

# Selenium Transformations in Salinity-Affected Agricultural Drainage Water Management Areas of California as Determined by Selenium Stable Isotope Ratios

Mitchell Herbel<sup>1</sup>, Suduan Gao<sup>2</sup>, and Thomas Johnson<sup>3</sup>

<sup>1</sup>USDA-ARS, George E. Brown, Jr., Salinity Laboratory, Riverside, CA, mherbel@ussl.ars.usda.gov.

<sup>2</sup>USDA-ARS, SJVASC, Water Management Research Unit, Parlier, CA

<sup>3</sup>Dept. of Geology, University of Illinois, Champagne-Urbana, IL.

## 1 INTRODUCTION

The trace element selenium is of high concern in many salt-affected areas of the Western U.S. and the world due to its potential to become toxic to plants and wildlife at elevated concentrations. In many agricultural regions in the Western San Joaquin Valley of California, evapoconcentration of irrigation drainage water has increased Se concentrations in soils, sediments, and shallow ground waters, which has posed a significant risk to wildlife (Tanji et al., 1986). To decrease the effects of salinity, and to a lesser extent, trace elements, on irrigated agriculture and wildlife in the San Joaquin Valley, various management strategies have been tested and/or implemented (Engberg et al., 1998). For example, saline drainage waters could be mixed with lower salinity waters and re-used on crops, applied to more salt-tolerant plants, impounded in evaporation basins, or passed through wetlands to facilitate removal of hazardous trace elements. The effects of these strategies on Se biogeochemical cycling are relatively unknown.

Predicting the behavior (speciation), transport, and fate of Se in these drainage water management regions is challenging due to the ability of Se to exist in multiple oxidation states and in various inorganic and organic forms. Fortunately, Se has six naturally occurring stable isotopes (masses 74, 76, 77, 78, 80, and 82), thus, measuring and comparing specific Se isotope ratios in select samples from Se affected localities may provide a means to better determine the fate of Se in these water management systems. In this investigation we measured Se isotope ratios in various water, soil and plant samples from the experimental Tulare Lake Drainage District (TLDD) flow-through wetland (recently decommissioned), which was used as a model system to understand the dynamics of Se after it enters the wetland as Se(VI) in agricultural drainage water. By measuring and comparing <sup>80</sup>Se/<sup>76</sup>Se ratios, we were able to show that the major transformation product for aqueous Se(VI) was sedimentary organic Se and Se(0) via biological assimilation and mineralization (Herbel et al., 2002). In this way, Se isotopes can be used to better characterize and predict Se transport and biogeochemical cycling.

## 2 STUDY METHODS

Surface and pore water samples were collected from the TLDD flow-through wetlands and transported to the laboratory for filtration, acidification with HNO<sub>3</sub> to pH 2, and refrigeration. Macrophyte samples were rinsed, dried at 60°C for 5 d, and ground and sieved to pass

through a 40-mesh screen. Sediment samples were collected in 5 cm diameter acrylic tubes, immediately capped, and frozen at  $-4^{\circ}\text{C}$ . Total selenium concentrations in the surface and pore waters were determined by digestion with  $\text{HNO}_3\text{-HClO}_4$  (Zasoski and Burau, 1977). Selenium speciation in the waters and select sediment extracts was determined by direct analysis using hydride generation-atomic absorption spectrometry (HG-AAS) for Se(IV) and 6 N HCl reduction at  $100^{\circ}\text{C}$  for Se(IV)+Se(VI), the difference being Se(VI). Organic-Se was the difference between total soluble Se and Se(IV)+Se(VI). Plant tissues were digested using  $\text{HNO}_3\text{-H}_2\text{O}_2$  (Zarcinas et al., 1987). Sedimentary Se was sequentially extracted using KCl (soluble),  $\text{K}_2\text{HPO}_4$  (adsorbed), NaOH (organic-Se), and  $\text{Na}_2\text{SO}_3$  (elemental Se) (Gao et al., 2000); Se in each extract was then converted to Se(VI) by total digestion using  $\text{HNO}_3$ -persulfate and then to Se(IV) by 6 N HCl reduction. All Se was quantified using HG-AAS.

For Se isotope ratio analysis, Se(VI) was selectively extracted for analysis from surface and pore waters using ferric hydroxide precipitation (Nakishima, 1979) followed by 6N HCl reduction. Total Se in plant and soil digests was converted to Se(IV) by 6 N HCl reduction. The Se(IV) in all samples was mixed with an  $^{82}\text{Se}/^{74}\text{Se}$  double spike and purified by conversion to  $\text{H}_2\text{Se}$  in a  $\text{NaBH}_4\text{-HCl}$  flow-through system, with the Se being trapped in concentrated  $\text{HNO}_3$  (Johnson et al, 1999). After evaporation of the acid the Se was deposited on an Re filament for negative thermal ionization mass spectrometry analysis. The  $^{80}\text{Se}/^{76}\text{Se}$  ratios were determined by iterative measurement of the various Se isotopes using a Finnigan 261 mass spectrometer, followed by a data reduction routine which used the double spike values to correct mass discrimination during purification and Se isotope measurement. Values were reported as  $\delta^{80/76}\text{Se}$  (‰) using equation 1:

$$\delta^{80/76}\text{Se}(\text{‰}) = \frac{\left(\frac{^{80}\text{Se}}{^{76}\text{Se}}\right)_{\text{sample}} - \left(\frac{^{80}\text{Se}}{^{76}\text{Se}}\right)_{\text{std}}}{\left(\frac{^{80}\text{Se}}{^{76}\text{Se}}\right)_{\text{std}}} \times 1000 \quad (1)$$

using MH495 ( $\text{SeO}_2$  in  $\text{HNO}_3$ ) as the standard Se for comparison to the samples.

### 3 RESULTS AND DISCUSSION

Dissolved Se concentrations, speciation, and  $\delta^{80/76}\text{Se}$  values of the Se(VI) across two of the flow-through cells are shown in Figure 1. The major forms of soluble Se changed from predominantly Se(VI) to Se(IV) and Org-Se across the cells from inlet to outlet, reflecting biological reduction and conversion in the water column and/or sediments. The  $\delta^{80/76}\text{Se}$  values of the Se(VI) showed little change from the inlet to outlet, remaining near 3.7‰. The Se content and  $\delta^{80/76}\text{Se}$  values for the plant digests and sediment sequential extracts are listed in Table 1. The  $\delta^{80/76}\text{Se}$  for the plant digests averaged  $2.91 \pm 0.20$ ‰, a minor but significant decrease from the Se(VI) in the water column. The Se content and  $\delta^{80/76}\text{Se}$  values for the sediment extracts are listed for only the  $\text{K}_2\text{HPO}_4$ , NaOH, and  $\text{Na}_2\text{SO}_3$  extracts, which solubilize the major pools of sedimentary Se (adsorbed, organic, and elemental forms). Compared to the  $\delta^{80/76}\text{Se}$  values for Se(VI) in the water column,  $\delta^{80/76}\text{Se}$  values for Se in the 0-5 cm  $\text{K}_2\text{HPO}_4$  sediment extracts were similar, but  $\delta^{80/76}\text{Se}$  values for Se in the 0-5 cm NaOH and  $\text{Na}_2\text{SO}_3$  extracts were significantly lower ( $p < 0.05$ ). The  $\delta^{80/76}\text{Se}$  values for Se in the macrophytes were similar to  $\delta^{80/76}\text{Se}$  values for Se in the 0-5 cm NaOH and  $\text{Na}_2\text{SO}_3$  extracts.

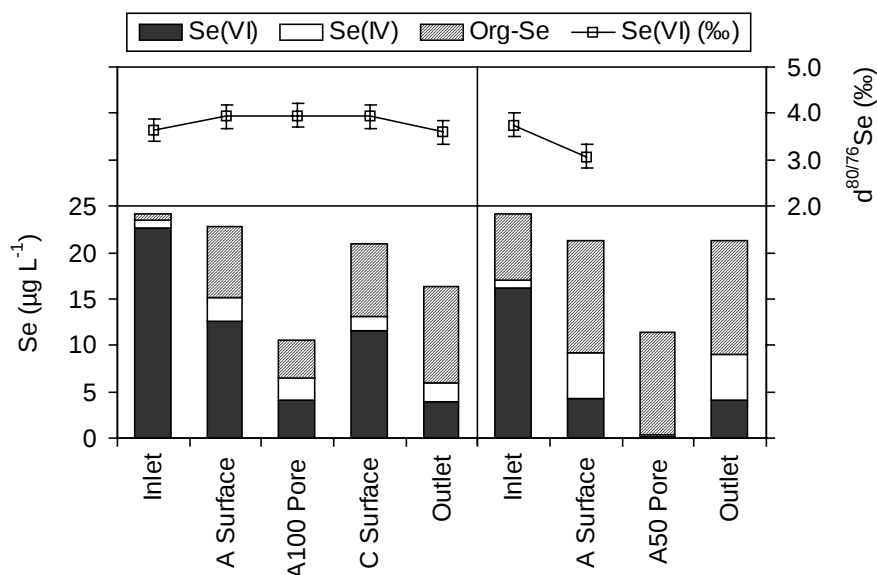


Figure 1. Selenium speciation and  $\delta^{80/76}\text{Se}$  values for Se(VI) in TLDD flow-through wetland surface and pore waters.

Table 1. Selenium concentrations and  $\delta^{80/76}\text{Se}$  values in macrophytes and sediment sequential extracts from the TLDD flow-through wetlands.

|                                           | Samples | Selenium Concentrations  | $\delta^{80/76}\text{Se}$ | $\delta^{80/76}\text{Se}$ Average | $\delta^{80/76}\text{Se}$ Standard Deviation |
|-------------------------------------------|---------|--------------------------|---------------------------|-----------------------------------|----------------------------------------------|
|                                           | (No.)   | (mg/Kg)                  | (‰)                       | (‰)                               | (‰)                                          |
| <i>Macrophytes</i>                        |         |                          |                           |                                   |                                              |
| Rabbitsfoot Grass                         | 1       | 8.55                     | 2.80                      |                                   |                                              |
| Saltmarsh Bulrush-shoots                  | 1       | 4.33                     | 2.97                      |                                   |                                              |
| Saltmarsh Bulrush (roots)                 | 1       | 13.93                    | 2.63                      |                                   |                                              |
| Cattail                                   | 1       | 8.46                     | 3.01                      |                                   |                                              |
| Widgeon Grass                             | 1       | 15.02                    | 3.15                      |                                   |                                              |
|                                           | 5       |                          |                           | 2.91                              | 0.20                                         |
| <i>Sediment Sequential Extracts</i>       |         |                          |                           |                                   |                                              |
| K <sub>2</sub> HPO <sub>4</sub> (0-5 cm)  | 3       | 0.15 - 0.34 <sup>†</sup> |                           | 3.63                              | 0.30                                         |
| K <sub>2</sub> HPO <sub>4</sub> (5-10 cm) | 2       | 0.01 - 0.10              |                           | 1.59                              | 1.40                                         |
| NaOH (0-5 cm)                             | 4       | 0.38 - 0.60              |                           | 3.01                              | 0.26                                         |
| NaOH (5-10 cm)                            | 2       | 0.10 - 0.11              |                           | 5.25                              | 0.16                                         |
| Na <sub>2</sub> SO <sub>3</sub> (0-5 cm)  | 4       | 0.33 - 0.44              |                           | 3.28                              | 0.24                                         |
| Na <sub>2</sub> SO <sub>3</sub> (5-10 cm) | 4       | 0.09 - 0.19              |                           | 2.69                              | 0.32                                         |

<sup>†</sup> - indicates range of values

Grouping the  $\delta^{80/76}\text{Se}$  values by sample type and sediment depth, statistical analysis reveals some likely Se cycling scenarios that can reflect primarily Se reduction pathways. Selenium stable isotope fractionation, characterized by  $\epsilon$  in (‰), has been shown to be substantial ( $> 3\text{‰}$ ) only during microbial and chemical reduction of Se(VI) to Se(IV) and Se(IV) to Se(0) (Johnson and Bullen, 2004). Fractionation is minor ( $< 1\text{‰}$ ) during other important Se transformation processes, such as adsorption onto mineral surfaces, oxidation from reduced forms, plant or algae uptake, volatilization of organic selenides, etc. The minor differences between  $\delta^{80/76}\text{Se}$  values for Se(VI) in the water column and Se in the macrophytes are similar to the  $\delta^{80/76}\text{Se}$  differences between Se(VI) in the water column and Se in the organic and elemental phases in the sediments. If Se(VI) reduction was occurring primarily by microbial

respiratory (dissimilatory) reduction in the sediments, one would expect Se in these phases, particularly the  $\text{Na}_2\text{SO}_3$  extract which best removes Se(0), to be much lighter isotopically (i.e.,  $\ll 3\text{‰}$  found for Se(VI) in the water column) (Johnson and Bullen, 2004). This was not observed. These values are more reflective of plant uptake of Se(VI) and Se(IV) from the water column followed by mineralization of the organic Se in the plant tissues to Se(0), which is expected to result in only minor fractionation (Figure 2).

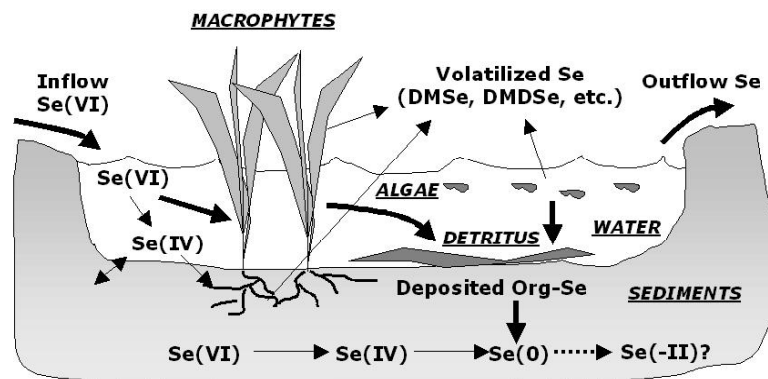


Figure 2. Selenium cycling scenarios in the TLDD flow-through wetland as determined by  $\delta^{80/76}\text{Se}$  values. Major fluxes are indicated by heavy arrows; minor fluxes are indicated by light arrows.

### 3 CONCLUSIONS

Selenium stable isotope ratio analysis revealed that for the TLDD flow-through wetland, plant uptake of Se from the water column followed by deposition of plant material and mineralization from organic Se to Se(0), is the dominant transformation pathway for Se in this agricultural water management system. Selenium stable isotope ratios can similarly be used to elucidate Se sources and transformation pathways in other salinity-affected regions in the San Joaquin Valley, CA (Herbel et al., 2002), and throughout the world.

### 4 REFERENCES

- Engberg, R.A., D.W. Westcot, M. Delamore, and D.D. Holz. 1998. Federal and state perspectives on regulation and remediation of irrigation-induced selenium problems. P. 1-25. In W.T. Frankenberger Jr. and R.A. Engberg (ed.). *Environmental chemistry of selenium*. New York: Marcel Dekker.
- Gao, S., K.K. Tanji, D.W. Peters, and M.J. Herbel. 2000. Water selenium speciation and sediment fractionation in a California flow-through wetland system. *Journal of Environmental Quality* 29:1275-1283.
- Herbel, M.J., T.M. Johnson, K.K. Tanji, S. Gao, and T.D. Bullen. 2002. Selenium stable isotope ratios in California agricultural drainage water management systems. *Journal of Environmental Quality* 31:1146-1156.
- Johnson, T.M. and T.D. Bullen. 2004. Mass-dependent fractionation of selenium and chromium isotopes in low-temperature environments. *Reviews in Mineralogy and Geochemistry* 55:289-317.
- Johnson, T.M., M.J. Herbel, T.D. Bullen, and P.T. Zawislanski. 1999. Selenium isotope ratios as indicators of selenium sources and oxyanion reduction. *Geochimica et Cosmochimica Acta* 63(18):2775-2783.
- Nakashima, S. 1979. Flotation separation and atomic absorption spectrometric determination of selenium(IV) in water. *Analytical Chemistry* 51:654-656.
- Tanji, K.K., A. Lauchli, and J. Meyer. 1986. Selenium in the San Joaquin Valley. *Environment* 28(6):6-39.
- Zarcinas, B.A., B. Cartwright, and L.R. Spouncer. 1987. Nitric acid digestion and multi-element analyses of plant material by inductively coupled plasma spectrometry. *Communications in Soil Science and Plant Analysis* 18:131-146.
- Zasoski, R.J. and R.G. Burau. 1977. A rapid nitric-perchloric acid digestion procedure for multi-element tissue analyses. *Communications in Soil Science and Plant Analysis* 8:425-436.