

Evaluation of Mineral Deposits Along the Little Wind River, Riverton, Wyoming, Processing Site

December 2014



**U.S. DEPARTMENT OF
ENERGY**

Legacy
Management

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Appendix

Appendix A *Work Plan to Sample Mineral Deposits Along the Little Wind River Riverton, Wyoming, Processing Site*

Abbreviations

| | |
|------------------------|--|
| COC | contaminant of concern |
| DOE | U.S. Department of Energy |
| EPA | U.S. Environmental Protection Agency |
| GEMS | Geospatial Environmental Mapping System |
| g | grams |
| GPS | Global Positioning System |
| kg | kilograms |
| $\mu\text{R}/\text{h}$ | microroentgens per hour |
| mg | milligrams |
| mg/kg | milligrams per kilogram |
| mg/L | milligrams per liter |
| Mn | manganese |
| Mo | molybdenum |
| MTL | maximum tolerable level |
| SAP | Sampling and Analysis Plan for U.S. Department of Energy Office of Legacy Management Sites |
| SO_4 | sulfate |
| SRNL | Savannah River National Laboratory |
| TDS | total dissolved solids |
| U | uranium |

1.0 Introduction

In 2012, the U.S. Department of Energy (DOE) began reassessing the former Riverton, Wyoming, Processing Site area for potential contaminant sources impacting groundwater. A flood in 2010 along the Little Wind River resulted in increases in groundwater contamination (DOE 2013). This investigation is a small part of continued efforts by DOE and other stakeholders to update human health and ecological risk assessments, to make a comprehensive examination of all exposure pathways to ensure that the site remains protective through established institutional controls.

During field inspections at the Riverton Site in 2013, a white evaporitic mineral deposit was identified along the bank of the Little Wind River within the discharge zone of the groundwater contamination plume. In December 2013, Savannah River National Laboratory (SRNL) personnel collected a sample for analysis by X-ray fluorescence (Figure 1 shows the type of material sampled). The sample had a uranium concentration of approximately 64 to 73 parts per million. Although the uranium in this mineral deposit is within the expected range for evaporitic minerals in the western United States (SRNL 2014), DOE determined that additional assessment of the mineral deposit was warranted.



Figure 1. Example of a Mineral Deposit Sampling Location

In response to the initial collection and analysis of a sample of the mineral deposit, DOE developed a work plan (*Work Plan to Sample Mineral Deposits Along the Little Wind River, Riverton, Wyoming, Processing Site* [DOE 2014]) to further define the extent of these mineral deposits and the concentration of the associated contaminants (Appendix A). The work plan addressed field reconnaissance, mapping, sampling, and the assessment of risk associated with the mineral deposits adjacent to the Little Wind River. The objectives of the work plan were to:

- Identify the extent of the mineral deposits.
- Determine concentrations of contaminants of concern (COCs), manganese, molybdenum, sulfate, and uranium, in the mineral deposits and associated soil.
- Determine if these mineral deposits pose unacceptable risks to human health or the environment.

This report details the results of the investigation prescribed in the work plan, including field reconnaissance and mapping, concentrations of COCs, an evaluation of potential risks, and a search for any correlation of the mineral deposits with site conditions.

2.0 Field Reconnaissance and Mapping

Visual inspection of the north bank of the Little Wind River and oxbow lake (within the institutional control boundary) was conducted to identify areas of mineral deposits resulting from the evaporation of groundwater seeps. Field reconnaissance was conducted at the oxbow lake, the section of the river where the groundwater plume is expected to intersect the river, and areas on either side of the plume. A global positioning system (GPS) device was used to map the linear extent of each expression of a mineral deposit, and the vertical thickness of the deposits was measured and recorded. With the exception of location MD-01, vertical thickness of the mineral deposits was measured from the base of the deposit to the top of the deposit where it outcropped at the river bank. Location MD-01 was away from the river bank and oriented in a horizontal plane on flat ground, and, therefore, had zero vertical thickness. Photographs were taken of each sampling location (to provide additional documentation of the mineral deposit) and of other items of interest. Figure 1 shows a typical mineral deposit. Representatives from the Wind River Environmental Quality Commission participated in the sampling event.

Photographs taken during this sampling event are available for viewing with dynamic mapping via the Geospatial Environmental Mapping System (GEMS) website at <http://gems.lm.doe.gov/#&site=RVT>. Results of the reconnaissance and mapping are listed in Table 1 and shown in Figure 2. Table 1 documents the concentrations of COCs in the samples and how these compare to benchmark levels. Details of the methods and the basis for the benchmark concentrations are presented in the following section.

Mineral deposits were most often associated with south-facing river banks on the north side of the Little Wind River, possibly due to increased sun exposure, which enhanced evaporation and mineral deposit formation.

Table 1. Mineral Deposit Field and Analytical Data Compared to Ecological Benchmarks^a

| Sample Location | Radiological Reading on Contact ($\mu\text{R}/\text{h}$) | Radiological Reading at 3 Feet ($\mu\text{R}/\text{h}$) | Vertical Thickness of Mineral Deposit (Inches) | Manganese (Benchmark = 1,000 mg/kg) | Molybdenum (Benchmark = 5–10 mg/kg) | Sulfate (Benchmark = 4,500 mg/kg) | Uranium (Benchmark = 100–400 mg/kg) |
|-----------------|--|---|--|-------------------------------------|-------------------------------------|-----------------------------------|-------------------------------------|
| MD-01 | 24.0 | 20.0 | 0 (horizontal) | 250 | 0.59 | 83,000^b | 1.4 |
| MD-02 | 17.3 | 21.3 | 13 | 260 | 0.42 | 5,400 | 1.8 |
| MD-03 | 22.0 | 18.6 | 16 | 210 | 0.26 | 66,000 | 1.4 |
| MD-04 | 20.0 | 19.4 | 21 | 350 | 0.35 | 35,000 | 2.6 |
| MD-05 | 15.3 | 18.0 | 21 | 230 | 0.29 | 66,000 | 2.5 |
| MD-06 | 18.0 | 14.6 | 40 | 250 | 0.69 | 100,000 | 2.5 |
| MD-07 | 17.3 | 20.3 | 24 | 190 | 0.51 | 69,000 | 2.7 |
| MD-08 | 23.3 | 18.0 | 5 | 400 | 0.41 | 48,000 | 4.4 |
| MD-09 | 22.0 | 17.3 | 13 | 290 | 0.57 | 73,000 | 8.8 |
| MD-10 | 22.0 | 18.0 | 25 | 230 | 0.57 | 66,000 | 12 |
| MD-11 | 16.6 | 14.0 | 32 | 220 | 0.26 | 71,000 | 3.5 |
| MD-12 | 18.6 | 20.0 | 32 | 180 | 1.8 | 120,000 | 25 |
| MD-13 | 13.0 | 24.0 | 15 | 180 | 3.4 | 130,000 | 27 |
| MD-14 | 18.0 | 18.0 | 35 | 340 | 1.9 | 62,000 | 30 |
| MD-15 | 22.0 | 20.0 | 30 | 210 | 0.49 | 95,000 | 6.5 |
| MD-16 | 20.0 | 13.3 | 23 | 230 | 1.2 | 140,000 | 16 |
| MD-17 | 26.6 | 17.0 | 16 | 260 | 2.9 | 47,000 | 13 |
| MD-18 | 16.6 | 18.0 | 12 | 230 | 7 | 110,000 | 46 |
| MD-19 | 16.6 | 12.6 | 32 | 270 | 15 | 72,000 | 66 |
| MD-20 | 26.0 | 21.3 | 24 | 240 | 1.6 | 90,000 | 46 |
| MD-21 | 18.6 | 20.0 | 48 | 240 | 1.0 | 160,000 | 51 |
| MD-21 Duplicate | — | — | — | 240 | 1.2 | 220,000 | 55 |
| MD-23 | 24.0 | 16.0 | 13 | 450 | 0.74 | 82,000 | 6 |
| MD-24 | 22.6 | 19.3 | 21 | 450 | 0.45 | 71,000 | 14 |
| MD-25 | 17.3 | 23.3 | 11 | 190 | 0.68 | 53,000 | 2.6 |
| MD-26 | 16.6 | 16.6 | 9 | 330 | 0.44 | 67,000 | 3.6 |
| MD-27 | 14.6 | 10.6 | 24 | 250 | 0.49 | 110,000 | 5.1 |

Table 1 (continued). Mineral Deposit Field and Analytical Data Compared to Ecological Benchmarks^a

| Sample Location | Radiological Reading on Contact ($\mu\text{R}/\text{h}$) | Radiological Reading at 3 Feet ($\mu\text{R}/\text{h}$) | Vertical Thickness of Mineral Deposit (Inches) | Manganese (Benchmark = 1,000 mg/kg) | Molybdenum (Benchmark = 5–10 mg/kg) | Sulfate (Benchmark = 4,500 mg/kg) | Uranium (Benchmark = 100–400 mg/kg) |
|---------------------------|--|---|--|-------------------------------------|-------------------------------------|-----------------------------------|-------------------------------------|
| MD-27 Duplicate | — | — | — | 240 | 0.43 | 110,000 | 4 |
| MD-29 | 27.3 | 18.6 | 25 | 250 | 0.6 | 65,000 | 3.6 |
| MD-30 | 16.6 | 16.0 | 23 | 230 | 0.38 | 39,000 | 2.2 |
| MD-31 | 16.6 | 20.6 | 21 | 200 | 0.33 | 47,000 | 2.4 |
| MD-32 | 23.3 | 14.6 | 28 | 210 | 0.38 | 170,000 | 7.2 |
| MD-33 | 22.6 | 12.0 | 18 | 230 | 0.54 | 69,000 | 5.2 |
| MD-34 | 20.0 | 10.6 | 25 | 200 | 0.96 | 85,000 | 4.6 |
| Background | 24.0 | 20.0 | — | 250 | 0.59 | 83,000 | 1.4 |
| Minimum | 13 | 10.6 | 5 | 180 | 0.26 | 5,400 | 1.4 |
| Maximum | 27.3 | 24 | 48 | 450 | 15 | 220,000 | 66 |
| Mean | 19.8 | 17.6 | 22 | 257 | 1.44 | 85,255 | 14.2 |
| Standard Deviation | 3.7 | 3.4 | 9.4 | 69 | 2.7 | 43,073 | 18.0 |

Notes:

^a Benchmark values from *Mineral Tolerance of Animals* (NRC 2005).

^b Values in red text exceed the benchmark value.

Abbreviations:

$\mu\text{R}/\text{h}$ = microroentgens per hour
mg/kg = milligrams per kilogram

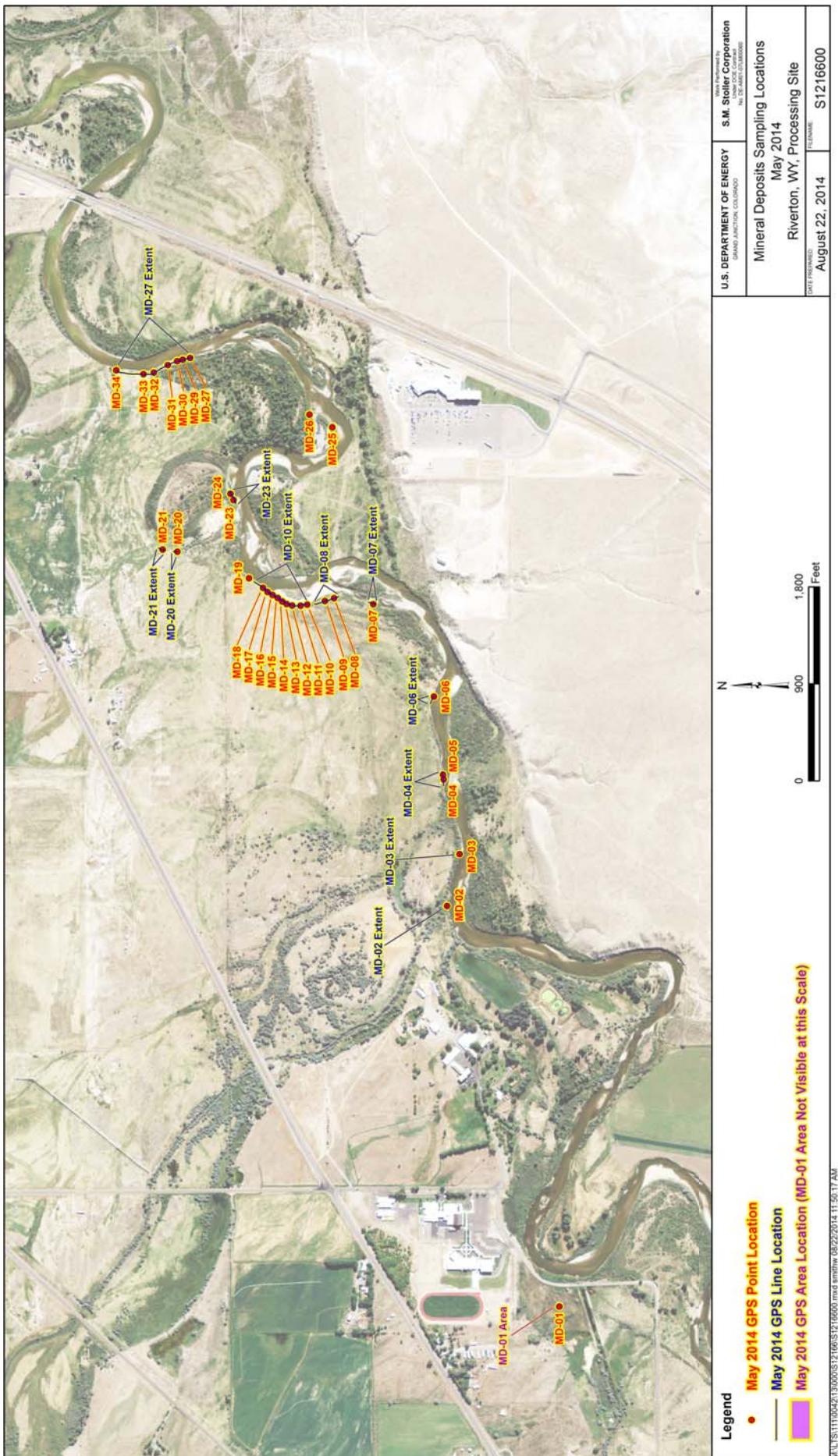


Figure 2. Mineral Deposit Sampling Locations and Extent of Mineral Deposits

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3.0 Sampling and Analysis

3.1 Sampling Protocol

Samples were collected every 50 feet across 27 “extents” (Figure 2) where mineral deposits were located. Where a mineral deposit was less than 50 feet long, one sample was collected at that isolated deposit at eight locations. A total of 32 locations were sampled, and two duplicate samples were collected. GPS coordinates were recorded at each sample location. Samples were numbered consecutively starting with MD-02 on the west side of the reconnaissance area, and one sample (MD-01) was collected near the upstream sampling location to provide background data (Figure 2).

The sample collection technique consisted of scraping a thin layer of mineral deposit and soil along the width of the mineral deposit and placing the material into a pre-cleaned, 250 milliliter, high-density polyethylene bottle. Both soil and mineral deposit material were included in the sample to represent potential biological uptake or ingestion.

General sampling protocols specified in the *Sampling and Analysis Plan for U.S. Department of Energy Office of Legacy Management Sites* (SAP) (LMS/PRO/S04351) guided the sampling effort. SAP protocols applicable to this project include pre-trip planning, chain-of-custody, quality control, sample identification and handling, analytical program requirements, equipment decontamination, and documentation.

3.2 Analytical Methods

Samples were analyzed for manganese, molybdenum, sulfate, and uranium by the ALS Laboratory Group (a DOE-Consolidated Audit Program audited laboratory) using the U.S. Environmental Protection Agency (EPA)-approved preparation and analytical methods shown in Table 2.

Table 2. Analytical Requirements

| Constituent | Preparation Method | Analytical Method | Detection Limit (mg/kg) |
|-------------|--------------------|-------------------|-------------------------|
| Manganese | SW-846 3050B | SW-846 6020 | 3 |
| Molybdenum | SW-846 3050B | SW-846 6020 | 5 |
| Sulfate | SW-846 9056 | SW-846 9056 | 5 |
| Uranium | SW-846 3050B | SW-846 6020 | 1 |

3.3 Sample Results

Table 1 shows the results and summary statistics from analysis of the mineral deposits.

3.4 Comparison with Screening Benchmarks

It is anticipated that the data presented in this report will be used in conjunction with analyses of other environmental media to prepare a comprehensive risk assessment for the Riverton site. The data evaluation presented in this report is not a substitute for that risk assessment and looks at only one potential pathway (ingestion) for exposure to the mineral deposits only. However, to put the sampling results into context, concentrations are compared to available screening levels from accepted sources such as EPA's Regional Screening Levels (EPA 2014) and National Research Council's benchmarks (NRC 2005). Screening levels are typically used in the scoping phase of a risk assessment to help focus and guide further data collection. Where screening levels are not available, results are discussed in the context of standard risk assessment assumptions. It is anticipated that these assumptions will be refined in light of the broader conceptual site model during completion of the comprehensive risk assessment.

3.4.1 Human Health Risk from the Mineral Deposits

It is possible that some human exposure could occur; however, because of the remote location of the deposits and the limited frequency and duration of any potential exposure pathway (inhalation, ingestion, or dermal absorption), risk to human health is considered insignificant. To address the small potential for risk to human health, the mineral deposits were scanned with radiological instruments to determine if there is a potential for radiological exposure above background.

Two radiological measurements (gamma) were made at each location; one measurement on contact with the mineral deposit and a second measurement 3 feet from the deposit in air. All gamma measurements were averaged over a 1-minute count time and are shown in Table 1.

Observations from Table 1 include:

- Radiological measurements on contact with the mineral deposit were near the background value. For example, the maximum value of 27.3 microroentgens per hour ($\mu\text{R}/\text{h}$) at location MD-029 was within 3.3 $\mu\text{R}/\text{h}$ of the background reading of 24.0 $\mu\text{R}/\text{h}$ at location MD-01, and all radiological measurements on contact with the mineral deposit were less than 2 standard deviations from the mean.
- Eleven of the 32 measurements in air at 3 feet from the mineral deposits were equal to or higher than the measurement on contact with the mineral deposit, which indicates background radiation levels.
- Uranium concentrations in the mineral deposits correlate poorly with the gamma exposure rates measured on contact with the mineral deposit, as shown in Figure 3.

Based on these observations, the radiological measurements are interpreted to represent background conditions and are not influenced by the mineral deposits; therefore, there is no unacceptable risk to human health due to gamma radiation from the mineral deposits.

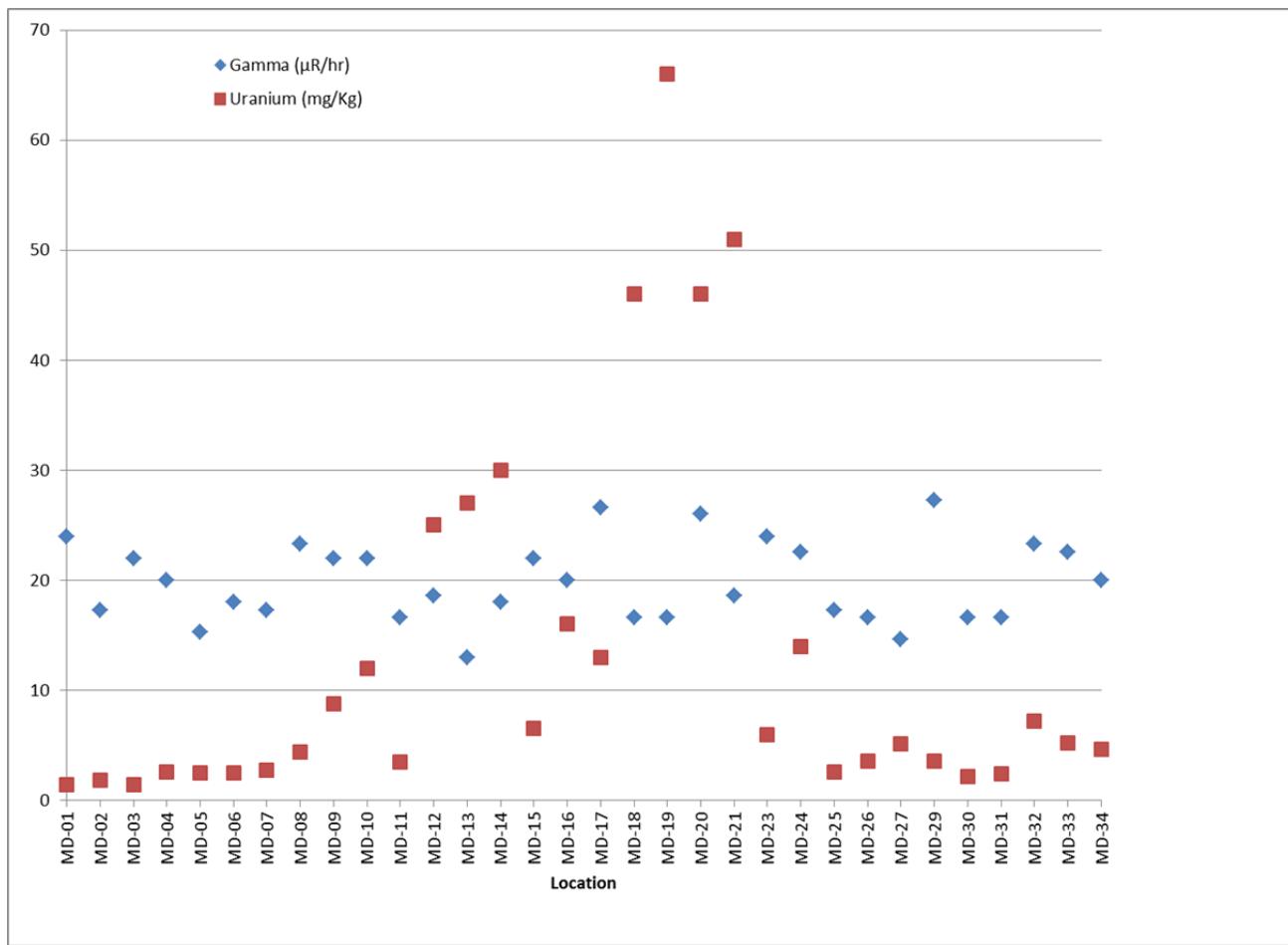


Figure 3. Uranium Concentrations Versus Radiological Measurements

Table 3 lists EPA's screening values for nonradiological constituents in residential soil for comparison to those in the mineral deposits. The EPA screening concentrations are considered acceptable for regular ingestion in a residential setting. Concentrations of manganese, molybdenum, and uranium in the mineral deposit samples are well below the EPA screening values.

Screening values have not been developed for sulfate. However, the Institute of Medicine of the National Academies (2004) has estimated that the average diet, based on supermarket foods, contains 200 to 1,500 milligrams (mg) of inorganic sulfate per day. An approximately equal amount of sulfate is ingested in drinking water and beverages per day; organic sulfate from protein intake also contributes to daily intake. Total average sulfate intake for humans is estimated at 4,400 mg/day. EPA's estimated upper-end soil ingestion rate is 200 mg/day (EPA 2011). Ingestion of 200 mg/day of soil containing the highest concentration of sulfate in the mineral deposits (220,000 mg/kg) would result in a sulfate intake of 44 mg/day. This is just 1 percent of the estimated daily total intake and would not be considered a health risk. The mineral deposits, therefore, are not a threat to human health, even if ingested on a regular basis.

Table 3. Benchmark Values to Address Human Health Risks

| Constituent | Benchmark Values (mg/kg) | Comments |
|-------------|--------------------------|---|
| Manganese | 1,800 | Residential soil ingestion ^a |
| Molybdenum | 390 | Residential soil ingestion ^a |
| Sulfate | N/A | The Institute of Medicine (2004) reports that average total intake of sulfate per day is 4.4 g; an estimated upper tendency soil ingestion rate is 200 mg/day (EPA 2011); ingestion of 200 mg of soil at 220,000 mg/kg sulfate (maximum result from this investigation) results in ingestion of 44 mg (0.044 g) of sulfate, or 1 percent of the estimated daily total intake. |
| Uranium | 230 | Residential soil ingestion ^a |

Notes:

g = grams

^a Benchmark values from EPA's Regional Screening Level Summary Table, May 2014, available at:

http://www.epa.gov/reg3hwmd/risk/human/rb-concentration_table/Generic_Tables/docs/master_sl_table_run_MAY2014.pdf

3.4.2 Ecological Risk from the Mineral Deposits

Ecological risks have been examined for mineral deposits associated with evaporation ponds or highly saline lacustrine environments (DOI 1998; USFWS 1993; Bauder et al. 2007). In these cases the deposits and associated water bodies tend to be widespread and may serve as a significant source of water for birds, macroinvertebrates, and other ecological receptors. A major concern in such areas is bioconcentration of metals in the food chain. The mineral deposits at the Riverton site are of a much different nature, as they are associated with groundwater and capillary fringe along a narrow, discontinuous band along the river bank. They may also be temporary features that are dissolved or washed away by heavy rains or rising river stage. As such, they do not represent a distinct habitat that supports significant fauna or flora (e.g., nesting habitat for birds), but are most likely to be encountered only occasionally by wildlife or livestock using the river or the wider site area.

For this evaluation, it is assumed that the receptor most likely to encounter the mineral deposits is a horse or cow grazing in the area and using the river for water. Some plants have been observed growing near the deposits, and it is possible that animals grazing on this vegetation could ingest the minerals and soil adhering to the plants. Because available literature contains abundant information about the toxic effects of chemical constituents on cattle, cows were selected as the representative receptor for this analysis.

In order to put potential exposures to the mineral deposits in perspective, data on their chemical composition were examined in comparison to feeding habits and dietary requirements of cattle. This evaluation is not intended to be a risk assessment, but presents bounding calculations that may be used to determine if further analysis of this issue is warranted in a future risk assessment.

As a starting point, benchmarks for the COCs at the site (manganese, molybdenum, sulfate, and uranium) were obtained from the literature. The benchmarks represent the maximum tolerable levels (MTLs) in feed for cattle. An MTL is a dietary level that will not impair animal health or performance. While it is unrealistic to think that cattle would consume feed quantities of the mineral deposits, if constituent concentrations in the mineral deposits are below those

benchmarks, they can clearly be eliminated as a concern. Benchmarks used were based on recommendations of the National Research Council (NRC 2005). Table 4 summarizes the benchmarks used; these are also included with the sampling results in Table 1.

Table 4. Benchmark Values to Address Ecological Risk^a

| Constituent | Benchmark Values | Comments |
|-------------|------------------|---|
| Manganese | 1,000 mg/kg | Typically safe level for swine, cattle, sheep, and poultry |
| Molybdenum | 5 to 10 mg/kg | Based on cattle (most sensitive) with adequate copper |
| Sulfate | 4,500 mg/kg | Maximum dietary sulfate for beef cattle and other ruminants (as sulfate [SO ₄]) |
| Uranium | 100 to 400 mg/kg | Maximum tolerable intake for domestic animals |

^aBenchmark values from *Mineral Tolerance of Animals* (NRC 2005).

Based on comparison of results (Table 1) with the ecological benchmarks (Table 1 and Table 4), concentrations of manganese, molybdenum, and uranium in the mineral deposits are all sufficiently low enough to be of no concern. One result for molybdenum exceeded the highest benchmark; all manganese and uranium results were below benchmarks. These three constituents can be eliminated from further consideration for ecological receptors. However, all sulfate results, including the background location, exceeded the sulfate benchmark, and this constituent therefore requires additional evaluation.

Table 5 provides sulfur dietary intake and toxicity data for cattle. This information is used in the subsequent bounding calculations. Data on food and soil intakes for cattle were obtained from an American Petroleum Institute risk assessment for cattle (API 2004). That risk assessment summarized intake rates from several other studies. Ranges provided were consistent with other estimates from the literature. To be conservative, the calculations used average to high-end intake values for these ranges, and calculated intakes are compared to low-end toxicity values.

Table 5. Parameters Used in Bounding Calculations

| Parameter | Range | Source |
|--|---|----------|
| MTL of sulfur (as sulfur [S]) in cattle | 0.15 percent to 0.4 percent (1,500 to 4,000 mg/kg as S, or 4,500 to 12,000 mg/kg as sulfate [SO ₄]) | NRC 2005 |
| Single dose acute toxicity level for cattle (as S) | 250 to 300 g as S (750 to 900 g as SO ₄) | NRC 2005 |
| Daily intake rate of soil for cattle | 0.1 to 2.56 kilograms per day (kg/day) | API 2004 |
| Daily intake rate of food | 11.4–13.5 kg/day | API 2004 |

Abbreviations:

g = grams

S = sulfur

SO₄ = sulfate

A cow consuming 12 kg of food per day (average of the daily intake range) with a concentration at the lower end of the MTL range (4,500 mg/kg as sulfate [SO₄]) would consume 54,000 mg (54 grams [g]) of sulfate per day. This rate represents the maximum permissible sulfate consumption rate for the remaining calculations.

It is extremely unlikely that all of the soil consumed by an animal would come from the area containing minerals deposits. However, to bound the potential impacts of ingestion of mineral deposits by cattle, calculations were completed assuming that 1 percent and 100 percent of the soil ingested by an animal came from areas with mineral deposits. An ingestion rate of 2 kg of soil per day was assumed, which is at the high end of the soil intake range provided in Table 5. Highest, average, and background mineral deposit concentrations were used in the calculations. The calculated amount of sulfate ingested is compared to the low-end values for the maximum permissible and acutely toxic ranges. Results are presented in Table 6.

Table 6. Bounding Calculation Results for Sulfate Ingestion by Cattle

| Soil Consumption Rate from Mineral Deposits (kg/day) (Percent of Soil Ingested) | Soil Concentration (mg/kg as SO ₄) | Sulfate Ingested (g) | Percent of Permissible Sulfate (54 g as SO ₄) | Percent of Acutely Toxic Level (750 g as SO ₄) |
|---|--|----------------------|---|--|
| 0.001 (0.05 percent) | 220,000 (max.) | 0.22 | 0.41 | 0.03 |
| 0.001 (0.05 percent) | 85,255 (mean) | 0.085 | 0.16 | 0.01 |
| 0.001 (0.05 percent) | 83,000 (bkgd.) | 0.08 | 0.15 | 0.01 |
| 0.02 (1 percent) | 220,000 (max.) | 4.4 | 8 | 0.6 |
| 0.02 (1 percent) | 85,255 (mean) | 1.7 | 3.1 | 0.2 |
| 0.02 (1 percent) | 83,000 (bkgd.) | 1.7 | 3.1 | 0.2 |
| 2 (100 percent) | 220,000 (max.) | 440 | 815 | 59 |
| 2 (100 percent) | 85,255 (mean) | 171 | 317 | 23 |
| 2 (100 percent) | 83,000 (bkgd.) | 166 | 307 | 22 |

Abbreviations:

bkgd. = background level

max. = maximum level

In addition to the 1 percent and 100 percent of soil-ingested calculations, another set of calculations was completed to better relate the bounding calculations to actual site conditions. It was assumed that the fenced area encompassing the mineral deposits could be used for grazing, and the total area within the fencing was determined. The lateral extent of mineral deposits was also determined (Figure 4). It was assumed that the mineral deposits had 2 feet of vertical thickness over their entire lateral extent, for a total of approximately 3,390 square feet, or 0.05 percent of the entire fenced area of nearly 6.5 million square feet. Table 6 also provides related calculations about ingestion, including calculations that assume mineral deposits are 0.05 percent of the total soil consumed.

These results indicate that incidental ingestion of the mineral deposits (e.g., if 0.05 percent or 1 percent of soil ingested is mineral deposits) would represent only a small portion of the permissible amount of sulfate intake. Approximately 92 percent to 97 percent of sulfate could be obtained from other sources. Even if 100 percent of the soil ingested was from the most highly contaminated mineral deposits, the total dose would be less than the lowest acutely toxic level. Based on the average mineral deposit concentration, a cow would need to ingest approximately one-third of its soil intake from areas with mineral deposits to reach the maximum permissible chronic level (assuming this is the only source of sulfate in its feed). Intakes calculated for background and average mineral deposit concentrations are similar.

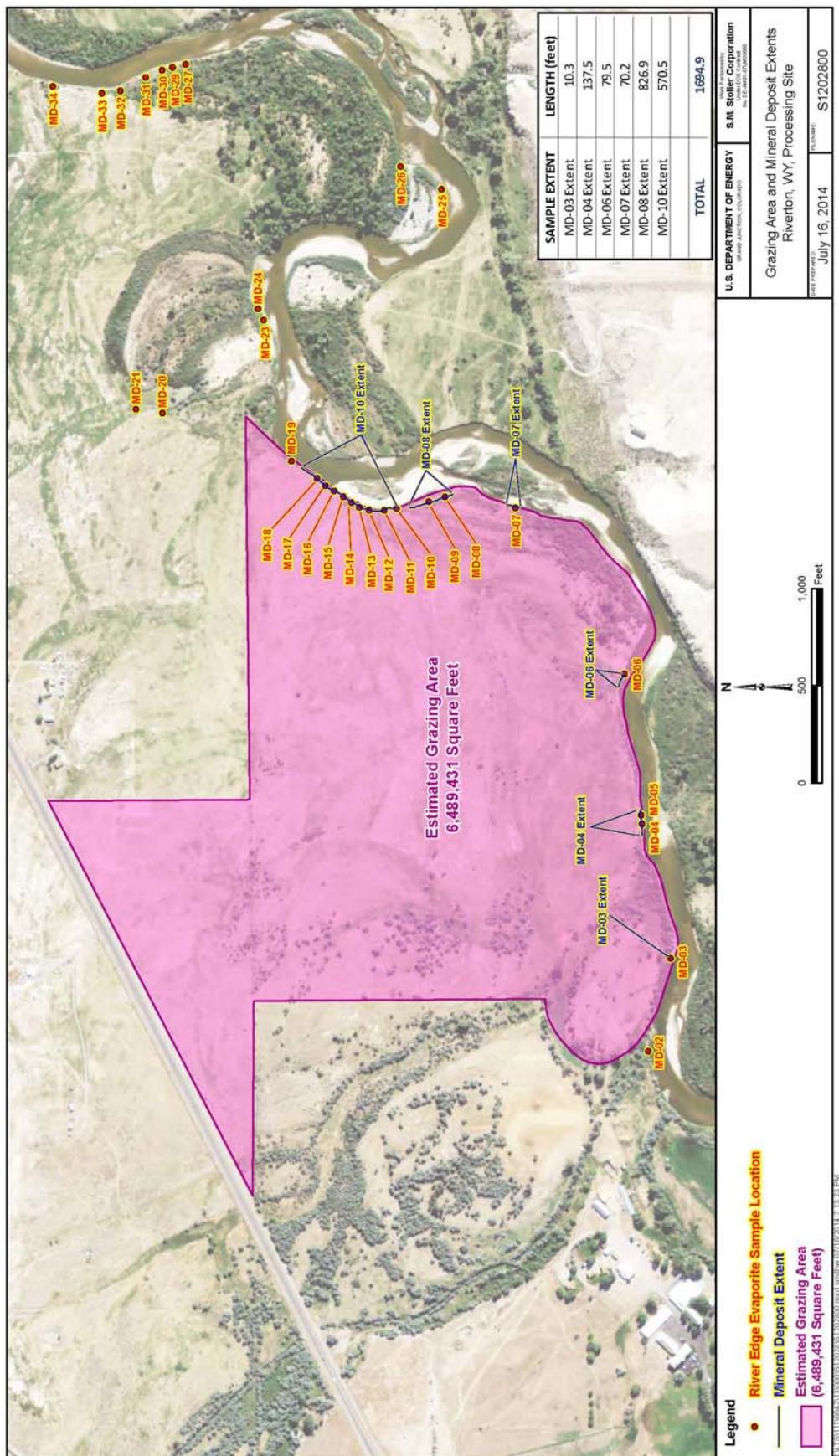


Figure 4. Estimated Grazing Area and Mineral Deposit Extent

Besides the fact that ranges are associated with the input parameters used in this evaluation, other uncertainties must be considered in interpreting the results. These include:

- More information is needed on potential receptors of concern at the site. Horses and cows have been observed using properties adjacent to the areas with the mineral deposits.
- The areas containing the mineral deposits do not contain significant amounts of forage, as they are located on steep riverbank areas. Grazing animals are likely to derive only a very small amount of their feed from these areas.
- The elemental content of potential forage in the site area is unknown and would contribute to the diet of animals grazing on that land.
- Grazing probably occurs for only a portion of the year. It is likely that supplemental feed would need to be provided, particularly for the winter months.
- Limited toxicity data are available for horses and other animals that might use the land and encounter the mineral deposits.
- Some animals are known to deliberately ingest soil to satisfy a sodium deficiency, and the mineral deposits have a measured sodium concentration of 162,000 mg/kg (SRNL 2014).
- The variability in background mineral deposit concentrations is unknown, but mean concentration of sulfate in the mineral deposits in the plume area is essentially the same as the background concentration.

3.5 Correlation of Mineral Deposits with Groundwater Plume

To better understand if site groundwater conditions influence COC concentrations in the mineral deposits, concentrations of COCs in the mineral deposit samples were spatially compared to COCs in the groundwater contaminant plume. Information on the contaminant plume was derived from the Riverton 2012 Enhanced Characterization Report (DOE 2013) from shallow groundwater samples collected using a Geoprobe with direct-push technology. The comparison of the mineral deposits with the contaminant plume was achieved by comparing plume COCs in a line perpendicular to the plume flow direction. This comparison used a line going through mineral deposit sample location MD-02 and Geoprobe sample line T06 (see the cross-plume line in Figure 5). A line parallel to the plume direction was defined by Geoprobe sample points T04-09 and T08-03, because these points provide a good parallel line on the southwest boundary of the molybdenum plume (based on Figure 38 in the 2012 Enhanced Characterization Report [DOE 2013]). Using this parallel line (i.e., the pink line in Figure 5), all of the T06 line groundwater samples and new MD series mineral deposit samples were projected onto the cross-plume line.

To provide a comparison between contaminant plume groundwater (Geoprobe line T06) and the mineral deposit samples, a maximum COC concentration was calculated in milligrams per kilogram assuming the plume groundwater was fully evaporated (Table 7). These units are milligrams of COC divided by kilograms of total solids that would be deposited from full evaporation; they were calculated using the total dissolved solids value that was computed using all constituents measured in the groundwater. The COC maximum concentrations for uranium (U), molybdenum (Mo), sulfate (SO₄), and manganese (Mn) compared to measured values from the mineral deposit samples are provided in Figure 6 through Figure 9, respectively. In all of these figures, MD-02 is the zero point, and the T06-10 line is provided as a location reference.

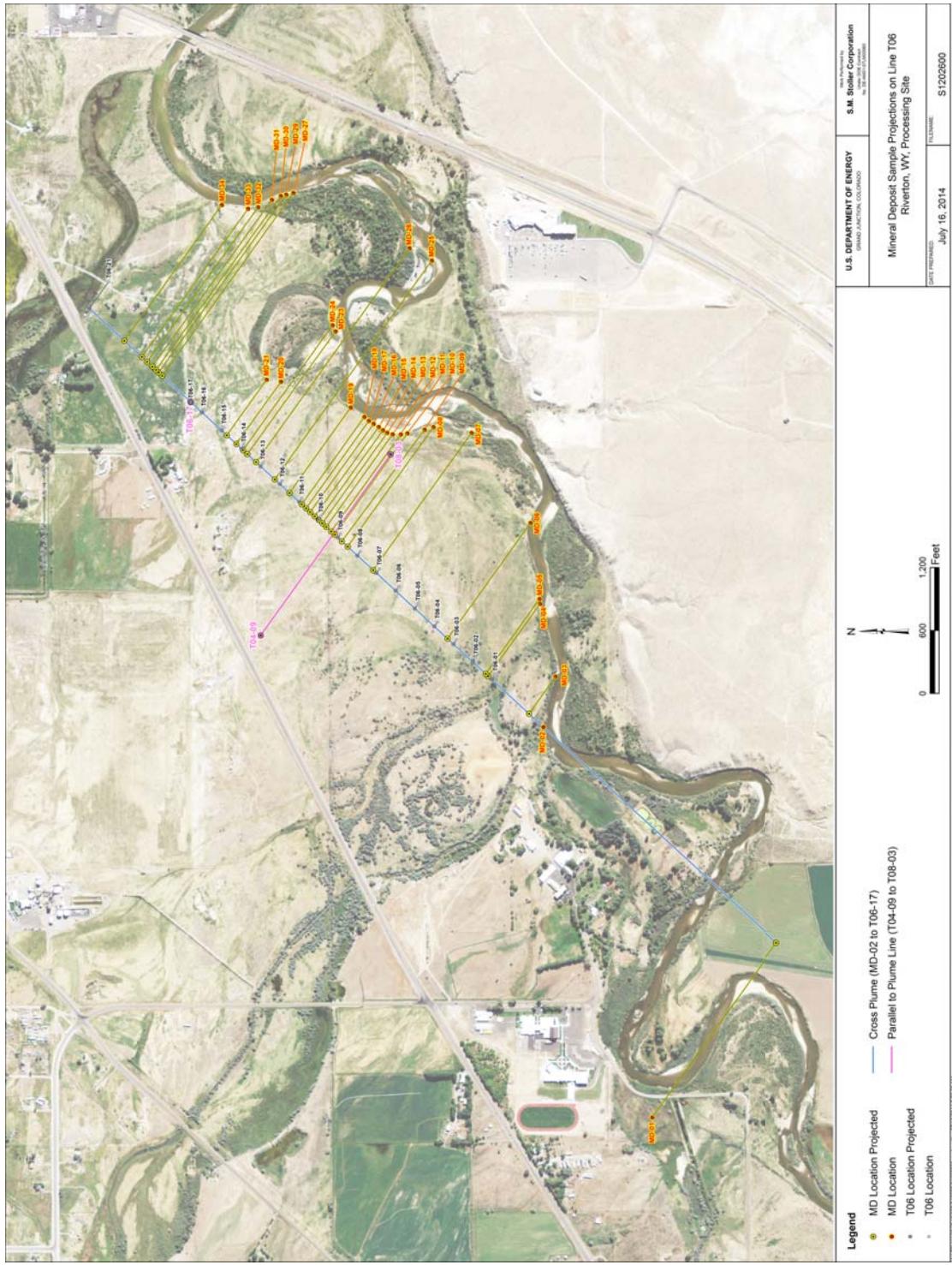


Figure 5. Mineral Deposit Sample Projections on Line T06, Riverton, Wyoming, Processing Site

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Table 7. Data for Evaporated Groundwater Along Line T06

| Location | Calculated TDS (mg/L) | Groundwater Mn (mg/L) | Evaporated Mn (mg/kg) | Groundwater Mo (mg/L) | Evaporated Mo (mg/kg) | Groundwater U (mg/L) | Evaporated U (mg/kg) | Groundwater SO ₄ (mg/L) | Evaporated SO ₄ (mg/kg) |
|----------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|----------------------|----------------------|------------------------------------|------------------------------------|
| T06-01 | 2,228 | 1.2 | 539 | 0.013 | 5.8 | 0.051 | 22.9 | 1,200 | 538,600 |
| T06-02 | 2,684 | 1.7 | 633 | 0.083 | 30.9 | 0.024 | 8.9 | 1,500 | 558,867 |
| T06-03 | 3,052 | 1.4 | 459 | 0.012 | 3.9 | 0.020 | 6.6 | 1,700 | 557,012 |
| T06-04 | 2,193 | 0.67 | 306 | 0.020 | 9.1 | 0.029 | 13.2 | 1,200 | 547,196 |
| T06-05 | 4,772 | 0.17 | 36 | 0.083 | 17.4 | 0.17 | 35.6 | 2,900 | 607,712 |
| T06-06 | 5,108 | 2.8 | 548 | 0.11 | 21.5 | 0.18 | 35.2 | 3,100 | 606,891 |
| T06-07 | 6,710 | 1.7 | 253 | 0.17 | 25.3 | 0.30 | 44.7 | 4,100 | 611,028 |
| T06-08 | 5,947 | 0.85 | 143 | 0.25 | 42.0 | 0.60 | 100.9 | 3,600 | 605,347 |
| T06-09 | 5,522 | 0.64 | 116 | 0.31 | 56.1 | 0.96 | 173.9 | 3,400 | 615,719 |
| T06-10 | 6,172 | 2.7 | 437 | 0.96 | 155.5 | 1.4 | 226.8 | 3,900 | 631,886 |
| T06-11 | 3,750 | 1.4 | 373 | 0.97 | 258.7 | 0.58 | 154.7 | 2,300 | 613,333 |
| T06-12 | 2,141 | 1.1 | 514 | 0.34 | 158.8 | 0.58 | 270.9 | 1,200 | 560,486 |
| T06-13 | 2,055 | 2.2 | 1,071 | 0.075 | 36.5 | 0.66 | 321.2 | 1,200 | 583,942 |
| T06-14 | 1,239 | 0.67 | 541 | 0.030 | 24.2 | 0.16 | 129.1 | 600 | 484,262 |
| T06-15 | 850 | 0.70 | 824 | 0.014 | 16.5 | 0.075 | 88.2 | 350 | 411,765 |
| T06-16 | 829 | 0.060 | 72 | 0.0050 | 6.0 | 0.056 | 67.6 | 310 | 373,945 |
| T06-17 | 1,258 | 0.18 | 143 | 0.0048 | 3.8 | 0.055 | 43.7 | 580 | 461,049 |
| T06-21 | 595 | 0.087 | 146 | 0.0046 | 7.7 | 0.0096 | 16.1 | 120 | 201,819 |

Abbreviations:

TDS = total dissolved solids

Mn = manganese

Mo = molybdenum

U = uranium

SO₄ = sulfate

mg/L = milligrams per liter

Notes:

TDS is not a laboratory measurement, but a calculation of total mass from all measured constituents in solution.

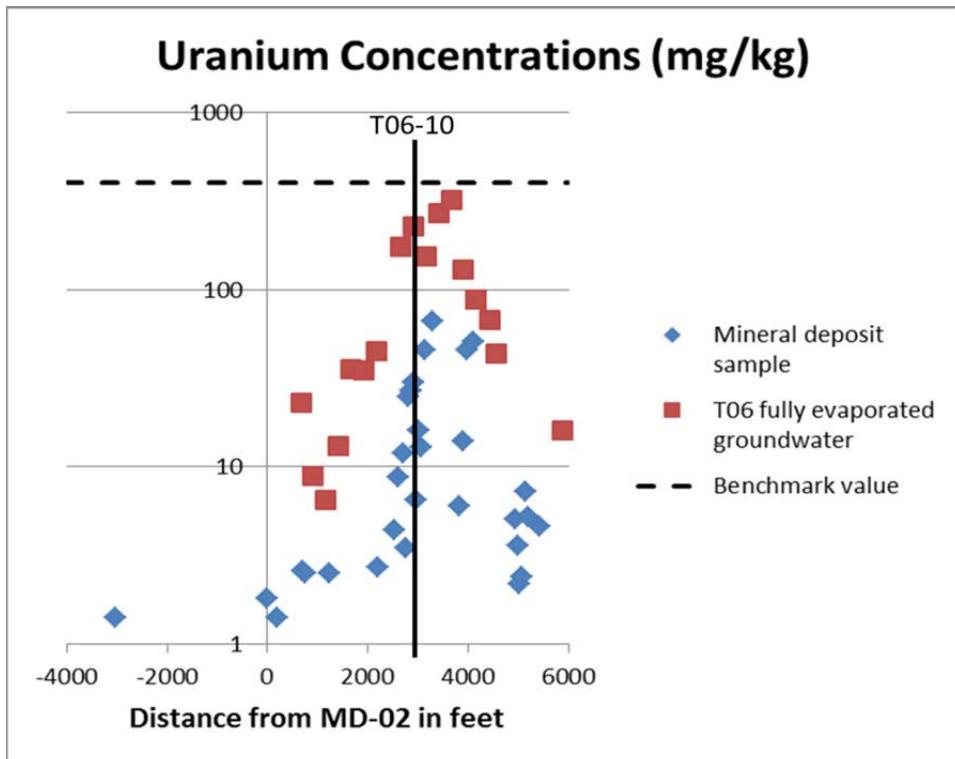


Figure 6. Uranium in Mineral Deposits and Fully Evaporated Groundwater

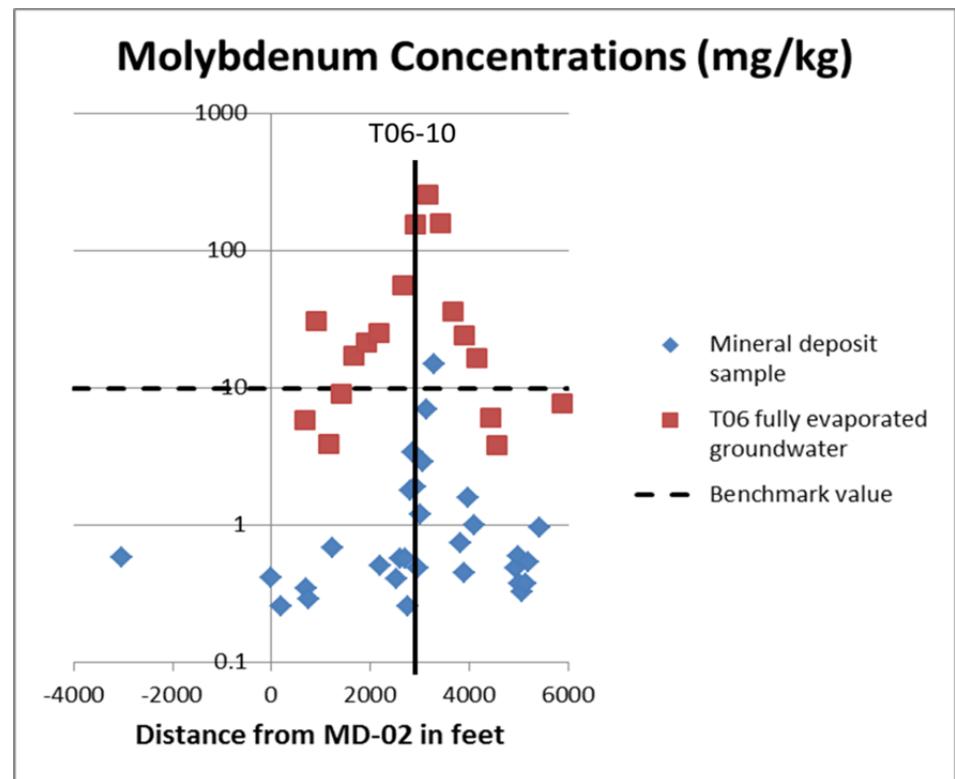


Figure 7. Molybdenum in Mineral Deposits and Fully Evaporated Groundwater

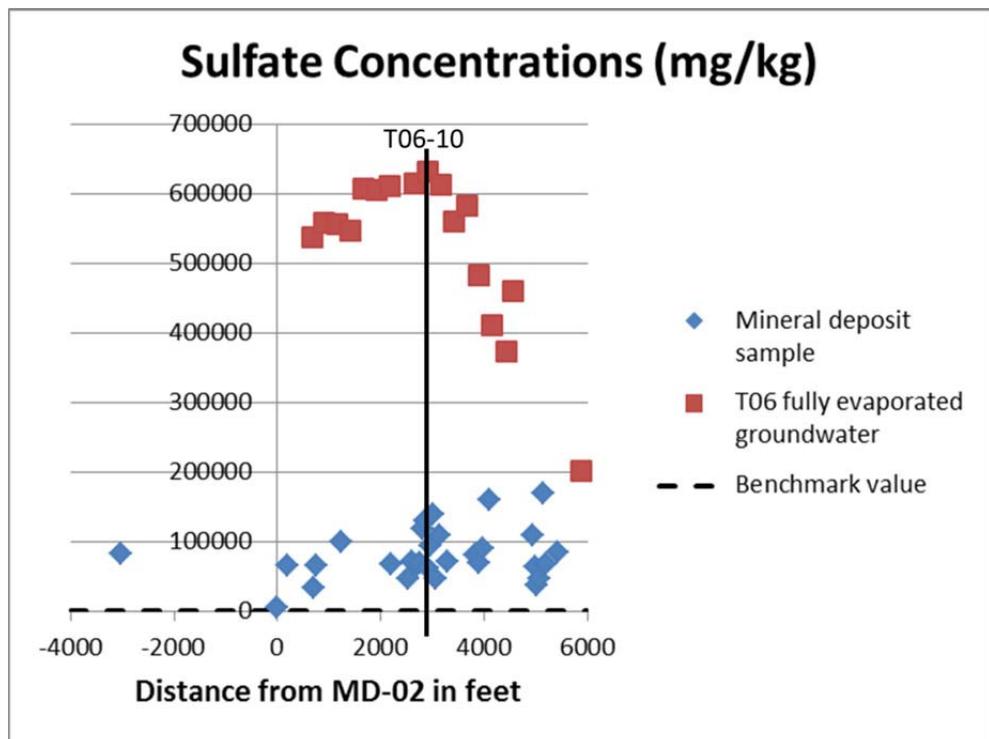


Figure 8. Sulfate in Mineral Deposits and Fully Evaporated Groundwater

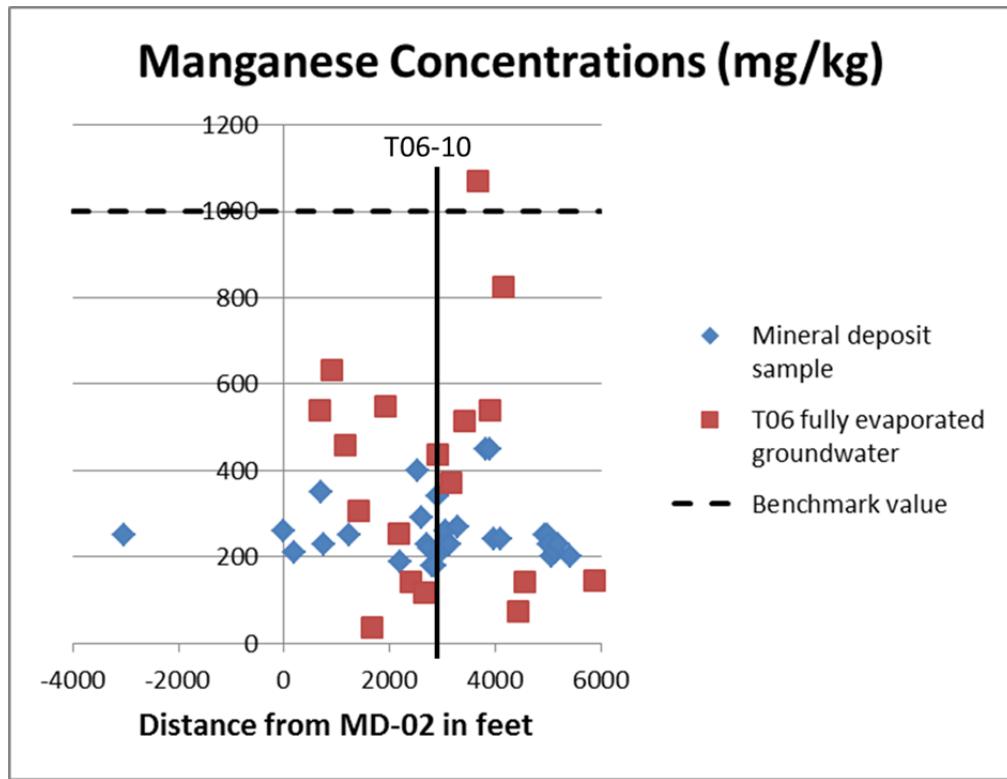


Figure 9. Manganese in Mineral Deposits and Fully Evaporated Groundwater

The background mineral deposit sample MD-01 is labeled as a negative distance from MD-02 to Geoprobe point T06-10 (Figure 5). Otherwise the term T06-10 line, could be confused with the other and is also projected to the cross-plume line. Samples MD-25 and MD-26 were not included in Figure 6 through Figure 9 because of their location. The projection lines of these two samples intersect river meanders and cross the river two times (Figure 5). Thus, these samples are much less likely to be within the plume discharge zone. This conclusion is also based on the lower concentrations of U and Mo in these samples compared to concentrations in samples MD-16 through MD-21; however, these concentrations are still slightly elevated compared to background sample MD-01 (Table 1).

The resulting figures for U and Mo (Figure 6 and Figure 7, respectively; note the logarithmic scale) show very good matching trends between the mineral deposit samples and the evaporated groundwater. These figures indicate that U and Mo concentrations in the mineral deposit samples appear to be controlled by evaporation of discharging plume groundwater, but do not reach the maximum concentrations that would be indicated by full groundwater evaporation. This might be due to solubility controls, but it could also be influenced by dilution during the sampling process (inclusion of some underlying soil material). In addition, the plume samples increase in U and Mo concentrations approximately 2,000 to 2,500 feet from MD-02, where concentrations in the mineral deposit samples are still near background (Figure 6 and Figure 7). This may be an artifact of not having a full alignment between the plume area discharge and the mineral deposit samples. It is also important to note that the maximum U and Mo concentrations in groundwater do not necessarily correspond with the maximum U and Mo concentrations in totally evaporated groundwater (Table 7). This difference is due to the total solids values, mainly controlled by sulfate concentrations. For example, a high U concentration in groundwater may be “diluted” by an even higher total solids value. As a result, the maximum U concentration in groundwater does not always correspond with the maximum U concentration in fully evaporated groundwater.

Sulfate (Figure 8) does not show the same trend as the plume correlation for U and Mo. Similar to the groundwater plume (DOE 2013), the high sulfate to the southwest and a decrease in sulfate in to the northeast are readily apparent in the evaporated groundwater samples (Figure 8). However, the mineral deposit samples do not show any clear trend and are much lower in overall concentrations. It is likely that sulfate precipitation is solubility controlled and that only specific sulfate minerals precipitate at the conditions found at the Riverton site. Two sulfate-bearing minerals (blödite and thenardite) have been identified in the riverbank mineral deposits, according to a recent Riverton groundwater contamination report (SRNL 2014). Geochemical modeling in that report also indicated a specific mineral precipitation order based on the overall amount of evaporation. Similar to that report, the groundwater samples from line T06 were entered into the geochemical modeling program PHREEQC (Parkhurst and Appelo 2013), and evaporation was modeled. Evaporation sequences derived for this study are similar to the evaporation sequences used in the groundwater contamination report (SRNL 2014), but mineral database differences and a lack of information on the total amount of evaporation make exact mineral precipitation predictions uncertain. In any case, the data for sulfate concentrations in the mineral deposit samples do not show much variation (Figure 8), which is consistent with a sulfate mineral solubility control and the identified sulfate minerals.

Manganese does not form a distinct plume at the Riverton site. As a result, the Mn concentrations in the mineral deposit samples and the evaporated groundwater do not show any distinct trends (Figure 9). Overall, the Mn concentrations in the mineral deposit samples

are similar to the maximum concentrations of Mn derived from evaporated groundwater. Generally, Mn is not soluble under fully oxidizing conditions at the surface and may be fully precipitated in the mineral deposit samples.

4.0 Conclusions

Evaluation of the mineral deposits identified and sampled along the Little Wind River can be summarized as follows:

- Radiation (gamma) measurements from the mineral deposits are near background levels and do not pose any additional risk to human health.
- Ingestion of mineral deposits is not considered to be a threat to human health based on EPA screening levels for residential soil. Uranium, molybdenum, and manganese concentrations are all (except for one molybdenum result) below dietary benchmarks for domestic animals. Therefore, these three constituents can be eliminated from further consideration for ecological receptors.
- All sulfate results, including the background location, exceeded the sulfate benchmark for cattle and therefore required additional evaluation. Based on the average mineral deposit concentration, a cow would need to ingest approximately one-third of its soil intake from areas with elevated mineral concentrations to reach the maximum permissible chronic level. This is not a realistic scenario based on the limited extent of the mineral deposits compared to the area available for grazing. However, future analyses are needed to examine other receptors of concern and contributions to forage from soil and plants.
- Uranium and molybdenum concentrations measured in the mineral deposits generally correspond with possible plume discharge zones. Sulfate appears to have a solubility control, and manganese does not show any distinct trends.
- This investigation is a small part of continued efforts by DOE and other stakeholders to update human health and ecological risk assessments. These efforts will provide a comprehensive examination of all exposure pathways to ensure that site conditions remain protective through established institutional controls.

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Appendix A

Work Plan to Sample Mineral Deposits Along the Little Wind River, Riverton, Wyoming, Processing Site

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Work Plan to Sample Mineral Deposits Along the Little Wind River, Riverton, Wyoming Processing Site

May 2014



**U.S. DEPARTMENT OF
ENERGY**

Legacy
Management

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**Work Plan to Sample Mineral Deposits
Along the Little Wind River
Riverton, Wyoming, Processing Site**

May 2014

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Abbreviations

| | |
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| COCs | contaminants of concern |
| DOE | U.S. Department of Energy |
| EPA | U.S. Environmental Protection Agency |
| GPS | global positioning satellite |
| JSA | Job Safety Analysis |
| mg/kg | milligrams per kilogram |
| SAP | <i>Sampling and Analysis Plan for U. S. Department of Energy Office of Legacy Management Sites</i> |

1.0 Introduction

In previous field trips to the Riverton site, a white mineral deposit resulting from evaporation of groundwater seepage along the bank of the Little Wind River has been observed. In December 2014, a sample was collected by Savannah River personnel and was subsequently analyzed using an X-ray fluorescence technique (Figure 1 shows a photograph the type of material that was sampled). The sample was found to have a uranium concentration of approximately 64 to 73 parts per million, which is “in the expected range for evaporative minerals in the western United States” (DOE 2014a). Although the uranium in this mineral deposit is likely related to activities associated with the former uranium mill site at Riverton, this level of uranium concentration can occur naturally in other geologic media; for example, uranium concentrations were measured from 50 to 200 milligrams per kilogram (mg/kg) in the Pennsylvanian Hartville Formation in Wyoming (McKelvey et al. 1955) and up to 102 mg/kg in soils (USGS 2013).

The work described in this plan will further define extent of these mineral deposits and the concentration of the associated contaminants. This plan addresses field reconnaissance, mapping, sampling, and assessment of risk associated with these mineral deposits adjacent to the Little Wind River. The objectives of this work are to:

- Identify the extent of the mineral deposits.
- Determine concentrations of contaminants of concern (COCs) in the mineral deposits and associated soil.
- Determine if these mineral deposits pose unacceptable risk to human health or the environment.

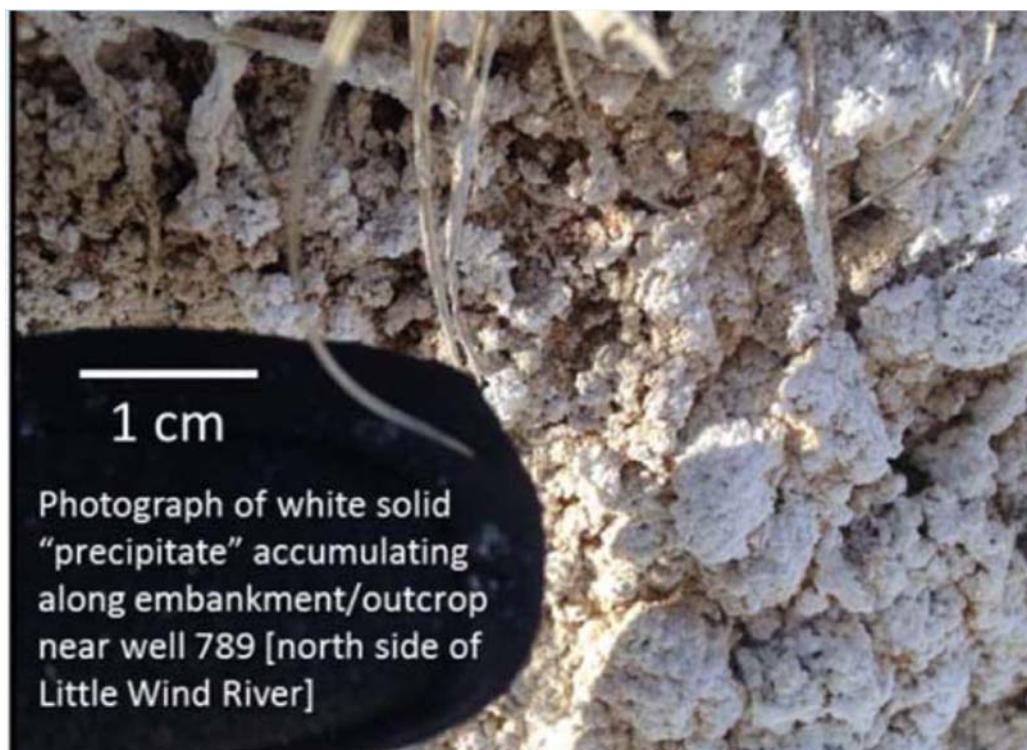


Figure 1. Example of a Mineral Deposit (DOE 2014a)

2.0 Field Reconnaissance and Mapping

Visual inspection of the north bank of the Little Wind River and oxbow lake will be conducted to identify areas of mineral deposits resulting from evaporation of groundwater seeps. Field reconnaissance will focus on the oxbow lake and the section of the river where the groundwater plume is expected to intersect the river but will also include areas on either side of the plume (Figure 2). A global positioning satellite (GPS) device will be used to map the linear extent of each expression of a mineral deposit, and the thickness of the deposits will be measured and recorded. Photographs will be taken at each sampling location to provide additional documentation of the mineral deposit.

3.0 Sampling Protocol

Samples will be collected every 50 linear feet in areas where mineral deposits are located. If an isolated mineral deposit is found that is less than 50 feet, one sample will be collected at each isolated deposit. A maximum of 50 samples will be collected. GPS coordinates will be collected at each sample location. Samples will be consecutively numbered starting with MD-02 on the west side of the reconnaissance area as shown in Figure 2. One sample will be collected (MD-01) near the upstream sampling location to provide background data.

Samples will be collected by scraping a thin layer of mineral deposit and soil along the width of the mineral deposit and placing the material into a 250 milliliter high-density polyethylene bottle. Both soil and mineral deposit material in the sample are expected to represent potential biological uptake or ingestion.

General sampling protocols specified in the *Sampling and Analysis Plan for U. S. Department of Energy Office of Legacy Management Sites* (SAP) (DOE 2014b) will be used to guide the sampling effort. Protocols in the SAP that are applicable to this project include pre-trip planning, chain-of-custody, quality control, sample identification and handling, analytical program requirements, equipment decontamination, and documentation.

Analytical Methods

Samples will be analyzed for manganese, molybdenum, sulfate, and uranium using an approved DOE-Consolidated Audit Program audited laboratory using EPA-approved preparation and analytical methods shown in Table 1.

Table 1. Analytical Requirements

| Constituent | Preparation Method | Analytical Method | Detection Limit (mg/kg) |
|-------------|--------------------|-------------------|-------------------------|
| Manganese | SW-846 3050B | SW-846 6020 | 3 |
| Molybdenum | SW-846 3050B | SW-846 6020 | 5 |
| Sulfate | SW-846 9056 | SW-846 9056 | 5 |
| Uranium | SW-846 3050B | SW-846 6020 | 1 |

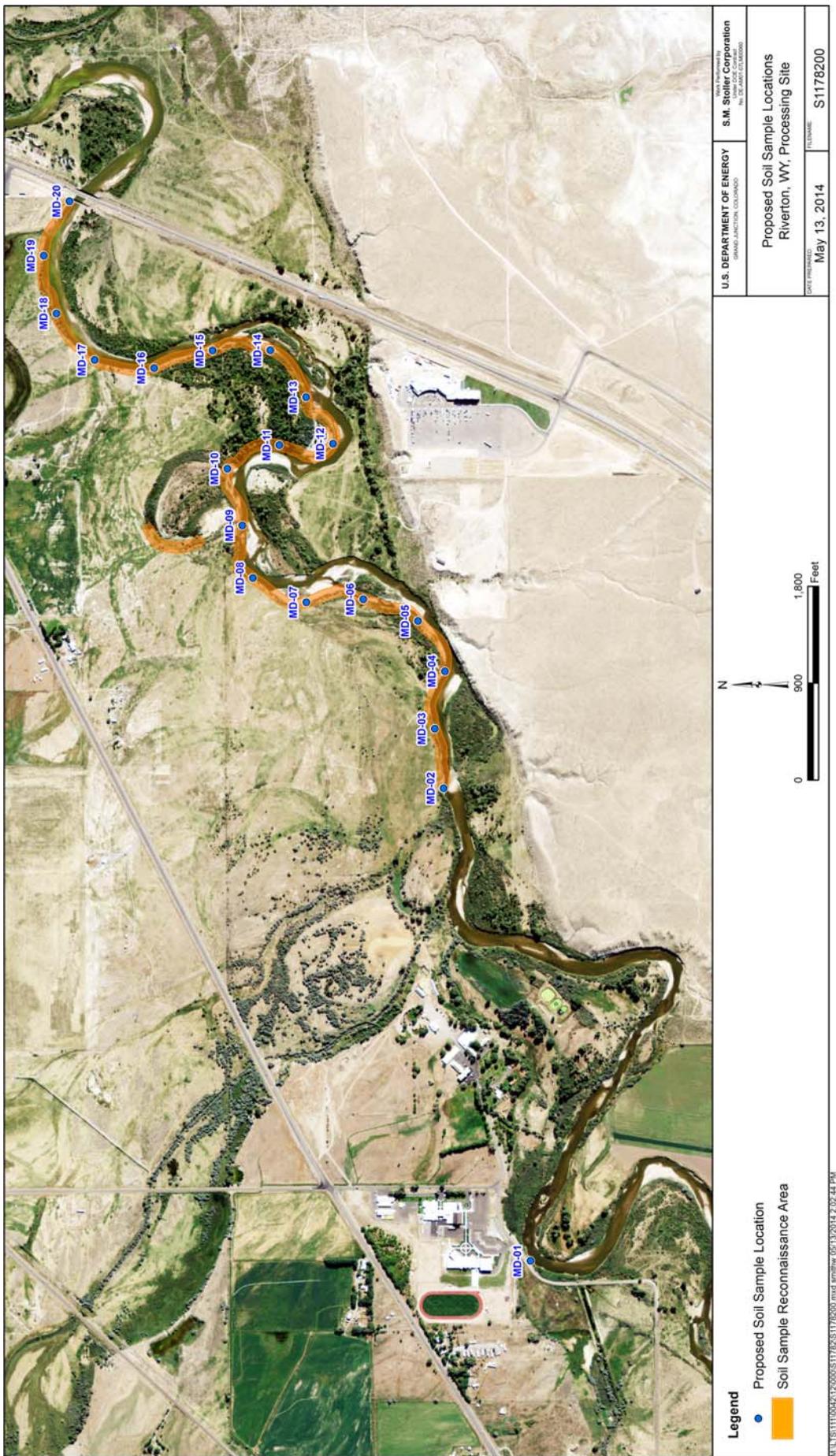


Figure 2. Proposed Mineral-Deposit Reconnaissance Area and Soil Sample Numbering Scheme.

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4.0 Risk Assessment

4.1 Human Health Risk

It is possible that some human exposure could occur; however, because of the remote location and the limited exposure frequency and duration that could occur from any potential exposure pathway (inhalation, ingestion, or dermal absorption), risk to human health is considered insignificant. To address the small potential for risk to human health, the mineral deposits will be scanned with radiological instrumentation to determine if there is a potential for radiological dose. The gamma radiation readings from the field instrument will be converted to dose rate and compared to the DOE public dose limit of 100 millirem/year limit (DOE 2011). Radiological instrumentation will have a current calibration and will be operationally checked prior to use.

Gamma readings will be used to guide sampling of the mineral deposits. If gamma readings are above background on contact with the mineral deposit, then a sample will be collected at the highest gamma reading at each 50 foot interval. Two gamma readings will be recorded at each sample location – one on contact with the mineral deposit and one 3 feet away from the mineral deposit. A background range of gamma readings also will be recorded in an area away from the mineral deposits.

4.2 Ecological Risk

The primary risk to the environment from the mineral deposits will likely be ingestion by animals; therefore, concentrations will be compared to benchmark values derived from *Mineral Tolerance of Animals* (National Research Council 2005), which are listed in Table 2. If COC concentrations of mineral deposit samples are below the benchmark values or ranges in Table 2, then risk from exposure to the mineral deposits will be considered insignificant. If the concentrations are within or exceed the benchmark ranges listed in Table 2, then additional assessment of the risk will be conducted. Note that this work plan is focused on the mineral deposits; additional biota samples may be collected in the future, if necessary, to further assess risk to human health and the environment.

Table 2. Benchmark Values to Address Risk^a

| Constituent | Benchmark Values | Comments |
|-------------|------------------|---|
| Manganese | 1,000 mg/kg | Typically safe level for swine, cattle, sheep, and poultry. |
| Molybdenum | 5 to 10 mg/kg | Based on cattle (most sensitive) with adequate copper. |
| Sulfate | 1,500 mg/kg | Maximum dietary sulfur for beef cattle and other ruminants. |
| Uranium | 100 to 400 mg/kg | Maximum tolerable intake for domestic animals. |

^a Benchmark values from *Mineral Tolerance of Animals* (National Research Council 2005).

5.0 Health and Safety

Sampling will be conducted according to the Job Safety Analysis (JSA) *Water Sampling and Minor Well Maintenance at LM Sites* (expires 2/26/2015) for general hazards encountered during field work. The main hazards associated with this work – driving, working near water, and working near ledges are addressed in this JSA.

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