



KAFB BFFS
ST-106 and SS-111

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 6
1445 Ross Avenue, Suite 1200
Dallas, Texas 75202-2733

August 8, 2014

MEMORANDUM

FROM: *Laurie King*
Section Chief
Federal Facilities Section (6PD-F)

TO: John Kieling
Hazardous Waste Bureau Chief
New Mexico Environment Department

RE: **RCRA Facility Investigation Reports, Groundwater Zone and Vadose Zone, Bulk Fuels Facility Spill, Solid Waste Management Units ST-106 and SS-111, Kirtland Air Force Base, Albuquerque, New Mexico, March 2014**

As requested by the New Mexico Environment Department (NMED), the United States Environmental Protection Agency (EPA) is providing comments on the following five (5) specific areas of the above referenced reports:

1. Compound Specific Isotope Analysis
2. Shortcomings of the Groundwater Model
3. Radius of Influence of the SVE System
4. Biodegradation of Contaminants
5. Slug Test Data

These comments do not reflect all that may be forthcoming from the EPA on the RFI Reports, but are provided to NMED for their consideration. If you have any questions concerning these comments, please contact Paul Torcoletti at 214-665-6494 or at torcoletti.paul@epa.gov, Tara Hubner at 214-665-7246 or at hubner.tara@epa.gov, or Scott Ellinger at 214-665-8408 or at ellinger.scott@epa.gov.

Compound Specific Isotope Analysis (CSIA)

On July 1, 2014, the EPA's National Risk Management Research Laboratory in Ada, Oklahoma ("Ada lab") provided their comments on the CSIA and biological parameters analysis. The memorandum is provided as Attachment 1.

Shortcomings of the Groundwater Model

1. **Boundary Conditions (North, South, East, & West Boundaries):** Simulated groundwater flow in the CB&I local model adjacent to specified head boundaries is inconsistent with the expected curvature of the cone of depression existing in southeast Albuquerque.

KAFB4220



- Examples of inconsistent boundary flow are shown in figure 4-9 (for years 1980 and 1990) and figure 4-10 (1995, 2000, and 2005). Given the presence of the cone of depression in S.E. Albuquerque, the expected simulated pattern should be concave (inward) from each boundary
 - Local model flow near specified boundaries suggests a fundamental problem with conceptualization of the groundwater system, such as a lack of hydraulic connection between flow boundaries and areas of major groundwater extraction such as the Ridgecrest and Burton well fields.
 - The installation of piezometers at key locations near local model boundaries would provide important head data for defining boundary conditions. Additional data are necessary because boundary flow problems were not overcome during model calibration with existing data. Boundary problems may have been caused by the large difference in scale between the USGS regional model and the local model. Head data from the Del Sol Divider and Jerry Cline Park wells can provide some data for the north boundary. Piezometers are needed for the south, west, and east boundaries.
2. **Vertical Discretization with Subdivided Basin Floor Fluvial Deposits:** The basin floor fluvial deposits (QTsa) in Connell et al. (1998) are subdivided into A1 and A2 stratigraphic units based on electric log responses. These units can be identified in Miles 1, Burton 4, Charles 5, Charles 6, Kirtland 15, Kirtland 16, the VA hospital well, Ridgecrest 5, and the Trumbell wells.
- A1 and A2 have lower hydraulic conductivity than overlying and underlying strata based on visual examinations of well cuttings (NMED staff). A rough estimate is ten to one hundred times less. Potential effects of A1 and A2 on flow and transport (especially EDB transport) to production wells should be examined.
 - A1 and A2 could be included as either dipping or horizontal geologic strata, but dipping layers will intersect production well screens at different depths than horizontal layers. Although the USGS regional model used horizontal layers, dipping layers seem more appropriate for the local model.
- (Connell, S.D., Allen, B.D., and Hawley, J.W., 1998, Subsurface stratigraphy of the Santa Fe group from borehole geophysical logs, Albuquerque area, New Mexico: New Mexico Geology, Vol 20, No. 1.)
3. **Pattern of Hydraulic Conductivity:** Using the pattern of hydraulic conductivity contained in the USGS regional model for the CB&I local model omits important aquifer test conductivity data collected from Ridgecrest and Burton wells. In addition, the USGS regional model report (McAda and Barroll, 2002) states that the regional model is most sensitive to hydraulic conductivity. Utilizing the broad pattern of hydraulic conductivity from the regional model in the local model carries over potential limitations to local model.
- The USGS regional model is not detailed enough to include important data and modeling assumptions for depositional channel geometry created by the ancestral Rio Grande for the EDB

plume area. Further, it is not clear whether anisotropy in the local model sufficiently accounts for the north-south orientation of channel deposits.

- Developing potential designs for hydraulic controls of the EDB plume will require increased definition of hydraulic conductivity as described above.

(McAda, D.P., and Barroll, P., 2002, Simulation of ground-water flow in the middle Rio Grande basin between Cochiti and San Acacia, New Mexico: U.S. Geological Survey Water-Resources Investigations Report 02-4200).

4. **Tijeras Arroyo and the Kirtland Perched Zone:** Tijeras arroyo and the Kirtland perched zone are important hydraulic features that potentially affect the southern local model boundary. A modeling analysis of sources of water to the perched zone at Sandia National Laboratories and connections to the regional aquifer are described in Balleau 2002 (SAND-2011-0005P). The nearness of these hydraulic features to the local model indicates an evaluation is necessary of how they may affect boundary conditions. (Balleau Groundwater, Inc., 2002, Model of a perched zone of saturation at Sandia National Laboratories, New Mexico.)
5. **Boundary Conditions, Pathlines, and EDB Source Release Time:** RFI section 5 describes the use of particle pathlines to estimate the time of EDB source term release by noting differences in pathlines between 1970 and 1980. Considering that the determination of local model boundary conditions may be problematic as noted above for the 1980 period, the pathline analysis and estimate of EDB release time needs additional consideration. A sensitivity analysis of local model boundary conditions would help place limits on the range of possible EDB release times.
6. **Model Sensitivity Analysis Needed:** The RFI should include a model sensitivity analysis. This includes describing the approach to the sensitivity analysis, presenting the input parameters selected for the investigation (and which ones were excluded), how model boundary conditions were treated during the analysis, the ranges of parameters tested, a description of the relevance of sensitivities to local model objectives, and other factors. Determining local model sensitivities to changes in boundary conditions, hydraulic conductivity, and pumping rates are especially important.
7. **Assumptions for Production Well Pumping Rates:** A number of actual and assumed production well pumping rates and scenarios have been provided by the Albuquerque-Bernalillo County Water Utility Authority, Kirtland AFB, and the Veterans Administration. These include pumping during a selected reference year, a high-flow pumping case, and a potential worst case scenario. The RFI should thoroughly discuss how rates were applied for each of these scenarios, and the resulting output for flow and mass transport.
8. **Running Mass Transport using both Calculated and Mapped EDB Concentrations:** The local model generates a calculated EDB plume based on fuel contacting the water table in approximately 1980. The calculated plume for 2013 is shown in figure 6-3. The 2013 EDB plume as mapped from monitoring well data (in quarterly reports) has a substantially different geometry and contaminant distribution than the plume in figure 6-3. The CB&I local model could be strengthened by

performing a sensitivity analysis using the both the 2013 mapped concentrations, and the 2013 calculated concentrations, as starting concentrations and then comparing output between the two.

9. **Reproduction of 2013 EDB Plume Extents:** Page M-20 of the RFI report states that overall, transport simulations for both EDB and benzene were able to reproduce the year 2013 respective plume extents. However, the EDB plume extent shown on the map is actually 1000 feet or so further eastward than the calculated/modeled plume extent.
10. **Modeling Objective:** The objective of Kirtland's modeling is to develop a local groundwater flow and solute transport model for use in simulating current and future migration of the EDB and benzene plumes. The RFI contains no results for future transport. Figures 6-2 through 6-7 show EDB and benzene plumes through 2013.

Radius of Influence of the SVE System

Appendix G – ROI Test Report

1. Section 5.1 - Please explain why an "edge of the ROI" value of 0.2 in WC was used in determination of the ROI. Why was this method chosen to determine ROI instead of alternative approaches?
2. Section 7 – The report states "The decreasing ROI with depth observed during the majority of the tests indicates that the vadose zone at SWMU ST-106 is anisotropic, with vapor flowing more freely horizontally than vertically". In the tab just prior to this statement, the remediation monitoring results of the CATOX SVE system are shown. Based on these results, it appears that the ROI increases with depth.
3. General Comments – How do the resulting ROIs compare with the geology? Could there be a coarsening of lithology with depth causing a higher ROI? Also what was the relation between the extraction well screen depth and the observation well screen depths? Did the tests where the extraction well and observation wells were screened at similar depths show a quicker response and/or higher measured vacuum? This could be a sign that preferential air flow is horizontal. Which set of test data provided representative data for determining ROI for current and future SVE corrective measures?

Biodegradation of Contaminants

The CSIA and biological parameters analysis comments from Ada lab (Attachment 1) include comments on biodegradation of benzene and ethylene dibromide (EDB).

Slug Test Data

General Comments

1. Properly designed and analyzed slug tests are useful to gather discrete, order of magnitude estimates of hydraulic conductivity and to perhaps identify spatial variations in hydraulic conductivity within an area of interest. Slug tests should continue to be performed on new monitoring wells installed at

the KAFB site. However, the limitations of slug test data are well recognized by the scientific community and environmental practitioners and should be articulated in Appendix H-1. Consider the following:

- EPA (1993) emphasizes that slug tests provide very limited information on the hydraulic properties of the aquifer and often produce results which are only accurate within an order of magnitude. This guidance further observes that many experts believe there is too much reliance on slug tests in site characterization and contamination studies and recommends that slug tests be performed in initial site studies to assist in developing a site conceptual model and to inform the design of pumping tests. Kruseman and de Ridder (1994) observe that “...slug tests cannot be regarded as a substitute for conventional pumping test. From a slug test for instance, it is only possible to determine the characteristics of a small volume of aquifer material surrounding the well, and this volume may have been disturbed during well drilling and construction.” Butler and Healey (1998) report that “...a large body of field data indicates that the hydraulic conductivity (K) estimates obtained from a series of slug tests is, on average, considerably lower than that obtained through pumping tests in the same formation.” The Groundwater RFI Report Appendix H-1 states that the slug test data can be used to “...assist in the design of subsequent pumping tests.” Additional aquifer characterization is needed and pumping tests are the most appropriate technique to obtain defensible hydrogeologic parameter data necessary to support groundwater modeling efforts, remedy evaluation and remedy selection. Reasonable agreement between pumping test and slug test results will likely increase overall confidence in use of the slug test dataset. (US EPA, 1993. *Suggested Operating Procedures for Aquifer Pumping Tests*, United States Environmental Protection Agency, Office of Research and Development, February) (Kruseman G.P. and de Ridder, N.A., 1994, *Analysis and Evaluation of Pumping Test Data*, 2nd Edition, International Institute for Land Reclamation and Improvement.)
 - Per Butler and Healey (1998), the degree of well development typically performed to produce representative samples for laboratory analysis, may not be sufficient to adequately restore damage to the formation caused by drilling and well installation. Incomplete development may result in “skin effects” that can be particularly pronounced in slug test analysis (versus pumping tests). Stanford and McElwee (2000) recommend that well development be evaluated by repeated slug testing rather than typical methods such as parameter stabilization and turbidity measurements. The degree to which wells at the fuel spill site were adequately developed for the purposes of slug testing is undetermined and introduces uncertainty regarding the reliability of slug test results. (Butler J.J. Jr. and Healey J.M., 1998, *Relationship Between Pumping-Test and Slug-Test Parameters: Scale Effect or Artifact?*, *Ground Water*, Vol. 36, No. 2) (Stanford K.L. and McElwee C.D., 2000, *Analyzing Slug Tests in Wells Screened Across the Water Table: A Field Assessment*, *Natural Resources Research*, Vol. 9, No. 2.)
2. Include slug test-related field notes, forms and recovery data (electronic files or print outs) in the Groundwater RFI Report. Without this information, a reviewer cannot adequately assess slug test

variables presented in Table 5-9 and on the individual slug test solutions in Appendix H-3, such as screen length (for water table wells), water column height and initial height (H_0).

3. Notwithstanding concerns regarding the slug test results presented in the Groundwater RFI Report, properly conducted and analyzed slug tests can provide useful point estimates of hydraulic conductivity, especially when performed at multiple locations and depths. It appears that additional qualitative and/or quantitative spatial analysis could have been performed beyond simply placing hydraulic conductivity estimates on a map (Figure H-5). Are there any statistically significant differences between shallow, intermediate and deep populations? Are there any lateral and/or vertical spatial variations that may warrant additional consideration or study? For instance, three of the lower hydraulic conductivity estimates in the shallow zone are from the three shallow wells downgradient of the EDB plume (KAFB-106201, 204 & 207). The available K estimates also suggest that hydraulic conductivity increases with depth in this same area based upon slug test results from the deep zone wells (KAFB-106203, 206 & 209). Use of these slug test data should be maximized within the confines of their limitations.

Specific Comments

4. The list of slug tested wells provided in Table 4-4 does not match the list of wells presented in Table 5-9, with several (eleven) wells omitted from Table 4-4. Please resolve this discrepancy.
5. It is apparent that the text of Appendix H-1 provided to the EPA on optical disk was not updated to reflect all slug test activities as of the date of the RFI Report submittal. Resolve the discrepancies identified in the following bullets:
 - Groundwater RFI Report Appendix H makes reference to Figures H-1 through H-5 and Table H-1, none of which were included in the electronic copy provided to the EPA, nor were they identified in on-line postings of the RFI report. Presumably, these tables and figures are the same as those referenced in Appendix H of recent Quarterly Reports. The footers for the figure and table title pages in RFI Report Appendix H reference the 2011 third quarter report.
 - Groundwater RFI Report, Section 5.2.5: The hydraulic conductivity values summarized in the first bullet match what is presented in Table 5-9, but do not match the information contained within Appendix H.
 - Appendix H-1, Section 1.2: The text indicates that 36 mechanical slug tests were performed in 18 wells. According to Table 5-9 (and the fourth quarter 2012 quarterly report) mechanical slug tests were performed in 26 wells.
 - Appendix H-1, Section 1.3: The text indicates that 76 pneumatic slug tests were performed in 19 wells. According to Table 5-9 (and the fourth quarter 2012 quarterly report) pneumatic slug tests were performed in 22 wells.
 - Appendix H-1, Section 1.5.2: The hydraulic conductivity values presented in the first bullet are not consistent with Table 5-9.
6. Appendix H-1, Section 1.4.1: This section describes analytical assumptions and changes to those assumptions through testing and analysis of slug test data. It would be helpful to better articulate

how changes in assumptions affect the resulting analysis and conductivity estimates. For instance, problems were identified with the assumption of instantaneous change in head. This section would be improved by explaining how the erroneous early time data could affect the slug test results (e.g. bias estimates of K high or low, etc.) and how the effect of this variance was minimized in the ensuing analyses and selection of K values.

7. Appendix H-1, Section 1.4.1.2: The sensitivity analysis performed demonstrating that aquifer thickness was not a significant input for analysis should be provided to substantiate this assertion.
8. Appendix H-1, Section 1.4.1.2: What is the basis for selecting the filter pack thickness as the aquifer thickness? The filter pack and surrounding natural formation located above or below the screened interval is not developed and should not be included. Therefore, in the absence of knowing the actual aquifer thickness, it seems more appropriate and consistent to use the saturated screen length as the aquifer thickness. This is consistent with the fact that the slug test is only affecting a small vertical segment of the aquifer coincident with the length of the saturated well screen.
9. Appendix H-1, Section 1.4.1.3: Please describe the potential causes and result of "skin effects" on the applicable slug test analyses.
10. Appendix H-1, Section 1.4.3: The lack of correlation of slug test results with laboratory hydraulic conductivity values and field characterization of aquifer materials is not surprising considering that the vast majority of remolded laboratory samples and field characterizations of soil type were collected/observed after the samples had traveled 500+ feet up the drill string in the return air stream. Accurate sampling or visual characterization of subsurface soils collected in this manner can be complicated by variations in uphole air velocity, lag time of returned-cuttings samples, sample mixing and balling as the cuttings are moved uphole in the return air stream, periods of lost circulation and no cuttings return, uncertainty regarding the validity of the cuttings and depths from which they were drilled, and skill/experience of both the driller(s) and the borehole logger(s).
11. Section H-2: This section regarding field verification of test procedures is underdeveloped and it is difficult to understand the evaluation that was performed. The description and information provided is insufficient to substantiate the assertions made. For instance, what is the significance of values being within "two standard deviations of the mean"? A table (or tables) devoted to these comparisons, including the results of statistical analyses performed, would be a significant improvement.

Table 5-9

12. Recommend that the static depth to water measurement (below ground surface) collected just prior to the start of each slug test be included in Table 5-9.
13. Suggest that the relative depth range (shallow, intermediate, deep) for each well be included in this table.

14. Apparent rounding differences were noted throughout Table 5-9 and the slug test analysis sheets, to include H_0 values and well specifications (casing and borehole radius). While the effect on the actual analysis is negligible, the inconsistency is confusing.
15. For the KAFB 10610, slug in test, the "initial height" is listed as 2.4 ft, which is assumed to be the initial displacement (H_0). Examination of the slug test analysis sheets for this well indicates values ranging from 3.36 to 4 ft. Please explain: 1) where the value of 2.4 came from, and 2) why there are different H_0 values for a single falling head test?
16. For the KAFB-10610 slug out test, the H_0 value listed is 2.8 feet, which matches the value for the selected best fit solution. However, the slug test analysis sheets for this test show range of H_0 values from 2.815 to 3 ft. Is this a function of rounding?
17. For KAFB-106032 only the QC-IN and QC-OUT data are provided – the initial slug test is omitted. Please explain why these data were excluded or add them to the table. Examination of the slug test analysis sheets for the initial "slug in" test indicates an H_0 value of 10.12 ft. This seems excessively large compared to other tests using the same size slug in 4-inch diameter wells. Please explain this apparent discrepancy.
18. Appendix H-1 states that the sand pack thickness was used to represent aquifer thickness. For wells screened across the water table, the aquifer thickness is often greater than the water column height. While it is known that the aquifer extends below the completion depth of all monitoring wells, it is confusing to base the aquifer thickness on the length of a filter pack that is partially unsaturated. As stated previously, if the sensitivity analysis indicates that aquifer thickness is not an important variable, then consider consistently using the saturated screen length as the aquifer thickness so that all analyses are performed on the same basis.
19. Even when using the filter pack length as a substitute for aquifer thickness, there are inconsistencies in how the filter pack length was established – in some cases it was based only on the length of the 10/20 filter pack whereas in other cases the overlying 20/40 filter pack was included. While inconsequential with respect to the end result, the inconsistency is confusing.

Review of Slug Test Analysis Sheets (H-3)

20. With the exception of KAFB-106160, -106161 and -160201 through 209, the well radius was set equal to the casing radius for all slug test analyses, whereas the borehole radius was used as the well radius for the eleven wells identified above. Use of the borehole radius as the well radius is the accepted industry standard for wells with filter packs (Butler, 1997). For the KGS model with skin effect, the well skin radius was set equal to the borehole radius, which is appropriate. What is the basis for the difference in approach and what affect does this have on slug test results? The analyses should be performed consistently for all wells and the well radius should be set equal to the borehole radius. (Butler J.J. Jr., 1997, The Design, Performance, and Analysis of Slug Tests, Lewis Publishers)

ATTACHMENT 1

ADA LAB CSIA REVIEW MEMO



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
NATIONAL RISK MANAGEMENT RESEARCH LABORATORY
GROUND WATER AND ECOSYSTEMS RESTORATION DIVISION
P.O. Box 1198 Ada, OK 74820

OFFICE OF
RESEARCH AND DEVELOPMENT

July 1, 2014

MEMORANDUM

SUBJECT: Review of Compound-Specific Isotope Analysis (CSIA) and Biological Parameters Analysis, Kirtland Air Force Base, New Mexico (14-R06-002)

FROM: David S. Burden, Ph.D., Director 
Ground Water Technical Support Center

TO: Tara Hubner, P.G.
Environmental Scientist
U.S. EPA Region 6

In response to your request, EPA's Ground Water Technical Support Center (GWTSC) has completed a technical review for the Kirtland Air Force Base Site, New Mexico. Specifically, the review focused on reviewing documents concerning compound-specific isotope analysis (CSIA) and biological parameters sampling results from samples of ground water from Kirtland Air Force Base (KAFB; the Site), and associated portions of Albuquerque, New Mexico. The review was conducted by Dr. John T. Wilson (microbiologist and subcontractor to the Dynamac Corporation) and Dr. Dan Pope of the Dynamac Corporation a contractor to the GWTSC. I have reviewed the comments and concur with them. If you have any questions, please contact me at your convenience.

Introduction

The GWTSC was tasked to determine if (1) the sampling results are usable for assessing the degradation of ethylene dibromide (EDB) and benzene in ground water at the Site, and (2) based on the results is degradation of EDB and benzene occurring.

Specific questions requested by EPA Region 6 to be considered in this review are:

Were samples collected at the appropriate locations within the plume to determine if degradation is occurring? If not, what locations would be more appropriate?

Were the appropriate analytical methods used for the CSIA sampling (i.e. separating EDB from the other fuel components by two-dimensional gas chromatography)?

Following a conference call with staff of EPA Region 6, the following questions were requested to be considered:

What comments or suggestions could be provided that would improve the documentation of the data quality of the CSIA analysis of subsequent samples?

How many additional times should the site be sampled for CSIA analyses before the site is adequately characterized with respect to fractionation of benzene and EDB during degradation of benzene and EDB in ground water?

The site-related documents reviewed or used for additional site information provided by EPA Region 6 included the following information:

- *Figure 5-52 Sample Locations For EDB And Benzene CSIA Analyses And Biological Parameters, Third Quarter 2013 Bulk Fuels Facility Kirtland Air Force Base, New Mexico. (Figure 5-52)*
- *KAFB-013-0008c_App L_GW Degradation Analysis.pdf. (GW Degradation Analysis).*
- The following attachments to *KAFB-013-0008c_App L_GW Degradation Analysis.pdf.*
 - *KAFB_AppL_All_figures.pdf*
 - *Attachment 1 Benzene Regression.pdf*
 - *Attachment 2 EDB Regression.pdf.*
- Final reports of analysis of stable isotope ratios of carbon in benzene and EDB, and concentrations of benzene and EDB with the following titles:
 - *43132 Final Reports.pdf* Collectively (ZymaX Final Reports)
 - *43133 Final Reports.pdf*
 - *43135 Final Reports.pdf*
 - *43136 Final Reports.pdf*
 - *43137 Final Reports.pdf*
 - *43141 Final Reports.pdf*
 - *43143 Final Reports.pdf*
 - *43146 Final Reports.pdf*
 - *43172 Final Reports.pdf*
 - *43178 Final Reports.pdf*
 - *43181 Final Reports.pdf*
 - *43186 Final Reports.pdf*
 - *43194 Final Reports.pdf*
 - *43201 Final Reports.pdf*

The following information was downloaded from a U.S. Air Force web page identified by EPA Region 6.

- *Ground Water and Soil Analytical Results Quarterly_Rpt_July-Sept 2013_ALLTables.pdf* (GW Concentrations Sept 2013)

The following information was consulted for context:

- *SIMULATED MASS TRANSPORT OF 1,2-DIBROMOETHANE IN GROUNDWATER OF SOUTHEAST ALBUQUERQUE, NEW MEXICO, prepared for New Mexico Environment Department by Scott Ellinger, U.S. EPA Region 6. Draft September 16, 2013.* (GW Mass Transport Model).

In 1999, a jet fuel leak was discovered at the KAFB Bulk Fuels Facility (BFF) Spill site. Located within the western portion of KAFB, the BFF has two solid waste management units (SWMUs) designated as ST-106 and SS-111. The component of the BFF Spill remediation effort related to investigation and remediation of the vadose zone near the Former Fuel Offloading Rack (FFOR) is designated as ST-106. The non-aqueous phase liquid (NAPL)-impacted ground water component of the project is designated as SS-111. Benzene and EDB have partitioned from the NAPL to moving ground water, and formed plumes of benzene and EDB that extend to the northeast in the direction of water supply wells. The primary concern is whether benzene or EDB contamination can reach water supply well KAFB-3 on KAFB or the City of Albuquerque water supply wells Ridgecrest 3 or Ridgecrest 4.

Summary and Recommendations

After review of the available information, It was determined that samples were collected at the appropriate existing wells within the plume to determine if degradation is occurring. However, the wells KAFB-106105 and KAFB-106106 were available and perhaps could have provided useful data.

A determination that biodegradation is occurring requires a comparison of samples at the source of contamination where the extent of degradation is minimal to the samples down gradient of the source where degradation should be more extensive. It was determined that the number of samples in the source and the number of samples down gradient of the source were adequate to determine whether biodegradation of EDB and benzene was occurring.

Based on the reported isotopic fractionation of benzene and EDB, as much as 90% of the benzene and 77% of the EDB that was originally present (i.e., introduced into the ground water from the fuel release) in the ground water was degraded. The remainder of the attenuation can be attributed to a non-fractionating process such as dilution in the well.

After comparing the standard operating procedure (SOP) that was used for the KAFB CSIA analysis of EDB and benzene to the recommendations in the U.S. EPA guide for analysis of

stable isotopes (Hunkeler et al., 2008), we found that insufficient information was available in the SOP to determine whether appropriate analytical methods were used for the CSIA sampling.

Based on review of the KAFB CSIA SOP and the KAFB CSIA analytical data reports, it is unlikely that EDB was separated from the other fuel components by two-dimensional gas chromatography, which is the method outlined in Wilson et al. (2008) to attain complete separation of EDB from the petroleum hydrocarbons. If the compounds are not separated, the values determined for the stable isotope ratio of EDB will be in error. The KAFB CSIA analytical reports indicated that there were problems with the CSIA analysis when petroleum hydrocarbons are present. That is, all of the CSIA data reviewed from the Site ground water with high concentrations of EDB and high concentrations of petroleum hydrocarbons were flagged with either a J (less than optimal reproducibility) or a U (a ratio could not be determined).

Hunkeler et al. (2008) recommends that wells at a site be sampled for CSIA in three phases: a preliminary sampling to determine if the organic compounds are fractionating, a main investigation to understand the distribution of fractionation and thus degradation at a site, and a long term control to document that degradation continues over time (Section 5.3). Hunkeler et al. (2008) recommends that the main investigation be done in two campaigns. Each well should be sampled twice with several months of elapsed time between the sampling campaigns. This provides statistical control on the variation in isotopic fractionation in each well. The reviewers consider the data presented in the GW Degradation Analysis to be the first campaign of the main investigation. It is recommended that the wells at the Site be sampled and analyzed for CSIA a second time before EPA makes any decision about the contribution of natural biodegradation of EDB to MNA at the site.

It is recommended that the following wells be sampled as part of the second campaign of the main investigation.

Well Number (prefixed by KAFB-)

10610	106035	106064	106088
10614	106036	106070	106089
10617	106037	106072	106092
10619	106042	106076	106105
10625	106055	106082	10628-510
106022	106057	106086	106105
10610	106035	106064	106106

If MNA is selected as the remedy for EDB in ground water at KAFB, it is recommended that the Site be resampled for CSIA analysis every five years.

The reviewers suggest that the SOP for CSIA analysis of EDB and benzene should be examined and updated as needed to provide adequate documentation of the data quality for CSIA analysis. The SOP should be examined to determine if it provides baseline separation of EDB from the

petroleum hydrocarbons for each sample that is analyzed (See Figure 2.2 of Hunkeler et al. (2008) for an example of the necessary baseline separation).

As described in Section 2.4.3 of Hunkeler et al. (2008), a series of working standards with decreasing concentrations should be analyzed to determine the concentration threshold or working limit for EDB when analysis is done using the SOP. If the concentration threshold or working limit is higher than 0.05 µg/L, it is recommended that the SOP be modified to attain a concentration threshold or working limit of 0.05 µg/L.

General Comments

The reviewers found that the number of samples in the source and the number of samples down gradient of the source were adequate to determine whether biodegradation of EDB and benzene was occurring.

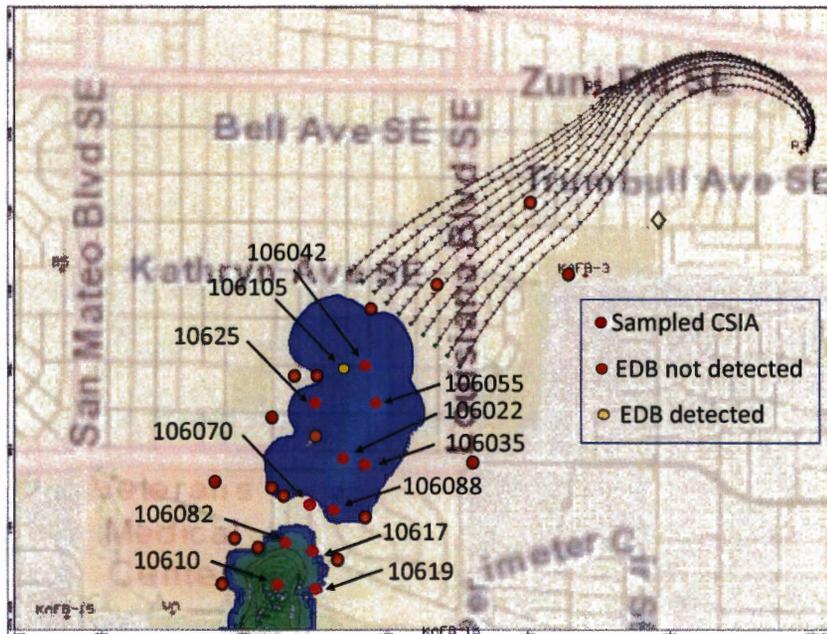
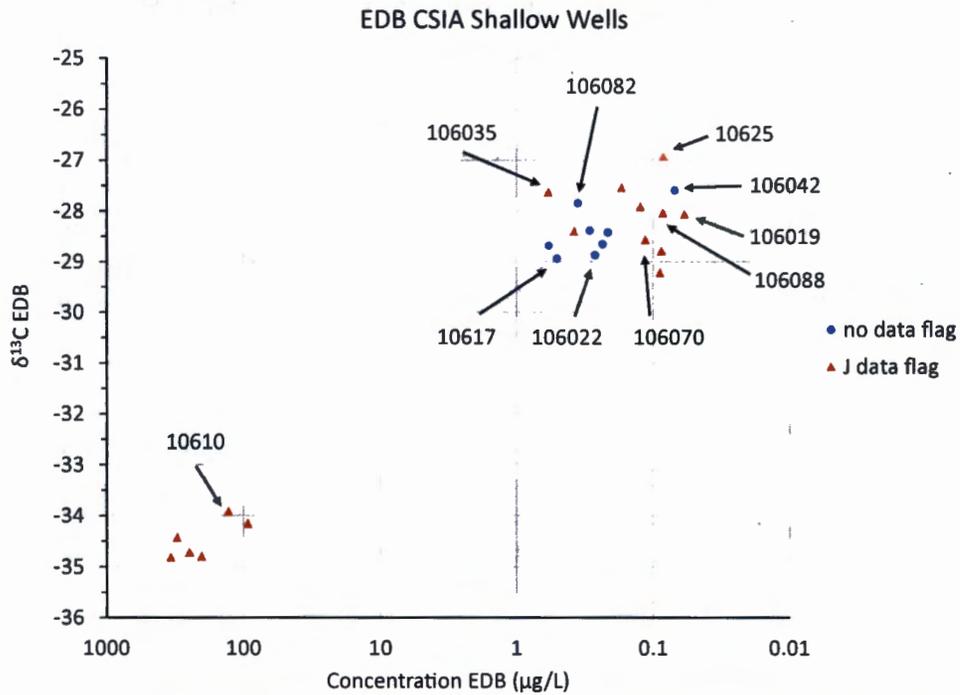
To evaluate the extent of fractionation of EDB and the reduction in concentration of EDB against the location of the sampling point in the flow of ground water to potential water supply wells, the reviewers located the wells that were sampled for CSIA within figures that predicted the flow of ground water from the BFF to City of Albuquerque wells Ridgecrest 3 or Ridgecrest 4. Data and figures were compiled from Figure 5-52, GW Degradation Analysis, GW Mass Transport Model, and GW Concentrations Sept 2013.

The flow at the water table is presented in Figure 13 of the GW Mass Transport Model, and the flow deeper in the aquifer at the level of well screens of the city wells is presented in Figure 12 of the GW Mass Transport Model. The data overlay for flow near the water table is presented in Figure 1. The data overlay for flow at depth is presented in Figure 2. Each figure also has a chart that compares the stable carbon isotopic ratio of EDB ($\delta^{13}\text{C}$) against the concentration of EDB at various locations. The chart plots all the data that were available. The data for wells that sample the shallow aquifer are labeled in Figure 1 and data for wells that sample the intermediate and deep aquifer are labeled in Figure 2.

Examination of the chart in Figure 1 demonstrates that the values of $\delta^{13}\text{C}$ and concentrations fall into two distinct and well-separated regions. If the concentration of EDB is near or greater than approximately 100 µg/L, the value of $\delta^{13}\text{C}$ varies from -35‰ to -34‰. The samples were taken from the area that has residual fuel hydrocarbons. If the concentration of EDB is less than approximately 1µg/L, the value of $\delta^{13}\text{C}$ varies from approximately -29‰ to -27‰. These samples were taken from the area that does not have residual fuel hydrocarbons. There are no samples with concentrations between 100 and 1µg/L and no samples with values of $\delta^{13}\text{C}$ between approximately -34‰ and -29‰.

Whatever process causes the reduction in concentration occurs rapidly. Compare the location of wells KAFB 10610 and KAFB 106082 in the flow field and in the chart in Figure 1. It should take approximately five years for water to flow from well KAFB 10610 and KAFB 106082. The concentration of EDB drops by 360 fold. The first order rate constant for degradation of EDB

would be 1.2 per year. This rate of degradation is consistent with rates that have been determined for anaerobic biodegradation of EDB at gasoline spill sites (Wilson et al., 2008).



Particle pathlines in model layer 3.

Figure 1. Comparison of the position along the flow path in ground water to the change in values of $\delta^{13}\text{C}$ for EDB and concentrations of EDB for flow near the water table.

As the ground water moves further away from the source of EDB, the extent of fractionation of carbon isotopes and the extent of attenuation in concentration are much less extensive. Compare wells KAFB 16082 and KAFB 10617 at the margin of the source to well KAFB 106042 at the furthest extent of the EDB plume. The attenuation is only tenfold, and the fractionation is only 1.5‰.

Figure 2 makes the same comparison for wells that are screened in the deeper portion of the aquifer. The behavior of EDB in the deeper wells is equivalent to behavior in the shallow wells. The reduction in concentration is greater and the extent of fractionation is greater in well KAFB 106086, KAFB 106088, KAFB 106089, and KAFB 106072 which are closer to the source than KAFB 106057 which is farthest from the source. Once the ground water moves past the wells that are immediately proximate to the source, there is little additional reduction in concentration of EDB and little additional fractionation of EDB.

This is the behavior that would be expected if the attenuation in concentration and fractionation was caused by anaerobic biodegradation of EDB by bacteria that use EDB as an electron acceptor to metabolize petroleum hydrocarbons (Henderson et al., 2008). When the petroleum hydrocarbons are degraded, they are no longer available to support the biodegradation of EDB.

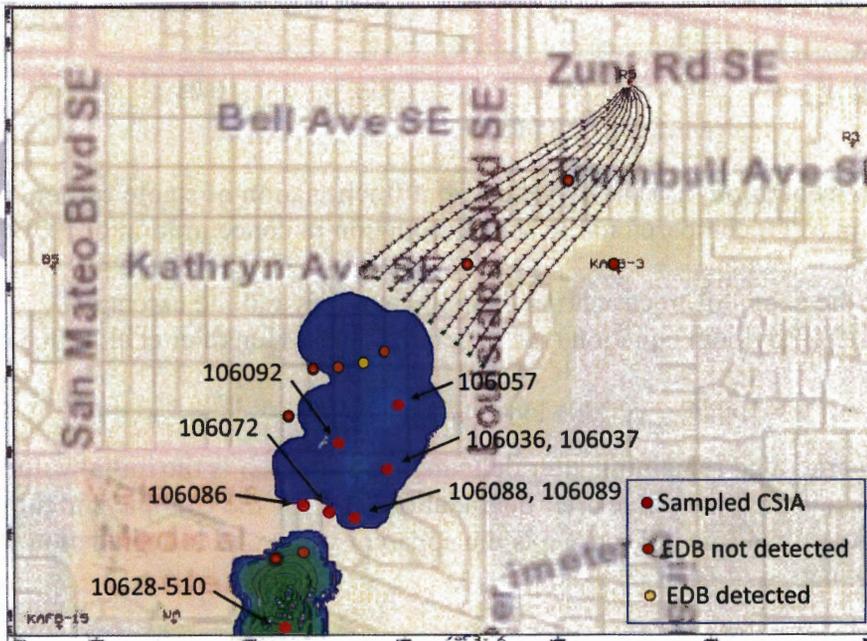
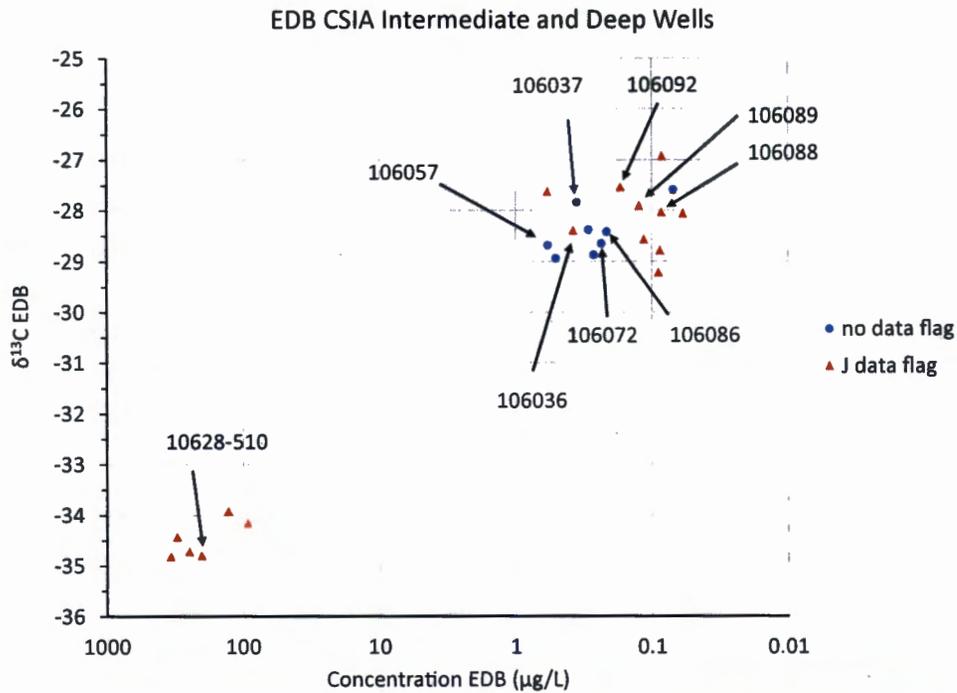


Figure 2. Comparison of the position along the flow path in ground water to the change in values of $\delta^{13}\text{C}$ for EDB and concentrations of EDB for flow deeper in the aquifer.

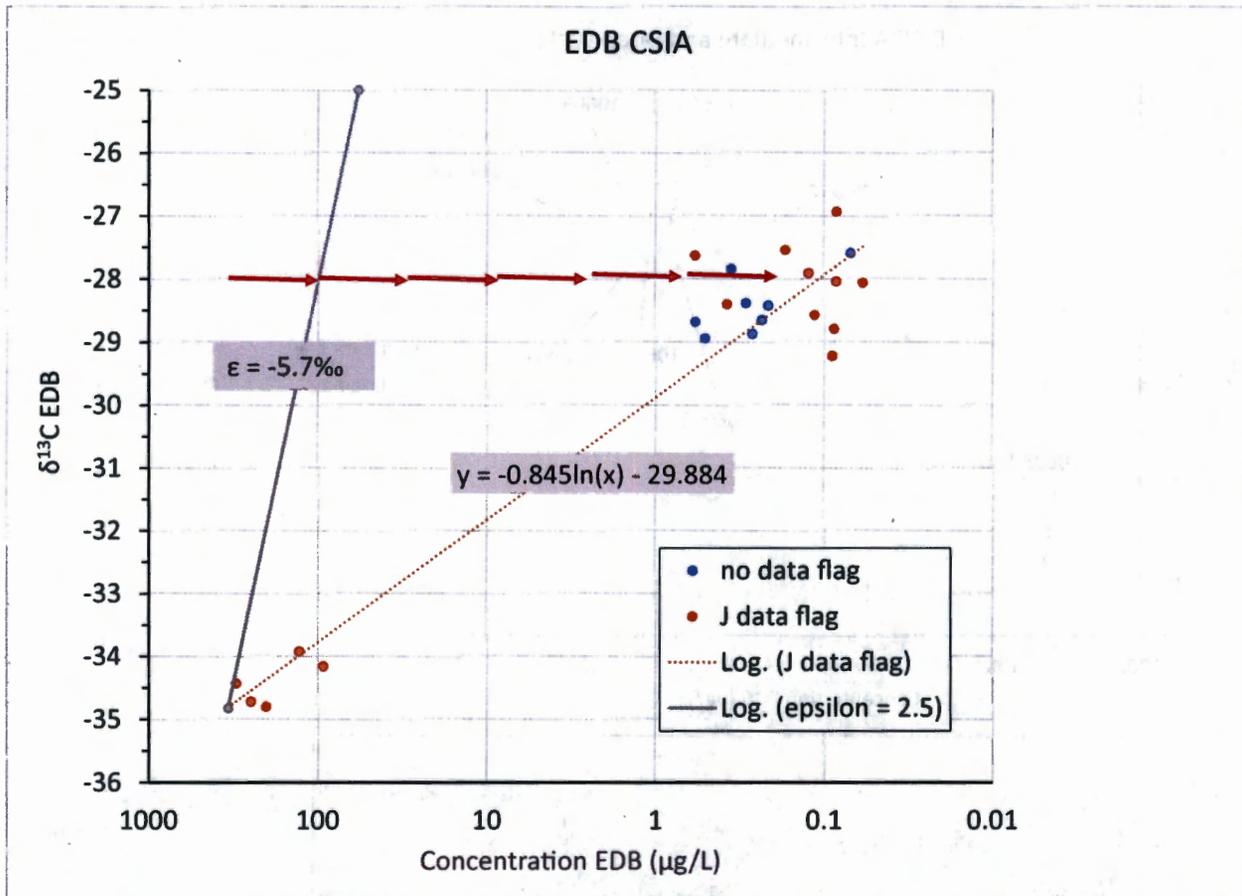


Figure 3. Reduction in concentration of EDB expected from fractionation of stable carbon isotopes in EDB (change in $\delta^{13}\text{C}$) compared to the actual reduction in concentration of EDB.

The relationship between the extent of fractionation of stable isotopes and the extent of degradation often follows the Rayleigh equation (see equation 7.17 in Hunkeler et al. (2008):

$$f = [(\delta^{13}\text{C}_{\text{final}}/1000+1)/(\delta^{13}\text{C}_{\text{initial}}/1000+1)]^{1000/\epsilon}$$

where f is the fraction of compound remaining after degradation, $\delta^{13}\text{C}_{\text{initial}}$ is the initial value before degradation, $\delta^{13}\text{C}_{\text{final}}$ is the final value after degradation, and ϵ is the isotopic enrichment factor. The slope of the dotted red line in Figure 3 is the apparent value of ϵ if degradation were responsible for all the attenuation of EDB.

There is only one value reported in the literature for anaerobic biodegradation of EDB (Henderson et al., 2008). That value is -5.7‰. The grey line in Figure 3 is the relationship that would be expected between concentrations of EDB and the value of $\delta^{13}\text{C}_{\text{final}}$ when EDB is removed by anaerobic biodegradation. The actual removal is much more extensive. There must be a considerable contribution of a non-fractionating processes, such as dilution in the well bore, to the attenuation of EDB in ground water along the flow path. The red arrow in Figure 3 to the left of the grey line is the extent of removal that can be attributed to anaerobic biodegradation. Roughly 77% of the original mass should have been removed. Compare the stacked red arrows

to the right of the grey line. The effect of dilution or some other non-fractionating process is five times more important.

Figure 4 makes the same comparisons for fractionation of $\delta^{13}\text{C}$ in benzene and attenuation of benzene in ground water.

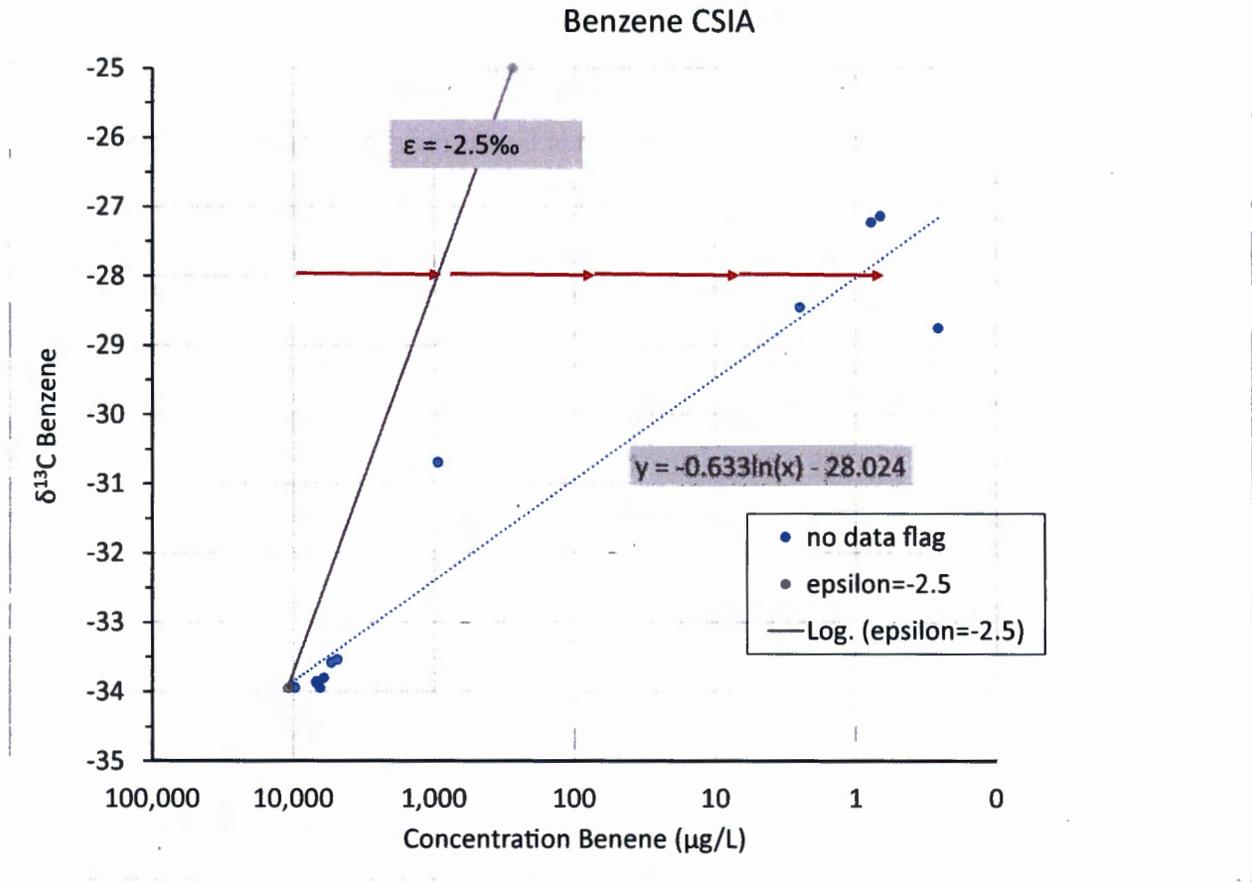


Figure 4. Reduction in concentration of benzene expected from fractionation of stable carbon isotopes in benzene (change in $\delta^{13}\text{C}$) compared to the actual reduction in concentration of benzene.

In the wells with the lowest concentration of benzene, anaerobic biodegradation could be expected to remove approximately 90% of the benzene originally in the ground water. The contribution of dilution or some other non-fractionating process was important for attenuation of benzene as well, accounting for most of the attenuation. However, dilution was not as important as for EDB. This is probably because the benzene plume was shorter than the EDB plume.

With regard to the comment that the reviewers find that it is unlikely that EDB was separated from the other fuel components by two-dimensional gas chromatography, as was done in Wilson et al. (2008).

In Wilson et al. (2008) there is a discussion of the need for two-dimensional gas chromatography to successfully determine the isotopic ratio of EDB in the presence of gasoline hydrocarbons. The isotopic ratio is determined on carbon dioxide produced from the combustion of the substance being analyzed. If there is a co-eluting compound, the co-eluting compound will contribute to the isotopic ratio. As a consequence, successful determination of the isotopic ratios requires base line separation of the compound for which the isotopic ratio is being determined. There are compounds in gasoline that elute near EDB. To achieve baseline separation it is necessary to first separate EDB on one gas chromatography column, then take the compounds that elute from the first column and separate them again on a second column with separate properties. This is called two-dimensional gas chromatography.

As the concentration of the compound being analyzed is lower, the determined value of $\delta^{13}\text{C}$ becomes more variable. At some concentration, the variability becomes greater than the data quality objective. The general objective is to be within a value of 0.5‰ of the nominal value of a known standard. The data presented below are from Appendix C of Wilson et al. (2008). At a concentration of EDB of 4.2 $\mu\text{g/L}$, four replicates vary by 0.7‰ and the sample standard deviation was 0.3096‰. The minimum concentration that could be used to determine the $\delta^{13}\text{C}$ was taken to be 4.2 $\mu\text{g/L}$. Notice in the Table C.1 below, as the concentration increased above 4.2 $\mu\text{g/L}$, the standard deviation was less.

Table 3. Synopsis of data from Table C.1. of Wilson et al. (2008) showing the reproducibility of $\delta^{13}\text{C}$ values for EDB prepared by a purge and trap sampler from ground water containing aqueous solutions of EDB and gasoline.

Run #	Conc $\mu\text{g/L}$	EDB		
		$\delta^{13}\text{C}$		
			Mean	Stan dev
1975	3.6	-27.7		
1976	4.2	-27.9	-27.475	0.3096
1979	4.2	-27.5		
1981	4.2	-27.2		
1982	4.2	-27.3		
1973	4.8	-27.8		
1984	8.4	-27.3	-27.26	0.2302
1986	8.4	-27.6		
1988	8.4	-27.3		
1990	8.4	-27.1		
1991	8.4	-27		
1971	12	-27.6		
1972	21.6	-28.2		
1974	36	-28.3	-28.42	0.1095
1978	36	-28.3		
1980	36	-28.5		
1985	36	-28.5		
1989	36	-28.5		
1977	48	-28.0		

Table 4 below compares the concentrations of EDB by either EPA Method 8011 or EPA Method 8260 to the value of $\delta^{13}\text{C}$.

Table 4. Relationship between concentration of EDB and reported values of $\delta^{13}\text{C}\%$ in the Kirtland AFB study.

Entry number	Well number	ZymaX file number CSIA	Zymax file number VOA	CSIA EDB $\delta^{13}\text{C}\%$	Conc. EDB 8260 $\mu\text{g/L}$	Conc. EDB 8011 $\mu\text{g/L}$
1	106064	43178	43178	J -34.82	320	340
2	10614	43181	43181	J -34.43	230	305
3	106076	43204	43204	J-34.72	210	248
4	10628	43194	43194	J -34.80	220	202
5	10610	43181	43181	J -33.92	95	129
6	106059	43178	43178	J -34.16	87	92.9
7	106079	43172	43172	U	<18	45.5
8	1069	43186	43186	U	<7.2	14.1
9	106055	43186	43186	U	<0.36	1.59
10	106035	43135	43135	J-27.63	<0.36	0.583
11	106057	43137	43137	-28.68	0.85	0.582
12	10617	43133	43135	-28.94	<0.36	0.509
13	106036	43135	43135	J -28.40	<0.36	0.377
14	106082	43136	43136	-27.84	<0.36	0.357
15	106037	43135	43135	-28.38	<0.36	0.292
16	10622	43132	43135	-28.87	<0.36	0.267
17	106058	43172	43172	U	<0.36	0.241
18	106072	43141	43141	-28.65	<0.36	0.235
19	106086	43141	43141	-28.42	<0.36	0.215
20	106092	43143	43143	J -27.54	<0.36	0.17
21	106089	43143	43143	J -27.91	<0.36	0.124
22	106070	43137	43137	J -28.57	<0.36	0.114
23	106065	43194	43194	J -29.22	<0.36	0.0894
24	106065A	43194	43194	J -28.79	<0.36	0.0872
25	106080	43178	43178	U	<1.8	0.0871
26	106088	43137	43137	J -28.04	<0.36	0.085
27	10625	43133	43135	J -26.93	<0.36	0.0845
28	106042	43133	43135	-27.59	<0.36	0.0699
29	10619	43132	43135	J -28.06	<0.36	0.059
30	106073	43146	43146	J -28.17	<0.36	not detected
31	106075	43146	43146	J -28.22	<0.36	not detected
32	106083	43136	43136	-28.09	<0.36	not detected

The Zymax Final Reports have a notation that a quality identifier “J” means the *target analyte produced a low peak signal and the result is considered usable to ± 1-2%, but not the standard 0.5%*. A quality identifier of “U” means that *either there was no peak corresponding to the target analyte or that such a peak did not produce a reliable CSIA result*.

In the first 6 entries, the concentrations are above 90 µg/L by EPA Method 8011, yet the CSIA data are flagged with a “J.” In data entries 7, 8, and 9, the concentrations are 45.5, 14.1 and 1.59 µg/L by EPA Method 8011, yet the CSIA data are flagged with a “U.”

In data entries 23 through 32, the concentrations are less than 0.1 µg/L by EPA Method 8011. Of these ten entries, one is flagged with a “U”, seven are flagged with a “J” and two have no flag. Entry 32 reports a value of $\delta^{13}\text{C}$ for EDB without a flag even though EDB was not detected.

The CSIA data provided by ZymaX on ground water at the Kirtland AFB site provide no documentation of the minimum concentration that can provide a determination of $\delta^{13}\text{C}$ at a defined data quality. ZymaX reported values of $\delta^{13}\text{C}$ for EDB without a flag when concentrations were less than 0.4 µ/L. These values are tenfold lower than the minimum concentration in the study of Wilson et al. (2008).

Specific Comments

GW Degradation Analysis, Page L-ix.

The following statement is made.

“The microbial data show that the benzylsuccinate synthase and phenol monooxygenase genes appear to be involved in the degradation of benzene, and by association, possibly other aromatic hydrocarbon compounds.”

The presence of the genes do not mean that they are involved in the degradation of benzene. The presence of the genes indicate that organisms are present that have the capability to synthesize enzymes that are able to degrade benzene.

The qPHE gene is a mono-oxygenase that only functions when molecular oxygen is available. It is a predictor of aerobic benzene biodegradation, but not of anaerobic benzene biodegradation. The qbssA gene is a predictor of anaerobic biodegradation of alkylbenzenes with a methyl function, but not of benzene itself.

GW Degradation Analysis, Page L-6

The following statement is made:

“For degradation of petroleum hydrocarbons under anaerobic conditions such as exist in the NAPL plume area at the BFF, benzylsuccinate synthase (bssA) and phenol

monooxygenase (PHE) are two functional bacterial gene markers in anaerobic bacterial degradation of the monoaromatic hydrocarbons benzene, toluene, ethylbenzene, and xylene (Weelink et al., 2010)."

Weelink et al. (2010) does not claim that PHE or bssA are involved in anaerobic degradation of benzene.

GW Degradation Analysis, Page L-7.

The following statement is made:

"As presented in Section 4, both of these genes show abundant counts in the BFF NAPL area and in the downgradient dissolved plume. These results indicate that anaerobes capable of degrading benzene and other monoaromatic hydrocarbons are present in the plume."

As discussed above, neither of these genes are markers for anaerobic biodegradation of benzene. **GW Degradation Analysis, Page L-9.**

The following statement is made with respect to benzene degradation:

"The form of the Rayleigh equation used for this purpose is:

$$R_t/R_i = f(\alpha-1)$$

Where:

$R_t = \delta^{13}\text{C}$ in the remaining undegraded compound

$R_i = \delta^{13}\text{C}$ in the original undegraded source

$f =$ Mass fraction of the remaining undegraded compound

$\alpha =$ Fractionation factor for the compound of interest"

There is an error in this definition of R_t and R_i . These parameters are the actual ratio of ^{13}C to ^{12}C in the sample, and are not the values of $\delta^{13}\text{C}$ of the sample as reported from the analysis of SCIR.

Their form of the equation is correct. It can be easily converted to the form used in their reference Weelink et al. (2010). If the mass fraction remaining (f) is represented by C_t/C_o [the ratio of the final concentration to the initial concentration], and the original un-degraded compound is R_o instead of R_i , the Rayleigh equation used in Appendix L becomes

$$R_t/R_o = (C_t/C_o)(\alpha-1).$$

The fractionation factor (α) is related to the isotopic enrichment factor (ϵ) as follows:

$$\epsilon = (\alpha - 1) * 1000$$

(See equation 7.3 in Hunkeler et al., 2008).

Substituting $\epsilon/1000$ for $\alpha-1$, the Rayleigh equation becomes

$$R_t/R_o = (C_t/C_o) \epsilon/1000.$$

This is the form of the Rayleigh equation in equation 2 of their reference Weelink et al. (2010).

It is surprising that Page L-9 used $\delta^{13}\text{C}$ for R in the Rayleigh equation. Page L-7 and L-8 properly define R and $\delta^{13}\text{C}$.

As a result, GW Degradation Analysis is in error when it attempts to use the Rayleigh equation to estimate the extent of biodegradation.

GW Degradation Analysis, Page L-26.

The following statement is made:

“The majority of the benzene CSIA $\delta^{13}\text{C}$ results within the NAPL area is in the range of -33 to -34‰ as shown on Appendix L, Figure 4-25. It is assumed this represents the non-degraded benzene $\delta^{13}\text{C}$ ratio. This is a conservative assumption because it is likely that some degradation has occurred. The lightest benzene ratios are in the range of -27‰. Application of the Rayleigh equation [$R_t/R_i = f(\alpha-1)$] (discussed in Section 2.1.2) to these ratios with a benzene fractionation factor (α) of -2.8‰ and solving for f is as follows:

$$f = [27/34]1.003$$

yields a fraction remaining of 0.80, which is equal to a destroyed fraction of 0.20.”

The text is in error. The value of (ϵ) is -2.8‰, not the value of α . The value of $\alpha = (\epsilon/1000)+1$. Inserting the value for ϵ , the value of $\alpha = (-2.8/1000)+1 = 0.9972$. The value of $\alpha-1 = -0.0028$.

The equation should have been

$$f = [F_t/F_i]^{1/(\alpha-1)} = [(27/1000+1)/(34/1000+1)]^{1/-0.0028} = 0.076$$

The amount degraded is 1-f. As much as 92% of the benzene was biodegraded between the source and the down-gradient wells.

To be appropriately conservative, GW Degradation Analysis used a value of ϵ that estimated the highest value for f and the least extensive degradation. It is possible that the extent of removal was even greater.

The same comments apply to fractionation of EDB.

GW Degradation Analysis, Pages L-22 and L-23.

The following statement is made:

"The majority of the EDB $\delta^{13}C$ results within the NAPL area is in the range of -34 to -35 per ‰ as shown on Appendix L, Figure 4-26. It is assumed that this represents the non-degraded EDB $\delta^{13}C$ isotopic ratio. This again is a conservative assumption because it is likely that some degradation has occurred. The lightest EDB ratios are in the range of -27‰. Application of the Rayleigh equation to these ratios with an EDB fractionation factor of -5.7‰ and solving for f is as follows:

$$f = [27/35]1.01$$

yields a fraction remaining of 0.77, which is equal to a destroyed fraction of 0.23. This shift in ratios indicates that a minimum of 23 percent of the original mass of EDB has been degraded."

The text is in error. The value of (ϵ) is -5.7‰, not the value of α . The value of $\alpha = (\epsilon/1000)+1$. Inserting the value for ϵ , the value of $\alpha = (-5.7/1000)+1 = 0.9943$. The value of $\alpha-1 = -0.0057$.

The equation should have been

$$f = [F_t/F_i]^{1/(\alpha-1)} = [(-27/1000+1)/(-35/1000+1)]^{1/-0.0057} = 0.23$$

As much as 77% of the EDB was degraded between the source and the down-gradient wells.

GW Degradation Analysis, Page L-14.

The following statement is made:

"Two types of regression analyses were performed on the EDB and benzene concentrations and degradation indicator compounds. The coefficient of determination (R^2) of each regression was assessed as a general goodness-of-fit to a first-order exponential decay curve. In addition, the quantitative assessment of each regression was tested using standard exponential analysis of variance (ANOVA) regression methods with an $\alpha = 0.05$ level of significance (SAS Institute, 2012). The null hypothesis, H_0 , was that there was no trend in the data, and the alternate hypothesis, H_a , was that there was a trend. The ANOVA regression results were used to quantitatively assess the overall regression, the slope of the regression line, and the intercept of the regression line. For statistically significant regressions, the slope of the trend line defined whether the concentration was increasing (+) or decreasing (-)."

The coefficient of determination for the regression is not an appropriate evaluation of the goodness of fit. Neither is an analysis of variance to compare the trend of the data to no trend. The data are being interpreted in terms of attenuation with distance along a flow path. The question is not whether the plume is attenuating, but how much. Will EDB be attenuated to concentrations that are below action levels before the plume reaches a receptor? The best evaluation of the goodness of fit to the trend in concentration is the confidence interval on the slope of the regression. This topic is discussed in detail in Wilson, (2011).

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