

Transmittal letter for 2015, Rev.1 report (September 2015)

The original version of this report included results from redox measurements collected in surface water and sediment at multiple locations in the North and South Walnut Creek drainages. Measurements of dissolved oxygen were collected concurrently in surface water at the same locations. After the original report was issued in April 2015, it was identified that the redox data presented in the April report were invalid because of problems related to the measurement probe. The available dissolved oxygen data were re-examined and it was determined that the general findings related to oxidizing and reducing conditions described in the 2015 report remained valid. However, the redox data were deleted from the original report and the report was re-issued as Revision 1 with a September 2015 date.

**EVALUATION OF WATER QUALITY VARIABILITY FOR
URANIUM AND OTHER SELECTED PARAMETERS IN WALNUT CREEK
AT THE ROCKY FLATS SITE**

**PREPARED FOR:
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PROJECT 071-091.020

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EXECUTIVE SUMMARY

This report, prepared by Wright Water Engineers, Inc. (WWE) on behalf of Stoller Newport News Nuclear (SN3), summarizes the current findings from an ongoing study initiated to address specific questions raised by SN3 regarding uranium in surface water at the Rocky Flats Site (RFS). The study addresses the distribution, transport mechanisms, sources and composition of uranium, in terms of its natural versus anthropogenic fractions, with a focus on the North and South Walnut Creek drainages. Other water quality parameters related to the transport of uranium at RFS are also evaluated.

SN3 is a prime contractor to the United States Department of Energy (DOE) Office of Legacy Management (LM), which is responsible for ongoing surveillance and monitoring activities at the site.

The following questions were evaluated and are discussed in this report:

- 1) How do concentrations of natural uranium observed globally and throughout Colorado compare with the uranium concentrations observed in the RFS Walnut Creek drainages?
- 2) What are the primary mechanisms by which concentrations of uranium in surface water may significantly increase and decrease?
- 3) Are previously unrecognized anthropogenic uranium sources suggested by the data?

Findings related to these questions are summarized below:

Presence of Natural Uranium in the Environment

- Naturally occurring uranium is ubiquitous in the environment. Significant natural deposits of uranium are distributed across Colorado. For example, in the Ralston Creek drainage basin, approximately 5 miles southwest of RFS, the Schwartzwaldner mine is identified as the largest vein-type uranium deposit in the United States.

- As a result of the widespread presence of natural uranium sources in Colorado, multiple public water systems have uranium measured in the source water wells, with at least 10 systems identified that have uranium concentrations in one or more wells that have exceeded the 30 µg/L drinking water Maximum Contaminant Level (MCL).

Presence of Anthropogenic Uranium in the Environment

- Natural uranium can be modified to create anthropogenic forms by separating and collecting the three isotopes in natural uranium (U-234, U-235 and U-238) through the use of diffusion and centrifugal processes. Two types of anthropogenic uranium, “enriched” and “depleted,” differ from natural uranium chiefly in their relative percentages of U-235 and are characterized as follows:
 - Enriched uranium has a higher fraction of U-235 (up to 97% U-235, compared with approximately 0.72% for natural uranium) and is used for nuclear reactor fuel and in weapons.
 - Depleted uranium has a lower fraction of U-235 than natural uranium and a higher fraction of U-238 compared to the approximate 99.27% of U-238 in natural uranium. The reduced fraction of U-235 makes depleted uranium less radioactive than natural uranium. Because of its high density, depleted uranium is used in applications such as armor plating on military vehicles, munitions, counterweights on aircraft control surfaces and as ballast for ships.
- The chemical processes that control the environmental mobility of uranium (speciation, dissolution, chemical precipitation, and sorption) are essentially identical whether the uranium is of anthropogenic or natural isotopic composition.
- At RFS, the work conducted historically involved anthropogenic uranium, in either “enriched” or “depleted” forms, which was received from other facilities in the DOE complex. Work at RFS did not involve uranium from natural sources. As a result,

environmental media at RFS (i.e., soil, surface water, groundwater, etc.), can have a mixture of uranium from both natural and anthropogenic sources.

- Determining whether uranium is from natural or anthropogenic sources, or a combination of both, can be accomplished by analyzing the composition of the uranium isotopes in samples using specialized analytical techniques. In surface water at WALPOC, the fraction of uranium from natural sources has been determined to average approximately 78 percent (described further below).

RFS Site-Specific Uranium Stream Standard

- The Colorado Water Quality Control Commission Regulation 38 established a site-specific uranium standard of 16.8 µg/L for Segments 4a and 5 on Woman Creek and Segments 4a, 4b and 5 on Walnut Creek. The site-specific standard is the lower end of a 16.8 µg/L – 30 µg/L range for the statewide stream standard for uranium in a drinking water supply. For context, the 16.8 µg/L and 30 µg/L values were determined as follows:
 - The 16.8 µg/L lower limit of the statewide stream standard for uranium is based on protection of human health from chemical toxicity. The 16.8 µg/L value is based on a daily drinking water consumption rate of 2 liters per day, with no duration because it is related to toxicity, not a lifetime dose.
 - The 30 µg/L upper limit of the statewide stream standard for uranium is the EPA drinking water MCL, adopted by Colorado Department of Public Health and Environment (CDPHE) that has been determined to be an acceptable concentration in public drinking water supplies, taking treatability and laboratory detection limits into account. The 30 µg/L value is based on an additional lifetime cancer risk of 10^{-4} (meaning the normal cancer mortality risk would increase from 20 percent to 20.0001 percent [20 plus 10^{-4}]) for a population consuming drinking

water that contains 30 µg/L of uranium, based on a consumption rate of two liters of water per day for 70 years.

- At RFS, compliance with the 16.8 µg/L stream standard in Walnut Creek is monitored, in accordance with the Rocky Flats Legacy Management Agreement (RFLMA), at the Walnut Creek Point-of Compliance (WALPOC) monitoring location. Per RFLMA, at WALPOC, a 30-day average concentration of uranium that exceeds 16.8 µg/L defines a reportable condition; a 12-month rolling average concentration of uranium that exceeds 16.8 µg/L defines a reportable condition and triggers an evaluation of compliance with the remedy performance standard.

General Chemical Factors that Govern Uranium Concentrations and Transport that are Not Specific to RFS

- Uranium concentration and mobility in aqueous environments are mainly governed by four chemical processes: precipitation, complexation, sorption, and colloid formation. All of these processes can be influenced by: redox potential, pH, and water quality, which determine the aqueous speciation and dissolved/solid equilibria of uranium and thereby govern the movement of uranium in the environment.
 - Redox potential determines whether uranium species occur predominantly in the sparingly soluble reduced state U(IV) or in the more highly soluble and mobile oxidized state U(VI).
 - The solubility of the more highly soluble U(VI) species (mainly oxides, hydroxides and carbonate complexes) is further dependent on pH and other water chemistry parameters.
 - U(VI) species that have been reduced to low solubility U(IV) species can be re-oxidized back again to soluble U(VI) species, resulting in former sinks for immobilized U(IV) species changing into sources for mobile U(VI) species.

- In water, sediments, and soils with negative redox potentials, oxidants other than oxygen, particularly nitrate, can restore or maintain significant levels of soluble U(VI) species.

Chemical Factors Specific to RFS

- Where stream conditions are anaerobic (flow dominated by anaerobic groundwater inputs, deeper ponded water, wetlands, bottom sediments, etc.), nitrate from the Solar Ponds Plume (either in treated effluent from the Solar Ponds Plume Treatment System [SPPTS] as measured at monitoring location SPOUT or, alternatively, in groundwater that is not collected by the SPPTS) can oxidize U(IV) species to U(VI) species and mobilize uranium. This mechanism becomes much less important when groundwater and stream conditions are aerobic, such as following extreme storm events like that which occurred in September 2013.
- Storm events of relatively smaller magnitude, in terms of rainfall or snowmelt depth, produce different conditions in surface and groundwater at RFS than large storms. The primary result of smaller storms is dilution from surface runoff that generally lowers uranium concentrations in the Walnut Creek drainages, despite short-term surface conditions that are generally aerobic and that facilitate mobilization of uranium.
- The effect of very large storms is an initial short-term dilution period caused by increased runoff which first results in lower uranium concentrations in surface water. This is followed by a prolonged long-term effect of increased dissolved oxygen in groundwater entering the Walnut Creek drainages. Where anaerobic waters become aerobic, immobilized U(IV) species can be oxidized to soluble U(VI) species, helping to mobilize and increase concentrations of uranium in surface water.

RFS Data - Spatial and Temporal Variability

- North Walnut Creek

- Along North Walnut Creek, uranium concentrations measured at individual monitoring locations are highly variable from upstream monitoring station SW093 down to station GS11 (Pond A-4 outfall), indicating the presence of significant uranium source(s) and sink(s) as average uranium concentrations increase and then decrease going downstream along the channel reach.
- The uranium load measured at GS13 is approximately two times greater than the uranium load measured at upstream monitoring location SW093 (based on total loads measured at both locations from January 2010 through March 2014). The source of the uranium observed at GS13 appears to be a combination of: 1) groundwater with a higher relative uranium concentration that is not collected by the SPPTS and enters the channel upstream from GS13, 2) uranium in channel sediments located between SW093 and GS13, and/or 3) groundwater or periodic surface runoff entering North Walnut Creek from the north side of the channel.
- Flows from SPOUT are approximately 2 percent of the flow volume compared to station GS13. The uranium load from SPOUT is approximately 5 percent of the uranium load measured at GS13 (based on total loads measured at both locations from January 2010 through March 2014). In contrast, the nitrate load delivered from SPOUT is approximately 20 percent of the total nitrate load measured at GS13, based on data for the same period.

- South Walnut Creek

- Along South Walnut Creek, average uranium concentrations measured at individual monitoring locations generally decrease from upstream monitoring

station GS10 down to station GS08 at the Pond B-5 outfall, indicating uranium removal along this channel reach.

- At GS10, uranium concentrations vary widely temporally and in a cyclical, seasonal pattern, with the highest concentrations typically observed during the first two to three months each calendar year when a larger fraction of the flow at GS10 during those months is attributed to groundwater.
- The uranium load is higher at GS10 than at B5INFLOW (downstream monitoring location) in most months evaluated, indicating that uranium removal occurs between those two locations. This is consistent with areas where sorption and precipitation occur, which can create sinks for uranium as it is transported down the drainage. Uranium deposited between GS10 and B5INFLOW is intermittently mobilized and transported downstream, generally during periods with higher flows.
- Immediately downstream from GS10, between B5INFLOW and GS08 (Pond B-5 outfall), removal of uranium in Pond B-5 is most likely to occur during periods with increased flows when elevated concentrations of suspended sediments are likely to exist, which leads to proportionately greater removal of uranium bound to sediments via settling processes, even when the pond is in flow-through mode.
- North Walnut Creek Compared with South Walnut Creek
 - The pattern of uranium concentrations and loads in North Walnut Creek differs from that in South Walnut Creek. In North Walnut Creek, uranium concentrations and loads generally increase in a downstream direction, from monitoring location SW093 to A2EFF, indicating a uranium source or sources in that reach (such as an inventory of uranium in the channel sediments or groundwater with elevated uranium concentration that enters the channel), before decreasing in concentration

further downstream at station GS11 (Pond A-4 outfall). In contrast, in South Walnut Creek, uranium concentrations and loads generally decrease from the uppermost location down to the inlet to Pond B-5, indicating uranium removal over the length of the channel reach.

- WALPOC

- Measured uranium concentrations in individual flow-paced composite samples collected at WALPOC were below the 16.8 µg/L standard until after the September 2013 flood event. Shortly after that event, multiple samples contained uranium at concentrations above the standard. Not until mid-May 2014, approximately eight months after the September 2013 flood event, did all subsequent sample results return to concentrations below the 16.8 µg/L standard, with three consecutive sample results at WALPOC with concentrations below 16 µg/L (sample dates from 5/12/14 through 5/21/14). Stream flows at WALPOC were continuous for the entire post-flood period into mid-May 2014.

Anthropogenic Versus Natural Uranium

- In North Walnut Creek, the measured fraction of natural uranium (versus anthropogenic uranium) at SW093 (approximately 90 percent) is higher than at downstream locations GS13 (approximately 71 to 75 percent) and in discharges from Pond A-4 (74 to 75 percent). The decrease of the natural uranium fraction at the further downstream locations reflects inputs of anthropogenic uranium from potentially multiple sources (e.g., SPOUT discharges, groundwater not collected by the SPPTS, and channel sediments with anthropogenic uranium). Each of the locations represents a “snapshot” of the uranium isotopic distribution in a specific part of the drainage; the changes in natural uranium fraction from one location to another are likely gradual transitions from one monitoring location to another, with the data reflecting the relative consistency of the natural uranium percentage from GS13 down the drainage to Pond A-4.

- In South Walnut Creek, progressing from upstream to downstream, the measured fraction of natural uranium at FC4EFF, in the upstream portion of the drainage, was approximately 71 to 74 percent. At downstream location GS10, the natural uranium fraction fluctuates broadly, ranging from 43 to 78 percent. Downstream from GS10 at location GS08 (Pond B-5 outfall), the measured natural uranium percentage increases, ranging between 76 and 80 percent.
- The percentage of natural uranium at WALPOC does not vary substantially with changes in measured uranium concentrations or stream flow rate, with an average natural fraction of 78 percent based on 21 samples analyzed from September 2011 through April 2014, with results ranging from approximately 75 to 83 percent natural uranium. For the same samples used for the isotopic analyses, the uranium concentrations had greater relative variability than the natural percentage values, with concentrations ranging from 1.7 $\mu\text{g/L}$ to 22.9 $\mu\text{g/L}$.
- At specific monitoring locations, limited isotopic data collected from samples following the September 2013 flood indicate that during the post-flood period the percentage of natural uranium decreased slightly when concentrations of total uranium increased. While this relationship is apparent at several locations, particularly in South Walnut Creek, GS10 is the only location to have more than three sample results to base this observation. Since both natural and anthropogenic uranium respond in the same way to changes in water chemistry, the relatively minor increase in the anthropogenic fraction may indicate contributions from other anthropogenic sources that don't normally contribute to the uranium load in the stream. These other intermittent sources could potentially include sub-surface anthropogenic uranium that is mobilized when exposed to increased levels of groundwater and/or increased contributions from sources with higher than average anthropogenic fractions, such as an increased volume of groundwater from the former Solar Evaporation Ponds area that is not collected by the SPPTS. This suggests that during and following the September 2013 flood event, previously immobile anthropogenic uranium sources may have been mobilized, possibly by a rising

groundwater table contacting anthropogenic uranium that normally is above the groundwater elevation, and/or by increased mobilization by surface flows of specific anthropogenic sources, such as bed sediments located near anthropogenic inputs to stream flow.

SPPTS Operations

- The uranium load contributed from the SPPTS effluent at SPOUT was approximately 5 percent of the uranium load measured at GS13 based on data from January 2010 through March 2014. During time periods when the SPPTS has been least effective removing uranium, there has not been a corresponding increase in uranium concentrations downstream at GS13, further supporting the understanding that flows from SPOUT do not have a substantial effect on uranium concentration in North Walnut Creek.
- The nitrate load delivered from SPOUT was approximately 20 percent of the total nitrate load measured at GS13 based on data from January 2010 through March 2014. This is an appreciably larger fraction of the nitrate load in North Walnut Creek contributed by SPOUT compared to the fraction of uranium load contributed by SPOUT.

Ponds A-4 and B-5

- Pond A-4 – Uranium concentrations at station GS11 (Pond A-4 outfall) for the batch-release mode pond operations (mean: 7.2 µg/L; median: 6.6 µg/L) are lower compared to the flow-through mode, pre-2013 storm conditions (mean: 11.9 µg/L; median: 13.3 µg/L). When analyzed in conjunction with data for GS12 (or adjacent monitoring location A3AFF) located immediately upstream from Pond A-4, data indicate a significant reduction of uranium concentration occurs in Pond A-4 during batch-release mode operations (i.e., pond operations prior to late September 2011). The pond provides a reduction in the uranium concentration but not specifically to anthropogenic uranium. Approximately three quarters of the uranium in Pond A-4 is from natural sources.

- Pond B-5 - Uranium concentrations at station GS08 (Pond B-5 outfall) for the batch-release mode pond operations (mean: 9.3 µg/L; median: 8.5 µg/L), are not substantially different compared to the flow-through mode, pre-2013 storm conditions (mean: 9.9 µg/L; median: 8.8 µg/L). Reasons for the limited difference in uranium concentrations regardless of operating configuration in Pond B-5 are not fully understood, but differences between B-5 and A-4, in terms of uranium removal effectiveness, might be related to uranium concentrations in the sediment, and/or the nature of the sediments, including sorption strength for uranium, and the relative effectiveness of sedimentation processes in the two ponds. As noted previously, uranium removal in Pond B-5 is most likely to occur during periods with increased flows when elevated concentrations of suspended sediments are likely to exist, which leads to proportionately greater removal of uranium bound to sediments via settling processes. Approximately three quarters of the uranium in Pond B-5 is from natural sources.

EVALUATION OF WATER QUALITY VARIABILITY FOR URANIUM AND OTHER SELECTED PARAMETERS IN WALNUT CREEK AT THE ROCKY FLATS SITE

1.0 INTRODUCTION AND BACKGROUND INFORMATION

1.1 Introduction

This report, prepared by Wright Water Engineers, Inc. (WWE) on behalf of Stoller Newport News Nuclear (SN3), summarizes the current findings from an ongoing study initiated to address specific questions raised by SN3 regarding uranium in surface water at the Rocky Flats Site (RFS). The study addresses the distribution, transport mechanisms, sources and composition of uranium, in terms of its natural versus anthropogenic fractions, with a focus on the North and South Walnut Creek drainages. Other water quality parameters related to the transport of uranium at RFS are also evaluated.

SN3 is a prime contractor to the United States Department of Energy (DOE) Office of Legacy Management (LM), which is responsible for ongoing surveillance and monitoring activities at the site.

1.2 RFS Background Information

1.2.1 Site Description and History

The RFS, located approximately 16 miles northwest of Denver, Colorado, was formerly used to produce components for nuclear weapons. The site was originally developed by the United States Atomic Energy Commission (AEC) in 1952 and served as a weapons component manufacturing facility until 1994. During production operations, radionuclides released to the environment included plutonium-239, americium-241, tritium and uranium.

The work conducted historically at RFS involved uranium that was modified, in either “enriched” or “depleted” forms, which was received from other facilities in the DOE complex

(collectively referred to as “anthropogenic” uranium). The work conducted at the facility did not involve uranium from natural sources. (Note: Since the different types of uranium have different isotopic compositions, samples can be analyzed to determine whether the uranium in environmental media at RFS is from anthropogenic sources, natural sources [which are abundant in the region], or a combination of the two; this topic is addressed in Section 3.4).

In 1994, the mission of the site was officially transitioned to one of environmental remediation, decommissioning, demolition and removal of production facilities and, ultimately, restoration/revegetation of the site. The environmental remediation, restoration and “closure” phase was completed in October 2005. Closure of the site resulted in a different hydrologic regime compared to that which existed during the production and operations phase, because: 1) water that was formerly supplied to the site for domestic and industrial purposes, and discharged as treated wastewater, was eliminated, and 2) runoff from the site was reduced substantially because of impervious surfaces (i.e., buildings and pavement) being removed. The reduction in water volume flowing across the site also had an effect on the movement of uranium (both naturally occurring and anthropogenic) across the site.

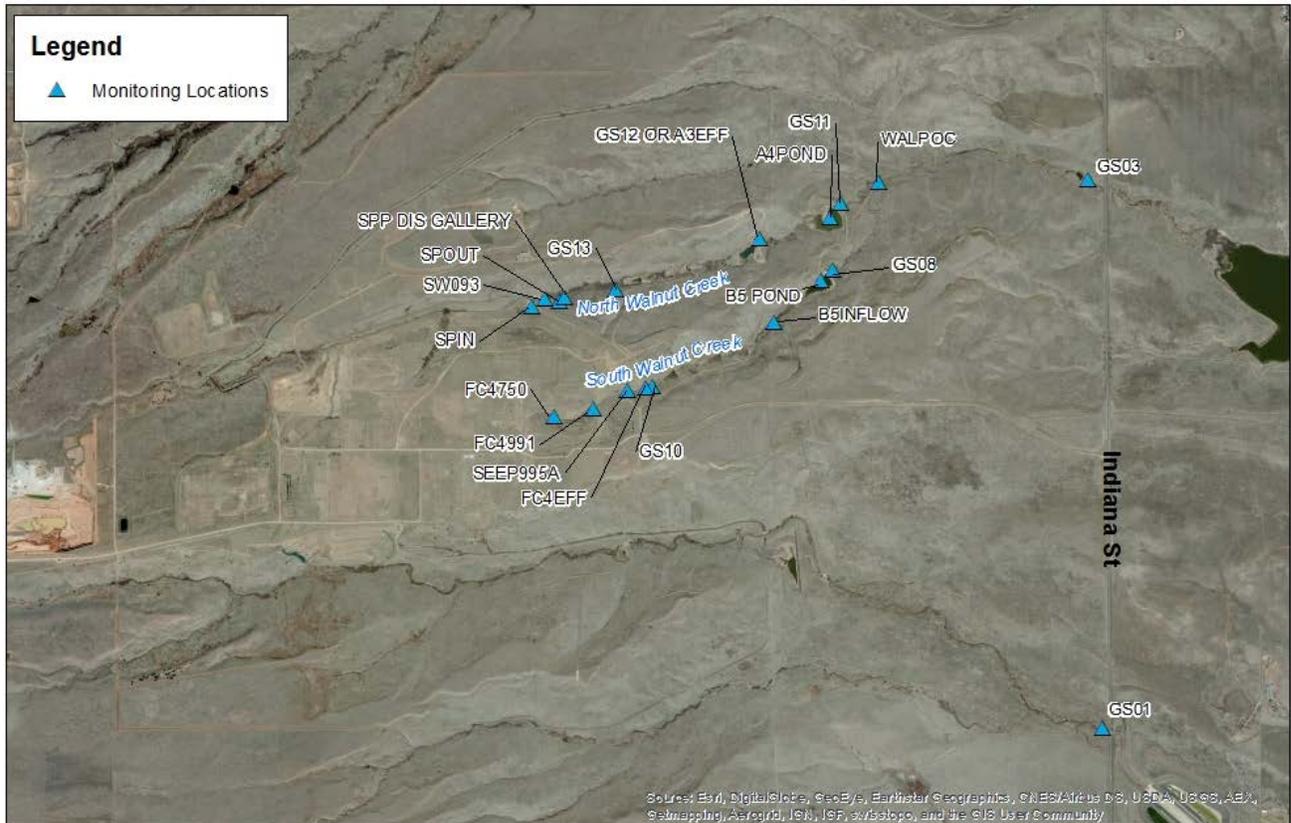
Since site closure activities were completed in 2005, other major changes and/or relevant events at the site, in terms of surface water management, have included:

- Removal of all interior dams on Walnut Creek via the construction of engineered breaches, from 2009 through 2012 (this included breaching dams A-1, A-2 and A-3 on North Walnut Creek and dams B-1, B-2, B-3 and B-4 on South Walnut Creek [see Figure 1])¹.
- Changing the operations of terminal dams A-4 (North Walnut Creek) and B-5 (South Walnut Creek) from batch discharge to flow-through operation.

¹ Dam C-1, in the Woman Creek drainage, was breached in 2003, but is not addressed in this report.

- Occurrence of the driest calendar year, in 2012, that has been recorded by site rain gages since 1993, with an average total precipitation depth of 7.21 inches measured at gages located across the site.
- Occurrence of the largest recorded rainfall event in site history (from September 9 through September 15, 2013, total rainfall depths ranging from 5.21 to 8.30 inches were measured at six rain gages located across the site, averaging 6.5 inches). This was determined to be approximately a 100-year rainfall event for the site (for a 7-day period), per the NOAA Atlas 14, Volume 8 (NOAA, 2013a; NOAA, 2013b).

Figure 1. Selected RFS Surface Water Monitoring Locations Used in Study



Note: Figure 1 shows surface water monitoring locations that are most frequently referenced in this report. A map of all monitoring locations referenced in this study is provided in Appendix A (Figure A.1).

1.2.2 Site Regulatory Background

A brief description of the historical evolution of regulations for uranium in surface water at RFS is provided below. A summary of uranium regulations for surface water in Colorado is provided in Section 1.4.

RFS Site-Specific Uranium Standard

Through March 2009, the site-specific standards for uranium (U) that applied at RFS were:

- North and South Walnut Creeks: 10 picocuries per liter (pCi/L) (equivalent to approximately $14.9 \mu\text{g/L}$)², measured at Point of Compliance (POC) monitoring location GS03 (Walnut Creek just east of Indiana Street).
- Woman Creek: 11 pCi/L (equivalent to approximately $16.4 \mu\text{g/L}$), measured at POC monitoring station GS01 (Woman Creek just east of Indiana Street).

These values were based on ambient concentrations of uranium determined during the former operations period at the Site. During that period, naturally-occurring uranium contributed to the ambient concentrations measured in surface water, with natural uranium comprising approximately 78 percent of the uranium observed at monitoring location GS03 (at Walnut Creek and Indiana Street) for a sample collected in May 2002, prior to closure of the site.

Another important factor that influenced ambient uranium concentrations during the operations period was the large relative volume of water historically imported to the site (for industrial purposes, restrooms, irrigation, etc.) and then discharged into South Walnut Creek after being treated at the former on-site wastewater treatment plant (WWTP). Prior to closure of the site, an average of approximately 195 acre-feet per year was discharged from the WWTP into South Walnut Creek (based on discharge data from 1997 to 2001) (Kaiser-Hill, 2002). In terms of

² The conversion from pCi/L to $\mu\text{g/L}$ (0.67 pCi per μg of uranium) is based on the isotopic composition of uranium from a natural source.

stormwater runoff during the same time period, the annual volume measured in North and South Walnut Creeks combined (averaged from 1997 through 2001 at stations SW093 and GS10 combined), was approximately 284 acre-feet per year (Kaiser-Hill, 2002).

For comparison, in the post-closure condition, the average annual stormwater runoff volume measured in North and South Walnut Creeks combined was approximately 137 acre-feet per year (based on flow data from stations SW093 and GS10 in 2010 and 2011, which were typical years in terms of precipitation [see Section 3.1]); during those years, no discharges of treated effluent from the WWTP were added to the stream flows because the WWTP was removed in 2004.

The historic discharges of imported, treated water from the WWTP, in conjunction with the higher volume of stormwater runoff from impervious surfaces (i.e., buildings and pavement) that formerly existed at RFS, resulted in dilution and lowering of uranium concentrations in surface water flowing from the site. The historic industrial-era conditions described above and the corresponding ambient concentrations of uranium in surface water at that time are not representative of the current, post-closure conditions.

In 2009, DOE unsuccessfully petitioned the Colorado Water Quality Control Commission (WQCC) to revise the site-specific uranium standard to the statewide basic standard for uranium, 30 micrograms per liter ($\mu\text{g/L}$), which is the same as the United States Environmental Protection Agency (EPA) Maximum Contaminant Level (MCL) for drinking water. In recognition of the changed conditions following closure of the site (as described in Section 1.2.1), the WQCC revised the site-specific standard to 16.8 $\mu\text{g/L}$ (equivalent to approximately 11.6 pCi/L of natural U). During the revision proceedings, the WQCC requested that if a higher ambient standard was warranted, the Site should collect additional data justifying this need. In 2011, the 16.8 $\mu\text{g/L}$ standard was defined as the lower end of the Colorado basic statewide standard for uranium for domestic water supply, which has a range from 16.8 $\mu\text{g/L}$ to 30 $\mu\text{g/L}$ (note that the uranium concentration is measured as a metal mass per unit volume of water, versus radioactivity per unit volume of water).

At RFS, compliance with the 16.8 µg/L stream standard in Walnut Creek is currently monitored, in accordance with the Rocky Flats Legacy Management Agreement (RFLMA), at the Walnut Creek Point-of Compliance (WALPOC) monitoring location (see Figure 1). The Point of Compliance for Walnut Creek was moved from GS03 (just west of Indiana Street) to WALPOC (at the eastern boundary of the Central Operable Unit) on September 12, 2011. Per RFLMA, at WALPOC, a 30-day average concentration of uranium that exceeds 16.8 µg/L defines a reportable condition; a 12-month rolling average concentration of uranium that exceeds 16.8 µg/L defines a reportable condition and triggers an evaluation of compliance with the remedy performance standard.

The 16.8 µg/L site-specific standard for uranium at RFS is the lower end of the 16.8 µg/L - 30 µg/L range for Colorado basic statewide standard for uranium in a domestic water supply, and is less than the 30 µg/L MCL for drinking water, though the receiving streams from RFS are not used for domestic water supply.³

Further information on uranium standards in surface water in Colorado is provided in Section 1.4. Additional information on the RFS site-specific standard is provided in Section 1.4.3.

1.2.3 Basis for Current Study: Water Quality Trends in Walnut Creek

As discussed above, the purpose of this study is to address questions related to water quality and evolving changes in water quality in the Walnut Creek drainage. Relevant observations regarding water quality in Walnut Creek are summarized below:

³ For types of water use other than domestic water supply, Regulation 38 provides the following equations to calculate the uranium standard:

Aquatic life (acute): $e^{(1.102[\ln(\text{hardness})] + 2.7088)}$

Aquatic life (chronic): $e^{(1.102[\ln(\text{hardness})] + 2.2382)}$

North Walnut Creek – Surface Water Uranium Concentrations

Water quality monitoring in the North Walnut Creek drainage following closure of the site identified trends that raised questions being addressed by this study. At all surface water monitoring locations in North Walnut Creek upstream of terminal Pond A-4 and at WALPOC (the Walnut Creek Point of Compliance monitoring location), uranium concentrations for individual samples have intermittently been detected at levels that exceed 16.8 µg/L, recognizing that the site-specific standard is monitored at WALPOC and regulatory responses are based on 30-day average and 12-month rolling average concentrations (see Sections 1.4.3 and 3.2.1). Also, it is noted that uranium concentrations at specific monitoring locations in North Walnut Creek upstream of Pond A-4 have intermittently been detected at levels above the 30 µg/L MCL for drinking water.

Discharges from Pond A-4, measured at station GS11, have generally been below 16.8 µg/L. However, four flow-paced composite samples that were collected starting in October 2013 and into May 2014 (i.e., starting approximately one month after the large September 2013 storm event), collectively had an average uranium concentration of approximately 24 µg/L, with individual sample results ranging from approximately 19 to 29 µg/L.

Expanded monitoring to better understand uranium fate and transport processes in both North and South Walnut Creeks has been conducted for over four years and is ongoing.

South Walnut Creek – Surface Water Uranium Concentrations

Similar to North Walnut Creek, surface water uranium concentrations in South Walnut Creek upstream of terminal Pond B5 have a variable range of uranium concentrations that periodically exceed the site-specific standard and, for reference purposes, the 30 µg/L MCL for drinking water. In early 2011, a composite sample collected at station GS10 had a result of approximately 90 µg/L, or more than twice the highest concentration in previous samples at that location. That sample result was followed by other samples with results above the prior normal. Although

routine cycles of relatively higher and lower uranium concentrations have historically been observed at GS10, the high results in early 2011 were outside the range of normally observed conditions prior to that time. Since mid-2011, sample results with greater than 30 µg/L of uranium have been observed routinely at GS10. Prior to early 2010, no samples had been measured with concentrations at that level.

Walnut Creek Point of Compliance – Surface Water Uranium Concentrations

Since the WALPOC station was first installed and monitoring initiated in September 2011, all uranium sample results were below the 16.8 µg/L site-specific uranium standard until October 2013 (approximately one month after the large September 2013 storm event), when multiple consecutive composite sample results at WALPOC were measured above 16.8 µg/L. This continued into April 2014. Uranium concentrations up to approximately 23 µg/L were measured at WALPOC during that period. However, starting in mid-May 2014, subsequent samples at WALPOC returned to lower concentrations, including three samples from mid-May 2014 measured below 16 µg/L.

It is noted that the data set evaluated in this report generally includes data collected through March 2014, though at some locations data through June 2014 are plotted, evaluated and discussed. Generally, the time period of data evaluated will be identified in the discussion of the report.

1.3 General Uranium Background Information

1.3.1 Occurrence of Natural Uranium in the Environment

Naturally occurring uranium is ubiquitous in the environment. It is a metal found in all rock types in varying small concentrations and its abundance varies by location as a function of local geologic formations that contain uranium. Uranium is widely dispersed in the earth's crusts, rocks and soils at concentrations of approximately 2 – 4 parts per million (ppm) (Abdel-Sabour, 2014; TRSL, 2001) and in seawater at approximately 2 to 3.7 parts per billion (ppb) (Kathren,

1984). For perspective, uranium is more abundant than gold, silver, mercury, antimony, or cadmium, and approximately as abundant as tin, cobalt, lead, molybdenum, and arsenic (Abdel-Sabour, 2014; Todorov, 2006; UNSCEAR, 1993).

Awareness that natural uranium is a common constituent in geologic material, soils, and waters is of particular importance at RFS because the majority of uranium measured in surface water and groundwater at the site is from natural sources. Natural uranium is composed of three isotopes in the following approximate percentages:

- U-234: 0.006%
- U-235: 0.72%
- U-238: 99.27%

Natural uranium is distinguished from anthropogenic uranium by measuring the isotopic composition, using analytical methods discussed in Section 3.5.

Mineral Sources of Natural Uranium in Colorado

Elevated concentrations of natural uranium are present in granite, metamorphic rocks, lignites, monazite sand and phosphate deposits, as well as in the uranium-rich minerals of uraninite, carnotite, and pitchblende (EPA, 2000). High concentrations of uranium in the South Platte River Basin are directly related to the local geology. The local bedrock, particularly the crystalline rocks (primarily granitic) in the mountains and marine shales and coal deposits in the plains, are naturally high in uranium. Sediments derived from crystalline rocks in the mountains are transported by the streams eastward onto the plains (Dennehy, et al., 1998) and “roll-front” type uranium deposits, similar to those in the Uravan belt in Montrose County, are found primarily in the northeast section of the state (Colorado Division of Reclamation, Mining and Safety [CDRMS], 2014).

Because of the relative natural abundance of uranium in Colorado, uranium has historically been mined throughout the state and Colorado ranks third for uranium reserves, behind Wyoming and

New Mexico (CDMRS, 2014). Significant natural deposits of uranium are distributed across Colorado and include: Montrose County, where the UraVan mineral belt contains an estimated 1,200 historic mines; Larimer County, where the EPA lists at least 25 mines or mineable occurrences of uranium (Larimer County Environmental Advisory Board, 2008), and; Jefferson County, where the largest vein-type uranium deposit in the United States exists at the Schwartzwalder mine, located approximately 5 miles southwest of RFS in the Ralston Creek drainage (Zielinski et al., 2007).

Natural Uranium in Groundwater and Surface Water

Globally, uranium in natural waters is typically present in concentrations between 0.1 and 10 µg/L. Concentrations greater than 1 µg/L generally occur in water associated with uranium ore deposits and much higher concentrations of natural uranium are possible (Weiner, 2013); a 90-meter deep well in Finland had a uranium concentration near 15,000 µg/L (Hem, 1992).

In the United States, the Colorado Plateau and Rocky Mountains are two of the primary areas with uranium in groundwater. In contrast, in the eastern United States, concentrations of uranium in groundwater are typically low (EPA, 2004).

A Colorado Geological Survey of 104 water wells studied natural groundwater contamination in the Cheyenne Basin of Colorado (in Weld County, north of Greeley) and found water high in uranium in many of the major aquifers (Kirkham, et al., 1980). Review of the study results indicates 90 of the wells sampled do not meet current EPA standards for uranium in drinking water (CGS, 2015).

With respect to surface water and sediments, geochemical sampling of 82 stream waters and 87 stream sediments within mountainous areas immediately west of Denver was conducted by the U.S. Geological Survey in October 1994 (Zielinski et al., 2007). The primary purpose was to evaluate regionally the effects of geology and past mining on the concentration and distribution

of uranium. In surface water, concentrations ranged from less than 1 µg/L to 65 µg/L, with most values less than 5µg/L.

Natural Uranium in Colorado Public Drinking Water Systems

As a result of the widespread presence of natural uranium sources in Colorado, 33 public water systems participate in the *Colorado Radionuclides Abatement and Disposal Strategy* (CO-RADS) project. The purpose of CO-RADS is to provide technical assistance with the goal of resolving drinking water radionuclide violations in order to comply with one or more of the Colorado radionuclide drinking water MCLs⁴ (CDPHE, 2009). Review of CO-RADS records indicates at least 10 of the systems have uranium measured in one or more source water wells at concentrations that have exceeded the 30 µg/L drinking water MCL, with concentrations ranging as high as 280 µg/L.

1.3.2 Occurrence of Anthropogenic Uranium in the Environment

General Description of Anthropogenic Uranium

Natural uranium can be modified to create anthropogenic forms by separating and collecting the three isotopes in natural uranium (U-234, U-235 and U-238) through the use of diffusion and centrifugal processes. Two types of anthropogenic uranium, “enriched” and “depleted,” differ from natural uranium chiefly in their relative percentages of U-235, as described below:

- Enriched uranium has a higher fraction of U-235 (up to 97% U-235, compared with approximately 0.72% for natural uranium) and is used for nuclear reactor fuel and in weapons.

⁴ *Colorado has adopted the USEPA’s radionuclide drinking water MCLs of:

Adjusted gross alpha activity: 15 pCi/L

Combined radium 226/228: 5 pCi/l

Uranium: 30 µg/L

Beta and photon particle activity: 4 mrems/yr

Note that uranium is the indirect source of most of the non-uranium radioactivity listed above as a result of daughter products in the decay chains of U-235 and U-238. A small amount of the non-uranium radioactivity is also from daughter products in the Th-232 decay chain.

- Depleted uranium is a remnant of the enrichment process. Most U-235 has been removed from depleted uranium, leaving a higher U-238 fraction than the approximate 99.27% of U-238 in natural uranium. The reduced fraction of U-235 in depleted uranium causes it to be approximately 40 percent less radioactive than natural uranium, for a given mass. Because of its high density, depleted uranium is used in applications such as armor plating on military vehicles, munitions, counterweights on aircraft control surfaces and as ballast for ships.

The chemical processes that control the environmental mobility of uranium (speciation, dissolution, precipitation⁵, and sorption) are essentially identical for natural or anthropogenic uranium. In any environmental system, the particular forms of uranium present (e.g., dissolved, sorbed, or precipitated) will be the same under the same environmental conditions whether the uranium is composed entirely of natural isotopic composition, entirely anthropogenic composition, or any ratio between. The concentration of uranium present at a given location and time in surface water or groundwater is not related to the isotopic makeup of the uranium source(s).⁶

Anthropogenic Uranium at RFS

The work conducted historically at RFS involved anthropogenic uranium, in either “enriched” or “depleted” forms, which was received from other facilities in the DOE complex. The work conducted at RFS did not involve uranium from natural sources. Because of the high

⁵ With respect to chemical processes, “chemical precipitation” means the change of uranium species from soluble and dissolved (most mobile forms) to insoluble and solid (less mobile forms). It does not refer to atmospheric deposition of rain or snowfall.

⁶ This is a “rule of thumb” that is applicable to nearly all chemical processes. However, variations have been measured in natural uranium for the mass ratios of U-238/U-235 (ratios of 137.792 to 137.961, respectively) and U-235/U-234 (ratios of 83.63 to 164.17, respectively), that can be attributed to relatively minor geochemical processes (e.g., alpha-recoil damage to the crystalline lattice of uranium-containing minerals that enables isotope-selective leaching) and very small changes in the kinetics of chemical and biological reactions due to mass differences of the isotopes that result in small-but-measurable mass fractionation. None of the natural mass fractionation processes significantly affect the observed mobility of the different uranium isotopes at RFS (Brennecke, 2011; Buerger, 2009).

concentration of uranium naturally present at RFS, environmental media at the site (i.e., soil, surface water, groundwater, etc.), can have uranium from both natural and anthropogenic sources.

Determining whether uranium is from natural or anthropogenic sources, or a combination of both, can be accomplished by analyzing the composition of uranium isotopes in samples using specialized analytical techniques, as discussed in Section 3.5.

1.4 Uranium Regulations for Surface Water in Colorado

1.4.1 EPA and Colorado - Uranium MCL for Drinking Water

The EPA established drinking water standards for several radioactive contaminants as part of the Radionuclides Rule in order to protect public health. This involved the following major rulemakings:

- 1976 - The original Radionuclides Rule was promulgated to establish the current MCL⁷ for combined radium and gross alpha particle activity (uranium was not regulated then).
- 2003 - The Revised Rule took effect in December 2003 and, among other changes, included creation of the 30 µg/L MCL value for uranium. (Note: The basis of the 30 µg/L MCL is discussed below under the Statewide Stream Standards).

The CDPHE Water Quality Control Division (WQCD) adopted the 30 µg/L MCL for uranium as part of the Colorado Primary Drinking Water Regulations (CPDWRs) (CDPHE, 2009).

1.4.2 Statewide Stream Standard

The statewide stream standard with respect to uranium in surface water is as follows:

⁷ MCL is defined by the Safe Drinking Water Act as “the maximum permissible level of a contaminant in water which is delivered to any user of a public water system.”

- CDPHE Water Quality Control Commission, Regulation 31, Basic Standards and Methodologies for Surface Water (5 CCR 1002-31) (Regulation 31) (CDPHE, 2013).
 - Table III of Regulation 31 establishes a statewide Domestic Water Supply standard for uranium of 16.8 µg/L - 30 µg/L (30-day standard). The effective date for this hyphenated standard was January 1, 2011.
 - The 16.8 µg/L lower limit of the statewide stream standard for uranium is based on protection of human health from chemical toxicity. The 16.8 µg/L value is used in the absence of any toxicological data and is calculated using Equation 1-1 for non-carcinogens per WQCC Policy 96-2 (Human Health-Based Water Quality Criteria and Standards)⁸. Equation 1-1 (see footnote below) is identical to the equation used by EPA for calculating Maximum Contaminant Level Goals (MCLGs) for chemical toxicity and is based on a daily drinking water consumption rate of 2 liters per day (CDPHE, 2012; EPA, 2011). Because the acceptable risk level for chemical toxicity is not based on an incremental lifetime risk factor, MCLGs are calculated by an equation that is not related to a lifetime dose (40 CFR Part 141).
 - The 30 µg/L upper limit of the statewide stream standard for uranium is the EPA drinking water MCL that was adopted by CDPHE. The MCL value has been determined to be an acceptable concentration in public drinking water supplies, taking treatability and laboratory detection limits into account. The 30 µg/L value is based on an additional lifetime cancer risk of 10⁻⁴ (meaning the normal cancer mortality risk would increase from

⁸ WQCC Policy 96-2, Equation 1-1: $MCLG (\mu\text{g/L}) = (\text{RfD} \times 70 \times 1000 \mu\text{g/mg} \times \text{RSC}) / (2 \times \text{UF})$, where: RfD (Reference Dose) = 0.0006 mg/kg-day; 70 = weight of avg. adult (kg); RSC(Relative Source Contribution factor) = 0.8; 2 = daily drinking water consumption (L/day); UF (Uncertainty Factor) = 1.0).

20 percent to 20.0001 percent [20 plus 10^{-4}]) for a population consuming drinking water that contains 30 µg/L of uranium, based on a consumption rate of two liters of water per day for 70 years (CDPHE, 2008).

- Implementation of the 16.8 µg/L - 30 µg/L hyphenated standard is addressed in Table III of Regulation 31, which has the following note (Note 13) with respect to a standard with a range of values:

Whenever a range of standards is listed and referenced to this footnote, the first number in the range is a strictly health-based value, based on the Commission's established methodology for human health-based standards. The second number in the range is a maximum contaminant level, established under the federal Safe Drinking Water Act that has been determined to be an acceptable level of this chemical in public water supplies, taking treatability and laboratory detection limits into account. Control requirements, such as discharge permit effluent limitations, shall be established using the first number in the range as the ambient water quality target, provided that no effluent limitation shall require an "end-of-pipe" discharge level more restrictive than the second number in the range. Water bodies will be considered in attainment of this standard, and not included on the Section 303(d) List, so long as the existing ambient quality does not exceed the second number in the range. (Note: emphasis added with underlined text).

- Table III has the following note (Note 17) with respect to uranium:

"When applying the table value standards for uranium to individual segments, the Commission shall consider the need to maintain radioactive materials at the lowest practical level as required by Section 31.11(2) of the Basic Standards regulation."

1.4.3 RFS Site-Specific Uranium Stream Standard

Within the South Platte River Basin, where RFS is located, the following regulations apply:

- CDPHE Water Quality Control Commission, Regulation 38, Classifications and Numeric Standards – South Platte River Basin, Laramie River Basin, Republican River Basin, Smoky Hill River Basin (5 CCR 1002-38) (Regulation 38) (CDPHE, 2013).
 - Regulation 38 establishes a site-specific uranium standard of 16.8 µg/L for Segments 4a and 5 on Woman Creek and Segments 4a, 4b and 5 on Walnut Creek (see Appendix A, Figure A.2). As discussed under the “Statewide Stream Standard” text above, 16.8 µg/L is the lower end of the 16.8 µg/L – 30 µg/L range for the statewide stream standard for uranium in a drinking water supply.
- Rocky Flats Legacy Management Agreement (RFLMA) (DOE, 2007)
 - At RFS, compliance with the 16.8 µg/L stream standard in Walnut Creek is monitored, in accordance with RFLMA, at the Walnut Creek Point-of Compliance (WALPOC) monitoring location. Per RFLMA, at WALPOC, a 30-day average concentration of uranium that exceeds 16.8 µg/L defines a reportable condition; a 12-month rolling average concentration of uranium that exceeds 16.8 µg/L defines a reportable condition and triggers an evaluation of compliance with the remedy performance standard.

1.5 Questions Addressed by Current Study

The following questions regarding uranium transport in surface water at the RFS, identified by SN3, are addressed in this report:

- 1) How do concentrations of natural uranium observed globally and throughout Colorado compare with the uranium concentrations observed in the RFS Walnut Creek drainages?

- 2) Other than predictable and measurable variations in surface flow (such as the diluting effects of storm events and associated runoff and the concentrating effects of low surface water flow and an increased proportion of baseflow/groundwater recharge), what are the primary mechanisms by which concentrations of uranium in surface water may significantly increase and decrease?
- 3) Are previously unrecognized anthropogenic uranium sources suggested by the data?

1.6 Report Format

The questions addressed by this study (i.e., questions 1 through 3 above) have some overlap in terms of their subject matter. To avoid redundancy in the responses to the questions, rather than providing separate responses to each individual question, this report is organized into sections which collectively address the different questions as outlined in Table 1:

Table 1. Summary of Report Sections and Study Questions Addressed

Report Section	Section Title	Study Question(s) Addressed
1.0	Introduction and Background Information	1
2.0	Chemical and Site-specific Factors that Govern Uranium Concentration and Transport in Aqueous Environments. This includes: <ul style="list-style-type: none"> • General controls (Section 2.1) • RFS-specific conditions (Section 2.2) 	2
3.0	RFS Data Analysis This includes: <ul style="list-style-type: none"> • Spatial and temporal variability of uranium and nitrate (Section 3.3) • Determination of anthropogenic uranium (Section 3.5) 	3

Evaluation of Water Quality Variability for Uranium and
Other Selected Parameters in Walnut Creek at the Rocky Flats Site

Report Section	Section Title	Study Question(s) Addressed
4.0	Site Operations - Effects on Uranium Concentrations This includes: <ul style="list-style-type: none">• Solar Ponds Plume Treatment System (Section 4.1)• Ponds A-4 and B-5 (Section 4.2)	2
5.0	Summary	All questions

2.0 CHEMICAL AND SITE-SPECIFIC FACTORS THAT GOVERN URANIUM CONCENTRATION AND TRANSPORT IN AQUEOUS ENVIRONMENTS

This section provides an overview of the primary factors that govern the concentration and transport of uranium in aqueous environments. Uranium concentrations and mobility depend on the relative proportions of uranium that are associated with dissolved and solid species; under a given range of stable geochemical conditions, dissolved species travel with surface and groundwater flow and are the most mobile, while solid species, precipitated and sorbed, are less mobile and move only when surface sediments and subsurface colloids are carried by water flow. In addition to water movement, chemical factors that influence the dissolved/solid equilibria (i.e., chemical speciation) of uranium also have important roles in determining the distribution and transport of uranium at any given site. The aqueous geochemistry is the same whether the uranium is from natural or anthropogenic sources.

The following two sections discuss the aqueous chemistry of uranium: Section 2.1 presents basic chemical principles that are generally applicable to all sites and Section 2.2 addresses chemical and environmental factors specific to RFS.

2.1 General Uranium Chemistry

2.1.1 Chemical Processes

Uranium concentration and mobility in aqueous environments, at RFS and elsewhere, are mainly governed by four chemical processes: precipitation, complexation, sorption, and colloid formation (Silva and Nitsche, 1995):

- Precipitation/dissolution reactions are influenced by uranium concentrations, redox potential, pH, complexation reactions and evapotranspiration. Evapotranspiration can, in some conditions, cause the precipitation of uranium minerals near the top of the water table which later may be mobilized via dissolution when the water table rises.

- Complexation reactions occur in aerobic groundwater and surface water between the highly soluble uranyl cation $U(VI)O_2^{2+}$ and several complexing cations and anions, mainly calcium, magnesium, carbonate, and hydroxide. These complexation reactions influence the amount of uranium that is available for other reactions (sorption and/or precipitation). The calcium/magnesium/carbonate complexes are the most important because they greatly increase the solubility of uranium minerals and decrease the extent of sorption to sediments, which act to increase uranium mobility.
- Sorption/desorption reactions are site- and time-specific, depending on how the water quality is influenced by environmental conditions. Water quality parameters that are important for understanding these influences include pH, dissolved oxygen, redox potential, alkalinity, hardness, nitrate, temperature, uranium concentrations, and total dissolved solids. Sorption/desorption reactions mainly involve sorption of soluble U(VI) species to solid sediments, mainly Fe(III) oxyhydroxides and organic matter (e.g., wetland humus), potentially followed by desorption initiated by changes in redox potential, pH, and/or a decrease in water-phase uranium concentrations. (Note: Redox measurements were taken in surface water and sediments for this study, in conjunction with measurements of dissolved oxygen, but the redox data were subsequently rendered invalid because of issues related to the measurement probe. New measurements of redox potential are planned for the future).
- Colloid formation – Colloids (very small [sub-micron sized] particles that can have sorbed or precipitated uranium) can both facilitate and impede the transport of highly insoluble compounds, facilitating transport in anoxic aquifers and surface waters and impeding transport when oxic conditions exist and the uranium can be readily soluble (Zaenker, et al., 2007).

Subsequent transport of uranium depends on site-specific environmental and climate conditions that determine surface and groundwater flow characteristics. The three chemical factors of redox potential, pH, and water quality (i.e., concentration and nature of dissolved species), discussed

below, act in concert as the major determinants of which aqueous chemical species are formed with uranium and their chemical states (dissolved, solid, or sorbed).

2.1.2 Redox Potential

Although any existing system depends on the three chemical factors described above, redox potential is often regarded as the first to consider when evaluating uranium behavior. Redox potential determines whether uranium species occur predominantly in the sparingly soluble reduced U(IV) state or the more highly soluble oxidized U(VI) state, as outlined below:

- At negative redox potentials (reducing conditions):
 - U(IV) forms relatively insoluble and less mobile uranium species such as solid uraninite (UO_2).
 - Sorption of both U(IV) and U(VI) species to soil solids is enhanced.
- At positive redox potentials (oxidizing conditions):
 - U(VI) forms more soluble and mobile uranium species such as uranyl ion, UO_2^{2+} , and its complexes.
 - In calcium-carbonate-type waters, such as those which predominate at RFS, the most important complexes are the strong uranyl-carbonate and uranyl-calcium-carbonate complexes [UO_2CO_3 , $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$, $\text{CaUO}_2(\text{CO}_3)_3^{2-}$, and $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$]; these complexes, especially the uranyl-calcium-carbonate complexes, can inhibit sorption of U(VI) to solids, thereby increasing the uranium's mobility.

Effects of Dissolved Oxygen on Redox Potential

In surface water, the redox potential is chiefly determined by the chemical and biological oxygen demands. Oxygen-saturated water tends to have positive redox potentials and oxygen-depleted water tends to have negative redox potentials. Thus, highly oxygenated surface waters such as shallow streams and turbulent waters that rapidly equilibrate with atmospheric oxygen, and which contain only small amounts of oxygen-demand from carbonaceous matter, tend to contain mobile U(VI) species. Oxygen-depleted surface waters that are slow moving or deeper with higher oxygen-demand (e.g., wetlands) tend to contain less-mobile U(IV) species (Owen, 1992).

In the subsurface, where oxygen equilibration with the atmosphere is greatly retarded, the oxygen content of groundwater depends on how rapidly groundwater is recharged by oxygenated surface water, compared to how rapidly bacteria, feeding on subsurface organic matter, can deplete oxygen levels. Hem (1985) notes uranium concentrations greater than 1000 µg/L occurring in natural water associated with uranium ore deposits and describes a 90-meter deep well in Helsinki, Finland with a uranium concentration near 15,000 µg/L was measured.

Redox Reversibility

While the expectation that highly oxygenated waters will have positive redox potentials and support mainly soluble and mobile U(VI) species is generally reliable, the converse expectation, that oxygen-depleted waters will contain mostly low solubility U(IV) species, cannot always be assumed. Because redox reactions are reversible, U(VI) species that have been reduced to low solubility U(IV) species can be re-oxidized back again to soluble U(VI) species. In water, sediments, and soils with negative redox potentials, oxidants other than oxygen such as nitrate, can restore and maintain significant levels of soluble U(VI) species.

Several studies have shown that the rate of oxidation of U(IV) to U(VI) by nitrate in oxygen-depleted waters can be enhanced greatly when mediated by the commonly occurring bacterium *Thiobacillus denitrificans* (Beller, 2005; Pokharel, 2013). The microbially-mediated oxidation by

nitrate can be so effective at mobilizing uranium that it has been known to hinder efforts to immobilize uranium at sites undergoing remediation, such as in cases where a treatment system or constructed wetland is created in an attempt at reductive immobilization of U(IV) species (Wei-Min Wu, et al., 2010).

The importance of redox reversibility can be illustrated by the following feasible example:

Oxygenated stream water carrying dissolved U(VI) species enters a wetland zone where oxygen is depleted and the redox potential is negative, facilitating the reduction of U(VI) to U(IV) and immobilizing much of the uranium in the wetland as precipitated and sorbed U(IV) species. Then, a new oxidant such as nitrate is introduced to the wetland, which re-oxidizes U(IV) back to mobile U(VI), changing the wetland from a uranium sink to a uranium source, a condition that will continue until the nitrate (and any other non-oxygen oxidant) is depleted.

2.1.3 pH and Water Quality

In addition to the redox potential, the behavior of uranium depends on pH and other water quality properties such as dissolved oxygen, the presence of other oxidizing agents such as nitrate, and complexing agents.

Solubility, sorption, complexation and colloid formation are all sensitive to the water pH. In general, uranium solubility (in pure water where only hydroxyl complexation can occur) decreases rapidly as pH increases from around pH 2 ($U_{aq} = \sim 2.5$ g/L) to pH 4 ($U_{aq} = \sim 10^{-6}$ g/L), remaining fairly constant to pH 8 and then increasing in solubility again to pH 10 ($U_{aq} = \sim 10^{-4}$ g/L). However, in calcium carbonate waters, where strong and highly soluble U(VI) carbonate complexes species become dominant, higher solubilities ($\sim 10^{-4}$ g/L) occur at a pH value as low as 5 and remain high beyond pH 10 (depending on carbonate concentration) (Langmuir, 1997).

The carbonate complexes are also important because, in addition to facilitating U(IV) oxidation to U(VI) and greatly increasing the solubility of uranium minerals, they limit the extent of

uranium sorption to sediments in oxidized waters, further increasing uranium mobility (Langmuir, 1997).

2.1.4 Theoretical Principles: Natural Versus Anthropogenic Uranium

The chemical properties of natural and anthropogenic uranium with respect to speciation, dissolution, precipitation, and sorption are essentially identical (Weiner, 2013). In any environmental system, the particular forms of uranium present (e.g., dissolved, sorbed, or precipitated) will be the same under the same environmental conditions whether the isotopic makeup of the uranium is 100 percent natural, 100 percent anthropogenic, or any ratio between. The concentration of total dissolved uranium that is present at a given location and time in a stream is not related to the isotopic makeup of the uranium sources.

However, the proportion of natural versus anthropogenic uranium in a water sample from a stream depends on the proportions of natural and anthropogenic uranium in the different contributing sources and the relative contributions of these sources to the sample collected. This principal applies whether the system is in theoretical equilibrium or, as for any real environment such as RFS, in dynamic disequilibrium.

Determining whether uranium at a particular location is from natural or anthropogenic sources can be accomplished by analyzing the composition of the uranium isotopes in the sample, as discussed in Section 3.5.

2.2 Conditions Specific to RFS

Many factors, in addition to the relative proportions of surface runoff and groundwater to stream channel flow noted in Question 1, influence the concentrations and transport of uranium in surface water at RFS. Numerous site-specific environmental conditions and chemical properties of water and sediments affect uranium chemistry and influence uranium distribution and transport. These environmental conditions and chemical properties must be considered singly

and in total when addressing the question of which chemical and physical mechanisms have an observable effect on uranium concentrations in surface water at RFS.

Important site-specific factors at RFS that control uranium concentrations and transport can be generally grouped into three categories,

1. Uranium sources (mass, form, and location of natural and anthropogenic);
2. Environmental conditions (e.g., rainfall events, surface flow, groundwater elevation and flow, residence time in ponds, wetland area effects, streambed sediment composition, and bacterial populations [i.e., sulfate- and nitrate-reducing bacteria]);
3. Chemical properties (e.g., measured values of chemical and mineral composition, pH, dissolved oxygen and redox potential, etc.) of surface water, groundwater, soils, and stream-bed sediments. Most site-specific chemical properties at RFS are discussed in detail in the RFS Data Analysis section (Section 3.0) and are not repeated here, where only a few additional observations concerning nitrate and pH are added.

These topics are discussed below:

Uranium sources

The uranium sources of interest at RFS are those that contribute uranium, in dissolved or particulate form, from the source area(s) to WALPOC. These include:

1. Ambient natural uranium from surface and subsurface minerals and stream channel sediments which is transported as a dissolved species or suspended sediments (as precipitated and sorbed U) and transported in surface waters that ultimately flow through WALPOC. (Note: as discussed previously, natural uranium is ubiquitous in the environment).

2. Anthropogenic uranium in stream channel sediments which is transported as dissolved species or suspended sediments by surface waters that ultimately flow through WALPOC.
3. Anthropogenic uranium in subsurface sources which is mobilized by groundwater and transported as a dissolved species before flowing to the surface and flowing to WALPOC in a drainage channel.

Environmental Conditions

The availability and influence of the different uranium sources depends strongly on environmental conditions, which can vary seasonally (with randomly unique events) and by physical features of a site, both natural and engineered, (e.g., channels, wetland zones, dams, groundwater treatment systems, etc.). These conditions affect the transport of uranium at any site. Important site-specific environmental conditions at RFS include the following:

- Precipitation rates and volumes (for both rainfall and snowmelt), which influence the flows and volumes of groundwater and surface waters, which in turn affect the movement of contaminants from sources into streams, as well as the chemistry of waters on the surface and in the subsurface.
- The fraction of groundwater flow, relative to surface flow, that contributes to channel flow in North and South Walnut Creeks is seasonally dependent, with occasional random extremes of wet or dry periods. Groundwater normally contains higher relative concentrations of uranium than surface water.
- Changes in groundwater elevation, which may bring groundwater into contact with additional uranium-containing material in the subsurface.
- Movement of sediments carrying precipitated and sorbed uranium to downstream stream segments depends on flow rates and stream channel characteristics.
- Environmental conditions which influence the chemical properties of surface water and groundwater, including:

- The volume of and rate of precipitation, which can influence chemical conditions of waters at the site. For example, the prolonged, heavy rainfall event that occurred at RFS in September 2013, from which the recharge rate appears to have dominated subsurface bacterial activity, resulted in a prolonged condition of highly oxygenated groundwater over the entire site (the effects of this storm are discussed in the Data Analysis section [Section 3.0]).
- Physical features such as wetlands, mineral and organic soil content, subsurface microbial activity, etc. (Owen, 1992).

Chemical properties of surface water and groundwater at RFS

In waters saturated with oxygen and at positive redox potentials, oxygen is always the strongest and most important oxidant. However, in waters with relatively low concentrations of dissolved oxygen and negative redox potentials, nitrate may become an important oxidizing agent. Under these conditions, nitrate can oxidize slightly soluble U(IV) species to highly soluble U(VI) species, thereby increasing their mobility.

In some areas at RFS, one of the most important chemical characteristics of the surface water and groundwater, in terms of uranium mobility, is the presence of nitrate. Although the background concentration of nitrate at RFS is relatively low, as measured in South Walnut Creek, conditions are different in North Walnut Creek where nitrate concentrations are substantially higher, with measurements as high as 140 mg/L at monitoring location GS13 (see Figure 1) as recently as December 2012. The elevated nitrate concentrations in North Walnut Creek are attributed to sources in the area of the former Solar Evaporation Ponds which impact North Walnut Creek water quality upstream from GS13. The presence of high levels of nitrate in oxygen-depleted groundwater and surface waters at RFS can facilitate the microbially-mediated oxidation of immobilized U(IV) species to highly mobile U(VI) dissolved species.

3.0 RFS DATA ANALYSIS

3.1 Meteorological Conditions

Water quality data collected during periods of both routine and extreme meteorological conditions are desirable to account for the variable effects that precipitation can have on water quality in the system being evaluated. The types of meteorological conditions represented in the water quality data evaluated for this report include the following:

- “Normal” Conditions – The average annual precipitation depth recorded at RFS since 1993 has been 12.25 inches per year (based on calendar year records). The rainfall depths in 2010 (11.64 inches) and 2011 (13.12 inches) are both representative of “normal” precipitation conditions. Data from both years were used in the analyses for this study.
- “Wet” Conditions – The September 2013 storm event, which delivered approximately 6.5 inches of rainfall over approximately 7 days, had a prolonged effect on not only the flow rates measured in the stream channels, but also on the environmental chemistry of the site, which directly affected uranium concentrations in surface water, as described in previous sections of the report. The extent of the “lag time” associated with the effects of the September 2013 storm is still being determined. To visualize the effect of the September 2013 rainfall on water volumes measured at stream gages across the site, see Figures F.1 and F.6 [in Appendix F, for North Walnut Creek] and Figures G.1 and G.6 [in Appendix G, for South Walnut Creek]).

The 7.67 inches of rainfall recorded in September 2013 was the wettest single month on record. The 15.75 inches of rainfall occurring during 2013 was the third wettest year recorded by site rain gages since 1993. Only 1995 (16.49 inches) and 2004 (16.91 inches) had more precipitation. Based on these data, it can be reasonably stated that data for an extreme precipitation event have been collected and utilized in this analysis.

- “Dry” Conditions – The recorded precipitation depth during 2012 was 7.21 inches, which is the driest year recorded by site rain gages since 1993. The 0.00 inches of precipitation recorded in March 2012 has been equaled only one other month (December 2002), in terms of dry conditions, during the 21 year precipitation record. While more extreme drought conditions can, and likely will, occur at the site, the 2012 data used in this study are representative of water quality at the site during “dry” conditions.

3.2 Data Collection Methods

Water data presented and discussed in this report were collected by RFS personnel. Different types of sample collection methods are used at different locations and for different analytes. A general summary of the sample locations and respective data collection methods for data presented and discussed in this report is presented in Table 2 (Refer to Appendix A, Figure A.1 for sample locations).

Table 2. Surface water data locations and data collection methods

Drainage	Sample Location	Uranium Sample Method		NO ₃ + NO ₂ (All Grab Samples)	Other Parameters
		Flow-Paced	Grab		
North Walnut Creek	SW093	Yes	Yes	Yes	Yes ²
	SPIN	No	Yes	Yes	Yes ²
	SPOUT	No	Yes	Yes	Yes ²
	SPPDG	No	Yes	No	Yes ²
	GS13	Yes	Yes	Yes	Yes ²
	GS12 or A3EFF	Yes	Yes	Yes	Yes ²
	GS11 (Pond A4 Outfall)	Yes	No	Yes	Yes ²
	GEOFC3INF	No	No	No	Yes ¹
	GEOFC3EFF	No	No	No	Yes ¹
	GEOA1INF	No	No	No	Yes ¹
	A1EFF	No	Yes	No	Yes ²
	GEOA1	No	No	No	Yes ¹
	A2EFF	No	Yes	No	Yes ²
	GEOA3INF	No	No	No	Yes ¹
A3EFF	No	Yes	No	Yes ²	

Evaluation of Water Quality Variability for Uranium and
Other Selected Parameters in Walnut Creek at the Rocky Flats Site

Drainage	Sample Location	Uranium Sample Method		NO ₃ + NO ₂ (All Grab Samples)	Other Parameters
		Flow-Paced	Grab		
North Walnut Creek (cont'd)	GEOA3EFF	No	No	No	Yes ¹
	A4POND	No	No	No	Yes ²
South Walnut Creek	GS10	Yes	Yes	No	Yes ²
	FC4750	No	Yes	No	Yes ²
	FC4991	No	Yes	No	Yes ²
	FC4EFF	No	No	No	Yes ²
	SEEP995A	No	No	No	Yes ²
	B3OUTFLOW	No	Yes	No	Yes ²
	POM2	No	No	No	Yes ²
	B5INFLOW	Yes	Yes	Yes	Yes ²
	B5POND	No	Yes	No	Yes ²
	GS08 (Pond B-5 Outfall)	Yes	No	No	Yes ²
	GEOB1INF	No	No	No	Yes ¹
	GEOB4INF	No	No	No	Yes ¹
	GEOB5INF	No	No	No	Yes ¹
Walnut Creek	WALPOC	Yes	Yes	Yes	Yes ²

Notes:

1) Other parameters include: pH, dissolved oxygen, temperature, SO₄, Fe, H₂S, NO₃ and NO₂.

2) Other parameters include isotopic analyses conducted at Lawrence Berkeley National Laboratory.

3.2.1 Uranium Data

Two types of sample collection methods are used for surface water uranium data discussed in this report:

1. Continuous flow-paced composite samples - Automated sampling units collect individual grab samples as a function of flow rate at the monitoring location. The individual samples are combined into a flow-weighted composite sample that is representative of the water quality over the entire sample collection period, which is variable and typically ranges from a few days to several months, varying in large part to the amount of stream flow that occurs. At the same locations where automated composite samples are collected, continuous flow measurement is also conducted. The uranium concentration

and stream flow volume data can be combined to estimate the uranium load at a given location for a specific time period.

2. Grab samples – Grab samples for uranium are collected by manually filling a sample bottle at a specific, documented time. In some cases grab samples are routine biweekly samples and in other cases they may not be collected routinely.

Note: Analyses of the isotopic composition of uranium samples, discussed in Section 3.5, are from selected samples collected by both continuous flow-paced and grab sample methodologies. The routine uranium analysis is for total (not isotopic) uranium.

3.2.2 Nitrate Data

Nitrate sample results, as discussed in this report, refer to results for nitrate + nitrite as nitrogen ($\text{NO}_3 + \text{NO}_2$ as N). Due to sample hold-time and preservation requirements, these samples are all collected using a grab sample methodology; none are collected using a flow-paced composite approach. Consequently, nitrate grab samples often do not reflect the dilution effects of periods with high flow rates, and the potential for nitrate results to be biased high is typically higher than for samples collected using a continuous flow-paced method. Sampling personnel are not always able to be on-site to collect a grab sample when flow rates are high, in contrast to automated sampling equipment that can capture samples during runoff events at any time of the day or night. Calculated average concentrations, loads, etc. also may be biased high. As a result, any comparisons of the characteristics of uranium data and nitrate data must take this into consideration.

3.2.3 Other Parameters

Other water quality parameters, in addition to uranium and nitrate, are also measured at some locations and are evaluated in this report. These other parameters include: pH, dissolved oxygen, temperature, SO_4 , Fe, H_2S , NO_3 and NO_2 . All are collected via either in-situ measurement or by grab sample.

3.3 Spatial and Temporal Variability

Analysis of the spatial and temporal variability of RFS surface water data in North and South Walnut Creeks are presented for uranium (Section 3.3.1) and nitrate (Section 3.3.2).

3.3.1 Uranium Concentrations and Loads

Surface water uranium data, including mass balance analyses, were evaluated to assess their spatial variability in order to identify potential sources and/or sinks of uranium in the North and South Walnut Creek drainages. In addition, temporal variability was evaluated to assess whether seasonal or other temporal trends could be identified. Surface water monitoring data were plotted to compare uranium concentrations and uranium loads at monitoring locations in both drainages. Data plots were developed for all monitoring locations to facilitate comparisons between locations for the following types of data:

- Uranium concentrations (monthly flow-weighted average and maximum values [$\mu\text{g/L}$])
- Water volume flow (liters per month)
- Uranium loads (average monthly values [$\mu\text{g/month}$])

Data from January 1997 through March 2014 (and later at some locations) are included on each of the plots (see Appendix B, Figures B.1 through B.7 for North Walnut Creek and Appendix C, Figures C.1 through C.3 for South Walnut Creek), except for locations where data are not available back to 1997 (for example, WALPOC was installed as a monitoring location in 2011). The uranium concentration plots also include the following uranium water quality standards for reference:

- The site-specific uranium standard that applied through March 2009 (10 pCi/L [equivalent to approximately 14.9 $\mu\text{g/L}$]).

- The site-specific uranium standard that has applied from April 2009 to the present (16.8 µg/L), which is monitored for regulatory compliance at WALPOC, based on 30-day and 12-month rolling average uranium concentrations.
- The uranium MCL for drinking water (30 µg/L).

3.3.1.1 North Walnut Creek

For North Walnut Creek, data plots of surface water uranium concentration, water volume and uranium loads are presented in Appendices B and F for locations SW093, SPIN (Solar Ponds Plume Treatment System [SPPTS] influent monitoring location), SPOUT (SPPTS effluent monitoring location), GS13, GS12 (or A3EFF), GS11 (Pond A-4 outfall), and WALPOC. A summary of the different data plots developed for this analysis is provided in Table 3.

Table 3. Description of data plots and tables – Uranium in North Walnut Creek (Appendices B and F)

Data plot description	Figure(s) and Table(s) in Appendices B and F
SW093, SPIN, SPOUT, GS13, GS12 (or A3EFF), GS11 and WALPOC – Monthly average and maximum uranium concentrations, water volume, and loads, by location	Figures B.1 – B.7 (Note that all figures use same scale for comparison purposes)
Annual uranium loads in North Walnut Creek, by location (2010 – 2013)	Figure B.8
Monthly uranium loads in North Walnut Creek, by location (2010 – 2014)	Figures B.9 – B.14
Solar Ponds Plume Treatment System performance, by month (2010 – March 2014)	Figure B.15
Average uranium concentrations, by location, North Walnut Creek (1/27/2010 – 4/30/2014) (period with available data for all locations)	Figure B.16
WALPOC uranium concentrations, September 2011 – May 2014	Figure B.17
Uranium loads in North Walnut Creek	Table B.1

Data plot description	Figure(s) and Table(s) in Appendices B and F
Water volumes at North Walnut Creek monitoring locations (annual totals for 2010 - 2013 and monthly totals for 2010 - 2014), for comparison purposes with uranium load and concentration plots.	Figures F.1 – F.7 and Table F.1

Review of the uranium concentration and loading data plots listed in Table 3 leads to the following observations regarding North Walnut Creek and WALPOC:

Uranium Concentrations in North Walnut Creek and at WALPOC

- Average uranium concentrations at monitoring locations along North Walnut Creek (for the period from 1/27/2010 to 4/30/2014) are summarized on Figure B.16. (Note: The average uranium concentrations shown on Figure B.16 provide a general reference for the spatial variability of uranium concentrations along North Walnut Creek, but do not distinguish between different specific site conditions, such as different operating protocols for Pond A-4 or conditions following the September 2013 flood event, which are discussed later in this report.)
- Along North Walnut Creek, uranium concentrations measured at individual monitoring locations are highly variable spatially from upstream monitoring station SW093 (Figure B.1) down to station GS11 at the Pond A-4 outfall (Figure B.6), indicating the presence of significant uranium source(s) and sink(s) as average uranium concentrations increase and then decrease going downstream along this channel reach. (Note: the uranium concentrations on Figures B.1 through B.6 are plotted on common scales to facilitate comparisons between locations.)
- In terms of temporal variability, observed uranium concentrations indicate seasonal patterns are not as distinct in North Walnut Creek (and at WALPOC) as in South Walnut Creek (particularly at GS10). Specific observations include the following:

- At SW093, uranium concentrations are generally well below 16.8 µg/L (except for one sample (flow-composited) collected from November 2009 to January 2010) (Figure B.1). In contrast, farther downstream, station GS13 samples are routinely above 16.8 µg/L (Figure B.4).
- At GS13, uranium concentrations are higher than at upstream location SW093 and frequently are above 16.8 µg/L, with a limited number of individual sample results over 60 µg/L (see Figure B.4). In addition, uranium concentrations at GS13 vary significantly over time, though a clear seasonal pattern or a relationship to concentrations measured at SPOUT (Figure B.3.a) are not apparent, recognizing that the uranium load (and, therefore, effect) from SPOUT is relatively minor compared to the load measured at GS13. Regarding discharges from SPOUT, it is noted that testing and development of improved long-term treatment methods for the SPPTS is ongoing. The focus on the SPPTS has been to identify better treatment approaches that are effective as well as sustainable (see footnote 8 in Section 3.3.2.1).
- At GS11 (Pond A-4 outfall), measured uranium concentrations for individual flow-paced composite samples increased significantly in 2012, 2013, and 2014 (up to 5/20/14), averaging 15.2 µg/L over that period with a maximum result of 29 µg/L. In contrast, sample results from March 2007 through 2011 had an average uranium concentration over that period of 7.4 µg/L and a maximum individual sample result of 13.5 µg/L (see Figure B.6).
 - The increased uranium concentrations measured at GS11 (Pond A-4 outfall) correspond with the transition from batch-release mode to flow-through mode in Pond A-4 in September 2011. During the time period when uranium concentrations were increasing in Pond A-4 discharges (from 2012 to end of available data set, in May 2014), the uranium concentrations at locations upstream from Pond A-4, such as SW093 and

GS13, were at or below their normal range observed after site closure in 2005 (see Figure B.1 [SW093] and Figure B.4 [GS13]), further suggesting that the increased uranium concentrations in A-4 discharges starting in 2012 and continuing since then are not attributed to a new upstream uranium source, but instead are likely related to changing the pond operating protocol from batch mode to flow-through mode. The increased residence time of water during batch mode operations in the terminal pond allowed increased chemical precipitation of low solubility uranium species and increased sorption of uranium to pond sediments in deeper pond water containing low dissolved oxygen.

- At WALPOC, measured uranium concentrations were below the 16.8 µg/L standard until the September 2013 flood event, after which multiple samples were measured above the standard (see Figure B.17). Not until May 2014, approximately eight months after the September 2013 flood event, did sample results return to concentrations below the 16.8 µg/L standard (three consecutive sample results at WALPOC, the most recent data analyzed for this study, had concentrations below 16 µg/L [sample dates from 5/12/14 through 5/21/14]).

Uranium Loads in North Walnut Creek and at WALPOC

- The channel reach between monitoring locations SW093 and GS13 has a substantial gain in uranium load (see Figure 1):
 - The uranium load measured at GS13 is approximately two times greater than the uranium load measured at upstream monitoring location SW093, based on total loads measured at both locations from January 2010 through March 2014 (Figures B.9 through B.11). (Note: If the September 2013 uranium loads are excluded from this analysis, because of the extreme conditions that month, the uranium load at GS13 is still approximately two times greater than at SW093).

- The increased uranium load observed at GS13 cannot be attributed solely to a gain in water volume between stations SW093 and GS13. Although the stream frequently has a slight gain in water volume in that reach (see Figures B.1 through B.7), the increased water volume at GS13 is proportionately substantially less than the increased uranium load in the same reach, indicating: 1) the inflow of water between SW093 and GS13 has a higher uranium concentration than the water flowing in North Walnut Creek (e.g., subsurface flows that are not collected by the SPPTS) and/or 2) there is a uranium source between SW093 and GS13 that is mobilized and transported to GS13 (for example, channel sediments or wetland area(s), or both, with elevated concentrations of uranium that increase the uranium concentration in surface water, and/or 3) groundwater and/or periodic surface runoff enters North Walnut Creek from the north side of the channel. (Note. extensive historic characterization did not identify anthropogenic sources of uranium on the north side of North Walnut Creek; however, natural uranium from groundwater or surface runoff could potentially cause this increased uranium load).
- The increased load observed at GS13 is temporally consistent:
 - When uranium load data are evaluated on an annual basis, the increased load at GS13, relative to SW093, occurs every year, from 2010 through 2013 (see Figure B.8).
 - When uranium load data are evaluated on a more frequent time step (i.e., monthly total loads) the increased load at GS13 still occurs nearly every month from 2010 through the present, with few exceptions (see Figures B.9 to B.14), indicating that the gaining load at GS13 is not seasonally dependent.

- Effluent from the SPPTS monitored at SPOUT (located between SW093 and GS13) (see Figure 1) contributes only a minor fraction of the increased uranium load observed at GS13.
 - The SPOUT effluent, which is located “off-line” from the main North Walnut Creek channel and discharges to the subsurface via the SPPTS Discharge Gallery comprises approximately 5 percent of the uranium load measured at GS13 (based on total loads measured at both locations from January 2010 through March 2014). The relatively minor input load of uranium from SPOUT to GS13 occurs despite SPOUT having the highest average uranium concentration of any of the surface water monitoring locations analyzed. This occurs because of the low relative water volume discharged by SPOUT (SPOUT discharges account for approximately 2 percent of the volume measured downstream at GS13), resulting in the small relative uranium load from SPOUT (Figure B.2) compared with GS13 (Figure B.4).
 - The small relative contribution of uranium load provided by SPOUT compared to GS13 occurs in all months analyzed from 2010 through March 2014 (see Figures B.9 through B.14).

3.3.1.2 *South Walnut Creek*

Data plots of surface water uranium concentration, water volume and load for South Walnut Creek monitoring locations are compiled in Appendix C (includes plots for locations GS10, B5INFLOW, GS08). A summary of the different data plots developed for the South Walnut Creek data analysis is provided in Table 4.

**Table 4. Description of data plots – Uranium in South Walnut Creek
(Appendices C and G)**

Data plot description	Figure(s) in Appendices C and G
GS10, B5INFLOW, GS08 - Monthly average and maximum uranium concentrations, water volume, and loads, by location	Figures C.1 – C.3
Summary of annual uranium loads in South Walnut Creek, by location (2010 – 2013)	Figure C.4
Monthly uranium loads in South Walnut Creek, by location (2010 – 2014) (includes expanded scale plot for 2013 loads)	Figures C.5 – C.10
Average uranium concentrations, by location, South Walnut Creek (1/27/2010 – 4/30/2014)	Figure C.11
Uranium loads in South Walnut Creek	Table C.1
Water volumes at South Walnut Creek monitoring locations (annual totals for 2010 - 2013 and monthly totals for 2010 - 2014), for comparison purposes with uranium load and concentration plots.	Figures G.1 – G.7 and Table G.1

Review of the uranium concentration and loading data plots listed in Table 4 leads to the following observations regarding South Walnut Creek:

Uranium Concentrations in South Walnut Creek

- Average uranium concentrations at monitoring locations along South Walnut Creek (for the period 1/27/2010 to 4/30/2014) are summarized on Figure C.11. (Note: The measured uranium concentrations shown on Figure C.11 provide a general reference for the variability of uranium concentrations along South Walnut Creek, but do not distinguish between different specific site conditions, such as different operating protocols for Pond B-5 or changes in site geochemical conditions following the September 2013 flood event, which are discussed later in this report.)
- Along South Walnut Creek, uranium concentrations measured at individual monitoring locations generally decrease from upstream monitoring station GS10 (Figure C.1) down to station GS08 at the Pond B-5 outfall (Figure C.3), indicating uranium removal along

this channel reach and the formation of temporary uranium “sinks” (Figures C.1 through C.3). (Note: the uranium concentrations on Figures C.1 through C.3 are plotted on common scales to facilitate comparisons between locations). Uranium deposited between GS10 and B5INFLOW is intermittently mobilized and transported downstream given certain flow and/or oxidizing conditions (see discussion below regarding uranium loads in South Walnut Creek).

- Observations at specific locations along South Walnut Creek, including temporal variability and seasonal patterns, include the following:
 - At GS10, uranium concentrations vary widely temporally, and in a cyclical, seasonal pattern, with the highest concentrations typically observed during the first two to three months each calendar year (see Figure C.1). This supports the understanding that a larger fraction of the flow at GS10 during those months is attributed to groundwater and, as a result, elevated concentrations of uranium will be discharged into surface flows. However, other potential sources of uranium (e.g., mobilization of sediments upstream of GS10, or contributions of uranium from specific seeps upstream of GS10) are also possible.
 - At GS08 (Pond B-5 outfall), uranium concentrations (monthly flow-weighted averages) increased significantly in 2012, 2013 and through March 2014, compared to prior monitoring results dating back to site closure in 2005 (Figure C3).
 - During the time period when uranium concentrations were increasing in Pond B-5 discharges, the uranium concentrations at monitoring locations upstream from Pond B-5 were variable:
 - At GS10, uranium concentrations generally remained within their normal range observed after site closure in 2005 (see Figure C.1).

- At B5INFLOW (located immediately above Pond B-5), available data are limited but uranium concentrations were higher in 2012 and 2013 compared to 2010 through 2011 (see Figure C.2), with several samples in 2012 and 2013 exceeding 16.8 µg/L.
- While the increased uranium concentrations measured in Pond B-5 discharges correspond with the transition from batch-release mode to flow-through mode in Pond B-5 in September 2011 (Figure C.3), based on monitoring data from the B5INFLOW location, it appears that the increase in uranium concentrations measured in Pond B-5 discharges since September 2011 may be the result of both: 1) the changed operating protocol (from batch-release mode to flow-through mode), and 2) increased concentrations in the upstream flow (including elevated uranium when groundwater comprises a larger fraction of inflows during dry periods, and/or when elevated groundwater levels or oxidizing conditions mobilized uranium sources during extremely wet periods; see B5INFLOW data). The increased residence time of water in Pond B-5 during batch mode operation allowed increased chemical precipitation of low solubility uranium species and increased sorption of uranium to pond sediments in deeper pond water containing low dissolved oxygen. Changing Pond B-5 to flow-through mode reduced the efficiency of these uranium removal processes.
- Uranium Loads in South Walnut Creek
 - The annual and monthly uranium loads are frequently higher at GS10 than at B5INFLOW (the next monitoring location downstream), indicating that uranium removal, or a “sink,” occurs between those two locations during most months and generally more so during drier periods with lower flows, such as in 2012. (See the summary of annual loads [Figure C.4] and monthly load data [Figures C.5 through C.10]). This pattern of uranium load removal in the channel downstream from GS10 was observed for all but five months from 2010 through March, 2014

(the exceptions being October, 2011; March, April and September, 2013; and February, 2014).

- Between B5INFLOW and GS08 (Pond B-5 outfall), reduction of uranium loads is intermittent, but is generally more pronounced during periods with higher flows, such as April, May and September in 2013 (see Figures C.8 and C.9). Increased concentrations of suspended sediments are likely to exist in conditions with higher flow, which leads to increased removal of uranium bound to sediment via settling processes in Pond B-5, even when the pond is in flow-through mode. (Note: this observation is made while recognizing the increased uncertainty regarding flow measurement and water quality during the September 2013 flood event, which added uncertainty to the uranium load calculation for that month in particular).

3.3.2 Nitrate Concentrations and Loads

For reasons discussed in Section 2.2, an evaluation of uranium concentrations and loads in RFS surface water must also address nitrate since it is prevalent in certain areas of the site, particularly in North Walnut Creek (as a result of historic activities), and because nitrate can facilitate uranium mobility via oxidation processes (Wu, et al., 2010).

Similar to the approach used for uranium, the data analysis for nitrate in surface water at RFS involves assessing spatial variability, including mass balance analyses, to identify potential sources and/or sinks of nitrate because of the role that nitrate can play in mobilizing uranium. In addition, temporal variability was evaluated to assess whether seasonal or other temporal trends could be identified. It is noted that care must be taken when comparing nitrate and uranium data because, as discussed in Section 3.1, nitrate samples are collected only as grab samples whereas uranium samples are collected as flow-paced composite samples for compliance purposes and as grab samples for bi-weekly data.

Surface water monitoring data were plotted to compare nitrate concentrations and loads at monitoring locations in both drainages. Data plots were developed for all monitoring locations to facilitate comparisons between locations for the following types of data:

- Nitrate concentrations (monthly average and maximum values [mg/L])
- Water volume discharged (liters per month)
- Nitrate loads (average monthly values [mg/month])

Data from January 1997 through the most currently available data are included on each of the plots (where data exist), except for where data are not available back to 1997.

3.3.2.1 North Walnut Creek

For North Walnut Creek, data plots of surface water nitrate concentration, water volume, and nitrate loads are presented in Appendices D and F for locations SW093, SPIN, SPOUT, GS13, GS12 (or A3EFF), GS11 (Pond A-4 outfall) and WALPOC. A summary of the different data plots developed for this analysis is provided in Table 5.

Table 5. Description of data plots and tables – Nitrate in North Walnut Creek (Appendices D and F)

Data plot description	Figure(s) in Appendices D and F
SW093, SPIN, SPOUT, GS13, GS12 (or A3EFF), GS11 and WALPOC – Monthly average and maximum nitrate concentrations, water volume, and loads, by location	Figures D.1 – D.7
Summary of annual nitrate loads in North Walnut Creek, by location (2010 – 2013)	Figure D.8
Monthly nitrate loads in North Walnut Creek, by location (2010 – 2014)	Figures D.9 – D.14
Solar Ponds Plume Treatment System Performance, by month (2010 – March 2014)	Figure D.15
Average nitrate concentrations, by location, in North Walnut Creek	Figure D.16

Data plot description	Figure(s) in Appendices D and F
Pond A-4 Nitrate Grab Sample Data (NO ₃ + NO ₂ as N), 2010 - April 2014	Figure D.17
Water volumes at North Walnut Creek monitoring locations (annual totals for 2010 - 2013 and monthly totals for 2010 - 2014), for comparison purposes with uranium load and concentration plots.	Figures F.1 – F.7 and Table F.1

Review of the nitrate concentration and loading data plots listed in Table 5 leads to the following observations:

Nitrate Concentrations in North Walnut Creek and at WALPOC

- Average nitrate concentrations for all North Walnut Creek locations are summarized on Figure D.16. (Note: The average nitrate concentrations shown on Figure D.16, calculated from samples collected from 1/27/10 through 4/30/14, provide a general reference for the variability of nitrate concentrations along North Walnut Creek. However, the average concentrations presented on Figure D.16 do not distinguish between different specific site conditions, such as different operating protocols for Pond A-4 or different configurations at the SPPTS. To assess the variability of nitrate concentrations at individual locations in the north Walnut Creek drainage, refer to Figures D.1 through D.6.)
- Nitrate concentrations measured at North Walnut Creek monitoring locations are spatially variable from upstream monitoring station SW093 (Figure D.1) down to station GS11 at the Pond A-4 outfall (Figure D.6), indicating the presence of significant nitrate source(s) and sink(s) as average nitrate concentrations rise and then fall going downstream along this channel reach, similar to the spatial variation observed for uranium. (Note: the nitrate concentrations on Figures D.1 through D.6 are plotted on common scales to facilitate comparisons between locations.)

- Nitrate concentration data and temporal variability are discussed below for individual locations in the North Walnut Creek drainage:
 - SW093 - Nitrate concentrations at SW093 have historically been generally below the 10 mg/L RFLMA standard for nitrate plus nitrite, with two exceptions for the period reviewed (from 2010 through May 2014), with both exceptions occurring following periods of elevated rainfall (or snowmelt) and resulting recharge to the area of the former Solar Evaporation Ponds, as described below:
 - From 4/22/10 through 6/2/10, in four consecutive grab samples at SW093, nitrate was measured at concentrations ranging from 25 to 35 mg/L. These elevated nitrate sample results followed a period of high precipitation and resulting recharge to the former Solar Evaporation Ponds area in March and April of 2010, as shown on Figure F.2 (water volume plot for 2010), as well as hillside seepage from the area north of the former Solar Evaporation Ponds with elevated nitrate concentrations reaching SW093 (SN3, 2014). The high relative precipitation during this period, is evident based on a comparison of Figure F.2 with other months and years (Figures F.3 – F.7).
 - From 9/19/13 to 11/26/13, in five consecutive grab samples at SW093, nitrate was measured at concentrations ranging from 15 to 46 mg/L. Again, the elevated nitrate sample results followed a period of high rainfall (the September 2013 storm event), as shown on Figures F.5 and F.6, which resulted in increased recharge to the former Solar Evaporation Ponds area. The September 2013 storm event started on 9/10/13, with the highest runoff rates occurring on 9/12/13. The following week, on 9/19/13, a grab sample was 15 mg/L nitrate; subsequent samples were higher, including: 35 mg/L (10/15/13), 41 mg/L (10/30/13); 39 mg/L

(11/13/13), and 46 mg/L (11/26/13), before decreasing, as reflected on Figure D.1.

- SPOUT – At the SPPTS effluent monitoring location SPOUT, which is located “off-line” from the main North Walnut Creek channel and discharges to the subsurface via the SPPTS Discharge Gallery, the water has a substantially higher average nitrate concentration compared to any other monitoring location in the North Walnut Creek drainage (except for SPIN – the influent monitoring location to the SPPTS).⁹

The average nitrate concentration at SPOUT is greater than 250 mg/L (NO₃ + NO₂ as N), for samples collected from 1/27/10 through 4/30/14. (Note: Refer to Figures D.2.a and D.2.b which show recent increasing nitrate concentrations at SPOUT).

- Although the water volume discharged from SPOUT is minor compared to the flows in the main North Walnut Creek channel (SPOUT flows represent approximately two percent of the flow volume compared to station GS13), because of the high nitrate concentration in SPOUT discharges, the nitrate load delivered from SPOUT was approximately 20 percent of the total nitrate load measured at GS13 (based on data from January 2010 through March 2014.) Unlike uranium, with its abundant natural background, the primary source of nitrate at RFS (from the Solar Ponds Plume [SPP]) is clearly known.

⁹ Contact Record 2009-01 approved testing and development of improved long-term treatment methods for the SPPTS. The Contact Record notes that replacing the original media with fresh media would not result in adequate treatment over the long term, would be costly and difficult, and would need to be repeated every few years. Therefore, the focus on the SPPTS has been to identify better treatment approaches that are effective as well as sustainable, from a cost and maintenance perspective.

Regarding the uncertainty of nitrate measurements, at in-stream locations such as GS13, there is a greater likelihood of overestimating nitrate loads when using grab sample results (compared with using flow-paced composite sample results) because of the timing of the grab sampling. In contrast, at SPOUT, since the discharge is from an engineered system that does not fluctuate in the same manner as a stream channel, the uncertainty of the nitrate measurements is less. Consequently, if the nitrate loads at GS13 are more likely to be overestimated than at SPOUT, the relative contribution of nitrate from SPOUT to GS13 may be underestimated (i.e., it may likely be greater than 20 percent).

- At GS13, the average nitrate concentration (approx. 28 mg/L) was higher compared to upstream location SW093 (approx. 7 mg/L) for the period from 1/27/10 – 4/30/14 (see Figure D.16). Some of the increased nitrate concentration at GS13 can be accounted for by the input of nitrate from SPOUT (located between SW093 and GS13).
 - At A1EFF, located downstream from GS13 (see Figure 1), Figure D.18 shows a plot of nitrate versus uranium (using grab sample data for each) to assess the relationship between the two. The plot shows two separate trends, both with positive correlations between uranium and nitrate concentrations. The trend with the higher uranium concentrations could potentially represent a unique source of both uranium and nitrate, which is mobilized only periodically; this theory, however, has not been substantiated.
- Pond A-4 discharges, measured at GS11, consistently had nitrate concentrations fluctuating at levels less than the RFLMA 10 mg/L standard prior to September 2013. However, at a separate sampling location in Pond A-4 upstream from GS11, grab samples collected from the pond following a 5-month lag after the

September 2013 storm have had nitrate concentrations that increased to as high as 18 mg/L from February through April 2014 (see Figure D.17). While the increase in nitrate concentrations in Pond A-4 coincides with a spike in nitrate loads at SW093 in March 2014 (see Figure D.14), the relative proportions of nitrate loads at SW093 and GS11 (Pond A-4 outfall) did not change during that time; this suggests that the increase in nitrate concentrations observed in the A-4 discharges was likely the result of the increased nitrate load from the high baseflow following the extreme storm event in September 2013.

- At WALPOC, the average nitrate concentration has been approximately 3 mg/L, based on 34 grab samples collected from 9/12/11 to 6/4/14. Results during that time period ranged in concentration from non-detected to approximately 8.7 mg/L, with all but one of the results greater than 5 mg/L occurring following the large storm in September 2013. The nitrate concentration increase at WALPOC following the large storm event reflects increased concentrations of nitrate at all the upstream monitoring locations in North Walnut Creek following the storm, as well as minimal biological reduction of nitrate occurring during the cold winter months (see Figures D.1 through D.6).

Nitrate Loads in North Walnut Creek and at WALPOC

- To assess the increased nitrate concentrations at GS13, review of North Walnut Creek nitrate load data indicates a substantial portion of the nitrate load entering GS13 is from a source other than SW093 or SPOUT (see annual load analysis Figure D.8). Review of monthly nitrate load analyses for 2010 to 2014 (time frame selected based on available data for multiple locations in the drainage) shows an additional nitrate load to GS13 (from a source other than SW093 or SPOUT) for most months from 2010 through March 2014 (taking into account that flow was not present at GS13 for some months) (see Figures D.9 to D.14).

- The increase in nitrate load at GS13 cannot be explained merely by a gain in water volume (see the annual average water balance [Figure F.1] and monthly water balance plots [Figures F.2 through F.7]). The gain in water volume from the combined SW093+SPOUT to GS13 is not the same proportion as the increase in nitrate load, indicating that the water entering North Walnut Creek upstream from GS13 (other than that contributed by SW093 and SPOUT) has nitrate at a higher concentration than the water flowing in North Walnut Creek. Based on the presence of the SPP, the only known groundwater source of nitrate in this area, it appears that a portion of the SPP is not collected by the SPPTS and enters the North Walnut Creek channel between SW093 and GS13, increasing nitrate loads and concentrations at GS13 and farther down North Walnut Creek. Overall, month after month, nitrate loads are frequently higher at GS13 than at any other location sampled in the North Walnut Creek drainage (see North Walnut Creek monthly load plots, Figures D.9 to D.14).

3.3.2.2 *South Walnut Creek*

Data plots of surface water nitrate concentration, water volume, and nitrate loads at South Walnut Creek location GS08 (Pond B-5 outfall) are presented in Appendix E.¹⁰ A summary of the different data plots developed for this analysis is provided in Table 6.

¹⁰ Nitrate data are available in South Walnut Creek only at GS08 (Pond B-5 outfall) because the majority of nitrate sampling at RFS is conducted in the North Walnut Creek drainage as a result of the plume associated with the former Solar Evaporation Ponds.

**Table 6. Description of data plots and tables – Nitrate in South Walnut Creek
(Appendices E and G)**

Data plot description	Figure(s) in Appendices E and G
GS08 – Monthly average and maximum nitrate concentrations, water volume, and loads	Figure E.1
Water volumes at South Walnut Creek monitoring locations (annual totals for 2010 - 2013 and monthly totals for 2010 - 2014), for comparison purposes with uranium load and concentration plots.	Figures G.1 – G.7 and Table G.1

Review of the nitrate concentration and loading data plot listed in Table 6 leads to the following observations:

Nitrate Concentrations in South Walnut Creek

Although historic depictions of the nitrate groundwater plume originating from the area surrounding the former Solar Evaporation Ponds have indicated that a portion of this groundwater migrates to South Walnut Creek, data collected over the last decade or more continue to demonstrate that any such pathway is relatively insignificant. Therefore, nitrate measurements in South Walnut Creek are extremely limited compared to North Walnut Creek.

- At the 995 seep locations (SEEP995, SEEP995A, SEEP995B and SEEP995C), 27 samples collected since the September 2013 storm event (from 10/1/13 through 12/30/13) ranged from 0.4 to 7.5 mg/L (all below the RFLMA standard of 10 mg/L). These data indicate that this area in South Walnut Creek has not had elevated nitrate concentrations as a result of increased recharge in the area of the former Solar Evaporation Ponds; this contrasts to the demonstrated nitrate response observed in the North Walnut Creek drainage following the September 2013 storm event discussed previously.

- At Pond B-5, two nitrate measurements since 2010 have yielded samples with nitrate concentrations of approximately 0.2 mg/L.
- Grab samples at other locations in South Walnut Creek (GEOB1INF, GEOB4INF and GEOB5INF) also have had the majority of nitrate sample results below 10 mg/L (see Appendix I, Figures I.1 through I.3). However, variability exists in the data set, as demonstrated by an individual sample result of 12 mg/L nitrate at GEOB5INF on 11/17/13. Though it appears that specific elevated result may have been related to the 2013 flood event, it is difficult to confirm, since a result of 10 mg/L was also measured at GEOB5INF in May 2014.
- In addition to the surface water data described above, groundwater samples from wells in the Building 991 and 995 area (including wells 99305, 99405, 91305) also consistently report non-detects or concentrations of nitrate less than 10 mg/L, further supporting the observations made at the surface water locations with respect to negligible observed effects in the South Walnut Creek drainage in terms of increased nitrate concentrations resulting from the former Solar Evaporation Ponds area.

3.3.3 Other Parameters

Evaluation of data for multiple chemical parameters, other than uranium and nitrate (such as pH, dissolved oxygen, sulfate and sulfide), are plotted and tabulated in Appendix H (for North Walnut Creek monitoring locations), Appendix I (for South Walnut Creek monitoring locations) and Appendix J (for other parameters in both North and South Walnut Creeks). Summaries of the findings are provided in Section 3.3.3.1 (for North Walnut Creek) and in Section 3.3.3.2 (for South Walnut Creek). Note that the sample locations for these other parameters, while still in North and South Walnut Creeks, differ from those discussed in prior sections for uranium and nitrate (see Appendix A, Figure A.1).

3.3.3.1 North Walnut Creek

- pH: pH shows no significant temporal (or spatial) trends. The average value from all monitoring locations was 7.36, with a range of 8.88 to 6.53.
- Dissolved Oxygen – Dissolved oxygen shows an important temporal change during the period between December 2012 and July 2014.
 - Between December 5, 2012 and July 10, 2013, dissolved oxygen saturation was consistently low (average range at all stations: 35.3% to 56.8%), with minimal diurnal variation. For surface waters, these values represent reducing conditions (indicative of negative redox conditions), with little plant photosynthesis occurring, and are consistent with a groundwater-dominated stream flow (low groundwater dissolved oxygen resulting from subsurface bio-consumption of dissolved oxygen, not relieved by sufficient oxygenated recharge water). Under these conditions and absent any influx of oxygenated water, uranium is expected to mostly be present as low solubility U(IV) species, but is potentially susceptible to mobilization by nitrate.
 - Change in Dissolved Oxygen - Sometime between 7/10/2013 and 11/07/2013, stream conditions changed to relatively higher dissolved oxygen saturation (average range: 78% to 87%), with the shift occurring during the period with heavy rainfall in September 2013, (see Figures H.1 through H.6 and Tables H.1 through H.6).
 - Persistence of Current Aerobic Conditions - The aerobic conditions have persisted, with a slow decline in dissolved oxygen concentrations as measured in mid-July 2014. (Note: The July 2014 dissolved oxygen samples were at only three locations [FCINF, FCEFF and A1INF] due to limited water flow at sample locations in mid-summer.) These data are consistent with a flood-triggered mechanism in which the heavy rainstorms of September 2013 recharged the

groundwater with oxygenated water more rapidly than subsurface bio-consumption could deplete it. Where the oxygen-rich groundwater entered North Walnut Creek, it provided: 1) increased mobilization of uranium in subsurface deposits, thereby causing elevated concentrations of uranium in groundwater to be issued to surface drainages, and 2) an increase in dissolved oxygen concentrations in the stream channels, thereby enhancing uranium transport to WALPOC via mobilization of uranium in channel sediments.

- Sulfate and hydrogen sulfide - Sulfate and hydrogen sulfide were included in the chemical parameters analyzed because the reduction of sulfate to hydrogen sulfide would indicate very strong reducing conditions. However, substantial changes in hydrogen sulfide concentrations were never observed.
- Uranium in sediment – Uranium concentrations in sediment in North Walnut Creek fluctuate by location (six locations sampled) but generally are higher upstream compared to downstream (Appendix J, Figure J.3). Based on samples collected on 11/8/12, concentrations of uranium in sediment in the North Walnut Creek drainage range from slightly more than 1 mg/kg at the uppermost sampling location GEOFC3INF to approximately 7 mg/kg at the most downstream location GEOA3EFF (see Figure A.1 for sample locations). It is noted that pond sediments were not removed from North Walnut Creek during site closure activities.
- Hardness and alkalinity – Hardness and alkalinity data for six North Walnut Creek monitoring locations, collected from 12/24/13 to 4/30/14, are presented in Appendix J (Figures J.5 and J.7, respectively). Both hardness and alkalinity generally declined over the sampling period at most monitoring locations (ranging from approximately 500 to 600 mg/L in December 2013 down to 370 to 510 mg/L in April 2014). This reflects the proportionately larger contribution from groundwater during the winter months. Pond A-4 was an exception, with lower hardness values than the other locations until mid-February, after which hardness was comparable for all locations. Similarly, alkalinity in

Pond A-4 was also lower than the upstream stations until mid-February, at which time the alkalinity increased to a level comparable with the other upstream monitoring locations.

- Total Suspended Solids (TSS) and Uranium – Data are presented for TSS versus uranium at monitoring locations SW093 and GS11 (Pond A-4 outfall) in the North Walnut Creek drainage, as well as for locations in South Walnut Creek and at WALPOC (Appendix J, Figure J.9). The date ranges for the available data sets vary by location and while no relationship between uranium and TSS is apparent, the data suggest historically more TSS at GS11 (Pond A-4 outfall) than at GS08 (Pond B-5 outfall).

3.3.3.2 *South Walnut Creek*

- pH: pH values in South Walnut Creek are similar to those in North Walnut Creek, with an average of 7.4, with a range of 6.84 to 8.05 and showing no significant spatial or temporal trends (see Appendix I).
- Dissolved Oxygen – Dissolved oxygen shows the same temporal change in South Walnut Creek (see Appendix I) that was observed in North Walnut Creek.
 - Before 7/10/2013, dissolved oxygen saturation was consistently relatively low (average range at all stations: 42.4% to 55.0%), with minimal diurnal variation. For surface waters, these values represent reducing conditions in stream water and sediments (indicative of negative redox conditions), with little plant photosynthesis occurring, and are consistent with a groundwater-dominated stream flow (low groundwater dissolved oxygen resulting from subsurface bio-consumption of dissolved oxygen, not relieved by sufficient oxygenated recharge water). Under these conditions, uranium is expected to mostly be present as low solubility U(IV) species, but is potentially susceptible to mobilization by nitrate. As in North Walnut Creek, the grab sample nitrate data are inconsistent in some cases for reasons that are not fully understood.

- Change in Dissolved Oxygen - Sometime between 7/10/2013 and 11/07/2013, stream conditions changed to relatively higher dissolved oxygen saturation (average range: 77.5% to 87.1%), with the shift occurring during the period with heavy rainfall in September 2013, (see Figures I.1 through I.3 and Tables I.1 through I.3).
- Persistence of Current Aerobic Conditions - The aerobic conditions created by the September 2013 storm event appear to have persisted, with a slow decline in dissolved oxygen concentrations continuing into mid-July 2014, as observed at two of the three locations sampled (see Figures H.1 through H.3). Where the oxygen-rich groundwater entered South Walnut Creek, it provided: 1) increased mobilization of uranium in subsurface deposits, and 2) an increase in dissolved oxygen concentrations in the stream channels, thereby enhancing uranium transport to WALPOC via mobilization of uranium in channel sediments.
- Sulfate and hydrogen sulfide – Substantial changes in hydrogen sulfide were never observed.
- Uranium in sediment – Uranium concentrations in sediment in South Walnut Creek fluctuate by location (three locations sampled), with the highest concentration, approximately 14 mg/kg, measured upstream at location GEOB1INF. Concentrations near 2 mg/kg were measured at downstream locations GEOB4 and GEOB5INF (Appendix J, Figure J.4). For historical reference, pond sediments were removed from Ponds B-1, B-2 and B-3 as part of site closure activities and replaced with clean fill.
- Hardness and alkalinity – Hardness and alkalinity data for six South Walnut Creek monitoring locations, collected from 12/24/13 to 4/30/14, are presented in Appendix J (Figures J.6 and J.8, respectively). Both hardness and alkalinity generally declined over the sampling period at most monitoring locations (ranging from approximately 650 to 700 mg/L in December 2013 down to 470 to 530 mg/L in April 2014). This reflects the

proportionately larger contribution from groundwater during the winter months. Pond B-5 was an exception, with lower hardness values than the other locations until mid-February, after which hardness was comparable for all locations. Similarly, alkalinity in Pond B-5 was also lower than the upstream stations until mid-February, at which time the alkalinity increased, though it remained lower than at all but one other location for all sample dates.

- Total Suspended Solids (TSS) and Uranium – Data are presented for TSS versus uranium at monitoring locations GS10 and GS08 (Pond B-5 outfall) in the South Walnut Creek drainage, as well as for locations in North Walnut Creek and at WALPOC (Appendix J, Figure J.9). The date ranges for the available data sets vary by location and while no relationship between uranium and TSS is apparent, the data suggest historically less TSS in Pond B-5 than at GS11 (Pond A-4 outfall).

3.4 Meteorological Conditions Effects

The relationship of uranium to the findings for other water quality parameters discussed in Section 3.3.3 is shown on Figure J.1, where uranium concentrations in North and South Walnut Creeks and at WALPOC are plotted over a time span that includes the heavy rainfall in September 2013 (the 7.67 inches of rainfall recorded for the entire month in September 2013 was the wettest month on record since site precipitation records were kept beginning in 1993).

At each monitoring location illustrated on Figure J.1, uranium concentrations (from flow-paced composite samples) were relatively lower just prior to and during the September rain event and abruptly began to increase following the storm. The increased uranium concentrations at WALPOC persisted until mid-May 2014, at which time a decline in concentrations was observed, with three consecutive samples all below the 16.8 µg/L standard (sample dates 5/12/14 through 5/21/14). At some locations, particularly GS10 (Figure J.1), uranium concentrations in samples collected after the September 2013 flood remained within the pre-flood range but are more uniform and generally higher than in samples collected immediately prior to the September

2013 event. The extended duration of elevated uranium in the Walnut Creek surface water drainages is believed to have resulted from, among other factors:

- An increased proportion of groundwater, with elevated uranium concentrations relative to surface water.
- Increased oxygen concentration in groundwater, which facilitates mobilization of uranium.
- Higher groundwater elevations which can cause groundwater to remain in contact with different subsurface sources with higher uranium content (e.g., Solar Ponds Plume, subsurface sediments, “evaporite-type” deposits at the water table interface, etc.).
- Increased oxygen concentration in surface water, which facilitates mobilization of uranium associated with streambed sediments (see Figure J.1 and Figures H.1 through H.6 and Figures I.1 through I.3).

The prolonged period of discharges of oxygen-rich groundwater can continue for an extended period due to the low hydraulic conductivity materials through which the groundwater flows to reach surface water. These conditions would be expected to facilitate oxidizing conditions and mobilization of uranium in any location, including at RFS or elsewhere.

- Data suggest that as long as the Solar Ponds Plume and sediment sources remain, it can be expected that a future storm of a magnitude comparable to the September 2013 event will have a similar effect of initiating prolonged periods of relatively higher uranium concentrations in surface water monitoring locations across the site. The important characteristic of the September 2013 storm that differentiates it from lesser storms appears to be that the shallow groundwater and, as a result, surface water became oxygenated to such an extent that subsurface microbial activity and slow groundwater movement had not yet returned dissolved oxygen concentrations in surface water to the lower pre-storm levels, based on the available monitoring data through 7/23/14 at some

locations. With lesser storms, the oxygen content of the recharged groundwater was low enough that subsurface conditions and, ultimately, surface water returned to lower dissolved oxygen concentrations more rapidly through biological activity.

3.5 Determination of Uranium from Anthropogenic Sources

The work conducted historically at RFS involved forms of anthropogenic uranium, both enriched and depleted, that was received from other facilities in the DOE complex, but did not involve uranium from natural sources. As a result of the historic activities, residual quantities of anthropogenic uranium remain in the environment at RFS. Primary sources of anthropogenic uranium at the site from which uranium is transported in the North and South Walnut Creek drainages and which have been previously documented and characterized include: 1) the former Solar Evaporation Ponds area with elevated concentrations of uranium in groundwater (Kaiser-Hill, 2005), and 2) sediments with anthropogenic uranium in both North Walnut Creek and South Walnut Creek, which were previously characterized for isotopic ratios by a Los Alamos National Laboratory (LANL) study for the purpose of determining the anthropogenic fractions (Efurud et al., 1993), though the site has been altered substantially since those samples were collected. In addition, other uranium source locations were previously documented in the Historical Release Report (EG&G, 1994), though many of those sources were removed during site remediation activities.

To evaluate more current conditions with respect to distinguishing between anthropogenic versus natural uranium, results of uranium isotopic composition analyses (i.e., analyses of the content of individual isotopes as well as ratios of U-234/U-238, U235/U-238 and U236/U-238) were reviewed for analyses conducted from 2002 through 2014 from locations throughout the site, for both surface water and groundwater. The analyses were conducted at LANL and the Lawrence Berkeley National Laboratory (LBNL) and involved the use of Thermal Ionization Mass Spectrometry (TIMS) and Multicollector-Inductively Coupled Plasma/Mass Spectrometry (MC-ICP/MS) analytical techniques (LANL, 2011; LBNL, 2013a; LBNL, 2013b). Results were used

to address the question of whether previously unrecognized anthropogenic sources of uranium have been identified at the site (Question 3).

3.5.1 Surface Water Isotopic Uranium Analyses

Results of the isotopic composition analyses for surface water samples are presented in Table 7. Plotted results from isotopic analyses are provided in Appendix K for individual sample locations.

Table 7. Summary of isotopic composition of uranium at selected surface water monitoring locations

Drainage/ Water Source	Location	Number of Samples Analyzed at LANL and/or LBNL	Sample Date Range	Average U Concen. of Samples Analyzed at LANL and/or LBNL ⁽¹⁾ (µg/L)	Percent Natural Uranium (%)			Data Plot (Appen. K)
					Min. %	Max. %	Avg. %	
Walnut Creek	WALPOC	21	9/22/11 - 4/8/14	13.4	74.85%	82.60%	77.96%	K.1 and K.2
North Walnut Ck.	SPIN	3	6/6/08 - 4/20/11	57.4	47.80%	62.00%	57.2%	-
	SW093	3	12/6/07 - 4/20/11	8.6	90.90%	92.70%	91.87%	K.3
	SPOUT	2	3/17/10 - 4/20/11	31.4	57.70%	65.10%	61.40%	K.4
	SPPDG	5	6/8/02 - 3/17/10	51.4	41.40%	67.20%	51.6%	-
	GS13	5	5/1/02 - 4/20/11	29.6	71.30%	74.80%	72.63%	K.5
	A1EFF	2	3/17/10 - 4/20/11	31.8	69.60%	73.10%	71.35%	-
	A2EFF	2	3/17/10 - 4/20/11	43.15	70.70%	70.90%	70.80%	-
	A3EFF	2	3/7/10 - 4/20/11	37.80	72.50%	72.70%	72.60%	-
	GS12	1	4/2/14	23	-	-	73.68%	K.6
	A4POND	1	2/13/14	20	-	-	74.88%	K.7
	GS11	2	2/13/14 - 4/2/14	28	73.65%	74.27%	73.96%	K8
South Walnut Ck.	FC4750	1	9/28/11	17.6	-	-	70.90%	-
	FC4991	1	9/28/11	5	-	-	78.30%	-

Evaluation of Water Quality Variability for Uranium and
Other Selected Parameters in Walnut Creek at the Rocky Flats Site

Drainage/ Water Source	Location	Number of Samples Analyzed at LANL and/or LBNL	Sample Date Range	Average U Concen. of Samples Analyzed at LANL and/or LBNL ⁽¹⁾ (µg/L)	Percent Natural Uranium (%)			Data Plot (Appen. K)
					Min. %	Max. %	Avg. %	
South Walnut Ck. (cont'd)	SEEP995A	2	9/30/13 - 11/25/13	15.25	59.67%	68.14%	63.91%	K.10
	FC4EFF	2	9/30/13 - 11/25/13	14.9	71.17%	73.86%	72.52%	K.9
	GS10	17	5/1/02 - 11/25/13	17.38	43.29%	77.84%	65.91%	K.11 and K.12
	B3OUTFLOW	2	3/17/10	15.3	74.3%	76.60%	75.45%	-
	POM2	2	8/28/08 - 3/17/10	24.65	69.10%	75.4%	72.3%	-
	B5INFLOW	3	3/7/10 - 4/2/14	14.63	75.85%	78.50%	77.12%	K.13
	B5POND	2	9/16/08 - 2/13/14	2.70	78.80%	80.32%	79.56%	K.14
	GS08	2	2/13/14 - 4/2/14	17.0	75.79%	79.97%	77.88%	K.15

Notes:

1) Uranium concentrations of samples analyzed at LANL or LBNL are provided for reference with results of isotopic analyses. Uranium concentrations provided by LANL and LBNL are not used for compliance purposes.

Summaries of the isotopic uranium data for different surface water sample locations are provided below, beginning with results at WALPOC followed by isotopic results from monitoring locations upstream.

WALPOC

The average natural uranium composition at WALPOC, as shown in Table 7, is approximately 78%, based on isotopic uranium analyses conducted on 21 samples collected from 9/22/11 to 4/8/14. The proportion of natural uranium measured in those samples has remained relatively consistent over that time period, with reported values ranging from approximately 75% to 83% (see Figure K.1).

There is no apparent temporal relationship at WALPOC between the uranium concentration in samples and the measured percentage of natural uranium, based on two years of available data (see Figure K.2). A short-term fluctuation in isotopic composition of uranium at WALPOC was

associated with the September 2013 flood event, when the percentage of natural uranium dropped from approximately 80% to 75% for samples collected from runoff between 9/13/13 and 9/16/13 (see Figure K.1). However, that change was within approximately 1% of the lowest natural fraction observed previously.

The isotopic analyses conducted at WALPOC through 4/18/14 include samples from a broad range of precipitation and runoff conditions, including a prolonged dry period in 2012 and the extreme runoff conditions associated with the September 2013 storm event (see Figures F.1 through F.7). The range of conditions for the current data set increases the confidence that the composition of uranium from natural sources in surface water at WALPOC can be expected to not deviate substantially from the existing range of sample results (approximately 75% to 83% of the uranium from natural sources).

Locations Upstream from WALPOC

At locations upstream from WALPOC, the following observations can be made regarding the percentage of natural uranium:

- North Walnut Creek (discussed in order from upstream to downstream locations):
 - SW093 - all isotopic samples (through 4/20/11) have greater than 90 percent natural uranium (Figure K.3).
 - SPOUT – the percentage of natural uranium in samples varies from approximately 65 percent to less than 60 percent, based on two samples (Figure K.4), reflecting the anthropogenic composition of the groundwater being treated from the Solar Ponds Plume (Figure K.4).
 - GS13 – The percentage of natural uranium, ranging from 71 to 75 percent, reflects a substantial decrease in the natural uranium fraction compared to SW093 (upstream), and reflects the effects from SPOUT inflows and other sources with anthropogenic uranium between SW093 and GS13 (e.g., subsurface flows that are

not collected by the SPPTS, sediment in the channel with anthropogenic uranium, etc.); this also supports the understanding that the gain in uranium load that occurs between SW093 and GS13 (discussed previously in Section 3.3.1.1 and shown on Figure K.5) is from a source (or sources) with a higher fraction of anthropogenic uranium compared to the uranium at SW093.

- GS12, A4POND, GS11 (Pond A-4 outfall) – The natural uranium percentage is in the same range (from 74 to 75 percent) at all these locations, based on a limited sample set (Figures K.6 – K.8).
- South Walnut Creek (discussed in order from upstream to downstream locations):
 - FC4EFF – Natural uranium percentage ranged from 71 to 74 percent, with an inverse relationship between natural percentage and uranium concentration (i.e., when uranium concentration increased, the natural percentage decreased) (Figure K.9). Note that this observation is based only on two samples approximately two months apart.
 - SEEP995A – Natural uranium percentage ranged from 60 to 68 percent, with an inverse relationship between natural percentage and uranium concentration (Figure K.10). Note that this observation also is based only on two samples approximately two months apart. Also noteworthy is that SEEP995A is an off channel seep with an indeterminate zone of entry to South Walnut Creek and three other seeps in the immediate vicinity, as well as other seeps nearby (e.g., SEEP988).
 - GS10 – 17 samples with isotopic uranium results at GS10 indicate substantial fluctuation in the percentage of natural uranium compared to other locations at the site, ranging from approximately 43 percent to nearly 78 percent in samples analyzed from 2002 to 2014 (Figure K.11). An inverse relationship between

natural percentage and uranium concentration is indicated for several samples (Figure K.11). Plotting natural uranium percentage versus uranium concentration (Figure K.12), shows that all results greater than 60 µg/L are composed of less than 60% natural uranium, indicating that an anthropogenic source (or sources) upgradient from GS10 may be contributing a larger share of the uranium at GS10 when concentrations are elevated.

- B5INFLOW – The natural percentage of uranium ranges from approximately 76 to 79 percent and indicates an inverse relationship between natural uranium percentage versus uranium concentration, though the data set limited to only three sample results (Figure K.13).
- B5POND and GS08 (Pond B-5 outfall) – The natural percentage of uranium was approximately 80 percent at B5POND (only 1 sample) and ranges between 76 and 80 percent at GS08 (3 samples). An inverse relationship between natural uranium percentage versus uranium concentration at GS08 may be indicated (Figure K.15).

3.5.1 Groundwater Isotopic Uranium Analyses

Table 8 provides a summary of results for isotopic uranium analyses for selected groundwater wells that had at least one sample analyzed for isotopic composition from 2011 through 2013:

Table 8. Summary of isotopic composition of uranium at groundwater wells

Drainage/ Water Source	Well #	Number of Samples Analyzed	Sample Date Range	Average U Concen. of Samples Analyzed ¹ (µg/L)	Percent Natural Uranium (%)			Data Plot (Appen. K)
					Min. %	Max. %	Avg. %	
Ground- water	79102	2	6/22/04 - 5/14/12	655.5	0.00%	0.00%	0.00%	K.16
	79302	1	10/29/13	182.8	87.14%	87.14%	87.14%	K.17
	79502	1	10/29/13	11	96.81%	96.81%	96.81%	K.18
	91305	2	8/9/05 - 10/10/11	47.0	90.80%	94.36%	92.58%	K.19
	99405	3	8/8/05 - 4/20/11	415.3	99.90%	100.00%	99.95%	K.20

Note: Sample results presented in Table 8 are from wells with isotopic analyses conducted at both LANL and LBNL. Uranium concentrations from LANL and LBNL are for reference, but not for compliance purposes.

Results presented in Table 8 are discussed below:

- Well 79102 (located in the northwest section of the former Solar Evaporation Ponds area [see Figure K.22]) – The percentage of natural uranium is 0% (2 samples), with a corresponding average uranium concentration of approximately 650 µg/L (Figure K.16). One of the isotopic analyses was conducted at LANL in 2004 (801 µg/L) and one was conducted at LBNL in 2012 (510 µg/L). Isotopic analysis results from this well indicate a source of high concentration, anthropogenic uranium in groundwater in the North Walnut Creek drainage.
- Well 79302 (located in the northern section of the former Solar Evaporation Ponds area [see Figure K.22]) – The percentage of natural uranium is approximately 87% (1 sample), with a corresponding uranium concentration of approximately 183 µg/L (Figure K.17).
- Well 79502 (located in the southern section of the former Solar Evaporation Ponds area [see Figure K.22]) – The percentage of natural uranium is approximately 96% (1 sample), with a corresponding average uranium concentration of approximately 11 µg/L (Figure K.18).
- Well 91305 (located in the upper reach of South Walnut Creek [see Figure K.22]) – The percentage of natural uranium is approximately 93% (2 samples), with a corresponding average uranium concentration of approximately 47 µg/L (Figure K.19).
- Well 99405 (located in the upper reach of South Walnut Creek [see Figure K.22]) – The percentage of natural uranium is greater than 99% (3 samples), with a corresponding average uranium concentration of approximately 415 µg/L (Figure K.20).

In addition to the limited sample set of isotopic analyses for wells 79102, 79302, 79502, 91305 and 99405 presented in Table 8, Figure K.22 displays results for isotopic and uranium concentration analyses for a much larger group of groundwater wells that had samples analyzed for isotopic composition. These other isotopic results are provided for reference to give a

general indication of which areas of the site have: 1) high relative concentrations of uranium in groundwater, and 2) high relative fractions of anthropogenic uranium.

4.0 EFFECT OF SITE OPERATIONS ON URANIUM CONCENTRATIONS

4.1 Solar Ponds Plume Treatment System Operations

The SPPTS influent uranium and nitrate concentrations (measured at the SPIN monitoring location) and effluent uranium and nitrate concentrations (measured at the SPOUT monitoring location) were evaluated to assess the performance of the SPPTS and its effect on uranium and nitrate concentrations in North Walnut Creek.

The relative effectiveness of the treatment system, in terms of percent removal, is plotted on Figure B.15 for uranium (see Appendix B) and Figure D.15 for nitrate (see Appendix D). As noted previously (see footnote 8 in Section 3.3.2.1), testing and development of improved long-term treatment methods for the SPPTS is ongoing, and the focus on the SPPTS has been to identify better treatment approaches that are effective as well as sustainable, from a cost and maintenance perspective. For both plots, the monthly water volumes measured at SPOUT are provided for reference regarding whether it was a relatively wet period or dry period and the effect the conditions had on the performance of the SPPTS.

4.1.1 SPPTS and Uranium in North Walnut Creek

Overall, the reduction in uranium load discharged monthly from SPOUT, compared to SPIN, varies widely, with the most effective uranium treatment (approximately 80 percent removal of uranium) occurring in early 2011 and the least effective uranium treatment (less than 20 percent removal of uranium) occurring in early 2014, based on monthly time intervals. There does not appear to be a clear relationship between flow rate and treatment system effectiveness, though on several occasions where high flow rates have passed through the system (such as June 2010, April 2012 and September 2013), a period has followed with decreased effectiveness by the SPPTS, suggesting the system's treatment capacity for uranium may have been reduced during

those high flow periods. Also noteworthy has been the upward trend in uranium concentrations entering the SPPTS (as measured at SPIN) (Figure B.3.b). Overall, the system's effectiveness for uranium removal appears to have trended downward from 2010 to the present (Figure B.15) while the uranium concentration in SPOUT discharges has trended higher (Figure B.2.a).

During periods where the SPPTS was less effective for uranium (for example, February 2014) (see Figures B.2 and B.15), there is not a clear corresponding increase in uranium observed at GS13 (see Figure B.4), suggesting the relationship between SPPTS uranium removal performance and downstream water quality in North Walnut Creek may not be strong, which is expected since the SPOUT uranium load is approximately 5 percent of the uranium load at GS13 (measured from 2010 through March 2014).

4.1.2 SPPTS and Nitrate in North Walnut Creek

Nitrate removal effectiveness in the SPPTS, based on SPIN versus SPOUT nitrate loads, has declined substantially from 2010 to the present (see Figures D.2 and D.15). The most rapid decrease in nitrate removal efficiency occurred from December 2013 (approximately 55 percent nitrate removal) to February 2014 (no nitrate removal). This period of substantially decreased effectiveness for nitrate removal directly followed the period of extreme prolonged rainfall in September 2013, indicating that the increased volume through the treatment system may have decreased the system's performance. (Note: communication with RFS personnel indicates that the diminished system performance in later 2013 and early 2014 is linked to reduced residence time in the system because of higher flow rates, resulting in reduced treatment effectiveness).

Similar to uranium, there is not a clear relationship between nitrate discharge from SPOUT (Figures D.2 and D.15) and nitrate concentrations observed at GS13 (Figure D.4), suggesting the link between SPPTS nitrate removal performance and downstream water quality in North Walnut Creek may not be strong. While the nitrate load from SPOUT, relative to the overall drainage load, is clearly larger than for uranium, the subsequent removal kinetics are different, making comparisons difficult. Adding to the complexity of comparing nitrate and uranium data is the

different sampling protocols used (i.e., grab samples for nitrate versus flow-paced composite samples for uranium).

Relevant transport mechanisms for uranium include elevated oxygen concentrations in groundwater and surface water (in particular during the post-flood condition), which causes uranium to remain in solution; removal of uranium from the water column relies, in part, on reducing conditions in the deeper sediments. In contrast, nitrate mobility relies on denitrification in the deeper sediments. Furthermore, increased nitrate in the system will increase uranium mobility.

4.2 Pond A-4 and B-5

Box-plots and scattergrams were developed to provide a statistical summary for evaluating uranium data at surface water monitoring locations GS11 (Pond A-4 outfall), GS08 (Pond B-5 outfall) and WALPOC. The range of uranium concentrations observed was evaluated for three distinct pond operating protocols:

- Condition 1 - (samples from 3/1/07 – 9/27/11): Batch mode operations at terminal dams A-4 and B-5.
- Condition 2 – (samples from 9/27/11 – 9/12/13): Flow-through operations at terminal dams A-4 and B-5, prior to the flood event in September 2013.
- Condition 3 – (samples from 9/13/13 – 5/14/14): Flow-through operations at terminal dams A-4 and B-5, during and after the flood event in September 2013.

Box plots and scattergrams for GS11, GS08 and WALPOC are provided in Appendix J, Figure J.2. Summary statistics for the evaluation are provided in Table 9, followed by an assessment of the results:

Table 9. Summary Statistics – Uranium Concentrations for Varying Site Conditions at GS08, GS11 and WALPOC

Statistic	GS11 (A-4 Outfall)			GS08 (B-5 Outfall)			WALPOC	
	Batch Release Mode	Flow-Through Mode, Pre-2013 Storm	Flow-Through Mode, Post-2013 Storm	Batch Release Mode	Flow-Through Mode, Pre-2013 Storm	Flow-Through Mode, Post-2013 Storm	Flow-Through Mode, Pre-2013 Storm	Flow-Through Mode, Post-2013 Storm
No. of observations	32	13	4	29	13	10	17	14
Minimum	3.744	4.845	1.330	5.870	5.390	4.340	3.210	1.990
Maximum	11.800	17.500	29.000	15.141	17.200	20.400	15.100	22.850
1st Quartile	5.760	8.040	8.508	7.140	5.990	8.310	7.565	15.888
Median	6.600	13.300	18.150	8.485	8.820	12.450	11.400	19.025
3rd Quartile	8.558	14.700	26.300	10.400	11.900	15.750	12.600	20.975
Mean	7.240	11.893	16.658	9.299	9.904	12.394	10.544	16.699
Standard deviation (n)	1.972	3.843	11.145	2.790	4.123	4.894	3.180	6.557
Lower bound on mean (95%)	6.518	9.476	-3.820	8.219	7.310	8.704	8.859	12.770
Upper bound on mean (95%)	7.963	14.311	37.135	10.378	12.497	16.084	12.230	20.628
Geometric mean	6.982	11.166	10.165	8.923	9.109	11.267	9.911	13.890

The statistical summary results presented in Table 9 provide a reference to evaluate the uranium concentrations historically observed at WALPOC, GS11 and GS08, under varying conditions at the site.

- GS11 (Pond A-4 outfall) – Differences between the uranium concentrations are distinct for each of the three conditions evaluated. Approximately 74 to 75 percent of the uranium passing through Pond A-4 is from natural sources.
 - Uranium concentrations for the batch-release mode (mean: 7.2 µg/L; median: 6.6 µg/L) are substantially lower compared to the flow-through mode, pre-2013 storm conditions (mean: 11.9 µg/L; median: 13.3µg/L). This indicates that a reduction of uranium concentration occurs in Pond A-4 during batch-release mode operations.

- Uranium concentrations are substantially lower in the flow-through mode, pre-2013 storm conditions (mean: 11.9 $\mu\text{g/L}$; median: 13.3 $\mu\text{g/L}$) compared to the flow-through mode, post-storm conditions (mean: 16.7 $\mu\text{g/L}$; median: 18.2). This indicates that the ongoing changed chemical conditions of the site following the September 2013 storm resulted in a higher concentration of uranium in Pond A-4 discharges compared to the pre-storm condition, to the extent that the mean concentration of discharges during the post-storm period approached 16.8 $\mu\text{g/L}$ and the median concentration exceeded that level.
- GS08 (Pond B-5 outfall) – Differences between the uranium concentrations at GS08 for each of the three conditions evaluated are not as distinct as the differences observed at GS11 (Pond A-4 outfall). Approximately 76 to 80 percent of the uranium passing through Pond B-5 is from natural sources.
 - Uranium concentrations for the batch-release mode (mean: 9.3 $\mu\text{g/L}$; median: 8.5 $\mu\text{g/L}$), while lower, are not substantially different compared to the flow-through mode, pre-2013 storm conditions (mean: 9.9 $\mu\text{g/L}$; median: 8.8 $\mu\text{g/L}$). This indicates that batch-release mode operations in Pond B-5 had a limited difference in terms of reducing uranium concentrations compared to flow-through mode operations, prior to the September 2013 storm.
 - Uranium concentrations are substantially lower in the flow-through mode, pre-2013 storm conditions (mean: 9.9 $\mu\text{g/L}$; median: 8.8 $\mu\text{g/L}$) compared to the flow-through mode, post-storm conditions (mean: 12.4 $\mu\text{g/L}$; median: 12.5 $\mu\text{g/L}$). This indicates that the ongoing changed chemical conditions of the site following the September 2013 storm resulted in a higher concentration of uranium in Pond B-5 discharges compared to the pre-storm condition, and made a larger difference in uranium concentrations in discharges than did changing pond operating protocols at Pond B-5.

- WALPOC – Differences between the uranium concentrations are distinct for the two conditions evaluated¹¹:
 - Uranium concentrations are substantially lower in the flow-through mode, pre-2013 storm conditions (mean: 10.5 µg/L; median: 11.4 µg/L) compared to the flow-through mode, post-storm conditions (mean: 16.7 µg/L; median: 19.0 µg/L). This indicates that the ongoing changed chemical conditions of the site following the September 2013 storm resulted in a significantly higher concentration of uranium at WALPOC compared to the pre-storm condition, to the extent that the mean concentration at WALPOC during the post-storm period has approached the site-specific 16.8 µg/L standard and the median value exceeded the standard. It also indicates that the uranium concentrations at WALPOC are more closely tied to Pond A-4 discharge concentrations than to Pond B-5 discharges, which is logical since the uranium load from A-4 discharges is substantially higher than the load from Pond B-5 discharges.

5.0 SUMMARY

Key points from the analyses discussed in the report are summarized below:

5.1 Chemical and Site-Specific Factors that Govern Uranium Concentration and Transport in Aqueous Environments

General Factors - Not Specific to RFS

- Uranium concentration and mobility in aqueous environments are mainly governed by four chemical processes: precipitation, complexation, sorption, and colloid formation. All of these processes can be influenced by: redox potential and dissolved oxygen, pH,

¹¹ Data from batch mode operations at WALPOC were not evaluated since monitoring at WALPOC began in September 2011 at the same time when Ponds A-4 and B-5 were switched to flow-through mode.

and water quality, which determine the aqueous speciation and dissolved/solid equilibria of uranium and thereby govern the movement of uranium in the environment.

- Redox potential determines whether uranium species occur predominantly in the sparingly soluble reduced state U(IV) or the more highly soluble oxidized state U(VI).
 - U(IV) forms relatively insoluble and less mobile uranium species such as solid uraninite (UO₂).
 - U(VI) forms more soluble and mobile uranium species such as uranyl ion, UO₂²⁺, and its complexes.
- Because redox reactions are reversible, U(VI) species that have been reduced to low solubility U(IV) species can be re-oxidized back again to soluble U(VI) species, changing former sinks for immobilized U(IV) species into sources for mobile U(VI) species.
- In water, sediments, and soils with negative redox potentials, oxidants other than oxygen, particularly nitrate, and oxyhydroxides, can restore/maintain significant levels of soluble U(VI) species.
- The solubilities and sorption strengths of different U(IV) and U(VI) species are also pH dependent.

Factors Specific to RFS

- Uranium measured in surface flows at RFS originates from several sources, including natural subsurface minerals and groundwater; groundwater from the former Solar Evaporation Ponds area, which ultimately flows to the surface and which contains both natural and anthropogenic uranium; and streambed sediments, which also are composed of both natural and anthropogenic uranium.

- When stream conditions are anaerobic, nitrate from the former Solar Evaporation Ponds area (e.g., flows exiting from SPOUT or groundwater not collected by the SPPTS) can oxidize U(IV) species to U(VI) species and mobilize uranium. This mechanism becomes much less important when groundwater and stream conditions are aerobic, such as following extreme storm events (e.g., September 2013).
- Storm events of relatively smaller magnitude, in terms of rainfall or snowmelt volume, produce different conditions in surface and groundwater at RFS than large storms. The primary result of smaller storms is dilution from surface runoff that generally lowers uranium concentrations in the Walnut Creek drainages.
- The effect of very large storms is an initial short-term dilution period caused by increased runoff which results in lower uranium concentrations in surface water. This is followed by a prolonged period with increased concentrations of dissolved oxygen which helps to mobilize and increase concentrations of uranium in surface water.
- Large storms also generate a prolonged period with a higher than normal volume of groundwater, with a higher relative concentration of uranium than surface water, flowing to the surface, which results in an extended period with elevated uranium concentrations in surface water.

5.2 RFS Data Analysis

Spatial and Temporal Variability

- North Walnut Creek
 - The uranium load measured at GS13 is approximately two times greater than the uranium load measured at upstream monitoring location SW093 (based on total loads measured at both locations from January 2010 through March 2014). Other than the relatively small contribution from the SPPTS, the source of the uranium observed at GS13 appears to be a combination of: 1) groundwater with a higher

relative uranium concentration that is not collected by the SPPTS and enters the channel upstream from GS13, 2) uranium in channel sediments located between SW093 and GS13, and/or 3) groundwater or periodic surface runoff entering North Walnut Creek from the north side of the channel.

- Flows from SPOUT are approximately 2 percent of the flow volume compared to flows at station GS13. The uranium load from SPOUT was approximately 5 percent of the uranium load measured at GS13 (based on total loads measured at both locations from January 2010 through March 2014). However, the nitrate load delivered from SPOUT was approximately 20 percent of the total nitrate load measured at GS13 for the same period.
- South Walnut Creek
 - At GS10, uranium concentrations vary widely temporally, and in a cyclical pattern, with the highest concentrations typically observed during the first two to three months each year, which supports the understanding that a larger fraction of the flow at GS10 during those months is attributed to groundwater
 - The uranium load is substantially higher at GS10 than at B5INFLOW (the next monitoring location downstream), indicating that uranium removal occurs between those two locations.
- WALPOC - Measured uranium concentrations were below the 16.8 µg/L standard until the September 2013 flood event, after which multiple samples were measured above the standard (see Figure B.17). Not until May 2014, approximately eight months after the September 2013 flood event, did sample results return to concentrations below the 16.8 µg/L standard (three consecutive sample results at WALPOC, from 5/12/14 through 5/21/14, had concentrations below 16 µg/L).

Meteorological Effects

The effects of the September 2013 event persisted (with an apparent slow return to pre-storm conditions) for approximately 8 months. The extended period of increased groundwater flow to surface water created an abnormally higher fraction of groundwater relative to surface runoff water in stream flows for a prolonged period compared to normal seasonal trends. Data indicate that the effects from the groundwater pulse, in terms of uranium concentrations in surface water, began to subside in Walnut Creek in May 2014.

Anthropogenic Versus Natural Uranium

- In North Walnut Creek, progressing from upstream to downstream, the fraction of natural uranium at SW093 (approximately 90 percent natural) decreases at GS13 (approximately 71 to 75 percent natural), reflecting inputs of anthropogenic uranium from potentially multiple sources (i.e., SPOUT discharges, groundwater that is not collected by the SPPTS and/or channel sediments with anthropogenic uranium). Further downstream, the fraction of natural uranium increases in discharges from Pond A-4 (74 to 75 percent natural) compared to locations upstream in North Walnut Creek.
- In South Walnut Creek, progressing from upstream to downstream, the fraction of natural uranium decreases then increases. From FC4EFF, in the upstream portion of the drainage (approximately 71 to 74 percent natural) the natural uranium decreases downstream at station GS10 (which fluctuates broadly, ranging from 43 to 78 percent natural). GS10 may reflect inputs from the SEEP995A area (an off-channel seep, which fluctuates more broadly than other locations, and which ranges from 60 to 68 percent natural uranium); GS10 isotopic data also reflect an inverse relationship between natural uranium percentage and uranium concentration. Downstream from GS10 at Pond B-5, the natural uranium percentage increases, ranging between 76 and 80 percent natural.
- At WALPOC, the variability in the range of uranium concentrations is not primarily a function of changes in the fraction of anthropogenic uranium. The percentage of

anthropogenic uranium at WALPOC does not vary substantially with changes in measured uranium concentrations.

- The percentage of natural uranium in WALPOC samples has ranged from approximately 75 to 83 percent, with an average value of 78 percent, based on 21 samples analyzed from September 2011 through April 2014. The isotopic uranium samples collected from WALPOC, collected throughout the existence of monitoring at WALPOC, have been collected during climatic conditions ranging from the driest year (2012) to the wettest month (September 2013) recorded at RFS since 1993.
- Isotopic data collected from samples following the September 2013 flood period indicate that, during this period, the percentage of natural uranium decreases slightly when concentrations of total uranium increase, at specific locations (based on limited data). This suggests that previously immobile anthropogenic uranium sources were mobilized during and following the flood event. A potential explanation is that a rising groundwater table might contact anthropogenic uranium that previously existed above the pre-storm groundwater level.
- Groundwater samples analyzed at LBNL for isotopic composition indicate a broad range of anthropogenic uranium fractions. However, when comparing the more recent isotopic results with prior isotopic sample results, the more recent results do not provide information that indicates a previously unknown source of anthropogenic uranium in groundwater.

5.3 Site Operations Effects on Uranium Concentrations

SPPTS Operations

- The uranium load contributed from the SPPTS effluent at SPOUT was approximately 5 percent of the uranium load measured at GS13 based on data from January 2010 through March 2014. During time periods when the SPPTS has been least effective removing

uranium, there has not been a corresponding increase in uranium concentrations downstream at GS13, further supporting the understanding that flows from SPOUT do not have a substantial effect on uranium concentration in North Walnut Creek.

- In comparison with SPOUT, a more significant source of anthropogenic uranium in North Walnut Creek appears to come from groundwater from the former Solar Evaporation Ponds area that is not collected by the SPPTS. The effect of anthropogenic uranium in groundwater not collected by the SPPTS is reflected at station GS13 and at other monitoring locations further downstream. All of these downstream locations contain substantially less natural uranium (approximately 75 percent) compared to the upper part of the drainage, as measured at SW093, which has approximately 90 percent natural uranium.
- Although the water volume discharged from SPOUT is minor compared to the flows in the main North Walnut Creek channel (SPOUT flows were approximately two percent of the flow volume compared to station GS13), because of the high nitrate concentration in SPOUT discharges, the nitrate load delivered from SPOUT was approximately 20 percent of the total nitrate load measured at GS13 based on data from January 2010 through March 2014. This is an appreciably larger fraction of the nitrate load in North Walnut Creek contributed by SPOUT compared to the fraction of uranium load contributed by SPOUT.

Pond A-4 and B-5

Box-plots and scattergrams were developed to provide a statistical summary for evaluating uranium data at surface water monitoring locations GS11 (Pond A-4 outfall), GS08 (Pond B-5 outfall) and WALPOC. The range of uranium concentrations observed was evaluated for three distinct pond operating protocols and site conditions: 1) Batch mode, 2) Flow-through operating mode, pre-2013 flood, and 3) Flow-through operating mode, post-2013 flood. Results of the analysis indicate:

- Pond A-4 - Uranium concentrations for the batch-release mode (mean: 7.2 $\mu\text{g/L}$; median: 6.6 $\mu\text{g/L}$) are lower compared to the flow-through mode, pre-2013 storm conditions (mean: 11.9 $\mu\text{g/L}$; median: 13.3 $\mu\text{g/L}$), indicating that a greater reduction of uranium concentration occurs in Pond A-4 during batch-release mode operations. The pond provides a reduction in the uranium concentration but not specifically to anthropogenic uranium. Approximately three quarters of the uranium in Pond A-4 is from natural sources.
- Pond B-5 - Uranium concentrations for the batch-release mode (mean: 9.3 $\mu\text{g/L}$; median: 8.5 $\mu\text{g/L}$), are comparable to the flow-through mode, pre-2013 storm conditions (mean: 9.9 $\mu\text{g/L}$; median: 8.8 $\mu\text{g/L}$), indicating that historic batch-release mode operations in Pond B-5 had a relatively limited difference on uranium concentrations compared to flow-through mode operations. Approximately three quarters of the uranium in Pond B-5 is from natural sources.

6.0 REFERENCES

- Abdel-Sabour, M.F., 2014. Uranium fixation and Removal from Different Soil Types: Review. *Journal of Nuclear Energy Science and Power Generation Technology*. 3:3. 1000126.
- Beller, Henry R., 2005. "Aerobic, Nitrate-Dependent Oxidation of U(IV) Oxide Minerals by the Chemolithoautotrophic Bacterium *Thiobacillus denitrificans*." *Applied and Environmental Microbiology* 71.4 (2005): 2170-2174.
- Brennecke, G. A., 2011, Uranium Isotope Variations in Nature: Mechanisms, Applications, and Implications, PhD. Thesis, Arizona State University.
- Buerger, S., S.F. Boulyga, J.A. Cunningham, A. Koepf, J. Poths, 2009, "The range of variation of uranium isotope ratios in natural uranium samples and potential application to nuclear safeguards." International Atomic Energy Agency, Safeguards Analytical Services, Austria, IAECA-CN-184/256.
- CDRMS (Colorado Division of Reclamation, Mining and Safety). 2014. Uranium Mining in Colorado.
- CDPHE (Colorado Department of Public Health and Environment). 2008. Colorado Radionuclide Abatement and Disposal Strategy (CO-RADS). Final Report Radionuclide Risk Assessment Analysis Report, Appendix B. Prepared by Malcom Pirnie, Inc. for CDPHE. March 2008.
- CDPHE (Colorado Department of Public Health and Environment). 2009. Colorado Radionuclide Abatement and Disposal Strategy (CO-RADS) Phase 2 and 3 Summary Report. Prepared by Malcom Pirnie, Inc. for CDPHE. March.
- CDPHE (Colorado Department of Public Health and Environment). 2012. Water Quality Control Commission. Policy 96-2. Amended October 9, 2012.

- CDPHE (Colorado Department of Public Health and Environment). 2013. Water Quality Control Commission Regulation No. 31. The Basic Standards and Methodologies for Surface Water (5 CCR 1002-31). Effective January 31, 2013.
- CDPHE (Colorado Department of Public Health and Environment). 2014. Water Quality Control Commission Regulation. Regulation 38, Classifications and Numeric Standards – South Platte River Basin, Laramie River Basin, Republican River Basin, Smoky Hill River Basin (5 CCR 1002-38). Effective June 30, 2014.
- CGS (Colorado Geological Survey). 2014. CGS website:
<http://coloradogeologicalsurvey.org/water/water-quality/>.
- Dennehy, K.F., D. W. Litke, C. M. Tate, S. L. Qi, P. B. McMahon, B. W. Bruce, R. A. Kimbrough, and J. S. Heiny, 1998. Water Quality in the South Platte River Basin, Colorado, Nebraska, and Wyoming, 1992-95. USGS Circular 1167.
- DOE (U.S. Department of Energy), 2007. Rocky Flats Legacy Management Agreement, Rocky Flats Environmental Technology Site, Golden, Colorado, February.
- Efurd, D.W., D.J. Rokop and R.E. Perrin, 1993. Characterization of the Radioactivity in Surface Waters and Sediment Collected at the Rocky Flats Facility, Final Report, Los Alamos National Laboratory, LA-UR-93-4373.
- EPA (U. S. Environmental Protection Agency), 2000. Radionuclides Notice of Data Availability Technical Support Document. Targeting and Analysis Branch Standards and Risk Management Division Office of Ground Water and Drinking Water United States Environmental Protection Agency.
- EPA (U. S. Environmental Protection Agency), 2000. Cancer Risk Coefficients for Environmental Exposure to Radionuclides. Federal Guidance Report No. 13. EPA 402-R-99-001. September 1999.
- EPA (U. S. Environmental Protection Agency), State of Colorado and DOE, 2007. Rocky Flats Legacy Management Agreement. Federal Facility Agreement and Consent Order. February 2007.

- EPA (U. S. Environmental Protection Agency), 2011. Letter dated August 4, 2011 from Carol Campbell to Peter Butler, CDPHE, regarding 2010 Revisions to the Basic Standards and Methodologies for Surface Waters.
- Hem, J.D., 1985. Study and Interpretation of the Chemical Characteristics of Natural Water. United States Geological Survey Water-Supply Paper 2254.
- Kaiser-Hill, 2002. Site-Wide Water Balance Model Report of the Rocky Flats Environmental Technology Site. May.
- Kaiser-Hill, 2005. Final Interim Measure/Interim Remedial Action for Groundwater at the Rocky Flats Environmental Technology Site. June 21.
- Kathren, R.L., 1984. Radioactivity in the Environment. Distribution and Surveillance. New York, NY: Harwood Academic Publishers, 93-115.
- Kirkham, R. M., W. J. O'Leary, J. W. Warner, 1980. Information Series 12. Hydrogeologic and Stratigraphic Data Pertinent to Uranium Mining, Cheyenne Basin, CO. Colorado Geological Survey.
- Langmuir, D. 1997, *Aqueous Environmental Geochemistry*, Upper Saddle River, Prentice Hall, Inc.
- Larimer County Environmental Advisory Board, 2008. Report on In Situ Leach and Open-Pit Mining. February.
- LANL, 2011. Thermal Ionization Mass Spectrometry Uranium Results for 2011 RFETS Waters.
- LBNL, 2013a. U Isotopic Compositions and Concentrations of Rocky Flats Water Samples Collected During 9/13/13 to 11/25/13 and Submitted to LBNL. John N. Christensen. Report date 3/20/13.
- LBNL, 2013b. U Isotopic Compositions and Concentrations of the First Batch of Rocky Flats Water Samples Submitted to LBNL. John N. Christensen. Report date 9/16/13.

- NOAA, 2013a. NOAA Atlas 14, Hydrometeorological Design Studies Center, Precipitation Frequency Data Studies Center, <http://hdsc.nws.noaa.gov/hdsc/pfds/>.
- NOAA, 2013b. Exceedance Probability Analysis for the Colorado Flood Event, 9 - 16 September 2013, Hydrometeorological Design Studies Center, National Weather Service National Oceanic and Atmospheric Administration. September 24, 2013.
- Owen, Douglass E., James K. Otton. 1992. "Mountain Wetlands: Efficient Uranium Filters - Potential Impacts." U.S. Geological Survey, MS-939, Denver, CO (1992).
- Pokharel, Rasesh, 2013. Oxidative dissolution of Bio-U(IV)O₂(s) in presence of nitrate and iron under anaerobic conditions using flow-through columns. M.S. thesis, University of California, Merced, 60 p.
- Silva, RJ and Nitsche, H, 1995. Actinide Environmental Chemistry. *Radiochimica Acta*, **70/71**, 377-396.
- SN3, 2014. Verbal communication with SN3 personnel (G. Squibb).
- Todorov, P.T; E.N. Illieva, 2006. Contamination with Uranium from Natural and Anthropological Sources, Rom. Journal of Physics, 51: 27-34.
- TRSL (The Royal Society London), 2001. The Health Hazards of Depleted Uranium Munitions, Part I. The Royal Society London.
- UNSCEAR (United Nations Scientific Committee on the Effects of Atomic Radiation), 1993. Report to the General Assembly, with scientific annexes, New York.
- Wu, Wei-Min, Jack Carley, Stefan J. Green, Jian Luo, Shelly D. Kelly, Joy Van Nostrand, Kenneth Lowe, Tonia Mehlhorn, Sue Carroll, Benjaporn Boonchayanant, Frank E. Löffler, David Watson, Kenneth M. Kemner, Jizhong Zhou, Peter K. Kitanidis, Joel E. Kostka, Philip M. Jardine and Craig S. Criddle, 2010. Effects of Nitrate on the Stability of Uranium in a Bioreduced Region of the Subsurface. *Environmental Science Technology* 44.13 (2010): 5104-5111. doi: 10.1021/es1000837).

- Weiner, E. R. 2013. Applications of Environmental Aquatic Chemistry. A Practical Guide. Third Edition. CRC Press. Boca Raton, FL.
- Zaenker, Harald, Kai-Uwe Ulrich, Kai-Uwe Ulrich, Karsten Opel and Vinzenz Brendler, 2007. The Role of Colloids in Uranium Transport: a Comparison of Nuclear Waste Repositories and Abandoned Uranium Mines. IMWA Symposium 2007: Water in Mining Environments, R. Cidu & F. Frau (Eds), 27th - 31st May 2007, Cagliari, Italy.
- Zielinski, R. A., J.K. Otton, R.R. Schumann, and L. Wirt. 2007. Uranium in Surface Waters and Sediments Affected by Historical Mining in the Denver West 1:100,000 Quadrangle, Colorado. Scientific Investigations Report 2007-5246. United States Geological Survey.

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