UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
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October 14, 1999

Mr. John Burleson
BRAC Environmental Coordinator
Stratford Army Engine Plant
Stratford, CT 06497

Re: Draft Pilot-Scale Treatability Study Work Plan
Chromium and VOC Groundwater Operable Unit 2

Dear John:

The United States Environmental Protection Agency (EPA) has reviewed the draft document entitled "Pilot-Scale Treatability Study Work Plan, Chromium and VOC Groundwater Operable Unit (OU) 2, EE/CA, Stratford Army Engine Plant". The document is dated September 27, 1999.

EPA's comments on the above-mentioned document are provided in Attachment I to this letter.

If you have any questions regarding this matter, please contact me at (617)918-1387.

Sincerely,

Meghan F. Cassidy

Meghan F. Cassidy
Remedial Project Manager

Enclosure

cc: Jeff Frye/Army Corps of Engineers
Beth Shields/Army Corps of Engineers
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ATTACHMENT I

The following are the United States Environmental Protection Agency's (EPA's) comments on the draft document entitled "Pilot-Scale Treatability Study Work Plan, Chromium and VOC Groundwater Operable Unit (OU) 2, EE/CA, Stratford Army Engine Plant". The document is dated September 27, 1999.

General Comments

1. The general concept of in situ reduction of the Cr(VI) and oxidation of the TCE seems to be well conceived, and the results of the bench experiments are encouraging. The bench-top experiments clearly demonstrate the efficacy of the ferrous iron and the potassium permanganate treatments. The proposed pilot test is critical, because it will help to address questions concerning the role of transport of the reductant or oxidant to the target contaminants that were not confronted in the "batch" experiments on the bench-top The bench-scale experiments achieve complete mixing of the reactants, while the *in situ* application requires that mixing be achieved by dispersion due to the flow along tortuous pathways within the porous soil. Without mixing, the injected fluid will simply displace the contaminated groundwater toward the extraction well, and the system will effectively be operating as a pump-and-treat approach. Only the field-scale test can answer this critical question.

2. The bench-scale and pilot-scale tests separate the issues of remediation of Cr(VI) contamination and TCE contamination. However, it appears that there are areas where both are present at high levels, particularly in the area of the historic B-2 chromium plating facility at depths of -10 to -40 feet MSL. (For example, WP-99-04 with 700 µg/L Cr(VI) and WP-99-09 with 130,000 µg/L TCE are in close proximity.) Has the in situ remediation for *both* contaminants in the same domain been considered? How will the proposed treatments interact? For example, has the re-oxidation of Cr(III) to Cr(VI) by reaction with MnO_2 been considered? Oxidation of the TCE by potassium permanganate leaves MnO_2 as a product (see, e.g., reaction shown on p. 2-3), while manganese oxides have been shown to oxidize Cr(III) (see, e.g., [1], [2]).

3. The Work Plan does not speculate on possible configurations for full-scale remedial systems, should the pilot tests support such an effort. Is it envisioned that a distribution of "five-spot" injection / extraction cells might be employed in a full-scale effort? Have issues of scaling up from the pilot tests been considered? For example, if the same configuration were to be used, but at larger dimensions, would the mixing of injectate and contaminated groundwater be the same? (For example, it is widely observed that dispersion - and hence mixing of the reactants - is scale-dependent.) Or, if a different configuration were to be employed in order to remediate larger areas, would inferences from the pilot test carry over directly to the new geometry? (The degree of mixing of injectate and contaminated groundwater might be expected to be rather sensitive to the configuration.)

4. The experimental design appears to be flawed to the extent that evaluation of the effects of different solution concentrations cannot be determined based on our understanding of the description of the experiment in Section 3.2.1 With four test lobes in each treatment area, each receiving a different solution concentration, the experiment must be capable of determining the change in the mass of hexavalent chromium in each lobe. It is not clear from the experimental design how this would be done The description of the experiment in Section 3 2 1 appears to refer to the entire test area rather than each test lobe. The work plan should better explain the proposed work or correct the apparent deficiencies in the experimental design.

5. The experimental design encompasses, in a sense, four experiments conducted simultaneously at each area (i.e., the hexavalent chromium test area and the TCE test area). Because of an interest in looking at the response to different concentrations of reactants in the injectate, the design proposes to introduce a different concentration at each injection well (see p. 3-2, sec 3.2.1 and p. 3-4, sec. 3.3.1), so that a different experiment is done within each of the four "lobes" of the flow field. While this is a clever design that addresses an important independent variable within a single experimental run, the price paid is that the analytical results obtained from the extraction well may become somewhat ambiguous. That is, the chemistry observed at the mid-point piezometers along each of the four direct pathways from injection to extraction clearly reflects processes along those paths, while the chemistry at the central well results from a combination of the processes within the four lobes, each of which is different. Detailed numerical transport modeling of the experimental configuration may prove to be valuable in interpreting the results, particularly those from the central well, and should be considered as an integral part of the pilot test.

6. As design concepts for remediation of the dissolved TCE plume move forward, the likelihood of the presence of DNAPL at the site should not be neglected. With concentrations in the plume approaching the aqueous solubility limit, there is a strong indication that free-phase DNAPL may be present. In the long term, this could replenish a dissolved-phase plume after an elaborate and costly effort to remove the dissolved phase has been completed. An aggressive DNAPL investigation should be considered in parallel with the effort to remediate the known plume.

7. A better summary description of the groundwater plumes (hexavalent chromium and VOCs) is required to properly evaluate this work plan. While this information is probably available in other documents for the site, this work plan needs to provide enough information to allow it to be evaluated on its own. Only Appendix C contains information about the vertical extent of the plumes and that the greatest contaminant concentrations are found at approximately 30 to 35 feet below ground surface. Also, the depth to groundwater is not presented in the work plan text, but is only found in Appendix C. The work plan should include this information in an appropriate location in the work plan, not just in Appendix C.

8. Several times in the work plan (page 3-1 and Appendix C, for example) it is stated that a recirculating well system will be created to execute this pilot test of the in situ technologies However, Figure 11 appears to show that all extracted groundwater will be pretreated then discharged to the CWTP sewer Please clarify the meaning of the references to a recirculating system, which would suggest that a portion of the extracted groundwater would be returned through the injection wells, or delete the references

Specific Comments

1. Page iii The title of Figure 9 does not match the title on Figure 9 in Appendix A Please correct the title in the List of Figures.

2. Page 1-4, §1.2.3 Please include the depth range from which the groundwater samples were collected for the fourth and fifth bullets.

In the sixth bullet, were these parameters monitored for all 189 of the samples mentioned in the fourth and fifth bullets? Please clarify.

3. Page 1-5, §1.2.3 The second half of the first sentence in the last paragraph for this section mentions "... detectable chromium at depths...." Does this refer to hexavalent chromium or total chromium? Please clarify the text.

4. Page 1-5, §1.2.4 In the first bullet in this section, please add the depth range from which the samples were collected.

5. Page 1-7, §1.2.5, ¶6 The bench-scale experiments demonstrated that the TCA was not readily oxidized by the reagents tested. Has further consideration been given to the possibility of in situ treatment of the TCA? If so, what are the alternative additives? If not, what alternative remedial schemes (e g , pump and treat, etc.) might be considered?

6. Page 1-7, §1.2.5, ¶6 The text notes that the bench-scale experiments showed that the pH had to be kept low in order to prevent "excessive" precipitation of trivalent chromium and ferric iron. Is this simply a qualitative judgment? Were criteria established for the mass of precipitates that would likely lead to problematic plugging of the porous medium (assuming that this is the concern)? If so, what are they?

7. Page 2-2, §2.2.1 The last sentence in the second to last paragraph refers to a final round groundwater sampling conducted one week after system shutdown However, Figure 12 and Table 4 state that two rounds of sampling will occur one and two weeks after shutdown. Clarify this discrepancy.

8. Page 2-5, §2.5.2 Are there relevant CTDEP RSR criteria for soil that could be evaluated for this pilot test? Please add if appropriate.

9. Page 3-1, §3.1 In the first paragraph, include the depth at which the screens will be set

10. Page 3-2, §3.2.1 Based on the ferrous sulfate dosing rate described in this section, the accuracy of the third sentence in the first paragraph is questionable. It appears that only two lobes will have enough ferrous sulfate to treat the estimated mass in their respective lobe Provide additional information to support the information presented.

11. Page 3-2, §3.2.1 Please clarify the meaning of the last sentence in the first paragraph. It appears that the sentence is saying that the injected solution will have a pH of 2.5, but could be read that a pH of 2.5 is the goal for the groundwater in the test lobe. If, as discussed in Section 2.2.1, the goal is to achieve a pH of less than 4 in the groundwater in the test lobe, how was it determined that a pH of 2.5 in the injection solution would achieve this? If a pH of 2.5 is in fact the goal for the groundwater in the test lobe, how was the necessary amount of chemical to achieve this determined? Was this calculated using the dilution rate for the injected solution and the buffering capacity of the groundwater? Please explain and clarify.

12. Page 3-2, §3.2.1 Where would the soil samples, referred to in the first sentence of the third paragraph, be collected? Are such samples proposed for each lobe of each test area? Note that Tables 4 and 6 do not account for the referenced soil samples. Please provide information to address these issues.

13. Page 3-3, §3.2.1 The first sentence on page 3-3 states that the concentration of hexavalent chromium will be monitored at the perimeter (of the treatment area). However, Table 4 shows that all wells and piezometers will be sampled on installation. Will the concentrations at the perimeter only be used to characterize the hexavalent chromium concentration of all water that flows into the test area over the course of the experiment? Will there be any differentiation made for each test lobe? Provide clarifying information.

The second sentence states that $Cr(VI)_{OUT}$ will be estimated using the concentration of hexavalent chromium sent to the industrial wastewater treatment plant and the net flow rate of one gpm to the plant. Since this does not appear to be a recirculating system (see previous comments), the average flow rate to the treatment plant will be approximately five gpm not one gpm. Also, it is not clear where samples would be collected to determine the concentration of hexavalent chromium in extracted groundwater. Because the concentration of hexavalent chromium in the extraction well discharge is expected to vary over time it would not be appropriate to collect grab samples from the discharge line. Also, it would not be appropriate to collect samples after the carbon adsorption units because some removal of metals through the carbon would be expected. It appears that a frac tank and pump is required upstream of the carbon adsorption units so that a sample from each filled frac tank can be collected and analyzed for hexavalent chromium to characterize that entire volume. Using the concentration and volume of the frac tank contents, the mass of hexavalent chromium can be calculated Provide information to better describe how $Cr(VI)_{OUT}$ will be determined.

Please indicate which wells, piezometers, or other sample locations will be used to perform the mass balance analysis for each of the treatment lobes so the effectiveness of the various solution concentrations can be evaluated

The work plan would benefit from the inclusion of sample calculations to clarify how the various mass terms in the mass balance would be calculated.

14. Page 3-2, §3.2.1, ¶1 It was noted in the bench-scale experiments that twice the stoichiometric ratio of ferrous sulfate to chromate was required to reduce the Cr(VI). How is this result interpreted, and how might that interpretation relate to the pilot- or full-scale attempt to reduce Cr(VI) in situ? Is the excess ferrous sulfate being oxidized by something else? This may be significant because of the concern for plugging of the porous medium by iron oxide, and the desire to introduce the minimum mass of iron. Could dissolved oxygen (DO) in the groundwater have contributed significantly to the oxidation of the ferrous sulfate (see, e.g., [3])? Was DO in the agitated samples in the bench experiment comparable to that in *in situ* groundwater? One reason to be concerned is that this excess iron oxide may contribute to potential clogging of the porous medium, and it is desirable to minimize this impact. It is noted that DO measurements will be acquired in the course of sampling (e.g , Table 8); particular care should be taken with these data, as they are important, yet it is difficult to obtain reliable analyses of DO from field instruments.

15. Page 3-2, §3.2.1, ¶1 The proposed experiment for reduction of Cr(VI) will use sulfuric acid "... to achieve a pH of approximately 2.5 ..." Is the intent to keep the solution pH at 2.5 over the entire path from injection to extraction? Has dilution by ambient water been considered in determining the target pH of the injectate? Is it possible that the mass of added sulfate (as both ferrous sulfate and sulfuric acid) in the injection solution will result in the precipitation of solid phases containing Cr(VI), in the presence of other groundwater ions (e.g., $Ca(Cr,S)O_4 2H_2O$)?

16. Page 3-3, §3.2.1, ¶2 The text states that piezometers will be placed at locations corresponding to "... travel times from the injection well to the extraction well of 1.0, 1.5, and 2.0 days." Should this read "... from the injection well to the piezometer?" How are these predicted travel times reconciled with the prediction (e.g., Appendix C) that the travel time from injection well to extraction well is about 1.5 days? The travel times to the piezometers must be less than that to the extraction well.

17. Page 3-3, §3.2.2 The text does not specify whether the groundwater samples are to be filtered or unfiltered. Please clarify and provide the rationale.

18. Page 3-4, §3.3.1, ¶2 The proposed experiment for oxidation of TCE will employ a solution "... adjusted to achieve a pH of less than 5.0." What will be used to make this pH adjustment? Is the intent to keep the solution pH below 5.0 over the entire path from injection to extraction? Has dilution by ambient water been considered in determining the target pH of the injectate?

19. Page 3-4, §3.3.1 Based on the potassium permanganate dosing rate described in this section, the accuracy of the last sentence in this first paragraph is questionable Although the dosing rate from the bench-scale testing was not referenced here, it is presumed to be 1.5 moles of potassium permanganate per mole of TCE. Therefore, only two lobes will have enough potassium permanganate to treat the estimated mass in their respective lobe. Please delete or rewrite this sentence.

20. Page 3-4, §3.3.1 Please clarify the meaning of the last sentence in the second paragraph. It appears that the sentence is saying that the injected solution will have a pH of 5.0 but could be read that a pH of 5.0 is the goal for the groundwater in the test lobe.

How was it determined that a pH of 5.0 in the injection solution is appropriate? If a pH of 5.0 is in fact the goal for the groundwater in the test lobe, how was the necessary amount of chemical to achieve this determined? Was this calculated using the dilution rate for the injected solution and the buffering capacity of the groundwater? Provide clarifying information.

21. Page 3-4, §3.3.1 All the comments on page 3-3 of Section 3.2.1 also pertain to this section. However, if a frac tank is used upstream of the carbon adsorption units, the mass balance will need to account for (or ignore with justification) TCE that volatilizes into the air space above the liquid collected in the tank.

22. **Page 3-4, §3.3.3 and Table 7** Manganese should be added to the analyte list for the TCE experiment. This will allow an internal check on the fate of the oxidant as it reacts with the TCE. Also, the addition of large quantities of manganese to the groundwater may pose a risk to downgradient receptors. This may need to be assessed if full-scale remediation by this method is implemented, so that a full understanding of the fate and transport of manganese will be essential.

23. Page 4-1, §4.2 The third sentence in the second paragraph refers to the monitoring of piezometers located outside the test areas; however, Tables 4 and 6 do not appear to include such piezometers and the titles of the tables suggest that only piezometers in the test areas are included in these tables. Please clarify what is intended by this sentence and provide an appropriate table.

24. Figure 1 This figure references the Installation Restoration Program at the Massachusetts Military Reservation in the title block. Please correct the reference.

25. Figure 2 Notes 1 and 3 are not pertinent to this figure. Please delete them.

26. Figure 8 Will it be necessary to avoid the drain lines that cross each of the test areas when installing wells and piezometers?

The wall along the southwestern edge of the hexavalent chromium test area may make it difficult to install the injection well at the proposed location. Please review and revise the work plan as necessary.

27. Figure 9 Are the existing piezometers screened at the required elevation for the pilot test? The required elevation is 27 to 37 feet below ground surface according to Appendix C.

28. Figure 10 Does the backflow preventer meet the stated design criteria for the proposed use?

This figure shows, and the bill of material confirms, that the discharge line from each metering pump will split to dose two injection wells from each metering pump. Control of the chemical flow in this configuration may prove difficult. Each discharge line will need to be calibrated properly. Chemical injection valves installed at the end of each discharge line are recommended.

29. Figure 11 It is understood that this figure is not a design drawing, but the carbon units should be plumbed and valved to allow change out of spent units unless the units are sized to last for the entire pilot test.

Please refer to comments on the experimental design in Sections 3.2.1 and 3.3.1. It does not appear that this layout will satisfy the requirements to achieve the pilot test objectives. For example, where would samples of extracted groundwater be collected for hexavalent chromium and TCE? Please edit this layout and the work plan as necessary or clarify the work plan in support of this layout.

30. Tables 1 & 2 Why doesn't Test Area 2 list ferrous sulfate in the Treatment Solution column?

31. Table 3 Consider adding chemical injection valves at the discharge end of each chemical metering line to better control the chemical addition rate to each injection well.

Presumably, a drum of (dilute) sulfuric acid will also be provided. A drum of sodium hydroxide solution would also be recommended for pH adjustment. Will separate drums of acid and base be provided for each test area and will drum pumps by shared by each area? Please edit as necessary.

32. Table 4 Comparing this table with the description of the experimental design in Section 3.2.1, there appear to be anomalies in the table that require correction.

The first sentence in the third paragraph of Section 3.2.1 refers to "before" and "after" samples for soil and groundwater; however, samples collected immediately after the test are not included in this table. Please edit the work plan to correct this discrepancy.

Sampling included in this table needs to address the fact that the experimental design requires evaluation of each test lobe independently

Will PZ-99-02 also be sampled (for groundwater) at the beginning (and end) of the pilot test? Please correct as necessary.

Clarify where extracted groundwater will be sampled for the mass balance calculations.

33. Tables 4 and 6 The tables show the sampling frequency for groundwater samples at the piezometers and the extraction wells. The sampling schedule is strongly predicated on the prediction that the travel time for the injectate from the injection well to the extraction well is 2 days (i.e., the sampling is concentrated around 48 hours to resolve the "breakthrough"). What is the basis of this prediction for the travel time? (It is not discussed explicitly in the text.) Is the proposed sampling schedule based on the distribution of arrival times of particles in the particle tracking calculations shown in Appendix C? What is the relationship between the prediction of a travel time of 1.5 days along the most direct path (see, e.g., Appendix C) and the two days around which the sampling is centered? If significant injectate and/or reaction products arrive at the extraction well as early as 36 hours after start-up, the sampling program will not resolve the breakthrough in detail. It may be prudent to perform more detailed transport modeling in order to reduce uncertainty in the travel time to guide the sampling schedule, or to consider adding sampling events to resolve possible earlier breakthrough. It should be noted that the particle tracking calculations employed to date, while effective in mapping out the advective flow field, do not address dispersion, which is critical to the mixing process required to achieve in situ reduction or oxidation of the contaminants, and will spread out the breakthrough curve for reactants to some extent.

34. Table 5 The table indicates no TOC analyses for the soil samples. Has the site soil been characterized previously for TOC? If not, this should be added to the analyses proposed for the pilot test program. Organic carbon could play a role in the processes affecting Cr(VI) distribution. For example, oxidation of organic carbon in the soil may reduce some Cr(VI), even in the absence of the ferrous iron.

35. Table 5 Addition of dissolved organic carbon (DOC) to the analyte list for the groundwater samples should be considered. DOC has been shown to influence the formation of soluble organic complexes with Cr(III) [4].

36. Table 5 Analysis for ferrous iron should be added for the pre-test groundwater ("Groundwater - Collected during installation") in order to characterize the background ferrous iron. Although under the strongly oxidizing conditions observed in the test area, the concentration of ferrous iron in solution should be negligible, this should be verified by pre-test analyses.

37. Tables 5 and 7 Modify these tables as required in response to comments made and associated resolution of comments that impact these two tables. For example, soil and groundwater collected immediately after the test, and sampling of extracted groundwater for mass balance calculations.

38. Table 6 Discrepancies similar to those identified in Table 4 exist between Table 6 and the text in Section 3.3.1. Please make the necessary corrections.

Will PZ-99-01 also be sampled (for groundwater) at the beginning (and end) of the pilot test? Please correct as necessary.

Clarify where extracted groundwater will be sampled for the mass balance calculations.

39. Table 7 The table indicates an analysis only of Cr(VI) during the test, and only at the extraction well. Why is characterization of Cr(VI) during the test limited to the extraction well? Total Cr and Cr(VI) should be characterized throughout the domain during the test, as well as afterward, due to the potential complexity of the interaction between Cr(VI) and the permanganate solution

40. Table 8 This table refers to on-site analyses for VOCs, chromium, and iron species; however, it is not clear from the work plan that an on-site laboratory is planned. Please review and correct as necessary.

Please identify sampling that will be conducted in support of the mass balance calculations and add that to this table. Note that the experimental design requires evaluation of the various test lobes independently to determine the effect of various chemical dosages.

This table appears to be more complete than Table 4, 5, 6, and 7.

41. Appendix C The second paragraph refers to a recirculating system; however, it appears that a recirculating system will not be used. Please correct as appropriate.

What is the 4-foot hot zone referred to at the top of the second page of text? Please clarify this in the text of the work plan.

On the second page of text, is the porosity consistent with the apparently tight formation found at the sight? Is the assumption of a porosity of 0.3 supported by field investigations at the site? Please explain or document if possible.

References

[1]. Eary, L. E., and D. Rai, Kinetics of chromium(III) oxidation to chromium(VI) by reaction with manganese dioxide, *Environmental Science and Technology*, **21**, 1987, 1187-1193.

[2]. Rai, D., L. E. Eary, and J. M. Zachara, Environmental chemistry of chromium, *The Science of the Total Environment*, **86**, 1989, 15-23.

[3]. Eary, L. E., and D. Rai, Chromate removal from aqueous wastes by reduction with ferrous ion, *Environmental Science and Technology*, **22**, 1988, 972-977.

[4]. Masscheleyn, P. H., J. H.Pardue, R. D. DeLaune, and W. H. Patrick, Jr., Chromium redox chemistry in a lower Mississippi Valley bottomland hardwood wetland, *Environmental Science and Technology*, **26**, 1992, 1217-1226.