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Simulating reactive transport of selenium coupled with nitrogen in a regional-scale irrigated groundwater system

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SUMMARY

The contamination or deficiency of Selenium (Se) has become a critical issue in watershed systems world-wide during the past half-century, with either elevated or deficient Se concentrations in groundwater, surface water, soils, and associated vegetation. Regardless of the reason for concern, there is a basic need for tools for use in assessing baseline concentrations and mass loadings in large-scale environmental systems and for exploring remediation strategies. This paper presents the application of UZF-RT3D, a multi-species variably-saturated reactive transport model for groundwater systems, and its recently developed Se agricultural and chemical reaction module to a regional study site (50,600 ha) along the irrigated Arkansas River Valley in southeastern Colorado. The study region has been monitored for Se contamination during the previous decade, with all segments of the Arkansas River impaired with respect to Se. The Se reaction module accounts for near-surface Se cycling due to agricultural practices, oxidation–reduction reactions, and sorption, and includes a nitrogen cycle and reaction module due to the dependence of Se transformation and speciation on the presence of nitrate (NO_3). Of prime importance is the role NO_3 plays in oxidation of residual Se from marine shale, which is prevalent throughout the study region, along with its inhibition of Se chemical reduction to less toxic forms. The model is corroborated against groundwater solute concentrations, mass loadings of solutes to the Arkansas River, relationships between solutes within the groundwater system, and overall regional statistics of groundwater solute concentration. Results indicate that the model is successful in replicating the major spatial and temporal patterns in Se and NO_3 contamination and transport, hence providing a tool that can be used with confidence to explore remediation schemes.

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1. Introduction

The presence of elevated Selenium (Se) concentrations in aquifer and surface water systems has emerged as a serious concern in regions worldwide during the last half-century (Seiler, 1997; Afzal et al., 2000; Mizutani et al., 2001; Zhang et al., 2008; Hudak, 2010). Although an essential micro-nutrient for humans and animals (Combs et al., 1986; Aro et al., 1998), a narrow range exists between dietary deficiency and toxic levels. In recent decades, this "essential toxin" (Stolz et al., 2002; Fernández-Martínez and Charlet, 2009) has caused deformities and death among water fowl and fish populations in surface waters hydraulically connected to contaminated aquifer systems (Flury et al., 1997; Hamilton,

1998; Skorupa, 1998). In many instances, Se contamination occurs in irrigated agricultural aquifer systems underlain by shale from which Se is released via oxidation–reduction processes (Seiler, 1995, 1997; Bailey et al., 2012). Conversely, Se deficiency in soils and crops has been linked to diseases among both animal (Aro et al., 1998; Kishchak, 1998) and human (Alfthan et al., 1995; Peng et al., 1995; Wang and Gao, 2001) populations.

Whether the nature of the problem is one of elevated or of deficient concentrations, methodologies and tools need to be developed that can support evaluation of the current level of concentration for a particular groundwater system and exploration of remediation strategies. Due to the spatial variability in land management practices and geologic formations, both of which strongly influence the level of Se contamination (Seiler, 1995), analysis at the regional scale ($\sim 10^4$–10^5 ha) is essential. Whereas spot sampling of groundwater and surface water can provide a general assessment of the concentration for a particular region (e.g., Gates et al., 2009; Hudak, 2010), other techniques are required to determine the cause of Se availability and movement

within the aquifer system, and to identify potential remediation strategies. Due to the complexity of Se fate and transport dynamics in an aquifer system, which include oxidation–reduction (redox) reactions with dissolved oxygen (O_2) and nitrate (NO_3) (e.g., Weres et al., 1990; White et al., 1991; Bailey et al., 2012), sorption, along with spatio-temporal mass inputs and sinks, the development and use of numerical models is an appealing approach.

Numerical models designed for Se fate and transport dynamics thus far have been limited to one-dimensional (1D) soil profile models (Alemi et al., 1988, 1991; Fio et al., 1991; Liu and Narasimhan, 1994; Guo et al., 1999; Mirbagheri et al., 2008) and a small-scale two-dimensional (2D) vertical profile model (Tayfur et al., 2010). Se transport has been simulated in a regional-scale watershed using a three-dimensional (3D) model (Myers, 2013), although Se was treated as a conservative solute. For the 1D studies, Se transport was subject to sorption and redox reactions, while boundary conditions and forcing terms were kept basic (e.g., steady inflow rate and constant concentration of Se within the influent). Mirbagheri et al. (2008) incorporated a more complete set of Se cycling processes for a 1D model, including volatilization, mineralization and immobilization, and plant uptake. Tayfur et al. (2010) applied the same modeling processes to a small-scale (3-m soil profiles) 2D vertical cross-section to simulate Se transport in both saturated and unsaturated soil zones.

More recently, the model used by Bailey et al. (2013a) in assessing Se transport in soil profiles at a test site in southeastern Colorado accounted for Se cycling in the root and soil zone and the dependence of redox reactions on the presence of organic carbon (OC). The model also accounted for the reactive transport of O_2 and NO_3, with the latter governed by Nitrogen (N) cycling. Modeling framework consisted of incorporating Se and N modules into UZF-RT3D (Bailey et al., 2013b), which is linked with MODFLOW-NWT (Niswonger et al., 2011) and simulates the reactive transport of multiple interacting chemical species in variably-saturated groundwater systems. Although chemical reactions governing the release of Se from marine shale have been implemented in the modeling framework, the model has until now not been applied at a large enough scale to require their use.
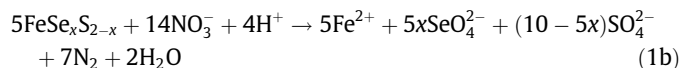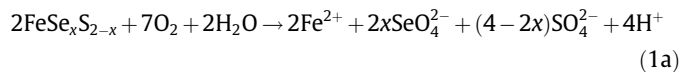
There are two objectives of this paper. The first is to present a numerical modeling tool that can be used to simulate the reactive transport of Se species in a regional-scale irrigated agricultural groundwater system underlain by marine shale. The second objective is to test the tool to establish its credibility in evaluating remediation strategies. The tool was developed by applying UZF-RT3D and the accompanying Se and N reaction modules developed by Bailey et al. (2013a) to a regional study site along the alluvial valley of the Arkansas River in southeastern Colorado, with the groundwater flow pattern and sources/sinks provided by a calibrated and tested groundwater flow model for the same region (Morway et al., 2013). Of particular interest is the influence of marine shale, which underlies the alluvial aquifer and also is present as outcrops and weathered residuum throughout the region, on the source and mobilization of Se in the aquifer. Spatial distributions of irrigation water, canal and river seepage, and crop cultivation, each with associated Se concentration and Se mass residue, also are included. Guided by global sensitivity analysis, the model is calibrated and tested against observed groundwater solute concentration, calculated daily mass loading of solutes from the aquifer and ungauged surface flows to the Arkansas River, observed relationships between solutes in the groundwater, and regional statistics of groundwater solute concentrations. Following a summary of the Se and N reaction modules for UZF-RT3D, the climate, geology, and field monitoring network of the study region is presented, followed by a description of the calibration and testing of the model for the study region.

2. Simulating Se and N reactive transport at the regional scale

2.1. Conceptual model of Se and N reactive transport

Se is present in water systems primarily in the four oxidation states of +VI (selenate SeO_4^{2-}), +IV (selenite SeO_3^{2-}), 0 (elemental selenium Se^0), and -II (selenide Se^{2-}). Selenide can occur in forms such as solid Se found in geologic formations in the form of seleno-pyrite (-II) ($FeSe_xS_{2-x}$), in which Se substitutes for Sulfur (S) in pyrite (FeS_2) (Bye and Lund, 1982), organic selenomethionine (-II) (SeMet), and gaseous dimethylselenide $(CH_3)_2Se$ (-II) (DMSe, a product of the volatilization of SeMet). SeO_4, SeO_3, and SeMet are soluble, whereas Se^0 and other forms of Se^{2-} are insoluble. SeO_4 is one of the most toxic Se species, is a weak sorbent (Ahlrichs and Hossner, 1987), and has been reported to account for 90–95% of soluble Se in oxygenated agricultural waters (Masscheleyn et al., 1989; Gates et al., 2009; Gerla et al., 2011), and hence is the primary target in Se contamination remediation.

Microbially-mediated chemical reactions (Oremland et al., 1990) reduce SeO_4 to SeO_3 and SeO_3 to either immobile Se^0 or mobile SeMet (Ellis and Salt, 2003). SeMet can then be volatilized to non-toxic DMSe (Calderone et al., 1990; Frankenberger and Arshad, 2001). SeO_3 also can sorb strongly to soil surface sites (Balistrieri and Chao, 1987). Chemical reductions, however, are inhibited by the presence of O_2 and NO_3 (Oremland et al., 1989; Weres et al., 1990; White et al., 1991; Zhang and Moore, 1997). A more detailed description of these processes is provided in Bailey et al. (2013a). SeO_4 also can be released from shale formations containing seleno-pyrite (Seiler, 1995) via autotrophic reduction of O_2 or NO_3 (Wright, 1999; Stillings and Amacher, 2010):

$$2FeSe_xS_{2-x} + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 2xSeO_4^{2-} + (4-2x)SO_4^{2-} + 4H^+$$
(1a)

$$5FeSe_xS_{2-x} + 14NO_3^- + 4H^+ \rightarrow 5Fe^{2+} + 5xSeO_4^{2-} + (10-5x)SO_4^{2-} + 7N_2 + 2H_2O$$
(1b)

Se fate and transport in an irrigated alluvial stream-aquifer system is represented in Fig. 1A. This conceptualization is the result of numerous field studies conducted during the previous decades. Sources of Se in watersheds like this are Se-bearing geologic formations, particularly marine shale (Williams and Byers, 1934; Moxon et al., 1938; Schultz et al., 1980; Kulp and Pratt, 2004). This residual Se in either outcropped or bedrock shale is subject to oxidation by O_2 in leaching soil water and groundwater and, more recently, by NO_3-laden water resulting from over-fertilization and over-irrigation of cultivated area. Once released from shale, typically in the form of SeO_4, Se is transported through the aquifer to either shallow soil zones or to surface water discharge points (Fig. 1A), with transport tempered by possible sorption and redox reactions that lead to immobilized, volatilized, and/or precipitated forms of Se. In regions downstream from Se source locations, Se-laden river water may be diverted into canal networks (Fig. 1A), resulting in Se transport to the root zone and shallow soil zones via infiltrating irrigation water and canal seepage (Fig. 1A).

If present in the root zone in cultivated areas, Se is subject to cycling in the plant-soil system similar to other nutrients (Shrift, 1954; Stolz et al., 2002). The conceptual model of Se fate and transport in an agricultural soil system is shown in Fig. 1B. All redox reactions as discussed previously are shown, including the chemical reduction of O_2 and NO_3 (denitrification), and the nitrification and volatilization of ammonium (NH_4). Soil organic matter is composed of litter (fast-decomposing), humus (slow-decomposing), and manure. Solute mass is taken up by crop roots throughout the growing season and incorporated into the plant material. At harvest the dead root mass of the crop, with associated organic