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Contaminants from cretaceous black shale: II. Effect of geology, weathering, climate, and land use on salinity and selenium cycling, Mancos Shale landscapes, southwestern United States

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ABSTRACT

The Cretaceous Mancos Shale (MS) is a known nonpoint source for a significant portion of the salinity and selenium (Se) loads in the Colorado River in the southwestern United States and northwestern corner of Mexico. These two contaminants pose a serious threat to rivers in these arid regions where water supplies are especially critical. Tuttle et al. (companion paper) investigates the cycling of contaminants in a Colorado River tributary watershed (Uncompahgre River, southwestern Colorado) where the MS weathers under natural conditions. This paper builds on those results and uses regional soil data in the same watershed to investigate the impact of MS geology, weathering intensity, land use, and climate on salt and Se storage in and flux from soils on the natural landscape, irrigated agriculture fields, areas undergoing urban development, and wetlands. The size of salinity and Se reservoirs in the MS soils is quantified. Flux calculations show that during modern weathering, natural landscapes cycle salt and Se; however, little of it is released for transport to the Uncompahgre River (10% of the annual salinity and 6% of the annual Se river loads). When irrigated, salinity and Se loads from the MS soil increase (26% and 57% of the river load, respectively), causing the river to be out of compliance with Federal and State Se standards. During 100 years of irrigation, seven times more Se has been removed from agricultural soil than what was lost from natural landscapes during the entire period of pedogenesis. Under more arid conditions, even less salt and Se are expected to be transported from the natural landscape. However, if wetter climates prevail, transport could increase dramatically due to storage of soluble phases in the non-irrigated soil. These results are critical input for water-resource and land-use managers who must decide whether or not the salinity and Se in a watershed can be managed, what sustainable mitigation strategies are possible, and what landscapes should be targeted. The broader implications include providing a reliable approach for quantifying nonpoint-source contamination from MS and other rock units elsewhere that weather under similar conditions and, together with results from our companion paper, address the complex interplay of geology, weathering, climate, and land use on contaminant cycling in the arid Southwest.

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1. Introduction

Nearly 36 million people and 4.5 million acres of farmland in the United States and Mexico depend on the Colorado River (U.S. Department of Interior, 2005). Serageldin (2000) considers this river one of the most stressed in the world because of increasing salinization, with damages estimated at \$380 million per year in the United States alone (U.S. Department of Interior, 2005). In addition to salinization, selenium (Se) loading is of concern because Se concentrations exceed the U.S. Environmental Protection Agency's freshwater aquatic life chronic criteria ($5 \mu\text{g L}^{-1}$) in some reaches

of the river inhabited by threatened and endangered species of fish (Hamilton, 1998), and Se impacts the habitat of other wildlife in the area such as waterfowl (Presser et al., 1994; Butler et al., 1996). Much of the salinity and most of the Se loads in the Colorado River are sourced from rocks in the upper Colorado River Basin (UCRB). Tuttle and Grauch (2009) estimated that a third of the 2005 solute load in the river at Cisco, Utah (equivalent to dissolution of $1,400,000 \text{ t a}^{-1}$ gypsum), and nearly all the Se (22 t a^{-1}) were derived from the Mancos Shale (MS) in western Colorado.

In 1974, the U.S. Congress passed the Colorado River Basin Salinity Control Act. The purpose of the act is to control the salinity of water delivered to users in the United States and Mexico by constructing, operating, and maintaining projects in the Colorado River Basin. As of 2011, these efforts have reduced salinity loading in

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the river by 1,200,000 tons per year; however, it is estimated that an additional 660,000 tons per year of salinity are needed to meet the 2030 goal of 1,900,000 tons per year (U.S. Bureau of Reclamation, 2011). To target this additional salinity reduction, a more in-depth understanding of salinity sources and transport in the basin is required. This includes determining the role of natural weathering, climate, and land use on salinity. Because salinity and Se weathering cycles overlap (Tuttle et al., companion paper), reducing salinity will help reduce Se.

A number of studies have described salinity and Se derived from the MS in the UCRB and its tributary watersheds (e.g., Butler et al., 1991, 1996; Clark, 1995; Engberg, 1999; Brummer et al., 2002; Butler and Leib, 2002; Fisher, 2005; Kenney et al., 2009). None of these studies have quantified the geochemical cycles on different MS landscapes that control the distribution of salinity and Se between soil and mobile aqueous phases in the watershed, the goal of this study. This paper builds on results from Tuttle et al. (companion paper), which describe the geochemical processes that control salinity and Se during pedogenesis and erosion of the MS weathering naturally in the Uncompahgre River watershed (Fig. 1). Geochemical surveys provide regional data for salinity and Se on two MS landscapes in the watershed. The first landscape is located upland from the floodplain on the Gunnison Gorge National Conservation Area (GGNCA) and has not been disturbed by development or irrigation (Figs. 1 and 2; referred to as natural landscape). The effects of geology and weathering intensity on reservoirs and fluxes for this landscape are quantified. Comparison with results from the regional survey on the second landscape (floodplain) shows the effect of climate and land use on reservoir size and contaminant fluxes. Salinity and Se cycling on the Uncompahgre River floodplain are further constrained with data from detailed studies of soil irrigated for variable lengths of time and laboratory leaching experiments. These results provide

understanding of processes that control water quality in the watershed now and in the future. Together with the companion paper, this study provides resource managers with a quantitative approach for managing landscapes in semiarid to arid climates elsewhere where black shale weathers under similar conditions.

2. Study area

The Uncompahgre River in southwestern Colorado is a tributary to the Gunnison River that flows into the Upper Colorado River (Fig. 1). The climate in our study area is semiarid with less than 25 cm of precipitation per year. Beginning in 1908, the U.S. Bureau of Reclamation created the Uncompahgre (irrigation) Project (UP), which provides an average of $412 \text{ km}^3 \text{ a}^{-1}$ ($334,400 \text{ acre-feet a}^{-1}$; U.S. Bureau of Reclamation, 1982) of diverted Gunnison River water for irrigating 334 km^2 of farmland in the lower portion of the watershed. The amount of diverted water is nearly twice that of the natural flow of the Uncompahgre River just above the UP.

Mancos Shale and derived soil are exposed over 725 km^2 (25% of the watershed). A brief description of the MS geology is in Tuttle et al. (companion paper). The study area is in the lower portion of the watershed and covers 356 km^2 of MS. This includes 116 km^2 of natural MS outside the UP (54 km^2 on the GGNCA) and 240 km^2 on the floodplain (119 km^2 irrigated soil, 103 km^2 non-irrigated soil, 18 km^2 wetlands). The natural MS landscape occurs as deeply incised pediments adjacent to the Black Canyon Uplift (Fig. 2) that weathers into rolling hills and wide valleys westward. The soil is a silty clay loam. Mancos Shale soil on the floodplain (Adobe Soil) occurs on alluvial fans, fan remnants, and stream terraces with slopes less than 1° (Fisher, 2005). Agricultural fields produce a variety of crops once flushed of readily soluble salts; however, even soils that have been irrigated for nearly 100 years still release

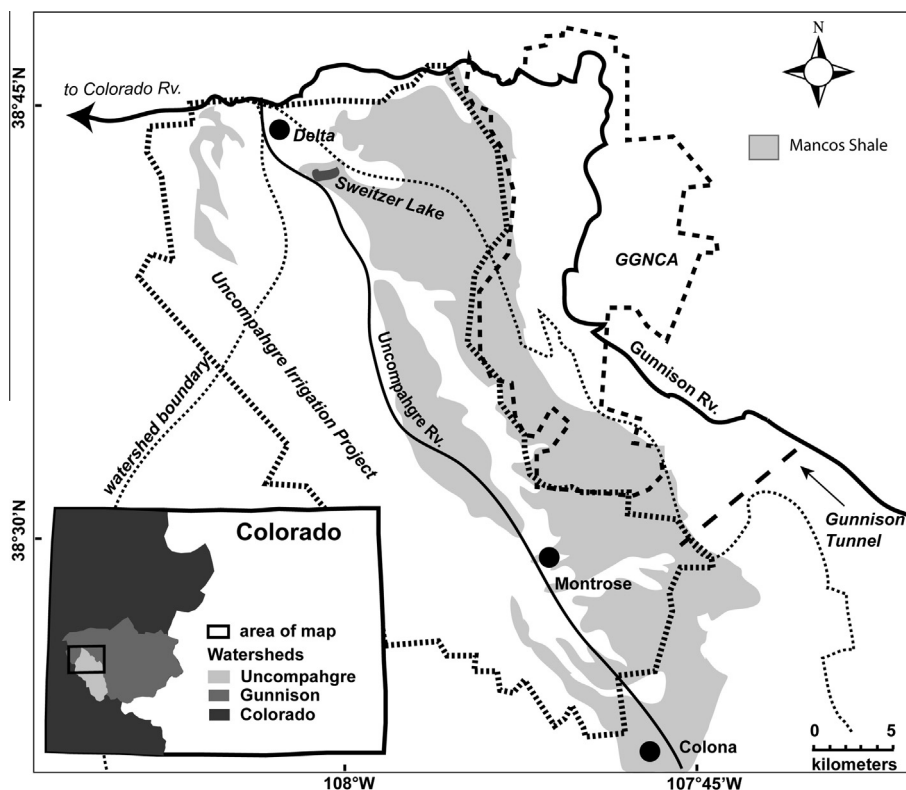


Fig. 1. Map of the study area showing the lower Uncompahgre River watershed, the extent of Mancos Shale (outcrops and derived soil), Gunnison Gorge National Conservation Area (GGNCA), Uncompahgre (irrigation) Project (UP), Gunnison diversion tunnel, and Sweitzer Lake.

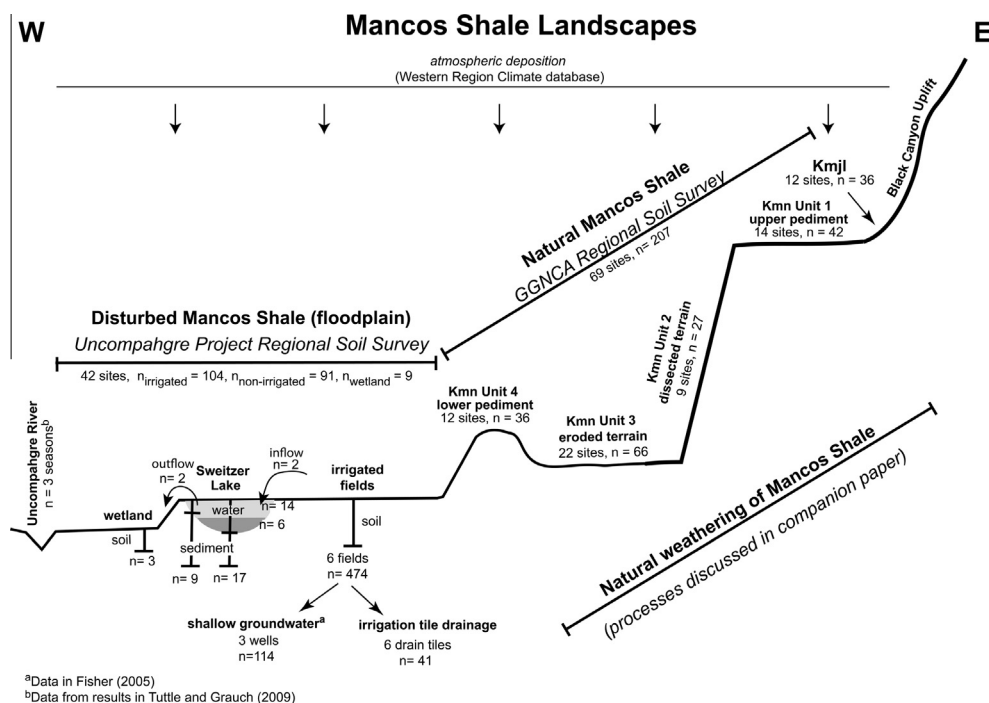


Fig. 2. Schematic showing the sampling sites imposed on a generalized east–west transect across the watershed. The different geological and variably weathered units are noted (see Fig. 3). At each site, the number and type of samples collected are designated. GGNCA, Gunnison Gorge National Conservation Area.

appreciable amounts of salinity and Se to irrigation water (Tuttle et al., 2005; this study).

Because the MS has low permeability due to its fine-grained, clay-rich characteristics, salinity- and Se-laden irrigation return water is removed from fields through subsurface drains. Drainage water then flows into a variety of water bodies including canals, reservoirs, shallow alluvial aquifers, and the Uncompahgre River. Sweitzer Lake is a small recreational reservoir (0.54 km²) on MS and is filled by diverting irrigation return water (details about the lake and surrounding area are in Thomas, 2009). High Se concentrations occur in the lake (Butler et al., 1991; Thomas, 2009; this study), making stocking of fish a serious challenge. Low survival rates have been reported for many species (Barnhart, 1957; Butler et al., 1996; Skorupa, 1998) and advisories warning of Se contamination of the surviving fish are posted at the lake.

3. Materials and methods

3.1. Sample collection

The samples collected for this study (Fig. 2) include soils across the GGNCA and UP; sediment from Sweitzer Lake; and water from drain tiles, shallow groundwater wells, Sweitzer Lake, and the Uncompahgre River. In 2005, a regional soil survey collected three depths of soil (0–5, 5–25, and 25–45 cm) from sites located on a 2.6-km² (1-mi²) grid covering the GGNCA. Soil samples were collected with an auger, dried, and ground to less than 75 μm for bulk chemistry, and sieved to less than 2 mm for extraction. A detailed account of sampling and a tabulation of the chemical data are in Tuttle et al. (2007). Between 1999 and 2005, the U.S. Bureau of Reclamation and the Natural Resources Conservation Service collected samples across the UP. Soil at each site was collected with an auger and homogenized over soil horizon intervals. During the same time, the U.S. Bureau of Reclamation collected samples from six fields in three

irrigated sites (north, central, and south portions of the UP). Each field was 0.1–0.2 km² (30–50 acres) and had been irrigated for variable amounts of time (<5 to >50 years). Soil samples were collected with an auger and homogenized over each horizon interval as above. The U.S. Bureau of Reclamation also sampled water multiple times throughout the year from subsurface drains located 2.4–3.6 m below the surface of these fields. The U.S. Geological Survey sampled shallow groundwater beneath one field throughout one year from wells screened at depths below those of the drain tiles (see Fisher, 2005, for well details).

In 2004, Sweitzer Lake water and sediment were sampled (Fig. 2). Physical and chemical conditions of the lake water (pH, conductivity, temperature, oxidation–reduction potential, and dissolved oxygen) were characterized with a field-calibrated Hydro-lab multi-parameter sonde. Water samples were collected with a peristaltic pump from the surface, and along depth profiles in areas where bottom water in the deep portion of the lake was hypoxic (low oxygen) and where the water column was fully oxygenated (shallow portion). Inflow and outflow samples were also collected. Precautions were taken to prevent trace-metal contamination during sample collection. Samples were filtered (0.45 μm) into acid-washed bottles, cation samples acidified with ultra-pure nitric acid, and all samples refrigerated until analyzed. Sediment cores were taken with a gravity corer from below the anoxic and oxygenated water-columns and from a small wetland just below the overflow dam. Sediment was extruded on site from plastic liners into acid-washed amber bottles under an atmosphere of N₂ to preserve the redox condition of the sediment and immediately refrigerated. Sediment samples for total chemistry were split in the laboratory and dried prior to grinding (<70 μm). A sample split was kept under N₂ for sulfur speciation and isotopic analyses.

During 2005, the solutes carried by the Upper Colorado River above Cisco, Utah and tributaries (including the Uncompahgre River) were inventoried. Three seasons in the calendar year were

sampled as a subset of the U.S. Geological Survey synoptic sampling program (high-water flow, irrigation flow, and base flow). Detailed accounts of sampling and the chemical data for this inventory are in Tuttle and Grauch (2009). Water samples were treated as above.

3.2. Soil extraction

Soil samples were extracted using the saturated paste extract technique (SPE) instead of the many water:solid-ratio extracts because SPE best approximates field saturation conditions during irrigation. Not all salts are fully removed during the SPE as gypsum is oversaturated; however, the readily soluble salts such as thenardite, components of double sulfate salts such as glauberite ($\text{NaSO}_4 \cdot \text{CaSO}_4$), and distinct selenates, if present, readily dissolve. The extracts were prepared by mixing the dried, sieved soil with distilled water into a smooth paste with a consistency comparable to that of pudding (U.S. Department of Agriculture, 2004). The amount of water added relative to the dry weight of the soil is reflected in the percent saturation, which is used to calculate solute concentrations to a dry-weight basis. The pH of the paste and conductivity of the filtrate (0.45 μm) were measured with instruments calibrated using standard procedures. Samples for analyses were treated the same as the aqueous samples above.

3.3. Analytical

Soil from GGNCA regional soil survey and Sweitzer Lake sediment were analyzed for bulk chemical composition by SGS Canada, Inc., Canada. Major elements were analyzed by lithium metaborate fusion/inductively coupled plasma optical emission spectrometry (ICP-OES). Minor and trace elements were analyzed by four-acid digestion/inductively coupled plasma mass spectrometry (ICP-MS). Arsenic (peroxide fusion) and Se (three-acid digestion) were analyzed by hydride generation-atomic absorption spectrometry. The C_{total} and S_{total} were analyzed by combustion; $C_{\text{carbonate}}$ by coulometric titration; C_{organic} by difference; Cl by ion selective electrode; and thallium by graphite furnace atomic adsorption spectrometry. The SGS quality was monitored internally by the U.S. Geological Survey. Most elements have RSDs below 15%. A summary of the entire element suite for GGNCA soils is in Table S1 (online supplement). All UP soils collected by the U.S. Bureau of Reclamation and Natural Resources Conservation Service were analyzed in-house for Se_{total} and Se_{ex} by three-acid digestion/hydride generation-atomic absorption spectrometry.

Analyses of sulfur species in Sweitzer Lake followed procedures of Tuttle et al. (1986) and Rice et al. (1993). A brief description of these procedures is in Tuttle et al. (companion paper). Sulfur isotopes were determined on the barite and Ag_2S produced during speciation using a continuous flow isotope ratio analysis coupled with a thermal combustion/elemental analyzer system. The sulfur isotopic values were calculated from:

$$\delta = ((R_{\text{sample}} - R_{\text{standard}}) / R_{\text{standard}}) \times 1000,$$

where R is the isotopic ratio ($^{34}\text{S}/^{32}\text{S}$); and reported in parts per thousand (‰) deviation from the composition of Vienna Canyon Diablo Troilite (VCDT). Replicate analyses reproduced to within $\pm 0.1\%$.

The GGNCA SPE extracts and Sweitzer Lake aqueous samples were analyzed in-house by ICP-OES (cations), ion chromatography (anions), and ICP-MS (minor and trace elements). Total dissolved carbon and dissolved organic carbon (DOC) were commercially obtained (Huffman Laboratories, Denver, Colorado) and analyzed by combustion. Inorganic carbon (reported as HCO_3^-) was obtained by difference. Selenium was analyzed by hydride generation/atomic adsorption spectrometry. Mercury in Sweitzer Lake samples was

analyzed by flow injection-cold vapor-atomic fluorescence spectrometry. Analyses were considered acceptable for this study if charge balance was within $\pm 10\%$. Total dissolved solid (TDS) data are the sum of major ions, DOC, and dissolved SiO_2 . Summaries of the entire element suite for GGNCA extracts and Sweitzer Lake waters are in Tables S2 and S3 (online supplement).

3.4. Leaching experiments, tile-drainage, and groundwater

Two leaching experiments were performed on UP soil. In the first experiment, dried, ground, and well-irrigated (>50 years) soil was sequentially extracted with distilled water 10 times. This experiment was designed to investigate the transformation of relatively stable phases to readily soluble salt and Se in irrigated soil. The saturation paste extract method described in Section 3.2 was used and the sample was dried and ground after each extraction.

The second experiment was designed to quantify the impact of land-use change on previously non-irrigated soil. Examples of this type of change include farming on previously non-irrigated soil and developing tracts of natural landscapes that require excavation of subsurface MS soil. The experiment passed three pore volumes of distilled water through columns (2" diameter by 18" long) packed with non-irrigated, newly irrigated (<5 years), and well-irrigated (>25 years) dried, ground soil. Soils were not dried between extractions and leachate was collected after each pore volume.

Solutions from these experiments, drain-tile drainage and shallow groundwater were treated as above for conductivity and Se analyses. Complete chemistry was not analyzed in these samples, so conductivity data were converted to total dissolved solid (TDS) using the relation between TDS and conductivity in samples from the same area (Butler et al., 1991):

$$\text{TDS (mg L}^{-1}\text{)} = -279 + 0.924 * \text{EC } \mu\text{S/cm, } r = 1.$$

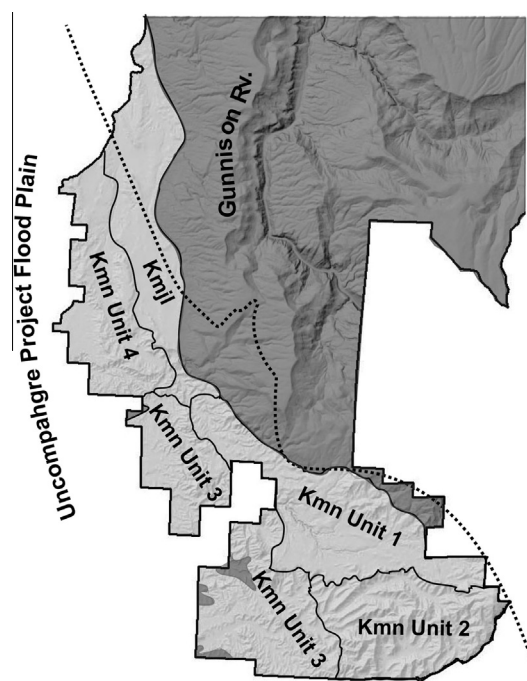


Fig. 3. Map showing the extent of the Juana Lopez Member (Kjlm) and variably weathered Niobrara Member (Kmn) units within the study area on the GGNCA (Unit 1 least weathered to Unit 4 most weathered). Dashed line is the watershed boundary.

Table 1

Means for selected parameters for unweathered MS members in core (Tuttle et al., companion paper), soil on the GGNCA derived from these members, GGNCA soil within the Uncompahgre watershed and from four variably weathered units of the Niobrara Member, soil from the UP based on land-use classification, and soil from farms irrigated for variable lengths of time. (), percentage of total extracted. Data for soil depth 0–45 cm, except farm data, which is for 0–150 cm.

Members	n_{samples}	Salt _{GE} wt.% (generating potential) ^a			Se _{total} (mg kg ⁻¹)
<i>Unweathered Mancos shale (core, 150 m depth)</i>					
Niobrara	56	3.8			1.3
Juana Lopez	42	9.4			1.1
<i>Regional GGNCA soil data (0–45 cm depth)</i>					
Members	n_{sites}^b	Salt _{GE} (wt.%)	Salt _{ex} (wt.%)	Se _{total} (mg kg ⁻¹)	Se _{ex} (μg kg ⁻¹)
Niobrara	56	4.3	0.21 (5%)	1.6	39 (2%)
Juana Lopez	12	1.5	0.08 (6%)	1.3	12 (1%)
<i>GGNCA soil from Niobrara weathered units (0–45 cm depth)</i>					
Unit ^c	n_{sites}	Salt _{GE} (wt.%)	Salt _{ex} (wt.%)	Se _{total} (mg kg ⁻¹)	Se _{ex} (μg kg ⁻¹)
Unit 1 (upper pediment)	14	3.3	0.13 (4%)	1.2	11 (1%)
Unit 2 (dissected pediment)	9	0.87	0.09 (10%)	1.3	11 (1%)
Unit 3 (eroded terrain)	22	5.8	0.33 (6%)	2.0	125 (6%)
Unit 4 (lower pediment)	12	8.6	0.25 (3%)	1.8	40 (2%)
<i>Regional up data (0–45 cm depth)</i>					
Land use	n_{sites}	n_{samples}	Salt _{ex} (wt.%)	Se _{total} (mg kg ⁻¹)	Se _{ex} (μg kg ⁻¹)
<i>Irrigated soil</i>					
All	20	60	0.10	3.0	29 (.01)
Crop	9	27	0.09	3.3	20 (.01)
Development	3	9	0.26	3.1	95 (.03)
Pasture	8	24	0.08	2.8	29 (.01)
<i>Non-irrigated soil</i>					
All	17	51	0.38	4.4	230 (.05)
Rangeland	15	45	0.36	4.4	220 (.05)
Development	2	6	0.57	4.2	335 (.08)
<i>Wetland soil</i>					
All	3	9	1.0	10	3100 (.30)
<i>Farm data (0–150 cm depth)</i>					
Location (time irrigated)	Field size (m ²)	n_{samples}	Salt _{ex} (wt.%)	Se _{total} (mg kg ⁻¹)	Se _{ex} (μg kg ⁻¹)
South Field 1 (<5 y)	101,000	86	1.2	5.6	595 (.11)
South Field 2 (<5 y)	121,000	32	1.0	9.4	1200 (.13)
North Field (25–50 y)	121,000	3	0.10	2.1	5.4 (<.01)
Central Field 1 (>50 y)	158,000	158	0.09	4.1	23 (<.01)
Central Field 2 (>50 y)	57,000	120	0.09	4.7	45 (<.01)
Central Field 3 (>50 y)	69,000	59	0.10	5.3	17 (<.01)

^a Salt_{GE} generating potential is gypsum equivalence calculated from S_{total} concentrations (dominant S-mineral in core is pyrite).

^b Data for GGNCA sites are depth-weighted means calculated from three depth intervals sampled (0–5, 5–25, 25–45 cm).

^c Unit 1 is a flat pediment at the base of the Black Forks Uplift. Unit 2 is a deeply incised landscape weathering into Unit 1. Unit 3 is eroded landscape to west of Units 2 and 3. Unit 4 is lower pediment with an alluvial surface (farthest west).

4. Results and discussion

4.1. Natural Mancos Shale landscapes

Tuttle et al. (companion paper) described the processes that occur during natural weathering and pedogenesis of the MS. Results showed that salt and Se reservoirs vary in size across the natural MS landscape and appear to be sensitive to a variety of factors. To capture the effect of two important variables (geology and extent of weathering), the regional GGNCA soil data (0–45 cm depth interval) are divided with respect to subsurface geology (Juana Lopez and Niobrara Members) and relative extent of weathering of the Niobrara as determined from geomorphology (Fig. 3). The Juana Lopez Member on most the GGNCA occurs on the flank of the Black Canyon Uplift, where the MS dips steeply to the west. This unit designated as Kmjl was sampled in the northern portion of our study area. The Niobrara Member (Kmn) extends from an eastern, relatively flat pediment surface in the southeastern portion of the GGNCA just west of the uplift (Kmn Unit 1) and grades into a dissected pediment to the south (Kmn Unit 2), and an erosional terrain to the west (Kmn Unit 3). In the northern portion of the study area, a wide Kmn pediment surface (Kmn Unit 4) may have been subjected to more alluviation as MS paleosols are found

beneath 1 m of MS alluvium in one of our trenches. Alluvial processes such as these likely intensify as the landscape steps down onto the UP floodplain to the west (Figs. 2 and 3). The Kmn units on the floodplain and the natural landscape are more or less stratigraphic equivalents as the dip on the Niobrara Member is less than 6° (Hansen, 1971) on the flanks of a shallow syncline that runs through our study area just west of the Black Canyon uplift.

4.1.1. Geology

Niobrara and Juana Lopez Members in core contain little to no gypsum or other sulfate salts. Most of the sulfur in unweathered samples is in pyrite with rare sphalerite and copper/nickel sulfides. Sulfur isotopes of salt on the MS landscape show that the sulfate is derived from oxidation of these sulfides during weathering, with gypsum dominating the salt mineralogy (Tuttle et al., companion paper). Salt_{GE} generating potential (Table 1) is calculated to represent the amount of gypsum that could form when sulfides in unweathered shale oxidize, and is calculated from total sulfur core data. The Juana Lopez Member has the potential to generate much more salt than the Niobrara, but the 0–45 cm soils derived from these members show the opposite, with the Niobrara soil containing much more salt_{GE} than the Juana Lopez soil. The amount of salt extracted from soil of both members is only about 0.06 of the

salt_{GE}. Tuttle et al. (companion paper) showed that gypsum accumulates along bedding planes of incipiently weathered Niobrara shale and in subsurface Niobrara soil. The gypsum along shale bedding planes is attributed to weathering near a paleo-water table and the gypsum in soil is an ongoing accumulation from infiltration of sulfate-rich runoff. The Juana Lopez Member is stratigraphically lower than the Niobrara, but is topographically higher on the flanks of the Black Canyon Uplift. It is possible that the higher salt concentration in the Niobrara is due to salinity cycling from the topographically higher Juana Lopez Member to the down-gradient Niobrara in either paleo-groundwater or surface runoff. Salinity data from trenches on Juana Lopez GGNCA terrain could help constrain this hypothesis.

The amounts of Se_{total} in the Niobrara and Juana Lopez Members are similar (Table 1). The amount of the Se_{ex} is small, representing less than 0.03 of the Se_{total}. Comparison of the Se and salt data for the two members and their derived soil support the hypothesis in Tuttle et al. (companion paper), showing that processes variably redistributing salt in the MS soil do not necessarily control Se distribution.

4.1.2. Weathering intensity

Spatial trends of salt and Se in Niobrara soil appear to be related to different geomorphic areas that we believe reflect weathering intensity. In the south half of the GGNCA along the flank of the Black Canyon Uplift (Kmn Unit 1; Fig. 3), a relatively flat pediment surface is thought to be the least weathered Niobrara unit in the study area. This terrain is partially covered by terrace and pediment deposits (Wisconsin Glacial Episode; Hansen, 1971). These deposits are now thin and in many places removed entirely, but could have shielded the MS pediment surface from extensive weathering in the past. Niobrara soils on the pediment contain 3.3 wt.% salt_{GE} (Table 1), of which 0.04 is extractable, and 1.2 mg kg⁻¹ Se_{total}, of which only 0.01 is extractable. These concentrations are all slightly less than the average for all GGNCA soil derived from the Niobrara Member. Salt_{GE} and Se_{total} concentrations are very similar to those in the unweathered Niobrara; however, adjustment of values using bulk density indicates that the shallow soil has lost both of these constituents relative to parent shale (Tuttle et al., companion paper).

Niobrara terrain in the southeastern portion of the GGNCA (Kmn Unit 2) consists of narrow valleys and steep slopes developed during dissection of the Unit 1 pediment surface. Compared to the pediment soil in Unit 1, Unit 2 soil has low salt_{GE} and salt_{ex} concentrations and similar Se_{total} and Se_{ex} concentrations (Table 1). Appreciable amounts of salt have been removed from Unit 2 soil, much more than what is extractable in Unit 1. This suggests a shift in sulfate phase from relatively insoluble gypsum (Unit 1) to soluble sulfates such as sodium sulfate (Unit 2) that can be easily leached from the soil. Data from footslope and alluvial valley trenches in Tuttle et al. (companion paper) describe this process. In addition, the steep terrain in this unit may enhance runoff, leaching solutes from the shallow soil and transporting them from the site.

Niobrara Unit 3 west of Units 1 and 2 is an eroded terrain of wide valleys and rolling hills. We interpret this terrain as having once been analogous to Unit 2, but more weathered as evidenced by the wider valleys and gentler slopes. Salt_{GE}, salt_{ex}, Se_{total} and Se_{ex} concentrations are significantly greater than in Units 1 and 2 (Table 1). The dramatic increase seen in Unit 3 may be due to accumulation of solutes carried in runoff from Units 1 and 2. Because of shallow gradients in Unit 3, runoff may have more time to infiltrate and evaporate due to slower flow rates through the unit.

Niobrara Unit 4 in the northwest quadrant of our GGNCA study area is mostly flat with some steep slopes on the east eroding into an upper pediment surface. A portion of this terrain has paleosols covered by thick alluvium as revealed in one of our trenches. Tuttle

et al. (companion paper) report that all trenches in this unit are more intensely weathered than those in Unit 2. We conclude that Unit 4 is the most intensely weathered unit in the natural study area. Salt_{GE} concentration for this terrain is 8.6 wt.% with about 0.3 of it being extractable (Table 1). Gypsum crystals were found on the soil surface at some of the sample sites. Whether this gypsum formed when the water table was higher, as proposed for gypsum found in trenches (Tuttle et al., companion paper), or during alluviation, is unknown. The source of the sulfate is oxidized MS pyrite as indicated by the sulfur isotopic signature. Total Se concentration of 1.8 mg kg⁻¹ is similar to that of Unit 3, but less of it is extracted. This unit is situated just above the modern floodplain.

4.2. Regional survey of Mancos Shale floodplain soils

All of the MS soil in the UP included in our study area is on the Niobrara Member and, most of the alluvium is derived from the Niobrara Member. In the non-irrigated soil in the UP, the Se_{total}, salt_{ex}, and Se_{ex} are greater than in Kmn Unit 4 (most weathered and adjacent to the floodplain) (Table 1). Clues to these elevated concentrations can be found in the wetlands, where soils contain 0.59 wt.% salt_{ex}, 12 mg kg⁻¹ Se_{total} and 1100 µg kg⁻¹ Se_{ex}. These relatively high concentrations are due to reduced Se phases that accumulate under reducing conditions inherent in most saturated sediment. Paleo-wetlands and backwaters formed during river flooding and avulsion likely covered much of the floodplain at one time or another. As these wetlands dried, reduced phases such as sulfides and selenides oxidized. Resulting iron oxides provided adsorption sites for selenite. This process is essentially the same as that proposed for the Se-enriched iron bands found in trenches on the GGNCA and that are thought to have formed at a paleo-water table (Tuttle et al., companion paper). Adsorbed selenite is not readily soluble, but over time, some selenite oxidizes to selenate, the dominant Se phase in waterways and our extracts. Similar redox processes would affect sulfate (salinity) as well, but concentrating effects are smaller compared to Se due to the inherent large reservoir of sulfate in all MS soil. Although the high Se_{ex} in wetland sediment samples is likely due in part to oxidation during sample preparation, the data provide a good proxy for estimating Se mobilization when wetlands on the floodplain drain and the soil dries.

4.2.1. Irrigation

Leaching by irrigation water has a profound effect on soluble salts and Se in the soil (Table 1). Irrigated soil in areas undergoing development contains more extractable salt and Se than soil in irrigated crop fields and pasture possibly because the soil is disturbed to a greater depth during development (e.g., subdivisions, golf courses, etc.) than when the land is farmed. Although irrigation reduces the amount of salinity and Se in the soil, irrigation return water continues to have poor water quality, with Se often out of compliance with State and Federal standards. The sequential leaching experiment (Fig. 4a) shows that even after 10 extractions of soil irrigated for more than 50 years, salt and Se are mobile. By the sixth extraction, Se_{ex} values are 17 µg kg⁻¹, where they remain during subsequent extractions. Salt_{ex} concentrations stay relatively constant at 0.11 wt.% throughout the entire experiment. The constant salinity concentration is controlled by gypsum solubility, whereas that for Se is likely controlled by the rate of oxidation of reduced Se phases (elemental Se or selenite) to selenate.

Farm data illustrate the effect of irrigation time on salt and Se concentrations in agricultural fields (Table 1). The pore-volume leach data in Fig. 4b show the effect of irrigation on previously non-irrigated soils, soil irrigated less than 5 years, and those irrigated for greater than 25 years. Non-irrigated soils and soils in fields irrigated for less than 5 years have similar salt_{ex} and Se_{ex} depletion trends. In pore volume 1, fields irrigated for >25 years

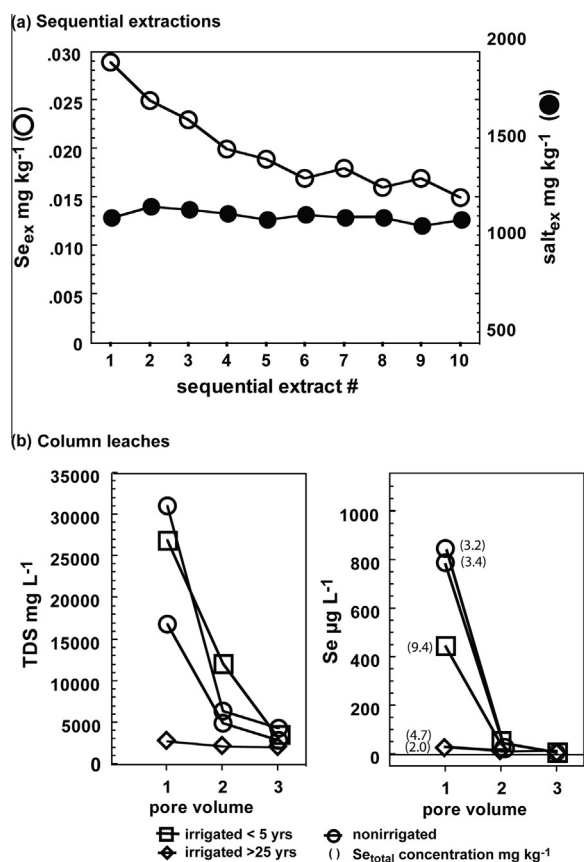


Fig. 4. Experimental results from (a) sequential extractions of an irrigated soil from the central portion of the Uncompahgre (irrigation) Project (salt_{ex} and Se_{ex} concentrations on a dry soil-weight basis), and (b) TDS and Se concentrations in solutions from 3 sequential pore-volume extractions of non-irrigated and irrigated soil from the Uncompahgre (irrigation) Project. Starting Se_{total} concentrations (mg kg⁻¹) in the soil are in parentheses.

have salt_{ex} and Se_{ex} concentrations that are one to two orders-of-magnitude less than in soils irrigated less than 5 years because they have been flushed of a large portion of the readily soluble constituents. The three soil types converge within two pore volumes, approaching the final concentration in the sequential leaching experiment.

Assuming irrigated soils originally had the same Se_{total} concentrations as non-irrigated soils, 6.7×10^8 g of Se (5.6 g m^{-2}) have been removed from the 0 to 150 cm interval since irrigation began. This amount is nearly 200 times the 2005 river's Se load, and is seven times greater than the 0.8 g m^{-2} lost from weathering profiles on natural landscapes during the entire period of pedogenesis

(calculated from data in Tuttle et al., companion paper). Pore-volume leaching data show that Se fluxes would have been very large shortly after irrigation began, but would rapidly decline to the steady concentrations observed today. The sequential leach data show that although Se and salt concentrations have declined over time, irrigated soils will continue to be a potent nonpoint source of contamination well into the future.

4.3. Water management

4.3.1. Drain-tile drainage and shallow groundwater

Drain tiles are installed in irrigated fields because low permeability of the underlying MS retards infiltration. In the fields sampled, the tiles were 2.4–3.6 m deep. The composition of the tile drainage (Table 2) is used to estimate the amount of contaminants that infiltrate the irrigated soil, acknowledging that the irrigation water may have picked up some salinity and Se during transport in the canals or application to fields upstream. The TDS and Se in waters from drain tiles in the central (irrigated >50 years) and south (irrigated <5 years) fields are similar, and, in the north field (25–50 years) concentrations are lowest. All Se values far exceed the U.S. Environmental Protection Agency's freshwater aquatic life chronic criteria of $5 \mu\text{g L}^{-1}$. Drainage eventually discharges into canals or directly into the stream/river system.

Some irrigation water not captured by the drain tiles flows into the shallow subsurface, further interacting with MS. Shallow groundwater sampled from wells in a central UP field contained similar total solutes as the tile drainage, but had significantly more Se (Table 2). The large groundwater Se concentration likely results from redox cycling in the shallow subsurface that sequesters Se in solid phases when anoxic conditions occur intermittently throughout the year and partially remobilizes Se when aerobic conditions prevail. This sequestered Se may be responsible for the elevated Se reported in UP waterways that drain previously irrigated land undergoing urban development (Moore, 2011).

4.3.2. Sweitzer Lake

Near the mouth of the Uncompahgre River, irrigation return water is impounded to form a recreational reservoir (Fig. 1). Sweitzer Lake has a maximum depth of 7.5 m and at the time of sampling, the water column was stratified. The thermocline did not extend into the shallower portions of the lake where sediment is deposited from an oxygenated water column. The reducing conditions of lake sediment provided an opportunity to quantify sequestration of sulfate as pyrite and dissolved Se as selenide in mineral phases. Fig. 5 summarizes the salt and Se concentrations at Sweitzer Lake. At the time of sampling, TDS and Se concentrations in the reservoir inflow were about half those in water draining fields nearby (north field; Table 2); however, bottom water and outflow concentrations were nearly the same as from the nearby drain tile,

Table 2

pH, total dissolved solids (TDS), and Se concentration in water from drain tiles; shallow groundwater in central fields; Sweitzer Lake inflow, surface water, hypoxic bottom water (b.w.), oxygenated bottom water, and surface outflow; and Uncompahgre River at Delta during spring runoff, summer irrigation season, and winter base flow. na, not analyzed.

Sample	n	pH	DO (mg L ⁻¹)	TDS (mg L ⁻¹)	Se (µg L ⁻¹)
Drain tiles (south; <5 y irr.)	8	7.3	na	2680	75
Drain tiles (central; >25 y irr.)	28	7.4	na	2580	79
Drain tiles (north; 5–25 y irr.)	5	7.2	na	2000	31
Shallow groundwater (central)	114	6.9	1.3	2970	240
Sweitzer L. inflow	2	8.3	na	1120	18
Sweitzer L. surface	11	7.8	5.6	2150	12
Sweitzer L. hypoxic b.w.	6	7.4	1.3	2130	6.2
Sweitzer L. oxygenated b.w.	3	7.9	5.9	2120	12
Sweitzer L. surface outflow	1	8.0	5.7	2130	11
Uncompahgre R. spring	1	7.8	na	810	8.6
Uncompahgre R. summer	1	7.9	na	915	9.0
Uncompahgre R. winter	1	8	na	1350	18

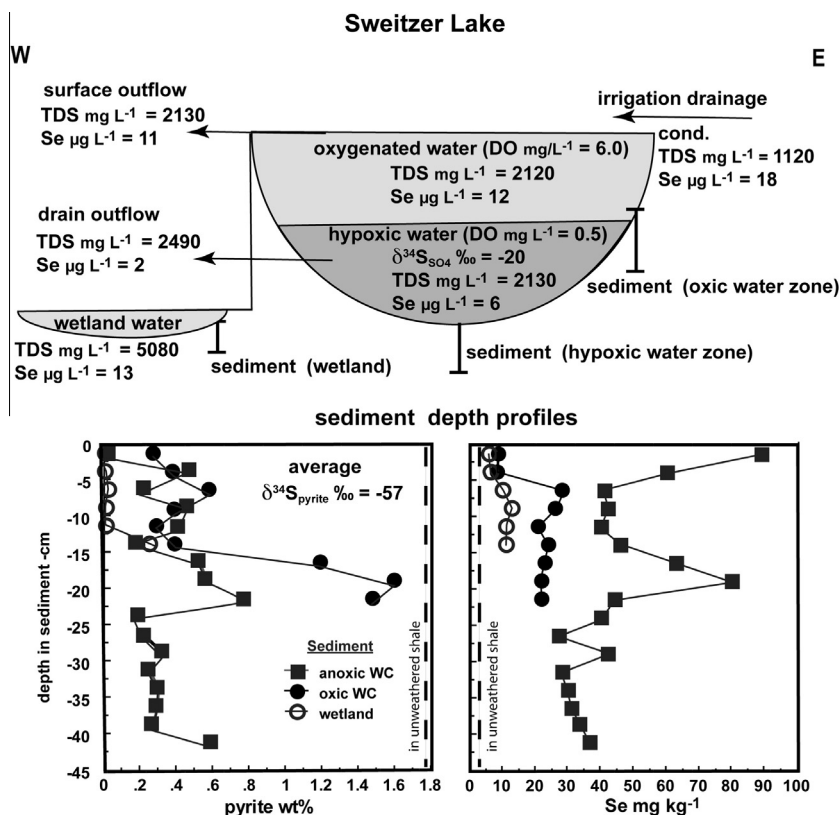


Fig. 5. East–west transect of Sweitzer Lake showing concentrations of TDS and dissolved Se in inflow, outflow, surface water, and below-thermocline water; depth profiles of pyrite and Se_{total} in the lake sediment overlain by hypoxic to anoxic and oxygenated water column and in wetland sediment; and $\delta^{34}\text{S}$ for dissolved sulfate and sediment pyrite.

suggesting that subsurface flow into the lake occurs (Fig. 5). Isotopes of S in sulfate from the lake water and inflow are around -20‰ , indicating that most of the salinity is derived from MS soil. Se concentrations in shallow lake waters are less than in the nearby drain tile and drop to $6.2 \mu\text{g L}^{-1}$ below the thermocline. The decrease in Se through the water column is due to removal of Se by reduction and sequestration in the sediment as discussed above.

Sediment profiles (Fig. 5) show that pyrite and stable Se phases (likely selenide) form rapidly below the sediment water interface. Sulfide is produced from bacterial sulfate reduction that further fractionates the sulfur (average isotopic composition of pyrite is -57‰), and pyrite concentrations at depth reach values close to those in unweathered MS. Lake sediment also accumulates Se. This process is enhanced below the thermocline where sediment has an average Se concentration of 43mg kg^{-1} (values as high as 90mg kg^{-1}) compared to 19mg kg^{-1} in sediment from the shallow portion of the lake overlain by oxygenated water. These Se concentrations far exceed the 1.2mg kg^{-1} in unweathered MS. If Sweitzer Lake was drained and the sediment oxidized, a larger soluble Se reservoir would be produced than in the oxidized wetland sediment discussed in Section 4.2.

5. Cycling of salinity and Se in the Uncompahgre River watershed

Cycling of salinity and Se for the lower portion of the Uncompahgre River watershed is reflected in three budgets calculated from: (1) data for surface water in the watershed (water budget); (2) the GGNCA regional data scaled to include all natural MS landscapes in the watershed outside of the UP (natural landscape budget); and (3) regional data for irrigated, non-irrigated, and wetland

soil (UP landscape budget). Details on the construction of these budgets are in the [online supplement](#).

5.1. Salinity and Se cycling based on water budget

The water budget (Fig. 6 and Table 3) identifies water sources and quantifies their salinity and Se loads to the river in 2005. The budget was constructed with 2005 climate data; 2005 measured flow rates and loads; 2005 irrigation diversion data, estimated water delivery data, and evaporation records (last two variables are estimated from data in [U.S. Bureau of Reclamation, 1982](#)). Salinity and Se loads in the river are derived from multiple sources within the watershed. Precipitation in the watershed supplies less than 1% of the river's salinity load and about 2% of the Se load. The river above Colona delivers 31% of the river's 2005 salinity load and 4% of the Se load. Gunnison River water diverted into the watershed for irrigation (Fig. 1) brings in 29% of the river's salinity load and 6% of the Se load. Tributaries below Colona, but outside the UP delivered 7% of the salinity and 5% of the Se to the river. After accounting for these loads, we assume the remainder of the salinity and Se in the river is derived from the irrigated and non-irrigated landscapes within the boundary of the UP (33% of the salinity and 83% of the Se loads).

The water balance shows more inflow to the watershed than recovered as outflow. This discrepancy could be due to error or uncertainty in input data, deep percolation of water that discharges outside the watershed, or moisture retained in the soil, or a combination of these possibilities. Although we have no direct data to test these possibilities, measurements of moisture in irrigated soils are consistent with soil moisture retention of 13 wt.% moisture in irrigated soils. The calculated amounts of salinity and Se that would be associated with this moisture could be as high

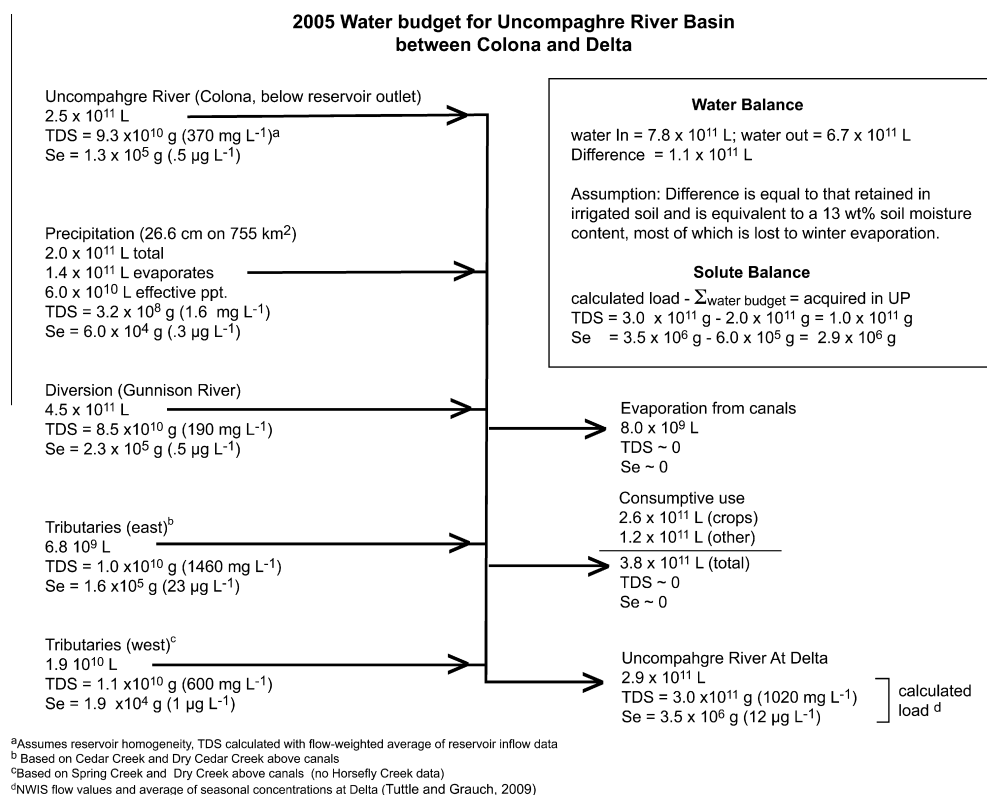


Fig. 6. The 2005 water budget for Uncompahgre River watershed between Colona and Delta.

Table 3

Sources of salt and Se in the Uncompahgre River and their estimated contribution to annual river load (water budget) and Mancos Shale (MS) contributions to the annual river load. (Scaled GGCA and Uncompahgre Project flood plain budget).

Sources	Salt (g a ⁻¹)				Selenium (g a ⁻¹)			
	Water budget	% River salt load	Scaled GGCA/UP MS salt budget	% River salt load	Water budget	% River Se load	Scaled GGCA/UP MS Se budget	% River Se load
Precipitation in UP ^a	3.2×10^8	0.1			6.0×10^4	2		
River above Colona	9.3×10^{10}	31 ^b			1.3×10^5	4		
MS above Colona			2.3×10^{10}	8			1.3×10^5	4
Diversion water	8.5×10^{10}	29			2.3×10^5	6		
Tributaries below Colona and outside UP	2.1×10^{10}	7			1.8×10^5	5		
MS in Tributaries below Colona and outside UP			3.8×10^9	1			4.8×10^4	2
Acquired from the UP	1.0×10^{11}	33			2.9×10^6	83		
Acquired from MS on UP			8.8×10^{10}	29			2.5×10^6	71
MS Soil irrigated (tailwater)			3.1×10^{10}	10			5.9×10^5	17
MS Soil irrigated (tile drainage)			4.6×10^{10}	15			1.4×10^6	40
MS Soil non-irrigated			1.1×10^{10}	4			4.8×10^5	14
Sum	3.0×10^{11}	100	1.1×10^{11}	38	3.5×10^6	100	2.7×10^6	77
2005 Load in Uncompahgre River at Delta	3.0×10^{11}				3.5×10^6			

^a TDS and Se derived from precipitation above Colona are included in River above Colona; TDS and Se derived from precipitation below Colona, but outside UP are included in tributaries below Colona and outside UP.

^b Eight percent of the total river load at Delta is from Mancos Shale landscapes upstream from Colona as determined with sulfur isotopes.

as 6.9×10^{10} g salt (25% of the 2005 Uncompahgre River's annual salinity load) and 2.9×10^6 g Se (80% of the river's Se load).¹ Moisture evaporation during the dry winter would form sulfate minerals (gypsum, thenardite, and glauberite) and selenate minerals. When moist conditions return with the next irrigation season, gypsum and the CaSO₄ portion of glauberite would be left behind and the sodium sulfate solubilized in irrigation water. Selenate, if present,

would be mobilized as well. This process provides a mechanism for production of the relatively large amount of gypsum found in irrigated soils.

5.2. Salinity and Se cycling on natural landscapes (scaled GGCA budget)

The salinity and Se cycles for the natural landscape are based on GGCA regional soil data and provide reservoir inventories (0–45 cm depth interval) and contaminant fluxes. Reservoir concentrations (on a per m² basis) are calculated from bulk soil

¹ Amounts calculated from the hypothetical 13% soil moisture and the geometric mean of SPE concentrations for 0–150 cm in irrigated fields.

chemistry or extract chemistry, and soil density. Reservoir size is the concentration times the areal extent. Fluxes are calculated from surface (0–5 cm) extract chemistry, rainfall simulation data (90% infiltration, 10% runoff), and annual rainfall rates (Elliott et al., 2007). Although the data are specific to the GGNCA (53.5 km²), we assume that the processes that control reservoirs and fluxes in GGNCA units are the same that control fluxes across the entire natural MS landscape above the floodplain (an additional 62 km² within the study area). We also assume that the landforms on the GGNCA are a good representation of those across the entire natural landscape below Colona. This second assumption was tested with a Lidar elevation model (online supplement) that shows the terrain sampled in our study physically represents the broader area of natural Mancos Shale landscape in the study area. Therefore, we conclude that our data provide reasonable estimates for the entire 116 km² of natural landscape below Colona.

Reservoir data for the five units across the GGNCA are in Fig. 7a and reflect the geology and weathering intensities discussed in Section 4.1. Collectively, the soil on the natural landscape below

Colona contains 3.1×10^{12} g salt_{GE}, (average of 26,900 g m⁻²) of which 3.2×10^{11} g is extractable (10% of total). Applying the results from our rainfall simulation experiments (10% runoff), the amount of salt that is transported is estimated to be 3.8×10^9 g a⁻¹. The natural landscape also contains 1.1×10^8 g Se_{total} (average of 985 mg m⁻²) of which 3.6×10^6 g are extractable (3% of total). We calculate that 4.8×10^4 g a⁻¹ Se are transported in runoff.

Using $\delta^{34}\text{S}_{\text{SO}_4}$ data (Tuttle and Grauch, 2009), we estimate that 25% of the river's salinity load at Colona is derived from MS soil upstream. We have no constraint on what portion of the small amount of Se associated with this source is derived from MS. Based on other data indicating MS is the major source of Se in the watershed, we assign the entire amount (4% of the river load) to MS landscapes upstream of Colona. We have no data to determine whether the loads are from natural landscapes or irrigated land, but no large irrigation project such as the UP serves the area, so we have included the solutes and Se in the natural landscape budget (Table 3).

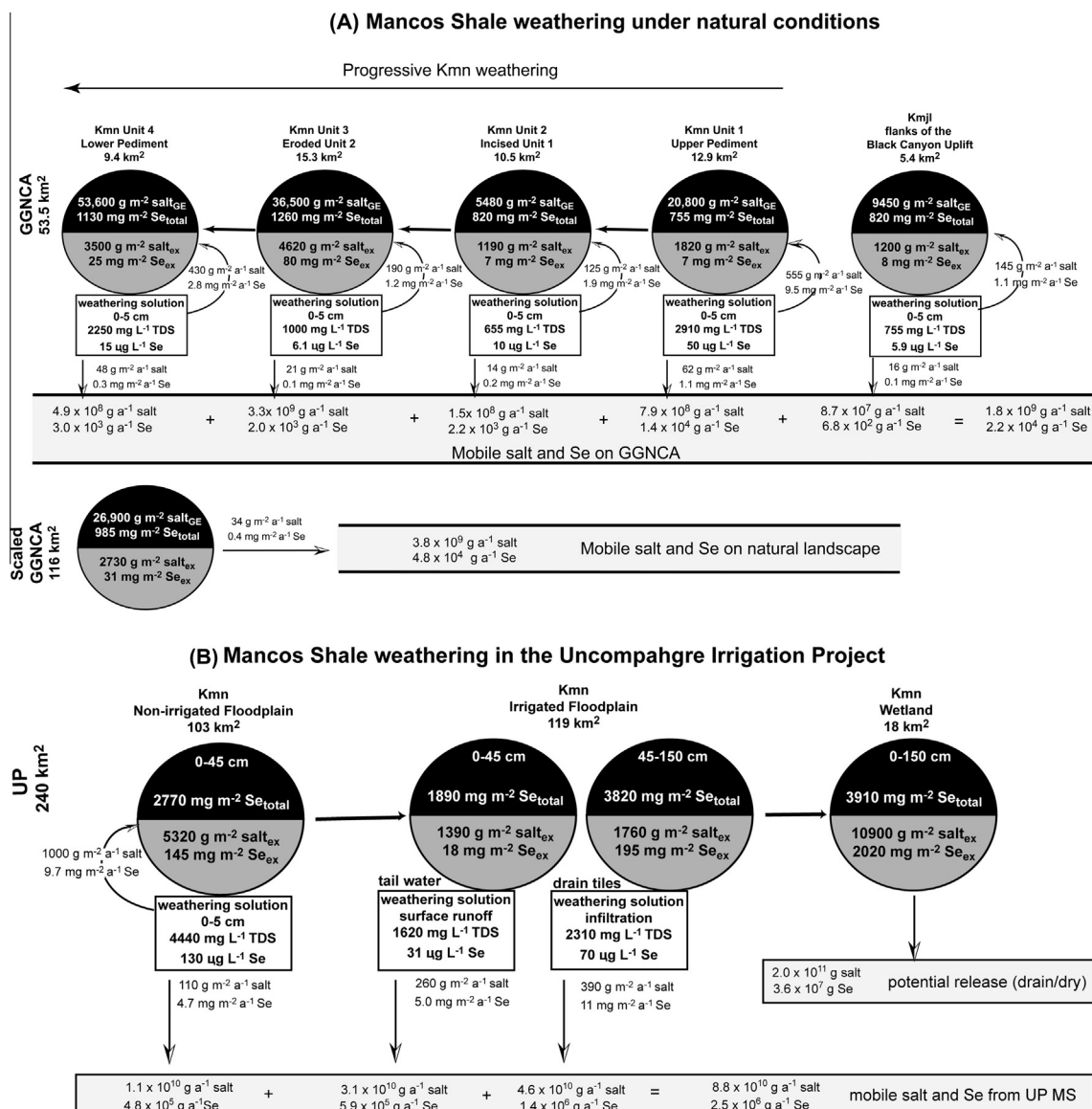


Fig. 7. Salinity and selenium reservoir concentrations and contaminant fluxes for (a) geological and weathered units on the GGNCA and the scaled natural landscape and (b) irrigated, non-irrigated, and wetland soil in the Uncompahgre (irrigation) Project floodplain.

5.3. Salinity and Se cycling on the Uncompahgre (irrigation) Project floodplain

Reservoir inventories on the UP (0–45 cm) are calculated from bulk soil chemistry or extract chemistry, and soil density (Fig. 7b). Inventories for a deeper reservoir in irrigated soil (45–150 cm) are included because irrigation water infiltrates to greater depths than rainfall. Wetland inventories are for 0–150 cm. No inventory of salt_{CE} for the UP was possible because total sulfur data were not available for UP soils. Fluxes for non-irrigated soils are calculated in the same manner as those for natural landscapes (0–5 cm extract chemistry, rainfall simulation experiment results (90% infiltration, 10% runoff), and annual rainfall rates (Elliott et al., 2007)). Fluxes for irrigated soil are calculated using 0–45 cm extract chemistry (greater depth interval because of deeper infiltration), annual irrigation application rates (U.S. Bureau of Reclamation, written commun., 2007), and tailwater and baseflow estimates (U.S. Bureau of Reclamation, 1982). No flux estimates were calculated for wetlands as we assume that solutes remain in the waterlogged soil. However, extract data were used to calculate how much salt and Se could be mobile if all the current wetlands were drained and the soil dried during changes in land use or climate.

Across the UP, non-irrigated (0–45 cm) MS soil contains 5320 g m⁻² salt_{ex}, twice the amount as in the same soil interval on natural MS landscapes (Fig. 7a and b). This increase reflects processes that fix sulfur in the soil as reduced phases (pyrite or elemental S) during flooding and river avulsion. Oxidation of these phases to sulfates occurs when the soil dries. Irrigated MS soil (0–45 cm) contains 1390 g m⁻² salt_{ex}, much less than non-irrigated soil due to continuous leaching of the sodium sulfate salts with irrigation water. Because the amount of salt contributed to the river load each year is similar, the soluble portion of salt in the soil must be renewed each year by transformation of relatively insoluble phases to soluble phases. In the deeper interval (45–150 cm), irrigated soil contains similar amounts of salt_{ex} as in shallower depths. The amount of salt_{ex} here is also controlled by sulfate mineral solubility as well as removal of solutes with tile drainage and groundwater recharge.

Total and extractable Se reservoir concentrations are much greater in non-irrigated soil on the UP compared to the natural landscape; however, similar proportions of Se_{total} are extractable (0.03 and 0.05). Irrigated soil also contains more Se_{total} than the natural landscape; however, the loss of Se during irrigation is evident when Se_{total} and Se_{ex} reservoir concentrations are compared to those for non-irrigated soil in the UP. In deeper irrigated soil, the Se_{total} increases by a factor of two relative to shallow irrigated soil while the Se_{ex} increases by over an order-of-magnitude. Processes that control the large increase in extractable Se relative to extractable salt are not readily apparent, but possibilities are competing Se–S reduction/oxidation rates, pyrite-selenide stability, gypsum–glauberite–thenardite stability relative to selenite-selenate mineral stability, and selenite adsorption. Because the irrigation water interacts with a deeper soil interval (0–45 cm in our model) than rain (0–5 cm), more salt and Se are transported from irrigated soil than from non-irrigated UP soil (Fig. 7b). This model calculates that the MS floodplain landscape contributes 8.8 × 10¹⁰ g a⁻¹ salt and 2.5 × 10⁶ g a⁻¹ Se to the river. Comparing these amounts to those calculated for the entire UP floodplain (1.0 × 10¹¹ g salt and 2.9 × 10⁶ g Se), we conclude that over 86% of the contaminants coming from the area within the UP are from MS soil.

The concentration of Se_{total} in wetland soil is similar to that in deeper irrigated soil (Fig. 7b); however, the amount of extractable salt and Se is nearly an order-of-magnitude greater. The amount of salt that could potentially be mobilized upon draining and drying

of the wetland soil is twice that collectively transported each year from the other UP soils, and the amount of Se is an order-of-magnitude greater. The disparity between potential salt and Se supplies in the wetland likely is due to (1) redox cycling in wetland soil (see Section 4.2) that preferentially favors sequestration of Se relative to S (observed in Sweitzer Lake sediment), (2) different reduction/oxidation rates for Se and S, (3) less soluble sulfate minerals relative to selenate minerals, and (4) enhanced selenite desorption.

5.4. Summary of salinity and Se cycling in the watershed

Gypsum solubility controls the large concentrations of salt in MS soil. During incipient weathering of the shale, pyrite oxidizes at the water table. Gypsum forms as the water table recedes (Tuttle et al., companion paper). Gypsum also forms in MS soil from centuries of weathering. During weathering, rain and snowmelt dissolve calcite and thenardite at the soil surface and solutes are carried deeper into the soil as the moisture infiltrates. In the sub-surface, evapotranspiration leaves behind gypsum and enriches soil moisture in Na₂SO₄. Under extreme dryness, soil moisture evaporates and forms soluble Na₂SO₄ salts and, eventually, reacts with gypsum to form glauberite. Formation of salts by this weathering process is ongoing across the natural MS landscape and, due to the dry climate, only a relatively small portion of the solutes in the river today are sourced from them. When MS soil is irrigated, Na₂SO₄ readily dissolves, supplying the river with over a third of its salinity load. Because gypsum solubility is limited in the irrigated soil, it provides a constant salinity supply. If wetter climatic conditions were to prevail, larger amounts of salinity from the natural landscape would be expected. If irrigation were to stop and the land to remain undeveloped, salinity storage in the soil would increase and supply to waterways would decrease.

Most of the Se in MS soil occurs in immobile phases such as adsorbed selenite and the less abundant selenide and elemental Se. The mobile Se phase is selenate associated with soil moisture or Na₂SO₄ salt, and forms through (pseudo) equilibrium reactions between soluble and insoluble Se phases. Similar to salinity, Se from the natural landscape contributes little to the river load and most Se is from irrigated soil. Selenium appears to be preferentially mobilized relative to salt during irrigation. A similar disparity is seen in wetland soil where S and Se mobility is differentially controlled by redox, solubility, and sorption processes.

6. Implication of results

Fig. 8 summarizes the contribution of each Mancos Shale (MS) landscape to the salinity and Se loads in the Uncompahgre River as calculated in the scaled GGNCA and UP budgets. The MS landscapes account for 25% of the area in the Uncompahgre River watershed and supplies 38% of the Uncompahgre River's salinity load. Of the 38%, irrigated soil supplies 66% (26% in tailwater and 40% in tile drainage), 10% is from non-irrigated land in the UP, and 24% from the natural landscape. We assume that none of the loads are derived from wetlands as long as they remain saturated. The MS contributes 77% of the Se load in the Uncompahgre River. Of the 77%, 75% is attributed to irrigated soil (22% from tailwater and 53% tile drainage), 18% to non-irrigated soil in the UP, and 7% to the natural landscape.

Statistical models estimating salt and Se loading have been used to evaluate salt and Se reduction projects for the Colorado River Basin (e.g., Anning et al., 2007; Kenney et al., 2009; Leib et al., 2012; Linard, 2013). Our results based on process-oriented research provide an independently derived comparison for these statistically based estimates. Comparisons between the two methods are not exact because sampling periods and geologic classifications vary

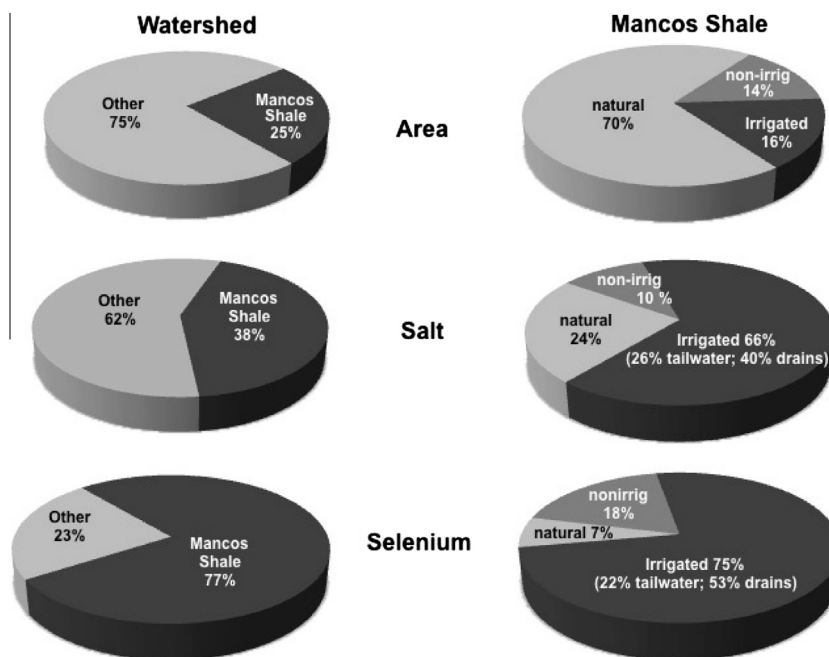


Fig. 8. Contribution of the Mancos Shale to the area of the watershed and the annual salinity and Se loads in the Uncompahgre River at Delta. The area, salinity, and Se contributions from Mancos Shale are further divided into contribution by land use.

between them. Regardless, if we assume environmental conditions are relatively constant over time and Mancos Shale represents all the high salinity yielding Mesozoic rocks in the watershed, then comparison of our results with the statistical approach is possible.

For example, we compared our results to those of Kenney et al. (2009), who present a U.S. Geological Survey, Spatially Referenced Regressions on Watershed Attributes (SPARROW) surface-water quality model, estimating salinity loadings to the Upper Colorado River and its major tributaries. The SPARROW model variables include rock type (divided by age and salinity class), land use (specifically, irrigated agriculture and reservoirs), point-source contributions, and landscape transport characteristics. For the Uncompahgre watershed (09144250 station), the SPARROW model predicts that 60% of the river's salt load is from irrigated high-salinity yielding Mesozoic rock, with no contribution from weathering of these rocks under natural conditions (Kenney et al., 2009). Our budget shows that 38% of the salt load is derived from MS within the same watershed (25% from irrigated MS landscapes and 13% from weathering of natural MS landscapes; Table 3). Discussion of the possible causes for disagreement is beyond the scope of this paper; however, data from this study suggest that, at least in the Uncompahgre watershed, statistical processes may overpredict salt loads derived from irrigated MS landscape and underpredict contributions related to natural weathering processes.

The broader implications of this paper provide water-resource and land managers data for making informed policy decisions. For example, in this watershed results provide quantitative data to support recommendations that sprinklers replace flood irrigation to lower the amount of tailwater and deep percolation, improving groundwater and return water quality. Results show that sediment in wetlands, ponds, and reservoirs will release Se to the environment at highly accelerated rates when dried and sediments are exposed to ambient weathering conditions. This scenario could be accelerated by climate change, water diversion, or dredging. The data show that the natural landscape contributes moderate amounts of salt that will be difficult to mitigate; however, it contributes little Se contamination due to the partial

decoupling of the salinity and Se cycles during weathering and solute transport. In addition, results identify the types of data and protocols necessary to address specific issues in future studies related to nonpoint-source contamination from rocks weathering in arid to semiarid climates.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apgeochem.2013.12.011>.

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