

Interim Natural Attenuation Report
for the
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Nutley, New Jersey

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Interim Natural Attenuation Report

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EXECUTIVE SUMMARY

This Interim Natural Attenuation Report is an interim progress report that provides preliminary evidence in support of a future Monitored Natural Attenuation (MNA) remedy that may be proposed in the site-wide Remedial Action Workplan.

MNA has been preliminarily evaluated within the context of the current hydrogeologic conceptual site model (CSM). The CSM is an integral component of the approach to MNA under the New Jersey Department of Environmental Protection (NJDEP) (2012) MNA guidance document. The CSM combines the regional and site data into an integrated, dynamic CSM to be used in describing site conditions and in developing, implementing, and optimizing remedial actions. The CSM is dynamic and will evolve as more data are gathered. Therefore, the CSM presented in this report has evolved from the CSM presented in the April 2014 Groundwater Remedial Investigation (RI) Report.

Natural attenuation includes a number of physical, chemical, and biological processes that can reduce the concentration, mobility, toxicity, and/or mass of contaminants in groundwater. Natural attenuation processes considered in this report are: dispersion, diffusion, dilution, sorption, and biotic and abiotic degradation.

The general CSM for the Site includes the following:

- Groundwater primarily occurs, with local variability, within 20 feet below ground surface (bgs) in the bedrock fractures/partings and occasionally within the overburden beneath the Site.
- Most of the bedrock fractures are oriented northeast to southwest and are cross-cut by a subordinate, north-northwest to south-southeast trending fracture system. Vertical fractures are numerous and extensive in some areas, and interconnect the low-angle bedding plane fractures. The greatest frequency of fractures is found in the central and southwestern portions of the Site within the shallow, intermediate and deep bedrock and is associated with a documented regional fault system.
- The groundwater flow regime has been conceptually divided for ease of assessment into seven, elevation-based hydrostratigraphic zones (S1 through S3 and D1 through D4).

- The groundwater gradient in Zone S1 is generally from the north and northwest to the south and southeast with local variability. Several “V” shapes in the groundwater contours in Zone S1 illustrate zones of converging groundwater gradient which is typically associated with either higher hydraulic conductivity zones or groundwater discharge zones.
- The horizontal groundwater gradients in Zones S2 to D3 are generally from the northwest to the southeast, with local variability. Converging groundwater gradients from the east and from the west toward the center of the Site also occur within Zones S2 and S3. An eastern gradient is shown on the eastern side of the Site in Zone S3 and a northeastern gradient appears to exist in Zone S2 in a small isolated area in the northeastern corner of the property. However, as described in Section 4.2.3 of the Site-Wide Groundwater Progress Report (December 2014), the wells showing this gradient in Zone S2 (wells MW-271B and MW-61B) have few transmissive fractures and may be in poor communication with water bearing fractures in Zone S1 and may not be representative of groundwater conditions throughout this area.
- There are significant downward vertical gradients between Zone S1 to the deeper intervals (S2, S3) in key areas of the Site such as in the IA-12 area under the Clifton-Allwood Municipal Sewer (CAMS) and several other areas. Upward vertical gradients are inferred from Zone D1 to the shallower Zone S3 within the southern-southeastern portion of the Site.
- The horizontal and vertical groundwater gradients only represent the potential for groundwater flow and that groundwater gradients do not equate to groundwater flow, as the hydraulic conductivity needs to be considered as well. Steep hydraulic gradients generally coincide with zones of either relatively small hydraulic conductivity or limited hydraulic capacity (diffusivity). In contrast, mild/low hydraulic gradients coincide with zones of either relatively high hydraulic conductivity or large diffusivity.
- The hydraulic conductivity varies widely across the Site within the shallow and deep zones reflective of heterogeneous and anisotropic water bearing zones. The horizontal hydraulic conductivity was estimated to vary from 0.001 to 230 feet/day.
- The horizontal hydraulic gradient was estimated to vary from 0.006 to 0.20. The vertical hydraulic gradient was estimated to vary from 0.36 downward to horizontal and up to 0.6 upward.
- Different volatile organic compounds (VOCs) have been detected in groundwater at the Site, some of which originated off-site. The most prevalent constituents present in groundwater are chlorinated VOCs (specifically, tetrachloroethene [PCE], trichloroethene [TCE], cis-1,2-dichloroethene [cis-1,2-DCE] and vinyl chloride [VC]), which have been detected throughout the shallow and deep groundwater zones across and along the boundaries of the Site. The distribution of chlorinated VOCs (CVOCs) in groundwater generally correlate with the groundwater gradients defined within the bedrock aquifer system, as well as site features such as the Valley Drain and municipal sewer. Other VOCs detected in groundwater at the Site include 1,1,1-trichloroethane (1,1,1-TCA) and its breakdown daughter products 1,1-dichloroethane (1,1-DCA) and 1,1-dichloroethene (1,1-DCE); chloroform and its breakdown daughter product methylene chloride; 1,4-dioxane; chlorobenzene; and benzene and toluene. Some of these secondary VOC impacts are localized with a limited horizontal and vertical extent.
- The sampling results from off-Site monitoring wells installed north of Route 3 indicate that PCE has been discharged off-Site from one or more upgradient sources, transported within

the CAMS to both off-Site and on-Site locations, and released into the environment from multiple compromised sections (off-Site and on-Site) of the municipal sewer which enters and traverses the Roche Site. Once released to the groundwater, the VOCs migrate down the groundwater gradient. For example, releases upstream of Roche have resulted in total chlorinated ethene concentrations at upgradient wells MW-201A (Zone S1) and MW-201 (Zone S2) of 2,894 µg/L and 3,954 µg/L, respectively, as shown on Figures 3 and 4.

- There is another off-Site VOC source(s) located upgradient of the Roche Site that has produced a separate chlorinated VOC plume (total VOCs in excess of 100 µg/L) which enters the Roche Site between Zone S2 and Zone D2 approximately 1,350 feet west of the guard shack (south of Route 3). The furthest upgradient, on-site well, MW-266B, in Q2 2014 contains low PCE (2.2 µg/L), TCE (11 µg/L), but much higher 1,1,1-TCA (54 µg/L) and its degradation products 1,1-DCA (246 µg/L) and 1,1-DCE (224 µg/L).
- The groundwater quality data for on-Site wells installed east of the municipal sewer area (along the northern boundary of the Roche property), also suggest that there is another off-Site VOC source located upgradient of the Roche Site that has produced a separate CVOC plume with total chlorinated ethenes of about 2,000 µg/L at well MW-271C (see Figure 5) and characterized by nearly 100% PCE. This plume enters the Roche property between Zone S3 and D2, approximately 850 feet east of the guard shack (south of Route 3).
- On the western portion of the Site, in IA-10, the direction of groundwater flow and distribution of 1,1,1-TCA and its breakdown products in deep groundwater (Zones D1, D2 and D3) indicates that this contamination is derived from potentially multiple off-Site sources.
- As noted in this CSM, the CAMS contributed to the CVOC plume through apparent leaks in the sewer pipe at several locations along its alignment. This results in superimposing multiple releases of VOCs into what could be viewed as a continuous plume on Figures 3 through 6. In reality, these multiple sources contribute to the VOC plume, extending the plume from IA-12 that may otherwise be shorter than currently observed. This is an important point, because it affects the assessment of attenuation and degradation rates.
- The Valley Drain storm sewer acts as a linear groundwater discharge feature. This observation provides the explanation for an upward gradient on the southern side of the facility, and may provide an explanation for the presence of VOCs in shallow zones without the presence of a source of VOCs.

Multiple Lines of Evidence for Natural Attenuation

As described in the NJDEP (2012) MNA guidance document, the three lines of evidence for natural attenuation were evaluated, including Primary Lines of Evidence (Contaminant Trends: Reduction/Stability), Secondary Lines of Evidence (Geochemistry), and Tertiary Lines of Evidence (Microbiological and Isotope Analyses). These lines of evidence used site-wide data, primarily from zones S1, S2, and S3, and focused on degradation of the chlorinated ethenes PCE, TCE, cis-1,2-DCE, and vinyl chloride. The data for these lines of evidence for natural attenuation provided the following conclusions:

Primary Lines of Evidence – Contaminant Plume Characteristics

- Degradation Trends: Breakdown daughter products of PCE/TCE (as well as other CVOCs) are detected throughout the Site. CVOC speciation indicates that degradation daughter products are more dominant than parent compounds at several key areas of the Site.
- Temporal Distribution: A long history of VOCs is available at some wells on the Site. In particular, CVOC plumes in IA-12 and IA-7 demonstrate that the CVOC concentrations have been essentially stable for the duration of monitoring from as early as 1996 to the present. This suggests that the CVOC plume is at steady state with regard to source loading and migration. Continued quarterly monitoring is being conducted to extend this temporal distribution throughout the Site.
- Spatial Distribution: Based on the observed concentrations shown in Figure 5, the length of the VOC plume in Zone S3 from the upgradient property line (northernmost boundary of IA-12 along Route 3) to the furthest extent of VOCs (i.e., the southeastern tip of IA-15, as measured along the central axis of the plume(s) shown on Figure 5) is approximately 2,500 ft. This compares to conservatively predicted groundwater migration distances in Zones S1 to S3 of at least 5,000 to 12,500 ft. over a 30-year timeframe. This demonstrates that the CVOCs in groundwater have not migrated as far as expected based on average groundwater flow. Therefore, the CVOCs are significantly attenuated compared to groundwater flow.
- Concentration vs. Distance Trend: A concentration versus distance graph for IA-12 illustrates the total chlorinated ethenes concentration from the source down the highest concentration of the plume, regardless of zone. This concentration-distance graph demonstrates the concentration decline downgradient of the release from the CAMS in IA-12. This apparent trend follows the expected exponential decline for natural attenuation of VOCs downgradient of a source, for the entire distance from IA-12 to just upgradient of the next known or potential release area (increased concentrations) of VOCs from the CAMS in IA-3.

Secondary Lines of Evidence – Geochemistry and Physical Characteristics

- Organic substrate for microbiological degradation is present as measured by Total Organic Carbon (TOC), but at relatively low concentrations and is potentially a limiting factor for significant biodegradation of CVOCs.
- Geochemical conditions (i.e., pH and redox conditions) are generally conducive for reductive dechlorination of the CVOCs.
- Biotic Degradation by-products monitoring, particularly for dissolved gases including ethene and carbon dioxide demonstrates that there is evidence of degradation generally through the center of the Site.
- Abiotic degradation is a potentially significant contributor to CVOC degradation, particularly in the presence of iron-bearing minerals under anaerobic conditions. The confirmed presence of even low, infrequent detections of acetylene is evidence that abiotic degradation may be occurring at the Site.
- Analysis of the distribution of major ions indicates that dilution (diffusion and dispersion) is a significant factor in natural attenuation at the Site with an overall reduction due to dilution of 67% based on site wide average chloride concentration reductions from Zone S1 to Zone S3.

- The presence of natural organic matter, albeit at low levels, indicates that sorption is contributing to the natural attenuation of CVOCs on site, particularly in less porous and less transmissive zones, where advection is less dominant.
- Matrix diffusion is also expected to be an important natural attenuation process given the relatively high matrix porosity compared to the effective fracture porosity, particularly in the vicinity of less transmissive and isolated (less connected) fractures, where advection is less dominant and in zones of high contaminant concentrations.

Tertiary Lines of Evidence – Microbiology and Isotopes

- Bacteria capable of degrading CVOCs were found at every monitoring well that was sampled. These wells were selected to represent source areas, plume axis and plume fringe areas. These bacteria have been reported at moderate to high populations at several locations.
- Isotopic fractionation was detected in groundwater samples from several monitoring wells on and offsite that indicate some level of PCE-TCE-*cis*-1,2-DCE degradation. However, the degree of fractionation/enrichment within water (liquid phase) appears generally low, indicating that current rates of degradation may be limited.

1.0 INTRODUCTION

On behalf of Hoffmann-La Roche Inc. (Roche), TRC Environmental Corporation (TRC) has prepared this Interim Natural Attenuation Report to evaluate the occurrence of natural attenuation of the primary constituents of concern (COCs) listed in the April 2014 Site-Wide Groundwater Remedial Investigation Report (Groundwater RI Report). The Groundwater RI Report presented the findings of the remedial investigation conducted at the 120-acre Roche facility (Site), located at 340 Kingsland Street, in the Township of Nutley, Essex County, New Jersey. The location of the Roche facility is provided as Figure 1.

This Interim Natural Attenuation Report is an interim progress report that provides preliminary evidence that supports the occurrence of natural attenuation processes at the Site. The report documents the findings of an initial natural attenuation assessment in support of a future monitored natural attenuation (MNA) remedy that may be proposed for certain groundwater zones or affected areas in the site-wide Remedial Action Workplan. This Interim Natural Attenuation Report follows the New Jersey Department of Environmental Protection's (NJDEP's) Technical Requirements for Site Remediation (TRSR) (N.J.A.C. 7:26E) and is in compliance with applicable guidance and Remedial Investigation (RI) Workplans previously approved by the NJDEP. In particular, this Baseline MNA Report follows the NJDEP guidance titled *Monitored Natural Attenuation, Technical Guidance* (NJDEP 2012). The Groundwater RI Report characterized the groundwater conditions, identified contaminant sources and potential receptors, and delineated the extent of groundwater contamination.

The objectives of this Interim Natural Attenuation Report are to:

- (1) Provide a comprehensive analysis of shallow and deep groundwater conditions that support natural attenuation in areas being targeted for active Interim Remedial Measures (IRMs). The presence and rate of natural attenuation will be used in the selection, design, and cleanup objective for these interim groundwater remedies; and,
- (2) Establish a site-wide baseline of key natural attenuation parameters (*i.e.*, diffusion, dispersion, sorption, and degradation), consistent with NJDEP Technical Guidance, to support a potential MNA remedy for portions of the chlorinated volatile organic compound (CVOC) plume in shallow and deep hydrostratigraphic zones under the Roche site that will not be the target of more active remedies and in IRM areas after the IRM has been completed.
- (3) Identify areas for future study and investigation to better define the key natural attenuation parameters, where needed.

2.0 SITE CHARACTERIZATION

2.1 Characterization Activities

This Interim Natural Attenuation Report is a supplement to the information presented in the Groundwater RI Report and relies heavily on the information presented in that report. In addition to the data presented in the Groundwater RI Report, two rounds of sampling for natural attenuation parameters have been conducted, and the results are summarized in this report. The two rounds of MNA sampling included a large round of sampling in February 2014 and a smaller early summer round of sampling in June 2014. The sampling program from the February 2014 and the June 2014 events are included in Table 1.

The Groundwater RI Report relied on the September 2013 (2013-Q3) sampling event for its characterization of the distribution of VOCs in the Site groundwater. As recommended in the Groundwater RI Report, quarterly sampling is continuing, with sampling events in December 2013 (2013-Q4), March 2014 (2014-Q1), and June 2014 (2014-Q2). Quarterly sampling will continue for a minimum of eight quarters as required by NJDEP for characterization and non-parameter statistical analyses of groundwater quality trends¹. In addition to these quarterly sampling data, groundwater sampling has occurred at some Site monitoring wells for many years. Data from these sampling events are contained in the Roche database. Data from the historic groundwater sampling and the quarterly sampling events are used, where applicable, in this Interim Natural Attenuation Report to characterize Site conditions. Data from historic groundwater sampling are used primarily to assist in characterizing VOC trends at wells.

2.1 Conceptual Site Model

The Conceptual Site Model (CSM) combines the regional and site data, including the geologic, hydrogeologic, and the biogeochemical soil and water quality data, into an integrated, dynamic elaboration to be used in describing site conditions and in developing, implementing, and optimizing remedial actions. The CSM is dynamic and will evolve as more data are gathered. The CSM presented in prior reports is used to assist in gathering additional site data, and implementing pilot studies or IRMs. Data from these actions are integrated into the CSM, balancing these new data with existing data, progressively updating the CSM to explain the site data and contaminant trends to the extent possible. This process uses the concepts of maintaining multiple working hypotheses and using multiple lines of evidence to describe the processes at work at the Site. Therefore, it should be expected that the CSM, for example, as presented in the Groundwater RI Report, will evolve and be refined as will the CSM presented in this report.

2.1.1 Geology

¹ Additional sampling will be conducted, during and after the 8 quarters, for Interim Remedial Measure (IRM) performance monitoring, site-wide Remedial Action Workplan (RAW) performance monitoring and Classification Exception Area (CEA) monitoring.

Regionally, the Site lies within a portion of the Newark Basin that has a deep section of primarily sedimentary rocks.

Locally, the bedrock is overlain by up to 30 feet of glacial deposits of the Rahway till and anthropogenic fill. The overburden is generally composed of sand with silt and discontinuous layers of clay with silt. The first bedrock unit encountered beneath the overburden is a weathered and competent reddish-brown sandstone and siltstone of the Passaic Formation. Based on borehole geophysical logging observations across the Site, most of the bedrock fractures are oriented northeast to southwest and are cross-cut by a subordinate, north-northwest to south-southeast trending fracture system. Vertical fractures are numerous and extensive in some parts of the Site and interconnect the low-angle bedding plane fractures in these areas. The greatest frequency of fractures is found in the central and southwestern portions of the Site within the shallow, intermediate and deep bedrock. This highly fractured system is likely associated with a documented regional fault system (Volkert 2007). This is based on the observation that the two faults on the Volkert geologic map, if extended to the south, align with the natural stream feature (approximate Valley Drain location). The presence of these fault zones is supported by surface geophysical survey data collected from the Site illustrating a higher density of fractures through this zone. The local and regional system of fractures and faults constitute the structural framework affecting local and regional groundwater flow.

There are two hydrogeologic CSMs for groundwater flow in the Passaic Formation throughout the Newark Basin. These CSMs are:

- The Leaky Multi-Aquifer System (LMAS), as described by Michalski (1990) for certain sites in the Newark Basin. This model describes groundwater flow occurring principally in bedding plane fractures with limited vertical fracturing and limited hydraulic connectivity between these transmissive bedding plane fractures.
- The continuum-flow model (CFM), as described by Knapp (1904), Vecchioli (1965) and Spayd (1985), consists of steeply dipping (near vertical) fractures that serve as major conduits for groundwater recharge, storage and flow (Herman 2010).

The extensive network of vertical fractures throughout much of the Site and its surroundings is an important component of the CSM for the Site. The bedrock at the Site may be conceptualized locally and regionally by a hybrid CFM-LMAS model. The Groundwater RI Report concluded that the fractured rock behaves as a CFM on a large scale; however, fracture patterns will affect groundwater flow on a smaller scale. The S1, S2 and S3 zones seem to represent a CFM in the central and southwestern portions of the site. This is based on the combination of geologic data indicating significant vertical fracturing in these areas and the low vertical hydraulic gradients measured in these areas². The LMAS model may apply to

² Groundwater flow interpretations must integrate the groundwater gradient and hydraulic conductivity as well as effective porosity. Areas of low hydraulic conductivity may create steep hydraulic gradients but may result in relatively low groundwater flow rates. In contrast, areas of higher hydraulic conductivity may result in low hydraulic gradients although with higher groundwater flow rates. However, these are two end components of a continuous relationship that includes effective porosity.

other portions of the Site. This may be supported by significant downward vertical hydraulic gradients between the S1, S2 and S3 zones, suggestive of minimal vertical fracturing and limited vertical hydraulic connection. In addition, across most of the Site (except the southern portion of the site), moderate to significant downward vertical hydraulic gradients exist between the S3 zone and the underlying D zones, suggestive of minimal vertical fracturing and limited vertical hydraulic connection.

As described in the Groundwater RI Report, the Site and its surroundings were characterized by hundreds of boreholes and monitoring wells installed within the overburden and bedrock across the Site and its surroundings to assess groundwater flow and quality conditions. In addition, numerous additional wells have been installed through multiple Pre-Design Investigations (PDI) throughout the site.

The groundwater system at the Site was conceptually separated into seven, elevation-based hydrostratigraphic zones (S-1 through S-3 and D-1 through D-4) that extend from the ground surface to greater than 700 feet below ground surface (bgs), as shown below.

Hydrologic Zone	Elevation Interval (ft. MSL)
S-1	>80
S-2	50 to 80
S-3	0 to 50
D-1	-100 to 0
D-2	-250 to -100
D-3	-400 to -250
D-4	Below -400

In addition, the Site has been separated into 15 investigative areas (IA-1 through IA-15) for the purpose of structuring the investigation and organizing IRMs. These IAs are shown on Figure 2.

2.1.2 Groundwater Conditions

Horizontal groundwater gradients in all of the hydrostratigraphic zones are generally from the northern portion of the Site to the south and southeast, with locally varying flow components to or from surface water features such as streams. The June 2014 groundwater potentiometric surface maps for Zones S1, S2 and S3 are shown on Figures 3, 4, and 5. These maps also include the distribution of total chlorinated ethenes for each zone. As will be described in Section 2.2.4, it is apparent on these maps that the distribution of chlorinated ethenes generally follows the groundwater gradients of the potentiometric surface maps.

Figure 3, the potentiometric map for Zone S-1, is also the water table map for the Site. This map illustrates the general horizontal gradient from the north and northwest to the south and southeast with local variability. This map indicates the presence of several “V” shapes in the groundwater contours pointing in an upgradient direction. These “V” shapes in groundwater contour maps illustrate zones of converging groundwater flow, which is typically associated with either higher hydraulic conductivity zones or groundwater discharge zones. A primary “V” shape in the water

table map occurs in IA-12 near the north central portion of the Site and is coincident with a fracture zone identified by the surface geophysical survey. Other “V” shapes in the S1 potentiometric map occur to the west of IA-12, in IA-4, further west, in IA-10, and a long “V” oriented to the southwest parallel to the railroad tracks from the south side of IA-9, through IA-11 and just south of IA-15. This long “V” is oriented generally along a long fracture zone identified by the surface geophysical survey but is also close to St. Paul’s Brook and the Valley Drain. A survey of the Valley Drain (in March 2013) in the vicinity of Building 716 (south of IA-15) showed water leaking into the Valley Drain in that area, demonstrating that groundwater flow into the Valley Drain occurs at least during a portion of the year.

The Groundwater RI Report concluded that, in general, the bedrock to the east and southeast of the Site has a much lower hydraulic conductivity than the bedrock immediately under the middle of the Site. This permeability contrast has a controlling influence on groundwater flow, the distribution of groundwater constituents, and the shape of the chlorinated VOC plume.

Groundwater gradients in the lower hydrostratigraphic zones (S2 and S3) are generally similar to the S1 potentiometric map with the exception that the variation in potentiometric contours are somewhat subdued, with broader, less angular contour lines compared to Zone S1. This is probably due to less influence by surficial features and variations in recharge from location to location. Notable exceptions to the similarity between S1, S2 and S3 gradients are:

- In the northeastern corner of the Site (IA-12), the gradient in S1 is to the southwest, whereas the gradient in S2 is to the northeast, and in S3 the gradient is to the east. These differences in gradient and flow patterns in this localized area may indicate that there is potentially a limited vertical connection among the zones, allowing differences in horizontal gradients with depth. This will be reviewed with future monitoring to determine whether this observation persists.
- In the eastern portion of the Site, the gradient in S1 is to the south in IA-12 and IA-3 and changes to southeast in IA-7, whereas in S2 and S3 the gradient is more easterly. This localized variability may also indicate a limited vertical hydraulic interconnectivity among different hydrostratigraphic zones in this area.

There is a significant downward vertical gradient from Zone S1 to the deeper intervals (Zones S2 and S3) throughout much of the Site. The magnitude of the downward gradient varies across the Site, probably depending on the vertical conductance, with steeper gradient where there is more resistance to vertical flow. Groundwater gradient is upward in the immediate vicinity of groundwater discharge areas, such as along the Saint Paul’s Brook and Valley Drain in Nichol’s Park. These vertical groundwater gradient patterns are illustrated in the cross sections with potentiometric lines and hydraulic conductivity ranges in Appendix N of the Groundwater RI Report.

As stated in the Groundwater RI Report, hydraulic gauging studies have shown that there is currently no significant influence (e.g., gradient reversal) on the groundwater flow regime from locally active water supply wells.

2.1.3 Constituents of Concern

As described in the Groundwater RI Report, the constituents of concern (COCs) at the Site consist of a group of volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), pesticides and metals as listed in a table on page 47 of the Groundwater RI Report and reproduced below. However, the most prevalent groundwater COCs at the Site are chlorinated VOCs, specifically tetrachloroethene (PCE), trichloroethene (TCE) and their degradation products, cis-1,2-dichloroethene (*cis*-1,2-DCE) and vinyl chloride (VC) (and to a lesser extent 1,1-dichloroethene [1,1-DCE], 1,1,1-trichloroethane [1,1,1-TCA], and 1,1-dichloroethane [1,1-DCA]).

VOCs	SVOCs	Pesticides	Metals
1,1,1-Trichloroethane	1,4-Dioxane	Dieldrin	Aluminum
1,1-Dichloroethane	2-Methylnaphthalene	Lindane	Antimony
1,1-Dichloroethene	2-Methylphenol	Chlordane	Arsenic
1,2-Dichloroethane	3&4-Methylphenol		Barium
1,2-Dichloropropane	bis(2-Ethylhexyl)phthalate		Beryllium
2-Butanone (MEK)	Benzo(a)anthracene (BaA)		Cadmium
Benzene	Benzo(a)pyrene		Chromium
Chlorobenzene	Benzo(b)fluoranthene		Cobalt
Chloroform	Benzo(k)fluoranthene		Iron
cis-1,2-Dichloroethene	Dibenz(a,h)anthracene		Lead
Cyclohexane	Hexachlorobenzene (Hbenz)		Manganese
Methylcyclohexane	Indeno(1,2,3-cd)pyrene		Nickel
Methylene chloride	Pentachlorophenol		Sodium
Tetrachloroethene	Tentatively Identified Compounds (TICs)		Thallium
Toluene			Zinc
trans-1,2-Dichloroethene			
Trichloroethene			
Vinyl Chloride			

2.1.4 Contaminant Distribution – Chlorinated Ethenes

The Groundwater RI Report presents the distribution of chlorinated VOCs as CVOC isoconcentration maps (See Groundwater RI Report Figures 23 to Figure 29) for each of the elevation-defined hydrostratigraphic zones and on cross sections with isoconcentration contours (Groundwater RI Report Figures 36 through Figure 40). These figures present data from the September 2013 (2013Q3) sampling event. As recommended in the Groundwater RI Report, quarterly groundwater monitoring has continued. Data from these addition sampling rounds will

be presented in the Annual Groundwater Progress Report being prepared concurrently with this Interim Natural Attenuation Report.

A recent summary of the distribution of the total chlorinated ethenes (the sum of PCE, TCE, *cis*-1,2-DCE, and VC) for Zones S1, S2 and S3 are shown in Figures 3, 4, and 5. A maximum value for Zones S1, S2, and S3 are mapped as a composite for these zones in Figure 6. These maps of total chlorinated ethenes reflect the maximum concentrations between September 2013 and August 2014 with the data presented in Appendix B. The percentage of different chlorinated ethenes is presented as pie chart maps for Zones S1, S2, and S3 in Figures 7, 8 and 9. The pie chart maps use the same maximum values as in Figures 3, 4, 5, and 6.

Several releases of CVOCs and plumes of CVOCs were identified in the Groundwater RI Report based on the presence of an area of elevated CVOC concentrations at the water table and decreasing concentrations in downgradient groundwater. These sources and plumes of CVOCs, as described in detail in the Groundwater RI Report, are presented below, with additional observations based on data collected since the Groundwater RI Report. The plumes are as follows:

- **IA-9 Process Pipe** – The highest total chlorinated ethenes concentration detected in the data presented in this report (data in Appendix B) is at S-1 well MW-170 (shown as 146,689 µg/L on Figure 3 and Appendix B). This is located in IA-9 and is associated with a Roche process pipe. However, this area of VOCs was shown to be localized and delineated by surrounding wells in Zones S-1 (Figure 3) and S-2 (Figure 4), delineating the horizontal and vertical extent of this small zone of chlorinated ethenes. The chlorinated ethenes in this area consist of parent compound PCE, but the highest concentration is the daughter product *cis*-1,2-DCE (87,700 of the 146,689 µg/L) at well MW-170. This is illustrated as a fingerprint for this area in the pie chart map for Zone S1 (Figure 7).
- **Clifton-Allwood Municipal Sewer** – Several sources of PCE were identified along the length of the existing Clifton-Allwood Municipal Sewer and a former length of the municipal sewer in IA-12, IA-3, IA-7 and IA-11 (as described below). The municipal sewer has been shown to have breaches through video surveys of the sewer in IA-12. Pipe breaches similar to those observed in IA-12 are expected to be present elsewhere north and south of IA-12. Based on the presence of PCE and its breakdown products directly associated with the length of the sewer, it is clear that there were historically a number of releases of PCE. The presence of *cis*-1,2-DCE as the primary constituent present in the vicinity of the sewer line demonstrates that significant degradation has occurred along the municipal sewer line through the Roche property. The municipal sewer slopes to the south, which coincides with the groundwater gradient through this area (see Figure 3). The groundwater plumes associated with the Clifton-Allwood Municipal Sewer include the following:
 - **Clifton-Allwood Municipal Sewer North of Route 3 (Off-Site)** – The release(s) north of Route 3 have created an upgradient CVOC plume(s) that appears to extend vertically from the water table down to Zone D2 and laterally comingles with the VOC plume beneath the sewer breach in IA-12 (see Figures 3 through 6). Concentrations of total chlorinated ethenes, shown in Zones S1 and S2 upgradient

of the Roche property at wells MW-201A and MW-201 (Figures 3 and 4) are 2,894 and 3,953 µg/L, respectively.

- **IA-12 Clifton-Allwood Municipal Sewer** – The second highest chlorinated ethenes concentration in the dissolved phase on the Site was identified in IA-12 adjacent to the CAMS at well MW-60 and historically at MW-80. Chlorinated ethenes in these wells have ranged as high as 10,000 to 60,000 µg/L. This is illustrated in time-concentration graphs for select wells (see Figure 10).

The chlorinated ethenes in well MW-60 consist primarily of PCE (50,100 µg/L of the total chlorinated ethenes of 60,830 µg/L). However, other wells in this area have a high percentage of *cis*-1,2-DCE, as shown in the Zone S1 and Zone S2 pie chart maps (Figures 7 and 8).

Angled drill holes under this municipal sewer demonstrated the presence of small quantities of dense non-aqueous phase liquid (DNAPL) using NAPL FLUTes (TRC 2015 IA-12 PDI). This DNAPL was shown to be present below the municipal sewer in one of two investigated locations, to depths of approximately 41 ft. bgs. The presence of DNAPL explains the presence of chlorinated ethenes with concentrations up to 60,000 µg/L.

Groundwater concentrations in the highest concentration areas, close to and at the same elevation of the DNAPL, have a great deal of variation through time, as illustrated at wells MW-60 and MW-80 (see Figure 10). Note that the DNAPL was found from about elevation 88 ft. to 109 ft. above mean sea level (msl) and these wells are screened between elevations 101 ft. to 116 ft. (MW-60) and 104 ft. to 114 ft. (MW-80) msl. This variation is likely due to small shifts in the groundwater regime between these wells and the DNAPL source under the municipal sewer resulting in concentration fluctuations. As shown in Figure 10, the maximum values detected in these wells (*i.e.*, the maximum concentrations present in the groundwater) are shown to be stable. This is an important consideration in assessing the attenuation/degradation character of this plume as described in Section 3.0.

- **IA-3/IA-7 Clifton-Allwood Municipal Sewer** – A small plume of PCE and daughter products was detected in Zone S1 well MW-139 located proximal to the former Clifton-Allwood Municipal Sewer, south of Building 115 (see Figure 3). The VOC distribution in this area suggests that there is a potential release from this former municipal sewer near MW-139. Below this area in Zone S2, elevated chlorinated ethene concentrations were detected in well MW-253B (Zone S2) (587 µg/L total chlorinated ethenes on Figure 4), which is hydraulically downgradient from S1 well MW-139. The chlorinated ethenes in both of these wells are primarily *cis*-1,2-DCE (see Zone S1 pie chart map on Figure 7), indicating significant degradation has occurred.

- **IA-7 Clifton-Allwood Municipal Sewer** – The VOC distribution suggests that MW-218 is located near a release of VOCs potentially from the former municipal sewer, creating a small plume that extends into IA-11. VOC concentrations at MW-218 (2,834 µg/L) decline to much lower concentrations in nearby wells (e.g., 1,152 µg/L at MW-292A). Zone S1 wells around well MW-218 (see Figure 3) serve to delineate the horizontal extent of this small plume area. The Zone S1 pie chart map (Figure 7) illustrates that while PCE is over 50% of the total chlorinated ethenes in the largest circle (*i.e.*, the highest concentration at well MW-218), the surrounding wells have higher percentages of daughter products than at MW-218 and lower concentrations.

- **IA-11 Parking Lot 903** – The groundwater within IA-11 (Parking Lot 903) contains mainly PCE, TCE, *cis*-1,2-DCE, 1,1-DCE and VC. As shown on total chlorinated ethenes maps for Zones S1 through S3 (Figures 3, 4, and 5), the areal limits of the shallow CVOC plume in IA-11 have generally been defined, although additional delineation may be needed for remedy design. Along the southern boundary, the CVOC plume extends from IA-11 potentially into Nichols Park in Zones S2, S3, and D1. However, in Zone S1 the chlorinated ethenes plume appears to be limited by St. Paul’s Brook in Nichols Park, with only limited VOCs south of the brook (shown as 9.9 µg/L at well MW-144A on Figure 3). In the deeper Zones S2 and S3 (Figures 4 and 5), the chlorinated ethenes plume is shown to have the potential to extend beyond St. Paul’s Brook.

As shown in the pie chart maps for Zones S1 through S3 (Figures 7 – 9) the VOCs fingerprints in this area vary significantly. These variations include the following:

- The shallow (Zone S1), western portion of IA-11 contains significant daughter products, *cis*-1,2-DCE and VC. While this speciation may be due to enhanced bioremediation that began in 2006, there is evidence that a similar distribution was present prior to enhanced bioremediation efforts. This is shown at well MW-33 in Zone S1 in the time concentration graphs in Figure 10, where pre-2006 concentrations of PCE were around 100 µg/L with daughter products TCE and *cis*-1,2-DCE at about 20 µg/L and 80 µg/L, or about 50% of the total chlorinated ethenes. This is consistent with the source of PCE from a municipal sewer (*i.e.*, the sewage creating anaerobic, nutrient-rich conditions for biodegradation).
- In Zone S3, throughout IA-11, PCE is the predominant chlorinated ethene (see Figure 9), with only limited exceptions.
- Zone S2 in the western portion of IA-11 has a transition between the degradation fingerprint in Zone S1 and the PCE predominance in Zone S3.
- In the northern portion of the park and to the west of IA-11 the chlorinated VOCs are predominantly TCE. In the southern portion of the park (*e.g.*, MW-257B) the VOCs are generally similar to the PCE dominated fingerprint in IA-11.
- Further downgradient of IA-11, in the vicinity of IA-15 (*e.g.*, MW-112) through the southern portion of the park (*e.g.*, MW-257B), the presence of the daughter products (*cis*-1,2-DCE and VC) is not as prevalent, indicating

that the extent of VOC migration from IA-11 is limited to a smaller area than the furthest extent of chlorinated ethenes shown in Zones S1 and S2 (Figures 3 and 4).

- **IA-15** – This area is located in the southern end of the Roche property. Groundwater gradients in IA-15 and to the south, show potential flow is converging towards the Valley Drain located just north of the dam on St. Paul’s Brook. In addition, there are vertically upward gradients from S3 to S2 to S1 on and immediately south of IA-15. The VOCs present within this area are limited to PCE with low concentrations of TCE, cis-1,2-DCE and chloroform (see Figures 7, 8, and 9). The VOCs present within Zones S-2 and S-3 in this area are not consistent with the presence of the daughter products present at the water table in upgradient areas (*i.e.*, IA-11, IA-7, etc.). Rather, the predominance of PCE at IA-15 in S1, S2, and S3 is similar to the PCE dominance in Zone S3 in IA-13, Zone S3 of IA-11, and the eastern portion IA-11, IA-7, IA-3, and IA-12.
- **Western Border of IA-10 and Adjacent Former Deluxe Check Facility** – The bulk of the CVOC contamination at the adjacent former Deluxe Check property originates from a source area on the eastern side of the former Deluxe Check building, where one or more buried drums with the bottom cut off were discovered, and in an area where a former subsurface waste fluid tank received solvent wastes. CVOCs were detected at high (>1,000 µg/L) concentrations 10 years ago in shallow (Zone S1) monitoring wells on Roche property adjacent to the former Deluxe Check facility. Higher concentrations were historically present, upgradient, at the former Deluxe Check facility. In addition to PCE and its breakdown products, the releases at the former Deluxe Check site included 1,1,1-TCA and its breakdown products.

In IA-10 the highest current CVOC concentrations detected on-Site were in Zone S1 well MW-259A, which is in the vicinity of the loading dock of former Building 104 (near the western border of the Roche Site). As shown on Figure 3, well MW-259A has a total chlorinated ethenes concentration of 423 µg/L, with a majority of that as *cis*-1,2-DCE (see Figure 7 pie chart map).

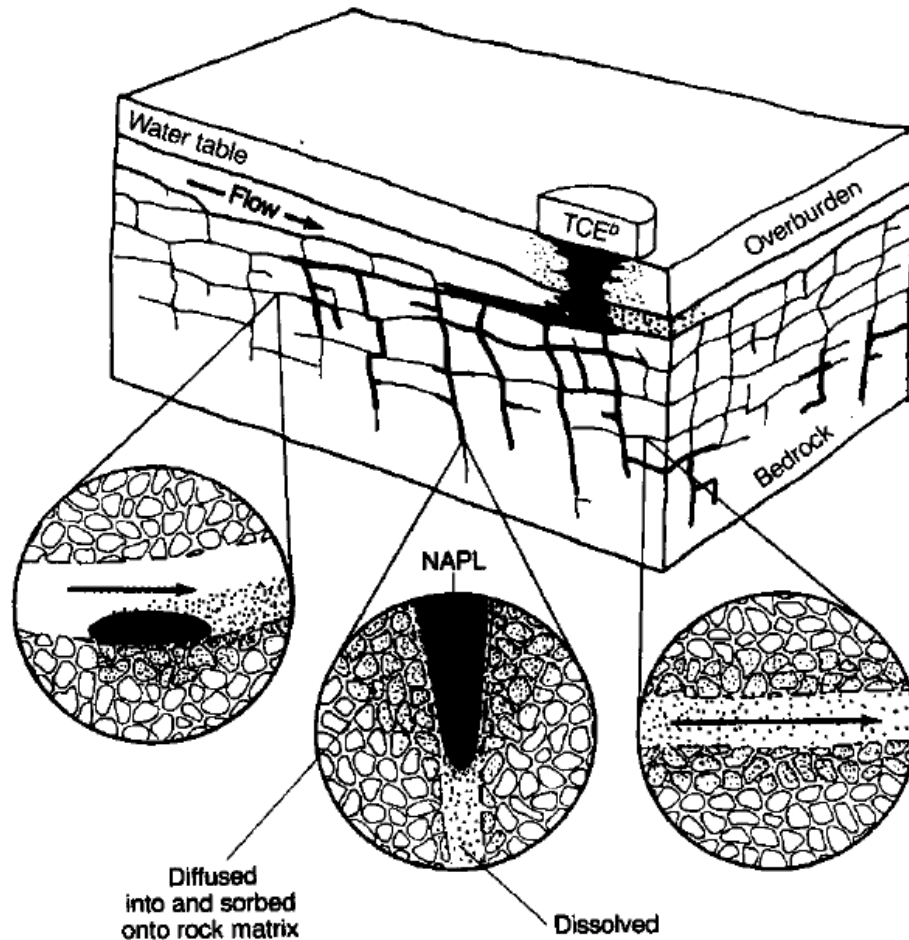
- **Southern Region of IA-10** – As shown on Figure 3, a broad, diffused plume area of low CVOC concentrations (less than 100 µg/L) is observed in IA-10, extending from former Building 103 southward to the intersection of Kingsland Street and Bloomfield Avenue. However, the fingerprint of the CVOCs (see Figure 7) shifts from a mix of PCE and TCE and daughter products in the vicinity of Building 103 to primarily TCE northwest of Building 70. This zone of principally TCE and daughter products extends to the southwest in Zones S2 and S3 where it blends with the VOCs in IA-11.
- **Former Nova Electric** – A significant TCE release to groundwater occurred from this facility located to the southeast of IA-15. There are wells with no exceedances in Zones S-1, S-2, and S-3 between the VOC plumes on the Roche Site and on the former Nova property. In addition, differences in speciation show a strongly TCE enriched signature on the Former Nova Electric site and no corollary on the adjacent Roche property, which indicates that the sources/releases are separate and different.

3.0 LINES OF EVIDENCE FOR CHLORINATED ETHENES NATURAL ATTENUATION

The NJDEP (2012) MNA guidance document outlines the use of multiple lines of evidence to present information to “provide added levels of confidence that MNA represents a viable remedy”. These tiers of data evaluation are commonly referred to as “primary”, “secondary” and “tertiary” lines of evidence. The primary line of evidence includes evaluating plume behavior and contaminant trends that *directly* demonstrate natural attenuation. The secondary line of evidence consists of geochemical data that *indirectly* indicate that natural attenuation processes are occurring at the Site (i.e., contributing processes). The tertiary line of evidence involves microbiological and isotopic studies that can be used as supporting lines of evidence to confirm natural attenuation.

Natural attenuation includes a number of physical, chemical, and biological process that can reduce the concentration, mobility, toxicity, and/or mass of contaminants in groundwater. Natural attenuation processes considered in this report are: dispersion, diffusion, dilution, sorption, and degradation (biotic and abiotic).

Diffusion is one of two mechanisms (diffusion and dispersion) that result in mixing of the groundwater containing the COCs with the ambient groundwater. Diffusion is the movement (on a molecular scale) of a fluid from an area of higher concentration to an area of lower concentration until the concentrations equilibrate. In a fractured rock network, concentrations of constituents flowing through the fractures can diffuse into the matrix porosity of the rock, particularly in zones where advection is less dominant. To illustrate the magnitude of the rock matrix porosity, testing of the bedrock in IA-12 has demonstrated that the rock matrix has a porosity of 4% to 15.5%. The discrete fracture network model of Parker and Cherry (2011) describes a dual-porosity model where contaminant fate and transport is controlled by groundwater flow and contaminant migration through an extensive fracture network. The porosity of the rock matrix comes into play through diffusion of contaminants into the rock matrix. As described by Parker and Cherry (2011) contaminant diffusion into the matrix can attenuate migration of the contaminants within the fracture network. However, without degradation in the matrix, contaminants within the matrix would also diffuse back into the fracture network, extending the plume persistence through time, as shown in the illustration below.



From MacKay and Cherry, 1989.

Dispersion is the other mechanism (besides diffusion) that results in mixing of groundwater. It is a mechanical process that spreads the contaminant front away from the source due to variation in groundwater velocity and tortuosity in the flow field, as groundwater flows through the porous media or fractured rock system. Dispersion can occur on a small scale, as groundwater flows through the tortuous paths of individual grains of porous media and on a large (macro) scale as groundwater flows through large-scale heterogeneities and fracture networks. The combined effect of diffusion and dispersion is dilution of contaminant concentrations and spreading of the contaminant mass longitudinally and transversely to groundwater flow.

Sorption is a process whereby some of the dissolved phase constituent attaches (adsorbs) to the surface of the aquifer matrix (and fracture surfaces) by physical-chemical attraction. Sorption to the surface of the aquifer matrix may be temporary or permanent. Sorption of organic compounds is typically controlled by the content of native organic material on the aquifer matrix, but can also be affected by the rock mineralogy.

Degradation of organic compounds can occur through biotic and abiotic pathways. Biotic degradation of most CVOCs in groundwater occurs by oxidation-reduction reactions that are predominantly carried out by bacteria in the environment (ITRC 1999). Bacteria in the environment can breakdown CVOCs through reductive dechlorination, co-metabolism, and direct oxidation. The type of biodegradation depends on the availability of carbon sources (i.e., food as typically measured by TOC), the CVOCs present, the geochemical conditions in the groundwater, among other factors. Abiotic degradation of CVOCs can occur through multiple processes. For example, abiotic reactions may include reductive elimination, hydrogenolysis, dehydrohalogenation, hydrolysis, etc. (EPA 2009). A number of these processes, especially for the chloroethenes, has been most frequently documented when the CVOCs are in contact with various forms of reduced iron minerals. Biotic and abiotic degradation will reduce the concentration of the parent compound and often produce breakdown products or by-products that can be measured in the groundwater.

The discrete fracture network model of Parker and Cherry (described above) has been extended by EPA (2009) and Schaefer (2013) to include the potential for degradation to be occurring through abiotic degradation by iron bearing minerals within the rock matrix. If degradation is occurring within the rock matrix, the matrix porosity could play an important role in the process of natural attenuation at the Site.

Evidence of natural attenuation occurring at the Site is presented for these three lines of evidence in the following sections.

3.1 Primary Lines of Evidence – Plume Behavior - Contaminant Reduction

3.1.1 Potential Groundwater Migration Distance – Spatial Distribution

An important component of the primary line of evidence for the occurrence of natural attenuation is to determine whether contaminants have migrated as far as expected based on groundwater migration since release of the contaminants. If the groundwater travel distance is much greater than the observed extent of groundwater contaminants, then there must be one or more natural attenuation mechanisms at work to retard the contaminant migration. This evaluation would not discriminate between which attenuation mechanism is occurring, just that there is some form or combination of sorption or degradation occurring to retard migration of the contaminants.

The date of contaminant release and groundwater velocities are rarely known explicitly at remediation sites; therefore, we use a range of potential release dates and hydrologic properties in our evaluation. Data from the Site investigation are used in this section to estimate groundwater migration rates and travel distances during the time frame of potential releases.

Groundwater velocities through the Site vary with hydraulic conductivity, hydraulic gradient, and effective porosity. The hydraulic conductivity of the fractured rock has been extensively tested at the Site through over 700 tests using packer test, slug tests in wells, and pumping tests. The range in hydraulic conductivity is summarized in Table 2 from the hydraulic conductivity tests presented in Appendix A. This summary indicates a large range in hydraulic conductivity, but that the average value for Zones S1 (2.9 ft/day) and S2 (2.67 ft/day) are approximately the same, with Zone S3 somewhat higher, at 6.65 ft/day. The high end hydraulic conductivity for S1 and S2 are the

maximum values measured, as shown on Table 2, 20 ft/day for Zones S1 and S2 and 155 ft/day for Zone S3. The average hydraulic conductivity values are very similar to the hydraulic conductivity estimates used in the Groundwater RI Report's CEA calculation (see Groundwater RI Report Appendix V where hydraulic conductivity for S-1 = 3.7 ft/day, S-2 = 5.5 ft/day, and S-3 = 8.6 ft/day). Differences in these estimates are minor and are based on a somewhat larger data set than available in the Groundwater RI Report.

These averages and maximum values of hydraulic conductivity are used in Table 3 to calculate a range in potential groundwater travel distances for Zones S1 and S2 and for Zone S3.

The average hydraulic gradient used in Table 3's estimate of groundwater velocity is from the Groundwater RI Report that states the average lateral hydraulic gradient along the longest flowpath (from the northwest corner to the southeast corner) of the Site is 0.013. For purposes of this estimate, we assume that the range in gradient through the Site through time varies $\pm 20\%$ from this average of 0.013.

The effective porosity of the rock used in Table 3 for estimating groundwater velocity, is the fracture porosity. The range in fracture porosity presented in Table 3 (average of 5% to a low of 2%) is based on literature values and judgment based on observations of rock core samples. Carleton (1999) reported an estimated effective porosity for a site in the Newark Basin to be from 0.037% to 0.076%. In contrast the, EPA (1999) guidance document provides an estimate for sandstone of 10% to 40%. The range in effective porosity used in Table 3 is an average of 5% to a low of 2%. The very low values from Carleton would result in very large natural groundwater velocities, whereas the 10% to 40% EPA values are too high for the fracture dominated effective porosity for the Site's sandstone. Continued testing at the Site will be used to refine values of effective porosity, but the range, 2% to 5%, is considered a reasonable range for use in Table 3 for estimating a range of potential travel distances. As shown in Table 3, the 2% value is entered into the high column as it results in a higher travel velocity and travel distance.

Using these inputs in Table 3 results in a range of groundwater flow velocity estimates. For Zones S1 and S2 the range is from an average of 0.70 ft/day to a high of 16 ft/day or 260 ft/year to 5,700 ft/year. Zone S3 ranges from an average of 1.7 ft/day to a high of 121 ft/day or 623 ft/year to 44,000 ft/year.

No information is available on when potential releases occurred. However, a reasonable range for this calculation would be at least 20 years to a potential maximum of 50 years before present. Using this range in Table 3 yields an average groundwater travel distance of 5,000 ft. in Zones S1 and S2 to 12,500 ft. in Zones S3. These maximum travel distances are unreasonably high (i.e., 284,000 ft. to 2,200,000 ft.) using a combination of the high estimates for each input parameter. The average travel distances of 5,000 ft. and 12,500 ft for Zones S1/S2 and S3, respectively, are reasonable estimates for groundwater migration to have occurred on the Site since a potential release of contaminants.

As described in Section 2.1.4, the longest extent of the observed VOCs from the upgradient property line is approximately 2,500 ft in Zone S3. Comparison of this maximum extent of VOCs to the average travel distances (5,000 ft. to 12,500 ft.) illustrates another line of evidence that there

must be some form of attenuation occurring to result in a smaller extent of VOCs observed on the Site than would be expected based on groundwater travel times. As stated above, this natural attenuation may be in the form of diffusion, dispersion, sorption and/or degradation. Continued evaluation of natural attenuation processes will be used to determine the processes responsible for this apparent attenuation.

3.1.2 Temporal Distribution

The temporal distribution of VOCs at the Site is in the process of being determined through the eight quarters of VOC monitoring, beginning with the 2013 Q3 sampling event in September 2013. 2014 Q1 and 2014 Q2 have been completed and will be reported in subsequent MNA and annual reporting. However, there are some wells with an extensive history of monitoring; for example, wells in IA-12, and one well each in IA-11 and IA-7 are shown in Figure 10. The time concentration graphs in Figure 10 indicate that the source concentrations in IA-12 have been stable for essentially the duration of their history. As described in Section 2.2.4 for IA-12, the wide swings in concentration are probably due to small changes in the groundwater regime. Likewise, the concentrations at wells PW-37 in IA-7 and MW-33 in IA-11 show a stable concentration over time. Therefore, these areas have data to suggest that the sources have been present and unchanged for the long term history presented in these graphs.

Insufficient data are available to determine whether the downgradient extent of VOCs is stable. One of the goals of the on-going quarterly VOC sampling events is to document the stability of the downgradient extent of the plume. For purposes of this Interim Natural Attenuation Report, we will make the assumption that the downgradient extents of VOCs are stable. This assumption will be thoroughly evaluated in subsequent MNA evaluation.

3.1.3 IA-12 Concentration versus Distance Profile

Figure 11 illustrates the concentration versus distance downgradient from well MW-60 in IA-12. The wells posted on this figure are generally along the center axis of the plume. This figure clearly shows that as the groundwater moves away from the source area, chlorinated ethenes concentrations decline. The straight line fit through the data points from zero to 1,000 ft. downgradient is an exponential trend line that shows a strong correlation coefficient. This exponential trend line is used, as described by EPA (2002), to fit the trend expected based on the governing equation for contaminant migration in groundwater. Extending this trend line beyond 1,000 ft. illustrates the expected concentrations downgradient of IA-12 if there were no other sources of VOCs contributing to the groundwater. However, as described above, IA-3 contributes VOCs to the groundwater beginning at well MW-139. Therefore, downgradient groundwater concentrations are increased due to this downgradient source.

3.1.4 Breakdown Products of PCE and TCE

Reductive dechlorination of PCE and TCE produces breakdown products of cis-1,2 DCE and VC. These breakdown products are not present in the parent PCE and TCE and are direct evidence of degradation. Cis-1,2 DCE has been reported in virtually every IA where PCE and TCE are present. VC is also reported at many wells throughout the Site. The absence of cis-1,2 DCE and VC in source areas and downgradient does not necessarily mean that reductive dechlorination is not taking place, since both of these compounds can be readily degraded.

Ethene can also be a breakdown product of PCE and TCE, however its presence or absence is less dispositive of PCE and TCE degradation, since it can be formed by the breakdown of other compounds, e.g., 1,1,1-TCA. Ethene can also be readily degraded by a wide variety of aerobic and anaerobic microbes, so it typically does not persist in many groundwater settings.

3.2 Secondary Lines of Evidence – Geochemistry

Secondary lines of evidence for natural attenuation include the presence of conditions that are needed to support biological or abiotic degradation and as indicators of the occurrence of degradation or attenuation of contaminants. Understanding aquifer geochemical conditions is important for the determination of aquifer capacity to degrade contaminants. The following sections describe the information available. The EPA MNA guidance document (EPA 1998) described the concentrations of constituents that are conducive for reductive dechlorination processes. These reductive dechlorination processes biologically degrade PCE to TCE to *cis*-1,2-DCE, to VC to ethene and ethane and then to carbon dioxide and water. In this evaluation, the EPA concentration limits are used to evaluate each constituent.

3.2.1 Reductive Dechlorination

3.2.1.1 Organic Substrate

Organic substrate is the food needed for microbial growth. This is measured in laboratory testing as the TOC that is dissolved in a groundwater sample. Figure 12 presents the results of TOC from the February 2014 MNA sampling event. As described by EPA (1998) a concentration of 20 mg/L of TOC is ideal to support the bacteria that are needed for biological degradation. As shown in Figure 12, the TOC present throughout much of the aquifer is 5 mg/L or less. The only well with over 20 mg/L is at well MW-186-2 (20.7 mg/L) in IA-2. There are several scattered wells with TOC greater than 5 mg/L. The TOC at these wells would provide some substrate to support biological activity, but it is not expected to support a robust biological population.

3.2.1.2 Terminal Electron Acceptors

Terminal electron acceptors are constituents that are used by biological respiration. The comparison to human respiration is that we take in oxygen as an electron acceptor (energy source) and exhale carbon dioxide. Bacteria can utilize a variety of electron acceptors, and their respiration causes changes in groundwater chemistry that can be measured. For example, under aerobic conditions, bacteria can use dissolved oxygen as their terminal electron acceptor with a resulting decrease in dissolved oxygen and an increase in carbon dioxide. As the oxygen is depleted, conditions become increasingly anaerobic, and subsequent electron acceptors are utilized, e.g., nitrate, manganese, iron, sulfate, and carbon dioxide. The geochemical condition is named for the primary electron acceptor being used. Data supporting these discussions are presented in Table 4 General Natural Attenuation Parameters, Table 5 Dissolved Gases, and Appendix C1 Field Parameter Data. Terminal Electron Acceptors Processes (TEAP) are described, going from aerobic to progressively more strongly anaerobic:

- **Aerobic Conditions** – Use of dissolved oxygen (DO) reduces the DO in groundwater. As shown in Appendix C, the DO ranges from 0.2 mg/L to 8.8 mg/L with almost 50% of the measurements below 2 mg/L.

- **Nitrate-Reducing Conditions** – Bacteria can use dissolved nitrate as a terminal electron acceptor, typically when DO has been depleted. Evidence for nitrate-reducing conditions is when nitrate concentration in groundwater declines to less than 1 mg/L. As shown on Figure 13, the concentration of dissolved nitrate throughout the Site is typically less than 1 mg/L throughout the center of the Site, with only a few outlier wells exhibiting nitrate concentrations higher than 2 mg/L. Along the southwestern and southern portion of the Site, there is a greater number of wells with nitrate greater than 2 mg/L, indicating that the groundwater is not strongly reducing and, based on this parameter alone, would not indicate reducing conditions.
- **Manganese-Reducing Conditions** – Following depletion of DO and nitrate in the groundwater, bacteria can use solid manganese dioxide from the soils or rock as a terminal electron acceptor, which increases the dissolved manganese in groundwater. Concentrations greater than 50 µg/L typically indicates the presence of manganese-reducing conditions. As shown on Figure 14, the dissolved manganese indicates manganese-reducing conditions throughout the same region as nitrate-reducing conditions.
- **Iron-Reducing Conditions** – In the next more strongly reducing condition, iron-reducing conditions, bacteria can use solid iron-bearing minerals from the soils or rock as a terminal electron acceptor. This increases the dissolved (ferrous) iron in groundwater to concentrations typically greater than 300 µg/L. As shown on Figure 15, the dissolved iron indicates iron-reducing conditions throughout a somewhat smaller region shown as having nitrate- and manganese-reducing conditions.
- **Sulfate-Reducing** – Bacteria can use dissolved sulfate as a terminal electron acceptor, which reduces the sulfate concentration in groundwater to much less than background, and can reduce sulfate concentrations to less than 1 mg/L. As shown on Figure 16, the sulfate concentration is typically greater than 20 mg/L, showing there is relatively little sulfate reduction, indicating that there is little evidence of wide spread sulfate-reducing conditions. While there may be localized zones of sulfate-reducing conditions, it is not a prevalent condition.
- **Methanogenic Conditions** – Bacteria can use dissolved carbon dioxide as a terminal electron acceptor, which produces dissolved methane in the groundwater. Concentrations of methane greater than 500 µg/L indicate significant methanogenic conditions. As shown on Figure 17, there are a few locations with methane concentrations in excess of 500 µg/L, but only in widely distributed locations. However, the presence of methane in most locations indicate that there are localized zones of methanogenic conditions distributed around the Site.

In summary, these analyses demonstrate that the geochemical conditions across most of the Site are anaerobic. The anaerobic conditions are predominantly iron reducing, with localized zones throughout the Site that are methanogenic. The lack of Site-wide sulfate-reducing or methanogenic conditions are understandable based on the high iron mineral content of the Passaic Formation. The color of the red sandstones and siltstones are indicative of high iron oxide mineral content. These data indicate that the system, at ambient geochemical conditions, is well “poised” (i.e., the redox equivalent term for buffering of pH) at iron reducing TEAP level.

3.2.1.3 Degradation By-Products

Carbon dioxide is a product of aerobic bacterial respiration and an endproduct of organic compound degradation. This includes degradation of chlorinated ethenes. Results for carbon dioxide at the Site are shown in Figure 18. As described by EPA (2002), the presence of carbon dioxide at least two times higher than background is one of many indicators of natural attenuation of chlorinated ethenes. However, the background concentration of carbon dioxide is difficult to determine due to the presence of upgradient contamination. For purposes of this evaluation, a concentration of less than approximately 10 mg/L is used as background, primarily based on carbon dioxide concentrations southwest of the Site (i.e., the red labeled values).

On Figure 18, the carbon dioxide values less than 10 mg/L are shown as red, between 10 mg/L and 25 mg/L are shown as yellow, and greater than 25 mg/L as green to illustrate background, greater than background, and at least twice background, respectively. This illustrates that, based on carbon dioxide values, there is evidence of degradation generally through the center of the Site.

Degradation by-products of reductive dechlorination also include ethane and ethene. Table 5 presents the results of analysis of dissolved gases for the February 2014 and June 2014 sampling rounds. Dissolved gas data from the source zones show elevated concentrations of ethane and ethene. These data provide strong supporting lines of evidence that degradation of the chlorinated ethenes by reductive dechlorination is occurring within the groundwater plume.

3.2.2 Abiotic Degradation

Abiotic degradation of chlorinated VOCs has been demonstrated to be a significant mechanism of natural attenuation of chlorinated VOCs. EPA (2009) published an extensive summary of abiotic mechanisms. Abiotic degradation is the degradation of organic molecules via direct contact with reactive elements or minerals. The most common example of abiotic degradation (chemical reduction) of chlorinated ethenes is the use of zero valent iron in groundwater treatment walls. However, reactive elements and minerals are also naturally occurring and, as shown by EPA (2009) and others (Schaefer 2013), can play an important role in the degradation of chlorinated organic compounds. The primary class of minerals that promote abiotic degradation are iron-bearing minerals. EPA (2009) goes into great detail describing the minerals, mechanisms, and degradation products. Generally, the primary conditions that support abiotic degradation are the presence of iron-bearing minerals under an anaerobic environment. The degradation products described by EPA (2009) may include *cis*-1,2-DCE and VC, like biological degradation; however, the more commonly referenced degradation products are acetylene, ethene, ethane and carbon dioxide. One of the studies referenced by EPA (2009) demonstrated degradation of TCE directly to carbon dioxide without any intermediate daughter products.

Based on their red color, the Passaic Formation rocks contain significant concentrations of iron-bearing minerals. Section 3.2.1 concludes that the groundwater throughout most of the Site is primarily at an iron-reducing redox potential. Therefore, the iron minerals deposited in the Passaic Formation as oxidized iron minerals tend to be reduced. As described by EPA (2009), these conditions tend to form metastable iron minerals that are the most reactive with the CVOCs.

Groundwater samples were analyzed for the abiotic degradation products of CVOCs, i.e., acetylene, ethene, ethane, and carbon dioxide. Collection and analysis of acetylene is difficult because of its very high volatility. Special septa have to be used in the sample bottles to try to

keep acetylene in the closed sample bottle. In addition, acetylene is highly biodegradable, so it is probably very short lived in the environment. Considering these obstacles detecting acetylene, even at very low concentrations, may be significant if the results are reproducible in subsequent rounds.

Like acetylene, ethene and ethane are also abiotic degradation products of chlorinated ethenes. Ethene and ethane were much more widely detected in Site monitoring wells as compared to acetylene, potentially supporting an abiotic degradation pathway. However, the presence of ethene and ethane in groundwater is less dispositive of an abiotic degradation pathway than the presence of acetylene, since ethene and ethane are also breakdown products of biotic reductive dechlorination.

As described by Schaefer (2013), abiotic degradation can occur within the fractures and within the matrix of the rock. However, much more intimate contact between the groundwater and the iron-bearing minerals occurs within the rock matrix. Therefore, the abiotic degradation may be occurring within the rock matrix, with little evidence of the degradation products being present in the high-permeability fracture zones. Therefore, direct detection of these abiotic degradation mechanisms may not be evident from the groundwater sampling, which collects groundwater samples primarily from the fractures.

3.2.3 Aquifer Geochemical Conditions

The general geochemistry is illustrated as pie charts of the primary anions and cations in Figures 19 through 24. The primary differences in the general geochemistry is illustrated on these maps as changes in the concentration of chloride in the anion maps and for sodium in the cation maps. These maps show a distinct change from being chloride and sodium dominated in Zone S1 to being progressively less chloride and sodium dominated in Zones S2 and S3. The high chloride and sodium in the uppermost zone is most likely attributable to the application of road salt and subsequent infiltration of rainfall carrying dissolved sodium and chloride to the water table. Locally, some chloride could result from degradation of chlorinated VOCs; however, the potential contribution from the degradation of CVOCs is limited, in that CVOC concentrations greater than several hundred mg/L are very limited on the Site. As groundwater migrates vertically deeper, the geochemistry becomes progressively more calcium carbonate dominated, as carbonates dissolve into the groundwater from the soil and rock matrix.

The following table presents some chloride summary statistics for each zone. As shown in this table, there are two columns for chloride, one with all chloride data and one without values in excess of 3,000 mg/L as these appear to be outliers in S1. [Note that the chloride concentration outliers occurred in S1 and are likely associated with local infiltration of road salt impacted surface water. These values were excluded because their extent was limited in areal extent and not representative of typical shallow groundwater quality.

SAMPLE ID:	Chloride (mg/L)	Chloride without outliers (mg/L)
S1 Average	1230	665
S2 Average	518	518

S3 Average	267	267
D1, D2, and D3 Average	180	180
Dilution Factors		
S1 to S2	0.58	0.22
S2 to S3	0.48	0.48
S1 to S3	0.78	0.60
S3 to D1	0.33	0.33

Chloride without outliers - eliminated values greater than 3,000 mg/L
Dilution factors calculated as (S1-S2)/S1, (S2-S3)/S2, (S1-S3)/S1, (S3-D1)/S3

As shown in this summary, using the chloride data without the outliers, it appears that the chloride concentration drops from an average of 665 mg /L in Zone S1 to 518 mg/L in Zone S2, and 267 mg /L in Zone S3. This results in reductions of:

- 22% from S1 to S2,
- 48% from S2 to S3,
- 60% from Zones S1 to S3.

As the only source of these reductions is dilution (*i.e.*, chloride is not attenuated through other means, it appears to be a good measure of the amount of dilution (*i.e.*, diffusion and dispersion) that can be applied to organic contaminant concentration between each of these zones. These values can be used as site-wide averages; however, dilution in any one location could use area-specific chloride values.

3.3 Tertiary Lines of Evidence – Microbiological and Isotopes

3.3.1 Microbial Analyses

Characterization of functional genes and structural components of microbes present in Site groundwater across the Site was conducted using Quantitative Polymerase Chain Reaction (qPCR) and Phospholipid fatty acid (PLFA) analysis. The 29 analyses indicate the presence of halo-respiring bacteria (e.g., *Dehalococcoides* and *Dehalobacter*) as well as functional genes capable of aerobic co-metabolization of chlorinated ethenes. The results of sampling showed that halo-respiring bacteria were found at every monitoring well that was sampled. In many locations, these bacteria have been reported at moderate to high populations. The qPCR and PLFA data are presented in Appendix D, along with Figure D1 showing the abundance of the different strains of halo-respiring bacteria. Not surprisingly, the bacteria are most abundant in areas where breakdown products of PCE/TCE are also present, e.g., IA-10 B104 and IA-12 source areas.

3.3.2 Compound-Specific Isotope Analyses

Compound-specific isotope analysis (CSIA) was performed on groundwater samples collected from 18 Site wells in February 2014. CSIA results are presented in Appendix E. Isotopic fractionation detected in groundwater samples from wells within IA-3, IA-7, IA-9, IA-12, and

offsite 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 observed here is not sufficient to perform such an analysis.

Evidence for natural attenuation is most compelling in IA-12. However, the degree of fractionation/enrichment is generally low, indicating that current rates of degradation along the primary flow pathways are very slow.

4.0 CONCLUSIONS

The objectives for this Interim Natural Attenuation Report are to provide an in-depth understanding of the existing biogeochemical conditions in areas of elevated concentrations being targeted for IRMs as well as for Site-wide to support a potential MNA remedy for the CVOCs outside of the IRM areas. The report followed the MNA Report outline described in the NJDEP 2012 MNA guidance, presenting the CSM and the multiple lines of evidence for natural attenuation, including the Primary Lines of Evidence as Contaminant Reduction, the Secondary Lines of Evidence through the Site's geochemistry, and the Tertiary Lines of Evidence through microbiological and CSIA data.

Hydrogeologic Conceptual Site Model:

The hydrogeologic CSM is based on the Groundwater RI Report with some additional insights developed from continued groundwater sampling, monitoring well installation, and analysis. The additional insights include:

- Clifton-Allwood Municipal Sewer – The Clifton-Allwood Municipal Sewer that runs through the center of the Site, from north to south, as well as a former segment in IA-3, IA-7, and IA-11, was recognized as a source of PCE and possibly other CVOCs to groundwater in the Groundwater RI Report. However, further definition of this source shows that it has contributed to the CVOC plume through apparent leaks in the sewer pipe at several locations along its alignment.
- The Valley Drain storm water conveyance pipeline south of the Roche property in Nichols Park is present below the water table and acts as a groundwater discharge area in this part of the Site area. This creates upward groundwater flow toward the Valley Drain adjacent to the drain in this area.
- The fingerprint of groundwater quality at IA-15 is different than at known sources along the Clifton-Allwood Municipal Sewer and consists primarily of PCE.
- The source of PCE in Zone S3 upgradient of IA-15 is not known; however, the VOC fingerprint is similar to the VOC fingerprint at well MW-271C on the upgradient Site boundary in the northeastern end of IA-12. However, there are no wells present in Zone S3 to confirm the continuity of VOCs between MW-271C to MW-8C and wells to the south.
- Groundwater travel distances – An important line of evidence for natural attenuation is a comparison of the observed extent of VOCs with the expected groundwater migration since a potential date of release. Based on an expected potential source release from 20 years ago, the range in groundwater migration distances is 5,000 ft. to 12,500 ft. for Zones S1 to S3 compared to a CVOC maximum plume length of 2,500 feet. This line of evidence demonstrates that some form of attenuation is occurring to retard migration of the VOCs. Continued evaluation of natural attenuation will help discern the mechanisms for this attenuation.

Multiple Lines of Evidence for Natural Attenuation

As described in the NJDEP (2012) MNA guidance document, the three categories of evidence for MNA were evaluated, including Primary Lines of Evidence (Contaminant Reduction), Secondary

Lines of Evidence (Geochemistry), and Tertiary Lines of Evidence (Microbiological and Isotope Analyses). These lines of evidence provided the following conclusions:

Primary Lines of Evidence – Contaminant Reduction

- Temporal Distribution – A long history of VOCs on the Site is available at some wells on the Site. In particular, CVOC plumes in IA-12 and IA-7 demonstrate that the CVOC concentrations have been essentially stable for the duration of monitoring from 1996 to the present. This suggests that the CVOC plume is at steady state with regard to source loading and migration. Continued quarterly monitoring is being conducted to extend this temporal distribution throughout the Site.
- Spatial Distribution – As described above, the observed extent of VOCs (2,500 ft.) is much smaller than the range in potential groundwater distances in Zones S1 through S3 (5,000 ft. to at least 12,500 ft.), demonstrating that some form of natural attenuation is occurring.
- Concentration vs. Distance Graph – The concentration versus distance graph (Figure 11) for IA-12 demonstrates the concentration decline downgradient of the release from the Clifton-Allwood Municipal Sewer in IA-12. This trend follows the expected exponential decline for natural attenuation of VOCs downgradient of a source for the distance upgradient of the next known source of VOCs from the Clifton-Allwood Municipal Sewer in IA-3.
- Breakdown Products – Reductive dechlorination of PCE and TCE produces breakdown products of cis-1,2 DCE and VC. These breakdown products are not present in the parent PCE and TCE and are direct evidence of degradation. Cis-1,2 DCE has been reported in virtually every investigative area where PCE and TCE are present. VC and low concentrations of ethene and ethane are present in many areas of the Site as well.

Secondary Lines of Evidence – Geochemistry

- Organic Substrate for microbiological degradation is present, but at relatively low concentrations (i.e., TOC concentrations are typically 5 mg/L or less, with limited areas up to 20 mg/L).
- Monitoring of the terminal electron acceptors in groundwater demonstrates that dissolved oxygen and dissolved nitrate have been consumed, and there is significant dissolved manganese and dissolved iron in groundwater. These data indicate that the groundwater is anaerobic and is under iron-reducing conditions, with localized zones of methanogenic conditions distributed around the Site. Where present, these conditions are conducive for complete reductive dechlorination of the CVOCs.
- Biotic Degradation By-Products monitoring, particularly for carbon dioxide, demonstrates that there is evidence of biotic degradation generally through the center of the Site.
- Abiotic Degradation is a potentially significant contributor to CVOC degradation, particularly in the presence of iron-bearing minerals under anaerobic conditions. Both of these conditions (anaerobic groundwater in an aquifer with high concentrations of iron-bearing minerals) are present at the Site. In addition, recent studies at other sites have shown abiotic degradation can occur within the matrix of the rock with little evidence observed in the fractures of this abiotic degradation that may be occurring in the matrix (i.e., little evidence in groundwater monitoring wells that collect samples from the more permeable fracture zones and not from the rock matrix).

- Abiotic degradation products are similar to biological degradation products and by-products (e.g., ethene, ethane, and carbon dioxide). However, acetylene is distinctive to abiotic degradation. The confirmed presence of even low, infrequent detections of acetylene is evidence that abiotic degradation may be occurring at the Site.
- Major Ions – The major ions (chloride, sodium, calcium, carbonate, etc.) illustrate that there is a source of sodium chloride (e.g., road salt) on the Roche property in Zone S1 groundwater. Chloride is a conservative tracer in groundwater, so it is reduced concentrations in downgradient locations is a direct indication of dilution.
- Dilution Factors – Reduction in chloride concentrations from Zone S1 to S2 indicates a reduction due to dilution of 28% and 54% from Zones S2 to S3, with an overall reduction due to dilution of 67% between Zones S1 and S3. This suggests that one of the mechanisms of CVOC attenuation is dilution, through the processes of diffusion and dispersion.

Tertiary Lines of Evidence – Microbiology and Isotopes

- Microbiology –Halorespiring bacteria were found at every monitoring well that was sampled. In many locations, these bacteria have been reported at moderate to high populations. The bacteria are most abundant in areas where breakdown products of PCE/TCE are also present.
- CSIA – 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. However, the degree of fractionation/enrichment is generally low, indicating that current rates of degradation are very slow.

5.0 RECOMMENDATIONS

Recommendations based on this Interim Natural Attenuation Report are as follows:

- As recommended in the Groundwater RI Report, quarterly monitoring should be continued to further evaluate trends and assess plume stability.
- An additional MNA sampling event should be, and has been, conducted in the late summer to supplement the winter MNA sampling event to assess seasonal variations in the data.
- Further evaluation of abiotic degradation and matrix diffusion should be conducted to determine the mechanisms and rate of degradation. Because the abiotic degradation mechanism is likely occurring within the matrix of the rock, we would expect to see little evidence of this in the groundwater samples, since the groundwater samples are collected from the rock fractures. Therefore, a laboratory study should be completed to assess abiotic degradation of CVOCs within the rock matrix.

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