U.S. Department of Energy
Hanford Site

September 29, 2020

20-SGD-0071

Mr. Ben W. Simes, Program Manager
U.S. Environmental Protection Agency
1200 Pennsylvania Ave. NW
MC 5106R
Washington, District of Columbia 20460

Dear Mr. Simes:

300-FF-5 OPERABLE UNIT ENHANCED ATTENUATION URANIUM SEQUESTRATION COMPLETION REPORT, SGW-63113 Rev 0

This letter transmits the 300-FF-5 Operable Unit Enhanced Attenuation Uranium Sequestration Completion Report, SGW-63113 Rev 0, for your information.

If there are any questions, please contact me, or your staff may contact John Sands, of my staff, on (509) 372-2282.

Sincerely,

Michael W. Cline Digitally signed by Michael W. Cline Date: 2020.09.29 16:09:26 -07'00'

Michael W. Cline, Director
Soil and Groundwater Division
Richland Operations Office

SGD:JPS

Attachment

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SGW-63113
Revision 0

300-FF-5 Operable Unit Enhanced Attenuation Uranium Sequestration Completion Report

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Contractor for the U.S. Department of Energy
under Contract DE-AC06-08RL14788

CH2MHILL
Plateau Remediation Company

P.O. Box 1600
Richland, Washington 99352

Approved for Public Release;
Further Dissemination Unlimited

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Executive Summary

This report presents the initial performance evaluation of the enhanced attenuation (EA) for uranium contamination in a portion of the 300 Area of the Hanford Site. Cleanup of the 300 Area is being accomplished under the *Comprehensive Environmental Response, Compensation, and Liability Act of 1980*[1] (CERCLA) in accordance with the 300 Area Record of Decision (ROD)[2]. Uranium is identified as a contaminant of concern in both soil and groundwater. Part of the selected remedy for uranium contamination in the 300 Area is EA using polyphosphate solutions to sequester the uranium and reduce the mass of mobile uranium migrating into the groundwater.

The polyphosphate treatment was implemented at a 1.2 ha (3 ac) area of high residual uranium contamination that provides a continuing source of contamination to the groundwater. The EA remedy was conducted in two stages. Stage A was implemented from November 6 through 18, 2015, within an area of approximately 0.3 ha (0.75 ac). Polyphosphate solutions were applied to the vadose zone using a near-surface drip infiltration system and subsurface injection wells. Soil, groundwater, and electrical resistivity tomography data were collected and analyzed from Stage A to improve performance of Stage B treatment[3].

Design refinements made to Stage B to improve the effectiveness of the EA remedy included the following:

- Eliminated near-surface infiltration of the polyphosphate solution
- Used injection wells with two screens to better deliver polyphosphate solution to the two target zones (periodically rewetted zone [PRZ] and lower vadose zone [LVZ])

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[1] *Comprehensive Environmental Response, Compensation, and Liability Act of 1980*, 42 USC 9601, et seq., Pub. L. 107 377, December 31, 2002. Available at: https://www.csu.edu/cerc/researchreports/documents/CERCLASummary1980.pdf.

[2] EPA, Ecology, and DOE, 2013, *Hanford Site 300 Area Record of Decision for 300-FF-2 and 300-FF-5, and Record of Decision Amendment for 300-FF-1*, U.S. Environmental Protection Agency, Washington State Department of Ecology, and U.S. Department of Energy, Olympia, Washington. Available at: https://pdw.hanford.gov/arpir/pdf.cfm?accession=0087180.

[3] SGW-59614, 2016, *300-FF-5 Operable Unit Enhanced Attenuation Stage A Delivery Performance Report*, Rev. 0, CH2M HILL Plateau Remediation Company, Richland, Washington. Available at: http://pdw.hanford.gov/arpir/pdf.cfm?accession=0072777H.

- Increased the number of injection wells to distribute polyphosphate solution evenly throughout Stage B area
- Injected three pore volumes of polyphosphate solution to the PRZ, approximately twice the number of pore volumes injected to the PRZ during Stage A
- Injected three pore volumes of polyphosphate solution to the LVZ instead of infiltrating polyphosphate solution to the LVZ
- Eliminated aquifer injections
- Increased the number of groundwater monitoring wells, the sampling frequency, and the monitoring duration
- Extended the time until collection of post-treatment soil samples to allow longer reaction time between the polyphosphate solution and the sediment

Stage B was implemented within a 0.9 ha (2.25 ac) area. Polyphosphate injections were delivered to the PRZ and LVZ from September 4 through 20, 2018. Cross-borehole electrical resistivity tomography and downhole sensor data were collected continuously before, during, and following the injection period through late October and early November 2018, respectively. Groundwater monitoring data were collected at selected PRZ and aquifer monitoring wells daily during the injection period. Monthly samples were collected following the injections, with final samples collected during the higher river water stage in June 2019. Groundwater samples were collected monthly before, during, and after injections through October 2019 at 13 wells. Soil samples were collected before and 6 months after treatment from six collocated borehole pairs to compare uranium concentrations, phosphate distribution, and uranium leaching characteristics. Soil samples also were collected from three unpaired post-treatment boreholes to evaluate spatial distribution of phosphate and uranium leaching characteristics.

The target volumes of polyphosphate solution were effectively delivered to the PRZ and LVZ for the most part, but the distribution was not uniform across the treatment area. Near-surface infiltration during Stage A resulted in a variable fraction of the phosphate reaching the deeper portion of the vadose zone, while injection to the PRZ and LVZ (during Stages A and B) resulted in some local mounding near the injection wells. In some locations within the treatment area, the polyphosphate solution moved

preferentially downward to the aquifer, resulting in less effective lateral transport and treatment.

Overall, the EA treatment was deemed successful in sequestering the labile uranium fraction present in the PRZ and LVZ. During both stages, polyphosphate injections produced a rapid peak in phosphate concentrations in the aquifer and PRZ wells, followed by a gradual decline. On average, the mass of phosphate delivered during Stage B, through each of the injection wells, was 1,557 kg to the PRZ and 1,216 kg to the LVZ. Uranium concentrations in the 24 monitoring wells decreased during and immediately following polyphosphate injections with the exception of three wells that had nominal increases in uranium concentrations during injections followed by sharp declines. The downgradient groundwater wells monitored during and following the polyphosphate injections had lower uranium concentrations, below or near the cleanup level, compared to pre-treatment concentrations.

Three types of laboratory tests were conducted using soil samples from pre-treatment and post-treatment boreholes to evaluate the reduction in uranium mobility and leachability in the post-treatment samples. The results of these analyses confirmed that there were measurable reductions in the mobile uranium fraction following treatment. Bicarbonate solution extractions using Stage B samples showed that the fraction of mobile uranium decreased an average 63% from pre-treatment to post-treatment sediments as a result of the polyphosphate treatment. Sequential liquid extractions using Stage B samples showed that high-solubility uranium minerals decreased on average from 59% to 37% (of the total extracted uranium) and low-solubility uranium minerals increased on average from 35% to 54% as a result of the polyphosphate injections. One-dimensional column leach experiments using Stage B samples showed an average 59% decrease in uranium leaching (from the fraction leached to total uranium) for the post-treatment samples.

While the uranium mobility and leachability were reduced following polyphosphate treatment, the total mass of uranium was comparable in the pre-treatment and post-treatment soil analyses. This was further confirmed based on groundwater monitoring data that showed limited increases in uranium concentrations during or after polyphosphate injections. Therefore, flushing of uranium mass during injections was minimal. The reduction of the labile uranium fraction, increase in the relatively immobile uranium fraction, and decrease in downgradient uranium groundwater concentrations are attributed to polyphosphate treatment sequestering uranium.

Detailed geochemical reactive transport modeling and system-scale flow and transport modeling was conducted to evaluate the impact of polyphosphate injection on uranium sequestration. The results of reactive transport modeling indicated precipitation of calcium-phosphate phases along with other in-situ geochemical reactions that result in reducing the labile uranium fraction consistent with the field observations during and after the injections. The system-scale modeling used to make longer-term predictions indicate that the uranium concentrations in groundwater following treatment continue to decline to asymptote-based concentrations indicating the effectiveness of the polyphosphate treatment. The modeling indicated that the uranium concentrations in wells within and around the treatment area will largely remain below the cleanup level except during the short-term seasonal increases in river stage.

Evaluation of the EA remedy performance is ongoing. It is too early to draw conclusions on how phosphate treatment has impacted the estimated cleanup timeline for the 300-FF-5 Operable Unit. Data collected from continued monitoring of wells in and around the treatment area over the longer term will be used to estimate the timeframe to achieve the uranium cleanup level in the groundwater. Evaluation of long-term groundwater monitoring will continue to further elucidate the performance of the 300 Area EA remedy (including Stages A and B) as part of the CERCLA five-year review process.

Contents

1 Introduction 1-1

1.1 Purpose 1-2
1.2 Site Description 1-2
1.2.1 Background 1-2
1.2.2 Physical Setting 1-8
1.2.3 Enhanced Attenuation Remedy Timeline 1-18
1.3 Uranium Sequestration Technology 1-18
1.3.1 Treatability Tests 1-19
1.3.2 Enhanced Attenuation Remedy 1-19

2 Uranium Sequestration Implementation 2-1

2.1 Stage B Objectives 2-1
2.2 Stage B Design 2-1
2.2.1 Stage B Enhanced Attenuation Area 2-2
2.2.2 Stage B Injection Wells 2-2
2.2.3 Stage B Monitoring Wells 2-7
2.2.4 Stage B ERT System 2-11
2.2.5 Stage B Chemical Mixing Skids and Site Infrastructure 2-15
2.2.6 Stage B Enhanced Attenuation System Configuration 2-15
2.2.7 Stage B Timing and Order of Treatment 2-16
2.3 Stage B Deviations from Design 2-19

3 Sampling and Monitoring Methods 3-1

3.1 Soil Sampling and Analysis 3-1
3.1.1 Pre-Treatment Sampling and Analysis 3-2
3.1.2 Post-Treatment Sampling and Analysis 3-3
3.1.3 Laboratory Tests on Pre-Treatment and Post-Treatment Samples 3-7
3.1.4 Radiological Contamination of Backfill Material 3-9
3.2 Groundwater Sampling and Monitoring 3-10
3.2.1 Manual Monitoring 3-10
3.2.2 Automated Monitoring 3-15
3.3 Operations Monitoring 3-16
3.4 Electrical Resistivity Tomography 3-18
3.5 Long-Term Groundwater Monitoring 3-18
3.6 Data Management 3-18

4 Sampling and Monitoring Results 4-1

4.1 Soil Sampling and Analysis 4-1
4.1.1 Uranium and Phosphate Analytical Results 4-1

4.1.2 Uranium and Phosphate Leachability Characteristics Test Results 4-7
4.2 Groundwater Sampling and Monitoring 4-12
4.2.1 Manual Monitoring 4-12
4.2.2 Automated Monitoring 4-28
4.3 Operations Monitoring 4-36
4.4 Electrical Resistivity Tomography 4-46
4.4.1 Pre-Treatment Monitoring 4-47
4.4.2 Monitoring During Treatment 4-48
4.4.3 Post-Treatment Monitoring 4-53
5 Enhanced Attenuation Performance Evaluation 5-1
5.1 Effectiveness of Phosphate Delivery and Distribution 5-1
5.1.1 Evaluation of Phosphate Delivery and Distribution During Treatment 5-1
5.1.2 Evaluation of Phosphate Distribution Post-Treatment 5-2
5.2 Impacts of Polyphosphate Injections on Uranium Mobility Reduction 5-12
5.2.1 Changes in Total Uranium Distribution in the Vadose Zone 5-12
5.2.2 Changes in Uranium Leaching in the Vadose Zone 5-17
5.2.3 Uranium Solid Phase Analysis in the Vadose Zone 5-18
5.2.4 Changes in Total Uranium Concentrations in the Aquifer 5-19
5.3 Uranium Fate and Transport Modeling 5-19
5.3.1 Geochemical Modeling: Kinetic Sorption-Desorption Parameters 5-20
5.3.2 Near-Field Reactive Transport Modeling 5-22
5.3.3 System-Scale 3-D Flow and Transport Modeling Parameters 5-36
5.3.4 System-Scale 3-D Flow and Transport Modeling Results and Projections 5-43
6 Conclusions 6-1
6.1 Delivery and Distribution of Polyphosphate Treatment Solution in the Subsurface 6-1
6.1.1 Vadose Zone and PRZ Phosphate Delivery 6-1
6.1.2 Phosphate Distribution Within the Vadose Zone, PRZ, and Aquifer 6-2
6.2 Impacts to Uranium Mobility and Leachability 6-2
6.3 Impact to Local Uranium Concentrations and Chemistry 6-2
6.4 Numerical Modeling to Assess Future Impacts 6-2
6.5 Conclusions 6-2
7 References 7-1

Appendices

A 300-FF-5 Operable Unit Enhanced Attenuation Bibliography ..... A-i

B Enhanced Attenuation Stage B Soil and Groundwater Sample Analytical Data ..... B-i

C Automated Field Measurements for Enhanced Attenuation Stage B Monitoring Wells ..... C-i

D Enhanced Attenuation Stage B Mixing Skids Analytical Data ..... D-i

E Long-Term Groundwater Monitoring Analytical Data ..... E-i

Figures

Figure 1-1. Map of the Hanford Site, 300 Area, and 300 Area Industrial Complex 1-3

Figure 1-2. Aerial View of a Portion of the 300 Area Industrial Complex Showing the Stage A and B Enhanced Attenuation Areas and Nearby Waste Sites 1-4

Figure 1-3. 300 Area Geology 1-10

Figure 1-4. Cross Section of the General Geologic Features of the 300 Area Industrial Complex and Stage A and B Enhanced Attenuation Areas 1-11

Figure 1-5. Composite Log for the 399-1-162 Aquifer Monitoring Well 1-13

Figure 1-6. Hanford Formation Isopach Map and Ringold Formation Structural Elevation Map in the Enhanced Attenuation Area 1-15

Figure 1-7. Elevations of the Periodically Rewetted Zone and Lower Vadose Zone in the Enhanced Attenuation Area 1-17

Figure 1-8. Timeline of Documents and Activities Supporting Implementation of the Enhanced Attenuation Remedy 1-18

Figure 1-9. Uranium Sequestration Mechanisms via Phosphate Addition as an In Situ Remediation Approach 1-20

Figure 1-10. Uranium Mobility Change with Polyphosphate Treatment 1-21

Figure 2-1. Stage B Injection Well Locations in Four Injection Zones 2-3

Figure 2-2. Stage B Well Designs Without ERT Electrodes 2-5

Figure 2-3. Stage B Well Designs with ERT Electrodes 2-6

Figure 2-4. Forty-Eight Injection Wells and Nineteen Monitoring Wells Drilled for Stage B 2-8

Figure 2-5. Stage B EA Area Monitoring Well Locations 2-10

Figure 2-6. Stage B ERT Well Locations 2-13

Figure 2-7. Stage B Enhanced Attenuation System Configuration 2-16

Figure 3-1. Sampling Locations for the Stage A and B Pre-Treatment and Post-Treatment Wells 3-2

Figure 3-2. Location of Stage B Pre-Treatment Wells Selected for Uranium Leachability Tests 3-3

Figure 3-3. Location of Six Pre-Treatment and Nine Post-Treatment Stage B Boreholes 3-6

Figure 3-4. Locations of 13 Stage B Monthly Groundwater Monitoring Wells 3-11

Figure 3-5. Locations of 24 Stage B Monitoring Wells 3-12

Figure 3-6. Locations of AWLN Stations Monitored for EA Operations 3-17

Figure 4-1. 3-D Plane View and Cross Section of EA Area with Excavation Footprint and Uranium Soil Samples from Stages A and B Below 108.5 m Elevation 4-3
Figure 4-2. Uranium Concentration Depth-Discrete Profiles in Pre-Treatment and Post-Treatment Borehole Pairs 4-5
Figure 4-3. Uranium and Phosphate Concentration Depth-Discrete Profiles of Pre-Treatment and Post-Treatment Borehole Pairs and Unpaired Post-Treatment for the Stage B EA Area 4-6
Figure 4-4. Geochemical Simulations of Targeted Polyphosphate Injection Solution 4-11
Figure 4-5. Uranium and Phosphate Concentrations in Groundwater Samples from Wells Within the Treatment Area Collected from August through October 2018 4-13
Figure 4-6. Uranium and Phosphate Concentrations in Groundwater Samples from Wells Outside of the Treatment Area Collected from August through October 2018 4-14
Figure 4-7. Uranium and Phosphate Concentrations in Groundwater Samples from Wells Within the Treatment Area Collected from August through June 2019 4-15
Figure 4-8. Uranium and Phosphate Concentrations in Groundwater Samples from Wells Outside the Treatment Area Collected from August 2018 through June 2019 4-16
Figure 4-9. Phosphate Concentrations in the Aquifer and PRZ on September 5, 2018 (During Treatment) 4-17
Figure 4-10. Phosphate Concentrations in the Aquifer and PRZ on September 9, 2018 (During Treatment) 4-18
Figure 4-11. Phosphate Concentrations in the Aquifer and PRZ on September 13, 2018 (During Treatment) 4-19
Figure 4-12. Phosphate Concentrations in the Aquifer and PRZ on September 18, 2018 (During Treatment) 4-20
Figure 4-13. Phosphate Concentrations in the Aquifer and PRZ on September 19, 2018 (During Treatment) 4-21
Figure 4-14. Phosphate Concentrations in the Aquifer and PRZ on September 23, 2018 (After Treatment) 4-23
Figure 4-15. Phosphate Concentrations in the Aquifer and PRZ on September 27, 2018 (After Treatment) 4-24
Figure 4-16. Uranium and Phosphate Concentrations in Groundwater Samples from Well 399-1-73 Collected from August through October 2018 4-25
Figure 4-17. Temporary Arsenic and Vanadium Concentration Increases in Well 399-1-17A Following Stage A and B Polyphosphate Treatments 4-27
Figure 4-18. Comparison of Downhole Sensor Specific Conductance with Specific Conductance from Groundwater Samples and Phosphate Concentration for PRZ Well 399-1-73 4-30
Figure 4-19. Comparison of Downhole Sensor Specific Conductance with Specific Conductance from Groundwater Samples and Phosphate Concentration for PRZ Well 399-1-152 4-31
Figure 4-20. Comparison of Downhole Sensor Specific Conductance with Specific Conductance from Groundwater Samples and Phosphate Concentration for PRZ Well 399-1-148 4-32
Figure 4-21. Comparison of Downhole Sensor Specific Conductance with Specific Conductance from Groundwater Samples and Phosphate Concentration for PRZ Well 399-1-149 4-33
Figure 4-22. Comparison of Downhole Sensor Specific Conductance with Specific Conductance from Groundwater Samples and Phosphate Concentration for PRZ Well 399-1-147 4-34

Figure 4-23. Comparison of Downhole Sensor Specific Conductance with Specific Conductance from Groundwater Samples and Phosphate Concentration for PRZ Well 399-1-154 4-35
Figure 4-24. Skid 1 Daily Sample Solution Concentrations.....4-37
Figure 4-25. Skid 2 Daily Sample Solution Concentrations.....4-38
Figure 4-26. Total Injection Volumes Per Well Per Zone at Skid 1.....4-44
Figure 4-27. Total Injection Volumes per Well per Zone at Skid 2 4-45
Figure 4-28. Stage A and B Treatment Area Layout with Clusters 1, 2, and 3 4-46
Figure 4-29. Pre-Treatment Baseline ERT Images in the A-A' Plane for Each Cluster (top) and the Corresponding Interpretations (bottom).....4-47
Figure 4-30. Twice Daily Images of ERT Amendment Distribution in Cluster 1.....4-49
Figure 4-31. Twice Daily Images of ERT Amendment Distribution in Cluster 2.....4-51
Figure 4-32. Twice Daily Images of ERT Amendment Distribution in Cluster 3.....4-52
Figure 5-1. Measurement of the Change in Solid Phase Phosphorus in Stage B from Pre-Treatment to Post-Treatment.....5-4
Figure 5-2. Comparison of the Change in Total Phosphorus (Post-Treatment Minus Pre-Treatment) in Stage B Paired Boreholes with Respect to Depth 5-5
Figure 5-3. Representative 2-D Elemental Maps using SEM-EDS of Pre-Treatment Borehole 399-1-123 (top) and Post-Treatment Borehole C9729 (bottom) Sediments Showing an Increase in Phosphorus in the Solid Phase After Polyphosphate Injection 5-6
Figure 5-4. Groundwater Uranium, Phosphate, and Specific Conductivity Concentrations at Downgradient Well 399-1-23 5-7
Figure 5-5. Groundwater Uranium, Phosphate, and Specific Conductivity Concentrations at Downgradient Well 399-1-17A 5-8
Figure 5-6. Groundwater Uranium, Phosphate, and Specific Conductivity Concentrations at Downgradient Well 399-1-7 5-9
Figure 5-7. Groundwater Uranium, Phosphate, and Specific Conductivity Concentrations at Downgradient Well 399-2-2 5-10
Figure 5-8. Uranium Concentrations and Water-Level Elevation Data at Downgradient Well 399-1-17A 5-11
Figure 5-9. Correlation Between the Fraction of Mobile Uranium (Post-Treatment Minus Pre-Treatment) with the Change in Solid Phase Phosphorus for Stage B Sediment Samples.....5-14
Figure 5-10. Change in the Fraction of Uranium (Post-Treatment Minus Pre-Treatment) Extracted in Six Sequential Steps from 19 Pairs of Sediments where Uranium Mobility Decreases with Each Successive Extraction Step 5-15
Figure 5-11. Comparison of Total Uranium Measured in Six Sequential Extractions in Pre-Treatment (red) and Post-Treatment (green) Sediments 5-16
Figure 5-12. Sequential Extraction of Uranium Minerals of Relevance to the 300 Area of the Hanford Site.....5-17
Figure 5-13. Uranium and Phosphate Leaching over Time in 1-D Column Experiments for Stage B Pre-Treatment and Post-Treatment Sediment Sample Pairs 5-18

Figure 5-14. Representative 2-D Elemental Maps using μ-XRF of Post-Treatment Sediments from Borehole C9729 for Uranium (in green) Overlaid with Copper (left), Calcium (middle), and Iron (right) (in red) 5-19
Figure 5-15. Comparison of Uranium Release Rate Constants for All the Pre-Treatment and Post-Treatment Soil Samples 5-21
Figure 5-16. Comparison of Derived K_d Value for the Pre-Treatment and Post-Treatment Samples 5-21
Figure 5-17. Uranium Sequestration Mechanisms via Phosphate Addition as an In Situ Remediation Approach 5-22
Figure 5-18. Near-Field Reactive Transport Model Domain in Radial Coordinates with Distribution of Hydrogeologic Units (upper figure) and the PRZ and LVZ Injection Screen Intervals Along with Observation Nodes (lower figure) 5-24
Figure 5-19. 3-D Near-Field Reactive Transport Model Calculated Aqueous Saturation Profiles a) Before Injections, b) After the First PRZ, c) Second PRZ, d) First LVZ, and e) Second LVZ Injection Periods 5-26
Figure 5-20. 3-D Near-Field Reactive Transport Model Geochemical Evolution Plots Showing Aqueous Species at a) 0.5 m Distance from LVZ Injection Screen and b) 0.5 m Distance from PRZ Injection Screen 5-28
Figure 5-21. 3-D Near-Field Reactive Transport Model Showing Minerals Favored to Form over Time at a) 0.5 m Distance from LVZ Injection Screen and b) 0.5 m Distance from PRZ Injection Screen 5-29
Figure 5-22. 3-D Near-Field Reactive Transport Model Time-Series Plots of Log Molar Ratio HPO_4/HCO_3 and pH for 0.5 m Distance from a) LVZ Injection Screen and c) PRZ Injection Screen and Mineral Stability Phase Diagrams b) with Uranium and d) without Uranium 5-30
Figure 5-23. 3-D Near-Field Reactive Transport Model HPO_4^{2-} Profile a) Before Injections, b) After the First PRZ, c) Second PRZ, d) First LVZ, and e) Second LVZ Injection Periods 5-32
Figure 5-24. 3-D Near-Field Reactive Transport Model Total Aqueous Uranium Profile a) Before Injections, b) After the First PRZ, c) Second PRZ, d) First LVZ, and e) Second LVZ Injection Periods 5-33
Figure 5-25. 3-D Near-Field Reactive Transport Model pH Profile a) Before Injections, b) After the First PRZ, c) Second PRZ, d) First LVZ, and e) Second LVZ Injection Periods 5-34
Figure 5-26. 3-D Near-Field Reactive Transport Model Hydroxyapatite Profile a) Before Injections, b) After the First PRZ, c) Second PRZ, d) First LVZ, and e) Second LVZ Injection Periods 5-35
Figure 5-27. System-Scale 3-D STOMP Model Domain to Evaluate Remedy Performance 5-37
Figure 5-28. System-Scale 3-D STOMP Model Domain with Recharge Boundary at the Top Surface 5-38
Figure 5-29. Monitoring Locations with Transducers within 300 Area Showing River Gauge (SWS-1) and Monitoring Wells 5-40
Figure 5-30. Daily Averaged Columbia River Stage Data at SWS-1 (300 Area River Gauge) 5-41
Figure 5-31. Zones of Variable Hydraulic Conductivity for the Hanford Unit in the Unconfined Aquifer within the System-Scale 3-D STOMP Model 5-42

Figure 5-32. Spatial Distribution of Uranium Soil Concentration Based on Interpolation of Soil Sampling Data Collected from Various Boreholes 5-43
Figure 5-33. Comparison of System-Scale 3-D STOMP Model Simulated Hydraulic Heads with Observed Heads at Wells 399-1-17A and 399-1-7 5-45
Figure 5-34. Comparison of System-Scale 3-D STOMP Model Simulated Groundwater-Riverwater Mixing Fraction with Observed Data at Wells 399-1-17A and 399-1-7 5-46
Figure 5-35. Comparison of System-Scale 3-D STOMP Model Simulated Uranium Concentrations in Groundwater with Observed Data at Wells 399-1-17A and 399-1-7 5-47
Figure 5-36. Comparison of System-Scale 3-D STOMP Model Simulated Groundwater Uranium Concentrations During the Post-Treatment Period with Observed Data at Wells 399-1-17A and 399-1-7 5-48
Figure 5-37. System-Scale 3-D STOMP Model Simulated Longer Term Groundwater Uranium Concentrations at Wells 399-1-17A and 399-1-7 5-49
Figure 5-38. Simulated Uranium Plumes for (a) January 2019 and (b) June 2019 5-50
Figure 5-39. Simulated Uranium Plumes for: (a) January 2021 and b) June 2021 5-51
Figure 5-40. Simulated Uranium Plumes for: (a) January 2024 and (b) June 2024 5-52
Figure 5-41. Simulated Uranium Plumes for: (a) January 2027 and (b) June 2027 5-53
Figure 5-42. Simulated Uranium Plumes for: (a) January 2029 and (b) January 2039 5-54
Figure 5-43. Comparison of the Cumulative Mass Flux of Uranium Across the Approximate Water Table Between the Base Case with Treatment and the No-Action Case Without Treatment (Relative to Year 2009) 5-55
Figure 6-1. Summary Images of the Changes in Electrical Conductivity during Stage B Polyphosphate Injections in Clusters 1 through 3 6-2
Figure 6-2. Uranium and Phosphate Concentrations in Aquifer Wells in and Downgradient of the Treatment Area from August 2018 through June 2019 6-2
Figure 6-3. Change in Leached Uranium Comparing Pre-Treatment to Post-Treatment 6-2
Figure 6-4. Summary of Fraction of Uranium Leached out of Mobile Phases Compared to Least Mobile Phases with Total Uranium Leached with Carbonate Extractions 6-2

Tables

Table 1-1. Companion Documents for the Uranium Sequestration Remedy Required by the Groundwater Addendum of the RDR/RAWP 1-5
Table 2-1. Stage B Monitoring Well Locations 2-9
Table 2-2. Summary of Stage B Uranium Sequestration Operations at Skid 1 2-17
Table 2-3. Summary of Stage B Uranium Sequestration Operations at Skid 2 2-18
Table 3-1. Stage A Pre-Treatment and Post-Treatment Boreholes with Planned Soil Samples 3-4
Table 3-2. Stage B Pre-Treatment and Post-Treatment Boreholes with Planned Soil Samples 3-5
Table 3-3. Post-Treatment Stage B Boreholes with Opportunistic Soil Sampling 3-7
Table 3-4. Stage B Pre-Treatment and Post-Treatment Samples Selected for Laboratory Tests 3-8

Table 3-5. Sampling Frequency for 30 Stage B Wells 3-12
Table 3-6. Constituents Monitored in Groundwater Samples 3-14
Table 4-1. Range of Stage B Pre-Treatment Uranium and Copper Soil Concentrations 4-7
Table 4-2. Percent of High, Moderate, and Low Mobility Uranium Before and After Stage B Treatment 4-8
Table 4-3. Average Flow Rates into PRZ and LVZ 4-39
Table 4-4. Skid 1 Total Volume of Solution Injected into PRZ and LVZ 4-40
Table 4-5. Skid 2 Total Volume of Solution Injected into PRZ and LVZ 4-41
Table 5-1. Solution Chemical Composition 5-25

Terms

1-D	one-dimensional
2-D	two-dimensional
3-D	three-dimensional
μ-XRF	micro X-ray fluorescence
APS	Advanced Photon Source
AWLN	Automatic Water Level Network
bgs	below ground surface
CUL	cleanup level
DQO	data quality objective
EA	enhanced attenuation
EHM	equivalent homogeneous medium
ERT	electrical resistivity tomography
EXAFS	extended x-ray absorption structure
FS	feasibility study
Hf	Hanford formation
K_d	solid to liquid partitioning coefficient
LVZ	lower vadose zone
OU	operable unit
PNNL	Pacific Northwest National Laboratory
PRZ	periodically rewetted zone
RDR/RAWP	remedial design report/remedial action work plan
RI	remedial investigation
Rlm	Ringold Formation member of Wooded Island – lower mud unit
ROD	record of decision
Rwie	Ringold Formation member of Wooded Island – unit E
SAP	sampling and analysis plan
SEM-EDS	scanning electron microscopy energy dispersive X-Ray spectroscopy
XANES	X-ray near edge structure

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1 Introduction

This report presents the initial performance evaluation of the enhanced attenuation (EA) implemented to sequester residual uranium that provides a continuing source of contamination to groundwater in a portion of the 300-FF-5 Operable Unit (OU) in the 300 Area of the Hanford Site.

The 300 Area encompasses approximately 105 km^2 (40 mi^2) adjacent to the Columbia River in the southern portion of the Hanford Site (Figure 1-1). The 300 Area includes a smaller operations area, called the 300 Area Industrial Complex, comprising several facilities and waste disposal sites that supported uranium fuel production and research and development activities. Past contaminant releases at waste disposal sites in the 300 Area Industrial Complex resulted in persistent uranium contamination within the underlying soil and groundwater.

Completion of the soil and groundwater cleanup is being performed under the *Comprehensive Environmental Response, Compensation, and Liability Act of 1980* in accordance with EPA et al., 2013, *Hanford Site 300 Area Record of Decision for 300-FF-2 and 300-FF-5, and Record of Decision Amendment for 300-FF-1* (hereinafter called the 300 Area Record of Decision [ROD]). Uranium is identified as a contaminant of concern in both soil and groundwater. Part of the selected remedy for uranium contamination in the 300 Area Industrial Complex is EA of uranium using polyphosphate solutions to sequester and reduce the mass of mobile uranium migrating into the groundwater. The polyphosphate solutions interact with the sediment to form calcium-phosphate minerals that can react with residual uranium, thereby sequestering the uranium in situ.

The polyphosphate treatment was implemented at a 1.2 ha (3 ac) area of high residual uranium contamination that is a persistent source of uranium contamination to groundwater in the 300 Area Industrial Complex in accordance with the 300 Area ROD (EPA et al., 2013). Implementation of the remedy occurred in two sequential stages (A and B), as described in DOE/RL-2014-13-ADD2, *Remedial Design Report/Remedial Action Work Plan Addendum for the 300 Area Groundwater* (hereinafter called the remedial design report/remedial action work plan (RDR/RAWP]).

Stage A was implemented from November 6 through 18, 2015, in accordance with DOE/RL-2014-42, *300-FF-5 Operable Unit Remedy Implementation Sampling and Analysis Plan* (hereinafter called the sampling and analysis plan [SAP]; as modified by TPA-CN-0762, TPA-CN-0820, TPA-CN-0827, TPA-CN-0867, and TPA-CN-0883). During Stage A, polyphosphate solutions were infiltrated into the shallow vadose zone and injected into the periodically rewetted zone (PRZ) and top of the unconfined aquifer within an area of approximately 0.3 ha (0.75 ac) (Figure 1-2). The Stage A operations and treatment performance were evaluated to identify refinements needed for design and operation of Stage B.

Stage B was implemented from September 4 through 20, 2018, in accordance with DOE/RL-2014-42-ADD1, *300-FF-5 Operable Unit Remedy Implementation Sampling and Analysis Plan Addendum for Stage B Uranium Sequestration* (hereinafter called the SAP addendum; as modified by TPA-CN-0828, TPA-CN-0835, and TPA-CN-0868). During Stage B, polyphosphate solutions were injected into the lower vadose zone (LVZ) and PRZ within a 0.9 ha (2.25 ac) area adjacent to Stage A (Figure 1-2).

The EA treatment performance was evaluated through several lines of evidence (Section B2.5 of the SAP and Section 1.2 of the SAP addendum). These lines of evidence include the following:

- The change in uranium leachability following polyphosphate application
- The delivery and distribution of phosphate to the LVZ, PRZ, and top of the aquifer

- The decrease in the timeframe to achieve the uranium cleanup level (CUL) in groundwater predicted by fate and transport modeling
- The change in uranium concentrations in groundwater following polyphosphate application

This report is the seventh and final companion document required by the RDR/RAWP for the uranium sequestration remedy (Table 3-1 in DOE/RL-2014-13-ADD2). All of the required companion documents for the uranium sequestration remedy have been completed (Table 1-1).

1.1 Purpose

The purpose of this report is to present the results and evaluate the initial performance of the EA remedy. Stage A treatment performance was evaluated in SGW-59614, *300-FF-5 Operable Unit Enhanced Attenuation Stage A Delivery Performance Report*. This report provides the details on implementation of Stage B treatment and evaluates the initial performance of the EA remedy from the combined Stage A and B treatment results.

Information on the final design and installation of the Stage A uranium sequestration system is described in SGW-59455, *300-FF-5 Operable Unit Stage A Uranium Sequestration System Installation Report*.

Information on the final design and installation of the Stage B uranium sequestration system is described in SGW-60778, *300-FF-5 Operable Unit Stage B Uranium Sequestration System Installation Report*.

1.2 Site Description

The 300 Area is located adjacent to the Columbia River in the southern portion of the Hanford Site (Figure 1-1). This part of the Columbia River is within the Hanford Reach, a nontidal, free-flowing section of the Columbia River in southeastern Washington State. The Hanford Reach extends from the Priest Rapids Dam northwest of the Hanford Site to the slack water of Lake Wallula, which was created by McNary Dam southeast of the Hanford Site.

1.2.1 Background

Operations in the 300 Area began in 1943. The 300 Area Industrial Complex included the buildings and facilities where the majority of uranium fuel production and research and development activities took place. Large volumes of liquid waste containing uranium were discharged to the soil column through waste disposal sites in the 300 Area Industrial Complex. Contaminant releases at waste sites resulted in uranium contamination in groundwater that exceeds the 30 µg/L CUL in the 300 Area ROD (EPA et al., 2013). The following seven waste sites were historically the main contributors of groundwater uranium contamination: former liquid waste disposal sites 316-1, 316-2, 316-3, and 316-5; and former solid waste disposal sites 618-1, 618-2, and 618-3 (Table 1 in the 300 Area ROD) (Figure 1-1).

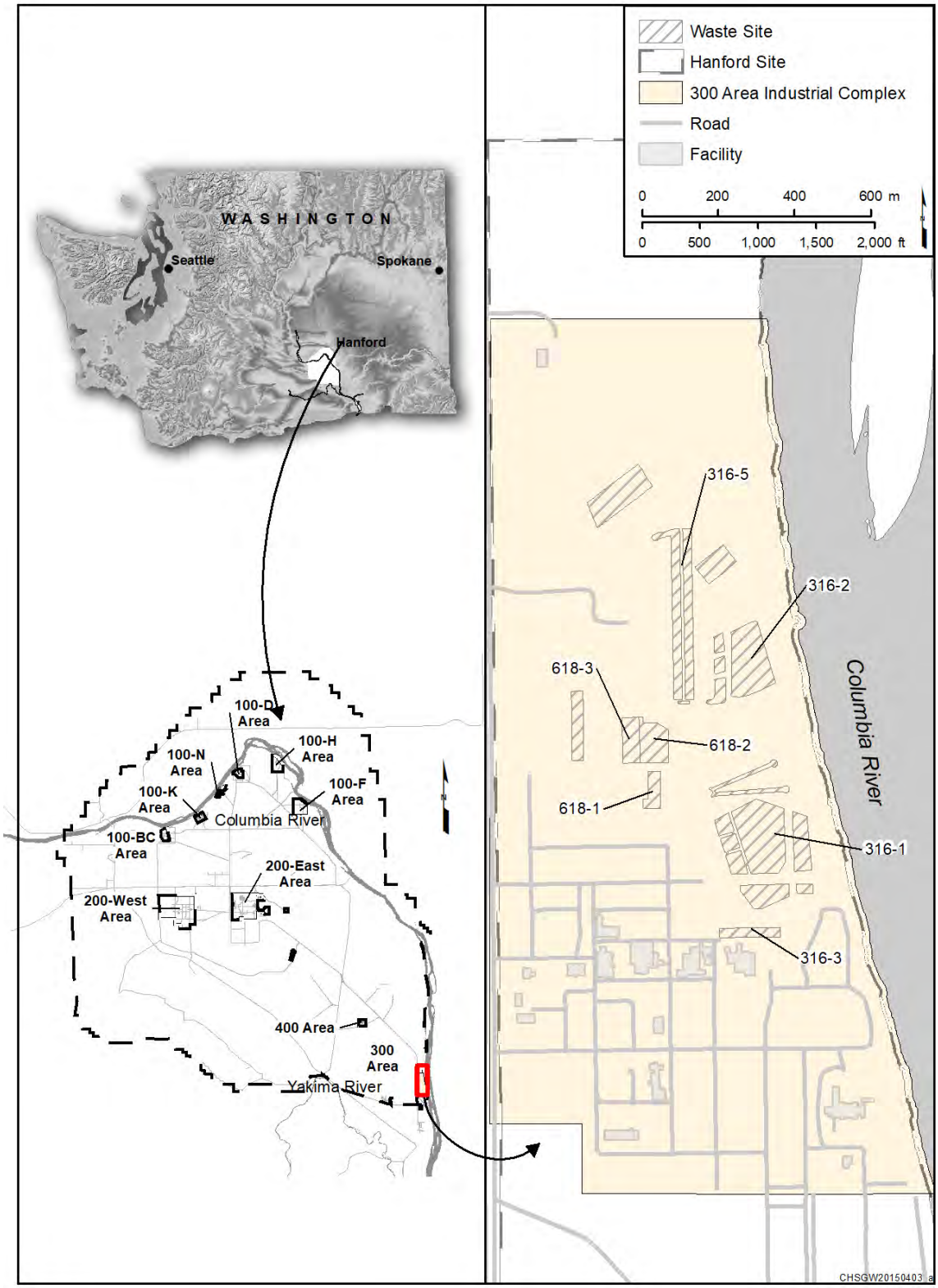


Figure 1-1. Map of the Hanford Site, 300 Area, and 300 Area Industrial Complex

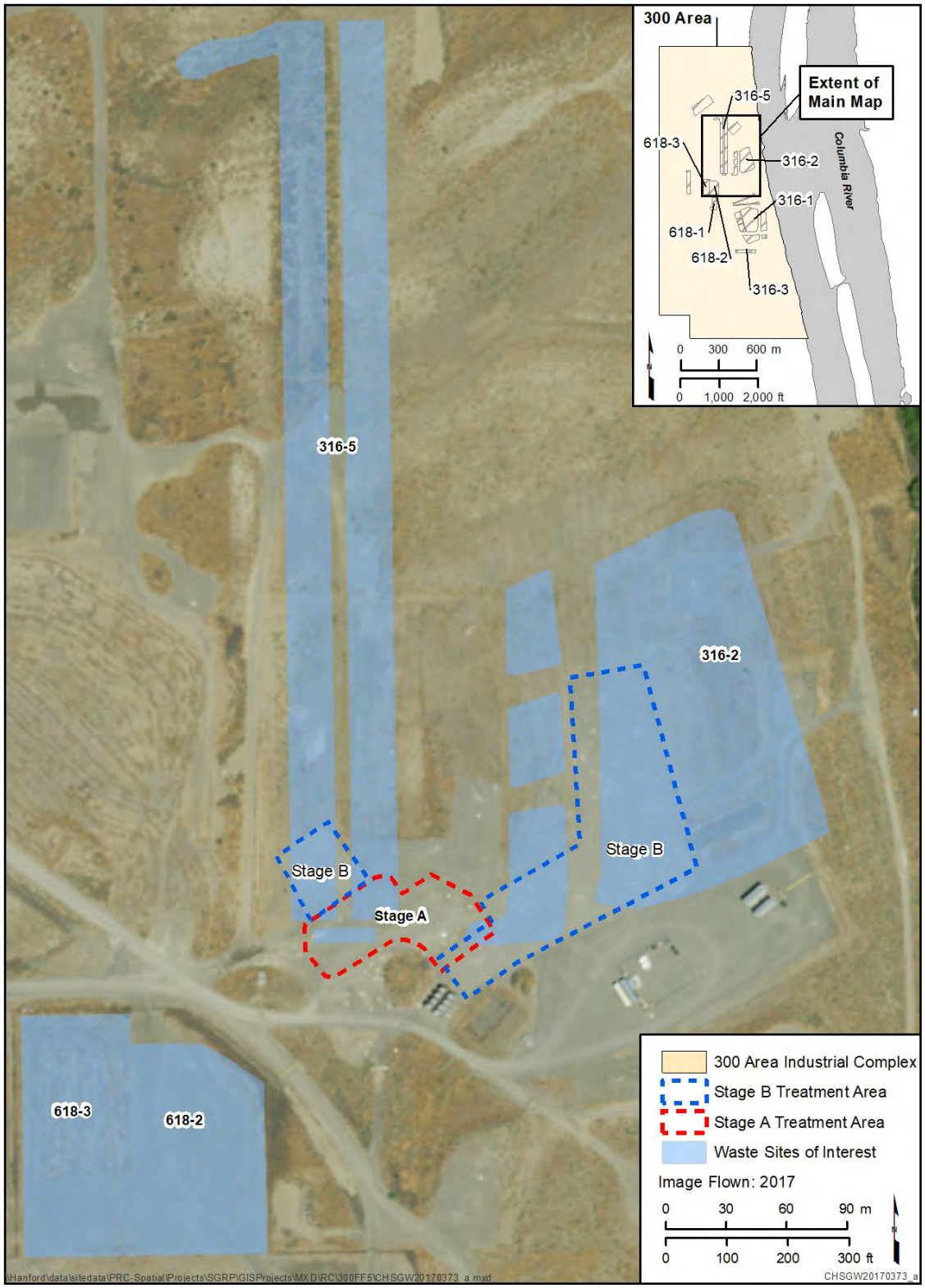


Figure 1-2. Aerial View of a Portion of the 300 Area Industrial Complex Showing the Stage A and B Enhanced Attenuation Areas and Nearby Waste Sites

Table 1-1. Companion Documents for the Uranium Sequestration Remedy Required by the Groundwater Addendum of the RDR/RAWP

Document*	Purpose/Content*	Completed Document Number and Title	Completed Document Date Published
Sampling Instructions for Post-ROD Investigation	Describes the drilling and sampling procedures for refining the location of the enhanced attenuation areas.	SGW-56993, *Sampling Instruction for the 300-FF-5 Operable Unit Supplemental Post ROD Field Investigation* (as modified by TPA-CN-656)	August 2014
Remedy Implementation SAP	Describes the waste management procedures; well installation and sampling procedures for the well, piezometer, and infiltration system installation for the Stage A and B uranium sequestration implementation. Includes the performance monitoring plan, which describes groundwater monitoring locations, parameters, and frequency of sampling for both the MNA and groundwater monitoring. Describes the evaluation methods for plume mapping, water level mapping and refining the CSM, groundwater modeling, statistical analysis, and enhanced attenuation treatment performance. Describes the phosphate formulations, injection and infiltration volumes and rates, operations and maintenance requirements for phosphate solution storage, distribution, and delivery, infiltration schedule, and monitoring during injection and infiltration.	DOE/RL-2014-42, *300-FF-5 Operable Unit Remedy Implementation Sampling and Analysis Plan* (as modified by TPA-CN-0762, TPA-CN-0820, TPA-CN-0827, TPA-CN-0867, and TPA-CN-0883)	September 2015
		DOE/RL-2014-42-ADD1, *300-FF-5 Operable Unit Remedy Implementation Sampling and Analysis Plan Addendum for Stage B Uranium Sequestration* (as modified by TPA-CN-0828; TPA-CN-0835; and TPA-CN-0868)	December 2016
Supplemental Post-ROD Field Investigation Summary	Summarizes findings from the supplemental post-ROD field investigation and includes proposed injection well, infiltration system, and piezometer locations for the Stage A uranium sequestration implementation.	SGW-58830, *300-FF-5 Supplemental Post-ROD Field Investigation Summary*	July 2015

Table 1-1. Companion Documents for the Uranium Sequestration Remedy Required by the Groundwater Addendum of the RDR/RAWP

Document*	Purpose/Content*	Completed Document Number and Title	Completed Document Date Published
Stage A Uranium Sequestration System Installation Report	Summarizes Stage A injection well, infiltration system, and piezometer installation results.	SGW-59455, *300-FF-5 Operable Unit Stage A Uranium Sequestration System Installation Report*	March 2016
Stage A Delivery Performance Report	Summarizes Stage A infiltration and injection results including refinements for Stage B.	SGW-59614, *300-FF-5 Operable Unit Enhanced Attenuation Stage A Delivery Performance Report*	December 2016
Stage B Uranium Sequestration System Installation Report	Summarizes Stage B injection well, electrical resistivity, and downhole monitoring system installation results.	SGW-60778, *300-FF-5 Operable Unit Stage B Uranium Sequestration System Installation Report*	January 2019
Uranium Sequestration Completion Report	Documents completion of uranium sequestration remedy and results.	SGW-63113, *300-FF-5 Operable Unit Enhanced Attenuation Uranium Sequestration Completion Report* (this document)	September 2020

Source: Table 3-1 in DOE/RL-2014-13-ADD2, *Remedial Design Report/Remedial Action Work Plan Addendum for the 300 Area Groundwater*.

Note: Complete references are provided in Chapter 7.

*Column from Table 3-1 in DOE/RL-2014-13-ADD2.

CSM = conceptual site model

MNA = monitored natural attenuation

RAWP = remedial action work plan

RDR = remedial design report

ROD = record of decision

SAP = sampling and analysis plan

Portions of two former liquid waste disposal sites with higher uranium contamination are located in the EA area (Figure 1-2). The primary waste stream disposed to these two waste sites was process waste from 300 Area uranium fuel fabrication facilities as described below.

- The 300 Area North Process Pond (316-2 waste site), part of which was located within the eastern Stage B area, was originally a single, unlined infiltration basin that was later subdivided into six small settling ponds and one large infiltration basin over an area of approximately 40,000 m^2 (10 ac). The seven sections were separated by 3.7 m (12 ft) wide interior dikes and were surrounded by an exterior dike 4.6 m (15 ft) wide and 3 m (10 ft) high. Some of the subdividing dikes were removed to cover the bottom of the site after deactivation of the pond in 1975. The inlet for the pond was in the southwest corner (Section 1.2.1 of BHI-01298, *300-FF-1 Operable Unit North Process Pond Scraping Disposal Area Verification Package*). From 1948 to 1975, this waste site was used to dispose of cooling water and low-level liquid process waste from the 300 Area fuel fabrication facilities and the early laboratories. Beginning in 1963, the pond received laboratory waste that was below discharge limits (Section 1.2.2 of BHI-01298). Lack of infiltration was a problem for the pond. Between 1948 and 1969, the basins were periodically dredged to improve infiltration when sludge in the bottom of the pond slowed the percolation rate. The sludge contained large amounts of uranium and copper and was deposited on the pond dikes and in a disposal area at the south end of the pond (618-12 waste site) or a landfill at the north end (300-50 waste site) (Section 1.2.2 of BHI-01298). The 316-2 waste site was remediated from May 1998 to June 1999 by excavating contaminated soil (Section 2.5 of BHI-01298). In the southwest corner of the site, excavation to remove contaminated soil approached 6.1 to 6.7 m (20 to 22 ft) below ground surface (bgs) (Section 2.5.2 of BHI-01298). Backfilling and regrading operations were initiated in November 2003 and completed in February 2004. Clean fill material was imported from a preapproved borrow site to supplement the excavated soil that had been stockpiled during remedial actions and cleared for back fill use (Section 4.13.1 of DOE/RL-2004-74, *300-FF-1 Operable Unit Remedial Action Report*).

- The 300 Area Process Trenches (316-5 waste site), part of which was located in the northwestern section of the Stage A area and western Stage B area, consisted of two parallel, unlined trenches, each 468 m (1,535 ft) long, 3 m (10 ft) wide, 3.7 m (12 ft) deep, and spaced 15 m (50 ft) apart (Section 1.2.1 of BHI-01164, *300 Area Process Trenches Verification Package*). From 1975 to 1994, the trenches received liquid process waste from the 300 Area uranium fuel fabrication facilities and waste from 300 Area laboratories that was below discharge limits (Section 1.2.2 of BHI-01164). The effluent was discharged at the south ends of the trenches, which operated alternately (Section 1.2.1 of BHI-01164). In 1991, the site was partially remediated through an expedited response action, which uniformly excavated 0.3 m (1 ft) and 1.3 m (4 ft) of contaminated soil from the sides and bottom of each trench, respectively. The contaminated soil was stockpiled at the north ends of the trenches (Section 1.2.3 of BHI-01164). The site was remediated from July 1997 through February 1998 by excavating contaminated soil in the stockpiles. The deepest excavation was 4.3 m (14 ft) in the western portion of the stockpiled soil (Section 2.5 of BHI-01164). Backfilling and regrading operations were initiated in November 2003 and completed in February 2004. Clean fill material was imported from a preapproved borrow site to supplement the excavated soil that had been stockpiled during remedial actions and cleared for back fill use (Section 4.13.1 of DOE/RL-2004-74).

Solid waste was disposed in burial grounds and shallow landfills from 1943 through the 1950s. Two former solid waste burial grounds are located southwest of the EA area (Figure 1-2).

- The Solid Waste Burial Ground No. 2 (618-2 waste site) consisted of three east-west trenches ranging from 49 to 55 m (160 to 180 ft) long and 9 to 15 m (30 to 50 ft) wide; each trench was assumed to be 4.6 m (15 ft) deep. The trenches were used from 1951 through 1954 to dispose of contaminated equipment, materials, and laboratory wastes from 300 Area Industrial Complex facilities. The uranium waste was solid metal (uranium oxide) cuttings from fuel fabrication facilities (Section 2.0 of CVP-2006-00010, *Cleanup Verification Package for 618-2 Burial Ground*). Solid Waste Burial Ground No. 2 was remediated from November 2004 through August 2006 by excavating contaminated material to a depth of approximately 6 m (20 ft) and backfilling (Sections 3.1 and 3.5 of CVP-2006-00010). A location in the middle trench was excavated to groundwater (14.5 m [47.6 ft] bgs) (Section 3.3.1 of CVP-2006-00010).

- The Dry Waste Burial Ground No. 3 (618-3 waste site) consisted of one north-south trench that was 105.2 m (345 ft) long, 30.5 m (100 ft) wide, and 4.6 m (15 ft) deep. The waste site was used in 1954 and 1955 to dispose of uranium-contaminated construction debris from the 311 Building and debris from remodeling the 313 Metal Fabrication Building and 303-J and 303-K Buildings in the 300 Area Industrial Complex (Section 2.0 in CVP-2006-00005, *Cleanup Verification Package for 618-3 Burial Ground*). Dry Waste Burial Ground No. 3 was remediated from September through October 2004 by excavating contaminated material (Section 3.1 in CVP-2006-00005) to a depth of approximately 5 m (16 ft) (Figure 3 in CVP-2006-00005).

The other three waste sites that historically contributed uranium contamination to groundwater are farther south in the 300 Area Industrial Complex (Figure 1-1).

1.2.2 Physical Setting

The following sections provide a summary of the site geology and hydrogeology for the 300 Area Industrial Complex and EA area. Detailed information on the geology and hydrogeology of the 300 Area is presented in Chapters 3 and 4 of the 300 Area remedial investigation (RI)/feasibility study (FS) report (DOE/RL-2010-99, *Remedial Investigation/Feasibility Study for the 300-FF-1, 300-FF-2, and 300-FF-5 Operable Units*). Detailed information on the geology and hydrogeology of the EA area is presented in ECF-300FF5-16-0087, *Determination of Vadose Zone Uranium Concentration Distribution Extents and Development of a Three-Dimensional Geologic Framework Model for the 300-FF-5 Operable Unit, Hanford Washington*, and ECF-HANFORD-13-0029, *Development of the Hanford South Geologic Framework Model, Hanford Site, Washington*.

1.2.2.1 Geology

The ground surface in the 300 Area Industrial Complex is relatively flat, except for the steep embankment that slopes to the Columbia River. The surface elevation for the 300 Area Industrial Complex is approximately 115 m (377 ft) (Executive Summary in DOE/RL-2010-99).

The stratigraphic units that underlie the 300 Area Industrial Complex, from youngest to oldest, are the eolian (windblown) surficial deposits, Hanford formation (Hf), and Ringold Formation. These sediments overlie the Columbia River Basalt Group bedrock (Section 3.4.2 of DOE/RL-2010-99) (Figure 1-3):

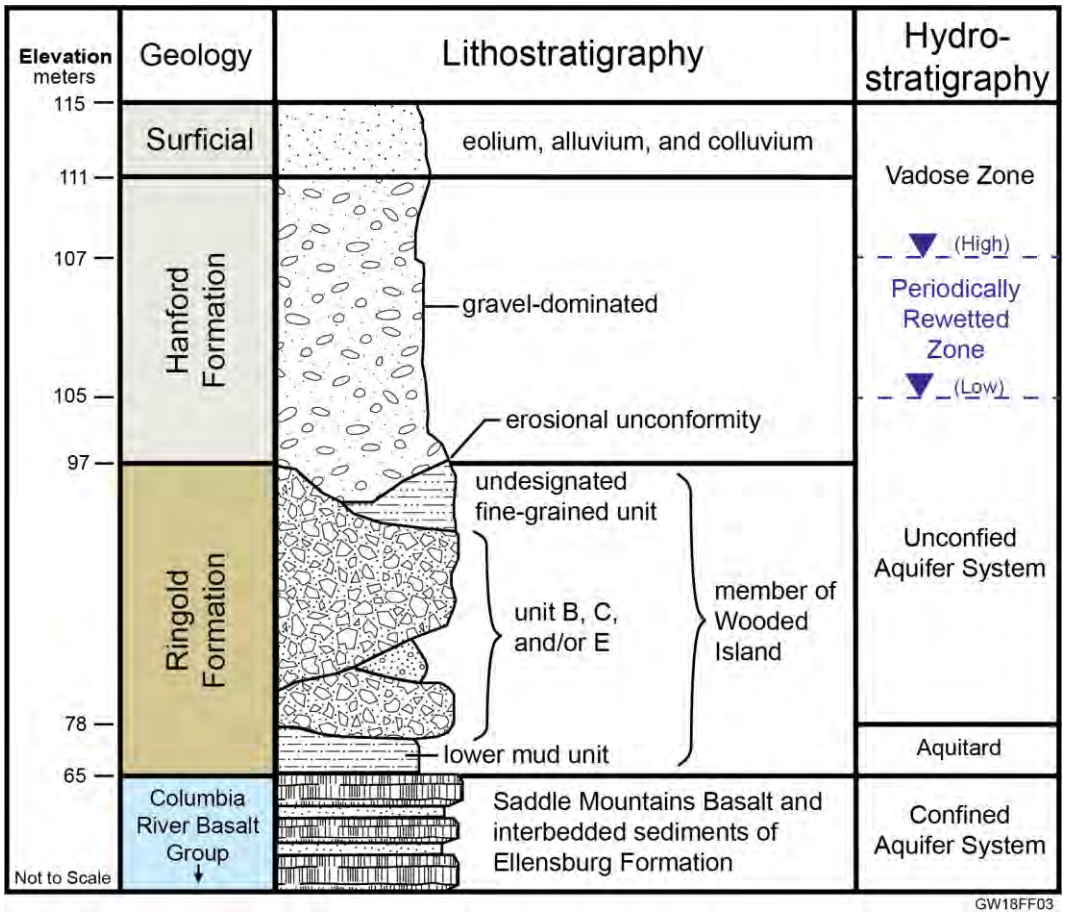
- Eolian deposits (Holocene age)/Backfill: The most recently deposited sediment contains eolian sand and/or gravel-dominated backfill deposited within waste sites that were excavated during remediation. These deposits overlie most of the 300 Area Industrial Complex, with a typical thickness of approximately 1 to 6 m (3 to 20 ft) (Section 3.4.2.3 of DOE/RL-2010-99).

- Hf (Pleistocene age): In the 300 Area Industrial Complex, the Hf cataclysmic flood deposits are primarily composed of clast-supported, muddy sandy gravel with a typical range in thickness from 12 to 24 m (40 to 80 ft). The Hf is thickest over paleochannels carved into the underlying Ringold Formation by the Pleistocene cataclysmic floods. In contrast to the Ringold Formation, the Hf is generally unconsolidated due to its much younger age and insufficient amount of time for weathering or secondary alteration and cementation to take place within the sediments. The depth of burial for the Hf is shallower, so relatively little compaction has occurred. As a result, the Hf permeability is generally several orders of magnitude greater than that of the Ringold Formation (Section 3.4.2.2 of DOE/RL-2010-99).
- Ringold Formation (late Miocene to Pliocene age): The Ringold Formation is an unconsolidated to semiconsolidated sedimentary sequence deposited on the basalt by the ancestral Columbia River. The gravel-dominated Ringold Formation upper coarse unit (Ringold Formation member of Wooded Island – unit E [Rwie]) is up to 24 m (80 ft) thick and is composed of pebble-cobble gravel compacted within a matrix of fine- to medium-grained sand with silt. A relatively fine-grained interval of silt and fine sand occurs at or near the top of the Rwie in parts of the 300 Area Industrial Complex. The Rwie overlies the Ringold Formation member of Wooded Island – lower mud unit (Rlm), a silt and clay-dominated layer, which ranges up to 24 m (80 ft) thick. These Rlm fine-grained, low-permeability sediments are an aquitard that significantly impedes the downward flow of groundwater and forms the base of the unconfined aquifer system overlying the basalt (Section 3.4.2.2 of DOE/RL-2010-99).

Injection and monitoring wells were installed to support implementation of the EA remedy for uranium. During drilling of the wells, only the gravel-dominated sediment of the backfill, Hf, and Rwie were encountered (Chapter 3 of SGW-59465, *Borehole Summary Report for the Installation of Nine Injection Wells, Twenty-One Monitoring Wells, and Three Boreholes in the 300-FF-5 Operable Unit*, and Chapter 3 of SGW-61092, *Borehole Summary Report for the Installation of Forty Eight Injection Wells and Nineteen Monitoring Wells at the 300-FF-5 Operable Unit, FY 2017*). The Rwie was not fully penetrated during drilling of EA remedy wells (e.g., wells 399-1-93, 399-1-136, and 399-1-162; shown in Figure 1-4).

Backfill placed into the remediated 316-2 North Process Pond and 316-5 300 Area Process Trenches is composed of Hf sandy cobble gravel and clast-supported gravel. Large boulders are often present throughout the backfill material. Backfill in the 316-5 300 Area Process Trenches is present from the ground surface to 4.9 to 5.5 m (16 to 18 ft) bgs. Backfill in the 316-2 North Process Pond extends from ground surface to no greater than 7.5 m (25 ft) bgs. Disturbed surface sediments surrounding the trenches and the pond extend from ground surface to approximately 0.6 m (2 ft) bgs (Section 1.2.2.1 of SGW-59614).

The Hf underlies the EA area between 0.6 and 15.4 m (2 and 50 ft) bgs (Figure 1-5 in this report and Figures 1-6 and 1-7 in SGW-59614). Rip-up clasts composed of silt and gravelly silt, present in abundance throughout the Hf, are encountered sporadically throughout the EA area. Rip-up clasts are typically composed of nonindurated to very well indurated, massive to finely laminated silt, clayey silt, and gravelly silt (Figure 1-5). The rip-up clasts encountered throughout the EA area range in size from a few centimeters (inches) up to 1.2 m (4 ft). The inferred contour map of the contact between the Hf and Ringold Formation is shown in Figure 1-6.



Source: Figure 7-3 in DOE/RL-2018-66, *Hanford Site Groundwater Monitoring Report for 2018*.

Figure 1-3. 300 Area Geology

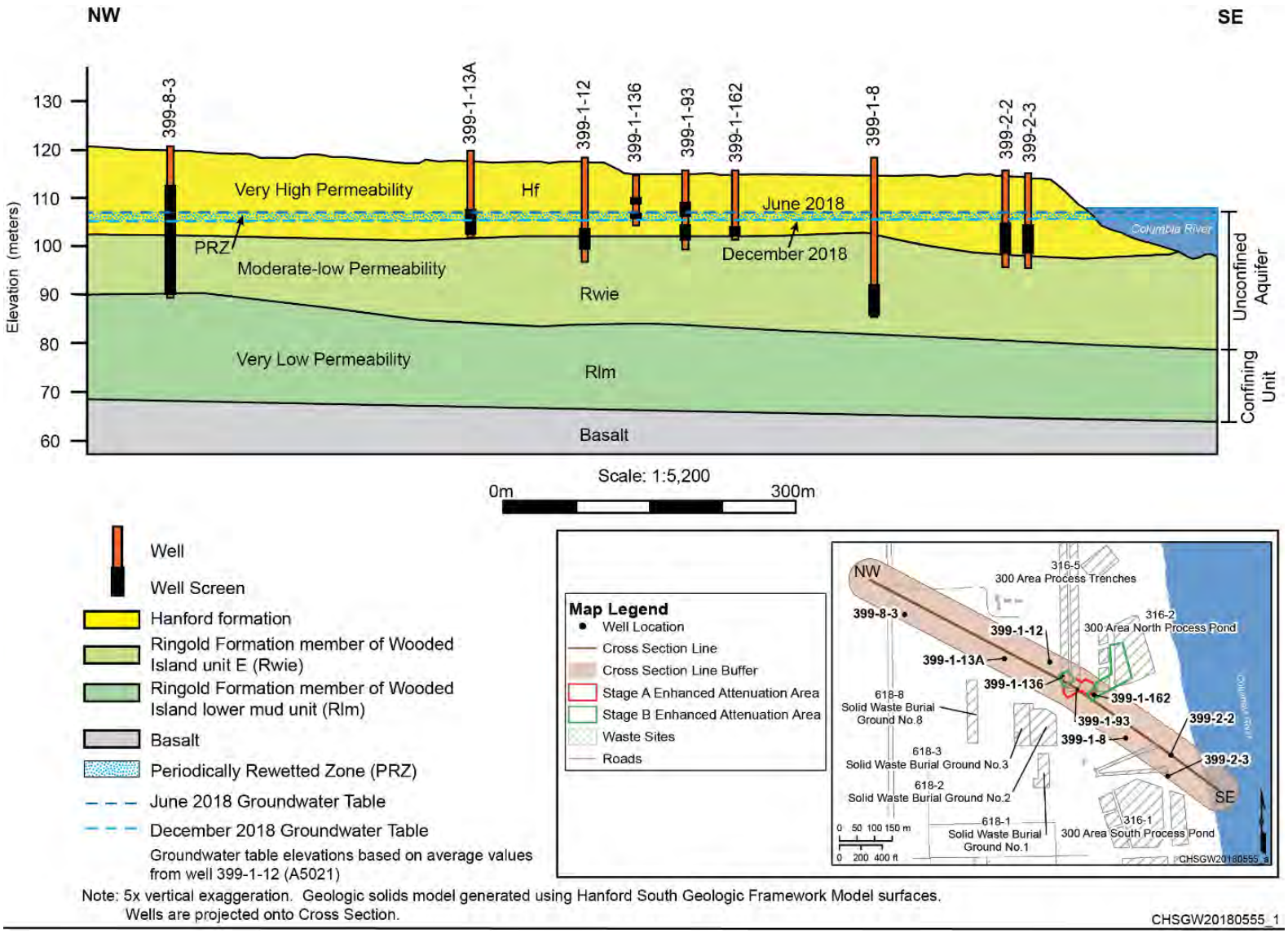


Figure 1-4. Cross Section of the General Geologic Features of the 300 Area Industrial Complex and Stage A and B Enhanced Attenuation Areas

The gravel-dominated Rwie is present across the EA area between 11.4 and 15.5 m (37 and 50.5 ft) bgs (Figure 1-5 in this report and Figures 1-6 and 1-7 in SGW-59614). The silty sand to silt, fine-grained Ringold Formation subunit that locally overlies the gravel-dominated Rwie in the vicinity of the 316-1 South Process Pond was not encountered during drilling in the EA area. However, stratigraphically equivalent, discontinuous sand lenses were encountered in the top meter (top few feet) of the Rwie in some of the deep injection and monitoring wells.

1.2.2.2 Hydrogeology

The vadose zone in the 300 Area Industrial Complex consists primarily of backfill materials and unconsolidated gravel and sand of the Hf. The average thickness of the vadose zone is 10 m (33 ft). However, the vadose zone thickness varies with the seasonal stages of the Columbia River and distance inland from the river. Rising groundwater elevations resulting from higher Columbia River stages seasonally saturate lower portions of the vadose zone, while lower river stages result in falling groundwater elevations that de-water these same lower portions of the vadose zone. These fluctuating groundwater elevations define the PRZ (Figure 1-4). Generally, wells adjacent to the river within the 300 Area Industrial Complex show larger variations in water level elevation in response to river stage changes than wells located at increasing distance from the shoreline (Section 2.4.3 of PNNL-22048, *Updated Conceptual Model for the 300 Area Uranium Groundwater Plume*).

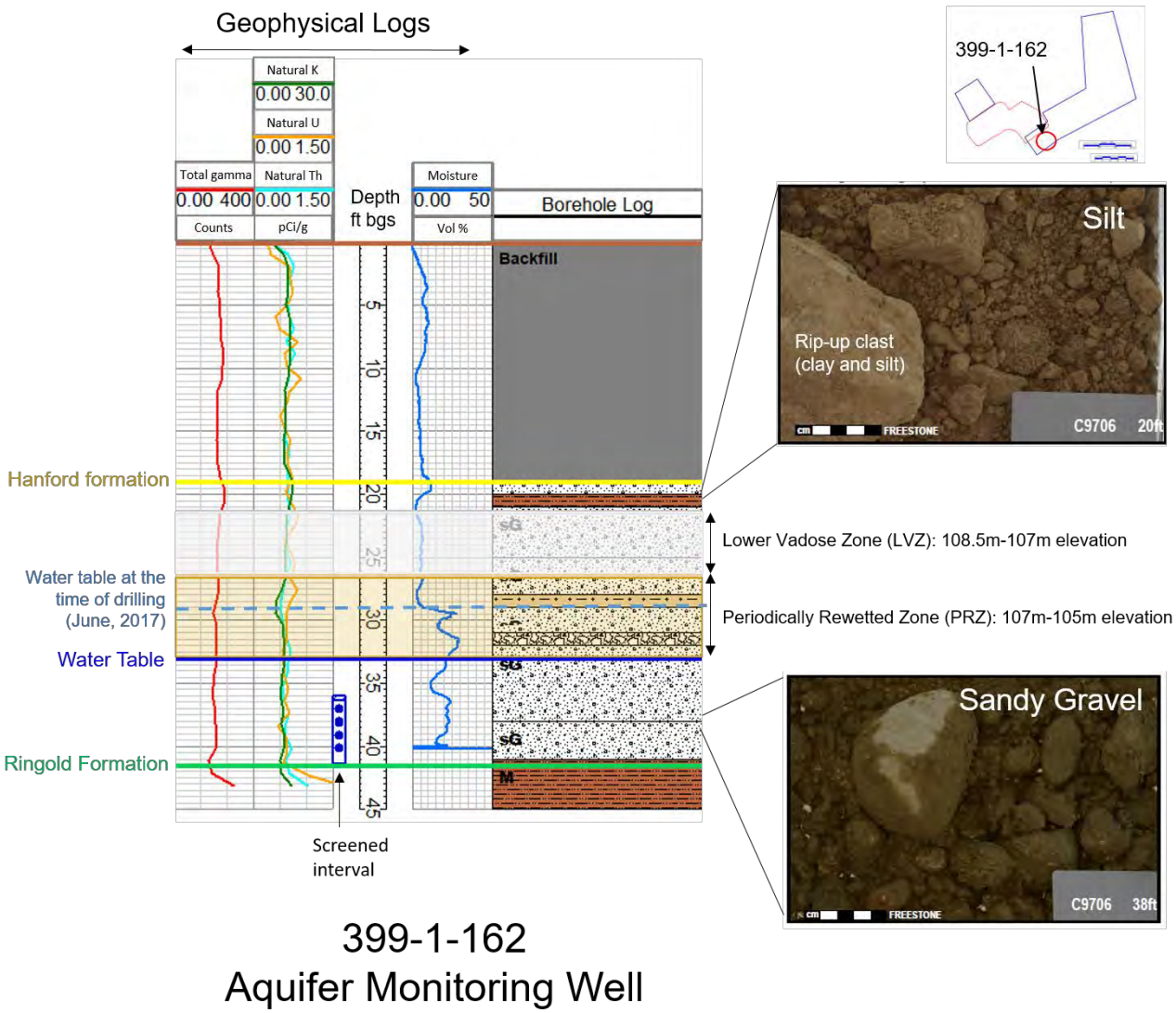
In the EA, the PRZ is defined as the portion of the vadose zone from 105 to 107 m (344.5 to 351 ft) elevation that is contacted by typical seasonal changes in the groundwater elevation (Figure 1-7). The LVZ, from 107 to 108.5 m (351 to 356.0 ft) elevation, represents the portion of the vadose zone contacted by increases in groundwater elevation in atypical high-water years. The low-water elevation of the water table is 105 m (344.5 ft). These elevations used to define the LVZ, PRZ, and top of the low-water-table aquifer are based on the hydrograph for well 399-1-17A.

The unconfined aquifer occurs in the highly permeable, gravel-dominated Hf and in the underlying, less permeable gravel-dominated Rwie.

Paleochannels carved into Rwie sediments are filled with Hf sand and gravel and may act as preferential pathways for groundwater flow and for intrusion of river water during periods of high river stage. The Rlm is a confining layer (i.e., aquitard) that forms the base of the unconfined aquifer and is characterized by very low-permeability fine-grained sediment. This hydrologic unit prevents further downward movement of groundwater contamination to the deeper aquifers. The thickness of the unconfined aquifer along the Columbia River shoreline is about 25 m (80 ft).

Groundwater in the unconfined aquifer discharges to the Columbia River via upwelling through the riverbed and riverbank seeps. The flux from the unconfined aquifer is very low compared to the flow of the river. Because the river stage regularly fluctuates up and down, flow beneath the shoreline oscillates back and forth, with river water intruding into the unconfined aquifer and mixing with groundwater at times. When the river stage drops quickly to a low elevation, riverbank seeps appear.

Groundwater flow velocities beneath the 300 Area in the Hf portion of the aquifer can be relatively rapid, with a velocity of 15.2 m/d (50 ft/d) estimated during a tracer test in December 2006 (PNNL-17708, *Three-Dimensional Groundwater Models of the 300 Area at the Hanford Site, Washington State*). However, the hydraulic gradients change direction in response to river stage, which fluctuates on seasonal and multiyear cycles. Consequently, groundwater flow is not always directed toward the river.



399-1-162
Aquifer Monitoring Well

Source: Geophysical logs, borehole log, and sediment photographs are from SGW-61092, *Borehole Summary Report for the Installation of Forty Eight Injection Wells and Nineteen Monitoring Wells at the 300-FF-5 Operable Unit, FY 2017*.

Figure 1-5. Composite Log for the 399-1-162 Aquifer Monitoring Well

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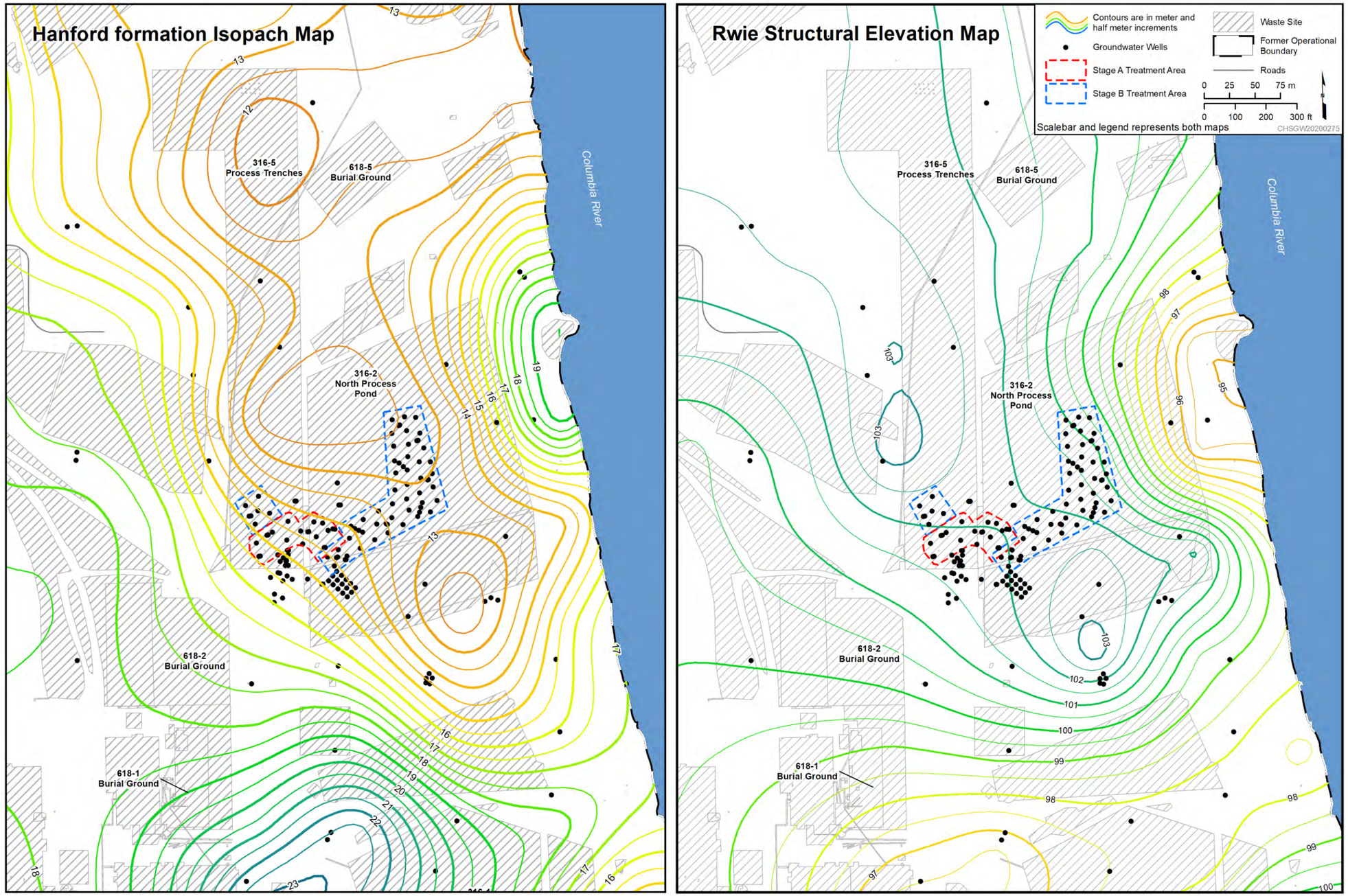

Figure 1-6. Hanford Formation Isopach Map and Ringold Formation Structural Elevation Map in the Enhanced Attenuation Area

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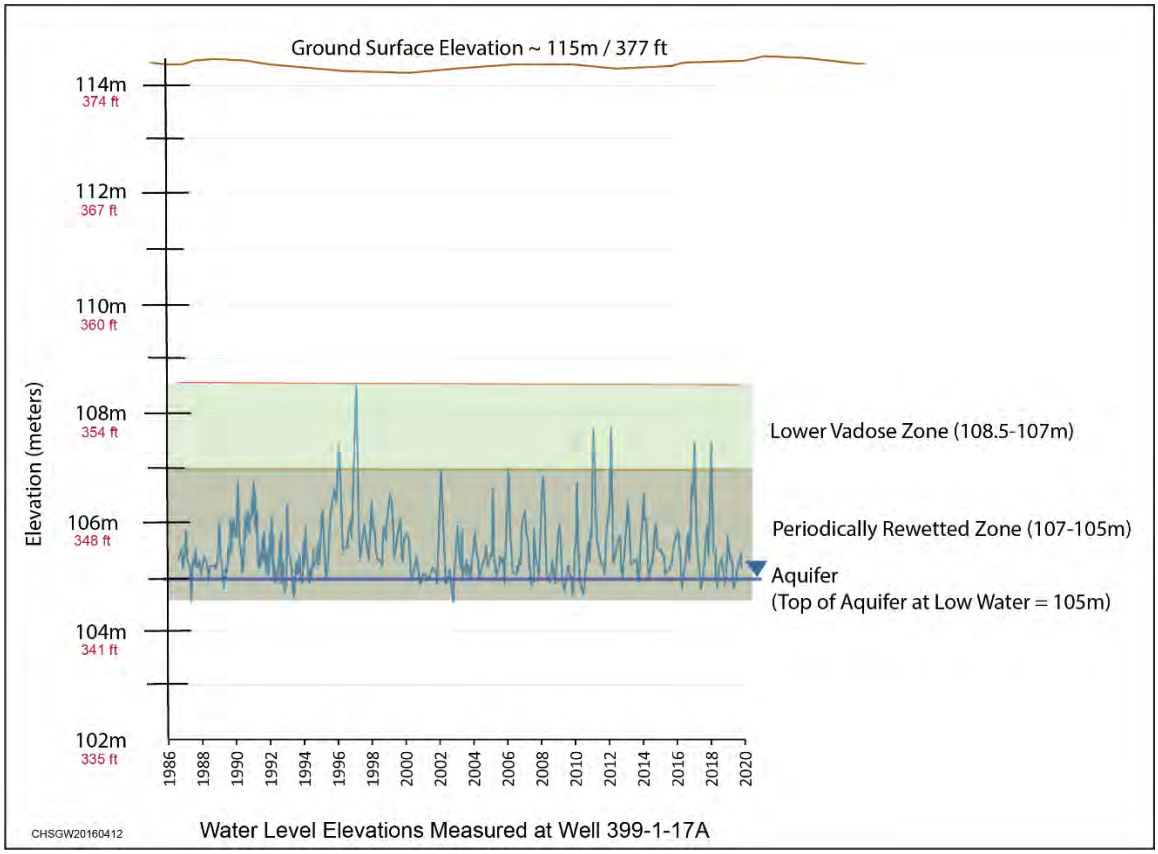


Source: Modified from Figure 1-8 in SGW-59614, *300-FF-5 Operable Unit Enhanced Attenuation Stage A Delivery Performance Report*.

Figure 1-7. Elevations of the Periodically Rewetted Zone and Lower Vadose Zone in the Enhanced Attenuation Area

In general, regional groundwater flow converges on the 300 Area from the northwest, west, and southwest, inducing a southeast or east flow direction in the 300 Area (Section 3.6.1.3 of DOE/RL-2010-99). During periods of extended high river stage (typically May through June), water flows from the river into the aquifer.

The rise and fall of the river stage creates a dynamic zone of interaction between groundwater and river water affecting groundwater flow patterns, contaminant transport rates (e.g., uranium in groundwater), groundwater geochemistry, contaminant concentrations, and contaminant attenuation rates.

1.2.2.3 Movement of Uranium Contamination

Residual uranium contamination remaining in the vadose zone resulted from active liquid waste discharge of uranium-bearing solutions during 300 Area operations. Uranium soil concentrations vary within the soil column, with higher concentrations associated typically with finer grained sediments. Uranium is mobilized during periodic rewetting of the lower portion of the vadose zone due to Columbia River stage fluctuations. The groundwater within the PRZ leaches residual uranium and drains under gravity, providing a pathway for dissolved uranium to reach the aquifer. Due to periodic river stage fluctuations and depending upon the inland distance from the river, the groundwater flow direction can change over a wide area and distribute the dissolved uranium within the aquifer. Uranium sorption is generally lower in groundwater as compared to river water due to the relatively higher concentrations of bicarbonate which strongly complex uranium, keeping it in the aqueous phase. As a result of mixing of river water and

groundwater, the alkalinity also varies spatially and temporally within the aquifer and can lead to variable speciation and sorption of uranium aqueous complexes. The amount of uranium leaching from the PRZ is affected by both the degree of saturation of the sediments and the alkalinity of the solution. The combination of uranium desorption and dilution in the river water/groundwater mixing zone results in a varying distribution of uranium concentrations in the aquifer.

1.2.3 Enhanced Attenuation Remedy Timeline

The 300 Area ROD (EPA et al., 2013) was issued in November 2013. Figure 1-8 shows the chronology of the significant activities, investigations, and decisions completed after issuance of the ROD that support implementation of uranium sequestration at the Stage A and Stage B EA areas. In Figure 1-8, key documents and decisions are shown above the timeline; investigations and actions are shown below the timeline. Appendix A of this document contains a bibliography that provides information on the documents shown on the timeline. Environmental investigations and remedial actions conducted in the 300 Area before the 300 Area ROD was issued are summarized in the 300 Area RI/FS report (Section 1.3 of DOE/RL-2010-99).

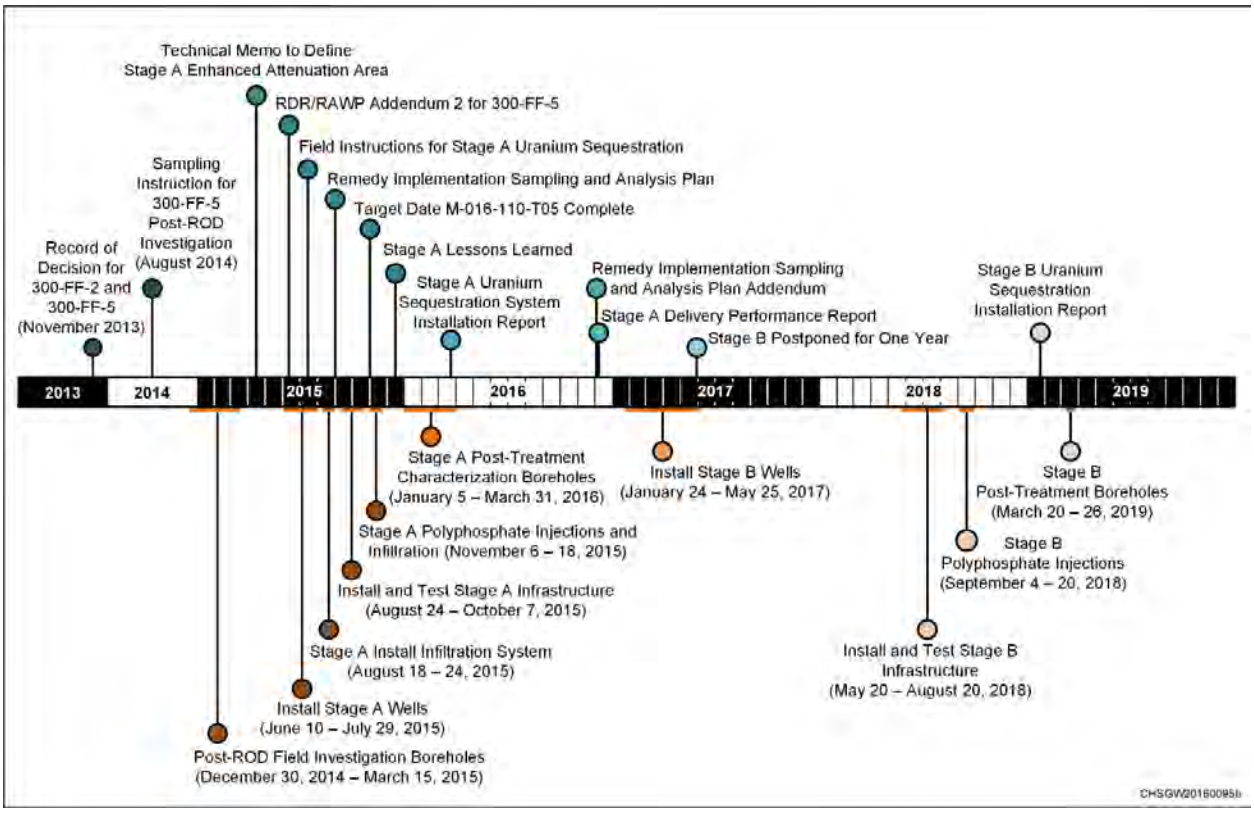


Figure 1-8. Timeline of Documents and Activities Supporting Implementation of the Enhanced Attenuation Remedy

1.3 Uranium Sequestration Technology

The uranium sequestration technology was developed during treatability tests, and the technology was adapted for use as the EA remedy.

1.3.1 Treatability Tests

A treatability test was conducted at the 300 Area Industrial Complex to evaluate the use of polyphosphate as a remedial technology to sequester uranium (PNNL-18529, *300 Area Uranium Stabilization Through Polyphosphate Injection: Final Report*). The treatability test included both laboratory and field studies. The laboratory studies evaluated applying polyphosphate to vadose zone and PRZ sediments to immobilize uranium and prevent it from leaching to the aquifer. The field study evaluated direct sequestration of dissolved uranium in groundwater by injecting polyphosphate into the aquifer.

Laboratory tests demonstrated that when a soluble form of polyphosphate is injected into uranium-bearing saturated porous media, immobilization of uranium can occur due to surface complexation, incorporation, coating, and formation of relatively insoluble uranyl-phosphate minerals, such as autunite ($Ca(UO_2)_2(PO_4)_2 \cdot nH_2O$) (PNNL-18529; Wellman et al., 2008, "Sequestration and retention of uranium(VI) in the presence of hydroxylapatite under dynamic geochemical conditions").

Results of the field study demonstrated that, upon direct injection, the polyphosphate amendment could be effectively distributed over a relatively large lateral extent. Monitoring wells located at a radial distance of 23 m (75 ft) showed phosphate concentrations as high as 40% to 60% of the injection concentrations, which indicated that uranium sequestration could be effectively implemented on a full field scale.

Laboratory-scale column studies (PNNL-21733, *Use of Polyphosphate to Decrease Uranium Leaching in Hanford 300 Area Smear Zone Sediment*) also were conducted to evaluate short- and long-term effects of polyphosphate treatment on uranium leaching from 300 Area PRZ sediments. Under idealized laboratory conditions, a wide range of polyphosphate treatments resulted in significant (average 54%) decreases in leached uranium mass in columns run for up to 1 year. Polyphosphate treatment decreased uranium leaching through the formation of calcium-phosphate precipitates coating uranium surface phases, uranium adsorption to precipitates, or slow formation of uranium-phosphate precipitates. The simulated phosphate delivery strategy that resulted in the greatest decrease in uranium leaching involved maximizing stop-flow conditions to increase phosphate-sediment reaction time before groundwater advection combined with the use of high-concentration (approximately 50 mM) polyphosphate solutions.

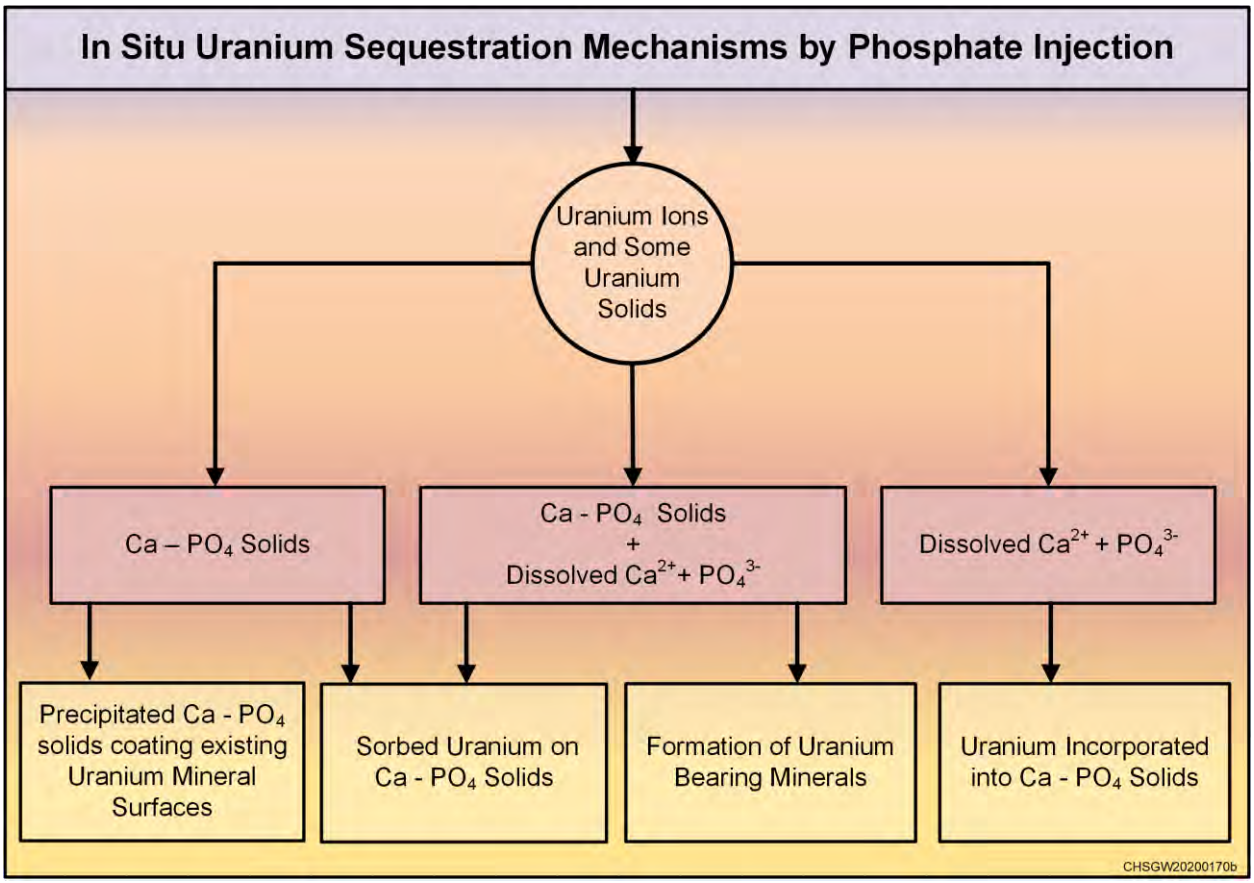
1.3.2 Enhanced Attenuation Remedy

Based on results of the treatability tests, uranium sequestration using polyphosphate solutions was adapted for use as a remedy for uranium in the 300 Area. Treatment during Stages A and B used the same polyphosphate solution concentrations based on a mixture of sodium and potassium orthophosphate (NaH_2PO_4 and KH_2PO_4) and sodium pyrophosphate ($Na_4P_2O_7$). The blend of orthophosphate and pyrophosphate solutions was used to take advantage of the reaction kinetics of each compound. Orthophosphate combines with naturally occurring calcium in the vadose zone pore water for rapid formation of the calcium-phosphate solid. Pyrophosphate hydrolyzes, or breaks down, slowly to orthophosphate over time, which allows for enhanced transport of phosphate to the LVZ and PRZ followed by formation of the calcium-phosphate solid.

The residual uranium contamination is typically present as secondary precipitates and as adsorbed complexes on sediment surfaces. A conceptual model of uranium sequestration mechanisms expected in the field was developed based on previous work (Mehta et al., 2016, "Effect of reaction pathway on the extent and mechanism of uranium(VI) immobilization with calcium and phosphate," and Mehta, 2017, "Geochemical evaluation of uranium sequestration from field-scale infiltration and injection of polyphosphate solutions in contaminated Hanford sediments"). The multiple mechanisms for uranium sequestration that occur during phosphate addition can be broadly grouped into four types: sorption of aqueous uranium to calcium-phosphate solids; formation of uranium-bearing minerals; precipitation and

coating of calcium-phosphate solids on uranium mineral surfaces; and uranium incorporation in calcium-phosphate solids (Figure 1-9).

The primary sequestration mechanism is deemed to be the formation of an amorphous (unstructured) monocalcium phosphate that precipitates and coats sediments containing uranium and thereby reduces the dissolution of uranium-bearing mineral phases. Over months to years, this rind is expected to crystallize to form a stable calcium-phosphate mineral, hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), which has very low solubility (Figure 1-10). During crystallization, some incorporation of uranium into the hydroxyapatite structure is also expected.[1]



Source: Modified from Mehta et al., 2016, "Effect of reaction pathway on the extent and mechanism of uranium(VI) immobilization with calcium and phosphate."

Figure 1-9. Uranium Sequestration Mechanisms via Phosphate Addition as an In Situ Remediation Approach

[1] In literature, the terms hydroxyapatite and hydroxylapatite are both used to refer to the calcium-phosphate mineral $Ca_{10}(PO_4)_6(OH)_2$. These terms may be used interchangeably in this document.

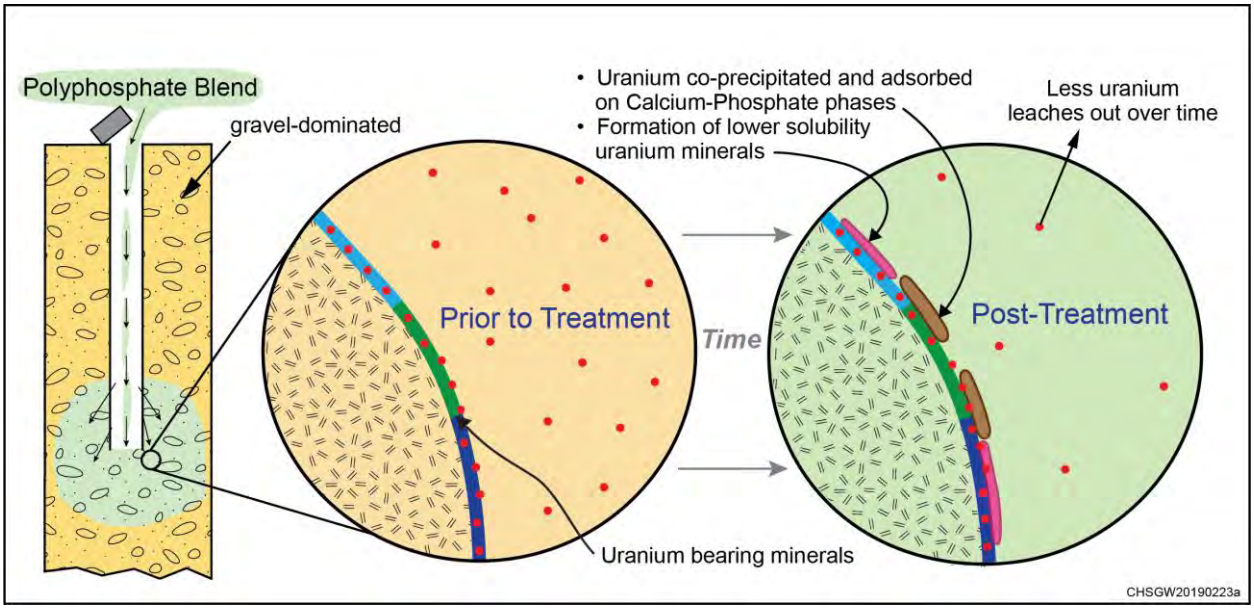


Figure 1-10. Uranium Mobility Change with Polyphosphate Treatment

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2 Uranium Sequestration Implementation

This chapter provides an overview of the approach used to implement uranium sequestration in the Stage B EA area. Sections 2.1 and 2.2 summarize the objectives, design, and implementation of the Stage B polyphosphate injections. Section 2.3 briefly discusses changes that were made from the original Stage B design during implementation. An overview of the approach used to implement uranium sequestration in the Stage A EA area is provided in Chapter 2 of SGW-59614.

2.1 Stage B Objectives

The objectives for the Stage B polyphosphate injections to sequester uranium include the following elements summarized from Sections 1.1 and 1.2 of DOE/RL-2014-42-ADD1:

- Deliver three pore volumes of polyphosphate solution uniformly to the LVZ and PRZ
- Achieve targeted treatment solution concentrations; achieve injection flow rate and volume
- Evaluate the distribution of phosphate over time in the LVZ, PRZ, and top of the aquifer
- Determine the short-term impact (<1 year) to local uranium groundwater concentrations and chemistry
- Determine the change, if any, observed in the leachability of uranium after treatment

The effectiveness of Stage B polyphosphate injections in meeting these objectives is evaluated in this report.

The objectives for the Stage A polyphosphate applications were similar to those for Stage B (Section 2.1 of SGW-59614). One additional objective of Stage A treatment operations, monitoring, and evaluation was to apply experience and lessons learned to Stage B. The effectiveness of Stage A polyphosphate injections in meeting the Stage A objectives is evaluated in SGW-59614.

2.2 Stage B Design

As specified in the 300 Area ROD (EPA et al., 2013), EA using uranium sequestration involves infiltrating and injecting polyphosphate solutions into the vadose zone, PRZ, and top of the aquifer to sequester, or bind, residual mobile uranium by forming insoluble minerals. The target area for application of the polyphosphate solutions is a 1.2 ha (3 ac) area containing a persistent source of mobile uranium that contributes to contamination of the underlying groundwater. Uranium sequestration in the EA area is anticipated to reduce the mobility of the uranium, thereby slowing the rate of uranium leaching into the groundwater.

The EA remedy was implemented in two stages in accordance with the RDR/RAWP (Section 3.1.1 of DOE/RL-2014-13-ADD2). Stage A was implemented on a smaller scale (0.3 ha [0.75 ac]) in November 2015. The Stage A results were used to improve the conceptual design for Stage B implementation on a larger scale (0.9 ha [2.25 ac]) in September 2018. Based on lessons learned in Stage A, the following changes were made to improve delivery of polyphosphate to the target zones of interest for Stage B:

- Eliminating near-surface infiltration lines and injecting directly into the LVZ and PRZ
- Increasing the spatial density of injection wells to provide more uniform spatial coverage of the EA area in the absence of infiltration

- Eliminating injections to the aquifer and injecting into the PRZ instead (Sections 2.1.1.1 and 2.1.1.2 of DOE/RL-2014-42-ADD1)

The Stage A infiltration system was installed 1.8 m (6 ft) bgs. Stage A post-treatment soil samples showed variable vertical distribution of phosphate. A larger proportion of the phosphate that was delivered through surface infiltration precipitated on soils in the upper vadose zone at an elevation higher than 108.5 m [356 ft]). Areas with lower wetting front velocities exhibited higher concentrations of phosphate at shallow depths followed by a sharp decline in concentrations with increased depth. Areas with higher velocity showed more phosphate traveling deeper into the vadose zone. To maximize the delivery of phosphate to the LVZ and PRZ where the contamination is present, a combination of LVZ and PRZ injections were used in Stage B instead of near-surface infiltration.

One of the Stage A design objectives of combining near-surface infiltration with PRZ injections was to provide more uniform horizontal and vertical coverage of the EA area than could be achieved with injection alone. During Stage A, nine injection wells were used. The Stage B area was three times larger, and 27 injection wells would have provided a similar horizontal coverage in the PRZ (Section 3.2.1.2 of DOE/RL-2014-13-ADD2). Because Stage B included only injections, the number of injection wells was increased from 27 to 48 to provide more uniform spatial coverage of the PRZ and LVZ in the Stage B area.

During Stage A, phosphate injected through the aquifer injection wells was quickly diluted when it mixed with groundwater and migrated downgradient. Phosphate injected into the PRZ was able to infiltrate slowly to the top of the aquifer and sustain higher and more persistent phosphate concentrations in the aquifer.

The design of the Stage B uranium sequestration system as it was installed and implemented is described in SGW-60778. The design of the Stage A uranium sequestration system as it was installed and implemented is described in SGW-59455.

2.2.1 Stage B Enhanced Attenuation Area

The final Stage A EA area was based on the results of the post-ROD field investigation conducted from December 30, 2014, to January 15, 2015. An updated conceptual site model and three-dimensional (3-D) model of uranium concentrations in the soil were generated from the field investigation and used to finalize the Stage A area outline (SGW-58830, *300-FF-5 Supplemental Post-ROD Field Investigation Summary*). The Stage B area outline, generally based on the conceptual site model developed for Stage A, was formalized in the SAP addendum (Figure 2 in DOE/RL-2014-42-ADD1).

2.2.2 Stage B Injection Wells

Forty-eight injection wells were drilled between February 1 and May 23, 2017, for the Stage B EA implementation, as specified in DOE/RL-2014-42-ADD1, in accordance with SGW-60287, *Description of Work for the Installation of Forty Eight Injection Wells and Nineteen Monitoring Wells in the 300-FF-5 Groundwater Operable Unit, FY17*. The injection wells were drilled using a sonic drill rig. A summary of the drilling and well construction details is contained in SGW-61092.

The injection well locations were based on modeling results, which predicted that a well injecting into the PRZ and LVZ could have an 8 m radius of influence (ECF-300FF5-16-0137, *Radius of Influence Estimates for Injection Wells in Support of Stage B Enhanced Attenuation Remedy for the Hanford Site 300 Area Vadose Zone*). Each injection well was installed to target full spatial coverage across the Stage B EA area with minimal overlap (Figure 2-1). The Stage B EA area was divided into four injection zones, each of which included 12 injection wells spaced approximately 16 m apart.

All injection wells were constructed using 15 cm (6 in.) diameter Schedule 80 polyvinyl chloride (PVC) flush joint pipe for the sumps and risers and two 50-slot, 1.5 m (5 ft) long screened intervals, with one screen in the LVZ and one screen in the PRZ (Figure 2-2). The screens were separated by a bentonite or grout seal within the annulus to limit hydraulic communication between injection intervals and inflatable packers within the wellbore to allow isolated injections into either the LVZ or the PRZ. The LVZ screens extend from elevations of approximately 109.5 to 108 m (depths of 5.5 to 7 m [18 to 23 ft] bgs). The PRZ screens extend from elevations of approximately 106.5 to 105 m (depths of 8.5 to 10 m [28 to 33 ft] bgs), which are coincident with the seasonal high and low water table, respectively.

Twelve of the 48 injection wells were installed with electrical resistivity tomography (ERT) electrodes that necessitated the use of a nonbentonite grout seal (Figure 2-3). Bentonite grout has a high electrical conductivity that interferes with ERT measurements, and a variance was obtained to use a nonbentonite grout seal instead (Appendix G of SGW-61092). The wells were sealed with a high-strength, low-permeability, and low-conductivity grout mixture that was one part type 1 Portland cement and three parts DS-325 Hess Pozzolan (Pumice) at a 0.5 water-to-cement ratio. The mixture was tested to ensure optimal ERT system measurements could be obtained using this grout (PNNL-28619, *Stage B Uranium Sequestration Amendment Delivery Monitoring Using Time-Lapse Electrical Resistivity Tomography*).

The target drilled depth of the boreholes was approximately 10.8 m (35.0 ft) bgs for the injection wells without ERT electrodes and 13.6 m (44.2 ft) bgs for the injection wells with ERT electrodes.

Final well development of the lower screens of the injection wells was conducted by over-pumping to obtain maximum flow rates. The upper screens of injection wells were not developed because the upper screens are located above the seasonal low water mark and were dry. Table 2-7 of SGW-61092 summarizes the well development data for the injection wells. Appendix D of SGW-61092 contains the well development and testing data.

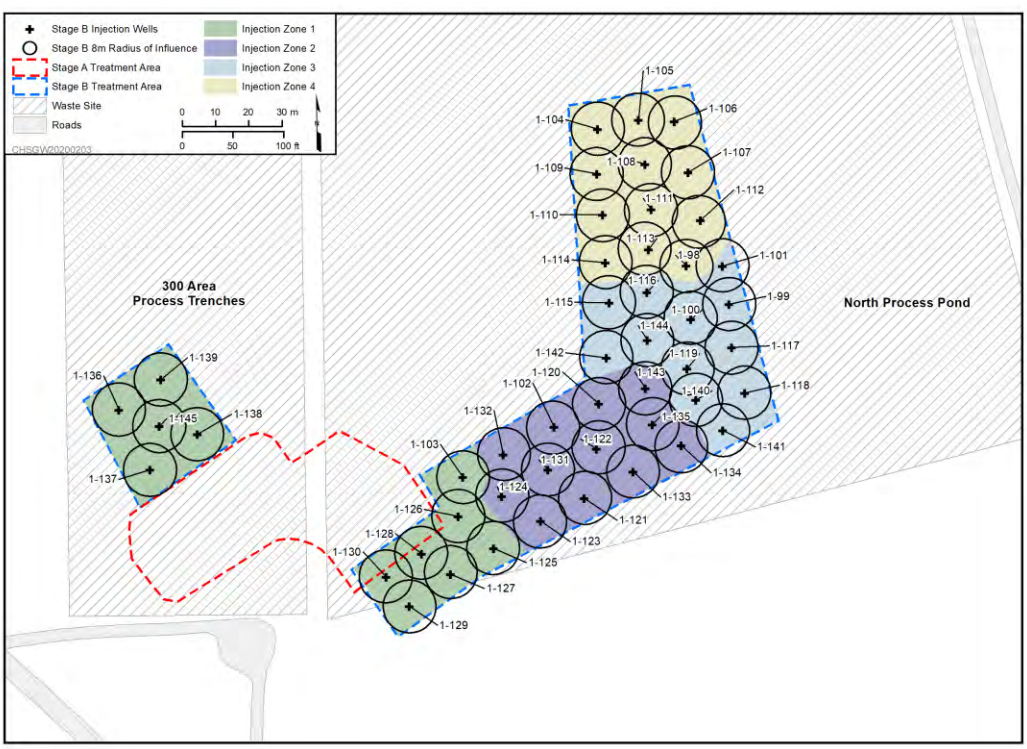

Figure 2-1. Stage B Injection Well Locations in Four Injection Zones

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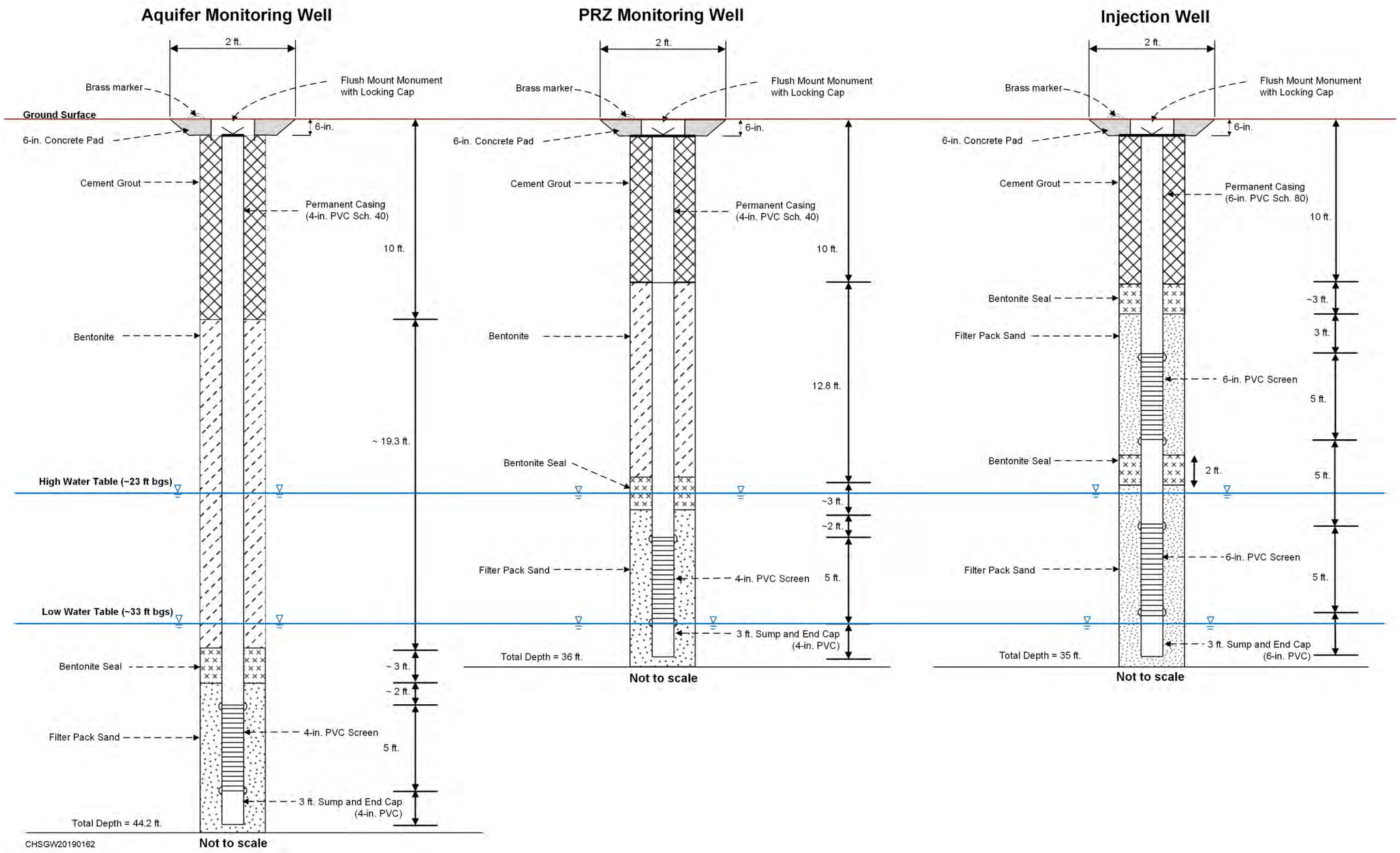

Figure 2-2. Stage B Well Designs Without ERT Electrodes

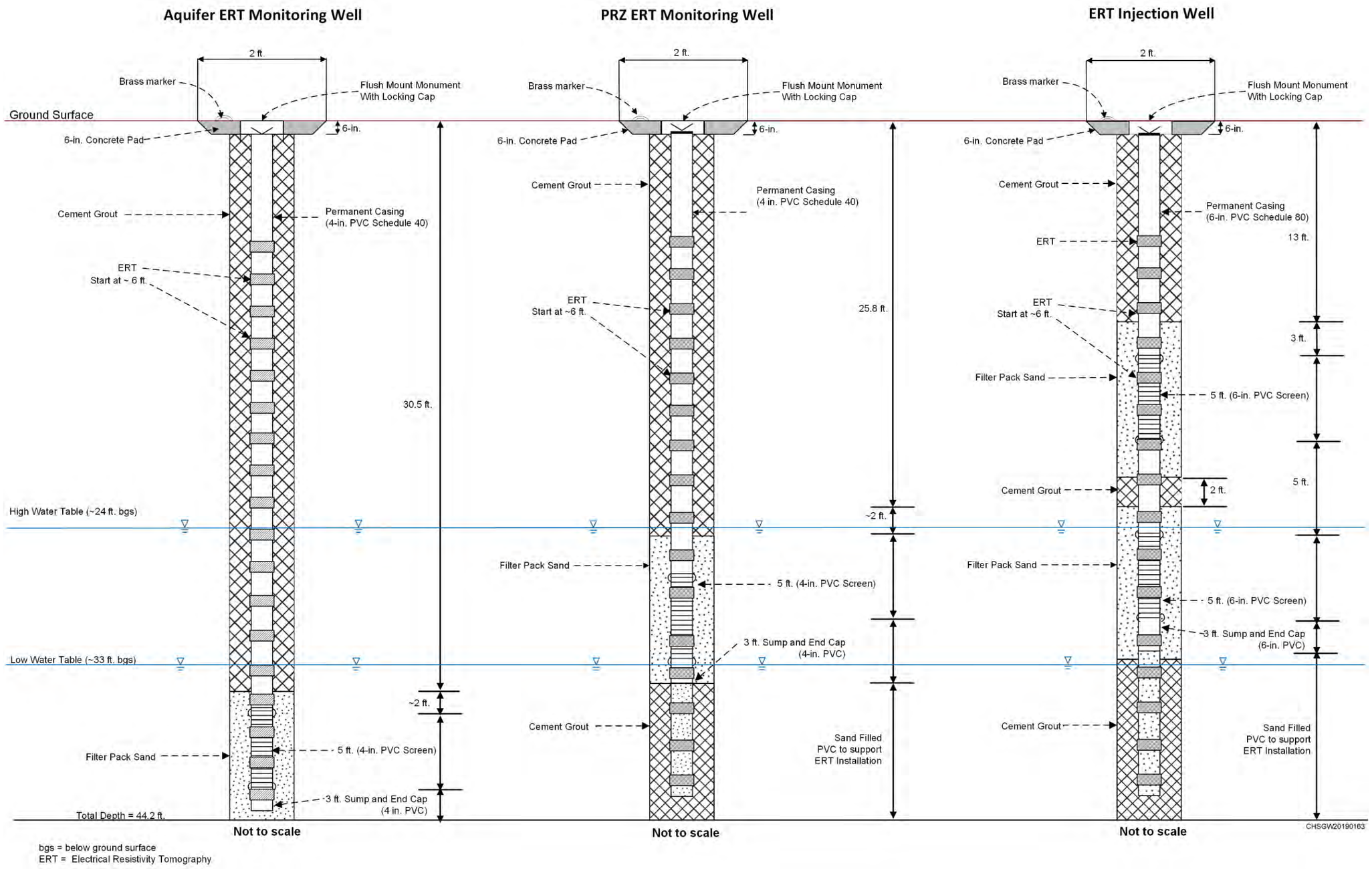

Figure 2-3. Stage B Well Designs with ERT Electrodes

2.2.3 Stage B Monitoring Wells

The Stage B groundwater monitoring system consisted of 24 monitoring wells: 19 new wells and 5 existing wells. The 19 new monitoring wells were drilled between January 24 and May 25, 2017, as specified in DOE/RL-2014-42-ADD1, in accordance with SGW-60287 (Figure 2-4). The monitoring wells were drilled using a sonic drill rig. A summary of the drilling and well construction details is contained in SGW-61092.

Sixteen new monitoring wells and two existing monitoring wells were located within the Stage B EA area near the intersections of predicted radii of influence for injection wells. The 18 wells within the Stage B EA area consisted of 9 collocated well pairs. For each well pair, one well is screened in the PRZ and one well is screened in the aquifer to enable monitoring of both depths (Table 2-1). Three new aquifer monitoring wells and three existing aquifer monitoring wells were located downgradient of the Stage B area (Figure 2-5).

Three of the paired wells have the two monitoring wells 4 m (13 ft) apart. These three pairs were designed to straddle the injection zones so that monitoring could parse out the influence from each phase of injection. The other six pairs have a nominal distance between the two wells. These six pairs are distributed throughout the rest of the Stage B area so that at least one pair was in the middle of an injection zone.

All of the new monitoring wells were constructed using 10 cm (4 in.) diameter, Schedule 40 PVC pipe with 1.5 m (5 ft) long screens and 0.9 m (3 ft) long sumps. The eight new PRZ wells were screened from elevations of approximately 106.3 to 104.8 m (depths of 8.5 to 10 m [28 to 33 ft] bgs). The 11 new aquifer wells were screened from elevations of approximately 104.3 to 102.8 m (depths of 10.4 to 12.0 m [34.3 to 39.3 ft] bgs). The one existing PRZ well was screened from elevations of 106.2 to 104.6 m (depths of 8.7 to 10.2 m [28.3 to 33.3 ft] bgs). The four existing aquifer monitoring wells were screened from elevations of approximately 107.7 to 100.5 m (depths of 8.7 to 16.0 m [28.6 to 52.4 ft] bgs).

Six of the new monitoring wells were installed with ERT electrodes. The nonbentonite grout, described in Section 2.2.2, was used to seal the monitoring wells with ERT electrodes.

Table 2-13 of SGW-61092 summarizes the well development data for the new monitoring wells. Appendix D of SGW-61092 contains the well development and testing data.

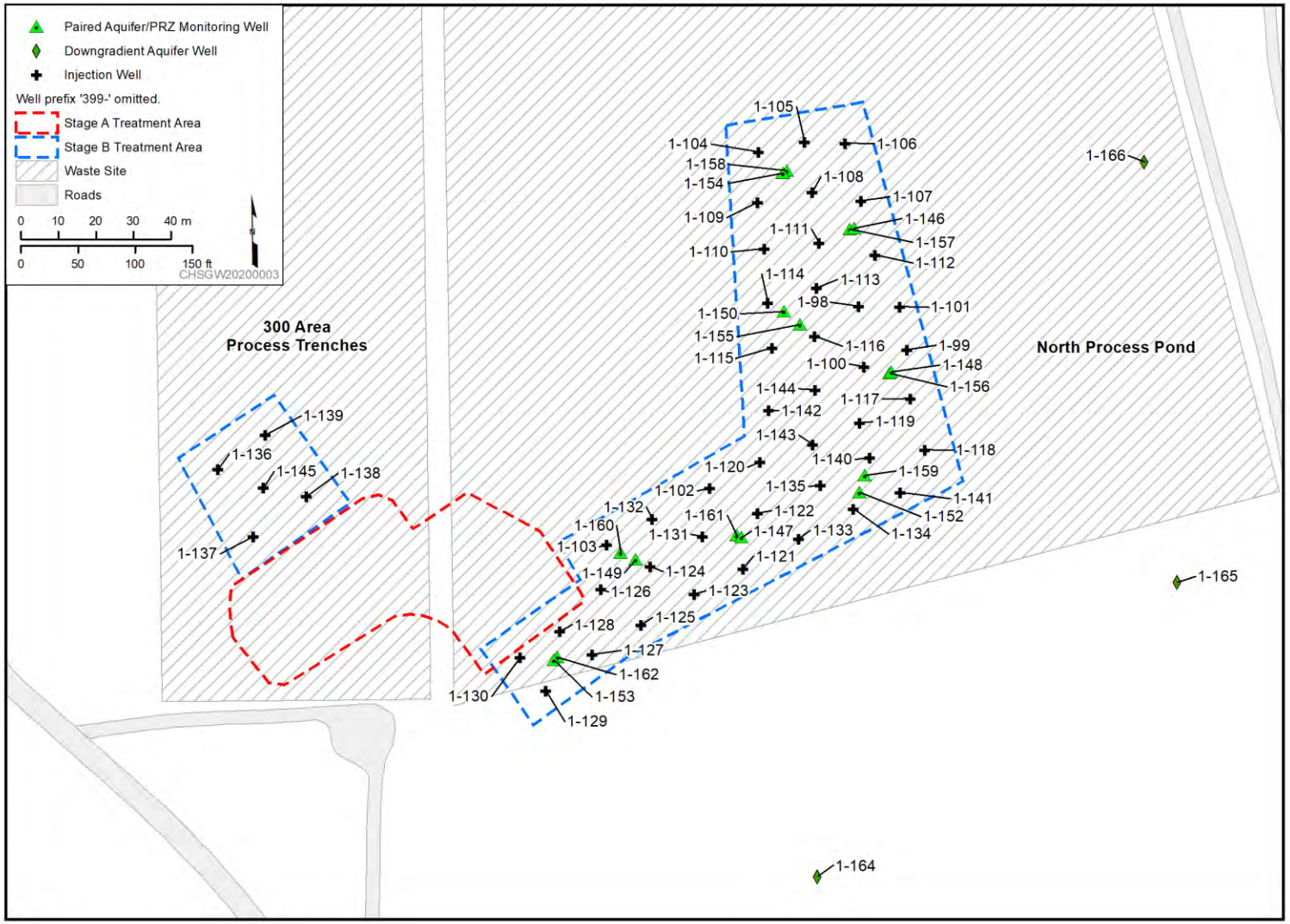

Figure 2-4. Forty-Eight Injection Wells and Nineteen Monitoring Wells Drilled for Stage B

Table 2-1. Stage B Monitoring Well Locations

Well	Injection Zone	Type	Well	Injection Zone	Type
Paired Aquifer and PRZ Wells in Stage B Enhanced Attenuation Area					
399-1-72*	1	Aquifer	399-1-73*	1	PRZ
399-1-162	1	Aquifer	399-1-153	1	PRZ
399-1-160	1	Aquifer	399-1-149	2	PRZ
399-1-161	2	Aquifer	399-1-147	2	PRZ
399-1-159	3	Aquifer	399-1-152	2	PRZ
399-1-156	3	Aquifer	399-1-148	3	PRZ
399-1-155	3	Aquifer	399-1-150	4	PRZ
399-1-157	4	Aquifer	399-1-146	4	PRZ
399-1-158	4	Aquifer	399-1-154	4	PRZ
Aquifer Wells Downgradient of the Enhanced Attenuation Area					
399-1-7*			399-1-164		
399-1-17A*			399-1-165		
399-1-23*			399-1-166		

*Existing well.

PRZ = periodically rewetted zone

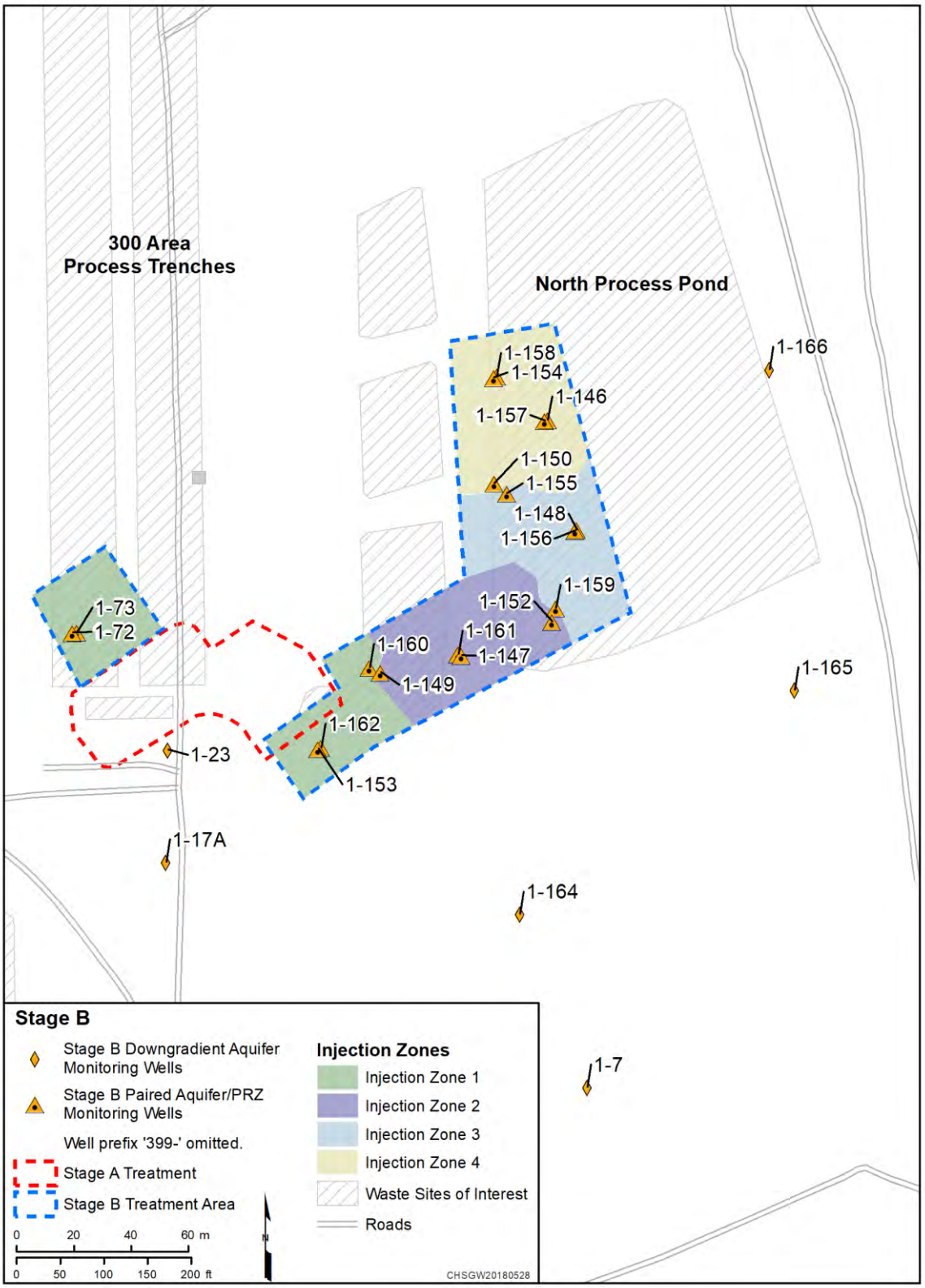

Figure 2-5. Stage B EA Area Monitoring Well Locations

2.2.4 Stage B ERT System

Twelve injection wells and six monitoring wells were instrumented with downhole ERT electrodes. The electrodes enable cross borehole ERT imaging near the instrumented wells for both pre-treatment geologic characterization and time-lapse monitoring of the treated zone during and after treatment. The Stage B area has three clusters of ERT wells, each with four injection wells and two monitoring wells (Figure 2-6). Each cluster consists of an A-A' plane and a B-B' plane. Wells in the A-A' plane were horizontally spaced approximately 4.3 to 5.5 m (14.1 to 18.0 ft) apart and wells in the B-B' plane were horizontally spaced approximately 11.5 to 12 m (38 to 40 ft) apart. The three pairs of PRZ/aquifer monitoring wells in the ERT clusters are on the A-A' planes and were spaced approximately 4 m (13 ft) apart to support the ERT monitoring design. The Stage B ERT clusters were positioned along the margins of two injection zones to bridge the zones (e.g., cluster 1 bridges injection zones 1 and 2; cluster 2 bridges injection zones 2 and 3; and cluster 3 bridges injection zones 3 and 4). This design facilitated determination of the radius of influence for individual injection wells and chronicled the coalescence between injection zones using time-lapse ERT imagery. The three pairs of PRZ and aquifer monitoring wells in the ERT clusters were spaced approximately 4 m (13 ft) apart to facilitate spacing of wells along the ERT line in the A-A' plane.

At each well, 16 electrodes were installed from 2.0 to 13.25 m (6.6 to 43.5 ft) bgs at 0.75 m (2.5 ft) spacing (Figure 2-3). At each electrode installation, a 10 cm (3.9 in.) tall stainless-steel wire mesh was attached to the outside of the PVC casing. The electrode was then attached to a multiconductor ERT cable through a stainless-steel cylinder ("takeout") internally attached to one of the conductors (i.e., wires) within the ERT cable (Section 2.2 of PNNL-28619).

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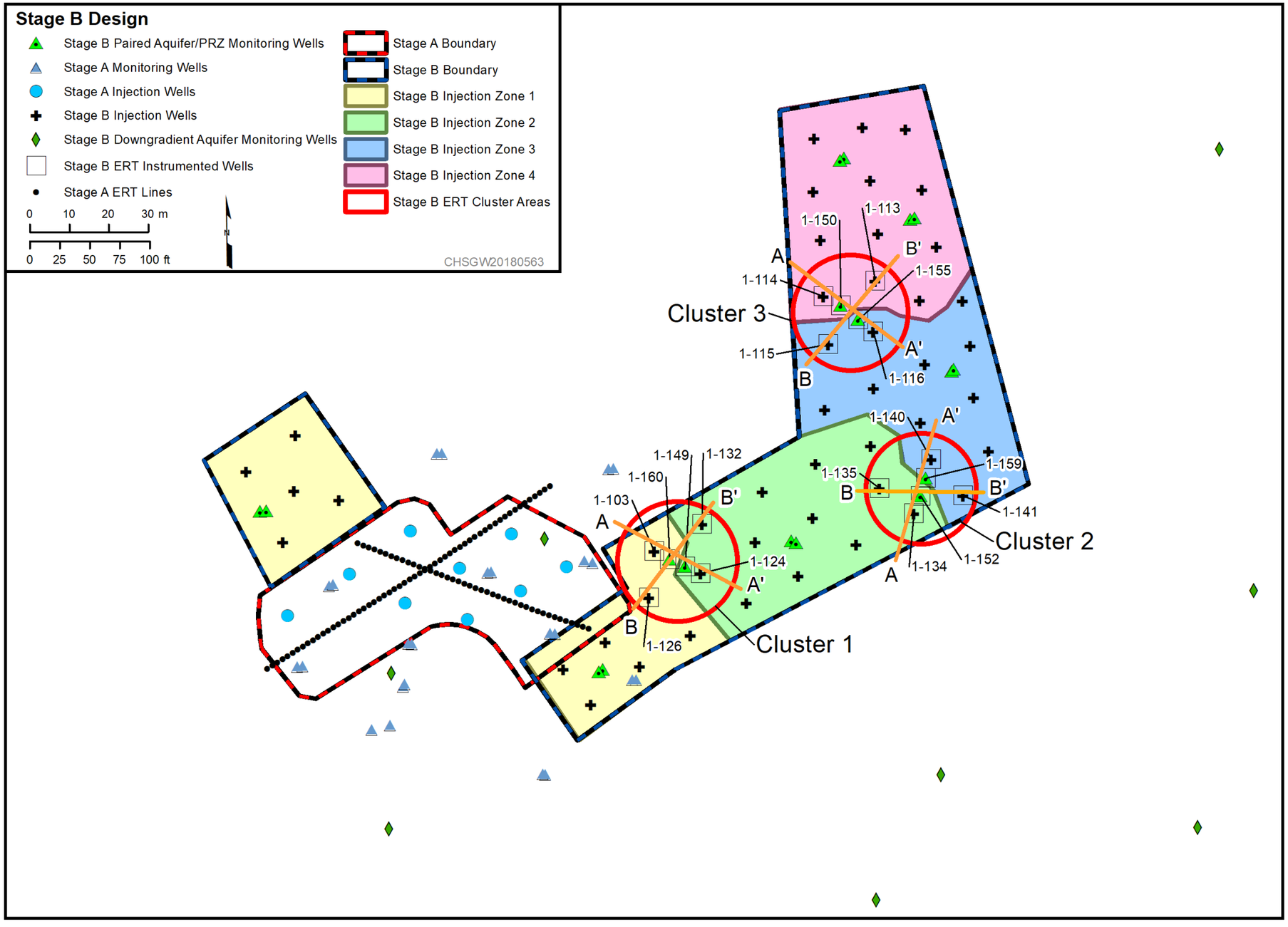

Figure 2-6. Stage B ERT Well Locations

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2.2.5 Stage B Chemical Mixing Skids and Site Infrastructure

Two remediation skids were designed and constructed as part of the apatite permeable reactive barrier remedy for the 100-NR-2 OU (DOE/RL-2010-29, *Design Optimization Study for Apatite Permeable Reactive Barrier Extension for the 100-NR-2 Operable Unit*). The remediation skids were used for the 300-FF-5 OU EA remedy in Stages A and B. Each remediation skid is capable of delivering polyphosphate solution at a targeted flow rate of up to 1,135 L/min (300 gal/min) (DOE/RL-2010-29). Each skid delivered polyphosphate solution to six wells at a time during the treatment period. The target design flow rate was 189 L/min (50 gal/min) to each well. Totalizers and sample ports were provided on each skid to monitor injection volumes and collect samples of the polyphosphate solution. Details of the chemical mixing skids and chemical storage tanks are provided in Chapter 2 of SGW-60778.

Concentrated polyphosphate solutions were delivered to the 300 Area in tanker trucks during the injection phase and stored in seven 30,283 L (8,000 gal) chemical storage tanks. The concentrated polyphosphate solutions were a mixture of sodium and potassium orthophosphate (NaH_2PO_4 and KH_2PO_4) and sodium pyrophosphate ($Na_4P_2O_7$) and were transferred from the tanks to the remediation skids using aboveground hoses.

Feed water from the Columbia River was obtained using two submersible pumps, and hoses were used to convey the river water to the remediation skids. The river water was filtered and then blended with the concentrated polyphosphate solutions in an inline mixing chamber to achieve the target injection phosphate concentration of 8,236 mg/L. Following mixing, a manifold distributed the diluted polyphosphate solutions to transfer hoses for distribution to the injection well network.

2.2.6 Stage B Enhanced Attenuation System Configuration

Figure 2-7 is an aerial view of the Stage B uranium sequestration system showing the locations of the river pumps, chemical mixing skids, chemical storage tanks, and Stage B treatment area. The color-coded hoses were used to deliver the polyphosphate solution from the mixing skids to the injection wells. When the schedule required injection into a different injection zone, the appropriate set of injection hoses was connected to the chemical mixing skids.

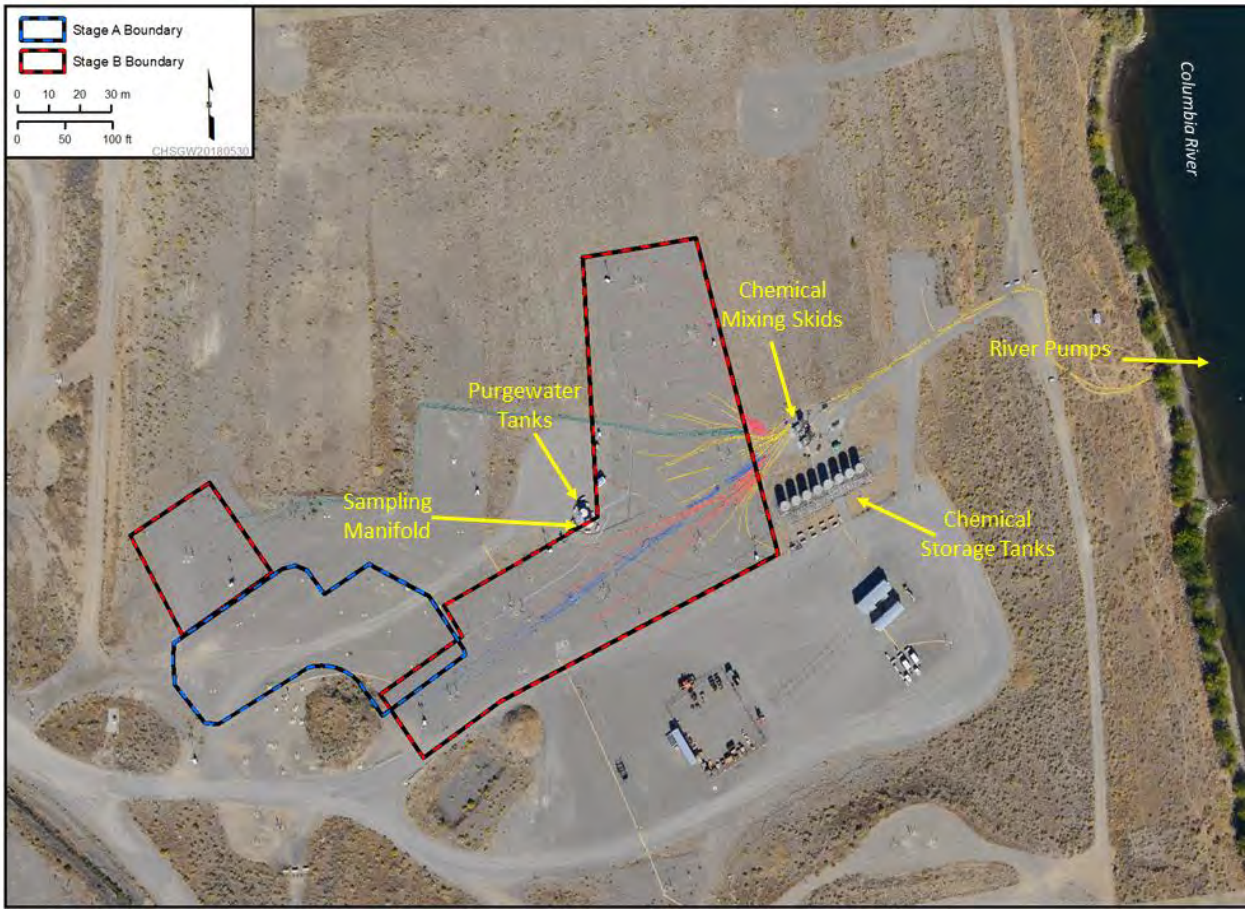

Figure 2-7. Stage B Enhanced Attenuation System Configuration

2.2.7 Stage B Timing and Order of Treatment

Design of the Stage B EA treatment system specified application of polyphosphate solutions using direct injection into the LVZ and PRZ. Stage B injections occurred over 17 days from September 4 through 20, 2018. Tables 2-2 and 2-3 summarize the daily polyphosphate solution injections for each remediation skid detailed in ECF-300FF5-19-0005.

Polyphosphate solution was injected through 48 injection wells into the PRZ and LVZ in four zones of 12 wells each (Figure 2-1). The solution was injected simultaneously into all 12 wells in a zone for a period of approximately four days with one change from injection into the PRZ to injection into the LVZ. Injections typically lasted 7.5 hours each day. The design sequence for the Stage B injections was to inject polyphosphate into the PRZ for the first half of the injection period for a zone and then change to injection into the LVZ for the second half of the injection period for a zone. The design objective was to inject the PRZ injection well screens with a solution volume equivalent to three PRZ pore volumes (193,500 L [51,100 gal]) and to inject the LVZ injection well screens with a solution volume equivalent to three LVZ pore volumes (145,200 L [38,400 gal]) (Table 5 of DOE/RL-2014-42-ADD1). After the approximately 4-day injection period for a zone was complete, the system began injections to the 12 injection wells in the next zone.

During injections, the vadose zone conditions were continuously monitored at the 18 monitoring and injection wells installed with ERT sensors. The ERT data provided near-real time imaging to monitor the lateral and vertical migration of the polyphosphate solution. These data were accessible through a secure

password-protected website and used to evaluate the delivery of polyphosphate to the LVZ and PRZ and the radius of influence for each injection well.

Table 2-2. Summary of Stage B Uranium Sequestration Operations at Skid 1

Operation Day (Date)	Injection Wells	Vadose Zone Target		Average Injection Rate Achieved (L/min [gal/min])	Injection Zone	Duration of Operations (Hours)
		PRZ	LVZ			
1 (09/04/2018)	399-1-129 399-1-136 399-1-137 399-1-138 399-1-139 399-1-145	Yes	No	170 [45]	1	6
2 (09/05/2018)		Yes	No	170 [45]	1	7
3 (09/06/2018)		Yes	No	170 [45]	1	6
4 (09/07/2018)		No	Yes	170 [45]	1	7
5 (09/08/2018)		No	Yes	170 [45]	1	8
6 (09/09/2018)	399-1-143 399-1-132 399-1-124 399-1-120 399-1-102 399-1-131	Yes	No	174 [46]	2	8
7 (09/10/2018)		Yes	No	189 [50]	2	8
8 (09/11/2018)*		Yes	Yes	189 [50]	2	9
9 (09/12/2018)		No	Yes	174 [46]	2	6
10 (09/13/2018)	399-1-99 399-1-100 399-1-101 399-1-115 399-1-116 399-1-144	Yes	No	178 [47]	3	9
11 (09/14/2018)		Yes	No	174 [46]	3	9
12 (09/15/2018)*		Yes	Yes	174 [46]	3	9
13 (09/16/2018)		No	Yes	182 [48]	3	6
13 (09/16/2018)	399-1-104 399-1-105 399-1-106 399-1-107 399-1-108 399-1-109	Yes	No	182 [48]	4	1
14 (09/17/2018)		Yes	No	182 [48]	4	9
15 (09/18/2018)		Yes	No	182 [48]	4	7
16 (09/19/2018)		No	Yes	182 [48]	4	9
17 (09/20/2018)		No	Yes	182 [48]	4	4

*Change from PRZ to LVZ

LVZ = lower vadose zone

PRZ = periodically rewetted zone

Table 2-3. Summary of Stage B Uranium Sequestration Operations at Skid 2

Operation Day (Date)	Injection Wells	Vadose Zone Target		Average Injection Rate Achieved (L/min [gal/min])	Injection Zone	Duration of Operations (hours)
		PRZ	LVZ			
1 (09/04/2018)	399-1-103 399-1-125 399-1-126 399-1-127 399-1-128 399-1-130	Yes	No	174 [46]	1	6
2 (09/05/2018)		Yes	No	174 [46]	1	7
3 (09/06/2018)		Yes	No	178 [47]	1	6
4 (09/07/2018)		No	Yes	174 [46]	1	7
5 (09/08/2018)		No	Yes	174 [46]	1	6
6 (09/09/2018)	399-1-121 399-1-122 399-1-123 399-1-133 399-1-134 399-1-135	Yes	No	174 [46]	2	8
7 (09/10/2018)		Yes	No	185 [49]	2	8
8 (09/11/2018)*		Yes	Yes	189 [50]	2	9
9 (09/12/2018)		No	Yes	174 [46]	2	6
10 (09/13/2018)	399-1-117 399-1-118 399-1-119 399-1-140 399-1-141 399-1-142	Yes	No	182 [48]	3	9
11 (09/14/2018)		Yes	No	182 [48]	3	9
12 (09/15/2018)*		Yes	Yes	182 [48]	3	9
13 (09/16/2018)		No	Yes	182 [48]	3	6
13 (09/16/2018)	399-1-98 399-1-110 399-1-111 399-1-112 399-1-113 399-1-114	Yes	No	182 [48]	4	1
14 (09/17/2018)		Yes	No	182 [48]	4	9
15 (09/18/2018)		Yes	No	182 [48]	4	7
16 (09/19/2018)		No	Yes	182 [48]	4	9
17 (09/20/2018)		No	Yes	182 [48]	4	5

*Change from PRZ to LVZ

LVZ = lower vadose zone

PRZ = periodically rewetted zone

Monitoring during Stage B polyphosphate treatment included pre-treatment (baseline) groundwater and soil sampling; monitoring of skid system parameters and polyphosphate injection solution concentrations, ERT, and groundwater during treatment; and post-treatment groundwater and soil sampling and ERT monitoring. Sampling and analysis requirements are described in Chapter 3 of the SAP addendum (DOE/RL-2014-42-ADD1). Sampling and monitoring methodology is described in Chapter 3 of this report.

2.3 Stage B Deviations from Design

This section summarizes instances where implementation and operation of the Stage B treatment and monitoring differed from the design presented in DOE/RL-2014-42-ADD1. The impact of the deviations is also discussed.

The SAP addendum (Table 5 of DOE/RL-2014-42-ADD1) states that geophysical logging will be conducted at nine of the selected monitoring or injection wells used for ERT monitoring during Stage B. The logging plan was adjusted to collect neutron moisture data that could be converted to volume percent moisture. At the time of Stage B operations, neutron moisture data could only be converted if collected in boreholes that were 20 cm (8 in.) diameter or smaller. Injection boreholes were 25 cm (10 in.) diameter, so neutron logging was only conducted in 20 cm (8 in.) diameter monitoring boreholes. Nine monitoring wells were selected for geophysical logging across the Stage B area (399-1-139, 399-1-150, 399-1-156, 399-1-157, 399-1-158, 399-1-159, 399-1-160, 399-1-161, and 399-1-162) (SGW-61092). One monitoring well from each ERT cluster was selected for neutron moisture logging: well 399-1-160 is located within ERT cluster 1; well 399-1-159 is located within ERT cluster 2; and well 399-1-150 is located within ERT cluster 3. The neutron moisture log data were intended to provide the baseline moisture content of the soils near the ERT wells. While the intent of the data need was not explicitly met by selecting wells only in ERT clusters, the nine selected wells did provide a baseline moisture content for the Stage B area.

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3 Sampling and Monitoring Methods

This chapter describes the methods used for sampling, analysis, and monitoring of soil, groundwater, polyphosphate solutions, and electrical resistivity before, during, and after completion of Stage B treatment activities to determine the initial site conditions and the changes during and following implementation of the EA remedy. The sampling and monitoring methods used for the Stage A EA remedy can be found in Chapter 3 of SGW-59614.

3.1 Soil Sampling and Analysis

Soil samples were collected from the LVZ and PRZ during borehole drilling both before and after application of polyphosphate solutions. The soil samples were analyzed for uranium content. Data to evaluate uranium mobility and leachability were collected based on the following five laboratory tests (PNNL-29650, *Evaluation of the Change in Uranium Mobility in Sediments from the Hanford 300-FF-5 Stage B Polyphosphate Field Injection*):

1. Sequential extraction tests use six increasingly stronger solutions to quantify how uranium in the sediment samples is distributed among porewater and mineral phases. Solid phases that require stronger solutions to remove the uranium are considered to be less mobile and have slower leaching characteristics. These extractions also provide data on co-contaminants, metals, and phosphate (Section 4 of PNNL-29650).

2. Carbonate batch extraction tests evaluate the quantity of uranium that is readily solubilized into the aqueous phase through 1,000-hour bicarbonate extractions, helping define the most mobile portion of uranium in a sediment sample.

3. Flow-through column leach tests on repacked sediments that contained the full grain size distribution provide information about the mass and rate of uranium release to the groundwater.

4. Identification of uranium mineral surface phase(s) and surface coating(s) can be used to interpret uranium leaching behavior based on the types of phases present.

5. Phosphate extraction tests quantify the amount of phosphate precipitate that formed at field scale as a result of polyphosphate injection.

Comparison of data from the pre-treatment and post-treatment boreholes was used to evaluate the distribution of phosphate and the sequestration of uranium after treatment. The following sections describe the methods used and the criteria for selection of the Stage B pre-treatment and post-treatment borehole samples for testing.

Soil sample analytical data and uranium mobility and leachability test results are summarized in Section 4.1 of this report. The Stage B analytical data are provided in Appendix B; the Stage A analytical data are provided in Appendix A of SGW-59614. Uranium mobility and leachability test results for Stage B samples are provided in PNNL-29650. Results for Stage A samples are provided in Snyder and Cantrell, 2016, *Analytical Data Report for Sediment Samples Collected From 300-FF-5 OU, Wells C8933, C8936, and C8938*; PNNL-24911, *Analytical Data Report for Sediment Samples Collected From 300-FF-5 OU, Wells C8940 and C9451*; and PNNL-25420, *Analytical Data Report for Sediment Samples Collected from 300-FF-5: Boreholes C9580, C9581, and C9582*; all three reports are included in Appendix A of SGW-59614.

3.1.1 Pre-Treatment Sampling and Analysis

Pre-treatment soil samples were collected from five boreholes prior to the Stage A injections; three of these boreholes were within the Stage A area (Figure 3-1). The pre-treatment samples were analyzed for uranium concentrations but were not analyzed for phosphate concentrations. Criteria for selection of borehole locations are described in Sections 3.1.1 and 3.1.2 of SGW-59614.

Forty-eight injection wells and 19 monitoring wells were drilled and constructed for the Stage B EA implementation in accordance with SGW-60287. Twenty of these wells were preselected for continuous sediment sample collection; these wells were sampled at 0.8 m (2.5 ft) intervals from 6.1 to 9.9 m (20 to 32.5 ft) bgs (Figure 3-1). Opportunistic samples were also collected from 16 wells at depths where unexpected geologic conditions (e.g., rip up clasts or discolored soils) occurred and at depths where field readings (volatile organic compounds and beta/gamma counts) were above background. Samples were collected for laboratory analysis of uranium, metals, anions, phosphate, and alkalinity. The six pre-treatment wells with the highest persistent concentration of uranium throughout the borehole, based on the laboratory analyses, were selected for future analyses of uranium mobility and leachability (Figure 3-2). In total, 30 Stage B pre-treatment samples (5 samples from each of the six wells) were retained for future testing.

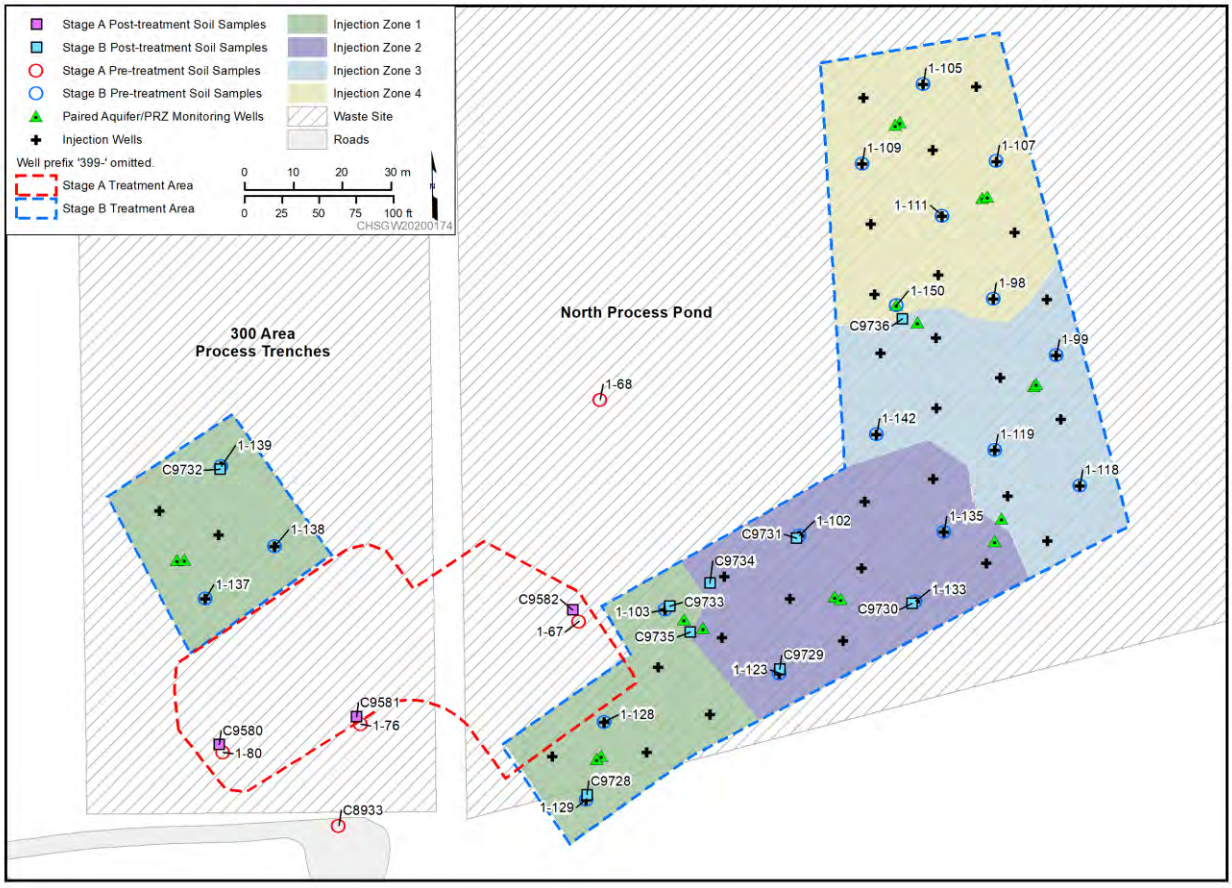

Figure 3-1. Sampling Locations for the Stage A and B Pre-Treatment and Post-Treatment Wells

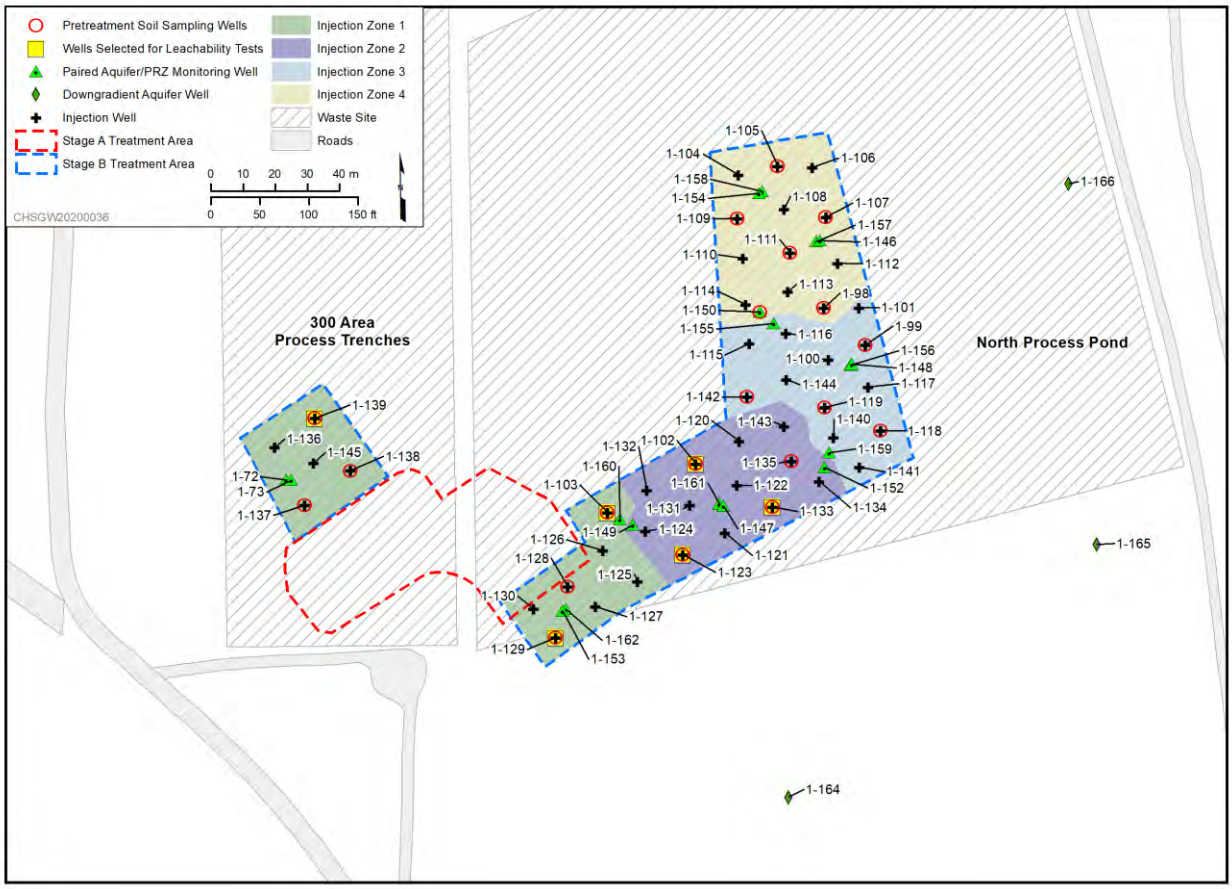

Figure 3-2. Location of Stage B Pre-Treatment Wells Selected for Uranium Leachability Tests

3.1.2 Post-Treatment Sampling and Analysis

Three Stage A post-treatment boreholes were drilled at locations adjacent to the three Stage A pre-treatment boreholes within the Stage A area (Figure 3-1 and Table 3-1). The post-treatment soil samples were collected at the same depth intervals that were selected for the pre-treatment soil samples. The samples were analyzed for uranium, calcium, phosphorus, and anions (chloride, fluoride, nitrate, nitrite, phosphate, and sulfate). Results are provided in Section 4.1.1.1 of SGW-59614. Results of the leachability tests, mineral phase analyses, and flow-through column tests for Stage A soil samples are provided in PNNL-25420, *Analytical Data Report for Sediment Samples Collected from 300-FF-5: Boreholes C9580, C9581, and C9582*.

Table 3-1. Stage A Pre-Treatment and Post-Treatment Boreholes with Planned Soil Samples

Stage A Pre-Treatment Borehole	Stage A Post-Treatment Borehole
Paired Boreholes	
399-1-80 (C9451)	C9580
399-1-76 (C8940)	C9581
399-1-67 (C8936)	C9582
Unpaired Boreholes	
C8933	Not applicable
399-1-68 (C8938)	Not applicable

The data quality objective (DQO) process used to develop the Stage B EA design specified that up to nine post-treatment boreholes would be drilled and sampled 6 months after Stage B polyphosphate treatment completion (Table 5 in DOE/RL-2014-42-ADD1). Following Stage B implementation, nine post-treatment borehole locations were identified using the following criteria:

- Location of one borehole within 1 m (3.3 ft) of each of the six Stage B pre-treatment wells with samples retained for paired pre-treatment and post-treatment analyses.
- Presence of phosphate at the six pre-treatment borehole locations, as determined by laboratory analysis of phosphate in pre-treatment samples from the LVZ and PRZ and wetting front distribution from preliminary ERT images.
- Presence of uranium at the six pre-treatment borehole locations, as determined by laboratory analysis of uranium in pre-treatment samples from the LVZ and PRZ and uranium concentrations in groundwater before injections.
- Presence of metals (e.g., copper, manganese) at the six pre-treatment borehole locations, as determined by laboratory analyses of pre-treatment samples, which could potentially form metal precipitates that increase subsurface conductivity affecting ERT imaging and form uranium metal minerals.
- Location of three additional post-treatment boreholes radially distant from injection wells to evaluate phosphate distribution laterally and vertically.

The nine Stage B post-treatment boreholes are shown in Figure 3-3 and listed in Table 3-2.

Table 3-2. Stage B Pre-Treatment and Post-Treatment Boreholes with Planned Soil Samples

Stage B Pre-Treatment Borehole	Stage B Post-Treatment Borehole
Paired Boreholes	
399-1-139 (C9683)	C9732
399-1-129 (C9673)	C9728
399-1-103 (C9647)	C9733
399-1-123 (C9667)	C9729
399-1-133 (C9677)	C9730
399-1-102 (C9646)	C9731
Unpaired Boreholes	
Not applicable	C9734
Not applicable	C9735
Not applicable	C9736
399-1-98 (C9642)	Not applicable
399-1-99 (C9643)	Not applicable
399-1-105 (C9649)	Not applicable
399-1-107 (C9651)	Not applicable
399-1-109 (C9653)	Not applicable
399-1-111 (C9655)	Not applicable
399-1-118 (C9662)	Not applicable
399-1-119 (C9663)	Not applicable
399-1-128 (C9672)	Not applicable
399-1-135 (C9679)	Not applicable
399-1-137 (C9681)	Not applicable
399-1-138 (C9682)	Not applicable
399-1-142 (C9686)	Not applicable
399-1-150 (C9694)	Not applicable

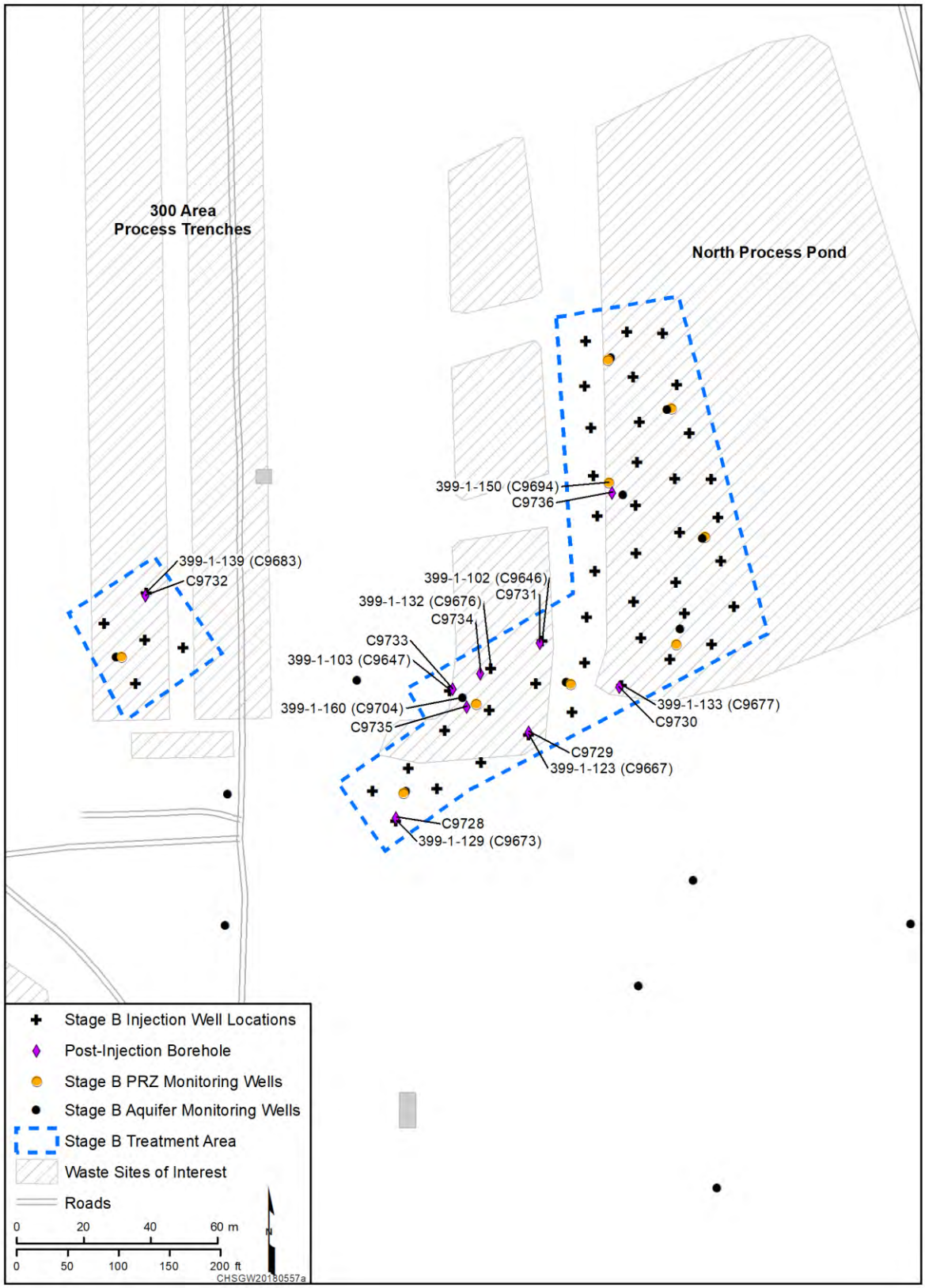

Figure 3-3. Location of Six Pre-Treatment and Nine Post-Treatment Stage B Boreholes

Soil samples were collected from the nine post-treatment boreholes at 0.8 m (2.5 ft) intervals from 6.1 to 9.9 m (20 to 32.5 ft) bgs, coincident with the pre-treatment well sample depths for comparability. The samples from six post-treatment boreholes were paired with the samples from the six pre-treatment wells (Table 3-2).

Seven opportunistic samples were collected within the backfill (0 to 6.1 m [20 ft] bgs) from six of the post-treatment boreholes based on beta/gamma detections above background by field instrumentation (Table 3-3). Two of the opportunistic samples were selected for laboratory analysis based on persistent beta/gamma readings above background throughout the backfill, paired pre-treatment borehole field readings, and geophysical logs (3.0 m [10 ft] at C9729 and 4.6 m [15 ft] at C9735). These samples from the backfill were not considered for further analysis of uranium mobility.

Table 3-3. Post-Treatment Stage B Boreholes with Opportunistic Soil Sampling

Borehole Identification	Depth (m [ft])	Rationale
C9729	3.0 [10]	Onsite beta/gamma detections above background and unknown black oily substance
	4.6 [15]	
C9730	3.0 [10]	Onsite beta/gamma detections above background
C9731	4.6 [15]	Onsite beta/gamma detections above background
C9733	6.1 [20]	Onsite beta/gamma detections above background
C9734	4.6 [15]	Onsite beta/gamma detections above background
	6.1 [20]	
C9735	4.6 [15]	Onsite beta/gamma detections above background and unknown black oily substance

Source: Section 1.3 of SGW-63544, *Borehole Summary Report for the Installation of Nine Boreholes in the 300-FF-5 Operable Unit, FY2019*.

3.1.3 Laboratory Tests on Pre-Treatment and Post-Treatment Samples

The five laboratory tests outlined in Section 3.1 were used to evaluate changes in uranium mobility and leachability after application of the polyphosphate treatment solutions. The rationale for selection of the samples for each test is provided in this section.

The DQO process used to design the Stage B EA evaluation specified that up to 18 pre-treatment and up to 18 post-treatment soil samples would be needed for evaluation of uranium mobility using sequential extraction tests, mineral phase analyses, and bicarbonate extraction tests; and that up to 12 of these pre-treatment and up to 12 of these post-treatment samples would be needed for evaluation of uranium leachability using column leach tests (Table 5 of DOE/RL-2014-42-ADD1). Following Stage B implementation, pre-treatment and post-treatment samples were selected for uranium mobility sequential and bicarbonate extractions using the following criteria:

- Target the PRZ interval (107 to 105 m [351 to 344 ft] elevation)
- Uranium soil concentrations >10 mg/kg

- Range in coincident copper soil concentrations (indicator of contamination)
- Vertical uranium profiles in characterized pre-treatment boreholes for understanding uranium mobility with depth

Using these criteria, 19 pairs of the collocated pre-treatment and post-treatment samples were selected for uranium sequential extractions and 1,000-hour bicarbonate extractions (laboratory tests 1 and 2) (Table 3-4). Six samples were selected from the unpaired post-treatment boreholes (two from each of the three unpaired boreholes) for spatial coverage of the Stage B EA area.

Table 3-4. Stage B Pre-Treatment and Post-Treatment Samples Selected for Laboratory Tests

Numbers of Samples	Laboratory Test				
	1: Uranium Sequential Extraction	**2: Uranium 1,000-Hr Bicarbonate Extraction**	**3: Uranium 1-D Column Leach**	**4: Surface Mineral Phase Analysis**	**5: Phosphate Extraction**
Number of pre-treatment samples	19	19	10	2	30
Number of post-treatment samples	25	25	14	2	25

Note: Table 3-1 in PNNL-29650, *Evaluation of the Change in Uranium Mobility in Sediments from the Hanford 300-FF-5 Stage B Polyphosphate Field Injection*, provides the borehole numbers and sample depths.

1-D = one-dimensional

Sequential extractions 1 and 2 target readily mobile (aqueous and adsorbed) uranium phases, extractions 3 and 4 target high-solubility and readily leachable uranium-bearing carbonate and silicate mineral phases, extraction 5 targets iron oxides that may co-precipitate uranium, and extraction 6 targets low-solubility uranium precipitates. Extractions 4 through 6 should be considered operationally defined and not necessarily proving direct association with the targeted phases. However, they provide evidence for predictions of future mobility based on the step in which they are extracted. Batch carbonate extractions for 1,000 hours target the fraction of mobile uranium.

Two pairs of collocated pre-treatment and post-treatment samples were selected for surface mineral phase analysis (laboratory test 4) based on their relatively high uranium and copper concentrations (Section 3.9 of PNNL-29650). The samples were analyzed at the Advanced Photon Source (APS) at Argonne National Laboratory using the micro x-ray fluorescence (μ-XRF), extended x-ray absorption fine structure (EXAFS), and x-ray near edge structure (XANES) measurement techniques. The Argonne National Laboratory instrumentation can analyze uranium phases at concentrations of <50 μg/g, which is one of the lowest method detection limits available for surface phase analysis. The μ-XRF creates two-dimensional (2-D) maps of elements to determine which minerals are associated with uranium. The EXAFS identifies what atoms are closest to uranium, and XANES identifies the valence state of the uranium. These analyses help to identify the mineral phases with which uranium is associated including relatively insoluble uranyl-phosphate minerals. Low energy elements (e.g., silicon and phosphorus) could not be detected at APS because of limitations in analyzing radioactive samples. Therefore, scanning electron microscopy energy dispersive X-ray spectroscopy (SEM-EDS) was used at the Environmental

Molecular Sciences Laboratory at Pacific Northwest National Laboratory (PNNL) to map low-energy elements.

All 30 of the Stage B pre-treatment samples were selected for phosphate analysis using nitric acid extraction (laboratory test 5) to establish background concentrations of phosphate in the Stage B EA area prior to injections.

The one-dimensional (1-D) uranium column leach test samples were selected based on the following criteria:

- Concentrations of uranium, copper, and phosphorus were above background level
- Availability of sequential extraction data for the sampled depth for both pre-treatment and post-treatment samples
- Samples adequately represent the Stage B treatment area both spatially and vertically
- All nine post-treatment wells have at least one-column leach sample selected
- Proximity to ERT clusters

Ten pairs of collocated pre-treatment and post-treatment soil samples and four post-treatment soil samples from unpaired boreholes were selected for column leach testing (laboratory test 3) (Table 3-4). Because three of the post-treatment boreholes were unpaired with pre-treatment boreholes, an even distribution of 12 pre-treatment and 12 post-treatment column leach samples was determined to not provide adequate spatial coverage of the Stage B EA area. However, the total number of 24 column leach samples specified in the DQO for the Stage B design was maintained. The four post-treatment samples selected from the unpaired wells were used to evaluate the lateral distribution of the phosphate and confirm ERT imaging results.

3.1.4 Radiological Contamination of Backfill Material

During drilling of the pre-treatment and post-treatment boreholes, field screening detected radiological contamination above background in the backfill material. This contamination was unexpected because clean backfill was used to remediate the 300 Area North Process Pond and 300 Area Process Trenches (Section 1.2.1 in this report). Contingency samples were collected from the boreholes where radiological contamination above background was detected. Three contingency samples from pre-treatment boreholes and two samples from post-treatment boreholes were submitted for laboratory analysis of metals, anions, gross alpha/beta, gamma energy analysis, americium-241, uranium isotopes, and strontium-90. Cesium-137, uranium, uranium isotopes, and gross alpha/beta were detected. Geophysical logs confirmed detections of man-made radionuclides in the backfill as well.

The statistical sampling method used during waste site remediation determined that the backfill was clean, but the individual sample results from isolated sampling depths based on field instrumentation, laboratory analyses, and geophysical logs show some minor contamination; the maximum cesium-137 concentration based on laboratory analyses was 0.169 pCi/g. However, these backfill soils are not in the PRZ and the contamination is not considered an issue for protection of groundwater from uranium flux from the PRZ. This contamination does not affect the numerical modeling for EA from a performance evaluation view.

3.2 Groundwater Sampling and Monitoring

Groundwater sampling and monitoring was conducted prior to, during, and following the Stage B uranium sequestration polyphosphate treatment injections. Manual and automated monitoring associated with Stage A treatment operations is described in Section 3.2 of SGW-59614. The following sections describe manual and automated monitoring associated with Stage B treatment operations.

3.2.1 Manual Monitoring

In May 2017, the U.S. Department of Energy, Richland Operations Office and the U.S. Environmental Protection Agency agreed to postpone implementation of Stage B operations for 1 year to perform and evaluate additional groundwater monitoring prior to the start of the Stage B treatment (TPA-CN-0784). In accordance with the SAP addendum (Table 5 in DOE/RL-2014-42-ADD1), six aquifer wells were monitored monthly starting in January 2017. Monthly monitoring began at five wells in September 2017 and at two wells in March 2018 as part of additional groundwater monitoring during the 1-year postponement (TPA-CN-0828). These 13 aquifer wells continued to be monitored monthly through October 2019 (Figure 3-4).

Groundwater was sampled from 15 aquifer wells and 9 PRZ wells during Stage B operations to evaluate the distribution of the polyphosphate solution and the short-term impacts to uranium concentrations (Table 5 of DOE/RL-2014-42-ADD1) (Figure 3-5). Baseline samples for the Stage B EA area were collected in August 2018 from 14 of the 15 aquifer monitoring wells; baseline sampling at one well (399-1-23) was unsuccessful due to an electrical problem at the well. Baseline samples were not collected from PRZ wells because these wells were dry prior to the start of injections. During treatment, all 24 aquifer and PRZ wells were sampled daily during injections and for 1 week after the last day of injections (September 4 through 27, 2018), and then weekly for 1 month (October 3 through 24, 2018). Eight aquifer wells and one PRZ well were then sampled monthly for 6 months (November 2018 through April 2019) (Figure 3-5). Opportunistic samples were collected at eight PRZ wells in November 2018 when the PRZ was saturated. Opportunistic samples were collected at all 24 wells in June 2019 during high river stage conditions.

Seven of the 13 aquifer wells monitored monthly were part of the set of 15 aquifer wells monitored daily, weekly, and monthly. As a result, 30 wells were monitored to support Stage B operations. The sampling frequency and duration for each monitoring well is provided in Table 3-5.

The Stage B DQO identified the importance of collecting all groundwater samples at the same time in order to better evaluate the trends. A sampling manifold was designed to enable coincident sampling of multiple wells. During polyphosphate injections, 10 Stage B aquifer wells and 8 Stage B PRZ wells were sampled from a sampling manifold. The wells were purged for 5 minutes, approximately three borehole volumes, before sampling.

Configuration of the sampling system resulted in difficulty sampling the eight PRZ wells. Because the submersible pumps installed in the wells were not compatible with the adjustable frequency drive installed to control the pumps, the pumps were operated at full speed (Section 2.7.1.1 of SGW-60778). During daily sampling operations this caused the PRZ wells to run dry for multiple sampling events and resulted in missed samples. Wells 399-1-146 and 399-1-154 were not successfully sampled during daily sampling because of this pump issue. Because of the number of missed PRZ daily samples, the opportunistic samples at the PRZ wells in November 2018 and June 2019 were needed to fill data gaps.

Based on the average low water levels in the PRZ wells, it was determined that further sampling of these PRZ wells using the manifold sampling system would likely result in unsuccessful sampling events. Instead, the PRZ wells were sampled using a bailer during the weekly and opportunistic sampling events.

The PRZ wells were not sampled in the first week of October during the transition from the manifold configuration to sampling using a bailer. Typically, 1.9 to 5.7 L (0.5 to 1.5 gal) was bailed from a well prior to taking the sample. Bailing agitates the water column and disturbs sediment in the sump of the well, resulting in high sample turbidity.

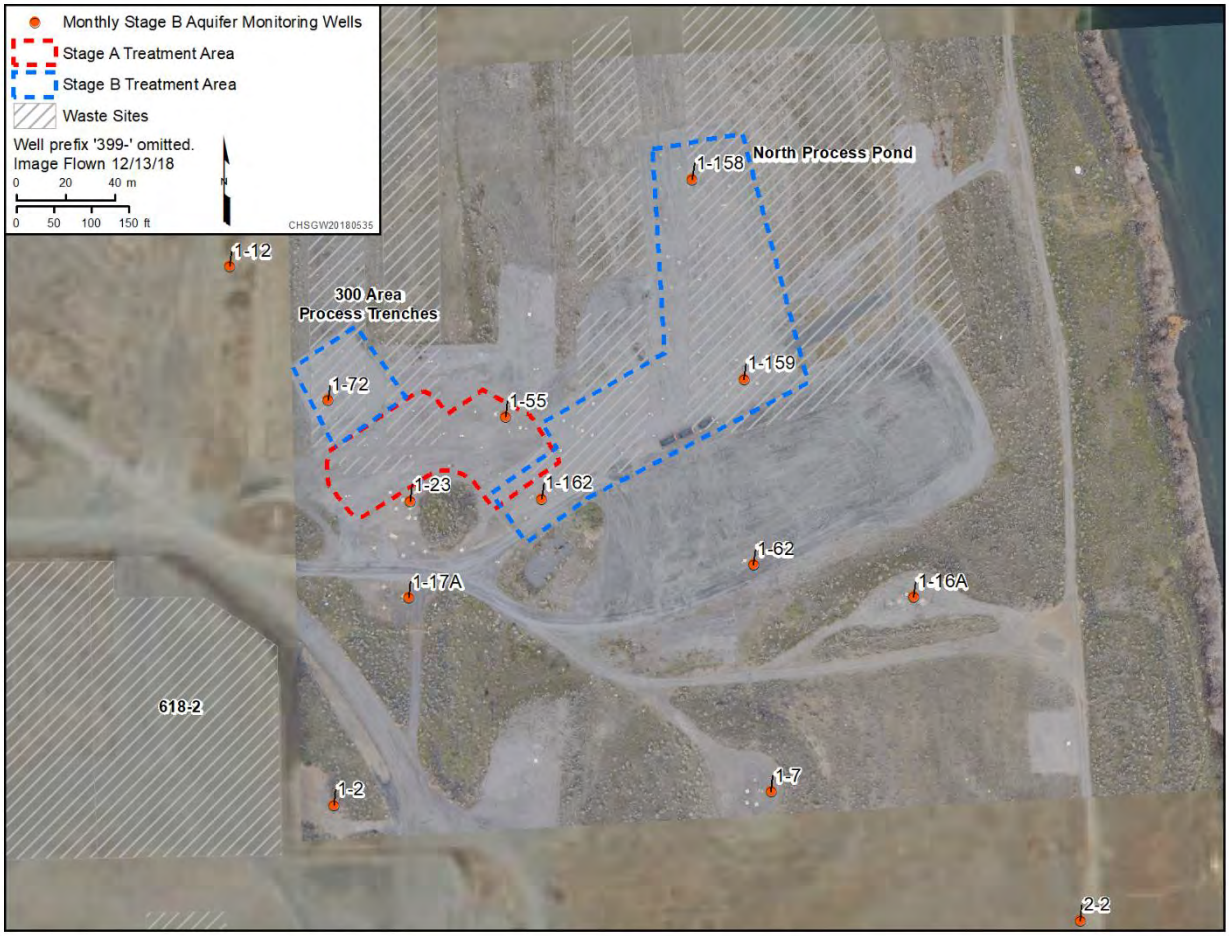

Figure 3-4. Locations of 13 Stage B Monthly Groundwater Monitoring Wells

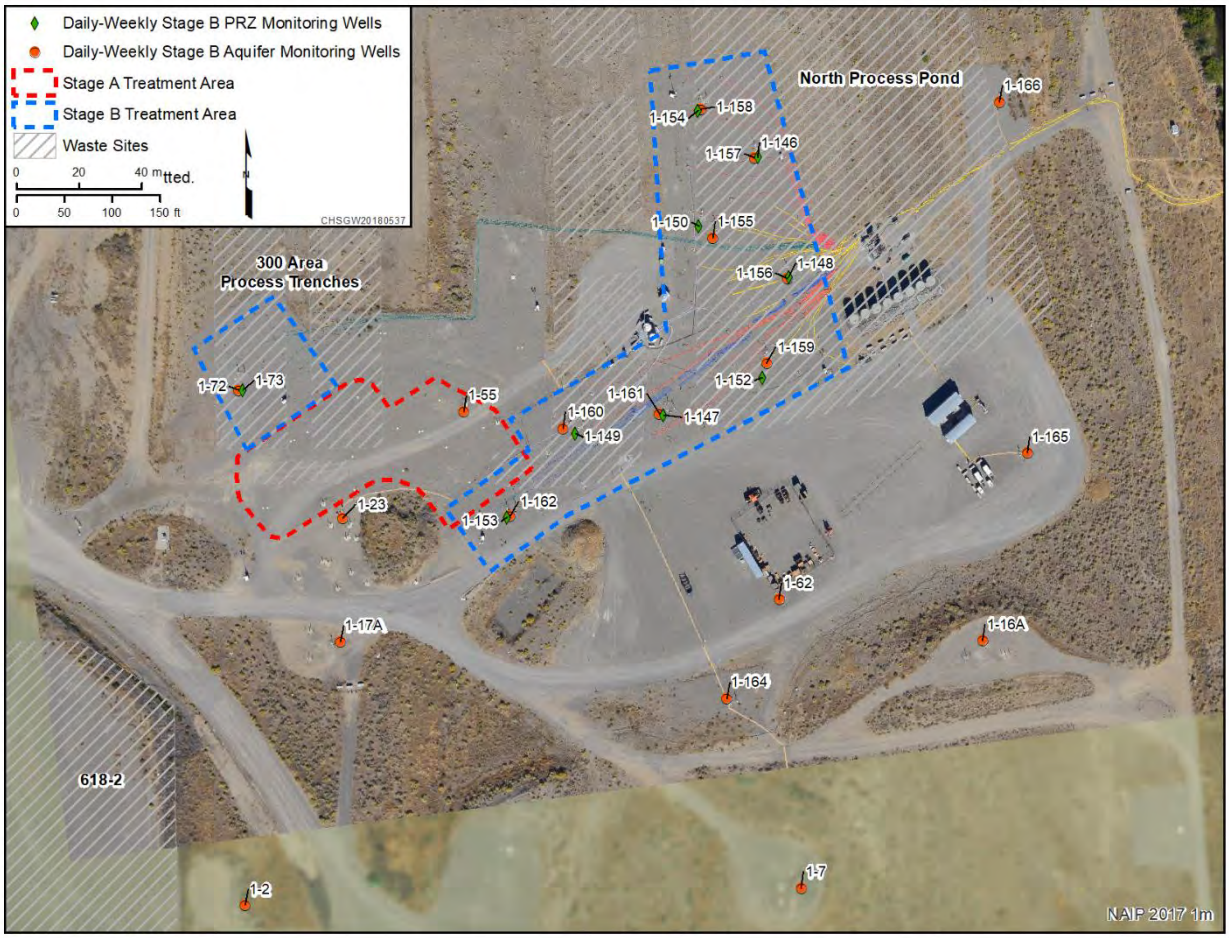

Figure 3-5. Locations of 24 Stage B Monitoring Wells

Table 3-5. Sampling Frequency for 30 Stage B Wells

Well Name	Well ID	Zone Monitored	Sampling Frequency
399-1-146	C9690	PRZ	Daily and weekly in September and October 2018; opportunistic sampling in November 2018 and June 2019
399-1-147	C9691	PRZ	Daily and weekly in September and October 2018; opportunistic sampling in November 2018 and June 2019
399-1-148	C9692	PRZ	Daily and weekly in September and October 2018; opportunistic sampling in November 2018 and June 2019
399-1-149	C9693	PRZ	Daily and weekly in September and October 2018; opportunistic sampling in November 2018 and June 2019
399-1-150	C9694	PRZ	Daily and weekly in September and October 2018; opportunistic sampling in November 2018 and June 2019
399-1-152	C9696	PRZ	Daily and weekly in September and October 2018; opportunistic sampling in November 2018 and June 2019

Table 3-5. Sampling Frequency for 30 Stage B Wells

Well Name	Well ID	Zone Monitored	Sampling Frequency
399-1-153	C9697	PRZ	Daily and weekly in September and October 2018; opportunistic sampling in November 2018 and June 2019
399-1-154	C9698	PRZ	Daily and weekly in September and October 2018; opportunistic sampling in November 2018 and June 2019
399-1-155	C9699	Aquifer	Daily and weekly in September and October 2018; monthly from November 2018 through April 2019; opportunistic sampling in June 2019
399-1-156	C9700	Aquifer	Daily and weekly in September and October 2018; monthly from November 2018 through April 2019; opportunistic sampling in June 2019
399-1-157	C9701	Aquifer	Daily and weekly in September and October 2018; monthly from November 2018 through April 2019; opportunistic sampling in June 2019
399-1-158	C9702	Aquifer	Monthly from September 2017 through October 2019; daily and weekly in September and October 2018
399-1-159	C9703	Aquifer	Monthly from September 2017 through October 2019; daily and weekly in September and October 2018
399-1-160	C9704	Aquifer	Daily and weekly in September and October 2018; monthly from November 2018 through April 2019; opportunistic sampling in June 2019
399-1-161	C9705	Aquifer	Daily and weekly in September and October 2018; monthly from November 2018 through April 2019; opportunistic sampling in June 2019
399-1-162	C9706	Aquifer	Monthly from September 2017 through October 2019; daily and weekly in September and October 2018
399-1-164	C9708	Aquifer	Daily and weekly in September and October 2018; monthly from November 2018 through April 2019; opportunistic sampling in June 2019
399-1-165	C9709	Aquifer	Daily and weekly in September and October 2018; monthly from November 2018 through April 2019; opportunistic sampling in June 2019
399-1-166	C9710	Aquifer	Daily and weekly in September and October 2018; monthly from November 2018 through April 2019; opportunistic sampling in June 2019
399-1-17A	A5028	Aquifer	Monthly from January 2017 through October 2019; daily and weekly in September and October 2018
399-1-23	C5000	Aquifer	Monthly from January 2017 through October 2019; daily and weekly in September and October 2018

Table 3-5. Sampling Frequency for 30 Stage B Wells

Well Name	Well ID	Zone Monitored	Sampling Frequency
399-1-7	A5040	Aquifer	Monthly from January 2017 through October 2019; daily and weekly, in September and October 2018
399-1-72	C8934	Aquifer	Monthly from September 2017 through October 2019; daily and weekly in September and October 2018
399-1-73	C8935	PRZ	Daily and weekly in September and October 2018; monthly from November 2018 through April 2019; opportunistic sampling in June 2019
399-1-12	A5021	Aquifer	Monthly from March 2018 through October 2019
399-1-16A	A5025	Aquifer	Monthly from January 2017 through October 2019
399-1-2	A5035	Aquifer	Monthly from March 2018 through October 2019
399-1-55	C7654	Aquifer	Monthly from January 2017 through October 2019
399-1-62	C8027	Aquifer	Monthly from September 2017 through October 2019
399-2-2	A5044	Aquifer	Monthly from January 2017 through October 2019

ID = identification
PRZ = periodically rewetted zone

During the injections, five Stage B aquifer wells and one PRZ well were sampled using a portable pump. After completion of the daily and weekly sampling, all 15 aquifer wells and 1 PRZ well were sampled using a portable pump. Wells were sampled using a portable pump after three borehole volumes were purged. For the nine aquifer wells within the Stage B area, the average purge volume during monthly sampling (November 2018 through June 2019) was 150 L (40 gal).

During review, the analytical data from the weekly samples that were collected at five of the eight PRZ wells were rejected because insufficient water levels prevented collection of representative samples. It was determined that the water level at the time of sampling was below the bottom of the well screen, indicating that the samples taken were from stagnant water in the blanked section of well casing below the screen (sump) rather than from saturated sediments in the PRZ.

Groundwater samples were analyzed for the constituents listed in Table 3-6. Analytical results for the groundwater samples are summarized in Section 4.2. These data are provided in Appendix B.

Table 3-6. Constituents Monitored in Groundwater Samples

Characteristics	Metals	Anions
Bicarbonate alkalinity	Arsenic	Chloride
Carbonate alkalinity	Calcium	Nitrate
Total alkalinity	Iron	Nitrite

Table 3-6. Constituents Monitored in Groundwater Samples

Characteristics	Metals	Anions
pH*	Phosphorus	Phosphate
Specific conductance*	Potassium	Sulfate
Oxidation-reduction potential*	Magnesium	—
Dissolved Oxygen*	Manganese	—
Temperature*	Sodium	—
—	Uranium	—

*Field parameter

3.2.2 Automated Monitoring

Automated groundwater measurements were obtained from selected monitoring wells before, during, and following Stage B uranium sequestration treatment.

3.2.2.1 In Situ Measurements

Downhole multi-parameter sensors connected to data loggers at the surface were deployed at all 24 aquifer and PRZ monitoring wells for continuous monitoring of water levels and field parameters (dissolved oxygen, specific conductance, temperature, pH, and oxidation-reduction potential) (Figure 3-5). Water levels and field parameters were measured and recorded in situ every 30 minutes from July 14, 2017, approximately 1 year prior to injections, to November 7, 2018, 1 month following injections. The sensor data were stored on the data loggers and manually downloaded. The data were evaluated in conjunction with the ERT data to assess the distribution and migration of the polyphosphate solution in the PRZ and aquifer.

In July 2018, maintenance was performed to inspect and recalibrate sensors to correct any instrument drift that may have occurred after 1 year of continuous operations; the dissolved oxygen sensors were also replaced prior to the expiration date (Section 2.8.1 of SGW-60778).

The downhole sensors are designed to operate while fully submersed in water. During injection operations, water levels mounded near PRZ wells and sensors were fully submerged, and these data were retained. Data collected when water levels were below the PRZ sensors (e.g., low river stage and intermittently during operations) were filtered out because they were considered unrepresentative of PRZ conditions.

During operations, some of the sensors and data loggers failed. The data logger at well 399-1-157 failed during injection operations and was replaced in late September 2018, but it was discovered in early October 2018 that the pressure-sensing element had also stopped working. After discussions with the project scientists, the decision was made to not replace the nonworking sensors because there was sufficient groundwater sampling data from this well, and adequate groundwater sample and downhole sensor data from surrounding wells, to alleviate any data gaps. Well 399-1-17A experienced electrical issues during October 10 to 17, 2018, which caused the data logger to reset itself and resulted in a brief loss of data during this reset period. No mechanical replacements or repairs were needed to address this instrumentation issue. PRZ well 399-1-150 experienced a data logger failure during the last week of

October 2018. Since the data loggers were scheduled to be removed from the system during the first week of November 2018, no attempt was made to replace this data logger.

Analytical results for the automated groundwater measurements are discussed in Section 4.2.2. These data are provided in Appendix C of this document.

3.2.2.2 Water Level Monitoring

Seven groundwater wells (399-1-12, 399-1-16A, 399-1-17A, 399-1-23, 399-1-7, 399-2-2, and 399-8-1) in a greater area around the Stage B EA area and the 300 Area river gauge (station SWS-1) were monitored as part of the local automated water level network (AWLN) (Figure 3-6). Water level, temperature, and specific conductance were logged at 15-minute intervals during 2018 and stored on data loggers. These data were used to monitor the groundwater chemistry changes and the likely extent of migration of the polyphosphate solution and to evaluate the hydraulic impact of the injections on nearby water levels. These same wells were used during Stage A polyphosphate treatment, and the results for the Stage A automated groundwater measurements are presented in Chapter 4 of SGW-59614. Results for the automated groundwater measurements are discussed in Section 4.2.2. These data are provided in Appendix C of this document.

3.3 Operations Monitoring

This section describes the operations monitoring associated with Stage B treatment. Results for the operations monitoring during Stage B are discussed in Section 4.3 and provided in Appendix D of this document. Operations monitoring associated with Stage A treatment is described in Section 3.3 of SGW-59614.

Field measurements and samples for laboratory analysis were collected to evaluate achievement of targeted treatment solution concentrations, injection flow rates, and injection volumes (Section 2.1).

Volumes of filtered river water and polyphosphate solution entering the injection mixing skids for blending and of the blended polyphosphate solution being injected through wells were measured continuously using inline totalizers that were mounted on the mixing skid piping. The volumes of polyphosphate solution injected through individual wells were monitored using six in-line totalizers on each skid. Flow rates were calculated hourly by operations personnel using the volumes monitored at the inline totalizers. These data and calculations are provided in ECF-300FF5-19-0005.

Samples of the polyphosphate treatment solution were collected once in the morning after startup of daily injections and then approximately every 4 hours throughout the duration of daily operations. Field measurements of pH, temperature, specific conductance, oxidation reduction potential, and dissolved oxygen were recorded for each sample by operations personnel.

Injection solution samples for laboratory analysis were collected from each skid at the start of injections and once daily thereafter for each day of treatment. One baseline sample of filtered river water was collected for each skid prior to the start of polyphosphate injections. The polyphosphate solution and river water samples were analyzed at an offsite laboratory for alkalinity, calcium, magnesium, phosphorus, potassium, sodium, uranium, chloride, phosphate, and sulfate. Analysis of the phosphate results had a 3-day turnaround time to allow adjustments of the total phosphate concentration in the treatment solutions to be made in the field.

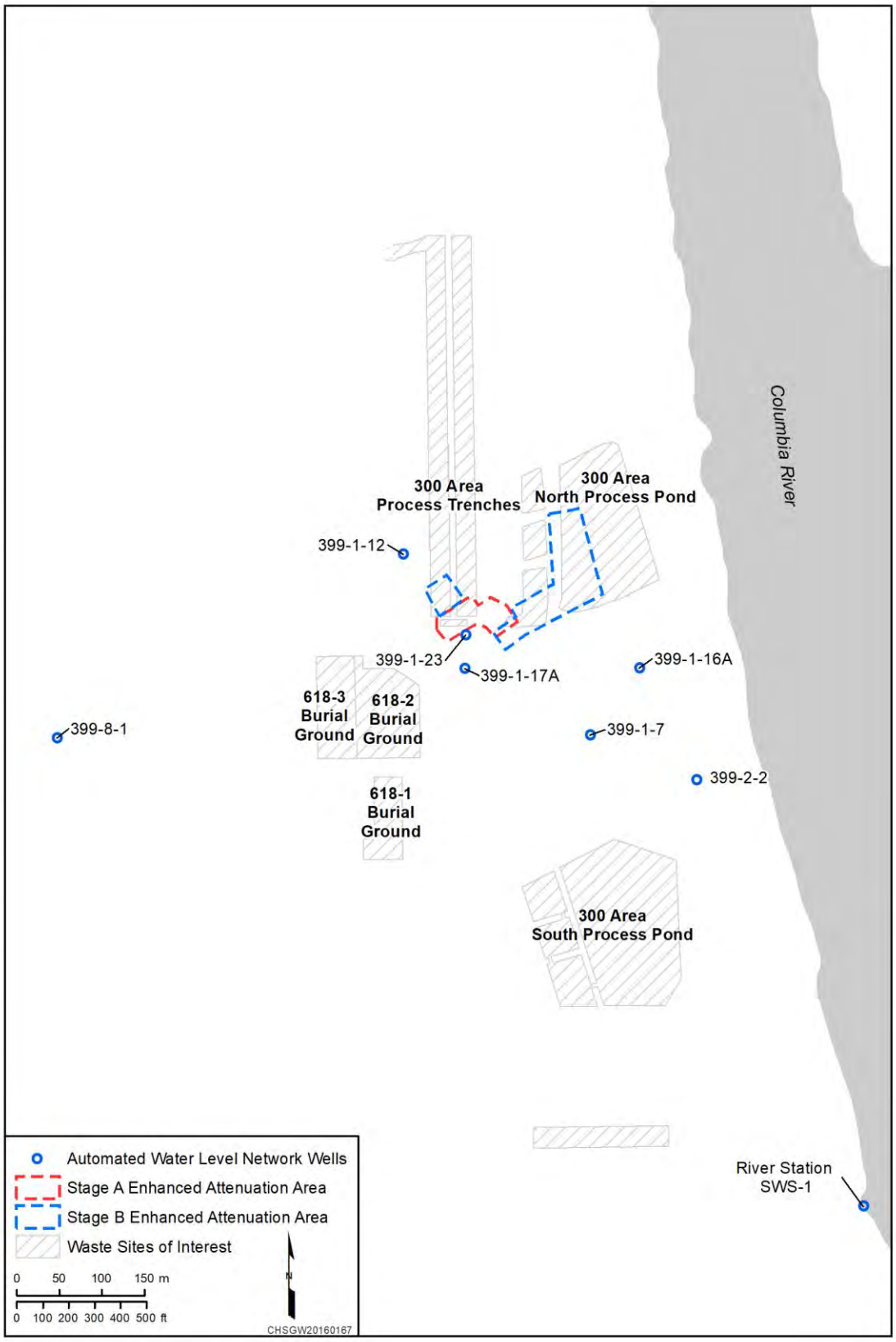

Figure 3-6. Locations of AWLN Stations Monitored for EA Operations

3.4 Electrical Resistivity Tomography

Real-time ERT was conducted in the Stage A and B areas to monitor the spatial and temporal changes in bulk electrical conductivity associated with the migration of the polyphosphate amendment through the targeted vadose treatment zone. The surface array ERT for Stage A operations is described in Section 3.4 of SGW-59614. This section describes the borehole-based ERT surveys associated with Stage B operations. Results for the Stage B ERT monitoring are discussed in Section 4.4. A detailed description of the ERT operations and imaging interpretation is provided in PNNL-28619.

ERT data were collected from August 30, 2018, to October 26, 2018, with the exception of four brief (1 to 4 hours) interruptions due to power outages. Baseline ERT surveys were collected prior to polyphosphate injections in order to image pre-treatment subsurface structure and establish baseline conditions. Injection of the polyphosphate solution increased bulk electrical conductivity in the vadose zone and the PRZ by increasing both the degree of saturation and the pore fluid electrical conductivity. Time-lapse ERT images of the corresponding changes in bulk conductivity provided a proxy measure of when and where the injected solution reached a given portion of the ERT imaging zone. Baseline ERT imaging (i.e., the pre-treatment image) was subtracted from the time-lapse images to reveal the changes in bulk conductivity caused by the injection of polyphosphate solution. ERT imaging surveys were conducted at 12-minute intervals. The time-lapse surveys were collected and processed continuously, and each survey was submitted to a webserver for near-real time visualization. The turnaround time from the beginning of a survey until time-lapse images were available on the website was approximately 15 to 30 minutes. The time-lapse images were then analyzed to investigate solution delivery performance and timing.

3.5 Long-Term Groundwater Monitoring

Semiannual long-term groundwater monitoring samples were collected from four downgradient wells (399-1-17A, 399-1-7, 399-2-1, and 399-2-2) during December (typically low river stage) and June (typically high river stage) in accordance with the SAP (DOE/RL-2014-42). These wells were sampled for water levels, field parameters (specific conductance, dissolved oxygen, temperature, turbidity, and pH), uranium, and gross alpha. Analytical results for these groundwater samples are summarized in Section 4.2. These data are provided in Appendix E of this document.

3.6 Data Management

Data review and verification were conducted in accordance with the SAP (Section 4.4 of DOE/RL-2014-42). The CH2M HILL Plateau Remediation Company Sample Management and Reporting organization, in coordination with the 300-FF-5 OU project team, ensured that analytical data were appropriately reviewed, managed, and stored in accordance with the applicable programmatic requirements governing data management. All samples submitted to analytical laboratories were accompanied by appropriately filled out chain-of-custody forms.

Data review and verification were performed to confirm sampling and chain-of-custody documentation was complete. This review included linking sample numbers to specific sampling locations, reviewing sample collection dates and preparation and analysis dates to assess whether holding times were met, and reviewing quality control data to determine whether analyses met the data quality requirements specified in the SAP (DOE/RL-2014-42).

The 300-FF-5 OU technical lead reviewed the analytical data to evaluate potential data errors and submitted requests for data review on questionable data. Results of the request for data review process were used to flag the data appropriately in the Hanford Environmental Information System database

and/or to add comments. Example data review flags applied as a result of the request for data review process are "Y," indicating the data are suspect but cannot be confirmed to be incorrect, and "R," indicating the data are known to be incorrect and are rejected.

Data validation was performed by a third-party data validation contractor based on the results of the quality control samples for specified sets of analytical data. Data validation was performed on a minimum of 5% of the analytical data in the set. Five data validation reports were completed to evaluate analytical results for five sets of analytical data: polyphosphate injection solution samples from the mixing skids; groundwater samples collected daily and weekly; groundwater samples collected monthly; soil samples collected from pre-treatment boreholes; and soil samples collected from post-treatment boreholes. The results of the data validation reports are included in the data usability assessment reports.

The data usability assessment process compares completed field sampling activities to those proposed in corresponding sampling documents and provides an evaluation of the resulting data. The purpose of the data usability assessment is to determine whether quantitative data are of the correct type and are of adequate quality and quantity to meet the project DQOs. Each data usability assessment was performed on 100% of the data in a specified set of analytical data. Data usability assessments were completed for the following three sets of analytical data:

- Polyphosphate injection solution samples from the mixing skids; SGW-64537, *Data Usability Assessment for 300-FF-5 Stage B Skids*, concluded that given the high degree of acceptable data, the analytical results are considered usable for their intended purposes.
- Soil samples; SGW-64538, *Data Usability Assessment for 300-FF-5 Stage B Soils*, concluded that given the high degree of acceptable data, the analytical results are considered usable for their intended purposes.
- Groundwater samples; SGW-64539, *Data Usability Assessment for 300-FF-5 Stage B Groundwater*, concluded that given the high degree of acceptable data, the analytical results are considered usable for their intended purposes

All operational monitoring and field measurements data for the two mixing skids were recorded on datasheets by operations personnel. The original datasheets were reviewed by operations personnel and transferred to the 300 Area field lead following completion of injections. The 300 Area field lead provided the datasheets to the Sample Management and Reporting organization for archiving.
The datasheets are included in ECF-300FF5-19-0005.

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4 Sampling and Monitoring Results

This chapter provides the results for sampling and monitoring soil, groundwater, polyphosphate solutions, and electrical resistivity before, during, and after the polyphosphate treatment to determine the initial site conditions and the changes resulting from implementation of the Stage B EA remedy. Results of the Stage A EA remedy are summarized in Chapter 4 of SGW-59614.

4.1 Soil Sampling and Analysis

Soil sampling and analysis was conducted before and after application of polyphosphate treatment solutions. Samples were analyzed for uranium and phosphate concentrations and tested for uranium leachability characteristics.

During Stage A of the EA remedy, sediment samples from five pre-treatment boreholes were analyzed for uranium (Section 3.1 of SGW-59614). Samples from the three post-treatment boreholes were analyzed for uranium, calcium, phosphorus, and anions. The three post-treatment boreholes were collocated with the three pre-treatment boreholes that were located in the Stage A area (Table 3-1) (Figure 3-1). Ten pre-treatment samples and nine post-treatment samples from the Stage A boreholes were analyzed for uranium leachability (Section 4.1 of SGW-59614).

During Stage B of the EA remedy, sediment samples were analyzed for uranium content as well as indicators of mobility and leachability (Section 3.1 of this report). The samples from the six pre-treatment wells with the highest persistent concentrations of uranium throughout the borehole were submitted for additional analysis (Section 3.1 of this report). Nine boreholes were drilled and sampled 6 months after Stage B injections to determine post-treatment characteristics of the vadose zone (Section 3.1.2 of this report). Six of the post-treatment boreholes were drilled adjacent to the six pre-treatment boreholes with samples, resulting in six collocated borehole pairs. Three additional, unpaired Stage B post-treatment borehole locations were selected to evaluate delivery to the targeted PRZ and LVZ treatment zones (Figure 3-2). Samples from each of these post-treatment boreholes were analyzed for metals, anions, phosphate, and alkalinity.

Nineteen samples from the six Stage B pre-treatment boreholes and 25 samples from the nine Stage B post-treatment boreholes were selected for comprehensive tests on uranium leachability, mineral phase association, and soil characteristics to determine pre-treatment and post-treatment characteristics of the vadose zone. PNNL-29650 presents a detailed discussion of the results of sediment analyses.

4.1.1 Uranium and Phosphate Analytical Results

Sediments in the Stage A and B areas contain elevated concentrations of uranium from waste disposal. Total uranium concentrations in pre-treatment and post-treatment samples were comparable, because the goal of treatment was to decrease contaminant mobility, not mass. Pre-treatment samples showed elevated uranium concentrations above 300 Area background[2] at 16 of the 20 Stage B boreholes and at all 5 Stage A boreholes. Post-treatment samples showed elevated uranium concentrations above the background concentration at all nine Stage B and all three Stage A boreholes. Stage B results are provided in Appendix B and Stage A results are provided in Section 4.1.1.1 of SGW-59614.

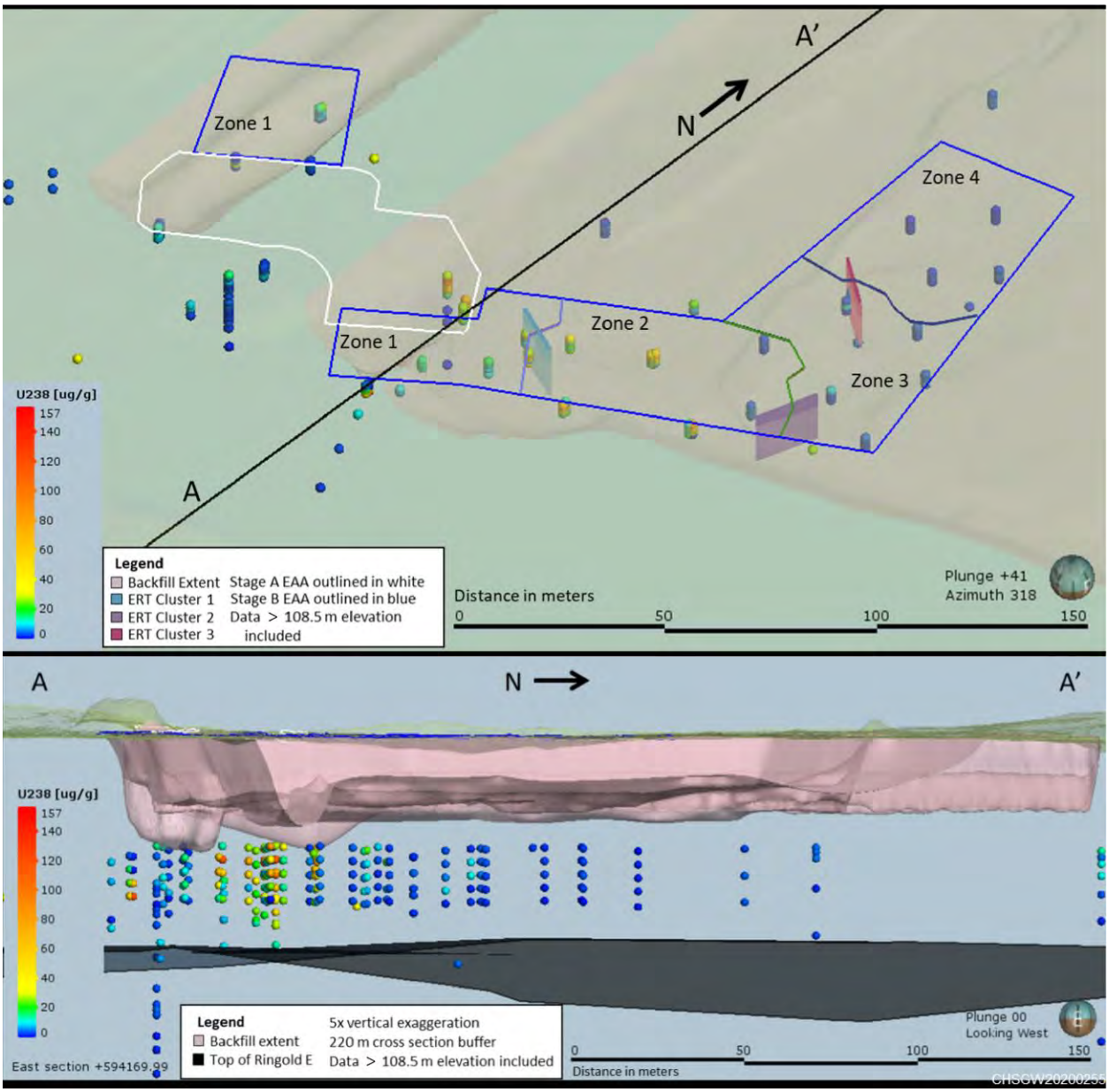
Uranium concentrations ranged from 0.438 to 85.4 mg/kg for Stage B pre-treatment sediment samples, which was comparable to the Stage A pre-treatment concentrations of 0.141 to 41.4 mg/kg

[2] The background uranium concentration in the 300 Area soil has been previously calculated as 3.21 mg/kg (ECF-300FF5-11-0151, *Groundwater Flow and Uranium Transport Modeling in Support of the 300 Area FF-5 RI/FS Document*).

(Section 4.1.1.1 of SGW-56914). Post-treatment uranium concentrations ranged from 1.31 to 175 mg/kg (Stage B) and from 1.2 to 100 mg/kg (Stage A).

The pre-treatment boreholes within zones 1 and 2 of the Stage B EA area consistently had higher uranium concentrations than boreholes in zones 3 and 4 (Table 4-1). The highest uranium concentrations from zones 1 and 2 were >10 times the 300 Area background concentration and were collected from the LVZ and PRZ at depths of approximately 6 to 9 m (20 to 30 ft) bgs. Figures 4-1 and 4-2 illustrate total uranium concentrations in the Stage B pre-treatment and post-treatment boreholes. Uranium concentrations in pre-treatment boreholes from zones 1 and 2 are coincident with higher concentrations of copper. In comparison, zones 3 and 4 soil samples had lower concentrations of uranium and copper (Table 4-1). The spatial variability in uranium and copper concentrations in soils is likely reflective of residual influence from the former 316-2 North Process Pond waste site, which was host to sludge high in uranium and copper. During remediation of the 316-2 North Process Pond, excavation depth was variable based on detectable contamination (Figure 4-1). In zones 1 and 2, where the depth of backfill is the deepest (4.6 to 6 m [15 to 20 ft] bgs) also correlates with the highest concentrations of uranium and copper. In zones 3 and 4 the backfill depth is 3.0 to 3.7 m (10 to 12 ft) bgs and the uranium and copper concentrations indicate less impact from waste discharges in the LVZ and PRZ.

Results of sediment sampling for phosphate show that EA treatment increased the concentrations of phosphate in most locations (Figure 4-3). Stage B pre-treatment phosphate concentrations were near or below quantitation limits in most samples (average of 2.72 µg/g, including duplicate samples and nondetect values) (Appendix B of this report). In eight of the nine post-treatment Stage B boreholes, phosphate was detected in all of the samples from the PRZ (deeper than 8 m [26 ft] bgs). The exception was unpaired zone 4 borehole C9736, where phosphate was detected in only one of the two samples from 9.14 m (32 ft) bgs. The average phosphate concentration in the post-treatment sediment samples was 217.2 µg/g (including duplicate samples and nondetect values) (Appendix B of this report). Detected post-treatment phosphate concentrations ranged from 3.99 µg/g (C9728) to 862 µg/g (C9732). Phosphate was also detected in all three post-treatment Stage A boreholes, ranging from 7.05 µg/g (C9581) to 3,680 µg/g (C9580).



Reference: ECF-300FF5-16-0087, *Determination of Vadose Zone Uranium Concentration Distribution Extents and Development of a Three-Dimensional Geologic Framework Model for the 300-FF-5 Operable Unit, Hanford Washington*.

Figure 4-1. 3-D Plane View and Cross Section of EA Area with Excavation Footprint and Uranium Soil Samples from Stages A and B Below 108.5 m Elevation

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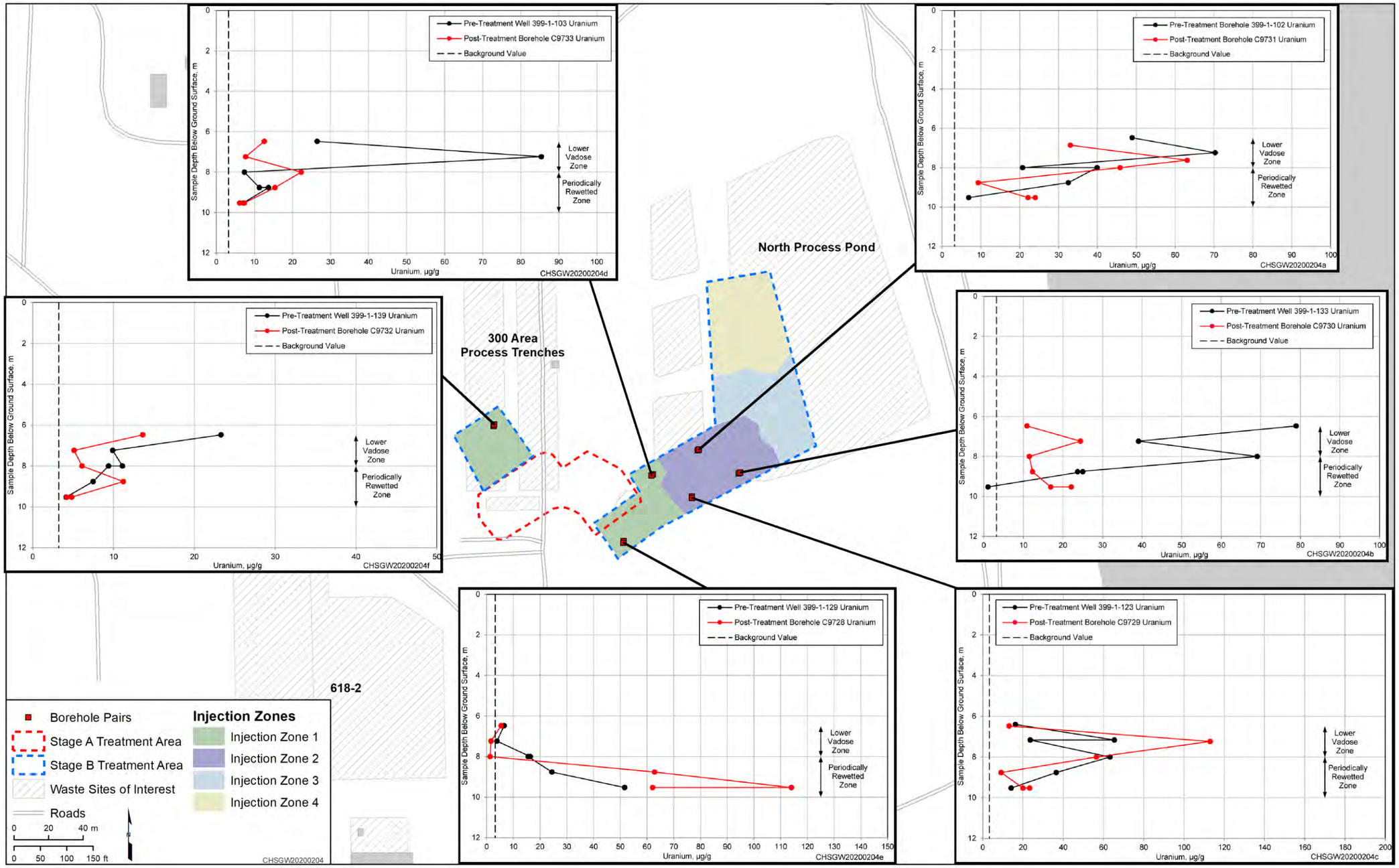


Figure 4-2. Uranium Concentration Depth-Discrete Profiles in Pre-Treatment and Post-Treatment Borehole Pairs

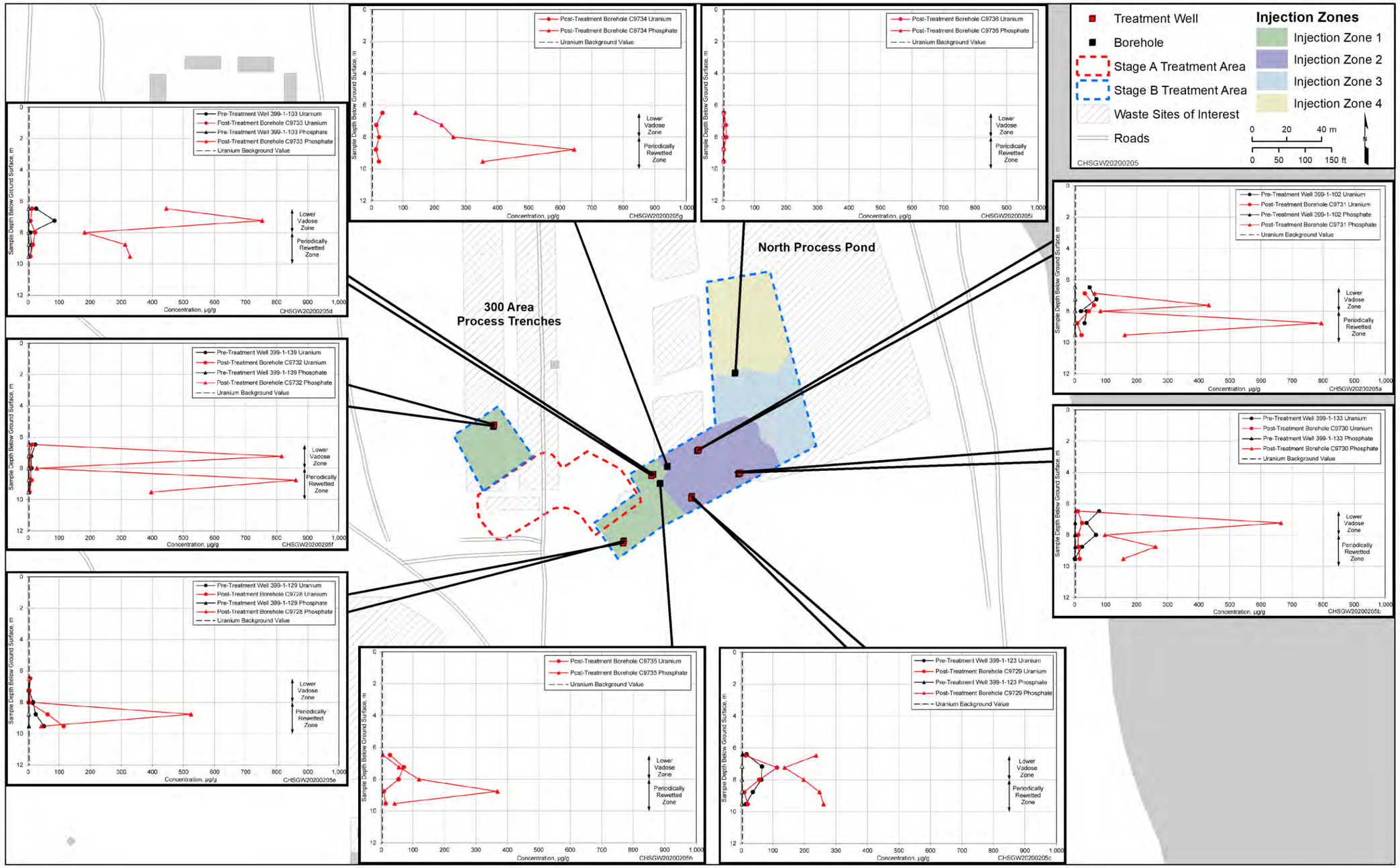


Figure 4-3. Uranium and Phosphate Concentration Depth-Discrete Profiles of Pre-Treatment and Post-Treatment Borehole Pairs and Unpaired Post-Treatment for the Stage B EA Area

Table 4-1. Range of Stage B Pre-Treatment Uranium and Copper Soil Concentrations

Injection Zone	Uranium (mg/kg)	Copper (mg/kg)
1	0.438 - 85.4	9.34 - 1,000
2	1.05 - 78.9	20 - 1,620
3	1.64 - 9.58	13 - 325
4	0.786 - 9.58	4.22 - 107

4.1.2 Uranium and Phosphate Leachability Characteristics Test Results

Four types of leachability tests (Section 3.1 of this report) were conducted on pre-treatment and post-treatment sediment samples: sequential extraction tests using six liquid extraction solutions in series, 1,000-hour carbonate solution extraction tests, 1-D flow-through column leach tests, and nitric acid phosphate extraction tests.

Analytical results from both Stage A and B pre-treatment samples indicated there was a high concentration of uranium in the sediments and much of it was potentially mobile. The ranges of total extracted uranium concentrations in the Stages A and B pre-treatment sediments were comparable (7 to 126 mg/kg in Stage A samples, 10 to 94 mg/kg in Stage B samples), with elevated uranium concentrations in the Stage A area and in zones 1 and 2 of the Stage B area, which are adjacent or close to the Stage A area. Stage A and B labile uranium fractions (i.e., from the 1,000 hour labile extraction) were nearly equal (43% and 42.5±9.6%, respectively).

The ranges of total extracted uranium concentrations in Stage A and B post-treatment samples also were comparable (2 to 105 mg/kg in Stage A samples, 3 to 136 mg/kg in Stage B samples). The Stage B labile uranium fraction was 15.6±14.3%, an average of 63% less mobile uranium as a result of the polyphosphate treatment based on carbonate extractions (Section 6.0 of PNNL-29650).

Sections 4.1.2.1 through 4.1.2.4 provide additional discussion.

4.1.2.1 Sequential Extractions

Sequential extraction tests using six increasingly strong acid solutions were performed to determine the concentration and distribution of uranium and phosphate in the Stage A and B pre-treatment and post-treatment sediment samples. Sequential extraction results for other selected metals in Stage B samples were also analyzed (Section 4 of PNNL-29650). Results for the Stage A sequential extraction tests can be found in Section 4.1.1.2 of SGW-59614. The term extraction as used in this report refers to the removal of contaminants in the presence of solutions of varying aggression in order to estimate long-term release of contaminants.

Extractions 1 and 2 targeted readily mobile (aqueous and adsorbed) uranium phases, extractions 3 and 4 targeted high solubility uranium-bearing carbonate and silicate mineral phases, extraction 5 targeted iron oxides that may co-precipitate uranium, and extraction 6 targeted low solubility uranium precipitates. Extractions 4 through 6 should be considered operationally defined and do not necessarily prove direct association with the targeted phases. However, they provide evidence for predictions of future mobility based on the step in which they are extracted.

Sequential extraction tests were conducted on 19 pairs of Stage B pre-treatment and post-treatment sediment samples from the six paired boreholes and six samples from the three unpaired post-treatment boreholes. For the 19 pre-treatment and post-treatment Stage B sample pairs, the post-treatment samples showed significantly less mobile uranium compared to pre-treatment samples (Table 4-2). The total uranium that could be extracted from the post-treatment sediment samples was on average 33.2±50.8% lower than the total uranium that could be extracted from corresponding pre-treatment samples (Section 4.2.1 of PNNL-29650).

Table 4-2. Percent of High, Moderate, and Low Mobility Uranium Before and After Stage B Treatment

Uranium Mobility (Extractions)	Pre-Treatment	Post-Treatment
Highly mobile; rapid contaminant release (1 and 2)	6.7%	3.4%
Soluble precipitates; moderate to slow contaminant release (3 and 4)	58.6%	37.2%
Associated with low solubility precipitates; slow to very slow contaminant release (5 and 6)	34.8%	54.3%
Concentration range (and average)	10.3 to 94.1 (52.2) mg/kg	2.99 to 136 (34.0) mg/kg

To better understand which uranium minerals dissolve in which extraction fluids, sequential extractions were also conducted with three relatively higher solubility uranium minerals (uranophane and Na-boltwoodite, which are hydrous uranium silicates, and uranyl carbonate) and two relatively lower solubility uranium minerals (autunite and torbernite, which are uranium phosphate minerals). Results showed uranium carbonate minerals primarily dissolve in sequential extractions 3 and 4, hydrous uranium silicates dissolve in sequential extractions 3 and 4, and uranium phosphate minerals dissolve in sequential extraction 6. This indicates that uranium silicates, in addition to the targeted uranium carbonates, are extractable in steps 3 and 4. Therefore, uranium in 300 Area sediments in these extracts may be associated with either phase. Moreover, uranium in these extractions are still considered readily leachable whether present as carbonates or silicates.

Previous results further indicate that exposure of uranium carbonate and silicate phases to 70 mM polyphosphate (Section 3.4 of PNNL-29650) for 16 hours led to significant dissolution followed by precipitation after sufficient calcium sulfate was dissolved to favor formation of secondary phases. Therefore, it is possible that the decrease in uranium in extracts 3 and 4 in post-treatment sediments from Stage B are due to dissolution of uranium carbonate and silicate phases followed by reprecipitation as lower solubility phases over time.

Sequential extractions for phosphate concentrations were performed for the pre-treatment and post-treatment samples to evaluate the presence and distribution of precipitated phosphate following treatment. Because phosphate initially precipitates as amorphous calcium phosphate and then crystallizes over time to the stable mineral hydroxyapatite, sequential extractions 3, 4, 5, and 6 each dissolve some precipitated phosphate. In the pre-treatment samples, analysis of phosphate in extractions 1 (aqueous) and 2 (adsorbed) were all less than detection limits. Phosphate concentrations in half of the pre-treatment samples in extraction 3 (acetate pH 5) were nondetect. All of the phosphate results from extractions 4, 5, and 6 in the pre-treatment samples were detections. Pre-treatment sample phosphate extraction results varied from borehole to borehole and within discrete depth intervals (Section 4.5, Figures 4.46 through

4.48 of PNNL-29650). Some of the total extractable phosphate was natural and some was a uranium co-contaminant, which include copper and phosphate (Sections 2.0 and 5.1 of PNNL-29650). The average phosphate increase from pre-treatment to post-treatment sediments based on extractions 3 through 6 was 1,329 µg/g (Section 5.1 of PNNL-29650).

4.1.2.2 1,000-Hour Carbonate Solution Extractions

The 19 pre-treatment and post-treatment paired sediment samples and 6 unpaired post-treatment samples from Stage B boreholes were also subjected to a 1,000-hour carbonate extraction on the <2 mm (0.1 in.) grain size fraction of the sediments. This solution exchanges aqueous carbonate with mineral phases in order to target potentially mobile uranium associated with soluble phases like calcite or uranium-carbonates. Pre-treatment results show that the average mobile fraction of uranium detected is 42.5±9.6% (Table 4.3 in PNNL-29650). Comparison of the mobile fractions extracted from these carbonate extractions and the acetic acids extractions (sequential extractions 3 and 4) confirm that most of the uranium is potentially associated with carbonate mineral phases. Post-treatment extractions removed an average of 15.6±14.3%, or an average of 63% less mobile uranium compared to pre-treatment samples based on the carbonate extractions (Section 5.2 of PNNL-29650).

4.1.2.3 One-Dimensional Flow-Through Column Leach Tests

1-D flow-through column leach tests were performed on 10 paired pre-treatment and post-treatment samples and four unpaired post-treatment samples from Stage B boreholes to investigate changes in uranium leachability following treatment in terms of the release rate from sediments into groundwater and porewater. The term leach in this report refers to the ability of a contaminant to be remobilized in groundwater as measured under conditions simulating the natural subsurface (i.e., artificial groundwater). Results showed high variability in uranium mobility within zones 1 and 2 of the Stage B EA area. The amount of extractable uranium in the pre-treatment sediments varied from 3.19 to 45.35 µg/g, and the fraction of uranium leached from the sediments varied from 2.5% to 54% (Section 4.3.1 of PNNL-29650).

Column leach tests performed on zone 1 and zone 2 post-treatment sediment samples showed moderate uranium concentrations varied both laterally and vertically. The amount of total extractable uranium in post-treatment zone 1 samples ranged from 0.383 to 29.13 µg/g, and the amount of uranium leached in columns varied from 0.3% to 6% (Section 4.3.1 of PNNL-29650). The amount of total extractable uranium in post-treatment zone 2 samples ranged from 1.91 to 12.6 µg/g, and the amount of uranium leached varied from 2% to 35% (Section 4.3.1 of PNNL-29650). Unpaired post-treatment borehole C9736, which straddles zones 3 and 4 of the Stage B EA area, showed a moderate amount of uranium leaching (39%) (Section 4.3.1 of PNNL-29650). Overall, uranium leaching in 1-D column experiments decreased an average of 58.9±53.2% from pre-treatment to post-treatment samples (Section 4.3.2 of PNNL-29650). Morever, uranium leaching decreased in 9 of the 10 paired sediment samples with the 10th pair receiving limited phosphate.

4.1.2.4 Nitric Acid Phosphate Extraction Tests

Phosphate extractions were conducted on pre-treatment and post-treatment Stage B sediment samples using a 0.5 M nitric acid solution for a short period of time (15 minutes) to maximize dissolution of the newly precipitated phosphate phase (on mineral grains) and minimize dissolution of natural phosphate in the sediment. The increase in phosphate from pre-treatment to post-treatment samples averaged 206 µg/g (Section 4.5 of PNNL-29650). Results of the phosphate extraction in pre-treatment and post-treatment pairs show small increases in some post-treatment sediments, and large phosphate increases at a few depths (Figures 4.46 through 4.49 in Section 4.5 of PNNL-29650).

Phosphate extraction results using a 0.5 M nitric acid solution for the Stage A pre-treatment sediments had an average phosphate concentration of 1,750 µg/g. This elevated concentration is likely due to residual phosphate existing in the Stage A EA area from past liquid discharges (Section 6.3 of ECF-300FF5-16-0091, *Uranium Transport Modeling in Support of the Stage A Enhanced Attenuation Remedy at 300-FF-5 Operable Unit*). Results from post-treatment samples showed that phosphate concentrations were typically higher than 2,000 µg/g for samples that received significant polyphosphate solutions during Stage A treatment (Section 6.3 of ECF-300FF5-16-0091). Laboratory phosphate results and sequential extraction phosphate results for the Stage A samples are presented in Section 4.1 of SGW-59614.

4.1.2.5 Uranium Solid Phase Analysis on Pre-Treatment and Post-Treatment Sediment Samples

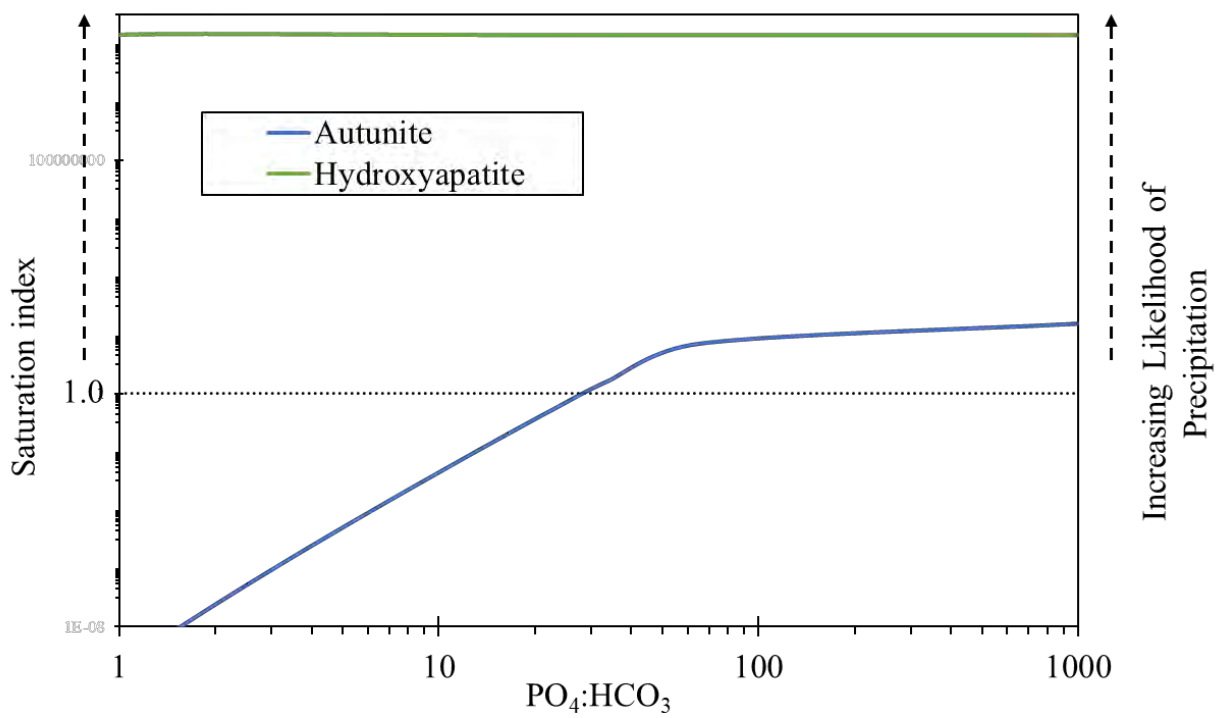
Several methods of solid phase analysis were conducted on two pre-treatment/post-treatment borehole pairs [C9967 (399-1-123)/C9729 and C9673 (399-1-129)/C9728] primarily to identify uranium precipitate composition, morphology, and oxidation state (Section 3.1.3 of this report). Detailed results are provided in Section 4.4 of PNNL-29650. These techniques showed that uranium was (1) present mostly in the +6 oxidation state, (2) consistent with copper-uranyl-phosphate in some pre-treatment and post-treatment samples, and (3) associated primarily with iron, copper, calcium, bismuth, and zinc. SEM-EDS showed an increase in phosphate precipitates after treatment.

Uranium was primarily present in the +6 valence state (via XANES), consistent with previous studies of North Process Pond sediments impacted by historic waste releases prior to polyphosphate injection. For the pre-treatment/post-treatment borehole pair 399-1-129 (C9673)/C9728 located in zone 1, µ-XRF shows uranium associated with copper, iron, and calcium as well as trace metals such as bismuth, titanium, and zinc mostly in the pre-treatment sediments. For the pre-treatment/post-treatment pair 399-1-123 (C9667)/C9729 located in zone 2, µ-XRF strongly correlated uranium with copper, iron, bismuth, and zinc. For both borehole pairs, weak correlations of uranium with calcium and titanium were observed, with slightly higher amounts of calcium in both post-treatment boreholes. This weak correlation may indicate possible calcium phosphate species (e.g., calcium-uranyl-phosphate phases like autunite) or carbonate species (e.g., co-precipitation with calcite) in association with uranium. Sediments from pre-treatment boreholes 399-1-129 (C9673) and 399-1-123 (C9667) exhibited some small uranium particles with no strong correlation to other elements mapped. This suggests that there are either discrete uranium particles (e.g., oxides or hydroxides) or uranium in association with lighter elements (e.g., silicon and phosphorus) that were not measurable at APS. A conglomerate of particles including calcium and phosphorus was identified by SEM-EDS in the post-treatment sample from borehole C9729 at 7.62 m (25 ft) bgs, which is likely the calcium phosphate mineral apatite. However, due to limitations with SEM-EDS instrument detection limits for uranium and operational constraints at the APS facility (inability to simultaneously analyze uranium and phosphate surface phases due to radiological control restrictions), it was not possible to simultaneously measure phosphorus and uranium to determine if there was an increase in uranium phosphate species (e.g., autunite group minerals) in post-treatment sediments relative to pre-treatment sediments.

Geochemical speciation modeling was used to complement solid phase characterization since results were inconclusive as to the major phases controlling sequestration of uranium (e.g., determining if conditions favored formation of specific uranium phases or apatite coatings). Previous studies have identified multiple mechanisms that may decrease uranium mobility: (1) phosphate precipitation (e.g., apatite group minerals) that can structurally incorporate uranium, (2) autunite mineral group precipitation (e.g., $Ca(UO_2)_2(PO_4)_2 \bullet 10\text{-}12H_2O$), (3) aqueous uranium sorption to precipitated calcium-phosphate phases, and (4) mineral coating of existing uranium surface phases (PNNL-17818, *300 Area Treatability Test: Laboratory Development of Polyphosphate Remediation Technology for In Situ Treatment of*

Uranium Contamination in the Vadose Zone and Capillary Fringe; PNNL-17480, *Challenges Associated with Apatite Remediation of Uranium in the 300 Area Aquifer*; Wellman et al., 2008; Mehta et al., 2016; Lammers et al., 2017, "Groundwater uranium stabilization by a metastable hydroxyapatite"). While these models cannot predict uranium incorporation with or coating by secondary minerals (e.g., apatite and calcite), they can identify the phases that are thermodynamically favorable to precipitate in the subsurface geochemical environment during polyphosphate injection and following re-introduction of groundwater and river water through natural exchange processes.

The potential precipitation of apatite and uranium phases was investigated via modeling in Geochemist's Workbench. It shows that apatite precipitation is favored from pH 6.5 to 8 with the injection solution (i.e., 87 mM phosphate, 61 mM carbonate). These results are similar to precipitates reported by Mehta et al., 2016. Under the injection solution conditions with a high bicarbonate concentration, simulations indicate that uranyl carbonate minerals (e.g., andersonite, $Na_2Ca(UO_2)(CO_3)_3 \bullet 6H_2O$, and grimselite, $K_3Na(UO_2)(CO_3)_3 \bullet H_2O$)) are the most likely to form initially. However, phosphate remains in the immediate area due to precipitation (e.g., hydroxyapatite) and sorption, where it may slowly dissolve or desorb into porewaters. Porewater bicarbonate in cores (6 months after injection) are near natural concentrations indicating that the high bicarbonate from injection solutions has likely advected from the system. Therefore, in the long-term, bicarbonate is expected to be less than phosphate in porewaters based on the solubility of apatite. Moreover, uranium may be favored to precipitate as autunite group minerals over time (Figure 4-4). Figure 4-4 shows that autunite ($Ca(UO_2)_2(PO_4)_2 \bullet 10\text{-}12H_2O$) precipitation is favored with increasing phosphate while hydroxyapatite is highly favored throughout the range of conditions (Section 4.4.4 of PNNL-29650). This trend is consistent with previous modeling and the hypothesis that apatite acts as a source for additional autunite formation (PNNL-17818). Moreover, it has been shown experimentally in laboratory column experiments (Lammers et al., 2017).



Note: Showing autunite and hydroxyapatite precipitation predicted with respect to the molar ratio of phosphate to bicarbonate.

Figure 4-4. Geochemical Simulations of Targeted Polyphosphate Injection Solution

4.2 Groundwater Sampling and Monitoring

The following sections provide results of vadose zone pore water and groundwater monitoring and sampling before, during, and after application of polyphosphate solutions to the LVZ and PRZ. The purpose of the sampling was to evaluate short-term impacts to uranium and phosphate concentrations and other groundwater chemistry parameters.

4.2.1 Manual Monitoring

This section summarizes results of manual groundwater monitoring (Section 3.2.1 of this report). Analytical results for the samples collected as part of operational monitoring are provided in Appendix B of this report, and analytical results for the samples collected as part of the long-term monitoring are provided in Appendix E. The PRZ wells are screened above the average water table and only provide representative samples when the water table is high due to elevated river stage or polyphosphate injections in nearby wells. As a result, fewer PRZ samples are available than aquifer samples. The data for Stage A groundwater concentration observations are presented in Section 4.2.1 of SGW-59614.

Pre-treatment phosphate concentrations in groundwater monitoring wells surrounding the Stage B treatment area ranged from 0.205 to 16.1 mg/L. These concentrations were higher than pre-treatment concentration during Stage A, which ranged from 0.082 to 0.27 mg/L in aquifer wells. These results indicate the Stage B pre-treatment samples detected residual phosphate from the Stage A treatment.

Stage A treatment included injections into the aquifer and the PRZ. There was no significant increase in phosphate concentrations during aquifer injections despite the proximity of the monitoring wells to the injection wells. This was attributed to dilution in the aquifer, and therefore Stage B treatment did not include injections into the aquifer.

Concentration trends of phosphate in the aquifer monitoring wells based on daily and weekly sampling during and following Stage B treatment (August through October 2018) are shown in Figures 4-5 and 4-6. Trends of phosphate in aquifer monitoring wells during daily, weekly, and monthly sampling (August 2018 through June 2019) are shown in Figures 4-7 and 4-8. Figures 4-9 through 4-15 show the areal distribution of phosphate based on daily sampling during and following treatment in September 2018. With the exception of PRZ wells 399-1-146 and 399-1-154 (in zone 4), where no daily samples could be collected due to low water, all aquifer and PRZ wells indicate the injection wells successfully delivered an elevated concentration of phosphate to the monitoring wells within their radius of influence. A summary of the phosphate groundwater concentration observations for each Stage B injection zone during polyphosphate injections is provided below.

Zone 1: During injections into the PRZ (September 4 to 6, 2018), phosphate concentrations in the PRZ and aquifer monitoring wells in zone 1 increased to a range of 22.1 to 7,360 mg/L (Figures 4-5 and 4-9). During injections into the LVZ (September 7 to 8, 2018), phosphate concentrations increased to a range of 1,810 to 7,970 mg/L (Figures 4-5 and 4-9).

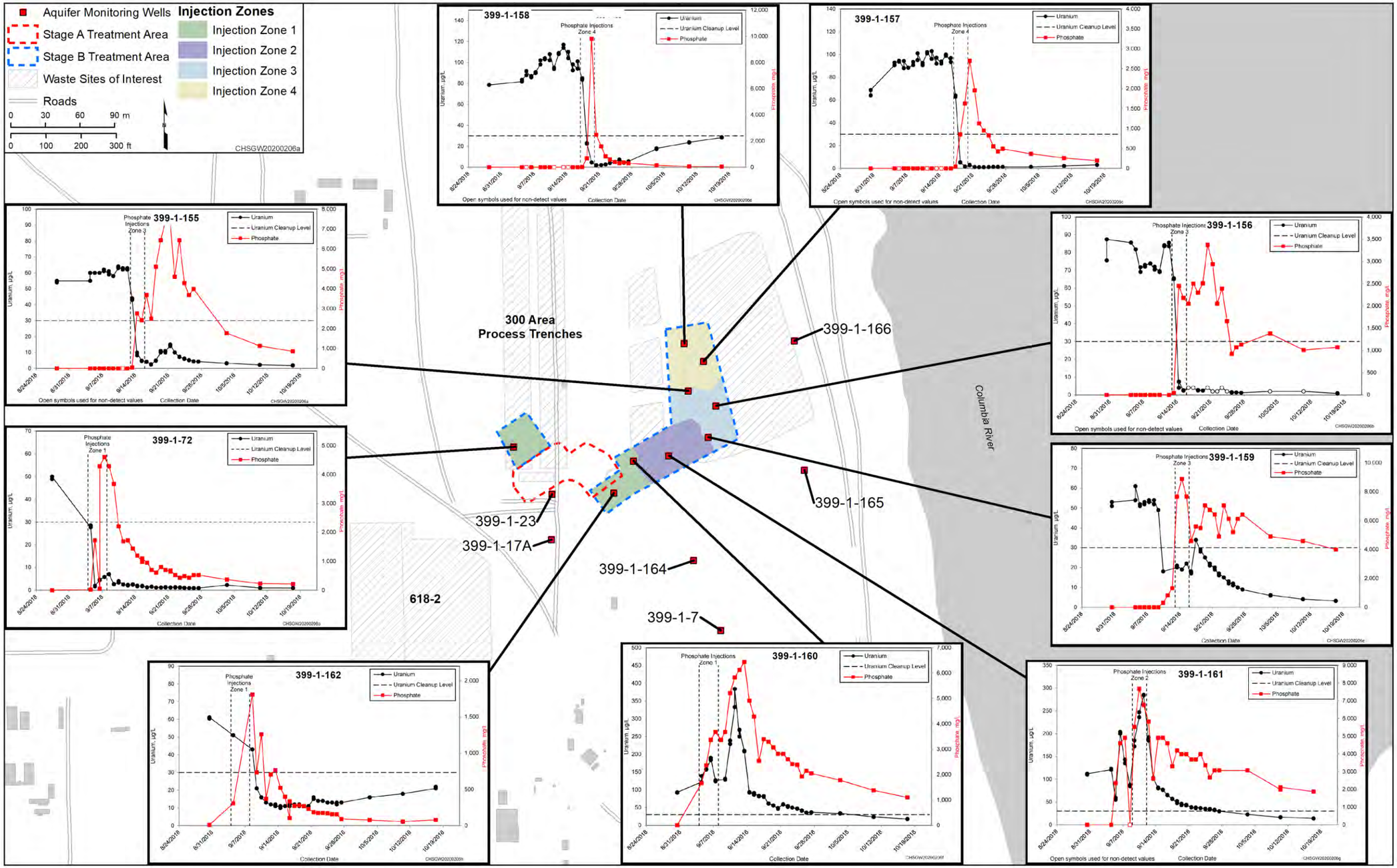


Figure 4-5. Uranium and Phosphate Concentrations in Groundwater Samples from Wells Within the Treatment Area Collected from August through October 2018

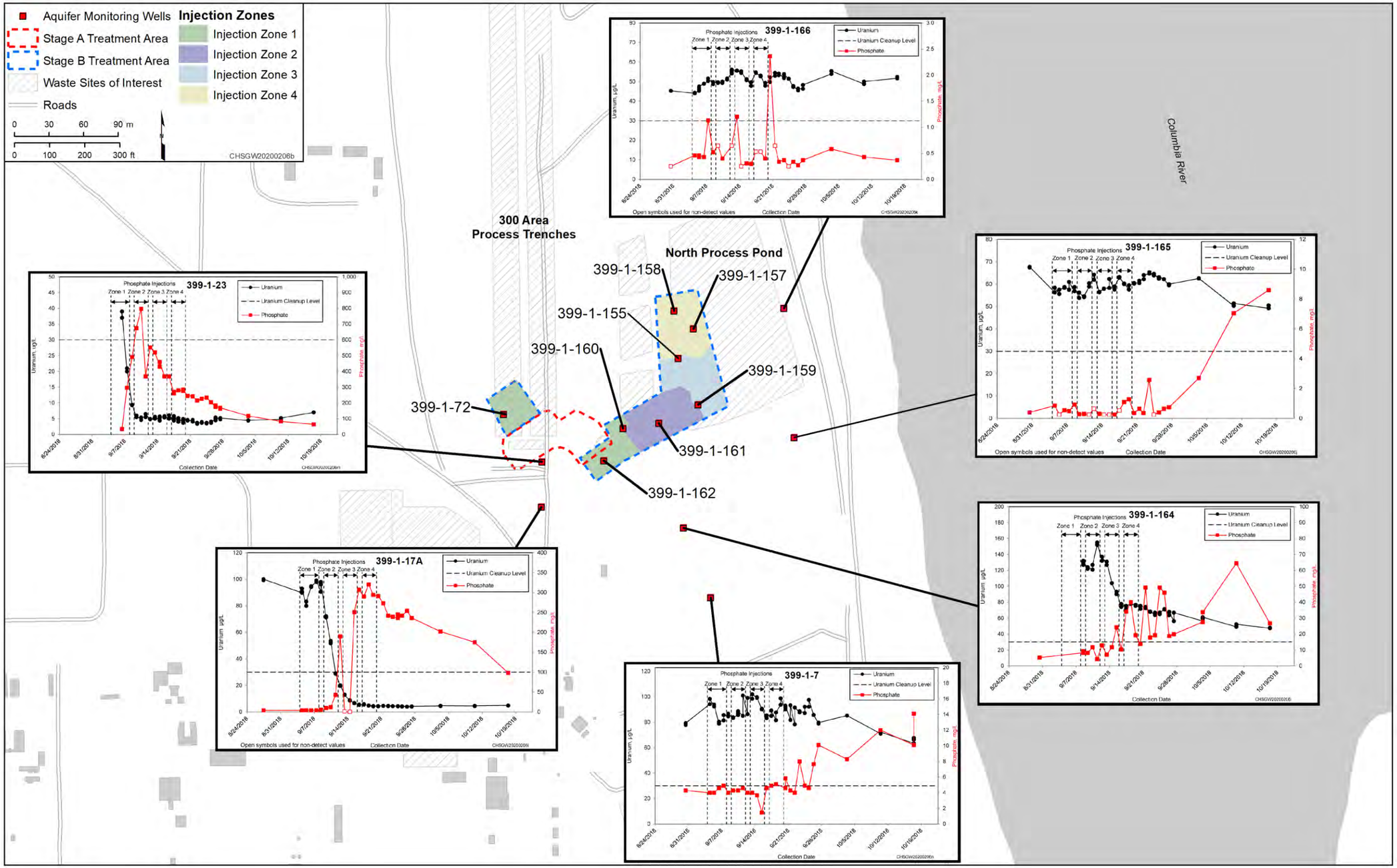


Figure 4-6. Uranium and Phosphate Concentrations in Groundwater Samples from Wells Outside of the Treatment Area Collected from August through October 2018

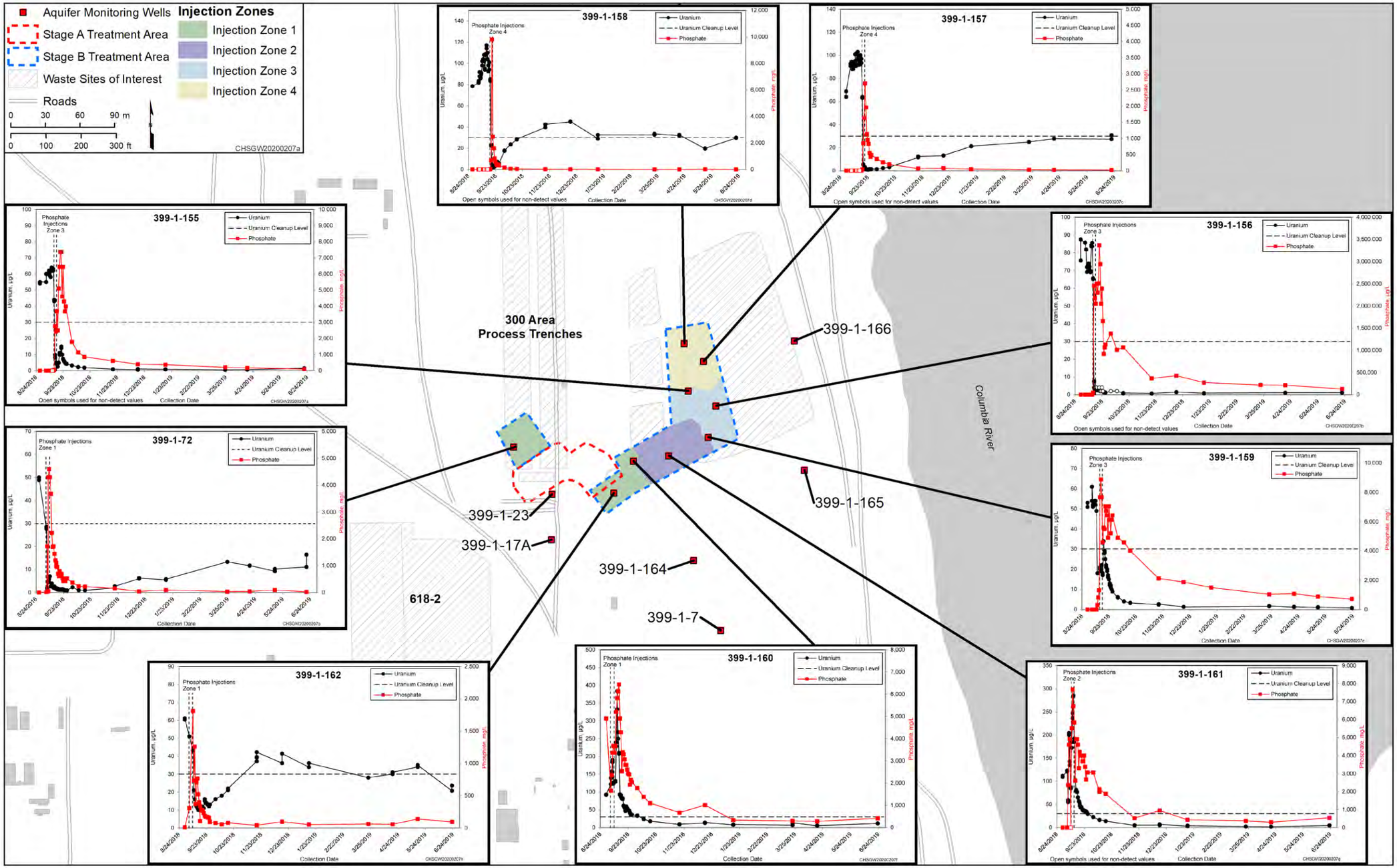


Figure 4-7. Uranium and Phosphate Concentrations in Groundwater Samples from Wells Within the Treatment Area Collected from August through June 2019

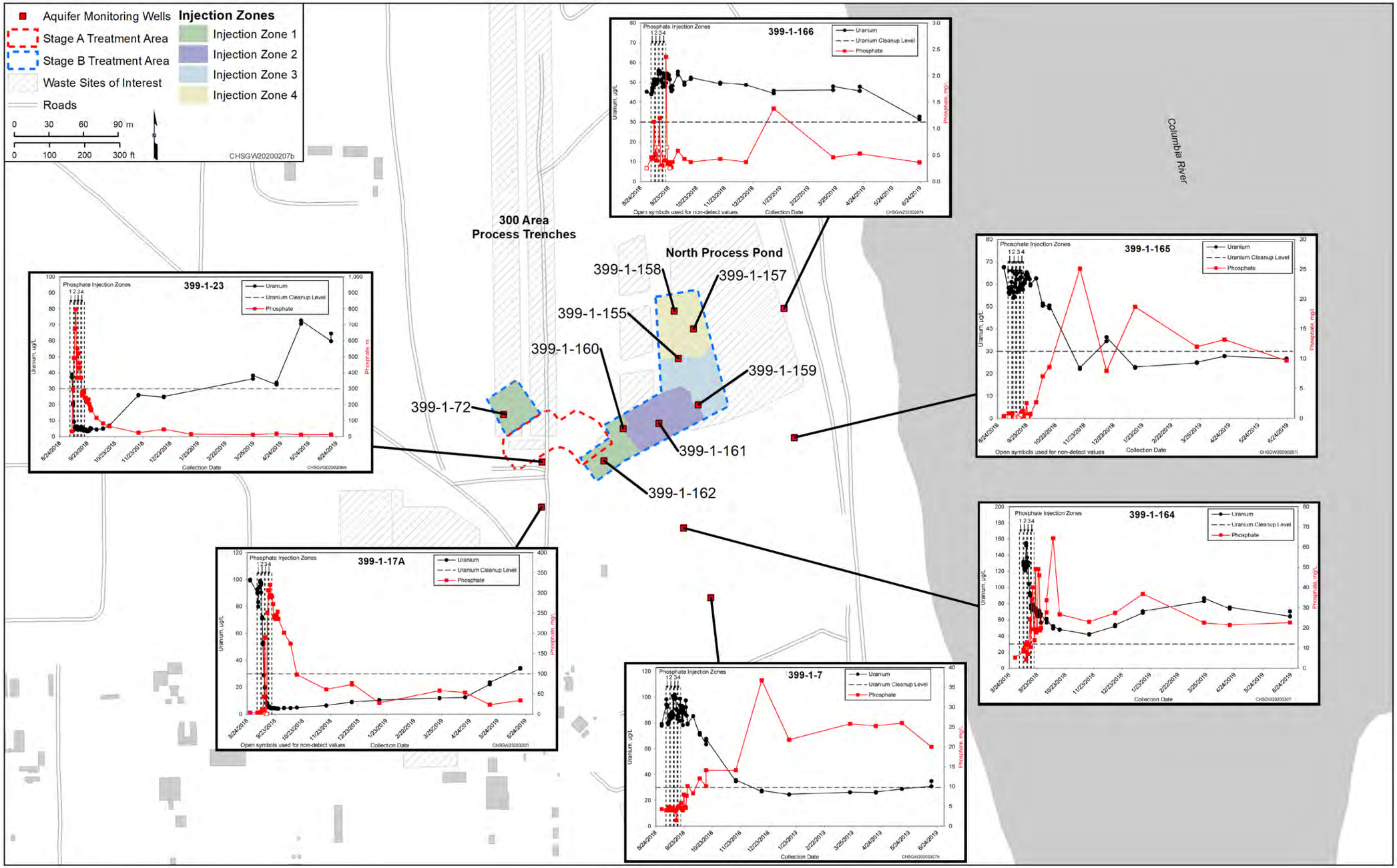


Figure 4-8. Uranium and Phosphate Concentrations in Groundwater Samples from Wells Outside the Treatment Area Collected from August 2018 through June 2019

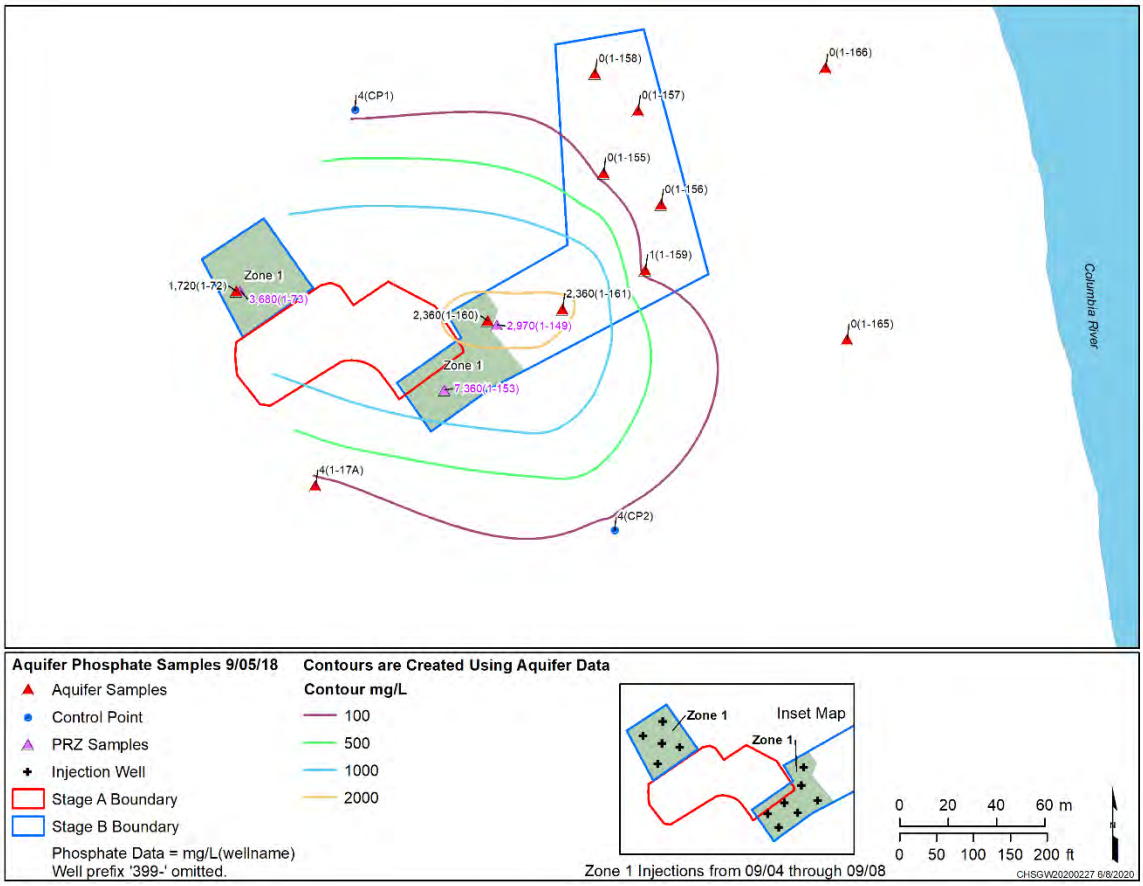


Figure 4-9. Phosphate Concentrations in the Aquifer and PRZ on September 5, 2018 (During Treatment)

Zone 2: During injections into the PRZ (September 9 to 11, 2018), phosphate concentrations in the PRZ and aquifer monitoring wells in zone 2 increased with a range of 368 to 9,510 mg/L (Figure 4-5). Figure 4-10 shows the rise in phosphate in concentrations on the first day of zone 2 injections. During injections into the LVZ (September 11 to 12, 2018), phosphate concentrations increased to a range of 368 to 7,360 mg/L (Figure 4-5).

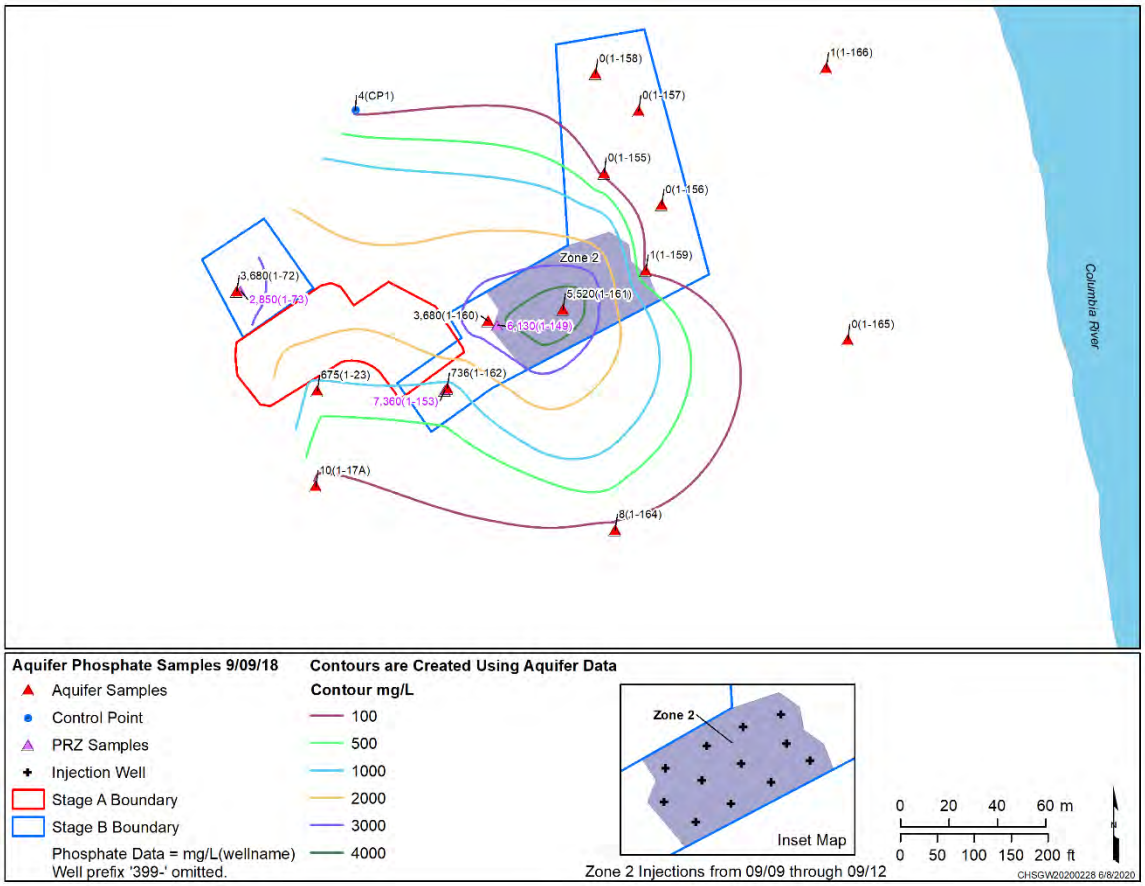


Figure 4-10. Phosphate Concentrations in the Aquifer and PRZ on September 9, 2018 (During Treatment)

Zone 3: During injections into the PRZ (September 13 to 15, 2018), phosphate concentrations in the PRZ and aquifer monitoring wells in zone 3 ranged from 46 to 8,890 mg/L (Figure 4-5). Figure 4-11 shows the range of phosphate concentrations at the start of zone 3 injections. During injections into the LVZ (September 15 to 16, 2018), phosphate concentrations ranged from 2,050 to 7,670 mg/L (Figure 4-5).

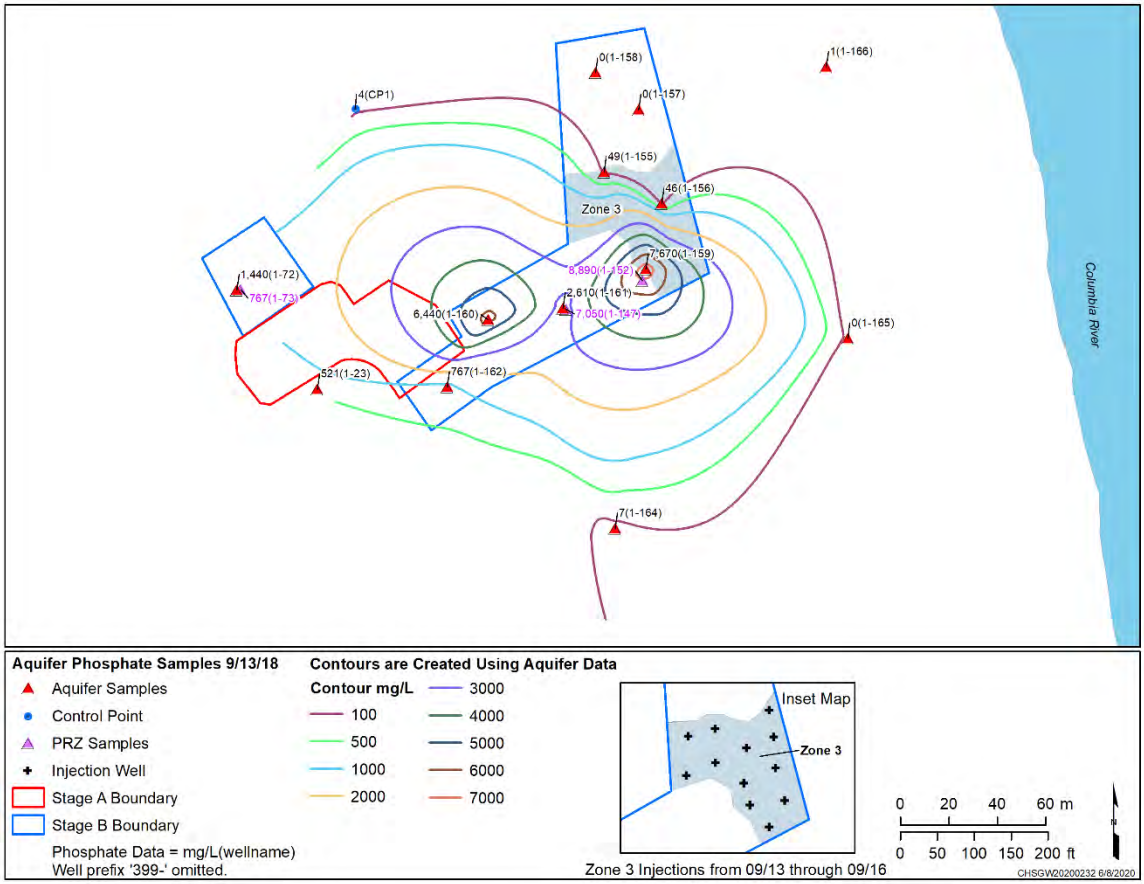


Figure 4-11. Phosphate Concentrations in the Aquifer and PRZ on September 13, 2018 (During Treatment)

Zone 4: During injections into the PRZ (September 16 to 18, 2018), phosphate concentrations in the PRZ and aquifer monitoring wells in zone 4 ranged from 20 to 5,700 mg/L (Figures 4-5 and 4-12). During injections into the LVZ (September 19 to 20, 2018), phosphate concentrations ranged from 1,640 to 9,810 mg/L (Figures 4-5 and 4-13).

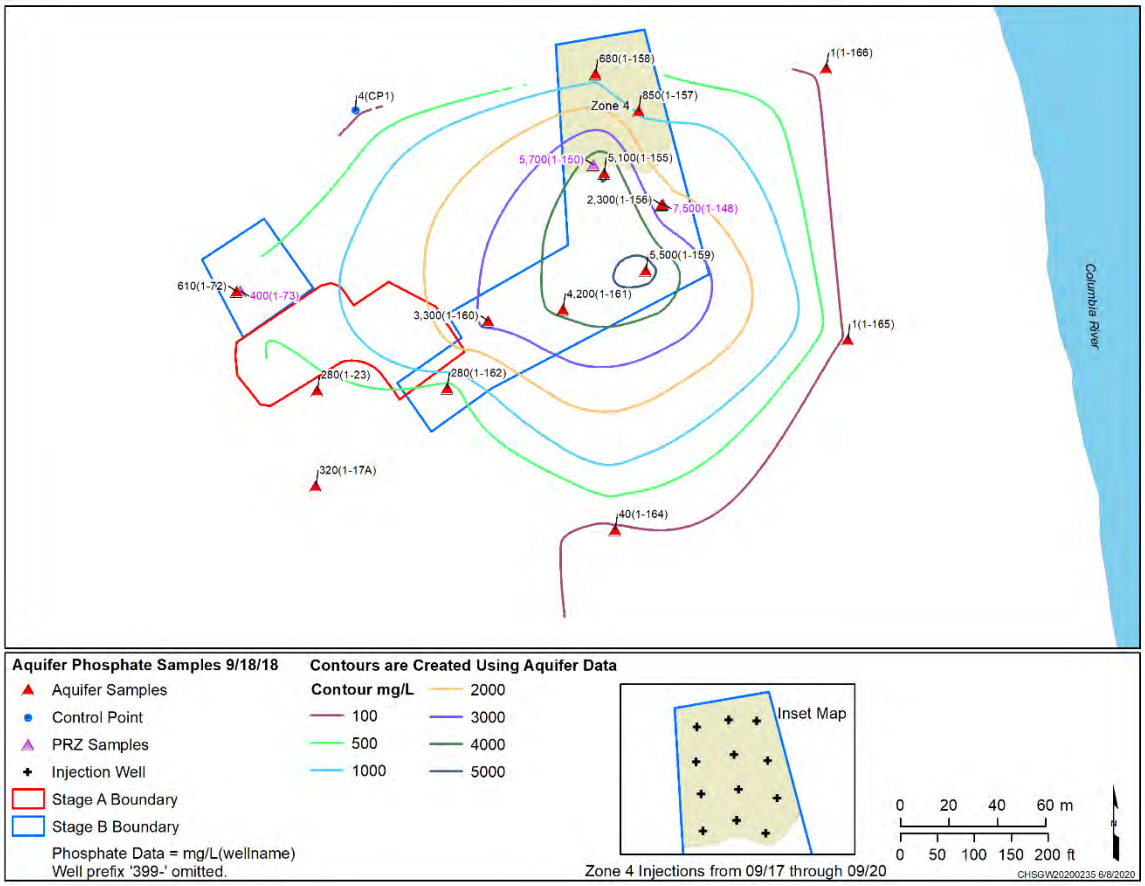


Figure 4-12. Phosphate Concentrations in the Aquifer and PRZ on September 18, 2018 (During Treatment)

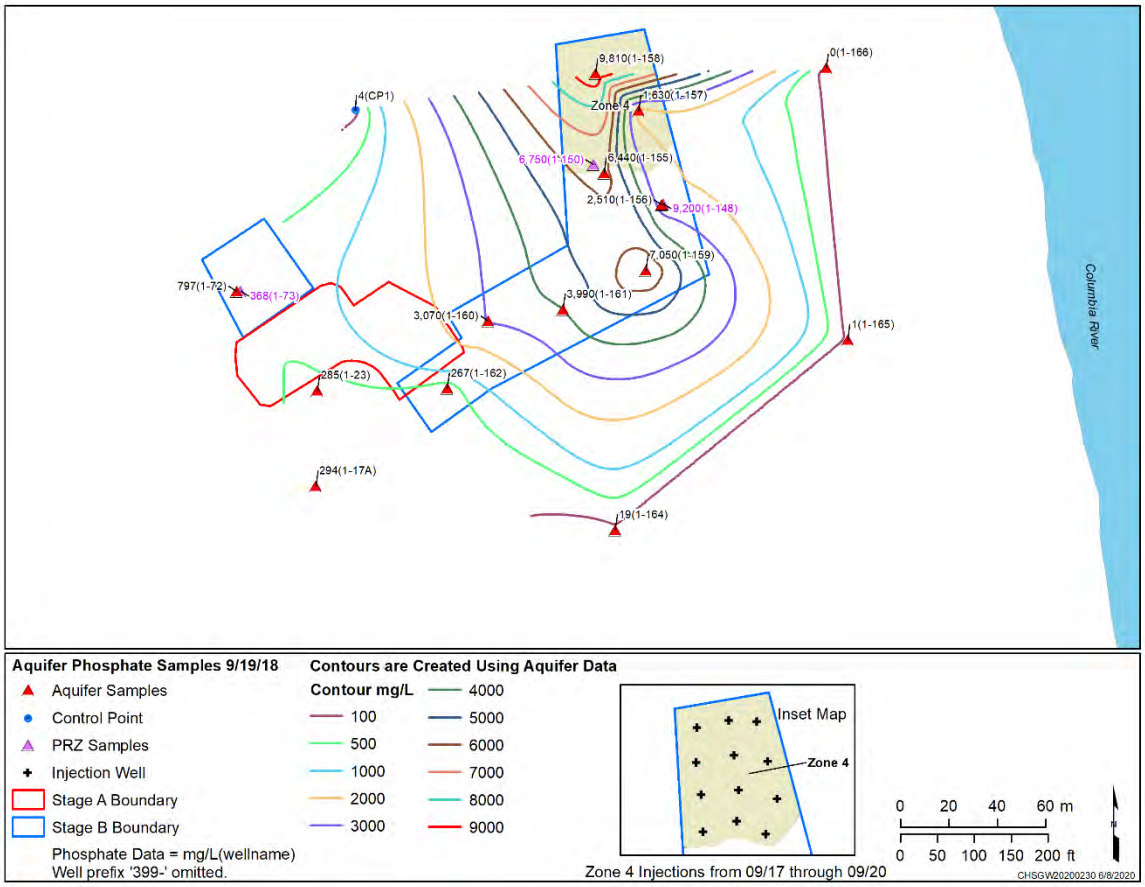


Figure 4-13. Phosphate Concentrations in the Aquifer and PRZ on September 19, 2018 (During Treatment)

The phosphate concentration trends observed during PRZ injections in Stages A and B were similar. During both stages, polyphosphate injections produced a rapid peak in phosphate concentrations in the aquifer and PRZ wells, followed by a gradual decrease. Figures 4-14 and 4-15 exhibit the start of the gradual decline of phosphate concentration post-treatment with the contours. This suggests that both Stages A and B injections to the PRZ were effective in delivering a high concentration of phosphate to the aquifer and PRZ for short durations.

During Stage B treatment, phosphate concentrations averaged approximately 3,300 mg/L at aquifer wells and approximately 6,300 mg/L at PRZ wells. Direct comparison of phosphate concentrations at paired PRZ and aquifer monitoring wells showed that the phosphate concentrations in PRZ wells were typically equal to or greater than the paired aquifer well concentrations, which indicates that there was some dilution of phosphate as it migrated and mixed with groundwater.

Three aquifer wells showed phosphate concentrations lower than average for aquifer wells, and significantly lower than their paired PRZ wells during Stage B treatment:

- Aquifer well 399-1-162, located in zone 1, had the lowest overall phosphate concentrations among the aquifer wells (Figure 4-5). Paired PRZ well 399-1-153 showed phosphate concentrations that were similar to other PRZ wells.
- Aquifer well 399-1-156, located in zone 3, had much lower phosphate concentrations than paired PRZ well 399-1-148.

- Aquifer well 399-1-157, located in zone 4, had phosphate concentrations lower than most other aquifer wells (Figure 4-5). The paired PRZ well (399-1-146) was not successfully sampled during daily sampling operations.

Wells that were located near the border of a neighboring injection zone exhibited secondary phosphate peaks, prolonged periods of high phosphate concentrations, or partial recovery of phosphate concentrations during injections in the neighboring zone. Aquifer/PRZ well pair 399-1-156/399-1-148, located in zone 3, showed elevated phosphate for 1 week after the end of injections to zone 3, which coincided with the beginning of injections to zone 4 (Figure 4-5). Aquifer/PRZ well pairs 399-1-159/399-1-152 and 399-1-156/399-1-148, located in zone 3, are all generally downgradient of zone 4, which may explain the prolonged or secondary peaks of phosphate concentrations exhibited in these wells. Aquifer well 399-1-159 did not show a clear declining trend in phosphate concentrations until October 2018 (Figure 4-5).

Near-field downgradient aquifer wells 399-1-17A, 399-1-23, 399-1-164, and 399-1-165 began to show elevated phosphate concentrations within 1 to 2 weeks after the start of injections in zones 1 through 3, which are located upgradient of these wells (Figure 4-6). Far-field downgradient aquifer wells (e.g., 399-2-2) began to show elevated concentration of phosphate in October and November 2018 (1 to 2 months after treatment). Well 399-1-166, which is cross gradient to groundwater flow in the Stage B area, did not exhibit a change in phosphate concentrations during or following injections (Figures 4-6 and 4-8).

In the weekly post-treatment samples, all wells except aquifer well 399-1-162 exhibited decreasing phosphate trends. Generally, aquifer and PRZ well aqueous phosphate concentrations were <2,000 mg/L for both Stages A and B during the weekly sampling events. However, concentrations in two aquifer wells and five PRZ wells remained above 2,000 mg/L for 1 to 4 weeks after Stage B injections. This suggests that either phosphate was continuing to infiltrate down through the LVZ and PRZ or polyphosphate solutions may have persisted in some areas of the aquifer and PRZ and did not rapidly dilute and migrate in the groundwater.

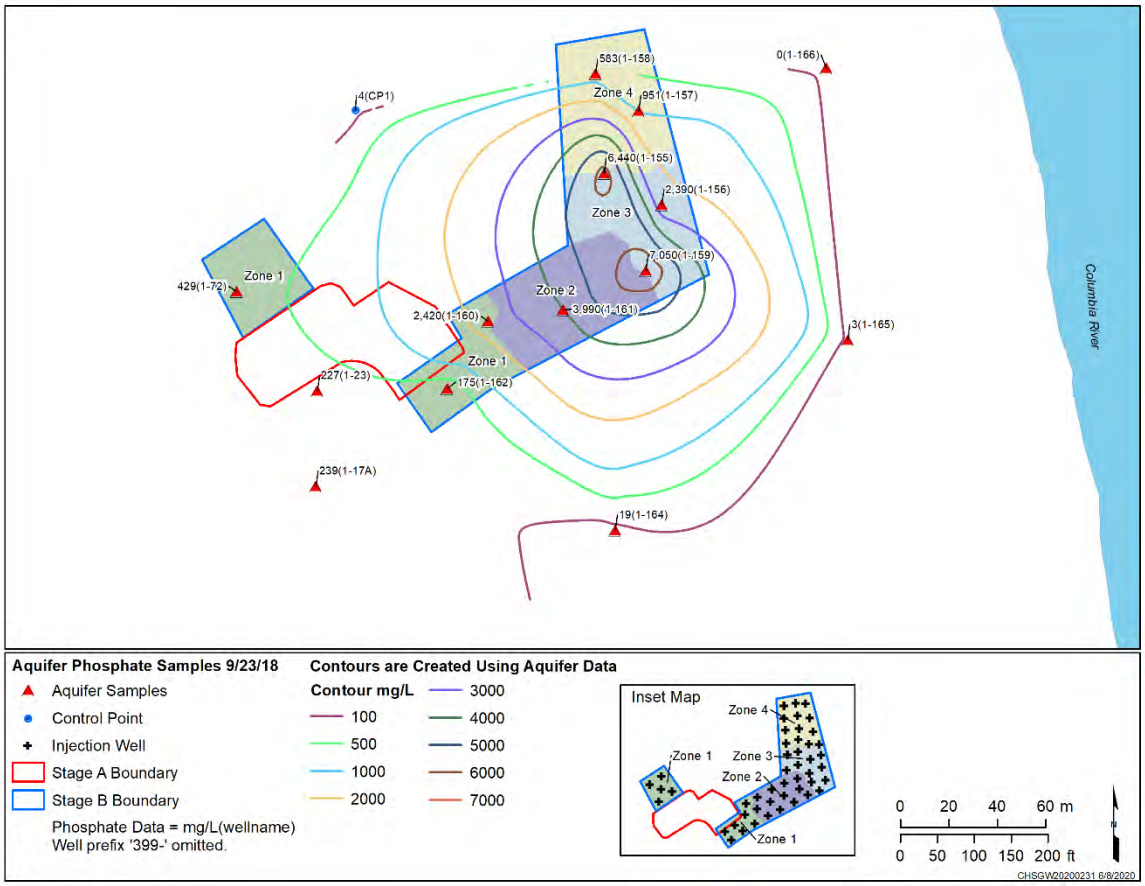


Figure 4-14. Phosphate Concentrations in the Aquifer and PRZ on September 23, 2018 (After Treatment)

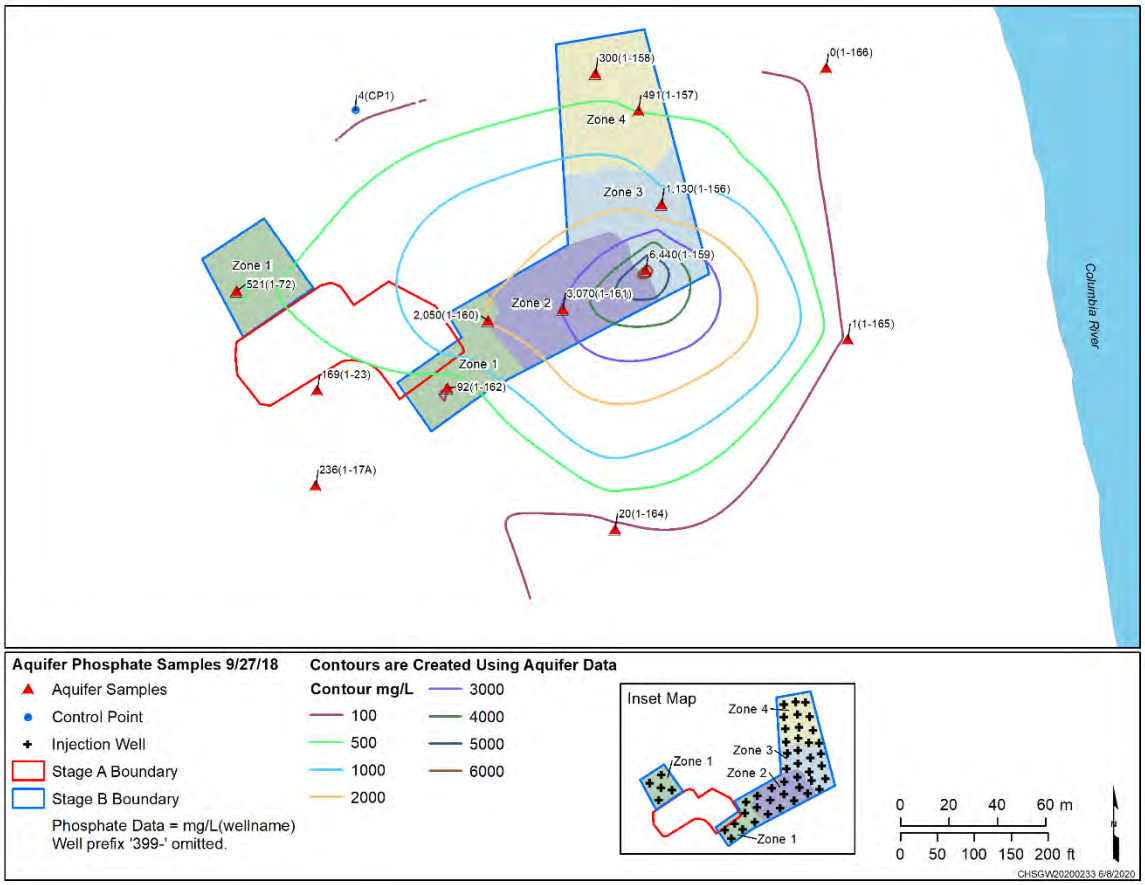


Figure 4-15. Phosphate Concentrations in the Aquifer and PRZ on September 27, 2018 (After Treatment)

PRZ wells 399-1-146 and 399-1-154, located in zone 4, were not successfully sampled during daily sampling but were sampled weekly in October 2018. Phosphate concentrations did not exceed 500 mg/L, but were greater than average pre-treatment baseline values. The paired aquifer wells showed a brief phosphate peak and a significant decrease in concentrations immediately after injections. This indicates that zone 4 may have had more dilution and quicker migration of the polyphosphate solution in the groundwater, which is consistent with the results for the ERT imaging analysis of cluster 3 (PNNL-28619). Results from ERT imaging in cluster 3 indicated there may have been rapid draining of polyphosphate solution toward the water table after injections.

Variable phosphate drainage to the aquifer was observed in Stage A during weekly sampling (Section 4.2.1 of SGW-59614). The western area of Stage A drained faster than the eastern area of Stage A, which was consistent with ERT data. This indicates that there is heterogeneity in the character of the subsurface sediments in the Stage A and B areas and that ERT provides a reliable measure to observe polyphosphate solution wetting front migration by tracking changes in the bulk conductivity of the sediment and pore water. ERT is unlikely to be able to track actual phosphate precipitation because phosphate precipitation is unlikely to change the bulk conductivity of the system.

Monthly sampling performed for 6 months to 1 year after injections showed that all wells within and downgradient of the Stage B treatment area exhibited a steady decline in phosphate concentrations, but only well 399-1-23 had returned to pre-treatment baseline phosphate concentrations (Figure 4-8).

Uranium concentrations in aquifer and PRZ wells responded almost immediately to phosphate injections. All Stage B monitoring wells were sampled daily to evaluate whether the injections may be flushing uranium in the LVZ and PRZ soils to the aquifer. It was suspected that minor uranium flushing occurred during Stage A operations but the monitoring data were inconclusive (Section 4.2.1 of SGW-59614). Application of the polyphosphate solutions with higher ionic strength would be expected to temporarily mobilize uranium. Of all the Stage B aquifer monitoring wells, only 399-1-160 and 399-1-161 exhibited increases in uranium concentrations during injections with peaks of 384 and 285 µg/L, respectively (Figure 4-5). The elevated uranium concentrations lasted 4 days and then the uranium concentrations dropped precipitously like the other Stage B monitoring wells. These two aquifer monitoring wells with nominal uranium increases (399-1-160 and 399-1-161) are in the portion of Stage B where the highest concentrations of uranium were observed in the soils. The uranium concentration increases in groundwater do not represent a significant portion of the uranium mass in that portion of the Stage B area. PRZ monitoring well 399-1-73 had a large uranium increase during 2 days of phosphate injections, reaching a maximum of 3,600 µg/L uranium on September 7, 2018 (Figure 4-16). However, the paired aquifer monitoring well 399-1-72 had uranium concentrations of 6 µg/L on September 7, 2018, consistent with the period before injections and far below the CUL (Figure 4-5). Increases in uranium concentration were not observed at any of the wells downgradient of 399-1-160 and 399-1-161 during Stage B operations (Figure 4-6). Uranium mass mobilized to the groundwater during Stage B injections appears to be relatively inconsequential and the resulting decrease in uranium concentrations in the groundwater over time is due to polyphosphate treatment rather than removal of uranium mass from the system.

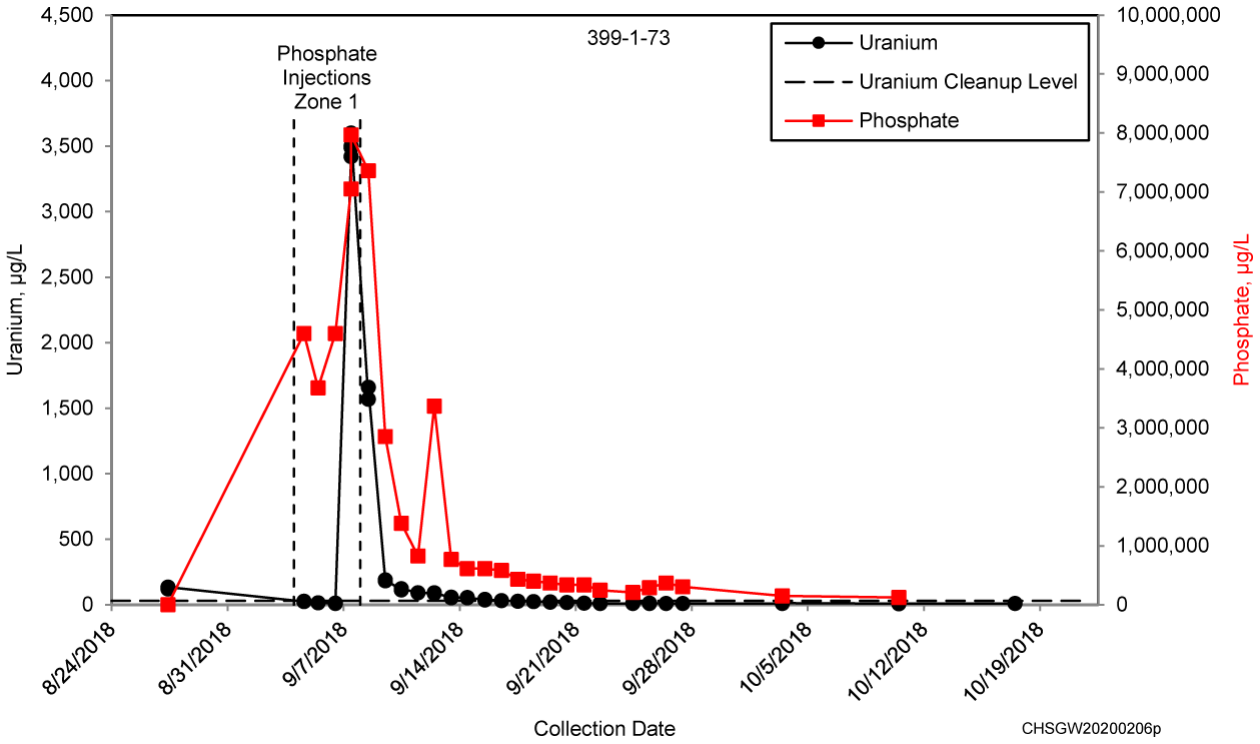


Figure 4-16. Uranium and Phosphate Concentrations in Groundwater Samples from Well 399-1-73 Collected from August through October 2018

Trend plots of phosphate, specific conductance, and uranium indicate that as polyphosphate was injected into the PRZ and LVZ during Stage B, there was a corresponding decrease in uranium concentrations for all 24 wells. Concentrations remained low or continued to decline in most of the wells for up to 6 months

after injections. A summary of the groundwater concentration observations for each Stage B injection zone 6 to 12 months following injections is provided below.

1. Zone 1: Four of the five aquifer and PRZ wells had uranium concentrations near or below the 30 µg/L CUL during the period of polyphosphate injections (Figure 4-5). All five wells reported uranium concentrations below the CUL 8 months later during the high river stage sampling event in June 2019 (Figure 4-7). Phosphate concentrations for the aquifer monitoring wells remained persistently above background levels for 6 to 12 months after injections (Figure 4-7).

2. Zone 2: Uranium concentrations in the three PRZ wells and one aquifer well declined during and after treatment (Figure 4-5). All had uranium concentrations below the CUL 8 months after injections during the high river stage sampling event (Figure 4-7). Phosphate concentrations remained above background levels 6 to 8 months after zone 2 injections (Figure 4-7).

3. Zone 3: Uranium concentrations in the three aquifer wells fell below 5 µg/L during treatment and remained below this concentration 6 to 12 months after treatment (Figures 4-5 and 4-7). Concentrations in the one PRZ well were below the 30 µg/L CUL. Phosphate concentrations remained three orders of magnitude higher than the baseline values for the aquifer wells 6 to 12 months after treatment (Figure 4-7).

4. Zone 4: All three PRZ and two aquifer wells in this zone had uranium concentrations less than the uranium CUL during the polyphosphate injection period in September 2018 (Figure 4-5). PRZ well 399-1-150 did not exceed the uranium CUL at any time (maximum concentration about 20 µg/L). The four other wells in this zone began to exhibit increasing uranium trends starting in October 2018, and concentrations remained at or above the uranium CUL 6 months after treatment (Figures 4-5 and 4-7). The average phosphate concentrations at these wells were consistently lower than the averages for aquifer wells or PRZ wells in other zones.

Uranium concentrations in downgradient monitoring wells decreased as phosphate concentrations increased (Figure 4-6). Three of the six downgradient wells had uranium concentrations below the CUL by December 2018 (Figure 4-8). Uranium concentrations in wells 399-1-164 and 399-1-166 remained above the uranium CUL during and after treatment (through June 2019) (Figures 4-6 and 4-8). Overall, wells downgradient of the Stage A and B EA areas exhibited decreased uranium concentrations during the polyphosphate treatment (Section 4.2.1 of SGW-59614). Most of the wells within and downgradient of the Stage A and B EA areas reached uranium concentrations near or below the uranium CUL during and after the polyphosphate treatment.

Stage A and B groundwater monitoring results showed an increase in trace metals such as arsenic and vanadium during and after polyphosphate injections. Concentrations were highest in treatment zone wells and declined after treatment, but arsenic remained above the 10 µg/L drinking water standard in June 2018 in some wells. Downgradient wells also increased temporarily, but declined to levels near or below the drinking water standard by June 2019 (Figure 4-17). Concentrations of trace metals subsequently declined as phosphate concentrations declined. Both arsenic and vanadium are likely naturally occurring and possibly were mobilized by dissolution of iron oxides and clay minerals from interaction with phosphate-bearing solutions. Vanadium could also be made available from dissolution of a uranium-bearing mineral such as carnotite (a potassium-uranium-vanadium mineral).

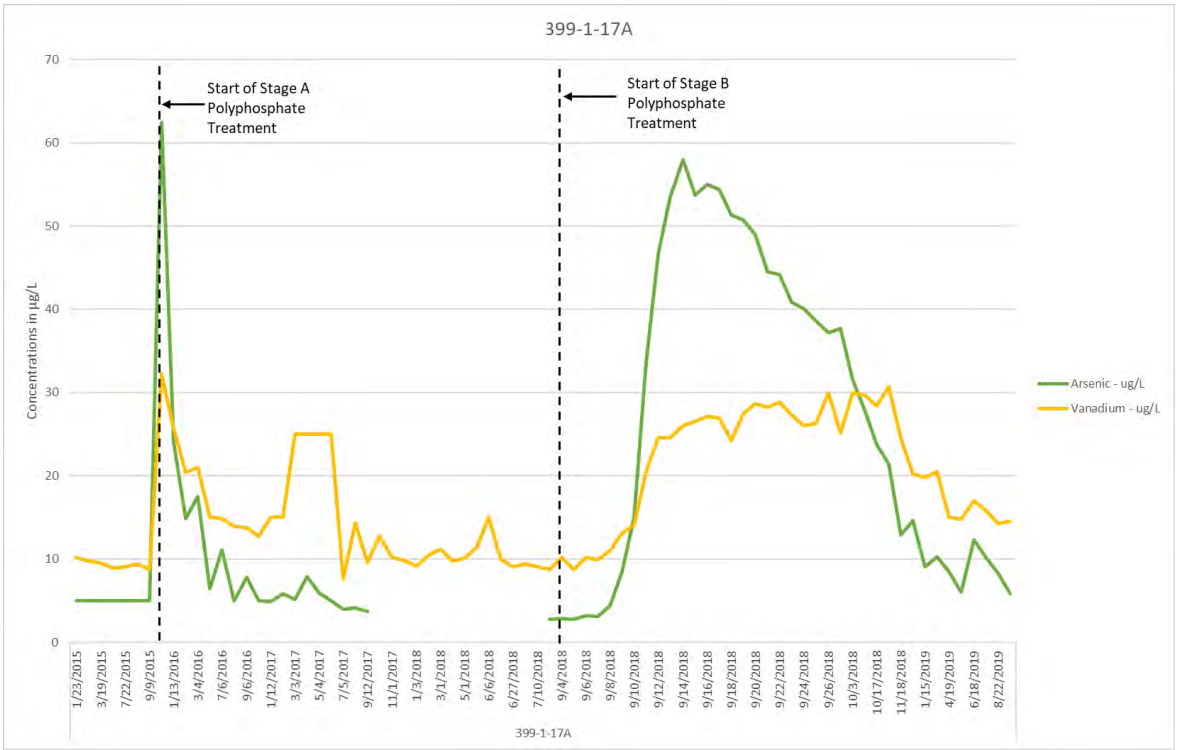


Figure 4-17. Temporary Arsenic and Vanadium Concentration Increases in Well 399-1-17A Following Stage A and B Polyphosphate Treatments

4.2.2 Automated Monitoring

Many observation and testing redundancies were built into the performance of field activities for this project to make sure there was a robust data set that could be used in evaluating project performance. The automated monitoring at aquifer and PRZ well locations described in Section 3.2.2 of this report was used because limited groundwater accessibility was anticipated at the PRZ wells, which were screened above the water table. The collection of continuous specific conductance measurements could be correlated with phosphate injections and help corroborate the ERT results that would verify the delivery of polyphosphate solution to the PRZ. Analytical results for the automated groundwater monitoring measurements are summarized in Appendix C of this report. Detailed results for the Stage A automated monitoring are reported in in Section 4.2 of SGW-59614.

4.2.2.1 In Situ Monitoring

Downhole instruments were installed in the 24 aquifer and PRZ monitoring wells to monitor multiple groundwater parameters during phosphate injections. The instrumentation was operated and data were collected and recorded at 30-minute intervals from July 2017 until November 2018. Automated specific conductance data were collected to assess phosphate migration. In addition, groundwater samplers recorded daily measurements of specific conductance using field instrumentation during daily sampling activities and specific conductance was analyzed at laboratories from the groundwater sample analyses. Therefore, for each sampling event for phosphate there are two data sources for specific conductance and any observed increases in specific conductance would indicate the presence of the higher ionic strength polyphosphate solutions during injections as polyphosphate solution reached the monitoring locations.

PRZ specific conductance measurements could not be collected during every 30-minute automated or daily field sampling collection interval because the PRZ well screened intervals are above the pre-injection groundwater surface and phosphate injections did not consistently increase the level of the groundwater surface into the PRZ well screens. In addition, some automated measurement data could not be collected because of intermittent technical problems with the monitoring equipment. However, the representative PRZ data when comparing continuous specific conductance from the downhole sensors, phosphate concentrations, and specific conductance values analyzed from the groundwater samples show the following qualitative results: the EA treatment did affect the PRZ and the LVZ and corroborate groundwater sample analyses and ERT imaging (discussed in Section 4.4 of this report):

- All PRZ wells in zones 1, 2, and 3 show response to injections within their respective zones. Figures 4-18 through 4-20 show wells 399-1-73 (zone 1), 399-1-152 (zone 2), and 399-1-148 (zone 3) displaying peaks in both specific conductance from the downhole sensors and groundwater data during the respective injection times. Trending of specific conductance values are similar over time at all the wells exhibiting a response to phosphate injections. The phosphate concentrations analyzed from collected PRZ groundwater data also display similar increasing trends with the specific conductance values.

- PRZ wells 399-1-149 and 399-1-147, located in zone 2, have continuous specific conductance data from downhole instruments that show responses from zone 1 injections as well as zone 2 injections. Figures 4-21 and 4-22 show in situ and groundwater specific conductance data and phosphate concentrations over time for wells 399-1-149 and 399-1-147. Well 399-1-149, located 8.7 and 12.1 m (28.5 and 39.7 ft) away from zone 1 injectors, shows an increasing trend in specific conductance from zone 1 injections from September 6 through 8, 2018. The increasing trend in downhole sensor specific conductance is also corroborated by increasing groundwater specific conductance values and phosphate concentrations. The groundwater sample analyses from September 7, 2018 were flagged as suspect values that were low and out of trend and therefore not included in the figure for

well 399-1-149. However, with the qualitative correlation between both specific conductivity values and phosphate concentrations from other sampling events at this well, the phosphate concentration in the PRZ at this well on September 7, 2018, is estimated to have been around 6,000,000 µg/L. The phosphate concentrations and specific conductivities continue to increase during zone 2 injections. At well 399-1-147, which is located in the middle of zone 2, the downhole sensor data display peaks in specific conductance between 6,000 and 8,000 µS/cm on September 5 and 6, 2018, during zone 1 injections. The nearest zone 1 injectors are >30 m (98 ft) away from well 399-1-147. Peaks in specific conductance are then noted after injections in zone 2 start on September 9 through 12, 2018. Correlations with both specific conductance values and phosphate concentrations at sampling events after September 10, 2018, indicate that the phosphate concentration in the groundwater sample from September 9, 2018, (which was rejected) was around 7,000,000 µg/L.

- Downhole specific conductance values in the PRZ wells in zone 2 do not show response from zone 3 injections during September 13 to 16, 2018. Well 399-1-152, located near the border between zones 2 and 3, shows a downhole specific conductance response to zone 2 injections (Figure 4-19). Qualitative analysis indicates that the concentration of phosphate at this well would have been around 8,000,000 µg/L. In addition, at well 399-1-152, the downhole specific conductance values show a response to zone 3 LVZ injections. The nearest injection wells were approximately 9 to 10 m (30 to 33 ft) away from this PRZ well. The analyzed specific conductance values and phosphate concentration values also show a similar increase during the zone 3 injections.

- PRZ well 399-1-148 located in zone 3 does not show influence from injections in zones 1 and 2 during September 4 to 12, 2018. During zone 3 injections, downhole specific conductance values peak only on September 15, 2018, to 2,350 µS/cm and do not correlate well with the specific conductance data analyzed from groundwater samples. The specific conductance and phosphate concentrations from the groundwater samples indicate the injected solution was in the PRZ at this well location through zone 3 injections and gradually decrease afterwards. It is possible that the sensor was above the groundwater water level and data could only be measured when the water level mounded creating the peak seen on September 15, 2018, during zone 3 injections (Figure 4-20).

- PRZ wells 399-1-150, 399-1-146, and 399-1-154 located in zone 4 do not indicate responses in downhole specific conductance during or after injection operations from September 4 to 20, 2018 (Figure 4-23). The specific conductance data and phosphate concentrations from groundwater samples cannot be correlated due to poor data quality.

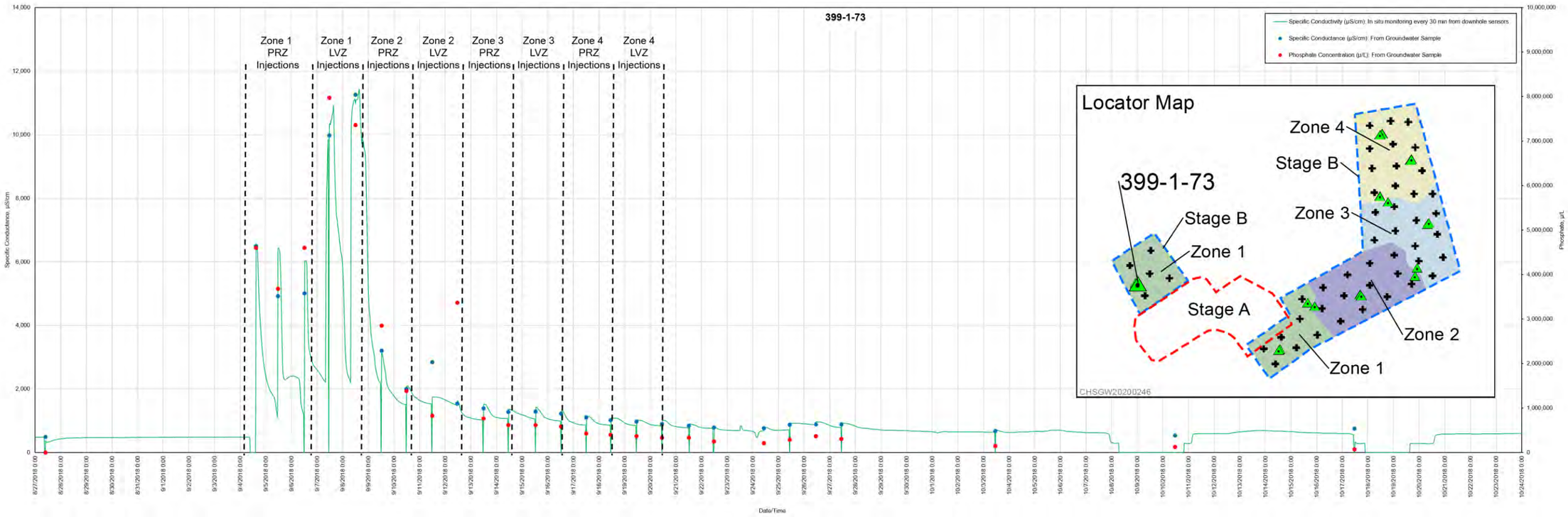


Figure 4-18. Comparison of Downhole Sensor Specific Conductance with Specific Conductance from Groundwater Samples and Phosphate Concentration for PRZ Well 399-1-73

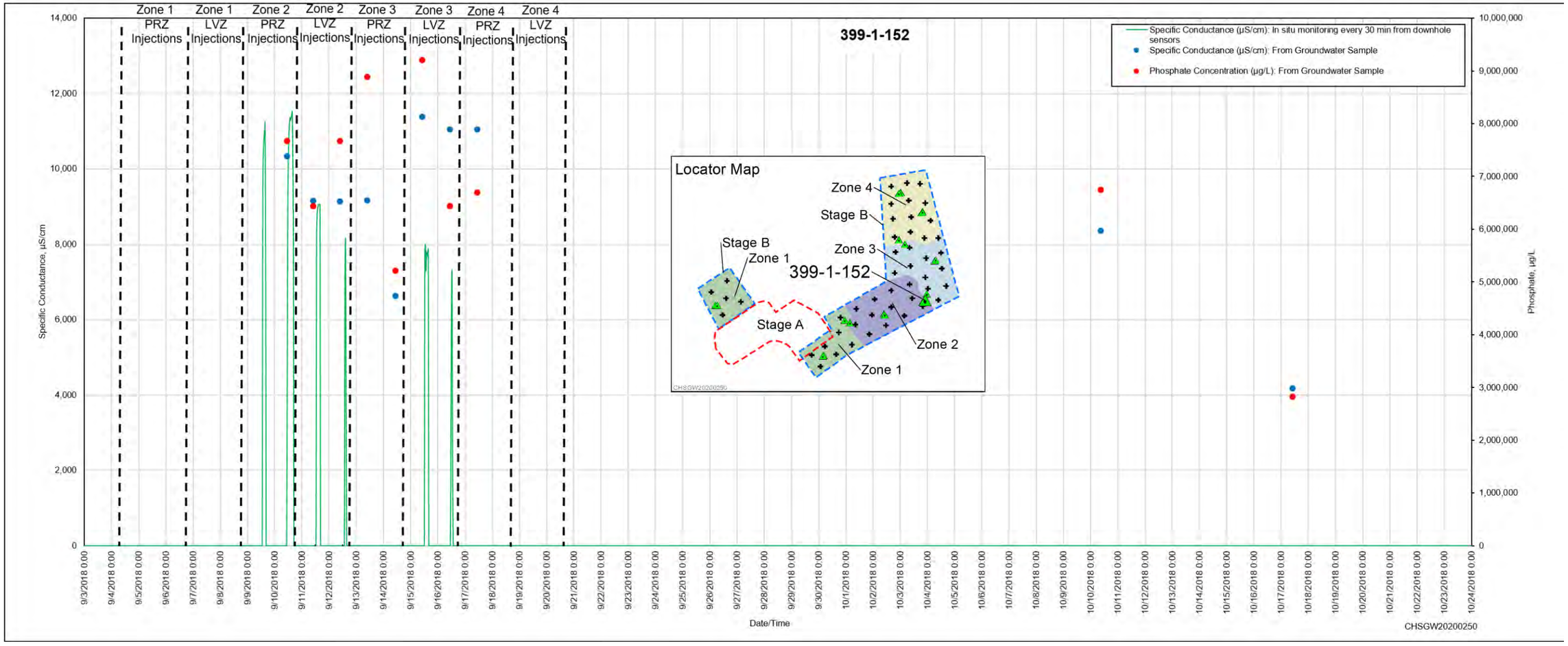


Figure 4-19. Comparison of Downhole Sensor Specific Conductance with Specific Conductance from Groundwater Samples and Phosphate Concentration for PRZ Well 399-1-152

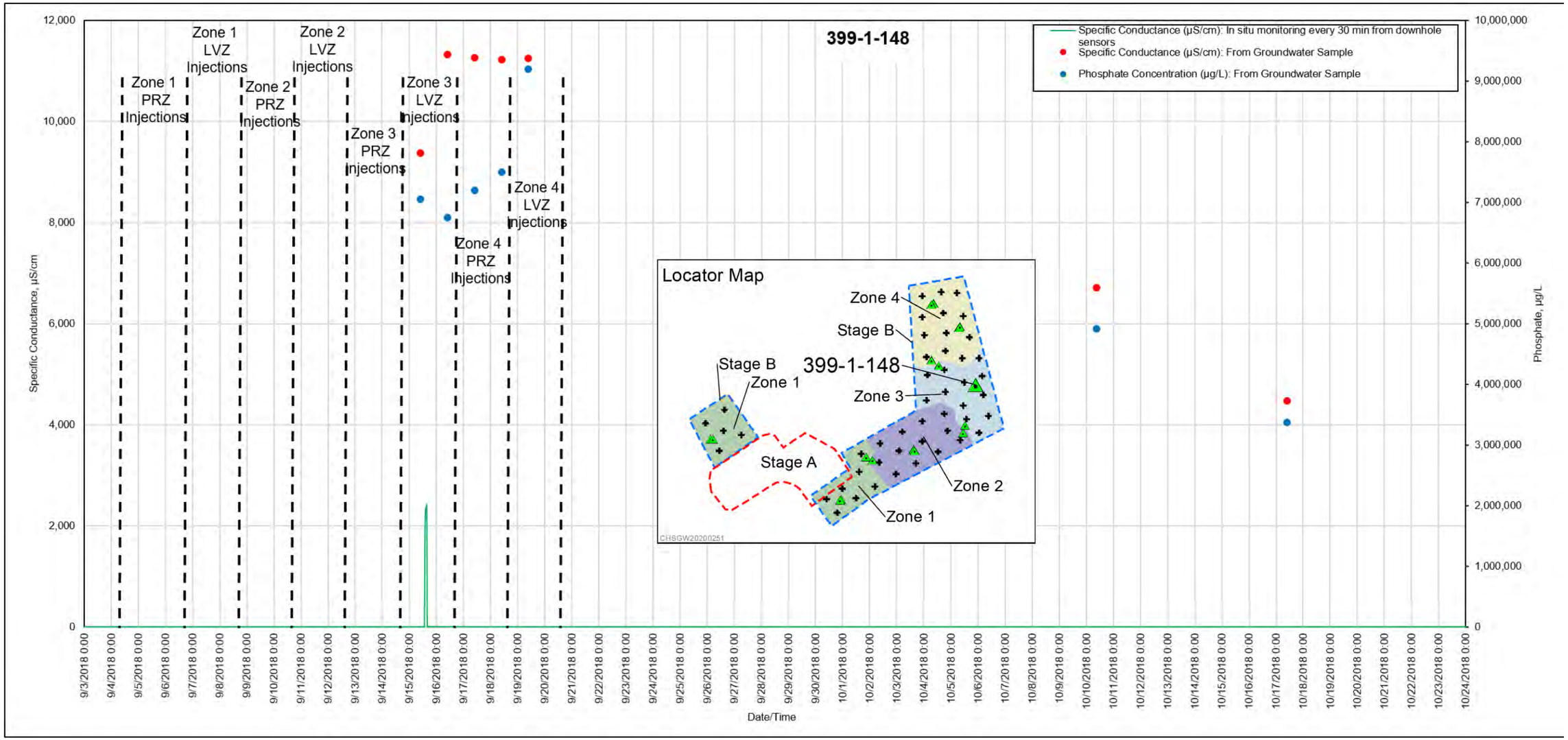


Figure 4-20. Comparison of Downhole Sensor Specific Conductance with Specific Conductance from Groundwater Samples and Phosphate Concentration for PRZ Well 399-1-148

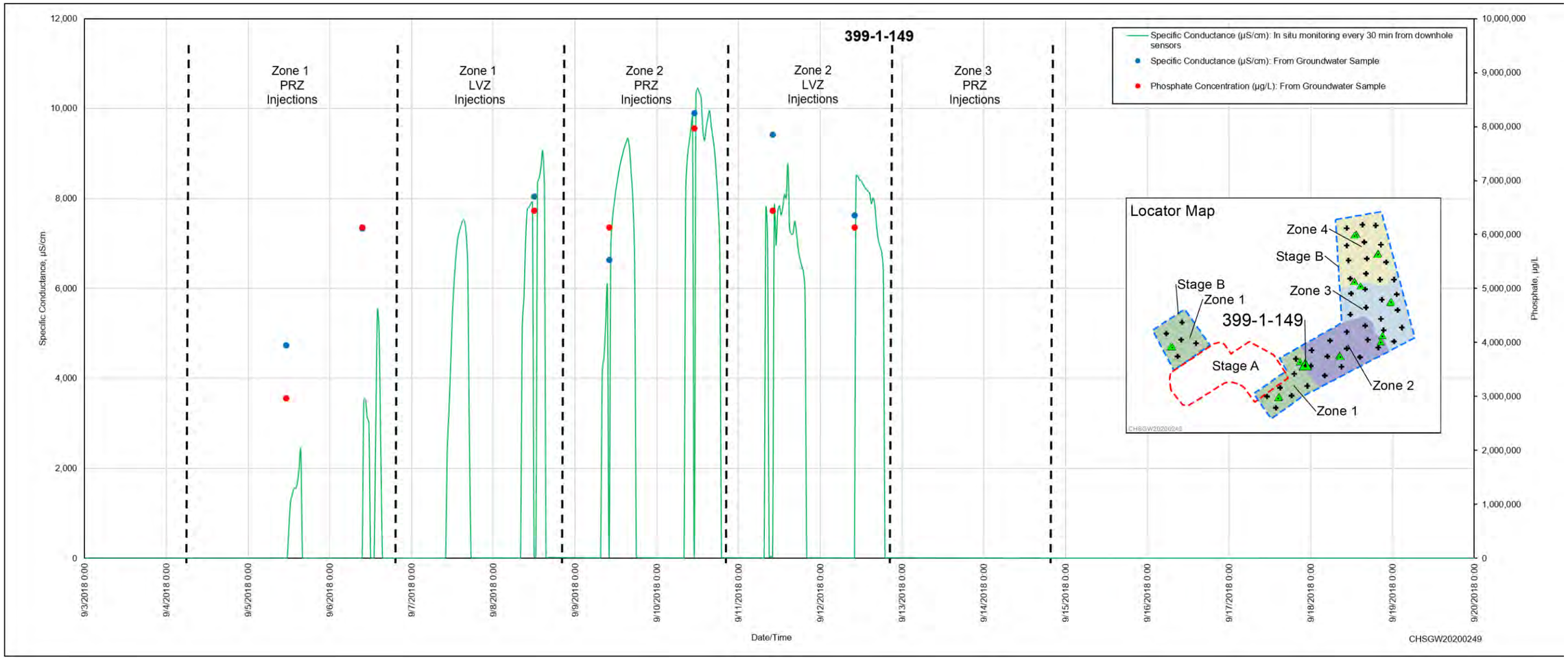


Figure 4-21. Comparison of Downhole Sensor Specific Conductance with Specific Conductance from Groundwater Samples and Phosphate Concentration for PRZ Well 399-1-149

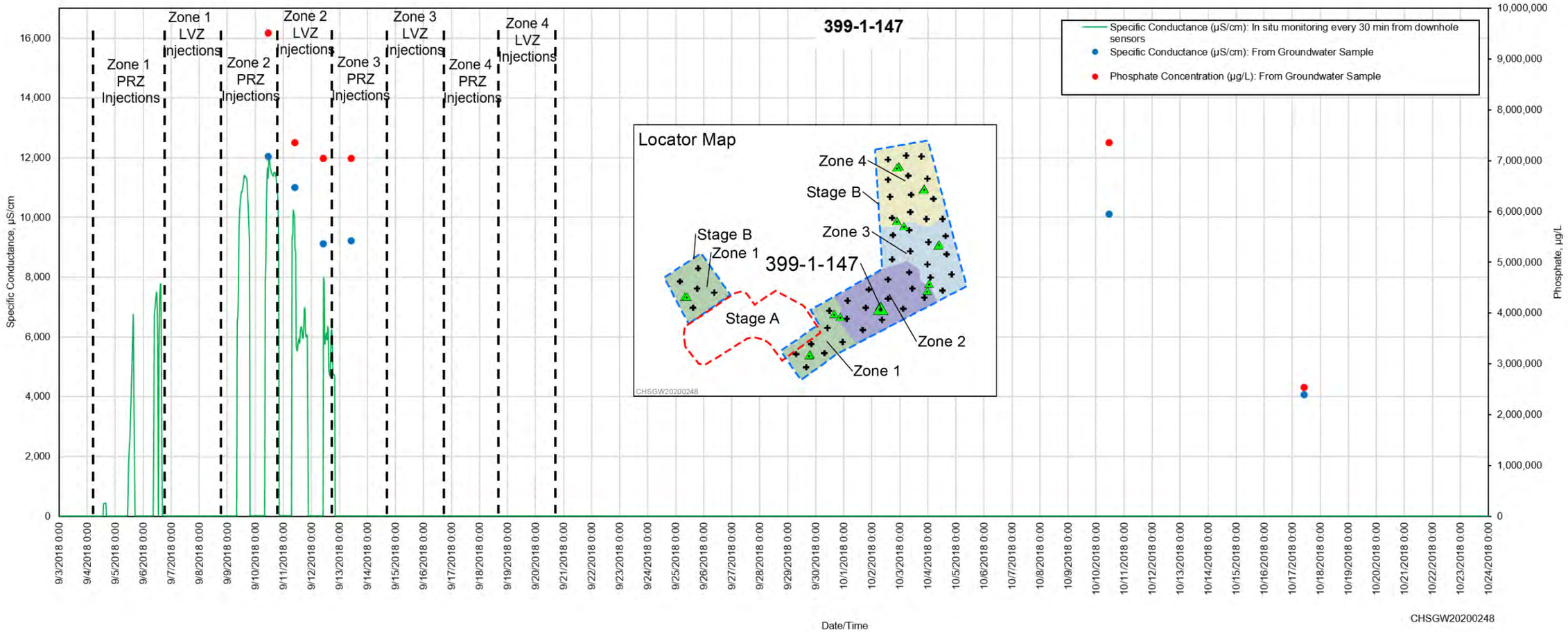


Figure 4-22. Comparison of Downhole Sensor Specific Conductance with Specific Conductance from Groundwater Samples and Phosphate Concentration for PRZ Well 399-1-147

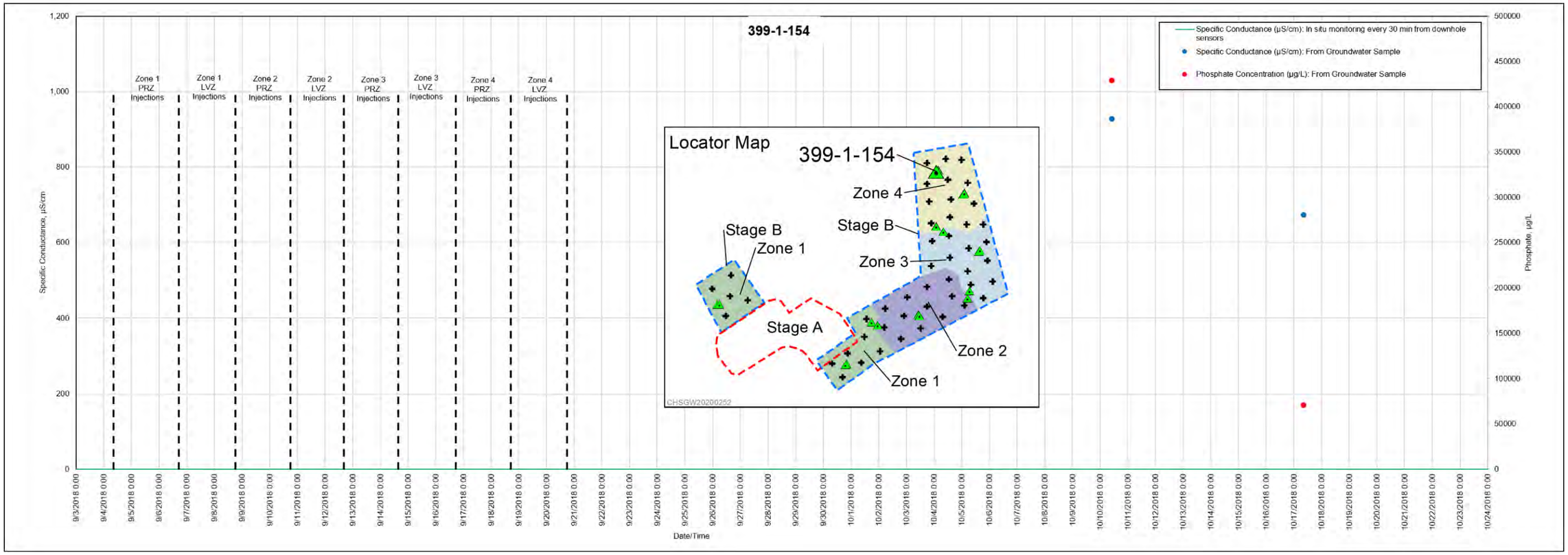


Figure 4-23. Comparison of Downhole Sensor Specific Conductance with Specific Conductance from Groundwater Samples and Phosphate Concentration for PRZ Well 399-1-154

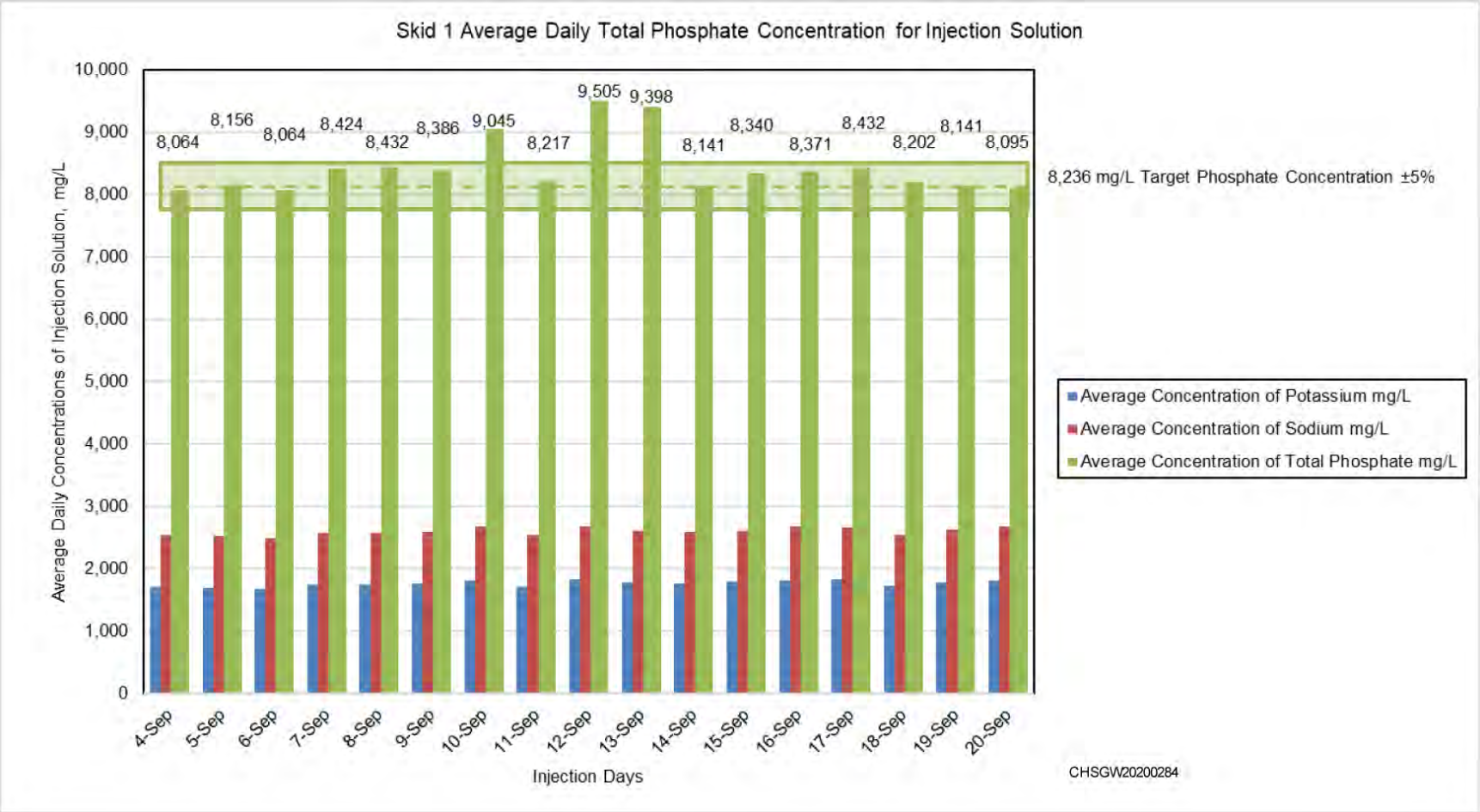
4.2.2.2 Water Level Monitoring

Seven groundwater wells in the vicinity of the Stage A and B injection areas and the 300 Area river gauge were continuously monitored as part of the 300-FF-5 OU AWLN. The water levels and river stage measured before, during, and after the injections were used in the numerical fate and transport modeling described in Chapter 5 of this report and in ECF-300FF5-19-0086, *STOMP Modeling Calculations in Support of the Stage B Sequestration of Uranium at 300-FF-5 Operable Unit*. The monitoring data are provided in Appendix C of this report.

4.3 Operations Monitoring

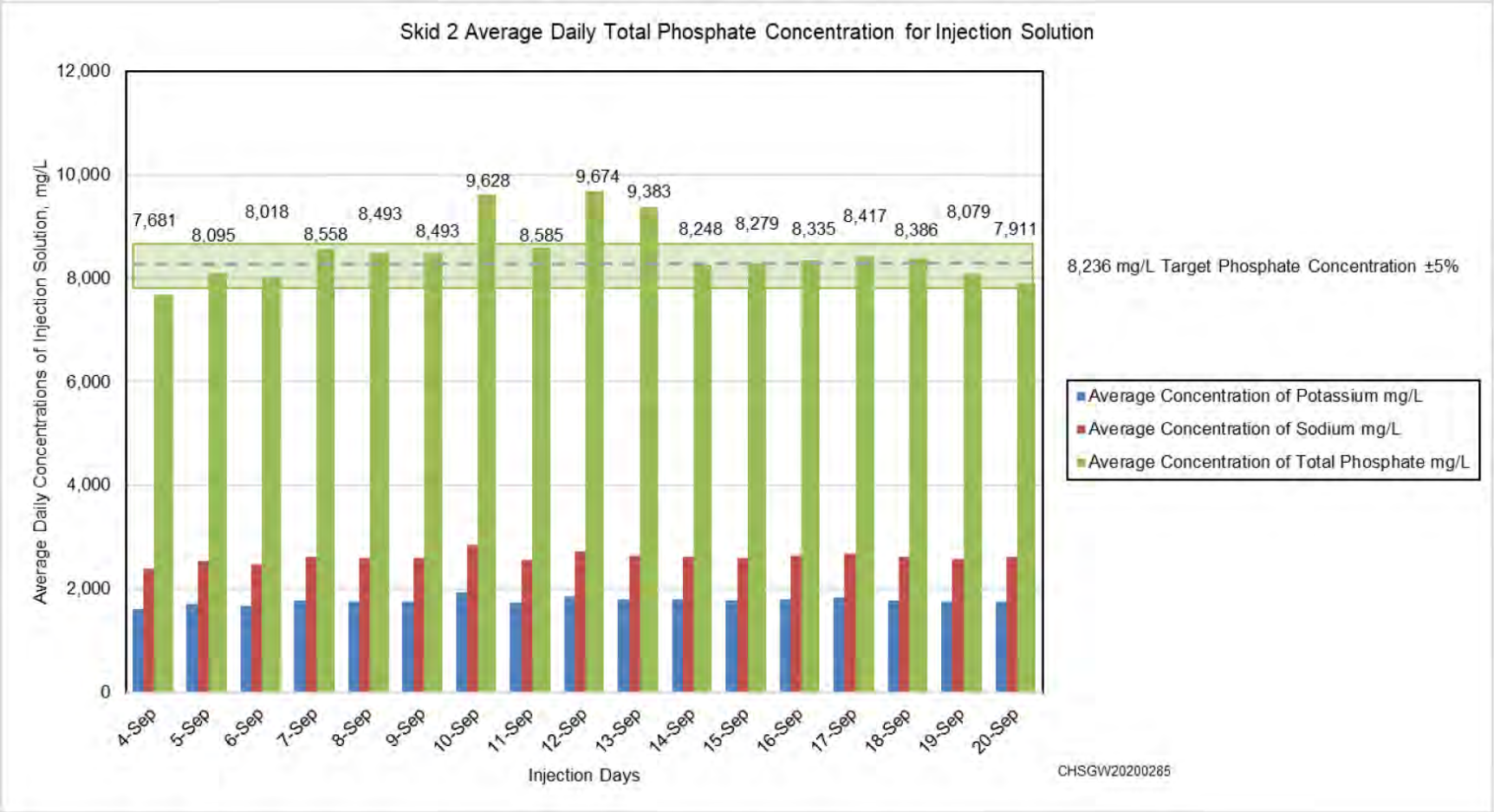
This section summarizes the results of operations monitoring of the Stage B injection system. Detailed information for the injection volumes is provided in ECF-300FF5-19-0005. Analytical data for the skid polyphosphate solution samples are provided in Appendix D of this report.

The Stage B polyphosphate injections started on September 4, 2018, and continued through September 20, 2018 (Section 2.2.7 of this report). Target treatment solution concentrations were 2,430 mg/L ±5% orthophosphate (measured as phosphorus) and 256 mg/L ±5% pyrophosphate (measured as phosphorus) (Table 4 in DOE/RL-2014-42-ADD1). These phosphorus concentrations are equivalent to a total phosphate concentration in the blended polyphosphate solution of 8,236 mg/L (using a conversion factor of 3.06618). The average concentrations of total phosphate in the injection solution sampled at the skids were within 5% of 8,236 mg/L for 13 of the 17 operational days (Figures 4-24 and 4-25). Average sodium and potassium concentrations varied in proportion to the average phosphate concentrations, with the sodium concentrations being slightly greater than potassium concentrations. The blended polyphosphate solution samples generally had a pH between 7 and 7.6, meeting the target pH of 7 to 7.5 identified in Section 2.5 of SGW-60778.



Note: Total phosphate concentrations are reported using phosphorus converted to phosphate assuming that all of the phosphorus from orthophosphate and pyrophosphate is present as phosphate.

Figure 4-24. Skid 1 Daily Sample Solution Concentrations



Note: Total phosphate concentrations are reported using phosphorus converted to phosphate assuming that all of the phosphorus from orthophosphate and pyrophosphate is present as phosphate.

Figure 4-25. Skid 2 Daily Sample Solution Concentrations

Each skid was capable of injecting 6 wells at a time for a total of 12 wells simultaneously in each zone (Section 2.2.7 of this report). The skids monitored the volume of river water and polyphosphate solution delivered to the skid for blending as well as the volume of blended solution injected through each well to the PRZ or LVZ (Section 3.3 of this report). The volume data were used to calculate the flow rate of fluid injected at each of the wells (ECF-300FF5-19-0005).

The target injection flow rate of solution into the PRZ and LVZ was 189 L/min (50 gal/min) or more, or as close to 189 L/min (50 gal/min) as achievable in the field (Table 5 of DOE/RL-2014-42-ADD1). Each skid was capable of delivering up to 1,135 L/min (300 gal/min) of solution that was injected simultaneously to six wells (Section 2.2.5 of this report). The average flow rates for injections into the PRZ and LVZ in injection zones 1 through 4 ranged from 170 L/min (45 gal/min) to 185 L/min (49 gal/min) (Table 4-3). The average flow rates for injections into the PRZ and LVZ for each day of injection ranged from 170 L/min (45 gal/min) to 189 L/min (50 gal/min) (Tables 2-2 and 2-3). The average flow rates to individual wells ranged from 121 L/min (32 gal/min) to 261 L/min (69 gal/min) (Tables 4 and 6 in ECF-300FF5-19-0005). The lowest daily average flow rates in Tables 2-2 and 2-3 are within 10% of the target.

Table 4-3. Average Flow Rates into PRZ and LVZ

Injection Zone	Injection Days	Skid 1		Skid 2		Met Flow Rate Target?
		PRZ (L/min [gal/min])	LVZ (L/min [gal/min])	PRZ (L/min [gal/min])	LVZ (L/min [gal/min])	
1	09/04/2018 to 09/08/2018	170 (45)	170 (45)	174 (46)	174 (46)	Yes
2	09/09/2018 to 09/12/2018	182 (48)	182 (48)	185 (49)	182 (48)	Yes
3	09/13/2018 to 09/16/2018	174 (46)	178 (47)	182 (48)	182 (48)	Yes
4	09/16/2018 to 09/20/2018	182 (48)	182 (48)	182 (48)	182 (48)	Yes

LVZ = lower vadose zone
PRZ = periodically rewetted zone

The design volumes for the total amount of polyphosphate solution injected into the LVZ and PRZ were 6,970,000 L (1,841,300 gal) and 9,289,800 L (2,454,100 gal), respectively (Table 3 in DOE/RL-2014-42-ADD1). The volume injected into the LVZ was 7,085,734 L (1,871,853 gal), 2% higher than the design volume (Tables 7 and 8 in ECF-300FF5-19-0005). The volume injected into the PRZ was 9,126,302 L (2,410,914 gal), 2% lower than the design volume. Knowing the total volume of solution injected into the PRZ and LVZ and the concentration of phosphate in the solution (8,236 mg/L), the total masses of phosphate delivered to the PRZ and LVZ is calculated to be 75,164 and 58,358 kg (165,709 and 128,658 lb), respectively.

The target injection volumes were 193,500 L (51,100 gal) ±5% of solution per PRZ well screen and 145,200 L (38,400 gal) ±5% of solution per LVZ well screen (Table 5 of DOE/RL-2014-42-ADD1). The total volumes of solution injected into the PRZ and LVZ are summarized in Tables 4-4 and 4-5. The total volumes injected into the PRZ and LVZ for each well are shown in Figures 4-26 and 4-27 relative to the target volumes. The mass of phosphate delivered through each PRZ and LVZ well screen is calculated to approximately 1,566 and 1,216 kg (3,452 and 2,680 lb), respectively.

Table 4-4. Skid 1 Total Volume of Solution Injected into PRZ and LVZ

Zone	Days	PRZ or LVZ	Total Volume Injected (L)	Total Volume Injected (gal)	Met Target Volumes?
1	09/04/2018 to 09/06/2018	PRZ	1,027,274	271,377	No
	09/07/2018 to 09/08/2018	LVZ	932,665	246,384	Yes
2	09/09/2018 to 09/11/2018	PRZ	1,176,847	310,890	Yes
	09/11/2018 to 09/12/2018	LVZ	874,733	231,080	Yes
3	09/13/2018 to 09/15/2018	PRZ	1,194,051	315,435	Yes
	09/15/2018 to 09/16/2018	LVZ	882,103	233,027	Yes
4	09/16/2018 to 09/18/2018	PRZ	1,160,725	306631	Yes
	09/19/2018 to 09/20/2018	LVZ	904,899	239,049	Yes

Source: Table 7 in ECF-300FF5-19-0005, *Injection Volumes for 300-FF-5 Stage B Injections and Sampling*.

LVZ = lower vadose zone

PRZ = periodically rewetted zone

Table 4-5. Skid 2 Total Volume of Solution Injected into PRZ and LVZ

Zone	Days	PRZ or LVZ	Total Volume Injected (L)	Total Volume Injected (gal)	Met Target Volumes?
1	09/04/2018 to 09/06/2018	PRZ	1,057,451	279,349	No
	09/07/2018 to 09/08/2018	LVZ	833,347	220,147	No
2	09/09/2018 to 09/11/2018	PRZ	1,186,280	313,382	Yes
	09/11/2018 to 09/12/2018	LVZ	882,031	233,008	Yes
3	09/13/2018 to 09/15/2018	PRZ	1,161,803	306916	Yes
	09/15/2018 to 09/16/2018	LVZ	873,147	230,661	Yes
4	09/16/2018 to 09/18/2018	PRZ	1,161,872	306934	Yes
	09/19/2018 to 09/20/2018	LVZ	902,809	238,497	Yes

Source: Table 8 in ECF-300FF5-19-0005, *Injection Volumes for 300-FF-5 Stage B Injections and Sampling*.

LVZ = lower vadose zone

PRZ = periodically rewetted zone

Skid 1 did not meet the target injection volume for the PRZ for five of the six wells in injection zone 1. Skid 2 did not meet the target injection volume for the PRZ for five of the six wells in injection zone 1 and did not meet the target injection volume for the LVZ for two of the six wells in injection zone 1. However, overall, between the two injection skids, the combined target injection volume of 16 million L (4.3 million gal) was met.

Totalizer values from both skids indicate that during the first 3 days of injections, three pore volumes of polyphosphate solution were not successfully delivered to the PRZ in 10 of the 12 wells in injection zone 1 (Tables 7 and 8 in ECF-300FF5-19-0005). PRZ injection volumes for zone 1 were not met due to the totalizers being reset on both skids on day one of injections. The operations worksheets note that the totalizers on the first day were reset to zero during operations and do not reflect the accurate measurement of total injection volume for September 4, 2018. The first day of injection operations was planned for modifying and balancing the injection system, however, the system needed only minor fine-tuning. After approximately 4.5 hours of successful injections, the operations field personnel decided to pause injections, zero the totalizers, restart injections, and start recording the volumes and flow rates in the daily operations worksheets. It was estimated that 23,091 L (6,100 gal) of blended solution was injected into each well before the totalizers were reset and the daily records began. The estimated 23,091 L (6,100 gal) of solution was not included in the total skid volumes because this was not documented in the daily operations worksheets. It is possible the target volume was achieved but it was not documented. PRZ wells 399-1-138 and 399-1-125 in zone 1 did receive the target volume.

Skid 2 did not successfully deliver three pore volumes of polyphosphate solution to the LVZ in wells 399-1-125 and 399-1-126 in injection zone 1. Wells 399-1-125 and 399-1-126 experienced some ponding on the ground surface on September 7, 2018. The injection flow rate into wells 399-1-125 and 399-1-126 was decreased on September 7, 2018, and the flow rate was increased at neighboring wells within zone 1 to reduce overflow. Once the ponding was managed, the flow rate was gradually increased at wells 399-1-125 and 399-1-126, but the total volumes injected did not reach the target.
Wells 399-1-121 and 399-1-123 in zone 2 also experienced ponding on the ground surface during injections on September 12, 2018, to the LVZ but did receive the target volume. Ponding during injections into the LVZ was likely because the LVZ zone in the injection wells was undeveloped.

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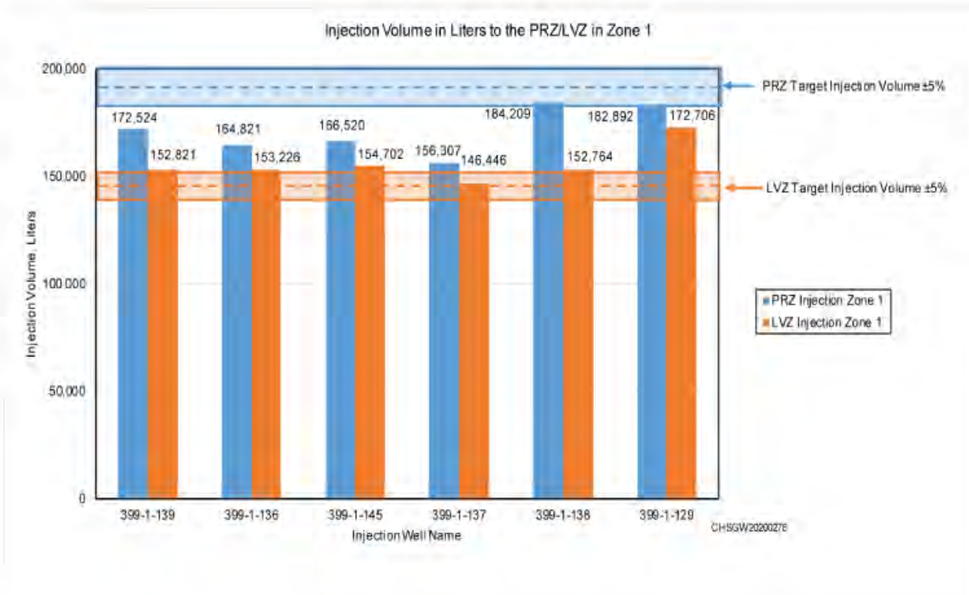
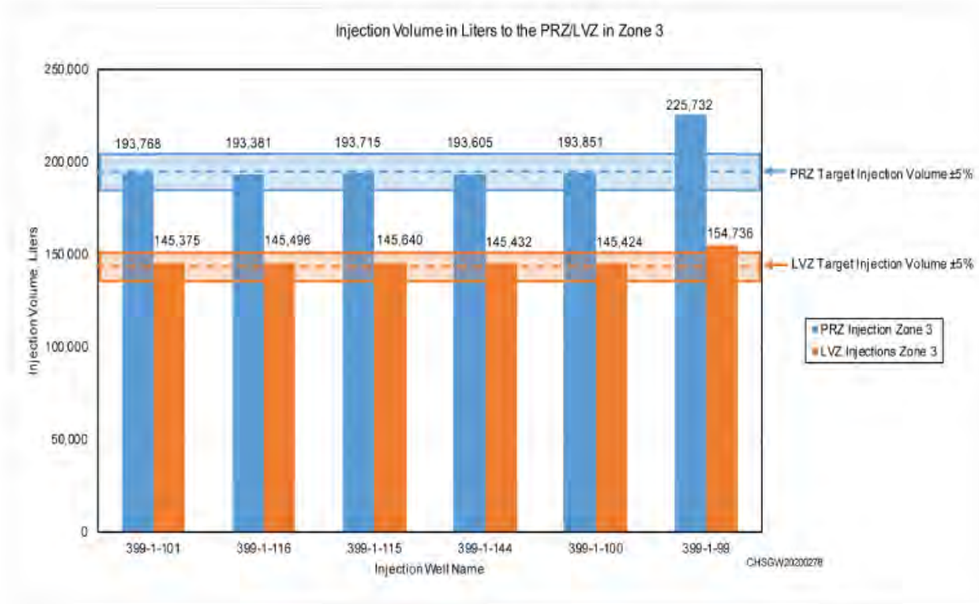




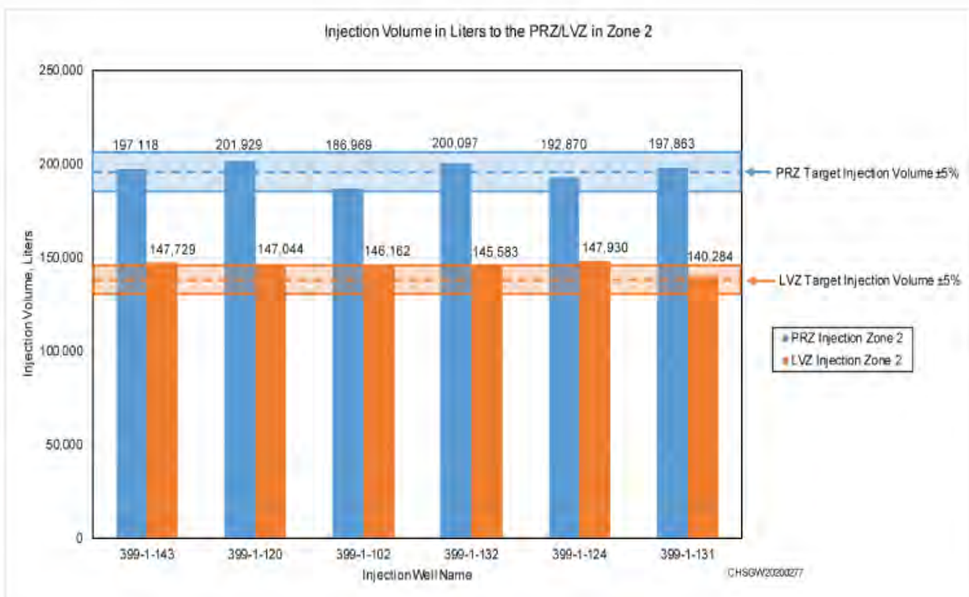
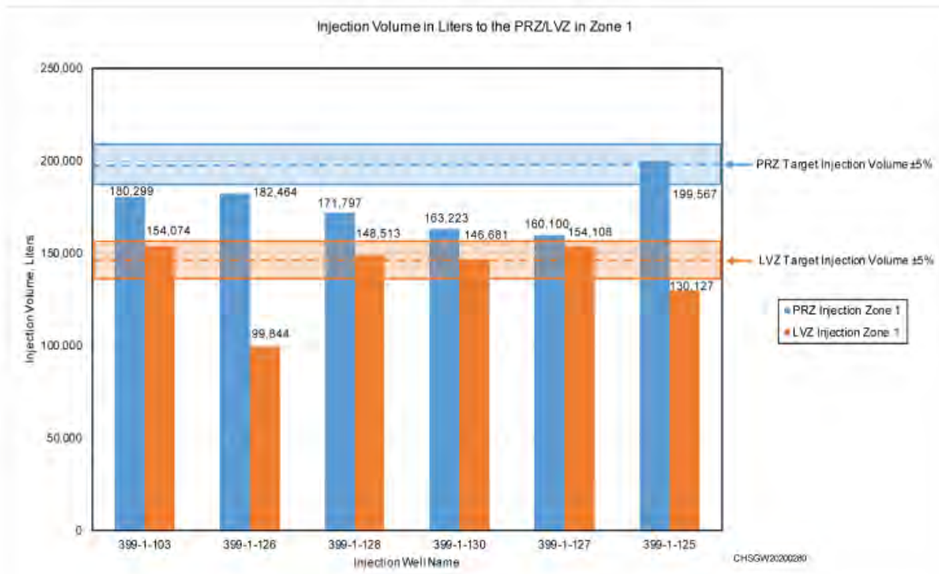
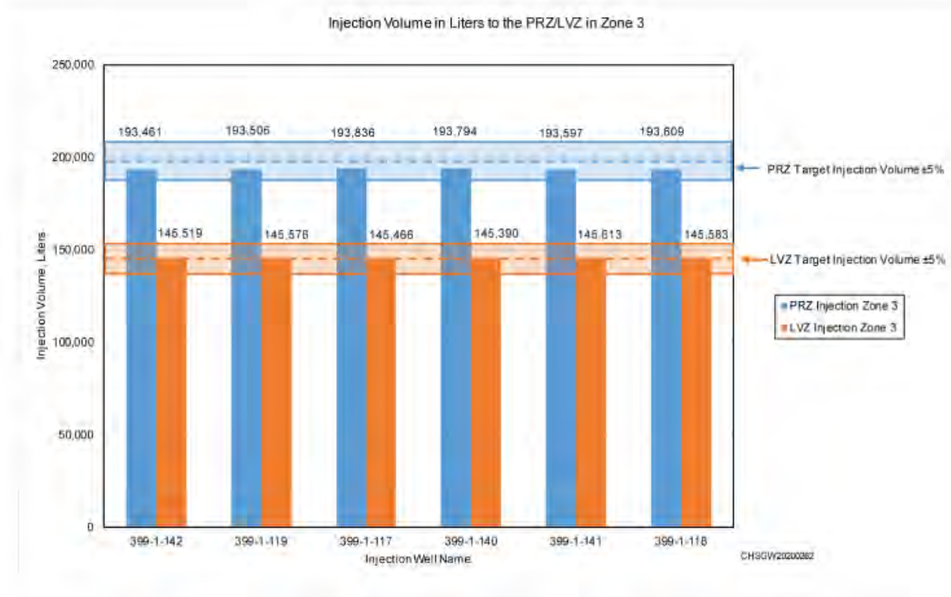


Figure 4-26. Total Injection Volumes Per Well Per Zone at Skid 1





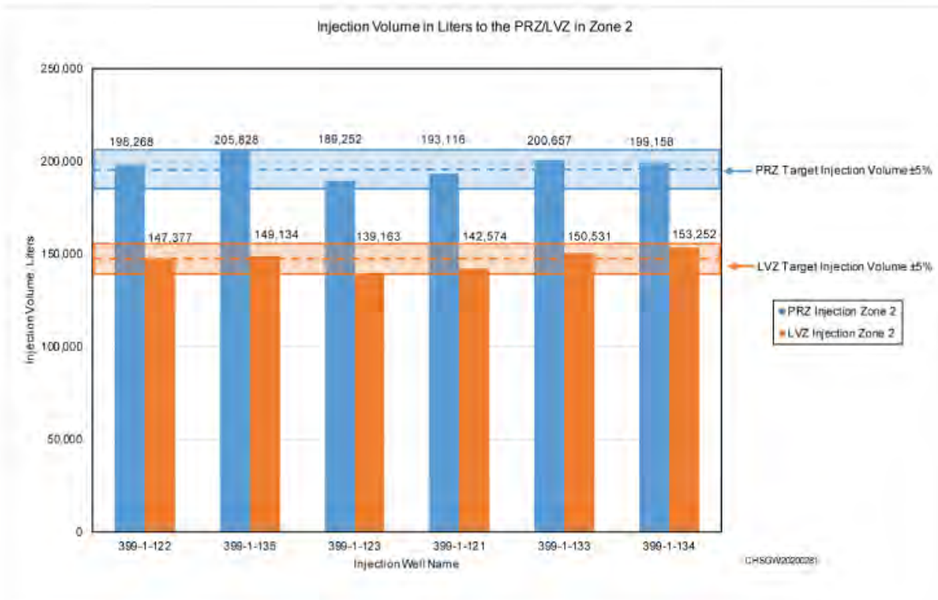
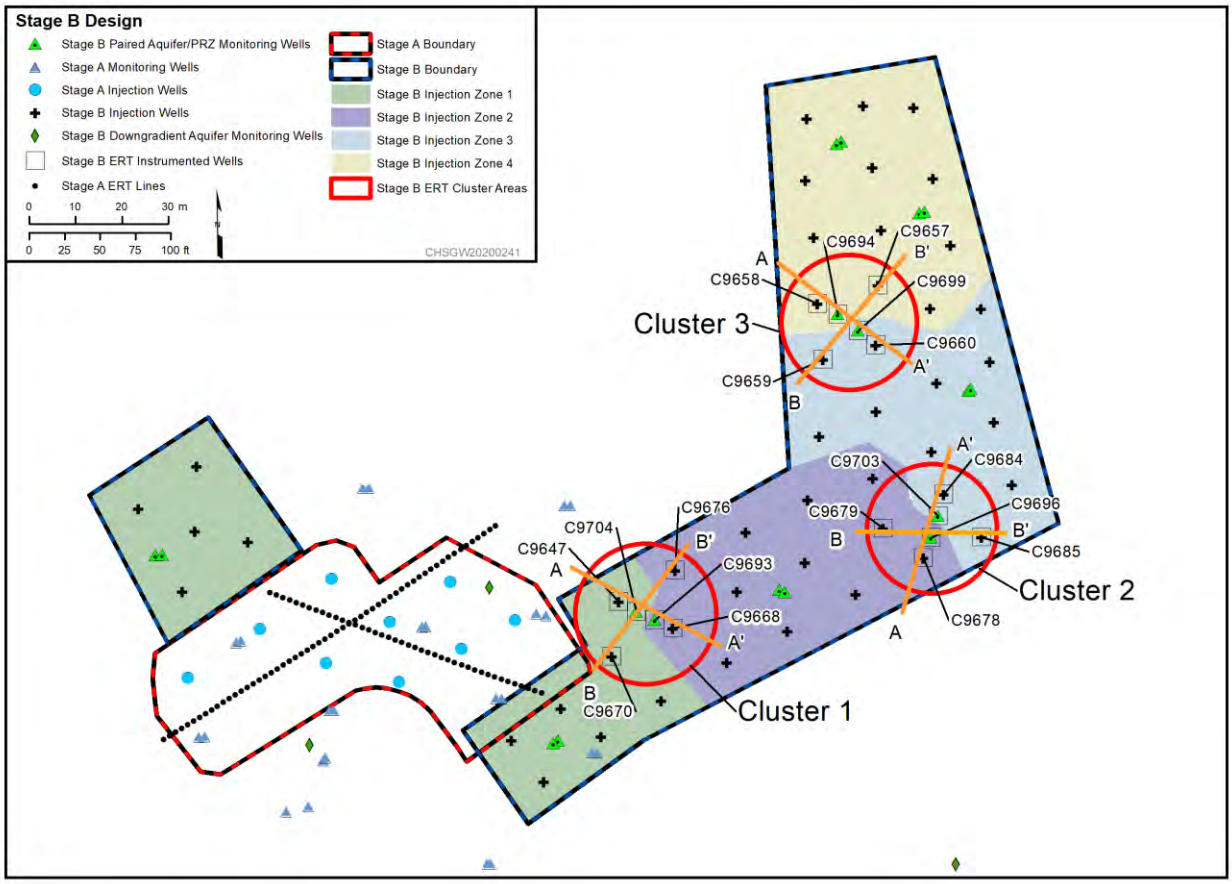


Figure 4-27. Total Injection Volumes per Well per Zone at Skid 2

4.4 Electrical Resistivity Tomography

Time-lapse ERT was used to image the spatial and temporal changes in electrical conductivity corresponding to migration of the polyphosphate injection solution through the vadose zone. The ERT system array is described in Section 2.2.4 (of this report), and the data collected are described in Section 3.4. The ERT data and interpretations are provided in PNNL-28619. A discussion of the data collected from the Stage A ERT is provided in Section 4.4 of SGW-59614.

The Stage B ERT clusters were designed to produce high-resolution cross-borehole ERT images of changes in total electrical conductivity, which is related to the polyphosphate solution distribution. Each cluster consisted of two arrays of wells along planes A-A' and B-B' (Figure 4-28). Horizontal well offset for the B-B' plane (11.5 to 12 m [38 to 39 ft]) was greater than the well offset for the A-A' plane (4.3 to 5.5 m [14 to 18 ft]). The B-B' plane well offset proved to be too large to provide adequate cross-hole resolution between the B-B' wells. Therefore, results for the A-A' plane are emphasized in the data analysis as the most useful to support interpretation of polyphosphate solution delivery (Section 2.1 of PNNL-28619).

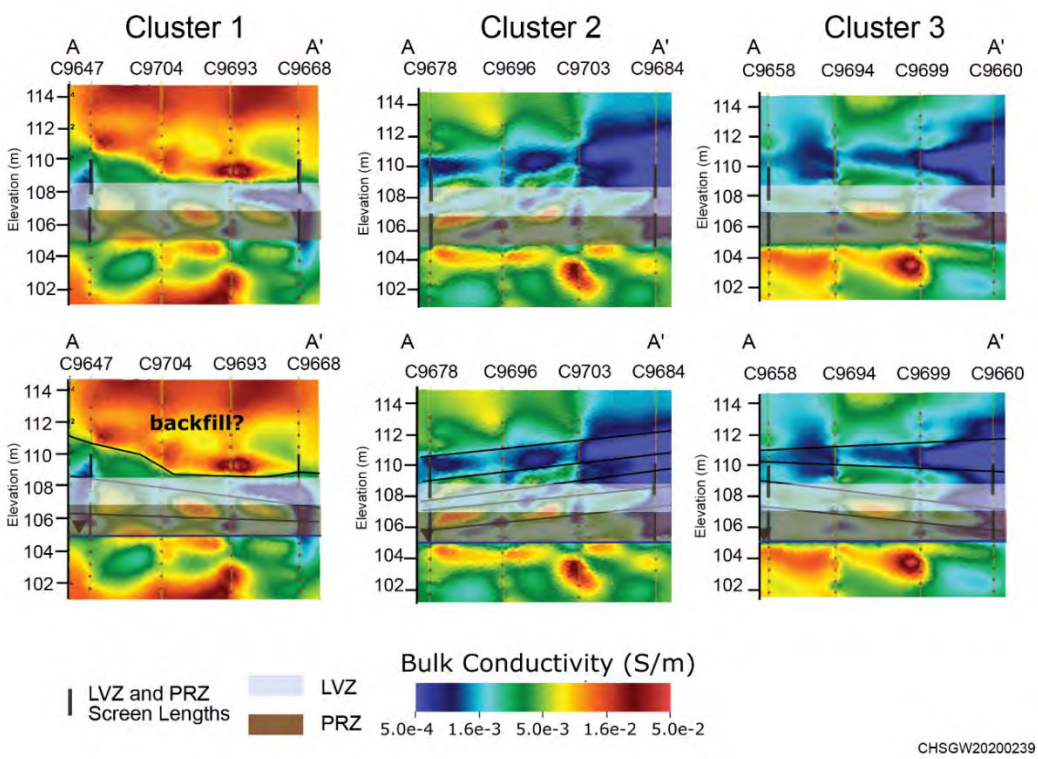


Source: Modified from PNNL-28619, *Stage B Uranium Sequestration Amendment Delivery Monitoring Using Time-Lapse Electrical Resistivity Tomography*.

Figure 4-28. Stage A and B Treatment Area Layout with Clusters 1, 2, and 3

4.4.1 Pre-Treatment Monitoring

The baseline ERT image refers to the image of bulk conductivity distribution prior to injection of the polyphosphate solution. The baseline ERT image is critical because it is subtracted from every time-lapse image to reveal the change in bulk conductivity with time. In this way, the changes in bulk conductivity can be attributed to the increase in saturation, pore fluid conductivity, and/or precipitate conductivity due to the injection of polyphosphate solution. The baseline image also can be used to interpret geologic structure, zones of high conductivity co-contaminant migration, or other properties related to spatial variations in porosity, saturation, pore fluid conductivity, texture, and mineralogy (Figure 4-29).



Reference: Figure 15 in PNNL-28619, *Stage B Uranium Sequestration Amendment Delivery Monitoring Using Time-Lapse Electrical Resistivity Tomography*.

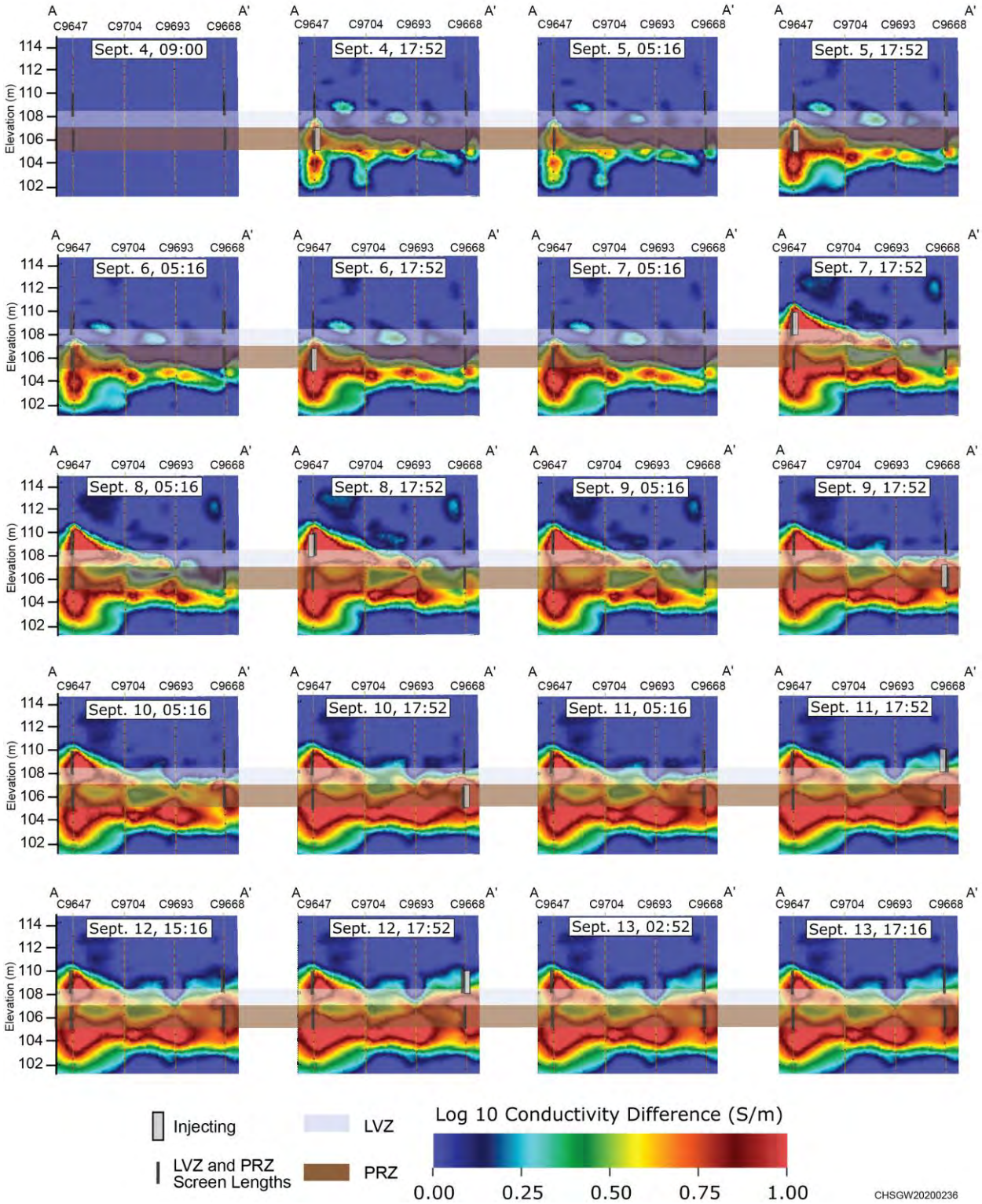
Figure 4-29. Pre-Treatment Baseline ERT Images in the A-**A'** Plane for Each Cluster (top) and the Corresponding Interpretations (bottom)

Figure 4-29 shows the baseline ERT images at the three ERT clusters that were collected on September 4, 2018, prior to the start of injections in zone 1. The images show the spatial variability in bulk conductivity for each cluster and the increased saturation across the water table. All three clusters exhibit some amount of layering in the subsurface with alternating conductive and resistive layers. Cluster 1 exhibits elevated conductivity above the 109 m (358 ft) elevation and clusters 2 and 3 exhibit layered bulk conductivity from the 105 to 110 m (345 to 361 ft) elevation. Cluster 1 is located in the area with the deepest excavation and backfill (Figure 4-1) with demonstrably higher conductivities from ground surface to the water table than those measured in clusters 2 and 3. The high conductivity observed in cluster 1 is correlated with high concentrations of metals (specifically copper) in soil samples. This may indicate that cluster 1 is more influenced by residual waste site contamination at the LVZ and PRZ depths than clusters 2 and 3.

4.4.2 Monitoring During Treatment

Cross-borehole ERT cluster 1 is located across zones 1 and 2 (Figure 4-28). Injection of the polyphosphate solution occurred on September 4 through 8, 2018, in zone 1 and September 9 through 12, 2018, in zone 2. Selected ERT images for cluster 1 from September 4 through 13, 2018, are shown in Figure 4-30. Two images are shown for each day, one image before and one image during the injections on that day. The two injection wells and two monitoring wells are shown in each image. The two screened intervals are shown for each injection well. In the images during the injections, the well screen receiving the polyphosphate solution is shown in grey.

Imaging during injections into the PRZ in zone 1 suggest that the polyphosphate solution mounded above the PRZ screen in injection well 399-1-103 (C9467) on September 4 (day 1 of PRZ injections) and spread over 4 m (13 ft) laterally to monitoring well 399-1-160 (C9704) through the PRZ (Figure 4-30). Increases in bulk conductivity below the water table indicate that the polyphosphate solution exhibited density-driven downward flow in the saturated zone and pressure-driven radial flow at or near the water table. Post-treatment draining and dilution, and corresponding decreases in the vadose zone conductivity, occur in every image in between each injection. Injection into the LVZ at zone 1 started on September 7, 2018, and showed that mounding occurred above the top of the LVZ screen. The elevated bulk conductivity in the zone 1 portion of cluster 1 after September 8 suggests lateral delivery of the injected solution over 8 m (26 ft) to the 399-1-149 (C9693) monitoring well. This is further supported by the prolonged elevated concentrations of phosphate in groundwater samples at well 399-1-160 (C9704), which is adjacent to the injection well. This monitoring well is near the border of zones 1 and 2 and initially showed increased phosphate concentrations during injections into zone 1 (Figure 4-5). Phosphate concentrations continued to increase at this well after the conclusion of injections into zone 1 on September 8, 2018, and peaked on September 13, 2018, which marked the end of injections into zone 2 and start of injections into zone 3. Injections into zone 2 during September 9 through 12, 2018, indicate that significant mounding occurred above the PRZ screen in the injection well 399-1-124 (C9668) but not above the LVZ screen. The bulk conductivity was more elevated on the side of the ERT cluster nearer injection well 399-1-103 (C9647) in zone 1 in comparison to the side nearer zone 2. Lack of mounding above the LVZ screen during injections to zone 2 indicate that sediment permeability was high enough to inhibit backpressure and mounding over the top of the screen.



Source: Modified from Figure 17 in PNNL-28619, *Stage B Uranium Sequestration Amendment Delivery Monitoring Using Time-Lapse Electrical Resistivity Tomography*.

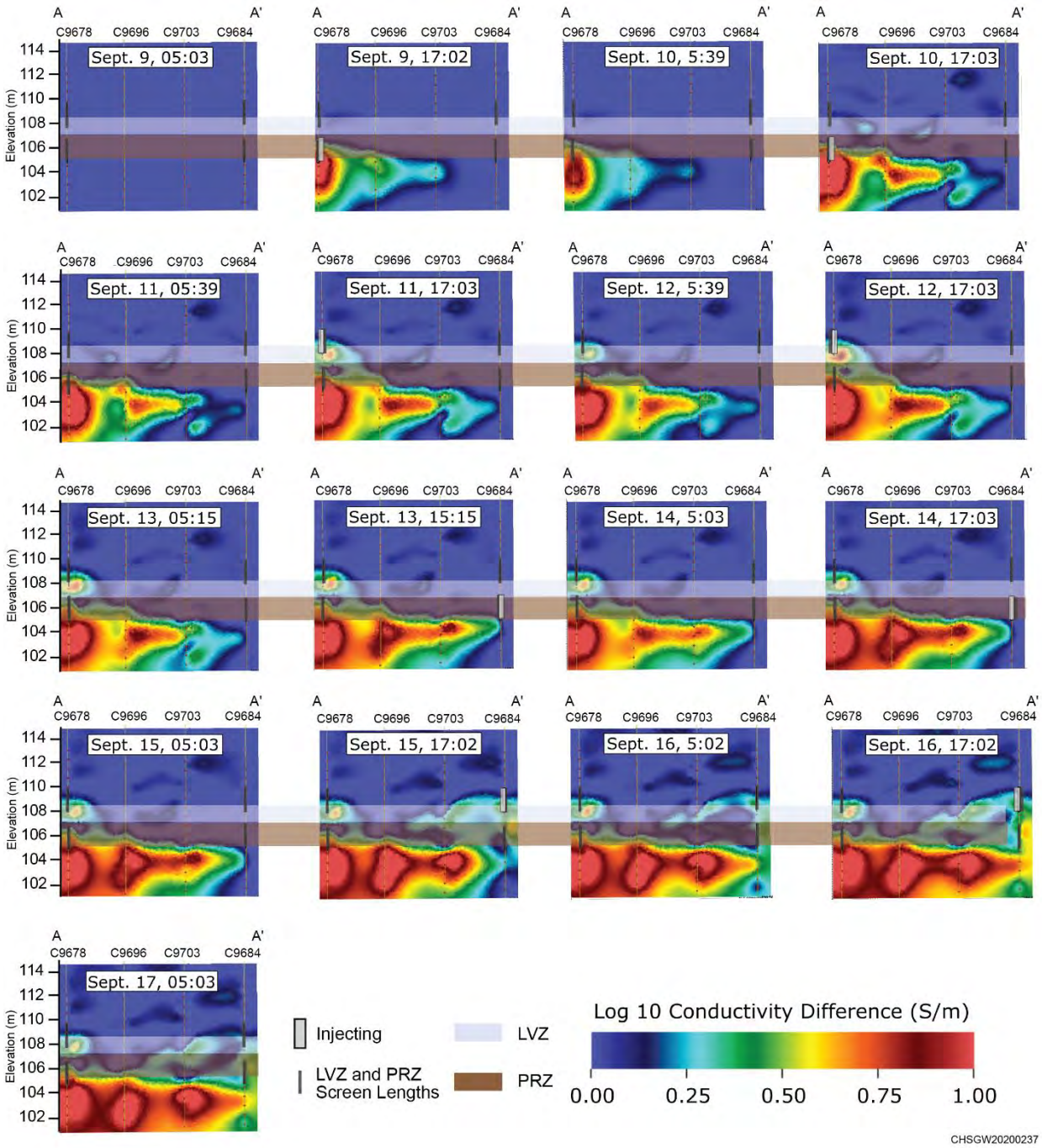
Figure 4-30. Twice Daily Images of ERT Amendment Distribution in Cluster 1

Overall, the cluster 1 ERT images suggest that injection to zone 1 and 2 in cluster 1 exhibited a radius of influence of at least 8 m (26 ft) resulting in lateral transport that impacted all of the PRZ and much of the LVZ.

Cross-borehole ERT cluster 2 is located across zones 2 and 3 (Figure 4-28). Injection of the polyphosphate solutions to zones 2 and 3 occurred on September 9 to 12 and 13 to 16, 2018, respectively. ERT imaging suggests that the polyphosphate injection solution reached the top of the PRZ screen of the four wells in cluster 2 during injections of zone 2 but did not overtop the screened interval (Figure 4-31).

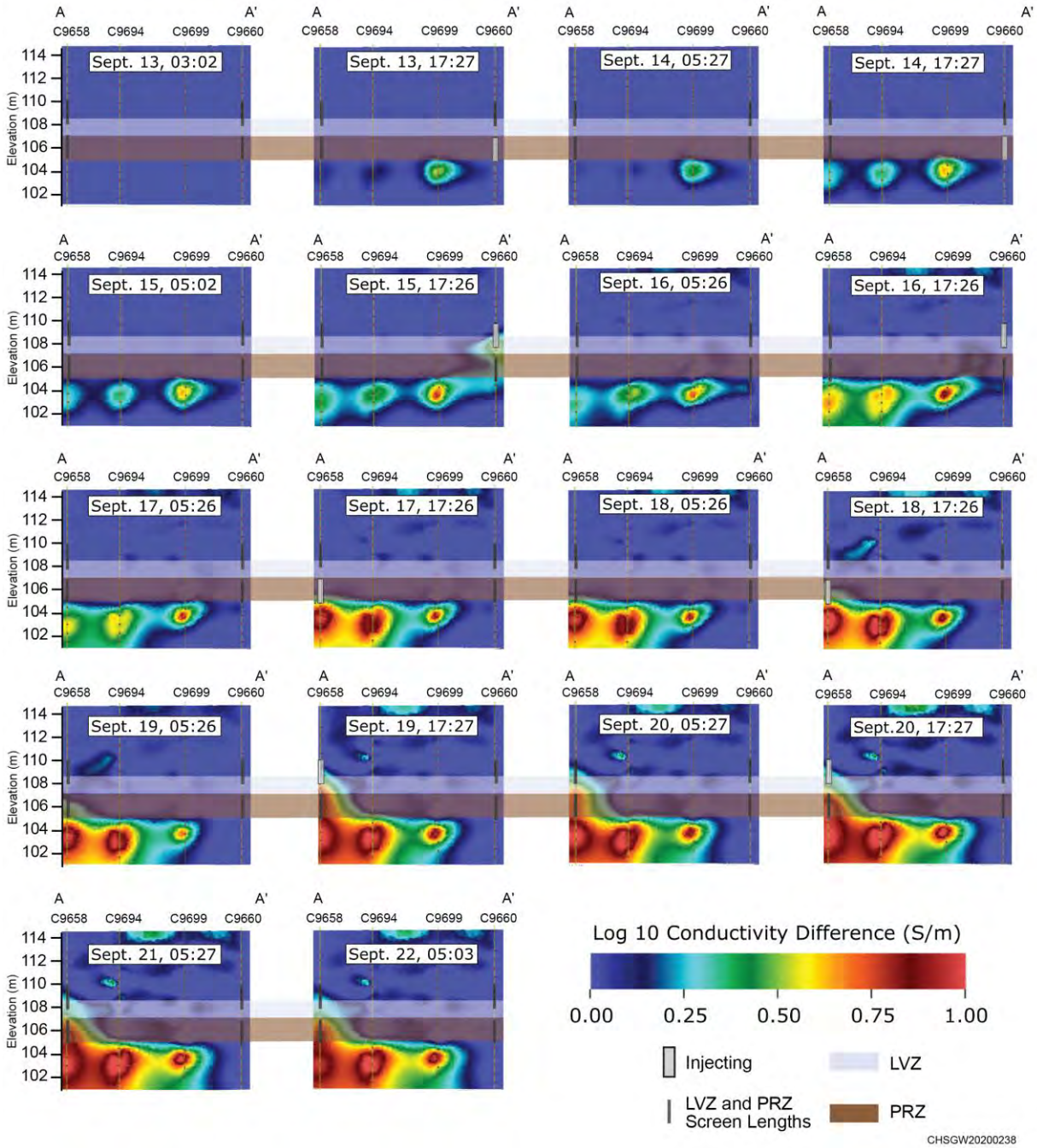
Laterally the polyphosphate injection solution appeared to extend 4.7 m (15 ft) to monitoring well 399-1-152 (C9696). Injection into zone 3 from September 13 to 16, 2018, shows that mounding did not extend above the screens for the PRZ or the LVZ. Lateral transport during this time appeared to extend approximately 6.5 m (21 ft) between wells 399-1-159 (C9703) and 399-1-152 (C9696) through the PRZ. The radius of influence from injections in zone 2 appears to be smaller than at cluster 1, although the A-A' plane of each cluster only shows a two dimensional view of the system. So while the imaging of zone 2 injections at cluster 2 indicate a roughly 5 to 7 m (16 to 23 ft) radius of influence, it is possible that injection from this zone is asymmetric in its influence. The orientation of the A-A' plane of cluster 1 is perpendicular to the A-A' plane at cluster 2. If injections followed a more elliptical shape, the A-A' plane in cluster 2 may represent the shorter radius of the injection influence while the A-A' plane in cluster 1 demonstrates the longer radius. In short, it is difficult to determine the absolute radius of influence in the absence of a 3-D image.

ERT cluster 3 is located across zones 3 and 4 (Figure 3-28). Injections of polyphosphate solutions to zones 3 and 4 occurred on September 13 to 16 and 16 to 20, 2018, respectively. ERT imaging at cluster 3 showed degrading measurement quality over the course of the monitoring period, and these measurements were removed. The removed measurements were mostly associated with injection wells 399-1-114 (C9658) and 399-1-116 (C9660). This resulted in decreased image resolution in comparison to clusters 1 and 2. Reduced resolution at injection well 399-1-116 (C9660) near the PRZ resulted in no response near this well during the injections, and therefore no interpretations could be made concerning polyphosphate solution distribution. Increases in bulk conductivity near the water table indicate that the polyphosphate injection solution did reach wells 399-1-155 (C9699), 399-1-150 (C9694), and 399-1-114 (C9658), which indicates lateral, pressure-driven transport at the water table. However, over the injection period to zone 3 there was no indication from ERT imaging that the polyphosphate injection solution reached the PRZ and LVZ at well 399-1-155 (C9699), 4 m (13 ft) away (Figure 4-32).



Source: Modified from Figure 18 in PNNL-28619, *Stage B Uranium Sequestration Amendment Delivery Monitoring Using Time-Lapse Electrical Resistivity Tomography*.

Figure 4-31. Twice Daily Images of ERT Amendment Distribution in Cluster 2



Source: Modified from Figure 19 in PNNL-28619, *Stage B Uranium Sequestration Amendment Delivery Monitoring Using Time-Lapse Electrical Resistivity Tomography*.

Figure 4-32. Twice Daily Images of ERT Amendment Distribution in Cluster 3

Bulk conductivities on September 17, 2018, one day after injection finished in zone 3, indicate that the values quickly returned to baseline values. This may be because of rapid draining of the polyphosphate injection solution to the water table after injections stopped. The following observations based on aquifer data from wells in zones 3 and 4 appear to support this conclusion. Phosphate concentrations in aquifer wells in zone 4 show a short-lived peak with a rapid decline in concentrations back to nearly baseline.

Monitoring wells downgradient of zone 4 show prolonged elevated phosphate concentrations with peaks in data that correlate with timing of injections into zone 4. Baseline ERT measurements at well 399-1-116 (C9660) exhibited relatively low bulk conductivity in the baseline image vadose zone, which may indicate coarser-grained materials. Coarser-grained materials are not conducive to horizontal flow and may have inhibited lateral migration of the polyphosphate solution here. Borehole logs from wells in cluster 3 indicate similar lithologies as at clusters 1 and 2. The sediments are a combination of silty sandy gravel, sandy gravel, and gravel. There were no silt-rich rip-up clasts observed in any of the ERT wells. However, residual effects of discharges may reduce the porosity of the subsurface sediments and subsequently impede the vertical permeability of the system. In areas where effects of residual contamination are less, the sandy gravels may produce more of an isotropic system with horizontal permeability being nearly equal to vertical permeability. ERT imaging of injections to zone 4 indicate that mounding of the injection solution was minimal above the water table and the lateral extent did not reach the monitoring wells in the cluster. The absence of significant mounding seen through ERT is consistent with the lack of sufficient water to sample the two PRZ wells in zone 4. Two PRZ monitoring wells, 399-1-146 (C9690) and 399-1-154 (C9698), were not successfully sampled during the daily sampling campaign, which indicates that there was poor lateral distribution of the polyphosphate injected into the LVZ and PRZ. Overall injections in zone 3 and 4 at cluster 3 appeared to have behaved far more isotropically than in clusters 1 and 2 with less lateral spreading of polyphosphate injection solution. However, cluster 3 should not be considered representative of zones 3 and 4 overall due to the limitations in imaging on one side of the A-A’ plane.

4.4.3 Post-Treatment Monitoring

Real-time ERT data were collected through October 2018. All three ERT clusters exhibited overall declines in bulk conductivities following the completion of injections to their respective vadose zones, indicating draining of polyphosphate solution to the saturated zone, and possibly some influence from phosphate precipitation (which may decrease pore fluid conductivity). ERT imaging also indicated that increased bulk conductivities remained in the saturated zone of each ERT cluster through September 2018.

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5 Enhanced Attenuation Performance Evaluation

The expected outcome of the EA remedy using polyphosphate treatment is the reduction in uranium concentrations in groundwater downgradient of the EA treatment area (Appendix B of DOE/RL-2014-42). This remedy is also expected to result in less seasonal variation in uranium concentrations in the underlying groundwater because the uranium is sequestered in situ within the LVZ and PRZ by precipitation of phosphate minerals. The Stage A EA performance evaluation is presented in Chapter 5 of SGW-59614. This chapter discusses the Stage B EA initial performance evaluation and the overall outcome of the Stage A and B EA remedy on uranium sequestration.

The evaluation of the Stage B EA is based on the following design objectives developed for Stage B (Section 1.2 of DOE/RL-2014-42-ADD1):

- Determine the delivery and distribution of phosphate in the vadose zone, PRZ, and aquifer.
- Determine short-term impacts (<1 year) to local uranium groundwater concentrations and groundwater chemistry.
- Determine the change, if any, observed in the leachability of uranium after treatment.

This evaluation uses multiple lines of evidence collected from monitoring data, laboratory experiments, and numerical modeling in accordance with Table 5 in DOE/RL-2014-42-ADD1 to determine the treatment effectiveness. Each line of evidence was used to answer multiple questions and corroborate findings in other data sets.

5.1 Effectiveness of Phosphate Delivery and Distribution

Phosphate delivery and distribution in the vadose zone, PRZ, and aquifer during Stages A and B were evaluated using ERT imaging, groundwater sampling, soil sampling, injection solution monitoring, downhole sensor monitoring, and comparison of pre-treatment and post-treatment results. Each of these sampling media allowed for spatial and temporal analysis of phosphate delivery and distribution. Both Stages A and B achieved target goals for delivery of polyphosphate solution to the PRZ through injections. While ERT, downhole sensor data, and groundwater monitoring showed that the lateral distribution of phosphate was generally effective in the targeted treatment zones, the spatial distribution of phosphate varied where subsurface heterogeneity influenced the solution migration.

5.1.1 Evaluation of Phosphate Delivery and Distribution During Treatment

ERT imaging, downhole sensor monitoring, injection volume and solution concentration monitoring, and groundwater sampling were conducted during polyphosphate treatment to monitor the distribution and delivery of polyphosphate in the Stage B area. The data collected from these systems indicate that the required 16.3 million L (4.3 million gal) of polyphosphate solution was delivered to the vadose zone, PRZ, and aquifer during Stage B; however, the polyphosphate solution was not distributed evenly across the Stage B EA area. This spatial variability can be attributed to local heterogeneities in permeability in the Hf affecting lateral migration of the solutions and the ability of different injection wells to accept fluids at the same rates.

The monitoring systems in zones 1 and 2 indicated good spatial distribution of phosphate in both the LVZ and PRZ. Images of the elevated bulk conductivity in cluster 1 suggests lateral delivery of the injected solution that impacted all of the PRZ and much of the LVZ. Phosphate concentrations were elevated during zone 1 and 2 injections in groundwater samples from well 399-1-160 (C9704), which is adjacent to the zone 1 injection well in cluster 1. The specific conductance data from the downhole sensors in the

zone 1 and 2 PRZ wells also indicate response to the polyphosphate injections (Figures 4-18, 4-19, 4-21 and 4-22).

The monitoring systems in zone 3 indicated good spatial distribution of phosphate in the PRZ. The ERT images in cluster 2 show lateral distribution of phosphate solution in the PRZ and aquifer. Downhole sensor data and groundwater phosphate concentration data from all PRZ wells in zone 3 show responses to the zone 3 injections (Figure 4-20).

The monitoring systems in zone 4 indicated limited distribution of phosphate. Because the ERT images had reduced resolution, they could not be used to evaluate the polyphosphate solution distribution. Downhole sensor data in PRZ wells located in zone 4 do not indicate responses to zone 4 injections (Figure 4-23). The specific conductance data and phosphate concentrations from groundwater samples cannot be correlated due to poor data quality.

5.1.2 Evaluation of Phosphate Distribution Post-Treatment

This section evaluates the distribution of phosphate both within and downgradient of the injection zones for the months after injections.

5.1.2.1 Post-Treatment Distribution of Phosphate in the Vadose Zone

Following injection of polyphosphate, precipitation of phosphate minerals is expected (initially as amorphous phases, then monocalcium phosphate, $Ca(H_2PO_4)_2$, with eventual crystallization of hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$) (Sumner, 2000, “Soil Fertility and Plant Nutrition”). The goal is to form these solid phases throughout the injection area to maximize attenuation of uranium. Therefore, both aqueous and solid phase phosphorus (as total phosphorus and phosphate) in the vadose zone sediments were analyzed alongside ERT data in order to track the distribution of solutions and formation of the targeted solid phases. In addition, Stage B sequential phosphate extractions using groundwater (a synthetic formula to mimic 300 Area groundwater) were analyzed for total phosphorus to estimate aqueous and adsorbed phosphorus in pre-treatment and post-treatment sediments. Further, for Stages A and B, sediment extractions with 0.5 M nitric acid, and sequential extractions were analyzed for total phosphorus and phosphate (with the exception of pre-treatment samples for sequential extractions in Stage A).

Due to impacts of previous waste disposal operations, phosphorus was widely distributed in the sediments prior to polyphosphate injections. The average phosphate concentrations were 1,750±80 µg/g and 365±223 µg/g as phosphate in pre-treatment samples analyzed for Stages A and B, respectively, for 0.5 M nitric acid extracts (PNNL-24911, PNNL-29650). Following injection of polyphosphate, the average phosphate concentration increased by 137 and 123 µg/g in Stage A and B samples, respectively, for 0.5 M nitric acid extracts. Phosphorus analyzed in sequential extractions in Stage B showed larger differences in pre-treatment to post-treatment sediments, with an increase of 183 µg/g in extraction #5 (Figure 5-1) and 123 µg/g in extraction #6 (Section 4.5 of PNNL-29650).

A comparison of the total phosphorus concentrations in pre-treatment and post-treatment samples based on the sequential extractions for Stage B shows that the total phosphorus increased in all but three post-treatment borehole samples. Moreover, total phosphate in the porewater was as high as 1,000 mg/L 6 months after injections with 10 of 13 post-treatment sediments receiving high phosphate based on aqueous phosphate in column leach experiments (Section 4.5 in PNNL-29650).

Figure 5-2 provides an overview of the total phosphorus distribution with depth and distance across the paired pre-treatment and post-treatment samples analyzed for Stage B in sequential extraction #5. These results showed that while phosphorus increases in the subsurface following treatment, there was

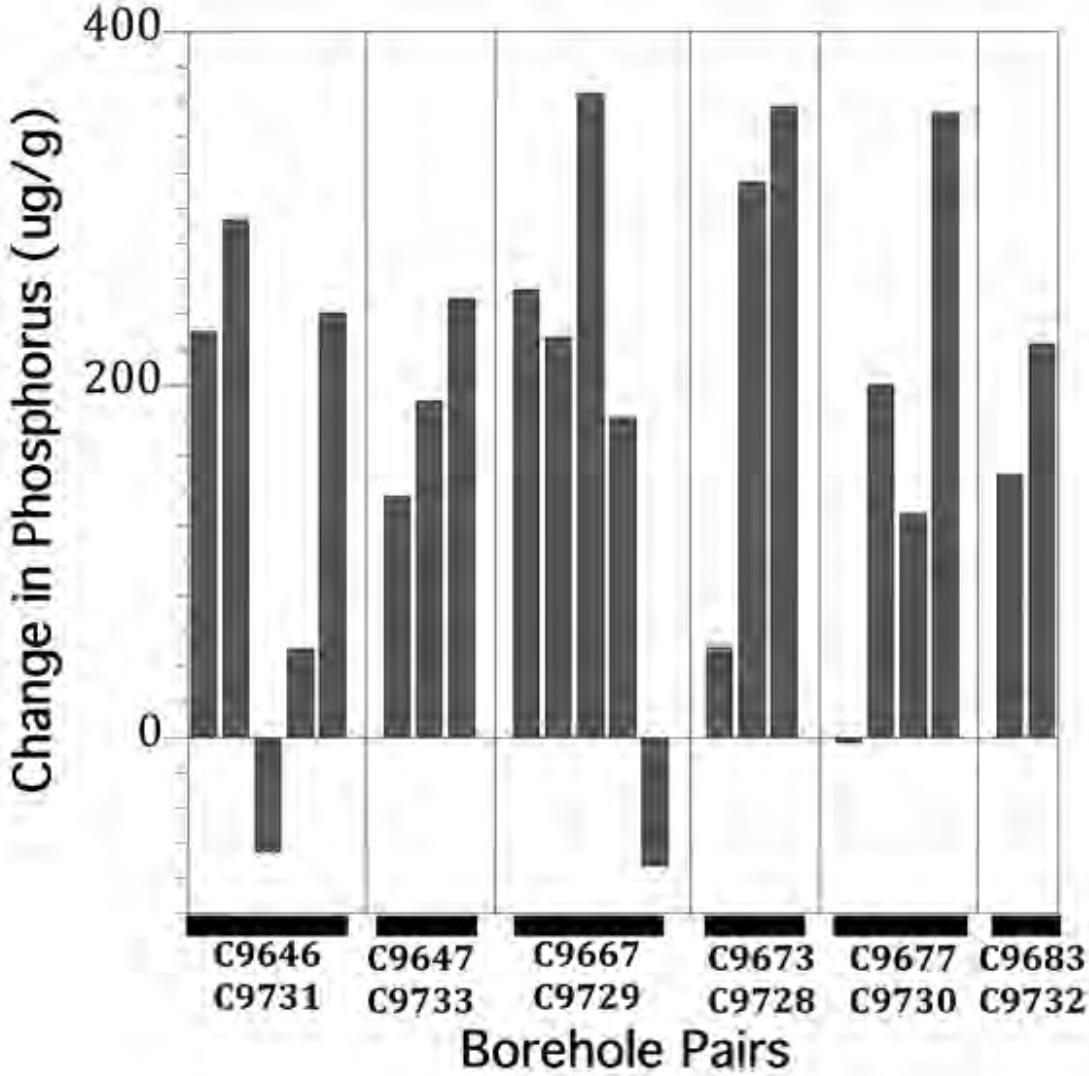
significant variability in the lateral distribution and an insignificant correlation of delivery with depth (Section 4.5 of PNNL-29650). Post-treatment borehole C9736, between injection zones 3 and 4 and approximately 6 m (20 ft) from each of the four injectors around it, may have received lower phosphate due to its greater distance from injectors. However, post-treatment borehole C9735 in zone 1, also approximately 6 m (20 ft) from injectors, had elevated phosphate throughout the LVZ and PRZ. Some sample depths in post-treatment boreholes C9731 (7.62 m [25 ft] bgs) and C9733 (9.14 m [30 ft] bgs) located in zone 2 had lower phosphate concentrations suggesting some gaps in delivery. In Stage A, elevated phosphate concentrations high in the section (e.g., in post-treatment borehole C9580 at 5 m [16.4 ft] bgs) were attributed to silt layers which slowed movement of solutions during infiltration and increased adsorption (Section 4.1.2 in SGW-59614). Similar subsurface heterogeneities may have impacted lateral distribution in Stage B as shown by the variability with respect to depth and borehole (Figure 5-2). Despite these few exceptions, results suggest that phosphate was effectively delivered to the majority of targeted areas based on extraction analyses of soil samples collected after 6 months for Stage B.

Microscopy of the solid phase corroborated that a significant mass of phosphate precipitated from the polyphosphate solution injections into sediments (Figure 5-3). Phosphorus was identified in 6 of 11 micron-scale maps collected in the post-treatment sample (C9729, 7.62 m [25 ft] depth) compared to 1 of 7 maps in the pre-treatment samples (399-1-123 [C9667], 7.62 m [25 ft] depth). The extractions and SEM-EDS analyses are consistent with precipitation of calcium-phosphate phases as predicted by geochemical equilibrium simulations which showed that apatite was highly favored to precipitate under the conditions induced by the polyphosphate injection (Section 4.4.3 in PNNL-29650).

5.1.2.2 *Post-Treatment Distribution of Phosphate in the Aquifer*

ERT imaging and groundwater monitoring data collected after the conclusion of Stage B injections indicated that residence times of the polyphosphate solution varied among the injection zones. High baseline conductivity areas in ERT images prior to injections in zones 1 and 2 may represent finer grained rip-up clasts of lower permeability interbedded with coarser grained sediments. Additionally, residual waste that coated the sediments increased anisotropy of the system under zones 1 and 2 promoting lateral transport of the solution and may have also caused phosphate solution to persist in some areas of the aquifer and PRZ rather than migrating to groundwater and being diluted. Geologic heterogeneity created conditions for increased lateral transport in zones 1 and 2, but in zones 3 and 4, where mounding was not as apparent, vertical transport to groundwater was more prevalent.

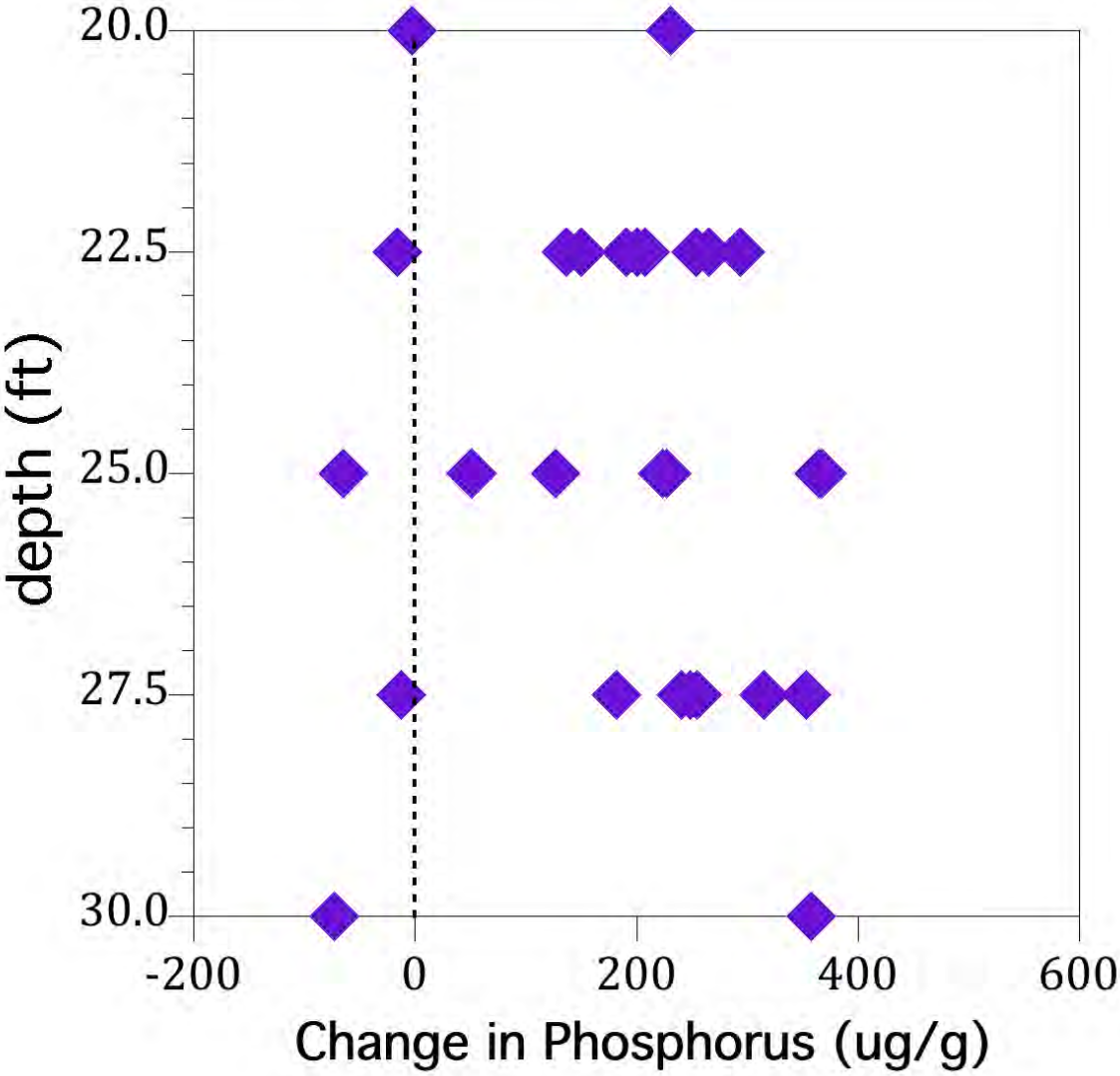
The time until the arrival of phosphate at downgradient wells depended in part on the distance from the EA area to the well. Downgradient groundwater monitoring wells closest to the Stage A and B areas saw the earliest increases in phosphate concentrations following injections. Well 399-1-23, the downgradient well closest to the Stage A area and zone 1 of the Stage B area, exhibited increases in phosphate and specific conductance within 4 days after the commencement of injections, with maximum concentrations of 800 mg/L and 1,200 µS/cm, respectively (Figure 5-4). The higher maximum phosphate and specific conductance concentrations at well 399-1-23 during Stage B than during Stage A may reflect the higher volume of solution injected during Stage B. Well 399-1-23 displayed the highest maximum concentrations of phosphate and specific conductance during both stages, most likely because it is the downgradient well closest to the injection sites. However, well 399-1-23 also may be within a preferential pathway for groundwater flow.



Note: Each bar for each borehole pair represents a different depth.

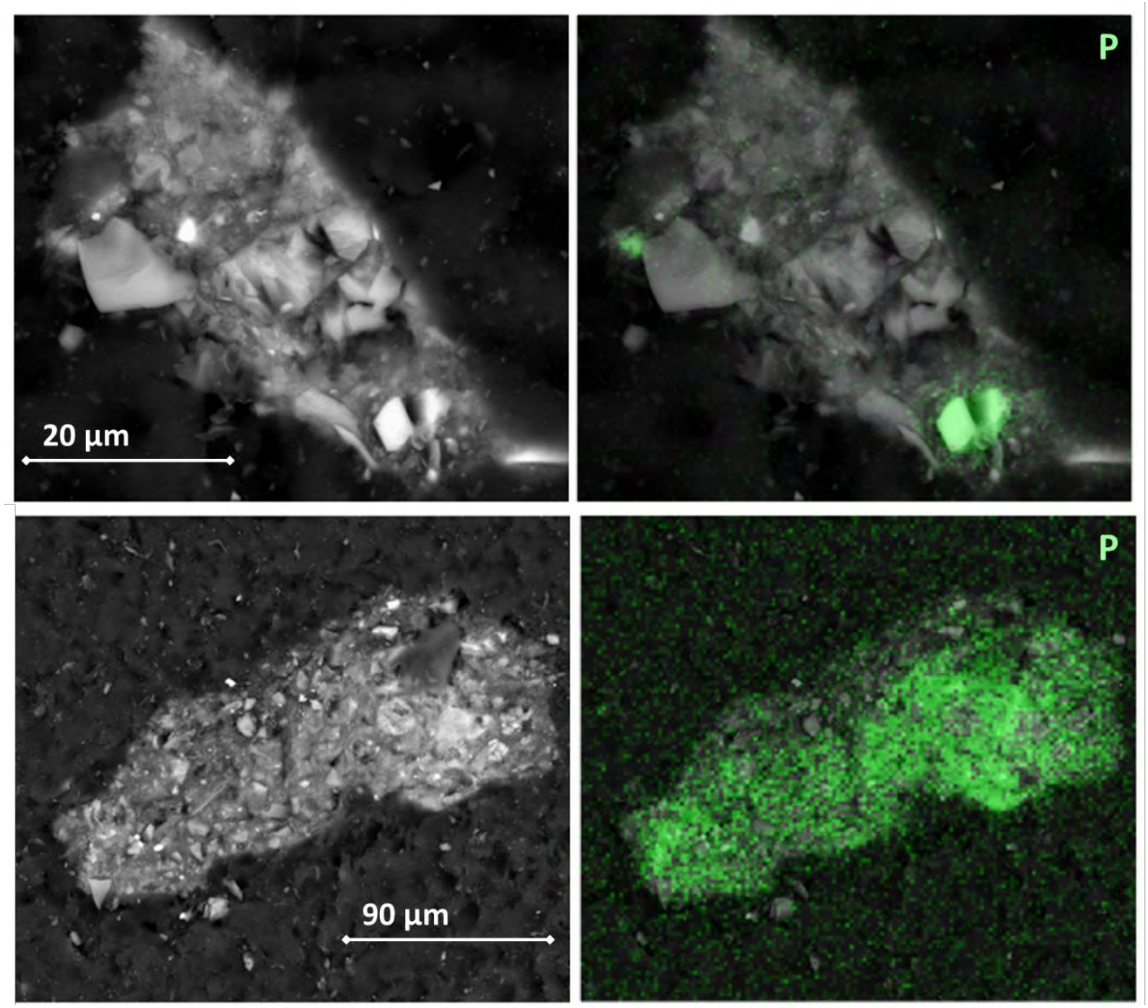
Source: Figure 4.51 in PNNL-29650, *Evaluation of the Change in Uranium Mobility in Sediments from the Hanford 300-FF-5 Stage B Polyphosphate Field Injection*.

Figure 5-1. Measurement of the Change in Solid Phase Phosphorus in Stage B from Pre-Treatment to Post-Treatment



Source: Figure 4.52 in PNNL-29650, *Evaluation of the Change in Uranium Mobility in Sediments from the Hanford 300-FF-5 Stage B Polyphosphate Field Injection*.

Figure 5-2. Comparison of the Change in Total Phosphorus (Post-Treatment Minus Pre-Treatment) in Stage B Paired Boreholes with Respect to Depth



Notes: Uranium was below detection limits for SEM-EDS, approximately 500 µg/g (Section 4.4.3 of PNNL-29650, *Evaluation of the Change in Uranium Mobility in Sediments from the Hanford 300-FF-5 Stage B Polyphosphate Field Injection*).

Electron backscatter produced an image of the particle surface (left) and phosphorus mapping was overlaid in green (right), depicting the change in distribution of phosphate following polyphosphate treatment. Both samples are from 7.62 m (25 ft) bgs.

Figure 5-3. Representative 2-D Elemental Maps using SEM-EDS of Pre-Treatment Borehole 399-1-123 (top) and Post-Treatment Borehole C9729 (bottom) Sediments Showing an Increase in Phosphorus in the Solid Phase After Polyphosphate Injection

Wells farther downgradient also display increases in phosphate concentration and specific conductivities above background levels after Stage A and B injections. In contrast to well 399-1-23, these wells show maximum phosphate and specific conductance concentrations no higher than 350 mg/L and 800 µS/cm, respectively (Figures 5-5 through 5-7). Increases in phosphate concentration and specific conductivity were observed at well 399-2-2, the downgradient well furthest from the Stage A and B areas, for 1 to 6 months after the start of injections. The phosphate and specific conductance concentrations were higher at well 399-2-2 than at well 399-1-7 after Stage B injections (Figures 5-6 and 5-7). Although not shown, well 399-1-16A, which is closer and directly downgradient of zones 3 and 4, displayed increases in phosphate concentration <1 month after injections. The higher concentrations at wells 399-2-2 and 399-1-16A, which are more directly downgradient of zones 3 and 4, may reflect the higher amount of polyphosphate fluid drained to the aquifer in that part of the Stage B area.

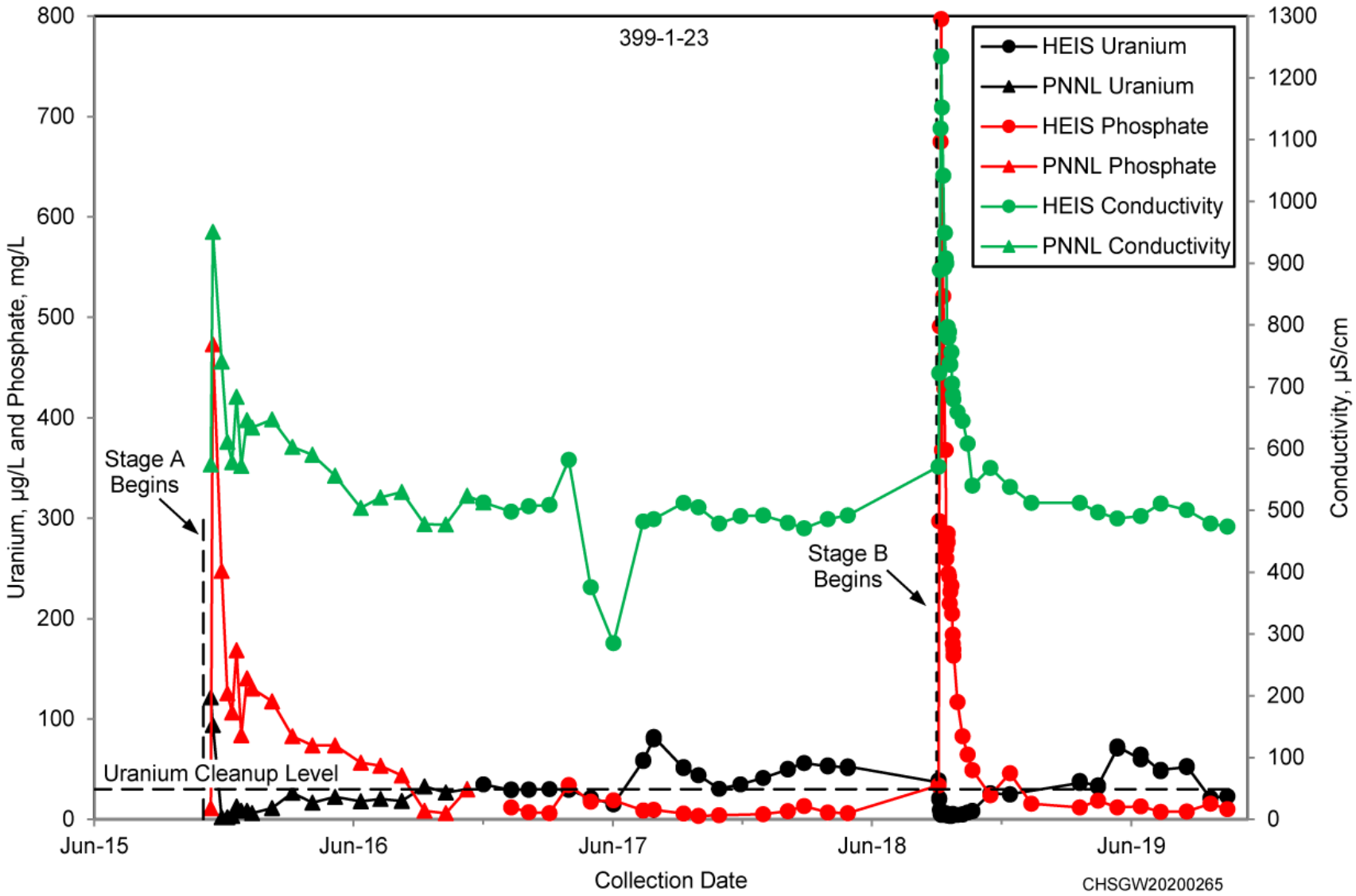


Figure 5-4. Groundwater Uranium, Phosphate, and Specific Conductivity Concentrations at Downgradient Well 399-1-23

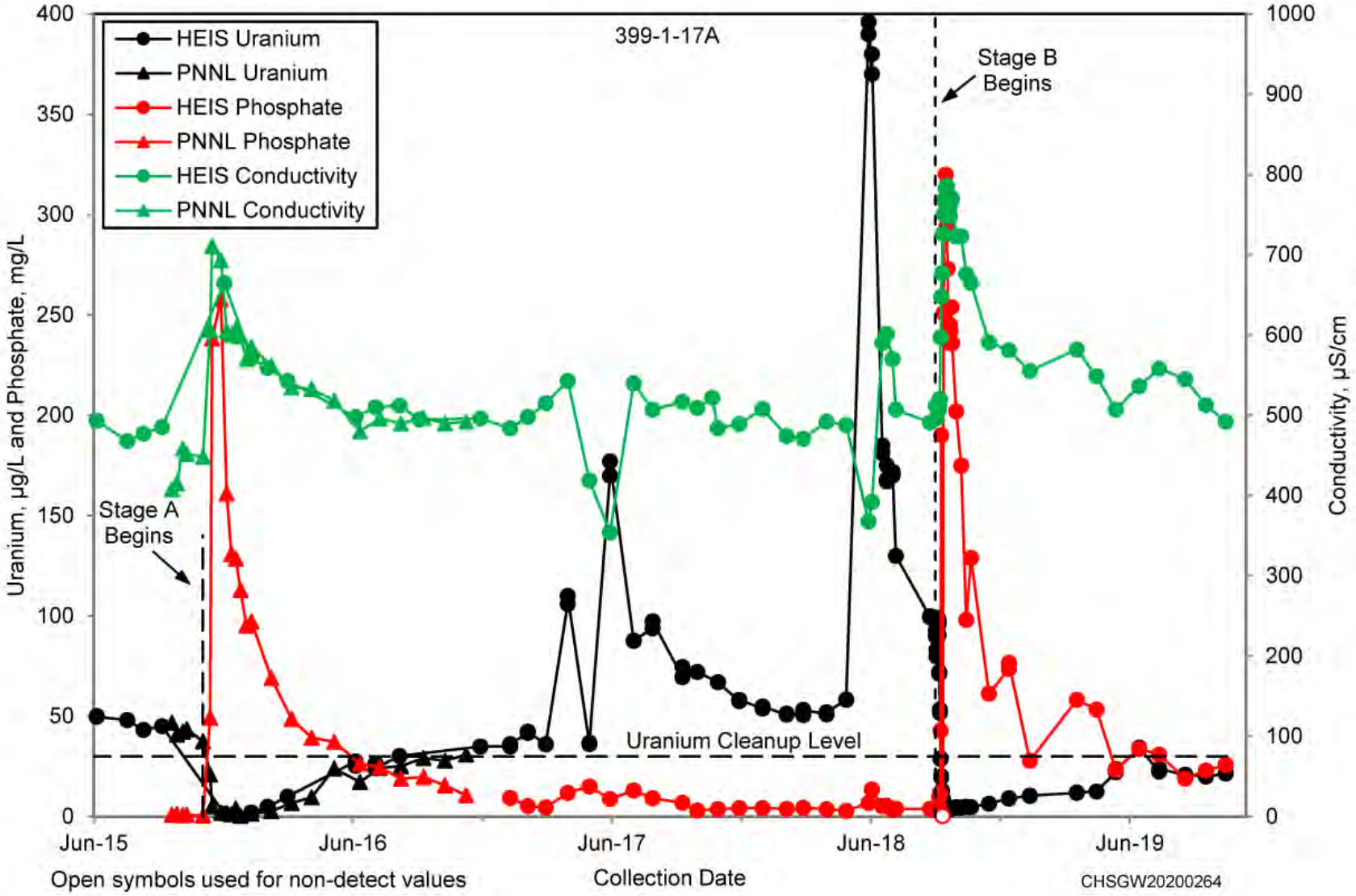


Figure 5-5. Groundwater Uranium, Phosphate, and Specific Conductivity Concentrations at Downgradient Well 399-1-17A

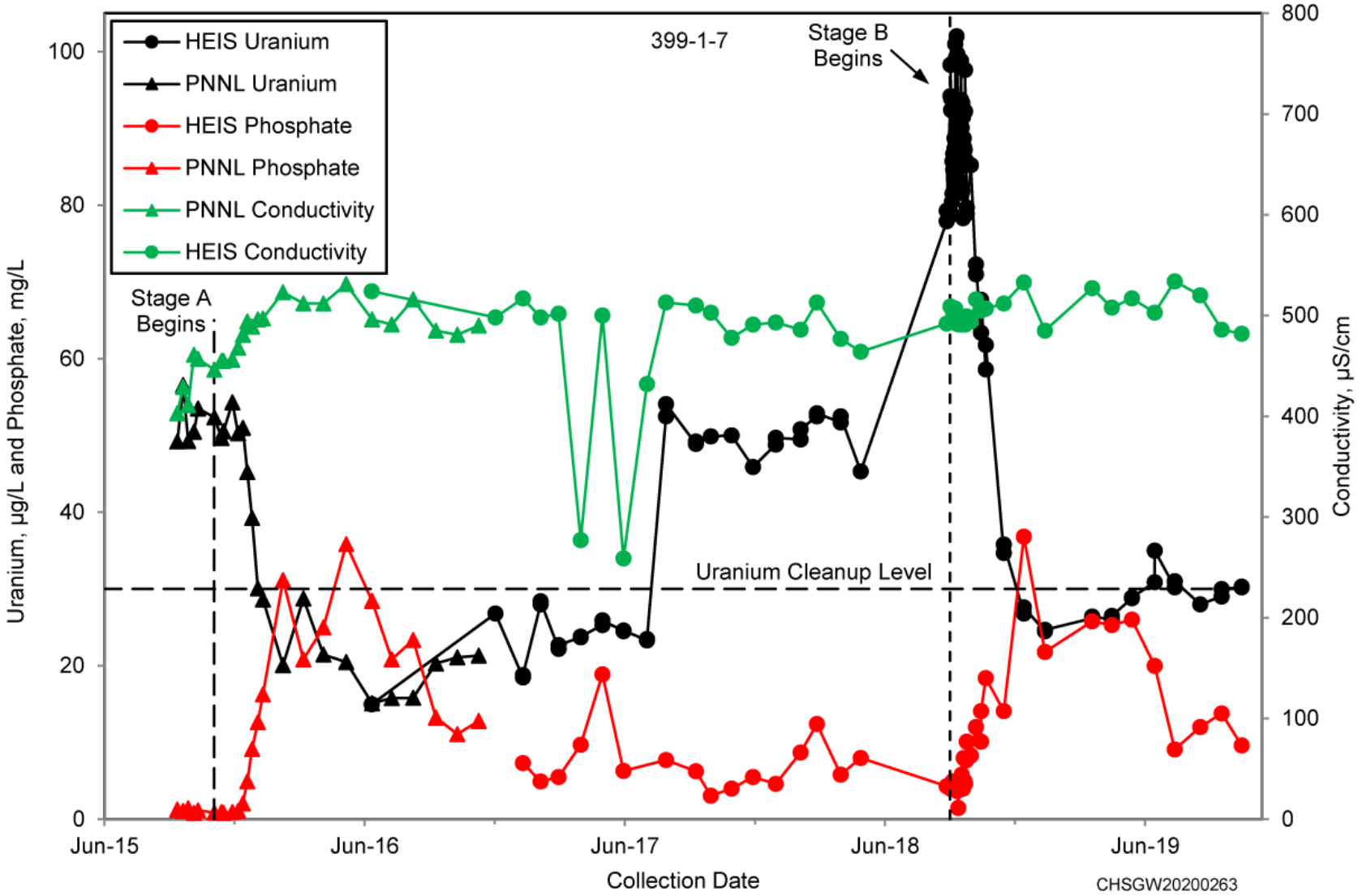


Figure 5-6. Groundwater Uranium, Phosphate, and Specific Conductivity Concentrations at Downgradient Well 399-1-7

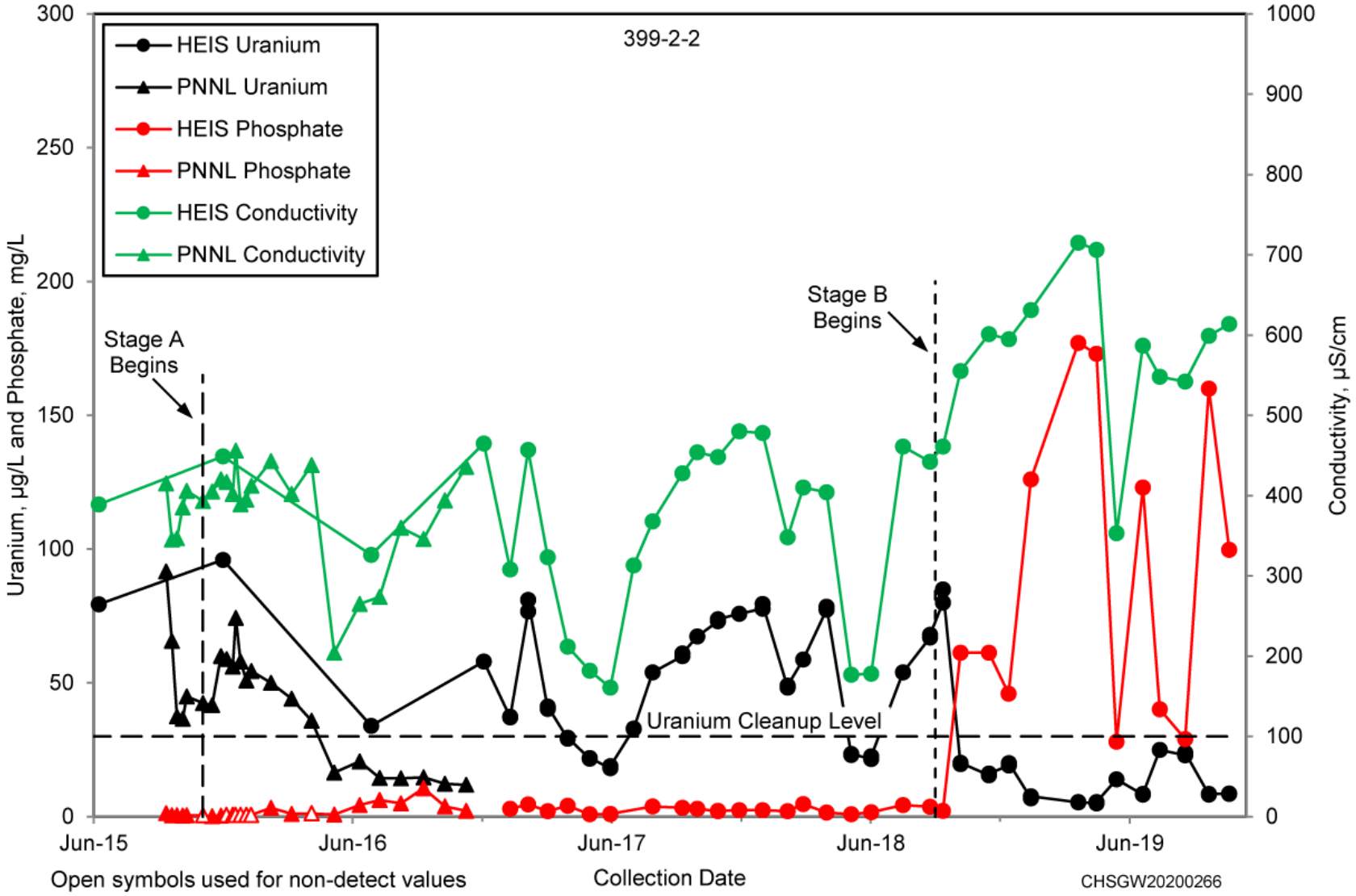


Figure 5-7. Groundwater Uranium, Phosphate, and Specific Conductivity Concentrations at Downgradient Well 399-2-2

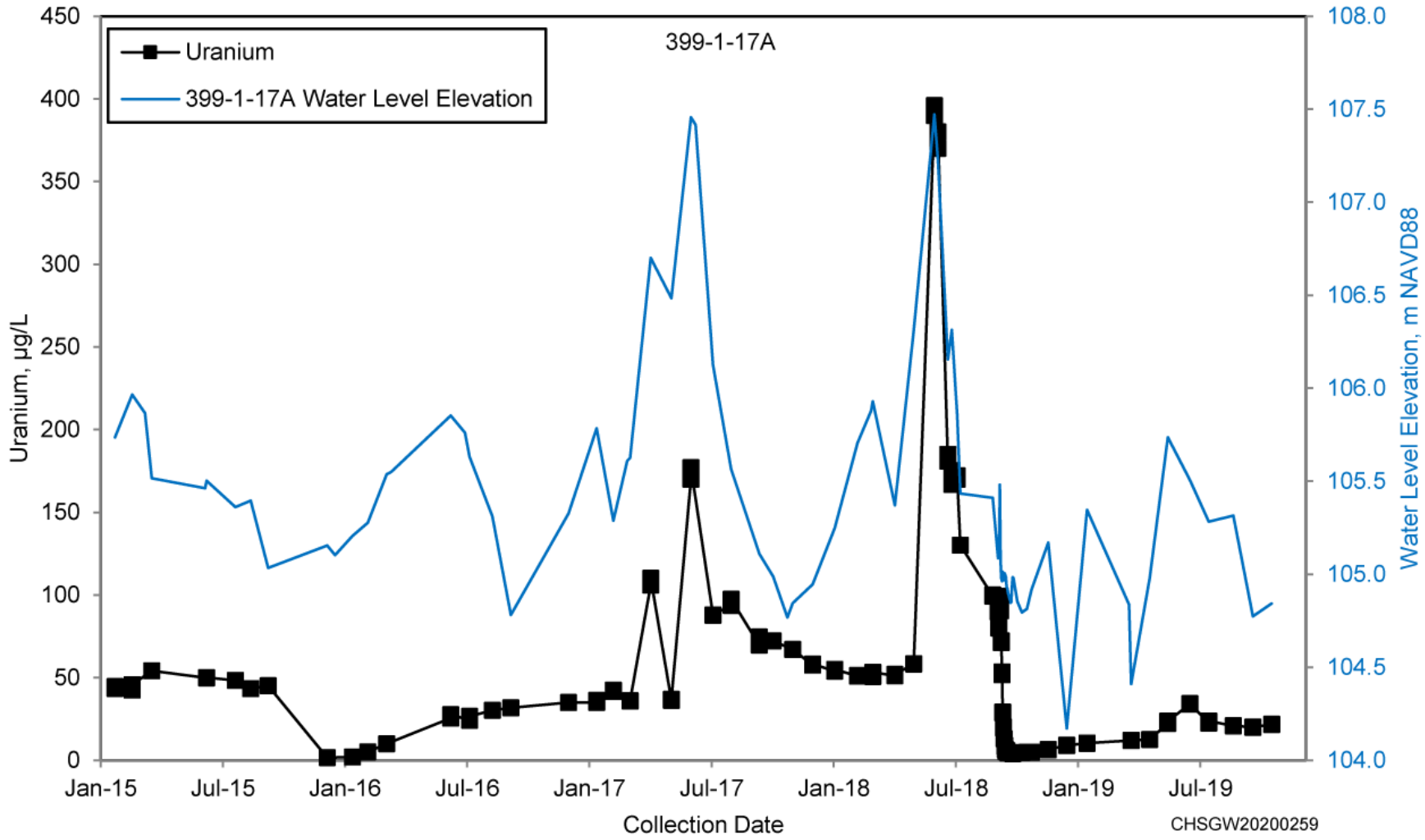


Figure 5-8. Uranium Concentrations and Water-Level Elevation Data at Downgradient Well 399-1-17A

Uranium concentrations in these four downgradient wells declined below the CUL with the increase in phosphate concentrations (Figures 5-4 through 5-7). Well 399-1-16A (not shown) also displayed a decline in uranium concentrations to below the CUL through June 2019. The decline in uranium concentrations in both wells 399-1-16A and 399-2-2 indicates that there was enough phosphate treatment into zones 3 and 4 to affect the system and decrease uranium concentrations. The uranium concentration increased in well 399-1-17A in June 2018 in response to the seasonal water level increase (Figure 5-8).

5.2 Impacts of Polyphosphate Injections on Uranium Mobility Reduction

The reduction in uranium mobility following the polyphosphate injections was evaluated using changes in groundwater uranium concentrations and results of laboratory tests on pre-treatment and post-treatment soil samples. The laboratory tests included sequential and carbonate extractions, 1-D column leach tests, and solid phase elemental mapping

5.2.1 Changes in Total Uranium Distribution in the Vadose Zone

Sequential and carbonate extractions showed that the overall mobility of uranium decreased after polyphosphate solution injections. Some initial mobilization of uranium may have occurred (Section 5.3.2 of this report), due to the conditions created by polyphosphate solution injection (e.g., high ionic strength). However, the ability to extract uranium from sediments decreased as summarized below.

Due to the variability of natural uranium in sediments and impacts from historic waste disposal, the total uranium extracted based on the sum of the sequential extractions was variable in both pre-treatment and post-treatment sediments. In Stage A, the sum of total uranium extracted in pre-treatment and post-treatment sediments was 32±36 µg/g and 42±35 µg/g, respectively (Snyder and Cantrell, 2015; PNNL-24911; PNNL-25420). In Stage B, the sum of total uranium in pre-treatment and post-treatment extractions was 52±27 µg/g and 34±32 µg/g, respectively (Section 4.2.1 of PNNL-29650). However, in 14 of 19 pre-treatment and post-treatment pairs of sediment samples analyzed in Stage B, the total uranium as measured by the sum in the sequential extractions was lower in the post-treatment samples. These results could suggest that some uranium was initially mobilized by the polyphosphate injection solutions. However, uranium concentrations in 300 Area soils are rarely consistent from borehole to borehole. There is large uncertainty in the range of uranium concentrations that stems from sample to sample variability and normalization to the total sediment weight. By design, samples selected for pre-treatment analyses are biased toward the highest uranium concentrations and other wells near those selected had lower uranium concentrations in soil samples prior to phosphate treatment. As discussed in Section 4.2.1 of this report, groundwater monitoring data within the treatment area suggest there was limited mobilization initially based on increases in uranium in the first 2 days after injection began, with no evidence of uranium mobilization observed in downgradient wells. The decrease in groundwater uranium concentrations over time are due to precipitation of phosphate phases which sequester uranium and reduce migration to the aquifer.

The extraction results further show that the mobility of uranium decreased based on the different sequential extractions. For example, the mobile uranium fraction in Stage B for pre-treatment sediments is 0.425±0.096 and for post-treatment samples is 0.156±0.143, which is an average of 63% less mobile uranium as a result of the polyphosphate treatment based on carbonate extractions of 44 sediments including 19 pre-treatment and post-treatment pairs. There was also a strong correlation between the increase in solid phase phosphate as determined by oxalate extractions (#5) and the decrease in pre-treatment to post-treatment mobile uranium fraction determined by the carbonate extractions (R^2 = 0.88), suggesting that the delivery of phosphorus via polyphosphate injections may be correlated with decreasing uranium mobility (Section 5.5 of PNNL-29650) (Figure 5-9).

Moreover, the six sequential extractions for Stage B samples also showed that the most mobile uranium (i.e., aqueous and adsorbed as measured in extracts #1 and #2, respectively) decreased from 6.7% to 3.4% (average of the total extracted uranium); the higher solubility uranium minerals decreased from 58.6% to 37.2% (extracts #3 and #4); and the low-solubility uranium minerals increased from 36.8% to 54.3% (i.e., oxalate and nitric acid extracts #5 and #6, respectively). The increases and decreases are based on comparison of 19 pre-treatment and post-treatment sediment pairs. These changes in mobility results from pre-treatment to post-treatment are shown in Figure 5-10, where the red blocks indicates the most mobile uranium phases and green blocks indicates the least mobile uranium phases. Detailed results and discussion are in Section 4.2.2 of PNNL-29650. In Stage A, the post-treatment uranium fraction in the acetic acid extractions increased as compared to the pre-treatment uranium fraction with averages of 48±6% and 19±3%, respectively. This result may suggest an initial shorter term increase in relatively soluble uranium phases (e.g., uranyl carbonates or silicates), although the smaller sampling pool must be noted (21 versus 44 sediment samples in Stages A and B, respectively).

Moreover, uranium increases were not significant from pre-treatment to post-treatment samples in Stage A for the oxalate and nitric acid extractions, and the trends with respect to pairs suggest a decrease in uranium for the nitric acid extraction of post-treatment samples. However, because the post-treatment sediment samples were collected at different times following injection (2 months following treatment in Stage A and approximately 6 months following treatment in Stage B), it is likely that the samples represent differing progress in the reaction of uranium with phosphate precipitates. Therefore, results from Stage A may indicate that the formation of less mobile uranium phases is still ongoing in the first month following polyphosphate injections with some initial mobilization of uranium due to the conditions created by the polyphosphate solutions (e.g., relatively high ionic strength). In Stage B, results show that, although total uranium content is variable across the injection area, total extractable uranium decreased in all but the following three pre-treatment and post-treatment borehole sample pairs (Figure 5-11):

- 399-1-123 (C9667)/C9729 at 6.86 m (22.5 ft) bgs
- 399-1-129 (C9673)/C9728 at 8.38 m (27.5 ft) bgs
- 399-1-128 (C9672)/C9728 at 9.14 m (30 ft) bgs

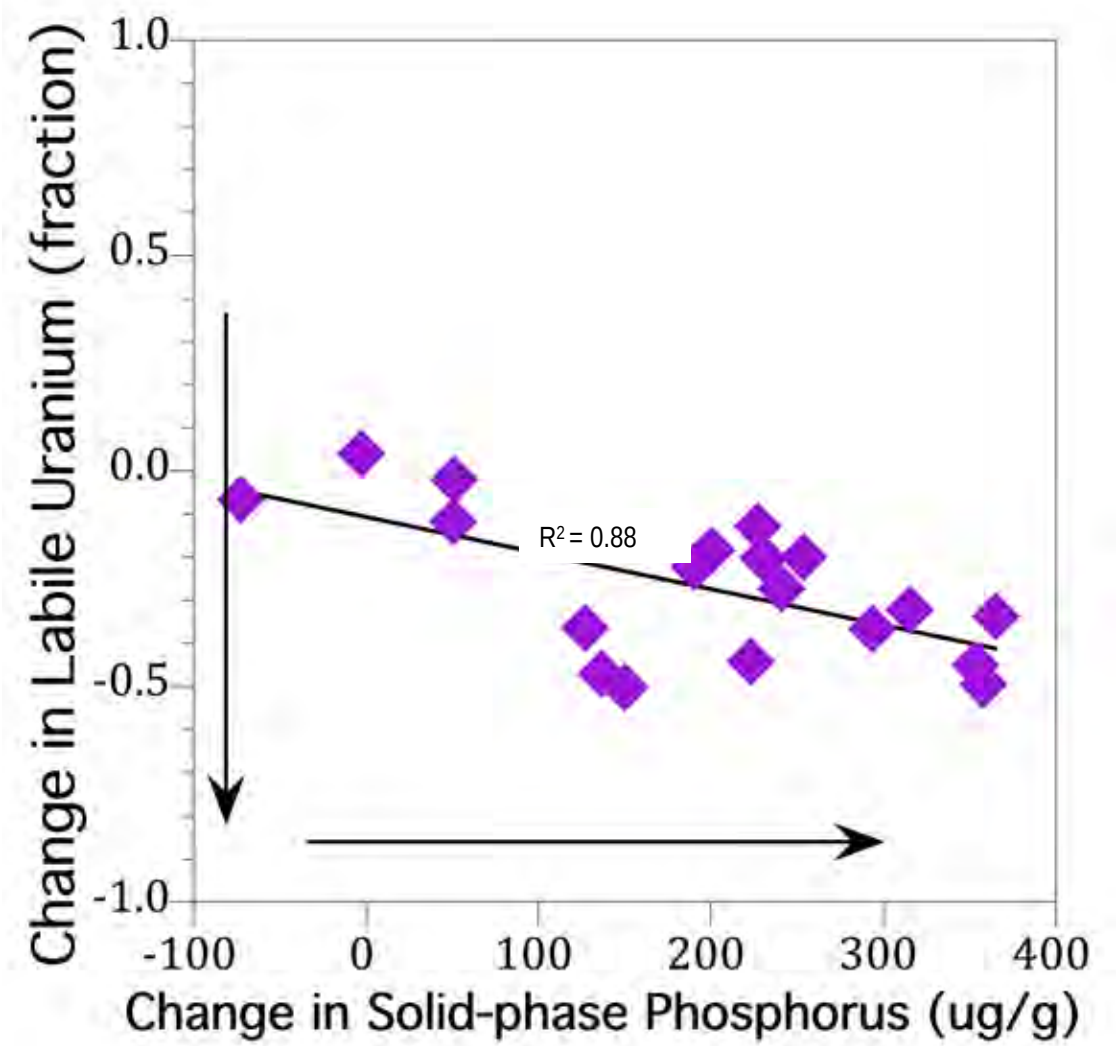
It is possible that the decrease in uranium in the mobile fractions (based on carbonate solution extractions) is due to transformation of high-solubility uranium minerals and adsorbed species in pre-treatment samples to lower-solubility uranium minerals in post-treatment sediments. The transformation is due to dissolution of uranophane [$Ca(UO_2)_2(HSiO_4)_2 \bullet 5H_2O$] or Na-boltwoodite [$Na_2(UO_2)SiO_4 \bullet 1.5H_2O$] and desorption processes followed by secondary sorption and co-precipitation induced by the polyphosphate solutions. The transformation rationale is based on separate batch experiments, which showed that uranium silicates (uranophane and Na-boltwoodite) and uranium carbonates (uranium-substituted calcite) are intermediate solubility uranium minerals (solubilized in carbonate extractions) that may continue to release uranium to the groundwater over time and that uranium phosphate minerals (autunite and torbernite) are lower-solubility minerals (solubilized with oxalate and nitric acid extractions) (Section 4.2.3 of PNNL-29650) (Figure 5-12).

Further, these 300 Area sediments have previously been shown to contain metatorbernite [$Cu(UO_2)_2(PO_4)_2 \bullet 8H_2O$], uranophane [$Ca(UO_2)_2(HSiO_4)_2 \bullet 5H_2O$], and aqueous and adsorbed uranium (Wang et al., 2005, “Cryogenic laser induced fluorescence characterization of U(VI) in Hanford vadose zone pore waters”; Arai et al., 2007, “Spectroscopic evidence for uranium bearing precipitates in vadose zone sediments at the Hanford 300-Area site”). These compositions are consistent with previous research

that has identified multiple mechanisms that decrease uranium mobility with polyphosphate injection including the following:

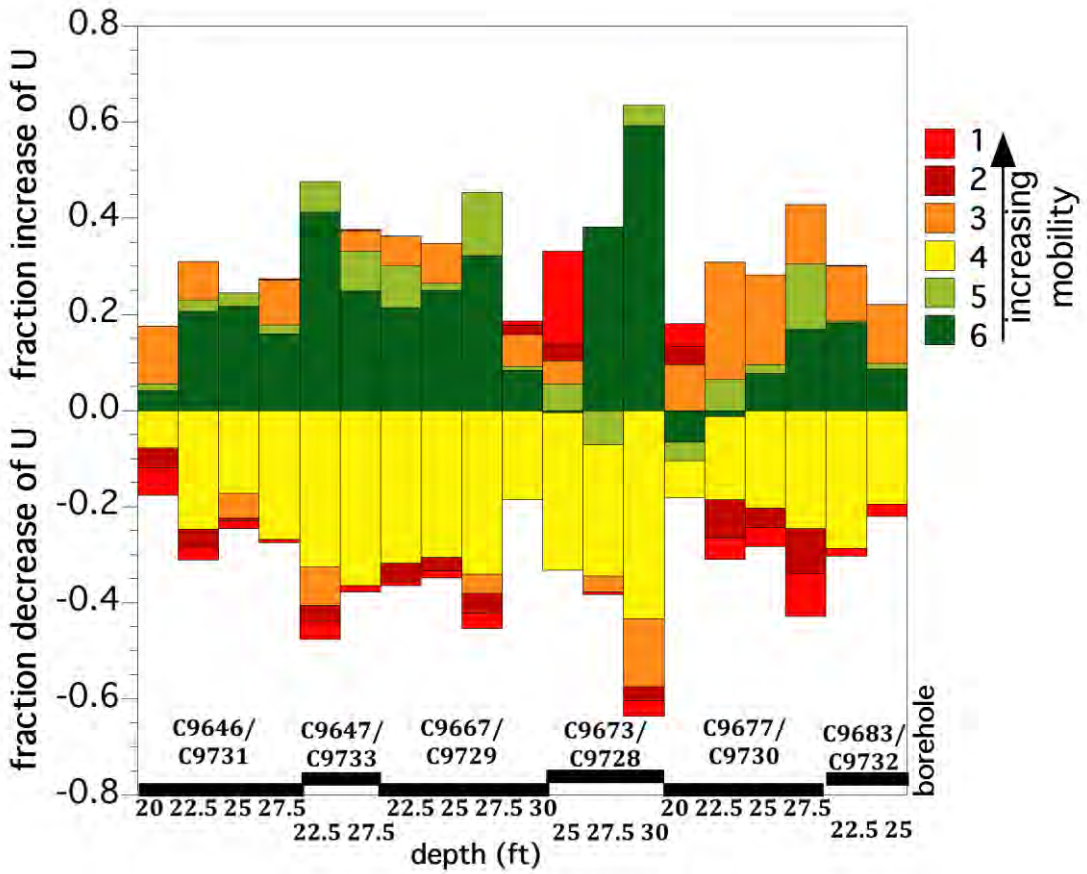
- Precipitation of a low-solubility uranium-phosphate mineral (autunite)
- Precipitation of a calcium-phosphate mineral (apatite) that can structurally incorporate uranium
- Precipitation of calcium-phosphate that coats existing uranium phases (i.e., uranium in calcite, uranium in iron-oxides), reducing uranium leaching
- Aqueous calcium-uranium-carbonate species adsorption onto apatite (Wellman et al., 2008; PNNL-17818; PNNL-17480; Mehta et al., 2016; Lammers et al., 2017)

Section 5.2.3 of this report describes additional characterization of solid phases for identification of uranium sequestration mechanisms.



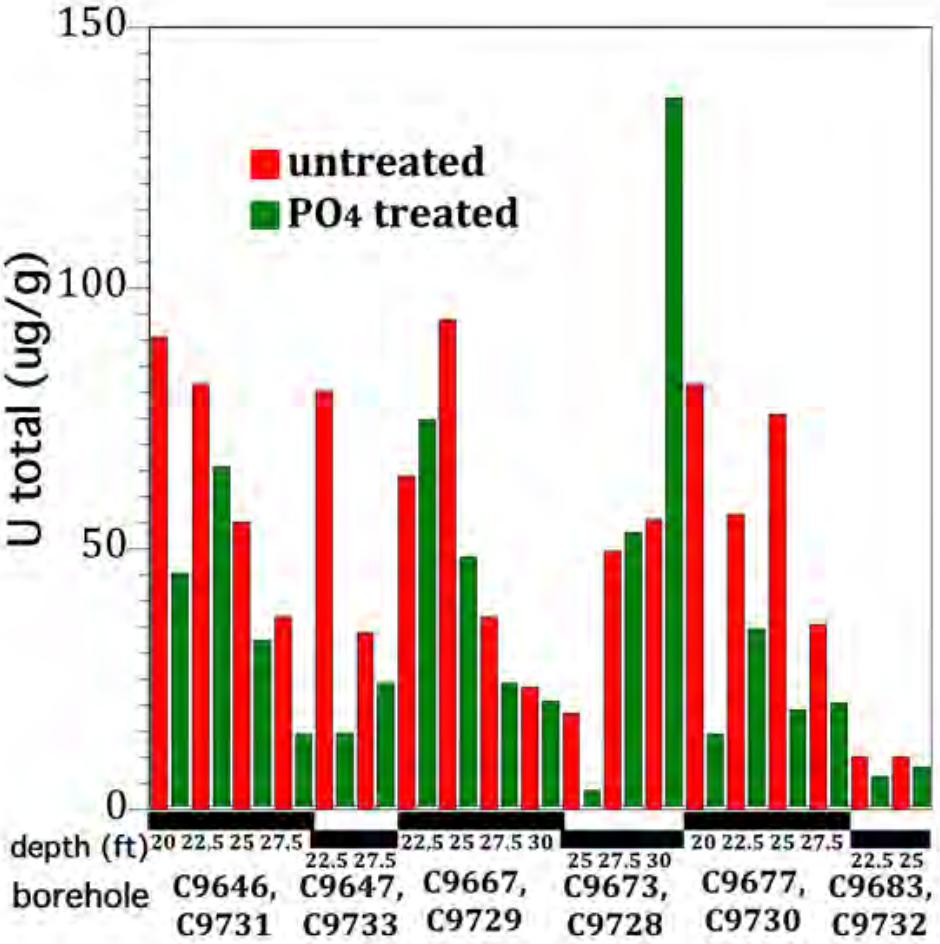
Source: Figure 5.8 in PNNL-29650, *Evaluation of the Change in Uranium Mobility in Sediments from the Hanford 300-FF-5 Stage B Polyphosphate Field Injection.*

Figure 5-9. Correlation Between the Fraction of Mobile Uranium (Post-Treatment Minus Pre-Treatment) with the Change in Solid Phase Phosphorus for Stage B Sediment Samples



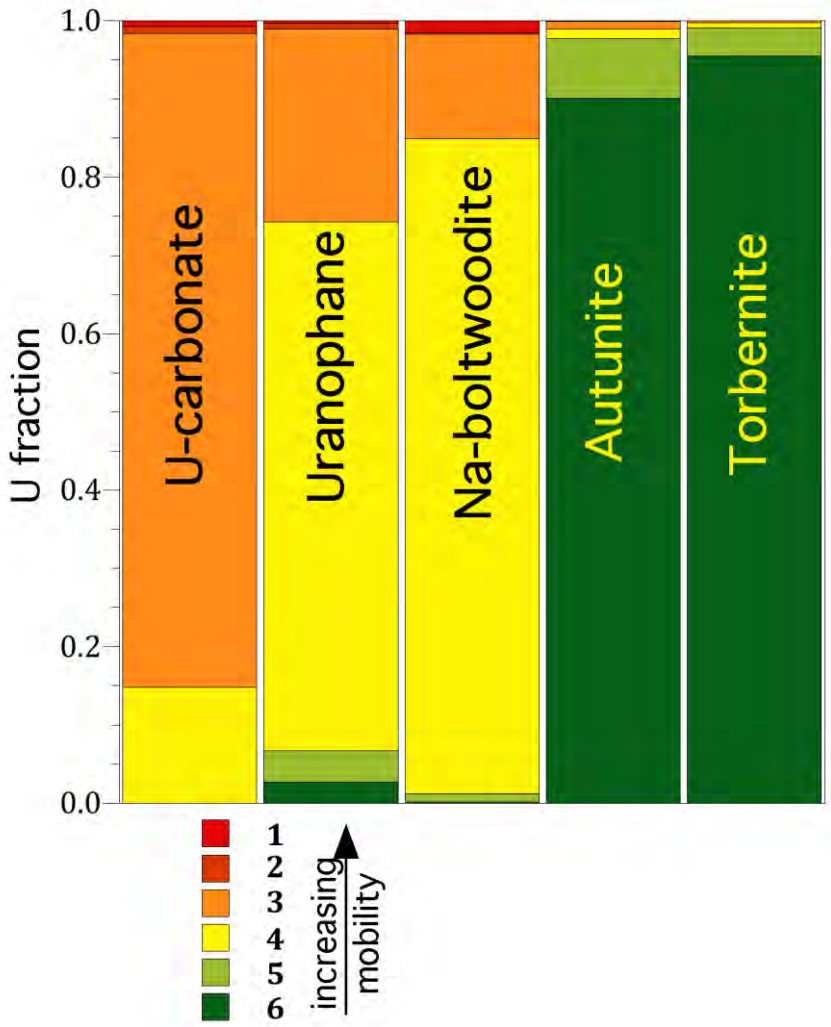
Source: Figure 5.4 in PNNL-29650, *Evaluation of the Change in Uranium Mobility in Sediments from the Hanford 300-FF-5 Stage B Polyphosphate Field Injection*.

Figure 5-10. Change in the Fraction of Uranium (Post-Treatment Minus Pre-Treatment) Extracted in Six Sequential Steps from 19 Pairs of Sediments where Uranium Mobility Decreases with Each Successive Extraction Step



Source: Figure 4.16 in PNNL-29650, *Evaluation of the Change in Uranium Mobility in Sediments from the Hanford 300-FF-5 Stage B Polyphosphate Field Injection*.

Figure 5-11. Comparison of Total Uranium Measured in Six Sequential Extractions in Pre-Treatment (red) and Post-Treatment (green) Sediments



Source: Figure 4.20 in PNNL-29650, *Evaluation of the Change in Uranium Mobility in Sediments from the Hanford 300-FF-5 Stage B Polyphosphate Field Injection*.

Figure 5-12. Sequential Extraction of Uranium Minerals of Relevance to the 300 Area of the Hanford Site

5.2.2 Changes in Uranium Leaching in the Vadose Zone

The 2-month-long, 1-D column leach experiments included stop-flow events that were selected to quantify the uranium release rate from sediments (discussed in Section 5.3.1 of this report). During the leach experiments, the 100 pore volumes that passed through the columns were equivalent to a few years to tens of years at field scale depending on the pore water or groundwater flow rate (i.e., sediment samples in the PRZ will have considerably less pore water flux than sediment samples in groundwater). Of the 10 pre-treatment and post-treatment borehole sediment pairs, 9 pairs showed a decrease in uranium leaching for the post-treatment experiment. One pair showed an increase (399-1-123 [C9667]/C9729 at 9.14 m [30 ft] bgs, located in the southwest corner of injection zone 2), although this sediment sample did not receive significant phosphate.

Figure 5-13 compares leaching of uranium and phosphate in two pre-treatment and post-treatment sample pairs. Sample pair 399-1-129 (C9673)/C9728 at 8.38 m (27.5 ft) bgs received significant phosphate

delivery, and sample pair 399-1-123 (C9667)/C9729 at 9.14 m (30 ft) bgs did not receive significant phosphate delivery. The change in uranium leaching was dependent on the amount of phosphate (if any) delivered to that location, as measured by solid phase extracted phosphate and aqueous phosphate in the first few effluent samples of each leach experiment (Section 5.1.2 of this report). These results provide field-based evidence that phosphate injection decreased uranium mobility.

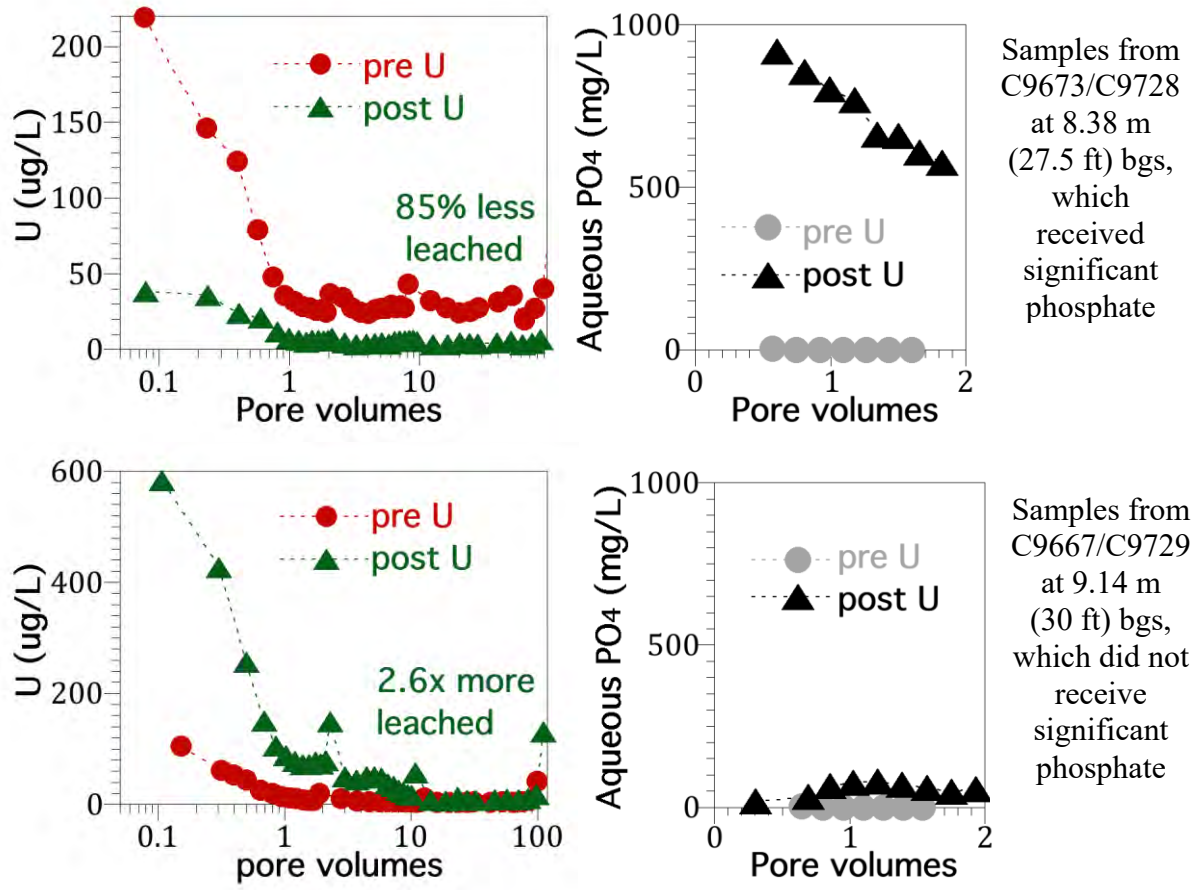


Figure 5-13. Uranium and Phosphate Leaching over Time in 1-D Column Experiments for Stage B Pre-Treatment and Post-Treatment Sediment Sample Pairs

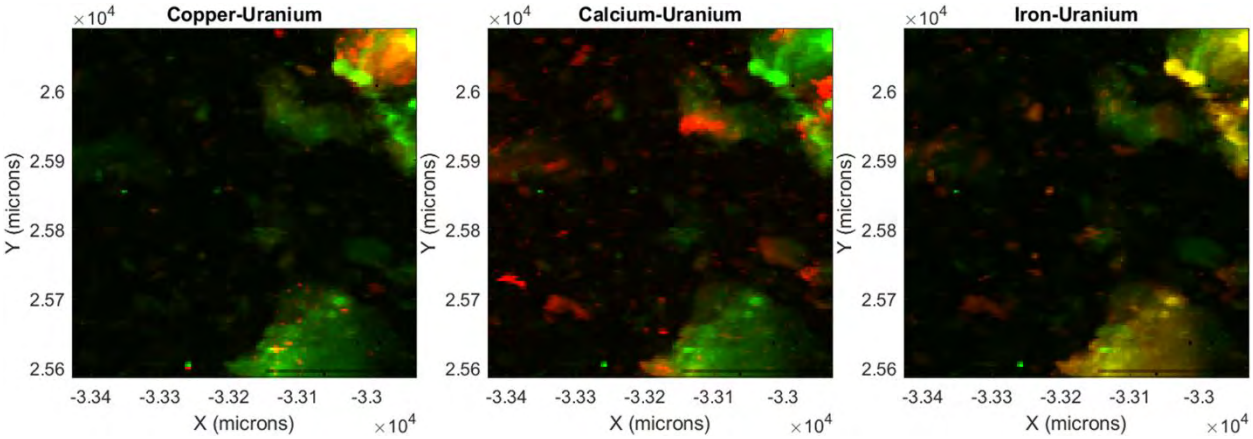
5.2.3 Uranium Solid Phase Analysis in the Vadose Zone

Complementary solid phase techniques (2-D elemental maps using µ-XRF data collected at APS, 2-D elemental maps using SEM-EDS data collected at PNNL) were performed on two pairs of Stage B pre-treatment and post-treatment sediment samples to investigate the four mechanisms of uranium sequestration and to confirm phosphate delivery and precipitation (Section 5.1.2.1 of this report).

These data show that uranium is primarily associated with copper and, to a lesser extent, iron and calcium (Section 5.3 of PNNL-29650). Copper was a significant co-contaminant disposed with uranium and has been directly identified previously in association with uranium as the low-solubility mineral metatorbernite [$Cu(UO_2)_2(PO_4)_2 \cdot 8H_2O$ – a member of the meta-autunite group of minerals] (Arai et al., 2007). Although it was not directly identified in these characterization studies, µ-XRF and EXAFS data collected at APS also suggest similar phases (PNNL-29650). Furthermore, there is the potential to form autunite phases over time as bicarbonate present in injection solutions is advected from the area and re-equilibrated with groundwater (Section 5.1.1 of this report). However, due to the similar structures of

autunite [$Ca(UO_2)_2(PO_4)_2$•10-12H_2O] and metatorbernite, these minerals could not be differentiated by EXAFS (Section 4.4.2 of PNNL-29650).

Calcium was observed near uranium precipitates in µ-XRF maps, consistent with the formation of calcium-phosphate coatings on the surfaces of post-treatment sediments (Figure 5-14). Figure 5-14 also shows a strong association of iron and copper (e.g., torbernite phases) with uranium due to historic waste disposal. Although uranium could not be mapped simultaneously with phosphorus using µ-XRF at APS, phosphorus was identified separately by SEM-EDS at PNNL in 6 of 11 micron-size mapping locations in the post-treatment sample (C9729, 7.62 m [25 ft] bgs) as compared to 1 of 7 locations in the pre-treatment sample (399-1-123 [C9667], 7.62 m [25 ft] bgs) as shown in Figure 5-14. These results suggest that the large increase in low-solubility uranium minerals may be due to (a) precipitation of autunite, (b) apatite coating existing uranium surface phases, or (c) other uranium phases (i.e., uranium carbonates) co-precipitating with apatite.



Source: Figure 4.36 in PNNL-29650, *Evaluation of the Change in Uranium Mobility in Sediments from the Hanford 300-FF-5 Stage B Polyphosphate Field Injection*.

Note: Uranium detection limit was approximately 1 µg/g. Samples are from 7.62 m (25 ft) bgs.

Figure 5-14. Representative 2-D Elemental Maps using µ-XRF of Post-Treatment Sediments from Borehole C9729 for Uranium (in green) Overlaid with Copper (left), Calcium (middle), and Iron (right) (in red)

5.2.4 Changes in Total Uranium Concentrations in the Aquifer

Of the 18 groundwater wells in the injection zones monitored to support Stage B operations, all but 3 (wells 399-1-157, 399-1-146, and 399-1-158) exhibited uranium concentrations below the uranium CUL (30 µg/L) after injections through June 2019. However, it should be noted that 399-1-157, 399-1-146, and 399-1-158 have uranium concentrations of 30.8, 35.2, and 30 µg/L, respectively. Four of the six downgradient monitoring wells also achieved uranium concentrations below the CUL after treatment. Further, most wells also exhibited a decrease in aqueous uranium concentrations within the first 3 months; the exceptions in zone 4 are attributed to poor phosphate distribution due to heterogeneity in the system. Overall, uranium concentrations in the aquifer within and downgradient of the Stage A and B areas decreased after polyphosphate solution application (Figures 4-6 through 4-8).

5.3 Uranium Fate and Transport Modeling

System-scale models were developed to evaluate the impact of phosphate injection on uranium fate and transport within and around the EA areas defined by Stage A and B treatment footprints. Two numerical models are developed to evaluate the processes that would occur in the subsurface as a result of the polyphosphate injections. One is a reactive transport model that is used to simulate, on a local scale, the

evolving geochemical conditions from injection of phosphate-rich solutions contacting the uranium bearing vadose zone sediments associated with Stage B treatment (ECF-300FF5-19-0089). The simulated changes in geochemical conditions are compared with the field observations to gain insight into key processes that would occur due to interaction of sediment with the injected solution. The second is a 3-D large-scale flow and transport model to assess the longer term impacts of uranium sequestration on dissolved concentrations in the aquifer and its effect on the nature and extent of the uranium plume that travels toward the Columbia River (ECF-300FF5-19-0086).

Given that a key model parameter is the one that controls the uranium sorption-desorption behavior, this section first discusses the parameter estimation approach based on 1-D column leaching tests (described in Chapter 4 and prior sections of Chapter 5 of this report and PNNL-29650). Then development and modeling results from the detailed reactive transport model are presented to evaluate the uranium transport behavior near an injection well along with other geochemical changes. After this, the results of the 3-D flow and transport model are presented to evaluate the net impact of Stage A and B treatments on uranium mass flux to the aquifer and on the long-term concentrations in the aquifer.

5.3.1 Geochemical Modeling: Kinetic Sorption-Desorption Parameters

Flow-through column tests were performed on sediment samples collected from the Stage B area prior to and following polyphosphate treatment (described in Section 4.1.2.3 and Section 5.2.2 of this report and Section 4.3 of PNNL-29650). The column tests are used to evaluate the leaching behavior of uranium under saturated conditions and, therefore, provide useful information for quantifying the desorption rates. A single-site kinetic sorption-desorption model is developed to estimate the kinetic rates. The mathematical model is described in Appendix D of the ECF-300FF5-19-0086 and is based on fitting the model to the experimental data. Both the forward and reverse (backward) reaction rate constants are estimated. The forward rate constant is used to estimate the sorption behavior from liquid onto the sediment while the reverse rate constant estimates the desorption or dissolution rates. The results of the parameter estimation process are presented in Figure 5-15 for the 10 pre-treatment and post-treatment sample pairs and the additional unpaired post-treatment samples. While the reverse rate constants for the post-treatment samples have generally decreased compared to pre-treatment samples, the more important aspect is the relative change between the forward and reverse rate constants. This relative change in rate constants is presented in terms of the solid to liquid uranium partitioning coefficient (K_d), which is calculated from the ratio of forward to reverse rate constants. The K_d values are presented separately for the pre-treatment and post-treatment sample pairs in Figure 5-16. The results indicate that the K_d values increased appreciably in the majority of the post-treatment sample pairs and, therefore, the intended goal of phosphate injection to sequester uranium was met. For some samples, the increase in K_d was over an order of magnitude, which indicates a significant reduction in leaching in the future. The average increase in K_d was approximately a factor of 10.

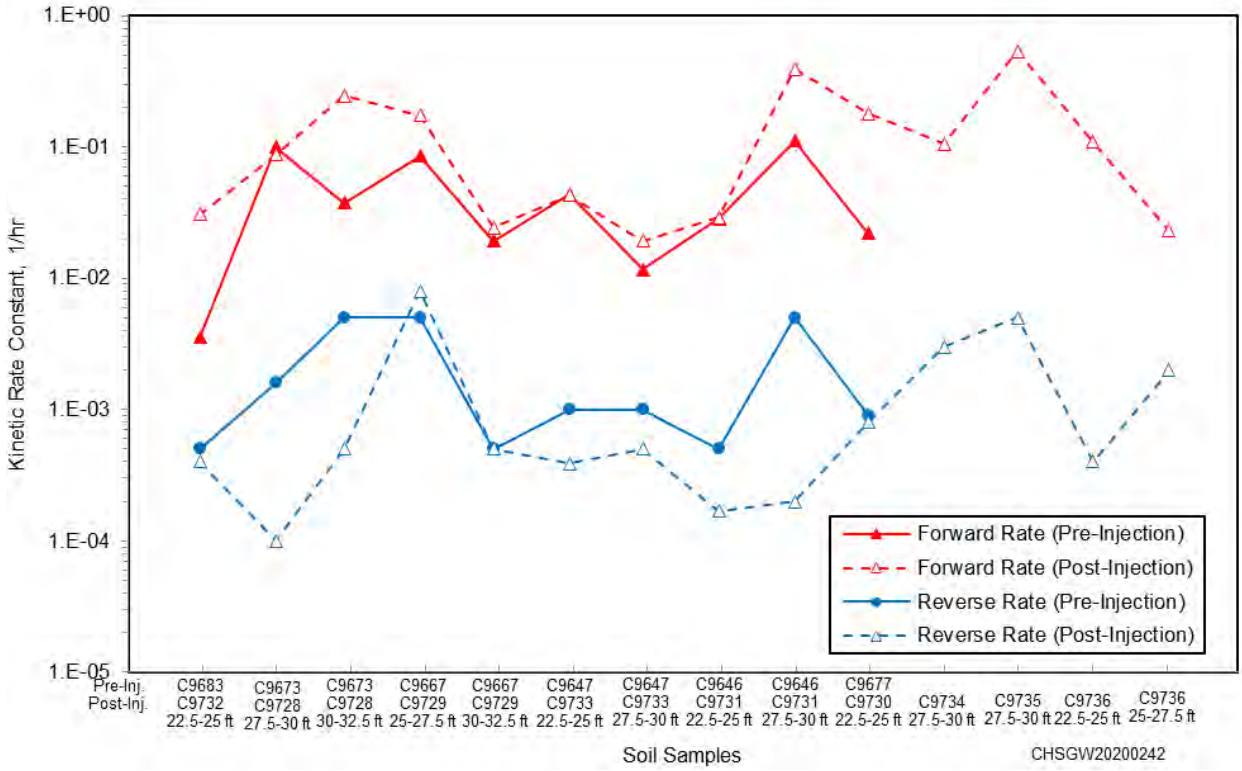


Figure 5-15. Comparison of Uranium Release Rate Constants for All the Pre-Treatment and Post-Treatment Soil Samples

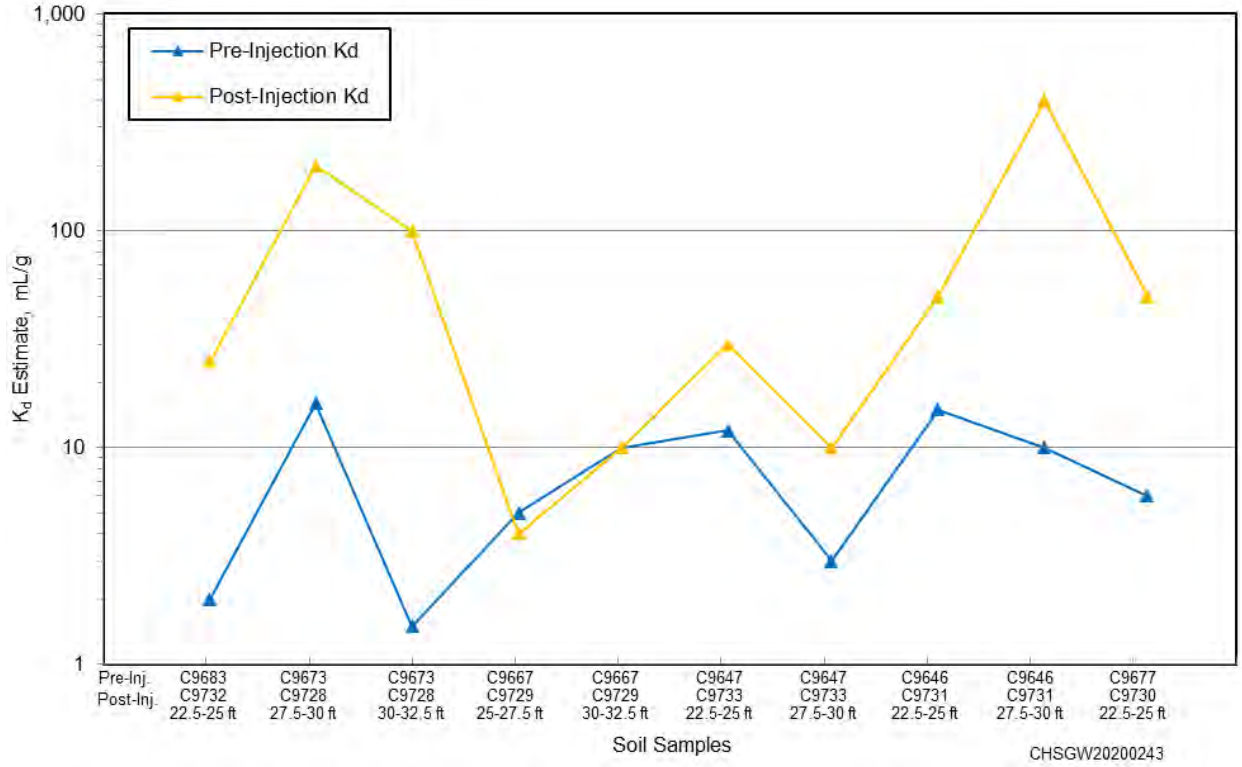
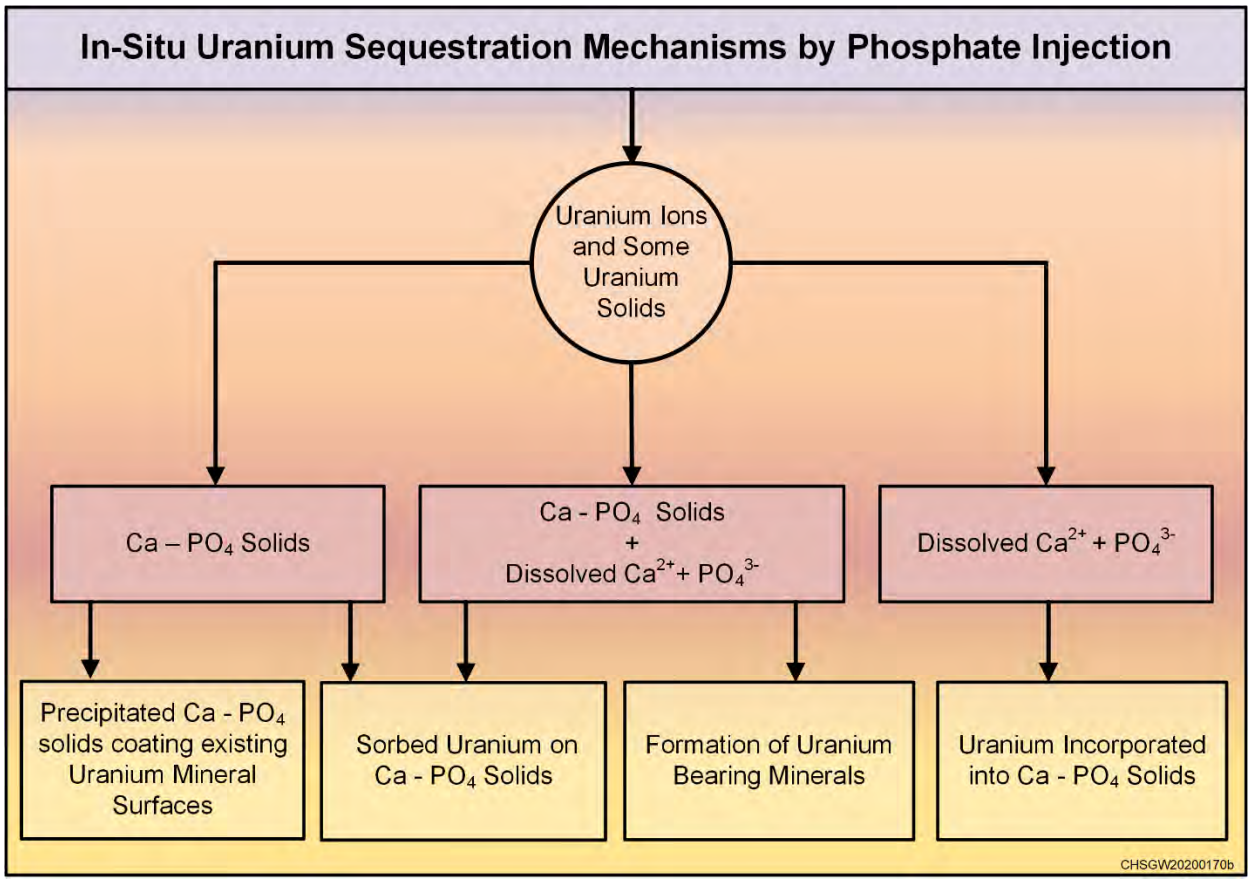


Figure 5-16. Comparison of Derived K_d Value for the Pre-Treatment and Post-Treatment Samples

5.3.2 Near-Field Reactive Transport Modeling

A conceptual model of uranium sequestration mechanisms expected in the field, based on previous work (Mehta et al., 2016, and Mehta, 2017), is developed first to support subsequent modeling. Multiple mechanisms for uranium sequestration occur during phosphate addition which can be broadly grouped into: sorption of aqueous uranium to calcium phosphate solids (e.g., hydroxyapatite), formation of uranium bearing minerals (e.g., autunite), precipitation and coating of calcium phosphate solids on uranium mineral surfaces, and uranium incorporation in calcium phosphate solids (Figure 5-17).



Source: Modified from Mehta et al., 2016, "Effect of reaction pathway on the extent and mechanism of uranium(VI) immobilization with calcium and phosphate."

Figure 5-17. Uranium Sequestration Mechanisms via Phosphate Addition as an In Situ Remediation Approach

The effect of interaction of injected solution with sediments was investigated by developing a near-field reactive transport model. The focus was on evaluating the effects in the vicinity of the injection well. The model was built based on experience gained during Stage A remedy evaluation and by incorporating the following processes and conditions that control uranium transport:

- Variably saturated flow conditions will exist during and following the injection of polyphosphate solutions in the vadose zone and need to be modeled appropriately given the nonlinear change in unsaturated hydraulic conductivity as a function of saturation.
- Spatially and temporally varying concentrations of polyphosphate will exist in the vadose zone as the radius of injection expands leading to concentration gradients.

- The impact of injection on flow in the vadose zone and saturated zone needs to be considered in three dimensions.
- Ion-exchange reactions will occur as the available in-situ calcium exchanges with injected sodium- and potassium-rich solutions.
- Surface complexation of uranium with iron (and manganese) mineral reactive surfaces present in the subsurface need to be considered. In addition, aqueous complexation of uranium with bicarbonate and phosphate needs to be considered.
- Impact of formation of calcium-phosphate solid precipitates and their effect on uranium leaching rates needs to be considered given that studies have shown uranium release is kinetically controlled.
- Upscaling of the effects of solution-surface reactions to assess the geochemical evolution over time from injections over spatial scales ranging from meter to tens of meters.

The 3-D simulation of a single generalized injection well is undertaken to evaluate the geochemical impacts that occur during and directly after polyphosphate injections in the vadose zone near the water table. The results can be considered representative of conditions that would exist within the Stage B injection area. Because the 3-D axisymmetric model is constructed using radial coordinates to simulate the injection well (at the axis of model) a radial symmetry is assumed.

Calculations are performed using VS2DRTI software (developed by the U.S. Geological Survey: Healy et al., 2018, "VS2DRTI: Simulating Heat and Reactive Solute Transport in Variably Saturated Porous Media"), which couples the flow and transport with the geochemical modeling capabilities of PHREEQC (Parkhurst and Appelo, 2013, "Description of Input and Examples for PHREEQC Version 3: A Computer Program for Speciation, Batch-reaction, One-dimensional Transport, and Inverse Geochemical Calculations") for performing reactive transport model. The details of the model development are presented in ECF-300FF5-19-0089, *Geochemical Evaluations and Reactive Transport Modeling in Support of Stage B Enhanced Attenuation Remedy at 300-FF-5 Operable Unit*. Some key features of the model are summarized below.

The domain dimensions of 16 m (52.5 ft) horizontally (radius length) and 20 m (65.6 ft) vertically were found sufficient to capture horizontal contaminant mobility in the vadose zone. The domain is generated in radial coordinates with the leftmost side representing the centerline of a 3-D cylinder and the rightmost side representing the outermost edge. A height of 0.25 m (0.82 ft) was used for the vertical cell discretization. Horizontal discretization was defined by successive cell widths increasing by a factor of 1.2, such that a minimum cell width of 0.01 m (0.033 ft) was located near the injection well (leftmost domain edge) and 2.68 m (8.53 ft) furthest from the well (rightmost domain edge). A total of 2,400 nodes centered in each grid cell are used in calculations for the simulation. Figure 5-18 presents the model domain along with hydrogeologic units considered. An equivalent homogenous medium (EHM) approach is taken for each hydrogeologic unit defined such that the flow properties are equivalent throughout the defined domain for a given unit. The hydrogeologic units within the model domain consist of unsaturated (or variably saturated) Hf, saturated Hf, and saturated Rwie. Average hydrogeologic unit thicknesses were used based on a surface elevation of 115 m (377 ft) and average water table elevation of 105 m (344.5 ft) such that the Hf unsaturated zone is 10 m (33 ft) thick, the Hf saturated zone is 3 m (10 ft) thick, and the Rwie saturated zone is 7 m (23 ft) thick.

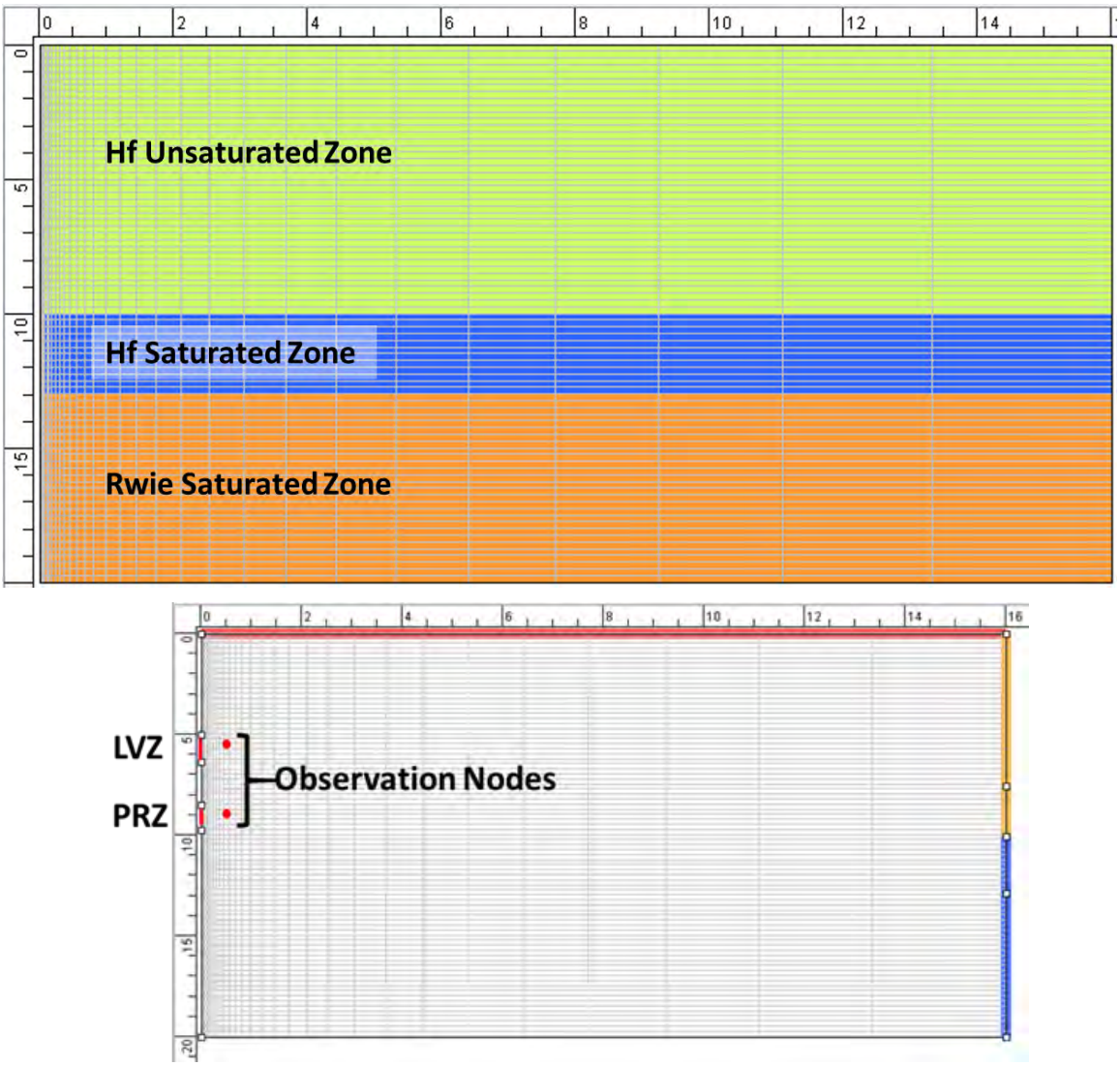


Figure 5-18. Near-Field Reactive Transport Model Domain in Radial Coordinates with Distribution of Hydrogeologic Units (upper figure) and the PRZ and LVZ Injection Screen Intervals Along with Observation Nodes (lower figure)

Recharge periods are used to define changes in boundary conditions (e.g., periods of remedy injections and when no injections are occurring) over specified lengths of time. This model assumes a start time of midnight prior to injections and includes two periods of 8 hours (0.33 day) each to represent PRZ injections and two 8 hour (0.33 day) periods of LVZ injections during approximately similar start/end times of a typical workday (8 a.m. to 4 p.m.). Each of the four injection periods is separated by a period of 16 hours (0.66 day) to represent inactive times (from end of the current workday to start of next workday). A final period of 10 days is included at the end of the fourth injection to see near-term evolution of chemistries after remedy implementation.

The existing thermodynamic database (*llnl.dat*) included with the VS2DRTI software was supplemented to include additional uranium carbonate and uranium phosphate aqueous species, mineral phases, and surface complexation reactions (ECF-300FF5-19-0089). Two solutions chemistries are considered in the model as shown in Table 5-1, one representing the background porewater chemical composition prior to injection and the other being the injected solution composition.

Table 5-1. Solution Chemical Composition

Constituent	Solution 1[a]	Solution 2[b]
Sodium (mg/L)	26.7	2,605.76
Potassium (mg/L)	8.0	1,769.39
Phosphorus (mg/L)[c]	--	2,605.76
pH	7.5	7.6
Calcium (mg/L)	53.1	17.64
Magnesium (mg/L)	12.6	4.55
Chloride (mg/L)	25.0	1.17
Bicarbonate (mg/L)	129.5	3,666.90
Sulfate (mg/L)	58.5	28.46
Nitrate (mg/L)	31.9	0.48
Iron (mg/L)	0.05	--
Uranium (mg/L)	0.10	--

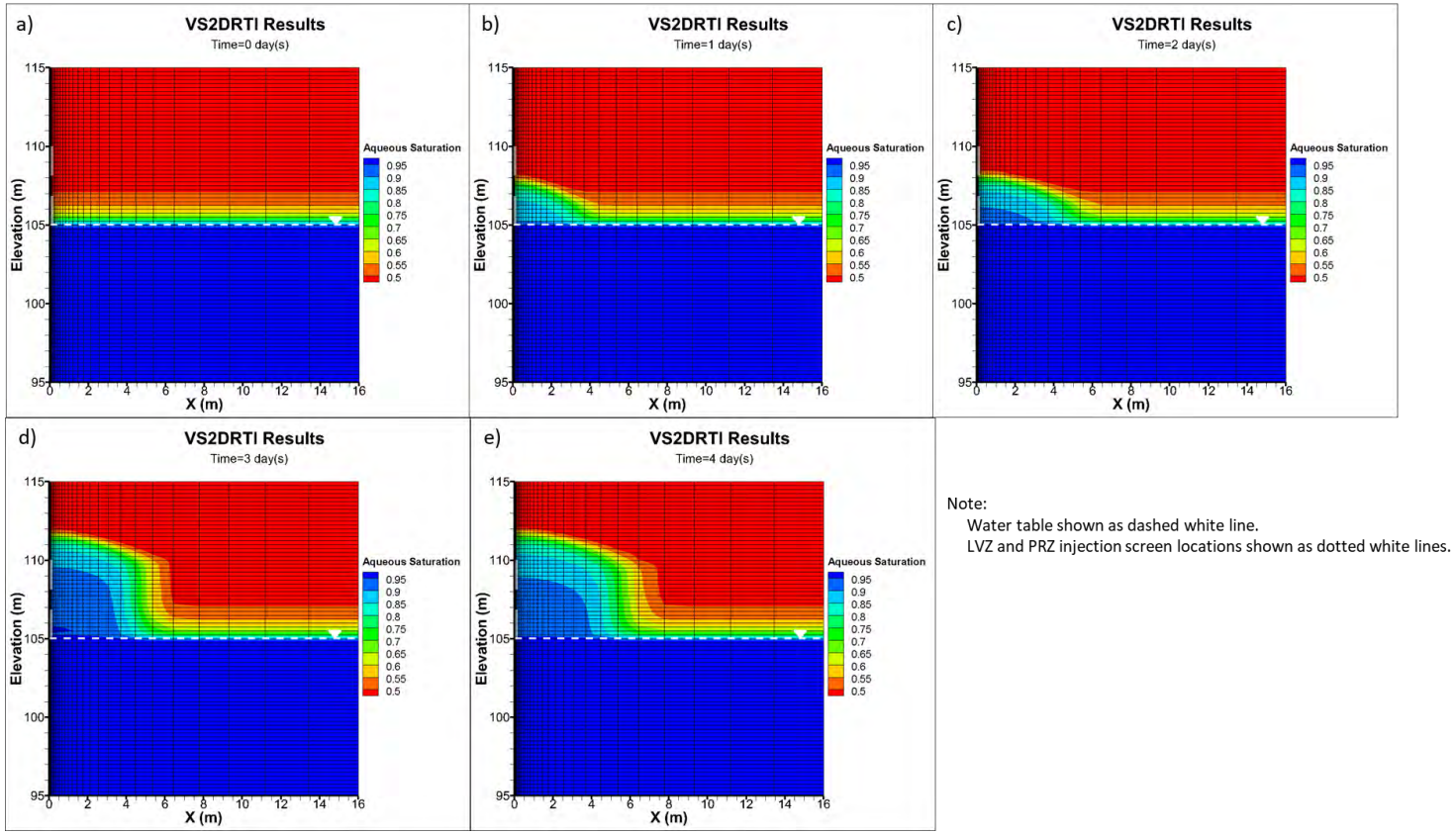
a. Background porewater chemistry.

b. Remedy injection solution.

c. As phosphate.

Kinetic mineral dissolution and precipitation is modeled for both calcite and uranium precipitates using reaction rates. The mass of reactants are based on site-specific data from laboratory experiments conducted on the Stage A and B sediments. The initial molar amount of calcite is based on the sum of weak and strong acid extractions of calcium from sequential extractions, while 1,000-hour carbonate batch extraction uranium data are used to define the amount of uranium available for release from sediments.

Flow field results from the 3-D near-field reactive transport model show extensive mounding of solution above the groundwater table as a result of remedy injections into the PRZ and LVZ. Aqueous saturation results are presented at 0-, 1-, 2-, 3-, and 4-day time periods (Figure 5-19). Increases in water saturation are observed from approximately 5 m (16 ft) horizontally and 3 m (10 ft) vertically above the water table after two successive injection periods to the PRZ (Figure 5-19, inset c), though the greatest saturation (values >0.9) extends approximately 3 m (10 ft) horizontally and 1 m (3 ft) vertically above the water table. Little change was observed to the horizontal extent after the remaining two LVZ injection periods reaching approximately 6 m (20 ft), though the vertical extent did reach approximately 7 m (23 ft) above the water table (Figure 5-19, inset e). Saturations >0.9 reached between 3 to 4 m (10 to 13 ft) horizontally and vertically above the water table.



Note:
Water table shown as dashed white line.
LVZ and PRZ injection screen locations shown as dotted white lines.

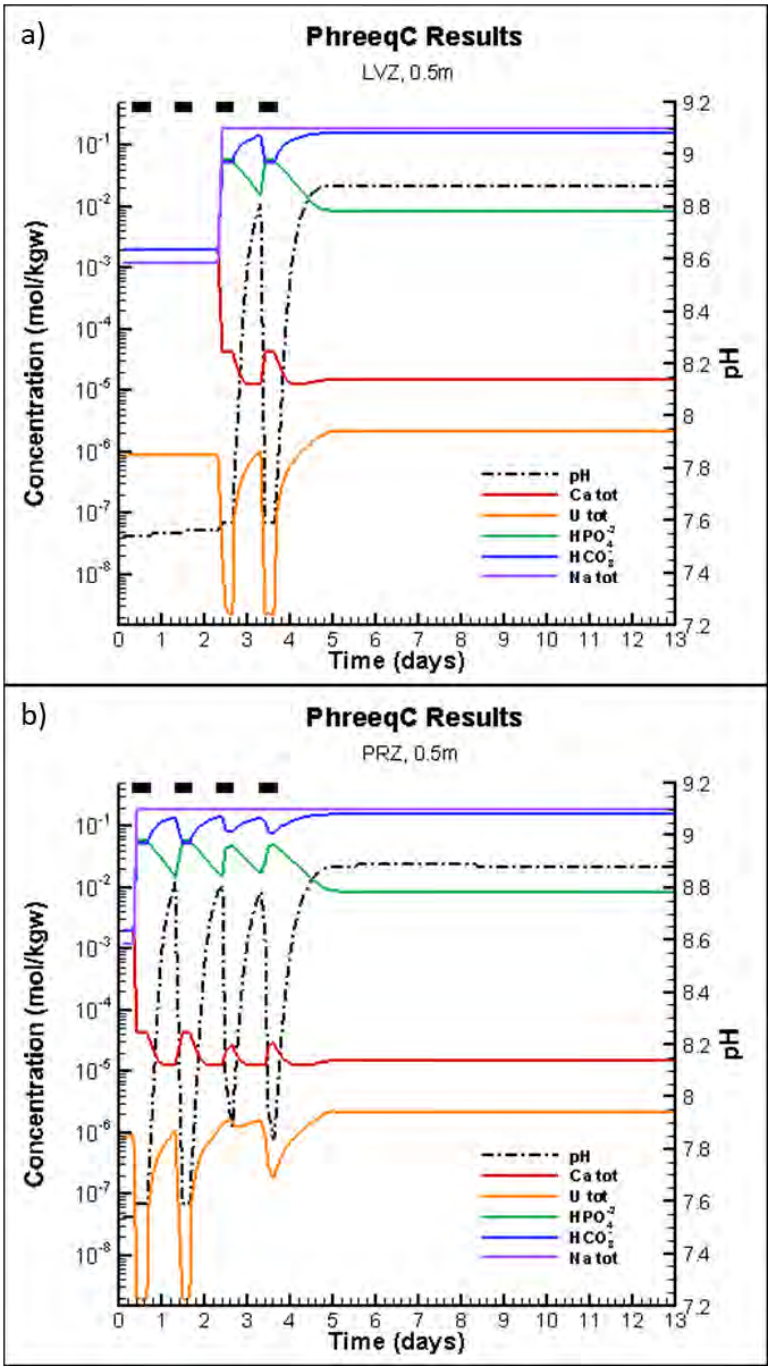
Figure 5-19. 3-D Near-Field Reactive Transport Model Calculated Aqueous Saturation Profiles a) Before Injections, b) After the First PRZ, c) Second PRZ, d) First LVZ, and e) Second LVZ Injection Periods

Time-series plots for major system aqueous constituents including hydrogen phosphate (HPO_4^{2-}), uranium (present mainly as uranyl-carbonate or uranyl-phosphate species), calcium, sodium, bicarbonate (HCO_3^-), and pH are shown near the LVZ and PRZ injection screens (Figure 5-20). These results are extracted from the two observation nodes shown in Figure 5-18. A sharp increase in sodium, bicarbonate, and phosphate concentration occurs at the first instance of injection in the PRZ and LVZ reflecting injected solution composition. Uranium and calcium show a sharp decrease in concentration during the injections, while bicarbonate and phosphate concentrations remain high. Between injection periods, pH, uranium, and bicarbonate concentrations show a gradual increase while calcium and phosphate concentrations decrease. The gradual increase in bicarbonate concentration is attributed to kinetically controlled dissolution of calcite from changes in pH and other ongoing reactions in the subsurface, while the increase in uranium concentration results from kinetic dissolution of the existing uranium mineral assemblage (assemblage of uranium bearing silicates, carbonates, and phosphate minerals). The decrease in phosphate and calcium between the injection periods results from their consumption during mineral precipitation (formation of hydroxyapatite) and sorption. Changes in pH range from 7.6 during times of injection (matching the injection solution pH) and increasing to 8.9 between injection periods. After all remedy injections are completed (approximately at day 5), all constituent concentrations level off reflecting establishment of near steady-state conditions over the duration of the simulation.

Mineral composition time-series plots are compiled in Figure 5-21. The amount of uranium precipitates (mineral assemblage mass) is shown to be in excess throughout the simulation with little observable change. No kinetic limits were imposed on mineral precipitation or dissolution for all minerals modeled with the exception of calcite and uranium mineral assemblage. The precipitation of calcium-phosphate bearing phases, such as hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), occurs at the onset of injections and increases to approximately 10^{-2} mol (per kg water). The excess of calcium in pore waters due to displacement from exchange sites and calcite dissolution, in addition to phosphate from remedy solution injection, create favorable conditions for hydroxyapatite precipitation. It is worth noting that the simulation indicates that hydroxyapatite reaches saturation and precipitation is favorable. Calcite decreases with time during all four remedy injection periods in the PRZ and the last two injection periods in the LVZ.

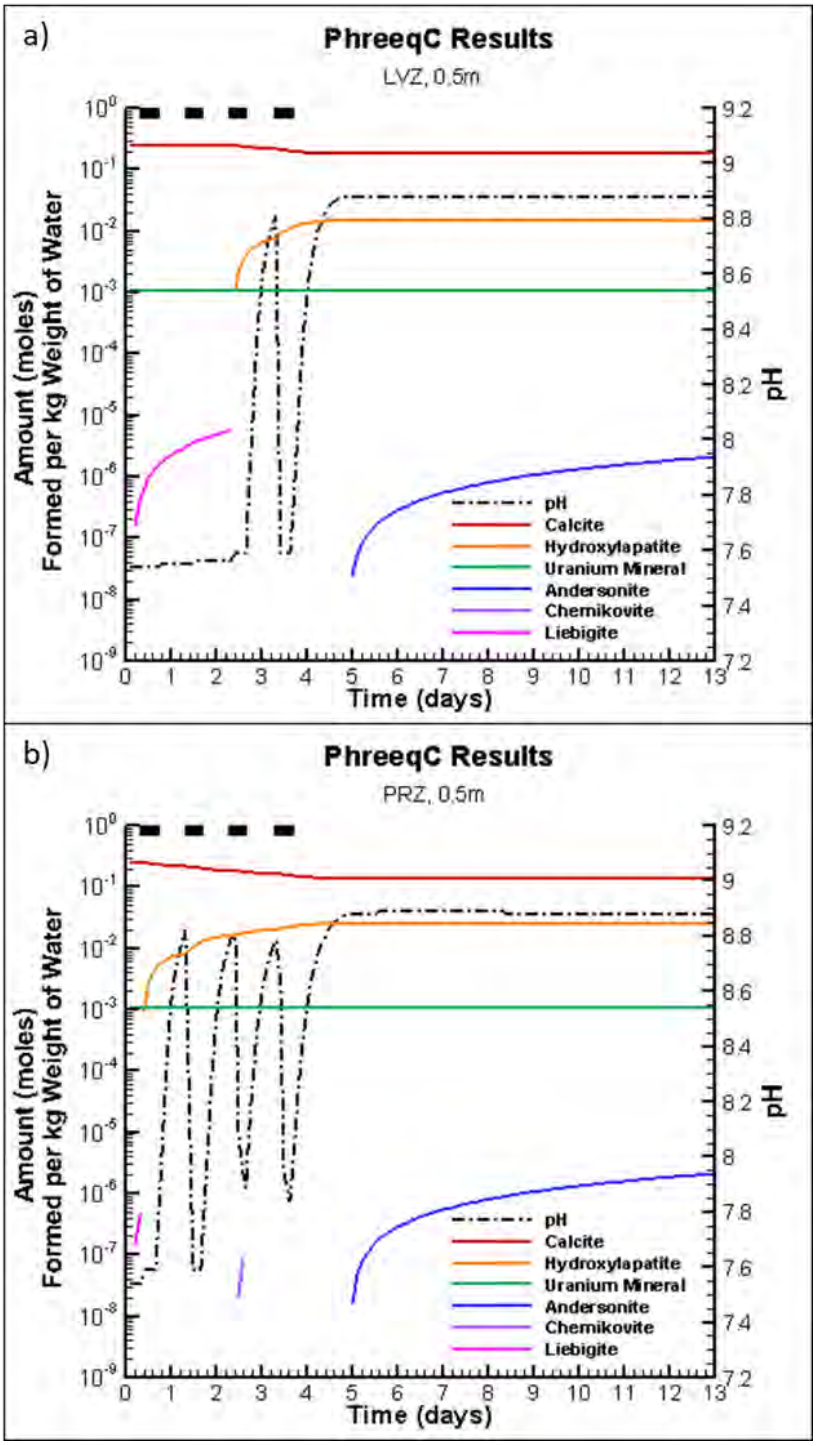
Formation of uranium-bearing mineral phases, liebigite ($Ca_2UO_2(CO_3)_3(H_2O)_{10}$), chernikovite ($(UO_2)HPO_4(H_2O)_4$), and andersonite ($Na_2CaUO_2(CO_3)_3(H_2O)_6$), are found to be thermodynamically favorable at different times during the simulation. Liebigite and chernikovite are favored to precipitate early on during the remedy injections in the PRZ and LVZ; however, they are not favored in the post-treatment period. Andersonite is the most favored to form and exist in the post-treatment period over the simulated duration, increasing from approximately 10^{-8} mol to 10^{-6} mol (per kg water).

3-D Remedy Injection modeling results were compared to mineral phase diagrams (Figure 5-22) to provide model confidence. The logarithmic molar ratio of hydrogen phosphate to bicarbonate (Log HPO_4^{2-}/HCO_3^-) represents the relative amount of phosphate to bicarbonate in the system such that high phosphate concentrations relative to bicarbonate produces positive values while greater bicarbonate concentrations relative to phosphate produces negative values. Log HPO_4^{2-}/HCO_3^- values range from 0.05 during injections to -1.3 after all remedy injection periods. As discussed in Figure 5-21, predictions of both hydroxyapatite and andersonite precipitates formed during 3-D Remedy Injection simulation, can be understood by evaluating the phase diagrams under the chemical conditions immediately following injections (Figure 5-22 inserts b and d, respectively). If the precipitated apatite is assumed to be a phosphate source with the adsorbed uranium on the apatite, a simulation in groundwater shows that autunite may be favored to precipitate (Figure 4.44 of PNNL-29650). This has also been shown to occur experimentally with a column of apatite with aqueous uranium injection slowly forming autunite (Lammers et al., 2017).



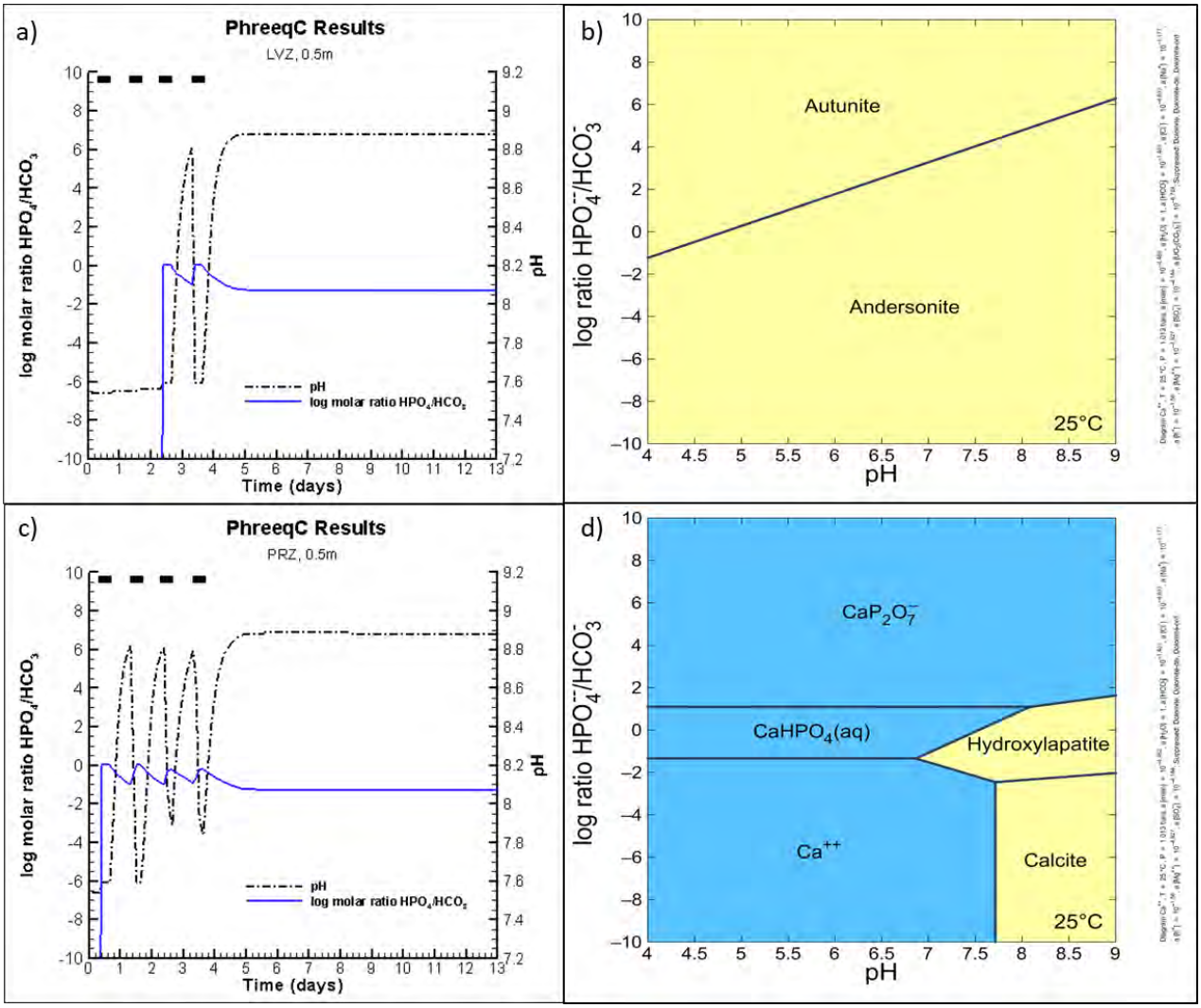
Note: Injection periods indicated by black bars.

Figure 5-20. 3-D Near-Field Reactive Transport Model Geochemical Evolution Plots Showing Aqueous Species at a) 0.5 m Distance from LVZ Injection Screen and b) 0.5 m Distance from PRZ Injection Screen



Note: Injection periods indicated by black bars.

Figure 5-21. 3-D Near-Field Reactive Transport Model Showing Minerals Favored to Form over Time at a) 0.5 m Distance from LVZ Injection Screen and b) 0.5 m Distance from PRZ Injection Screen



Note: Injection periods are indicated by black bars in (a) and (c).

Figure 5-22. 3-D Near-Field Reactive Transport Model Time-Series Plots of Log Molar Ratio HPO_4/HCO_3 and pH for 0.5 m Distance from a) LVZ Injection Screen and c) PRZ Injection Screen and Mineral Stability Phase Diagrams b) with Uranium and d) without Uranium

2-D plots from the 3-D Remedy Injection Model are presented at 0-, 1-, 2-, 3-, and 4-day time periods for phosphate shown as HPO_4^{2-}, aqueous uranium, pH, calcite, and hydroxyapatite to evaluate constituent extents (Figure 5-23 through Figure 5-26, respectively).

Changes in phosphate molar concentration and extent are shown in Figure 5-23. Phosphate extents mirror increases in aqueous saturation due to remedy injections in the vadose zone, with greatest extents of approximately 6 m (20 ft) horizontally and vertically above the water table after all injection periods. Groundwater phosphate concentrations rapidly increase during the injection periods and remain primarily in the saturated zone.

Aqueous uranium concentrations show an increased reaction front as a result of remedy solution injections (Figure 5-24). As high concentrations of injected solution enter the system, the readily available uranium in the porewater and on surface sites is displaced. This is shown by increased aqueous uranium

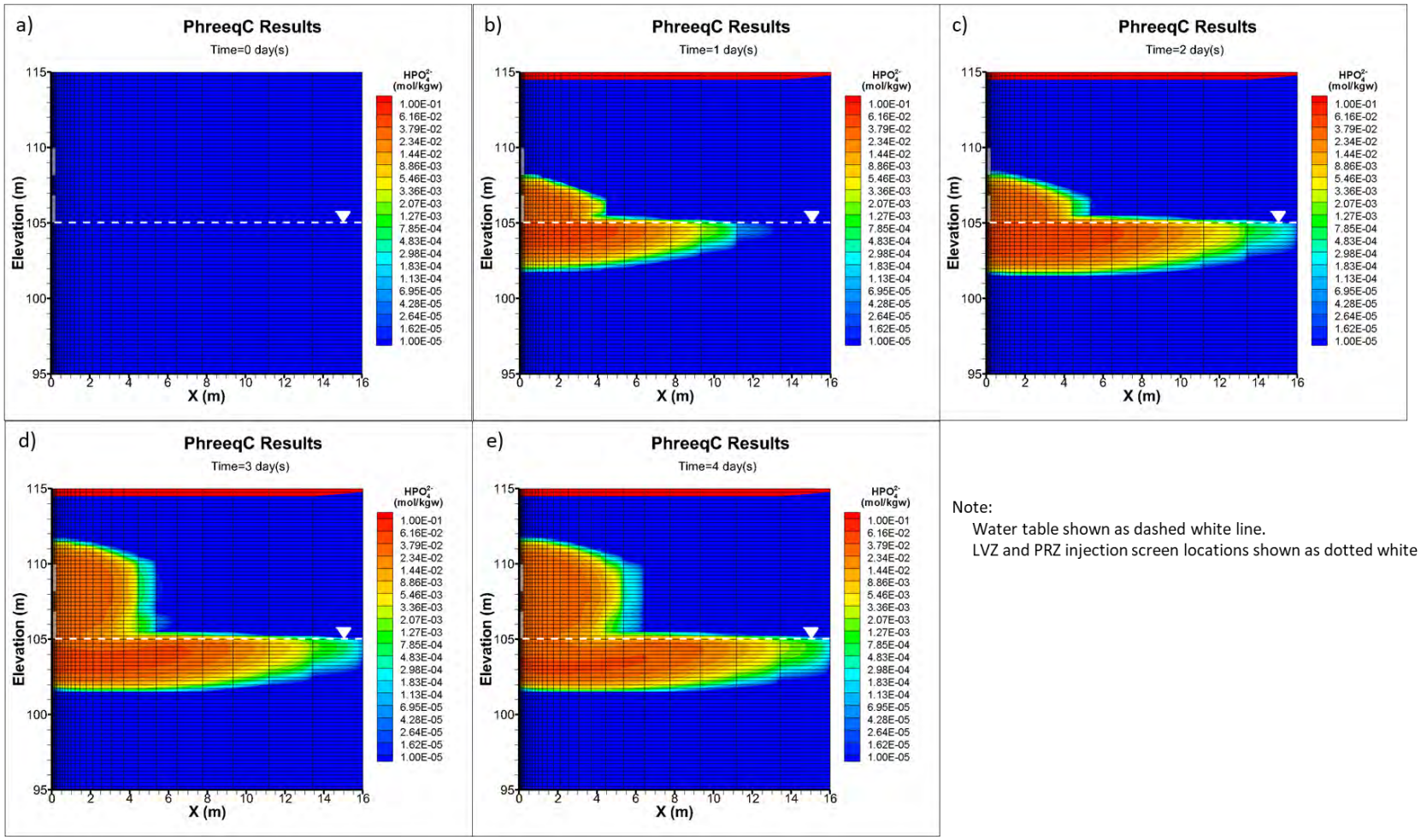
concentrations at the furthest edge of the solution front, with decreasing concentrations near the injection sites.

The system pH evolves as shown in Figure 5-25. In the vadose zone it increases from about 7.5 to 8.8. The increase in pH is largely controlled by calcite dissolution and from variably increased bicarbonate content due to injection. Modeled 3-D remedy solution injections indicate favorable conditions for sustained hydroxyapatite formation (Figure 5-26). Approximately 2.0×10^{-2} moles of hydroxyapatite (per kilogram of water) precipitate near the PRZ injection screens with amounts $>1.4\times10^{-2}$ moles of hydroxyapatite (per kilogram of water) precipitating within the zone that is 4 m (13 ft) horizontally from the injection location and 6 m (20 ft) vertically above the water table.

The near-field reactive transport modeling indicates favorable conditions for multiple mechanisms of uranium sequestration, including formation of stable uranium mineral phases, adsorption of aqueous uranium complexes, and precipitation of calcium-phosphate minerals that reduce the labile uranium concentrations, consistent with the conceptual model indicated in Figure 5-26. The results of the geochemical reactive transport modeling are consistent with the field observations and laboratory analyses conducted on pre- and post-treatment sediment samples. For example, the model simulations indicate the following:

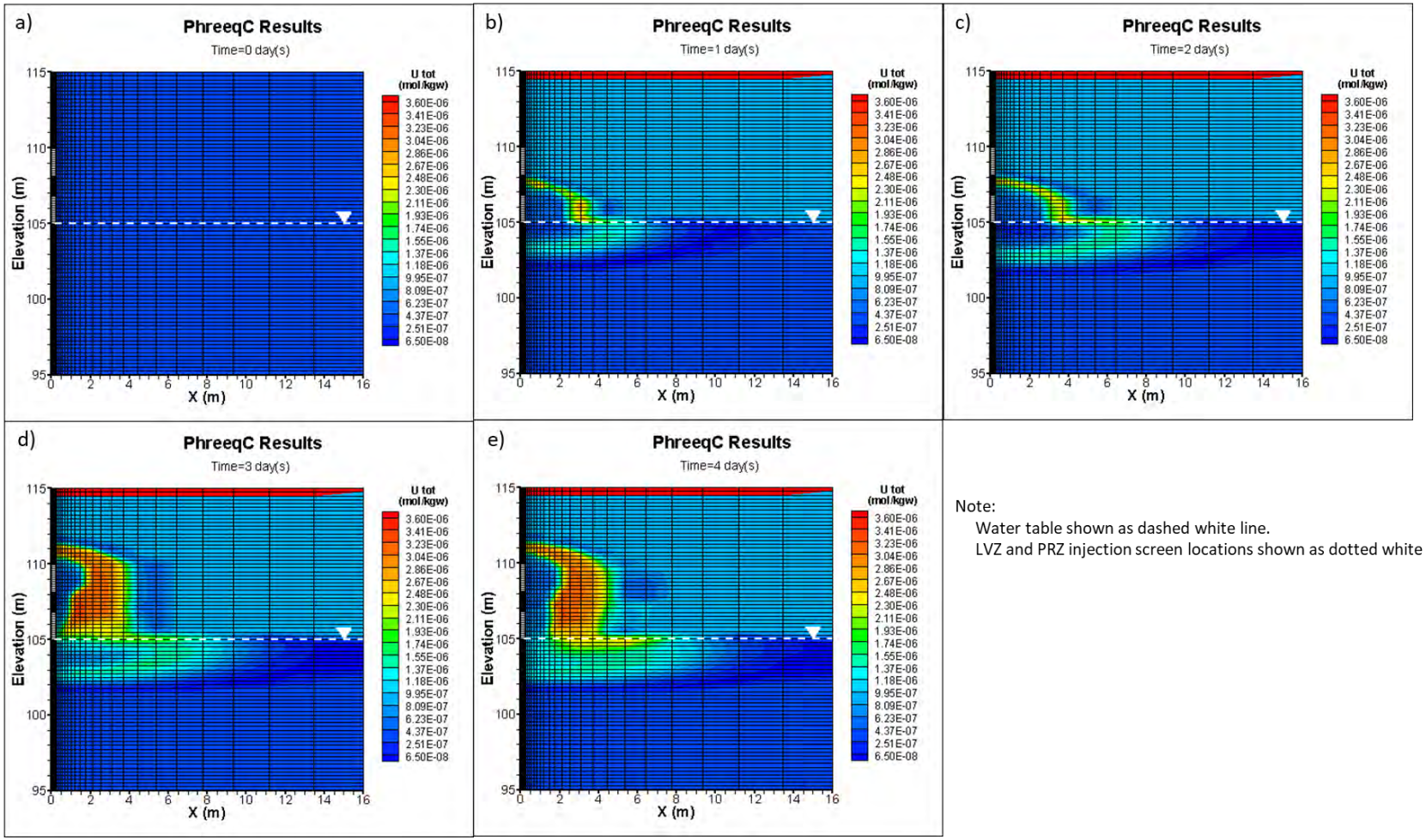
- Elevated saturation developing in the PRZ approximately 4 to 6 m (13 to 20 ft) laterally from the injection well (Figure 5-25), which is consistent with the ERT measurements at cluster 1 during injections (Figure 4-30)
- Precipitation of hydroxyapatite in the vadose zone sediments (Figure 5-26), which is consistent with solid phase analysis indicating calcium-phosphate precipitation in post-treatment samples (Section 4.1.2)
- Some dissolution of existing moderately soluble uranium mineral phases and re-precipitation as lower solubility (more stable) minerals, which is consistent with sequential extraction results

Additional comparisons of near-field reactive transport modeling results to field data are discussed in ECF-300FF5-19-0089.



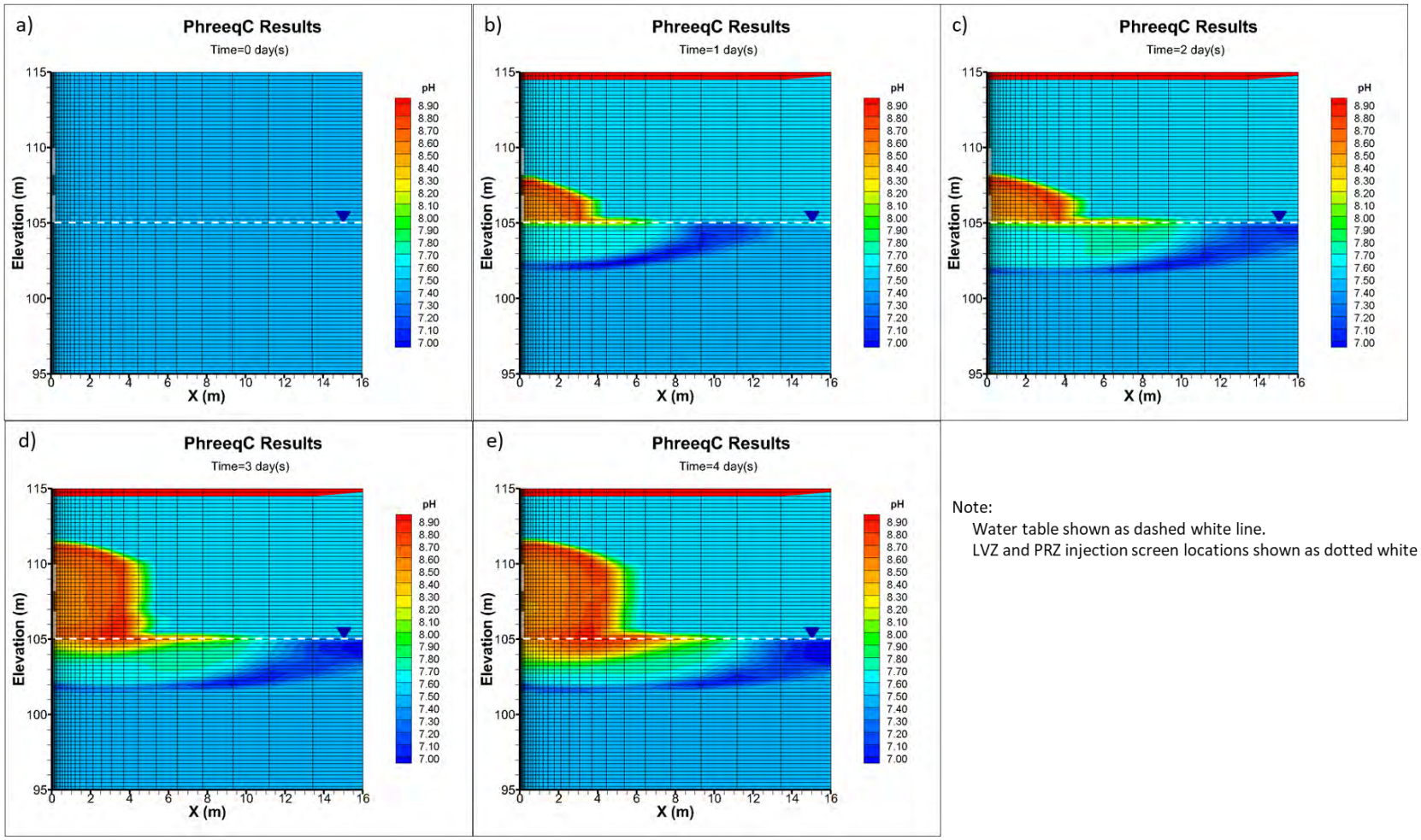
Note:
Water table shown as dashed white line.
LVZ and PRZ injection screen locations shown as dotted white lines.

Figure 5-23. 3-D Near-Field Reactive Transport Model HPO_4^{2-} Profile a) Before Injections, b) After the First PRZ, c) Second PRZ, d) First LVZ, and e) Second LVZ Injection Periods



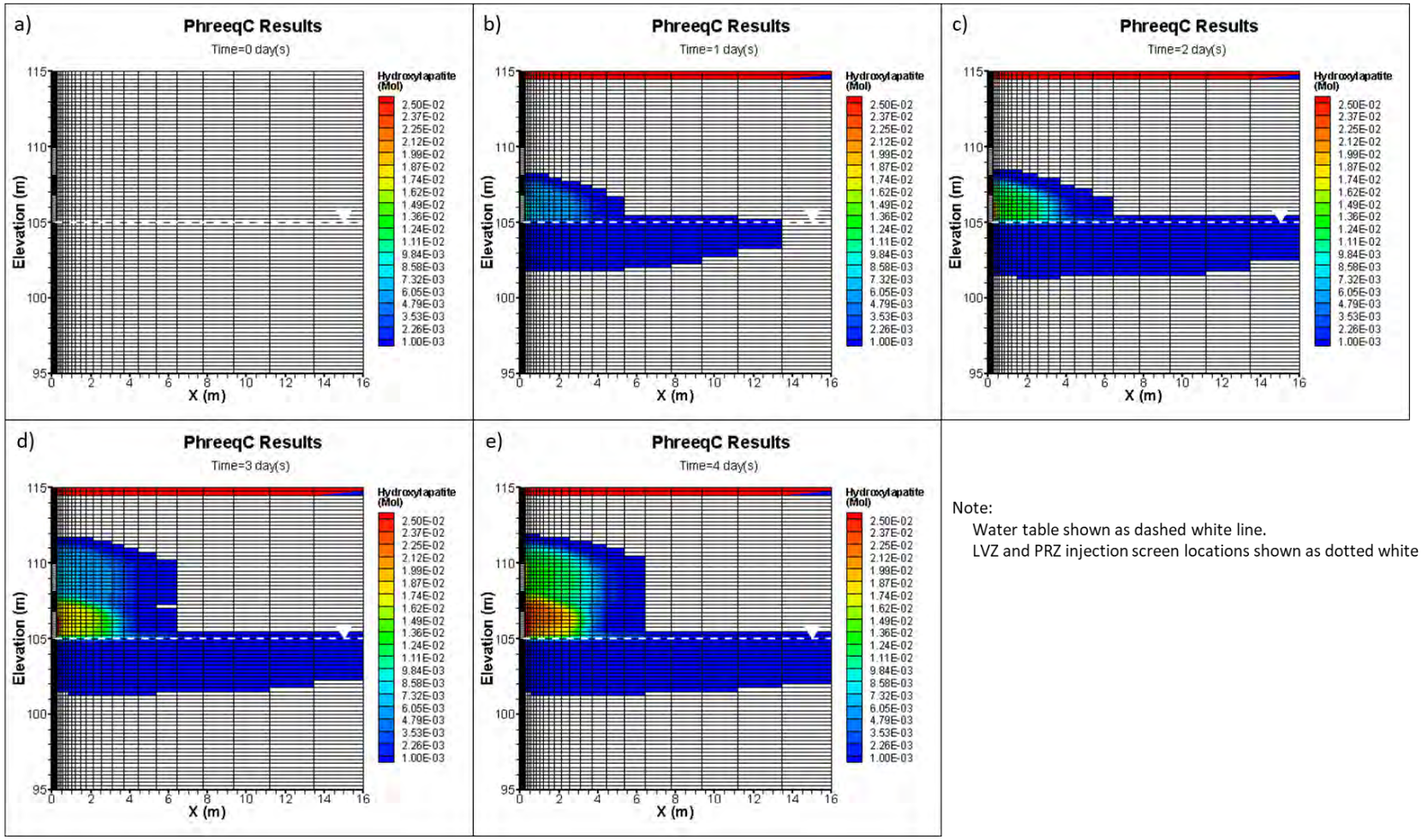
Note:
Water table shown as dashed white line.
LVZ and PRZ injection screen locations shown as dotted white lines.

Figure 5-24. 3-D Near-Field Reactive Transport Model Total Aqueous Uranium Profile a) Before Injections, b) After the First PRZ, c) Second PRZ, d) First LVZ, and e) Second LVZ Injection Periods



Note:
Water table shown as dashed white line.
LVZ and PRZ injection screen locations shown as dotted white lines.

Figure 5-25. 3-D Near-Field Reactive Transport Model pH Profile a) Before Injections, b) After the First PRZ, c) Second PRZ, d) First LVZ, and e) Second LVZ Injection Periods



Note:
Water table shown as dashed white line.
LVZ and PRZ injection screen locations shown as dotted white lines.

Figure 5-26. 3-D Near-Field Reactive Transport Model Hydroxyapatite Profile a) Before Injections, b) After the First PRZ, c) Second PRZ, d) First LVZ, and e) Second LVZ Injection Periods

5.3.3 System-Scale 3-D Flow and Transport Modeling Parameters

A system-scale 3-D flow and transport model is developed to evaluate the net impact of Stage A and B treatments on uranium mass flux to the aquifer and on the long-term concentrations in the aquifer. The model evaluates the changes in water table elevation from river stage fluctuations, leaching of uranium from periodic rewetting, and effects of phosphate treatment. The system-scale 3-D model is intended to capture the existing conceptual site models and integrate it into a comprehensive numerical model for evaluating the net impact of the remedy. It synthesizes all the relevant information for conducting fate and transport modeling to evaluate the uranium concentrations in the aquifer in the vicinity of EA areas defined by the footprints of Stages A and B. The understanding gained from evaluation of near-field reactive transport model regarding various geochemical processes on controlling the release of uranium prior to and following the injection is applied in the system-scale 3-D model. This is implemented by abstraction of kinetic sorption-desorption parameters and upscaling them to adjust for gravel fraction and uranium labile fraction.

The PNNL multi-processor capable extreme-scale STOMP©[3] (eSTOMP©) simulator, a highly scalable (parallel) version of STOMP (PNNL-15782, *STOMP: Subsurface Transport Over Multiple Phases Version 4.0: User's Guide*) was selected to develop the fate and transport model. The steps utilized in the development of the system-scale model and its application includes the following:

1. Construct representative 3-D models for the 300-FF-5 OU using site-specific descriptions of the local physical and hydrogeologic conditions.
2. Calibrate the groundwater flow and transport model to measured water-levels and groundwater-river water mixing (using electrical conductivity as the conservative tracer) at selected wells.
3. Develop spatial uranium distribution in sediment based on available sampling data and correct it for gravel fraction and the labile fraction before incorporating it in the model.
4. Develop representative kinetic sorption/desorption parameters at the scale of the model to evaluate the long-term uranium trends prior to Stage A and B treatment and following the treatment.
5. Simulate phosphate injection and uranium transport to calculate the change in sediment and groundwater uranium concentrations over time.

A summary level discussion regarding the flow and transport model is presented here based on details presented in ECF-300FF5-19-0086.

The 3-D STOMP model domain of 600 m (1,968 ft) by 600 m (1,968 ft) is selected in such a way that it covers the Stage A and B EA area along with a number of monitoring wells in the vicinity (Figure 5-27). In the plan view the grid spacing varies spatially from 3 to 30 m (10 to 98.4 ft) with finer grid spacing in and around the EA area. Vertically, the model extends from the ground surface elevation (115 m [377 ft]) to the bottom elevation (95 m [312 ft]) located in the Rwie. The vertical grid spacing was chosen to be 0.5 m (1.6 ft).

[3] Subsurface Transport Over Multiple Phases (STOMP©) (and its derivative works, including eSTOMP) is copyrighted by Battelle Memorial Institute, 1996.

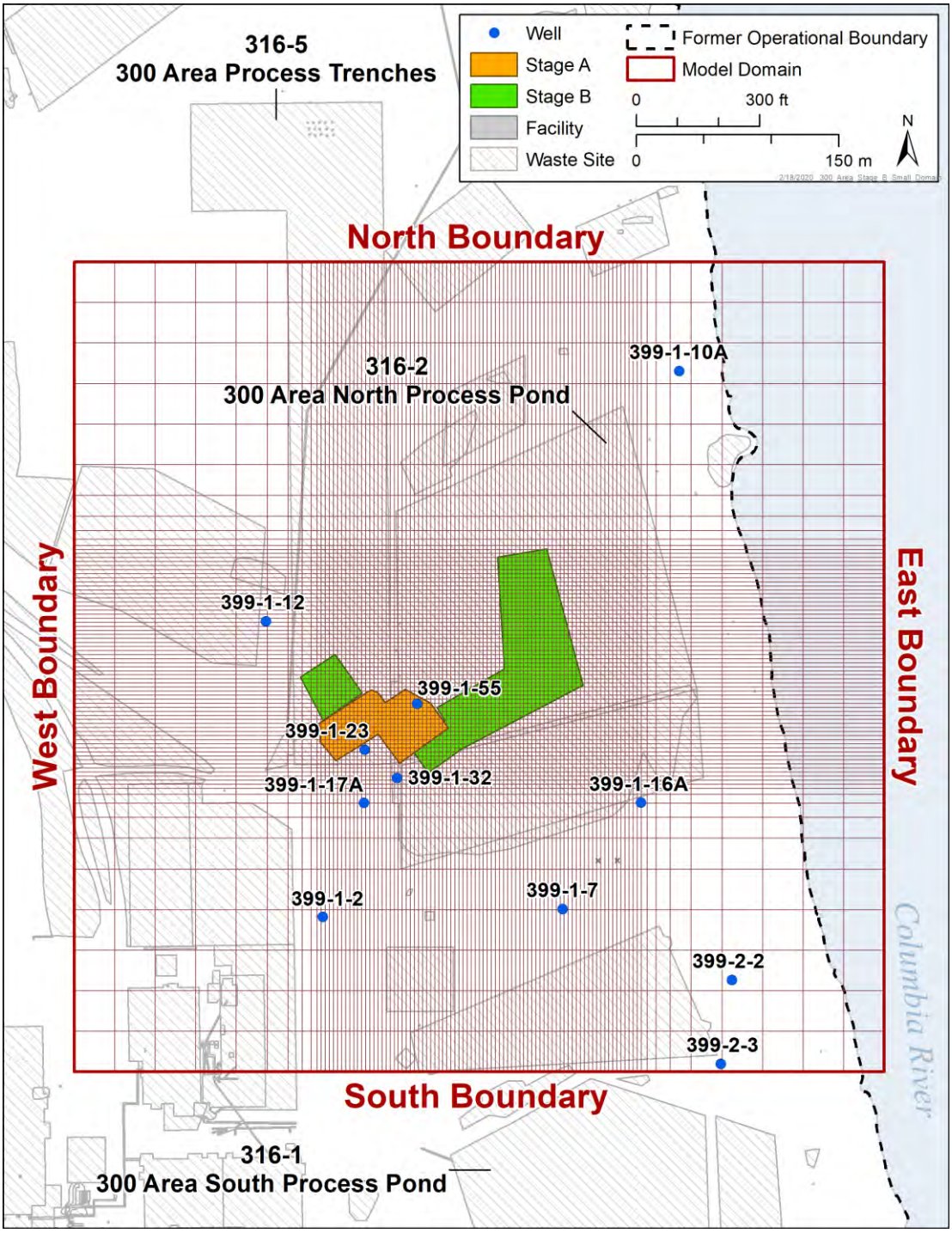


Figure 5-27. System-Scale 3-D STOMP Model Domain to Evaluate Remedy Performance

The assignment of hydrostratigraphic units is based on integrating the regional geology with local scale borehole lithology into a detailed geologic framework model described in ECF-300FF5-16-0087. Where information was available the spatial extent and distribution of sediment classes based on borehole logs were identified including any silt lenses or gravel-dominated zones. However, because detailed information on lithologic heterogeneity was not available throughout the model domain, an EHM modeling approach is used to represent the heterogeneity. For EHM modeling, upscaling for macroscopic field-scale flow and transport parameters was accomplished as follows (ECF-300FF5-19-0086):

- The vadose zone heterogeneous geologic media at the 300-FF-5 OU is conceptualized as being comprised of multiple EHM.
- Each heterogeneous hydrostratigraphic unit is treated as an anisotropic EHM having upscaled (effective) flow and transport properties.
- Upscaled flow properties and the macroscopic anisotropy for the field scale are based on a variable moisture (tension) dependent anisotropy model.

Macrodispersivity estimates for various hydrostratigraphic units are based on a combination of numerical simulation results, stochastic solutions, and 200 East Area tracer experiments.

The aerially applied recharge rate was based on the analysis of lysimeter drainage at the South Caisson located in the Buried Waste Test Facility of the 300 North Area over the period July 1985 to June 1993 (PNL-10285, *Estimated Recharge Rates at the Hanford Site*). Over the 8-year period of record, the recharge ranged from 2.4 to 11.1 cm/yr (0.9 to 4.4 in./yr) with an average of 5.54 cm/yr (2.2 in./yr). Drainage data from the lysimeter reflects a nonvegetated cover and medium to coarse sand. The recharge boundary condition in the model (Figure 5-28) was specified as a Neumann (specified flux) boundary condition with a flux of 5.54 cm/yr (2.2 in./yr).

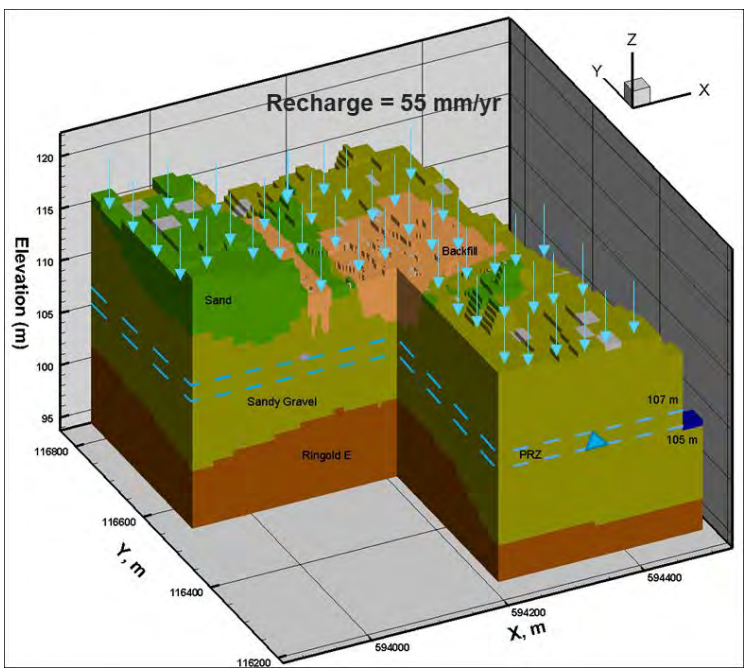


Figure 5-28. System-Scale 3-D STOMP Model Domain with Recharge Boundary at the Top Surface

Hourly Columbia River stage data from the river stage recorder in the 300 Area (river gauge station SWS-1) was used to set a time-varying hydrostatic pressure boundary on the east. The SWS-1 river gauge is located on the west bank of the Columbia River (Figure 5-29). Eight nearby AWLN monitoring wells (wells with downhole transducers for automated water level measurements) were used for model calibration (Figure 5-29). The river stage data were collected manually beginning in 1991 approximately at monthly intervals; the automated hourly measurements were available beginning in January 2004. The river stage data were implemented in the model by averaging the hourly data over a daily cycle for the period January 1, 2009, through December 31, 2018 (Figure 5-30). Over this period, the minimum and maximum river stages were 104.25 and 108.78 m (342.04 and 356.88 ft), respectively. The median stage over the period was 105.26 m (345.36 ft). The hydraulic gradient along the river was interpolated from two stations (319 and 321), based on the Modular Aquatic Simulation System 1D model results (PNNL-22886, *System-Scale Model of Aquifer, Vadose Zone, and River Interactions for the Hanford 300 Area – Application to Uranium Reactive Transport*). The interpolated gradient along the river of 3.19E-04 m/m was used in the model.

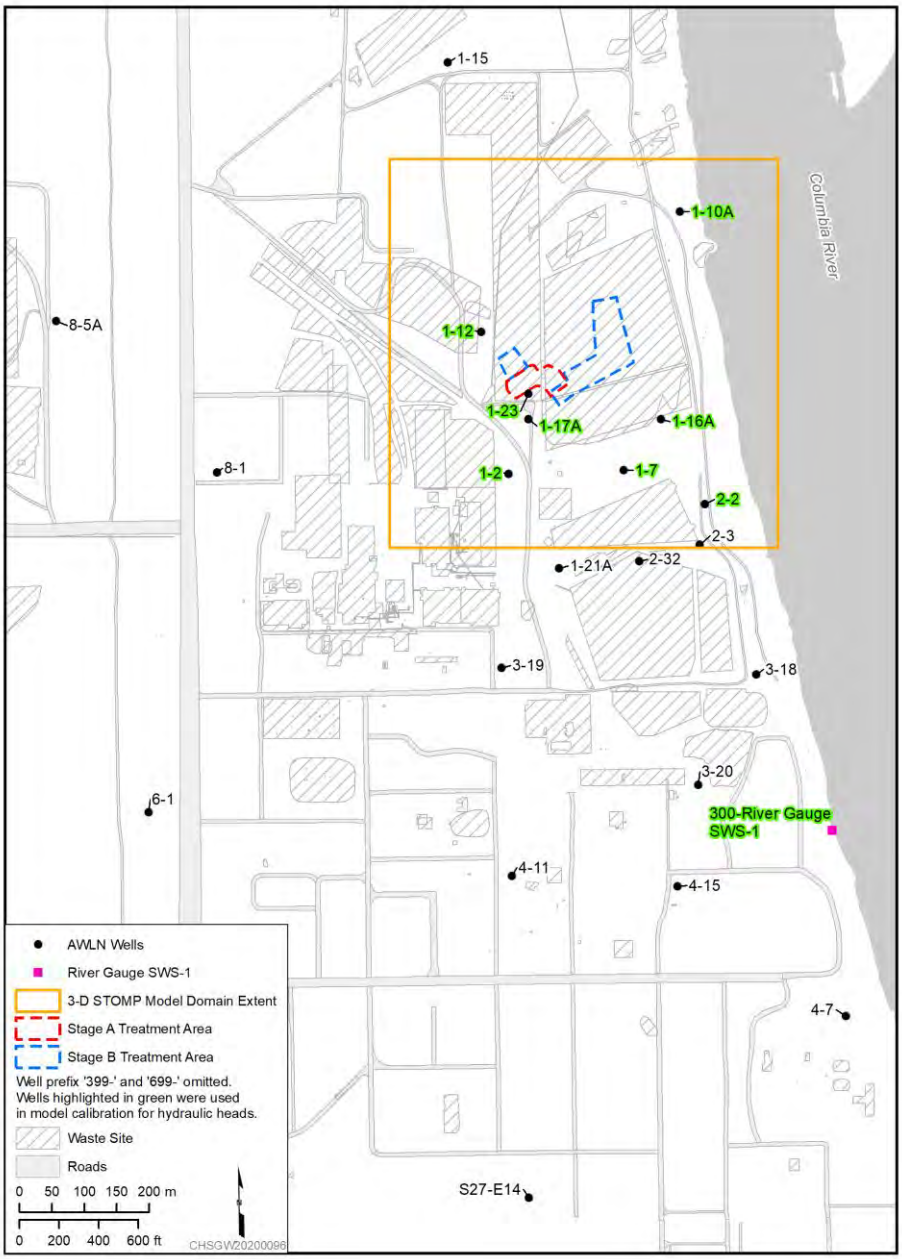
The water level data from well 399-1-12 were used to interpolate time-varying hydrostatic pressures at the western boundary nodes, while well 399-1-10A was used for the northern boundary nodes and well 399-1-2 was used for the southern boundary nodes. The hourly water levels were averaged over a daily time period from 2009 through 2018 and then applied as the boundary conditions. The daily averaged water levels were extrapolated along the entire length of the respective boundaries by assuming a constant gradient of 2.35E-4 m/m based on evaluation of the water table maps in the Hanford Site Groundwater Monitoring Reports that are produced annually.

Based on evaluation of spatial and temporal trends in river and groundwater mixing, uranium concentration plume maps, and geologic information on preferential pathways within the surficial aquifer (e.g., paleochannels), the saturated zone Hf unit was divided into the following three different hydraulic conductivity zones (Figure 5-31):

1. Saturated Hanford 1 zone: This zone covers most of the model domain and was assigned a saturated hydraulic conductivity of 4,000 m/d (13,123 ft/d) based on tracer test data and information assembled in Appendix B of ECF-300FF5-19-0086.

2. Saturated Hanford 2 zone: This zone defines an area of higher hydraulic conductivity (paleochannel) where the preferential movement of uranium and phosphate has been observed. The saturated hydraulic conductivity of 6,000 m/d (19,685 ft/d) was assigned to this zone that resulted in a better match to uranium concentrations.

3. Saturated Hanford 3 zone: A lower hydraulic conductivity zone of 1,000 m/d (3,281 ft/d) near the river was assigned to dampen the effect of river stage fluctuations at the river-aquifer interface due to the presence of a lower permeability lithologic unit near the base of the river channel.



Note: Highlighted locations are used in the System Scale 3-D STOMP Model Hydraulic Head Calibration.

Figure 5-29. Monitoring Locations with Transducers within 300 Area Showing River Gauge (SWS-1) and Monitoring Wells

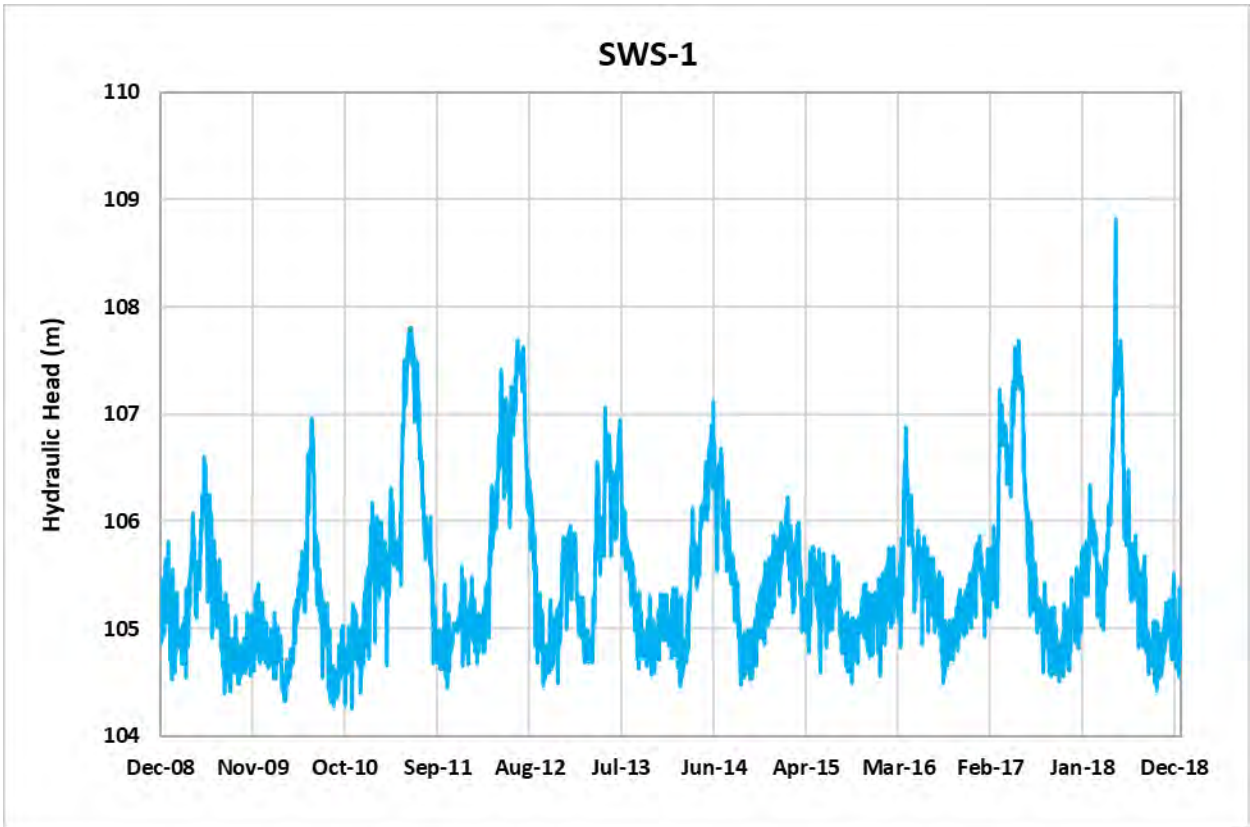


Figure 5-30. Daily Averaged Columbia River Stage Data at SWS-1 (300 Area River Gauge)

The saturated hydraulic conductivity of the Rwie that is located below the saturated zone Hf unit is set at 10 m/d (33 m/d).

A 3-D uranium distribution was developed based on compilation of all available uranium sediment data. The details of the data compilation and development of the 3-D uranium distribution can be found in ECF-300FF5-16-0087. The plan view of the spatial distribution is shown in Figure 5-32 at interpolated elevation of 107 m (351 ft) (PRZ). Since the uranium sediment concentrations were determined on <2 mm (0.1 in.) size sediment, the soil concentrations were corrected for gravel content for the purpose of applying uranium mass on the bulk volume basis. This correction is necessary as almost all of the uranium mass is associated with the <2 mm (0.1 in.) size fraction and a negligibly small amount is associated with the gravel fraction. A 60% gravel correction factor was applied. An additional adjustment was made to account for the component of uranium that would be exchangeable or labile. This was considered to be 60% based on evaluations presented in ECF-300FF5-16-0091. For the initial conditions set-up, any soil uranium mass interpolated to be in the backfill material was removed along with any uranium mass in the aquifer as it was deemed to be nonlabile.

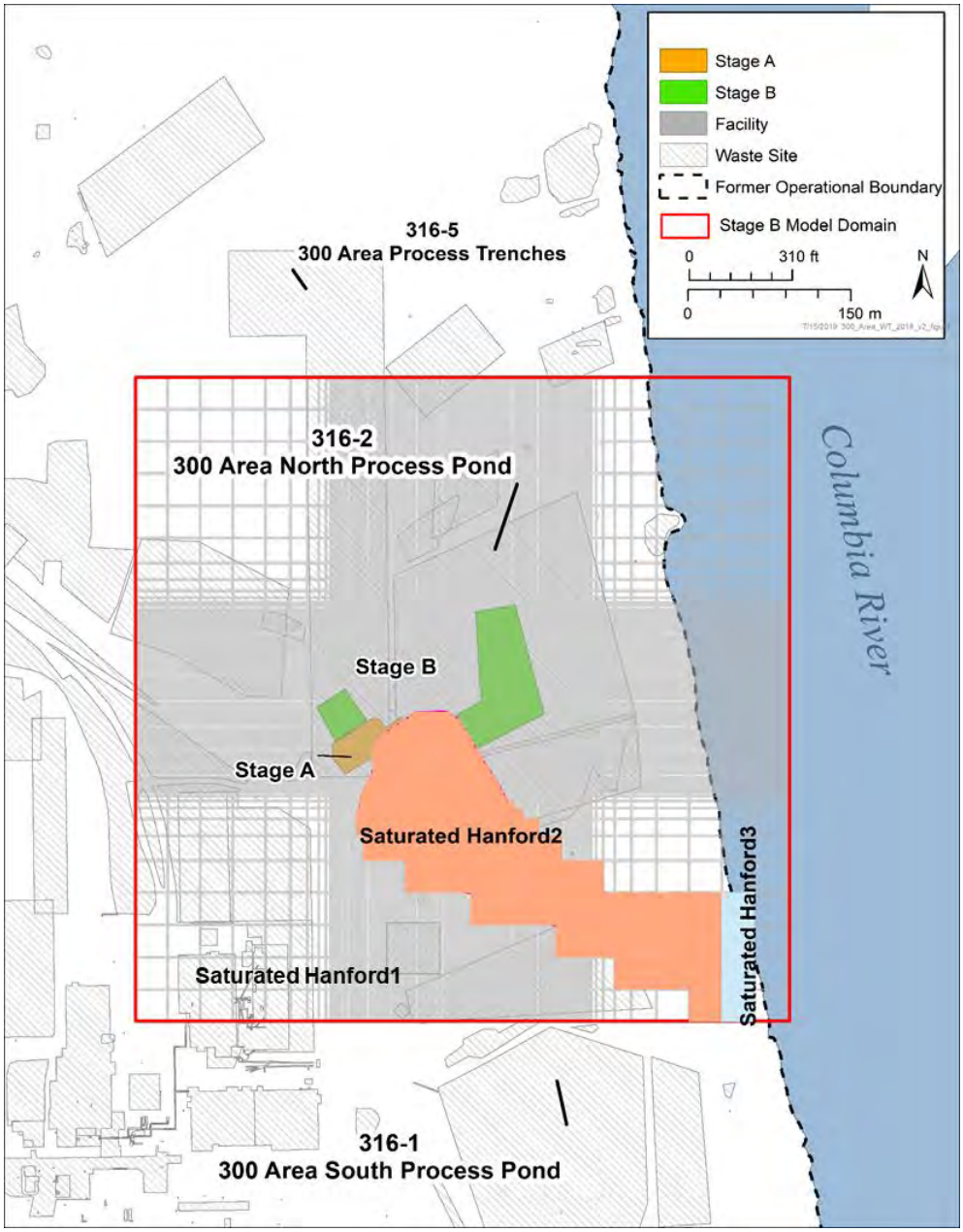


Figure 5-31. Zones of Variable Hydraulic Conductivity for the Hanford Unit in the Unconfined Aquifer within the System-Scale 3-D STOMP Model

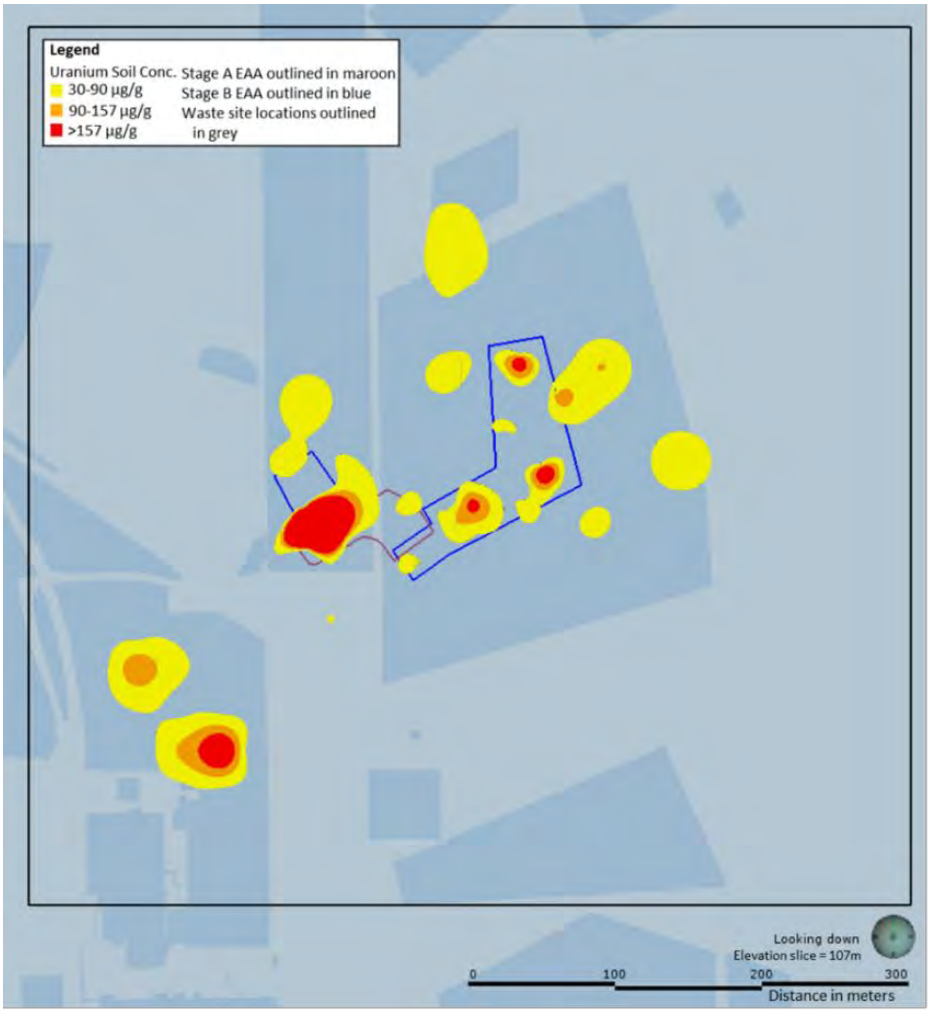


Figure 5-32. Spatial Distribution of Uranium Soil Concentration Based on Interpolation of Soil Sampling Data Collected from Various Boreholes

5.3.4 System-Scale 3-D Flow and Transport Modeling Results and Projections

The simulated hydraulic heads based on the system-scale 3-D flow modeling are presented in Figure 5-33 for two monitoring wells (399-1-17A and 399-1-7) to illustrate the modeling results. These two wells not only have long-term monitoring records but are representative of the uranium concentrations in the aquifer and have been used consistently to delineate the uranium plumes. Monitoring well 399-1-17A is located just south of the Stage A and B treatment zone, while well 399-1-7 is located farther downgradient approximately midway between the treatment zone and the river (Figure 5-29). The hydraulic head comparison results presented in Figure 5-33 are representative of excellent matches throughout the model domain providing confidence in the choice of hydraulic parameters and the representation of boundary conditions. The time varying groundwater-riverwater mixing fractions were also estimated at various AWLN wells based on electrical conductivity measurements to indirectly evaluate conservative (unretarded) solute transport across the model domain. Based on end-member mixing of river water and upgradient groundwater, the electrical conductivity of the two end-members can be used to calculate the groundwater-riverwater mixing fraction at any well over the monitoring period. The results are compared to the simulated mixing fractions for the two monitoring wells in Figure 5-34 over the 10-year period. The results show good match between the model simulated values

and the observations indicating that both temporal and spatial component of a conservative tracer (river water) is properly represented, thereby providing further confidence in the model to simulate both flow and transport processes at the scale of the model domain.

The results of the simulated uranium concentrations are compared to the monitoring records for the past 25 years (1995-2019) at the two representative wells (Figure 5-35). The simulations were conducted by applying the daily averaged hydraulic head boundary conditions compiled for the 10-year period (2009-2018) to the past. The model simulations were started in 1989 and the 10-year cycle was repeated to generate the results with the objective to get the uranium concentration trends consistent with the observations, particularly over the past 10-year time interval (excluding short-term transient effects during Stage A and B treatments in November 2015 and September 2018, respectively). The simulated uranium concentrations are consistent with the observations and indicate that despite inherent uncertainty in initial uranium mass distribution in the subsurface and in the mass release behavior under variably saturated conditions, the parameters used in the model are reasonable for the system-scale evaluation and that all the relevant processes and features are represented adequately at the scale of the model domain. It further indicates that the model can be used to predict future uranium concentrations over the next 20 to 30 years with reasonable degree of confidence.

Figure 5-36 presents the results of the simulation focused on the time periods just before and after Stage B treatment (September 2018). The simulated uranium concentrations in the post-treatment period drop and stay low consistent with the observations at both representative wells. These results provide confidence in the parameters used to simulate the uranium leaching rates for the post-treatment period within the model domain. A longer term predictive simulation is carried out for the next 20-year time period to estimate the future concentrations using the system model. The results are presented for the two wells in Figure 5-37 to illustrate the changes over time. The dissolved uranium concentrations continue to decline following treatment but reach asymptote-based concentrations that are below the CUL of 30 µg/L. Other than the short-term seasonal increases in uranium concentration due to river stage fluctuations during summer, the concentrations stay below the CUL for remainder of the year.

The simulated spatial uranium plume maps are presented in Figure 5-38 for two time periods in year 2019 corresponding to the seasonal low water table (January) and high water table (June) conditions. Also presented are uranium concentration contours based on observations that are influenced by higher concentrations at wells 399-1-55 and 399-1-62. Outside of those two wells the uranium concentrations appear to remain low as indicated by the 30 µg/L concentration contour indicating effectiveness of the treatment. Figures 5-38 through 5-42 show snapshots of predicted uranium plumes in selected years. Over time the spatial extent of uranium plume (with concentration exceeding 30 µg/L) continues to decline.

Of particular interest is the time evolution of the uranium mass transport from the vadose zone to the water table. For this, the mass flux rate and cumulative mass across the 105 m (344.5 ft) elevation plane (average water table) using the system scale 3-D flow and transport model was computed for the base case (which includes effects of Stage A and B treatments) and compared to a sensitivity case (a "no-action case") where effects of Stage A and B treatment are not modeled. The results are presented from 2009 onward in terms of cumulative mass released to the water table (Figure 5-43). The extrapolation to start of year 2040 suggests that about 240 kg (529 lb) less uranium reaches the groundwater in the base case due to the Stage A and B treatment in the EA area.

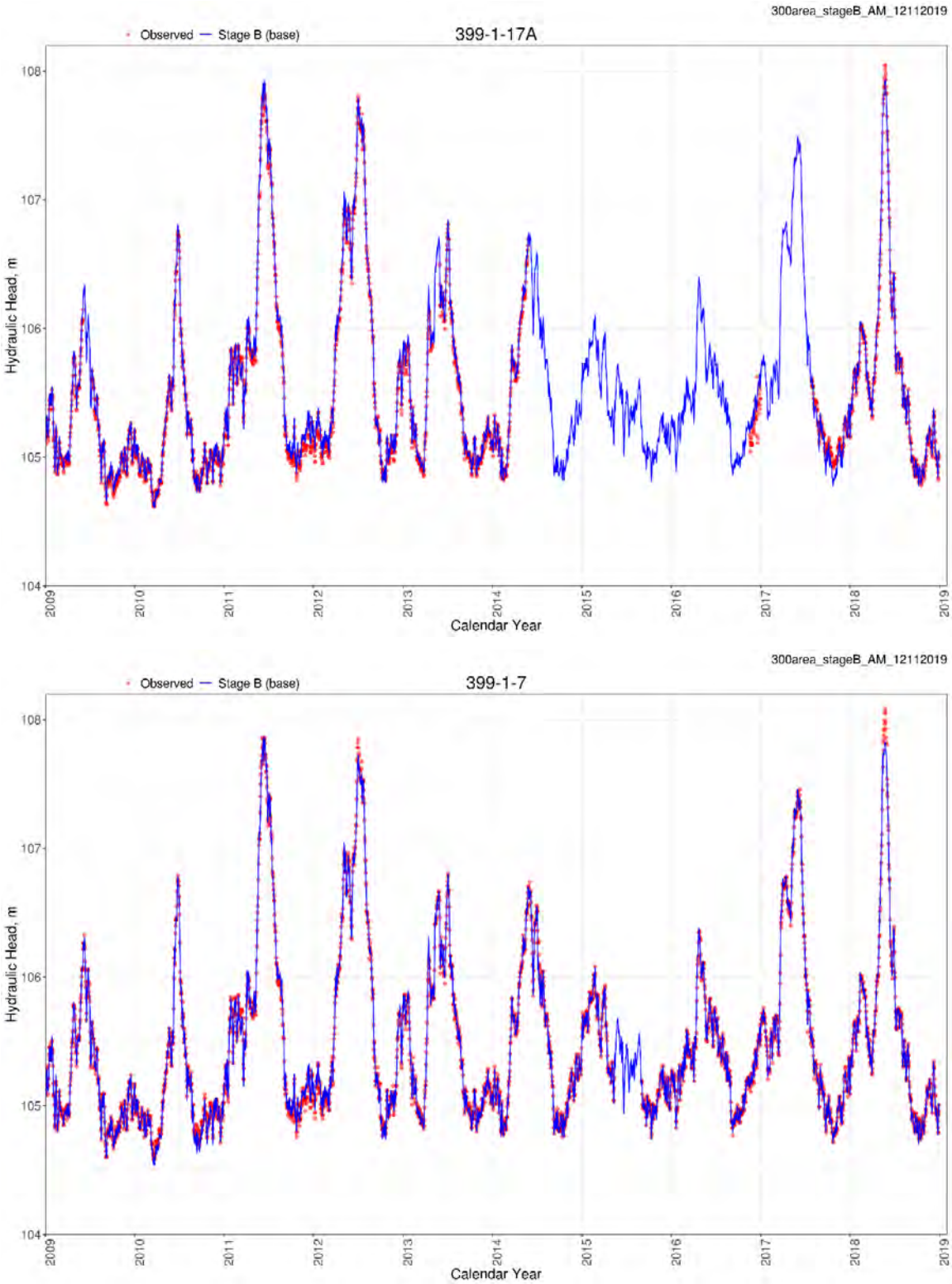


Figure 5-33. Comparison of System-Scale 3-D STOMP Model Simulated Hydraulic Heads with Observed Heads at Wells 399-1-17A and 399-1-7

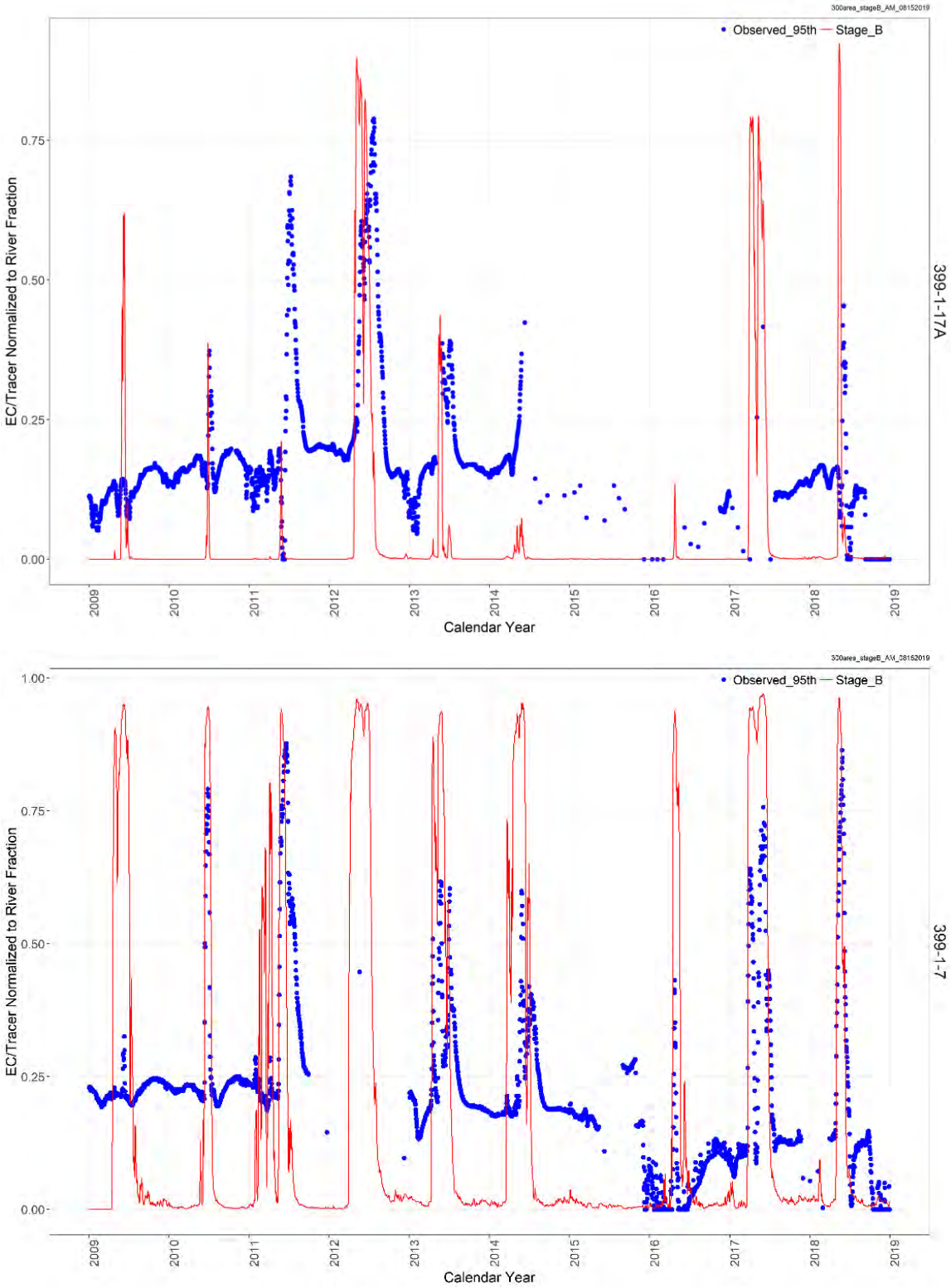


Figure 5-34. Comparison of System-Scale 3-D STOMP Model Simulated Groundwater-Riverwater Mixing Fraction with Observed Data at Wells 399-1-17A and 399-1-7

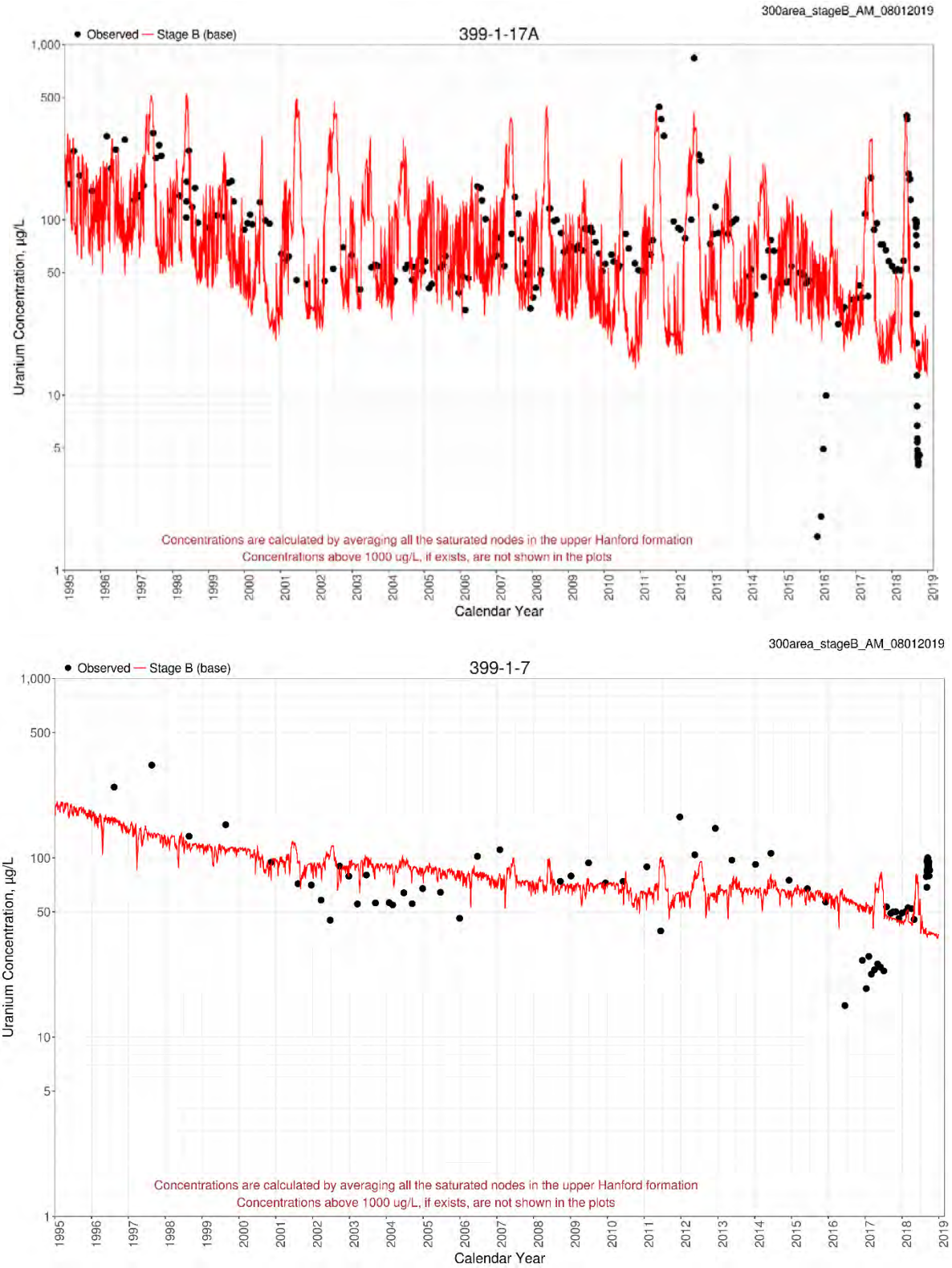
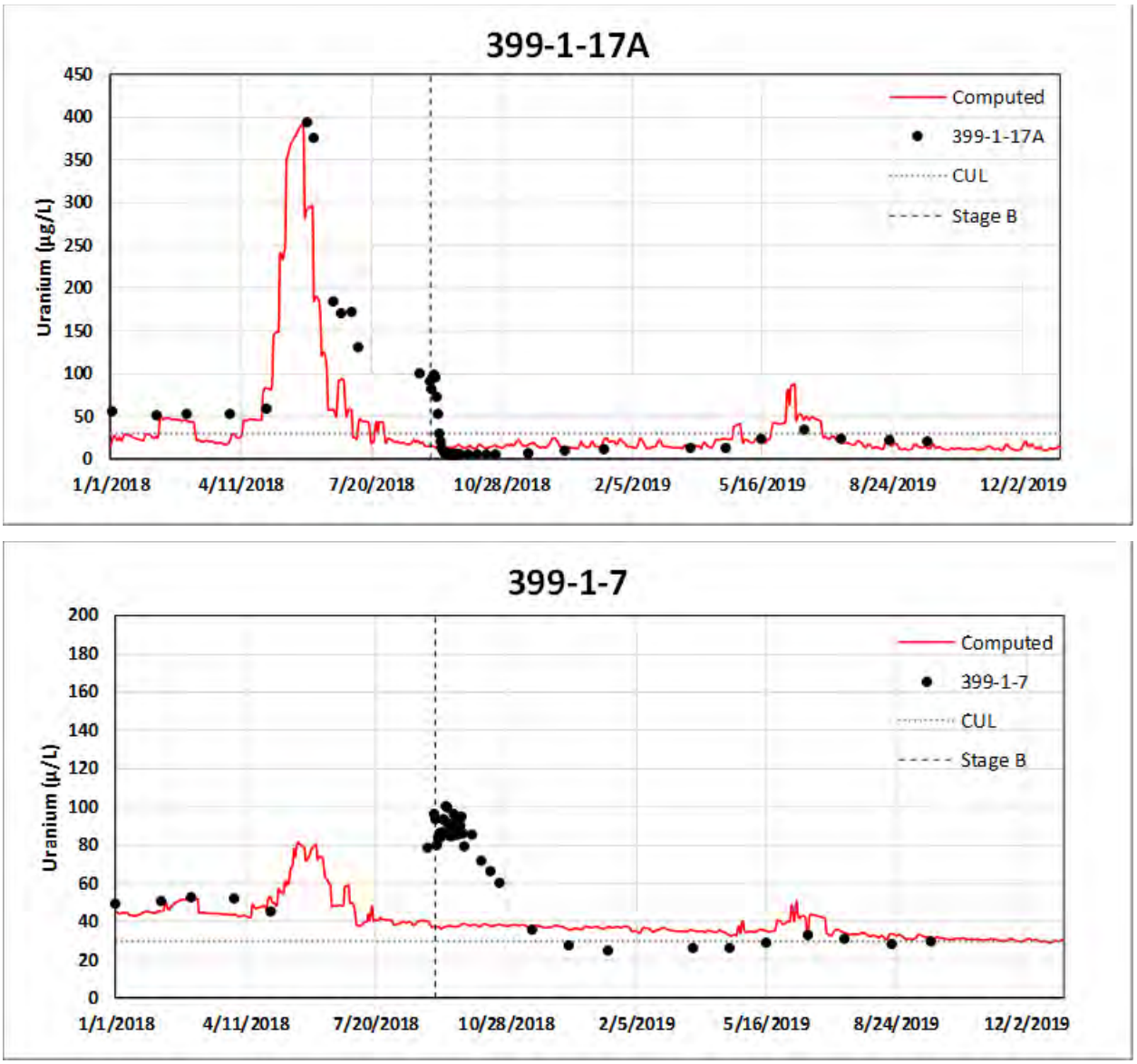
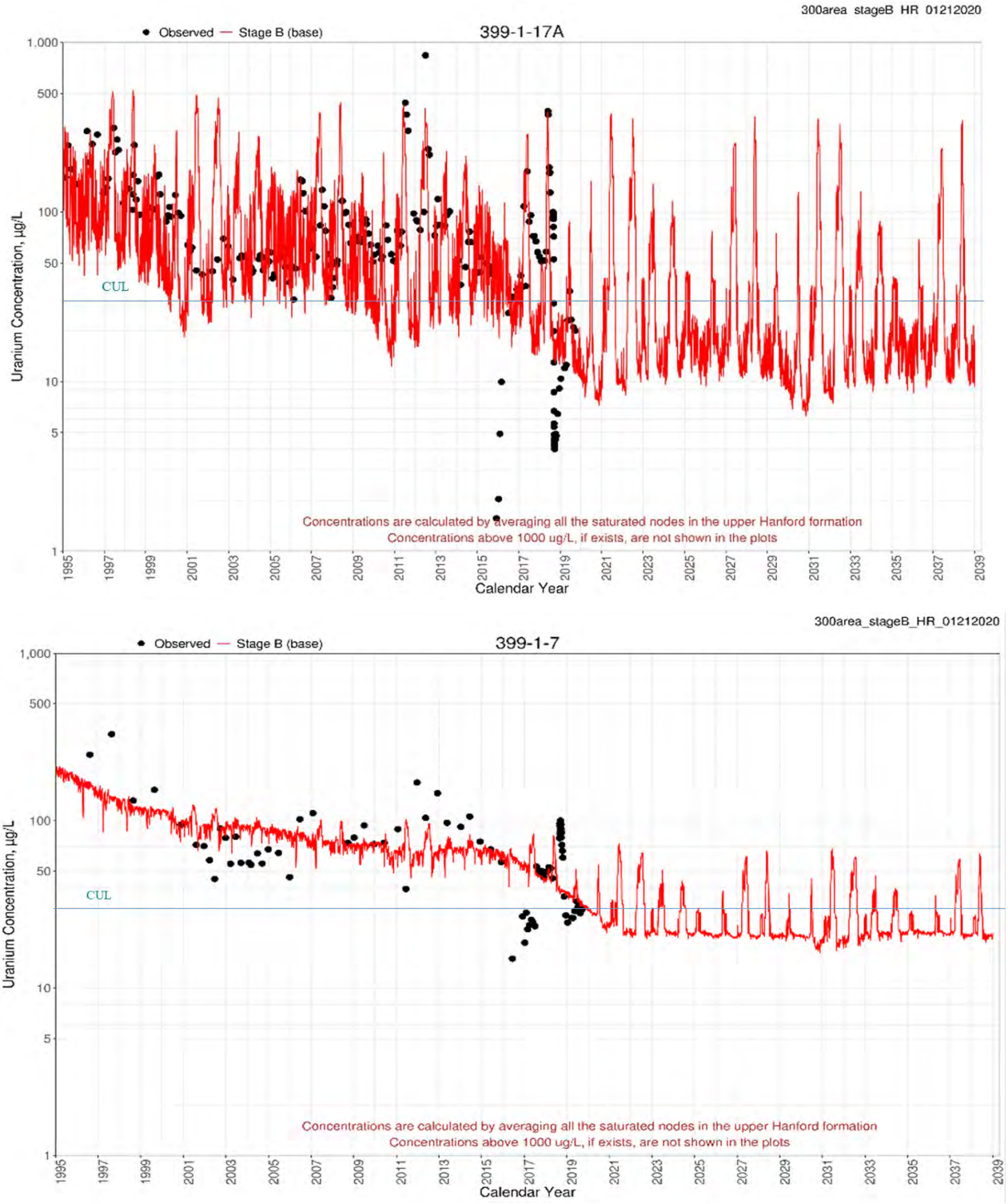


Figure 5-35. Comparison of System-Scale 3-D STOMP Model Simulated Uranium Concentrations in Groundwater with Observed Data at Wells 399-1-17A and 399-1-7



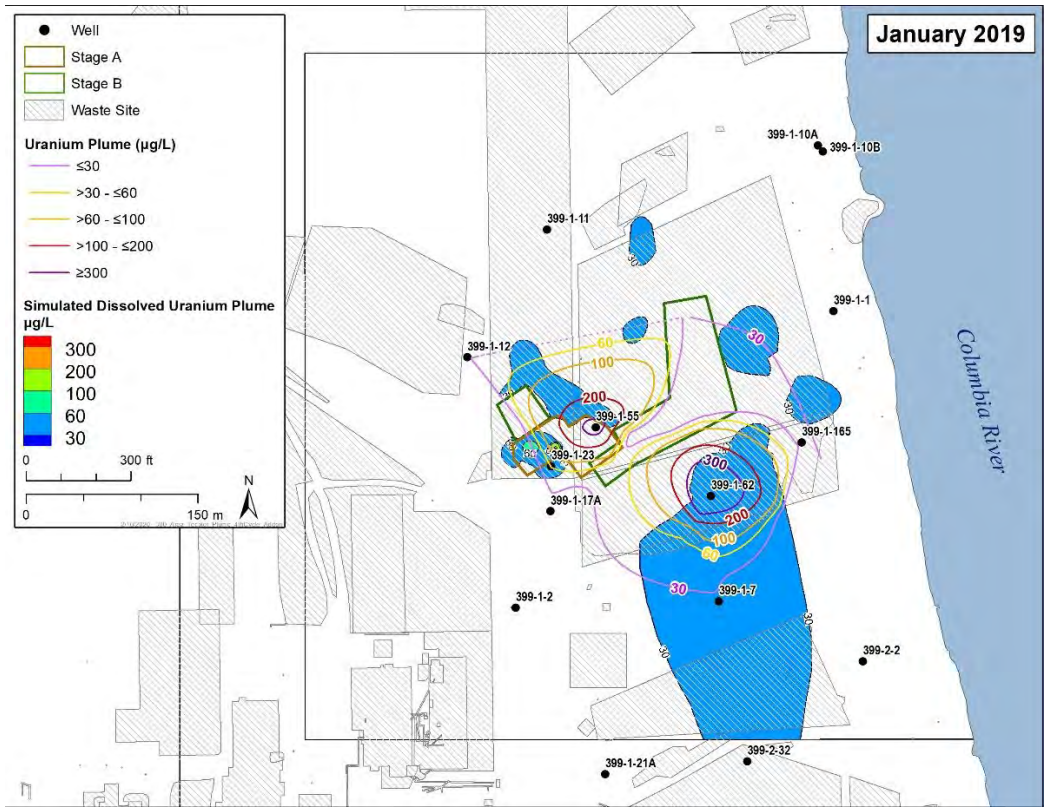
CUL = cleanup level (30 µg/L)

Figure 5-36. Comparison of System-Scale 3-D STOMP Model Simulated Groundwater Uranium Concentrations During the Post-Treatment Period with Observed Data at Wells 399-1-17A and 399-1-7



CUL = cleanup level (30 µg/L)

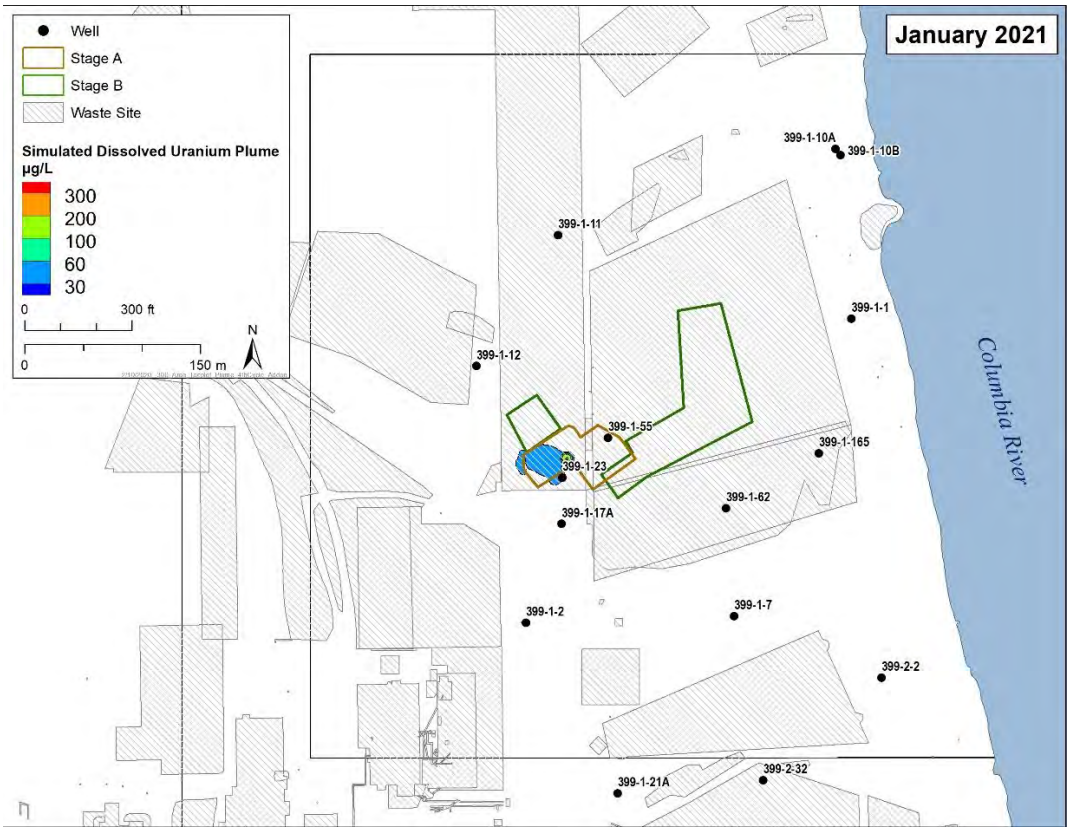
Figure 5-37. System-Scale 3-D STOMP Model Simulated Longer Term Groundwater Uranium Concentrations at Wells 399-1-17A and 399-1-7



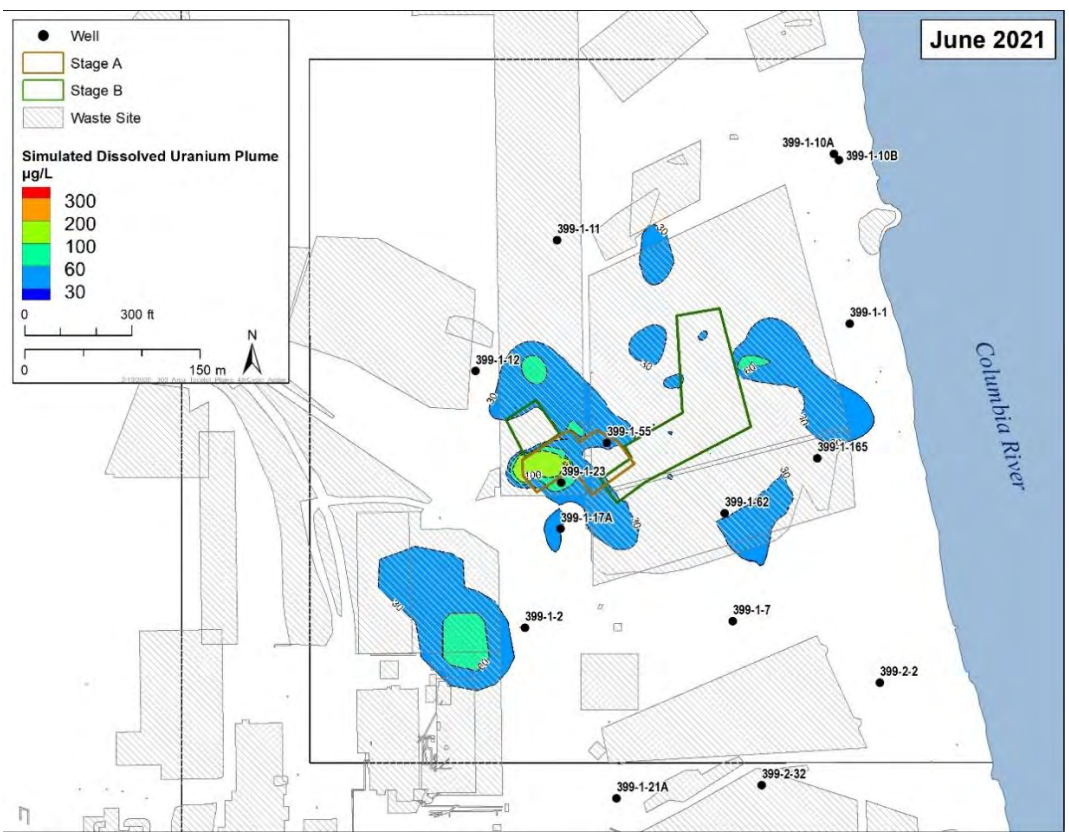
(a)

(b)

Figure 5-38. Simulated Uranium Plumes for (a) January 2019 and (b) June 2019

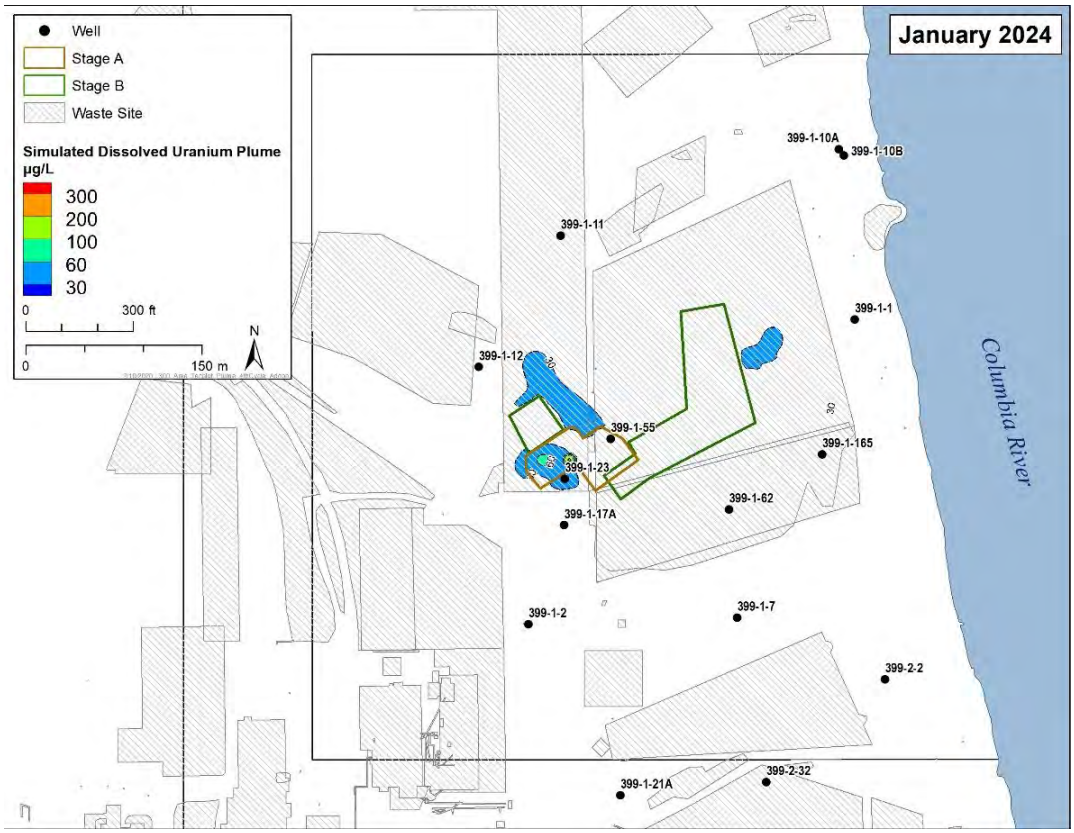


(a)

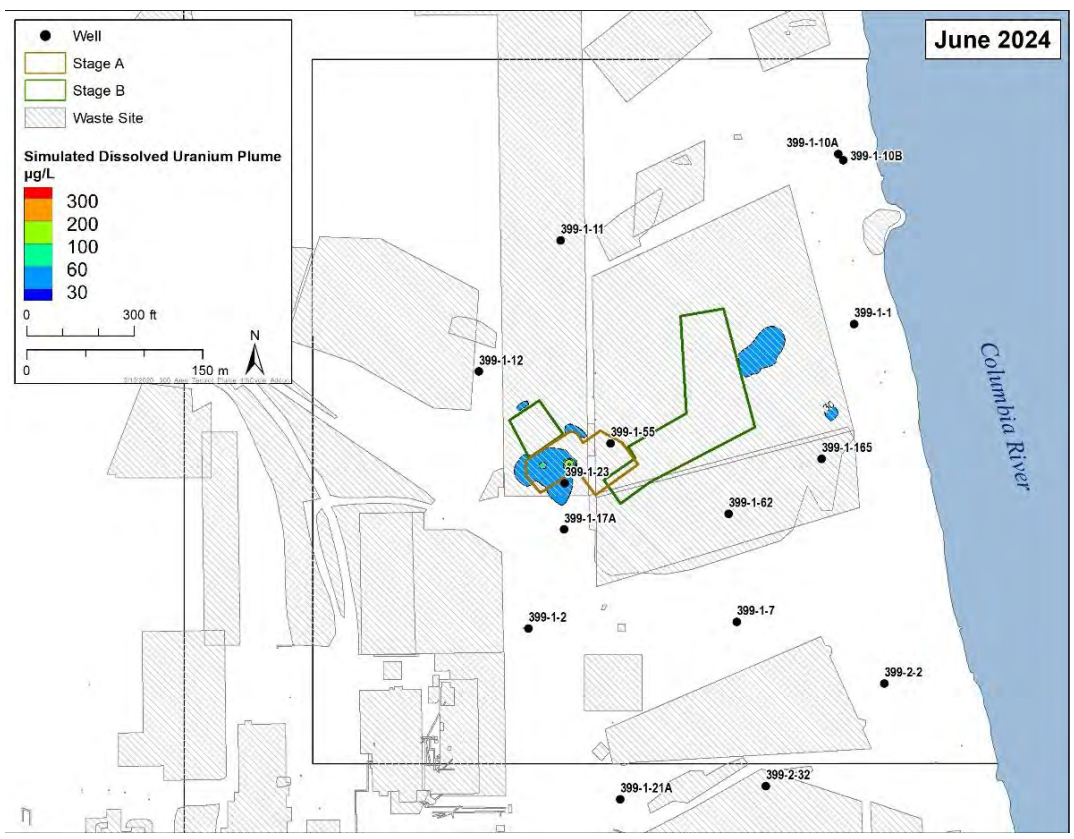


(b)

Figure 5-39. Simulated Uranium Plumes for: (a) January 2021 and b) June 2021



(a)



(b)

Figure 5-40. Simulated Uranium Plumes for: (a) January 2024 and (b) June 2024

(a)

(b)

Figure 5-41. Simulated Uranium Plumes for: (a) January 2027 and (b) June 2027

(a)

(b)

Figure 5-42. Simulated Uranium Plumes for: (a) January 2029 and (b) January 2039

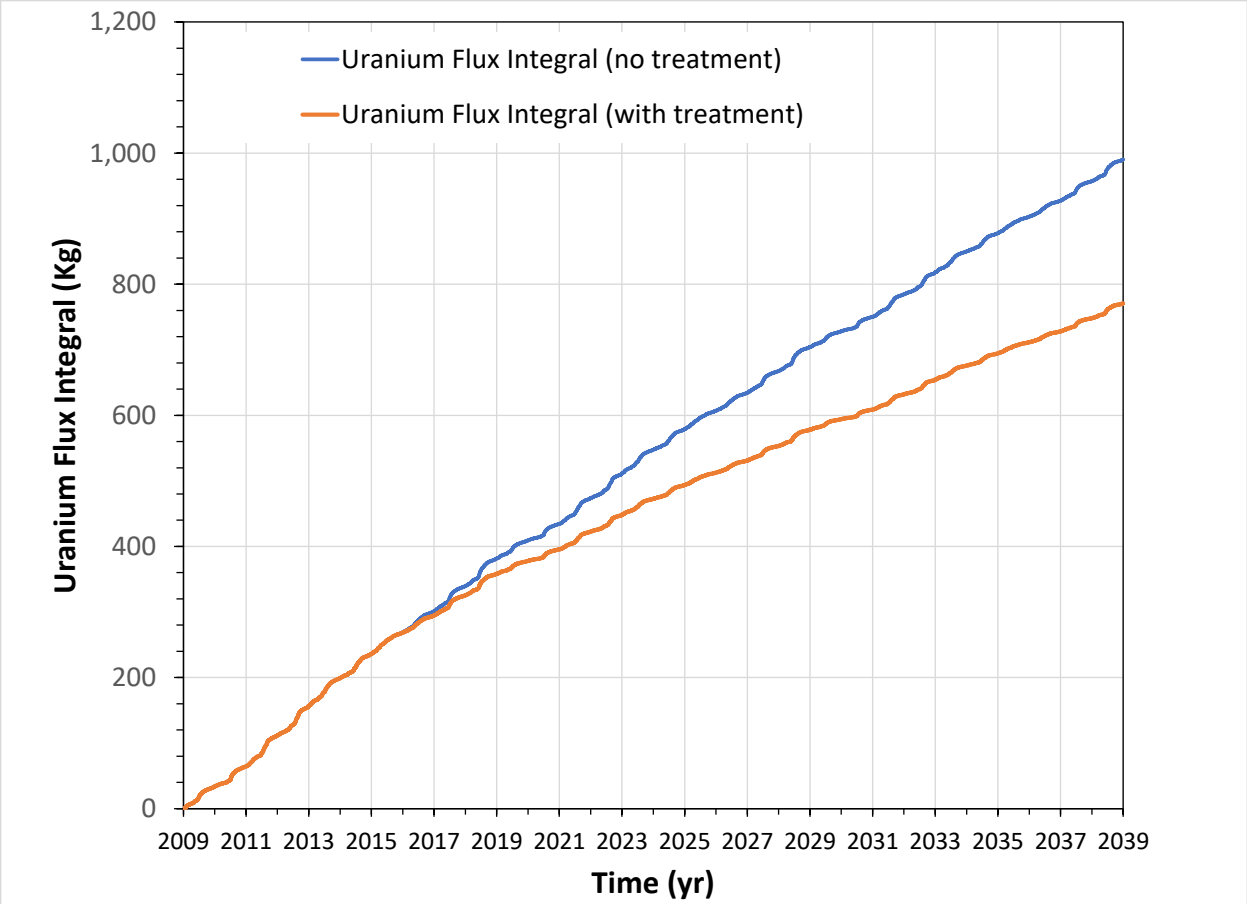


Figure 5-43. Comparison of the Cumulative Mass Flux of Uranium Across the Approximate Water Table Between the Base Case with Treatment and the No-Action Case Without Treatment (Relative to Year 2009)

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6 Conclusions

The 300 Area ROD (EPA et al., 2013) identified uranium as a contaminant of concern in soil and groundwater. Part of the selected remedy for uranium contamination in the 300 Area is EA using polyphosphate solutions to sequester uranium and reduce its mobility in the vadose zone, PRZ, and top of the aquifer. This report presents the initial performance evaluation of the EA remedy for uranium contamination in a portion of the 300 Area of the Hanford Site.

The EA remedy was implemented in the 1.2 ha (3 ac) area where the conceptual site model indicated the most concentrated uranium is replenishing the uranium groundwater plume. Concentrated phosphate solution mixed with river water was applied in 0.3 ha (0.75 ac) in November 2015 (Stage A) and in the remaining 0.9 ha (2.25 ac) in September 2018 (Stage B). The Stage A application of the amendment served to test the field-scale implementation plan, and the lessons learned during Stage A (Sections 3.8 and 6.3 in SGW-59614) were used to improve the design and operation of Stage B. During Stage A, the polyphosphate solution was delivered to the subsurface via near-surface buried infiltration drip lines and PRZ and aquifer injection wells. While the polyphosphate solution was delivered to the PRZ in most of the Stage A area, Stage B was designed to directly inject the solutions to the LVZ and PRZ.

Stage B injections were conducted via 48 closely spaced injection wells by first injecting solutions into the PRZ and then into the LVZ to maximize the residence times. The LVZ was operationally defined to range from the 108.5 to 107 m (356 and 351 ft) elevation, while PRZ was defined from the 107 to 105 m (351 and 345 ft) elevation. During and following the injections, continuous ERT imaging was undertaken along with automated water level monitoring at selected locations. In addition, groundwater and PRZ monitoring wells were sampled at varying time intervals for a period of 1 year. Before the injections and 6 months after the injections, pre-treatment and post-treatment boreholes were drilled and soil samples were collected for laboratory analyses and leaching tests.

The effectiveness of the treatment can be assessed by grouping the relevant information into the following three categories: (1) the delivery and distribution of the polyphosphate treatment solutions in the subsurface, (2) impacts to uranium mobility and leachability, and (3) numerical modeling to assess future impacts. Each section presents a summary of key observations or major conclusions.

6.1 Delivery and Distribution of Polyphosphate Treatment Solution in the Subsurface

The delivery and distribution of the polyphosphate solution to the targeted treatment zones were monitored by groundwater monitoring, ERT imaging, and downhole automated instrumentation during and after the injections. Six months after the injections, post-treatment boreholes were drilled and soil samples were collected for phosphate extraction. The extractions evaluated the change in solid phase phosphate in the sediments.

6.1.1 Vadose Zone and PRZ Phosphate Delivery

For Stage B, the blended solution was injected at a target volume roughly equivalent to three pore volumes of the LVZ and PRZ based on the size of the Stage B area of 0.9 ha (2.25 ac). The Stage B injection volumes for each well ranged from 156,307 to 225,732 L (41,292 to 59,632 gal) of polyphosphate solution delivered to the PRZ with an average of 190,131 L (50,227 gal), which is within 5% of the target volume. Similarly, a range of injection volumes from 99,844 to 172,705 L (26,376 to 45,624 gal) were delivered to the LVZ with an average of 147,619 L (38,247 gal), also within 5% of the target delivery volume. Overall, injection rates ranged from 121 to 261 L/min (32 to 69 gal/min) with an average rate of 181 L/min (48 gal/min).

During Stage A, the average volume of solution injected into each PRZ injection well was 201,054 L (53,113 gal) and the average volume injected into each aquifer injection well was 188,634 L (49,832 gal). The infiltration rate for Stage A ranged between 198 to 316 L/min (52 to 84 gal/min) and the rate of injection was approximately 1,136 L/min (300 gal/min).

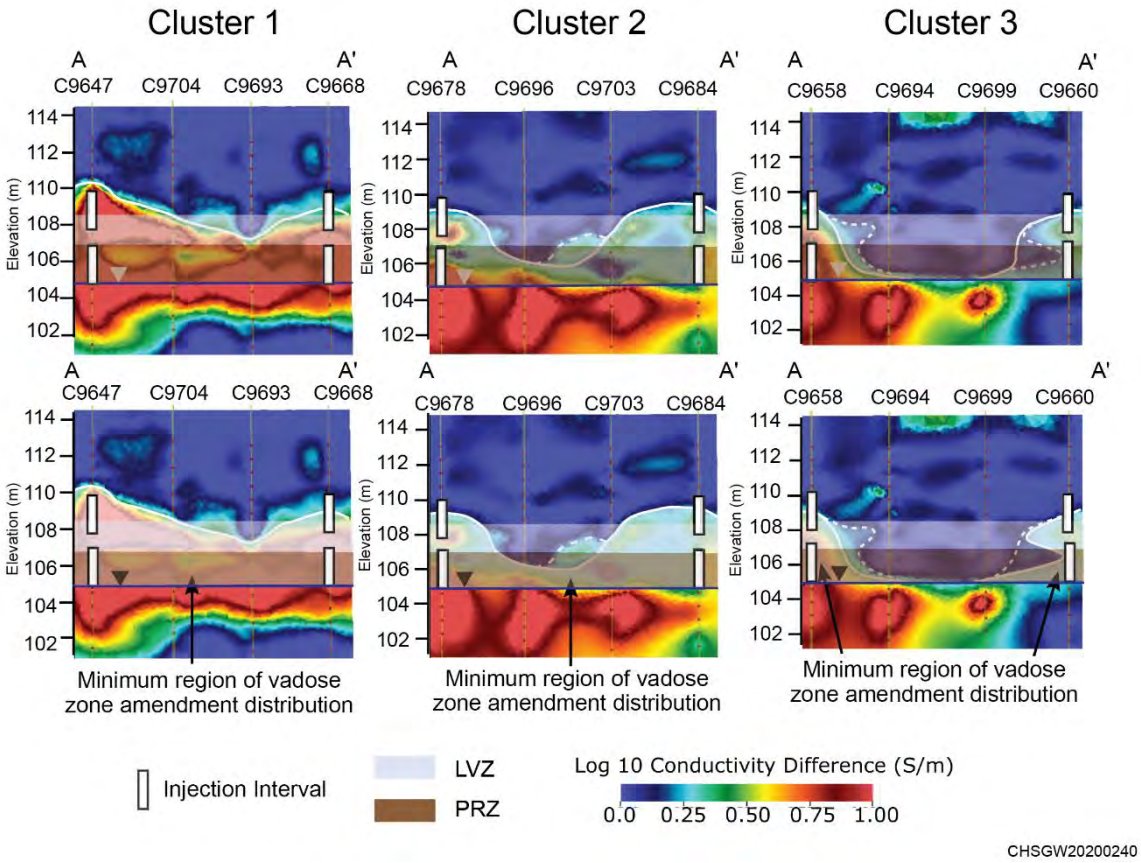
Polyphosphate solutions (90% orthophosphate and 10% pyrophosphate) were injected at a target concentration of 8,236 mg/L total phosphate during the Stage A and B EA remedy. The target pH was between 7.0 and 7.5. On average, the mass of phosphate delivered during Stage B, through each of the 48 wells, was 1,566 kg (3,452 lbs) to the PRZ and 1,216 kg (2,680 lbs) to the LVZ. The total mass of phosphate injected was 75,164 kg (165,708 lbs) into the PRZ and 58,358 kg (128,657 lbs) into the LVZ. For Stage A, the target treatment mass of phosphate was 20,969 kg (46,229 lbs) for infiltration, 15,387 kg (33,922 lbs) for PRZ injection, and 15,387 kg (33,922 lbs) for aquifer injection as prescribed in the RDR/RAWP (DOE/RL-2014-13-ADD2). Target masses were met during Stage A and B operations (Section 4.3 in this report; Appendix I in SGW-59614).

6.1.2 Phosphate Distribution Within the Vadose Zone, PRZ, and Aquifer

Phosphate was effectively distributed in the portions of the subsurface targeted for the uranium sequestration remedy, namely the PRZ and upper aquifer. As expected, there was some variability in the phosphate concentration distribution, due in large part to the inherent heterogeneity of the system. Several lines of evidence were employed to evaluate the distribution of phosphate in the Stage A and B sediments.

ERT was used to evaluate amendment delivery by imaging the change in subsurface electrical conductivity caused by the injection and infiltration of polyphosphate solution. Stage A employed two surface ERT arrays that imaged a 2-D cross section of the subsurface with the intent to track the polyphosphate infiltration from ground surface to the aquifer (Section 3.4 of SGW-59614). Stage B employed real-time cross-borehole arrays in three clusters of 6 instrumented wells (18 wells total) straddling the different injection zones in the treatment area. As shown in Figure 6-1, the change in conductivity within the PRZ and LVZ varied spatially across the three clusters. Cluster 1 monitored injections in zones 1 and 2 as it spans the border between zones 1 and 2 (Figures 4-28 and 4-30), and cluster 2 was positioned across injection zones 2 and 3 (Figures 4-28 and 4-31). The most comprehensive distribution of the injected fluids occurred in the PRZ and most of the LVZ of clusters 1 and 2.

Cluster 3, positioned across injection zones 3 and 4, had some signal loss and imaging issues but overall showed less lateral flow than clusters 1 and 2 (Figures 4-28 and 4-32. However, it should be noted that the absolute radius of influence is difficult to determine in the absence of a 3-D image. As discussed in Section 4.4.2 of this report, the spatial variability of phosphate distribution throughout the PRZ and LVZ shown by the ERT images is hypothesized to be influenced by the differences in sediment permeability and degrees of anisotropy across the four injection zones. The downhole sensor specific conductance data associated with PRZ wells also showed variability in responses from the injections. The variability in polyphosphate solution migration is also corroborated by the concentration of phosphate in the soils when pre-treatment borehole samples were compared to post-treatment borehole samples.



Source: Modified from Figure S.1 in PNNL-28619, *Stage B Uranium Sequestration Amendment Delivery Monitoring Using Time-Lapse Electrical Resistivity Tomography*.

Top row is maximum increase in conductivity observed over the monitoring period. Bottom row shows the corresponding interpretation of the amendment-distribution zone above the water table.

Figure 6-1. Summary Images of the Changes in Electrical Conductivity during Stage B Polyphosphate Injections in Clusters 1 through 3

Pre-treatment and post-treatment sampling was conducted to evaluate phosphate concentration changes in sediments (detailed in Section 4-1 of this report). Post-treatment soil samples collected and analyzed 2 months later for Stage A and 6 months later for Stage B exhibited increases in phosphate concentrations from depths of 6.1 to 9.1 m (20 to 30 ft) bgs. Stage B pre-treatment phosphate concentrations in soils were near or below quantitation limits in most samples (average of 2.72 µg/g) (Appendix B of this report). Phosphate in post-treatment samples increased to an average concentration of 217 µg/g and ranged from 1.85 µg/g (C9736, located on the border between zones 3 and 4) to 862 µg/g (C9732, located in zone 1) (Appendix B of this report). Post-treatment borehole C9736 phosphate concentrations were near background for all samples and correlated to the variable distribution of conductivity observed in the ERT cluster 3 images. However, 87% of the other post-treatment soil samples had phosphate concentrations 10 to 100 times the pre-treatment values.

Aqueous phosphate concentrations in PRZ and aquifer monitoring wells in and downgradient of treatment zones 1 through 4 are higher following the polyphosphate injections (Figure 6-2). The phosphate concentration trends observed during injections in Stages A and B were similar. During both stages, polyphosphate injections produced a rapid peak in phosphate concentrations in the aquifer and PRZ wells,

followed by a gradual decline. This suggests that both Stage A and B injections to the PRZ were effective in delivering high concentrations of phosphate to the subsurface sediments.

In the 4 weeks after injections, aqueous phosphate concentrations in aquifer and PRZ wells gradually decreased within the treatment area. Aquifer wells farther downgradient of the treatment areas began to show elevated concentrations in phosphate 1 to 2 months after the end of injections but then exhibited gradual decreases in phosphate concentrations (Figure 6-2). This gradual decline suggests either phosphate was continuing to infiltrate down through the LVZ and PRZ or polyphosphate solutions may have persisted in some areas of the aquifer and PRZ and did not immediately dilute and migrate in the groundwater. Monthly sampling performed for 6 months to 1 year after injections showed wells within and downgradient of the Stage B treatment area exhibited a steady decline in phosphate concentrations. Aquifer and PRZ wells continued to have phosphate concentrations at least five times their pre-treatment concentrations during the monthly sampling.

6.2 Impacts to Uranium Mobility and Leachability

Stage A and B polyphosphate injections resulted in a measurable reduction of the labile uranium fraction throughout the treatment area. Correspondingly, the polyphosphate injections increased the less soluble uranium mineral fraction, thereby reducing the rate at which uranium leaches into the groundwater. Several lines of evidence were employed to evaluate the change in uranium mobility in the Stage A and B sediments. Stage A analyses and results can be found in Section 4.1.2 of SGW-59614, Stage B results are in Section 4.1.2 of this report and are discussed below. Three types of leachability tests and solid phase elemental mapping were conducted on pre-treatment and post-treatment sediment samples to evaluate uranium mobility and leachability as follows:

- Sequential extractions on 19 samples from paired pre-treatment and post-treatment Stage B boreholes and 6 samples from unpaired post-treatment boreholes
- 1,000-hour carbonate solution extractions on 19 samples from paired pre-treatment and post-treatment Stage B boreholes and 6 samples from unpaired post-treatment boreholes
- 1-D flow-through column leach tests on 10 samples from paired pre-treatment and post-treatment Stage B boreholes and four samples from unpaired post-treatment boreholes
- Uranium solid phase analyses on two pairs of Stage B pre-treatment and post-treatment borehole samples

The results of these analyses confirmed that there were measurable reductions in the labile uranium fraction throughout the treatment area (Figures 6-3 and 6-4). 1,000-hour carbonate solution extractions exchange carbonate in aqueous solution with calcite and dissolve highly soluble uranium phases in the carbonate solution. The mobile uranium fraction for Stage B pre-treatment sediments is 0.425±0.096, and for Stage B post-treatment samples is 0.156±0.143, or an average of 63% less mobile uranium as a result of the polyphosphate treatment based on carbonate extractions of sediment samples from 19 pre-treatment and post-treatment pairs (shown as purple bars on Figure 6-4).

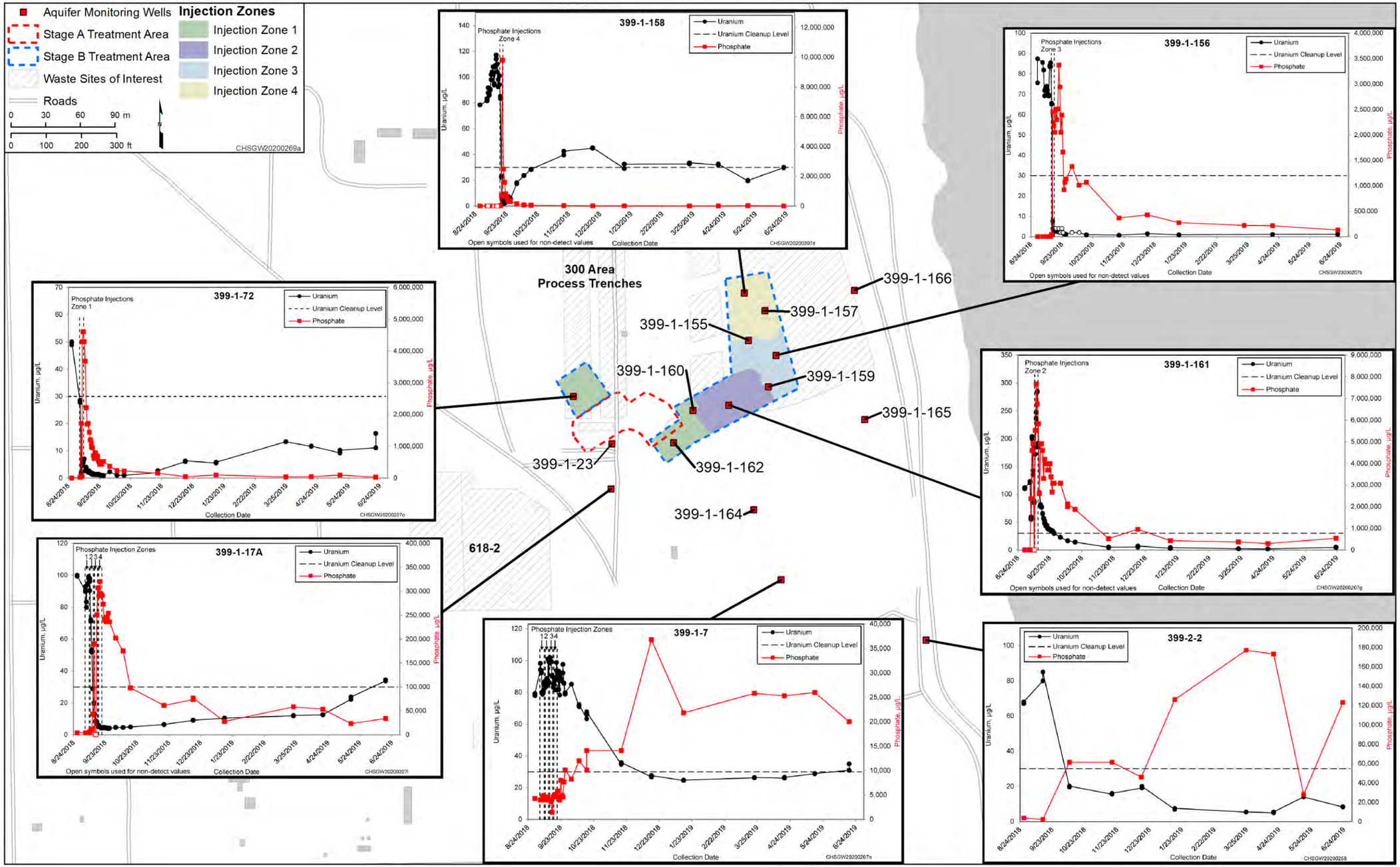


Figure 6-2. Uranium and Phosphate Concentrations in Aquifer Wells in and Downgradient of the Treatment Area from August 2018 through June 2019

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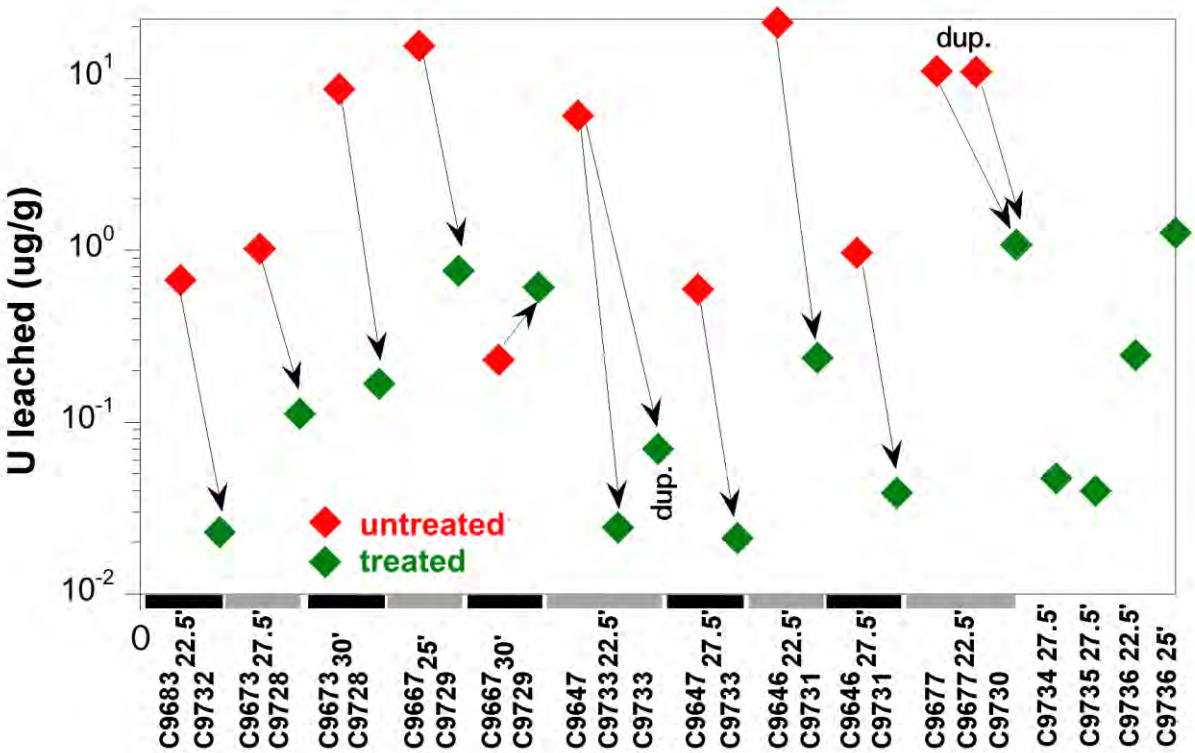
Sequential extraction results (Table 4-2 of this report) indicate a reduction in the fraction of (1) highly mobile uranium phases with rapid contaminant release that can be extracted by extractions 1 and 2, (2) soluble precipitates that can be extracted by extractions 3 and 4, and (3) an increase in the least mobile uranium fraction associated with low-solubility precipitates that can be extracted by extractions 5 and 6. Results of sequential extractions conducted on sediments showed that high-solubility uranium minerals decreased from 58.6% to 37.2% (of the total extracted uranium) and low-solubility uranium minerals increased from 34.8% to 54.3% as a result of the phosphate injections based on comparison of 19 pre-treatment and post-treatment sediments (Figure 6-4). The extractable uranium fraction associated with extractions 3 and 4 indicate high-solubility uranium minerals while the uranium fraction associated with extractions 5 and 6 indicate low-solubility uranium minerals. These results also confirm that there was a measurable reduction in the labile uranium fraction following treatment.

The 1-D leach experiments were conducted with pre-treatment and post-treatment sediments to measure the change in uranium mobility (i.e., uranium mass and concentration released) and to measure the rate of uranium release from the sediment. For Stage B, the uranium mobility measured in 26 1-D column leach experiments showed a 58.9±53.2% decrease in uranium leaching (fraction leached to total uranium) for the post-treatment samples (detailed discussion in Section 5.2 of PNNL-29650; shown as blue bars on Figure 6-4). These experiments also showed that the uranium release rates were one to three orders of magnitude less in post-treatment sediments relative to pre-treatment sediments (Figure 6-3). A general trend of increasing measured phosphate precipitate to measured decrease in uranium leaching was observed.



Source: Modified from Figure 4.31 in PNNL-29650, *Evaluation of the Change in Uranium Mobility in Sediments from the Hanford 300-FF-5 Stage B Polyphosphate Field Injection*.

Figure 6-3. Change in Leached Uranium Comparing Pre-Treatment to Post-Treatment

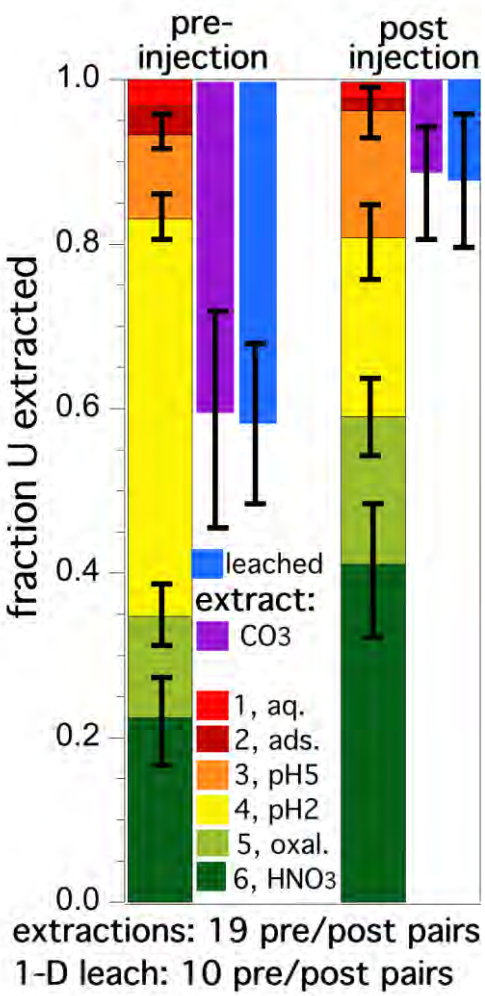


Figure 6-4. Summary of Fraction of Uranium Leached out of Mobile Phases Compared to Least Mobile Phases with Total Uranium Leached with Carbonate Extractions

The leachability and mobility of uranium is reduced through co-precipitation, sorption, and coating (Figure 5-17, Section 5.3.2 in this report). Phosphate extractions were conducted on pre-treatment and post-treatment sediments to evaluate the change in newly precipitated phosphate phases on mineral grains versus natural phosphate in the sediments. Phosphate extractions results show that a significant mass of calcium-phosphate bearing solids precipitate from the polyphosphate solution injected into sediments. This indicates that the large increase in low-solubility uranium minerals may be due to (a) precipitation of autunite, (b) calcium-phosphate solids coating existing uranium surface phases, or (c) other uranium phases (i.e., uranium carbonates) co-precipitating with calcium-phosphate solids (such as hydroxyapatite).

Calcium was observed near uranium precipitates in μ-XRF maps, consistent with the formation of calcium-phosphate coatings on the surfaces of post-treatment sediments (Figure 5-14 in this report). Additionally, phosphorus was identified separately by SEM-EDS in 6 of 11 micron-size mapping locations in the post-treatment sample as compared to 1 of 7 locations in the pre-treatment sample.

6.3 Impact to Local Uranium Concentrations and Chemistry

While the uranium mobility and leachability have been reduced following Stage A and Stage B treatment, total uranium mass in the EA area is comparable in pre-treatment and post-treatment sediment analyses. As detailed in Section 4.1.1 of this report, the goal of uranium sequestration is to decrease the mobility of the uranium, not the mass. Prior to treatment, Stage B uranium concentrations in soils ranged from 0.438 to 85.4 µg/g and Stage A uranium concentrations ranged from 0.141 to 41.4 µg/g. Post-treatment, Stage B uranium concentrations ranged from 1.31 to 175 µg/g and Stage A concentrations ranged from 1.2 to 100 µg/g (Section 4.1.1 of this report and Section 4.1.1.1 of SGW-59614). Uranium concentrations in monitoring wells decreased during and immediately following polyphosphate injections with some exceptions (Figure 6-2). Three wells had nominal increases in uranium concentrations during injections followed by sharp declines similar to the concentration declines observed in other monitoring wells. Uranium peaks were not observed in the downgradient monitoring wells during or after phosphate injections. Therefore, flushing of uranium mass during injections was minimal and the resulting decrease in uranium concentrations over time in and downgradient of the treatment area is attributed to polyphosphate treatment sequestering uranium (Figure 6-2).

Uranium concentrations decreased in all 24 wells to below the 30 µg/L CUL as the polyphosphate solution was injected into the PRZ and LVZ. Uranium concentrations in downgradient monitoring wells decreased as phosphate concentrations increased. Three of the five downgradient wells had uranium concentrations below the CUL by December 2018. Concentrations remained low or continued to decline after December 2018. The long-term monitoring wells shown in Figure 6-2 exhibited uranium concentrations near or below the 30 µg/L CUL.

6.4 Numerical Modeling to Assess Future Impacts

Monitoring observations and results of pre-treatment and post-treatment extraction and leach tests provided information that could be used in numerical models to assess the impact of Stage A and B treatment on uranium contamination in the groundwater. Near-field reactive transport modeling indicates favorable conditions for multiple mechanisms of uranium sequestration including formation of stable uranium mineral phases, adsorption of aqueous uranium complexes, and precipitation of calcium-phosphate minerals that reduce the labile uranium concentrations consistent with the conceptual model (Figure 5-17).

Experimental results from 1-D flow-through column leach tests were fitted to quantify the kinetic release model for uranium from the pre-treatment and post-treatment samples. Both forward and reverse rate constants for uranium were estimated from which an effective K_d was determined that represents the partitioning of uranium mass between sorbed and dissolved phases. The K_d values increase in the majority of the post-treatment samples when compared to the pre-treatment sample pairs, with an average increase by factor of 10. The 3-D system scale flow and transport modeling shows that the dissolved uranium concentrations continue to decline following treatment but reach asymptote-based concentrations indicating the effectiveness of Stage A and B treatment. The modeling indicated that for wells within and around Stage A and B treatment zones the uranium concentrations will remain below the CUL except during the short-term seasonal increases in uranium concentration due to river stage fluctuations. The system-scale 3-D flow and transport model predicts around 240 kg (529 lbs) less uranium will reach the groundwater over the next approximately 20-year time period as a result of Stage A and B treatments. Data collected from the continued monitoring of wells in and around the treatment area over the longer term will be used to further refine the fate and transport model parameter estimates to predict the timeframe to achieve the uranium CUL in the groundwater.

6.5 Conclusions

Field-scale uranium sequestration by infiltration and injection of a polyphosphate solution has reduced the mobility and leachability of uranium in a 1.2 ha (3 ac) portion of the 300 Area. Large volumes of polyphosphate were injected into the PRZ, LVZ, and aquifer which caused the concentration of phosphate in the sediments and groundwater to increase by multiple orders of magnitude. Less mobile uranium-bearing mineral phases formed as a result of the treatment. Uranium concentrations in groundwater wells both in and downgradient of the treatment zone have decreased to near the CUL of 30 µg/L or lower. Numerical modeling predicts over 240 kg (529 lbs) of uranium will be prevented from reaching groundwater over the next 20 years.

Evaluation of the enhanced attenuation remedy performance is ongoing. It is too early to draw conclusions on how phosphate treatment has impacted the estimated cleanup timeline for the 300-FF-5 OU. Data collected from continued monitoring of wells in and around the treatment area over the longer term will be used to estimate the timeframe to achieve the uranium CUL in the groundwater. Evaluation of long-term groundwater monitoring will continue to further elucidate the performance of the 300 Area remedy (including Stage A and B enhanced attenuation) as part of the CERCLA 5-year review process.

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SGW-59614, 2016, *300-FF-5 Operable Unit Enhanced Attenuation Stage A Delivery Performance Report*, Rev. 0, CH2M HILL Plateau Remediation Company, Richland, Washington. Available at: http://pdw.hanford.gov/arpir/pdf.cfm?accession=0072777H.

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SGW-60778, 2019, 3*00-FF-5 Operable Unit Stage B Uranium Sequestration System Installation Report*, Rev. 0, CH2M HILL Plateau Remediation Company, Richland, Washington. Available at: https://pdw.hanford.gov/document/0063871H.

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SGW-64537, 2020, *Data Usability Assessment for 300-FF-5 Stage B Skids*, Rev. 0, CH2M HILL Plateau Remediation Company, Richland, Washington. Available at: https://pdw.hanford.gov/document/AR-03859.

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Appendix A

300-FF-5 Operable Unit Enhanced Attenuation Bibliography

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A1 Bibliography

The record of decision (EPA et al., 2013, *Hanford Site 300 Area Record of Decision for 300-FF-2 and 300-FF-5, and Record of Decision Amendment for 300-FF-1*) for the 300 Area was signed in 2013. Part of the selected remedy for uranium contamination in the 300 Area is enhanced attenuation using polyphosphate solutions to sequester the uranium and reduce the mass of mobile uranium migrating into the groundwater. Table A-1 provides a bibliography of key documents that supported and evaluated implementation of the enhanced attenuation remedy using uranium sequestration.

Table A-1. Chronological Summary of Key Documents Associated with the 300-FF-5 Operable Unit Enhanced Attenuation Remedy

Document	Issue Date	Description
EPA et al., 2013, *Hanford Site 300 Area Record of Decision for 300-FF-2 and 300-FF-5, and Record of Decision Amendment for 300-FF-1*, U.S. Environmental Protection Agency and U.S. Department of Energy, Richland, Washington, Richland, Washington.	November 2013	The final ROD specified EA of uranium using polyphosphate solutions to sequester the uranium and reduce the mass of mobile uranium migrating into the groundwater. The remedy also included MNA, groundwater monitoring, and ICs.
SGW-56993, 2014, *Sampling Instruction for the 300-FF-5 Operable Unit Supplemental Post ROD Field Investigation*, Rev. 0, CH2M HILL Plateau Remediation Company, Richland, Washington.	August 2014	This sampling instruction describes drilling and sampling procedures for refining the location of Stage A and Stage B EA areas.
SGW-58261, 2014, *Description of Work for Borehole Drilling, Sampling, and Construction of Monitoring Wells in Support of the 300-FF-5 OU Supplemental Post ROD Field Investigation*, Rev. 0, CH2M HILL Plateau Remediation Company, Richland, Washington.	October 2014	This DOW describes the drilling, construction, development, and sampling activities associated with installation of three characterization boreholes, two of which were completed as groundwater monitoring wells.
TPA-CN-656, 2015, *Tri-Party Agreement Change Notice Form: SGW-56993, Sampling Instruction for the 300-FF-5 Operable Unit Supplemental Post ROD Field Investigation*, *Rev 0*, dated March 31, U.S. Department of Energy, Richland Operations Office, and U.S. Environmental Protection Agency, Richland, Washington.	April 2015	This change notice adds two boreholes to SGW-56993. Boreholes C8940 and C9451 were identified for pre-treatment soil sampling following selection of the refined Stage A EA area.
Snyder, M.M.V., and K.J. Cantrell, 2016, *Analytical Data Report for Sediment Samples Collected From 300-FF-5 OU, Wells C8933, C8936, and C8938*, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.	April 2015	This is the data report for soil samples collected from supplemental post-ROD boreholes C8933, C8936, and C8938.

Table A-1. Chronological Summary of Key Documents Associated with the 300-FF-5 Operable Unit Enhanced Attenuation Remedy

Document	Issue Date	Description
SGW-58589, 2015, *Borehole Summary Report for the Installation of 2 Wells and Drilling of 1 Borehole in the 300-FF-5 Operable Unit, FY2015*, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington.	April 2015	This report summarizes field activities for the drilling and construction of two monitoring wells and one characterization borehole associated with the 300-FF-5 OU supplemental post-ROD field investigation.
SGW-58736, 2015, *300-FF-5 Enhanced Attenuation Area Stage A Location Selection*, Rev. 0, CH2M HILL Plateau Remediation Company, Richland, Washington.	April 2015	This technical memorandum summarizes the field effort conducted during the post-ROD field investigation and provides the proposed location of the Stage A EA area for polyphosphate injection/infiltration.
DOE/RL-2014-13, 2015, *Integrated Remedial Design Report/Remedial Action Work Plan for the 300 Area (300-FF-1, 300-FF-2 & 300-FF-5 Operable Units)*, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington.	May 2015	This integrated RDR/RAWP addresses all three OUs in the 300 Area and is accompanied by two addenda. The addenda correspond to the two distinct media (soil and groundwater). The document is written in three parts: an integrated RDR/RAWP that contains common information to support remedy implementation, an addendum containing information specific to waste site/soil-specific remedies for the 300-FF-2 OU, and an addendum containing information specific to groundwater-specific remedies for the 300-FF-5 OU and uranium sequestration elements implemented at the 300-FF-1 and 300-FF-2 OUs.
DOE/RL-2014-13-ADD2, 2015, *Remedial Design Report/Remedial Action Work Plan Addendum for the 300 Area Groundwater*, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington.	June 2015	The RDR/RAWP addendum for 300 Area groundwater describes the work elements, construction management and oversight, schedule, and cost specific to EA using uranium sequestration in the vadose zone and PRZ, MNA, and groundwater monitoring.
SGW-58830, 2015, *300-FF-5 Supplemental Post-ROD Field Investigation Summary*, Rev. 0, CH2M HILL Plateau Remediation Company, Richland, Washington.	June 2015	This report summarizes observations and measurements made during the field activities conducted as part of the supplemental post-ROD field investigation.
SGW-58553, 2015, *Description of Work for the Installation of Twenty Two Monitoring Wells and Nine Injection Wells in the 300-FF-5 Operable Unit, FY2015*, Rev. 0, CH2M HILL Plateau Remediation Company, Richland, Washington.	June 2015	This DOW describes the drilling, construction, development, and sampling activities associated with installation of 22 monitoring wells and 9 injection wells in the 300-FF-5 OU to support Stage A of the EA remedy.
SGW-58976, 2015, *Field Instructions for Uranium Sequestration in the 300 Area*, Rev. 0, CH2M HILL Plateau Remediation Company, Richland, Washington.	July 2015	This document provides the field instructions and technical guidance for implementation of the Stage A uranium sequestration activities in the 300 Area Industrial Complex.

Table A-1. Chronological Summary of Key Documents Associated with the 300-FF-5 Operable Unit Enhanced Attenuation Remedy

Document	Issue Date	Description
DOE/RL-2014-42, 2015, *300-FF-5 Operable Unit Remedy Implementation Sampling and Analysis Plan*, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington.	September 2015	This SAP presents the plans for 300-FF-5 OU remedy implementation, performance monitoring, and groundwater monitoring.
PNNL-24911, 2016, *Analytical Data Report for Sediment Samples Collected From 300-FF-5 OU, Wells C8940 and C9451*, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.	November 2015	This is a data report for soil samples collected from boreholes C8940 and C9451.
1232138/181431, 2015, "100/300 Area Unit Manager Meeting Minutes," U.S. Department of Energy, Richland Operations Office, Washington State Department of Ecology, U.S. Environmental Protection Agency, Richland, Washington, November 12.	November 2015	The submission of *300-FF-5 Operable Unit Remedy Implementation Sampling and Analysis Plan,* DOE-RL-2014-42, Draft A, to the U.S. Environmental Protection Agency completed the Hanford Facility Agreement and Consent Order Target Date M-016-l10-T05.
TPA-CN-700, 2015, *Tri-Party Agreement Change Notice Form: DOE/RL-2014-13-ADD2, Remedial Design Report/Remedial Action Work Plan Addendum for the 300 Area Groundwater, REV. 0*, dated November 17, U.S. Department of Energy, Richland Operations Office, and U.S. Environmental Protection Agency, Richland, Washington.	November 2015	This change notice revises the project schedule to reflect the time required to obtain Stage A EA post-treatment data and the deferment of the Stage B EA implementation from FY2016 to FY2017.
SGW-59369, 2015, *Description of Work for the Installation of Three Boreholes in the 300-FF-5 Groundwater Operable Unit, FY2016*, Rev. 0, CH2M HILL Plateau Remediation Company, Richland, Washington.	December 2015	This DOW describes the drilling, construction, decommissioning, and sampling activities associated with installation of three post-treatment characterization boreholes in the 300-FF-5 OU to support Stage A of the EA remedy.
SGW-59455, 2016, *300-FF-5 Operable Unit Stage A Uranium Sequestration System Installation Report*, Rev. 0, CH2M HILL Plateau Remediation Company, Richland, Washington.	March 2016	This report provides the final design and installation of the Stage A uranium sequestration system. This report also provides lessons learned on the installation of the Stage A system.
PNNL-25420, 2016, *Analytical Data Report for Sediment Samples Collected from 300-FF-5: Boreholes C9580, C9581, and C9582*, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.	May 2016	This is a data report for soil samples collected from boreholes C9580, C9581, and C9582.

Table A-1. Chronological Summary of Key Documents Associated with the 300-FF-5 Operable Unit Enhanced Attenuation Remedy

Document	Issue Date	Description
SGW-59465, 2015, *Borehole Summary Report for the Installation of Nine Injection Wells and Twenty-One Monitoring Wells in the 300-FF-5 Operable Unit, FY 2015*, Rev. 0, CH2M HILL Plateau Remediation Company, Richland, Washington.	July 2016	This borehole summary report describes field activities for installing and sampling 33 wells as part of the Stage A uranium sequestration remedial action for the 300-FF-5 OU.
SGW-60243, 2016, *300-FF-5 Operable Unit Stage B Uranium Sequestration Functional Requirements*, Rev. 0, CH2M HILL Plateau Remediation Company, Richland, Washington.	October 2016	This document provides the Stage B uranium sequestration system design and installation criteria.
SGW-59614, 2016, *300-FF-5 Operable Unit Enhanced Attenuation Stage A Delivery Performance Report*, Rev. 0, CH2M HILL Plateau Remediation Company, Richland, Washington.	December 2016	This report presents the results and performance evaluation of the Stage A enhanced attenuation remedy implemented during November 2015.
DOE/RL-2014-42-ADD1, 2016, *300-FF-5 Operable Unit Remedy Implementation Sampling and Analysis Plan Addendum for Stage B Uranium Sequestration*, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington.	December 2016	This addendum to DOE/RL-2014-42, *300-FF-5 Operable Unit Remedy Implementation Sampling and Analysis Plan*, describes the implementation, performance monitoring, and groundwater monitoring of the Stage B EA remedy for the 300-FF-5 OU.
SGW-60287, 2016, *Description of Work for the Installation of Forty Eight Injection Wells and Nineteen Monitoring Wells in the 300-FF-5 Groundwater Operable Unit, FY17*, Rev. 0, CH2M HILL Plateau Remediation Company, Richland, Washington.	December 2016	This DOW describes the drilling, construction, development, and sampling activities associated with installation of 48 injection wells and 19 monitoring wells in the 300-FF-5 OU to support Stage B of the EA remedy.
ECF-300FF5-16-0137, 2017, *Radius of Influence Estimates for Injection Wells in Support of Stage B Enhanced Attenuation Remedy for the Hanford Site 300 Area Vadose Zone*, Rev. 0, CH2M HILL Plateau Remediation Company, Richland, Washington.	January 2017	This ECF provides estimates of the radius of influence created within the vadose zone during the remedial action of injecting polyphosphate solutions into the PRZ within the Stage B EA area.
TPA-CN-0784, 2017, *Tri-Party Agreement Change Notice: DOE/RL-2014-13-ADD2, Rev. 0: Remedial Design Report/Remedial Action Work Plan Addendum for the 300 Area Groundwater*, dated May 31, U.S. Department of Energy, Richland Operations Office, U.S. Environmental Protection Agency, and Washington State Department of Ecology, Richland, Washington.	June 2017	This change notice modifies the Stage B EA project schedule to reflect postponement of the Stage B EA implementation from FY2017 to FY2018 for additional groundwater monitoring.

Table A-1. Chronological Summary of Key Documents Associated with the 300-FF-5 Operable Unit Enhanced Attenuation Remedy

Document	Issue Date	Description
SGW-61092, 2017, *Borehole Summary Report for the Installation of Forty Eight Injection wells and Nineteen Monitoring Wells at the 300-FF-5 Operable Unit, FY 2017*, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington.	October 2017	This borehole summary report describes field activities for installing and sampling 67 wells as part of the Stage B uranium sequestration remedial action for the 300-FF-5 OU.
TPA-CN-0827, 2018, *Tri-Party Agreement Change Notice Form: DOE/RL-2014-42, 300-FF-5 Operable Unit Remedy Implementation Sampling and December 2016 Analysis Plan Addendum for Stage B Uranium Sequestration, Rev. 0*, dated August 16, U.S. Department of Energy, Richland Operations Office, and U.S. Environmental Protection Agency, Richland, Washington.	August 2018	This change notice adds 28 groundwater monitoring wells to support fate and transport model calibration and clarifies the development and use of groundwater models to evaluate remedy performance.
TPA-CN-0828, 2018, *Tri-Party Agreement Change Notice Form: DOE/RL-2014-42-ADD1, Rev. 0, 300-FF-5 Operable Unit Remedy Implementation Sampling and December 2016 Analysis Plan Addendum for Stage B Uranium Sequestration, Rev. 0*, dated August 16, U.S. Department of Energy, Richland Operations Office, and U.S. Environmental Protection Agency, Richland, Washington.	August 2018	This change notice revises the Stage B EA schedule following postponement of Stage B uranium sequestration as modified by TPA-CN-784, *Tri-Party Agreement Change Notice: DOE/RL-2014-13-ADD2, Rev. 0: Remedial Design Report/Remedial Action Work Plan Addendum for the 300 Area Groundwater*, and adds 7 groundwater monitoring wells (13 wells total) to the pre- and post-Stage B monthly monitoring network
SGW-60778, 2019, *300-FF-5 Operable Unit Stage B Uranium Sequestration System Installation Report*, Rev. 0, CH2M HILL Plateau Remediation Company, Richland, Washington.	January 2019	This report provides the final design and installation of the Stage B uranium sequestration system. This report also provides lessons learned on the installation of the Stage B system.
TPA-CN-0835, 2019, *Tri-Party Agreement Change Notice Form: DOE/RL-2014-42-ADD1, Rev. 0, 300-FF-5 Operable Unit Remedy Implementation Sampling and December 2016 Analysis Plan Addendum for Stage B Uranium Sequestration*, dated January 31, U.S. Department of Energy, Richland Operations Office, and U.S. Environmental Protection Agency, Richland, Washington.	February 2019	This change notice revises the uranium completion report schedule following postponement of Stage B uranium sequestration as modified by TPA-CN-784 and TPA-CN-0828.

Table A-1. Chronological Summary of Key Documents Associated with the 300-FF-5 Operable Unit Enhanced Attenuation Remedy

Document	Issue Date	Description
SGW-63046, 2019, *Description of Work for the Installation of Nine Boreholes in the 300-FF-5 Groundwater Operable Unit, FY2019*, Rev. 0, CH2M HILL Plateau Remediation Company, Richland, Washington.	February 2019	This DOW describes the drilling and sampling activities for nine post-injection boreholes as part of the Stage B uranium sequestration remedial action for the 300-FF-5 OU.
SGW-62900, 2019, *Sampling Instruction for Uranium Sequestration Stage B Post-Injection Boreholes in the 300-FF-5 Operable Unit*, Rev. 0, CH2M HILL Plateau Remediation Company, Richland, Washington.	February 2019	This sampling instruction provides the details for drilling and sampling nine post-injection boreholes as part of the Stage B uranium sequestration remedial action for the 300-FF-5 OU.
SGW-63235, 2019, *Sampling Results for Unplanned Release of Groundwater During Uranium Sequestration Stage B Operations in the 300-FF-5 Operable Unit*, Rev. 0, CH2M HILL Plateau Remediation Company, Richland, Washington.	May 2019	This report presents the sampling results for shallow soil samples collected in the area of an unplanned release of groundwater during Stage B EA operations.
SGW-63544, 2019, *Borehole Summary Report for the Installation of Nine Boreholes in the 300-FF-5 Operable Unit, FY 2019*, Rev. 0, CH2M HILL Plateau Remediation Company, Richland, Washington.	June 2019	This borehole summary report describes field activities for drilling, sampling, and decommissioning nine post-injection boreholes as part of the Stage B uranium sequestration remedial action for the 300-FF-5 OU.
TPA-CN-0867, 2019, *Tri-Party Agreement Change Notice Form: DOE/RL-2014-42, 300-FF-5 Operable Unit Remedy Implementation Sampling and Analysis Plan, Rev. 0*, dated September 23, U.S. Department of Energy, Richland Operations Office, and U.S. Environmental Protection Agency, Richland, Washington.	September 2019	This change notice revises DOE/RL-2014-42 to support the Stage B EA operations as implemented in 2018 and the monitoring for fate and transport model calibration added to the SAP by TPA-CN-0827.
TPA-CN-0868, 2019, *Tri-Party Agreement Change Notice: DOE/RL-2014-42-ADD1, 300-FF-5 Operable Unit Remedy Implementation Sampling and Analysis Plan Addendum for Stage B Uranium Sequestration, Rev. 0*, dated September 25, U.S. Department of Energy, Richland Operations Office, and U.S. Environmental Protection Agency, Richland, Washington.	September 2019	This change notice revises DOE/RL-2014-42-ADD1 to be consistent with Stage B EA operations as implemented in 2018.

Table A-1. Chronological Summary of Key Documents Associated with the 300-FF-5 Operable Unit Enhanced Attenuation Remedy

Document	Issue Date	Description
TPA-CN-0883, 2020, *Tri-Party Agreement Change Notice Form: DOE/RL-2014-42, 300-FF-5 Operable Unit Remedy Implementation Sampling and Analysis Plan, Rev. 0*, dated April 14, U.S. Department of Energy, Richland Operations Office, and U.S. Environmental Protection Agency, Richland, Washington.	April 2020	This change notice revises DOE/RL-2014-42 to add 13 monitoring wells that will be sampled quarterly for 1 year in the Stage B enhanced attenuation area to support fate and transport model calibration.
ECF-300FF5-19-0005, 2020, *Injection Volumes for 300-FF-5 Stage B Injections and Sampling*, Rev. 1, CH2M HILL Plateau Remediation Company, Richland, Washington.	August 2020	This ECF presents the Stage B polyphosphate injection volumes and injection rates delivered to the PRZ and vadose zone for the dates of 09/04/2018 through 09/20/2018.

DOW	=	description of work	OU	=	operable unit
EA	=	enhanced attenuation	PRZ	=	periodically rewetted zone
ECF	=	environmental calculation file	RAWP	=	remedial action work plan
FY	=	fiscal year	RDR	=	remedial design report
IC	=	institutional control	ROD	=	record of decision
MNA	=	monitored natural attenuation	SAP	=	sampling and analysis plan

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Appendix B

Enhanced Attenuation Stage B
Soil and Groundwater Sample Analytical Data

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B1 Introduction

This appendix provides laboratory analytical data for the following two sets of samples:

- Soil samples collected before and following polyphosphate treatment
- Groundwater samples collected before, during, and following polyphosphate treatment

B1.1 Stage B Soil Sample Analytical Data

The pre-treatment and post-treatment soil samples were collected from boreholes installed to implement the 300-FF-5 Operable Unit Stage B enhanced attenuation remedy. Soil samples were planned and collected at 20 of the pre-treatment wells (19 of the 48 injection wells and 1 of the 19 monitoring wells) drilled in 2017. Opportunistic samples were also collected from 14 of these injection wells and 3 of these monitoring wells. Soil samples were planned and collected at nine post-treatment boreholes drilled in 2019. Opportunistic samples were also collected from six of these post-treatment boreholes.

All of the pre-treatment and post-treatment planned and opportunistic samples were analyzed for concentrations of uranium, metals, anions, phosphate, and alkalinity. The data were queried from the Hanford Environmental Information System database on June 3, and June 5, 2020, and compiled into the spreadsheets listed in the table below; the files are available on request.

Microsoft® Excel® Spreadsheets	
File Name	**Description**
Soil - Analytical Results_6-3-2020_C9642-C9706.xlsx	Contains the analytical results for samples collected at pre-treatment boreholes.
Soil - Analytical Results_6-5-2020_C9728-C9736.xlsx	Contains the analytical results for samples collected at post-treatment boreholes.

B1.2 Stage B Groundwater Analytical Data

Groundwater samples collected from 30 monitoring wells used to support implementation of the Stage B enhanced attenuation remedy. The wells were monitored before, during, and following application of polyphosphate solutions in the Stage B enhanced attenuation area. All of the samples were analyzed for concentrations of uranium, metals, anions, and alkalinity. The data were queried from the Hanford Environmental Information System database on April 14, 2020, and compiled into the spreadsheet listed in the table below; the file is available on request.

Microsoft Excel Spreadsheet	
File Name	**Description**
GW - Analytical Results_4-14-2020_StageB.xlsx	Contains the groundwater monitoring data.

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Appendix C

Automated Field Measurements for Enhanced Attenuation Stage B Monitoring Wells

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C1 Automated Field Measurements for Enhanced Attenuation Stage B Monitoring Wells

This appendix provides the automated field measurements collected to support implementation of the Stage B enhanced attenuation (EA) remedy. Automated groundwater measurements were collected using dataloggers installed in 24 monitoring wells screened in either the periodically rewetted zone or the aquifer. The wells were monitored for water level and field parameters (specific conductivity, temperature, pH, and oxidation-reduction potential) every 30 minutes from June 23, 2017, to November 7, 2018 (i.e., before, during, and following application of polyphosphate solutions in the Stage B EA area). Spreadsheet "Stage_B_Data_Logger_Pivot.xlsx" (available on request) contains the data.

Automated water level measurements were collected from seven groundwater wells (399-1-7, 399-1-12, 399-1-16A, 399-1-17A, 399-1-23, 399-2-2, and 399-8-1) around the Stage B EA area and the 300 Area river gauge (SWS-1). The wells and gauge are part of the automated water level network in the 300-FF-5 Operable Unit. The automated water level network logs water levels every 15 minutes. During the Stage B EA operations, specific conductivity and temperature were also logged in these wells. All of the automated water level network data are provided in the following spreadsheets, which are available on request.

Microsoft® Excel® Spreadsheets	
399-1-7_combined_4Q19.xlsx	399-1-23_combined_4Q19.xlsx
399-1-12_combined_4Q19.xlsx	399-2-2_combined_4Q19.xlsx
399-1-16A_combined_4Q19.xlsx	399-8-1_combined_4Q19.xlsx
399-1-17A_combined_4Q19.xlsx	SWS-1_combined_4Q19.xlsx
Stage_B_Data_Logger_Pivot.xlsx	

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Appendix D

Enhanced Attenuation Stage B Mixing Skids Analytical Data

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D1 Enhanced Attenuation Stage B Mixing Skids Analytical Data

This appendix provides the polyphosphate solution sample analytical results for the two injection mixing skids used to support implementation of the Stage B enhanced attenuation remedy.

Injection solution samples were collected from each skid at the start of injections and once daily thereafter for each day of treatment. A Columbia River sample was collected prior to mixing with polyphosphate chemicals. The samples were analyzed for carbonate and bicarbonate alkalinity, calcium, magnesium, potassium, sodium, chloride, phosphate, and sulfate. The data are presented in the spreadsheet listed below, which is available upon request.

Microsoft® Excel® Spreadsheet	
File Name	**Description**
Miscellaneous Material_4-16-2020_Skids.xlsx	Contains the analytical data.

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Appendix E

Long-Term Groundwater Monitoring Analytical Data

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E1 Long-Term Groundwater Monitoring Analytical Data

This appendix provides the analytical results for long-term groundwater monitoring samples collected semiannually from 4 wells in accordance with DOE/RL-2014-42, *300-FF-5 Operable Unit Remedy Implementation Sampling and Analysis Plan*. Wells 399-1-17A, 399-1-7, 399-2-1, and 399-2-2 are scheduled to be monitored in June (high water conditions) and December (low water conditions) for 5 years. Analytical results for semiannual samples collected from December 2015 through December 2019 are provided in the attached spreadsheets. All of the samples were analyzed for concentrations of uranium, metals, anions, and alkalinity. Water levels were measured each time a sample was collected. The data were queried from the Hanford Environmental Information System database; the spreadsheets are listed in the table below and available on request.

Microsoft® Excel® Spreadsheets	
Groundwater (GW) - LTM_DEC15.xlsx	Groundwater (GW) - LTM_JUN18.xlsx
Groundwater (GW) - LTM_JUN16.xlsx	Groundwater (GW) - LTM_DEC18.xlsx
Groundwater (GW) - LTM_DEC16.xlsx	Groundwater (GW) - LTM_JUN19.xlsx
Groundwater (GW) - LTM_JUN17.xlsx	Groundwater (GW) - LTM_DEC19.xlsx
Groundwater (GW) - LTM_DEC17.xlsx	Groundwater (GW) - WL.xlsx

E2 Reference

DOE/RL-2014-42, 2015, *300-FF-5 Operable Unit Remedy Implementation Sampling and Analysis Plan*, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington. Available at: https://pdw.hanford.gov/document/0079669H.

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