# Assessing and Modeling Irrigation-Induced Selenium in the Stream-Aquifer System of the Lower Arkansas River Valley, Colorado

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**Abstract.** Water quality data on dissolved selenium (Se) have been collected since April 2003 in a study area of the irrigated lower Arkansas River Valley, Colorado. Data have been obtained from 22 surface water locations and from 59 ground-water monitoring wells using low-flow sampling techniques. GIS mapping and statistical analysis were used to characterize the occurrence, severity, and spatial-temporal distribution of Se in the study area. Results indicate dissolved Se concentrations ranging from about 0 to 3760 micrograms per liter ($\mu$g/l), with a median of 16.6 ($\mu$g/l) in the ground water, including three significant "hot spots". River concentrations range from 4.2 to 23.0 $\mu$g/l, often exceeding stream standards for aquatic habitat. Relationships are explored between Se concentrations and more-easily- monitored indicators such as electrical conductivity, sulfate concentration, and nitrate concentration. Statistically significant non-linear relationships exist between Se, sulfate, and nitrate concentration. Uranium (U) concentrations also are found to have a significant relationship with Se. Since high U concentrations have earlier been linked to marine shale and shale-derived soils in the Valley, the relationship between U and Se concentrations suggests a similar linkage between Se and the presence of shale formations. This relationship will be explored further with additional sampling events to test its validity   A model of the selenium transport process in the unconfined aquifer, as affected by irrigation practices, is currently being developed and will be calibrated using field data.

## 1. Introduction

The Lower Arkansas River Valley in Colorado is an intensively irrigated, alluvial basin comprised of underlying marine sedimentary rocks. With these characteristics, dissolution and mobilization of metals and minerals, such as selenium (Se), can lead to transport into canals and the Arkansas River and a consequent threat to the health and safety of animals and aquatic life. The study described herein aims to describe the extent to which these processes are

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occurring as non-point source pollution to the river and to provide the background for possible total maximum daily load (TMDL) development.

Thirteen segments of the Arkansas River are designated as"water quality limited" with respect to Se and/or Fe and have been placed on the current Clean Water Act 303(d) list (CDPHE 2002) for TMDL development, along with six segments on the current Monitoring and Evaluation List (CDPHE 2002).  In order to set appropriate water quality standards, the Colorado Water Quality Control Division of the Colorado Department of Public Health and Environment (CDPHE), is in the process of determining the nature of the elevated levels of Se in the stream-aquifer system of the Arkansas River.

The study area consists of a segment of irrigated alluvial valley extending about 60 km from Lamar, Colorado to the Colorado-Kansas border along the Arkansas River.  The Lower Arkansas River Basin is underlain by seleniferous Upper Cretaceous and Tertiary marine sedimentary rocks, as well as shale outcroppings that serve as a source of Se in the overlying soils.  The study area encompasses approximately 54,300 ha of land, including about 25,700 ha under irrigation.  It is sufficiently large to capture the diversity of soils, hydrogeology, irrigation and drainage infrastructure, and crops that are characteristic of the portion of the Arkansas River downstream of John Martin Reservoir.

Approximately 59 monitoring wells and 22 surface water monitoring points have been sampled nineteen times over the past three years for dissolved Se, iron (Fe), pH, specific conductance (*EC*), temperature, dissolved oxygen (*DO*), oxidation-reduction potential (*ORP*), and major salt ions using low flow sampling techniques.  Analytical analysis has been provided by Olson Biochemistry Labs at South Dakota State University in Brookings, SD and Ward Laboratories, Inc. in Kearney, NE.  A map of the study region, showing GIS coverage of individual fields and locations of monitoring sites is shown in Figure 1.
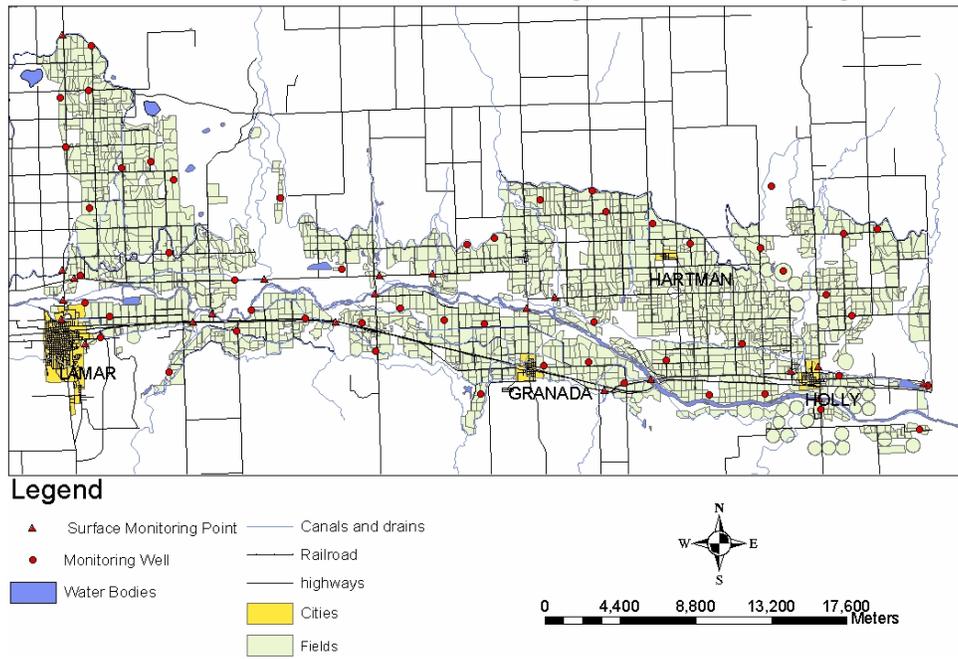


**Figure 1.**  The study area and sampling locations.

## 2. Data Analysis

### 2.1 General Statistics

Histograms of the data collected and analyzed to date (through the January 10-14, 2006 sampling event) were plotted as shown in Figures 2 to 4 for ground water, all surface water, and Arkansas River samples, respectively. In order to visually examine the relevance of measured concentrations of $C_{Se}$ along the study area, current standards are indicated on each histogram. For ground water comparison, the 20 (µg/l) Colorado groundwater standard for agricultural use (CDPHE 2001a) is shown. The Arkansas River, irrigation canals, and drains are compared against the Colorado chronic aquatic life standard (also referred to as the table value standard, TVS) of 4.6 µg/l (CDPHE 2001b) and the temporary lower Arkansas River segment 1c standard of 14 µg/l (CDPHE 2003). Data indicate levels of Se in the study area that exceed use protective standards.



Colorado Ground Water
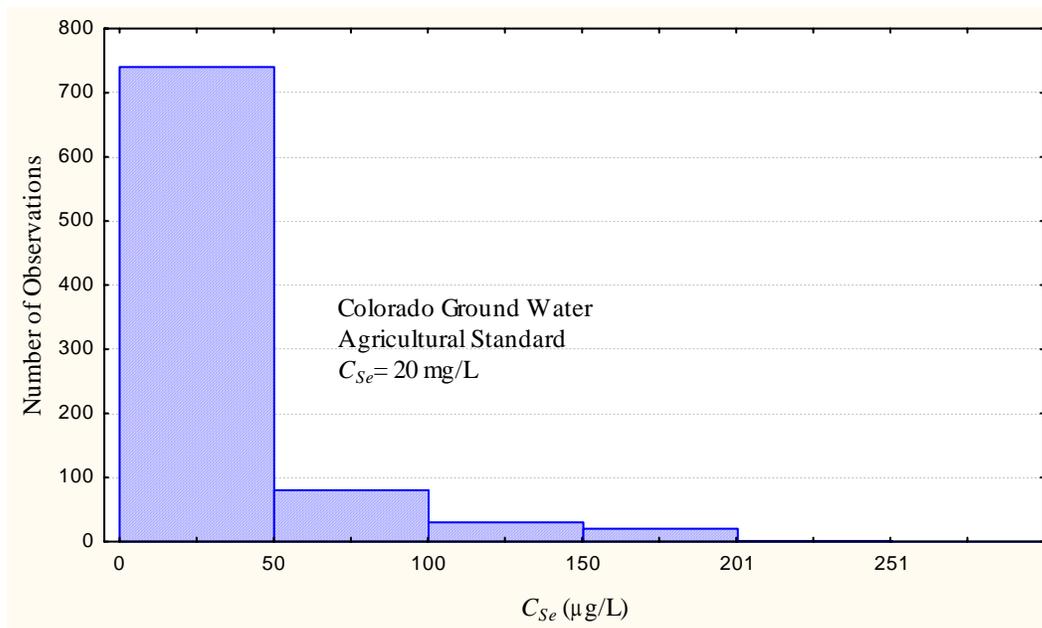Agricultural Standard
$C_{Se}= 20$ mg/L

**Figure 2.** Total dissolved selenium in ground water samples collected April 25 – May 3 2003 to January 10-14, 2006.
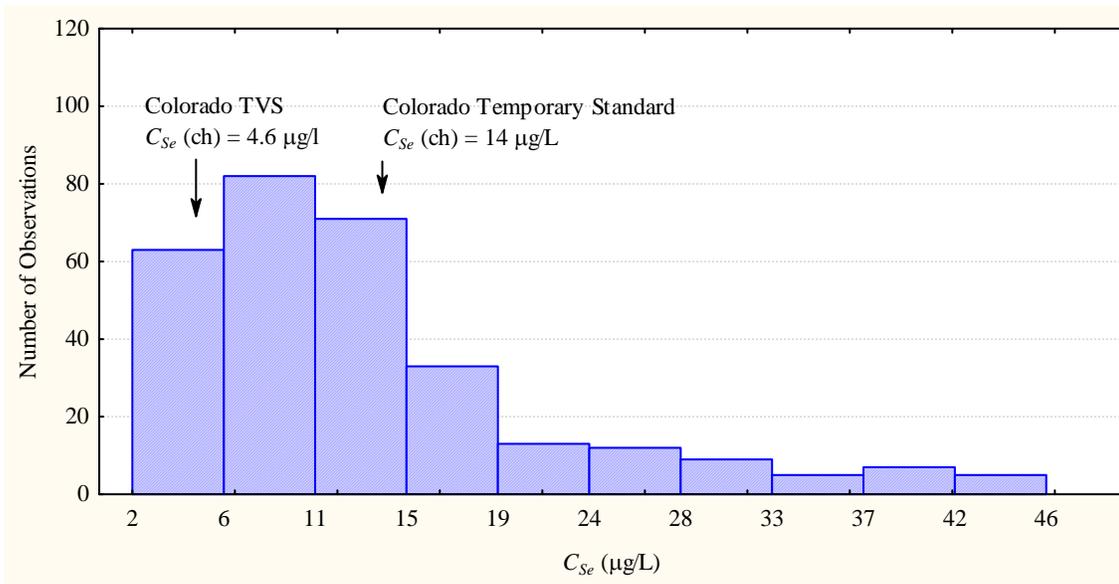
**Figure 3.** Total dissolved selenium in surface water samples collected from April 25 – May 3 2003 to January 10-14, 2006.
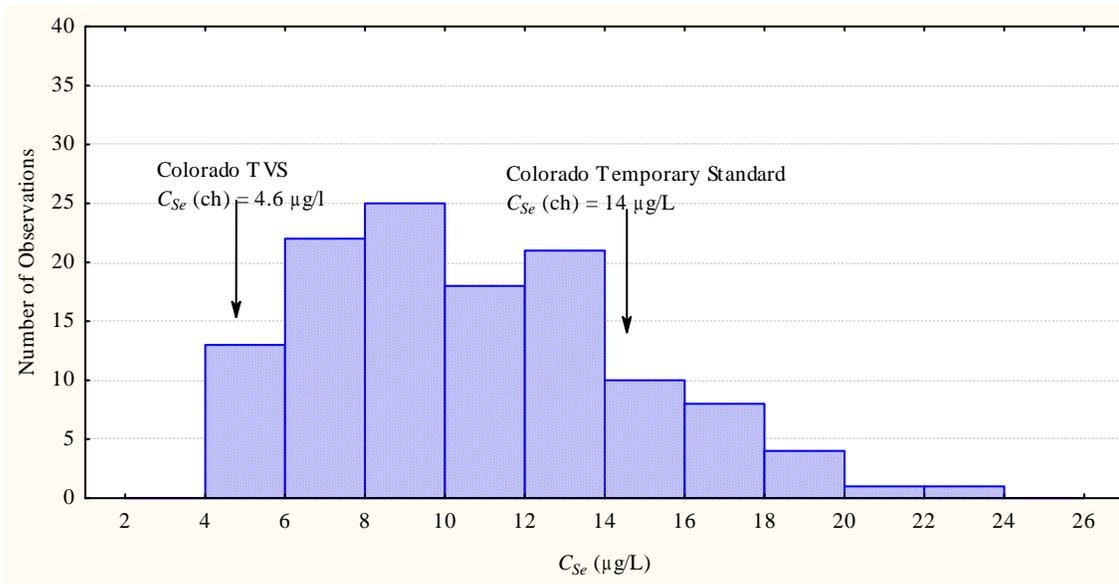


**Figure 4.** Total dissolved selenium in Arkansas River samples collected from April 25 – May 3, 2003 to January 10-14, 2006.

Summary statistics of $C_{Se}$ for all ground water, surface water, and river data are presented in Table 1. The Se concentrations in ground water samples range over five orders of magnitude. This skews the sample mean right of the median, as is apparent from the large variance and skewness. The maximum value of 3760 µg/l was determined from a sample taken at a monitoring well north of Lamar on June 30, 2004. The samples collected throughout the rest of the sampling period at this well also indicated consistently high $C_{Se}$. The

monitoring well was destroyed by field harvesting operations in late summer 2004. Two new wells were installed nearby in November 2005. One well was dry and the other contained a selenium concentration of only 15.7 µg/l when sampled during January 2006.

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**Table 1.** Summary statistics of dissolved Se (µg/l).

|  | *Ground Water* | *Surface Water* | *Arkansas River* |
|---|---|---|---|
| *Size of Population* | 954.0 | 210.0 | 135.0 |
| *Mean* | 70.6 | 13.9 | 10.7 |
| *Median* | 16.6 | 11.5 | 10.2 |
| *Maximum* | 3760.0 | 46.2 | 23.0 |
| *Minimum* | 0.4 | 0.5 | 4.2 |
| *Standard Deviation* | 373.5 | 10.6 | 4.0 |
| *Skewness* | 8.9 | 1.2 | 0.6 |

## 2.2    Spatial and Temporal Statistical Analysis

From the histograms, it is clear that the probability distributions of the data are not normally distributed. Therefore Se concentrations were analyzed in time series using nonparametric statistics to avoid biased results. The box and whisker plots shown in Figures 5 and 6 illustrate a summary of the statistical analysis. The central squares on the plot represent the median Se concentration at each point in time. The top and bottom of the rectangles represent the 75th and 25th percentiles, while the whiskers extend to the non-outlier range by the data set. The highest and lowest values were omitted from the data sets to decrease biasing by extreme values. Outliers were systematically determined as values that are higher than the 75th percentile value by more than two times the difference between the 25th and 75th percentile values. The outliers are shown on the plot.

Figure 5 indicates the median of each ground water data set is not substantially changing over time. However, it appears that the variability in $C_{Se}$ in ground water changes throughout the year. The degree to which this occurs depends on recharge rates, drainage rates, and river flow rates, which will be explored.

Figure 6 indicates seasonal patterns of $C_{Se}$ in the Arkansas River. There is higher $C_{Se}$ during low flow months and lower $C_{Se}$ during high flow months. The low flows occur during fall and winter months while high flows occur during the spring and summer months.
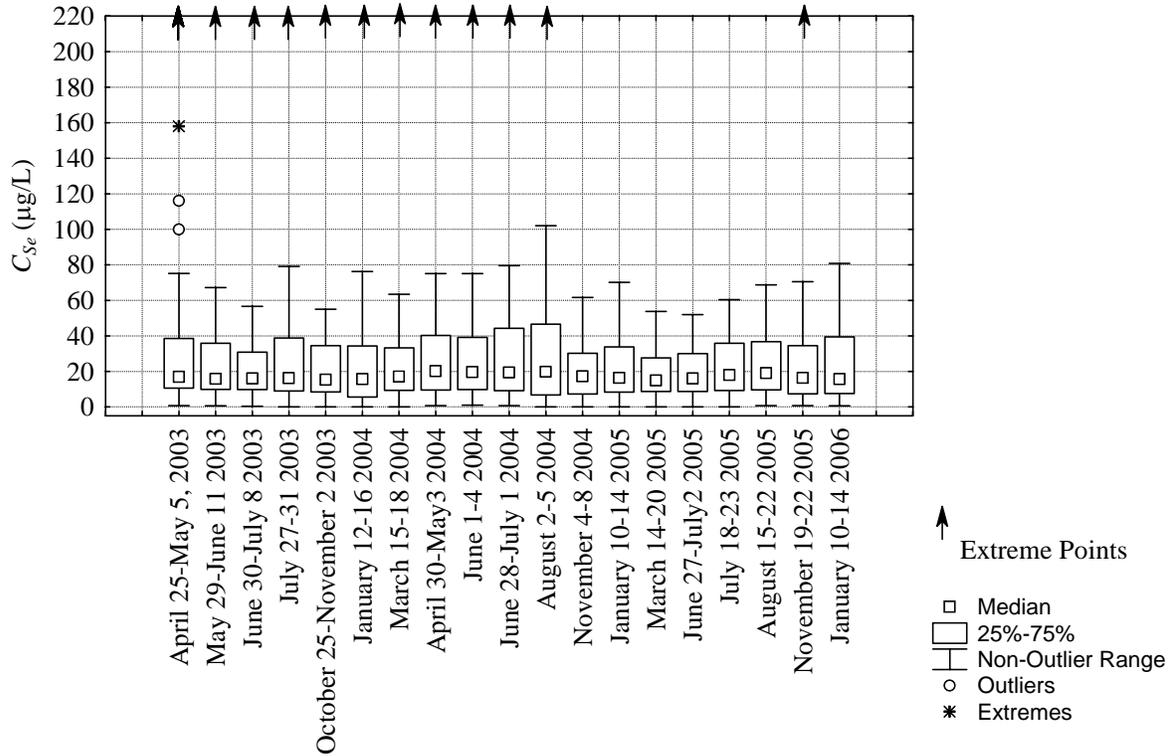
**Figure 5.** Box and Whiskers plot of dissolved Se in the ground water at continuously-sampled sites in the study area.
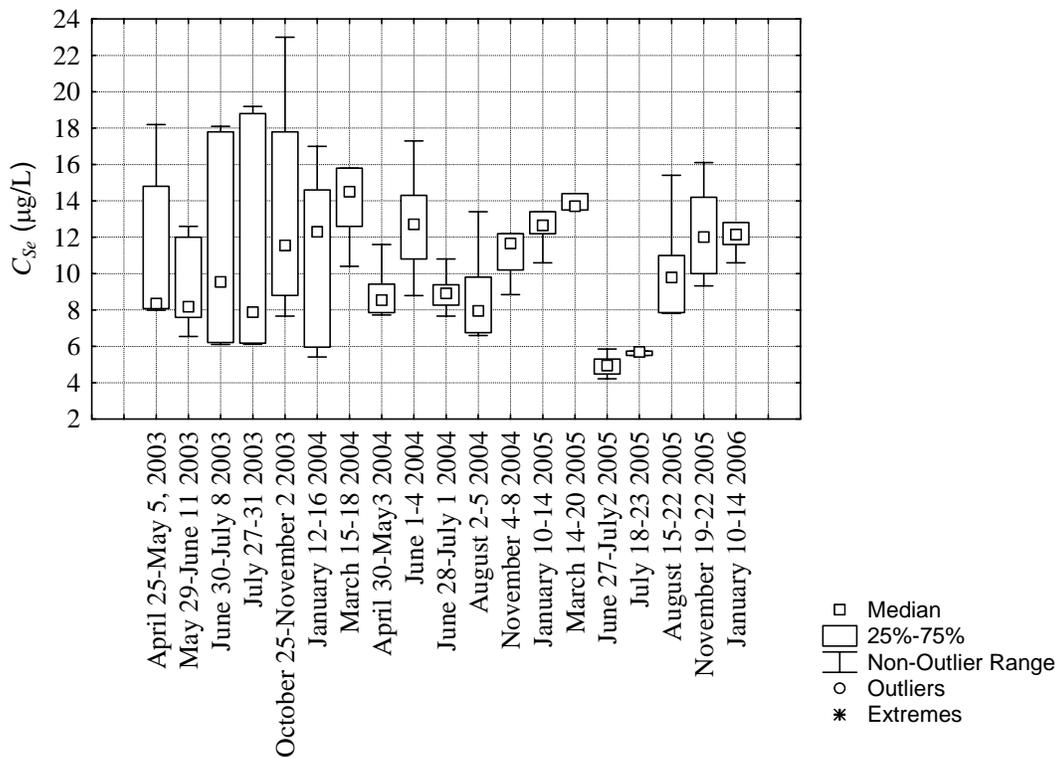


**Figure 6.** Box and Whiskers plot of dissolved Se at continuously-sampled sites in the Arkansas River.

Figures 7 and 8 provide examples of GIS contour maps of $C_{Se}$ developed for summer and winter sampling events in 2005, respectively. The contours were estimated in GMS$^{TM}$ (BYU 2005) utilizing the "natural-neighbor" interpolation method. The study area has relatively low Se concentrations uniformly throughout the middle portion. However, the eastern portion of the study area has two distinct hot-spots, which change in magnitude depending on the season.

Ground water samples collected during the period of July 18 – 23, 2005 were analyzed for dissolved uranium concentration, $C_U$. A GIS color-gradient contour map shown in Figure 9 reveals significant spatial variation in $C_U$ within the study area. High $C_U$ values are generally found in areas of high $C_{Se}$, as was earlier noted in a study by Zielinski et al. (1995). Additional samples for uranium from 15-20 ground water monitoring wells are planned for the March 2006 sampling period. The wells chosen for uranium sampling will be located where the highest values of $C_{Se}$ have been detected. All of the ground water monitoring wells will be sampled for uranium during the May sampling event.

## 2.3    Water Quality Relationships

Relationships were explored between $C_{Se}$ and several in-situ monitored variables including *EC*, *DO*, and *ORP*. Dissolved Se is thermodynamically in equilibrium as selenate, Se(VI), in highly oxidized environments such as the lower Arkansas River Valley, although it can be stable as selenite [Se(IV)] in fairly oxidized environments. In order to empirically explore the possibility of determining Se concentrations from ORP measurements, a laboratory analysis was conducted for selenite in the July 27 - 31, 2003 data set. Using total dissolved selenium and selenite analysis, the amount of selenate was calculated. Approximately half of the samples analyzed for selenite were below the detection limit and the data indicate that over 90 percent of Se in the study area is oxidized to selenate. This suggests that waters in the lower Arkansas River valley may be sufficiently oxidized and that the ORP may not be a limiting factor for Se dissolution.
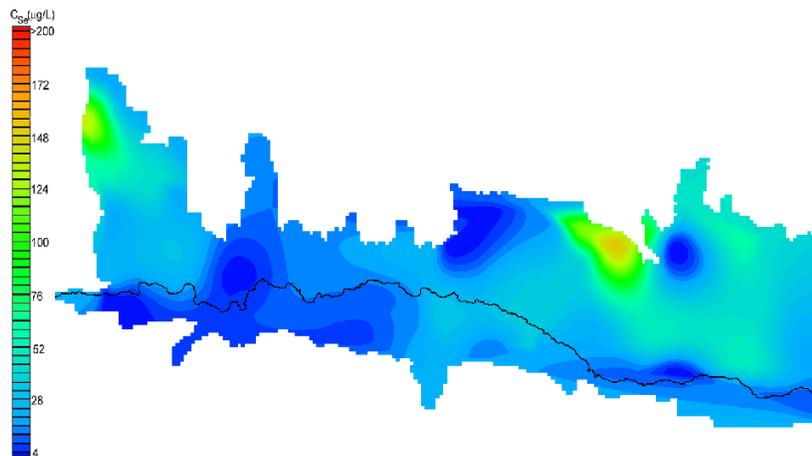


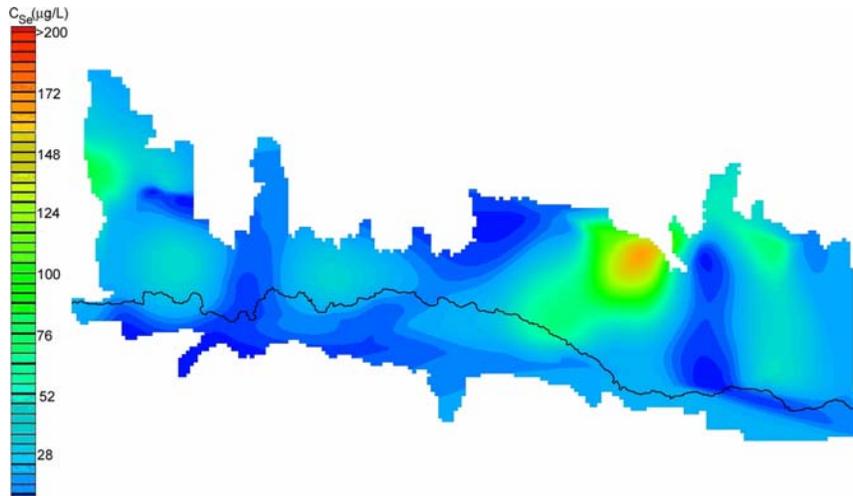**Figure 7.**  Contour plot of $C_{Se}$ from samples collected during July 18 – 23, 2005.

**Figure 8.** Contour plot of $C_{Se}$ from samples collected during January 10-14, 2006.

Although there does not appear to be a statistically significant relationship between Se concentration and *ORP*, the combination of low dissolved Fe and selenite concentrations indicates that the majority of the ground water and all of the surface waters in the Arkansas River Valley may be sufficiently oxidized to allow for the dissolution and mobilization of $C_{Se}$. Therefore, *ORP* monitoring may not be useful in quantifying $C_{Se}$ in the Valley. However, there are a limited number of cases where ground water maintains high levels of dissolved salts but does not contain high levels of $C_{Se}$. In some of these cases the ORP values are very low.
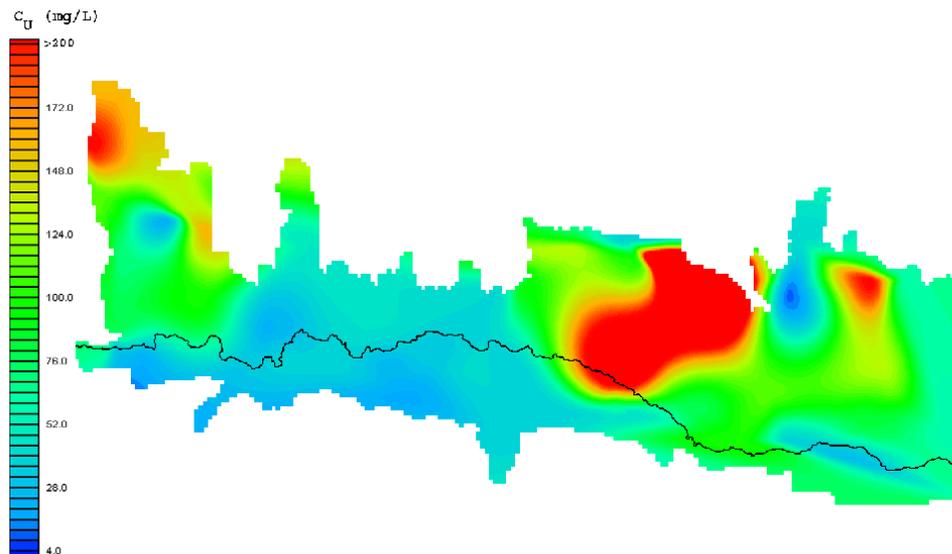


**Figure 9**. Contour plot of U concentration from samples collected during July 18 – 23 2005.

Using the least-squares criteria, a two parameter power function was fit to the groundwater data using the Levenberg-Marquardt estimation procedure

(Moré 1977). Extreme data points stand out in the ground water relationship and it is unclear from the depiction what type of relationship (if any) exists. In order to examine the relationships within the bulk of the data set, extreme values were removed where the *EC* was greater than 12 decisiemens per meter (dS/m) and where $C_{Se}$ was greater than 240 (µg/l) as shown in Figure 10. There appears to be considerable uncertainty in the relationship, as indicated by the scatter about the fitted curve.
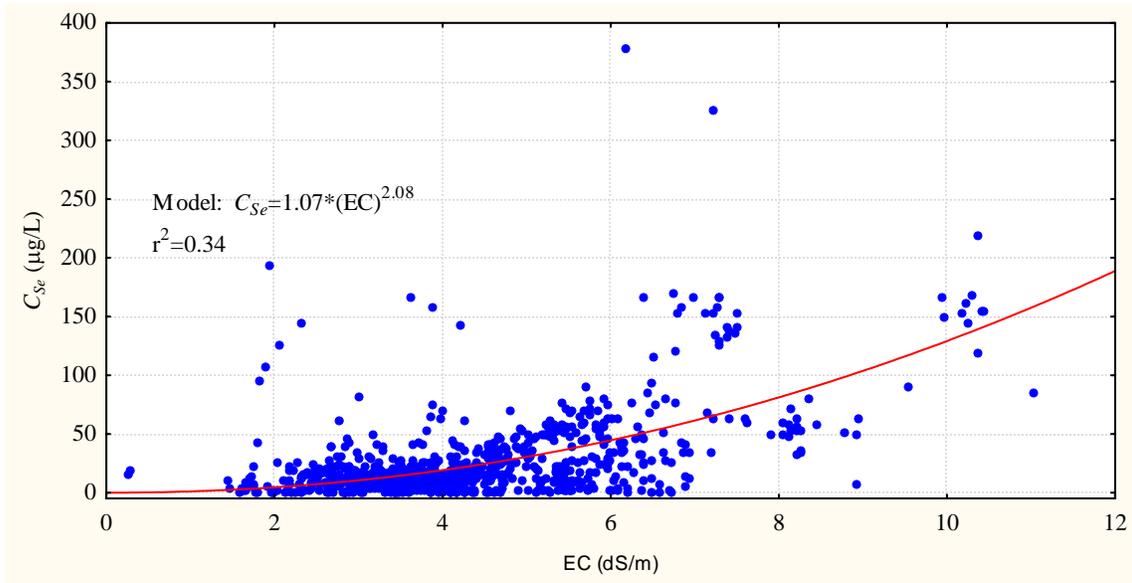


**Figure 10.** Se concentration versus EC in the ground water samples (excluding data when EC>12 dS/cm or Se>240 µg/L).

Further relationships were explored between $C_{Se}$ and the major salt ions. The most promising bivariate relationship was between $C_{Se}$ and sulfate concentration, $C_{SO_4}$, in the surface water as shown in Figure 11. A multivariate nonlinear regression with $C_{SO_4}$ and nitrate concentration, $C_{NO_3}$, explained even more of the variance in $C_{Se}$, as may be seen in the observed values of $C_{Se}$ versus the values predicted by the fitted multivariate equation as shown in Figure 12.
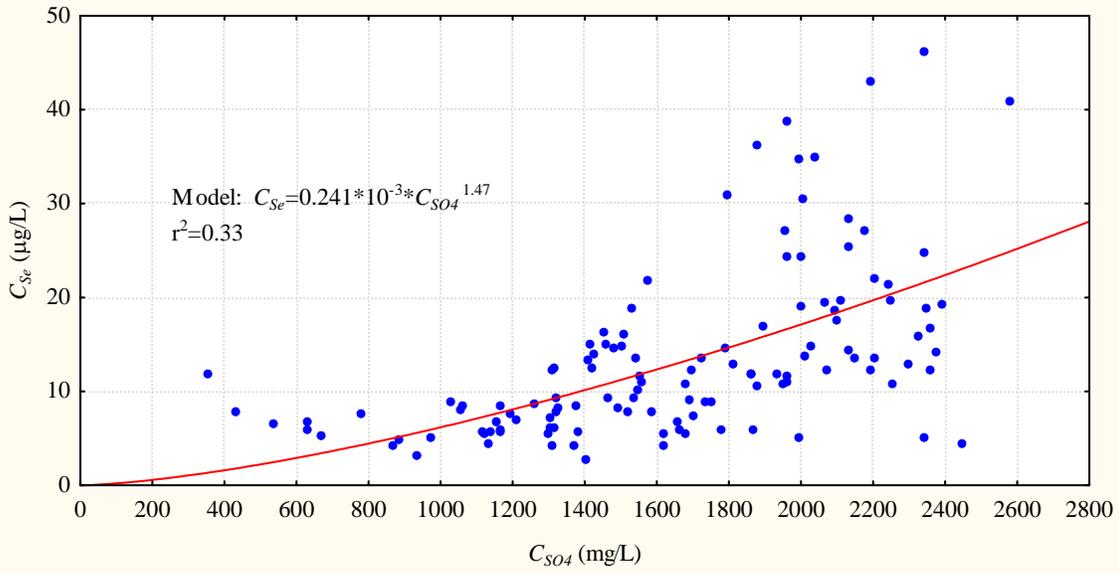
**Figure 11.** Se concentration versus SO$_4$ concentration for all surface water samples.
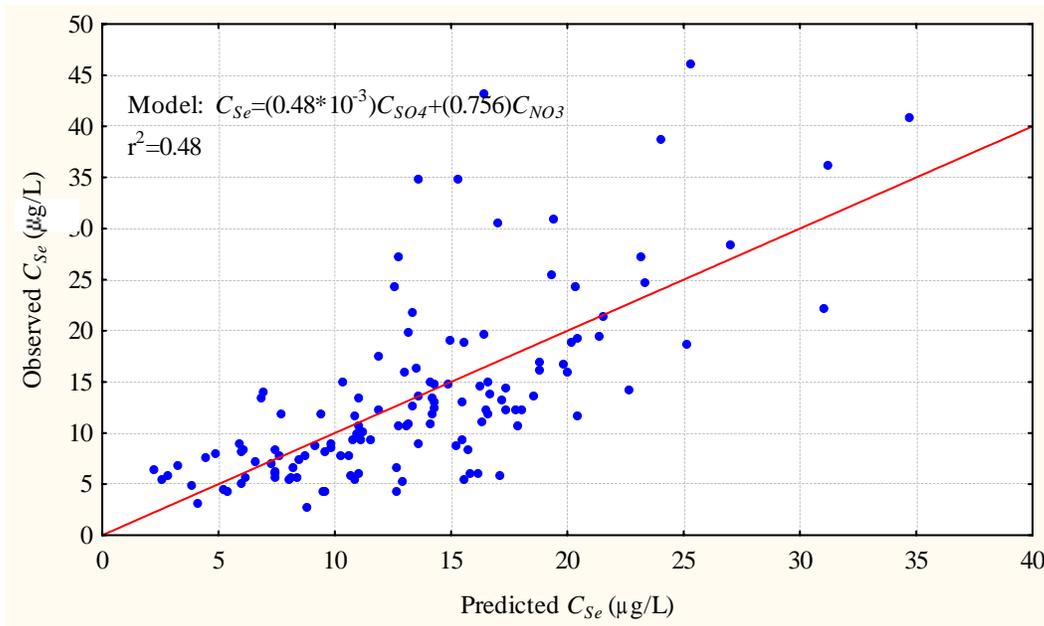


**Figure 12.** Observed Se concentrations in surface water compared to concentrations predicted by a multivariate relationship with SO$_4$ and NO$_3$ concentrations.

## 3. Conclusions and Future Research Plans

Overall, selenium concentrations in the study area are higher than the 20 (µg/l) Colorado groundwater standard for agricultural use (CDPHE 2001a). The selenium concentrations vary across the Arkansas River Basin, but three

main "hot spots" have been detected in the region.  There does not appear to be significant seasonal fluctuation in the central tendency of dissolved Se concentrations in the continuously-monitored ground water data.  However, it appears that the variability of Se in the ground water slightly increases during the irrigation season (from approximately June and July) and decreases during the off season (approximately November through March ).  Further analysis exploring relationships between Se concentrations and average recharge rates, drainage rates, and river flow rates are needed to verify this phenomenon.

Concentrations of dissolved Se in the Arkansas River have routinely exceeded the current standard for aquatic habitat.  The mean sampled river concentration is a little over double the standard.

The ground water and surface waters in the Arkansas River Valley may be sufficiently oxidized to allow for the dissolution and mobilization of Se. Therefore, *ORP* monitoring may not be useful in quantifying Se concentration in the Valley.

Significant relationships exist between Se concentration and *EC* and $SO_4$ concentration.  Nonlinear forecasting relationships were developed between Se concentration and *EC,* $SO_4$, and $NO_3$ concentration data.  Uranium sampling was performed on July 18-23, 2005, and it appears that there is a significant relationship between uranium and selenium concentrations.  Since high U concentrations have earlier been linked to marine shale and shale-derived soils in the Valley (Zeilinski et al 1995), the significant relationship between $C_{Se}$ and $C_U$ suggests a similar linkage between $C_{Se}$ and the presence of shale formations. Additional sampling will be performed in March and May of 2006 to help enhance this relationship.  Also, monitoring wells in a region upstream of the current study area will be sampled during summer 2006 to further explore selenium and uranium concentrations.

A flow and balance model of the unconfined aquifer in the study area using Groundwater Modeling System (GMS$^{TM}$) software version 6.0 (BYU 2005) is currently being developed and calibrated against field data with salinity and selenium concentrations.  A steady state model is initially being created, and transient flow and transport models will be produced once the steady state model is calibrated and running properly. This model will be used to predict selenium concentrations under a variety of improved water management alternatives.

## Acknowledgements

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