A Study of Uranium and Arsenic in the Treasure Valley Aquifer System, Southwestern Idaho

Year 1, 2017-2018

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IDWR

Contents

1 Executive Summary

The Treasure Valley Aquifer System (TVAS) in southwestern Idaho contains well-documented uranium and arsenic concentrations over the U.S. Environmental Protection Agency (EPA) maximum contaminant levels (MCL) of 30 $\mu g\ L^{-1}$ and 10 $\mu g\ L^{-1}$, respectively (EPA, 2009). The area is home to over 630,000 people, and the population is projected to reach 1.5 million by 2040 (Bartolino and Vincent, 2017; SPF Water Engineering, 2016). As the majority of the region's domestic and municipal water use is sourced from the aquifer system, the Idaho Department of Water Resources (IDWR) has deemed it important to have current and robust knowledge of the spatial and temporal extent of uranium and arsenic in the groundwater (Bartolino and Vincent, 2017). Previous studies have characterized a possible source for uranium (Hansen, 2011) and a source mechanism for arsenic (Busbee et al., 2009), but each was completed using small datasets, limiting the spatial and temporal conclusions and management recommendations regarding the contaminants.

In this study, the spatial and temporal characterization of the contaminants and the source and release mechanism of uranium are investigated, with the goal of developing well monitoring and construction recommendations. Uranium is the primary focus of this study, however, arsenic distributions in the TVAS and its correlation with uranium will be explored. The first year of the study has been completed, with a focus on various pre-determined tasks requested by IDWR as well as other constituent exploration-based activities. Task-related work included literature review, water quality dataset compilation, point coverage maps of water quality constituents, and cross section construction, while other activities included uranium redox score generation, basic statistics of compiled datasets, and completion of a thesis proposal associated with Boise State University.

Following the completion of Year 1 activities and tasks, several key observations can be made involving uranium and arsenic in the TVAS.

1. A large water quality dataset has been compiled that includes well sample measurements of uranium, arsenic, alkalinity, nitrate, and other water quality constituents. The compiled dataset contains information with a wide range of locations spread throughout Treasure Valley and at a variety of depths.
2. Preliminary results indicate several spatial characteristics of uranium in the TVAS; uranium is present at high concentrations and with high variability, geographic hotspots of high uranium concentrations appear to be present, and high concentrations seem to be associated with shallow depths within the aquifer.
3. High uranium concentrations appear to be associated with oxidizing environments in the TVAS, decreasing to below the MCL in reducing environments.

The knowledge gained in this study will provide IDWR and other natural resource managers in the Treasure Valley with groundwater management recommendations that will inform decisions with implications in public health, land development, and domestic and municipal water quality. The key observations from the first year of this study will be further explored and will lead the direction of the study in Year 2.

2 List of Figures

3 Introduction

Elevated levels of uranium and arsenic in drinking water represent a global water quality issue. Arsenic is typically present in natural waters at a range of < 0.5 µg L^{-1} to 5000 µg L^{-1}, and elevated concentrations can be found in groundwater around the globe (Smedley and Kinniburgh, 2002). Uranium groundwater concentrations commonly range from < 0.1 µg L^{-1} to 100 µg L^{-1} (Siegel and Bryan, 2005). The health effects connected to consumption of uranium include increased cancer risk and kidney toxicity, and of arsenic include skin damage, circulatory system complications, and increased cancer risk (EPA, 2009). In the United States, the contaminants are regulated by the US Environmental Protection Agency (EPA) with a maximum contaminant level (MCL) of 30 µg L^{-1} for uranium and 10 µg L^{-1} for arsenic.

The Treasure Valley Aquifer System (TVAS) in western Idaho contains documented uranium and arsenic concentrations, up to 110 µg L^{-1} and 120 µg L^{-1}, respectively (Hansen, 2011; Busbee et. al., 2009). The contaminants historically show elevated concentrations with high spatial variability throughout the region.

The goal of this study is to explore the nature of uranium in the TVAS with a focus on the identification of spatial or temporal trends, correlation with constituents such as arsenic, and the development of management recommendations for the use of IDWR and other water managers in the Treasure Valley.

Year 1 activities focused the completion of the critical initial steps of the study: (1) Water quality dataset compilation and (2) Exploration of the spatial and temporal characteristics of uranium and arsenic in the TVAS. These initial steps are designed to lead the direction of the remainder of the study with informed hypotheses and adequate water quality data. The majority of the tasks and activities listed below have been completed, with the remaining tasks and activities continuing into Year 2.

3.1 Literature Review

Uranium and arsenic in the TVAS have been the focus of studies by Idaho government organizations and academic institutions for several decades. Substantial work has been completed documenting the source, source release mechanism, and spatial nature of each contaminant.

3.1.1 Uranium and Arsenic Sources

Potential sources of elevated concentrations of uranium in the Treasure Valley Aquifer System and associated surface waters have been explored in several different studies (Hansen, 2011; Cosgrove and Taylor, 2007). Uranium is likely leached from surficial sediments by irrigated water and further mobilized via subsequent complexation with carbonates (Hansen, 2011).

Arsenic in the TVAS tends to be largely limited to shallow, oxidizing waters, and the likely source is surficial sediments with substantial amounts of water soluble arsenic (Busbee et. al., 2009).

3.1.2 Uranium Source Release Mechanism

The presence and concentration of dissolved uranium in groundwater can be attributed to the system's redox status, presence of complexing agents, sorption capability, or direct contact with a uranium source (Hansen, 2011).

In oxidizing natural waters, uranium is commonly present in its U(VI) form as a uranyl oxycation, UO_2^{2+} or UO_2OH^+, and reacts with aqueous anions and cations to form complexes that can greatly affect the nature of the contaminant in a given system (Hansen, 2011; McKinley et. al., 2007). The specific uranium complexes that form, such as UO_2F^- or $UO_2(CO_3)_2^{2-}$, are dependent on the pH and specific geochemistry of the water (Fetter, 1992). Uranium in carbonate-rich, oxidizing waters at mid to high pH readily forms uranyl-carbonate complexes, increasing the mobility and dissolved concentrations of uranium, while decreasing its adsorption to mineral surfaces (Cumberland et. al., 2016; Stewart et. al., 2008).

3.1.3 Arsenic Source Release Mechanism

Arsenic is typically present in groundwater systems as two inorganic species dictated by redox status, arsenite (+3 redox state) and arsenate (+5), each hydrolyzed in aqueous solutions to form oxyanions (Hagan, 2004; Busbee et. al., 2009). Arsenite oxyanions are the more mobile species at the pH of natural waters, as the lower charge resists adsorption to aquifer sediments (Hagan, 2004). The specific species' presence depends on the oxidizing or reducing nature of the water, which also generally dictates the source release mechanism and abundance of the contaminant in natural waters. Reductive dissolution, in which arsenic-laden sediments in reducing environments release the reduced arsenite species into the groundwater, is the among the most commonly cited release mechanisms in arsenic-contaminated waters (Busbee et. al., 2009; Smedley and Kinniburgh, 2002; Erbs et. al., 2010).

Busbee et. al. (2009) documented a robust release mechanism for arsenic, characterized by leaching of surficial sediments due to increased infiltration spurred by the onset of irrigation in Treasure Valley. Prior to the onset of irrigation in the Treasure Valley, arsenic in surficial sediments was relatively stable, with limited transportation to greater depths and transferred to iron oxides. Since the onset of irrigation, arsenic has been mobilized by increased infiltration in the oxidizing waters of TVAS (Busbee et. al., 2009). This release mechanism contrasts the common arsenic source mechanism of reductive dissolution, and in the TVAS, arsenic concentrations seem to decrease the more reducing the waters become (Busbee et. al., 2009).

3.1.4 Spatial Characterization of Uranium

The spatial characteristics of uranium in the TVAS have been presented in two main studies, Hansen (2011) and Cosgrove and Taylor (2007). Hansen (2011) used a dataset made up of samples from around 100 public water system wells and around 60 private systems to explore the spatial characterization of uranium in the Treasure Valley. Cosgrove and Taylor (2007) also explored the spatial nature of uranium in the region, mostly restricted to the spatial extent of Canyon County. Each study found widespread, elevated uranium concentrations with high spatial variability, but limited conclusions were made regarding the spatial characterization of the depth of uranium concentrations.

3.1.5 Spatial Characterization of Arsenic

The spatial characteristics of arsenic in the TVAS have been presented mainly in the study by Busbee (2009), with limited attention paid by several other studies (Neely and Crockett, 1998; Hagan, 2004). Busbee (2009) found that elevated arsenic concentrations tend to be near the water table in oxidizing waters, and the majority of arsenic concentrations from the study above the MCL of 10 $\mu g\ L^{-1}$ were within or above the sediment redox transition. Geographically, groundwater arsenic concentrations tend to be higher to the west and south of Lake Lowell and lower to the north of the lake (Busbee, 2009).

3.1.6 Geology

The TVAS resides within the western Snake River Plain, an intracontinental rift basin of Neogene age in southwestern Idaho (Woods and Clemens, 2002). The regional Snake River Plain spans the southern half of Idaho in an arcuate shape (Neely and Crockett, 1998). The western Snake River Plain basin, about 300 km long and 70 km wide and bounded by the Boise Front Foothills to the northeast and the Owyhee Foothills to the southwest, trends southeast to northwest and is filled with 2-3 km of sedimentary fill that overlies basaltic rock (Woods and Clemens, 2002; Neely and Crockett, 1998). The deep sedimentary fill in the basin is made up of the homogenous mudstones of the Chalk Hills and Glenns Ferry Formations and the overlying 60 to 90 meters of interbedded silts, mudstones, and sandstones of the Glenns Ferry and Pierce Park Formations, formed in an active rift environment consisting of the episodic formation and drainage of ancient lakes (Woods and Clemens, 2002). The shallow, overlying sediments are composed of gravels, fluvial sediments, and alluvium, formed in a fluvial dominated depositional environment (Woods and Clemens, 2002; Hansen, 2011).

A basin-wide sediment color transition from brown (overlying) to gray or blue (below) exists within the Snake River Group sediments (Petrich and Urban, 2004). This transition is referred to as the ‘sediment redox transition' in Busbee (2009) and is likely a signature from the historic water table, at which the redox environment was oxidizing above and reducing below.

3.1.7 Hydrology/Hydrogeology

The TVAS consists of a group of aquifers within the sedimentary units of the Idaho Group and the Snake River Group (Petrich and Urban, 2004). The system is generally divided into two main flow systems, a shallow, local system consisting of gravels, fluvial sediments, and alluvium; and a deep, regional system, made up of ancient lake sediments and monotonous sandstones (Hutchings and Petrich, 2002; Petrich and Urban, 2004). The general direction of groundwater flow is west, southwest, and northwest, depending on location and depth (Neely and Crockett, 1998). Recharge in the shallow aquifer system is mainly derived from seepage attributed to the canal system in the region and infiltration from agricultural irrigation, with smaller contributions coming from mountain front and tributary groundwater recharge, underflow from the Idaho batholith, and Treasure Valley precipitation (Hutchings and Petrich, 2002).

4 Year 1 Tasks and Activities

4.1 Task-Related Work

This section summarized progress on Year 1 tasks and activities.

4.1.1 *Task 1:* Review all existing publications that contain relevant data and interpretations.

Task 1 is complete. An extensive literature review has been completed of existing publications related to arsenic and uranium in the Treasure Valley Aquifer System (TVAS), summarized above in Section 3, Introduction. The literature review has provided a necessary background of the hydrology, hydrogeology, and land use of the Treasure Valley Aquifer System as well as the knowledge and study of uranium and arsenic in the system to date. Year 2 will include continued literature review to explore new sources of understanding of the dynamics of uranium and arsenic in groundwater and further exploration of the Treasure Valley Aquifer System.

4.1.2 *Task 2:* Investigate data sources with arsenic and uranium ground water results.

Task 2 is complete. Data has been gathered from DEQ, USGS, and the Statewide Program for arsenic and uranium, as well as detailed well logs and water chemistry data from the City of Meridian. Additional data will be gained by sampling IDWR-affiliated and municipal wells in data deficient areas.

4.1.3 *Task 3:* Compile key water quality data into an electronic database.

Task 3 is complete. Water quality data have been compiled into three separate databases using MS Excel and ArcGIS relating to the source (IDWR, DEQ, and USGS in Figures 1, 2, & 3, respectively).

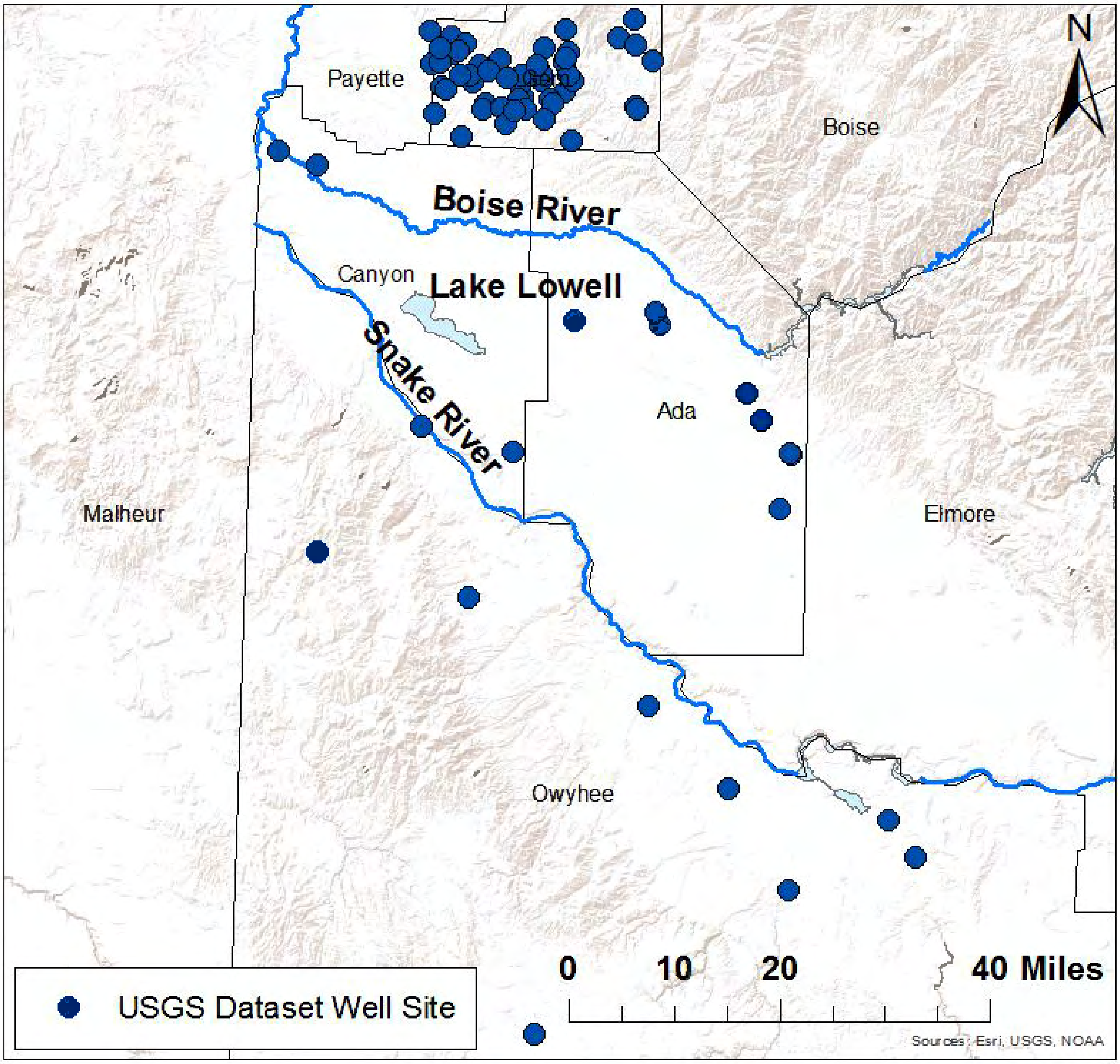

***Figure 1**: Well sites included in the USGS uranium dataset.*

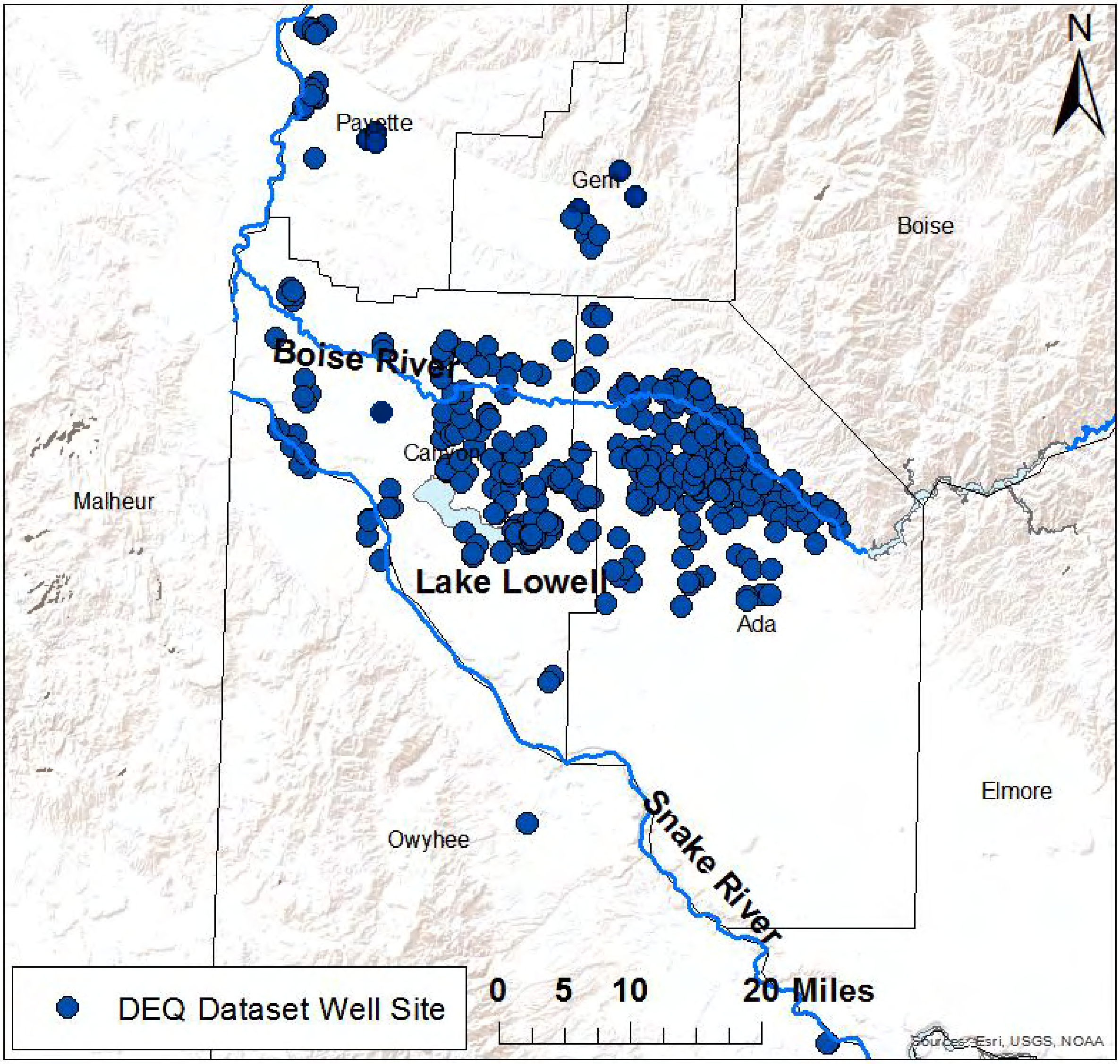

***Figure 2**: Well sites included in the DEQ uranium dataset.*

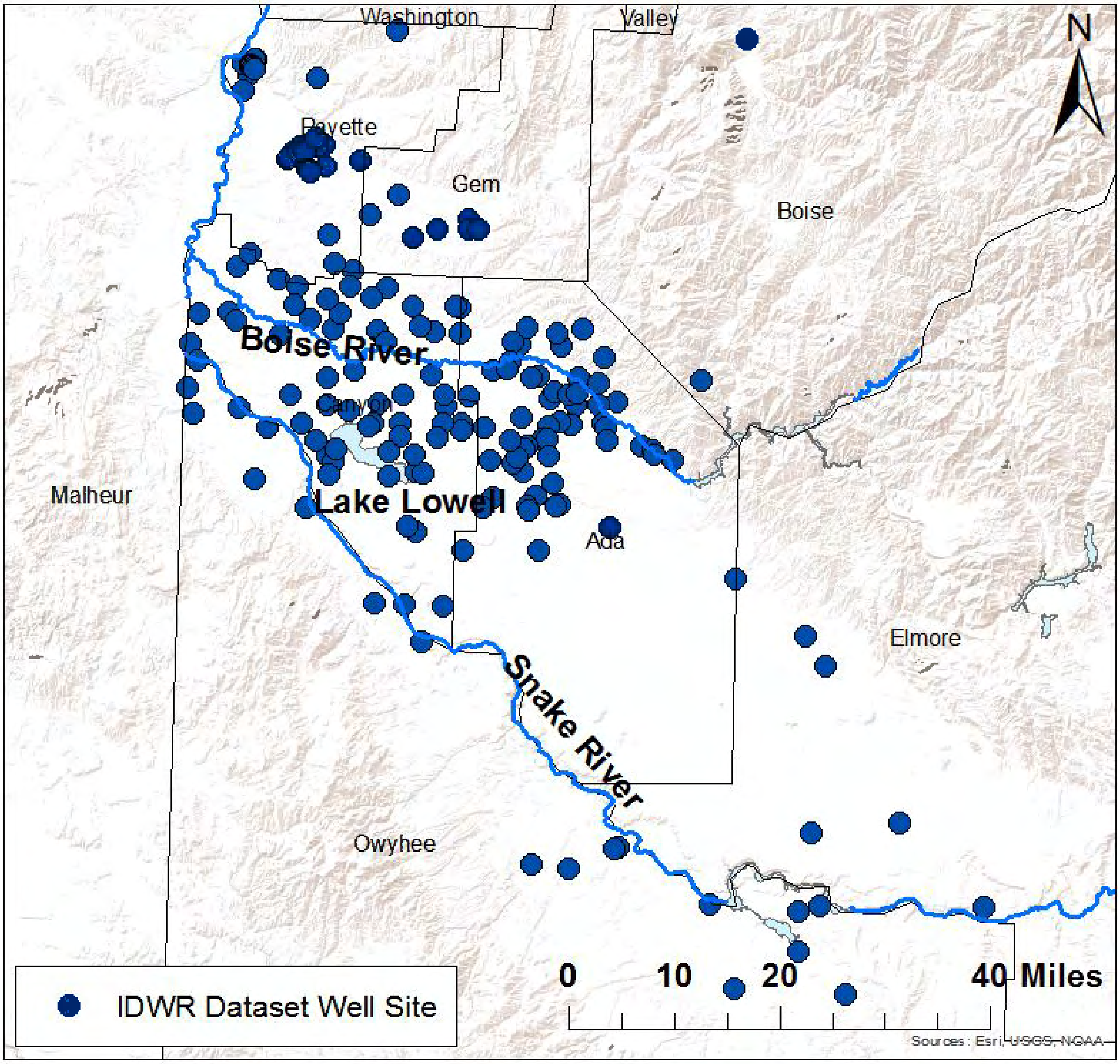

***Figure 3**: Well sites included in the IDWR uranium dataset.*

4.1.4 *Task 4:* Match well driller's reports with water quality records in the database.

Task 4 is complete. Well logs have been gathered with water quality records to explore constituent correlation with depth and for cross section construction. Task 4 will continue into Year 2 with new cross sections and exploration of the role of stratigraphy on uranium and arsenic transport.

4.1.5 *Task 5:* Evaluate the quality of wells for assessing contamination

Task 5 is complete, though modified. Well driller reports have been extensively reviewed and assessed for their utility in providing insight into the subsurface nature of arsenic and uranium in the TVAS. The well driller reports were not specifically ranked, but various factors were used to assess whether the information presented was accurate and useful. Such factors included: presence of screened interval and sufficient casing, detailed stratigraphic log, legibility, and information about water table elevation.

4.1.6 *Task 6:* Create point coverage maps of wells and water quality results.

Task 6 is complete. Point coverage maps have been created for arsenic, uranium, nitrate, alkalinity, and other water quality constituents using ArcGIS (e.g., Figure 4). These maps will provide important insight into the spatial distribution of the contaminants and will inform future hypotheses to explore.

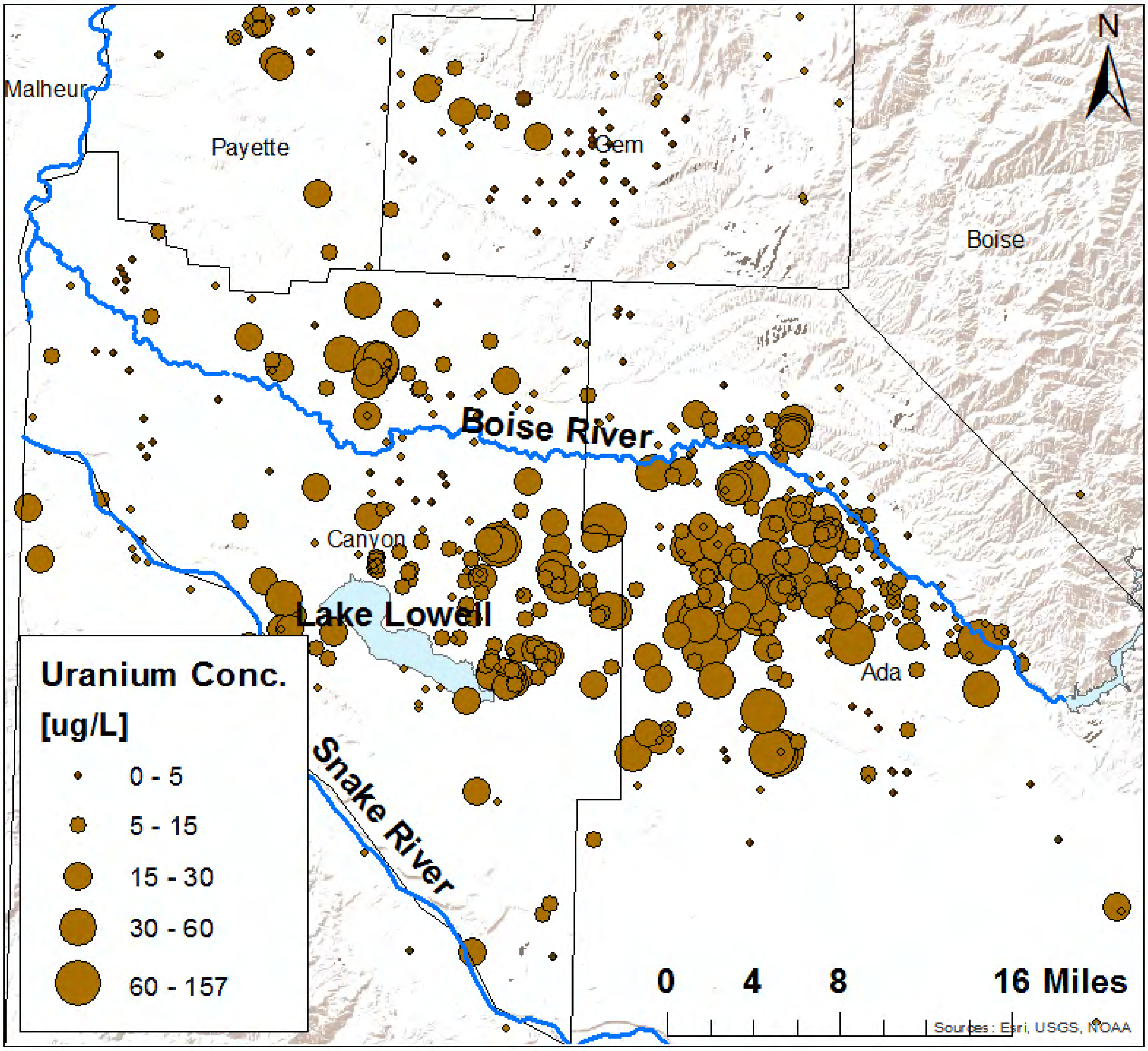

Figure 4: Point coverage map of average uranium concentrations in the Treasure Valley Aquifer System (1991-2017).

4.1.7 *Task 7:* Create cross sections showing water quality results and well construction.

Task 7 is in progress. Four cross sections have been completed (Figures 5, 6, 7, 8, & 9) and will continue to be constructed as needed in the coming year. These sections will provide important insight into the nature of uranium and arsenic in the TVAS, specifically when considering the association of elevated levels of the contaminants with the sediment redox transition.

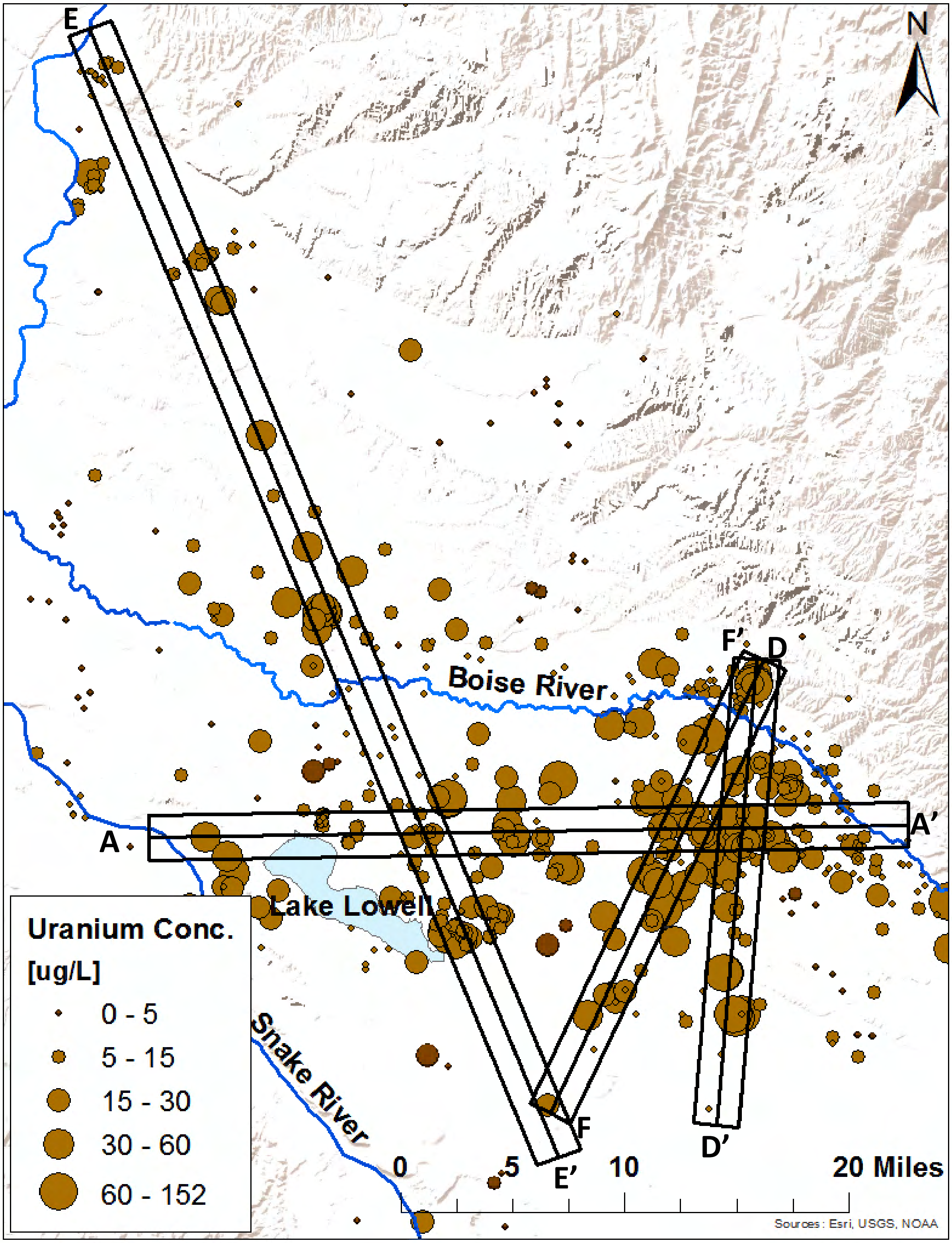

***Figure 5**: Orientation and layout of cross sections created for the study. Each section line has a one-mile buffer used to maximize data used in cross section construction.*

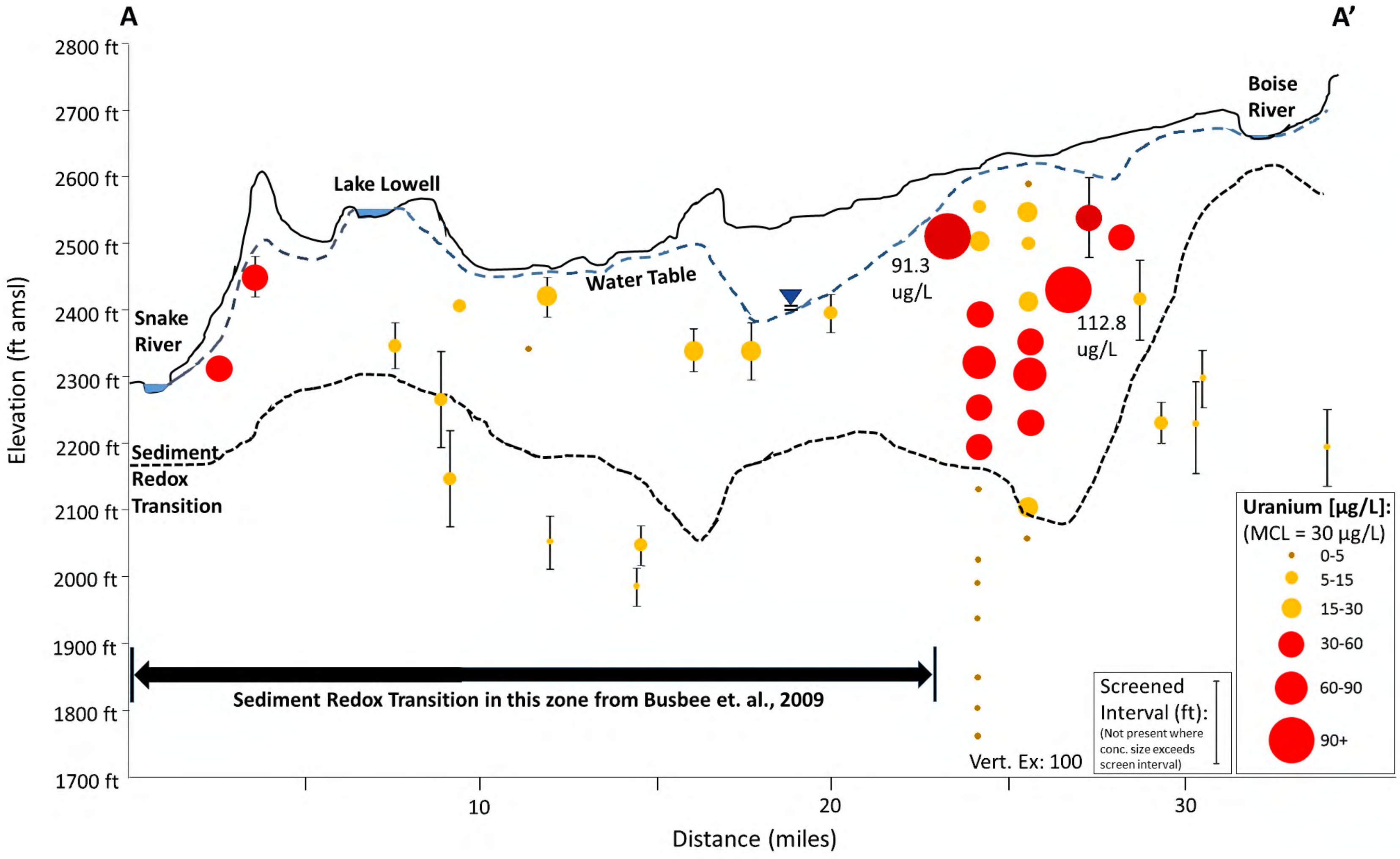

***Figure 6**: Cross Section A-A' showing uranium concentrations and the correlating water table and Sediment Redox Transition. The Sediment Redox Transition from Busbee (2009) where indicated by black arrows, otherwise interpolated using the depth of the blue clay layer in the corresponding well logs.*

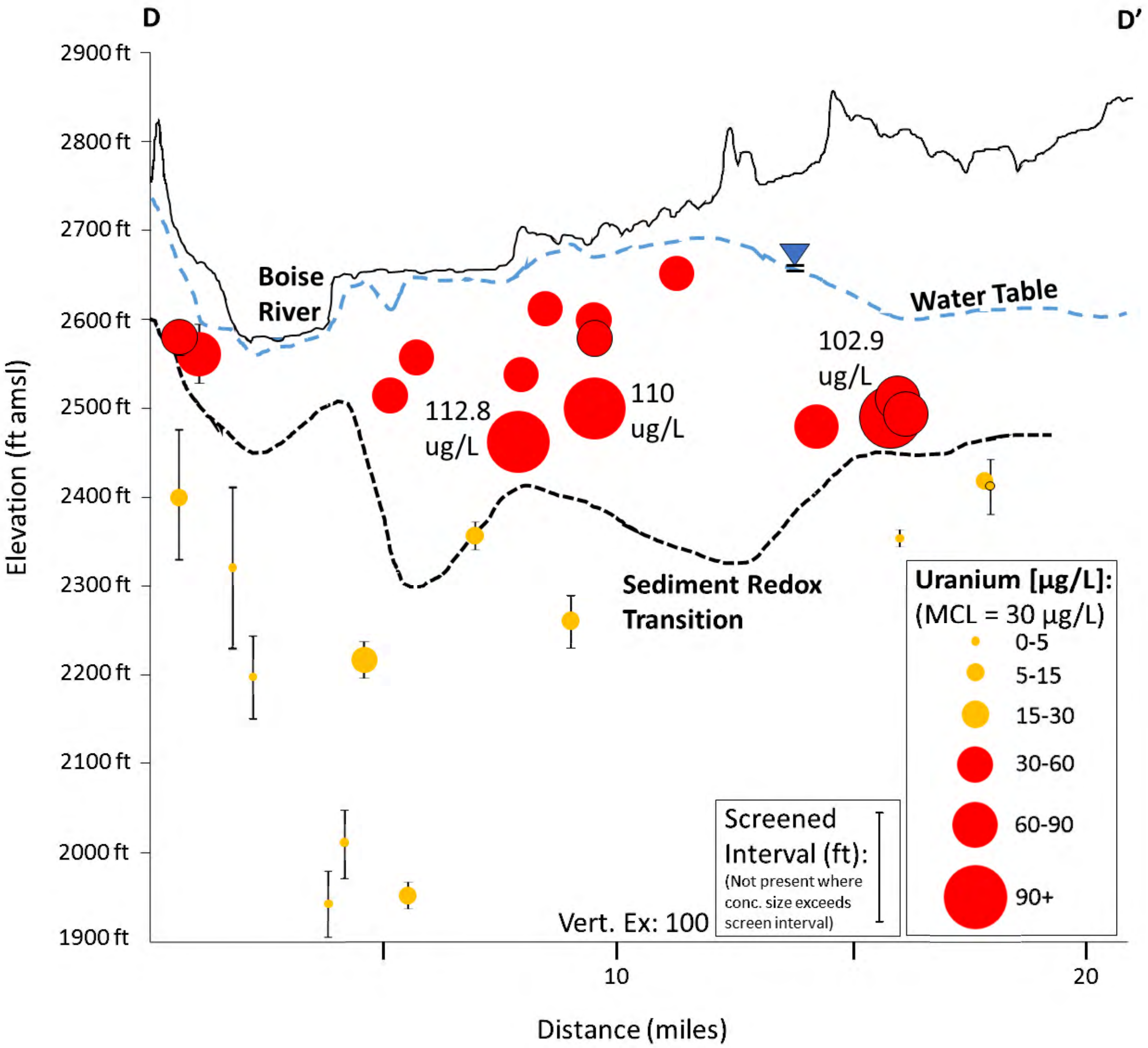

Figure 7: *Cross Section D-D' showing uranium concentrations and the correlating water table and Sediment Redox Transition. The Sediment Redox Transition has been interpolated using the depth of the blue clay layer in the corresponding well logs.*

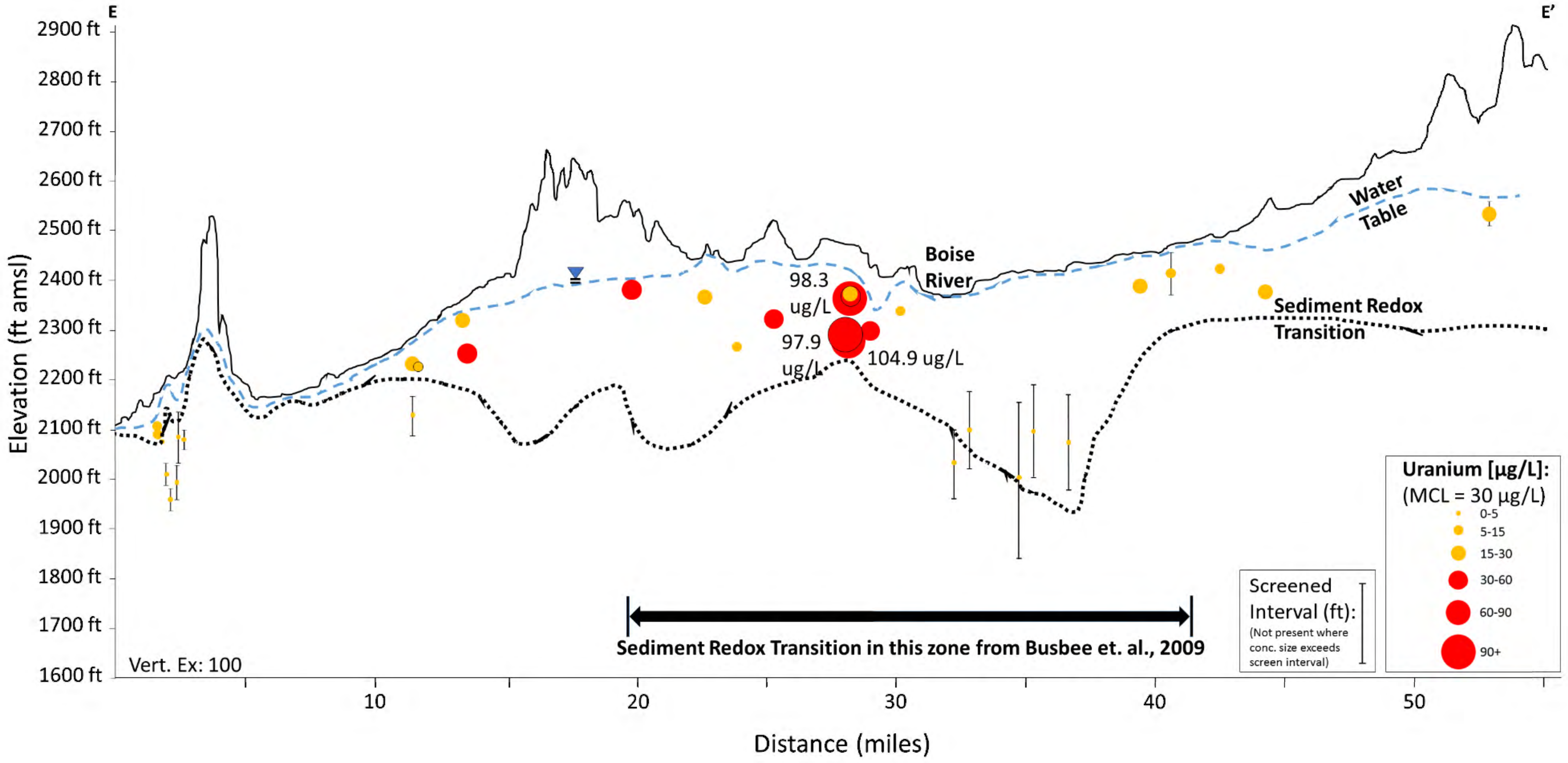

***Figure 8**: Cross Section E-E' showing uranium concentrations and the correlating water table and Sediment Redox Transition. The Sediment Redox Transition from Busbee (2009) where indicated by black arrows, otherwise interpolated using the depth of the blue clay layer in the corresponding well logs.*

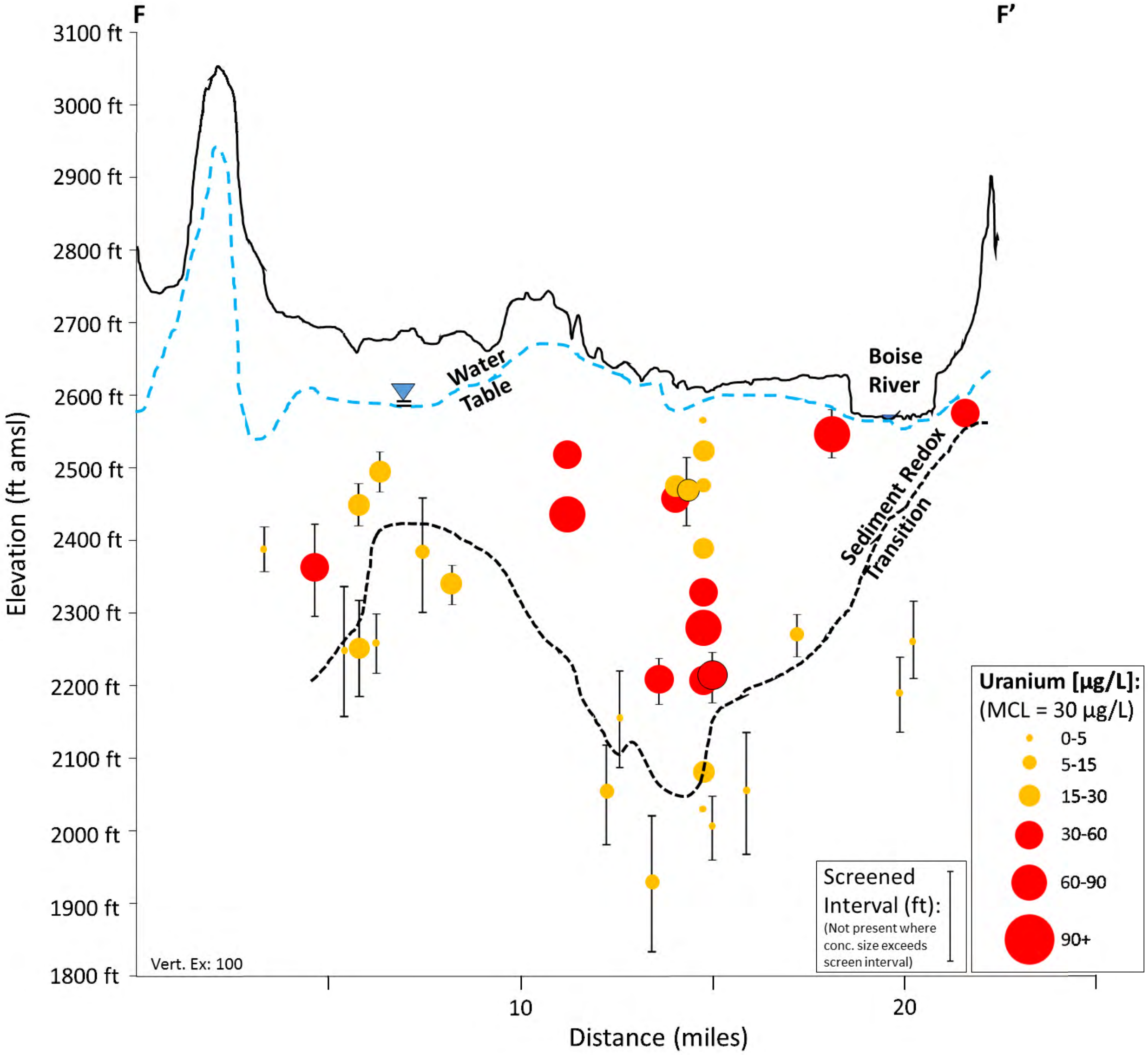

Figure 9: *Cross Section F-F' showing uranium concentrations and the correlating water table and Sediment Redox Transition. The Sediment Redox Transition has been interpolated using the depth of the blue clay layer in the corresponding well logs.*

4.1.8 *Task 8:* Using the maps and cross sections, identify locations needing additional testing.

Task 8 is in progress. Specific geographic locations and stratigraphic intervals have been identified that require additional testing to inform the nature of uranium and arsenic in the groundwater. Such areas include near the City of Caldwell and at depths greater than the sediment redox transition.

The process of deciding locations for further testing will need to consider three questions: (1) Where are well data limited horizontally and vertically? (2) Where are the areas with the highest population density? (3) Where are the areas with high domestic well density? Answering these questions will allow the selection of locations in which further testing will aid in understanding uranium and arsenic in the aquifer system and highlight areas of concern when considering human health.

4.1.9 *Task 9:* Identify wells for possible sampling.

Task 9 is in progress. Following the completion of the identification of geographic areas and stratigraphic intervals that need additional testing, Task 8, applicable wells will be identified to fill the data gaps.

5 Further Activities

This section describes notable activities undertaken that are not described under specific tasks.

5.1 Development of a Redox Score to Help Delineate Uranium Contamination

IDWR Statewide Ambient Monitoring data were used to create a redox score correlating to each uranium sample based on scoring criteria borrowed from Busbee (2009). The criteria are gleaned from water chemistry data using constituents commonly indicative of redox status: O_2, NO_3, Fe, Mn, and NH_3. The following criteria each result in a (+1) to the overall redox score, indicating an oxidizing environment: (1) dissolved oxygen (O_2) greater than 0.5 mg/L and (2) combined nitrate/nitrite (NO_3/NO_2) greater than 0.5 mg/L. The following criteria each result in a (-1) to the overall redox score, indicating a reducing environment: (1) ammonia (NH_3) concentrations greater than nitrate/nitrite concentrations, (2) dissolved iron (Fe) greater than 100 µg/L, and (3) dissolved manganese (Mn) greater than 50 µg/L. For each groundwater uranium sample the redox score is summed up, providing insight into the sampled environment: the more negative a score, the more reducing the environment (Figure 10). Uranium concentrations are only used in Figure 10 if all five redox scoring criteria are present in the corresponding water quality data.

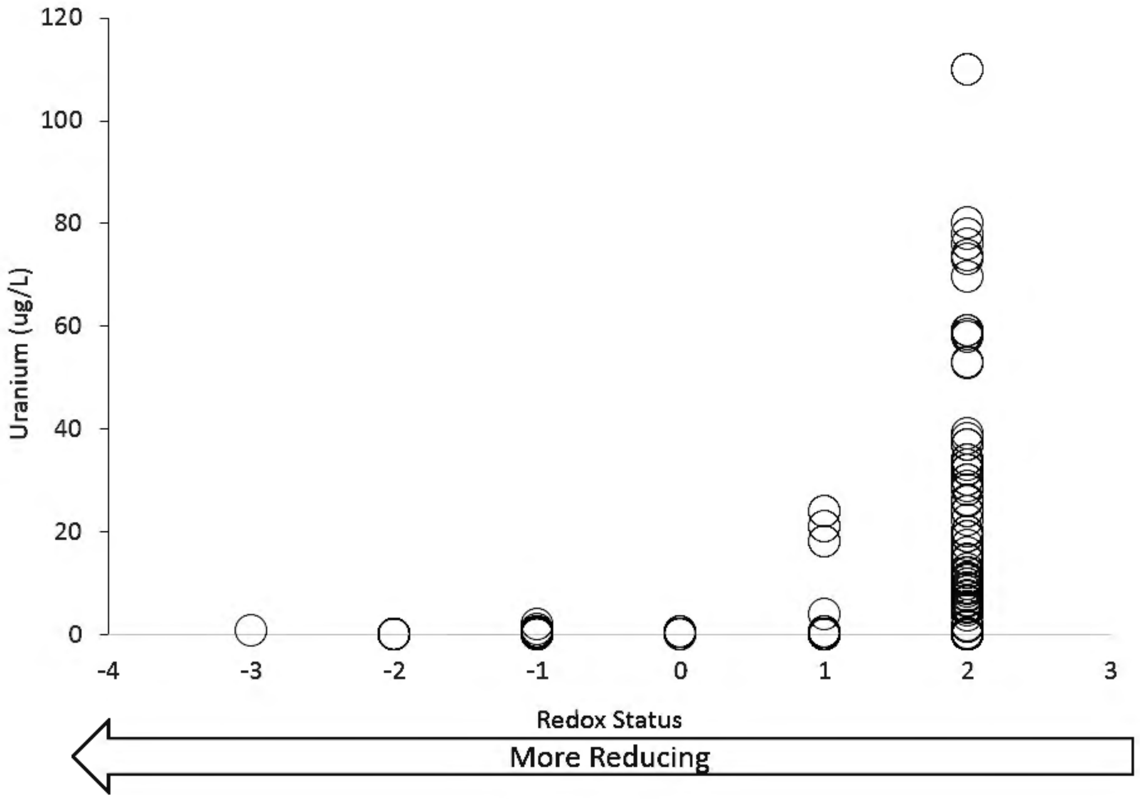

Figure 10*: Total dissolved uranium concentration and the correlating aqueous redox status. Samples from IDWR dataset, 1991-2017.*

5.2 Basic Statistics

Basic statistical tests have been performed on the current IDWR and DEQ datasets. Moving forward, complex statistical analyses will be instituted using the R statistical packages, guidance from Dr. H.P. Marshall at Boise State University, and examples provided by USGS, IDWR, and other research institutions.

5.3 Thesis Proposal and Write-up

Gus Womeldorph presented his thesis proposal in early April 2018 and completed the corresponding thesis write-up, a requirement for the M.S. in Hydrologic Sciences at Boise State University. The write-up includes in-depth background knowledge of uranium and arsenic in the TVAS (see ‘Literature Review’ in the Introduction), and a project “roadmap” with a detailed research plan and expected results.

5.4 Digitization of Sediment Redox Transition Surface

The sediment redox transition surface shown in Busbee (2009) has been redigitized in order to better use the information for this study (Figure 11). This surface may provide important insight into the nature of uranium in the TVAS and has aided in cross section construction.

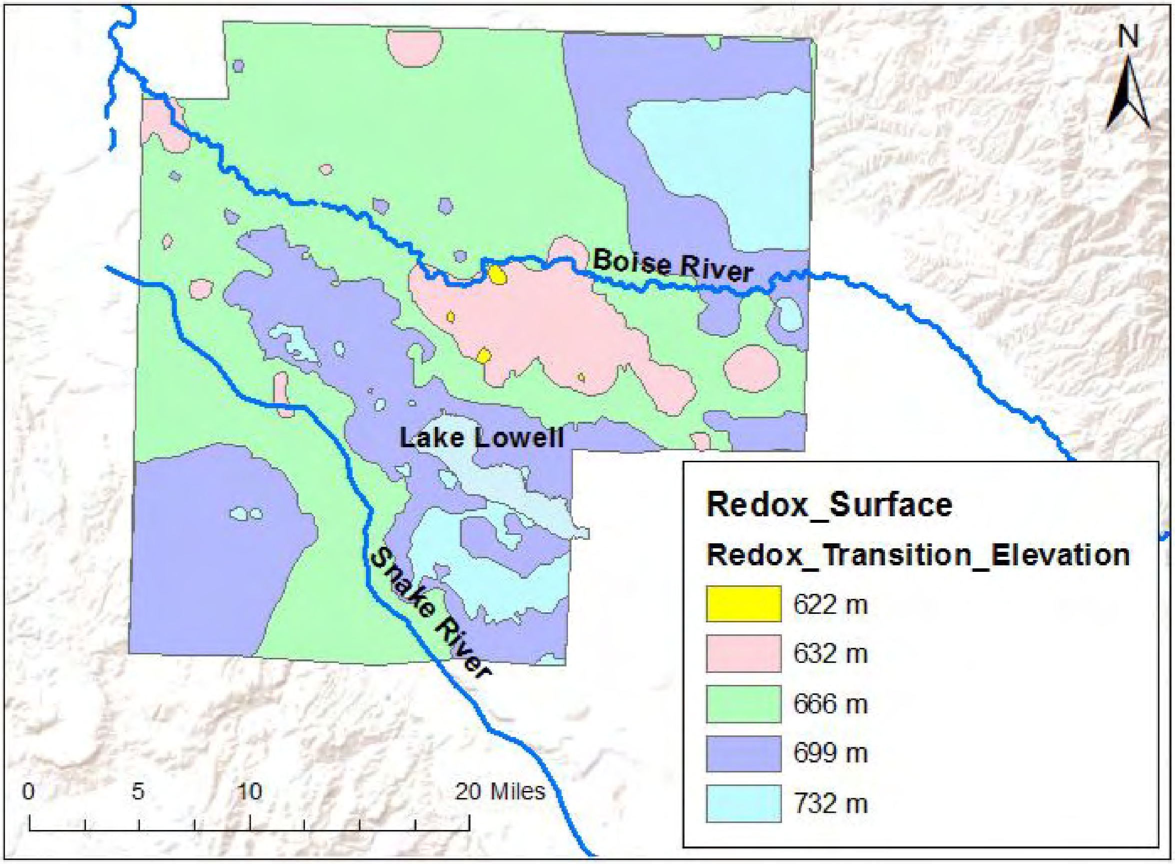

***Figure 11**: Redigitization of the Busbee (2009) sediment redox transition in the Treasure Valley Aquifer System.*

6 Observations and Future Work

6.1 Large Compiled Dataset

A large water quality dataset has been compiled from three organizations, USGS, DEQ, and IDWR, with data on various constituents including uranium, arsenic, alkalinity, and nitrate, among others. The data represent wells from five counties in the Treasure Valley (Ada, Canyon, Gem, Owyhee, and Payette) from a large variety of depths below ground surface. The temporal scale of the dataset ranges from over 50 measurements in a well over a 20-year span to just one measurement in a well. This information will allow for detailed investigations into the nature of uranium and arsenic in the TVAS, both spatially and temporally.

6.2 Spatial Characteristics of Uranium Concentrations

The spatial distribution of uranium concentrations in the Treasure Valley Aquifer System are highly variable and cover a range of values, from non-detect to greatly exceeding the MCL of 30 µg/L. High uranium concentrations appear to be present in hotspots throughout the Treasure Valley, such as in the Boise-Meridian metro area. There also appears to be a relationship between high uranium concentrations and shallow zones of the TVAS. Further study will use statistical analyses to provide evidence behind any possible spatial patterns and to gain a greater understanding of the spatial characteristics of uranium concentrations in the TVAS.

6.3 Redox Status and Uranium Concentrations

One key observation made following Year 1 activities is there appears to be an association with uranium concentrations and the redox status of the aquifer environment (oxidizing or reducing). The completed cross sections (Figures 5, 6, 7, 8, & 9) and the graph of uranium concentration redox status (Figure 10) may indicate that uranium concentrations greater than the MCL of 30 µg/L typically occur in oxidizing environments. This observation is consistent with the conclusions found in previous groundwater uranium studies from around the globe (Cumberland et. al., 2016; Hansen, 2011; Stewart et. al., 2008).

Further investigations will attempt to validate this observation using statistics and inclusion of newly gathered water quality data.

6.4 Treasure Valley Aquifer System Uranium and Arsenic Study, Year 2

Year 2 of the Treasure Valley Aquifer System Uranium and Arsenic study will consist of three main activities: (1) Identification of data gaps and subsequent collection of new water quality data, (2) statistical analysis of possible spatial and temporal trends of uranium and arsenic in the TVAS, (3) continued exploration of the activity and nature of uranium and arsenic in the TVAS, and (4) management recommendations.

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