

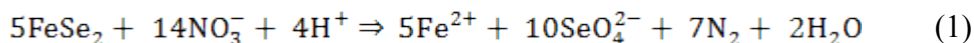
Mobilization and reactive transport of selenium in a stream-aquifer system: From field monitoring toward remediation modeling

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Abstract. Predicting the fate and transport of redox-sensitive species in ground water systems requires an accurate characterization of the distribution and concentrations of all related (or interdependent) chemical constituents and the reaction rates at which these constituents interact. Ground and surface water sampling of chemical and physical properties in the stream-aquifer system of Colorado's Arkansas River is providing an emerging picture of the nature and extent of selenium (Se) contamination as well as the strengths of correlations between Se and other constituents. Results from almost six years of field measurements, along with a detailed review of the literature, have led to a conceptual model of a redox-sensitive aquifer system wherein oxidants such as dissolved oxygen (DO) and nitrate, driven by extensive recharge from irrigation and canal seepage, mobilize sulfide and selenide species from shale bedrock and shale-derived soils. These species, dependent on the redox environment, are either reduced to immobile forms or transported through the shallow aquifer to surface water bodies. This conceptual model will be further refined through sampling along a transect of multi-level piezometers, thus enabling chemical characterization in the vertical dimension of the aquifer. This sampling, coupled with laboratory analyses of soil samples to quantify reaction kinetics, will allow the calibration of a vertical-profile reactive-transport ground water model wherein the fate and transport of DO, nitrate, and Se species are modeled. Insights from this modeling exercise will assist in developing a regional-scale, three-dimensional, reactive transport model of the Arkansas River system, providing a tool for exploring best management practices and remediation schemes.

1. Introduction

During the last few decades, high selenium (Se) concentrations in ground water and surface water supplies as well as wildlife habitats has emerged as a worldwide concern (Haygarth 1994), particularly in regions where intensively irrigated alluvial valleys overly or are in connection with Se-bearing geologic formations. Se, as a trace constituent in all igneous rocks, is present in all soils, although significantly high concentrations of Se occur mostly in marine shale deposits (Taylor 1964), wherein Se exists as a sulfur-substituting constituent in pyrite (FeS₂), forming the mineral "selenopyrite" (FeSe₂). The mobilization of selenate (SeO₄), a highly toxic Se species, from bedrock shale occurs as FeSe₂ is oxidized by NO₃, as represented by the following oxidation-reduction (redox) reaction:



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In this redox reaction, FeSe₂ is oxidized to mobilize SeO₄ into the surrounding ground water, whereas NO₃ is reduced (“denitrified”) to N₂. Mobilized SeO₄ undergoes an advection-dispersion transport path retarded by reduction to immobile forms or adsorption onto aquifer sediments, eventually entering surface water bodies, where it can bioaccumulate through the food chain and attain toxic concentrations (Lemly 2004). This paper describes the processes that govern the mobilization and transport of Se species, outlines numerical modeling efforts involving the fate and transport of Se and other redox-sensitive species, and presents data collection results and future modeling efforts regarding the reactive transport of Se in Colorado’s Lower Arkansas River Basin (LARB). The intent of the modeling is first, to understand the reactive nature of the aquifer, and second, to explore remediation schemes and best-management practices to either prevent the mobilization of SeO₄ or to reduce it to non-toxic forms.

1.1. Se Chemistry

Se exists principally in the four oxidation states of selenide Se²⁻ (-2 valence), elemental selenium Se (0 valence), selenite SeO₃ (+4 valence), and selenate SeO₄ (+6 valence) (Table 1). SeO₄ and SeO₃, the most oxidized Se species, are much more soluble than reduced Se forms, Se and Se²⁻. Between SeO₄ and SeO₃, SeO₄ is by far the dominant form in agricultural drainage water, with Masscheleyn et al (1989) reporting SeO₄ accounting for about 95% of total Se. The movement of Se species in ground water systems is governed by redox reactions, which controls the speciation of Se, and adsorption processes, which retard SeO₄ and SeO₃ (Figure 1). Under highly oxidizing conditions, SeO₄ and SeO₃ are the principle Se constituents, whereas Se and Se²⁻ become dominant in oxygen-depleted, reducing conditions.

Table 1. Characteristics of Se Species.

Se Species	Oxidation State	Solubility	Adsorption	Oxidizing conditions	Reducing conditions	Toxicity
Selenate <i>SeO₄</i>	+6	yes	weak	Present	Absent	yes
Selenite <i>SeO₃</i>	+4	yes	strong	Present	Absent	no
Elemental Se <i>Se</i>	0	no	none	Absent	Present	no
Selenide <i>Se²⁻</i>	-2	no	none	Absent	Present	yes

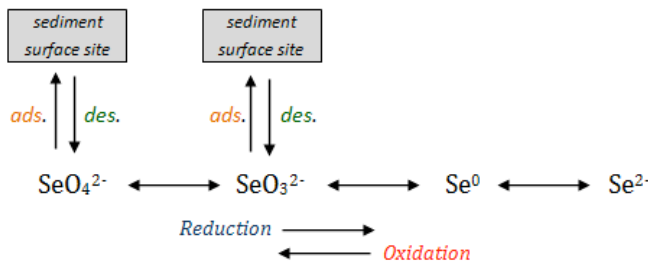


Figure 1. Speciation of Se due to oxidation-reduction reactions, and adsorption of selenate and selenite onto soil surface sites (ads. = adsorption; des. = desorption).

Redox reactions, inherently slow, are catalyzed and driven by bacterial respiration, which uses organic matter (OM) and mineral substrate as a source of energy through electron transfer between the donors (OM and mineral substrate), which are oxidized, and acceptors [oxygenated species such as dissolved oxygen (DO), NO_3 , and SeO_4], which are reduced. DO, which supplies the microbial population the greatest quantity of energy per mole (McMahon and Chapelle 2008), is preferentially reduced, followed by NO_3 , SeO_4 , MnO_2 , Fe(III), SO_4 , and U(+6) (Korom 1992). Studies (Korom 1992) have noted a dramatic decrease in the concentration of NO_3 and other oxidized species within the first few meters below the water table, as conditions become anaerobic. Inhibited consumption of electron acceptors occurs when an electron acceptor with a higher redox potential is present in solution. Hence, under laboratory conditions, the inhibition of SeO_4 reduction in the presence of NO_3 , and the immediate reduction of SeO_4 upon depletion of NO_3 , has been observed (Weres et al 1990). Correlation between DO, NO_3 , and SeO_4 also has been reported by White and Dubrovsky (1994) and Wright (1999), with the conclusion that the presence of DO and NO_3 allow SeO_4 to remain in solution and undergo uninhibited transport.

Adsorption of the soluble Se species (SeO_4 and SeO_3) onto surface soil sites can be an important sink of Se in the ground water system. SeO_3 , similar in its adsorption capacity to phosphate, is strongly adsorbed onto surface sites (Ahlrichs and Hossner 1987; Neal et al 1987), whereas SeO_4 , similar in its adsorption capacity to SO_4 , is weakly adsorbed (Ahlrichs and Hossner 1987; Fio et al 1991). As reported by Fio et al (1991), the difference in adsorption capacities of SeO_4 and SeO_3 means that SeO_4 can be easily leached from the unsaturated zone, whereas SeO_3 is resistant to leaching. However, under reducing conditions, SeO_4 can be reduced rapidly to SeO_3 , thus retarding its transport.

1.2. Modeling the Fate and Transport of Redox-Sensitive Species: A Review

Many studies have been performed to determine the speciation of Se and the rate at which it occurs (Marten and Suarez 1997; Losi and Frankenberger 1998), as well as the adsorption of SeO_4 and SeO_3 . Specifically, they have relied on laboratory batch studies to determine reaction rate coefficients for kinetic rate laws of redox reactions and equilibrium isotherms for adsorption reactions. Redox reactions are normally approximated by first-order reaction rate laws. An equilibrium approach for adsorption, rather than a time-dependent, kinetic approach, is justified by the rapid time to equilibrium (Neal et al 1987). In some instances, these rate coefficients and isotherms have then been incorporated into reactive transport numerical models in order to calibrate the models and predict the fate and transport of Se species. Due to the redox reactions depending on microbial, electron donor, and electron acceptor density, rate coefficients are site-specific.

Numerical modeling studies involving Se fate and transport have been confined to one-dimensional soil profile models wherein Se transport in saturated or unsaturated conditions is subject to adsorption processes, redox reactions, or both (Table 2). For most studies, only adsorption has been simulated. Incorporation of redox reactions was first included by Liu and Narasimhan (1994) in their modeling study of the vertical movement of Se in the aquifer underlying the Kesterson reservoir. They also

highlighted the importance of bacterial characterization on Se transport. Guo et al (1999) simulated the reduction and equilibrium adsorption of SeO_4 and SeO_3 in saturated soil columns, with SeO_4 reduction rates being estimated through calibration. Mirbagheri et al (2008) incorporated all governing processes involving Se species in the unsaturated zone, including advective-dispersive transport, adsorption, redox reactions, and volatilization.

Although Se fate and transport modeling has been restricted to 1D processes, other modeling studies dealing with redox-sensitive species, such as Frind et al (1990) and Postma et al (1991) in Europe, provide a framework for modeling Se fate and transport in a more complex aquifer system. Due to horizontal “redox fronts” in the aquifer, in which a sharp division occurs between oxidizing and reducing ground water conditions, these two studies sampled constituent concentrations in the vertical direction via multi-level sampling in preparation for numerical modeling. Other modeling studies followed suit (Tesoriero 2000). These studies have all modeled redox reactions using first-order kinetic approximations. Other models have employed more sophisticated models wherein the kinetics are represented by double –Monod microbial kinetic models, wherein the microbial, electron donor, and electron acceptor concentrations, and their influence on the chemical reaction, are accounted for through time (Molz et al 1986; Brun and Engesgaard 2002). These more complex models, however, have a large number of parameters that each need quantification.

Table 2. Summary of Se Reactive Transport Numerical Modeling Studies.

Study	Model Dimension	Saturated	Unsaturated	Adsorption		Redox
				SeO_4	SeO_3	
Alemi et al 1988	1D	x		x		
Fio et al 1991	1D	x		x	x	
Alemi et al 1991	1D		x	x	x	
Liu and Narasimhan 1994	1D	x				x
Guo et al 1999	1D	x		x	x	x
Mirbagheri et al 2008	1D		x	x	x	x

This paper presents selected results from a long-term sampling project, a conceptual model of Se fate and transport based on sampling results as well as the literature, and finally a framework for modeling the fate and transport of Se species in a stream-aquifer system. Following the pattern of other numerical modeling studies involving redox-sensitive species, the first phase of modeling will be dependent on field sampling from a battery of nested piezometers along a ground water flow transect located within the LARB. Constituent concentrations determined from ground water samples as well as laboratory-determined redox and adsorption rates will provide parameter and boundary condition values for the two-dimensional, vertical profile reactive transport model. The two-dimensional layout will be used to investigate sensitivity of all model parameters. Insights gained from this modeling exercise, coupled with already-acquired sampling in

the surrounding region, will provide the necessary information to construct a three-dimensional, regional scale reactive transport model.

2. Field Work: Methods and Selected Results

Due to the immense size of Colorado's LARB, approximate 235 km between Pueblo, CO and the Kansas state line, two regional scale study regions have been established. Comprising a total area of approximately 50,600 ha (125,000 ac), of which about 26,400 ha (65,300 ac) are irrigated from canals or pumping wells, the upstream study region is located upstream of John Martin Reservoir and extends between just west of the town of Manzanola to near Las Animas. Samples are routinely taken from 45 ground water observation wells, 4 locations in tributaries and drains, and 10 locations along the river (Figure 2). Samples are also taken from an additional 69 observation wells on an aperiodic schedule for use in expanding the dataset.

The second study region is located downstream of John Martin Reservoir and stretches between the city of Lamar and the Colorado-Kansas state line. The farthest west well of the downstream study region is located approximately 30 km east of the eastern edge of the upstream study region. The downstream region covers a total of about 55,200 ha (136,300 ac), of which about 33,000 ha (81,600 ac) are irrigated from canals that divert water from the river or from alluvial pumping wells. A total of 47 ground water observation wells, 12 locations in tributaries and drains, and 6 locations along the river have been routinely monitored for Se and related constituents. An additional 59 observation wells in this region were sampled aperiodically.

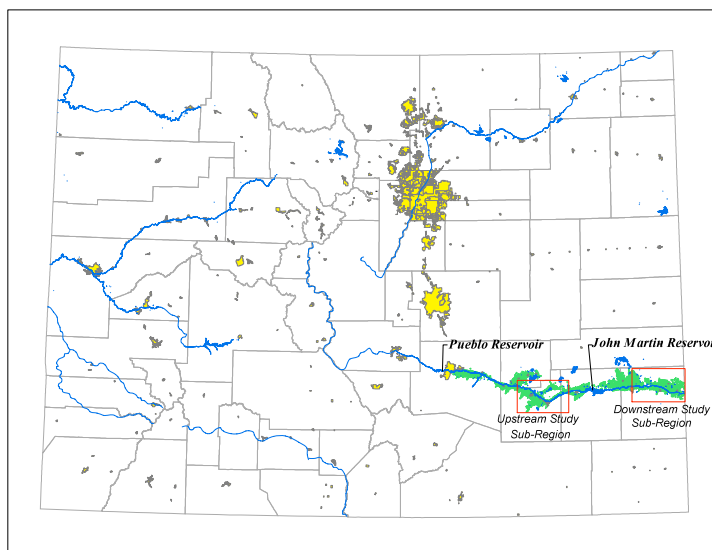


Figure 2. Image of Colorado showing the outlined boundaries of the upstream and downstream study regions in the Lower Arkansas River Basin.

Water table levels and electrical conductivity (EC) have been consistently sampled in the upstream region from as early as April 1999. Sampling for Se concentrations in ground water and surface water began in April 2003 in the downstream region and June 2006 in the upstream region. Sampling events occur approximately 7 times per year

and typically alternate each time between the upstream and downstream regions. Currently, there have been 8 and 34 sampling events in the upstream and downstream regions, respectively. Using calibrated YSI 600QS Multiparameter Sampling Systems™ several in-situ water quality measurements are taken from each specified ground and surface water point. These consist of water table depth, pH, temperature, specific conductance, DO concentration, and oxygen reduction potential. Water samples are also taken from each point and are analyzed for concentrations of Se, U, Na, K, Ca, Mg, NO₃, SO₄, Cl, CO₃, HCO₃, and B.

Values of the Pearson correlation coefficient, r_P , were computed between a given variate X and a variate Y (designated as X-Y), between logs of the variates (log X-log Y), and between a variate and the log of a variate (log X-Y and X-log Y) for the concentrations and properties measured in the LARB study regions. Numerous variate pairs were discovered to be moderately or strongly correlated. The highest correlation found was a linear (X-Y) relationship between C_{Se} and C_{NO3} in the downstream ground water dataset. Details may be found in a forthcoming paper by Gates et al (2009). This strong correlation suggests the potential to drastically reduce the loading of Se to the stream system that takes place due to the widespread practice of using nitrogen fertilizers in irrigated crop production. Contour plots generated using a natural-neighbor method (Figure 3) show relative “hot spots” as well as an illustration of the correlation between C_{Se} and C_{NO3} .

The relationship between C_{Se} and the upgradient distance to Se-rich shale deposits also has been explored (Gates et al 2009). First, underlying shale deposits were located in ArcGIS by georeferencing existing USGS maps. Next, in order to show general ground water flow directions, water table contour lines were generated by importing water table data from an existing MODFLOW model into ArcGIS. Finally, distances between monitoring wells and upgradient shale deposits, L_s , were estimated using the ArcGIS measurement tool. While the downstream region yielded scattered results, the upstream region showed a strong inverse relationship between average C_{Se} in monitoring wells and values of L_s . The upstream region has a much larger quantity and extent of identified underlying shale deposits, hence a much higher likelihood of ground water sampling points being located near shale deposits. This may explain why little to no correlation has been found between average C_{Se} and L_s downstream.

Further analysis has shown that a multivariate relationship between C_{Se} , C_{NO3} , C_{DO} , and L_s exists. If oxic conditions are needed to mobilize Se then it is reasonable to expect that if the average C_{NO3} or C_{DO} at a ground water sampling point is above a certain threshold value and L_s is small then its average C_{Se} should be relatively large. The correlation between log C_{Se} and log L_s has been found to significantly increase when removing C_{Se} samples in which corresponding C_{NO3} and C_{DO} values were low or L_s was high. Currently, this multivariate relationship between C_{Se} , C_{NO3} , or C_{DO} and L_s is being explored with the intent of determining how high the oxidant concentrations of C_{DO} and C_{NO3} must be to mobilize deposited or immobilized Se (Gates et al 2009).

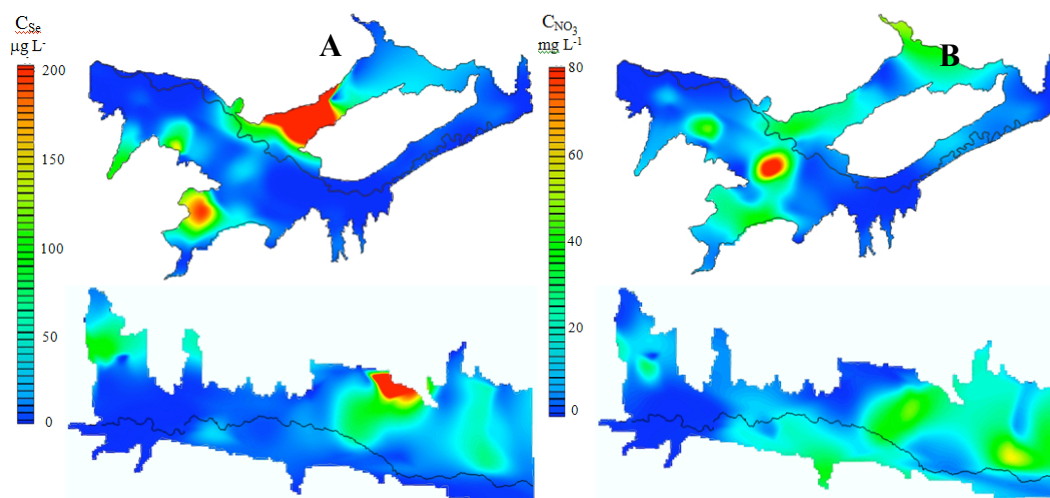


Figure 3. Contour plots of (A) C_{Se} (estimated using the “natural neighbor” interpolation method) from samples collected during August 14-15, 2008 in the upstream study region (upper image) and during November 17-19, 2007 in the downstream study region (lower image); and (B) C_{NO_3} for the same two time periods.

3. Conceptualization of System

Results from the field, coupled with a review of the literature, lead to a conceptual model of Se mobilization and transport in a stream-aquifer system (Figure 4), wherein oxidants such as DO and NO_3 , driven by extensive recharge from irrigation and canal seepage, mobilize SeO_4 from shale bedrock and shale-derived soils containing selenopyrite ($FeSe_2$). SeO_4 , dependent on the redox environment, either is reduced to immobile forms or is transported through the shallow aquifer to surface water bodies, where dissolved concentrations and return flow rates determine the pattern of Se loading to the river system. When DO and NO_3 are present in the ground water, SeO_4 is retarded only by adsorption processes. However, once DO and NO_3 are reduced by bacterial respiration, SeO_4 becomes the dominant electron acceptor, and through oxidation of OM or mineral substrate is reduced to SeO_3 , which typically adsorbs strongly to aquifer sediment, and immobile elemental Se. Reduced forms of Se such as elemental Se also can be re-oxidized to SeO_3 and SeO_4 , thus creating the possibility of transport being retarded and accelerated in a cyclical pattern depending on the redox condition of the aquifer through which the ground water is flowing. Sources and sinks of all species involved in the fate and transport Se, due to recharging water and chemical reactions, are summarized in Table 3.

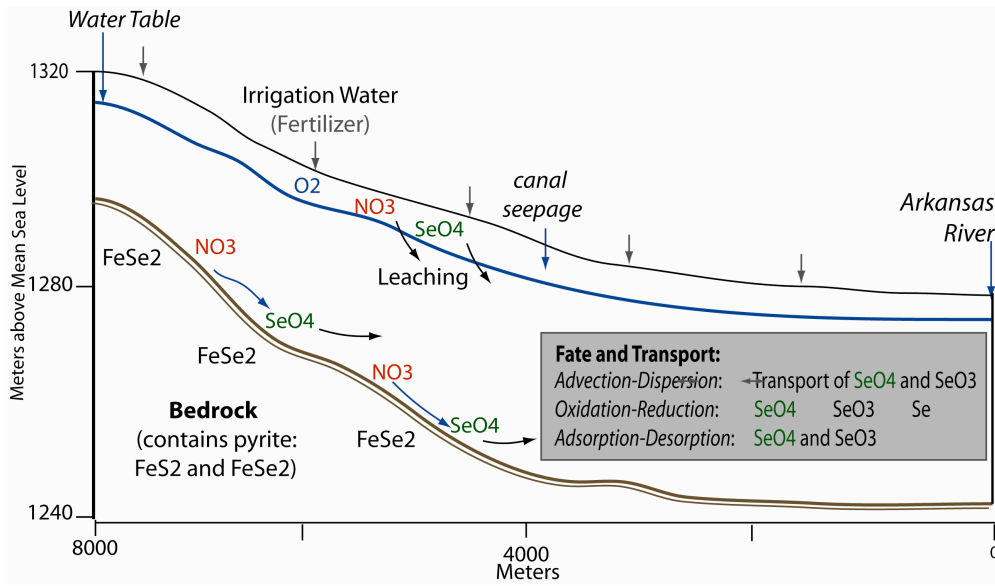


Figure 4. Conceptual Model of Se mobilization and transport in an irrigated stream-aquifer system.

Table 3. Sources and Sinks of Se Species and Species Affecting Se speciation. (All Adsorption and Redox Reaction Rates Require Quantification through lab methods)

Species	Source	Sink
DO	Recharging waters	Oxidation of substrate
		Oxidation of NO ₂
		Oxidation of SeO ₃
		Oxidation of Se
NO ₃	Leaching from unsaturated zone Oxidation of NO ₂	Oxidation of substrate
		Oxidation of SeO ₃
		Oxidation of Se
SeO ₄	Leaching from unsaturated zone Desorption Oxidation of SeO ₃ by O ₂ Oxidation of SeO ₃ by NO ₃ Oxidation of FeSe ₂ by O ₂ Oxidation of FeSe ₂ by NO ₃	Adsorption
		Oxidation of substrate
SeO ₃	Leaching from unsaturated zone Desorption Oxidation of Se by O ₂ Oxidation of Se by NO ₃ Reduction of SeO ₄	Adsorption
		Oxidation of substrate
		Oxidation of SeO ₃ by O ₂
		Oxidation SeO ₃ by NO ₃
Se	Reduction of SeO ₃	Oxidation of Se by O ₂
		Oxidation of Se by NO ₃

substrate = organic matter (OM) or seleno-pyrite (FeSe₂)

4. Modeling the Fate and Transport of Se in the Lower Arkansas River Basin

4.1. Theoretical Development of Se Reactive Transport Model

Reactive transport involves the transport processes of advection and dispersion for a constituent as well as the reactions involving that constituent during its transport. This is summarized mathematically by the following Advection-Dispersion-Reaction (ADR) equation, as presented by Clement et al (1997) in his development of a three-dimensional, multi-species reactive transport modeling code (RT3D):

$$R \frac{\partial C}{\partial t} = -\frac{\partial}{\partial s}(vC) + \frac{\partial}{\partial s}\left(D \frac{\partial C}{\partial s}\right) + \frac{q}{n}C_s + r \quad (2)$$

where the four terms on the right-hand side represent advection, dispersion, source/sink mixing, and reaction, respectively, and C is aqueous-phase concentration of the constituent [ML^{-3}]; D is the hydrodynamic dispersion (incorporates diffusion and mechanical dispersion) [L^2T^{-1}]; v is the pore velocity [LT^{-1}]; n is the soil porosity, q is the volumetric flux of water, representing sources and sinks [units]; C_s is the concentration of the constituent of the source/sink [ML^{-3}]; and r is the time-dependent reactions that occur in the aqueous phase [$\text{ML}^{-3}\text{T}^{-1}$]. Adsorption of the constituent, which is normally assumed to be equilibrium in nature, is taken into account by use of the retardation factor R , on the left-hand side of the equation. A separate ADR equation is written for all species to be included in the model, and the resulting system of equations is solved simultaneously.

In the case of Se fate and transport, the reaction equation r represents the rate at which the constituent is either consumed or produced via redox reactions, and can be presented by the following first-order kinetic reaction rate law:

$$r = \frac{dC}{dt} = k C_R \quad (3)$$

where $[C]$ is the concentration of the constituent being considered [ML^{-3}], k is the reaction rate coefficient [T^{-1}], and C_R is the concentration of the reactant [ML^{-3}]. If C is consumed, k is negative, and equation (3) represents first-order decay. If first-order kinetics is assumed for all redox processes in the system (refer to Table 3), thus assuming that the reactant is in limitless supply, then each redox reaction can be approximated using the form of equation (3), which is then inserted into the ADR equation. Following this same pattern, and using the sources and sinks found in Table 3, the following reaction equation can be written for the fate and transport of SeO_4 in a ground water system:

$$r_{\text{SeO}_4} = \frac{\partial C_{\text{SeO}_4}}{\partial t} = k_1 C_{\text{O}_2} + k_2 C_{\text{NO}_3} + k_3 C_{\text{SeO}_3} + k_4 C_{\text{SeO}_3} - k_5 C_{\text{SeO}_4} \quad (4)$$

where k_1 to k_5 are the reaction rate coefficients for the oxidation of FeSe_2 by O_2 , oxidation of FeSe_2 by NO_3 , oxidation of SeO_3 by O_2 , oxidation of SeO_3 by NO_3 , and the reduction of SeO_4 as it oxidizes aquifer substrate, respectively. Rate coefficients would depend on soil type, aquifer zone, and temperature. The ADR equation would also

include a retardation factor R specific to the adsorption of SeO_4 on soil surface sites. Similar reaction equations representing the net rate of consumption and production can be written for DO, NO_3 , SeO_3 , and Se. The model employed by Clement (1997), RT3D, allows user-defined kinetics to be incorporated into the model framework.

Some models incorporate more complex kinetic rate laws in order to allow the rate coefficient to adapt to the changing chemical environment. As redox reaction rates are a function of time-dependent factors (microbial, electron donor, and electron acceptor concentrations), a more elegant characterization of kinetic rate laws adopts a microbial kinetics approach, wherein both constituent and microbial consumption/production are modeled (Clement 1997; Brun and Engesgaard 2002). The equations form a coupled system, as the rates are a function of the concentrations of all interacting species considered in the system. However, the sophistication of this kinetic model is tempered by the increasing number of parameters which require quantification, and thus becomes a question of the amount of data which can be acquired from the field. Specifically, spatial and temporal concentrations of microbial populations, electron donors and electron acceptors, and laboratory-determined kinetic rates and coefficients must all be quantified.

4.2. Numerical Modeling

Using the ADR equation for each species involved in the fate and transport of Se, the first phase of modeling in the LARB will consist of a representative two-dimensional, saturated, vertical profile model, similar to those found in Frind et al (1990) and Postma et al (1991). The 2D model will be used to calibrate to field conditions and to explore sensitivity of model parameters such as reaction rate coefficients. Accuracy of the model parameters will be dependent on field sampling and laboratory soil analysis.

Sampling of ground water constituents will take place along a ground water flow path (Figure 5), which has been delineated using a calibrated MODFLOW ground water model. Sampling will occur at batteries of multiple-level nested piezometers along the transect in order to characterize concentrations in the vertical dimension of the aquifer (Figure 6). Drilling of the piezometers along the transect are planned to take place before the summer of 2009, whereupon preliminary sampling will take place in order to assess the spatial redox conditions of the aquifer. These preliminary sampling events will determine the subsequent sampling procedure and frequency. It is anticipated that samples will be collected 3-4 times during the irrigation season and 3 times during the off-season.

To supply the model with parameter values consistent with conditions found in the LARB, laboratory batch studies will be conducted to determine the redox and adsorption capacity of soils along the transect as a function of initial, DO, and NO_3 concentrations, as well as temperature. As the redox capacity of the soil will be dependent on the availability of an active microbial population and adequate electron donor content, multiple soil samples from representative areas will be taken and used in the laboratory studies.

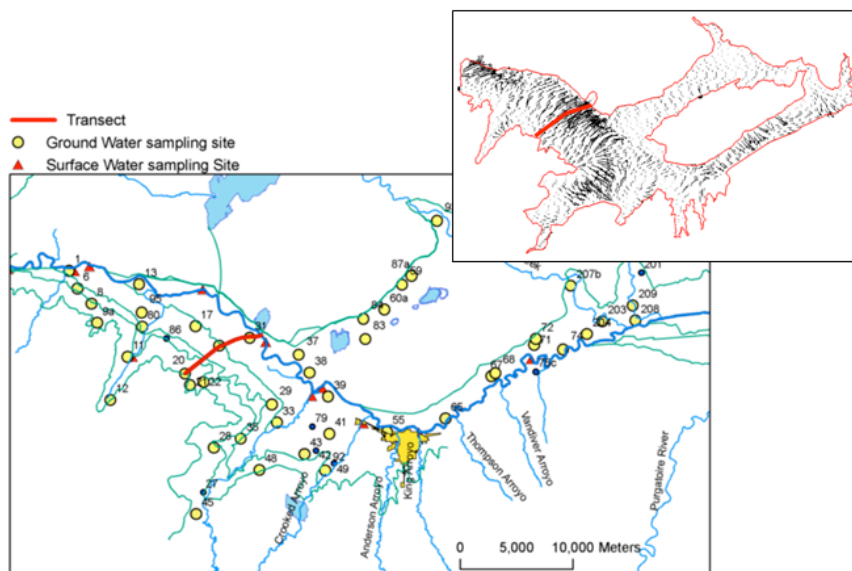


Figure 5. Preliminary proposed transect for vertical and transverse sampling of Se and related properties, with map at upper right showing average ground water flow vectors obtained from a calibrated MODFLOW simulation. Circles indicate current ground water sampling locations. Triangles indicate current surface water sampling locations.

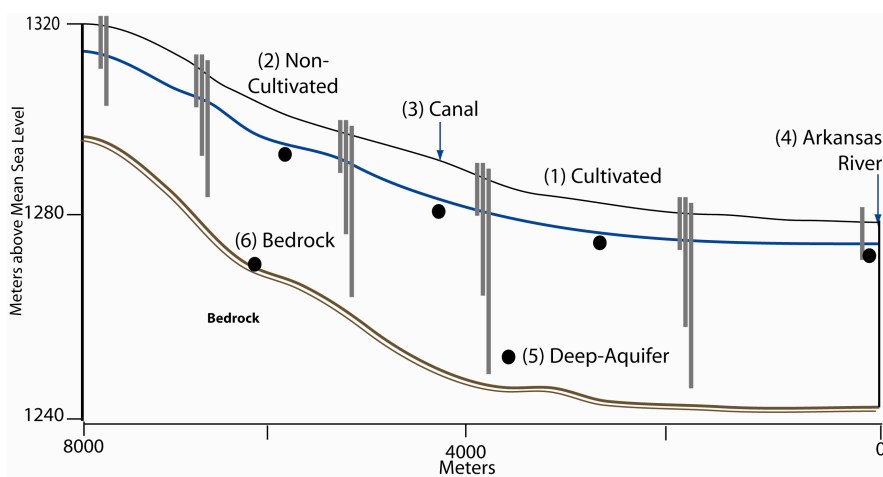


Figure 6. Placement of nested piezometers along a ground water flow path in the Lower Arkansas River Basin, near Rocky Ford, CO. Dark circles indicate soil sampling sites for determination of reaction kinetics.

Currently these areas include (referring to Figure 6) (1) cultivated areas, (2) non-cultivated areas, (3) riparian zones near canals, (4) riparian zones near the Arkansas River, and (5) deep-aquifer areas, with (6) bedrock samples also being analyzed in batch studies in order to quantify the rate at which SeO_4 is released due to FeSe_2 oxidation by DO and NO_3 . Assuming first-order reaction kinetics, each reaction will be represented by equation (3). If microbial population and electron donor concentrations are not uniform and in limited supply, then modeling using microbial kinetics will be explored. However, this will require many more soil samples and laboratory batch

studies. Adsorption batch studies will also be undertaken to establish equilibrium isotherms for SeO_4 and SeO_3 .

Results of field sampling and laboratory analysis will provide valuable insights into the distribution Se species and the rate of reactions various regions of the aquifer. It is anticipated that batch studies will allow redox patterns to be established according to land surface type, and that redox reaction rates and adsorption isotherms can be incorporated into the vertical profile model on a section by section basis, e.g. reaction rates provided for aquifer sections underlying cultivated regions will be different than reaction rates provided for sections underlying non-cultivated sections. Simulations will be run to assess the sensitivity of model parameters and the rate at which Se species are transported in the aquifer system. Anticipated key model parameters are electron donor distribution and concentration and reaction rate coefficients. In the case of microbial kinetics, bacterial distribution and concentration will be key model parameters.

Insights gained from the vertical profile simulations will assist in developing a regional-scale, three-dimensional, reactive transport model of the Arkansas River system, providing a tool for exploring best management practices and remediation schemes. The regional-scale model will be calibrated using the field work results from the ongoing region-wide sampling program. Anticipated remediation methods to be explored will consist of internal schemes, wherein the already-present SeO_4 will be reduced and immobilized by adding high electron donor concentration to the aquifer, as well as preventative schemes, wherein NO_3 input and excess recharge into the aquifer will be lowered, so as to minimize the mobilization of SeO_4 from FeSe_2 minerals contained in the shale bedrock and the aquifer substrate.

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