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NSWC CRANE
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DEPARTMENT OF THE NAVY
CRANE DIVISION
NAVAL SURFACE WARFARE CENTER
300 HIGHWAY 361
CRANE, INDIANA 47522-5000

IN REPLY REFER TO:

5090
Ser 095/0053

09 MAR 2000

U.S. Environmental Protection Agency, Region V
Waste, Pesticides, & Toxics Division
Waste Management Branch
Illinois, Indiana, and Michigan Section
Attn: Mr. Peter Ramanauskas (DW-8J)
77 West Jackson Blvd.
Chicago, IL 60604

Dear Mr. Ramanauskas:

Crane Division, Naval Surface Warfare Center (NAVSURFWARCENDIV Crane) submits for review and approval two (2) copies of the Response to December 1999 Comments and Replacement Pages for the Audit Demonstration Report - Field Test Kits and Wiley Mill Riffle Splitter for Full Scale Bioremediation Operations included as enclosure (1). The required certification statement is included as enclosure (2).

NAVSURFWARCENDIV Crane point of contact is Ms. Christine D. Freeman, Code 09511, telephone 812-854-4423.

Sincerely,

Phillip A. Veith, for
JAMES M. HUNSICKER, DIRECTOR
ENVIRONMENTAL PROTECTION DEPARTMENT
BY DIRECTION OF THE COMMANDER

Encl:
(1) Response to Comments/Replacement Pages Audit Demonstration Report - Field Test Kits & Wiley Mill Riffle Splitter
(2) Certification Statement

Copy to:
[redacted]
IDEM (D. Griffin)
MK Cleveland
SOUTHNAVFACENGCOM (Code 1864)
TolTest Crane

RESPONSES TO COMMENTS
DRAFT AUDIT DEMONSTRATION REPORT - FIELD TEST KITS AND WILEY MILL/RIFFLE SPLITTER
DATED MARCH 1999
NAVAL SURFACE WARFARE CENTER
CRANE, INDIANA

Comments by Region V EPA, Peter Ramanauskas, December 1999.

Wiley Mill/Riffle Splitter Study

Comment

1. Referring to Table 2-1, note how in a large set of cases the standard homogenization technique produces lesser analyte concentrations than the procedure involving the Wiley Mill/Riffle Splitter (WM/RS). Also, this table should also reflect the standard deviation in data associated with the reported averages for each analyte concentration. A more definite indication of analytical reporting limit should also be shown here. (One can infer from the presented information that the RL is about 12.5 ppm for most analytes, however.)

Response

1. Table 2-1 was revised and issued June 1999 as part of responses to EPA Region V comments. The revised pages are dated 5/14/99. The revised table includes standard deviation and individual cross section results for each compound where contaminants were detected above reporting limits.

Comment

2. After reviewing Table 2-1 data, one might conclude that the WM/RS is affecting the samples. The WM/RS may be increasing the surface area of the samples relative to samples prepared using the standard homogenization technique. This could have the effect of permitting more solvent penetration during soil extraction, with the result of higher analyte concentrations in environmental samples. Such a phenomenon would have an impact on the Day 0 samples especially, upon which an objective standard for % bioremediation/degradation is founded. (It might take a few days longer to degrade the contaminants to below the 90% removal/detoxification level if the WM/RS procedure is utilized.)

Response

2. Table 2-1 was revised on 5/14/99 which provides the individual cross section results for each compound where contaminants were detected above reporting limits. A consistently higher analyte concentration is not obtained with the WM/RS. The rate of degradation of the explosives will be proportional to the concentration and provided that the

measurements are made using the same homogenization technique, the rate of reduction is not anticipated to be impacted using either technique.

Actually, assuming that the surface area is greater using the WM/RS, it is likely that the duration to degrade the compounds to the 90% level would be less. If surface area was significantly increased using the WM/RS when the compost consists of large pieces of straw, manure, and soil there would be a higher concentration of analytes on Day 0. Then on Day Final when more thoroughly degraded compost exists, the WM/RS would not significantly impact the surface area on Day Final compost. This would result in a higher Day 0, and a lower or comparable Day Final result, which would reduce the days required to degrade the contaminants below the 90% removal/detoxification level.

Based upon the results obtained in relation to the cleanup objectives and the analytical techniques utilized, the results of the standard and WM/RS are considered comparable.

Comment

3. On page 2-6, the techniques used for rinsing equipment are stated. It should be clarified as to whether or not the WM/RS device was also decontaminated in this manner as well. Were any blanks taken as an indication of how effectively the WM/RS was cleaned? Note that in the last paragraph on page 2-14 it is mentioned that the approved technique for decontaminating field equipment is inappropriate for the WM/RS due to its delicate construction.

Response

3. The WM/RS equipment was not rinsed between samples and no rinseate blanks were collected for this equipment. The WM/RS equipment was decontaminated using a brush to remove course material and wiped clean to remove small particulates between samples. The method described in the QAPP is not appropriate because the bearings of this machine cannot come in direct contact with water.

Comment

4. In Table 2-2, page 2-9, given that a result was recorded for RDX (2,960P ug/kg), why is there a 0% RPD indicated for this analyte?

Response

4. The field duplicate sample did not show the presence of RDX above the reporting limit, therefore, no percent difference could be calculated.

Comment

5. Referring to page 2-10, 3rd full paragraph, (and Table 2-3 as well), it should be clarified whether the MS/MSD samples were prepared using the WM/RS, or through standard

homogenization. How did WM/RS QC data compare to analogous data prepared using the standard homogenization method? Also, in this same paragraph, there is a reference to the Day 5 sample, when shouldn't this refer to a Day 0 sample from S-005 instead? (I thought that Day 5 samples were not included in this study.)

Response

5. Page 2-10 was revised and issued June 1999 as part of responses to EPA Region V comments. The revised pages are dated 5/14/99. The revised text describes that three matrix spikes were preformed during the WM/RS sampling, two matrix spikes were performed on samples produced through regular homogenization, and one matrix spike was performed on a sample collected using the WM/RS. Table 2-3 was also revised with the revision dated 5/14/99.

   The reference to the Day 5 was incorrect and was changed to refer to a Day 0 sample from S-005.

Comment

6. Referring to the Summary, I am skeptical about conclusions stated in the 3rd paragraph concerning the perceived lack of bias between results generated from WM/RS samples versus samples derived using standard homogenization. SWOK doesn't perform a laboratory homogenization step which grinds the samples to particularly finer size upon arrival in the lab. It is apparently more of a disaggregation step, leading to the proportioning of a more representative sample. But it may be the case that the WM/RS does produce a finer particle size in the field, which increases the efficiency of solvent extraction in the lab. The ratio of 78% to 22% higher results achieved using the WM/RS does strike me as a "biased" value. Perhaps some discussion of the importance of the consequences should be initiated (and inserted into the document).

Response

6. If the assumption is made that the WM/RS produces a finer particle size in the field, which increases the efficiency of the solvent extraction in the lab, then there would be a more significant effect of using the WM/RS on Day 0 sampling. When the compost consists of large pieces of straw, manure, and soil decreasing the particle size would lead to higher surface volume and increased efficiency of solvent extraction. Therefore, there would be a higher concentration of analytes on Day 0. Then on Day Final when a more thoroughly degraded compost exists, the WM/RS would not significantly impact the surface area of the compost. The overall effect, would result in a higher Day 0, and a lower, or value comparable to standard homogenization Day Final value. By providing this "bias" to Day 0 samples, the days required to degrade the contaminants below the 90% removal/detoxification level would be reduced. The data reported for Day Final clearly shows that there is little difference between either homogenization technique. Based upon the results obtained in relation to the cleanup objectives and the analytical techniques utilized, the results of the standard and WM/RS are considered comparable.

Comment

7. There are a couple of typos in the final paragraph of the Summary presented on page 2-14. Note the word "extened" in the 4th from last line. In the 3rd line from end of page the word "be" should be deleted.

Response

7. The corrections have been made.

Comment

8. Text should be added explaining why the RDX MSD data in Table 2-3 is so poor.

Response

8. Text on Page 2-10 explains the table results and offers the probable cause for the levels outside acceptable limits for Day 0 sample results for the target compounds. An additional explanation was included in the responses to comments issued June 1999, Question/Response 4 and are summarized below:

   RDX spiking data is usually poor on Day 0 due to the high concentration of RDX initially found in the compost matrix relative to the spiking concentration. Concentrations of RDX initially in the sample are often more than 100 times the spiking concentration. At this level, the spike cannot be sufficiently distinguished from variability of the sample.

Field Test Kit Analysis

Comment

9. Referring to Table 3-1, the 11 out of 12 false negatives resulting for the field use of the RDX test kit for Day 60 samples does seem to be a highly significant outcome. This implies that a "nondetect" field result almost certainly means it will be detected in the laboratory on Day 60. Why even bother to use the test kit under these circumstances? Please clarify the text to indicate why the test kit would still be useful under these circumstances, referring to reporting limits (field vs. lab) and pertinent screening levels.

Response

9. The false negative readings are further discussed in the summary Section 3.5. Response 7 of Responses to EPA Region V Comments issued June 1999 and are summarized below:

   RDX has a reporting limit of 0.88 mg/kg in the field test kit, and a laboratory' reporting limit of 0.25 mg/kg by Southwest Laboratories. In Day 60 samples, the laboratory reported all 12 samples with RDX concentrations greater than 1.66 mg/kg and an average RDX concentration of 7.77 mg/kg. Since all the RDX concentrations were greater than 1.66 mg/kg, RDX should have been detected in the field test kits that have a reporting

limit of 0.88 mg/kg. The field test kits had one positive value of 1.1 mg/kg detected. The remaining eleven sample results have been flagged as false negatives for RDX.

Each one of the positive results were flagged by the laboratory with a "P" code, which represents a deviation of greater than 40% between the primary and secondary confirmation column. From the case narrative, Southwest laboratories stated, "Due to differences in the concentration of RDX in the quantitation and confirmation columns, some of the samples were randomly selected, re-dispensed, and re-analyzed. The concentrations of RDX in the re-analyzed samples were the same as the original analysis. Therefore, the original analysis was submitted." As stated by Southwest Laboratories, the re-analysis confirmed the original values determined from the primary column. The large difference between the primary and the confirmation column may be due to chromatographic interferences co-eluting with the target analyte. The levels were not detected in the field test kits which may indicate that these values are indeed interferences. In addition concentrations of RDX detected in Day 60 exceeded levels detected in Day 10, and Day 40 which may further demonstrate an interfering peak in the laboratory analysis.

Comment

10. Are RDX matrix 8330 column interferences a commonly experienced difficulty in day 60 samples? Why can't the laboratory adjust column conditions to circumvent this problem?

Response

10. Chromatographic interferences have not been experienced to any significant degree in previous testing. Chromatographic interferences exhibited in this study were at levels near the reporting limits and significantly below the industrial clean up levels. Because the clean-up levels are well above the laboratory reporting limits and concentration levels typically seen on Day Final, the interference levels should and have not presented any difficulties during routine operations.

    The laboratory followed standard operating procedures for calibration, quantification, and quality control procedures as established by EPA methodology. General chromatography specifications established in Solid Waste Method 8000 and HPLC analysis specified by Method 8330 were used to establish the standard operating procedure used by the laboratory.

Comment

11. On page 3-5, it is mentioned that the LCS and LCSD samples may consist of either clean soil or water spiked with known amounts of target analytes. It should be clarified which type of matrix was selected for this (soil) study by SWOK.

Response

11. The matrix type of the LCS and LCSD is comparable to the samples analyzed in the analytical batch. Compost and soil samples are prepared using clean soil as the LCS. Rinse blanks, field blanks and any other liquid samples are prepared in their own analytical batches with LCS and LCSD consisting of organic free deionized water.

Comment

12. Referring to page 3-15, 2nd paragraph, the text should be revised to indicate whether re-analysis of samples for RDX incorporated re-extraction steps. There is a typo in this paragraph. The word, "inferring" should be changed to "interfering".

Response

12. Response 9 of the Responses to EPA Region V Comments issued June 1999 addressed this comment and is summarized below. Re-analysis did not entail re-extraction. Re-analysis was performed by the laboratory to confirm values detected in the primary column because of the increased variability seen between the primary and secondary column. This analysis was performed within holding time, but was not reported by the laboratory. The high false negatives are most likely due to interferences seen in the analysis of RDX as discussed above in Response 9.

    The word interfering has been corrected.

Comment

13. The statement, "In cases where the laboratory detected either TNT or RDX below the level achievable by the appropriate field test kit, results were deemed to be in agreement...." is a bit confusing. Is this concept incorporated into data presented in Table 3-1? Does this mean that a false negative would not be recorded if the lab detected an analyte below the reporting limit of the (respective) field test kit?

Response

13. This is correct. Detection limit differences between the laboratory and the field test kits were already factored into account in the development of Table 3.1. False negatives are not recorded in Table 3.1 if the laboratory reported values were below the reporting limit of the field test kits.

<u>Appendices</u>

Comment

14. Just some random questions. In several injection reports, there is mentioned that the Calibration file was last modified on April 27, 1982. Can this be correct?

Response

14. This should be April 27, 1998. Records of calibration standards provided show that all calibrations were performed in 1998.

Comment

15. Also, it does appear if several other columns were used for both studies other than those identified in the approved QAPP & SWOK - method 8330 SOP. This creates difficulty in resolving the alleged RDX matrix contamination in the field Test Kit study noted for Day 60 samples. What were the accepted retention time windows for RDX in this study?

Response

15. Retention time windows are established for each instrument at the time of calibration. Calibration records for every instrument and every column have been provided for all analysis performed for this study which state the acceptable retention time window for each compound.

Comment

16. Why are there two separate or multiple injection reports provided for the confirmation column result when all the resulting peaks appear to have been resolved on one injection?

Response

16. Only one injection is performed on each column. The confirmation column in many instances uses two multi-compound calibration standards. The primary column uses a single multi-compound calibration standard. After a single injection was performed, half of the compounds are quantified using calibration A standards, and the remaining half of the compounds are quantified using calibration B standards. The two reports represent the two standards used in calibration.

Comment

17. It would be helpful if the sample name, designation, or scheme for naming samples (such as BIO-S-001-00-05-2-R2) would be inserted near the beginning of the Appendix such that one could envision more readily where in the pile the samples were taken from for each study.

Response

17. The nomenclature used for naming samples was identified in the approved QAPP. Standard Operating Procedure 3.0 found in Appendix A discusses the scheme for naming samples, and was followed for this study.

Comment

18. In Appendix E, Form 1 for EPA sample no. BIOS00515031R2, the result for SWOK is given as "1,000 U ug/kg". However information on the associated injection report indicates the result should have been 1,994 ug/kg. Please explain (or resolve) this apparent discrepancy.

Response

18. The injection report for the primary column indicates that RDX was quantified at 1,994 ug/kg. Referring to the stamped page numbers of the analytical data package found on the bottom right hand corner of the page, the chromatogram for this injection is provided in Appendix E on page 19. This chromatogram shows a wide peak that actually extends beyond the retention time window. On the confirmation column which is provided on page 22, RDX was not identified within the retention time window. Because the qualification of RDX was not made on both the primary and secondary column, the analyte was not reported, therefore the reporting limit of 1000 ug/kg was reported with a "U" data qualifier.

Comment

19. In Appendix P, injection report for sample BIO-N-30%-60-A1, isn't the peak for RDX a little outside the retention window for RDX, as deferred to the calibration data associated with this study? (Please explain.)

Response

19. The primary column's retention time (RT) window for RDX is 7.36 to 7.49 minutes. The retention time for the peak quantified as RDX was 7.536 which is outside of the window for the primary column, however the analyst's experience and judgement were utilized for interpretation of this data because it was slightly outside of the RT window. This judgement made by the analyst is described on page C2-40, item 7.4.8 of the approved QAPP.

Comment

20. Referring to Appendix P, injection report for sample BIO-N-30%-60-A1, please clarify which is the confirmation data for samples & calibration? What are the accepted RDX windows for both primary and confirmation columns for this run? Note that some of the retention times do not correspond to page 13 of 16 (p. C2-43) in the approved QAPP. In order to evaluate the claim that matrix interferences were at large in the case of the Day 60 RDX samples, more information must be provided concerning QC acceptance criteria for RDX.

Response

20. Referring to the stamped page numbers of the analytical data package found on the bottom right hand corner of the page, the primary column injection report is on page 23 and the confirmation column injection report is on page 25 and 27 representing the

quantitation of the two calibration standards used in the confirmation column. The primary column was calibrated on 6/30/98 and calibration information begins in Appendix Q on page 159. The primary column's retention time (RT) window for RDX 7.36 to 7.49 minutes. The retention time for the peak quantified as RDX was 7.536 which is outside of the window for the primary column. The analyst's experience and judgement were utilized for interpretation of this data because it was slightly outside of the RT window, and the worst case was presented in the data. The secondary column was calibrated on 7/16/98 and the calibration information begins in Appendix Q on page 230. The RT window for RDX was 7.46 to 7.89 and the RT for the peak quantified as RDX was 7.648 which is inside the window for the confirmation column. The calibration procedures used by the lab are identified on page C2-39 of the approved QAPP and were followed during this analysis. Many of the RDX peaks on the primary column are slightly outside the RT window, but are within the secondary column window. The analyst used his/her judgement to identify all peaks as positive values flagged with a "P" codes to identify the large difference between the quantitation of the two columns. By identifying that almost every RT for the primary column is outside of the window by approximately 0.05 minutes and that there is greater than 40% difference between the quantitation of the primary and confirmation column, a matrix interference is most likely causing some chromatographic interference which cannot be resolved by the methodology.

Audit Demonstration Report
Field Test Kits and Wiley Mill/Riffle Splitter
Full-Scale Bioremediation
NSWC Crane, Crane, Indiana

ERRATA SHEET

Additional comments from EPA have been addressed in the enclosed response to comments. The following pages incorporate changes made to the Audit Demonstration Report as a result of the EPA comments.

1. Remove binder cover and spine and discard. Replace with attached "green-colored" binder cover and spine.

2. Remove inside cover and signature page and discard. Replace with attached cover and signature page.

3. Remove Page 2-9 and 2-10 dated 5/14/99 and discard. Replace with new pages 2-9 dated 5/14/99 and 2-10 dated 3/03/00.

4. Remove page 2-13 and 2-14 dated 5/14/99 and discard. Replace with new page 2-13 dated 5/14/99 and 2-14 dated 3/03/00.

5. Remove page 3-14 and 3-15 dated 5/14/99 and discard. Replace with new page 3-14 dated 5/14/99 and 3-15 dated 3/03/00.

5090
Ser 095/0053

09 MAR 2000

The letter Ser 095/0053 was for the submittal of response to comments and replacement pages for the Bioremediation Audit Demonstration Report. The replacement pages have been incorporated into the previously submitted report on 03/29/99.

I certify under penalty of law that this document and all attachments were prepared under my direction or supervision in accordance with a system designed to assure that qualified personnel properly gather and evaluate the information submitted. Based on my inquiry of the person or persons who manage the system, or those persons directly responsible for gathering the information, the information submitted is, to the best of my knowledge and belief, true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment for knowing violations.

Phillip R. Keith, Acting

SIGNATURE

DIRECTOR, ENVIRONMENTAL PROTECTION DEPARTMENT
BY DIRECTION OF THE COMMANDER

TITLE

3/9/00

DATE

Enclosure (2)