

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

Joseph P. Donnelly¹

Graduate Research Assistant and MS candidate, Civil Engineering Department, Colorado State University, Fort Collins

Timothy K. Gates²

Professor, Civil Engineering Department, Colorado State University, Fort Collins

Abstract. Water quality data on Se and Fe have been collected since April 2003 in a study area of the lower Arkansas River valley, Colorado. Data were obtained from 19 surface water locations and from 50 ground water monitoring wells using low-flow sampling techniques. GIS mapping and statistical analysis were used to characterize the occurrence, severity, and spatial and temporal distribution of Se and Fe in the study area. Results indicate dissolved Se concentrations ranging from about 0 to 3560 µg/L with a median of about 16 µg/L in the ground water, including two significant hot spots. River concentrations range from 5.4 to 23 µg/L, often exceeding stream standards. Dissolved Fe concentrations in the wells range from about 0 to 1560 µg/L, however only about twenty percent of the samples were above the analytical detection limit. Relationships were explored between Se concentrations and more-easily monitored indicators such as electrical conductivity and sulfate concentration. Statistically significant non-linear relationships exist between Se and these constituents and will be tested for predictive capability.

1. Introduction

Intensive irrigation of alluvial soils, derived from underlying marine sedimentary rocks, can accelerate dissolution and mobility of metals, like selenium (Se) and iron (Fe), in the underlying alluvial aquifer that flows to the river. Consequently, the concentration of these dissolved metals in ground waters and surface waters can rise to levels that may threaten the health and safety of humans, animals, and aquatic life. Evidence suggests that these processes are occurring as non-point source pollution in the lower Arkansas River Valley of Colorado. The study described herein aims to provide the background for an agricultural TMDL development on a river-segment scale.

Thirteen segments of the Arkansas River are designated “water quality limited” with respect to Se and/or Fe and are 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

¹ Civil Engineering Department
Colorado State University, Fort Collins, CO 80523-1372
Tel: (970) 491-5387
e-mail: Joseph.Donnelly@colostate.edu

² Civil Engineering Department
Colorado State University, Fort Collins, CO 80523-1372
Tel: (970) 491-5043
e-mail: tkg@engr.colostate.edu

Control Division is in the process of determining the nature of the elevated levels of Se and Fe in the Arkansas River.

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

Approximately 50 monitoring wells and 19 surface water monitoring points have been sampled six times over the past nine months for dissolved Se, dissolved 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 a GIS coverage of individual fields and the location of monitoring sites is shown in Figure 1.

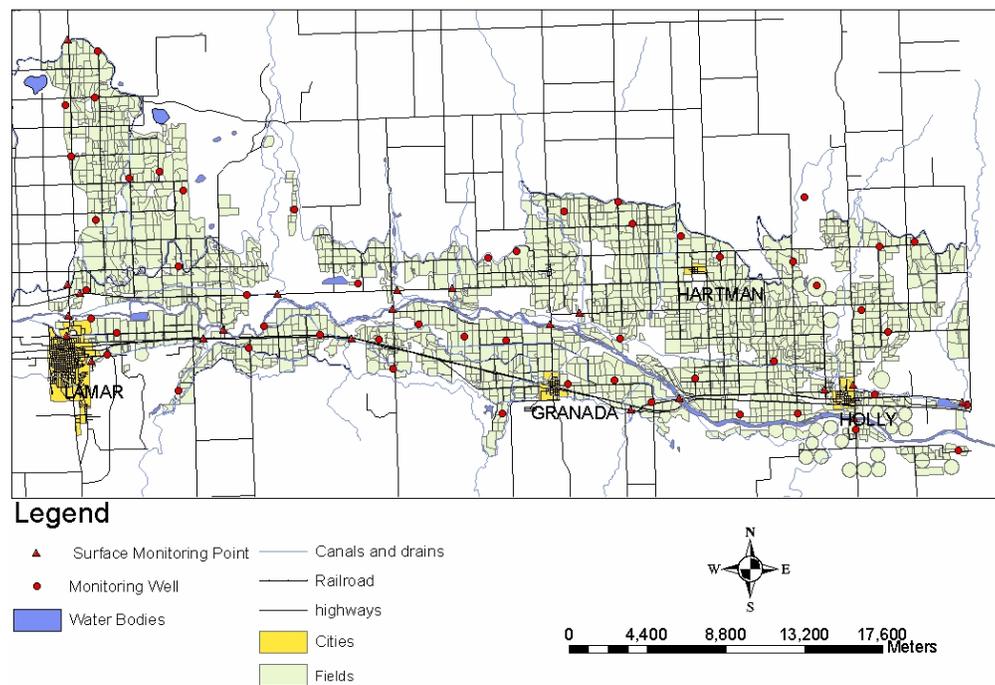


Figure 1. The study area and sampling locations

2. Data Analysis

2.1 General Statistics

Histograms were completed of Se and Fe concentrations for six sample sets collected to date. The histograms were developed using STATISTICA[®] (StatSoft 2003) and are included in Figures 2 through 5. To visually examine

the relevance of measured concentrations of Se in the study area, standards were indicated on each histogram. For ground water assessment, the 20 $\mu\text{g/L}$ Colorado ground water standard for agricultural use (CDPHE 2001a) was included. The Arkansas River samples were compared against the Colorado chronic aquatic life standard of 5.0 $\mu\text{g/L}$ (CDPHE 2001b) and the temporary lower Arkansas River segment 1c standard of 14 $\mu\text{g/L}$ (CDPHE 2003). There appear to be Se levels in the study area that exceed use these protective standards.

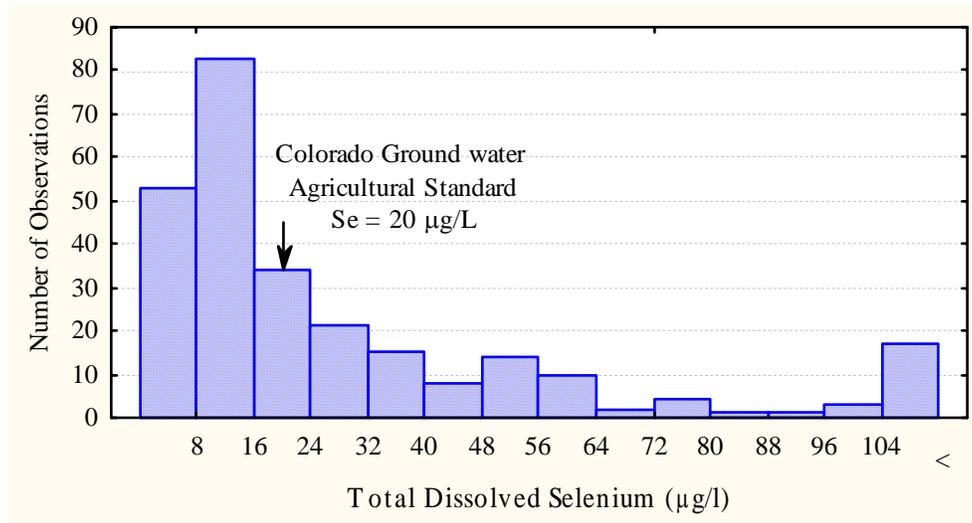


Figure 2. Total dissolved selenium in ground water samples

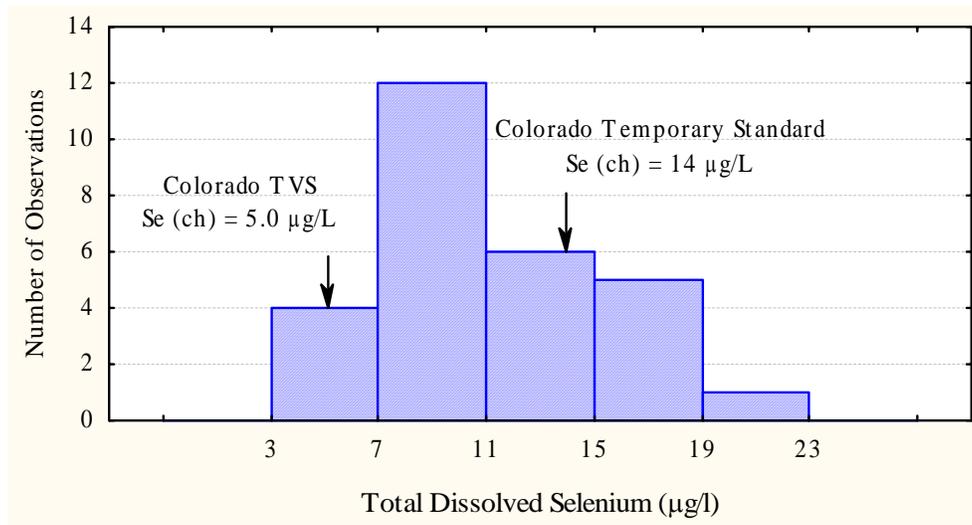


Figure 3. Total dissolved selenium in Arkansas River samples

Dissolved Fe concentrations are relatively low in the study area. All dissolved Fe concentrations in the Arkansas River are below the analytical detection limit of 10 $\mu\text{g/L}$. The Colorado chronic dissolved Fe standard is 300 $\mu\text{g/L}$ (CDPHE 2001b), significantly higher than the data depicted on the Fe histograms and indicating very little soluble Fe in the study area.

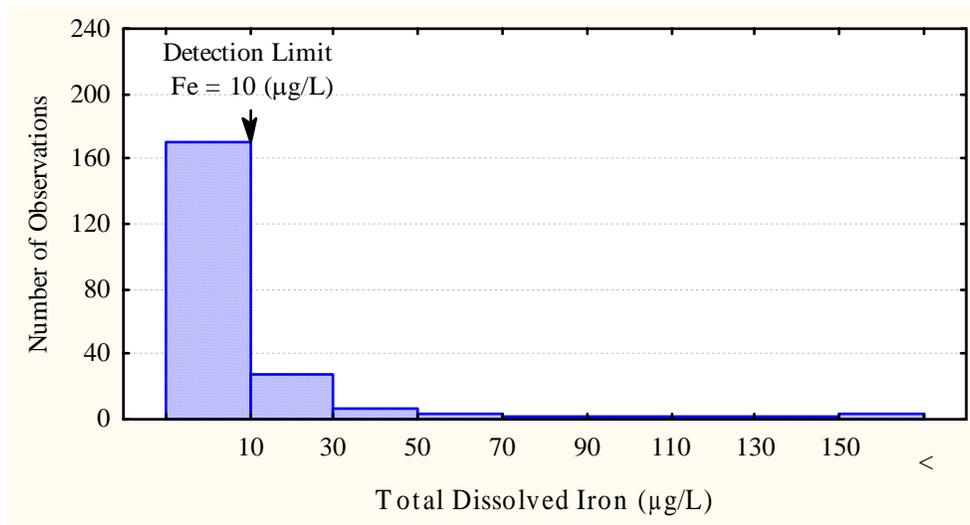


Figure 4. Total dissolved iron in ground water samples

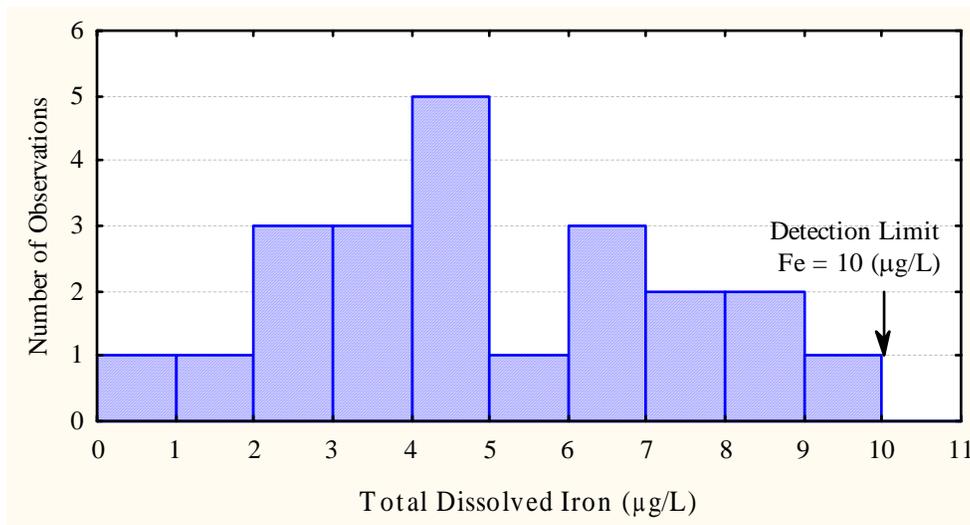


Figure 5. Total dissolved iron in Arkansas River samples

Statistical summaries of the Se and Fe data are given in Tables 1 and 2. The ground water Se samples range over five orders of magnitude. This skews the sample mean right of the median, as is apparent from the large standard deviation and skewness. The maximum value of 3560 µg/L was determined from a sample taken at well number 306 on April 26, 2003. Throughout the rest of the study, samples collected at this well indicate consistently high Se concentrations.

Dissolved Fe concentrations are relatively low throughout the study area. Concentrations from the analytical analysis were reported, even when below the analytical detection limit. Negative numbers were assumed to be zero. The median and mean dissolved Fe concentrations in each data set are below the analytical detection limit. The exception occurs in the ground water where there is a mean dissolved Fe concentration of 23.2 µg/L. The mean is skewed right primarily from one Fe concentration data point of 1560 µg/L which was taken at well 347 on April 28, 2003. The remaining Fe concentrations ana-

lyzed at this well are significantly below the detection limit indicating that the single high dissolved Fe concentration is a legitimate outlier in the data set. Due to low and non-existent dissolved Fe concentrations in the study area, no further analysis was completed for dissolved Fe.

Table 1. Summary statistics of dissolved Se ($\mu\text{g/L}$)

Statistic	Ground water	Surface Water	Arkansas River
Size of Population	265	81	28
Mean	102.41	14.11	11.55
Median	16	11	9.975
Maximum	3560	43.2	23
Minimum	0.2	2.45	5.41
Standard Deviation	493.94	9.58	4.72
Skewness	6.45	1.42	0.71

Table 2. Summary statistics of dissolved Fe ($\mu\text{g/L}$)

Statistic	Ground water	Surface Water	Arkansas River
Size of Population	219	71	22
Mean	23.20	6.73	4.99
Median	3.7	5.2	4.55
Maximum	1560	30.4	9.73
Minimum	0	0.4	0.6
Standard Deviation	117.64	5.23	2.38
Skewness	11.02	1.95	0.25

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 whiskers plot in Figure 6 illustrates a summary of the statistical analysis. The central squares on the plot represent the median Se concentration at each point in time. The outer squares represent the 25th and 75th percentiles while the whiskers extend to the non-outlier range of the data set. The highest and lowest values were omitted from the data set to decrease biasing from extreme values. Outliers were systematically determined as values that are more than two times the difference of the 25th and 75th percentiles higher than the 75th percentile. The outliers are shown on the plots.

The results indicate that the median of each data set is not changing over time. However, it appears that the variability of the data decreases during the irrigation season (from approximately April through October) and increases during the off season (approximately November through March). Contrary to the results, more variability was expected during the irrigation season when the hydraulic gradient in the ground water increases from recharge due to excess irrigation. However, due to drought conditions in southeastern Colorado over the sampling period, minimal irrigation water was applied over the summer months. Further analysis exploring relationships between Se concentrations and average recharge rates, drainage rates, and river flow rates are needed to verify this phenomenon.

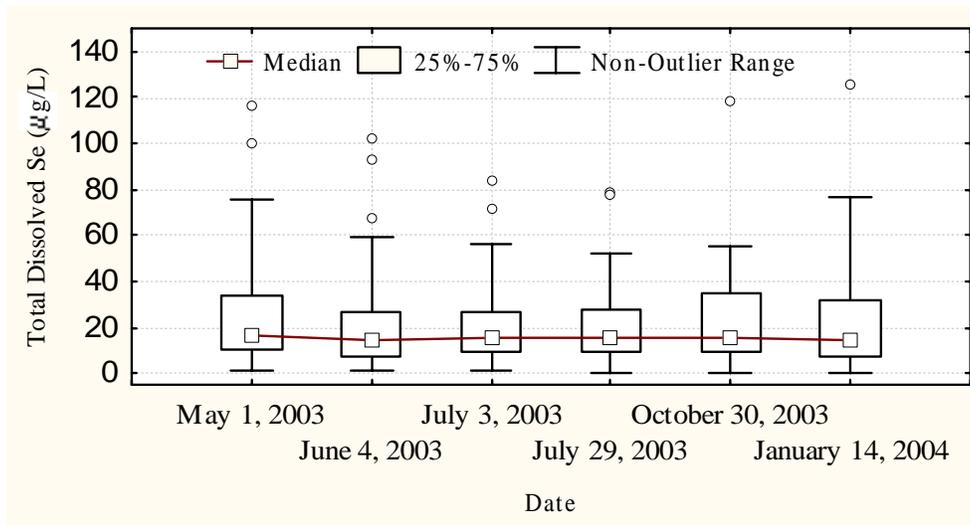


Figure 6. Box and Whiskers plot of dissolved Se data

Figures 7 and 8 provide samples of GIS maps of Se developed during the mid-summer and fall sampling events. The contours were estimated in GMS™ (BYU 2003) utilizing the “natural-neighbor” interpolation method.

The contour plots depict the spatial variability in Se throughout the study area. The western “hot-spot” is centered around well number 306, which has consistently indicated high levels of Se. The study area has relatively low Se concentrations uniformly throughout the middle portion. The eastern portion of the study area has two distinct hot-spots, which seem to change in magnitude throughout time. In series, the contour maps depict some temporal variation as revealed from the slightly changing shape of the hot-spots in the eastern portion of the region.

During the coming year, five additional wells will be completed and routinely monitored to help understand the extent and significance of the hot-spots located in the study area.

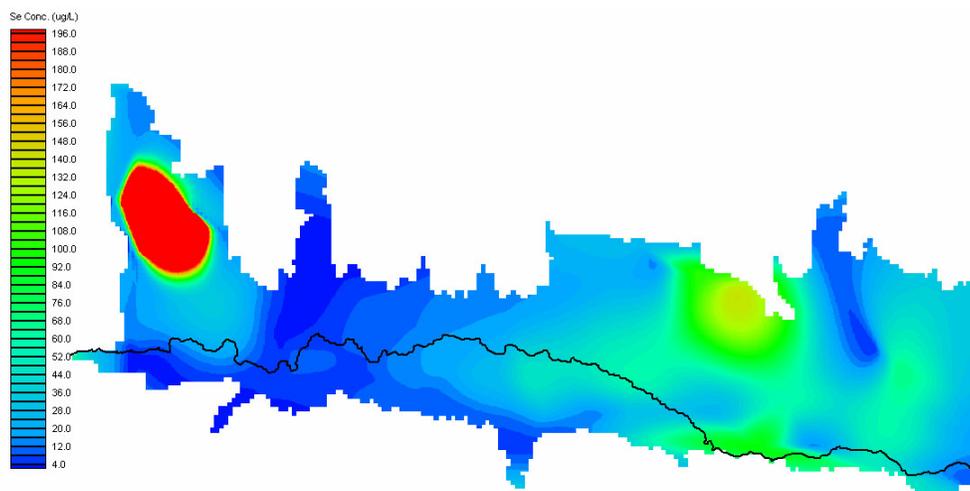


Figure 7. Contour plot of Se from samples collected from May 29 to June 11, 2003

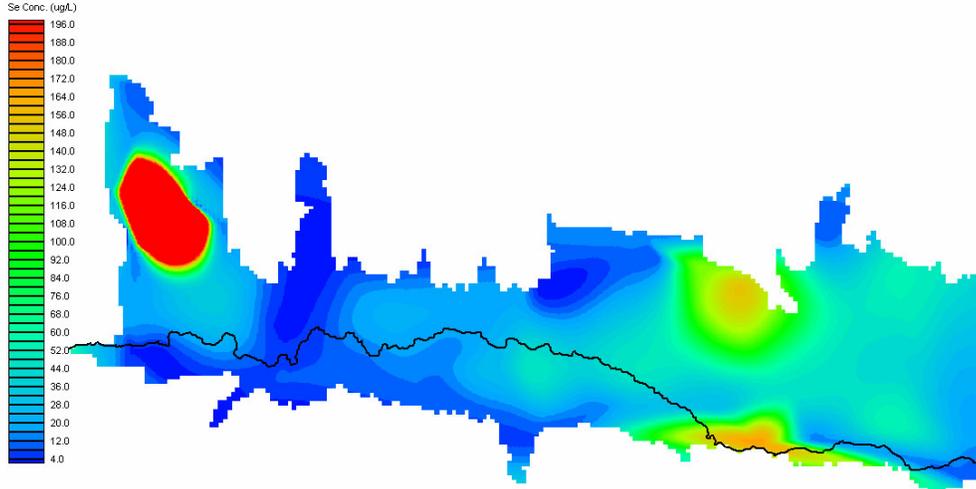


Figure 8. Contour plot of Se from samples collected from Oct. 25 to Nov. 2, 2003

2.3 Relationships Between Water Quality Variables

Relationships were explored between Se concentration and *EC*, pH, *DO*, *ORP*, nitrate (NO_3) concentration, and sulfate (SO_4) concentration. There appears to be significant correlation between Se and *EC* and SO_4 , however there is little to no correlation between Se and the other monitored constituents. Figure 9 shows a scatter plot of Se concentration versus *EC*. Data collected from wells 306 and 371 stand out in the plot and it is unclear from the depiction in Figure 9 what type of relationship (if any) exists. In order to examine relationships within the bulk of the data set, data from wells 306 and 371 were removed from the population and Figures 10 and 11 were produced.

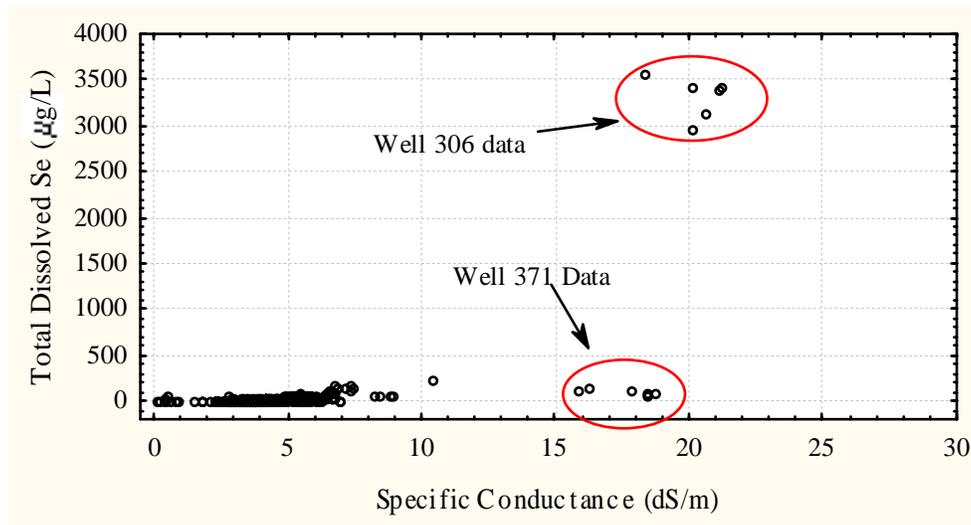


Figure 9. Dissolved Se versus EC

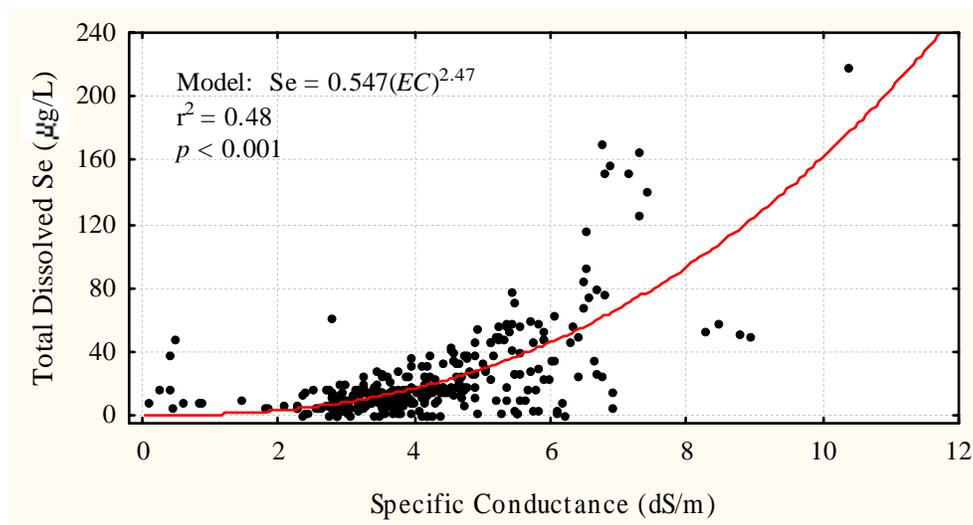


Figure 10. Dissolved Se versus EC (excluding data from wells 306 and 371)

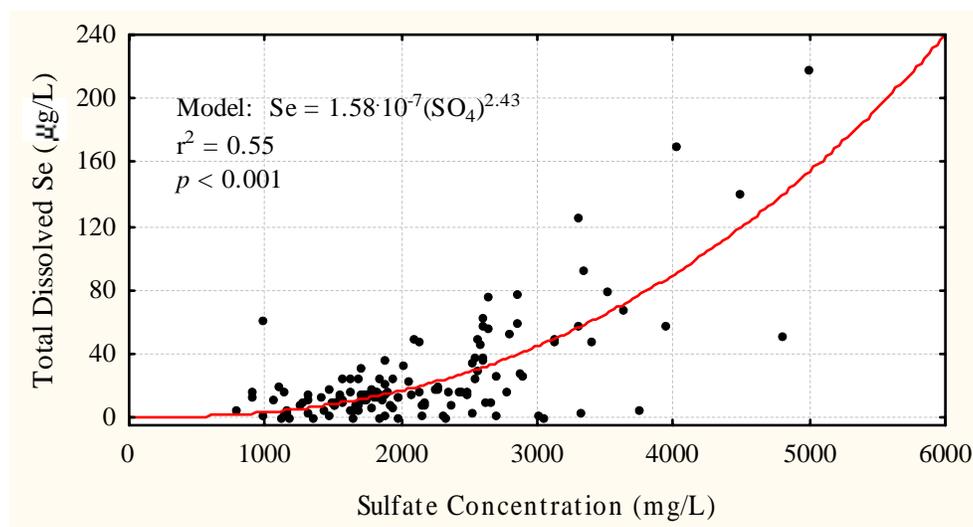


Figure 11. Dissolved Se versus SO_4 (excluding data from wells 306 and 371)

Previous research has attempted to correlate Se with both *EC* and SO_4 at Kesterson Reservoir in California. Linear relationships were developed between Se and SO_4 where SO_4 concentrations remained below 4000 mg/L (White et al 1991). Additional nonlinear power relationships were quantified by Fujii and Deverel (1989) for Se and *EC* data from Kesterson Reservoir. However, both of these studies were completed in a smaller region where elevated Se levels are primarily the result of evaporative concentration. It is apparent from the Arkansas River data that the best-fit relationship will be nonlinear. Using STATISTICA[®] (StatSoft 2003) and a least-squares regression criteria, a two parameter non-linear model was fit with the Levenberg-Marquardt algorithm (Moré 1977). The resulting relationships are depicted in the figures 10 and 11. Although the *p*-levels indicate the fitted relationships are statistically significant, there appears to be substantial uncertainty about each relationship. The estimated relationship was removed from the Se con-

centration values and the resulting residuals were plotted and fit with normal probability distributions as shown in figures 12 and 13.

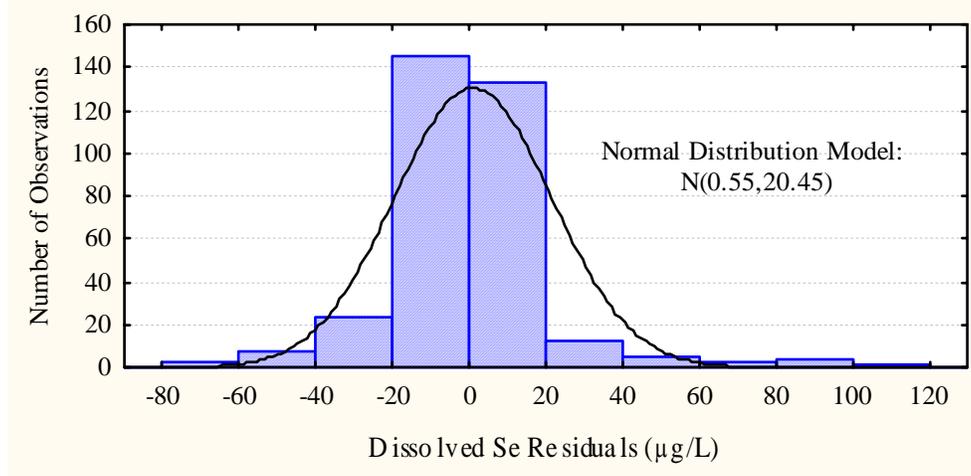


Figure 12. Selenium residuals from the Se-EC correlation

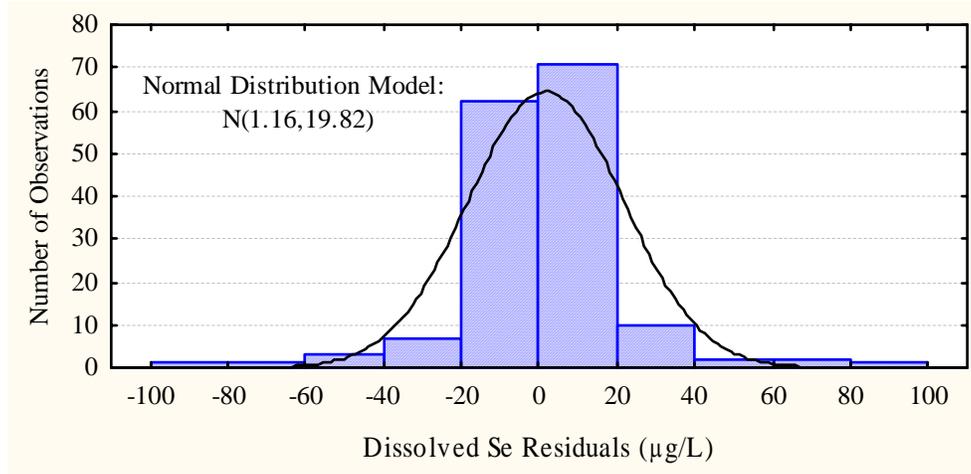


Figure 13. Selenium residuals from the Se-Sulfate correlation

Combining the nonlinear regression models with the uncertainty demonstrated by the residuals, three parameter-forecasting models were produced. The forecasting relationships are shown in Equations 1 and 2. The values of ε_1 and ε_2 represent normal random residuals for Se in the *EC* and *SO₄* (expressed as concentration) relationships, respectively, generated from a probability distribution model of the form $N(\text{mean}, \text{standard deviation})$:

$$\text{Se} = 0.547\text{EC}^{2.47} + \varepsilon_1 \quad (1)$$

Where : $\varepsilon_1 \in N(0.55,20.45)$

$$\text{Se} = 1.58 \cdot 10^{-7} \text{SO}_4^{2.43} + \varepsilon_2 \quad (2)$$

Where : $\varepsilon_2 \in N(1.16,19.82)$

Although using SO_4 concentration to predict dissolved Se concentration seems to provide more reliability, *EC* data are easier and less costly to monitor than SO_4 . If the resulting reliability of each equation proves to be marginal, it may not be worth the additional expense of collecting SO_4 data for Se estimation. During the coming year, approximately 40 additional wells will be sampled and analyzed for Se, SO_4 , and *EC*. This independent data will be used to test the predictive capability of each forecasting model.

3. Significance of Results and Plans for Future Work

Overall, dissolved Se concentrations in the study area are higher than expected while dissolved Fe concentrations are significantly lower than expected. As such, more focus and effort will be made to collect additional Se samples, while dissolved Fe samples will be reduced.

DO, *ORP*, pH, and temperature are not strongly correlated with Se concentration in the lower Arkansas River valley samples; however, *DO* and *ORP* data indicate that the water in the shallow alluvial aquifer and surface water is fairly oxidized. This helps to explain the relatively high levels of dissolved Se and low levels of dissolved Fe in the study area. Dissolved Se is thermodynamically in equilibrium as selenate, Se(VI), in oxidized environments although it can be stable as selenite, Se(IV), in less oxidized environments. It was assumed that the total dissolved Se is present primarily in these two oxidation states. In order to empirically explore the possibility of determining Se concentrations from *ORP* measurements, a laboratory analysis was conducted for selenite in a subset of the data. Using total dissolved selenium and selenite analysis, the amount of selenate was calculated. The data indicate that over 90 percent of Se is in the most oxidized form, selenate (SeVI). This shows that waters in the lower Arkansas River valley may be sufficiently oxidized and that the *DO* and *ORP* may not be a limiting factor for Se dissolution.

Fe in the natural environment exists in two oxidation states: ferrous Fe(II) and ferric Fe(III). Ferric Fe is the oxidized form of Fe. At the pH range of natural waters (about 5 to 9) ferric Fe will precipitate to ferric hydroxide and ferric oxyhydroxides, which are largely insoluble (i.e. will not pass through a 0.45 μm filter). Therefore, assuming there is a source of Fe in the underlying bedrock and soils in the study area, the sampling results indicate that Fe is present in the oxidized insoluble state throughout the surface and ground waters of the study area.

Since ground and surface water in the lower Arkansas River Valley is fairly oxidized, it may be unnecessary to test for dissolved Fe in the following years of data collection. Possibly, Fe exists in the study area in an oxidized ferric state and is insoluble in the oxidized environment. Hence, future sampling will include total recoverable Fe samples in the surface water samples.

EC is a surrogate measure of the total dissolved ions in the water. Although dissolved Se only accounts for a fraction of these ions, there is physical rationale to propose a significant relationship between the two constituents. Also, Se has similar chemical characteristics to sulfur, the central atom of the SO_4 compound. These elements are each in the oxygen group and have the same four oxidation states (McNeal and Balistrieri 1989).

It appears that there is more variability of Se concentration in the ground water during the off season as opposed to the irrigation season. After a complete year of data collection, a statistical analysis, including the Seasonal Kendall test, will be used to test if the central tendency of Se concentration is indeed changing over time. Furthermore, following continued study, it is hoped that evidence of the impact of the drought on Se and Fe concentrations will emerge from this database.

Acknowledgements. The support of the Environmental Protection Agency, the Colorado Water Quality Control Division, the Natural Resources Conservation Service, the Colorado Agricultural Experiment Station, and Colorado State University is gratefully acknowledged.

References

- Brigham Young University (BYU), 2003: The department of defense ground-water modeling system: GMS, Version-3.1.
- Colorado Department of Public Health and Environment (CDPHE), Water Quality Control Commission, 2001a: Regulation Number 41 – The Basic Standards for Ground water, 65.
- Colorado Department of Public Health and Environment (CDPHE), Water Quality Control Commission, 2001b: Regulation Number 31 – The Basic Standards and Methodologies for Surface Water, 169.
- Colorado Department of Public Health and Environment (CDPHE), Water Quality Control Division, 2002: Water Quality Limited Segments Still Requiring TMDLs – Colorado’s 2002 303(d) List and Monitoring and Evaluation List, 46.
- Colorado Department of Public Health and Environment (CDPHE), Water Quality Control Commission, 2003: Regulation Number 32 - Classification and Numerical Standards for Arkansas River Basin, 81.
- Fujii, R., and Deverel, S. J., 1989: Mobility and Distribution of Selenium and Salinity in Ground-water and Soil of Drained Agricultural Fields, Western San Joaquin Valley of California. *Selenium in Agriculture and the Environment*, New Orleans, LA, Soil Science Society of America, Inc., 233.
- McNeal, J. M., and Balistrieri, L., S., 1989: Geochemistry and Occurrence of Selenium: An Overview. *Selenium in Agriculture and the Environment*, New Orleans, LA, Soil Science Society of America, Inc., 233.
- Moré, J., J., 1977. The Levenberg-Marquardt Algorithm: Implementation and Theory. *Lecture Notes in Mathematics* (Berlin), **630**, 105-116.
- StatSoft®, 2003: STATISTICA, Version 6.1.
- White, A. F., Benson, S.M., Yee, A.W., Wollenberg, H. A., and Flexser, S., 1991: Groundwater Contamination at Kesterson Reservoir, California .2. Geochemical Parameters Influencing Selenium Mobility. *Water Resource Research*, **27**, 1085-1098.