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REGION IX
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ARIZONA DEPARTMENT OF ENVIRONMENTAL QUALITY
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MEMORANDUM

SUBJECT: Williams ST12 Fuels Spill Site; Air Force Proposal for Enhanced Bioremediation to Address Remaining Contamination

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As you are aware, the Steam Enhanced Extraction (SEE) Remedy for Williams Site ST12 was terminated in April 2016 after having removed over 2.5 million pounds of hydrocarbons from the subsurface. At the time of shutdown and dismantling of the SEE system, thousands of pounds of hydrocarbons were still being removed on a daily basis, and the criteria established in the RD/RA Work Plan for SEE had not been consistently attained. EPA and ADEQ objected to termination of the remedy as premature and subsequently invoked informal dispute.

Significant hydrocarbon mass remains in the subsurface; between four to ten million pounds, by AFs own estimates as reported in the Addendum #2 RD/RA Work Plan for Enhanced Bioremediation (EBR). It appears that the SEE remedy as designed may have only targeted half of the LNAPL mass at the site. AF is now asking to proceed with Enhanced Bioremediation for the remainder of the LNAPL at the site. EPA and ADEQ have already submitted substantial comments on AFs proposal which have not been satisfactorily resolved and remain significant concerns going forward. The fact that a large quantity of LNAPL remains behind at the site requires a re-assessment of our remedial progress and a critical evaluation of the path forward.

At the time of the 2013 Record of Decision Amendment (RODA) signature, it was not anticipated that there would be large quantities of remaining LNAPL, especially untreated mobile LNAPL still rich in benzene and BTEX compounds at the site following termination of SEE. As the RODA specified attainment of remedial action objectives within 20 years, we now need to understand how expectations for the longevity of this remedy have changed given the current site conditions. We also need to understand the feasibility and cost/benefit of the options going forward.

When the ST12 remedy was first described to the agencies, it was assumed that SEE would be employed to remove almost all of the LNAPL source in order to create optimal conditions for Enhanced Bioremediation (EBR) to degrade dissolved phase residual contaminants. Given that the construction costs associated with thermal technologies significantly outweigh the operational costs, thermal remedies are almost always run until the contaminant source is completely removed, as the industry standard for this technology. If essentially all of the LNAPL source material had been removed by SEE, there would have been no need for further hydraulic containment following SEE, so it was not included in the RODA. This understanding is documented in the January 4, 2013 draft proposed plan (attached) which described the remedy as follows: *"After most of the LNAPL is removed by SEE, the remedial action would transition to enhanced bioremediation"*. This language evolved in subsequent documents to specify performance criteria for the SEE system which the agencies believed were intended to signal when most of the LNAPL had been removed. However, as we have previously explained, the performance criteria specified in the Remedial Design/Remedial Action Work Plan (RD/RAWP) had not been consistently attained at the time the SEE system was terminated and dismantled.

While the Agencies were aware that some LNAPL would remain after SEE, the large amounts of mobile LNAPL that now appear to remain at ST12 within and surrounding the SEE treatment area significantly reduces the possibility that the planned EBR will be successful in meeting the 2013 RODA goals. The current remaining mass estimate still needs to be verified by post SEE sampling. An updated estimate of remaining LNAPL mass and BTEX concentrations residing within the LNAPL mass within specific locations and depths is critical to 1) resolve uncertainties of amendment mass loading required for successful implementation of EBR, 2) enable specific areas and depth zones to be targeted for treatment 3) evaluate the impact of amendment upon groundwater quality, 4) estimate the anticipated timeframe to meet remedial action objectives, and 5) define milestones for monitoring EBR remedy success against baseline conditions. Appropriate and agreed-upon baseline conditions would need to be established in order to be able to monitor remedy performance. AF's responses to agency comments provided to date have not provided this information and have not resolved these concerns.

The AF's letter of November 17, 2016 expresses concerns that elevated post steam temperatures are necessary for successful EBR implementation as *"partially dependent upon taking advantage of the increased solubility and dissolution of contaminants of concern (COCs) from LNAPL occurring at elevated temperatures"*, and, *"increased anaerobic degradation at the higher temperatures is currently establishing microbial populations that can be further enhanced for bioremediation of COCs. If extended extraction is used for hydraulic containment instead of establishing EBR reagent distribution, deterioration of conditions favorable to the anaerobic EBR approach will occur due to introducing cooler groundwater and higher dissolved oxygen levels."* While elevated temperatures may in general enhance bacterial growth and metabolism, this is

generally true for only a narrow range of temperatures for any given species. Upon significant changes in temperatures, it would be expected that major changes in the microbial population mix would occur, quite possibly causing reduction or cessation of COC degrading activity. AF has not presented any data to show that significant and active populations of high-temperature-adapted microorganisms, capable of degrading the COCs at the rates necessary to achieve Site remedial goals are present. Further, LNAPL is currently present within a wide range of variable temperature zones both inside and outside the SEE treatment zone, as the characterization data being collected now shows that there is considerable LNAPL outside of the heated zone. Thus, if "high" temperatures are critical for biodegradation, the existence of LNAPL at widely variable temperatures across the site may already be problematic.

Other factors, including the rate of mass loading of sulfate amendment and the subsequent changes that this causes to the geochemistry of the subsurface can also affect the degradation rate and would need to be carefully monitored and controlled. We did not see acknowledgement or preparations to address these considerations in the RD/RAWP Addendum 2. (Please see attached journal article, *Engineered Anaerobic Bio-Oxidation Systems for Petroleum Hydrocarbon Residual Source Zones with Soluble Sulfate Application Suthersan et al., Ground Water Monitoring & Remediation, 31(3):41-46, 2011)*

Recently, during the 5 Year Review inspections for the Lawrence Livermore site where a smaller 100,000 cubic yard thermal application was implemented it was documented that subsurface temperatures within the former treatment area still remain elevated by a few degrees above the surrounding aquifer twenty years after termination of thermal treatment. In comparison, the 410,000 cubic yard SEE application at ST12 is the largest and deepest ever implemented and can be expected to remain at elevated temperatures for many years, even with ongoing extraction for containment. The same conditions that enhance solubility and dissolution of contaminants conducive to EBR also increase the mobility of contaminants, which are the most significant concern the regulatory agencies have for maintaining the future protectiveness of the remedy. <u>Contaminants cannot be allowed to migrate away from the site and create a more extensive groundwater plume.</u>

Based upon our analysis of the most recent soil boring and groundwater data, migration of the dissolved phase already appears to be occurring. For example, the data from the existing sentry wells provided on November 30, 2016 indicated increasing benzene concentrations at W-36 which doubled between 8/31 and 11/1, and is now 1600 μg/l. We also note in the November 11, 2016 weekly report that several interior Thermal Treatment Zone wells in the Lower Saturated Zone (LSZ) which previously were shown to be free of LNAPL following SEE treatment now have over a foot of LNAPL in them. Further, LNAPL was present in several steam injection wells in both the UWBZ and LSZ in the post SEE monitoring phase, so even near the SEE injection wells, LNAPL is still present in mobile form. It is probable that any diminishing of LNAPL movement into some monitoring wells is only because the driving pressure gradient (i.e., drawdown) to move the LNAPL into such wells has diminished following termination of extraction, not because LNAPL has been depleted from the subsurface. These observations indicate that LNAPL within the treatment area was not completely recovered and could migrate off site if not contained.

Numerous recent characterization borings, including CZ-23, UWBZ-37, LSZ-43, LSZ-45, LSZ-46, UWBZ28/LSZ51, UWBZ33/LSZ48, SB19/LSZ61, LSZ44, had PID readings or analytical results indicative of contamination exceeding the MCL for benzene, and it is not clear that the containment system currently being constructed will be adequate to contain the plume in these areas. Once the containment system is operating, an assessment of the capture zone should be undertaken, and necessary improvements to the system must be made.

The EBR application as described in the Addendum 2 RD/RAWP is a much larger effort than was anticipated at the time of the 2013 RODA signature. The large amount of amendment proposed to be injected to degrade the remaining LNAPL cannot be permitted to degrade water quality downgradient of the site and must therefore also be contained. It does not appear that the interim containment system now being constructed has been designed to be capable of also treating extracted EBR amendment or the arsenic contaminant it contains; the treatment system will require an upgrade to treat the extracted amendment before EBR application could begin. If AF is concerned that cooler water from outside of the Site should not enter the EBR treatment area, the containment system should be reconfigured to extract from perimeter wells to meet that objective. The costs of long term containment should be included when evaluating the costs of EBR and should also be weighed against performing additional SEE to eliminate the bulk of LNAPL as was intended under the current remedy specified in the 2013 RODA.

The efficacy of EBR to treat such a large mass of remaining LNAPL is highly questionable and unprecedented in that this has never been attempted anywhere else on a comparable scale, and has not been adequately pilot tested at this site. LNAPL cannot be expected to directly biodegrade; the LNAPL components must first dissolve into the aqueous phase for degradation to occur. LNAPL structure is highly important in terms of dissolution rates: mobile LNAPL bodies (as opposed to small, dispersed globules, and residual LNAPL in pores) will greatly slow movement of COCs (i.e., benzene) from LNAPL to groundwater. The modelling effort employed in the RD/RAWP Addendum 2 does not account for mass transfer limitations of dissolution, thus, the remedial timeframe for EBR was significantly underestimated.

The attached paper, *Engineered Anaerobic Bio-Oxidation Systems for Petroleum Hydrocarbon Residual Source Zones with Soluble Sulfate Application Suthersan et al., Ground Water Monitoring & Remediation, 31(1):45-49, 2011* states "The presence of a NAPL source zone leads to inherent uncertainty with regard to achieving remediation endpoints as the NAPL extent and structure (i.e., surface area) is unknown."; and, "we note that the technology will be effective at NAPL-contaminated sites only if the trapped NAPL can be remediated, i.e., if the amount of residual NAPL is small, and if the presence of any perched aquifers does not affect the results." Furthermore, "The presence of a smear zone, where porosity is consumed to varying extents by residual separate-phase PHCs, can present a challenge to effective reagent delivery." Currently, the smear zone at ST12 extends nearly 100 feet from the water table to 230 feet below ground surface and contains mobile as well as residual LNAPL; it cannot be expected that it can be treated adequately by amendment injection.

It has also come to our attention that AF's Preliminary Assessment for Perfluorinated Compounds (PFCs PA) identified the area of ST12 as the site of at least 2 spills where PFC firefighting foams were applied and allowed to soak into the ground. Although we currently have no data to assess

the situation, a follow on Site Inspection has been recommended. EPA deferred remedy protectiveness for ST12 on the 2016 Five Year Review pending resolution of data gaps for PFCs. This uncertainty also contributes to the difficulty in determining the most appropriate path forward for ST12 at this time, as the ultimate remedy needs to be compatible with and address all of the potential concerns at the site. For example, it was recently reported that perfluoroalkyl fatty acids (PFFA) precursors as found in firefighting foams may biotransform under aerobic conditions but not under anaerobic conditions such as currently proposed for the Site. (AECOM /Arcadis NEWMOA webinar presentation November 11, 2016.)

Additional comments on AFs proposal for Enhanced Bioremediation provided by Dr. Dan Pope of CSS-Dynamac are also attached. Our joint agency technical team continues to conclude that AFs termination of the SEE system was premature, and AFs proposal for Enhanced Bioremediation is also premature.

Attachments