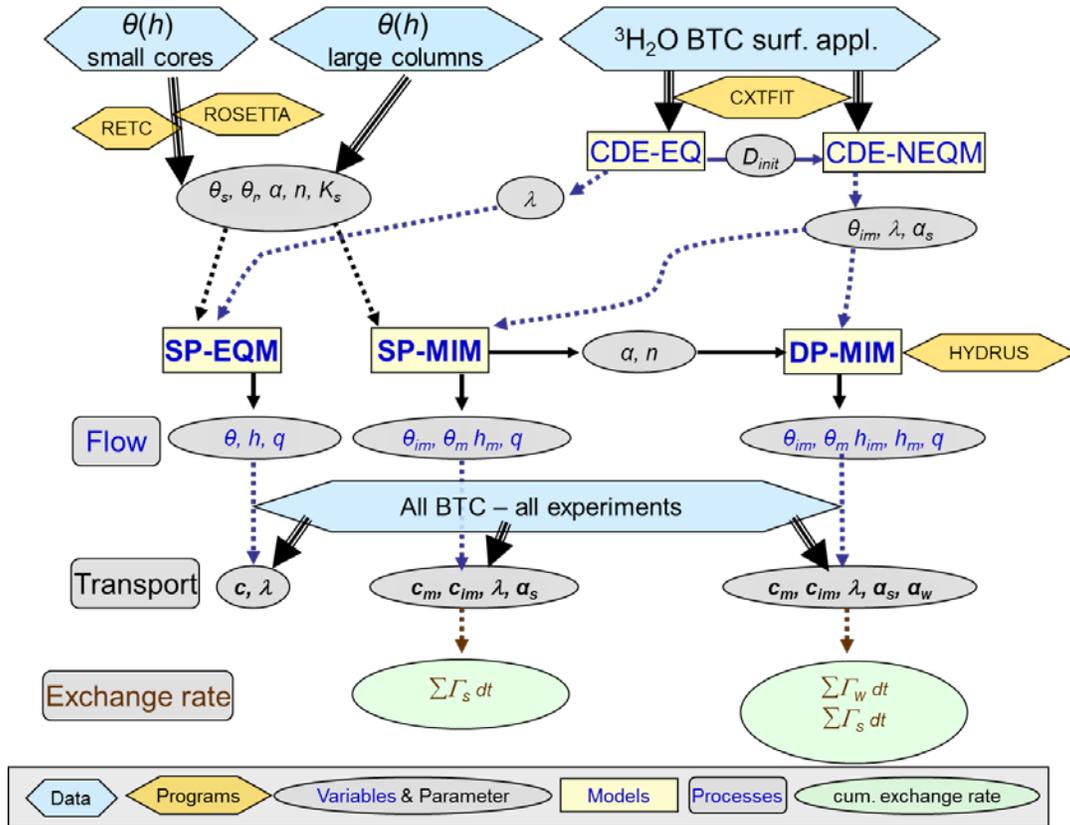


Figure 1. Overview of the complex stepwise analysis of mass exchange in the leaching experiments, illustrating the data input from small cores and larger intact columns, breakthrough curves (BTC) for $^3\text{H}_2\text{O}$ and Br for steady flow (top row), variably-saturated flow and transport during surface application and injection (of slurry) for intermittent irrigation (bottom), and the resulting exchange rates and the used programs, models, flow and transport parameter derivations.

Soil Hydraulic Model Parameters

From the experimental conditions (Glæsner et al., 2011a, b, c), the volumetric water contents at -5 and -100 cm from each intact soil column as well as eight values of the water retention curve from 100 cm^3 intact core samples were available for each soil texture-type in the pressure head range between -4 and -300 cm. Two approaches were carried out to find optimized single porosity vGM (van Genuchten, 1980) soil hydraulic parameters:

- A) Soil hydraulic functions were estimated using pedotransfer functions with the ROSETTA program (Schaap et al., 2001) as implemented in HYDRUS. ROSETTA estimates were based on data of texture, bulk density, and water content at -100 cm, which we used instead of that at -330 cm. Since the ROSETTA fit did not match the two retention values at -5 and -100 cm available for each soil column, the value of θ_s was manually adjusted based on the vGM equation (van Genuchten, 1980), such that the fitted matched the

observed θ -value at -5 cm. With the manually fitted θ_s and the ROSETTA fitted θ_r , n and α values as initial estimates, the α -values of the vGM function were again optimized using the RETC program (van Genuchten et al., 1991), assuming $m=1-1/n$ to fit the retention values at -5 and -100 cm. The values of K_s were fitted such that $K(h)$ function (van Genuchten, 1980) matched the observed K -value at $h = -5$ cm.

- B) The water retention data from 100 cm³ soil cores of each texture were fitted with the RETC program using the optimized vGM-parameters from step A) as initial estimates. The value of θ_s was fixed, and θ_r , n , and α were fitted. For the loam, the optimized values for n were not allowed to drop below $n = 1.2$ (fixed minimum) to avoid numerical problems. The resulting α and n values based on soil core retention data were applied to all columns of each texture class, whereas θ_s and θ_r values were adjusted to match the measured water contents at -100 cm and -5 cm of each individual column using the vGM equation (van Genuchten, 1980).

The parameter sets were finally tested by describing the experiments with the vGM parameters in HYDRUS, such that simulated θ -values were matching the measured ones during drainage (at -100 cm) and irrigation (at -5 cm) for each column.

For the double porosity flow model parameters, the identical values of α and n obtained from above were used for both mobile and immobile pore water regions in order to minimize parameter identification. The fractions θ_m and θ_{im} were obtained from CXTFIT results (above). For the loamy sand and the sandy loam columns, the mobile pore water region θ_{sm} and θ_{rm} were defined as 0.9-times, and the immobile region θ_{sIm} and θ_{rIm} as 0.1-times the values of the vGM parameters. For the loam, θ_{sm} and θ_{rm} were 0.4-times, and θ_{sIm} and θ_{rIm} were 0.6-times the values of the vGM parameters. Values of the water exchange coefficient, α_w , were fitted using the optimization routine provided in the HYDRUS program.

Solute Transport and Mass Exchange Parameters

The transport parameter θ_{im} obtained with CXTFIT from ³H₂O solute transport was not further fitted; however, λ and α_s of columns subjected to injection were fitted in HYDRUS using the average values of the parameters from columns of the same texture that were subjected to surface application as initial values. For analyzing Br leaching, we used the parameters obtained from ³H₂O as initial estimates in all columns and then fitted the values of λ and α_s for Br in HYDRUS. For intermittent irrigation, solute transport parameters, λ and α_s , obtained during steady flow, were used as initial estimates in HYDRUS and then fitted to the effluent data of the respective soil columns.

2.2.2. Initial and Boundary Conditions

Conditions in HYDRUS were different for columns subjected to surface application or injection of slurry (mixed with Br). Surface application of slurry was treated as a flux boundary condition with a flux rate of 32.4 cm d⁻¹ for 10 min, assuming that a pulse of 70 mL of water in applied slurry per column was mixed within the first 1 cm layer for 10 min after application at day 11 (2 days prior to irrigation).

Slurry injection as an initial condition was assumed to be fully mixed with the soil of a vertical layer of 2.5 cm in 6.5 - 9 cm depth for the loamy sand and the sandy loam, and a layer of 7 cm thickness in 4 - 11 cm depth for the loam columns. The full mix of slurry and soil in the layers of the whole column was required when assuming a 1D vertical model. The slurry injection introduced Br and additional water. This application-induced increase in water contents was considered proportional to the available water storage porosity, hence the vertical thickness of the injection layer was chosen the smallest layer possible that could store the additional slurry water without exceeding the porosity. Due to a larger fraction of smaller pores in the loam (Glæsner et al., 2011a), the higher water-filled porosity at -100 cm at the time of slurry injection resulted in the assumed larger layer for the loam in which slurry was mixed as compared to the other two soils.

Upper boundary conditions in HYDRUS were set to atmospheric with a surface layer. The lower boundary was set to a seepage face condition of 0 cm when irrigation was initiated; hereafter, a seepage face condition of -5 cm was imposed after 2.5 - 12.5 hours. These changes of lower boundary conditions required us to split the simulation runs in a series of interrupted model periods per run. Hence, end conditions of a previous period were applied as initial conditions in the subsequent period during each simulation run. Transport of $^3\text{H}_2\text{O}$ was described as concentration flux at the upper boundary and with zero concentration gradient at the lower boundary, whereas Br was described (see above) in the initial condition in the form of a resident concentration. The flow domain was spatially discretized using 200 nodes.

3. Leaching of Irrigation Tracer ($^3\text{H}_2\text{O}$)

Simulations using ROSETTA-derived parameters for $^3\text{H}_2\text{O}$ transport yielded only small differences as compared to those results obtained with the optimized RETC retention parameter set (data not shown). We, therefore, used optimized RETC retention parameters in all solute transport simulations.

The NEQM in CXTFIT fitted the $^3\text{H}_2\text{O}$ BTCs before slurry application better than the EQM in all soil textures (Fig. 2), even though the NEQM fit improved more with increased clay content, as the degree of nonequilibrium transport increased with increasing clay content observed by earlier breakthrough and larger tailing (e.g., Flüher et al., 1996). In HYDRUS, applying DP-MIM did, however, not improve the fitting of $^3\text{H}_2\text{O}$ in an injected column during continuous irrigation compared with the simpler models (Fig. 3, left).

Simulations of intermittent irrigation conditions improved with increasingly complex models from SP-EQ to SP-MIM to DP-MIM (Fig. 3, right). One explanation for improved simulation with increasingly complex models for the increased complex experimental setup during intermittent conditions could be the inclusion of solute and water exchange in the more complex models, as increased exchange of solute as well as of water is expected as new pressure and concentration gradients arise within the soil when pores are emptied for water during interruptions.

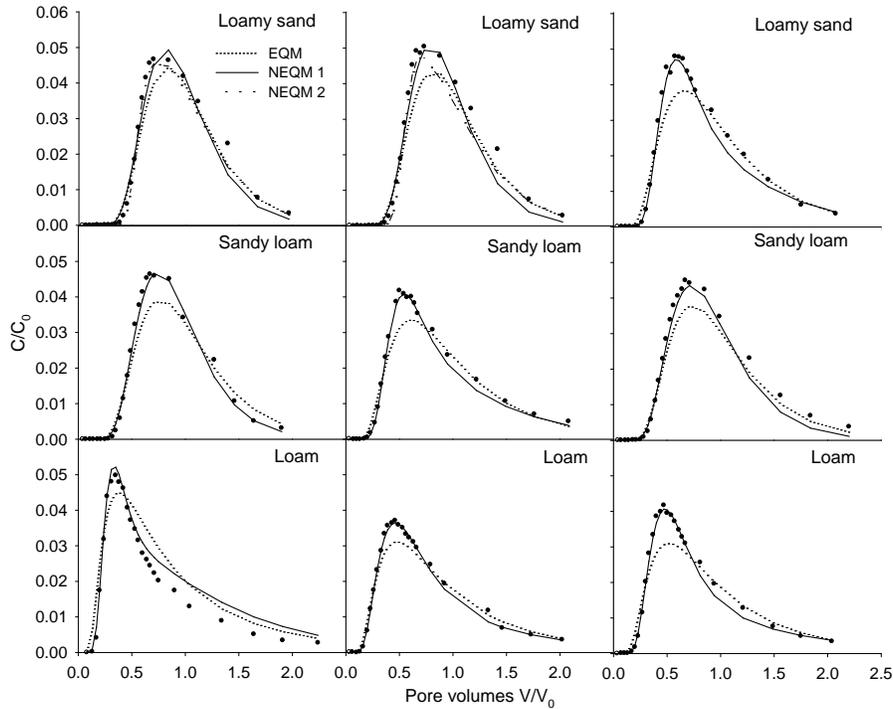


Figure 2. $^3\text{H}_2\text{O}$ BTCs in surface applied triplicate columns from the three soil textures using EQM and NEQM in CXTFIT for curve fitting for steady flow (continuous irrigation).

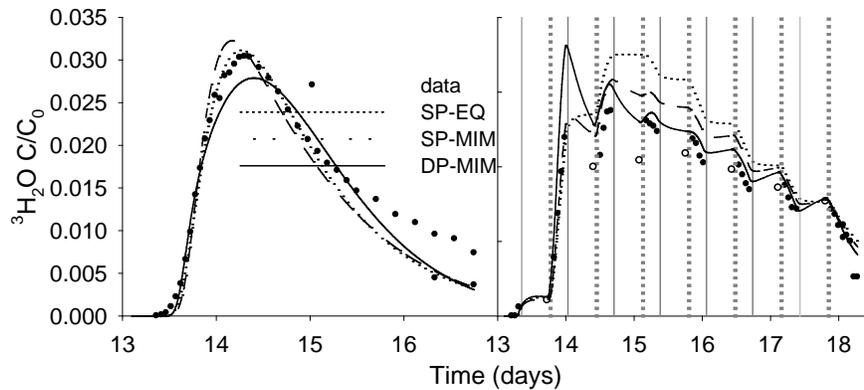


Figure 3. $^3\text{H}_2\text{O}$ BTCs after injection with continuous (left) and intermittent (right) irrigation using SP-EQ (dotted line), SP-MIM (dashed line), and DP-MIM (solid line) in HYDRUS. Only one column from each experiment is shown. Open symbols represent samples collected during interruptions; vertical solid lines represent interruptions; and vertical dotted lines represent initiation of irrigation.

Water exchange during continuous irrigation occurred only from mobile to immobile pore water regions (positive values) (Fig. 4). Water exchange during intermittent irrigation occurred from mobile to immobile pore regions during irrigation and from immobile to mobile pore regions (negative values) during irrigation interruptions (Fig. 4), resulting in lower cumulative mass exchange of water from mobile to immobile pore regions during intermittent conditions.

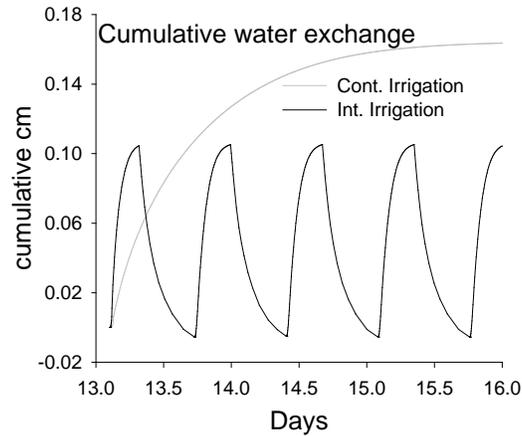


Figure 4. Cumulative water exchange for continuous and intermittent irrigation using the DP-MIM approach.

The importance of water exchange for solute transport is evident, as a substantially larger exchange of $^3\text{H}_2\text{O}$ occurred when applying DP-MIM compared with SP-MIM (Fig. 5). This is explained by the additional advective solute mass exchange of $^3\text{H}_2\text{O}$ caused by assuming water exchange between the pore regions in the DP-MIM. However, for solute exchange, higher cumulative $^3\text{H}_2\text{O}$ exchange from mobile to immobile pore regions is recorded for intermittent irrigation as compared with continuous irrigation, which is due to “diffusive” mass exchange of $^3\text{H}_2\text{O}$ being the main mechanism for $^3\text{H}_2\text{O}$ exchange caused by concentration differences between pore regions compared to “advective” exchange of $^3\text{H}_2\text{O}$ with water caused by pressure head gradients. The high fluctuations in cumulative water exchange (Fig. 4) are therefore not so evident in the cumulative $^3\text{H}_2\text{O}$ exchange (Fig. 5). This was further confirmed by decreased mass recovery of leached $^3\text{H}_2\text{O}$ when changing the boundary conditions from continuous (86.6 %) to intermittent (76.4 %) irrigation (Glæsner et al., 2011c).

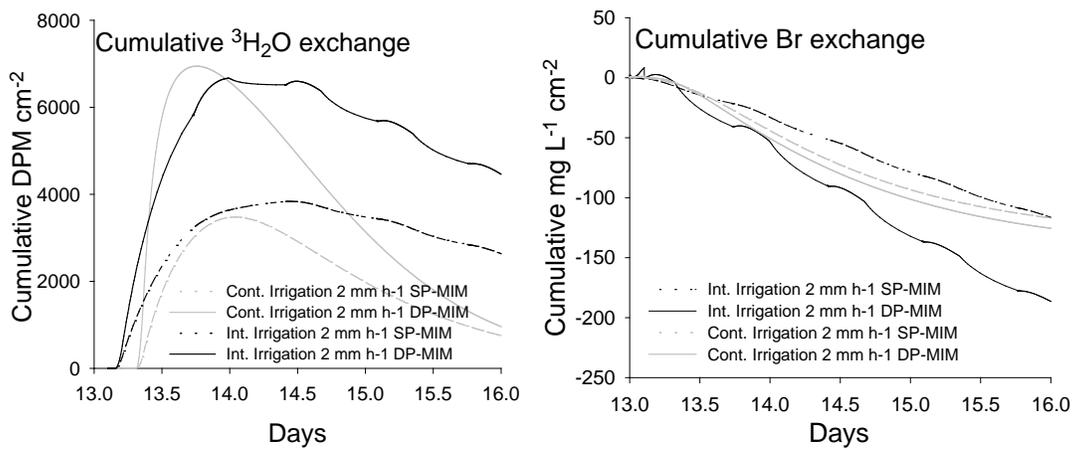


Figure 5. Cumulative $^3\text{H}_2\text{O}$ and Br exchange for continuous and intermittent irrigation simulated with the SP-MIM and DP-MIM approaches.

4. Leaching of Slurry Tracer (Bromide)

Bromide BTCs, when slurry was applied both to the soil surface and injected into the soil, were simulated less well than $^3\text{H}_2\text{O}$, but the models still gave good simulation fits (Fig. 6). That BTCs of Br were less well fitted compared with $^3\text{H}_2\text{O}$ reflects that Br was applied with slurry which has a different consistency and viscosity than water (Kumar et al., 1972; Frey et al., 2012).

Injection of slurry decreased mass recovery of bromide (60.2 %) compared with surface application (80.6 %) in the loam soil, but not in the other soils (Glæsner et al., 2011a). The authors suggested this to be due to protection of solutes from the few preferential flow paths in the more fine-textured soil. This hypothesis was confirmed in this study by lower cumulative mass exchange from immobile to mobile pore regions during injection compared with surface application in the loam, whereas no difference was observed in the loamy sand and sandy loam when using SP-MIM, even though no statistical significance was found (Table 1). The highly heterogeneous nature of the different columns challenges statistical analysis of the results.

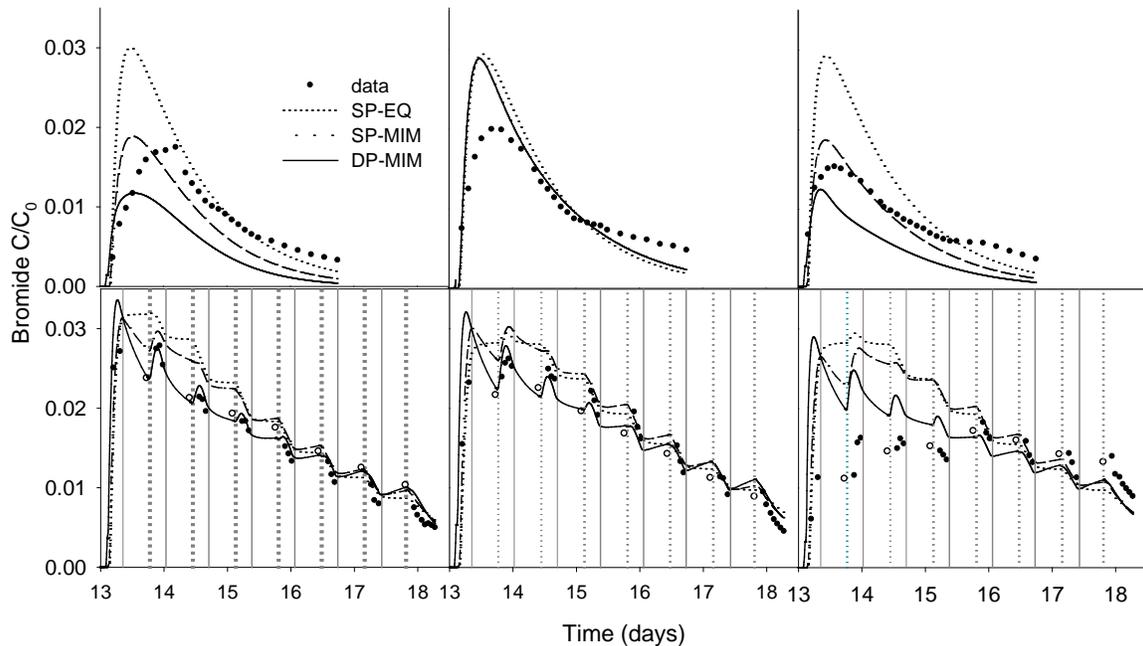


Figure 6. Bromide BTCs after injection with continuous (upper) and intermittent irrigation (lower) using SP-EQ (dotted line), SP-MIM (dashed line), and DP-MIM (solid line) in HYDRUS. Open symbols represent samples collected during interruptions; vertical solid lines represent interruptions; and vertical dotted lines represent initiation of irrigation.

Table 1. Averaged cumulative mass exchange of Br after 1.2 eluted PV using SP-MIM and DP-MIM. Positive values represent exchange from mobile to immobile pore regions, whereas negative values represent exchange from immobile to mobile pore regions. Statistical differences at the 5% level are given by different letters.

Experiment	SP-MIM	DP-MIM
	mg L ⁻¹ cm ⁻²	mg L ⁻¹ cm ⁻²
Loamy sand – surface application	-0.01 (0.00) ^a	-16.79 (13.7) ^a
Loamy sand – injection	-0.61 (0.49) ^a	-3.11 (1.04) ^a
Sandy loam – surface application	-0.01 (0.00) ^a	-17.91 (14.4) ^a
Sandy loam – injection	-4.64 (1.14) ^a	-1.42 (0.81) ^a
Loam – surface application	-127.45 (28.4) ^a	-140.27 (8.46) ^a
Loam – injection	-58.46 (0.13) ^a	-124.21 (8.59) ^a
Loam – injection - continuous	-127.73 (21.5) ^a	-170.23 (47.1) ^a
Loam – injection - intermittent	-175.02 (3.18) ^a	-272.56 (4.20) ^a

During intermittent conditions, in similarity to ³H₂O, simulation fits increased with increased model complexity (Fig. 6). The Br mass exchange values were all negative (Fig. 5), indicating that exchange of injected Br is only directed from the immobile to the mobile pore water region, which corresponds well with Br being placed within the intact columns at -100 cm, when only pores <30 μm were saturated. Though the water content of the slurry added to higher pore classes being saturated, Br was assumed to diffuse into the water-filled porosity at the time of application, hence the immobile region. Mass recovery of Br in the effluent during continuous irrigation (45.5% ± 2.5) was lower than during intermittent irrigation (59.3% ± 5.2) (Glæsner et al., 2011c). This is fully supported by the cumulative exchange analysis, demonstrating higher mass exchange from immobile to mobile pore regions during intermittent irrigation (Fig. 5), thereby resulting in higher effluent mass recovery.

5. Conclusions

The role of mass exchange was analyzed using different models implemented in HYDRUS-1D. Both single and double porosity water flow and mobile-immobile solute transport models described the data well. However, as experimental conditions became more complex, the more complex models described the data better by including solute and water exchange between pore water regions. Injection decreased leaching of solutes compared with surface application in a loam, but not in the more coarse-textured soils, which could be described by decreased solute exchange from immobile to mobile pore regions in the loam by the model based analysis. Introducing rainfall interruptions (and variably-saturated flow) led to higher leaching of injected slurry compounds compared with steady flow conditions, explained by increased mass exchange from immobile to mobile pore water regions during interruptions in the model based analysis. The results suggest considering more natural boundary conditions when trying to obtain improved understanding of nutrient leaching after slurry application.

References

- Coelho, B. R. B., R. C. Roy, E. Topp, and D. R. Lapen, Tile water quality following liquid swine manure application into standing corn, *Journal of Environmental Quality*, 36, 580–587, 2007.
- De Jonge, L. W., P. Moldrup, G. H. Rubæk, K. Schelde, and J. Djurhuus, Particle leaching and particle-facilitated transport of phosphorus at field scale, *Vadose Zone Journal*, 3, 462–470, 2004.
- Flühler, H., W. Durner, and M. Flury, Lateral solute mixing processes - A key for understanding field-scale transport of water and solutes, *Geoderma*, 70, 165-183, 1996.
- Gerke, H. H., Preferential flow descriptions for structured soils, *Journal of Plant Nutrition and Soil Science*, 169, 382-400, 2006.
- Glæsner, N., C. Kjaergaard, G. H. Rubæk, and J. Magid, Interacting effects of soil texture and placement of dairy slurry application. I. Flow characteristics and leaching of nonreactive components, *Journal of Environmental Quality*, 40, 337-343, 2011a.
- Glæsner, N., C. Kjaergaard, G. H. Rubæk, and J. Magid, Interacting effects of soil texture and placement of dairy slurry application. II. Leaching of phosphorus forms, *Journal of Environmental Quality*, 40, 344-350, 2011b.
- Glæsner, N., C. Kjaergaard, G.H. Rubæk, and J. Magid, Effect of irrigation regimes on mobilization of nonreactive tracers and dissolved and particulate phosphorus in slurry-injected soils, *Water Resources Research*, 47, W12536, 2011c.
- Jarvis, N. J., A review of non-equilibrium water flow and solute transport in soil macropores: principles, controlling factors and consequences for water quality, *European Journal of Soil Science*, 58, 523–546, 2007.
- Kronvang, B., G. H. Rubæk, and G. Heckrath, International Phosphorus Workshop: Diffuse phosphorus loss to surface water bodies - Risk assessment, mitigation options and ecological effects in river basins, *Journal of Environmental Quality*, 38,1924-1929, 2009.
- Kumar, M., H. D. Bartlett, and N. N. Mohsenin, Flow properties of animal manure, *Transactions ASAE*, 15, 718-722, 1972.
- Maguire R. O., P. J. A. Kleinman, C. J. Dell, D. B. Beegle, R. C. Brandt, J. M. McGrath, and Q. M. Ketterings, Manure application technology in reduced tillage and forage systems: A review, *Journal of Environmental Quality*, 40, 292-301, 2011.
- Schaap, M. G., F. J. Leij, and M. Th. van Genuchten, ROSETTA: a computer program for estimating soil hydraulic parameters with hierarchical pedotransfer functions, *Journal of Hydrology*, 251, 163-176, 2001.
- Šimůnek, J., and M. Th. van Genuchten, Modeling nonequilibrium flow and transport processes using HYDRUS, *Vadose Zone Journal*, 7(2), 782-797, 2008.
- Šimůnek, J., M. Th. van Genuchten, and M. Šejna, Development and applications of the HYDRUS and STANMOD software packages, and related codes, *Vadose Zone Journal*, 7(2), 587-600, 2008.
- Toride, N., F. J. Leij, and M. Th. van Genuchten, The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments, Version 2.0, *Research Report No. 137*, US Salinity Laboratory, USDA, ARS, Riverside, CA, USA, 1995.
- van Genuchten, M. Th., A closed-form equation for predicting the hydraulic conductivity of unsaturated soils, *Soil Science Society of America Journal*, 44, 892-898, 1980.
- van Genuchten, M. Th., and P. J. Wierenga, Mass-transfer studies in sorbing porous-media. I. Analytical solutions, *Soil Science Society of America Journal*, 44, 473-480, 1976.
- van Genuchten, M. Th., and F. N. Dalton, Models for simulating salt movement in aggregated field soils, *Geoderma*, 38, 165-183, 1986.
- Van Genuchten, M. Th., F. J. Leij, and S. R. Yates, The RETC code for quantifying the hydraulic functions of unsaturated soils, Version 1.0, *EPA Report 600/2-91/065*, US Salinity Laboratory, USDA, ARS, Riverside, CA, USA, 1991.
- Webb, J., B. Pain, S. Bittman, and J. Morgan, The impacts of manure application methods on emissions of ammonia, nitrous oxide and on crop response – a review, *Agriculture, Ecosystem and Environment*, 137, 39-46, 2010.
- Wehrer, M., and K. U. Totsche, Detection of non-equilibrium contaminant release in soil columns: delineation of experimental conditions by numerical solutions, *Journal of Plant Nutrition and Soil Science*, 166, 475-483, 2003.

