Direct methods to calculate the mass exchange between solutes inside and outside aggregates in macroscopic model for solute transport in aggregated soil

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ABSTRACT

Macroscopic modeling of solute transport in aggregated soil is often based on the dual-domain approach assuming that water flow occurs mainly in the inter-aggregates pores while the water inside the aggregates is stagnant; the solutes in the two waters can exchange driven by molecular diffusion. Since such a mass exchange is not measurable, practical modeling often uses pre-defined empirical memory functions to describe it with the parameters in the functions calculated by calibration against experimental measurement. It is hence difficult to verify that the calibrated memory functions correctly describe the mass exchange process or just to bridge the model and the measurements in that a shift from the experimental conditions could invalidate the model. Furthermore, most researches on such mass exchanges are for inert tracers, while most solutes in soil are reactive. How to link the mass exchange rates for inter tracer and reactive solutes is poorly studied. The purpose of this paper is to present direct methods to calculate the mass exchange rates for inert tracer and reactive solute using x-ray tomography and pore-scale simulations. Sample of an aggregated soil is scanned using x-ray microtomography by assuming, judged by visual observation in imaging the soil, that the sizes of the inter-aggregate pores are larger than 40 μm and using 40 μm as the resolution can separate the inter-aggregate pores from the aggregates. The aggregates are assumed to be permeable and their ability to conduct solute is described by an effective diffusion coefficient. We then numerically simulate the movement of both inert tracer and reactive solute from the inter-aggregate pores into the aggregates using pore-scale modeling. The simulated solute concentration in all voxels is sampled and then volumetrically averaged to calculate the average mass exchange rates between solute inside and outside the aggregates in the soil image. For reactive solute, we take nitrate as an example and analytically link its mass exchange rate to that for the inert tracer assuming that the nitrate reduction is a first-order kinetics. We also analytically establish the relationship between the mass exchange rates of solutes with different molecular diffusion coefficients, and verify this relationship against the results directly calculated from the pore-scale simulations. We additionally examine the accuracy of the commonly used empirical memory functions against those directly calculated from pore-scale simulations, finding that none of these functions can accurately describe the mass exchange process. To verify these directly- calculated mass exchange rates, we apply them to model the leaching of the inert tracer and the reactive nitrate in an aggregated soil column.

1. Introduction

The interaction between soil microbes and organic matters aggregates soil, yielding a hierarchical structure in which the pores inside the aggregates are much smaller than the pores between the aggregates (Bronick and Lal, 2005; Neretnieks, 1980; Rao et al., 1980). When modeling water flow and chemical transport in such structured soils, the water inside the aggregates is often assumed to be stationary compared with the water outside them, yet solutes can move between the two driven by molecular diffusion (Knabner et al., 1996; Yang et al., 2014). Mass exchange between the two waters depends on geometry and diffusivity of the aggregates, while in macroscopic models these aggregate processes cannot be explicitly resolved and they are instead described by a model known as memory functions in the literature

(Haggerty and Gorelick, 1995).

The early models for chemical transport in aggregated soils assumed that the mass exchange rate is proportional to the difference between solute concentrations inside and outside the aggregates (Coats and Smith, 1964), which leads to an exponential memory function. Practical applications of the exponential memory function, however, show that its parameter needs to change with flow rate in order to match experimental data (Bromly and Hinz, 2004; Gao et al., 2010; Pang et al., 2002), raising a speculation over its correctness in capturing the mass exchange process because there is no theoretical basis for the exchange rate coefficient to depend on water velocity (Gouze et al., 2008; Zhang et al., 2008). Recent study based on pore-scale simulations indeed reveals that the real memory function decreases with time more steadily than predicted by the exponential function in early stage even though it declines approximately exponentially in the late stage (Hu et al., 2014). This is consistent with previous analysis which suggested that the temporal change of the mass transfer rate between solute in mobile and immobile water in structured media is likely to be multiple scales (Haggerty et al., 2004; Haggerty et al., 2000). As such, more complicated memory functions have been proposed, including gamma (Chen and Wagenet, 1997), modified gamma (Cvetkovic, 2012), log-normal (Russo et al., 2010) and fractal (Schumer et al., 2003) functions. However, these functions are empirical lacking explicit link to geometry and diffusivity of the aggregates. Another approach is the multi-region model (Ginn, 2009; Haggerty and Gorelick, 1995), and Berkowitz et al. view it as a special case of their continuous random time walk model (Berkowitz et al., 2006; Dentz and Berkowitz, 2003). The multi-region model is evolved from the multi-rate model initially developed to describe heterogeneous adsorption (Donado et al., 2009; Zhang et al., 2008). When applied to mass exchange between solute inside and outside the aggregates, it divides the aggregates into a number of regions and the solute in each region can exchange directly with the solute outside the aggregates at a rate proportional to their concentration difference. Although the multi-rate and multi-region models are mathematically the same (de Dreuzy et al., 2013), their implications are different when applied to solute in aggregated soil as the adsorptive solutes are not bioavailable for roots and microbes to take up.

Most studies on memory function focus on inert tracers (de Dreuzy et al., 2013), while solutes in soils such as nitrate, ammonium and phosphate are reactive. A salient example is nitrification and denitrification in nitrogen cycling (Ebrahimi and Or, 2015; Ebrahimi and Or, 2014). In soils, the biogeochemical reactions mediated by microorganisms dwelling in aggregates proceed only when substrates are available (Kremen et al., 2005). Some substrates, such as oxygen and fertilizers, move through the inter-aggregates pores downward first prior to diffusing into the aggregates. Meanwhile, the soil needs to remove the products of its biochemical reactions out of the aggregates. Thus, the mass exchange between substrates inside and outside the aggregates modulates most biogeochemical reactions but is difficult to measure. A possible method is to use the mass exchange calculated from inert tracer to estimate the mass exchange for reactive solutes, but this has not been well documented.

Solute diffusion in soil aggregates can be directly calculated once their geometry and diffusivity are known (Willmann et al., 2010). The advent in x-ray micro-tomography over the last decade has opened an avenue to visualize the interior structure of opaque soil (Baveye et al., 2010; Flavel et al., 2012; Mooney et al., 2012; Wildenschild and Sheppard, 2013), and it has been increasingly used with pore-scale modeling to study a wide range of transport processes in porous media (Blunt et al., 2013; Chen et al., 2008) which would remain unknown otherwise, such as the relationship between solute residence time and pore structure (Bijeljic and Blunt, 2006), discontinuity of concentration at sharp interface between two media (Zhang et al., 2010), and the role of aggregate geometry in regulating nitrogen and carbon cycling in ecosystems (Ebrahimi and Or, 2016).

The purpose of this paper is to show how to directly calculate the

mass exchange between solutes inside and outside the aggregate. Samples of an aggregated soil are scanned using x-ray tomography at resolution of 40 μm assuming, judged by visual observation in imaging the soil, that most inter-aggregate pores are larger than 40 μm, and using 40 μm as the resolution can approximately separate the inter-aggregate pores and the aggregates. The aggregates are permeable and their ability to diffuse solute is described by an effective diffusion coefficient, and the solute movement within the aggregates is numerically simulated using the pore-scale model we previously developed (Zhang and Gao, 2016). The simulated solute concentration in all voxels are sampled, and they are then volumetrically averaged to calculate the average mass exchange rates for both inert and reactive solutes over the image. For reactive solute, we take denitrification of nitrate as an illustrative example and analytically link its mass exchange rate to that for the inert tracer.

In arable soils, the intra-aggregate pores proximal to the aggregate surfaces are rich in oxygen and minerals nutrients, thereby promoting microbial growth. Accumulation of microbial biomass could reduce the ability of the aggregate surfaces to diffuse solutes. We consider such less-diffusible zones and investigate their significance in impacting solute movement between waters inside and outside the aggregates. To examine the accuracy of the commonly used empirical memory functions in the literature, we fit them to the average mass exchange rates calculated directly from the pore-scale simulations. To verify the directly-calculated the mass exchange rates, we apply them to model the leaching of the inert tracer and the reactive nitrate in an aggregated soil column.

2. Materials and methods

2.1. The macroscopic equations for solute transport in aggregated soil

Solute transport in aggregated soils is often described by the dual-domain approach assuming that water inside the aggregates is immobile and water movement occurs only through the inter-aggregate pores. The solute can move from one water to another driven by molecular diffusion. In one dimension, the volumetric average transport equation for a soluble species in the soil is (Gerke and van Genuchten, 1993):

$$\frac{\partial \theta C_m}{\partial t} = \frac{\partial}{\partial z}\left(\theta D \frac{\partial C_m}{\partial z}\right) - \frac{\partial q C_m}{\partial z} - \frac{\partial Q_{im}}{\partial t} + S, \tag{1}$$

where θ is inter-aggregate porosity, C_m is volumetric average concentration of the solute between the aggregates, z is the coordinate, D is the hydrodynamic dispersion coefficient, q is the volumetric average water flow rate (the Darcy's flow rate) and $\partial Q_{im}/\partial t$ is the mass exchange rate due to solute moving into or out of the aggregates, S is a source/sink term describing the loss or gain due to reaction taking place outside the aggregates. In general, $\partial Q_{im}/\partial t$ can be written as follows:

$$\frac{\partial Q_{im}}{\partial t} = \int_0^t \theta_{im} \frac{\partial C_m}{\partial \tau} f(t - \tau) d\tau, \tag{2}$$

where θ_{im} is intra-aggregate porosity and $f(t)$ is called as memory function, satisfying $\int_0^\infty f(t) dt = 1.0$ for inert tracer and $\int_0^\infty f(t) dt \neq 1$ for reactive solutes.

The most common approach to describe the mass exchange in aggregated media is the multi-region model by dividing the aggregates into a number of regions, and the solute in each region can exchange directly with solute outside the aggregates at a rate proportional to their concentration difference:

$$\frac{\partial \theta_{im} C_{im}}{\partial t} = \sum_{j=1}^N \theta_j \beta_j (C_m - C_j), \tag{3}$$

where θ_j is the volumetric fraction of region j, C_{im} is the volumetric average concentration of solute within the aggregates, C_j is the volumetric average concentration in region j, β_j is the mass exchange rate