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New York State Department of Environmental conservation
625 Broadway
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RECEIVED
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REMEDIAL BUREAU A
DIV. OF ENV. REMEDIATION

Re: CSIA sampling

Dear Mr. Harrington:

Northrop Grumman Systems Corporation has retained several consulting firms, including Ramboll Environ, Environmental Standards, Inc. and Arcadis U.S., Inc., with expertise on the interpretation of compound specific isotope analysis (CSIA) laboratory data and interpretation to review two reports: NYSDEC Standby Engineering Contract D007625-27 WA#27 Grumman Aircraft Engineering Corporation/Naval Weapons Industrial Plant NYSDEC Site #130003A/13000B Draft CSIA Results report prepared by Henningson, Durham & Richardson Architecture and Engineering, P.C. (HDR), dated April 12, 2016; and CSIA Forensic Report Grumman Aerospace Bethpage Facility (NYSDEC Site Number 130003) CSIA Projects #18232, 18233 & 18242 report prepared by Pace CSIA Center of Excellence (Pace), dated April 6, 2016. The Pace report includes data provided by Pace Analytical Energy Services (PAES), which will also be referred to as the PAES data package in this letter.
The evaluation demonstrates that the reports are not scientifically valid and that the results are inconclusive. Further, there is no peer-accepted framework for interpreting 1,4-dioxane CSIA results for environmental samples. Thus, further sampling for additional CSIA testing is unlikely to yield meaningful results.
General comments:

- Interpretation of the CSIA data occurred out of context of the conceptual site model. It is unlikely that mixing of the two plumes emanating from the Former Bethpage Facility (represented by wells GM73D2 and RE122D1) and the Bethpage Community Park site (represented by well BCP MW-4-1) actually occurs to any significant extent.
- The primary conclusion from the Pace report was that the CSIA results for TCE and 1,4-dioxane in site groundwater were inconclusive. Both HDR and Pace provide recommendations for an expanded scope for additional sampling and CSIA analysis without providing appropriate justification for this recommended expansion in scope.

Additional investigations utilizing CSIA for TCE and 1,4-dioxane are not likely to yield better results for a variety of reasons, including those set forth below:

- Regardless of whether or not one- or two-dimensional CSIA is applicable for 1,4-dioxane, as discussed below, use of CSIA for distinguishing sources of 1,4-dioxane in groundwater and other environmental samples is not established within peer-reviewed literature. There is also a very limited body of information regarding the potential range of 1,4-dioxane carbon and hydrogen isotopic compositions for 1,4-dioxane that was used as a stabilizer for chlorinated solvent. Furthermore, changes in isotopic composition (carbon, hydrogen) associated with degradation of 1,4-dioxane has not been sufficiently reported/published within the scientific community, and therefore, interpretation of 1,4-dioxane CSIA results does not rely on scientifically-accepted methodology.
- CSIA is most powerful when a "multi-dimensional" analysis can be conducted (i.e., multiple isotopes).
  - For TCE, the Pace laboratory no longer offers hydrogen isotope analysis for chlorinated solvent compounds because the method utilized could result in erroneous data (HCl generation upon pyrolysis may cause interference and inaccurate results[1]). Evaluation of TCE, therefore, is limited to two isotopes (carbon and chlorine). The use of two-dimensional CSIA analysis for TCE for additional sampling locations is likely to continue to provide equivocal results.
  - 1,4-dioxane concentrations presented in this study are generally too low for hydrogen isotope analysis. Only two of six samples collected during the initial investigation had sufficient concentrations of 1,4-dioxane (greater than 10 µg/L) for hydrogen isotope analysis, which precludes using CSIA for hydrogen, and reduces the results to a one-dimensional dataset. The utility of a one-dimensional isotopic dataset is questionable.

<u>Comments on the PAES Package include the following:</u>

- The PAES data report states that the laboratory "focused their efforts" on proving that the concentration aspects of the extraction process did not alter the $\delta^{13}C$ in 1,4-dioxane. No results of those efforts or demonstrations are presented. This stated objective is problematic; a proper scientific approach would be to examine the effect, if any, of the extraction, rather than to only seek to support a desired outcome.
- The PAES data report does not provide adequate information to support a position that the 1,4-dioxane was within the working range of the IRMS instrument. The information needed to complete that evaluation would include the percent recovery obtained during

[1] Kuder, T. and P. Philp. 2013. Demonstration of compound-specific isotope analysis of hydrogen isotope ratios in chlorinated ethenes. *Environmental science and Technology* 47: 1461-1467.

liquid-liquid extraction; however, this information was not available due to the PAES' omission of the use of a surrogate standard.

- The PAES data packages did not contain raw data for sample preparation, calibrations and analysis and, therefore, cannot be verified. This is a particular concern given that PAES' reported detections of CCl4, Freons®, dichloropropene, and (only) o-xylenes in select samples suggest potential artifacts and/or false positives.

Comments on the Pace report include the following:

The Pace Report contains an introductory section describing the site, a methodology section presenting the theory of CSIA, followed by a section discussing the results of bulk compositional analysis and CSIA of trichloroethene (TCE), and 1,4-dioxane in six groundwater samples collected from the site. The methodology section contains numerous errors and unsupported assumptions and does not convey a thorough understanding of the behavior of stable isotopes in the environment. Specific examples include, with regard to methodology:

- Page 5, first paragraph, states, "... (1) unlike petroleum hydrocarbon products, which are mixtures of certain hydrocarbons with useful biomarkers..." Although petroleum hydrocarbon products are mixtures of hydrocarbon compounds, not all petroleum hydrocarbon products contain compounds that are classified as biomarkers. For example, diesel fuel may contain biomarkers, but gasoline does not. This statement by Pace overstates the utility of petroleum hydrocarbon forensics, and casts doubt on application of general environmental forensics principles, including CSIA.

- Page 5, fifth paragraph, states that "the isotopic composition of the raw materials; the chemical reactions employed in the manufacturing; any separation steps and all of the temperatures involved" results in "particular isotopic composition unique to the particular chemical lot." This statement is not correct; two compounds generated by entirely different manufacturers may share identical isotopic compositions. While the isotopic composition of a specific "chemical lot" depends on the parameters noted, it is not necessarily the case that those parameters will yield a "unique" isotopic composition.

- Page 6, last paragraph, states that "For an isotopic ratio to significantly change, a bond must be broken" and that "degradation of a compound is the only significant cause of increasing isotopic composition." This is not correct, as it is widely known that significant fractionation occurs during evaporation or volatilization and during diffusion transport of constituents in various media.

- Page 6, last paragraph, states, "That means degradation of a compound is the only significant cause of increasing isotopic composition (deltas) for that compound." As described in the previous comment, degradation of a compound is not the *only* significant cause of isotope shifts. Contributions of constituents from an additional source can cause shifts in isotopic composition.

- Page 6, last paragraph, states, "This makes CSIA an ideal tool to look for difference in the composition of minimally degraded chemicals that are otherwise indistinguishable." In fact, this statement highlights CSIA's incompatibility as a tool for this project. Different TCE degradation pathways have been demonstrated to result in significantly different changes in isotopic compositions. For example, changes in the stable carbon isotopic composition of TCE to more positive delta values are small for aerobic degradation of TCE compared with anaerobic degradation of TCE. Therefore, there could be substantial aerobic degradation of TCE with a

minimal change in the stable carbon isotope delta values. This is also true for chlorine isotopes of TCE. Since the groundwater system at the Site is generally more aerobic than anaerobic, substantial degradation of TCE could occur before a measureable change in TCE carbon or chlorine isotopic composition occurs.

The following comments pertain to the Results and Discussion Section of the Pace Report:

- Page 12, second paragraph: The report purports to rely on knowledge of site-specific hydrogeology (e.g., flow direction), and the conceptual site model for the plume (e.g., releases of solvents with other organic carbon sources, indication of the presence of daughter products that demonstrate biodegradation); however, the basis for these site-specific conditions are not provided. In comparing the results, there is no discussion of how the samples may or may not be representative of groundwater from similar aquifer units, how the pumping operations may be impacting groundwater flow directions, whether geochemical conditions do in fact indicate conditions conducive to reductive dechlorination, etc. To present the isotope results and bulk concentration information without discussion of how the results integrate with other hydrogeologic and geochemical data means the report's conclusions are speculative.
- Page 12, paragraph following Table 1, states "As seen in Table 1, contaminants were detected in the highest concentrations at locations between the presumed upgradient well, BCP MW-4-1 and the presumed downgradient well, TT101D2." However, the highest concentrations of 1,4-dioxane, vinyl chloride, *cis*-dichloroethene, PCE, 1,1-dichloroethane, and 1,1,1-trichloroethane were observed at the presumed upgradient well; and only TCE and Freon-113 were reported to present at their highest levels between the presumed upgradient and presumed downgradient wells. Thus, PAES/Pace's own data do not support the Pace statement.
- Page 12, paragraph following Table 1, states "TCE in well BCP MW-4-1 (99 µg/L) is being biodegraded into its daughter products cDCE (390 µg/L) and then VC (390 µg/L)." The Pace report provides no supporting data to substantiate this claim. It is entirely possible that the source of chlorinated solvents in that well could be derived from PCE, or separate releases.
- Page 13, first paragraph, lists alternate sources for 1,4-dioxane as 1,1,1-TCA stabilization and deicers, but 1,4-dioxane is also used in many unmentioned products, including paint strippers, dyes, greases, varnishes, waxes, and personal care products including shampoo.
- Page 14, last paragraph, states that Figure 6 suggests that all of the variation in isotopic enrichment (*i.e.*, both $\delta^{13}C$ and $\delta^{37}Cl$ on TCE) can be explained by biodegradation. However, there is some variation in $\delta^{13}C$ that is independent of $\delta^{37}Cl$ across TT101D2, GM73D2, and RE122D1.
- Page 14, last sentence, states "The most heavily degraded TCE is that furthest upgradient. This is typical of a mature source area where there is no longer a dissolved phase or an ongoing leak." Initially, this does not make sense. However, there is still a dissolved phase plume in the source area near BCP MW-4-1; otherwise, chlorinated compounds would not be detected in groundwater. Indeed, support for this statement is absent, and it has not been demonstrated that such isotopic behavior is "typical." Various levels of degradation may be associated with different areas within a large plume. In many cases, these differences are

related to the presence/absence of specific microbial communities, availability of nutrients or carbon sources, remediation history, or a variety of other geochemical conditions. It is not clear why an upgradient location would necessarily be prone to any more degradation than another area in the plume based on the information provided in the report.

- Page 15, third paragraph, states, "The slope of the line predicted by EQ 4 is a ratio of the enrichment factors. Reductive dechlorination is the most common biodegradation mechanism for TCE, and Wiegert, et al (2013) have specified the ratio of enrichment factors for that process as 0.37 ± 0.11. With a 90% one tailed confidence interval, the slope on the line in Figure 6 is 0.63 ± 0.16. Thus within that limit they are statistical [sic] indistinguishable." The overlap on these two slopes is 0.01, which is not supportive of the conclusion that all of the TCE was derived from a single source, as indicated by the following sentence in the Pace report: "It can't be ruled out that there is more than one source ..."

- Page 15, fourth paragraph, states, "It can't be ruled out that there is more than one source and that the limited sample set and the extensive degradation in BCP-MW-4-1 and BPOW3-4 have made it such that this study can't identify the additional sources." The report has not demonstrated that there has been "extensive degradation" of TCE in groundwater at BPOW3-4. There is a small shift (maximum of 1.93‰) in the carbon isotopic value of TCE in groundwater at BPOW3-4 compared with upgradient locations and the chlorine isotope values are not different within the margin of analytical error (±0.5‰). The USEPA 2008 CSIA Guidance document[2] has the following recommendation, "To ensure reliable interpretation, we recommend that fractionation on the order of 2‰ be used as a criterion for positive identification of degradation in order to minimize the possibility of an erroneous interpretation." This was not done.

- Page 16, second paragraph, states, "Most samples have concentrations of 1,4-D that are too low (<10 µg/L) for a reliable hydrogen CSIA. No significant difference is observed between 1,4-D obtained in samples BCP MW-4-1 and RE122D1 (-60‰ vs. -58‰), considering the analytical precision for hydrogen isotope analysis could be up to 20‰ for the low 1,4-D sample RE122D1 (12.9 µg/L)." This statement brings into question the utility of running hydrogen isotope analysis for samples with low 1,4-dioxane concentrations, perhaps less than about 20 µg/L, due to potentially large margins of error in the hydrogen isotope results for low 1,4-dioxane concentration samples.

- Page 16, third paragraph, states, "Unlike TCE, 1,4-D is resistant to natural biodegradation in groundwater, and could retain its isotopic fingerprint in the groundwater system." There is no available peer-reviewed literature demonstrating that 1,4-dioxane does indeed retain its isotopic fingerprint in groundwater.

- Page 16, third paragraph, states, "Without considering any degradation induced isotope enrichment effect, multiple sources of 1,4-D release may exist at the GABF site as those

[2] http://advancedtools.us/resources/guidance/csia/EPA_guide_for_CSIA.pdf

highlighted in blue and yellow (Table 3), and those highlighted in orange may become co-mingled." The language regarding the co-mingling of sources appears to imply that the values in the middle are the products of mixing of plumes represented by the upgradient and downgradient wells. However, the reported results for $\delta^{13}C$ and $\delta^{2}H$ for 1,4-dioxane clearly do not support the apparent implication.

- Page 16, Summary, the report notes that "...the TCE plume had a single source; however, that could not be absolutely determined because of a number of confounding issues (e.g., potential effect of biodegradation)." This summary, which appears to represent Pace's conclusions, does not appear to be supported by any particular data presented in the report. If other "confounding issues" were identified, they should be described. The report continues to note that "Overall, the most significant factor limiting the level of certainty in the conclusions made in this interpretation was the limited sample size." While recommending a next phase of sampling, the report fails to acknowledge the numerous issues that will significantly hamper any future studies, including the absence of 1,4-dioxane at sufficient concentrations to yield hydrogen isotope ratios, and the inability of the Pace laboratory to provide isotope ratios for hydrogen in TCE. Additional CSIA sampling would be subject to the same limitations, and would likely produce similar inconclusive results. Moreover, this Summary conflicts with page 15 of Pace's own report that states, "It can't be ruled out that there is more than one source and that the limited sample set and the extensive degradation in BCP-MW-4-1 and BPOW3-4 have made it such that this study can't identify the additional sources."

Specific comments on the HDR report are as follows:

- Page 2, last paragraph, notes that the primary purpose of collecting this data was to evaluate the utility and value of forensics studies to identify the specific source(s) of the known groundwater contamination. The report further concludes that the "study holds value and as part of a well-designed sampling program should be an element of additional work at this site." As noted with regard to similar assertions in the Pace report, it is unlikely that additional sampling will yield scientifically valid and reliable results.

Thank you for your consideration of these comments.

Sincerely,

Edward J. Hannon
Manager ESH&M
Northrop Grumman