SECTION 319 NONPOINT SOURCE POLLUTION CONTROL PROGRAM
WATERSHED ASSESSMENT/PLANNING PROJECT FINAL REPORT

Identifying Arkansas River Selenium and Nitrogen Best Management

by

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May 2017

Revised July 2017

This project was conducted in cooperation with the State of Colorado and the United States Environmental Protection Agency, Region 8.

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EXECUTIVE SUMMARY

PROJECT TITLE: Identifying Arkansas River Selenium and Nitrogen Best Management

PROJECT START DATE: 26 October 2012

PROJECT COMPLETION DATE: 30 June 2016

FUNDING

TOTAL BUDGET: $457,431

TOTAL EPA GRANT: $256,620
WQIF State Match (Cash): $59,459
Other Non-Federal Match (Cash): $125,337
Other Non-Federal Match (In-Kind):

TOTAL EXPENDITURES OF EPA FUNDS: $256,620
TOTAL SECTION 319 MATCH ACCRUE: $184,796
BUDGET REVISIONS: None
TOTAL EXPENDITURES: $441,416

SUMMARY ACCOMPLISHMENTS

Computational models, supported by field data, were developed and applied to find ways to amend land and water management to lower selenium and nitrogen pollution in Colorado's Lower Arkansas River and its alluvial groundwater aquifer. A number of alternative best management practices (BMPs) were assessed, with input from stakeholders, according to their technical impact and socio-economic feasibility. Considered BMPs include reduced irrigation application, lease-fallowing of irrigated land, canal sealing to reduce seepage, reduced fertilizer application, and enhanced riparian buffers. Results suggest that selenium and nitrate concentrations could be lowered using different means by at least as much as about 10% and 30%, respectively, in the river within a representative study region. Refinement and extended application of the computational models, along with enhanced socioeconomic evaluation, is underway. Preliminary recommendations were made for future work and for the development of a pilot implementation program to test these BMPs in the field in view of widespread adoption.

INTRODUCTION

The Lower Arkansas River Valley (LARV), one of Colorado's most productive agricultural regions, is vulnerable to a number of irrigation-induced pollutants that exceed regulatory standards. The Valley is underlain by Upper Cretaceous marine and Tertiary sedimentary rocks, which serve as a source of salts and trace elements, like selenium (Se). As water from excess irrigation and canal seepage comes into contact with the marine shale, dissolved oxygen (O_2) and nitrate (NO_3) in the water oxidizes immobile Se into a dissolved form, leading to the transport of Se to the drainage network and eventually to the river. Besides triggering the release of Se from marine shale, NO_3 also prevents dissolved forms of Se from being chemically reduced to immobile or less-toxic forms. In addition, irrigation of crops increases the consumptive use of water in the watershed, leading to evaporative concentration of solutes already present. Consequently, concentrations of both Se and N in ground water and surface water can rise to levels that threaten livestock, aquatic life in the streams, and human health.

The concentrations of dissolved Se species in groundwater and in overland return flows have resulted in the designation of all segments of the Lower Arkansas River as "water quality limited" with respect to Se and their placement on the current Clean Water Act 303(d) list for development of Total Maximum Daily Load (TMDL). Gates et al (2009, 2016) report measured Se concentrations in two study regions along the Arkansas River that amount to between 1.4 and 3.7 times, respectively, the chronic standard of 4.6 $\mu g\ L^{-1}$ (85th percentile) for total dissolved Se.

In addition to Se, N is a pollutant of growing concern in the LARV. Elevated concentrations of NO_3 in surface water and groundwater in the LARV, presumably from over-fertilization of cultivated fields, have been observed in data gathered over the last several years (Gates et al 2009, 2016). Median measured NO_3-N concentrations are about 1.5 mg L^{-1}, approaching the Colorado interim standard of 2 mg L^{-1} for total N (NO_3 plus nitrite pus ammonium), at 11 locations sampled over 2006 – 2011 in an upstream study region (USR) near La Junta and at eight locations sampled over 2003 – 2011 in a downstream study region (DSR) near Lamar (Figure 1). Possible implications of high NO_3-N concentrations, in addition to effects on Se, include eutrophication for ecosystems and methemoglobinemia, or "blue-baby" syndrome for human populations.

Elevated concentrations of Se and N constitute an on-going threat to the bioenvironmental system within the LARV as well as to downstream regions. Ways must be found to lower concentrations toward compliance without impairing the agricultural productivity of the Valley. Specifically, an enhanced watershed plan aimed at investigating, implementing, and monitoring mitigation procedures is needed at this time and is consistent with the priorities outlined in the 2012 Colorado NPS Management Plan, specifically that by 2025, nonpoint sources will no longer be a cause of impairments. This report describes the methods and results of a project that provides tools and preliminary guidance toward the implementation of strategies to solve these key water quality problems.

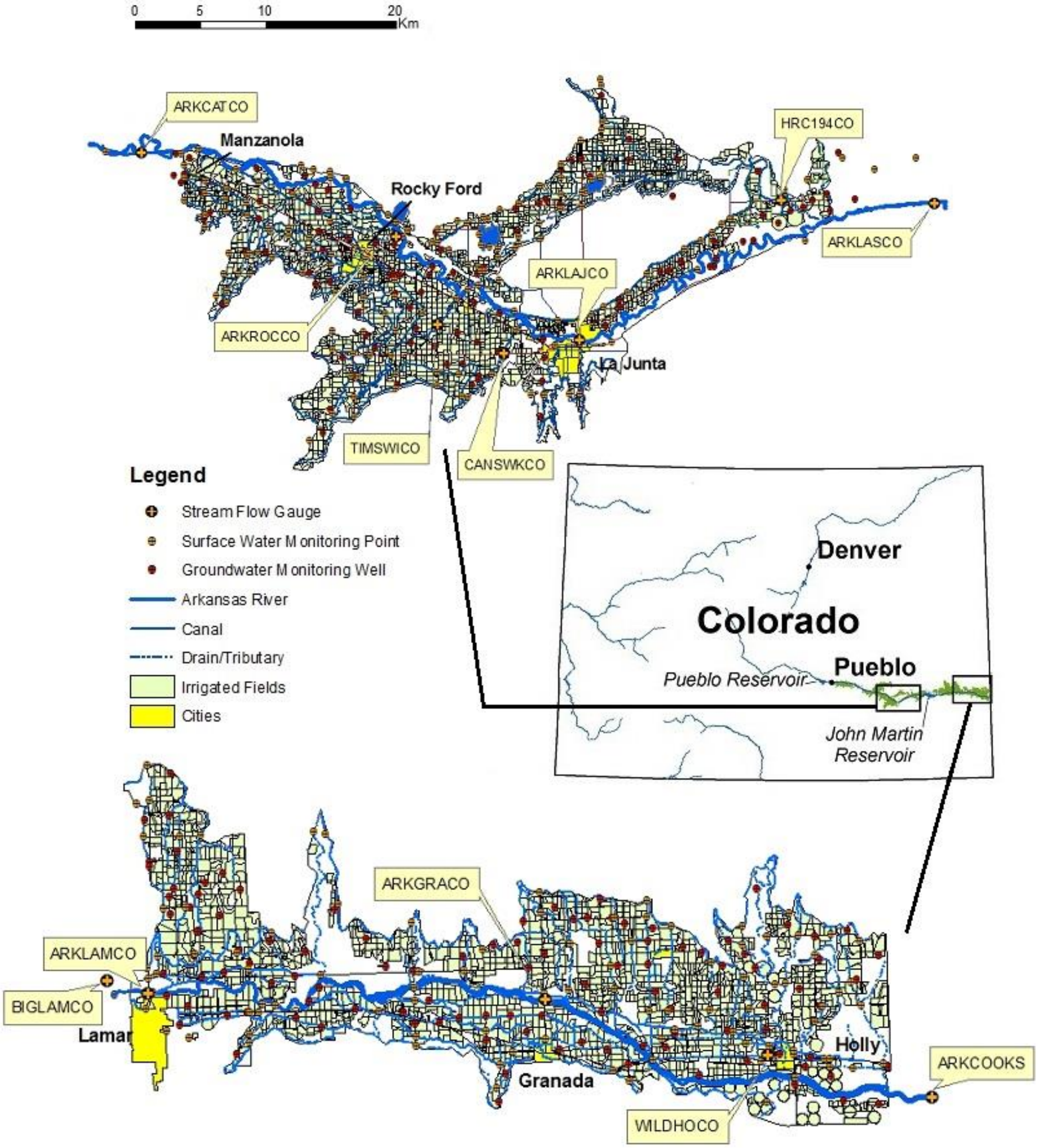


Figure 1. The upstream study region (USR) and downstream study region (DSR) in the LARV, showing locations of streamflow gages, surface water monitoring sites, and groundwater monitoring wells.

PROJECT GOAL, OBJECTIVES, TASKS, AND ACCOMPLISHMENTS

The overall goal of this project was to enhance the Lower Arkansas Watershed Plan by detailing best management practices (BMPs), and outlining a means for their future pilot implementation, which will aid in diminishing the mass loadings and concentrations of Se and N in the surface waters of the LARV and bring them into closer conformity with regulatory standards. This involved developing and using modeling tools to investigate practical, economically-viable, and socially-acceptable BMPs, as identified in collaboration with stakeholders and the watershed community. The accomplishments toward meeting this goal under the objectives and tasks laid out in the project implementation plan (PIP) are presented below.

OBJECTIVE 1: Identify representative key stakeholders in the LARV and form a stakeholder group to guide the planning process, facilitate communication, and promote community involvement.

Task 1: Identify key stakeholders in the LARV through an assessment of local elected officials, extension offices, soil and water conservation districts, water conservancy districts, National Resources Conservation Service, parks and recreation services, state fish and wildlife programs, landowners, canal companies, CWQCD, and other water and resource management agencies.

Accomplishments under Objective 1, Task 1: A pilot group of 25 stakeholders, mostly farmers, from the LARV were surveyed in three phases as part of this project. In an effort to gage the socio-economic perceptions of these stakeholders regarding the alternative land and water BMPs being considered, a form of multi-criteria decision analysis (MCDA), called analytic hierarchy process (AHP), was used as described in Heesemann (2016) and as summarized below under "Accomplishments under Objective 1, Task 2".

Another group of stakeholders, consisting of about 12 farmers and 18 representatives of local and state water agencies, accepted an invitation from the Colorado State University (CSU) project team to join the Arkansas River Management Action Committee (ARMAC). Membership includes personnel from the NPS Pollution Control Program of the Colorado Department of Public Health and Environment (CDPHE). The aim of the ARMAC is to make recommendations on behalf of the LARV for future land and water management actions that will help improve water quality in the river, the groundwater aquifer, and soils, while increasing profitability and sustainability of irrigated agriculture and possibly saving water. This will involve evaluation of the technical, socioeconomic, and administrative viability of alternative management actions with the assistance of the CSU team. The committee is a clearing house for the presentation, discussion and consideration of ideas and potential BMPs.

A broader group of about 400 LARV farmers were identified and sent a confidential survey to solicit their views. The survey examined opinions about water quality problems and prospective BMPs.

Task 2: Establish forums of communication with stakeholders and the broader watershed community, in order to identify issues of concern, establish specific goals of the watershed plan related to Se and N, and propose and discuss feasible management strategies.

Accomplishments under Objective 1, Task 2: In the AHP MCDA method, rankings of alternative BMPs by the pilot group of stakeholders were derived by comparing them two at a time (pairwise comparisons) based on either actual measurements (i.e. cost, efficiency, etc.) or on relative strength of preferences and feelings (Saaty 1987). The hierarchical structure of the AHP is illustrated in Figure 2, including from top to bottom the main criteria, sub-criteria, and BMP alternatives.

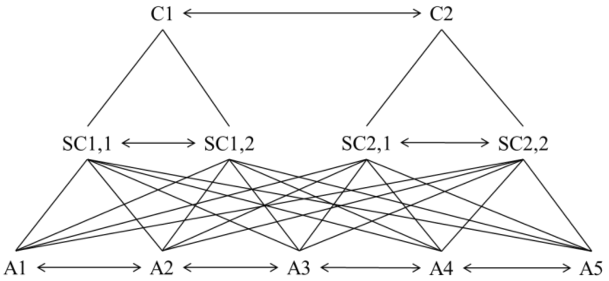


Figure 2. General AHP structure, including main criteria (C1, C2), sub-criteria (SC1,1, SC1,2, SC2,1, SC2,2), and alternatives (A1, A2, A3, A4, A5). The hierarchical structure of the AHP is shown, whereby pairwise comparisons are made at each level (arrows) with respect to the criteria preceding them (lines).

The AHP uses a hierarchical structure to assess the complex relationship between criteria and alternatives by breaking them into sets of pairs that can be easily compared. The method also ensures that the elements being compared at each level (i.e. main criteria, sub-criteria, and alternatives) are of the same magnitude and can therefore in fact be reasonably compared (Saaty 1990). At each level, pairwise comparisons are made between all elements at that level in regard to the preceding criteria (main criteria are compared only with main criteria since there are no higher level criteria) (Heesemann 2016).

The first phase in applying the AHP process was to conduct a preliminary oral interview of selected stakeholders. Questions in this dialogue were framed to gain insight into stakeholder views about the major issues facing the LARV, the cause of those issues, and possible solutions. One-on-one or two-on-one [researcher(s) to stakeholder] interviews were held with five farmers and one a water conservancy district employee in May 2014 in Rocky Ford, Colorado. The views expressed by the stakeholders in this preliminary interview were taken into account in preparing an AHP survey.

The AHP survey was developed for submission to stakeholders in the USR of the LARV and was approved by Colorado State University's Institutional Review Board. The structure of the final survey is summarized in Table 1, showing the main criteria and sub-criteria that were used to evaluate five considered classes of BMPs: reduced irrigation application (RI), canal sealing to reduce seepage (CS), lease-fallowing of irrigated land (LF), reduced fertilizer application (RF), and enhanced riparian buffer zones (ERB).

Table 1. The AHP survey structure administered to a pilot group of stakeholders in the LARV USR.

Main Criteria	**Sub-Criteria**	**BMP Alternatives**
Cost of BMP Implementation	Upfront	Reduced fertilization (RF)
	On-going	Reduced irrigation (RI)
	Service	Canal sealing (CS)
Ease of BMP Implementation	Willingness	Land-fallowing (LF)
	Incentives	Enhanced riparian buffer (ERB)
	Avoiding legal hurdles	
	Cooperation	
Economic Benefits from BMP Implementation	Water efficiency	
	Crop yield	
	Avoiding legal or regulatory restrictions	
Off-farm Environmental Benefits from BMP Implementation	Nitrogen reduction	
	Selenium reduction	
	Salinity reduction	

To reduce the required number of pairwise comparisons in the AHP survey, the sub-criteria were excluded from the typical hierarchical structure. Instead, survey participants were asked to strictly rank the sub-criteria (i.e. directly ranking 1-3 or 1-4, with 1 being the most preferred) in regard to the associated main criteria. Thereby, more data could be obtained about each of the main criteria without increasing the difficulty and time required to complete the survey. Participating stakeholders then were asked to rank the main criteria by a series of pairwise comparisons using the modified Saaty scale shown in Table 2. The alternative BMPs also were compared using this scale, whereby surveyed stakeholders scored each pairwise comparison in relation to each of the main criteria (Heesemann 2016).

In the next phase, a preliminary survey was conducted individually and confidentially with eight additional stakeholders in October 2014, at Colorado State University's Arkansas Valley Research Center (AVRC) in Rocky Ford. The content and structure of the survey was thoroughly explained to each participant prior to its completion. Questions of participants were answered and noted so that the survey could be revised as needed. Feedback from the participants indicated that only minor survey adjustments were required.

Table 2. Modified Saaty scale used for the AHP BMP survey in the LARV USR (Heesemann 2016).

Importance	**Definition**
1	Equally
2	Somewhat More
3	Much More
4	Very Much More
5	Absolutely More

The final phase of the survey was issued at the Annual AVRC Advisory Council meeting held in December 2014 in Rocky Ford. The written survey was issued to 12 LARV stakeholders confidentially but in a group setting.

Figure 3 displays the average relative importance scores determined by the AHP analysis for the 25 surveys, along with estimated margins of error (MOE) (Heesemann 2016). The results indicated that the criterion of economic benefits is the most important to the surveyed stakeholders, within the given MOE. The second most important main criterion was cost. In contrast to the comparison of economic benefits and cost with all other criteria, there was overlap in the MOE associated with ease of implementation and environmental benefits; thus, it was not possible to determine the relative importance of these two criteria with respect to each other.

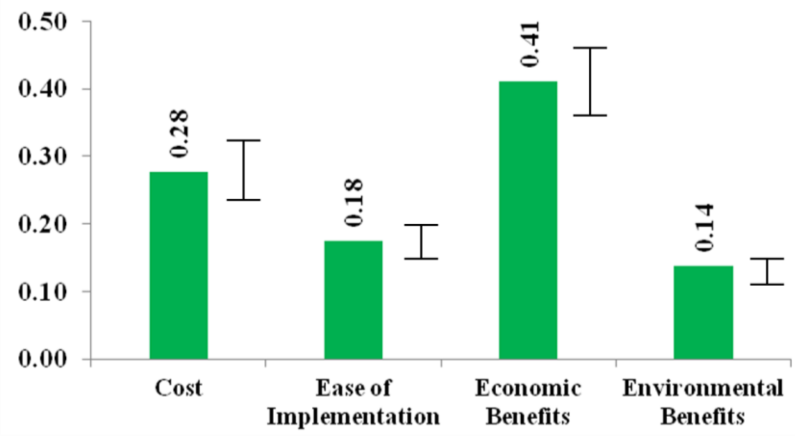


Figure 3. Average main criteria relative importance scores with MOE bars associated with a 95% confidence interval.

Average relative importance scores of sub-criteria are shown in Figure 4. The economic benefits sub-criterion that was most important to surveyed shareholders appeared to be crop yield, although this conclusion cannot be stated with much confidence since all three of the economic benefits considerations sub-criteria show overlap in their MOE. Upfront costs were the most important cost-related sub-criterion. Under the ease of implementation main criterion, incentives rank as the highest sub-criterion, suggesting incentives will be needed by stakeholders to offset any economic burdens associated with BMP implementation. Salinity reduction far outweighed both N reduction and Se reduction sub-criteria associated with environmental benefits. High levels of soil salinity are well known to reduce crop yield, which was the highest ranking sub-criterion under the highest ranking main criterion.

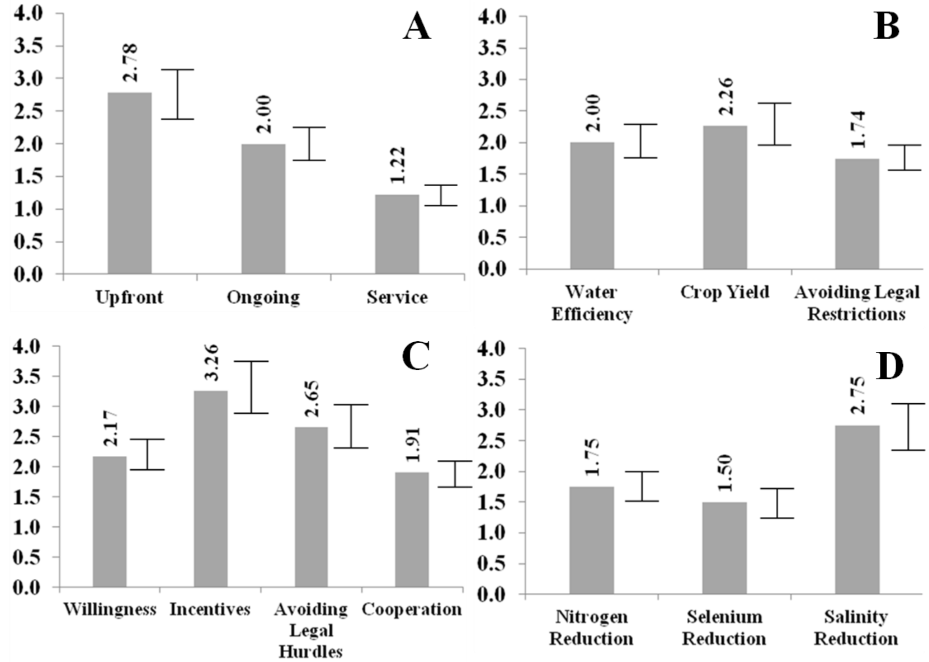


Figure 4. Average sub-criteria ranks with MOE bars associated with a 95% confidence interval.

Figure 5 depicts the average relative importance scores for the BMP alternatives. The BMP most preferred among the stakeholder surveys analyzed by AHP appeared to be RI. However, considering the MOE, RF also could be ranked first. Overlaps in the MOE for the CS, LF, and RF BMPs also occurred, making it difficult to assign ranks for these BMPs. The ERB BMP appears to be the least preferred among the surveyed, although there is slight overlap of the MOE for ERB and that for CS.

Four meetings between CSU project members and the ARMAC were held in La Junta in the LARV between March 2015 and April 2016. The ARMAC was briefed on data and modeling results regarding current water quality, crop productivity, and water use conditions and on the assessment of considered BMPs. Preliminary study results were assessed and guidance was sought from ARMAC members regarding how to make BMPs practicable as well as effective. ARMAC members agreed to share their experience and expert opinions in the on-going identification and evaluation of additional prospective BMPs.

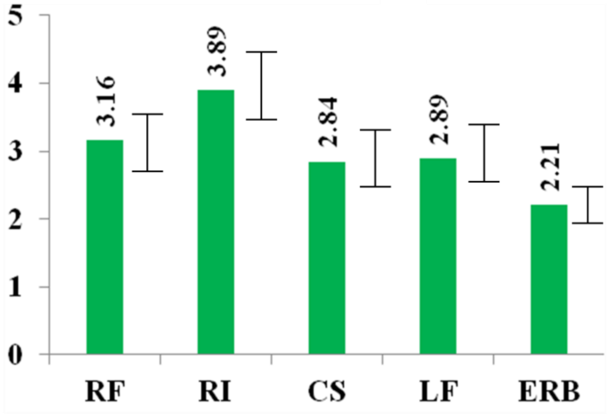


Figure 5. Average BMP ranks with error bars associated with a 95% confidence interval.

A website (www.coloradoarmac.org) was set up for exchange of information, including access to GIS-based data and model results through the eRAMs platform, as described below. The website facilitates interaction between stakeholders and water specialists and evaluation of the pros and cons of available land and water BMP options.

A broad survey of farmers was designed for discovering views and preferences regarding the severity of water quality problems in the LARV and the most practicable ways to address them. The response rate was about 38% (151). There were 79 useable surveys where farmers irrigated. The remaining returned surveys indicated that they did not irrigate. About 14% of farms indicated that they irrigated with sprinkler systems, less than 2% used drip irrigation, and the remaining farms used flood irrigation, which is consistent with estimated use of these systems in the LARV. The average size of these farms was 364 acres and the most commonly produced crops were alfalfa, corn and wheat. Farmers were more concerned with water quantity for irrigation than water quality. Respondents indicated that they were about equally responsible for water quality problems with industry, but laid little blame on urban sources.

As shown in the Figure 6, surveyed farmers ranked salinity higher than Se, and Se higher than nutrients (including N), as problems on their own farms. Respondents said they lacked reliable sources of information to make them aware of water quality problems in the LARV. Over 70% said that cost was an impediment to controlling salinity and Se, but only half said the same about nutrients. Likewise, about half thought salinity and Se were difficult to control, but less than 30% felt that nutrients were difficult to control.

Over half of respondents felt that it is the responsibility of both farmers and the government to address water quality problems, but 79% said they did not trust the government in these matters. Almost 100% of farmers said that is in their best interest to invest in irrigation management to ensure long term success. Nearly 40% have already tried reduced fertilizer application to mitigate pollution and approximately 20% have tried reduced irrigation, canal sealing, or lease following. Three quarters felt that protecting the environment is not the most important role in being successful, and about two-thirds said that pollution mitigation costs more than it is worth. Nevertheless, 92% said that a slight decrease in farming profits is acceptable to adopt these practices. Over 80% of producers were motivated to adopt pollution mitigating technologies to avoid regulations. On the flip side, the most common reasons given for not adopting a high-efficiency irrigation system were threats to water rights, requirements to purchase replacement water, and limited knowledge. Surveyed farmers seemed united in feeling that if they do not change their current practices then both water quality and quantity will be at risk in the future. The final evaluation and ranking of a refined set of BMPs, to be recommended by the ARMAC for consideration, has not yet been conducted.

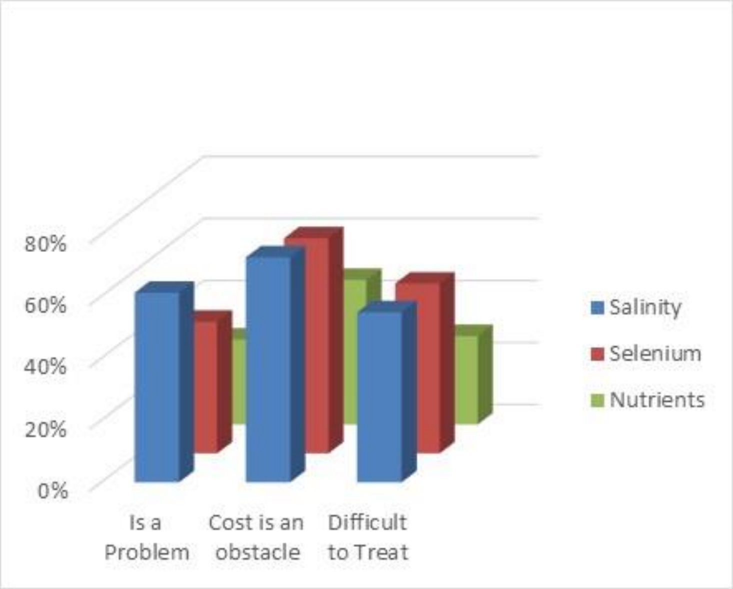
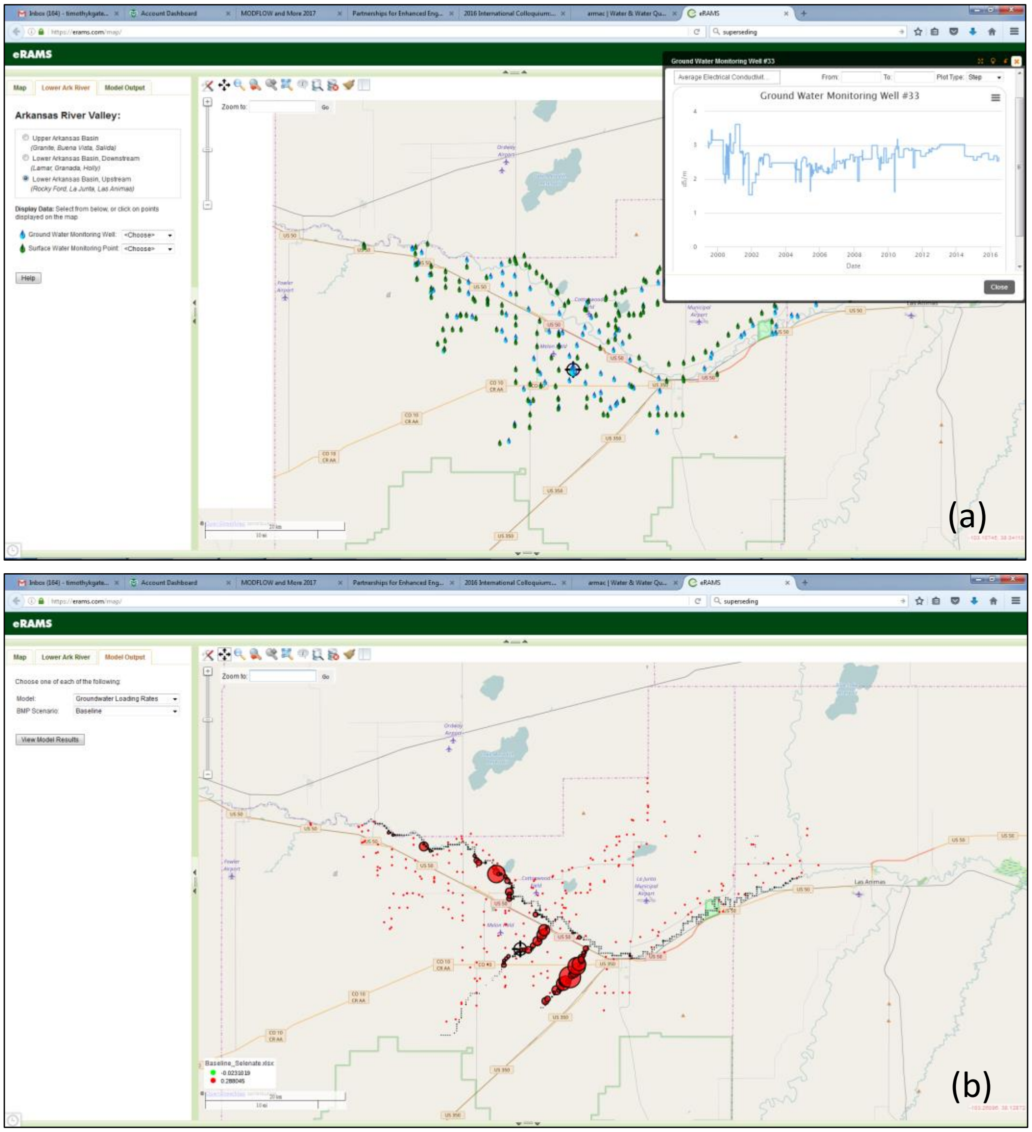


Figure 6. Summary of surveyed farmers' concerns about implementing BMPs to control salinity, Se, and nutrient water quality problems in the LARV.

<u>OBJECTIVE 2:</u> Characterize and assess current watershed conditions in relation to Se and N, and develop a plan that provides for delineation and eventual implementation of BMPs to enhance conditions in relation to specified criteria.

Task 3: Collate, store and analyze data to identify water quality concerns, in order to identify geographic regions of highest concern. The environmental Risk Assessment and Management System (eRAMS) will be used to store and retrieve geospatial data, observed hydrologic and water quality time series data, and modeling results corresponding to alternative management (i.e., BMP) scenarios.

Accomplishments under Objective 2, Task 3: The existing CSU SQL database, containing Se and N concentrations measured in groundwater monitoring wells and at surface water sites, was linked to eRAMS to allow access to data using GIS. Data gathered over the period 1999 – 2012, as described in Gates et al (2016), were used to calibrate, test, and support the models developed and used in this project. The eRAMS platform link was incorporated into the ARMAC website. In addition to data access, model estimates under current baseline conditions and under proposed alternative BMPs are made available through eRAMS. Data and results are displayed spatially on maps of the USR and DSR study regions using GIS. Example screenshots of the eRAMS display, accessed through the ARMAC website, are shown in Figure 7.


Arkansas River Valley:

○ Upper Arkansas Basin (Granite, Buena Vista, Salida)
○ Lower Arkansas Basin, Downstream (Lamar, Granada, Holly)
● Lower Arkansas Basin, Upstream (Rocky Ford, La Junta, Las Animas)

Display Data: Select from below, or click on points displayed on the map

Ground Water Monitoring Well: <Choose>
Surface Water Monitoring Point: <Choose>

Plot Type: Step

Choose one of each of the following:

Model: Groundwater Loading Rates
BMP Scenario: Baseline

Figure 7. eRAMS screenshots of (a) plot of electrical conductivity measured in a groundwater monitoring well in the USR and (b) model-simulated total Se loading in the USR for baseline conditions.

Task 4: Estimate the magnitude, source locations, and timing of pollutant loading under existing watershed conditions. The estimation procedure involves the use of the newly-developed numerical model RT3D-AG (Bailey et al 2013), which uses results of a calibrated MODFLOW-UZF flow model (Morway et al 2013), capable of simulating the fate and transport of Se and N species in agricultural groundwater systems. Modifications for use in the proposed project include incorporating in-stream flow and chemical processes using an enhanced stream routing and transport model, based upon a modification of the OTIS model (Runkel 1998).

Accomplishments under Objective 2, Task 4: The calibrated RT3D-AG (a variant of UZF-RT3D) model was applied to estimate historic baseline conditions of groundwater concentrations and loading of Se and N to the stream system in the LARV. The flow variables predicted by MODFLOW-UZF were used in the RT3D-AG model. MODFLOW-UZF employs a finite difference approximation of the three-dimensional governing equations for saturated groundwater flow with the one-dimensional (vertical) equation for unsaturated flow. The model predicts groundwater hydraulic head, saturated and unsaturated groundwater flow, and water content in the unsaturated zone. Its implementation, calibration, and application to the USR and DSR are described in Morway et al (2013). Application of the RT3D-AG model to predict the concentration and transport of dissolved Se and N species in the saturated and unsaturated zones for historic baseline conditions in the USR is described by Bailey et al (2013, 2014).

To simulate Se and N concentrations within the stream system of the LARV, dynamic links were set up between the MODFLOW-UZF groundwater flow model and the SFR2 stream flow model and also between the RT3D-AG groundwater reactive transport model and the OTIS-QUAL2E stream reactive transport model. Like the groundwater flow and transport models, the SFR (Prudic et al. 2004) and OTIS-QUAL2E models are finite difference approximations of the flow and reactive transport governing equations, respectively. OTIS-QUAL2E combines OTIS (Runkel 1998), used as the advection-dispersion solute transport engine, with QUAL2E (Brown and Barnwell 1987) which simulates the basic in-stream water quality processes for Se species, dissolved oxygen, N species, and algae (Bailey and Ahmadi 2014). The final developed model that couples groundwater reactive solute transport with surface water reactive solute transport is referred to as RT3D-OTIS.

The RT3D-OTIS numerical model developed for this project is based on the conceptual model of hydro-chemical processes illustrated in Figure 8. The hydrological processes (simulated by MODFLOW-SFR) are labeled in blue text; the chemical transport processes in the soil and groundwater system (simulated by RT3D-AG) are labeled in red text; and the chemical transport processes in the stream network (simulated by OTIS-QUAL2E) are labeled in green text. The chemical processes simulated by OTIS-QUAL2E are further illustrated in Figure 9. The conceptual basis for the OTIS-QUAL2E and RT3D-AG models, along with the integrated RT3D-OTIS model, is described in the following. More details about these component and integrated models are provided in Sections A1 – A3 of the Appendices.

Figure 8 represents stream-aquifer processes affecting N and Se fate and transport in both naturally vegetated and cultivated land, the principal land surface processes including applying irrigation water, canal seepage from earthen canals, N fertilizer loading, ET, tailwater runoff from irrigated fields, and runoff from rainfall events. Irrigation water, canal seepage, and runoff also contain dissolved N and Se mass in the form of NH_4, NO_3, NO_2, SeO_4, and SeO_3.

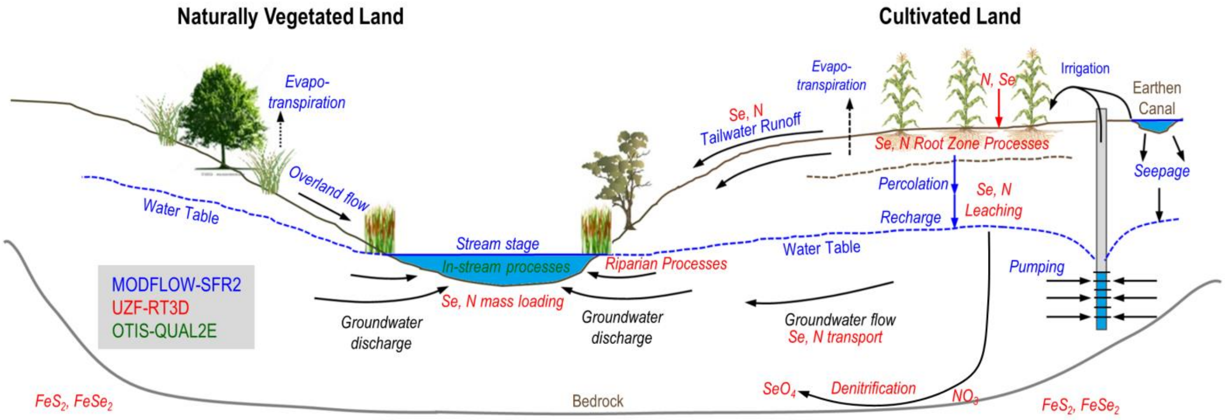


Figure 8. Principal hydro-chemical processes governing fate and transport of N and Se species in an agricultural stream-aquifer system.

Root zone processes include chemical reactions such as nitrification, denitrification, sorption, and Se chemical reduction (SeO_4 reduction to SeO_3, and SeO_3 reduction to elemental Se), with each reaction requiring the mediation of microbial populations. Other processes include crop uptake of NH_4, NO_3, NO_2, SeO_4, and SeO_3, mineralization and immobilization, volatilization of SeO_3 and SeO_4, with any N and Se species not taken up by crops leached through the vadose zone to the water table. Once in the saturated zone of the aquifer, NO_3, SeO_4, and SeO_3 are transported through the aquifer via advection and dispersion processes, with the latter occurring due to spatially-varying groundwater velocities based on spatially-varying hydraulic conductivity. Chemical reactions such as denitrification and Se chemical reduction also can occur in the saturated zone. Of particular interest is the autotrophic denitrification (and also autotrophic reduction of DO) in the presence of pyrite (FeS_2), which is contained in abundance in marine shale. Such shale is present in the LARV in the near-surface, sometimes as outcrops, and also as the bedrock underlying the alluvial materials. This process is assumed to be a major source of Se into the saturated zone of the aquifer.

An important aspect of the groundwater and surface water system is the influence of NO_3 on Se transformation chemistry. As redox-sensitive species, SeO_4 and SeO_3 depend on the succession of terminal e^--accepting processes. Due to energy demands, microbes in the subsurface media first utilize O_2, followed by NO_3, SeO_4, Mn(IV), Fe(III), and finally SO_4 (Korom 1992; McMahon and Chapelle 2008) in the so-called "redox ladder". Since O_2 is found in abundance in the unsaturated zone, NO_3 reduction (denitrification) usually only occurs below the water table (Korom 1992), where it is denitrified if microbes and electron donors (organic carbon in the case of heterotrophic bacteria or inorganic material, like shale, in the case of autotrophic bacteria) are present, or transported via advection through the subsurface system. Due to this preferential consumption of species, each species acts as an inhibitor of the reduction of species with lower redox potentials. With O_2 and NO_3 present in the system, SeO_4 reduction to SeO_3 is inhibited, thus allowing SeO_4 to remain in the dissolved phase and undergo transport through the groundwater system.

When the water table is above the river stage, groundwater near the exposed surface water can discharge to the river. N and Se mass in the discharged groundwater can then be transported downstream through the stream network. On the other hand, if the water table is below the river stage, then river water can discharge (seep) to the aquifer, and N and Se mass in the river water can load to the aquifer. Often, groundwater discharge and stream seepage can occur concurrently within the same reach of the river, and also can occur cyclically throughout the year at a given point depending on the current hydrologic patters, e.g. high stream stage in the spring due to snowmelt can cause stream seepage to the aquifer, whereas low stream stage and high water tables recharged from irrigation water later in the season can cause groundwater discharge to the stream network.

The exchange of water between the stream and aquifer, and the associated dissolved N and Se mass loaded with the water, is depicted in the left picture in Figure 9. The flow exchange rates are simulated by the MODFLOW-SFR model that uses the Streamflow Routing Package (SFR2) to calculate groundwater-surface water exchange flow rates and simulate stream discharge and stream stage. These flow rates are used by RT3D-AG to calculate the mass of dissolved N and Se that loads to the stream network via groundwater discharge. Once N and Se is in the stream network, transport and chemical alteration in the downstream direction is simulated by OTIS-QUAL2E, with main processes shown in Figure 8 (diagrams on the right-hand side). OTIS-QUAL2E requires stream discharge, stream stage, the cross-sectional area of flow, the lateral flow rates (groundwater discharge rates), and the N and Se concentration in the lateral groundwater flow. These values for each grid cell are supplied by MODFLOW-SFR and RT3D-AG.

The main processes of transport in the stream are advection, with solutes flowing with the surface water (due to flow rates and velocity), and dispersion, with solute mass spreading longitudinally due to difference in local surface water velocity. The chemical reactions that also influence N and Se concentrations are depicted in Figure 9. N mass is governed by processes represented in QUAL2E, which includes transformation between the various N species (organic N, NH_4, NO_2, and NO_3), denitrification, uptake by algae, and the processes that affect algae concentration (algal respiration, photosynthesis, etc.) and O_2. The Se module designed for this project is similar to the N cycling processes in QUAL2E, with transformation processes between the Se species, and uptake by algae and aquatic plants. Sorption of SeO_4 and SeO_3 to suspended sediments and bed sediments also occur.

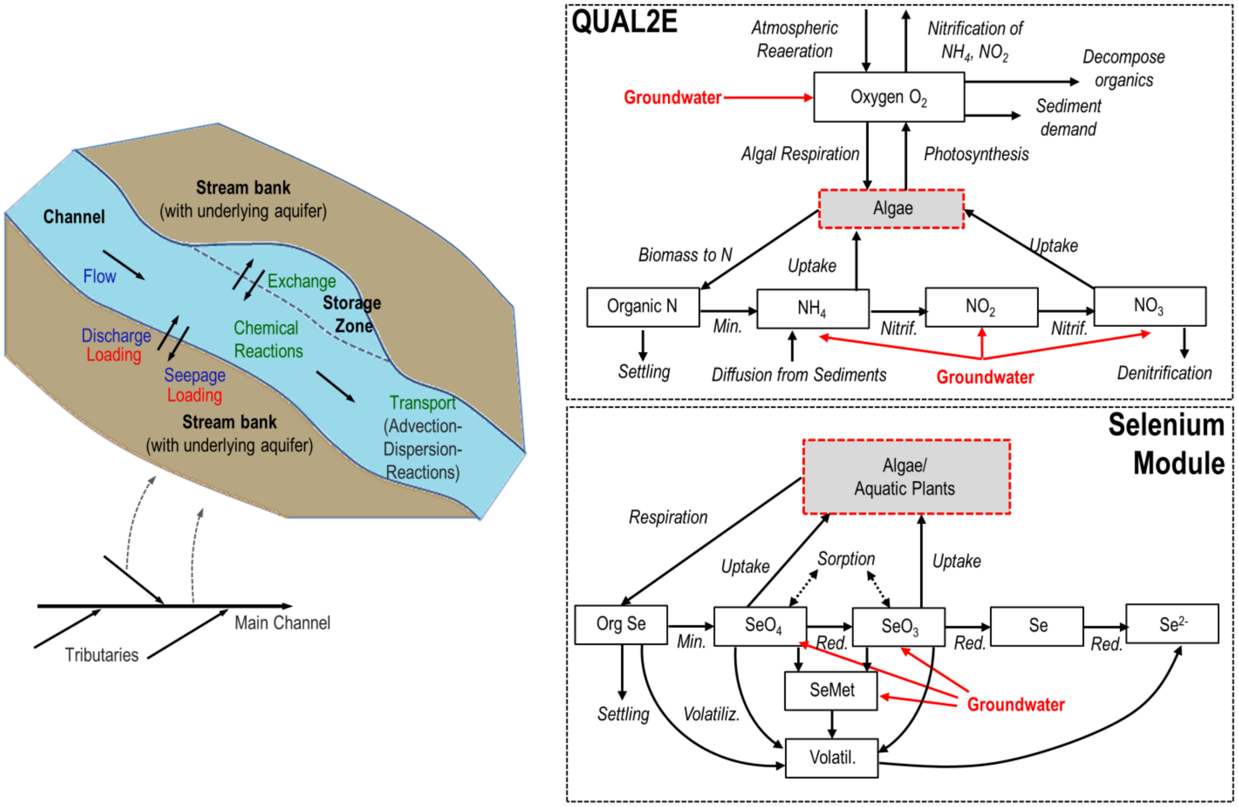


Figure 9. (Left) Conceptual model of reactive solute transport in streams, with surface water interacting with the adjacent and underlying aquifer; (Right) Species' mass transfer in QUAL2E (top), which simulates O_2, Algae, and N species fate and transport in a stream channel, and in the Se module for QUAL2E (bottom).

Parameters associated with the MODFLOW-UZF groundwater flow model were calibrated and tested for the USR as described in Morway et al (2013). Application of the MODFLOW-SFR model, which links subsurface flows predicted by MODFLOW-UZF to flows in the stream system, required additional calibration. Values of surface runoff resulting from rainfall were refined in the MODFLOW-SFR model using the NRCS curve number method as described in USDA-NRCS (1986). Other refinements included the representation of Holbrook Reservoir using the reservoir (RES) package in MODFLOW and the introduction, using the river (RIV) package, of Adobe Creek on the western border of the modeled domain. Surface runoff from irrigation was modeled using a variable tailwater runoff fraction following the procedure of Morway et al (2013). Values of streambed conductance for the Arkansas River and its tributaries which were employed in the MODFLOW-UZF model of the USR by Morway et al (2013) were adjusted in the MODFLOW-SFR model to achieve reasonable compliance with the previous calibration reported in Morway et al (2013) as well as a good match with available target variables. Target variables included flow rates and flow depths measured by the US Geological Survey (USGS) and the Colorado Division of Water Resources (CDWR) at stream gauges in the tributaries and in the Arkansas River, measured groundwater levels, and total return flows from the irrigated valley to the Arkansas River as estimated from river mass balance analysis.

The RT3D-AG model originally was calibrated and tested for application to the USR as described by Bailey et al (2014, 2015b, 2015c). Influential parameters were identified and calibrated manually and automatically using the Parameter Estimation (PEST) software (Doherty 2007). These parameters included chemical reaction rates, NH_4 fertilizer application, seasonal uptake of Se and N by crops, and concentrations of NO_3 and SeO_4 in irrigation water. Calibration targets, against which simulated variables were compared, included statistics of measured groundwater concentrations and groundwater mass loading to streams estimated by stream mass balance analysis.

The RT3D-OTIS model was developed in this project by linking the RT3D-AG groundwater reactive transport model to the stream system. In doing so, a few refinements were made to the RT3D-AG model. These refinements included extending the baseline simulation of the USR from the period January 2006 – December 2009 to the period January 1999 – December 2009, and enhancing the calculation of saturated-zone solute concentrations in the computational cells containing the water table. The resulting RT3D-OTIS model was calibrated for the USR by adjusting selected model parameter values in an attempt to reasonably match key variables predicted by the model to target values based upon analysis of field data. The selection of parameters for calibration was guided by sensitivity analysis (Bailey et al 2014, 2015b, 2015c; Heesemann 2016). Calibrated parameters consisted of those associated with chemical reactions and solute transport in both groundwater and streams: groundwater chemical reduction rates, half-saturation constant for oxidation of Se from shale, riparian zone chemical reduction rates, stream chemical reaction rates, stream sediment sorption for Se, and NO_3 concentration increase in surface runoff. Manual calibration and automated calibration with PEST were used to evaluate and match simulated results against an analysis of field data for the following calibration target variables: groundwater and stream concentrations of Se and NO_3-N, and mass loading of Se and NO_3-N to the streams.

Contours of time-averaged groundwater concentrations of total Se simulated by RT3D-OTIS in the USR over the baseline period April 1999 to October 2009 is shown in Figure 10. A similar plot of NO_3-N concentration is shown in Figure 11. Time-averaged cumulative Se and N mass loading rates simulated by the models along the Arkansas River and its tributaries in the USR over the baseline period are shown in Figures 12 and 13, respectively. Among other factors, the timing and distribution of the discharge of Se and N mass from the groundwater aquifer to the river and tributaries influences the timing and distribution of Se and N concentration in these same streams.

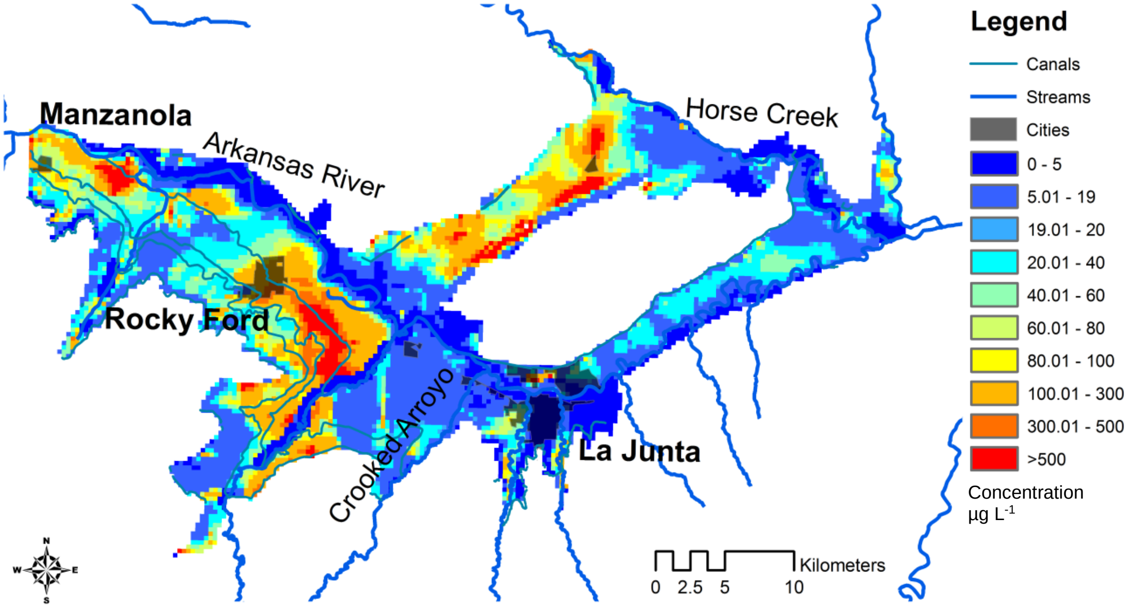


Figure 10. Contour plot of simulated average Se concentration in groundwater in the USR over the period April 1999 – October 2009.

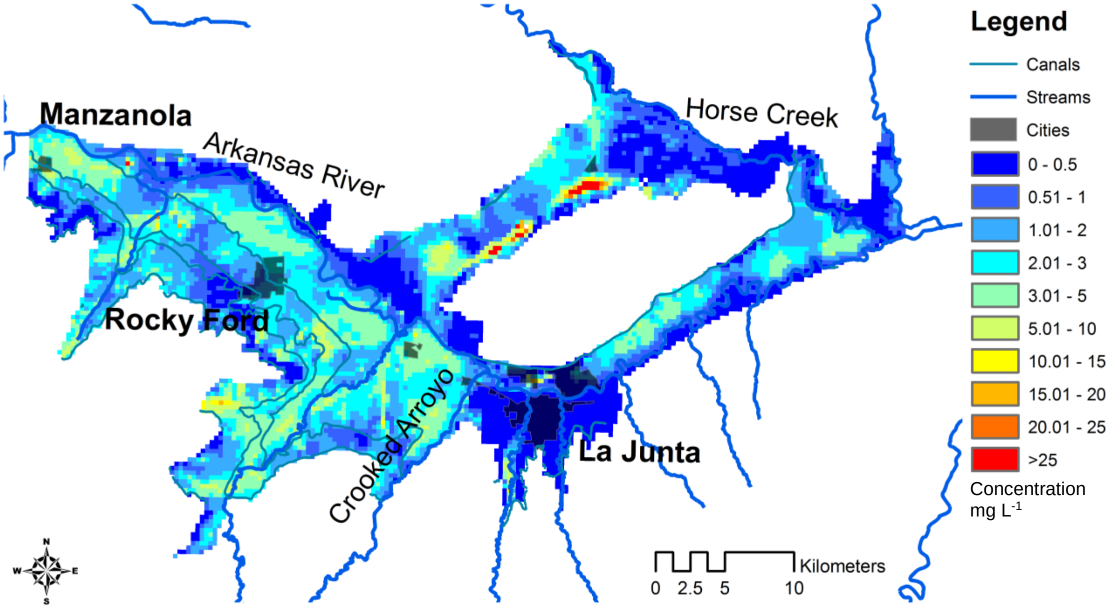


Figure 11. Contour plot of simulated average NO_3-N concentration in groundwater in the USR over the period April 1999 – October 2009.

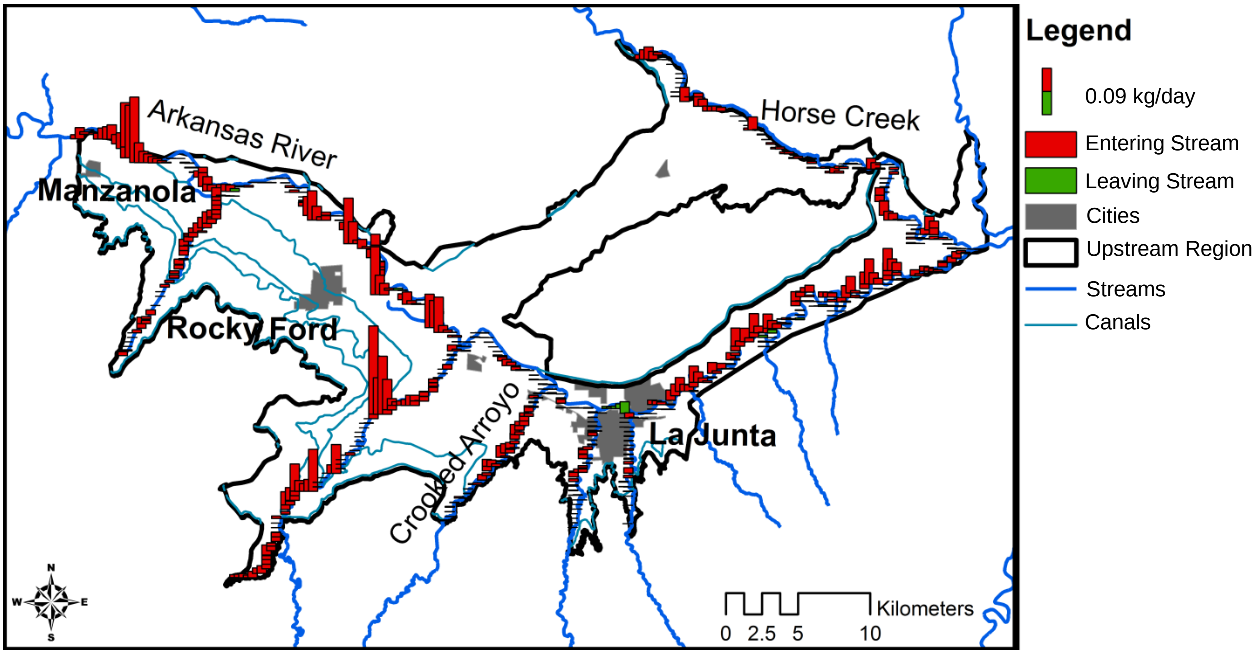


Figure 12. The spatial distribution of cumulative simulated Se mass loadings to streams in the USR over the baseline period.

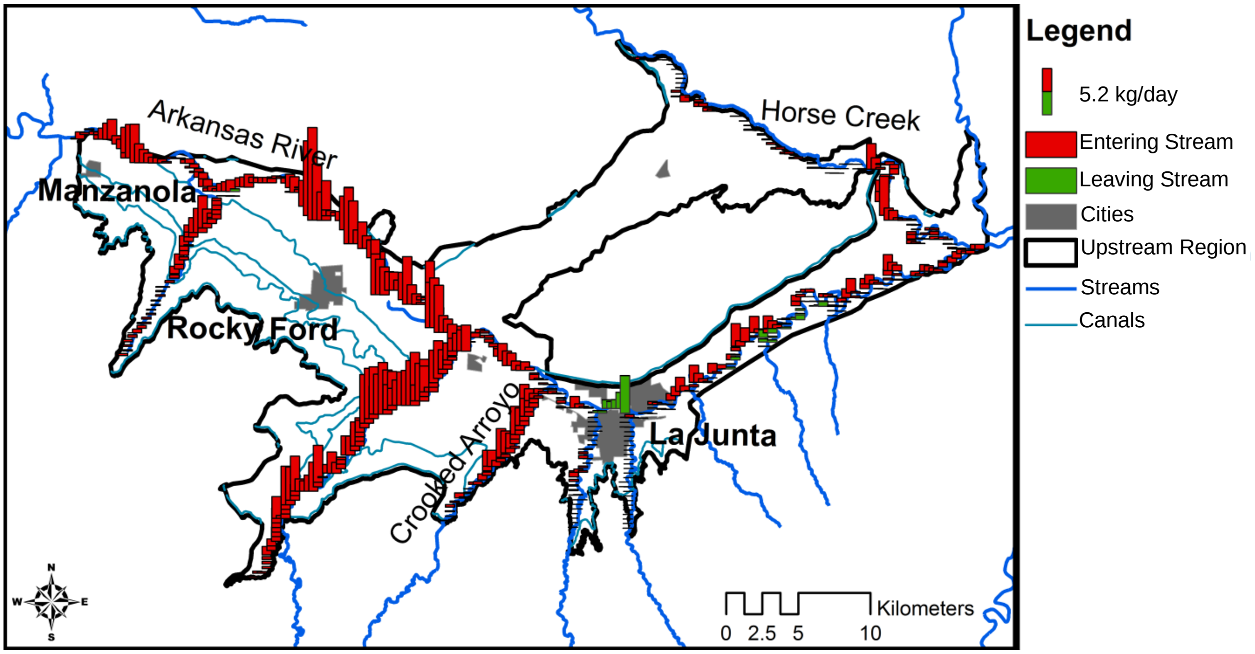


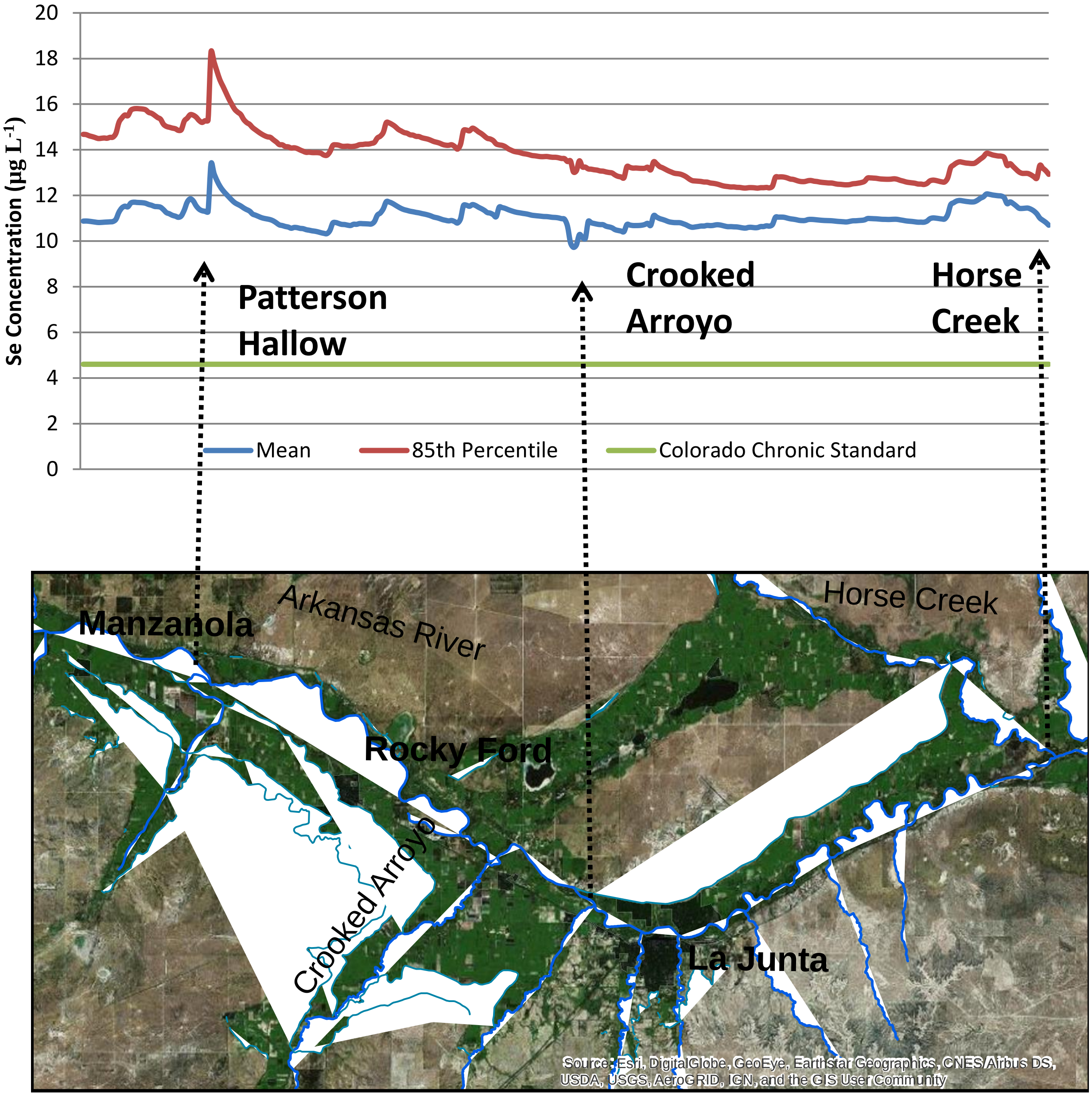
Figure 13. The spatial distribution of cumulative simulated NO_3-N mass loadings to streams in the USR over the baseline period.

A plot of model-simulated total Se and total N concentrations along the Arkansas River in the USR, averaged over the baseline period January 1999 – December 2009, are shown in Figures 14 and 15, respectively. Figure 14 shows the mean simulated value, the 85th percentile value, and the state chronic standard of 4.6 $\mu g\ L^{-1}$ for Se. Figure 15 shows the mean simulated value, median value, and the Colorado interim standard for total N of 2.0 $mg\ L^{-1}$.

Task 5: Establish a set of feasible BMPs. This will be accomplished with the aid of stakeholders and CWQCD personnel by first, identifying practical management practices that achieve the overall environmental goals and ranking these practices; second, establishing criteria, against which the BMPs will be evaluated; and third, using RT3D-AG, stream modeling, and appropriate socioeconomic assessment methods within the eRAMS platform to evaluate the BMP effectiveness.

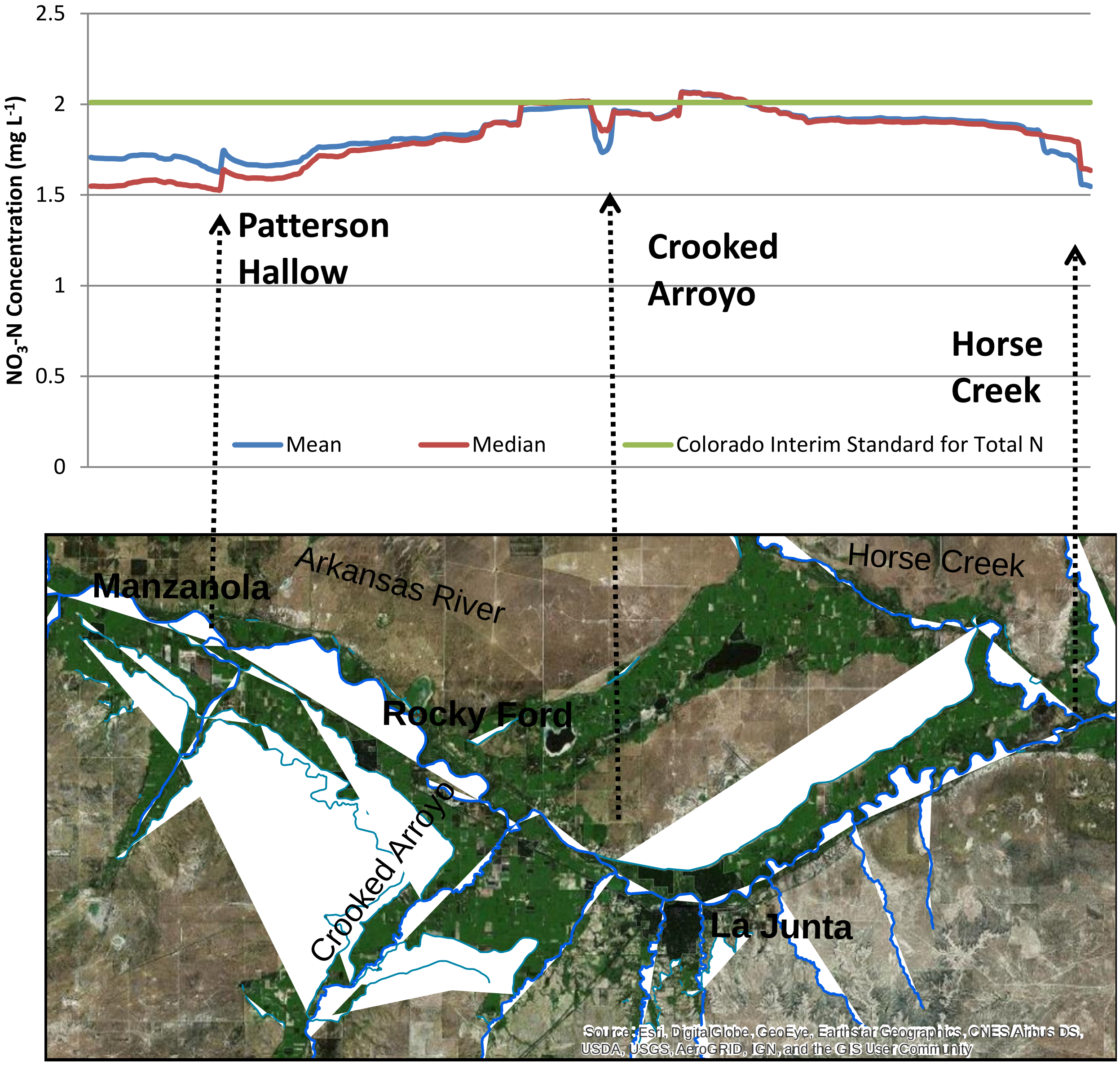
Accomplishments under Objective 2, Task 5: The groundwater and surface water models were applied to estimate the impact of several levels of implementation within the five classes of BMPs in the USR, described in "Accomplishments under Objective 1, Task 2". Baseline conditions and conditions as altered by each BMP were analyzed over a 40-yr period consisting of successive simulations of historic conditions over January 1999 – December 2009. This method allowed estimation of long-term effects of BMP implementation in relation to baseline conditions. The following BMPs have been examined so far: reduced fertilizer application by 10%, 20%, and 30% (RF10, RF20, and RF30, respectively); reduced irrigation application by 10%, 20%, and 30% (RI10, RI20, and RI30); rotational lease –fallowing of 10%, 20%, and 30% of the irrigated land (LF10, LF20, and LF30); canal sealing to reduce seepage by 20%, 40%, 60%, and 80% (CS20, CS40, CS60, and CS80); combination of RI30, LF30, and CS80; and combination of RI30, LF30, CS80, and RF30. Additional combinations are planned for upcoming consideration.

Example contour plots of simulated *lowering* of Se and NO_3-N concentrations in groundwater in the USR from the baseline condition are shown in Figures 16 and 17, respectively, for the RI30LF30CS80RF30 combined BMP. The values depicted in Figures 16 and 17 represented temporal-averages over the simulated 40-yr period. The simulated lowering of mass loading rate of Se and NO_3-N to the streams in the USR for this BMP is shown in Figures 18 and 19, respectively. Figure 20 shows predictions of the 85th percentile Se concentrations along the Arkansas River in the USR for the simulated 40-yr period for baseline conditions, for several individual BMPs at intensive levels of implementation (RI30, RF30, CS80, and LF30), and for the BMP combinations of RI30LF30CS80 and RI30LF30CS80RF30. A similar plot is shown in Figure 21 for predicted median NO_3-N concentrations along the Arkansas River in the USR. Figures 22 and 23 depict the 40-yr time series of predicted total Se concentration and NO_3-N concentration, respectively, averaged over the downstream quarter (about 12 miles) of the Arkansas River in the USR, compared to respective baseline conditions. Table 3 summarizes the estimates of percent reduction in Se and NO_3-N concentration along the Arkansas River in the USR and near the downstream end of the reach for these and other BMPs considered to date.



Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community

Figure 14. Simulated total Se concentration along the Arkansas River in the USR averaged over the historic baseline period.



Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community

Figure 15. Simulated NO_3-N concentration along the Arkansas River in the USR averaged over the historic baseline period.

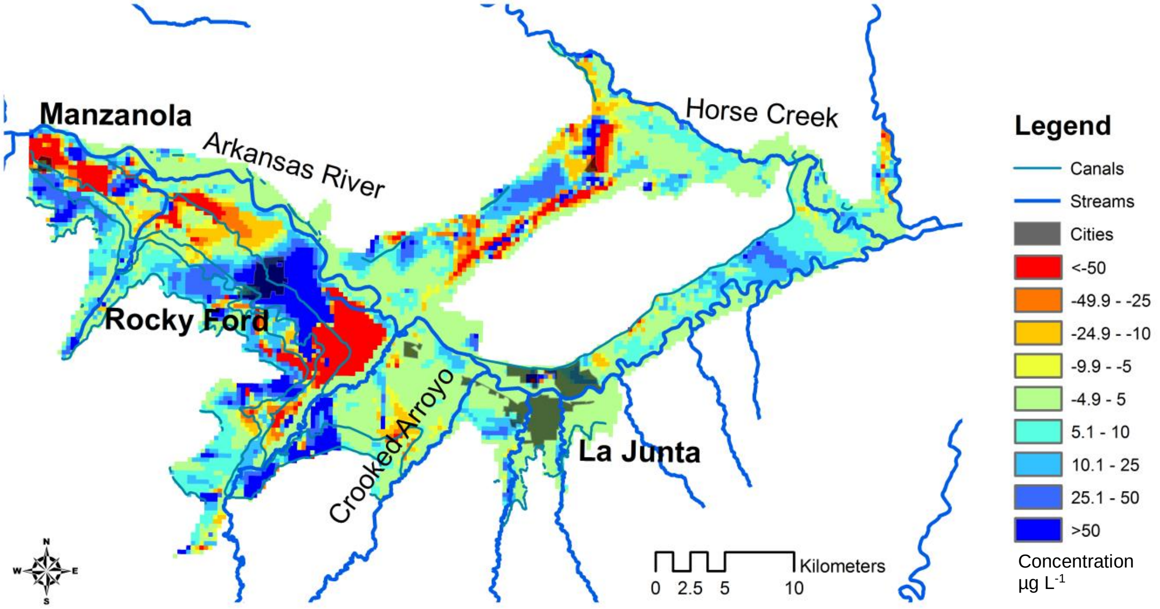


Figure 16. Simulated lowering of total Se concentration in groundwater under the RI30LF30CS80RF30 BMP compared to the baseline, averaged over the 40-yr simulated period.

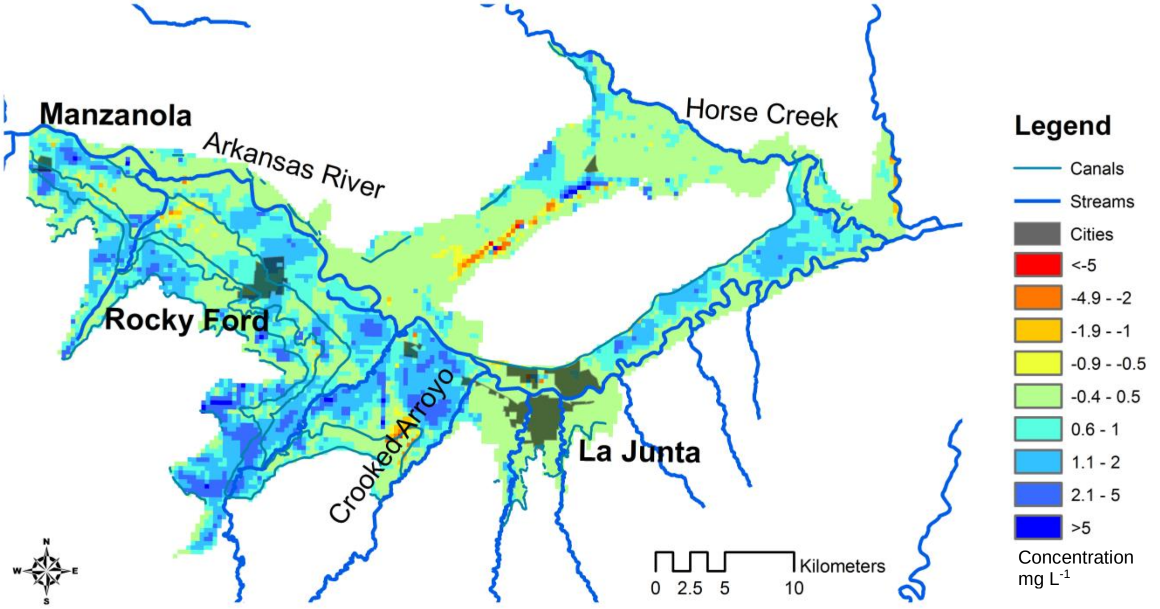


Figure 17. Simulated lowering of NO_3-N concentration in groundwater under the RI30LF30CS80RF30 BMP compared to the baseline, averaged over the 40-yr simulated period.

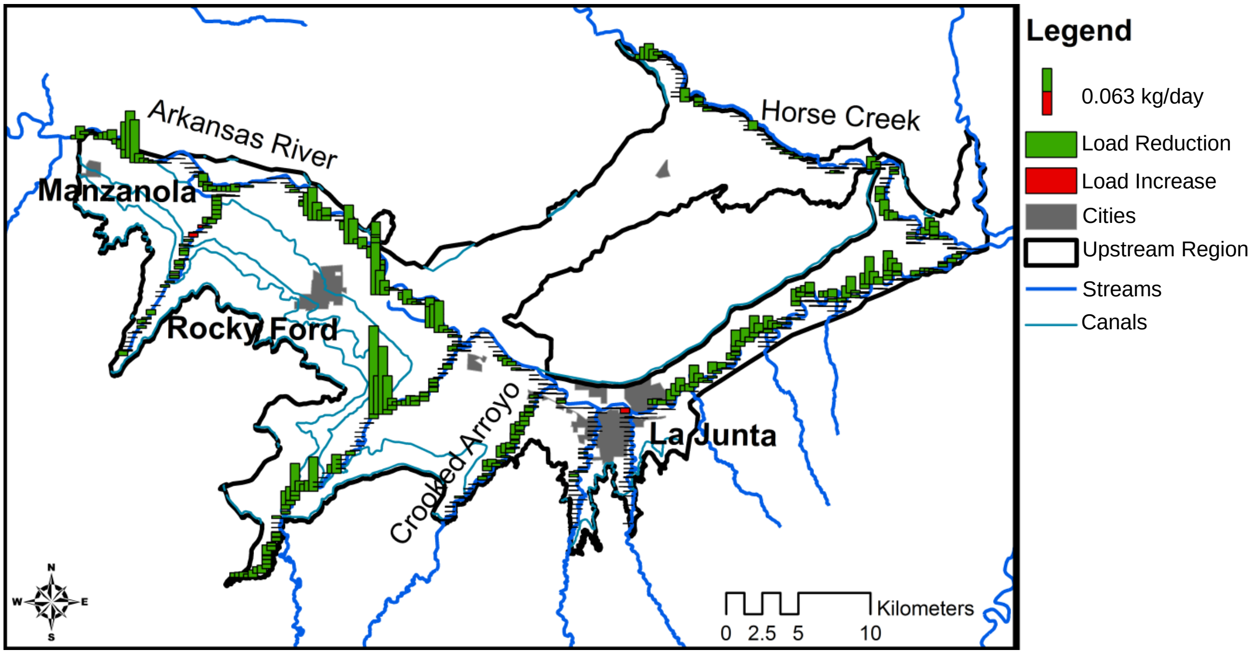


Figure 18. Simulated lowering of average loading rate of total Se to the streams in the USR from the baseline over the 40-yr simulation.

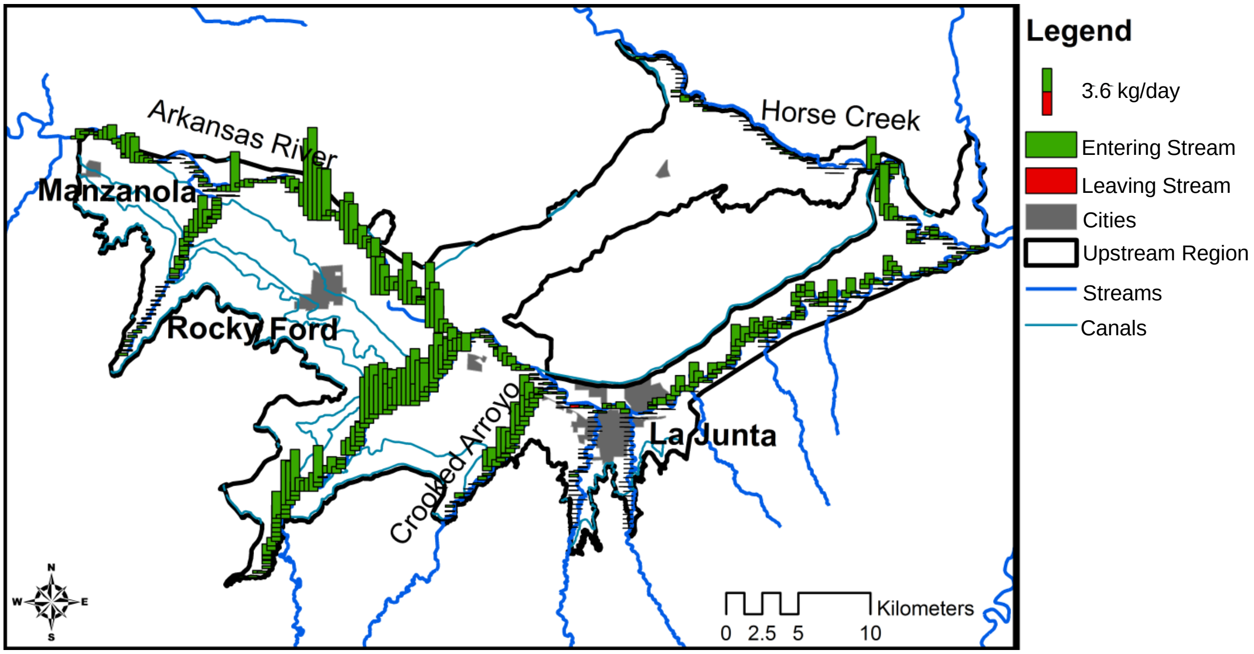


Figure 19. Simulated lowering of average loading rate of NO_3-N to the streams in the USR from the baseline over the 40-yr simulation.

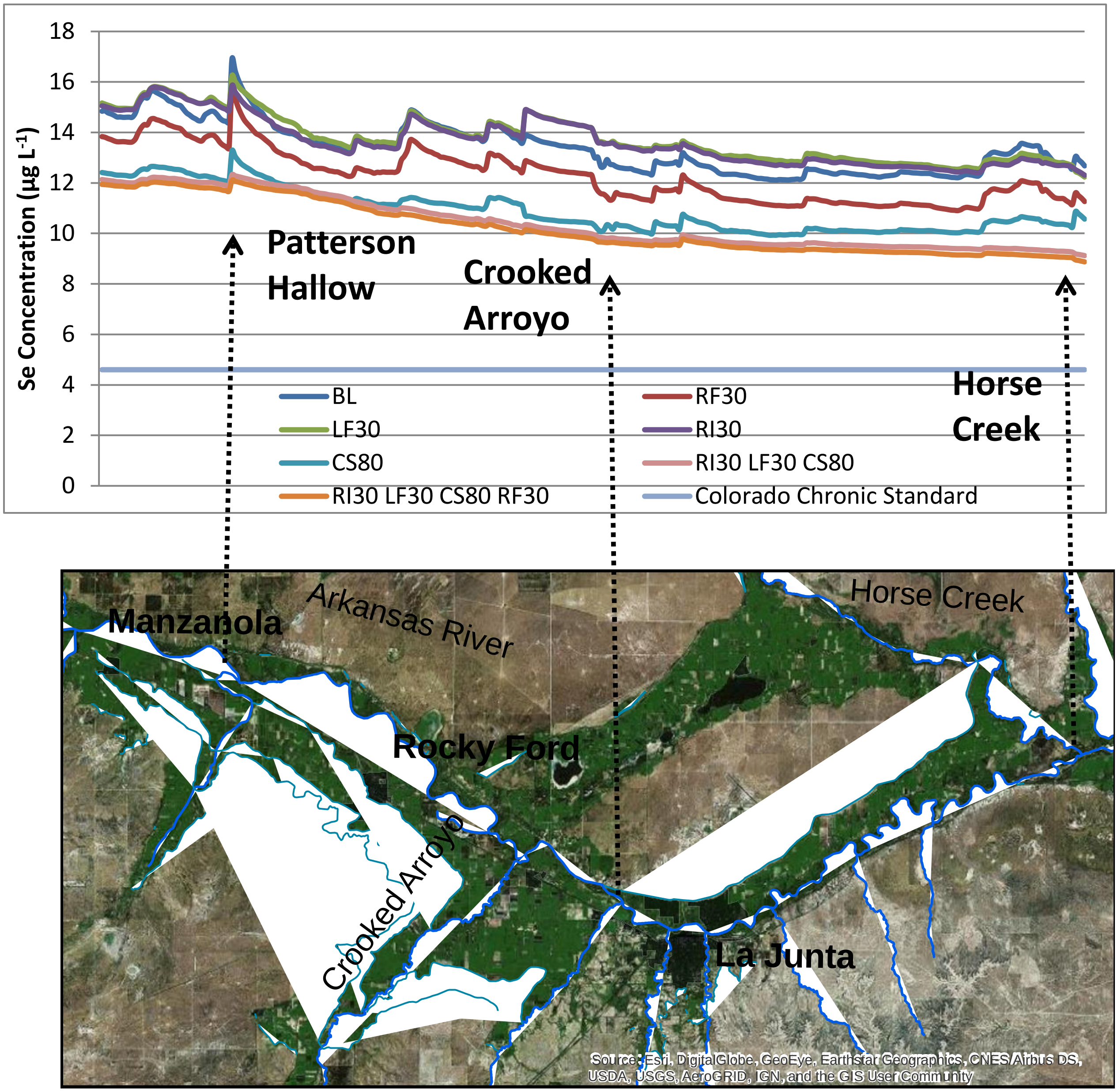
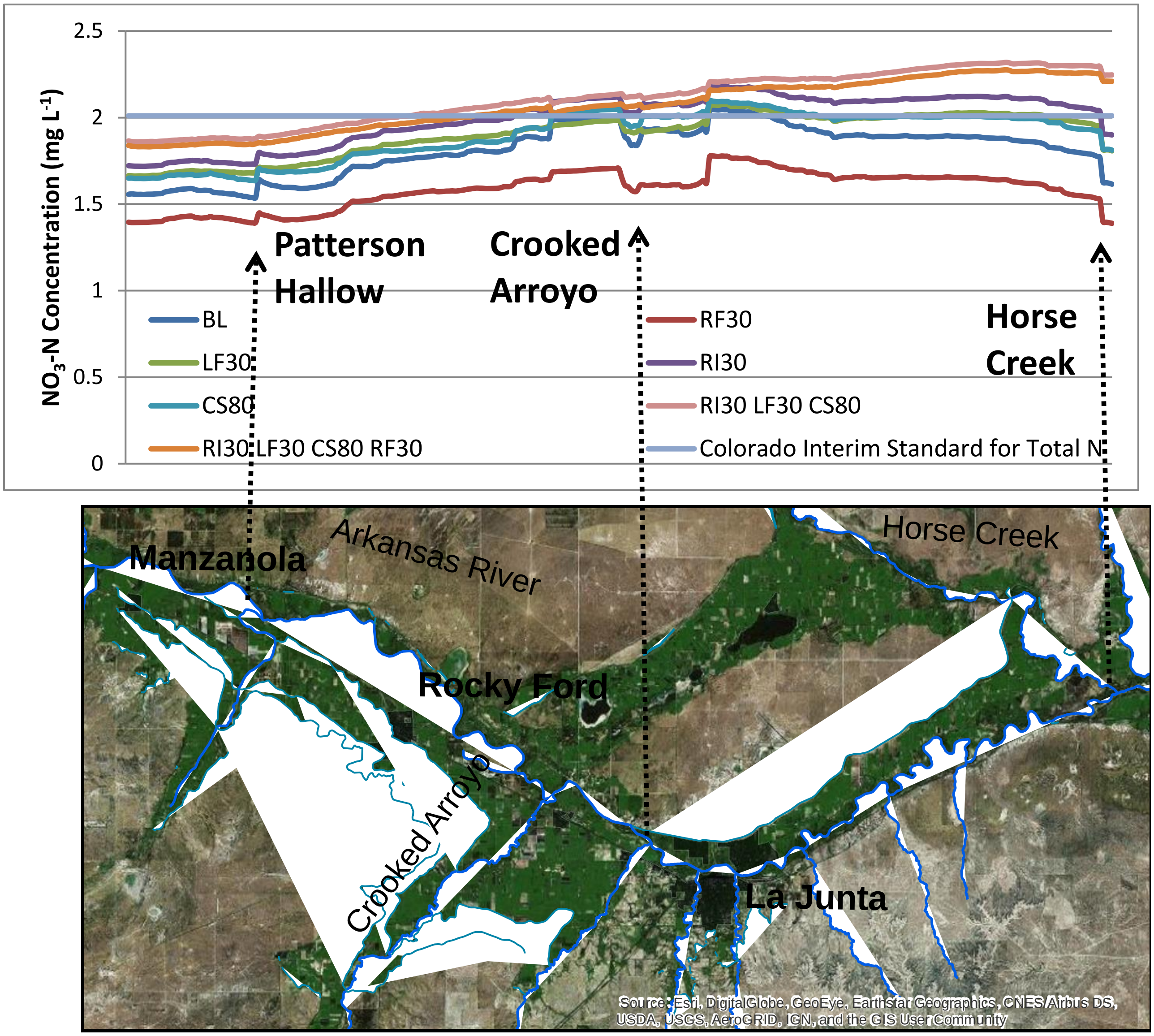


Figure 20. Simulated 85th percentile of total Se concentration along the Arkansas River in the USR averaged over the 40-yr simulation period for baseline and selected BMP conditions.



Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community

Figure 21. Simulated median NO_3-N concentration along the Arkansas River in the USR averaged over the 40-yr simulation period for baseline and selected BMP conditions.

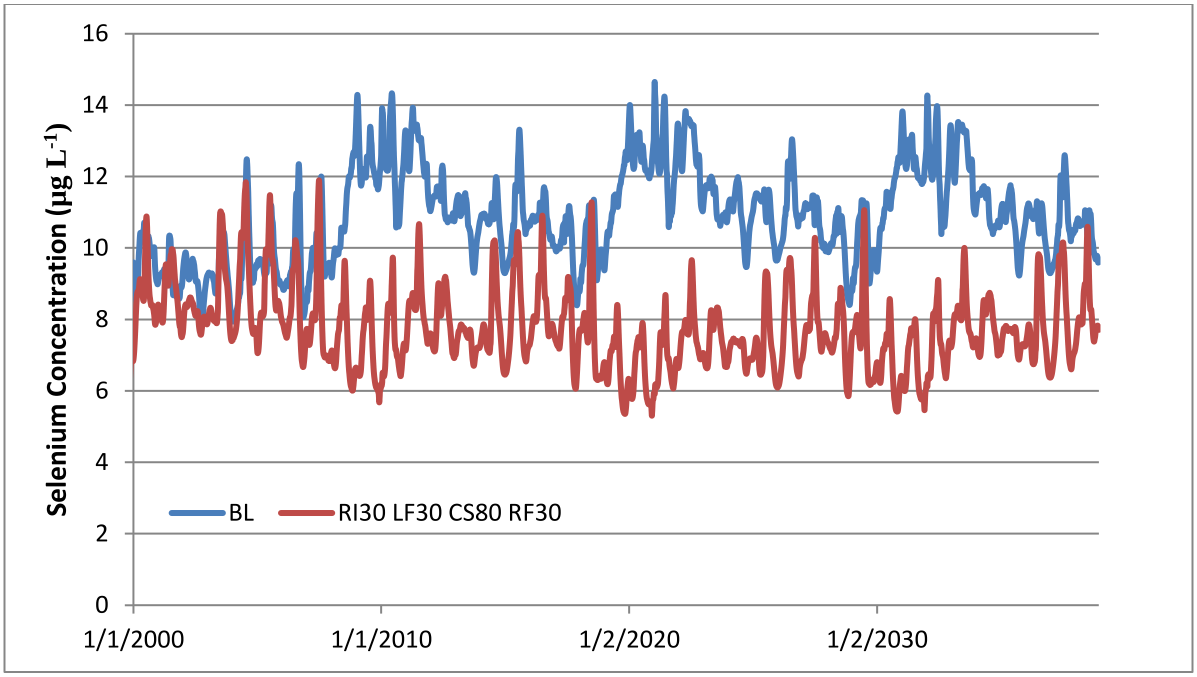


Figure 22. Times series of simulated total Se concentration, averaged along the downstream quarter of the Arkansas River in the USR, over the 40-yr simulation period for baseline and BMP RI30LF30CS80RF30 conditions.

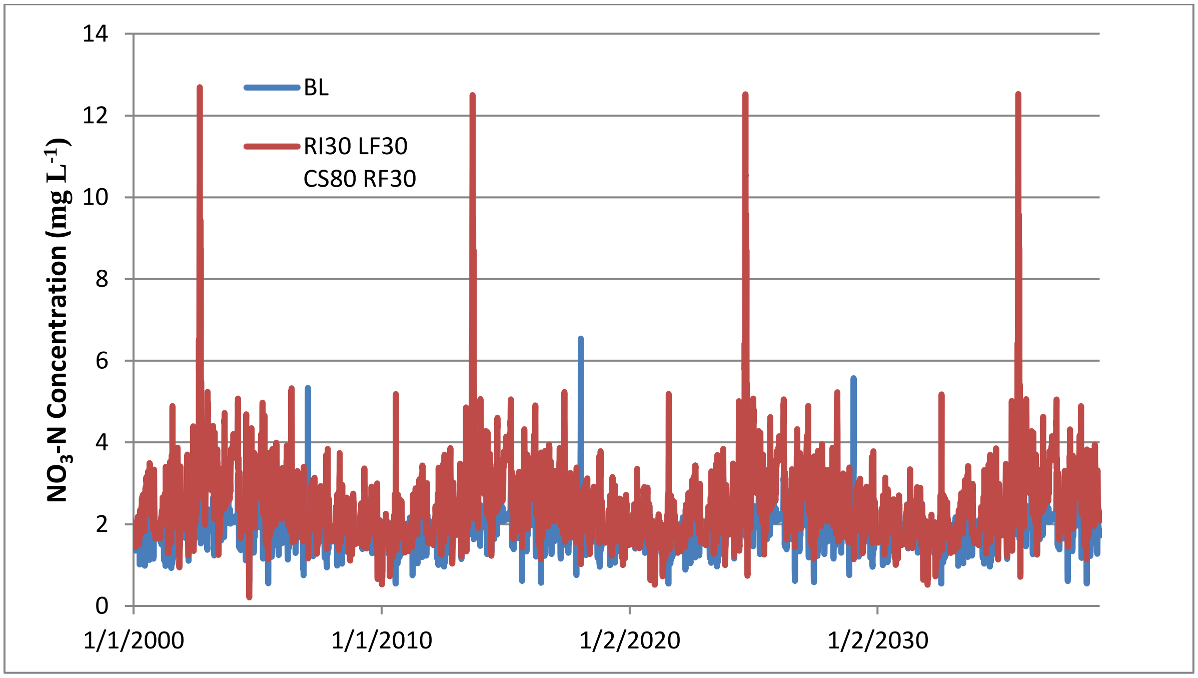


Figure 23. Times series of simulated total Se concentration, averaged along the downstream quarter of the Arkansas River in the USR, over the 40-yr simulation period for baseline and BMP RI30LF30CS80RF30 conditions.

Table 3. Simulated percent reductions from the baseline in time-averaged total Se concentrations and NO_3-N concentrations over the 40-yr simulation period, averaged over the entire river length within the USR and over the downstream third of the river in the USR.

BMP	Percent Reduction in Time-Averaged Concentration Over Entire River in USR		Percent Reduction in Time-Averaged Concentration Over Downstream Third of River in USR	
	Selenium Reduction (%)	Nitrate Reduction (%)	Selenium Reduction (%)	Nitrate Reduction (%)
RF30	8.0%	10.9%	9.2%	10.4%
RF20	5.7%	7.8%	6.6%	7.4%
RF10	2.9%	4.1%	3.4%	3.9%
LF30	-2.0%	-7.1%	-0.9%	-8.7%
LF20	-2.0%	-3.8%	-1.2%	-4.7%
LF10	-0.1%	-1.2%	0.3%	-1.5%
RI30	-0.5%	-12.2%	0.8%	-13.7%
RI20	-1.1%	-8.4%	-0.6%	-9.2%
RI10	-0.9%	-4.6%	-1.0%	-4.8%
CS80	18.9%	-8.3%	19.9%	-9.9%
CS60	14.0%	-5.2%	14.6%	-6.3%
CS40	9.3%	-3.5%	9.8%	-3.9%
CS20	3.5%	-3.1%	3.4%	-3.6%
RI30 LF30 CS80	23.03%	-25.99%	26.08%	-31.42%
RI30 LF30 CS80 RF30	24.7%	-23.4%	27.9%	-28.8%

The results presented here suggest that decreases in Se concentration of up to about 28% could potentially be achieved near the downstream end of the Arkansas River reach in the USR through combinations of improved land and water management practices. In contrast, NO_3-N concentrations could be dropped by reduced fertilizer applications but not by reduced irrigation application or reduced canal seepage. The working hypothesis for this unexpected result is that in the USR the riparian corridor adjacent to the Arkansas River and its tributaries is very effective in chemically reducing NO_3-N in the high-concentration groundwater flows that pass through this corridor (including the stream hyporheic zone) and discharge to the river. The end result is that, under baseline conditions, groundwater return flows to the river serve to dilute NO_3-N concentrations in the river. Apparently, if rates of groundwater discharge to the river were to be diminished by BMPs that decrease irrigation return flows, the dilution effect would decline and river concentrations would increase. On the other hand, reduced fertilization BMPs do not alter groundwater return flow rates to the river but they accentuate the diluting effect by creating even lower NO_3-N concentrations in the return flows. Modeling and field data support this hypothesis, but further confirmation is needed.

It is noteworthy that the considered RI and LF BMPs are predicted by the model to result in a slight increase (though, in some cases a slight decrease) in time-averaged Se concentration in the Arkansas River in the USR. It seems that using these BMPs to reduce diffuse recharge to the groundwater under irrigated lands results in a net concentrating effect within a diminished volume of stored groundwater, offsetting the impact of these BMPs on lowering the rates of groundwater return flow. Apparently, the processes of mobilization and inhibited chemical reduction of Se are not modified enough under these scenarios to sufficiently alter stream loading patterns throughout the region so as to reduce stream concentrations. It is important to realize that under different conditions than those considered here, stand-alone RI and LF BMPs may decrease stream concentrations. Preliminary assessments indicate that this would be the case for such BMPs when they are targeted to specific areas within the USR or implemented in other regions of the LARV with differing characteristics, such as the DSR.

To represent multiple objectives in farmer's land and water management decisions, the tradeoffs of economic and pollution impacts for each BMP were considered. To represent non-financial considerations, institutional constraints were included which farmers revealed were important in an in-person survey conducted early on in the project. Studies that compare economic and environmental tradeoffs are common and are often represented in a Pareto trade-off frontier that shows only the most efficient combinations of cost and environmental outcomes. Engineering approaches to estimate environmental outcomes, pollution from Se in this case, typically utilize field studies and models to determine impacts of implemented practices and to project relative cost-efficiency for pollution abatement strategies. Economic approaches represent costs by taking into account shadow prices or resource rents and opportunity costs associated with each engineering practice.

Pareto frontiers were constructed to evaluate the BMPs of canal sealing, reduced irrigation, land fallowing, and combinations of these three options, where cost was on the vertical axis and pollution was on the horizontal axis. The economic analysis focused solely on the private costs and benefits (reduced costs) since implementation is voluntary. The discounted net present cost (NPC) of each of the BMPs depends on the up-front fixed costs as well as the on-going costs of maintenance, replacement costs, opportunity costs, and reduced costs accumulating due to BMP implementation over time. Examples of opportunity costs may be crop benefits foregone upon fallowing whereas reduced costs may include an increase in crop yield associated with less waterlogging and salinization and reduced costs of fertilizer. Costs were simulated for each BMP over 38 years in order to be on the same time scale as the physical model (Sharp et al 2016).

The combined impact of economic and pollutant modeling can be seen in Figure 24. Three BMP's are shown at three levels of implementation that increase the degree to which Se mass loading to the river is reduced. Notably, the curves slope downward, which indicates that costs are reduced when pollution is reduced. If this were true, or the only thing that mattered, then farmers would already be adopting these solutions. Therefore, consideration also was given to institutional constraints that might explain this phenomenon.

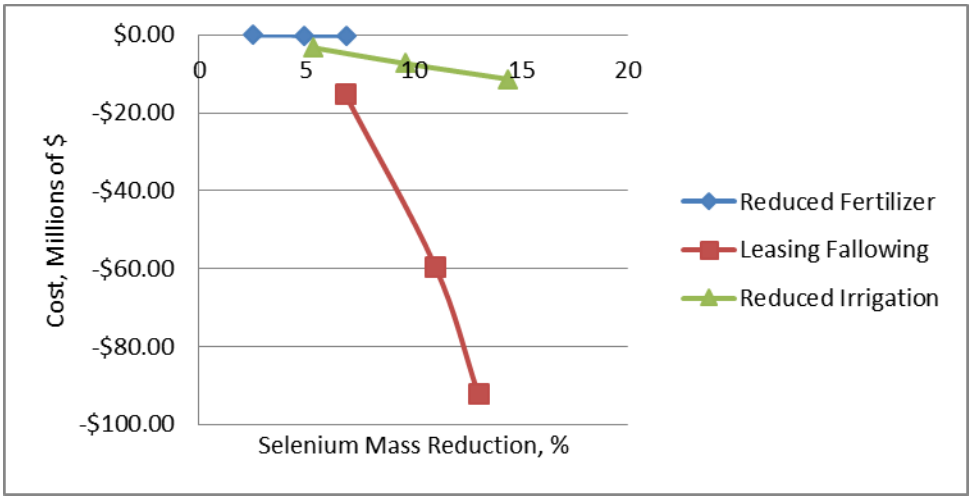


Figure 24. Basin-wide trade-off curves between cost and percent reduction in Se mass loadings for three levels of intervention (basic, intermediate, and aggressive) for selected individual practices (Sharp et al 2016).

Pollution control often depends on the rules of the game in addition to the physical environment or monetary costs, which often are given so much emphasis in a frontier. These rules can make moving from one practice to another along the frontier infeasible and therefore must be considered in any policy or analysis about why farmers adopt, or do not adopt BMPs. Farmers were asked through an in-person qualitative survey to identify institutional constraints that affect how they are able to manage or change their land and water.

One of the hurdles that farmers revealed was the requirement to buy replacement water to satisfy a compact between Colorado and Kansas that may be violated when farmers switch from traditional gravity-fed irrigation systems to high-efficiency systems like center pivot sprinklers. Figure 25 shows how buying replacement water alters the Pareto frontiers and provides a valuable example about why farmers might not be installing pivot systems when they appear so economically desirable. Under low levels of reduced irrigation farmers would not have to pay for augmentation and the Pareto frontier slopes down, but as irrigation needs increase, so does the need for replacement, which tilts the Pareto frontier upward to the expected relationship where farmers have to pay out of their own pockets to make changes that reduce pollution.

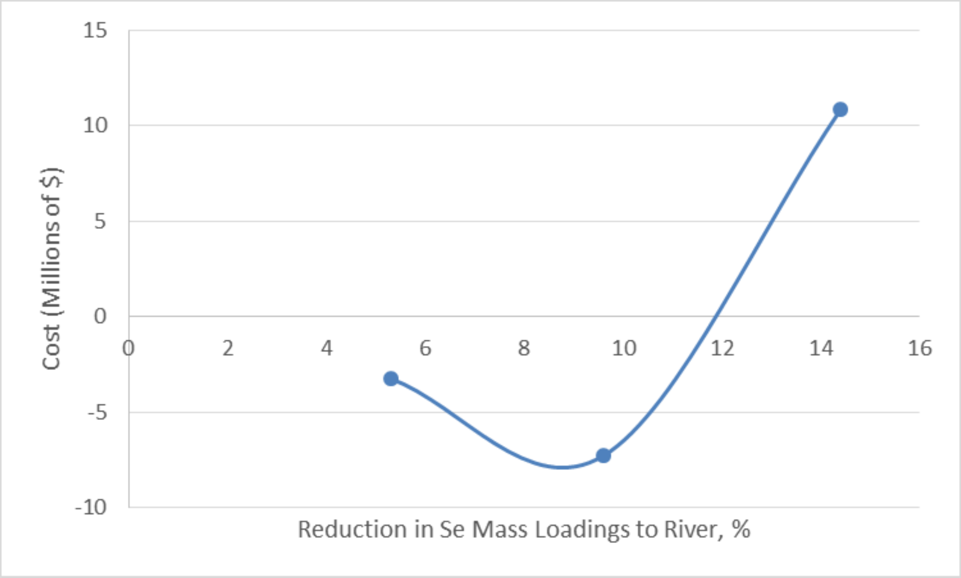


Figure 25. Cost of the reduced irrigation practice when augmenting at various levels of implementation.

Task 6: Prepare a preliminary plan for a pilot implementation and assessment program, with a timeline for BMP adoption and evaluation. This also includes proposed mechanisms for adapting and funding.

Accomplishments Under Objective 2, Task 6: Model development, testing, and application to estimate the impact of BMP alternatives on Se and N pollution in the USR took longer than expected. Also, the finding that NO3-N concentration is predicted to increase in the Arkansas River under implementation of the BMPs found most effective in decreasing total Se concentration needs to be further assessed, especially from an the perspective of economic tradeoffs. Thus, as described in the section "EVALUATION OF GOAL ACHIEVEMENT" below, a technical and socio-economic assessment and ranking of a full suite of BMP alternatives has not yet been completed. Consequently, a preliminary plan for pilot implementation has not been prepared as of the completion of this final report. This effort is on-going and is expected to be completed by summer 2017.

Task 7: Prepare a report describing the proposed BMPs, their expected impact, and a preliminary plan for pilot implementation. Before publication, a draft will be given to stakeholders, CWQCD personnel, and interested watershed residents for potential feedback; and appropriate refinement will be made.

Accomplishments Under Objective 2, Task 7: Due to the pending completion of Task 6, the report described in Task 7 has not been prepared and reviewed by CDPHE personnel and by the ARMAC. The report on expected BMP impacts and preliminary plan for pilot implementation is expected to be submitted by summer 2017. In the meantime, some preliminary thoughts are offered as follows:

(1) Model results to date indicate that the individual BMPs most effective in lowering total Se concentrations in the Arkansas River in the USR are reduced fertilizer application (RF) and sealing of irrigation canals (CS). Alternatives RF30 and CS80 are predicted to lower total Se concentration averaged over the entire river reach within the USR by about 8% and 19%, respectively. The predicted impact near the downstream end of the reach is a reduction by about 9% and 20%, respectively. To achieve more substantial impacts will require BMPs that combine multiple improvements, including lease fallowing (LF) and reduced applied irrigation (RI). For example, the RI30LF30CS80RF30 BMP is predicted to lower reach-averaged and end-of-reach concentrations in the river by about 25% and 28%, respectively. Corresponding values for the RI30LF30CS80 BMP are 23% and 26%.

(2) Only RF BMPs were predicted by the model to lower NO_3-N concentrations in the Arkansas River. Adoption of RF30 was predicted to lower reach-averaged and end-of-reach NO_3-N concentrations by about 11% and 10%, respectively. All of the considered individual water BMPs (RI, LF, and CS), along with combination alternatives that included these BMPs, were predicted to cause increases in NO_3-N concentrations in the river. This is attributed to a diluting effect on subsurface irrigation return flows passing through the river riparian corridor, brought about by heterotrophic chemical reduction. Enhancement of chemical reduction of NO_3-N by altering the riparian buffer may be an effective way to lower concentrations in the river even when return flows are diminished by the adoption of alternative water BMPs.

(3) Surveys indicate that the BMPs most preferred among farmers are RI and RF alternatives. However, farmers also appear open to implementing the LF and CS alternatives.

(4) Economic analysis suggests that net private benefits increase with increasing levels of adoption of RF, RI, and LF BMPs.

(5) A major concern among stakeholders is how to implement BMPs that would improve water quality while maintaining compliance with the Arkansas River Compact. This is arguably the strictest constraint on the implementation of water BMPs. An effective and economical way must be found to replace depletions to flows returning to the river, brought about by water BMP adoption, while maintaining the improved water quality benefits.

(6) Consideration should be given to a pilot implementation of BMPs over an area of the USR with the following characteristics:

   a. Adequate data on baseline conditions (irrigation practices, surface water flows and quality, groundwater flows and quality, soil characteristics and quality, crop characteristics and yields, economic costs and benefits, etc) are available;
   b. Area is large enough and monitoring period is long enough that BMP adoption would allow measurable changes in conditions;
   c. A large number of farmers are interested and willing to cooperate;
   d. Irrigation water delivery is relatively reliable.

A tentative recommended area that meets the above criteria is the vicinity serviced by the Catlin Canal on the south and bounded by Timpas Creek on the west, Crooked Arroyo on the east, and the Arkansas River on the north, as indicated in Figure 26.

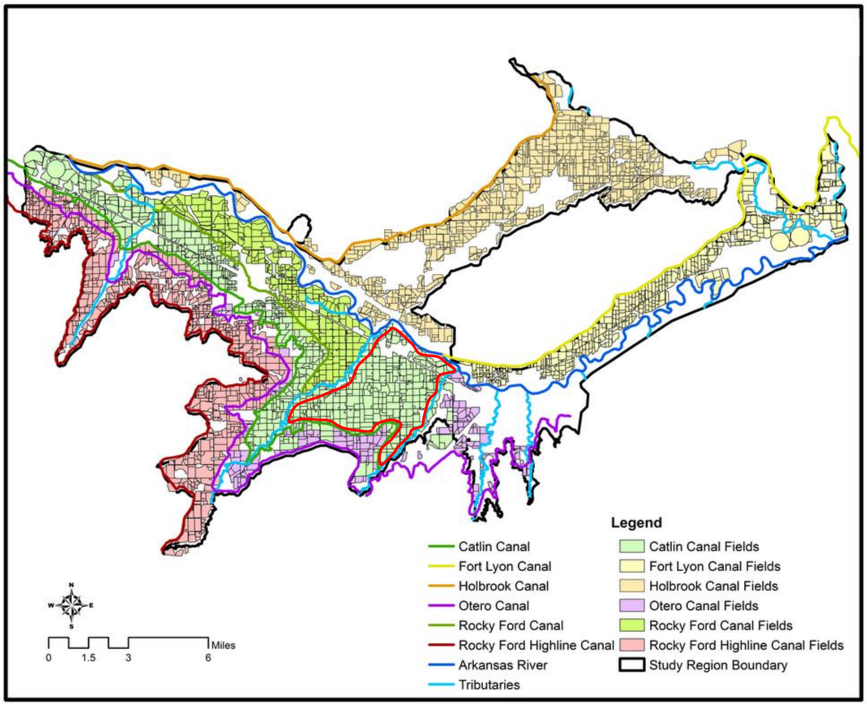


Figure 26. Recommended area for possible implementation of pilot program to test BMPs.

OBJECTIVE 3: Manage the project in accordance with all federal, state, and organization funding requirements and report on project implementation.

Task 8: Ensure that objectives and tasks are accomplished within the estimated schedule; ensure compliance with general procedures and protocol described in the project implementation plan; maintain accounting and matching funds records; and ensure that costs are kept within specified budgetary guidelines.

Accomplishments Under Objective 3, Task 8: The principal investigator and the project accountant worked to achieve project objectives in a timely manner and in compliance with budgetary constraints and financial requirements.

Task 9: Hold progress report meetings, complete semi-annual reports, final reports, and reimbursement requests within the prescribed schedule. Where appropriate, prepare refereed journal articles documenting key findings.

Accomplishments Under Objective 3, Task 9: Periodic progress and planning meetings were held between the CSU project team members and the CDPHE project supervisors. Written and oral reports of project progress were given to CDPHE personnel over the course of the project. Reimbursement requests and financial reports also were submitted.

Five refereed journal articles were published under partial funding from this project: Bailey et al (2014, 2015a, 2015b, 2015c) and Sharp et al (2016). Two MS theses also were published: Romero (2016) and Heesemann (2016). Details are given in the References section.

EVALUATION OF GOAL ACHIEVEMENT

The goal of this project was in large part attained through successful organization and interaction with key stakeholders; the development and calibration of models for reasonably simulating the transport of Se and N pollutants in the surface and subsurface flows of the LARV; the successful application of the models in preliminary assessment of how a number of alternative land and water BMPs might bring about improved water quality conditions; and the gathering of feedback from stakeholders regarding the utility, practicality, and economic feasibility of the considered BMPs. Goal achievement was limited, however, in the following regards:

(1) An initial set of BMPs, of different classes and at different levels of intensity, have been simulated and evaluated for the USR. However, the full suite of BMPs envisioned for consideration, especially combinations of classes and various levels of intensity, have not yet been assessed. The resources and timeframe of this project allowed only an initial launch into the analysis of BMPs for the DSR.

(2) Economic assessment of potential BMP implementation has been successfully initiated and valuable stakeholder input has been documented. The need remains, though, to refine cost estimates, to better assess economic benefits (especially associated with environmental enhancement), and to clarify potential roadblocks to broad adoption by stakeholders.

(3) A preliminary recommendation of an area for pilot implementation of BMPs has been made. However, due to the limitations cited above, extended and enhanced analysis is needed before a more comprehensive plan of action can be crafted for the entire LARV.

(4) A report recommending pilot implementation of BMPs has not yet been completed for review by CDPHE or ARMAC.

FUTURE ACTIVITY RECOMMENDATIONS

The following future activities are recommended:

(1) A full suite of BMPs, including more levels of intensity for individual BMPs and additional BMP combinations, need to be simulated with the USR models (This effort is nearing completion under funding from another project). Moreover, the impact of targeting specific areas of the USR for implementation of specific BMPs needs to be explored;

(2) BMPs that include enhanced riparian buffer (ERB) alternatives must be considered for their potential to lower not only total Se concentrations in the Arkansas River, but also NO_3-N concentrations;

(3) A refined economic analysis, especially of potential benefits of alternative BMPs, should be completed (This effort is nearing completion under funding from another project);

(4) A separate modeling effort, currently underway, to evaluate how reservoir and river alterations could be amended to insure that BMPs can be implemented in compliance with the Arkansas River Compact must be completed; and

(5) Efforts should be completed in refining, calibrating, and applying flow and reactive transport models for evaluation of potential BMP impacts in the DSR.

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APPENDICES

A1. RT3D-AG Model: Se and N Reactive Transport in Variably-Saturated Groundwater Systems

The fate and transport of Se species in the soil-groundwater system is simulated using a solution to the advection-dispersion-reaction equation, which describes the conservation of Se mass in the system. The following equations describe the transport of SeO4, SeO3, and SeMet according to advection, dispersion, sorption, sources and sinks (e.g. groundwater pumping, irrigation water, canal seepage, aquifer/river exchange), fertilizer, crop uptake, mineralization and immobilization, chemical reduction, and release of Se from marine shale due to autotrophic reduction of both O_2 and NO_3:

$$\frac{\partial\left(C_{SeO_4}\theta\right)}{\partial t}R_{SeO_4} = -\frac{\partial}{\partial x_i}\left(\theta v_i C_{SeO_4}\right)+\frac{\partial}{\partial x_i}\left(\theta D_{ij}\frac{\partial C_{SeO_4}}{\partial x_j}\right)+q_f C_{f_{SeO_4}}+F_{SeO_4}-U_{SeO_4}+\varepsilon\left(r^{min}_{s,Se}-r^{imm}_{s,Se}\right) + \theta\left(r^{auto}_{f,SeO_4}-r^{het}_{f,SeO_4}\right) \quad (1)$$

$$\frac{\partial\left(C_{SeO_3}\theta\right)}{\partial t}R_{SeO_3} = -\frac{\partial}{\partial x_i}\left(\theta v_i C_{SeO_3}\right)+\frac{\partial}{\partial x_i}\left(\theta D_{ij}\frac{\partial C_{SeO_3}}{\partial x_j}\right)+q_f C_{f_{SeO_3}}+F_{SeO_3}-U_{SeO_3} + \theta\left(r^{het}_{f,SeO_4}-r^{het(Se_s)}_{f,SeO_3}-r^{het(SeMet)}_{f,SeO_3}\right) \quad (2)$$

$$\frac{\partial\left(C_{SeMet}\theta\right)}{\partial t} = -\frac{\partial}{\partial x_i}\left(\theta v_i C_{SeMet}\right)+\frac{\partial}{\partial x_i}\left(\theta D_{ij}\frac{\partial C_{SeMet}}{\partial x_j}\right)+q_f C_{f_{SeMet}}-U_{SeMet}+\theta\left(r^{het(SeMet)}_{f,SeO_3}-r^{het}_{f,SeMet}\right) \quad (3)$$

where D_{ij} is the hydrodynamic dispersion coefficient [L^2T^{-1}], v is the average seepage velocity [L_bT^{-1}] where b denotes the bulk phase, ϕ is the soil porosity [$L_f^3L_b^{-3}$], q_s is the volumetric flux of water representing sources and sinks of the species [$L_f^3T^{-1}L_b^{-3}$], C_{s_k} is the concentration of the source or sink [$M_fL_f^{-3}$], r represents the rate of all reactions that occur in the aqueous phase for the k^{th} species [$M_fL_f^{-3}T^{-1}$], ρ_b is the bulk density of the porous media [$M_bL_b^{-3}$], and C_k^* is the concentration of the k^{th} species sorbed on solids [$M_f M_b^{-1}$]. The retardation factor R_k represent sorption of the species, and is equal to $1 + (\rho_b K_{d_k})/\phi$, where K_d is the partitioning coefficient [$L_f^{-3}M_b$]. Typically, only SeO_3 sorbs strongly to aquifer materials. Similar equations can be written for NH_4, NO_3, and O_2:

$$\frac{\partial\left(C_{NH_4}\theta\right)}{\partial t}R_{NH_4} = -\frac{\partial}{\partial x_i}\left(\theta v_i C_{NH_4}\right)+\frac{\partial}{\partial x_i}\left(\theta D_{ij}\frac{\partial C_{NH_4}}{\partial x_j}\right)+q_f C_{f_{NH_4}}+F_{NH_4}-U_{NH_4}+\varepsilon\left(r_{s,N}^{min}-r_{s,N}^{imm}\right) + \theta\left(-r_f^{nit}-r_f^{vol}\right) \tag{4}$$

$$\frac{\partial\left(C_{NO_3}\theta\right)}{\partial t} = -\frac{\partial}{\partial x_i}\left(\theta v_i C_{NO_3}\right)+\frac{\partial}{\partial x_i}\left(\theta D_{ij}\frac{\partial C_{NO_3}}{\partial x_j}\right)+q_f C_{f_{NO_3}}+F_{NO_3}-U_{NO_3}+\theta\left(r_f^{nit}-r_{f,NO_3}^{het}-r_{f,NO_3}^{auto}\right) \tag{5}$$

$$\frac{\partial\left(C_{O_2}\theta\right)}{\partial t} = -\frac{\partial}{\partial x_i}\left(\theta v_i C_{O_2}\right)+\frac{\partial}{\partial x_i}\left(\theta D_{ij}\frac{\partial C_{O_2}}{\partial x_j}\right)+q_f C_{f_{O_2}}+\theta\left(-r_{f,O_2}^{het}-r_{f,O_2}^{auto}\right) \tag{6}$$

These equations are solved for each finite different grid cell in the model domain. Hence, each grid cell (in the case of the Upstream Study Region, each 250 m x 250 m area) has a concentration of each species for each day of the simulation. These concentration values then can be compared to observed data from groundwater monitoring wells, sampled between 2006 and 2009, to verify that the model is working correctly. Complete explanation of these equations can be found in recent publications (Bailey et al. 2014, Bailey et al., 2015a, Bailey et al., 2015b).

A2. OTIS-QUAL2E Model: 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 DO, N species, and algae (Bailey and Ahmadi, 2014). The inclusion of DO 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 DO and NO_3. QUAL2E processes simulate the reactive behavior of DO, 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, DO fate, algal growth and respiration, and algal uptake of N and DO. Specific processes include atmospheric reaeration, algal respiration, sediment oxygen demand, nitrification of NH_3, and oxidation of NO_2. Algal growth rate 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 DO, depending on the reaction.

The original OTIS code (Runkel, 1998) was capable of handling solute transport only in one stream. In this project, the OTIS code (FORTRAN) provided by the USGS was modified to include solute transport in a system of connected streams (i.e. tributaries delivering water and solute mass to the main stem of the Arkansas River). The original code could handle the transport of multiple solutes, but they could not interact chemically. As N and Se species can interact, specifically SeO_4 and SeO_3 chemical reduction depends on the concentration of NO_3 in the water column, the OTIS code was modified to solve simultaneously a system of equations using the 4th-order Runge-Kutta ordinary differential equation solver.

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:

$$\frac{\partial C_j}{\partial t} = -\frac{Q}{A}\frac{\partial C_j}{\partial x} + \frac{1}{A}\frac{\partial}{\partial x}\left(AD\frac{\partial C_j}{\partial x}\right) + \frac{q_L}{A}\left(C_{L_j} - C_j\right) + S_j + R_j \qquad j = 1,\ldots,n \tag{7}$$

$$S_j = \bar{\rho}\lambda_{s_j}\left(C_j^* - K_{d_j}C_j\right) \tag{8}$$

Sorbate on the streambed:

$$\frac{\partial C_j^*}{\partial t} = -\frac{S_j}{\bar{\rho}} \tag{9}$$

Solid-phase species on the streambed:

$$\frac{\partial C_k^s}{\partial t} = R_k \qquad k = 1,\ldots,m \tag{10}$$

where n is the number of dissolved-phase species, m 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 solute concentration of the k^{th} solid-phase species [MM^{-1}], t is time [T], Q is the volumetric flow rate [L^{3}T^{-1}], A is the main channel cross-sectional area [L^2], x is distance [L], D is the dispersion coefficient [L^{2}T^{-1}], q_L is the lateral inflow rate [L^{3}T^{-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^{3}M^{-1}], S represents the change in solute mass on the streambed [ML^{-3}T^{-1}], and R represents the change in solute mass due to biochemical reactions [ML^{-3}T^{-1}].

For representation of the Se biochemical processes (algal uptake, algal biomass conversion to organic Se, settling, mineralization and assimilation, volatilization, chemical reduction) presented in Section “Accomplishments under Objective 2, Task 4”, first-order reaction rate laws similar in form to those used in QUAL2E are adopted. The chemical reactions governing Se cycling in the OTIS-QUAL2E-Se model include only chemical reduction. Although chemical oxidation does occur in natural systems, Se redox reactions proceed much faster in the direction of reduction, with the slow rate of oxidation exacerbated in aquatic environments with high DO and nutrient concentrations. 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.

Se_{org}, SeO_4, SeO_3, Se_{vol}, and SeMet are treated as dissolved-phase species (Figure 8), with fate and reactive transport simulated using Equation (7), whereas Se^0 and Se^{2-} are treated as solid-phase species on the streambed (Figure 8), with transformations simulated using Equation (10). Solute mass exchange between the water column and the streambed due to sorption is represented by Equation (8), and is operative only for SeO_4 and SeO_3 (Figure 8). Concentrations of sorbed SeO_4 and sorbed SeO_3 are calculated using Equation (3). The change in mass due to biochemical reactions (*R*) in Equations (7) and (10) 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:

$$R_{Se_{Org}} = \left(\alpha_{Se} C_{alg} \gamma_{alg}\right) - \left(\sigma_{Se_{org}} C_{Se_{org}}\right) - \left(\lambda^{min}_{Se_{Org}} C_{Se_{org}}\right) - \left(\lambda^{vol}_{Se_{Org}} C_{Se_{org}}\right) \qquad (11)$$

$$R_{SeO_4} = \Big[\left(\lambda^{min}_{Se_{Org}} C_{Se_{Org}}\right) + \left(\lambda^{min}_{SeMet} C_{SeMet}\right) - \left(fr_{SeO_4} \alpha_{Se} \mu_{alg} C_{alg}\right) - \left(\lambda_{SeO_4} C_{SeO_4}\right) - \left(\lambda^{assim}_{SeO_4} C_{SeO_4}\right) - \left(\lambda^{vol}_{SeO_4} C_{SeO_4}\right)$$

(12)

$$R_{SeO_3} = \left(\lambda_{SeO_4} C_{SeO_4}\right) - \left[\left(1 - fr_{SeO_4}\right) \alpha_{Se} \mu_{alg} C_{alg}\right] - \left(\lambda_{SeO_3} C_{SeO_3}\right) - \left(\lambda^{vol}_{SeO_3} C_{SeO_3}\right) - \left(\lambda^{assim}_{SeO_3} C_{SeO_3}\right) \qquad (13)$$

$$R_{Se^0} = \left(\lambda_{SeO_3} C_{SeO_3}\right)^s - \left(\lambda_{Se^0} C^s_{Se^0}\right) \qquad (14)$$

$$R_{Se^{-2}} = \left(\lambda_{Se^0} C^s_{Se^0}\right) + \left(\lambda_{Se_{vol}} C_{Se_{vol}}\right) \qquad (15)$$

$$R_{Se_{vol}} = \left(\lambda^{vol}_{Se_{Org}} C_{Se_{org}}\right) + \left(\lambda^{vol}_{SeO_4} C_{SeO_4}\right) + \left(\lambda^{vol}_{SeO_3} C_{SeO_3}\right) + \left(\lambda^{vol}_{SeMet} C_{SeMet}\right) - \left(\lambda_{Se_{vol}} C_{Se_{vol}}\right) \qquad (16)$$

$$R_{SeMet} = \left(\alpha^{SeMet}_{Se} C_{alg} \gamma_{alg}\right) - \left(\sigma_{SeMet} C_{SeMet}\right) - \left(\lambda^{vol}_{SeMet} C_{SeMet}\right) - \left(\lambda^{min}_{SeMet} C_{SeMet}\right) \qquad (17)$$

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 parameter variable is defined in the Nomenclature table.

Each first-order rate coefficient λ_j shown in Equations (11)-(17) is modified from a base value, $\lambda_{j,20}$ (at T = 20 °C) according to the water temperature T_{water} of the current day of the simulation:

$$\lambda = \lambda_{20} 1.083^{(T_{water} - 20)} \tag{18}$$

The fraction of algal Se uptake corresponding to SeO_4 uptake in Equation (12) is calculated according to the following equation, where f_{SeO_4} is the algal preference factor for SeO_4 (as opposed to SeO_3):

$$fr_{SeO_4} = \frac{f_{SeO_4} C_{SeO_4}}{\left(f_{SeO_4} C_{SeO_4} + \left(1 - f_{SeO_4}\right) C_{SeO_3} \right)} \tag{19}$$

The chemical reduction of SeO_4, SeO_3, Se^0, and Se_{vol} is tempered by the presence of DO and NO_3 using inhibition constants which impede the rate of Se reduction. For SeO_4 reduction, the base rate constant is modified according to:

$$\lambda_{SeO_4} = \lambda_{SeO_4,20} \left(\frac{I_{O_2}}{I_{O_2} + C_{O_2}} \right) \left(\frac{I_{NO_3}}{I_{NO_3} + C_{NO_3}} \right) \tag{20}$$

where I_{O_2} and I_{NO_3} are the DO and NO_3 inhibition constants [ML^{-3}] and indicate the concentrations of DO 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 $\lambda_{Se_{vol}}$.

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 (µg/g) 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 (14). 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 7) is solved using a Crank-Nicolson finite-difference solution (Runkel, 1998), with the stream network divided into physically-uniform reaches and each reach 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 reach 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.

A3. RT3D-OTIS Model: Coupling Groundwater-Surface Water Reactive Transport of N and Se Species

The processes of coupling groundwater flow and solute transport with surface water flow and solute transport were described briefly in Section "Accomplishments under Objective 2, Task 4". RT3D-AG runs on a daily time step, i.e. groundwater solute concentration of N and Se species are simulated for each cell of the finite difference grid for each day of the simulation. OTIS-QUAL2E, however, runs on an hourly time step. Thus, at the end of each day in the simulation, the groundwater solute concentrations simulated by RT3D-AG are provided to surface water cells if there is groundwater discharge to the stream. The concentrations are taken by OTIS-QUAL2E, and transport of the solutes then is simulated for the same 24 hours, on the hourly time steps. At the end of the 24 hours, any stream seepage to the aquifer is provided with solute concentration simulated by OTIS-QUAL2E, so that solute mass is transferred from the stream system to the groundwater system.

Another important aspect of coupling solute transport in the watershed system is the transport of solute mass from irrigated fields to the stream network via tailwater runoff. This process was included in the RT3D-OTIS model by tracking the volume of calculated tailwater runoff for each irrigated field, and adding it to the appropriate adjacent stream reach. The concentration of N and Se species in the applied irrigation water also is tracked, and included in the tailwater runoff as it is loaded to the stream reach. The water added to a given stream reach on a daily basis is thus the summation of groundwater discharge and tailwater runoff.

MODFLOW-SFR consists of a single FORTRAN program, and RT3D-AG consists of a single FORTRAN code. QUAL2E-OTIS is included as a subroutine within the RT3D-AG code, called at the end of the daily time step, and thus the RT3D-OTIS code is a single FORTRAN code and executable. This greatly facilitates the linkage between groundwater and surface water. The flow of data within the coupled groundwater and surface water solute transport system is shown in the Figure 27. MODFLOW-SFR simulates groundwater head, groundwater flow, streamflow, and groundwater-surface water exchange rates, which are supplied to RT3D-OTIS on a weekly basis. The weekly flow rate values are divided by 7 to provide daily flow rates, to coincide with the RT3D-OTIS daily time step. For each transport time step (1 day), the mass balance equation for each solute is solved according to advection, dispersion, and chemical reactions, with OTIS-QUAL2E then called to perform daily surface water solute transport according to advection, dispersion, and chemical reactions. Before OTIS-QUAL2E solves the surface water mass balance equations, groundwater solute concentration data is prepared as input to OTIS-QUAL2E along with lateral inflow rates from MODFLOW-SFR. Once OTIS-QUAL2E is finished solving the equations over the 24 hourly time steps, surface water solute concentration data are prepared as input into RT3D-AG for the next day's simulation.

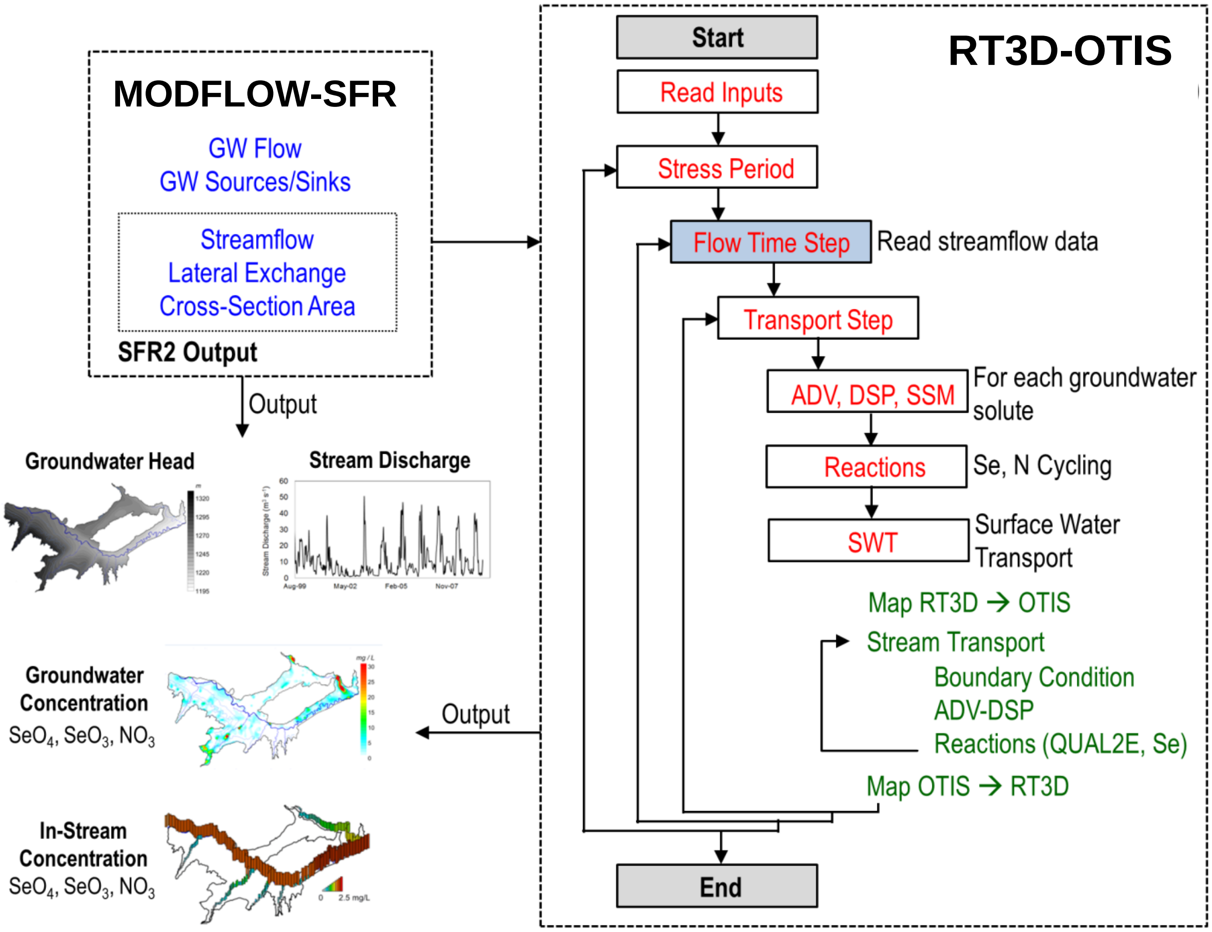

Figure 27. Diagram of data flow between flow and reactive transport models.