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FOR INCLUSION IN THE ADMINISTRATIVE RECORD

August 15, 2007

Ms. Anna Krasko, Project Manager
United States Environmental Protection Agency
Region 1
One Congress Street
Boston, Massachusetts 02114

RE: Summary of Findings Regarding Cosolvency at MW-05S – Centredale Manor Restoration Project, North Providence, Rhode Island

Dear Ms. Krasko:

At the June 12, 2007 meeting among Emhart's technical consultants and EPA technical staff, its consultants from Battelle, RIDEM, and the USACE, EPA suggested that there was adequate relevant peer-reviewed literature to substantiate EPA's claim that the elevated concentrations of 2,3,7,8-TCDD reported in unfiltered groundwater samples from monitoring well MW-05S are, at least in part, due to the effects of cosolvency or enhanced solubility as a result of the co-occurrence of tetrachloroethylene (PCE) and trichloroethylene (TCE). Additionally, on June 14, 2007, EPA sent us email correspondence citing seven technical journal articles that purportedly support EPA's theory that cosolvency may be occurring at monitoring well MW-05S.

After review of the technical articles cited by EPA, we conclude that there is no supporting basis for EPA's theory that the occurrence of PCE and TCE in groundwater at monitoring well MW-05S would enhance the aqueous solubility of 2,3,7,8-TCDD. In fact, we conclude that the cited literature invalidates EPA's theory that enhanced solubility is occurring. Moreover, the cited literature refutes EPA's assertion that reduced 2,3,7,8-TCDD sorption to soil is occurring as the result of the co-occurrence of PCE and TCE. Thus, the notion that the mobility of 2,3,7,8-TCDD in the vicinity of monitoring well MW-05S is enhanced due to the presence of PCE and TCE is not supported by the research data.

This correspondence provides a meta-analysis of the literature cited by EPA in its June 14, 2007 email correspondence, and discusses the purported relevance of each referenced article to what is known about the existing conditions at monitoring well MW-05S.

Meta-Analysis of Literature

AMEC conducted a thorough review of the literature cited by EPA and found that the information presented in the papers seems to follow a progression from the investigation of simple systems in the earlier papers to the investigation of more complex systems in the more recent literature. The typical experiment discussing enhanced solubility in the earlier papers involved the use of solutions consisting of water, a solute (e.g., anthracene or another hydrophobic organic compound (HOC)), and a completely miscible solvent, such as methanol or acetone. The investigators evaluated the effect of increasing aqueous-phase solvent concentration on the solubility of the HOC. Typically, these experiments used solvent-water solutions with solvent concentrations ranging from 5% to 100%. Because the solvents used in the experiments were completely miscible, the investigations only evaluated the effect of a single phase on HOC enhanced solubility.

Similarly, earlier experiments conducted to evaluate the effect of cosolvents on reduced soil sorption only evaluated the influence of completely miscible solvents at very high concentrations (e.g., methanol-water solutions at 5% to 100% methanol). Again, because the solvents used were completely miscible, the investigations only evaluated the effect of a single phase on HOC sorption.

Although the experiments using a variety of completely miscible solvents and HOCs showed enhanced solubility and reduced soil sorption with increased solvent concentrations, the conditions applied in these experiments were not similar to the known conditions at monitoring well MW-05S. EPA's June 30, 2005 *Interim-Final Remedial Investigation Report* prepared by Battelle (RI Report) states that the primary chemical constituents in the water and soil in the vicinity of monitoring well MW-05S include PCE and 2,3,7,8-TCDD, with smaller amounts of TCE. There are no data to suggest that a completely miscible solvent, such as methanol or acetone, is present in the soil or groundwater at monitoring well MW-05S. Therefore, the literature cited by EPA evaluating enhanced solubility and/or reduced sorption due to the presence of percent levels of a completely miscible solvent cannot be used to objectively assess the conditions at monitoring well MW-05S.

It is not until data from experiments published in 1990 and 1994, in papers by Pinal et al., Rao et al., and Li and Andren, that the effects of partially miscible solvents on enhanced HOC solubility and decreased sorption were explored. In those experiments, the investigators explored the effects of enhanced solubility of HOCs in water from the addition of TCE, as well as in water-acetone mixtures. The conclusion reached from these studies is that *a partially miscible solvent, such as TCE or PCE, has no appreciable effect on the solubility or sorption of HOCs until the concentration of the partially miscible solvent dissolved in water is 1% (10,000 mg/l) or greater.* This situation will occur for PCE only when it is present in a ternary solution. An example of a ternary solution is TCE, water, and a completely miscible solvent, where the completely miscible solvent is at high percent levels in water. However, as noted above, there is no mention in the RI Report of any completely miscible solvents (like acetone) in the groundwater at MW-05S.

The following discussion provides a synopsis of each of the research papers cited by EPA in

the June 14 email correspondence and addresses the application of the research data to monitoring well MW-05S. The discussion of the papers is presented in the same order in which they were listed in EPA's June 14 email correspondence.

Title: Solubility of Polychlorinated Biphenyls in Water/Alcohol Mixtures. 1. Experimental Data

Authors: An Li and Anders W. Andren

Journal Citation: *Environ. Sci. Technol.* 1994, *28,* 47-52.

Article Summary: Li and Andren (1994) investigate solubility of three PCB congeners in mixtures of water and normal alcohols (1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol). Li and Andren conclude that "the rapid drop of PCB solubility as the cosolvent alcohols change from butanol to octanol may indicate that cosolvency of water-immiscible solvents is dominantly limited by the amount of cosolvent dissolved in water." Li and Andren also state that the observed decrease in the cosolvency effect of immiscible alcohols as their polarity decreases is in agreement with the findings of Pinal et al. (1990).

Application to MW-05S: Although Li and Andren focused on alcohols and PCBs, neither of which have been reported in soil or water samples from MW-05S, their data supports the findings of Pinal et al. (1990), discussed below. In summary, the immiscible[1] and non-polar solvents reported in groundwater samples from MW-05S, principally PCE and TCE, are not anticipated to increase the solubility of HOCs, such as PCBs or dioxin, in water.

Title: Cosolvency of Partially Miscible Organic Solvents on the Solubility of Hydrophobic Organic Chemicals

Authors: R. Pinal, P.S.C Rao, L.S. Lee, P.V. Cline, and S.H. Yalkowsky

Journal Citation: *Environ. Sci. Technol.* 1990, *24,* 639-647.

Article Summary: Pinal et al. (1990) study the effects of the non-polar partially miscible organic solvent (PMOS) TCE cosolvency on the water solubility of HOCs naphthalene and anthracene (by itself and in the presence of varying amounts of a completely miscible organic solvent (CMOS) (e.g., methanol)). In all cases the PMOS or the PMOS/CMOS solution was mixed with water. Pinal et al. conclude that a non-polar PMOS can alter the HOC solubility if it is present in solution at concentrations in excess of 10,000 mg/l (>1%). The authors further state that "non-polar PMOS, such as TCE, octanol, toluene, and other similar hydrocarbons, are not expected to have appreciable cosolvency."

Application to MW-05S: TCE has been reported in groundwater samples from well MW-05S at concentrations as high as 2.5 mg/l, several orders of magnitude below the 10,000 mg/l

[1] Note that Li and Andren use the term "immiscible" while other authors use the term "partially miscible" to describe compounds that have very limited solubility in water. The terms are interchangeable.

threshold suggested by Pinal et al. for the initiation of cosolvency effects on HOCs (like dioxin) in water. Additionally, the nonpolar solvent, PCE, has been reported in groundwater samples from MW-05S at concentrations up to 61 mg/l, again several orders of magnitude below the 10,000 mg/l threshold suggested by Pinal et al. The combined total of the maximum concentrations of TCE and PCE (63.5 mg/l) is only 0.635% of the threshold level suggested by Pinal et al. for initiation of observable cosolvent effects on HOCs in water. Given this information, it can be concluded that cosolvency effects from PCE and/or TCE are not occurring in MW-05S, and that enhanced dioxin water solubility is not plausible with respect to the groundwater in this well.

Title: Cosolvency and Sorption of Hydrophobic Organic Chemicals

Authors: P.S.C Rao, L.S. Lee, and R. Pinal

Journal Citation: *Environ. Sci. Technol.* 1990, *24,* 647-654.

Article Summary: Rao et al. (1990) study the effects of the non-polar PMOS TCE cosolvency on the sorption of HOCs anthracene and diuran to soil. Rao et al. conclude that non-polar PMOS are likely to have negligible effects on HOC sorption from predominantly aqueous solutions (i.e., where the concentration of a CMOS, such as methanol, is less than 30%). Rao et al. also note that non-polar PMOS, either dissolved in the aqueous phase or present as a separate liquid phase (i.e., NAPL), did not influence HOC sorption to soil, which suggests that the presence of a non-polar PMOS as a separate liquid will have a minimal impact on HOC sorption.

Application to MW-05S: Dissolved TCE and PCE have been reported in soil samples from MW-05S at concentrations as high as 26 and 300 mg/kg, respectively. Also, as discussed above, dissolved TCE and PCE have been reported in groundwater samples from well MW-05S at concentrations as high as 2.5 mg/l and 61 mg/l, respectively. Moreover, TCE and PCE are both non-polar PMOS.

However, there is no indication that a CMOS, such as acetone or methanol, is present at concentrations greater than 30%. Based on the conclusions from Rao et al., there is no evidence that dioxin or any other HOC would have experienced a reduction in sorption to soil as a result of the presence of the non-polar PMOS TCE and PCE. Therefore, it reasonably can be concluded that, even in the presence of TCE and PCE, dioxin in soil would not be expected to undergo enhanced transport from the soil to the underlying groundwater.

Title: Sorption of Organic Chemicals by Soil from Multi-Solvent and Multi-Sorbate Mixtures

Authors: P.S.C Rao and L.S. Lee

Journal Citation: In *Health and Environmental Research on Complex Mixtures,* R.H. Gray, E.K. Chess, P.J Mellinger, R.G Riley (eds.), DOE Symposium Series 62, 24th Hanford Life Science Symposium, Pacific Northwest Labs, Richmand, WA. Pp. 457-471.

Article Summary: The subject paper provides a review of experiments concerning cosolvency that had been conducted to date. The paper addresses solubility and sorption changes of HOCs in the presence of water/CMOS mixtures, water/PMOS mixtures and water HOC sorption from multi-sorbate mixtures. Much of the article presents the results of CMOS/water mixtures. However, one portion titled "HOC Sorption from Immiscible Solvent Mixtures" evaluates how PMOS (in this case, toluene and n-pentane) in water affect the sorption of two herbicides (terbacil and atrazine) to soil. In all cases studied, the volume ratio of water to immiscible solvent was larger than 10. The authors conclude that "the presence of an immiscible organic solvent did not measurably affect herbicide sorption."

Application to MW-05S: Although the chemicals used in the experiments are not identical to those present in MW-05S, the results are consistent with the previously summarized papers in that an immiscible solvent will not have a measurable effect (reduction) on the sorption of HOC to soil. Again, the data presented in Rao and Lee indicate that reduced soil sorption is not occurring at MW-05S as the result of the co-occurrence of 2,3,7,8-TCDD and chlorinated solvents. Thus, enhanced transport of 2,3,7,8-TCDD due to cosolvency is not occurring at MW-05S.

Title: Solvophobic Approach for Predicting Sorption of Hydrophobic Organic Chemicals on Synthetic Sorbents and Soils

Authors: K.B. Woodburn, P.S.C. Rao, M. Fukui, and P. Nkedi-Kizza

Journal Citation: *Journal of Contaminant Hydrology.* 1988, *1*, 227-241.

Article Summary: Woodburn et al. discuss the findings from their experiments evaluating the effects of solute sorption on a model and natural solid phase in the presence of three cosolvents. The solutes used in the experiments included a variety of polycyclic aromatic hydrocarbons, alkylbenzenes, halobenzenes, and pesticides. The cosolvents used included acetone, methanol, and acetonitrile.

Application to MW-05S: The applicability of the information presented in Woodburn et al. to MW-05S is very limited because the systems they evaluated are significantly different than the known conditions at MW-05S. For example, while the cosolvents used by Woodburn et al. span a wide range of polarities, all three are completely miscible in water. This contrasts

with the data from MW-05S, where the potential cosolvents are non-polar compounds with very limited solubility. Additionally, the most dilute solvent solutions used in the experiments were between 5% and 10% dissolved solvent in water. The highest concentration solvent solutions were 100% solvent (i.e., pure solvent). In contrast, the maximum concentration of potential cosolvents reportedly dissolved in water at MW-05S is approximately 0.006 %, about three orders of magnitude lower than the lowest concentration used by Woodburn et al.

In addition, more recent work by co-authors of the present paper, Pinal et al. (1990) and Rao et al. (1990), evaluated the effects of non-polar cosolvents with limited solubility and found that their aqueous (i.e., dissolved) concentration must exceed 1% before appreciable sorption or solubility effects are noted. As noted above, the reported dissolved concentrations of the non-polar solvents in MW-05S are more than two orders of magnitude less than 1%. In fact, the solvents reported in MW-05S, principally PCE and TCE, cannot have dissolved concentrations above 1% unless a suitable ternary solvent, such as methanol, were present at elevated concentrations. Nevertheless, there is simply not enough TCE and PCE to reach the 1% threshold. Thus, no cosolvency effects on dioxin solubility or sorption is expected at MW-05S.

Title: Influence of Organic Cosolvents on Sorption of Hydrophobic Organic Chemicals by Soils.

Authors: P. Nkedi-Kizza, P.S.C Rao and A.G. Hornsby

Journal Citation: *Environ. Sci. Technol.* 1985, *19*, 975-979

Article Summary: Nkedi-Kizza et al. assess the sorption of anthracene, diuron and atrazine by soils from aqueous solutions and binary solvents consisting of methanol-water and acetone-water.

Application to MW-05S: As discussed for Woodburn et al., the solvents used in the binary mixtures, methanol and acetone, are completely miscible in water. Also, the minimum concentration of cosolvents in water is 5%. Using the same information from Pinal et al. (1990) and Rao et al. (1990) expressed above for Woodburn et al., we conclude that no cosolvency effects are occurring at MW-05S.

Title: Sorption and Transport of Hydrophobic Organic Chemicals in Aqueous and Mixed Solvent Systems: Model Development and Preliminary Evaluation

Authors: P.S.C Rao, A.G. Hornsby, D.P Kilcrease, and P. Nkedi-Kizza,

Journal Citation: *J.Environ. Qual.* 1985, Vol. 14, no. 3.

Article Summary: Rao et al. present the theoretical basis for the manner in which HOCs may behave in aqueous and mixed solvent mixtures. To verify these theories, Rao et al. rely on the work presented in Nkedi-Kizza et al. (1985) and Woodburn et al. (1985), both of which are reviewed and summarized above. In general, the work of Nkedi-Kizza et al. (1985) and Woodburn et al. (1985) focus on the evaluation of the effects of CMOS, such as methanol and acetone, on the sorption of HOCs.

Application to MW-05S: The work of Nkedi-Kizza et al. (1985) and Woodburn et al. (1985), and thus the reported findings in Rao et al., (1985), are not comparable to the conditions at MW-05S where there are no reported concentrations of miscible organic solvents, such as methanol or acetone. In contrast, MW-05S is reported to contain concentrations of only partially miscible solvents, PCE and TCE, which have not been shown to have an effect on cosolvency at the levels reported.

Conclusions

Based on the information known about the soil and groundwater at monitoring well MW-05S, and the data presented in the papers cited by EPA, we conclude the following:

- MW-05S contains no free product in groundwater.
- MW-05S is not reported to contain any completely miscible solvents, such as methanol or acetone, in the solid (soil) or liquid (groundwater) phases.
- The highest reported levels of PCE and TCE in groundwater at monitoring well MW-05S are 61 mg/l and 2.5 mg/l, respectively.
- For partially miscible solvents, such as TCE and PCE, to have an appreciable effect on cosolvency or reduced sorption, the concentration in the dissolved aqueous phase must exceed 10,000 mg/l.
- The maximum reported concentration of dissolved, aqueous phase partially miscible solvents in MW-05S is 0.635% of the threshold at which cosolvency effects would be observed.
- The water solubilities of TCE and PCE are 1,100 mg/l and 150 mg/l, respectively.
- Given the absence of a high concentration (percent range) of miscible solvent and the aqueous solubilities of TCE and PCE, the dissolved aqueous phase concentrations of PCE or TCE in groundwater at monitoring well MW-05S could not approach the 10,000 mg/l threshold cited in literature for cosolvency effects by immiscible solvents to occur.
- No cosolvency of dioxin by PCE or TCE is occurring at MW-05S.
- Enhanced transport of 2,3,7,8-TCDD is not occurring at monitoring well MW-05S as

the result of the co-occurrence of PCE and/or TCE.

The papers that EPA has cited to support the theory that there is cosolvency or enhanced solubility of 2,3,7,8-TCDD at monitoring well MW-05S due to the presence PCE and/or TCE do not support EPA's claim. Many of the papers are simply not applicable due to the differences in systems examined by the researchers and the conditions that exist at monitoring well MW-05S. However, even with respect to those papers that examine systems that are similar to the conditions at MW-05S (e.g., the presence of a partially miscible solvent and a hydrophobic organic compound in water), the research clearly demonstrates that enhanced solubility of the hydrophobic organic compound, 2,3,7,8-TCDD, is not occurring. Moreover, the relevant research leads to the conclusion that reduced sorption to soil (and thus higher mobility) of 2,3,7,8-TCDD has not occurred at monitoring well MW-05S.

The results of the meta-analysis further support and augment the information and analysis presented in our June 8, 2007 letter, in which we discuss EPA's flawed conceptual site model for the groundwater to surface water pathway and its inappropriate interpretation of the SPMD results. Given the overwhelming evidence contradicting EPA's position, we request that EPA reconsider its conceptual site model for the groundwater to surface water pathway and its interpretation of the SPMD results.

Sincerely,

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