SECOND 2008 SEMIANNUAL MONITORING REPORT
CHEVRON CINCINNATI FACILITY
HOOVEN, OHIO

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1.0 INTRODUCTION

Chevron Environmental Management Company (Chevron) is performing final groundwater corrective measures implementation and monitoring of the remedy performance at the former Gulf Refinery located approximately 20 miles west of Cincinnati, Ohio, near the intersection of Ohio State Route 128 and US Highway 50, as shown on Figure 1-1. The groundwater remedy was designed to be protective of human health and the environment, with the long-term objective of reducing dissolved phase hydrocarbon concentrations to meet cleanup objectives. Achieving the long-term objective will take many years; therefore the following interim objectives have been adopted for the groundwater remedy:

- Monitor soil vapor concentrations and prevent unacceptable migration of volatile petroleum hydrocarbons into indoor air
- Measure the stability of LNAPL and dissolved phase petroleum hydrocarbons
- Remove recoverable LNAPL to agreed upon end-points
- Stabilize the west bank of the Great Miami River to prevent erosion of soils containing petroleum hydrocarbons

Groundwater remediation and monitoring efforts are being conducted in accordance with a November 2006 Administrative Order on Consent (2006 AOC) between Chevron and the United States Environmental Protection Agency (USEPA; Docket No: RCRA-05-2007-0001). The primary components of the groundwater remedy specified in the 2006 AOC include:

- Re-establishment of natural hydraulic conditions beneath the facility, Hooven, and off-site properties to the southwest (commonly referred to as the Southwest Quadrant) through discontinuance of year round groundwater recovery (although, as subsequently discussed, hydraulic containment via groundwater extraction from the production wells situated along the facilities eastern boundary were resumed in March 2009)
- Focused LNAPL removal during periods of extreme low water table conditions through high-grade pumping over the next decade
- Combined operation of the horizontal soil vapor extraction (HSVE) system beneath Hooven with high-grade recovery
- Continued seasonal operation of the Gulf Park biovent system during low water table conditions

- Engineered stabilization of the bank of the Great Miami River at the former refinery and Gulf Park to prevent erosion of soil containing petroleum hydrocarbons
- Long-term monitoring of natural source zone attenuation including dissolved and vapor phase biodegradation

A fundamental concept of the final groundwater remedy is the continued stability of the LNAPL and dissolved contaminant plumes. The majority of recoverable LNAPL has been removed from beneath the former refinery and off-site properties over the past two decades. This is especially true in the upper and middle reaches of the smear zone, where LNAPL saturations are low. High-grade recovery is intended to focus on remaining LNAPL removal within the lower reaches of the smear zone and core portions of the plume with the highest remaining LNAPL saturations. However, it is understood that the long-term remedy objective will be accomplished primarily through natural processes that drive contaminant degradation and removal over time.

A detailed discussion of the objectives and activities to be conducted to achieve the groundwater remedy goals, are described in the documents titled, *Remedy Implementation Plan (RIP) for Final Groundwater Remedy, Chevron Cincinnati Facility* (Trihydro 2007a) and *Operation, Maintenance, and Monitoring (OMM) Plan for Final Groundwater Remedy, Chevron Cincinnati Facility* (Trihydro 2007b).

Some components of the RIP and OMM plan were amended with a June 30, 2008 modification to the 2006 AOC, which was put in place per US EPA plans for conducting an independent vapor monitoring program in Hooven. The timing and scope of vapor and groundwater monitoring in Hooven was adjusted slightly during the second half of 2008 per this Order amendment, but was largely consistent with the intent of the original OMM Plan. The Order amendment would have restricted horizontal soil vapor extraction (HSVE) system operation during the second half of 2008, but it turned out that groundwater trigger elevations were never reached during the second half of the year and there were not any high-grade or HSVE system operations during the reporting period. The US EPA’s Hooven vapor monitoring program was not completed by the end of 2008, so plans for monitoring and system operation during 2009 were further clarified in a February 18, 2009 letter from USEPA to Chevron. The results of any modifications to 2009 system operation and monitoring results per the 2009 AOC clarification letter will be addressed in future semiannual reports.

1.1 SUMMARY OF SITE CONCEPTUAL MODEL

A detailed site conceptual model (SCM) for groundwater was presented in the *First 2008 Semiannual Monitoring Report, Chevron Cincinnati Facility, Hooven, Ohio* (Trihydro 2009). A summary of the SCM is provided herein including updates made using data collected during the second half of 2008. Figure 1-2 shows a diagrammatic SCM for the facility, Hooven, and Southwest Quadrant.

1.1.1 SETTING

Refinery operations at the former Gulf Oil refinery began in 1931. Chevron acquired Gulf Oil Company in 1985 and that same year, an oily sheen was observed on the Great Miami River along the southeast portion of the facility. Hydraulic containment measures were implemented to minimize migration of petroleum hydrocarbons off-site. The refinery ceased production in 1986 and the refinery infrastructure was subsequently dismantled. Interim measures performed at the facility since early 1985 focused on hydraulic control of LNAPL and dissolved phase petroleum hydrocarbons by extracting groundwater and creating inward hydraulic gradients. These measures were expanded to include excavation of refinery related wastes; soil vapor extraction and six-phase heating beneath the Islands; bioventing beneath Gulf Park; and operation of the HSVE system designed to remove hydrocarbons beneath State Route 128 and Hooven. Historic remediation activities have recovered millions of gallons of LNAPL.

The former refinery is situated in a glacial valley incised into Ordovician-age shale and partially filled with glacial outwash and fluvial deposits of the Great Miami River (Spieker and Durrell 1961, Spieker 1968, Watkins and Spieker 1971). The surficial fluvio-glacial aquifer ranges from approximately 20 to 100 feet thick, and is composed of dominantly coarse sediment, referred to as the Buried Valley Aquifer. An upward fining sequence is present in areas along the riverbank and flood plain on the former refinery. In addition, a clayey-silt layer is exposed at the ground surface in the western portion of Hooven with a thickness of at least 10 feet along the western edge of town. This layer serves as an apparent aquiclude with runoff flowing eastward over the shallow aquiclude before descending towards the groundwater table and joining regional flow.

Groundwater within the Buried Valley Aquifer generally flows from north to south, although episodic flooding tends to result in redirection of the flow to the west for periods ranging from days to weeks dependant on the magnitude of the flood event. A partially penetrating sheet pile wall was installed as part of the riverbank stabilization measures between September and December 2008. It is not anticipated that the partial penetrating wall will affect hydraulic conditions within the Buried Valley Aquifer under ambient conditions or episodic flood events.

1.1.2 SOURCE

Refinery operations terminated in 1986, and the distribution of LNAPL stabilized as gravity and capillary forces approached equilibrium. Vertical smearing of the LNAPL occurred over time as a result of seasonal fluctuation of the water table, leaving some LNAPL within the pore spaces below and above the water table. The top and bottom of the "smear zone" are roughly coincident with the historic high and low groundwater elevation. Therefore, some smear zone is exposed above the water table, even during periods of seasonal high groundwater, although the maximum exposure of LNAPL occurs during periods of low water table. The thickness of the smear zone generally increases from inches at the plume periphery, to as much as 20 feet in locations of the production wells. The depth to the top of the smear zone varies across the site, from as little as 10 feet near the Great Miami River, to approximately 30 feet across most of the former process areas and tank farms, to about 60 feet under the town of Hooven.

Petroleum hydrocarbon liquids are a mixture of hundreds of individual compounds from many families, including aliphatics, aromatics, paraffins, isoparaffins, olefins, and naphthalenes. Each compound has somewhat different physical, chemical, and toxicological properties, but some are sufficiently volatile and toxic to pose a potential human health risk via dermal contact, ingestion, and inhalation if present at sufficient concentration. In the area adjacent to the distribution of LNAPL, some hydrocarbons dissolve in groundwater and migrate as solutes in the aqueous phase. Volatilization from LNAPL or dissolved phase hydrocarbons can produce vapors in the unsaturated zone immediately above the water table.

1.1.3 PLUME STABILITY

A fundamental concept of the final groundwater remedy is the continued stability of LNAPL and dissolved phase petroleum hydrocarbons. The majority of recoverable LNAPL has been removed from beneath the former refinery and off-site properties over the past two decades. This is especially true in the upper and middle reaches of the smear zone, where LNAPL saturations are low. High-grade recovery is intended to focus on removal of LNAPL within the lower reaches of the smear zone and core portions of the plume with the highest remaining LNAPL saturations. However, it is understood that the long-term remedy objective will be accomplished primarily through natural processes that drive contaminant degradation and removal over time.

The LNAPL and dissolved phase plume boundaries are generally coincident at the up-gradient and lateral edges of the smear zone (i.e., western limit in Hooven and eastern limit along the Great Miami River), where dissolved phase petroleum hydrocarbons are generally indicative of LNAPL within the smear zone. Whereas, in the primary flow direction towards the south, a dissolved phase “halo” extends several hundred feet down-gradient from the LNAPL plume boundary.

Dissolved phase plume stability is expected to continue over the long-term, however, it is anticipated that some re-distribution of dissolved phase hydrocarbons may occur at the down-gradient edge of the plume after discontinuance of year round containment. It is anticipated that the dissolved phase plume stability will become re-established during the first few years after pumping is discontinued. Thus, the detection of dissolved phase contaminants farther down-gradient than in recent years will not necessarily represent an expansion of the plume footprint relative to its maximum historical extent.

The primary driver for dissolved phase plume stability is believed to be active biodegradation at the down-gradient limits of the plume. Most petroleum hydrocarbons are readily degradable by soil microorganisms in the presence of oxygen (O_2), a process referred to as aerobic biodegradation. Petroleum hydrocarbons are also degraded by soil microorganisms in the absence of O_2 via anaerobic respiration, but generally at a lower rate compared with aerobic degradation.

The pathway for migration of petroleum hydrocarbon in soil vapor into structures located in Hooven and the Southwest Quadrant is considered incomplete. Soils within the vadose zone to the west of the refinery are predominantly sand and gravel, which allow water to drain relatively freely; therefore, the pore-spaces are mostly air-filled, which provides a pathway for vapor migration. The migration of hydrocarbon vapors from the vapor source at depth is retarded by biological degradation where soil microbes metabolize hydrocarbon vapors as a source of energy. Beneath Hooven, where the vadose zone is nearly 60 feet thick, the hydrocarbon vapors are generally reduced through aerobic biodegradation where O_2 in the atmosphere diffuses down into the unsaturated zone and is reduced along with the petroleum hydrocarbon vapors.

Microbiological degradation can also occur in the absence of O_2, where secondary oxidizers such as iron, sulfate, nitrates, etc. are reduced producing methane. Methane will diffuse upward and is generally degraded at shallower intervals where O_2 concentrations are sufficient. Anaerobic degradation is typically observed in the deeper intervals above the LNAPL and dissolved phase plume; however anaerobic conditions can persist in the intermediate portions of the vadose zone during seasonally low water table conditions or if a secondary sources of petroleum hydrocarbons are present in the shallow subsurface utilizing available O_2.

Biodegradation is a primary driver not only for stability of the vapor and dissolved phase petroleum hydrocarbons, but also for hydrocarbon mass reduction throughout the plume. Aerobic and anaerobic processes reduce contaminant mass in the dissolved and vapor phase. Whenever O_2 is available, aerobic biodegradation processes predominate. Aerobic degradation processes are the dominant mechanism for reductions in petroleum hydrocarbon concentrations in the plume periphery. Within the interior portions of the plume where dissolved oxygen is depleted, anaerobic biodegradation processes will tend to dominate. These anaerobic processes are expected to continue throughout the entire smear zone, given the relatively consistent supply of petroleum hydrocarbons (i.e., source of carbon) from the smear zone.

1.1.4 RECEPTOR

Receptors that have the potential to be affected by dissolved and LNAPL petroleum hydrocarbons include residents within Hooven, commercial workers in business situated in the Southwest Quadrant, sensitive ecological communities along the Great Miami River, visitors and workers employed in remedy support and redevelopment activities on the former refinery, and trespassers coming onto the facility property. As the groundwater beneath the facility, Hooven, or Southwest Quadrant is not used for drinking purposes or secondary uses (e.g., irrigation, bathing, etc.) ingestion and dermal contact with dissolved phase petroleum hydrocarbons associated with the former refinery will not occur. Administrative and engineering controls, as well as personal protective equipment will be used as appropriate to prevent site workers and visitors from unacceptable levels of exposure to LNAPL or dissolved phase petroleum hydrocarbons during redevelopment on the former refinery. Bank stabilization measures along the Great Miami River prevent soil containing petroleum hydrocarbons from eroding into the Great Miami River.

With respect to vapor intrusion, the receptor would be any occupant of a building on the former refinery, in Hooven, or to the southwest if subsurface vapors entered that building at concentrations that pose a potential health risk. If soil vapors diffuse within the “zone of influence” of a structure without degrading, they will become available to be transported into the structure via advection and convection through drains, cracks, utility entrances, sumps, or other permeable discontinuities in the building floor or basement walls. Wind load on the side of a building, barometric pressure changes, HVAC system operation, or temperature differences can all contribute to building depressurization that can drive advection. Most of these processes are reversible, so soil gas generally flows both into and out of buildings under varying conditions. Atmospheric air also enters buildings through doors, windows, and small openings, and the rate of air exchange in buildings typically reduces soil vapor concentrations by a factor of 100 to

10,000 (Johnson 1999), depending on building design, construction, use, maintenance, soil conditions, weather conditions and similar factors.

The vapor intrusion pathway in Hooven was demonstrated to be incomplete during the subsurface investigation completed in 2005, through characterization of the contaminant source, soil vapor, and migration pathway. In addition, the soil vapor data collected from the nested monitoring wells from 1997 to 1999 and following the 2005 investigation have also indicated vapors from the plume are not migrating from the smear zone to indoor air within the residences, businesses, or school at concentrations sufficient to pose an unacceptable excess health risk. In portions of the Southwest Quadrant overlying the smear zone, commercial structures were constructed with a passive vapor barrier beneath the slab as a protective measure for inhibiting migration of vapors into the building, if present.

1.1.5 SECONDARY SOURCES

There are several potential secondary sources of LNAPL and dissolved phase petroleum hydrocarbons within proximity of the former refinery. These include a former service station (currently a non-commercial automotive service center) located directly north of the facility, former operations at the Dravo quarry including several diesel and gasoline underground storage tanks removed in 1991, the Kroger service station, dry wells installed in the Southwest Quadrant, the Whitewater Reclamation (formerly Golsch) construction and demolition landfill, as well as local point sources in the Southwest Quadrant and Hooven.

Volatile petroleum hydrocarbons are ubiquitous in indoor and outdoor air from industrial and commercial sources, automobiles, combustion sources (e.g., gasoline, fuel oil, natural gas, etc.), combustion byproducts (e.g., diesel, wood, coal, candles, etc.), water treatment chemicals and byproducts, a variety of different consumer products, small power tools, tobacco smoke, glues, household cleaners, carpeting, and furniture. Indoor air often contains measurable concentrations of volatile and semivolatile compounds from household activities, consumer products, building materials, furnishings, and outdoor air sources. In addition, urban areas can have shallow releases of hydrocarbons to the subsurface from gasoline powered tools (lawnmowers, chainsaws, trimmers, snow blowers, etc.), vehicles with leaks of oil or gas, runoff from roads, and similar sources. Therefore, it is common to detect low concentrations of hydrocarbon vapors in the shallow subsurface.

1.2 PURPOSE

The primary purpose of this report is to provide a summary of the operations and monitoring conducted in accordance with the 2006 AOC, RIP (Trihydro 2007a), and OMM Plan (Trihydro 2007b) from July 1, 2008 to December 31, 2008. In addition, this report will provide a summary of the additional infrastructure that was installed in accordance with the RIP (Trihydro 2007a) in support of the groundwater remedy. The remainder of this report is organized into the following sections:

- Section 2.0 – Describes the infrastructure, methods, and results of groundwater and soil vapor monitoring activities conducted during the second semiannual reporting period in 2008.
- Section 3.0 – Presents the preliminary qualitative and quantitative lines of evidence supporting the efficacy of natural attenuation mechanisms to degrade petroleum hydrocarbons within the smear zone over the course of the remedy.
- Section 4.0 – Provides details related to the bank stabilization and sheet pile barrier construction activities performed along the west bank of the Great Miami River between September and December 2008.
- Section 5.0 – Describes the results of biovent system operation and groundwater monitoring conducted in Gulf Park.

2.0 MONITORING NETWORK AND RESULTS

The primary component of the final groundwater corrective measures is routine monitoring to evaluate the progress towards meeting the interim and long term remedy objectives. The monitoring network has been established to meet multiple performance and compliance monitoring criteria including collection of data to support remedial system operation; confirmation of high-grade pumping and HSVE system effectiveness; determination of compliance at boundaries where sensitive receptors are present; and evaluation of natural attenuation mechanisms. For the purpose of this report, monitoring has been divided into the following activities:

- Fluid level gauging including continuous monitoring using pressure transducers as well as weekly, monthly, and bimonthly manual measurements
- Groundwater sampling to demonstrate dissolved phase plume stability, protection of sensitive receptors, and efficacy of monitored natural attenuation
- Vertical nested groundwater monitoring to analyze dissolved-phase profiles to evaluate potential differences in the rate of LNAPL mass loss and degradation in the dissolved phase at different depths across the site
- Lysimeter installation and monitoring to collect data regarding precipitation infiltrate to assist in understanding electron acceptor flux into the upper plane of the smear zone
- ROST monitoring to confirm stability of the LNAPL plume at the lateral edge of the smear zone
- LNAPL and soil core analysis to track changes in LNAPL composition over time
- River monitoring to ensure that dissolved phase contaminants do not impact surface water by migrating past the barrier wall located between the smear zone and the west bank of the Great Miami River
- Vapor monitoring to track the vapor intrusion pathway beneath Hooven and evaluate natural attenuation mechanisms in the vadose zone

The following sections describe the results of monitoring conducted to support the groundwater remedy between July 1 and December 31, 2008. A description of the methods used for installation, monitoring, and analysis have been previously described within the RIP (Trihydro 2007b) and OMM Plan (Trihydro 2007a). Additional information pertinent to these activities is described herein when deviations from these plans was necessary.

2.1 FLUID LEVEL MONITORING

Pressure transducers are generally deployed across the monitoring well network listed on Figure 2-1 to evaluate rapid fluctuations in hydraulic conditions across the facility. It should be noted that pressure transducers are relocated as the goals of short term monitoring change such as during flood events or high-grade recovery. Transducers log groundwater elevations on a daily basis. High frequency groundwater elevation data recorded using the pressure transducers are provided in Appendix A.

Manual fluid level gauging is conducted on a bimonthly basis in each of the monitoring wells located in the facility, as well as in Hooven and the Southwest Quadrant. In addition, fluid levels are gauged weekly in select groundwater monitoring wells, and river bank gauging point RBGP-44 located along the west bank of the river. Weekly gauging in these wells is conducted to supplement the bimonthly fluid level measurements in tracking trends in river and groundwater table elevations, as wells as in LNAPL thickness across the Facility, Hooven, Southwest Quad and Gulf Park.

Appendix B provides manual fluid level gauging data collected during the second half of 2008. Potentiometric surface maps for July, September, and November 2008 generated using data collected during bimonthly monitoring are provided as Figures 2-2 through 2-4. During each of the events conducted during the second half of 2008, groundwater flow in the Buried Valley Aquifer was generally to the south, consistent with monitoring events conducted since the termination of hydraulic containment in January 2008. During the November 2008 event, the groundwater monitoring wells situated in Hooven could not be gauged as the USEPA Superfund Technical Assessment & Response Team was performing vapor monitoring, limiting access to these wells.

2.2 DISSOLVED PHASE MONITORING

Dissolved phase monitoring is conducted at the Facility, Hooven, and Southwest Quadrant to assess plume stability, evaluate natural attenuation within the saturated portions of the smear zone, and measure performance of the final groundwater remedy.

Groundwater samples are analyzed for the constituents of concern including benzene, ethylbenzene, toluene, total xylenes, chlorobenzene, arsenic, and lead. Benzene is the constituent most frequently reported in groundwater samples above remedial objectives, with historic concentrations as high as 13 milligrams per liter (mg/L). Dissolved phase benzene is not generally detected more than a few hundred feet outside the LNAPL smear zone, due to intrinsic biodegradation at the plume periphery. Although as discussed in Section 1.1.3, re-distribution of dissolved phase hydrocarbons was anticipated and may have occurred at the down-gradient edge of the plume after continuous containment pumping was discontinued in 2008.

Groundwater samples are also collected from selected wells for analysis of natural attenuation indicators including alkalinity, total calcium, total chloride, chemical oxygen demand, ferric iron (Fe3+), ferrous iron (2+), total iron, dissolved manganese, total manganese, methane, nitrogen, nitrogen as ammonia, nitrate, nitrite, total potassium, total sodium, sulfate, sulfide, and total organic carbon.

Field forms for groundwater samples collected between July and December 2008 are included in Appendix C. Laboratory analytical reports for groundwater samples collected during the second 2008 semiannual monitoring event are provided in Appendix D-1. Data validation reports for each of the analytical packages provided by the laboratory are provided in Appendix D-2. The following subsections present the results of dissolved phase monitoring conducted between July and December 2008. Interpretation of the dissolved phase analytical results is provided in Section 3.0.

2.2.1 SENTINEL AND POINT OF COMPLIANCE MONITORING

There are three sentinel and four point of compliance monitoring wells located at the down-gradient edge of the dissolved phase plume in the Southwest Quadrant. The sentinel and point of compliance monitoring networks are presented on Figure 2-5.

Groundwater samples were collected from the sentinel and point of compliance monitoring wells MW-131 through MW-134 on July 8 and 9, 2008, as these wells were newly installed in late 2007 and are being monitored on a quarterly basis for the first two years. Groundwater samples were collected from the entire sentinel and point of compliance network again in mid-November 2008. Groundwater analytical results for the dissolved phase constituents of concern are provided on Table 2-1. Dissolved arsenic and lead were detected in sentinel well MW-131 at concentrations of 0.0155 mg/L and 0.0225 mg/L respectively during the November 2008 sampling event. As reported in the *Evaluation of Background Metal Concentrations in Ohio Soils* (Cox-Colvin & Associates, Inc. 1996) and the *Closure Plan Review Guidance for RCRA Facilities* (OEPA 1999), several metals including arsenic and lead are naturally occurring in soils across Ohio and the United States. Arsenic and lead have been sporadically detected in groundwater collected from monitoring wells located throughout the Southwest Quad over the more than two decades of monitoring. There were not any reported detections of dissolved lead or arsenic in the point of compliance monitoring wells in the groundwater samples collected in July and November 2008.

Benzene was detected above the groundwater remedial objectives at a concentration of 0.13 mg/L in the sample collected from sentinel well MW-35 on November 19, 2008. Benzene was also reported at a similar concentration in the duplicate sample collected from this well. Confirmation groundwater sampling and assessment activities to evaluate the source of the dissolved phase benzene were conducted during the first and second quarter of 2009. These activities included installation of five additional groundwater monitoring wells (wells MW-138 through MW-142, as shown on Figure 2-5) during the first quarter 2009, collection of monthly groundwater samples from selected newly installed and existing monitoring wells, and resumption of hydraulic controls through groundwater extraction using production wells PROD_15 and PROD_24. Additionally, a letter work plan to assess the soil vapor profile beneath the structures in the Southwest Quad that are not underlain by a passive vapor barrier was submitted to the USEPA on May 8, 2009. It should be noted that none of the constituents of concern were reported above laboratory detection limits in groundwater samples collected from the point of compliance wells during the second half of 2008. The groundwater sample collected from point of compliance well MW-133 was reported with dissolved phase benzene concentrations above the remedial goal during the subsequent monitoring event during the first quarter 2009. These results will be presented in the next semiannual monitoring report.

2.2.2 PERIMETER, INTERIOR, AND SUPPLEMENTAL MONITORING

As discussed in the SCM presented in Section 1.0, the LNAPL and dissolve-phase petroleum hydrocarbons are thought to be laterally stable and degrading over time, although the dissolved phase benzene detections in well MW-35 has resulted in additional testing and evaluation in the Southwest Quad. Remaining LNAPL in the smear zone is gradually depleted through several mass loss mechanisms including dissolution into groundwater and subsequent dispersion and biodegradation, as well as volatilization and degradation within the vadose zone. As such, groundwater samples were collected from three groups of monitoring wells for evaluation of natural attenuation mechanisms within the saturated zone: perimeter, interior plume and supplemental monitoring wells.

- Perimeter groundwater monitoring wells include those wells situated at the margins of the smear zone but not considered to be compliance boundaries for dissolved phase petroleum hydrocarbons in the saturated zone. Monitoring wells that are included in this network include MW-26R, MW-33, MW-48S, MW-85S, MW-94S, MW-95S, MW-100S, MW-104S, and MW-115S.

- Interior plume monitoring wells are those wells located within the smear zone that will be tracked on a consistent basis over the course of the remedy and include ten wells: MW-10, MW-17, MW-18R, MW-20S, MW-22, MW-58S, MW-81S, MW-85D, MW-88, MW-93S, and MW-96S. A groundwater sample could not be collected from monitoring wells MW-20S, MW-58S, and MW-96S during the second semiannual monitoring event due to the presence of LNAPL within the well.

- Supplemental monitoring wells include additional wells that will be targeted for sampling to support MNA evaluation purposes. The supplemental well network may be modified based upon data gaps identified during previous monitoring events. Supplemental monitoring wells sampled during the second semiannual monitoring event in 2008 include wells L-1RR, L-3R, MW-21, MW-33, MW-51, MW-64, MW-80, and MW-99S.

Groundwater analytical results for the dissolved phase constituents of concern reported in samples collected from the perimeter, interior plume, and supplemental monitoring wells are provided on Table 2-2.

Groundwater samples were also collected from 12 monitoring wells for analysis of natural attenuation indicators during the second semiannual monitoring event including wells L-1RR, MW-18R, MW-33, MW-35, MW-38, MW-51, MW-81S, MW-85S, MW-100S, MW-112, MW-114, and MW-115S. Groundwater analytical results for the dissolved phase natural attenuation indicators are included on Table 2-3. It should be noted that the nitrite as nitrogen results reported for monitoring wells MW-93S and NW-21ID were rejected due to the samples exceeding the 48-hour hold time prior to analysis.

2.3 VERTICAL NESTED GROUNDWATER MONITORING WELLS

Between March 6 and April 2, 2008, vertically nested groundwater monitoring wells were constructed at the grouped media sample locations adjacent to MW-18R, MW-20S, MW-21, and MW-93S, in accordance with details presented in the RIP (Trihydro 2007b). These nested wells were installed with short screened intervals (generally two feet in length) to evaluate the dissolved-phase vertical profile and potential differences in the rate of intrinsic biodegradation across the saturated portions of the smear zone. The screened intervals in each nest were established at the approximate top of the groundwater table, the middle and bottom of the smear zone, and 10-15 feet below the smear zone. The vertical spacing of the screened intervals within each nested well is a function of the thickness of the smear zone. Lithologic logs, well construction details, and the Ohio Department of Natural Resources Well Logs and Drilling Reports (ODNR Form 7802.03) for the vertical nested groundwater monitoring wells are provided in Appendix E.

Intervals NW-18IS, NW-21IS, NW-21ID, and NW-21D were sampled in conjunction with monitoring wells MW-18R, MW-21, and MW-93S during the second semiannual monitoring event in December 2008. Several intervals including NW-18ID, NW-18D, NW-20ID, NW-93D were sampled in January 2009 per approval from the USEPA. Due to relatively low water table conditions during the second semiannual event for 2008, nested monitoring wells NW-18S, NW-20S, NW-20IS, NW-21S, NW-93S, and NW-93IS were dry. Monitoring well MW-20S and the deep interval in vertical nested well NW-20 could not be sampled due to the presence of LNAPL in these wells. Additionally, the intermediate-deep interval in nested well NW-93 could not be sampled as the screen had filled with silt.

Groundwater samples were analyzed for the constituents of concern and natural attenuation indicator parameters, as provided on Table 2-4a and 2-4b respectively. It should be noted that the nitrite as nitrogen results reported for monitoring wells MW-93S and NW-21ID were rejected due to the samples exceeding the 48-hour hold time prior to analysis. These two samples were collected on December 23, 2008 and may not have been delivered to the laboratory or subsequently analyzed on an expedited basis.

2.4 LYSIMETERS

Between September 22 and September 30, 2008, two soil moisture lysimeters were constructed at each grouped media location, in accordance with details presented in the RIP (Trihydro 2007b). The lysimeters will be used to measure the makeup of recharge water (particularly oxidizers) from infiltrating precipitation and evaluate the contribution to biodegradation within the upper limits of the saturated zone. A shallow and deep lysimeter were installed at each grouped media location, the first set at a depth above the smear zone and the second set at an average groundwater elevation within or near the upper smear zone limit. Placement of each lysimeter was a function of the elevation of the top of the smear zone.

Each lysimeter consists of a small ceramic receptacle (4-inch diameter by 18 inches tall) placed into a borehole to the target depth. The ceramic receptacle has two Teflon or nylon tubes extending to the ground surface, a pressure-vacuum access tube and a sample discharge tube. The ceramic cup wicks precipitation infiltrate from the vadose zone, which can subsequently be extracted by applying pressure to the receptacle.

2.4.1 LYSIMETER INSTALLATION

An 8-inch soil boring was installed to the target depth using a hollow stem auger drilling technique. After the borehole was completed, approximately two inches of No. 20 silica sand was emplaced at the total depth to encourage hydraulic communication between the porous ceramic receptacle and the native formation. The porous ceramic cup was then embedded in the sand. The remainder of the annular space around the body of the ceramic receptacle was backfilled with the No. 20 sand and deionized water was poured down the inside of the augers to flush and compact the sand around the receptacle. The remainder of the annular space in the borehole was backfilled with soil cuttings sifted through a 0.25-inch mesh screen to remove any coarse deposits. Each lysimeter was completed within a flush mounted well vault installed into a concrete pad no more than 1-foot in diameter to prevent impediment of precipitation into the subsurface. Lithology logs and construction diagrams for the completed lysimeters: L-18S, L-18D, L-20S, L-20D, L-21S, L-21D, L-93S and L-93D are included in Appendix F.

In accordance with the OMM Plan (Trihydro 2007a) the shallow and/or deep lysimeters will be sampled on a semiannual basis. If the deep lysimeter is below the water table, only the shallow lysimeter will be sampled. Infiltrating precipitation collected from the lysimeters will be analyzed for the constituents of concern and natural attenuation indicators starting with the first 2009 semiannual monitoring event.

2.5 ROST MONITORING

Three ROST monitoring transects (RT-1 through RT-3) are in place perpendicular to the leading edge of the LNAPL plume, as shown in Figure 2-5. ROST technology was identified as the preferred tool for monitoring the potential for LNAPL migration at the leading edge of the plume because it is designed to provide rapid real-time analysis of the physical and chemical characteristics of the distribution of petroleum hydrocarbons to distinguish between soils containing LNAPL and those outside of the smear zone.

The ROST monitoring transects consist of blank polyvinyl chloride (PVC) casing above the smear at three locations within each transect: an interior location (I) situated at the approximate lateral limit of the smear zone, an intermediate location (M) located 20-feet from the approximate lateral limit of the smear zone, and an outer location (O) installed 40-feet from the approximate lateral limit of the smear zone. ROST technology and installation methodology is presented in greater detail in the RIP (Trihydro 2007b).

Monitoring within the ROST monitoring wells was conducted between December 16 and 17, 2008. The tool was advanced from approximately 5 feet above the water table to approximately 5 feet below the water table in each of the wells. ROST monitoring results are provided in Appendix G. Data collected during the second half of 2008 indicate that the smear zone is stable. There was not an indication of the presence of LNAPL within any of the intermediate or outer ROST monitoring wells based on laser induced fluorescence measurements in the three transects.

2.6 SMEAR ZONE SOIL CORING

Soil cores were generally collected within the interior of the smear zone during November and December 2008 from the grouped media sampling locations 18, 20, and 21; adjacent to monitoring well MW-58; as well as 550-feet south of grouped media location 21, in the north tank farm. Soil cores from grouped media sampling location 93 are slated to be collected during the first quarter of 2009.

The smear zone coring was completed using a direct push drilling technique with soil collected within 2-inch acetate liners that were approximately 5-feet in length. Heterogeneity was accounted for by collecting four cores at each location. The first of the four cores was continuously logged from the ground surface to several feet below the bottom of the smear zone. The recovered soil within each core was visually described and logged in general accordance with the Unified Soil Classification System. An aliquot of soil from 5-foot sections of the recovered core was field screened for total organic vapors using a RAE Systems™ MiniRae® 2000 photoionization detector. The total organic vapor results were recorded on the lithologic logs included in Appendix H.

Based upon the lithologic log, the depth intervals for the top, middle, and bottom of the smear zone were established for the four soil cores at each location. The top of the smear zone was located within the unsaturated zone, the middle was established near the vadose-saturated zone interface, and the bottom of the smear zone was situated within the saturated zone. Samples were collected within the top, middle, and bottom of the smear zone intervals based upon observed petroleum hydrocarbons or elevated total organic vapor measurements. An approximate 18-inch long section of the acetate liner was cut and immediately capped at the selected interval within each portion of the smear zone. Soil cores were analyzed for selected volatile organic constituents, as well as total petroleum hydrocarbons. The laboratory analytical results are provided in Appendix I. Soil cores will be collected at the grouped media sampling locations and other selected locations within the smear zone every five years to evaluate changes in the smear zone composition and vertical LNAPL distribution.

2.7 RIVER MONITORING

River monitoring was conducted during the second semiannual monitoring period according to activities required prior to construction of the riverbank stabilization measures as outlined in the OMM Plan (Trihydro 2007b). Groundwater monitoring was conducted in three existing monitoring wells situated along the west bank of the Great Miami River: MW-26R, MW-48S, and MW-85S. These wells are monitored as part of the perimeter monitoring network and dissolved phase analytical results are provided on Table 2-2.

Surface water samples were not collected from locations immediately adjacent to each of these three groundwater monitoring wells during the second semiannual monitoring period due to the construction activities associated with construction of the partially penetrating sheet pile wall and riverbank stabilization measures. As discussed in Section 4.0, the barrier wall performance monitoring network was constructed in December 2008. Groundwater and surface water monitoring along the west bank of the Great Miami River was conducted using the barrier wall performance monitoring network during the first 2009 semiannual monitoring event and the results from that sampling will be reported with the first 2009 semiannual results report.

Observations for hydrocarbon sheening on the river surface were conducted on a weekly basis during the second half of 2008. Sheen observations are conducted at ten monitoring points established along the Great Miami River based on areas of concern identified during historic monitoring. Starting on August 11, sheen observation frequency increased to twice a week while the groundwater elevation as measured in well MW-20S was near the 464.8 amsl trigger level, as these are the conditions under which sheening has been observed in the past. Results of sheen observations at the Facility are presented in Table 2-5. A single sheen was noted on the surface water at Monitoring Point No. 10 on July 24, 2008. A slight sheen was also observed on the water’s edge at Monitoring Points No. 3 and No. 4 on August 22 and August 28, 2008.

LNAPL was not detected in any of the monitoring wells situated on the west bank of the river between July and December 2008. Therefore, the sheen observations reported at Monitoring Points No. 3, No. 4, and No. 10 did not trigger any additional response, as construction of corrective measures along the river bank was already underway.

2.8 VAPOR MONITORING

There were three soil vapor monitoring events conducted at the facility and Hooven during the second half of 2008. Soil vapor samples were collected from the nested monitoring wells located in Hooven (VW-93, VW-96, VW-99, and VW-127 through VW-130) between September 5 and September 11, 2008 and again between December 8 and December 14, 2008. Soil vapor samples were collected from the three nested monitoring wells on the facility between September 24 and September 25, 2008.

Table 2-6 provides a summary of soil vapor samples collected from the nested vapor monitoring wells since September 2005. During September 2008, soil vapor samples were collected from each of the intervals in the nested wells on-site and in Hooven with the exception of the 20 and 25-foot intervals in well VW-18, the 40-foot probe in nested well VW-20, and the 60-foot interval in vapor well VW-99, which were submerged beneath the water table; as well as the 50-foot probe in well VW-130, which was installed in the dolomite bedrock. During the December 2008 soil vapor monitoring event, samples were collected from each of the soil vapor probes in the nested wells in Hooven, with the exception of the 60-foot interval in well VW-93, as it was submerged beneath the water table; the 10-foot probe in well VW-99A, which is a redundant probe; and the 50-foot probe in well VW-130. Field forms for the vapor monitoring activities conducted in September and December 2008 are provided as Appendix J.

2.8.1 STATIC VACUUM/PRESSURE

Prior to initiating sampling activities, the static pressure or vacuum within the nested soil gas probes was assessed to determine whether there were any gradients that might induce soil gas flow. A summary of the static pressures or vacuums measured in the nested soil gas probes during the monitoring event conducted during the second half of 2008 is provided on Table 2-7. In general, the initial static pressure or vacuum measurements were between 0.00 and 0.20 inches of water, which is in the range that can be produced from wind and barometric pressure. The following anomalies were noted in the initial vacuum and pressure measurements during the September and December monitoring events:

- The 5-foot probes in nested monitoring wells VW-18 and VW-21 were reported with elevated vacuum measurements during the September monitoring events that may be attributed to soil moisture drainage around the screen or water within the tubing.
- There were elevated pressure readings in the 30, 35, and 45 through 60-foot probes in nested vapor well VW-93 during December 2008, ranging as high as 2.80 inches of water within the 55-foot interval.
- Vacuum was measured in each interval in nested well VW-96 with the exception of the 5 and 15-foot intervals during sampling in September 2008, with a maximum of 1.10 inches of water reported in the 30-foot probe.
- There was a slight pressure (0.30 inches of water) in the 50-foot interval in well VW-99 and a slight vacuum (0.34 and 0.31 inches of water) within the 15 and 30-foot intervals of nested vapor well VW-127 during the September monitoring event.

- There was a slight pressure (ranging from 0.30 to 0.50 inches of water) measured in the 25 and 30-foot intervals in nested well VW-96, the 50 and 60-foot intervals in well VW-99, as well as the 5-foot probe in nested vapor monitoring well VW-127 during the December 2008 monitoring event.
- A vacuum was reported in the 10-foot through 50-foot probes in nested well VW-127 during sampling performed in December 2008, with a maximum vacuum of 0.70 inches reported in the 15-foot interval.

The HSVE system was not operating during this timeframe and these residual vacuum and pressure measurements are likely associated with water table fluctuations and LNAPL redistribution within the smear zone unless otherwise noted.

2.8.2 SOIL GAS PERMEABILITY

Pneumatic testing was performed at each probe by measuring the differential pressure over increasing soil vapor extraction rates. The gas permeability of geologic materials around the nested soil gas probes was estimated using data collected through pneumatic testing and is included on Table 2-7. Soil gas permeability within the nested probes were primarily between 1E-7 to 1E-8 square centimeters (cm^2) with specific capacities (flow rate per unit of vacuum applied) ranging from 1.0 to 128 cubic centimeters per second per inch of water column (cm^3/sec•in H_2O), which are typical for medium grained sands. Soil gas permeability calculated in the 5 and 10-foot interval in soil vapor monitoring well VW-21, the 30-foot interval in well VW-127, and the 15-foot interval within nested well VW-128 were estimated at 1E-9 cm^2 with specific capacities between 0.1 and 2.0 cm^3/sec•in H_2O, which are representative of finer grained sands. Whereas, soil gas permeability in the 15-foot intervals in nested vapor monitoring wells VW-18, VW-20, and VW-21; the 25-foot interval within well VW-20; as well as the 5-foot interval in well VW-129 were estimated at 1E-6 cm^2 with a specific capacity between 38 and 238 cm^3/sec•in H_2O indicative of coarse sand and gravel deposits. The soil probes within nested vapor wells VW-18, VW-20, and VW-21 were developed prior to sampling in September 2008 by injecting distilled water and/or ultra high purity grade nitrogen through the probe to remove drilling fines from the screened interval, resulting in the increase in soil gas permeability measured during the September monitoring events.

2.8.3 VAPOR DIFFUSION COEFFICIENT

The vapor diffusion coefficient (VDC) is defined as the “ease” at which vapors can move through the vadose zone soils. Vapors are transported more easily through soils with a high VDC. Estimation of this parameter is important in estimating hydrocarbon mass loss rates in the vapor phase, as well as updating the site conceptual model over time.

A discussion on estimation of the VDC based on data collected during the second half of 2008 is presented herein. Further discussion on the use of the VDC will be presented in future semiannual monitoring reports.

There are two primary approaches for estimating the VDC of vadose zone soils. The first method involves mathematical approximation of the VDC based on the physical properties of the soil. One example of a mathematical solution for estimating the VDC is the Millington-Quirk (1960) equation, which relates the VDC to the soil porosity and moisture content. The second approach includes in-situ estimation of the VDC through tracer gas injection and recovery. A tracer test method was described by Johnson et al. (1998) using sulfur hexafluoride or helium as a tracer gas. This technique has previously been used to estimate the VDC beneath Hooven (Johnson 1997).

The VDC of selected intervals in nested wells VW-18, VW-20, VW-21, and VW-93 were estimated using a mathematical approximation and a tracer test methodology during the second half of 2008. The tracer method involves injection of 300 milliliters of ultra high purity grade helium into the vapor point with an airtight syringe followed by injection of a known volume of ambient air. The volume of ambient air injected into each vapor point is equal to the volume of ambient air present in the tubing between the ball valve at the top of the interval and the soil vapor probe at depth, such that the helium is displaced into the formation around the vapor probe. An instantaneous sample was collected by purging the same volume of ambient air and helium that was injected to the vapor point using the airtight syringe. After purging, approximately 300 milliliters of soil gas were sampled into a 1-liter Tedlar bag and the instantaneous helium concentration was measured. This helium concentration was recorded as the “time zero” concentration. The vapor probe and line were then flushed with 10-liters of ambient air. This procedure was subsequently repeated and helium concentrations recorded over two successive time intervals (approximately 20 and 60 minutes) following injection of the tracer gas. The change in helium concentration recorded over the three injection intervals (approximately 0, 20, and 60 minutes) during tracer testing can be used to estimate the VDC of the formation or fill material surrounding the soil vapor probe using the equations provided in Johnson et al. (1998) for a point source.

The VDC was also estimated using the Millington-Quirk (1960) equation. Soil cores were collected adjacent to each of the grouped media locations and samples were submitted for geophysical properties such as porosity and volumetric soil moisture from one foot intervals corresponding to the depth of the soil vapor probes within each nested vapor well. Soil core geophysical analytical results are provided in Appendix K. This ex-situ method is expected to be generally less reliable than in-situ tracer testing, as collection of soil cores tends to bias towards recovery of fine deposits such as silts, clays, and fine sands, whereas coarse gravels, pebbles and cobbles are not recoverable. Nonetheless, the mathematical approximation of the VDC is useful for comparison to estimates derived via tracer testing.

The VDC for the intervals in nested monitoring wells VW-18, VW-20, VW-21, and VW-93 estimated using the helium tracer method and Millington-Quirk equation are included on Table 2-7. The VDC values ranged from 3.26E-4 square centimeters per second (cm^2/s) within the 10-foot interval in VW-18 to 2.75E-2 cm^2/s in the 60-foot interval in VW-93, with an average VDC of 7.5E-3 cm^2/s using the helium tracer method. Whereas, the values estimated using the Millington-Quirk equation ranged from 3.29E-4 cm^2/s within the 30-foot interval in VW-93 to 5.85E-2 cm^2/s in the 10-foot interval in VW-21, with an average of 1.1E-2 cm^2/s. On average, the two methods for calculating the VDC compared reasonably well. For individual point estimates, there did not appear to be a correlation with depth as depicted on Figure 2-6. Overall, the Millington-Quirk estimates serve as supporting evidence that the VDCs estimated using the helium tracer test are reasonably accurate.

2.8.4 NESTED SOIL GAS ANALYTICAL RESULTS

A summary of the soil vapor analytical results for the deep nested monitoring wells is provided on Table 2-8. The target analytes have been divided into four classes on these tables including: (a) petroleum related constituents, (b) solvent related constituents, (c) water treatment related and other constituents, and (d) fixed gases. Soil vapor analytical results for samples collected on the facility and in Hooven during the September and December 2008 monitoring events are provided in Appendix L-1. The Tier 3 data validation reports for each event are included in Appendix L-2.

2.8.4.1 PETROLEUM RELATED CONSTITUENTS

Of the 22 constituents commonly found in gasoline that were included on the target analyte list, 17 were detected in soil gas samples collected from one or more of the nested monitoring wells in September 2008; 19 of the target constituents were detected in at least one sample collected from the nested wells sampled during December 2008. The highest measured concentrations in Hooven were reported in the 55-foot intervals in nested wells VW-99 and the 60-foot interval in nested well VW-96, consistent with previous sampling events. The concentration of petroleum related constituents reported in samples collected from wells VW-18, VW-20, and VW-21, situated on the facility, were generally one to two orders of magnitude greater than concentrations reported in samples collected from nested wells VW-96 and VW-99 in Hooven.

Concentrations of petroleum related constituents in the deep source probes were comparable between the September and December monitoring events; whereas concentrations in the remainder of the probes in nested vapor wells VW-96 and VW-99 increased by several orders of magnitude over this timeframe. With the exception of 2,2,4-trimethylpentane detected in vapor samples collected from nested well VW-96, there were not any other petroleum related constituents detected throughout the soil vapor profile in the nested wells situated in Hooven during the September or December 2008 monitoring events. Historic soil and vapor data collected from nested well VW-96 have indicated a secondary source of volatile petroleum hydrocarbon vapors between 20 and 25 ft-bgs. Assessment activities were conducted during the first 2009 semiannual monitoring event to evaluate potential impacts from secondary sources, including 1) the installation of several soil borings and collection of cores for laboratory analysis of volatile and semivolatile organic constituents at target intervals based on physical observations and total organic vapor measurements, 2) installation of ROST borings adjacent to vapor well VW-96, and 3) collection of soil vapor samples for field screening of fixed gases during three additional monitoring events. Results of these assessment activities will be provided in subsequent routine monitoring reports.

There were sporadic detections of petroleum related constituents in the samples collected from the remaining nested wells in Hooven including VW-93 and VW-127 through VW-130. It should be noted that vapor samples collected from the 5 and 10-foot intervals in nested well VW-127 during September 2008 were reported with elevated concentrations of benzene, cyclohexane, hexane, and heptane, indicative of a surface source. These chemicals were either not detected in subsequent depth intervals or were detected at concentrations several orders of magnitude below those observed in the 5 and 10-foot intervals. These chemicals were previously reported in the 5 and 10-foot samples collected from this well in April 2008 when a natural gas odor was detected during sampling. None of these constituents were reported in samples collected from the 5 and 10-foot probes in well VW-127 during sampling in December 2008.

2.8.4.2 SOLVENT RELATED CONSTITUENTS

Acetone, 2-butanone, and isopropanol were the most frequently detected solvent related constituents in the soil vapor samples collected from the nested wells in Hooven, with an overall frequency of detection in the primary samples of 72%, 62%, and 49% during the September monitoring event and 46%, 30%, and 3% during the December event. Acetone and isopropanol were also detected in the 5 and 10-foot probes in well VW-20 in September 2008. They were the only solvents detected in the soil vapor samples collected on Site. Acetone, 2-butanone, and isopropanol are considered common laboratory contaminants as they are used for cleaning and preparation of samples within the analytical laboratory.

Tetrachloroethene was reported in samples collected from 15 to 40 ft-bgs in nested well VW-99 in September 2008, as well as 30 to 50 ft-bgs in well VW-127 during the September and December monitoring events. Additionally, 1,1,1-trichloroethene and carbon tetrachloride were reported in the intermediate and deeper samples (greater than 10 ft-bgs) collected from monitoring well VW-129, situated outside of the smear zone and dissolved phase impacts, in September 2008. None of the solvent constituents were measured continuously from the deepest intervals to the shallow soil vapor probes within any of the nested wells during monitoring conducted in September and December 2008.

2.8.4.3 WATER TREATMENT RELATED AND OTHER CONSTITUENTS

Nine of the 22 water treatment related and other chemicals were detected during the September and December monitoring events in the soil vapor samples collected in Hooven. Constituents detected included, from most to least frequently detected: dichlorodifluoromethane; ethanol; carbon disulfide; trichlorofluoromethane; chloroform; chloromethane; chloroethane; 1,2-dichlorobenzene; and 1,2,4-trichlorobenzene. The frequency of detection of these constituents during the December event (1.6%) was nearly half of that reported during the September monitoring event (3.5%). None of the 22 water treatment related or other constituents were reported in any of the samples collected from the nested monitoring wells on the facility in September 2008.

During the September event, dichlorodifluoromethane and trichlorofluoromethane were reported in the soil gas samples collected from each of the intervals in nested wells VW-129 and during the December event dichlorodifluoromethane was reported in soil vapor samples collected from the 5, 20, 30, and 40-foot intervals in nested well VW-130. Nested wells VW-129 and VW-130 are located in the central and western portions of Hooven outside of the distribution of LNAPL and dissolved phase constituents associated with the refinery, suggestive of a secondary source for these two constituents.

2.8.4.4 FIXED GASES

Fixed gas concentrations including O_2, CO_2, and CH_4 were measured during purging of the nested probes to determine that steady state conditions had been achieved prior to the collection of the soil gas sample for laboratory analysis and as a quality assurance/quality control measure of the analytical results. Field screening results indicated that the fixed gas measurements were generally stable prior to collecting samples from the nested soil vapor wells. The fixed gas measurements are included on the field forms provided in Appendix J.

The O_2 and CO_2 analytical results for the soil gas samples are summarized on Table 2-8d. The O_2 and CO_2 concentrations recorded in the field can be compared to the fixed gas results provided by the laboratory as a measure to validate the field results. Correlation plots showing the field reported O_2 and CO_2 concentrations and the laboratory analytical data for samples collected from the nested wells in September and December 2008 are provided as Figure 2-7 and 2-8, respectively. During the September event, CO_2 concentrations reported in the field were generally comparable to the laboratory reported results with few outliers; however there appeared to be an increasing low bias for O_2 concentrations measured in the field, with lower O_2 concentrations. During the December monitoring event, concentrations of CO_2 reported using field instruments appear to be biased slightly high with an increasing bias as concentrations of CO_2 increase. The O_2 results reported in the field show the inverse of this during sampling in December 2008, with a low bias compared to the laboratory results which appears to increase with lower O_2 concentrations.

The fixed gas results from the deep nested soil vapor wells situated within the distribution of the LNAPL and dissolved phase petroleum hydrocarbons on the facility and Hooven generally show decreasing $O_{2,}$ increasing CO_2, and increasing CH_4 with depth, indicative of aerobic and anaerobic degradation of petroleum hydrocarbon vapors in the unsaturated zone. In areas outside the plume, the O_2 and CO_2 concentrations were generally consistent throughout the vadose zone, and CH_4 was not detected in soil gas.

During monitoring in September 2008, CH_4 was detected in each of the intervals in nested wells VW-18 and VW-21, as well as the deep intervals in nested wells VW-20, VW-96, and VW-99. Additionally, methane was elevated in the 5 and 10-foot samples collected from nested well VW-127. A natural gas odor was detected near this nested vapor monitoring well during sampling and elevated concentrations of several petroleum related constituents were reported in the soil gas samples collected from these two probes as previously described herein.

Methane was not measured in samples collected from the 5 and 10-foot probes in well VW-127 during December 2008. However, methane was reported from the deep intervals in nested well VW-96 up to the 5-foot probe. Methane was also reported in the deep and intermediate intervals in nested well VW-99 during sampling in December 2008, but not within the shallow intervals. As previously described, secondary sources of volatile petroleum hydrocarbons are suspected near vapor well VW-96, and additional assessment activities are being conducted near this well.

2.8.5 OUTDOOR AIR ANALYTICAL RESULTS

A single “floating” outdoor air canister was collected each day soil vapor samples were collected in September 2008 with the exception of September 11, as sampling activities only spanned a few hours this day and an insufficient volume of ambient air would have been collected over this short time frame for laboratory analysis. This “floating” sample remained secured outdoors and the Summa canister was open, collecting a sample, while the team was engaged in soil vapor monitoring activities. The Summa canister was shut, and not collecting a sample, during transport or when sampling activities were not being conducted.

Two outdoor ambient air samples were collected each day when soil vapor monitoring was conducted during December 2008, with the exception of December 14, as sampling activities were only conducted during the morning. One sample was collected at a fixed location in the center of Hooven and the second “floating” ambient air sample was placed in the care of the sample team each day.

The ambient air samples were collected using a 6-liter Summa canister suspended approximately five feet above the ground surface using a flow-controller calibrated to collect the sample over an eight hour period. Outdoor air analytical results are summarized on Table 2-9. Both petroleum and non-petroleum related constituents were detected at low concentrations in the outdoor air samples. Benzene, toluene, and isopropanol were detected in more than half the samples. Acetone, 2-butanone chloromethane, dichlorodifluoromethane, ethanol, and trichlorofluoromethane were detected in every sample.

The outdoor air constituent concentrations reported for the September and December 2008 monitoring events were compared to the 50th percentile values from the *Summary of Indoor and Outdoor Levels of Volatile Organic Compounds from Fuel Oil Heated Homes in New York State* (NYDOH 2005). These average outdoor air concentrations are included on Table 2-9. The reported results for the outdoor air samples were generally within the range of the average ambient air data with the exception of concentrations of acetone, chloromethane, dichlorodifluoromethane, and trichlorofluoromethane, which were detected at concentrations an order of magnitude greater than the published average outdoor air concentrations. These four compounds are not petroleum related constituents. In addition, several petroleum and non-petroleum related constituents were detected above the average ambient air values presented on Table 2-9 within the “floating” outdoor air sample collected on September 5, 2008. The reported concentrations are indicative of a secondary, ambient source of impacts in outdoor air during sampling on this day.

2.8.6 METEOROLOGICAL DATA

Appendix M presents hourly meteorological data collected from the weather station located at the scale house on the facility during September and December 2008. During September 2008, ambient temperatures oscillated daily, ranging from 49.9 to 94.8 degrees Fahrenheit (ºF). There was 1.86 inches of precipitation recorded during September with only a slight variation in barometric pressure (29.5 to 30.4 inches of mercury). The wind direction was variable with a maximum speed of 37 miles per hour (mph) and an average of 1.3 mph.

In contrast, during December 2008, temperatures ranged between 4.8 and 70.3ºF, with a total of 4.92 inches of precipitation measured over the month. Barometric pressures were comparable to those measured in September, ranging from 29.3 to 30.6 inches of mercury. The wind direction was variable with a maximum speed of 22 mph and an average of 4.9 mph.

3.0 INTERPRETATION

Data collected during the second half of 2008 and included herein demonstrate that the intrinsic processes in the saturated and unsaturated zones are degrading petroleum hydrocarbons in the smear zone. These same processes are reducing dissolved and vapor phase petroleum hydrocarbons to levels that are protective of sensitive receptors at the point of compliance boundaries in Hooven and the Southwest Quadrant. In general, natural attenuation occurs as constituents present in smear zone partition to groundwater and soil vapor, where they are biodegraded via aerobic and anaerobic processes. There are two general lines of evidence provided herein to support the efficacy of natural attenuation processes to degrade petroleum hydrocarbons at a rate that will achieve remedial goals for groundwater (i.e. maximum contaminant levels) in a timeframe comparable to active remedial measures. The primary lines of evidence demonstrate the stability of petroleum hydrocarbons in the smear zone beneath the Site and protectiveness of sensitive receptors (Section 3.1); as well as meaningful trends of decreasing constituent concentrations over time (Section 3.2). The secondary lines of evidence, discussed in Section 3.3, includes evaluation of hydrogeochemical data that demonstrate indirectly the natural attenuation mechanisms are acting to transform hydrocarbon constituents, reduce concentrations, and inhibit mobility of the LNAPL, dissolved phase, and vapor phase impacts. Baseline qualitative and quantitative lines of evidence were discussed in the *First 2008 Semiannual Monitoring Report, Chevron Cincinnati Facility, Hooven, Ohio* (Trihydro 2009). Updates to these lines of evidence for which data was collected during the second half of 2008 are included herein.

3.1 PLUME STABILITY AND PROTECTIVENESS OF SENSITIVE RECEPTORS

During execution of the final groundwater remedy at the Site, Chevron must continue to demonstrate that the LNAPL and dissolved phase plumes are stable and that sensitive receptors remain protected (USEPA 1999). If the extent of the LNAPL, dissolved, or vapor phase petroleum hydrocarbons are determined to be mobile or impacting sensitive receptors above risk based limits, contingency measures would be employed as outlined in the OMM Plan (Trihydro 2007a). In response to the dissolved phase benzene detections in the sentinel monitoring well MW-35 in November 2008, as well as subsequent monitoring results collected in January 2009 in the Southwest Quad, groundwater containment was resumed using production wells PROD_15 and PROD_24. Approximately 1,725,000 gallons of groundwater have been pumped each day from these two wells since March 29, 2009, with the majority recovered from well PROD_15 (approximately 900 gallons per minute). Pumping was temporarily discontinued between May 1 and May 5, 2009 as the main electric breaker at the biological treatment system was replaced, and again between May 7 and May 9, 2009 as repairs were required in the treatment system reactor. Hydraulic containment of groundwater down-gradient of the facility has been confirmed on a weekly basis since pumping resumed. In addition, monthly groundwater samples have been collected from selected monitoring wells in the Southwest Quad to track the performance of hydraulic containment on the dissolved phase benzene concentrations. Subsequent reports will provide the fluid level and groundwater analytical results for monitoring conducted during the first and second 2009 semiannual monitoring events. Per requirements in the 2006 Order, Chevron will also submit a work plan by October 1, 2009 describing the results of assessment activities and contingency measures to remediate dissolved phase benzene concentrations, if the source is determined to be the smear zone associated with historic releases from the former refinery.

3.1.1 LNAPL

As discussed in the *Update to Site Conceptual Model and Summary of Remedial Decision Basis* (Chevron Cincinnati Groundwater Task Force 2005) and outlined within the *First 2008 Semiannual Monitoring Report, Chevron Cincinnati Facility, Hooven, Ohio* (Trihydro 2009), LNAPL within the smear zone is stable. This determination was made based on (1) the age of the release; (2) a decrease in LNAPL gradients, transmissivity, and saturations due to natural degradation and engineered recovery; (3) morphology of the smear zone with a “thicker” core which thins at the lateral edges; (4) there having been no expansion of LNAPL beyond the originally defined limits of the smear zone; and (5) preferential depletion of petroleum related constituents within the LNAPL at the soil gas and groundwater interface (otherwise referred to as outside-in weathering of the plume).

Data collected during the second half of 2008 continue to support that the smear zone is stable. The LNAPL plume has not expanded at the down-gradient limits based on the laser induced fluorescence measurements in the three ROST monitoring transects conducted on December 16 and 17, 2008. Additionally, LNAPL was not measured in any of the sentinel or point of compliance monitoring wells installed in the southwest quadrant or in any of the wells located beyond the smear zone extent in Hooven during gauging events conducted in July, September, and November 2008. Fluid level gauging within the performance monitoring network installed along the west bank of the Great Miami River began during the first quarter 2009 to confirm the stability of the smear zone along the restored river bank.

Historical petrophysical tests on soil cores collected in the saturated portions of the smear zone indicate two-phase (water-oil) LNAPL residual saturation ranges from about 18 to 25% for the Site. Data collected from the facility show an exponential decrease in the ability of LNAPL to migrate at saturations below 20 to 25%. Field testing completed in the late 1990s indicates that the two-phase LNAPL saturations in the majority of the plume were below residual values (i.e., immobilized). Additional smear zone coring conducted in November 2008 were used along with estimates of soil bulk density, LNAPL density, and soil porosity to estimate the LNAPL saturations in the upper, middle, and lower portions of the smear zone across the Facility and Hooven. Average saturations in the upper portion of the smear zone were between 0.2% and 2.3%, in the middle of the smear zone ranged from 0.3% to 3.4%, and within the lower portions of the smear zone were between 0.9% and 6.1%. These saturations are below the residual values and the plume is considered immobile.

3.1.2 DISSOLVED PHASE

None of the dissolved phase constituents of concern were detected above risk based limits within the point of compliance groundwater monitoring wells during the second 2008 semiannual monitoring event. As previously described in Section 2.2.1, benzene was detected in the groundwater sample collected from sentinel well MW-35 at a concentration of 0.13 mg/L in November 2008. It is not currently known whether there is a secondary source of the dissolved phase benzene in this portion of the Southwest Quad. If the source of the benzene in the sentinel well was the smear zone associated with releases from the former refinery, it is expected that other petroleum related constituents would have been measured in the groundwater samples collected in November 2008 and that similar concentrations of benzene would have been detected in the samples collected from the other sentinel and monitoring wells situated beyond the down-gradient limits of the smear zone. Instead, dissolved phase benzene appears to be isolated to this one location. Additionally, the ROST results were similar between April and December 2008, indicating that the smear zone was stable.

While these benzene detections may represent re-equilibration of the dissolved phase halo subsequent to two decades of hydraulic containment, they may also be related to potential alternate sources of contaminants in the area around the well. Overall, it is not thought to indicate significant dissolved phase plume mobility. Confirmation groundwater sampling and assessment activities to evaluate the source of the dissolved phase benzene were conducted during the first half of 2009 and will be provided in subsequent semiannual reports.

The dissolved phase concentrations will also be monitored using the performance monitoring network installed along the stabilized bank of the Great Miami River (described in Section 4.6) beginning in the first quarter 2009. Hyporheic and surface water quality results will be compared to Ohio surface water quality standards to ensure that sensitive ecological receptors are protected within the Great Miami River.

3.1.3 VAPOR PHASE

In order to evaluate protectiveness of human health from migration of deep soil vapors into structures located in Hooven, the data from the nested wells is compared to the conservative risk based screening standards. Screening standards are concentrations that are sufficiently low that any results below these can safely be considered to pose no significant risk. Screening standards are developed with consideration for uncertainty, and are designed to be overly protective; therefore, concentrations above the screening levels do not necessarily pose an unacceptable risk.

Table 3-1a through 3-1c provide the screening level evaluation for the deep soil gas samples for gasoline related, solvent related, and water treatment related and other constituents, respectively. The residential air screening values (assuming a risk of 1E-5 for carcinogenic constituents and a Hazard Quotient of 1 for non-carcinogenic constituents) provided on the USEPA Regional Screening Level tables (2009) were used with the semi-site specific attenuation factors from Figure 3a of the OSWER Draft VI Guidance (USEPA 2002) to determine if any of the constituents identified in the deep soil vapor monitoring points posed a potential risk to human health. Attenuation factors provided on Figure 3a are based on statistical comparison of concentration ratios for non-biodegradable or recalcitrant chlorinated hydrocarbon compounds measured in subsurface soil vapor and indoor air. The resultant attenuation factors (concentration of constituent in indoor air compared to the concentration in soil vapor) are used as a screening step to identify where vapor intrusion may be possible based on the presence of contaminants of concern in soil gas. Application of these screening attenuation factors are extremely conservative for this evaluation, since they do not account for attenuation due to aerobic biodegradation, which is the chief mechanism limiting vapor transport beneath the Site.

The screening level evaluation was applied to the deep soil vapor samples collected from 20 ft-bgs or greater. The data collected from the shallow probes was not evaluated because vapor concentrations at depths less than 20 ft-bgs have been shown to be indistinguishable between locations over hydrocarbons from the former refinery and locations that were outside of the area of groundwater and LNAPL impacts. Based on Figure 3a of the OSWER Draft VI Guidance, an attenuation factor of 0.002 was applied to samples collected from depths of 20 ft-bgs, 0.001 was used to screen soil vapor data from greater than 20 ft-bgs to 35 ft-bgs, and an attenuation factor of 0.0007 was used to screen data greater than 35 ft-bgs. Note that the attenuation factors shown on Figure 3a of the OSWER Draft VI Guidance correspond to the depth below the foundation. For this evaluation the depth of the basement was conservatively assumed to be 5 ft-bgs; therefore, a sample depth of 20 ft-bgs corresponds to a depth of 15 feet as shown on Figure 3a.

The soil vapor samples collected from the 60-foot interval from nested well VW-96 during September and December 2008 and the 60-foot interval from well VW-99 in December 2008 were reported with several petroleum related constituents (benzene; ethylbenzene; hexane; 1,2,4-trimethylbenzene; and 1,3,5-trimethylbenzene) above the screening levels for residential air. The remainder of the reported results in the soil vapor samples collected from the 20 to 60 ft-bgs intervals in Hooven were below the screening standards during the September and December 2008 monitoring events. The reporting limits for several other petroleum and non-petroleum related constituents including allyl chloride; benzyl chloride; bromodichloromethane; 1,3-butadiene; carbon tetrachloride; chloroform; dibromochloromethane; 1,2-dichloroethane; 1,2-dibromomethane; 1,4-dichlorobenzene; 1,2-dichloropropane; 1,4-dioxane; hexachlorobutadiene; naphthalene; tetrachloroethene; 1,1,2,2-tetrachloroethane; 1,2,4-trichlorobenzene; 1,1,2-trichloroethane; and vinyl chloride were occasionally reported above the screening levels in samples collected from nested wells VW-96 and VW-99 during September and December 2008. None of the constituents were detected above the screening standards from the source at depth to the 20-foot interval in any of the vapor wells installed in Hooven indicating that the vapor intrusion pathway is incomplete. This is consistent with the results reported within the *2005 HHRA* (Trihydro and GeoSyntec 2005) and the *10-Year Soil Vapor Retrospective Report* (Trihydro and GeoSyntec 2008).

Benzene; ethylbenzene; hexane; 1,2,4-trimethylbenzene; and 1,3,5-trimethylbenzene were also reported in several of the soil gas samples collected from nested wells VW-20 and VW-21 above their respective screening values. Benzene was the only constituent measured in each of the probes installed from the source at depth to the 20-foot probe in nested wells VW-20 and VW-21 at concentrations exceeding the screening standards for a residential scenario. The reporting limits for several constituents found in gasoline, solvent, and water treatment chemicals were measured above the residential screening standards. Nested vapor well VW-21 was installed in the north tank farm on the former refinery property, where there are not any structures. Nested vapor well VW-20 is situated near the facility’s office and maintenance buildings. There are currently preventative measures in place to mitigate vapor intrusion into the occupied structures. In addition, this portion of the facility is currently used for industrial purposes and is slated to be used for commercial and industrial purposes in the future following implementation of engineered and institutional controls.

3.2 CONSTITUENT TRENDS

It is expected that the data collected over the course of the remedy will show a meaningful trend of decreasing hydrocarbon mass and/or constituent concentrations over time. Analyses that may be used in evaluating the progress of the long term remedy in meeting remedial goals (i.e., MCLs in groundwater) include evaluation of temporal trends in contaminant concentrations, LNAPL mass, or LNAPL saturations; comparisons of observed contaminant distributions with predictions; as well as comparison of calculated attenuation rates with those necessary to meet remedial goals within the required time frame. These analyses can be complicated as a result of variation in the petroleum hydrocarbon distribution across the site, temporal fluctuations related to seasonal and longer term trends, heterogeneity in the vadose and saturated zones across the plume footprint, along with measurement variability. These complications necessitate the use of multiple lines of evidence and expanded monitoring networks to reduce uncertainty.

3.2.1 LNAPL AND SOIL CORE CONSTITUENT TRENDS

Figure 3-1 shows the mole fraction of benzene in LNAPL samples collected in 1997, 1999, and 2005 from four sets of wells (MW-1R/PROD_20, MW-58/PROD_12, PROD_15, and MW-96S) on a logarithmic-linear scale. This figure also shows the decline in the average mole fraction of benzene for all the LNAPL samples collected over this timeframe. The trends presented on this figure depict a first order degradation rate for benzene in the LNAPL since 1997.

As the LNAPL saturation and transmissivity continue to decrease across the smear zone over time, it may become infeasible to collect LNAPL samples for laboratory analysis. As a result, smear zone soil coring will be conducted to provide a means of measuring LNAPL composition. As described in Section 2.6, soil coring was conducted in November and December 2008. The mole fraction of volatile organic constituents of concern, including benzene, within the LNAPL were calculated using the soil core analytical results. To complete these calculations using the soil cores instead of LNAPL samples, two main assumptions must be made:

1. The majority of organic matter measured in the smear zone soil is present in the form of LNAPL. Therefore, both the laboratory results for individual constituents of concern and the total petroleum hydrocarbon ranges are representative of LNAPL.
2. The total petroleum hydrocarbon results used to estimate the molecular weight of the LNAPL within the soil core are comprised of 100% aliphatic compounds. This is a conservative assumption because this will tend to provide a lower estimate of the molecular weight of the LNAPL and therefore a higher estimate of the mole fraction results.

The estimated mole fraction of benzene, toluene, ethylbenzene, and total xylenes in smear zone LNAPL calculated using soil cores collected from the group media locations on the facility are summarized on Figure 3-2. The data are averaged for the four cores collected at each location, with error bars denoting one standard deviation. This data can be used to infer the dominant attenuation mechanisms at each sampling location. For instance, the benzene mole fraction estimated using cores collected at smear zone locations SZ-20 and SZ-21 are lower at the top and middle of the smear zone in comparison to the bottom. This suggests that volatilization may be the dominant process for benzene depletion at these locations. Whereas, at smear zone location SZ-18 similar benzene mole fractions were observed in the top, middle, and bottom of the smear zone, which suggests that benzene attenuation rates within the dissolved and vapor phase are similar.

Figure 3-2 also depicts the total petroleum hydrocarbon concentrations measured in the upper, middle, and bottom of the smear zone at the group media locations on the former refinery. Total petroleum hydrocarbons are significantly higher at the base of the smear zone. It is estimated that more than 80% of the mass loss by natural attenuation mechanisms occurs within the vadose zone, preferentially degrading petroleum hydrocarbons within the upper portions of the smear zone. This follows from the large flux plane (i.e., the top of the smear zone) for vapor, where there is a large contact area between the smear zone and the vadose zone. The attenuation attributable to groundwater is a secondary mechanism. This groundwater dissolution and subsequent biodegradation is rate limited as electron acceptors are rapidly depleted from up-gradient groundwater and precipitation.

Benzene mole fractions estimated within the soil cores collected in November and December 2008 were compared to the mole fraction benzene in LNAPL shown on Figure 3-1. There was general agreement between benzene mole fractions reported in the LNAPL samples collected in 2005 and smear zone soil cores collected in 2008, with slightly higher concentrations estimated in the soil cores. This is likely a function of the conservative assumptions used in calculating mole fraction benzene in LNAPL from the soil core samples. Soil core and LNAPL samples will be collected on approximate five year cycles over the course of the remedy to measure changes in the LNAPL composition and depletion of benzene from the smear zone.

3.2.2 DISSOLVED PHASE CONSTITUENT TRENDS

The distribution of selected dissolved phase benzene, toluene, ethylbenzene, and total xylenes in groundwater as well as total petroleum hydrocarbons concentrations for samples collected during the second 2008 semiannual monitoring event are displayed on Figure 3-3. It is useful to evaluate the dissolved phase constituent trends in two ways. First, dissolved phase constituent trends within individual groundwater monitoring wells can be used to assess spatial variability in engineered mass removal and intrinsic biodegradation processes across the smear zone footprint and identify areas that are not behaving as predicted. Second, groundwater quality trends can be averaged within areas of the smear zone (i.e., up-gradient, interior, down-gradient) to assess overall trends in natural attenuation processes. For discussion purposes, there are two areas up-gradient of the smear zone, one to the north of the facility property and the second to the west along the Buried Valley Aquifer-bedrock interface in Hooven.

3.2.2.1 TRENDS WITHIN INDIVIDUAL MONITORING WELLS

While useful for inferring source zone depletion of individual constituents, temporal trends observed in the dissolved constituent concentrations collected from individual wells can also be essential indicators of plume stability and progress toward meeting remedial goals. In the absence of remedial efforts, (i.e. HSVE system operation), decreasing dissolved phase concentrations over time within the plume area indicate that natural attenuation processes are acting to reduce contaminant mass and concentrations. Trend analyses should be conducted in monitoring locations situated throughout the distribution of petroleum hydrocarbons to assess the range of dominant intrinsic processes acting on the plume. Temporal trends in individual wells may also indicate changes in climatic, hydrogeochemical, contaminant release, site reuse, or other conditions unrelated to attenuation processes and need to be evaluated in the context of other lines of evidence.

Historically, groundwater samples have not been collected from the interior plume monitoring wells due to the presence of LNAPL during sampling. For the purpose of this analysis, trends are inferred for wells that have groundwater data from at least three monitoring events spanning three separate years. Of the ten interior plume wells, seven (MW-10R, MW-18R, MW-20S, MW-22, MW-58S, MW-88, and MW-96S) do not have data that meet these criteria. Constituent of concern concentrations reported in the samples collected from interior monitoring well MW-85D were all reported below the remedial goals, which is expected as this well is screened in the deeper portions of the Buried Valley Aquifer, well below the vertical distribution of dissolved phase petroleum hydrocarbons. Dissolved phase trends for the two remaining interior plume monitoring wells (MW-17 and MW-81S) are provided on Figure 3-4 and Figure 3-5. Monitoring well MW-17 is located in the interior of the smear zone and dissolved phase benzene concentrations continue to be measured at concentrations above remedial goals. There is a slight decreasing trend in benzene concentrations over time. This decreasing trend will become more pronounced over time as the smear zone up-gradient of MW-17 becomes depleted and attenuation continues from the “outside-in.” Monitoring well MW-81S is situated in the southwest limit of Hooven adjacent to State Route 128. Dissolved phase constituent concentrations in this well show a clear decreasing trend between 1996 and 2008. This trend is likely associated with startup of the groundwater production, LNAPL recovery, and HSVE systems between 1999 and 2000, focused on remediation of petroleum hydrocarbons beneath Hooven. There was a slight rebound in dissolved phase benzene concentrations observed in samples collected in December 2008 that may be related to discontinuance of pumping and shutdown of the HSVE system for more than a year.

Similar to data limitations observed with trend analyses using the interior plume monitoring wells, of the eight supplemental groundwater monitoring wells (L-1RR, L-3R, MW-21, MW-33, MW-51, MW-64, MW-80, and MW-99) only wells MW-21, MW-33, MW-64, and MW-99 had sufficient data (i.e., results from at least three monitoring events spanning more than three years) to complete a trend analysis. The dissolved phase results for the constituents of concern reported in samples collected from well MW-33 have remained below MCLs over time. As presented on Figure 3-6, dissolved phase benzene concentrations reported in supplemental monitoring well MW-21 showed a first order degradation rate over time. This well is situated outside the footprint of remedial measures at the facility and these decreasing trends are indicative of natural attenuation processes. The dissolved phase benzene concentrations reported in samples collected from monitoring wells MW-64 (Figure 3-7) and MW-99 (Figure 3-8) also show a decreasing trends over time. These two monitoring wells are located on the eastern and western edge of the smear zone, respectively, and demonstrate preferential depletion of benzene along the smear zone margins.

Temporal analysis of the dissolved phase results can be performed for three additional monitoring wells (MW- 85S, MW-93S, and MW-115S) located within the distribution of hydrocarbons at the facility, as these wells have a sufficient monitoring history with concentrations above remedial goals. Figures 3-9 through 3-11, show decreasing trends in dissolved phase benzene concentrations over time in these three monitoring wells. Monitoring wells MW-85S and MW-115S are located outside the influence of historic remedial efforts along the Great Miami River and in the southwest quadrant, respectively. Trends within these two wells are considered indicative of natural attenuation processes. Well MW-93S is located in Hooven and the trends observed in the groundwater analytical results from this well most likely have been influenced by hydraulic and vapor recovery efforts since 1999.

The average first order degradation rate estimated using the dissolved phase analytical results from six monitoring wells (MW-21, MW-81S, MW- 85S, MW-93S, and MW-115S) is approximately 7.0×10^{-4} per day. This compares well with previously estimated first order decay rates for the benzene mole fraction in LNAPL. The average estimated first order decay rate for benzene in LNAPL, based on LNAPL and smear zone soil samples collected between 1997 and 2008, is 5.3×10^{-4} per day.

As additional dissolved phase data is collected, it will be possible to make meaningful decisions regarding the temporal trends across the distribution of hydrocarbons. Attenuation rates will be compared over time within individual wells installed across the plume and progress towards meeting the remedial goals will be further considered.

3.2.2.2 AVERAGE TRENDS ACROSS SMEAR ZONE

Table 3-2 provides the average dissolved phase constituent concentrations measured in the up-gradient, interior, and down-gradient portions of the smear zone during the second half of 2008. The average dissolved phase constituent and total petroleum hydrocarbon concentrations are indicative of ongoing natural attenuation processes, with preferential LNAPL depletion at the smear zone boundaries. The average dissolved phase benzene concentration was 0.01 mg/L in samples collected from the monitoring wells located in the two up-gradient areas while the average concentration of dissolved phase benzene within the smear zone was 1.30 mg/L. Down-gradient of the smear zone, the average benzene concentration was 0.019 mg/L. This indicates that attenuation processes such as dispersion, sorption, and biodegradation reduce the dissolved phase concentration, reduce mobility of the plume, and/or transform constituents of concern as the plume exits the smear zone.

The average dissolved phase benzene concentration trends for selected monitoring wells located in the up-gradient (MW-21 and MW-22), interior (L-1RR, L-3R, MW-17, and MW-18R), and down-gradient (MW-48S, MW-94S, and MW-115S) portions of the smear zone are presented on Figure 3-12. Dissolved phase concentrations depicted were reported during the Fall 2002, Fall 2004, and Fall 2008 monitoring events and are averaged for the up-gradient, interior, and down-gradient wells. Irrespective of the well locations, there is a decreasing trend in the dissolved phase benzene concentration reported between 2002 and 2008, indicative of benzene depletion from the smear zone. These decreasing trends are more pronounced at the margins of the smear zone compared to the interior portion of the plume. At its margins, the smear zone is thinner and LNAPL saturations are lower. In addition, as reported on Table 3-2, groundwater enriched in electron acceptors intercepts the smear zone north of the facility and again to the southeast of the Buried Valley Aquifer-bedrock interface in Hooven creating a situation whereby petroleum hydrocarbons including benzene are attenuated more quickly along the margins than the interior of the smear zone. These observations are consistent with the expectation of outside-in attenuation of petroleum hydrocarbons within the smear zone.

As the up-gradient portion of the smear zone is depleted of petroleum hydrocarbons, the benzene removal rates from the interior portion of the smear zone will increase as “outside-in” weathering continues. It is anticipated that the dissolved phase benzene concentrations reported in monitoring wells L-1RR and MW-17 will show trends similar to those currently observed in wells MW-21 and MW-22. This may then be followed by a similar transition in the dissolved phase benzene trends observed in monitoring wells L-3R and MW-18R. Over time, it is expected that benzene concentrations in groundwater will continue to decrease across the smear zone, eventually approaching remedial goals (i.e., USEPA MCL).

3.2.3 VAPOR PHASE CONSTITUENT TRENDS

As with temporal analysis of the dissolved constituents of concern, soil vapor results from samples collected above the LNAPL plume (i.e., vapor source) should be considered as a line of evidence to demonstrate the effectiveness of natural attenuation mechanisms to degrade the smear zone over time. Vapor source trend analyses will be conducted using data collected from soil vapor monitoring wells installed across the distribution of petroleum hydrocarbons to assess the rate of attenuation in various portions of the plume. The trends observed in the vapor source should be evaluated in the context of the other lines of evidence to identify secondary causes of variation such as seasonal fluid level fluctuations or longer term cyclical events such as droughts.

For the purpose of this analysis, trends are inferred for wells that have source vapor data for at least three monitoring events over at least three years. Monitoring wells VW-93, VW-96, and VW-99 have a sufficient monitoring history to complete temporal analyses and are located over the smear zone. Figures 3-12 through 3-14 show the concentration of benzene and total petroleum hydrocarbons reported in the vapor source in nested wells VW-93, VW-96, and VW-99 over the past decade. A first order degradation rate is observed in the vapor source concentration since 1997, with a two to five order of magnitude decrease in benzene and total petroleum hydrocarbon concentrations. This rapid decrease in concentrations is attributable primarily to startup of groundwater, LNAPL, and soil vapor recovery systems in Hooven between 1999 and 2000.

3.3 GEOCHEMICAL INDICATORS OF NATURAL ATTENUATION

Characterization of geochemical variations in the vadose and saturated zones provides evidence of the types of biodegradation processes that are thought to be attenuating petroleum hydrocarbons in the smear zone. Many of the processes attenuating hydrocarbons in the smear zone cannot be measured directly (e.g., biological transformation of contaminants). However, the processes may cause changes in geochemical parameters, leaving an observable “footprint” that can be related qualitatively and quantitatively to the natural attenuation processes (National Research Council 2000). In general, geochemical species serve as electron acceptors and are reduced during microbial degradation (i.e., oxidation) of petroleum hydrocarbons.

3.3.1 DISSOLVED PHASE CONSTITUENTS

During microbial degradation of petroleum impacts, the dissolved oxygen concentrations steadily decrease until anaerobic conditions prevail. Once anaerobic conditions exist and multiple potential electron acceptors are available, microorganisms preferentially use the electron acceptor that is thermodynamically most favorable. The general order of preference for anaerobic hydrocarbon biodegradation based on the Gibb's energy of the reaction is:

- Denitrification (reduction of nitrate), with the eventual production of molecular nitrogen
- Reduction of manganese from Mn4+ to Mn2+
- Reduction of ferric iron (Fe3+) to ferrous iron (Fe2+)
- Sulfate reduction, with eventual production of sulfide
- Reduction of carbon dioxide and generation of methane

These microbial processes generally segregate into distinct zones dominated by oxygen, nitrate, ferric iron, sulfate, and carbon dioxide reduction. Furthermore, given the different electron acceptors consumed and final products produced it is theoretically possible to differentiate the "zones" of microbial processes across the smear zone.

If dissolved oxygen is present in groundwater above 0.5 mg/L, then aerobic biodegradation of petroleum hydrocarbons is the dominant process. If dissolved oxygen concentrations are less than 0.5 mg/L, but nitrate concentrations exceed 1.0 mg/L, then denitrification dominates. Because nitrite is an unstable intermediate product of denitrification, the presence of measurable nitrite concentrations is indicative of nitrate reduction. If groundwater is deprived of dissolved oxygen, nitrate, and nitrite; but concentrations of ferrous iron are greater than 0.5 mg/L then iron reduction will be the dominant biodegradation process. If groundwater is depleted in ferrous iron but contains concentrations of sulfate above 1.0 mg/L and hydrogen sulfide above 0.05 mg/L, then sulfate reduction will be the predominant process. Finally, if the groundwater is depleted in all the electron acceptors and byproducts, with the exception of methane greater than 0.2 mg/L, then methanogenesis is the predominant process degrading petroleum hydrocarbons. When applied at a field scale this differentiation of microbial zones commonly encounters uncertainties as many of the byproducts of microbial metabolism (such as ferric iron, hydrogen sulfide, and methane) are readily transported down-gradient. Figure 3-16 presents the proportion that each reduction-oxidation process contributes to natural attenuation within the saturated zone as measured during the first and second half of 2008. Sulfate reduction and methanogenesis account for more than 90% of smear zone natural attenuation within the saturated zone.

The spatial distribution of electron acceptors measured during the second 2008 semiannual monitoring event is displayed on Figures 3-17. Nitrate and sulfate concentrations were higher up-gradient of the smear zone compared to within the smear zone. Specifically, the average nitrate and sulfate concentrations in up-gradient groundwater, as provided in Table 3-2, were 5.41 and 70.5 mg/L, respectively. Sulfate enriched water enters the smear zone with groundwater flowing from the north of the facility and bedrock-aquifer interface in the western portions of Hooven. Groundwater flowing from the west in Hooven also contains elevated nitrate. The average sulfate concentration within the smear zone was 13.0 mg/L, with the majority of the samples reported as non-detect for sulfate. Nitrate was not detected above the reporting limit (0.04 mg/L) within the smear zone. Dissolved phase sulfate and nitrate concentrations did not rebound in the down-gradient portions of the smear zone as observed in the Spring 2008, which may be related to lower water table conditions, with the supply of these constituents to the smear zone being somewhat lower.

The spatial distribution of reduced species and attenuation byproducts including dissolved iron, manganese, and methane are depicted on Figure 3-18. The concentration of each of these oxidation byproducts was higher within the smear zone compared to up-gradient and down-gradient conditions. As reported in Table 3-2, the average dissolved iron, manganese, and methane concentrations up-gradient of the smear zone were 0.015, 0.18, and 0.007 mg/L, respectively. Average dissolved iron, manganese, and methane concentrations within the smear zone were 11.44, 0.615, and 11.13 mg/L, respectively. This significant increase in the concentrations of these dissolved phase products indicates iron and manganese reduction of dissolved phase petroleum hydrocarbons, as well as methanogenic processes that transform dissolved hydrocarbons to methane. Down-gradient of the smear zone dissolved iron concentrations decrease to 0.085 mg/L.

Figure 3-19 shows the concentration of dissolved phase benzene versus distance through the centerline of the smear zone with a comparison to sulfate, iron, and methane concentrations. Dissolved phase manganese was not included on these distances versus concentration plots as manganese reduction represents less than 1% of the total smear zone mass loss in the saturated zone. Additionally, nitrate was not included on this figure as denitrification is only a significant mechanism for natural attenuation in the southern portions of the smear zone. As portrayed on Figure 3-19, iron and sulfate reduction, as well as methanogenesis primarily occur within 1,000 feet down-gradient of the smear zone boundary where available electron receptors are fully reduced. Thus, the efficacy of intrinsic processes to further degrade petroleum hydrocarbons in the saturated zone is significantly reduced within several hundred feet of the smear zone boundary at the northern portion of the former refinery. Benzene concentrations rebound within the interior of the smear zone and then are reduced at the down-gradient limits of the smear zone, as methanogenic conditions prevail. These distances versus concentration plots further support an “outside-in” weathering of the smear zone.

3.3.2 VAPOR PHASE CONSTITUENTS

Aerobic degradation of hydrocarbon vapors occurs (often in a relatively thin zone) where the concentrations of O_2 and volatile constituents in the soil vapor are optimal for the growth of petrophyllic bacteria. Aerobic degradation has the potential to reduce soil gas concentrations by several orders of magnitude, as long as the supply of O_2 is not rate limiting (Roggemans et al. 2001). CO_2 is produced as a result of aerobic biodegradation of hydrocarbons. The expected vertical profiles of O_2 and CO_2 concentrations in the presence of aerobic biodegradation tend to be mirror images. Depth profiles of petroleum related constituent, O_2, and CO_2 concentrations provide qualitative evidence of the occurrence of aerobic biodegradation in the vadose zone.

- For cases where there is little or no hydrocarbon source at depth, the hydrocarbon vapor profiles will show results at or near the reporting limit (i.e., background or non-detectable concentrations) from the deepest to the shallowest portions of the vadose zone. The concentration of O_2 will be nearly constant throughout the unsaturated zone and CO_2 concentrations will be very low or not detectable.

- If there is a significant hydrocarbon source at depth and aerobic biodegradation is not significant, the hydrocarbon vapor profile would show a linear decrease in vapor concentration with increasing distance above the source. In other words, the steady-state soil vapor profile due to diffusion will be linear with the highest concentration at the water table and the lowest concentration at the ground surface assuming the contaminant source is within groundwater and the overlying geology is relatively uniform. Degradation occurs whenever there are hydrocarbon vapors and O_2 is available, so this condition would only occur where O_2 is either prevented from entering the subsurface, or consumed completely at a rate faster than oxygen can be supplied.

- Where there is a significant hydrocarbon source at depth and aerobic biodegradation is significant, the hydrocarbon vapor profile will show a decrease in hydrocarbon concentration with increasing distance above the plume that is more rapid than that expected due to diffusion alone. The VOC concentration profile will show three distinct zones. The first zone is from the source to a depth where active aerobic biodegradation is not occurring. This zone is representative of anoxic conditions where diffusion is the primary transport mechanism and hydrocarbon vapor concentrations decrease in a linear profile, if at all. The second portion of the profile represents the active zone of aerobic biodegradation (which can be relatively thin compared to the thickness of the unsaturated zone), where there is rapid attenuation of hydrocarbon concentrations coinciding with consumption of O_2 and generation of CO_2

(Johnson et al. 1999). It is not uncommon to see O_2 concentrations decrease from atmospheric levels (20.9%) to 1-2% and CO_2 concentrations increase from less than 1% in the atmosphere to several percent in areas where aerobic degradation is active (DeVaull et al. 1997). In the third zone (above the biologically active layer) hydrocarbon concentrations are typically very low or not detectable and there is generally elevated O_2 and minimal CO_2. These profiles may vary if there are significant stratigraphic layers of different geologic materials, but this is not the case beneath the former refinery or Hooven.

Petroleum hydrocarbon constituent, O_2, and CO_2 profiles were created for each of the deep nested wells for the September and December 2008 monitoring events, as described in the subsections below. The vertical soil vapor profiles were grouped into four general categories, based on the location of the nested vapor monitoring wells:

- Overlying undisturbed portions of the LNAPL smear zone (VW-18 and VW-21)
- Overlying affected portions of the LNAPL smear zone (VW-20, VW-93, VW-96, and VW-99)
- Overlying dissolved phase petroleum hydrocarbons (VW-127 and VW-128)
- Background areas outside the distribution of petroleum related hydrocarbons attributed to the former refinery (VW-129 and VW-130)

3.3.2.1 PROFILES FOR AREAS ABOVE UNDISTURBED PORTIONS OF THE SMEAR ZONE

Total volatile petroleum hydrocarbon (TVPH) concentration profiles (Figure 3-20a and 3-21a) and benzene concentration profiles (Figure 3-20b and 3-21b) were prepared for samples collected from nested monitoring wells VW-18 and VW-21 in September 2008. TVPH is a mixture of petroleum hydrocarbon constituents whose composition can vary significantly both spatially (sample interval in each nest) and temporally (across sample events). TVPH was estimated by summing the mass of the detected volatile hydrocarbon constituents shown in Table 2-8a. For constituents that were reported as “non-detect”, half the detection limit was used as a surrogate in the estimation.

The profiles for nested vapor wells VW-18 and VW-21 generally show increasing benzene and TVPH concentrations with depth. In September 2008, the TVPH source term vapor concentrations were greater than 5,000 mg/m^3 directly above the saturated portion of the smear zone with a slight decline in vapor concentration to the shallow 5-foot intervals. Fixed gas concentrations reported in samples collected from monitoring well VW-18 and VW-21 indicate that anaerobic conditions are predominant in the vadose zone beneath the up-gradient and interior portions of the smear zone. O_2 concentrations are generally low (approximately 2 to 4%) throughout the profile. Anaerobic degradation mechanisms may account for the slight decrease in constituent concentrations observed in nested well VW-21, where CH_4 increased from 2% to 10% between the 5- and 15-foot intervals. Whereas, in well VW-18, methane concentrations remained above 35% in the vadose zone and there is a linear decrease in the TVPH concentrations, consistent with a diffusive profile. This data indicates that biodegradation of petroleum hydrocarbons within the vadose zone may be limited in these portions of the smear zone during the September 2008 monitoring event.

3.3.2.2 PROFILES FOR AREAS ABOVE TREATED PORTIONS OF THE SMEAR ZONE

TVPH profiles for wells VW-20, VW-93, VW-96, and VW-99 are provided along with O_2 and CO_2 profiles as Figures 3-22a through 3-25a, respectively. The benzene profiles are presented as Figures 3-22b through 3-25b. When historic data was available for a well, the September and December 2008 profiles were compared to the historic profiles. Generally, TVPH was reported as a single concentration value in the soil gas samples collected prior to 2005.

The September 2008 TVPH and benzene profiles from nested wells VW-96 and VW-99, overlying LNAPL impacts, show a rapid decrease in TVPH and benzene concentrations from the deepest probe to a depth between 40 and 50 ft-bgs. The soil vapor profile from samples collected from nested well VW-20 during the September 2008 event, as well as the profiles from nested wells VW-96 and VW-99 during the December 2008 event show a more gradual decrease in TVPH and benzene concentrations for the source to between 20 and 30 ft-bgs, with a rapid decrease above 20 ft-bgs. It should be noted that the TVPH concentrations in nested well VW-96 remained consistent throughout the soil vapor profile in December 2008, primarily as a result of elevated aliphatic hydrocarbons including hexane and 2,2,4-trimethylpentane.

Surface sources of petroleum related constituents can be observed in the 10 ft-bgs samples from well VW-99 and the 20 ft-bgs interval in nested well VW-96. Several of the historic profiles are suggestive of secondary sources of volatile petroleum hydrocarbon vapors between 20 and 25 ft-bgs within nested vapor well VW-96. As previously described, assessment activities were conducted during the first half of 2009 to evaluate whether there is a secondary source in proximity to this nested well.

The rapid reduction in constituent concentrations observed in the profiles for wells VW-20, VW-96, and VW-99 also coincide with decreasing O_2, increasing CO_2, and increasing CH_4 profiles from ground surface to the LNAPL plume at depth. These fixed gas profiles indicate aerobic biodegradation is the primary process responsible for the observed hydrocarbon concentration decreases observed during the September and December 2008 monitoring event. Although the active zone of aerobic biodegradation is observed in shallower portions of the vadose zone in December compared to September 2008.

The petroleum hydrocarbon profiles prepared using the analytical results from nested well VW-93 situated over the LNAPL plume show continuously low concentrations from the deepest to the shallowest intervals. The concentration profile for O_2 and CO_2 are relatively constant across the vadose zone. The source vapor concentrations measured in this well have decreased dramatically over the past ten years due to the combined effects of aerobic biodegradation and corrective measures system operation. The TVPH and benzene profiles prepared using data collected from this well between 1997 and 1999 (shown on Figure 3-23a and Figure 3-23b) are representative of a typical aerobic biodegradation profile. The more recent profiles, including the profile for data collected in September and December 2008, are consistent with a limited hydrocarbon source (i.e., concentrations near background or reporting limits throughout the profile) most likely due to operation of the HSVE system since 2000.

Overall, the hydrocarbon, O_2, CO_2, CH_4 profiles are consistent with the results from deep nested soil gas monitoring conducted over the past decade. These profiles are indicative of an active zone of aerobic biodegradation rapidly degrading petroleum hydrocarbon constituents from the source in the deeper portions of the vadose zone beneath Hooven.

3.3.2.3 PROFILES FOR AREAS ABOVE THE DISSOLVED PHASE PLUME

Vertical profiles for benzene measured in deep nested wells VW-127 and VW-128 are provided along with O_2 and CO_2 profiles as Figure 3-26 and Figure 3-27, respectively. Soil vapor monitoring has been intermittently conducted at nested wells VW-127 and VW-128 since the Spring 2005 subsurface investigation. Both of these nested vapor monitoring wells are located over dissolved phase plume, and LNAPL may be exposed during extreme low water table events or during high-grade pumping, as was the case during the second half of 2007. The benzene screening value is shown on these two profiles for reference. Profiles were not constructed for TVPH for these nested wells because of the low frequency of detection for nearly all of the TVPH constituents.

The September and December 2008 vapor profiles for these wells are consistent with cases where there is a limited hydrocarbon source at depth, similar to the recent profiles prepared using data from nested well VW-93. There are consistent, relatively low concentrations of hydrocarbons from near the water table to 10 ft-bgs with a minor reduction in O_2 and slight increase in CO_2 with depth.

The vapor profiles for the April and September 2008 monitoring events show a reverse gradient from the ground surface to shallow depths caused by detections of benzene in the 5, 10, and 15-foot intervals in nested well VW-127. As previously described herein, a natural gas odor was detected near nested vapor monitoring well VW-127 during sampling and elevated concentrations of several other target analytes were also reported in the soil gas sample collected from this probe. Benzene was not reported in samples collected from these three soil vapor probes during monitoring conducted in December 2008.

3.3.2.4 PROFILES FOR AREAS OUTSIDE OF THE PLUME

Routine vapor monitoring has been conducted at least annually using nested well VW-129 since the subsurface investigation in the Spring 2005. Until the April 2008 event, nested vapor monitoring well VW-130 had not been sampled since completion of the subsurface investigation in May 2005. Vertical profiles for benzene, O_2, and CO_2 prepared using soil gas data collected from these two nested wells are presented as Figures 3-28 and 3-29, respectively. There were not any reported detections of benzene within any of the monitoring intervals in these two wells during the September and December 2008 monitoring events. In addition, the O_2, and CO_2 concentrations are similar to atmospheric conditions throughout the vadose zone at these two locations. These vapor profiles are consistent with there being no source of petroleum hydrocarbons present at depth.

3.4 SUMMARY OF LINES OF EVIDENCE OF NATURAL ATTENUATION

Performance monitoring for any corrective measures program is necessary to demonstrate that the remedy is progressing as anticipated and will meet remedial goals while ensuring that sensitive receptors remain protected. The USEPA has established additional performance monitoring criteria for remedies incorporating intrinsic natural attenuation processes for degradation of residual impacts (USEPA 1999, USEPA 2003). Performance monitoring programs in these cases must be designed to:

1. Demonstrate that natural attenuation is occurring according to expectations
2. Detect changes in environmental conditions (e.g., hydrogeologic, geochemical, microbiological, or other changes) that may reduce the efficacy of any of the natural attenuation processes

3. Identify any potentially toxic and/or mobile transformation products (although this process is not typical of biodegradation of petroleum hydrocarbons and has not been observed in samples collected at the Chevron Cincinnati Facility)
4. Verify that the LNAPL or dissolved phase plume is not expanding down-gradient
5. Verify no unacceptable impact to down-gradient receptors
6. Detect new releases of contaminants to the environment that could impact the effectiveness of the natural attenuation remedy

These performance monitoring criteria have been achieved during this second semiannual monitoring event based upon the qualitative and quantitative lines of evidence used to demonstrate the stability of petroleum hydrocarbons in the smear zone, protectiveness of sensitive receptors, transformation of petroleum hydrocarbon constituents via intrinsic processes, as well as decreasing petroleum hydrocarbon constituent concentrations and mass over time. During the second semiannual monitoring event changes in both the dissolved phase and vapor phase conditions at the point of compliance boundaries were identified. Contingency measures, assessment activities, and additional monitoring have been implemented to determine the nature and source of the dissolved phase benzene encroachment at the sentinel monitoring well MW-35, as well as TVPH measured in soil vapor samples collected from the shallow intervals in nested monitoring well VW-96. Subsequent reports will detail the results of these activities.

4.0 BANK STABILIZATION AND BARRIER CONSTRUCTION

On December 28, 2006, Chevron submitted an evaluation of containment options for petroleum hydrocarbons present near the west bank of the Great Miami River within the *Evaluation of Engineering Options along the Great Miami River, Chevron Cincinnati Facility* to fulfill Section VI.11.g of the 2006 AOC. The USEPA provided comments regarding that document and it was subsequently revised and finalized. The preferred option included stabilization of the river bank combined with installation of a partially penetrating sheet pile wall to prevent erosion of bank soils in contact with the smear zone. Upon approval of the preferred option concept by the USEPA, Chevron proceeded to prepare detailed designs for the remedy, and submitted them in a document titled *Remedial Measures Work Plan for Sheet Pile Barrier and Bank Stabilization along the Great Miami River, Chevron Cincinnati Facility*. Based on comments to the design, Chevron subsequently revised the plans and submitted the final approved design in an updated report dated September 10, 2008.

The bank stabilization and barrier construction activities were completed between September and December 2008 in general accordance with this work plan. As-built drawings showing the riverbank stabilization measures and alignment of the sheet pile barrier wall is provided on Figure 4-1. Additional details regarding construction activities are provided below, organized by main project components and presented in the general order they were performed.

4.1 SITE PREPARATION

Construction activities commenced on September 15, 2008 with tree clearing and grubbing of the affected portions of the west bank. An approximate 3.4-acre area, extending from the river's edge to the access road was cleared to allow for grading of a low-sloping bench. Following vegetation clearing, topsoil was stripped and stockpiled for subsequent placement as the last lift on the re-contoured low-sloping bench. In addition the Hooven Ditch, an ephemeral storm water drainage channel passing through the proposed barrier wall alignment, was redirected to the north. Riprap armoring was applied to the reconstructed ditch to limit erosion and potential migration of the channel behind the barrier over time.

4.2 SHEET PILE BARRIER WALL

Prior to installation of the sheet piles, a work platform was constructed along the length of the barrier to accommodate pile driving activities. Along the southern third of the proposed barrier alignment, where the river bed was below water, an earthen cofferdam was built using material from several gravel bars within the channel. Then, the region between the cofferdam and existing bank was backfilled with additional river derived gravel to complete the work platform. Along the central and northern portions of the proposed barrier, the river bed was naturally exposed due to seasonal low flow conditions within the Great Miami River, allowing access for necessary equipment.

Pile driving activities began in late September and were completed by October 22, 2008. The partially penetrating steel sheet pile barrier wall was installed with piles driven from north to south. Sheet piles consisted of 2.5-foot wide by 30-foot tall Roll Form Group EZ88 steel piles. The piles were driven into the ground surface using a track-mounted RAM sheet pile driver to a top-of-pile target elevation of approximately 472 ft-amsl at the northern limits of the barrier sloping down to approximately 471 ft-amsl at the southern tie in of the wall. The sheet piles were delivered in seal-welded pairs with a water-swelling sealant applied to the non-welded joint interlocks.

A professionally licensed surveyor established control points throughout the project area and completed an as-built survey of the constructed sheet pile barrier wall. Each of the sheet piles were emplaced within 4 inches of the target depth, with the vast majority driven within 2-inches of the design elevation. Piling was driven without refusal except for one area near the southernmost tie-in. Piling in this area was relocated approximately six inches to the east and the remaining sections of the wall realigned accordingly to avoid large glacial deposits (i.e., boulders) within the Buried Valley Aquifer.

4.3 HORIZONTAL AIR SPARGE PIPING

As part of the river bank stabilization measures, contingency horizontal air sparge lines were installed along the inland portions of the barrier between the existing smear zone limits and the sheet pile wall. Figure 4-2 shows the location of the eight air sparge lines (five at the downstream segment and three at the upstream segment) installed along the reconstructed west bank. The sparge lines were emplaced along the two portions of the west bank where the smear zone was in close contact with the former river bank. Each sparge line consists of a bundle of two-inch diameter, schedule 80 PVC pipes with a unique 100-foot screened interval. Utilizing multiple sparge lines with uniquely screened intervals results in enhanced delivery of air across the saturated zone and minimizes uneven air delivery, which can occur when using a single line with an extended horizontal screen. The upstream sparge piping was trenched to an approximate depth of 460 ft-amsl, whereas downstream the sparge piping was emplaced at an approximate depth of 462 ft-amsl. The terminal ends of all sparge lines were capped slightly above ground surface. A 6-inch diameter steel bollard approximately 4-feet tall was placed immediately upstream of the terminal ends of each cluster to protect the sparge piping from debris in the river and assist with locating the terminal ends in the future should air sparing be required.

4.4 LOW-SLOPING BENCH

Grading activities began following installation of the partially penetrating sheet pile wall and the air sparge piping to create a low-sloping bench along the west bank of the Great Miami River. The existing bank was re-contoured using primarily river gravel with some native soils (river silts) to the proposed grade. Gravel was borrowed from the existing gravel bars, placed in 8-inch lifts, and compacted using low ground pressure equipment (e.g., bulldozer) and a sheepsfoot roller. Native soils were emplaced in a similar fashion above the gravel. A topsoil layer (staged during site preparation activities) was placed and compacted as the final lift along the low-sloping bench.

4.4.1 RIP RAP REVETMENT SYSTEM

A riprap revetment system was constructed along the outboard portion of the sheet pile barrier to protect the partially penetrating wall from scouring during future flood events. Prior to positioning riprap, river gravel was placed outboard of the barrier at the angle of repose (i.e., the maximum angle of a stable slope). A woven geotextile fabric (SKAPS W300) was installed over the gravel and anchored into trenches at base of the sheet pile wall and at the end of the reconstructed low-sloping bench. Approximately 4,500 cubic yards of ODOT Class A riprap was then placed overtop the geotextile fabric. An adequate volume of riprap was applied in order to be “self-launching”, where riprap will fall into and protect against areas of deep river scour should they occur adjacent to the barrier.

4.4.2 FLOOD TOLERANT VEGETATIVE COVER

Over the remainder of the low-sloping bench, flood-tolerant vegetation was planted to protect the newly formed bank from erosion. Preparation for the vegetative cover consisted of applying a Green Armor™ system. The Green Armor™ system is a turf reinforcement mat (Enkamat® TRM) into which a flexible growth medium (Flexterra® FRM) is applied. Turf reinforcement matting was anchored into rock trenches to limit uplift or damage during flood events. Approximately 50,000 live tree stakes consisting of equal portions of Silky Willow, Silky Dogwood, Eastern Nine Bark, and Elderberry were planted at an approximate density of two per square yard within the Green Armor™. Re-vegetation and stabilization measures were completed on December 22, 2008.

4.5 EXCAVATION OF NON-PROJECT AREA SOILS AND SEDIMENTS

Hydraulic modeling was completed to evaluate potential stresses on the barrier wall and stabilized riverbank during flood conditions within the Great Miami River. The model results indicated that during intervals of high flow, the flood control levee adjacent to former SWMU-10 may constrict the channel resulting in increased shear stress along the proposed barrier wall. Therefore, the height of the flood control levee was reduced north of the sheet pile wall to decrease shear stress and potential scour during flood events.

In addition, sediments were excavated from portions of the East Island Channel (channel located east of Islands No. 1 and No. 2 as described in the 2006 AOC) in order to reduce upstream flood elevations (i.e., achieve no rise to the modeled 100-year flood elevation) and further reduce potential shear stress along the partially penetrating sheet pile wall. Historically, flow through this channel had only occurred under high water conditions, hindered by sedimentation at the northern and southern limits of the channel. Over 85,000 tons of soils and sediments were excavated, staged, and then reutilized as clean fill along the reconfigured bank and other historic SWMUs.

4.6 BARRIER WALL PERFORMANCE MONITORING NETWORK

The Barrier Wall Construction plans included a work plan titled *Performance Monitoring Plan, Sheet Pile Barrier Along Great Miami River, Chevron Cincinnati Facility, Hooven, Ohio* (Trihydro 2007). The plan specified measures to characterize baseline conditions and monitor performance of the partially penetrating sheet pile wall during implementation of the final corrective measures for groundwater. The performance of the sheet pile wall will be monitored by observing the hydraulic gradients in groundwater and surface water, as well as evaluating groundwater, hyporheic water, and surface water quality over time.

In accordance with this plan, a monitoring network was constructed between November 10 and December 29, 2008. The monitoring network is comprised of three monitoring transects along the northern, central, and southern portions of the barrier wall as illustrated on Figure 4-2. Each transect includes a groundwater monitoring nest (shallow, intermediate, and deep wells) situated inboard of the sheet pile wall and a groundwater monitoring nest located on the outboard side of the wall. In addition, a hyporheic/surface water monitoring well was also constructed outboard of the wall at each monitoring transect. A description of the installation and construction details is provided in the following subsections.

4.6.1 INBOARD MONITORING WELL CONSTRUCTION DETAILS

Figures 4-3 through 4-5 depict the screened intervals for the inboard monitoring nests installed at the northern, central, and southern monitoring transect respectively. A typical diagram for the inboard monitoring wells is provided on Figure 4-6. The shallow, intermediate, and deep groundwater monitoring wells were installed along the interior portions of the barrier wall using ten feet of prepacked screen. The prepacked screens are constructed of 2-inch diameter, 0.010-inch factory-slotted polyvinyl chloride (PVC) with a sand pack encased in a fine stainless steel mesh around the PVC screen. The screen interval within the shallow well was generally installed between 460 and 475 ft-amsl based on the range of historical fluid level elevations recorded in nearby monitoring wells. The intermediate wells were generally screened at an elevation between 435 and 455 ft-amsl across the bottom of the partially penetrating sheet pile wall. The deep wells were typically completed with the screen interval between 420 and 440 ft-amsl with the top of screen installed approximately ten feet below the bottom of the wall.

Schedule 40 flush-threaded blank PVC casing was installed from the top of the prepack screens to approximately two to three feet above the ground surface. Within the intermediate and deep inboard groundwater monitoring wells, 7.5 feet of prepacked granular bentonite was emplaced above the filter pack and the borehole was allowed to collapse to approximately two feet below ground surface. Within the shallow inboard wells, approximately 6-inches of hydrated bentonite chips were placed above the pre-packed screens. The wells were completed at the surface with a 6-inch diameter steel outer protective casing with locking lid. The protective casings were backfilled with concrete and supported by a 2-foot by 2-foot square concrete pad. A 6-inch diameter bollard with concrete pad was installed on the upstream side of the monitoring wells to protect the wells from debris during future flood events. Lithology logs (for deep wells) and a well log and drilling report (ODNR Form 7802.03) are provided in Appendix N.

4.6.2 OUTBOARD MONITORING WELL INSTALLATION

Three groundwater monitoring wells and one hyporheic/surface water monitoring well were installed at the northern, central, and southern monitoring transects (Figures 4-3 through 4-5) outboard of the sheet pile wall. The deep monitoring well was installed vertically, immediately adjacent to the barrier wall. The intermediate well was installed at an angle of 20 degrees from vertical. The shallow groundwater monitoring well was installed 40 degrees from vertical, and the hyporheic/surface water monitoring well was installed at approximately 60 degrees from vertical.

During barrier wall construction, supportive steel I-beams were driven inboard and outboard of the sheet pile wall to support installation of the shallow groundwater and hyporheic/surface water monitoring wells at each transect. Before well construction began, 6-inch steel pipes were driven into the river bed at the appropriate angles to help protect the wells from damage during flood events. Perforated stainless steel casing was used for the hyporheic/surface water well at similar depths as the proposed well screens. The protective casings were welded to the I-beams at the shallow and hyporheic/surface well locations to further protect the wells from damage. The sediment within the outer protective steel casings was removed using a vacuum truck prior to installation of the borehole to the proposed depth.

The groundwater monitoring wells were constructed using twenty to thirty five feet of two-inch diameter, prepacked screen depending on the target depth and angle of installation. Schedule 40 flush-threaded PVC blank casing was installed from the top of the screen interval to approximately 6-inches below the top of the outer steel casing. Between 2.5 and 7.5 feet of prepacked granular bentonite was placed above the screen interval within each of the outboard groundwater monitoring wells. The length of prepacked bentonite seal depended upon the distance between the top of the screen and the bottom of the outer protective steel casing. The bottom of the protective steel casings were sealed with approximately 2-feet of bentonite chips and then grouted to within 2-feet of the top of casing using a cement-bentonite grout (95% cement/5% powdered bentonite).

The hyporheic/surface water well was screened continuously throughout the perforated stainless steel outer casing using 2-inch diameter prepacked screens. The annulus between the prepacked screens and the perforated stainless casing was filled with No. 5 silica sand. Each of the 6-inch diameter protective steel outer casings were completed with a cast aluminum locking lid. A 6-inch diameter bollard with concrete pad was installed on the upstream side of the monitoring wells to protect the wells from impacts during future flood events. Typical well completion diagrams for the outboard groundwater monitoring wells and the hyporheic/surface water monitoring wells are provided on Figure 4-6. Lithology logs (for deep wells) and a well log and drilling report (ODNR Form 7802.03) are provided in Appendix N.

4.6.3 MONITORING WELL DEVELOPMENT AND LICENSED SURVEY

Between February 17 and 19, 2009 the barrier performance monitoring wells were developed to remove accumulated sediments from the boring and well casing potentially introduced during drilling and well construction activities. The newly installed wells were developed by mechanically surging the well followed by over-pumping using an air lift technique, until stabilization of water quality parameters, or a minimum of ten casing volumes of water had been removed. Purge water recovered from each well during development was discharged to the on-site wastewater treatment facility.

The top of casing and surface elevations, as well as, northing and easting coordinates of the inboard and outboard monitoring wells were measured by a professionally licensed surveyor, relative to mean sea level and the Ohio state plane coordinate system, respectively. A permanent mark on each well casing was established as the measuring point.

5.0 GULF PARK

A former products transfer pipeline corridor, consisting of five 6-inch diameter lines that connected the former refinery with a loading terminal on the Ohio River, was located beneath the Gulf Park property. The pipelines carried three grades of gasoline, kerosene, aviation fuel, diesel, and fuel oil during use between 1930 and the mid-1980s. Hydrocarbon-stained soil was discovered in Gulf Park in January 1993 at approximately 10 to 14 feet below grade. Several subsurface investigations to define soil and groundwater conditions and the extent of petroleum hydrocarbons were conducted between 1993 and 1994.

Based upon the findings of these investigations, a bioventing system was installed in the area that is now the westernmost soccer field at Gulf Park in 1996. It consists of 14 air injection wells designed to deliver approximately 30 to 35 standard cubic feet per minute (scfm) to each injection well, and a blower. Valve controls for the air injection wells installed in the soccer field area are located in a nearby Valve Control Shed (VCS No.1). A bioventing system expansion was installed between August and October 2000, consisting of an additional 38 bioventing wells constructed of 2-inch diameter PVC casing and 0.010-inch slotted screen. These bioventing wells were completed below grade and connected to a separate Valve Control Shed (VCS No. 2). Figure 5-1 shows the layout of the two bioventing systems installed at Gulf Park.

There are two primary lines of evidence used to evaluate the remedy performance at Gulf Park. First, soil vapor data is collected from selected nested wells installed in the shallow and deep portions of the vadose zone to evaluate fixed gas concentrations during times when the bioventing system is active and inactive. Second, dissolved phase monitoring is conducted annually in Gulf Park to evaluate temporal and spatial trends in the dissolved phase constituents of concern, as well as natural attenuation indicators. Groundwater monitoring was not conducted in Gulf Park during the second half of 2008 and therefore is not discussed herein. Groundwater samples were collected for the constituents of concern and natural attenuation indicators in June 2009 and will be reported within the *First 2009 Semiannual Monitoring Report*.

5.1 BIOVENT SYSTEM PERFORMANCE MONITORING

Bioventing stimulates intrinsic biodegradation of petroleum hydrocarbons in the vadose zone by injecting air at low flow rates to provide sufficient oxygen to sustain aerobic microbial activity. Airflow is injected at rates designed to maximize oxygen delivery to the subsurface while minimizing volatilization of hydrocarbon constituents, thus

eliminating the necessity for vapor intrusion or ambient air pollution control measures.
Startup and shutdown criteria for the biovent system are related to groundwater trigger levels beneath Gulf Park. Historic soil vapor monitoring data indicate that higher respiration rates occur within the lower portions of the smear zone. However, this portion of the smear zone is only exposed above the groundwater table during low water table conditions. The groundwater level is typically above the trigger level elevation from January through June and below the trigger level intermittently from June through December. The period of low water table conditions is considered the seasonal bioventing operation period. Figure 5-2 presents the hydrographs from the trigger monitoring wells for 2006 through 2008. As shown, groundwater elevations were below the trigger elevation from July 31, 2008 until January 2009, when water levels began fluctuating around the trigger elevations within wells GPW-5S and TH-2.

The bioventing system at Gulf Park was operated continuously from August 12 though the end of 2008, with the exception of outages due to power failure from September 14 through September 17 and November 29 through December 1. Each bioventing well has a valve to regulate air flow and a port used for monitoring temperature, pressure, and air flow. The system monitoring activities collected during operation of the biovent system in 2008 consisted of:

- Recording operational parameters (pressure, flow rate, and temperature) periodically at the process blower in order to document blower performance.
- Measuring the air flow parameters in each of the biovent wells weekly in order to document airflow to each injection well.
- Gauging fluid levels within the system “trigger” wells (GPW-5S and TH-2) weekly to determine the schedule for system startup and shutdown.
- Collecting field measurements of soil vapor composition including total organic vapor, pressure, and fixed gas concentrations (O_2, CO_2, and CH_4) to qualitatively evaluate system effectiveness.

5.1.1 BIOVENT SYSTEM PERFORMANCE RESULTS

During system inspections and each time air flow adjustments were made, performance parameters for active (i.e., valve not closed) injection wells were monitored within VCS No. 1 (Lines BV-1 through BV-14) and VCS No. 2 (BVW-1 through BVW-38). Biovent wells in VCS No. 1 contain analog, vane-style flow meters, which allow for measuring instantaneous flow rates. Biovent lines located in VCS No. 2 were installed with sensor ports to allow for measurement of pressure, temperature, and differential pressure in order to calculate standard air flow rate. Pressure in the individual biovent wells in VCS No. 2 was measured using a digital manometer. Injection air temperature measurements for the biovent expansion system were collected from dedicated dial gauge thermometers installed on each vent line. Flow rates measured at individual biovent well lines were measured using a Dwyer flow sensor manufactured to measure differential pressure in a 2-inch diameter pipe. The flow sensor was connected to a digital manometer, and differential pressure values provided by the manometer were recorded. The recorded values were later converted to volumetric flow rates and corrected to standard conditions.

During 2008 operations, biovent system control valves were periodically adjusted to deliver a target 35 scfm of air to each biovent well. Based upon average flow rates measured at the biovent wells and recorded operation times, approximately 385,000,000 scfm of process air was injected into the expanded biovent system area during the 2008 period of operation. The biovent well performance measurements, including dates and time of operation, are presented in Appendix O.

5.1.2 SOIL VAPOR MONITORING RESULTS

Soil vapor conditions including fixed gases (O_2, CO_2, and CH_4), total organic vapor, and pressure were measured within selected nested vapor monitoring points including VP1-25S, VP1-25D, VP1-50S, VP2-25S, VP2-50S, VP3-35S, VP4-25S, VP4-25D, VP6-35S, based on access to the vapor points and water table elevation. Due to the groundwater elevation at the time of measurement, several of the deeper vapor monitoring points could not be monitored. Several other points have been destroyed over time by maintenance workers at Gulf Park. Soil vapor field measurements were collected prior to system start-up on August 12, 2008 and again while the system was active on October 14, 2008. Results of field measurements collected from accessible vapor monitoring points during the second half of 2008 are included in Appendix N.

Table 5-1 presents the results of fixed gas and total organic vapor measurements collected from soil vapor monitoring points during August and October 2008. Comparison of the fixed gas concentrations measured prior to system start-up and when the system was active indicates that bioventing has a measurable impact on subsurface vapor composition within the intended limits of the systems. A significant increase in subsurface O_2 content is accompanied with a measureable decrease in CO_2 and CH_4 concentrations.

O_2 concentrations in the western portion of Gulf Park (measured using wells VP2, VP4, and VP6) were negligible and

CH_4 concentrations were reported as high as 75.8% prior to system startup, indicating anoxic conditions throughout the vadose zone. Whereas, in the eastern limits of the biovent system (measured using data collected from wells VP1 and VP3) O_2 concentrations were reported between 12 and 13% and CH_4 was not detected. Following system start-up, O_2 concentrations were approximately the same as atmospheric levels and CH_4 was not detected within the influence of the system, with the exception of near well VP2-50S, where O_2 concentrations remained below 12% and CH_4 remained at 2.6%. This also corresponds to the area with the highest reported total organic vapor concentrations during monitoring in August and October.

These field screening results may be used in the future to terminate bioventing in portions of the system where aerobic conditions prevail throughout the year and petroleum hydrocarbons have been depleted. Additional air delivery can then be supplied to those portions of the Park where petroleum hydrocarbons persist and anaerobic conditions are observed during periods when the system is inactive.

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