

# Review of the Natural Flushing Groundwater Remedy at the Old Rifle Legacy Management Site, Rifle, Colorado

July 2011



U.S. DEPARTMENT OF  
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## Abbreviations

1-D	one-dimensional
2-D	two-dimensional
3-D	three-dimensional
ACL	alternate concentration limit
ALARA	as low as reasonably achievable
COC	contaminant of concern
DO	dissolved oxygen
DOC	dissolved organic carbon
DOE	U.S. Department of Energy
EM	Office of Environmental Management
EPA	U.S. Environmental Protection Agency
ERSP	Environmental Remediation Sciences Program
FE(II)	ferrous iron
Fe(III)	ferric iron
ft	feet
ft <sup>3</sup> /day	cubic feet per day
GCAP	Groundwater Compliance Action Plan
gpm	gallons per minute
IFRC	Integrated Field Research Challenge
LM	Office of Legacy Management
MCL	maximum concentration limit
µg/L	micrograms per liter
µS/cm	microsiemens per centimeter
mg/L	milligrams per liter
mL/g	milliliters per gram
mV	millivolts
NABIR	Natural and Accelerated Bioremediation Research
NH <sub>4</sub>	ammonium
NRC	U.S. Nuclear Regulatory Commission
ORP	oxidation-reduction potential
PEIS	Programmatic Environmental Impact Statement
redox	oxidation-reduction

SC	Office of Science
SOWP	Site Observational Work Plan
TEAP	terminal electron acceptor process
TI	technical impracticability
USGS	U.S. Geological Survey
U(VI)	hexavalent uranium
U(IV)	tetravalent uranium
U-234	uranium-234
U-238	uranium-238
UAR	uranium activity ratio
UMTRA	Uranium Mill Tailings Remedial Action (Project)
UMTRCA	Uranium Mill Tailings Radiation Control Act

## Executive Summary

A review of environmental information collected at the Old Rifle, Colorado, Legacy Management Site indicates that the natural attenuation of uranium contamination in the alluvial aquifer at the site is not progressing as quickly as numerical modeling projected. This discrepancy calls into question the validity of the selected compliance strategy of natural flushing. Groundwater uranium concentration data collected at the site since 1996, when the surface cleanup was completed, through 2010 show that, in recent years, uranium levels have tended to either remain relatively constant or gradually increase.

Numerous published and unpublished sources of information have been examined to determine why uranium concentrations in the aquifer are not attenuating. Initially, data and modeling analyses presented in the Site Observational Work Plan (DOE 1999) were reviewed. This review was followed by assessments of recent hydraulic and water chemistry data collected at numerous on-site locations used to monitor both groundwater and surface water. The assessment resulted in an updated understanding of local groundwater flow processes, water sources recharging the alluvial aquifer, and background biogeochemical processes in the subsurface.

To a large extent, this investigation has relied on data collected by scientists participating in research at the site under a U.S. Department of Energy (DOE) initiative called the Rifle Integrated Field Research Challenge (Rifle IFRC). Several reports and papers prepared by IFRC researchers were examined to identify phenomena that can impact natural flushing processes. Enhanced bioremediation experiments, as well as other studies performed by the IFRC team, provide valuable insight into various flow, transport, and biogeochemical processes that potentially have a bearing on the fate of dissolved uranium in alluvial groundwater.

Collectively, the data, reports, and papers reviewed in this study reveal that processes affecting the fate and transport of uranium in the site's groundwater system are more complex than assumed. Significant physical and biogeochemical heterogeneity and temporally variable flow and transport processes characterize the subsurface. Complex phenomena that potentially contribute to persistently elevated uranium concentrations in Old Rifle site alluvium include the slow diffusion of uranium from low-permeability sediments, the occasional mobilization of uranium in the vadose zone, and the natural inflow of uranium in recharge sources north of the site. Such complexities not only limit the degree to which existing technologies can be used to fully characterize local subsurface media but also severely hamper modeling of contaminant transport in the alluvial aquifer on a site-wide scale. Consequently, natural flushing of uranium contamination cannot be reliably forecast at this time. While it is not possible to definitively state that natural flushing cannot achieve the uranium standard in the permitted timeframe, current trends strongly suggest that this is the case.

This report recommends ways to monitor the groundwater system in coming years and discusses prospects for future predictive modeling. A review of the site's regulatory status indicates that a decision framework specifically developed for the Uranium Mill Tailings Remedial Action (UMTRA) Project provides for several compliance strategies that are alternatives to natural flushing.

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## 1.0 Introduction

This report presents findings from a review of available environmental information on the Old Rifle, Colorado, Legacy Management Site (Old Rifle site; the site) near Rifle, Colorado. The site was previously managed under the former Uranium Mill Tailings Remedial Action (UMTRA) Project administered by the U.S. Department of Energy (DOE). The Site Observational Work Plan (SOWP; DOE 1999) for the Old Rifle site was finalized in 1999, and the Groundwater Compliance Action Plan (GCAP; DOE 2000), which established the groundwater remedy for the site, was completed in 2000. The recommended compliance strategy for uranium was “natural flushing” of the site’s alluvial aquifer. Natural flushing is a form of monitored natural attenuation. It depends on a combination of aquifer discharge to the nearby Colorado River and ambient geochemical processes to reduce contaminant concentrations in the groundwater. A numerical model prepared in support of the SOWP had indicated that natural flushing over a 10-year period would meet the applicable groundwater standard for uranium, which is the primary contaminant of concern (COC). The U.S. Nuclear Regulatory Commission (NRC), the regulatory authority for UMTRA sites, approved the GCAP in early 2002, setting in motion a process under which the performance of the remedy could be evaluated.

Groundwater monitoring has continued at the Old Rifle site during the 9 years since NRC approved the GCAP. The first year of post-GCAP monitoring was conducted by the DOE Office of Environmental Management (EM). In early 2003, the DOE Office of Legacy Management (LM) took over administration of the site and has overseen the groundwater monitoring since that time. Semiannual monitoring data collected by both EM and LM suggest that dissolved uranium levels in the alluvial groundwater are not attenuating.

In addition to monitoring efforts by EM and LM, the DOE Office of Science (SC) has sponsored research at the site since the early 2000s; the research largely focuses on the use of enhanced bioremediation technology to decrease dissolved uranium levels in the alluvial groundwater. In 2006, SC established the former milling property as one of three Integrated Field Research Challenge (IFRC) sites in the United States; work began under the Rifle IFRC in 2007. The DOE research has been managed through multiple SC programs, including the Natural and Accelerated Bioremediation Research Program, the Environmental Remediation Sciences Program, and, most recently, Subsurface Biogeochemical Research. SC-sponsored activities have shown success at immobilizing uranium within individual test areas of about 0.1 acre or less through manipulation of groundwater oxidation-reduction (redox) chemistry, but recent IFRC reports corroborate multiple years of uranium concentration data, collected by DOE, that indicate little, if any, progress in the sitewide attenuation of uranium contamination. Analyses presented in this report provide some insight into the reasons for the lack of remediation progress.

The groundwater system at the Old Rifle site is complex. The system is characterized by substantial heterogeneity of the aquifer sediments and significant flow and transport transients, both of which contribute to variable biogeochemical processes that strongly influence dissolved uranium levels. Complex phenomena that appear to contribute to persistently elevated uranium concentrations in Old Rifle alluvium include the slow diffusion of uranium from low-permeability sediments, the occasional mobilization of uranium in the vadose zone, and the natural inflow of uranium in recharge sources north of the site.

Subsurface system complexities limit the degree to which existing technologies can be used to fully characterize groundwater flow and transport processes at the Old Rifle site. Similarly, it is currently difficult, if not impossible, to accurately simulate the transport of uranium in local groundwater on a sitewide scale. As a consequence, natural flushing of uranium contamination from site groundwater cannot be reliably forecast. Despite such obstacles, this report examines the prospects for predictive simulation of contaminant fate at the site, using different modeling alternatives that range from simple to very complex. Regardless of the type of site-scale model that might be used for predictive purposes, the information presented in this study strongly suggests that continued natural flushing processes over the next 100 years will not produce a groundwater system that meets the applicable uranium standard.

This report recommends ways to monitor the groundwater system in coming years, with the intent of better discerning the progress of natural flushing. An assessment of the site's current regulatory status is also provided.

## 2.0 Objectives and Scope

This study has four objectives:

- Develop an updated conceptual model of groundwater flow and associated contaminant transport in the alluvial aquifer at the Old Rifle site;
- On the basis of the updated conceptual model and field information collected at the site since publication of the GCAP in 2000, develop potential explanations for the apparent lack of progress of natural flushing at the site through 2010;
- Assess the prospects for reliable predictive modeling of the natural flushing remedy; and
- Recommend a path forward regarding environmental monitoring at the site.

Several investigative activities have been carried out to meet these objectives, beginning with a review of the SOWP and GCAP. Hydraulic data collected at numerous groundwater monitoring locations have been analyzed to assess groundwater flow patterns and sources of water to the alluvial aquifer. Chemical data from LM monitoring wells and surface water sampling locations have been evaluated to identify significant temporal trends in concentration or other indicators of subsurface chemical processes.

To a large extent, this investigation has relied on IFRC data as well as reports and papers prepared by IFRC investigators to identify possible reasons why natural flushing is not progressing as predicted. Biostimulation experiments and other studies performed by the IFRC team at several different locations have demonstrated that microbially mediated chemical reactions in groundwater leading to immobilization of uranium can be enhanced by the injection of organic carbon nutrients. The experiments have provided valuable insight into various flow and biogeochemical processes that influence the fate of dissolved uranium in alluvial groundwater. Where relevant to the natural flushing remedy, those processes are discussed in this report.

Though several COCs were identified at the Old Rifle site (see Section 3.3.1), this study focuses almost exclusively on the fate of uranium in the subsurface. This contaminant is the most abundant in the alluvial aquifer and has been considered the contaminant most likely to flush naturally from the aquifer because of its relatively high mobility in the aqueous phase, in comparison to the transport characteristics of other COCs.

### **3.0 Site Description and Background Information**

The Old Rifle site is a former ore-processing facility located in Garfield County, Colorado, approximately 0.3 mile east of the city of Rifle, Colorado. The site is situated on a relatively low-lying alluvial terrace created by a floodplain meander of the Colorado River (Figure 1). The terrace is bounded on its south side by a steep slope that abruptly descends to the river and on the north by U.S. Highway 6.

#### **3.1 Site History**

The Old Rifle processing plant was constructed in 1924 for the production of vanadium. The plant closed in 1932 due to a shortage of vanadium ore, but ore processing resumed in 1942 in response to an increased demand for vanadium during World War II. The mill continued to operate until 1946, when it was modified to include the recovery of uranium as well as vanadium. Ore processing continued until 1958, when the plant was replaced with a new mill located approximately 3 miles west of the Old Rifle site.

Buildings used in the ore-processing operations were in the east half and midsection of the site (Figure 1), in areas lying on both sides of an unlined ditch (on-site ditch) that traverses the site in a north-south direction. Vanadium and uranium ores were stockpiled in the east end of the site, and the tailings produced by the milling were placed across a large area that covered most of the site's west half (Figure 1). During milling years, ponds designed to contain mill-process waters were often constructed over large portions of the former mill tailings area.

A relatively flat tailings pile that existed at the site at the end of the ore-processing years was stabilized in 1967 in accordance with State of Colorado regulations. The facility became an UMTRA Project site in 1978 with passage of the Uranium Mill Tailings Radiation Control Act (UMTRCA). Approximately 13 acres of tailings remained at the site when UMTRCA was enacted, but no structures remained. Surface remediation of the Old Rifle site began in spring 1992 and was completed in October 1996. Tailings and contaminated sub-tailings soils were removed from the site and relocated to a disposal site approximately 6 miles to the north-northwest. Fine-grained soils from off site were imported and used as fill to replace contaminated sediments that had been relocated. The fine-grained replacement fill was applied across most of the site and today commonly comprises the uppermost 5 to 10 feet (ft) of local surficial material.

Criteria used to determine the depth to which sub-tailings soils and other contaminated soils were excavated and transported off site were based on standards for soil concentrations of radium-226. Because the radium-226 criteria did not reflect the depth distribution of other mill-related contaminants that migrated into the subsurface, several inorganic contaminants remained in sub-fill sediments at many locales.



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Site Features Old Rifle, CO, Processing Site	
DATE PREPARED: December 27, 2010	FILENAME: S0727100

Figure 1. Site Features—Old Rifle, Colorado, Processing Site

## 3.2 Hydrogeology

Groundwater flow at the Old Rifle site occurs primarily within a surficial aquifer composed of Holocene-age alluvium that was deposited by the ancestral Colorado River. The alluvium consists mostly of sandy gravels and gravelly sands interspersed with silts and clays. Sediments described as clayey gravels, silty gravels, and sandy silts are also reported in logs for boreholes drilled into the aquifer. The fine-grained fill that was used to replace contaminated alluvium that was excavated is typically described as silty sand and silt that also contains fine-grained sands, subrounded gravels, clays, and roots. The alluvial aquifer is underlain by the Tertiary Wasatch Formation, an erosion-resistant geologic unit consisting mostly of variegated claystone, siltstone, and sandstone. Depth to the top of the Wasatch from land surface (i.e., from the top of the fill where present) typically varies between 20 and 30 ft.

The alluvial aquifer extends northward to just south of Highway 6, where resistant sedimentary rocks of the Wasatch Formation ascend steeply 40 to 60 ft. Much of the Wasatch face near the aquifer's north boundary is covered with alluvium and colluvium that has descended from elevated areas north of Highway 6. The Colorado River forms the south boundary of the aquifer, and the aquifer's east and west ends are located in areas where the outcropping Wasatch Formation abuts the river (Figure 1), effectively pinching the alluvium out. The areal extent of the alluvial aquifer takes up most of the area contained within the site's property boundary (Figure 1).

The low-permeability Wasatch Formation is thousands of feet thick beneath the site and generally acts as a strong aquitard, such that very little, if any, water appears to be exchanged between unweathered Wasatch sediments and the overlying alluvium. Descriptions in the SOWP (DOE 199) of the geologic logs for three wells drilled more than 30 ft into the Wasatch Formation at the site indicate that the uppermost 8 to 13 ft of the formation tends to be weathered and is in hydraulic communication with the overlying alluvial aquifer. Signs of weathering and fracturing are visually observed in the uppermost portion of the Wasatch in elevated outcrops of the formation just north of Highway 6.

Under base-flow conditions on the Colorado River, the bottom 10 or 15 ft of the alluvial sediments are typically saturated. Groundwater levels in the alluvial aquifer can increase by as much as 5 to 6 ft during late spring and early summer, when surface water discharge and river stage increase substantially due to snowmelt runoff from mountainous terrain in the region. As a consequence, piezometric levels in the aquifer may at times rise above the base of the surficial fill in some locations.

Analyses of aquifer test data collected in support of the SOWP (DOE 1999) resulted in estimates of hydraulic conductivity for the alluvial aquifer that varied from 100 to 125 ft/day. Values used in various studies to represent the alluvium's porosity have ranged between 0.25 and 0.35 (25 to 35 percent). The geometric mean of hydraulic conductivities estimated from slug tests in upper, weathered portions of the underlying Wasatch Formation was 0.017 ft/day (DOE 1999), a value that is more than 3 orders of magnitude less than the hydraulic conductivities ascribed to the alluvial aquifer. An investigation of co-located hydraulic heads in the alluvium and Wasatch Formation at multiple well nests across the site under non-pumping conditions revealed little or no driving force for vertical groundwater migration from one hydrogeologic unit to the other.

Past assessments of the alluvial groundwater flow system during periods of both low runoff and high runoff for the river indicate that groundwater flow in the aquifer is predominantly toward the south-southwest and southwest, although groundwater in the eastern half of the site tends to flow more directly to the west during high-river stage (DOE 1999). Virtually all of the groundwater in the aquifer discharges to the Colorado River. On the basis of previously prepared maps of the aquifer's potentiometric surface, calculated horizontal hydraulic gradients across the site vary from 0.003 to 0.006 ft/ft.

The predominant flow direction of south-southwest to southwest in the alluvial aquifer implies that much or most of the site groundwater derives from water sources north of Highway 6. These sources consist of subsurface inflow from older Quaternary alluvium north of the highway, much of which appears to migrate downward into weathered and fractured portions of the underlying Wasatch before migrating horizontally beneath the highway and recharging the alluvial aquifer. However, some of the inflowing water in the older alluvium apparently fails to migrate downward into Wasatch Formation sediment prior to reaching the site, which results in groundwater seeps on the north side of the highway. One of the seeps is located west of Ash Avenue (Figure 1), which intersects Highway 6 from the northwest. Areal recharge through sediments in higher elevation areas north of the site, either from natural infiltration of precipitation or anthropogenic water sources, is likely to be the origin of water in this seep. The seep water flows into an unlined ditch that parallels the highway on its north side, which in turn conveys water eastward to a culvert under Ash Avenue and then to a culvert under Highway 6, which feeds water to the on-site ditch (Figure 1).

Multiple seeps are present on the north side of Highway 6 in an area of thick vegetation located just east of Ash Avenue (Figure 1). The groundwater discharged there also flows into an unlined ditch that parallels the highway and feeds the on-site ditch via the culvert beneath the highway. The source, or sources, of the groundwater feeding these latter seeps is unknown. As in the case of the seep located west of Ash Avenue, some of this water may derive from natural or anthropogenic recharge in areas lying farther to the north. Alternatively, it is possible that some or all of the surface seepage here can be attributed to infiltration and downward percolation of surface water in two detention lagoons located on a mesa directly north of the site's east end (Figure 1). The City of Rifle periodically disposes of treated Colorado River water via pipelines to the lagoons, where it tends to pond, evaporate and support in-lagoon vegetation. Because the delivery rate of city water to the lagoons can at times be hundreds of gallons per minute (gpm), the potential also exists for some infiltrated water from this source to migrate downward and outward in multiple directions, including to the seep area east of Ash Avenue. Similarly, some of the lagoon water might migrate more directly to the south-southwest and directly recharge the easternmost third of the alluvial aquifer.

The conceptual model of groundwater flow developed for the SOWP (DOE 1999) attributed additional aquifer inflows to surface water seepage losses along the unlined on-site ditch (Figure 1). Areal recharge from precipitation on the site and possible upflow from the underlying Wasatch Formation were considered relatively minor contributors to alluvial aquifer groundwater. The SOWP conceptual model did not directly address potential inflows of river water to the aquifer; boundary conditions used to represent the river in the numerical groundwater flow model developed for the site indirectly accounted for this possibility.

## 3.3 Water Chemistry

### 3.3.1 Contaminants

The SOWP identified arsenic, selenium, uranium, and vanadium as COCs in alluvial groundwater at the Old Rifle site, and uranium is the most abundant and widely spread contaminant. Mill-related processes contributed many other inorganic constituents to the groundwater system, some of which continue to impact subsurface geochemical processes, but the aqueous concentrations of these additional constituents in the alluvial aquifer are not considered threats to human health or the environment.

Much of the groundwater contamination currently detected in the aquifer likely resulted from rainfall and melting snow that leached uranium and vanadium ores stored on the east end of the site and from leaching of tailings deposited on the ground surface in the west half of the site. Downward-seeping water from the various mill-water ponds that were occasionally used in the former mill tailings area (Figure 1) also probably contributed tailings-derived aquifer contamination, as did the leaching of contaminants present in the former mill buildings area.

Several types of chemicals used to process the ores undoubtedly added to the inorganic constituent mass that remains in the site's subsurface today. The impacts of most of these chemicals and related chemical residues were likely to have been observed in the former mill tailings area. Though the exact quantities of chemicals used in the milling process are unknown, dissolved inorganic constituents that probably exhibited increased concentrations due to their use included ammonia, bicarbonate, carbonate, chloride, sodium, and sulfate (DOE 1999, Merritt 1971).

To assess the potential for a continued source of groundwater contamination in the subsurface, samples from soils directly beneath the former tailings and ore stockpile areas were collected in the late 1990s (DOE 1999) and analyzed for arsenic, molybdenum, selenium, uranium, and vanadium. The soil testing revealed that concentrations of arsenic, uranium, and vanadium were generally higher than those for molybdenum and selenium, and selenium concentrations were nondetectable. The highest uranium and vanadium concentrations were mostly detected in a sample collected beneath the former ore storage area. Of interest was the fact that uranium concentrations in soil samples collected from two off-site points in a river floodplain about 0.8 mile east-northeast of the site were generally of the same magnitude as concentrations in samples collected beneath the former tailings area.

Site characterization in support of the SOWP also included the collection of surface water samples from a variety of locations. Analyses of several samples collected from seeps north of the highway, the unlined ditch north of the highway into which the seeps fed, and the on-site ditch indicated that uranium in these surface waters ranged from 0.02 to 0.055 milligram per liter (mg/L). Given that all of these waters were considered representative of major recharge sources for the alluvial aquifer (Section 3.2), the reported uranium concentration range indicated that site groundwater could naturally contain uranium at levels approaching 0.03 to 0.05 mg/L. Thus, the background concentration of uranium at the site had the potential to exceed the 0.044 mg/L UMTRA standard for uranium.

Considerable attention was given in the SOWP to the estimation of a representative sediment-water distribution coefficient, or  $K_d$ , for each COC in the site's alluvial groundwater. A reliable estimate of  $K_d$  was considered critical for assessing the subsurface migration because it reflected

the degree to which a contaminant would sorb to aquifer sediments along its transport path, with increasing  $K_d$  values signifying greater sorption. Correspondingly, the  $K_d$  value adopted for a COC controlled the rate at which its advective transport (due to average linear groundwater velocity) and, therefore, flushing, would be retarded (Freeze and Cherry 1979).

Laboratory batch tests conducted in accordance with a 1987 American Society for Testing and Materials standard was applied to sediment samples from a floodplain location upriver of the site to estimate  $K_d$  values for all COCs. The test method generated multiple  $K_d$ s for uranium, ranging from 0.2 to 0.9 milliliters per gram (mL/g). These values were considered too large for the alluvial aquifer because a large fraction of the sediments in the test samples consisted of coarse-grained sands and gravels, which were expected to contribute little to uranium sorption in the subsurface. Subsequent adjustment of the original  $K_d$  values to reflect the large percentage of coarse materials resulted in a set of final estimated  $K_d$ s ranging from 0.2 to 0.3 mL/g, which suggested that uranium in the alluvial aquifer would be relatively mobile and its advective transport only mildly retarded.

### **3.3.2 Historical Distribution of Uranium in the Alluvial Aquifer**

Aqueous constituent concentrations measured at several alluvial wells in 1998 during preparation of the SOWP showed that the largest amount of dissolved uranium mass at the time was present in groundwater underlying the former tailings area. As illustrated in a map of contoured uranium concentrations from a sampling event in May 1998 (Figure 2), uranium concentrations approaching 0.3 mg/L were detected in the west half of the site, and concentrations of about half this value were detected in groundwater on the site's east end. Measured uranium concentrations were noticeably lower in the site's midsection, such as in the vicinity of the on-site ditch. Here, the uranium levels here exceeded the UMTRA groundwater standard of 0.044 mg/L for uranium, which is based on assumed secular equilibrium between isotopes of uranium-234 (U-234) and uranium-238 (U-238). The lowest uranium concentrations were observed at wells located along the aquifer's northwest border.

The areal distribution of aqueous-phase uranium shown in Figure 2 suggests that in 1998, 40 years after cessation of Old Rifle milling operations, a majority of the uranium remaining in groundwater could be attributed to leaching of tailings that had previously covered much of the site's west half. A smaller but nevertheless significant mass of uranium detected in groundwater in the east third of the site was likely caused by leaching of ore that was historically stored there. The presence of uranium concentrations in the central part of the site that were noticeably lower than concentrations observed to the west and east suggested that historical leaching of surface contamination in this area was possibly less than in other site locales. It is also possible that the relatively low uranium levels in the site's midsection were attributable to dilution by fresh surface water seeping into the subsurface from the on-site ditch.

The uranium concentrations posted in Figure 2 for alluvial aquifer wells in May 1998 represent a snapshot in time, and aqueous uranium concentrations measured at some of these same wells in November 1998 were noticeably different from those shown in the figure. This observation illustrates how uranium concentrations can change between sampling events. Despite such temporal variability, the general pattern of uranium distribution shown in Figure 2, with the highest uranium levels beneath the east and west portions of the site and lower concentrations in between, is consistently maintained.

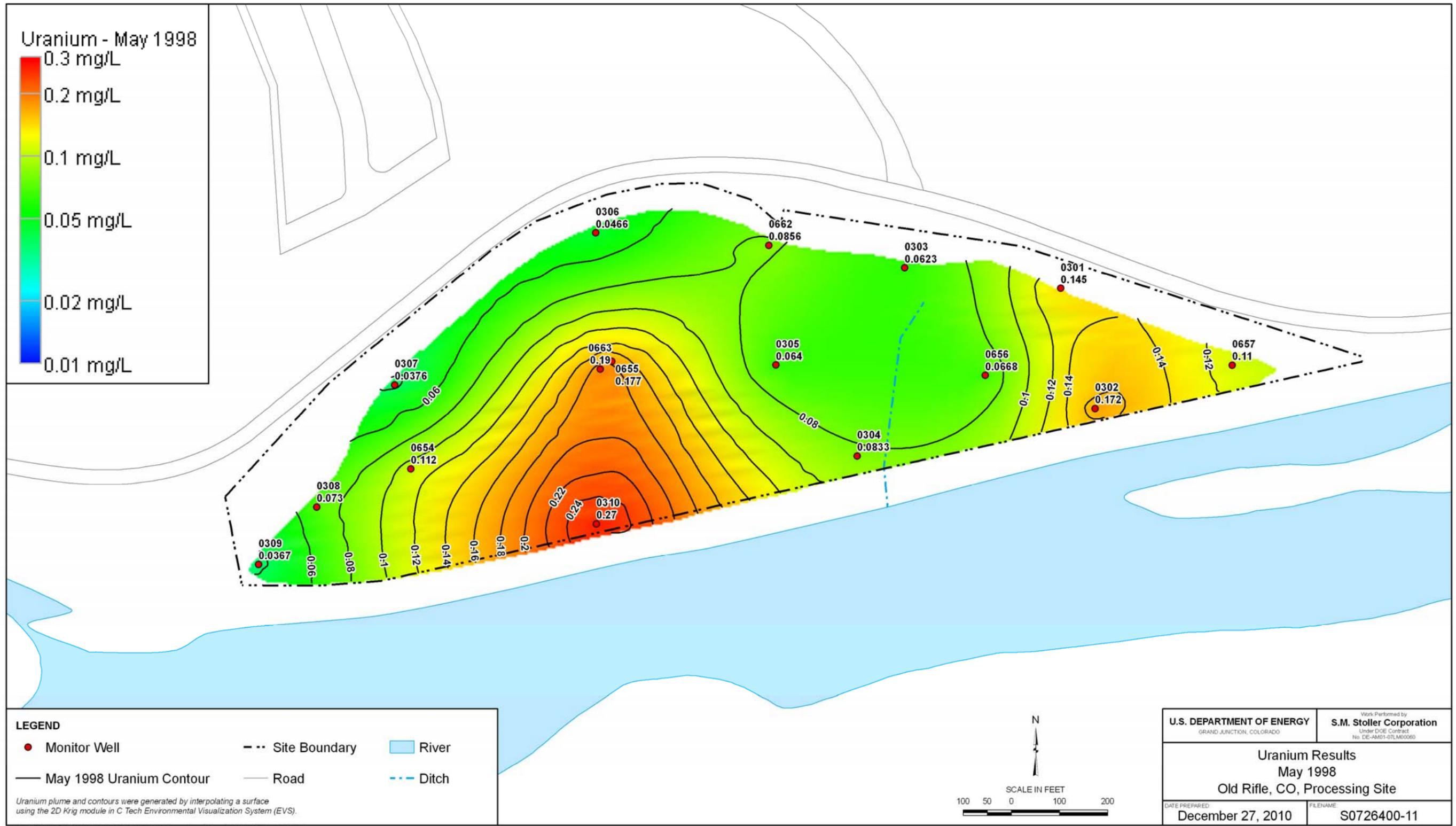


Figure 2. Uranium Concentrations in the Alluvial Aquifer in May 1998

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### 3.3.3 Ambient Groundwater Chemistry

The general chemistry of water in the site's subsurface strongly affects the fate of uranium remaining in groundwater as a legacy of historical milling operations. Pertinent chemical characteristics of groundwater in the alluvial aquifer, derived primarily from the SOWP (DOE 1999), are summarized in this section.

The specific conductance of alluvial aquifer groundwater varies from about 1,800 to 5,000 microsiemens per centimeter ( $\mu\text{S}/\text{cm}$ ), which is reflective of total dissolved solids concentrations of approximately 1,500 to 4,500 mg/L. Alkalinity concentrations typically fall in the range of 300 to 600 mg/L as calcium carbonate and are indicative of relatively high dissolved bicarbonate concentrations. Dissolved nitrate levels are low; most reported concentrations for this constituent are less than 2 mg/L. Sulfate concentrations, which commonly vary between 500 and 2,000 mg/L, are elevated ostensibly as a result of past milling activity at the site. The pH of the groundwater is circumneutral to slightly basic (6.8 to 8.5).

The redox state of the alluvial groundwater is manifested in a variety of chemical indicators. Dissolved oxygen (DO) concentrations in most horizons within the saturated zone are typically less than 0.3 mg/L (DOE 1999), which signifies anoxic conditions. However, DO levels measured in the shallowest parts of the saturated zone may have values as large as 2 to 2.5 mg/L, and DO concentrations show a tendency to increase during periods of higher groundwater elevation (Yabusaki et al. 2007) in late spring and early summer. Dissolved iron concentrations tend to be relatively high, ranging from 0.003 mg/L to as high as 3 mg/L and averaging near 0.5 mg/L. Similarly, aqueous manganese concentrations are somewhat elevated, and concentrations as high as 2 mg/L are common. The oxidation-reduction potential (ORP) of the groundwater ranges from  $-250$  millivolts (mV) to about 100 mV (DOE 1999). Overall, these characteristics are representative of a slightly reducing chemical environment. Such a redox state suggests that uranium has the potential to naturally occur in a precipitated solid state at some locations within the subsurface.

The low DO and nitrate concentrations in site groundwater provide a subsurface environment that is conducive to the immobilization of uranium using techniques that manipulate redox chemistry. Specifically, biogeochemical reactions that depend on the presence of these two constituents (i.e., aerobic respiration and denitrification) tend to consume only minor amounts of the organic carbon injected by IFRC personnel during biostimulation experiments (see Section 4.1.1), which makes more organic carbon available for reactions that cause uranium to precipitate out of solution.

### 3.4 DOE Modeling

A groundwater flow and transport model was developed for the SOWP (DOE 1999) to assess the effectiveness of natural flushing as a groundwater remedy. Groundwater flow was numerically represented using the U.S. Geological Survey (USGS) code MODFLOW (McDonald and Harbaugh 1988), and contaminant transport was modeled with the USGS simulator MT3D (Zheng 1990). Flow and transport in the aquifer were assumed to occur solely within a two-dimensional (2-D) horizontal plane.

### 3.4.1 Groundwater Flow Model

Recharge sources included in the model were represented using prescribed flows in several parts of the flow domain, including at seep locations close to Highway 6 and along the ditch paralleling the highway on its north side. Prescribed flow conditions were also applied along the length of the on-site ditch to account for recharge from this surface water source. A minor amount of recharge from areal infiltration of precipitation on the site was also taken into account. The southern aquifer boundary coincided with the north bank of the Colorado River, which was simulated using prescribed values of hydraulic head.

A trial-and-error approach was applied to calibrate a steady-state version of the flow model, using a set of groundwater elevations collected from site wells during a monitoring event in 1998 as calibration targets. A uniform hydraulic conductivity of 110 ft/day was employed in the final calibrated model, and prescribed flow boundary conditions were adjusted to achieve an acceptable match between computed groundwater elevations and the head calibration targets. A water budget reported for the steady-state flow model (DOE 1999) indicated that water inflow sources north of Highway 6 contribute 6,113 cubic feet per day (ft<sup>3</sup>/day), or 31.8 gpm, of recharge to the alluvial aquifer. Inflow to the aquifer from seepage losses along the on-site ditch amounted to 2,484 ft<sup>3</sup>/day (12.9 gpm) in the model, and the assumed average recharge rate from areal infiltration of precipitation was limited to 18 ft<sup>3</sup>/day (0.09 gpm). All water losses from the aquifer in the steady-state model occurred as discharge to the river.

### 3.4.2 Transport Model

MT3D simulations of uranium transport accounted for advection and dispersion (Freeze and Cherry 1979) within the aquifer as well as retarded uranium migration due to constituent sorption on aquifer sediments. Contaminant sorption was modeled as a linear equilibrium process using a uniform and constant value of the soil-water partition coefficient, or  $K_d$ , considered representative of uranium in the alluvial aquifer. Several different values of longitudinal and transverse horizontal dispersivity were tested in the model before adopting a final set of values for these parameters to be used in predictive simulations.

A probabilistic, or stochastic, modeling approach was taken to predict how natural flushing of uranium would progress at the site. One hundred Monte Carlo simulations, each with a different combination of randomly generated values of stochastic parameters, were conducted to generate a suite of numerical results from which the predicted flushing time for uranium could be ascertained. Stochastic (uncertain) parameters in the Monte Carlo simulations included aquifer hydraulic conductivity, longitudinal and transverse horizontal dispersivities, and the uranium  $K_d$ , the last of which was allowed to range between 0.0 and 0.2 mL/g. Aquifer porosity was maintained at a uniform value of 0.25 (25 percent), and the concentration of uranium in recharge waters from north of Highway 6 and on-site ditch seepage was assumed to be 0.038 mg/L in all model runs. The uranium concentrations shown in Figure 2 for conditions in May 1998 were used to develop a spatially distributed set of starting concentrations in each simulation.

Each of the 100 Monte Carlo simulations accounted for 100 years of uranium transport. All of the stochastic model runs predicted that ambient background flow and transport conditions would cause uranium to effectively flush from the alluvial aquifer within 10 simulation years. The largest predicted uranium levels in all model runs after 10 years of flushing were only

slightly higher than the 0.038 mg/L concentration assigned to the major recharge sources in the model.

### **3.5 DOE Compliance Strategy Selection**

Based on the information discussed above and the conceptual model developed in the SOWP, DOE was required to select a compliance strategy for site groundwater. Because the modeling showed that natural flushing would achieve the groundwater standard for uranium in a timeframe less than 100 years, DOE selected natural flushing (similar to monitored natural attenuation) as the groundwater compliance strategy for the Old Rifle site (see Section 10.1.3 for further discussion). As noted previously, NRC concurred on this compliance strategy, as described in the GCAP (DOE 2000), in 2002. As part of the compliance strategy, annual monitoring has been required to support the natural flushing evaluation. In addition to monitoring, research at the Old Rifle site has been ongoing to study uranium attenuation mechanisms. Section 4.0 summarizes the activities associated with and results from that research.

## **4.0 IFRC Studies**

Consistent with DOE's goal of uranium attenuation in groundwater, studies by SC researchers at the Old Rifle site began in the early 2000s and have continued through the first half of 2011 (Long 2011). As described in Section 1.0, many of these investigations have been conducted as part of the Rifle IFRC, which began in 2007. The earliest research work comprised experiments aimed at reducing aqueous-phase uranium concentrations in portions of the site's alluvial aquifer comprising less than 0.1 acre. Specifically, uranium was immobilized through subsurface application of an organic carbon amendment that stimulates microbially mediated precipitation of uranium as a solid. As discussed in the following sections, field-scale tests of this form of biostimulation, using acetate as an amendment, have confirmed that this type of stimulation does, for some time, locally reduce dissolved uranium concentrations. Since the earliest experiments and continuing to the present, efforts have been made to more thoroughly understand the geochemistry and microbiology associated with biostimulation. In more recent years, Rifle IFRC researchers have also strived to better describe ambient, background phenomena in the alluvial aquifer, focusing on more detailed characterization of hydrological, contaminant-transport, geochemical, and microbiological processes in areas separate from those subjected to biostimulation. In addition, experiments have been conducted that promote flushing of uranium by enhancing levels of naturally occurring constituents, such as bicarbonate ions, in groundwater. These stimulations induce mobilization of uranium adsorbed to sedimentary materials that constitute the alluvium.

A key goal of the IFRC initiative has been to develop quantitative models that simulate the various flow, transport, geochemical, and microbial processes that occur in the alluvial aquifer, under both biostimulated and ambient background conditions. The models have proved particularly beneficial, not only for synthesizing the numerous physicochemical phenomena that impact the fate of uranium in the aquifer, but also for projecting the results of future experiments.

It should be mentioned that one IFRC task parallels efforts by LM to better understand reasons for the persistence of relatively high uranium concentrations in the alluvial aquifer at the Old Rifle site. This work tacitly acknowledges that natural flushing processes have not been

successful in the manner that DOE originally anticipated and provides reinforcement for many of the analyses and findings presented in this report. The specific research activities that IFRC personnel carried out to identify and better understand processes contributing to uranium persistence in groundwater are not addressed in this present study. Nonetheless, readers should be aware that findings developed thus far under the IFRC effort generally comport with reasons presented in this report (see Section 7.0) for recalcitrant uranium in Old Rifle groundwater.

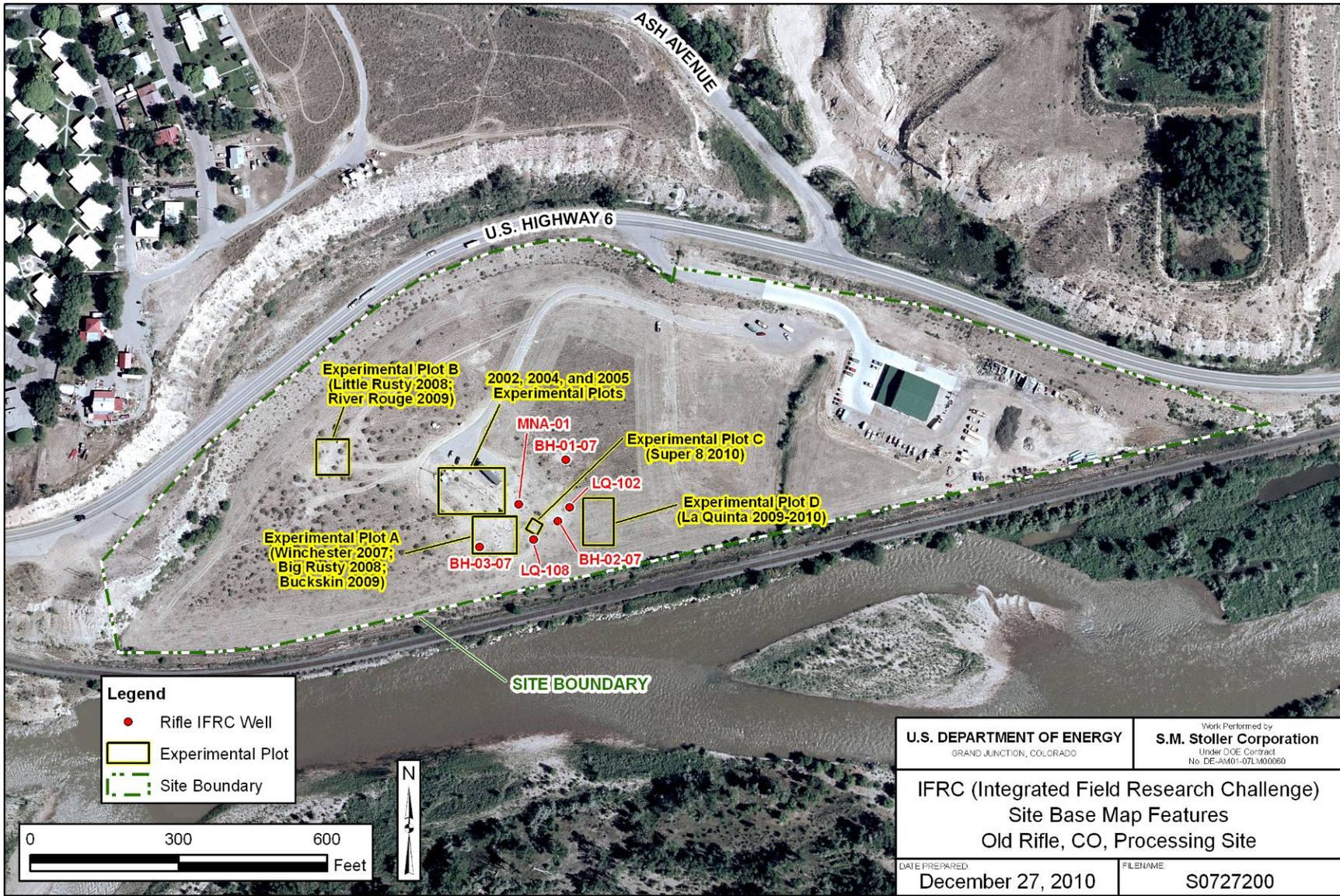
The SC investigations have been concentrated in rectangular areas on the west half of the site. Figure 3 shows the locations of the study areas, along with the adopted names and applicable dates (in parentheses) for several explicit experiments that have been or are being performed at the plots. More than one experiment is typically performed within a study area. The first three enhanced biostimulation tests were performed in the area identified as the location of “2002, 2004, and 2005 experimental plots.” Because the Old Rifle site was not designated an IFRC location until 2006, these earliest biostimulation investigations are also referred to as pre-IFRC experiments. New, detailed biostimulation experiments have since been conducted at Plots A and C; investigations at Plots B and D (Figure 3) have primarily focused on the characterization of natural background processes in the alluvial aquifer.

Subsequent parts of this section describe the general groundwater chemistry associated with the biostimulation experiments (Section 4.1.1), the monitoring networks and techniques used to conduct and evaluate the experiments (Section 4.1.2), relevant findings from the biostimulation experiments (Section 4.1.3), the presence of chemically reduced zones in the alluvial aquifer under natural background conditions (Section 4.2), studies designed to characterize processes affecting uranium mobility in groundwater (Section 4.3), and models of some of the IFRC experiments (Section 4.4).

## **4.1 Biostimulation Experiments**

### **4.1.1 Biogeochemical Reactions**

The primary goal of each biostimulation experiment at the Old Rifle site is to use biological processes to promote chemically reducing conditions in uranium-contaminated parts of the alluvial aquifer. Specifically, the aim is to enhance biologically mediated iron reduction, a redox reaction wherein subsurface microorganisms metabolize organic carbon and in the process transfer electrons from a donor chemical (electron donor) to solid-phase ferric iron Fe(III) (Anderson et al. 2003). The IFRC experiments use acetate as the electron donor, and Fe(III) is provided by iron oxyhydroxide and phyllosilicate minerals in the alluvial aquifer matrix. Microbially mediated iron reduction is also referred to as a terminal electron acceptor process (TEAP) in that it facilitates the transfer of electrons to the oxidant Fe(III); in the process of accepting electrons, solid Fe(III) is converted into dissolved ferrous iron Fe(II). Though a generic group of microbes referred to as iron reducers are generally responsible for mediating iron reduction in the environment, *Geobacter* species have been specifically identified as the microorganisms primarily responsible for iron reduction in Old Rifle alluvium (Anderson et al. 2003).



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Figure 3. IFRC Experimental Plots at the Old Rifle Site

Iron-reducing microbes are also capable of facilitating uranium reduction (Anderson et al. 2003), a TEAP in which electrons from an organic carbon source (e.g., acetate) are transferred to dissolved hexavalent uranium U(VI), resulting in the production of tetravalent uranium U(IV). Dissolved U(VI) may be present as a free uranyl ion ( $\text{UO}_2^{2+}$ ), but is more commonly present in aqueous-phase chemical complexes (Sections 4.1.3 and 6.1.2). Minerals containing U(IV) generated by the U(VI) reduction have low solubility and precipitate out of solution. It has traditionally been assumed that the U(IV) generated through biostimulation automatically occurs in the subsurface as uraninite  $\text{UO}_{2(s)}$ . However, work over the past 3 years at the Rifle IFRC and other locations has shown that the biogenic U(IV) is initially present in solid forms different from uraninite. Continued research dealing with this phenomenon has shown that these early forms of U(IV) have the potential to eventually transform into uraninite (Section 4.1.3).

Biostimulated iron reduction decreases U(VI) concentrations in areas of the alluvial aquifer downgradient of an organic carbon application as long as a supply of the electron acceptor Fe(III) is available. However, after about a month of acetate injection, iron reduction tends to be overtaken by biologically mediated sulfate reduction (Long 2011), the next thermodynamically favored TEAP, in which dissolved sulfate becomes the electron acceptor. It has long been known that some sulfate-reducing microbes (sulfate reducers) are also capable of reducing U(VI) depending on local subsurface conditions and the electron donor material driving the sulfate reduction. However, IFRC researchers have shown that the sulfate reducers stimulated by acetate amendments at the Rifle site do not contribute to U(VI) reduction, thus indicating that biologically driven precipitation of uranium during site biostimulation tests is solely attributable to the activity of iron-reducing bacterial species (Long 2011). After sulfate reduction becomes the dominant TEAP in a biostimulation test, iron-reducing bacteria continue to reduce uranium in the presence of Fe(III), but the rate at which U(IV) is generated by iron reducers is noticeably less than occurred when microbial iron reduction predominated. Recent biostimulation experiments conducted by IFRC personnel have been aimed at identifying means of enhancing and sustaining microbially mediated iron reduction with the intent of maximizing uranium immobilization.

#### **4.1.2 Test Plots and Monitoring**

Each biostimulation test is performed using an array of wells laid out in a rectangular pattern. Injection wells near the upgradient end of the well array are used to deliver acetate amendment to the aquifer, and multiple rows of wells oriented perpendicular to the ambient groundwater flow direction (Figure 4) are used to monitor the downgradient effects of the experiment on dissolved concentrations of numerous constituents, including acetate, U(VI), and Fe(II). “Background” wells located upgradient of the injection wells are used to characterize the chemistry of ambient water feeding into the test plot.

The sizes of the biostimulation injection and monitoring plots vary among tests, depending on the objectives of the experiment being conducted. However, in general, the dimensions of a rectangular test area typically fall in a range that facilitates experimental control. As shown in the schematic in Figure 4, the widths of the test areas tend to range between 25 and 50 ft, and the plot lengths, extending from the background wells to the farthest downgradient monitor wells, are typically 50 to 70 ft. Hence, the area included in the test monitoring is less than 0.1 acre. Figure 5 presents an areal view of the well layout used in the first biostimulation test, which began in spring 2002 within the “2002, 2003, and 2005 experimental plot” areas (Figure 3). As

indicated in the figure, three rows of five monitor wells were used for this test, and the distances from the injection array to monitoring rows were 12, 24, and 48 ft, respectively. The average distance between wells in each monitoring row was about 9 ft, and the row of injection wells was about 48 ft long.

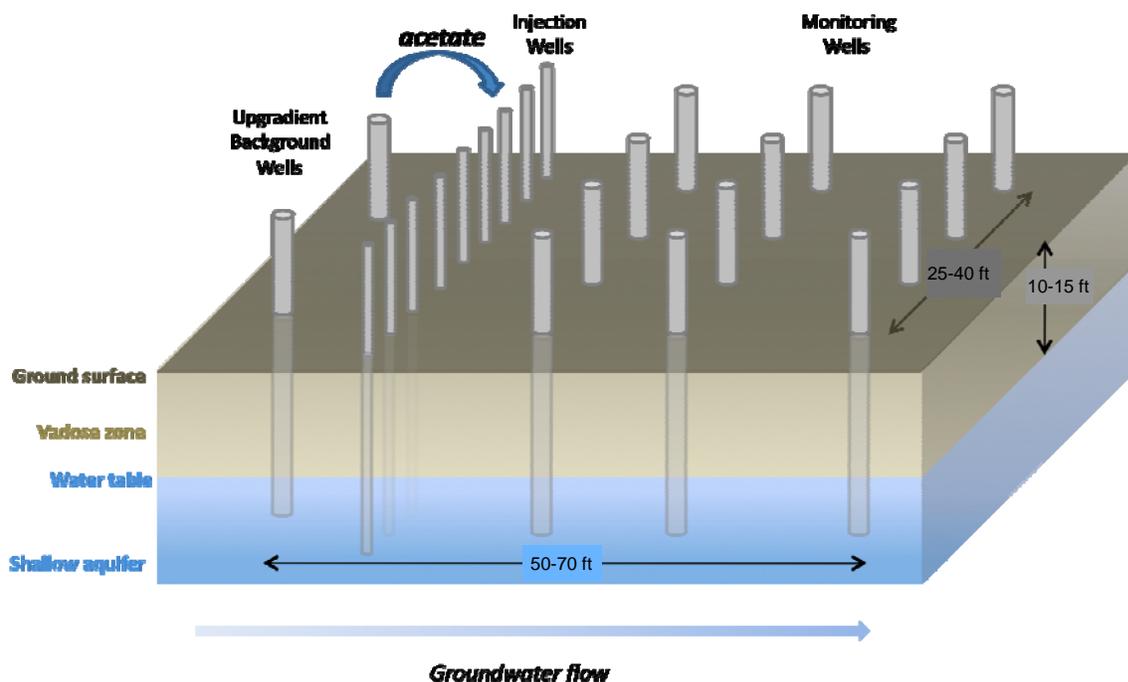


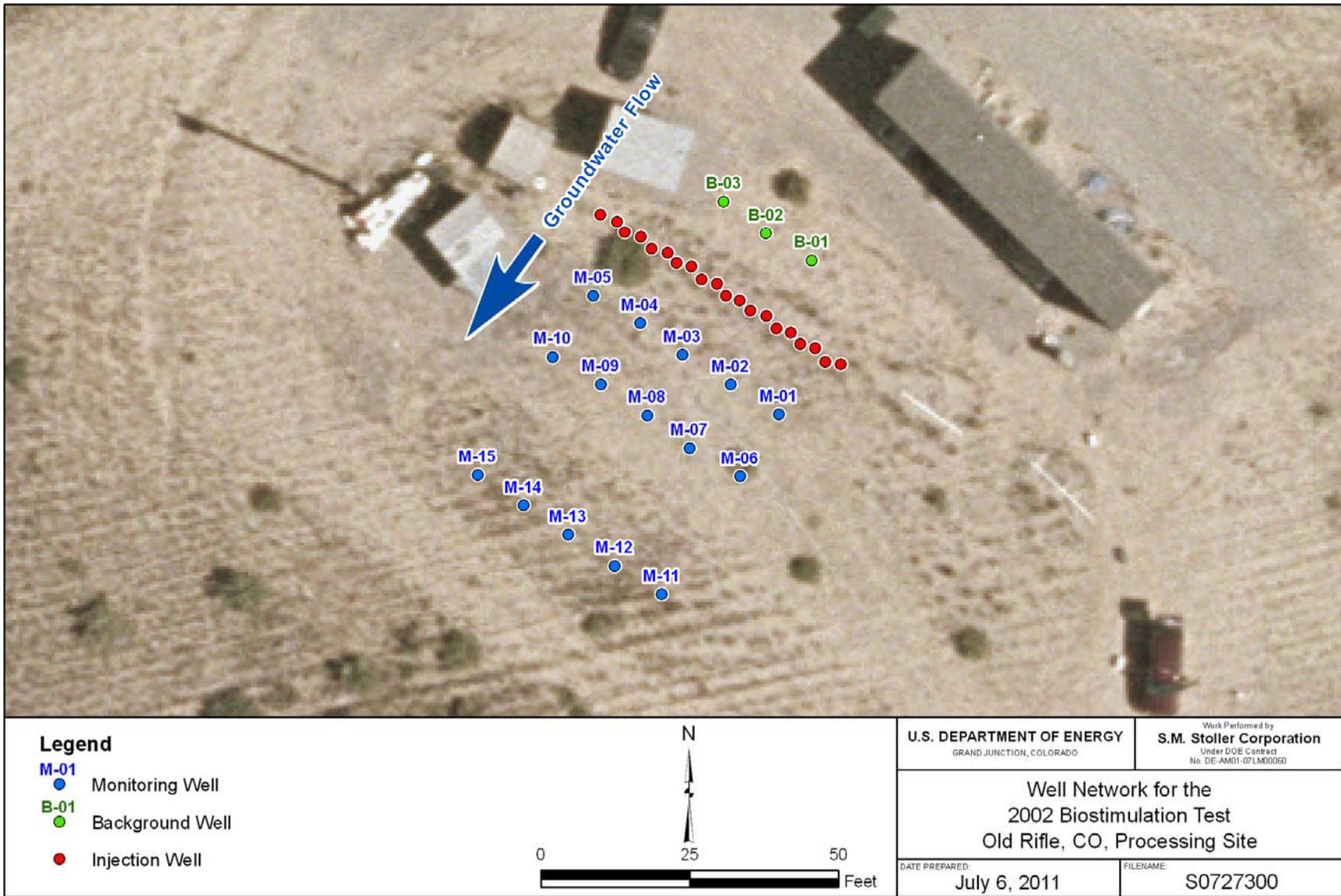
Figure 4. Typical Configuration of Wells in a Biostimulation Test

It is common for multiple biostimulation events to be conducted at a given test plot. Specific reasons for carrying out successive tests vary, though in most cases the motivation is to change test variables (e.g., acetate concentrations, amendment application duration) and study the concomitant impacts on biologically mediated iron, uranium, and sulfate reduction. A second experiment was conducted in summer 2003 at the field plot shown in Figure 5, the location for the first biostimulation test that began in spring 2002. During the 2003 experiment, injected acetate concentrations were 3 times those used in the 2002 test.

Occasionally, multilevel sampling wells are installed within the biostimulation test array for the purpose of discerning and analyzing vertical flow and transport processes. Drill cores of alluvial aquifer sediment are also sometimes collected and chemically analyzed to better understand the solid-phase chemistry associated with iron, uranium, and sulfate bioreduction.

#### 4.1.3 Relevant Findings

Throughout the various biostimulation tests conducted to date, researchers have identified chemical complexes of uranium, calcium, and carbonate ( $\text{Ca-UO}_2\text{-CO}_3$  ternary complexes) as the primary U(VI) species in groundwater. This finding is expected, given the relatively large concentrations of alkalinity (300 to 600 mg/L as calcium carbonate) in subsurface water at the site (Section 3.3.3). Though the ternary complexes are relatively mobile in groundwater, the biostimulation tests have demonstrated that the application of acetate amendment does



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Figure 5. Layout of Wells in the 2002 Biostimulation Experiment

successfully lead to the creation of solid U(IV) species, and that dissolved uranium concentrations in the resulting chemically reduced zones can be decreased to less than the UMTRA groundwater standard of 0.044 mg/L.

One of the observed effects of biologically induced sulfate reduction results in the generation of dissolved sulfide. IFRC experiments have shown that much of the biogenic sulfide combines with the dissolved Fe(II) produced by iron reduction to form iron sulfide precipitates. The presence of these precipitates has been confirmed through the analysis of drill cores collected upon the completion of some of the biostimulation tests. An interesting finding stemming from the study of dissolved sulfide generated by the biostimulation tests is that the sulfide has a tendency to react with dissolved U(VI) and, in the process, abiotically reduce the U(VI) to solid-phase U(IV) (Long 2011). One of the products of this chemical reaction is elemental sulfur, which also appears as a solid on aquifer materials. This finding is considered important because it demonstrates that, under sulfate-reducing conditions, abiotic chemical reactions are an important contributor to the removal of U(VI) from solution, and should be considered in addition to bioreduction processes when attempting to ascertain the effects of biologically reduced conditions on the fate of uranium.

Biostimulation applications are ultimately judged for their ability to immobilize uranium over long-term periods. Invariably, at least some biogenic U(IV) is re-oxidized to aqueous U(VI) as upgradient groundwater flows into the area impacted by the biostimulation. Relatively high alkalinity concentrations in the background groundwater enhances the redissolution of U(IV), as do occasional natural influxes of DO. As discussed subsequently in Section 4.3, a recent biostimulation experiment conducted in Experimental Plot C has shown that methods designed to mobilize uranium in the subsurface may actually help lengthen the period over which U(VI) concentrations remain depressed due to biostimulation.

As mentioned in Section 4.1.1, the solid-phase U(IV) generated by biostimulation initially occurs in forms different from uraninite. Specifically, the biogenic U(IV) is present in the form of solid-phase monomeric complexes that tend to be associated with solid-phase iron and sulfur in the subsurface (Long 2010). In late 2010, an experiment designed to observe the evolutionary behavior of biogenic U(IV) encased in wells at the Buckskin experimental site (Plot A in Figure 3) showed that, with about a year of aging, monomeric U(IV) did transform into uraninite. This finding encouraged IFRC researchers because uraninite is considered less likely than monomeric U(IV) to be re-oxidized by inflowing water containing relatively high alkalinity.

This, in turn, implies that reduced uranium produced by biostimulation may be slow to reoxidize and re-dissolve in site groundwater, and therefore, could help maintain concentrations of U(VI) below the UMTRA groundwater standard (0.044 mg/L).

## 4.2 Naturally Reduced Zones

IFRC work in recent years inadvertently led to the discovery of multiple zones in the subsurface that are naturally reducing (e.g., Long 2010). The presence of the naturally reduced zones was not entirely unexpected, given that previous site characterization efforts have occasionally revealed alluvium dominated by fine-grained sediments and containing organic debris, the combination of which has the potential to induce natural biodegradation and consumption of the

thermodynamically favorable electron acceptors (e.g., DO, nitrate, iron, sulfate). The identification of such zones, combined with a general interest of uranium on a sitewide scale, eventually led to a new IFRC experimental task (LaQuinta) and a rectangular study area (Plot D in Figure 3) that focused on characterizing the origin of, composition of, and processes occurring within the naturally reduced areas. This research is of great interest because it is believed that the reduced zones not only have the capacity to be subsurface sinks for uranium but also can act as long-term sources of uranium in groundwater.

Investigations of the sediments in the naturally reduced zones indicate that they are dominated by fine-grained materials such as clays and silts that are typically dark gray to black in color. Examination of solid-phase components of the reduced zones shows a significant presence of sulfide minerals, including pyrite. U(IV) is present in the reduced sediments, and analyses of the pyrite (Qafoku et al. 2009) show the presence of both solid-phase U(VI) and U(IV). Relatively high levels of total organic carbon provide evidence of a biological origin for the reduced zones, as do the presence of microbial communities dominated by iron reducers, sulfate reducers and bacteria that facilitate fermentation.

IFRC research conducted thus far on naturally reduced zones at Old Rifle has not shed light on the relative abundance of these features in the alluvial subsurface. However, it has been shown that surface geophysical characterization methods based on electrical resistivity potentially provide a non-invasive means for identifying the locations of buried chemically reduced zones. Further understanding of their overall abundance and the nature of the physicochemical phenomena occurring within them may prove to be important in future years even if the zones comprise only a few percent of the alluvial aquifer. Their potential to act as long-term sources of aqueous-phase U(VI) could detrimentally impact the success of any applied remediation strategy.

### **4.3 Uranium Mobility**

A thorough understanding of processes that influence the mobility of U(VI) in the site's alluvial aquifer is considered critical by IFRC researchers, not only for assessing the efficacy of efforts to effect sustainable immobilization of uranium through biostimulation, but also to ascertain the influence of engineered uranium mobilization techniques on the long-term fate of uranium. Accordingly, several IFRC experiments, in both the laboratory and the field, have been conducted to study in detail uranium mobility under various subsurface conditions.

Consistent with the effort to improve knowledge of uranium mobility, a key IFRC objective has been to improve both the conceptualization and quantification of U(VI) sorption processes under ambient conditions (Long 2011). A test aimed at pursuing this objective was performed at the Little Rusty site (in Experimental Plot B) in fall 2008. The purpose of the test was to accelerate desorption of U(VI) from alluvial sediments by injecting sodium bicarbonate (Long 2009) upgradient of an array of monitor wells used to monitor both sorption and desorption in the subsurface. Using the results of laboratory-batch reaction tests performed earlier (Hyun et al. 2009) on sediments from the Little Rusty area, the bicarbonate was expected to combine with dissolved calcium and sorbed U(VI) to form aqueous Ca-UO<sub>2</sub>-CO<sub>3</sub> ternary complexes that are relatively mobile, with the net result being increased concentrations of U(VI) in impacted areas and the creation of additional sorption sites for upstream influent U(VI). The Little Rusty test was distinct in the sense that it was designed to assess sorption/desorption processes in an ambient, non-biostimulated environment.

A Rifle IFRC quarterly report (Long 2009) indicates that a sorption model based on the Hyun et al. (2009) application of surface complexation theory to the above-mentioned batch reaction tests provided a useful tool for simulating uranium and desorption processes at Little Rusty. The quarterly report also mentions that tracer breakthrough data at a downstream multi-level monitor well showed the presence of considerable aquifer heterogeneity, with groundwater at depth (25 ft) in the aquifer migrating much faster than water in shallower portions of the aquifer. Results from the Little Rusty test have not yet been formally reported. Eventual publication of the test results and analysis are expected to show that sorption and desorption of U(VI) are complex processes that vary spatially and temporally, and that are heavily influenced by water pH and aqueous concentrations of calcium, bicarbonate, and U(VI).

The Super 8 experiment, initiated in 2010 in Plot C, provides a more recent test of methods used to enhance uranium mobility by injecting sodium bicarbonate into the alluvial aquifer. Though one of the objectives of the test was to replicate and extend the test conducted at Little Rusty, Super 8 was also designed to study uranium mobility under conditions in which acetate was injected into the aquifer (Long 2011). Thus the Super 8 experiment differed from the Little Rusty test in the sense that uranium mobility could be studied under the iron-reducing conditions created by aquifer amendment with organic carbon.

The Super 8 experiment was designed such that half of the experimental plot accounted for the effects of bicarbonate-induced desorption followed by acetate biostimulation some distance downgradient, and the other half functioned as a control affected only by acetate amendment. In this way, the design enabled a direct comparison of uranium reduction rates under typical and amended bicarbonate concentrations. Test results showed that U(VI) concentrations in the zone affected only by sodium bicarbonate injections were about 2 to 3 times the concentration of U(VI) entering the experimental plot in inflowing groundwater from the north. Data collected from the test also indicated that the rate of uranium reduction occurring in the bicarbonate-amended half of the test was virtually indistinguishable from the rate in the control half that was subjected to biostimulation only (Long 2011). A key interpretation stemming from the latter observation is that, as U(VI) is bioreduced and precipitated from groundwater, the enhanced levels of Ca-UO<sub>2</sub>-CO<sub>3</sub> ternary complexes generated by bicarbonate amendment do not retard bioreduction. The decreased U(VI) concentrations occurring in areas subjected to combined bicarbonate enhancement and bioreduction also stand the chance of persisting longer than those achieved solely through biostimulation.

Recent IFRC experiments shed light on how and at what rate biogenic U(IV) will be re-oxidized and, as a consequence, mobilized in the form of U(VI) complexes in groundwater. These tests, which involved the installation of pure, laboratory-generated biogenic uraninite in wells at Buckskin test site, showed that release of U(IV) under site-specific field conditions was 50 to 100 times slower than was indicated by laboratory flow-through reactor experiments under oxic conditions (Long 2010). A subsequent modeling analysis of the conditions under which these experiments were conducted suggested that the slow oxidation in the field was mostly due to a diffusion barrier created by the sample cells in which the biogenic uraninite was placed. Because natural sediments are expected to create much larger diffusion barriers than those attributed to the sample cells, a logical conclusion derived from the in-well tests of U(IV) release is that oxidation of reduced uranium in alluvial sediments under background conditions is inherently slow (Long 2011).

## 4.4 IFRC Models

Much of the mathematical modeling performed in support of IFRC research has focused on simulation of numerous chemical reactions that occur in groundwater in response to subsurface injections of acetate. The objective of the reactive transport simulations has been to provide reasonable matches to the observed results of biostimulation tests and, as a consequence, identify which reactions and transport processes exert significant influence on the fate of uranium in site groundwater. Most of the IFRC modeling efforts have also accounted for relatively complex sorption processes that differ considerably from the manner in which sorption of uranium to alluvial sediments was handled in the model developed for the SOWP (Section 3.4.2). As discussed in the following section, one of the IFRC modeling investigations concentrated solely on uranium sorption processes that occur naturally in the alluvial aquifer without influences from biostimulation activities.

### 4.4.1 Surface Complexation Modeling

The use of a spatially uniform and temporally constant sorption distribution coefficient ( $K_d$ ) to model sediment-water partitioning of a constituent dissolved in groundwater has several shortcomings. Not only does the “constant  $K_d$ ” approach fail to take into account the availability and mineral composition of the sediment surfaces upon which the sorption takes place, but it also neglects the effects that variable water chemistry can have on the distribution of the constituent between water and sediment phases. When the impacts of these factors are taken into consideration, researchers tend to find that the  $K_d$  for a specific chemical can vary greatly in both space and time. Accordingly, models that allow for a spatially and temporally varying  $K_d$  dependent on ambient aquifer conditions are likely to provide more realistic appraisals of groundwater remedies.

To overcome the limitations of uranium transport models that adopt a constant  $K_d$ , models based on surface complexation theory (e.g., Davis et al. 2004) have been developed. A considerable amount of aquifer sediment characterization is necessary for the development of surface complexation models capable of accurately simulating sorption processes at specific field sites, but the efforts put into such characterization can prove worthwhile if they are appropriately applied in model simulations that account for spatially and temporally variable sorption as affected by aquifer geochemistry.

Hyuan et al. (2009) developed a site-specific surface complexation model, using data from batch reaction tests on a sediment sample collected from a floodplain location about a mile upriver of the Old Rifle site and on a composite sediment sample collected from two locations at the Little Rusty site (at Plot B in Figure 3). The sample from the upriver location was considered representative of non-contaminated, background conditions in floodplain materials deposited by the Colorado River, whereas the Little Rusty composite sample was potentially impacted by Old Rifle mill activity. The purpose of this model development, based on laboratory analysis of soil samples, was to provide a surface complexation simulator that could be applied to follow-up experiments involving field-scale reactive transport under ambient chemically oxidizing conditions. Subsequent to the Hyun (2009) study, surface complexation modeling was applied to the 2008 Little Rusty field investigation addressing accelerated uranium desorption of sediments at the Little Rusty site (Section 4.3).

Though the results of the Little Rusty field study have yet to be formally reported, modeling by Hyun et al. (2009) of the laboratory-derived results indicated that partitioning of U(VI) between groundwater and sedimentary materials in the alluvial aquifer was strongly affected by water pH and U(VI), calcium, and bicarbonate concentrations. The effective  $K_d$ s for U(VI) determined for the sampled sediments varied from about 0.5 to 20 mL/g (Hyun et al. 2009) for a range of geochemical conditions considered representative of the alluvial aquifer. These  $K_d$  values, by themselves, indicate that uranium transport in the alluvial aquifer is considerably more retarded than was assumed for uranium in the DOE modeling. They also suggest that the solid-phase uranium available in the alluvial aquifer as a contaminant source is much larger than was assumed for the DOE modeling. As mentioned in Section 3.4.2, the maximum value of  $K_d$  used in the SOWP modeling of uranium flushing was 0.2 mL/g, which suggests minimal retardation.

#### 4.4.2 Reactive Transport Modeling

This section describes four separate reactive transport models that have been developed to support IFRC quantitative assessments of enhanced uranium bioreduction processes at the site test plots. All four models have been shown to perform reasonably well in matching the concentrations of dissolved species observed during biostimulation tests. All account for the transport and fate of multiple components in the subsurface and are based on chemical reactions that influence aqueous U(VI) concentrations as well as solid-phase concentrations of both U(IV) and U(VI). The complexity of the models has increased with each successive modeling project in an effort to more fully understand the numerous factors that influence the fate of uranium.

Yabusaki et al. (2007) were the first to simulate the effects of a biostimulation experiment at the site. Their model accounted for one-dimensional (1-D) flow and transport during the first enhanced bioremediation test that began in spring 2002 at the test plot shown in Figure 5, within the rectangular zone defining the boundary of the 2002, 2004, and 2005 experimental plots (Figure 3). Because test results from the acetate injections were collected at an array of wells over the test area, average constituent concentrations along each row of wells oriented perpendicular to the ambient flow direction downgradient from the injection gallery were used to calibrate the 1-D reactive transport model. The model simulated both the effects of an initial acetate-injection phase lasting about 4 months in 2002, and the effects of the follow-up injection phase beginning in spring 2003. The flow model was constructed to maintain a uniform and steady Darcy velocity of 0.25 ft/day throughout the test plot during both amendment-injection phases.

The Yabusaki et al. (2007) transport model was developed using the simulator HYDROGEOCHEM (Yeh et al. 2004, Fang et al. 2006). No attempt was made in the model to simulate sorption of U(VI) on aquifer sediments because the retardation of uranium advection due to such processes was considered relatively minor. Three TEAPs driven by microbial consumption of acetate—iron reduction, uranium reduction, and sulfate reduction—were accounted for using dual Monod rate law algorithms incorporated into the model code. The model accounted for several aqueous- and solid-phase species, including dissolved acetate, Fe(II), Fe(III), U(VI), U(IV), and sulfate, as well as two microbial populations (iron reducers and sulfate reducers). Despite the fact that their model was limited to 1-D transport, Yabusaki et al. (2007) managed to approximately match measured concentrations of dissolved constituents at most test gallery wells over time, indicating that key processes were mostly accounted for in the simulations. The relatively simple reactive transport model used in this case identified several steps that could be taken with future models to improve simulations of bioreduction phenomena.

As follow-up to the Yabusaki et al. (2007) modeling, Fang et al. (2009) performed more detailed simulations of the 2002/2003 experiments at the test plot shown in Figure 5 using a version of HYDROGEOCHEM that handled many more reactions and constituents than were incorporated into the earlier model. Four different TEAPs associated with two different microbial populations (iron reducers and sulfate reducers) were included in the updated model; two of the reactions accounted for uranium and sulfate reduction, and the other two represented reduction of Fe(III) in phyllosilicates and iron oxides, respectively. As in the Yabusaki et al. (2007) model, acetate consumption was simulated using a dual Monod kinetics formulation. An extensive reaction network was incorporated into the Fang et al. (2009) model, which included abiotic chemistry as described by more than 30 equilibrium reactions and 6 kinetic reactions. Sorption and desorption processes were simulated using a surface complexation model that accounted for several aqueous and solid species in the subsurface.

Fang et al. (2009) initially simulated the geochemical conditions observed during the 2002 biostimulation experiment included in the Yabusaki et al (2007) analysis. As with the earlier model, the new flow and transport model was 1-D, and the simulated Darcy velocity field was treated as steady and uniform. In addition to acetate, dissolved concentrations of 10 primary species were simulated, including those for uranyl, calcium, iron, carbonate, and sulfate ions. After using the 2002 experimental data to develop a set of calibrated parameters for the new model, the calibrated reaction simulator was then applied to the 2003 experimental results and subsequently to an entirely new biostimulation test (Winchester) in 2007 within Experimental Plot A (Figure 3). This latter modeling application performed well in capturing the observed dynamics in pH and concentrations of U(VI), Fe(II), sulfate, and acetate. The 1-D simulations performed by Fang (2009) of the 2002, 2003 and 2007 experiments highlighted the importance of integrating abiotic chemical reactions with biologically mediated processes to achieve a more thorough quantitative description of the many processes affecting enhanced bioremediation of subsurface uranium.

A reactive transport modeling investigation by Li et al. (2009) focused on potential aquifer porosity reduction resulting from mineral precipitation and biomass accumulation induced by biostimulation experiments at the Old Rifle site. Like the Fang et al. (2009) study, this modeling effort accounted for multiple biogeochemical reactions associated with consumption of acetate as well as several abiotic reactions taking place in the subsurface. Kinetic biogeochemical reactions were handled using dual Monod reaction rate laws, and surface complexation modeling was employed to simulate sorption effects. The modeling was conducted using the code CrunchFlow (Steefel 2007).

The CrunchFlow simulator was initially applied to simulate the results of laboratory column-based biostimulation experiments using sediments collected from the site. Upon developing a calibrated set of model parameters from analysis of the column tests, the model was subsequently used to simulate the geochemical processes induced by the 2002/2003 field tests. As in the case of the Yabusaki et al. (2007) and Fang et al. (2009) efforts, the model simulated flow and transport processes within a 1-D domain. With the model taking account of biomass produced during both microbially driven iron and sulfate reduction as well as solid mass generation in the form of mineral precipitates, Li et al. (2009) projected that these mass forms could take up as much as 1.5 percent of available pore space in a zone located a short distance downgradient of the tests' acetate injection gallery. This amount of pore clogging was not considered to be problematic in relatively coarse-grained sediments consisting of relatively clean

sands or gravels, but it was thought to have significant effects on flow and uranium transport in finer-grained media.

A follow-up modeling investigation by Li et al. (2010) was significant because it represented the first formal effort to simulate 2-D horizontal (depth-averaged) flow and fate and transport associated with an IFRC enhanced bioremediation test. An underlying objective of this new study was to further assess the possible effects of mineral precipitation and biomass accumulation on aquifer porosity. As with the foregoing Li et al. (2009) study, multiple biogeochemical reactions and abiotic chemical reactions, as well as sorption in accordance with surface complexation theory, were included in the 2-D simulations. The 2002/2003 experiments were again the subject of the modeling investigation, and the simulator applied was CrunchFlow. Unlike earlier modeling studies, the flow domain was treated as being heterogeneous rather than homogeneous; thus, simulated flow fields were no longer uniform in space, and local Darcy and average linear velocities were spatially variable. The 2-D hydraulic conductivity field used in the simulations was derived using the code TOUGH2 (Pruess et al. 1999) and associated automated inverse techniques as applied to bromide tracer data collected from the well array for the 2002/2003 experiments.

The Li et al. (2010) modeling indicated that aquifer heterogeneity could significantly influence pore-clogging phenomena in the Old Rifle site alluvial aquifer. Modeling results suggested that accumulated biomass and mineral precipitation associated with stimulated iron and sulfate reduction processes could occupy more than 5 percent of the subsurface pore volume in certain areas downgradient of the acetate injection.

## **5.0 More Recent Alluvial Aquifer Conditions**

LM contractor personnel have been collecting and analyzing groundwater monitoring data on a semiannual basis primarily to assess the progress of natural flushing. These assessments indicate that subsurface flow patterns at the site and the distribution of uranium contamination have changed very little since 1998, when groundwater conditions were documented in support of the SOWP (DOE 1999). Sections 5.1 through 5.3 describe the general findings regarding groundwater flow and uranium contamination at the site in recent years.

### **5.1 Groundwater Flow**

Groundwater elevation data collected at 10 on-site monitoring wells in April 2007 were used to prepare a potentiometric surface map for the alluvial aquifer. An aerial photograph of the surface (Figure 6) indicates that groundwater movement continues to be dominated by flow toward the southwest and south-southwest, in the direction of the Colorado River, with slight variations from this pattern occurring in a few distinct locales. In the north-central portion of the site, a short distance south of Highway 6, plotted groundwater level contours (Figure 6) suggest that the local flow direction is more directly toward the south. This conceptualization supports the hypothesis that subsurface inflows from north of the highway represent a major source of groundwater recharge to the alluvial aquifer. Water level contours near the eastern end of the site exhibit a northwest–southeast orientation that is almost perpendicular to the river, suggesting that groundwater flow here is more parallel to the river than elsewhere in the aquifer. In general,

these groundwater flow patterns comport with those that were adopted in the conceptual model developed for the SOWP.

The potentiometric surface presented in Figure 6 indicates that horizontal hydraulic gradients at the site range between 0.003 and 0.006 ft/ft. Assuming that hydraulic conductivities of the alluvial aquifer sediments average 125 ft/day and that aquifer porosity is 30 percent, the hydraulic gradients mentioned translate into average linear groundwater velocities ranging between 0.8 and 2.5 ft/day.

## **5.2 Spatial Distribution of Uranium**

An updated uranium plume map, similar to the one in Figure 2 for the alluvial aquifer in May 1998, has been prepared using uranium concentrations measured at site wells in April 2007. Though the number of monitoring locations used to prepare this figure is substantially fewer than the number of permanent and temporary wells that were available in 1998, the distribution of uranium concentrations in 2007 (Figure 7) appear to be similar to the distribution observed during preparation of the SOWP. By and large, the 2007 plume map supports the observation that dissolved uranium concentrations have not decreased in response to 9 years of through-flow by waters that enter the site north of Highway 6 and eventually discharge to the river. Similarly, the highest uranium levels in the late 2000s continue to be observed beneath the former tailings area west of the on-site ditch. Lesser amounts of apparent uranium contamination are detected east of the ditch (Figure 7), in an area that was likely impacted by leachates from the former ore stockpile area in the eastern half of the former mill buildings area.

A single uranium concentration of 0.062 mg/L in well 0304, about 50 ft west of the on-site ditch (Figure 7), supports the SOWP conceptual and numerical models, which assumed that recharge to the alluvial aquifer from the ditch helped dilute contaminant concentrations both under and on either side of the ditch. If seepage water from the ditch containing relatively low levels of uranium remains a significant source of alluvial groundwater today, local groundwater mounding caused by the recharge provides a reasonable explanation for the two areas of higher uranium concentrations on the east and west halves of the site.

## **5.3 Uranium Concentration Histories**

The apparent lack of natural flushing progress to date is also seen in updated temporal plots of uranium concentration at multiple on-site wells. Figure 8, which presents the uranium concentration histories for six widely spaced wells using semiannual monitoring data through 2010, shows that on-site uranium concentrations have tended to remain elevated since 1998. Though concentrations have fluctuated considerably between consecutive sampling events at well 0310, the uranium levels reported for the remaining locations have either remained fairly constant for 12 years or have gradually increased in the past 5 years (well 0656). Given that there are no obvious downward trends in uranium concentration at these locations, it is safe to conclude that ambient groundwater flows through the alluvial aquifer system have not induced the natural flushing results predicted by the SOWP modeling.

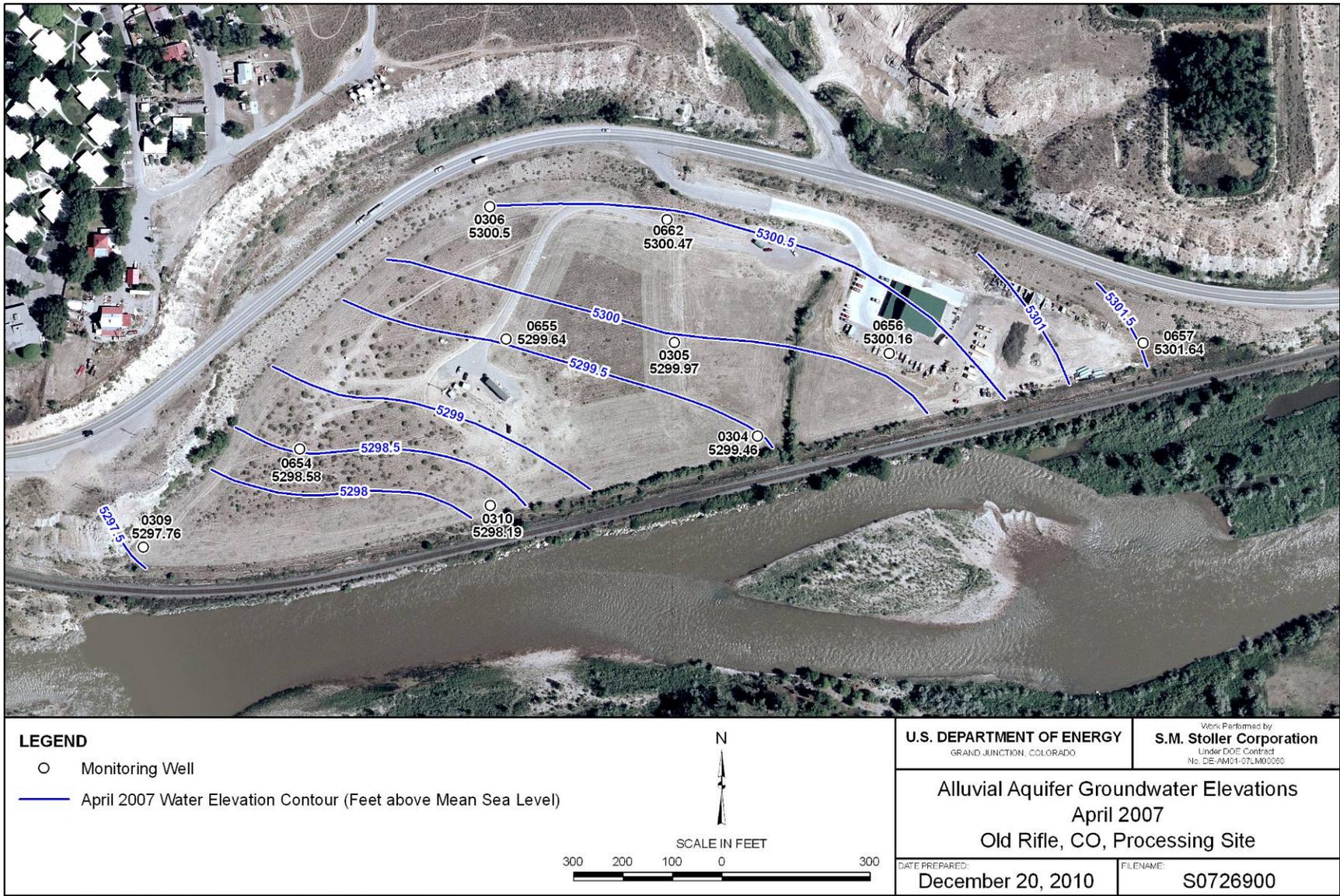


Figure 6. Potentiometric Surface for the Alluvial Aquifer in April 2007

## 6.0 Updated Conceptual Model

### 6.1 Subsurface System Complexity

#### 6.1.1 Physical Heterogeneities Affecting Groundwater Flow and Transport

Much of the complexity associated with the Old Rifle groundwater system exists in the form of aquifer heterogeneity. Well logs for the numerous DOE and IFRC wells that have been drilled in the alluvial aquifer at the site indicate that the composition of alluvial sediments ranges from coarse sands and gravels to silts and clays. It is common for a single log to show distinct layers of fine-grained materials interspersed with larger sand and gravel horizons. Though the IFRC work has not focused on the physical characterization of aquifer sediments, descriptions of sediment test plot areas as well as the results of modeling efforts by IFRC researchers have provided valuable additional evidence of substantial aquifer heterogeneity.

Little characterization work has been done to contrast the hydraulic characteristics of the sands and gravels with those of the silts and clays, but the hydraulic conductivities of the coarser-grained materials are likely as much as 3 or 4 orders of magnitude larger than the conductivities of the fine-grained sediments. Moreover, even when an alluvial material at one location appears to be virtually identical to material at a different location (e.g., both are coarse-grained sand), it is possible that the hydraulic conductivities of the materials could differ by a factor of two or more. Such spatial variations in hydraulic conductivity can lead to local groundwater flow directions that diverge significantly from the overall, background flow orientation, which in turn signifies more tortuous flow paths than are generally assumed for the alluvial aquifer system.

The physical heterogeneity of Old Rifle alluvial sediments probably contributes to slow removal of subsurface uranium on a sitewide scale largely because of the disparate groundwater velocities occurring in coarser, high-permeability sediments versus the velocities in finer-grained, low-permeability materials. The more permeable sediments that are connected form preferential pathways (mobile domain) in which contaminant migration is relatively rapid, and the low-permeability zones (immobile domain) slowly feed contaminants into those pathways (Zheng and Gorelick 2003, Bianchi et al. 2010). In some cases, the flow velocity in the less-permeable sediments may be so small that contaminant transport out of them is effectively governed by molecular diffusion rather than the process of advection. Such rate-limited mass transfer, which is capable of taking place even in small areas with dimensions of a few tenths of a foot or less, can cause long-lasting persistence, or tailing, of uranium concentrations at the site's monitoring wells.

As discussed in Section 3.4, the numerical model prepared for the SOWP was based on 2-D horizontal flow, in which the hydraulic conductivity assigned to each location was considered a vertically averaged value of local material layers. Overall, this approach appeared to adequately represent general flow directions over distances of hundreds of feet, but the 2-D model obviously did not capture more localized vertical flow components. Without more detailed studies of local groundwater movement, the potential for three-dimensional (3-D) flow to strongly influence transport of contaminants cannot be discounted.

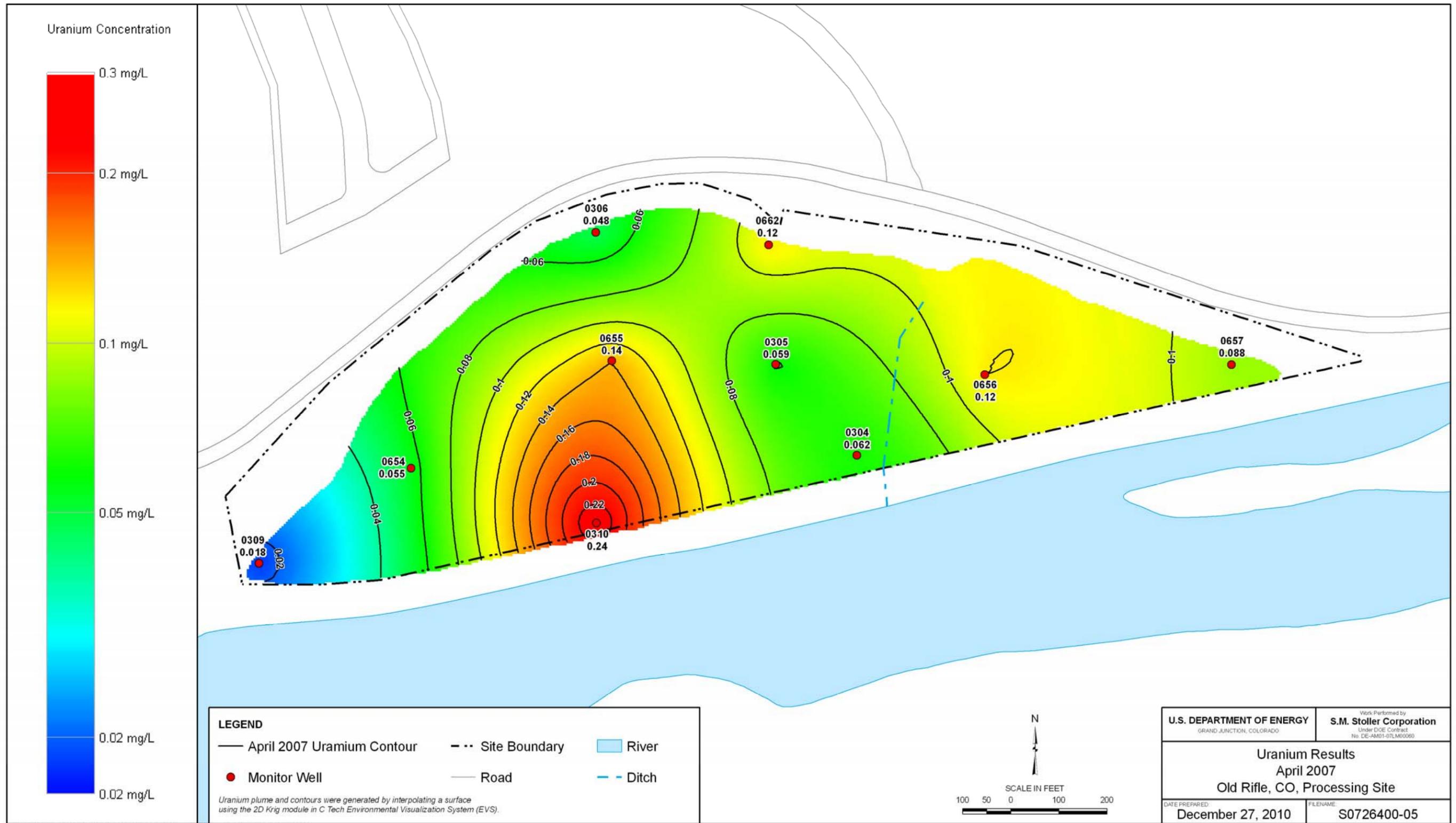


Figure 7. Uranium Concentration in the Alluvial Aquifer in April 2007

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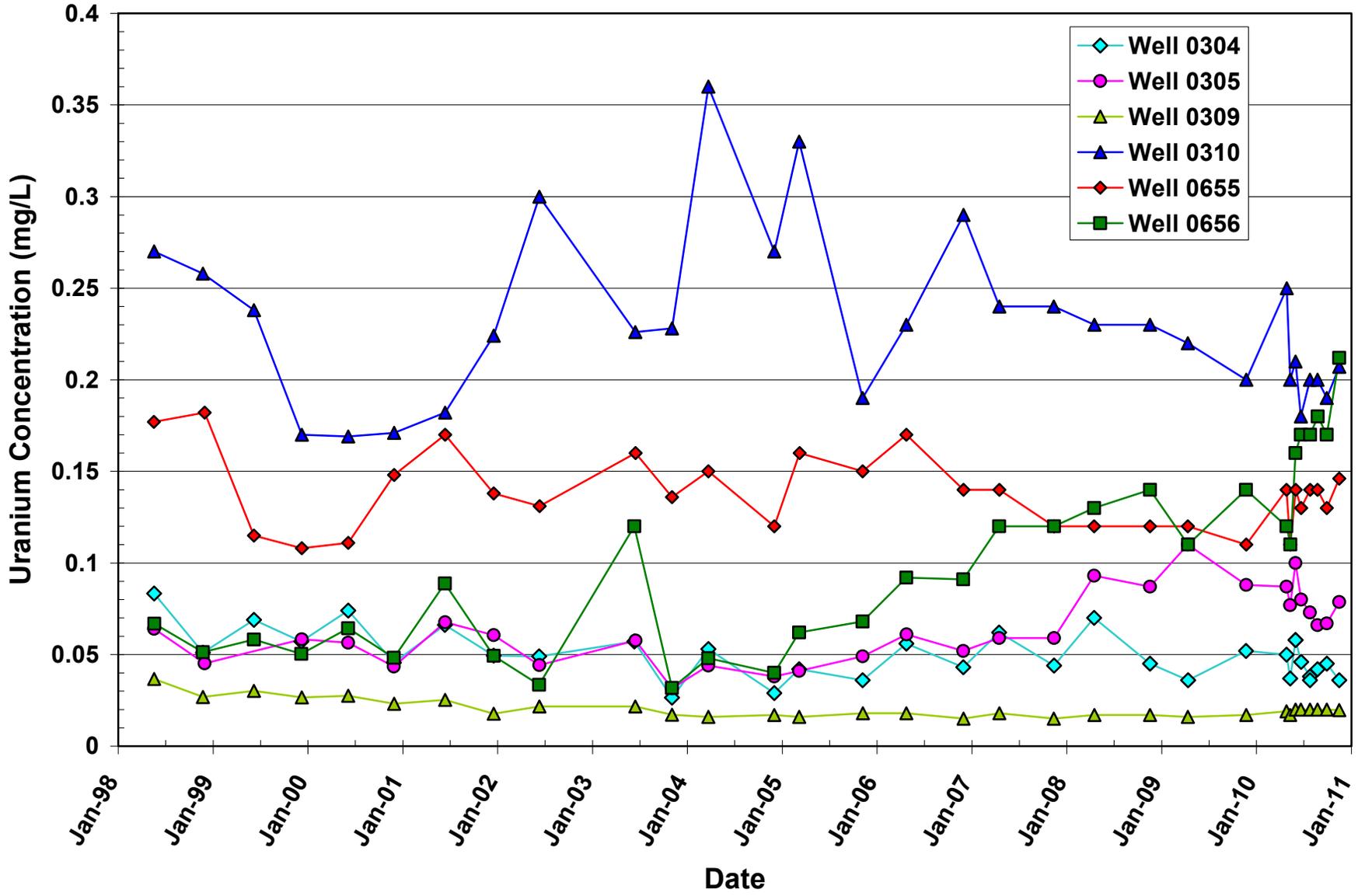


Figure 8. Uranium Concentration Histories at Several On-Site Wells

Logs prepared for the numerous boreholes drilled on the Old Rifle site indicate that the interface between the alluvial aquifer and the underlying Wasatch Formation is irregular, with depressions up to 3 ft deep occurring in the Wasatch surface. At one of the IFRC experimental plots, the logs from monitoring wells show a localized depression with dimensions of 5 to 10 ft wide and several tens of feet long. It is unclear whether the Wasatch surface depressions comprise portions of more extensive paleochannels that traverse the floodplain area, and whether these features significantly influence transport of contaminants in the alluvial aquifer. At a minimum, the irregular surface of this bedrock formation adds to the complexity of the alluvial groundwater flow system at the site.

### 6.1.2 Biogeochemical Heterogeneity

The IFRC work has provided considerable evidence that, in addition to being physically heterogeneous and complex, the alluvial aquifer is also chemically heterogeneous (Vrionis et al. 2005, Li et al. 2010). Moreover, on the basis of reported water chemistry results from DOE and IFRC wells and biogeochemical analyses of sediment cores, the heterogeneity appears in both aqueous and solid phases within the shallow subsurface. Aqueous-phase variability is seen in different forms of dissolved U(VI) or heterogeneous distributions of electron acceptors, such as sulfate. An example of solid-phase chemical variability is spatially changing mineral types within the alluvial sediments.

Mobile U(VI) in groundwater at the Old Rifle site has the potential to migrate in multiple chemical forms. Though it can migrate as the free uranyl ion at low pH, it tends to form complexes with anions in the aqueous phase. Carbonate, sulfate, phosphate, fluoride, chloride, and dissolved organic carbon are all potential ligands for the uranyl ion at circumneutral and alkaline pH values; however, most of the U(VI) in the alluvial aquifer appears to be transported as Ca-UO<sub>2</sub>-CO<sub>3</sub> ternary complexes (Section 4.1.3) due to the relatively high alkalinity present at the site (Section 3.3.3). Nevertheless, the possibility that multiple U(VI) complexes could exist in the subsurface adds to the complexity of uranium transport and natural flushing processes.

The rate of flushing at the site under natural conditions is heavily influenced by uranium sorption onto and desorption from the sediments in the alluvial aquifer. As discussed in Section 4.4, IFRC modeling analyses have clearly demonstrated that the uniform  $K_d$  approach applied in the DOE modeling for the SOWP does not capture the complex nature of sorption under actual field conditions. In particular, the IFRC work confirms that the  $K_d$  for uranium will vary both spatially and temporally depending on sediment type and a variety of chemical indicators, such as pH and dissolved U(VI), bicarbonate, and calcium concentrations. Assessment of natural flushing processes should take into consideration the results of the laboratory tests on alluvial sediment samples (Hyun et al. 2009), which indicated that the  $K_d$  for uranium at the site was capable of varying by more than an order of magnitude under a range of chemical conditions representative of the site groundwater system.

The naturally reduced zones discovered in the alluvial aquifer further highlight the effects that sediment heterogeneity can have on in situ biogeochemical processes. The reduced zones are typically found in fine-grained, lower-permeability materials, suggesting that the types of sediments with the highest concentrations of U(IV) are also likely to be dominated by slow diffusive transport of U(VI). Thus, even if the naturally reduced zones only compose a relatively small percentage of the aquifer, they can be expected to strongly influence long-term rates of U(IV) mobilization for the site as a whole.

Another factor possibly leading to variable bioreduction of U(VI) on a sitewide scale is the spatial variability of nutrients required for microbial growth. Nitrogen and phosphate are essential nutrients that typically play significant roles in microbial metabolism. Dissolved ammonium (NH<sub>4</sub>) has been shown to be an important source of nutrient nitrogen for biologically driven iron reduction by *Geobacter* species (Mouser et al. 2009). However, its concentration in site alluvial groundwater can vary with location by orders of magnitude, which implies that its availability to support biologically mediated iron and uranium reduction can vary significantly in space as well. The reasons for the wide variation in NH<sub>4</sub> levels at the site are unclear, but evidence suggests that they may be related to natural variations in organic matter and organic carbon content in the aquifer sediments (Mouser et al. 2009). Alternatively, the possibility exists that concentration variations reflect differential mass loading of milling-related ammonium to the subsurface.

An IFRC study conducted by N'Guessan et al. (2008) of the biostimulation experiment begun in 2002 provided further evidence of natural bioreduction of U(VI) in the alluvial aquifer in areas that apparently do not contain the fine-grained sediments typically associated with naturally reduced zones. The study pointed out that, at a single time prior to injection of acetate, the concentration of U(VI) in a background well upgradient of the injection gallery was noticeably higher than the U(VI) concentration at a well about 24 ft downgradient of the injection gallery. This pre-test finding implied that natural attenuation of uranium via ambient biological processes was occurring near the upgradient edge of the experimental plot, but no attempt was made to quantify the apparent attenuation rate. The findings of N'Guessan et al. (2008) also had bearing on the many issues that should be taken into account when characterizing the mechanisms that affect natural flushing. In particular, the researchers discovered that removal of U(VI) unexpectedly continued for about 1.5 years after cessation of biostimulation injections, and that the apparent lack of uranium mobilization with reintroduction of oxidizing water could be largely attributed to U(VI) sorption onto the sediment microbial community. Thus, analysis of this experiment revealed alternative means by which U(VI) could be immobilized that had not been considered in previous experiments focused on biologically driven production of U(IV) or sorption of U(VI) to sediments themselves.

Section 6.4 presents a more detailed discussion of the relevant biogeochemical phenomena in the alluvial aquifer, as elucidated in IFRC reports and papers.

### **6.1.3 System Transients**

Temporal variability of subsurface flow and transport processes adds to the complexity of the groundwater system at the Old Rifle site. For example, seasonal highs in water levels induced by high runoff in the Colorado River during April through June make it possible for groundwater to entrain constituents from sediments that normally reside in the vadose zone during other months. Though difficult to identify on the basis of semiannual monitoring, minor to moderate changes in groundwater flow direction probably occur during the high-runoff months and not at other times. It is also probable that the infiltration and subsequent downward seepage of rainfall or melted snow on the site will periodically add recharge to the groundwater system. Despite the fact that several feet of fine-grained materials were used to replace contaminated sediments excavated during surface remediation of the site, the heterogeneity of the replacement materials and desiccation cracks within them make it possible for such recharge to occur in at least some locales. Because this latter type of seepage into the aquifer consists of oxic water, the recharge

from it has the capacity to not only impact local flow direction for a time but also to noticeably change water chemistry in at least the shallowest portions of the saturated zone.

Collection of analyte concentration data during some of the enhanced bioremediation experiments conducted by IFRC personnel has revealed a form of short-term chemical variability in the alluvial aquifer. In particular, it has been shown that U(VI) concentrations at some upgradient wells in the experimental plots can double or decrease by half over the course of about a year. Note that the upgradient wells are located in areas with some of the largest on-site total uranium concentrations, and they are unaffected by the injection of organic carbon sources at hydraulically downgradient wells. Consequently, the variations in concentration reflect natural, ambient conditions, the cause of which is unknown. This observation emphasizes that uranium concentration contour maps, such as those presented in Figure 2 and Figure 7, should be viewed only as snapshots, despite the fact that uranium concentrations have not changed drastically since the late 1990s.

## **6.2 Sources of Alluvial Groundwater**

Hydrologic processes that contribute water to the alluvial aquifer strongly affect the distribution of dissolved uranium in the aquifer at any given time. This section reviews the four sources of alluvial groundwater that were mentioned in the SOWP (DOE 1999) and provides an updated perspective on their impact on the fate of uranium.

### **6.2.1 Subsurface Inflow**

Recently prepared maps of the potentiometric surface in the alluvial aquifer (Figure 6) support the original conceptual model of the site, which assumed that the primary source of groundwater in the aquifer is subsurface inflow from north of Highway 6. It is unclear whether the inflowing water occurs along the entire length of the highway in the vicinity of the site, but the existence of surface seeps just north of the highway on both sides of Ash Road (Figure 1) indicates that groundwater is entering the site's alluvial aquifer at multiple locations. These seeps appear to occur in areas where the presence of relatively impermeable Wasatch Formation prevents water in the basal portion of the older alluvium from discharging directly to the site's alluvial aquifer. At other locations north of the highway, it is possible that the upper portion of the Wasatch Formation is fractured, rendering it more permeable and capable of transmitting water from the overlying alluvium directly to the alluvial aquifer south of the highway.

The seep lying west of Ash Road was recently added to the list of monitoring locations for the site (location 0395). Though the flow emanating from this area has not been quantified, analytical results for the limited number of samples collected there help shed light on the possible effects of inflowing water from north of Highway 6 on the uranium chemistry of the alluvial aquifer. The water chemistry of the seep at 0395 is also of interest because it might be used to identify the recharge mechanism for the locally inflowing water. The recharge is likely to take place at least thousands of feet north of the seep, but, as mentioned in Section 3.2, it is unknown whether the recharge occurs naturally or is of anthropogenic origin. Subsequent sections of this report address this issue.

Without key water chemistry data from multiple portions of the long (~300 ft) seep area east of Ash Avenue, the recharge source, or sources, for the seep water remains uncertain. The

possibility that some of this seep water stems from recharge in the city detention basins suggests that knowledge of the basin water's chemical signature would assist in tracking its migration within the alluvial aquifer. In addition, further investigation of groundwater levels and water chemistry in a series of on-site wells in the alluvial aquifer immediately south of the highway would help to identify general locations of inflow associated with the seeps and quantify the inflow rates.

### **6.2.2 Recharge from the On-Site Ditch**

The updated conceptual model also assumes that some of the surface water flowing in the on-site ditch seeps into the subsurface and recharges the alluvial aquifer. Because little to no hydraulic data exist for alluvial groundwater under and near the ditch, the evidence for this form of recharge is mostly in the form of relatively low contaminant concentrations at a few monitoring wells located on either side of the ditch. Accordingly, the quantity of recharge from this apparent source remains unknown. Previous stream gaging measurements on the ditch at the outlet of the culvert under Highway 6 and a short distance upstream of the river on two separate occasions helped illustrate the variability associated with ditch loss measurements. In September 1998, the gaged flow at the culvert outlet was 86 gpm, and the downstream flow measurement was about 60 gpm, indicating that the ditch was losing approximately 26 gpm to a combination of downward seepage and evapotranspiration between Highway 6 and the river. Subsequent stream gaging in February 1999, when evapotranspiration would have been insignificant, showed flows of about 40 and 32 gpm at the upstream and downstream locations, respectively, for a loss of approximately 8 gpm. These two loss values represented about 30 percent and 20 percent, respectively, of the flow in the ditch at its upstream gaging location just south of Highway 6. Because the stream gaging results using flow meters can often be in error by 10 percent or more, these previously computed ditch losses should be considered rough estimates. More reliable estimates of ditch losses might be made using alternative forms of flow measurement in the ditch (e.g., Parshall flumes) in combination with the installation and monitoring of wells located adjacent to the ditch at several points along its length.

### **6.2.3 Inflow of River Water**

During the past few years, considerable interest has been given to the interactions between water stage in the Colorado River and groundwater levels in the alluvial aquifer. This interest was recently demonstrated in an IFRC quarterly report published in July 2010 (Long 2010) that examined ways in which groundwater levels in key on-site wells could be predicted using Colorado River stage data from a USGS gaging station located greater than 25 miles upstream of the Old Rifle site. The report formally discussed river-aquifer interaction phenomena that have long been known about the site, namely, that a local increase in river stage during the high-runoff months of April through June produces corresponding and relatively rapid increases of up to 5 or 6 ft in on-site groundwater levels at key wells used to monitor the uranium plume.

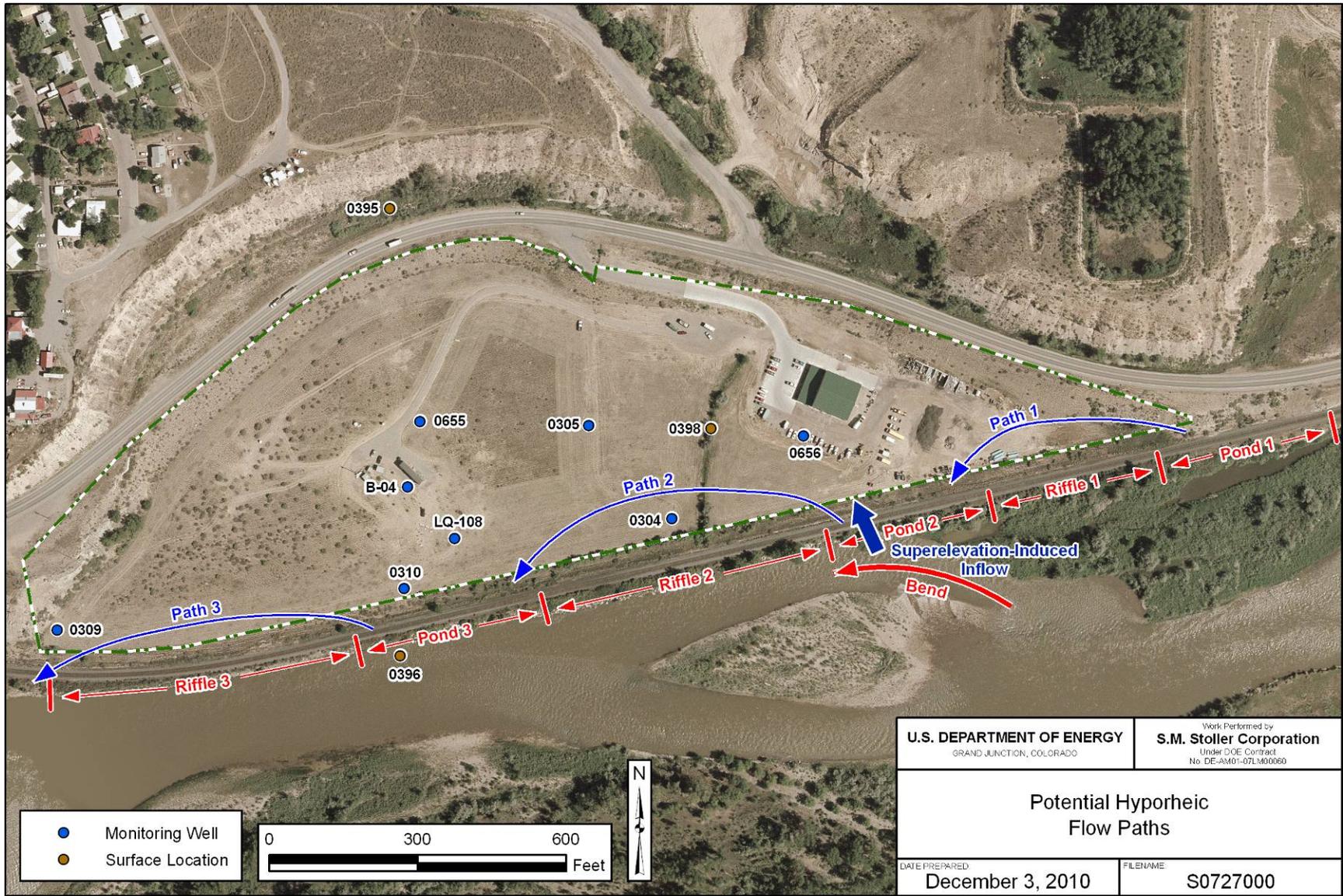
Correspondingly, subsequent decreases in river flow and stage in the following months of August and September cause equally responsive drops in on-site water levels. The IFRC report (Long 2010) identifies this correlation between river stage and local groundwater elevation as being important for better understanding of groundwater flow patterns on a sitewide scale and any corresponding changes in biogeochemical conditions, but the report does not identify how flow and biogeochemical responses to river flow variations might be manifested.

Though the IFRC quarterly report (Long 2010) did not address the effect of river changes on on-site groundwater flow patterns, IFRC personnel have previously suggested that a temporary reversal of flow direction occurs in the alluvial aquifer during initial periods of increased river flow in late spring, and a significant effect of this phenomenon is loss of river water to the aquifer and subsequent groundwater flow from near the riverbank toward the north. As yet, a detailed investigation of the hypothesized flow change has not been conducted, but inspection of river stage data from the upriver gaging station suggests that the flow reversals are difficult to sustain and that seasonal incursions of river water into the aquifer are minimal. This is because river flows, and correspondingly, river stages, tend to increase gradually over the month- to two-month-long rising limb of the spring runoff. As a consequence, groundwater elevations throughout the alluvial aquifer are expected to respond relatively quickly and proportionally to the increase in river stage, thereby maintaining a net discharge to the river from the site as a whole.

Assuming that a net discharge of groundwater from the alluvial aquifer to the river predominates throughout each year, it is helpful to assess whether the river is capable of contributing minor amounts of surface water to near-river portions of the aquifer even during average-runoff periods on the river. Such contributions to the groundwater system could be occurring in hyporheic flow paths (e.g., Winter et al. 2002), which are created naturally by surface water entering the aquifer at specific locations and eventually returning to the river at other locations farther downstream. Hyporheic zone processes at the site are significant because mixing of local groundwater with the river-derived water, which tends to be saturated with dissolved oxygen, can influence biogeochemical processes in the near-river subsurface.

The existing monitoring well network at the site is insufficient for identifying hyporheic zone flow processes, if any are actually present. However, the potential existence of on-site hyporheic flow paths can be speculated upon using visual observations of pool and riffle sequences in the river reach abutting the site. In accordance with flow patterns typically observed in floodplain groundwater systems (e.g., Winter et al. 2002), it can be assumed that river water seeps into the subsurface near the downstream end of a river pool preceding (upstream of) a riffle and then discharges back to the river near the downstream end of the riffle. Such patterns are governed by basic hydraulic principles, which state that water flows from a point of higher water elevation to another of lower elevation, and the potential for flow between them increases in proportion to the difference in water level.

Three separate hyporheic flow paths associated with distinct pond and riffle sequences are postulated from the above-mentioned approach. As shown in Figure 9, inflow to the groundwater system from the easternmost hyporheic path (Path 1) appears to result from ponding (Pond 1) created by thick vegetation locally obstructing river flow. In contrast, ponding at the upstream end of Path 2 (Pond 2) is attributed to superelevation of the river surface where river water flows directly into the riverbank at the end of a local river bend. Similarly, the ponding that appears to take place at the upstream end of Path 3 is attributed to west-northwestward-flowing river water that intercepts and mildly obstructs surface water near the tail of Riffle 2.



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Figure 9. Potential Hyporheic Flow Paths at the Old Rifle Site

Of the three postulated hyporheic paths, Path 1 is considered the most likely to exist. This contention is based partly on the estimated drop in river surface elevation along Riffle 1, which, based solely on rough observations in the field, is significantly larger than drops along Riffles 2 and 3. In addition, the groundwater elevation contours in the vicinity of Riffle 1 (Figure 6) tend to be oriented perpendicular to the river, which suggests that groundwater in this area tends to flow toward the west, or more parallel to the river rather than toward it. In contrast, measured water elevations in the vicinity of and just north of postulated Paths 2 and 3 indicate that groundwater flow there is oriented toward the south-southwest (Figure 4), or more perpendicular to the river.

#### **6.2.4 Episodic Recharge from Infiltration of Precipitation**

Because most of the site was covered with fine-grained, low-permeability fill after the removal of radioactively contaminated sediments during surface remediation, the low rate of areal recharge adopted in the SOWP model (0.07 inch per year) was probably appropriate for the purpose of developing a long-term, sitewide water budget. However, the effects of recharge from precipitation on groundwater flow and transport in the alluvial aquifer are probably different from what was assumed during the DOE modeling. Specifically, recharge from rainfall and snowmelt probably varies spatially across the site rather than being distributed uniformly (see Section 6.1.3). Moreover, the recharge from precipitation is also temporally variable because it takes place mostly during or shortly after on-site rainfall and snow events. The combination of both types of variability suggests that precipitation recharge will exhibit relatively acute influences on groundwater in the alluvial aquifer. Assuming that the magnitudes of localized sporadic recharge processes are small due to limited infiltration into fine-grained surface sediments, the overall effects on groundwater flow direction and rate will be minor. However, the possibility exists that the oxic water occasionally contributed to the aquifer by infiltrated precipitation can mobilize uranium in both the vadose and saturated zones.

Evidence for possible episodic recharge and contribution of oxic water to the saturated zone was observed during the 2002/2003 IFRC biostimulation experiments (Yabusaki et al. 2005). Specifically, DO concentrations at three of the test plots' background wells noticeably increased between April and June 2003, and the spikes in DO correlated with a local groundwater elevation increase of more than 4.5 ft. Though an IFRC report (Long 2009) suggested that seasonal DO increases are caused by scavenging of oxygen entrapped in the lower part of the vadose zone by a rising water table, the possibility exists that spatially variable episodic recharge can also contribute DO to the saturated zone. More detailed studies of vadose zone flow and transport processes above areas that exhibit periodic DO spikes would help identify their causes. Because the background wells that show the DO increases in spring 2003 are located more than 300 ft north of the river, inflow of oxic river water to the aquifer and its subsequent migration toward the wells over a limited period of about 3 to 4 months is not considered a feasible explanation.

### **6.3 Distinguishing Natural Background Uranium from Mill-Related Uranium Contamination**

Given that the conceptual model developed for the SOWP (DOE 1999) and this updated conceptual model single out natural waters north of Highway 6 as the primary source of alluvial groundwater at the site, it stands to reason that significant portions of the alluvial aquifer contain natural uranium rather than mill-related contamination. To better understand where the natural

recharge waters might be dominant on site, efforts were made in 2010 to identify chemical means of distinguishing natural background uranium from mill-related contamination. As part of these efforts, additional uranium concentration data were collected that shed further light on the background concentration of this constituent at the site.

### 6.3.1 Uranium Isotope Ratios

One of the tools used to help identify sources of dissolved uranium at the site involved the examination of uranium isotope distributions in water samples collected at several monitoring locations. Specifically, the ratio of the activity concentrations for U-234 and U-238 was calculated under the hypothesis that mill-related contamination would have a U-234/U-238 value, or uranium activity ratio (UAR), that was noticeably different from that of naturally derived uranium. The logic applied was based on similar work by Zielinski et al. (1997), who showed that the UAR in contaminated groundwater samples collected at a former uranium mill site near Cañon City, Colorado, exhibited ratios generally reflective of secular equilibrium ( $UAR \cong 1$ ), while those of natural waters had ratios greater than 1.3. The Cañon City study built upon previous work by Cowart and Osmond (1977) that suggests natural waters tend to show an excess of U-234 activity in comparison to that of U-238 at the mineral/water interface during prolonged mild leaching of subsurface uranium-bearing rock by groundwater. This excess comprises a form of isotopic fractionation related to alpha recoil displacement (Cowart and Osmond 1977) of the U-234 atom from its U-238 parent, with the net effect of enhanced leachability of U-234. In contrast, high-grade uranium ores with more recent histories of open-system alteration appear to be mixtures of materials with both  $UAR < 1$  and  $UAR > 1$ , which, when leached over periods of just a few decades or more, yield waters with a UAR of  $1.0 \pm 0.1$  (Zielinski et al. 1997).

Tests of the UAR hypothesis at the Old Rifle site were conducted using samples collected at both groundwater and surface water monitoring locations on and near the site in April and June 2010. Table 1 and Table 2 list the resulting uranium mass and activity concentrations along with related isotopic UARs from the April and June sampling events, respectively, and a source designation (mill-related versus natural) is assigned to each listed monitoring location. Figure 10 and Figure 11 present corresponding aerial photographs of the uranium analytical results.

Results from the April 2010 monitoring generally comport with the findings of Zielinski et al. (1997) in that groundwater monitoring locations believed to exist within or on the edge of mill-contaminated areas (0304, 0305, 0310, 0310, 0655, 0656, B-04, LQ-108) show UARs between 1.0 and 1.1, whereas all other groundwater and surface water monitoring locations exhibit ratios of 1.4 or more. The UAR of 1.42 at the single monitoring location on the Colorado River (0396) is expected because U-234/U-238 ratios in stream and river waters typically show U-234 enrichment (Zielinski et al. 1997). Likewise, the UAR of 1.62 for the surface water sample collected from the on-site ditch (0398) is not surprising, since the ditch is fed by a natural drainage system upstream of Highway 6.

Table 1. Uranium Concentrations and Isotope Activity Ratios in April 2010

Location	On Site/ Off Site	Medium (SW/GW) <sup>a</sup>	Uranium Mass Concentration ( $\mu\text{g/L}$ ) <sup>b</sup>	U-234 Activity Concentration (pCi/L) <sup>c</sup>	U-238 Activity Concentration (pCi/L) <sup>c</sup>	Uranium Activity Ratio (UAR)	Presumed Source (Natural/ Mill-Related)
0304	On	GW	50	17	16.4	1.04	Mill-Related
0305	On	GW	87	30.7	28.3	1.08	Mill-Related
0309	On	GW	19	10.5	5.71	1.84	Natural
0310	On	GW	250	68.9	64.5	1.07	Mill-Related
0395	Off	SW	25	13.1	8.29	1.58	Natural
0396	Off	SW	1.4	1.06	0.748	1.42	Natural
0398	On	SW	16	7.39	4.55	1.62	Natural
0655	On	GW	140	47.2	44.4	1.06	Mill-Related
0656	On	GW	120	47.7	43.8	1.09	Mill-Related
B-04	On	GW	170	61.4	59.7	1.03	Mill-Related
LQ-108	On	GW	240	90.7	84.9	1.07	Mill-Related

<sup>a</sup> GW = groundwater, SW = surface water

<sup>b</sup>  $\mu\text{g/L}$  = micrograms per liter

<sup>c</sup> pCi/L = picocuries per liter

Table 2. Uranium Concentrations and Isotope Activity Ratios in June 2010

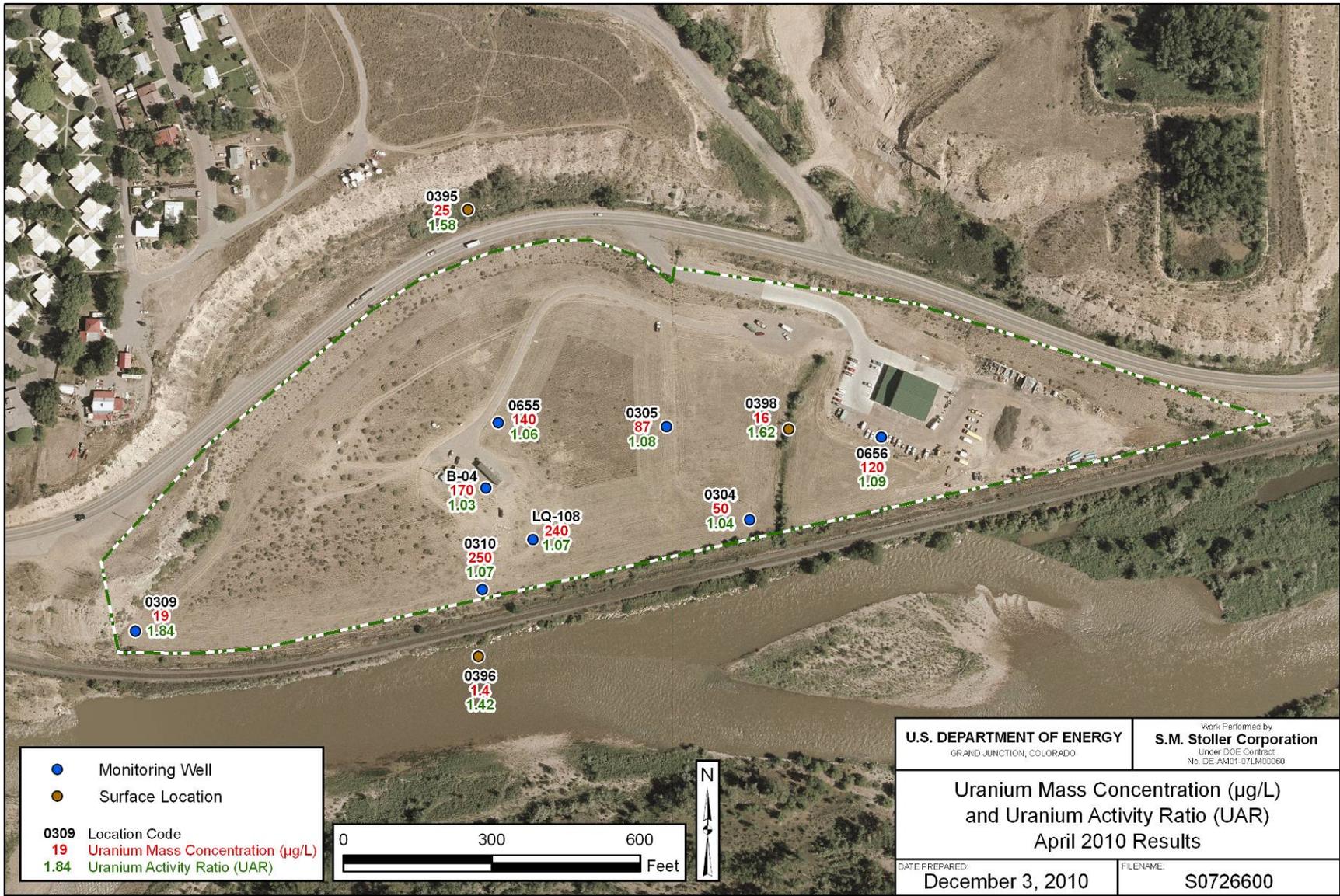
Location	On Site/ Off Site	Medium (SW/GW) <sup>a</sup>	Uranium (U) Mass Concentration ( $\mu\text{g/L}$ ) <sup>b</sup>	U-234 Activity Concentration (pCi/L) <sup>c</sup>	U-238 Activity Concentration (pCi/L) <sup>c</sup>	Uranium Activity Ratio (UAR)	Preliminary Assessment (Natural/ Mill-Related)
0304	On	GW	46	19.1	13.9	1.37	?
0305	On	GW	80	33.3	28.8	1.16	Mill-Related
0309	On	GW	20	12.3	7.28	1.69	Natural
0310	On	GW	180	73.2	67.4	1.09	Mill-Related
0395	Off	SW	28	14.7	8.88	1.66	Natural
0396	Off	SW	1	0.416	0.466	0.89	?
0398	On	SW	14	6.83	4.7	1.45	Natural
0655	On	GW	130	52.6	47.2	1.11	Mill-Related
0656	On	GW	170	59.9	55.3	1.08	Mill-Related
B-04	On	GW	210	81.4	75.3	1.08	Mill-Related
LQ-107	On	GW	150	53.5	49.9	1.07	Mill-Related
LQ-108	On	GW	130	49.4	47.3	1.04	Mill-Related

<sup>a</sup> GW = groundwater, SW = surface water

<sup>b</sup>  $\mu\text{g/L}$  = micrograms per liter

<sup>c</sup> pCi/L = picocuries per liter

April 2010 results for the remaining surface water sample, collected at the seep north of Highway 6 (0395), are significant because the reported uranium mass concentration here is relatively high (25 micrograms per liter [ $\mu\text{g/L}$ ]), yet the corresponding UAR is reflective of natural water (1.58). These values tend to confirm SOWP findings that natural sources of alluvial aquifer groundwater located north of the highway can contribute dissolved uranium to the aquifer at levels that are more than half the UMTRA maximum concentration limit (MCL) of 44  $\mu\text{g/L}$  for this constituent.



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Figure 10. Uranium Concentrations and Uranium Activity Ratios at Selected Monitoring Locations in April 2010



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Figure 11. Uranium Concentrations and Uranium Activity Ratios at Selected Monitoring Locations in June 2010

The calculated UAR of 1.84 during April 2010 for location 0309 in the westernmost corner of the site suggests that uranium in groundwater in the vicinity of this well is naturally occurring rather than legacy contamination from mill operations. This observation, when combined with groundwater flow directions inferred from the site's potentiometric surface (Figure 6) and the fact that the April uranium mass concentration of 19 µg/L at well 0309 is similar in magnitude to the concentration of 25 µg/L at seep 0395, suggests that groundwater in the aquifer's east corner may originate as natural water north of the highway rather than leached tailings water.

An additional monitoring location, well LQ-107, was included in the uranium analyses performed on June 2010 samples (Table 2 and Figure 8). By and large, the uranium concentrations and UARs from the June monitoring event were similar to those reported for the April event. However, uranium data at two locations made it difficult to ascertain whether the samples were reflective of a natural or mill-related uranium source. The calculated UAR of 1.37 at well 0304 was not representative of mill-related uranium despite the fact that the analyses for this location in April 2010 were indicative of uranium contamination. One potential explanation for the higher UAR at well 0304 in June was increased recharge from the on-site ditch, which is about 50 ft west of the well. If flows in the ditch were high due to spring runoff, it is possible that ditch water with a UAR reflective of natural water seeped downward into the subsurface and mixed with local groundwater, thereby producing a UAR reflective of isotope disequilibrium.

A UAR of 0.89 at river sampling location 0396 was considered anomalous because the river is always expected to be representative of natural waters. This discrepancy was attributed to analytical error caused by the very low mass and activity concentrations reported here for uranium in June 2010.

### **6.3.2 Additional Chemical Indicators**

Water samples collected by the LM contractor during 2010 were submitted for tritium analyses with the intended purpose of helping to distinguish natural uranium from mill-related uranium contamination. Given that groundwater discharging at seeps immediately north of Highway 6 originated as natural recharge farther to the north, the potential existed for seep waters to have tritium concentrations reflective of atmospheric conditions prior to above-ground testing of nuclear explosive devices in the 1950s and 1960s. If this were the case, the seep tritium levels were expected to be less than 3 picocuries per liter (pCi/L), whereas the tritium concentrations in all other waters affected by the atmospheric testing were expected to range from 15 to 30 pCi/L. Accordingly, the possibility existed that naturally occurring groundwater in the alluvial aquifer just south of Highway 6 would also exhibit a low-tritium signature, which could in turn indicate the co-presence of naturally occurring uranium.

Though the tritium analyses were subject to considerable uncertainty, all of the reported concentrations, including those for water samples collected at the seeps, fell in the range of 15 to 30 pCi/L. This result indicated that tritium could not be used to help distinguish areas of naturally derived uranium contamination from those affected by mill-related contamination.

Since summer 2010, IFRC personnel have also been attempting to identify explicit chemical fingerprints for different sources of alluvial aquifer groundwater. These efforts have focused on analysis of the stable isotopes oxygen-18 and deuterium. The oxygen-18 and deuterium data collected so far are considered preliminary but will be included in future studies aimed at distinguishing natural waters from mill-derived contamination.

## 6.4 Biogeochemistry

### 6.4.1 Background Microbial Processes

Both the site characterization information collected during preparation of the SOWP (DOE 1999) and additional data and investigations conducted in recent years, particularly in association with IFRC projects, suggest that microbial processes affecting alluvial groundwater chemistry are common under ambient background conditions at the Old Rifle site. For example, low nitrate concentrations collected in support of the SOWP and IFRC work indicate that any nitrate fed to the aquifer is likely to be quickly consumed by microbially mediated denitrification. Similarly, relatively high concentrations of dissolved iron (Fe[II]) in groundwater indicate that background iron reduction driven by microbial processes is likely. In addition, very low levels of DO (<0.3 mg/L) combined with relatively low values of oxidation-reduction potential signify the presence of conditions that are somewhat chemically reducing, which could be the result of biologically mediated redox reactions. These lines of evidence by themselves do not indicate that sulfate reduction is occurring throughout the alluvial aquifer, but conditions amenable to pervasive iron reduction do appear likely.

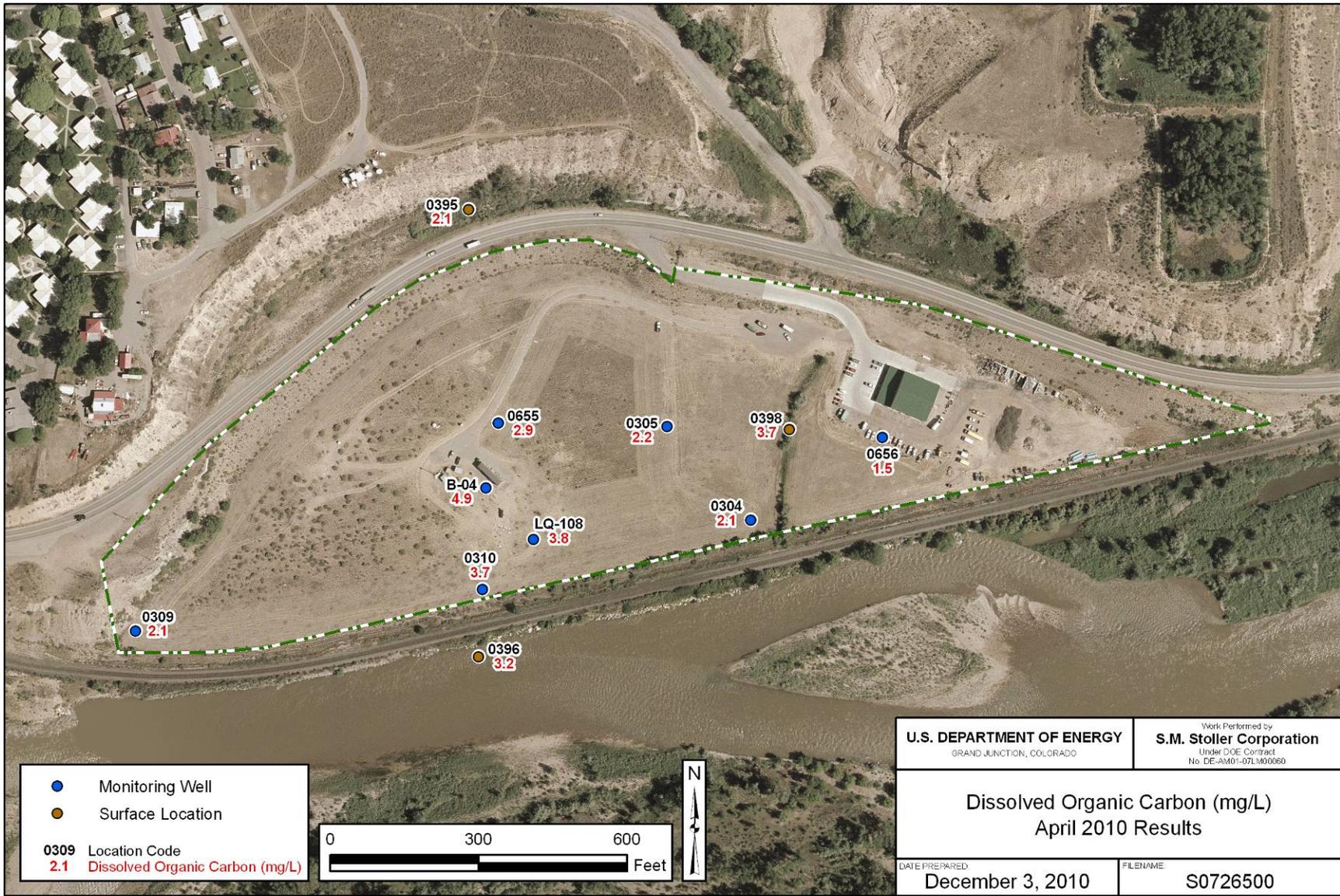
The discovery of naturally reduced sediment zones (e.g., Long 2008) in the subsurface has shown that some portions of the aquifer are more reducing than others, and the presence in these zones of other chemical data indicative of biologically mediated iron as well as sulfate reduction implies that background microbial metabolism in these isolated zones can also influence ambient groundwater chemistry. Whether the naturally reduced zones represent sinks or sources for dissolved uranium, or both, remains to be determined. The N'Guessan (2008) study that presents evidence possibly indicative of natural bioreduction of uranium upgradient of IFRC experimental plots also supports the presence of background microbial processes.

If biological activity in the form of microbial iron reduction is pervasive in the alluvial aquifer, a natural source of electron donor chemicals is needed. IFRC studies have suggested that much of donor source is ultimately attributable to solid organic matter co-existing with the alluvial sediments that compose the aquifer. To help assess how these and other potential organic carbon sources are manifested in local water chemistry, recently measured concentrations of dissolved organic carbon (DOC) at several monitoring locations were examined.

Figure 12 and Figure 13 are aerial photographs showing measured DOC levels on and near the site in April 2010 and June 2010, respectively. Both figures indicate that wells screened in the alluvial aquifer maintain DOC concentrations ranging between about 2 and 5 mg/L, and a similar concentration range is observed at surface water monitoring locations that include the seep north

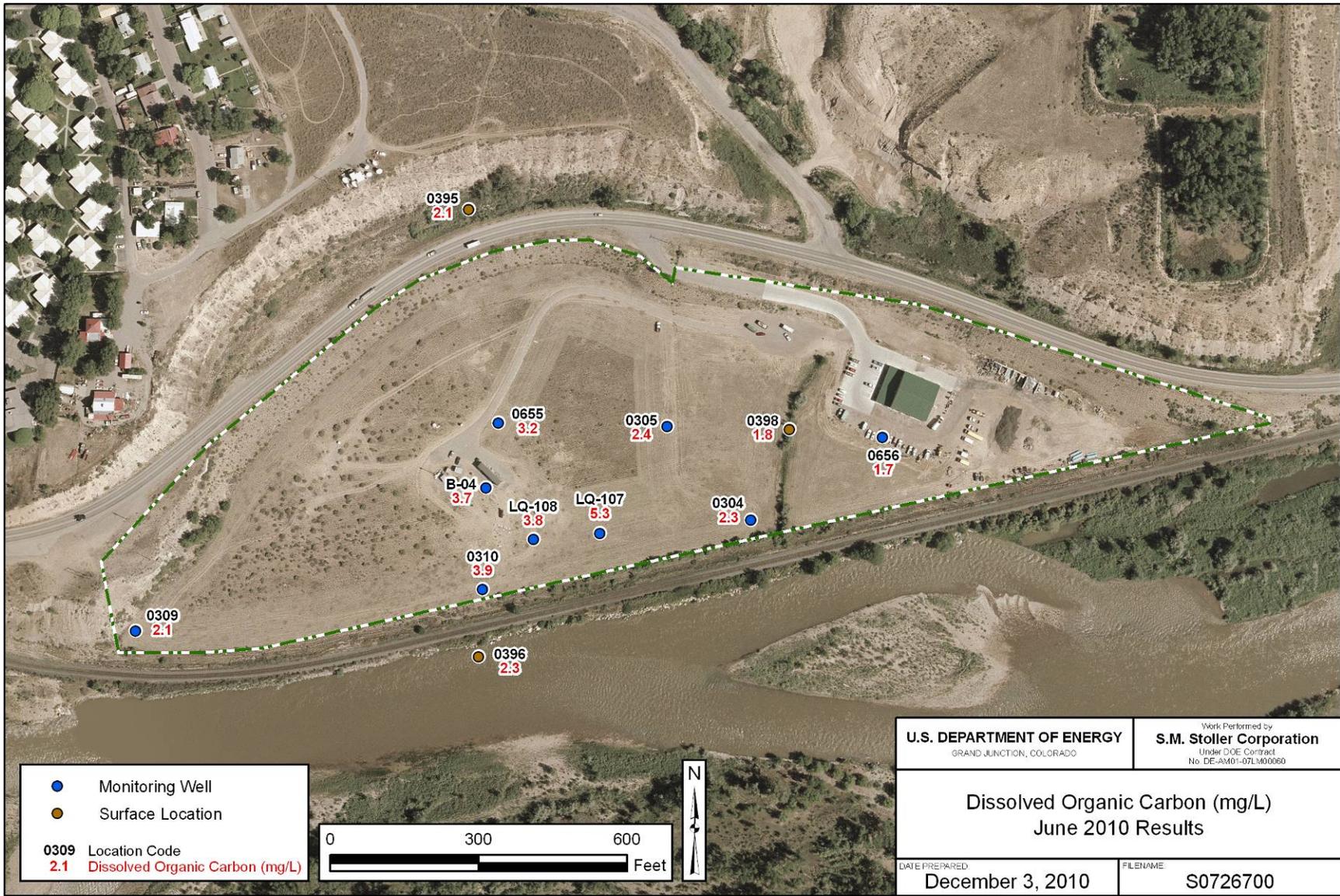
of Highway 6 (0395), the on-site ditch (0398), and the Colorado River (0396). Though it is unclear what percentage of the DOC is labile and, therefore, available for biologically mediated chemical reactions in the subsurface, the reported concentrations by themselves do suggest that ambient background microbial processes are likely.

To date, thorough analyses of the dissolved chemicals contributing to DOC in local water have not been performed. Assuming that at least a portion of the DOC consists of dissolved acetate that originated from the dissolution of solid organic matter in alluvial sediments, it is likely that the acetate was produced through a series of natural fermentation reactions occurring in the subsurface (e.g., Bartlett et al. 2010) rather than directly resulting from the leaching of buried organic solids.



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Figure 12. Dissolved Organic Carbon Concentrations at Selected Monitoring Locations in April 2010



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Figure 13. Dissolved Organic Carbon Concentrations at Selected Monitoring Locations in June 2010

The DOC concentration of 2.1 mg/L reported for both April and June 2010 (Figure 12 and Figure 13) at the seep above Highway 6 (location 0395) is of interest because it suggests that recharge to the alluvial aquifer due to subsurface inflow from off-site water sources is an additional source of organic carbon that sustains on-site microbial processes. Similarly, the two DOC concentrations in surface water from the on-site ditch (3.7 and 1.8 mg/L) are significant because recharge due to seepage losses from the ditch could influence microbial activity locally in the subsurface.

#### **6.4.2 Oxidation and Dissolution of Uranium**

As previously discussed, research into the speciation and stability of the reduced uranium produced during biostimulation experiments at the IFRC plots revealed that the solid-phase uranium created consists of “monomeric U(IV)” rather than uraninite (Long 2010). This finding has bearing on the persistence of uranium in the subsurface at the Old Rifle site, because the rate at which the monomeric form reoxidizes and subsequently dissolves in groundwater as a U(VI) species is expected to be greater than the equivalent rate associated with uraninite. The variation in rates is attributed in part to abundant cation impurities in the natural uraninite. Results from some of the most recent IFRC testing—which show that, with aging, monomeric U(IV) eventually transforms into uraninite (Long 2011)—suggest that biogenic U(IV), whether created naturally due to background iron reduction or via biostimulation, will tend to mobilize in groundwater relatively slowly. Regardless of the form of U(IV) present in the alluvial aquifer, oxidation of the reduced uranium and its eventual dissolution as a U(VI) species increases with the presence of increased DO and alkalinity concentrations.

An investigation by Qafoku et al. (2009) of the chemistry of naturally reduced sediments at the site reported that at least a portion of the U(IV) and some U(VI) in the reduced zones was incorporated into solid-phase iron sulfides, including pyrite. Moreover, some of the pyrite exhibited framboidal structure. Qafoku et al. (2009) indicated that the interaction of aqueous U(VI) with the framboidal pyrite was complex, with possible augmentation of uranium in the pyrite resulting from the interaction. Alternatively, the research also indicated that the pyrites incorporated into the naturally reduced zones at the site were capable of acting as long-term sources of aqueous U(VI) in groundwater.

The recent experiments on uranium redissolution involving the installation of pure, laboratory-generated uraninite in wells at the Buckskin site (see Section 4.3) also suggest that release of biogenic U(IV) under Old Rifle field conditions is very slow. Though much of the slow release observed in these experiments was attributed to diffusion from the sample cells containing the uraninite (Long 2010), the much larger diffusion barrier associated with lower-permeability alluvial sediments is expected to greatly limit the oxidation of U(IV) under background conditions. Though these findings pertain solely to reduced uranium, they are also relevant to the mobilization of U(VI) in low-permeability sediments.

## **7.0 Potential Causes of Persistently High Uranium Concentrations**

An evaluation of the updated conceptual model suggests that three potential phenomena are contributors to the high uranium concentrations currently observed in Old Rifle site groundwater. These phenomena, summarized below in Sections 7.1 through 7.3, comport with explanations by IFRC researchers (Long 2011) for the persistence of elevated uranium concentrations in Old

Rifle groundwater. It is important to note that none of the potential causes of persistently high concentrations of dissolved uranium has yet been identified as a dominant explanation for the limited progress of natural flushing to date.

## **7.1 Slow Diffusion of Uranium from Low-Permeability Zones**

As discussed in Section 6.1.1, preferential flow processes in heterogeneous porous media are characterized by the slow release of dissolved constituents from the lower-permeability portions (immobile domain) of an aquifer to the more conductive portions (mobile domain), which produces long-term tailing of constituent concentrations in monitoring wells screened in the preferential flow paths. In effect, water molecules in the low-permeability zones move so slowly that the effective mechanism for transporting U(VI) to the mobile domain is molecular diffusion in response to concentration gradients. The visually observed heterogeneity of alluvial aquifer sediments suggests that the aquifer is capable of sustaining preferential flow effects, and the lack of declining uranium levels at key monitoring wells since 1998 (Figure 8) possibly indicates diffusion-limited transport and concentration tailing.

By itself, the concept of dual-domain porous media (Flach et al. 2004) provides what is fundamentally a physical explanation for slow attenuation of uranium contamination at the site. However, as the updated conceptual model indicates, several chemical processes could also contribute to the release of uranium from low-permeability zones.

## **7.2 Mobilization of Vadose Zone Uranium**

Surface remediation at the site using only radium-226 concentrations as cleanup criteria made it possible for several mill-derived inorganic constituents to remain undetected in the vadose zone below the former tailings pile and the ore-storage area. Indeed, the leaching tests conducted on soil samples from beneath the former tailings and ore piles (Section 3.3) suggested that uranium could remain in the vadose zone. Accordingly, occasional mobilization of uranium that remains in the vadose zone today should be considered a potential long-term contributor to saturated zone uranium. The fact that alluvial groundwater levels increase up to 6 ft during high-river-runoff months implies that a rising water table could periodically leach uranium from the vadose zone. Similarly, it is also possible that downward seeping moisture from episodic precipitation events could leach uranium from the vadose zone.

The exact mechanisms through which uranium is mobilized in the vadose zone remain uncertain. A more thorough study of vadose zone processes represents the most reliable means to identify and characterize this potential source of saturated-zone contamination.

## **7.3 Uranium in Subsurface Inflow**

Data presented in this study and collected over the past several years clearly demonstrate that recharge sources to the alluvial aquifer from multiple areas north of Highway 6 contribute a portion of the on-site dissolved uranium seen today. The uranium concentrations measured for this investigation at the seep discharging just north of Highway 6 and west of Ash Road (0395) (Section 6.3.1) imply that a background concentration of 25 to 30 µg/L would be representative of subsurface inflows from north of the site. However, historical data collected from various off-site sampling locations indicate that uranium levels in potential aquifer recharge sources north of

the highway are temporally and spatially variable and may at times reach concentrations as high as 55 µg/L. Additional investigation of the chemistry of water seeps north of the highway as well as in alluvial groundwater just south of the highway would assist in better defining such variability. It can be concluded that the highest uranium concentrations observed in on-site wells (0.1–0.25 µg/L) are not due solely to background uranium contributions from north of Highway 6.

## 8.0 Prospects for Predictive Modeling

With a new understanding of the complexity of subsurface flow and biogeochemical processes in Old Rifle groundwater, the prospects for developing numerical models capable of successfully predicting the future progress of sitewide natural flushing can be discussed. The types of models included in this assessment range from the relatively simple one applied in the SOWP to the much more detailed simulators developed by IFRC researchers in recent years.

The predictive success of any model applied to the site will greatly hinge on the model's ability to match uranium concentration histories at numerous monitoring wells throughout the site. At a minimum, this will mean that the model is capable of capturing any long-term concentration trends, if present, at key wells. If the temporal plots of uranium concentration presented in Section 5.2 for six on-site wells (Figure 8) are used as a guide, the likelihood is small that any model developed at this time would project successful flushing of uranium in the alluvial aquifer within the next 100 years. For example, if the model originally employed by DOE to assess natural flushing were reapplied to the site with the intent of roughly duplicating the concentration histories shown in Figure 10, either the assumed uranium source mass or the uniform  $K_d$  employed in the model, or both, would probably be many times higher than values originally adopted for these model features, and predicted flushing time would extend well beyond 100 years.

To address the possibility that slow diffusion of uranium from low-permeability zones in the alluvial aquifer is a major cause of slower contaminant release (Section 6.1.1), a dual-domain simulator might be applied. This type of model has been successfully employed in a variety of studies (e.g., Flach et al. 2004, Zheng et al. 2010) in an effort to capture concentration tailing phenomena and is conceptually logical because it directly accounts for contaminant mass exchange between the mobile and immobile domains. Yet the key parameters used to simulate the mass exchange are effectively nothing more than model-fitting parameters, because they have no true physical basis. Though a dual-domain simulator could be developed to approximate the uranium concentration histories shown in Figure 8, it also would probably predict a natural flushing scenario extending beyond 100 years.

Regardless of the type of model used, a reliable estimate of the total current uranium inventory in the alluvial aquifer is crucial for accurately predicting future flushing. Strictly speaking, this means that all uranium that has the potential to eventually migrate in groundwater to the river would have to be accounted for, including the uranium mass sequestered in low-permeability sediments, sorbed to aquifer sediments, and existing in vadose zone sediment possibly subject to periodic leaching. Because most currently available site characterization techniques still rely heavily on the drilling of boreholes and collecting samples for analysis, accomplishing this task in the next few years would be extremely difficult and very expensive.

The multicomponent reactive transport models developed by IFRC researchers during the past several years have demonstrated that it is possible to produce fairly reliable simulators of many of the complicated flow, sorption, and biogeochemical processes occurring in site alluvium in response to biostimulation experiments. It is currently possible to apply numerical simulators that collectively account for several tens of chemical constituents, both equilibrium and kinetic reactions between the constituents, mineral precipitation, microbial population dynamics, and sorption and desorption processes for key analytes via surface complexation modeling. As the research models have grown increasingly complex with each successive application, IFRC personnel have added greatly to a knowledge base that will be crucial to understanding the eventual fate of uranium on a sitewide basis. However, the inputs to these complex models have also risen proportionately, and many of them vary both spatially and temporally. Thus, it is unclear how the numerous parameters used in these advanced models could be ascertained for the entire alluvial aquifer if they were needed for predicting the site-scale fate of uranium. The use of IFRC models to project future concentrations of dissolved uranium at the site would probably be most beneficial if applied to active remediation schemes such as those based on biostimulation or enhanced mobilization, rather than natural processes.

The proceedings from a recent DOE workshop (DOE 2010) hosted by the Office of Biological and Environmental Research under SC provides some insight into how future predictive models might be developed to better predict the fate of contaminants like uranium on a site-wide scale. The approaches discussed involve the use of principles and methods integral to a research field called complex systems science. The science, as applied to the subsurface, acknowledges that the holistic behavior of a groundwater system includes features at higher spatial scales that cannot be readily derived from the sum of features observed at smaller scales. Key to this is the concept of emergent behavior, which comprises system features that do not cleanly derive from examining all individual components of subsurface processes but are discerned at a greater scale due to the multiple interactions between those components. The goals of this approach are to identify macroscopic laws for the larger-scale system and develop a predictive model that comports with such laws. The type of simulator resulting from the approach can be referred to as more of a phenomenological model, in lieu of a fully mechanistic one, because it derives from examination of the interaction of multiple processes on larger-scale behavior rather than being built from the bottom through a simple additive combination of many small-scale processes.

It is difficult, if not impossible, to foresee what form of model will, or can, be developed to reliably predict the fate of uranium in the Old Rifle site alluvial aquifer. So far, the methods used to develop IFRC models of ever-increasing complexity appear to be following a more-traditional “bottom-up” approach rather than attempting to identify larger-scale emergent behaviors. The hope is that findings from the numerous plot-scale biostimulation experiments and other IFRC research will eventually be translated into a model or models capable of accurately simulating groundwater remediation effects for the site as a whole.

## **9.0 Recommendations for Monitoring**

This section provides several recommendations for groundwater monitoring that will assist in developing an improved understanding of local subsurface flow and transport processes, particularly if natural flushing remains a component of the groundwater remedy at the site.

Suggestions include installing new wells and adding some existing IFRC wells to the current LM monitoring network. Note that some or all of the recommended monitoring steps may not be relevant if a new compliance strategy were adopted that is less dependent on continued groundwater monitoring.

Though the following discussion focuses solely on the use of wells to monitor groundwater, it is important to mention that site characterization activities that extend beyond simple monitoring might be considered in the future, particularly if they can contribute to a clearer understanding of processes affecting uranium contamination in the alluvial aquifer. Though the types of characterization that would assist this purpose depend somewhat on the compliance strategy that is taken at the site, examples include the drilling and sampling of wells that intersect groundwater in Wasatch Formation sediments underlying Highway 6 and improved measurements of flows in upstream and downstream portions the on-site ditch.

## 9.1 New Well Installation

This report has highlighted the likelihood that portions of the alluvial aquifer underlying the site contain uranium that has a natural origin, specifically as a result of subsurface inflows to the aquifer from areas north of Highway 6. Though the nature of the uranium in these inflows has not been fully characterized, existing chemical analyses indicate that U(VI) concentrations in the inflowing water are as high as 25 to 30  $\mu\text{g/L}$ , but concentrations could be higher in some areas and at certain times. Additional chemical characterization efforts focused on the analysis of uranium isotopes, and analyses of isotopes of oxygen and hydrogen (deuterium) are expected to help distinguish natural U(VI) influxes from mill-related uranium contamination. To avoid the unnecessary remediation of natural uranium, five to six new wells are proposed for installation in areas where groundwater is potentially dominated by the natural inflows. Decisions regarding specific well locations would be made by taking into account site-specific criteria, but most of the wells would likely be evenly spaced along a narrow band of alluvium just south of the highway, and one additional well would be placed near the aquifer's west boundary in the vicinity of IFRC Experimental Plot B. After initial water testing aimed at discerning the source of uranium at these locations, monitoring would be focused on identifying temporal variations in concentrations of naturally derived uranium from north of the highway.

New well installations are also recommended at multiple locations located within 50 ft of and on either side of the on-site ditch. It is expected that these wells would not only help quantify recharge created by ditch water losses along its length, but also help to ascertain whether such recharge is flushing any local residual uranium contamination from the former mill. The data collected at these monitoring sites could prove valuable if they identify a swath of aquifer that is responding positively to the influx of uncontaminated surface water.

Natural flushing at the site could be tracked more comprehensively using additional monitoring wells installed east of the on-site ditch, particularly in the vicinity of the former ore storage area. Currently, monitoring of uranium concentrations east of the ditch is limited to a single well (0656), which is insufficient for delineating uranium levels in areas closer to the Colorado River and the east end the site.

## 9.2 IFRC Wells

Monitoring of several of the background wells employed during the various IFRC experiments would improve delineation of subsurface uranium contamination in several locales west of the on-site ditch. Existing candidate wells that should be considered for this purpose include the multiple background wells previously installed at the IFRC plot used for the 2002, 2004, and 2005 experiments and those within Plots A, B, C, and D.

A strong possibility exists for a 5-year extension of current SC-funded research at the Old Rifle site. If this occurs, researchers plan to investigate hydrological and biogeochemical processes occurring for the site as a whole. LM will coordinate with these efforts to maximize accrued research and applied science benefits. The extended research effort will involve the installation of additional wells that serve the needs of both LM and SC.

## 10.0 Regulatory Analysis

### 10.1 Regulatory Assessment

Standards for the cleanup of residual radioactive materials from inactive uranium-ore processing sites were published by the U.S. Environmental Protection Agency (EPA) in 40 CFR 192. Standards for the cleanup of land and buildings were put in place well before those for groundwater were finalized. As a result, the UMTRA surface program was nearly completed by the time the groundwater regulations were finalized in January 1995. DOE's final Programmatic Environmental Impact Statement (PEIS) (DOE 1996) for the groundwater program was issued in October 1996 and provided the framework for selecting groundwater compliance strategies. DOE's authorization to conduct further surface cleanups expired in 1998.

Cleanup standards for the surface program were based on meeting numerical criteria for radium-226 in uranium mill tailings and tailings-contaminated soils. Background and planning documents published by EPA and DOE in support of the UMTRA groundwater standards and groundwater program are premised on the assumption that cleanup under the surface program was adequate in achieving source removal for groundwater contamination, even though the groundwater standards address constituents other than radium.

Surface cleanup at the Old Rifle site was completed in October 1996, and fieldwork to characterize post-surface-remediation conditions and to support selection of a groundwater compliance strategy was conducted in 1998. The site conceptual model, fate and transport model, and preliminary compliance strategy options presented in the SOWP (DOE 1999) led to the selection of natural flushing as the compliance strategy, which was finalized with NRC concurrence in the GCAP in 2002.

### **10.1.1 40 CFR 192 Groundwater Standards**

EPA established several standards that can apply to groundwater at Title 1 UMTRCA sites. These include (1) background levels, (2) maximum concentration limits (MCLs), (3) alternate concentration limits (ACLs), and (4) supplemental standards. Several criteria are provided in 40 CFR 192.11(e) whereby supplemental standards could apply. These criteria are:

- (1) The concentration of total dissolved solids is in excess of 10,000 mg/L (not milling-related); or
- (2) Widespread, ambient contamination not due to activities involving residual radioactive materials from a designated processing site exists that cannot be cleaned up using treatment methods reasonably employed in public water systems; or
- (3) The quantity of water reasonably available for sustained continuous use is less than 150 gallons per day.

The regulations also provide for an “extended period” of remediation of up to 100 years at Title I sites where groundwater cleanup may be “reasonably accomplished in full or in part through natural flushing.” Institutional controls are specified as a critical component of a natural flushing remedy, to ensure protectiveness during the extended remediation period.

### **10.1.2 DOE’s Programmatic Environmental Impact Statement**

DOE’s PEIS (DOE 1996) provides the decision framework for selecting a groundwater remediation strategy at a given site. This “decision tree” was accepted by NRC and incorporated into their standard review plan for Title I sites with contaminated groundwater (NRC 2000). Figure 14 is a reproduction of the decision tree flow chart. According to the PEIS, three basic compliance strategies may be applied at a site: (1) no remediation, (2) natural flushing, or (3) active remediation. In addition, a combination of natural flushing and active remediation is a further option. According to the decision tree, the preferred compliance strategies are no remediation, followed by natural flushing, followed by active remediation (with or without natural flushing) in order to achieve one of the standards.

### **10.1.3 Rationale for Compliance Strategy Selection**

Compliance strategies have been selected and proposed for all Title I sites, though not all have received regulatory approval from NRC. The compliance strategy selection process, as has been conducted to date, is discussed here and is relevant to reevaluating the compliance strategy for the Old Rifle site.

The compliance strategy selection process at Title I sites first involves a determination of the applicability of supplemental standards based on the criteria for classifying groundwater as “limited use.” For sites with limited-use groundwater, it is assumed that any beneficial groundwater uses would not require improvements in water quality, and no remediation is required. For sites with groundwater that is not considered to be limited use, the selection of an appropriate compliance strategy requires the identification of appropriate groundwater standards (e.g., MCLs, ACLs) and a means for achieving those standards (e.g., passive versus active remediation).

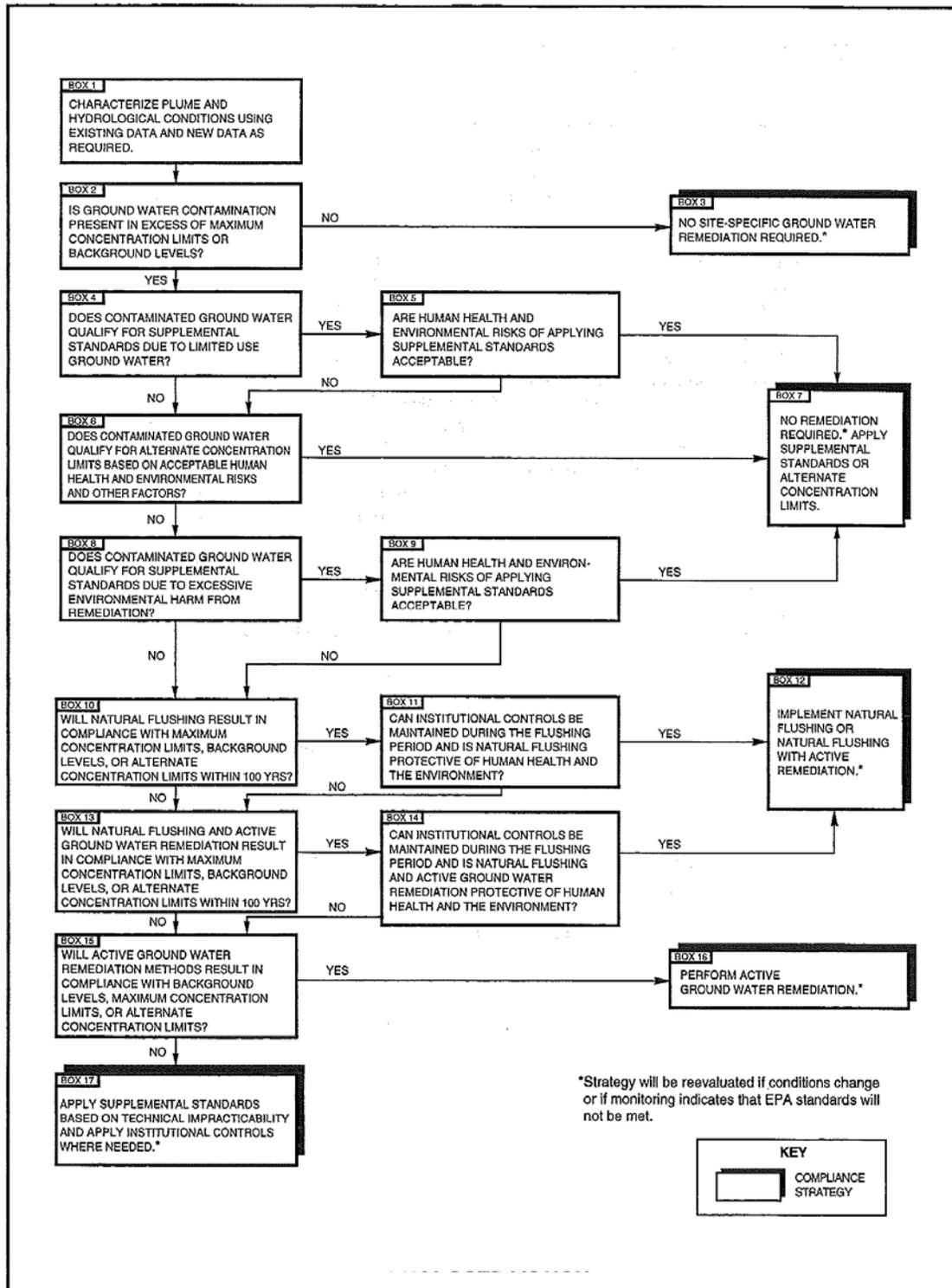


Figure 14. Ground Water Compliance Strategy Decision Process (from DOE 1996)

Two major assumptions have guided DOE's compliance strategy selection process at Title I sites, including the Old Rifle site. The first is that the most stringent standards should be met if possible. This meant that MCLs or background concentrations were assumed to be the default standards. The second assumption is that passive remediation (i.e., natural flushing) is preferable to conducting active remediation. Therefore, if modeling predicted that MCLs or background levels could be met in groundwater within the 100-year timeframe permitted for natural flushing, this was the preferred compliance strategy. Other options were considered only if it was determined that natural flushing was unlikely to achieve MCLs or background levels. At Title I sites where it was determined that natural flushing could not achieve MCLs or background levels, the selected compliance strategies usually involved either (1) active remediation to continue to try to meet MCLs, or (2) no remediation, with the application of less stringent cleanup standards (usually ACLs). At one site, the proposed strategy was to continue to employ natural flushing, but to establish less stringent cleanup goals (e.g., ACLs) that would be met at some future time. At some sites, multiple compliance strategies were selected to address different constituents.

Note that the flow chart in Figure 14 is not strictly consistent with the rationale presented above. Box 6 in the flow chart appears to provide for the use of ACLs before necessitating an evaluation of either natural flushing or active remediation. This implies that if ACLs can be demonstrated to be protective, no remediation is required, and neither passive nor active remediation need be considered. The text in the PEIS confirms that DOE anticipated applying ACLs in lieu of performing remediation, so long as institutional controls (ICs) were applied as needed and the remedy could be demonstrated to be protective. It is potentially significant that NRC accepted this decision-making logic and placed this figure in its standard review plan published as NUREG-1724 (NRC 2000).

According to Figure 1, the compliance strategy of "last resort" is the application of supplemental standards on the basis of technical impracticability (TI; Box 17). This compliance strategy would be appropriate where no method of remediation—passive or active—is likely to achieve applicable cleanup standards. Institutional controls are employed to prevent unacceptable exposures. This alternative has not been selected for any Title I site to date, primarily because NRC has been reluctant to approve this approach without extensive evidence to demonstrate that active remediation would not be effective. This is consistent with the fact that the TI compliance strategy is not actually referred to as a "no remediation" strategy, as is the case with limited-use groundwater. However, data compiled on the application of TI to CERCLA groundwater cleanups has shown that most of the approved TI waivers for those sites were "front-end" decisions made because of the documented complexity of the sites—not based on failed attempts at active remediation (USAEC 2004). The study recommends an earlier consideration of TI for all sites that have complex contaminant and hydrogeologic characteristics.

Because of the separation of the UMTRA surface and groundwater cleanup programs, the "no remediation" compliance strategy is misleading for most Title I sites, particularly those where tailings were removed and disposed of at an off-site location. At these sites, source removal was performed, which significantly reduced the contaminants in groundwater and stabilized groundwater plumes. The justification for any groundwater compliance strategy should "take credit" for the source removal remedy component. However, surface remediation was focused only on meeting cleanup standards for radium-226 in soil. Soil sampling conducted as part of the groundwater cleanup program suggests that other constituents in soil that were not addressed

during surface cleanup may remain at levels that could have a continuing impact on groundwater quality. As presented in the natural flushing evaluation report (DOE 2011), residual uranium in soil at the Old Rifle site may serve as a long-term source of groundwater contamination.

## **10.2 Protectiveness of Human Health and the Environment**

The ultimate goal in the selection of any groundwater compliance strategy is the protection of human health and the environment. This requires an evaluation of contamination present, potential pathways for exposure, and potential receptors. Contaminated groundwater at the Old Rifle site is laterally and vertically isolated from any other aquifer by the presence of bedrock that bounds the alluvial aquifer on its north side and underlies it as well. As a consequence, the contaminated groundwater discharges from the site to the Colorado River. However, river flows, even at low stages, are so high that discharged groundwater quickly mixes with river water; river water quality adjacent to the site is indistinguishable from background river concentrations. Therefore, there are no unacceptable risks to potential receptors in the river.

Institutional controls in the form of a quitclaim deed have been placed on the Old Rifle site to prevent the use of groundwater. Therefore, there are no complete exposure pathways to contaminated groundwater and no unacceptable risks associated with use of the site.

## **10.3 Reconsideration of the Old Rifle Compliance Strategy**

Because technical information presented in this report strongly suggests that natural flushing processes will not successfully remove uranium from the alluvial aquifer within a reasonable timeframe, an alternative compliance strategy at the site should be considered. The process for selecting a revised strategy, based on the decision framework discussed above and illustrated in Figure 14, is quite detailed and beyond the scope of this study. If and when the strategy is reconsidered, it is recommended that several possible options be examined, each with its distinct benefits and drawbacks.

# **11.0 Conclusions**

Several conclusions are drawn from the information and analyses presented in this report:

- Contrary to modeling predictions presented in the SOWP, uranium concentrations in groundwater at the Old Rifle site have not attenuated during the past 10 years in response to ambient natural flushing processes. Uranium levels at most on-site wells have remained relatively constant over that time or have gradually increased in recent years.
- Alluvial aquifer zones with the greatest uranium contamination in groundwater are located beneath the former mill tailings area on the west half of the site (0.1–0.3 mg/L), and beneath the former ore stockpile area on the site's east end (0.1–0.15 mg/L). Groundwater with lower uranium concentrations is found in between these two zones, including in the vicinity of the on-site ditch, which may lose surface water to the subsurface and dilute local aquifer sections impacted by former mill processes.

- Biostimulation experiments and other studies conducted by IFRC personnel at the site since 2002 show that flow, geochemical, and biological processes in the site's subsurface are complex, and especially more complex than was assumed during preparation of the SOWP.
- The numerous site complexities revealed through recent IFRC research efforts indicate that accurate modeling of subsurface flow and biogeochemical phenomena at the site is very challenging, particularly given that required model inputs increase with each new effort to simulate the impacts of IFRC biostimulation experiments.
- Recent IFRC modeling of the partitioning of uranium between groundwater and sediments indicates that the sorption distribution coefficient ( $K_d$ ) for uranium in the site's alluvial aquifer can vary from 0.5 to 20 mL/g, suggesting that uranium transport in the aquifer can be moderately to heavily retarded. The uranium transport modeling used in the SOWP to evaluate natural flushing was probably overly optimistic because the maximum uranium  $K_d$  employed in the simulations was 0.2 mL/g, which suggested minimal retardation. Use of such a low  $K_d$  in the SOWP model meant that the total mass of uranium in the alluvial aquifer system was underestimated.
- An updated site conceptual model presented in this report indicates that groundwater flow and concomitant uranium transport is strongly affected by physical and biogeochemical heterogeneities in the subsurface, groundwater system transients, recharge due to seepage losses from an on-site ditch, and recharge attributed to subsurface inflows from areas north of the site.
- Though seasonal increases in river stage on the nearby Colorado River can increase site groundwater levels by as much as 5 to 6 ft each year, inflows of river water to the alluvial aquifer during spring runoff months (April–June) are thought to be minimal. This is because river flows tend to increase gradually over the month- to 2-month-long rising limb of the spring runoff, and groundwater elevations throughout the alluvial aquifer are expected to respond relatively quickly and proportionally to the increase in river stage, thereby maintaining a net discharge to the river.
- An assessment of potential hyporheic flow processes at the site suggests that near-river portions of the aquifer might be influenced by river losses at a few locations, but areas farther from the river are probably not impacted by river water.
- Concentration data collected in 2010 showed that uranium isotopes can potentially be used to distinguish site-related uranium contamination from ambient uranium occurring in recharge from subsurface inflows north of the site as well as from seepage losses along the on-site ditch. The usefulness of additional chemical indicators for distinguishing mill-related contamination from naturally occurring uranium in groundwater has yet to be determined.
- Water chemistry data from several groundwater and surface water monitoring locations on and near the site indicate that ambient concentrations of DOC (~2–5 mg/L) are sufficiently high to support multiple background biogeochemical reactions in the subsurface.
- Potential causes of persistently high uranium concentrations in parts of the alluvial aquifer include slow diffusion of uranium from low-permeability sediments, occasional mobilization of uranium in the vadose zone, and natural inflow of uranium in recharge sources north of the site. Chemically reduced zones that are naturally occurring represent possible long-term sources of uranium contamination.

- Groundwater system complexities limit the capacity of existing numerical models to simulate uranium transport in the alluvial aquifer on a sitewide scale; as a consequence, natural flushing of uranium contamination cannot be reliably forecast or controlled. Any model developed at this time to match uranium concentration histories at multiple on-site wells would likely predict that the time needed to complete natural flushing of mill-related uranium contamination from the alluvial aquifer would exceed 100 years.
- It is not possible at this time to definitively state that natural flushing cannot achieve the uranium standard within the next 100 years, but uranium concentration histories at several on-site wells and phenomena contributing to flow and transport complexities suggest that this is the case.
- Several new wells are recommended for installation at the Old Rifle site to enhance the monitoring network currently used to track uranium contamination in groundwater. Five to six of the new wells would be located along a narrow band of alluvium just south of Highway 6 for the purpose of detecting naturally inflowing groundwater underneath the highway, and others would be located close to the on-site ditch and in the east third of the site.
- The decision logic specifically developed for the UMTRA Project will be followed if the decision is made to consider alternative compliance strategies. Reconsideration of the compliance strategy would likely involve assessment of several different options, each with its distinct benefits and drawbacks.

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