Reactive Transport of Manure-Derived Nitrogen in the Vadose Zone: Consideration of Macropore Connectivity to Subsurface Receptors

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Macropores can be important conduits for surface-derived nutrients to reach subsurface receptors. Accordingly, nutrient reactive transport processes in macroporous soils need to be well understood. In this study, steady-state two-dimensional reactive transport simulations with MIN3P-THCm (version 1.0.519.0) were used to elucidate how soil macropore connectivity to tile drains can influence N transformations following liquid swine manure (LSM) applications to soil. Four different soil scenarios were considered: homogeneous sand, homogeneous clay loam, and clay loam with discrete macropores connected to or disconnected from the bottom boundary used to represent tile drain outflow. In relation to the homogeneous soils, macropores, overall, facilitated chemical diffusion into the adjacent soil matrix along their length and broadly augmented O₂ ingress into the soil profile. These processes combined to critically control the spatial distribution of NH₄+ oxidation reaction products. When used in transient simulation mode with field data observed at experimental tile-drained plots that received LSM application, the model showed that simulated nitrate mass losses to tile are considerably higher and most realistic under the connected macropore scenario compared with the homogeneous or disconnected macropore scenarios.

Many surface and groundwater pollution problems are related to excess nutrients derived from agricultural production practices (Ritter et al., 2002; Kelly et al., 2015; Liang et al., 2014). Preferential flow in agricultural soils can directly and significantly contribute to many of these pollution burdens (Gärdenäs et al., 2006; Ulén et al., 2014). Soil macropores facilitate preferential flow to groundwater and artificial subsurface drainage systems (tile drains) (Frey et al., 2013) and, as such, are important soil features to rigorously consider in agronomic and land management prescriptions (Ghodrati and Jury, 1992; Turpin et al., 2007a) and water pollution vulnerability assessments (Gerke and van Genuchten, 1993; Jarvis, 2007; Beven and Germann, 2013; Frey et al., 2016). Also, macropores can profoundly impact physical, chemical, and biological processes in the bulk soil by virtue of their capacity to preferentially introduce O₂, organic matter, and fertilizer amendments to depth within a soil profile (Lapen et al., 2008; Kuncoro et al., 2014a, 2014b; Colombi et al., 2017), all of which impact soil microbiology and biogeochemical reactions germane to nutrient transformations (Paul, 2014). Some of the most important macropores in agricultural soils are worm burrows generated by Lumbricus terrestris (Shipitalo and Butt, 1999), but there are other important macropores that include, but are not limited to, soil desiccation cracks and abandoned root channels (Turpin et al., 2007b; Ulén et al., 2014). The degree and nature of macropore hydraulic connectivity (Allaire et al., 2002; Fox et al., 2012; Petersen et al., 2012; Hruby et al., 2016) also strongly influence water flow and chemical transport and reaction processes, as some are connected directly to subsurface receptors (e.g., groundwater and tile drains) while others are not (Frey and Rudolph, 2011; Frey et al., 2012a). The nature of this connectivity needs to be considered explicitly because the macropores directly
connected to tile drains, for instance, may be most important in terms of the rapid movement of land-surface-derived contaminants to subsurface water flow systems (e.g., tile drains) (Fleming and Bradshaw, 1992; Fox et al., 2004; Akay and Fox, 2007; Frey et al., 2016).

A substantial body of literature has been produced regarding N transformations and transport in agricultural soils (i.e., Lee et al., 2006; Berlin et al., 2013, 2014a; Li et al., 2015). And while some studies have characterized or modeled macropore connectivity in soil in the context of flow (Akay et al., 2008; Klaus and Zehe, 2010), there is a need to elucidate dynamic chemical transformations and transport in soil macropores under various degrees of macropore connectivity (Jarvis et al., 2017). This may be especially true for high-rate liquid manure and biosolid applications that have great potential to convey N-derived constituents quickly, and at significant concentrations, to subsurface receptors (Larsbo et al., 2009; Frey et al., 2013, 2016).

Manure application to land is performed as a means to fertilize crops, but in many regions of the world, it is also a pragmatic necessity for farmers to empty their manure lagoons seasonally (Ribaudo et al., 2003). Manure (e.g., liquid swine manure) N exists primarily in the form of NH₄⁺ and organic N (Fernando et al., 2002; Mayer and MacQuarrie, 2010): a s ra a 0

where

is the saturation of the aqueous phase (m³ H₂O m⁻³ void), Sₜ is the specific storage coefficient (m⁻¹), b is hydraulic head (m), t is time (s), φ is porosity (m³ void m⁻³ porous medium), kₕ is the relative permeability (dimensionless), K is the hydraulic conductivity tensor (m s⁻¹), and Qₜ is a source-sink term (m³ H₂O m⁻³ porous medium s⁻¹). Both Sₜ and kₕ are calculated using the van Genuchten unsaturated soil hydraulic functions (van Genuchten, 1980).

Reactive Transport

This study used the MIN3P-THCm (version 1.0.519.0) reactive transport code (Mayer et al., 2002; Bea et al., 2016) to simulate N transformations in agricultural soils following liquid manure application—specifically, N transformation processes in and around macropores connected to, as well as disconnected from, subsurface tile drains. Despite the importance of macropore connectivity in tile-drained landscapes with respect to environmental water quality, to our knowledge there are few documented studies that assess macropore connectivity (or lack thereof) and manure application within a reactive transport framework. The underlying experimental data and conceptual framework for the simulations described here were built on the liquid swine manure (LSM) land application experiment described by Frey et al. (2013).

Methods

Model Description

This study required a model that accommodates physically based variably saturated flow and advanced reactive transport processes. Accordingly, MIN3P-THCm (version 1.0.519.0), a well-supported and widely applied three-dimensional multicomponent reactive transport code was selected (Mayer et al., 2002; Steefel et al., 2015; Bea et al., 2016). MIN3P-THCm uses the Richards equation based flow solution within a globally implicit, finite-volume, adaptive time stepping framework that allows transport and reaction processes to be solved simultaneously. In this simulation work, a discrete macropore approach was used, where a narrow vertical conduit with very high hydraulic conductivity (K) and porosity was discretized to represent the macropore. The extensive reactive transport functionality in MIN3P-THCm includes simultaneous advective and molecular diffusive transport in the aqueous and gas phases; however, advective gas transport was not used for this study. In MIN3P-THCm, chemical reactions relevant to agricultural nutrient cycling include kinetically controlled C and N transformation processes, mineral dissolution–precipitation, and ion exchange.

Flow

In MIN3P-THCm, variably saturated flow is solved with the assumption of incompressible fluid, no hysteresis, and a passive air phase (Mayer et al., 2002):

\[
S_t \frac{\partial b}{\partial t} + \phi \frac{\partial S_t}{\partial t} - \nabla \cdot (k_{fa} \nabla b) - Q_a = 0
\]

where \(S_t\) defines the saturation of the aqueous phase (m³ H₂O m⁻³ void), \(S_t\) is the specific storage coefficient (m⁻¹), \(b\) is hydraulic head (m), \(t\) is time (s), \(\phi\) is porosity (m³ void m⁻³ porous medium), \(k_{fa}\) is the relative permeability (dimensionless), \(K\) is the hydraulic conductivity tensor (m s⁻¹), and \(Q_a\) is a source-sink term (m³ H₂O m⁻³ porous medium s⁻¹). Both \(S_t\) and \(k_{fa}\) are calculated using the van Genuchten unsaturated soil hydraulic functions (van Genuchten, 1980).

Reactive Transport

The globally implicit transport solution in MIN3P-THCm, relevant to the simulations performed here, considers reaction and transport processes simultaneously leading to a system of equations with \(N_a\) dissolved components in the aqueous phase (Mayer et al., 2002; Mayer and MacQuarrie, 2010):

\[
\frac{\partial}{\partial t} \left( S_a \phi T_a^s + \frac{\partial}{\partial t} \left( S_g \phi T_g^g \right) + \frac{\partial T_a^s}{\partial t} + \nabla \cdot \left( q_a T_a^s \right) - \nabla \cdot \left( S_a \phi D_a \nabla T_a^s \right) \right) - Q_a^{in} = 0
\]

for \(j = 1, N_a\). \(N_a\) where \(t\) is time (s); \(\phi\) is porosity (m³ void m⁻³ porous medium); \(S_a\) is the saturation of the aqueous phase (m³ H₂O m⁻³ void); \(S_g\) is the saturation of the gaseous phase (m³ gas m⁻³ void) calculated based on the water-phase saturations \(S_a\) obtained from solution of the relation \(S_a = 1 - S_g\); \(T_a^s\), \(T_g^g\), and \(T_a^s\) are the total aqueous component (mol L⁻¹ H₂O), gas-phase component (mol L⁻¹ gas), and adsorbed component concentrations (mol dm⁻³ bulk porous medium), respectively; \(q_a\) is the Darcy velocity flux vector; \(D_a\) is the aqueous-phase hydrodynamic dispersion tensor (m² s⁻¹) and \(Q_a^{in}\) is the source-sink term (mol L⁻¹ H₂O s⁻¹).
\( \mathbf{D}_g \) is the gas-phase diffusion tensor (m\(^2\) s\(^{-1}\)); \( Q_{j}^{\text{ex}} \) is an external source and sink term (mol dm\(^{-3}\) porous medium), which defines mass fluxes across the domain boundaries for the aqueous and gas phases; \( Q_{j}^{\text{in}} \) is the internal source and sink due to dissolution–precipitation reactions and intra-aqueous kinetic reactions (mol dm\(^{-3}\) porous medium); and \( N_c \) defines the number of components. For further detailed description of the MIN3P-THCm model formulation, see Mayer et al. (2002).

The equilibrium gas dissolution–exsolution reactions are integrated into the model through Henry’s law coefficient, \( H_i \) (dimensionless):

\[
H_i = \frac{p_{i}^{g}}{C_i^a} \quad \text{for } i = 1, N_g
\]

where \( p_{i}^{g} \) and \( C_i^a \) are the partial pressures and dissolved concentrations of the gases, respectively, and \( N_g \) is the number of gases considered. The intra-aqueous reactions are represented by kinetic reactions, optionally with inhibition terms:

\[
R_i = -k_i^a \left( \prod_{j = 1, K_j^a > 0}^{N_i} \left( \frac{T_j^a}{K_j^a} \right) \prod_{j = 1, K_j^a > 0}^{N_i} \left( \frac{K_j^a - T_j^a}{K_j^a + T_j^a} \right) \right)
\]

for \( i = 1, N_i \)

where \( R_i^a \) is the reaction rate (mol L\(^{-1}\) s\(^{-1}\)), \( k_i^a \) is the rate constant (mol L s\(^{-1}\)), \( K_j^a,\text{mo} \) is the half-saturation constant (mol L\(^{-1}\)), \( K_j^a,\text{in} \) is inhibition constant for aqueous components (mol L\(^{-1}\)), and \( N_i \) is the number of kinetic intra-aqueous reactions. Sorption reactions were described using a cation exchange formulation.

**Modeling Approaches**

The conceptual model (Fig. 1), on which this work is based, is derived from an actual liquid swine manure (LSM) application field experiment (Frey et al., 2013). The behavior of a theoretical conservative tracer (Br\(^-\)) was incorporated into the simulations here to shed light on the nature of solute transport in the simulated flow domains. Given that the primary focus of this work is on N transformations and O\(_2\) transport characteristics in relation to nitrification and denitrification, the following reactions are presented in detail, as they are the major reactions influencing the fate and transport of manure-derived N:

1. First nitrification reaction (Nit-1): \( \text{NH}_4^+ \) oxidation to \( \text{NO}_2^- \) (Reddy and Patrick, 1975):

\[
\text{NH}_4^+ + \frac{3}{2} \text{O}_2(aq) \rightarrow \text{NO}_2^- + \text{H}_2\text{O} + 2\text{H}^+
\]

2. Second nitrification reaction (Nit-2): \( \text{NO}_2^- \) oxidation to \( \text{NO}_3^- \) (Reddy and Patrick, 1975):

\[
\text{NO}_2^- + \frac{1}{2} \text{O}_2(aq) \rightarrow \text{NO}_3^-
\]

3. Denitrification reaction (Denit):

\[
\frac{5}{2} \text{CH}_2\text{O}_{(aq)} + 2\text{NO}_3^- \rightarrow \text{N}_2(aq) + \frac{5}{2} \text{CO}_2^- + 3\text{H}^+ + \text{H}_2\text{O}
\]

4. Dissolved organic matter oxidation [\( \text{CH}_2\text{O}_{(aq)} \) Oxi]:

\[
\text{CH}_2\text{O}_{(aq)} + \text{O}_2(aq) \rightarrow \text{CO}_3^- + 2\text{H}^+
\]

Fig. 1. Conceptual model showing N transformation pathways resulting from a theoretical liquid swine manure (LSM) application to the land surface. The first and second nitrification reactions and the denitrification reaction are shown as Nit-1, Nit-2, and Denit, respectively. The disconnected and connected macropores are represented by DC-Macropore and C-Macropore, respectively.
After manure application, a significant portion of the NH₄⁺ is immobilized through sorption following a cation exchange process involving Ca²⁺ and Na⁺ as provided in Table 2. The equilibrium constant (log K) values for ion exchange reactions do not change with temperature in MIN3P. The temperature dependence of sorption is not easily quantified. Enthalpy (ΔH) values, particularly site-specific values, are not available. Nitrification commences through the oxidation of NH₄⁺ to NO₂⁻ by autotrophic NH₄⁺ oxidizing bacteria (e.g., *Nitrosomonas*) in the presence of O₂ (Eq. [5]). This NO₂⁻ is unstable and readily reduced or oxidized to other N species. The presence of oxic conditions, generally observed in the unsaturated zone, promotes nitrification, although some studies have shown that nitrification can also occur under anoxic conditions (Schmidt and Bock, 1998). In this study, it was assumed that NO₂⁻ produced in the initial nitrification processes along with any existing NO₃⁻ will be further oxidized to NO₃⁻ by autotrophic NO₂⁻-oxidizing bacteria in the presence of O₂ (Eq. [6]). Nitrate is more stable than NO₂⁻, very soluble in water, and is not subject to sorption onto negatively charged surfaces, which are typical of agricultural soils (Behnke, 1975; Lee et al., 2006). However, under anoxic conditions, denitrification is expected, whereby NO₃⁻ is reduced to N₂ and N₂O gases (Saggar et al., 2013). In this study, it was assumed that denitrification goes to completion with the end product N₂(aq) (Eq. [7]), given that the focus of this study is on aqueous NH₄⁺ and NO₃⁻. However, the presence of O₂(aq) does inhibit the denitrification reaction via the rate expression of Eq. [7] (Table 3). At low to near-neutral pH, NH₄⁺ is the dominant N species between NH₄⁺ and NH₃. Considering the pH range (pH 4.7–7.8) in this study and due to the high solubility of NH₃ in water, NH₃ was not included in the simulation.

Dissolved organic matter oxidation is represented by a biodegradation reaction mediated by a microbial population, with the stoichiometry of the reaction expressed by Eq. [8] (Lee et al., 2006; Berlin et al., 2014a). Soil organic matter was included in the simulations to capture its contribution to the O₂ demand of the soil (Eq. [9]). Rate expressions for the reactions (Eq. [5–9]) are provided in Table 3. The rate constants for the reactions (Eq. [5–8]) were calculated using the expressions provided in Table 4, where constant biomass populations were assumed. The substrate utilization rates, the biomass concentration, and the biomass inhibition terms were adapted from Lee et al. (2006) (Table 5). These values, particularly the substrate utilization rates, significantly influence the reaction rates in the model (MacQuarrie and Sudicky, 2001; Lee et al., 2006). It is important to note that biomass was assumed constant in this calculation. Calcite was included as an acid-consuming agent for low-pH rainwater and the acidity generated due to the oxidation of organic matter (Table 2). Gas dissolution–exsolution reactions and Henry’s law constants for O₂(g), N₂(g), and CO₂(g) are provided in Table 2.

### Configuration of the Simulation Domains

Four different soil profile configurations were conceptualized and incorporated into simulation frameworks so that soil structure and soil composition influences on N and O₂ fate and transport can be evaluated.
A rectangular mesh was used to discretize the domain, with 38 nodes along the axis and 120 nodes along the axis for the Sand scenario. In the second scenario, the macropore is 0.8 m deep (tile depth) and 0.005 m wide. The third scenario represents a clay loam with uniform bulk hydraulic conductivity (K-Bulk), the fourth scenario is a clay loam with uniform bulk hydraulic conductivity (K-Bulk), the third scenario represents a clay loam with uniform bulk hydraulic conductivity (K-Bulk), and the fourth scenario, which most represents soil pores associated with tile drainage contamination potential in the Frey et al. (2013) experiment, is a clay loam with a macropore connected drainage receptor simulating dead-end earthworm burrows, abandoned root channels, finite soil cracks, etc. (DC-MP), and finally, the fourth scenario, which most represents soil pores associated with tile drainage contamination potential in the Frey et al. (2013) experiment, is a clay loam with a macropore connected from surface to tile (C-MP). The respective height and width of the domains are 0.81 m (z direction) to accommodate the macropore geometry and to determine the macropore contribution to the total mass outflux from the macroporous domains.

**Initial and Boundary Conditions**

The initial conditions for each scenario were established using a constant water flux of 2.95 × 10⁻¹ cm d⁻¹ (3.41 × 10⁻⁸ m s⁻³), consistent with the average yearly precipitation rate at the Frey et al. (2013) field site, applied to the upper surface of the domains until steady-state flow conditions were achieved. For the flow solution, a first-type boundary condition (pressure head = 0 m) was defined for the bottom boundary, while both lateral boundaries were no-flow (Fig. 2). For transport, a mixed-type boundary condition was configured across the top of the domain; which in MIN3P-THCm facilitates a specified aqueous-phase mass flux together with a diffusive gaseous-phase mass flux based on a fixed concentration in an atmospheric boundary layer present directly above the top surface. For the simulations performed in this study, the mixed type boundary allows gas-phase movement into and out of the system. At the base of the domain, a second-type (free-exit) boundary condition was used in the transport solution. A thin (0.01 m) high conductivity (similar to the hydraulic conductivity of sand in this study) recharge spreading layer was used in the three steady-state clay loam scenarios to

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**Table 2. Exchange reaction between Ca²⁺ and Na⁺ and between NH₄⁺ and Na⁺ (and equilibrium constants; gas dissolution–exsolution reactions and Henry’s law constants for O₂(g)–O₂(aq), N₂(g)–N₂(aq), and CO₂(g)–CO₃²⁻; and the reaction stoichiometry and equilibrium constant for calcite.**

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction</th>
<th>Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cation exchange</td>
<td>Ca²⁺–Na⁺ exchange</td>
<td>log K = 0.7959†</td>
</tr>
<tr>
<td>NH₄⁺–Na⁺ exchange</td>
<td>NH₄⁺ – Na⁺ ↔ NH₄⁺ × Na⁺</td>
<td>log K = 0.6021†</td>
</tr>
<tr>
<td>Gas dissolution–exsolution</td>
<td>O₂(g)–O₂(aq)</td>
<td>log H = −2.898‡</td>
</tr>
<tr>
<td></td>
<td>N₂(g)–N₂(aq)</td>
<td>log H = −3.184‡</td>
</tr>
<tr>
<td></td>
<td>CO₂(g)–CO₃²⁻</td>
<td>log H = −18.16§</td>
</tr>
<tr>
<td>Mineral reaction</td>
<td>CaCO₃ → Ca²⁺ + CO₃²⁻</td>
<td>log K = −8.48†</td>
</tr>
</tbody>
</table>

† From WATEQ4F database (http://www.phreeplot.org/pphtml/wateq4f.dat.html).
‡ Molins et al. (2010).
§ From Minteq database (http://www.phreeplot.org/pphtml/minteq.dat.html).

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**Table 3. Reaction rate expressions, where the half-saturation constants for NH₄⁺, NO₂⁻, NO₃⁻, O₂, and CH₂O(aq) are represented as K_{nit[NH4]}^\text{max}, K_{nit[NO2]}^\text{max}, K_{nit[NO3]}^\text{max}, K_{Oxid[O2]}^\text{max}, and K_{Denit[CH2O]}^\text{max}.” The O₂(aq) inhibition constant is represented as K_{oxid[O2]}^\text{eff}, and the effective rate constant for calcite dissolution is represented by k_{CaCO3}^\text{eff}.**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>First nitrification reaction</td>
<td>R_{NH4–NO2} = − k_{NH4–NO2} max [NH4⁺]/(K_{nit[NH4]} × [NO₂⁻])/(O₂(aq))</td>
</tr>
<tr>
<td>Second nitrification reaction</td>
<td>R_{NO2–NO3} = − k_{NO2–NO3} max [NO₂⁻]/(K_{nit[NO2]} × [NO₃⁻])/(O₂(aq))</td>
</tr>
<tr>
<td>Denitrification reaction</td>
<td>R_{CH2O–NO3} = − k_{CH2O–NO3} max [CH₂O(aq)]/(K_{nit[CH2O]} × [NO₃⁻])/(K_{nit[NO3]} × [NO₃⁻])</td>
</tr>
<tr>
<td>Dissolved organic matter oxidation reaction</td>
<td>R_{CH2O(aq)–O2(aq)} = − k_{CH2O–O2} max [CH₂O(aq)]/(O₂(aq))/(K_{nit[CH2O]} × [O₂(aq)])</td>
</tr>
<tr>
<td>Soil organic matter oxidation reaction</td>
<td>R_{CH2O(aq)–O2(aq)} = − k_{CH2O–O2} max [CH₂O(aq)]/(O₂(aq))/(K_{nit[CH2O]} × [O₂(aq)])</td>
</tr>
<tr>
<td>Calcite dissolution reaction</td>
<td>R = k_{CaCO3}^\text{eff} × (1 − IAP/K_{sp})</td>
</tr>
</tbody>
</table>

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**Table 4. Expressions for the reaction rate constants (Lee et al., 2006; Berlin et al., 2014b), where k_{nit[NH4]}^\text{max}, k_{nit[NO2]}^\text{max}, k_{nit[NO3]}^\text{max}, and k_{max} refer to the maximum substrate utilization rate for the respective reactions. The concentrations of autotrophic NH₄⁺ oxidizing biomass is X₁, NO₂⁻ oxidizing biomass is X₂, and heterotrophic biomass is X₃.”**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>First nitrification reaction</td>
<td>k_{NH4–NO2} = k_{nit[NH4]} \max × nit[NH4] × (k_{b1} + X)</td>
</tr>
<tr>
<td>Second nitrification reaction</td>
<td>k_{NO2–NO3} = k_{nit[NO2]} \max × nit[NO2] × (k_{b2} + X)</td>
</tr>
<tr>
<td>Denitrification reaction</td>
<td>k_{CH2O–NO3} = k_{nit[CH2O]} \max × Denit[CH2O] × (k_{b3} + X)</td>
</tr>
<tr>
<td>Dissolved organic matter oxidation reaction</td>
<td>k_{CH2O(aq)–O2(aq)} = k_{nit[O2]} \max × oxid[O2] × (k_{b3} + X)</td>
</tr>
</tbody>
</table>

mesh was further refined (40 nodes between 0.0 and 0.01 m and 40 nodes between 0.01 and 0.25 m along the x axis; 120 nodes between 0.0 and 0.81 m along the z axis) to accommodate the macropore geometry and to determine the macropore contribution to the total mass outflux from the macroporous domains.
facilitate lateral transfer of the incident water across the low-
K soil (clay loam matrix) to the higher K macropore, where water can infiltrate more rapidly.

Each steady-state simulation consisted of a surface application of LSM (applied at a rate of 80 m$^3$ ha$^{-1}$, with a total spread-out time of 65 h) followed by 5000 h of rainwater influx applied at a constant rate of 3.41 $\times$ 10$^{-8}$ m s$^{-1}$. The LSM composition is described in Table 1. Under steady-state conditions, the effects of transport and mass transfer processes allow the intricacies of the geochemical processes to be illustrated, whereas inclusion of transient flow conditions shows the additional effects of changes in water flux on the overall solute fluxes. Thus it is beneficial to evaluate the scenarios with steady-state simulations first.

For transient-flow simulations, which evaluated model performance against observed tile effluent data (Frey et al., 2013), the initial conditions were established following the same method as described above for the clay loam scenarios. After the steady-state flow conditions were established, LSM (Table 1) was applied for 5 min at a uniform inflow rate of 2.31 $\times$ 10$^{-2}$ cm d$^{-1}$ or 2.67 $\times$ 10$^{-5}$ m s$^{-1}$ (volumetrically equivalent to the 80 m$^3$ ha$^{-1}$ manure application of Frey et al. [2013]) to represent the field application. However, subsequent water inflow after the 5-min-long LSM application was based on the observed rainfall received during the study period described by Frey et al. (2013). It is important to note that due to the short duration (5 min) of the LSM application, the thickness of the spreading layer in the DC-MP

![Fig. 2. Model domain, and flow and reactive transport (RT) boundary condition (BC) configuration, for the four simulated soil scenarios: homogeneous sand, homogeneous clay loam (K-Bulk), and clay loam with discrete macropores connected to (C-MP) or disconnected from (DC-MP) the bottom boundary.](image-url)
scenario was increased to 0.04 m to avoid ponding as a result of the high LSM application rate.

Soil Hydraulic Properties

The soils represented in this work span a range of particle-size distributions wherein macroporosity would be fundamentally contrasting (Table 6). Despite the fact that the physical properties of the soils change with depth, homogeneous hydraulic parameters were assumed for each pore domain (matrix and macropores) to simplify interpretation of the influence of macropores on reactive transport.

Hydraulic properties of the sand and clay loam soils (Table 6) were obtained from the Rosetta Lite v. 1.1 module within HYDRUS-1D (Schaap et al., 2001; Šimůnek et al., 1998). The hydraulic conductivity of the K-Bulk soil ($K_{\text{bulk}}$) was calculated using the following relationship from Gerke and van Genuchten (1993):

$$K_{\text{bulk}} = w_{\text{mp}}K_{\text{mp}} + (1-w_{\text{mp}})K_{\text{m}}$$

where $w_{\text{mp}}$ is the macropore volumetric weighting factor ($m^3 m^{-3}$), $K_{\text{mp}}$ is the macropore hydraulic conductivity ($m s^{-1}$), and $K_{\text{m}}$ is the matrix hydraulic conductivity ($m s^{-1}$). Macropore hydraulic properties (Table 6) were derived from Frey et al. (2012b, 2016), inferring that macropores are highly permeable, low-water-retention soil pores that facilitate gravity flow. Thus, macropore flow constraints are primarily imposed by boundary soil conditions along macropore walls and macropore bottoms.

Temperature Sensitivity

Temperature has a strong influence on mineral and gas solubilities as well as reaction rates (Griffin et al., 2002; Tromans, 1998). To evaluate the influence of temperature on the fate and transport of manure-derived N, a set of simulations was performed at 10°C (typical late autumn temperature when manure amendments are commonly applied in eastern Canada) and 25°C (a periodically high summer and spring surface soil condition in eastern Canada. The apparent activation energies for the first nitrification reaction (86.99 kJ mol$^{-1}$ [20.79 kcal mol$^{-1}$]), second nitrification reaction (116.98 kJ mol$^{-1}$ [27.96 kcal mol$^{-1}$]), and denitrification reaction (202.00 kJ mol$^{-1}$ [48.28 kcal mol$^{-1}$]) were obtained from Saad and Conrad (1993) based on similar soil types. The activation energy for the organic matter oxidation reaction (70.00 kJ mol$^{-1}$ [16.73 kcal mol$^{-1}$]) was obtained from Thiessen et al. (2013). Gas-phase temperature dependence parameters from the default MIN3P-THCm database were used except for $O_2(g)$, which was obtained from Moore and Stanitski (2015). Outside of the temperature sensitivity tests, all simulation results reported here were based on 10°C ambient temperature consistent with conditions associated with the autumn LSM experiments of Frey et al. (2013).

Chemical Parameters

Rainwater chemistry, LSM chemistry, and background pore water chemistry are given in Table 1. Liquid swine manure samples for chemical analyses were collected according to Frey et al. (2013). The soil pore-water samples were collected at the 10-, 25-, 45-, and 75-cm soil depths from the field site of Frey et al. (2013) prior to the LSM application. The manure and pore-water samples were analyzed for pH, Eh, alkalinity, anions, cations, and trace metals at commercial laboratories (SGS Canada Inc., Lakefield, ON, Canada; and EXOVA Environmental, Ontario, Canada) (Table 1). Chemical parameters that were not measured, including rainwater chemistry and some components of both the pore water and LSM were derived from literature values (Table 1). The pore-water chemistry taken prior to the LSM application was used as an initial soil chemical condition in the model scenarios.

Sorption and Reactive Transport Parameters

Sorption plays an important role in NH$_4^+$ immobilization. For the Sand scenario, the sorption capacity is 1.2 cmol dm$^{-3}$ bulk soil, whereas for the clay loam scenarios, respective values ranged between 21.0 and 30.4 cmol dm$^{-3}$ bulk soil on a soil depth basis (Supplemental Table S1). The organic C content, CH$_2$O(s), assigned in the model domain (Supplemental Table S1) was derived from measured organic matter contents at the Frey et al. (2013) site. The longitudinal dispersivity ($\alpha_x$), and transverse vertical dispersivity ($\alpha_y$), were respectively assigned as 0.1 and 0.001 m (Mayer et al., 2002). The aqueous-phase diffusion coefficient ($D_a$) and gaseous-phase diffusion coefficient ($D_g$) were assigned as $2.4 \times 10^{-5}$ and $2.1 \times 10^{-5}$ m$^2$ s$^{-1}$ (Mayer et al., 2012).

Results

Steady-State Modeling

Bromide Transport

As expected, the presence of the continuous macropore in the C-MP scenario led to the earliest ($\sim 0.2$ h after the start of LSM application) arrival of Br$^-$ at the base of the domain (Fig.

Table 6. Hydraulic parameters† of sand, clay loam matrix, macropores, and bulk (macropore + matrix) clay loam soils obtained in part from the Rosetta Lite version 1.1 module within HYDRUS-1D. The hydraulic parameters of macropore and matrix shown here were assigned for the macropore and matrix zones of the disconnected macropore and connected macropore scenarios.

<table>
<thead>
<tr>
<th>Soil type</th>
<th>$\theta_r$</th>
<th>$\theta_s$</th>
<th>$\alpha$</th>
<th>$n$</th>
<th>$K_r$</th>
<th>$l$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m$^{-1}$</td>
<td>m$^{-1}$</td>
<td>m$^{-1}$</td>
<td>m$^{-1}$</td>
<td>m$^{-1}$</td>
<td>m$^{-1}$</td>
</tr>
<tr>
<td>Sand</td>
<td>0.05</td>
<td>0.37</td>
<td>3.53</td>
<td>3.18</td>
<td>7.44 x 10$^{-5}$</td>
<td>0.5</td>
</tr>
<tr>
<td>Clay loam matrix</td>
<td>0.08</td>
<td>0.44</td>
<td>1.58</td>
<td>1.41</td>
<td>9.47 x 10$^{-7}$</td>
<td>0.5</td>
</tr>
<tr>
<td>Macropore</td>
<td>0.05</td>
<td>0.90</td>
<td>5.64</td>
<td>2.49</td>
<td>5.00 x 10$^{-2}$</td>
<td>0.5</td>
</tr>
<tr>
<td>Bulk clay loam</td>
<td>0.08</td>
<td>0.44</td>
<td>1.58</td>
<td>1.41</td>
<td>1.00 x 10$^{-3}$</td>
<td>0.5</td>
</tr>
</tbody>
</table>

† $\theta_r$, residual soil moisture content; $\theta_s$, saturated soil moisture content; $\alpha$, $n$, and $l$, van Genuchten soil hydraulic function parameters for unsaturated soils; $K_r$, saturated hydraulic conductivity.
3). Bromide arrival times in the K-Bulk and Sand scenarios were longer, at ~32 and ~155 h post-application (hpa), respectively. It is important to note that hpa 0 refers to the end of the 65 h of LSM application. The Br\(^{-}\) arrival in the DC-MP scenario was ~25 hpa.

The greatest Br\(^{-}\) mass outflow rate was predicted in the C-MP scenario (5.0 \times 10^{-4} \text{ mol m}^{-2} \text{ d}^{-1}) at 85 hpa. The maximum Br\(^{-}\) mass outflow rates in the Sand, K-Bulk, and DC-MP scenarios were 2.3 \times 10^{-4} \text{ mol m}^{-2} \text{ d}^{-1} at 1487 hpa, 1.9 \times 10^{-4} \text{ mol m}^{-2} \text{ d}^{-1} at 1741 hpa, and 1.7 \times 10^{-4} \text{ mol m}^{-2} \text{ d}^{-1} at 1010 hpa, respectively. Hydraulic properties of the soil matrix strongly govern Br\(^{-}\) transport under low steady-state flow conditions, as evidenced by results from the Sand scenario, which has relatively low water retention characteristics and is therefore drier under equivalent pressure heads than the soil matrix in the K-Bulk scenario (Fig. 4).

When the results from the Sand and C-MP scenarios are compared, the C-MP facilitated higher early time (<500 hpa) rates of Br\(^{-}\) discharge because of preferential flow through the macropore. The Br\(^{-}\) mass retention (percentage of applied mass) in the K-Bulk scenario (5.3%) was lower than in the DC-MP (11.1%) and C-MP (17.2%) scenarios at the end of the simulation (5000 hpa) because of its high hydraulic conductivity and uniform, one-dimensional flow field, which promoted domain flushing, compared with the two MP scenarios in which preferential flow promoted Br\(^{-}\) mass retention within the soil matrix. The lower mass retention in the K-Bulk scenario compared with the macropore scenarios was consistent with the higher cumulative mass outflux and lower mass retained in the K-Bulk domain (Fig. 3). In further contrast, the Sand scenario retained the least amount of Br\(^{-}\) mass (2.3%) among the four scenarios, with the domain being nearly flushed of Br\(^{-}\) (97.7% of applied Br\(^{-}\) leached) by 5000 hpa.

**Reaction Rates**

The rate constants for the first and second nitrification reactions, denitrification reaction, and dissolved organic matter oxidation were calculated (based on the parameters presented in Table 5) to be 1.34 \times 10^{-9}, 3.85 \times 10^{-9}, 6.69 \times 10^{-9}, and 6.69 \times 10^{-9} \text{ mol L}^{-1} \text{ H}_2\text{O s}^{-1}, respectively. Using these coefficients, spatially and temporally distributed reaction rates for Eq. [5–8] were obtained from the MIN3P-THCm output (reported in Fig. 5–7). The effective rate constant for a CH\(_2\)O(s) oxidation reaction (Eq. [9]) is provided in Table 5, and the spatial and temporal changes of the reaction rate in all four scenarios are presented in Fig. 7.

For the Sand scenario, the first nitrification (Eq. [5]) reaction was limited to the top 0.27 m and declined after 2500 hpa due to the low sorption capacity and low water retention characteristics of the sand, which led to NH\(_4^+\) depletion at the top boundary (Fig. 5 and 8; Table 6; Supplemental Table S1). Similar to the Sand scenario, the first nitrification reaction was also limited to the top of the K-Bulk domain (within 0.35 m from surface). The strong influence of macropores on the spatial distribution of the first nitrification reaction was evident in both the DC-MP and

![Fig. 3. Bromide mass outflux rate, cumulative Br\(^{-}\) mass outflux, and Br\(^{-}\) mass in the domains for the four simulated soil scenarios: homogeneous sand, homogeneous clay loam (K-Bulk), and clay loam with discrete macropores connected to (C-MP) or disconnected from (DC-MP) the bottom boundary; hpa is hours post application.](image-url)
C-MP scenarios, with the highest reaction rates predicted along the macropores (as well as across the top soil surface).

The rate of the second nitrification reaction (Eq. [6]) was dependent on multiple factors that included the production of NO$_2^-$ from the first nitrification reaction (Supplemental Fig. S1), NO$_2^-$ concentration in the manure, the availability of O$_2$ in the domain, and the oxidation of CH$_2$O$_{(aq)}$ and CH$_2$O$_{(s)}$. Due to the contribution of NO$_2^-$ from two different sources (from the LSM and the product of the first nitrification reaction) and the availability of O$_2$, the early-time (1 hpa) rates of the second nitrification reaction were overall higher than those associated with the first nitrification reaction (Fig. 5). However, the spatial patterns of the two nitrification reactions were similar, and the strong influence of the macropores was again evident. Overall, the production of NO$_3^-$ is closely related in both space and time to the availability of reactants, which are governed by soil texture and structure. The depth of penetration of the macropores largely controls the depth of maximum NO$_3^-$ production, which is demonstrated by the differences in the NO$_3^-$ production depth between the DC-MP and C-MP scenarios. However, because of its high mobility, NO$_3^-$ readily spreads throughout the domain (Fig. 8).

The reaction rates for denitrification (Eq. [7]) were directly dependent on the availability of NO$_3^-$, CH$_2$O$_{(aq)}$, CH$_2$O$_{(s)}$, O$_2$(aq), and O$_2$(g) (Fig. 8; Supplemental Fig. S2–S3; Supplemental Table S1). Because CH$_2$O$_{(aq)}$ was depleted by 5000 hpa in all but the C-MP scenario (Supplemental Fig. S2), denitrification was occurring only in the C-MP scenario at 5000 hpa (Fig. 6; Supplemental Fig. S1). The oxidation of CH$_2$O$_{(aq)}$ and CH$_2$O$_{(s)}$ (Eq. [8–9]) indirectly contributed to the nitrification-denitrification processes by the consumption of O$_2$(aq). In the 1 to 2500 hpa time interval, maximum denitrification rates were closely aligned with the highest coincident concentrations of NO$_3^-$ and CH$_2$O$_{(aq)}$ (Fig. 6 and 8; Supplemental Fig. S2). Although the reaction rate diminished with time for the CH$_2$O$_{(aq)}$ oxidation reaction, no significant changes in reaction rate were predicted for the CH$_2$O$_{(s)}$ oxidation reaction. The consistent reaction rate of the CH$_2$O$_{(s)}$ oxidation reaction during 1 to 5000 hpa (Fig. 7) compared with the CH$_2$O$_{(aq)}$ oxidation reaction (Fig. 7) helped to keep O$_2$ concentrations within a range that prevented amplified nitrification.

**Effect of Sorption**

Within the soil matrix in the K-Bulk scenario, adsorbed NH$_4^+$ was effectively constrained to the top 0.63 m of the
domain during the entire 5000 hpa simulation (Supplemental Fig. S4). The presence of the preferential flow paths in the DC-MP and C-MP scenarios facilitated localized rapid vertical migration of NH$_4^+$, which with time spread laterally into the soil matrix (Fig. 8). The macropore continuity influences on the flow regime, which, along with the vertical change in sorption capacity within the domain, played an important role in the distribution of the aqueous- and solid-phase NH$_4^+$ (Fig. 8; Supplemental Fig. S4). Because of the lower sorption capacity of sand compared with clay loam (Supplemental Table S1), NH$_4^+$ migrated much faster in the Sand domain and was depleted at the top surface by ~5000 hpa. In contrast, NH$_4^+$ persisted near the top surface of the clay loam domains until the end of the simulation (Fig. 8).

**Effect of Dissolved Oxygen**

The domains were all initially saturated with dissolved O$_2$ [O$_2$(aq)]. Following the manure application, O$_2$(aq) was consumed during the oxidation of manure-derived NH$_4^+$ and aqueous-and solid-phase organic C [CH$_2$O(aq) and CH$_3$O(s)]. Because MIN3P-THCm allows gas-phase O$_2$ to replenish depleted O$_2$(aq) (Supplemental Fig. S2 and S3), an assessment of how macropores influence O$_2$ distributions, in both phases, could be made. Results show that O$_2$(aq) depletion is highly dependent on manure-derived NH$_4^+$ and CH$_2$O(aq) distributions within the simulation domains and the diffusion of O$_2$(g) into (and through) the domain as affected by macropores (Supplemental Fig. S2).

The macropore in both the C-MP and DC-MP scenarios provided a pathway for O$_2$(g+aq) (sum of diffusive O$_2$(g) influx...
and advective–diffusive O$_2$(aq) influx, dominated by the O$_2$(g) influx] to transmit vertically into the domain (Supplemental Fig. S2). There was a distinct difference in O$_2$(aq) observed at about 0.17 and 0.20 m below the top surface in the DC-MP and C-MP scenarios after the initial consumption of O$_2$(aq) (within 1 hpa), which reflects the influence of gas-phase diffusion of atmospheric O$_2$ and the associated impacts of the macropores as replenishing conduits (Supplemental Fig. S2 and S3). Organic matter oxidation reaction and nitrification reactions also played important roles in the distribution of O$_2$ in all model domains (Fig. 5 and 7). Continuous O$_2$ replenishment processes muted spatial differences in concentrations for a specific scenario in the long term (to 5000 hpa) (Supplemental Fig. S2 and S3); however, during the 65-h LSM application time period, concentrations were more dramatically affected spatially as impacted by direct LSM inputs (Supplemental Fig. S3).

**Nitrogen Transformation and Transport**

Manure-derived NH$_4^+$ reached the bottom outflow boundary in the Sand scenario by $\sim$4 h after the start of LSM application due to the sand’s relatively high hydraulic conductivity and low sorption capacity (Supplemental Table S1), while in the C-MP scenario, NH$_4^+$ reached the outflow boundary by $\sim$1 h after the start of LSM application due to preferential transport (Fig. 9). However, these early arrivals of NH$_4^+$ at the bottom of the simulation domain of the Sand scenario are not visible on the plot because NH$_4^+$ concentrations increased slowly during the early stage of the simulation. Due to the low mobility of NH$_4^+$ in the clay loam soil matrix for DC-MP and K-Bulk, there was no significant NH$_4^+$ mass outflow for these scenarios (Fig. 9). For the Sand scenario, NH$_4^+$ was depleted at the top of the domain by $\sim$5000 hpa, whereas for the K-Bulk, DC-MP, and C-MP scenarios, NH$_4^+$ persisted to a greater degree at the surface at 5000 hpa (Fig. 8). The NH$_4^+$ transport regimes were notably different between homogeneous and macroporous soil configurations overall (Fig. 8). In both the Sand and K-Bulk scenarios, NH$_4^+$ migrated downward in a uniform front, whereas as expected in the DC-MP and C-MP scenarios, the macropores facilitated localized preferential downward transport of NH$_4^+$. The two-dimensional plots also show a distinguishable increase in pressure head in the DC-MP scenario compared with the C-MP scenario, which led to a subtle lateral pressure head gradient and higher water saturation in the DC-MP scenario (Fig. 4). The lateral gradient promoted the lateral migration of NH$_4^+$ into the soil matrix in the DC-MP scenario (Fig. 8). At 1 hpa, zones of high NH$_4^+$ retention were somewhat aligned with elevated NO$_3^-$ (Fig. 8); however, at this early stage of the simulation, NO$_3^-$ distribution was largely dependent on the modest pore-water NO$_3^-$ concentrations in the soil (Table 1). At longer simulation times, zones of elevated NO$_3^-$ are more closely aligned with the zones that exhibit the highest geochemical activity.

The presence of the macropore in the clay loam scenarios played an important role in the lateral migration of the N species. In both the DC-MP and C-MP scenarios, NO$_3^-$ and NO$_2^-$ were elevated in the vicinity of the macropores throughout the entire 5000 hpa simulation (Fig. 8; Supplemental Fig. S1), which resulted from the O$_2$(g+aq) influx through the macropore (Supplemental Fig. S2 and S3). The influence of macropore continuity is also evident, with the DC-MP scenario displaying a greater late-time (2500–5000 hpa) NO$_3^-$ distribution throughout the soil matrix compared with the C-MP scenario (Fig. 8). Comparing the NO$_3^-$ distribution between the DC-MP and C-MP scenarios highlights how free-drained macropores can limit N movement into the matrix, whereas disconnected
Macropores provide conduits that enhance the distribution of N throughout the soil matrix by facilitating lateral nutrient redistribution (Fig. 8). The late-time (2500–5000 hpa) NO$_3^-$ distribution in the DC-MP and C-MP domains (Fig. 8) shows depletion of NO$_3^-$ in the regions surrounding macropores (in the absence of new N sources) over longer time frames, in part due to back-diffusion across the matrix–macropore interface (which promoted denitrification in the matrix adjacent to macropore walls). Both NH$_4^+$ and NO$_3^-$ are shown to move through the two homogeneous soil scenarios with a uniform front (Fig. 8), and with faster breakthrough rates in the sand domain than that of the K-Bulk scenario (Fig. 9).

Elevated concentrations of N$_2$(aq) were simulated at the base of the DC-MP domain around 2500 hpa (Supplemental Fig. S1), and after 2500 hpa, the denitrification reaction rate was reduced significantly (Fig. 6). Elevated N$_2$(aq) concentrations predicted between 2500 and 5000 hpa in the C-MP scenario (Supplemental Fig. S1) coincided with more prominently expressed denitrification reaction rates at 5000 hpa (Fig. 6).

**Temperature Influence**

As expected, initial O$_2$(aq) saturation levels decreased when the temperature was increased from 10 to 25°C. Conversely, the higher temperature increased nitrification rates, which led to an
earlier increase in \( \text{NO}_3^- \) at the base of the simulation domain and higher \( \text{NO}_3^- \) and lower \( \text{NH}_4^+ \) concentrations in the outflow from the Sand and C-MP scenarios. No significant \( \text{NH}_4^+ \) reached the bottom of the domain in the K-Bulk and DC-MP scenarios due to a higher sorption capacity of the clay loam soil and the absence of macropore connectivity to the bottom of the domain (Fig. 9). The increased nitrification rates promoted the early-time consumption of \( \text{O}_2\text{(aq)} \) in the near surface, which in turn led to a higher flux of \( \text{O}_2\text{(aq+g)} \) across the top boundary (Fig. 9). In all four scenarios, the \( \text{NO}_3^- \) breakthrough curve was notably influenced by the higher nitrification rates, with increased peak concentrations observed for the 25°C scenarios (Fig. 9). In the C-MP scenario, there is also a notable change in the shape of the \( \text{NO}_3^- \) breakthrough curve at early times, where at 25°C, \( \text{NO}_3^- \) breakthrough displays a stronger preferential transport regime. It is evident from the results of the temperature-sensitivity tests that \( \text{O}_2\text{(aq)} \) availability was not a limiting factor on nitrification rates at 25°C. Hence under these same conditions in a field setting, it could be expected that higher temperatures will have a significant influence on \( \text{NO}_3^- \) leaching for all scenarios. However, higher temperatures had a more pronounced impact on \( \text{NO}_3^- \) leaching in the clay loam scenarios than the sand scenario, where the lower sorption capacity of the sand facilitated leaching of a significant portion of the N source (\( \text{NH}_4^+ \)) out of the bottom of the domain (Fig. 9).

### Transient Simulation Results

The results from the transient reactive transport simulations (Fig. 10) are presented here to demonstrate that the steady-state
modeling discussed thus far captures the primary N fate and transport processes associated with LSM applications on macroporous soils.

Both C-MP and DC-MP scenarios reproduced the observed declines in NO$_3^-$ concentrations (during the first 60 h after the start of manure application) due to the post-manure-application rainfall, which transmitted event water via macropores directly to the tiles (Frey et al., 2013), and facilitated the appearance of NH$_4^+$ in the tile effluent without it being oxidized to NO$_3^-$ (evidenced by higher observed NH$_4^+$ concentrations at the tile effluent during this time) (Fig. 10). Although the early-time (0–200 hpa) NO$_3^-$ concentrations were in reasonable agreement with the field observations in the DC-MP and K-Bulk scenarios, the late-time NO$_3^-$ concentrations were considerably underestimated in all but the C-MP scenario. Due to the presence of the 0.3-m-thick clay loam layer at the bottom of the macropore, very low concentrations of NH$_4^+$ and its transformation products were observed in the outflow of the DC-MP scenario (Fig. 10). For NO$_2^-$, the RMSE was best in the DC-MP scenario.

Notwithstanding the simplified flow regime used to represent the tile-drained field scenario, the basic conceptual representation of preferential flow and reactive transport utilized here with the MIN3P-THCm model incorporated the key components required to emulate nitrification and NO$_3^-$ release following LSM applications on macroporous tile-drained soils.

Discussion and Conclusions

Macropores have received considerable attention with respect to contaminant transport in agricultural soil environments (Beven and Germann, 1982, 2013; Jarvis, 2007; Köhne et al., 2009). Experimental studies have documented that macropores directly connected to tile drainage systems were responsible for a large proportion of tile effluent contamination following the land application of liquid fertilizer amendments (Lapen et al., 2008; Frey et al., 2013; Colombi et al., 2017). Direct connectivity of open-surface macropores with the subsurface drainage is not required for rapid drain flow response; however, for a noticeable effect on the arrival time, surface connected macropores need to extend at least halfway to the drain (Akay and Fox, 2007; Akay et al., 2008). Allaire-Leung et al. (2000) found that the solution in macropores open at the surface and at the bottom of a soil column reached the bottom of the column ~100 times faster (relative to other macropore configurations) by bypassing most of the soil matrices, and furthermore, the breakthrough time for that macropore column was much faster than any other pore continuity treatment. The macropore in the C-MP scenario in this study transmitted approximately 97% of the total water discharge, which is consistent with the findings of other studies (Haws et al., 2005) including those conducted on the same soils (Lapen et al., 2008; Frey et al., 2013, 2016). However, the implication of macropore connectivity to subsurface hydrological receptors in the context of N transport and transformations extends beyond just influences on flow.
Although a significant portion of LSM-derived NH$_4^+$ was initially immobilized through sorption, a portion of the NH$_4^+$ was subjected to simultaneous nitrification processes, which was reflected in the distribution of NH$_4^+$, the production of NO$_3^-$, variations in the distribution of sorbed NH$_4^+$ across the four soil scenarios examined, and the distribution of soil organic C in different layers (Fig. 8; Supplemental Fig. S4; Supplemental Table S1).

Because nitrification is a primary N transformation process associated with land application of LSM (Rochette et al., 2001; Chantigny et al., 2002), the relative concentrations of NO$_3^-$ in the hydrological or soil environment (which may be made available to crop or other plant use) will be highly dependent on the availability of O$_2$\textsubscript{(aq)}, which is governed by pore geometry and connectivity, soil water contents, and gas-phase diffusion of O$_2$. The results of this study demonstrate that macropores can have a significant influence on O$_2$\textsubscript{(aq)} ingress in the soil (Hendriks et al., 1999), which in turn facilitates the first and second nitrification reactions, as well as organic C oxidation in the deeper part of the DC-MP and C-MP domains. Because the denitrification reaction was dependent on the availability of CH$_2$O\textsubscript{(aq)} and O$_2$\textsubscript{(aq)}, this reaction was indirectly influenced by the CH$_2$O\textsubscript{(aq)} oxidation reaction, the CH$_2$O\textsubscript{(g)} oxidation reaction, and second nitrification reaction. In comparison to nitrification reaction rates, denitrification rates were very low across all four soil scenarios due to the capacity for all scenarios to facilitate adequate inputs of both aqueous- and gas-phase O$_2$ to the systems. However, production of N$_2$\textsubscript{(aq)} at the base of the domain in all scenarios, particularly the C-MP and DC-MP scenarios, suggests the potential occurrence of denitrification in the connected and disconnected macroporous clay loam soils was probably linked to preferential transport of NO$_3^-$ and O$_2$ to depth.

In terms of mass movement, the greatest downward movement of NH$_4^+$ mass occurred in the Sand scenario, where low sorption capacity (relative to the clay loam) limited sorption. The maximum rate of NO$_3^-$ mass loss was not appreciably different among the three clay loam scenarios; however, because of the connected preferential flow path, the earliest NO$_3^-$ breakthrough occurred...
in the C-MP scenario. While the importance of preferential flow paths on N cycling in agricultural soils has been demonstrated, the steady-state modeling results here highlight that the mere presence of connected macropores may not lead to significantly greater mass loss of reactive constituents with time, and that all aspects of the flow and reactive transport system (i.e., matrix–macropore interactions, pore connectivity, water retention characteristics, soil chemistry) need to be considered.

In addition to enhancing the downward propagation of nutrient mass, macropores have been shown to facilitate the diffusion of chemical constituents into the soil matrix, which has been widely noted in previous works (Rahman et al., 2004; Cey and Rudolph, 2009; Koestel and Larsbo, 2014). However, this study has also demonstrated that macropores can facilitate O$_2$ ingress into the soil profile, which in turn supports oxidation reactions and increased vertical distribution of oxidation reaction products, such as NO$_3^-$.- Besides the differences in mass arrival at the base of the model domain, one of the key observations was that the disconnected macropore promoted the accumulation of NO$_3^-$ at depth within the soil matrix compared with the C-MP scenario, which is in part attributed to pore-geometry-induced differences in the pressure-head and water-saturation distributions. In addition to being a mass source for the surrounding soil matrix (under mass influx conditions), macropores are demonstrated here to be a conduit whereby incident water can propagate deep into the soil profile, which in turn provides opportunity for advective and dispersive solute flushing of the soil matrix in the vicinity of the macropore, leading to steeper lateral concentration gradients in the domain.

Macroporosity in agricultural tile drained soil environments is often highly variable, in terms of density and the degree of hydraulic connection (Petersen et al., 2012). In this study, an arbitrary depth for a disconnected macropore was chosen for comparative purposes (according to Akay and Fox, 2007) because there are many connected, dead-end (disconnected), and buried pores in an agricultural soil environment of unknown spatial and structural disposition. Thus, simplifying macropore characterization in reactive transport models could be a means of reducing modeling and parameterization complexities. Regarding the N species examined here, especially NO$_3^-$, the transient C-MP model with a highly simplified parameterization of macropore connectivity is certainly one approach to specifically simulate critical N transformations and N losses to tiles in macroporous soils. To account for N loading to both shallow groundwater and tiles, however, model spatial domains would need to be expanded to include pores contributing directly to tile drains as well as shallow groundwater.

Overall, we attempted to explicitly document model parameterization and initialization to make the work interpretable and applicable to conditions beyond those immediately examined (van der Laan et al., 2014). Our study suggests that soil temperature, structure, and composition and macropore connectivity to tile drains can have a significant influence on N behavior, particularly following liquid manure applications. Proof-of-concept demonstration of the modeling methodology for transient applications shows promise in that key NH$_4^+$ and NO$_3^-$ transport characteristics observed in previous field work were captured substantially in the connected macropore scenario, even though the model domain was heavily simplified. Accordingly, there is considerable opportunity to further develop this modeling approach to refine and capture additional reactions, such as those that resolve N gas production, within the reactive transport framework.

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References


