LMS/RVT/S36212

Riverton, Wyoming, Processing Site: 2020 Geochemical Condition Assessment

April 2022

U.S. DEPARTMENT OF ENERGY | Legacy Management

This document has been designed for online viewing.

Contents

Figures

Tables

Appendixes

Abbreviations

amsl	above mean sea level
bgs	below ground surface
BLRA	baseline risk assessment
cm	centimeters
CO_2	carbon dioxide
CSM	conceptual site model
DI	deionized
DO	dissolved oxygen
DOC	dissolved organic carbon
DOE	U.S. Department of Energy
DQO	data quality objective
EPA	U.S. Environmental Protection Agency
ET	evapotranspiration
EVS	Earth Volumetric Studio
Fe/Mn	iron-manganese
ft	feet
ft bgs	feet below ground surface
FTA	former tailings area
GCAP	Groundwater Compliance Action Plan
LM	Office of Legacy Management
MCL	maximum contaminant level
mg/kg	milligrams per kilogram
mg/L	milligrams per liter
mm	millimeters
mV	millivolts
NPDES	National Pollutant Discharge Elimination System
NRC	U.S. Nuclear Regulatory Commission
NRZ	naturally reduced zone
ORP	oxidation-reduction potential
pCi/g	picocuries per gram
PV	pore volume
S&G	sand and gravel

SI	saturation index
SSMA	Saint Stephen’s Mission Area
UMTRA	Uranium Mill Tailings Remedial Action Project
UMTRCA	Uranium Mill Tailings Radiation Control Act
V	velocities
VMR	Verification Monitoring Report

Executive Summary

Historical milling operations and associated tailings disposal caused surface and groundwater contamination at the Riverton, Wyoming, Processing Site (Site). Surface remediation was completed in 1989 by removing the tailings to radioactivity standards for radium. The current compliance strategy for groundwater remediation is natural flushing with institutional controls to below 0.044 milligrams per liter (mg/L) for uranium and below 0.10 mg/L for molybdenum within 100 years (from 1998). After Site flooding and high recharge events, data indicate that uranium and molybdenum are not naturally flushing as predicted and may not naturally attenuate below standards by 2098. Therefore, the U.S. Department of Energy Office of Legacy Management plans to revise the Site Groundwater Compliance Action Plan (GCAP), which will potentially have a new Site compliance strategy. In preparation for a new GCAP, this report (1) reviews the evolution of the conceptual site model, (2) quantitatively evaluates natural flushing rates across the Site, (3) summarizes field and column geochemical data collected through 2020 to evaluate potential controls on uranium and molybdenum mobility, and (4) determines data gaps, which when addressed, can improve a Site reactive transport model for use in evaluating Site compliance strategies.

The geology of the Site is approximately 5 feet (ft) of silt underlain by approximately 15 ft of alluvial sands and gravels (S&G) (surficial aquifer). This is underlain by the Wind River Formation, with interbeds of shale, siltstone, and sandstone up to 1500 ft below ground surface. The surficial aquifer has some hydraulic connection to the upper 50 ft of the Wind River Formation (semiconfined aquifer) but does not appear to have a connection to the regional zone of typical groundwater use near the 400 to 500-foot-deep (confined aquifer) level. The groundwater flow direction is northwest to southeast toward the Little Wind River for both the surficial and semiconfined aquifers. Limited information is available at the Site on the confined aquifer, but groundwater in this aquifer is presumed to flow toward water supply wells near the town of Riverton, Wyoming. Other anthropogenic influences on the groundwater flow regime are irrigation in surrounding fields and retention ponds associated with a sulfuric acid plant (Plant) that was once part of the former uranium mill.

The surficial aquifer continues to be contaminated with uranium, molybdenum, and sulfate while the semiconfined aquifer is contaminated only with sulfate. The confined aquifer has not been contaminated. The origin of these contaminants is the former tailings impoundment along with an ongoing source of sulfate from the Plant. The conceptual site models through time are as follows:

- **Tailings in place (before 1990):** The tailings were a source of low-pH metal-rich fluids and pH buffering. This created conditions that removed most metals, except for uranium and molybdenum. Sulfate is controlled at solubility limits for gypsum. Other significant reactions included the dissolution of calcite, production of carbon dioxide, and the precipitation of iron and aluminum oxyhydroxides (which can sorb uranium and molybdenum). Uranium, molybdenum, and sulfate plumes were heading toward the Little Wind River along the direction of groundwater flow in the surficial aquifer with uranium moving faster than molybdenum. Uranium and molybdenum mobility controls had not been quantified.
- **After tailings removal (1990 to 2010):** With the tailings removed, ongoing sources of uranium, molybdenum, and sulfate were not considered. This is reflected in contaminant transport modeling that considers the original tailings source, no ongoing source, and

predicts natural flushing within 100 years. This modeling did include contaminant sorption and a probabilistic approach to account for heterogeneity, both of which were considered the main controlling properties for uranium and molybdenum transport in the surficial aquifer. The Site GCAP was established in 1998, and it relies on this modeling with a compliance strategy of natural flushing to below standards for uranium and molybdenum within 100 years, with institutional controls in place during that time.

- **Post-2010 flood through 2020:** Identified solid-phase contamination (includes uranium, molybdenum, and sulfate) exists in two main compartments: (1) the unsaturated zone over the contaminant plumes near the Little Wind River (referred to as the Saint Stephen's Mission Area [SSMA]) and (2) the saturated zone under the former tailings area (FTA). Based on groundwater data, the unsaturated zone at the FTA also likely has solid-phase contamination that has not been directly measured. Contaminants are released to the underlying groundwater in the FTA and SSMA after flooding or large recharge events. Natural flushing occurs between recharge events, except for consistent contaminant release in the south-central FTA with contaminants in the saturated zone. Loss of contaminants from the groundwater to the solid phase occurs in saturated zone SSMA sediments that have high organic carbon content. Release of those contaminants back to the water phase occurs under oxic conditions with column testing, but release under anoxic conditions (more likely to occur in the field) has not been evaluated. Loss of water from the Plant retention ponds likely contributes to ongoing sulfate plumes in the surficial and semiconfined aquifers.

Natural flushing was evaluated using plume maps from various years, trend data in individual wells, three-dimensional mapping using Earth Volumetric Studio (EVS), and effluent concentrations from column testing data. Flushing in some areas in fewer than 100 years is possible. However, full Site flushing in fewer than 100 years is not likely due to remaining secondary sources at the FTA and the SSMA. Significant considerations in evaluating Site flushing times are (1) the flooding or large recharge event frequencies that can release contaminants from the unsaturated zone and (2) the FTA contaminant source must be flushed out (upgradient source zone) before the SSMA unsaturated zone (downgradient retention) will stop storing contaminants wicked up from the underlying groundwater. Likewise, the SSMA unsaturated zone must be flushed before the SSMA saturated zone can start to be flushed. The different zones considered for flushing and associated controls and time frames are as follows:

- **Former ore storage area:** Past starting location of the uranium and molybdenum plumes may be experiencing natural flushing based on groundwater data from 1983 versus 2012, but limited solid-phase data are available, and no groundwater data are available after 2012.
- **South-east FTA:** Natural flushing in the saturated zone is progressing for uranium, molybdenum, and sulfate based on plume maps. Well trend data indicate flushing by 2077. Spikes in uranium and sulfate concentrations after wet years indicate the possibility of upgradient unsaturated zone sources. Limited solid-phase data are available in this area.
- **South-central FTA:** One well (0718) downgradient of this area has spikes in uranium, molybdenum, and sulfate concentrations after wet years indicating the possibility of upgradient unsaturated zone sources. Solid-phase data in this area are limited. Natural flushing is occurring as uranium, molybdenum, and sulfate sources from the saturated zone solid phase are released into the groundwater. Flushing times were calculated with multiple methods. Mass balance data indicate flushing by 2086 with current groundwater contaminant concentrations and by 2165 at slightly lower concentrations. Well trend data have a limited period of record but have variable trends (some increasing, some decreasing)

with flushing times greater than 100 years (2098). Column flushing times upscaled to the field indicate a mid-range estimate of 190 years for uranium and 96 years for molybdenum. Sulfate flushing times could not be estimated due to its continuous release from gypsum ($CaSO_4 \cdot 2H_2O$) dissolution in the columns. Powellite ($CaMoO_4$) dissolution is indicated in the plume and column data. Release of calcium and sulfate from the Plant likely suppresses gypsum and powellite dissolution and thus increases flushing times estimated from the column tests (which used deionized or background groundwater with lower calcium and sulfate concentrations).

- **SSMA unsaturated zone source:** Natural flushing in this area is delayed as the silt wicks up groundwater contaminants into the unsaturated zone due to capillary action. Past groundwater contaminant concentration declines in this area occurred in between flooding events. Excess uranium and molybdenum have been measured in the solid phase. Silt-containing columns over the contaminant plumes release more uranium, molybdenum, and sulfate than background silt columns. Column flushing times upscaled to the field indicate midrange estimates of 110 years for uranium, 38 years for molybdenum, and 66 years for sulfate. This estimate relies on an assumption of flooding every 5 years and no upgradient contaminant sources. Thus, these flushing times must be added to the FTA flushing time estimates.
- **SSMA saturated zone source:** The solid phase sources of uranium, molybdenum, and sulfate are mainly from the unsaturated zone. Contaminant sources in the saturated zone are variably indicated from solid-phase and column data with contaminant concentration differences with depth and location. Some column data indicate limited uranium and molybdenum sorption on S&G with relatively quick contaminant release. Other columns indicate gypsum and powellite dissolution. Areas with high organic carbon content (naturally reduced zone [NRZ]) are a sink for contaminants released from the unsaturated zone that could later be released to the groundwater. Column testing with oxic influent water is not necessarily representative of field conditions just below the NRZ and possible release mechanisms under anoxic conditions are not well understood. The SSMA saturated zone will not flush until the FTA (unsaturated and saturated zones) and the SSMA unsaturated zone are flushed. Estimates of additional flushing times for the SSMA saturated zone were not completed since the other sources already exceeded 100 years.
- **Semiconfined aquifer:** Natural flushing in this zone was not thoroughly evaluated, but it is considered possible for sulfate (only contaminant currently present) if the source of sulfate in the surficial aquifer declines. The sources of sulfate in the surficial aquifer are (1) dissolution of gypsum in the FTA, and (2) Plant retention ponds and outfall water.

Data from current groundwater geochemical conditions, solid-phase data, and column studies were evaluated for uranium and molybdenum fate and transport controls with the following observations:

- Background silt columns can release uranium and molybdenum above standards for a few pore volumes, as the silt naturally accumulates evaporites (like gypsum and sodium sulfates) along with small amounts of metals.
- FTA silt is difficult to distinguish as fill or native material. Only one column of FTA silt was completed, and it released more molybdenum than uranium. The reason for this is not understood, but it is possible that molybdenum sorbs more strongly to iron-manganese (Fe/Mn) oxyhydroxides precipitated at the top of the water table.

- SSMA silt can have an extended release of uranium and molybdenum, but molybdenum flushes to below standards in less pore volumes than uranium.
- Overall, the geochemistry appears to indicate mineral controls by calcite, gypsum, and powellite. Uranium and molybdenum also appear to be controlled by sorption/desorption processes. Additional geochemical modeling and reactive transport modeling will be necessary to fully quantify these processes and their influence on uranium and molybdenum mobility.

Ongoing work with groundwater tracer test studies at the FTA and SSMA under the Applied Studies and Technology Program will help provide information on uranium and molybdenum mobility controls. These evaluations will provide additional constraints on geochemical input parameters for a Site reactive transport model.

Data quality objectives were developed to determine potential data gaps for consideration before developing a Site reactive transport model. Recommendations to address these data gaps are summarized below:

- Sample groundwater and solid phase at the past head of uranium and molybdenum plumes (e.g., well 0101 area, former ore storage) to confirm possible flushing in this area.
- Solid-phase unsaturated zone sampling, within and upgradient of the south-east FTA to confirm distribution of source zone mass of uranium, molybdenum, and sulfate.
- Groundwater sampling via temporary piezometers between prior transects 02 and 03 (Figure 37) to confirm the start of the uranium, molybdenum, and sulfate plumes; this will be used as a guide for solid-phase sampling in this area.
- Unsaturated and saturated zone solid-phase sampling upgradient of the south-central FTA (between transects 02 and 03, Figure 37) to confirm distribution of source mass of uranium, molybdenum, and sulfate.
- During FTA solid-phase sampling, sample more discrete intervals at the top of the water table where the potential precipitation of Fe/Mn oxyhydroxides with sorbed uranium and molybdenum might exist.
- Between the Plant retention ponds and the FTA boundary, confirm the groundwater geochemistry before it enters the FTA, either with a new monitoring well or a temporary piezometer. This groundwater geochemistry can potentially influence the flushing rate of contaminants from the solid phase at the FTA.
- Complete geochemical modeling of column tests (Section 6.0) and field tracer testing (Section 7.0). Completion of this work will provide geochemical input parameters for Site reactive transport modeling.
- Additional column testing on S&G below the NRZ at well 0855 for uranium release using anoxic background groundwater. This influent water type is likely to occur at this area once all other areas have flushed to below standards.
- Addition of transducers for water level variations and specific conductance probes for overall geochemical variations at the FTA. This can provide information on water/sediment interaction at the top of the water table and possible groundwater inputs from the Plant.

Once data gaps are addressed and a Site reactive transport model is developed, this model will be used to evaluate compliance strategies as part of a revised GCAP.

1.0 Introduction

1.1 Background

The Riverton, Wyoming, Processing Site (Site) is regulated under Title I of the Uranium Mill Tailings Radiation Control Act (UMTRCA) and is managed within the Uranium Mill Tailings Remedial Action (UMTRA) Program. The Site is managed by the U.S. Department of Energy (DOE) Office of Legacy Management (LM), and the regulator is the U.S. Nuclear Regulatory Commission (NRC). Historical milling operations and associated tailings disposal caused surface and groundwater contamination to the Site. Surface remediation was completed in 1989 by removing the tailings to radioactivity standards for radium (DOE 1991; DOE 1998a). Supplemental standards were applied to 231 verification grids due to thorium-230 contamination in the absence of radium-226, at depth, and within the saturated zone (DOE 1991). As outlined in the Groundwater Compliance Action Plan (DOE 1998b) (GCAP) that was approved by the NRC (NRC 1999), the current compliance strategy for groundwater remediation is natural flushing with institutional controls to below applicable standards for uranium and molybdenum within 100 years. Multiple mill process-related constituents were identified in the groundwater, but only uranium, molybdenum, and sulfate were sufficiently distributed to form volumetrically sufficient aqueous plumes (DOE 1998b). Only uranium and molybdenum were selected as indicator constituents for compliance monitoring (DOE 1998b) with maximum concentration limits of 0.044 milligrams per liter (mg/L) and 0.10 mg/L, respectively (DOE 1998a).

Highlight Box 1: Current Riverton Groundwater Compliance Standards:

Uranium = 0.044 mg/L and Molybdenum = 0.10 mg/L

Groundwater meeting those concentrations in 100 years (2098) with institutional controls in place.

Due to Site flooding and high recharge events, recent data indicate that uranium and molybdenum are not naturally flushing as predicted and may not naturally attenuate below their maximum concentration limits within 100 years (DOE 2018). DOE 1998b indicates that a formal corrective action will be implemented if "compliance monitoring indicates that observed concentration decreases are not in general accordance with out-year predictions." Therefore, LM is planning on revising the GCAP to reevaluate the Site compliance strategy.

1.2 Purpose and Objective

This report summarizes geochemical data collected through 2020 to (1) evaluate natural flushing progress and possible time frames, (2) provide information on the current site conditions that can be used to inform the GCAP revision, and (3) determine potential data gaps that might need to be addressed before completing a revised GCAP.

1.3 Review of Contaminant Mobility Controls

1.3.1 Uranium

Except for uranium minerals that form in waters with high vanadium concentrations (i.e., carnotite [$K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$] and tyuyamunite [$Ca(UO_2)_2V_2O_8 \cdot H_2O$]), uranium is soluble under oxidizing conditions, namely as U(VI), where it forms the uranyl oxycation,

UO_2^{2+} (aq) (Choppin 2007; Maher et al. 2013). Uranyl forms stable aqueous complexes with a range of inorganic (e.g., carbonate) and organic (e.g., humic and fulvic acids) ligands. Uranyl and its complexes can also sorb to mineral and colloid (both inorganic and organic) surfaces and have a particular affinity for iron and manganese (oxyhydr) oxide minerals (Maher et al. 2013). The stability of sorbed uranium is dependent on pH conditions, competing ion concentrations, redox conditions, and existing stable aqueous complexes. Uranium is known to form soluble complexes with carbonate, with more recent information on uranyl complexes with carbonate and alkaline earth metals (calcium, magnesium, strontium, and barium) (Dong and Brooks 2006).

Reduced uranium, typically as uranium (IV), is sparingly soluble and preferentially precipitates to form insoluble minerals like uraninite, UO_2(s), and noncrystalline solids (Loreggian et al. 2020; EPA 2007). In microbial respiration pathways, uranium can be utilized as an electron acceptor (i.e., reduced) during iron- and sulfate-reducing conditions, typically followed by precipitation as a U(IV) species (Konhauser 2007; Moon et al. 2010; Wall and Krumholz 2006). The redox reactivity of aqueous and surface complexes of uranium is an area of ongoing research. Depending on the coordinating ligand(s) or mineral surface, uranium may be more or less resistant to redox reactions. Carbonate complexes, some of the most abundant in natural waters, are likely to shield oxidized uranium from reductants, at least to a certain extent (Bender and Becker 2020).

1.3.2 Molybdenum

Molybdenum often occurs with uranium ores as it is also a redox sensitive element. Smedley and Kinniburgh (2017) provide detailed information on molybdenum geochemistry that is summarized as follows: (1) under oxidizing condition, it occurs as Mo(VI) as the molybdate anion (MoO_4^{2-}), and under reducing conditions it occurs as molybdenum (IV); (2) molybdenum is relatively mobile in oxic groundwater conditions but can form powellite ($CaMoO_4$) in waters with high calcium and molybdenum concentrations; (3) enrichments of molybdenum in oxic sediments are often attributed to adsorption onto iron, manganese, and aluminum oxides and organic matter, with sorption affinity varying with pH; and (4) under strongly reducing conditions, molybdenum is present as a very insoluble molybdenum-sulfide mineral and can be incorporated into pyrite. Conlan et al. (2012) reported molybdate mobility is limited by powellite and wulfenite ($PbMoO_4$) precipitation under neutral pH conditions with aqueous calcium and lead present. Conlan et al. (2012) indicate that batch experiments demonstrate that wulfenite forms almost instantaneously, but powellite formation is kinetically limited and has the capacity to significantly reduce molybdenum concentrations in the presence of calcite. Lead is not a current contaminant of concern at the Site, but it may have been released during tailings oxidation. Calcium, along with the precipitation of powellite, is potentially a control for molybdenum mobility at the Site.

Compared to uranium, molybdenum sorption is reversed based on pH due to the negative charge on the predominant ion. Thus, the uranyl cation will sorb more strongly at a higher pH, and the molybdate anion will sorb more strongly at a lower pH (Smedley and Kinniburgh 2017). For the Site, with relatively neutral pH values, this difference may not currently be significant. However, any future remedial scenarios might need to account for this reversal in sorption affinity with pH.

1.3.3 Sulfate and Manganese

While uranium and molybdenum are the main indicator contaminants at the Site, sulfate was identified as having a significant contaminant plume sourced from mill tailings and discharge from the upgradient sulfuric acid plant (DOE 1998a; DOE 1998b). Sulfate mobility is mainly controlled by the precipitation of gypsum ($CaSO_4$), albeit affected groundwater at the Site can have sulfate concentrations in the thousands of milligrams per liter sulfate before gypsum solubility is reached. Gypsum solubility can also control calcium concentrations, which can maintain calcium concentrations in the hundreds of milligrams per liter calcium and influence the formation of powellite, as discussed above. For uranium, gypsum solubility is also significant, as additional calcium from gypsum can suppress the dissolution of calcite and potentially reduce alkalinity. In turn, reduced alkalinity can reduce uranium mobility, as discussed above.

Manganese was identified as being released by the oxidation of the uranium mill tailings but, after tailings removal, did not create a volumetrically significant contaminant plume (DOE 1998a; DOE 1998b). Manganese is controlled by pH and redox conditions, like iron, with manganese being mobile under low pH and possible reducing conditions that were present in the surficial aquifer below the tailings impoundment. With mixing of more oxidizing upgradient groundwater and buffering by calcite that increased the pH, manganese and iron oxyhydroxides likely precipitated downgradient from the tailings impoundment, thereby removing manganese and iron from solution. These precipitates can sorb uranium and molybdenum and delay their natural flushing. Precipitated manganese and iron oxyhydroxides from the tailings fluids have not been directly identified, although solid-phase data are available from total sample digestions (DOE 2016). Currently, elevated manganese and iron concentrations can be used to identify more reducing conditions in the groundwater, which would occur regardless of any tailings-derived iron and manganese being present on the solid phase. No original tailings pore fluids remain at the Site.

1.4 Report Overview

In preparation for revising the GCAP, this report provides a current Site geochemical condition assessment, which is presented as follows:

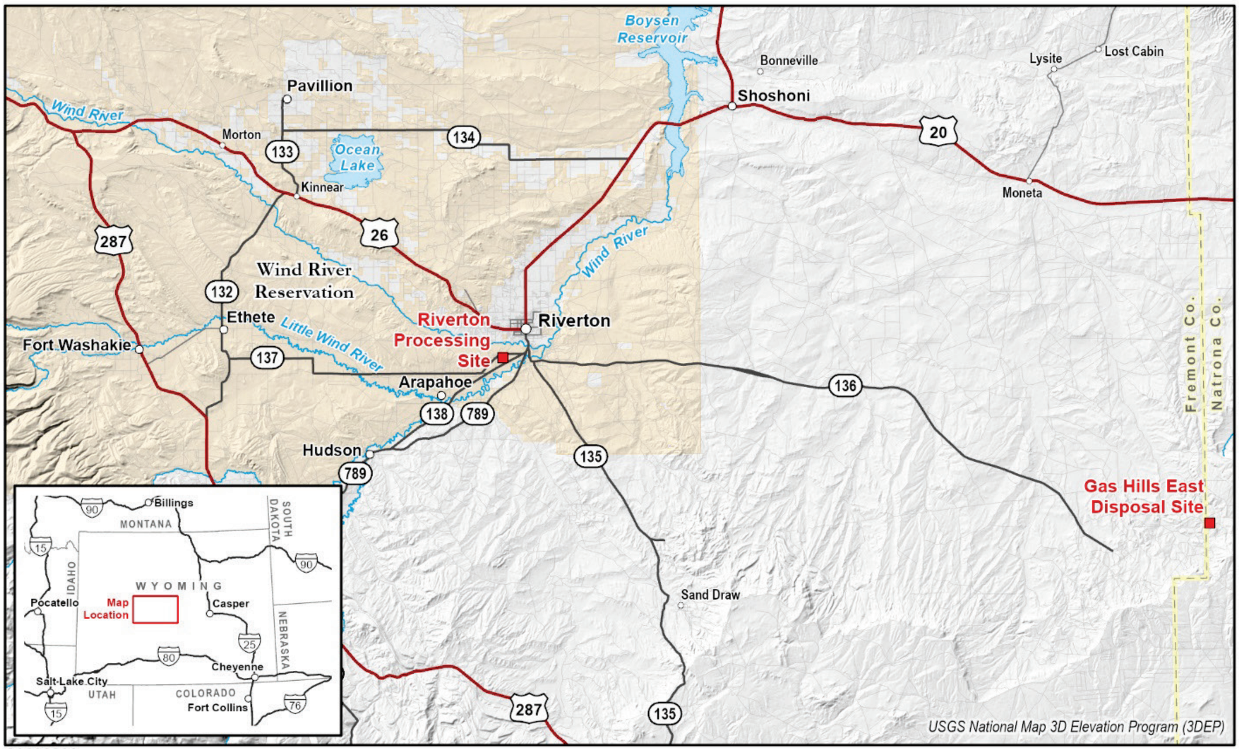
- Section 2.0: Nongeochemistry-related site details including: location, geology, and groundwater flow conditions.
- Section 3.0: The evolution of the geochemical conceptual site model (CSM) through time as (1) before moving the tailings in 1989; (2) after moving the tailings, but before 2010; and (3) after the 2010 flood through 2020, along with the current geochemical CSM.
- Section 4.0: Quantitative evaluations of natural flushing using well trends and overall mass balance.
- Section 5.0: Current Site geochemical conditions that could influence uranium and molybdenum mobility, based on most recent data.
- Section 6.0: Details on column studies that include how these data supplement and support the CSM. Column studies provide additional information on natural flushing rates and contaminant mobility. Geochemical modeling that gives quantitative uranium sorption parameters are provided.

- Section 7.0: Ongoing work, which includes tracer studies being completed at the Site under the Applied Studies and Technology (AS&T) Program.
- Section 8.0: Approach to identifying data gaps using the data quality objectives approach.
- Section 9.0: Final recommendations.
- Section 10.0: References.

2.0 Nongeochemistry-Related Site Details

2.1 Site Location and Site Features

The Riverton Site is in central Wyoming (Fremont County) 2 miles southwest of the town of Riverton and is within the boundaries of the Wind River Indian Reservation (Figure 1). The Site is on river alluvium between the Wind River and the Little Wind River (Figure 1). Figure 2 shows the monitoring network, the Site boundaries, location of the former tailings, and the institutional control boundary.



S3692200

Figure 1. Riverton, Wyoming, Processing Site Location (from DOE 2021a)

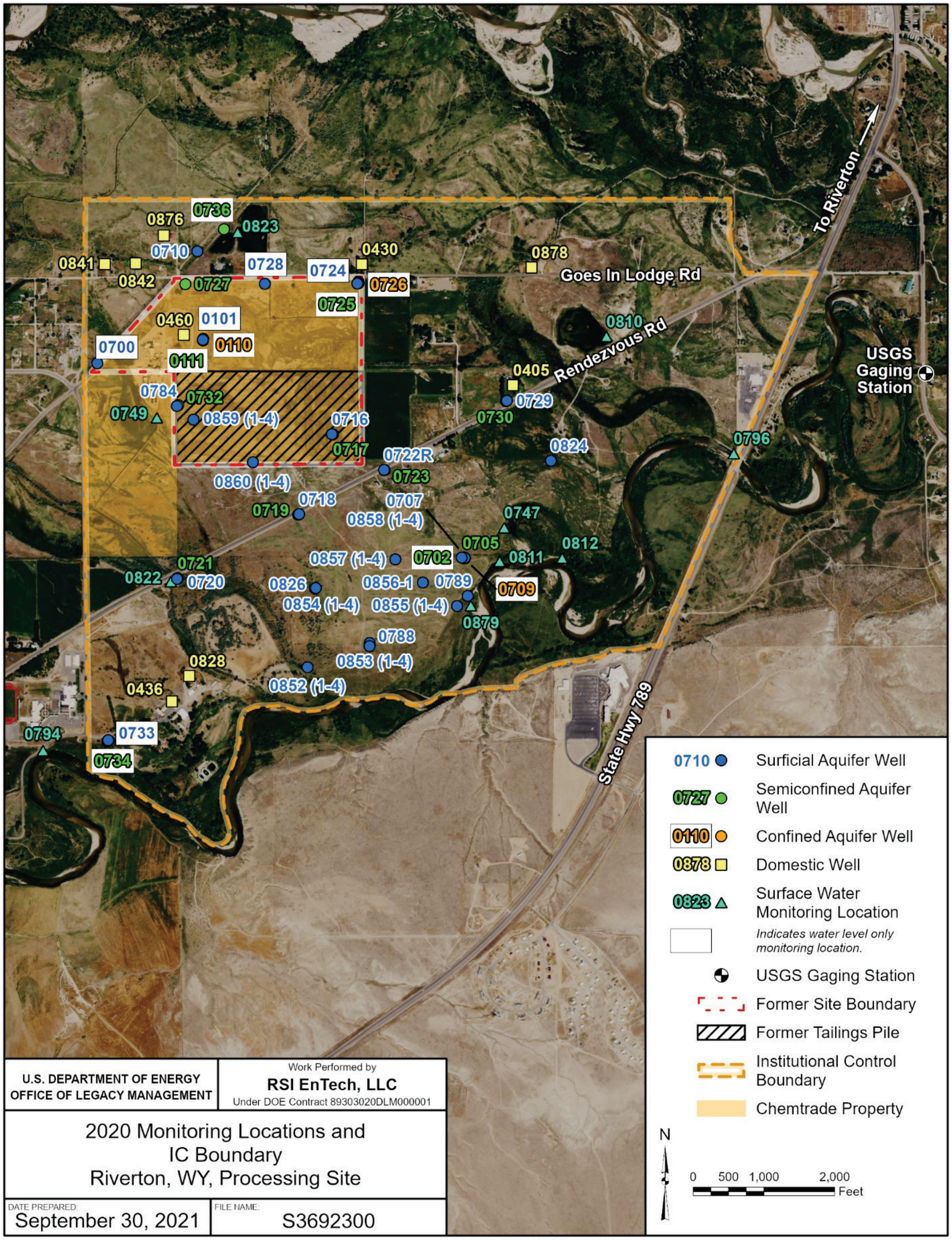


Figure 2. Site Features and Current Monitoring Network

2.2 Hydrogeology

The geology underlying the Site was first confirmed in DOE 1977 (Figure 3) as approximately 15 to 20 feet (ft) of alluvial sands and gravels (S&G) underlain by the Wind River Formation, with interbeds of shale, siltstone, and sandstone up to 1500 ft below ground surface (bgs). A northwest to southeast cross section is provided in DOE 1998b and reproduced here in Figure 4 (note that the cross-section location is provided in the figure inset). DOE 1998a defined the three main aquifers: (1) a surficial unconfined aquifer (surficial aquifer), (2) a middle semiconfined aquifer, and (3) a deeper confined aquifer. The surficial S&G aquifer can contact various units of sandstone, siltstone, or shale within the Wind River Formation (Figure 4). In addition, well logs and surficial aquifer trenches (DOE 2016) identify a silt layer occurring from 2 to 5 feet below ground surface (ft bgs) before encountering the underlying S&G. As seen in Figure 3 and Figure 4, the interbedded nature of the Wind River Formation makes the definition of distinct aquitard and aquifer units difficult. However, the first confining unit with depth (leaky shale aquitard) at an elevation of 4900 to 4920 ft above mean sea level (amsl) (Figure 4), is relatively continuous, as is the underlying sandstone unit (semiconfined sandstone aquifer) at an elevation of approximately 4880 to 4910 ft amsl (Figure 4). The deeper confined sandstone aquifer is composed of multiple interbed of sandstone and shale (Figure 4). A simplified conceptual summary of the hydrogeology across the Site is provided in Figure 5.

For the current wells across the Site (well locations are in Figure 2 and well logs can be found at https://gems.lm.doe.gov/#site=RVT), (1) wells installed at approximately 20 bgs or less (variable elevations with topography) are within the surficial aquifer, (2) semiconfined aquifer wells have well screens between 4885 to 4925 ft amsl (top elevation depends on Site topography and the variable nature of the bedrock subunits) and are completed in the first sandstone layer below any shale/siltstone layers that were encountered (Figure 4, except for well 0736, where no distinct shale/siltstone layer was encountered before completing the well), and (3) the three confined aquifer wells (0110, 0709, and 0726) are screened at various intervals between 4805 to 4885 ft amsl. Well 0110 is screened in a sandstone unit within the shale aquitard (Figure 4), and wells 0709 and 0726 are screened in the uppermost, greater than 10-foot-thick sandstone within the confined aquifer (Figure 4). The bottom of the well 0709 screen is at a 4 ft higher elevation than the top of the well screen at well 0726. Given the distance between these wells, it is difficult to determine if they are screened in the same sandstone interbed. Locally, the most productive sandstones in the confined aquifer are 300 to 400 ft bgs (Figure 3) at approximately 4540 to 4640 ft amsl, which is 100 to 200 ft deeper than the Site cross section in Figure 4 and deeper than any Site confined aquifer monitoring wells.

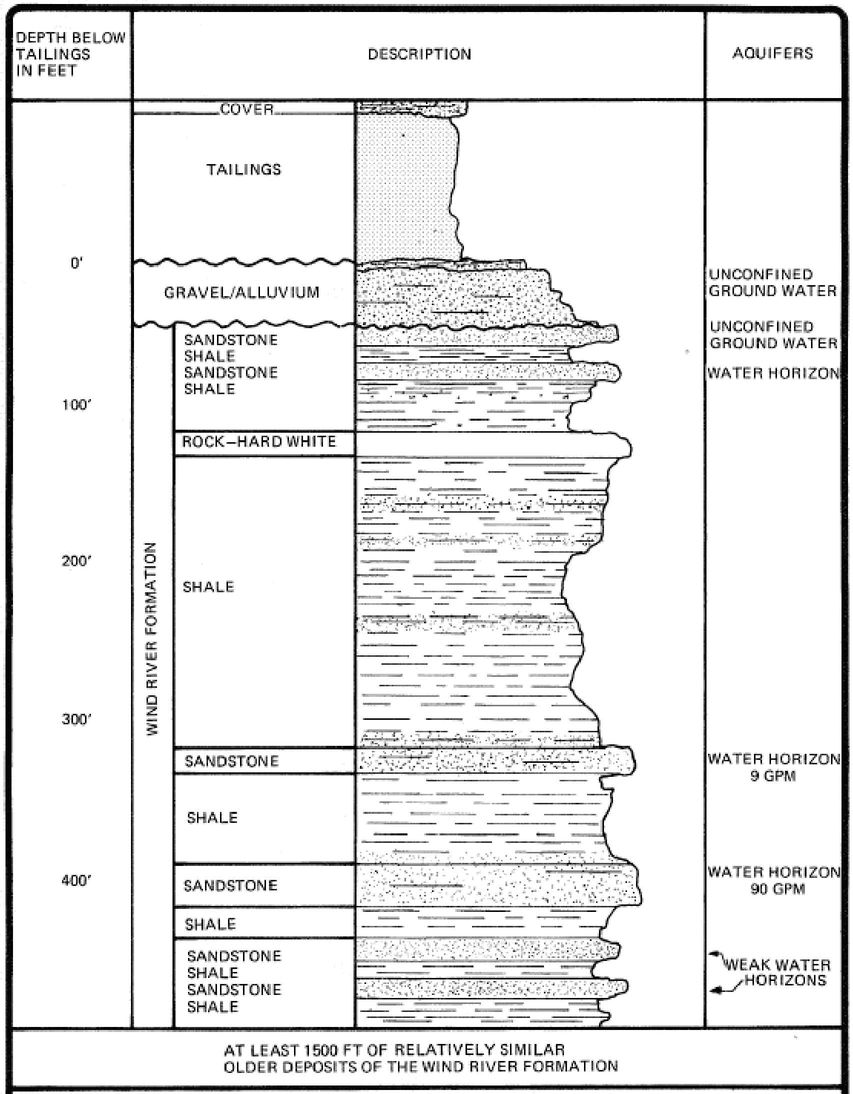


FIGURE 2-5. SIMPLIFIED LOG OF WELL AT THE SITE 130-16

Figure 3. Stratigraphy at the Riverton Site (from DOE 1977, when tailings were still in place)

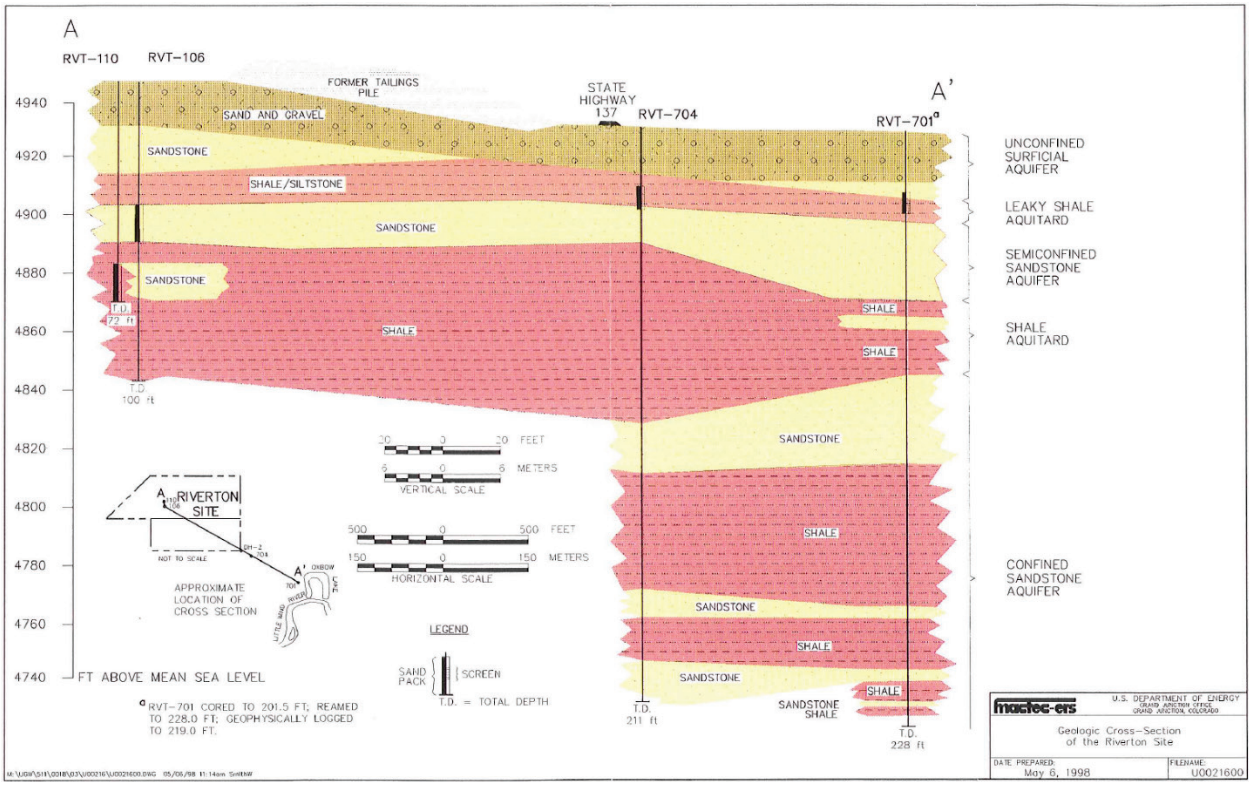


Figure 4. Cross Section of the Riverton Site (northwest [A] to southeast [A'], see inset). Figure is directly from DOE 1998b.

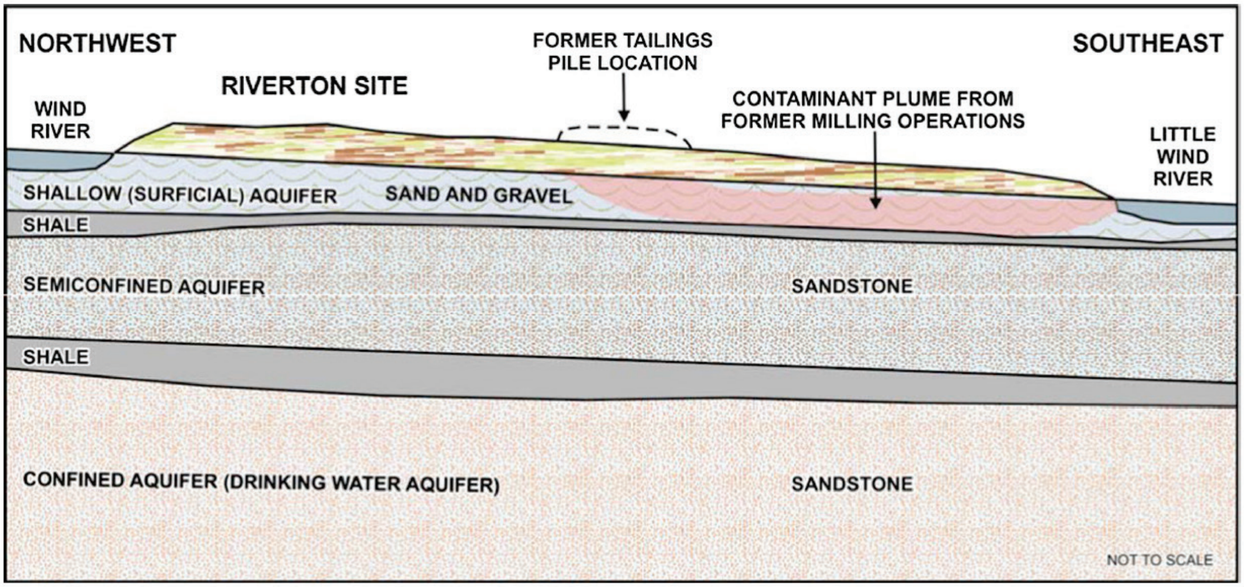


Figure 5. Conceptual Cross Section at the Riverton Site (from Dam et al. 2015). Overall groundwater flow direction is left to right.

2.3 Groundwater Flow

2.3.1 Hydraulic Head Distributions

The surficial aquifer groundwater flow direction is northwest to southeast toward the Little Wind River, as defined by a line perpendicular to the groundwater elevation contours. This overall interpretation of groundwater flow direction has not changed through time (Figure 6, Figure 7, and Figure 8), even with changing well configurations. For the groundwater elevation map of the surficial aquifer in 1983 (Figure 6), the tailings had not been removed yet (rectangular area). Thus, the groundwater below the tailings impoundment does show some slight mounding likely due to excess recharge through the tailings. The current Chemtrade sulfuric acid plant (Plant) retention ponds and the former tailings area (FTA) are identified on Figure 8. Groundwater mounding around the retention ponds is not apparent, but there are no surrounding monitoring wells (Figure 8).

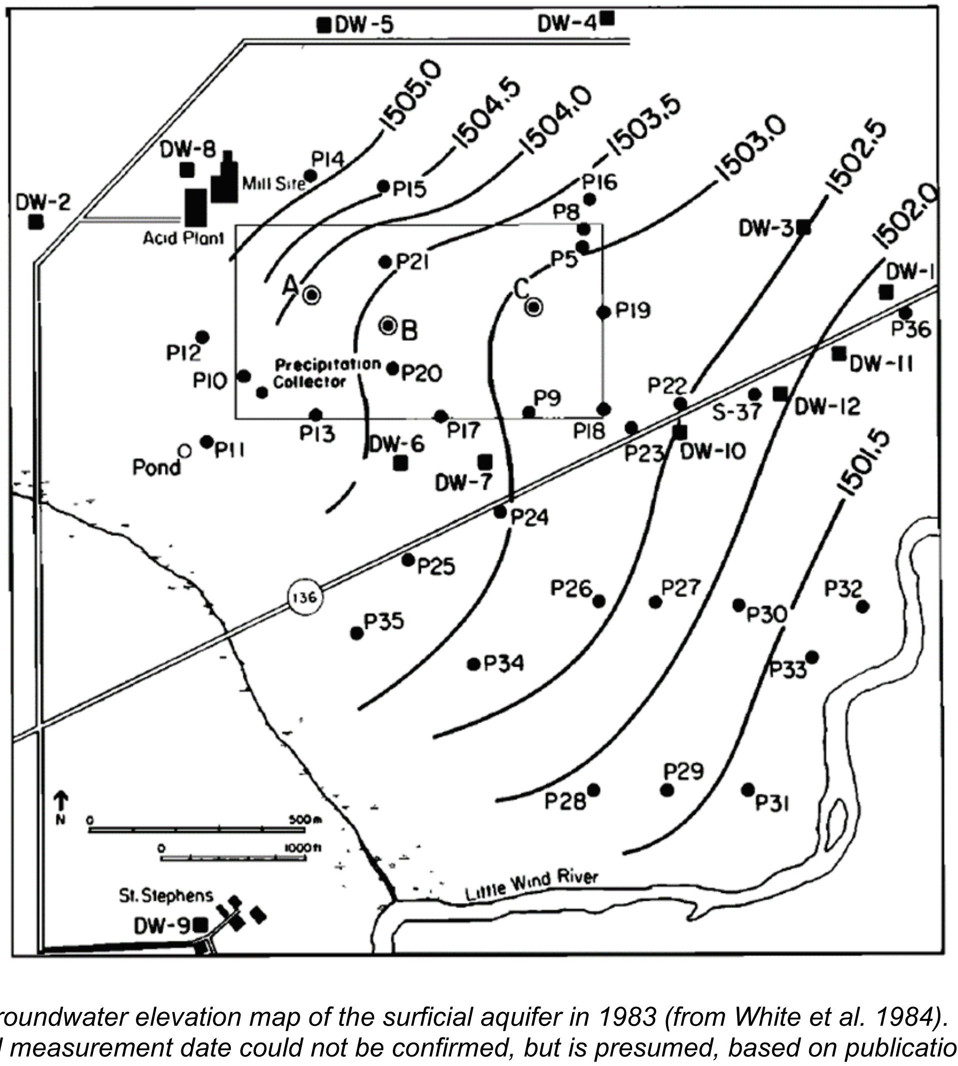


Figure 6. Groundwater elevation map of the surficial aquifer in 1983 (from White et al. 1984). Units are in meters and measurement date could not be confirmed, but is presumed, based on publication date and similar data in DOE 1987. DW indicates domestic wells in the Wind River Formation, P indicates piezometers in the alluvium, and A, B, C sites are nested suction water samplers completed in the tailings. Rectangle is the approximate dimensions of the tailings pile. It is presumed that the groundwater elevations of the surficial aquifer are based only on the piezometers (P designation), based on data in DOE 1987.

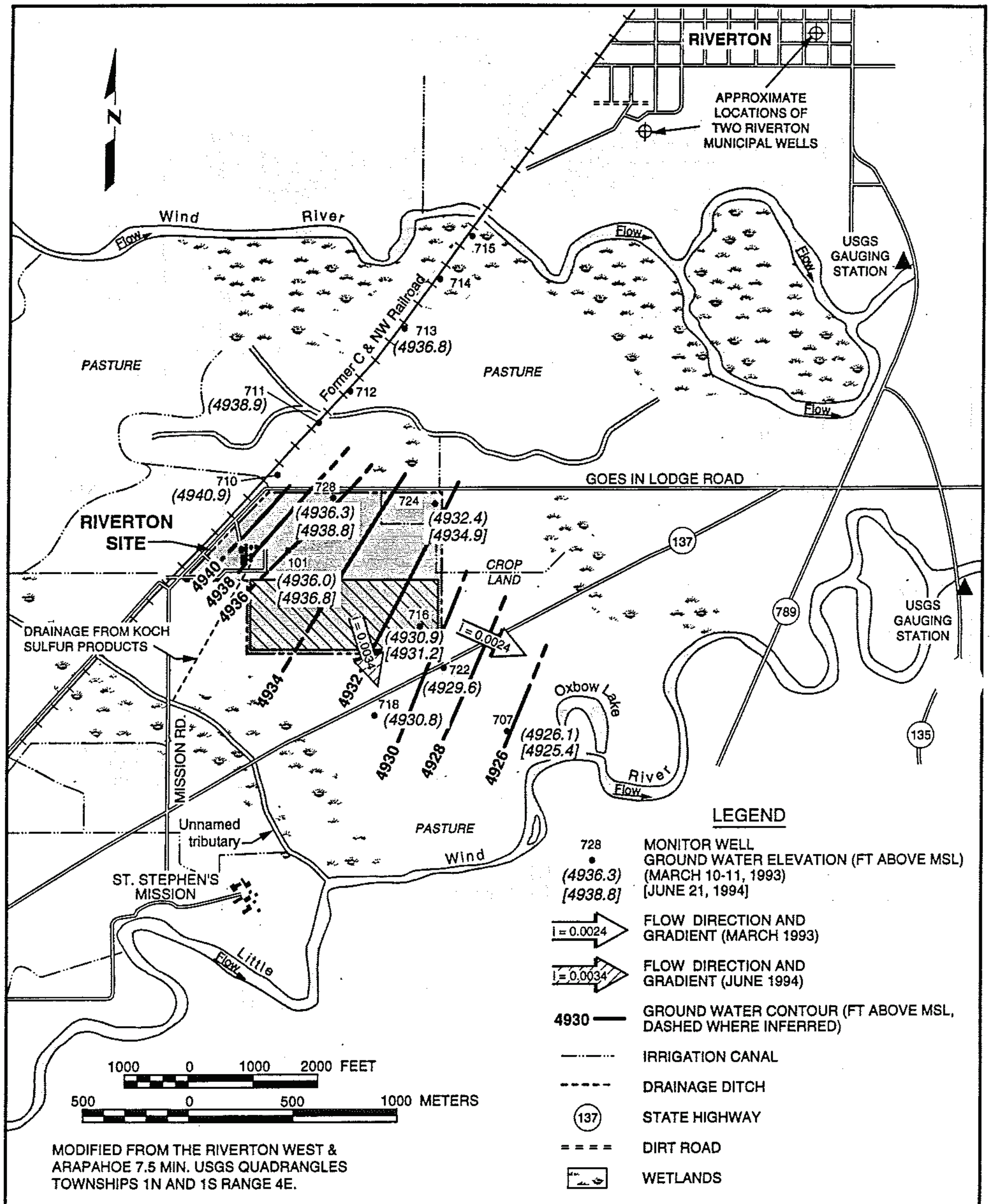


FIGURE 2.4
GROUND WATER ELEVATIONS IN THE SURFICIAL AQUIFER
RIVERTON, WYOMING, SITE

Figure 7. Groundwater Elevation Map of the Surficial Aquifer in 1993 and 1994 (from DOE 1995)

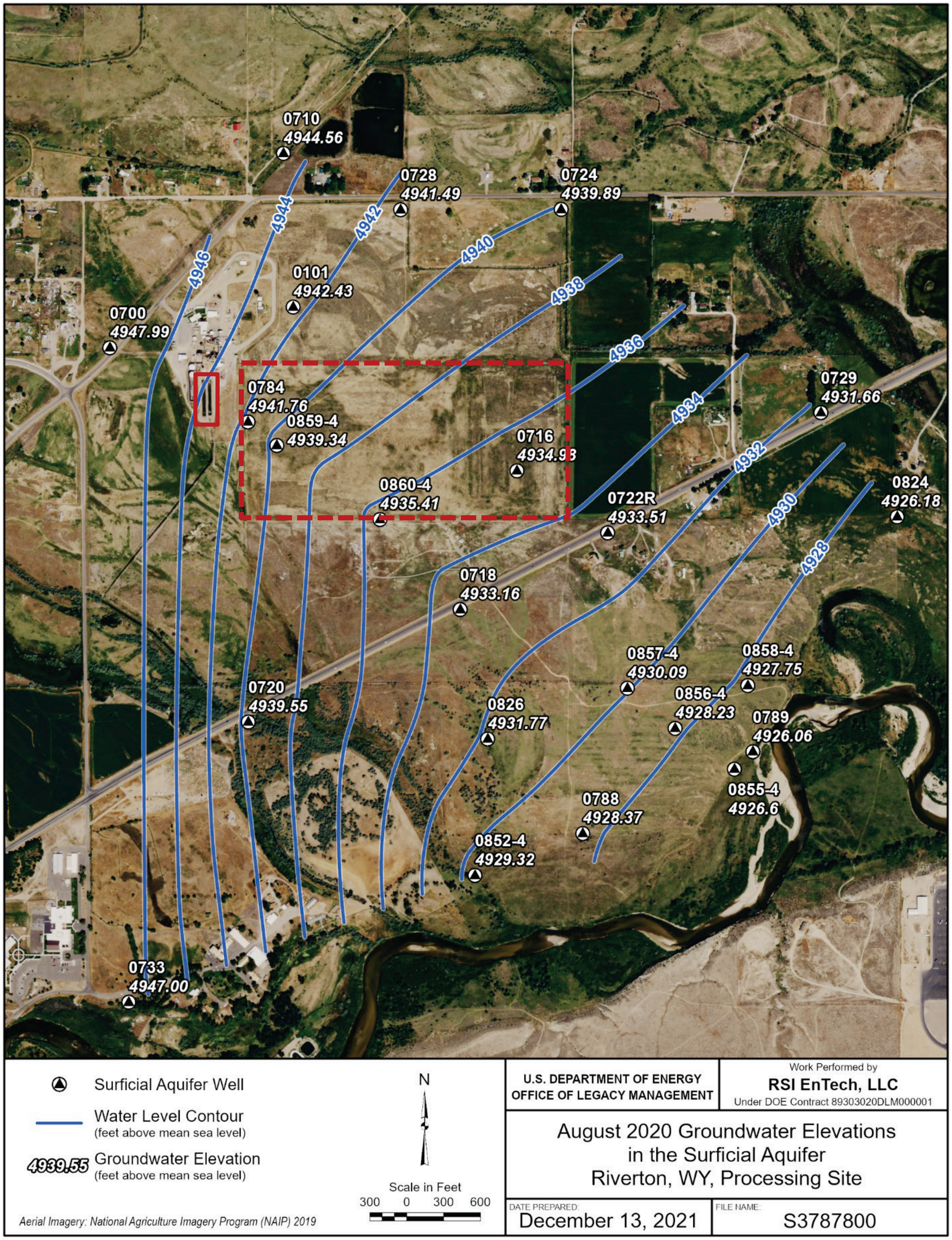


Figure 8. Groundwater Elevation Map of the Surficial Aquifer in 2020 (from DOE 2021a). (The solid red rectangle highlights two retention ponds associated with the Chemtrade sulfuric acid plant. The dashed red rectangle highlights the FTA.)

Similarly, the semiconfined aquifer groundwater flow direction is northwest to southeast. This overall interpretation of groundwater flow direction has not changed through time (Figure 9 and Figure 10), even with a slightly different monitoring well configuration. Vertical gradients between the surficial and the semiconfined aquifer exist (DOE 2021a), with an overall downward gradient within the Site boundary (see Figure 27 in DOE 2020a). No semiconfined aquifer wells were discussed in White et al. 1984, as the focus of investigations in that time frame was on the surficial aquifer.

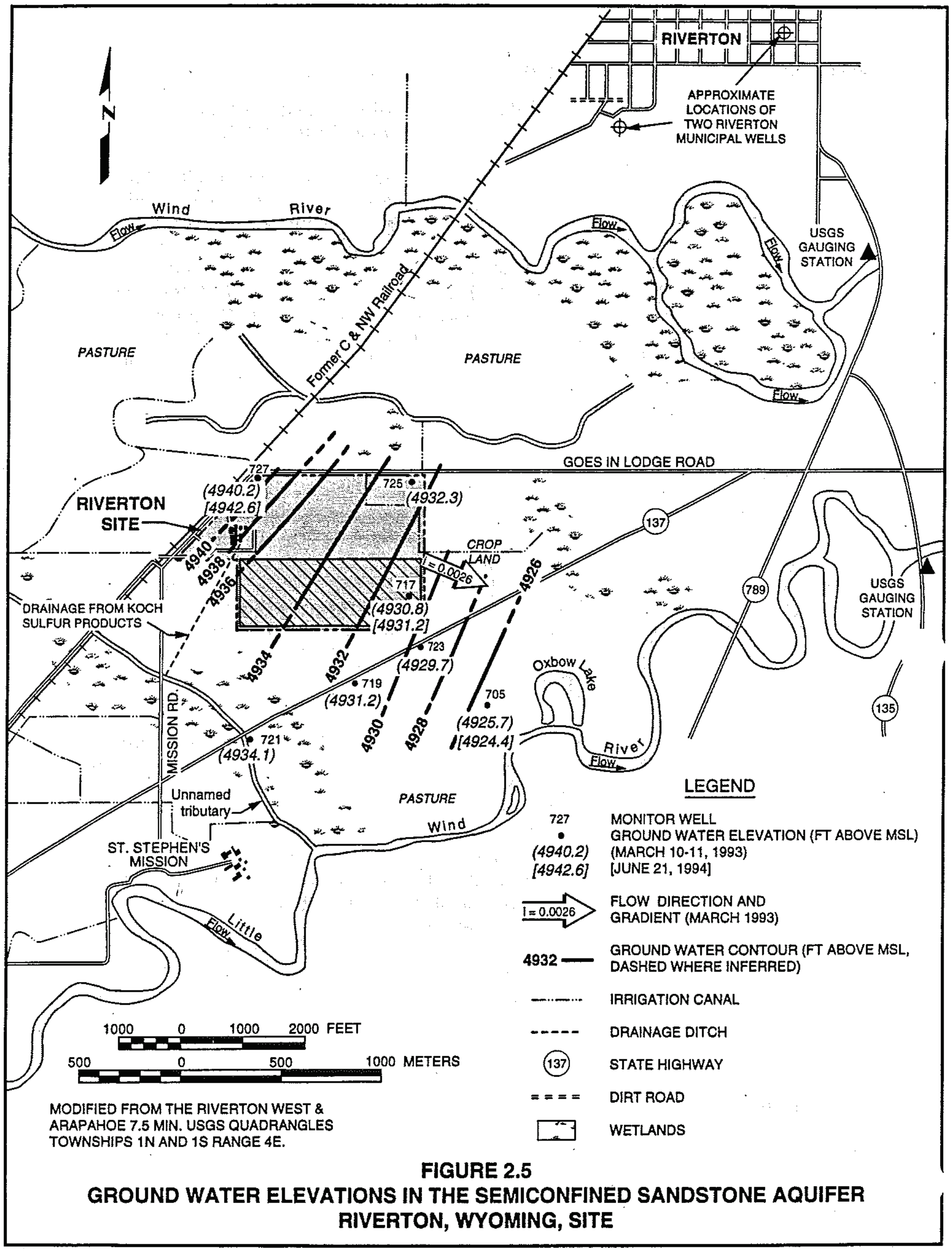


FIGURE 2.5
GROUND WATER ELEVATIONS IN THE SEMICONFINED SANDSTONE AQUIFER
RIVERTON, WYOMING, SITE

Figure 9. Groundwater Elevation Map of the Semiconfined Aquifer (from DOE 1995)

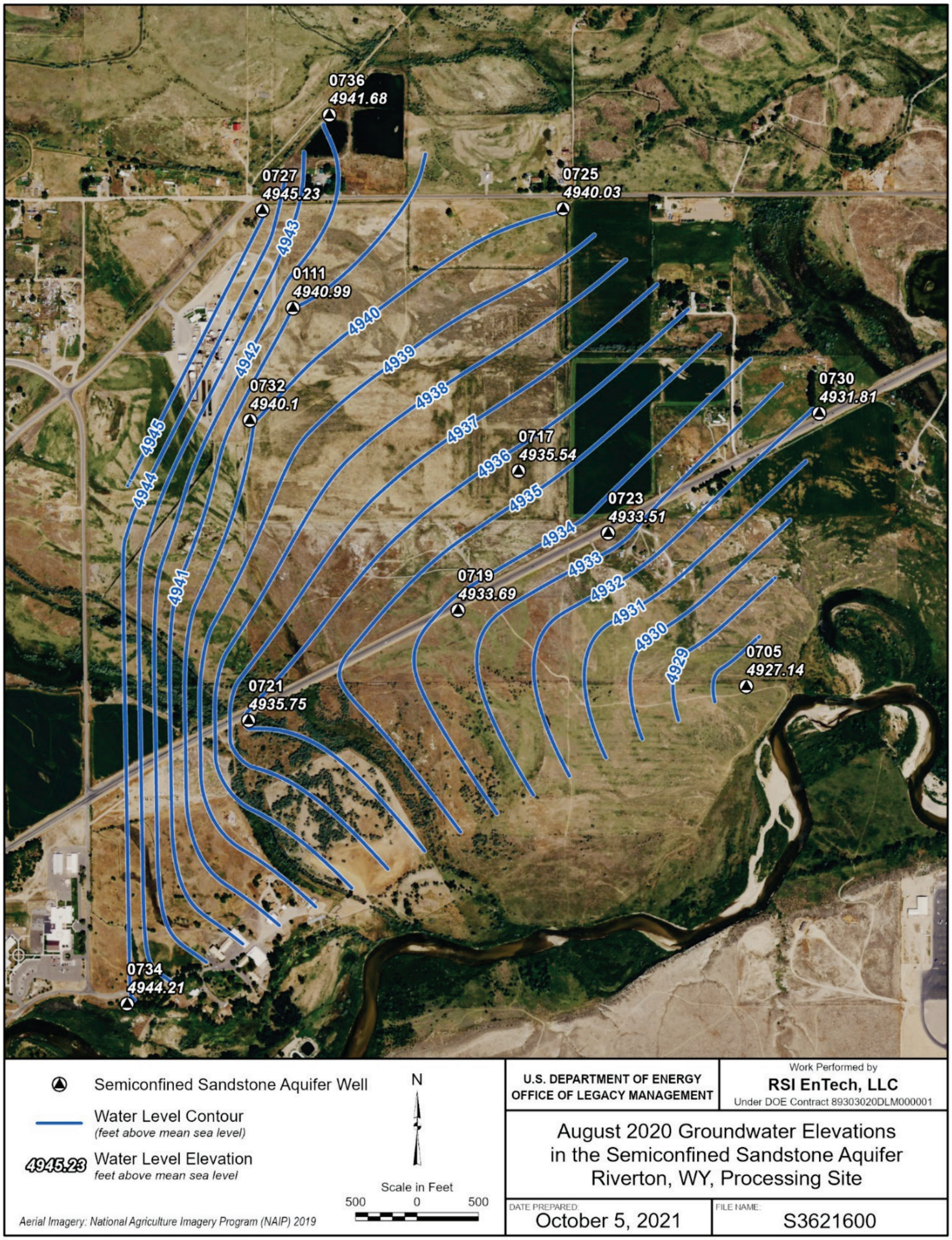


Figure 10. Groundwater Elevation Map of the Semiconfined Aquifer

It is presumed that the Little Wind River is the groundwater discharge area for the alluvial aquifer and possibly from the semiconfined aquifer, given a prominent bedrock outcrop south of the Little Wind River with a higher topographic elevation (bottom right, tan area in Figure 10). Historically, there have been three wells on the south side of the Little Wind River (wells 0706 and 0809, surficial aquifer wells installed in 1984 and 2004, respectively, and well 0735, a semiconfined aquifer well installed in 1995). A review of the data from all three wells did not indicate any uranium contamination. These three wells have been abandoned, as scouring of the Little Wind River makes the current location of these past wells within the river channel. Data and well locations can be found at https://gems.lm.doe.gov/#site=RVT.

Highlight Box 2: Groundwater Flow Direction Summary

Unconfined aquifer: Flow is northeast to southwest with discharge to the Little Wind River

Semiconfined aquifer: Flow is northeast to southwest with likely discharge to the Little Wind River

Confined aquifer: Flow direction at the site is unknown, not enough consistent well completions. Presumed to flow towards the town of Riverton.

Given the variable screen depths for the confined aquifer monitoring wells, there are not enough data to confirm an overall groundwater flow direction in the confined aquifer wells. In the 1980s, groundwater flow in the confined aquifer at the Site was toward the town of Riverton (see Figure C.2.20 in DOE 1987) due to pumping in deep wells within the Wind River Formation for the municipal water supply (DOE 1987). This regional groundwater flow is likely not connected to the groundwater flow in the Site confined aquifer wells that are completed at much shallower depths (discussed in Section 2.2).

2.3.2 Anthropogenic Hydraulic Considerations

Two anthropogenic hydraulic considerations that can add water to the surficial aquifer are (1) irrigation in nearby agricultural fields and (2) retention ponds associated with the Plant (Figure 8). Recharge from excess irrigation is quantified in DOE 2020a as part of the water balance for a Site groundwater flow model. No prior consideration of the retention ponds could be found. According to National Pollutant Discharge Elimination System (NPDES) Permit No. WY-0034207 Statement of Basis (https://www.epa.gov/sites/default/files/2020-11/documents/wy0034207-chemtrade-sob-2020.pdf), the average flow of total wastewater from the Plant was 202,000 gallons per day between April 2013 through March 2014. Based on measurements in DOE 2016 at the Plant outfall of 175,000 gallons per day (converted from 0.27 cubic feet per second), the possible loss to groundwater is 27,000 gallons per day, albeit with limited measurements. Wastewater treatment consists of mixing, neutralizing, settling, and nonbiological aeration before going to an outfall ditch. The aeration step occurs in two large retention ponds (Figure 8) that are presumably unlined and were dug directly into the S&G of the surficial aquifer. The height of the water within the retention ponds compared to the water table is unknown. In any case, the high permeability of the sediments likely creates a significant loss of water from the retention ponds to the surficial aquifer, even though no groundwater mounding is apparent (Figure 8). In addition, added water from the retention ponds to the surficial aquifer could create enough additional hydraulic head to provide the downward hydraulic gradient from the surficial aquifer to the semiconfined aquifer in this area (see Figure 27 in DOE 2020a).

Google Earth imagery was reviewed to identify when the Plant retention ponds were created. One pond was visible in imagery from July 1994, and imagery before that date was too low in resolution for any identification. The current two pond configuration (Figure 8) can be seen in imagery from September 2006. Geochemistry of water in the retention ponds and the associated outfall are discussed in Section 3.3.

3.0 Evolution of the Geochemical Conceptual Site Model (CSM)

3.1 Before Tailings Removal (before 1990)

Early data from DOE 1977 and DOE 1981 focused on radioactivity measurements of radium-226 as a measurable decay product of uranium that was not removed in the milling process. With the tailings being the source material, contamination was detected (1) up to 5 ft below the bottom of the tailings and (2) as windblown tailings surrounding the tailings impoundment itself up to 0.3 mile away (DOE 1981). While the potential for nearby groundwater and surface water was recognized, no measurements of radium-226 in groundwater or surface water exceeded U.S. Environmental Protection Agency (EPA) standards of 15 picocuries per liter (gross alpha activity) (DOE 1981). These reports also measured radon emanation from the tailings. At that time, the focus was on remedial alternatives for stabilizing the tailings impoundment based mainly on reducing exposure to radioactivity.

More detailed groundwater and surface water data were collected by various entities from 1980 to 1985 (extensive summary can be found in Appendix C, “Water,” in DOE 1987). The first geochemical CSM is provided in White et al. 1984 (also discussed in DOE 1987), based on detailed tailings pore water and surficial aquifer groundwater sampling. The geochemical CSM in White et al. 1984 is “Except for elevated uranium and molybdenum concentrations, current radionuclide and trace metal transport is limited by the near-neutral pH conditions of the groundwater. Significant reactions include the dissolution of calcite, production of CO_2, and precipitation of gypsum and the hydroxides of iron and aluminum.” These reactions were identified using tailings pore water geochemistry with depth along with geochemical modeling. Additional data from around 1983 (exact dates are not specified in White et al. 1984 but are presumed to be from between 1981 to 1983 based on data in DOE 1987), which supported these reactions, included measured pH along with uranium, molybdenum, and sulfate plumes (Figure 11). The contouring from Figure 11 is also provided on a consistent base map (uranium in Figure 12, molybdenum in Figure 13, sulfate in Figure 14, and pH on Figure 15) that matches plume map figures for later dates.

White et al. 1984 recognized that most of the metals (e.g., copper, nickel, aluminum, manganese, iron, and zinc) present in the low-pH tailings pore water precipitated as that pore water was buffered by calcite within the tailings, while uranium and molybdenum can remain mobile. This buffering reaction creates a slightly lower pH zone in the surficial aquifer groundwater (Figure 11 and Figure 15) as the calcite dissolution also produces excess CO_2 and precipitates gypsum (White et al. 1984). Whether the low-pH conditions like the tailings pore water (pH <4) ever occurred in the underlying surficial aquifer or remained just within the tailings is unclear. In addition, molybdenum does not appear to be as mobile as uranium downgradient of the tailings impoundment (Figure 11, Figure 12, and Figure 13).

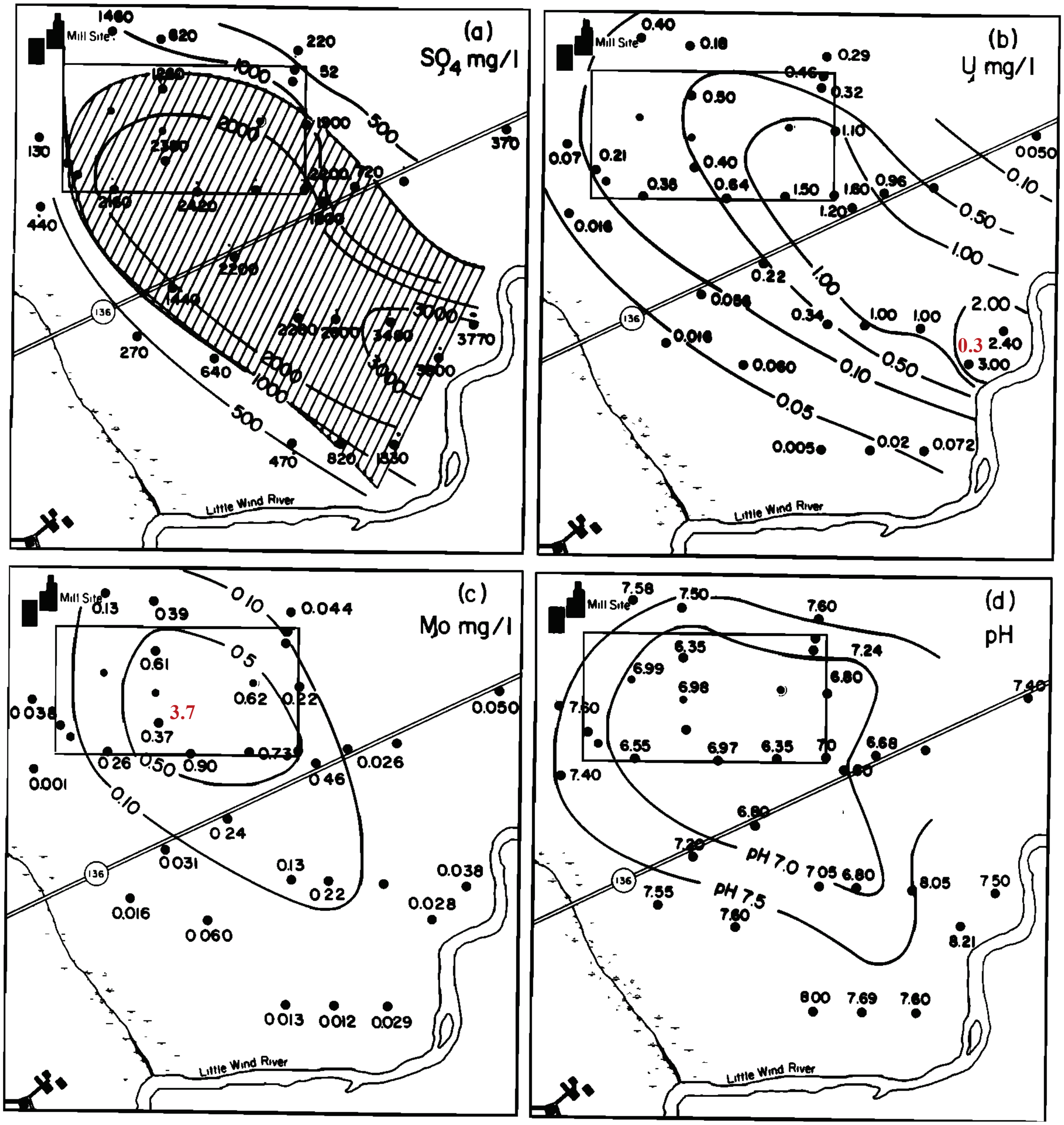


Figure 11. Geochemical data for the surficial aquifer including (a) sulfate in mg/L, (b) uranium in mg/L, (c) molybdenum in mg/L, and (d) pH in standard units. Rectangle is the tailings impoundment. The shaded area in (a) is the extent of gypsum saturation. From White et al. 1984. Data collection date is presumed to be around 1983 based on the timing of Lawrence Berkley National Laboratory analyses listed in DOE 1987. Note that two data points were incorrectly labeled based on the data table in White et al. 1984. Those points are relabeled in red with the appropriate change in the decimal place.

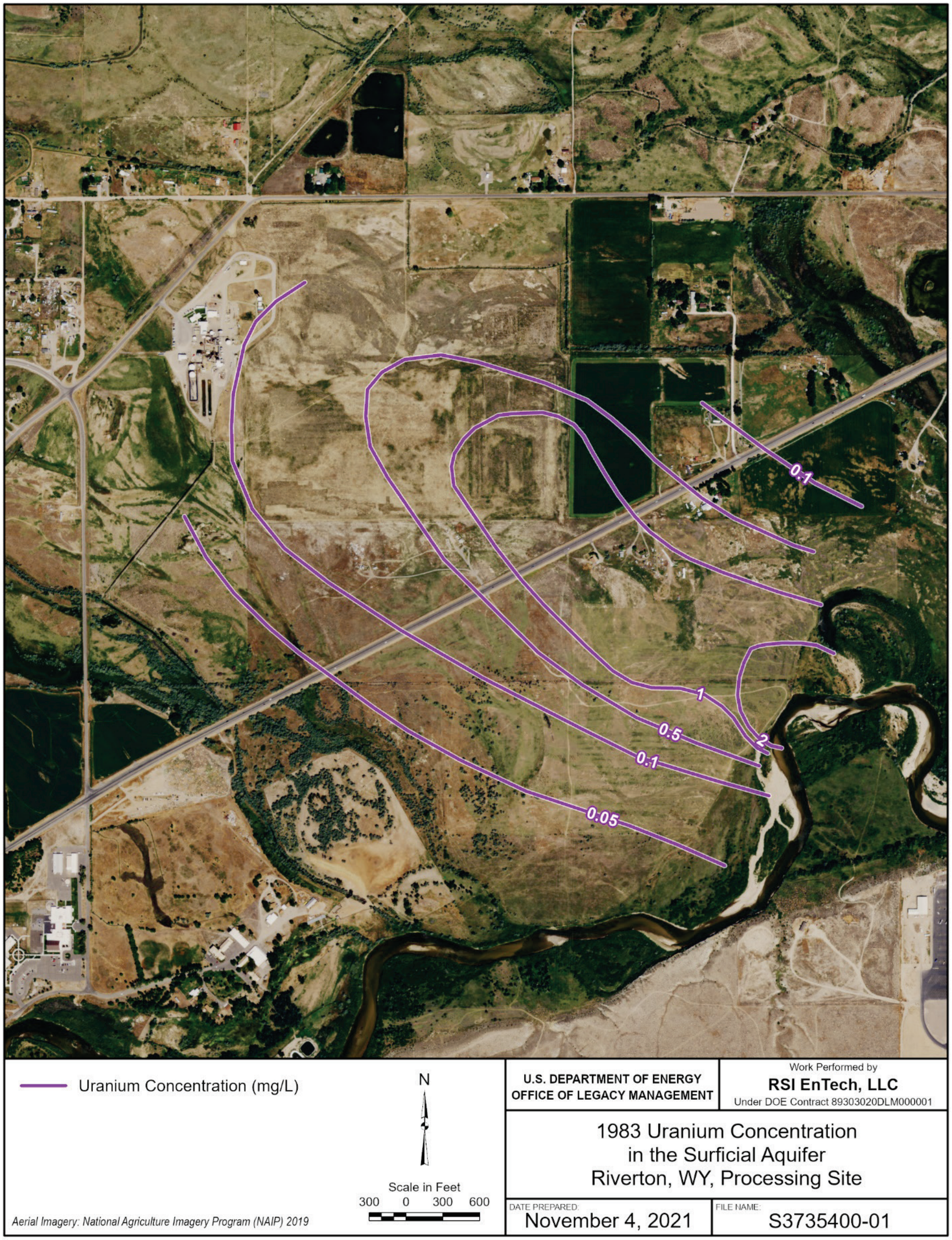


Figure 12. Uranium Contours from Figure 11 on a Consistent Base Map

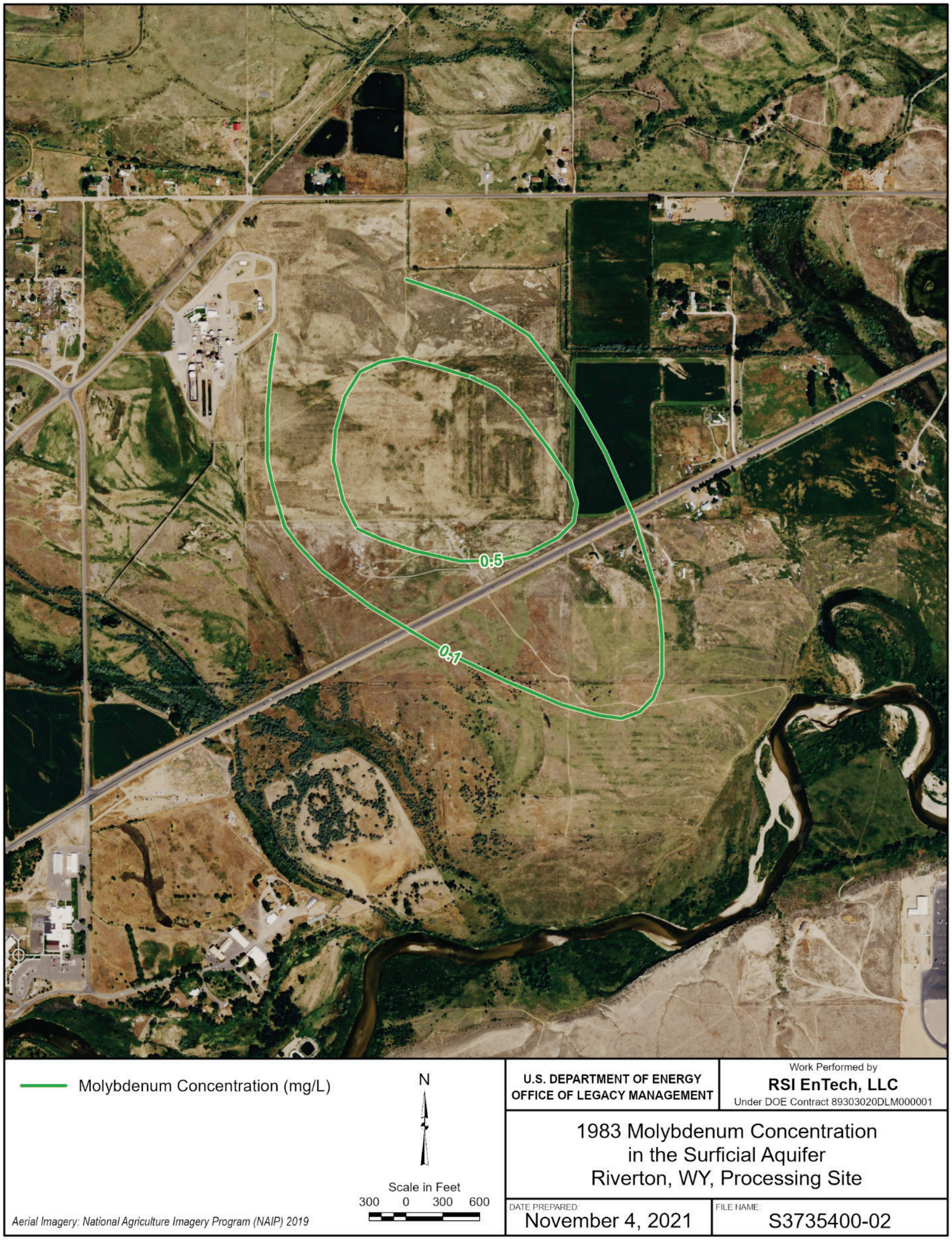


Figure 13. Molybdenum Contours from Figure 11 on a Consistent Base Map

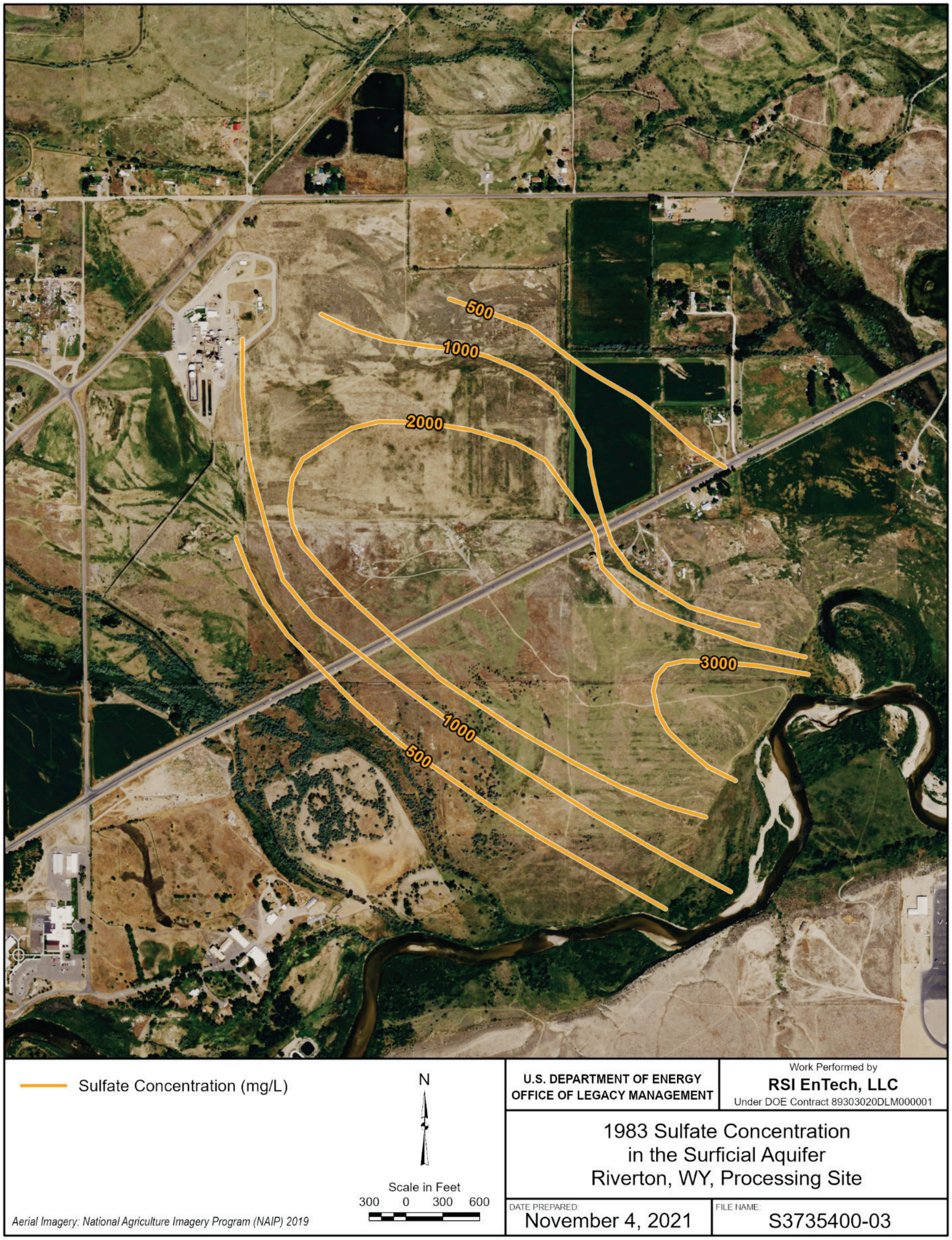


Figure 14. Sulfate Contours from Figure 11 on a Consistent Base Map

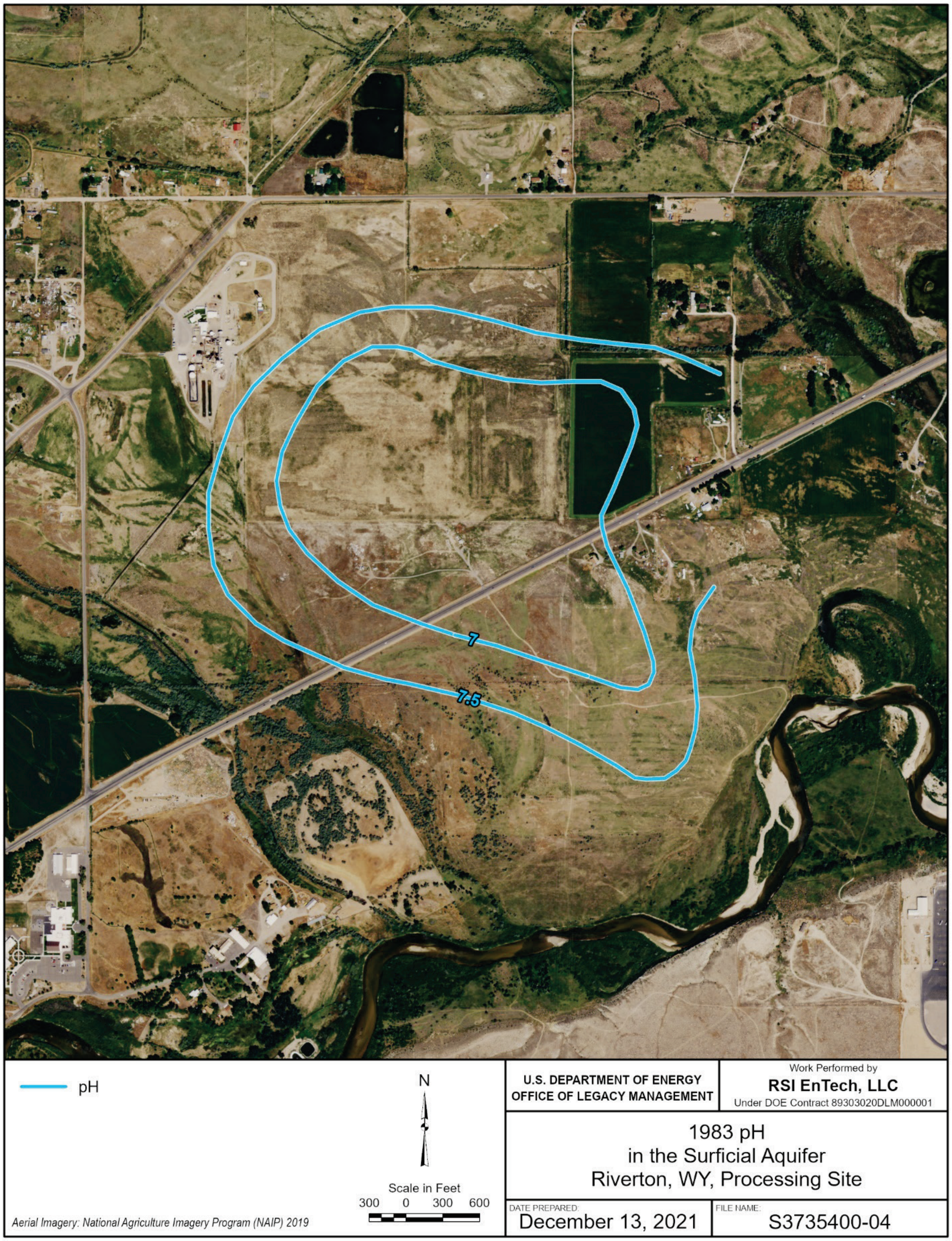


Figure 15. pH Contours from Figure 11 on a Consistent Base Map

Highlight Box 3: Summary of CSM Before Tailings Removal

Tailings are a source of low-pH metal-rich fluids.

pH buffering creates conditions that removes most metals, except for uranium and molybdenum.

Uranium, molybdenum, and sulfate plumes are heading toward the Little Wind River along the direction of groundwater flow in the surficial aquifer.

Gypsum can limit sulfate concentrations, uranium is moving faster than molybdenum, but uranium and molybdenum mobility controls have not been determined.

Narasimhan et al. 1986, a companion article to White et al. 1984, uses a mixing model coupled with a geochemical model to conclude that, at most, 1.7% of the tailings pore water is needed to produce the surficial aquifer geochemistry observed in Figure 11. Narasimhan et al. 1986 determined this mixing percentage using measured pH, oxidation-reduction potential (ORP), calcium, magnesium, sodium, potassium, iron, aluminum, silicon, chlorine, and carbon (total alkalinity) and sulfate values with controls from predicted minerals of interest: calcite, gypsum, gibbsite, and iron hydroxide. The dissolution of gypsum is used to model the sulfate plume at that time (1983, equivalent to a sulfate plume calculated for 20 years after the end of active tailings deposition). Narasimhan et al. 1986 found a reasonable match between the measured and modeled sulfate plumes. Potential mobility controls for uranium and molybdenum and possible plume configuration with the tailings removed are not discussed.

Some semiconfined aquifer wells were installed in the 1980s, but these wells are considered part of the unconfined or confined system (DOE 1987). This was before a separate distinction of the semiconfined system was identified. As such, no separate discussions or interpretations of the geochemistry in the semiconfined aquifer could be found.

3.2 After Tailings Removal (1990 to 2010)

Remediation standards for tailings removal required radiological analyses for radium-226 to be below 5 picocuries per gram (pCi/g) (plus background) in the top 15 centimeters (cm) of sediment and below 15 pCi/g (plus background) in deeper sediment. Confirmation of meeting these standards is provided in DOE 1991 that indicates background values of 1.9 pCi/g with 1.3 Ci/g as a measurement detection limit. Gridded maps with verification sampling are provided in DOE 1991. In addition to remedial verification, these data provide information on where some residual solid-phase contamination was left in place (below standards, but above background), including thorium-230 contamination at depth with the absence of radium-226 below the water table (area with supplemental standards). Solid-phase analyses for any residual uranium and molybdenum in the FTA were not completed.

DOE 1994 states:
“Surface remediation was completed at the former uranium mill site in Riverton, Wyoming, in 1990. Residual radioactive materials (contaminated soil and debris) were removed and Disposed of at Union Carbide Corporation's (Umetco) nearby Gas Hills Title II facility…. The contaminant plume extends offsite to the south and east…. Fifteen monitor wells installed in 1993 were sampled to better define the contaminant plume and to provide additional water

quality data for the baseline risk assessment…Most of the monitor wells installed during previous field studies were decommissioned during the surface remedial actions at the site."

Contaminant plume maps from 1993 and 1997 along with well numbers and locations are provided in DOE 1994, DOE 1995, and DOE 1998a. Well 0788 was not installed until July 26, 1995 and provides plume definition on the southwest side of the contaminant plumes that is not provided in DOE 1994 and DOE 1995; thus, the 1997 plume maps from DOE 1998a are reproduced here. For the surficial aquifer, this includes uranium (Figure 16), molybdenum (Figure 17), and sulfate (Figure 18), plus sulfate for the semiconfined aquifer (Figure 19). Note that data from 1995 have been added for well 0732 on Figure 19, but the contouring was not changed from the original figures in DOE 1998a. It is unclear why the contouring for uranium and molybdenum is so tightly spaced compared to sulfate on the northeast side of the plume. This is an area with limited well coverage.

A variety of contaminants originating from the Site are identified in DOE 1995 as occurring in the surficial aquifer, but this list is narrowed down to manganese, molybdenum, sulfate, and uranium based on only these elements exceeding guidelines (DOE 1998b). However, a distinct manganese plume emanating from the tailings impoundment was not identified. DOE 1995 also recognizes the semiconfined aquifer as being affected by sulfate from the uranium milling processes (the only other contaminant detection was molybdenum at the 0.1 mg/L standard in 1995 in well 0732, and all subsequent samples have been below that value). Compared to the time before the tailings were moved (Section 3.1 and Figure 9), the uranium and sulfate plumes in the surficial aquifer are quite similar, but the molybdenum plume in 1997 has higher concentrations near the Little Wind River, comparatively. No contamination was detected in the confined aquifer (DOE 1998a).

Sediment samples were collected in 1993 (for iron, lead, manganese, molybdenum, and uranium) and 1995 (prior list plus constituents arsenic, copper, nickel, vanadium, and zinc) at various surface water sampling locations (DOE 1995; DOE 1998a) with the goal of comparing downgradient sediments with background to test the possibility of contaminants accumulating in areas of groundwater discharge. In DOE 1995, the baseline risk assessment (BLRA) indicates that the results were inconclusive. DOE 1998a (i.e., the final site observational work plan) added additional analytes and more sample locations, and it included vegetation sampling. Some elements in sediment and vegetation did exceed benchmark standards, which helped identify locations for continued sampling (Table 5-1 in DOE 1998a). From a geochemical CSM standpoint, the most significant finding is elevated uranium and molybdenum (location 744, Table 4-9) (DOE 1998a just outside of the northeast edge of the FTA, in Plate 1) at 28 milligrams per kilogram (mg/kg) and 11 mg/kg compared to background concentrations of 1.1 mg/kg and <1 mg/kg, respectively. No solid phase samples were taken within the FTA.

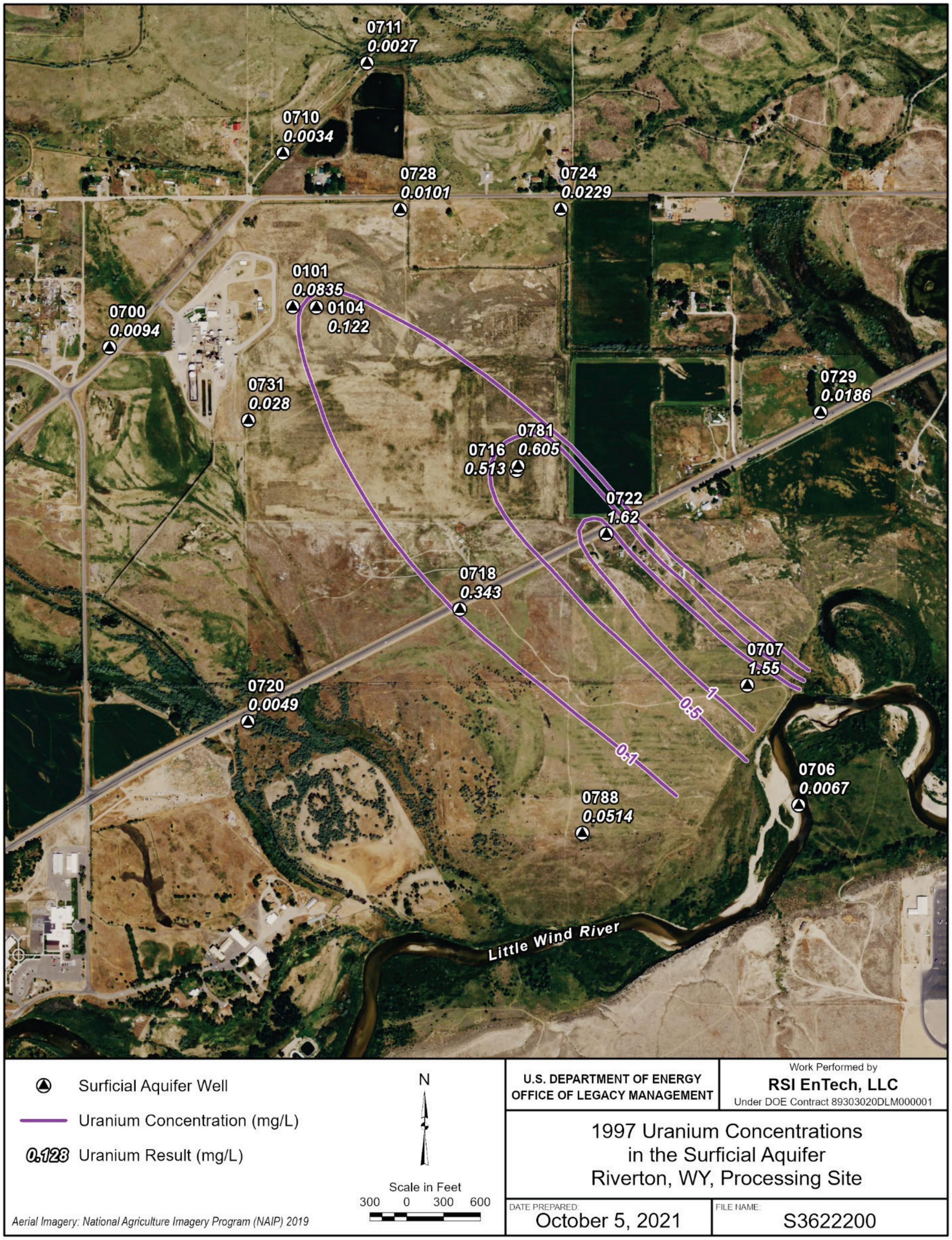


Figure 16. Uranium Concentrations in the Surficial Aquifer in 1997 (after DOE 1998a)

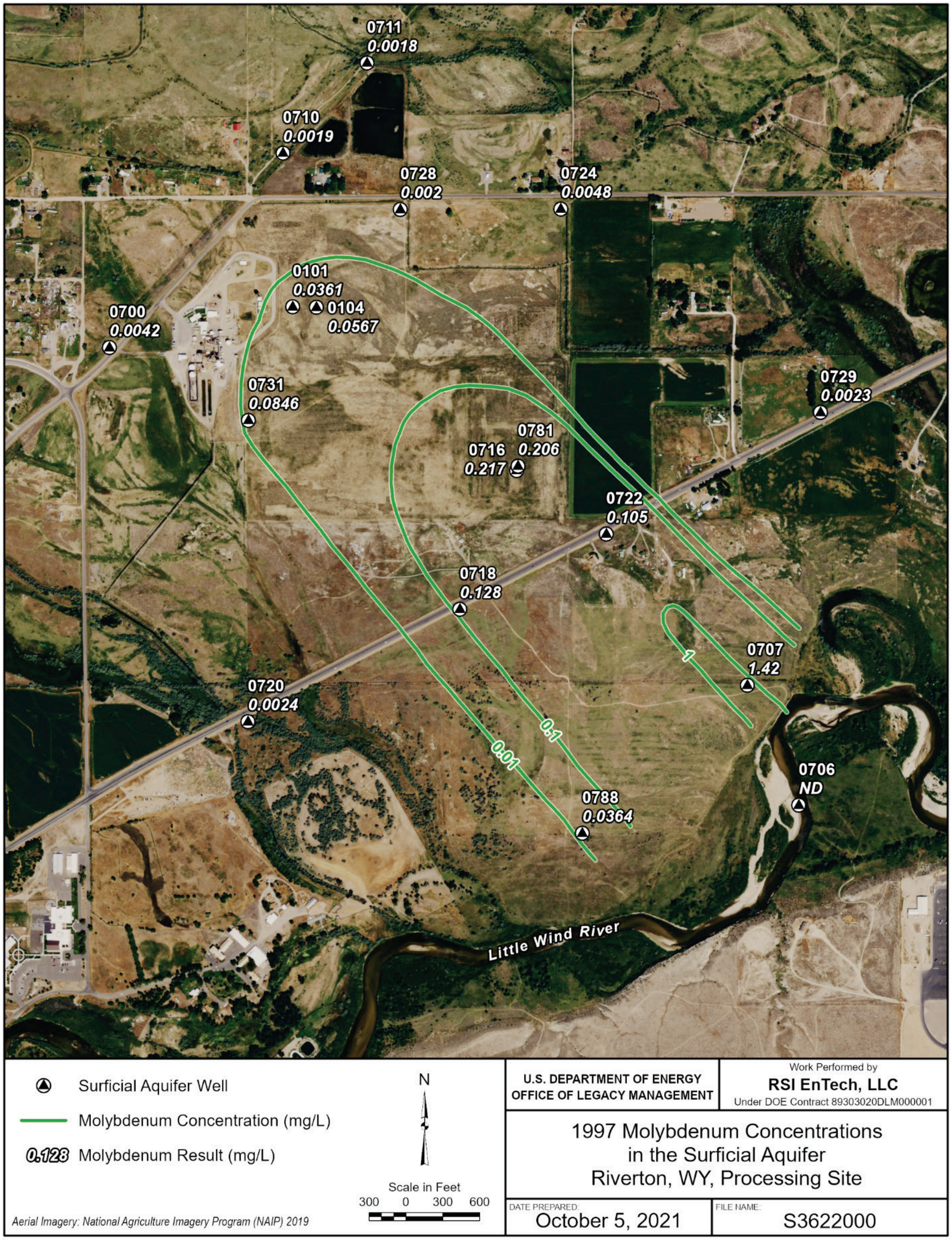


Figure 17. Molybdenum Concentrations in the Surficial Aquifer in 1997 (after DOE 1998a)

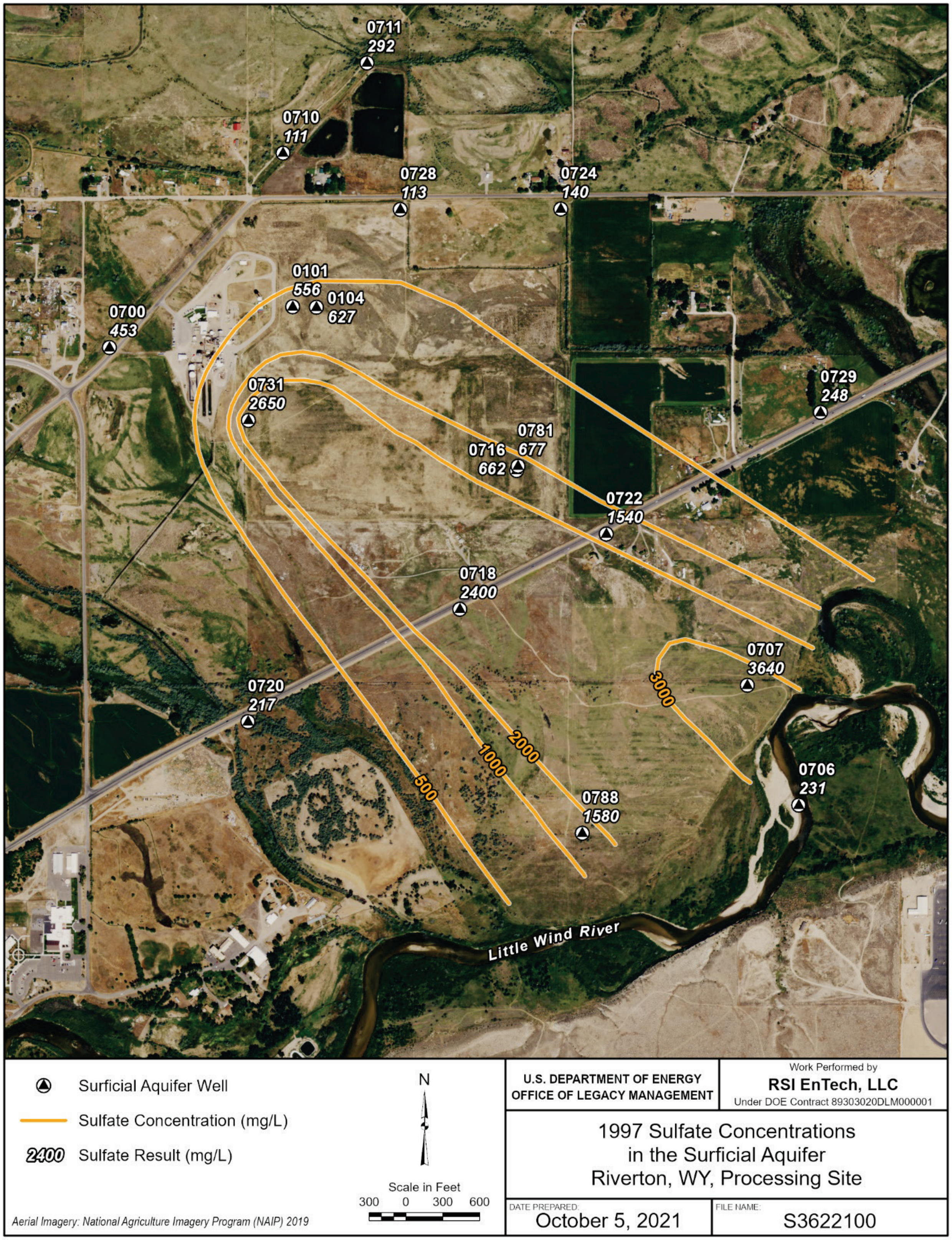


Figure 18. Sulfate Concentrations in the Surficial Aquifer in 1997 (after DOE 1998a)

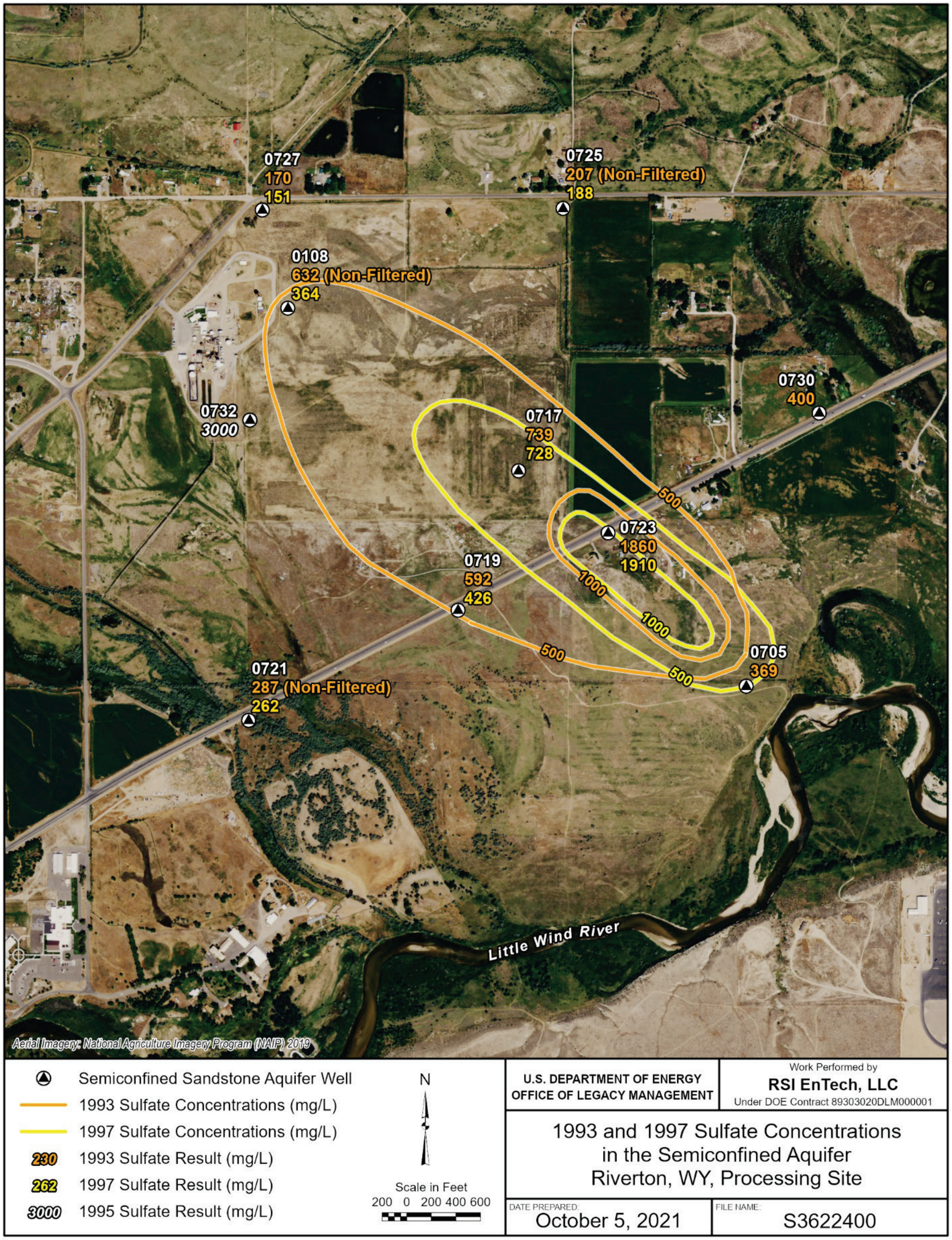


Figure 19. Sulfate Concentrations in the Semiconfined Aquifer in 1993 and 1997 (after DOE 1998a). Note the addition of well 0732 with sulfate data from July 18, 1995, at 3000 mg/L (data from EQuIS database) that likely indicates a sulfate source from the sulfuric acid plant. Contouring from DOE 1998a has not been changed.

Highlight Box 4: Summary of previous CSM (After Tailings Removal but Before 2010)

Tailings, as a primary source of contamination, have been removed with no ongoing inputs into the groundwater.

Highest contaminant concentrations have moved toward the Little Wind River in the direction of groundwater flow.

Uranium and molybdenum will continue to naturally flush to the Little Wind River until groundwater concentrations are below standards within 100 years.

For the surficial aquifer, the Site CSM provided in DOE 1998a is "Contaminants present in the surficial aquifer are moving with the ground water downgradient from the processing site to the Little Wind River. Since uranium ore processing was begun in 1958, groundwater movement has transported the centroid of ground water contamination southeast to the vicinity of monitor well 707, located approximately 3000 ft (900 m) from the tailings pile area." In addition, DOE 1998a indicates that "Contaminant concentrations in the plume are influenced by the dispersive effects of dilution and by chemical reactions such as oxidation/reduction, sorption onto the aquifer matrix, coprecipitation with other mineral phases, microbial reactions, and advective transport of ground water. With distance from the source, dispersive effects will decrease the concentration of all contaminants in the plume." These geochemical reactions were evaluated with geochemical modeling and used to conceptually describe the fate and transport of individual contaminants (DOE 1998a). Quantitative prediction of future contaminant transport was only done for uranium and molybdenum using the computer code GANDT (Knowlton et al. 1997). The Riverton GANDT model included an unsaturated zone source term (former tailings) that lasted for 10 to 15 years from 1958 (timing range that matched contaminant plumes in 1997), after which no ongoing contaminant sources were considered (DOE 1998a). In the saturated zone, contaminant transport processes included advection, dispersion, and retardation using a sorption distribution coefficient. A key feature of the GANDT model was a probabilistic framework (i.e., Monte Carlo approach) to account for uncertainty in hydraulic conductivities for contaminant movement and fate. The final results predicted uranium and molybdenum concentrations reaching background levels before 2097 (within 100 years from 1997) (DOE 1998a).

Based on these GANDT model results, the proposed compliance strategy for the Site was 100-year natural flushing (DOE 1998a). This strategy is reiterated in DOE 1998b with details on continued surface water, groundwater (surficial and semiconfined aquifers), sediment, and vegetation sampling for uranium, molybdenum, manganese, and sulfate with the following caveat "when the remediation goals are met for manganese, molybdenum, and uranium, it will be assumed that millsite-related sulfate has flushed through the surficial aquifer as well." It was recognized during the GANDT modeling that continued sulfate release to the surficial aquifer from the Plant was likely (DOE 1998a, Appendix D). The 100-year natural flushing with compliance monitoring for uranium and molybdenum is officially proposed in the final Riverton GCAP (DOE 1998c) and accepted by NRC (NRC 1999); it was considered supported by the following: (1) 15 years of water quality data, (2) probabilistic flow and solute transport modeling, (3) enforceable institutional controls, and (4) a compliance monitoring framework to ensure that contaminant concentrations decrease as predicted (DOE 1998c).

To summarize, the 1998 Site, CSM considers (1) the mill tailings as being the primary source of contaminants, (2) the primary source has been removed with any residual sources not being considered, (3) the highest groundwater contaminant concentrations that were under the former tailings are now near the Little Wind River, and (4) contaminant concentrations across the Site will continue to decline as the contaminants remain relatively mobile and are discharged to the Little Wind River. The 1998 CSM does not change until 2010. The only additional documentation before 2010 is a revised monitoring plan (DOE 2009).

Consistent with the 1998 CSM, natural flushing of uranium and molybdenum at well 0707 near the Little Wind River (Figure 16 and Figure 17) was relatively consistent with the GANDT modeling predictions through 2009 (Figure 20), as reported in the 2009 Verification Monitoring Report (DOE 2010) (VMR). However, duration of natural flushing for uranium at wells 0707 and 0718, based on trend data, was calculated to be 160 years (Figure 21). No action was taken at that time based on the following statement: “Although 160 years is longer than the 100-year regulatory limit and 19 years may underestimate flushing time, estimates will likely change as more data are collected” (DOE 2010).

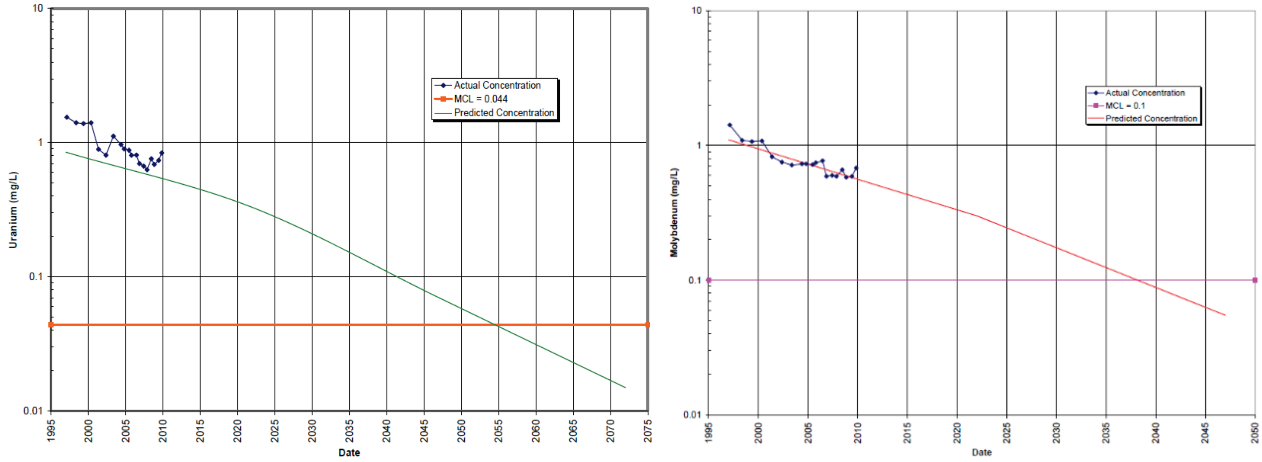


Figure 20. Uranium and Molybdenum Concentrations in Well 707, Actual Versus Predicted (from DOE 2010)

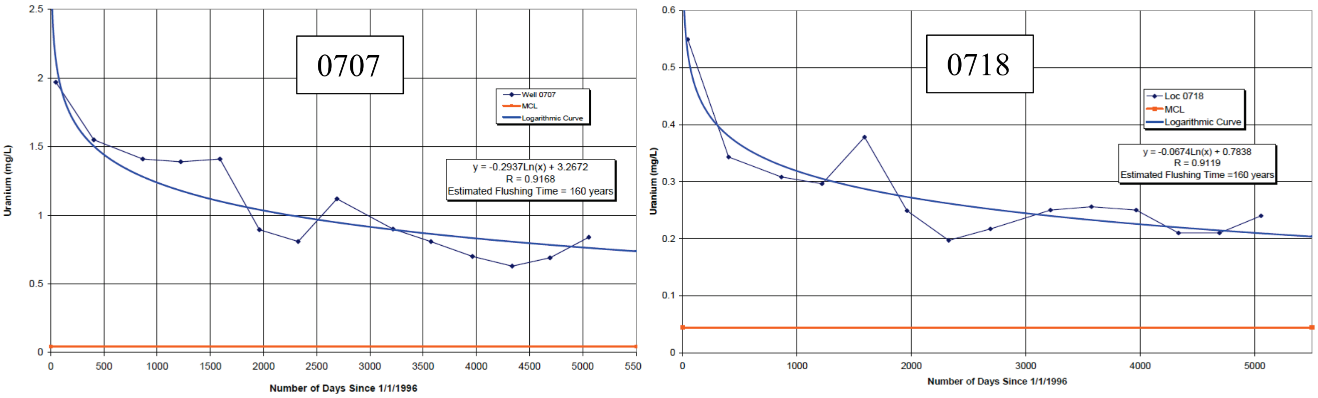


Figure 21. Estimated flushing time for uranium in well 0707 and 0718 based on measured data. Note that 0 days is equivalent to January 1,1996, and 5000 days is equivalent to January 1, 2009 (from DOE 2010).

3.3 Post-2010 Flood Event Through 2020

The second largest Little Wind River streamflow and flooding event in recorded history happened on June 9, 2010. The largest flooding event occurred June 17, 1963, at the end of the uranium milling operation when environmental sampling was not occurring. The 2010 flooding event surrounded wells 0707 and 0789 with floodwaters. These wells then experienced significant spikes in uranium and molybdenum concentrations just after the flood event (Figure 22). Wells that were not flooded (0716, 0718 and 0722/0722R) did not experience concentration spikes (Figure 22).

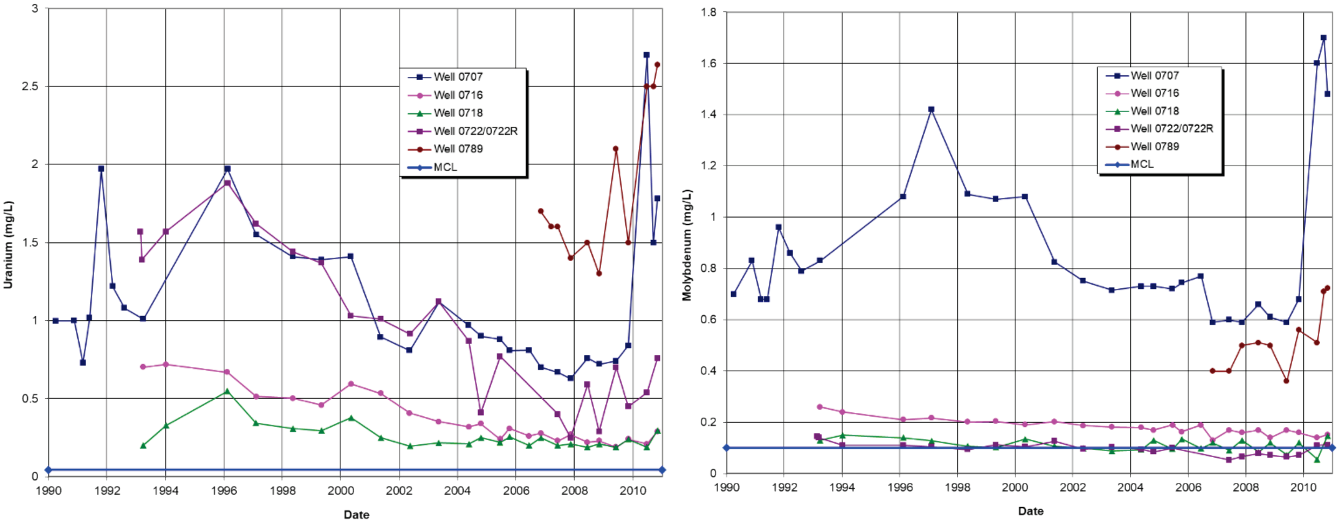


Figure 22. Groundwater Uranium and Molybdenum Concentrations Through Time at Selected Wells (from DOE 2011)

The 2010 flooding event indicated that the conceptual model of continued natural flushing was not accurate. This led to additional work that is summarized in DOE 2013 and DOE 2016. This work included (1) Site sediment sampling, (2) higher resolution sampling of the contaminant plumes, and (3) an updated contaminant transport model. To briefly summarize the results, DOE 2013 and DOE 2016 identified: (1) elevated solid-phase uranium and molybdenum concentrations in the saturated zone at the FTA and in the unsaturated zone near the Little Wind River, (2) ongoing Site-related groundwater contamination below the FTA and near the Little Wind River from these secondary sources, and (3) that uranium concentrations may remain above standards after the 100-year natural flushing period when river flooding events are included in updated transport modeling. In addition, DOE 2014 identified evaporite deposits above the uranium plume near the Little Wind River that had elevated solid-phase uranium concentrations. These results were summarized as part of an updated CSM in Dam et al. 2015 that highlighted the previously unidentified secondary contaminant sources.

Additional work reported in DOE 2019 tracked uranium, molybdenum, and sulfate concentrations in multilevel wells near the Little Wind River on a near monthly basis for 3 years (2016 through 2018). This sampling confirmed concentrations spikes of all three constituents after flooding and large recharge events. In fact, during the 3-year sampling period, the third, fourth, and fifth largest Little Wind River discharge events occurred February 10, 2017, May 8, 2016, and June 9, 2017, respectively. The 2017 events were created by flooding due to an ice jam (February 10, 2017) and a large mountain snowmelt runoff (June 9, 2017) and the 2016 event was a large early spring rain (May 8, 2016). The 2010 and 2016–2017 flooding events, along with other high Little Wind River stage events correlate with higher uranium and molybdenum concentrations in well 0707 (Figure 23). Well 0707 is collocated with well 0858 (Figure 2). Well 0858 was sampled monthly for 3 years, whereas well 0707 is currently sampled annually (but has a longer period of record, Figure 23).

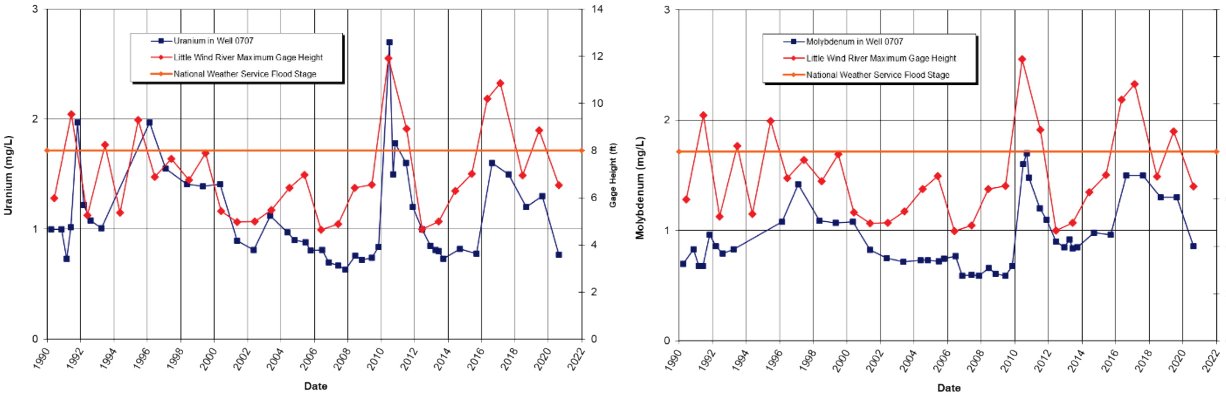


Figure 23. Groundwater Uranium and Molybdenum Concentrations in Well 0707 Through Time Compared to Little Wind River Gage Heights (from DOE 2021a)

Overland flooding in 2016 and 2017 stopped between wells 0856 and 0857 (Figure 2) and flooding conditions have not been observed at well 0857. Uranium and molybdenum concentrations in wells outside of the river flooding zone (wells 0716 and 0718, see Figure 2) do not see the same concentration spikes with the 2010 flooding event (Figure 24 and Figure 25), though well 0716 does show a uranium increase in 2011 (Figure 24). In addition, well 0718 shows an increase in sulfate late in 2010 (Figure 26). The largest influence in these wells is likely due to the large rain event in 2016 with subsequent dissolution of contaminants in the upgradient unsaturated zone. This created delayed uranium and sulfate spikes in both wells and a molybdenum spike only in well 0718 (Figure 24, Figure 25, and Figure 26). These data suggest the presence of uranium, molybdenum, and sulfate in the unsaturated zone upgradient of well 0718 and the presence of uranium and sulfate in the unsaturated zone upgradient of well 0716.

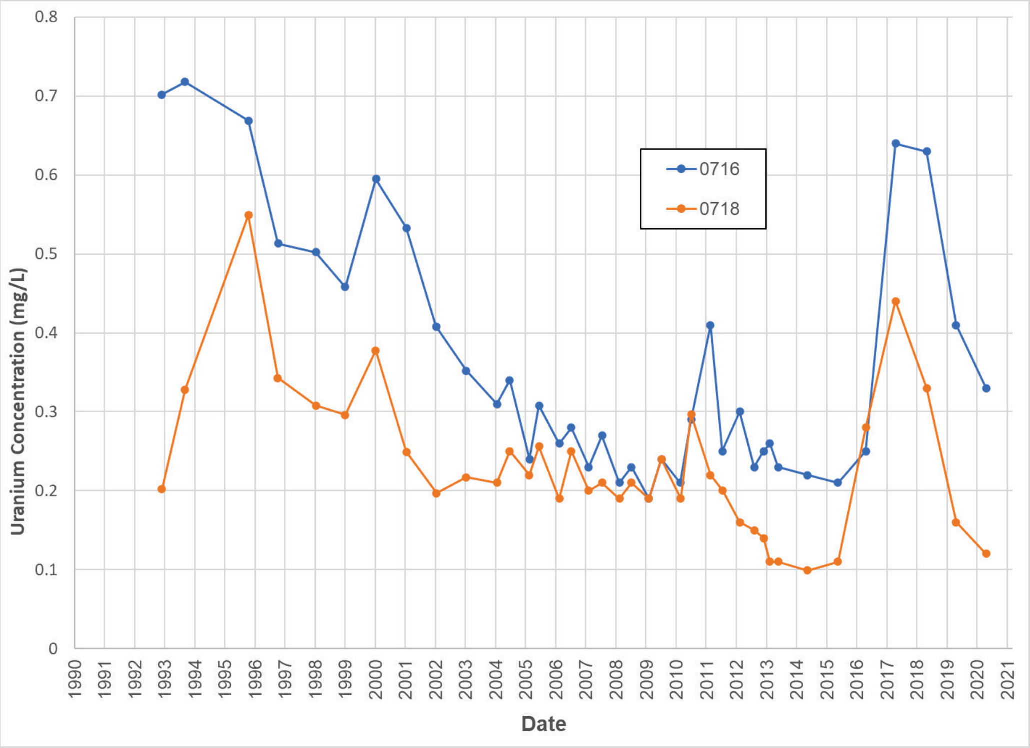


Figure 24. Groundwater Uranium Concentrations in Wells 0716 and 0718 Through Time

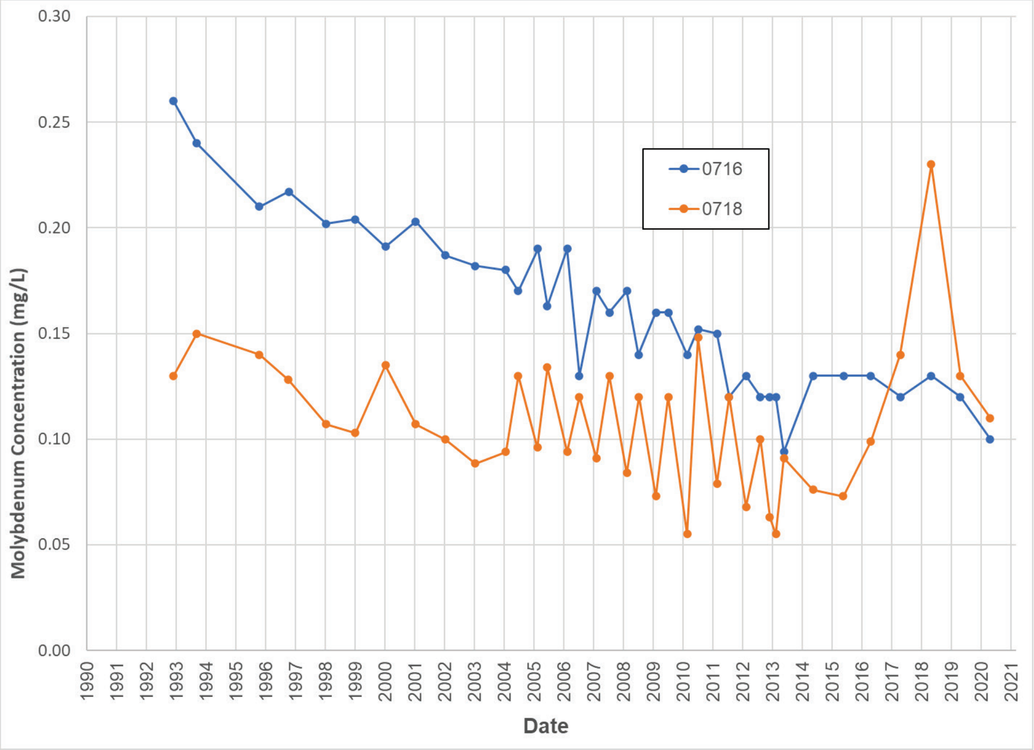


Figure 25. Groundwater Molybdenum Concentrations in Wells 0716 and 0718 Through Time

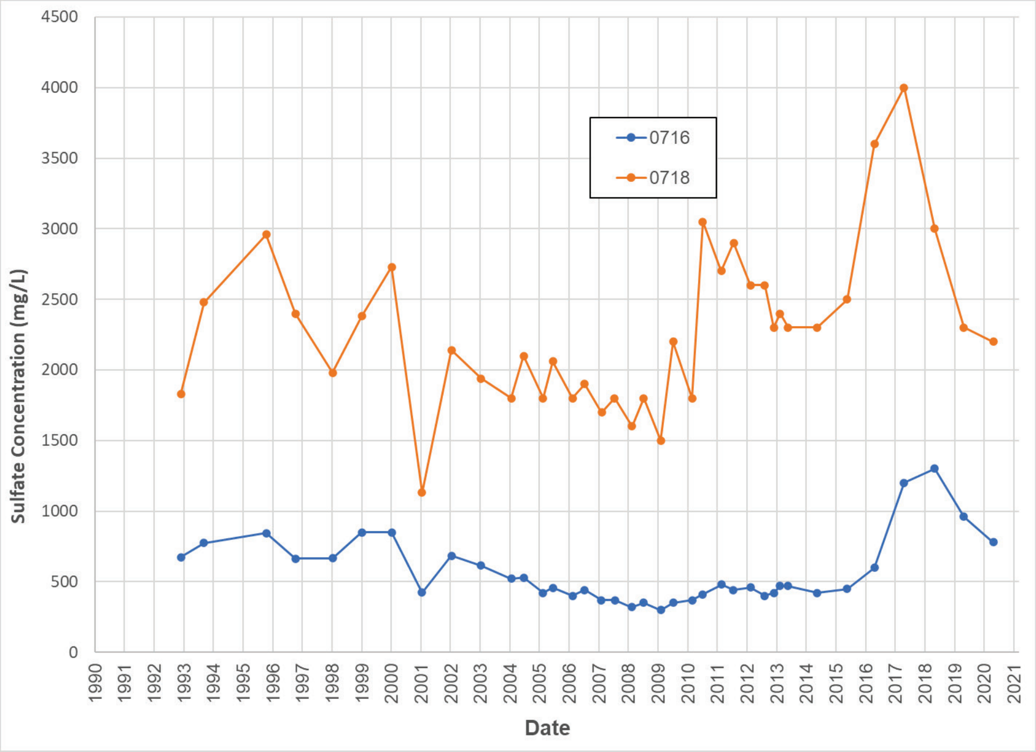


Figure 26. Groundwater Sulfate Concentrations in Wells 0716 and 0718 Through Time

Highlight Box 5: Summary of updated CSM (After 2010)

Residual contamination (uranium, molybdenum, and sulfate) exists in the following compartments:

1) **Unsaturated zone over the contaminant plumes at the SSMA near the Little Wind River (have solid phase confirmation). Contaminants are released during flooding events to the underlying groundwater.**
2) **Saturated zone at the FTA (have solid phase confirmation). Contaminants are released continuously, albeit in localized areas.**
3) **Unsaturated zone at the FTA (indirect evidence via groundwater concentrations). Contaminants are released to the underlying groundwater in certain areas only with large recharge events.**

Loss of water from the Plant retention ponds likely contributes to ongoing sulfate plumes in the surficial and semiconfined aquifers.

Contaminant plumes in 2020 for uranium, molybdenum, and sulfate in the surficial aquifer are provided in Figure 27, Figure 28, and Figure 29, respectively. The 2020 sulfate plume in the semiconfined acquired is provided in Figure 30. Compared to contaminant plumes from past years, the general configuration of all these plumes is not much different. This confirms the overall CSM of the groundwater flow direction from northwest to southeast in both the surficial and semiconfined aquifers and confirms a continuing source of contaminants to the groundwater from the former tailings and mill-site area in both aquifers and from sediments near the Little Wind River in the surficial aquifer. The semiconfined aquifer continues to have uranium and molybdenum concentrations that are below standards (0.044 and 0.01 mg/L respectively, see data in DOE 2021a). It is notable that there is a stronger downward gradient from surficial aquifer well 0784 to semiconfined aquifer well 0732 compared to other well pairs (DOE 2020a). In addition, well 0784 has high sulfate concentrations (2000 mg/L in 2020) yet low uranium (0.0028 mg/L in 2020) and molybdenum (0.034 mg/L in 2020) concentrations at the start of the sulfate plume in the surficial aquifers (Figure 29). It is possible that the groundwater with higher sulfate concentrations and less uranium and molybdenum in well 0784 in the surficial aquifer (Figure 29) and well 0732 in the semiconfined aquifer (Figure 30) are due to water loss from the retention ponds related to the Plant. This corresponds with similar concentrations of sulfate, uranium, and molybdenum at well 0749 in the Plant outfall ditch (DOE 2021a). Contaminant concentrations in the retention ponds or in the groundwater between the FTA and the retention ponds (upgradient of wells 0784 and 0732) have not been measured.

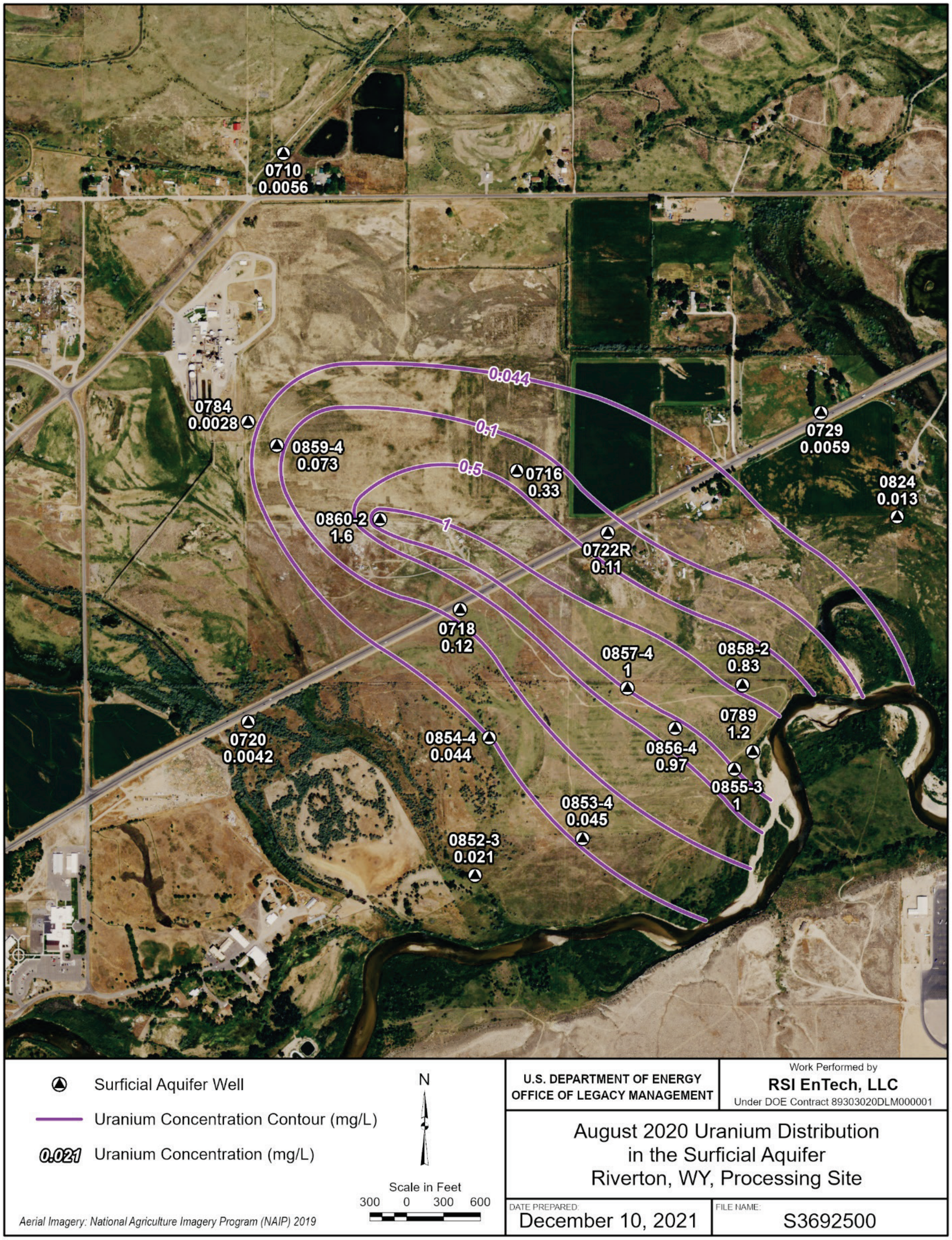


Figure 27. August 2020 Groundwater Uranium Concentrations in the Surficial Aquifer (after DOE 2021a)

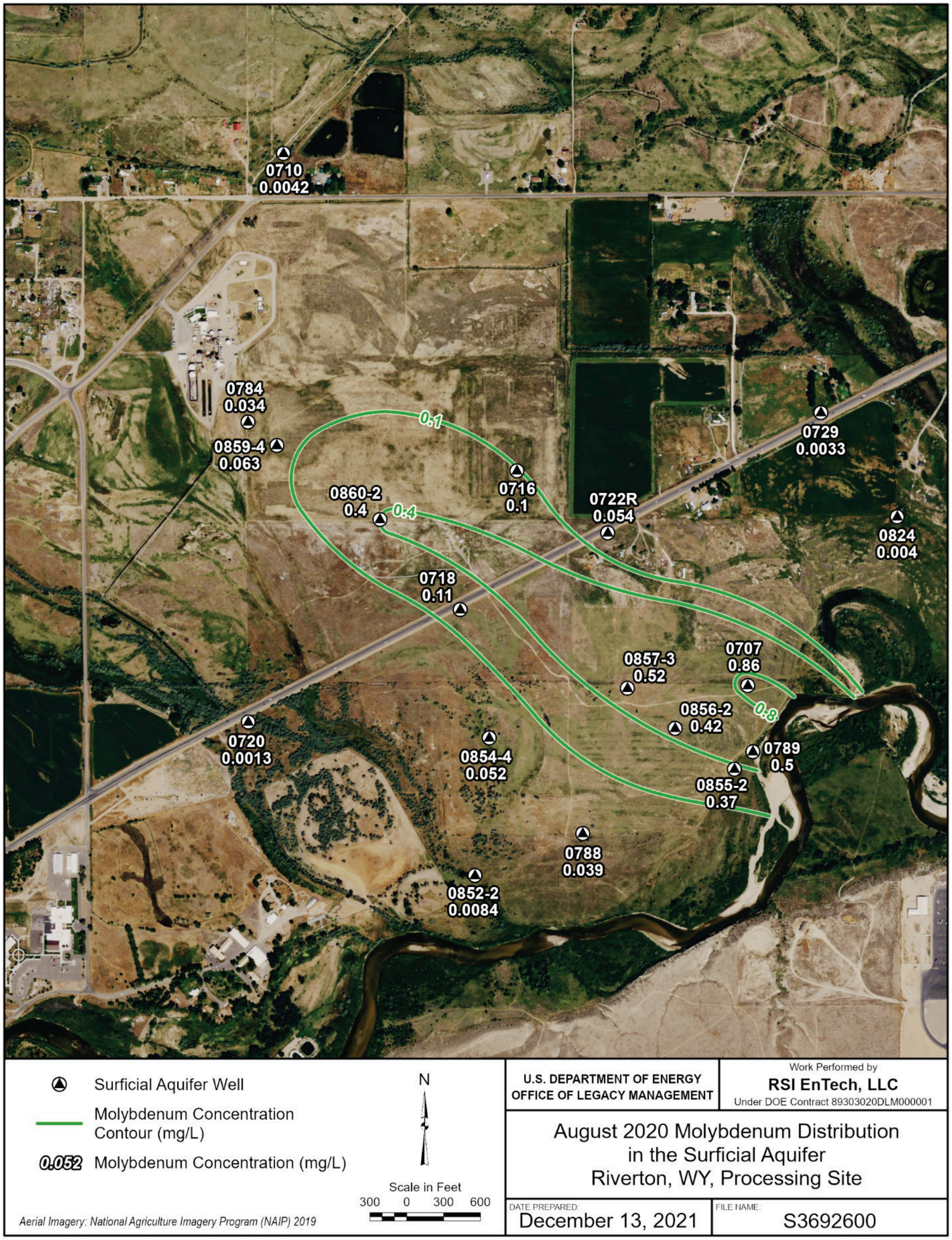


Figure 28. August 2020 Groundwater Molybdenum Concentrations in the Surficial Aquifer (after DOE 2021a)

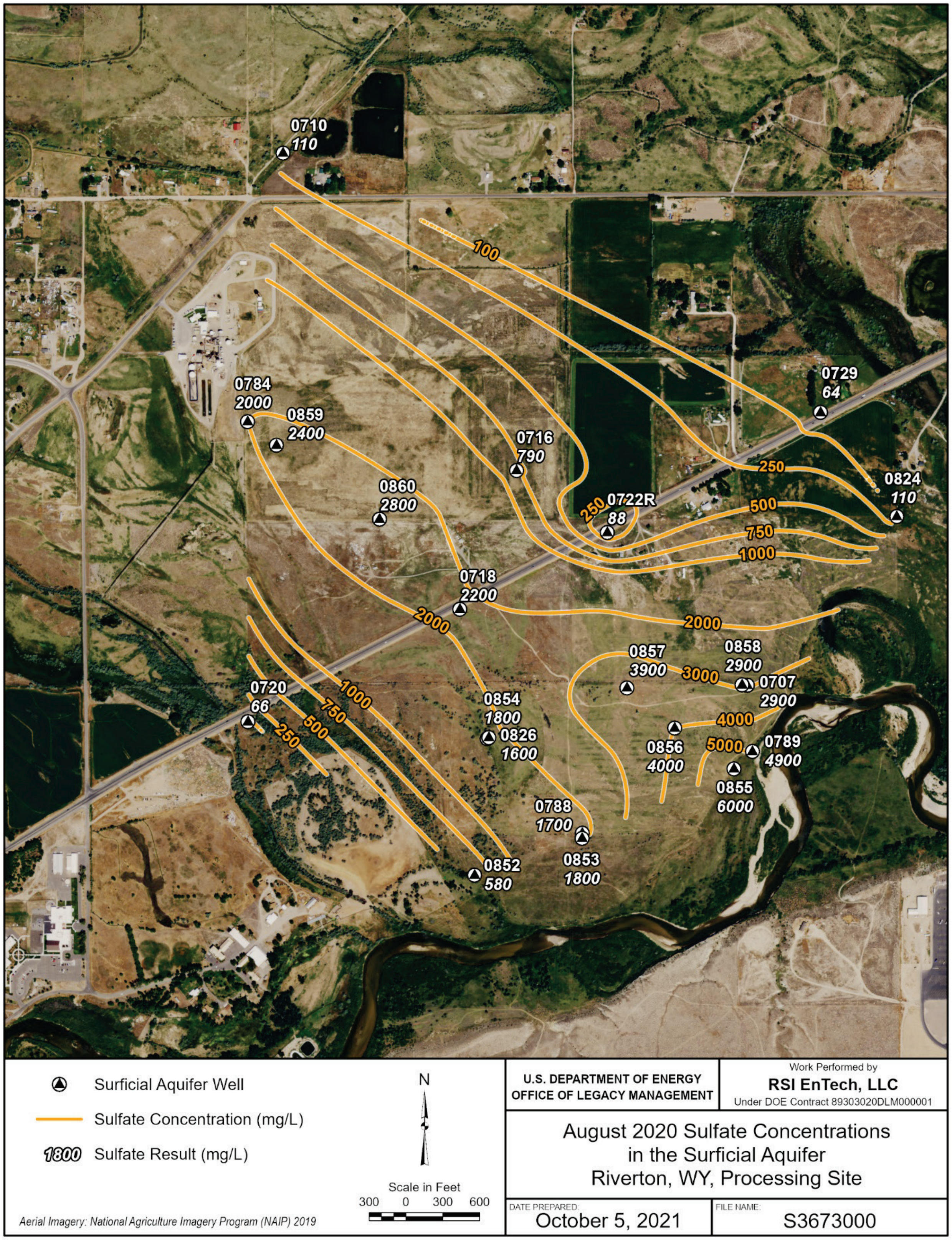


Figure 29. August 2020 Groundwater Sulfate Concentrations in the Surficial Aquifer

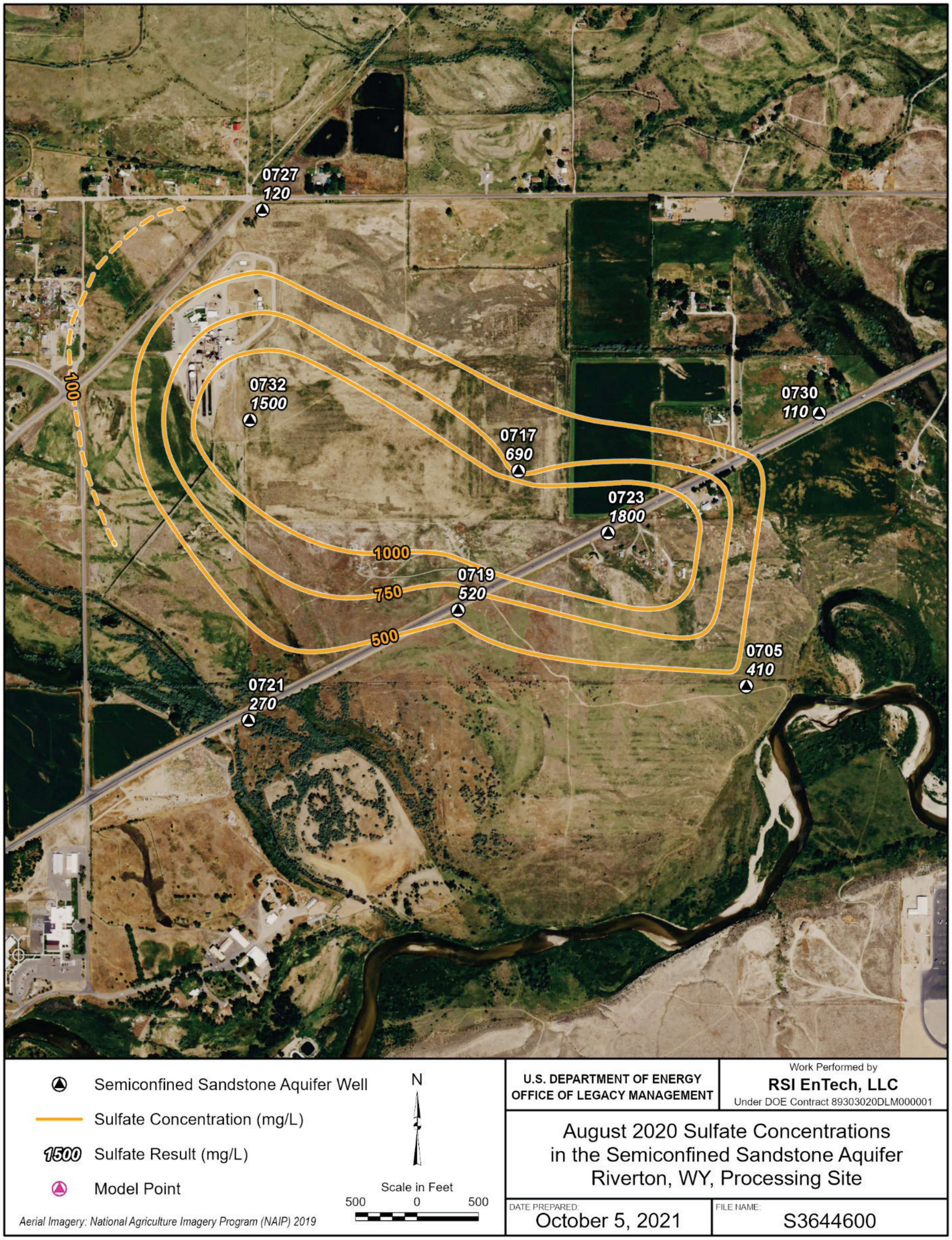


Figure 30. August 2020 Groundwater Sulfate Concentrations in the Semiconfined Aquifer

3.4 Natural Flushing Through Time

Contaminant plume concentration data are compared by overlaying low and high concentration contours from the 1983, 1997, and 2020 plumes for uranium, molybdenum, and sulfate (Figure 31 through 36). Additional data from temporary well point transects in 2012 and 2015 are also used (Figure 37, 38, and 39). The area near the Little Wind River that experiences flooding is referred to as the Saint Stephen's Mission Area (SSMA) on the figures mentioned below. The results are summarized as follows:

- **Figure 31:** 0.1 mg/L uranium plume: Overall this plume is similar through time with possible natural flushing at the head of the plume in the former ore storage area. The 0.1 mg/L head of the plume in 1983 was defined by piezometer P14 with a concentration of 0.4 mg/L (Figure 6 and Figure 11) and well 0104 in 1997 with a concentration of 0.12 mg/L (Figure 16). Well 0104 and nearby well 0101 (Figure 16) in the former ore storage area were not sampled again after 1998 (well 0101 exists, but well 0104 was abandoned). In addition, temporary well point T02-09 just downgradient from well 0101 had a uranium concentration of 0.12 mg/L uranium in 2012 (Figure 37 and Figure 38). Thus, current data on natural flushing in the former ore storage area after 2012 is unknown, and the contouring in 2020 (Figure 27) does not reach that area, likely due to a lack of data. In addition, most of the eastern FTA is contoured above 0.2 mg/L uranium in DOE 2016 based on data collected in 2012 with the highest uranium concentration being 0.27 mg/L in temporary well point T03-14 (Figure 37 and Figure 38). Thus, natural flushing may be occurring in the areas just north and west of well 0716 (Figure 27), but there is no well control in that area. Also, the western edge of the 0.1 mg/L uranium contour in the south-central FTA moves significantly to the east in 1997; this is probably due to a lack of well control in that area in 1997.
- **Figure 32:** 1 mg/L uranium plume: natural flushing is occurring in the south-east FTA with concentrations <1 mg/L after 1997 as the head of the 1 mg/L uranium plume moved downgradient near the road. Uranium concentrations above 1 mg/L in the south-east FTA are well characterized by data from 1983 (Figure 11 and Figure 38). Continued declines in uranium concentrations in the south-east FTA were measured in well 0716 (Figure 27) until uranium concentration spikes occurred in 2017 and 2018 after the wet years of 2016 and 2017 (DOE 2019). After 1997, the head of the 1 mg/L uranium plume shifted to the south-central FTA that is currently measured by well 0860 (Figure 27). This well was installed in 2015 after data from temporary well point T03-08 had a uranium concentration of 1.1 mg/L in 2012 (Figure 37 and Figure 38). Uranium concentrations greater than 1 mg/L likely existed in this area before 2012 but were not detected due to the prior well configurations. In 1997, there were no wells in the south-central FTA (Figure 16). In 1983, piezometers P13, P17, and P20 had uranium concentrations of 0.36, 0.64, and 0.40 mg/L, respectively (Figure 37 and Figure 38), none of which were located exactly at well 0860 (collocated with T03-08) but did surround it (Figure 37 and Figure 38). As such, an ongoing uranium source likely exists near well 0860 that was not detected by any prior well configurations. Elevated solid-phase uranium concentrations were detected from core samples collected when well 0860 was installed (DOE 2016). Uranium concentrations in the multilevel ports of well 0860 have not shown spikes in uranium after 2017 like well 0716 did. The top port (0860-2) has shown some increase in uranium concentrations after it was installed, whereas the deeper ports 0860-3 and 0860-4 have shown relatively stable uranium

concentrations near 0.8 to 1.0 mg/L (Appendix A). Thus, upgradient sources of solid-phase uranium in the saturated zone is likely, and unsaturated zone sources are possible.

- **Figure 33:** 0.1 mg/L molybdenum plume: This plume reached the river sometime between 1983 and 1997 (based on piezometer points P30 and P32 [Figure 6 and Figure 11] and well 0707 in 1997 [Figure 17]). Thus, the 0.1 mg/L molybdenum plume appears to have a slower velocity than the 0.1 mg/L uranium plume. The head of the 0.1 mg/L molybdenum plume was in the former ore storage area in 1983 and 1987. This plume has similar well control issues in the former ore storage area as the 0.1 mg/L uranium plume discussed above, but wells 0101 and 0104 were both below 0.1 mg/L molybdenum in 1997 (Figure 17). Temporary well point T02-09 just downgradient from well 0101 had a molybdenum concentration of 0.09 mg/L in 2012 (Figure 37 and Figure 38). Thus, natural flushing in the former ore storage area appears to be likely, but continued progress is unknown with the abandonment of well 0104 and discontinued sampling of well 0101.
- **Figure 34:** Overall, molybdenum concentrations are less than uranium concentrations, so a 0.5 mg/L molybdenum plume comparison is more appropriate for higher molybdenum concentration contouring. The 0.5 mg/L molybdenum contour is limited to the SSMA, as the results appear to show significant natural flushing of molybdenum in the FTA. However, data from temporary well points completed in 2012 and 2015 show a very narrow molybdenum plume starting at point T03-09 with concentrations of 0.94 and 0.98 mg/L, respectively (Figure 37 and Figure 39). DOE 2016 shows a molybdenum contour of 0.8 mg/L detected by a series of temporary well points that does not encompass any existing monitoring wells (see Figure 23 in DOE 2016). T03-09 is the next point north and east of T03-08 (and well 0860) with the highest molybdenum concentration in the south-central FTA and is in between piezometers P20 and P17 (Figure 6) with measured molybdenum concentrations of 3.7 and 0.9 mg/L, respectively, in 1983 (Figure 37 and Figure 39).
- **Figure 35:** 500 mg/L sulfate plume: This plume does not show much change from 1983 to 2020 and is likely due to the dispersed nature of sulfate from the FTA and the Plant. The large curve, near the south-east FTA, in the 500 mg/L contour in 2020 occurs around well 0722R (Figure 29), which may have experience enhanced natural flushing due to irrigation in the field just to the north of this well.

Highlight Box 6: Summary of Natural Flushing Based on Plume Mapping

Former Ore Storage Area: Past start of the uranium and molybdenum plumes may be experiencing natural flushing, but unclear without more recent sampling.

South-east FTA: Natural flushing in the saturated zone is progressing for uranium, molybdenum, and sulfate. Possible unsaturated zone source for uranium and sulfate based on concentration spikes after wet years (see Section 3.3)

South-central FTA: Natural flushing is limited with ongoing uranium, molybdenum, and sulfate sources in the saturated zone. U and Mo plumes are slightly offset. Additional unsaturated zone source(s) cannot be ruled out.

SSMA: Limited natural flushing, with ongoing sources of uranium, molybdenum, and sulfate in the unsaturated zone.

Semiconfined aquifer: Limited natural flushing overall, but possible flushing at the head of the plume at well 0732.

- **Figure 36:** 3000 mg/L sulfate plume: This plume also does not show much change from 1983 to 2020, which is likely due to a continued contribution of sulfate from the unsaturated zone in the SSMA after flooding or other large recharge events. In 2009, sulfate in well 0707 had flushed to 1900 mg/L (Appendix A) after an extended period of no flooding before the flooding event in 2010, which increases sulfate in well 0707 to 7000 mg/L on June 24, 2010.

For the semiconfined aquifer, the sulfate plume from the 1990s to 2020 is relatively similar. The biggest difference is a decline in sulfate at well 0732 from 3000 mg/L in 1995 (Figure 15) to 1500 mg/L in 2020 (Figure 30). This may be due to a continued decline in sulfate releases from the Plant (DOE 2021a).

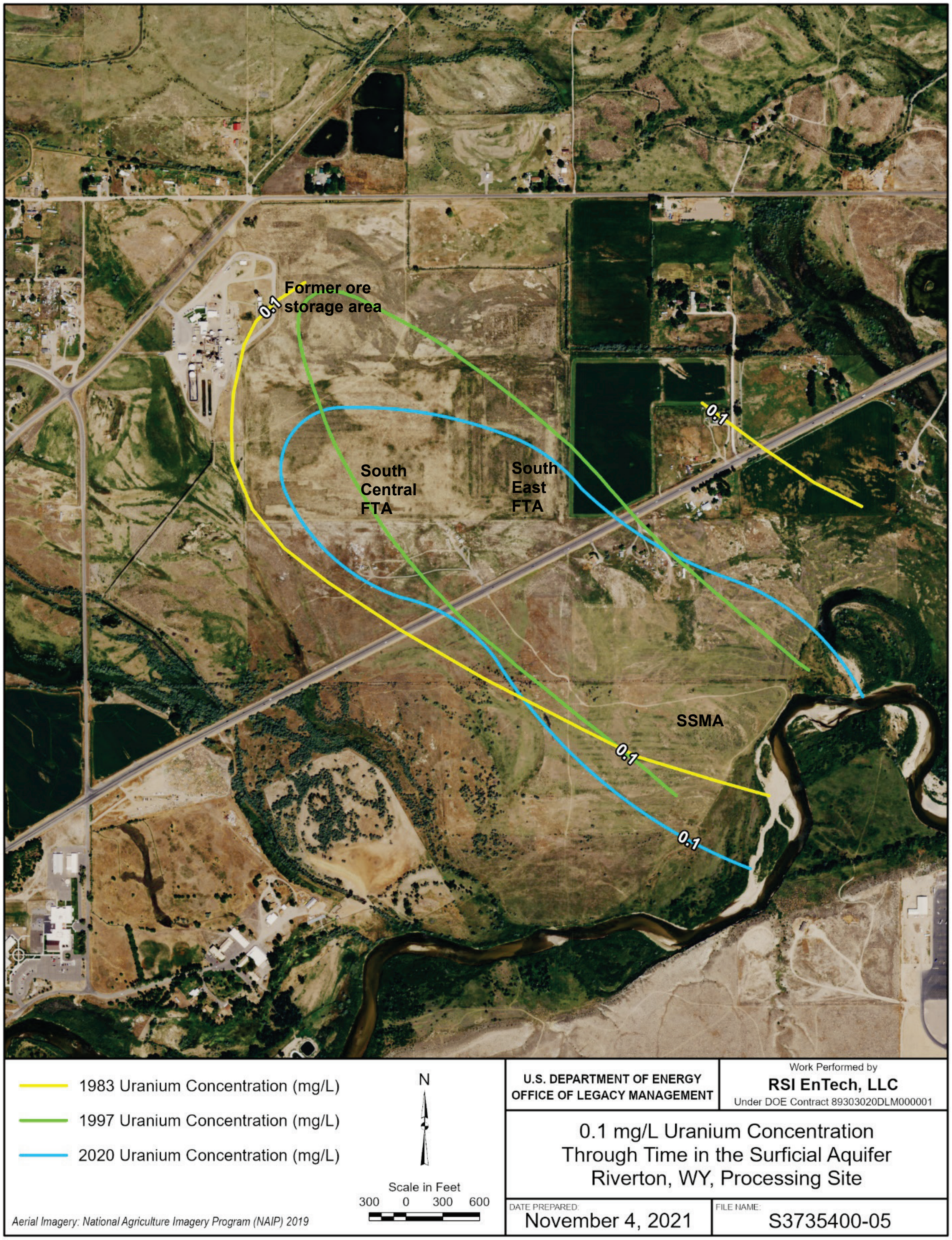


Figure 31. 0.1 mg/L Uranium Concentration Contours in the Surficial Aquifer Through Time

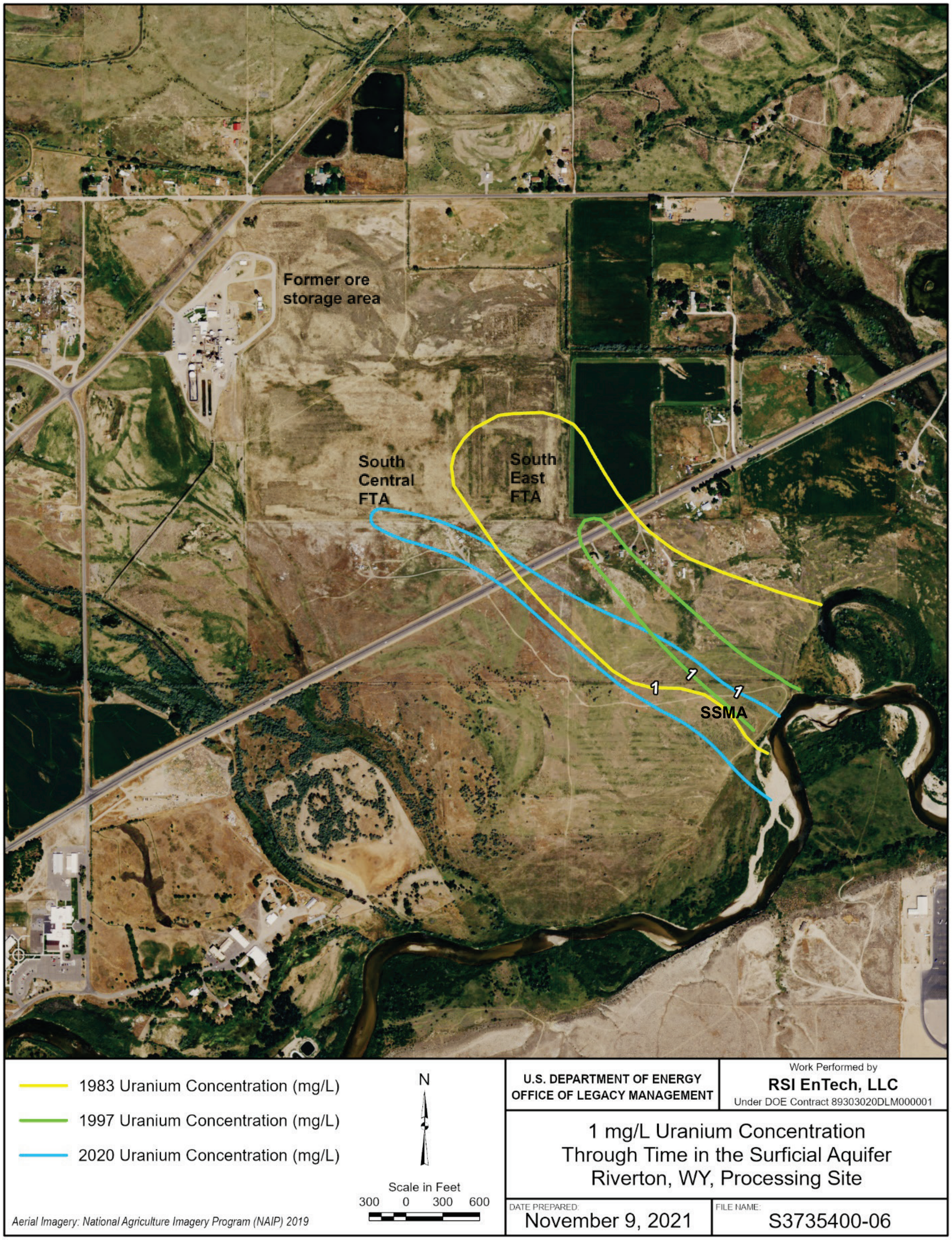


Figure 32. 1 mg/L Uranium Concentration Contours in the Surficial Aquifer Through Time

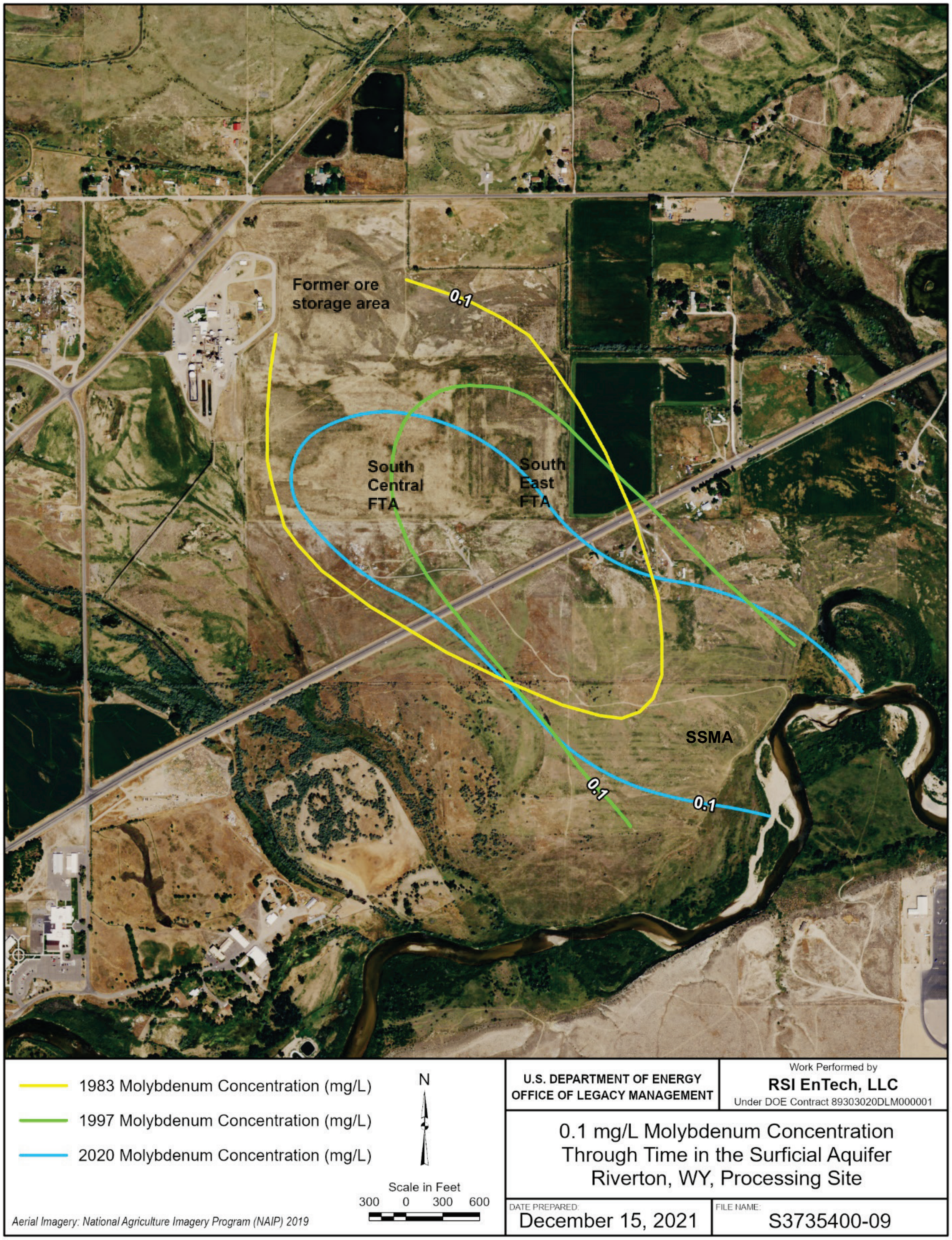


Figure 33. 0.1 mg/L Molybdenum Concentration Contours in the Surficial Aquifer Through Time

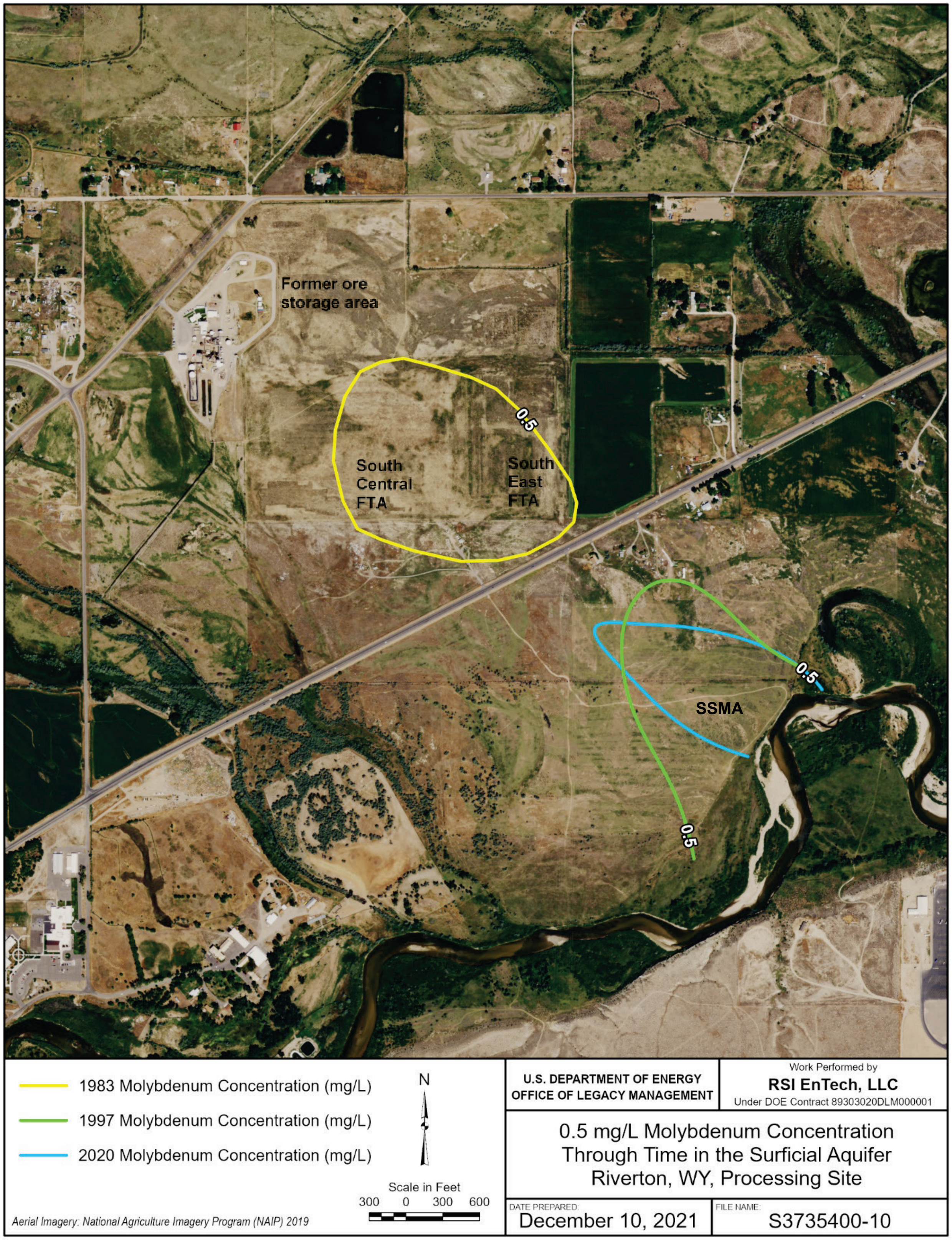


Figure 34. 0.5 mg/L Molybdenum Concentration Contours in the Surficial Aquifer Through Time

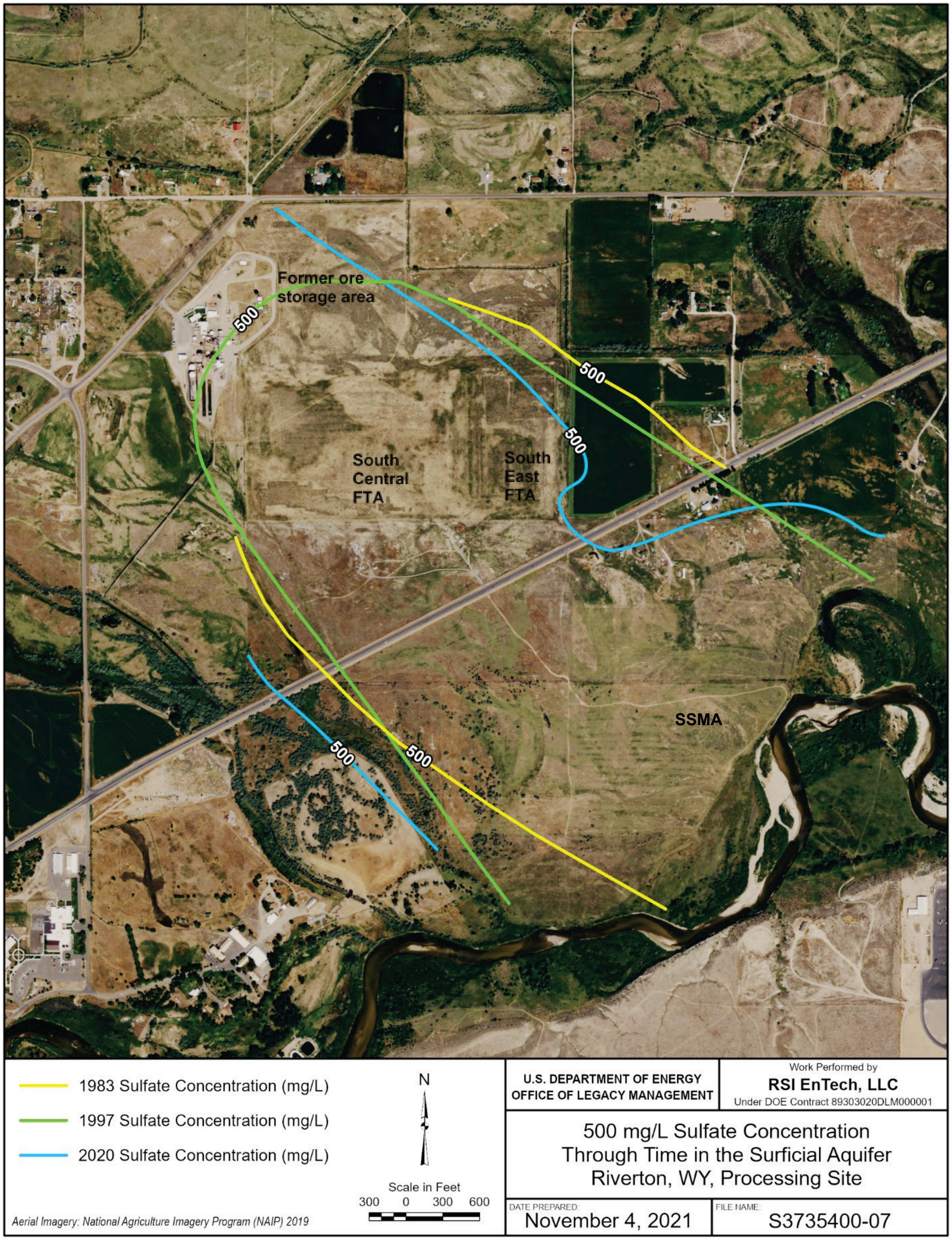


Figure 35. 500 mg/L Sulfate Concentration Contours in the Surficial Aquifer Through Time

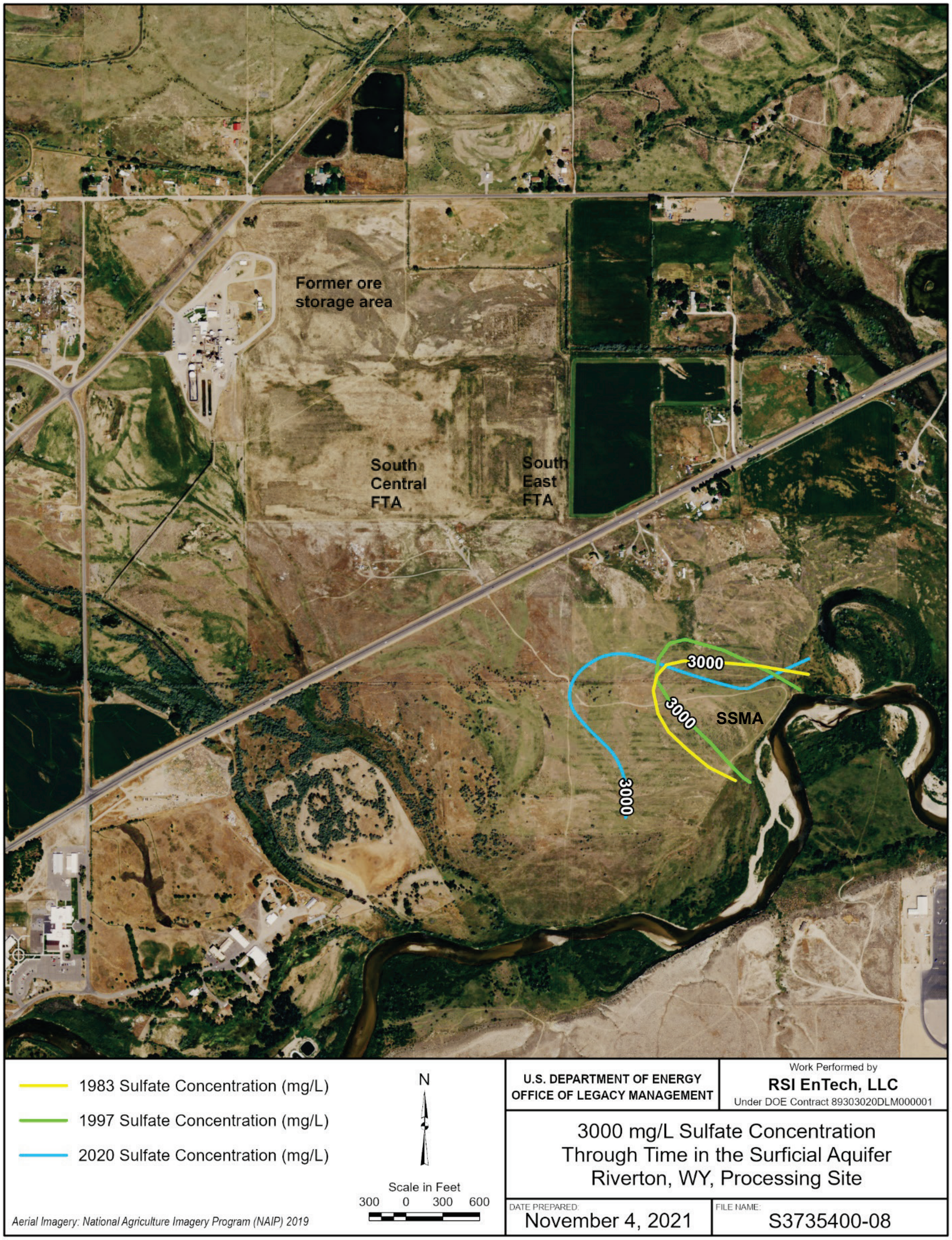


Figure 36. 3000 mg/L Sulfate Concentration Contours in the Surficial Aquifer Through Time

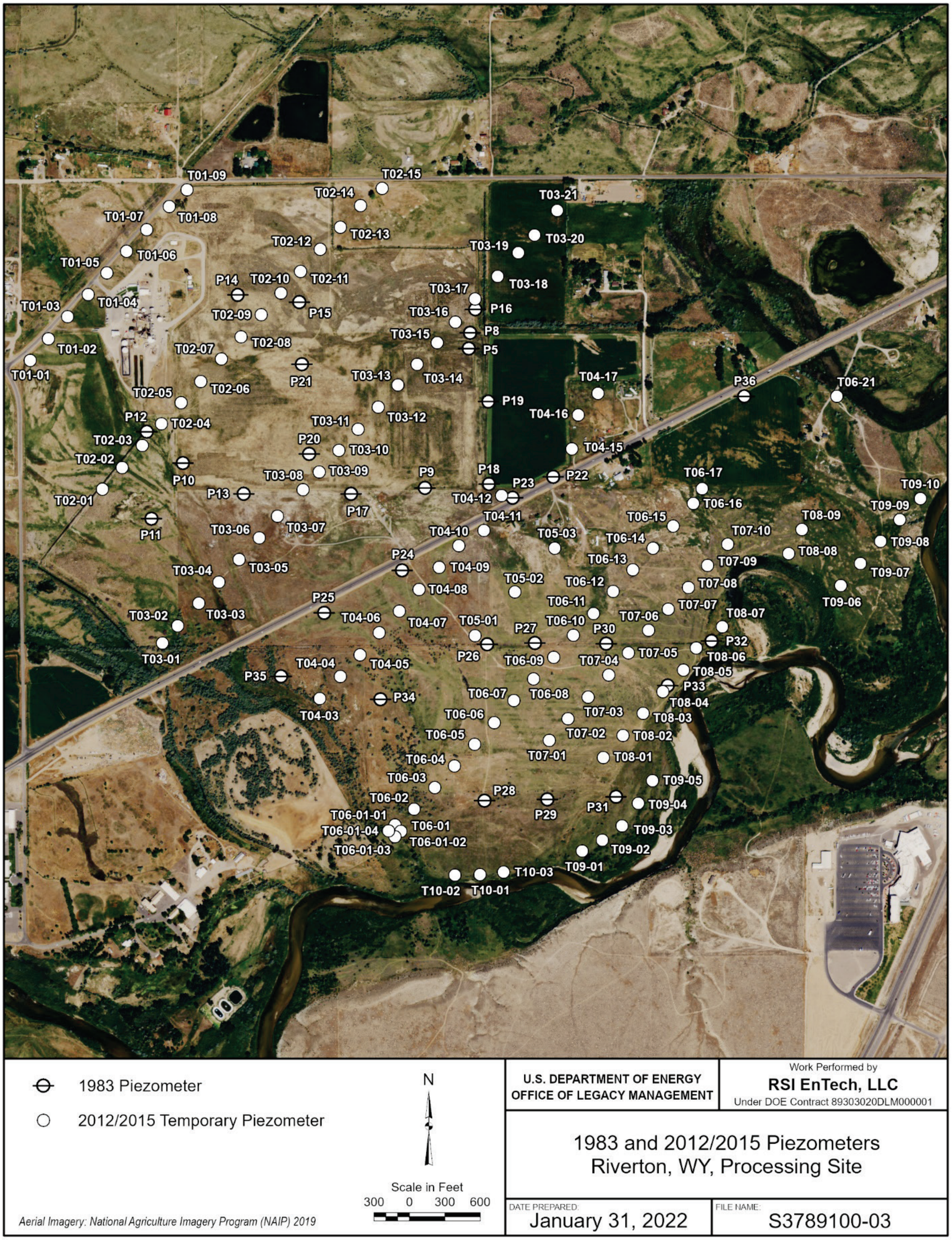


Figure 37. Identification Numbers for Piezometers in 1983 and Temporary Well Point Transects Done in 2012/2015

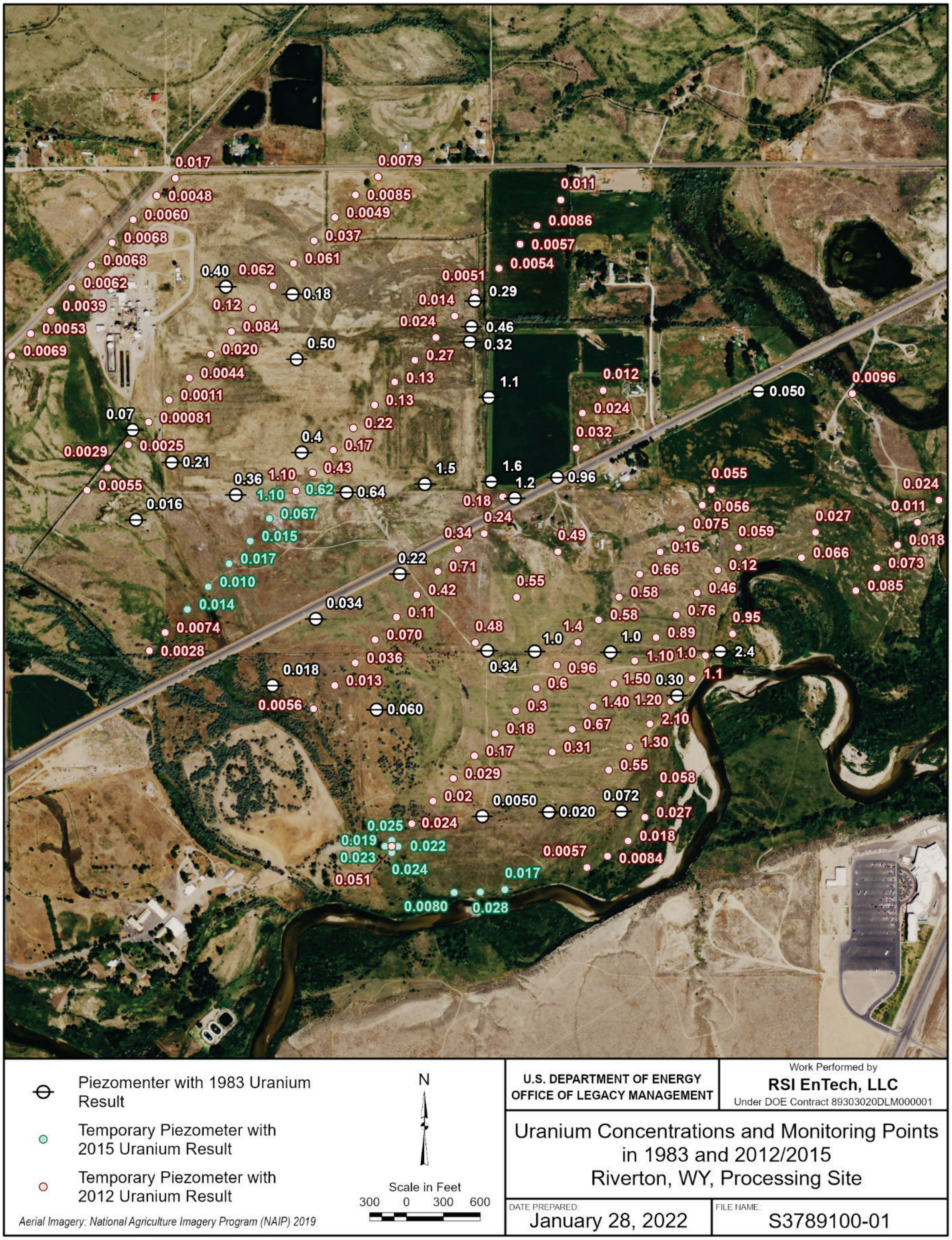


Figure 38. Uranium Concentrations and Monitoring Points from 1983 Compared to Temporary Well Point Transects Done in 2012/2015

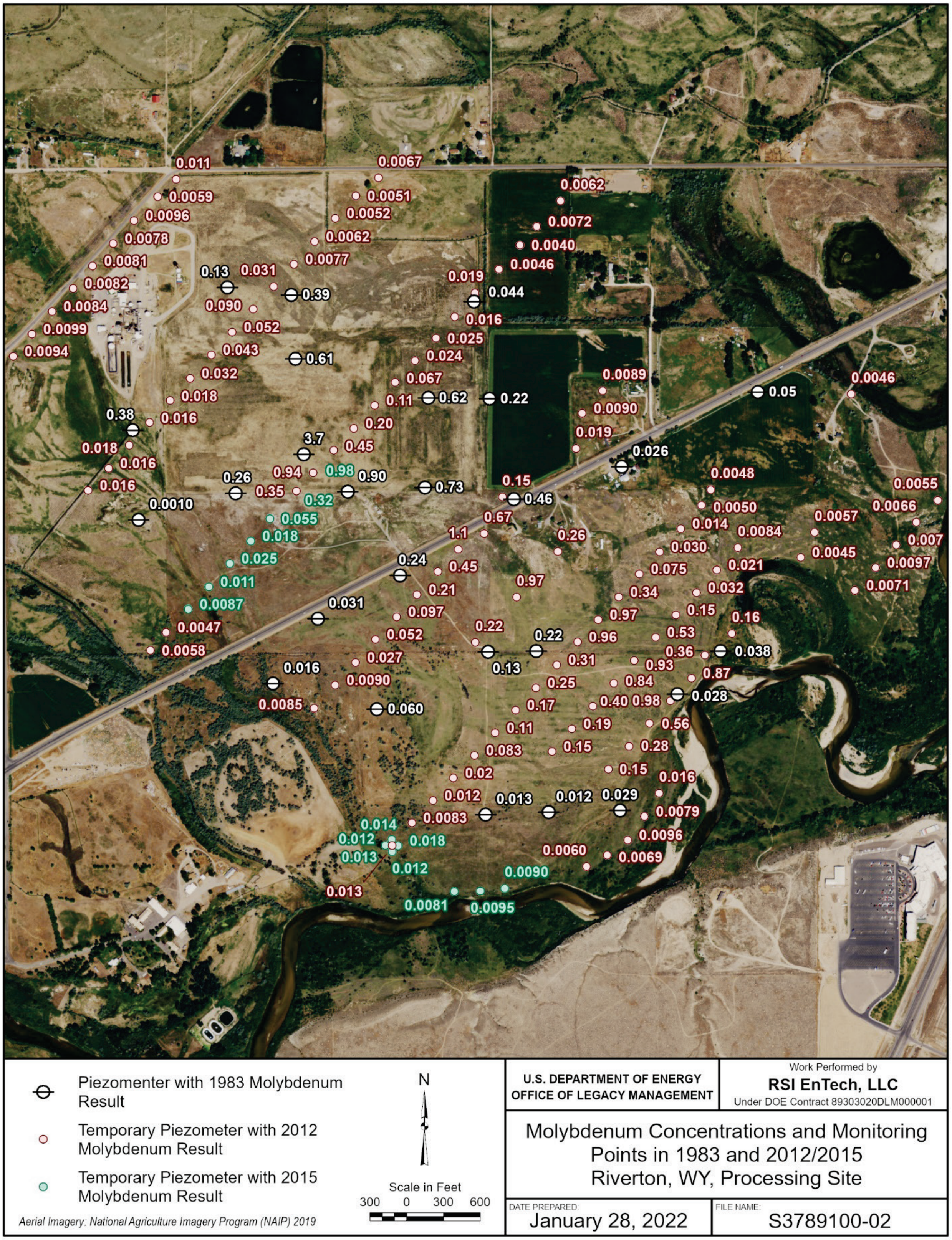


Figure 39. Molybdenum Concentrations and Monitoring Points from 1983 Compared to Temporary Well Point Transects Done in 2012/2015

4.0 Quantitative Evaluations of Natural Flushing Time

As part of the conceptual model, Section 3.4 qualitatively shows the potential for natural flushing in the former ore storage area and the south-east FTA. In the sections below, well trends (Section 4.1), plume visualization and contaminant mass with Earth Volumetric Studio (EVS) (Section 4.2), and mass balance removal rates (Section 4.3) are used to more quantitively evaluate natural flushing time frames.

4.1 Well Trends

All existing wells in the surficial aquifer were evaluated for natural flushing times by matching the trends of existing data through 2020 using an exponential curve fit in Excel (Appendix A). Appendix A also includes graphs of all measured analytes through time and all of the surficial aquifer groundwater data through 2020. Results are summarized in Table 1 for estimated natural flushing dates for all wells that reported uranium or molybdenum above standards (0.044 mg/L and 0.10 mg/L, respectively) in 2020. Well 0853-4 was not included as it was just above the standard with a uranium concentration of 0.045 mg/L in 2020. Well 0788 was not included as it was below standards in 2020 but has experienced flood related spikes in uranium concentrations in the past. In addition, compared to the 700-series wells (0707, 0716, 0718, 0722R, and 0789), the 800-series wells (0855 through 0860), only have a 5-year period of record and well 0101 has a period of record that ends in 1998 (Table 1).

Based on groundwater concentration trends, natural flushing for uranium and molybdenum within a 100-year time clock (ending date of 2098, based on the GCAP being finalized in 1998, DOE 1998c) looks possible at the upgradient portion of the contaminant plumes (wells 0101 and 0859), the south-east FTA (wells 0716 and 0722R), and south of the south-central FTA (well 0718), with faster flushing times for molybdenum (Table 1 and Appendix A). However, spikes in uranium and molybdenum concentrations at well 0718 and spikes in uranium concentrations in well 0716 occur after wet periods (Figure 24 and Figure 25) indicate the concentrations of these contaminants could exceed the standards beyond the end of any defined flushing period. This is likely due to upgradient, residual uranium and molybdenum sources in the unsaturated zone.

Natural flushing times of longer than 100 years for uranium and molybdenum are variable (Table 1) for wells within the core of the plume (wells 0855, 0856, 0857, 0858, 0860, 0707, and 0789). Essentially, these wells highlight the areas within the current 0.5 mg/L uranium contour in Figure 27 and the 0.4 mg/L molybdenum contour in Figure 28. Thus, the outer edges of the plume are flushing faster than the plume core, with the possibility of ongoing uranium and molybdenum sources near and upgradient of well 0860. Solid-phase uranium and molybdenum in the surficial aquifer sediments at well 0860 are up to two times background (DOE 2016). The ongoing plume near well 0860 is defined by uranium concentrations at temporary well point T03-08 with 1.1 mg/L in 2012 and 2015 (Figure 38) and molybdenum concentrations at temporary well point T03-09 of 0.94 and 0.98 mg/L in 2012 and 2015, respectively (Figure 39). Well T03-08 was collocated with well 0860 while well T03-09 was 200 ft northeast of well T03-08. The increasing uranium and molybdenum trends in well 0860-2 (Table 1, shallowest well point) may be an indication of unsaturated zone sources upgradient of well 0860. Uranium and molybdenum concentration trends in wells 0860-3 and 0860-4 have been relatively stable from 2015 to 2020 (Table 1 and Appendix A), like the stable concentrations in the temporary well points between 2012 and 2015.

Sources of uranium and molybdenum in the unsaturated zone in the SSMA that contribute to elevated concentrations in the underlying groundwater have been confirmed (DOE 2016; DOE 2019). Thus, longer flushing times in that area are expected and are difficult to quantify. The flushing times listed in Table 1 are based on current data. Future spikes in uranium and molybdenum concentration in the groundwater are expected with future flooding events, but the timing of those events and overall groundwater concentrations cannot be predicted. In any case, elevated uranium and molybdenum concentrations at the SSMA will persist as long as ongoing sources are still present at the FTA near well 0860 (upgradient of the SSMA).

Sulfate flushing times based on concentration trends were not evaluated, but concentrations at the end of the period of record for the wells are included in Table 1. These data indicate potential flushing of sulfate in the former ore storage area and the south-east FTA based on sulfate concentrations being much less than 2000 mg/L (typical of concentrations higher than this within the sulfate plume, Figure 29). Natural flushing is not indicated at the upgradient edge of the contaminant plumes near well 0784 and 0859 (Figure 29) likely due to an ongoing sulfate source from the Plant which is defined by temporary well points T02-04 through T02-07 (see Figure 24 in DOE 2016). Sulfate release from gypsum under the FTA is also a likely sulfate source, which will be discussed further in Section 5.3.

Highlight Box 7: Summary of Natural Flushing Based on Groundwater Concentration Trends

Same overall results as the summary in Box 6.

Quantitative addition is the potential for less than 100-year natural flushing of uranium and molybdenum in the former ore storage area, the south-east FTA (well 0716), and south of the south-central FTA (well 0718), see Table 1. However, future concentration spikes past a 100-year natural flushing period are possible based on existing data.

Based on current concentration trends, greater than 100 years for natural flushing is indicated at the south-central FTA (well data starts in 2015) and the SSMA (well data starts in 1987) due to the presence of ongoing solid-phase sources.

Table 1: Estimates of Natural Flushing Dates Based on Groundwater Concentration Trends Shown in Appendix A

Well	Area Description	Period of Record	Uranium Flushing Year	Molybdenum Flushing Year	End of Record Sulfate (mg/L)	Comments
0101	Former ore storage area	1983 to 1998	2026	1983	410	Not sampled since 1998
0859-3	Upgradient edge of plumes	2015 to 2020	2021	2015	2200	
0859-4	Upgradient edge of plumes	2015 to 2020	2031	2015	2400	
860-2	South-central FTA	2015 to 2020	Increasing trend	Increasing trend	2800	

Table 1. Estimates of Natural Flushing Dates Based on Groundwater Concentration Trends Shown in Appendix A (continued)

Well	Area Description	Period of Record	Uranium Flushing Year	Molybdenum Flushing Year	End of Record Sulfate (mg/L)	Comments
860-3	South-central FTA	2015 to 2020	No trend	No trend	2200	
860-4	South-central FTA	2015 to 2020	2292	2394	2200	
718	Slightly south of being downgradient of south-central FTA and well 0860	1993 to 2020	2062	2012	2200	Temporary rise in uranium and molybdenum in 2017 and 2018 (see Figures 24 and 25), molybdenum was 0.10 mg/L in 2012
716	South-east FTA	1993 to 2020	2077	2020	780	Temporary rise in uranium in 2017 and 2018 (see Figures 24 and 25), molybdenum was 0.10 mg/L in 2020
722R	Downgradient of south-east FTA and well 0716	2007 to 2020	2078	2016	88	
0857-2	Nonflooding SSMA	2015 to 2020	2121	2032	3800	
0857-3	Nonflooding SSMA	2015 to 2020	2066	2119	3800	
0857-4	Nonflooding SSMA	2015 to 2020	2257	Increasing trend	3900	
0856-2	SSMA	2015 to 2020	Increasing trend	Increasing trend	3900	
0856-3	SSMA	2015 to 2020	2050	2185	4000	
0856-4	SSMA	2015 to 2020	2038	2034	4400	
0858-2	SSMA	2015 to 2020	Increasing trend	2085	2600	
0858-3	SSMA	2015 to 2020	Increasing trend	2129	2900	
0858-4	SSMA	2015 to 2020	Increasing trend	Increasing trend	2900	
707	SSMA	1987 to 2020	2441	Increasing trend	2900	
789	SSMA	2006 to 2020	No trend	No trend	4900	
0855-2	SSMA	2015 to 2020	2068	Increasing trend	6100	
0855-3	SSMA	2015 to 2020	2066	Increasing trend	6000	
0855-4	SSMA	2015 to 2020	2235	Increasing trend	5400	

Note: Flushing times beyond the 100-year time period (2098) are highlighted in red.

4.2 Plume Visualization and Contaminant Mass with EVS

EVS allows for the creation of three-dimensional visualization of groundwater, solid-phase contaminant concentrations, and groundwater elevations. For plume visualization when presenting to stakeholders, EVS output was created for data spanning 2016–2018 (EVS files are in Appendix B). This output focuses on the spikes in uranium and molybdenum concentrations near the Little Wind River in the SSMA, showing concentration spikes after flooding events with high groundwater elevations contacting the contaminated, near-surface silt in this area. This work used the multilevel groundwater quality data from wells installed in the SSMA in 2015 (DOE 2016; DOE 2019) along with annual sampling data.

In addition to the plume visualizations, EVS was used to contour and estimate the mass of uranium and molybdenum from water-phase and solid-phase data reported in DOE 2016. The EVS files and figures with water-phase and solid-phase contoured concentrations of uranium and molybdenum are in Appendix B. The results are summarized in Table 2 by splitting out silt material (generally unsaturated) from the underlying S&G (generally saturated). The estimation of contaminated silt material covers the area over the uranium plume footprint (> 0.044 mg/L uranium [Figure 27]) using silt data from 2012 and 2015 in boreholes and trenches (DOE 2016). The silt data did not include the higher uranium concentrations in reduced zone silts near and below the water table at borehole 0855.

S&G contamination is most prevalent at the FTA (DOE 2016), but is only measured at wells 0859 and 0860 (wells that were completed after coring, Figure 2). Thus, estimation of uranium and molybdenum mass in the overall FTA besides boreholes 0859 and 0860 has more uncertainty due to the lack of data. However, a comparison between the full FTA footprint and a limited footprint near boreholes 0859 and 0860 provide a potential range of contaminant mass (Table 2). Elevated uranium concentrations on the solid phase are found in S&G likely associated with additional organic carbon content below the reduced zone silts at borehole/well 0855 (DOE 2016). Elevated molybdenum concentrations occur in the S&G near borehole/well 0858. These concentrations on S&G outside of the FTA were not included in Table 2.

Table 2. Solid-Phase Uranium and Molybdenum Masses Calculated from EVS

Analyte	Zone	Area	Total Mass (kg)	Background Mass (kg)	Mill-Related Mass (kg)
Uranium	Silt	Uranium plume footprint	5970	4140 (3620–4920)	1830 (1050–2340)
Uranium	Gravel beneath former tailings impoundment	Full tailings impoundment footprint	3520	920 (770–1080)	2600 (2450–2750)
Uranium	Gravel beneath former tailings impoundment	Limited tailings footprint bound by boreholes 0859 and 0860	640	170 (140–200)	470 (450–500)
Molybdenum	Silt	Uranium plume footprint	1970	670 (540–850)	1300 (1110–1430)
Molybdenum	Gravel beneath former tailings impoundment	Full tailings impoundment footprint	3080	350 (230–550)	2730 (2530–2850)
Molybdenum	Gravel beneath former tailings impoundment	Limited tailings footprint bound by boreholes 0859 and 0860	560	60 (40–100)	500 (460–520)

Notes: Ranges shown in parentheses represent values calculated from the 95% confidence limits on mean background analyte concentrations. Background mass is calculated using the solid-phase uranium and molybdenum concentrations from borehole 0852 and applied to the considered zone and area.

Abbreviation: kg = kilograms

4.3 Using Mass Balance

Bounding calculations can be done to estimate flushing times at the FTA using the EVS calculated masses and groundwater mass removal rates. Groundwater removal rates are considered in a line perpendicular to the plume for (1) the whole plume above 0.044 mg/L uranium (T03-07 to T03-15 in Figure 25 of DOE 2016) which is 2000 ft in length, and (2) the core of the plume near well 0860 (T03-07 to T03-10 in Figure 25 of DOE 2016) which is 800 ft in length. Average uranium concentrations of 0.3 mg/L are applied to No. 1 based on uranium values for T03-07 through T03-15 in 2012/2015 (DOE 2016) and 0.5 mg/L are applied to No. 2 based on uranium values for T03-07 through T03-10. Using a typical surficial aquifer groundwater flow rate of 1 ft/day (DOE 2020a and tracer testing near well 0860, unpublished data), the saturated aquifer thickness of 8.2 ft measured at well 0860 on August 18, 2020, and the uranium concentrations listed above, mass removal rates can be calculated (Table 3). This results in 0.14 kg/day and 0.093 kg/day uranium removal rates along the longer (No. 1) and shorter lengths (No. 2), respectively. Using the mill-related uranium masses in Table 2 of 2600 kg of uranium for the whole FTA applied to the longer length perpendicular to the plume (No. 1) and 470 kg of uranium for the more limited area applied to the shorter length (No. 2) gives 51 and 14 years from 2015 for flushing years of 2066 and 2029 (Table 3). The above calculations assume uranium mass removal rates remain constant based on 2012/2015 measured values (DOE 2016). To test a lower mass flushing rate, lower uranium concentrations of 0.1 mg/L for No. 1 and 0.2 mg/L for No. 2 gives flushing years of 2165 and 2049, respectively (Table 3). These lower concentrations give lower mass removal rates and thus a higher bound on the flushing year (Table 3).

The above calculations for uranium were also done for molybdenum. The only difference was the use of slightly different lengths and locations perpendicular to the molybdenum plume. Thus, (1) the whole plume above 0.1 mg/L molybdenum uses T03-07 to T03-13 with a length of 1500 ft and an average concentration of 0.3 mg/L and (2) the core of the plume to the northeast of well 0860 uses T03-08 to T03-10 with a length of 700 ft and an average concentration of 0.5 mg/L. Concentrations are the same as for uranium, but the narrower plume results in slightly lower mass removal rates and the same or slightly longer flushing times (Table 3).

Highlight Box 8: Summary of Natural Flushing Based on Mass Balance

100-year natural flushing of uranium and molybdenum in the FTA is unclear, albeit possible, only if additional residual sources are not detected and current high-flushing concentrations continue.

Flushing at the SSMA was not calculated, as flushing there depends on flooding events that cannot be predicted. SSMA flushing would require FTA flushing to be completed first.

Estimates of natural flushing times in the FTA are highly uncertain since there are only two locations that have solid-phase uranium and molybdenum concentration with depth. In addition, these calculations assume a constant removal concentration, which is realistic with the current data (DOE 2016 and Appendix A), but may not be the case in the future. Given the uncertainty in the solid-phase data and future mass removal rates, estimates straddle the 100-year natural flushing time at the FTA. Areas with higher solid-phase uranium and molybdenum concentrations are also quite likely, especially for molybdenum, given the offset in the molybdenum plume to the northeast of well 0860 where higher molybdenum concentrations were detected in 1983 (Figure 11), which could increase flushing times.

Table 3. Mass Balance Flushing Calculation for the FTA

Analyte	Contaminated Area Considered	Average Concentration (mg/L)	Average Mass Removal Rate (kg/day)	Lower Bound Concentration (mg/L)	Lower Bound Mass Removal Rate (kg/day)	Average Flushing Year	Higher Bound Flushing Year (Lower Bound Concentration)
Uranium	No. 1-FTA full area 80 acres	0.3	0.14	0.1	0.047	2066	2165
Uranium	No. 2-FTA limited area 16 acres	0.5	0.093	0.2	0.037	2029	2049
Molybdenum	No.1-FTA full area 80 acres	0.3	0.10	0.1	0.035	2086	2165
Molybdenum	No. 2-FTA limited area 16 acres	0.5	0.082	0.2	0.033	2032	2057

Note: Flushing times beyond the 100-year time period (2098) are highlighted in red.

Using mass balance to calculate flushing times for the measured mass of uranium and molybdenum in the silt unsaturated zone (Table 2) was not completed. Release of uranium and molybdenum to the groundwater is dependent upon high recharge or flooding events, or both. As such, this will require probabilistic modeling (DOE 2019) that is beyond the scope of this report and should be included in any future sitewide reactive transport modeling. In any case, the process of groundwater contamination wicking into the silt layer means flushing of silt or unsaturated zone contaminants cannot occur until the underlying groundwater is no longer contaminated (i.e., FTA flushing must be complete first). Flushing times in the various Site sediments (FTA, SSMA, saturated and unsaturated zones) are also evaluated in Section 6.0 based on column studies.

5.0 Current Geochemical Conditions that Could Influence Uranium and Molybdenum Mobility

5.1 Introduction

When the former tailings where present, low-pH fluids were produced by the oxidation of pyrite along with any sulfuric acid disposal in the tailings impoundment, which created a slightly lower pH zone (Figure 11, Figure 15, and White et al. 1984). As directly stated in the abstract of White et al. 1984 “Significant reactions include the dissolution of calcite, production of CO_2, and precipitation of gypsum and the hydroxide of iron and aluminum.” These are typical reactions that occur below oxidizing sulfide-rich tailings that are exposed to the atmosphere or meteoric water. In this case, the low-pH water is buffered by calcite (often producing some excess carbon dioxide) and the dissolution of calcium from the calcite makes the resulting solution supersaturated with respect to gypsum due to the high sulfate concentrations (from sulfide oxidation).

Since the tailings were removed, the remaining controls on the surficial aquifer geochemistry are related to upgradient groundwater and recharge water interacting with the remaining solid phase. Each of the water phase and solid phase constituents that could influence uranium and molybdenum mobility are discussed below. Only the geochemistry in the surficial aquifer is considered, since uranium and molybdenum are not detected above standards below the surficial aquifer. Sulfate in the semiconfined aquifer likely moves in a conservative manner with minimal mineral control. No semiconfined aquifer wells currently have sulfate concentrations that exceed gypsum solubility limits (evaluated using a data mining application that runs the geochemical computer modeling code PHREEQC [Parkhurst and Appelo 2013] directly with the database).

The discussion below highlights potential controls on uranium and molybdenum mobility. However, given the complexity of these controls, the best way to make a quantitative evaluation of future mobility is to include the knowledge of the Site geochemistry in a reactive transport model. Such a model will allow for the incorporation of multiple control mechanisms that can be used to quantify uranium and molybdenum fate and transport.

To highlight the geochemical controls, the temporary piezometer data from 2012/2015 were used to create site wide maps of pH, alkalinity, calcium, sodium, manganese, and magnesium, plus, gypsum saturation indices (SIs) (Appendix C). SI is used to evaluate solubility estimates of minerals with the surrounding solution. SIs greater than zero suggests potential mineral precipitation, while a value below zero suggests potential mineral dissolution. SIs near zero represent equilibrium. The 2012/2015 data along with gypsum, calcite, and carbon dioxide saturation indices are provided in Appendix C, where the saturation indices were calculated using PHREEQC and the phreeqc.dat database through a data mining application. These data were also evaluated using PHREEQC for the saturation indices of uraninite, and powellite. Uraninite saturation indices were calculated using the phreeqcU_V.dat database which includes new thermodynamic data from Dong and Brooks (2006) and Guillaumont et al. (2003). Powellite saturation indices were calculated using the minteq.v4.dat database that includes molybdenum thermodynamic information. All PHREEQC input and output files and the respective databases are provided in Appendix C.

For simplicity, the 2012/2015 temporary piezometer data were evaluated in four upgradient to downgradient lines to compare geochemical changes along the groundwater flow paths. These lines are (1) southwest area outside of the contaminant plumes (Table 4), (2) along the uranium plume centerline (Table 5), (3) along the molybdenum plume centerline (Table 6), and (4) northeast area outside of the contaminant plumes (Table 7). Confirmation of the 2012/2015 geochemistry is provided in Table 4, Table 5, and Table 7 using the most recent data from existing nearby monitoring wells. Locations of the four lines are provided in Figure 40 along with stiff diagrams at selected locations along transects T01, T03, and T06. Locations and lines are color coded for groundwater types as follows:

- Blue = background groundwater (Table 4 through Table 7 and Figure 40)
- Green = southwest of contaminant plumes and downgradient of the Plant outfall (thus, added sulfate), Table 4 and Figure 40
- Bold black = Plant outfall (Table 4 only)
- Orange = centerline of uranium plume (Table 5 and Figure 40)
- Red = centerline of molybdenum plume (Table 6 and Figure 40)
- Black = surficial aquifer wells (Table 4, Table 5, Table 7)

Details on the constituents in Table 4 through Table 7 and the associated geochemistry are discussed in subsequent subsections, but overall trends are as follows:

- Concentrations of uranium, molybdenum, major cations, and major anions increase going downgradient across the whole Site. This is likely due to all dissolved constituents being stored in the unsaturated zone and then being released in higher concentrations to the groundwater after recharge events. This effect increases as it gets closer to the Little Wind River.
- Table 4 (southwest of the contaminant plumes) represents groundwater conditions that are influenced by the Plant outfall.
- Table 7 (northeast of the contaminant plumes) represents the most consistent natural groundwater conditions without any anthropogenic influence.
- The uranium and molybdenum plumes are offset slightly (Figure 40) and are both characterized by elevated calcium, sulfate, sodium, and manganese.

Table 4. Overall Geochemistry Southwest of the Contaminant Plumes

Location	Sample Date	U mg/L	Mo mg/L	Alkalinity mg/L as $CaCO_3$	Ca mg/L	SO_4 mg/L	Gypsum SI unitless	Na mg/L	Cl mg/L	Mg mg/L	Specific Conductance µmhos/cm	Mn mg/L
T01-02	8/24/2012	0.0053	0.0099	240	96	270	-1.2	110	23	22	840	0.24
T02-02	8/22/2012	0.0029	0.016	160	73	580	-1.0	230	26	8.7	1400	0.27
T03-03	8/27/2015	0.014	0.0087	370	200	570	-0.69	170	18	44	1600	0.40
T04-03	8/26/2012	0.0056	0.0085	450	180	910	-0.61	310	29	48	2300	1.7
T06-02	8/26/2012	0.024	0.0083	430	340	1500	-0.25	420	57	98	3200	1.7
0710	8/20/2019	0.0068	0.0026	210	86	210	-1.3	60	22	20	1100	0.040
0720	8/20/2019	0.0041	0.0016	210	73	77	-1.7	26	3.8	18	590	0.0015
0852-4	8/21/2019	0.035	0.011	390	230	1100	-0.46	350	62	59	2900	1.5
0749	**8/20/2019**	**0.0027**	**0.034**	**100**	**620**	**1800**	**0.035**	**190**	**16**	**2.4**	**3000**	**0.097**

Notes:
Blue text = background groundwater
Green text = southwest of contaminant plumes and downgradient of the Plant outfall (thus, added sulfate)
Black text = surficial aquifer wells
Bold black text = Plant outfall

Abbreviations:
Ca = calcium
$CaCO_3$ = calcium carbonate
Cl = chloride
Mg = magnesium
µmho/cm = micromhos per centimeter
Mn = manganese
Mo = molybdenum
Na = sodium
SO_4 = sulfate
U = uranium

Table 5. Overall Geochemistry Along the Uranium Plume Centerline

Location	Sample Date	U mg/L	Mo mg/L	Alkalinity mg/L as $CaCO_3$	Ca mg/L	SO_4 mg/L	Gypsum SI unitless	Na mg/L	Cl mg/L	Mg mg/L	Specific Conductance µmho/cm	Mn mg/L	$CaMoO_4$ SI unitless	Uraninite SI unitless
T01-06	8/23/2012	0.0068	0.0078	260	120	310	-1.1	99	28	30	26	0.091	-2.2	-9.7
T02-09	8/23/2012	0.12	0.09	320	180	500	-0.76	140	46	46	1400	0.18	-1.1	-8.0
T03-08	8/21/2012	1.1	0.35	310	500	2600	0.0050	580	55	54	4100	2.1	-0.42	-7.2
T04-09	8/27/2012	0.71	0.45	370	470	2600	-0.019	660	77	76	4500	2.0	-0.34	-6.0
T06-10	8/27/2012	1.4	0.96	440	440	3900	-0.016	1200	130	220	6500	2.7	-0.17	-6.5
T07-04	8/25/2012	1.5	0.84	470	460	4000	0.011	1300	180	220	7100	3.4	-0.21	-6.6
T08-03	8/25/2012	2.1	0.56	500	450	5300	0.035	1700	300	320	8600	1.1	-0.48	-6.5
710	8/20/2019	0.0068	0.0026	210	86	210	-1.3	60	22	20	1100	0.040		
784	8/20/2019	0.0045	0.044	140	420	1800	-0.11	320	31	27	3200	1.3		
0859-4	8/20/2019	0.095	0.073	210	460	2600	-0.012	540	28	65	4600	2.0		
0860-4	8/20/2019	0.90	0.31	290	390	2200	-0.11	510	41	53	42003	1.4		
0857-4	8/21/2019	1.6	0.70	450	570	5200	0.13	1600	380	260	9100	3.4		
789	8/21/2019	1.9	0.54	540	380	6100	-0.012	2100	390	320	11000	0.62		

Notes:
Blue text = background groundwater
Orange text = centerline of uranium plume
Black text = surficial aquifer wells

Abbreviations:
Ca = calcium
$CaCO_3$ = calcium carbonate
$CaMoO_4$ = calcium molybdate (powellite)
Cl = chloride
Mg = magnesium
µmho/cm = micromhos per centimeter
Mn = manganese
Mo = molybdenum
Na = sodium
SO_4 = sulfate
U = uranium

Table 6. Overall Geochemistry Along the Molybdenum Plume Centerline

Location	Sample Date	U mg/L	Mo mg/L	Alkalinity mg/L	Ca mg/L	SO$_4$ mg/L	Gypsum SI unitless	Na mg/L	Cl mg/L	Mg mg/L	Specific Conductance (µmhos/cm)	Mn mg/L	CaMoO$_4$ SI unitless	Uraninite SI Unitless
T01-06	8/23/2012	0.0068	0.0078	258	120	310	-1.1	99	28	30	26	0.091	-2.2	-9.7
T02-09	8/23/2012	0.12	0.09	320	180	500	-0.76	140	46	46	1423	0.18	-1.1	-8.0
T03-09	8/22/2012	0.43	0.94	356	380	2600	-0.10	780	38	49	4467	0.74	-0.12	-8.4
T04-10	8/27/2012	0.34	1.1	398	350	2000	-0.19	590	44	63	2377	1.5	-0.013	-6.5
T05-02	8/29/2012	0.55	0.97	382	320	2100	-0.21	630	59	80	3951	1.0	-0.12	-7.2
T06-11	8/27/2012	0.58	0.97	382	490	2300	-0.031	550	66	99	3726	1.4	0.051	-6.7
T07-05	8/25/2012	1.1	0.93	424	450	3300	-0.012	900	110	170	5570	2.1	-0.11	-6.8
T08-04	8/25/2012	1.2	0.98	427	500	3900	0.057	1000	160	200	6458	1.2	-0.093	-7.3

Notes:
Blue text = background groundwater
Orange text = centerline of uranium plume
Red text = centerline of molybdenum plume

Abbreviations:
Ca = calcium
CaMoO$_4$ = calcium molybdate (powellite)
Cl = chloride
Mg = magnesium
µmho/cm = micromhos per centimeter
Mn = manganese
Mo = molybdenum
Na = sodium
SO$_4$ = sulfate
U = uranium

Table 7. Overall Geochemistry Northeast of the Contaminant Plumes.

Location	Sample Date	U mg/L	Mo mg/L	Alkalinity mg/L as $CaCO_3$	Ca mg/L	SO4 mg/L	Gypsum SI unitless	Na mg/L	Cl mg/L	Mg mg/L	Specific Conductance µmhos/cm	Mn mg/L
T01-09	8/23/2012	0.017	0.011	210	66	110	-1.6	56	8.1	14	590	0.034
T02-12	8/23/2012	0.037	0.0062	200	86	140	-1.4	35	11	19	640	0.017
T03-16	8/21/2012	0.014	0.016	200	69	120	-1.6	48	6.7	17	600	0.070
T04-16	8/24/2012	0.024	0.0091	240	93	120	-1.5	40	6.3	21	680	0.18
T06-21	8/28/2012	0.0096	0.0046	390	140	120	-1.4	51	9.6	32	900	0.087
T08-09	8/28/2012	0.027	0.0057	350	110	320	-1.1	120	20	39	1200	0.36
T09-10	8/28/2012	0.024	0.0055	330	110	180	-1.3	84	12	29	1000	0.19
710	8/20/2019	0.0068	0.0026	210	86	210	-1.3	60	22	20	1100	0.040
729	8/21/2019	0.0060	0.0031	290	80	62	-1.8	32	6.3	20	930	0.32
824	8/21/2019	0.018	0.0043	310	93	140	-1.4	66	8.0	26	960	0.0075

Notes:
Blue text = background groundwater
Black text = surficial aquifer wells

Abbreviations:
Ca = calcium
Cl = chloride
Mg = magnesium
µmho/cm = micromhos per centimeter
Mn = manganese
Mo = molybdenum
Na = sodium
SO_4 = sulfate
U = uranium

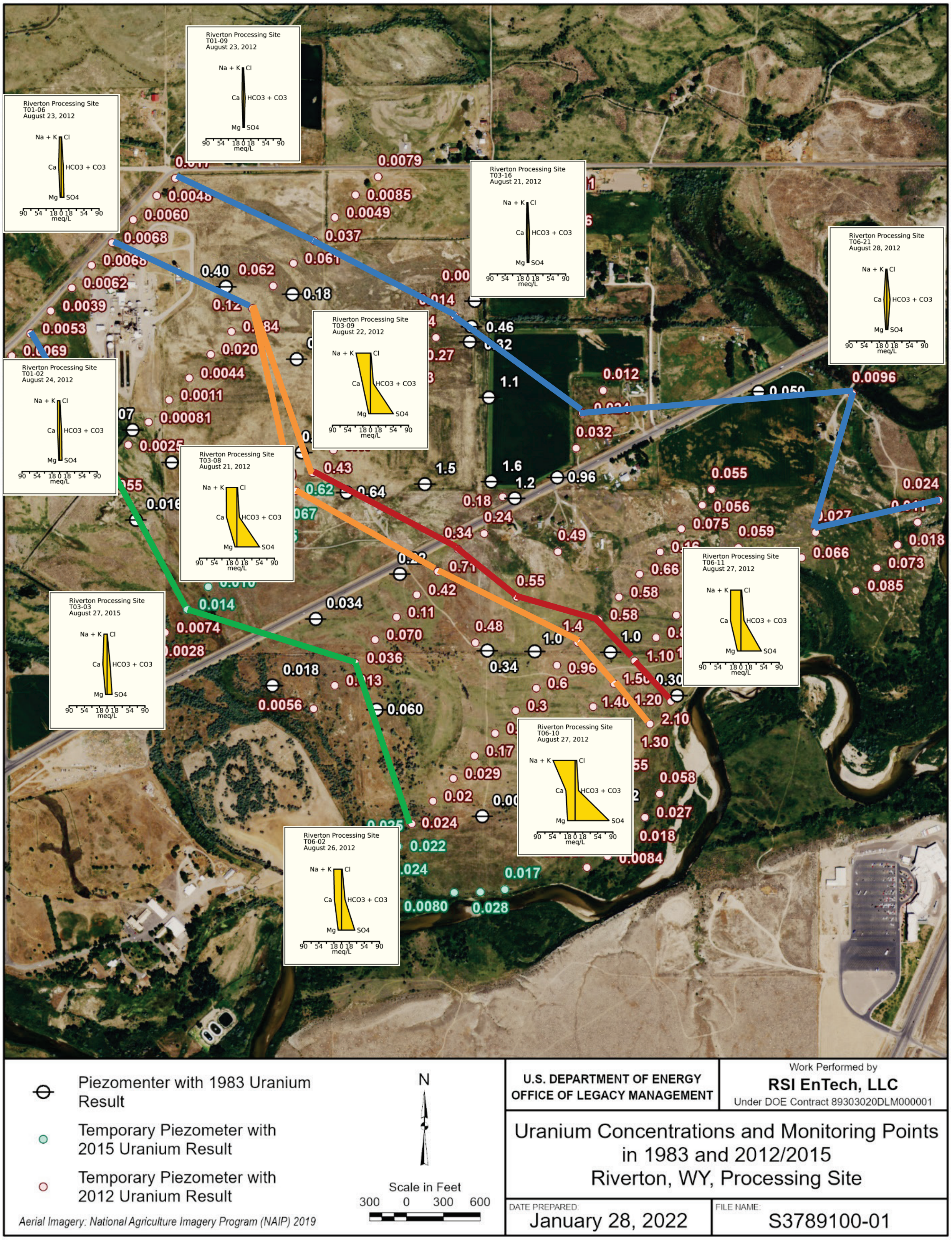


Figure 40. Four Lines Going Downgradient to Match Tables 4 through 7 with Stiff Diagrams for 2012/2015 Temporary Piezometer Data

5.2 Carbonate system (pH, alkalinity, calcium, calcite, and carbon dioxide)

Overall, the carbonate system across the Site appears to be near equilibrium to slightly supersaturated with respect to calcite (SI values above 0.0 represent supersaturated conditions). For August 2019, the calcite SI range was -0.45 to 0.46 with a median value of 0.18 and results were similar for the 2012/2015 data with a range of -0.23 to 0.76 and a median of 0.15. As a result, the pH across the Site in August 2019 was near neutral (range of 6.6 to 7.4 with a median of 7.1). In August 2020 it was consistently near neutral with a range of 6.8 to 7.3 and a median of 7.1. Likewise, the carbon dioxide concentration for August 2019 was -2.1 to -1.1 with a median of -1.5 log atmospheres, which is typical of shallow groundwater having about 100 times more carbon dioxide than the atmosphere. Given these consistencies in pH, calcite SI, and carbon dioxide concentration, these constituents were not included in Table 4 through Table 7.

Albeit close to equilibrium with calcite, increases in calcium and alkalinity do occur going downgradient naturally (Table 7) and within the contaminant plumes (Table 4, Table 5, and Table 6). This is likely due to higher calcite concentrations in the unsaturated zone closer to the Little Wind River that is then released during recharge events. Minimal solid phase calcite data are available, but X-ray diffraction work at well 0858 (unpublished data) indicate 4.6 weight percent calcite in the unsaturated zone compared to 0.84 weight percent calcite in the saturated zone.

5.3 Gypsum

Calcium and sulfate addition, without added alkalinity likely occurs at the Plant retention ponds and at the outfall (Table 4). In 2019, the Plant outfall ditch was at equilibrium with respect to gypsum. Downgradient from the outfall ditch, the surficial aquifer groundwater has higher calcium and sulfate (Table 4 and Figure 40) compared to the northeast area with background groundwater (Table 7 and Figure 40). This results in a gypsum SI in T06-02 of -0.25 compared to a value of -1.4 at T06-21 (Table 4 and Table 7). High calcium and sulfate concentrations are present in transects T02 and T03 below the former tailings, which is also downgradient of the Plant retention ponds (Figure 37). The gypsum SI maximums in transect T02 are -0.18 at T02-05 and 0.0050 at T03-08(Appendix C). Gypsum SIs near zero continue from the Plant area and the south-central FTA all the way to the Little Wind River (Appendix C). Thus, gypsum likely controls the maximum concentrations of calcium and sulfate. Similar calcium and sulfate concentrations with similar gypsum SIs are present in the existing monitoring wells compared to the temporary piezometer transects (Table 4).

The presence of gypsum in the FTA is likely and X-ray diffraction data (unpublished) at borehole/well 0859 did indicate gypsum at 6.6 weight percent. However, gypsum is unlikely to dissolve downgradient of the Plant retention ponds and outfall due to the continued input of calcium and sulfate to the groundwater. Dissolution of gypsum would only occur if Plant discharge variation occurs such that calcium and sulfate concentrations are lower than the gypsum solubility limits.

In the south-east FTA area, any gypsum that was present in the saturated zone has now likely dissolved. High calcium and sulfate concentrations present in 1983 (location P18 in White et al., 1984, calcium = 720 mg/L and sulfate = 2200 mg/L) were near background in 2012 (T04-12) and in nearby well 0716 were 37 and 479 mg/L, respectively in September 2013.

However, calcium and sulfate spiked in this well up to 120 and 1300 mg/L, respectively in 2018, indicating a possible upgradient source of gypsum in the unsaturated zone in the south-east FTA.

5.4 Redox

A review of previous data in surficial aquifer monitoring wells (Appendix A) indicate that dissolved oxygen (DO) and ORP, when measured, are typically less than 1 mg/L and less than 50 millivolts (mV), respectively. These data are consistent with a suboxic aquifer. Some data indicate occasional influx of recharge that makes some locations temporarily oxic, especially in areas near the Little Wind River after flooding events (DO > 2 mg/L and ORP > 50 mV).

The 2012/2015 temporary piezometer transects provide the best data to determine redox conditions across the Site for the surficial aquifer. DO ranges from 0.40 to 2.1 mg/L with a median of 0.68 mg/L. These measurements were completed with DO probes that are not considered very accurate below 1 mg/L. ORP probe measurement ranged from -2.1 to -140 mV with a median of -62 mV. These ORP measurements are considered qualitative data that confirm the surficial aquifer is generally suboxic.

Based on the above, manganese data from the 2012/2015 the temporary piezometer transects (Figure 41) are the best indicator of redox conditions across the site, with high manganese concentrations indicating more reducing conditions. Transect data are consistent with monitoring well data (Table 4, Table 5, Table 7) where higher manganese concentrations generally occur (1) near the start of the contaminant plumes, (2) within and on the southwest side of the contaminant plumes, and (3) near the Little Wind River (Figure 41). No continued contaminant release of manganese is known; thus, manganese concentrations are considered indicative of reducing conditions. Reducing conditions starting at the FTA are possibly created by degradation of oil and grease released into the Plant retention ponds and outfall (allowed up to 10 mg/L based on NPDES Permit No. WY-0034207) and the manganese concentrations do generally correlate with sulfate concentrations (Figure 42). In addition, unknown organic contaminant releases at the FTA during or after milling are a possibility. The former uranium mill did use an amine-decanol-kerosene solution for uranium solvent extraction (Merritt 1971), but it is unknown if this kerosene solution was ever disposed of in the tailings impoundment. Reducing conditions closer to the Little Wind River are likely due to higher organic carbon contents in the aquifer sediments.

Higher iron concentrations are also an indicator of more reducing conditions. Limited iron measurements are available but were completed at all monitoring wells in 2015. Iron concentrations in 2015 were greater than 0.5 m/L in wells 0853 through 0860, which defines the same three reducing zones discussed above. The highest iron and manganese concentrations in 2015 were from wells 0859 and 0860, both completed in the FTA and downgradient of the Plant retention ponds. Wells 0859 and 0860 are multilevel wells with three ports. As part of ongoing work (Section 7.0), data from those locations in June 2021 indicate reducing conditions increase with depth. For well 0859, iron concentrations increase from 1.6 to 8.4 mg/L with depth and manganese concentrations increase from 0.35 mg/L to 1.9 mg/L. Likewise, for well 860, iron and manganese concentrations increase from < 0.0005 mg/L for both, to 4.7 and 1.6 mg/L, respectively. These data likely reflect precipitation infiltration and the top of the water table experiencing oxygen influx. DO and ORP measurements at the top port of well 0860 were

2.0 mg/L and 130 mV (slightly oxic conditions). These data indicate the potential for the precipitation of iron and manganese oxyhydroxides at the top of the water table.

Figure 41. Manganese from 2012/2015 Data

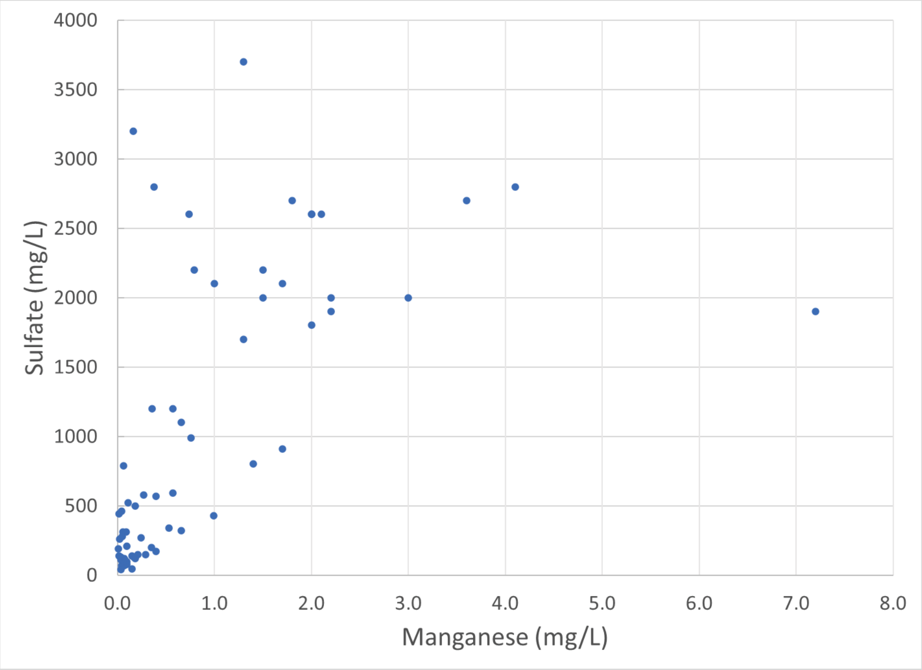


Figure 42. 2012/2015 Manganese Versus Sulfate for Transects 01 Through 06

5.5 Other Major Cations and Anions

In general, all the major cations and anions increase going toward the Little Wind River. The major difference from the natural system compared to anthropogenic inputs are a large contribution of sodium and sulfate, plus calcium to a lesser extent (Table 4 through Table 7 and Figure 40). Sodium discharge at the Plant is a possibility as outfall concentrations at well 0749 have been as high as 2700 mg/L in 1995, albeit current concentrations are much lower (190 mg/L in 2019, Table 4). At two boreholes in the FTA (0859 and 0860), sodium concentrations are elevated in the unsaturated zone compared to the saturated zone (DOE 2016), but are not above background concentrations. Current sodium concentrations at wells 0859 and 0860 (Table 5) continue to be elevated above background (Table 7).

Higher sodium and sulfate concentrations near the Little Wind River are due to the dissolution of sodium sulfate salts in the unsaturated zone. Most of the sodium and sulfate in the unsaturated zone near the river likely originated from the mill site, either due to tailings disposal or Plant discharge water. Likewise, the increasing calcium in groundwater near the river is likely due to evaporative concentration of calcium that was originally produced by the calcite dissolution that buffered the low-pH tailings fluids. Currently, additional calcium is produced by excess calcium from the Plant outfall water and gypsum dissolution at the FTA.

5.6 Influences on Uranium and Molybdenum Mobility

5.6.1 Uranium

PHREEQC calculations were completed on all the temporary piezometer transects using the measured ORP to calculate pe. Using the phreeqcU_V.dat database (Appendix C), precipitation of uraninite was not indicated. Thus, the main mobility control for uranium appears to be sorption, albeit incorporation into precipitated minerals (e.g., gypsum) below the FTA is also a possibility. Uranium sorption can be controlled by complexation in solution (less sorption) and different solid-phase mineralogy, such as more iron/manganese oxyhydroxides, or organic carbon (more sorption). Changes in pH could influence uranium sorption, if current conditions were altered. Likewise, changes in redox conditions might change uranium sorption, but this is an area of ongoing research.

Additional uranium complexation and mobility is enhanced by the addition of calcium, magnesium, and bicarbonate (Dong and Brooks 2006). Based on the above discussions, the addition of calcium and magnesium downgradient of the Plant and the addition of calcium, magnesium, and bicarbonate heading toward the Little Wind River (Figure 40) needs to be considered. Based on the PHREEQC output, the most abundant uranium complexes occur with calcium, magnesium, and carbonate with a very small amount of uranyl sulfate complexes (5 orders of magnitude less). Calcium, sodium, and magnesium bicarbonate complexes are indicted, and may compete for uranium bicarbonate complexation.

On the solid phase, greater amounts of iron and manganese precipitation as iron/manganese (oxyhydr)oxide minerals can limit mobility. Iron and manganese likely precipitated below and downgradient of the former tailings, but the amount of existing precipitates is unknown. With the identified reducing conditions within the plume, these precipitates may have already dissolved, but could be reprecipitated at the top of the water table. High solid-phase organic carbon content in the surficial aquifer have been identified at the riverbank, the oxbow lake, and at well 0855 (DOE 2016) with elevated uranium concentrations.

Highlight Box 9: Summary of Uranium and Molybdenum Mobility Controls

Uranium: Mobility could be influenced by prior mineral precipitation below the FTA (incorporation into gypsum or sorption, or both, to iron/manganese oxyhydroxides). Reducing conditions starting at the head of the plume and near the Little Wind River do not appear to influence uranium mobility. Main mobility control is likely sorption in the saturated zone and retention in the unsaturated zone near the river upon evapotranspiration.

Molybdenum: Mobility in the saturated zone is likely controlled by the precipitation of powellite. Dissolution of powellite may be limited by high calcium concentration from the Plant outfall and possible gypsum dissolution. Retention occurs in the unsaturated zone near the river upon evapotranspiration. Sorption in the saturated zone is likely based on the literature.

Quantification of uranium and molybdenum fate and transport will require a reactive transport model.

Evaluating the quantitative interplay between groundwater and solid-phase geochemistry is beyond the scope of this report but will need to be included in any future site reactive transport models. However, changing site conditions in the future should be considered, such as discontinued release of calcium at the Plant outfall that would create conditions favorable to gypsum dissolution under the FTA. Once gypsum is dissolved, calcium concentrations would decrease, and uranium mobility might also decrease. Similarly, Plant outfall changes could reduce the groundwater oxygen demand and possibly precipitate iron and manganese if slightly more oxic conditions occur, which could also decrease uranium mobility. Thorough reactive transport modeling using various scenarios will be needed to test the interplay from these possible geochemical interactions.

5.6.2 Molybdenum

Based on information in Smedley and Kinniburgh (2017) for molybdenum under oxic conditions, the current major control on molybdenum at the Site is likely sorption of the molybdate anion onto iron, manganese, and aluminum oxides and organic matter, with sorption affinity varying with pH. The lack of oxygen at the Site is not considered enough to change molybdenum sorption controls, but this has not been evaluated. In fact, the minteq.v4.dat database with PHREEQC does not include the reduced molybdenum (IV) species, so potential molybdenum sulfide precipitation could not be determined.

Given saturation indices of powellite near equilibrium (Table 5 and Table 6) and the reduced molybdenum mobility compared to uranium in 1983 (Section 3.4), the precipitation of powellite when the tailings impoundment existed seems reasonable. Mineralogic analyses to detect powellite have not been done. Conlan et al. (2012) indicated that batch experiments of acid producing mine waste did produce powellite and reduced molybdenum concentrations in the presence of calcite, albeit kinetically limited.

Molybdenum mobility is further evaluated with data from Site column studies (Section 7.0). Overall, any future changes in Site conditions must be considered carefully because (1) increases in pH could mobilize sorbed molybdate, which is reversed from the uranyl cation; (2) more oxidizing conditions that precipitate iron/manganese oxides could increase molybdenum sorption (similar to uranium); and (3) reduced calcium concentrations could create conditions more favorable to powellite dissolution. The current high calcium concentrations from the Plant outfall and possible gypsum dissolution are potentially suppressing the dissolution of powellite with calcium as a common cation. Like uranium, thorough reactive transport modeling using various scenarios will be needed to test the interplay from these possible geochemical interactions. However, finding the necessary thermodynamic data for molybdenum could be challenging.

6.0 Column Studies

6.1 Solid-Phase Sample Locations and Objectives

Column testing was conducted in response to the CSM update and data gaps identified in (DOE 2016). Column tests were conducted on 22 samples collected from eight locations to better constrain the geochemical mechanisms and release rates of contaminant transfer from sediment to groundwater and to see how different geochemical conditions affect these release processes. Sediment samples used for the column testing were collected from Site background locations, including from outside of the uranium and molybdenum plumes (boreholes 0852, 0880, 0882, and 0884, see Figure 43), a location near the start of the uranium plume at the FTA (borehole 0859, see Figure 44), and within the uranium plume at the SSMA near the Little Wind River (boreholes 0855, 0856, and 0858, see Figure 44). Use of solid-phase material for column testing was selected to quantitatively test different zones within and outside of the contaminant plumes to verify or update the CSM and use the resulting data to estimate natural flushing times. Additional geochemical modeling of the column data is planned to provide data for input parameters in a site reactive transport model but is beyond the scope of this report. Sample depths, material types, influent water types, and test objectives for each column are shown in Table 8.

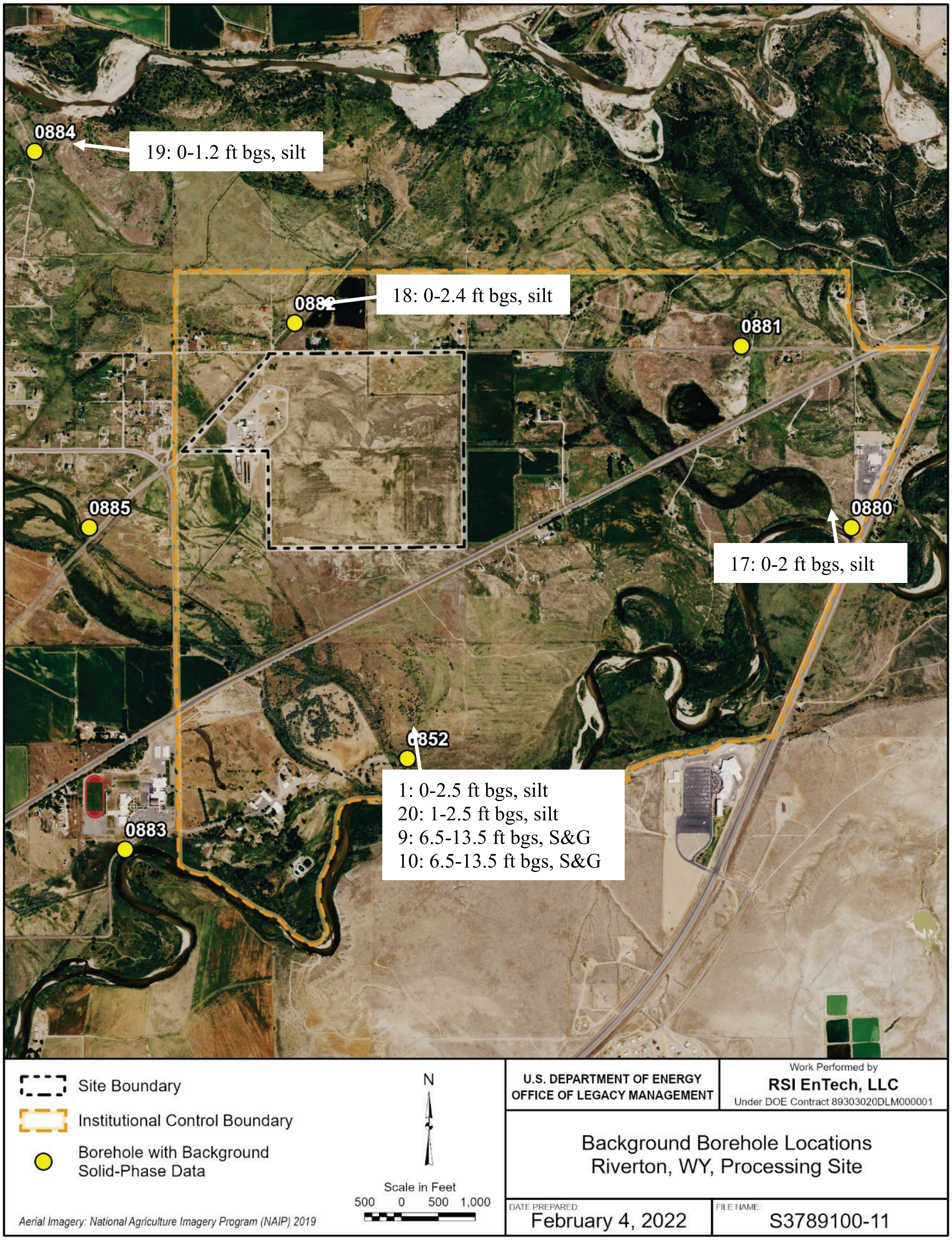
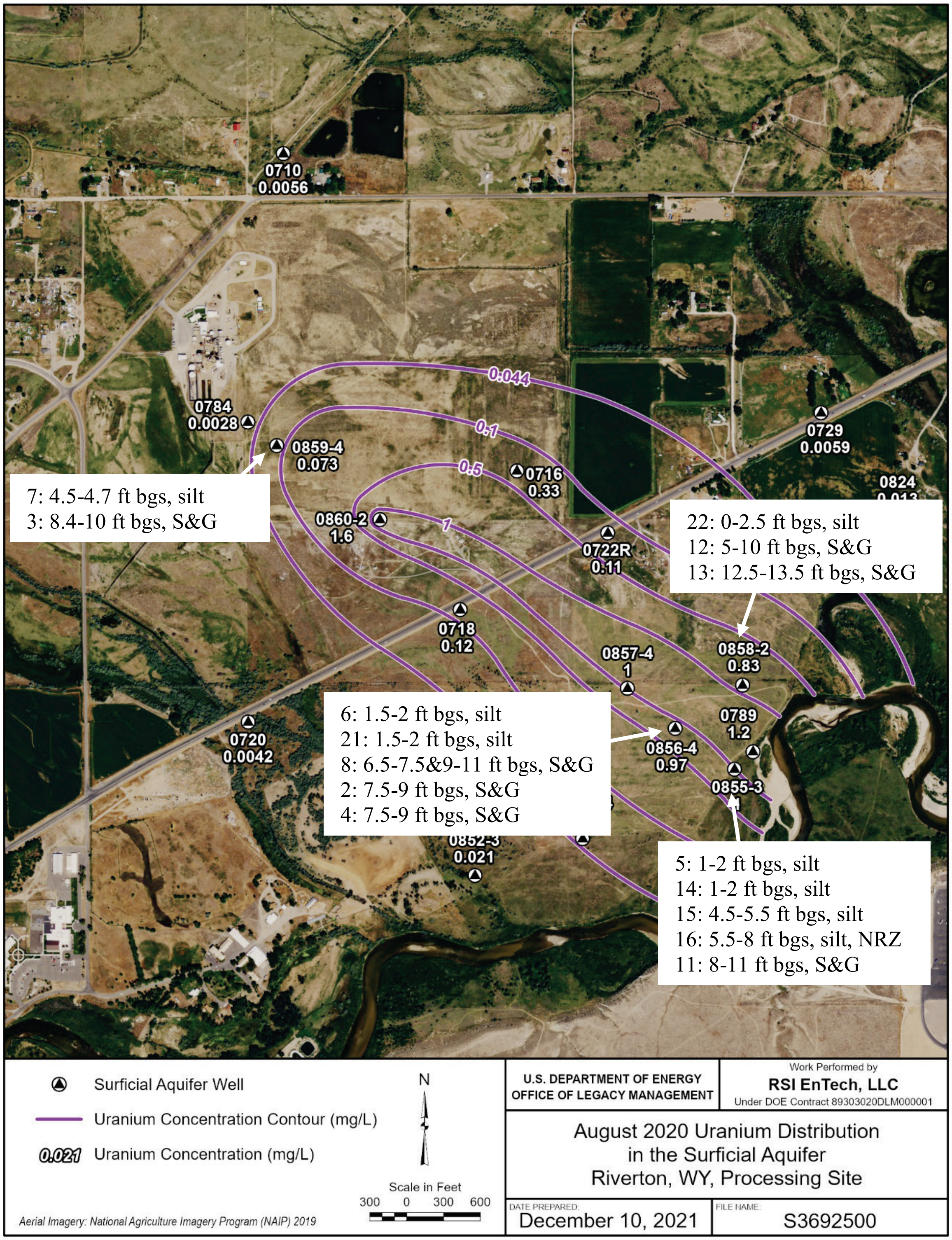


Figure 43. Locations with background sediments. Sediments used in column testing are indicated with column numbers listed on the left from shallowest to deepest for each location. Sample depth and media type are listed on the right.



7: 4.5-4.7 ft bgs, silt
3: 8.4-10 ft bgs, S&G

22: 0-2.5 ft bgs, silt
12: 5-10 ft bgs, S&G
13: 12.5-13.5 ft bgs, S&G

6: 1.5-2 ft bgs, silt
21: 1.5-2 ft bgs, silt
8: 6.5-7.5&9-11 ft bgs, S&G
2: 7.5-9 ft bgs, S&G
4: 7.5-9 ft bgs, S&G

5: 1-2 ft bgs, silt
14: 1-2 ft bgs, silt
15: 4.5-5.5 ft bgs, silt
16: 5.5-8 ft bgs, silt, NRZ
11: 8-11 ft bgs, S&G

U.S. DEPARTMENT OF ENERGY
OFFICE OF LEGACY MANAGEMENT

Work Performed by
RSI EnTech, LLC
Under DOE Contract 89303020DLM000001

August 2020 Uranium Distribution
in the Surficial Aquifer
Riverton, WY, Processing Site

DATE PREPARED:
December 10, 2021

FILE NAME:
S3692500

Figure 44. Locations with sediments used in column testing that are within the contaminant plumes at the FTA and SSMA. Column numbers are listed on the left from shallowest to deepest for each location. Sample depth and media type are listed on the right.

Table 8. Column Testing Summary

Column Number	Borehole ID	Sample Depth (feet bgs)	Area	Material	Influent Waters	U (mg/kg)	Max. U in Effluent (mg/L)	Mo (mg/kg)	Max. Mo in Effluent (mg/L)	Test Objective
1	852	1-2.5	BG	Silt	DI	1.2	0.040	0.16	0.10	Leaching of background silt
20	852	1-2.5	BG	Silt	Acidic DI	1.2	0.070	0.16	0.020	Repeat of column 1 with added acidity
17	880	0-2	BG	Silt	Acidic DI	2.4	0.023	0.26	0.070	Leaching of background silt
18	882	0-2.4	BG	Silt	Acidic DI	2.7	0.25	0.58	0.36	Leaching of background silt
19	884	0-1.2	BG	Silt	Acidic DI	1.3	0.10	0.21	0.13	Leaching of background silt
9	852	6.5-13.5	BG	S&G	710	0.62	0.051	0.26	0.12	Leaching of background S&G with BG GW
10	852	6.5-13.5	BG	S&G	856-4, 710	0.62	n/a	0.26	n/a	Test desorption, add contamination and then BG GW
7	859	4.5-4.7	FTA	Silt	DI	1.9	0.072	1.9	1.00	Leaching for FTA unsaturated zone, bottom of the fill material
3	859	8.4-10	FTA	S&G	DI, 710	4.6	0.51	3.1	1.10	Test FTA uranium release with DI and background GW
6	856	1.5-2	SSMA	Silt	DI	7.3	0.19	0.70	0.98	Leaching of contaminated silt
21	856	1.5-2	SSMA	Silt	Acidic DI	7.3	0.15	0.70	0.90	Repeat of column 6 with added acidity
22	858	0-2.5	SSMA	Silt	Acidic DI	5.4	0.93	1.9	3.5	Leaching of contaminated silt
5	855	1-2	SSMA	Silt	DI	4.1	0.86	0.35	0.42	Leaching of contaminated silt
14	855	1-2	SSMA	Silt	Acidic DI	4.1	0.63	0.35	0.37	Repeat of column 5 with added acidity
15	855	4.5-5.5	SSMA	Silt	Acidic DI	4.1	0.74	0.48	0.49	Leach silt above NRZ
16	855	5.5-8	SSMA	Silt	Acidic DI	14	2.4	1.1	1.6	Leach NRZ material
8	856	6.5-7.5&9-11	SSMA	S&G	710	0.60	0.31	0.54	0.15	Test desorption in contaminant plume near river
11	855	8-11	SSMA	S&G	710	3.5	5.8	0.37	0.96	Test desorption in contaminant plume near river
12	858	5-10	SSMA	S&G	710	1.2	1.1	3.6	1.9	Test desorption in contaminant plume near river

Table 8. Column Testing Summary (continued)

Column Number	Borehole ID	Sample Depth (feet bgs)	Area	Material	Influent Waters	U (mg/kg)	Max. U in Effluent (mg/L)	Mo (mg/kg)	Max. Mo in Effluent (mg/L)	Test Objective
13	858	12.5-13.5	SSMA	S&G	710	0.72	0.39	0.48	0.45	Test desorption in contaminant plume near river
2	856	7.5-9	SSMA	S&G	DI, 856-4, 710	0.62	0.14	0.67	0.39	Test sorption/desorption on S&G within the plume
4	856	7.5-9	SSMA	S&G	856-4, 710	0.62	n/a	0.67	n/a	Same as column 2, but start with contaminated water

Abbreviations:
710 = background well
BG = background
DI = deionized water
FTA = former tailings area
GW = groundwater
Mo = molybdenum
n/a = not applicable
NRZ = naturally reduced zone
U = uranium

6.2 Methods

6.2.1 Column Setup and Testing Procedures

For use in column testing, core sediment was air dried in aluminum pans until all samples had no observable moisture in them (minimum of 7 days). Once dry, the sediments were sieved and the fraction that passed the No. 10 sieve (<2 millimeters [mm]) was collected separately for testing.

Columns were built from plastic and plexiglass with a 2.5-inch inside diameter and 18 inches in length. They were dry-packed in lifts of approximately 2 inches, with tamping of the material between lifts to a height of about 9 inches, depending on the amount of available material. The bottom of each column had a mesh filter disk that holds the sediment in the column but allows water to enter the column. A piece of mesh was placed on top of the soil with approximately 2.5- inch of acid-washed 5 mm glass beads on top of the mesh to help hold the sediment in place. A sample collection tube was then inserted into the glass beads to the top surface of the sediment and water samples were removed from the column via a syringe. The final volume, mass, and density of sediment in each column is provided in Appendix D with each individual column file.

Flow was delivered via laboratory peristaltic pumps (Masterflex L/S) into the bottom of the columns at approximately 1 to 3 milliliters per minute. Enough influent water was pumped into the column to saturate the sediment (one pore volume [PV]), and then the saturated column sat for 24 hours. The next day, another PV of water was introduced into the column, pushing the prior PV out of the sediment. This effluent PV was collected, filtered, and analyzed. Approximately one PV of influent water and collected effluent was cycled once every 24 hours until the column test was completed. The types of influent water used included deionized (DI) water, acidic DI water (addition of 0.001 M HCl), Site background groundwater (well 0710), and Site contaminated groundwater (well 0856-4). Acidic DI water was used on some column tests to lower the column pH from that determined in tests with straight DI water addition, to get closer to field conditions.

Influent water types for each column test are listed in Table 8. All influent waters were exposed to the atmosphere and were considered oxic when analyzed and during column testing. Analytical data for each type of influent water are shown in Table 9 and are also included in the data file in Appendix D for each column test. Influent groundwaters were collected on two different dates and did have some significant geochemical differences (Table 9). Analyses were not completed for DI water, which was assumed to have minimal dissolved constituents and an equilibrium pH of near 5.5. When using the different groundwaters as influent waters, that water was pumped from a sealed collapsible container to minimize degassing. However, the pH in the influent containers were periodically checked and carbon dioxide gas was bubbled in as necessary to maintain the pH within +/- 0.2 units of the pH when the water was collected.

All samples were collected in one aliquot and filtered through a 0.45-micron filter. The filtered sample was then split into two aliquots. One aliquot was immediately analyzed in the laboratory for pH, temperature, specific conductance, and alkalinity via titration. The remaining portion of this aliquot was kept at 4 degrees °C for subsequent analyses for anions by ion chromatography (ThermoFisher Aquion) and dissolved organic carbon (DOC) (Shimadzu Total Organic Carbon-L). The other aliquot was acidified to pH <2 with nitric acid and subsequently analyzed for cations and metals via inductively couple plasma—optical emission spectroscopy

(Perkin Elmer DV7000) and uranium via kinetic phosphorescence (Chemchek KPA-11). The full analyte list includes pH, temperature, specific conductance, alkalinity, DOC, chloride, sulfate, calcium, magnesium, sodium, potassium, iron, manganese, silica, molybdenum, uranium, and vanadium. Analytical procedures followed the LM Grand Junction *Environmental Sciences Laboratory Procedures Manual* (DOE 2021b).

Table 9. Geochemistry of Column Influent Waters (Average of Analyses)

Influent Water Type	pH	Alkalinity (mg/L as $CaCO_3$)	DOC (mg/L)	Cl (mg/L)	SO_4 (mg/L)	U (mg/L)	Mo (mg/L)	Ca (mg/L)	Na (mg/L)	K (mg/L)	Mn (mg/L)
0856-4 Contaminated Site Water (from 5/2016)	7.3	440	35	460	6200	2.7	0.41	490	2100	18	1.3
0856-4 Contaminated Site Water (from 8/2016)	7.8	510	71	1100	11,000	5.7	0.82	460	4200	3.5	3.0
0710 Background Site Water (from 4/2016)	7.7	300	10	130	1000	0.029	<0.020	360	160	5.5	0.010
0710 Background Site Water (from 9/2016)	7.9	210	3.5	33	260	0.0089	<0.020	120	73	2.9	<0.010
Acidic Deionized Water	2.9	n/a	n/a	32	<0.50	<0.002	<0.010	14	13	0.090	<0.010

Abbreviations:
Ca = calcium
$CaCO_3$ = calcium carbonate
Cl = chloride
K = potassium
Mn = manganese
Mo = molybdenum
Na = sodium
n/a = not available
SO_4 = sulfate
U = uranium

6.2.2 Geochemical Modeling

Geochemical modeling was performed using the modeling program PHREEQC (Parkhurst and Appelo 2013) to determine mineral precipitation and dissolution potential (i.e., SIs) within the columns. All column PHREEQC modeling used the minteq.v4.dat (Appendix C) database for the inclusion of molybdenum thermodynamics. Uranium minerals in the columns were not directly evaluated (but are included in the minteq.v4.dat database) since the column influent waters were oxidized and the Site does not have significant vanadium concentrations. Thus, typical uranium minerals such as uraninite and carnotite are not likely to precipitate in the column studies.

6.3 Results

Column testing results are provided in Appendix D with a separate folder for each column test. Each folder has an Excel file specific to each column test with (1) a data tab, (2) tabs with graphs of each analyte, (3) a tab that combines graphs with multiple analytes, and (4) tabs with graphs for mineral and carbon dioxide SIs. In addition to the main Excel file, each folder also has the PHREEQC input files used for calculating the SIs (column # SI.pqi). Additional folders are provided that have graphs in Excel files to compare multiple column results together. The discussions below focus on uranium, molybdenum, and sulfate in the column effluent with separate discussions on silt versus S&G materials.

The silt material was collected from the unsaturated zone (except for column 16) and leached with DI or acidic DI water. The S&G material was collected from the saturated zone and was leached with background groundwater from well 0710. S&G columns 2 and 3 were first leached with DI water and S&G columns 2, 4, and 10 also used a contaminated groundwater (well 0856-4) with the influent series (Table 8).

6.3.1 Silt Columns

Background silt was collected at seven locations (boreholes 0880 through 0885 and borehole/well 0852, Figure 43) with column tests completed at four of those locations (boreholes 0880, 0882, 0884, and 0852, see Table 8 and Figure 43). The median uranium and molybdenum concentrations on the background silt material are 1.5 and 0.23 mg/kg, respectively. For comparison, the median uranium and molybdenum concentrations on the background S&G in borehole 0852 are 0.59 and 0.14 mg/kg, respectively. Molybdenum is not naturally present at the Site in significant concentrations and is a good indicator of a mill-related influence. In fact, the above solid-phase background concentrations include estimated concentrations for samples that were below 0.19 mg/kg molybdenum (thus, were below the typical 0.20 mg/kg detection limit but still reported). Overall, uranium is more detectable above detection limits in background samples and has solid-phase concentrations in the silt that are higher than in the S&G.

Columns 1, 5, and 6 were leached with DI water and repeated with acidic DI (columns 20, 14, and 21) (Table 8), giving similar results (Appendix D). For consistency, only the acidic DI columns are discussed further. Maximum leaching of uranium and molybdenum in the background silt columns does indicate the potential to release these constituents above their respective groundwater standards for a few PVs, but at much lower concentrations than the contaminated silt at the SSMA (Figure 45, Figure 46, Table 8). One silt column was completed with FTA sediments at 4.5 to 4.7 ft bgs (column 7). Sediments for column 7 were selected because the boring log indicated these sediments were likely at the bottom of the fill material (silt with up to 20% clay) in the unsaturated zone (DOE 2016) and would represent leaching through the fill. Solid-phase uranium in column 7 was within the range of background silt, but with elevated molybdenum compared to background (Table 8). Thus, column 7 was included as background for uranium (Figure 45) but included with the SSMA silt columns for molybdenum (Figure 46). Molybdenum release in column 7 was not below the 0.10 mg/L standard until PV 8 (Figure 46). The source of this molybdenum is likely mill related, but it is not clear if the column 7 material was native material below the former tailings or fill material that was contaminated by molybdenum wicked up from underlying sediments or the groundwater. The highest water table at this location was 6.2 ft bgs in 2017, which was below the depth of column 7 sediment collection. Visual determination of fill material silt versus native silt from the core material was difficult (author experience).

When comparing background silt columns, column 18 from borehole 0882 stands out as having higher uranium and molybdenum concentrations in the solid phase and higher column effluent concentrations (Table 8, Figure 45 and Figure 46). This location is close to the site boundary (Figure 43), just north of the former mill site and just outside of an area with surface contamination from windblown material identified by radiological measurements above radium standards (see Figure 4-1 in DOE 1998a). Thus, it is possible that this location cannot strictly be considered naturally occurring background. Likewise, the groundwater from the “background” well at this location (0710) can be quite variable (Table 9).

Highlight Box 10: Summary of Results from Silt Columns

Background silt columns can release uranium and molybdenum above standards for a few PVs and naturally accumulates evaporites (like gypsum and sodium sulfates).

FTA silt is difficult to distinguish as fill or native material. One column of FTA silt releases more molybdenum than uranium.

SSMA silt can have an extended release of uranium and molybdenum, but molybdenum flushes to below standards in less PVs. SSMA silt zone NRZ could release uranium and molybdenum with oxidized groundwater, which is unlikely to occur with current conditions.

Overall geochemistry appears to indicate mineral controls by calcite, gypsum, and powellite. Uranium and molybdenum also appear to be controlled by sorption/desorption processes. Additional geochemical modeling and reactive transport modeling will be necessary to fully quantify these processes and their influence on uranium and molybdenum mobility that determines remedy timeframes.

Overall, in the contaminated columns, it is apparent that molybdenum flushes to below standards in fewer PVs than uranium (Figure 45 and Figure 46). In these columns, molybdenum is at or below standards by PV 7; whereas, uranium is not below standards until PV 10 and column 15 does not go below standards even after 14 PVs. Column 22 has the highest maximum molybdenum effluent concentration of 3.5 mg/L with effluent water having near equilibrium conditions with respect to powellite for the first three PVs (SI > -0.20, Appendix D). Molybdenum is flushed to below the 0.10 mg/L standard at PV 8 for column 22 (Figure 46). The solid-phase material for this column has elevated molybdenum concentrations and is from a location with higher molybdenum concentrations in the groundwater (column 22 is from location 0858 which is next to well 0707, Figure 28). The other columns did not indicate the possibility of powellite dissolution (SIs < -0.20). Thus, molybdenum mobility is likely controlled by desorption after powellite is dissolved.

All of the SSMA silt columns are over the uranium plume and indicate significant release of uranium (Figure 45). The initial drop in uranium effluent concentrations at PV 2 for these columns (Figure 45) corresponds to lower initial alkalinity concentrations (Appendix D) which may decrease the desorption of uranium. Alkalinity may be suppressed by the presence of gypsum (discussed below), as the common cation affect with calcium may suppress the dissolution of calcite. For all of the SSMA silt columns, PV 1 has gypsum SIs near zero (Appendix D). Column 21 has a lower maximum uranium release concentration, but effluent concentrations do not consistently go below the standard until PV 10 (Figure 45). The high pH range in this column of 8.6 to 9.6 may influence the uranium release rates (Appendix D) or the uranium may be in a less soluble phase. Other columns typically have an effluent pH of 7.2 to 8.0.

In contrast to uranium and molybdenum, significant sulfate release occurs in background silt columns as well as the FTA and SSMA silt columns (Figure 47). Sulfate concentration trends are similar to calcium trends (Appendix D). These data indicate that the naturally occurring silt likely concentrates gypsum that can be released during recharge events. However, sulfate release at the SSMA is near 25,000 mg/L at PV 1 compared to near 10,000 mg/L for the background and FTA silt column (Figure 47 and Appendix D). Sulfate is flushed to near or below background groundwater concentrations within three PVs (Figure 47) if the presence of gypsum is not indicated (gypsum is indicated by saturation indices near zero along with elevated calcium and sulfate). When the gypsum SI is near zero, calcium concentrations remain nearly constant (Appendix D). Gypsum in background columns 7 (FTA 0859) and 19 (location 0884) last for 4 PVs. Gypsum in SSMA silt columns 14, 15, and 22 last for 14, 6, and 4 PVs, respectively. The end of gypsum dissolution was identified as a gypsum SI less than -0.25, a decrease in calcium (Appendix D), and a decrease in sulfate (Figure 47).

Column 16 (0855: 5.5–8 ft) is not included in the discussion above on the other SSMA unsaturated zone silt, as this column material is from the saturated zone. Column 16 material is from a naturally reduced zone (NRZ) with high silt and organic carbon content. The elevated uranium and molybdenum concentrations in this NRZ are likely related to the organic carbon. The previous evaluation of the reducing conditions in the groundwater with transect data did not indicate the potential for uraninite precipitation and recent work indicates that uranium (IV) can sorb to organic carbon under anoxic conditions (Bone et al. 2017). The NRZ material is generally below the top of the water table, so column 16 would only represent an extreme event with influx of oxidized water due to a low river stage followed by a high river stage event. Even after an extreme event, it is likely that anoxic conditions would be reestablished relatively quickly. With the continuous addition of oxic, acidic DI water, column 16 is not representative of typical field conditions. In any case, column 16 does release uranium and molybdenum at high concentrations (2.4 and 1.6 mg/L, respectively), likely due to desorption. However, molybdenum is flushed to below the 0.10 mg/L standard by PV 7; whereas, uranium is not flushed to below the 0.044 mg/L standard even when the column test is discontinued at 14 PVs (uranium is 0.15 mg/L). These data appear to indicate stronger sorption of uranium to the organic carbon than occurs for molybdenum under oxidizing conditions.

All of the SSMA unsaturated zone silt columns indicate a potential release of uranium, molybdenum, and sulfate during flooding or other large recharge events. In addition, the first PV on these columns all release high sodium and chloride concentrations (up to 12,000 and 2000 mg/L, respectively). This is indicative of evaporites occurring in the unsaturated zone of the SSMA. Along with the release of high calcium and sulfate concentrations from gypsum or sodium sulfates, this column work confirms a release mechanism by evaporite dissolution for these constituents that are also found in the underlying groundwater (Appendix C).

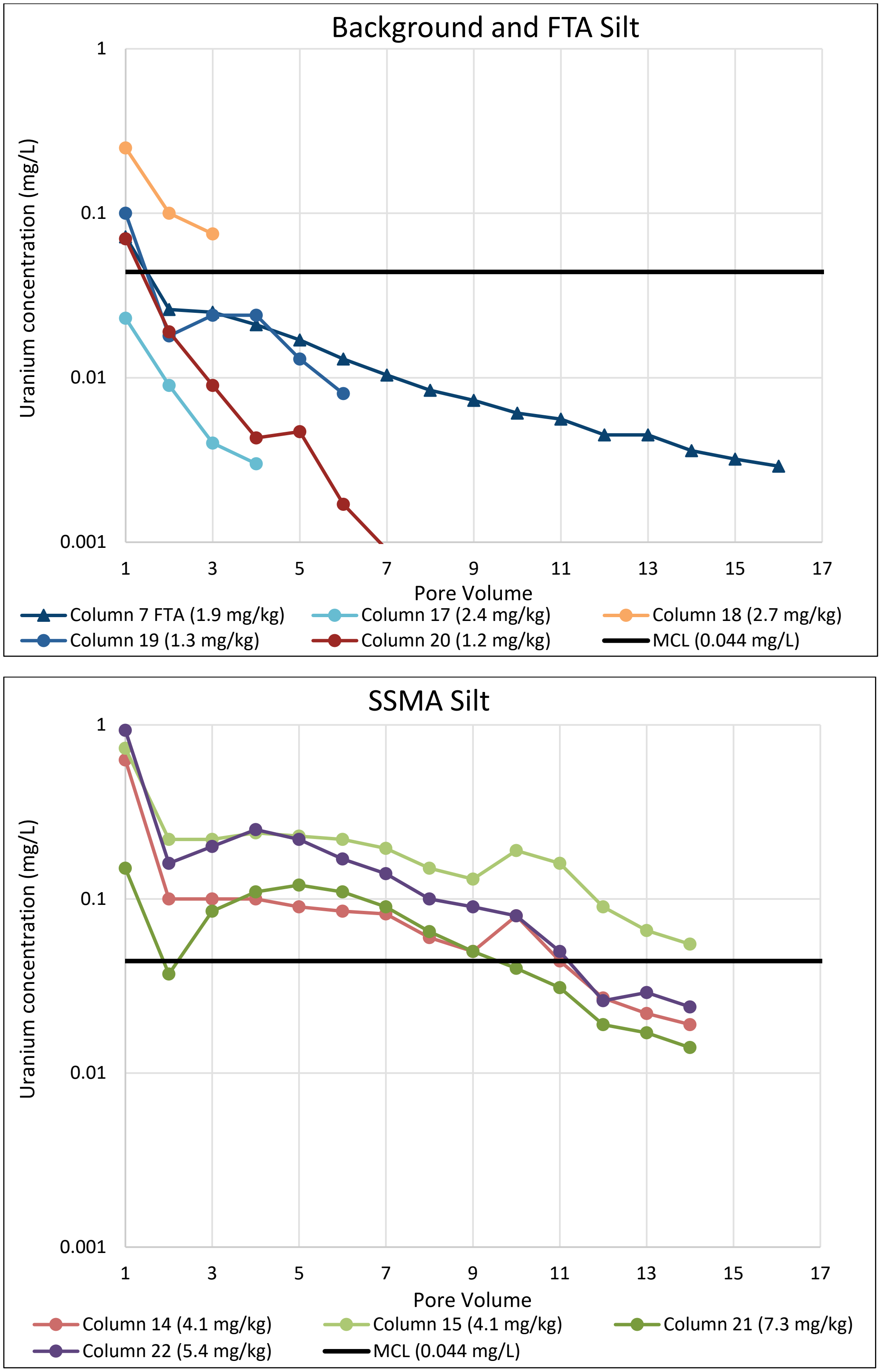


Figure 45. Uranium concentrations in silt columns effluent. Solid-phase uranium concentrations are provided as a reference for each column.

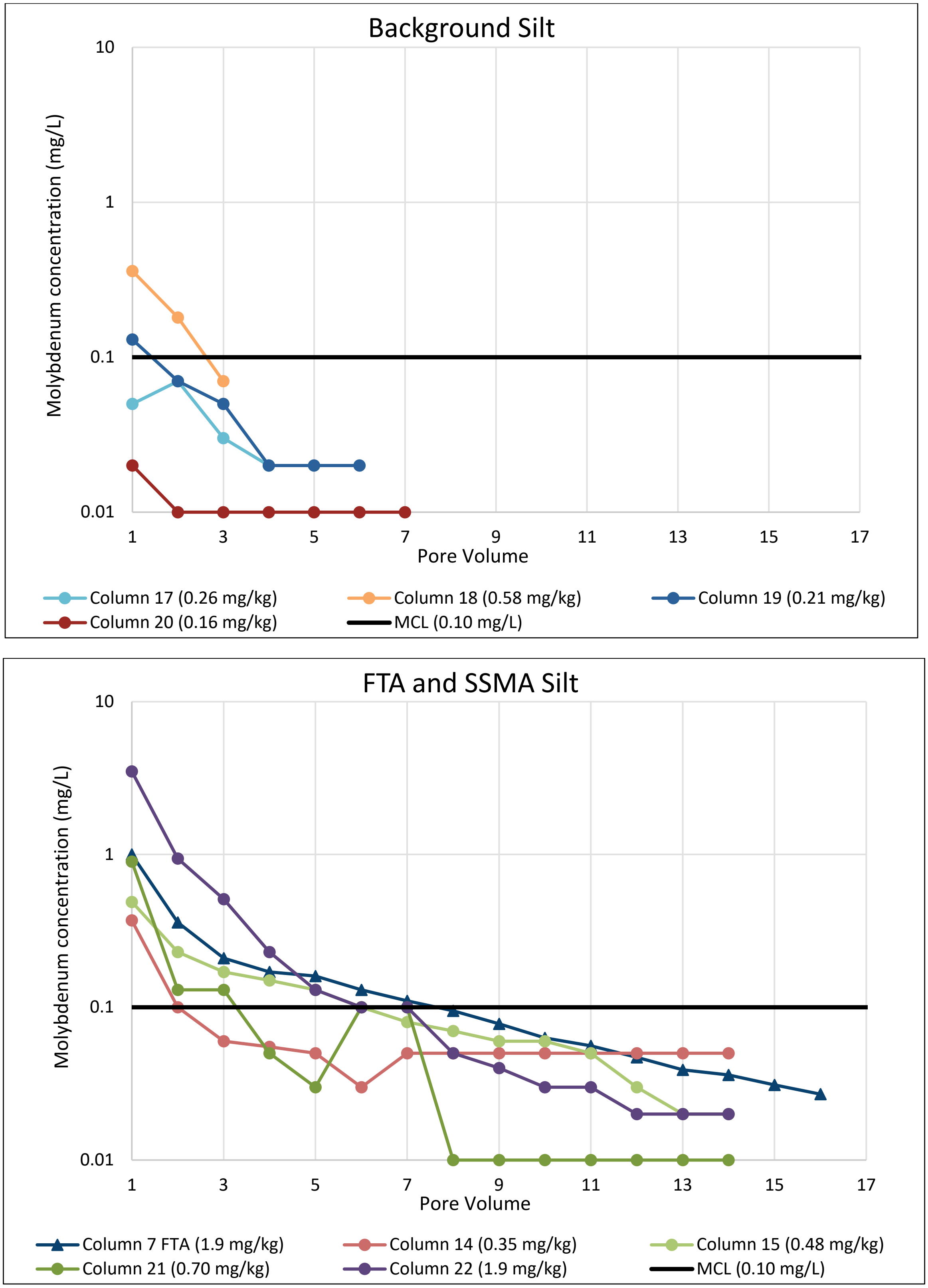
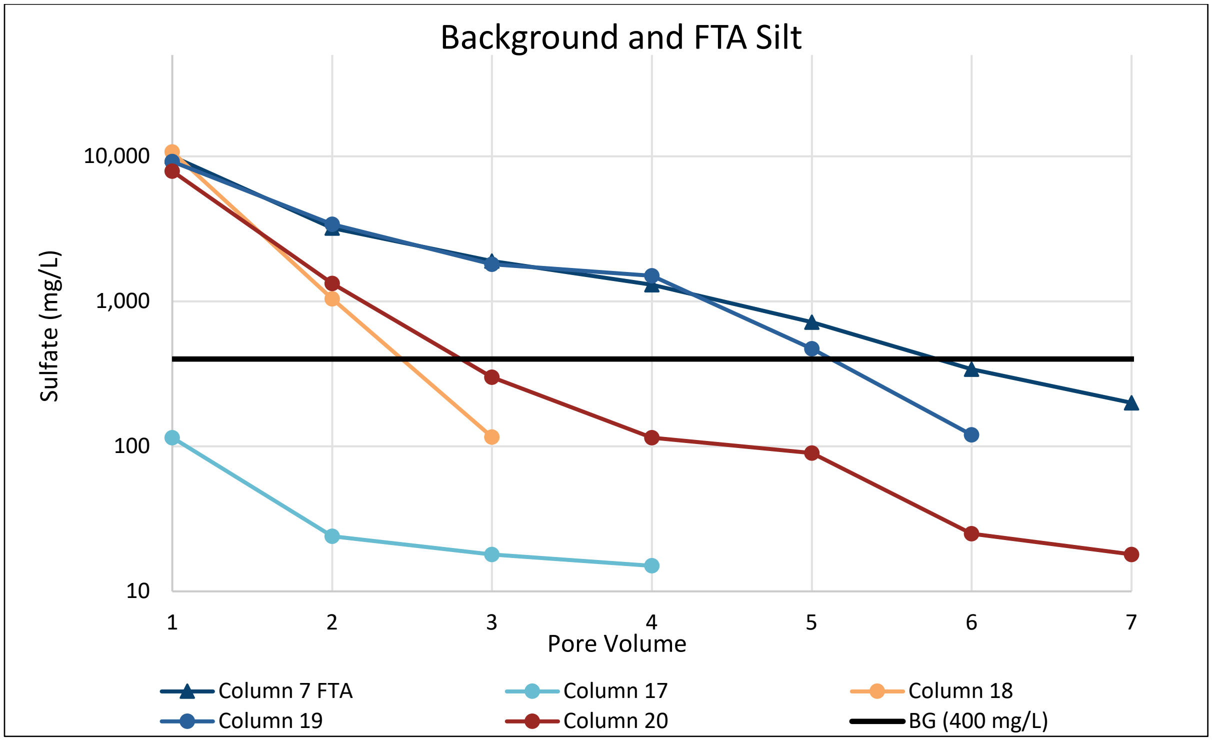


Figure 46. Molybdenum concentrations in silt columns effluent. Solid-phase molybdenum concentrations are provided as a reference for each column.



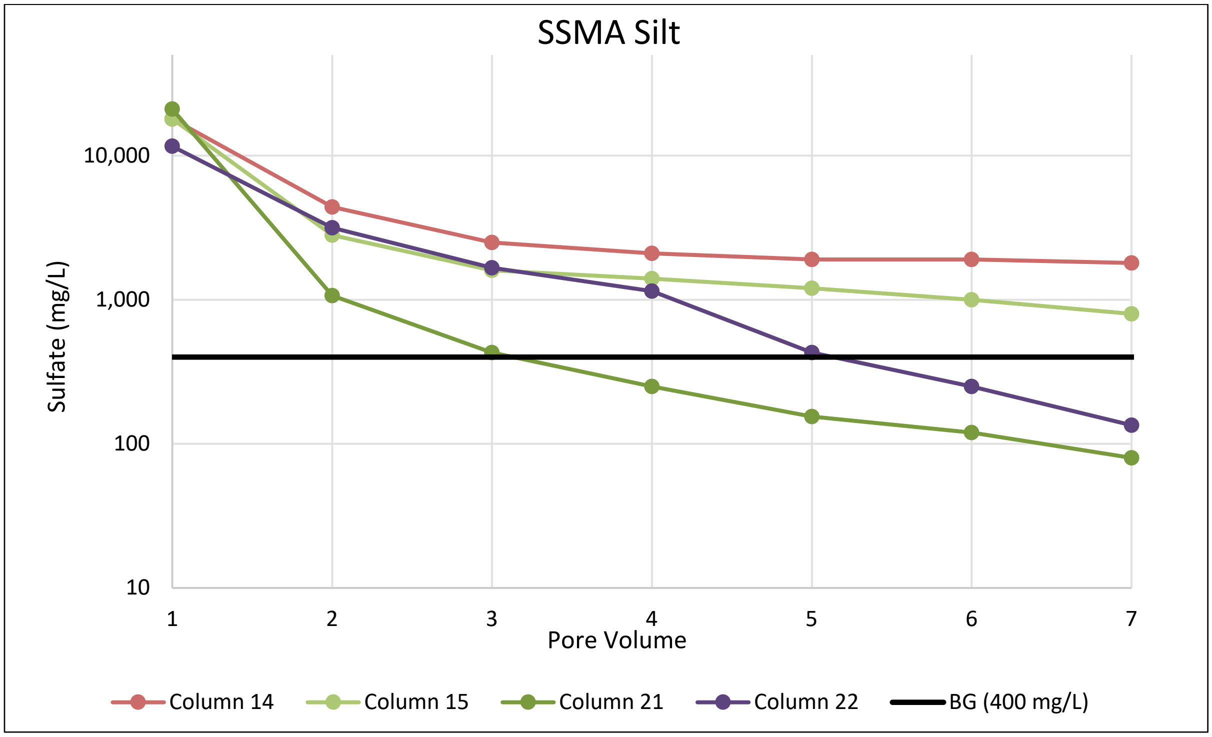


Figure 47. Sulfate Concentrations in Silt Columns Effluent

6.3.2 S&G columns

Columns 2, 4, and 10 were designed to test the sorption and desorption of uranium and molybdenum with the introduction of contaminated plume water (Table 8). These more complex column data will be used with geochemical modeling to derive sorption parameters for a site reactive transport model and are not discussed further in this report. In addition, the initial influent for column 3 was DI water for 17 PVs, which was then switched to background groundwater (well 0710). All other S&G columns had well 0710 groundwater as the initial influent.

Column 9 is the only column for testing background S&G (borehole 0852). Borehole 0852 was converted to a monitoring well and is outside of the contaminant plumes (except sulfate). Column 9 indicates that uranium and molybdenum are released in the first two PVs slightly above standards (Figure 48 and Figure 49), albeit almost within an analytical data error range of -10%. The "background" groundwater from well 0710 used for column 9 had a uranium concentration of 0.029 mg/L (Table 9 and Appendix D). Well 0710 is near borehole 0882, which, as previously discussed, may have a small amount of mill-related uranium and molybdenum in the unsaturated zone. Some sulfate is released from column 9, but it quickly flushes and is equivalent to the influent concentration at PV 3 (Figure 50). Sulfate was also relatively high at 1000 mg/L when the water from well 0710 was collected, compared to a typical background value of less than 400 mg/L. At PV 8, column 9 starts to have detectable iron in the effluent and the effluent uranium concentration continues to be lower than the influent uranium concentration of 0.029 mg/L (Figure 48). This potentially indicates stronger sorption with the onset of more reducing conditions within the column.

One column test (column 3) was completed on the S&G at the FTA (location 0859). Sediments for column 3 were selected because they had a slight petrochemical odor and had elevated solid-phase uranium and molybdenum. For column 3, elevated solid-phase uranium and molybdenum correspond with elevated releases of uranium and molybdenum to the column effluent (Table 8). Column 3 effluent stands out as having a relatively constant uranium release (Figure 48) and a slowly declining molybdenum release (Figure 49). Throughout this column test, calcium and sulfate concentrations were near 650 and 1500 mg/L respectively (Appendix D and Figure 50), which correspond to equilibrium with gypsum (SI near zero). With the DI influent, uranium in the column effluent did not go below 0.12 mg/L throughout the test (Figure 48) and molybdenum did not go below 0.10 mg/L until PV 17 (Figure 49). Uranium concentrations increased at PV 18 with the introduction of background ground (Appendix D) and that portion of the column test is used to calculate uranium flushing rates (Section 6.3.3.1). Groundwater uranium concentrations at well 0859-4 from 2015 through 2020 have been very similar to the column effluent with an average concentration of 0.11 mg/L uranium and groundwater molybdenum concentrations continue to slowly decline (in 2020 the concentration of molybdenum was 0.062 mg/L in well 0859-4). In 2019, the calcium concentration in 0859-4 was 460 mg/L, sulfate was 2,400 mg/L and the gypsum SI was -0.012.

Additional geochemical modeling of column 3 will help with the understanding of the complex interplay of the geochemistry. However, for the first four PVs, the SIs are near zero (+/- 0.25) for calcite, gypsum, and powellite, which suggest that these minerals control the geochemistry of column 3 and well 0859 for calcium, sulfate, and molybdenum. No uranium minerals are suggested with the PHREEQC saturation indices, but uranium has the potential to be incorporated into gypsum (Lin et al. 2018). Uranium release in this column is likely controlled by both mineral dissolution and sorption controls. Such controls will need to be considered for sitewide reactive transport modeling, along with incoming groundwater geochemistry from upgradient that can influence the uranium, molybdenum, and sulfate release from the solid phase.

Column 11 consists of S&G at well 0855 below an NRZ silt (column 16). Solid-phase uranium concentrations are elevated (Table 8), presumably due to sorption of uranium on organic carbon related to the overlying NRZ. Solid-phase molybdenum is not elevated (Table 8), but this location is somewhat south of the highest groundwater molybdenum concentrations (Figure 28). The highest uranium release concentrations are seen in column 11 (up to 5.8 mg/L, Figure 48) and molybdenum is flushed faster than uranium to below standards in 5 PVs versus greater than 17 PVs for uranium (Figure 48 and Figure 49). At end of testing, the uranium concentration was 0.13 mg/L (Figure 48). Unlike column 16 where field conditions introducing continuously oxidized groundwater is not likely due to the low hydraulic conductivity of the silty NRZ, the permeable S&G of column 11 could potentially receive oxidized water after a large upgradient recharge event. Thus, column 11 represents a worst-case scenario of uranium and molybdenum release in this area. Iron concentrations increase after PV 7 (Appendix D), which may indicate the onset of reducing conditions within the column.

Highlight Box 11: Summary of Results from S&G Columns

A background S&G column shows minimal potential to release uranium and molybdenum above standards.

FTA S&G columns have an extended release of uranium, molybdenum, and sulfate.

SSMA S&G columns can have extended releases of uranium, molybdenum, and sulfate to varying degrees. This variation can occur with a depth increase of just a few feet or a location difference within the contaminant plumes. “Cleaner” S&G occur with depth and areas with less molybdenum in groundwater.

Like the silt columns, overall geochemistry appears to indicate mineral controls by calcite, gypsum, and powellite. Uranium and molybdenum are also likely controlled by sorption/desorption processes.

Additional geochemical modeling and reactive transport modeling will be necessary to fully quantify these processes and their influence on uranium and molybdenum mobility that determines remedy timeframes.

Columns 8, 12, and 13 are from the SSMA within the contaminant plumes with relatively low solid-phase uranium concentrations. Even with the low solid-phase uranium concentrations, all three columns release uranium above 0.044 mg/L for several PVs (Figure 48). Elevated solid-phase molybdenum occurs in column 12 (Table 8). Sediments from column 12 and 13 are from location 0858 near well 0707 within the center of the molybdenum plume (Figure 28), albeit column 13 sediments were collected slightly deeper than column 12 sediments and have less molybdenum (Table 8). Even though column 13 is from sediments with the uranium and molybdenum plumes, its effluent concentrations are similar to background (column 9) with only slightly more molybdenum released on PV 1 and three PVs (PV 3,4,5) with uranium release above 0.044 mg/L (Figure 48). Like column 3 at the FTA, the SSMA column 12 is supersaturated with respect to calcite and near equilibrium with respect to gypsum for the whole column test, which maintains elevated calcium and sulfate concentrations (Appendix D and

Figure 50). Powellite is near equilibrium through PV 10 and manganese is released up to 19 mg/L with supersaturated conditions for rhodochrosite (Appendix D). Thus, like column 3, additional geochemical modeling will be necessary to better understand the complex interplay of the geochemistry in column 12. Column 8 also indicates gypsum dissolution with elevated calcium and sulfate concentrations (Appendix D and Figure 50). Column 8 has uranium release above 0.044 mg/L for 12 PVs even with solid-phase uranium of only 0.60 mg/kg (Figure 48) and molybdenum release is minimal (Figure 49).

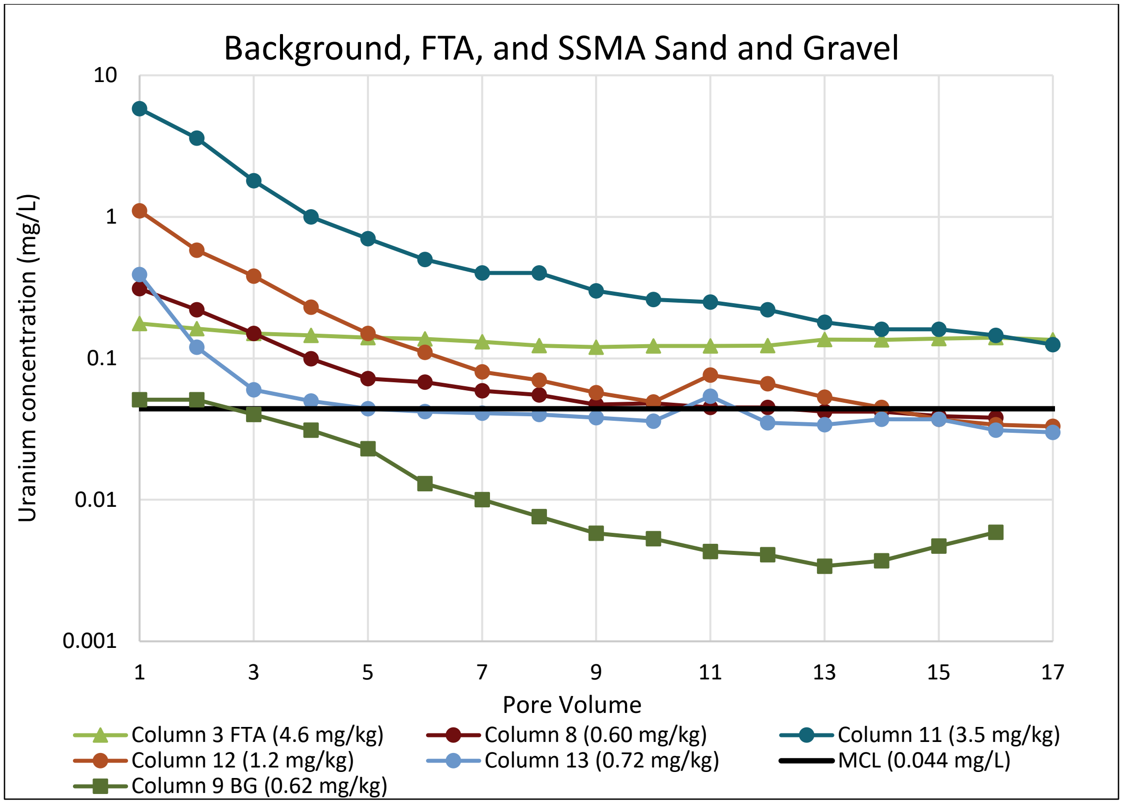


Figure 48. Uranium concentrations in S&G columns effluent. Influent water was from well 0710 which had 0.029 mg/L uranium (except for column 3 with DI influent). Solid-phase uranium concentrations are provided as a reference for each column.

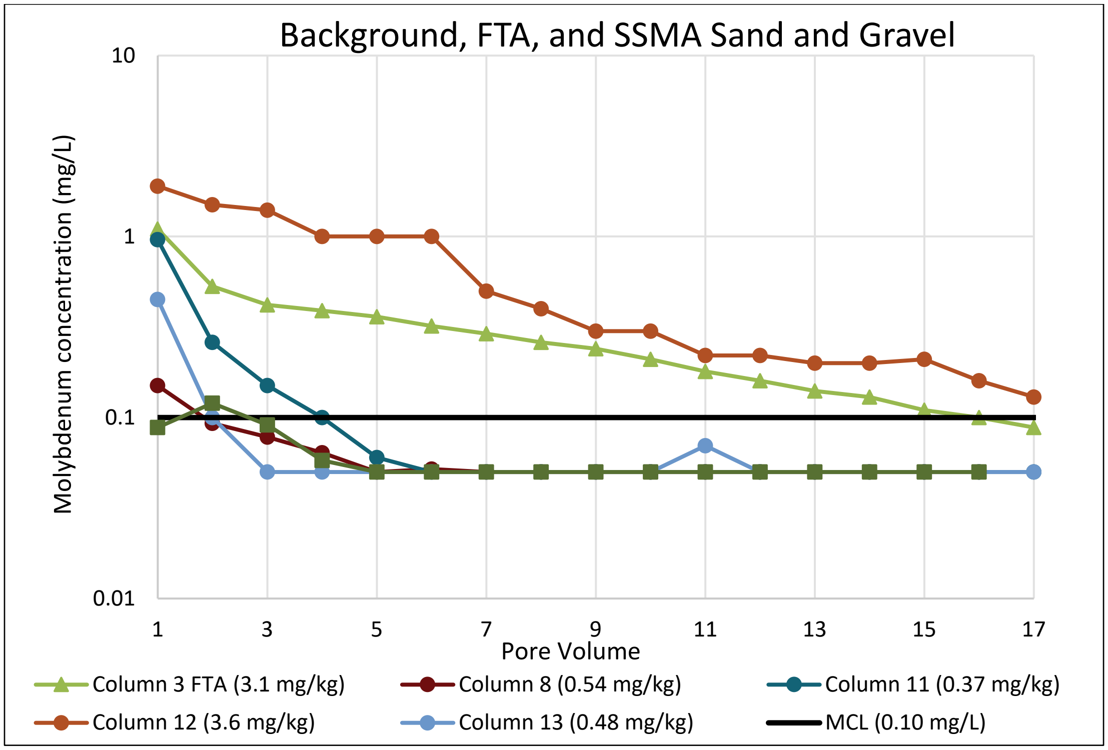


Figure 49. Molybdenum concentrations in S&G columns effluent. Influent water was from well 0710 which had <0.020 mg/L molybdenum (except for column 3 with DI influent). Solid-phase molybdenum concentrations are provided as a reference for each column.

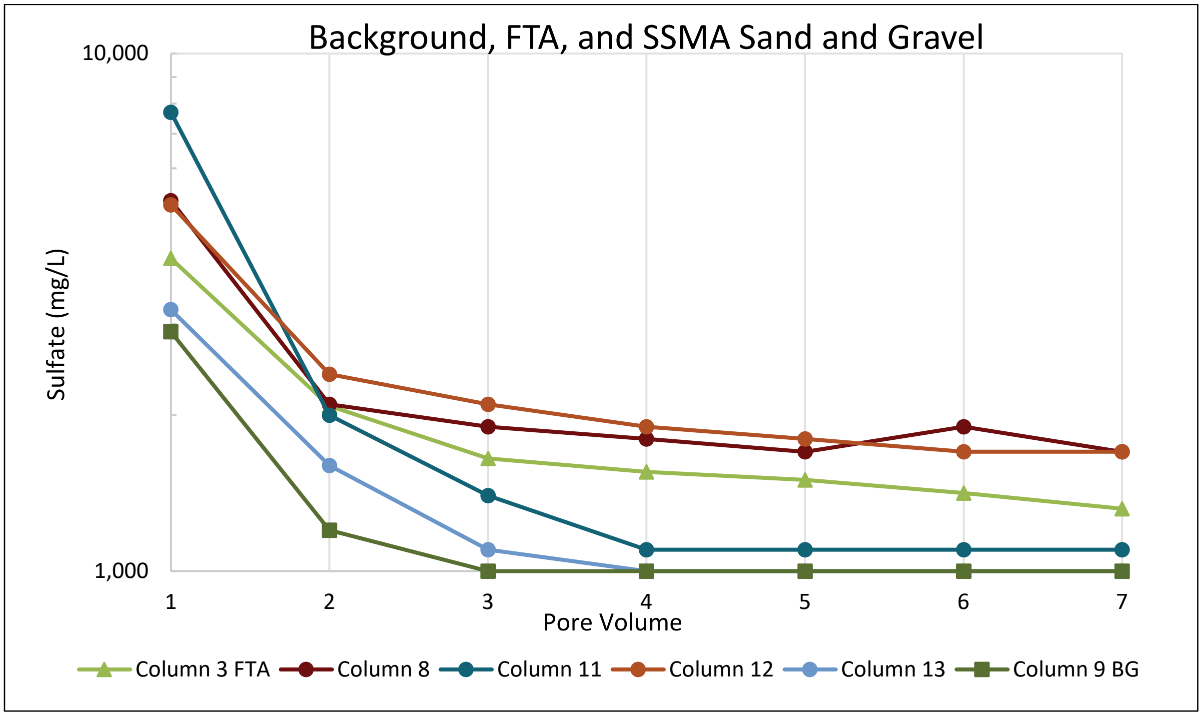


Figure 50. Sulfate concentrations in S&G columns effluent. Influent water was from well 0710 which had 1000 mg/L sulfate (except for column 3 with DI influent). BG = approximate background sulfate concentration.

6.3.3 Estimated flushing times using column data

Estimates of field flushing times for uranium, molybdenum, and sulfate were evaluated for (1) the FTA saturated zone using column 3 and (2) the SSMA unsaturated zone using column 15. Flushing per year was calculated using column PVs, groundwater velocity and flow path length. This information was used to convert the number of PVs flushed in a column test to a flushing time at the Site. Flushing times are calculated as the time required for concentrations to be reduced to their respective maximum contaminant level (MCLs): 0.044 mg/L for uranium and 0.1 mg/L for molybdenum. Flushing times for sulfate are included, albeit it does not have a specified MCL for the Site. Sulfate flushing was considered complete at 400 mg/L, which is a typical maximum background groundwater concentration (DOE 2013). Linear interpolation was used to estimate flushing times when contaminant limits fell between experimental measurements. When column tests were ended before contaminant concentrations were reduced to the goal, concentrations were extrapolated by fitting an exponential decay curve to column test data. Calculations specific to each scenario are presented in Appendix E.

The following general assumptions were made for estimating flushing times:

- Aqueous contaminant concentrations in effluent samples from column tests 3 and 15 provide representative concentrations flowing out of the saturated and unsaturated zones, using sediments sampled from those zones.
- The sediments used in the column tests are representative of the zones they originated from.
- Contaminants in the saturated zone groundwater move vertically into the vadose zone during the time between floods due to factors including capillary action, evapotranspiration (ET), and sorption. Reentrainment of 20% of the contaminant mass is assumed to occur after every flood event (purely an assumption to represent the mechanism, not based on any direct observations or literature).
- The aquifer porosity is 0.35 and the thickness of the unsaturated zone is 5 ft based on the DOE 2016.
- There is a finite mass of contaminants present in the sediments.

6.3.3.1 Scenario 1 Saturated Zone FTA (Column 3)

The column 3 results completed with sediments collected from the FTA in 2015 were used to determine the required number of PVs flushed to meet MCLs in the saturated zone. The number of PVs flushed was then converted to an amount of time using the groundwater velocity and the longest flow path through the FTA based on August 2012 and August 2015 contaminant and water level measurements (DOE 2016). Average groundwater velocities (V) of 0.5 ft per day (ft/day) (V-Low), 1 ft/day (V-Mid), and 1.5 ft/day (V-High) were evaluated based on the results of borehole dilution tests, aquifer tests, and tracer tests (DOE 1998a). The flow path used for this analysis is 2150 ft long and was calculated as starting at the northwest corner of the FTA and following the groundwater flow direction defined by a line perpendicular to the surficial aquifer groundwater elevations (Figure 8).

Column 3 was the only column representative of the saturated zone beneath the FTA. This column test used DI water as influent for the first half of the column test before switching to background groundwater for the second half of the experiment. For the first half of the test, molybdenum concentrations steadily decline, possibly due to the dissolution of powellite (Section 6.3.2) with the introduction of DI water. Sulfate concentrations remain constant near 1500 mg/L throughout the test (Appendix D) due to the dissolution of gypsum (Section 7.3.2). Uranium concentrations were low and relatively steady (0.12 to 0.15 mg/L) from 1 to 17 PVs before increasing up to 0.51 mg/L from 17 to 21 PVs with the introduction of background groundwater. Because of this, only the second half of the experiment was used for the analysis of uranium flushing which represents a faster flushing rate with background groundwater instead of DI water. For uranium only, the number of PVs required for flushing was assumed to start at the maximum uranium concentration with 21 PVs into the test being the first PV flushed.

Results from this scenario indicate flushing times greater than 100 years for uranium (120 to 370 year), spanning 100 years for molybdenum (64 to 190 years), and sulfate flushing time could not be estimated (Table 10). Sulfate flushing time could not be estimated due to continuous sulfate release for the whole column test (Appendix D).

Groundwater quality transects for uranium and molybdenum (Figure 38 and Figure 39) indicate increasing groundwater concentration going from transect 02 (goes near well 0859 with sediment for column 3) to transect 03 (goes near well 0860 with sediment data, but no column data). Solid phase data for uranium and molybdenum in the saturated zone for column 3 (0859) are 4.6 and 3.1 mg/kg, respectively and a maximum for 2.7 and 2.5 mg/kg at borehole/well 0860, respectively. At location 0860, molybdenum on the solid phase reaches a hole maximum of 3.3 mg/kg at the top of the water table (9 ft bgs). With background S&G concentrations for uranium and molybdenum of 0.59 and 0.14 mg/kg, respectively, these data indicate a continuing source of these elements in the saturated zone of the FTA. The extent of the source of uranium and molybdenum in the FTA saturated zone beyond the interval between location 0859 and 0860 is unknown, but a source along the whole FTA flow path was applied for these calculations.

For flushing calculations, it is important to note that uranium and molybdenum release was greater with the introduction of different waters into the column (Section 6.3.2) than what occurs in the field. For column 3, the maximum uranium release of 0.51 mg/L with background groundwater compares to a 2020 groundwater concentration in 0859 of 0.072 mg/L. Likewise, the column 3 maximum molybdenum release of 1.1 mg/L (PV 1) and 0.53 mg/L (PV 2) with DI water compares to a much lower 2020 groundwater concentration for molybdenum of 0.062 mg/L. These data indicate that flushing rates at the FTA may increase with the introduction of cleaner background groundwater. This could be especially true for molybdenum if it is being released from powellite. For powellite, the common cation influence of high calcium concentrations from Plant discharge or gypsum dissolution could suppress powellite dissolution and keep molybdenum concentrations lower in the actual groundwater. Thus, the flushing times in Table 10 for molybdenum may be underestimated for actual field conditions, as the column condition flushing with a lower calcium influent has not occurred in the field yet.

Table 10. Estimated Flushing Times for Scenario 1, Saturated Zone Underneath the FTA

	Flushing Times (years)		
	V-Low	**V-Mid**	**V-High**
Uranium	370	190	120
Molybdenum	190	96	64
Sulfate	No estimate		

6.3.3.2 Scenario 2 Unsaturated Zone SSMA (Column 15)

Scenario 2 models the flushing of the unsaturated zone near the river due to periodic flooding, assuming the unsaturated zone becomes fully saturated under flooding conditions. This approach assumes that floodwater displaces existing water in the saturated zone, and the contaminant mass leached out of the unsaturated zone into the floodwater moves into the saturated zone. Twenty percent of the water and contaminant mass from the saturated zone is assumed to move back up into the vadose zone after flooding due to capillary action and ET. Therefore, the time to reach concentration limits depends on how many PVs are flushed by each flooding event; how often flooding events happen; and the extent contaminants being retarded by factors such as capillary action, ET, and sorption.

Data from column test 15, which used a sediment sample from the SSMA unsaturated zone, were used to determine the number of PVs required to flush uranium, molybdenum, and sulfate. The calculated flushing time reflects the number of PVs required to meet concentrations of 0.044, 0.10, and 400 mg/L, respectively, in pore water in the unsaturated zone and eliminate further impacts to the saturated zone after flooding. These calculations also assume no additional upgradient groundwater inputs of these contaminants.

The number of years required to reach respective concentration was estimated assuming that: (1) 0.5, 1, or 2 PVs are flushed from the unsaturated zone during each flood; (2) flooding occurs every 2, 5, or 10 years: 20% of the contaminant mass is returned to the unsaturated zone due to capillary action and ET between flooding events; and (3) 80% of the specified PV is effectively flushed from the unsaturated zone during each flooding event.

Flood frequency estimates were based on discharge data from the Little Wind River assuming flows of approximately 8000 cubic ft per second or greater are required for flooding (DOE 2016; DOE 2018). Eleven significant flood events were observed from 1963 to 2019 (approximately one flood every 5 years). However, five significant flood events have been observed between 2010 and 2019 (one flood every 2 years).

Flushing times were estimated for the following scenarios:

- Low flood frequency and low flushing volume per flood: One flood every 10 years and 0.5 PVs flushed per flood (10 year, 0.5 PV)
- Moderate flood frequency and moderate flushing volume per flood: 1 flood every 5 years and 1 PV flushed per flood (5 year, 1 PV)
- High-flood frequency and high flushing volume per flood: 1 flood every 2 years and 2 PVs flushed per flood (2 year, 2 PV)

Estimated flushing times for the SSMA unsaturated zone are summarized in Table 11. The 5 year, 1 PV scenario is the most likely flooding and flushing scenario based on historical Little Wind River discharge data. Results in flushing times ranging from 38–110 years, depending on the contaminant, but the overall range of potential flushing times is 7.6 to 450 years.

Table 11. Estimated Flushing Times for Scenario 2, Contaminants in the Unsaturated Zone at the SSMA

	Flushing Times (years)		
	10 yr, 0.5 PV	**5 yr, 1 PV**	**2 yr, 2 PV**
Uranium	450	110	22
Molybdenum	150	38	7.6
Sulfate	260	66	13

Abbreviation: yr = year

6.3.3.3 Consideration of Scenarios 1 and 2 Together

Highlight Box 12: Summary of Flushing Times from Column Data

Natural flushing times considering both the FTA and the SSMA range from 140 to 820 years for uranium and 72 to 340 years for molybdenum. A reasonable estimate for overall flushing times for uranium and molybdenum are 300 and 130 years, respectively.

If molybdenum flushing is controlled by powellite dissolution, the above flushing rates may be even longer, as these times are estimated using column test data, which do not include continued calcium inputs to groundwater from the Plant that could suppress powellite dissolution.

Sulfate natural flushing at the SSMA is on the order of 13 to 260 years. The rate of sulfate flushing could not be estimated for the FTA due to ongoing gypsum dissolution and Plant inputs to the groundwater.

The prior sections consider scenarios 1 and 2 separately. However, with the consideration of contaminants wicking up from the groundwater into the unsaturated zone, scenario 2 cannot start until scenario 1 (upgradient FTA flushing) is complete. Using the middle range groundwater velocity for scenario 1 (Table 10) and the 5 year, 1 PV flushing in scenario 2 (Table 11), this gives an estimated uranium flushing time of 300 years and an estimated molybdenum flushing time of 130 years. These estimates do not include the time for groundwater to flow from the FTA to the Little Wind River, which is on the order of 10 years, given the high groundwater flow velocities. A combined sulfate flushing time is not calculated, as the time depends on sulfate release by the Plant and the unknown mass of gypsum to be dissolved at the FTA. The faster flushing of molybdenum is reflective of the faster declines of molybdenum concentrations in the column results and its higher MCL value.

7.0 Ongoing Work

7.1 AS&T Tracer Studies

Like the tracer studies that were completed at the LM Field Support Center at Grand Junction, Colorado (Paradis et al. 2020), tracer injection has also been completed at the Site. This work was done under LM's AS&T Program. The objective of this work at both sites is to test techniques for determining geochemical input parameters for future reactive transport modeling. At the Riverton Site, multiple injections of river water and background groundwater were completed. All injection fluids had tracer additions to confirm the water source, and some had added alkalinity to test possible enhanced flushing of uranium. At this time, only some of the analytical analyses have been completed and report writing has not started. This work focused on the FTA and SSMA as two areas with ongoing uranium and molybdenum source zones. Interpretations of the field data using reactive transport modeling is planned, as this will provide geochemical reaction parameters at a pilot field scale. Results from these pilot field-scale tracer tests will provide initial input parameters for a Site reactive transport model. A summary of the field tests is provided below.

7.1.1 SSMA

Tracer testing at the SSMA was completed in an area just upgradient from well 0855. The goal of the testing in this area was to determine uranium and molybdenum fate and transport in the unsaturated and saturated zone. A gallery of 13 wells was installed in the surficial aquifer along with an infiltration basin. All 13 wells were sampled to track the movement of fluids in the surficial aquifer. Injection and infiltrations at the SSMA used traced Little Wind River water to provide test conditions similar to a flooding event. Testing was completed during the summer months (June, July, August, and September) and all tests were done under natural gradients (no pumping).

The tests and year they were completed are as follows:

- 2020 saturated zone single-well injection
- 2020 unsaturated zone infiltration
- 2021 unsaturated zone infiltration with alkalinity added

7.1.2 FTA

Tracer testing at the FTA was completed using a gallery of 15 wells installed in the surficial aquifer in an area just upgradient from well 0860. Additional tests were completed in wells 0859 and 0860. The goal of the testing in this area was to determine uranium and molybdenum fate and transport in the saturated zone. All 15 wells were sampled to continuously track the movement of fluids in the surficial aquifer. Wells 0859 and 0860 have three ports in each that were sampled after the traced water injections. All injection water used background groundwater to test a natural flushing approach. Testing was completed during the summer months (June, July, August, and September) and all tests were done under natural gradients (no pumping).

The tests and year they were completed are as follows:

- 2020 one single-well injection without added alkalinity
- 2020 two single-well injections with added alkalinity
- 2021 four single-well injections (wells 0859 and 0860), two with added alkalinity

8.0 Data Quality Objectives

Data quality objectives (DQOs) were developed in general accordance with EPA guidance (EPA 2006). This DQO process is intended to identify any data gaps and provide a systematic planning tool for developing scientifically sound and cost-effective data collection plans. Thus, these DQOs will guide any future data gap work plans before a Riverton GCAP revision occurs. Implementation of the DQO process generally follows the seven major planning steps recommended by EPA:

[1] State the Problem
    [a] Define the problem that necessitates the study.
[2] Identify the Study Objectives
    [a] Identify the key questions and study objectives along with identifying alternative actions or outcomes.
[3] Identify Information Inputs
    [a] Identify the types and sources of information needed to address study questions and objectives.
[4] Define the Study Boundaries
    [a] Identify the spatial boundaries and temporal limits of the study.
[5] Develop the Analytic Approach
    [a] Identify parameters of interest and develop the logic for inference.
[6] Specify Performance and Acceptance Criteria
    [a] Develop performance criteria for new data being collected.
[7] Plan for Obtaining Data
    [a] Define the plan that meets performance criteria for obtaining the required data.

This report discusses steps [1] and [2] along with a summary table of available data and potential data gaps (Table 11), followed by a recommendations section (Section 9.0). The remaining DQO process steps will be discussed further as part of a subsequent work plan that identifies (1) available data in relation to necessary information inputs, (2) data gaps in addressing the study objectives, and (3) defines a plan for obtaining information to address data gaps (steps [3] through [7]).

8.1 Step No. 1: State the Problem

Evaluations of human health and ecological risks associated with contamination related to the Site are presented in the BLRA (DOE 1995). The BLRA determined that risks to human health can be mitigated by applying institutional controls to restrict access to contaminated groundwater in the vicinity of the Site (DOE 1995) and an alternate water supply has been provided. The BLRA recommended that contaminated groundwater at the Site not be used for livestock or irrigation uses. In addition, the BLRA concluded that limited environmental sampling and available guidelines from regulatory agencies were not sufficient to fully evaluate the possible long-term impacts of the affected ground water or surface water on plants or animals (DOE 1995). An updated risk assessment (Argonne 2021) was conducted to determine if the Site is protective of human health for traditional Native American cultural uses of plants, consumption of livestock, or wildlife, and from contact with surface water either through consumption of catch (fish) or direct contact (dermal and incidental ingestion), which had not been evaluated in prior risk assessments. Argonne 2021 concluded that “Based on the results of this update in combination with past completed remedial action and ongoing monitoring activities and IC implementation, it is concluded that the current conditions at the Riverton site are protective of human health and the environment given the continuous monitoring and oversight provided by DOE and the collaboration with NANRO [Northern Arapaho Natural Resources Office] and the Northern Arapaho community for the implementation of the ICs that are in place at the site.” However, Site surface water data indicated that some Site concentrations of contaminants exceeded screening benchmarks from various agencies for aquatic species, suggesting further evaluation may be warranted. Potential influences on aquatic biota was not evaluated, only that screening values were exceeded (Argonne 2021).

The final compliance strategy for the Site (DOE 1998c) is “to allow natural flushing to meet the EPA ground water standards within a performance period of 100 years, starting in 1998, and coupled with institutional controls and compliance monitoring.” Uranium and molybdenum were selected as indicator constituents for compliance monitoring (DOE 1998c). DOE 1998c also states that “In the unlikely event that the compliance monitoring indicate that observed concentration decreases are not in general accordance with the predictions, then the process of applying the decision framework developed in the Final Programmatic Environmental Impact Statement [PEIS, DOE 1996] for the Uranium Mill Tailings Remedial Action Ground Water Project (October, 1996) to the site conceptual model would be implemented as formal corrective action.”

As discussed in this Report, previous predictions of uranium and molybdenum decreases are not being met and the following problem statement is defined:

The groundwater compliance strategy outlined in the 1998 GCAP for the Site (DOE 1998c) was based on the risk of mill-related contamination exposures as outlined in the BLRA (DOE 1995). This strategy consisted of the application of supplemental standards for thorium, institutional controls on groundwater use, and natural flushing of uranium and molybdenum to below MCLs within 100 years (2098). Natural flushing has not occurred as original predicted. Thus, with new data collection, Site CSMs and transport modeling have been updated. This information has indicated that 100-year natural flushing in all areas of the Site is not viable.

DOE plans to develop a reactive transport model for the Site that includes all current data and all relevant geochemical processes. DOE would like to identify any remaining data gaps before this Site reactive transport model is developed. Once appropriate compliance strategies are identified, the final Site reactive transport will be used to evaluate available remedial techniques that could be implemented to achieve a new compliance strategy. The final compliance strategy selection will be documented in a revised GCAP.

8.2 Step No. 2: Identify the Study Objectives

The following four study objectives and associated study questions were developed to identify any Site data gaps.

- **DQO 1:** Evaluate the existing predictions and CSMs for uranium, molybdenum, and sulfate fate and transport.
    - What was the prediction methodology, CSM, and basis for development of the current GCAP?
    - How have predictions and CSMs been updated and what were they based on?
    - Is 100-year natural flushing still a viable strategy for the Site?
- **DQO 2:** Delineate the current distribution of uranium, molybdenum, and sulfate in the water and solid phases and remaining source mass.
    - How sufficient is the delineation of the water phase plumes?
    - How sufficient is the delineation of the source mass distribution?
    - Are the data adequate for use in a reactive transport model?
- **DQO 3:** Define the geochemical processes at the Site that likely influence uranium, molybdenum, and sulfate fate and transport.
    - What modeling tools and observations are needed to define these processes?
    - Are the processes well enough understood and are the data adequate for use in a reactive transport model?
    - Can the geochemical processes be incorporated into a reactive transport model to reasonably quantify natural flushing times with a desired level of certainty?
- **DQO 4:** If a 100-year natural flushing strategy for the site is no longer viable, determine an appropriate compliance strategy for the Site.
    - What are the potential Site compliance strategies besides natural flushing?
    - Will a Site reactive transport model be adequate for evaluating compliance strategy alternatives?
    - Are the data available to complete a cost/benefit analysis of all the compliance strategy alternatives, in order to make a final defensible selection?

Preliminary answers, available information, and identified data gaps for the above objectives and questions are summarized in Table 12. This table will be revisited during the subsequent work plan development.

Table 12. Data Quality Objectives and Study Questions with Answers, Available Information, and Data Gaps

Data Quality Objectives	Study Questions	Answer/Available Information	Data Gaps
1	What was the prediction methodology, CSM, and basis for development of the current GCAP?	GANDT model (DOE 1998a), no ongoing sources, sorption controlled only, with sorption parameters based on laboratory data and general literature.	Ongoing source zones were not identified and not included.
	How have predictions and CSMs been updated and what were they based on?	DOE 2013 recognized an unsaturated zone source term at the SSMA. DOE 2013 used MODFLOW 2000 and MT3DMS with a larger sorption coefficient than DOE 1998a based on laboratory testing but did not include additional source terms. DOE 2016 updates the CSM with new source term data. This report provides new predictions based on mass balance and column testing.	Source term data and stronger sorption on organic carbon near the Little Wind River have not been included in any predictions.
	Is 100-year natural flushing still a viable strategy for the Site?	No, based on DOE 2013 and this report showing additional source zone mass. Some areas might flush, but strategy requires flushing in all areas.	Limited data on source zone mass at the FTA, which adds uncertainty to flushing predictions.
2	How sufficient is the delineation of the water phase plumes?	Good three-dimensional data. Data are in DOE 2016, DOE 2019, annual VMRs, and LM database.	None.
	How sufficient is the delineation of the source mass distribution?	Good definition in the SSMA, but only two boreholes in the FTA. Data are in DOE 2016 with solid-phase data from boreholes and trenches.	Additional definition of source zone mass in the FTA.
	Are the data adequate for use in a reactive transport model?	Generally, yes, using data from DOE 2016 and this report. Greatest uncertainty occurs with source mass at the FTA, variations in groundwater geochemistry upgradient of the FTA from the Plant, and possible sorption changes for uranium and molybdenum with redox conditions and high organic carbon content.	Additional definition of source zone mass in the FTA. Data on upgradient groundwater coming into the FTA with Plant influences. Sorption variability with redox conditions.
3	What modeling tools and observations are needed to define these processes?	Geochemical and reactive transport modeling with geochemical analyses of all major constituents in the water and solid phase.	Confirmation of the presence of powellite. Molybdenum transport at the Site has not been thoroughly considered before.
	Are the processes well enough understood and are the data adequate for use in a reactive transport model?	Processes of mineral dissolution and sorption are understood, but still need to be quantified from field and column testing.	Geochemical modeling of column and field data. Minteq.v4.dat database for molybdenum should be evaluated. Variable sorption with redox changes.

Table 12. Data Quality Objectives and Study Questions with Answers, Available Information, and Data Gaps (continued)

Data Quality Objectives	Study Questions	Answer/Available Information	Data Gaps
3 (continued)	Can the geochemical processes be incorporated into a reactive transport model to reasonably quantify natural flushing times?	Yes, current reactive transport models can account for multiple geochemical processes coupled with groundwater flow to quantify flushing times. Unsaturated zone transport complexity may need to be simplified to have more reasonable simulation run times.	Models rely on empirical data (e.g., field and column work); thus, the quality of those data should be reevaluated during work plan development.
4	What are potential compliance strategies besides natural flushing?	See Figure 5-1 in DOE 1998a based on DOE 1996. Individually or in a combination: alternate concentration limits, active remediation, technical impractability, and institutional controls.	Potential alternatives have not been determined.
	Will a Site reactive transport model be adequate for evaluating compliance strategy alternatives?	Yes. Similar approach was completed for Monticello, Utah, Processing Site (DOE 2020b).	Data gaps as listed already for model inputs (DQO 3).
	Are data available to complete a cost/benefit analysis of all the compliance strategy alternatives, in order to make a final defensible selection?	Not yet.	Sitewide reactive transport model to compare alternatives. Data analyses on cost versus risks of the various alternatives.

9.0 Recommendations

The following items are recommendations to fill in data gaps that have been identified in this Report. The development of a detailed work plan that follows the DQOs discussed in Section 8.0 is recommended. The recommendations below assume that these data gaps will be used in a new Site reactive transport model. This model will be part of a new GCAP to compare remedial alternatives and associated cost/benefit analyses, leading to a new compliance strategy selection. The recommendations are as follows:

- Sample well 0101 to confirm potential flushing in this area (former ore storage area). Additional solid-phase samples in the unsaturated and saturated zones near well 0101 to determine distribution of source zone mass of uranium, molybdenum, and sulfate in this area.
- Unsaturated zone solid-phase sampling upgradient of the south-east FTA to confirm distribution of source zone mass of uranium, molybdenum, and sulfate.
- Groundwater sampling via temporary piezometers between transects 02 and 03 (Figure 37) to confirm the start of the uranium, molybdenum, and sulfate plumes and potentially use as a guide for solid-phase sampling in this area.
- Unsaturated and saturated zone solid-phase sampling upgradient of the south-central FTA (between transects 02 and 03, Figure 37) to confirm distribution of source mass of uranium, molybdenum, and sulfate in this area.

- During FTA solid-phase sampling, sample more discrete intervals at the top of the water table. This is a zone with possible iron and manganese oxyhydroxide precipitation that could sorb uranium and molybdenum. For any new FTA solid phase samples, consider doing a subset of samples for sequential extractions on iron, manganese, uranium, and molybdenum. The goals of these analyses are (1) determining the amount of precipitated iron and manganese oxyhydroxides and (2) determining the amount of sorbed versus precipitated uranium and molybdenum. Scanning electron microscopy is recommended on samples with high molybdenum concentrations to determine whether powellite is present.
- Between the Plant retention ponds and the FTA boundary, confirm the groundwater geochemistry before it enters the FTA, either with a new monitoring well or a temporary piezometer. This groundwater geochemistry can potentially influence the flushing rate of contaminants from the solid phase at the FTA.
- Complete geochemical modeling of column tests (Section 6.0) and field tracer data (Section 7.0). Completion of this work will provide input parameters for Site reactive transport modeling.
- Additional column testing on the S&G below the NRZ at well 0855 for uranium release. Suggest repeating column 11 with the introduction of anoxic background groundwater. Column 11 had the highest uranium release concentration using oxic background groundwater. However, it is not well understood if uranium release from high organic content sediments will still occur under anoxic conditions. Such testing will help determine potential reactive transport mechanism in these areas that might occur in the future. It is unclear if NRZ areas will remain long-term sinks or will later become source zones due to the high uranium content on the solid phase.
- Addition of transducers for water level variations and specific conductance probes for overall geochemical variations at the FTA. This can provide information on the potential for water/sediment interaction at the top of the water table. Specific conductance probes can provide data on geochemical variations due to possible Plant retention pond inputs to the groundwater.

10.0 References

Argonne (Argonne National Laboratory), 2021. *Riverton, Wyoming, Processing Site: An Environmental Risk Assessment Update*, Environmental Science Division Argonne National Laboratory, Lemont, Illinois, September.

Bender, W.B., and U. Becker, 2020. “Resolving the Kinetics of Individual Aqueous Reaction Steps of Actinyl (AnO_2^+ and AnO_2^{2+}; An = U, Np, and Pu) Tricarbonate Complexes with Ferrous Iron and Hydrogen Sulfide from First Principles,” *Radiochimica Acta*, V. 108, No. 3, p. 165–184.

Bone, S.E., J.J. Dynes, J. Cliff, J.R. Bargar, 2017. “*Uranium (IV) adsorption by natural organic matter in anoxic sediments,*” Proceedings of the National Academy of Sciences of the United States of America, 114(4), 711–716, https://www.pnas.org/content/114/4/711.

Choppin, G.R. 2007. “Actinide Speciation in the Environment,” *Journal of Radioanalytical and Nuclear Chemistry*, V. 273, No. 3, p. 695–703.

Conlan, M.J.W., K.U. Mayer, R. Blaskovich, and R.D. Beckie, 2012. “Solubility Controls for Molybdenum in Neutral Rock Drainage,” *Geochemistry: Exploration, Environment, Analysis*, 12 (1), pp. 21-32.

Dam, W.L., S. Campbell, R.H. Johnson, B.B. Looney, M.E. Denham, C.A. Eddy-Dilek, and S.J. Babits, 2015. “Refining the Site Conceptual Model at a Former Uranium Mill Site in Riverton, Wyoming, USA,” *Environmental Earth Sciences*, DOI 10.1007/s12665-015-4706-y, 74(10), pp. 7255–7265, https://link.springer.com/article/10.1007%2Fs12665-015-4706-y.

DOE (U.S. Department of Energy), 1977. *Phase II – Title I Engineering Assessment of Inactive Uranium Mill Tailings Riverton Site, Riverton, Wyoming,* prepared for the U.S. Department of Energy, Grand Junction, Colorado, by Ford, Bacon, and Davis, Utah, Inc., Salt Lake City, Utah, December.

DOE (U.S. Department of Energy), 1981. *A Summary of the Engineering Assessment of Inactive Uranium Mill Tailings Riverton Site, Riverton, Wyoming,* prepared by the U.S. Department of Energy, UMTRA Project Office, Albuquerque Operations Office, Albuquerque, New Mexico, by Ford, Bacon, and Davis, Utah, Inc., Salt Lake City, Utah, August.

DOE (U.S. Department of Energy), 1991. *Riverton Wyoming Final Completion Report*, Albuquerque Operations Office, Albuquerque, New Mexico, December.

DOE (U.S. Department of Energy), 1987. *Environmental Assessment for Remedial Action at the Riverton Uranium Mill Tailings Site, Riverton, Wyoming*, DOE/EA-0254, prepared by the U.S. Department of Energy, UMTRA Project Office, Albuquerque Operations Office, Albuquerque, New Mexico.

DOE (U.S. Department of Energy), 1994. *UMTRA Project Water Sampling and Analysis Plan, Riverton, Wyoming,* DOE/AL/62350-117, prepared by the U.S. Department of Energy, UMTRA Project Office, Albuquerque Operations Office, Albuquerque, New Mexico. March.

DOE (U.S. Department of Energy), 1995. *Baseline Risk Assessment of Ground Water Contamination at the Uranium Mill Tailings Site near Riverton, Wyoming,* DOE/AL/62350-65 Rev. 1, prepared by the U.S. Department of Energy, UMTRA Project Office, Albuquerque Operations Office, Albuquerque, New Mexico, September.

DOE (U.S. Department of Energy), 1996. *Final Programmatic Environmental Impact Statement for the Uranium Mill Tailings Remedial Action Ground Water Project,* DOE/EIS–0198, prepared by the U.S. Department of Energy, UMTRA Project Office, Albuquerque Operations Office, Albuquerque, New Mexico, October.

DOE (U.S. Department of Energy), 1998a. *Final Site Observational Work Plan for the UMTRA Project Site at Riverton, Wyoming*, U0013901, Grand Junction Office, February.

DOE (U.S. Department of Energy), 1998b. *Environmental Assessment of Ground Water Compliance at the Riverton, Wyoming, Uranium Mill Tailings Site*, DOE/EA-1261, Grand Junction Office. September.

DOE (U.S. Department of Energy), 1998c. *Final Ground Water Compliance Action Plan for the Riverton, Wyoming, Title I UMTRA Project Site*, attached to letter from DOE to NRC, 22 September.

DOE (U.S. Department of Energy), 2009. *Long-Term Management Plan for the Riverton, Wyoming, Processing Site*, LMS/RVT/S01187, Office of Legacy Management, Grand Junction, Colorado, September.

DOE (U.S. Department of Energy), 2010. *Verification Monitoring Report for the Riverton, Wyoming, Processing Site, Update for 2009*, LMS/RVT/S06093, Office of Legacy Management, Grand Junction, Colorado, April.

DOE (U.S. Department of Energy), 2011. *Verification Monitoring Report for the Riverton, Wyoming, Processing Site, Update for 2010*, LMS/RVT/S07202, Office of Legacy Management, Grand Junction, Colorado, February.

DOE (U.S. Department of Energy), 2013. *Enhanced Characterization of the Surficial Aquifer, Riverton, Wyoming, Processing Site Data Summary Report,* LMS/RVT/S09545, Office of Legacy Management, January.

DOE (U.S. Department of Energy), 2014. *2013 Verification Monitoring Report for the Riverton, Wyoming, Processing Site*, LMS/RVT/S11203, Office of Legacy Management, Grand Junction, Colorado, April.

DOE (U.S. Department of Energy), 2016. *2015 Advanced Site Investigation and Monitoring Report, Riverton, Wyoming, Processing Site,* LMS/RVT/S14148, Office of Legacy Management, September.

DOE (U.S. Department of Energy), 2018. *2017 Verification Monitoring Report, Riverton, Wyoming, Processing Site,* LMS/RVT/S17242, Office of Legacy Management, July.

DOE (U.S. Department of Energy), 2019. *Three Years of Multilevel Monitoring Data at the Riverton, Wyoming, Processing Site That Show Contaminant Increases After River Flooding Events and a Large Recharge Event,* LMS/RVT/S26137, Office of Legacy Management, October.

DOE (U.S. Department of Energy), 2020a. *Riverton, Wyoming, Processing Site, Numerical Groundwater Flow Modeling Update,* LMS/RVT/S28497, Office of Legacy Management, January.

DOE (U.S. Department of Energy), 2020b. *Monticello Mill Tailings Site Operable Unit III – Groundwater Flow and Contaminant Transport Model Report,* LMS/MNT/S30707, Office of Legacy Management, November.

DOE (U.S. Department of Energy), 2021a. *2020 Verification Monitoring Report, Riverton, Wyoming, Processing Site,* LMS/RVT/S32810, Office of Legacy Management, March.

DOE (U.S. Department of Energy), 2021b. *Environmental Sciences Laboratory Procedures Manual*, LMS/PRO/S04343, Office of Legacy Management, continuously updated, prepared by the LMS contractor for the U.S. Department of Energy Office of Legacy Management.

Dong, W., and S.C. Brooks, 2006. "Determination of the Formation Constants of Ternary Complexes of Uranyl and Carbonate with Alkaline Earth Metals (Mg2+, Ca2+, Sr2+, and Ba2+) Using Anion Exchange Method," *Environmental Science & Technology*, 40(15):4689–4695.

EPA (U.S. Environmental Protection Agency), 2006. *Guidance on Systematic Planning Using the Data Quality Objectives Process*, EPA QA/G-4, Washington, D.C., February.

EPA (U.S. Environmental Protection Agency), 2007. *Monitored Natural Attenuation of Inorganic Contaminants in Ground Water, Volume 1 – Technical Basis for Assessment*, October.

Guillaumont R., T. Fanghanel, J. Fuger, I. Grenthe, V. Neck, D. Palmer, and M.H. Rand, 2003. "Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium," *Chemical Thermodynamics*, Vol. 5, OECD Nuclear Energy Agency, Elsevier Science, Amsterdam.

Knowlton, Jr., R.G., D.M. Peterson, and H. Zhang, 1997, *Analysis of Natural Attenuation as the Preferred Ground Water Alternative at the DOE UMTRA Site Near Riverton, WY*, prepared by Sandia National Laboratories, August.

Konhauser, K. 2007. Introduction to Geomicrobiology. Blackwell Publishing, Malden, Massachusetts.

Lin, J., W. Sun, J. Desmarais, N. Chen, R. Feng, P. Zhang, D. Li, A. Lieu, J.S. Tse, and Y. Pan, 2018. "Uptake and Speciation of Uranium in Synthetic Gypsum ($CaSO_4 \bullet 2H_2O$): Applications to Radioactive Mine Tailings," *Journal of Environmental Radioactivity*, 181, pp. 8-17, https://doi.org/10.1016/j.jenvrad.2017.10.010.

Loreggian, L., A. Novotny, S.L. Bretagne, B. Bartova, Y. Wang, and R. Bernier-Latmani, 2020. "Effect of Aging on the Stability of Microbially Reduced Uranium in Natural Sediment," *Environmental Science & Technology*, V. 54, No. 1, p. 613-620.

Maher, K., J.R. Bargar, and G.E. Brown, Jr., 2013. "Environmental Speciation of Actinides," *Inorganic Chemistry*, V. 52, p. 3510-3532.

Merritt, R.C., 1971. *The Extractive Metallurgy of Uranium*, Colorado School of Mines Research Institute, Johnson Publishing Co, Golden, Colorado.

Moon, H.S., L. McGuinness, R.K. Kukkadapu, A.D. Peacock, J. Komlos, L.J. Kerkhof, P.E. Long, and P.R. Jaffé, 2010. "Microbial Reduction of Uranium Under Iron- and Sulfate-Reducing Conditions: Effect of Amended Goethite on Microbial Community Composition and Dynamics," *Water Research*, V. 44, No. 44, p. 4015–4028.

Narasimhan, T.N., A.F. White, and T. Tokunaga, 1986. *Groundwater Contamination from an Inactive Uranium Mill Tailings Pile: 2. Application of a Dynamic Mixing Model*, Water Resources Research 22(13):1820–1834.

NRC (U.S. Nuclear Regulatory Commission), 1999. *Acceptance of the Final Groundwater Compliance Action Plan for the Riverton, Wyoming Title I UMTRA Site*, Memo to Ray Plieness, U.S. Department of Energy, Grand Junction, Colorado, May 3, 1999.

Parkhurst, D.L., and C.A.J. Appelo, 2013. "Description of Input and Examples for PHREEQC Version 3—A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations," USGS Techniques and Methods 6-A43, https://pubs.usgs.gov/tm/06/a43/.

Smedley, P.L. and D.G. Kinniburgh, 2017. "Molybdenum in Natural Waters: A Review of Occurrence, Distributions and Controls," *Applied Geochemistry*, 84, 387–432.

Wall, J.D., and L.R. Krumholz, 2006. "Uranium Reduction," *Annual Review of Microbiology*, V. 60, p. 140-166.

White, A.F., J.M. Delany, T.N. Narasimhan, and A. Smith, 1984. "Groundwater Contamination from an Inactive Mill Tailings Pile, 1. Application of a Chemical Mixing Model," *Water Resources Research* 20(11): 1743–1752.

Appendix A

Surficial aquifer wells: data, analyte graphs, and flushing times

Please see separate .zip file for this data

Appendix B

EVS files for water and solid-phase volume calculations and plume visualization

Please see separate .zip file for this data

Appendix C

2012/2015 piezometer data: figures and PHREEQC files

Please see separate .zip file for this data

Appendix D

Column data: Graphs and PHREEQC files

Please see separate .zip file for this data

Appendix E

Flushing times calculated with columns 3 and 15

Please see separate .zip file for this data