

THESIS

FINDING LAND AND WATER MANAGEMENT PRACTICES TO REDUCE SELENIUM AND NITRATE
CONCENTRATIONS IN AN AGRICULTURAL RIVER VALLEY APPLYING
A REGIONAL-SCALE STREAM-AQUIFER MODEL

Submitted by

Christopher David Shultz

Department of Civil and Environmental Engineering

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Colorado State University

Fort Collins, Colorado

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Master's Committee:

Advisor: Timothy K. Gates

Ryan T. Bailey
Dana L. K. Hoag

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ABSTRACT

FINDING LAND AND WATER MANAGEMENT PRACTICES TO REDUCE SELENIUM AND NITRATE CONCENTRATIONS IN AN AGRICULTURAL RIVER VALLEY APPLYING A REGIONAL-SCALE STREAM-AQUIFER MODEL

The long-term practice of irrigated agriculture within the Lower Arkansas River Valley (LARV) in southeast Colorado has contributed to a number of land and water management concerns, including elevated concentrations of dissolved selenium (Se) and nitrate (NO_3) in the stream-aquifer system. The goal of this study was to develop and calibrate a stream-aquifer flow and reactive transport model to simulate conditions within a representative region of the LARV, then to apply the model to evaluate the potential effectiveness of alternative land and water best management practices (BMPs) to improve conditions. Using a MODFLOW-SFR model to simulate groundwater and stream flow, linked to an RT3D-OTIS model to simulate reactive transport of solutes, enabled comprehensive regional-scale modeling of the coupled stream-aquifer system. Through an extensive calibration and testing process, including manual and automated calibration using PEST, parameter values were estimated and runs were conducted to describe spatiotemporal distributions of groundwater levels and concentrations, mass and return flow rates to streams, and stream concentrations for baseline conditions. Similar runs were conducted for individual and combined BMPs to analyze their effectiveness in reducing groundwater and stream water pollution from Se and NO_3 , assuming their broad implementation over the study regions. The considered BMPs include two land BMPs, namely reducing applied fertilizer application (RF), and enhancing riparian buffer zones (ERB); and three water BMPs, reducing applied irrigation (RI), lease-fallowing irrigated land (LF), and canal sealing to reduce seepage (CS). Results reveal substantial spatial and temporal variability in Se and NO_3 concentrations over the region. Moreover, they show that

by implementing such BMPs, Se and NO₃ groundwater concentrations could be lowered by as much as 23% and 40%, respectively, and stream concentrations of Se and NO₃ could be lowered by as much as 57% and 33%, respectively. The most effective stand-alone land BMP was ERB, and the most effective stand-alone water BMP was CS. By coupling groundwater and stream flow modeling, this study has provided a number of insights not perceived in precursor modeling studies in the study region which examined only groundwater concentrations and mass loading. Some of these findings include: (1) BMPs which alter water management alone are likely to result in an increase in NO₃ concentration in the streams (this is because the chemical reduction of groundwater return flows through the riparian zone is so effective under baseline conditions that practices which lower rates of return flow, without also substantially lowering concentrations, diminish the dilution effect on stream flow), (2) lower mass loading of Se and NO₃ to streams due to a BMP does not necessarily imply a lowering of stream concentration since there are interactive effects of concurrent reductions in return flow rates, and (3) though there are prospects for substantial lowering of total Se concentrations in streams in the LARV, it is unlikely that the current Colorado chronic standard of 4.6 µg L⁻¹ for total Se could ever be achieved practically. Furthermore, the linked models presented in this thesis could be applied to other irrigated stream-aquifer systems to simulate reactive transport of Se and NO₃.

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CHAPTER 1: Introduction

1.1. Challenges in Irrigated Agriculture

With a rapidly increasing global population projected to reach 9 billion by 2044 (U.S. Census Bureau 2016), increasing pressure will be put on the agricultural industry to keep up with the growing demand of feeding the world. Maintaining irrigated agricultural regions is critical to sustaining the high production required. However, conversion from natural ecosystems to irrigated crop land along with corresponding changes in land and water use and management in these regions has led to a number of water quantity and quality concerns.

Several issues have emerged which threaten the long-term sustainability of irrigated agriculture including high water tables and water quality degradation. Irrigation-induced high water tables present under some cultivated land has led to waterlogging of crops, salinization of soils, and non-beneficial consumptive use of water (Scanlon et al. 2007; Pimentel et al. 1997; Gates et al. 2012). This waterlogging and soil salinity reduces potential crop yields, while the non-beneficial consumptive use wastes water on vegetation with no economic value that could otherwise be used for agricultural production. Water quality is also a concern in many agricultural systems. Nutrients [e.g. nitrogen and phosphorous] applied on crop lands are transformed and transported by water as it flows through the groundwater system and surface drains which return back to streams. In some regions, trace elements also present water quality concerns. As groundwater interacts with geology, oxidation-reduction (redox) processes cause trace elements to be expelled. Due to these processes, selenium (Se) contamination has emerged as a widespread issue in recent years in the Western United States. This originated in the 1980s with the discovery of contamination in the Kesterson National Wildlife Refuge in the San Joaquin Valley, California, where significant concentrations of Se lead to bioaccumulation and waterfowl mortality (Nolan and Clark 1997). Se, present in the bedrock as seleno-pyrite (FeSe_2), is oxidized into mobile species of Se, then transported to the surface water systems. This oxidation process is

accelerated by the presence of electron acceptors such as dissolved oxygen (DO) and nitrate (NO_3) present in the groundwater. Se, NO_3 , uranium (U), and other salts present in the hydrologic system are further concentrated through high rates of evapotranspiration (ET) on the crop land leading to evaporative concentration of the solutes.

These challenges are prevalent in the Lower Arkansas River Valley (LARV) in Southeastern Colorado (Figure 1.1), which represents a large and productive agricultural region in the state. The LARV faces problems related to water quality and high water tables which are further perpetuated by inefficient irrigation practices. These challenges in irrigated agriculture must be adequately addressed to ensure sustained agricultural production that meet future demands for food and fiber and supports the rural economy of the area.

1.2. Irrigation Related Concerns in Colorado's LARV

1.2.1. Description of Study Area

The LARV is located in southeastern Colorado between Pueblo, Colorado and the Colorado-Kansas border shown in Figure 1.1. The region is semi-arid and is heavily irrigated with many canals and wells used for irrigation. The LARV sits atop an alluvial aquifer formed over time from the deposition of sediment along the river and in the floodplain. In past research by Colorado State University (CSU), two major study areas have been examined: the Upstream Study Region (USR) and the Downstream Study Region (DSR). For this thesis, modeling working was conducted for the USR. The USR represents a large region within the LARV representative of the portion lying upstream of John Martin Reservoir, which relies heavily on irrigation from canal diversions and groundwater pumping to promote crop production. Major cities include Rocky Ford and La Junta, with Las Animas located a few miles east of the downstream end of the model boundary. The primary crops in the region include alfalfa, corn, sorghum, and grains, with some area being cropped with melons and vegetables.

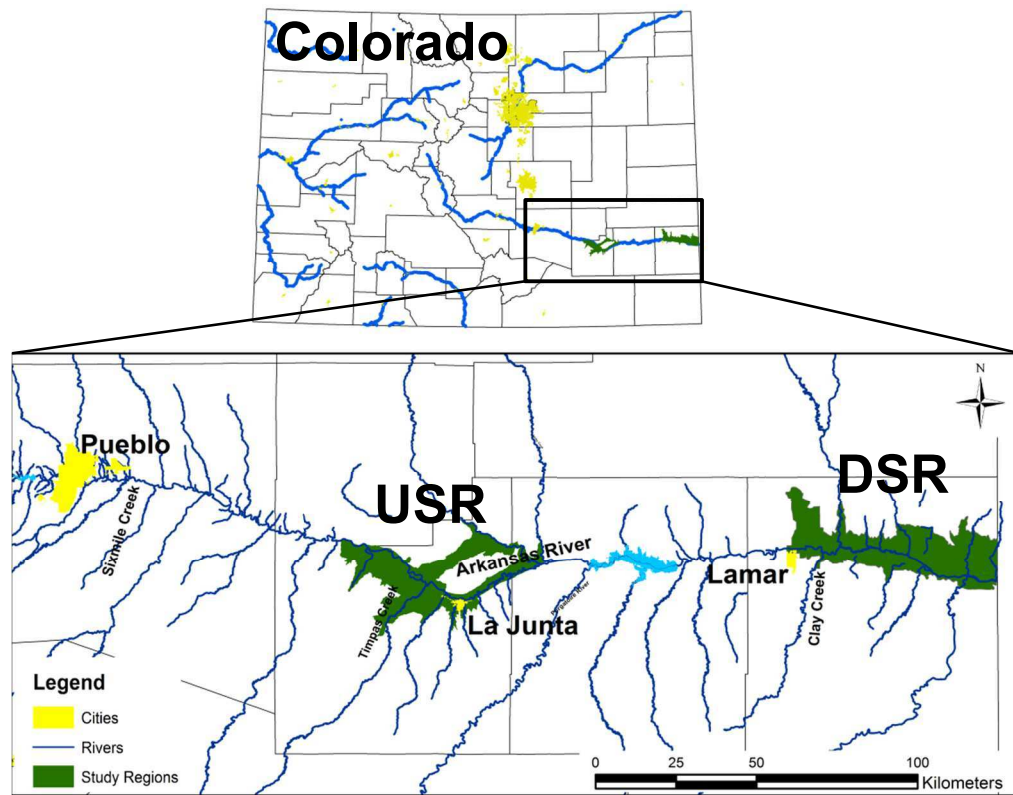


Figure 1.1: The Upstream Study Region (USR) and Downstream Study Region (DSR), the two primary CSU regional-scale study regions in the LARV.

The portion of the LARV that lies within the USR consists of about a 75 kilometer stretch of the Arkansas River with an underlying alluvial aquifer and a number of tributaries. The major tributaries within the model domain are Patterson Hollow, Timpas Creek, Crooked Arroyo, King Arroyo, and Horse Creek. The stream and canal system and cropped fields are shown in Figure 1.2. Tributaries are primarily fed by irrigation returns which then flow to the Arkansas River. In most cases, the Arkansas River and its tributaries are gaining, meaning that water flows from the groundwater into the streams.

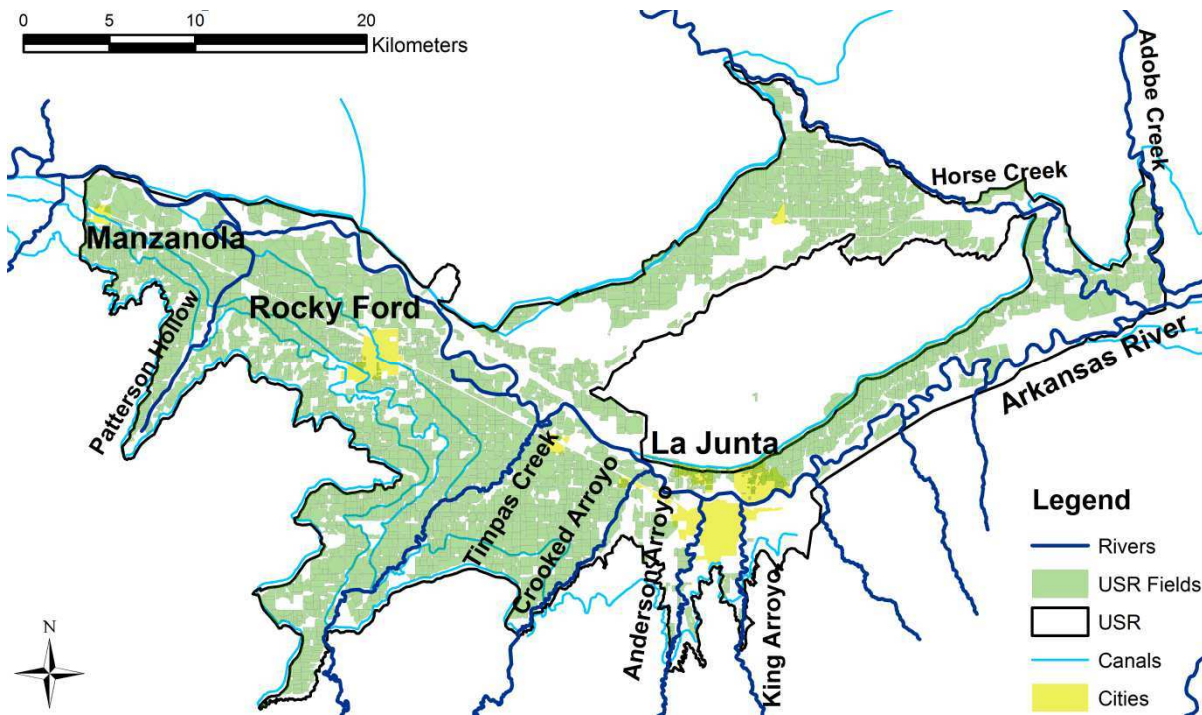


Figure 1.2: Map of USR in LARV showing the Arkansas River, fields, canals, cities, and major tributaries.

Agriculture in the region relies heavily on irrigation due to the large difference between crop ET and rainfall. Due to the need for supplemental water, a network of irrigation canals was created as large scale agricultural production began in the late 19th century. Some 25 canals help support about 270,000 irrigated acres in the LARV (Gates et al. 2012). Canals within the USR include the Highline Canal, Otero Canal, Catlin Canal, Rocky Ford Canal, Fort Lyon Canal, Holbrook Canal, Fort Lyon Storage Canal, and Las Animas Consolidated Canal. These canals represent a fraction of those in the valley. To further support the crop land, about 2,400 irrigation wells pump water from the aquifer in the USR. Historically, a vast majority of irrigation was done via applied surface water with Gates et al. (2012) reporting that less than 5% of irrigation was applied using sprinkler or drip technologies. In recent years, sprinklers have increased in popularity, now representing nearly 20% of the irrigated agriculture in the valley.

Soils in the USR range from sandy to clayey, with a large portion of the soils being clay or clay loam texture. The LARV is underlain by marine shale which acts as the bedrock beneath the alluvial

aquifer (Scott 1968, Sharps 1976, Morway et al. 2013). This bedrock layer contains mineral forms of Se and U, which become mobilized by redox processes. In some locations, this shale layer emerges at the ground surface in the form of shale outcrops (Gates et al. 2012).

1.2.2. Non-Beneficial Consumptive Use

In the LARV, infiltrated water from irrigation and canal seepage causes water tables to be elevated to a level at which flows upward to contribute to ET. This occurs when the water table is within the root zone of plants or water from the groundwater rises into the root zone of plants through capillary action. Under naturally-vegetated and fallow land this upflux amounts to losses to non-beneficial plants and direct soil evaporation which reduce the amount of water that could be appropriated to other beneficial uses downstream. This non-beneficial ET has been estimated to be approximately 31,500 acre-feet of water per year within the USR (Morway et al. 2013).

1.2.3. Water Quality Issues

Numerous water quality issues have been discovered in the LARV including problems with salinity, Se, U, and NO₃. Over time much of the same water is used repeatedly as it travels downstream along the Arkansas River. As water in excess of ET returns to streams from irrigation, it picks up salts from the soil and surrounding geology. Water lost from the system through ET concentrates these salts in the water supply. This increased salinity in the applied water hinders crop uptake of water and ET, potentially reducing crop yields. Furthermore, nutrients and trace elements such as Se, NO₃, and U dissolve in irrigation water as it returns to the Arkansas River. These solutes have the potential to harm wildlife, livestock, and humans. NO₃ is picked up from fertilizer applied to fields, whereas Se and U enter during redox interactions between groundwater return flows and the shale bedrock. Gates et al. (2009, 2016) presented results from field studies showing elevated concentrations of Se, NO₃, and U. Another study by Miller et al. (2010) showed similar results of elevated Se and U concentrations. These studies have concluded that the Se concentrations in the Arkansas River and its tributaries consistently exceed

state chronic standards of $4.6 \mu\text{g L}^{-1}$. However, field data from Gates et al. (2009, 2016) shows that the average NO_3 as nitrogen ($\text{NO}_3\text{-N}$) concentrations typically are under the interim state standard of 2.0 mg L^{-1} for total nitrogen (N).

1.2.4. Arkansas River Compact Constraints

By the late 19th century, all reliable flows in the Arkansas River in Colorado had already been appropriated, including much upstream of the LARV (MacDonnell 1999). As the flows from the Arkansas River into Kansas became increasingly depleted, the state of Kansas took the state of Colorado to court in 1901. A U.S. Supreme Court decision in 1907 ruled that while flows into Kansas had been reduced, the benefits that Colorado received from using the water outweighed the harm to Kansas (MacDonnell 1999). In 1948, John Martin Reservoir was completed and, in 1949, Kansas and Colorado created the Arkansas River Compact. This compact had two major purposes. First, it was made to settle disputes between the states of Kansas and Colorado regarding water use from the Arkansas River. Second, the compact explained who controls John Martin Reservoir and the water that is stored in it. The compact explains that the Army Corps of Engineers is in charge of managing and releasing water from the reservoir in the case of a flood, but both Kansas and Colorado can ask for “water equivalent to the river flow” to be released from the reservoir when needed (Kansas-Colorado 1949). Since the creation of the compact, multiple lawsuits have been filed between Kansas and Colorado. Most recently, in 1995, the U.S. Supreme Court ruled that groundwater pumping had depleted water that was agreed to come into Kansas, which forced an end to some of the pumping in the LARV (MacDonnell 1999; Kansas v. Colorado 2009). The Arkansas River Compact makes it difficult to implement changes in water management by improving irrigation efficiencies and sealing irrigation canals since these practices alter the rates and patterns of return flows to the river, and therefore alter flows entering Kansas in the Arkansas River itself. In recent years, formal methods have been adopted to allow for some changes in water management, but there are still serious limitations.

1.2.5. Prospects for Improvement of Conditions in the LARV

Past work has shown promising land and water Best Management Practices (BMPs) to reduce Se and NO₃ groundwater concentrations and mass loading to stream (Bailey et al. 2015a, 2015b). These BMPs include reducing applied irrigation, sealing of irrigation canals, fallowing of agricultural lands, reducing applied fertilizer, and enhancing riparian buffer zones. Bailey et al. (2015a, 2015b) concluded that these BMPs could significantly reduce mass loading to the Arkansas River and its tributaries. The investigation in this thesis will examine the same BMPs to determine their effectiveness in lowering concentrations within the Arkansas River in addition to reexamining the effectiveness of BMPs on mass loading and groundwater concentrations.

1.3. Research Objectives

The overall goal of this research is to develop, calibrate, and apply a computational model to assess the impacts of alternative BMPs on lowering Se and N concentrations in the stream-aquifer system of the USR of the LARV. This goal will be achieved through the following objectives:

1. Build a conceptual model for the coupled stream-aquifer system to understand the means of reactive solute transport through the system as a whole.
2. Check and modify the previously-developed stream-aquifer reactive transport model to ensure that the model performs consistently with physical laws and assumptions and to eliminate any bugs in the model code.
3. Perform calibration and testing on the stream-aquifer model using available field observations and mass balance estimates.
4. Analyze alternative BMPs for their effectiveness in reducing the Se and NO₃ concentrations compared to the baseline condition (current practices) and in relation to Colorado's current regulatory standards.

5. Interpret results to form conclusions and recommendations for future management decisions that could yield improved water quality for the region.

1.4. Thesis Structure

Chapter 2 is a review of the literature, examining previous modeling studies for Se and NO₃ and for potential BMPs to reduce their concentrations. The end of the chapter focuses on previous work that has been undertaken within the LARV.

Chapters 3 and 4 represent journal papers prepared to describe the work completed on the development and application of the coupled model. Chapter 3 details the model coupling, calibration, and application to simulate baseline conditions, with reference to related work completed by previous CSU researchers. Chapter 4 then describes the application of the calibrated model to assess prospective changes due to application of alternative land and water BMPs.

Chapter 5 contains concluding remarks including results from the model calibration and simulation of BMPs, as well as recommendations of the best BMPs and future work. Finally, the Appendices contain material providing additional detail on model refinements, the calibration process, BMPs results, and the simulation of reservoir storage.

CHAPTER 2: Literature Review

2.1. Irrigation-Induced Nonpoint Source Pollution

In order to sustain agricultural production for the future, agricultural regions themselves must be sustained. Tilman et al. (2002) reported that while only 16% of agricultural lands are irrigated, these areas account for 40% of the total agricultural production globally. However, the success of irrigation practices has come with costs, including the degradation of water quality over time. Inefficiencies in irrigation practices have increased return flows to surface water systems both through the groundwater and tailwater runoff. As the water returns to the streams, it picks up salts from the soil and surrounding geology. The further evapoconcentration of these salts that occurs from water application and crop use leads to elevated concentrations far above what would have been present prior to development of the regions. In order to sustain these irrigated agricultural regions, long-term water quality degradation must be mitigated or resolved.

In recent years, coupled stream-aquifer models have become increasingly popular in order to more accurately represent hydrologic systems (Fleckenstein et al. 2010). These models are useful in representing flow and reactive transport in complex systems with prevalent stream-aquifer interactions and/or hyporheic exchange. In the past, several model couplings have been used to represent the systems. Hussein and Schwartz (2010) used FTSTREAM and FTWORK (Faust et al. 1993) to model stream-aquifer flow and reactive transport of tetrachloroethylene (PCE) and trichloroethylene (TCE). Additionally, there have been several past studies using coupled SWAT (Arnold et al. 1996), MODFLOW (McDonald and Harbaugh 1988), and MT3D (Zheng 1990) models to simulate reactive transport of nutrients in stream-aquifer systems (Narula and Gosain 2013; Conan et al. 2003). Bailey et al. (2016) created an updated SWAT-MODFLOW coupling to examine stream-aquifer interaction in a watershed in southern Oregon. Finally, the U.S. Geological Survey (USGS) has recently released an updated version of MT3DMS (Zheng and Wang 1999) (a groundwater reactive transport model) called MT3D-USGS (Bedekar

2016) which, when used in conjunction with MODFLOW, computes flow and reactive transport in the groundwater system and routes solutes in streams.

2.2. Se Pollution in Irrigated Regions

Se contamination of surface water (Engberg and Sylvester 1993; May et al. 2008), groundwater (Hudak 2010; Alfthan et al. 1995), and soils (Zhang et al. 2008) due to underlying geology is becoming a concern in the United States and around the world. Se naturally occurs in the forms selenate (SeO_4), selenite (SeO_3), elemental Se (Se^0), and selenide (Se^{2-}), having oxidation states of +6, +4, 0, and -2, respectively. In the western United States, the Se is stored in shale bedrock from the Cretaceous period in the form of FeSe_2 (Presser et al. 1994). During redox reactions, the mineral form of Se, along with the sulfur (S) in pyrite (FeS_2), is oxidized, transforming the Se into the species SeO_4 and SeO_3 (Gates et al. 2009). These oxidized species of Se are aqueous and mobile, allowing the Se to enter and move through the hydrologic system.

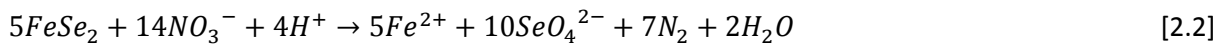
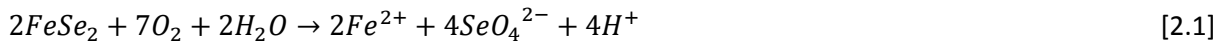
Se is an essential micronutrient for life in small quantities, however in moderate amounts it can be toxic. When dissolved Se is present in surface water systems, it can be consumed by fish, replacing the S in amino acids in the fish's eggs and altering the structure of the resulting protein, resulting in deformities (EPA 2016). Furthermore, Se has a known ability to bioaccumulate in the aquatic food chain thereby affecting birds (Presser et al. 1994; Hamilton 2004). The state of Colorado has set the chronic and acute standards for Se to be $4.6 \mu\text{g L}^{-1}$ and $18.4 \mu\text{g L}^{-1}$, respectively (CDPHE 2016). In 2016, the Environmental Protection Agency (EPA) released new standards for Se that include values for fish tissue (egg/ovary, whole body, and muscle tissue) as well as lowering the Se standard to $3.1 \mu\text{g L}^{-1}$ for lotic waters and $1.5 \mu\text{g L}^{-1}$ for lentic waters (EPA 2016).

2.2.1. Redox-Affected Se Pollution in Agricultural Hydrologic Systems

In an irrigated stream-aquifer system, inefficiencies in the conveyance of irrigation water through canals as well as from on field application cause seepage into the groundwater system. This

seepage water transports with it DO, taken from the air, and NO₃, from applied fertilizer, which have been dissolved into the water. Both these species, DO and NO₃, act as oxidizing agents during redox processes. Increasing their availability within the groundwater system thereby enables redox processes to occur, thus accelerating the release of Se into the dissolved phase (Bailey et al. 2012).

Figure 2.1 shows the redox ladder for select species of interest. The higher the redox couple is on the ladder, the more readily the species is reduced (left to right on the ladder). The same idea is true for oxidation; in lower rungs on the ladder, the species can be more easily oxidized (right to left on the ladder). Since oxidation and reduction occur as a coupled process, the presence of DO and NO₃, which can be readily reduced, accelerates the redox reaction that liberates SeO₄ and SeO₃ from bedrock. Figure 2.1 shows the redox reaction of sulfate (SO₄) and FeS₂ due to more readily available information on this process; a similar oxidation reaction would occur for SeO₄ and FeSe₂ due to similarities in the electron structure between Se and S. The stoichiometric redox equations resulting in the oxidation of Se due to DO and NO₃:



DO and NO₃ also inhibit the reduction of SeO₄ into forms that more readily can be removed from the system, since they are given higher preference when reduction occurs. Only when the oxidizing agent in a couple on a higher rung significantly diminishes will the solute on the next rung on the ladder begin to be reduced in an equilibrium state; this is evident when computing the reduction potential for these solutes at varying concentrations (Brezonik and Arnold 2011). Gates et al. (2009) suggested threshold concentrations that inhibit the reduction of Se to be 2.26 mg L⁻¹ for NO₃-N and 7 mg L⁻¹ for DO. This combination of facilitated oxidation and inhibited reduction is the root cause of elevated dissolved Se concentrations in irrigation-affected surface water and groundwater.

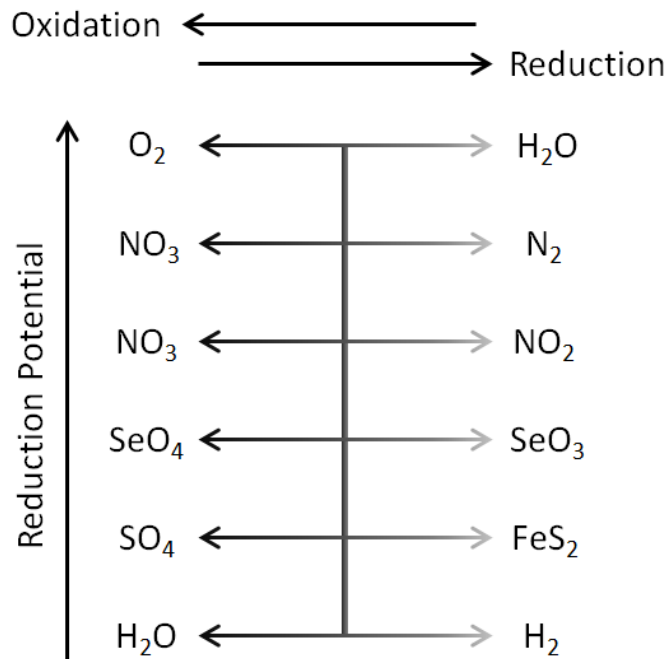


Figure 2.1: Oxidation-reduction ladder showing solutes of concern in order of reduction potential at pH=7.

2.2.2. Modeling and Control of Se Pollution

Engberg et al. (1998) outlined methods to control the Se concentration including preventing Se from entering the hydrologic system, capturing or removing Se that is present in the system, and reducing the effects of Se. Fundamentally, BMPs in literature tend to follow these approaches. Engberg et al. (1998) further evaluated the San Joaquin Valley Drainage Program, a multi-tiered program used to reduce irrigation induced Se problems in the irrigated valley. This program concentrated on removing Se from the system as well as making management changes to reduce Se coming into the system by reducing source Se, controlling drainage water, and altering land and groundwater management (Engberg et al. 1998). Lin and Terry (2003) treated irrigation drainage through a 10 cell wetland system, resulting in a reduction of the Se mass of 70%, mostly through sorption to sediment and volatilization. Amweg et al. (2003) examined the use of algae and bacteria for Se reduction, which resulted in reduced total Se but significantly increased the bioavailability of the Se. This shows the issues of relying on

bacteria to remove mobile Se; it must be removed from the system, while at the same time not becoming more accessible to other aquatic organisms.

In the past, several studies have analyzed Se in groundwater with numerical models. Tayfur et al. (2010) developed a 2-D finite element model designed to model both the saturated and unsaturated zones. This model was designed to handle redox processes, adsorption, volatilization, mineralization, and plant uptake. Additionally, it considers SeO_4 , SeO_3 , Selenomethionine (SeMet), and organic Se. Myers (2013) used MODFLOW and MT3D to simulate groundwater flow and transport of Se, respectively, to analyze a watershed where mines create an interaction between groundwater and the shale bedrock which contains Se. In this model, SeO_4 is the only species of Se that is considered and is treated as a conservative solute (Myers 2013). Ahmad et al. (2010) also used MODFLOW and MT3D to model solute reactive transport in the Kahota Industrial Triangle area. Their model accounted for advection, dispersion, sorption, and reactions. The work of Tayfur et al. (2010) is most similar to the LARV research. Their model was applied to two sites in the San Joaquin Valley in California, an area with a similar climate and land use to the LARV subject to Se issues.

2.3. NO_3 Pollution in Irrigation Return Flow

The prevalence of NO_3 in agricultural surface water and groundwater systems has become a widespread issue in recent decades (Carpenter et al. 1998; Spalding and Exner 1993). Across the United States, high levels of nutrients, including NO_3 , have been reported in surface water and groundwater systems coinciding with irrigated agriculture; these levels are often attributed to runoff and infiltration of applied nutrients due to inefficiencies in fertilizer and irrigation application (Muller et al. 1995; Spalding and Exner 1993). Excess nutrients in surface water systems can lead to eutrophication by causing rapid growth of algae. The decomposition of the algae robs the water of the dissolved oxygen resulting in fish kills, biodiversity loss, and hindering recreation (Mueller et al. 1995; Carpenter et al. 1998). In large concentrations, NO_3 in the water supply can also lead to methemoglobin in infants

(Carpenter et al. 1998). For these reasons, the EPA has set the maximum contaminant level (MCL) for $\text{NO}_3\text{-N}$ as 10 mg L^{-1} (2009). Additionally, the Colorado Department of Public Health and Environment (CDPHE) has placed an interim standard in the state of Colorado for $2,010 \text{ } \mu\text{g L}^{-1}$ on warm stream waters (CDPHE 2017).

2.3.1. Modeling and Control of NO_3 Pollution

In an effort to combat NO_3 contamination of water systems, BMPs have been evaluated in past studies to understand the most effective ways to reduce NO_3 (or N) concentrations and/or loadings. Some methods to reduce NO_3 include enhancing riparian buffers (Lee et al. 2010; Vaché et al. 2003; Sahu and Gu 2009), reducing or optimizing applied fertilizer or fertilizer loading (Rong and Xuefeng 2011; Liu et al. 2013; Lee et al. 2010; Trachtenberg and Ogg 1994; Molénat and Gascuel-Odoux 2002; Almasri and Kaluarachchi 2007), reducing applied irrigation (Rong and Xuefeng 2011), and changes in land management of agricultural land (Vaché et al. 2003; Lee et al. 2010; Liu et al. 2013). Results from these studies show the general effectiveness of land and water management practices in reducing the NO_3 loadings and thereby the in stream concentration (Vaché et al. 2003; Lee et al. 2010; Liu et al. 2013; Sahu and Gu 2009). Enhancing the riparian buffer zone or using vegetative strips has been found to be a particularly effective means of reducing nitrogen loading; by forcing the water to run slowly through a vegetated area, significant reduction of NO_3 can take place before the water enters the stream system.

Many previous studies have been undertaken to model the transport of NO_3 , in large part to understand the characteristics of groundwater systems. Wriedt and Rode (2006) modeled NO_3 transport in a lowland area that was predominantly cropland using a coupled soil and groundwater flow model. The groundwater processes were simulated with MODFLOW and Reactive Transport in 3-Dimensions (RT3D) (Clement 1997), while processes within the soil were simulated with a combination of mRISK-N (Wriedt 2004), SIMPEL (Hörmann 1998), and RISK-N (Gusman and Marino 1999) models (Wriedt and Rode 2006). In the study, NO_3 reactions were linked to the available pyrite in the surrounding geology

and organic matter; these were found to control the denitrification in the groundwater system (Wriedt and Rode 2006). Molénat and Gascuel-Oudou (2002) used MODFLOW and MT3D to model NO_3 in an agricultural watershed in France. This study also took into account the importance of denitrification reactions with the shale layer and used mass flux for the year to estimate the NO_3 leaching concentration. Their results showed significant reduction reactions occurring in NO_3 due to the pyrite in weathered shale, accounting for about half of the total denitrification (Molénat and Gascuel-Odou 2002). Almasri and Kaluarachchi (2007) used MODFLOW and MT3D to model a watershed in Washington State in the United States. In the study, NO_3 loads to groundwater were estimated by using the N inputs to the ground surface along with reactions removing the N in the groundwater system. They found that reducing surface applied N loads had a large effect on reducing NO_3 in groundwater (Almasri and Kaluarachchi 2007).

In some studies, surface water models have been used to understand NO_3 processes in rivers and streams. Several approaches have been used including SWAT (Arnold et al. 1996), QUAL2E (Brown and Barnwell 1987), and OTIS (Runkel 1998). SWAT is used for watershed management and models surface water routing, runoff, evapotranspiration, infiltration to groundwater, crop use, and nutrient loading. QUAL2E is a surface water quality model, which examines reactive solute transport in dendritic streams. OTIS is also a solute reactive transport and storage model for surface water systems. Lee et al. (2010) used SWAT to evaluate total N loading at the outlet of a watershed in South Korea. Sahu and Gu (2009) similarly used SWAT to evaluate outlet load of NO_3 in a watershed in Iowa. Azzellino et al. (2006) used QUAL2E to find in stream NO_3 concentrations in two agricultural watersheds in Italy. Herrman and Bouchard (2008) used OTIS to calculate the transient storage in an agricultural watershed in Ohio as part of a study examining removal of N.

Other studies have attempted to model NO_3 concentrations and movement between surface water and groundwater together. These models use SWAT with MODFLOW and MT3D. In these cases,

SWAT serves as the surface water model; stream gains or losses from SWAT then serve as forcing variables to the MODFLOW model, while nutrient load is transferred with the water. Narula and Gosain (2013) used this combined SWAT, MODFLOW, and MT3D model on a predominantly forested and agricultural watershed in India. This model also took into account the pyrite, amongst other compounds, in computing the denitrification in the groundwater. Conan et al. (2003) also used a similar type of coupled model for a watershed in France. In this case, pyrite was also taken into account in the reduction of NO_3 . The coupled model allowed for the modeling of the denitrification processes, which significantly reduced the total N in the system (Conan et al. 2003). Similar to the work in this thesis, these studies saw the necessity of including redox process, such with pyrite, to accurately represent the NO_3 cycling. In this work, the primary solute of concern is dissolved Se but it is important to capture reactive transport of NO_3 to accurately model the Se in the stream-aquifer system.

2.4. Lower Arkansas River Valley Past Research

There has been a long history of research work in the LARV. The LARV is shown in Figure 1.1 in the Introduction section along with the primary Colorado State University (CSU) study sites, the Upstream Study Region (USR) and the Downstream Study Region (DSR). Initial work by CSU began with monitoring and modeling irrigation related salinity and waterlogging problems that were developing in the region. Later work has addressed Se, NO_3 , and U pollution problems. Monitoring studies also have been conducted by the United States Geological Survey (USGS) and the CDPHE.

2.4.1. Flow and Salt Transport Modeling and Efforts to Address Waterlogging and Salinity in the LARV

Modeling efforts in the LARV began in an attempt to combat waterlogging and salinity problems in the region. These problems are caused directly by the transportation and application of irrigation water. During the conveyance of water, inevitably some of the water transported in irrigation canals seeps into the alluvial aquifer below, causing a higher than natural water table (Gates et al. 2006).

Furthermore, due to prominence of flood style irrigation and its inherent inefficiencies, a large amount of both tailwater runoff and deep percolation occur during irrigation events. This infiltration of water further increases the water tables.

High water tables are the root cause of waterlogging and salinity in the region. Waterlogging occurs when the root zone of a plant or crop is partially or totally immersed in the water table, leading to insufficient oxygenation of the roots and reduced yield. Additionally, high water tables contribute to water loss to riparian vegetation and plants on fallow lands that could be used for irrigation (Gates et al. 2006). The loss occurs both from water uptake to plants in constant contact with the groundwater or plants that reside in the vadose zone of soils that obtain moisture from the capillary rise of water from the groundwater table. Furthermore, these high water tables vary in height depending on well pumping, precipitation, or upstream irrigation. This repeated change in height causes the deposition of salts from the water into the soil, increasing soil salinity. These salts become dissolved and mobilized as the irrigation return flow runs through the soil and alluvial aquifer (Gates et al. 2006).

As the water travels downstream in the LARV, irrigation water that does not stay on the field through retained soil moisture returns to the Arkansas River or its tributaries in surface drains or the groundwater system. High return flows, due to the inefficient nature of flood irrigation, along with repeated reuse of water causes salinity to increase as the water travels further downstream. Some of these salts stay in the soil as the water infiltrates into the aquifer; this, in turn, increases salinity in the surface soils. These salts are inherently bad for the plant growth in the soil, making it more difficult for plants to uptake water from the soil even when the water is present, which reduces agricultural yield as well (Gates et al. 2006).

Early modeling work in the region was conducted by Konikow and Bredehoeft (1974), Konikow and Person (1985), and Person and Konikow (1986) in an effort to understand and control irrigation induced salinity issues. Konikow and Bredehoeft (1974) used an early computer model to examine

variations in hydrologic conditions and dissolved solid concentrations in a region of the LARV between La Junta, CO and the Bent-Otero county line. This study region now represents a portion of the USR examined in this thesis. A decade later, Konikow and Person (1985) reexamined long-term salinity changes to evaluate the necessity or further calibration of the original regional model. They found that, at minimum, a five-year long dataset would be necessary to “avoid a dominating influence of a short-term trend” (Konikow and Person 1985). Person and Konikow (1986) then recalibrated the original groundwater salinity model using an 11-year dataset to more accurately represent field conditions. A decade later, Goff et al. (1998) again recalibrated and applied the groundwater model developed by Konikow and Bredehoeft (1974), this time over a 24-year study period from 1971 to 1995. In the study, changes in irrigation management were analyzed using the calibrated model including a reduction in groundwater use for irrigation and a reduction in irrigated acreage. Results from the work show the potential for moderate reductions in groundwater salinity but limited reductions in the in stream salinity (Goff et al. 1998).

Dai and Labadie (2001) developed a river basin network model using MODSIMQ to model flows and QUAL2E to model water quality. This model was applied to the entire extent of the LARV from Pueblo, CO to the state line with Kansas. Using the surface water model, the study examined the surface management alternatives including implementing water quality constraints and improvements in irrigation efficiency.

Gates et al. (2002) created a steady-state groundwater model using the Groundwater Modeling System (GMS) software (BYU 1999) to model water table and salinity problems in the USR. GMS works as graphical user interface for MODFLOW and MT3D. After the model was constructed, Gates et al. (2002) investigated BMPs to reduce waterlogging and salinity such as increasing pumping, reducing recharge, and combinations of the two. Results shows that changes in pumping creates very small changes in the depth to water table, while increased irrigation efficiency (by reducing recharge) causes a

more substantial drop in the water table. All scenarios predicted small changes in groundwater salinity (Gates et al. 2002). This GMS model was further refined by Burkhalter and Gates (2005) and altered to model transient flow. Burkhalter and Gates (2006) then used this new model to review regional solutions including reducing recharge, reducing seepage, increasing pumping, placing subsurface drains, and combinations. This model output showed that BMPs, especially in combination, could significantly increase the depth of the water table and reduce salinity in the aquifer (Burkhalter and Gates 2006). Morway et al. (2013) created a new model in the same study area used by Burkhalter and Gates (2005, 2006) (USR) as well as another study area farther downstream in the LARV (DSR). These new models included longer simulation periods, the UZF1 package (Niswonger et al. 2006), and MODFLOW-NWT (Niswonger et al. 2011), and increased accuracy and representation of model input data such as precipitation, ET, and seepage from canals (Morway et al. 2013). Morway et al. (2013) examined BMPs including improving canal conveyance efficiency, enhancing irrigation efficiency, and lease fallowing and found a significant reduction in groundwater recharge under the BMPs scenarios, especially the combinations. Furthermore, these BMPs were found to be an effective means of lowering the water tables and decreasing non-beneficial consumptive use.

2.4.2. Field Studies for Se and NO₃

Gates et al. (2009) presented field data for groundwater wells and surface water points in the USR and DSR of the LARV. The work found an average groundwater Se concentration of 57.7 $\mu\text{g L}^{-1}$ and 33.0 $\mu\text{g L}^{-1}$ in the USR and DSR, respectively. The data showed average Se concentrations in the surface water to be 7.0 $\mu\text{g L}^{-1}$ for the USR and 10.7 $\mu\text{g L}^{-1}$ for the DSR, well above the CDPHE chronic standard of 4.6 $\mu\text{g L}^{-1}$. The study found NO₃ groundwater concentrations to be 10.2 mg L⁻¹ (2.30 mg L⁻¹ NO₃-N) and 9.5 mg L⁻¹ (2.15 mg L⁻¹ NO₃-N) for the USR and DSR, respectively, as well as in stream concentrations of 5.5 mg L⁻¹ (1.24 mg L⁻¹ NO₃-N) and 5.7 mg L⁻¹ (1.29 mg L⁻¹ NO₃-N) for the USR and DSR, respectively, on average (Gates et al. 2009). Gates et al. (2016) provided updated values of Se and NO₃ surface water and

groundwater concentrations in the LARV, which were of similar magnitude. Miller et al. (2010) has also reported on field data in the LARV. These reported concentrations in the Arkansas River, in or near the USR, were on average around $10 \mu\text{g L}^{-1}$, ranging from 9.9 to $12.2 \mu\text{g L}^{-1}$ temporal average concentrations (Miller et al. 2010). Ivahnenko et al. (2013) reported concentrations for 2009 and 2010, which averages similar to those in Miller et al. (2010). The differences in the averages in the Se concentrations between Gates et al. (2009) and Miller et al. (2010) inside the USR could be due to differences in timing when the samples were taken, locations, seasonal changes, number of samples, or the time span of the data. Data from Gates et al. (2009) represented the average of 57 different samples at 10 routinely sampled sites within the USR between 2006 and 2008, whereas the USGS data within or near the USR were sampled at 5 locations with between 29-71 samples within the time frame of 1976 to 2007 (Gates et al. 2009; Miller et al. 2010). Beyond the differences in the averages, both sample sets averaged well above the state of Colorado's chronic standard.

2.4.3. Reactive Transport of Se and N

Bailey et al. (2013b) used the MODFLOW model developed by Morway et al. (2013) which utilized the UZF1 package computing flow input information for the saturated and unsaturated zones as input forcing variables to a modified RT3D called UZF-RT3D. This model had the ability to compute variably saturated reactive transports of interacting solutes (Bailey et al. 2013b). Bailey et al. (2013a; 2014) then used the developed flow and reactive transport model to simulate Se coupled with N in the USR. The model computed groundwater flow in the agricultural basin then used the flows to drive solute transport. The advection-dispersion-reaction (ADR) equation was solved simultaneously for each species (Bailey et al. 2014). The Se species include SeO_4 , SeO_3 , and SeMet as dissolved phase Se as well as dimethylselenide (DMSe) and organic Se (litter, humus, and manure) in the reaction processes. In the model, Se entered the system from the shale bedrock through the reduction of DO or NO_3 , utilizing the ratio of S to Se in the rock.

Bailey et al. (2015b, 2015a) utilized the model calibrated by Bailey et al. (2014) to explore land and water management options to reduce dissolved Se and NO_3 , respectively, in the groundwater system of the USR. These studies examined reducing applied irrigation, fallowing irrigated land, canal sealing, reducing fertilizer application, enhancing riparian zones, and combinations as possible BMPs. Water management BMPs including reducing applied irrigation, fallowing irrigated land, and canal sealing worked to reduce the available DO, NO_3 , and dissolved Se by keeping more of the water in the river and reducing off-field runoff and groundwater return flows. Reducing fertilizer application lowered the NO_3 mass entering the stream-aquifer system. Enhancing riparian zones increased the rate of reduction of NO_3 and dissolved Se, accelerating the rate in which they leave the system before they reach the surface water. These land practices also curb the oxidation of Se from bedrock, and maximize the reduction of mobile Se by reducing the availability of NO_3 (Bailey et al. 2015b). Similar to Bailey et al. (2014, 2015b, 2015a), Tummalapenta (2015) created a groundwater model to analyze BMPs for the DSR using the coupled UZF-RT3D model. Bailey et al. (2015a), Bailey et al. (2015b), and Tummalapenta (2015) saw significant reductions in Se and NO_3 return mass loading, especially in the cases of combinations of BMPs for their respective model regions. In this thesis, the modeling effort of Bailey et al. (2015b, 2015a) is extended to examine the effectiveness of BMPs in reducing Se and NO_3 groundwater concentrations, solute mass loading to stream, and surface water concentrations using a stream-aquifer reactive transport model.

2.5. Description of Models Used

This section describes models used in the LARV USR regional model structure in the present study. The coupling and integration of these models is described in some detail in Chapter 3 of this thesis.

MODular finite difference groundwater FLOW model (MODFLOW) is a model designed to simulate saturated groundwater flow. MODFLOW is a fully distributed model which computes three-

dimensional saturated flow in groundwater systems. It is designed to run with optional packages to simultaneously model other parts of the aquifer system. In this project, several packages were used to accurately represent the stream-aquifer system including the UZF1 and SFR2 (Niswonger and Prudic 2005) packages. The addition of UZF1 enables the unsaturated zone, between the land surface and the aquifer, to be modeled. The UZF1 package takes into account infiltration and evapotranspiration (ET) and models one-dimensional flow through the unsaturated zone into the aquifer. Additionally, the addition of the Streamflow-Routing (SFR2) packages enables the modeling of stream-aquifer interaction. SFR2 routes water from upstream to downstream over the modeled region including the confluence of the main river and its tributaries. Interaction between the stream and adjacent aquifer is computed using Darcy's Law, using the head difference between the aquifer and the stream, streambed thickness, and streambed hydraulic conductivity (Prudic et al. 2004). In the previous model set-up used by Morway et al. (2013) and Bailey et al. (2015b, 2015a), the RIV (Harbaugh 2005) package was used to simulate stream-aquifer interaction. However, this package required a predefined stream stage, limiting its accuracy in modeling water management BMPs. By using the SFR2, changes in flow rates due to BMPs are modeled in the system, allowing for more accuracy in determining the return flow quantities and spatiotemporal variability.

The modeling in this thesis uses output from the modified MODFLOW model (including the SFR2 package) to feed a RT3D-OTIS coupled stream-aquifer reactive transport model. The coupling process and model descriptions are covered extensively in Chapter 3 of this thesis. The current modeling framework relies on the integration of three models RT3D, OTIS, and QUALE. RT3D is a finite difference solute transport model which solves for reactive-transport of saturated groundwater systems in three-dimensions (Clement 1997). As described above, the RT3D code was altered by Bailey et al. (2013b) to create UZF-RT3D, allowing for variably saturated reactive transport. OTIS computes advection, dispersion, transient storage, and lateral inflow/outflow of solutes in surface water systems (Runkel

1998). QUAL2E is a water quality management model that simulates advection, dispersion, and reactions for solutes in well mixed streams. The model uses finite-difference solutions for dendritic streams and can account for a number of reactive processes including nutrient cycling and algal processes, altering species concentrations (EPA 1995). Bailey and Ahmadi (2014) coupled the OTIS and QUAL2E models together for surface water modeling, using OTIS for advection and dispersion and QUAL2E to model the solute reactions. Discussion of the UZF-RT3D and OTIS-QUAL2E models will continue in great detail in Chapter 3.

CHAPTER 3: Simulating Selenium and Nitrogen Fate and Transport in Coupled Stream-Aquifer Systems of Irrigated Regions¹

3.1. Introduction

Se is an essential micro-nutrient for humans and animals, but at elevated concentrations in water and plant material it can lead to diseases such as selenosis, which can cause cirrhosis of the liver, neurological damage, fingernail brittleness, and hair loss in humans (Goldhaber 2003) along with nervous system defects, decrease in enzyme activity, and inhibition of tissue in water fowl and fish populations (Flury et al. 1997; Hamilton 1998; Kishchak 1998; Skorupa 1998). Se enters drinking water or consumable plants through its presence in soil, aquifer, and surface water systems, and often is released from geologic units such as Cretaceous marine shale in the presence of dissolved oxygen (O_2) and nitrate (NO_3) (Seiler 1995; Seiler 1997). There is a growing need to first, assess contamination levels in coupled aquifer-stream systems; and second, develop tools that can provide baseline conditions and quantify the comparative mobilization and movement of Se under varying land and water management practices.

Numerical models have been used more frequently in recent years to assess Se contamination and to investigate remediation strategies. Models used for simulating Se fate and transport in groundwater systems are based on a statement of solute mass conservation, with solute transport governed by advection, molecular diffusion, mechanical dispersion, sorption, and chemical reactions such as chemical reduction and oxidation. Early attempts at simulating Se transport focused on small-scale one-dimensional soil profiles models that accounted only for advection, dispersion, and sorption

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Christopher D. Shultz, *Department of Civil and Environmental Engineering, Colorado State University, 1372 Campus Delivery, Fort Collins, CO.*

Ryan T. Bailey, *Department of Civil and Environmental Engineering, Colorado State University, 1372 Campus Delivery, Fort Collins, CO.*

Timothy K. Gates, *Department of Civil and Environmental Engineering, Colorado State University, 1372 Campus Delivery, Fort Collins, CO.*

Brent E. Heesemann, *Parsons Corp., Denver, CO.*

Eric D. Morway, *Nevada Water Science Center, United States Geological Survey, Carson City, NV.*

(Alemi et al. 1988; Alemi et al. 1991; Fio et al. 1991). Redox reactions were included in the study of Liu and Narashimhan (1994) in a study of Se transport in groundwater at Kesterson Reservoir, California. Guo et al. (1999) initiated the use of first-order kinetics in a modeling scheme to simulate Se chemical reduction, followed by the work of Mirbagheri et al. (2008) and Tayfur et al. (2010) that included Se cycling in the soil-plant system for the first time. Bailey et al. (2013a) expanded on their work by including the influence of O_2 and NO_3 on Se transformation kinetics, necessitating the inclusion of nitrogen (N) cycling and transport. Their model used UZF-RT3D (Bailey et al. 2013b) as the base groundwater reactive transport model, which simulates multi-species reactive transport in variably-saturated porous media. Model results were compared against depth-dependent soil water concentration of NO_3 and selenite (SeO_4) at a field test site in the Lower Arkansas River Valley (LARV) in southeastern Colorado.

Several studies have attempted Se fate and transport simulation at larger scales. Two studies (Ahmad et al. 2010; Myers 2013) treated Se as a conservative solute in Pakistan and Idaho, respectively. A third study (Bailey et al. 2014) employed the Se module for UZF-RT3D at a regional (500 km^2) scale in the LARV, and accounted for all major Se and N sources/sinks in the agricultural environment, including fertilizer loading, groundwater pumping, seepage from earthen canals, groundwater-surface water exchanges, and Se release from marine shale that both outcrops and forms the bedrock layer in the alluvial aquifer system.

The calibrated and tested UZF-RT3D model was used to investigate the impact of land and water management strategies on Se groundwater concentrations and Se mass loading from the aquifer to the Arkansas River network. However, the model did not include solute transport within the stream network, and hence does not have the capability to translate mass loadings to in-stream concentration. Such capability is vital in coupled soil-aquifer-stream systems in order to compare in-stream concentration with the latest US Environmental Protection Agency recommended chronic standard (3.1

$\mu\text{g L}^{-1}$) (EPA 2016) or a State standard for aquatic habitat, and thereby to determine impacts of best management practices (BMPs) on downstream waterfowl and fish populations. To our knowledge, no studies have aimed at investigating Se fate and transport in a coupled groundwater-surface system and, whereas a number of models are available that simulate solute reactive transport in coupled groundwater-surface water systems (HydroGeoSphere, MIKE SHE, CATHY: Weill et al. 2011), none focus on Se species.

The objectives of this paper are two-fold. The first is to introduce a model for Se transport in coupled groundwater-surface water systems, with reactive transport in variably-saturated groundwater systems simulated by UZF-RT3D (Bailey et al. 2013b), and reactive transport in a network of streams simulated by a version of the 1D model OTIS (Runkel 1998) modified to account for Se cycling and transport using a revised chemical reaction module from the QUAL2E model (Brown and Barnwell 1987). Cycling and transport of N in both systems is included due to the influence of NO_3 on Se species' transformation. The coupled reactive transport model is referred to as RT3D-OTIS. Groundwater flow, groundwater hydraulic head, groundwater sources and sinks, streamflow, stream stage, and flow exchange rates between the aquifer and the stream network are provided by a MODFLOW-UZF groundwater model (Harbaugh 2005, Niswonger et al. 2006) that employs the streamflow routing (SFR2) package to constitute the groundwater-stream flow MODFLOW-SFR model. The second objective is to demonstrate the use of the flow and transport models through an application to a 500 km^2 study region in the Lower Arkansas River Valley (LARV) of southeastern Colorado. The MODFLOW-SFR model is based on a previously calibrated and tested MODFLOW-RIV model for the LARV (Morway et al. 2013), which represented streams using the RIV package, and is refined to reproduce field-observed groundwater hydraulic head, groundwater return flows estimated from river mass balance, evapotranspiration calculated from a remote sensing data algorithm, and gaged streamflow. The RT3D-OTIS model is calibrated and tested against groundwater Se and NO_3 concentration, Se and NO_3 mass loading from the

aquifer to the river network of the Arkansas River, and in-stream concentrations of Se and NO_3 at various monitoring sites in the stream network. Baseline conditions in the LARV are simulated to demonstrate the models' utility in profiling the likely long-term environmental consequences of irrigation-induced nonpoint source pollution in the absence of countervailing actions. The ultimate aim is to use the model to forecast outcomes of implementing alternative land and water BMPs relative to baseline conditions.

3.2. Conceptual Model of Se Fate and Transport in a Stream-Aquifer System

Se can exist in environmental water systems in four oxidation states: SeO_4 [Se(VI)], selenite (SeO_3) [Se(IV)], elemental Se (Se^0) [Se(0)], and selenide (Se^{2-}) [Se(-II)] (Masscheleyn and Patrick 1993). Selenide can be present in multiple forms, for example as organic selenomethionine (SeMet) and as gaseous Dimethylselenide (DMSe). SeO_4 , SeO_3 , and SeMet are soluble species, with SeO_4 being a weak sorbent to sediment (Ahlrichs and Hossner 1987) and SeO_3 being a strong sorbent (Balistrieri and Chao 1987). SeO_4 typically accounts for the vast majority of soluble Se (Gates et al. 2009; Gerla et al. 2011; Masscheleyn et al. 1989) and hence often is targeted for removal from the aqueous phase.

SeO_4 can be transformed to SeO_3 via microbial-mediated chemical reduction (Oremland et al. 1990; Masscheleyn and Patrick 1993; Ellis and Salt 2003), with further reduction to Se^0 and Se^{2-} possible. This process, however, is inhibited by the presence of O_2 and NO_3 (Weres et al. 1990; White et al. 1991; Zhang and Moore 1997; Bailey et al. 2012) due to microbial preference for higher-redox species. This inhibition is particularly significant in agricultural areas, wherein irrigation-induced drainage water discharging to streams can be high in O_2 and NO_3 . Within cultivated systems, Se mass can undergo cycling in the soil-plant-water system (Shrift 1964; Stolz et al. 2002), with Se being taken up into crop roots, converted to organic Se (Se_{org}) and then tilled back into the soil after harvest. Se_{org} can then be mineralized to mobile SeO_4 and SeO_3 , which in turn can be taken into the roots during the following growing season.

O₂ and NO₃ also can affect Se fate and transport through the oxidation of residual Se in marine Cretaceous shale, present as seleno-pyrite (-II) (FeSe_xS_{2-x}) in which Se substitutes for sulfur (S) in pyrite (FeS₂) (Bye and Lund 1982). Se is present in all soils (Byers 1937), but particularly in alluvial material overlying or adjacent to pyrite-bearing shale. Regions that are irrigated and loaded with N fertilizer can lead to O₂ and NO₃ coming into contact with pyrite-bearing shale, hence leading to Se mobilization and contamination of groundwater and nearby surface water (Seiler 1995; Seiler 1997). Due to marine sedimentary rock forming the bedrock beneath 805,000 km² in the western United States, many river basins have been found to be seleniferous (Seiler 1997). Se groundwater concentrations have been observed to be as high as 1,410 µg L⁻¹ in the LARV, Colorado (Gates et al. 2009, 2016) and 12,000 µg L⁻¹ in the San Joaquin Valley, California (Fujii et al. 1988), compared to the drinking water limit of 50 µg L⁻¹ set by the USEPA. Regions without marine sedimentary material present as bedrock also can experience extremely high Se groundwater concentrations. For example, Se concentrations in waste rock from phosphorite mining in southeastern Idaho were as high as 955 µg L⁻¹ (Mars and Crowley 2003). In a recent review of Se groundwater concentrations that compiled data from 14 contaminated regions worldwide, average concentration was 750 µg L⁻¹ (range: 0.9 µg L⁻¹) (Bailey 2016), although the average decreases to 220 µg L⁻¹ if the extremely high concentration values (12,000 µg L⁻¹) from the San Joaquin Valley are excluded.

Within stream environments, release of Se to the atmosphere can occur through volatilization (Lemly 1999). Dissolved Se can be taken up by algae (Bennett et al. 1986; Riedel et al. 1996; Baines et al. 2004), with Se_{org} released upon algal respiration. Settling of Se species' mass to the stream sediment bed also can occur, with further chemical reduction of these species occurring within the stream sediments. Se cycling (Masscheleyn and Patrick 1993; Lemly 1999; Chapman et al. 2010) occurs, with Se mass cycled between algal Se biomass, Se_{org}, SeO₄ and SeO₃ in the dissolved phase, and Se sorbed to sediment. More details regarding flow of Se mass in this system will be presented in Section 2.2.2. Within irrigated

alluvial river valleys, wherein typically a strong hydraulic connection exists between the alluvial aquifer and the stream network, Se mass also can be exchanged between the groundwater system and the surface water system, resulting in substantial Se mass loading to streams.

3.3. RT3D-OTIS Coupled Model for Se Fate and Transport

This section describes the model for Se species' reactive transport in coupled groundwater-surface water systems in an agricultural watershed. Because Se transformation chemistry in groundwater and surface is strongly affected by NO_3 and O_2 , the fate and transport of N species and of O_2 also is included in the model and are described herein. The equations for reactive transport in the aquifer will be presented first, followed by the equations for reactive transport in a network of stream channels. Finally, the method for exchanging water and solute mass between the two systems in a coupled modeling framework are presented.

The system under consideration by the modeling framework is shown in the stream-aquifer cross-section diagram of Figure 3.1. To the left of the stream is naturally vegetated land, and to the right is cultivated land. Processes simulated by the groundwater flow model MODFLOW-UZF are shown in blue text, and include irrigation from both canals and groundwater wells, evapotranspiration (ET), tailwater runoff from fields, percolate through the vadose zone, canal seepage, three-dimensional (3D) groundwater flow in the saturated zone, and water exchange with streams (either groundwater discharge or stream seepage). The streamflow routing package SFR2 is used in MODFLOW-SFR, so that streamflow and stream stage can be simulated in a river network. SFR2 employs a kinematic wave approximation of the governing open-channel flow equations (Szymkiewicz 2010). The system variables computed are vadose-zone volumetric water content, groundwater hydraulic head, and groundwater flow at each computational location (finite difference cell). Subsurface processes simulated by the UZF-RT3D component are shown in red text, and include Se and N cycling in the root zone, Se and N leaching in the vadose zone, Se and N transport in the saturated zone via advection, dispersion, and chemical

reactions, and the release of SeO_4 from bedrock and near-surface layers containing FeSe_2 . In-stream chemical transport processes are simulated by an OTIS-QUAL2E component, and will be described in the proceeding sections. The chemical species included in the transport model are listed in Table 3.1, and will be discussed in subsequent sections. Species' names in bold text are included only in stream solute transport.

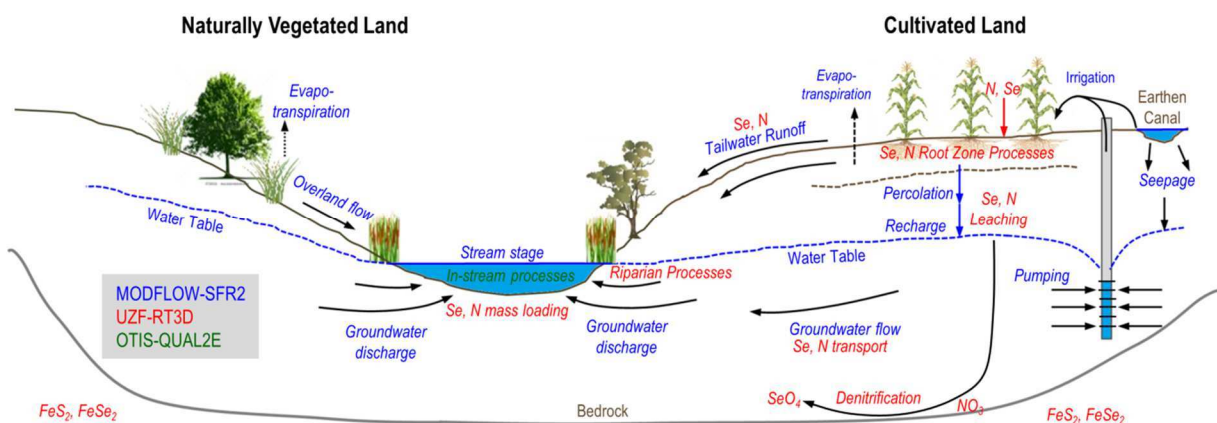


Figure 3.1: Conceptualization of flow and reactive transport processes addressed by the MODFLOW-SFR and RT3D-OTIS (including UZF-RT3D for groundwater and OTIS-QUAL2E for stream water) components of the coupled stream-aquifer system model.

Table 3.1: Chemical Species included in the coupled RT3D-OTIS reactive transport model.

Species Group	Mobile Species	Immobile Forms	Organic Forms
Selenium	Selenate (SeO_4)	Elemental Se (Se)	Litter Se (L_{Se})
	Selenite (SeO_3)	Seleno-Pyrite (FeSe_2)	Humus Se (H_{Se})
	Selenomethionine (SeMet)	Selenide (Se^{2-})	Manure Se (M_{Se})
Nitrogen	Ammonium (NH_4)		Organic Se
	Nitrate (NO_3)		Litter N (L_{N})
	Nitrite (NO_2)		Humus N (L_{N})
Other			Manure N (M_{N})
			Organic N
	Dissolved Oxygen (O_2)		
	Algae		

Bold = Species is only included in stream network transport (OTIS model)

3.3.1. Se and N Reactive Transport in Variably-Saturated Groundwater Systems

The reactive transport of Se species, N species, and O₂ in the subsurface (unsaturated and saturated zones) is simulated according to the following system of mass balance equations that quantifies the change in species concentration according to advection, dispersion, chemical reactions, and sources and sinks:

$$\frac{\partial(C_k \theta)}{\partial t} R_k = -\frac{\partial}{\partial x_i} (\theta v_i C_k) + \frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial C_k}{\partial x_j} \right) + q_s C_{s_k} + \theta r \quad k=1,2,\dots,m \quad [3.1]$$

where m is the total number of aqueous-phase species, C_k is the concentration of the k^{th} species [$M_f L_f^{-3}$] where f denotes the fluid phase, θ [$L_f^3 L_b^{-3}$] is volumetric water content that can change in space and time, where b denotes the bulk phase, D_{ij} is the hydrodynamic dispersion coefficient [$L^2 T^{-1}$], v is the average seepage velocity [$L_b T^{-1}$], q_s is the volumetric flux of water representing sources and sinks of the species [$L_f^3 T^{-1} L_b^{-3}$], C_{s_k} is the concentration of the source or sink [$M_f L_f^{-3}$], and r represents the rate of all reactions that occur in the aqueous phase for the k^{th} species [$M_f L_f^{-3} T^{-1}$]. R_k is the retardation term and is equal to $1 + (\rho_b K_{d_k}) / \phi$, where ρ_b is the bulk density of the porous media [$M_b L_b^{-3}$], ϕ is the soil porosity [$L_f^3 L_b^{-3}$], and K_d is the partitioning coefficient [$L_f^{-3} M_b$] for the k^{th} species. Within UZF-RT3D, Equation 3.1 is solved using a finite difference approach, with C_k solved at each grid cell for each transport time step.

Equation 3.1 is applied for each mobile species in the groundwater system, with sources and sinks (q_s) including fertilizer loading, crop uptake, surface water seepage, and groundwater pumping and reactions (r) including chemical reduction and oxidation, mineralization, and immobilization. Complete explanation of the mass balance transport equations is provided in Bailey et al. (2013a) and Bailey et al. (2013b), which describe the UZF-RT3D model and the UZF-RT3D Se transport module, respectively, and also Bailey et al. (2014), which describes the UZF-RT3D N transport module. Only the equations for SeO₄, NO₃, and O₂ are shown here:

$$\begin{aligned} \frac{\partial(C_{SeO_4}\theta)}{\partial t} R_{SeO_4} = & -\frac{\partial}{\partial x_i}(\theta v_i C_{SeO_4}) + \frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial C_{SeO_4}}{\partial x_j} \right) + q_s C_{sSeO_4} + F_{SeO_4} - U_{SeO_4} + \epsilon (r_{s,Se}^{min} - r_{s,Se}^{imm}) \\ & + \theta (r_{f,SeO_4}^{auto} - r_{f,SeO_4}^{het}) \end{aligned} \quad [3.2]$$

$$\frac{\partial(C_{NO_3}\theta)}{\partial t} = -\frac{\partial}{\partial x_i}(\theta v_i C_{NO_3}) + \frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial C_{NO_3}}{\partial x_j} \right) + q_s C_{sNO_3} + F_{NO_3} - U_{NO_3} + \theta (r_f^{nit} - r_{f,NO_3}^{het} - r_{f,NO_3}^{auto}) \quad [3.3]$$

$$\frac{\partial(C_{O_2}\theta)}{\partial t} = -\frac{\partial}{\partial x_i}(\theta v_i C_{O_2}) + \frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial C_{O_2}}{\partial x_j} \right) + q_s C_{sO_2} + \theta (-r_{f,O_2}^{het} - r_{f,O_2}^{auto}) \quad [3.4]$$

where the volumetric flow rate for each of the MODFLOW-SFR sources/sinks and the accompanying species concentration for each of the sources/sinks are contained in the terms q_s and C_s , respectively; F is the inorganic fertilizer application [$M_f L_b^{-3} T^{-1}$]; U_k is the potential uptake rate for the k^{th} species [$M_f L_b^{-3} T^{-1}$]; *min* and *imm* signify mineralization and immobilization, respectively; *auto* and *het* represent autotrophic and heterotrophic chemical reduction, and *nit* denotes nitrification, respectively.

The change in concentration of immobile species (see Table 3.1) is simulated using the following system of equations:

$$\frac{\partial(C_l \epsilon)}{\partial t} = \alpha_l P_{sol} + \epsilon r_{sol} \quad l = 1, 2, \dots, n \quad [3.5]$$

where l is the total number of solid-phase species; ϵ is the volumetric solid content [$L_s^3 L_b^{-3}$] with *sol* denoting the solid phase and is equal to $1 - \phi$; P_{sol} represents the mass application rate of all solid-phase sources mass inputs for the l^{th} solid-phase species [$M_s L_b^{-3}$] with α_l the fraction of P_{sol} attributed to the l^{th} species [-]; and r_{sol} represent the rate of all reactions that occur in the solid-phase for the l^{th} species [$M_s L_s^{-3} T^{-1}$]. For soil organic species (e.g. Se litter, L_{Se}), solid-phase source mass inputs include dead root mass and after-harvest stover, which are plowed into the top layers of soil at the end of the growing season. Solid-phase reactions include the transfer of mass between the litter, humus, and manure pools. Complete description of these equations for each species is presented in Bailey et al. (2013b).

All reaction rates in the UZF-RT3D model are considered to be governed by first-order kinetics, with Monod terms included to account for influence of other reactants and influential species. For brevity, only chemical reduction equations for SeO_4 and NO_3 are presented here, with complete description available in Bailey et al. (2013b):

$$r_{\text{NO}_3} = \lambda_{\text{NO}_3}^{\text{het}} C_{\text{NO}_3} \left(\frac{C_{\text{NO}_3}}{K_{\text{NO}_3} + C_{\text{NO}_3}} \right) \left(\frac{CO_{2,\text{prod}}}{K_{CO_2} + CO_{2,\text{prod}}} \right) \left(\frac{I_{O_2}}{I_{O_2} + C_{O_2}} \right) E \quad [3.6]$$

$$r_{\text{SeO}_4} = \lambda_{\text{SeO}_4}^{\text{het}} C_{\text{SeO}_4} \left(\frac{CO_{2,\text{prod}}}{K_{CO_2} + CO_{2,\text{prod}}} \right) \left(\frac{I_{O_2}}{I_{O_2} + C_{O_2}} \right) \left(\frac{I_{\text{NO}_3}}{I_{\text{NO}_3} + C_{\text{NO}_3}} \right) E \quad [3.7]$$

where $\lambda_{\text{NO}_3}^{\text{het}}$ and $\lambda_{\text{SeO}_4}^{\text{het}}$ are the first-order rate constants [T^{-1}] for denitrification and SeO_4 reduction, respectively, K_{NO_3} is the Monod half-saturation constant for NO_3 [$\text{M}_f\text{L}_f^{-3}$]; I_{O_2} and I_{NO_3} are the O_2 and NO_3 inhibition constants [$\text{M}_f\text{L}_f^{-3}$], included to simulate the effect of higher-redox species; and $CO_{2,\text{prod}}$ is the amount of CO_2 produced during organic matter decomposition. The term E [-] is the environmental reduction factor that accounts for the tempering of the reaction rate according to current soil temperature and soil moisture. Reaction rate equations can be applied specifically to the fluid or solid phase, for mineralization or immobilization, and for autotrophic or heterotrophic reactions.

3.3.2. Se and N Reactive Transport in a Stream Network

The base numerical models for the Se in-stream fate and transport model are OTIS and QUAL2E, with OTIS used as the advection-dispersion solute transport engine and QUAL2E providing the basic in-stream water quality processes for O_2 , N species, and algae (Bailey and Ahmadi 2014). Figure 3.2A shows the conceptual model of the stream system and its interactions with the adjacent aquifer. The inclusion of O_2 and N species in the Se species model is essential for accurate simulation of Se fate and transport due to the inhibition of Se chemical reduction processes in the presence of O_2 and NO_3 (e.g. Weres et al. 1990; White et al. 1991). QUAL2E processes simulate the reactive behavior of O_2 , organic N, ammonia (NH_3), nitrite (NO_2), NO_3 , algae, and carbonaceous biological oxygen demand (CBOD) in a 1D stream

network setting, with major reactions governing N cycling, O₂ fate, algal growth and respiration, and algal uptake of N and O₂. Specific processes include atmospheric reaeration, algal respiration, sediment oxygen demand, nitrification of NH₃, and oxidation of NO₂. These processes are shown in Figure 3.2B. Algae concentration (C_{alg}) is determined by algal growth rate which is a function of the availability of nutrients, light (solar radiation), and water temperature. Reactions are simulated using first-order kinetics, with terms included to condition reaction rates on the presence or absence of O₂, depending on the reaction.

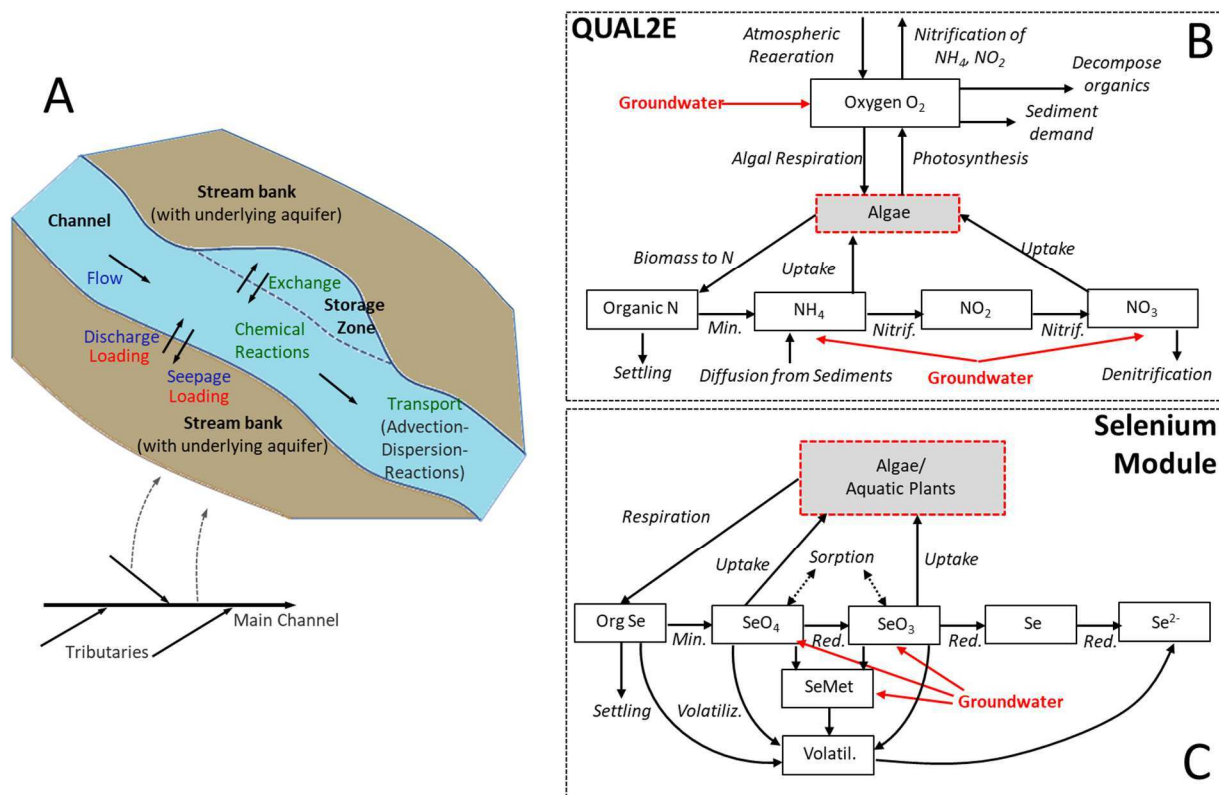


Figure 3.2: Conceptualization of (A) in-stream reactive transport processes addressed within OTIS-QUAL2E, with focus on (B) QUAL2E processes, and (C) the new Se processes module.

For 1D transport (i.e. solute concentration varies only in the longitudinal direction) that accounts for advection, dispersion, lateral inflow, lateral outflow, sorption, and biochemical reaction processes, the following partial differential equation (Runkel and Broshears 1991; Runkel 1998) is used

for each solute, with additional equations for the sorbate on the streambed (Bencala 1983) and the solid-phase species in the streambed:

Solute in the stream channel:

$$\frac{\partial C_j}{\partial t} = -\frac{Q}{A} \frac{\partial C_j}{\partial x} + \frac{1}{A} \frac{\partial}{\partial x} \left(AD \frac{\partial C_j}{\partial x} \right) + \frac{q_L}{A} (C_{L_j} - C_j) + S_j + r_j \quad j = 1, \dots, n \quad [3.8]$$

$$S_j = \bar{\rho} \lambda_{s_j} (C_j^* - K_d C_j) \quad [3.9]$$

Sorbate on the streambed:

$$\frac{\partial C_j^*}{\partial t} = -\frac{S_j}{\bar{\rho}} \quad [3.10]$$

Solid-phase species on the streambed:

$$\frac{\partial C_k^s}{\partial t} = r_{sol_k} \quad k = 1, \dots, w \quad [3.11]$$

where n is the number of dissolved-phase species, w is the number of solid-phase species in the streambed, C_j is the main channel concentration of the j^{th} dissolved-phase species [ML^{-3}], C_k^s is the main channel concentration of the k^{th} solid-phase species [MM^{-1}], t is time [T], Q is the volumetric flow rate [L^3T^{-1}], A is the main channel cross-sectional area [L^2], x is distance along the channel axis [L], D is the dispersion coefficient [L^2T^{-1}], q_L is the lateral inflow rate [$L^3T^{-1}L^{-1}$], C_{L_j} is the lateral inflow solute concentration of the j^{th} species [ML^{-3}], $\bar{\rho}$ is the mass of accessible sediment per volume of stream water [ML^{-3}], λ_s is the first order sorption rate coefficient [T^{-1}], C^* is the solute concentration on streambed sediment [MM^{-1}], K_d is the partition (distribution) coefficient [L^3M^{-1}], S represents the rate of change in solute mass concentration on the streambed [$ML^{-3}T^{-1}$], r represents the rate of change in solute mass concentration due to biochemical reactions [$ML^{-3}T^{-1}$], and r_{sol} represents the rate of change of solid phase species concentration due to biochemical reactions [$ML^{-3}T^{-1}$].

Chemical processes governing reactive transport of Se species in the stream system are shown in Figure 3.2C. Specific biochemical processes include algal uptake, algal biomass conversion to Se_{org} , settling, mineralization and assimilation, volatilization, chemical reduction, with first-order reaction rate laws adopted similar to those used in QUAL2E. The chemical reactions governing Se cycling include only chemical reduction. Although chemical oxidation does occur in natural systems, Se redox reactions proceed much faster in the direction of reduction (Cooke and Bruland 1987; Losi and Frankenberger 1998; Guo et al. 1999), with the slow rate of oxidation exacerbated in aquatic environments with high O_2 and nutrient concentrations (Losi and Frankenberger 1998). Hence, reduction rates represent the net chemical reduction of Se. For the current study, denitrification has been added as a first-order kinetic reaction, which proceeds at near-maximum rates when C_{O_2} is low.

Total organic Se (Se_{org}), excluding SeMet; SeO_4 ; SeO_3 ; total volatilized Se (Se_{vol}); and SeMet are treated as dissolved-phase species, with fate and reactive transport simulated using Equation 3.8, whereas Se^0 and Se^{2-} are treated as solid-phase species on the streambed, with transformations simulated using Equation 3.11. Solute mass exchange between the water column and the streambed due to net sorption is represented by Equation 3.9, and is operative only for SeO_4 and SeO_3 . Concentrations of sorbed SeO_4 and sorbed SeO_3 are calculated using Equation 3.10. The value of R in Equations 3.8 and 3.11 for Se_{org} , SeO_4 , SeO_3 , Se^0 , Se^{2-} , Se_{vol} , and SeMet is quantified by the following equations using first-order reaction rates, according to the sources and sinks for each species shown in Figure 3.2C:

$$r_{Se_{org}} = \left(\alpha_{Se} C_{alg} \gamma_{alg} \right) - \left(\sigma_{Se_{org}} C_{Se_{org}} \right) - \left(\lambda_{Se_{org}}^{min} C_{Se_{org}} \right) - \left(\lambda_{Se_{org}}^{vol} C_{Se_{org}} \right) \quad [3.12]$$

$$r_{SeO_4} = \left[\left(\lambda_{SeO_4}^{min} C_{SeO_4} \right) + \left(\lambda_{SeMet}^{min} C_{SeMet} \right) - \left(fr_{SeO_4} \alpha_{Se} \mu_{alg} C_{alg} \right) - \left(\lambda_{SeO_4} C_{SeO_4} \right) - \left(\lambda_{SeO_4}^{assim} C_{SeO_4} \right) - \left(\lambda_{SeO_4}^{vol} C_{SeO_4} \right) \right] \quad [3.13]$$

$$r_{SeO_3} = \left(\lambda_{SeO_4} C_{SeO_4} \right) - \left[\left(1 - fr_{SeO_4} \right) \alpha_{Se} \mu_{alg} C_{alg} \right] - \left(\lambda_{SeO_3} C_{SeO_3} \right) - \left(\lambda_{SeO_3}^{vol} C_{SeO_3} \right) - \left(\lambda_{SeO_3}^{assim} C_{SeO_3} \right) \quad [3.14]$$

$$r_{sol_{Se^0}} = (\lambda_{SeO_3} C_{SeO_3})^s - (\lambda_{Se^0} C_{Se^0}^s) \quad [3.15]$$

$$r_{sol_{Se^{-2}}} = (\lambda_{Se^0} C_{Se^0}^s) + (\lambda_{Se_{vol}} C_{Se_{vol}}) \quad [3.16]$$

$$r_{Se_{vol}} = (\lambda_{Se_{Org}}^{vol} C_{Se_{Org}}) + (\lambda_{SeO_4}^{vol} C_{SeO_4}) + (\lambda_{SeO_3}^{vol} C_{SeO_3}) + (\lambda_{SeMet}^{vol} C_{SeMet}) - (\lambda_{Se_{vol}} C_{Se_{vol}}) \quad [3.17]$$

$$r_{SeMet} = (\alpha_{Se}^{SeMet} C_{alg} \gamma_{alg}) - (\sigma_{SeMet} C_{SeMet}) - (\lambda_{SeMet}^{vol} C_{SeMet}) - (\lambda_{SeMet}^{min} C_{SeMet}) \quad [3.18]$$

where the subscripts of each variable refer to the Se species taking part in the process reaction; the superscripts *min*, *vol*, and *assim* refer to mineralization, volatilization, and assimilation; and α , γ , μ , σ , and λ refer to algal biomass fraction, algal death rate, algal growth rate, settling rate, and first-order rate coefficient, respectively.

Each first-order rate coefficient λ_j shown in Equations 3.12-3.18 is modified from a base value, $\lambda_{j,20}$ (at $T = 20^\circ\text{C}$) according to the water temperature T_{water} of the current day of the simulation (Brown and Barnwell 1987):

$$\lambda = \lambda_{20} 1.083^{(T_{water} - 20)} \quad [3.19]$$

The fraction of algal Se uptake corresponding to SeO_4 uptake is calculated according to the following equation, where f_{SeO_4} is the algal preference factor for SeO_4 (as opposed to SeO_3):

$$f_{SeO_4} = \frac{f_{SeO_4} C_{SeO_4}}{(f_{SeO_4} C_{SeO_4} + (1 - f_{SeO_4}) C_{SeO_3})} \quad [3.20]$$

The chemical reduction of SeO_4 , SeO_3 , Se^0 , and Se_{vol} is tempered by the presence of O_2 and NO_3 using inhibition constants which impede the rate of Se reduction, similar to those used for the reaction rates in groundwater shown in Equations 3.6 and 3.7. For SeO_4 reduction, the base rate constant is modified according to:

$$\lambda_{SeO_4} = \lambda_{SeO_4,20} \left(\frac{I_{O_2}}{I_{O_2} + C_{O_2}} \right) \left(\frac{I_{NO_3}}{I_{NO_3} + C_{NO_3}} \right) \quad [3.21]$$

where I_{O_2} and I_{NO_3} are the O_2 and NO_3 inhibition constants [ML^{-3}] and indicate the concentrations of O_2 and NO_3 at which λ_{SeO_4} is half of its base value. Similar equations are used for λ_{SeO_3} , λ_{Se^0} , and $\lambda_{Se^{2-}}$.

Both Se^0 and Se^{2-} are solid-phase species contained in the streambed sediment. The mass of Se that is transferred from dissolved-phase SeO_3 to solid-phase Se^0 via chemical reduction is converted to a solid concentration ($\mu g g^{-1}$) using the volume of stream water, the volume of accessible bed sediment, and the bulk density of the sediment. This is indicated by the s superscript for the SeO_3 reduction term in Equation 3.15. Once Se has become a particulate in the form of sorbed SeO_4 , sorbed SeO_3 , Se^0 , or Se^{2-} , it becomes a part of the net sediment sink where re-suspension into the water column does not occur.

The advection-dispersion equation (Equation 3.8) is solved using a Crank-Nicolson finite-difference solution (Runkel 1998), with the stream network divided into physically-uniform segments and each segment divided into a set of grid cells. Whereas the original OTIS model can be applied to a single stream and can account only for multiple, non-interacting species (Runkel 1998), the modeling code for this study was modified to simulate the fate of multiple interacting chemical species in a multi-stream network (Bailey and Ahmadi 2014). The 4th-order Runge-Kutta method was implemented to solve the system of ordinary differential equations required for simulating the kinetics of interacting species (Chapra 1997), and hence able to solve the QUAL2E and Se species' mass-balance equations. To implement OTIS in a multi-stream network, mass balance mixing calculations were used at stream junctions, with physical parameters and segment lengths of each stream specified.

The concentration for each solute is specified at the upstream end of the main stem of the stream and any originating tributaries. The model can operate under either steady or unsteady flow conditions. For steady, non-uniform flow, lateral inflow/outflow rates q_L are specified, with associated concentration values C_L for each solute. For a multi-stream network, flow rates are provided for each stream, with flow accumulating as tributaries discharge to the main stem of the channel. For unsteady,

non-uniform flow, segment-by-segment flow rates, lateral inflow/outflow rates, and cross-section areas must be provided by a streamflow routing model.

3.3.3. Coupling Groundwater-Surface Water Reactive Transport

Transfer of solute mass between the aquifer and streams occurs at each transport time step of the UZF-RT3D model. Typically, required time steps for the OTIS-QUAL2E component are much smaller than those for UZF-RT3D, e.g. an hourly time step vs. a daily time step. The data flow of the model is shown in Figure 3.3. The model begins by reading in all necessary inputs, including grid information, initial solute concentration for each grid cell in the aquifer and in the stream network and parameters defining chemical reactions in both the aquifer and the stream system. For each flow time step, volumetric water content, flow rates, and saturated zone hydraulic head values for each grid cell from a MODFLOW-SFR simulation (employing the SFR2 package) are read into the UZF-RT3D modeling code, followed by a loop through the transport time steps to simulate change in concentration of all species in the groundwater system due to advection (ADV), dispersion (DSP), source-sinking mixing (SSM), and chemical reactions (Reactions). The OTIS-QUAL2E subroutine (SWT) then is called, with groundwater concentrations in cells adjacent to streams used as input to OTIS for lateral inflow if groundwater discharge is simulated by MODFLOW-SFR, and surface water concentrations used for lateral outflow if stream seepage is simulated by MODFLOW-SFR. OTIS-QUAL2E then loops through the specified surface water transport time steps, and then maps concentration values to UZF-RT3D grid cells in preparation for the next groundwater transport time step.

All subroutine required for OTIS-QUAL2E and linking with UZF-RT3D are contained in a new Surface Water Transport (SWT) package within RT3D-OTIS, which can be turned off to revert to the original UZF-RT3D simulations.

3.3.4. Additions for Flow and Transport in Irrigated Areas

Two additional modifications to the code were made to account for the movement of water and associated solute mass in a managed irrigated area. First, additional subroutines were included to account for the effect of tailwater runoff, both flow rates and solute mass in the water, on nearby streams. Calculated tailwater volumes for each irrigated field can be added to the appropriate SFR2 stream segment at the same time step, with associated solute concentration equal to the concentration in the applied irrigation water. Solute concentration in the canal and applied irrigation water can be determined in one of two ways. First, it can be specified in UZF-RT3D input files according to field-sampled values; or second, it can be provided by the OTIS-QUAL2E-simulated concentration at the point of canal diversion from the main reach of the river, if this point is located within the model domain.

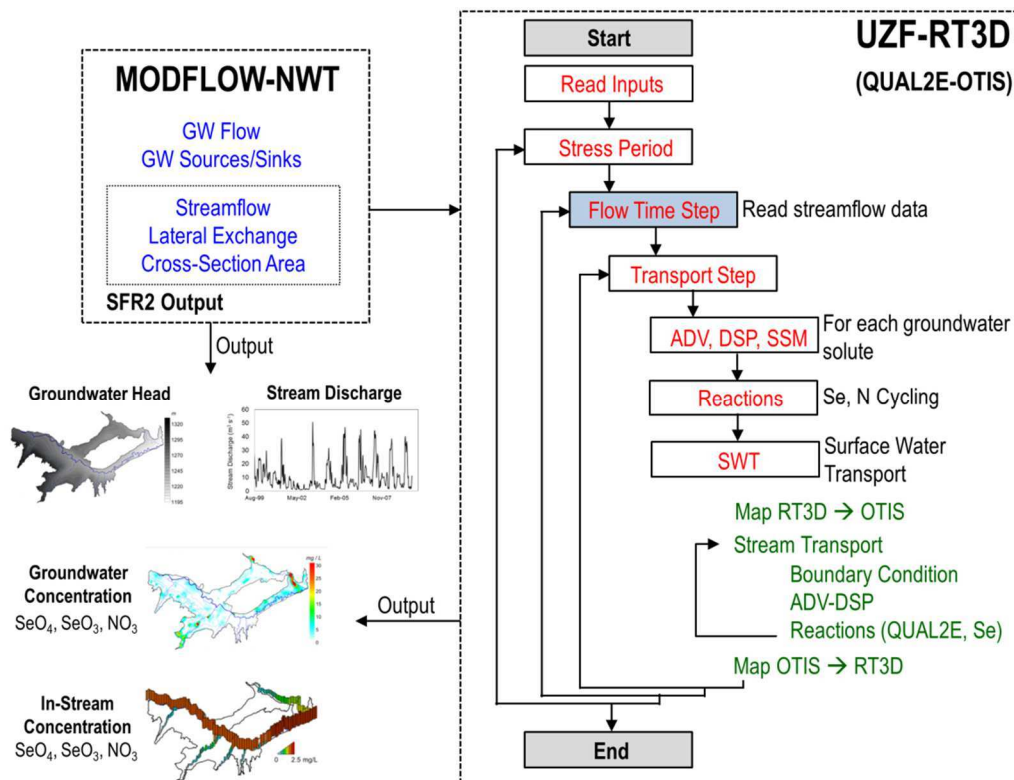


Figure 3.3: Coupling and major components of the stream and aquifer flow and transport models.

3.4. Application to the Lower Arkansas River Valley, Colorado

The LARV in semi-arid southeastern Colorado faces numerous challenges that are not uncommon in intensively-irrigated alluvial valleys. For more than 125 years, an extensive network of earthen canals has diverted irrigation flows from the Arkansas River for distribution over valley cropland which currently covers about 109,000 ha. Canal seepage and irrigation application in excess of crop evapotranspiration make their way back to the river and its tributaries in surface and subsurface flows. Subsurface return flows, coupled with evaporative concentration, have led to shallow saline groundwater tables which hinder crop productivity. Moreover, these excess flows, laden with O_2 and with NO_3 from applied fertilizers, move through weathered, near-surface, and bedrock Cretaceous shale formations dissolving and pushing salts, Se, and uranium (U) into the stream network (Gates et al. 2009 2016; Bern and Stogner 2017). Surface return flows also pick up salts, NO_3 , and Se in route back to the stream system. The result is river and tributary concentrations that threaten wildlife, livestock, and human health.

The performance of the developed stream-aquifer model is illustrated in application to a region that is representative of conditions in the LARV upstream of John Martin Reservoir. The region, called the upstream study region (USR), in contrast to a downstream study region (DSR) located downstream of John Martin Reservoir, covers about 50,600 ha (506 km²) (Figure 3.4). Field data gathered in the USR over 2006 – 2011 indicate that C_{Se} is about 3 times the CDPHE regulatory standard of 4.6 $\mu g L^{-1}$ and that the NO_3 species concentration (C_{NO_3-N}) alone is approaching the interim standard of 2 mg L^{-1} for total dissolved N ($NO_3 + NO_2 + NH_4$).

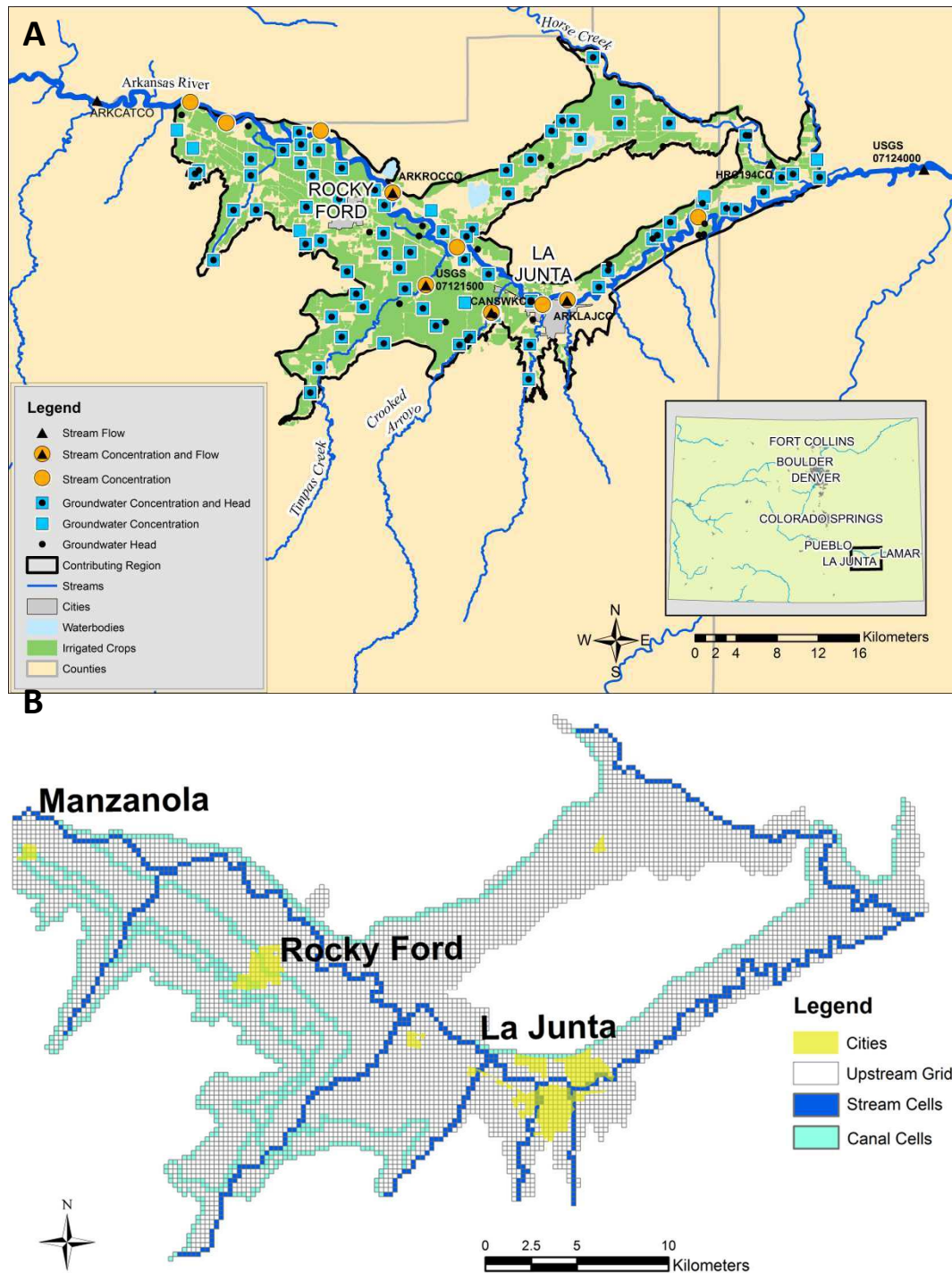


Figure 3.4: (A) The LARV USBR, showing the location of stream flow and concentration measurements, and groundwater head and concentration measurements; and (B) the areal finite difference computational cells for the coupled models.

The finite difference grid for the stream-aquifer model of the USR consists of 7777 cells of areal dimension 250 m x 250 m (Figure 3.4), with three vertical layers used in MODFLOW-SFR and seven overlapping vertical layers used in RT3D-OTIS. The river is represented by 44 segments in MODFLOW-SFR containing a total of 689 computational cells and by about 13 overlapping segments in RT3D-OTIS. The MODFLOW-SFR time steps are weekly and the RT3D-OTIS concurring time steps are daily, embedded with hourly time steps in OTIS. Groundwater flow and transport boundary conditions are treated as described in Morway et al. (2013) and Bailey et al. (2014).

3.4.1. Model Calibration and Testing

The procedure for calibrating and testing the MODFLOW-SFR and RT3D-OTIS models in application to the LARV USR is outlined in Figure 3.5 and generally follows the guidelines described by Anderson et al. (2015) and Zheng and Bennet (2002) for achieving a reasonable match between simulated and observed values of target variables. Calibration began with manual adjustment of SFR2 parameter values in MODFLOW-SFR to assure a comparable performance with the MODFLOW-RIV model previously calibrated and tested for the LARV USR by Morway et al. (2013). Next, the RT3D-OTIS model was calibrated using a “history matching” approach wherein manual and automated methods were guided by sensitivity analysis and applied to compare simulated values with values observed over a historic period. Finally, a 33-year model spin-up was performed using the calibrated model parameters and outputs were checked to assure they were physically reasonable. This resulted in a coupled model which was used to simulate long-term baseline conditions in the LARV USR.

3.4.1.1. MODFLOW-SFR Refined Calibration

Modeling flow and reactive solute transport in the Arkansas River and its tributaries, in consideration of the effects of groundwater flow exchange, required that the MODFLOW-RIV model, originally developed and calibrated by Morway et al. (2013), be altered to include the SFR2 package. Output from this updated MODFLOW-SFR model was compared with output from the original calibrated

MODFLOW-RIV model and with supplemental field data to guide a refined calibration that would ensure that the updated flow model adequately represents the system. Five calibration targets were used to assess the MODFLOW-SFR output: measured groundwater hydraulic heads, estimated groundwater return flows, unaccounted-for return flows derived from a river mass balance, evapotranspiration (ET) estimated from a satellite remote-sensing model, and gaged stream flow.

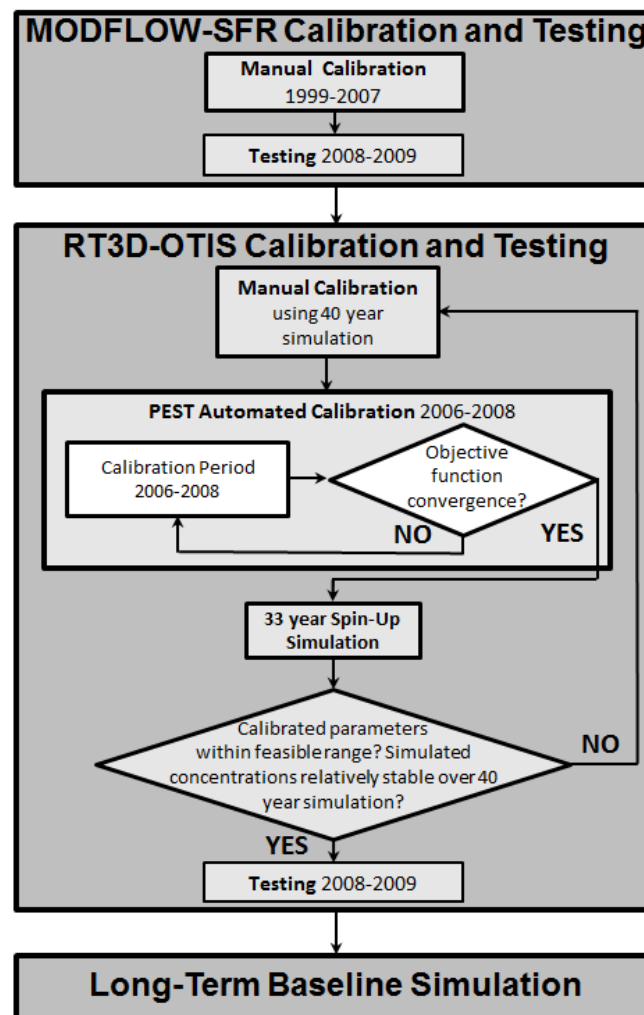


Figure 3.5: Workflow chart for calibration, testing, and application of the coupled flow and transport models for the LARV USR.

The unconfined groundwater hydraulic head computed by the MODFLOW-SFR model was compared to the hydraulic head derived from a total of about 8704 water table measurements taken

over the period April 1999 – October 2007 in 88 monitoring wells spread over the USR (Figure 3.4) and which were previously used to calibrate and test the MODFLOW-RIV model (Morway et al. 2013). The refined calibration of the MODFLOW-SFR model was tested against an additional 699 water table measurements from these wells gathered over November 2007 – December 2009. Simulated groundwater heads were compared to observed values using the sum of the squared residuals (differences), along with the mean and standard deviation of the residuals. In interpreting residual values it was important to take into account the difference in the temporal and spatial scales of the simulations and the observations. Simulated hydraulic heads represent averages over a time step of one week and over a 6.25 ha (250 m by 250 m) computational cell, whereas observed values are measured instantaneously in monitoring wells, each having a cross sectional area covering only a few square centimeters situated within a computational cell. Morway et al. (2013) estimated the uncertainty associated with the discrepancy in temporal scales by a statistical analysis of the residuals between groundwater levels measured hourly by pressure transducers and the corresponding weekly-averaged values in a number of monitoring wells in the LARV. They similarly assessed the uncertainty connected to the spatial scale discrepancy by analyzing in about two dozen intensively-monitored fields (of similar area to the computational cell size) the residuals between groundwater levels measured in multiple monitoring wells within a field and the corresponding spatial average over the field. Measurement error within an individual well was considered negligible ($\sim \pm 0.01$ m). Average residual values between the simulated and observed groundwater heads also were plotted over the model grid using inverse distance weighting to obtain estimates near the streams to aid in identifying locations where parameter adjustments were needed.

Groundwater return flow to the Arkansas River and its tributaries simulated by MODFLOW-SFR was compared to that simulated by the MODFLOW-RIV model previously calibrated by Morway et al. (2013) using groundwater return flow rates estimated from a river mass balance over the period April

1999 – March 2004 and was tested using similar data over the period April 2004 to October 2007. Also, in the current study a stochastic river mass balance model of the study region developed by Gates et al. (2017) for the period October 2006 to December 2009 afforded an additional calibration target. Gates et al. (2017) considered uncertainty associated with measurement error, regression relationships between variables, and spatial variability to estimate a probability distribution of daily unaccounted-for return flow, along with Se and NO₃ loading, to the Arkansas River along the USR. Unaccounted-for return flows are flows not directly accounted for in the river mass balance through gaged tributary flows, canal diversions, the La Junta wastewater treatment effluent, evaporative losses, or channel storage change. They include groundwater exchange with the Arkansas River, as well as surface flows to the river through ungaged tributaries and direct overland runoff. Values of these collective return flows simulated by MODFLOW-SFR were evaluated by plotting them in comparison to the statistics of the stochastic mass balance.

Finally, ET values computed by the MODFLOW-SFR model were compared to values for corn, a major crop in the area, along with those for six more minor crops, computed using the RESET model (Elhaddad and Garcia 2008, 2011) for the 2004, 2005, and 2006 irrigation seasons. Comparisons were not made for pasture or alfalfa, the dominant crop in the region, due to difficulties in estimating ET over long periods for these crops using RESET (Gates et al. 2012). RESET uses climatic data gathered by weather stations in the USR, along with crop growth data, to interpolate between instantaneous estimates of actual ET for these crops calculated from visible, infrared, and thermal bands detected by satellite images. The percent difference was computed between ET computed by MODFLOW-SFR on selected cropped cells (with greater than 99% crop coverage) and that estimated by the RESET model. Percent error in relation to RESET was not computed since remote sensing estimates of ET are still subject to considerable uncertainty; however, a percent difference comparison was deemed helpful since the two methods should reveal order-of-magnitude similarity.

Flow rates measured at six stream gages were compared to the flows simulated by MODFLOW-SFR for the stream segments (ranging in length from 25 m to 345 m, and averaging 229 m) containing or near the stream gages throughout the 1999-2009 simulation period. The gages used in the comparison are Colorado Division of Water Resources (CDWR) ARKROCCO on the Arkansas River near Rocky Ford, CDWR ARKLAJCO on the Arkansas River at La Junta, US Geological Survey (USGS) 07124000 on the Arkansas River at Las Animas, CO, USGS 07121500 on Timpas Creek at the mouth near Swink, CO., CDWR CANSWKCO on Crooked Arroyo near Swink, CO, and CDWR HRC194CO on Horse Creek at Highway 194 (Figure 3.4). The raw gage data, gathered on 15-min intervals, were averaged over each weekly time step used in the MODFLOW-SFR model for comparison. The magnitude and pattern of simulated and measured stream flows were compared visually in plots and quantitatively using the Nash-Sutcliffe Coefficient of Efficiency (NSCE) (Nash and Sutcliffe 1970), the coefficient of efficiency (E) (Legates and McCabe 1999), the volumetric efficiency (VE) (Criss and Winston 2008), and the coefficient of determination (R^2). These performance measures generally range from 0 to 1, with 1 indicating an ideal match between simulated and observed values; however, values for NSCE and E can be negative for cases of poor match. Uncertainty due to measurement error in the gaged flow was estimated using USGS accuracy ratings (Novak 1985) of “good” which indicates a 95% inter-percentile range (difference between the 97.5th percentile and the 2.5th percentile values) that corresponds to the range between $\pm$ 10% of the measured value for gages ARKLAJCO and 07124000; “fair” (95% inter-percentile range between $\pm$ 15% of the measured value) for gages ARKROCCO, 07121500, and CANSWKCO; and “poor” (95% inter-percentile range between $\pm$ >15% of the measured value) for HRC194CO. Data were not available for assessment of uncertainty associated with spatial scale discrepancy between flow rate simulated as an average over a stream segment and flow rate measured at a stream gage located within the stream segment.

Land surface elevation was used to delineate sub-watersheds within the model domain and total surface runoff from both irrigation and precipitation was routed from the MODFLOW cells within a sub-watershed to the associated SFR segment. The computations for surface runoff within each delineated sub-watershed were conducted external to MODFLOW-SFR and were added to the SFR input file for each stream segment.

To achieve a good match to the calibration targets, it was necessary to adjust only the values of streambed conductance assigned to the SFR2 stream reaches in the Arkansas River and its tributaries; values of other aquifer parameters, as previously calibrated and reported by Morway et al. (2013), were retained. Unit streambed conductance (defined as $c_{sb} = K_{sb}P_{sb}/M_{sb}$ where K_{sb} is the hydraulic conductivity of the streambed material [L/T], P_{sb} is the wetted perimeter of the streambed [L], and M_{sb} is the thickness of the streambed material [L]) is used in calculating the rate of stream-groundwater exchange employing computed values of the hydraulic gradient between the groundwater elevation adjacent to a stream cell and the water surface elevation in the stream (Prudic et al. 2004, Niswonger and Prudic 2005). Initial estimates of c_{sb} were taken from the previously-calibrated MODFLOW-RIV model. Values were adjusted manually within the SFR2 package to yield a sufficiently-calibrated MODFLOW-SFR model. This was accomplished by successively running the model and adjusting c_{sb} values until an acceptable match between plots of simulated results and the various calibration targets was obtained.

3.4.1.2. RT3D-OTIS Calibration and Testing

A calibration of stream reactive transport parameters, as well as an adjustment to the calibration by Bailey et al. (2014) of selected groundwater reactive transport parameters, was necessary to insure that the coupled RT3D-OTIS model adequately represents both groundwater and stream conditions in the LARV USR. Model input parameters were altered within a physically-realistic range of values reported in the literature to obtain simulated groundwater concentrations, mass loading to the Arkansas River, and stream concentrations that reasonably matched field observations and mass

balance estimates for both Se and NO₃. A recursive manual and automated calibration using the Parameter ESTimation (PEST) software package (Doherty 2016) was performed as part of the overall calibration process. Field data on Se and NO₃ concentrations and mass loads were available during 2006-2009, providing a model calibration period defined as June 19th, 2006 to March 20th, 2008 and a separate model testing period as March 21st, 2008 to October 31st, 2009. Six different calibration targets were assessed: average groundwater C_{Se} in defined grouping areas, average groundwater C_{NO_3-N} in the grouping areas, unaccounted-for mass loading of Se and NO₃ to the Arkansas River, C_{Se} in stream segments containing observations, and C_{NO_3-N} in stream segments containing observations.

Performance of the RT3D-OTIS model in predicting C_{Se} and C_{NO_3-N} in groundwater was judged using a methodology similar to that described by Bailey et al. (2014) who grouped measurements of groundwater concentration in monitoring wells according to the location of the wells within canal command areas. In the present study, concentration measurements were grouped within areas that were defined by their proximity to 13 respective OTIS stream segments along the modeled tributaries and the reaches of the Arkansas River located between the tributaries. The rationale for this grouping was the assumption that groundwater reactive transport parameters should be calibrated in a manner that achieves an acceptable match to both groundwater concentration targets within the grouping area and to surface water concentrations in the adjacent stream reaches. Depth-averaged simulated values of C_{Se} and C_{NO_3-N} in groundwater cells within each grouping area were compared with statistics of corresponding observed values. Analogous to the method used for groundwater levels and stream concentrations, uncertainty connected with differences in spatial and temporal scales of observed and simulated groundwater concentrations and with measurement error was described using a composite CV derived from a statistical analyses of the residuals of electrical conductivity (EC; measured as specific

conductance at 25°C) measured in multiple monitoring wells from temporal and spatial average EC values and of pairwise differences in duplicate sets of C_{Se} and C_{NO_3-N} samples.

Stochastic estimates by Gates et al. (2017) of unaccounted-for Se and NO_3 mass entering the Arkansas River also were used in the calibration process. The approach was similar to that described for the evaluation of unaccounted-for return flows simulated by MODFLOW-SFR. Results from the stochastic mass balance were available only for dates within the period October 1st 2006 to October 31st 2009 when both EC and flow data were available at the stream gages. Simulated mass loading over these dates were compared to statistics characterizing the estimated uncertainty in the river mass balance calculations. The time-averaged value of the ensemble CV was used as a composite measure of the level of uncertainty in Se and NO_3 loads computed by river mass balance analysis.

Stream concentrations determined from instantaneous water samples gathered in the field were compared to simulated values for each computational stream segment that contained a sample location and for the corresponding day that the sample was collected. Four dates of observations within the calibration period were available for use: 6/19/2006, 5/23/2007, 10/6/2007, and 3/20/2008; and five dates within the testing period were available: 6/23/2008, 8/14/2008, 1/15/2009, and 7/22/2009. In total, there are seven sampling locations within the Arkansas River and three within selected tributaries. Simulated and observed values were plotted and compared, keeping in mind the difference in temporal and spatial scales between simulations and observations. To estimate the uncertainty related to discrepancy in the temporal scale, an analysis was conducted of the temporal variability in the residuals of instantaneous (either 15-min or 30-min intervals) measurements of EC from the daily-average EC value, based upon a previously-determined correspondence of EC with C_{Se} and C_{NO_3-N} (Gates et al. 2017). The computed coefficient of variation (CV) of these residuals was used to represent the uncertainty associated with temporal-scale discrepancy between observed and simulated values of

C_{Se} and C_{NO_3-N} . The lack of synoptic samples, either in the present study or in the literature, from multiple locations along the extent of a modeled river segment (with lengths ranging from 32 m to 92 m, and averaging 57 m in OTIS) prevented a similar analysis of uncertainty associated with incongruity in the spatial scale. Instead, the CV representing uncertainty in spatial-scale discrepancy between C_{Se} and C_{NO_3-N} values measured at a point within a computational river segment and the model-computed average values over the river segment was assumed to be equal to the CV computed for the temporal-scale uncertainty. Uncertainty due to measurement error was assessed using the CVs of pairwise differences between values of C_{Se} in 40 duplicate sample sets and between values of C_{NO_3-N} in 108 duplicate sample sets from streams and groundwater. A composite measure of uncertainty derived from spatiotemporal variability and measurement error was computed as the square root of the sum of the squares (Casella and Berger 2002) of the CVs for temporal-scale discrepancy, spatial-scale discrepancy, and measurement error.

A combination of manual and automated calibration, guided by earlier investigations and sensitivity analyses, was used to adjust selected groundwater and surface water parameters to achieve an adequate match of RT3D-OTIS simulations to the six calibration targets within the LARV USR. The calibration procedure is outlined in the following steps, with more details provided in the appendices of Shultz (2017):

- (1) Several chemical reaction rates within the computational cells that represent the riparian corridor adjacent to the Arkansas River and its tributaries were selected for adjustment: rates of heterotrophic chemical reduction of NO_3 and SeO_4 , $\lambda_{NO_3}^{het}$ and $\lambda_{SeO_4}^{het}$, respectively; the rate of heterotrophic reduction of SeO_3 to elemental Se, $\lambda_{SeO_3}^{het(Se(0))}$; the rate of heterotrophic reduction of SeO_3 to mobile SeMet, $\lambda_{SeO_3}^{het(SeMet)}$; and the rate of heterotrophic reduction of SeMet, λ_{SeMet}^{het} ;

along with the Monod half-saturation constant for Se, K_{Se} . This approach was based upon previous studies which cite the key role that heterotrophic chemical reduction plays within riparian and hyporheic zones in lowering the concentration of redox-sensitive pollutants in waters exchanged with streams (Hill 1996, Spruill 2000, Vidon and Hill 2004, Dosskey et al. 2010, Ranalli and Macalady 2010, Bailey et al. 2015, Huizenga et al. 2017).

- (2) Results from a sensitivity analysis performed by Heesemann (2016) informed the choice of which stream reaction parameters to calibrate. Using a one-at-a-time (OAT) method which incrementally adjusted parameter values over a range of 0.1 to 10 times the initial values obtained from the literature (Bailey and Ahmadi 2014), Heesemann (2016) found that simulated values of C_{Se} and C_{NO_3-N} in the Arkansas River and tributaries were most sensitive to the stream reaction parameters λ_{SeO_4} , λ_{SeO_3} , $K_{d_{SeO_4}}$, $K_{d_{SeO_3}}$, $\lambda_{SeO_4}^{vol}$, and λ_{Se}^{vol} . Heesemann (2016) also discovered a need to adjust the groundwater chemical reduction parameters $\lambda_{NO_3}^{het}$ and $\lambda_{SeO_4}^{het}$ within the riparian corridor along with a parameter, DF_{NO_3-N} , that was used to scale estimates of C_{NO_3-N} in surface drainage from irrigated fields in relation to that in the irrigation water applied to the fields. Following these findings, and in consideration of other factors, the parameters λ_{SeO_4} , $\lambda_{SeO_4}^{vol}$, $\lambda_{SeO_4}^{assim}$, and DF_{NO_3-N} were chosen for calibration in the current study. With the aim of fine tuning model simulations of the total amount of Se and NO_3 adsorbed by streambed sediments, the mass of accessible sediment, $\bar{\rho}$, was chosen for calibration in lieu of the partitioning coefficients, $K_{d_{SeO_4}}$ and $K_{d_{SeO_3}}$, used to compute R_k in Eq. (8).
- (3) All parameters, including those selected for calibration, initially were set to values that had been previously determined by Morway et al. (2013), Bailey et al. (2014), Bailey and Ahmadi (2014), and Heesemann (2016). Next, a long-term (40-yr) simulation of the USR, consisting of 3.5

successive runs of 1999 – 2009 hydrologic and irrigation conditions, was conducted using RT3D-OTIS. Boundary conditions on river flow and C_{Se} and C_{NO_3-N} concentrations at the upstream end of the modeled reach of the Arkansas River along the reach were estimated using stream gage data and regression equations developed by Gates et al. (2017). These equations relate C_{Se} and C_{NO_3-N} to EC and Q at stream gage locations along the modeled reach and were extrapolated upstream to estimate concentrations of flows entering the model domain in the Rocky Ford Highline and Otero canals whose diversion headgates on the river are located about 54 km and 16 km, respectively, from the upstream boundary of the modeled reach. Due to lack of data, initial conditions on C_{Se} and C_{NO_3-N} along the modeled reach were set equal to estimated initial values at the upstream boundary. Resulting values of the variables related to the different calibration targets computed during the calibration period of June 19th, 2006 to March 20th, 2008 were examined as described above and a successive series of manual adjustment, followed by a re-run of the long-term simulation, was carried out. During the course of the manual calibration, it was deemed necessary to add $\lambda_{NO_3}^{auto}$, $\lambda_{NO_3}^{het}$, $\lambda_{SeO_4}^{het}$, $\lambda_{SeO_3}^{het(Se(0))}$, $\lambda_{SeO_3}^{het(SeMet)}$, λ_{SeMet}^{het} , and K_{Se} within the non-riparian areas to the set of parameters to be calibrated, in order to achieve a better match to observed values of C_{Se} and C_{NO_3-N} in both the streams and the groundwater grouping areas.

- (4) Using parameter values obtained from the manual calibration described in step (3), PEST was used, in conjunction with manual adjustment, to further refine the calibration. PEST iteratively adjusts parameter values to minimize the sum of the squared weighted residuals (the objective function) between the simulated values and observed values of all variables associated with the six designated calibration targets during the calibration period, June 19th, 2006 to March 20th, 2008:

$$\text{Min } \Phi = \sum_{i=1}^6 \sum_{j=1}^{N_i} (w_{u_i} w_{n_i} r_{i,j})^2 \quad (22)$$

Where Φ is the objective function, N_i is the number of variables associated with the i th calibration target, w_{u_i} is the weight assigned to address uncertainty in the variables associated with the i th calibration target, w_{n_i} is the normalization weight for all of the variables associated with the i th calibration target, and $r_{i,j}$ is the residual between the simulated value and observed value for the j th variable of the i th calibration target. The weights w_{n_i} were used to normalize the $r_{i,j}$ values of variables, which differ in number and measurement scale among the six calibration targets used in this study. Values of w_{n_i} were calculated by requiring the sum of squared products of each w_{n_i} with the observed variable values corresponding to the i th calibration target to be equal across all calibration targets. Each weight w_{u_i} was computed as the inverse of the estimated composite CV of the variables associated with the i th calibration target, thereby assigning a larger weight to values with a greater uncertainty. The calibrated parameter values determined by PEST were used in another 40-yr simulation to check for unreasonable long-term drift in simulated concentrations and loads. Such drift might indicate that parameter adjustments might have been excessive since their full effect on groundwater and stream concentrations could not be predicted within the relatively short calibration period. Further manual adjustment of PEST-calibrated parameter values was conducted to remove such long-term drift.

- (5) Using the final calibrated parameter values, the model was run for a 33-yr period as a spin-up simulation (Ajami et al. 2014). The spin-up simulation is used to achieve a dynamic equilibrium condition at the end of the 33-yr period that establishes the initial groundwater concentrations in the final baseline simulation.

(6) A further confirmation of the calibrated model was made by comparing model simulations to observed values within the test period, March 21st, 2008 to October 31st, 2009.

3.4.1.3. Calibration Results

3.4.1.3.1. MODFLOW-SFR Refined Calibration and Testing Results

Temporal averaged values of c_{sb} in the SFR stream segments, determined from manual calibration, varied from $0.67 \text{ m}^2 \text{ d}^{-1} \text{ m}^{-1}$ to $23,700 \text{ m}^2 \text{ d}^{-1} \text{ m}^{-1}$ with an average value of $537 \text{ m}^2 \text{ d}^{-1} \text{ m}^{-1}$ over the stream segments in the Arkansas River and from $0.005 \text{ m}^2 \text{ d}^{-1} \text{ m}^{-1}$ to $50.6 \text{ m}^2 \text{ d}^{-1} \text{ m}^{-1}$ with an average value of $9.7 \text{ m}^2 \text{ d}^{-1} \text{ m}^{-1}$ over the stream segments in the tributaries. These values are comparable to those reported and used in the literature for alluvial streams (Hunt et al. 2001, Chen and Shu 2002, Fox 2007).

In Figure 3.6 are frequency histograms of groundwater head residuals, computed as the difference between MODFLOW-SFR simulated groundwater head and the groundwater head observed in the monitoring well situated within each corresponding computational cell. These residuals, presented for both the calibration and testing periods, indicate a strong model performance in simulating groundwater head. On each histogram are black bars depicting the standard deviation inter-percentile range of the residuals, which is the range between the mean plus one standard deviation and the mean minus one standard deviation. The red bars represent a corresponding standard deviation inter-percentile range computed using the CV representing uncertainty due to spatial and temporal scale discrepancy between simulated and observed groundwater head, estimated as described above. Comparison of the red with the black bar provides an indication of the fraction of the total variability in the residuals that is contributed by scale discrepancy. The root mean square error (RMSE) of the simulated values compared to the observed values was 2.23 m and 2.83 m for the calibration and testing periods, respectively. The average residual was 0.02 m and 0.41 m for the calibration and testing periods, respectively. The calibration period residuals shown in Figure 3.6A for the MODFLOW-SFR

model are very similar to those determined for the MODFLOW-RIV model calibrated by Morway et al. (2013).

Figure 3.7 shows the simulated total groundwater return flows to both the Arkansas River and its tributaries on a week by week basis for both the MODFLOW-SFR model and the previously-calibrated MODFLOW-RIV. In Figure 3.8 the groundwater plus unmeasured surface return flow simulated by MODFLOW-SFR are compared to the mean and 95% inter-percentile range estimated by stochastic river mass balance (Gates et al. 2017). There is an estimated 95% probability that the actual groundwater plus unmeasured surface return flow lies within this range. These results reveal that while the MODFLOW-SFR model generally predicts larger groundwater return flows than the MODFLOW-RIV model over the calibration period, these higher rates bring the simulated total groundwater and unmeasured surface return flows closer to those estimated by the stochastic mass balance over the period October 2006 – December 2010. There are, however, some short-duration spikes in the mass balance estimates that are not captured in the MODFLOW-SFR simulation. One explanation for these spikes is the occurrence of large scale precipitation events. While MODFLOW-SFR routes precipitation applied to the land within the model domain, flows in tributaries coming into the model domain from precipitation runoff upstream are assumed to be negligible. Markers in Figure 3.8 show the time of precipitation events within the model domain that were estimated greater than 2.5 cm (1 inch) in depth. These events appear to account for some of the spikes in the mass balance results but not all of them. It is possible that other large precipitation events, occurring entirely outside of the model domain, are responsible for the remaining spikes.

ET from cropped cells computed by the MODFLOW-SFR model was compared to that computed by the RESET model over the same time period. The average percent differences over the years 2004 - 2006 were 0.1% for melons which cover about 1.5% of the cropped area in the USR over the 2004 – 2006 period, 0.2% for corn which covers about 9%, 5.4% for vegetables which covers about 1%, 12.8%

for beans which cover about 5%, 32.6% for onions which cover about 1%, 38.1% for spring grain which covers about 6%, and 44.3% for sorghum which covers about 12%. During the 2004 – 2006 period, when RESET data were available for comparison, the percentage of cropped area planted to corn was unusually low and that planted to sorghum was unusually high. During the cropping seasons within the entire calibration and testing period of 1999 – 2009, crop coverage percentages for corn and sorghum were 15.8% and 6.7%, respectively.

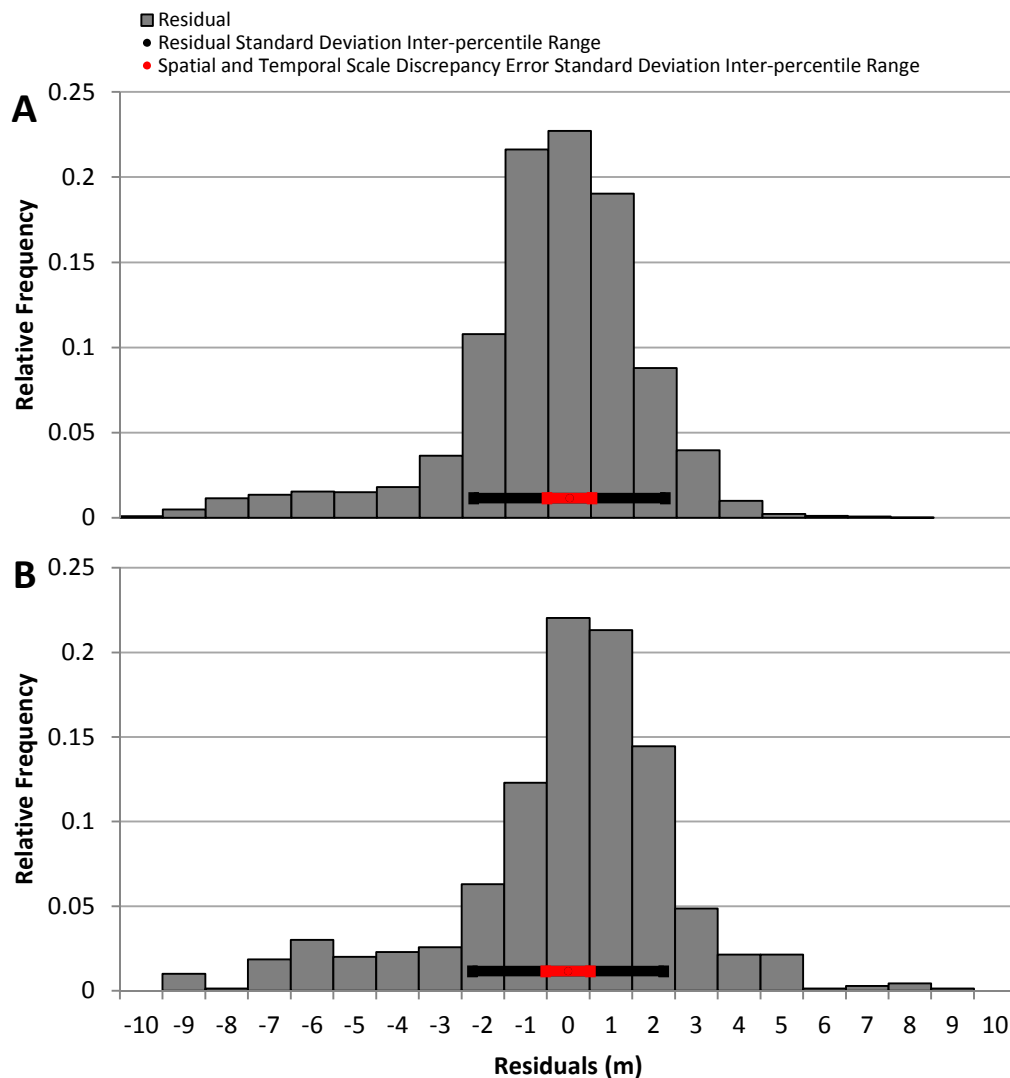


Figure 3.6: Frequency histograms of residuals of MODFLOW-SFR simulated minus observed groundwater elevations over (A) the January 1999 to October 2007 calibration period and (B) the November 2007 to December 2009 testing period.

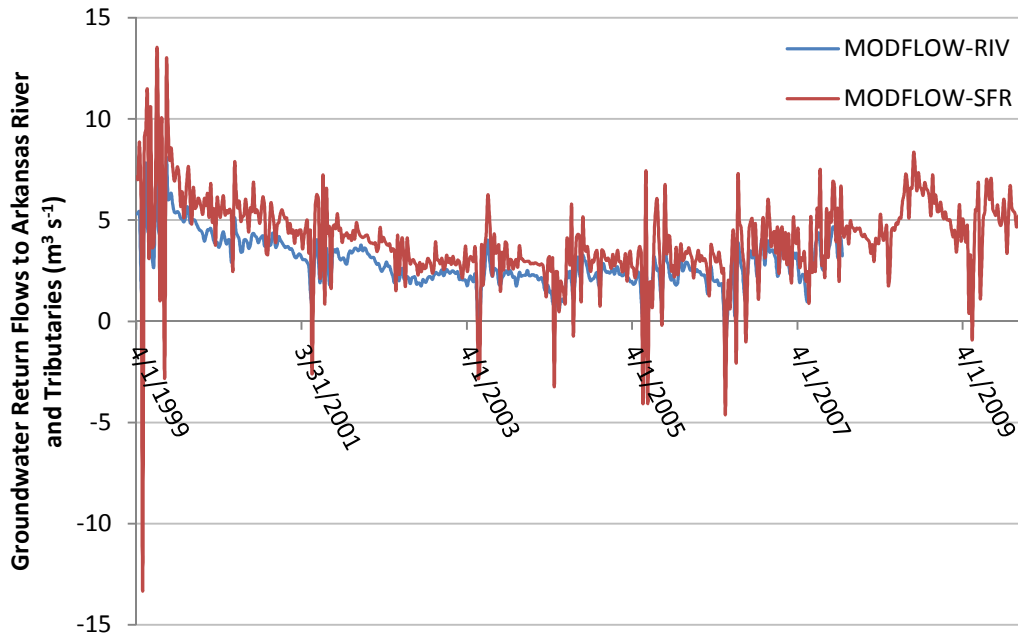


Figure 3.7: Comparison of total groundwater return flows to the Arkansas River and tributaries simulated by the MODFLOW-RIV (Morway et al. 2013) and MODFLOW-SFR models.

Finally, Figure 3.9 shows comparative time series of weekly average flow rate measured at stream gages ARKROCCO, ARKLAJCO, and 07124000 on the Arkansas River along with simulated flow rates which represent both a weekly average and an average over the corresponding river segment containing the stream gage. Uncertainty due to measurement error is depicted by the 95% inter-percentile range based upon the USGS accuracy rating. Though it could not be evaluated quantitatively, spatial scale discrepancy undoubtedly also contributes to ambiguity in the observed flow rates. These plots depict a generally good correspondence between simulated and observed streamflows in both magnitude and temporal variability. Table 2 summarizes the comparison of the model-predicted flows with the gaged values using the performance measures described above. Results indicate a fairly good match for the Arkansas River segments but a poorer match for the tributaries. The model performed more poorly in simulating tributary flows due to the assumption that inflow into the upstream end of

the tributaries from outside the model domain was typically negligible and due to difficulty in matching the timing and rate of return flows to tributaries.

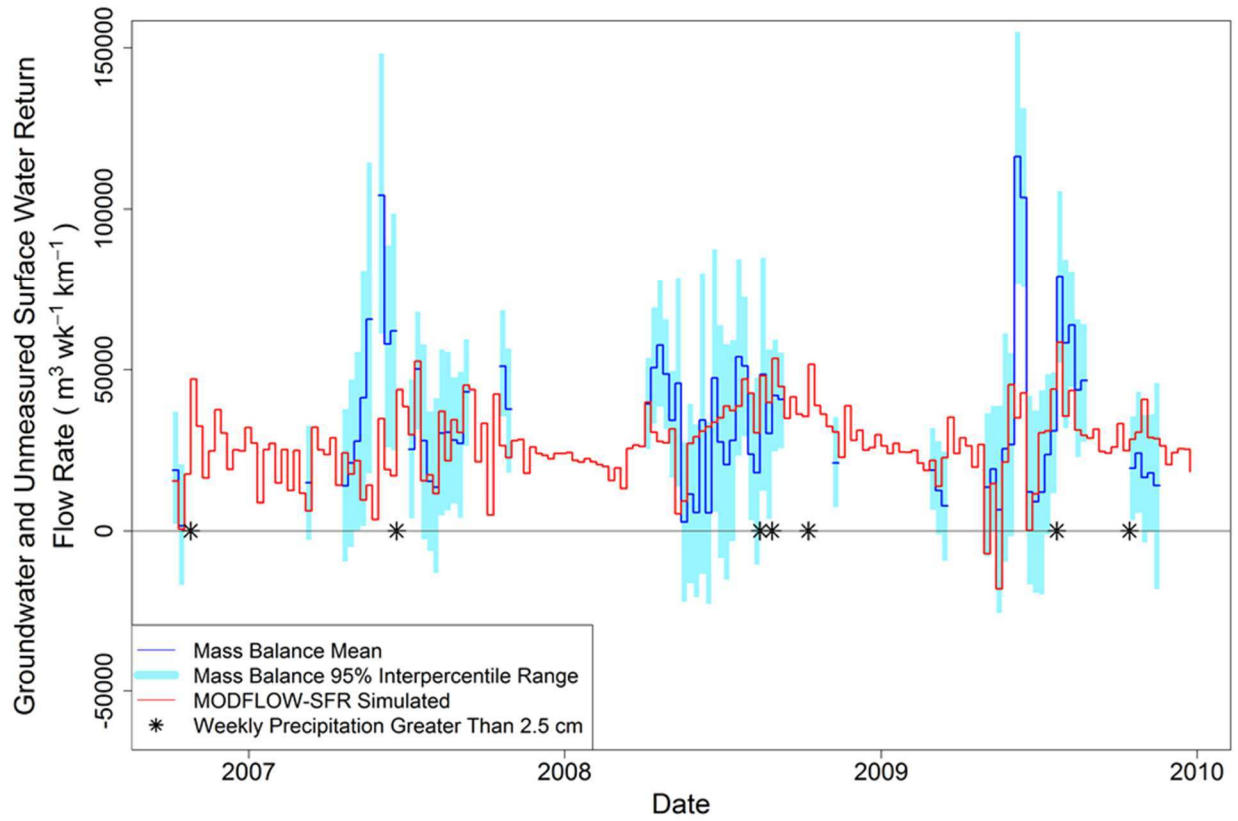


Figure 3.8: Comparison of return flows simulated by MODFLOW-SFR to the mean and 95% inter-percentile range estimated by stochastic river mass balance (Gates et al. 2017).

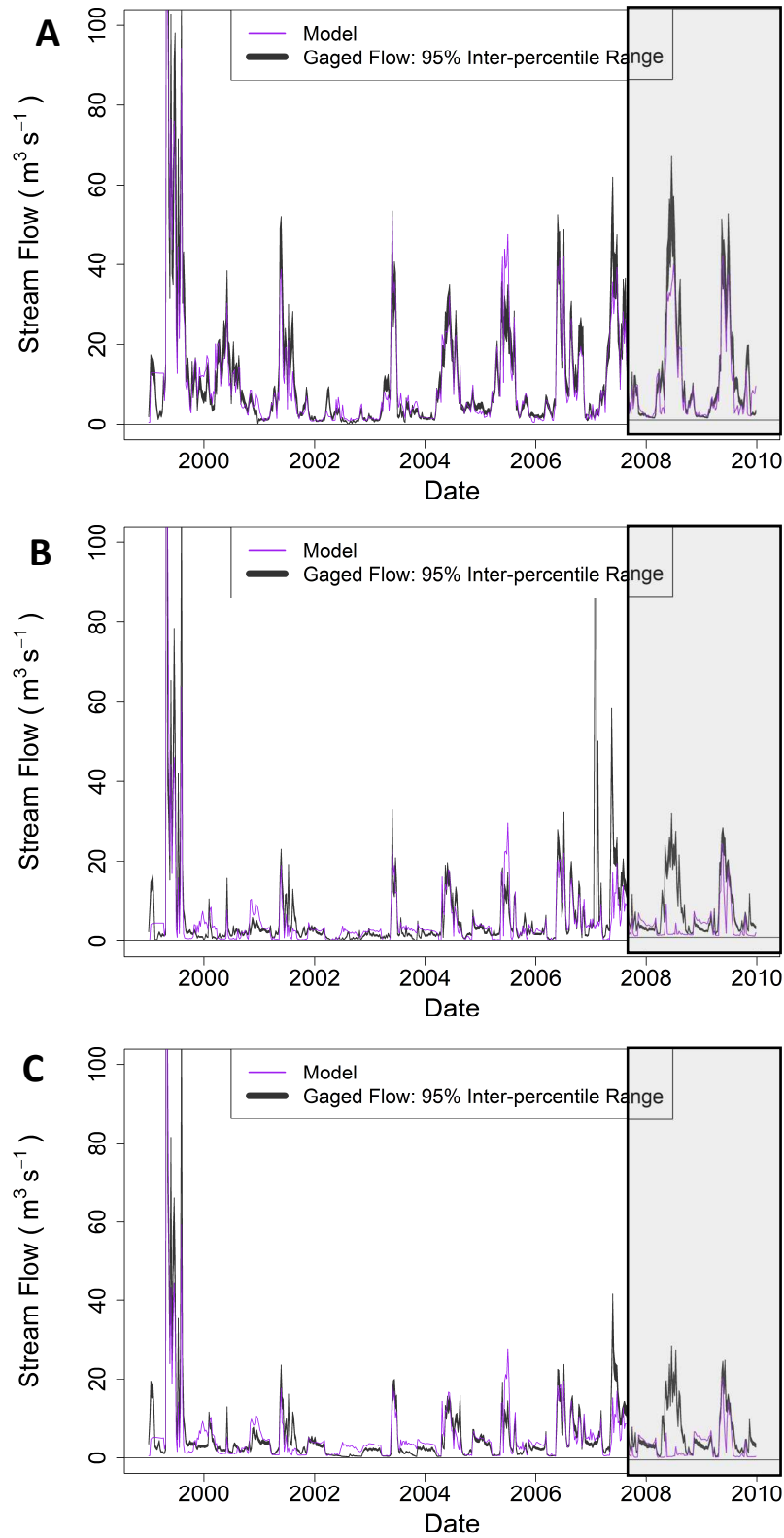


Figure 3.9: Comparison of MODFLOW-SFR -simulated and gaged flow at (A) ARKROCCO (B) ARKLAJCO (C) USGS 07124000. The November 2007 to December 2009 testing period is shaded.

Table 3.2: Comparison of MODFLOW-SFR output to stream gages.

	Timpas Creek	Crooked Arroyo	Horse Creek	Arkansas River at Rocky Ford	Arkansas River at La Junta	Arkansas River at Las Animas
NSCE	0.142	0.162	0.098	0.893	0.293	0.799
E	0.136	0.262	-0.133	0.718	0.460	0.481
VE	0.474	0.403	-0.058	0.745	0.426	0.524
R ²	0.481	0.255	0.307	0.898	0.306	0.855

3.4.1.3.2. RT3D-OTIS Calibration and Testing Results

Parameter values resulting from the RT3D-OTIS calibration process are summarized in Tables 3.3 and 3.4 for the groundwater and surface water parameters, respectively. These values fall within ranges reported in the literature.

Table 3.3: Final groundwater parameter values.

OTIS Stream Reach	$\lambda_{NO_3}^{auto}$ (day ⁻¹)	$\lambda_{NO_3}^{het}$ (day ⁻¹)		$\lambda_{SeO_4}^{het}, \lambda_{SeO_3}^{het(Se(0))}, \lambda_{SeO_3}^{het(SeMet)}, \lambda_{SeMet}^{het}$ (day ⁻¹)		K_{Se} (μg L ⁻¹)
		Riparian	Non-riparian	Riparian	Non-riparian	
1	2.00E-04	5.50E-03	2.00E-04	4.40E-02	1.00E-03	1.00
2	2.00E-04	5.50E-03	2.00E-04	6.50E+00	1.95E-01	10.00
3	5.20E-03	5.50E-03	5.20E-03	1.20E-01	1.00E-03	1.00
4	2.30E-03	5.50E-03	2.30E-03	4.22E+00	1.90E-01	1.00
5	6.20E-03	6.20E-03	6.20E-03	9.00E-02	9.00E-02	1.00
6	2.00E-04	5.50E-03	2.00E-04	8.50E-03	1.00E-03	1.00
7	2.00E-04	5.50E-03	2.00E-04	6.00E-03	1.93E-03	1.00
8	3.13E-02	3.50E-02	3.13E-02	6.50E+00	6.50E+00	10.00
9	3.13E-02	3.50E-02	3.13E-02	6.00E-03	2.00E-03	1.00
10	3.36E-02	3.50E-02	3.36E-02	1.40E-02	1.40E-02	1.00
11	1.28E-02	3.50E-02	1.28E-02	8.50E-03	1.11E-03	1.00
12	8.50E-02	8.50E-02	8.50E-02	1.30E-01	5.00E-02	1.00
13	3.16E-02	3.50E-02	3.16E-02	6.50E+00	6.50E+00	10.00

Table 3.4: Final surface water parameter values.

Parameters	
$\bar{\rho}$ (g m ⁻³)	6327.7
λ_{SeO_4} (day ⁻¹)	1.087
$\lambda_{SeO_4}^{assim}$ (day ⁻¹)	0.050
$\lambda_{SeO_4}^{vol}$ (day ⁻¹)	0.037
DF_{NO_3-N}	1.252

Konikow (2011) observes that “for transport models, we should not expect that the calculated concentrations will accurately match all variations observed in the field, or even in a single observation well. Rather, one should aim to reproduce major trends and locally averaged values.” Here we compare model-simulated average values of groundwater C_{Se} and C_{NO_3-N} within each of 13 grouping areas to the corresponding average observed values within the grouping area for both the calibration and testing periods, as shown in Figure 3.10. Also shown is the standard deviation inter-percentile range of the observations, representing uncertainty derived from scale discrepancy and from measurement error. In light of this uncertainty, simulated values are quite comparable to observations, especially for C_{Se} . Model under-prediction of C_{NO_3-N} compared to observations in some of the grouping areas may be due in part to the fact that the model-simulated averages are biased by low values computed within the riparian zone, where values are especially affected by chemical reduction, while the observed values do not fall within the riparian zone. Interestingly, the lower values of simulated groundwater concentrations in the testing period yield a better match to observed values for both C_{Se} and C_{NO_3-N} . A large incongruity is in grouping area 13 where the model output is much higher than the observed concentration. In this area there are very few groundwater monitoring wells, with the possibility that the few observed values are not representative of conditions in other parts of the grouping area.

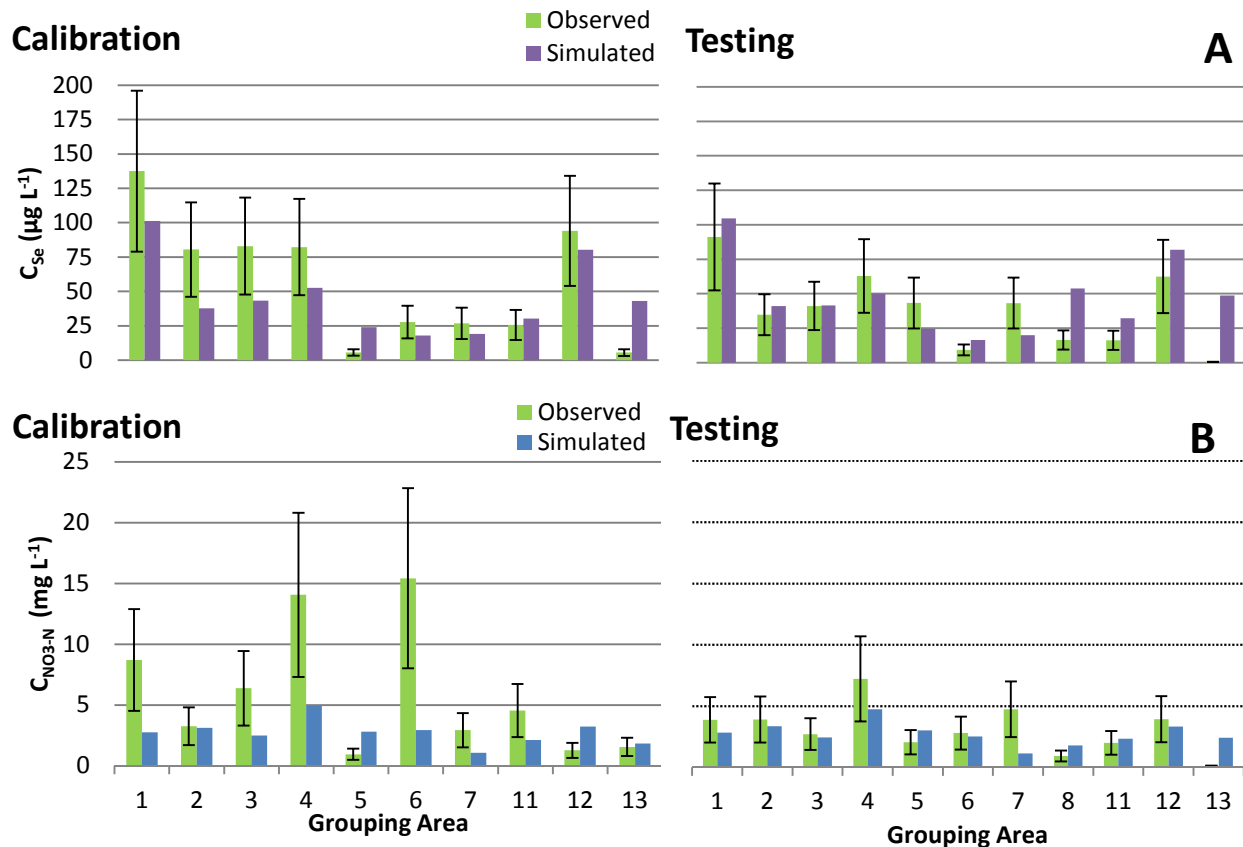


Figure 3.10: Grouping area average (A) C_{Se} and (B) C_{NO_3-N} values for the calibration and testing periods. Upper and lower whiskers depict plus or minus one standard deviation associated with uncertainty derived from discrepancy in the spatial and temporal scales of simulated and observed values and from measurement error.

Figure 3.11 shows the simulated mass loading of Se and NO_3 in groundwater and unmeasured surface water returns to the Arkansas River along with statistics of the mass loading computed from the stochastic river mass balance for a period over 2006 – 2009 (spanning portions of both the calibration and testing periods). The model-predicted mass loading is generally well-within the standard deviation inter-percentile range for both Se and NO_3 , but less so for NO_3 .

Time series plots of model-simulated C_{Se} and C_{NO_3-N} at seven locations along the Arkansas River and at locations within three tributaries are presented in Figure 3.12 along with observed values for the calibration and testing periods. Plots G and H in Figure 3.12 are enlarged in Figures 3.13 and 3.14

to display the standard deviation inter-percentile range associated with scale discrepancy and measurement error uncertainty in the observations of C_{Se} and C_{NO_3-N} , respectively. These comparisons indicate that predictions by the calibrated model provide a good match with available data in regard to magnitude and spatiotemporal variability of stream concentrations.

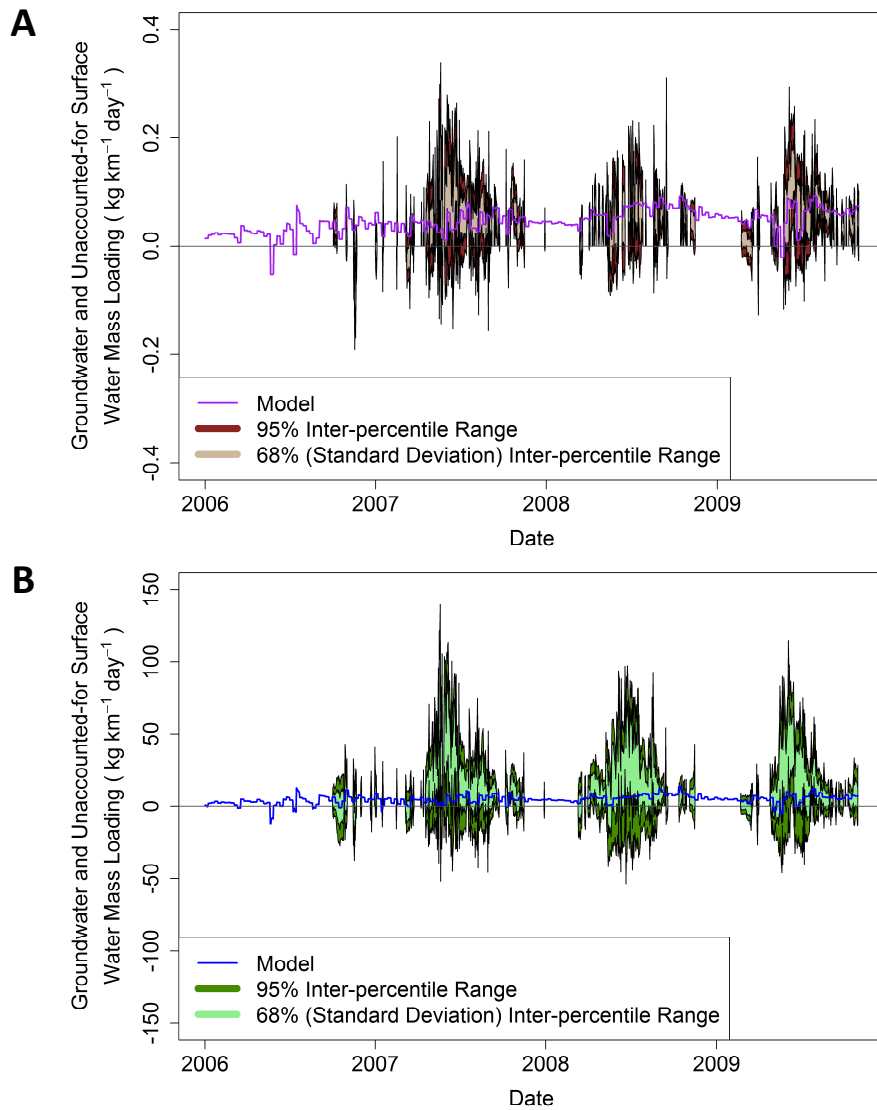


Figure 3.11: Simulated (A) Se and (B) NO₃-N unaccounted for mass loading to the Arkansas River compared to mass balance estimates.

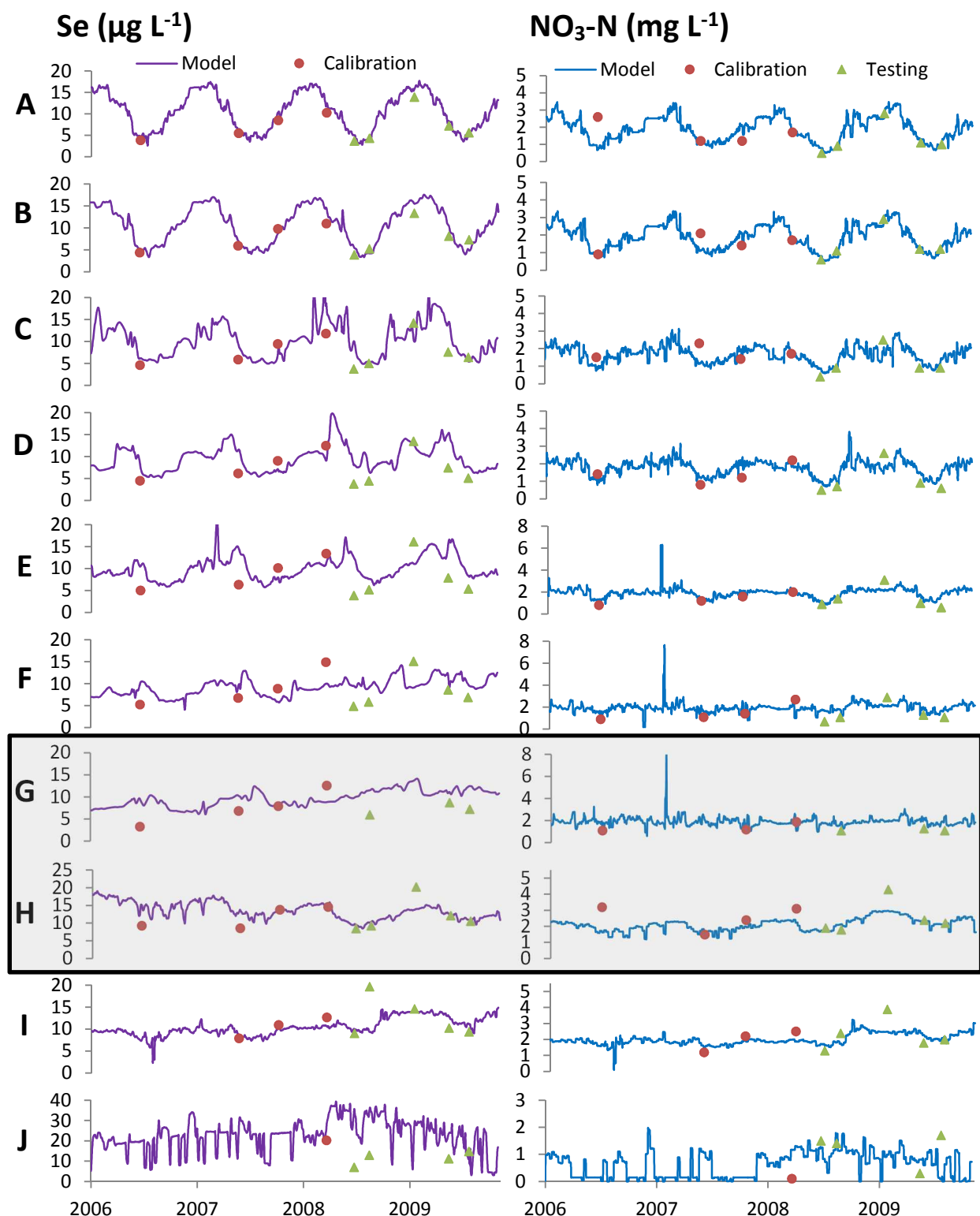


Figure 3.12: Observed and simulated surface water concentrations for dissolved Se and NO₃-N for (A) R3 (164), (B) R4 (167), (C) R5 (141), (D) R6 (12), (E) R7 (127), (F) R8 (95), and (G) R9 (162) along the Arkansas River (ordered upstream to downstream) and for (H) Timpas Creek (62), (I) Crooked Arroyo (74), (J) Anderson Arroyo (75). (G) and (H) are shown enlarged in Figure 3.13 and Figure 3.14 for detail.

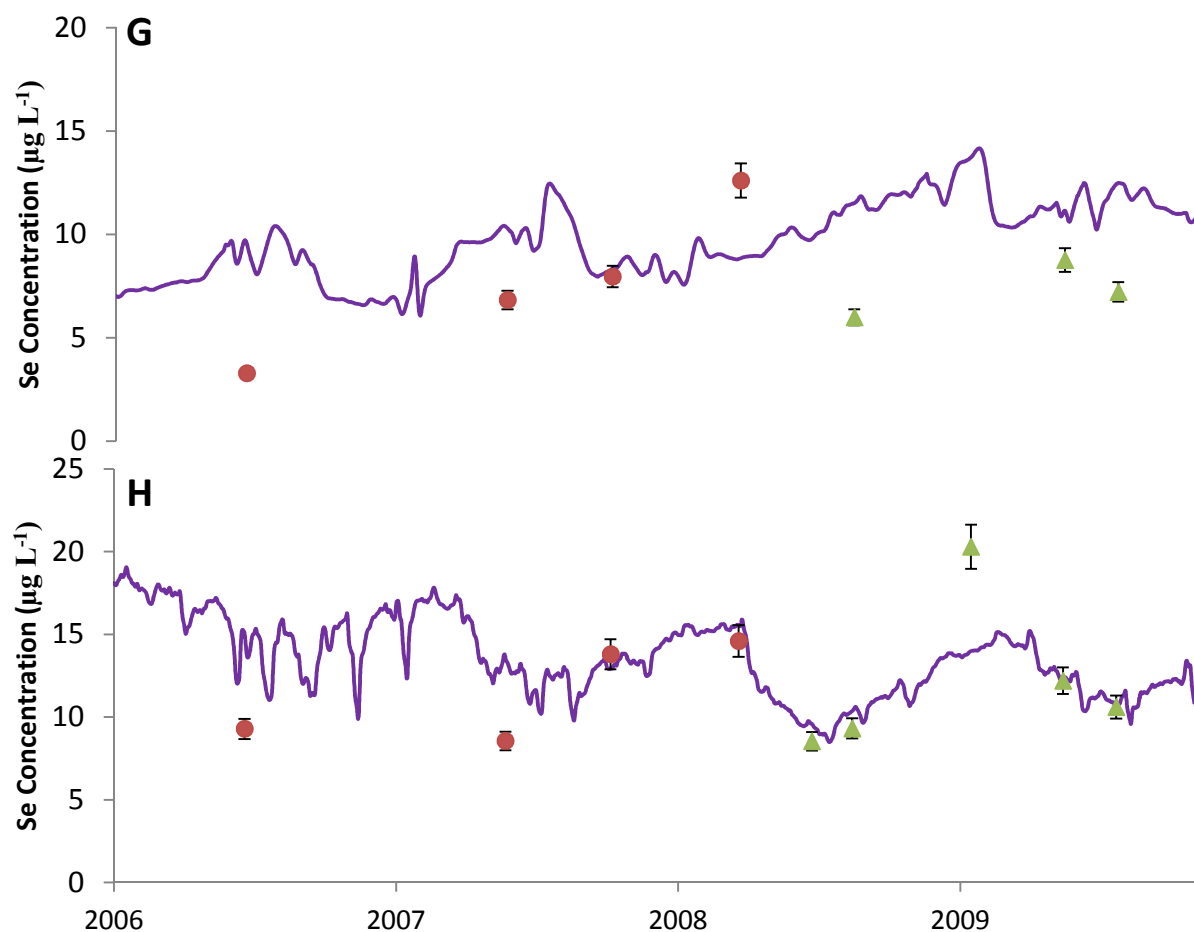


Figure 3.13: Observed and simulated Se surface water concentrations for (G) R9 (162), the downstream most Arkansas River point, and (H) Timpas Creek (62). Upper and lower whiskers depict plus or minus one standard deviation associated with uncertainty derived from measurement error.

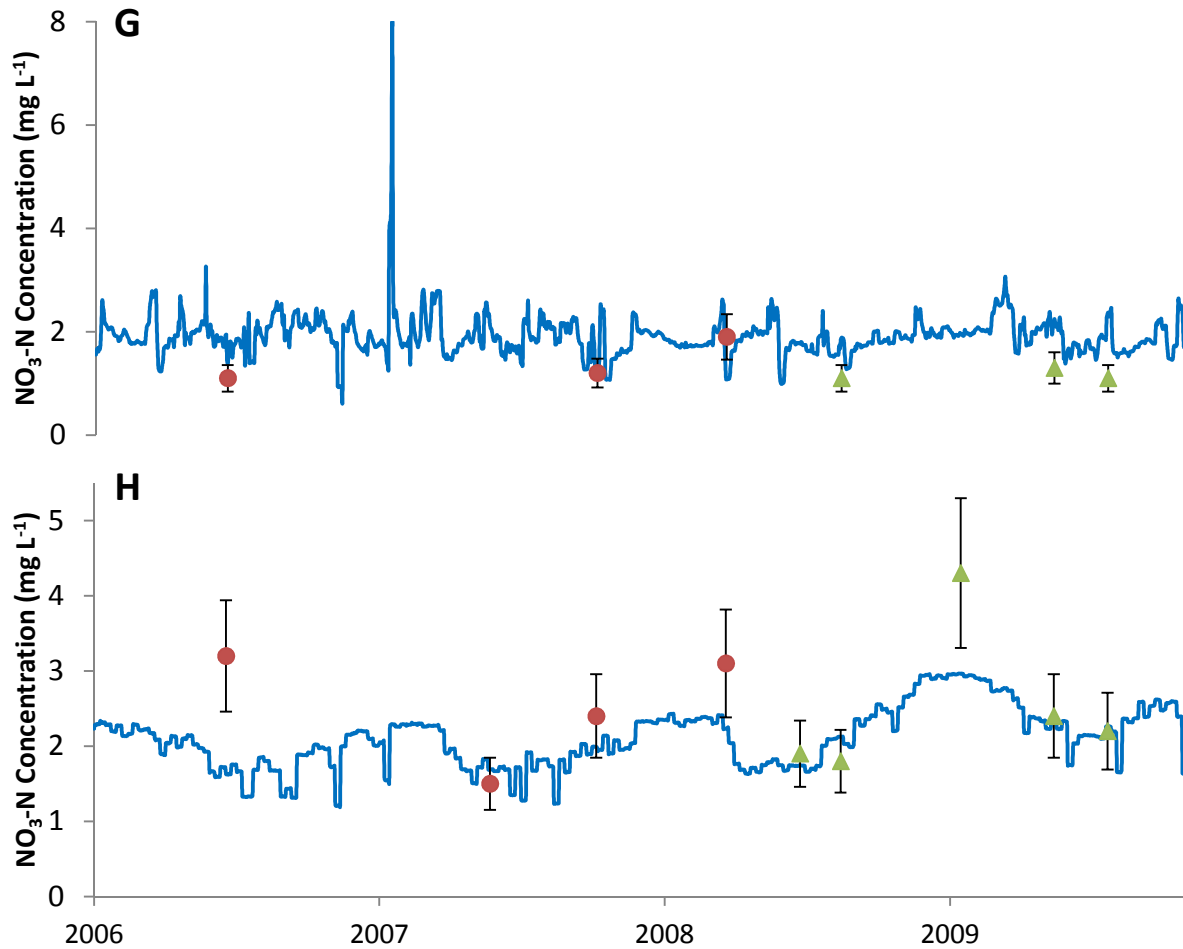


Figure 3.14: Observed and simulated NO₃-N surface water concentrations for (G) R9 (162), the downstream most Arkansas River point, and (H) Timpas Creek (62). Upper and lower whiskers depict plus or minus one standard deviation associated with uncertainty derived from measurement error.

3.5. Appraisal of Baseline Stream-Aquifer Conditions

A 40-year period was simulated using the calibrated coupled stream-aquifer model by repeating the historic period 1999-2009 three and a half times. The aim was to provide a representation of likely long-term baseline conditions against which forthcoming model predictions of impacts under alternative land and water BMPs could be evaluated.

Average simulated groundwater C_{Se} and C_{NO_3-N} over the long-term baseline period are shown in Figure 3.15. Time-averaged C_{Se} varies between $\approx 0 \mu\text{g L}^{-1}$ and $2614 \mu\text{g L}^{-1}$, with an overall average of

75.9 $\mu\text{g L}^{-1}$ over the region. The overall 85th percentile value of C_{Se} is 118.7 $\mu\text{g L}^{-1}$, compared to the CDPHE groundwater standard of 50 $\mu\text{g L}^{-1}$. For C_{NO_3-N} , time-averaged values span from ≈ 0 mg L^{-1} to 104.6 mg L^{-1} , averaging 1.9 mg L^{-1} over the region. At about 3.24 mg L^{-1} , the overall 85th percentile value is below the CDPHE chronic standard of 10 mg L^{-1} .

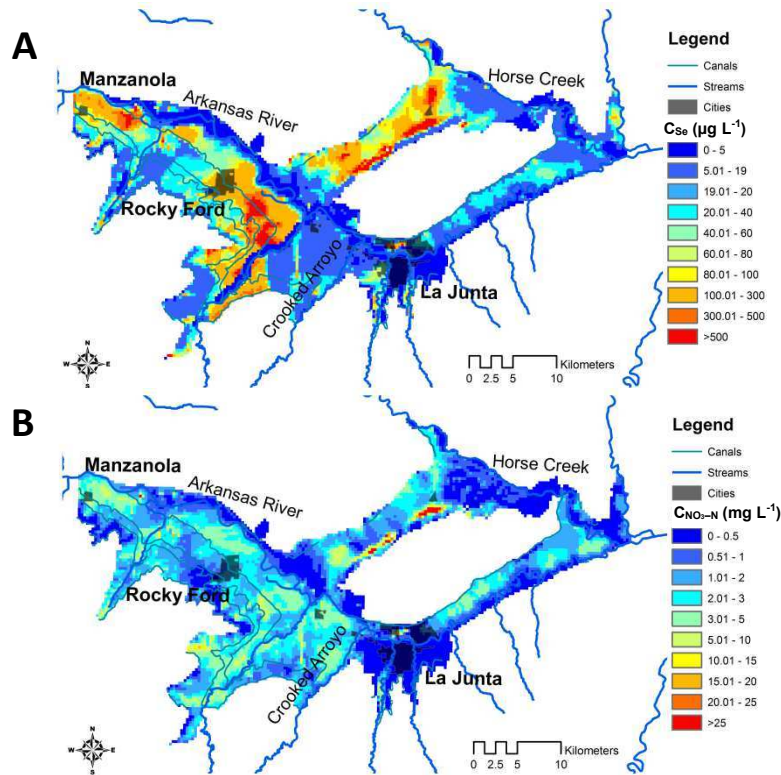


Figure 3.15: Simulated temporal average (A) C_{Se} and (B) C_{NO_3-N} in groundwater for long term baseline conditions.

Model predictions of baseline total mass loading of Se and $\text{NO}_3\text{-N}$ to the stream network are summarized in Figures 3.16 and 3.17, respectively. Included are plots of simulated time-averaged total return mass loading rates along the streams, along with time series plots of total mass loading. The considerable spatiotemporal variability over the region is apparent, revealing the need for distributed parameter models to guide decision-makers in targeting the location of interventions for effective pollution mitigation.

Finally, the 85th percentile value of C_{Se} over the simulated period is plotted along the extent of the Arkansas River within the USR in Figure 3.18, along with the current CDPHE regulatory standard. Baseline conditions indicate a large degree of violation extending from 2.6 to 3.7 times the standard along the river reach. Simulated average values of C_{NO_3-N} , also shown in Figure 3.18, spread from values equivalent to 76% to 102% of the plotted CDPHE interim standard for total N, demonstrating the reason for growing concern about N pollution in the LARV.

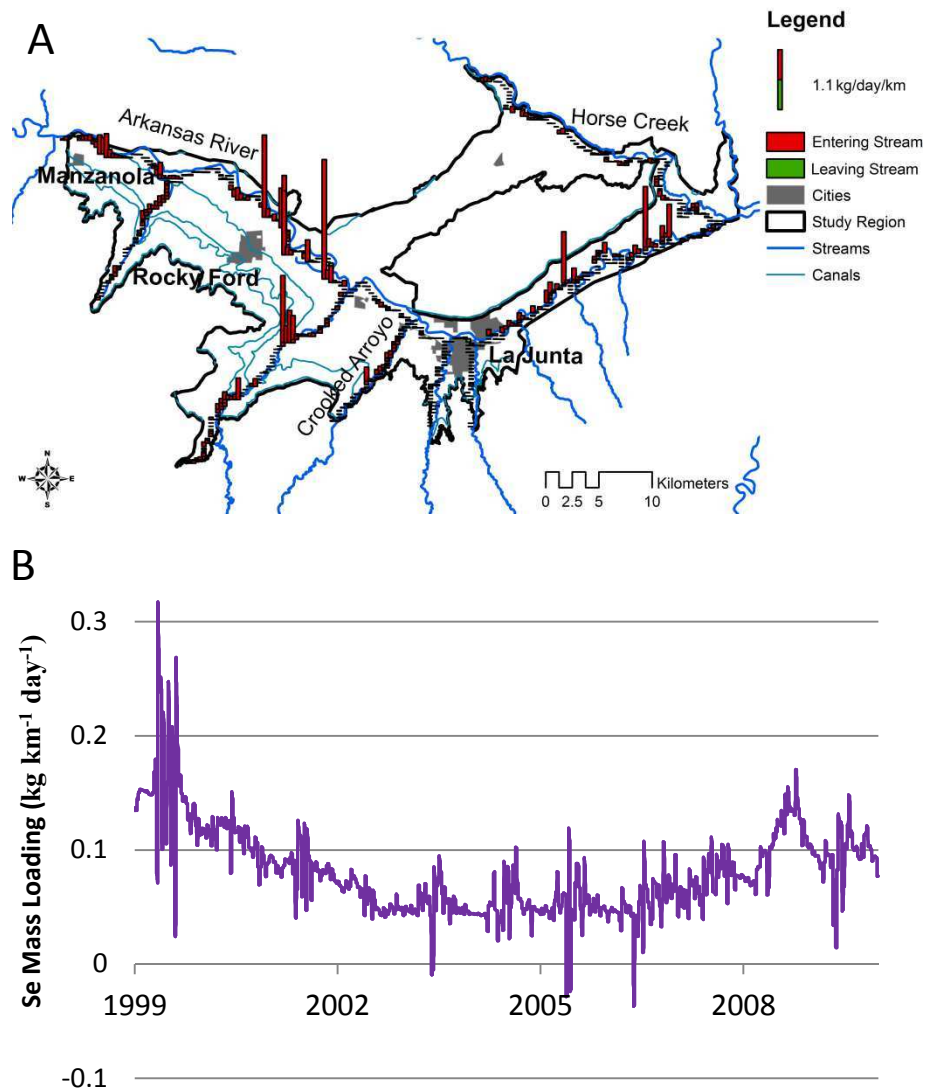


Figure 3.16: Simulated Se mass loading as (A) temporal averages along the stream system and (B) time series of spatial average along the stream system for long-term baseline conditions.

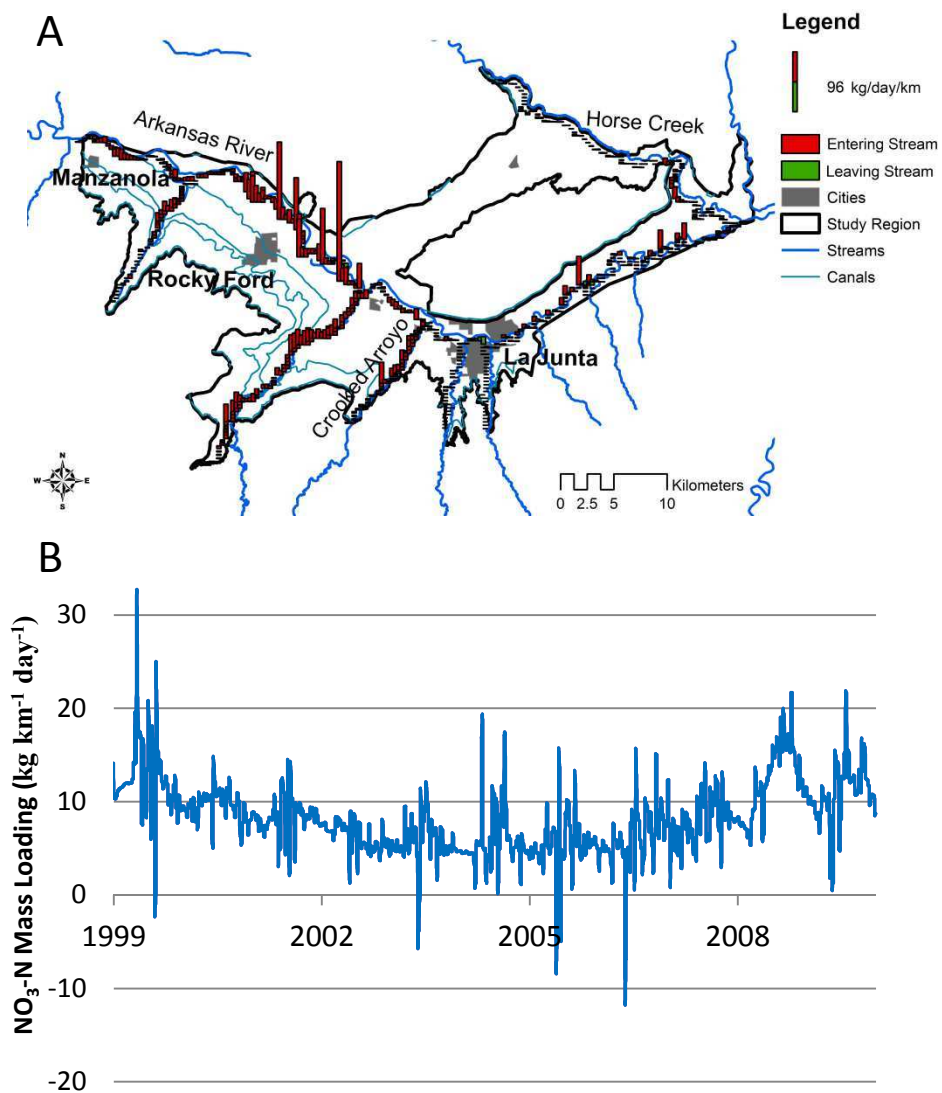


Figure 3.17: Simulated $\text{NO}_3\text{-N}$ mass loading as (A) temporal averages along the stream system and (B) time series of spatial average along the stream system for long-term baseline conditions.

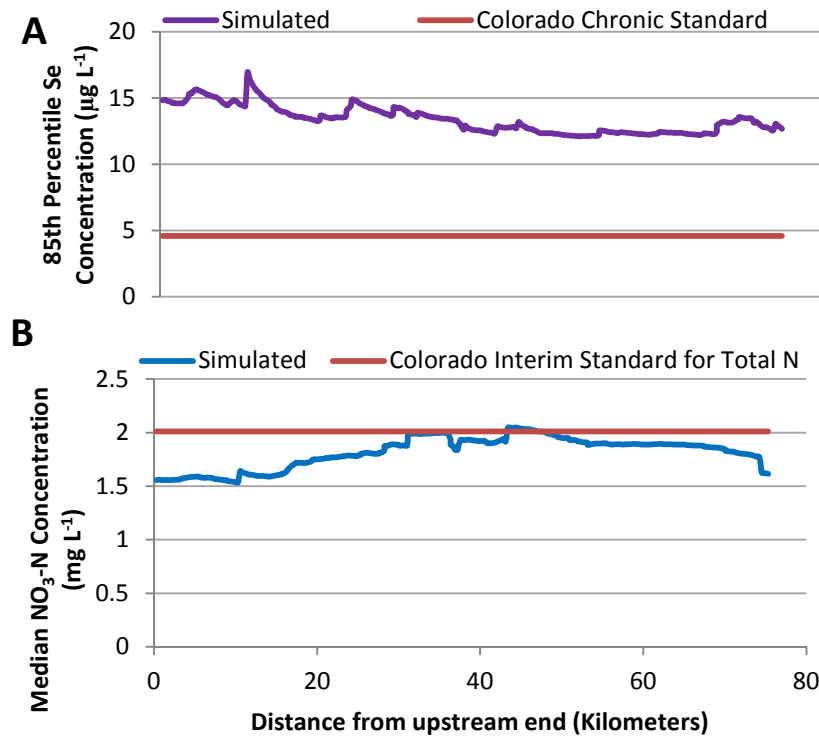


Figure 3.18: Simulated temporal average (A) C_{Se} and (B) $C_{\text{NO}_3\text{-N}}$ along the Arkansas River in comparison to the Colorado chronic standard for Se ($4.6 \mu\text{g L}^{-1}$) interim standard for total N (2.0mg L^{-1}).

3.6. Summary and Conclusions

Guided by a conceptualization of the major hydrological and chemical processes that influence the occurrence, movement, and interaction of aqueous selenium and nitrate in the environment, models of regional streamflow and reactive solute transport processes were melded with previously-developed and published groundwater flow and transport models. The aim was to enable accurate simulation of spatiotemporal distributions of selenium and nitrate within and between an aquifer and its interconnected streams. The resulting coupled stream-aquifer model addresses multi-species reactive transport, including advection, dispersion, sorption, autotrophic and heterotrophic redox reactions, soil-plant-water cycling, algal uptake and release, volatilization, and stream sediment cycling. It is showcased in application to a region in Colorado's Lower Arkansas River Valley, an area with a strong history of irrigated agriculture which faces challenges to control nonpoint source pollution to meet regulatory

standards. An extensive data set, gathered over a 10-yr period, along with the results of river flow and mass balance analyses, provided a rich set of targets for model calibration and confirmation. The groundwater-stream flow component model is found to reasonably concur with calibration targets of groundwater hydraulic head, return flows to streams, evapotranspiration, and streamflow by manually adjusting streambed conductance values while retaining previously-calibrated values of groundwater flow parameters. A suitable match to groundwater concentrations, mass loading to streams, and in-stream concentrations, taking into account uncertainties in available field-observed data, is achieved by a comprehensive calibration and testing of the groundwater-stream reactive transport component model.

Using the calibrated parameter values, the stream-aquifer model was run to describe long-term (40 year) baseline conditions in the LARV region. Spatial and temporal patterns of simulated concentrations reveal extreme violation of Colorado's selenium standards in both groundwater and streams and near-violation of the interim stream standard for total nitrogen by nitrate alone. Successful application to the LARV suggests the utility of the model for regional assessment of selenium and nitrogen in application to other similar stream-aquifer systems. The stage is now set for employing the model to forecast relative comparisons of conditions under alternative BMPs in the LARV with baseline conditions and to guide decisions about their future implementation.

CHAPTER 4: Finding Best Management Practices to Lower Selenium and Nitrate in Groundwater and Streams in an Irrigated River Valley²

4.1. Introduction

Over time, many water quality concerns have developed that are linked to irrigated agricultural water use. Along with high concentrations of total dissolved solids (TDS), nutrients and trace elements in irrigation return flows harm the environment, human health, and reduce crop yields.

Among nutrients that are applied as fertilizer, nitrogen (N), especially in the form of nitrate (NO_3), has become a widespread pollutant of concern in surface water and groundwater systems in recent decades (Carpenter et al. 1998; Muller et al. 1995; Spalding and Exner 1993). Mobilized by applied water, NO_3 is transported to groundwater and streams through inefficiencies in irrigation practices. Excess amounts can lead to eutrophication of surface water systems, promoting the growth of algae resulting in fish kills and biodiversity loss (Carpenter et al. 1998). Furthermore, elevated NO_3 concentrations also can lead to methemoglobinemia in infants (Fan and Steinberg 1996). For these reasons, the U.S. Environmental Protection Agency (EPA) (2009) has set a maximum contaminant level (MCL) for NO_3 as nitrogen ($\text{NO}_3\text{-N}$) to 10 mg L^{-1} and the Colorado Department of Health and Environment (CDPHE) has set an interim standard for total N in streams at 2.0 mg L^{-1} (CDPHE 2017).

Additionally, the prevalence of trace elements like selenium (Se) in groundwater (Hudak 2010; Alfthan et al. 1995) and surface water (Engberg and Sylvester 1993; May et al. 2008) systems has become a growing worry in the western United States and around the world. In many cases, Se is present within shale bedrock as seleno-pyrite (-II) ($\text{FeSe}_x\text{S}_{2-x}$) and is mobilized through oxidation-

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Christopher D. Shultz, *Department of Civil and Environmental Engineering, Colorado State University, 1372 Campus Delivery, Fort Collins, CO.*

Timothy K. Gates, *Department of Civil and Environmental Engineering, Colorado State University, 1372 Campus Delivery, Fort Collins, CO.*

Ryan T. Bailey, *Department of Civil and Environmental Engineering, Colorado State University, 1372 Campus Delivery, Fort Collins, CO.*

reduction (redox) processes into the groundwater as it returns to streams (Gates et al. 2009, Seiler 1995). High groundwater return rates due to inefficient irrigation practices and canal seepage act to promote this mobilization process. Furthermore, Bailey et al. (2012) showed that dissolved oxygen (DO) and NO_3 present in water both accelerate the mobilization of the seleno-pyrite and slow the reduction of dissolved species of Se. This presence of Se has been linked to toxicity problems in wildlife including fish and waterfowl, bioaccumulating in the food chain (Presser et al. 1994; Hamilton 2004). The state of Colorado has set a chronic Se standard for aquatic life protection to $4.6 \mu\text{g L}^{-1}$ in surface water systems (CDPHE 2016). Additionally, EPA (2016) recently released updated recommended standards for Se, lowering the standard for warm lotic waters to $3.1 \mu\text{g L}^{-1}$ and creating separate standards for fish tissue.

Because of the environmental and human health risks that these pollutants pose, a number of studies have been performed in the recent years to analyze the potential of land and water best management practices (BMPs) to drop concentrations. Many past studies have examined effective means of reducing NO_3 concentrations or mass loading in surface water. These BMPs include enhancing riparian buffers (Lee et al. 2010; Vaché et al. 2003; Sahu and Gu 2009) adjacent to streams, reducing or more efficiently applying fertilizer (Rong and Xuefeng 2011; Liu et al. 2013; Lee et al. 2010; Trachtenberg and Ogg 1994; Molénat and Gascuel-Oudoux 2002; Almasri and Kaluarachchi 2007), altering land tillage management and using vegetative filter strips (Vaché et al. 2003; Lee et al. 2010; Liu et al. 2013), and reducing applied irrigation (Rong and Xuefeng 2011). Results show that these BMPs can effectively lower NO_3 contamination. BMP modeling studies generally have reported results as changes in non-point source loading to surface water with moderate alterations in management causing a reduction in N loading of 5-10% and aggressive changes in management reducing N loads by 75-90% (Liu et al. 2013; Lee et al. 2010; Vaché et al. 2003; Sahu and Gu 2009).

Similarly, other studies have reviewed ways of lowering Se contamination in water systems. Engberg et al. (1998) examined the San Joaquin Valley Drainage Program, a multi-tiered approach to

reducing the Se problems caused by irrigation drainage, and outlined several methods to bring down Se concentration including preventing Se from entering the system, capturing or removing it, and allaying the effects of Se (Engberg et al. 1998). Lin and Terry (2003) used a ten-cell wetland system to treat irrigation drainage. The results showed 70% removal of Se from the water, mostly by sorption to sediment and volatilization. Amweg et al. (2003) studied the use of algae and bacteria to reduce Se in water. Results from the analysis showed that while Se was brought down, there was a significant increase in the bioavailable Se. Bailey et al. (2015a, 2015b) examined the effectiveness of mitigating water contamination from Se by diminishing groundwater return flows to streams and reducing available NO_3 in the system, thereby inhibiting the mobilization of Se. In these studies, the effects of decreasing applied irrigation water, fallowing irrigated land, sealing canals to lower seepage, reducing fertilizer application, and enhancing stream riparian buffers were analyzed for their impacts on lowering Se and NO_3 mass loading and groundwater concentrations in the Lower Arkansas River Valley (LARV) in southeastern Colorado. Results show that implementing these BMPs, especially in combination, could significantly decrease mass loading to the Arkansas River as well as strongly impact groundwater concentrations (Bailey et al. 2015a, 2015b).

In this paper, the analyses of Bailey et al. (2015a, 2015b) are expanded by examining the effects of BMPs on the reactive transport of Se and NO_3 in both groundwater and stream flow using coupled stream-aquifer models. The RT3D-OTIS model (Shultz et al. 2017), linked to MODFLOW-SFR, enables the regional-scale modeling of these solutes in an irrigated agricultural stream-aquifer system within the LARV under the influence of five BMPs (reduced applied irrigation, fallowing of agricultural lands, sealing of irrigation canals, reduced applied fertilizer, and enhanced riparian buffer zones), alone, and in combination. BMP effectiveness in lowering groundwater concentrations, decreasing mass loading to the stream network, and lessening stream concentrations for both Se and NO_3 is examined in

comparison to baseline (current) conditions. Insights from this analysis provide useful guidance in controlling Se and NO₃ contamination in similar irrigated agricultural river valleys.

4.2. Description of Study Region

The LARV (Figure 4.1) is located in southeastern Colorado situated between Pueblo, CO and the Kansas state line. The region is largely dominated by agriculture which, due to the semi-arid climate, relies heavily on irrigation through canal networks and pumped water. During previous work by Colorado State University (CSU), the area has been divided into two main study regions: the Upstream Study Region (USR) (Figure 4.2) which contains the Arkansas River reach extending from Manzanola to Las Animas and the Downstream Study Region (DSR) which encompasses the river reach from Lamar to the Kansas state line. In this study, flow and reactive transport of solutes in the stream-aquifer system was modeled in the USR. The modeled region consists of a 75-km stretch of the Arkansas River, several tributaries, and an alluvial aquifer that interacts with the stream network. The USR contains eight primary irrigation canals: the Rocky Ford Highline, Otero, Catlin, Rocky Ford, Fort Lyon, Holbrook, Fort Lyon Storage, and Las Animas Consolidated canals. About 575 pumping wells bring supplemental water to the crops. Major crops grown in the region include alfalfa, corn, sorghum, and wheat.

Large portions of the aquifer in the LARV, including within the USR, are underlain by or interspersed with near-surface marine shale geology (Scott 1968, Sharps 1976). Groundwater flows through the aquifer, mobilizing solute species from these rocks and their weathered residuum and transporting them to the river system. Among these solutes are Se and U (Bailey et al. 2012, Gates et al. 2009, 2016). Gates et al. (2009) reported on the scale of the groundwater and stream contamination from Se and U as well as NO₃ and other major salts. Findings from these extensive field data serve as the basis for the numerical modeling described in this study.

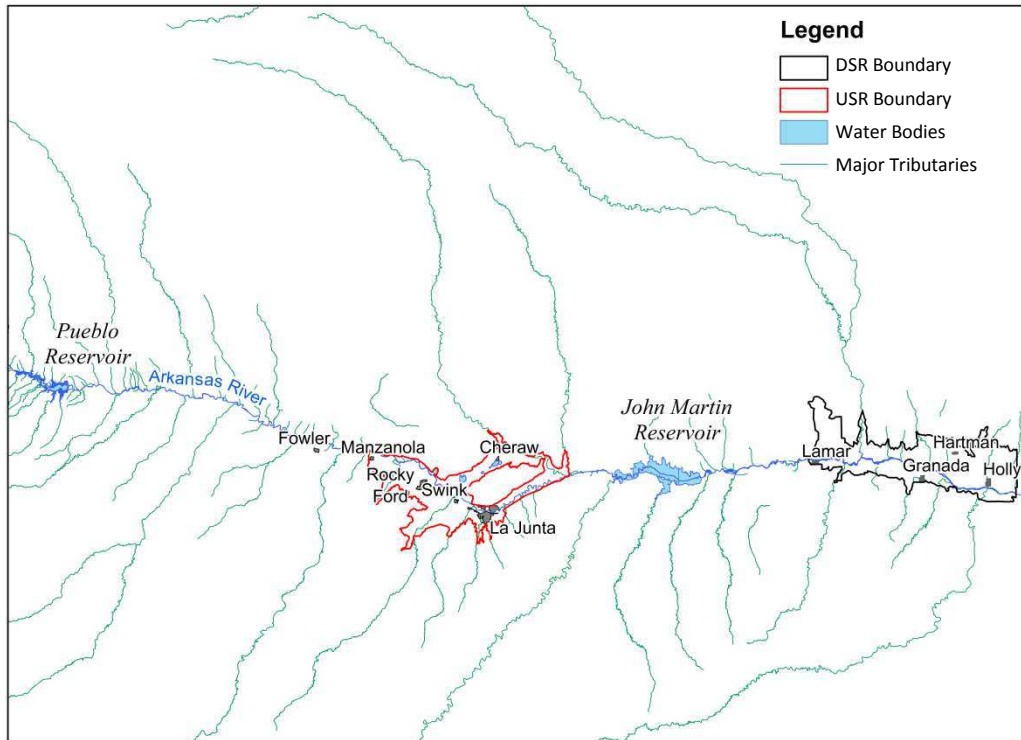


Figure 4.1: The LARV in southeastern Colorado with primary Colorado State University study regions.

In the USR, solute reactive transport in the hydrologic system is controlled heavily by irrigation practices. Natural aquifer recharge by precipitation and water returned to the stream network is accelerated by the use of supplemental water for irrigation. Some of the infiltrated irrigation water recharges the underlying aquifer and accelerates return flows to the river by increasing the head gradient between the aquifer and stream. The infiltrated irrigation water has a large supply of DO from the atmosphere and NO_3 oxidized from applied fertilizer. Other water recharges the groundwater through seepage from irrigation canals. As the groundwater returns to the river network, it comes in contact with the underlying bedrock where the availability of DO and NO_3 as electron donors in the

groundwater causes the aforementioned oxidation-reduction (redox) reactions to occur with selenopyrite within the shale bedrock.

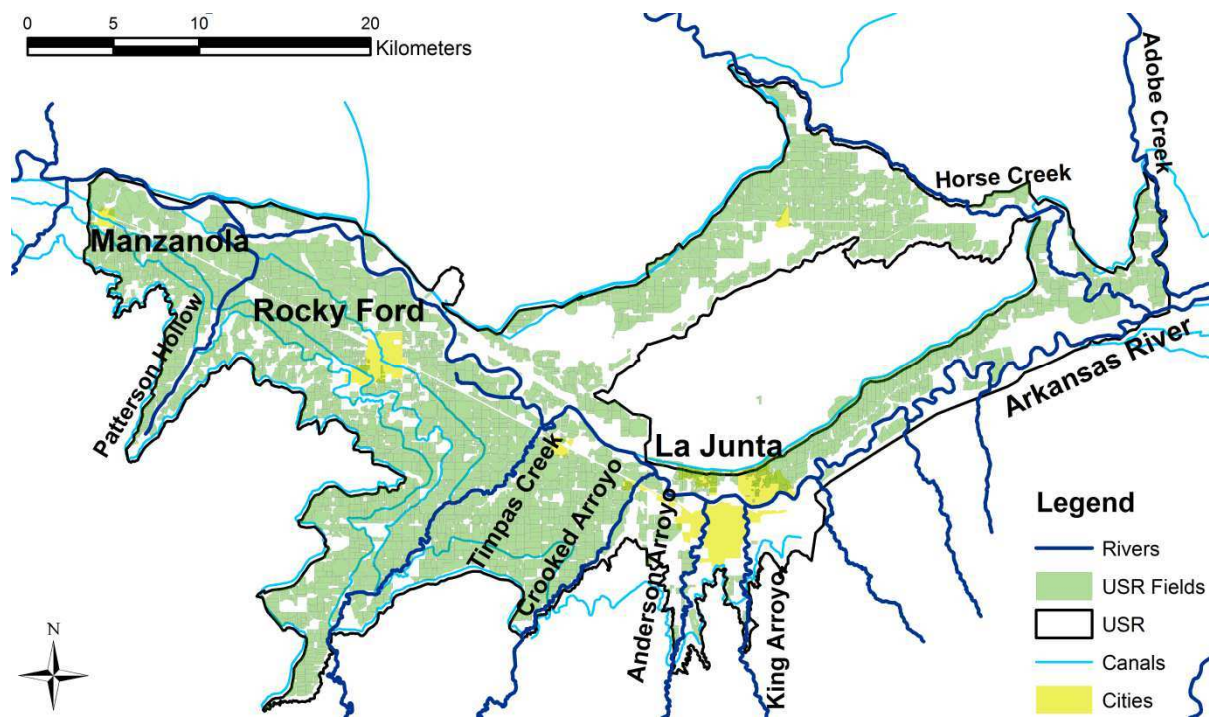


Figure 4.2: A map of the USR with the Arkansas River, fields, canals, major tributaries, and cities.

Groundwater, now containing mobilized Se, then flows through the aquifer to the Arkansas River and its tributaries. Additional water runs off fields due to inefficiencies in irrigation and returns in surface drainage to the streams. This aqueous Se exists primarily as selenate (SeO_4), selenite (SeO_3), or organic selenomethionine (SeMet), with SeO_4 representing the majority of the Se in the dissolved phase in the LARV (Gates et al. 2009). As water continues downstream where it is again applied, it picks up more Se from groundwater return flows in the bedrock and more NO_3 from fertilizer. Over time, this repeated reuse of water can push up the concentrations of the surface water and groundwater along the valley, depending upon chemical reactions within the streams and their adjacent riparian and hyporheic zones.

4.3. Methodology

4.3.1. Model Description

To accurately simulate hydraulic head and flows in the stream-aquifer system in the USR, MODFLOW-NWT (Niswonger et al. 2011) was used along with several modules, including the Unsaturated-Zone Flow (UZF1) (Niswonger et al. 2006) and Stream Flow Routing (SFR2) (Niswonger et al. 2005) packages. The original regional groundwater model developed by Morway et al. (2013) was modified by Shultz et al. (2017) to include the SFR2 package which allows for the simulation of flows in the Arkansas River and its tributaries. Groundwater and stream flow rates along with sinks and sources are taken from the MODFLOW-SFR output and are used as input forcing variables in the RT3D-OTIS reactive transport model. This RT3D-OTIS model represents a coupling of the UZF-RT3D model developed by Bailey et al. (2013) to simulate unsaturated and saturated zone groundwater reactive transport with a OTIS-QUAL2E model (Bailey and Ahmadi 2014) which simulates stream reactive transport. This model coupling of groundwater and streams and of flow and reactive solute transport allows for simulation of water and solute mass in the stream-aquifer system and serves as the basis for the BMP simulations presented here. A summary of the linked modeling processes are depicted in Figure 4.3.

To model the reactive transport of Se and NO₃ in groundwater, UZF-RT3D (Bailey et al. 2013) computes solute reactive transport using the advection-dispersion-reaction (ADR) equation:

$$\frac{\partial C_k}{\partial t} = -\frac{\partial(v_i C_k)}{\partial x_i} + \frac{\partial}{\partial x_i} \left(D_{ij} \frac{\partial C_k}{\partial x_j} \right) + \frac{q_s}{\phi} C_{s_k} + r \quad k = 1, \dots, m \quad [4.1]$$

where C_k is the concentration of the k^{th} species [ML⁻³], t is time [T], x_i is displacement along the i th coordinate direction [L], v_i is the pore velocity [LT⁻¹], D_{ij} is the hydrodynamic dispersion coefficient [L²T⁻¹], ϕ is soil porosity, q_s is net flow from sources and sinks [T⁻¹], C_{s_k} is the concentration of the net source and sink water of the k^{th} species [ML⁻³], r represents all possible reactions, and m is the total number of modeled species. Bailey et al. (2013) discuss the groundwater chemical reduction processes in detail. As

an example, the following equations representing chemical reductions for SeO_4 and NO_3 , respectively, are presented:

$$r_{\text{SeO}_4} = \lambda_{\text{SeO}_4} C_{\text{SeO}_4} \left(\frac{CO_{2,prod}}{K_{CO_2} + CO_{2,prod}} \right) \left(\frac{I_{O_2}}{I_{O_2} + CO_2} \right) \left(\frac{I_{NO_3}}{I_{NO_3} + C_{NO_3}} \right) E \quad [4.2]$$

$$r_{NO_3} = \lambda_{NO_3} C_{NO_3} \left(\frac{C_{NO_3}}{K_{NO_3} + C_{NO_3}} \right) \left(\frac{C_{NO_3}}{K_{NO_3} + C_{NO_3}} \right) \left(\frac{CO_{2,prod}}{K_{CO_2} + CO_{2,prod}} \right) \left(\frac{I_{O_2}}{I_{O_2} + CO_2} \right) E \quad [4.3]$$

where λ_{SeO_4} and λ_{NO_3} are first-order reaction rate constants [T^{-1}] for SeO_4 and NO_3 , respectively; K_j is the Monod half-saturation constant for species j ; $CO_{2,prod}$ is the CO_2 produced through decomposition of organic matter, I_j for species j is the inhibition constant [ML^{-3}]; and E [-] is an environmental reduction factor which accounts for soil temperature and moisture content.

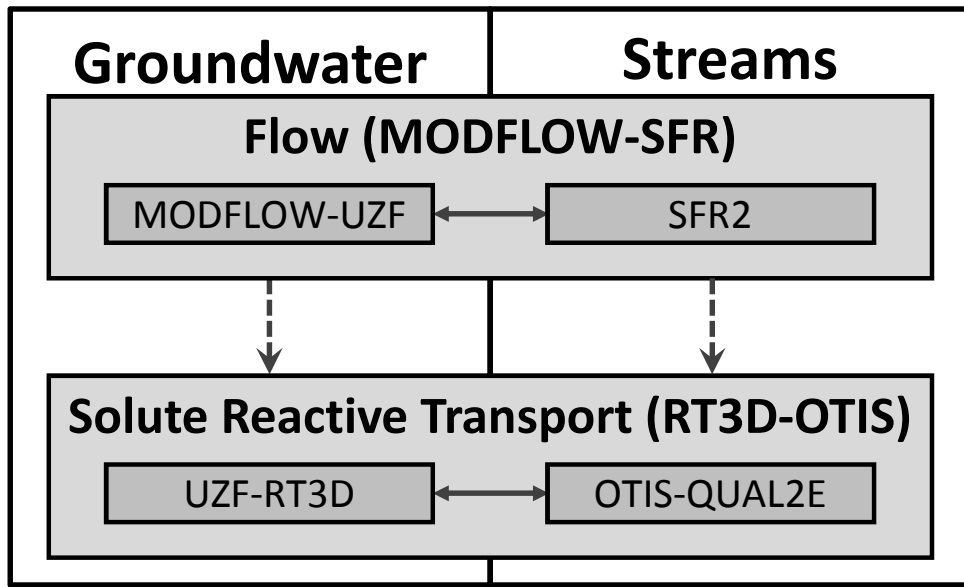


Figure 4.3: Linked modeling processes.

The stream network reactive transport model, OTIS-QUAL2E, was modified to include Se reactions and was coupled with the existing UZF-RT3D model to form the stream-aquifer reactive transport model RT3D-OTIS (Shultz et al. 2017). In-stream solutes are modeled in the OTIS-QUAL2E model using:

$$\frac{\partial C_j}{\partial t} = -\frac{Q}{A} \frac{\partial C_j}{\partial x} + \frac{1}{A} \frac{\partial}{\partial x} \left(AD \frac{\partial C_j}{\partial x} \right) + \frac{q_L}{A} (C_{L_j} - C_j) + S_j + R_j \quad j = 1, \dots, n \quad [4.4]$$

where C_j is the concentration of the j^{th} species [ML^{-3}], A is channel flow area [L^2], Q is the volumetric flowrate [L^3T^{-1}], D is the stream dispersion coefficient [L^2T^{-1}], q_L is the net lateral flow into the stream [$\text{L}^3\text{T}^{-1}\text{L}^{-1}$], C_{Lj} is the concentration of the net lateral inflow of the j^{th} species [ML^{-3}], S_j is the change in mass from sorption process of the j^{th} species [$\text{ML}^{-3}\text{T}^{-1}$], R_j is the change in mass from reactive processes of the j^{th} species [$\text{ML}^{-3}\text{T}^{-1}$], and n is the total number of modeled species. In-stream sorption is computed using:

$$\frac{\partial C_j^*}{\partial t} = -\frac{S_j}{\bar{\rho}} \quad [4.5]$$

where C_j^* is the concentration of the j^{th} species in the streambed sediment [MM^{-1}] and $\bar{\rho}$ is the mass of accessible sediment per volume of water [ML^{-3}]. Reaction equations are described in detail in Shultz et al. (2017) and Heesemann (2016). As an example, the reaction equation for SeO_4 is

$$r_{\text{SeO}_4} = (\lambda_{\text{Se}_{org}}^{\min} C_{\text{Se}_{org}}) + (\lambda_{\text{Se}_{Met}}^{\min} C_{\text{Se}_{Met}}) - (fr_{\text{SeO}_4} \alpha_{\text{Se}} \mu_{alg} C_{alg}) - (\lambda_{\text{SeO}_4} C_{\text{SeO}_4}) - (\lambda_{\text{SeO}_4}^{\text{assim}} C_{\text{SeO}_4}) - (\lambda_{\text{SeO}_4}^{\text{vol}} C_{\text{SeO}_4}) \quad [4.6]$$

where λ_j for species j is the first-order reaction rate constant [T^{-1}] with *min* referring to mineralization, *assim* referring to assimilation, and *vol* referring to volatilization, fr_{SeO_4} is the algae preference factor for SeO_4 , α_{Se} is the algal fraction that is Se, and μ_{alg} is the rate of algae growth [T^{-1}].

Past calibration and testing of the groundwater flow and reactive transport models in application to the LARV USR were undertaken by Morway et al. (2013) and Bailey et al. (2014), respectively. However, with the addition of the stream simulation in addition to the groundwater, a recalibration was necessary, a process explained in detail by Shultz et al. (2017). The groundwater parameters found by Morway et al. (2013) were assumed to be representative of the aquifer system, but with the addition of the SFR2 package, values of unit streambed conductance were manually calibrated to best match simulated groundwater hydraulic heads, groundwater and unaccounted-for surface return flows to streams, evapotranspiration, and stream flows to values estimated from field observations or from a river water balance. The RT3D-OTIS model was calibrated more extensively using

a combination of both manual and automated methods using PEST (Parameter ESTimation) (Doherty 2016). Groundwater concentrations, groundwater and unaccounted-for surface mass loading to streams, and stream concentrations were compared to field observations or river mass balance estimates. After testing model predictions against data sets independent of the calibration period, the coupled flow and reactive transport models were used to simulate long-term baseline conditions for Se and NO₃ mass loading to the stream network and concentrations in groundwater and streams. Results underscored the substantial violation of current Se concentration standards and the marginal violation of N concentration standards and the need to find effective solutions.

4.3.2. Assessment of BMPs

To simulate reactive transport in the stream-aquifer system for each of the considered BMPs, application of the RT3D-OTIS model was extended from the original 2006-2009 period considered by Bailey et al. (2014, 2015a) to a 1999-2009 period, as described by Shultz et al. (2017) for the baseline conditions. Since no surface water Se and NO₃ field data were collected in the USR before 2006, regression relationships developed by Gates et al. (2017) were used to relate stream flows and electrical conductivity (EC) measured prior to 2006 to in-stream Se and NO₃ concentrations. RT3D-OTIS simulation over the 1999-2009 period was repeated successively approximately three and half times to enable a 40 year long-term simulation of the solutes in the stream aquifer system. This extension of the simulation period was deemed necessary due to large groundwater residence time, taking as long as decades for infiltrated water to reach surface water bodies (Bailey et al. 2014).

Several BMPs were considered in order to reduce Se and NO₃ groundwater concentrations, mass loading, and stream concentrations. The BMPs considered in the analysis are referenced as (1) reduced irrigation (RI), (2) lease fallowing (LF), (3) canal sealing to reduce seepage (CS), (4) reduced fertilizer application (RF), and (5) enhanced riparian buffers (ERB). These BMPs were analyzed at basic, intermediate, and aggressive levels of implementation. In addition to the assessment of single BMP

scenarios, BMPs in combination were evaluated. The full set of considered BMP scenarios is summarized in Table 4.1. In the discussion that follows, BMPs are separated into water management BMPs (RI, LF, and CS) and land management BMPs (RF and ERB).

Modeling the BMPs involved modifying the input files of the linked flow and reactive transport model to reflect the changes in water and land management. Water management BMPs required some amendments to both MODFLOW-SFR and RT3D-OTIS input files, except in the case of CS which only required changes to MODFLOW-SFR input files. Land management BMPs required only changes in RT3D-OTIS input files.

RI BMPs constitute a change to more efficient irrigation practices. Crops are assumed to consume roughly the same amount of water; however, less water is applied to fields due to increased efficiency. This improved efficiency could be obtained by converting traditional surface irrigation to more efficient irrigation methods (such as sprinkler or drip) or by improving surface irrigation practices (grading the land surface, altering rates and timing of irrigation application, etc). Levels of RI simulated with the model ranged from 5-30 percent below simulated baseline conditions. The applied water on each cultivated field was reduced by the specified percentage, and a corresponding reduction was made in the modeled canal diversions. Additionally, an input in RT3D-OTIS which specifies the fraction of pumped water, canal water, and precipitation applied to each model cell had to be altered for each RI BMP, compared to baseline conditions.

Table 4.1: Summary of considered BMP scenarios.

Reduced Irrigation (%)	Lease Fallowing of Fields (%)	Canal Sealing to Reduce Seepage (%)	Reduced Fertilizer Application (%)	Enhanced Riparian Buffers to Increase Chemical Reduction Rates (factor)	BMP Level
RI	LF	CS	RF	ERB	
Single BMPs					
0	0	0	0	0	-
5	0	0	0	0	Basic
10	0	0	0	0	
15	0	0	0	0	
20	0	0	0	0	Intermediate
25	0	0	0	0	Aggressive
30	0	0	0	0	
0	5	0	0	0	Basic
0	10	0	0	0	
0	15	0	0	0	
0	20	0	0	0	Intermediate
0	25	0	0	0	Aggressive
0	30	0	0	0	
0	0	20	0	0	Basic
0	0	30	0	0	
0	0	40	0	0	
0	0	50	0	0	Intermediate
0	0	60	0	0	
0	0	70	0	0	Aggressive
0	0	80	0	0	
0	0	0	0	2	Basic
0	0	0	0	5	Intermediate
0	0	0	0	10	Aggressive
0	0	0	5	0	Basic
0	0	0	10	0	
0	0	0	15	0	
0	0	0	20	0	Intermediate
0	0	0	25	0	Aggressive
0	0	0	30	0	
Combination BMPs					
	✓	✓			Basic; Intermediate; Aggressive
✓		✓			Basic; Intermediate; Aggressive
	✓		✓		Basic; Intermediate; Aggressive
		✓	✓		Basic; Intermediate; Aggressive
✓	✓				Basic; Intermediate; Aggressive
✓			✓		Basic; Intermediate; Aggressive
✓	✓	✓			Basic; Intermediate; Aggressive
✓	✓		✓		Basic; Intermediate; Aggressive
✓		✓	✓		Basic; Intermediate; Aggressive
	✓	✓	✓		Basic; Intermediate; Aggressive
✓	✓	✓	✓		Basic; Intermediate; Aggressive
✓	✓	✓	✓	✓	Basic; Intermediate; Aggressive
		✓	✓	✓	Basic; Intermediate; Aggressive

LF BMPs entail fallowing irrigated fields for the purpose of leasing the water in excess of crop consumptive use to cities. Fallowing typically occurs for three out of ten years with associated water rights remaining with the irrigators. In the current study, a LF scenario was simulated as a fraction (ranging from 5-30%) of the cultivated fields fallowed (with no applied irrigation water) during any given year, as described by Morway et al. (2013). Lands were fallowed based on crop type, with corn, hay, and alfalfa fallowed before higher-valued crops. As in RI scenarios, canal diversions and fractions of applied water in RT3D-OTIS input were altered for LF scenarios. Additionally, RT3D-OTIS input files were amended to remove fertilizer application from fallowed fields.

Canals are assumed sealed using polymers, like linear anionic polyacrylamide (Susfalk et al. 2008, Martin 2014), to reduce seepage losses in CS scenarios. Currently, canals are not sealed or lined and a significant amount of conveyed water is lost to seepage to groundwater. To lessen seepage, the conductance of the canals is lowered, resulting in the seepage reduction ranging 20 to 80 percent from baseline conditions and canal diversions were decreased accordingly.

In the LARV, farmers commonly apply N fertilizers in excess of what is required for optimal crop yields. In BMPs that include RF, the input amount of fertilizer applied to all fields is lowered in RT3D-OTIS by amounts ranging from 5 to 30 percent from the baseline. Furthermore, a factor used to increase the NO_3 concentration of water running off the end of each irrigated field, compared to the concentration of the applied irrigation water, also was reduced.

Changing the dimensions, vegetative mix, and organic carbon composition of the riparian corridor adjacent to streams to accelerate the chemical reduction of dissolve NO_3 and Se is assumed in the considered ERB BMP scenarios. In these scenarios, reduction rates were increased by specified factors ranging from 2 to 10 times those under baseline conditions. While these factors result in chemical reduction rates within the feasible range reported in the literature, there is little information

available on the practicality of implementing such increases within the modeled region. Therefore, model output resulting from these scenarios must be interpreted with caution.

Apart from input file modifications for the single BMPs, other model modifications were necessary to adequately simulate the BMP scenarios. Water management BMPs alter flow patterns within and to the Arkansas River; in order to implement such BMPs on a region scale while insuring compliance with Colorado water law and the Arkansas River Compact with Kansas, new storage accounts likely would need to be set up in one or more on-stream or off-stream reservoirs. Application of BMPs which include RI, LF, and CS would involve reduced diversions of river flows to canals and would result in diminished surface and groundwater return flows to the river. Generally, this constitutes net increases in river flow during the irrigation season, compared to baseline conditions, and net reductions during the off season. New reservoir storage accounts would allow for water to be stored during times of net excess river flow due to reduced diversions to canals and to be released to the river over time to make up for net stream depletions due to reduced return flows.

Pueblo Reservoir was assumed to be available for water storage in analyzing the impact of alternative BMPs. Flows in the Arkansas River at the upstream end of the segment within the USR were altered so that river flows leaving the USR at the downstream end would remain the same under each BMP as during baseline conditions. This was done under the assumption that changes in reservoir management would enable reservoir releases resulting in properly timed upstream river flows. To compute the required storage and releases from Pueblo Reservoir, each BMP scenario was first simulated with the same river flows entering the USR as under the baseline. Next, the river flow computed for the BMP at the downstream end of the USR was compared with that computed for the baseline condition. The necessary reservoir storage was computed using the difference between the baseline and BMP flows when the BMP flows were less than the baseline (typically during the crop season).

Water was assumed released from reservoir storage to make up the difference when computed baseline flows exceed simulated BMP flows downstream (usually during the winter). Typically, the simulated overall total volume of water leaving the USR for a given year is greater under a water management BMP than under the baseline. This primarily results from a decline in calculated non-beneficial consumptive use from naturally-vegetated or fallow fields due to a predicted increase in water table depth in the region resulting from BMP implementation. This excess water is routed through the system to the downstream end of the USR, with only the water necessary to supplement low flows and to account for water loss due to reservoir water evaporation assumed stored in the reservoir. Water lost to reservoir evaporation is calculated based upon the additional storage volume in the reservoir. Water is assumed stored in the reservoir so that at the end of the 11-year simulation period there is approximately no storage remaining in the reservoir. This approach to reservoir storage was not meant to model the reservoir management or the river basin as a whole, but only to approximate river flows in the USR that would allow BMPs to be implemented.

A further model modification was made in an attempt to estimate the changes in Se and NO₃ concentrations that would occur at the upstream end of the river segment in the USR under a BMP if it was assumed to be implemented not only in the USR but also over the entire extent of the LARV. The change in upstream concentrations under a BMP were computed using the ratios of irrigated acreage and river length upstream of the USR to those within the USR. This resulted in a factor of 1.08 multiplied by the baseline concentration at the upstream end of the river segment for each simulated time step. A similar methodology was used to estimate the reduction in concentrations in flows diverted to canals with headgates located upstream of the USR. Due to significant spatial variability in computed Se and NO₃ concentrations along the river, the concentration changes due to a BMP were computed as averages over the downstream third of the Arkansas River segment within the USR.

4.4. Results and Discussion

Figure 4.4 shows the simulated temporal average groundwater concentrations of Se and NO₃ over the USR, illustrating the spatial variability of the concentrations over the extent of the aquifer. Figures 4.5 and Figure 4.6 depict the spatial distribution of temporal average total Se and NO₃ mass loading (groundwater and runoff), respectively, to the stream system over the 40-year long-term baseline period. Figure 4.7 shows the simulated 85th percentile of total dissolved Se concentration and median NO₃-N concentration in the Arkansas River in the USR averaged over the 40-year baseline simulation period in comparison to the Colorado chronic standard for Se of 4.6 µg L⁻¹ and the interim standard for total N of 2.0 mg L⁻¹. The model output highlights the significant spatial variability of the baseline concentrations and that the bulk of the mass loading occurs in the upstream portion of the USR.

A total of 67 BMP scenarios, including 39 combined BMPs, were analyzed for their effectiveness in reducing Se and NO₃ contamination in the USR. Due to the uncertainty associated with the practicality of its implementation, ERB was considered only as a single BMP and within a limited number of combined BMP scenarios. Every combined BMP scenario that included the remaining four single BMPs was implemented at basic, intermediate, and aggressive levels. Though scenarios that combined BMPs at different levels of implementation (e.g. an aggressive level implementation of one BMP along with a basic level implementation of another) could be tested, to limit the total number of considered BMPs and the associated computational requirements only single BMPs with the same level of implementation were combined together for this study. Additionally, for the single BMPs, smaller increments of implementation level were examined to more accurately estimate the relationship of implementation level to the resulting degree of Se and NO₃ reduction.

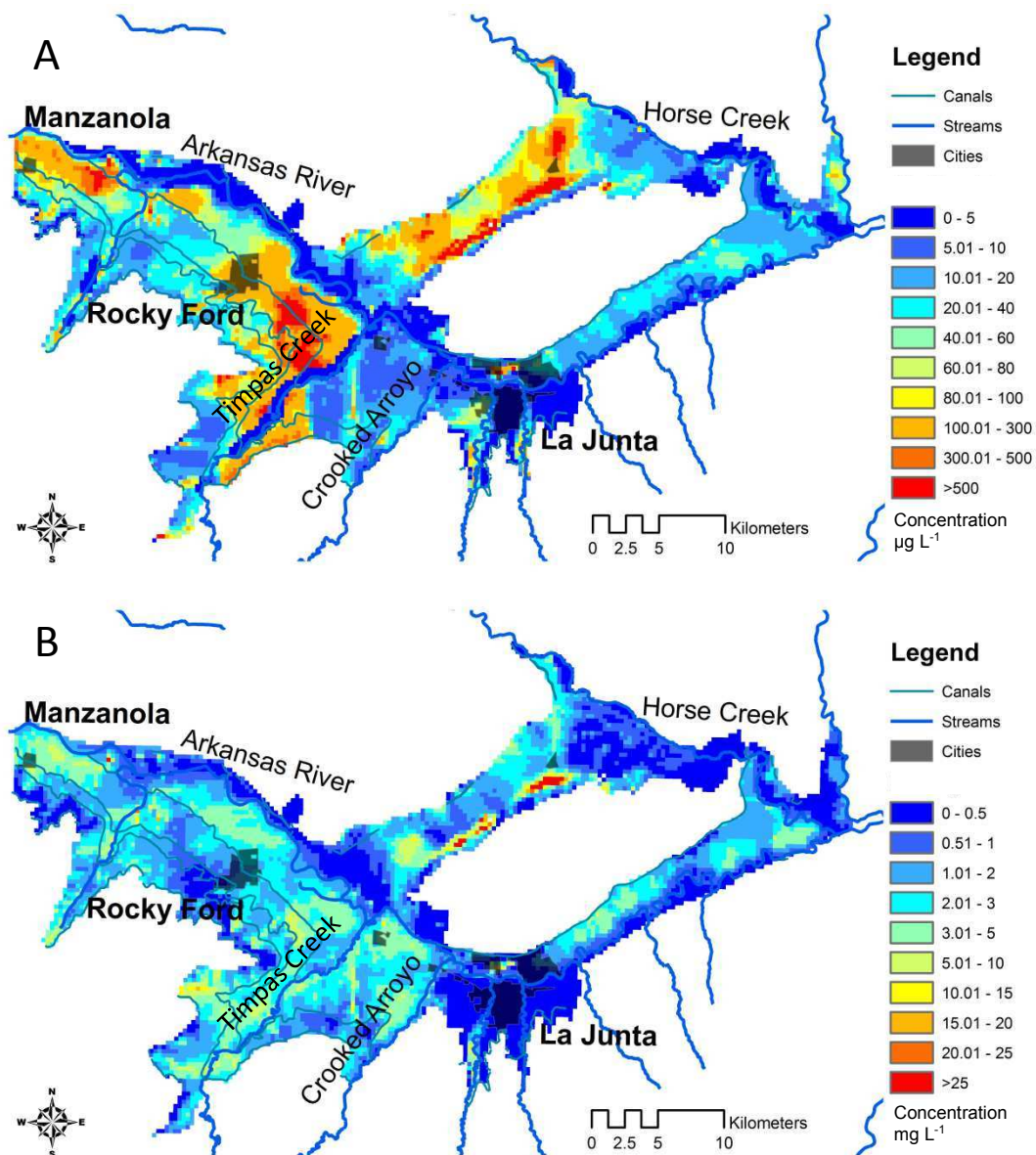


Figure 4.4: Simulated average groundwater concentrations in the USR for (A) Se and (B) NO_3 over the 40-year long-term baseline simulation.

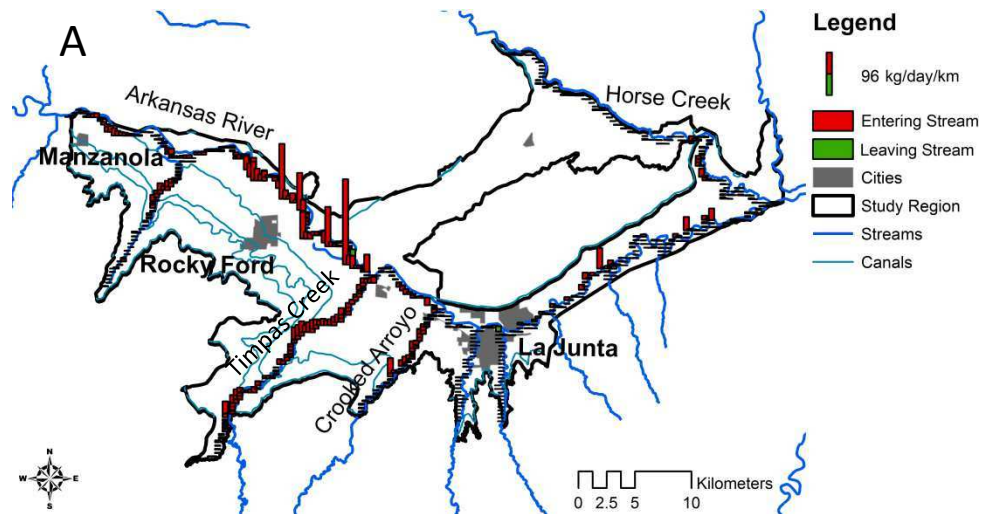


Figure 4.5: Simulated long-term baseline Se mass loading in the USR as spatial distribution of the temporal average rate.

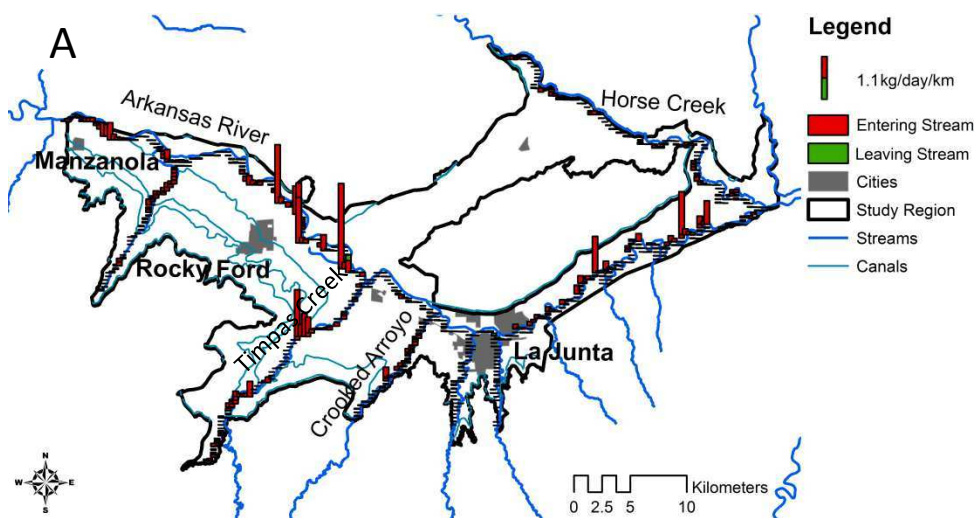


Figure 4.6: Simulated long-term baseline $\text{NO}_3\text{-N}$ mass loading in the USR as spatial distribution of the temporal average rate.

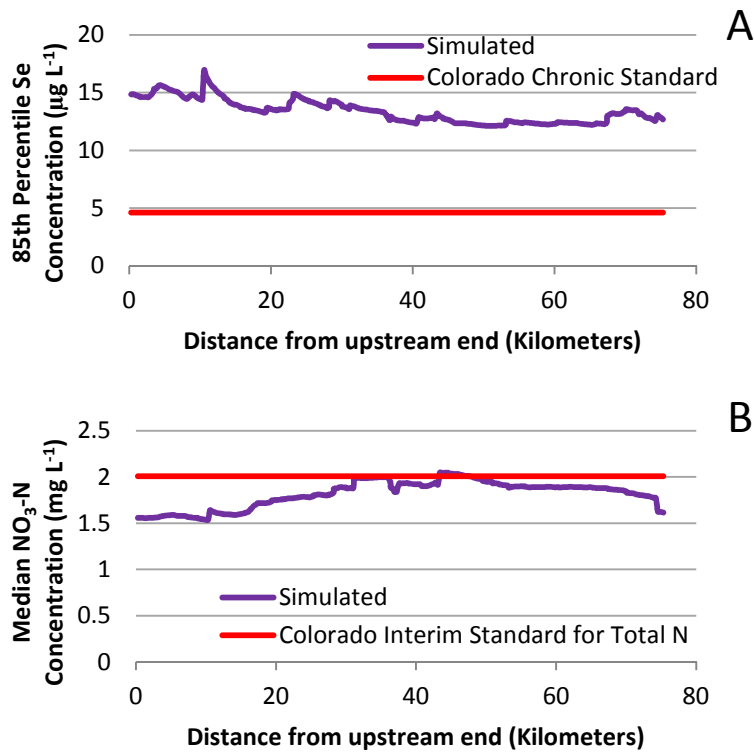


Figure 4.7: Simulated (A) 85th percentile C_{Se} and (B) median $C_{\text{NO}_3\text{-N}}$ over the 40-year baseline period along the Arkansas River within the USR.

The impact of BMPs on groundwater concentrations over the USR is illustrated in Figure 4.8 for the case of the RI30 LF30 CS80 RF30 combined BMP. Figure 4.8 shows the difference in the computed temporally averaged groundwater concentration for the baseline condition and the RI30 LF30 CS80 RF30 condition for C_{Se} and $C_{\text{NO}_3\text{-N}}$. In these plots, positive (blue shade) values indicate reductions in concentrations predicted to occur due to BMP implementation, while negative (red shade) values indicate predicted increases in concentrations. The C_{Se} plot displays substantial spatial variability in the effectiveness of the BMP to lower groundwater concentrations. While there is little net change in the concentration over the entire regions, there are areas where it is markedly reduced and others where it is markedly increased. This is likely due to the localized dominance of different BMPs over the spatial extent of the aquifer. Figure 4.8B, reveals a much more uniform reduction in $C_{\text{NO}_3\text{-N}}$ for this BMP, with

only a few instances of increased concentration, likely because most BMPs themselves result in a reduction in the concentration. For each of the water management BMPs the simulated effect of their implementation was found to be significantly variable across the region, especially for C_{Se} . The discovered nonhomogeneity in their effectiveness may point to the need to target the use of these BMPs to areas where they will be most effective in achieving concentration reductions.

The overall spatiotemporal average reductions in groundwater C_{Se} and C_{NO_3-N} over the final 11 years of the simulation period is summarized for each of the 67 BMPs in Figure 4.9. The BMPs are grouped by their respective types, with the level of implementation increasing from the most basic on the left of each group to the most aggressive on the right. The single BMPs, CS, ERB, and RF were found to be effective at reducing groundwater C_{Se} by 18.3%, 5.3%, and 2.3%, respectively, under the aggressive level scenarios, while RI and LF increased C_{Se} by 13.1% and 16.4%, respectively, under the aggressive level scenarios. The small reductions in C_{Se} under ERB and RF BMPs are likely due to a diminished availability of NO_3 to mobilize Se as well as to an enhanced chemical reduction of Se under the ERB scenario, while the larger reduction predicted for CS probably is due to altered subsurface flow patterns which diminish interaction between seepage-induced groundwater flow and the Se-containing shale formations. Additionally, predicted increases in the groundwater C_{Se} that occur under RI and LF may be due to increases in C_{Se} in flow that exits the unsaturated zone to recharge the water table, as affected by dissolution, evaporative concentration, and heterotrophic redox reactions; corresponding increases in C_{NO_3-N} in recharge water that contribute to inhibited chemical reduction of Se; and the slowing of return flows (by a reduced head gradient to the streams) allowing groundwater with available NO_3 and DO extended time to interact with bedrock and near-surface shale containing seleno-pyrite. Figure 4.9B shows lower predicted C_{NO_3-N} under LF and CS BMPs compared to the baseline. For the RI BMP,

significant spatial variability in simulated C_{NO_3-N} was found, with some locations showing an increase and others a decrease. The overall net increase in predicted average C_{NO_3-N} over the region under RI is likely because the same amount of fertilizer is assumed applied to fields but with less applied water. For lowering C_{NO_3-N} , the most effective single BMP was RF which, at the aggressive level, resulted in an average concentration 21.1% lower than the baseline.

Simulated reductions in Se and NO_3 mass loading and return flow rates to the Arkansas River and its tributaries from both groundwater and tail water runoff over the final 11 years of the simulation period are summarized in Figure 4.10. Model output indicates that all BMPs would lead to some, in cases substantial, lowering in mass loading of solutes to the Arkansas River, similar to the findings of Bailey et al. (2015a, 2015b). BMPs combined of RI, LF, CS, RF, and ERB have by far the largest simulated reduction mass loading, decreasing NO_3 loading by 90.8% and Se loading by 86.3%. Discrepancies between the values estimated by Bailey et al. (2015a, 2015b) and the current predictions could be attributed to a number of different causes including the inclusion of surface runoff mass loading, the simulation of stream flow levels using SFR2 and OTIS, and other recent modifications and enhancements further described in the appendices of Shultz (2017). Decreases in the return mass loading rates are attributed to two processes: changes in the rates of return flow entering the stream system and changes in solute concentrations within the return flows. Generally speaking, model results show that groundwater return flow (which makes up the majority of total return flow) has higher C_{Se} and lower C_{NO_3-N} than the receiving stream water. Low C_{NO_3-N} values likely are due to denitrifying reactions which occur in the groundwater, especially within the riparian zone, chemically reducing C_{NO_3-N} . Thus, if the concentrations of the return flow are not significantly altered by a BMP, a decrease in return flow rate would lead to a corresponding decrease in C_{Se} and increase in C_{NO_3-N} in the streams. These

processes must be taken into account when evaluating a BMP's effectiveness based on mass loading alone and are further highlighted below by the simulated changes in in stream concentrations.

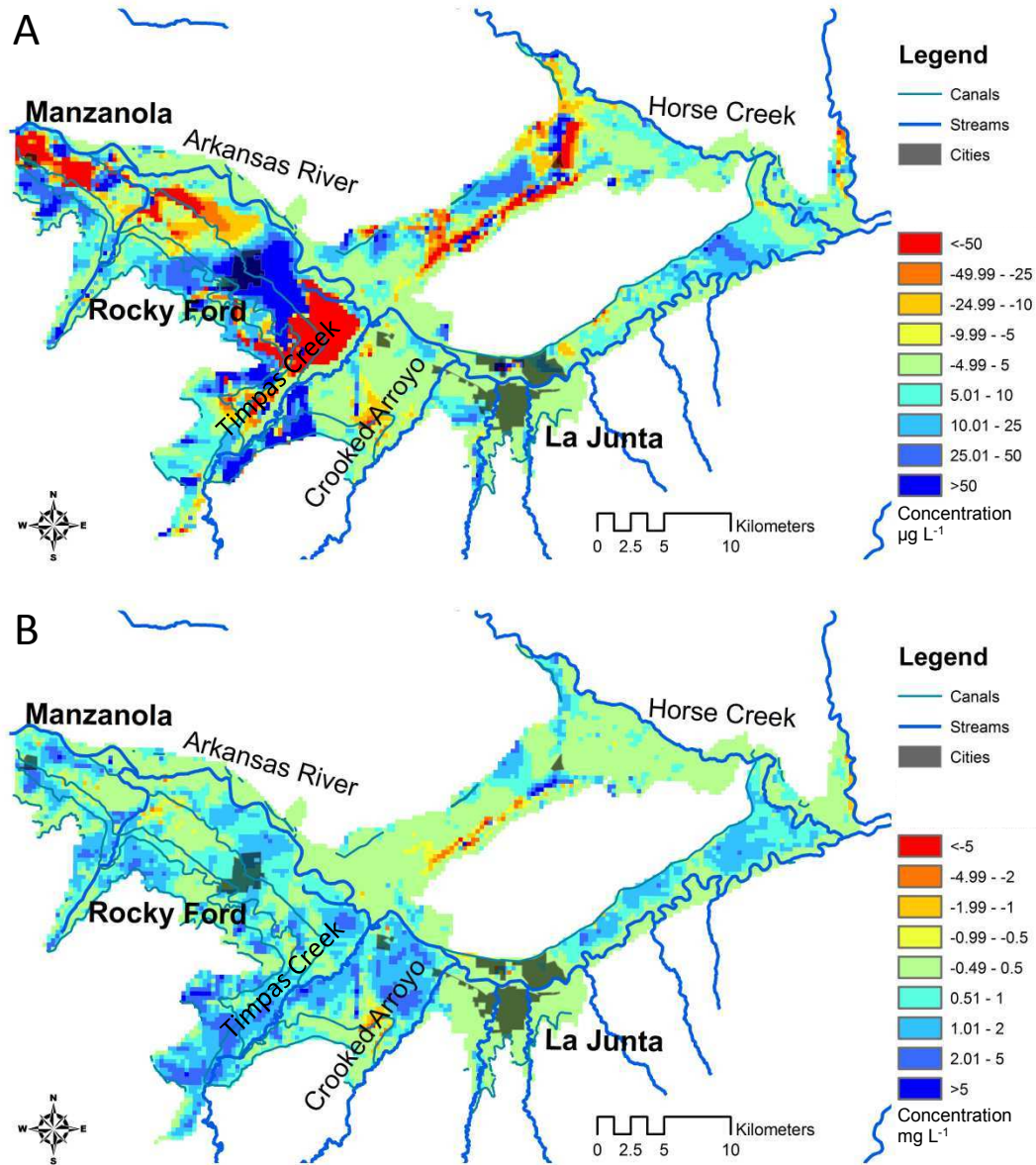


Figure 4.8: Simulated difference between the simulated baseline and RI30 LF30 CS80 RF30 BMP groundwater (A) C_{Se} and (B) C_{NO_3-N} over the 40 year period averaged temporally.

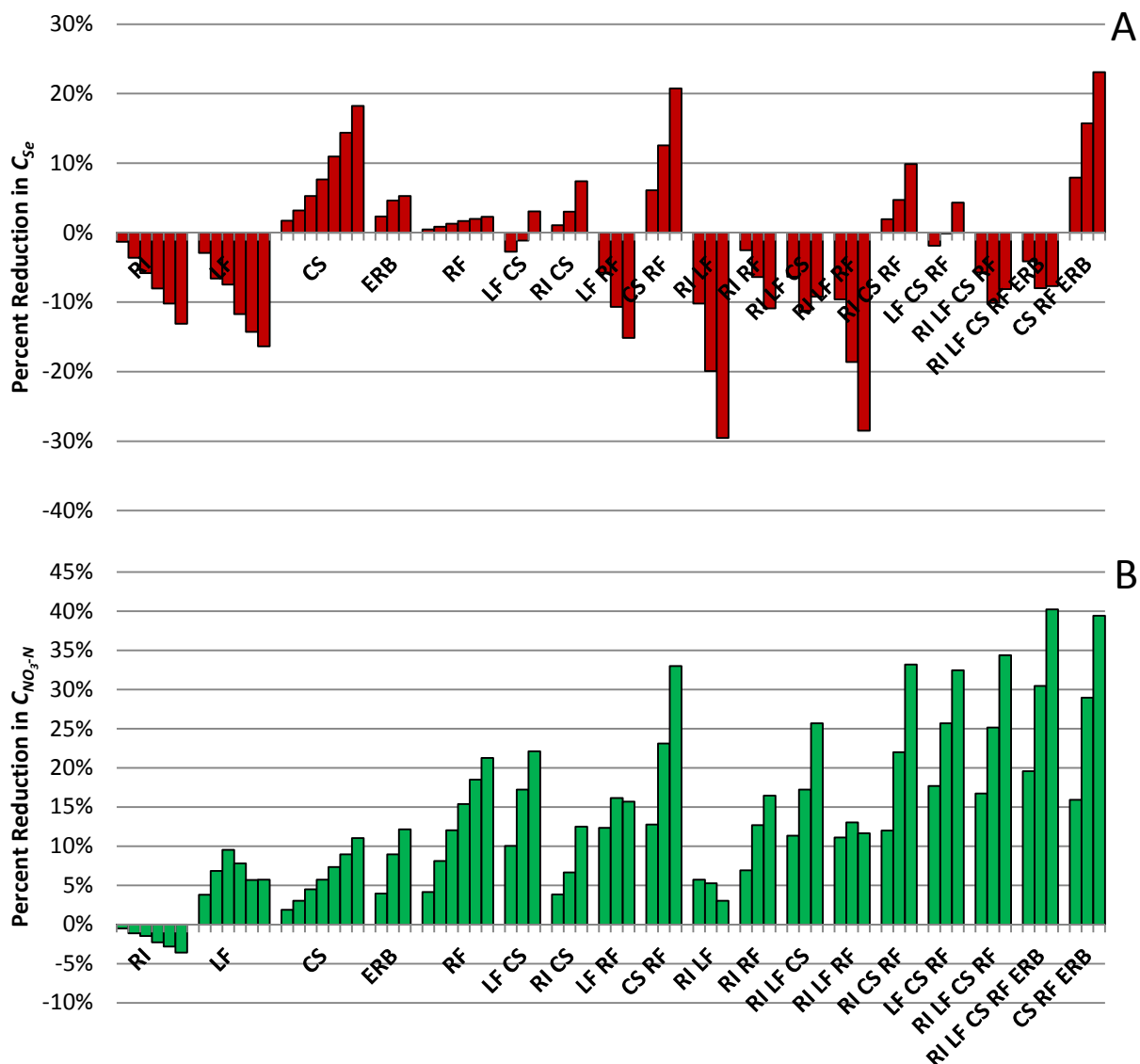


Figure 4.9: Simulated reduction in spatiotemporally averaged simulated groundwater (A) C_{Se} and (B) C_{NO_3-N} of the BMPs compared to the baseline condition.

The significant decrease in return flow rates shown in Figure 4.10B points to a difficulty in implementation of these BMPs on the regional scale. Water management BMPs lessen the amounts of water being diverted into the region, being applied to fields, and returning in excess to the river system. Results show that aggressive single water management BMPs could lower return flows by more than 10-20% of their current levels and some combined BMPs by more than 50%. These changes alter the amount and patterns of stream flow and potentially break Colorado water law which requires no harm

to the ability of downstream users to divert their appropriated water rights as well as violate the Arkansas River Compact which prohibits material change in the magnitude and pattern of river flows into Kansas. Such flow alterations must be remedied using reservoir storage and release or some other means.

Simulated C_{Se} and C_{NO_3-N} along the Arkansas River under baseline conditions and water select aggressive BMPs are shown in Figure 4.11. The BMPs include RF30, RI30, ERB10, LF30, CS80, and the combined BMP RI30LF30CS80RF30; representing the upper limit of aggressive implementation. Figure 4.11A shows that RI30 and LF30 have little effect on C_{Se} along the river reach and actually result in an increase in the concentration downstream of the mouth of Timpas Creek. This is likely due, at least in part, to the considerable increase in groundwater C_{Se} west of Timpas Creek (Figure 4.9) which causes a corresponding increase in return flow concentration. Thus, despite the fact that RI30 and LF30 substantially reduce the rate of groundwater return flow entering the Arkansas River, they are predicted to contribute to a net worsening counter-effect, including higher groundwater C_{Se} , which results in a net increase in C_{Se} along the Arkansas River. The RF30, CS80, and ERB10 BMPs are much more effective in the lowering C_{Se} in the river, with ERB10 being the most impactful. Figure 4.11B shows the effects of the same BMPs on C_{NO_3-N} . The water management BMPs (RI30, LF30, and CS80) result in an increase in C_{NO_3-N} when compared to the baseline. This increase in concentration is due to the relatively low C_{NO_3-N} in groundwater return flow that exists under the baseline. Since the groundwater returns flow contains a lower C_{NO_3-N} than the surface water, due to chemical reduction in the riparian zone (Huizenga et al. 2017), it acts to dilute the stream water. Therefore, when return flow volume is reduced under a water management BMP, less dilution of the stream water occurs, resulting in a higher in-

stream concentration than under baseline conditions. Thus, despite the reductions in overall mass loading shown in Figure 4.10A, the water management BMPs result in higher stream C_{NO_3-N} .

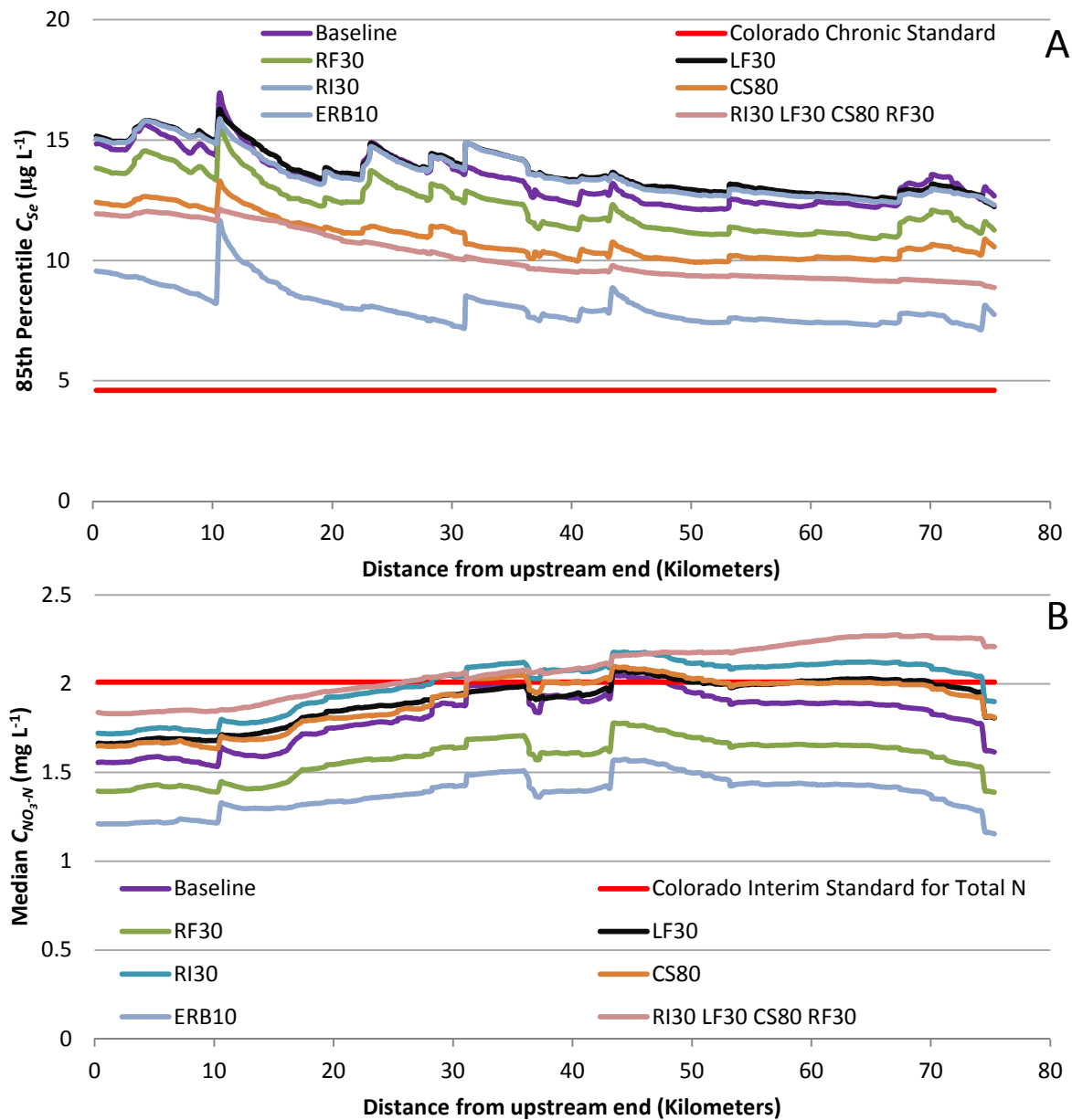


Figure 4.10: Simulated reduction in (A) Se and NO_3 mass loading and (B) average return flow rate to the Arkansas River and its tributaries of the BMPs compared to the baseline condition.

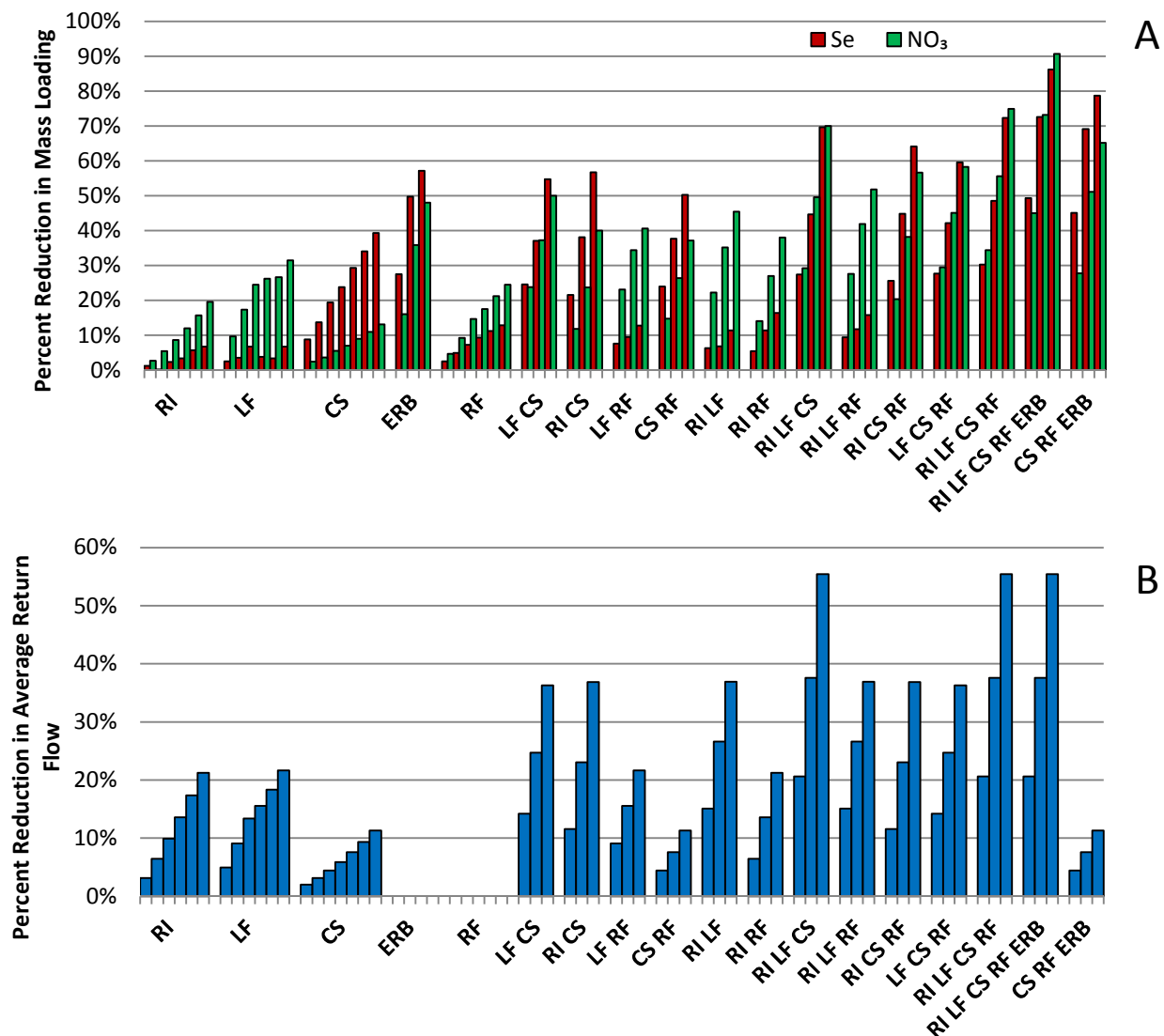


Figure 4.11: Simulated baseline and select BMPs (A) 85th percentile C_{Se} and (B) median C_{NO_3-N} over a 40-year period along the Arkansas River over the extent of the model domain.

There is also significant temporal variability in simulated concentration reduction along the Arkansas River, which is depicted for selected BMPs in the plots of percent reduction in C_{Se} averaged over the downstream third of the river reach within the USR in Figure 4.12. In addition to showing the large degree of temporal variability these plots reveal a trend of increasing impact over time. Most water management BMPs require 5 to 10 years to achieve their full effect on C_{Se} ; this is because of the rather slow nature of groundwater flow and solute reactions. The land management BMPs tend to keep increasing in effectiveness throughout the duration of the simulation period, implying that it takes over 40 years for their full effects to be realized. Due to the trends in BMP effectiveness, spatiotemporal average model output for groundwater concentration, mass loading, and stream concentration was examined over the final 11-year historical period.

Figure 4.13 shows the simulated spatial average reduction of the 85th percentile value of C_{Se} and of the median C_{NO_3-N} over the last 11 years of the simulation period for each of the 67 BMPs. While these results offer a general indicator of the overall effectiveness of the BMPs, the effectiveness varies over space and time as indicated in the preceding. For both single and combined BMPs there is a general correspondence between the predicted change in concentration, either positive or negative, and the level of implementation. ERB is found to be the most effective single BMP for lowering both C_{Se} and C_{NO_3-N} , resulting in an average reduction of 51.3% and 32.7%, respectively, at the aggressive level. Furthermore, CS RF ERB is the most effective combined BMP, resulting in an average reduction of 53.0% and 28.2%, respectively, at the aggressive level. Interestingly, the RI LF CS RF ERB combined BMP is predicted to be less effective in lowering concentrations than ERB alone at the aggressive level. This is likely because of the significant reduction in groundwater return flow rate that occurs in the implementation of the combined BMP. Since ERB is beneficial in chemically reducing solutes as they return through the riparian area, diminished return flow causes the BMP to be less effective.

Furthermore, though RI is generally ineffective in lowering C_{se} as a single BMP in combination with the CS BMP it results in a modest increase (about 2 percentage points) in the reduction of C_{se} when compared to CS alone at the aggressive level. This is probably due to alterations in flow patterns under the joint BMP implementation that cause it to be more effective than the respective single BMPs. Comparing decrease in mass loading (Figure 4.10A) and reduction in stream concentration (Figure 4.13) reveals that there is not necessarily a direct correspondence between the two. While BMPs such as RI and LF show significant decreases in mass loading, simulated stream concentrations remains unchanged or even increase slightly. In such cases, the reduction in mass loading corresponds primarily to a reduction in return flow rates back to the Arkansas River and its tributaries rather than to major alterations in solute processes. This is important to note when evaluating the effectiveness of BMPs based on impacts to solute mass loading alone.

Figure 4.13B depicts a number of BMPs that are predicted to result in reductions or only small increases in stream C_{NO_3-N} . These include the ERB, RF, and LF, RF single BMPs, CS RF combinations, RI RF combinations, RI LF RF combinations, RI CS RF combinations, LF CS RF combinations, RI LF CS RF ERB combinations, and CS RF ERB combinations, indicating that water management BMPs in combination with land management BMPs can result in modest reductions in stream C_{se} while keeping increases in C_{NO_3-N} at a minimum.

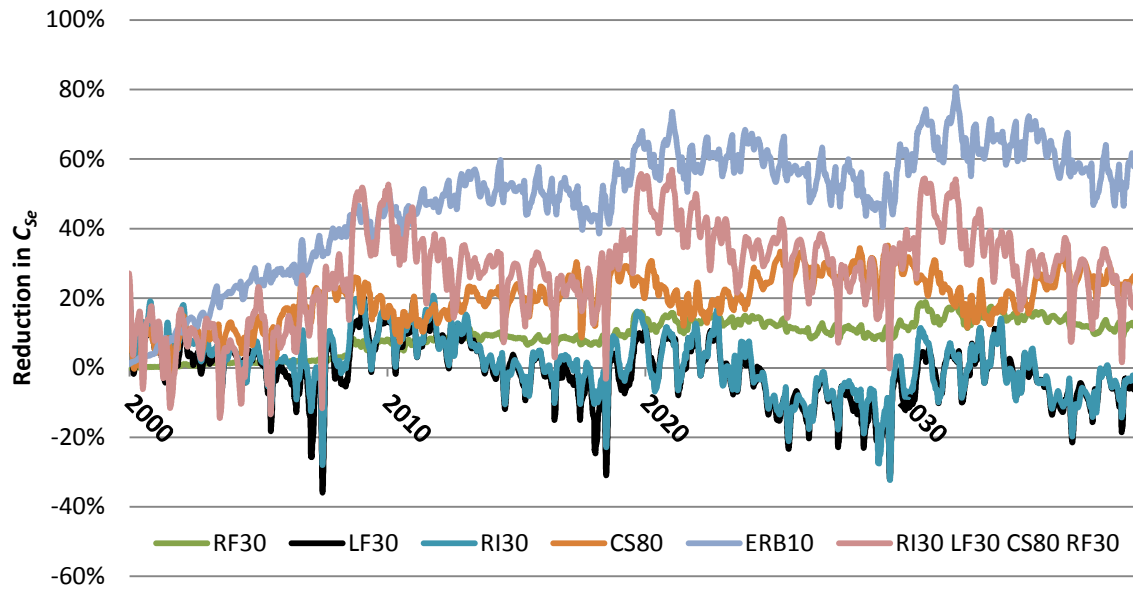


Figure 4.12: Simulated percent reduction in C_{se} over the downstream third of the Arkansas River reach within the USR for select BMPs.

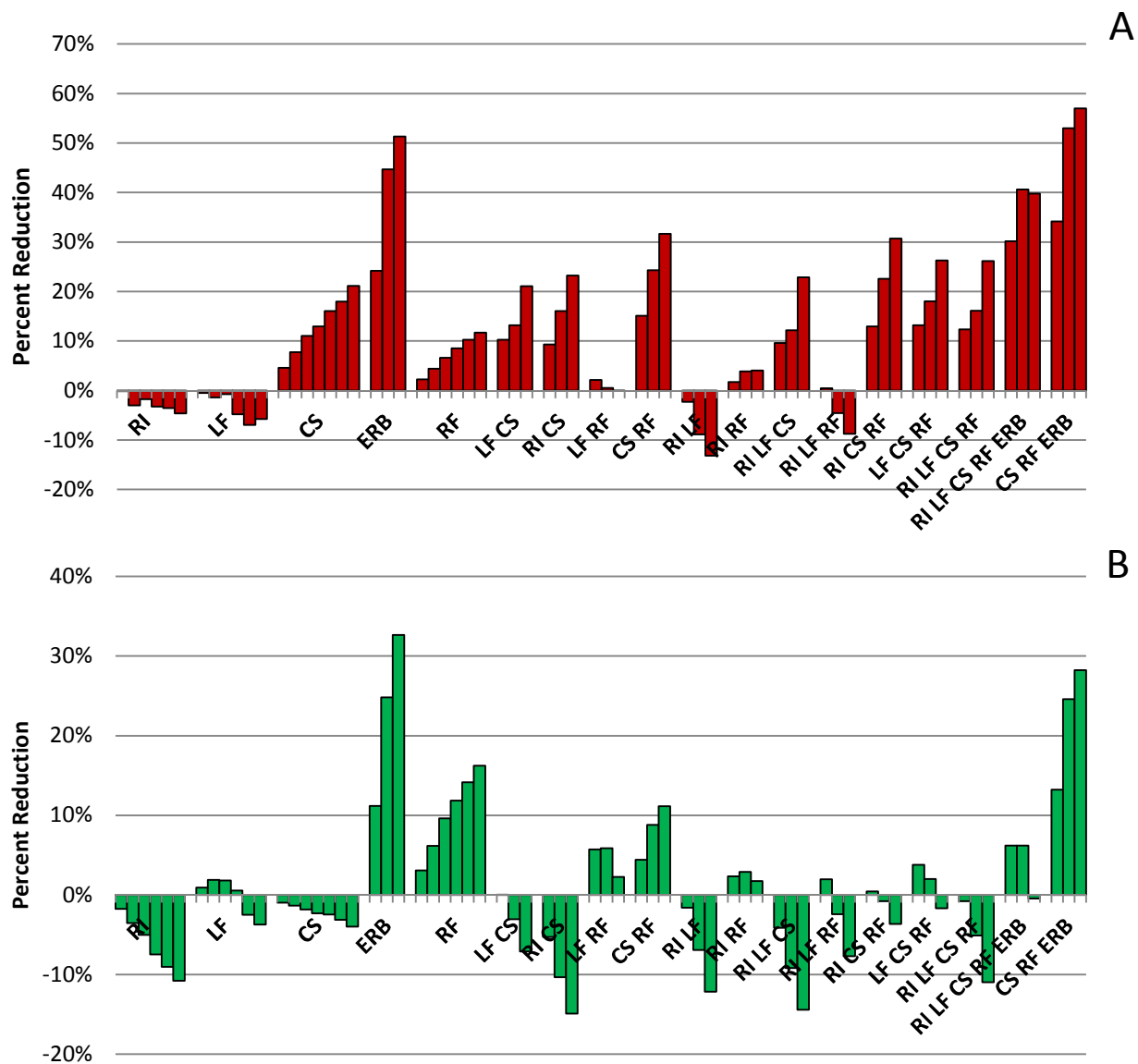


Figure 4.13: Simulated reduction in (A) 85th percentile C_{Se} and (B) median C_{NO_3-N} for different BMPs and levels of implementation compared to the baseline condition.

4.5. Summary and Conclusions

The calibrated stream-aquifer flow and solute transport model provides a framework for evaluating the potential of alternative land and water BMPs to decrease Se and NO₃ in groundwater concentrations, mass loading to streams, and stream concentrations in the LARV in Southeastern Colorado. Many stand-alone and combined BMPs were simulated for a 40-year period using MODFLOW-SFR linked with RT3D-OTIS, with the interactive nature of Se and NO₃ allowing for the potential of BMPs to lower contamination from both solutes. Results from this study also could prove useful for other regions facing similar issues, offering insight into prime methods for improving water quality affected by irrigated agriculture.

Modeling outcomes indicate that there are several means for achieving significantly lower Se and NO₃ concentrations in the region. Broad implementation of CS, RF, and ERB BMPs, alone and in combination, are all simulated to effectively decrease the Se concentration within the stream and groundwater systems, while the land management BMPs (RF and ERB) are found effective at reducing the NO₃ concentration. Results further indicate the benefit of implementing BMPs in combination with one another. For example, jointly implementing CS and RF is predicted to result in a large reduction of Se concentration in the river and has some positive effective on NO₃ concentration as well. Furthermore, the model suggests that joint implementation of CS and RI or LF would enhance the effectiveness of CS alone, though RI and LF are not impactful as stand-alone BMPs. The CS RF ERB combination appears to hold out the greatest promise for curtailing both Se and NO₃ pollution.

This study also highlights the marked spatial and temporal variability in the BMP impacts. Using this regional-scale modeling of broad BMP application as a guide, future analysis should focus on gaining an understanding of the best areas within the USR to target for implementation of BMPs. Additional work is being undertaken to ascertain the economic viability of using these BMPs not only to reduce Se and NO₃ concentrations, but also to control salinity which adversely impacts crop yield, in the hopes of

understanding which effective BMPs would be most practically feasible. Finally, future projects will analyze similar BMPs in the DSR to evaluate their effectiveness under different hydrological and agro-environmental conditions.

CHAPTER 5: Conclusions and Recommendations

As global population continues to grow in the future, society will be presented with new and difficult challenges to keep pace with food and fiber demands while limiting long-term land and water degradation. Within the LARV, transition of lands from natural ecosystems to irrigated agriculture has introduced a number of problems including high water tables, high soil salinity, and water quality issues related to Se and NO_3 and other pollutants. Over the span of nearly two decades, studies by researchers at Colorado State University have been conducted in the area in an effort to limit or reverse these land and water management problems in ways that would be mutually beneficial to the local agricultural industry and the environment.

In this study, effects of implementing BMPs in one representative region of the LARV, the USR, have been modeled in order to better understand methods for addressing Se and NO_3 pollution. NO_3 is present within the stream-aquifer system due to inefficiencies in fertilizer and irrigation application; applied nutrients runoff to streams and infiltrate into groundwater from deep percolation of applied irrigation. Se presence in the region is due to its mobilization from seleno-pyrite in the local bedrock and Se previously dissolved in the irrigation water. This Se is mobilized into groundwater and transformed as it returns to the Arkansas River and its tributaries by redox processes, which are accelerated due to the presence of NO_3 and DO. The presence of both Se and NO_3 in the stream-aquifer system has the potential to cause severe consequences ecologically and to human health; therefore, it is imperative to attempt to decrease these contaminant concentrations.

To analyze alternative land and water BMPs, a comprehensive stream-aquifer model using MODFLOW and RT3D-OTIS was developed and calibrated for the study region. In prior studies, only groundwater flow and reactive transport were simulated. To represent the stream-aquifer system as a whole, the SFR2 package was added to the MODFLOW model, simulating stream flow, and OTIS-QUAL2E was coupled with the existing UZF-RT3D model, simulating reactive transport. The addition of stream

flow and reactive transport modeling required an extensive calibration of the component models including a manual calibration of streambed conductance in the SFR2 package and a manual and automated calibration of stream and aquifer RT3D-OTIS parameter values. This calibration process matched simulated values to flow measured at stream gages, groundwater return flow, unaccounted for return flow, groundwater hydraulic head, evapotranspiration, groundwater concentrations, estimated unaccounted-for return mass loading to streams, and stream concentrations. Subsequent to calibration, simulated model results were tested against similar observed data from a period of time separate from that used for calibration.

Using the calibrated model parameter values, an 11-year historic period from 1999-2009 was repeated approximately three and a half times, for a total of 40 years, to simulate Se and NO₃ concentrations and loading under baseline (current) land and water management practices. Next, the calibrated model was used to simulate a number of alternative BMPs including reduced irrigation (RI), lease fallowing (LF), reduced fertilizer (RF), canal sealing (CS), and enhanced riparian buffer (ERB), along with their combinations, to determine the most effective means of reducing Se and NO₃ groundwater and stream contamination in the region.

Results show that there are several effective stand-alone BMPs for decreasing Se groundwater and stream concentrations including CS, RF, and ERB. The RI and LF BMPs, however, result in increases in the groundwater and surface water concentrations. The differences in the effectiveness of RI/LF versus CS is not entirely clear but may be due to changes in return flow patterns or interactions with the shale bedrock. However, the effects on NO₃ concentrations must also be considered in the BMP implementation. Model output indicates that while land management BMPs (RF and ERB) are also effective at reducing the NO₃ contamination, stand-alone water management BMPs (CS, RI, and LF) result in an increase in stream NO₃ concentrations because of a lowering of diluting groundwater flows, whose concentrations are decreased by denitrification in the riparian zone, entering the stream. Overall,

with long-term implementation of the BMPs, CS80 is the most effective single water management BMP for reducing Se and NO₃ concentrations in the groundwater resulting in decreases of 18% and 11%, respectively. CS80 was also the most effective water management BMP for lowering Se in stream concentrations, resulting in a reduction of 21%. Furthermore, while the majority of water management BMPs increase the in-stream NO₃ concentration, LF10 was the most effective at reducing it, resulting in a 2% reduction in the concentration. ERB10 was found to be the most effective land management BMP for Se in groundwater, reducing the concentration by 5%, while RF30 is the most effective land management BMP for NO₃ in groundwater, reducing the concentration by 21%. Finally, ERB10 was the most effective land management BMP for reducing Se and NO₃ in stream concentrations, resulting in a 51% and 33% reduction, respectively.

The effects of combined BMPs were found to not necessarily be additive of the single BMPs. This was the case in implementing CS and RI or LF together; the combination of these alterations in water management is more effective than the practices by themselves. Additionally, implementing water management and land management BMPs together, particularly the CS and RF combination and the CS, RF, and ERB combination, have the potential to significantly decrease Se in-stream concentrations while limiting negative effects or even having positive effects on NO₃. The aggressive combination of CS, RF, and ERB was found to be the most effective at lowering the Se groundwater concentration, resulting in a 23% reduction. The aggressive combination of RI, LF, CS, RF, and ERB was the most effective at reducing the groundwater NO₃ concentration, resulting in a 40% reduction. The aggressive CS, RF, and ERB BMP yielded a slightly lower reduction of 39%. Finally, the aggressive CS, RF, and ERB BMP also resulted in the largest in-stream reduction for Se and NO₃, 57% and 28%, respectively. It should be noted that the reduction in the stream NO₃ concentration under the CS, RF, and ERB BMP is less than the ERB BMP by itself, likely due to the reduction in return flows through the riparian area from the implementation of CS, making ERB less effective.

The model results also provide insight about using mass loading to estimate water quality improvements. The simulation output highlights that changes in solute mass loading to streams are not necessarily indicative of reductions in stream concentration, rather a decrease in solute loading may be due primarily to a decrease in the return flows to the stream. Furthermore, if the return flow concentration under baseline conditions is less than the in-stream concentration, due to chemical reduction and/or volatilization processes enroute, total mass loading under a BMP may be lowered but the in-stream concentration may increase.

Finally, simulation results show that it is likely not possible to reduce the in-stream concentrations of Se to levels below the state of Colorado's current chronic standard of $4.6 \mu\text{g L}^{-1}$. Only the aggressive ERB scenario came relatively close to the standard, but it is unknown whether the chemical reduction rates used to represent this BMP are feasible or realistic. Furthermore, such BMPs likely will not be implemented over the large, regional scale used in this model nor in the magnitude used in the aggressive BMPs. Nevertheless, results show the potential of this method for substantially lowering Se and NO_3 concentrations for the region.

Overall, this work suggests there are several effective ways to decrease Se and NO_3 concentrations within the region and within the LARV as a whole. While several BMPs are shown to be effective in reducing the contaminants, it is important to note that there is substantial spatial and temporal variability in the effectiveness of the BMPs, specifically in the groundwater concentrations for the water management (CS, RI, and LF) BMPs. Future work should entail using this spatial variability as an advantage, implementing the BMPs only where they would be most effective at reducing concentrations. This process may be particularly useful for the RI and LF BMPs in making them more effective at lowering in-stream Se concentrations, since concentration increases in the groundwater near Timpas Creek appear to be contributing to the negative effects of these BMPs. Furthermore, future studies of the Downstream Study Region (DSR) should involve similar modeling work, looking at Se and

NO₃ contamination within the stream-aquifer system. Due to differences between the study regions along similar lines as the spatial variability, land and water BMPs could have different relative effectiveness in that region. This future work also should include modeling uranium within the stream-aquifer system to understand the extent of contamination in relation to other constituents and methods to improve water quality in its regard.

REFERENCES

- Ahrlrichs, J. S., and Hossner, L. R. (1987). "Selenate and selenite mobility in overburden by saturated flow." *J. Environ. Qual.*, 16(2), 95-98.
- Ahmad, Z., Kausar, R., and Ahmad, I. (2010). "Highlighting the implications of selenium dispersion from disposal of Kahota Industrial Triangle area, Islamabad, Pakistan using three-dimension solute transport model." *Environ. Monit. Assess.*, 167, 565-579.
- Ajami, H., McCabe, M. F., Evans, J. P., and Stisen, S. (2014). "Assessing the impact of model spin-up on surface water-groundwater interactions using an integrated hydrologic model." *Water Resour. Res.*, 50(3), 2636 – 2656.
- Alemi, M.H., Goldhamer, D.A., and Nielsen, D. R. (1988). "Selenate transport in steady-state, water-saturated soil columns." *J. Environ. Qual.*, 17(4), 608-613.
- Alemi, M.H., Goldhamer, D.A., and Nielsen, D. R. (1991). "Selenate transport in steady-state, unsaturated soil columns." *J. Environ. Qual.*, 20, 89-95.
- Alfthan G., Wang D., Aro, A., Soverib, J. (1995) "The geochemistry of selenium in groundwaters in Finland". *The Science of the Total Environment*. 162, 93-103.
- Almasri, M.N., Kaluarachchi, J.J. (2007). "Modeling nitrate contamination of groundwater in agricultural watersheds". *Journal of Hydrology*. 343, 211– 229.
- Amweg, E.L., Stuart, D.L., Weston, D.P. (2003). "Comparative bioavailability of selenium to aquatic organisms after biological treatment of agricultural drainage water". *Aquatic Toxicology*. 63, 13-25.
- Anderson, M. P, Woessner, W. W., and Hunt, R. J. (2015). *Applied groundwater modeling: Simulation of flow and advective transport*. 2nd Ed., Elsevier, Inc., London.

- Arnold J.G., Williams J.R., Srinivasan R., King K.W., Griggs R.H. (1996). "SWAT — Soil and Water Assessment Tool (User manual)". Temple, TX: U.S. Department of Agriculture, Agricultural Research Service, Grassland Soil and Water Research Laboratory.
- Azzellino A., Salvetti R., Vismara, R., Bonomo, L. (2006). "Combined use of the EPA-QUAL2E simulation model and factor analysis to assess the source apportionment of point and non point loads of nutrients to surface waters". *Science of the Total Environment*. 371, 214–222.
- Bailey, R.T., Hunter, W.J., Gates, T.K. (2012). "The influence of nitrate on selenium in irrigated agricultural groundwater systems". *J. Environ. Qual.* 41(3), 783-92.
- Bailey, R.T., Gates, T.K., Halvorson, A.D. (2013a). "Simulating variably-saturated reactive transport of selenium and nitrogen in agricultural groundwater systems". *Journal of Contaminant Hydrology*. 149, 27–45.
- Bailey, R.T., Morway, E.D., Niswonger, R.G., Gates, T.K. (2013b) "Modeling Variably Saturated Multispecies Reactive Groundwater Solute Transport with MODFLOW-UZF and RT3D". *Ground Water*. 51(5), 752-61.
- Bailey, R.T. and Ahmadi, M. (2014). "Spatial and temporal variability of in-stream water quality parameter influence on dissolved oxygen and nitrate within a regional stream network." *J. Ecol. Model.* 277, 87-96.
- Bailey, R.T., Gates, T.K., Ahmadi, M. (2014). Simulating reactive transport of selenium coupled with nitrogen in a regional-scale irrigated groundwater system. *Journal of Hydrology*. 515, 29–46.
- Bailey, R.T., Gates, T.K., Romero, E.C. (2015a). "Assessing the effectiveness of land and water management practices on nonpoint source nitrate levels in an alluvial stream–aquifer system" *Journal of Contaminant Hydrology*. 179, 102–115.

- Bailey, R.T., Romero, E.C., Gates, T.K. (2015b). "Assessing best management practices for remediation of selenium loading in groundwater to streams in an irrigated region". *Journal of Hydrology*. 521, 341–359.
- Bailey, R.T., Wible, T.C., Arabi, M., Records, R.M., Ditty, J. (2016). "Assessing regional scale spatio-temporal patterns of groundwater–surface water interactions using a coupled SWAT-MODFLOW model". *Hydrol. Process*. 30, 4420–4433.
- Baines, S.B., Fisher, N.S., Doblin, M.A., Cutter, G.A., Cutter, L.S., and Cole, B. (2004). "Light dependence of selenium uptake by phytoplankton and implications for predicting incorporation into food webs." *J. Limnol. and Oceanography*, 49, 566-578.
- Balistrieri, L. S., and Chao, T. T. (1987). "Selenium adsorption by Goethite." *Soil Sci. Soc. Am. J.*, 51, 1145-1151.
- Bedekar, Vivek, Morway, E.D., Langevin, C.D., Tonkin, Matt. (2016). "MT3D-USGS version 1: A U.S. Geological Survey release of MT3DMS updated with new and expanded transport capabilities for use with MODFLOW". *U.S. Geological Survey Techniques and Methods* 6-A53, 69 p.
- Bencala, K.E. (1983). "Simulation of solute transport in a mountain pool-and-riffle stream with a kinetic mass transfer model for sorption." *Water Resour. Res.*, 19(3), 732-738.
- Bennett, W.N., Brooks, A.S., and Boraas, M.E. (1986). "Selenium uptake and transfer in an aquatic food chain and its effects on fathead minor larvae." *Archives Environ. Contam. Toxicol.*, 15, 513-517.
- Benson, B.B., and Krause Jr, D., (1980). "The concentration and isotopic fractionation of gases dissolved in freshwater in equilibrium with the atmosphere. 1. Oxygen". *Limnology and Oceanography*, 25(4), 662-671.
- Benson, B.B., and Krause Jr, D., (1984). "The concentration and isotopic fractionation of oxygen dissolved in freshwater and seawater in equilibrium with the atmosphere". *Limnology and Oceanography*, 29(3), 620-632.

- Bern, C. R., and Stogner, R. W., Sr. (2017). "The Niobrara formation as a challenge to water quality in the Arkansas River, Colorado, USA." *J. Hydrol., Regional Studies* 12 (2017), 181 – 195.
- Brezonik, P.L., Arnold, W.A. (2011). *Water Chemistry: An Introduction to the Chemistry of Natural and Engineered Aquatic Systems*. Oxford University Press: New York, NY.
- Brigham Young Univ. (BYU). (1999). "The department of defense groundwater modeling system: GMS v3.0 reference manual". Environmental Modeling Research Laboratory, Provo, Utah.
- Brown, L.C. and Barnwell, T.O. (1987). "The enhanced stream water quality models QUAL2E and QUAL2E-UNCAS: documentation and user manual." EPA/600/3-87/007. U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, GA.
- Burkhalter, J.P., Gates, T.K. (2005). "Agroecological Impacts from Salinization and Waterlogging in an Irrigated River Valley". *J. Irrig. Drain Eng.* 131, 197-209.
- Burkhalter, J.P., Gates, T.K. (2006). "Evaluating Regional Solutions to Salinization and Waterlogging in an Irrigated River Valley". *J. Irrig. Drain Eng.* 132, 21-30.
- Bye, R., and Lund, W. (1982). "Determination of selenium in pyrite by the atomic absorption-hydride generate technique." *Fresenius Z Anal. Chem.*, 313, 211-212.
- Byers, H. G. (1937). "The origin, distribution, and effects of selenium", edited by B. o. C. a. Soils, p. 326, Washington, D.C.
- Carpenter, S.R., Caraco, N.F., Correll, D.L., Howarth, R.W., Sharpley, A.N., and Smith, V. H. (1998). "Nonpoint pollution of surface waters with phosphorus and nitrogen." *Ecol. Appl.* 8(3), 559–568.
- Casella, G., and Berger, R. I. (2002). *Statistical inference*. Duxbury Press, Pacific Grove, Calif.
- Chapman, P.M., Adams, W.J., Brooks, M.L., Delos, C.G., Luoma, S.N., Maher, W.A., Ohlendorf, H.M., Presser, T.S., and Shaw, D.P. (2010). *Ecological assessment of selenium in the aquatic environment*. Soc. Environ. Toxicol. Chem. (SETAC), Pensacola, FL.
- Chapra, S.C. (1997). *Surface water-quality modeling*. McGraw-Hill Companies, Inc.; Singapore.

- Chen, X., and Shu, L. (2002). "Stream-aquifer interactions: Evaluation of depletion volume and residual effects from ground water pumping." *Groundwater*, 40(3), 284 – 290.
- Clement, T.P., (1997). "RT3D A modular computer code for simulating reactive multispecies transport in 3-dimensional groundwater systems". Richland, Washington, USA.
- Colorado Department of Public Health and Environment (CDPHE). (2016). "Regulation No. 32 Classifications and Numeric Standards for Arkansas River Basin." 5 CCR 1002-32.
- Colorado Department of Public Health and Environment (CDPHE). (2017). "Regulation No. 31 – The Basic Standards and Methodologies for Surface Water". 5 CCR 1002-31.
- Conan, C., Bouraoui, F., Turpin, N., de Marsily, G., Bidoglio, G. (2003). "Modeling Flow and Nitrate Fate at Catchment Scale in Brittany (France)". *J. Environ. Qual.* 32, 2026–2032.
- Cooke, T. D, and Bruland, K. W. (1987). "Aquatic chemistry of selenium: evidence of biomethylation." *Environ. Sci. Tech.*, 21, 1214 – 1219.
- Criss, R.E., Winston, W.E. (2008). "Do Nash values have value? Discussion and alternate proposals". *Hydrol. Processes.*, 22, 2723-2725.
- Dai, T., Labadie, J.W. (2001). "RIVER BASIN NETWORK MODEL FOR INTEGRATED WATER QUANTITY/QUALITY MANAGEMENT". *J. Water Resour. Plann. Manage.* 127(5), 295-305.
- Doherty, J. (2016). "PEST User Manual." Sixth Ed. Watermark Numerical Computing, Brisbane, Queensland, Australia.
- Dosskey, M. G., Vidon, P., Gurwick, N. P., Allan, C. J., Duval, T. P., and Lowrance, R. (2010). "The role of riparian vegetation in protecting and improving chemical water quality in streams." *J. Am. Water Resour. Assoc.*, 46(2), 261 – 277.
- Elhaddad, A., and Garcia, L. A. (2008). "Surface energy balance-based model for estimating evapotranspiration taking into account spatial variability in weather". *J. Irrig. Drain. Eng.* 134(6), 681 - 689.

- Elhaddad, A., and Garcia, L. A. (2011). "ReSET – raster: surface energy balance model for calculating evapotranspiration using a raster approach". *J. Irrig. Drain. Eng.* 137(4), 203 - 210.
- Ellis, D.R., and Salt, D. E. (2003). "Plants, selenium and human health." *Current Opin. Plant Biol.*, 6, 273-279.
- Engberg, R.A., and Sylvester, M.A. (1993). "CONCENTRATIONS, DISTRIBUTION, AND SOURCES OF SELENIUM FROM IRRIGATED LANDS IN WESTERN UNITED STATES". *J. Irrig. Drain Eng.* 119(3), 522-536.
- Engberg, R.A., Westcot, D.W., Delamore, M., and Holtz, D.D. (1998), "Federal and State perspectives on regulation and remediation of irrigation-induced selenium problems", in Frankenberger, W.T., Jr., and Engberg, R.A., eds., *Environmental Chemistry of Selenium*: New York, Marcel Dekker, Inc., 1–25.
- Fan, A.M., Steinberg, V.E. (1995). "Health Implications of Nitrate and Nitrite in Drinking Water: An Update on Methemoglobinemia Occurrence and Reproductive and Developmental Toxicity." *Regulatory Toxicology and Pharmacology* 23, 35-43.
- Faust, C.R., Sims, P.N., Spalding, C.P., Andersen, P.F., Lester, B.H., Shupe, M.G., Harrover, A. (1993). FTWORK: groundwater flow and solute transport in three dimensions. Documentation Version 2.8. Geo-Trans, Sterling, VA.
- Fenske, J.P., Leake, S.A., Prudic, D.E. (1996). "Documentation of a Computer Program (RES1) to Simulate Leakage from Reservoirs Using the Modular Finite-Difference Ground-Water Flow Model (MODFLOW)". U.S. GEOLOGICAL SURVEY Open-File Report 96 364.
- Fio, J. L., Fujii, R., and Deverel, S. J. (1991). "Selenium mobility and distribution in irrigated and nonirrigated alluvial soils." *Soil Sci. Soc. Am. J.*, 55, 1313-1320.
- Flury, M., W. T. Frankenberger, and Jury, W. A. (1997). "Long-term depletion of selenium from Kesterson dewatered sediments." *Sci. Total Environ.*, 198, 259-270.

- Fox, G. A. 2007. "Estimating streambed conductivity: guidelines for stream-aquifer analysis tests." *Trans. ASABE*, 50(1), 107 – 113.
- Fujii, R., Deverel, S. J., and Hatfield, D. B. (1988). "Distribution of selenium in soils of agricultural fields, Western San Joaquin Valley, California." *Soil Sci. Soc. Am. J.*, 52, 1274-1283.
- Gates, T.K., Burkhalter, J.P., Labadie, J.W., Valliant, J.C., Broner, I. (2002). "Monitoring and Modeling Flow and Salt Transport in a Salinity-Threatened Irrigated Valley". *J. Irrig. Drain Eng.* 128(2), 87-99.
- Gates, T. K., Garcia, L. A., and Labadie, J. W. (2006). "Toward optimal water management in Colorado's Lower Arkansas River Valley: monitoring and modeling to enhance agriculture and environment." Colorado Water Resour. Res. Inst. Completion Report No. 205, Colorado Agric. Exp. Station Tech. Report TR06-10, Colorado State Univ., Fort Collins, Colo.
- Gates, T.K., Cody, B.M., Donnelly, J.P., Herting, A.W., Bailey, R.T., and Price, J.M. (2009). "Assessing selenium contamination in the irrigated stream-aquifer system of the Arkansas River, Colorado." *J. Environ. Qual.* 38, 2344–2356.
- Gates, T. K., Garcia, L. A., Hemphill, R. A., Morway, E. D., and Elhaddad, A. (2012). "Irrigation practices, water consumption, & return flows in Colorado's Lower Arkansas River Valley: Field and model investigations." Colorado Water Institute Completion Report No. 221, Colorado Agricultural Experiment Station No. TR-12, Colorado State University, Fort Collins, CO.
- Gates, T.K., Steed, G.H., Niemann, J.D., and Labadie, J.W. (2016). "Data for Improved Water Management in Colorado's Arkansas River Basin: Hydrological and water quality studies." Special Report No. 24, Colorado Water Institute, Colorado State University, Fort Collins, CO
- Gates, T. K., Cox, J. T., and Morse, K. C. (2017). "Estimation of irrigation-induced return flows and pollutant loads to a river using a stochastic mass balance." To be submitted to *J. Hydrol.*

- Gerla, P.J., Sharif, M.U., and Korom, S.F. (2011). "Geochemical processes controlling the spatial distribution of selenium in soil and water, west central South Dakota." *J. Environ. Earth Sci.* 62, 1551-1560.
- Goff, K., Lewis, M.E., Person, M.A., Konikow, L.F. (1998). "Simulated Effects of Irrigation on Salinity in the Arkansas River Valley in Colorado." *Ground Water*. 36(1), 76-86.
- Goldhaber SB. (2003). "Trace element risk assessment: essentiality vs. toxicity." *Regul. Toxicol. Pharmacol.*, 38, 232–42.
- Guo, L., Frankenberger, W. T., and Jury, W. A. (1999). "Evaluation of simultaneous reduction and transport of selenium in saturated soil columns." *Water Resour. Res.*, 35(3), 663-669.
- Gusman, A.J., Marino, M.A., (1999). "Analytical modeling of nitrogen dynamics in soils and ground water". *Journal of Irrigation and Drainage Engineering*. 125(6), 330-337.
- Hamilton, S. J. (1998). "Selenium effects on endangered fish in the Colorado River basin." p. 297-314. In Frankenberger, W. T., and Engberg, R. A. (eds.), *Environmental chemistry of selenium*. Marcel Dekker, New York, New York, USA.
- Hamilton, S.J. (2004). "Review of selenium toxicity in the aquatic food chain." *Sci. of the Total Environ.* 326, 1-31.
- Harbaugh, A.W. (2005). "MODFLOW-2005, the U.S. Geological Survey Modular Ground-water Model – The Ground-water Flow Process". U.S. Geological Survey, Techniques and Methods 6-A16.
- Heesemann, B. R. (2016). "Assessing best management practices for the remediation of selenium in surface water in an irrigated agricultural river valley: Sampling, modeling, and multi-criteria decision making." MS Thesis, Dept. and Civil Environ. Engrg., Colorado State Univ., Fort Collins.
- Herrman, K., Bouchard, V. (2008). "An assessment of nitrogen removal from headwater streams in an agricultural watershed, northeast Ohio, U.S.A.". *Limnol. Oceanogr.* 53(6), 2573–2582.
- Hill, A. R. (1996). "Nitrate removal from stream riparian zones." *J. Environ. Qual.*, 25(4), 743 – 755.

- Hörmann, G., (1998). "Simpel – Speichermodelle zum Bodenwasserhaushalt". Ökologiezentrum der Universität Kiel. Version vom 26.06.2005.
- Hudak, P. F. (2010) "Nitrate, Arsenic and Selenium Concentrations in The Pecos Valley Aquifer, West Texas,USA". *Int. J. Environ. Res.* 4(2), 229-236.
- Huizenga, A., Bailey, R. T., and Gates, T. K. (2017). "Stream-aquifer and in-stream processes affecting nitrogen along a major river and contributing tributary." *J. Contam. Hydrol.*, 199, 24 – 35.
- Hunt, B., Weir, J., and Clausen, B. (2001). "A stream depletion field experiment." *Groundwater*, 39(2), 283 – 289.
- Ivahnenko, Tamara, Ortiz, R.F., and Stogner, R.W., Sr. (2013). "Characterization of streamflow, water quality, and instantaneous dissolved solids, selenium, and uranium loads in selected reaches of the Arkansas River, southeastern Colorado, 2009–2010." U.S. Geological Survey Scientific Investigations Report 2012–5234, 60 p.
- Kansas-Colorado (1949). "K.S.A. 82a-520 Arkansas River Compact." n.p. *Colorado Division of Water Resources*. Web. 26 June. 2017.
- Kansas v. Colorado. 556 U.S. 105. Supreme Court of the United States. (2009). *Supremecourt.gov*. n.d. Web. 26 June. 2017.
- Kishchak, I. T. (1998), "Supplementation of selenium in the diets of domestic animals." In Frankenberger, W. T., and Engberg, R. A. (eds.), *Enviromental chemistry of selenium*. Marcel Dekker, New York, New York, USA.
- Konikow, L. F. (2011). "The secret to successful solute-transport modeling." *Groundwater*, 49(2), 144 – 159.
- Konikow, L.F., Bredehoeft, J.D. (1974). "Modeling flow and chemical quality changes in an irrigated stream-aquifer system". *Water Resour. Res.* 10(3), 546-561.

- Konikow, L.F., Person, M. (1985). "Assessment of long-term salinity changes in an irrigated stream-aquifer system". *Water Resour. Res.* 21(11), 1611-1624.
- Lee, M., Park, G., Park, M., Park, J., Lee, J., Kim, S., (2010). "Evaluation of non-point source pollution reduction by applying best management practices using a SWAT model and QuickBird high resolution satellite imagery". *J. Environ. Sci.* 22(6), 826–833.
- Legates, D.R., and McCabe, G.J. (1999). "Evaluating the use of 'goodness of fit' measure in hydrologic and hydroclimatic model validation." *Water Resour. Res.*, 35, 233-241.
- Lemly, A.D. (1999). "Selenium transport and bioaccumulation in aquatic ecosystems: a proposal for water quality criteria based on hydrological units." *J. Ecotoxicol. Environ. Safety*, 42, 150-156.
- Lin, Z., Terry, N. (2003). "Selenium Removal by Constructed Wetlands: Quantitative Importance of Biological Volatilization in the Treatment of Selenium-Laden Agricultural Drainage Water". *Environ. Sci. Technol.* 37, 606-615.
- Liu R., Zhang P., Wang X., Chen Y., and Shen Z. (2013). "Assessment of effects of best management practices on agricultural non-point source pollution in Xiangxi River watershed". *Agricultural Water Management*. 117, 9-18.
- Losi, M. E., and Frankenberger, W. T. (1998). "Microbial oxidation and solubilization of precipitated elemental selenium in soil." *J. Environ. Qual.*, 27, 836-843.
- Lui, C. W., and Narasimhan, T. N. (1994). "Modeling of selenium transport at the Kesterson reservoir, California, U.S.A." *J. Contam. Hydrol.*, 15, 345-366.
- MacDonnell, Lawrence J. (1999). "From Reclamation to Sustainability: Water, Agriculture, and the Environment in the American West". *University Press of Colorado*. Print.
- Mars, J.C., and Crowley, J.K. (2003). "Mapping mine wastes and analyzing areas affected by selenium-rich water runoff in southeast Idaho using AVIRIS imagery and digital elevation data." *Remote Sens. Environ.*, 84, 422-436.

- Masscheleyn, P. H., Delaune, R. D. ,and Patrick, J. W. H. (1989). "Transformations of selenium as affected by sediment oxidation-reduction potential and pH." *Environ. Sci. Tech.*, 24, 91-96.
- Masscheleyn, P.H. and Patrick, W.H. Jr. (1993). "Biogeochemical processes affecting selenium cycling in wetlands". *Journal of Environmental Toxicology and Chemistry*, 12, 2235-2243.
- May, T.W., Fairchild, J.F., Petty, J.D., Walther, M.J., Lucero, J., Delvaux, M., Manring, J., Armbruster, M. (2008) "An evaluation of selenium concentrations in water, sediment, invertebrates, and fish from the Solomon River Basin". *Environ Monit Assess.* 137, 213–232.
- McDonald, M.G., Harbaugh, A.W., (1988). "A modular three-dimensional finite-difference ground-water flow model". Washington, USA.
- Miller, L.D., Watts, K.R., Ortiz, R.F., and Ivahnenko, T. (2010). "Occurrence and Distribution of Dissolved Solids, Selenium, and Uranium in Groundwater and Surface Water in the Arkansas River Basin from the Headwaters to Coolidge, Kansas, 1970–2009". U.S. Geological Survey, Reston, Virginia.
- Mirbagheri, S. A., Tanji, K. K. ,and Rajaei, T. (2008). "Selenium transport and transformation modelling in soil columns and ground water contamination prediction." *Hydrol. Processes*, 22(14), 2475-2483.
- Molénat, J., Gascuel-Odoux, C. (2002). "Modelling flow and nitrate transport in groundwater for the prediction of water travel times and of consequences of land use evolution on water quality". *Hydrol. Process.* 16, 479–492.
- Morway, E.D. (2014). "Regional-Scale Groundwater Flow and Salt Transport Models for Exploring Agro-Environmental Remediation Strategies in an Irrigated River Valley". Dissertation, presented to Colorado State University at Fort Collins, CO, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

- Morway, E.D., Gates, T.K., Niswonger, R.G. (2013). "Appraising options to reduce shallow groundwater tables and enhance flow conditions over regional scales in an irrigated alluvial aquifer system". *Journal of Hydrology* 495, 216–237.
- Mueller, D.K., Hamilton, P.A., Helsel, D.R., Hitt, K.J., Ruddy, B.C. (1995). "Nutrients in ground water and surface water of the United States; an analysis of data through 1992". *USGS Publications Warehouse*.
- Myers, T. (2013). "Remediation scenarios for selenium contamination, Blackfoot watershed, southeast Idaho, USA". *Hydrogeology Journal*. 21, 655–671
- Nash, J.E., Sutcliffe, J.V. (1970). "River flow forecasting through conceptual models: Part 1; A discussion of principles". *J. Hydrol.*, 10, 282- 290.
- Narula, K., Gosain, A. (2013). "Modeling hydrology, groundwater recharge and non-point nitrate loadings in the Himalayan Upper Yamuna basin". *Science of the Total Environment*. 468–469, S102–S116.
- Niswonger, R.G., S. Panday, and I. Motomu. (2011). "MODFLOW-NWT, a Newton formulation for MODFLOW-2005". 44. *U.S. Geological Survey Techniques and Methods 6-A37*. Reston, Virginia: USGS.
- Niswonger, R.G., and Prudic, D.E., (2005). "Documentation of the Streamflow-Routing (SFR2) Package to include unsaturated flow beneath streams—A modification to SFR1". *U.S. Geological Survey Techniques and Methods 6-A13*, 50 p.
- Niswonger, R.G., Prudic, D.E., and Regan, R.S. (2006). "Documentation of the unsaturated-zone flow (UZF1) package for modeling unsaturated flow between the land surface and the water table with MODFLOW-2005". *U.S. Geological Survey Techniques and Methods 6-A19*. Reston, Virginia: USGS.

- Novak, C. E. (1985). "WRD data reports preparation guide." Open File Report 85-480, U. S. Geological Survey, Reston, Virg.
- Oremland, R. S., Steinberg, N. A., Maest, A. S., Miller, L. G., and Hollibaugh, J. T. (1990). "Measurement of in situ rates of selenate removal by dissimilatory bacterial reduction in sediments." *Environ. Sci. Tech.*, 24, 1157-1164.
- Person, M.A., Konikow, L.F. (1986). "Recalibration and predictive reliability of a solute-transport model of an irrigated stream-aquifer system". *Journal of Hydrology*. 87, 145-165.
- Pimentel, D., Houser, J., Preiss, E., White, O., Fang, H., Mesnick, L., Barsky T., Tariche, S., Schreck, J., and Alpert, S. (1997). "Water Resources: Agriculture, the Environment, and Society". *BioScience*. 47(2), 97-106.
- Presser, T.S., Sylvester, M.A., Low, W.H. (1994). "Bioaccumulation of selenium from natural geologic sources in western states and its potential consequences." *Environmental Management*. 18(3), 423-436.
- Prudic, D. E., Konikow, L. F., and Banta, E. R. (2004). "A new streamflow-routing (SFR1) package to simulate stream-aquifer interaction with MODFLOW-2000." Open-file report 2004-1042, U. S. Geological Survey, Carson City, Nevada.
- Ranalli, A. J., and Macalady, D. L. 2010. "The importance of the riparian zone and in-stream processes in nitrate attenuation in undisturbed and agricultural watersheds – a review of the scientific literature." *J. Hydrol.*, 389, 406 – 415.
- Riedel, G.F., Sanders, J.G., and Gilmour, C.C. (1996). "Uptake, transformation, and impact of selenium in freshwater phytoplankton and bacterioplankton communities." *J. Aqua. Microb. Ecol.*, 11, 43-51.
- Rong, Y., Xuefeng, W. (2011). "Effects of nitrogen fertilizer and irrigation rate on nitrate present in the profile of a sandy farmland in Northwest China". *Procedia Environ. Sci.* 11, 726–732.

- Runkel, R.L. (1998). "One-dimensional transport with inflow and storage (OTIS): a solute transport model for streams and rivers." U.S. Geological Survey Water-Resources Investigation Report 98-4018, Denver, Colo.
- Runkel, R.L. and Broshears, R.E. (1991). "One-dimensional transport with inflow and storage (OTIS): a solute transport model for small streams." Final Report, Univ. Colo. Center for Advanced Decision Support for Water and Environmental Systems, Boulder, Colo.
- Sahu M., Gu, R. (2009). "Modeling the effects of riparian buffer zone and contour strips on stream water quality". *Ecological Engineering*. 35, 1167–1177.
- Scanlon, B.R., Jolly, I., Sophocleous, M., and Zhang, L. (2007) "Global impacts of conversions from natural to agricultural ecosystems on water resources: Quantity versus quality". *WATER RESOURCES RESEARCH*. 43, W03437.
- Scott, G.R., (1968). "Geologic and Structure Contour Map of the La Junta Quadrangle, Colorado and Kansas". U.S.G. Survey, Reston, Virginia.
- Seiler, R. L. (1995). "Prediction of areas where irrigation drainage may induce selenium contamination of water." *J. Environ. Qual.*, 24, 973-979.
- Seiler, R. L. (1997). "Methods to identify areas susceptible to irrigation-induced selenium contamination in the Western United States." Fact Sheet 038-97, National Irrig. Water Qual. Prog., U. S. Geological Survey, Washington, D.C.
- Sharps, J.A., (1976). "Geologic Map of Lamar Quadrangle, Colorado and Kansas". U.S.G. Survey, Reston, Virginia.
- Shrift, A. (1964). "A selenium cycle in nature?" *Nature*, 201, 1304-1305.
- Shultz, C. D. (2017). "Finding Land and Water Management Practices to Reduce Selenium and Nitrate Concentrations in an Agricultural River Valley Applying a Regional-Scale Stream-Aquifer Model". MS Thesis, Dept. Civil and Environ. Engrg., Colorado State Univ., Fort Collins.

- Shultz, C.D., Bailey, R.T., Gates, T.K., Heesemann, B., Morway, E.D. (2017). "Simulating Selenium and Nitrogen Fate and Transport in Coupled Stream-Aquifer Systems of Irrigated Regions". *Advances in Water Resources* (In Preparation).
- Skorupa, J. P. (1998). "Selenium poisoning of fish and wildlife in nature: Lessons from twelve real-world experiences." In Frankenberger, W. T., and Engberg, R. A. (eds.), *Environmental chemistry of selenium*. Marcel Dekker, New York, New York, USA.
- Spalding, R.F., Exner, M.E. (1993). "Occurrence of nitrate in groundwater: a review." *J. Environ. Qual.* 22, 392–402.
- Spruill, T. B. (2000). "Statistical evaluation of effects of riparian buffers on nitrate and ground water quality." *J. Environ. Qual.*, 29(5), 1523 – 1538.
- Stolz, J. F., Basu, P., and Oremland, R. S. (2002). "Microbial transformation of elements: the case of arsenic and selenium." *Int. Microbiol.*, 5(4), 201-207.
- Szymkiewicz, R. (2010). *Numerical modeling in open channel hydraulics*. Springer, Dordrecht, the Netherlands.
- Tayfur, G., Tanji, K., Baba, A. (2010). "Two-dimensional finite elements model for selenium transport in saturated and unsaturated zones". *Environ Monit Assess.* 169, 509–518.
- Tilman, D., Cassman, K.G., Matson, P.A., Naylor, R., Polasky, S. (2002). "Agricultural sustainability and intensive production practices". *Nature*. 418, 671-679.
- Trachtenberg, E., Ogg, C., 1994. Potential for reducing nitrogen pollution through improved agronomic practices. *Water Resour. Bull.* 30, 1109–1118.
- Tummalapenta, R.K. (2015). "Investigating Best Management Practices to Reduce Selenium and Nitrate Contamination in a Regional Scale Irrigated Agricultural Groundwater System: Lower Arkansas

- River Valley, Southeastern Colorado”. Thesis, presented to Colorado State University at Fort Collins, CO, in partial fulfillment of the requirements for the degree of Master of Science.
- United States Census Bureau. (2016). "International Data Base.", U.S. Dept. of Commerce, <<https://www.census.gov/population/international/data/idb/worldpopgraph.php>>
- United States Environmental Protection Agency (EPA). (2016). “Aquatic Life Ambient Water Quality Criterion for Selenium – Freshwater 2016”. EPA 822-R-16-006.
- United States Environmental Protection Agency (EPA). (2009). “National Primary Drinking Water Regulations”. EPA 816-F-09-004.
- United States Environmental Protection Agency (EPA). (1995). “QUAL2E Windows Interface User’s Guide”. Office of Water. EPA/823/B/95/003.
- U.S. Natural Resources Conservation Service (NRCS). (2004). *National Engineering Handbook*. Part 630 Hydrology. U.S. Department of Agriculture, Washington, D.C.
- Vaché, K.B., Eilers, J.M., Santelmann, M.V. (2002). “Water quality modeling of alternative agricultural scenarios in the U.S. Corn Belt”. *J. Am. Water Res. Assoc.* 38(3), 773–787.
- Vidon, P., and Hill, A. R. (2004). “Denitrification and patterns of electron donors and acceptors in eight riparian zones with contrasting hydrogeology.” *Biogeochem.*, 71, 259-283.
- Weill, S., Mazzia, A., Putti, M., and Paniconi, C. (2011). “Coupling water flow and solute transport into a physically-based surface-subsurface hydrological model.” *Adv. Water Resour.*, 34, 128-136.
- Weres, O., Bowman, H.R., Goldstein, A., Smith, E.C., Tsao, L., and Harnden, W. (1990). “The effect of nitrate and organic matter upon mobility of selenium in groundwater and in a water treatment process.” *J. Water Air Soil Pollution*, 49, 251-272.

- White, A. F., Benson, S. M., Yee, A. W., Wollenberg, J. H. A. and Flexser, S. (1991). "Groundwater contamination at the Kesterson Reservoir, California 2. Geochemical parameters influencing selenium mobility." *Water Resour. Res.*, 27(6), 1071-1084.
- Wriedt, G., (2004). "Modelling of nitrogen transport and turnover during soil and groundwater passage in a small lowland catchment of Northern Germany". Dissertation, Potsdam University, Germany.
- Wriedt, G., Rode, M. (2006) "Modelling nitrate transport and turnover in a lowland catchment system". *Journal of Hydrology*. 328, 157– 176.
- Zhang, Y., and Moore, J. N. (1997). "Reduction potential of selenate in wetland sediment." *J. Environ. Qual.*, 26, 910-916.
- Zhang, H.H., Wu, Z.F., Yang, C.L., Xia, B., Xu, D.R., Yuan, H.X. (2008). "Spatial Distributions and Potential Risk Analysis of Total Soil Selenium in Guangdong Province, China". *J. Environ. Qual.* 37, 780– 787.
- Zheng, C. (1990). "A modular three-dimensional transport model for simulation of advection, dispersion and chemical reactions of contaminants in groundwater systems". U.S.E.P.A Report.
- Zheng, C., Wang, P.P. (1999). "MT3DMS: a modular three-dimensional multispecies transport model for simulation of advection, dispersion, and chemical reactions of contaminants in groundwater systems". Documentation and user's guide. Contract report SERDP-99-1, US Army Corps of Engineers, Engineer Research and Development Center, Vicksburg, MS.
- Zheng, C., and Bennett, G. D. (2002). *Applied contaminant transport modeling*. 2nd ed. Wiley-Interscience, New York, NY.

APPENDIX A: Model Refinements

Along with the model coupling and calibration process presented in Chapter 3, several refinements and changes were necessary to more accurately represent field conditions in the basin within the MODFLOW and RT3D-OTIS models. These alterations represent changes in model inputs and RT3D-OTIS code from the models used by Heesemann 2016 and previously published papers such as Morway et al. (2013) and Bailey et al. (2014).

A.1. Converting RT3D-OTIS to 1999-2009

One significant refinement was the alteration of the historical simulation period in the RT3D-OTIS model to better align the solute transport model and the flow model. Previously, due to data availability, the forecasting simulation the UZF-RT3D model was run for 38 years by repeating the years 2006-2008 13 times. In contrast, MODFLOW was run for 44 years by repeating the years 1999 to 2009 four times. However, this had the potential to lead to discrepancies for a given year; a field could have been fertilized for one crop's requirements and irrigated or not irrigated due to the presence of a different crop. Therefore, RT3D-OTIS input files were altered so that they simulated the same 1999 to 2009 period as the MODFLOW model. The RT3D-OTIS model was able to be extended for the 1999 to 2009 period due to a regression relationship developed by Gates et al. (2017) that relates Se and NO₃ concentrations to Arkansas River flow and EC for a given time period. This allowed for an estimate (with some degree of error) of the concentration of the upstream end of the USR for any time when flow and EC measurements exist. The modification of the simulation period required extensive changes to input data including the total number of stress periods, percent of crops of each type in each cell, daily temperature, concentrations of canal diversion water, and fraction of canal water, pumped water, and rain water on each field. Alterations in the surface water model included the initial condition concentration, upstream boundary concentration, daily temperature, daylight hours, and solar radiation. Originally, the RT3D-OTIS model was converted to run for the full 44 years of the MODFLOW

simulation period, representing the 1999 to 2009 historical period repeated four times. However, this exceeded the maximum allowable memory for a program using the Intel Fortran Compiler so the simulation period of RT3D-OTIS was reduced to 40 years to avoid any unnecessary changes to the code to comply with the memory requirement.

A.2. Other Changes to the Groundwater Reactive Transport Model

Other refinements were made to the UZF-RT3D (Bailey et al. 2013b) portion of the RT3D-OTIS model. In the conversion from the 3 layer MODFLOW grid to the 7 layer RT3D grid for the groundwater cells, the previous assumption was that the water content for the divided up layers was the same fraction as the source layer. However, in reality, if the water table exists in one layer then the layer is split, the water content in the new layers would be variable depending on the location of the water table. Therefore, when computing the water contents for the 7 layer grid, the code now accounts for the location of the water table. Every layer below the water table has a saturated water content (effective porosity) and every layer above the water table contains the remaining water that was in the layer.

Furthermore, the layer in which the water table resides is now considered fully saturated. In reality, this layer would be partially saturated to some degree, ranging from zero to one hundred percent saturated. However, when mass is transferred to or from groundwater cells in the model, this mass transfer is computed as the concentration of the cell multiplied by the volume of water transferred. However, the volume that is transferred only consists of water from the aquifer, not the vadose zone, while the concentration of the transferred water previously consisted of both the saturated and unsaturated portions of the cell. This discrepancy has the potential to drastically overestimate the mass transferred for the top saturated layer of the model. To fix this, the water content in the layer in which the water table resides is now input into the RT3D model as being fully saturated.

Another change to the original RT3D model is that concentration from irrigation canals are now use the modeled in stream concentrations instead based on field data. This change would have a negligible effect on the model output concentration for the baseline, however, in the cases of land and water management practices that have an effect on in stream concentrations at diversions changes in seepage concentrations could have a significant effect on modeled concentrations.

A.3. Coupled RT3D-OTIS Changes

The solute transport between groundwater and the streams was also altered. Initially, a layer was read into the model for each stream cell; this layer represented the groundwater layer which fed the stream. In reality, however, the layer would not be constant through time or while running BMPs. The groundwater table varies in elevation depending on the time of the year and also between years depending on the magnitude and variability of precipitation and applied irrigation. Water management BMPs also alter the water table due to changes in return flows. For instance, the sealing of irrigation canals could drop the water table a few meters, in turn changing the top saturated layer. In this case, by using the same layer, an unsaturated layer would be feeding the stream cell, dramatically inflating the concentration of groundwater coming into the stream. The groundwater layer that feeds the stream now changes through time and for BMPs.

Additionally, the RT3D-OTIS code was changed so that all of the groundwater layers under the top layer flow into the stream proportionally according to their saturated thickness. When MODFLOW transports water to and from groundwater and streams in the SFR2 package, the water is moved using Darcy's Law, evaluating the streambed thickness, conductance, and difference in head between the groundwater and stream. This describes the quantity of water that moves from the groundwater to the stream, but does not describe the layer from which the water comes. Therefore, the assumption was made that water comes into the stream from all layers of the groundwater.

A.4. Changes to MODFLOW Model

Some changes were also made to the MODFLOW model developed by Morway et al. (2013) that now incorporates the SFR2 package. Incorrect crop data for 2008 and 2009 used in the water allocation process in creating the UZF1 file for MODFLOW was altered and new files were created. These changes in crops and applied water for 2008 and 2009 resulted in input file modifications in the RT3D-OTIS model as well. Additionally, the method of estimating runoff due to precipitation was changed to now use the Natural Resources Conservation Service (NRCS) direct runoff method (U.S. NRCS 2004). This alteration in the runoff estimation altered runoff routed the SFR2 stream segments as well as infiltration water from precipitation events. A single curve number was used uniformly throughout the extent of the USR obtained using the spatial average curve number due to soil texture and vegetative cover on the soil.

Another change to the MODFLOW model was the addition of the Fort Lyon Storage and Las Animas Consolidated Canal diversions in the SFR file, previously those canals had been neglected when computing the change in flow rates. These canals had already been accounted for when computing seepage. Additionally, river cross-sections in the SFR package are now being represented by 8 point cross-sections as opposed to rectangular channels using field data from Heesemann (2016) and other surveys yielded stream surveys between banks. The survey data was consolidated into 8 point cross-sections while still retaining the stream shape.

Furthermore, Holbrook Reservoir was added using the reservoir package (RES1) (Fenske et al. 1996) in MODFLOW. The RES1 package was used due to the availability of data on the reservoir's stage and concentration (Holbrook Canal feeds the reservoir) through time. Finally, Adobe Creek, which had initially been removed from the model when the SFR2 package was added, is once again being simulated in the MODFLOW RIV package in the same method that was used by Morway et al. (2013). The creek was not originally modeled in the SFR2 package because it enters the Arkansas River downstream of the model domain; however, it represents part of the downstream boundary of the MODFLOW model and is

useful in keeping groundwater elevations in that region of the model similar to field data and not near the ground surface.

A.5. La Junta, Colorado Waste Water Treatment Plant

Due to the large volume of effluent discharge, the city of La Junta's waste water treatment effluent was added to the model. In the MODFLOW model, the effluent discharge is treated as a short tributary stream to King Arroyo, a tributary of the Arkansas River. This methodology enabled solutes in the effluent to be assigned concentrations within the RT3D-OTIS model. Due to a lack of available data for the simulation period and the correlation of flows and solute concentrations over time, flow and concentrations of the effluent were estimated based on the day of the year using a fourth order polynomial. Flow, Selenium, and NO_3/NO_2 data was available from 2006-2011 and 2013-2016. Five day biochemical oxygen demand (BOD) was available from October of 2013 to December of 2016. Assuming a first-order reaction rate and a 20°C first order reaction rate (k) of 0.15 day^{-1} , the five day BOD was used to obtain an estimate of ultimate BOD used in the model input. Values for ammonia as nitrogen ($\text{NH}_3\text{-N}$) and electrical conductivity (EC) were only available from July of 2014 to December of 2016. $\text{NH}_3\text{-N}$ was needed as a solute input concentration and EC was used to calculate the DO of the water using a method developed by Benson and Krause (1980, 1984).

A.6. Changes in the Simulation of Water Management BMPs

Water Management BMPs (CS, RI, and LF) simulated in previous work by Bailey et al. (2015a, 2015b) only altered MODFLOW input files; however, management changes under RI and LF also have some effect on the input data in the RT3D-OTIS model. Both RI and LF alter the applied water on to fields, this applied waer is partitioned into a fraction of canal water, pumped water, and rain water on each field in the IRG input file. These fraction values are now altered in the IRG input files for each BMP using data from the MODFLOW UZF1 input file creation code. CS did not require this change because it does not alter the land applied water, only seeped water which is assigned a concentration in a different

part of the code. Additionally, under the LF BMPs, fallowed fields no longer have fertilizer applied to them. This required an alteration to the AGR input file for the LF BMPs. The fallowed fields were previously determined in creating the MODFLOW UZF1 files; for these same fields, fertilizer is no longer applied in the RT3D-OTIS model.

APPENDIX B: Supplementary Information on the Calibration Process

The calibration of the RT3D-OTIS model was done iteratively over a span of nearly a year and a half. Initially, only surface water parameters were calibrated similar to the approach of Heesemann (2016). However, in examining the surface water concentrations spatially along the Arkansas River, it became apparent that groundwater return flows to the river were significantly reducing the surface water Se concentrations over the extent of the USR. This result is counter to observed concentrations, which show spatially constant or slightly increasing concentrations of Se going downstream. To combat the low groundwater return flow concentration, groundwater parameters were added to the calibration process. Furthermore, NO₃ parameters were also included in the calibration due to the link between NO₃ reduction and Se reduction. The final list of groundwater parameters included: $\lambda_{SeO_4}^{het}$, $\lambda_{SeO_3}^{het(Se(0))}$, $\lambda_{SeO_3}^{het(SeMet)}$, λ_{SeMet}^{het} , and K_{Se} for Se and $\lambda_{NO_3}^{het}$ and $\lambda_{NO_3}^{auto}$ for NO₃, with the heterotrophic rates having separate values for the main groundwater and riparian groundwater. The final list of surface water parameters included: λ_{SeO_4} , $\lambda_{SeO_4}^{vol}$, $\lambda_{SeO_4}^{assim}$, DF_{NO_3-N} , and $\bar{\mu}$.

Calibration targets included surface water, groundwater, and estimated mass loading. Individual locations and times were compared for the surface water points. However, groundwater was separated into grouping areas based on the adjacent OTIS segment. All observed groundwater concentrations in each grouping area (Figure B.1) were averaged together, with the grouping area average concentration for each observation date then averaged together. Similarly, RT3D-OTIS output was averaged over all active cells in each grouping area for each day when observed groundwater concentrations were available. The grouping area average model output was then also averaged over the days for a single value for each grouping area. The parameter adjustments also took place over the same grouping areas, with a portion designated riparian. Finally, using the estimate of unaccounted for mass from Gates et al. (2017), groundwater return loads of Se and NO₃ to the Arkansas River were estimated. Gates et al.

(2017) estimated mass that entered the Arkansas River and ungaged tributaries. Using the estimate, the total return groundwater mass loading of Se and NO₃ over the simulation period was estimated. These estimates of mass loading were used as observations during the calibration process and were compared to the total predicted groundwater mass loading to Arkansas River segments in the model.

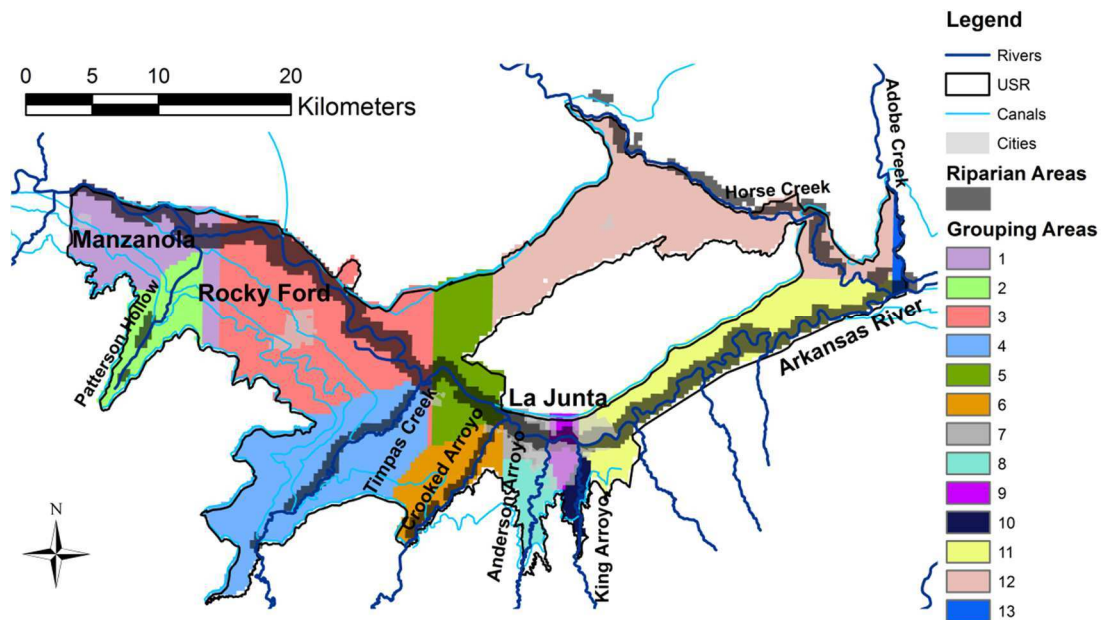


Figure B.1: USR grouping areas and riparian areas used in model calibration of groundwater concentrations.

Appendix C: Supplementary BMP Results

Table C.1: Percent reduction (positive) in the surface water Se concentration for single BMPs averaged over the entire 40-year simulation and the last 11-year historic period and averaged over the entire extent of the Arkansas in the USR and the downstream third of the Arkansas River in the USR.

	40 Year Average		Last 11 Year Average	
	Entire River Spatial Average	Downstream Third Spatial Average	Entire River Spatial Average	Downstream Third Spatial Average
RF30	8.34%	10.12%	11.68%	13.51%
RF25	7.30%	8.87%	10.24%	11.92%
RF20	6.06%	7.39%	8.54%	9.98%
RF15	4.65%	5.67%	6.60%	7.75%
RF10	3.08%	3.74%	4.39%	5.11%
RF5	1.60%	1.98%	2.28%	2.68%
LF30	-2.85%	-2.17%	-5.75%	-4.89%
LF25	-3.77%	-3.46%	-6.97%	-6.48%
LF20	-2.46%	-2.13%	-4.83%	-4.55%
LF15	0.48%	1.69%	-0.76%	0.64%
LF10	0.10%	0.09%	-1.39%	-1.82%
LF5	0.34%	0.49%	-0.49%	-0.75%
RI30	-1.83%	-1.05%	-4.64%	-3.84%
RI25	-1.20%	-1.01%	-3.54%	-3.34%
RI20	-1.45%	-2.06%	-3.27%	-4.15%
RI15	-0.23%	-0.21%	-1.75%	-2.32%
RI10	-1.18%	-1.74%	-3.03%	-4.10%
RI5	0.58%	0.49%	-0.13%	-0.40%
CS80	18.52%	18.73%	21.12%	21.19%
CS70	15.69%	15.25%	17.99%	17.44%
CS60	13.90%	13.38%	16.03%	15.53%
CS50	11.28%	10.69%	12.98%	12.46%
CS40	9.51%	9.30%	11.01%	11.15%
CS30	6.91%	6.23%	7.73%	7.26%
CS20	3.58%	3.81%	4.58%	4.79%
ERB10	39.55%	40.23%	51.29%	56.71%
ERB5	30.58%	30.74%	44.67%	48.52%
ERB2	15.23%	15.80%	24.16%	24.83%

Table C.2: Percent reduction (positive) in the surface water Se concentration for combination BMPs averaged over the entire 40-year simulation and the last 11-year historic period and averaged over the entire extent of the Arkansas in the USR and the downstream third of the Arkansas River in the USR.

	40 Year Average		Last 11 Year Average	
	Entire River Spatial Average	Downstream Third Spatial Average	Entire River Spatial Average	Downstream Third Spatial Average
LF30 CS80	20.99%	22.50%	21.07%	22.97%
LF20 CS60	13.41%	14.37%	13.17%	14.07%
LF10 CS40	10.09%	10.74%	10.25%	10.73%
RI30 CS80	22.38%	24.12%	23.20%	25.37%
RI20 CS60	15.87%	17.16%	16.05%	17.31%
RI10 CS40	9.44%	9.42%	9.29%	8.92%
RI30 LF30	-7.40%	-7.54%	-13.15%	-12.39%
RI20 LF20	-4.67%	-4.21%	-8.85%	-7.88%
RI10 LF10	-0.68%	-0.62%	-2.29%	-2.17%
LF30 RF30	1.52%	3.23%	-0.03%	1.54%
LF20 RF20	1.49%	2.78%	0.54%	1.59%
LF10 RF10	2.57%	3.24%	2.16%	2.46%
CS80 RF30	24.74%	25.84%	31.63%	33.68%
CS60 RF20	18.95%	19.49%	24.28%	25.17%
CS40 RF10	12.25%	12.63%	15.10%	16.00%
RI30 RF30	4.57%	6.56%	4.02%	5.90%
RI20 RF20	3.97%	4.60%	3.85%	4.04%
RI10 RF10	1.97%	2.17%	1.72%	1.60%
RI30 LF30 CS80	22.29%	24.74%	22.89%	26.23%
RI20 LF20 CS60	14.27%	15.32%	12.15%	13.44%
RI10 LF10 CS40	10.62%	11.94%	9.63%	11.05%
LF30 CS80 RF30	24.24%	26.35%	26.27%	28.85%
LF20 CS60 RF20	16.54%	18.10%	18.05%	19.77%
LF10 CS40 RF10	12.12%	13.23%	13.18%	14.22%
RI30 CS80 RF30	26.63%	29.04%	30.68%	33.51%
RI20 CS60 RF20	19.88%	21.79%	22.57%	24.62%
RI10 CS40 RF10	11.90%	12.33%	12.96%	13.14%
RI30 LF30 RF30	-4.17%	-3.65%	-8.77%	-7.51%
RI20 LF20 RF20	-1.59%	-0.52%	-4.53%	-3.00%
RI10 LF10 RF10	1.47%	1.99%	0.49%	0.96%
CS80 RF30 ERB10	44.71%	46.33%	56.99%	62.16%
CS60 RF20 ERB5	37.84%	37.96%	52.98%	56.64%
CS40 RF10 ERB2	23.48%	24.05%	34.18%	35.51%
RI30 LF30 CS80 RF30	23.85%	26.56%	26.16%	30.04%
RI20 LF20 CS60 RF20	16.60%	18.03%	16.14%	17.97%
RI10 LF10 CS40 RF10	12.48%	14.20%	12.37%	14.17%
RI30 LF30 CS80 RF30 ERB10	35.37%	38.26%	39.77%	44.66%
RI20 LF20 CS60 RF20 ERB5	33.72%	35.70%	40.61%	45.17%
RI10 LF10 CS40 RF10 ERB2	23.72%	25.97%	30.17%	32.70%

Table C.3: Percent reduction (positive) in the surface water NO₃ concentration for single BMPs averaged over the entire 40-year simulation and the last 11-year historic period and averaged over the entire extent of the Arkansas in the USR and the downstream third of the Arkansas River in the USR.

	40 Year Average		Last 11 Year Average	
	Entire River Spatial Average	Downstream Third Spatial Average	Entire River Spatial Average	Downstream Third Spatial Average
RF30	12.71%	12.87%	16.22%	16.44%
RF25	11.11%	11.32%	14.16%	14.45%
RF20	9.24%	9.54%	11.83%	12.21%
RF15	7.66%	7.95%	9.62%	9.91%
RF10	4.89%	5.17%	6.17%	6.43%
RF5	2.45%	2.56%	3.10%	3.20%
LF30	-4.97%	-7.02%	-3.71%	-6.03%
LF25	-3.77%	-5.21%	-2.51%	-4.23%
LF20	-0.95%	-2.44%	0.56%	-1.22%
LF15	0.24%	-0.97%	1.83%	0.29%
LF10	0.82%	0.19%	1.88%	1.08%
LF5	0.31%	-0.08%	0.92%	0.47%
RI30	-10.12%	-12.12%	-10.79%	-12.92%
RI25	-8.48%	-10.08%	-9.05%	-10.79%
RI20	-6.91%	-8.12%	-7.48%	-8.76%
RI15	-4.58%	-5.64%	-5.04%	-6.23%
RI10	-3.30%	-3.91%	-3.52%	-4.23%
RI5	-1.66%	-2.02%	-1.75%	-2.20%
CS80	-4.82%	-6.43%	-4.00%	-5.92%
CS70	-3.90%	-5.27%	-3.13%	-4.65%
CS60	-3.10%	-4.37%	-2.45%	-3.85%
CS50	-2.82%	-3.86%	-2.30%	-3.47%
CS40	-2.07%	-2.80%	-1.82%	-2.64%
CS30	-1.57%	-2.19%	-1.35%	-2.02%
CS20	-1.30%	-1.90%	-0.97%	-1.51%
ERB10	23.87%	24.80%	32.65%	34.21%
ERB5	16.71%	17.30%	24.82%	25.84%
ERB2	6.90%	7.29%	11.19%	11.74%

Table C.4: Percent reduction (positive) in the surface water NO₃ concentration for combination BMPs averaged over the entire 40-year simulation and the last 11-year historic period and averaged over the entire extent of the Arkansas in the USR and the downstream third of the Arkansas River in the USR.

	40 Year Average		Last 11 Year Average	
	Entire River Spatial Average	Downstream Third Spatial Average	Entire River Spatial Average	Downstream Third Spatial Average
LF30 CS80	-9.32%	-13.53%	-7.08%	-11.71%
LF20 CS60	-5.24%	-8.80%	-3.04%	-6.99%
LF10 CS40	-1.61%	-3.33%	0.05%	-2.02%
RI30 CS80	-15.13%	-19.28%	-14.88%	-19.42%
RI20 CS60	-10.48%	-13.38%	-10.34%	-13.44%
RI10 CS40	-5.50%	-6.78%	-5.30%	-6.78%
RI30 LF30	-13.31%	-16.28%	-12.14%	-15.37%
RI20 LF20	-8.29%	-11.06%	-6.93%	-10.12%
RI10 LF10	-2.68%	-4.10%	-1.59%	-3.25%
LF30 RF30	-0.60%	-2.90%	2.25%	-0.33%
LF20 RF20	3.05%	1.40%	5.87%	3.93%
LF10 RF10	3.75%	3.01%	5.71%	4.75%
CS80 RF30	6.83%	4.24%	11.16%	8.07%
CS60 RF20	5.63%	4.06%	8.79%	6.92%
CS40 RF10	2.88%	2.44%	4.43%	3.80%
RI30 RF30	-0.86%	-3.18%	1.75%	-0.93%
RI20 RF20	1.02%	-0.18%	2.88%	1.46%
RI10 RF10	1.23%	0.91%	2.33%	1.96%
RI30 LF30 CS80	-16.62%	-22.05%	-14.43%	-20.36%
RI20 LF20 CS60	-11.30%	-15.11%	-9.16%	-13.41%
RI10 LF10 CS40	-5.57%	-8.40%	-4.12%	-7.30%
LF30 CS80 RF30	-5.49%	-10.01%	-1.66%	-6.61%
LF20 CS60 RF20	-1.60%	-5.40%	2.01%	-2.24%
LF10 CS40 RF10	1.16%	-0.72%	3.77%	1.55%
RI30 CS80 RF30	-7.27%	-11.77%	-3.64%	-8.66%
RI20 CS60 RF20	-3.36%	-6.82%	-0.80%	-4.67%
RI10 CS40 RF10	-1.07%	-2.34%	0.44%	-1.19%
RI30 LF30 RF30	-10.27%	-13.27%	-7.68%	-11.12%
RI20 LF20 RF20	-5.06%	-7.90%	-2.41%	-5.78%
RI10 LF10 RF10	-0.02%	-1.46%	1.96%	0.18%
CS80 RF30 ERB10	19.38%	17.13%	28.24%	26.91%
CS60 RF20 ERB5	16.15%	14.62%	24.58%	23.35%
CS40 RF10 ERB2	8.16%	7.53%	13.24%	12.54%
RI30 LF30 CS80 RF30	-14.23%	-19.73%	-10.95%	-16.95%
RI20 LF20 CS60 RF20	-8.39%	-12.41%	-5.08%	-9.61%
RI10 LF10 CS40 RF10	-3.07%	-6.10%	-0.80%	-4.24%
RI30 LF30 CS80 RF30 ERB10	-6.34%	-11.78%	-0.46%	-6.41%
RI20 LF20 CS60 RF20 ERB5	-0.62%	-4.95%	6.20%	1.03%
RI10 LF10 CS40 RF10 ERB2	1.23%	-1.85%	6.21%	2.65%

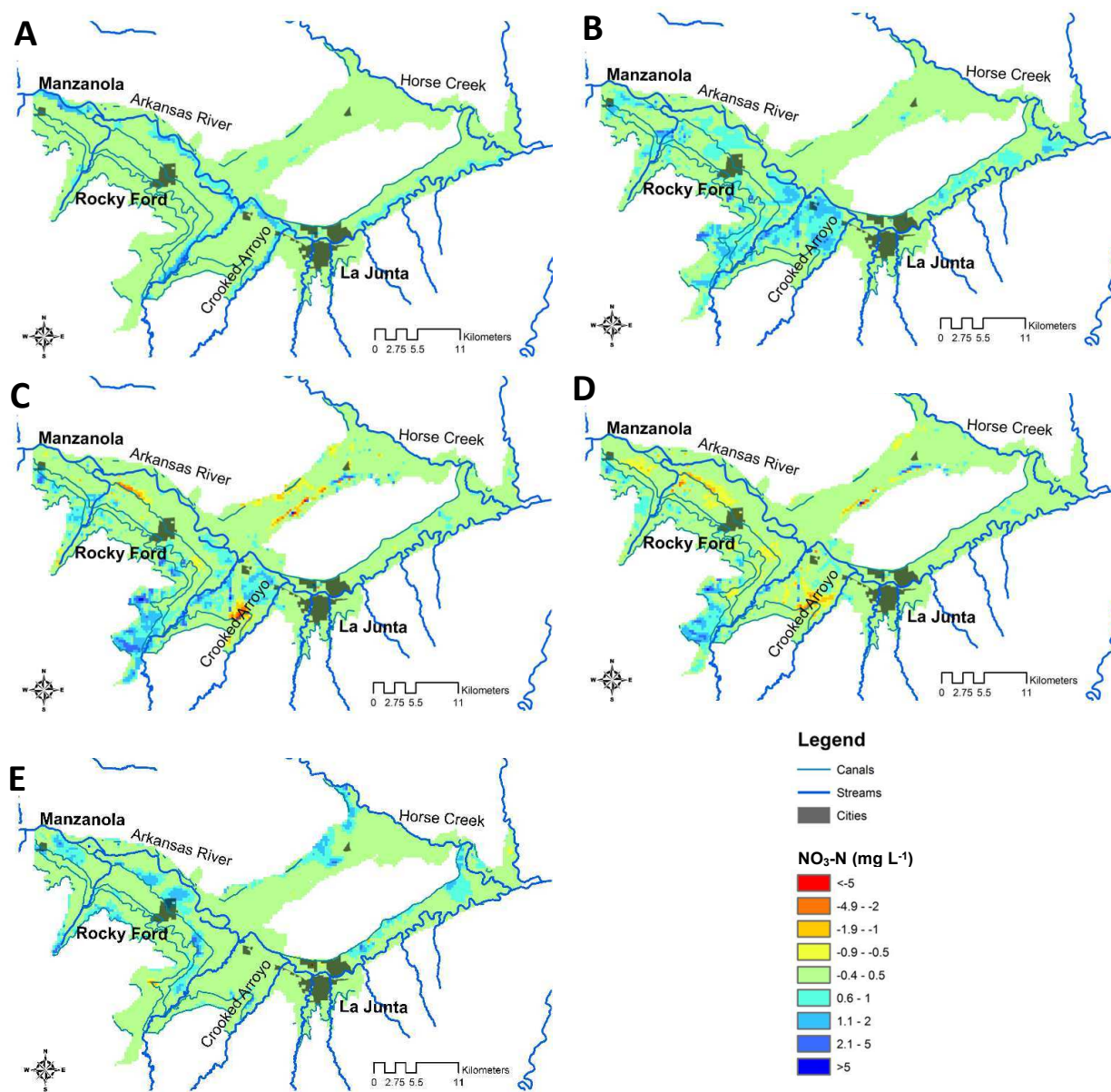


Figure C.1: Difference between temporal average baseline and (A) ERB10, (B) RF30, (C) LF30, (D) RI30, (E) CS80 $\text{NO}_3\text{-N}$ concentrations.

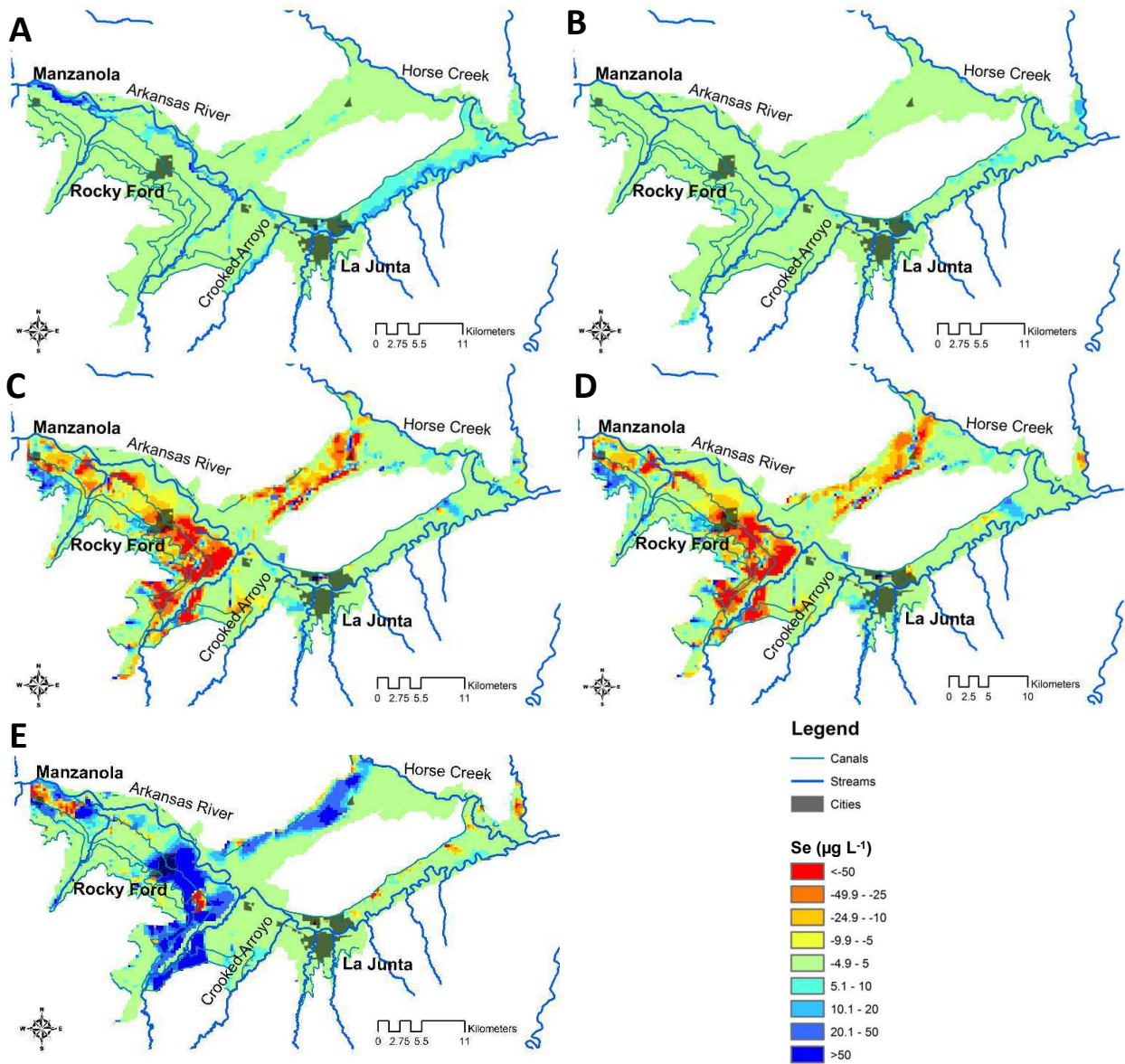


Figure C.2: Difference between temporal average baseline and (A) ERB10, (B) RF30, (C) LF30, (D) RI30, (E) CS80 Se concentrations.

APPENDIX D: BMP Flow and Reservoir Storage

The process of simulating reservoir storage to comply with the Arkansas River Compact with Kansas was discussed in Chapter 4 of this thesis. In water management BMPs (RI, LF, CS), flows from timesteps when the BMP condition had larger river flow were stored upstream of the USR and released when BMPs flows were lower than the baseline condition. Only the necessary water to supplement low flows and for reservoir evaporation was stored in the reservoir; excess water was routed through the system. In all cases, the model predicted larger average flows under BMPs than under the baseline. This excess flow is due a groundwater storage change (reduction in water tables) and a reduction in plant ET in the region. Figure D.1 shows the difference in flows between the RI30 BMP and the baseline over the first 11-year model historic period, where the plot is shaded when irrigation is occurring from mid-March to mid-November. Results from Figure D.1 as well as Figure D.2, showing other major BMPs, illustrate that these BMPs will have a large, positive impact on stream flow leaving the USR. It should be noted, however, that a large difference in the stream flows are due to the reduction in the Fort Lyon Canal diversion and there would be further reductions in return flows within the Fort Lyon Canal command area downstream of the USR.

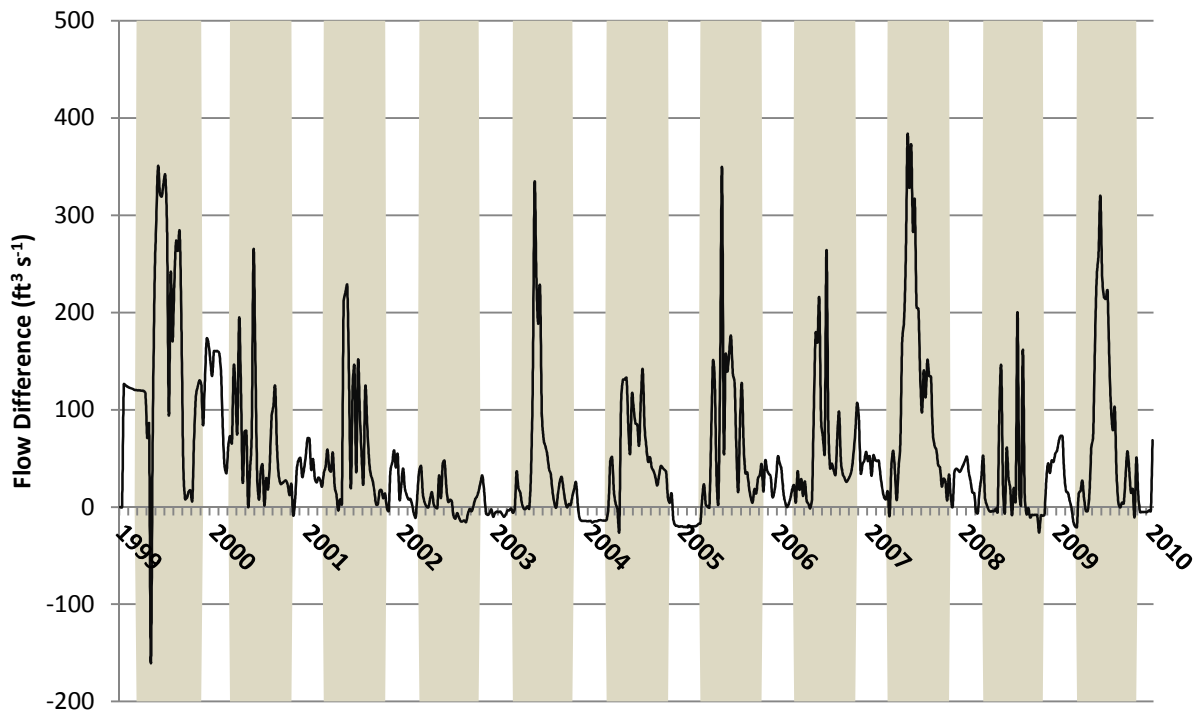


Figure D.1: Difference in flow at the downstream end of the USR between the RI30 BMP and the baseline.

Additionally, the modeling of reservoir storage and releases also provides a rough estimate of the total storage required to provide the supplemental water. The water is stored in such a way that at the end of the 11-year historic period the net water storage was zero; however, water can be stored between different water years. The storage was also allowed to go negative as long as the water volume was made up. Figure D.3 shows the simulated reservoir storage under the RI30 BMP scenario. The large spike at the beginning was due the smaller flows that occur in RI30 compared to the baseline for a timestep in 1999. Due to the nature of the code, an even amount of water was taken proportional to the excess flow the BMP had over the baseline so much of the large flows in earlier timesteps were not stored and the water was taken from existing reservoir storage. Based on this analysis, a rough estimate of storage required to implement the RI30 BMP within the USR would be about 4500 acre-ft.

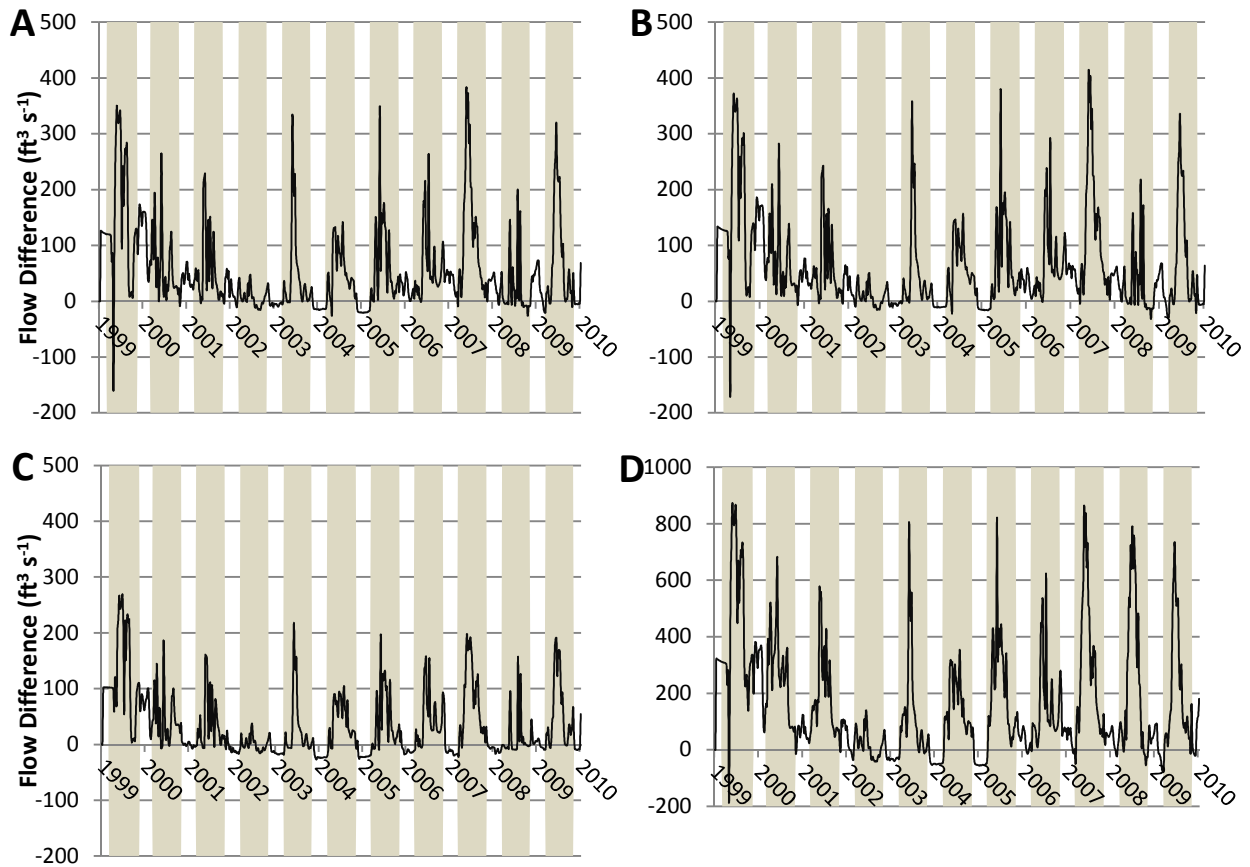


Figure D.2: Difference in flow at the downstream end of the USR between (A) RI30, (B) LF30, (C) CS80, (D) RI30 LF30 CS80 combined and the baseline condition.

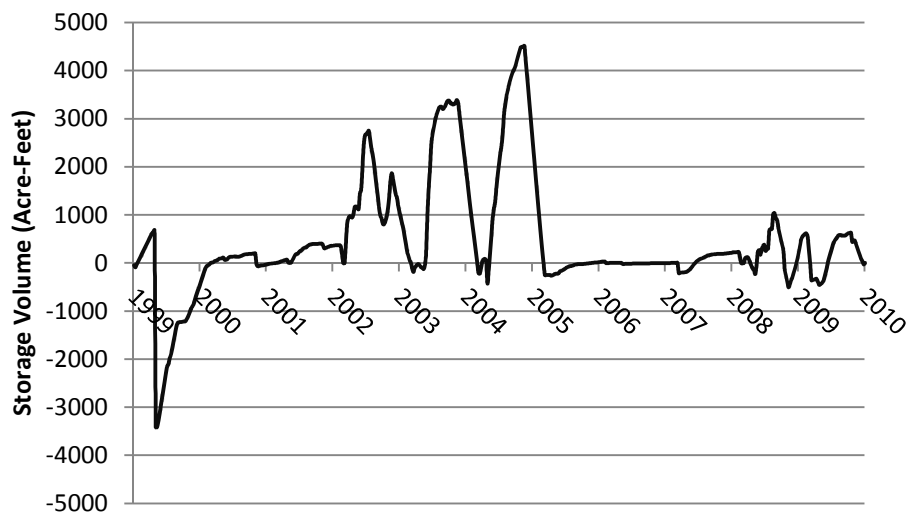


Figure D.3: Simulated reservoir storage over time under RI30 BMP.