amec

October 15, 2007
Ms. Anna Krasko, Project Manager
United States Environmental Protection Agency
Region 1
One Congress Street
Boston, Massachusetts 02114

RE: Centredale Manor Site: Alleged Facilitated Transport of Dioxin from MW-05S to the Woonasquatucket River

Dear Ms. Krasko:

We are writing on behalf of Emhart Industries, Inc. in furtherance of our prior correspondence disputing EPA's assertion that groundwater at the above-referenced Site is an ongoing source or a migration pathway of dioxin to the Woonasquatucket River. In your September 14, 2007 letter to David Scotti of Loureiro Engineering Associates, Inc. (LEA), you state that EPA believes that the data indicate the area around monitoring well MW-05S is likely acting as an ongoing source of 2,3,7,8-TCDD and volatile organic compounds (VOCs) discharging to the Woonasquatucket River. In our previous letters dated June 8, 2007 and August 15, 2007 on the matter of monitoring well MW-05S, we have provided the reasons why we do not believe the data are indicative of a dissolved 2,3,7,8-TCDD groundwater plume discharging to the Woonasquatucket River. In the September 14, 2007 letter, you provided a hyperlink (http://www.epa.gov/ada.download/issue/facili.pdf) in the context of explaining that there are several mechanisms at work which, individually or in combination, could be associated with the observed groundwater data.

The hyperlinked document, Superfund Ground Water Issue (Huling, 1989)[1], discusses the potential for enhanced solubility of hydrophobic organic compounds (HOC) as the result of cosolvency with other organic solvents present, and/or colloidal transport. Our August 15, 2007 letter provided a detailed review and analysis of the literature pertaining to the alleged cosolvency effect. It is important to note that the Huling (1989) document was published in August 1989; therefore, the author of that document did not have the benefit of the literature published after that date. This timing point is particularly important because the peer-reviewed literature that is most pertinent to conditions observed at monitoring well MW-05S was not published until 1990 and later. All of the literature cited for the effect of cosolvency in the Huling (1989) document evaluated the effect of high concentrations (percent levels) of completely miscible solvents (e.g., acetone, methanol, etc.) on the solubility of HOC. As discussed in our August 15, 2007 letter, these conditions do not exist at monitoring well MW-05S.

[1] Huling, 1989. Superfund Ground Water Issue – Facilitated Transport. U.S. Environmental Protection Agency, Office of Research and Development, Office of Solid Waste and Emergency Response. EPA/540/4-89/003. August.

The literature published subsequent to Huling (1989) evaluated the effect of chlorinated solvents on HOC solubility. The studies discussed found that for partially miscible solvents, such as trichloroethylene (TCE) and tetrachloroethylene (PCE), to have an appreciable effect on cosolvency or reduced sorption, the concentration in the dissolved aqueous phase must exceed 10,000 milligrams per liter (mg/l). Given the absence of a high concentration (percent range) of a completely 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 (Pinal et al, 1990[2] and Rao et al, 1990[3]). As a result, a cosolvency effect is not occurring at monitoring well MW-05S.

Further support for the conclusion that a cosolvency effect is not occurring at monitoring well MW-05S is evidenced by the semi-permeable membrane device (SPMD) data from monitoring well MW-05S. Based on Battelle's estimates, these data demonstrate that only approximately 2% of the dioxin present in the unfiltered water sample is in the dissolved formed. If chemical cosolvency were occurring at monitoring well MW-05S, a much higher percentage of the dioxin would be expected in the dissolved form. Clearly, however, this is not the case.

The other mechanism for enhanced solubility discussed in Huling (1989) is a colloidal process whereby HOC preferentially sorbs to colloids that are small enough to travel with groundwater through the soil pores. The data collected by EPA and its consultants cannot be used to confirm EPA's inference that dioxin is being mobilized toward the river via colloidally facilitated transport. For example, other than the SPMD deployment in the groundwater at monitoring well MW-05S, EPA has not attempted to quantify the proportion of dioxin sorbed to colloidal material. EPA's data derived from the SPMDs buried in the contaminated river bank sediment are in no way indicative of colloidal transport because SPMDs do not account for colloidally-bound chemicals. As the USGS states:[4]

> "Nonporous polymeric films such as low-density polyethylene (membrane of choice for SPMDs) contain transient cavities with maximum diameters of about 10 Å. These cavities are far too small to accommodate colloids or macromolecular dissolved organic carbon (DOC) such as humic acids.
>
> Also, comparisons of chemical concentrations determined by using traditional analytical methods for ultra-filtered river water (colloids and DOC > 50 Å diameter were removed)

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[2] R. Pinal, P.S.C Rao, L.S. Lee, P.V. Cline, and S.H. Yalkowsky. *Environ. Sci. Technol.* 1990, *24,* 639-647.

[3] P.S.C Rao, L.S. Lee, and R. Pinal. *Environ. Sci. Technol.* 1990, *24,* 647-654.

[4] http://wwwaux.cerc.cr.usgs.gov/SPMD/SPMD_questions.htm#7.%20Do%20SPMDs%20sample%20only%20dissolved%20or%20vapor%20phase%20chemicals?

and those estimated from SPMDs exposed to river water appear to confirm that SPMDs sample only dissolved residues, which are readily bioavailable."

Based on the USGS statements, the data from the SPMDs buried in the contaminated sediment cannot be used to assess whether colloids are transporting dioxin via groundwater because the SPMDs exclude colloids and, by extension, the chemicals that may be sorbed on the colloid.

Moreover, if EPA is theorizing that dioxin is being transported by colloids in groundwater, then the methods used by Battelle to estimate corresponding pore water concentrations of dioxins are not appropriate or valid. This is because the theory concerning the sampling of water by SPMDs includes only dissolved chemicals and does not include chemicals transported via colloids. As a result, the equations used by Battelle, their other shortcomings notwithstanding, are not appropriate to estimate pore water concentrations of dioxins sorbed to colloidal material.

To date, EPA's discussions regarding the theory that dioxin is being transported from monitoring well MW-05S to the Woonasquatucket River involve a notion that facilitated transport of dioxin is occurring due to cosolvency, colloidal transport, or some combination thereof. However, the most relevant peer-reviewed literature on the matter of cosolvency as it relates to monitoring well MW-05S, Pinal et al. (1990) and Rao et al. (1990), clearly demonstrates that the TCE and PCE present in groundwater at monitoring well MW-05S is not affecting the solubility of dioxin. This conclusion is substantiated by the results of the concurrent SPMD and unfiltered groundwater sampling at monitoring well MW-05S which, according to Battelle's calculations, demonstrates that approximately 2% of the dioxin in the unfiltered groundwater is actually dissolved in the water. The remaining 98% of the dioxin is particle-bound. Thus, if enhanced solubility due to cosolvency were occurring, the SPMD and unfiltered groundwater sampling results should be in relatively good agreement, yet they are not.

As for the notion that facilitated transport of dioxin is occurring due to colloidal transport, the data collected to date cannot possibly be used to confirm this theory. The data from monitoring well MW-05S (SPMD and unfiltered groundwater) suggest that a majority of the dioxin in water is sorbed to suspended particles. This outcome is not unexpected. As discussed above, SPMDs simply do not sample chemicals that are sorbed to suspended particles or colloids. Hence the difference in the unfiltered groundwater and SPMD samples' results from monitoring well MW-05S. Therefore, the SPMDs buried in the contaminated sediment did not sample chemicals that are sorbed to suspended particles or colloids in pore water.

The foregoing discussion raises the following question: If dioxin is not being transported as a result of chemical cosolvency and the SPMDs do not sample colloidally-bound chemicals, why are there relatively high levels of dioxin present in the SPMDs buried in the contaminated sediment? The likely answer is that the SPMDs were not adequately cleaned; therefore, contaminated sediment residue remained on the SPMD during the sample extraction phase. This answer is sensible because of the intimate contact of the sediment with the sediment-deployed SPMDs. Also, no studies ever have been conducted to assess the efficacy of the method employed by Battelle to clean the SPMDs of sediment residue. Thus, it is possible, and likely probable, that the Kimwipe cleaning was not effective in removing all sediment residue from the

surface of the SPMD. In addition, this answer is the only one that does not defy the available data, nor does it contradict all peer-reviewed scientific literature on cosolvency and SPMD sampling characteristics. In contrast, EPA's present position contradicts this literature.

To use the existing data in support of EPA's current theory, one must make the unreasonable and far-reaching assumptions that (1) the dioxin (which based on Battelle's data and calculations is overwhelmingly bound to suspended particles) in monitoring well MW-05S desorbs and becomes dissolved during the transport from monitoring well MW-05S to the Woonasquatucket River; and (2) by the time the dioxin reaches the SPMDs buried in the sediment, it is dissolved and available for SPMD uptake. This hypothesis is untenable, and there are no data to corroborate it. In fact, all the data and the scientific literature point to the conclusion that dioxin is not being transported from monitoring well MW-05S to the Woonasquatucket River. Accordingly, Emhart again requests that EPA reconsider its conceptual site model for the groundwater to surface water pathway, and its interpretation of the SPMD results.

Sincerely,

Russell E. Keenan, Ph.D.
Vice President
Technical Director, Risk Assessment

Patrick O. Gwinn
Senior Environmental Scientist

cc: Ms. Deidre Dahlen, Battelle
Eve Vaudo, Esq., U.S. EPA
Cornell Rosiu, U.S. EPA
Louis Maccarone, RIDEM
Jerome C. Muys, Jr., Esq.
Jeffrey M. Karp, Esq.
Laura Ford Brust, Esq.
Mr. Jeffrey Loureiro (LEA)
Mr. David Scotti (LEA)