

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH AND DEVELOPMENT
SITE CHARACTERIZATION AND MONITORING TECHNICAL SUPPORT CENTER

September 27, 2018

MEMORANDUM

SUBJECT: Third-Party Review and Technical Support to Evaluate Primary Responsible Parties' Claims Pertaining to Remaining Contaminants of Concern at the General Mills-Henkel Site

FROM: Jan Szaro
EPA Region 1 – Superfund & Technology Liaison

TO: Leah Evison
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Disclaimer: This memorandum contains scientific observations provided in response to a request for site technical support with limited scope. The observations herein are intended to address specific scientific questions posed to researchers and/or consultants with applicable experience. Therefore, the observations are written for a specific scientific audience within U.S. EPA Region 5. The observations provided are intended to assist U.S. EPA Region 5 with relevant and innovative science and engineering to help meet site-specific environmental goals. The observations are provided in good faith, and due to the limited scope of technical support requests, include substantial uncertainty. This memorandum is not to be considered the only source of information for decision making, nor should the information provided here be parsed. It would be advisable to consider this memorandum in conjunction with multiple lines of evidence including history, experience of site managers, and other pertinent information available to U.S. EPA Regional staff who retain the duties and responsibilities of all decisions and regulatory actions at the site.

This technical memorandum and the attached contractor work product were prepared in response to your request to the Site Characterization and Monitoring Technical Support Center (SCMTSC). An SCMTSC contractor, Battelle, prepared the attached product to summarize the requested site document review and offer suggestions.

This work product is intended to assess site conditions based on the document review and offer suggestions or explanations into apparent discrepancies between various site documents; this work product will assist EPA decision makers with planning future actions at the site. Neither the EPA nor its contractors evaluated the data collection and analysis protocols followed by the secondary government data sources provided by Region 5 or the potentially responsible party; therefore, the data received were assumed to meet Regional data quality criteria. We have reviewed and accepted our contractor's work product as having addressed the scientific and technical questions included in our technical directive to them. We find the results and observations in the work product to be scientifically and technically sound. Thank you for the opportunity to provide technical support on this important issue. Please feel free to contact me with any questions or comments.

cc: Felicia Barnett, EPA SCMTSC Director

Memorandum

Technical Support for General Mills-Henkel Site

**Contract No. EP-C-16-014
Task Order #001, TD 2-05**

Prepared for:



**U.S. Environmental Protection Agency
Region 5**

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September 27, 2018

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FINAL
Third-Party Review and Technical Support to Evaluate Potentially Responsible Parties' Claims Pertaining to Remaining Contaminants of Concern at the General Mills-Henkel Site

September 27, 2018

Introduction

A pump and treat system was in operation at the General Mills site from 1985 to 2010. Long-term monitoring performed after the system was shut down demonstrated its effectiveness to treat 1,1,1-trichloroethane (TCA) and other compounds. However, the concentration of trichloroethylene (TCE) remains elevated at the site. The Potentially Responsible Parties (PRPs) argue that TCE remains elevated because a portion of it is being transported to the site from an upgradient source. The PRPs state that the ratio of chlorinated volatile organic compounds (cVOCs) in soil can be used to infer what would have been in groundwater if there weren't any other nearby sources. The objective of this technical directive is to review available historical site documents to gain a thorough understanding of background information and conditions and provide a third-party opinion regarding the PRPs' claim. Specifically, the United States Environmental Protection Agency (USEPA) requested assistance to provide an opinion on two issues:

1. Can ratios of concentrations of various cVOCs, with similar properties to one another in soil, be expected to lead to similar ratios of concentrations, relative to one another, in groundwater?
2. Is it possible to use the provided data to model concentrations of relative ratios of various cVOCs that would likely have been present in groundwater if this soil were the only source of contamination (no contribution from other upgradient sources)? Further, if such modeling is possible, would the results obtained (as ranges of concentrations or ratios for various cVOCs relative to one another) provide reasonable confidence in such results?

Document Review

Battelle performed a review of the documents received from the EPA pertaining to the General Mills-Henkel Superfund Site. These documents included:

- Subsurface Soil Report (Soil Exploration Company, 1981)
- Site Characterization Study and Remedial Action Plan General Mills Solvent Disposal Site (Barr, 1983)
- Evaluation of Remedy Completeness at the General Mills/Henkel Corp. Superfund Site (GSI, 2017)
- Supplemental Report on VOC Sources and Remediation (Geosyntec et al., 2017)
- Technical Memorandum responding to a request for clarification on the Supplemental Report on VOC Sources and Remediation at the General Mills/Henkel Corp. Superfund Site (GSI, 2018)
- Technical Memorandum providing a follow-up to a January 26, 2018 Technical Meeting at the site (Geosyntec, 2018)

- An Excel file titled “East Hennepin Area Data Tables” that is a compilation of analytical results for soil, groundwater, and vapor samples.
- A variety of additional notes, figures, and soil data.

The first two documents listed provided site background information and contaminant of concern (COC) data as determined during preliminary investigations prior to implementing a pump and treat system to treat the COCs.

Results

Battelle used the information provided in the documents described above to support our evaluation and response to the two questions above posed by the EPA, which are provided below.

Can ratios of concentrations of various cVOCs, with similar properties to one another in soil, be expected to lead to similar ratios of concentrations, relative to one another, in groundwater?

A wide range of properties and site-specific conditions affect the fate and transport of contaminants from soil to groundwater and conversely from groundwater to soil. Some of the more important ones include the following:

- The partitioning coefficient (K_d), which is determined by multiplying the fraction of organic carbon (f_{oc}) by the organic carbon partitioning coefficient (K_{oc}). Assuming all other properties equal, the ratio of the molar concentration of contaminants in soil having similar K_d values would exhibit the same molar ratio in groundwater. However, compounds with higher K_d values preferentially will remain sorbed to soil, resulting in lower concentrations in groundwater and hence a ratio of concentrations different from that observed in soil.
- Abiotic and biotic degradation mechanisms and rates. Chemicals can be abiotically and biotically degraded via different pathways and at different rates. In addition, degradation of a parent compound can result in the formation of a daughter product that also is a site COC. Several examples of degradation mechanisms¹ for site COCs include:
 - TCE can be degraded via biotic and abiotic mechanisms. For the biotic mechanisms, both aerobic and anaerobic pathways are possible depending on the redox conditions in the groundwater. Under reducing conditions, the traditional biotic reductive dechlorination pathway produces cis-1,2-DCE, vinyl chloride, and ethene before being metabolized. Under aerobic conditions, monooxygenase enzymes can degrade TCE through a variety of pathways and the byproducts are not detectable by Method 8260B and ultimately are metabolized. For the abiotic mechanism, TCE can be degraded in the presence of reactive minerals to acetylene. The biotransformation of TCE under reducing conditions is associated with a faster degradation rate constant than biotransformation of lesser chlorinated compounds (e.g., vinyl chloride).
 - 1,1-Dichloroethane (1,1-DCA) is a daughter product of 1,1,1-trichloroethane (TCA) degradation and can be biotransformed to chloroethane via reductive dehalogenase enzymes before being metabolized.

¹ Mechanisms for biotic degradation were researched using the Biocatalysis/Biodegradation Database (<http://eawag-bbd.ethz.ch/index.html>).

- 1,2-Dichloroethane (1,2-DCA) undergoes hydrolytic dehalogenation producing chlorinated ethanol and acetic acid prior to being metabolized. Abiotic transformation of 1,2-DCA produces ethylene glycol or vinyl chloride – however at a very slow rate.
- cis-1,2-Dichloroethene (cis-1,2-DCE) is a daughter product of trichloroethene (TCE). Dehalogenase enzymes degrade cis-1,2-DCE as part of the reductive dechlorination pathway where ethene is produced prior to being metabolized. Abiotically, cis-1,2-DCE can undergo beta elimination in the presence of reactive minerals to produce acetylene.
- TCA can be degraded through biotic and abiotic mechanisms. The biotic mechanisms can occur via aerobic and anaerobic pathways. In reducing environments, TCA can be reductively dechlorinated to 1,1-DCA then chloroethane before ultimately being metabolized. In oxic environments, TCA can be biotransformed using monooxygenase enzymes to 2,2,2-trichloroethanol which can then be degraded via biotic TCE pathways. The abiotic mechanisms produce 1,1-DCE via dehydrochlorination and acetate by hydrolysis.

As illustrated above, biotransformation of the site COCs is a complicated process that is strongly affected by groundwater geochemistry. Differences in reaction mechanisms and rates (see Table 1) can, over time, result in different ratios of molar concentrations in groundwater compared to soil. Over time, as contaminants are degraded in the aqueous phase, a greater concentration gradient is generated, resulting in faster desorption and solubilization of contaminants into the aqueous phase, thereby depleting the mass on the solid phase and changing the molar concentration ratio. Models such as BIOCHLOR or NAS can be used to model relative changes in COC concentrations to understand changes over time. However, time series data and geochemical oxidation-reduction data such as dissolved oxygen, sulfate, and methane are required in order to model these changes, which were not available to Battelle at the time this evaluation was conducted.

- Fraction of contaminants in the vadose zone, frequency of rain events, and solubility of individual contaminants. These parameters contribute to the dissolution of contaminants in the vadose zone and transport into groundwater. In the source area, when surface releases occur, or in the case of the waste discharge point at the General Mills site, a portion of the vadose zone becomes saturated with contaminants. As rain events occur, contaminants that are less tightly bound to soil (i.e., lower K_d values) and have higher solubilities will tend to travel greater distance and impact groundwater, which can contribute to deviations between the molar ratio of contaminants in (saturated) soil and the molar ratio in groundwater.
- Henry's law constant (H_{cc}). Compounds having higher H_{cc} tend to volatilize more easily. Hence, concentrations of COCs in groundwater with higher H_{cc} will deplete faster than those with lower values, which over time can result in disproportionately lower concentrations in groundwater than in soil.

Table 1 summarizes various chemical and physical properties of the site COCs. Note the fraction of organic carbon, and therefore K_d , is not known and not included in Table 1. Instead the octanol-water coefficient (K_{ow}) for each COCs is included. Karickhoff *et al.* (1979) noted a linear relationship between K_{oc} and K_{ow} that depends on the type of contaminant. A variety of regression equations are available in the literature for conversion between K_{ow} and K_{oc} . In general, however, greater K_{ow} translates to greater K_{oc} and greater K_d (for a given fraction of organic carbon). The K_{ow} is the relative distribution of a contaminant between octanol and water assuming equilibrium conditions and provides a measure of the hydrophobicity of a contaminant. K_{ow} can be measured in the laboratory and the values are readily available.

Table 1. Chemical and Physical Properties of Site COCs

Compound	Molecular Weight (g/mol)	Density (g/cm ³)	C _{sat} (mg/L)	-log(H _{cc})	log K _{ow}	Solubility (mg/L @20C)	Half Life (days)	
							Biotic	Abiotic
Ethyl Benzene	106.2	0.86	168	0.5	3.2	152	5a ^a	NA
Xylene	106.2	0.86	176	0.59	3.24	175	17 ^a	NA
Toluene	92.2	0.87	556	0.6	2.69	535	5 (aerobic) ^b	NA
Benzene	78.1	0.88	1,748	0.65	2.17	1,750	58 (aerobic) ^b	NA
Chlorobenzene	112.6	1.11	459	0.8	2.78	500	280 – 580 ^b	NA
1,1-dichloroethane	99	1.18	5,077	0.61	1.79	550	NA	22,265 ^b
1,2-dichloroethane	99	1.25	8,426	1.27	1.46	8,690	63 – 165 ^b	25,915 ^b
cis-1,2-DCE	96.9	1.27	5,085	0.66	1.86	3,500	210 ^c	110–912.5 ^b
1,1,1-trichloroethane	133.4	1.34	1,304	-0.16	2.49	1,360	2.9 – 105 ^b	402-1387 ^d
TCE	131.4	1.46	1,093	0.31	2.42	1,000	277 – 1,210 ^b	23-49 ^e
Chloroform	119.4	1.48	8,453	0.84	1.95	8,000	NA	69,390 ^b
Carbon tetrachloride	153.8	1.59	885	-0.04	2.77	800	4.9 ^a	229,950 ^b

^a Suarez, Monica P., and Hanadi S. Rifai. "Biodegradation rates for fuel hydrocarbons and chlorinated solvents in groundwater." *Bioremediation Journal* 3, no. 4 (1999): 337-362.

^b Lawrence, S.J., 2006, Description, properties, and degradation of selected volatile organic compounds detected in ground water — A Review of Selected Literature: Atlanta, Georgia, U. S. Geological Survey, Open-File Report 2006-1338, 62 p., a Web-only publication at <http://pubs.usgs.gov/ofr/2006/1338/>

^c Median degradation rates from BIOCHLOR User’s Manual (V2.2) where signification BTEX is present to server as electron donor

^d Scheutz, Charlotte, Neal D. Durant, Maria H. Hansen, and Poul L. Bjerg. "Natural and enhanced anaerobic degradation of 1, 1, 1-trichloroethane and its degradation products in the subsurface—a critical review." *Water research* 45, no. 9 (2011): 2701-2723.

^e He, Y. T., J. T. Wilson, C. Su, and R. T. Wilkin. "Review of abiotic degradation of chlorinated solvents by reactive iron minerals in aquifers." *Groundwater Monitoring & Remediation* 35, no. 3 (2015): 57-75

NA – Not Available

As noted above, the molar ratio of concentrations of cVOCs in soil can, over time, differ from those measured in groundwater due to a variety of chemical and physical properties and site conditions. However, as shown in Table 1, the chemical and physical properties of TCE fall within the range of properties exhibited by the other cVOCs at the site. Hence, it is reasonable to assume that if the pump and treat system was able to adequately treat the other contaminants, then a similar level of treatment would be expected to be achieved for TCE².

Is it possible to use the provided data to model concentrations of relative ratios of various cVOCs that would likely have been present in groundwater if this soil was the only source of contamination (no contribution from other upgradient sources)? Further, if such modeling is possible, would the results obtained (as ranges of concentrations or ratios for various cVOCs relative to one another) provide reasonable confidence in such results?

VLEACH was used to simulate the migration of TCE contamination through the vadose zone in the vicinity of the historic source zone at the General Mills site and to evaluate the magnitude of TCE concentrations that could

² Battelle did not perform an analysis of the pump and treat remedy. This conclusion assumes that the results of the pump and treat system as reported by General Mills are correct.

potentially leach to groundwater. VLEACH is a one-dimensional finite difference vertical transport model that is designed to evaluate groundwater impacts from, and volatilization of, VOCs in the vadose zone (Dymanac, 1997).

An instantaneous source was assumed for the uppermost layer of the model (0 to 12 ft below ground surface [bgs]). The highest reported TCE concentration within this depth (25,000 $\mu\text{g}/\text{kg}$ in GP-3 in 2001 as reported in the East Hennepin Area data tables received from the EPA) was used as a conservative source concentration (i.e., worst-case scenario). The VLEACH model incorporates chemical-specific values for TCE. Values used for the Henry's Law constant and the water solubility for TCE were consistent with those in Table 1. Published values from the Department of Toxic Substance Control (DTSC, 1994a) were used for the organic carbon partition coefficient (K_{oc}) (86 mL/g) and the air diffusion coefficient (0.68 m^2/d).

The model incorporated a recharge rate of 0.625 ft/year, which was calculated as roughly one quarter of the annual precipitation (30 inches) measured in the vicinity of the site. Geologic data near the proposed release area (Barr Engineering, 1983) indicate fill and peat to a depth of roughly 10 ft bgs, underlain by alluvial sand. Conservatively, the alluvial sand was chosen to best describe the vadose zone lithology, given that peat typically has a very high fraction organic carbon (f_{oc}), which results in significant retardation of TCE contaminant migration. Vadose zone soil physical parameters representative of an alluvial sand were utilized during the simulation, including a bulk density of 1.35 g/cm^3 and an effective porosity of 0.3. Two f_{oc} values of 0.0005 and 0.005 were initially used based on measurements for similar sandy soil types as summarized in ITRC (2015).

Table 2 summarizes the VLEACH modeling simulations. The baseline VLEACH simulations performed using the input parameters discussed above predict fairly rapid migration of vadose zone TCE to groundwater. Based on the low end f_{oc} value of 0.0005, a maximum TCE concentration of 5,500 $\mu\text{g}/\text{L}$ is predicted to migrate to groundwater in 0.1 years. When the f_{oc} value is increased by an order of magnitude to 0.005, the maximum TCE leachate concentration decreases to 2,200 $\mu\text{g}/\text{L}$ and a similar migration timeframe is observed. During model simulations, it was noted that the model is highly sensitive to f_{oc} values, and that higher organic material in soil (higher f_{oc}), consistent with what would be observed in peat or shallow fill, would result in TCE retardation, and subsequently lower groundwater leachate concentrations. Accordingly, a sensitivity analysis was performed to evaluate the effect of higher f_{oc} values on groundwater concentrations. Additional simulations were performed using an f_{oc} more representative of peat to evaluate the associated impact on groundwater leachate concentrations. Increasing the f_{oc} to 0.05 and 0.5 increased the sorption potential and associated migration timeframe, resulting in lower groundwater leachate concentrations. Using a f_{oc} value of 0.05, a maximum leachate TCE concentration of 290 $\mu\text{g}/\text{L}$ is predicted to migrate to groundwater in 1.4 years. Increasing the f_{oc} value another order of magnitude to 0.5 yielded a maximum TCE leachate concentration of roughly 3 $\mu\text{g}/\text{L}$ that reaches groundwater in approximately 13 years. Assuming use of identical chemical- and soil-specific input parameters, additional modeling simulations indicated the ratio between soil and groundwater concentrations is linear, as shown in Table 2.

Additional model simulations were performed to evaluate migration of 1,2-DCA and 1,1,1-TCA soil concentrations to groundwater (see Table 2). These two chemicals were selected to evaluate how differences in chemical migration rates (i.e., higher and lower retardation rates) affect leachate concentrations and migration timeframes. All model input parameters remained the same, with chemical-specific values for 1,2-DCA and 1,1,1-TCA modified based on Table 1, DTSC (1994b) and EPA (1998). The simulations show that for a chemical with a lower K_{oc} (1,2-DCA – K_{oc} of 18), groundwater leachate concentrations are higher. Conversely, simulations with a chemical with a higher K_{oc} (1,1,1-TCA – K_{oc} of 150) predict lower groundwater leachate concentrations.

Table 2. Summary of Vadose Zone Modeling Simulations

Chemical	Source Concentration (ug/kg)	f_{oc}	Approximate Maximum Groundwater Leachate Concentration ($\mu\text{g/L}$)	Time of Maximum Groundwater Leachate Concentration (yr)
TCE	2,500	0.0005	550	0.1
		0.005	220	0.2
		0.05	29	1.4
		0.1	3	13
	25,000	0.0005	5,500	0.1
		0.005	2,200	0.2
		0.05	290	1.4
		0.5	30	13
	250,000	0.0005	55,000	0.1
		0.005	22,000	0.2
		0.05	2,900	1.4
		0.1	300	13
1,2-DCA	25,000	0.0005	19,000	0.1
		0.005	9,200	0.2
		0.05	1,700	1.4
		0.5	160	12
1,1,1-TCA	25,000	0.0005	3,500	0.1
		0.005	1,400	0.2
		0.05	170	1.5
		0.5	17	14

Given the model sensitivity to f_{oc} and other site-specific input parameters used in the model, direct measurement and subsequent use of soil parameter values would significantly enhance the accuracy of model predictions.

TCE concentrations measured in grab groundwater samples collected from the immediate vicinity of the former disposal area were found to be low (i.e., 36.5 $\mu\text{g/L}$) near the top of the water table (about 20 ft bgs), and were found to increase with depth (up to 136 $\mu\text{g/L}$ at about 40 ft bgs) (GSI, 2017). Similarly, concentrations were found to be much higher (629 $\mu\text{g/L}$ at about 52.5 ft bgs) at the upgradient boundary of the site. Although there may be a small contribution from any TCE remaining in soil in the immediate vicinity of the waste discharge area, it may be negligible compared to the TCE that appears to be entering the site from upgradient sources.

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