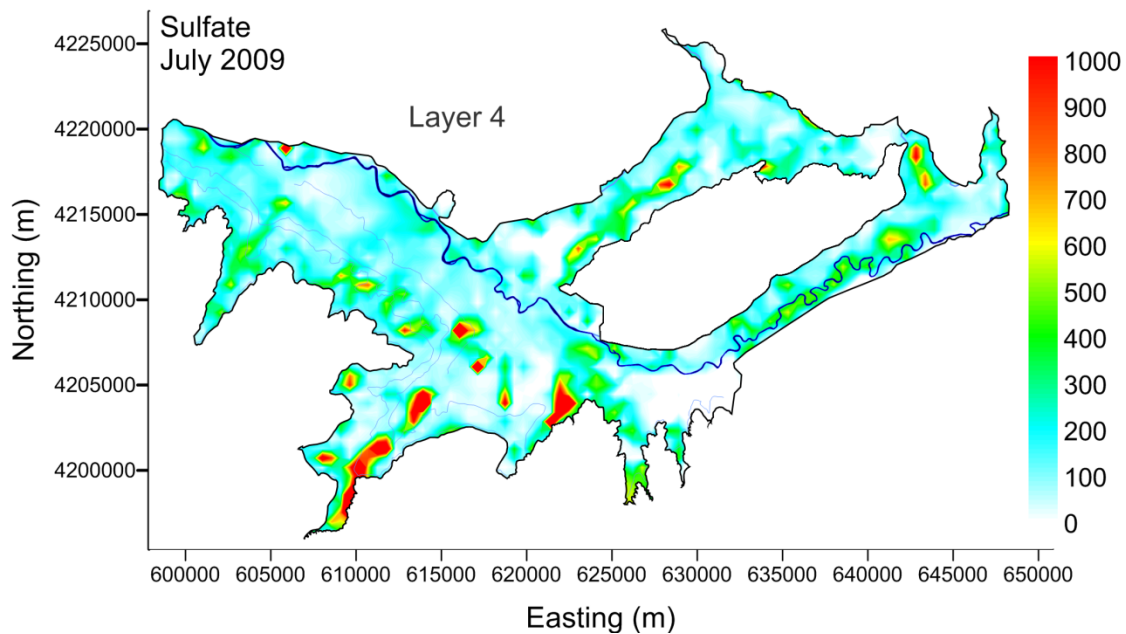


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# Developing a Framework for Simulating the Fate and Transport of Salinity Species in the Lower Arkansas River Valley, Colorado



Project Report, 2014-2015  
7/14/2015

**Project Title:** Developing a Framework for Simulating the Fate and Transport of Salinity Species in the Lower Arkansas River Valley, Colorado

**Report Summary:** This report summarizes the research activities accomplished during the time period July 1 2014 to May 15 2015. Activities include field data collection from the lysimeter site in Rocky Ford, CO; development and testing of an equilibrium chemistry module for salt ions and minerals; and coupling of the module with the numerical groundwater modeling code RT3D and initial testing at the regional scale.

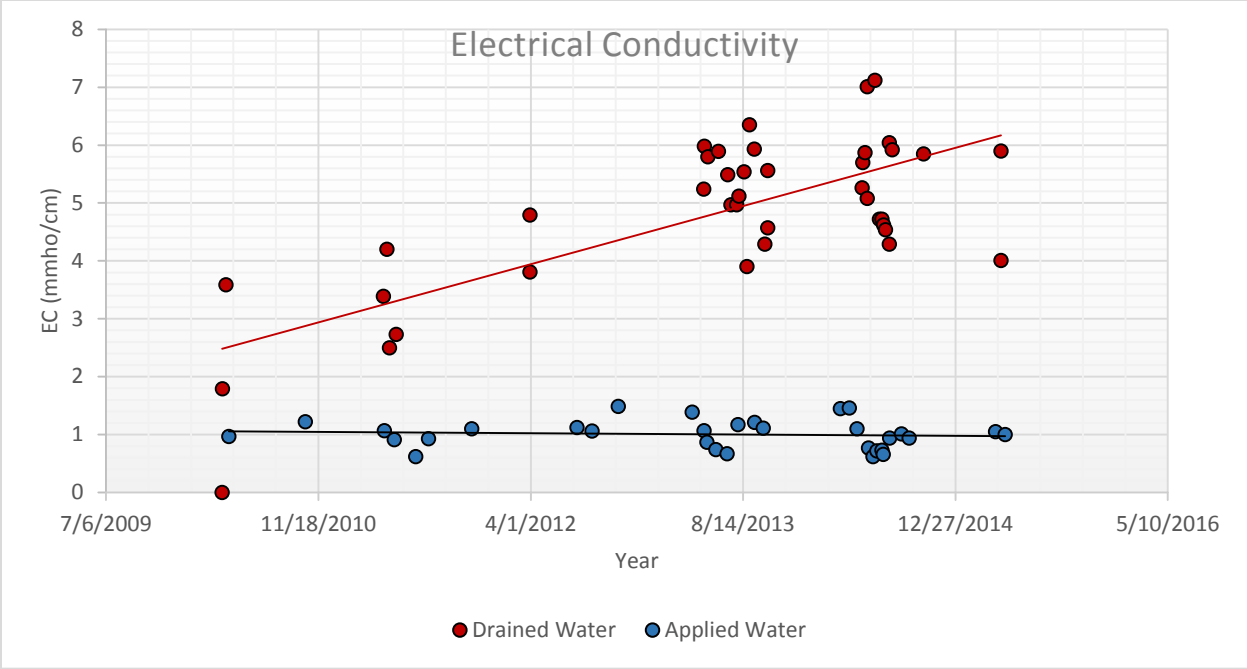
**Project Description:** The Lower Arkansas River Valley (LARV) in southeastern Colorado is a key resource for stakeholders in southeastern Colorado due to its valuable agriculture production. Because of a rising water table due to excessive irrigation and canal seepage, much of the soil-aquifer system in the valley has become salinized, thereby negatively impacting crop yield. High groundwater salinity loading to the Arkansas River stream network also impacts downstream areas, with saline river water diverted for application on irrigated fields. The overall aim of this project is to develop a numerical modeling framework capable of simulating the transport of salt ions within the stream-aquifer-soil system, so that current conditions of salinity can be assessed and possible remediation strategies in the region can be explored. This overall aim will be accomplished by the following specific objectives:

- 1- Collecting field data at multiple scales to enable small scale model testing; and
- 2- Developing a comprehensive salinity module that can be coupled with the UZF-RT3D model and that accounts for equilibrium chemistry and precipitation-dissolution processes;
- 3- Preliminary application of the coupled model at the large scale (~500 km<sup>2</sup>)

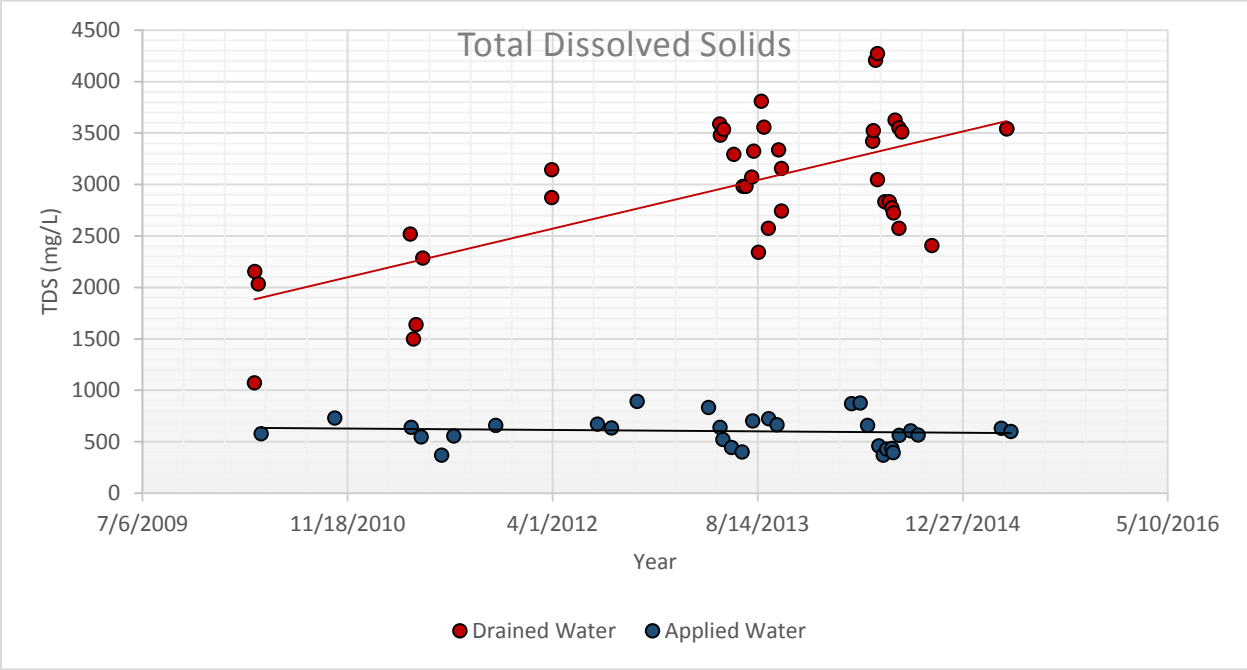
In the following sections, Lysimeter data collection, the development of the Equilibrium chemistry module, and the coupling of the module with UZF-RT3D are presented in detail.

## **1. Data Collection from Lysimeter Site**

There are two Lysimeters at the Arkansas Valley Research Center (AVRC) in Rocky Ford, CO: the Large Lysimeter, and the Reference Lysimeter. This project analyzed applied irrigation water, tail water, soil water, and drainage water (from the base of the lysimeter) to better understand the storage and movement of salt ions in a typical agricultural soil zone. Applied irrigation water and drained water, collected since 2009 and stored in a freezer at the AVRC, were tested for water quality indicators such as Electrical Conductivity (EC) and Total Dissolved Solids (TDS). For the 2014-2015 study period, personnel at the AVRC collected irrigation and drainage samples, which also were tested for EC and TDS. Figures 1 and 2 show the time series of EC and TDS, respectively, demonstrating the increase through time of both measures in the drainage water. Values of both indicators are above the EPA's criteria for acceptable irrigated water due to the quality (EPA recommended limit for EC: 1.5; for TDS: 500 mg/L). EC and TDS increases from 2009 and expected to be increased if no action taken.



**Figure 1.** Electrical Conductivity of Applied and Drained water



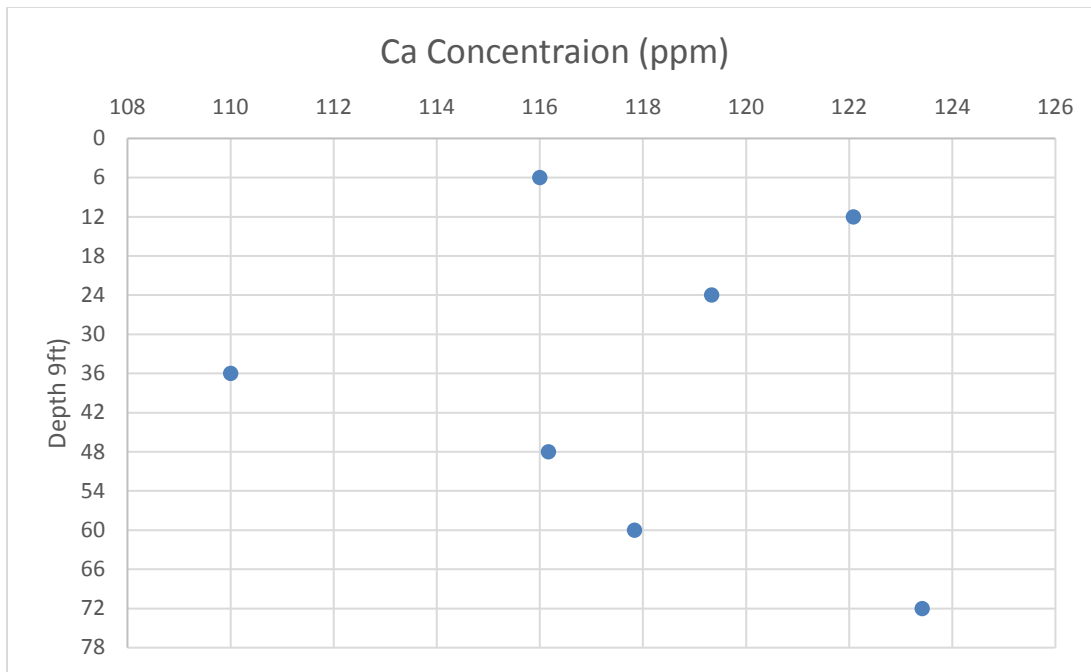
**Figure 2.** Total Dissolved Solids of Applied and Drained water

Samples of soil were collected from boreholes adjacent to the lysimeter site (see Figure 3). Samples were collected from three boreholes, so that results would not be biased to one site and thereby provide a more general assessment of soil salinity. For each borehole, soil was collected at each foot to a depth of five feet, except for the first foot below the ground surface in which two samples were taken. A total of four sampling events (June 21 2014, Nov. 11 2014, Sep. 11 2014, and April 21 2015) occurred during the project period. Samples were placed on ice and shipped to Ward Laboratory in Kearney, NE. The soil water was analyzed for Chloride, Calcium, Magnesium, Sodium, Sulfur, and Bicarbonate, SAR, EC, pH, and Nitrate. The data will be used to (1) assess salinity storage and movement in the soil profile; and (2) test the Equilibrium Chemistry module (see next section).

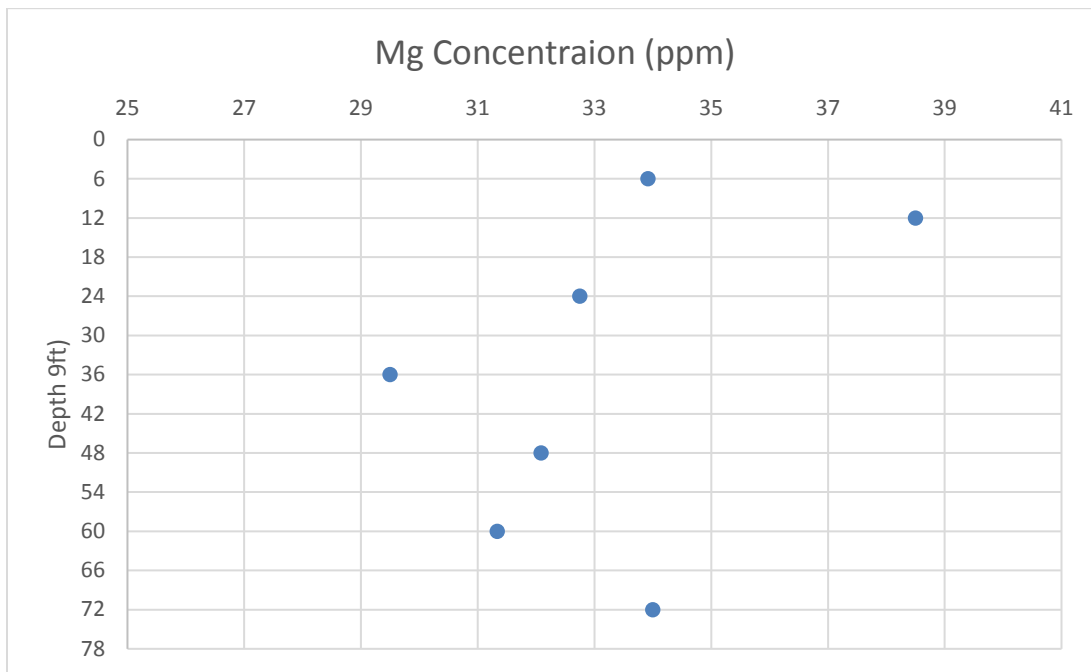


**Figure 3.** Boreholes for soil sampling, located adjacent to lysimeter at the AVRC, Rocky Ford, CO.

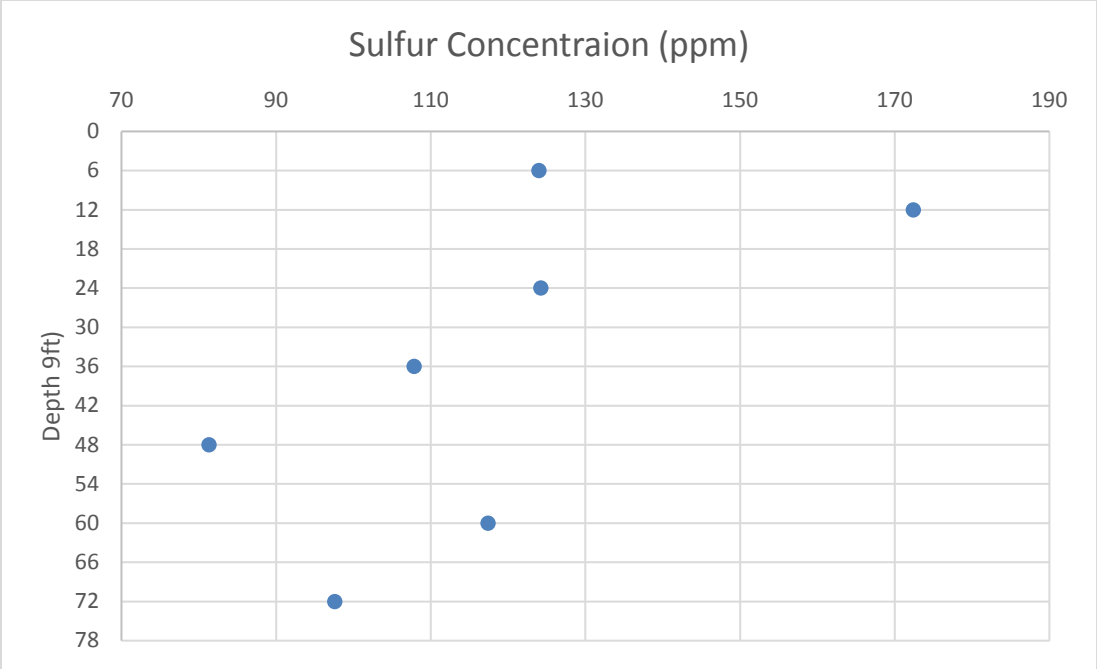
Average soil water concentration of Calcium, Magnesium, Sulfur, and Bicarbonate concentration through at each depth from the four sampling events is shown in Figures 4 to 5. It can be seen that Sulfur and Bicarbonate concentration increase with depth. All results from the four sampling events are summarized in Figures 8-18 for each water quality indicator using box plots.



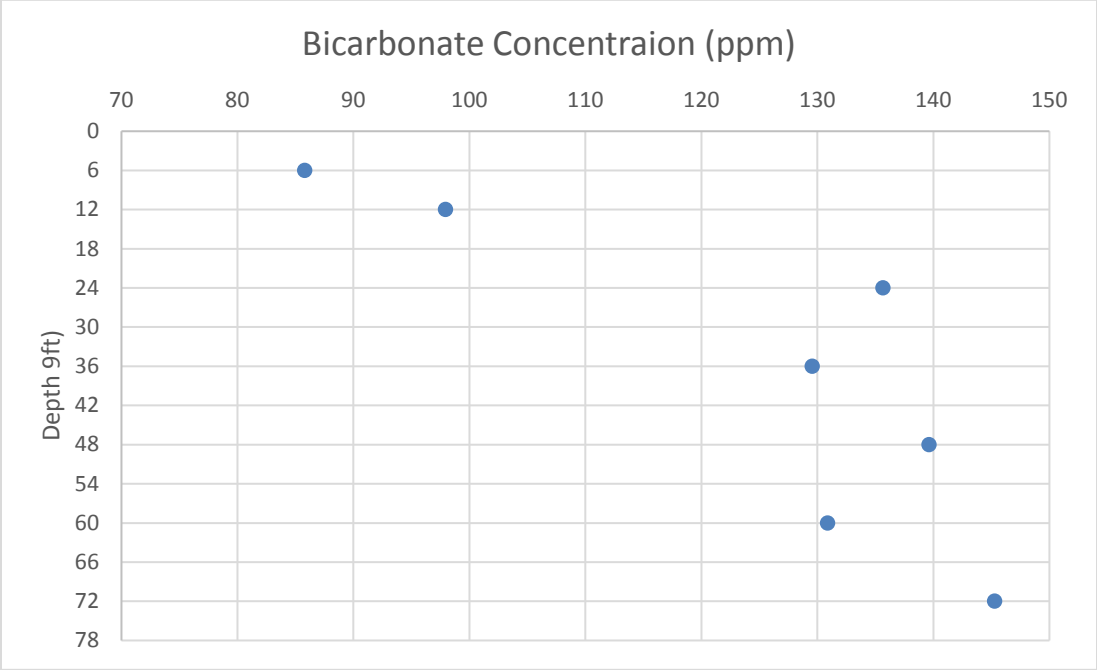
**Figure 4.** Calcium concentration through Lysimiter's soil profile



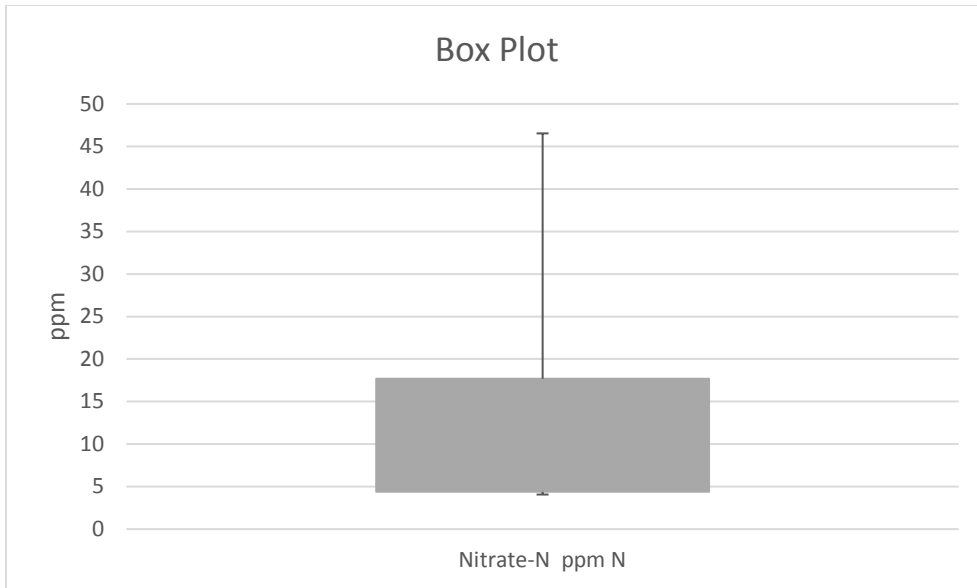
**Figure 5.** Magnesium concentration through Lysimiter's soil profile



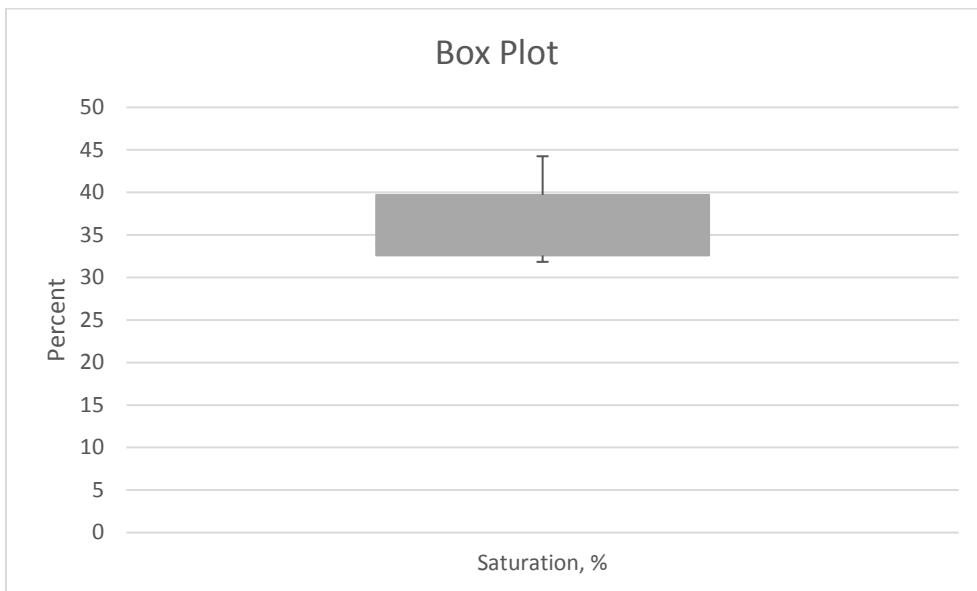
**Figure 6.** Sulfir concentration through Lysimiter’s soil profile



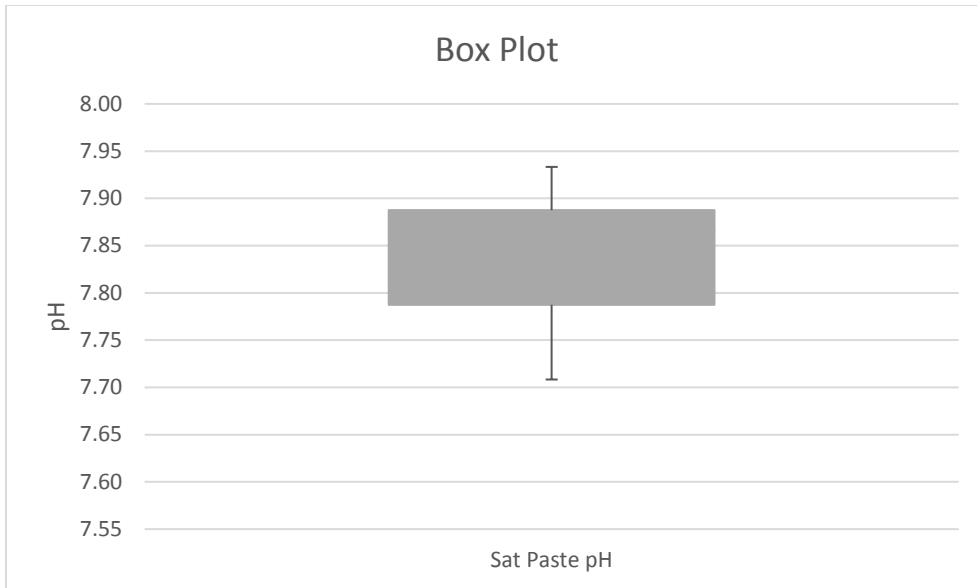
**Figure 7.** Bicarbonate concentration through Lysimiter’s soil profile



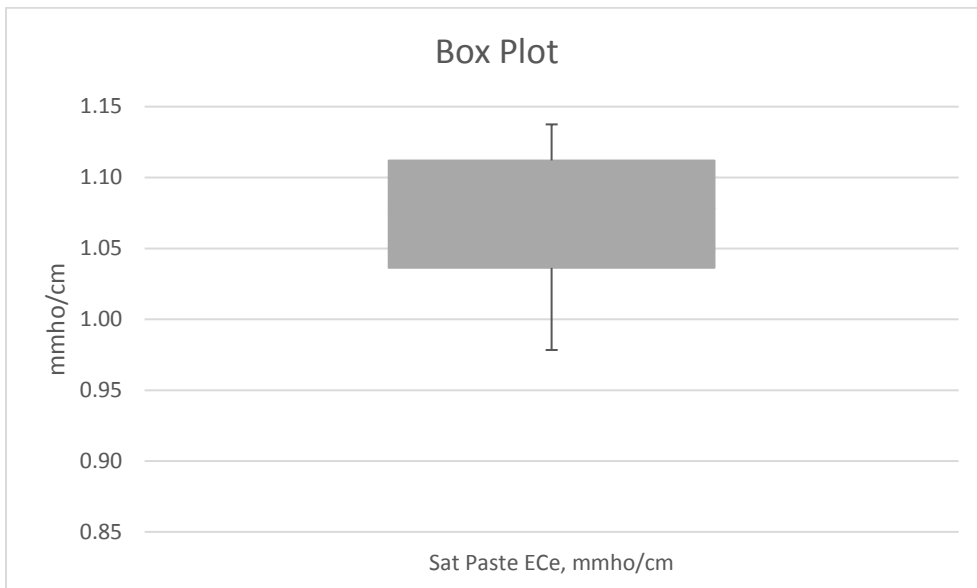
**Figure 8.** Distribution of Nitrate-N in Lysimeter soil profile up to six feet



**Figure 9.** Saturation in Lysimeter soil profile up to six feet

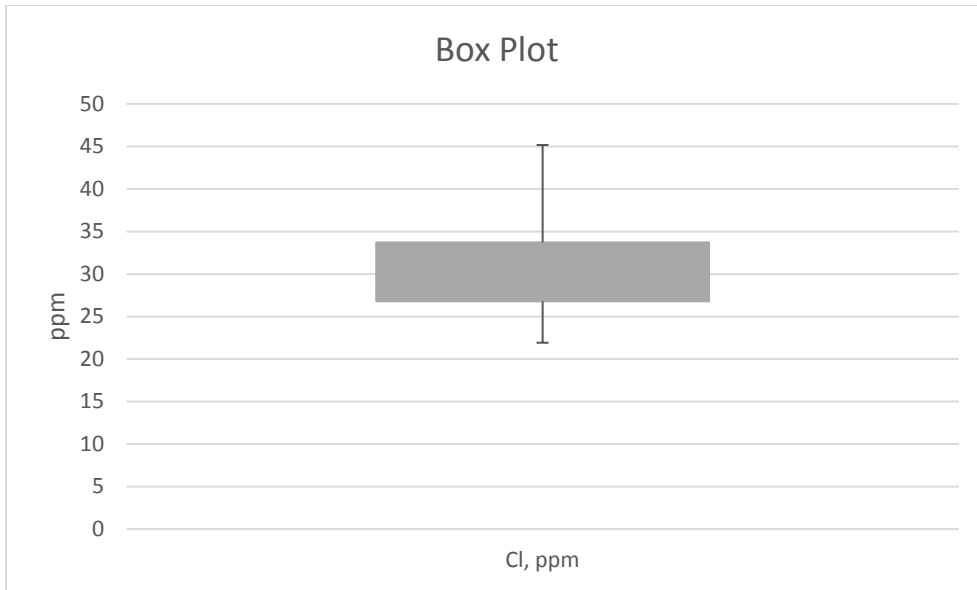


**Figure 10.** pH in Lysimeter soil profile up to six feet

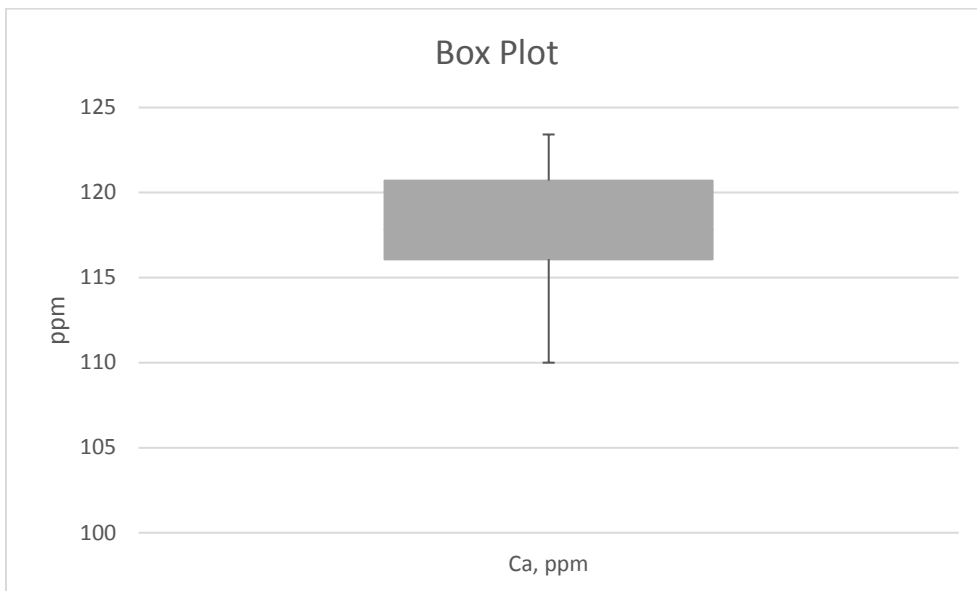


**Figure 11.** Electrical Conductivity in Lysimeter soil profile up to six feet

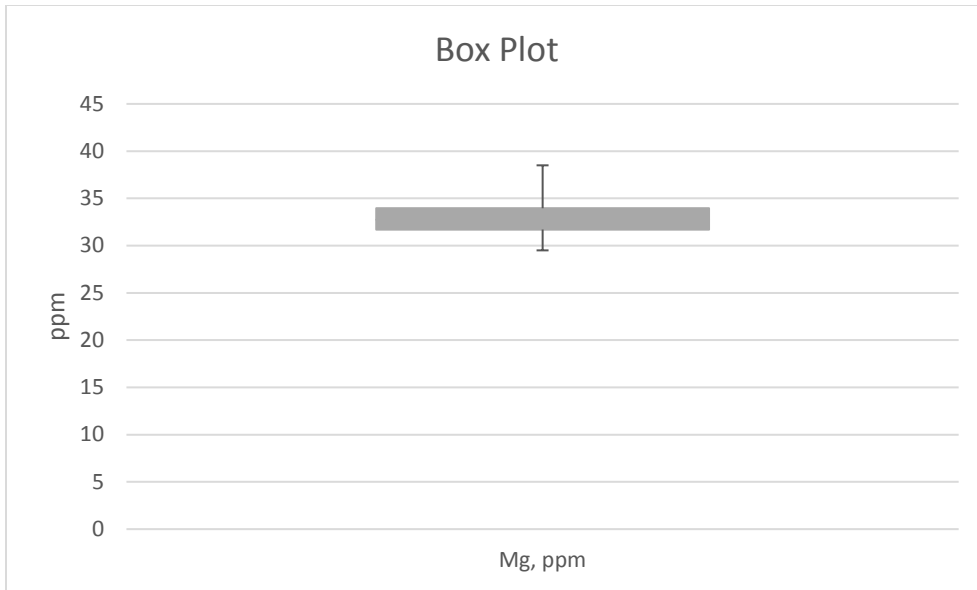




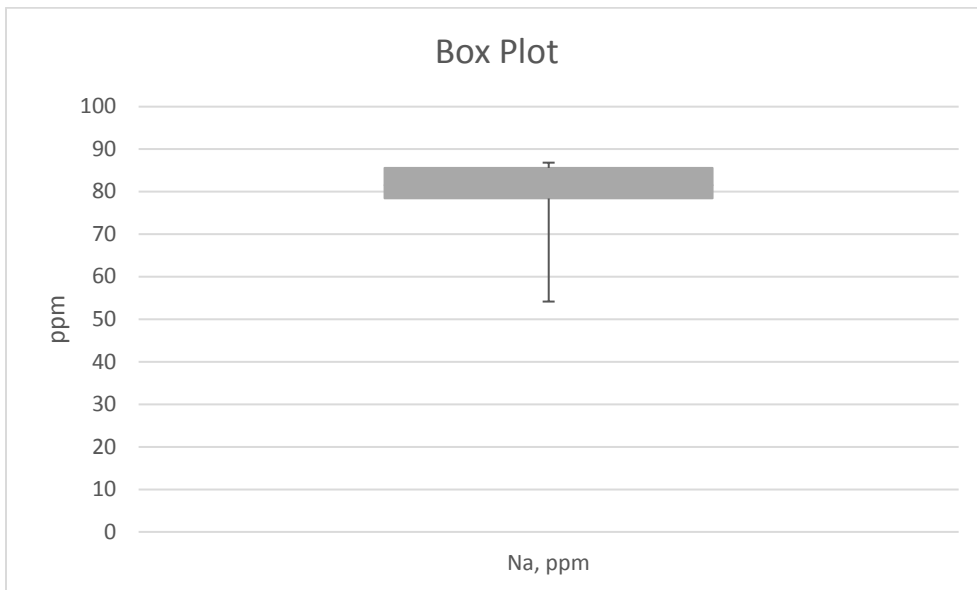
**Figure 12.** Distribution of Chloride in Lysimeter soil profile up to six feet



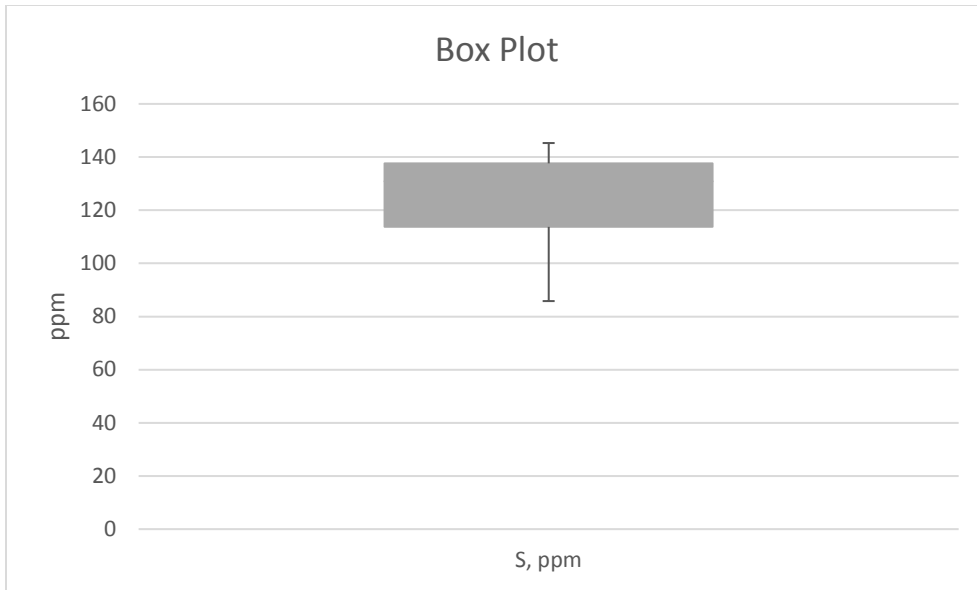
**Figure 13.** Distribution of Calcium in Lysimeter soil profile up to six feet



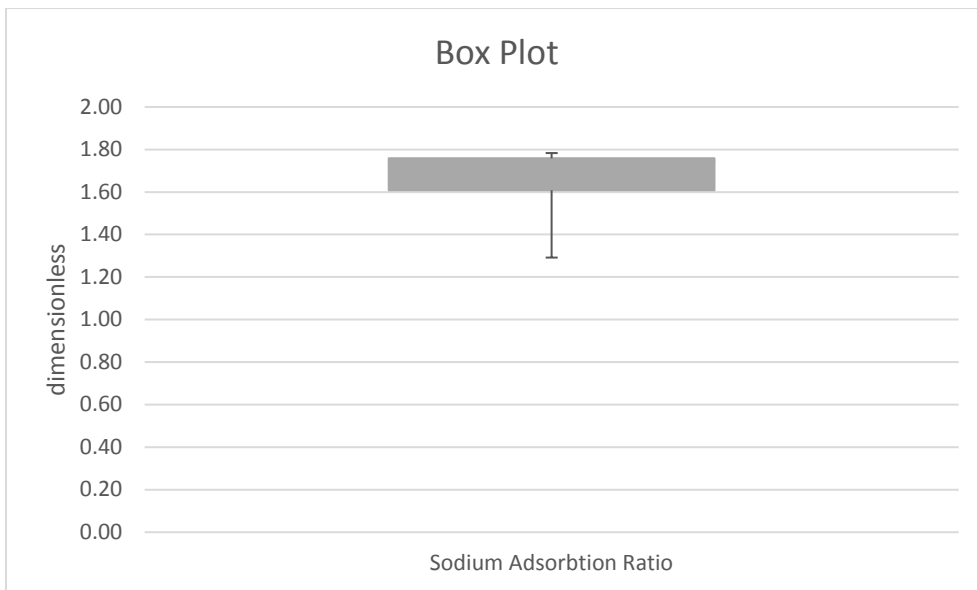
**Figure 14.** Distribution of Magnesium in Lysimeter soil profile up to six feet



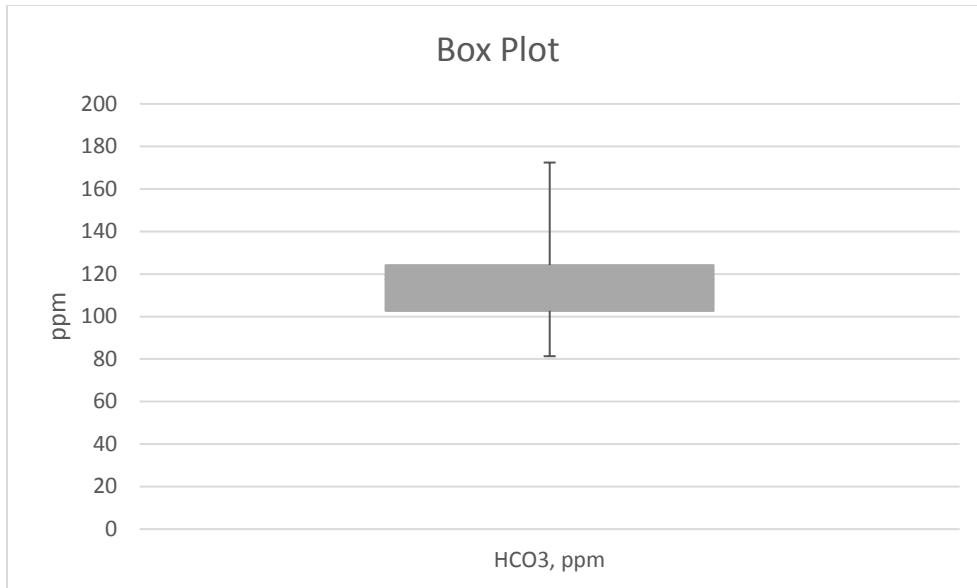
**Figure 15.** Distribution of Na in Lysimeter soil profile up to six feet



**Figure 16.** Distribution of Sulfur in Lysimeter soil profile up to six feet



**Figure 17.** Distribution of Sodium Adsorption Ratio in Lysimeter soil profile up to six feet



**Figure 18.** Distribution of Bicarbonate in Lysimeter soil profile up to six feet

## 2. Equilibrium Chemistry Module

The equilibrium chemistry module is intended to couple with UZF-RT3D to yield the complete set of required kinetic and equilibrium chemical reactions for salinity fate and transport in soil and groundwater systems. In previous years, only sulfur cycling and chemical kinetics have been used in UZF-RT3D to simulate sulfate (SO<sub>4</sub>) fate and transport, and resulting groundwater concentrations are less than measured values in the observation wells. A key component that is missing is precipitation-dissolution processes, in which salt minerals such as gypsum (CaSO<sub>4</sub>) dissolve and thereby increase soil and groundwater concentration of SO<sub>4</sub> and Ca. Since the interactions such ion-exchange, complexation, and precipitation/dissolution are not included in the RT3D model, developing an equilibrium chemistry package which can be coupled with transport model could decrease the discrepancy between simulated and observed data, and hence was a primary objective of the project.

Equilibrium chemistry is a state in which reactants and products have no tendency for further interactions. There are two main methods to implement equilibrium chemistry into the model: the stoichiometric method and the non-stoichiometric method. Determining the equilibrium concentration by stoichiometric method requires solving two sets of equations simultaneously (mass balance, mass action), while non-stoichiometric algorithm finds solutions by minimizing the Gibbs energy subject to constraints. Mass balance equations require that the amount of each species entering the system must be equal to the amount leaving. Mass action equations suggested by J.W Gibbs in 1873, means that equilibrium is attained when the Gibbs free energy of the system is at its minimum. Gibbs energy elements are shown in Equation 1, where  $g$  is the

Gibbs energy of the entire mixture,  $G$  is the Gibbs free energy of the system,  $R$  ( $=8.314 \text{ JK}^{-1}$ ) is the universal gas constant and  $T$  (K) is the absolute temperature:

$$g = \frac{G}{RT} \text{ Equation 1}$$

$$G = \sum_1^N n_i \mu_i \text{ Equation 2}$$

Equation 2 shows the free Gibbs energy of interactions where  $n_i$  is the number of moles of species  $i$  and  $\mu_i$  is the chemical potential of species  $i$ . Chemical potential for a specific species can be calculated by Equation 3:

$$\mu_i = \mu_i^\theta + RT \ln a_i \text{ Equation 3}$$

Where  $a_i$  is the chemical activity,  $\mu_i^\theta$  is the standard chemical potential,  $R$  ( $=8.314 \text{ JK}^{-1}$ ) is the universal gas constant, and  $T$  (K) is the absolute temperature.

The non-stoichiometric method is more efficient. Hence, considering that hundreds of thousands of equilibrium calculations may be required for particular groundwater simulations, this method is selected for the equilibrium chemistry module. In this method, for achieving the equilibrium concentration, two major steps needed to be taken into account. First, the concentration of each ion is calculated without the presence of any solids (i.e. salt minerals). Second, the precipitation or dissolution of salt minerals must be calculated.

Precipitation dissolution reactions have some differences in respect to other aqueous interactions. For instance, the activity of solids is equal to the unity. Hence, the excess amount of solid in saturated solution does not affect the concentration of dissolved ions into the solution. Basically, for considering the precipitation/dissolution reaction into the system, the solubility product of each solid must be identified. Solubility product indicates the maximum concentration of a specific species that a solution can hold without precipitation occurring. A trial solubility product of a certain mineral is first calculated to determine if a solution is undersaturated or saturated with respect to the solution concentrations. If the product is less than the solubility product, than the solid will dissolve into the solution until the trial solubility product is equal to the solubility product, depending on if enough mass of the corresponding solid exists. If not, it will dissolve completely. On the other hand, if the trial solubility product is greater than the solubility product, the ions precipitate into the solution until the trial solubility product is equal to the solubility product.

There are two main methods to implement the precipitation/dissolution reactions into the equilibrium chemistry model, both of which has their own advantages and disadvantages. In the first method, solids are added into the system one at a time and, based on the theory of “phase assemblage”, the direction of the reactions (precipitation/dissolution) will be specified. In the second method, all the ions which potentially could interact with each other and precipitate/dissolve into the solution are added to the system simultaneously. Although the first

method is easier to implement in a computer code since the user can add any solids of interest, it takes longer to solve in comparison with the second method. For the second method, the implementation is more difficult as the entire system of equations must be re-written for the addition a single ion. Furthermore, there are different mathematical algorithms to determine the equilibrium concentration, with varying run-times. A quadratic formula is used, based on recent papers in the literature, which is an extremely efficient method for calculating precipitation-dissolution processes. For an application to a 21,000 grid cell model of the study region upstream of John Martin Reservoir, equilibrium calculations for 1 day of simulation requires 3 hours using the exact solution. Using the quadratic formula approach, however, the run-time is only 60 seconds. This issue of run-time becomes extremely important when using the regional-scale model for best-management practice (BMP) assessment, in which model runs of several decades are required to determine the lasting effect of the BMPs on salinity in the groundwater and the Arkansas River stream network.

The equilibrium chemistry / precipitation/dissolution module is implemented in MATLAB. Since the reactive transport model UZF-RT3D is written FORTRAN, a novel coupling procedure is required to run the coupled model. UZF-RT3D is run for 1 day time step accounting for advection, dispersions, and chemical kinetics of each solute in the soil-aquifer system, whereupon the MATLAB routine is called and given the updated solute ion concentrations to calculate ion exchange, complexation, and precipitation-dissolution. This coupling was performed during the last few weeks of the project. The coupled model was applied to the study region upstream of John Martin Reservoir for a 10-year spin-up period. The simulation run-time was 3 days, and output results looked reasonable. Another project component is decreasing the model run-time by using parallelization. This can be performed because calculating the concentration at equilibrium using sequential non-iterative approach in each cell is independent from all the other cells. Hence, a block of cells can be run at the same time base on a number of assigned computer processors.

The next steps of the overall research project are:

- Apply coupled model to the AVRC soil profiles and test against soil water and drainage water concentrations
- Apply coupled model the upstream study region for the 2006-2009 study period, testing against groundwater concentrations, soil salinity concentrations, and groundwater salinity mass loadings to the Arkansas River
- Use the coupled model to assess the effects of BMPs on soil salinity, groundwater salinity, and groundwater salinity mass loadings to the Arkansas River.