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June 8, 2007

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

RE: Comments on EPA's Conceptual Model for the Groundwater to Surface Water Transport Pathway

Dear Ms. Krasko:

At the April 23, 2007 dialog meeting, the Battelle project team presented EPA's detailed analysis of the remedial alternatives for the source area groundwater. According to Battelle's presentation, it was stated that the shallow groundwater in the immediate vicinity of well MW-05 requires remediation due to the presence and transport of tetrachloroethylene and 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) to the Woonasquatucket River via groundwater flow. We are writing on behalf of Emhart Industries, Inc., to express significant concern with the conceptual site model for the transport pathway and the data that Battelle uses to reach the conclusion that remediation is warranted for the groundwater in the vicinity of MW-05.

Our concern regarding the conceptual site model for this transport pathway stems from the following:

1. The surface water data do not support a zonal influx of 2,3,7,8-TCDD to the Woonasquatucker River water column.

2. The data do not support the idea that 2,3,7,8-TCDD is dissolved in MW-05 groundwater.

3. The Semi-Permeable Membrane Device (SPMD) data cannot be used to assess flux of 2,3,7,8-TCDD to the overlying surface water.

Each of these points is discussed below.

ZONAL INFLUX OF 2,3,7,8-TCDD

According to the Remedial Investigation Report (RI), an analysis of surface water concentrations of dioxin showed that there are two zones in the Woonasquatucket River that display advective and diffusive flux of dioxin from the sediment to the water column, one adjacent to the Source Area Soils, and a second downstream of the Allendale Dam. The RI cites a 2004 sediment

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stability study as the basis for this analysis and conclusion[1]. Because the FS is focusing on the length of the river proximate to (i.e., west of) the source area, we evaluated the data that formed the basis for this conclusion.

The 2004 sediment stability study states that the analysis of dioxin flux is based on "total dioxin" although there are no descriptions as to how total dioxin is defined. Additionally, the sediment stability study states that the effect of sediment resuspension is not expected to be a significant factor in the assessment of the data. This is important because as stated at the April 2007 dialog meeting, EPA's decision to include a groundwater remedy in the FS is based not on total dioxin, but on the apparent need to control influx of 2,3,7,8-TCDD to the surface water. Also, the RI states that the working assumption is that there is an ongoing source of 2,3,7,8-TCDD to the surface water from advection of groundwater, diffusion of sediment pore water, or from bioturbation. However, the only way bioturbation will introduce 2,3,7,8-TCDD into the surface water is through the release of particles caused by macroinvertebrates mixing the sediment surface layer. Thus, bioturbation is by definition a form of sediment resuspension, which is contrary to EPA's conceptual model.

Review of the surface water data collected in 1999[2], which forms the basis for the advective and diffusive flux conceptual model, shows that there is no advective flux of 2,3,7,8-TCDD into the Woonasquatucket River adjacent to the Source Area or in Allendale Pond that can be attributed to the groundwater and/or pore water. Table 1 summarizes the data for surface water samples collected in October and November 1999 and analyzed for 2,3,7,8-TCDD. Table 1 lists the samples in order from upstream to downstream locations on the main stem of the Woonasquatucket River. Relative sample locations are noted in the table. In addition to the sampling notes, data on total and dissolved iron and aluminum are provided as are comments derived from sampling data sheets in TetraTech NUS (2000).

Table 1 shows that of the 10 surface water samples collected in this region, six were non-detect for 2,3,7,8-TCDD. The four samples that had detectable concentrations of 2,3,7,8-TCDD were at stations WRC-SW-2010, WRC-SW-2015, APB-SW-2029, and APB-SW-2034. Although the sediment stability study surmised that the effect of sediment resuspension should not be significant, the data from the field notes and the supplemental analytical data show otherwise.

For example, surface water sample APB-SW-2029 has a total (i.e., unfiltered) 2,3,7,8-TCDD concentration of 4,000 pg/l. However, the field notes for that station describe the water as "organic sheen noted; reddish iron oxide flock; clear to red" (TTNUS, 2000). Additionally, the colocated metals samples were analyzed for both total and dissolved metals. For samples APB-SW-2029, the total iron was 113,000 µg/l, whereas the dissolved (filtered) sample has only 435 µg/l of iron. Similarly, the total aluminum in this sample was 5,070 µg/l, and the dissolved

[1] Battelle, 2004. Final Technical Memorandum Sediment Stability Study. Centredale Manor Restoration Project Superfund Site, Providence RI. November.
[2] TetraTech NUS, 2000. Final Technical Memorandum Woonasquatucket River Sediment Investigation. Centredale Manor Restoration Project Superfund Site, Providence RI. June.

sample did not contain aluminum above the detection limit of 14 µg/l. Clearly, this sample had a significant amount of suspended particles as well as an "organic sheen". It is most likely that any 2,3,7,8-TCDD in this sample was associated with suspended particles.

Similarly, surface water sample WRC-SW-2010 had an estimated total 2,3,7,8-TCDD concentration of 10.3 pg/l. The field notes for this sample state that the water was "Clear w/ muck floating." Also, the turbidity of this station was approximately 3-4 times higher than other samples where the field notes described the water as "clear." Total and dissolved aluminum were 182 µg/l and 49 µg/l, and total and dissolved iron were 571 and 210 µg/l, respectively. Again, the data from the field notes and other supporting analytical data indicate that suspended particles were present. The data for this location is suspect given the apparent presence of suspended particles of "muck".

Sample APB-SW-2034 contained 4.3 pg/l 2,3,7,8-TCDD, though this value is reported as an EMPC value (Estimated Maximum Possible Concentration). The reported turbidity of this sample is approximately 4.5 times that for all samples without detectable levels of 2,3,7,8-TCDD. Also, the total vs. dissolved aluminum is 122 µg/l to 53.4 µg/l. There were no specific notes on the level of clarity of the water sampled in the sample log sheet. However, the turbidity data and the total vs. dissolved data indicate that suspended solids were in fact present at this sampling location.

Based on the data collected and observations of the sampling crew, the only sample whose 2,3,7,8-TCDD cannot be directly attributed to suspended particles is WRC-SW-2015. Thus, only one of the 7 samples collected downstream of MW-05 and upstream of Allendale Dam had detectable levels of 2,3,7,8-TCDD whose presence cannot be explained by the co-occurrence of suspended particles.

Clearly, these data do not support the conceptual model expressed in Section 5.3.2 of the RI report because they do not demonstrate in any way that mass transfer of pore water from the sediment bed to the water column (due to processes such as diffusion and/or groundwater advection) is occurring. Rather, the data demonstrate that where suspended solids occur, dioxin is detected in the surface water sample. This finding is not surprising given the levels of 2,3,7,8-TCDD detected in sediment samples in this stretch of the river.

SEMI-PERMEABLE MEMBRANE DEVICE (SPMD) DATA

EPA's use of the SPMD data to estimate sediment pore water concentrations of 2,3,7,8-TCDD is so uncertain and inaccurate that it makes the data unusable in determining whether the conceptual model is valid. There are many problems with using the SPMD data in the manner in which they have been used, each problem introducing very serious uncertainty. There are three primary areas where the SPMD data fail in terms of its relevance and applicability for use in this assessment. The three areas are:

- Inability to accurately predict dissolved concentrations of 2,3,7,8-TCDD in water;

- Significant lack of credible supporting peer-reviewed or Agency-approved guidance in applying the SMPD data as it has been for this site; and

- High probability for blank contamination interference.

Each of these points is discussed below.

Inability of SPMD to predict concentrations of 2,3,7,8-TCDD in water

As part of the 2005 SPMD sampling event, Battelle deployed an SPMD into monitoring well MW-05[3]. The MW-05 SPMD was deployed for 27 days, which is consistent with the other SPMD deployment times. Upon retrieval of the MW-05 SPMD, Battelle collected an unfiltered groundwater sample from MW-05 (CMS-GW-MW05S-05) that was analyzed for 2,3,7,8-TCDD. The reported result for 2,3,7,8-TCDD from that groundwater sample was 4,144 pg/l. This concentration is roughly consistent with the levels of total 2,3,7,8-TCDD found in this well in the past (approximately between 1,100 pg/l and 4,600 pg/l).

The SPMD sample from MW-05 (CMS-SPMD-MW05S-05) was found to contain 2,3,7,8-TCDD at 2,470 pg/SMPD. Using Equation 1 from Battelle's poster presentation on SPMDs[4] in conjunction with the sampling rate correction factors provided in the Draft Feasibility Study by Battelle (f = 0.25)[5], the following calculation can be made:

$$C_w = 2{,}470 \text{ pg/SPMD}/[(3.8 \text{ l/d} \times 0.25) \times 27 \text{ days}] = 96 \text{ pg/l}$$

Cw in the above equation is the estimated concentration of 2,3,7,8-TCDD in the water column of well MW-05, assuming that the SPMD-to-water sampling conversion used by Battelle is correct.

MW-05 is the *only* location where temporally and spatially colocated groundwater and SPMD data were collected. Thus this location serves as the only source of available data that can be used to evaluate the assumption that the SPMD-to-water conversion of 2,3,7,8-TCDD actually works. When these data are used for that purpose, however, it is clear that the model does not work. In fact, the concentration predicted using the SPMD-to-water conversion (96 pg/l) is only 2 percent of that detected in the MW-05 groundwater sample (4,144 pg/l).

Compared to the sediment-deployed SPMDs, which were likely in direct contact with large quantities of suspended or deposited sediment, and water column-deployed SPMDs, which were highly fouled by vegetation, the SPMD from MW-05 was probably placed in the best location to get good agreement between SPMD-to-water estimates and the actual water concentrations. This is due to the relatively low level of suspended solids in the well and the small amount of

[3] Battelle, 2005. Chemistry Data Report Task RI-13B Semipermeable Membrane Device (SPMD) Investigation. Centredale Manor Restoration Project Superfund Site, Providence RI. November
[4] Dahlen, D., G. Durell, T. Himmer, and C. Rosiu. Semi-Permeable Membrane Device Investigation at the Woonasquatucket River. Poster Presentation .
[5] Pers. Comm. with D. Dahlen. June 2007.

biofouling observed. It appears that the SPMD-to-water conversion use by Battelle was not able to reproduce the water sampling results at MW-05 even in the better than average conditions that existed in MW-05. If the results of the SPMD-to-water conversion are not representative for MW-05, they cannot be expected to be representative of the other locations where sampling rate interferences are likely far more problematic. Therefore, we have no confidence that the water concentrations derived with the SPMD-to-water conversions for either the sediment or the surface water samples are accurate, supportable, or useable for corroborating the Battelle conceptual model. Accordingly, there is no support for the assumption that 2,3,7,8-TCDD is dissolved in the groundwater and is being transported to the Woonasquatucket River via pore water diffusion and/or groundwater advection.

Lack of Peer-Reviewed or Agency-Approved Approach

The use of SPMDs to collect time-integrated water samples for the determination of relative concentrations hydrophobic compounds has been demonstrated in the peer-reviewed literature and has been used in the field with some success. Although there are a limited number of studies that use SPMD data to compute an estimated absolute concentration in the water column, Battelle cites no peer-reviewed or Agency-approved method which mimics the SPMD-to-water conversion approach that they used in the present study. Moreover, an SPMD-to-sediment pore water conversion is not found in the published literature.

Nearly all of the peer-reviewed literature cited by Battelle in support of the SPMD-to-water conversion focused on the sampling of water, primarily in a laboratory setting. Sediment sampling experiments cited by Battelle are also idealized laboratory experiments and cannot be expected to mimic the conditions of the system at the Woonasquatucket River.

Even Battelle states several potentially significant data gaps for this study, including:

- The lack of a known water flow and temperature used to derive the sampling rate value of 3.8 l/d for 2,3,7,8-TCDD;
- The effects of the very low flow rates encountered in the CMRP SPMD study on the sampling rate are not known;
- The flow rates for groundwater, river water and sediment pore water are not known for the CMRP site; and
- The effects of biofouling, temperature and facial velocity-turbulence effects are not known.

Huckins et al.[6]states that environmental conditions can have a significant impact on the SPMD sampling rates. For example, facial velocity-turbulence effects can affect the sampling rate by an order of magnitude, temperature can affect the sampling rate by a factor of 4, and biofouling can affect the sampling rate by a factor of 3 or 4. Combined these factors can affect the sampling rate by over two orders of magnitude. However, there were no efforts to measure or control for these effects in the CMRP SMPD sampling. As an example, effects from reduced interfacial velocity were assumed to be negligible, when the photographic evidence shows that significant velocity effects were likely at some locations.

Additionally, in the draft portion of the Feasibility Study provided to AMEC, Battelle derives a non-peer reviewed equation for PAH sampling rates vs. flow rate. Although an equation is derived, it is not used in the assessment. Rather, Battelle relies on professional judgment to pick sampling rate correction factors. There is no back up or explanation provided for how the sampling rate correction factors were chosen.

Battelle does not discuss what effect, if any, small particle adherence may play in the higher apparent adsorption of 2,3,7,8-TCDD in sediment. Booij et al.[7] state that small particles could, "escape the [SPMD] cleansing procedure (rinsing and wiping) applied before extraction." Booij et al. go on to state that small particles with a higher sorption capacity than bulk sediment materials, which are not cleansed from the SPMD, could result in a false positive.

Although we have not seen photographs of the SPMD cages as they were retrieved from the sediment, it is very likely that sediment particles backfilled the hole and infiltrated the SPMD cages such that the SPMD surface area was in direct contact with sediment. Indeed, the sediment-deployed SPMD cages that had the highest total 2,3,7,8-TCDD concentrations on a total SPMD basis were also the two locations where there was significantly higher 2,3,7,8-TCDD in the bulk sediment than at the other location. However, the plausibility of the higher levels of dioxin in sediment being the source of the dioxin in the SPMD is not discussed by Battelle.

The methods used to convert the SPMD data to pore water concentrations have not been established in the peer-reviewed literature nor is there an EPA-approved method for such a determination. In addition, there are more unknowns in the conversion process than there are knowns. Unknowns outlined above include media-specific sampling rates, effects of temperature, biofouling, facial velocity-turbulence, water flow rates, effect of sediment in contact with SPMD, and the efficacy of the water rinse/wiping cleaning procedure to effectively clean SPMD of all non-adsorbed 2,3,7,8-TCDD. Each of these unknowns can have a significant impact on the interpretation of the SPMD results. In fact, there are so many unknowns that a

[6] Huckins, J.N., J.D. Petty, J.A. Lebo, F.V. Almeida, K. Booij, D.A. Alvarez, W.L. Cranor, R.C. Clark, and B.B. Mogensen. Development of the Permeability/Performance Reference Compound Approach for In Situ Calibration of Semipermeable Membrane Devices. *Environ. Sci. Technol.* 2002. 36, 85-91.

[7] Booij, K., H.M. Sleiderink, and F. Smedes. Calibrating the Uptake Kinetics of Semipermeable Membrane Devices Using Exposure Standards. *Environ. Toxicol. Chem.* 1998. 17, 1236-1245.

conclusion regarding the disposition of 2,3,7,8-TCDD in the water surrounding the SPMD cannot be made with the available data.

SPMD Blank Contamination

As part of the overall SPMD study, Battelle collected an exposed SPMD trip blank. The jar housing the trip blank is opened during field activities and capped when field activities are completed. However, to our knowledge, the trip blank is neither removed from the jar nor configured inside the jar as are the deployed SPMDs inside the sampling cages so as to ensure maximum surface area exposure to the media of interest. Nevertheless, the trip blank was found to contain 83.37 pg 2,3,7,8-TCDD/SPMD, which is comparable to the quantities detected in the surface water-deployed SPMDs.

Battelle's explanation for the trip blank having such levels of 2,3,7,8-TCDD is the high efficiency of the SPMD at collecting TCDD (i.e., the 2,3,7,8-TCDD was scavenged from the air). The equation used by Battelle to back estimate 2,3,7,8-TCDD concentration requires that the amount of TCDD in the SPMD is proportional to the TCDD in the fluid passing over the sampler (water or air) and the volume of fluid to which the SPMD is exposed. This same variety of equation is used for air samples[8]. Also, Soderstrom and Bergqvist[9] have demonstrated that the wind speed to which the SPMD is exposed affects the sampling rate; increased wind speed = increased sampling rate.

The SPMD in the jar will be exposed to a volume of air determined by the volume of the jar and the time necessary for the air in the jar to be replaced by ambient air through diffusion and, given sufficient wind, air turbulence. Also, as mentioned above, the configuration of the trip blank SPMD is not designed to maximize its exposed surface area.

In contrast, the SPMDs that were deployed in the sediment, surface water and groundwater were exposed to the open air. The exposure volume will depend upon the time and wind velocity during this period of exposure. Based on the photograph taken of the retrieval of the SPMD in MW05 it can be seen that, at least for the case of this SPMD, the volume of air exposed to the MW05 SPMD is likely to be orders of magnitude higher than for the trip blank. This is surmised because the SPMD is in the direct path of the wind, unfurled where maximum exposure to the ambient air can occur. In short, it does not appear that the trip blank was deployed in a manner that would sufficiently determine the equivalent exposure to air-borne 2,3,7,8-TCDD when compared to the field sample. As a result, the data quality for all the SPMDs are considered suspect.

CONCLUSION

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[8] Ockenden, W.A., H.F. Prest, G.O. Thomas, A. Sweetman, and K.C. Jones. Passive Air Sampling of PCBs: Field Calculation of the Atmospheric Sampling Rates by Triolein-Containing Semipermeable Membrane Devices. *Environ. Sci. Technol.* 1998. 32 (10), 1538-1543.

[9] Soderstrom, H.S. and P.A. Bergqvist. Passive Air Sampling Using Semipermeable Membrane Devices at Different Wind-Speeds in Situ Calibration by Performance Reference Compounds. *Environ. Sci. Technol.* 2004. 38 (18), 4828-4834.

Based on the observations discussed above, we have significant concerns that EPA is employing a conceptual model of chemical transport that is not supported by valid data. Upon review of the 1999 surface water sampling data underlying the conceptual model, we believe that certain, important data were not included in EPA's initial evaluation of these data. When the complete set of data are considered in the analysis, the conceptual model of sediment pore water to surface water influx of 2,3,7,8-TCDD cannot be substantiated.

We have shown that the SPMD and water sampling data are internally contradictory because the data for MW-05, the only sampling point with data from both the water and the SPMD, shows a 43-fold difference in the concentration of 2,3,7,8-TCDD in water. The data from MW-05 simply does not substantiate the methods used to compute the surface water and sediment pore water concentrations. In fact, the data demonstrate how poorly the SPMDs estimate 2,3,7,8-TCDD concentrations in water. This fact, combined with the overwhelming number of unquantifiable factors, such as sampling rates, flow rates, effects of particles, biofouling, temperature, and facial velocity-turbulence, which are critically important in determining sampling rates, render the data unusable for a meaningful evaluation of the conceptual model.

Finally, we have concerns that contamination to the deployed SPMD samplers cannot be accurately assessed with the trip blank data. The only thing that we can discern from this data is that 2,3,7,8-TCDD may have been present in ambient air. However, as explained above, the degree to which the deployed SPMDs were exposed to the 2,3,7,8-TCDD in ambient air cannot be quantified.

We look forward to discussing this information with you at our June 12 meeting.

Sincerely,

Russ Keenan

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Table 1. Summary of 1999 Surface Water Sampling Data Adjacent to the Source Area at CMRP.

Sample ID	Location	Date	2,3,7,8-TCDD (pg/l)		Iron total (ug/l)	Iron dissolved (ug/l)	Aluminum total (ug/l)	Aluminum dissolved (ug/l)	Turbidity (NTU)	Notes
WRC-SW-2009	Upstream of source area soils	11/1/1999	7.2	U	229	232	44.2 J	46.3 J	1.4	
WRC-SW-2010	Adjacent to Brook Village, upstream of	11/2/1999	10.3	J	571	201	182	49 J	4.5	Clear w/ muck floating
WRC-SW-2011	Adjacent to Cap 2, ~200' downstream of MW-05	11/2/1999	5.2	U	242	189	56 J	140	1.3	Clear
WRC-SW-2012	Adjacent to Cap 2, ~400' downstream of MW-05	11/2/1999	4.9	U	335	157	67.6 J	34.9 J	1	
WRC-SW-2013	Dowstream of Cap 2, Upstream of Cap 1	11/1/1999	5.9	U	313	186	76.1	34.9 J	0.9	clear water
WRC-SW-2014	~300' downstream of Cap 1	11/1/1999	5.4	U	236	154	37 J	45.4 J	0.75	clear
WRC-SW-2015	~250' downstream of WRC-SW-2014	11/1/1999	44.4	J	234	155	35.8 J	38.8 J	0.9	oil sheen noted in sediment
APB-SW-2029	~250' upstream of Allendale Dam	10/29/1999	4000	J	113000	435	5070	14 U	3.9	Organic sheen noted; reddish iron oxide flock; clear to red
APB-SW-2034	~250' upstream of Allendale Dam	11/3/1999	4.9	EMPC	431	239	122	53.4	5.7	
APB-SW-2035	~100' upstream of Allendale Dam	11/3/1999	2.4	U	404	251	95.2	89	2	