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April 3, 2000

Commanding Officer
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DRAFT SURFACTANT ENHANCED SUBSURFACE REMEDIATION (SESR) DENSE, NON-AQUEOUS PHASE LIQUID (DNAPL) REMOVAL TREATABILITY STUDY RESULTS REPORT, ALAMEDA POINT SITE 5 (FEBRUARY 3, 2000)

Dear Mr. Wong:

The Department of Toxic Substances Control (DTSC) has reviewed the Draft Surfactant Enhanced Subsurface Remediation (SESR) Dense, Non-Aqueous Phase Liquid (DNAPL) Removal Treatability Stud Results Report for Alameda Point Site 5, dated February 3, 2000. The results appear to be inconclusive regarding the overall system performance at the site. A major concern is the ability of the injection/recovery well system to contain and capture injected surfactants and to prevent off-site migration, especially vertical migration, of any mobilized contaminants. On the positive side, a significant quantity of DNAPL (34 gallons) was reported to have been recovered from a relatively small volume. The site of the treatability study appears to be ideal for in-situ surfactant flushing: a shallow, relatively thin sand zone underlain by a less permeable clay layer, with significant concentrations of DNAPL identified in the vicinity of the sand-clay interface. To the extent other areas with similar conditions exist at the site, the in-situ surfactant flushing technology would have applicability.

Specific comments are enclosed. These address the following concerns:

- mass balance;
- effectiveness regarding capture of all injected fluids and preventing migration or mobilization of contaminants beyond the treatment cell;
- the decision not to use bromide as a conservative tracer;
- high concentrations of TCE and TCA in the clay layer beneath the test cell (Will a significant mass of contaminant remain in the underlying aquitard after treatment? Did the treatment mobilize contaminants into the underlying

aquitard? Do contaminants in the underlying aquitard represent a significant source of DNAPL which must be addressed?);

- the possibility that a significant amount of recovered DNAPL could have originated outside the treatment cell;
- swept volume;
- analysis of post-treatment groundwater results;
- discussion of QA/QC results;
- effects of other contaminants (e.g., TPH);
- report format.

The enclosed comments also contain suggestions for alternative methods to resolve some discrepancies or provide more accurate data, including sensitivity analysis of partitioning Interval Tracer Test results as a "reality check."

Please contact me at (510) 540-3767 if you have any questions regarding this letter.

Sincerely,

Mary Rose Cassa

Mary Rose Cassa, R.G.
Engineering Geologist
Office of Military Facilities

enclosure

cc: see next page

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MEMORANDUM

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TO: Mary Rose Cassa, R.G.
Office of Military Facilities
Site Mitigation

FROM: John Wesnousky, P.E.
Office of Pollution Prevention
and Technology Development

DATE: March 15, 2000

SUBJECT: ALAMEDA POINT SITE 5 (FORMER ALAMEDA NAVAL AIR STATION) SURFACTANT FLUSHING TREATABILITY STUDY RESULTS

Per your request I have reviewed the report entitled, "Surfactant Enhanced Subsurface Remediation (SESR) DNAPL Removal Treatability Study Results Report At Alameda Point (Site 5)," dated February 3, 2000. The subject report was prepared by SURBEC-ART Environmental for submittal to Tetra Tech EM Inc. and the U.S. Navy. Following are my comments concerning the results of this field scale treatability study.

General

Considerable data was collected to determine the mass of DNAPLs present before and after treatment by surfactant flushing. Unfortunately, the mass balances calculated from these data raise concerns with the overall accuracy of the results. That notwithstanding, the tests were generally favorable showing that surfactant flushing recovered a significant volume of DNAPL from the "test cell". The 35 gallons of DNAPL that were reported to have been recovered represent a reduction of 2000 to 3000 mg/kg if averaged over the volume of the test cell (20 ft. square by 4 ft. deep).

On a cautionary note, the pilot test data appear inconclusive on the system's effectiveness in capturing all of the injected fluids and preventing migration or mobilization of contaminants beyond the vertical and horizontal limits of the designed treatment cell. The above concern is based on the lack of closure in the mass balance for the tracers and the high levels of contaminants detected in the underlying clay layer after treatment.

Amount of DNAPL Removed or Recovered

Several lines of "evidence" or data were used to determine the amount of DNAPL removed. These included (a) the amount of free phase DNAPL actually separated and recovered from the groundwater effluent by the MPP (liquid-liquid extraction) system, (b) recovery well flow rates and DNAPL concentration data, (c) pre- and post-treatment soil core data, and (d) pre- and post-Partitioning Interwell Tracer Test (PITT) data. Of these data sets, the amount actually recovered should be considered the most accurate or "hardest" number. This was reported to be 35 gallons. The report does not provide a laboratory analysis of the recovered liquid. If the separated liquid was less than 100% DNAPL, as would be the case with an emulsion, the actual volume of DNAPL recovered would be proportionately less.

The calculated amount recovered based on recovery well flow rates and DNAPL concentrations was 65 gallons, almost twice the actual volume recovered by the MPP system. An explanation is not given to account for this difference. Figure 4.15 indicates that MPP system generally recovered above 80% and as high as 98% of the influent TCA/TCE concentrations. The system reportedly was designed to be 85% effective. Assuming 80% effectiveness, 44 gallons or less would have passed through the MPP unit. How is the 20 gallon difference explained? More importantly, if more than 35 gallons of VOC were actually recovered by the surfactant flushing operation, what is the fate in the environment or the system of the VOCs not recovered by the MPP unit.

There is some uncertainty in the 65 gallon calculation. Figure 4.14, a plot of the concentration over time indicates highly variable concentrations when samples were taken more frequently. Samples were taken more than days apart, especially after the first two days of operation. The result of integrating such data to determine the mass of contaminant recovered is subject to considerable uncertainty or error.

The amount of DNAPL recovered based on the Partitioning Interwell Tracer Tests (PITT) that were conducted before and after surfactant flushing ranged from 100 gallons to 560 gallons, depending on which of the three partitioning tracers were evaluated. These values are significantly higher than what was actually recovered or calculated based on concentration and flow rate data. These results are based on a number of assumptions and are admittedly qualitative. If the event any of these results were accurate, the question is the environmental fate of the mass not recovered by the system but somehow now gone from the treatment cell.

<u>Bench scale study and push-pull PITT test results</u>

The report references a bench scale study which was conducted to evaluate various surfactants, tracers and operational parameters. The results of these tests were not available for review, but apparently were issued in a Technical Memorandum (Surbec, 1999). Also, the results for a push-pull PITT test which was specified in the May 18, 1999 workplan is not included or referenced in the report.

<u>Conservative Tracer Results</u>

The workplan suggested that bromide would be used as a conservative tracer. The report indicates that both methanol and bromide were used as the conservative tracers in the pre-PITT (p. 2-11). There is no data or discussion on the results for a bromide tracer test. The report indicates specifically that bromide was not used in the post-PITT (p. 3-6). It is not clear that a bromide tracer test was actually performed or why methanol was selected as the conservative tracer in lieu of bromide. How was methanol selected as the best non-partitioning or conservative tracer to use? Methanol is an alcohol that is biodegradable and has application as a cosolvent to dissolve or mobilize DNAPLs in an in-situ flushing process. Bromide is generally regarded as conservative groundwater tracer and is commonly used to assess effectiveness of injection-extraction well systems. The reason that bromide was not used, if this was the case, should be explained. If bromide were used as the conservative tracer in the pre-PITT, then the data should be provided.

The recoveries of the tracers used in the pre- and post-PITT ranged from 59% to 157%, indicating considerable uncertainty in the results and methodology used. It is physically not possible to recover greater than 100% of the injected amount, but due to analytical error recovery values greater than 100 can result. The recoveries reported for methanol appear acceptable (113.7% and 95.8%); however the high variation in recoveries of the other tracers used at the same time raises concern over the accuracy of these results.

Tracer recovery was calculated based on concentration and flow rate data integrated over the test duration. The number of analyses and measurements used to calculate tracer recovery results increases uncertainty (i.e., the error in each analysis and measurement is additive). A more accurate method would have been to collect the recovered groundwater in the storage tanks which were available during the testing. Several replicate samples of the groundwater mixture and a single volume measurement would yield an accurate value of the mass of tracer recovered.

Soil Sampling Data

Table 4.5 presents the pre- and post-treatment soil boring sample data for TCE & TCA that were used to evaluate the system's effectiveness. A number of sample results are shaded indicating the sample was inadvertently collected from the clay aquitard underlying the treatment cell. All of these "shaded" results show elevated levels (520 mg/kg to 15,730 mg/kg of TCE & TCA) after treatment, but apparently are excluded from the removal effectiveness calculation because the samples were taken outside (below) the treatment cell. These results, however, raise significant issues. Will a significant mass of contaminant remain in the underlying aquitard after treatment? Did the treatment mobilize contaminants into the underlying aquitard? Do contaminants in the underlying aquitard represent a significant source of DNAPL which much be addressed.

Pre-treatment soil sample results tabulated in Figure 2.1 indicate limited data on contamination levels below the treatment cell (> 17 ft. deep) in the underlying clay layer. Results for monitoring well soil samples and one geoprobe boring (2A-G5), all located within the treatment cell, include two samples at 22 feet deep which have less than 1 mg/kg VOCs, and one sample at 19 feet deep with less than 8 mg/kg VOCs. Five of ten samples taken at 17 feet deep indicate very high levels of VOCs. Soil sampling data are not available on contamination levels for the immediate interval below the treatment cell (i.e., 17 to 19 ft.) to determine the mass of DNAPL that might be present in these clays. This is a concern in light of post-treatment sampling results noted in the above paragraph which indicate high VOC levels in the top of the clay zone after treatment. Soil sampling below the bottom of the treatment cell, 17 feet, was apparently not conducted after treatment.

An estimated 34 gallons of DNAPL was determined to be present in the untreated soil based on soil sample data. This estimate is briefly discussed but the actual calculation is not provided to verify the result or understand the calculation.

Pre- and post-treatment soil sample concentrations are presented in Table 4.5 and discussed in Section 4.2. Locations of post-SESR soil samples are shown on Figure 4.4 as X's and are labeled to correspond with adjacent injection or recovery wells. The report does not describe how these samples were collected, whether by geoprobe or otherwise. The "X" corresponding to FWI-1 should not be considered as a co-located sampling boring since it is offset a significant distance away.

Hydraulic Control Injection Wells FWI-1 and FWI-2

Fresh water was injected into two injection wells located outside the treatment cell boundaries to provide lateral hydraulic containment of the injected fluids. High levels of soil contamination were found at FWI-1. Groundwater VOC levels were found to be high at both wells. Mass flow balance for the SESR indicates recovery wells removed 20% more volume than was injected, and that FWI-1 & 2 accounted for about half of the volume injected. Given these conditions, a significant amount of the recovered DNAPL could have originated outside the treatment cell.

Although this may have been unavoidable in conducting a treatability test at this site, the relative impact of these conditions on the treatability study results should be analyzed and discussed.

Swept Volume

The groundwater pore volume of the defined treatment cell was calculated to be 5500 gallons (0.30 x 20 ft. x 20 ft. x 4 ft.) assuming a 0.30 porosity. I calculated 3590 gallons using a factor of 7.48 gal/ft^3. Based on results of both the pre-PITT and post-PITT for the conservative tracer (methanol), a swept pore volume of 8500 gallons was calculated, more than twice that of the defined treatment cell (3590 gallons). The report concludes that the swept pore volume includes flow paths outside the treatment cell and is therefore greater. Analyses of tracer concentrations outside the defined treatment cell were not provided to verify this. How do the modeling results for the flow paths of injection and recovery system compare with these results using the same parameters as field study. Given these concerns, as well as the variable mass balance results for the tracers, the swept pore volume figure should be considered very qualitative.

PITT tests

As noted in the report, PITT test results are subject to many assumptions which may not hold not hold true for the subsurface conditions throughout the treatment cell. It would be useful to know (reality check) what the range in results would be based on the uncertainties associated with the assumed values. A sensitivity analysis should be provided to evaluate how varying the assumed values affects the results.

Groundwater

Table 4-6 presents results of pre- and post-treatment groundwater samples collected from injection, recovery and monitoring wells within the treatment cell. High VOC concentrations (e.g. several mg/l to over 100 mg/l) were present at all sampling points after treatment. A number of the 20 sampling points showed an order of magnitude reduction in contaminant concentrations, while several showed little change or an increase in concentration (i.e., MRW-2, MRW-3 and MLS-2C).

Monitoring Wells MLS-1D and MLS-2D were installed and screened in a "clayey-sand" zone below the treatment cell (21.75 ft. to 22 ft. interval) to assess whether treatment might cause contamination of the underlying zone (i.e., cause contaminants to migrate vertically downward below the defined treatment cell). Results for these two locations show a decrease in concentration. How are these results explained given that these wells were screened below the influence of the injection and recovery wells. In the section on results, pre-PITT tracer concentration versus time plots are provided for MLS-1A & B (Figures 4-7 and 4-8) but not for the D interval or for any of the MLS-2 wells. In the Appendix, plots of tracer data for MLS-1D and MLS-2D for the post-PITT are given. These results suggest that MLS-2D is influenced but MSL-1D is not. These results are inconsistent with the concentration reduction in both wells. Tracer data for the "D" interval should be provided for the pre-PITT as well as the post-PITT.

QA/QC

There is no discussion of QA/QC results to confirm that analytical results summarized are within acceptable QA/QC limits.

Presence of Other Contaminants

Section 2.3.1.2 indicates a high level of TPH was detected in sample boring MS-2A-AE (820mg/kg at 7.5 ft.). This particular well is located within ten feet of the treatment cell boundary. The report indicates that groundwater gradient is variable at this location. Were soil samples analyzed to determine whether TPH was present in significant quantities in the defined treatment cell? This could be the case if the treatment cell were located down gradient. Presence of TPH would significantly affect validity of PITT test analyses for TCE and TCA.

Reporting Format

I found the report cumbersome to review. Results of tests are not consolidated in any one section, and in some cases only selected results are presented. Also, only selected calculations (spreadsheets) were provided (e.g., the post-PITT but not the pre-PITT calculations were provided; the calculation of the amount recovered based on soil sample data was not provided). In addition, figures were sometimes not correctly labeled (e.g., p.4-10 refers incorrectly to Figures 3-1 and 4.15).

In summary, results for treatability study are inconclusive regarding the overall system performance at the Alameda site. A major concern is the ability of the injection/recovery well system to contain and capture injected surfactants and to prevent off-site migration, especially vertical migration, of any mobilized contaminants. On the positive side, a significant quantity of DNAPL, 34 gallons, was reported to have been recovered from a relatively small volume. The site of the treatability study was somewhat ideal for in-situ surfactant flushing: a shallow, relatively thin sand zone (12 to 16 deep zone), underlain by a less permeable clay layer, with significant levels of DNAPLs identified in the vicinity of the sand-clay interface. To the extent other areas with similar conditions exist at the Alameda site, the in-situ surfactant flushing technology would have applicability. If you have any questions or concerns regarding the above comments, please contact me at (916) 322-2543.