Department of Energy
Savannah River Operations Office
P.O. Box A
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APR - 7 2022

Ms. Susan B. Fulmer, P.G., Manager
Federal Remediation Section
Division of Site Assessment, Remediation and Revitalization
Bureau of Land and Waste Management
South Carolina Department of Health and Environmental Control
2600 Bull Street
Columbia, South Carolina 29201

Mr. Jon Richards
Savannah River Site Remedial Project Manager
Superfund Division
U. S. Environmental Protection Agency, Region 4
61 Forsyth Street, SW
Atlanta, Georgia 30303

Dear Ms. Fulmer and Mr. Richards:

SUBJECT: Savannah River Site's Responses to the Regulatory Comments on the Effectiveness Monitoring Report (EMR) for the P-Area Groundwater (PAGW) Operable Unit (OU) Zero Valent Iron Permeable Reactive Barrier (ZVI-PRB) Removal Action (U) March 2019 through March 2021 (SRNS-RP-2021-00016, Revision 0, September 2021) SEMS Number: 81

The U. S. Department of Energy (DOE) is submitting the subject comment responses for your review. The U. S. Environmental Protection Agency (EPA) and the South Carolina Department of Health and Environmental Control (SCDHEC) provided comments on the report on January 05, 2022 and January 06, 2022, respectively. The report will not be revised; however, all comment responses will be included and/or addressed in the next report, as applicable. Please review these responses and provide your approval thirty (30) days from receipt. The time and effort that the SCDHEC and the EPA have given on the subject operable unit are greatly appreciated.

Questions from you or your staff may be directed to me at (803) 952-8365, or the DOE Program Manager, Mr. Philip Prater, at (803) 952-9333.

Sincerely,

Brian T. Hennessey

Digitally signed by Brian T. Hennessey
Date: 2022.04.06 12:53:36 -04'00'

Brian T. Hennessey
SRS Remedial Project Manager
Infrastructure and Area Completion Division

IACD-22-140

APR - 7 2022

Enclosures:
1. SRS Responses to the SCDHEC Comments on the Effectiveness Monitoring Report (EMR) for the P-Area Groundwater (PAGW) Operable Unit (OU) Zero Valent Iron Permeable Reactive Barrier (ZVI-PRB) Removal Action (U) March 2019 through March 2021 (SRNS-RP-2021-00016, Revision 0, September 2021) SEMS Number: 81
2. SRS Responses to the United States EPA Comments on the Effectiveness Monitoring Report (EMR) for the P-Area Groundwater (PAGW) Operable Unit (OU) Zero Valent Iron Permeable Reactive Barrier (ZVI-PRB) Removal Action (U) March 2019 through March 2021 (SRNS-RP-2021-00016, Revision 0, September 2021) SEMS Number: 81

cc w/o encl:
J. Blalock, SCDHEC-Columbia
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R. H. Pope, EPA-Atlanta

cc w/encl:
M. McRae, TechLaw, Inc.

SCDHEC Comments Received January 6, 2022

SPECIFIC COMMENTS

1. **Section 2.4, Removal Action Implementation and Monitoring Goals, Page 7 of 46, Paragraph 1:** The Report states, "Precipitation within the ZVI-PRB leads to a decreased performance as the porosity, and therefore the retention time within the barrier, will decrease." *Please clarify in the document if an abnormally high amount of rainfall has been considered when determining the performance and life of the ZVI-PRB.*

   Response: Clarification

   As described in the RADP for this RA, the ZVI-PRB was designed to target the highest concentrations of TCE contamination within the UAZ along the neck area. Potential changes in precipitation were considered in the design. A major concern is ensuring the ZVI media is not exposed to unsaturated conditions (period of abnormally low rainfall), which would allow for oxidation and therefore solidification of the ZVI-PRB and loss of porosity. Therefore, the top of the ZVI-PRB was set at ~14 meters (m) (45 feet [ft]) below ground surface (bgs). Currently the water table is ~12 m (39 ft) bgs, which allows up to 1.8 m (6 ft) of head loss before the ZVI-PRB could be impacted. It is not expected that water levels will fall to below the top depth of the ZVI-PRB. Historical water levels at P Area were considered during design while maximizing placement of the ZVI-PRB in treating contaminated groundwater.

   An abnormally high amount of rainfall would lead to a slightly higher water table elevation. However, the risk of increased concentrations of cVOC contamination bypassing by traveling over the ZVI-PRB is low. The majority of cVOC contamination is at depth in the UAZ, with low levels of TCE detections starting at 18 m (60 ft) bgs, ~4.6 m (15 ft) below the top of the ZVI-PRB.

   Abnormal rainfall, whether high or low, is not anticipated to have any impact on subsurface or groundwater characteristics in a way that would impact the ZVI-PRB performance and/or life expectancy.

   No changes to the document are proposed.

   Responsible Party: Adam Willey, (803) 646-4944, adam.willey@srs.gov

SCDHEC Comments Received January 6, 2022

2. **Section 2.4, Removal Action Implementation and Monitoring Goals, Page 7 of 46, Paragraph 1:** The Report states, "However, overtime, under normal circumstances, it is expected the ZVI will lose some of its reactivity." *Please clarify in the document what is the expected life of the ZVI and if there will be ample time for the removal action to be effective.*

Response: Agree with Clarification

The health and longevity of ZVI-PRBs is presented in Section 4.3. As part of the design phase of the PAGW OU ZVI-PRB, a bench scale treatability study was performed utilizing site groundwater, site soil, and the ZVI media used in construction. This study was designed to look at the ZVI-PRB performance over time and degradation in performance due to any incompatibilities. The following conclusions were made from the treatability study results (SRNS 2019), and will be added to the end of the first paragraph in this section in future EMRs:

- **Geochemistry of site groundwater, site soils, and ZVI material are favorable for extended long-term performance.**
- **No observation of mineral precipitation causing loss in reactivity towards cVOCs.**
- **No expectation of precipitation/clogging causing a significant loss in permeability, and therefore performance.**

Based on the results of the treatability study, the designed ZVI-PRB is expected to retain effectiveness and performance for at least 25 years, as has been observed in other PRB applications (SRNS 2019).

Responsible Party: Adam Willey, (803) 646-4944, adam.willey@srs.gov

References:

SRNS, 2019. ***Removal Action Design Plan (RADP) with Effectiveness Monitoring Plan (EMP) for the P-Area Groundwater (PAGW) Operable Unit (OU),*** **SRNS-RP-2019-00105, Revision 1, July 2019, Savannah River Nuclear Solutions, LLC, Savannah River Site, Aiken, SC.**

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USEPA Comments Received January 5, 2022

GENERAL COMMENTS

1. The Effectiveness Monitoring Report (EMR) for the P–Area Groundwater (PAGW) Operable Unit (OU) Zero Valent Iron Permeable Reactive Barrier (ZVI-PRB) Removal Action (U), March 2019 through March 2021, SEMS Number: 81, SRNS-RP-2021-00016, Revision 0, dated September 2021 (the Report), does not discuss the methane concentrations that were measured during the monitoring events. As such, it is uncertain how high concentrations of methane may impede reductive dechlorination, primarily due to microbial competition for nutrients. *Please revise the Report to include a discussion of methane generation and how high concentrations negatively impact the reductive dechlorination pathway.*

   Response: Clarification

   In this implementation of a ZVI-PRB as a Removal Action (RA) in the PAGW OU, the primary mechanism of chlorinated volatile organic compound (cVOC) degradation is interaction with ZVI. Degradation of cVOCs by microbial species that possibly might be present within the subsurface was not anticipated to play a role in cVOC mass flux reduction and therefore is not monitored or discussed. Savannah River Site (SRS) aquifers are highly oxygenated and do not support microbial species that are typically associated with reductive dechlorination.

   However, when a carbon source (e.g., food-grade guar) has been used, growth of anaerobic bacteria can occur. At the ZVI-PRB, dissolved organic matter and molecular hydrogen produced by anaerobic iron corrosion can be used as electron donors by various bacterial consortia. In the event there is a lack of efficient electron acceptors (e.g., dehalococcoides), sulfate-reducing and methanogenic bacteria can proliferate and coexist. The formation of methane is possibly related to the anaerobic processes associated with sulfate-reducing and methanogenic microbes in the presence of the food-grade guar. Further, recent studies have shown that ZVI enhances carbon dioxide reduction to methane in the presence of dissolved inorganic carbon (Wilkin et al 2018). Data from the in-wall monitoring wells indicate complete degradation of tetrachloroethylene (PCE) and trichloroethylene (TCE) with little, or no, intermediates (e.g., cis-1,2-dichloroethylene [cis-DCE], trans-1,2-dichloroethylene [trans-DCE], 1,1-dichloroethylene [DCE], chloroethene [vinyl chloride {VC}]) observed. Further, the final end-products of dechlorination, ethene and ethane, are not observed. These results are consistent with cVOC degradation by ZVI and not with microbial degradation.

   The effect of methane on ZVI-PRB performance is minimal as long as the gas is not entrained within the ZVI pore space and unable to escape. This is not the case at the PAGW OU since the ZVI-PRB is within an unconfined aquifer and gas can travel through many routes to the atmosphere.

In conclusion, consideration of the methane production, the role of microbial activity in degrading cVOCs, and microbial competition within the ZVI-PRB is important when implementing a technology such as ZVI, however, the focus of this RA is abiotic degradation of cVOCs by ZVI reactions. SRS does not believe microbial activity, or associated methane build-up, currently plays a significant role in cVOC degradation near the PRB and is not anticipated to result in any performance reduction of the ZVI-PRB at this time. These understandings are supported by the evidence above and no changes to the document are proposed.

Responsible Party: Adam Willey, (803) 646-4944, adam.willey@srs.gov

2. Based on the data presented in the Report, it is uncertain whether the current monitoring well network established for the upper aquifer zone (UAZ) and lower aquifer zone (LAZ) are adequate. For example, the plume maps prepared for the contaminant plumes in the UAZ and LAZ do not include associated monitoring well contaminant data. As such, an assessment of horizontal extents of the plume(s) could not be completed. Additionally, no cross-section maps were prepared demonstrating no data gaps exist in the vertical extent of contamination. *Please revise the Report to include this information to support adequate delineation of the vertical and horizontal extents of contamination in the UAZ and LAZ has been completed.*

Response: Clarification

The sole intention of data presented in the annual *Effectiveness Monitoring Report (EMR) for the P-Area Groundwater (PAGW) Operable Unit (OU) Zero Valent Iron Permeable Reactive Barrier (ZVI-PRB) Removal Action (U)* is to evaluate performance of the completed ZVI-PRB (Savannah River Nuclear Solutions, LLC [SRNS] 2021). Field activities in support of this RA were completed in January of 2020 and performance monitoring is planned for five years after completion, as agreed to by the United States Department of Energy (USDOE), the United States Environmental Protection Agency (USEPA), and the South Carolina Department of Health and Environmental Control (SCDHEC) in the *Removal Action Design Plan (RADP) with Effectiveness Monitoring Plan (EMP) for the P-Area Groundwater (PAGW) Operable Unit (OU)* (SRNS 2019). After five years, further reporting of the ZVI-PRB performance will be considered for inclusion in the biennial groundwater report for the PAGW OU, as agreed to in the *Sampling and Analysis Plan Addendum for the P-Area Groundwater Operable Unit (U)* (SRNS 2018).

The plume delineations used in the figures for the UAZ and LAZ of the Upper Three Runs Aquifer (UTRA) were generated from data acquired during the 2018 investigative work as described in the 2018 Sampling and Analysis Plan (SAP) (SRNS 2018) and presented in July of 2020 (Savannah River National Laboratory [SRNL] 2020). These data were later incorporated into the *Groundwater Report for the P-Area Groundwater (PAGW) Operable Unit (OU)* (SRNS 2020a). The plume delineations were presented in this EMR to indicate the relative location of the RA to the overall PAGW OU TCE plumes in the UAZ and LAZ. This EMR was not intended to provide an assessment of the overall

groundwater monitoring program for PAGW OU contamination. The plume extent delineation for the PAGW OU, and therefore adequacy of the monitoring well network, is evaluated in the biennial groundwater report for the PAGW OU. The most recent report that details groundwater conditions at the PAGW OU were presented in the *Groundwater Report for the P-Area Groundwater (PAGW) Operable Unit (U) April 2019 through March 2020 Data* (SRNS 2020a).

No changes to the document are proposed.

Responsible Party: Adam Willey, (803) 646-4944, adam.willey@srs.gov

3. It is unclear whether the large amount of grout used to complete the injection wells for the ZVI-PRB construction is negatively impacting groundwater pH in addition to elevating calcium concentrations in groundwater. Elevated pH levels have been recorded in groundwater since the implementation of the ZVI-PRB. Since the grout cement is likely to continue to leach to groundwater over time, increased pH levels could remain in groundwater for an extended period of time due to presence of grout. *Please revise the Report to discuss the impacts of leaching cement grout into the groundwater over time and how this impacts groundwater pH levels.*

Response: Agree with Clarification

The increase in pH was not unexpected as corrosion of ZVI results in alkaline (pH>9.5) groundwater with reducing conditions (oxidation-reduction potential [ORP {Eh}] <-100 millivolts [mV]). Other constructed PRBs with ZVI have also reported similar conditions. The primary source of elevated pH levels in anoxic condition is associated with the reaction of ZVI and water as illustrated below:

$$2Fe^0 + 4H_2O + 4e^- \rightarrow 2H_2 + 4OH^- + 2Fe^{2+} + 4e^-$$

Secondary to this process, leaching of the cement grout used to construct the frac injection wells could also be contributing to the increased pH levels. However, the contribution is significantly less when comparing the volume of grout in the frac injection wells to volume of the ZVI-PRB. Volumetrically, the total amount of grout for each of the 22 frac wells accounts for 1.48% of the total volume of ZVI. Therefore, even though leaching of the grout could be occurring, high groundwater pH is primarily attributed to groundwater interaction with the ZVI.

Future reports will provide similar discussion relative to the increased pH levels observed in groundwater at the ZVI-PRB.

Responsible Party: Adam Willey, (803) 646-4944, adam.willey@srs.gov

USEPA Comments Received January 5, 2022

SPECIFIC COMMENTS

1. **Section 4.2, ZVI-PRB cVOC Degradation, Page 16 of 46, Paragraph 3:** The Report states for PRW004DU, the parent and daughter products of reductive dechlorination are plotted over time in Figure 17 (CVOC Degradation at PRW004DU), Page 42 of 46; however, no indication is presented as to why PRW004DU was chosen for this example. *Please revise the text to add a sentence explaining why well PRW004DU was chosen over the other monitoring wells.*

   Response: Agree with Clarification

   Monitoring well PRW004DU provided a good representation of the reductive dechlorination trends expected west of the ZVI-PRB for the first year of monitoring. In future reports, the rationale for why specific monitoring well(s) were chosen for time-series plots will be provided.

   Responsible Party: Adam Willey, (803) 646-4944, adam.willey@srs.gov

2. **Figure 4. Trichloroethylene Plume Map for the Upper Aquifer Zone of the Upper Three Runs Aquifer (2018 Data), Page 29 of 46, and Figure 5. Trichloroethylene Plume Map for the Lower Aquifer Zone of the Upper Thee Runs Aquifer (2018 Data), Page 30 of 46:** Figure 4 and Figure 5 depict three sample location symbols that are not defined in the legend, and it is unclear what type of samples are collected or their significance. Additionally, the ZVI-PRB orientation depicted as a blue line in the neck area of the figure has not been defined in the legends. *Please revise the figures to define the three sample symbols and provide the definition of the ZVI-PRB orientation in the legends.*

   Response: Agree with Clarification

   The three locations included in both figures are for reference from the text. The location types will be added to the figure legends in future EMRs. Additionally, the ZVI-PRB trace will be identified in the legends on future EMRs.

   Revised Figure 4 and Figure 5 are included below as Figure CR-1 and Figure CR-2, respectively.

   Responsible Party: Adam Willey, (803) 646-4944, adam.willey@srs.gov

USEPA Comments Received January 5, 2022

3. **Figure 6. TCE Plume Cross-Section with ZVI-PRB Injection Wells, Page 31 of 46:** The figure does not depict or reference a map showing the plan view of the cross-section line provided on the figure. It is uncertain whether the cross-section line is equivalent to the ZVI PRB orientation line. *Please revise the Report to explain in the text and on a figure the location of the cross-section line presented on Figure 6.*

   Response: Agree with Clarification

   Figure 6 is a cross-section of the ZVI-PRB trace. This will be clarified in future EMRs with the revised Figure 7 (included below as Figure CR-3) and the following text revision:

   Section 2.4, Page 5 of 46, Paragraph 1:
   "The completed ZVI-PRB is estimated to be 80.5 linear meters (264 linear feet) long and has a cross-sectional area of 2,140 square meters (23,040 square feet) intersecting groundwater flow in the UAZ (Figure 6). Figure 6 is a cross-section of the ZVI-PRB trace (Figure 7) and ~~S~~soil concentrations for the plume ~~cross-section in Figure 6~~ are based on soil plug samples collected from soil cores collected along the ZVI-PRB trace as part of the PDI. There are high cVOC concentrations entrained within the low-permeability sediments of the area, which are reflected in soil plug samples."

   Figure 6 Caption:
   "Figure 6. TCE Plume North-South Cross-Section with ZVI-PRB Injection Wells"

   Responsible Party: Adam Willey, (803) 646-4944, adam.willey@srs.gov

4. **Figure 7. Effectiveness Monitoring Plan Locations, Page 32 of 46:** The small red box symbol used for PRW006C is not defined in the legend. *Please revise the legend in Figure 7 to include all symbols and definitions.*

   Response: Agree with Clarification

   The symbol for PRW006C was intended to be for "LAZ (1)" locations under the PRB EMP Proposed Well Locations heading. This symbol was corrected on the legend in the revised Figure 7 (Figure CR-3 included below) and will be included in future EMRs.

   Responsible Party: Adam Willey, (803) 646-4944, adam.willey@srs.gov

USEPA Comments Received January 5, 2022

5. **Figure 12. Time-Series Plot for TCE at Monitoring Wells Immediately West of ZVI-PRB, Page 37 of 46:** Several wells "immediately west" of the ZVI-PRB are missing from the figure and the justification is not clearly understood. For example, PRW007DU and PRW005DU are immediately west of the ZVI-PRB, but time-series plots are not presented on Figure 12. *Please revise Figure 12 to include all wells "immediately west" of the ZVI-PRB, or provide an explanation why time-series plots were not prepared for all wells immediately west of the ZVI-PRB.*

   Response: Agree with Clarification

   As described in the RADP, the Removal Action Report (RAR), and in the 2021 EMR, definitive conclusions on the ZVI-PRB impact to the down-gradient PAGW OU TCE plume will require more time and evaluation (SRNS 2019, SRNS 2020b, and SRNS 2021). This is due to expected back-diffusion of cVOCs into the clean groundwater front from cVOC mass adsorbed to the low permeability sediments just west of the ZVI-PRB. Therefore, for the first year results of ZVI-PRB performance monitoring, only the monitoring wells located in very close proximity and along the groundwater flow path were considered "immediately west" of the ZVI-PRB. In addition, PRW005 and PRW007 monitoring well clusters were installed in early 2020 and therefore limited data was available during the time period considered in this report.

   In future EMRs for the ZVI-PRB, all monitoring wells west of the ZVI-PRB will be included in TCE time-series plots within the main document body, or an explanation will be given for why monitoring wells were excluded.

   Responsible Party: Adam Willey, (803) 646-4944, adam.willey@srs.gov

6. **Table 1. Maximum Concentrations of PCE, TCE, and cis-DCE in the Three Plume Areas, Page 43 of 46:** Based on the information in Table 1, it is unclear if maximum concentrations for the neck and distal areas in the LAZ were measured prior to the ZVI-PRB installation, while those in the source area were measured post-ZVI-PRB installation. Additionally, it is unclear if the maximum concentrations for tetrachloroethylene (PCE) in the UAZ for the distal area and cis-DCE concentration in the neck area were also measured prior to ZVI-PRB installation. *Please revise the table to clarify this issue.*

   Response: Agree with Clarification

   The table note was removed to avoid confusion. All maximum concentrations in the table are from first half of 2019 sampling events, prior to the ZVI-PRB construction. The revised Table 1 is included as Table CR-1 and will be included in future EMRs.

   Responsible Party: Adam Willey, (803) 646-4944, adam.willey@srs.gov

References:

SRNL, 2020. ***2018 Sampling and Analysis Plan Addendum Data Review (Steel Creek and Elbow Areas), P-Area Groundwater Operable Unit,*** **SRNL-L3220-2020-00009, Core Team Information Meeting, July 15, 2020, Savannah River National Laboratory, Savannah River Site, Aiken, SC.**

SRNS, 2018. ***Sampling and Analysis Plan Addendum for the P-Area Groundwater Operable Unit (U),*** **SRNS-RP-2018-00261, Revision 1, August 2018, Savannah River Nuclear Solutions, LLC, Savannah River Site, Aiken, SC.**

SRNS, 2019. ***Removal Action Design Plan (RADP) with Effectiveness Monitoring Plan (EMP) for the P-Area Groundwater (PAGW) Operable Unit (OU),*** **SRNS-RP-2019-00105, Revision 1, July 2019, Savannah River Nuclear Solutions, LLC, Savannah River Site, Aiken, SC.**

SRNS, 2020a. ***Groundwater Report for the P-Area Groundwater (PAGW) Operable Unit (OU) (U),*** **SRNS-RP-2020-00621, Revision 0, October 2020, Savannah River Nuclear Solutions, LLC, Savannah River Site, Aiken, SC.**

SRNS, 2020b. ***Removal Action Report for the P-Area Groundwater Operable Unit Non-Time Critical Removal Action,*** **SRNS-RP-2020-00021, Revision 1, November 2020, Savannah River Nuclear Solutions, LLC, Savannah River Site, Aiken, SC.**

SRNS, 2021. ***Effectiveness Monitoring Report (EMR) for the P-Area Groundwater (PAGW) Operable Unit (OU) Zero Valent Iron Permeable Reactive Barrier (ZVI-PRB) Removal Action (U),*** **SRNS-RP-2021-00016, Revision 0, September 2021, Savannah River Nuclear Solutions, LLC, Savannah River Site, Aiken, SC.**

Wilkin, Richard T., T.R. Lee, M.R. Sexton, S.D. Acree, R.W. Puls, D.W. Blowes, C. Kalinowski, J.M. Tilton, and L.L. Woods, 2018. ***Geochemical and Isotope Study of Trichloroethene Degradation in a Zero-Valent Iron Permeable Reactive Barrier: A Twenty-Two-Year Performance Evaluation,*** **Environmental Science & Technology, 53:296-306.**

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USEPA Comments Received January 5, 2022

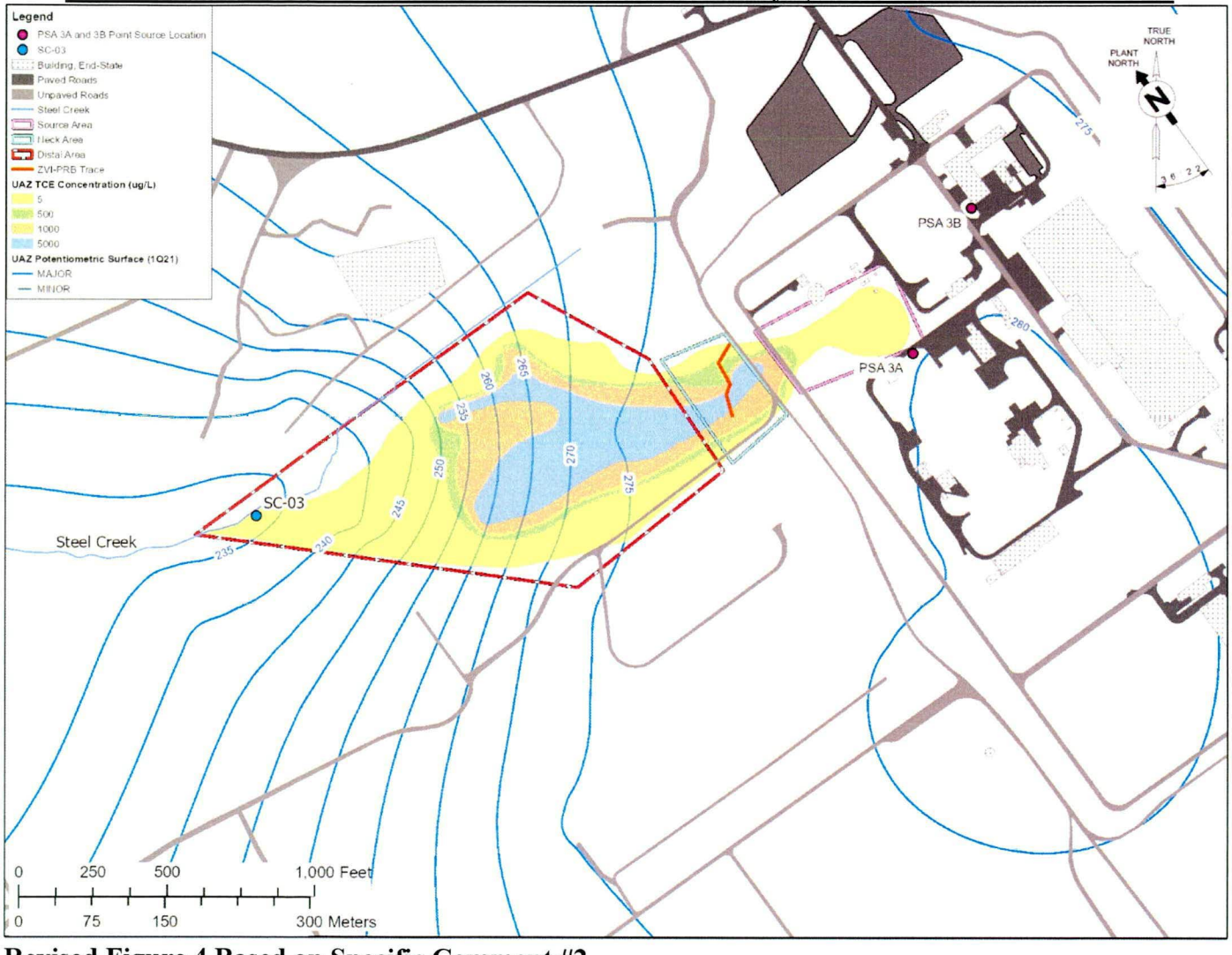

Figure CR-1. **Revised Figure 4 Based on Specific Comment #2**

USEPA Comments Received January 5, 2022

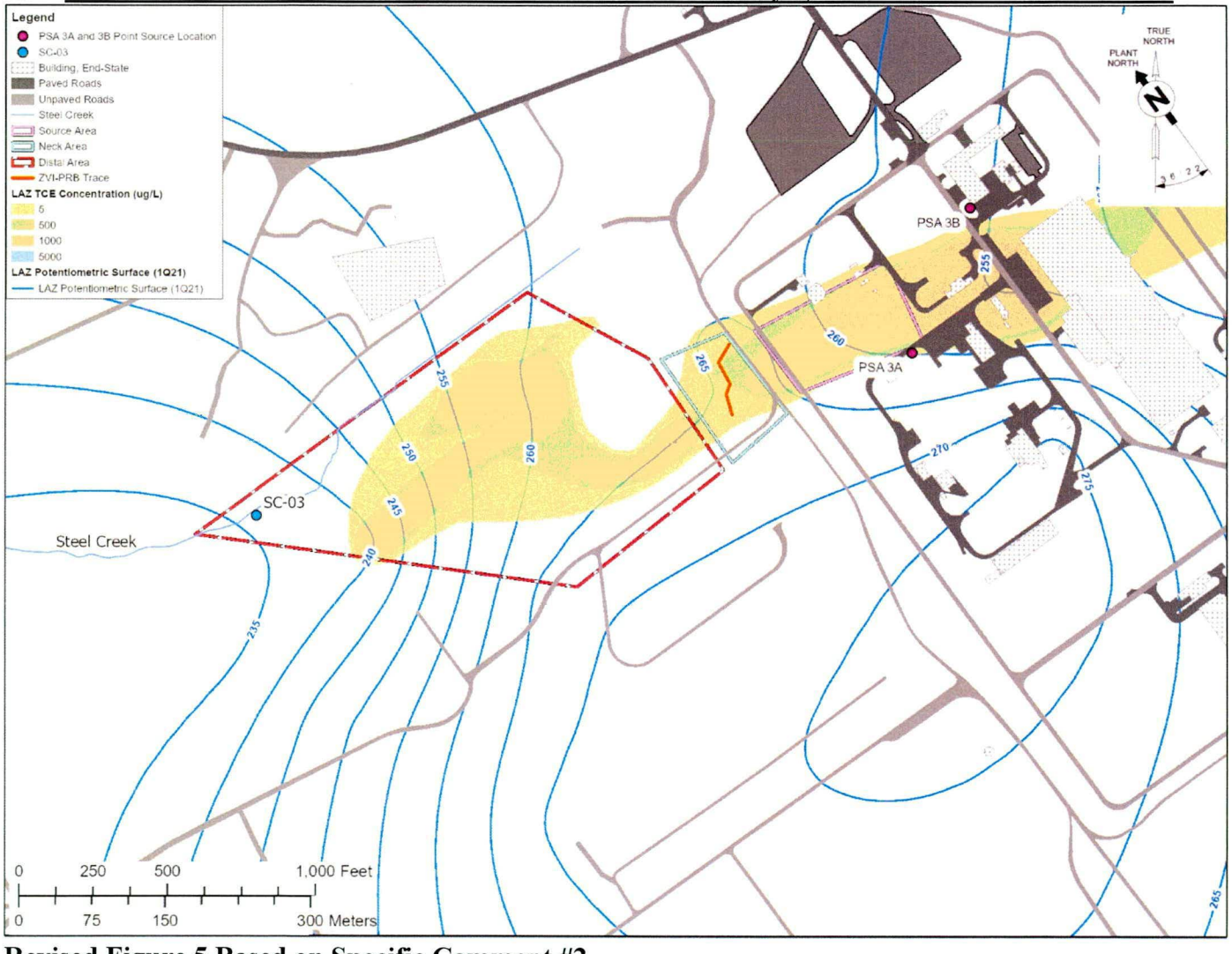

Figure CR-2. **Revised Figure 5 Based on Specific Comment #2**

USEPA Comments Received January 5, 2022

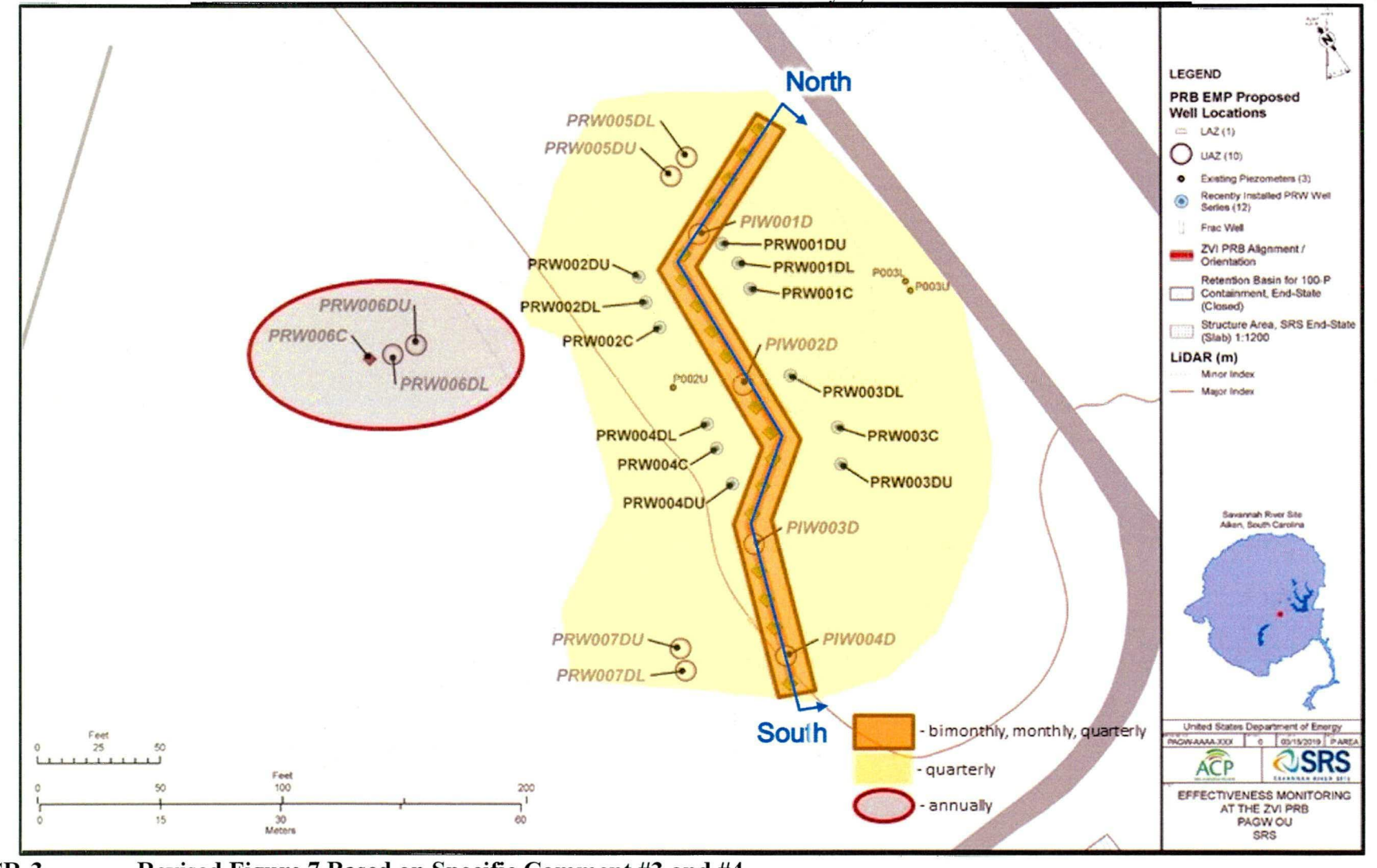

Figure CR-3. Revised Figure 7 Based on Specific Comment #3 and #4

USEPA Comments Received January 5, 2022

Table CR-1. Maximum Concentrations of PCE, TCE, and cis-DCE in the Three Plume Areas

Contaminant	MCL[1] *[µg/L]*	Maximum Concentration in UAZ *[µg/L]*			Maximum Concentration in LAZ *[µg/L]*		
		Source Area	Neck Area	Distal Area	Source Area	Neck Area	Distal Area
PCE	5	80.6	13.0	1.32	4.85	1.77	17
TCE	5	2,150	7,730	6,320	5,180	(791)	5,560
cis-DCE	70	195	892	(300)	69.0	138	168

[1] MCL – maximum contaminant level
Parenthesis indicate estimated values.