

Appendix G

Evaluation of Natural Attenuation at Gude Landfill

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EVALUATION OF NATURAL ATTENUATION AT GUDE LANDFILL

1. INTRODUCTION

Monitored natural attenuation (MNA) relies on (1) a combination of naturally occurring processes to decrease contaminant concentrations to acceptable levels, and (2) a program for monitoring these processes and resulting changes in contaminant levels. The U.S. Environmental Protection Agency (EPA 1997) defines MNA as:

“the reliance on natural attenuation processes (within the context of a carefully controlled and monitored clean-up approach) to achieve site-specific remedial objectives within a time frame that is reasonable compared to other methods. The “natural attenuation processes” that are at work in such a remediation approach include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil and ground water. These in-situ processes include biodegradation, dispersion, dilution, sorption, volatilization, and chemical or biological stabilization, transformation, or destruction of contaminants.”

For MNA to be a viable remedial technology for deployment at a given site, natural *in situ* conditions that promote the attenuation of contaminants must be present at the site. The natural attenuation occurring must also be protective of human health and the environment, with similar or greater protectiveness when compared to other remedial alternatives for the site.

This appendix to the Gude Landfill Assessment of Corrective Measures (ACM) evaluates the natural attenuation processes that are currently active at the Landfill, to assess the viability of MNA as a possible corrective measure technology. The most widespread site-related constituents of concern (COCs) at the Landfill are chlorinated volatile organic compounds (cVOCs), which will therefore be the focus of this MNA evaluation, although natural attenuation of other site-related volatile organic compounds (VOCs) will also be considered. The remedial action objective for groundwater at the Landfill is COC concentrations below maximum contaminant levels (MCLs) at the point of compliance, which is located at the property boundary. This evaluation was performed to assess whether MNA is an appropriate technology for achieving this objective. Section 2 below describes the most common mechanisms of natural attenuation, as they apply to the Landfill. Section 3 assesses the evidence for natural attenuation

occurring at the Landfill, including analysis of groundwater geochemistry, compound-specific isotope analysis (CSIA) of cVOCs, and statistical analysis of trends in COC concentrations.

2. MECHANISMS OF NATURAL ATTENUATION

2.1 PHYSICAL PROCESSES

Physical processes associated with groundwater flow, such as advection, diffusion, and dispersion, can cause dilution of dissolved constituents present within a contaminated groundwater plume. As the contaminated groundwater flows downgradient, the edges (top, bottom, sides, and front) of the plume mix with surrounding groundwater, which can result in lower contaminant concentrations. Attenuation of contaminants by physical processes generally occurs more slowly and over a longer distance than chemical or biological processes; therefore, this mechanism of attenuation is often insufficient to meet remedial goals at sites where COC concentrations are elevated substantially above acceptable limits and/or where a point of compliance that is located near the source, as is the case at the Landfill.

2.2 CHEMICAL PROCESSES

Chemical processes that occur independent of biological activity can cause attenuation of constituents in groundwater. For example, adsorption of metals to the soil or rock within the aquifer is a chemical reaction that can remove metals from the groundwater. Organic compounds can also be degraded by reaction with abiotic oxidizing agents within the aquifer. However, biologically mediated chemical reactions typically occur more rapidly, due to the influence of bacterial enzymes on reaction rates. Therefore, biological attenuation will be the focus of the evaluation presented in this appendix.

2.3 BIODEGRADATION PROCESSES

Biodegradation of cVOCs through reductive dechlorination is typically considered the primary driving force for rapid attenuation of cVOCs in groundwater. Reductive dechlorination occurs in low-oxygen, reducing groundwater, and requires the presence of a carbon substrate. Dechlorination of tetrachloroethene (PCE) and trichloroethene (TCE), which are two of the primary COCs at the Landfill, produces a series of daughter products which includes TCE (in the case of PCE degradation), cis-1,2-dichloroethene (DCE), and vinyl chloride (VC). This process can be mediated by a variety of bacteria, some of which can then degrade the cis-1,2-DCE and VC to ethane anaerobically. The presence of these daughter products in groundwater at the Landfill is evidence that reductive dechlorination is occurring.

Biodegradation of benzene and other petroleum constituents can occur either aerobically or anaerobically (with or without dissolved oxygen), although aerobic degradation is typically faster. This degradation does not necessarily require an additional carbon substrate, as the bacteria can use benzene as a carbon substrate. The byproducts of this degradation are carbon dioxide and water.

3. ANALYSIS

3.1 ANALYSIS OF GROUNDWATER GEOCHEMISTRY

As described above, the presence of daughter products (TCE, cis-1,2-DCE, VC) is one of the best lines of evidence that reductive dechlorination of PCE and/or TCE is occurring in an aquifer. In addition, various other groundwater characteristics can affect the rate of attenuation of cVOCs. These characteristics are identified and described in EPA's *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water* (1998). Pertinent characteristics for which data are available at the Landfill include general geochemical characteristics such as pH, oxidation-reduction potential (ORP), dissolved oxygen concentration, and the concentrations of nitrate and sulfate, which can compete with the cVOCs as reducing agents. The presence of reduced iron in groundwater can provide additional evidence of a low-ORP environment, favorable for reductive dechlorination.

To assess the evidence for and favorability of reductive dechlorination in the groundwater at the Landfill, the results of groundwater characterization during the March 2012 sampling event, in the wells where cVOCs have been detected at concentrations above MCLs, were assessed according to these criteria. The results of this evaluation are presented in Table E-1, with wells grouped as shown in the map of approximate remediation areas presented in the ACM (Northwest, West, Southwest, South, and Southeast).

The widespread occurrence of cVOC daughter products indicates that reductive dechlorination is occurring in all five areas. The presence of dissolved iron, often at concentrations over one (1) milligram per liter (mg/L), provides further evidence that the groundwater is reduced, particularly in the areas with the highest COC concentrations (the Northwest, South, and Southwest Areas). The pH is within or near the ideal range for dechlorination of five (5) to nine (9). Sulfate and nitrate concentrations have also been reported at sufficiently low concentrations that they should not substantially interfere with reductive dechlorination of the cVOCs through competition. Thus this analysis provides good support for the interpretation that reductive dechlorination is producing the daughter products observed at the Landfill.

The degradation of benzene can occur under a wide variety of conditions, and is also expected to occur under the observed conditions. Other potential COCs, such as methylene chloride, tend to persist under anaerobic conditions; however, the concentrations of this COC are typically less than three (3) times the MCL, and therefore may be effectively attenuated through physical or relatively slow biological processes.

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TABLE E-1 MONITORED NATURAL ATTENUATION EVALUATION

| | Northwest Area | | | | | | | | | | | |
|---|--|------------|-----------|------------|---------|------------|---------|------------|------------|------------|------------|------------|
| Well ⁽¹⁾ | OB-03 | | OB03A | | OB04 | | OB04A | | MW-13A | | MW-13B | |
| Analyte | 9/12 | Evaluation | 9/12 | Evaluation | 9/12 | Evaluation | 9/12 | Evaluation | 9/12 | Evaluation | 9/12 | Evaluation |
| Tetrachloroethene (µg/L) | 1.0 U * | | 1.0 U * | | 1.0 U * | | 1.0 U * | | 26 | | 27 | |
| Trichloroethene ⁽²⁾ (µg/L) | 76 | + | 18 | + | 1.0 U * | + | 1.0 U * | + | 30 | + | 28 | + |
| Dichloroethene ⁽²⁾ (µg/L) | 95 | + | 95 | + | 12.4 | + | 16.4 | + | 80 | + | 82 | + |
| Vinyl Chloride ⁽²⁾ (µg/L) | 18 | + | 16 | + | 1.0 U * | + | 1.0 U * | + | 8.6 | + | 9.8 | + |
| Nitrate (mg/L) | 0.2 U | + | 0.2 U | + | 0.2 U | + | 0.2 U | + | 2.08 | - | 2.08 | - |
| Sulfate (mg/L) | 13.1 | + | 21.2 | - | 18.3 | + | 11.5 | + | 4.0 U | + | 7.6 | + |
| Dissolved Iron (mg/L) (assumed to be majority Fe(II)) | 21.3 | ++ | 27.0 | ++ | 0.6 | + | 0.5 | + | 0.2 U | | 0.3 | |
| Dissolved Oxygen (mg/L) | 0.90 | + | 0.40 | ++ | 0.67 | + | 0.75 | + | 1.02 | | 0.56 | + |
| Oxidation-Reduction Potential (mV) (Summer 2010) | 50 | + | -26 | + | NA | | NA | | 170 | | 130 | |
| pH | 5.15 | + | 5.20 | + | 5.67 | + | 5.29 | + | 4.91 | - | 5.64 | + |
| Concentration Trends | | | | | | | | | | | | |
| Tetrachloroethene (µg/L) | D | ++ | NT | + | NT | + | NT | + | NT | + | NT | + |
| Trichloroethene (µg/L) | NT | + | NT | + | NT | + | NT | + | NT | + | NT | + |
| Dichloroethene (µg/L) | NT | + | NT | + | NT | + | NT | + | NT | + | NT | + |
| Vinyl Chloride (µg/L) | NT | + | NT | + | NT | + | NT | + | NT | + | NT | + |
| Notes: | <p>Bolded text denotes concentrations exceeding MCLs.</p> <p>⁽¹⁾ Wells represent the subset of sampled wells with chlorinated ethene concentrations above the Maximum Contaminant Level during the last 6 sampling events.</p> <p>⁽²⁾ Assumed daughter products of reductive dechlorination.</p> <p>*Not detected in March 2012, but detected within last 6 sampling events (applies only to PCE, TCE, DCE, VC)</p> <p>µg/L = Microgram(s) per liter mg/L = Milligram(s) per liter ++ = Highly Favorable + = Favorable - = Unfavorable I = Increasing Trend D = Downward Trend NT = No Significant Trend NA = Not Analyzed. Trends were not analyzed where the historical data contains fewer than four detects of a compound in a given well. NC = Not Conclusive, due to insufficient data Blank = Neutral</p> | | | | | | | | | | | |

TABLE E-1 MONITORED NATURAL ATTENUATION EVALUATION

| Well ⁽¹⁾ | South Area | | | | | | West Area | | | | | | | |
|---|--|------------|-----------|------------|---------|------------|-----------|------------|-----------|------------|---------|------------|---------|------------|
| | OB11 | | OB11A | | OB025 | | MW-7 | | MW-9 | | MW-6 | | OB01 | |
| | 9/12 | Evaluation | 9/12 | Evaluation | 9/12 | Evaluation | 9/12 | Evaluation | 9/12 | Evaluation | 9/12 | Evaluation | 9/12 | Evaluation |
| Tetrachloroethene (µg/L) | 40 | | 23 | | 1.0 U * | | 3.6 | | 14 | | 1.0 U | | 1.0 U | |
| Trichloroethene ⁽²⁾ (µg/L) | 34 | + | 25 | + | 1.0 U * | + | 3.6 | + | 1.0 U * | + | 1.0 U * | + | 1.0 U * | + |
| Dichloroethene ⁽²⁾ (µg/L) | 95 | + | 89 | + | 9.6 | + | 5.1 | + | 1.0 U | | 18 | + | 1.0 U * | + |
| Vinyl Chloride ⁽²⁾ (µg/L) | 14 | + | 13 | + | 1.0 U * | + | 1.0 U * | + | 1.0 U | | 1.0 U * | + | 1.0 U * | + |
| Nitrate (mg/L) | 0.2 U | + | 0.2 U | + | 0.2 U | + | 23 | - | 1.2 | - | 0.2 U | + | 2.1 | - |
| Sulfate (mg/L) | 10.3 | + | 15.7 | + | 61.8 | - | 11.0 | + | 4.0 U | + | 47 | - | 24 | - |
| Dissolved Iron (mg/L) (assumed to be majority Fe(II)) | 0.8 | + | 1.0 | ++ | 9.9 | ++ | 0.3 | - | NA | | 0.5 | + | 0.4 | |
| Dissolved Oxygen (mg/L) | 1.47 | | 1.01 | | 1.02 | | 1.22 | | 3.4 | | 1.14 | | 0.57 | + |
| Oxidation-Reduction Potential (mV) (Summer 2010) | NA | | NA | | NA | | 54 | | 109 | | NA | | NA | |
| pH | 5.31 | + | 5.36 | + | 5.98 | + | 5.04 | + | 5.23 | + | 5.44 | + | 5.14 | + |
| Concentration Trends | | | | | | | | | | | | | | |
| Tetrachloroethene (µg/L) | I | - | NT | + | NT | + | NT | + | NT | + | NA | | NT | + |
| Trichloroethene (µg/L) | I | - | NT | + | NT | + | NT | + | NA | | NA | | D | ++ |
| Dichloroethene (µg/L) | I | - | NT | + | I | - | NA | | NA | | NT | + | NT | + |
| Vinyl Chloride (µg/L) | NT | + | NT | + | NT | + | NA | | NA | | NA | | D | ++ |
| Notes: | <p>Bolded text denotes concentrations exceeding MCLs.</p> <p>⁽¹⁾ Wells represent the subset of sampled wells with chlorinated ethene concentrations above the Maximum Contaminant Level during the last 6 sampling events.</p> <p>⁽²⁾ Assumed daughter products of reductive dechlorination.</p> <p>*Not detected in March 2012, but detected within last 6 sampling events (applies only to PCE, TCE, DCE, VC)</p> <p>µg/L = Microgram(s) per liter mg/L = Milligram(s) per liter ++ = Highly Favorable + = Favorable - = Unfavorable I = Increasing Trend D = Downward Trend NT = No Significant Trend NA = Not Analyzed. Trends were not analyzed where the historical data contains fewer than four detects of a compound in a given well. NC = Not Conclusive, due to insufficient data Blank = Neutral</p> | | | | | | | | | | | | | |

TABLE E-1 MONITORED NATURAL ATTENUATION EVALUATION

| Well ⁽¹⁾ | Southwest Area | | | | Southeast Area | | | | | | | | Other | |
|---|--|------------|---------|------------|----------------|------------|---------|------------|------------|------------|------------|------------|---------|------------|
| | OB12 | | OB015 | | OB10 | | MW-4 | | OB08 | | OB08A | | OB105 | |
| | 9/12 | Evaluation | 9/12 | Evaluation | 9/12 | Evaluation | 9/12 | Evaluation | 9/12 | Evaluation | 9/12 | Evaluation | 9/12 | Evaluation |
| Tetrachloroethene (µg/L) | 27 | | 1.0 U * | | 1.0 U * | | 1.0 U * | | 1.0 U | | 1.0 U | | 1.0 U | |
| Trichloroethene ⁽²⁾ (µg/L) | 25 | + | 1.0 U * | + | 14 | + | 1.0 U * | + | 1.0 U | | 1.0 U * | + | 1.0 U * | + |
| Dichloroethene ⁽²⁾ (µg/L) | 32 | + | 1.0 U * | + | 26 | + | 1.0 U * | + | 15 | + | 20 | + | 15 | + |
| Vinyl Chloride ⁽²⁾ (µg/L) | 1.0 U * | + | 1.0 U * | + | 13 | + | 1.0 U * | + | 3.7 | + | 5.0 | + | 1.0 U * | + |
| Nitrate (mg/L) | 0.99 | + | 0.2 U | + | 0.2 U | + | 0.44 | + | 0.2 U | + | 0.2 U | + | 0.2 U | + |
| Sulfate (mg/L) | 4.6 | + | 37.9 | - | 4.0 U | + | 4.0 U | + | 4.1 | + | 4.0 U | + | 289 | - |
| Dissolved Iron (mg/L) (assumed to be majority Fe(II)) | 0.2 | | NA | | 1.6 | ++ | 0.4 | | 0.7 | + | 3.6 | ++ | 7.2 | ++ |
| Dissolved Oxygen (mg/L) | 0.87 | + | 2.11 | | 0.69 | + | 0.79 | + | 0.99 | + | 0.95 | + | 0.28 | ++ |
| Oxidation-Reduction Potential (mV) (Summer 2010) | 90 | | -35 | + | 24 | + | 74 | | NA | | NA | | 68.6 | |
| pH | 5.29 | + | 5.70 | + | 5.49 | + | 5.50 | + | 6.04 | + | 5.87 | + | 5.75 | + |
| Concentration Trends | | | | | | | | | | | | | | |
| Tetrachloroethene (µg/L) | NT | + | NA | | NT | + | NA | | NA | | NA | | NA | |
| Trichloroethene (µg/L) | NT | + | NT | + | D | ++ | NA | | NA | | D | ++ | NT | + |
| Dichloroethene (µg/L) | NT | + | NT | + | NT | + | NA | | NT | + | NT | + | NT | + |
| Vinyl Chloride (µg/L) | NT | + | D | ++ | NT | + | NA | | NT | + | NT | + | NT | + |
| Notes: | <p>Bolded text denotes concentrations exceeding MCLs.</p> <p>⁽¹⁾ Wells represent the subset of sampled wells with chlorinated ethene concentrations above the Maximum Contaminant Level during the last 6 sampling events.</p> <p>⁽²⁾ Assumed daughter products of reductive dechlorination.</p> <p>*Not detected in March 2012, but detected within last 6 sampling events (applies only to PCE, TCE, DCE, VC)</p> <p>µg/L = Microgram(s) per liter mg/L = Milligram(s) per liter ++ = Highly Favorable + = Favorable - = Unfavorable I = Increasing Trend D = Downward Trend NT = No Significant Trend NA = Not Analyzed. Trends were not analyzed where the historical data contains fewer than four detects of a compound in a given well. NC = Not Conclusive, due to insufficient data Blank = Neutral</p> | | | | | | | | | | | | | |

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3.2 COMPOUND-SPECIFIC ISOTOPE ANALYSIS

As cVOCs degrade, the ratio of stable isotopes in the contaminants will often change, and the extent of degradation can be determined based on the observed change in the ratio of stable isotopes. CSIA can provide definitive data to determine if biodegradation is occurring. Whereas many non-destructive processes that affect cVOCs in groundwater (dilution, sorption, etc.) have small or no isotopic effects, destructive processes including abiotic and biotic degradation generally result in changes in isotope ratios. The use of CSIA data in conjunction with other methods of assessing MNA can help determine if abiotic and biotic degradation are important factors for contaminant fate and transport in groundwater.

Several different stable isotopes can be used for CSIA, but for organic compounds such as the chlorinated solvents present in groundwater at the Landfill, the carbon isotopes ^{13}C and ^{12}C are appropriate and were therefore used in this study. In general, CSIA uses the ratio of the relative abundance of ^{13}C and ^{12}C of a given compound in an environmental sample and compares it to the abundance of the same isotopes in a standard. The result is expressed as “del” or “delta” ^{13}C , which is generally depicted as $\delta^{13}\text{C}$ and is given in parts per thousand (“per mil” or ‰). Del ^{13}C is calculated using the following equation (EPA 2008):

$$\delta^{13}\text{C} = \left[\frac{R}{R_s} - 1 \right] * 1000$$

where R is the ratio of ^{13}C to ^{12}C in the sample and R_s is the ratio in the standard.

Because the heavier isotope (^{13}C) forms bonds that are slightly stronger than those formed with the lighter isotope (^{12}C), biotic and abiotic degradation processes selectively act upon bonds involving the lighter isotope and cause the remaining parent contaminant to have a higher fraction of ^{13}C (Pirkle 2009). Therefore, degradation of a parent contaminant through these processes can be assessed by comparing $\delta^{13}\text{C}$ in the environmental sample to $\delta^{13}\text{C}$ in the “unfractionated” (i.e., non-degraded) source compound that was initially released into the environment.

Assuming there are no samples of the actual spilled material, there are three commonly used ways to estimate the $\delta^{13}\text{C}$ for the unfractionated compound that was released at the site (EPA 2008). The first is to assume that the $\delta^{13}\text{C}$ in the source matched published values for non-degraded pure product. This is acceptable for petroleum hydrocarbons and chlorinated ethenes

because the range of $\delta^{13}\text{C}$ is well characterized and relatively well constrained. As a compound degrades, the value of $\delta^{13}\text{C}$ can become more positive (more enriched in ^{13}C) than any reported value from commercially available products. When this occurs, degradation of the product is evident. A second approach is to use the most negative values of $\delta^{13}\text{C}$ for the organic contaminant in groundwater at the site as an estimate of $\delta^{13}\text{C}$ in the source. This can be appropriate for cVOCs because the fractionation due to biodegradation is large (tens of ‰) relative to the variation in assumed $\delta^{13}\text{C}$ in the source. The third approach is effective if there is a clear flow path for contaminants; it assumes that the $\delta^{13}\text{C}$ in the most upgradient well is approximately the same as the source material, and if the $\delta^{13}\text{C}$ in compounds farther downgradient is increasingly less negative, this is interpreted to indicate degradation along the flow path. However, this third approach could not be done at the Landfill because the spatial locations of the monitoring wells and the cVOC concentrations are such that an upgradient-downgradient flow path between monitoring wells containing cVOCs at concentrations high enough to perform CSIA is unavailable.

Table E-2, below, shows the $\delta^{13}\text{C}$ values for the cVOCs in groundwater samples at the Landfill, and provides comparison values from the literature for commercially available chlorinated solvents (EPA 2008). The $\delta^{13}\text{C}$ value for PCE in groundwater monitoring well MW-13A is less negative than the highest literature value, indicating that the PCE in MW-13A has almost certainly degraded. Additionally, the $\delta^{13}\text{C}$ values for PCE in the samples from each of the other wells where results are available (OB12, OB11, and OB11A) are on the less negative end of the range of published values. This provides less conclusive evidence of degradation in these wells. If it is assumed that the most negative $\delta^{13}\text{C}$ value (-23.93 per mil in wells OB11 and OB11A) is representative of non-degraded product, there is little evidence of degradation of PCE in any of the wells except MW-13A. However, this method is not ideal at the Landfill, as there is no independent basis for the assumption that the PCE in wells OB11 and OB11A is relatively undegraded and thus similar to the source material.

For TCE, all of the $\delta^{13}\text{C}$ values are within the range of non-degraded pure product reported in the literature. The presence of daughter products cis-1,2-dichloroethene and vinyl chloride are definitive indicators that TCE in groundwater at the Landfill has degraded, but it is unclear whether this degradation is significant enough to affect the isotopic composition of the TCE. In addition, $\delta^{13}\text{C}$ for TCE is lower (more negative) than for PCE in samples from each individual well. In general, if a parent compound and its daughters are degrading, $\delta^{13}\text{C}$ for each successive compound will be higher (less negative) than its parent. Based on a comparison of $\delta^{13}\text{C}$ values for PCE and TCE, it appears that, although some TCE is a result of PCE degradation, it is likely

that a source of TCE is also present in the Landfill and represents a source of chlorinated compounds to groundwater in the Landfill area.

A comparison of $\delta^{13}\text{C}$ values for TCE in samples from individual wells indicates that there is a fairly wide range between the lowest value (-31.12 per mil in OB11) and the highest value (-25.72 in OB03). If it is assumed that the $\delta^{13}\text{C}$ value for TCE in the source was similar to the $\delta^{13}\text{C}$ values for TCE in OB11, there may be evidence of significant degradation in the Northwest Area of the Landfill at OB03. However, OB11 and OB03 are located on opposite sides of the Landfill, and could thus contain TCE from different sources with different isotopic signatures.

All of the $\delta^{13}\text{C}$ values for DCE and VC are less negative than their respective parent compounds, as is expected if DCE and VC are forming through the common degradation pathway of TCE to DCE to VC. DCE and VC are rarely if ever present in groundwater as source compounds; rather, they are daughter compounds of TCE. Therefore, comparison of $\delta^{13}\text{C}$ values in site groundwater to the literature values for non-fractionated product may not be conclusive evidence that they are degrading. As with TCE, the least negative $\delta^{13}\text{C}$ values for DCE were reported in wells on the northwestern side of the Landfill (OB03 and OB04A), whereas the most negative values were reported in wells OB11 and OB11A.

TABLE E-2 DELTA ^{13}C VALUES FOR CHLORINATED VOLATILE ORGANIC COMPOUNDS IN GROUNDWATER SAMPLES COLLECTED FOR COMPOUND-SPECIFIC ISOTOPE ANALYSIS

| Well No. | $\delta^{13}\text{C}$ PCE | $\delta^{13}\text{C}$ TCE | $\delta^{13}\text{C}$ DCE | $\delta^{13}\text{C}$ VC |
|--|---------------------------|---------------------------|---------------------------|--------------------------|
| OB03 | -- | -25.72 | -22.91 | -20.49 |
| MW-13A | -21.98 | -27.58 | -25.70 | -23.67 |
| OB04A | -- | -- | -23.05 | -- |
| OB12 | -23.42 | -30.75 | -24.37 | -16.91 |
| OB11 | -23.93 | -31.12 | -26.87 | -21.17 |
| OB11A | -23.93 | -30.66 | -28.24 | -21.68 |
| OB11A (duplicate) | -23.68 | -30.34 | -27.84 | -21.28 |
| $\delta^{13}\text{C}$ Literature Range ⁽¹⁾ | -37 to -23 | -34 to -24 | -29 to -22 | -28 (1 value) |

⁽¹⁾ Literature range is the approximate range of reported $\delta^{13}\text{C}$ values for unfractionated chlorinated solvents. From EPA (2008), Figure 6.1.
PCE = Tetrachloroethene
TCE = Trichloroethene
DCE = cis-1,2-Dichloroethene
VC = Vinyl chloride
 $\delta^{13}\text{C}$ is expressed in per mil (‰)

Data Interpretation and Assessment of Uncertainty

In order to obtain definitive results in a CSIA study, the extent of fractionation must be greater than the total analytical uncertainty. Typically, the total analytical uncertainty is \pm one-half (0.5) ‰ (EPA 2008). Therefore, the observed fractionation limit is set at one (1) ‰ at a minimum. To ensure reliable interpretation, EPA recommends that a fraction limit of at least two (2) ‰ be used as a criterion for positive identification of degradation to minimize erroneous interpretation. Within each well, the enrichment along the degradation pathway from TCE to DCE to VC meets this criterion, indicating that degradation of those compounds has occurred in groundwater at the Landfill. This is not the case for PCE, however. The only definitive evidence of PCE degradation from CSIA is that $\delta^{13}\text{C}$ in MW-13A is less negative than the highest reported literature value. However, this does not mean that PCE degradation has not occurred; it just means that CSIA has not definitively shown its occurrence.

An additional factor that allows improved assessment of degradation is collection of samples that reflect high, intermediate, and low concentrations of organic contaminants. Degradation of higher concentrations of compounds can result in greater enrichment than degradation of lower concentrations, providing an additional criterion for analysis. Although the CSIA analysis was performed on samples from the wells with the highest cVOC concentrations, to improve the likelihood that a CSIA result would be obtained from each sample, concentrations in the samples were generally low (Table E-3, below). These relatively low concentrations are not indicative of proximity to an active source, which makes estimation of $\delta^{13}\text{C}$ in the source difficult. Performing CSIA only on wells with low concentrations of organic contaminants has been shown to have the potential to seriously underestimate the true contribution of degradation processes at a site (Wilson 2010).

TABLE E-3 CONCENTRATIONS OF CHLORINATED VOLATILE ORGANIC COMPOUNDS IN GROUNDWATER SAMPLES COLLECTED FOR COMPOUND SPECIFIC ISOTOPE ANALYSIS

| Well No. | PCE ($\mu\text{g/L}$) | TCE ($\mu\text{g/L}$) | DCE ($\mu\text{g/L}$) | VC ($\mu\text{g/L}$) |
|--|-------------------------|-------------------------|-------------------------|------------------------|
| OB03 | 2.4 | 80 | 150 | 28 |
| MW-13A | 27 | 32 | 110 | 13 |
| OB04A | 1.5 | 1.5 | 21 | 3.2 |
| OB12 | 37 | 35 | 55 | 8 |
| OB11 | 45 | 40 | 190 | 25 |
| OB11A | 21 | 25 | 110 | 21 |
| DCE = cis-1,2-Dichloroethene VC = Vinyl chloride PCE = Tetrachloroethene $\mu\text{g/L}$ = Micrograms per liter TCE = Trichloroethene | | | | |

Overall, the CSIA analysis provides evidence that degradation of TCE to DCE to VC is occurring. This supports the assumption that the DCE and VC present in groundwater at the Landfill are derived from degradation of TCE. Although the CSIA does not provide conclusive evidence of PCE degradation, this lack of conclusive evidence may be a result of the limitations to the study (including lack of analysis of source material, and low cVOC concentrations). Given the strong evidence for reductive dechlorination of cVOCs in groundwater at the Landfill, including the CSIA results for TCE-DCE-VC and the geochemical analysis described above, some degradation of PCE is likely occurring in the groundwater.

3.3 TREND ANALYSIS

Trend graphs for all constituents that have historically exceeded their MCLs in a given well during any monitoring event, are presented in Appendix A of the Gude Landfill ACM Report. These graphs allow visual interpretation of trends for each constituent in each well.

The data were also analyzed for statistically significant trends in constituents that have been reported at a concentration exceeding their respective MCLs within the last ten (10) sampling events (approximately five [5] years). Trend analysis was performed for metals and VOCs at each monitoring well that met this criterion and also meet the following requirements:

1. The monitoring well had been sampled at least four (4) independent times.
2. At least four (4) sample results were above the analytical detection limit for the given constituent.

The Mann-Kendall test for trend (Gilbert 1987) was used to identify constituents with an increasing or decreasing annual trend at the ninety-five (95) percent significance level. Concentrations reported below detection limits were treated as zero (0) for computing the yearly median concentration. Exact two (2)-sided probabilities for the null distribution of the Mann-Kendall test were obtained from Hollander and Wolfe (1973). The test results are presented in Appendix B of the Gude Landfill ACM Report.

Significant trends for constituents which have one or more reported MCL exceedances within the past ten (10) sampling events (approximately five [5] years) are presented in Table E-4 and discussed below. Wells are grouped for discussion by area of the Landfill, to support evaluation of MNA as an alternative in the different areas of the site.

Wells in the Northwest Area (OB03, OB03A, OB04, OB04A, OB102, MW-8, MW-13A, MW-13B)

The following constituents had decreasing trends in wells located in the Northwest Area:

- PCE and benzene in OB03
- Arsenic and benzene in OB03A

For all other constituents with MCL exceedances in the last ten (10) sampling events in the Northwest Area, there was no statistical trend, or no analysis could be performed due to insufficient data.

Wells in the West Area (MW-7, MW-9, MW-10, MW-11A, MW-11B)

The only COC in well OB01 had a decreasing trend:

- VC in OB01

Constituents with MCL exceedances in the last ten (10) sampling events have also been identified in MW-7 and MW-9, but had no statistical trend. Other wells in the West Area have no identified constituents with MCL exceedances in the last ten (10) sampling events, or no analysis could be performed due to insufficient data.

Wells in the Southwest Area (OB01, OB02, OB02A, OB015, OB12, MW-6)

The only COC in well OB015 had a decreasing trend:

- VC in OB015

Constituents with MCL exceedances in the last ten (10) sampling events have also been identified in OB12, but had no statistical trend. Other wells in the Southwest Area have no identified constituents with MCL exceedances in the last ten (10) sampling events.

Wells in the South Area (OB025, OB11, OB11A)

The following constituents with MCL exceedances in the last ten (10) sampling events had decreasing trends in wells located in the South Area:

- Methylene Chloride in OB011A

The following constituents with MCL exceedances in the last ten (10) sampling events had increasing trends in Well OB011, located in the South Area:

- 1,2-dichloroethane
- 1,2-dichloropropane
- Benzene
- Cadmium
- Cis-1,2-DCE
- Mercury
- Methylene chloride
- PCE
- TCE

For all other constituents with MCL exceedances in the last ten (10) sampling events in the South Area, there was no statistical trend.

Wells in the Southeast Area (OB08, OB08A, OB10, MW-3A, MW-3B, MW-4)

The following constituents with MCL exceedances in the last ten (10) sampling events had a decreasing trend:

- TCE in OB10

VC also has reported MCL exceedances in the last ten (10) sampling events in the Southeast Area (Wells OB08, OB08A, and OB10), but had no statistical trend. For the other constituents with MCL exceedances in the last ten (10) sampling events in the Southeast Area (TCE in MW-4), no analysis could be performed due to insufficient data.

Summary

Although each area of the Landfill assessed had a decreasing trend for at least one constituent with MCL exceedances in the last ten (10) sampling events, no areas had decreasing trends for the majority of these constituents. The only increasing trends were in the South Area, in Well OB011.

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TABLE E-4 TREND ANALYSIS RESULTS FOR CONSTITUENTS WITH EXCEEDANCE(S) DURING THE LAST TEN SAMPLING EVENTS, IN EACH PROPOSED REMEDIATION

| Well | Chemical | Decreasing Trend | Increasing Trend | No Trend | Insufficient Data |
|-----------------------|---------------------|------------------|------------------|----------|-------------------|
| Northwest Area | | | | | |
| OB03 | Tetrachloroethene | X | | | |
| OB03 | Benzene | X | | | |
| OB03 | 1,2-Dichloroethane | | | X | |
| OB03 | 1,2-Dichloropropane | | | X | |
| OB03 | Cis-1,2-DCE | | | X | |
| OB03 | Trichloroethene | | | X | |
| OB03 | Vinyl Chloride | | | X | |
| OB03A | Arsenic, total | X | | | |
| OB03A | Benzene | X | | | |
| OB03A | 1,2-Dichloroethane | | | X | |
| OB03A | 1,2-Dichloropropane | | | X | |
| OB03A | Cis-1,2-DCE | | | X | |
| OB03A | Tetrachloroethene | | | X | |
| OB03A | Trichloroethene | | | X | |
| OB03A | Vinyl Chloride | | | X | |
| OB04 | Vinyl Chloride | | | X | |
| OB04A | Arsenic, total | | | X | |
| OB04A | Methylene Chloride | | | X | |
| OB04A | Tetrachloroethene | | | X | |
| OB04A | Trichloroethene | | | X | |
| OB04A | Vinyl Chloride | | | X | |
| MW-8 | Nitrate | | | X | |
| West Area | | | | | |
| OB01 | Vinyl Chloride | X | | | |
| MW-10 | Chromium | | | X | |
| MW-11A | Chromium | | | X | |
| MW-6 | Cadmium | | | X | |
| MW-7 | Nitrate | | | X | |
| MW-7 | Trichloroethene | | | X | |
| MW-7 | Vinyl Chloride | | | | X |
| MW-9 | Chromium | | | X | |
| MW-9 | Tetrachloroethene | | | X | |
| Southwest Area | | | | | |
| OB015 | Vinyl Chloride | X | | | |
| OB12 | 1,2-Dichloropropane | | | X | |
| OB12 | Methylene Chloride | | | X | |
| OB12 | Tetrachloroethene | | | X | |
| OB12 | Trichloroethene | | | X | |
| OB12 | Vinyl Chloride | | | X | |

TABLE E-4 TREND ANALYSIS RESULTS FOR CONSTITUENTS WITH EXCEEDANCE(S) DURING THE LAST TEN SAMPLING EVENTS, IN EACH PROPOSED REMEDIATION

| Well | Chemical | Decreasing Trend | Increasing Trend | No Trend | Insufficient Data |
|-----------------------|------------------------|------------------|------------------|----------|-------------------|
| South Area | | | | | |
| OB11 | 1,1-Dichloroethene | | | X | |
| OB11 | 1,2-Dichloroethane | | | X | |
| OB11 | 1,2-Dichloropropane | | X | | |
| OB11 | Benzene | | X | | |
| OB11 | Cadmium, total | | X | | |
| OB11 | cis-1,2-Dichloroethene | | X | | |
| OB11 | Mercury, total | | X | | |
| OB11 | Methylene Chloride | | X | | |
| OB11 | Tetrachloroethene | | X | | |
| OB11 | Trichloroethene | | X | | |
| OB11 | Vinyl Chloride | | | X | |
| OB11A | 1,2-Dichloroethane | | | X | |
| OB11A | 1,2-Dichloropropane | | | X | |
| OB11A | Benzene | | | X | |
| OB11A | Cadmium, total | | | X | |
| OB11A | cis-1,2-Dichloroethene | | | X | |
| OB11A | Methylene Chloride | X | | | |
| OB11A | Tetrachloroethene | | | X | |
| OB11A | Trichloroethene | | | X | |
| OB11A | Vinyl Chloride | | | X | |
| OB025 | Chromium | | | X | |
| OB025 | Vinyl Chloride | | | X | |
| Southeast Area | | | | | |
| OB08 | Vinyl Chloride | | | X | |
| OB08A | Vinyl Chloride | | | X | |
| OB10 | Trichloroethene | X | | | |
| OB10 | Vinyl Chloride | | | X | |
| MW-4 | Trichloroethene | | | | X |

Note: COCs in each well are defined as constituents that have been reported at concentrations exceeding MCLs during at least one of the most recent 10 sampling events.

4. CONCLUSIONS

The analyses described above provide strong evidence that natural attenuation is occurring at the Landfill. Available groundwater geochemical data indicate conditions favorable for reductive degradation of COCs, and the widespread occurrence of cVOC daughter products (DCE and VC) strongly suggest that PCE and/or TCE degradation is occurring. CSIA provides additional evidence that reductive dechlorination is degrading TCE to DCE and then VC. The isolated trends of decreasing concentration observed for certain organic constituents in certain wells may also result from degradation.

Despite the degradation occurring, constituents persist at concentrations above MCLs, and trend analyses indicate that most constituents with concentrations above MCLs in most wells do not show statistically significant decreasing trends. Thus, it appears that COCs leaching from the source(s) within Landfill are currently being degraded at a rate that is insufficient to decrease concentrations to below MCLs by the time the groundwater reaches the property boundary point of compliance. The constituent concentrations at the property boundary are expected to naturally decrease in the future, when the sources of groundwater impacts within the Landfill are depleted, at which point the natural rate of degradation will be sufficient to achieve the remedial action objective for groundwater. The timeframe for this degradation of the source material cannot be estimated due to lack of characterization and lack of evidence of widespread decreasing trends in concentrations.

Although this evaluation indicates that the natural attenuation processes alone do not currently achieve the groundwater RAO, the documented attenuation processes could be utilized in combination with other technologies in designing an effective Corrective Measure Alternative for the Landfill. For example, excavation and removal of waste mass from the Landfill, particularly along the Landfill boundaries, could increase compliance with the groundwater RAO when combined with natural attenuation. Enhanced Bioremediation, including injection of substrates that promote natural attenuation, could also be used to increase the rate of degradation and thus decrease concentrations below MCLs at the point of compliance prior to depletion of the source material within the waste mass.

5. REFERENCES

Gilbert, R.O. 1987. Statistical methods for environmental pollution monitoring, New York: Van Nostrand Reinhold.

Hollander, M. and D. A. Wolfe. 1973. Nonparametric Statistical Methods. Wiley, New York.

Pirkle, R.J. 2009. Compound Specific Isotope Analysis: The Science, Technology and Selected Examples from the Literature with Application to Fuel Oxygenates and Chlorinated Solvents. Microseeps, Inc. July.

U.S. Environmental Protection Agency (EPA). 1997. Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites. OSWER Directive 9200.4-17. November.

U.S. Environmental Protection Agency (EPA). 2008. A Guide for Assessing Biodegradation and Source Identification of Organic Ground Water Contaminants using Compound Specific Isotope Analysis (CSIA). EPA 600/R-08/148. Available on-line at: www.epa.gov/ada. December.

Wilson, J.T. 2010. Stable Isotope Analyses to Understand the Degradation of Organic Contaminants in Ground Water. CLU-IN Internet Seminar, sponsored by U.S. EPA Technology Innovation and Field Services Division. 16 June 2010.