The Arkansas River and Shunganunga Creek Project
(Contract 2006-TMDL3)

An Extension of Contract 2005-TMDL4

Final Report

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for

Watershed Planning Section
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October 2007
Part I: Selenium levels in the water, fish, and sediment of the Arkansas River

Introduction

Selenium was the only trace constituent associated with irrigation drainage that was observed to be at elevated levels in water, bottom sediment, and biota within the Upper Arkansas River basin (Mueller et al. 1991). Selenium is usually associated with the clay content in rocks and so high concentration of selenium is often found in shales. Cretaceous marine shales and limestone are exposed extensively in that region. Thus, the main natural selenium source is runoff from the shales. Selenium becomes concentrated along the Arkansas River due to evapotranspiration and leaching of selenium by irrigation (Whitmer 2000).

This study focuses on the determination of spatial and temporal levels of selenium in water, fish, and sediment at selected sites along the upper Arkansas River in western Kansas. During the course of this study, we sampled multiple sites along the Arkansas River during four separate time periods (9/7/2005, 12/15/2005, 5/18/2006, and 9/11/2006). Prior to May 2006, our study area was the river downstream of the Colorado state line to Garden City, KS. We only sampled the Arkansas River near Coolidge, Kendall, and Lakin because the river was dry between Lakin and Garden City. In order to increase our sample size temporally and perhaps spatially we expanded our study area and extended the field season to late summer of 2006. In May 2006, we visited a large number of sites along the Arkansas River beginning near Holly (Colorado), then extending downstream to Coolidge, Kendall, Lakin, Deerfield, Garden City, Pierceville, Cimarron, Kinsley, Larned, and Great Bend (Figure 1, site pictures in Appendix A). During both the May and September 2006 visits we found most stream sites were dry below the Kendall site. Researchers have found that water seeps from the alluvial aquifer to the underlying Ogallala Formation between Lakin and Garden City (Mueller et al. 1991; Whitmer 2000), which in part may explain the lack of water in this segment of the river. Thus, river flow above Garden City was only observed at sites near Holly, Coolidge, Kendall, and Lakin (dry during the last two visits). Below Garden City only one of two sites located near Kinsley had water. The site at Highway 183 bridge crossing was dry whereas one to two feet of standing water was observed at both upstream and downstream of the Highway 50 crossing that was approximately 3 river miles downstream of the Highway 183 bridge site.

Selenium Levels in Water, Fish, and Sediment

This report summarizes selenium concentrations found in water, fish, and sediment samples taken at multiple sites along the Arkansas River in 2005 and 2006. Some seasonal and site variations in water-column concentrations of selenium were observed for the five sites having water during all or part of the study period (Figure 2). Six out of fourteen water samples (43%) collected from the five sites exceeded 5 µg/L, the water-column based chronic criterion for aquatic life that was published in 1987 (http://www.epa.gov/waterscience/criteria/selenium/). Sites near Holly, Coolidge, Kendall, and Lakin had selenium levels that exceeded 5 µg/L at times, especially during winter, while lower selenium levels were observed in late spring and summer. In addition, selenium levels appeared to be higher in upstream sites. Three out of four water samples collected from the Coolidge site exceeded the criterion. The Kinsley site consistently had relatively low selenium levels (1.7 µg/L in both May and September 2006).

The water-column based chronic criterion is currently being revised by the United States Environmental Protection Agency (USEPA) (http://www.epa.gov/waterscience/criteria/selenium/). The USEPA is proposing a whole-body...
fish tissue based criterion because fish tissue samples provide a better indicator of the presence of selenium in a particular waterbody and better account for the bioaccumulative property of selenium. Most fish species have whole-body selenium concentrations of less than 4 µg/g (DOI 1998). The proposed freshwater chronic criterion is 7.91 µg/g dry weight (dw).

Notched box plots (Figure 3) were constructed to show median and quartile distribution of selenium levels in fish tissue samples of all fish collected at each site in 2005 and 2006. Notched box plots can be used as an informal test of differences between treatments (e.g., sites) by observing if the notched areas between box plots do or do not overlap. If the notches of two boxes do not overlap, we may assume that the medians are significantly different (NCSS 1997). Care must be taken in interpreting the overlap of notches when examining more than two box plots as multiple comparisons require an adjustment in the value used to estimate significance thus limiting comparisons of multiple notched box plots to an informal interpretation of significance. Despite this limitation, it still appears that selenium levels in fish tissue samples of Holly, Coolidge, and Kendall sites were not different from one another (notches overlap), but were probably significantly different from those collected from Lakin and Kinsley sites.

A total of fifteen fish species were collected during the course of this study with the highest selenium level (14.5 µg/g dw) occurring in a central stoneroller (weight 2.15 g; length 2.5 in.) taken at the Coolidge site on 5/19/2006 (Figure 4). About 23% (46 out of 203) of collected fish in this study exceeded the proposed whole-body criterion (Table 1). Fathead minnow had the highest percentage of exceedance of the criterion (80%), followed by sand shiner (43%) and channel catfish (33%) while percent exceedances for all other species were below 25%. Selenium levels in fathead minnow ranged from 6.7 to 9.9 µg/g dw at the Kendall site and from 2.7 to 10.9 µg/g dw at the Coolidge site. However, it should be noted that all of these fathead minnow specimens were collected only during one collection period (5/19/2006). The other species that had exceedances of 25% or more were collected on more than one occasion and at more than one site, indicating that these species may have persistently high body burdens of selenium.

Only six fish (one plains killifish, two gizzard shad, and three common carp) were collected at the Lakin site and these were collected on a single sampling event early in our study (9/7/2005). Ice cover in December 2005 prevented our electrofishing at this site while in May and September of 2006 this site remained dry. At the Lakin site, only the plains killifish specimen had a high fish-fillet concentration of selenium (9.0 µg/g dw) whereas selenium levels in common carp and gizzard shad were much lower, ranging from 1.6 to 3.8 µg/g dw. At the Kinsley site, none of the analyzed fish samples were observed to exceed the whole-body criterion at any time, perhaps due to relatively low water-column selenium levels (1.7 µg/L) observed at this site.

Plains killifish, sand shiner, and red shiner were the most common fish collected temporally and spatially and hence were chosen to assess seasonal variation of selenium levels in fish tissue (Figures 5, 6, and 7). In general, there was no distinctive difference between selenium levels in fish tissue at Holly, Coolidge, and Kendall sites (also see Figure 3), perhaps in part because selenium concentrations of sediment and water at these sites are somewhat similar and fish are highly mobile and may move between sites. However, selenium levels in the plains killifish and red shiner specimens seemed to be higher in summer than in spring whereas for sand shiners, higher selenium levels were observed in spring and not summer.

Selenium concentration in sediment greater than 4 mg/kg dw is a concern because there is a potential for bioaccumulation in fish and wildlife while most soils have concentrations at or
below 2 mg/kg dw (Lemly and Smith 1987). In the western United State the baseline selenium concentration is 0.23 mg/kg (Whitmer 2000); however, selenium levels in the sediment associated with Arkansas River sites are higher and sometimes exceeded twice of this value. In general, selenium levels in sediment were higher in the three upstream sites when compared to Lakin and Kinsley sites (Figure 8). Nevertheless, the accumulation of selenium in sediment was not significant as selenium levels at all sites were much less than 4 mg/kg dw. Thus, it is likely that selenium level in sediment may not impose a potential risk to aquatic life within the study area.

Other Physical and Chemical Properties

The Arkansas River was generally clear (base flow turbidity was less than 50 NTU). However, this river was getting dryer. Holly, Coolidge, and Kendall sites had river flow whereas the Lakin site was dry during the last two visits in May and September 2006 (Kendall and Lakin sites are only about 16 river miles apart, also see Figure 1 and pictures in Appendix A). The Kinsley site was observed to have one to two feet of standing water during the last two visits. This site had rather different chemistry composition than those upstream sites.

The river water from Holly to Lakin sites had an average specific conductance of 3.96 ± 0.56 mS/cm whereas the Kinsley site had an average of 1.57 ± 0.12 mS/cm. Total phosphorus (TP) concentrations of all sites ranged from 5.6 to 133 µg/L and total nitrogen (TN) ranged from 0.30 to 2.47 mg/L. This river normally had chlorophyll $a$ concentrations less than 10 µg/L most of the time with the highest concentration observed at the Kendall site (39.6 µg/L), which also coincided with the timeframe when this site had the highest TP concentration (133 µg/L).

Conclusions

The Arkansas River remains saline. The selenium levels in the water of the upper Arkansas River still exceeded 5 µg/L at times (43%) and appeared to be higher in upstream sites and during winter. About 23% of all fish collected and analyzed for selenium exceeded selenium level of 7.91 µg/g dw. Fathead minnow, sand shiner, and channel catfish were fish species of concern (> 25% exceedances). Based upon common fish captured at most of the sites (plains killifish, sand shiner, and red shiner), there appeared to be seasonal variations in selenium levels in fish tissue but site differences were not obvious. The selenium concentration in sediment was relatively insignificant compared to selenium levels in water and fish tissue.
Literature Cited


Figure 1  Study area (shaded green) of the Arkansas River. Water samples could only be collected near Holly, Coolidge, Kendall, Lakin, and Kinsley (•). Δ designates dry stations (observed in May 2006). Site pictures are in Appendix A.
Figure 2  Selenium levels in water at multiple sites along the Arkansas River in 2005 and 2006.

Figure 3  The notched box plot of selenium levels in fish tissue of all collected fish species in the Arkansas River near Holly (n = 35), Coolidge (n = 89), Kendall (n = 55), Lakin (n = 6), and Kinsley (n = 18) in 2005 and 2006.
Figure 4  Vertical point plot of the fifteen fish species collected from the five sites in 2005 and 2006.
Figure 5  Error bar plot (mean ± 1 standard error) of collected plains killifish at different sites in 2005 and 2006.

Figure 6  Error bar plot (mean ± 1 standard error) of collected sand shiner at different sites in 2005 and 2006.
Red Shiner

Figure 7  Error bar plot (mean ± 1 standard error) of collected red shiner at different sites in 2005 and 2006.

Figure 8  Selenium levels in sediment at multiple sites along the Arkansas River in 2005 and 2006.
Table 1  Percentage of fish exceeded the draft chronic criterion

<table>
<thead>
<tr>
<th>Fish species</th>
<th>Number of Fish Collected</th>
<th>Percentage Exceeded 7.91 µg/g dw</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bluegill</td>
<td>7</td>
<td>0 %</td>
</tr>
<tr>
<td>Bullhead minnow</td>
<td>2</td>
<td>0 %</td>
</tr>
<tr>
<td>Central stoneroller</td>
<td>15</td>
<td>20 %</td>
</tr>
<tr>
<td>Channel catfish</td>
<td>15</td>
<td>33 %</td>
</tr>
<tr>
<td>Common carp</td>
<td>14</td>
<td>14 %</td>
</tr>
<tr>
<td>Fathead minnow</td>
<td>10</td>
<td>80 %</td>
</tr>
<tr>
<td>Gizzard shad</td>
<td>6</td>
<td>17 %</td>
</tr>
<tr>
<td>Green sunfish</td>
<td>2</td>
<td>0 %</td>
</tr>
<tr>
<td>Plains killifish</td>
<td>30</td>
<td>3 %</td>
</tr>
<tr>
<td>Red shiner</td>
<td>31</td>
<td>16 %</td>
</tr>
<tr>
<td>Sand shiner</td>
<td>42</td>
<td>43 %</td>
</tr>
<tr>
<td>Suckermouth minnow</td>
<td>6</td>
<td>17 %</td>
</tr>
<tr>
<td>Western mosquitofish</td>
<td>21</td>
<td>10 %</td>
</tr>
<tr>
<td>White sucker</td>
<td>1</td>
<td>0 %</td>
</tr>
<tr>
<td>Yellow bullhead</td>
<td>1</td>
<td>0 %</td>
</tr>
<tr>
<td><strong>TOTAL:</strong></td>
<td><strong>203</strong></td>
<td><strong>23 %</strong></td>
</tr>
</tbody>
</table>
Arkansas River near Holly (5-19-2006)

Arkansas River near Coolidge (5-19-2006)
Arkansas River near Kendall (5-19-2006)

Arkansas River near Lakin (5-19-2006)
Arkansas River near Pierceville (5-18-2006)

Arkansas River near Cimarron (5-18-2006)
Arkansas River near Kinsley at Highway 183 bridge crossing (5-18-2006)

Arkansas River near Kinsley at Highway 50 bridge crossing (5-18-2006)
Arkansas River near Larned (5-18-2006)
Part II: Dissolved-oxygen and SOD conditions in Shunganunga Creek in Topeka, Kansas

Introduction

Shunganunga Creek in Topeka, Kansas is listed under Total Maximum Daily Load (TMDL) as dissolved oxygen (DO) impaired stream by KDHE. The three selected study sites (in downstream order) were at the Shunga Glen Park, the Golden Avenue bridge crossing, and at the Croco Road bridge crossing (KDHE station 238).

Field sampling started in late June and ended in October 2006. AQUAsonde dissolved oxygen and temperature dataloggers were installed intermittently from early July to October 2006 to capture diurnal DO flux during summer and fall seasons. DO, pH, turbidity, specific conductance, water temperature, and salinity were measured in situ using a Horiba U-10 Water Quality Checker. A one-liter grab sample was collected for nutrients, chlorophyll a, and TOC analyses. Periphyton samples were collected for chlorophyll a analysis. A composite sediment sample, which consists of three sediment core samples collected near the AQUAsonde installation site, was used for potential sediment oxygen demand (pSOD) determination. The water chemistry data were attached as a separate spreadsheet.

Dissolved-Oxygen Conditions

In this study, DO concentration was measured using a Horiba U-10 Water Quality Checker. Figure 9 shows the DO measurements taken at the three sites during summer and fall 2006. Daytime DO concentrations were all above 5 mg/L (water-quality standard) and there were no distinctive differences among the three sites.

Photosynthetic activity by phytoplankton and periphyton (primary production) increases daytime DO concentration whereas respiration reduces DO. Hence, the minimum DO concentration often occurs at sunrise after an entire night of respiration without photosynthesis (Schnoor 1996). Thus, to better understand the diurnal DO cycle of this stream, an AQUAsonde dissolved oxygen and temperature datalogger was installed intermittently at the three sites and was set to record both DO and temperature readings at 10-minute intervals.

When a DO sensor is submerged in biologically active water (e.g., lakes and rivers), biofouling organisms can start adhering to the DO membrane surface. The biofilm that is formed on the membrane surface will adversely affect the sensor accuracy. Therefore, the initial and the endpoint DO data of the AQUAsonde were often compared to that of Horiba U-10 Water Quality Checker. When data discrepancy was found (>20% error), the AQUAsonde data were omitted (Figures 10 – 12). Most DO excursions happened during early morning hours and during summer months. Based upon time period when AQUAsonde data were available, daily min DO was determined (Figures 13 – 15). Shunga Glen Park site continued to have DO excursions even into the cooler months of fall perhaps in part due to substantial decomposition of fallen leaves at this site. Shunga Glen Park site had much denser riparian than the other two downstream sites (pictures in Appendix B). Table 2 summarizes number of days in which daily min DO was less than 5 mg/L at the three sites. The Shunga Glen Park site had the highest percentage of DO excursion, followed by Croco Road and Golden Avenue sites.
Table 2  Summary of daily min DO at the three sites along the Shunganunga Creek

<table>
<thead>
<tr>
<th>Sampling Site</th>
<th># of Days DO data available</th>
<th># of Days Daily Min DO &lt; 5 mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shunga Glen Park</td>
<td>50</td>
<td>25 (50%)</td>
</tr>
<tr>
<td>Golden Avenue</td>
<td>53</td>
<td>14 (26%)</td>
</tr>
<tr>
<td>Croco Road</td>
<td>75</td>
<td>29 (39%)</td>
</tr>
</tbody>
</table>

**Sediment Oxygen Demand (SOD)**

Sediment Oxygen Demand (SOD) is the sum of all biological and chemical processes in sediment that utilize oxygen. SOD studies are used in mathematical models that aid in determining waste load allocations, which in turn are used in determining TMDL and in NPDES permits. They are also useful in measuring the depletion of oxygen in waterbody that has been stratified. DO is depleted as a result of decay of organic matter and lack of exchange of oxygenated water from the upper layer.

In this study, three sediment core samples were collected at each site using a handheld Wildco sediment core sampler and the top 5 cm of each sediment sample was then composited into a single sample for potential SOD (pSOD) analysis (Matlock et al. 2003). PSOD was conducted within 48 hours of sample collection. During the experiment, the wet composite sediment was intentionally suspended to remove oxygen diffusion limitation and thus this allowed oxygen to be consumed at a maximum rate much like it would be in a resuspension event in the stream. For the first 10 minutes, DO reading was recorded at 1-minute intervals. PSOD is temperature-dependent and was conducted at 20 °C to imitate ambient environment conditions. The dry weight of sediment samples were determined by calculating the percent moisture by drying another aliquot of the samples.

Figures 16 – 18 show the pSOD plots of the three sites. The initial rate of oxygen consumption is determined to be pSOD, which is generally not realized in a stream because sediment is usually oxygen-diffusion limited. The first ten-minute oxygen consumption rate was used to calculate pSOD. It appeared that pSOD was higher at the upstream of Shunganunga Creek (Table 3) and that also coincided with the higher percentage of DO excursion observed at the upstream (Table 2).

Table 3  Summary of pSOD at the three sites along the Shunganunga Creek

<table>
<thead>
<tr>
<th>Sampling Site</th>
<th>pSOD (mg-O₂/g dw/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shunga Glen Park</td>
<td>26.6 ± 0.2</td>
</tr>
<tr>
<td>Golden Avenue</td>
<td>15.3 ± 1.4</td>
</tr>
<tr>
<td>Croco Road</td>
<td>4.1 ± 1.7</td>
</tr>
</tbody>
</table>
Additional Water Quality Information

Shunganunga Creek was observed to have good river flow at the three sites throughout the study period. The base flow turbidity was less than 90 NTU. Sestonic chlorophyll a concentrations were normally less than 20 µg/L, but higher at the Croco Road site most likely because the riparian vegetation minimally provides canopy over this stream site (pictures in Appendix B), thereby allowing more sunlight penetrating into the stream water. However, higher nutrient concentrations (total phosphorus and nitrogen) were often observed at the upstream of the Shunganunga Creek.

Conclusions

Shunganunga Creek was observed to have occasional low DO problems within the study area. Low DO concentrations were often seen during early morning hours and in summer months. DO excursion was more common at the upstream of Shunganunga Creek, in part, due to higher SOD.

Literature Cited


Figure 9  Bar plot of daytime DO concentrations at the three sites (in downstream order) of the Shunganunga Creek during summer and fall 2006.
Figure 10  Diurnal DO and temperature patterns of Shunganunga Creek at the Shunga Glen Park during summer and fall 2006.
Figure 11  Diurnal DO and temperature patterns of Shunganunga Creek at the Golden Avenue site during summer and fall 2006.
Figure 12  Diurnal DO and temperature patterns of Shunganunga Creek at the Croco Road site during summer and fall 2006.
Figure 13  Daily min, max, median, and mean DO concentrations of the Shunganunga Creek at the Shunga Glen Park.

Figure 14  Daily min, max, median, and mean DO concentrations of the Shunganunga Creek at the Golden Avenue site.
Shunganunga Creek - Croco site

Figure 15  Daily min, max, median, and mean DO concentrations of the Shunganunga Creek at the Croco site.

pSOD - Shunga Glen Park Site

Figure 16  PSOD plot of Shunganunga Creek at the Shunga Glen Park site.
Figure 17  PSOD plot of Shunganunga Creek at the Golden Avenue site.

Figure 18  PSOD plot of Shunganunga Creek at the Croco Road site.
Appendix B

Shunganunga Creek at the Shunga Glen Park (6-30-2006)

Shunganunga Creek at the Golden Avenue bridge crossing (6-30-2006)
Shunganunga Creek at the Croco Road bridge crossing (KDHE Station 238) (6-30-2006)