

Appendix E Compound-Specific Isotope Analysis

E1.0 Background

Compound-specific isotope analysis (CSIA) was performed on groundwater samples collected from 18 wells at the Hoffmann-La Roche Inc. (Roche) facility (Site), located at 340 Kingsland Street, in the Township of Nutley, Essex County, New Jersey, in February 2014. This appendix to the Baseline Monitored Natural Attenuation (MNA) Report is intended to present CSIA as a tertiary line of evidence for the occurrence of natural attenuation of chlorinated ethenes at the 120-acre facility. This appendix was prepared using guidance from the US Environmental Protection Agency's *A Guide for Assessing Biodegradation of Organic Ground Water Contaminants using Compound Specific Isotope Analysis (EPA 600/R-08/148, December 2008)*.

E2.0 CSIA Methodology and Interpretive Tools

E2.1 Carbon Isotope Fractionation

Many elements of biological interest have two or more common stable isotopes, with the lighter isotopes present in much greater abundance than their heavier counterparts. For example, the abundance of the light isotope of carbon (^{12}C) is 98.89 percent, and the abundance of the heavy isotope of carbon (^{13}C) is 1.11 percent. Under conditions in which abiotic or biotic degradation of a compound is occurring, the parent compound gains a progressively higher content of heavy isotopes. This is due to the fact that bonds between a heavier isotope and the atoms adjacent to it are stronger than the equivalent bonds of a lighter isotope. As a result, chemical or biologically mediated reactions of molecules that contain lighter isotopes occur more quickly than those that contain heavier isotopes. This process is called fractionation. Conversely, processes other than degradation that affect contaminant concentrations in groundwater, such as dilution, sorption, and volatilization, have very small or no isotopic effects.

The results of a CSIA analysis are reported as an isotope ratio, which is the concentration of the heavy isotope to the light isotope (i.e., $^{13}\text{C}/^{12}\text{C}$). The results of the sample and an internationally-used chemical standard, used to ensure consistency in analytical results from different instruments and laboratories, are reported in terms of the parameter "del", where the del value for ^{13}C is defined as:

$$\delta^{13}\text{C} = \frac{\frac{^{13}\text{C}}{^{12}\text{C}}_{\text{sample}} - \frac{^{13}\text{C}}{^{12}\text{C}}_{\text{standard}}}{\frac{^{13}\text{C}}{^{12}\text{C}}_{\text{standard}}} * 1000$$

The units for $\delta^{13}\text{C}$ ("del") are defined as per mil (parts per thousand, or ‰). In a system in which degradation is occurring, the value of del for a compound is expected to increase over travel distance and time. Note that the numerical value of del is dependent, in part, upon the laboratory standard, and is, alone, not particularly useful. It is the spatial and temporal trends in del that are used to indicate natural attenuation.

The magnitude of isotope fractionation can be expressed by the isotope fractionation factor (α_{PR}) that quantifies the difference in isotope ratio between the product (P) that is formed at a given time, e.g., cis-1,2-DCE; and the reactant (R), e.g., TCE, and is calculated using the isotope ratios for the parent (in this case $\delta^{13}C_R$) and daughter products (in this case $\delta^{13}C_P$), such as PCE-TCE and TCE-cis-1,2-DCE, to provide an indicator for degradation:

$$\alpha_{PR} = \frac{(\delta^{13}C_P + 1000)}{(\delta^{13}C_R + 1000)}$$

When degradation is occurring, α_{PR} is less than 1 as the $\delta^{13}C$ for the parent product becomes lighter and the $\delta^{13}C$ for the daughter product becomes heavier.

The isotope enrichment factor (ϵ_{PR}) gives the magnitude of isotope fractionation, expressed as:

$$\epsilon_{PR} = (\alpha_{PR} - 1) * 1000$$

The larger the fractionations during the reaction, the more negative the isotope enrichment factor.

E2.2 Hydrogen Isotope Fractionation

In the case of trichloroethene (TCE), fractionation of hydrogen between deuterium (2H , also known as “heavy” hydrogen), and the significantly more abundant “common” hydrogen (1H protium), can be used to differentiate manufactured TCE from degrading tetrachloroethene (PCE) (Wang and Smith, 2010). δ^2H for manufactured TCE is highly enriched due to the reactions of its synthesis, ranging from 466.9 ‰ and 681.9 ‰ in one study (Shouakar-Stash et al., 2003), whereas TCE degrading from PCE can be significantly depleted (as low as -300 ‰ or less). Results of δ^2H for TCE lower than the manufactured range can indicate that the TCE is a product of degradation.

E2.3 Rayleigh Model

If a single process for degradation controls the plume concentrations, the data will follow the Rayleigh model, which predicts a logarithmic enrichment pattern. Data that do not fall on a straight line on a semilog plot of $\delta^{13}C$ versus concentration may indicate other processes at work (e.g., mixing with other sources).

E3.0 Fractionation Results

In February 2014, groundwater samples were collected from 18 site wells and submitted to Zymax Forensics in Escondido, California, for CSIA analysis of tetrachloroethene (PCE), trichloroethene (TCE), and cis-1,2-dichloroethene (cis-1,2-DCE). $\delta^{13}C$ values for TCE and cis-1,2-DCE could not be obtained for three of these samples because analyte concentrations were too low for the analysis to be performed. Results are presented in Table E1 and discussed below in terms of designated site/source areas (see Section 2.2.4 of the main report). The analysis

below comprises only one sampling event and is therefore only a “snapshot” of natural attenuation as evidenced by CSIA.

- **IA-9 Process Pipe Corridor** – One well, MW-170, was sampled and analyzed for CSIA. Although the PCE-TCE enrichment factor is not currently favorable (slightly greater than 1), $\delta^2\text{H}$ for TCE is well below the manufactured range, indicating that it is a product of PCE depletion. The TCE-cis-1,2-DCE enrichment factor is currently moderately favorable (slightly less than 1), and the presence of cis-1,2-DCE at an elevated concentration indicates that TCE has in fact degraded.

- **Clifton-Allwood Municipal Sewer Corridor**

- **IA-12** – Four wells, MW-24, MW-60, MW-80A, and MW-233 were sampled and analyzed for CSIA. MW-60 has the highest chlorinated ethene concentrations, with a slightly favorable PCE-TCE enrichment factor and a $\delta^2\text{H}$ value indicating that TCE is a product of PCE depletion. The TCE-cis-1,2-DCE enrichment factor is currently moderately favorable, and the presence of cis-1,2-DCE at an elevated concentration indicates that TCE has in fact degraded.

MW-24, MW-80A, and MW-233C have significantly lower PCE concentrations than MW-60. The PCE-TCE enrichment factor is currently slightly unfavorable; however, the $\delta^2\text{H}$ value for MW-233C indicates that TCE is a product of PCE depletion. The TCE-cis-1,2-DCE enrichment factors are currently moderately favorable for MW-24 and MW-80A.

- **IA-3** – One well, MW-225B, was sampled and analyzed for CSIA. Although the PCE-TCE enrichment factor is not currently favorable (slightly greater than 1), $\delta^2\text{H}$ for TCE is well below the manufactured range, indicating that it is a product of PCE depletion. The TCE-cis-1,2-DCE enrichment factor is currently moderately favorable (slightly less than 1), and the presence of cis-1,2-DCE at an elevated concentration indicates that TCE has in fact degraded.
- **IA-7** – Four wells, MW-218, MW-218B, MW-212C, and PW-37PORT4, were sampled and analyzed for CSIA. Enrichment factors for PW-37PORT4 could not be obtained in the laboratory due to low analyte concentrations. For the remaining three wells, the PCE-TCE enrichment factors currently are slightly unfavorable, but the $\delta^2\text{H}$ value for MW-218 indicates that the TCE is a breakdown product of PCE. The TCE-cis-1,2-DCE enrichment factors are currently slightly unfavorable; however, the TCE concentrations are quite low.
- **IA-11** – Three wells, MW-63, MW-74, and MW-119, were sampled and analyzed for CSIA. The PCE-TCE and TCE-cis-1,2-DCE enrichment factors are currently slightly unfavorable.
- **IA-15 and Building 716** – Two wells from IA-15 (MW-112 and MW-221C) and three offsite wells located near Building 716 (MW-171A, B, and C) were sampled

and analyzed for CSIA. Enrichment factors for the IA-15 wells could not be obtained in the laboratory due to low analyte concentrations. For the MW-171 cluster, the PCE-TCE enrichment factors currently are slightly favorable, and TCE-cis-1,2-DCE enrichment factors are currently slightly unfavorable.

E4.0 Raleigh Model Analysis

To assess whether the Roche data fit the Raleigh model and thus comprise a single degradation process, $\delta^{13}\text{C}$ data for PCE were plotted versus the natural logarithm of the PCE concentration for designated site areas where CSIA was performed on at least three wells. The graph is shown on Figure E1.

The data for IA-12 appear to fit the Raleigh model, providing additional evidence for natural degradation of PCE. The data for areas IA-7, IA-11, and offsite (Building 716) are not linear, indicating influences from other processes, such as co-mingling, in addition to degradation. This is reasonable, as these areas are downgradient and thus more likely to be influenced by transport processes than IA-12, which is upgradient. However, the overall range of $\delta^{13}\text{C}$ on Figure E1 is approximately 1 ‰, which is within the analytical uncertainty of ± 0.5 ‰, and certainly within the recommended uncertainty range of ± 1 ‰ (EPA, 2008). With this in mind, even the well-behaved IA-12 data comprise a statistically insignificant slope, likely still indicating degradation, but very slow.

E5.0 Summary and Recommendations

Isotopic fractionation detected in groundwater samples from wells within IA-3, IA-7, IA-9, IA-12, and offsite (Building 716) indicate some level of PCE-TCE-cis-1,2-DCE degradation. It is not known whether this degradation is biotic or abiotic, or a combination of both. Although some studies have been performed to differentiate biotic from abiotic degradation using CSIA, the degree of fractionation here is not sufficient to perform such an analysis.

Evidence for natural attenuation is most compelling in IA-12, where CSIA results in each of the four wells sampled indicate favorable fractionation factors, and the Raleigh model is generally descriptive. However, the degree of fractionation/enrichment is generally low, indicating very slow rates of degradation, currently. Ongoing analysis for $\delta^{13}\text{C}$ would enable temporal trends and further substantiate the “snapshot in time” analysis presented here.

E6.0 References

Shouakar-Stash, O., Frappe, S.K., and Drimmie, R.J., 2003. *Stable hydrogen, carbon, and chlorine isotope measurements of selected chlorinated organic solvents*. Journal of Contaminant Hydrology, 60, 221-228.

US EPA, 2008. *A Guide for Assessing Biodegradation of Organic Ground Water Contaminants using Compound Specific Isotope Analysis*. EPA 600/R-08/148.

Wang, Y., and G.J. Smith, 2010. *Advanced Site Diagnostic Tool 3D-CSIA for In Situ Remediation*. Remediation 10.1002/rem.20273, 79-95.

**TABLE E1
COMPOUND SPECIFIC ISOTOPE ANALYSIS (CSIA) RESULTS**

Hoffmann-LaRoche Inc. - Nutley, New Jersey

Investigation Area	Well ID	Zone	Well Screen	Date Sampled	PCE		PCE to TCE		TCE			TCE to cis-1,2-DCE		cis-1,2-DCE	
					$\delta^{13}\text{C}$ (‰)	Conc. (µg/L)	α_{PR}	ϵ_{PR}	$\delta^{13}\text{C}$ (‰)	$\delta^2\text{H}$ (‰)	Conc. (µg/L)	α_{PR}	ϵ_{PR}	$\delta^{13}\text{C}$ (‰)	Conc. (µg/L)
IA-3	MW-225B	Clifton-Allwood Sewer	S2	2/20/14	-27.42	120	1.003	3.0	-24.54	74 JA	190	0.997	-2.8	-27.28	1,100
IA-7	MW-218	Clifton-Allwood Sewer	S1	2/20/14	-28.04	630	1.004	3.7	-24.49	65 JA	270	0.999	-1.5	-25.94	420
	MW-218B	Clifton-Allwood Sewer	S2	2/20/14	-27.88	67	1.002	2.3	-25.62	-	9.0	1.002	2.2	-23.50	20
	MW-212C	Clifton-Allwood Sewer	S3	2/19/14	-27.52	160	1.003	2.5	-25.07	-	42	1.001	1.5	-23.63	100
	PW-37PORT4	down/cross gradient	S3	2/20/14	-27.98	70	-	-	-	-	1.7	-	-	-	<2.0
IA-9	MW-170	IA-9 Pipeway	S1	2/17/14	-27.49	19,000	1.001	1.4	-26.15	55	10,000	0.997	-2.5	-28.63	57,000
IA-11	MW-63	downgradient	S2	2/19/14	-28.01	70	1.001	1.3	-26.73	-	23	1.007	7.1	-19.85	100
	MW-74	downgradient	S2	2/19/14	-27.70	40	1.003	2.7	-25.10	-	13	1.001	1.0	-24.08	120
	MW-119	downgradient	S3	2/17/14	-27.52	260	1.001	1.4	-26.13	-	22	1.002	1.7	-24.49	110
IA-12	MW-24	Clifton-Allwood Sewer	S1	2/19/14	-27.42	16	1.005	5.4	-22.20	-	41	0.998	-1.7	-23.84	670
	MW-60	Clifton-Allwood Sewer	S1	2/19/14	-27.82	11,000	0.996	-3.7	-31.42	61	3,500	0.999	-1.2	-32.63	2,900
	MW-80A	Clifton-Allwood Sewer	S1	2/20/14	-27.10	2.0	1.017	17.3	-10.31	-	20	0.988	-12.4	-22.56	580
	MW-233C	Clifton-Allwood Sewer	S3	2/19/14	-27.56	130	1.000	0.4	-27.13	76 JA	79	1.004	3.8	-23.45	170
IA-15	MW-112	downgradient	S1	2/20/14	-28.43	86	-	-	-	-	2.1	-	-	-	1.9
	MW-221C	downgradient	S3	2/20/14	-28.08	68	-	-	-	-	1.9	-	-	-	2.1
Off-site	MW-171A	Building 716	S1	2/17/14	-27.59	320	0.998	-1.9	-29.41	-	12	1.009	9.3	-20.35	17
	MW-171B	Building 716	S2	2/12/14	-27.41	260	0.997	-3.0	-30.30	-	11	1.008	8.1	-22.40	14
	MW-171C	Building 716	S3	2/12/14	-27.49	310	0.998	-1.7	-29.17	-	12	1.006	5.8	-23.52	18

Notes:

- Not analyzed or not calculated (typically because concentration was too low to perform the CSIA analysis)
- α_{PR} Isotope fractionation factor
- ϵ_{PR} Isotope enrichment factor
- $\delta^{13}\text{C}$ Carbon isotope ratio (parts per thousand, ‰)
- $\delta^2\text{H}$ Hydrogen isotope ratio (parts per thousand, ‰)
- JA Target analyte produced a lot peak signal and the result is considered usable to +/- 20 ‰, but not the standard = +/- 0.5 ‰

- PCE Tetrachloroethene
- TCE Trichloroethene
- cis-1,2 DCE cis-1,2-Dichloroethene

- < Parameter was not detected at or above the specified laboratory reporting limit.
- µg/L Micrograms per liter

- S1 First water to 80 feet above mean sea level (MSL)
- S2 80 feet to 50 feet above MSL
- S3 50 feet to 0 feet above MSL

 Favorable indicator for natural degradation.

Figure E1
Rayleigh Correlation - PCE

