



Groundwater transport modeling with nonlinear sorption and intraparticle diffusion



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ABSTRACT

Despite recent advances in the mechanistic understanding of sorption in groundwater systems, most contaminant transport models provide limited support for nonideal sorption processes such as nonlinear isotherms and/or diffusion-limited sorption. However, recent developments in the conceptualization of “dual mode” sorption for hydrophobic organic contaminants have provided more realistic and mechanistically sound alternatives to the commonly used Langmuir and Freundlich models. To support the inclusion of both nonlinear and diffusion-limited sorption processes in groundwater transport models, this paper presents two numerical algorithms based on the split operator approach. For the nonlinear equilibrium scenario, the commonly used two-step split operator algorithm has been modified to provide a more robust treatment of complex multi-parameter isotherms such as the Polanyi-partitioning model. For diffusion-limited sorption, a flexible three step split-operator procedure is presented to simulate intraparticle diffusion in multiple spherical particles with different sizes and nonlinear isotherms. Numerical experiments confirmed the accuracy of both algorithms for several candidate isotherms. However, the primary advantages of the algorithms are: (1) flexibility to accommodate any isotherm equation including “dual mode” and similar expressions, and (2) ease of adapting existing grid-based transport models of any dimensionality to include nonlinear sorption and/or intraparticle diffusion. Comparisons are developed for one-dimensional transport scenarios with different isotherms and particle configurations. Illustrative results highlight (1) the potential influence of isotherm model selection on solute transport predictions, and (2) the combined effects of intraparticle diffusion and nonlinear sorption on the plume transport and flushing for both single-particle and multi-particle scenarios.

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1. Introduction

Of the processes that affect the migration of dissolved contaminants in the subsurface, sorption to aquifer solids is believed to play a key role, especially in the absence of nonaqueous phase contamination. In particular, the influence of sorption on aquifer restoration has long been recognized (e.g. [1–5]), and the release of sorbed contaminants is an important component of modern multi-compartment conceptualizations of remediation processes (e.g. [6]). The prediction of cleanup times for hydrophobic organic contaminants (HOCs) can be strongly affected by assumptions used to model the sorption process, which typically include specification of an equilibrium sorption isotherm and, if applicable, a rate model [7–10]. Although potentially influential aspects of sorption

phenomena such as nonlinear equilibrium and/or kinetic limitations have been conceptualized for subsurface systems [11–15], only a few published field scale modeling studies have incorporated these processes [9,16,17], although some public domain software packages support a subset of the available models [18].

As the understanding of HOC sorption has evolved, recent developments have introduced complex isotherm expressions involving multi-parameter “dual mode” or “distributed reactivity” mechanisms [19–21]. However, in most groundwater contaminant transport models, HOC sorption is represented as a linear process, or by a limited number of nonlinear isotherms such as the Freundlich [22] or Langmuir [23] equation [18,24–27]. Also, the combination of intraparticle diffusion and nonlinear isotherms, while recognized as an appealing mechanistic conceptualization of “non-ideal” sorption processes (e.g. [13,28–31]) has been modeled primarily at the laboratory scale [31–35], with only a few studies conducted for intraparticle diffusion in two-dimensional domains [9].

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Nomenclature

Greek letters

Δt	time interval between T_1 and $T_1 + 1$ [T]
Δt_d	time interval between T_2 and $T_2 + 1$ [T]
ρ_b	bulk density of the porous media [M/L ³]
ρ_{bk}	bulk density for particle of identity k [M/L ³]
Δr	intraparticle node spacing in diffusion domain [L]
Δx	grid spacing in transport domain [L]

Roman letters

A	Polanyi isotherm parameter
B	Polanyi isotherm parameter
b	Langmuir isotherm parameter
C_l	volume averaged aqueous phase solute concentration in [M/L ³]
C_s	volume averaged sorbed solute concentration [M/L ³]
C_0	aqueous phase solute concentration at domain entrance [M/L ³]
Cr	Courant number
c_l	intraparticle aqueous phase solute concentration [M/L ³]
D	dispersion coefficient [L ² /T]
D_a	effective intraparticle diffusion coefficient [L ² /T]
D_a	Damkohler number for intraparticle diffusion
F	mesh Fourier number
K_p	partition coefficient in the Polanyi-partition isotherm [L ³ /M]
K_f	Freundlich isotherm parameter
nf	Freundlich isotherm parameter
n	aquifer porosity

n_p	intraparticle porosity
Pe	mesh Peclet number
Q_0	Langmuir isotherm parameter
Q_p	Polanyi isotherm parameter
q_s	intraparticle sorbed mass fraction [M/M]
r_k	radial distance from center of the particle of class k [L]
t	time [T]
v	groundwater velocity [L/T]
x	distance from the domain entrance [L]
S_w	solute aqueous solubility [M/L ³]

Subscripts/superscripts

l	aqueous phase
s	sorbed phase
i	node number for discretized transport domain (x)
j	node number for discretized particles (r)
k	particle identity for particle with identical diffusion and sorption characteristics
T_1	time sequence number for transport equation
T_2	time sequence number for diffusion equation

Abbreviations

ADRE	advective–dispersive–reactive–equation
HOC	hydrophobic organic contaminant
ODE	ordinary differential equation
MB	mass balance
PP	Polanyi-partition
TCE	trichloroethylene

The disconnect between the current mechanistic understanding of subsurface sorption and the lack of relevant modeling studies is most likely attributable to the significant computational burden of coupling field scale solute transport with grain scale diffusion processes. Thus, the primary purpose of this work is to present a modified computational algorithm designed to incorporate both aspects of “nonideal” sorption in a manner that can be scaled in a straightforward fashion to two- and three-dimensional applications. Although the focus of this work is on demonstrating the concepts through one-dimensional scenarios, the numerical algorithms have been designed to facilitate eventual extension to multidimensional field scale transport, for which the relative importance of grain scale processes remains largely unexplored.

To represent nonequilibrium (slow) sorption, we have adopted a traditional pore diffusion formulation, as detailed in Methods, which assumes that the rate of the sorption process is controlled by the physical transport of aqueous contaminants to sorbents located within the interior of soil grains, where local equilibrium is achieved. However, for nonlinear equilibrium, we have extended standard transport formulations to incorporate the emerging class of dual mode isotherms. As reviewed by Allen-King et al. [21], these models combine a nonlinear term to represent surface adsorption to “hard” carbon with a linear term based on partitioning to “soft” carbon. In particular, the Polanyi-partitioning (PP) isotherm presented below in Eq. (1) has been emphasized because of its mechanistically grounded “pore filling” expression for surface adsorption component [20,36].

$$q_s = Q_p 10^A \left[\log \left(\frac{S_w}{C_l} \right) \right]^B + K_p C_l \quad (1)$$

where q_s is the mass fraction of the contaminant in the sorbent phase [M/M], C_l is the aqueous concentration of solute [M/L³], Q_p

and A , B are Polanyi parameters, S_w is the solute aqueous solubility [M/L³], and K_p is the partition coefficient used in the PP formulation [L³/M] (see [21,36]).

At the time of this writing, the PP equation has not been utilized in published groundwater transport models and is therefore the focus of the numerical developments associated with this work. For comparison purposes, we also consider the commonly used nonlinear Freundlich and Langmuir isotherm expressions:

$$\text{Freundlich: } q_s = K_f C_l^{nf} \quad (2)$$

$$\text{Langmuir: } q_s = \frac{b Q_0 C_l}{1 + b C_l} \quad (3)$$

where K_f and nf are the Freundlich parameters and Q_0 and b are the Langmuir parameters. It is noted that both isotherms can be reduced to the more commonly used linear isotherm ($q_s = K_d C_l$) with appropriate specification of parameters.

In the next section, we present an efficient and accurate split-operator algorithm that can incorporate any isotherm expression into an intraparticle diffusion formulation, with a modular structure that can be coupled in a straightforward fashion to existing transport codes. The three-step numerical algorithm is based on the common split-operator decoupling of macroscopic advective–dispersive transport from local reaction processes, extended via a similar approach to decouple the local diffusion process from nonlinear sorption at intraparticle computational nodes. This approach avoids the use of ODE solvers and accommodates nonlinear isotherms by solving a single nonlinear algebraic mass balance equation for each macroscopic spatial node (for equilibrium sorption) or at intraparticle nodes (for diffusion limited sorption). Advantages of this approach are similar to other split-operator methods for reactive transport modeling, including reduced demand for

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