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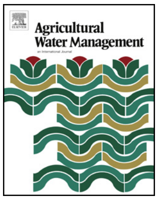

Modeling sulfur cycling and sulfate reactive transport in an agricultural groundwater system

Saman Tavakoli Kivi*, Ryan T. Bailey

Department of Civil and Environmental Engineering, Colorado State University, 1372 Campus Delivery, Fort Collins, CO, 80523-1372, United States

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ABSTRACT

Many irrigated agricultural areas worldwide suffer from salinization of soil, groundwater, and nearby river systems. Increasing salinity concentrations are due principally to a high water table that results from excessive irrigation, canal seepage, and a lack of efficient drainage systems, and lead to decreased crop yield. High groundwater salinity loading to nearby river systems also impacts downstream areas, where saline river water is diverted for application on irrigated fields. This paper presents a physically-based, spatially-distributed groundwater reactive transport model that simulates the fate and transport of sulfate, the principal salt ion in many salt-affected watersheds, in an agricultural groundwater system. The model, developed from the UZF-RT3D model that simulates chemical species transport in variably-saturated subsurface systems, accounts for sulfur cycling (crop uptake, organic matter decomposition, mineralization/immobilization) in the soil-plant system, oxidation-reduction reactions, including the oxidation of residual Sulfur in marine shale, and also the effect of dissolved oxygen and nitrate on sulfate chemical reduction. The model is tested at the small scale (i.e. soil profile) and at the regional scale (500 km^2) in the Lower Arkansas River Valley (LARV) in southeastern Colorado, an area acutely affected by salinization in the past few decades. Results demonstrate that although the major sulfate reactive transport processes are accounted for, the model consistently under-predicts measured soil and groundwater sulfate concentrations, pointing to the need for a comprehensive salinity module that accounts not only for advection, dispersion, sulfur cycling, and oxidation-reduction, but also salt ion equilibrium chemistry that includes the dissolution and precipitation of salt minerals in the soil-aquifer system. However, the model can be a useful tool to assess sulfate fate and transport in areas that are not dominated by salt mineral precipitation and dissolution.

1. Introduction

Salinization of soil and shallow groundwater is an almost inevitable problem in irrigated agricultural fields and a major challenge to sustain crop yield (Sparks, 2003; Gates et al., 2002; Morway and Gates, 2012; Lin and Garcia, 2008; Wichelns and Qadir, 2015; Vaze et al., 2003; Hutmacher et al., 1996). Approximately one-fourth of all irrigated lands in the world are impaired by high salinity (Rhoades, 1993; Ghassemi et al., 1995), with the salt-affected area increasing by approximately 1–1.5 million ha each year (Barghouti and Le Moigne, 1991). Within the United States, approximately one third of irrigated land is impaired (Tanji, 1990). Salt accumulates in top soil due to the presence of salt minerals in the soil and evaporative-concentration, with the latter occurring particularly in areas of shallow groundwater (Gowing et al., 2009). Shallow water tables result from poor natural soil drainage, poorly designed artificial drainage systems, and excessive water application. Furthermore, irrigation water often has high concentrations of salts. Salinization occurs particularly in arid and semiarid regions, due to high potential evapotranspiration, low rainfall rates, and hence the need for irrigation.

Irrigation-induced salinity is the principal water quality problem in the semi-arid region of the western United States, due to the extensive background quantities of salt in rocks and soils (El-Ashry et al., 1985). Specific areas with acute salinity problems include the Colorado River Basin, with the downstream areas of the Imperial Valley and the Coachella Valley experiencing the greatest salinity problems; the Rio Grande Basin of New Mexico and Texas; the Central Valley of California, particularly within the agriculturally-important San Joaquin Valley; the Yakima River Basin in Washington; the Snake River Basin in Idaho; and the

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* Corresponding author.
E-mail addresses: saman@engr.colostate.edu (S. Tavakoli Kivi), rtbailey@colostate.edu (R.T. Bailey).

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Arkansas and South Platte River Basins in Colorado, Nebraska, Kansas, and Oklahoma.

High ions concentration not only has a significant effect in soil and aquifer systems, but also can cause serious damage to surface water areas such as wetlands. For example, elevated sulfate contamination impaired the Florida Everglades by stimulating production of methyl mercury (Corrales et al., 2011). The tail water runoff from the agricultural area of the Everglades discharge to the wetlands and causes the high sulfate concentration.

To assess the implementation of practices to remediate soil and groundwater salinization, application of different tools or methodologies needs to be considered. Numerous field strategies have been attempted, including improving on-farm water management (van der Leedenet al., 1975), lining irrigation canals to reduce seepage to the aquifer (van der Leeden et al., 1975; Singh and Panda, 2012), dry-drainage practices (Tuteja et al., 2003; Konukcu et al., 2006), controlled multi-level subsurface drainage systems (Ayars et al., 2006; Hornbuckle et al., 2007), and increasing groundwater pumping volume (Singh and Panda, 2012). Generally these practices focus on the scale of a single field or multiple fields.

Investigators also have used an assortment of process-based salinity mass balance models, such as UNSATCHEM-2D (Šimůnek and Suarez, 1994) which predicts the major ion chemistry (precipitation-dissolution, cation exchange, complexation) for small-scale soil-water systems; and SAHYSMOD (Oosterbaan, 2005; Singh and Panda, 2012), an integrated agro-hydro-salinity model which can be applied to large-scale agricultural fields and is based on seasonal input data. SAHYSMOD has been applied to simulate the water and salt behavior in the semiarid irrigation area of Haryana State of India which has been impaired by – waterlogging and salinization for the last forty years (Singh and Panda, 2012). CATSALT (Tuteja and Vaze, 2003) is a distributed water balance model which is linked with the salt transport module. Tuteja et al. (2003) assessed the effect of landuse change on salt and water balance in Mandagery Creek catchment which is located in New South Wales of Australia using CATSALT. WATSUIT, a steady-state model which developed by Oster and Rhoades (1975), can calculate soil-water interaction with depth in the root zone. Gates et al. (2002), Burkhalter and Gates (2005), and Burkhalter and Gates (2006) used a MODFLOW-MT3DMS (Zheng and Wang, 1999) model for groundwater flow and salinity transport in the Lower Arkansas River Valley in southeastern Colorado to estimate the effects of management practices such as reducing the recharge rate from irrigation, reducing seepage from irrigation canals, and installing sub-surface drainage systems. They used total dissolved solids (TDS) as a surrogate for salinity.

In regards to assessing salinity problems at the regional and basin scale, we present in this paper a model that simulates the cycling of sulfur (S) and the related fate and transport of sulfate (SO_4) at multiple scales within an agricultural groundwater system. We focus on SO_4 since often it is the dominant ion in salt-affected groundwater. Reactive transport of S species is simulated using a reaction module imbedded in the UZF-RT3D model (Bailey et al., 2013a), a finite difference modeling code that simulates the transport of multiple interacting reactive chemical species in a variably-saturated groundwater environment. UZF-RT3D was developed by modifying RT3D (Reactive Transport in 3 Dimensions: Clement, 1997; Clement et al., 1998), a model that simulates reactive transport of multiple interacting chemical species in saturated groundwater systems, to include transport in the unsaturated zone. UZF-RT3D reads output from MODFLOW-NWT (Niswonger et al., 2011) simulations that employ the UZF1 (Unsaturated Zone Flow) package (Niswonger et al., 2006). The model has been used successfully to simulate reactive transport of nitrate (NO_3) and selenium (Se) in irrigated groundwater systems (Bailey et al., 2014). Specific processes represented in the S module include organic matter decomposition and mineralization, oxidation-reduction reactions, and mass inputs/outputs such as infiltrated irrigation fertilizer, canal seepage, groundwater pumping, and plant mass cycling. The model also accounts for the effect of dissolved oxygen (O_2) and nitrate (NO_3), and includes the fate and transport of selenium (Se) species as a constraint on the S cycling and transport parameter values.

The use of the model is demonstrated through application to a small-scale site (soil profile) and a regional-scale area (500 km^2) within the Lower Arkansas River Valley (LARV) in southeastern Colorado, where significant salinization has occurred in recent decades. To our knowledge, this is the first attempt at simulating S cycling in a reactive transport model, and at simulating SO_4 reactive transport at the regional scale. This study serves as a first step in representing salt chemistry in a regional-scale agricultural groundwater system. Following a presentation of S cycling and transport in soil and groundwater systems and its inclusion in UZF-RT3D, the application of the model to the study area will be presented.

2. Sulfur cycling and reaction module for UZF-RT3D

2.1. Sulfur cycling in agricultural subsurface systems

The principal processes governing S cycling in the soil and groundwater zone of an agricultural area are presented in Fig. 1. Cycling of S mass occurs as organic S is incorporated into soil organic matter, composed of litter (fast-decomposing) and humus (slow-decomposing), via plowing; mineralized to SO_4; and then taken up by crop roots during the growing season. S and SO_4 mass also are added to the subsurface via fertilizer, irrigation water, and canal seepage. SO_4 can be chemically reduced via a microbially-mediated reaction (Frind et al., 1990):

$$SO_4{}^{2-} + 2C_{org} + 2H_2O \rightarrow 2HCO_3{}^{-} + H_2S \tag{1}$$

This reaction, however, is inhibited by the presence of O_2 and NO_3 due to the succession of terminal electron (e^-)-acceptor processes. Furthermore, SO_4 can released from pyrite (FeS_2) via autotrophic reduction of O_2 and NO_3 (Frind et al., 1990; Postma et al., 1991; Pauwels et al., 1998):

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4{}^{2-} + 4H^+ \tag{2a}$$

$$5FeS_2 + 14NO_3{}^{-} + 4H^+ \rightarrow 5Fe^{2+} + 10SO_4{}^{2-} + 7N_2 + 2H_2O \tag{2b}$$

This process is represented in Fig. 1. Pyrite often can be found in Cretaceous marine shale.

2.2. Sulfur reaction module for UZF-RT3D

2.2.1. Mass balance equations

The S reaction module for UZF-RT3D consists of mass balance equations, chemical reaction rate laws, and sources and sinks of S mass (fertilizer loading, crop uptake, and loading in irrigation water and canal seepage) that are typical of agricultural systems. A glossary of model parameter terms is included at the end of the paper for reference. UZF-RT3D solves a system of advection-dispersion-reaction (ADR) equations for both dissolved-phase and solid-phase species in variably-saturated groundwater systems using a finite difference approach (Bailey et al., 2013a):

$$\frac{\partial\left(C_k\theta\right)}{\partial t}R_k = -\frac{\partial}{\partial x_i}\left(\theta v_i C_k\right) + \frac{\partial}{\partial x_i}\left(\theta D_{ij}\frac{\partial C_k}{\partial x_j}\right) + q_f C_{f_k} + \theta r_f \qquad k = 1, 2, \ldots, m \tag{3a}$$

$$\frac{\partial\left(C_l\varepsilon\right)}{\partial t} = \alpha_l P_s + \varepsilon r_s \qquad l = 1, 2, \ldots, n \tag{3b}$$

where C is solute concentration $[M_f L_f^{-3}]$, with f denoting fluid phase; D_{ij} is the hydrodynamic dispersion coefficient $[L^2T^{-1}]$; vis