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EVALUATION OF SELENIUM LOADING TO THE ARKANSAS RIVER NEAR PUEBLO, COLORADO

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A focused investigation was conducted on a 40-km reach of the Arkansas River in the vicinity of Pueblo, Colorado, to quantify the effect on selenium (Se) load of irrigation return flows compared to return flows from other sources. Results show that two tributaries that are minimally influenced by irrigated agriculture contributed the largest Se loads: 22% by Wild Horse Creek and 21% by Fountain Creek. Water quality, geology, and land use data suggest that the highest Se concentrations in groundwater are a result of natural dissolution processes from the underlying shale bedrock and shale residuum, and that Se concentrations in irrigated alluvial zones are not meaningfully higher than those in the non-irrigated alluvium. Within the study area, irrigation practices do not substantially increase Se concentrations in shallow groundwater. They do, however, increase total water and Se flux. The Se load from groundwater discharge and agricultural return flow estimated by three methods is likely between about 0.01 to 0.05 kg day⁻¹ per km, which is small relative to the total average Se load through the study reach (0.2 kg day⁻¹ per km). A simple mass balance Se load model was developed and the results indicate that only about 10 to 20 percent of the total Se source loads are derived from return flow from irrigated land. This study highlights the potential significance of natural and other Se sources relative to enhanced dissolution caused by irrigated agriculture, particularly in areas underlain by shale bedrock.

INTRODUCTION

In the 1980s, Se in irrigation drainwater caused wildlife deaths and deformities at Kesterton National Wildlife Refuge, California (Presser and Ohlendorf, 1987; Presser, 1994), illuminated the relationship between agricultural practices, Se mobilization and transport, and associated environmental hazards. During the past decade, regulatory and stakeholder interest in Se issues has increased regarding the transport, fate, and biotoxicity of Se in the Western United States (Lemly, 1999; Engberg, 1999; Seiler et al., 2003; Renner, 2005). In Colorado, USA, in particular, there is interest in the relationship between elevated Se in surface waters and irrigated agriculture, and the implications for water quality standards. For example, there are on-going multi-year studies addressing elevated Se in the Uncompahgre River Valley (Catlin, 2007) which is underlain by Mancos Shale and is located in western Colorado, and in the Lower Arkansas River Valley (Gates et al., 2006; Mueller Price and Gates, 2008) which is underlain by the Pierre Shale and Niobrara Formation and is located in the southeastern area of the state. Recently, the Colorado Department of Health and Environment (CDPHE) hosted a forum specifically focused on state-wide Se issues (CDPHE 2005). The work presented in this paper is a compilation of investigative work over the past decade conducted on behalf of the City of Pueblo (Colorado) to characterize Se sources and to estimate loading to the Arkansas River in the Pueblo area due to natural mineral dissolution, enhanced dissolution due to irrigated agriculture, and other anthropogenic sources.

The primary objective of early investigations in the mid- and late-1990s (Geraghty & Miller, 1994; ARCADIS, 1998) was to quantify the relationship between the occurrence of elevated Se concentrations in soils, bedrock, groundwater, and surface water and the geology and geochemical conditions found in the vicinity of the defined study area. The information obtained from these areas was used to assess sources of Se to the City of Pueblo sanitary sewer system and to the wastewater treatment plant. These initial studies also assessed the dynamics of these sources with respect to urbanization of the Pueblo area and Se concentrations in the Arkansas River, and concluded that the majority of Se in the City of Pueblo's Water Reclamation Facility discharge was naturally occurring and primarily a result of infiltration and inflow into the collection system. The rationale for the current discharge permit recognizes this condition, noting that "... much of the Se and sulfate loading in this segment comes from natural sources, and the wastewater treatment facility operated by the City of Pueblo appears to reduce Se loading by removing some of the Se that would otherwise reach the river." These studies also demonstrated that naturally-high Se concentrations are present in Fountain Creek (10 to 20 mg L⁻¹) Wild Horse Creek and several other tributaries draining non-agricultural land (often greater than 1,000 mg L⁻¹), and in groundwater in shale and weathered shale bedrock (up to 7,000 mg L⁻¹), suggesting, a component of the Se load in the study reach of the Arkansas River is from natural dissolution processes.

This paper presents the results of a focused field study intended to develop a better understanding of the relative significance of Se sources, and specifically to estimate the relative contribution from agricultural areas under irrigation, non-irrigated and urban areas, and other discharge. The study included synoptic water quality and streamflow measurement from 20 surface water sites and 23 groundwater monitoring wells over a 13-month period. Although the study was limited in duration, the observations were used to build a simple quantitative mass-balance model used to understand the relative strengths of Se sources and the impact of land use. This paper adds to the broader scientific literature because it characterizes Se sources and loading along a significant river reach and demonstrates the potential significance of natural Se dissolution relative to the

effects of irrigated agriculture on surface water Se load, specifically in areas underlain by seleniferous shale bedrock and shale residuum.

SELENIUM GEOCHEMISTRY AND GEOLOGIC CONSIDERATIONS

Selenium is widely distributed in the Earth's crust, but most Se occurs in association with S and sulfide minerals and may be concentrated to levels of 200 mg/kg in such settings (Kabata-Pendias and Pendias, 1984). Se is found as an isomorphous replacement element for sulfur in the sulfide crystal lattice of the minerals chalcopyrite and pyrrhotite. Se is easily oxidized during chemical weathering, and its subsequent mobility is controlled by local redox and pH conditions and the availability of sorbing phases. In aerobic (oxidizing) waters, and at moderate to high pH (> 6.6), Se is present as the oxyanions selenite (SeO_3^{-2}) and selenate (SeO_4^{-2}) (Hem, 1985). Selenite ions resulting from oxidation processes are stable and can migrate until they are adsorbed onto mineral or organic particles. Selenate ions are even more mobile under alkaline conditions and are less likely to be adsorbed. Selenate behaves similarly to sulfate (SO_4^{-2}) and is only weakly prone to sorption, while selenite may exhibit limited sorption to aquifer materials and sediment in some settings (Manning and Burau, 1995). Under reducing conditions and at low pH, Se exists in forms with low mobility, and elemental Se or metal selenides are likely to be formed (Elrashidi et al., 1987). In an oxygenated fluvial environment, sorption onto stream bed sediments or suspended solids and precipitation with hydrous iron oxides are the major controls on Se mobility (Freeze and Cherry, 1979). However, most Se in aquatic systems, particularly the selenate form, is transported in the dissolved state.

Sedimentary rocks cover more than three quarters of the Earth's land surface and are the principal parent material of agricultural soils (Lakin and Davidson, 1967). It is estimated that 58 percent of all sedimentary rocks are shales, which in turn contain the most elevated concentrations of Se (Anderson et al., 1961). Average Se concentrations found in Cretaceous age shales are nearly an order of magnitude higher than Se concentrations found in other sedimentary and magmatic rock types: Se concentrations typically found in shales and argillaceous sediments average from 0.4 to 0.6 mg/kg (Kabata-Pendias and Pendias 1984), while Cretaceous age shales, such as the Mancos Shale (located in western Colorado) and the Pierre Shale (major geologic unit in the study area), are the parent materials for much of the seleniferous soil found in the United States with an average Se concentration of about 2 mg kg⁻¹ (Lakin and Davidson, 1967). Consequently, high natural Se loads would be expected and there is significant potential for enhanced Se dissolution and loading due to irrigation practices in watersheds with significant Cretaceous age shales.

MATERIALS AND METHODS

Study Area

The study area is located near the City of Pueblo, Colorado at the confluence of the Arkansas River and Fountain Creek. (Figure 1). It is bounded on the north where Fountain Creek runs through the City of Fountain. The western and eastern boundaries along Fountain Creek include drainages into Fountain Creek as well as the Fountain Creek basin. The outlet of Pueblo Reservoir defines the upstream and western boundary for the Arkansas River in the study area. The hydrology of the Arkansas River in the study area is significantly affected by the operation of Pueblo Reservoir which provides significant winter storage and allows for additional water from west of the continental divide to be transferred and stored for irrigation in the Arkansas Basin. Western area drainages that flow into the Arkansas River are Williams Creek and Wild Horse Creek. The

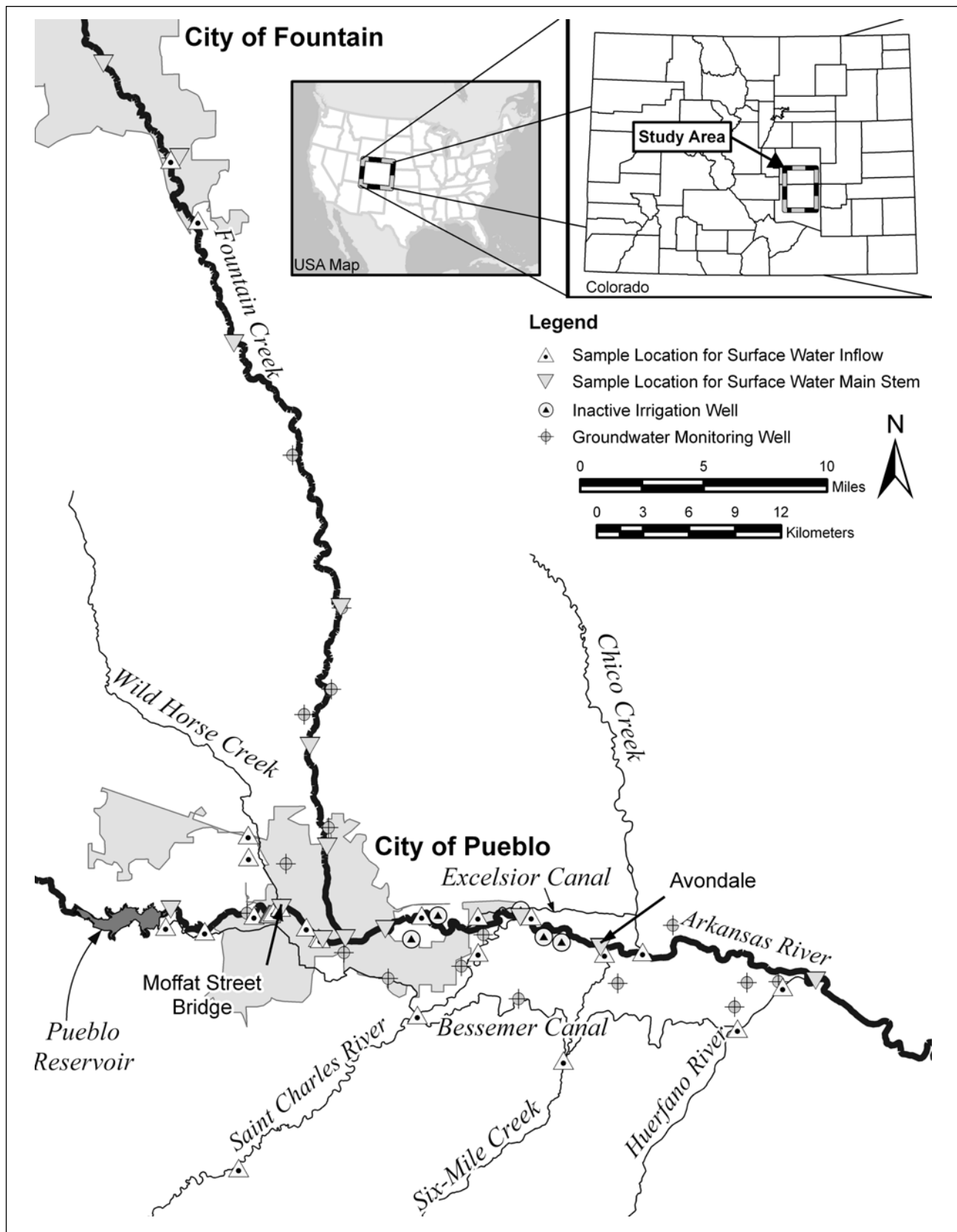


Figure 1. Study area boundaries and sampling site locations.

southern boundary of the study area (mainly east of Pueblo) is defined by the west to east flowing Bessemer Canal (irrigation canal) that terminates at the Huerfano River. Drainages into the Arkansas along Segment 1a include the St. Charles River, Six Mile Creek, and the Huerfano River

from the south. The northern boundary along this reach of the study area is essentially defined by the Booth and Excelsior canals that run along the upper contour of the irrigated valley lands north of the river. Chico Creek enters the Arkansas River from the north. Finally, the eastern boundary of the study area along the Arkansas is just below the confluence of the Huerfano River.

The land use adjacent to the Arkansas River is urban from immediately below Pueblo Reservoir to approximately 10 km downstream. Below Pueblo, agriculture is the dominant land use through the rest of the study reach to the confluence with the Huerfano River. Irrigated agriculture (primarily corn, alfalfa, grains, melons, and vegetables) occurs in the alluvial valley and depends on diversions from the Arkansas River and on irrigation wells completed in the Arkansas River alluvium. Based on a review of aerial photographs and satellite images, most agriculture in the study vicinity occurs on the southern side of the Arkansas River where the alluvial valley is more extensive. There are approximately 8,500 ha (21,000 acres) of irrigated land along the Arkansas River within the study area. The land use of the alluvial valley immediately adjacent to Fountain Creek within the study area is predominantly rangeland with only some limited irrigated agriculture. A small part of the watershed immediately upstream of the confluence of Fountain Creek and the Arkansas River is within the Pueblo urban area.

The climate in the study area is characterized as semiarid temperate continental. Daily mean air temperatures in the Pueblo area range from 7.2°C in December and January to higher than 32 °C in July with an annual average of 19°C. Total annual precipitation in Pueblo is approximately 0.30 m, and annual pan evaporation is approximately 1.50 to 1.80 m (Dunne and Leopold, 1978; US Bureau of Reclamation webpage [available at <http://www.usbr.gov/gp/>]). Precipitation can occur as snowfall between November and April; however, the months with the highest average precipitation are (in descending order): August, July, May, and June (Stronger, 2000).

Within the study area, the Arkansas River flows in a sand channel that overlies and is hydraulically connected with the underlying alluvial aquifer. Flows are also influenced by surface water diversions and groundwater pumping from the alluvial aquifer. There are several diversions and permitted discharges within the study area that affect the hydrology of the Arkansas River. The most significant surface water inflow in the study area is Fountain Creek which discharges to the Arkansas River near downtown Pueblo. Fountain Creek also flows in a sand channel that overlies and is hydraulically connected with the underlying alluvial aquifer. Upstream of the study area, streamflow in Fountain Creek is augmented by discharge of municipal wastewater from Colorado Springs and other communities. Streamflows in both Fountain Creek and the Arkansas River are characterized by three general flow regimes:

- The base-flow period begins in early October and extends until April. During this period, streamflow is generated from groundwater return flow within the watershed and flows are relatively uniform. Typical daily flows during this period are approximately 13 m³s⁻¹ for the Arkansas River and 3.5 m³s⁻¹ for Fountain Creek.
- The snowmelt period usually begins about mid-April and extends until mid-June. During this period, streamflows increase substantially from base-flow, usually peaking around mid-May. Typical daily flows during this period range from approximately 23 to 70 m³s⁻¹ for the Arkansas River and 4 to 8 m³s⁻¹ for Fountain Creek.
- The summer period begins around mid-June and usually extends until the end of September or the beginning of October. Streamflow during this period can be highly variable (particularly for Fountain Creek), and the variation in streamflow is driven primarily by afternoon and evening storm

events. Typical daily flows during this period range from approximately 15 to 30 m³s⁻¹ for the Arkansas River and 2.8 to 5.7 m³s⁻¹ for Fountain Creek.

The Bessemer Canal is the most significant diversion within the study area and represents the southern boundary of the study area. This canal draws water from Pueblo Reservoir and provides irrigation water to much of the agricultural areas south of the Arkansas River. The other active diversion within the study area is the Excelsior Canal. One important permitted discharge with respect to the magnitude of flows and Se loading is the City of Pueblo's Water Reclamation Facility outfall, which is located on the Arkansas River immediately downstream of the confluence of Fountain Creek. There are several other named and unnamed smaller tributaries and surface water flows that discharge to Fountain Creek and the Arkansas River within the study area.

The geology of the area has been mapped and described by Scott (1964), Sharps (1976), Scott et al. (1978), Tweto (1980), and Moore et al. (2002). The geologic formation of most interest in the Pueblo area with regard to Se is the Pierre Shale. In particular, lower units of the Pierre Shale contain iron concretions, gypsum, and selenite crystals (Scott, 1964), all of which are potential sources of dissolved Se. The lower unit (Sharon Springs Member) of the Pierre Shale outcrops along both sides of Fountain Creek from its confluence with the Arkansas River at Pueblo upstream to Pinon Bridge approximately 20 km to the north. North of Pinon Bridge, the Pierre Shale outcrops are present only on the west side of Fountain Creek. Quaternary age alluvial materials are present adjacent to Fountain Creek, the Arkansas River, and the various tributaries within the study area, and the majority of irrigated agriculture occurs on this alluvium. The alluvial deposits are particularly thick and extensive between the Bessemer Canal and the Arkansas River.

The Pierre Shale and the Niobrara Formation below it are the most seleniferous of the Upper Cretaceous formations found in south-central Colorado from Colorado Springs south to Pueblo (Howard, 1969). Several studies indicate that Se concentrations are high in the sediments along the east side of the Front Range in south-central Colorado (Moran, 1976; Trelease and Beath, 1949). Shacklette and Boerngen (1984) report data for surficial soil samples with high Se concentrations ranging from 0.7 to 5.0 mg kg⁻¹ in the Pueblo vicinity and trending south into northeast New Mexico. Data compiled by Trelease (1949) showing locations where Se concentrations in plants exceed 50 mg/kg indicate that the Pueblo area and the area east of the City of Pueblo yield some of the highest concentrations of such plants to be found anywhere in the Great Plains. Selenium was measured in soil samples collected from boreholes drilled at the Pueblo Depot Activity, located approximately 30 km east of Pueblo, at concentrations ranging from 0.7 to 16.5 mg kg⁻¹ (Geraghty & Miller, 1994). Se concentrations in soils and bedrock measured in early investigations range as high as 23 mg kg⁻¹ in outcrop and 13 mg kg⁻¹ in bedrock. The average Se concentration in the Pierre Shale surface samples (14.0 mg kg⁻¹) was much higher than the average Se concentration in the alluvium (0.77 mg kg⁻¹).

There is a topographic rise, known as Baculite Mesa, east of Fountain Creek beginning near Pinon and extending southward to within a few miles of the Arkansas River. Baculite Mesa is not used for agricultural purposes and, therefore, does not receive irrigation. Runoff from the mesa is entirely from precipitation events. The relative uplift of the mesa has resulted in increased erosion and the development of extensive surface drainage features east of Fountain Creek. Geologic maps for the area (Scott, 1964) show that many drainage features cut through the middle and lower Pierre Shale units and eventually discharge into Fountain Creek. The Sharon Springs member of the Pierre Shale is the most seleniferous member of the Pierre formation (Trelease and Beath, 1949).

The Fountain Creek alluvial aquifer is composed predominantly of sand and gravel and is up to 30 m thick in some areas. The aquifer behaves as a water table aquifer in the study area and is in hydraulic connection with Fountain Creek. The depth to groundwater is typically less than 6 m. Groundwater flow within the alluvial aquifer is generally to the south but is locally influenced by Fountain Creek. The average hydraulic conductivity values for the aquifer are relatively high, ranging from 1.4×10^{-3} to $5.6 \times 10^{-3} \text{ m s}^{-1}$ (Jenkins, 1964; Cain and Edelman, 1986). Values obtained from slug tests conducted for this study suggest that hydraulic conductivity values in the shallow intervals of the alluvial aquifer are lower, ranging from 3.5×10^{-6} to $3.5 \times 10^{-5} \text{ m s}^{-1}$. Several studies indicate that the reach of Fountain Creek north of Pueblo is predominately a gaining stream (Cain and Edelman, 1980; Cain et al., 1980; Cain and Edelman, 1986; ARCADIS, 1998). Near Pueblo, the Fountain Creek alluvium overlies the relatively impermeable Pierre Shale on either side of Fountain Creek.

Like the Fountain Creek alluvial aquifer, the Arkansas River alluvial aquifer is composed predominantly of sand and gravel and is highly permeable. Irrigation well depth in the Arkansas River Valley averages between 15 and 18 m and maximum depths rarely exceed 30 m (Topper et al., 2003). The aquifer behaves as a water table aquifer in the study area and is in hydraulic connection with the Arkansas River. The depth to groundwater is typically less than 12 m. Based on groundwater elevation contours, groundwater flow is generally toward the Arkansas River with an eastward component; however, local flow directions are likely influenced by tributary streams, canals, and extraction wells.

Burkhalter and Gates (2005) and Gates et al. (2006) summarized measurements of the hydraulic conductivities in the Lower Arkansas River alluvium near the town of La Junta (approximately 70 km downstream of the study area). In the upper 2 to 3 m of the water table, hydraulic conductivity values range from 1.1×10^{-8} to $1.2 \times 10^{-4} \text{ m s}^{-1}$. This is consistent with hydraulic conductivity values measured by slug testing for the current study, which indicate that hydraulic conductivity values in the shallow intervals of the aquifer are typically around $3.5 \times 10^{-6} \text{ cm s}^{-1}$. Hydraulic conductivity values measured in the deeper zones of the Lower Arkansas River valley alluvium are higher, ranging from 1.5×10^{-4} to $7.4 \times 10^{-2} \text{ m s}^{-1}$.

The shallow depth to groundwater and the relatively coarse-grained sediments (sands and gravels) for both the Fountain Creek and Arkansas River alluvial aquifers suggest that groundwater near the water table aquifer is well aerated (measured dissolved oxygen in alluvial groundwater generally exceeds 5 mg L^{-1} ; Cain and Edelman (1986); data from this study), which is an optimal condition for Se mobilization. This is particularly true for the selenate ion.

Several hundred Se measurements (unpublished data) collected by the City of Pueblo and the U.S. Geological Survey (USGS) over the past 20 years at various locations along both Fountain Creek and the Arkansas River were available for review prior to this study. Additionally, a few previous focused studies that contained some limited water quality information for the Fountain Creek basin were available. These studies and data indicate that the historical concentration of Se in lower Fountain Creek generally increases downstream, with a notably sharp increase between the monitoring station at Pinon Bridge (generally $< 10 \text{ mg L}^{-1}$, approximately 20 km upstream of the Arkansas River confluence) and further downstream (often $> 20 \text{ mg L}^{-1}$) (Edelman, 1988; Ruddy, 1991). Se concentrations in groundwater from the Fountain Creek alluvium were highly variable, ranging from less than 1 mg L^{-1} to 54 mg L^{-1} (Cain and Edelman, 1986). ARCADIS (1998) measured much higher average Se concentrations, ranging from 18.4 to $7,062 \text{ mg L}^{-1}$, in

groundwater more directly influenced by the shale bedrock and further from Fountain Creek and the Arkansas River. Existing data reviewed for this study indicate that Se concentrations in the Arkansas River immediately below Pueblo Reservoir average approximately 2 mg L^{-1} , are generally lower than 5 mg L^{-1} above the City of Pueblo, but often increase to above 10 mg L^{-1} downstream of the confluences of Wild Horse Creek (Se in Wild Horse Creek was frequently measured over $1,000 \text{ mg L}^{-1}$) and Fountain Creek. Prior to the study, the EPA-approved CDPHE aquatic habitat chronic table value standard for dissolved Se for the Arkansas River reach within the current study area was 4.6 mg L^{-1} .

Other studies have shown that salt and Se concentrations increase in the Lower Arkansas River valley toward the Kansas State line; however, the focus areas of these studies have generally been significantly downstream of the present study area (Gates et al. 2006). Between the community of Lamar (approximately 150 km downstream of the study area) and the Colorado-Kansas state line (a 65-km reach), Se concentrations in the river have been reported to range from 4.2 to 23 mg L^{-1} , with median concentrations in groundwater approximately 17 mg L^{-1} (Donnelly and Gates, 2005; Herting and Gates, 2006). For this same general area, Mueller Price and Gates (2008) reported that nonpoint source Se loading rates (including groundwater return flow and unaccounted surface return flow) on the average had a 90% probability of ranging between about 0.025 and $0.053 \text{ kg day}^{-1}$ per km (highest values typically occurred during the irrigation season), with an average of about $0.038 \text{ kg day}^{-1}$ per km.

Sampling Program

The sampling program for this focused study was developed from the existing information discussed above and included surface water samples were collected at 20 sites (which included sampling locations on the Arkansas River mainstem, tributaries, and canals) and groundwater samples at 23 wells (Figure 1) Nine surface water sampling events were conducted over a 13-month period January 2005 to February 2006. During sampling events, the streamflow was determined at all irrigation canals, several mainstem locations and a few tributary sampling locations from stage-discharge relationships established for permanent gauges at sampling locations. For all remaining small tributary sampling locations, streamflow was estimated by calculating the channel cross-sectional area from several stream depth measurements and multiplying the value by an average velocity estimated as 75 percent of the surface velocity. While this correction factor is estimated, it should be noted that flows for these small tributaries were generally less than $0.05 \text{ m}^3 \text{ s}^{-1}$, and therefore water balance errors and uncertainties introduced by this correction factor are small. The surface velocity was measured by timing the transport of a floating object along a specified distance. All surface water samples were collected as “grab” samples, not depth- or flow-integrated samples. To evaluate the potential variability associated with grab sampling, 27 field duplicate samples were collected during the sampling events. For samples with measured Se concentrations higher than 7 mg L^{-1} , the average absolute relative percent difference between the two measurements was 11 percent for total Se and 12 percent for dissolved Se. These results indicate the order of magnitude of the sum of the effects of sampling error, analytical error, and natural small-scale spatial and temporal variability among grab samples. These relative percent difference values can be used to represent the average uncertainty associated with measured values for grab samples at given locations within a stream cross section and over small periods of time.

The monitoring well network was designed to provide data at key locations of the study area, and included 16 monitoring wells and seven non-operating irrigation wells for a total of 23 monitoring

wells in the groundwater monitoring program (Figure 1). Twelve of these monitoring wells were newly installed for this study, and were drilled using hollow-stem auger techniques. During well development, limited aquifer testing (slug testing) was conducted at each newly installed well to estimate hydraulic conductivity values. The groundwater sampling program consisted of four quarterly groundwater monitoring events during 2005. Each event included measuring water levels and collecting groundwater samples from the 23 wells. The four groundwater sampling events were conducted in March, July, August, and October of 2005. Detailed descriptions and coordinates for all sampling locations and all water quality and flow data are available from the authors.

Se Analysis and Speciation

All groundwater and surface water samples were analyzed by the USGS certified laboratory at the City of Pueblo Water Reclamation Facility with the exception of Se speciation. All samples were analyzed for both total recoverable Se and dissolved Se (defined as Se measured in sample passed through a 0.45 mm filter). Twenty field and rinsate blanks were collected during the sampling events; dissolved Se values were below the analytical detection limit for all of these samples, supporting the integrity of the sample handling and decontamination procedures. Although Se was the primary focus of the study, samples were also analyzed for sulfate, iron, total organic carbon (TOC), and total dissolved solids (TDS).

For all sample results, the average ratio of dissolved Se to total Se was 92 percent; for all samples with total Se concentrations equal to or above 10 mg L⁻¹, the average ratio of dissolved Se to total Se is 97 percent. These results indicate that the majority of mobile Se in groundwater and surface water is in the dissolved phase, and that there is limited potential for Se sorption to stream sediment. This is consistent with what would be expected if most of the Se was present as the selenate species, which is expected given the aerobic condition of the groundwater and surface waters. To verify, five samples collected during the February 2006 surface water sampling event were submitted to an external laboratory for Se speciation. For all samples, the significant majority of the Se was present as selenate, and for the two samples with measured total Se higher than 10 mg L⁻¹, selenate represented an average of 97 percent of the total Se. These results support the assumption that selenate represented the majority of the Se measured in surface water, and provided the basis for the assumption of conservative Se transport (i.e., no significant sorption) in the study area groundwater and surface water systems.

RESULTS AND DISCUSSION

Surface Water Concentrations and Loads

Total and dissolved Se concentrations in the Arkansas River ranged from less than 0.97 to 23 mg L⁻¹, with mean and median values of 7.2 and 6.8 mg L⁻¹, respectively. The average concentration in the Arkansas River at the upstream boundary of the study area near Pueblo Reservoir was approximately 2 mg L⁻¹. Concentrations increased sharply to approximately 7 mg L⁻¹ in the Pueblo urban area and upstream of most heavily-irrigated lands and averaged approximately 9 mg L⁻¹ near the downstream study area boundary (Figure 2). Se concentrations in surface inflows to the Arkansas River varied significantly, from less than 0.97 mg L⁻¹ to 832 mg L⁻¹ (at Wild Horse Creek), with mean and median values of 66 and 16 mg L⁻¹, respectively. Se loads (calculated as the product of the sample concentration and the mean daily streamflow value) within the Arkansas River markedly increased along the study segment (Figure 3). Specifically, the mean daily average (range of values noted in parentheses) dissolved Se load increased from 2.0 kg day⁻¹ (0.6 to 4.6

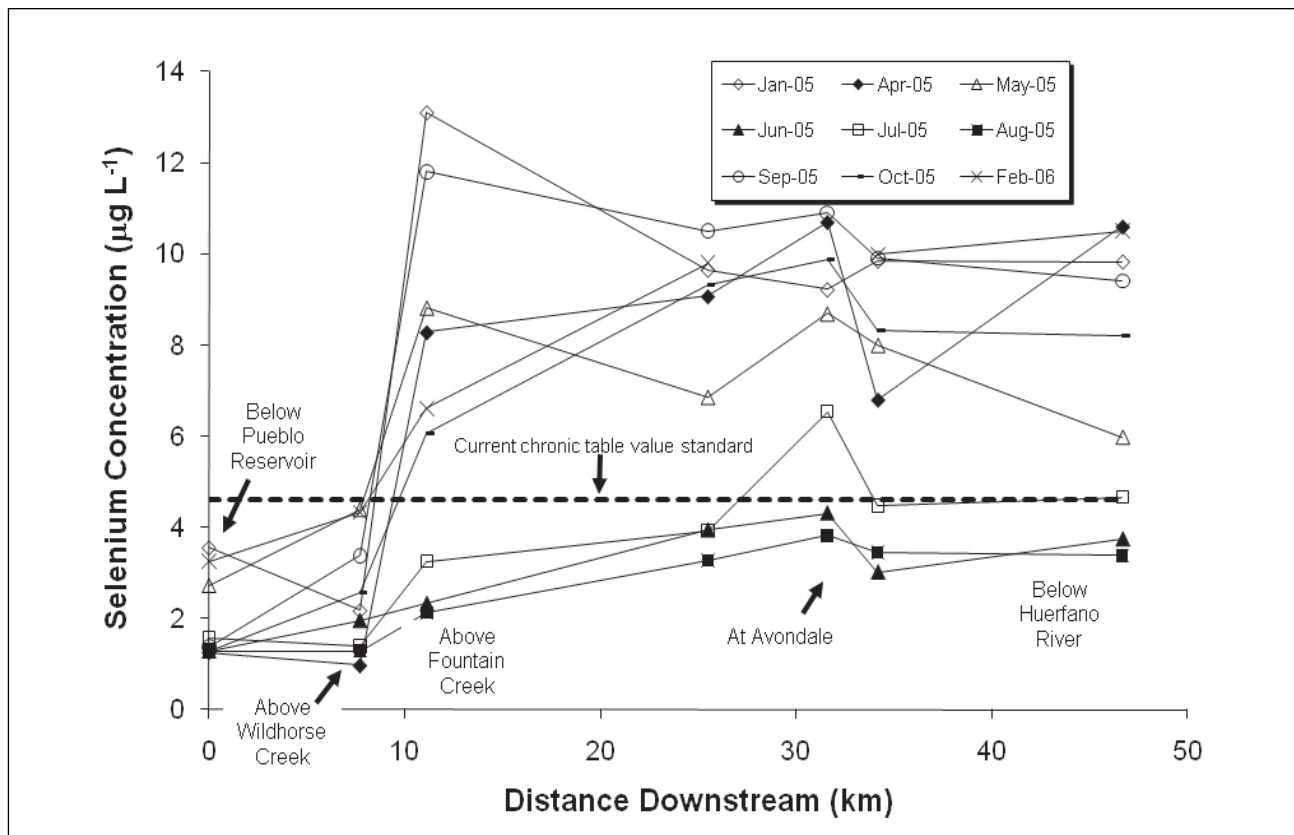


Figure 2. Measured Se concentrations in the Arkansas River within the study area reach.

kg day⁻¹) upstream of the City of Pueblo to 4.2 kg day⁻¹ (1.9 to 8.6 kg day⁻¹) in the downtown Pueblo area, and then to 9.2 kg day⁻¹ (5.0 to 13.2 kg day⁻¹) near the downstream study area boundary. It is important to note that surface water Se concentrations measured during the sampling period are consistent with available previously-measured values and ranges for the Arkansas River, Fountain Creek, Wild Horse Creek, and a few other tributaries. The source that contributed the largest and most variable load to the Arkansas River over the sampling periods was Wild Horse Creek with an average load of 2.8 kg day⁻¹ (22 percent of the total Se load from measured surface water sources) (Figures 4 and 5). The source that contributed the second largest load was Fountain Creek with an average load of 2.6 kg day⁻¹ (21 percent of the total Se load from measured surface water sources). There is little or no irrigated agriculture near these sources, however, it should be noted that urban land use activities such as lawn irrigation, that may result in an increased baseflow and Se loading as compared to natural conditions. Relative to Se loads from other surface water inflows, the Se load from Pueblo's Water Reclamation Facility exhibited very low temporal variability (Figure 5).

Sulfate concentrations in the Arkansas River generally corresponded to Se concentrations and ranged from 15.3 to 459 mg L⁻¹, with mean and median values of 202 and 172 mg L⁻¹, respectively. The average sulfate concentration in the Arkansas River at the upstream boundary of the study area near Pueblo Reservoir was approximately 114 mg L⁻¹. Concentrations increased to approximately 250 mg L⁻¹ near the downstream study area boundary. Sulfate concentrations in surface inflows to the Arkansas River ranged from 131 to 2,790 mg L⁻¹ (Huerfano River), with mean and median values of 938 and 958 mg L⁻¹, respectively.

Dissolved iron concentrations in the Arkansas River ranged from less than 0.1 to 40.3 mg L⁻¹, with mean and median values of 4.0 and 3.2 mg L⁻¹, respectively. The average iron concentration

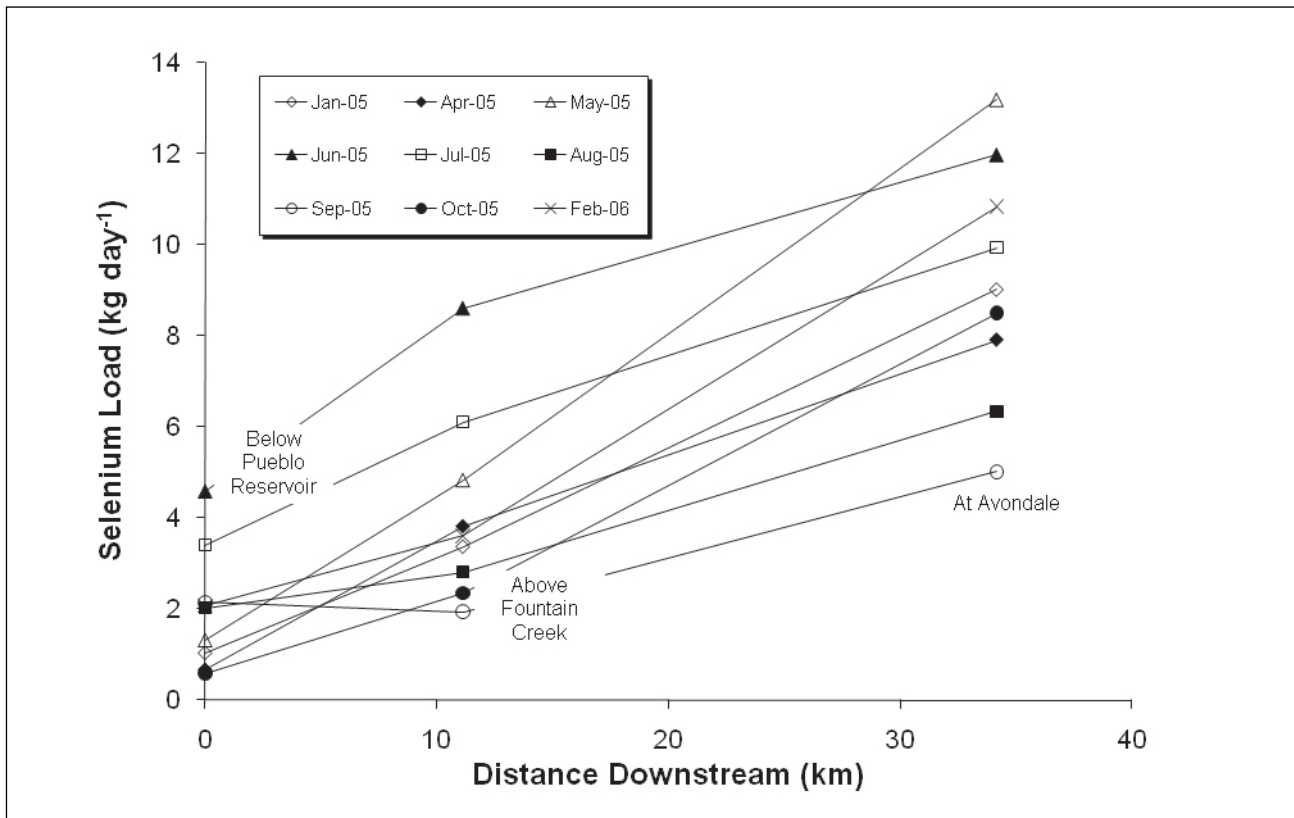


Figure 3. Calculated Se load in the Arkansas River within the study area reach.

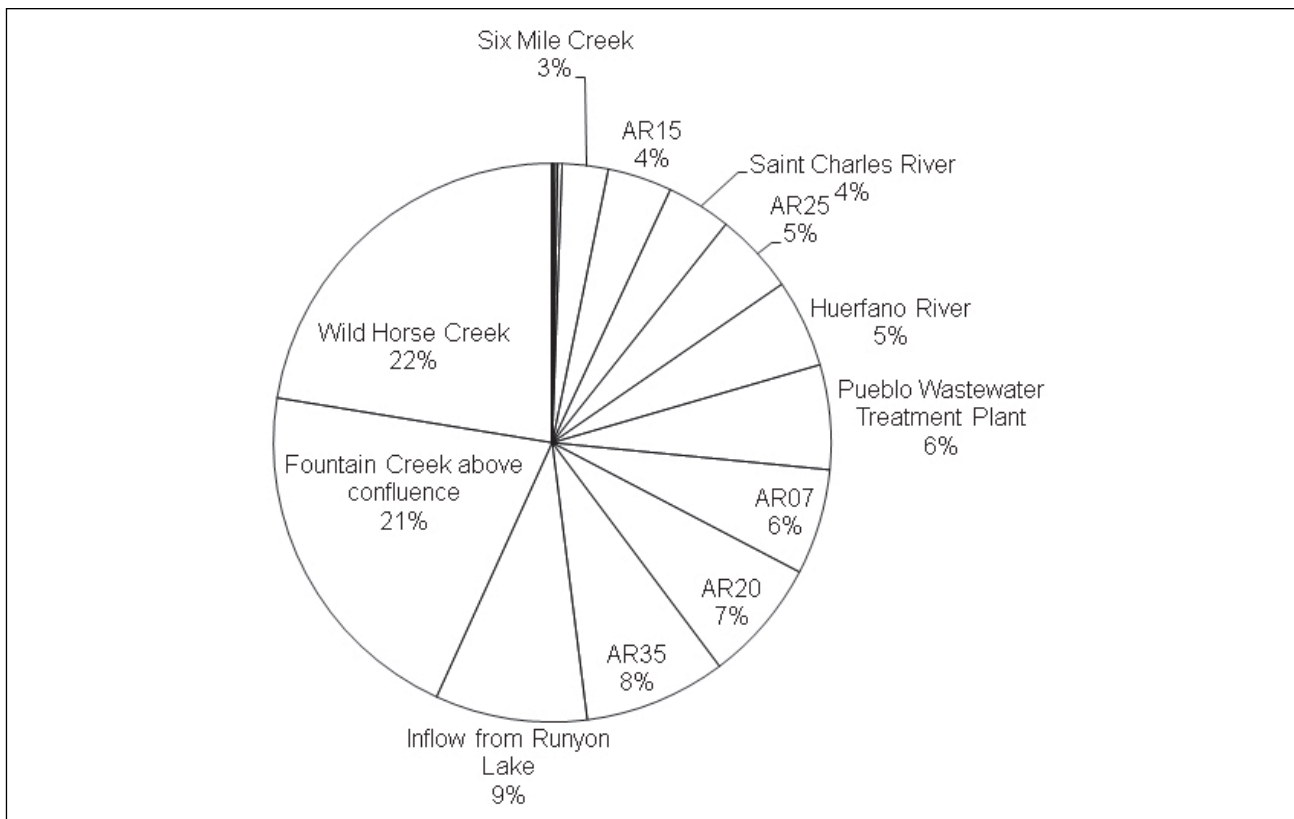


Figure 4. Relative average Se loads from surface water inflows to the Arkansas River. Unnamed tributaries are designated by sampling site locations (e.g., AR20); the specific locations of all sampling sites are included in the electronic supplementary materials.

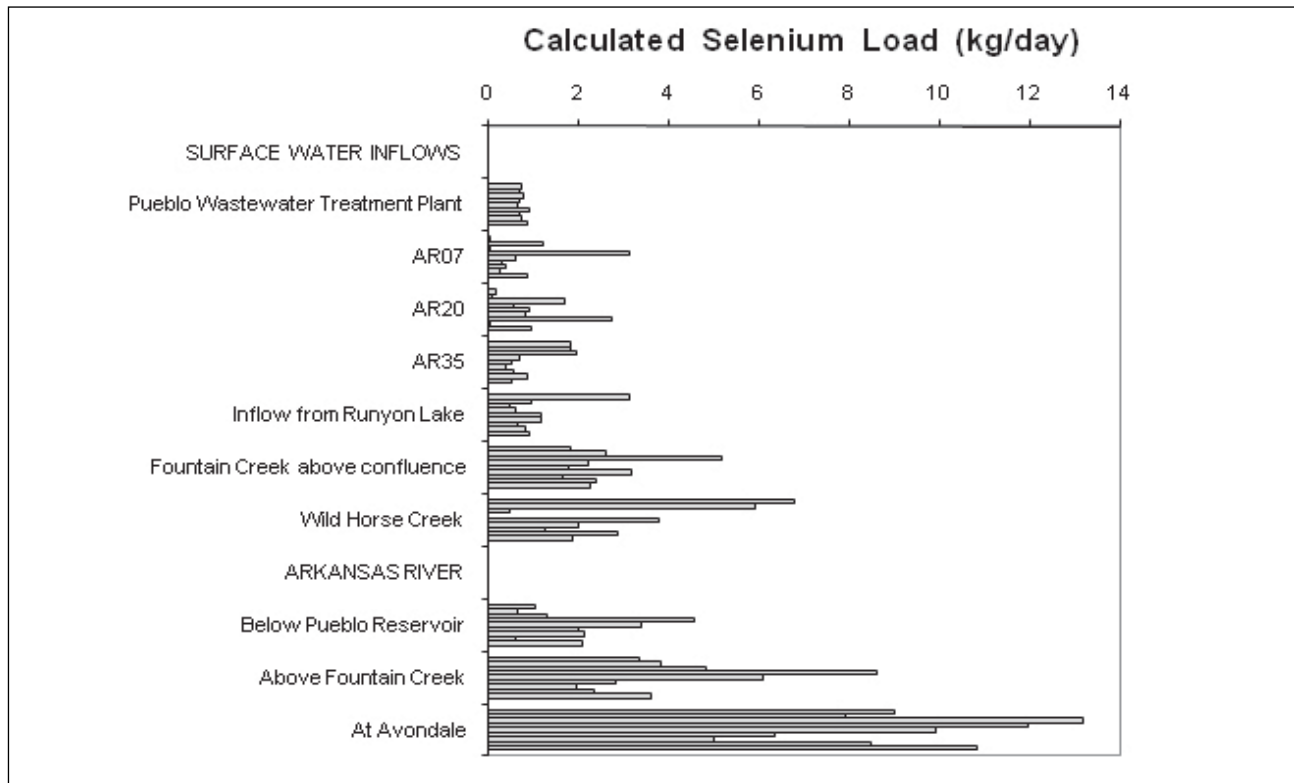


Figure 5. Calculated Se loads for each sampling event for the seven largest surface water inflows sources and the Arkansas River. The calculated load for an individual sampling event is represented by a horizontal bar. The sampling events are presented in chronological order from top to bottom for each location.

in the Arkansas River at the upstream boundary of the study area near Pueblo Reservoir was approximately 0.2 mg L^{-1} . Concentrations increased to approximately 7.3 mg L^{-1} near the downstream study area boundary. Iron concentrations in surface inflows to the Arkansas River ranged from less than 0.1 to 37.8 mg L^{-1} (Saint Charles River), with mean and median values of 2.8 and 0.3 mg L^{-1} , respectively.

Total organic carbon (TOC) concentrations in the Arkansas River ranged from 1.8 to 8.1 mg L^{-1} with mean and median values of 4.1 and 3.8 mg L^{-1} , respectively. The average TOC concentration in the Arkansas River at the upstream boundary of the study area near Pueblo Reservoir was approximately 3 mg L^{-1} . Concentrations were approximately 4.6 mg L^{-1} near the downstream study area boundary. Total organic carbon concentrations in surface inflows to the Arkansas River ranged from 1.7 to 37.9 mg L^{-1} with mean and median values of 6.0 and 4.8 mg L^{-1} , respectively.

Groundwater Concentrations

In the Fountain Creek area, dissolved Se concentrations in groundwater ranged from 1.9 to $1,950 \text{ mg L}^{-1}$; in the Pueblo area, dissolved Se concentrations ranged from less than 1.3 to $2,240 \text{ mg L}^{-1}$; and in the area of the main stem of the Arkansas River, dissolved Se concentrations ranged from less than 1.3 to 815 mg L^{-1} . Although the spatial distribution of groundwater quality data is limited to the study monitoring well network, groundwater concentrations of Se, sulfate, iron, and nitrate appear to be correlated to geology and land use. Statistical summaries of groundwater quality data grouped by land use are presented in Table 1. Conceptually, the following three primary groundwater zones were defined based on hydrogeology and land use.

- Non-irrigated Alluvial Zone – This zone represents coarse-grained river-deposited materials that are generally anticipated to exhibit strong hydraulic connection to a surface water body

hydraulically and are located in a largely non-irrigated area. The mean and median dissolved Se concentrations in this zone are 4.0 and 4.7 mg L⁻¹, respectively.

- Irrigated Alluvial Zone – This zone represents coarse-grained river-deposited materials that are located in heavily irrigated areas in the Arkansas Valley. The mean and median dissolved Se concentrations in this zone are 6.8 and 4.4 mg L⁻¹, respectively.

- Shale-Influenced Zone – This zone represents either shale-derived materials or coarse-grained river deposits located at the perimeter of the alluvial system. The chemistry of the groundwater in this zone is anticipated to be heavily influenced by the properties of the groundwater in this zone and by the geochemical properties of the Pierre Shale. However, it should be noted that significant irrigation and seepage from canals in these areas may occur depending on location, and these activities may dramatically enhance Se dissolution and mobilization. The mean and median dissolved Se concentrations in this zone are 602 and 386 mg L⁻¹, respectively.

These results suggest that the highest Se concentrations in groundwater result from natural and irrigation-induced dissolution processes from the Pierre Shale. Average concentrations in samples taken from shale-influenced zones are approximately 100 times higher than average concentrations in samples from both non-irrigated and irrigated alluvial zones. These results also indicate that the Se concentrations in the irrigated alluvial zones are not meaningfully higher than those in the non-irrigated alluvium. This suggests that, within the study area, Se concentrations are not significantly elevated due to enhanced dissolution of natural Se from alluvial materials by irrigation. However, because irrigation increases groundwater flows over those that occur under natural conditions, the total flux of Se moving through the irrigated alluvial zone is greater than it would be if the land were not irrigated. Based on groundwater elevations and streamflow data, the Arkansas River is a gaining river over the study area; therefore, Se in groundwater discharging to the river will contribute to the Se load in the river.

Table 1. Study period average dissolved Se concentrations in groundwater and associated land use.

Alluvium, minimal irrigation		Alluvium, irrigated				Shale Influenced	
Well ID	Concentration (µg L ⁻¹)	Well ID	Concentration (µg L ⁻¹)	Well ID	Concentration (µg L ⁻¹)	Well ID	Concentration (µg L ⁻¹)
FCA-01	6.00	ARA-01	19.29	ARA-03	4.72	FCA-05	1026.00
FCA-02	4.73	ARA-08	4.08	ARA-04	2.53	PA-02	1770.00
FCA-03	4.70	ARA-09	4.12	ARA-05	9.29	PA-03	15.30
FCA-04	2.75	ARA-10	5.43	ARA-07	18.48	PA-04	28.40
PA-01	1.60	ARA-12	3.60	ARA-11	5.21	ARA-02	163.38
		ARA-13	2.44	ARA-14	2.22	ARA-06	609.25
Median	4.70	Median	4.42			Median	386
Mean	3.95	Mean	6.78			Mean	602
Min	1.60	Min	2.22			Min	15.3
Max	6.0	Max	19.3			Max	1770
Standard deviation	1.8	Standard deviation	5.81			Standard deviation	694
CV	44%	CV	86%			CV	115%

CV - Coefficient of variation

Surface Water Mass Balance Model and Return Flow Load Estimation

A simple steady-state mass-balance model was used to estimate the Se loading throughout the study area. Specifically, this model estimates solute loading from each surface water inflow and at sampling points along the main stem of the Arkansas River. The most important model construction elements and assumptions include the following:

- Analyte loading was defined as the product of measured concentration and volumetric flow rates at sampling points. Instantaneously measured values of volumetric flow rate and solute concentrations at each sampling location were assumed to be average values over the sampling period. Hence, the effect of temporal variability, including time lags associated with solute movement along the streams, was assumed to be negligible in the analysis. Water samples were assumed to represent average solute concentrations over the entire stream cross-sections from which they were taken.
- The water and solute mass balances were closed by calculating the difference between all measured outflows from and inflows to the study segment or sub-segments. This difference, if positive, represented the unaccounted inflows to the segment. Such inflows would include groundwater return flows to the river as well as unmeasured nonpoint surface flows. Negative differences represented composite unaccounted outflows or sinks.
- A steady-state condition was assumed (no change in stored mass) within the river study reach over each sampling period.
- Internal sinks and sources (associated with dissolution and precipitation of solutes, adsorption/desorption to sediments, volatilization, etc.) were assumed to be negligible.

The results of the mass-balance model indicate that the average Se load to the Arkansas River, calculated as the net difference between measured external inflow sources and measured diversions, was 11.2 kg day^{-1} , which is similar to, but higher than, the average measured load of 9.2 kg day^{-1} within the main stem of the Arkansas River. This value does not include loads in unmeasured surface water and groundwater interactions with the river. Because the calculated load was nearly always somewhat higher than the measured load at the study boundary (7 of 9 events), it is likely that all major Se sources were measured and accounted for. Although the average difference in these values is relatively small (the average unaccounted Se load is only 18 % of the average total measured load from surface water inflows) the consistent negative difference in these values suggests that there are unaccounted outflows or processes that remove dissolved Se from the system (i.e., reduction of selenate to less-soluble forms).

These results demonstrate that the majority of the increase in Se load in the Arkansas River within the study segment is attributable to surface water inflows. If most of the Se load from the Saint Charles River and Six Mile Creek are assumed to be derived primarily from agricultural return flows, the Se loads from the rest of the surface water inflows are assumed to be primarily natural or non-agriculturally derived, and the contribution of groundwater return flow is assumed to be insignificant, the amount of Se measured in the Arkansas River at Avondale that is attributable to agriculture is approximately 9 %. Because the mass balance model does not “close” (i.e., the difference in the calculated load at Avondale is larger than the measured load at Avondale for most sampling events), it cannot be used to quantify the magnitude of Se loading from groundwater and unmeasured surface return flows. However, this result does suggest that the contribution of groundwater and unmeasured surface flow (i.e., unmeasured nonpoint source flows) along the

main stem of the study reach of the Arkansas River to the total Se load in the river was relatively small. Given the substantial variability in geologic conditions and Se concentrations, the actual groundwater discharge to the Arkansas River is difficult to quantify. However, the following additional independent analyses were conducted to estimate total unmeasured nonpoint source Se load to the river and Se load in groundwater flow to the river.

Daily average river flows recorded at Moffat Street (within the Pueblo urban center) and at Avondale, daily average tributary inflows recorded in Fountain Creek at the mouth and in the Saint Charles River a few miles upstream of the mouth, and daily average diversions to the Excelsior Canal were used to estimate daily average unmeasured nonpoint source inflows to the river reach (ungauged tributary flow plus direct groundwater flow), Q_{unps} , between 1975 and 2004 between Moffat Street and Avondale. Assuming no significant net storage change within the river reach yields:

$$Q_{unps} = Q_{ds} - Q_{us} + Q_{div} - Q_{in} \quad (1)$$

where Q_{ds} is the measured streamflow at the downstream gauge at Avondale, Q_{us} is the measured streamflow at the upstream gauge at Moffat Street, Q_{div} is the flow diverted from the river reach to the Excelsior Canal, and Q_{in} is the sum of measured surface water inflows to the river reach from Fountain Creek and the Saint Charles River. Using the average computed value of Q_{unps} for this river reach, and assuming this same rate of inflow to be uniform along the entire reach, the estimated average return flow rate over the considered period between Fountain Creek and the Huerfano River is about $0.9 \text{ m}^3 \text{ s}^{-1}$. Multiplying this flow by an average groundwater Se concentration range of 5 to 10 mg L^{-1} (as suggested by our measurements) yields an estimated range of Se loading to this 40-km reach of the Arkansas River from unmeasured nonpoint source flow of 0.38 to 0.73 kg day^{-1} (or about 0.01 to 0.02 kg day^{-1} per km). This result is consistent with the results of the mass-balance model, which suggest that the Se load from unmeasured nonpoint sources is small relative to the average net load accounting for using monitored diversions and surface water inflows to the Arkansas River. It is also consistent with Se load calculations by Mueller Price and Gates (2008) for a reach of the Arkansas River approximately 150 km downstream where agricultural nonpoint source return flows would be expected to be more predominant. They reported 90% probability intervals for nonpoint source Se loads to the river using data from 13 sample periods between July 2003 and August 2005: the smallest reported interval ranged between about 0.011 and $0.029 \text{ kg day}^{-1}$ per km in January 2004 and the largest between 0.038 and $0.084 \text{ kg day}^{-1}$ per km in June 2004.

As an additional analysis, daily average diversions to the Bessemer Canal and to the Excelsior Canal (using available data from between 1975 and 2004) were used to estimate the net daily volume of water that flows to the unconfined aquifer underlying the irrigated land and then eventually makes its way to tributaries and to the river. It was estimated that 20 % of daily average diversions seep out of the earthen canals to the underlying aquifer. Of the remaining 80 percent that is applied to irrigated farm land, it was estimated that about 35 % percolates through the root zone as over irrigation. These assumptions are based on extensive canal seepage tests and on-farm irrigation measurements made by Colorado State University in the Arkansas River Valley between 2001 and 2005 (irrigation monitoring revealed an average application efficiency of 55 %, with about 10 % of the applied water going to surface runoff and about 35 % going to deep percolation) (Gates et al., 2006). It was further assumed that about 15 percent of the total recharge to the

unconfined aquifer (including both seepage and over-irrigation) contributes to evapotranspiration via upflux from the shallow water table. Hence, it was estimated that the average net daily recharge rate to the unconfined aquifer, $Q_{net-rech}$, eventually flowing in the alluvial aquifer back to tributaries and to the main stem of the river, was:

$$Q_{net-rech} = [0.20 + 0.35(1 - 0.20)](0.85)Q_{div} \quad (2)$$

where, in this case, Q_{div} is the average total flow diverted from the river reach to the Bessemer and Excelsior Canals. $Q_{net-rech}$ was computed as about $1.6 \text{ m}^3 \text{ s}^{-1}$. Multiplying this flow by an average groundwater Se concentration range of 5 to 10 mg L^{-1} yields an estimated range of total Se loading in groundwater flow of 0.018 to $0.037 \text{ kg day}^{-1}$ per km to the tributaries and the mainstem of the Arkansas River between Fountain Creek and the Huerfano River. This result is again consistent with the results of the mass balance model, which suggests that the Se load from groundwater and unmeasured surface flows is small relative to the average net load accounted for in monitored surface water inflows and diversions.

The Se load from groundwater discharge and agricultural return flow estimated by the additional estimation methods described above are in close agreement with each other and are consistent with the results of the mass-balance model. Based on these analyses, the actual Se load attributable to groundwater and diffuse unmeasured surface flow is likely between about 0.01 to 0.05 kg day^{-1} per km along the study reach.

UNCERTAINTIES

The following is a limited discussion of the most important elements that potentially contribute to ambiguity in the study results:

Temporal Variability in Concentration: To evaluate the potential for natural variability in surface water concentrations over relatively short periods, samples were collected at inflows in Wild Horse Creek and unnamed inflow "AR-15", which are significant contributors of Se to the Arkansas River. For samples collected within two days of each other, the average absolute relative percent difference (a measure of variability) in dissolved Se concentrations was 12 %; for samples collected within 30 days of each other, the value was 12 %; and for samples collected more than 30 days apart, the value was 20 %. These results suggest that, during the study period, the natural variability in surface water samples collected at these locations over periods of 30 days or less was of the same order of magnitude as measurement error associated with discrete samples and analytical precision. Short-term temporal variability of Se concentration in groundwater is anticipated to be much lower.

Spatial Variability in Concentration: In this study, grab samples were taken near the midpoint of a stream cross section and were used to represent the average concentration over the entire cross section and no effort was made to estimate variability in concentration within the cross section of streams examined in this study. However, Mueller Price and Gates (2008) used field observations to estimate the spatial coefficient of variation of concentration within the cross section of the Arkansas River to be only about 5 %. Spatial variation across smaller tributaries and diversions is expected to be even smaller.

Streamflow Measurement: Uncertainty associated with streamflow measurements directly impacts the mass-balance model because solute loads are calculated as the product of measured streamflow and measured concentrations. The accuracy and precision for streamflow values

obtained from permanent gauges is assumed to be high, however, there is some uncertainty associated with the estimated flow values for most of the smaller surface water flows because they were manually estimated. Additionally, the mass-balance model is based on the assumption that flow values, either directly measured or obtained from reported daily averages at gauging stations, are representative of the entire sampling event. Although the uncertainty associated with manual gauging was not rigorously evaluated, duplicate flow measurements were occasionally conducted to demonstrate repeatability.

Selenium Storage Changes: This study neglected the effect of storage changes in Se loads that could occur along the river reach within a given sample period. Mueller Price and Gates (2008) demonstrated that mass storage changes within lower reaches of the Arkansas River can indeed be rather negligible compared to total calculated nonpoint source loads particularly under relatively steady hydrologic conditions (e.g., during baseflow); however, they can also be substantial when hydrologic conditions exhibit high temporal variability (e.g., during the irrigation season).

Study Duration: This focused study was relatively limited in duration and because hydrologic and irrigation conditions can vary significantly from year to year, the results should not be extrapolated to other years or river reaches without careful consideration. However, streamflows, irrigation draws, and Se concentrations measured during this study are consistent with available previously-measured values and ranges, and therefore, this study period can be considered representative of typical conditions.

The cumulative effects of these uncertainties on the study results are difficult to quantify without detailed uncertainty and sensitivity modeling; however, the magnitude of these individual uncertainties is consistent with the magnitude of expected uncertainties associated with this type of investigation. Although, more extensive spatial sampling over longer time periods would be necessary to refine estimates of the values of Se concentrations and loads in an absolute sense, the results of this sampling effort are believed to present reasonable estimates of the relative magnitudes of the different components of the Se balance along the study. While these various sources of uncertainty contribute to ambiguity surrounding specific estimated load values, they do not practically limit a comparative analysis of loading sources or the on the general conclusions of the study summarized in the following section.

SUMMARY AND CONCLUSIONS

Se concentrations within the Arkansas River and Fountain Creek markedly increased along the study segments of these surface waters (Figure 2): in the Arkansas River, the average concentration measured over the sampling periods increased by about 350 % from approximately 2 mg L⁻¹ upstream of the City of Pueblo to 9 mg L⁻¹ approximately 40 km downstream. Similarly, Se loads within the Arkansas River markedly increase along the study segment (see Figure 3): the mean daily average load estimated from data gathered during the nine sampling periods (conducted between January 2005 and February 2006) increased by 111 % from about 2.0 kg day⁻¹ upstream of Pueblo to about 4.2 kg day⁻¹ at Moffat Street and by 121 % from about 4.2 kg day⁻¹ at Moffat Street to about 9.2 kg day⁻¹ at Avondale. The source that contributed the largest and most variable load to the Arkansas River over the sampling periods was Wild Horse Creek with an average load of 2.8 kg day⁻¹ (22 percent of the total Se load from measured surface water sources) (see Figure 4). The source that contributed the second largest load was Fountain Creek with an average load of 2.6 kg day⁻¹ (21 percent of the total Se load from measured surface water sources). Both of these confluences

occur upstream of the most significant irrigated agriculture within the study reach. Over the nine sampling periods, the Pueblo Wastewater Treatment Plant contributed only about 6 % of the total measured surface water source loading to the river between Pueblo Reservoir and the Huerfano River. Because the primary source of Se entering Pueblo's Water Reclamation Facility is groundwater infiltrating into the sanitary sewer collection system rather than industrial processes that discharge Se, this actually represents another largely natural source of Se loading. The results of this study clearly demonstrate that the majority of Se in the study reach is attributable to tributaries above the confluence of Fountain Creek that drain land with minimal irrigated agriculture.

Although the Se load from groundwater and unmeasured surface return flow is uncertain, the nonpoint source Se load to the Arkansas River between Fountain Creek and the Saint Charles River (about 20-km reach with only limited irrigated agriculture) likely ranges between about 0.4 to 1 kg day⁻¹ along this reach. This accounts for about 3 to 8 percent of the estimated total measured surface water and nonpoint source loads to the Arkansas River between Pueblo Reservoir and the Saint Charles River. Assuming that Se loads from all surface water inflows above and within this reach are predominately a result of natural Se dissolution from geologic materials, it is estimated that more than 90 % of the Se load to the Arkansas River above the Saint Charles River is derived from natural and other non-agricultural sources.

Nonpoint source Se loads to the Arkansas River between Fountain Creek and the Huerfano River (about a 40-km reach draining land with significant irrigated agriculture) are uncertain, but are certainly small relative to other sources: the Se loading rates are likely between about 0.01 to 0.05 kg day⁻¹ per km. Assuming that Se loads from the Saint Charles River, Six Mile Creek, and groundwater return flows are derived predominately from agricultural return flows, it is estimated that, for the reach between Fountain Creek and the Huerfano River, only about 10 to 20 % of the total Se source load measured in the Arkansas River near the downstream boundary of the study area is derived from return flow from irrigated land along the river.

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REFERENCES

- Anderson, M.S., H.W. Lakin, K.C. Beeson, F.F. Smith, and E. Thanker. 1961. Selenium in agriculture. U.S. Department of Agriculture Handbook Number 200, Washington D.C., U.S. Government Printing Office.
- ARCADIS. 1998. Selenium source characterization: Investigation of naturally occurring selenium, Pueblo, Colorado, Final Report, 24 September 1998.
- Burkhalter, J.P., and T.K., Gates. 2005. Agroecological impacts from salinization and waterlogging in an irrigated river valley. *Journal of Irrigation Drainage Engineering*, Vol. 131, pp. 197-209.
- Cain, D., and P.R. Edelmann. 1980. Selected hydrogeologic data, Arkansas River Basin, Pueblo and Southeastern Fremont Counties, Colorado 1975-80. U.S. Geological Survey Open File Report 80-1185.
- Cain, D., and P.R. Edelmann. 1986. A reconnaissance water-quality appraisal of the Fountain Creek Alluvial Aquifer between Colorado Springs and Pueblo, Colorado, including trace elements and organic constituents. U.S. Geological Survey Water Resources Investigations Report 86-4085.
- Cain, D., B.J. Ryan, and P.J. Emmons. 1980. Hydrology and chemical quality of groundwater in Crowley County, Colorado. U.S. Geological Survey Water Resources Investigations Open File Report 80-681.

- Catlin, M. 2007. Best management practices for salinity and selenium. Sustaining Colorado's Watersheds Conference: Making the Water Quality Connections, Breckenridge, Colorado, October 2-4, 2007.
- Colorado Department of Health and Environment (CDPHE). 2005. Statewide selenium issues overview forum, 11 January 2005, Denver, Colorado.
- Donnelly, J.P., and T.K. Gates. 2005. Assessing irrigation-induced Se and iron in an irrigated portion of the Lower Arkansas River Valley in Colorado. In Proceedings of the EWRI World Water and Environmental Resources Conference., Anchorage, Alaska.
- Dunne, T., and L.B. Leopold. 1978. Water in environmental planning. W.H. Freeman and Company, New York.
- Edelmann, P.R. 1988. Water quality of Fountain and Monument Creeks, South-Central Colorado, with emphasis on relation of water quality to stream classifications, U.S. Geological Survey Water Resources Investigations Report 88-4132.
- Freeze, R.A., and J.A. Cherry. 1979. Groundwater. Prentice Hall, Inc.
- Elrashidi, M.A., D.C. Andriano, S.M. Workman, and W.L. Lindsay. 1987. Chemical equilibria of selenium in soils: A theoretical development. *Soil Science*, Vol. 144, pp. 141-452.
- Engberg, R.A. 1999. Selenium budgets for Lake Powell and the Upper Colorado River Basin. *Journal of the American Water Resources Association*, Vol. 35, pp. 771-786.
- Gates, T.K., L.A. Garcia, and J.W. Labadie. 2006. Toward optimal water management in Colorado's Lower Arkansas River Valley: Monitoring and modeling to enhance agriculture and environment. Colorado Water Resources Research Institute Completion Report No. 205, Colorado Agricultural Experimental Station Technical Report TR06-10, Colorado State University, Fort Collins, Colorado.
- Geraghty & Miller, Inc. 1994. Interim corrective action field investigation results for the Sanitary Landfill and adjacent areas, Pueblo Depot Activity, Pueblo, Colorado. Prepared for the U.S. Army Corps of Engineers, Omaha District, 5 November 1994.
- Hem, J.D. 1985. Study and interpretation of the chemical characteristics of natural water. United States Geological Survey Water-Supply Paper 2254, Third Edition, United States Government Printing Office.
- Herting, A.W., and T.K. Gates. 2006. Assessing and modeling irrigation-induced selenium in the stream-aquifer system of the Lower Arkansas River Valley, Colorado. In Hydrology Days 2006 Proceedings, Colorado State University, Fort Collins, Colorado.
- Howard, J.H. 1969. Selenium in the Upper Cretaceous Niobrara Formation and Pierre Shale of South-Central Colorado. Geological Society of America Special Paper 121.
- Jenkins, E.D. 1964. Groundwater in Fountain and Jimmy Camp Valleys, El Paso County, Colorado. US. Geological Survey Water Supply Paper 1583.
- Kabata-Pendias, A., and H. Pendias. 1984. Trace elements in soils and plants, CRC Press.
- Lakin H.W., and D.F. Davidson. 1967. The relation of the geochemistry of selenium to its occurrence in soils. In: Muth, OH (ed), Selenium in Biomedicine: A Symposium, Westport, Connecticut.
- Lemly, A.D. 1999. Selenium transport and bioaccumulation in aquatic ecosystems: A proposal for water quality criteria based on hydrological units. *Ecotoxicology and Environmental Safety*, Vol. 42, pp. 150-156.
- Manning, B.A., and R.G. Burau. 1995. Selenium immobilization in evaporation pond sediments by in situ precipitation of ferric oxyhydroxides. *Environmental Science & Technology*, Vol. 29, pp. 2639-2646.
- Moore, D.W., A.W. Straub, M.E. Berry, M.L. Baker, and T.R. Brandt. 2002. Generalized surficial geologic map of the Pueblo 1 degree x 2 degree Quadrangle, Colorado. U.S. Geological Survey, Denver, Colorado.
- Moran, R.E. 1976. Geochemistry of selenium in groundwater near Golden, Jefferson County, Colorado, Geological Society of America Abstracts, Annual Meeting, 8, Number 6, 1018 pp.
- Mueller Price, J., and T.K. Gates. 2008. Assessing uncertainty in mass-balance calculation of river nonpoint source loads. *Journal of Environmental Engineering*, Vol. 134, pp. 247-258.
- Presser, T.S. 1994. "The Kesterton effect". *Environmental Management*, Vol 18. Pp. 437-454.
- Presser, T.S., and H.M. Ohlendorf. 1987. Biogeochemical cycling of selenium in the San Joaquin Valley, California, USA. *Environmental Management*, Vol. 11, pp. 805-821.

- Renner, R. 2005. Proposed selenium standard under attack. *Environmental Science & Technology*, Vol. 39, pp. 125A-126A.
- Ruddy, B.C. 1991. Water quality variations and trends in monument and Fountain Creeks, El Paso and Pueblo Counties, Colorado, Water Years 1976-88, U.S. Geological Survey Water Resources Investigations Report 91-4176.
- Scott, G.R. 1964. Geology of the Northwest and Northeast Pueblo Quadrangles, Colorado, U.S. Geological Survey, Denver, Colorado.
- Scott, G.R., R.B. Taylor, R.C. Epis, and R.A. Wobus. 1978. Geologic Map of the Pueblo 1 degree x 2 degrees quadrangle, South-Central Colorado, U.S. Geological Survey, Denver, Colorado.
- Seiler, R.L., J.P. Skorupa, D.L. Naftz, and T. Nolan. 2003. Irrigation-induced contamination of water, sediment, and biota in the Western United States – Synthesis of data from the National Irrigation Water Quality Program. U.S. Geological Survey Professional Paper 1655.
- Shacklette, H.T., and J.G. Boerngen. 1984. Element concentrations in soils and other surficial materials of the conterminous United States, U.S. Geological Survey Professional Paper 1270, United States Government Printing Office.
- Sharps, J.A. 1976. Geologic map of the Lamar quadrangle, Colorado and Kansas. U.S. Geological Survey Miscellaneous Geologic Investigations Map I-944.
- Stronger, R. 2000. Trends in precipitation and streamflow and changes in stream morphology in the Fountain Creek Watershed, Colorado, 1939-99. U.S. Geological Survey Water Resources Investigation Report 00-4130, Denver, Colorado.
- Topper R., K.L. Spray, W.H. Bellis, J.L. Hamilton, and P.E. Barkman. 2003. Ground water atlas of Colorado. Colorado Geological Survey Special Publication #53.
- Trelease, S.F., and O.A. Beath. 1949. Se, its geological occurrence and its biological effects in relation to botany, chemistry, and agriculture. Nutrition, and Medicine, Published by the authors.
- Tweto, O. 1980. Geological map of Colorado, Compiled from 1969 Base Map by the U.S. Geological Survey.

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