

Environmental Sciences Laboratory

Analysis and Geochemical Modeling of Vanadium Contamination in Groundwater New Rifle Processing Site, Colorado

July 2010



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Abbreviations

ACL	alternate concentration limit
AFO	amorphous ferric oxyhydroxide
COCs	contaminants of concern
DOE	U.S. Department of Energy
GCAP	Ground Water Compliance Action Plan
ICP-MS	inductively coupled plasma mass spectrometry
ICs	institutional controls
LM	(DOE) Office of Legacy Management
µg/L	micrograms per liter
mg/kg	milligrams per kilogram
mg/L	milligrams per liter
mS/cm	millisiemens per centimeter
msl	mean seal level
ORP	oxidation-reduction potential
SOARS	System Operation and Analysis at Remote Sites
SOWP	Site Observational Work Plan
ZVI	zero-valent iron

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Executive Summary

This investigation examines the occurrence of a vanadium groundwater plume at the New Rifle Processing Site. Project documents indicate that vanadium is the only contaminant that will not flush in the 100-year time frame regulated for natural flushing. Groundwater compliance at the site is regulated through the Ground Water Compliance Action Plan (GCAP). The draft GCAP proposes an alternate concentration limit (ACL) of 50 milligrams per liter (mg/L) for vanadium, which is determined to be protective at the Colorado River point of compliance. This concentration value was selected in part because it was higher than any concentrations yet observed in groundwater samples. Institutional controls, including deed restrictions, are in place to prevent exposure to contaminated groundwater. However, the GCAP warns of possible exceedances to the ACL if the land surface is disturbed during construction activities. It was postulated that oxidation during surface disturbances could lead to desorption of vanadium, causing increased concentrations in groundwater, possibly exceeding the ACL. The City of Rifle has plans for land use that include construction activities, but deed restrictions require that these activities receive U.S. Department of Energy Office of Legacy Management (LM) approval. The current study was undertaken to better understand the nature of the groundwater vanadium system and chemical mechanisms that might cause exceedances of the ACL. The study is funded through LM's Applied Science and Technology program and covered 24 months, from February 2008 through February 2010. This project did not investigate human health or ecological risk factors associated with the groundwater vanadium plume; thus, recommendations regarding land use are not included. The goal of the project was to monitor the vanadium plume during a significant land disturbance—the construction of a wastewater treatment plant and associated aquifer dewatering—and to provide a reasonable explanation for the observed vanadium behavior. This information can then be used to update the GCAP.

In February 2008, dewatering began for installation of the wastewater treatment facility immediately east of the former mill site. Although details are lacking, it is likely that several hundred gallons per minute were pumped for 6 to 8 months. Under normal (non-pumped) conditions, groundwater at the site flows generally westerly or southwesterly subparallel to the Colorado River. Groundwater pumping for construction dewatering significantly altered this flow regime and caused groundwater to flow from the central portion of the site to the east. This dewatering event provided an opportunity to observe and evaluate modifications to the groundwater system during a construction-related disturbance.

Three new wells were installed at the eastern portion of the site to help monitor the groundwater table during dewatering. Six wells within the project area were equipped with monitoring instruments (specific conductance, water level, and oxidation-reduction potential) and connected to LM's System Operation and Analysis at Remote Sites (SOARS) network for real-time data analysis. Groundwater sampling of a network of wells was conducted at several times during the project, and an autosampler was used to track approximately weekly changes in vanadium concentrations in one of the more critical wells. Several samples of yellow-green soils that were exposed during construction were analyzed during this study. Vanadium concentrations in the yellow-green soils are high and are similar to concentrations in core samples collected at the site in 1999.

Vanadium concentrations in the groundwater exceeded the risk-based value of 0.33 mg/L in some monitoring wells. In some wells, the concentration exceeded this value by more than an

order of magnitude. One sample from well 0855 had a vanadium concentration of 1600 mg/L, the highest recorded on the site. Groundwater levels were affected by both the dewatering operation and changing water levels of the Colorado River. Influences on groundwater chemistry include influx from the Colorado River, local recharge, and contamination from the mill site. There is considerable variation in specific conductance (a measure of salt content) in some of these wells that is likely related to variable groundwater movements caused by dewatering from pumping.

One of the goals of the project was to better define the oxidation state of the groundwater. All chemical indicators of groundwater oxidation state suggest that the groundwater is oxidized relative to the vanadium system. Groundwater analyses from the entire New Rifle site form a tight cluster on a pE-pH diagram. With the exception of two points, the New Rifle groundwater data all plot in the V(+5) field suggesting that the groundwater is oxidized relative to the vanadium system.

The substantial increase in vanadium concentration to 1600 mg/L in well 0855 occurred during aquifer dewatering. The groundwater table at the time of this sampling had been drawn down to a level at which the well was nearly dry, and the small amount of water in the well was at the same elevation as a soil layer containing the highest concentration of vanadium observed at the site. The elevated concentration of dissolved vanadium is attributed to this thinning of the groundwater table, causing direct contact of a relatively small amount of water with the contaminated soil layer. When the water table is higher, the well receives groundwater that has contacted a variety of soil compositions, yielding a lower dissolved vanadium concentration.

To better understand the physical and geochemical partitioning of vanadium in the alluvial aquifer and to better predict effects that surface disturbance might have on vanadium concentrations in the groundwater system, mineral saturation indices were calculated from groundwater chemistry, and a one-dimensional transport model was developed to demonstrate geochemical interactions in the subsurface. The transport model invokes mineral precipitation, mineral dissolution, soil adsorption, and soil desorption. The model simulates chemical reactions occurring along a single stream tube as background-quality groundwater flows into the contaminated domain beneath a former mill pond. Adsorption is modeled using a surface complexation approach. The model predicts an extremely high initial effluent vanadium concentration caused by the dissolution of calcium vanadate, a highly soluble mineral. After the depletion of calcium vanadate, ferrous vanadate dissolves, yielding vanadium to solution but at a lower concentration. Finally, after ferrous vanadate is expended, desorption is the dominant process controlling aqueous vanadium concentrations. The variations observed in the modeled vanadium concentrations are consistent with the variations observed in well water samples. Dissolved uranium concentrations in the wells are much lower than the vanadium concentrations. The modeled uranium concentrations are also low due to equilibrium with uranyl-vanadate minerals. Thus, the model also helps explain the relatively low uranium concentrations detected in the New Rifle site groundwater system.

The groundwater analyses of samples collected for this study offer direct evidence that vanadium concentrations can exceed the ACL of 50 mg/L as a result of construction disturbance. Evidence presented suggests an alternate mechanism to the addition of oxygen (oxidation) as postulated in site documents. Instead, it is suggested that vanadium concentrations increase due to changing water levels that bring smaller amounts of groundwater into direct contact with vanadium-rich

soils. Most chemical indicators suggest that the aquifer is largely oxidized with respect to the vanadium system. Further oxidation would not dissolve vanadate minerals.

Vanadium at the New Rifle site is present in high concentrations in subsurface soils in a heterogeneous distribution. The soil vanadium is probably dominated by the +5 oxidation state occurring in vanadates and uranium vanadates and in vanadium adsorbed to soil particles, particularly those containing ferric oxides and oxyhydroxides. The vanadium in the soils was likely a residual from mill leachates that infiltrated the subsurface during milling and were not removed during site remediation in the early 1990s. Without removal of the vanadiferous soil layers, it is likely that vanadium concentration in the groundwater will remain at tens of milligrams per liter with occasional increases when contaminated soil layers are in more direct contact with a limited volume of groundwater.

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1.0 Introduction

This investigation examines the occurrence of a vanadium groundwater plume at the New Rifle, Colorado, Processing Site located about 2.3 miles west of the city of Rifle in Garfield County, Colorado (Figure 1). The New Rifle site was used to mill uranium and vanadium ores from 1958 through 1984. Milling processes included acid leaching, salt roasting, and solvent extraction, resulting in tailings piles covering approximately 33 acres (Merritt 1971). Liquids were stored in two holding ponds (called the gypsum and vanadium ponds) located east of the tailings piles (Figure 2). DOE conducted surface remediation at the site from 1989 to 1996; the remediation included removal of tailings, radiological contaminated materials, buildings, and structures. Groundwater in an alluvial cobble aquifer underlying the site contains elevated concentrations of vanadium and other site contaminants. The alluvium ranges from about 20 to 30 feet (ft) in thickness and is underlain by the Tertiary Wasatch Formation, which is composed predominantly of variegated claystone and siltstone interbedded with discontinuous fine-grained sandstone. Additional details on the milling history, groundwater regulations, site remediation, geology, and other site features are available in the Site Observational Work Plan (SOWP) (DOE 1999). The New Rifle site is currently managed by the U.S. Department of Energy (DOE) Office of Legacy Management (LM).

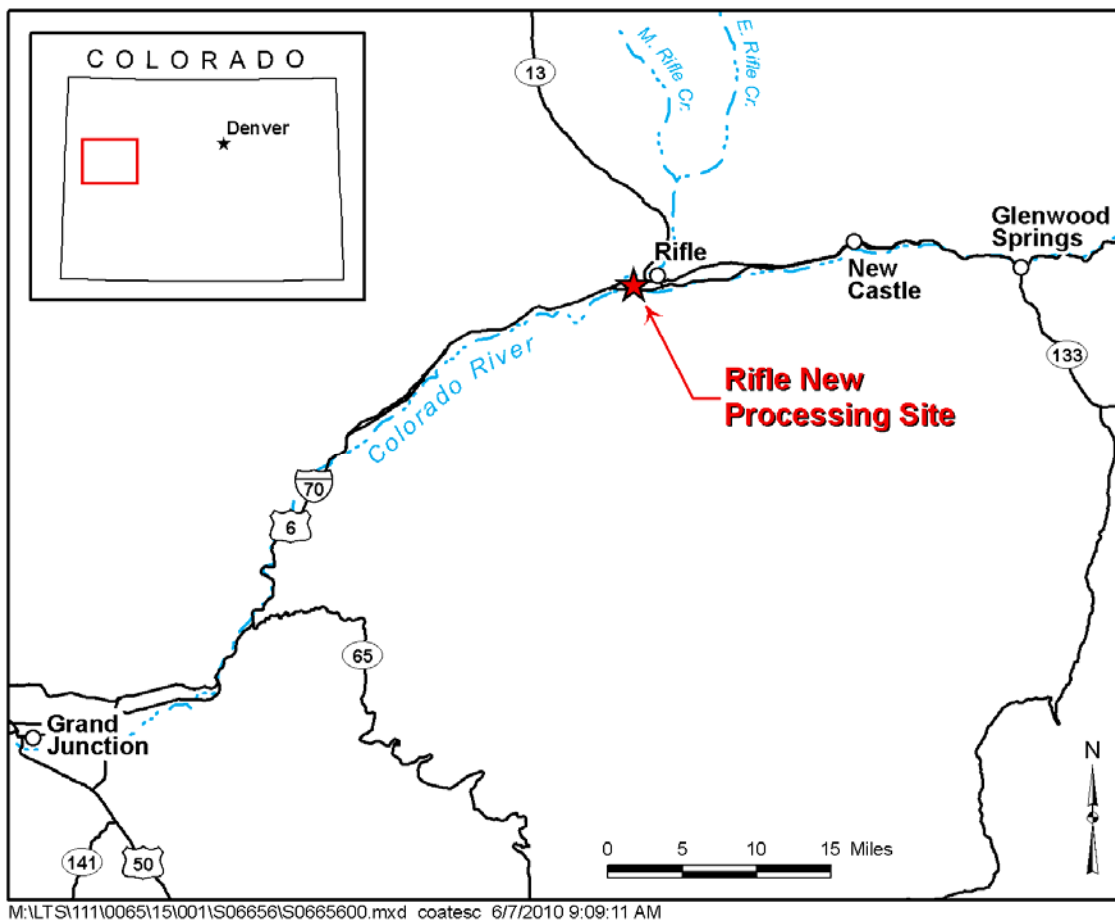


Figure 1. Location of the New Rifle Processing Site, Garfield County, Colorado



Figure 2. 1974 Photo of New Rifle Processing Site Showing Locations of Tailings Piles, Holding Ponds, Mill Buildings, Ore Storage Areas, and Colorado River Sampling Location 0322

Groundwater remediation is regulated under Subparts B and C of Title 40 *Code of Federal Regulations* Part 192 (40 CFR 192). Although vanadium is not listed in 40 CFR 192 as a contaminant at uranium and thorium mill sites, the concentrations at the New Rifle site exceed a risk-based value of 0.33 milligram per liter (mg/L), which assumes that groundwater is used as the primary source for drinking water (DOE 1999). Contaminants of concern (COCs) at the New Rifle site identified in the SOWP are ammonia, arsenic, fluoride, manganese, molybdenum, nitrate, selenium, uranium, and vanadium. Standards regulated by 40 CFR 192 of 0.05 mg/L, 0.1 mg/L, 44 mg/L, and 0.044 mg/L apply for arsenic, molybdenum, nitrate, and uranium, respectively. Alternate concentration limits (ACLs) of 200, 4.0, 0.05, and 0.33 mg/L were proposed for ammonia (as NH_4), manganese, selenium, and vanadium, respectively. A fluoride concentration limit was set at the drinking water standard of 4.0 mg/L. Based on aquifer transport modeling, concentrations of arsenic, molybdenum, nitrate, selenium, and uranium were expected to decrease to regulated levels within the 100-year period for natural flushing allowed under 40 CFR 192. Ammonia, fluoride, and manganese were also expected to flush naturally, although these contaminants were not specifically modeled. Modeling predicted that vanadium would not meet the 0.33 mg/L ACL for 300 years, the only COC that was predicted not to flush naturally within 100 years. The SOWP (page 7-4) notes that vanadium concentrations in some wells were decreasing at a higher rate than the model predicted, indicating that, for chemical reasons not well understood, natural flushing could be occurring faster than predicted by the transport model. Because of the apparent uncertainty in predicting vanadium fate and transport,

active remediation alternatives were evaluated for vanadium with the recommendation that pump-and-treat remediation using zero-valent iron (ZVI) as the treatment medium be pilot tested. In addition, characterization of vanadium concentrations in soil and groundwater was conducted in 2000 (DOE 2000a and 2000b). Those studies identified vanadium concentrations of up to 6190 milligrams per kilogram (mg/kg) in soil and up to 32 mg/L in groundwater. The highest concentrations of soil vanadium were approximately 10 ft below ground surface in areas of the former mill ponds.

Prototype testing of ZVI treatment was conducted by LM's Environmental Sciences Laboratory at the Grand Junction Office from September 27 through December 22, 2000 (DOE 2001). Favorable vanadium removal from the prototype tests led to construction of a full-scale pilot plant, which began operation in January 29, 2001. The plant consisted of a set of ZVI treatment columns, flocculation tanks, and an infiltration gallery. The flocculation removed iron that dissolved during ZVI treatment and provided supplemental removal of vanadium. The treated water was infiltrated back into the aquifer downgradient of the plant. The vanadium concentration in the groundwater plume did not decrease significantly during the operation of the pilot plant, and it was concluded that pumping was not an efficient method for aquifer restoration. High partitioning of vanadium to the solid particles in the aquifer was proposed as the reason for the inefficiency. Because of the inefficiency at decreasing aquifer vanadium concentrations, the pilot plant was discontinued on November 19, 2001, after treating 2.9 million gallons of groundwater.

In 2003, DOE reexamined the issue of vanadium in the groundwater based on the observation that concentrations in some wells appeared to be decreasing more rapidly than predicted by the transport model described in the SOWP. An analytical algorithm was used to describe localized vanadium transport using individual sets of time-concentration data (DOE 2003). In contrast to the previous transport modeling, the 2003 investigation concluded that vanadium concentrations were likely to meet the 0.33 mg/L ACL in 100 years.

In 2005, DOE prepared a Ground Water Compliance Action Plan (GCAP) (DOE 2005) to direct the groundwater remediation effort. Remediation concentration goals were the same as the concentration limits provided in the SOWP with the following exceptions: a risk-based standard of 155 mg/L was set for ammonia (decreased from 200 mg/L); background was set for manganese, and the historical background concentration was stated as 5.9 mg/L (increased from 4.0 mg/L); a combined standard of 10 mg/L (as N) was set for nitrate plus nitrite (modified from 44 mg/L as NO₃); and the standard for uranium was set at the greater of 0.044 mg/L or background, stated as 0.059 mg/L (increased from 0.044 mg/L). The remediation goal for vanadium in the GCAP remained at the risk-based value of 0.33 mg/L given in the SOWP. The GCAP maintains that "Evidence strongly suggests that disturbing the subsurface down into the water table tends to release vanadium from sorbed sites and increase concentrations in the groundwater. Consequently, future disturbance should be minimized. ICs [institutional controls] that prevent disturbance of the groundwater system ... [are needed]." The GCAP also states that vanadium concentrations in the groundwater system will decrease to the 0.33 mg/L remediation goal "if the groundwater system is not disturbed." Deed restrictions are described that would prohibit the use of groundwater and excavation or well construction for the site.

A second GCAP was prepared in 2006 (DOE 2006). Most remediation goals were the same as in the previous GCAP with the following exceptions: ammonia, fluoride, and manganese were

removed from the COC list. The remediation goal for selenium decreased from the ACL value of 0.05 mg/L in the SOWP to a background value of 0.036 mg/L (or maximum background level). The remediation goal for uranium increased from 0.059 mg/L given in the previous GCAP to 0.067 mg/L (or maximum background level). The ACL for vanadium increased from 0.33 to 50 mg/L. The higher vanadium ACL was determined to be protective at the Colorado River point of compliance and to be higher than any values observed in groundwater samples. Institutional controls (ICs) were established to eliminate exposure to contaminated groundwater through deed and zoning restrictions. The land has been deeded to the City of Rifle. Much of the land is within the growth corridor for the city, and the city would benefit from commercial and industrial construction in this area. Construction that contacts the contaminated groundwater is of concern. The 2006 GCAP contains a map in Appendix A, Part A1 showing areas of “No Disturbance” and “Limited Disturbance.” This map was filed with the quitclaim deed, presumably as a measure to control subsurface disturbances that could mobilize vanadium; however, the GCAP is vague on the meaning of “limited disturbance.” The exact nature of the restrictions is still under discussion, and the current study was intended to help provide information useful to the decision process.

In February 2008, dewatering began for installation of a wastewater treatment facility just east of the site (Figure 3 and Figure 4). Although details are lacking, it is likely that several hundred gallons per minute were pumped for 6 to 8 months. Water was discharged to the Colorado River. The pumping resulted in a lowering of the groundwater table within the study area extending at least as far west as well 0863 (Figure 5). Three new wells (0683, 0684, 0688) were drilled specifically for this study (Figure 5). These wells and existing wells 0215, 0857, and 0863 (Figure 5) were instrumented and connected to LM's System Operation and Analysis at Remote Sites (SOARS), but unfortunately, this detailed data collection network was not in place until a couple months after the onset of pumping.

Decisions on land use are closely tied to the eventual fate of vanadium in groundwater. Previous documents discuss mobilization and transport of vanadium in a broad sense. This study was undertaken to better evaluate the geochemical nature of the vanadium plume. The study is funded through LM's Applied Science and Technology program. The purpose is to provide a reasonable understanding of vanadium geochemistry as it applies to groundwater compliance. Information from the study will feed into the decision-making process for possible land use restrictions, additional characterization, and/or additional groundwater remediation. The study period covered 24 months, from February 2008 through February 2010.

2.0 Methods

In February 2008, the City of Rifle began dewatering for installation of a wastewater treatment facility near the eastern portion of the site. Thirty 12-inch-diameter wells (prefix CW) were used to extract groundwater at pumping rates in the hundreds of gallons per minute (Figure 3). Some of the dewatering wells were sampled for this study, although detailed pumping rates during the dewatering operation were unavailable. Some wells were assigned to DOE and continue to be monitored as part of the groundwater remediation effort. For the current study, three new monitoring wells were installed, real-time groundwater monitoring instruments were placed in six wells, groundwater samples were collected and analyzed, and soil samples were analyzed.

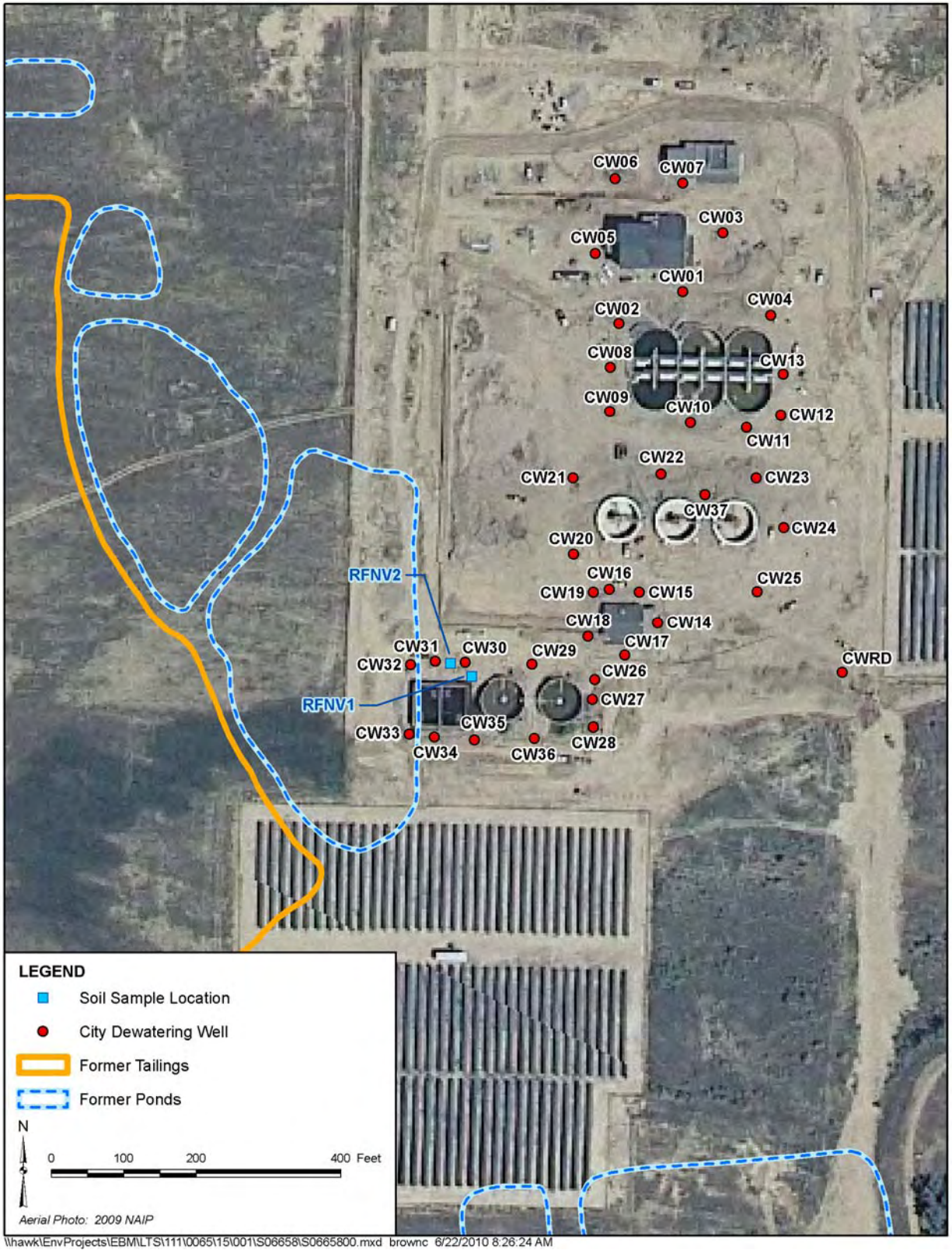


Figure 3. 2008 Aerial Photo of City of Rifle Wastewater Treatment Plant Showing Soil Sampling Locations (RFNV prefix) and the City's Dewatering Wells (CW prefix).



Figure 4. Photo of City of Rifle Wastewater Treatment Plant (taken May 3, 2010)

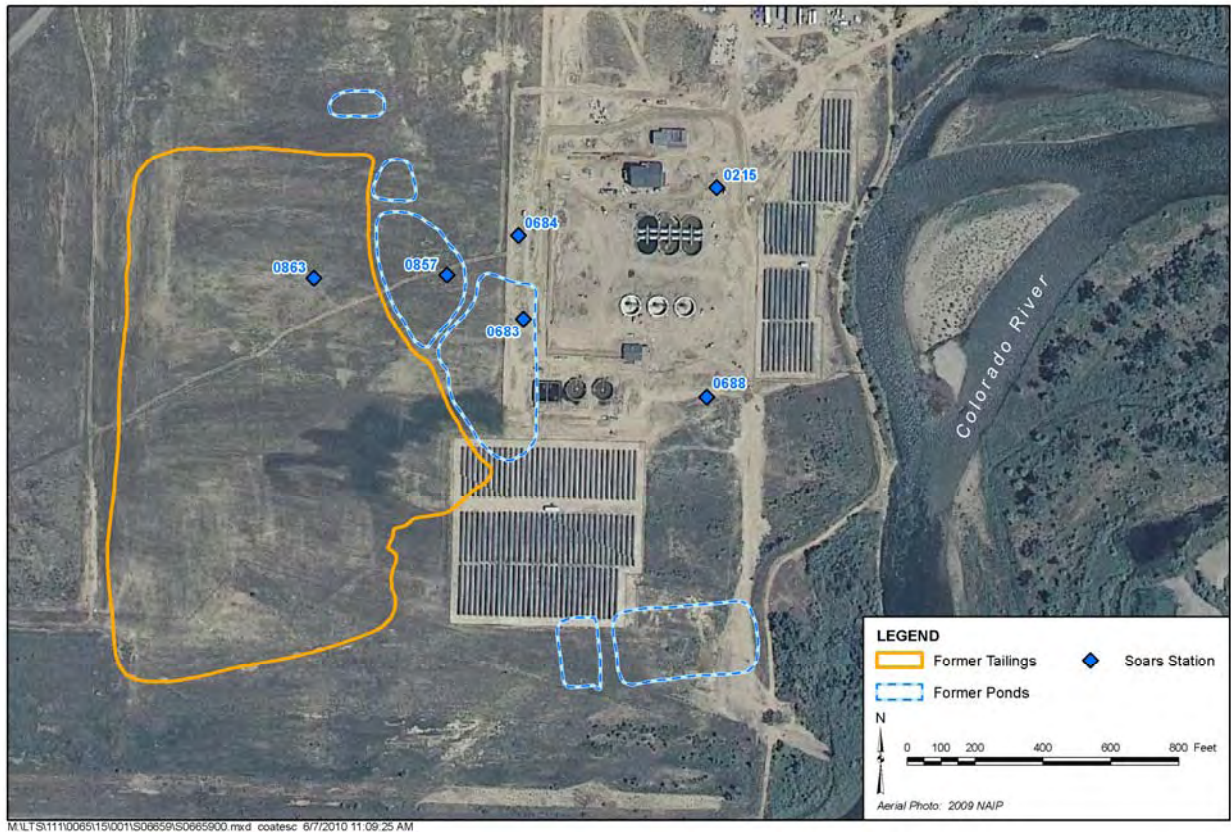


Figure 5. Locations of Monitoring Wells in the SOARS System (2008 Aerial Photo)

2.1 Well Installation

Wells 0683, 0684 and 0687 were installed for this project. The wells were drilled to depths of 18.4, 15, and 14.9 feet, respectively, by vibratory impact drilling using a Geoprobe. The well depths were limited by drilling refusal in the cobble-rich alluvium. Wells were completed with 5 ft of slotted (0.020 inch) well screen at the bottom of the well. Native soil was allowed to collapse around the casing, and a 1-ft plug of bentonite was placed at the ground surface. The locations and elevations were surveyed.

2.2 SOARS System

Between February and May of 2008, six wells within the project area were equipped with monitoring instruments (Figure 5). Data were collected at 5-minute intervals and automatically downloaded and graphed via the SOARS system. An example monitoring station at well 0857 is shown in Figure 6. The instruments measured oxidation-reduction potential (ORP), specific conductance, and water level using in situ sensors placed in the wellbores below the water table. Appendix A provides an analysis of the accuracy of the SOARS instruments.

ORP values were measured with Campbell Scientific Model CSIM11-ORP sensors. The ORP sensor uses a platinum electrode and was calibrated using Zobell solution when the probe was installed and twice during the project. The ORP data drifted downward during use, and much higher readings were reestablished after cleaning with 20 percent nitric acid. A detailed analysis of the ORP calibration data indicated that instrument drift was severe, and the ORP data should not be used (Appendix A). Thus, ORP values used for interpretation in this report were measured in flow-through cells during routine sampling events. ORP values were converted to Eh (potential relative to the standard hydrogen electrode) by the relationship:

$$Eh \text{ (millivolts [mV])} = ORP \text{ (solution, mV)} - ORP \text{ (Zobell, mV)} + Eh \text{ (Zobell, mV)}$$

Values of Eh were converted to pE (logarithm of the electron activity) by the relationship:

$$pE = Eh \text{ (mV)} / [2.3 * R \text{ (kcal / K - mol)} * T \text{ (deg- K)} * F^{-1} \text{ (C / mol)}]$$

where R is the gas constant (kcal per kelvin per mol), T is absolute temperature (kelvin), and F is the Faraday constant (coulombs per mole) (Stumm and Morgan 1981). At 25 °C, pE = Eh (volts)/0.059. Conversions to pE were needed for geochemical modeling.

Specific conductance was measured with a Campbell Scientific Model CS547A-L probe. The specific conductance probe was reasonably robust with minimal instrument drift. Specific conductance values were calibrated using commercial reagent-grade standards at the same frequency as the ORP. Water levels were measured with an In Situ Model PXD-261, 15-psi transducer calibrated with a hand-held electronic depth sonde. Water level measurements were accurate to about 0.1 ft. Detailed analysis of the calibration data for specific conductance and water level indicated that data collected with these instruments were reliable (Appendix A).



Figure 6. SOARS Station at Well 0857, Collects Data from Well 0857 and Weather Instruments

2.3 Groundwater Analyses

Groundwater samples were collected several times during the study. A peristaltic pump was used to pump groundwater from a well through a flow-through cell instrumented with sensors for ORP, pH, specific conductance, and temperature. The measurements were made according to methods AP(ORP-1), AP(pH-1), and AP(EC-1) in the *Environmental Sciences Laboratory Procedures* (STO 210). Alkalinity was measured in the field by titration with sulfuric acid (method AP[Alk-1] in STO-210). Samples were collected in plastic bottles. Samples for cations and metals were preserved by adding concentrated nitric acid to pH 2. All samples were kept on ice until laboratory analysis. Calcium, magnesium potassium, and sodium were analyzed by flame atomic absorption (STO-210 methods AP[AA-1], AP[Ca-1], AP[Mg-1], AP[K-1], and AP[Na-1]). Chloride, nitrate, and sulfate were analyzed by ion chromatography (STO-210, methods AP[Cl-2], AP[NO₃-4], and AP[SO₄-4]). Ammonia was analyzed by colorimetry (STO-210, method AP[NH₃-4]), and uranium was analyzed by kinetic phosphorescence (STO-210, method AP[U-2]). All vanadium analyses were conducted at a contract laboratory by inductively coupled plasma mass spectrometry (ICP-MS).

To better define the variation in contaminant concentrations in the high concentration portion of the vanadium plume, an autosampler was installed at well 0857 on May 7, 2008. A small amount of red-orange residue, probably iron oxyhydroxide, accumulated in the bottom of the plastic sample bottles in the autosampler. To avoid loss of constituents due to adsorption to this residue,

the bottles were agitated to homogenize and suspend the residue prior to splitting a sample for analysis. Samples were collected daily from May 7 through May 19, 2008; on 4-day intervals from May 19, 2008, through November 3, 2009; and weekly from November 9, 2009, through January 18, 2010. All samples from the autosampler were analyzed for uranium and vanadium by ICP-MS at a contract laboratory. Some samples were also analyzed for arsenic, molybdenum, and selenium. Chemical data collected during this project are provided as Appendix B.

2.4 Soil Analyses

Yellow-green discolored soils were uncovered in the southwestern portion of the construction area during excavation for the wastewater treatment plant. Contractor site personnel collected three samples of the discolored soil for this study. Sample material was biased toward fine-grained soil and excluded pebbles and cobbles. The samples were collected with a hand scoop and placed in plastic bags. One sample (“Yellow Soil”) was sieved to –10 mesh (<2 millimeters [mm]), air dried in the Environmental Sciences Laboratory, and then sent to a contract laboratory. The other two samples were further biased by hand selecting the most discolored material and sending it to a contract laboratory. At the contract laboratory, the samples were oven dried at about 105 °C and digested in a mixture of nitric acid (at 95 °C), hydrochloric acid, and peroxide (EPA procedure 3050B). Nitric acid and peroxide were repeatedly added until no further change was apparent. A separate extraction using the same procedure but without hydrochloric acid was conducted for vanadium analysis, because the chlorate ion interfered with the vanadium analysis. Iron was determined by ICP-emission; uranium and vanadium were determined by ICP-MS.

Personnel from the City of Rifle's contractor for the wastewater treatment system, Stanek, also collected discolored samples from a similar area. Less is known about the sampling and analysis methods used for the Stanek sampling; however, the data are included in this study. These samples were also collected with a hand scoop, presumably avoiding the larger pebbles and cobbles and were likely biased for discoloration and fines. It is likely that the samples were oven dried and extracted using EPA procedure 3050B, although that information was not available for this study. The Stanek samples were analyzed using ICP-emission for arsenic, molybdenum, selenium, uranium, and vanadium.

3.0 Results

3.1 Groundwater Elevations

Under normal (non-pumped) conditions, groundwater at the site flows generally westerly or southwesterly subparallel to the Colorado River (DOE 1999, SOWP Figure 5–11). Groundwater pumping for construction dewatering significantly altered this flow regime, causing groundwater to flow from the central portion of the site to the east, forming a groundwater divide near well 0863. As discussed in Section 3.2, lowering of the groundwater table by dewatering pumping increased direct contact of groundwater with contaminated soil zones and resulted in substantially higher vanadium concentrations in some wells.

Figure 7 shows a comparison of groundwater elevations in the 6 wells monitored with SOARS to the Colorado River discharge measured 28 miles upstream at the Glenwood, Colorado, USGS

gauging station. Construction dewatering began in mid-February 2008, about 3 months prior to the installation of the SOARS monitoring network. Thus, the earliest groundwater elevation data shown on Figure 7 had already been affected by the dewatering pumping. Documentation of pumping rates after startup was not available for this study; however, by observing water levels in well 0215, located within the main construction area, it is inferred that most of pumping occurred through about early November 2008.

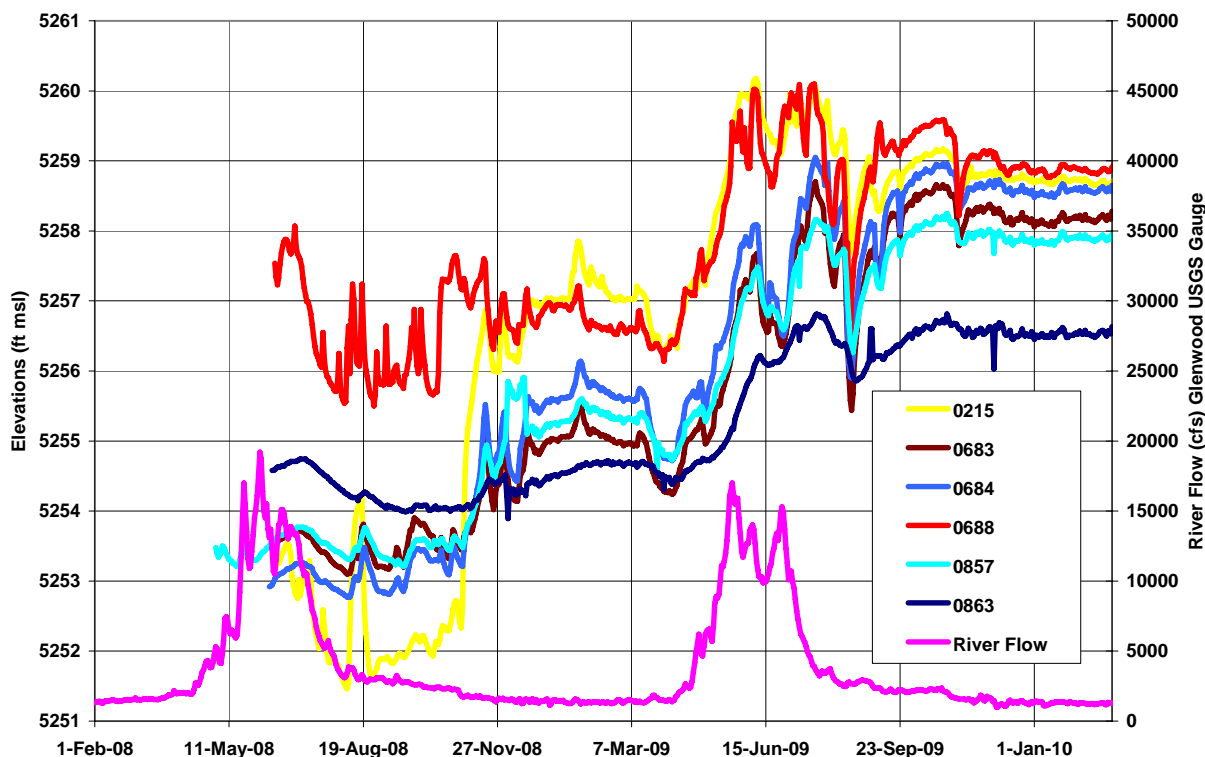


Figure 7. Colorado River Discharge Measured at the USGS Gauging Station, Glenwood Springs, Colorado, and Groundwater Elevations at the Project Site

Groundwater flow was affected by both the dewatering operation and water levels in the Colorado River. Monitoring well 0215 is located closest to the construction site and showed the lowest groundwater elevation from the start of monitoring on June 15, 2008, through November 3, 2008. After November 3, water levels increased in well 0215 at a faster rate than in all other wells and reached an elevation above that of the other wells. The water elevation in well 0215 mirrored that of well 0688 after November 3. The rapid increase in groundwater elevation in well 0215 was likely due to a relatively abrupt decrease in construction pumping in early November 2008.

Well 0688 is closest to the river and has continuously had the highest groundwater elevation. Because its location is somewhat removed from the main portion of the dewatering network (Figure 5), well 0688 seems more affected by river stage than by the dewatering operation. The highest water stage for the Colorado River is from about mid-May to mid-July (Figure 7). Most of the wells, in particular well 0688, had a slight increase in groundwater elevation during this

time period, probably caused by the higher river stage; however, the increase was negligible compared to the lower groundwater table caused by pumping.

With the exception of well 0688, well 0863 had the highest groundwater elevation during the high pumping period of February through November 2008. Wells farther west of well 0863 (not shown) had lower groundwater elevations, and thus well 0863 was near a groundwater divide with groundwater flowing both east and west. After early November 2008, groundwater elevations in the other wells increased more rapidly than in well 0863 as groundwater flow regained its non-pumped northeast to southwest direction. The groundwater table in all wells again showed increases during the May through July 2009 high-water stage of the river. Following a slight decrease as river stage subsided in July 2009, groundwater levels continued to increase in all wells and stabilized at levels that are similar to pre-pumping, as demonstrated by a long-term hydrograph for well 0215 (Figure 8).

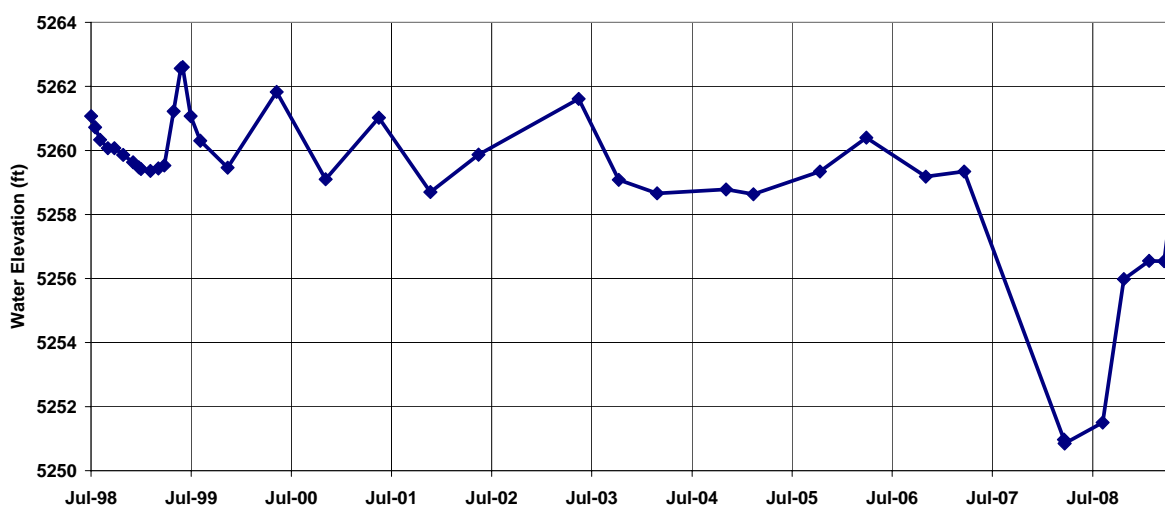


Figure 8. Long-Term Hydrograph of Well 0215 Showing Rebound to Nearly Non-Pumped Levels by May 21, 2009

3.2 Groundwater Major Ion Chemistry

Influences on groundwater chemistry include influx from the Colorado River, local recharge, and contamination from the mill site. Water chemistry is often classified by the ratios of major ions using a Piper diagram (Freeze and Cherry 1979, after Morgan and Winner 1962; and Back 1966). Colorado River water chemistry at the New Rifle site (location 0322) is a sodium chloride water with a significant proportion of calcium (Figure 9). Groundwater in the project area is mostly sulfate type with no predominant cation; however, cations are generally higher in calcium and low in magnesium (Figure 9). Groundwater also contains significant concentrations of dissolved solids compared to river water, as portrayed by the larger circles on the diamond portion of the Piper diagram.

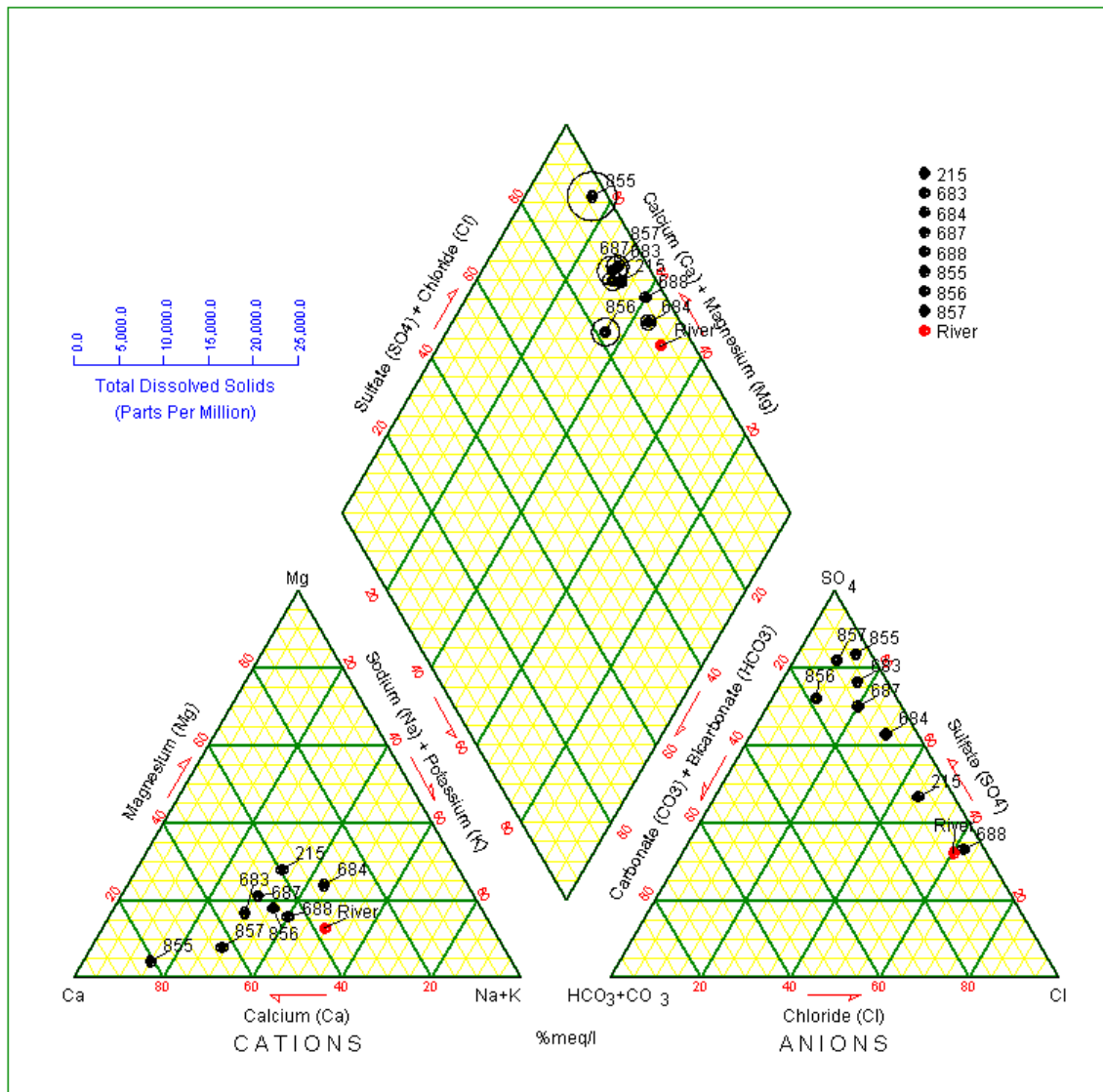


Figure 9. Piper Diagram of Groundwater and Colorado River Water
(Radii of circles on the diamond portion indicates the total dissolved solids concentrations)

Table 1 shows the distribution of major ions in two wells contaminated with vanadium. Values of pH are near neutral. Values of pE suggest relatively oxidized conditions with respect to most vanadium minerals. Nitrate concentrations are low. Sodium predominates over potassium, and calcium predominates over magnesium.

Table 1. Groundwater Composition in Samples Collected April 15, 2009

Analyte	Well 0855	Well 0857
pH	6.41	7.25
pE	7.2	4.7
Alkalinity (mg/L as CaCO ₃)	330	490
Calcium (mg/L)	780	340
Sodium (mg/L)	160	170
Potassium (mg/L)	8.6	17
Magnesium (mg/L)	25	26
Chloride (mg/L)	170	76
Sulfate (mg/L)	1500	890
Nitrate (mg/L as N)	17	2
Arsenic (µg/L)	2200	88
Molybdenum (µg/L)	18,000	510
Selenium (µg/L)	1800	320
Uranium (µg/L)	8.4	90
Vanadium (µg/L)	1,000,000	33,000

In situ measurements of specific conductance were made on 5-minute intervals in the six wells connected to the SOARS system. Specific conductance is the electrical conductance of a body of unit length and unit cross-sectional area at a specific temperature (Hem 1985). Measurement of specific conductance is straightforward and is readily integrated into remote monitoring systems. The instrument is robust and holds calibration well. Conductance of pure water is very low and increases with increasing concentrations of charged ions. Thus, specific conductance values directly correlate with dissolved salt content.

The specific conductance of the Colorado River at sampling location 0322, just south of the site, typically has a range of about 0.5 to 1.5 millisiemens per centimeter (mS/cm) with a mean of about 0.9 mS/cm. Specific conductance in the river is highest in the winter months and lowest during high river stage in late spring, early summer. Wells 0215 and 0688 have the lowest specific conductance values of the wells reflecting their location on the east side of the site nearest the river (Figure 10). Specific conductance in well 0688 ranges from about 0.5 to 1.2 mS/cm, similar to that in the river. Anomalously high specific conductance values in well 0215 in January and February 2010 were caused by the sensor placement in the sediment at the well bottom and are probably not reflective of the actual groundwater specific conductance. Other than these anomalous values, specific conductance in well 0215 ranged from about 0.6 to 2.3 mS/cm, slightly higher than in well 0688. Well 0215 is located in an area that was greatly affected by the dewatering pumping, and some of the variation in specific conductance probably reflects groundwater of varying values being intercepted by the well. However, well 0215 consistently had low concentrations of vanadium and other-site related contaminants, indicating that the variation in specific conductance is not due to contamination. Wells 0857, 0683, and 0684 had higher specific conductance values that probably indicate site contamination, at least in part. These wells are located in the eastern portion of the former mill site, and wells 0857 and 0683 are within the footprint of the former evaporation ponds. Specific conductance varies considerably in some of these wells and is likely related to variable groundwater conditions caused by dewatering pumping.

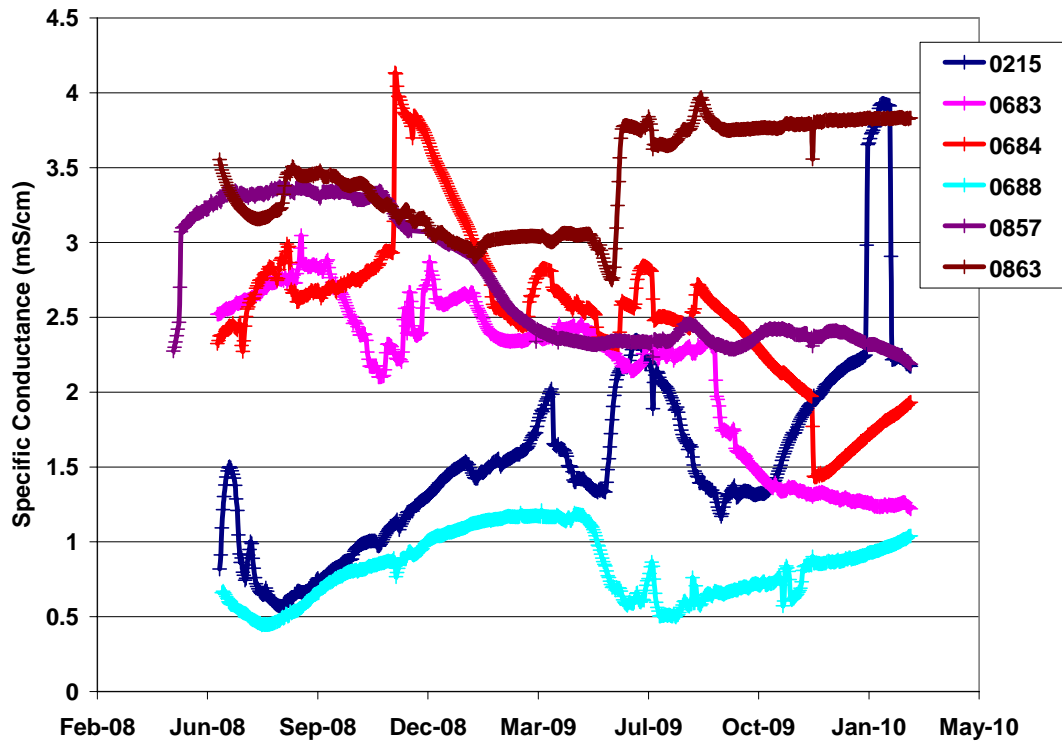


Figure 10. Specific Conductance in Groundwater

3.3 Vanadium in Groundwater

Vanadium concentrations in the groundwater exceed the risk-based value of 0.33 mg/L in some of the monitoring wells (Figure 11 and Figure 12). In some wells, the concentration exceeds this value by more than an order of magnitude. The highest vanadium concentrations (up to 810 mg/L in well 0855) are present in groundwater beneath one of the former mill ponds (Figure 12). The maximum concentration of vanadium detected in well 0855 is 1600 mg/L, which is also the highest vanadium value detected on the site. An approximately north-south line of wells (0688, CW25, CW23, CW12, 0215) has vanadium concentrations significantly less than the 0.33 mg/L goal, bracketing the eastern extent of contamination. Vanadium concentrations in groundwater beneath the former tailings pile are variable and range from 0.24 to 8 mg/L.

The anomalously high concentrations of vanadium in well 0855 are of particular interest in assessing compliance issues and are a focus of this study. The vanadium concentrations in well 0855 were approximately 20 mg/L from April 2000 through the start of dewatering pumping in February 2008 (Figure 13). After pumping began, the concentrations increased to a high of 1600 mg/L in February 2009 and have since been decreasing.

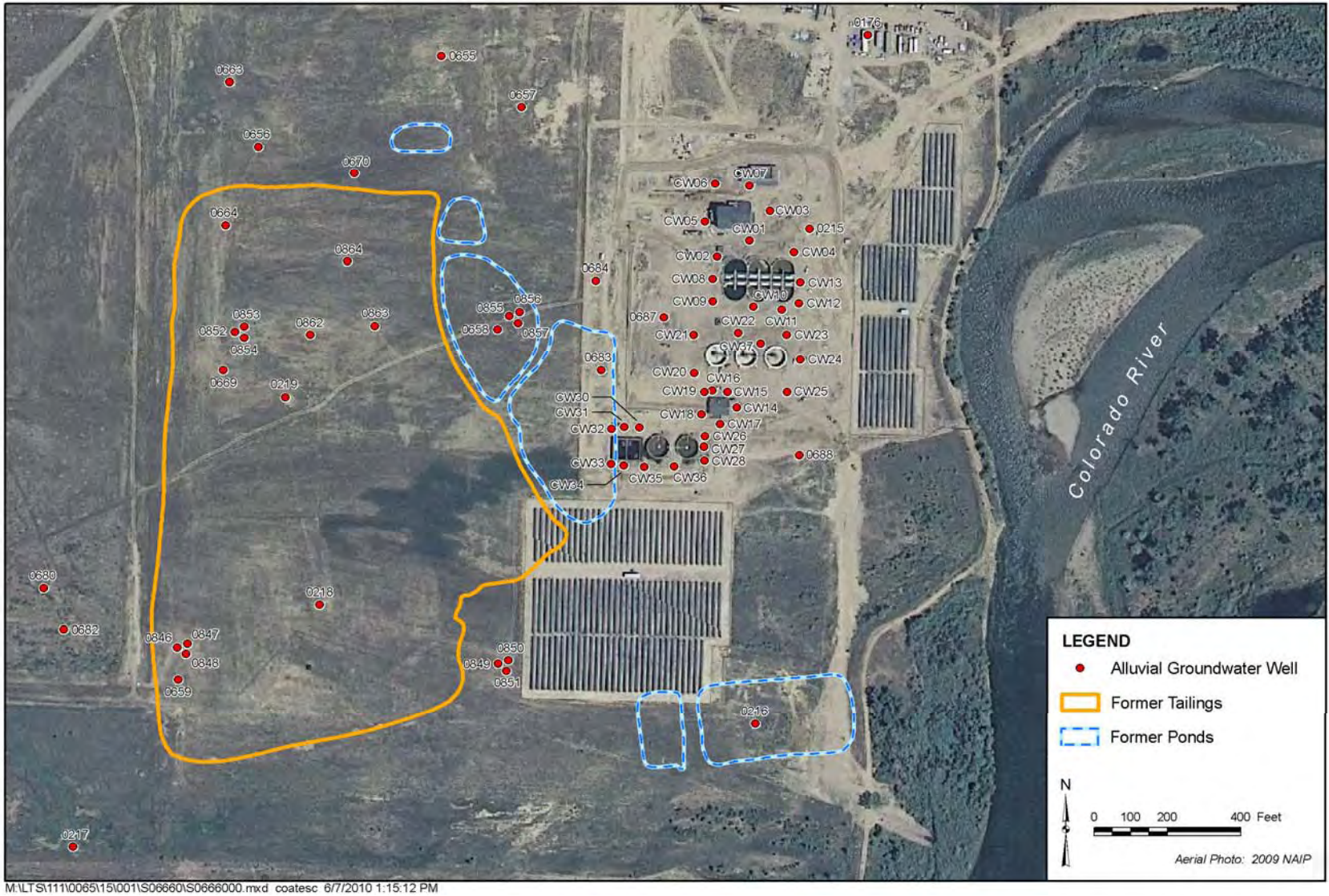


Figure 11. Location Map for Alluvial Groundwater Sampling Wells

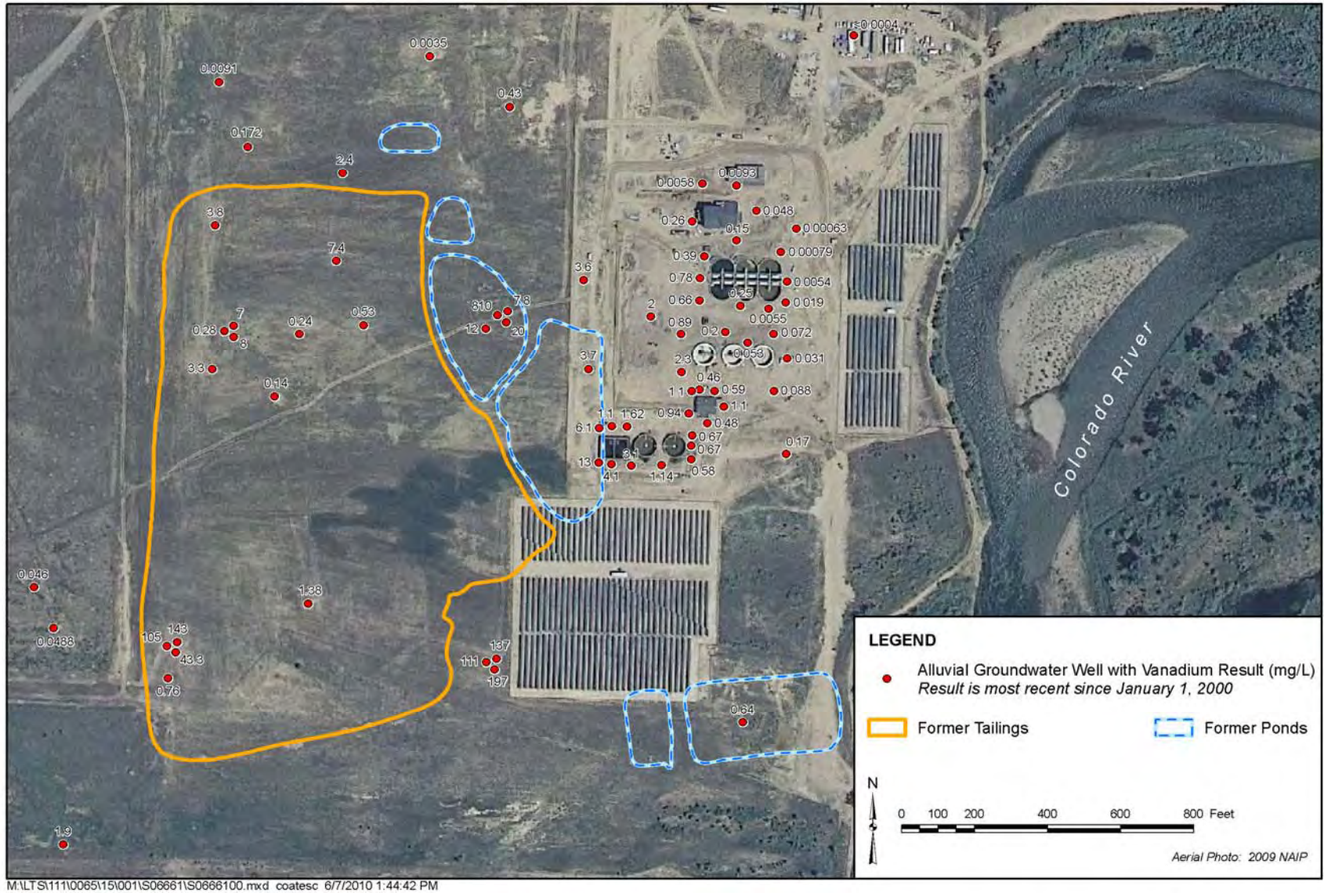


Figure 12. Vanadium Concentrations in Alluvial Groundwater Samples.
 Concentrations in most recent samples; in the date range April 25, 2000 through May 20, 2009

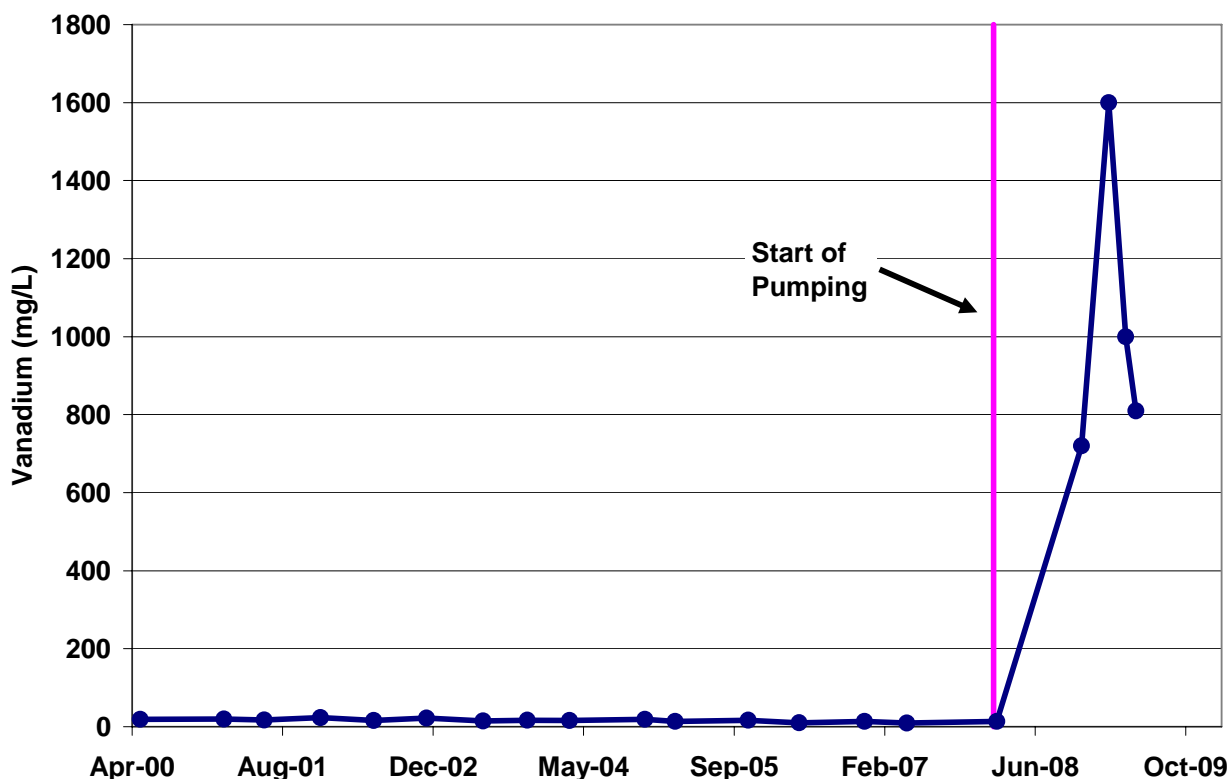


Figure 13. History of Vanadium Concentrations in Well 0855

Although well 0855 had the highest vanadium concentration, it was nearly dry and thus difficult to monitor and sample. Well 0857, located about 30 ft from well 0855 and completed at a greater depth, was selected for detailed monitoring during this study (Appendix D has logs of wells 0855 and 0857). Vanadium concentrations in well 0857 also increased following the initiation of pumping but peaked at 44 mg/L (Figure 14), substantially less than concentrations in well 0855. The increase in vanadium concentration occurred later in well 0857 than in well 0855; the concentration in well 0855 had increased to 720 mg/L by November 19, 2008, whereas the vanadium concentration in well 0857 was still at 6 mg/L on February 19, 2009. Following the peak vanadium concentration, the concentrations began to decrease but had not reached the pre-pumped values. Concentration in well 0855 had decreased to 810 mg/L by May 19, 2009, the most recent sampling time for this well. Concentration in well 0857 had decreased to 20 mg/L by January 18, 2010, and appears to have stabilized to some extent. The water sampled from well 0855 had a deep green color that was probably induced by the high vanadium concentration.

Concentrations of some other contaminants are also elevated in wells 0855 and 0857 (Table 2). In particular, arsenic, molybdenum, and selenium have relatively high concentrations in well 0855. Uranium has a low concentration in well 0855, suggesting that its aqueous concentration may be controlled by equilibrium with a uranium-vanadium mineral.

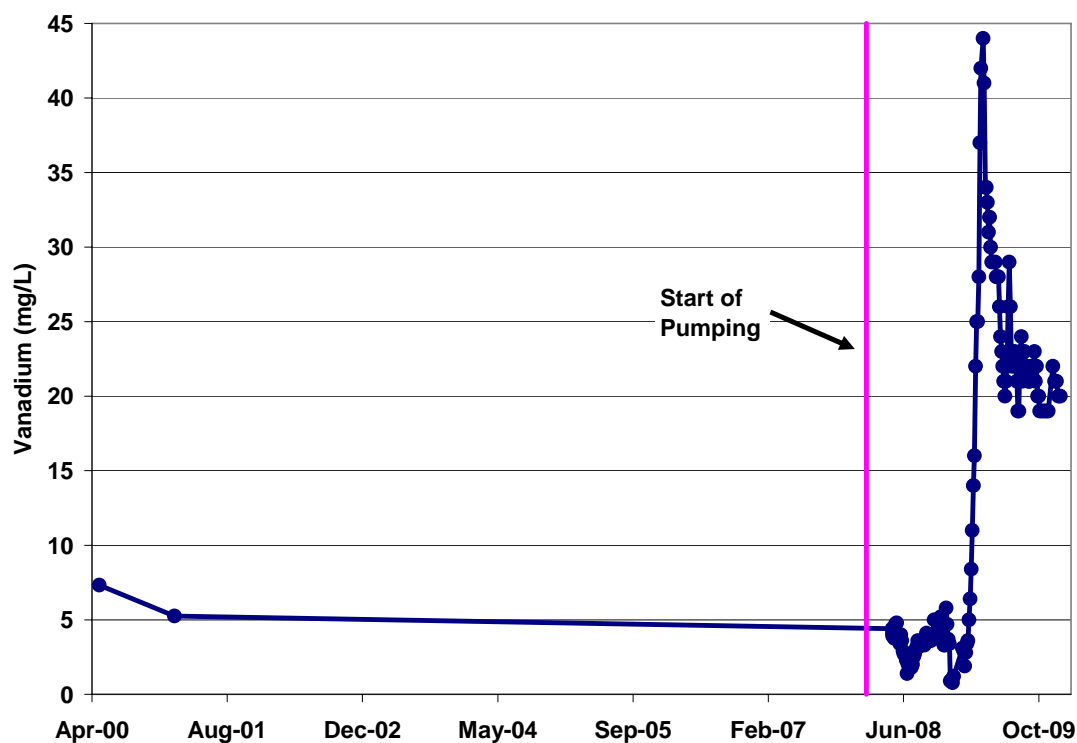


Figure 14. History of Vanadium Concentrations in Well 0857

Table 2. Concentrations of Contaminants in Wells 0855 and 0857 (mg/L) (sampled April 15, 2009)

Analyte	Well 0855	Well 0857
Arsenic	2.2	0.088
Molybdenum	18	0.51
Selenium	1.8	0.32
Uranium	0.0084	0.09
Vanadium	1000	33

3.4 Vanadium in Soil

During the excavation for the City's wastewater treatment plant, yellow-green discoloration was noted by Stanek personnel (Figure 15). Because of the possibility that the discolored soils contained contaminants that could pose a health risk to the construction workers, samples were collected and analyzed. The results of the analyses also provide data to help interpret the groundwater vanadium plume and are included here.

The samples were collected from an area at the southwestern portion of the construction site from trenches that had been excavated to a depth of about 4 or 5 ft (Figure 3). The samples submitted for analysis were biased toward fine-grained and discolored material. Thus, the results represent higher concentrations of the analyte than exist within the bulk aquifer medium. The discolored sediments contained visible amounts of gypsum.



Figure 15. Yellow-Green Staining on Alluvial Gravels in the Wastewater Treatment Plant Construction Area (Photo taken May 2009)

Vanadium concentrations in the samples ranged from 2200 to 9200 mg/kg and were reasonably uniform, considering the differences in locations and collection and handling methods used (Table 3). All vanadium values from the discolored area exceeded those of the background sample, which had 190 mg/kg. Samples with elevated vanadium also had higher concentrations of arsenic, molybdenum, selenium, and uranium.

Table 3. Analysis of Yellow-Green Soils

ID	Date Sampled	Location ^a	V (mg/kg)	As (mg/kg)	Fe (mg/kg)	Mo (mg/kg)	Se (mg/kg)	U (mg/kg)
1	2/6/2009	RFNV1	4700	NA	11,000	NA	NA	7.3
2	5/26/2009	RFNV2	7200	NA	11,000	NA	NA	16
3	5/26/2009	RFNV2	7400	NA	13,000	NA	NA	22
4	5/14/2009	RFNV2 ^b	2200	95	NA	9.5	37	16
5	5/14/2009	RFNV2 ^b	3600	48	NA	7.4	26	6.3
6	5/14/2009	RFNV2 ^b	4500	45	NA	9.7	20	<3.8
7	5/14/2009	RFNV2 ^b	7500	150	NA	15	36	6.6
8	5/14/2009	RFNV2 ^b	9200 ^c	490	NA	15	210	110
9	5/14/2009	Unknown ^d	190	14	NA	5.5	<7.8	11

NA = not analyzed

^aSee Figure 3 for locations

^bSample collected from trench at approximately this location

^cEstimated value

^dBackground (no discoloration) sample from unknown location

Vanadium concentrations in the yellow-green soils analyzed during this study are similar to those of core samples collected at the site in 1999 (Table 4). The highest vanadium concentration in the core samples was 6190 mg/kg, a value similar to the values of the yellow-green soils shown in Table 3. Many of the core samples had lower vanadium concentrations, but the samples were handled differently. The core samples were a homogenous blend of the selected depth interval and were not biased for color. The core sample with the highest vanadium also had the highest concentrations of arsenic, molybdenum, and uranium, a feature similar to the yellow-green soils. Although the highest concentrations of arsenic, molybdenum, and uranium are found in the same samples for both the yellow-green soil and the core samples, at lower concentrations no correlation between vanadium and these constituents is evident. The highest vanadium concentration in the core samples was from the 9 to 11 ft depth interval in well 0855, the well that had the highest groundwater concentration of vanadium.

Table 4. Concentrations of Constituents in Borehole Samples

Boring No.	Depth (ft)	V (mg/kg)	As (mg/kg)	Mo (mg/kg)	U (mg/kg)
RFN 846	7–9	105	3.76	5.93	0.73
RFN 847	11–14	143	2.91	5.46	1.08
RFN 848	18.5–19.5	43.3	1.15	4.21	0.66
RFN 849	8–9	111	3.62	1.56	0.57
RFN 850	13–14	137	3.09	1.93	0.67
RFN 851	3–4	36.5	2.46	6.89	2.05
RFN 851	19–20	197	2.47	5.17	0.6
RFN 852	11–12	5.23	2.15	3.38	30
RFN 853	16–17	202	1.32	3.11	3.24
RFN 854	5–6	2.24	0.95	0.16	0.51
RFN 854	20–22	169	1.56	1.2	0.54
RFN 855	9–11	6190	231	57.6	357
RFN 856	16–17	570	58.1	16.4	25.5
RFN 857	3–4	8.2	0.96	1.14	0.71
RFN 857	5–6	52.2	5.55	2.39	1.48
RFN 857	22–23	105	1.16	1.51	0.51

4.0 Discussion

The purpose of this study was to better understand the physical and geochemical partitioning of vanadium in the alluvial aquifer to make better predictions of its fate and transport, in particular to better predict any effects that surface disturbance might have on vanadium concentrations in the groundwater system. To address this issue, mineral saturation indices were calculated from groundwater chemistry, and a one-dimensional transport model was developed to demonstrate geochemical interactions in the subsurface.

4.1 Vanadium Chemistry

In groundwater systems, vanadium can exist in the +3, +4, and +5 oxidation states (Garrels and Christ 1965). Thus, the oxidation state may govern the mobility of the vanadium in groundwater

systems. Vanadate (vanadium +5) is the most common oxidation state in groundwater systems and forms anionic complexes with oxygen and hydroxide (Hem 1985). Solubility of metal vanadates, in particular ferrous vanadate, may control mobility of vanadium in groundwater systems, and vanadium has high solubility in alkaline solution (Hem 1985).

Hem (1985) provides some general concentration data for vanadium. Most public water supplies have less than 0.004 mg/L vanadium, although one system had a concentration of 0.070 mg/L. Average river water worldwide has 0.0009 mg/L vanadium. Some of the highest naturally occurring vanadium concentrations are found in thermal springs in concentrations up to several tenths of a milligram per liter. The concentration in seawater is 0.0002 mg/L, and the predominant species is $\text{VO}_2(\text{OH})_3^{2-}$ in the +5 oxidation state (Evans and Landergren 1974).

Evans and Landergren (1974) provide estimates of vanadium concentrations in the earth. The average concentration of vanadium in the earth's crust is 120 mg/kg. The highest concentrations of vanadium in naturally occurring minerals are found in magnetite and hematite, and iron ores have high vanadium concentrations. Red beds of the Colorado Plateau have relatively high concentrations of vanadium.

Vanadium adsorbs to a variety of minerals; adsorption to ferric oxide is more efficient than adsorption to manganese oxide, montmorillonite, or organic substances (Evans and Landergren 1974). Amorphous ferric oxyhydroxide shows high desorption of vanadium above pH 11 (Dzombak and Morel 1990). The distribution of vanadium in soils often correlates with the iron distribution, suggesting precipitation as ferrous vanadate or adsorption to ferric oxyhydroxide (Rai and Zachara 1986).

4.2 Redox State of New Rifle Alluvial Groundwater

Because vanadium occurs naturally in a variety of oxidation states, the oxidation of the groundwater is important in evaluating partitioning of vanadium between the mobile aqueous phase and the immobile solid phase. One approach to evaluating oxidation state is to examine existing New Rifle groundwater data in pE-pH space (Figure 16). The groundwater analyses form a tight cluster in an area with pE ranging from about 1 to 9, and pH ranging about 6.5 to 7.5. Groundwater samples containing high vanadium concentrations (more than 5 mg/L) form a slightly tighter cluster in the central portion of the same area. A smaller cluster of points ranging from about 10 to 13 is also present at higher pE values. A scattering of outliers that have pH values in excess of 9 are likely due to measurement errors.

With the exception of two points, the New Rifle groundwater data all plot in the V(+5) field, suggesting that the groundwater is oxidized relative to the vanadium system. Vanadium (+4) is not likely to have an influence on the New Rifle groundwater system, since it normally only occurs at low pH.

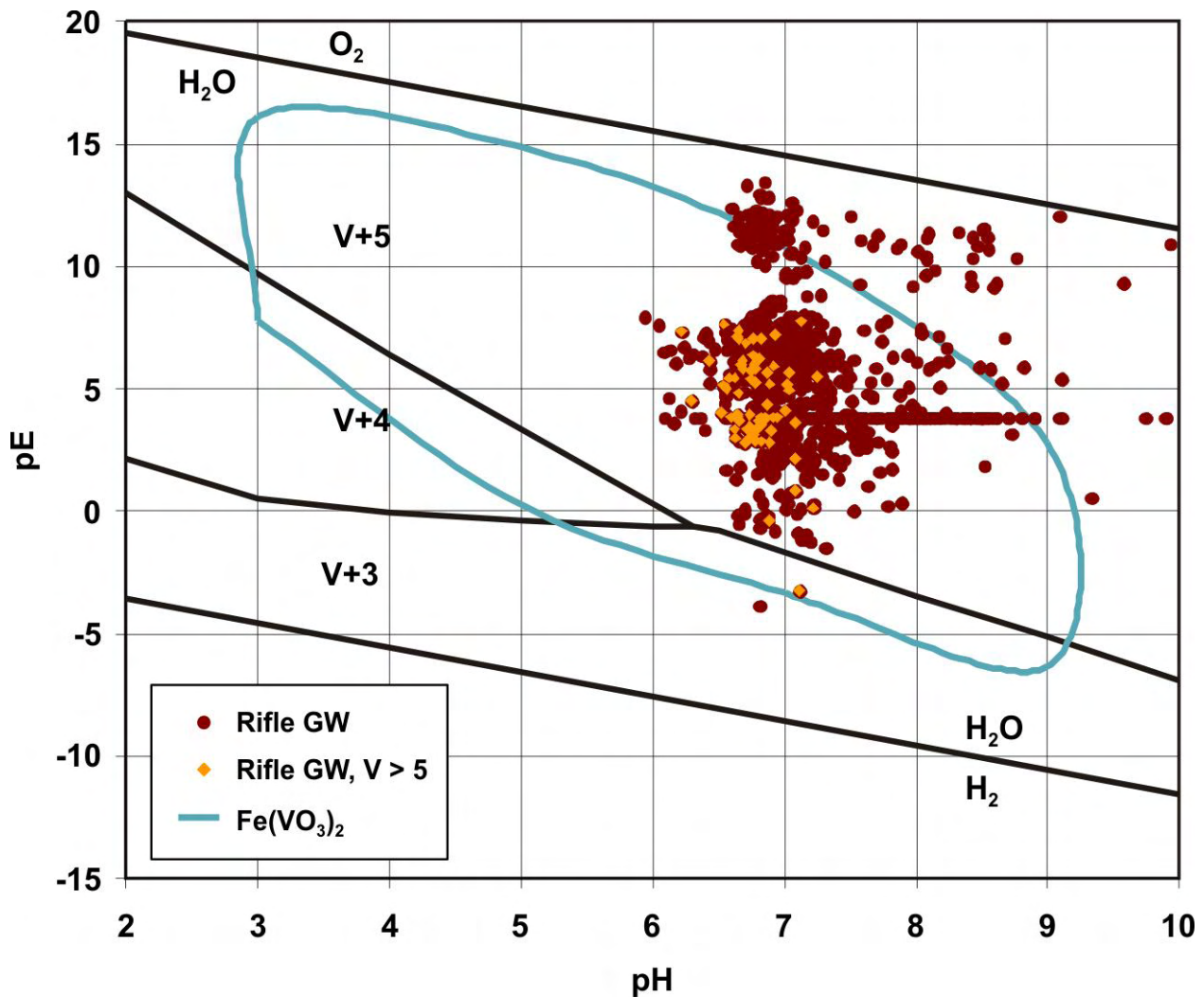


Figure 16. pE-pH Diagram Showing Lines of Equal Activities for Aqueous Vanadium Species, Stability Field for $\text{Fe}(\text{VO}_3)_2$, and Measured Values of New Rifle Alluvial Aquifer Groundwater. Orange symbols represent New Rifle groundwater vanadium analyses greater than 5 mg/L. Molar concentration of iron is 1 millimol per liter.

Eh values as calculated from ORP measurements are problematic in several ways. The measurement itself relies on a potential between the solution being measured and a reference electrode that are connected via a liquid junction. Ions must flow from the reference solution to the water in which the electrode is immersed and vice versa, with potential for salt contamination of the lower ionic strength solution (Langmuir 1971). Also, the liquid junction can become fouled and cause measurement errors. Problems with liquid junction and salt contamination may increase for probes immersed in well water for long time periods. Eh is often used to characterize the oxidation potential of a solution; however, this interpretation requires that the reactions being measured are fully and rapidly reversible, a condition rarely encountered in natural systems.

Because of these problems with Eh measurements, the investigation also included “redox couples” that might define the oxidation state of the system, or at least help to evaluate if various oxidation reactions are at equilibrium (Table 5). The pE values calculated from these redox

couples using the geochemical speciation program PHREEQC (Parkhurst and Appelo 1999) vary from 5.0 to 15 and are all suggestive of an oxidized groundwater system with respect to the vanadium system.

Table 5. Redox Parameters Calculated from Measured Concentrations of Redox Couples in Two Contaminated New Rifle Wells

Redox Couple	Well ^a	ORP (mV)	Eh (mV)	pE
Measured ORP	0855	190	430	7.2
	0857	35	275	4.7
Fe ²⁺ /Fe ³⁺	0855	265	505	8.9
	0857	44	284	5.0
N ³⁻ /N ⁵⁺	0855	190	430	7.6
	0857	122	362	6.4
O ²⁻ /O ⁰	0855	608	848	15
	0857	556	796	14

^aSamples were collected on 4/15/2009.

Often, the color of sediment can be used to draw general conclusions about the oxidation state. Yellow to red colors infer oxidized conditions with respect to the iron system because of the likely presence of iron oxide or oxyhydroxide minerals. In contrast, black coloration is often due to the presence of iron sulfide minerals and depicts more reducing conditions. Since the iron system has some chemical similarities to the vanadium system, inferences about the iron system might also apply to the vanadium system. The cores from the New Rifle site, including those within the vanadium contaminated area, are typically yellowish brown or light brown, supporting the inference of generally oxidizing conditions.

4.3 Mineral Saturation Indices

Mineral saturation indices were calculated from groundwater chemistry in two wells (0855 and 0857) located in an area containing the highest vanadium concentrations in groundwater. This effort was aimed at identifying possible mineralogical controls on the vanadium in the groundwater. Speciation and mineral saturation were calculated using the geochemical speciation program PHREEQC (Parkhurst and Appelo 1999). Because the thermodynamic database supplied with PHREEQC does not contain vanadium, the database was supplemented with the vanadium system from Peterson et al. (1987). A positive saturation index for a mineral indicates that the aqueous phase is oversaturated with that mineral, and the mineral would tend to precipitate from the water. A negative saturation index indicates that the mineral is undersaturated and, if present, would dissolve. In a system at equilibrium with both solid and aqueous phases, minerals would have saturation indices of zero. In the absence of disequilibrium, one or more minerals with saturation indices near zero are the most likely to be present in the subsurface system. Because of inherent uncertainties in measured concentrations and thermodynamic parameters, small deviations from zero are expected; thus, it was considered that minerals with saturation indices between minus one and plus one may be present.

Two uranium-vanadium minerals, tyuyamunite (Ca_{0.5}UO₂VO₄) and carnotite (KUO₂VO₄), are closest to equilibrium saturation in groundwater from wells 0855 and 0857 (Figure 17 and Figure 18). The vanadium minerals are color coded in the figures; minerals with red text are those with vanadate (vanadium in the +5 oxidation state). Ferrous vanadate (Fe_{0.5}VO₃) is slightly

oversaturated in both wells, and calcium vanadate ($\text{Ca}_{0.5}\text{VO}_3$) is slightly undersaturated. Based on this geochemical speciation approach, these four vanadate minerals are the most likely candidates to dominate the vanadium mineralogy in the alluvium. Analyses of the samples of yellow-green discolored soils and core samples provide some indication of mineralogy. The molar amounts of vanadium are approximately two orders of magnitude more than the molar amounts of uranium (Table 3 and Table 4) suggesting the dominance of discrete vanadium minerals over uranium-vanadium minerals.

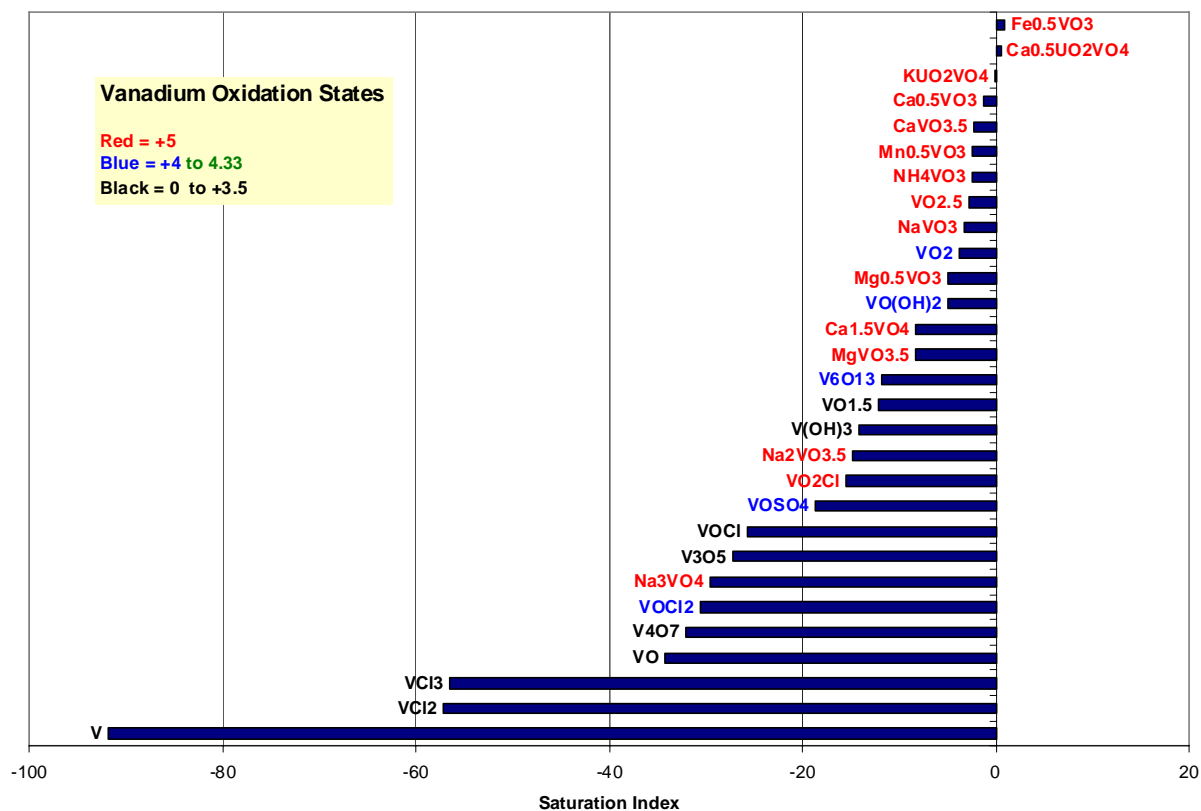


Figure 17. Vanadium Mineral Saturation Indices in Groundwater Sampled from Well 0855 on 4/15/2010. Oxidation states of vanadium are color coded. Minerals near the top are nearest to being in equilibrium with the water sample.

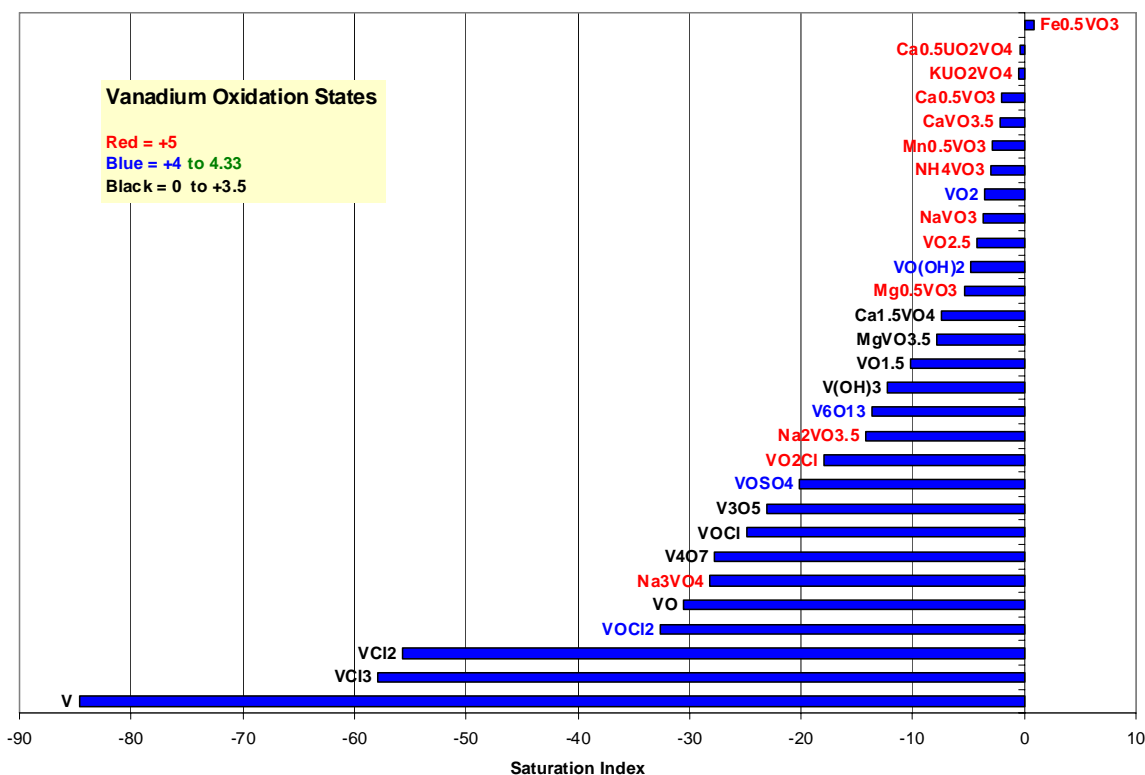


Figure 18. Vanadium Mineral Saturation Indices in Groundwater Sampled from Well 0857 on 4/15/2010. Oxidation states of vanadium are color coded. Minerals near the top are nearest to being in equilibrium with the water sample.

4.4 Correlation of Vanadium Concentration with Dewatering Event

The highest concentrations of vanadium in well 0855 and 0857 groundwater are in samples collected after the onset of groundwater pumping for construction of the City's wastewater treatment plant. Pumping began in February 2008 and caused drawdown of the groundwater table in the area of wells 0855 and 0857. The drawdown was about 3 ft in well 0855, which was sufficient to nearly dry up the well (Figure 19). A soil layer containing the highest vanadium contamination detected at the site exists near the bottom of the well (Table 4). The substantial increase (to 1600 mg/L) in vanadium concentration in the groundwater of well 0855 is attributed to the thinning of the groundwater table, which caused direct contact of a relatively small amount of water with the contaminated soil layer. Before pumping lowered the groundwater table, the column of water in the well had contact with a range of soils, most of which were lower in vanadium concentration than the layer depicted in Figure 19.

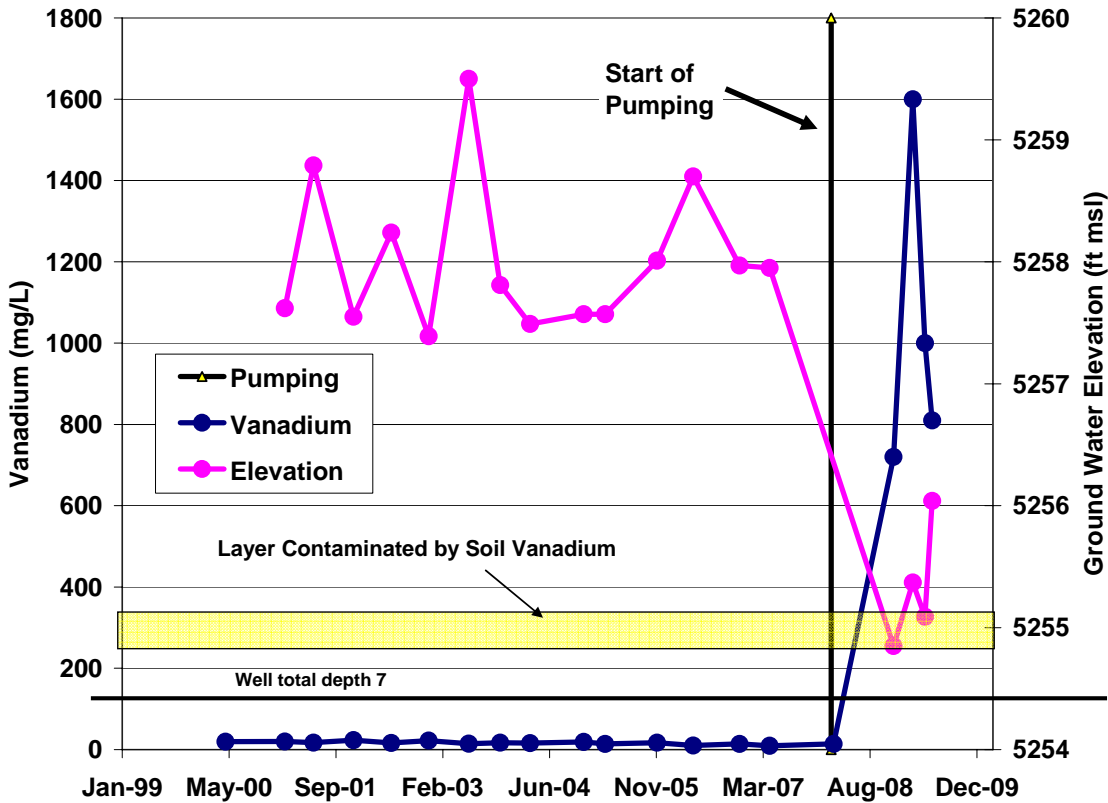


Figure 19. Vanadium Concentration, Groundwater Elevation, and Soil Vanadium Contamination in Well 855.

A similar trend was observed in well 0857 located 30 ft southeast of well 0855, but the vanadium concentrations are much less (Figure 20). Well 0857 was completed to 24 ft, and the water column was thicker than in well 0855, which was completed to 11 feet. Three core samples from well 0857 were analyzed and had much lower vanadium concentrations (maximum of 105 mg/kg) than the layer in well 0855 (Table 4). Therefore, even though well 0857 is close to well 0855, there is no direct contact of groundwater with the vanadium-rich soil layer. It is likely, however, that groundwater entering well 0857 has had contact with vanadium rich layers a short distance away. Groundwater data from well 0857 were collected with SOARS; groundwater was sampled using an autosampler, and the data are thus tightly spaced compared to those from well 0855 (Figure 20). Vanadium concentrations in well 0857 increased rapidly in February 2009, several months later than the increase in well 0855 (the first sample indicating increasing vanadium in well 0855 was collected November 19, 2008). The delay suggests that the highest vanadium concentrations may have originated away from well 0857 (perhaps nearer well 0855) taking a few months to migrate to the 0857 area. The groundwater elevation in well 0857 was already drawn down by the time the SOARS equipment was installed, and only the rebound is observable on Figure 20. In contrast to well 0855, the vanadium concentration is increasing during water table rebound rather than during maximum drawdown.

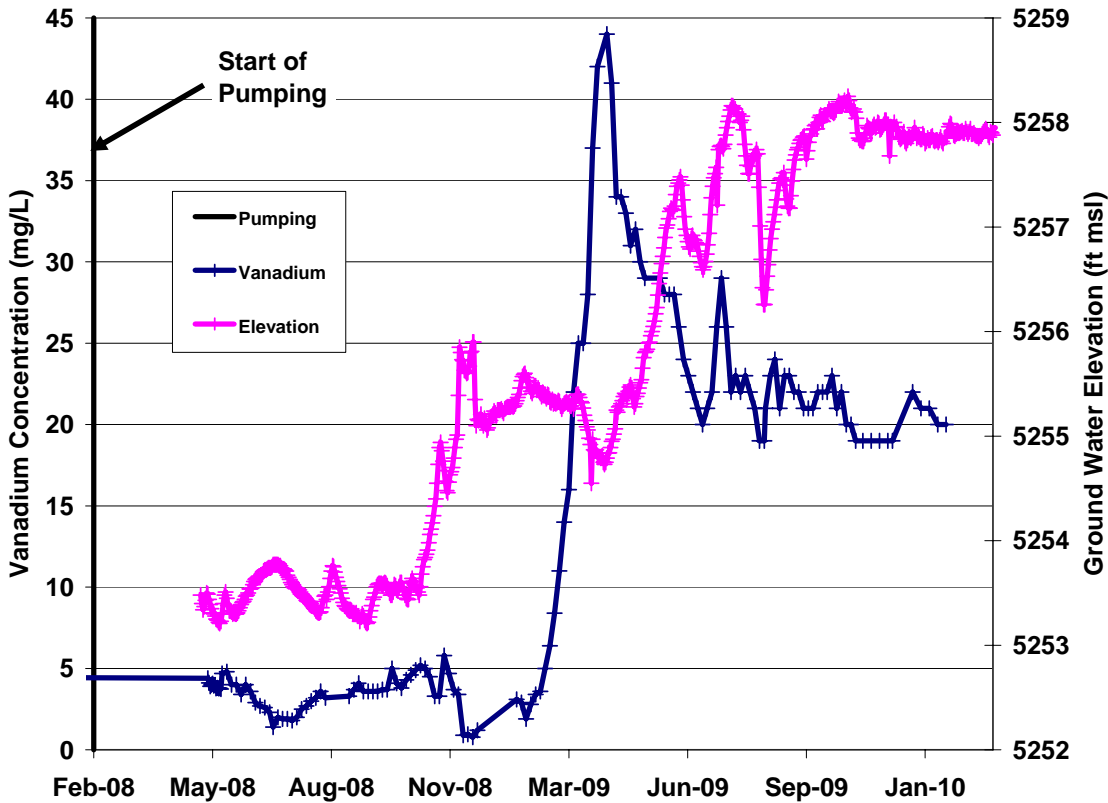


Figure 20. Vanadium Concentration and Groundwater Elevation in Well 857

4.5 Conceptual Model for Groundwater Vanadium

Soils underlying the former mill site have thin, discontinuous layers containing concentrations of vanadium up to at least 6190 mg/kg. Some soil contamination has recently been exposed by excavations for the wastewater treatment plant. Contaminated soils are particularly concentrated below the footprints of former evaporation ponds. It is likely that the soils were contaminated by mill liquors that percolated from the ponds into the subsurface during mill operation. DOE removed much of the contaminated soil during site remediation in the 1990s, but because cleanup verification was based on radiological criteria, metal contamination that percolated deeper than the radiological contamination could have been missed. Soil exceeding radiological criteria was excavated, removed from the site, and replaced with clean fill. Much of the vanadium contamination currently is in soils below the depth of the clean fill.

The contaminated soils have a green or yellow-green color and likely contain oxidized vanadium and uranium-vanadium minerals such as ferrous vanadate and tyuyamunite. Geochemical equilibrium analysis indicates that these minerals are close to saturation in the groundwater. In addition to mineral hosts, vanadium is likely adsorbed to soil particles such as ferric oxyhydroxide and, to a lesser extent, clay minerals.

An alternate explanation for increases in dissolved vanadium during construction dewatering is oxidation brought about by an incursion of atmospheric oxygen caused by water table drawdown. This explanation requires that minerals containing V(+3) or V(+4) be present in the subsurface. Although this concept cannot be ruled out, currently no data support the presence of reduced vanadium minerals. Existing data suggest the presence of an oxidized subsurface dominated by V(+5).

Conceptually, clean groundwater enters the area of the former mill site from upgradient. The background vanadium concentration in soil is probably similar to the 93 mg/kg value observed in upgradient boring 0844 (Figure 21). The flowing groundwater encounters contaminated soils beneath the former ponds, and vanadium is transferred from the solids to the aqueous phase. The vanadium transfer occurs through mineral dissolution and desorption (Figure 21).

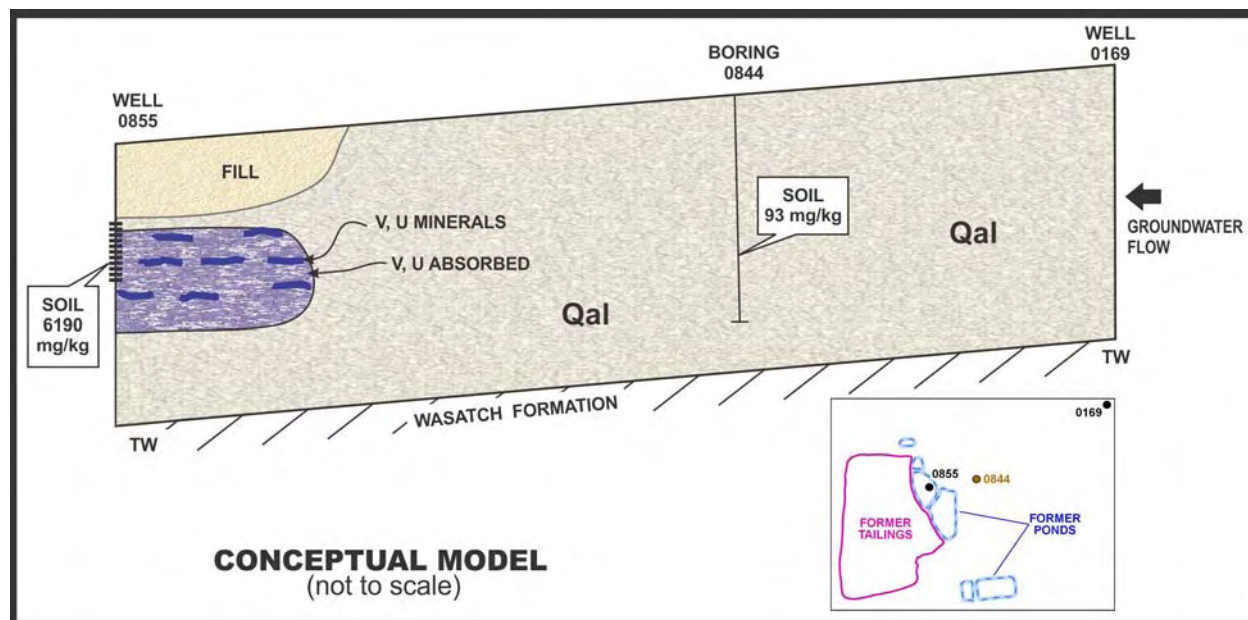


Figure 21. Conceptual Model of Vanadium System in New Rifle Alluvium

Dissolved vanadium concentrations vary with the fluctuating groundwater table. Vanadium concentrations increased in well 0855 during an extreme lowering of the groundwater table by construction dewatering. The fluctuating groundwater levels may simply cause changes in the proportions of groundwater that are in direct contact with a variety of contaminated soil layers.

4.6 Numerical Transport Model

To better exemplify the conceptual model presented in the previous section, a one-dimensional transport model was developed (Figure 22). The model invokes mineral precipitation, mineral dissolution, soil adsorption, and soil desorption. Model calculations were performed using the transport algorithm in PHREEQC. Surface complexation parameters for uranium are from Morrison et al. (1995). Surface complexation parameters for vanadium and all other cations are from Dzombak and Morel (1990). The vanadium surface complexation equilibrium constants were modified slightly to be internally consistent with the PHREEQC database by curve matching to the empirical data provided in Dzombak and Morel (1990). The only solid phase for

which uranium and vanadium surface complexation parameters are available is amorphous ferric oxyhydroxide (AFO). Thus, the adsorption portion of the model is limited to adsorption on AFO. This assumption is reasonable in that uranium and vanadium adsorption in many alluvial aquifers is likely dominated by AFO. Other adsorption sites likely occur on clay minerals and other silicates as well as other oxide minerals, but those are likely subordinate to AFO. Since the distribution of adsorption sites and the amount of AFO present in the New Rifle aquifer are not known, the adsorption model is not rigorous and is used to best fit site data. Input files for the PHREEQC modeling are provided as Appendix C.

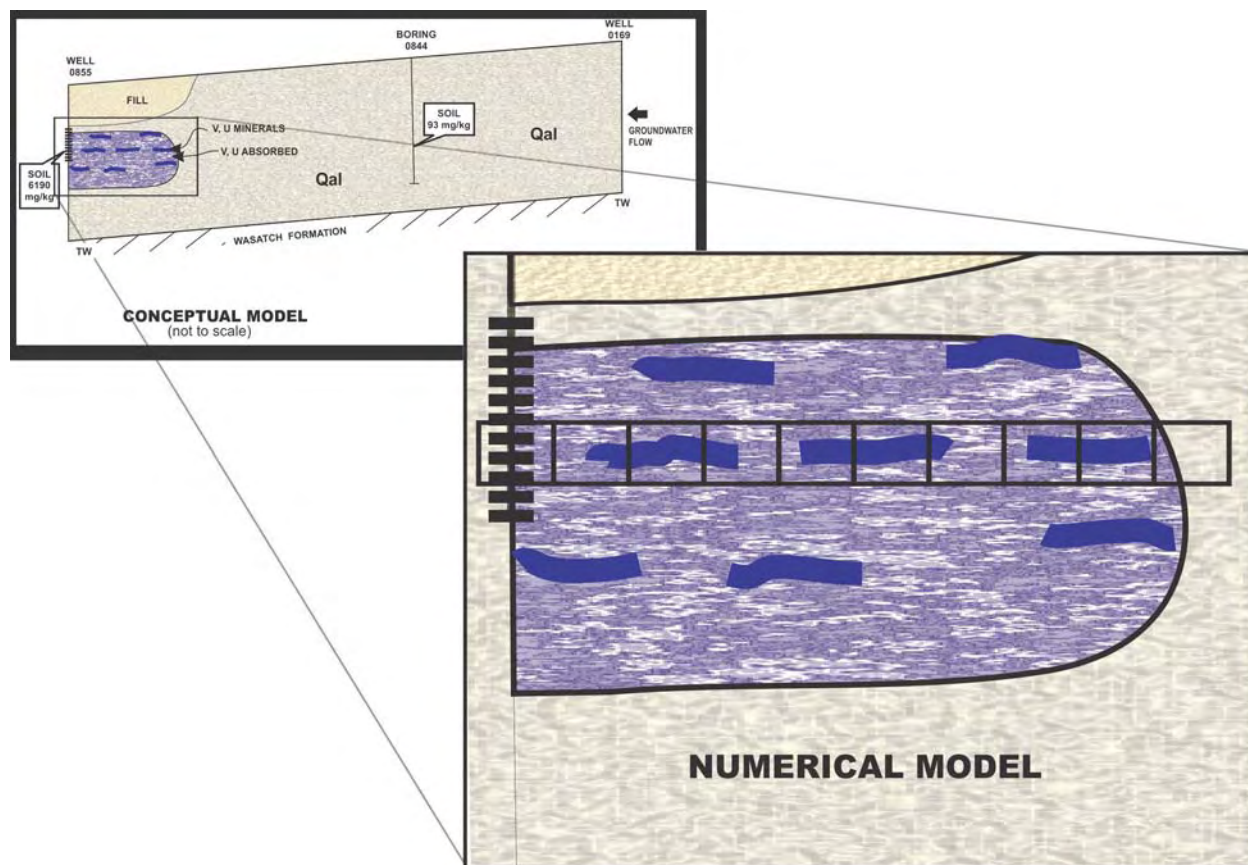


Figure 22. Numerical Representation of Vanadium Accumulation in New Rifle Alluvium. The 10 boxes represent the model cells positioned along a stream tube.

The model simulates chemical reactions occurring along a single stream tube as background-quality groundwater flows into the contaminated domain beneath a former mill pond (Figure 22). Each cell of the model initially contains uranium-vanadium minerals tyuyamunite and carnotite, the vanadium minerals Fe-vanadate and Ca-vanadate, and accessory minerals calcite, gypsum, and AFO (Table 6). An analysis of upgradient well 0169 is used for the background groundwater composition.

Adsorption sites are also present in each model cell. Adsorption is modeled using a surface complexation approach (Davis and Leckie 1978). The approach follows the two-layer adsorption model discussed by Stumm et al. (1970) with two distinct adsorption sites (weak and strong) as presented by Benjamin and Leckie (1981). Dzombak and Morel (1990) found that this combined

model matched well with a multitude of acid-base titration and cation-anion adsorption data. For simplicity, surface precipitation on adsorption surfaces as discussed by Dzombak and Morel (1990) was neglected. Adsorption parameters used in the model are presented in Table 6.

Table 6. Parameters Used in Numerical Model

Parameter	Value
Porosity	0.33
Rock Density	2.7 g/mL
Groundwater Density	1.0 g/mL
Chemical Parameters Included	H ⁺ , e ⁻ , Ca, Na, Mg, K, Cl, Fe, CO ₂ , NO ₃ , SO ₄ , U, V
Number of Cells in Domain	10
Number of Shifts ^a	500
Vanadium Concentration in Soil	5660 mg/kg
Influent Groundwater Composition	From well 0169 (Jan. 28, 1999)
Minerals Allowed	Tyuyamunite, carnotite, Fe-vanadate (Fe _{0.5} VO ₃), Ca-vanadate [Ca ₃ (VO ₄) ₂], calcite, gypsum, amorphous ferric oxyhydroxide [Fe(OH) ₃]
Specific Surface Area (AFO)	600 m ² /g
Concentration Weak Adsorption Sites ^b	0.192 mol/L _{water}
Concentration Strong Adsorption Sites ^b	0.0048 mol/L _{water}

^a For each shift, water is moved the length of one cell.

^b These site concentrations are equivalent to about 1% Fe as AFO.

m²/g = square meters per gram

mol/L = molar concentration in moles per liter

As background groundwater enters the upgradient cell (Cell 1) of the modeled stream tube, it reacts with minerals and adsorption sites that were initially in chemical equilibrium with the pore water. Although the concentrations vary throughout the stream tube, the water leaving the stream tube (the effluent) at model Cell 10 is used here as an example of the variations in vanadium concentrations that would be expected to occur in the subsurface. Detailed field knowledge of chemical variation along specific stream tubes is not available; however, it is possible to evaluate whether the variation in vanadium concentrations is consistent with the variation observed in available field data. The modeled effluent vanadium concentration is more than 17,000 mg/L after the first pore volume but rapidly decreases to about 180 mg/L (Figure 23). The vanadium concentration remains at this level until it again rapidly decreases to about 16 mg/L at pore volume 31, after which it slowly decays to 8 mg/L by pore volume 50. Uranium concentrations portray a mirror image of the vanadium trend but at much lower concentrations (Figure 23).

The extremely high initial effluent vanadium concentration is caused by the dissolution of calcium vanadate, a highly soluble mineral. The inventory of calcium vanadate is exhausted by pore volume 1.5, after which dissolved vanadium concentrations decrease (Figure 24). All vanadium-bearing minerals are in equilibrium with the aqueous phase through pore volume 28, when ferrous vanadate begins to dissolve. Ferrous vanadate becomes exhausted by pore volume 31, at which time the dissolved vanadium concentration decreases further. The dissolution of ferrous vanadate is coupled to other processes occurring in the chemical system. At pore volume 28, gypsum is precipitating at the expense of calcite, and AFO is precipitating. Depletion of dissolved iron caused by AFO precipitation results in dissolution of ferrous vanadate. A plot of the changes (deltas) in mineral masses better shows these relationships (Figure 25).

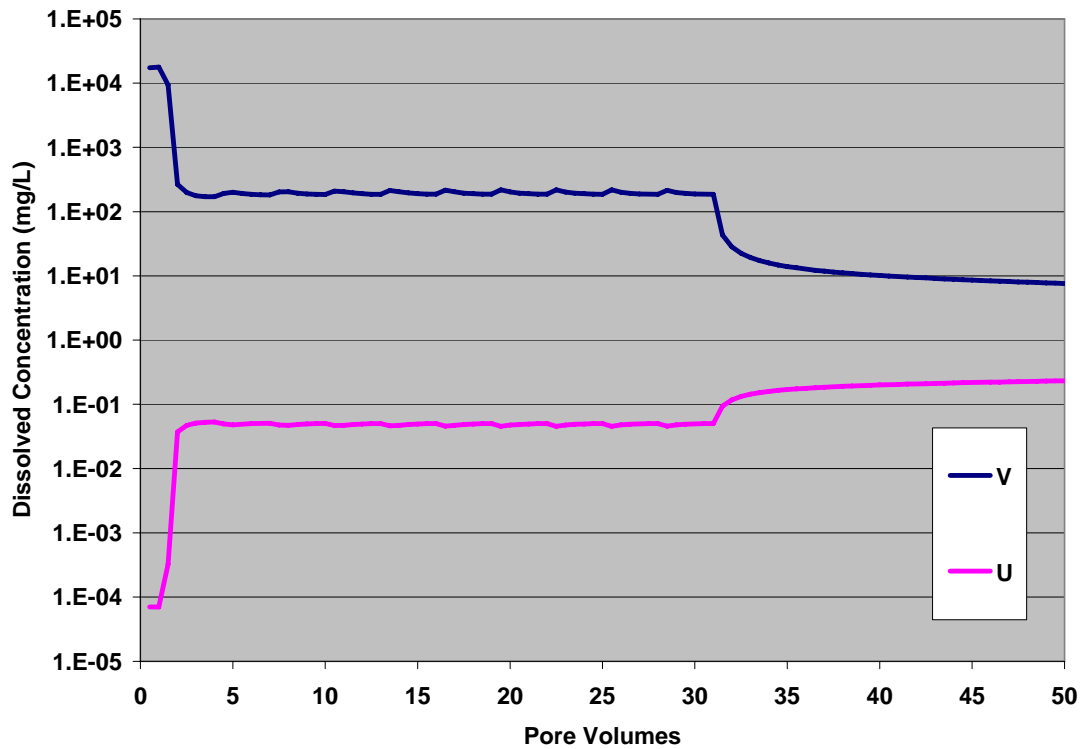


Figure 23. Modeled Effluent (Cell 10) Logarithmic Concentrations of Vanadium and Uranium

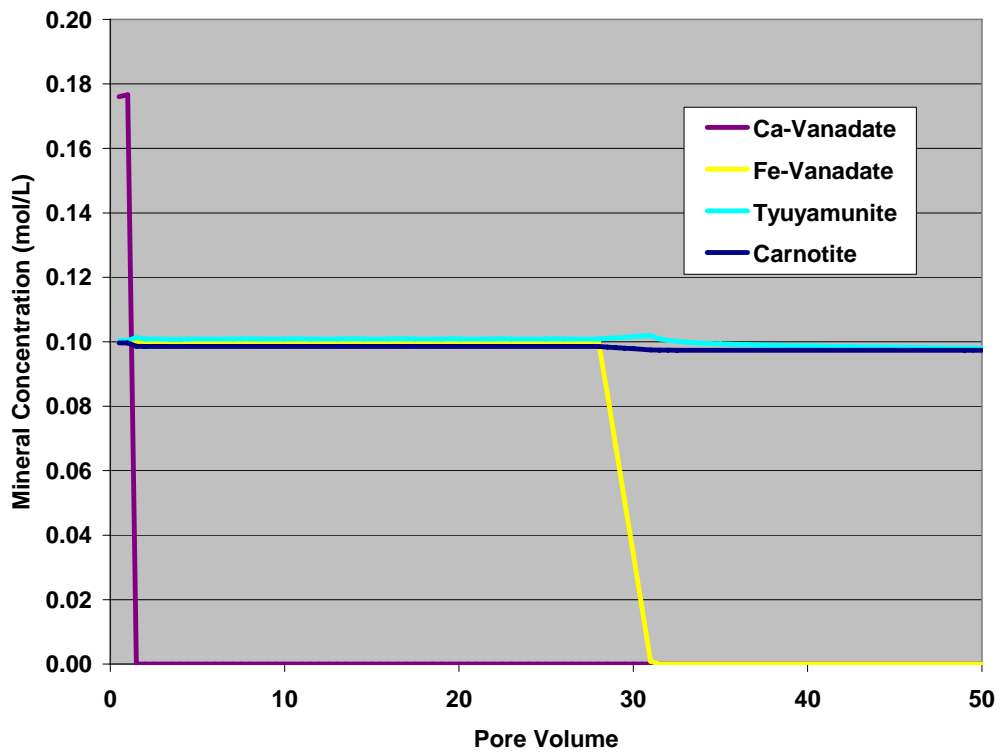


Figure 24. Modeled Effluent Concentrations of Vanadium-Bearing Minerals (in moles per liter of pore fluid). Initial concentrations: ferrous-vanadate, tyuyamunite, and carnotite are 0.1 mol/L; for Ca-vanadate, 0.3 mol/L.

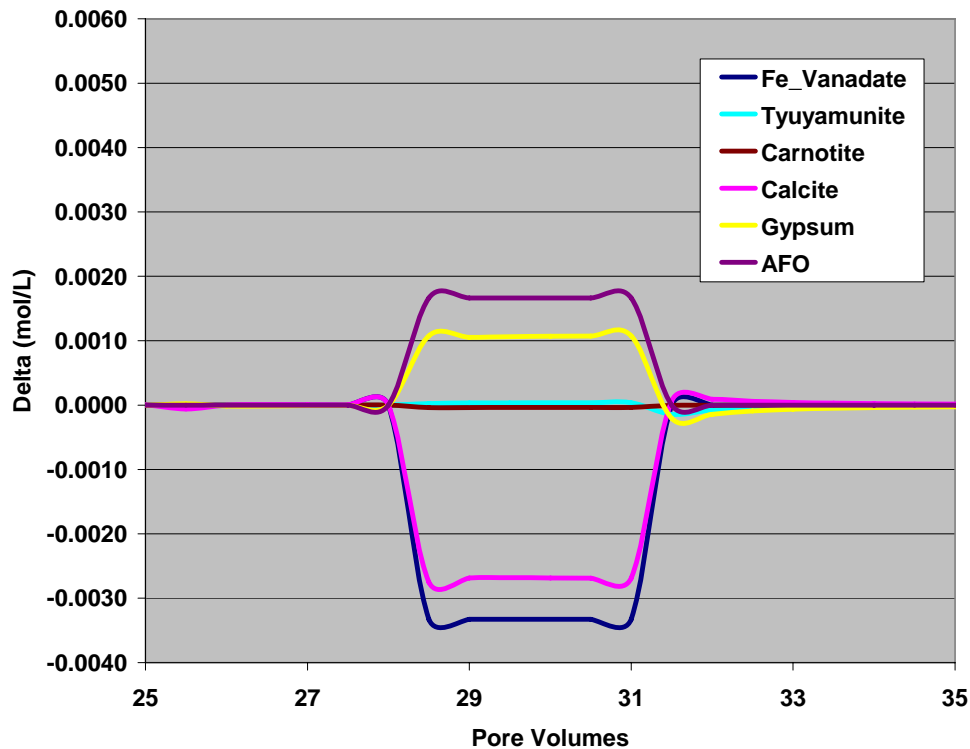


Figure 25. Modeled Changes (Delta) in Mineral Abundances. Positive values indicate mineral precipitation, negative values indicate dissolution, zero indicates that the mineral is at equilibrium with the aqueous phase.

In Figure 25, a zero value indicates that the mineral mass is not changing, whereas a positive value indicates the mass is being added to by precipitation, and a negative indicates that dissolution is occurring. After the depletion of ferrous vanadate, desorption is the dominant process controlling aqueous vanadium concentrations. Adsorption of vanadium, modeled by the AFO surface complex wOHVO_4^{3-} , parallels the aqueous concentrations (Figure 26). After the more soluble vanadates become exhausted at pore volume 31, vanadium slowly desorbs from these surfaces causing a long-lasting “tail” of lower concentration that is still significantly above background.

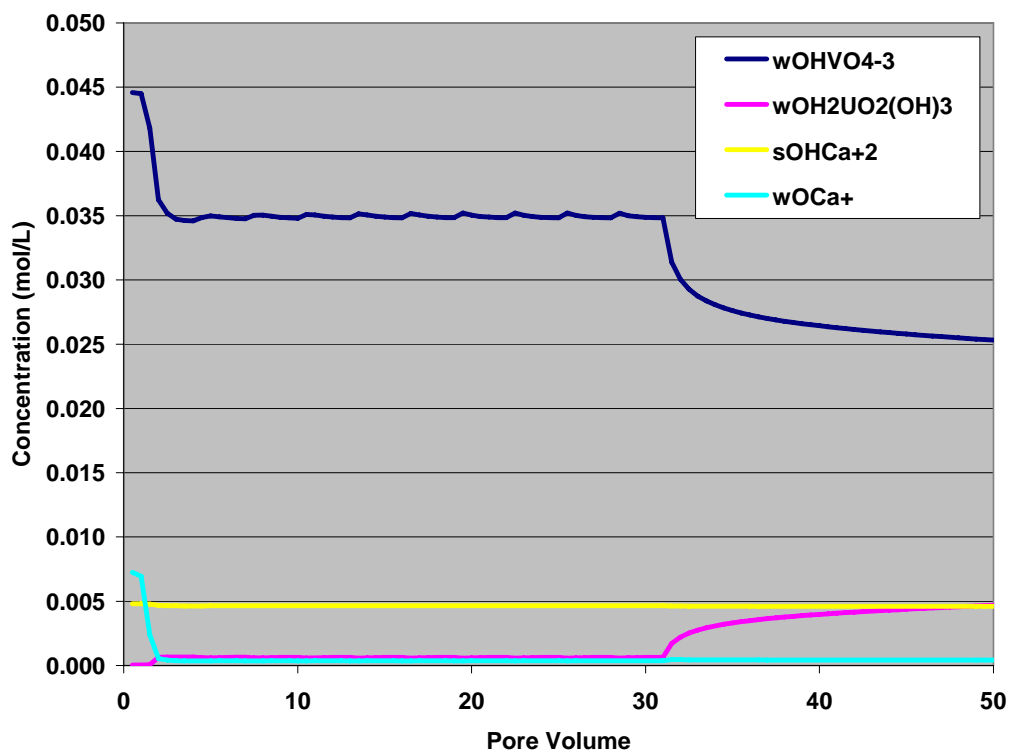


Figure 26. Modeled Effluent Concentrations of Adsorbed Species (in moles per liter of pore fluid)

The variation observed in the modeled vanadium concentrations are consistent with the variations observed in well water samples. Vanadium concentrations as high as 1600 mg/L were detected in samples from well 0855. These extreme concentrations could be caused by the presence of a highly soluble vanadate such as calcium vanadate. Once sufficient groundwater has contacted soils to remove the soluble phases, concentrations will decrease. Most of vanadium concentrations in the most concentrated portions of the plume at New Rifle vary around 10 to 50 mg/L. These concentrations are in general agreement with the modeled values prior to exhaustion of ferrous vanadate, and later when dissolved vanadium is controlled by desorption. Although not analyzed by x-ray diffraction, the yellow-green colors of the minerals observed in the vanadium-rich soils of the construction area are consistent with vanadates.

The vanadium concentration increased rapidly in well 0855 when the groundwater table was lowered. Lowering the groundwater table caused the well to nearly dry up, causing the decreased thickness of the water column in the well to be in direct contact with a soil layer containing the highest vanadium concentrations observed in the site soils. It is likely that the high concentration of vanadium in this soil layer is residue from mill liquors that percolated into the soils beneath a former mill pond. The contaminated soil was not removed during site remediation because it did not meet the radiometric standard that was used to verify soil removal. The mineralogy of the layer is unknown, but the vanadium-rich (1600 mg/L vanadium) groundwater in well 0855 had a yellow-green color, likely imparted by dissolution of vanadate minerals. Prior to the aquifer dewatering and during rebound from dewatering, well 0855 had lower concentrations of vanadium. These lower concentrations could be due to mixing of groundwater that had contact with soils containing vanadate minerals, soils containing only adsorbed vanadium, and soils that were relatively clean. Mixing of these groundwaters would be more pronounced with a higher

groundwater table. Well 0857 also had higher concentrations of dissolved vanadium during dewatering, possibly also due to a change in the amounts of groundwater contaminated by the variable soil compositions.

Dissolved uranium concentrations in wells 0855 and 0857 are much lower than the vanadium concentrations. The modeled uranium concentrations are low also, due to equilibrium with uranyl-vanadate minerals (tyuyamunite and carnotite). After depletion of iron vanadate at 31 pore volumes, uranium concentrations begin to increase slightly. The increasing dissolved uranium is from tyuyamunite dissolution being destabilized by the lower concentrations of dissolved vanadium during the desorption phase. Thus, the model results also help explain the relatively low uranium detected in the New Rifle groundwater system.

5.0 Conclusions

The goal of the project was to monitor the vanadium plume during a significant dewatering of the groundwater system and to provide a reasonable explanation for the observed vanadium behavior. This project did not investigate human health or ecological risk factors associated with the groundwater vanadium plume; thus, this document does not address recommendations regarding land use.

Vanadium at the New Rifle site is present in high concentrations in subsurface soils in a heterogeneous distribution. The soil vanadium is probably dominated by the +5 oxidation state occurring in vanadates and uranium vanadates and in vanadium adsorbed to soil particles, particularly those containing ferric oxides and oxyhydroxides. The vanadium in the soils was likely residue from mill leachates that infiltrated the subsurface during milling and were not removed during site remediation in the early 1990s.

High concentrations of vanadium up to 1600 mg/L have been detected in groundwater beneath former mill ponds. The vanadium contamination in the groundwater is explained by dissolution of soluble vanadate minerals and desorption from ferric oxyhydroxides. Of note, a ferrous vanadate with solubility that is coupled to the iron system may in part control vanadium distributions, and changes in redox with respect to the iron system could also affect vanadium concentrations. Lowering of the groundwater table during construction dewatering caused vanadium concentrations in some wells to increase. These increases are attributed to more direct contact with the vanadiferous soil horizons. After the highly soluble mineral fraction is depleted, vanadium concentrations decrease to levels (tens of milligrams per liter) that are characteristic of soil desorption. Without removal of the vanadiferous soil layers, it is likely that vanadium concentrations in the groundwater will remain at tens of milligrams per liter with occasional increases at times when contaminated soil layers are in contact with a limited thickness of groundwater.

6.0 References

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Appendix A

Instrument Calibration Summary Report

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Between February and May of 2008, six wells (0215, 0683, 0684, 0688, 0857, and 0863) within the project area were equipped with monitoring instruments (Figure A-1). Data were collected on 5-minute intervals and automatically downloaded and graphed via the SOARS (System Operation and Analysis at Remote Sites) system. A waste water treatment plant was being constructed in the project area during the study and it is likely that groundwater pumping for construction dewatering influenced groundwater levels and oxidation potentials. The study investigated the fate and transport of a vanadium plume in the shallow alluvial groundwater system resulting from a legacy uranium-vanadium milling operation near Rifle, Colorado. The study period was February 2008 through February 2010.

The SOARS system recorded oxidation-reduction potential (ORP), specific conductance, and water level from in-situ sensors placed in the wells below the water table. The ORP sensors were calibrated to Zobell solution. Specific conductance values were calibrated using commercial reagent-grade standards. Water levels were measured with water level transducers and calibrated against values measured manually with an electronic downhole depth sonde.

This appendix describes the accuracy of the ORP, specific conductance, and water level data collected during the study period. Data are presented from calibration checks made with standard solutions, and comparisons with measurements made using independent instruments. The goal is to determine the reliability of these data.

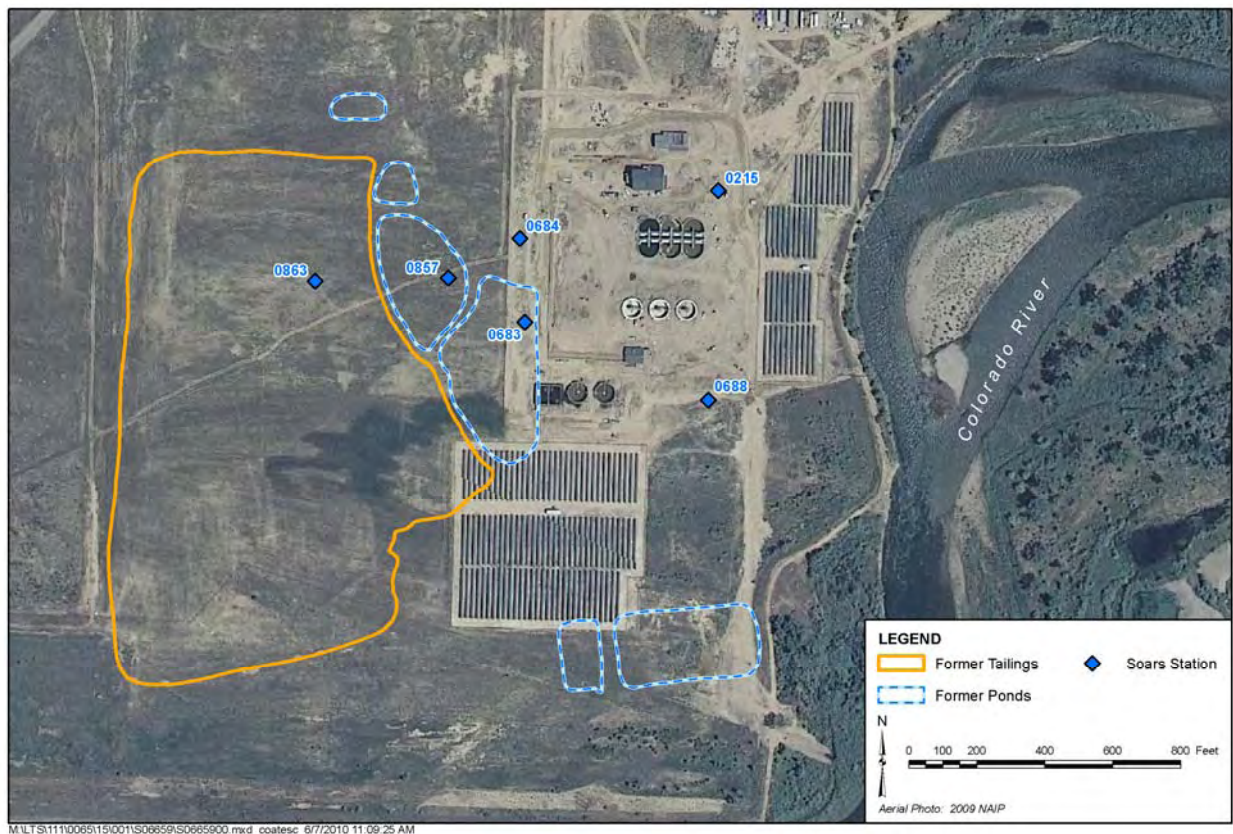


Figure A-1. Location Map Showing Instrumented Wells

Oxidation-Reduction Measurements

ORP was measured with a Campbell Scientific Model CSIM11-ORP gel-filled sensor (Figure A-2). ORP sensors were checked periodically by removing them from the wells and immersing them in Zobell solution. The theoretical ORP of Zobell is 231 mV at 25°C, and varies from 251 mV at 10 °C to 225 mV at 30 °C, the approximate temperature range during this study. For calibration checks, the temperature of the Zobell solution was measured and the theoretical potential corrected to this temperature value. At times, the sensors were cleaned by swirling in a 20% nitric acid solution. Fill solutions in the sensors were changed a couple times during the study.

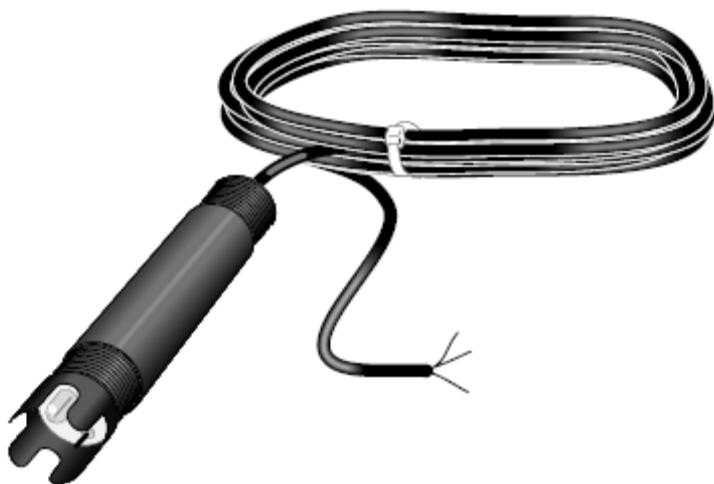


Figure A-2. ORP sensor Model No CSIM11-ORP-L (from Campbell Scientific product literature).

Zobell potentials were determined for six calibration events during the study period. The results are expressed as the deviations from the theoretical potentials in Figure A-3. On this graph, perfect agreement with the theoretical Zobell potential is represented by a zero value, whereas negative values indicate that the sensors are reading low.

In all except two cases, the measured ORP values of the Zobell were less than the theoretical potentials. Two measurements that most closely match the theoretical Zobell potentials are from Wells 0683 and 0684 in the April 2008 event (Figure A-3). New ORP sensors were installed in these two wells on March 21, 2008 and the measurements were taken about one month later on April 22, 2008. Thus, the sensors were relatively new and appear to have held their calibration for a month. Unfortunately, these are the only two checks that were made this soon after a new install. When checked with Zobell again about 4 months later, on August 14 2008, these same sensors (0683 and 0684) measured 90 and 70 mV, respectively, less than the theoretical potential (Figure A-3). In fact, all five ORP sensors checked in August 2008 were at least 50 mV low.

Other than the early results from Wells 0683 and 0684, the most accurate Zobell readings were from the September and April-May, 2009 calibration events (Figure A-3). During these events, the sensors were acid-washed prior to testing in Zobell solution. Zobell measurements made during the last two calibration events, July and December 2009, were well below the theoretical potentials.

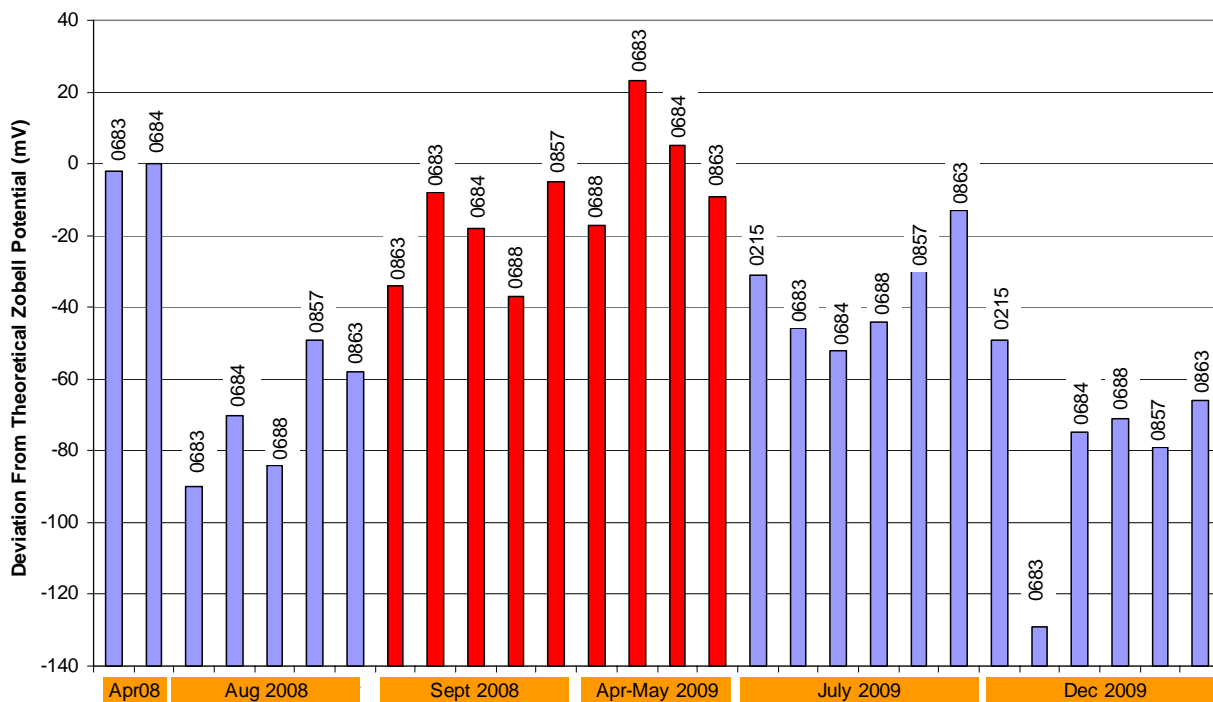


Figure A-3. Deviation from theoretical Zobell potential for the 6 calibration checks made on ORP sondes during the study period. Labels are the well numbers. Red bars are values that were measured following acid cleaning.

The extent and rate of drift to lower ORP values was investigated using the SOARS data following calibration events (Figure A-4 through Figure A-8). During a calibration event, ORP values of the sensors are altered by removing them from the wells, exposing them to the atmosphere, and immersing them in Zobell solution and rinse water. In some cases, the sensors were also immersed in nitric acid to clean them (these are marked "acid" on Figure A-5 through Figure A-8). If operating properly, readings should quickly rebound to nearly the ORP values that were being measured prior to the calibration event. The figures show the ORP values measured immediately prior to the calibration event, and 1 hour and 24 hours after placing the sensor back in the well.

In a few cases, the ORP values rebounded to nearly the same values as were measured prior to calibration within an hour, suggesting that the sensors were reacting quickly with the groundwater. Examples of this desirable behavior are found in Well 215 on 8/14/08, Well 684 on 4/22/08, and Well 863 on 9/4/08. Even the sensor in Well 0863, which had good response to the Zobell solution on 4/22/08 (Figure A-3), did not rebound to the prior groundwater potential after 24 hours (Figure A-5). In most cases, ORP values measured in groundwater an hour after reimmersion were higher than the prior groundwater values. From 1 to 24 hours, the values generally remained nearly constant or decreased. An exception is Well 0863 following the 7/9/09 calibration event in which rebound occurred between 1 and 24 hours (Figure A-8). Some other sensors eventually rebounded to nearly the same values as existed prior to the calibration event but took more time. Observations of longer term data (not shown, but available in SOARS) show

that following the 7/9/09 calibration event, Well 215 rebounded in about 8 days and Well 0684 rebounded in about 15 days.

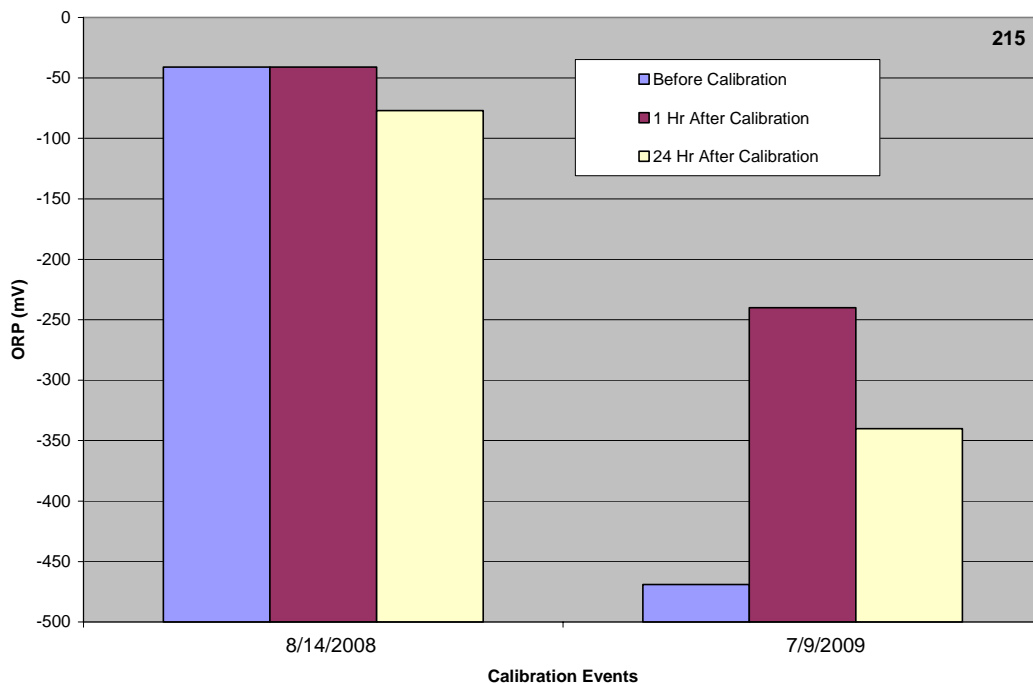


Figure A-4. ORP drift following calibration events for Well 0215. None of these were cleaned in acid.

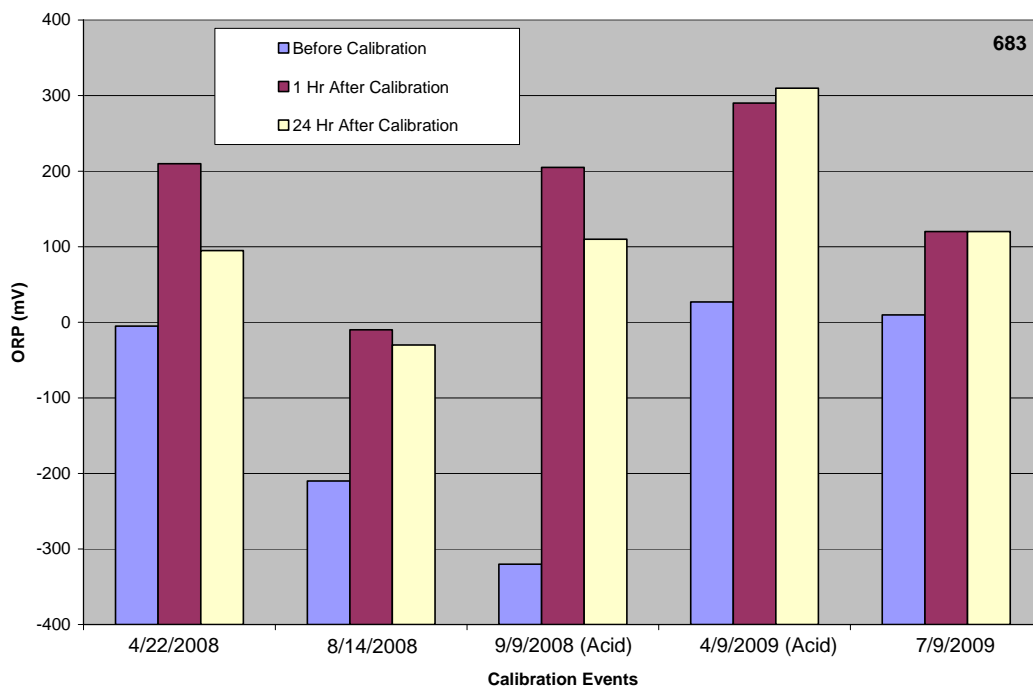


Figure A-5. ORP drift following calibration events for Well 0683. Those marked "acid" indicates they were cleaned prior to reinstallation in the well.

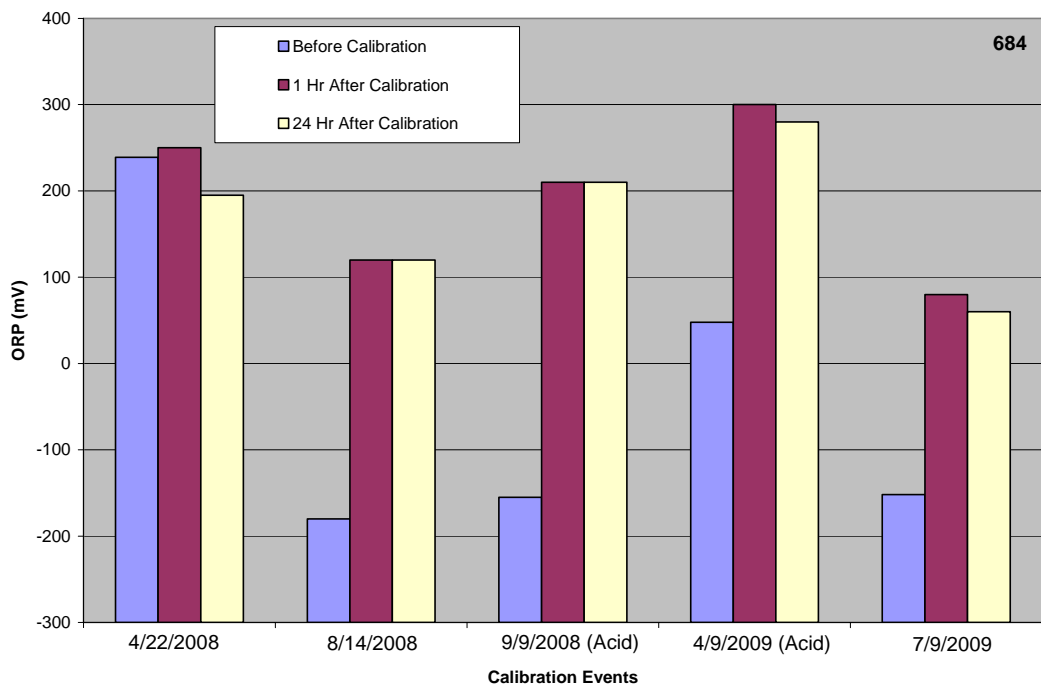


Figure A-6. ORP drift following calibration events for Well 0684. Those marked "acid" indicates they were cleaned prior to reinstallation in the well.

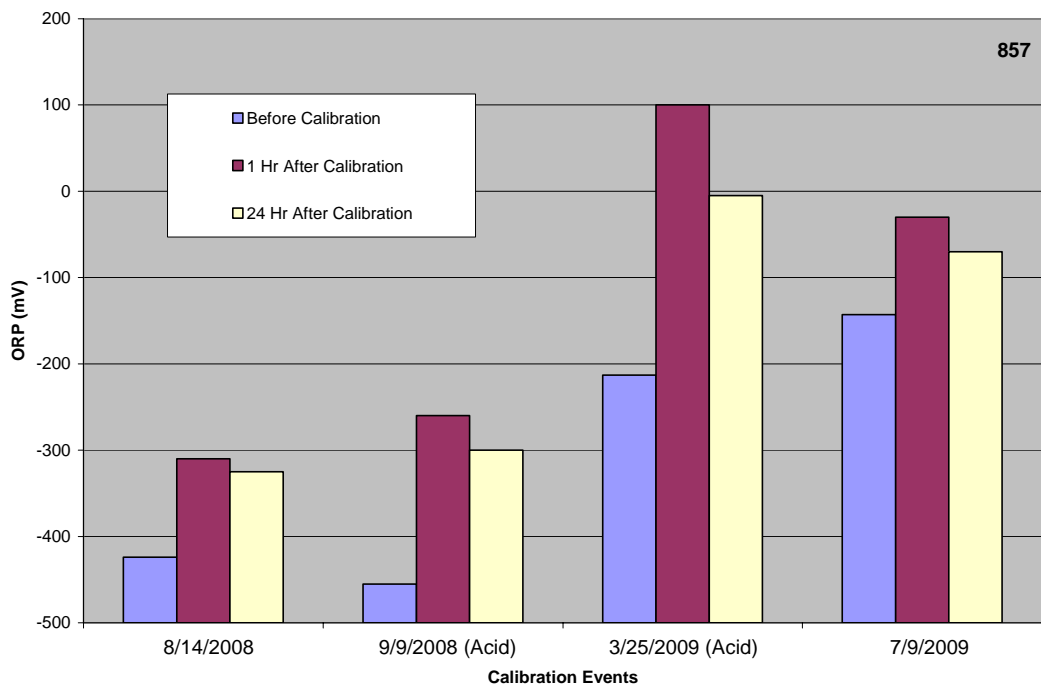


Figure A-7. ORP drift following calibration events for Well 0857. Those marked "acid" indicates they were cleaned prior to reinstallation in the well.

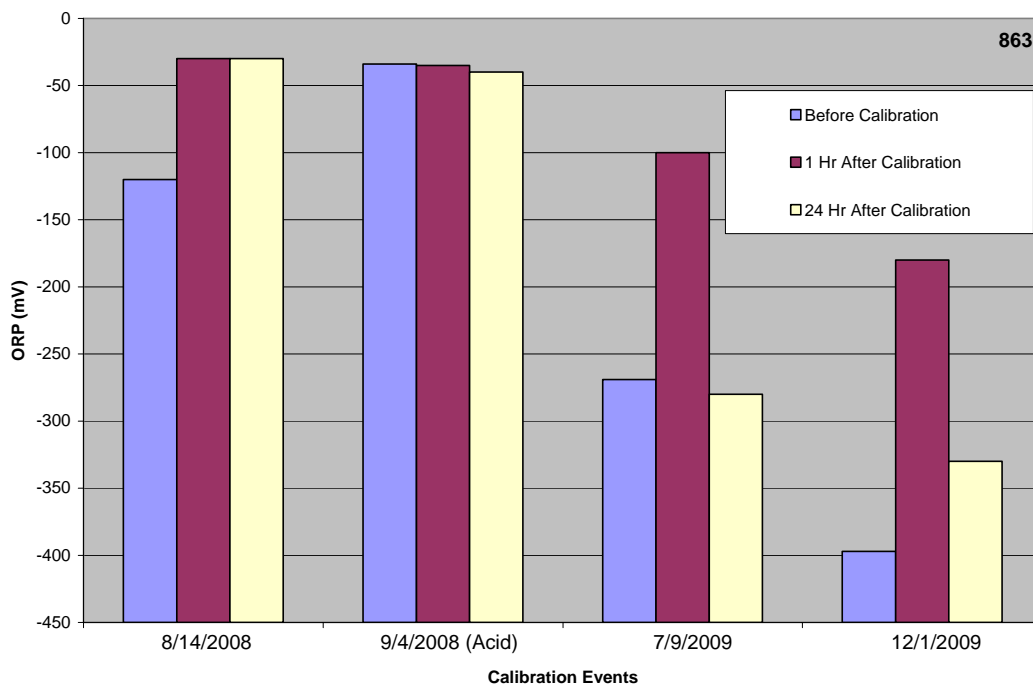


Figure A-8. ORP drift following calibration events for Well 0863. The one marked "acid" indicates it was cleaned prior to reinstallation in the well.

Groundwater was sampled during five events during the study period. ORP data available from these events is used as an additional indication of the reliability of the in situ ORP sensors. For a sampling event, groundwater was pumped from the well and ORP was measured in a flow-through cell using a sensor independent from the in situ sensor. The sensor used in the flow-through cell was calibrated with Zobell solution in a laboratory prior to the sampling events. Not all wells were sampled for all events.

In all but two cases, ORP values measured in a flow-through cell (labeled "field" on figures) are higher than values measured in situ (labeled "SOARS" on figures), in many cases much higher (Figure A-9 through Figure A-12). There appears to be better correlation between SOARS and field data in the earlier 4/15/08 sampling than in the later samplings although there are exceptions. This observation supports the suggestion discussed previously that new sensors may have functioned properly for a month, or perhaps several months.

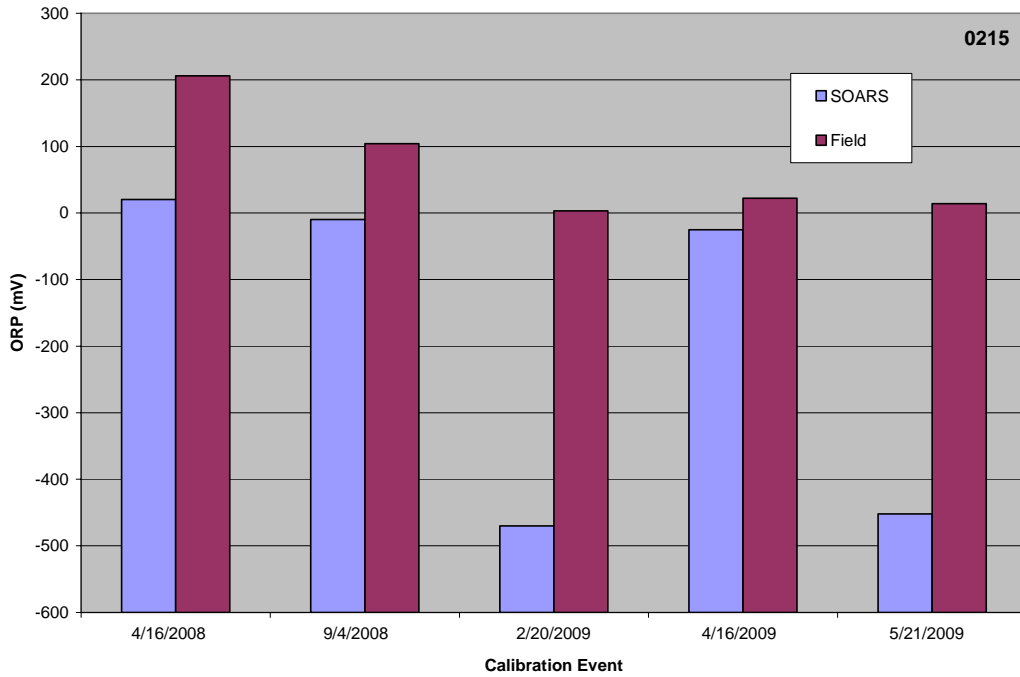


Figure A-9. Well 0215: Comparison of ORP measurements made with the in situ sensor and reported in SOARS, and field sampling values measured in a flow-through cell.

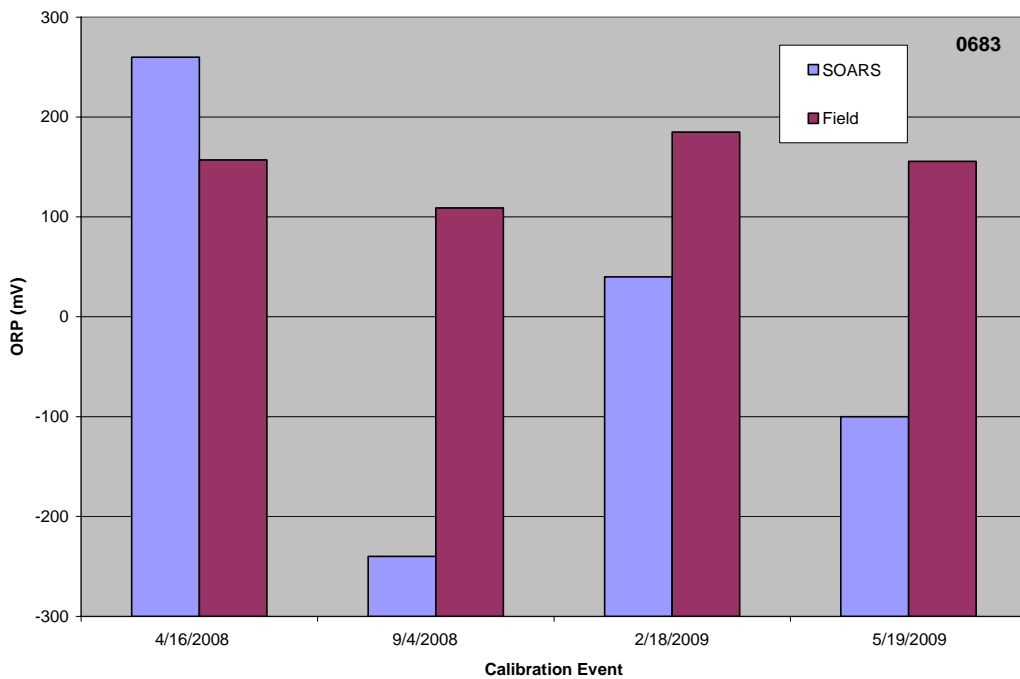


Figure A-10. Well 0683: Comparison of ORP measurements made with the in situ sensor and reported in SOARS, and field sampling values measured in a flow-through cell.

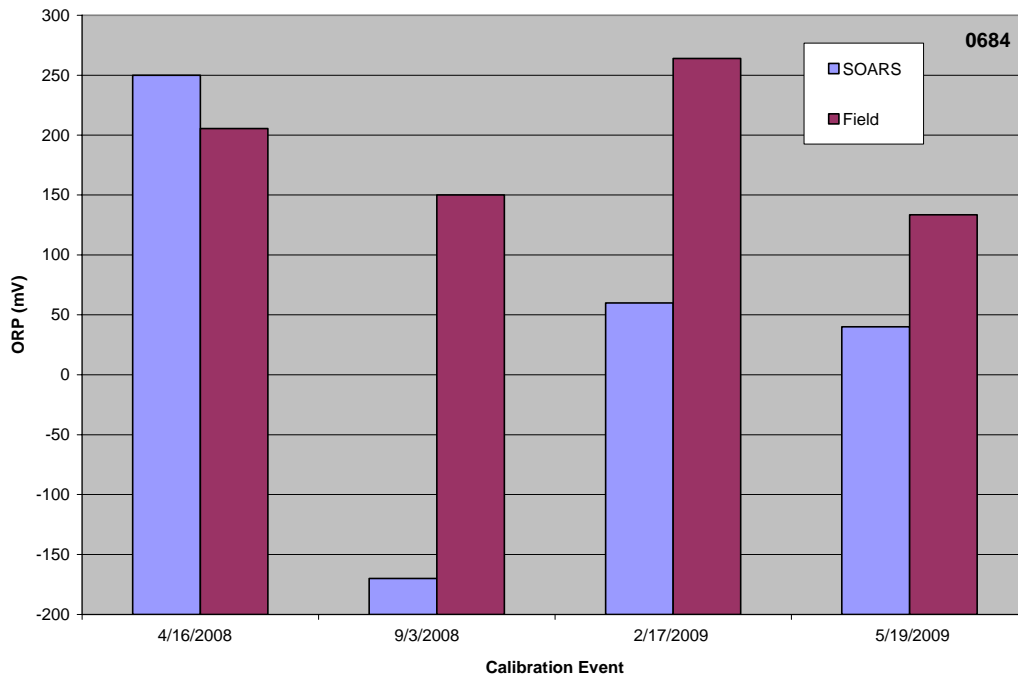


Figure A-11. Well 0684: Comparison of ORP measurements made with the in situ sensor and reported in SOARS, and field sampling values measured in a flow-through cell.

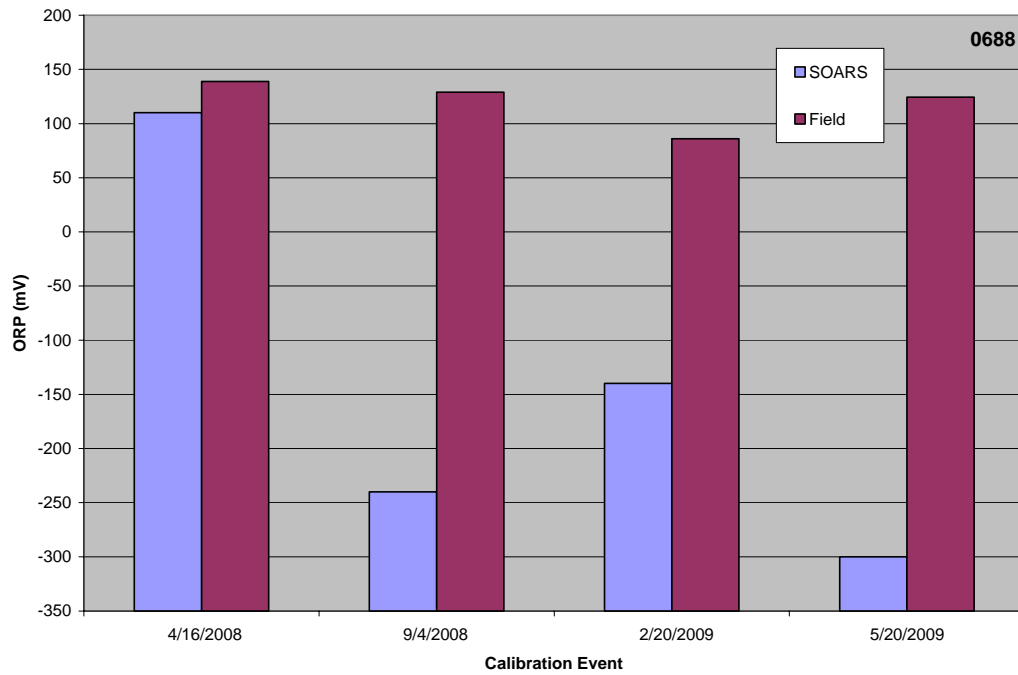


Figure A-12. Well 0688: Comparison of ORP measurements made with the in situ sensor and reported in SOARS, and field sampling values measured in a flow-through cell.

In addition to the data presented above, SOARS longer-term ORP data (not presented here) fluctuate significantly within a single well. Sometimes the values oscillate in a quasi-regular pattern and at times they seem rather erratic. At other times, the ORP signal is smooth and monotonous. While some of these patterns may be attributable to changing redox states in the aquifer due to the nearby groundwater pumping, some of the variation seems uncharacteristic of groundwater and is more likely due to instrument drift or malfunction.

These results suggest that ORP measurements may be accurate when the sensors are relatively new, but drift to lower values over time. Acid washing appears to help restore the sensors, but after several months of use even acid-washing is unable to completely restore them. It is likely that immersion in the groundwater in excess of one month may cause irreparable harm that cannot be restored with simple acid washing. Chemical alteration of the probe fill solution is another possible source of poor performance. Before accepting the results of any future in situ ORP data, sensors should be tested under controlled conditions to confirm reproducibility and accuracy of data, and determine sensor maintenance requirements.

Specific Conductance Measurements

Conductivity was measured with a Campbell Scientific Model CS547A-L conductivity sensor (Figure A-13). Results are expressed as specific conductance, the conductivity value normalized to 25°C. Temperature corrections were made using measurements from an internal temperature sensor and the manufacture's recommended algorithm. The sensors were immersed in groundwater through the well bores. Maintenance consisted only of periodic brushing of the electrode using the manufactures-supplied brush and recommended method.

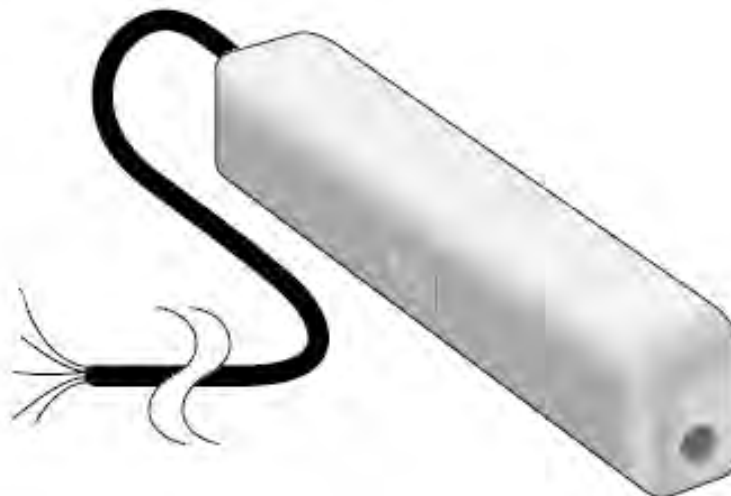


Figure A-13. Conductivity sensor, Model CS547A-L (from Campbell Scientific product literature).

Calibration checks were made using reagent-grade laboratory conductivity standards of deionized water (0 uS/cm), 1,000 uS/cm, and 10,000 uS/cm. Calibration checks were conducted at five times during the study period. Sensors were removed from the wells and immersed in calibration standards. The sensors were rinsed with deionized water between readings. None of the specific conductance probes were calibrated during the study, but rather the manufacturer's recommended calibration algorithms were used.

Specific conductance measurements of deionized water were generally close to the theoretical value of 0 uS/cm, with most between 0 and 10 uS/cm (Figure A-14). The higher values (up to 250 uS/cm) measured during the March 2008 calibration event were due to a slightly contaminated deionized water standard, an observation noted during the fieldwork. Specific conductance measured on the 1,000 uS/cm standard ranged from 930 to 1142 uS/cm, but most were within 50 uS/cm of the standard (Figure A-15). Values measured on the 10,000 uS/cm standard ranged from 9,003 to 11,711 uS/cm (Figure A-16). Many of these were near the 10,000 uS/cm standard; however, most were slightly higher. Given the wide range of calibration standards, these results indicate that the specific conductance measurements using the manufacturers algorithms for calibration and temperature correction are reasonably accurate. The results may have been slightly better had the probes been recalibrated regularly during the study.

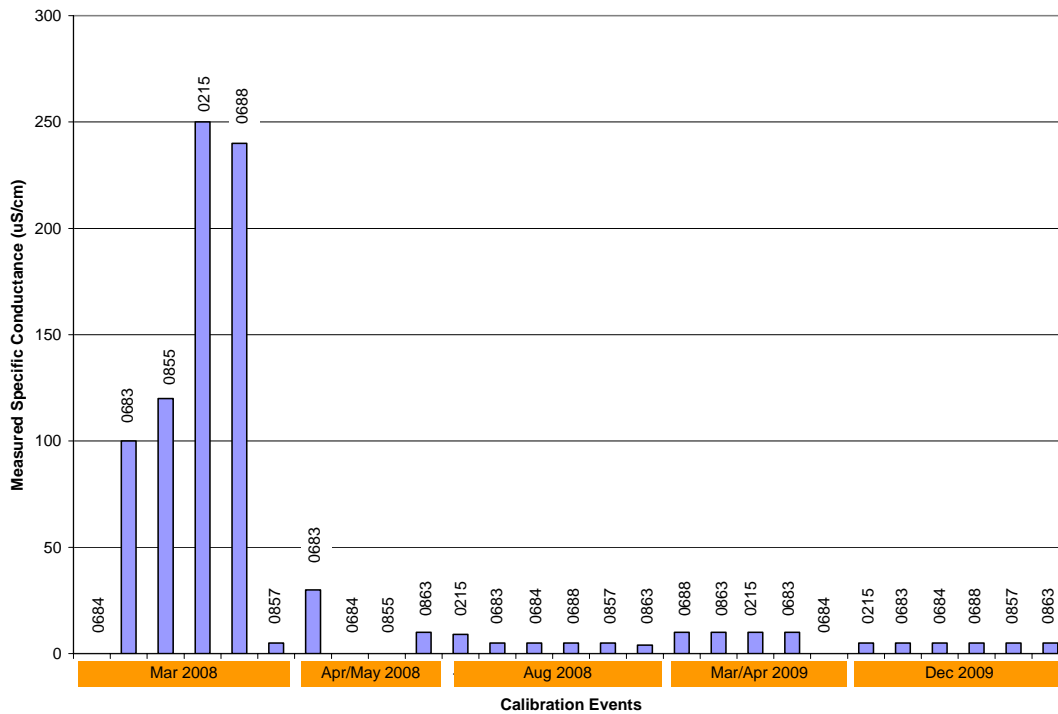


Figure A-14. Results of calibration of in situ specific conductance sensor with deionized water.

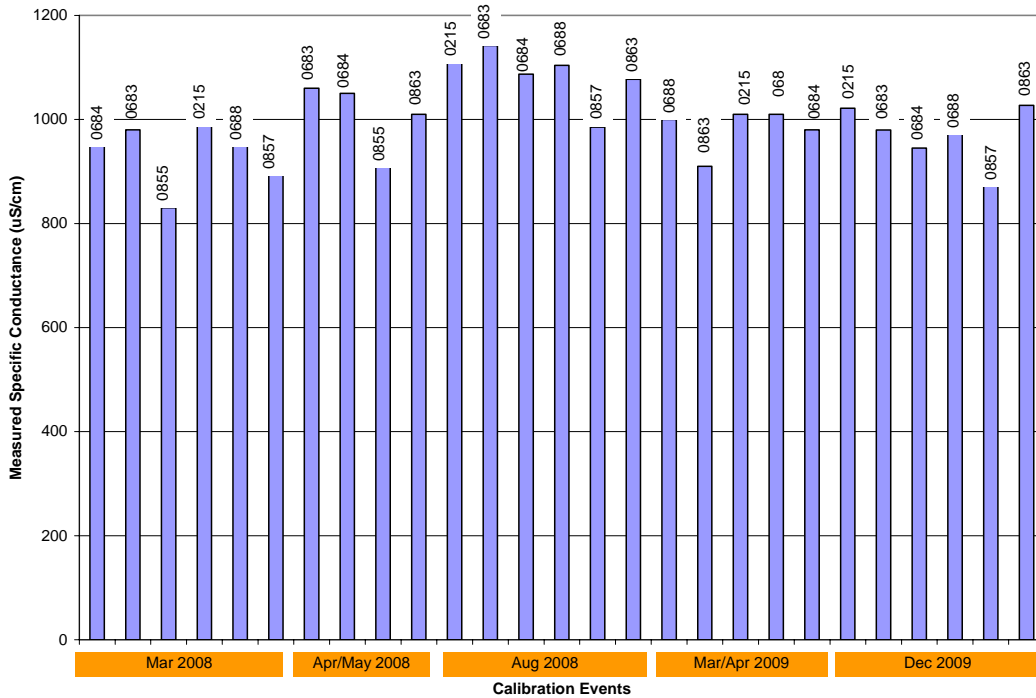


Figure A-15. Results of calibration of in situ specific conductance sensor with a 1,000 uS/cm conductivity standard.

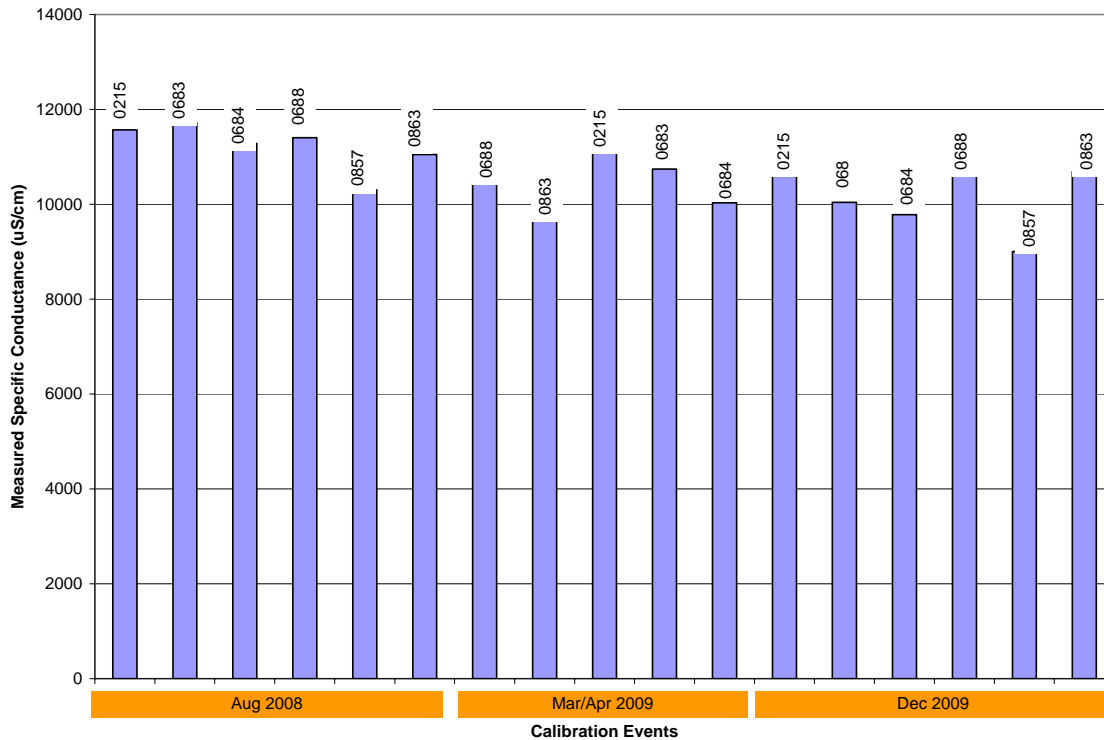


Figure A-16. Results of calibration of in situ specific conductance sensor with a 10,000 uS/cm conductivity standard.

In addition to checking calibration with standards, the accuracy of the in situ specific conductance probes were tested against measurements made using an independent probe in a flow-through cell during sampling events (Figure A-17 through Figure A-22). In most cases, the

specific conductance of the groundwater measured with the two independent instruments were within 10 % of each other. Measurements from wells 0215 and 0863 showed the most variation (Figure A-17 and Figure A-22, respectively). It is uncertain whether the occasional lack of agreement is due to sensor disagreement or to actual specific conductance variation while the sample is pumped through the flow cell.

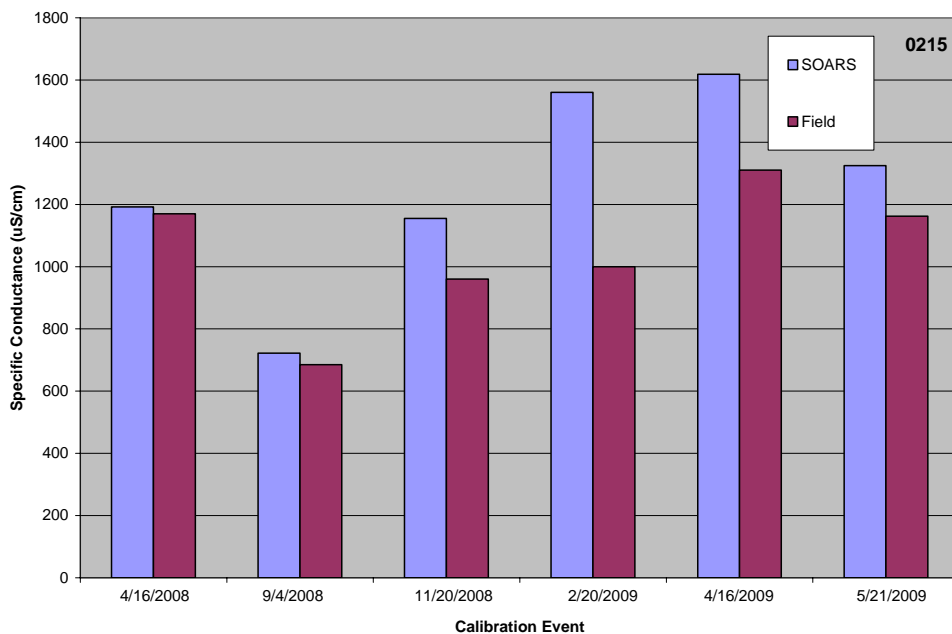


Figure A-17. Well 0215: Comparison of specific conductance measurements made with the in situ (SOARS) probe and those made with an independent sensor in a flow-through cell during sampling.

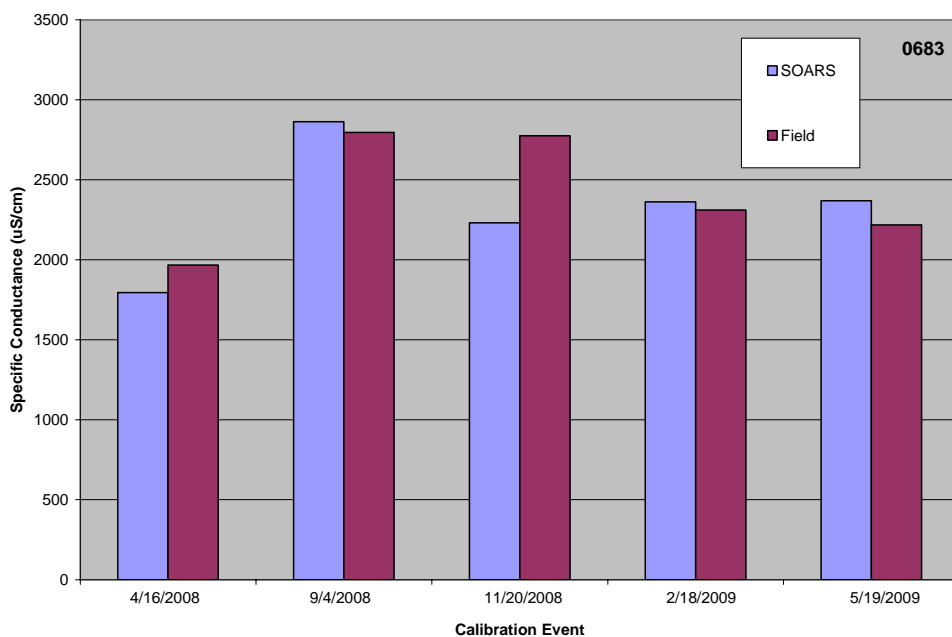


Figure A-18. Well 0683: Comparison of specific conductance measurements made with the in situ (SOARS) probe and those made with an independent sensor in a flow-through cell during sampling.

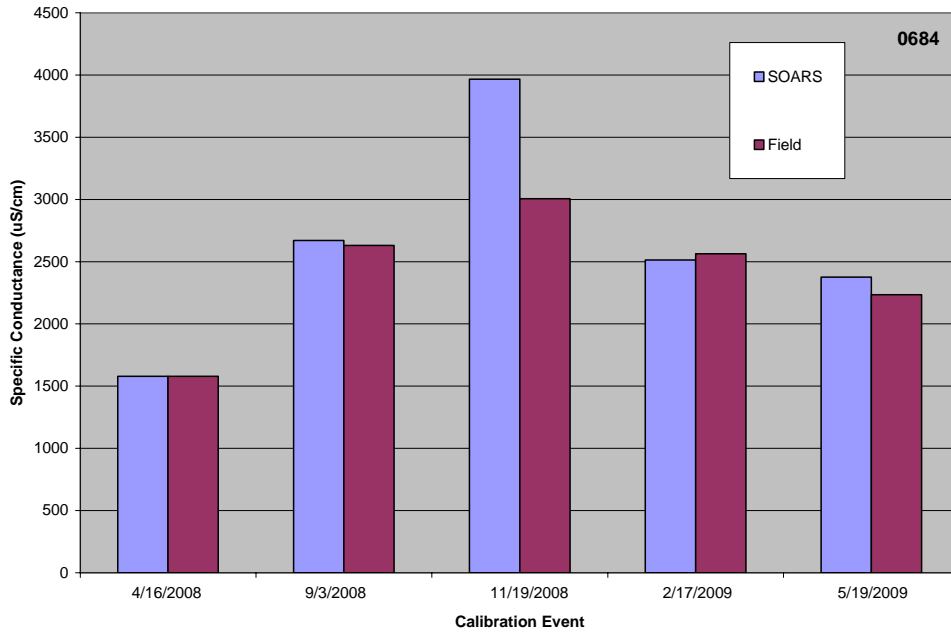


Figure A-19. Well 0684: Comparison of specific conductance measurements made with the in situ (SOARS) probe and those made with an independent sensor in a flow-through cell during sampling.

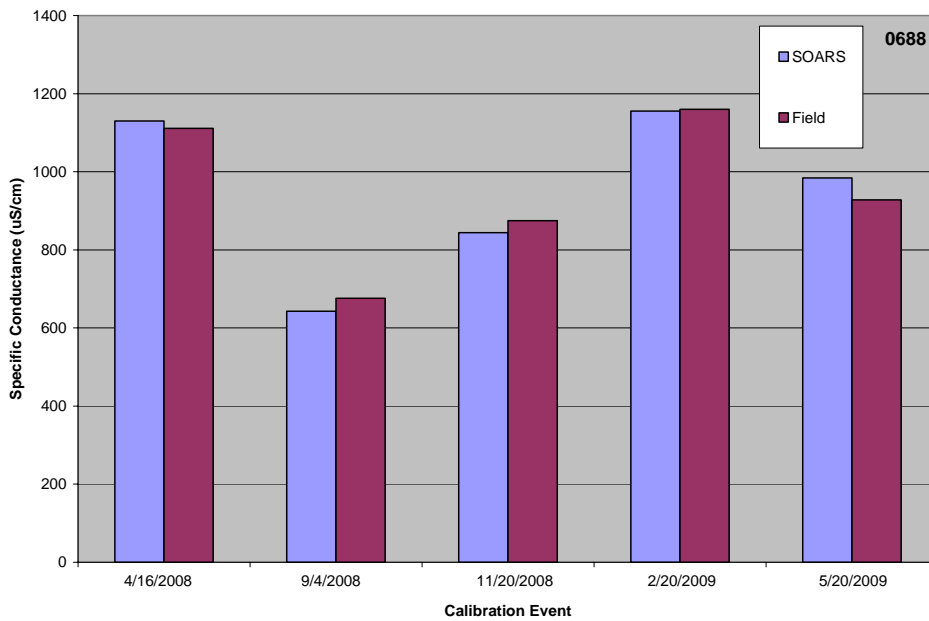


Figure A-20. Well 0688: Comparison of specific conductance measurements made with the in situ (SOARS) probe and those made with an independent sensor in a flow-through cell during sampling.

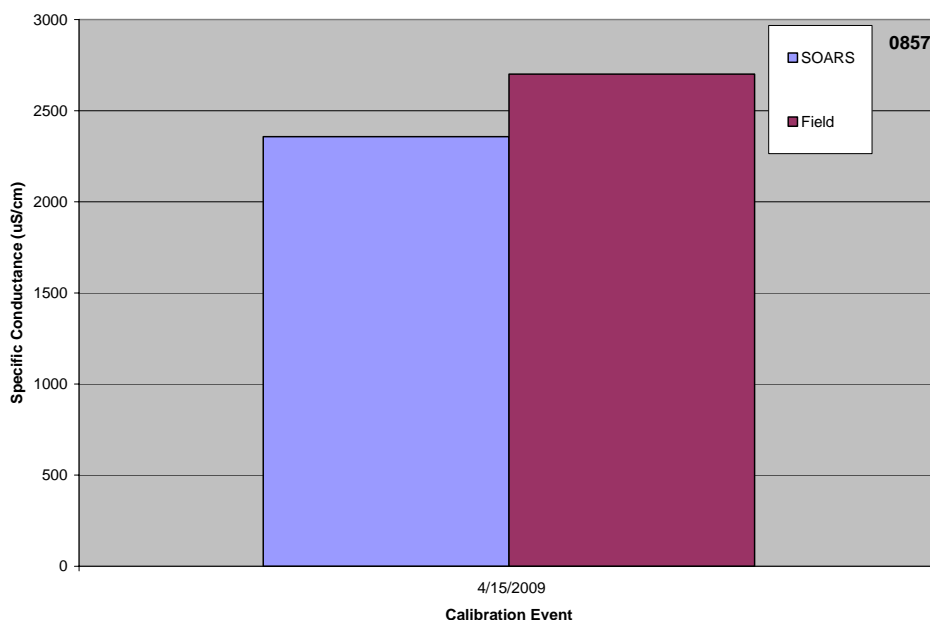


Figure A-21. Well 0857: Comparison of specific conductance measurements made with the in situ (SOARS) probe and those made with an independent sensor in a flow-through cell during sampling.

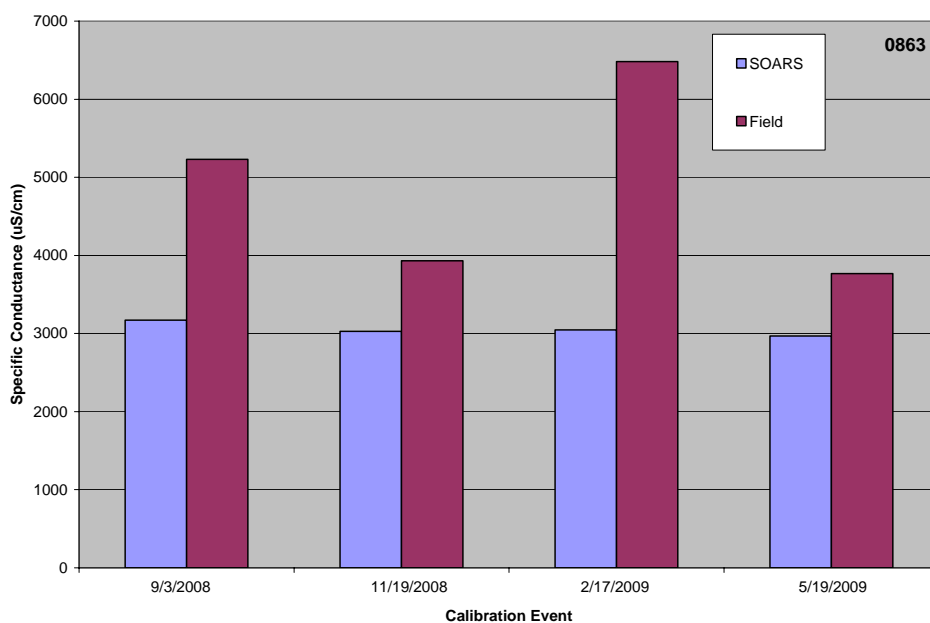


Figure A-22. Well 0863: Comparison of specific conductance measurements made with the in situ (SOARS) probe and those made with an independent sensor in a flow-through cell during sampling.

In contrast to the ORP probes which took many hours or days to rebound to the groundwater values following calibration, the specific conductance measurements rebounded soon (within minutes) after being replaced in the groundwater. The results indicate that the in situ specific

conductance values are reasonably accurate and robust. Additional care in maintaining the calibration of the probes could produce slightly more accurate values.

Water Level Measurements

Groundwater levels were measured with an In Situ Inc, Model PXD261 15 psi pressure transducer (Figure A-23). The transducers were calibrated to a known depth measured with a hand-held electronic water level sensor. The hand-held calibration sensor is accurate to about 0.01 ft. To ensure that the programmed slope equations were correct, depth to water values were rechecked after temporarily changing the position of the transducer by a known amount, usually 1 ft.



Figure A-23. In Situ Inc, Model PXD-261 pressure transducer used for water level determinations (from manufacturer's product information brochure).

Calibration data for the water level transducers during this study are presented in Figure A-24 through Figure A-30. The values recorded by SOARS closely match the values measured in the field using an electronic depth sensor. The differences between SOARS and manual values ranged from -0.45 to 0.56 ft and averaged 0.03 ft. Although the instruments (both the in situ transducer and the manual depth sensor) are capable of accuracy to within about 0.01 ft, due to calibration uncertainty it is likely that our depth-to-water data are routinely (without extended care in calibration) accurate only to about 0.1 ft. In 39 % of the calibration tests, the difference exceeded 0.1 ft as portrayed on a histogram in Figure A-31. Discrepancies greater than 0.1 ft are likely due to inadequate care in calibrating and maintaining the transducers. The discrepancies are more or less random with no apparent correlation to particular wells or calibration events.

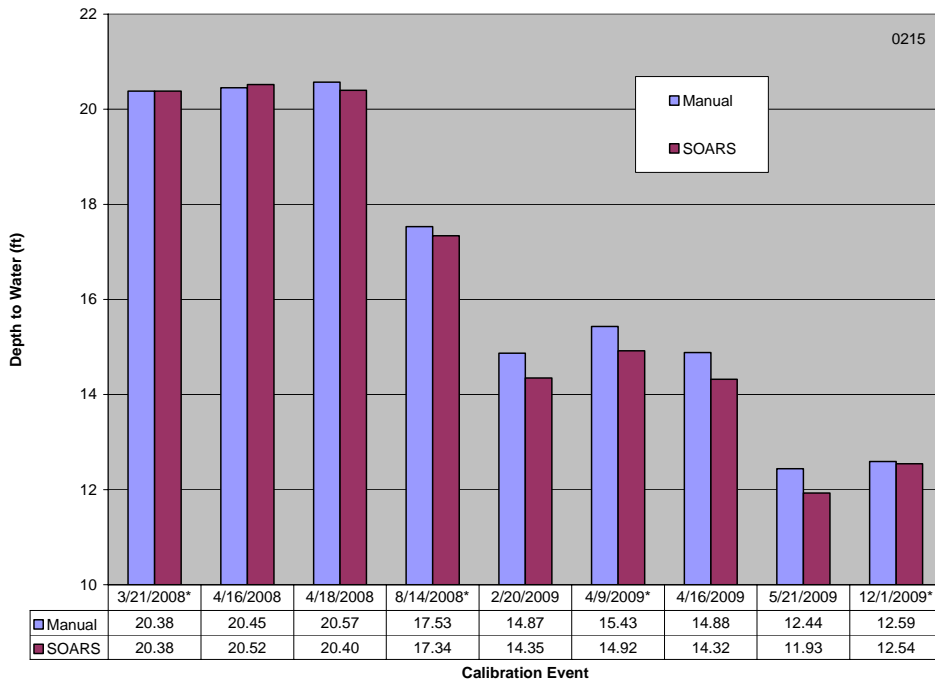


Figure A-24. Well 0215: Comparison of SOARS depth-to-water (ft) readings with manual readings using an electronic depth sonde. Asterik indicates

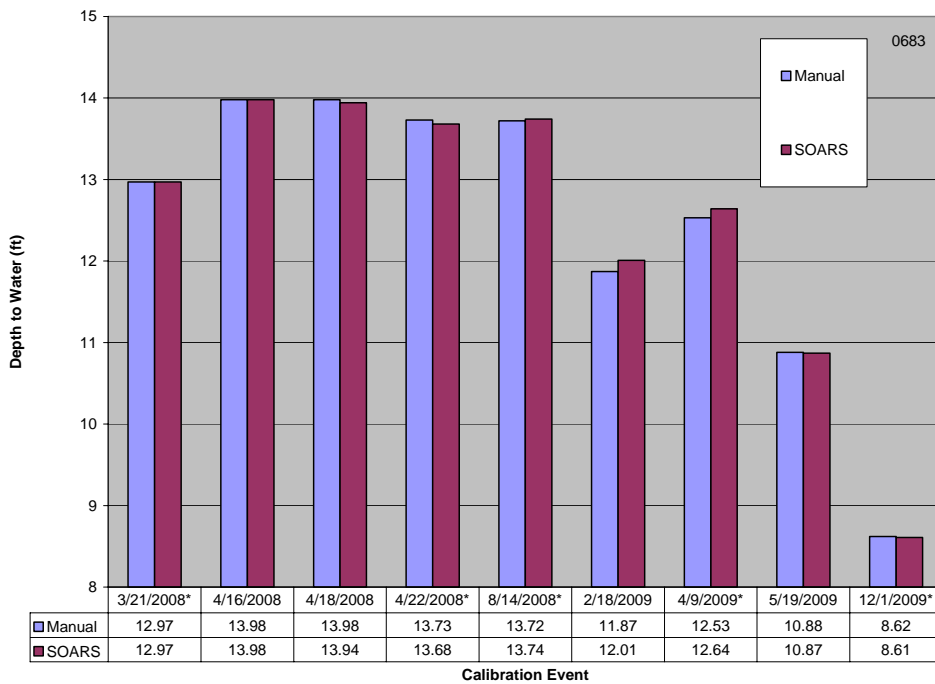


Figure A-25. Well 0683: Comparison of SOARS depth-to-water (ft) readings with manual readings using an electronic depth sonde.

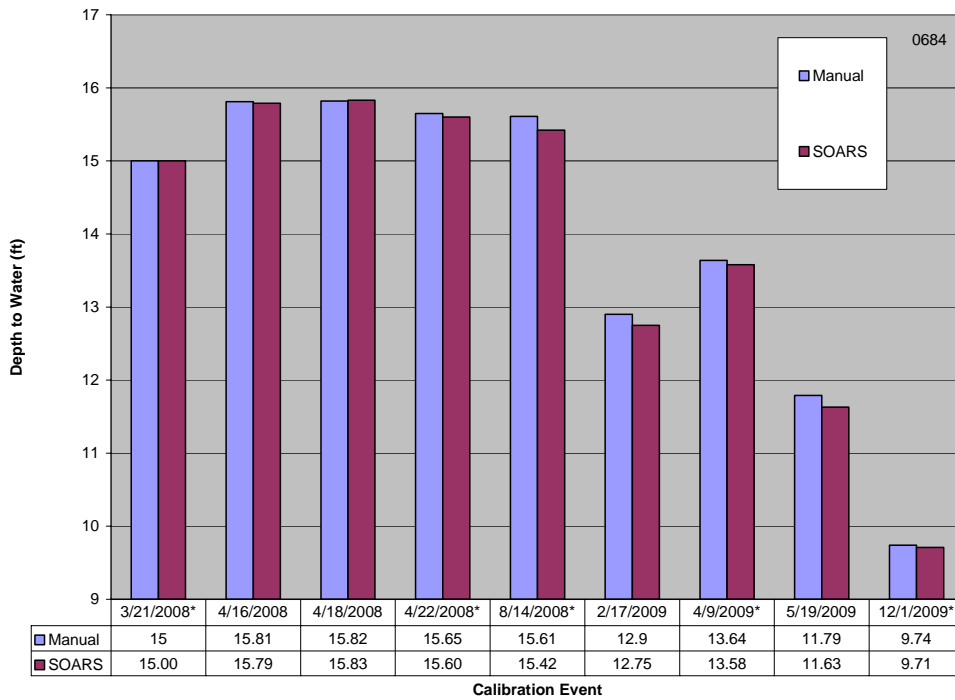


Figure A-26. Well 0684: Comparison of SOARS depth-to-water (ft) readings with manual readings using an electronic depth sonde.

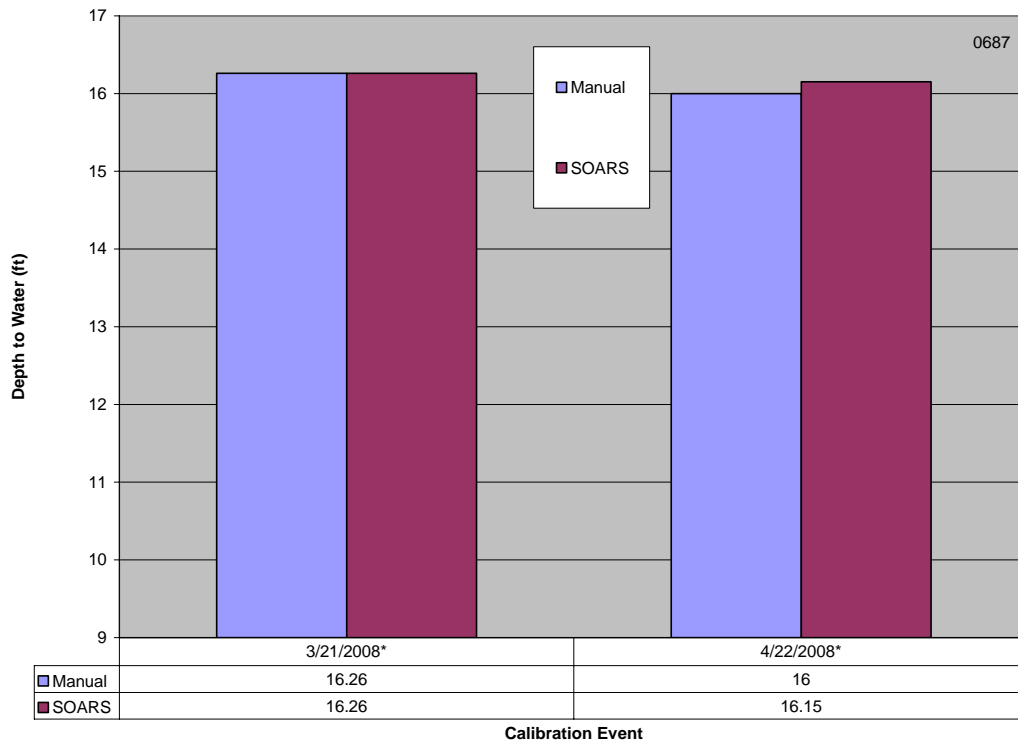


Figure A-27. Well 0687: Comparison of SOARS depth-to-water (ft) readings with manual readings using an electronic depth sonde.

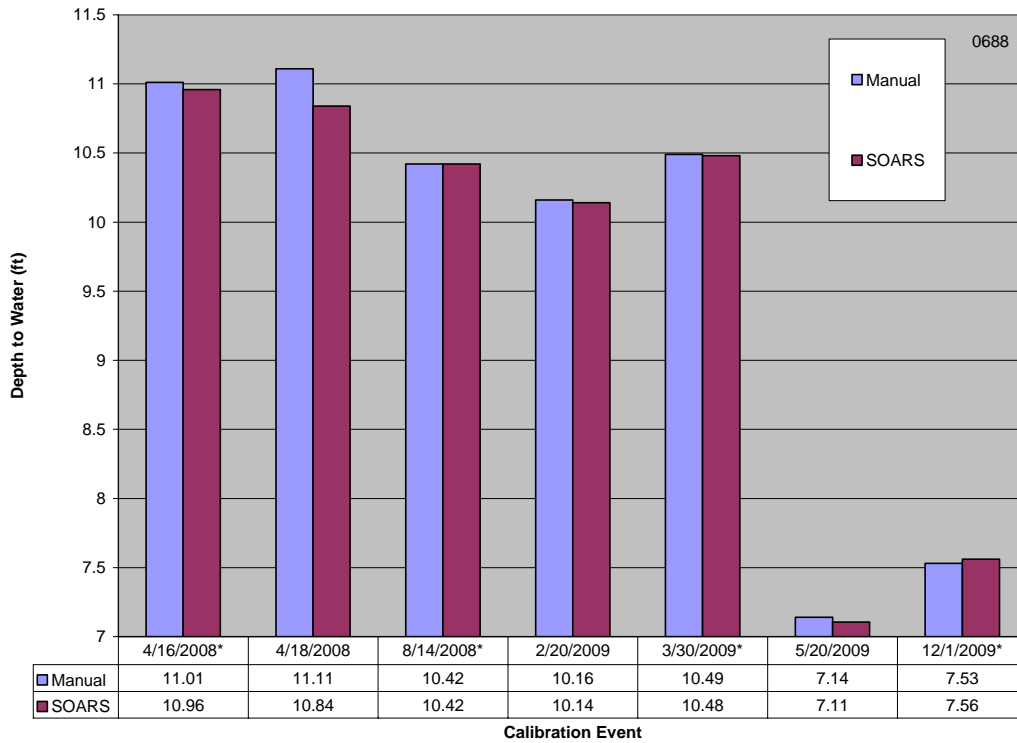


Figure A-28. Well 0688: Comparison of SOARS depth-to-water (ft) readings with manual readings using an electronic depth sonde.

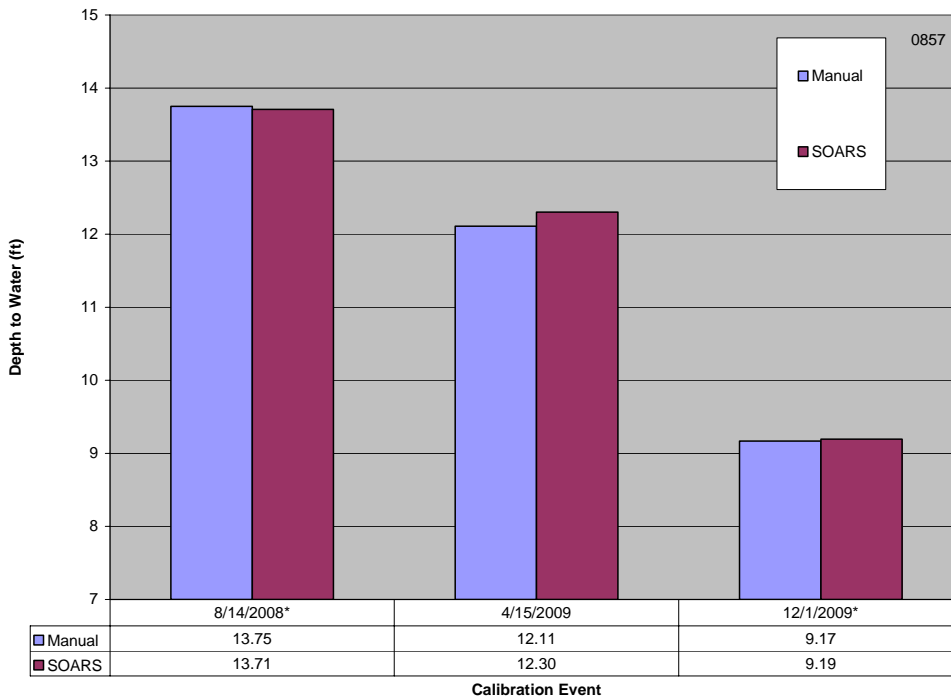


Figure A-29. Well 0857: Comparison of SOARS depth-to-water (ft) readings with manual readings using an electronic depth sonde.

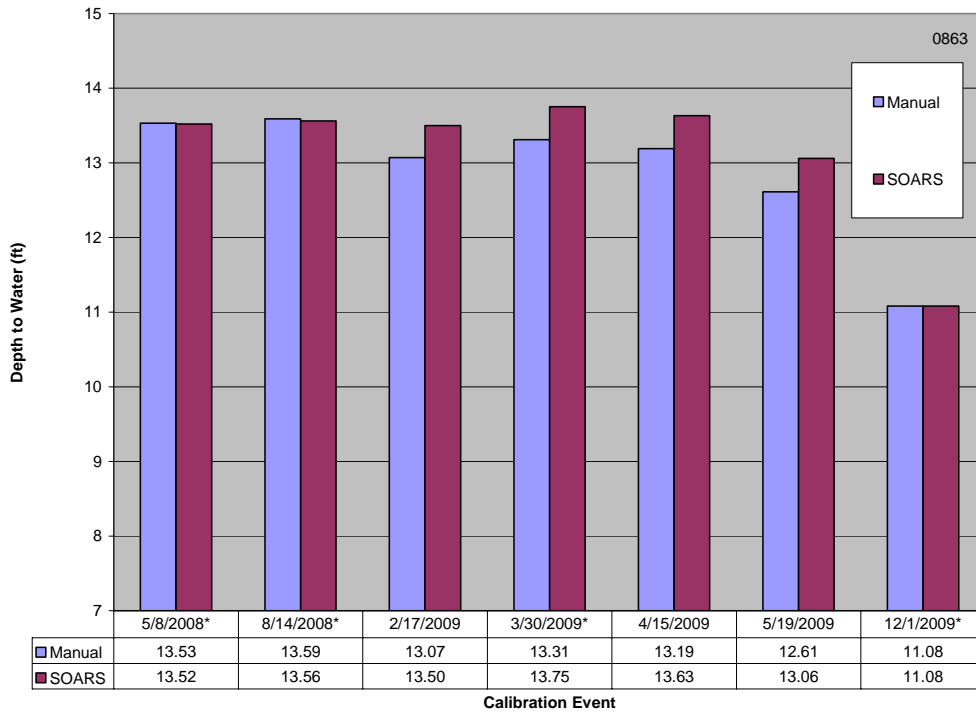


Figure A-30. Well 0863: Comparison of SOARS depth-to-water (ft) readings with manual readings using an electronic depth sonde.

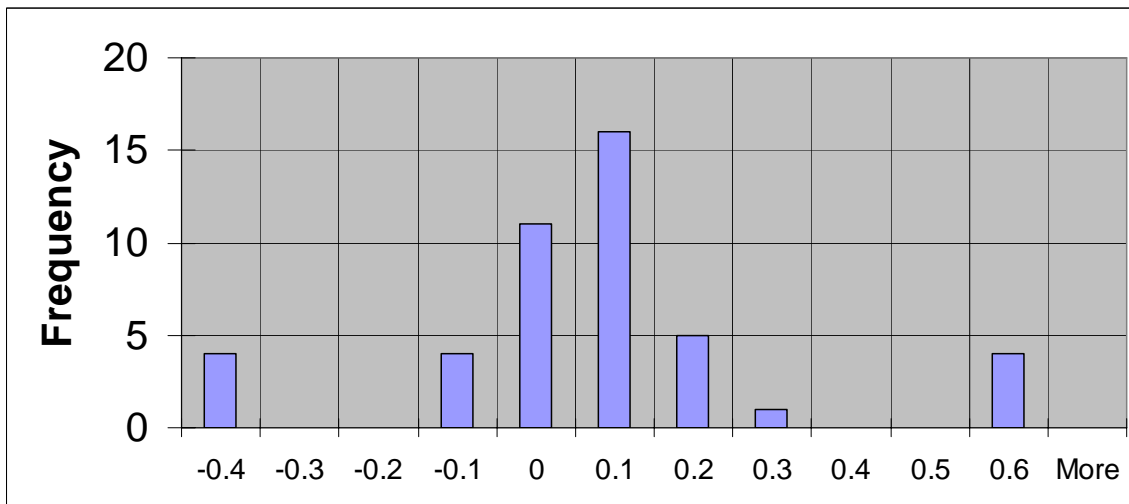


Figure A-31. Histogram of the differences between SOARS and manual water level determinations (ft) for the data presented in Figure A-24 through Figure A-29.

Summary and Conclusions

Some of the SOARS ORP measurements may accurately reflect the redox state of the groundwater, but because of issues with calibration the data should not be used. The failure of the ORP sensors to provide reliable data probably resides in the need for extensive calibration efforts which were not done during this study. ORP measurements are notoriously imperfect even with proper and painstaking calibrations. Imprecision occurs due to variations in the redox equilibrium state of the groundwater. It is recommended that rigorous tests of maintenance and calibration be conducted in the laboratory prior to future deployment of ORP probes. Specific conductance and water level transducer readings were reliable and can be used with confidence in most cases.

Appendix B
Chemical Data

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Well	Sampling Date/ Time	DTW ft	Well Depth ft	Water Temp C	Cond (µS/cm)	Dissolved O2 (mg/L)	pH	ORP (mV)	ORP Zobell	Temp Zobell	Corr. Factor For Eh	Eh Calc	Turbidity (NTU)	Alkalinity mg/L as CaCO3	As (ug/L)	Ca (mg/L)
664	11/19/08 0:00	16.51		14.1	2862		7.36	232	240	18	208	440	18.2			
664	2/17/09 0:00			10.33	2560		7.06	125.8					6.19			
664	4/15/09 0:00			16.8	2855	2.53	7.04	143					44.9	529	2.6	280
664	5/20/09 0:00															
668	4/28/08 14:30															
669	4/19/07 0:00				3892		6.91	149.5		11			38	287	4.8	
669	4/15/08 0:00				4349		6.91	115.4		13.31			10	302		
669	5/19/08 16:14															
669	7/1/08 0:00															
669	9/3/08 0:00															
669	11/19/08 0:00	12.99														
669	2/17/09 0:00			902	4256		6.7	129					823			
669	4/15/09 0:00			15.5	3975	4.48	6.92	81					653	274	5.6	530
669	5/19/09 0:00															
680	9/3/08 0:00															
680	11/20/08 0:00	9.25		13.9	4225		6.96	282					9.43			
680	2/18/09 0:00			6.6	4680		6.63	279					5.63			
680	5/21/09 0:00															
683	2/14/08 11:00	9.82	20	8.4	949	0.41	7.31	131	262	0.6	229	360	0.92	157	11	70
683	4/16/08 14:29	14	19.71	8.51	1966	1.38	7.2	157	244	9.26	225	382	3.03	319	15	200
683	7/1/08 0:00															
683	9/4/08 0:00															
683	11/20/08 0:00	12.53		14.2	2775		7.3	276	240	18	208	484	4.24			
683	2/18/09 0:00			10.1	2310		7.26	185					1.62			
683	5/19/09 0:00															
684	2/13/08 12:35	10.2	17	9.7	1294	0.59	7.31	183	245	13.3	214	397	7	221	3.9	69
684	4/16/08 12:44	15.83	16.9	9.6	1579	1.56	7.19	205.5	244	9.26	225	431	8.21	221	4.4	91
684	7/1/08 0:00															
684	9/3/08 0:00															
684	11/20/08 0:00	13.51		14.5	3005		6.97	326	240	18	208	534	3.26			
684	2/17/09 0:00			9.61	2564		6.8	264					1.45			
684	5/19/09 0:00															
687	2/13/08 14:20	9.7	16.9	9.5	928	0.4	7.55	141	245	13.3	214	355	6.08	190	2.5	56

Well	Sampling Date/ Time	DTW ft	Well Depth ft	Water Temp C	Cond (µS/cm)	Dissolved O2 (mg/L)	pH	ORP (mV)	ORP Zobell	Temp Zobell	Corr. Factor For Eh	Eh Calc	Turbidity (NTU)	Alkalinity mg/L as CaCO3	As (ug/L)	Ca (mg/L)
687	7/1/08 0:00															
687	9/4/08 0:00															
687	11/20/08 0:00	14.24		12.9	3275		7.19	247	240	18	208	455	28.1			
687	2/20/09 0:00			10.5	2010		6.98	298					7.05			
687	4/16/09 0:00			10.41	2074	2.67	7.11	101.1					1.45	331	2.7	210
687	5/21/09 0:00															
688	2/13/08 16:30	7.83		9.3	990	0.49	7.68	133	245	13.3	214	347	2.63	135	1.7	64
688	4/16/08 15:01	11.05	20.45	7.54	1111	1.55	7.51	138.8	244	9.26	225	364	1.22	95	0.73	92
688	9/4/08 0:00															
688	11/20/08 0:00	10.09		13.7	875		7.82	229	240	18	208	437	0.7			
688	2/20/09 0:00			7.8	1160		7.59	86					1.17			
688	5/20/09 0:00															
852	5/19/08 16:02															
852	7/1/08 0:00															
852	9/3/08 0:00															
852	11/19/08 0:00	12.72		14	4360		6.98	265	240	18	208	473	23.8			
852	2/17/09 0:00			8.8	2240		7	116					11.5			
852	5/19/09 0:00															
853	5/19/08 16:05															
853	7/1/08 0:00															
853	9/3/08 0:00															
853	11/19/08 0:00	12.81		13.6	2480		7.16	268	240	18	208	476	1.77			
853	2/17/09 0:00			9.4	2600		6.97	110					1.39			
853	5/19/09 0:00															
854	5/19/08 15:57															
854	7/1/08 0:00															
854	9/3/08 0:00															
854	11/19/08 0:00	12.83		13.8	2680		7.08	261	240	18	208	469	1.67			
854	2/17/09 0:00			10.3	2660		7.02	115					1.47			
854	5/19/09 0:00															
855	4/19/07 0:00				2485		6.82	-17.7		11.05			0.25	186	210	
855	2/12/08 13:50	10.05		9.1	3278	2.75	6.62	-18	245	13.3	214	196	18.8	205	270	568
855	11/19/08 0:00	12.39		17.3	6027		6.38	278	240	18	208	486	53.4			

Well	Sampling Date/ Time	DTW ft	Well Depth ft	Water Temp C	Cond (µS/cm)	Dissolved O2 (mg/L)	pH	ORP (mV)	ORP Zobell	Temp Zobell	Corr. Factor For Eh	Eh Calc	Turbidity (NTU)	Alkalinity mg/L as CaCO3	As (ug/L)	Ca (mg/L)
855	2/17/09 0:00			9.13	4266		6.21	224					61.7			
855	4/15/09 0:00			11.9	4100	0.72	6.41	190					76.5	330	2200	780
855	5/19/09 0:00															
856	5/19/08 15:13															
856	7/1/08 0:00															
856	9/3/08 0:00															
856	11/19/08 0:00	12.76		15.5	3270		7.13	317	240	18	208	525	3.65			
856	2/17/09 0:00			10.7	2692		7.05	248					2.88			
856	4/15/09 0:00			11.7	2560	0.36	6.41	210					9.05	973	23	230
856	5/19/09 0:00															
857	5/7/08 14:00															
857	5/8/08 14:00															
857	5/9/08 14:00															
857	5/10/08 14:00															
857	5/11/08 14:00															
857	5/12/08 14:00															
857	5/13/08 14:00															
857	5/14/08 14:00															
857	5/15/08 14:00															
857	5/16/08 14:00															
857	5/17/08 14:00															
857	5/18/08 14:00															
857	5/19/08 14:00															
857	5/23/08 14:00															
857	5/27/08 14:00															
857	5/31/08 14:00															
857	6/4/08 14:00															
857	6/8/08 14:00															
857	6/12/08 14:00															
857	6/16/08 14:00															
857	6/20/08 14:00															
857	6/24/08 14:00															
857	6/28/08 14:00															

Well	Sampling Date/ Time	DTW ft	Well Depth ft	Water Temp C	Cond (µS/cm)	Dissolved O2 (mg/L)	pH	ORP (mV)	ORP Zobell	Temp Zobell	Corr. Factor For Eh	Eh Calc	Turbidity (NTU)	Alkalinity mg/L as CaCO3	As (ug/L)	Ca (mg/L)
857	11/22/08 16:30															
857	11/26/08 16:30															
857	11/30/08 16:30															
857	12/4/08 16:30															
857	12/8/08 16:30															
857	12/12/08 16:30															
857	12/16/08 16:30															
857	12/20/08 16:30															
857	1/22/09 12:00															
857	1/26/09 12:00															
857	1/30/09 12:00															
857	2/3/09 12:00															
857	2/7/09 12:00															
857	2/11/09 12:00															
857	2/15/09 12:00															
857	2/19/09 12:00															
857	2/23/09 12:00															
857	2/27/09 12:00															
857	3/3/09 12:00															
857	3/7/09 12:00															
857	3/11/09 12:00															
857	3/15/09 12:00															
857	3/19/09 12:00															
857	3/23/09 12:00															
857	3/27/09 0:00															
857	3/31/09 0:00															
857	4/8/09 0:00															
857	4/12/09 0:00															
857	4/16/09 0:00															
857	4/20/09 0:00															
857	4/24/09 0:00															
857	4/28/09 0:00															
857	5/2/09 0:00															

Well	Sampling Date/ Time	DTW ft	Well Depth ft	Water Temp C	Cond (µS/cm)	Dissolved O2 (mg/L)	pH	ORP (mV)	ORP Zobell	Temp Zobell	Corr. Factor For Eh	Eh Calc	Turbidity (NTU)	Alkalinity mg/L as CaCO3	As (ug/L)	Ca (mg/L)
857	9/20/09 12:00														39	
857	9/24/09 12:00														39	
857	9/28/09 12:00														38	
857	10/2/09 12:00														43	
857	10/6/09 12:00														42	
857	10/10/09 12:00														41	
857	10/14/09 12:00														40	
857	10/18/09 12:00														41	
857	10/22/09 12:00														37	
857	10/26/09 12:00														39	
857	10/30/09 12:00														39	
857	11/3/09 12:00														38	
857	11/9/09 12:00															
857	11/16/09 12:00															
857	11/23/09 12:00															
857	11/30/09 12:00															
857	12/4/09 12:00															
857	12/21/09 12:00															
857	12/28/09 12:00															
857	1/4/10 12:00															
857	1/11/10 12:00															
857	1/18/10 12:00															
862	5/19/08 15:47															
862	7/1/08 0:00															
862	9/3/08 0:00															
862	11/19/08 0:00	13.06		13.6	4840		7.12	268	240	18	208	476	2.67			
862	2/17/09 0:00			10.6	6200		6.98	87					5.75			
862	2/17/09 0:00															
862	5/19/09 0:00															
863	5/19/08 15:25															
863	7/1/08 0:00															
863	9/3/08 0:00															
863	11/19/08 0:00	13.49		14.2	5230		7.04	205	240	18	208	413	2.9			

Well	Sampling Date/ Time	DTW ft	Well Depth ft	Water Temp C	Cond (µS/cm)	Dissolved O2 (mg/L)	pH	ORP (mV)	ORP Zobell	Temp Zobell	Corr. Factor For Eh	Eh Calc	Turbidity (NTU)	Alkalinity mg/L as CaCO3	As (ug/L)	Ca (mg/L)
863	2/17/09 0:00			10.1	3930		6.98	97					1.43			
863	4/15/09 0:00			12.3	6480	0.18	7.01	28					2.08	445	2.7	490
863	5/19/09 0:00															
864	5/19/08 15:35															
864	7/1/08 0:00															
864	9/3/08 0:00															
864	11/19/08 0:00	14.89		13.4	3410		7.18	202	240	18	208	410	558			
864	2/18/09 0:00			10.9	3180		7.06	175					65.3			
864	5/19/09 0:00															
CW-01	9/4/08 0:00															
CW-01	11/21/08 0:00	16.35		14.5	1265		7.19	206	240	18	208	414	1.03			
CW-02	5/19/08 11:20															
CW-02	7/1/08 0:00															
CW-02	9/4/08 0:00															
CW-02	11/21/08 0:00	16.42		14.1	1335		7.2	209	240	18	208	417	1.89			
CW-02	2/20/09 0:00			9.7	1341		7.3	72					3.69			
CW-02	5/21/09 0:00															
CW-03	9/4/08 0:00															
CW-03	11/21/08 0:00	14.6		13.6	1290		7.23	113	240	18	208	321	1.6			
CW-03	2/20/09 0:00			9.7	1175		7.39	14					3.26			
CW-03	5/21/09 0:00															
CW-04	7/1/08 0:00															
CW-04	9/4/08 0:00															
CW-04	11/21/08 0:00	13.2		13.4	945		7.42	206	240	18	208	414	0.63			
CW-05	11/21/08 0:00	16.84		13.5	2155		7.03	222	240	18	208	430	3.19			
CW-06	9/4/08 0:00															
CW-06	11/21/08 0:00	15.7		13.4	2185		7.01	56	240	18	208	264	9.13			
CW-06	2/20/09 0:00			10.4	2320		7.07	58					8.34			
CW-06	5/21/09 0:00															
CW-07	9/4/08 0:00															
CW-08	9/4/08 0:00															
CW-08	11/21/08 0:00	15.15		13.9	1460		7.28	212	240	18	208	420	1.12			
CW-08	2/20/09 0:00			9.4	1270		7.31	104					2.18			

Well	Sampling Date/ Time	DTW ft	Well Depth ft	Water Temp C	Cond (µS/cm)	Dissolved O2 (mg/L)	pH	ORP (mV)	ORP Zobell	Temp Zobell	Corr. Factor For Eh	Eh Calc	Turbidity (NTU)	Alkalinity mg/L as CaCO3	As (ug/L)	Ca (mg/L)
CW-08	5/21/09 0:00															
CW-09	5/19/08 11:00															
CW-09	9/4/08 0:00															
CW-09	11/21/08 0:00	16.82		14.3	1815		7.1	221	240	18	208	429	0.8			
CW-09	2/20/09 0:00			8.7	1510		7.15	292					2.95			
CW-09	5/20/09 0:00															
CW-10	9/4/08 0:00															
CW-10	11/21/08 0:00			12.5	1025		7.64	289	240	18	208	497	18.8			
CW-10	2/20/09 0:00			9	1200		7.75	270					3.33			
CW-11	9/4/08 0:00															
CW-11	11/21/08 0:00			12.9	960		7.72	300	240	18	208	508	5.98			
CW-11	2/20/09 0:00			5	1042		7.54	265					6.85			
CW-11	5/20/09 0:00															
CW-12	9/4/08 0:00															
CW-12	2/20/09 0:00			4.7	943		8.02	37					3.03			
CW-12	5/20/09 0:00															
CW-13	7/1/08 0:00															
CW-13	9/4/08 0:00															
CW-13	11/21/08 0:00	13.59		12.9	642		7.66	204	240	18	208	412	1.26			
CW-13	2/20/09 0:00			8.9	1115		7.38	95					3.41			
CW-14	9/4/08 0:00															
CW-14	11/21/08 0:00	14.28		13.6	1070		7.46	-126	240	18	208	82	15			
CW-15	7/1/08 0:00															
CW-15	9/4/08 0:00															
CW-15	11/21/08 0:00	13.75		13.2	962		7.51	334	240	18	208	542	22.2			
CW-15	2/19/09 0:00			8.8	1190		7.51	89					1.35			
CW-16	7/1/08 0:00															
CW-16	9/4/08 0:00															
CW-16	11/21/08 0:00	16.92		11.8	950		7.35	359	240	18	208	567	1.77			
CW-16	2/19/09 0:00			8	1410		7.37	103					1.43			
CW-16	5/21/09 0:00															
CW-17	9/4/08 0:00															
CW-17	11/21/08 0:00	11.02		12.9	910		7.49	153	240	18	208	361	8.5			

Well	Sampling Date/ Time	DTW ft	Well Depth ft	Water Temp C	Cond (µS/cm)	Dissolved O2 (mg/L)	pH	ORP (mV)	ORP Zobell	Temp Zobell	Corr. Factor For Eh	Eh Calc	Turbidity (NTU)	Alkalinity mg/L as CaCO3	As (ug/L)	Ca (mg/L)
CW-17	2/20/09 0:00			8	1170		7.44	103					1.83			
CW-18	7/1/08 0:00															
CW-18	9/4/08 0:00															
CW-18	11/20/08 0:00	14.63		13.5	930		7.27	152	240	18	208	360	7.48			
CW-18	2/19/09 0:00			8.5	1310		7.56	36					5.16			
CW-19	9/4/08 0:00															
CW-19	11/21/08 0:00			10.6	1055		7.28	273	240	18	208	481	11.2			
CW-19	2/19/09 0:00			8.5	1325		7.39	56					9.47			
CW-19	5/22/09 0:00															
CW-20	5/19/08 11:55															
CW-20	9/4/08 0:00															
CW-20	11/21/08 0:00	17.15		11.9	1240		7.44	345	240	18	208	553	0.98			
CW-20	2/19/09 0:00			9.8	1830		7.2	103					2.99			
CW-21	5/19/08 11:47															
CW-21	9/4/08 0:00															
CW-21	11/21/08 0:00	15.98		13.4	1825		7.23	348	240	18	208	556	0.92			
CW-21	2/19/09 0:00			10.3	1470		7.22	120					2.59			
CW-21	5/22/09 0:00															
CW-22	7/1/08 0:00															
CW-22	9/4/08 0:00															
CW-22	11/21/08 0:00	16.71		12.9	940		7.56	295	240	18	208	503	5.12			
CW-22	2/19/09 0:00			10	1110		7.42	19					3.49			
CW-22	5/22/09 0:00															
CW-23	2/19/09 0:00			10	1135		7.51	10					2.59			
CW-23	5/20/09 0:00															
CW-24	7/1/08 0:00															
CW-24	9/4/08 0:00															
CW-24	11/21/08 0:00	16.15		13.7	915		7.61	246	240	18	208	454	1.44			
CW-24	2/19/09 0:00			10.4	1100		7.62	40					1.37			
CW-25	7/1/08 0:00															
CW-25	9/4/08 0:00															
CW-25	11/21/08 0:00	12.51		13.6	890		7.71	272	240	18	208	480	0.78			
CW-25	2/19/09 0:00			8.9	1185		7.3	2					3.27			

Well	Sampling Date/ Time	DTW ft	Well Depth ft	Water Temp C	Cond (µS/cm)	Dissolved O2 (mg/L)	pH	ORP (mV)	ORP Zobell	Temp Zobell	Corr. Factor For Eh	Eh Calc	Turbidity (NTU)	Alkalinity mg/L as CaCO3	As (ug/L)	Ca (mg/L)
CW-26	7/1/08 0:00															
CW-26	9/4/08 0:00															
CW-26	11/20/08 0:00	12.39		12.7	1380		7.17	151	240	18	208	359	563			
CW-26	2/18/09 0:00			7.7	1975		7.19	166					117			
CW-26	5/20/09 0:00															
CW-27	5/19/08 14:15															
CW-27	7/1/08 0:00															
CW-27	9/4/08 0:00															
CW-27	5/20/09 0:00															
CW-28	5/19/08 14:11															
CW-28	7/1/08 0:00															
CW-28	9/4/08 0:00															
CW-28	11/20/08 0:00			13	1080		7.36	123	240	18	208	331	7.74			
CW-28	2/18/09 0:00			8.7	1220		7.36	172					19			
CW-28	5/20/09 0:00															
CW-30	5/19/08 12:37															
CW-31	5/19/08 13:44															
CW-31	7/1/08 0:00															
CW-31	9/4/08 0:00															
CW-31	11/20/08 0:00	13.22		14.7	1545		6.98	48	240	18	208	256	6.97			
CW-31	2/18/09 0:00			8.4	2815		7.42	183					47.2			
CW-31	4/17/09 0:00			8.66	1702	1.83	7.25	289.7					1.94	160	120	170
CW-31	5/20/09 0:00															
CW-32	5/19/08 13:46															
CW-32	7/1/08 0:00															
CW-32	9/4/08 0:00															
CW-32	11/20/08 0:00	10.95		13.5	1575		7.03	74	240	18	208	282	9			
CW-32	2/18/09 0:00			8	1530		7.34	180					1.31			
CW-32	4/16/09 0:00			9.51	1646	0.76	7.29	69					249	388	140	200
CW-32	5/21/09 0:00															
CW-33	5/19/08 13:52															
CW-33	7/1/08 0:00															
CW-33	9/4/08 0:00															

Well	Cl (mg/L)	K (mg/L)	Mg (mg/L)	Mo (mg/L)	Na (mg/L)	NH3-N (mg/L)	NO3 (mg/L)	NO3-NO2 as N (mg/L)	Fe (mg/L)	Mn (mg/L)	Se (µg/L)	SO4 (mg/L)	U (µg/L)	V (µg/L)	Sampling Method	Comments
201				1.9				98					86			
201													77	1.6		
201													80	0.67	Flow Cell	
201													81	0.63		
201													82	0.53		
201	150	19	62	1.9	360	93		61	0.014	3.2	65	2100	77	2.8	Flow Cell	Regular sampling
201													81	0.62		
215	200			0.017		5.4		0.01		0.4	0.52		13	0.13		
215	90	6.1	36	0.1	140	8	1		0.1	0.56	0.17	204	11	0.5	Flow Cell	redeveloped prior to sample
215	200	6.4	35	0.017	98	4.7		0.016	0.034	0.58	0.059	140	18	0.18	Flow Cell	
215													16	0.45		
215													29	0.4	Flow Cell	
215													20	0.58		
215	150	5.7	42	0.019	89	3.2		0.047	0.025	0.65	1.8	210	23	0.69	Flow Cell	Regular sampling
215													19	0.63		
219													84.2	1510		
219													200	1400		
219													35	140		
590				1.5		190		78		9.3	30		58	250		
590													76	420		
590													75	330	Flow Cell	
590													65	390		
590	300	28	54	1.5	420	170		73	0.02	11	56	2200	57	350	Flow Cell	
590													85	370		
657													33	430		
658				4.8		81		75		3.8	110		220	12000		
664				0.38		43		2.6		1.6	110		63	2100		
664				0.36		40		1.6					75	3200		
664													74.5	1270		
664													67	1800		
664													61	3300		

Well	Cl (mg/L)	K (mg/L)	Mg (mg/L)	Mo (mg/L)	Na (mg/L)	NH3-N (mg/L)	NO3 (mg/L)	NO3- NO2 as N (mg/L)	Fe (mg/L)	Mn (mg/L)	Se (µg/L)	SO4 (mg/L)	U (µg/L)	V (µg/L)	Sampling Method	Comments
664													64	940	Flow Cell	Limited water.
664													84	3600		
664	70	14	68	0.4	210	34		19	0.002	1.7	41	870	82	1800	Flow Cell	
664													85	3800		
668													131.4		Per. Pump	
669				1.8		140		8.5		3.1	3.5		120	1500		
669				0.91		42		0.23					76	2500		
669													56.9	3610		
669													50	2300		
669													42	1100		
669													75	2300	Pumped dry	
669													76	3000		
669	120	13	41	1.5	220	85		13	0.021	2.6	16	1700	69	3100	Flow Cell	
669													89	3300		
680													78	83		
680													120	80	Flow Cell	
680													150	44		
680													120	46		
683	104	6.4	36	0.14	103	10	1		0.1	0.81	10	135	17.1	1300	Flow Cell	new well
683	110	13	38	0.24	120	20		0.013	0.012	2	78	680	33	1400	Flow Cell	
683													35	710		
683													48	1500		
683													52	1900	Flow Cell	
683													97	3900		
683													90	3700		
684	126	13.4	35	0.12	138	19	3		0.1	0.96	230	226	22.9	2100	Flow Cell	new well
684	130	20	41	0.18	130	26		5.5	0.049	0.9	460	370	28	2300	Flow Cell	
684													34	2700		
684													49	2900		
684													68	2400	Flow Cell	
684													120	3800		
684													100	3600		

Well	Cl (mg/L)	K (mg/L)	Mg (mg/L)	Mo (mg/L)	Na (mg/L)	NH3-N (mg/L)	NO3 (mg/L)	NO3-NO2 as N (mg/L)	Fe (mg/L)	Mn (mg/L)	Se (µg/L)	SO4 (mg/L)	U (µg/L)	V (µg/L)	Sampling Method	Comments
687	107	10	21	0.1	118	14	1		0.1	0.72	160	103	17.3	1400	Flow Cell	new well
687													40	2300		
687													38	2400		
687													50	1900	Flow Cell	Limited water.
687													41	1900		
687	95	20	56	0.1	140	17		40	0.058	2.1	300	450	60	2200	Flow Cell	
687													50	2000		
688	134	9.1	18	0.16	120	10	1		0.1	0.73	20	131	14.2	320	Flow Cell	new well
688	180	5.3	20	0.019	92	2.1		0.46	0.011	0.61	8.5	130	9.5	150	Flow Cell	
688													5	230		
688													5.4	200	Flow Cell	
688													4.9	130		
688													8.2	170		
852													1060	74.6		
852													1100	130		
852													510	34		
852													760	24	Flow Cell	Limited water
852													1000	23		
852													550	280		
853													47.6	6600		
853													50	6000		
853													41	7900		
853													53	7300	Flow Cell	
853													66	7000		
853													74	7000		
854													38.3	7690		
854													42	7800		
854													39	7500		
854													49	7900	Flow Cell	
854													70	7800		
854													73	8000		
855				1.2		29		26		0.93	980		68	9400		

Well	Cl (mg/L)	K (mg/L)	Mg (mg/L)	Mo (mg/L)	Na (mg/L)	NH3-N (mg/L)	NO3 (mg/L)	NO3- NO2 as N (mg/L)	Fe (mg/L)	Mn (mg/L)	Se (µg/L)	SO4 (mg/L)	U (µg/L)	V (µg/L)	Sampling Method	Comments
855	121	6.6	20	2.04	133	60	5		1.2	1.14	300	1613	162.7	14000	Flow Cell	Redeveloped prior to sample. Parameters measured in lab?
855													32	72000		
855													6.4	2E+06		Purged dry. Green water. 0.4 L purged.
855	170	8.6	25	18	160	78		17	0.71	1.7	1800	1500	8.4	1E+06	Flow Cell	
855													10	81000		
856													24.6	6850		
856													39	14000		
856													27	7200		
856													30	6800	Flow Cell	
856													91	7600		
856	74	19	54	0.17	190	50		15	0.51	2.6	530	740	89	8600	Flow Cell	
856													79	7800		
857													12.5	4400		
857													12.9	4120		
857													12.6	3910		
857													13.6	4010		
857													13.4	4070		
857													13.5	3950		
857													14	3980		
857													13.1	3780		
857													13.1	3810		
857													12.8	3780		
857													13	3790		
857													12.9	3740		
857													8.2	4700		
857													6.4	4800		
857													3.7	4000		
857													3	4000		
857													3.3	3400		
857													15	4000		

Well	Cl (mg/L)	K (mg/L)	Mg (mg/L)	Mo (mg/L)	Na (mg/L)	NH3-N (mg/L)	NO3 (mg/L)	NO3-NO2 as N (mg/L)	Fe (mg/L)	Mn (mg/L)	Se (µg/L)	SO4 (mg/L)	U (µg/L)	V (µg/L)	Sampling Method	Comments
857													15	3600		
857													15	2900		
857													15	2700		
857													15	2600		
857													15	2300		
857													6.4	1400		
857													7.8	2000		
857													4.4	1900		
857													2.7	1900		
857													2.4	1800		
857													2.2	2000		
857													5.4	2500		
857													9.8	2700		
857													15	3000		
857													15	3200		
857													15	3600		
857													15	3200		
857													3.8	3300		
857													6.6	3700		
857													3.6	4100		
857													4.4	3600		
857													18	3600		
857													20	3600		
857													18	3600		
857													17	3700		
857													15	3700		
857													15	3800		
857													19	5000		
857													23	4100		
857													25	3800		
857													27	4300		
857													18	4600		

Well	Cl (mg/L)	K (mg/L)	Mg (mg/L)	Mo (mg/L)	Na (mg/L)	NH3-N (mg/L)	NO3 (mg/L)	NO3- NO2 as N (mg/L)	Fe (mg/L)	Mn (mg/L)	Se (µg/L)	SO4 (mg/L)	U (µg/L)	V (µg/L)	Sampling Method	Comments
857													17	4900		
857													17	5200		
857													16	5000		
857													21	4500		
857													26	3300		
857													29	3300		
857													38	5800		
857													29	4700		
857													34	3700		
857													32	3400		
857													33	900		
857													27	960		
857													31	780		
857													30	1200		
857													37	3100		
857													38	2900		
857													26	1900		
857													32	2800		
857													36	3400		
857													41	3600		
857													45	5000		
857													48	6400		
857													49	8400		
857													52	11000		
857													55	14000		
857													57	16000		
857													62	22000		
857													66	25000		
857													66	25000		
857													69	28000		
857													82	37000		
857													86	42000		

Well	Cl (mg/L)	K (mg/L)	Mg (mg/L)	Mo (mg/L)	Na (mg/L)	NH3-N (mg/L)	NO3 (mg/L)	NO3-NO2 as N (mg/L)	Fe (mg/L)	Mn (mg/L)	Se (µg/L)	SO4 (mg/L)	U (µg/L)	V (µg/L)	Sampling Method	Comments
857													92	44000		
857													92	41000		
857													92	34000		
857													94	34000		
857													90	33000		
857													88	31000		
857													90	32000		
857													93	30000		
857													94	29000		
857				0.44							530		110	29000		
857				0.4							540		120	28000		
857				0.35							490		110	28000		
857				0.37							520		120	28000		
857				0.33							500		100	26000		
857				0.33							430		98	24000		
857				0.32							400		97	23000		
857				0.31							430		91	22000		
857				0.3							410		90	21000		
857				0.3							420		93	20000		
857				0.31							420		93	21000		
857				0.32							460		94	22000		
857				0.47							790		56	26000		
857				0.42							790		69	29000		
857				0.35							770		78	26000		
857				0.35							710		85	22000		
857				0.34							700		110	23000		
857				0.35							580		100	22000		
857				0.36							500		100	23000		
857				0.38							510		110	22000		
857				0.46							480		120	21000		
857				0.4							500		100	19000		
857				0.36							470		89	19000		

Well	Cl (mg/L)	K (mg/L)	Mg (mg/L)	Mo (mg/L)	Na (mg/L)	NH3-N (mg/L)	NO3 (mg/L)	NO3- NO2 as N (mg/L)	Fe (mg/L)	Mn (mg/L)	Se (µg/L)	SO4 (mg/L)	U (µg/L)	V (µg/L)	Sampling Method	Comments
857				0.45							770		160	21000		
857				0.41							880		140	23000		
857				0.41							810		100	24000		
857				0.38							770		120	21000		
857				0.38							710		99	23000		
857				0.37							620		94	23000		
857				0.38							690		80	22000		
857				0.38							700		95	22000		
857				0.35							730		94	21000		
857				0.37							690		100	21000		
857				0.41							680		100	21000		
857				0.4							700		110	22000		
857				0.42							720		100	22000		
857				0.42							760		110	22000		
857				0.42							760		96	23000		
857				0.43							790		97	21000		
857				0.44							740		100	22000		
857				0.45							780		110	20000		
857				0.46							790		110	20000		
857				0.46							740		110	19000		
857													110	19000		
857													120	19000		
857													110	19000		
857													91	19000		
857													99	19000		
857													120	22000		
857													110	21000		
857													110	21000		
857													110	20000		
857													110	20000		
862													133	1280		
862													120	22000		

Well	Cl (mg/L)	K (mg/L)	Mg (mg/L)	Mo (mg/L)	Na (mg/L)	NH3-N (mg/L)	NO3 (mg/L)	NO3- NO2 as N (mg/L)	Fe (mg/L)	Mn (mg/L)	Se (µg/L)	SO4 (mg/L)	U (µg/L)	V (µg/L)	Sampling Method	Comments
862													84	1600		
862													95	210	Flow Cell	
862													98	220		
862													98	230		
862													110	240		
863													199	3400		
863													150	910		
863													140	470		
863													130	600	Flow Cell	
863													170	370		
863	180	21	35	1.6	390	290		0.056	0.32	3.6	1.9	2700	94	480	Flow Cell	
863													190	530		
864													45.9	4530		
864													44	4800		
864													40	5800		
864													40	7100	Flow Cell	
864													52	7900		
864													57	7400		
CW-01													48	660		
CW-01													18	150	Flow Cell	Pump OFF
CW-02													30.1	569		
CW-02													21	2200		
CW-02													18	48		
CW-02													26	350	Flow Cell	Pump OFF
CW-02													22	380		
CW-02													20	390		
CW-03													25	320		
CW-03													14	150	Flow Cell	Pump OFF
CW-03													13	140		
CW-03													14	48		
CW-04													19	1.1		
CW-04													12	2.2		

Well	Cl (mg/L)	K (mg/L)	Mg (mg/L)	Mo (mg/L)	Na (mg/L)	NH3-N (mg/L)	NO3 (mg/L)	NO3- NO2 as N (mg/L)	Fe (mg/L)	Mn (mg/L)	Se (µg/L)	SO4 (mg/L)	U (µg/L)	V (µg/L)	Sampling Method	Comments
CW-04													19	0.79	Flow Cell	Pump OFF
CW-05													30	260	Flow Cell	Pump OFF
CW-06													33	5.6		
CW-06													32	2	Flow Cell	Pump OFF, ORP dropping
CW-06													39	1.8		
CW-06													40	5.8		
CW-07													35	9.3		
CW-08													22	860		
CW-08													19	810	Flow Cell	Pump OFF
CW-08													20	1200		
CW-08													24	780		
CW-09													24	750		
CW-09													21	1200		
CW-09													18	890	Flow Cell	Pump OFF
CW-09													22	720		
CW-09													23	660		
CW-10													18	55		
CW-10													22	81	?	Pump ON
CW-10													27	250		
CW-11													15	5		
CW-11													24	1.2	?	Pump ON
CW-11													24	59		
CW-11													18	5.5		
CW-12													12	5.6		
CW-12													19	21		
CW-12													24	19		
CW-13													16	6.2		
CW-13													15	4.1		
CW-13													15	3.7	Flow Cell	Pump OFF
CW-13													26	5.4		
CW-14													11	1500		
CW-14													8.2	1100	Flow Cell	Pump OFF

Well	Cl (mg/L)	K (mg/L)	Mg (mg/L)	Mo (mg/L)	Na (mg/L)	NH3-N (mg/L)	NO3 (mg/L)	NO3-NO2 as N (mg/L)	Fe (mg/L)	Mn (mg/L)	Se (µg/L)	SO4 (mg/L)	U (µg/L)	V (µg/L)	Sampling Method	Comments
CW-15													9.5	1800		
CW-15													12	2100		
CW-15													8.4	1300	Flow Cell	Pump OFF
CW-15													9.6	590		
CW-16													21	1800		
CW-16													10	1600		
CW-16													8.8	1500	Flow Cell	Pump OFF
CW-16													17	840		
CW-16													7.1	460		
CW-17													11	1600		
CW-17													9.8	1200	Flow Cell	Pump OFF
CW-17													11	480		
CW-18													25	2000		
CW-18													16	2000		
CW-18													12	1400	Flow Cell	Pump OFF
CW-18													14	940		
CW-19													11	2100		
CW-19													9.3	1600	?	Pump ON
CW-19													19	1300		
CW-19													11	1100		
CW-20													14.3	1720		
CW-20													13	3200		
CW-20													17	1800	Flow Cell	Pump OFF
CW-20													42	2300		
CW-21													21.3	609		
CW-21													20	1100		
CW-21													29	970	Flow Cell	Pump OFF
CW-21													30	1200		
CW-21													22	890		
CW-22													16	710		
CW-22													17	490		
CW-22													20	160	Flow Cell	Pump OFF

Well	Cl (mg/L)	K (mg/L)	Mg (mg/L)	Mo (mg/L)	Na (mg/L)	NH3-N (mg/L)	NO3 (mg/L)	NO3- NO2 as N (mg/L)	Fe (mg/L)	Mn (mg/L)	Se (µg/L)	SO4 (mg/L)	U (µg/L)	V (µg/L)	Sampling Method	Comments
CW-22													26	140		
CW-22													28	200		
CW-23													16	59		
CW-23													15	72		
CW-24													7.9	35		
CW-24													7.4	68		
CW-24													11	57	Flow Cell	Pump OFF
CW-24													11	31		
CW-25													4.1	340		
CW-25													6.1	320		
CW-25													5.1	270	Flow Cell	Pump OFF
CW-25													6.1	88		
CW-26													42	880		
CW-26													21	820		
CW-26													23	780	Flow Cell	Pump OFF
CW-26													26	620		
CW-26													18	670		
CW-27													26.5	472		
CW-27													34	690		
CW-27													23	750		
CW-27													20	670		
CW-28													27.3	615		
CW-28													32	730		
CW-28													12	980		
CW-28													14	1100	?	Pump ON
CW-28													23	970		
CW-28													20	580		
CW-30													47	1620		
CW-31													25.3	1520		
CW-31													43	2500		
CW-31													29	2600		
CW-31													29	2900	Flow Cell	Pump OFF

Well	Cl (mg/L)	K (mg/L)	Mg (mg/L)	Mo (mg/L)	Na (mg/L)	NH3-N (mg/L)	NO3 (mg/L)	NO3-NO2 as N (mg/L)	Fe (mg/L)	Mn (mg/L)	Se (µg/L)	SO4 (mg/L)	U (µg/L)	V (µg/L)	Sampling Method	Comments
CW-31													130	3000		
CW-31	99	7.6	37	0.51	120	7.9		16	0.007	1.2	420	480	39	4100		
CW-31													16	1100		
CW-32													24	2600		
CW-32													29	2500		
CW-32													27	4100		
CW-32													26	6700	Flow Cell	Pump OFF
CW-32													32	4200		
CW-32	110	6.8	28	0.48	110	4.9		9.3	0.076	1.2	520	440	35	7500		
CW-32													36	6100		
CW-33													48.7	7250		
CW-33													38	4500		
CW-33													50	8900		
CW-33													43	9900	Flow Cell	Pump OFF
CW-33													34	8200		
CW-33	120	8.8	25	0.59	110	12		5	0.011	1.2	230	710	47	9100		
CW-33													45	13000		
CW-34													23.4	2120		
CW-34													35	5600		
CW-34													22	5100		
CW-34													14	3900	Flow Cell	Pump OFF
CW-34													20	4700		
CW-34	120	8.9	25	0.36	100	9.6		3	1.3	1.3	290	370	22	5100		
CW-34													19	4100		
CW-35													22.3	2580		
CW-35													29	2700		
CW-35													21	4400		
CW-35													14	3700	Flow Cell	Pump OFF
CW-35													30	3200		
CW-35	120	7.2	30	0.24	100	5.1		12	0.019	1.1	160	320	16	3700		
CW-35													16	3100		
CW-36													29.9	1140		Formerly CW-X2

Well	Cl (mg/L)	K (mg/L)	Mg (mg/L)	Mo (mg/L)	Na (mg/L)	NH3-N (mg/L)	NO3 (mg/L)	NO3- NO2 as N (mg/L)	Fe (mg/L)	Mn (mg/L)	Se (µg/L)	SO4 (mg/L)	U (µg/L)	V (µg/L)	Sampling Method	Comments
CW-37													17	27		
CW-37													10	53		
CWRD -01													21.8	778		
CWRD -01													16	440		
CWRD -01													21	930		
CWRD -01													19	1500	Open tap	
CWRD -01													18	1100		
CWRD -01													12	790		

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Appendix C

Input Files for PHREEQC Simulations

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I. Input for Construction of pE-pH Diagram

TITLE New Rifle, Colorado. Vanadium Aqueous Chemistry - Redox Plots.

SOLUTION 1 Simple Solution - V, e-, H+, Fe only

units mmol/L
pH 6.5 # To be varied
pe -0.6 # To be varied
density 1.0 # Condition
temp 25 # Condition
Fe 1 #from single value in well 0857
U 0.09
V 1 # Condition (1 mmol of V)

SOLUTION 2 Simple Solution - V, e-, H+ only

units mmol/L
pH 6.5 # To be varied
pe -0.7 # To be varied
density 1.0 # Condition
temp 25 # Condition
Fe 1 #from single value in well 0857
U 0.09
V 1 # Condition (1 mmol of V)

SOLUTION 3 Simple Solution - V, e-, H+ only

units mmol/L
pH 6.5 # To be varied
pe -0.8 # To be varied
density 1.0 # Condition
temp 25 # Condition
Fe 1 #from single value in well 0857
U 0.09
V 1 # Condition (1 mmol of V)

SOLUTION 4 Simple Solution - V, e-, H+ only

units mmol/L
pH 6.5 # To be varied
pe -0.9 # To be varied
density 1.0 # Condition
temp 25 # Condition
Fe 1 #from single value in well 0857
U 0.09
V 1 # Condition (1 mmol of V)

KNOBS

-iterations 1000 #100 is default
-tolerance 1e-10 #1e-14 is default
-pe_step_size 1 #5 is default
-step_size 10 #10 is default

SELECTED_OUTPUT

-file Phase_Diagram.sel
-totals V(5) V(4) V(3) V(2)

```

# -saturation_indices V_Fe_Vanadate
# -activities O2 H2
-pH true
-pe true
-simulation false
-state false
-solution true
-distance false
-time false
-step false

```

END

II Input for Determination of Mineral Saturation Indices

TITLE New Rifle, Colorado. Saturation Indices.

SOLUTION 1 Well 0855, Sampled 4/15/09

This well has the highest V concentrations (up to 1600 mg/L)

units mg/L

pH 6.41 # Measured pH = 6.41

Vary pE through water limits, pH constant at 7

Measured ORP = 190 mV, Eh ~ 430 mV (added 240)

pE = Eh(mV)/59 = 7.29

pe 7.2 #Calculated from ORP, pE = 7.2

density 1.1 #Assumed

temp 11.9

C 10

Alkalinity 330 as CaCO3 #Measured value is 330

As 2.2 #Measured 2.2

Ba 0.02 # No analysis

Ca 780 #Measured 780

Cl 170 #Measured 170

Fe(+2) 0.01 #Measured in field

Fe(+3) 0.70 #Difference of Tot Fe (0.71) and Fe+2 (0.01)

Fe 0.71 #Measured value of total Fe is 0.71

K 8.6 #Measured 8.6

Mg 25 #Measured 25

Mn 1.7 #Measured 1.7

Mo 18 #Measured 18

Na 160 #Measured 160

N(5) 17 as N #Analysis is for NO3+NO2, assumed all NO3

N(3) 0.1 as NO2 #Assumed low, included in NO3 analysis

N(-3) 78 as NH4

O(0) 0.72 as O2 #Measured 0.72

S(6) 1500 as SO4 #Measured 1500

Se 1.8 #Measured 1.8

U 0.0084 #Measured 0.0084

V 1000 #Measured value is 1000

KNOBS

-iterations 1000
-step_size 2
#-tolerance 1e-13
#-diagonal_scale false
END

TITLE New Rifle, Colorado. Saturation Indices.

SOLUTION 1 Well 0857, Sampled 4/15/09

This well has the highest V concentrations (up to 1600 mg/L)

units mg/L

pH 7.25 # Measured pH = 6.41

Vary pE through water limits, pH constant at 7

Measured ORP = 35 mV, Eh ~ 275 mV (added 240)

pE = Eh(mV)/59 = 4.66

pe 4.66 #Calculated from ORP, pE = 4.66

density 1.1 #Assumed

temp 13

Alkalinity 490 as CaCO3 #Measured value is 490

As 0.088

Ba 0.02 # No analysis

Ca 340

Cl 76

Fe(+2) 0.09 #Measured in field

Fe(+3) 0.07 #Difference of Tot Fe (0.16) and Fe+2 (0.09)

Fe 0.16 #Measured value of total Fe

K 17

Mg 26

Mn 2.1

Mo 0.51

Na 170

N(5) 2 as N #Analysis is for NO3+NO2, assumed all NO3

N(3) 0.1 as NO2 #Assumed low, included in NO3 analysis

N(-3) 61 as NH4

O(0) 0.49 as O2

S(6) 890 as SO4

Se 0.32

U 0.09

V 33 # Measured value is 33

END

III. Input for Advection Model

TITLE New Rifle: One-D model of interaction of BG water with contaminated soil

Use PHREEQC_SJM.DAT database

BG Water - Bkgd well 0169 1/28/1999 Most recent with full analysis

Contaminated soil modeled with various U-V minerals and AFO adsorption sites

PHASES

Fix_H+
H+ = H+
log_k 0.0

Fix_e-
e- = e-
log_k 0.0

SOLUTION 0 Well 0169, 1/28/1999 (most recent sampling with complete chemistry)

#Composition of back groundwater

units mg/L
pH 6.73 #6.73 measured
ORP +146, Eh~376, pE~6.37
pe 6.37 #O2(g) -0.68 #-0.68 is eq with atm
density 1.0 #Assumed
temp 10.2
Alkalinity 557
As 0.00031
Ca 157
Cl 85.7 #85.7 measured
Fe 0.0036
K 10 #Estimated value - no data available
Mg 121
Mn 0.297
Mo 0.0235
Na 252 charge
N(-3) 0.0978 as NH4
N(5) 20.6 as NO3
O(0) 8 as O2
S(6) 744 as SO4
Se 0.0176
Sp. Cond 2500
TDS na
Turb 9.63
U 0.000001 #measured 0.0366
V 0.000001 # measured 0.0023

Save Solution 0

End

Use Solution 0

EQUILIBRIUM_PHASES 1-10

Fix_H+ -7 HCl 10.0
Fix_e- -4 O2 10.0
CO2(g) -3.5
O2(g) 0.6

```

V_Tyuyamunite 0.0 0.1
V_Carnotite 0.0 0.1
V_Fe_Vanadate 0.0 0.1
Calcite 0.0 10
Gypsum 0.0 10
# V2O4 0.0 10.0
# V2O5 0.0 0.1
V_Ca_Vanadate 0.0 0.3 #Ca0.5VO3
# V_Ca3(VO4)2 0.0 0.5
# V_Ca2V2O7 0.0 0.1 #CaVO3.5
# V_Na_Vanadate 0.0 1.0 #NaVO3
# V_Na3VO4 0.0 0.1
# V_Na4V2O7 0.0 0.1
Fe(OH)3(a) 0.0 10.0
# Fe_hematite

```

SURFACE 1-10

```

# -equil with Solution 1
# -no_edl
Hfo_sOH 4.8e-3 600. 86.4 # 0.96 mol/L, 1% TOTFe
Hfo_wOH 0.192
# Hfo_sOH 5e-6 600. 0.09 #0.001 mol/L (~0.001 % TOTFe)
# Hfo_wOH 2e-4

```

Save Solution 1-10

END

SELECTED_OUTPUT

```

-file AAfinal_model.sel
-totals V U
-molalities Hfo_wOHVO4-3 Hfo_wOH2UO2(OH)3 Hfo_sOHCa+2 Hfo_wOCa+
-equilibrium_phases calcite gypsum V_Fe_Vanadate V_Tyuyamunite V_Ca_Vanadate

```

END

PRINT

```
-selected_out true
```

ADVECTION

```

-cells 10 #number of cells in model
-shifts 500 #number of shifts, movement of fluid to next cell; time steps
-punch 10
-punch_frequency 5
-print 10
-print_frequency 5

```

#User_Punch #Causes pore vols to be printed in selected output

```

# -heading Pore_Vol
# 10 punch (STEP_NO)/10

```

```
USER_GRAPH
  -headings Pore_Volumes  V V U Ca Fe pE pH
  -chart_title "Cell 10 Concentrations"
  -axis_titles "Pore_Volumes" "Effluent Concentration (mg/L)"
  -axis_scale x_axis 0 50 5
  -axis_scale y_axis 0 2100 200
  -axis_scale sy_axis 0 20 2
  -initial_solutions false
  -plot_concentration_vs t
  -start
  10 GRAPH_X (STEP_NO)/10
  20 GRAPH_Y TOT("V")*50942, TOT("V")*50942, TOT("U")*238029,
TOT("Ca")*40080, TOT("Fe")*55847
  30 GRAPH_SY -LA("e-"), -LA("H+")
-end
PRINT
  -user_graph true
END
```

Appendix D

Well Logs

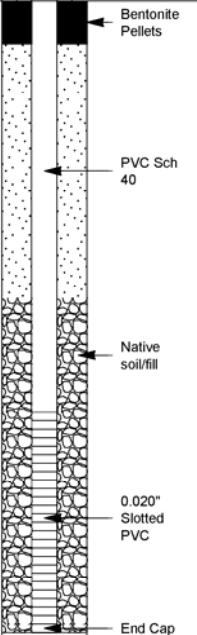
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MONITORING WELL COMPLETION LOG RFN01-0683						
PROJECT LM		WELL NUMBER RFN01-0683		DATE DRILLED 2/13/2008		
LOCATION RIFLE, CO		NORTH COORD. (FT) 624308.00		SURFACE ELEV. (FT NGVD) _____		
SITE Rifle New Processing Site		EAST COORD. (FT) 1347572.00		TOP OF CASING (FT) _____		
DRILLING METHOD GEOPROBE		HOLE DEPTH (FT) 18.40		MEAS. PT. ELEV. (FT) _____		
DRILL COMPANY S.M. Stoller		WELL DEPTH (FT) 18.40		SLOT SIZE (IN) 0.020		
RIG TYPE GEOPROBE		WATER LEVEL (FT BGS) _____		BIT SIZE(S) (IN) 2.75		
SURFACE CASING:		WELL INSTALLATION		INTERVAL (FT)		WATER LEVEL DATE _____
BLANK CASING:		2 in. PVC Sch 40		to 13.2		DRILLER Walters, J. / Trevino, J.
WELL SCREEN:		2 in. 0.02 Slotted PVC		13.2 to 18.2		LOGGED BY Walters, J.
SUMP/END CAP:		2 in. PVC Sch 40		18.2 to 18.4		SAMPLING METHOD _____
SURFACE SEAL:		Bentonite		0.0 to 1.0		DATE DEVELOPED 3/24/2008
GROUT:		_____		_____		REMARKS _____
SEAL:		_____		_____		_____
UPPER PACK:		20-40 Silica Sand		1.0 to 7.0		_____
LOWER PACK:		Natural Cave-in Material		7.0 to 18.4		_____
DEPTH (FT BGL)	ELEV. (FT NGVD)	BLOW COUNTS	SAMPLE INTERVAL (FT)	EXTENT	WELL DIAGRAM	GRAPHIC LOG
5	-5					
10	-10					
15	-15					
Total Depth 18.4 ft.						
<i>Stoller</i>		U.S. DEPARTMENT OF ENERGY GRAND JUNCTION, COLORADO			PAGE 1 OF 1 11/20/2008	

Well 0684

MONITORING WELL COMPLETION LOG RFN01-0684						
PROJECT <u>LM</u>		WELL NUMBER <u>RFN01-0684</u>		DATE DRILLED <u>2/12/2008</u>		
LOCATION <u>RIFLE, CO</u>		NORTH COORD. (FT) <u>624516.00</u>		SURFACE ELEV. (FT NGVD) _____		
SITE <u>Rifle New Processing Site</u>		EAST COORD. (FT) <u>1347572.00</u>		TOP OF CASING (FT) _____		
DRILLING METHOD <u>GEOPROBE</u>		HOLE DEPTH (FT) <u>15.00</u>		MEAS. PT. ELEV. (FT) _____		
DRILL COMPANY <u>S.M. Stoller</u>		WELL DEPTH (FT) <u>15.00</u>		SLOT SIZE (IN) <u>0.020</u>		
RIG TYPE <u>GEOPROBE</u>		WATER LEVEL (FT BGS) _____		BIT SIZE(S) (IN) <u>2.75</u>		
		WELL INSTALLATION		INTERVAL (FT)		WATER LEVEL DATE
SURFACE CASING:						DRILLER <u>Walters, J. / Trevino, J.</u>
BLANK CASING:		2 in. PVC Sch 40		to 9.8		LOGGED BY <u>Walters, J.</u>
WELL SCREEN:		2 in. 0.02 Slotted PVC		9.8 to 14.8		SAMPLING METHOD _____
SUMP/END CAP:		2 in. PVC Sch 40		14.8 to 15.0		DATE DEVELOPED <u>3/24/2008</u>
SURFACE SEAL:		Bentonite		0.0 to 1.0		REMARKS _____
GROUT:						_____
SEAL:						_____
UPPER PACK:		20-40 Silica Sand		1.0 to 7.0		_____
LOWER PACK:		Natural Cave-in Material		7.0 to 15.0		_____
DEPTH (FT BGL)	ELEV. (FT NGVD)	BLOW COUNTS	SAMPLE INTERVAL (FT)	EXTENT	WELL DIAGRAM	LITHOLOGIC DESCRIPTION
5	-5					0-15.0 ft. ALLUVIUM:
10	-10			Total Depth 15.0 ft.		
15	-15					
<i>Stoller</i>		U.S. DEPARTMENT OF ENERGY GRAND JUNCTION, COLORADO			PAGE 1 OF 1 11/20/2008	

Well 0687

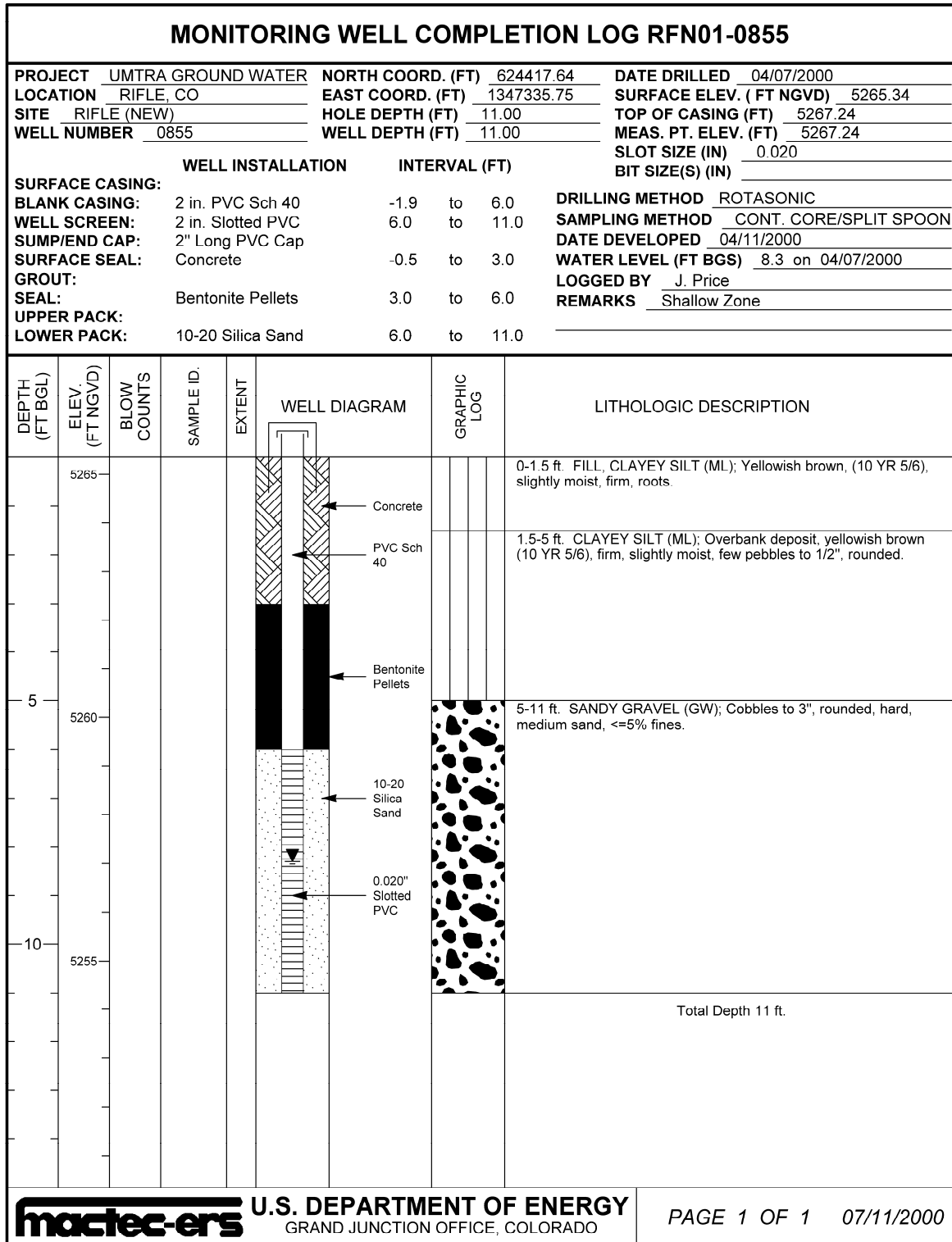
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PROJECT LM		WELL NUMBER RFN01-0687		DATE DRILLED 2/13/2008		
LOCATION RIFLE, CO		NORTH COORD. (FT) 624419.00		SURFACE ELEV. (FT NGVD) _____		
SITE Rifle New Processing Site		EAST COORD. (FT) 1347757.00		TOP OF CASING (FT) _____		
DRILLING METHOD GEOPROBE		HOLE DEPTH (FT) 14.90		MEAS. PT. ELEV. (FT) _____		
DRILL COMPANY S.M. Stoller		WELL DEPTH (FT) 14.90		SLOT SIZE (IN) 0.020		
RIG TYPE GEOPROBE		WATER LEVEL (FT BGS) _____		BIT SIZE(S) (IN) 2.75		
WELL INSTALLATION		INTERVAL (FT)		WATER LEVEL DATE _____		
SURFACE CASING:				DRILLER Walters, J. / Trevino, J.		
BLANK CASING: 2 in. PVC Sch 40		to 9.7		LOGGED BY Walters, J.		
WELL SCREEN: 2 in. 0.02 Slotted PVC		9.7 to 14.7		SAMPLING METHOD _____		
SUMP/END CAP: 2 in. PVC Sch 40		14.7 to 14.9		DATE DEVELOPED 3/24/2008		
SURFACE SEAL: Bentonite		0.0 to 1.0		REMARKS _____		
SEAL:				_____		
UPPER PACK: 20-40 Silica Sand		1.0 to 7.0		_____		
LOWER PACK: Natural Cave-in Material		7.0 to 14.9		_____		
DEPTH (FT BGL)	ELEV. (FT NGVD)	BLOW COUNTS	SAMPLE INTERVAL (FT)	EXTENT	WELL DIAGRAM	LITHOLOGIC DESCRIPTION
5	-5					0-14.9 ft. ALLUVIUM:
10	-10					
15	-15					Total Depth 14.9 ft.
<i>Stoller</i>		U.S. DEPARTMENT OF ENERGY GRAND JUNCTION, COLORADO			PAGE 1 OF 1 11/20/2008	

Well 0688

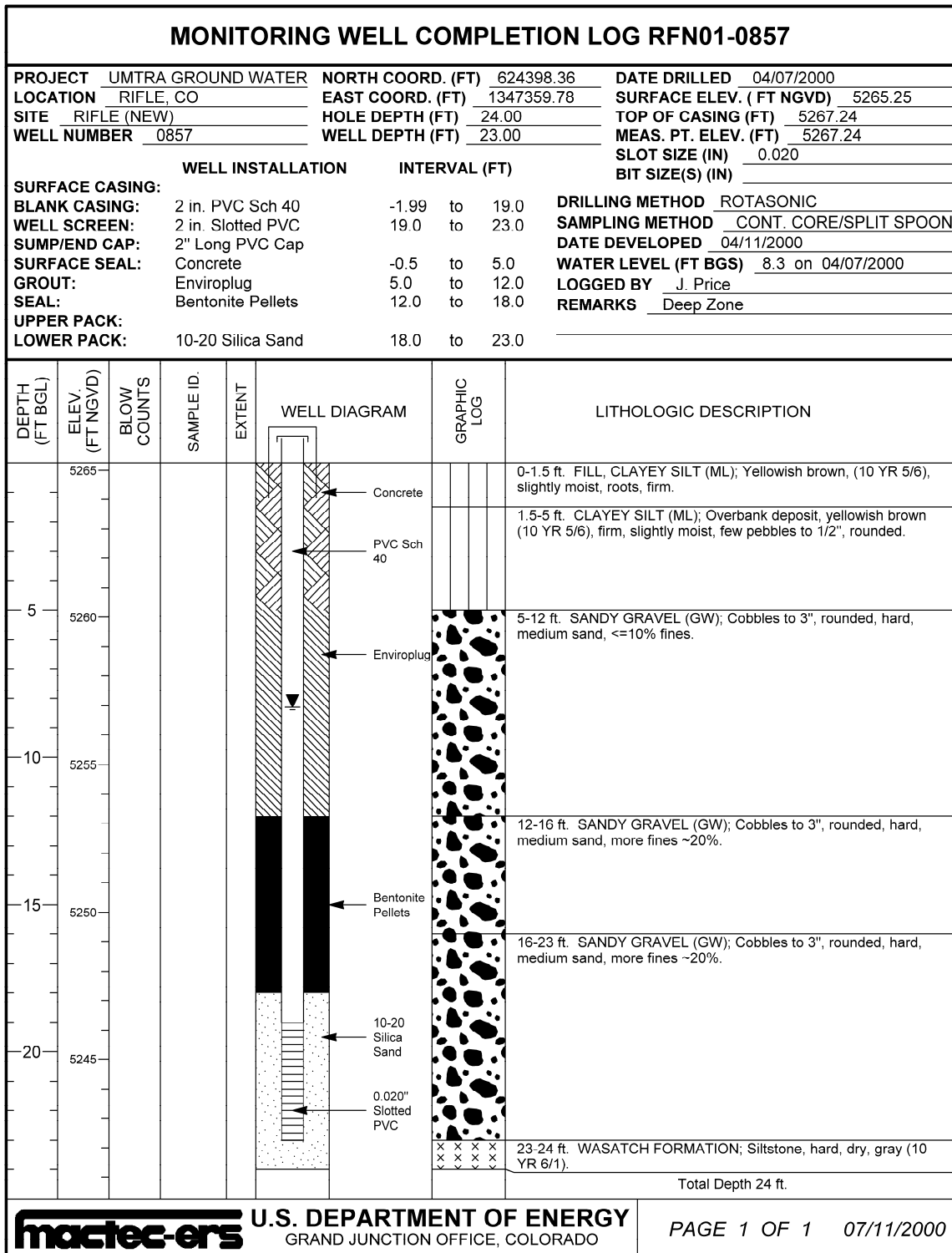
MONITORING WELL COMPLETION LOG RFN01-0688							
PROJECT LM		WELL NUMBER RFN01-0688		DATE DRILLED 2/13/2008			
LOCATION RIFLE, CO		NORTH COORD. (FT) 624037.00		SURFACE ELEV. (FT NGVD) _____			
SITE Rifle New Processing Site		EAST COORD. (FT) 1348127.00		TOP OF CASING (FT) _____			
DRILLING METHOD GEOPROBE		HOLE DEPTH (FT) 18.00		MEAS. PT. ELEV. (FT) _____			
DRILL COMPANY S.M. Stoller		WELL DEPTH (FT) 18.00		SLOT SIZE (IN) 0.020			
RIG TYPE GEOPROBE		WATER LEVEL (FT BGS) _____		BIT SIZE(S) (IN) 2.75			
SURFACE CASING:		WELL INSTALLATION		INTERVAL (FT)			
BLANK CASING: 2 in. PVC Sch 40				to 12.8			
WELL SCREEN: 2 in. 0.02 Slotted PVC		12.8		to 17.8			
SUMP/END CAP: 2 in. PVC Sch 40		17.8		to 18.0			
SURFACE SEAL: Bentonite		0.0		to 1.0			
GROUT:							
SEAL:							
UPPER PACK: 20-40 Silica Sand		1.0		to 7.0			
LOWER PACK: Natural Cave-in Material		7.0		to 18.0			
				WATER LEVEL DATE _____			
				DRILLER Walters, J. / Trevino, J.			
				LOGGED BY Walters, J.			
				SAMPLING METHOD _____			
				DATE DEVELOPED 3/24/2008			
				REMARKS _____			

DEPTH (FT BGL)	ELEV. (FT NGVD)	BLOW COUNTS	SAMPLE INTERVAL (FT)	EXTENT	WELL DIAGRAM	GRAPHIC LOG	LITHOLOGIC DESCRIPTION
5	-5						0-18.0 ft. ALLUVIUM:
10	-10						
15	-15						
							Total Depth 18.0 ft.
<i>Stoller</i>		U.S. DEPARTMENT OF ENERGY GRAND JUNCTION, COLORADO			PAGE 1 OF 1 11/20/2008		

Well 0855



Well 0857



Well 0863

MONITORING WELL COMPLETION LOG RFN01-0863						
PROJECT UMTRA GROUND WATER		NORTH COORD. (FT) 624389.81		DATE DRILLED 11/02/2000		
LOCATION RIFLE, CO		EAST COORD. (FT) 1346968.46		SURFACE ELEV. (FT NGVD) 5264.90		
SITE RIFLE (NEW)		HOLE DEPTH (FT) 26.00		TOP OF CASING (FT) 5267.77		
WELL NUMBER 0863		WELL DEPTH (FT) 26.00		MEAS. PT. ELEV. (FT) 5267.77		
WELL INSTALLATION INTERVAL (FT)				SLOT SIZE (IN) 0.020		
				BIT SIZE(S) (IN) 11.0		
SURFACE CASING:						
BLANK CASING:		6 in. PVC Sch 40		-2.87		to 10.5
WELL SCREEN:		6 in. SS Vee Wire Wrapped		10.5		to 25.5
SUMP/END CAP:		6 in. Stainless Steel		25.5		to 26.0
SURFACE SEAL:						
GROUT:						
SEAL:		Enviroplug		0.0		to 6.0
UPPER PACK:		20-40 Silica Sand		6.0		to 8.0
LOWER PACK:		10-20 Silica Sand		8.0		to 26.0
				DRILLING METHOD HAMMER CASING ADVANCE		
				SAMPLING METHOD		
				DATE DEVELOPED 11/02/2000		
				WATER LEVEL (FT BGS) 8.15 on 11/03/2000		
				LOGGED BY Pill, K.		
				REMARKS		

DEPTH (FT BGL)	ELEV. (FT NGVD)	BLOW COUNTS	SAMPLE ID.	EXTENT	WELL DIAGRAM	GRAPHIC LOG	LITHOLOGIC DESCRIPTION
	5260						0-7 ft. FILL, CLAYEY SILT (ML); yellowish brown (10 YR 5/6), slightly moist, firm, pebbles to 2 inches.
10							7-25 ft. SANDY GRAVEL (GW); yellowish brown (10 YR 5/6), slightly moist, cobbles to 4 inches, rounded, with medium sand, less than 15% fines. 12 ft. Becomes wet.
20							
	5250						
	5240						25-26 ft. WASATCH FORMATION, SHALE; very weathered, dark gray (7.5 YR N4), friable, dry. Total Depth 26 ft.
30							
	5230						
40							
	5220						

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