SECOND 2011 SEMIANNUAL MONITORING REPORT

CHEVRON CINCINNATI FACILITY

HOOVEN, OHIO

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EXECUTIVE SUMMARY

This report presents results of the routine monitoring conducted by Chevron Environmental Management Company (Chevron) between July 1, 2011 and December 31, 2011 at the former Gulf Oil refinery situated approximately 20 miles west of Cincinnati, Ohio. This report also summarizes the high-grade recovery and horizontal soil vapor extraction (HSVE) system operations during the second half of 2011. Monitoring during this semiannual period was performed in fulfillment of requirements provided in the 2006 Administrative Order on Consent (2006 AOC, Docket No. RCRA-05-2007-0001) following the methods described in the *Remedy Implementation Plan for Final Groundwater Remedy, Chevron Cincinnati Facility* (*RIP*, Trihydro 2007a) and the *Operation, Maintenance, and Monitoring Plan for Final Groundwater Remedy, Chevron Cincinnati Facility* (*OMM Plan*, Trihydro 2007b). Monitoring and groundwater corrective measures that were performed during the second 2011 semiannual period include:

- Fluid level gauging including continuous monitoring using pressure transducers as well as weekly, monthly, and bimonthly manual measurements to track hydraulic gradients and light non-aqueous phase liquid (LNAPL) occurrence.
- Rapid Optical Screening Tool (ROST) monitoring to confirm stability of the LNAPL plume at the lateral edge of the smear zone.
- River monitoring to evaluate groundwater and surface water quality adjacent to, beneath, and within the Great Miami River.
- Vapor monitoring in Hooven to confirm the protectiveness of inhabitants of structures overlying the distribution of petroleum hydrocarbons associated with releases from the former refinery.
- High-grade recovery and associated performance monitoring primarily using groundwater production well PROD_25 located in the Central High-Grade Area.
- HSVE system operation to recover additional hydrocarbon mass beneath Hooven and mitigate the effects of alternate sources of petroleum hydrocarbons within the shallow and intermediate portions of the vadose zone.
- Monthly vapor monitoring in selected nested wells in Hooven to confirm the effectiveness of the HSVE system.
- Operation and monitoring of the bioventing system in Gulf Park.
- Groundwater sampling in Gulf Park to demonstrate dissolved phase plume stability and efficacy of monitored natural attenuation.

- Installation of a southern sheet-pile barrier in Gulf Park to mitigate dissolved-phase contaminant flux to the Great Miami River.

Approximately 1,065 gallons of LNAPL was recovered during the high-grade recovery event performed in the Central Area between August and November 2011. An additional 5,567 pounds of organic carbon were recovered using the HSVE system during this event.

Monitoring results continue to demonstrate that the final groundwater remedy at the former refinery is progressing as anticipated and will meet remedial goals while ensuring that sensitive receptors remain protected. The United States Environmental Protection Agency (USEPA) has established performance monitoring criteria for remedies incorporating intrinsic natural attenuation processes (USEPA 1999, USEPA 2003). These performance monitoring criteria have been used to evaluate the progress of the final groundwater remedy at the Chevron Cincinnati Facility. Specifically the data collected at the Chevron Cincinnati Facility demonstrate the following:

1. Vapor phase natural attenuation indicators continue to demonstrate that intrinsic biodegradation is occurring within the vadose zone above the smear zone. Soil vapor samples collected during the second half of 2011 continue to demonstrate that petroleum hydrocarbon concentrations including benzene are decreasing and the smear zone mass is being depleted over time.
2. At the main Site, dissolved phase and hydrogeochemical monitoring was not performed within groundwater monitoring wells located within the smear zone during the second semiannual period in 2011, in accordance with the schedule provided within the *OMM Plan* (Trihydro 2007b). Evidence of dissolved phase degradation and natural attenuation processes occurring in the saturated zone will be presented in the first semiannual report for 2012. Within Gulf Park, dissolved phase natural attenuation indicators continue to demonstrate that intrinsic biodegradation is occurring within the saturated zone.
3. ROST and dissolved phase monitoring results verify that the LNAPL smear zone and dissolved phase plume is stable beneath the Southwest Quad and on the facility. Localized changes in dissolved phase conditions were identified at the point of compliance boundary in the Southwest Quad in November 2008 with benzene reported in groundwater samples collected from sentinel monitoring well MW-35 and point of compliance well MW-133. These changes have been associated with a localized release(s) in the Southwest Quad. Fluid level and groundwater monitoring results collected in the first half of 2010 confirm that constituents from the plume are not migrating to the point of compliance boundary. In March 2010, long-term operations and monitoring were reverted to the schedule outlined in the OMM Plan (Trihydro 2007b) following six months of monitoring with no additional detections of benzene in groundwater samples collected from wells MW-35 and MW-133. During groundwater monitoring performed in March and May 2011, low level detections (parts per billion range) of

benzene, ethylbenzene, and xylene were reported in groundwater samples collected from sentinel wells MW-35 and MW-131, as well as point of compliance well MW-120; however, groundwater flow directions during these monitoring events were primarily from the west to the east, which is perpendicular to the typical flow direction. During the second half of 2011, organic constituents of concern were not detected in any of the sentinel or point of compliance wells. Based on these recent monitoring results in the Southwest Quad, it is reasonable to conclude that the dissolved phase plume is stable and there has not been redistribution of constituents following termination of continuous hydraulic control (i.e., year round pumping) following execution of the 2006 AOC.

4. Dissolved phase monitoring conducted along the west bank of the Great Miami River showed that constituents of concern present in the smear zone are not migrating beneath the partial penetrating barrier wall. The surface water screening standards were not exceeded in any of the hyporheic or surface water samples collected during the second half of 2011 and sensitive receptors along the river bank remain protected.

1.0 INTRODUCTION

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 groundwater cleanup standards. Achieving this objective was estimated to take up to 42 years; therefore, the following interim objectives have been adopted for the groundwater remedy:

- Monitor soil vapor concentrations and prevent migration of volatile petroleum hydrocarbons into indoor air above risk based limits
- Measure the stability of LNAPL and dissolved phase petroleum hydrocarbons
- Remove recoverable LNAPL to agreed upon end-points
- Stabilize the bank of the Great Miami River on the main facility and in Gulf Park to prevent erosion of soils containing petroleum hydrocarbons

Groundwater remediation and monitoring efforts are being conducted in accordance with a 2006 AOC between Chevron and the 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 commercial properties to the southwest of the former refinery (commonly referred to as the Southwest Quad) through discontinuance of year round groundwater recovery.
- Focused LNAPL removal during periods of extreme low water table conditions through high-grade pumping over the next decade.
- Combined operation of the 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 phase petroleum hydrocarbons. The majority of recoverable LNAPL has been removed 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 portions of the smear zone with the highest remaining LNAPL saturations. However, it is understood that the long-term remedy objective will be accomplished primarily through natural attenuation 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 *RIP* (Trihydro 2007a) and the *OMM Plan* (Trihydro 2007b).

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 2009a). A summary of the SCM, including iterative updates made using assessment and routine monitoring results collected since early 2008, was provided in the semiannual reports and most recently updated in the *Five-Year Groundwater Corrective Measures Implementation Review, Chevron Cincinnati Facility, Hooven, Ohio* (*Five-Year Groundwater CMI Review*, Trihydro 2011b). Future updates to the SCM will be presented in subsequent groundwater corrective measures implementation reviews, which are provided every five years. Figure 1-2 shows a diagrammatic SCM for the facility, Hooven, and Southwest Quad.

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, 2011 to December 31, 2011.

This report will also provide a summary of additional assessment and remedial system operations performed during the second half of 2011 including high-grade recovery, additional soil vapor monitoring performed in Hooven and the Southwest Quad, as well as monitored natural attenuation in Gulf Park. The remainder of this report is organized into the following sections:

- Section 2.0 – Describes the infrastructure, methods, and results of monitoring activities conducted during the second semiannual monitoring period in 2011.
- 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.

- Section 4.0 – Provides the results of high-grade recovery operation completed between August and November 2011 including performance of the HSVE systems during this event.
- Section 5.0 – Describes the results of biovent system operation conducted in Gulf Park. This section also presents the results of natural attenuation indicator analyses in groundwater across the Park.

2.0 MONITORING NETWORK AND RESULTS

The primary component of the final groundwater corrective measures program 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
- Lysimeter 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 at the lateral edge of the LNAPL smear zone
- River monitoring to evaluate groundwater and surface water quality adjacent to, beneath, and within the Great Miami River

The following sections describe the results of monitoring conducted to support the groundwater remedy between July 1 and December 31, 2011. A description of the methods used for installation, monitoring, and analysis have been previously described within the *RIP* (Trihydro 2007a) and *OMM Plan* (Trihydro 2007b). 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. The 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 or more frequent basis. Groundwater elevation data recorded using pressure transducers are provided in Appendix A.

Pressure transducers were deployed during the entire second semiannual monitoring period in an expanded network (including wells MW-20S, MW-26R, MW-35, MW-44S, MW-48S, MW-79, MW-94S, MW-96S, MW-100S, MW-104S, MW-112, MW-131, MW-132, and RBGP-44) across the site, Hooven, and Southwest Quad.

Manual fluid level gauging is conducted on a bimonthly basis in each of the shallow monitoring wells located on the facility, Hooven, Southwest Quad, and Gulf Park. 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 LNAPL thickness.

Appendix B provides manual fluid level gauging data collected during the second half of 2011. Potentiometric surface maps for July, September, and November 2011 generated using data collected during bimonthly monitoring are provided as Figures 2-2 through 2-4. As shown on the July 2011 potentiometric surface map, groundwater flow in the Buried Valley Aquifer is primarily to the south and southwest under ambient (i.e., non-stressed) conditions. During high-grade recovery in September 2011, the groundwater flow conditions are significantly altered with predominant flow towards production well PROD_25 within the central portion of the facility. Following a flood event in November 2011, flow was primarily from the west to the east, which is perpendicular to the typical flow direction.

2.2 DISSOLVED PHASE MONITORING

Dissolved phase monitoring is conducted at the facility, Hooven, and Southwest Quad 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); therefore many of the analyses conducted as part of the final remedy monitoring focus upon benzene depletion within the smear zone. Dissolved phase benzene is not generally detected more than 200 feet outside the LNAPL smear zone due to intrinsic biodegradation at the plume periphery.

Field forms for groundwater samples collected between July and December 2011 are included in Appendix C. Laboratory analytical reports for groundwater samples collected during the second 2011 semiannual monitoring period 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. It should be noted that, Analytical Laboratory Services (ALS) located in Cincinnati, Ohio began analyzing groundwater and soil samples collected at the Chevron Cincinnati Facility beginning in 2011, following approval from the USEPA. The analytical summary reports provided by ALS in Appendix D-1 reference the laboratory reporting limits rather than the method detection limits. The method detection limits have been referenced on the summary tables and figures included within previous semiannual monitoring reports and remain so herein. Both the laboratory reporting limits (as listed on the analytical summary reports) and the method detection limits (included in the electronic data deliverable as well as the summary tables and figures) are below remedial goals for this project (USEPA MCLs). The following subsections present the results of dissolved phase monitoring conducted between July and December 2011.

2.2.1 SENTINEL AND POINT OF COMPLIANCE MONITORING

There are three sentinel wells (MW-35, MW-131, and MW-132) and four point of compliance monitoring wells (MW-37, MW-120, MW-133, and MW-134) located at the down-gradient edge of the dissolved phase plume in the Southwest Quad. 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 during November and December 2011, as part of semiannual monitoring activities in accordance with the schedule described in the *OMM Plan* (Trihydro 2007b).

Groundwater analytical results for the dissolved phase constituents of concern are provided on Table 2-1 and Figure 2-6. Organic constituents of concern (i.e., benzene, chlorobenzene, ethylbenzene, toluene, and xylene) were not detected in any of the sentinel or point of compliance wells during the second 2011 semiannual monitoring period.

Dissolved lead was detected in a sample collected from point-of-compliance well MW-37 during December 2011 at an estimated concentration of 0.007 mg/L. 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.

Based on these results and monitoring performed in the Southwest Quad over the past five years, it is reasonable to conclude that there has not been redistribution of constituents following termination of continuous hydraulic control.

2.2.2 PERIMETER, INTERIOR, AND SUPPLEMENTAL MONITORING

As discussed in the *Five-Year Groundwater CMI Review* (Trihydro 2011b) and supported by data collected to date, the LNAPL and dissolved phase petroleum hydrocarbons are laterally stable and degrading over time. 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. Groundwater samples are typically collected from three groups of monitoring wells for evaluation of natural attenuation mechanisms within the saturated zone: perimeter, interior plume, and supplemental monitoring wells. Per the schedule established within the *OMM Plan* (Trihydro 2007b), only the perimeter groundwater monitoring wells (MW-26R, MW-33, MW-48S, MW-85S, MW-94S, MW-95S, MW-100S, MW-104S, and MW-115S) were sampled during the second half of 2011. The analytical results for the dissolved phase constituents of concern reported in samples collected from the perimeter monitoring wells are provided on Table 2-2. The interior and supplemental monitoring wells will be sampled along with the perimeter wells during the first half of 2012 and the results reported in the first 2012 semiannual monitoring report.

2.3 LYSIMETERS

Lysimeters are used to measure the makeup of recharge water (particularly oxidizers) from infiltrating precipitation and evaluate the contribution of the makeup water to biodegradation within the upper limits of the saturated zone. Two soil moisture lysimeters were constructed at the grouped media locations near wells MW-18, MW-20, MW-21, and MW-93, in accordance with details presented in the *RIP* (Trihydro 2007a). Per the schedule established within the *OMM Plan* (Trihydro 2007b), these lysimeters were not sampled during the second half of 2011. The lysimeters will be sampled during the first half of 2012 and the results reported in the first 2012 semiannual monitoring report.

2.4 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 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 2007a).

ROST monitoring was completed within the three ROST transects on December 19 and 20, 2011 The tool was advanced from between 5 and 10 feet above the water table to between 5 and 10 feet below the water table in each of the monitoring locations. ROST monitoring logs are provided in Appendix E. Data collected during the December 2011 event indicate that the smear zone is stable as 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.

2.5 RIVER MONITORING

A partially penetrating sheet pile barrier wall and bank stabilization measures were installed along the west bank of the Great Miami River between September and December 2008. As part of these bank stabilization measures, a barrier wall performance monitoring network was installed along the restored river bank in accordance with the *Performance Monitoring Plan, Sheet Pile Barrier Along Great Miami River, Chevron Cincinnati Facility, Hooven, Ohio* (Trihydro 2007c). This work 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 is monitored by observing the hydraulic gradients in groundwater and surface water, as well as evaluating groundwater, hyporheic water, and surface water quality over time.

The barrier monitoring network is comprised of three monitoring transects along the northern, central, and southern portions of the barrier wall as illustrated on Figure 2-7. Each transect includes a groundwater monitoring nest (shallow, intermediate, and deep wells) situated inboard of the sheet pile wall and another nest 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 for the sheet pile wall, stabilization measures, and performance monitoring network is provided in the *Second 2008 Semiannual Monitoring Report, Chevron Cincinnati Facility, Hooven, Ohio* (Trihydro 2009b)

2.5.1 FLUID LEVEL MONITORING

Pressure transducers were deployed on December 1, 2009 in the groundwater and surface water monitoring wells in the northern and southern monitoring transects to evaluate horizontal and vertical gradients across the partial penetrating barrier wall. Transducers are programmed to record groundwater and surface water elevations at a four-hour frequency. High frequency groundwater elevation data recorded using the pressure transducers are provided in Appendix A. Manual fluid level gauging was also conducted on July 28 and September 29, 2011 to supplement the transducer data and measure LNAPL gradients (if present) within the inboard portions of the barrier wall. LNAPL was not detected in any of the monitoring wells situated on the west bank of the river during this gauging event. Manual fluid level measurements are included in Appendix B.

Transducer data from select monitoring wells was used to illustrate vertical hydraulic gradients on the interior and exterior of the barrier wall at the north and south monitoring transects (Figure 2-8 and Figure 2-9). Along the northern transect (shown on Figure 2-8), the groundwater elevation on the interior of the wall was generally coincident or lower than the surface water elevation from July through mid-November 2011 at which point a series of high river stage events occurred. Following each river stage peak, the groundwater elevation on the interior of the wall was temporarily higher than the surface water elevation. In general, there was a neutral to downward gradient on the outside of the wall leading up to the high river stage events. Following river stage peaks in late November and December, a brief upward gradient was observed on the outboard side of the wall, while the inboard gradient remained largely neutral. These results indicate that rapid and large fluctuations to surface water elevations can temporarily alter gradients and flow paths along the barrier.

At the southern transect (shown on Figure 2-9), groundwater elevations were generally higher than surface water elevations with brief reversals during rapid rises in river stage. Generally, there was an upward gradient observed on the outboard side of the partially penetrating sheet pile wall that briefly reversed during river stage increases. On the interior portions of the wall the vertical gradient was largely neutral, with increases during high river stage events, most notably during the December 6, 2011 flood event. These results indicate that despite the consistently lower river surface elevation relative to groundwater, a consistent downward inboard gradient was not observed and there is limited groundwater flux to the river along the southern transect as well.

2.5.2 GROUNDWATER, HYPORHEIC, AND SURFACE WATER MONITORING

The groundwater, hyporheic, and surface water monitoring wells were purged and sampled using a low flow methodology to prevent potential disturbance of the water quality. An inflatable packer system was used within the hyporheic/surface water zone monitoring wells to isolate a one foot interval within the uppermost portion of the water column to collect the surface water sample, and then to isolate a portion of the screen at the surface water/groundwater interface to collect the hyporheic water sample. Samples collected from the barrier monitoring network during December 2011 were analyzed for the dissolved phase constituents of concern. Field forms from this monitoring event are provided in Appendix C. Groundwater, hyporheic zone, and surface water analytical reports and data validation reports are included in Appendix D.

A summary of the groundwater results for constituents of concern are provided on Table 2-5. During the December 2011 monitoring event, volatile organic constituents of concern were not detected in any of the groundwater, hyporheic water, or surface water samples. Low level detections for arsenic (0.026 mg/L) and lead (0.013 mg/L) were reported in the sample from MW-136.

As reported in the first 2011 semiannual report, groundwater samples have also been collected and analyzed semiannually for monitored natural attenuation indicators during the June 2009, December 2009, May 2010, and November/December 2010 monitoring events. The intent of the natural attenuation monitoring program along the barrier wall was to collect data to define baseline conditions and then to make adjustments as warranted based on these initial results. However, quarterly dissolved phase analytical results demonstrate that there is not a dissolved phase or LNAPL source near the inboard or outboard portions of the barrier wall. Without the presence of a dissolved phase or LNAPL source, it is not expected that there will be any significant changes to the natural attenuation indicators as petrophyllic bacteria require a hydrocarbon source to proliferate and cause alterations to groundwater geochemistry.

A request to discontinue sampling and analysis for monitored natural attenuation indicators from the barrier wall network was sent to the USEPA via correspondence dated October 27, 2010. The USEPA requested additional groundwater samples be analyzed for the monitored natural attenuation indicators over a range of hydraulic conditions including during high-grade pumping from the facility groundwater production wells. Groundwater samples have been collected over a range of hydraulic conditions at the barrier monitoring network, ranging from 462.9 feet above mean sea level (ft-amsl) in September 2009 to 469.1 ft-amsl in March 2010. Additional samples were collected in December 2010 and analyzed for constituents of concern and monitored natural attenuation indicators during high-grade pumping. There were limited detections of the constituents of concern unrelated to the smear zone during the December 2010 event. Natural attenuation indicators showed that there was not any reduction in electron receptors (i.e., sulfate, iron, nitrate, etc.) by petrophyllic bacteria inboard of the barrier wall.

On June 13, 2011 Chevron again proposed to discontinue monitoring for natural attenuation indicators from the barrier wall network. The USEPA approved this request via correspondence dated December 1, 2011. Groundwater, hyporheic, and surface water samples will be collected and analyzed for dissolved phase constituents of concern on a semiannual basis for the next two years, annually for the following ten years, and biennially thereafter in accordance with the schedule within the *OMM Plan* (Trihydro 2007b). Groundwater samples will not be collected or analyzed for natural attenuation indicators until one or more volatile constituent is detected above the laboratory reporting limit at an inboard monitoring well on a consistent basis (two or more successive sampling events). Once this occurs, sampling and analysis for natural attenuation indicators will be resumed within the monitoring transect where dissolved phase constituents of concern were measured in accordance with the schedule described above.

2.6 VAPOR MONITORING

Soil vapor monitoring is conducted as part of the routine monitoring program associated with the final corrective measures program to: (1) confirm that there is not a completed pathway or an increase in incremental risk to residents in Hooven associated with intrusion of volatile constituents present in soil vapor that are associated with releases from the former refinery, (2) track remedial system effectiveness on reducing the mass of petroleum hydrocarbons present in the deep portions of the vadose zone, and (3) estimate natural smear zone depletion rates within the smear zone over the course of the final groundwater remedy. Soil vapor samples were collected from selected intervals within the nested monitoring wells in Hooven (VW-93, VW-96, VW-99, VW-128, and VW-129) in July 2011 prior to start-up of the HSVE system in accordance with the schedule established in the *RIP* (Trihydro 2007a) and *OMM Plan* (Trihydro 2007b). In addition, soil vapor samples were collected in September and October 2011 from the 10-, 20-, 30-, and 40-foot intervals in nested vapor monitoring wells VW-96 and VW-99 during operation of the HSVE system as stipulated within the USEPA AOC amendment dated June 23, 2010.

Field forms for the vapor monitoring activities conducted in July, September, and October 2011 are provided as Appendix F. Laboratory analytical reports for the soil vapor samples collected during each of these events are provided in Appendix G-1 and data validation reports for each of the analytical packages provided by the laboratory are included in Appendix G-2. It should be noted that a comprehensive summary of historical soil vapor monitoring results was presented in the *Hooven Vapor Site Conceptual Model Update, Chevron Cincinnati Facility, Hooven, Ohio* (*Hooven Vapor Update*, Trihydro 2010a). Historical soil vapor results collected prior to the second 2011 semiannual monitoring period are not included herein.

2.6.1 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 events conducted between July and October 2011 is provided on Table 2-3. In July 2011, prior to startup of the HSVE system the initial static pressure or vacuum measurements were between 0.0 and 0.5 inches of water, which is in the range that can be produced from wind and barometric pressure, with the exception of elevated vacuums reported in wells VW-20 and VW-21, and the 10-foot interval in nested well VW-18 on July 12, 2011. The increased vacuum observed in these probes may be associated with a decreasing water table during the time of the measurements. In September and October 2011, a vacuum was typically measured in the 10-, 20-, 30-, and 40- foot probes of well VW-96 during operation of the HSVE system. Pressure or vacuums below 0.05 were measured in the 10-, 20-, 30-, and 40- foot probes of well VW-99 with the exception of a 0.6 pressure in the 30-foot interval recorded on September 12, 2011.

2.6.2 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 2-3. Soil gas permeability within the nested probes (with the exception of the 5-foot intervals in nests VW-18 and VW-21) were between 1E-8 and 3E-7 square centimeters (cm^2) with specific capacities (flow rate per unit of vacuum applied) ranging from 1 to 38 cubic centimeters per second per inch of water column (cm^3/sec•in-H_2O), which are typical for medium to coarse grained sands. The 5-foot probes installed at nested wells VW-18 and VW-21 were installed within areas of compacted fill material with soil gas permeabilities more typical of fine grained sand and silt mixtures. It should be noted that soil gas permeability is directly related to moisture content within the sediment around the soil gas probe. Changes in the moisture content associated with infiltrating precipitation accounts for the variation in the permeability and specific capacity observed in an individual probe over time.

2.6.3 NESTED SOIL GAS ANALYTICAL RESULTS

A summary of the soil vapor analytical results for the nested monitoring wells is provided on Table 2-4. 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.

2.6.3.1 PETROLEUM RELATED CONSTITUENTS

During monitoring performed between July 2011 and October 2011, 15 of the 25 petroleum related constituents were detected in at least one of the samples collected from the nested soil vapor monitoring wells. Five of these constituents (1,2,4-trimethylbenzene, ethylbenzene, o-xylene, cyclohexane, and methyl cyclohexane) were detected at a frequency below 5%. Benzene, butane, heptane, hexane, m,p-xylene, 2,2,4-trimethylpentane, and 4-ethyltoluene occur at a slightly higher frequency of 6.3%. The remaining volatile petroleum related constituents including isopentane (8.3%), toluene (12.5%), and 1,3,5-trimethylbenzene (16.7%) occurred at a slightly greater frequency than other constituents.

The highest concentrations of petroleum related constituents were detected within the samples collected from the 55-foot interval of nested well VW-99 during the July 2011 monitoring event. Significantly lower concentrations at the 40-, 50-, and 55-foot intervals in well VW-96 were observed during this monitoring event. These intervals in both wells VW-96 and VW-99 are situated within the smear zone associated with releases from the former refinery and are representative of the vapor source.

During the July 2011 event, the concentrations of petroleum hydrocarbons measured above the vapor source within wells VW-96 and VW-99 decreased rapidly to the point where there were few reported detections above the 55-foot interval in either nested well. Volatile petroleum hydrocarbons were reported intermittently at low concentrations within the samples collected from nested wells VW-93 and VW-128 during the July 2011 monitoring event. These wells are located above portions of the smear zone which have been depleted by natural attenuation and remedial measures (VW-93) or above dissolved phase hydrocarbons (VW-128). Volatile petroleum hydrocarbons were not detected during this event within the samples collected from nested well VW-129, which is located beyond the lateral limits of petroleum hydrocarbons associated with the former refinery.

During the other two monitoring events performed in late-2011 while the HSVE system was operating, the majority of the petroleum hydrocarbons were reported as non-detect within the 10-, 20-, 30-, and 40-foot intervals within nested wells VW-96 and VW-99. It should be noted that concentrations were not elevated prior to start-up of the system within the shallow and intermediate intervals within these two nested wells and remained petroleum related hydrocarbons remained depleted irrespective of which line of the HSVE system was operating at the time the samples were collected.

2.6.3.2 SOLVENT RELATED CONSTITUENTS

There were six solvent related chemicals detected during monitoring conducted in the second half of 2011, of which only two were detected at frequencies greater than 5%: acetone (93.8%) and tetrachloroethane (18.8%). Acetone is ubiquitously used for residential and commercial purposes and is also considered a common laboratory contaminant, used for cleaning and preparation of samples within the laboratory. Tetrachloroethene was only reported in samples collected from nested well VW-99 during each of the monitoring events (irrespective of whether the HSVE was operating or shut down). This measured solvent is not associated with releases from the former refinery and is indicative of an alternate localized source beneath this portion of Hooven.

2.6.3.3 WATER TREATMENT RELATED AND OTHER CONSTITUENTS

Six of the 22 water treatment related and other chemicals were detected during the monitoring performed in the second half of 2011 with five constituents detected at a frequency greater than 5% including bromomethane (18.8%), dichlorodifluoromethane (10.4%), ethanol (18.8%), trichlorofluoromethane (8.3%), and chloroform (12.5%). Ethanol and chloroform were sporadically detected at low concentrations within each of the nests in Hooven during both operation and shut down of the HSVE system. Bromomethane was also detected at low concentrations in wells VW-96 and VW-99 irrespective of operations of the HSVE system. Trichlorofluoromethane was only reported in samples collected from nested well VW-129 while dichlorodifluoromethane was only measured in soil vapor samples collected from nested wells VW-128 and VW-129. Nested wells VW-128 and VW-129 are located in the central and western portions of Hooven outside of the distribution of petroleum-related hydrocarbons measured in soil vapor; therefore, an alternate source is suspected for these two constituents. Dichlorodifluoromethane and trichlorofluoromethane were historically used as freon within refrigerants and are ubiquitous in the environment. Freon use decreased in the 1980's after federal regulatory agencies banned its use due to detrimental effects on the ozone layer. Freons are commonly detected at elevated concentrations beneath landfills due to improper disposal practices.

2.6.3.4 FIXED GASES

Fixed gas concentrations including oxygen (O_2), carbon dioxide (CO_2), and methane (CH_4) were measured during purging of the nested probes to determine that steady state conditions had been achieved prior to the collection of a 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 F and the final O_2 and CO_2 concentrations measured from each probe before collecting the vapor sample for laboratory analysis are summarized on Table 2-3. The O_2, CO_2, and CH_4 results reported by the analytical laboratory are summarized on Table 2-4d. The O_2 and CO_2 concentrations recorded in the field were compared to the fixed gas results provided by the laboratory as a measure to validate the field results. Figures 2-10, 2-11, and 2-12 provide the correlation plots for O_2 and CO_2 measured during the July 2011 sampling event with the HSVE system off and the September and October events performed during operation of the HSVE system, respectively. There was good correlation between the field measurements and the laboratory reported concentrations of these two fixed gases during the July and October monitoring events. A leak within the equipment used to collect and monitor soil vapor during purging can be observed in the correlation plot for the September 2011 monitoring event. This leak resulted in elevated O_2 and reduced CO_2 in the field measurements compared to the laboratory results. This leak did not affect the final laboratory sample as the portion of the sample train which includes the equipment used during purging is isolated during collection of the final sample for laboratory analysis.

During the July 2011 sampling event, there was reduced O_2 and elevated CO_2 observed in the deepest probes in VW-96 (55-foot probes) and VW-99 (40-, 50-, and 55-foot probes). However, O_2 concentrations remained above the anoxic threshold (approximately 2%) throughout the vadose zone at these two locations, resulting in significant reduction of petroleum hydrocarbon concentrations to non-detect levels immediately above the vapor source in wells VW-96 and 5-feet above the smear zone in nested well VW-99 (more than 40 feet below basements in overlying structures). The effects of operating the HSVE system in early 2011 were still observed within the shallow and intermediate portions of the vadose zone where alternate sources present near nested vapor wells VW-96 and VW-99 are known to consume available O_2 at shallow depths limiting transport of O_2 to the intermediate and deeper portions of the vadose zone (Trihydro 2010a).

There was very little reduction in O_2 concentrations with depth observed in the vertical profiles for nested vapor monitoring well VW-128 (located above the dissolved phase plume) and well VW-93 (located above portions of the smear zone which have been depleted via natural attenuation and remedial measures). It should be noted that a similar reduction in O_2 concentrations was also observed in the vertical profile for well VW-129 (located in a background area outside the lateral extent of petroleum hydrocarbons associated with releases from the former refinery) during the July 2011 monitoring event.

O_2 concentrations rebounded during monitoring performed in September within nests VW-96 and VW-99 following start-up of the HSVE system and were reported near atmospheric conditions by October 2011. These fixed gases remained at near atmospheric levels throughout the vadose zone irrespective of which line of the system was being operated.

3.0 INTERPRETATION

Data collected during the second half of 2011 and included herein continue to demonstrate that intrinsic processes are degrading petroleum hydrocarbons in the smear zone. In general, natural attenuation occurs as constituents present in the 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., USEPA 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 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 (Section 3.3) demonstrate indirectly that 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 over the first five years of the groundwater remedy were summarized in the *Five-Year Groundwater CMI Review* (Trihydro 2011b). Updates to these lines of evidence for which data was collected during the second half of 2011 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 2007b).

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 2009a), 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 2011 continue to support that the smear zone is stable based on the laser induced fluorescence measurements in the three ROST monitoring transects conducted between December 19 and 20, 2011. Additionally, LNAPL was not measured in any of the sentinel or point of compliance monitoring wells installed in the Southwest Quad. Fluid level gauging within the performance monitoring network installed along the west bank of the Great Miami River also confirmed 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%. 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). Additionally, soil core samples were collected on the facility in November 2008 and soil saturations calculated using this data also demonstrated that LNAPL saturations within the upper, middle, and lower portions of the smear zone were below residual values. No soil cores or LNAPL samples were collected during the second half of 2011; therefore, an assessment of smear zone saturations will be provided upon collection of additional data during subsequent semiannual monitoring periods.

3.1.2 DISSOLVED PHASE

Dissolved phase constituents of concern (including benzene, toluene, ethylbenzene, xylene, chlorobenzene, dissolved arsenic, and dissolved lead) have not been measured within routine samples collected from the sentinel and point of compliance groundwater monitoring network with the exception of samples collected following flood events as described in the *First 2011 Semiannual Monitoring Report, Chevron Cincinnati Facility, Hooven, Ohio* (Trihydro 2012a) and the *Five-Year Groundwater CMI Review* (Trihydro 2011b). In addition, dissolved phase constituents have not been measured in groundwater or surface water at concentrations exceeding remedial goals along the Great Miami River. Arsenic and lead have been sporadically detected in groundwater collected from monitoring wells located throughout the Southwest Quad and along the river bank over the more than two decades of monitoring and are generally indicative of background metals measured in soils in Ohio 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).

3.1.3 VAPOR PHASE

In order to evaluate protectiveness of human health from migration of deep soil vapors into structures located in Hooven and the Southwest Quad, the data from the nested wells is compared to conservative risk based screening levels. Screening levels are concentrations that are sufficiently low that any results below these can safely be considered to pose no significant risk. They 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.

A screening level evaluation was not conducted for the buildings on the refinery as there are few buildings situated over the smear zone. Mitigation measures have been incorporated into those structures overlying the smear zone where there is the potential for volatile constituents to migrate into the structure. Proposed environmental covenants for any parcels redeveloped on the former refinery require mitigation measures including passive vapor barriers, and if necessary sub-slab depressurization or venting systems to be incorporated into the building design.

Table 3-1 provides the screening level evaluation for gasoline related constituents measured in soil vapor samples collected from the nested wells located in Hooven during the second half of 2011. The residential indoor air screening levels (assuming a lifetime incremental cancer risk of 1E-5 for carcinogenic constituents and a Hazard Quotient of 1 for non-carcinogenic constituents) provided on the USEPA Regional Screening Level (RSL) tables (USEPA 2009a) were divided by semi-site specific attenuation factors from Figure 3a of the USEPA Office of Solid Waste and Emergency Response (OSWER) *Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils (OSWER Draft VI Guidance*, USEPA 2002) to derive soil vapor screening levels (SVSLs). This approach for defining the SVSLs was developed in cooperation with USEPA Region V risk assessment staff and has been presented in previously submitted semiannual monitoring reports. Application of the attenuation factors from Figure 3a of the *OSWER Draft VI Guidance* is conservative for this evaluation, since these do not account for attenuation due to aerobic biodegradation, which is the chief mechanism limiting vapor transport beneath Hooven.

The November 2011 residential RSLs are used to define the SVSLs, as these were developed with the updates to the toxicity data for inhalation of many petroleum and non-petroleum related constituents, and as such represent the most current understanding of the health effects of inhaling the petroleum related constituents discussed herein. In December 2009, the USEPA Office of Inspector General identified that the indoor air screening levels provided in the *OSWER Draft VI Guidance* were outdated and may impede evaluation of the VI pathway (USEPA 2009b). In general, the RSLs are comparable or lower (more protective) than the screening levels provided within the *OSWER Draft VI Guidance*, with the exception of toluene, hexane, and 1,3-butadiene, which were higher. Four constituents (the alkylbenzenes [n-propyl-, n-butyl-, and sec-butyl-] and methyl cyclohexane) had screening levels in the *OSWER Draft VI Guidance* for which the USEPA did not calculate RSLs, as the most recent toxicity data did not support inclusion of these constituents as an inhalation risk.

It is worth noting that screening levels were not provided in the *OSWER Draft VI Guidance* or included as part of the RSL tables for 2,2,4-trimethylpentane. The constituent 2,2,4-trimethylpentane is a component of gasoline and has been detected in soil gas samples collected from the vapor source above the smear zone since 2005. In July 2007, the USEPA summarized the available hazard and dose-response assessment information for 2,2,4-trimethylpentane in the document titled *Toxicological Review of 2,2,4-Trimethylpentane* (USEPA 2007). This report is intended as a thorough review of the scientific understanding regarding the toxicology of 2,2,4-trimethylpentane with the stated purpose of providing "scientific support and rationale for hazard and dose-response assessment in the Integrated Risk Information System pertaining to chronic exposure." In other words, it specifically addressed the task of developing defendable reference concentrations (rfCs) and reference doses (rfDs) for chronic exposure to 2,2,4-trimethylpentane. This report was prepared by independent toxicologists and was subjected to peer review by both USEPA-internal and external toxicologists prior to finalization. The final version reflects an achieved common understanding among the multiple USEPA branches and concludes that there is insufficient data to develop defendable rfCs or rfDs for 2,2,4-trimethylpentane. As such, a screening evaluation for 2,2,4-trimethylpentane is not provided herein.

The screening level evaluation was applied to the deep soil vapor samples collected from 20 ft-bgs or greater in Hooven. The data collected from the shallow probes was not evaluated because vapor concentrations at depths less than 20 ft-bgs are attributable to alternate, surface-derived sources of petroleum hydrocarbons. 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.

During the monitoring events performed during the second half of 2011 there were no detections that exceeded the SVSLs in any of the samples collected from nested monitoring wells VW-93, VW-96, VW-99, VW-128, and VW-129. It should be noted that the laboratory detection limit for 1,2-dibromoethane exceeded the depth-specific SVSL in each of the deep soil gas samples collected from the nested wells in Hooven in July 2011. 1,2-dibromomethane has not been detected in any of the deep vapor samples collected across the refinery or Hooven during this or previous monitoring events. The soil vapor monitoring results collected in 2011 continue to demonstrate that there is not an unacceptable risk to the inhabitants in structures overlying the smear zone in Hooven.

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 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 DISSOLVED PHASE CONSTITUENT TRENDS

The distribution of total benzene, toluene, ethylbenzene, and xylenes (BTEX) in groundwater for samples collected during the second 2011 semiannual monitoring period are displayed on Figure 3-1. 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. 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, hydrocarbon release, site reuse, or other conditions unrelated to attenuation processes and need to be evaluated in the context of other lines of evidence.

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. These area averages are less sensitive to variations within individual wells that can sometimes complicate temporal analyses and provide an understanding of natural attenuation processes affecting the smear zone as a whole. 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.

Individual well and area-wide trend analyses performed using data collected from monitoring wells across the smear zone during previous semiannual monitoring events have demonstrated a first order degradation rate for benzene associated with both natural attenuation and engineered mass removal, with preferential depletion along the smear zone margins (i.e., outside-in weathering). Historically, groundwater samples are collected from a set of interior and supplemental groundwater monitoring wells (L-1RR, L-3R, MW-17, MW-21, MW-22, MW-38, MW-64, MW-81S, MW-85S, MW-93S, MW-99S, and MW-115S) for completing these temporal analyses. As groundwater samples were only collected from two of these interior and supplemental wells during the second 2011 monitoring period, per the schedule established in the *OMM Plan* (Trihydro 2007b), these trend analyses were not updated for this reporting period. However, the trend analyses will be updated as part of the first 2012 semiannual monitoring report as groundwater samples are scheduled to be collected across the interior and supplemental monitoring networks.

3.2.2 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.

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 3-2 through 3-4 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 15 years. 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 decrease in concentrations is partially attributable to operation of groundwater, LNAPL, and soil vapor recovery systems in Hooven beginning in 1999.

Reduction in the total volatile petroleum hydrocarbons (TVPH) and benzene concentrations has been more significant in well VW-93 compared to wells VW-96 and VW-99. As shown on Table 4-4, Line No. 2 (the closest extraction line to nested vapor well VW-93) has been run substantially less than Lines No. 1 and No. 3 (closest extractions lines near wells VW-96 and VW-99 respectively). This may be an indication that operation of the HSVE system alone does not fully account for the reduction of petroleum related constituents in the smear zone beneath Hooven. Alternate sources of petroleum hydrocarbons have not been observed in the soil vapor profiles from well VW-93; therefore, O_2 transport and aerobic biodegradation is not limited within the deeper portions of the vadose zone near this nested soil vapor monitoring well.

There was a significant increase in the TVPH concentrations in the vapor source (i.e., deepest sample) reported in wells VW-96 and VW-99 between September 2008 and October 2009 associated with extended shutdown of the HSVE system for more than 22 months during the USEPA investigation of the vapor intrusion pathway beneath Hooven. This trend was magnified during the September/October 2009 event by operation of the high-grade system. Induced depression of the water table during high-grade operation exposed the deepest portions of the smear zone containing the highest mole fraction of volatile petroleum hydrocarbons (Trihydro 2009b). This trend was again reversed with operation of the HSVE system during 2009, 2010, and 2011.

3.3 HYDROGEOCHEMICAL 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 constituents). 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, naturally occurring inorganic geochemical species serve as electron acceptors and are reduced during microbial degradation (i.e., oxidation) of petroleum hydrocarbons.

3.3.1 DISSOLVED PHASE CONSTITUENTS

As previously described, hydrogeochemical analyses were not performed during the second half of 2011 per the schedule established within the *OMM Plan* (Trihydro 2007b); and; therefore, these analyses were not updated or included herein. The natural attenuation indicators are scheduled to be collected again during the first semiannual 2012 monitoring period. Tables and charts depicting the spatial distribution of these indicators will be updated and presented as part of the first 2012 semiannual monitoring report.

3.3.2 VAPOR PHASE CONSTITUENTS

Aerobic degradation of petroleum hydrocarbons within the vadose zone occurs (often in a relatively thin zone) where the concentrations of O_2 and volatile constituents are optimal for the growth of petrophyllic bacteria. Aerobic degradation has the potential to reduce volatile petroleum related constituent 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 and O_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 (approaching atmospheric levels) throughout the unsaturated zone.

- Where there is a significant hydrocarbon source at depth and aerobic biodegradation of volatile constituents, the hydrocarbon vapor profile will show a decrease in hydrocarbon concentration with increasing distance above the source that is more rapid than that expected due to diffusion alone. The petroleum hydrocarbon 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. Methane is often measured within this zone. 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 (Johnson et al. 1999). It is not uncommon to see O_2 concentrations decrease from atmospheric levels (20.9%) to 1-2% (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. These profiles may vary if there are significant stratigraphic layers of different geologic materials, which is not the case beneath Hooven.
- For cases where there is a release of petroleum hydrocarbons at or near the ground surface that is unrelated to historical releases from the former refinery (referred to herein as an alternate source) that has migrated into the unsaturated zone, the vertical profiles will be different than the case of a single source at the bottom of the unsaturated zone. If the alternate source is minor, O_2 depletion may only be a few percent below atmospheric levels and vapor concentrations may be reduced to non-detectable or background levels within a few feet of the alternate source. However, where the alternate source is more significant, O_2 concentrations may be fully consumed and aerobic degradation may be limited, in which case, hydrocarbon vapors would be more persistent. Consumption of O_2 by an alternate source would also limit the supply of O_2 to deeper portions of the vadose zone, thereby reducing the effectiveness of aerobic biodegradation in deeper portions of the vadose zone where the vapor source is present. If this occurs, vapors from the source at depth diffusing upward and those associated with the alternate source diffusing downward may comingle at intermediate depths. Depending on the composition of the alternate source (i.e., petroleum versus non-petroleum) it may be difficult to distinguish whether the vapors are derived from shallow or deep sources. Additionally, the presence of alternate sources and preferential depletion of O_2 at shallow depths in the vadose zone may allow migration of vapors from the source at depth to shallower portions of the vadose zone than would otherwise occur if the alternate source was not present.

Vertical profiles for TVPH and O_2 were created for the nested vapor wells for monitoring events conducted during the second 2011 semiannual monitoring period, as described in the subsections below. The vertical soil vapor profiles were grouped into three general categories, based on the location of the nested vapor monitoring wells:

1. Overlying LNAPL, including nested wells VW-93 (Figure 3-4), VW-96 (Figure 3-5), and VW-99 (Figure 3-6)
2. Overlying dissolved phase petroleum hydrocarbons, as represented by nested well VW-128 (Figure 3-4)
3. Background areas outside the LNAPL and dissolved phase hydrocarbons, as represented by nested well VW-129 (Figure 3-4)

Profiles were constructed for TVPH, which is a mixture of hydrocarbon constituents whose composition can vary significantly both spatially (across depth intervals in each nest) and temporally (across sample events). TVPH was estimated by summing the mass of the detected volatile petroleum related hydrocarbon constituents shown in Table 2-4a. For constituents that were reported as “non-detect”, half the detection limit was used as a surrogate in the estimation of the TVPH concentration. CH_4 was not included in calculation of the TVPH values.

3.3.2.1 NESTED WELLS OVERLYING LNAPL

Vapor profiles for data collected in July 2011 from nested wells VW-96 and VW-99 show a rapid decrease in vapor concentrations from the source at 55 ft-bgs to 50 ft-bgs. A corresponding consumption of O_2 is noted in the fixed gas profiles at these depths, indicating that aerobic degradation is the primary mechanism for these reductions. A slight increase in vapor concentrations is observed in the TVPH profiles at 20 ft-bgs in well VW-96 during the October 2011 event, which is related to a previously identified alternate sources near this nested vapor monitoring well. Increasing concentration trends within the intermediate portions of the vadose zone is not consistent with vapor diffusion from a single source at the water table. Diffusion occurs as a result of a concentration gradient and results in movement of chemicals from areas of high concentration to areas of low concentration. The reverse concentration gradient at 20 ft-bgs is consistent with the presence of an alternate source of petroleum hydrocarbons that may have migrated downward into the vadose zone from a release at or near ground surface. The influence of alternate sources near well VW-99 were not observed during monitoring in the second half of 2011, possibly as a result of operation of the HSVE system in January and February.

The profiles for data collected in July 2011 for nested well VW-93 are consistent with those from a limited hydrocarbon source (i.e., concentrations near background or not detected throughout the profile). These results are similar with previous sampling events conducted since 2005. It is worth noting that historically the concentrations of TVPH measured above the smear zone in this well were similar to those measured in wells VW-96 and VW-99 and much higher than those observed since 2005. These data support that the vapor source concentrations have decreased dramatically due to the combined effects of aerobic biodegradation and corrective measures system operation, which is similar to trends observed in the LNAPL and soil core samples collected from this well.

3.3.2.2 NESTED WELLS OVERLYING DISSOLVED HYDROCARBONS

Nested vapor monitoring well VW-128 is located over the distribution of dissolved phase hydrocarbons but outside the area of residual LNAPL present in the smear zone. The TVPH profile for this well is consistent with cases where there is a limited hydrocarbon source at depth. The TVPH concentrations were non-detect throughout the vadose zone and there was a slight reduction in the O_2 concentrations with depth across the vadose zone.

3.3.2.3 NESTED WELLS OUTSIDE OF LNAPL AND DISSOLVED PHASE HYDROCARBONS

Vertical profiles of TVPH and fixed gases for nested vapor well VW-129 located outside the area of petroleum hydrocarbons associated with the former refinery show that there were not any reported detections of TVPH within any of the vapor samples and O_2 concentrations remained constant throughout the vadose zone.

3.4 SUMMARY OF LINES OF EVIDENCE SUPPORTING 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 such as CH_4 within the vadose zone.
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.

4.0 HIGH-GRADE RECOVERY

The high-grade pumping component of the groundwater remedy focuses on seasonal source removal of LNAPL from the lower reaches of the smear zone where the saturations remain the greatest. The purpose of high-grade recovery is to (1) further reduce LNAPL mobility at the lowest ambient water table conditions and (2) remove additional LNAPL mass from the smear zone. A summary of the high-grade recovery event conducted during the second half of 2011 is provided in this section.

4.1 2011 HIGH-GRADE SUMMARY

High-grade pumping began on August 30, 2011 with recovery from production well PROD_25 and concluded on November 7, 2011. As described in Section 2.1, transducers were deployed within a monitoring network across the high-grade area to collect continuous drawdown data. Groundwater elevation data collected from the transducers are provided in Appendix A. In addition, fluid levels were gauged within an expanded monitoring network at least once each week to evaluate changes in the LNAPL and groundwater elevations in response to high-grade pumping. Manual fluid level measurements are provided in Appendix B. Groundwater and LNAPL extraction rates from production well PROD_25 were compared weekly against operational logs at the biologically enhanced GAC and recovery volumes measured in Tank No. 291 and Tank No. 50 throughout the high-grade event. Table 4-1 provides a weekly summary of LNAPL recovery and Table 4-2 provides a summary of the daily groundwater extraction rate and fluid levels measured within production well PROD_25 during the 2011 high-grade event.

4.1.1 LNAPL RECOVERY

The 2011 high-grade event focused on additional LNAPL recovery within the central portion of the smear zone. Groundwater extraction rates were sustained between 1,100 and 2,600 gallons per minute (gpm) from start up through November 7, 2011. Figure 4-1 presents a summary of the LNAPL recovery and groundwater extraction rates measured in production well PROD_25, as well as groundwater drawdown and LNAPL thicknesses observed in proximal observation wells (MW-18R, MW-40, MW-56, MW-57, and MW-79) during the 2011 event. As shown on Figure 4-1 even during maximal drawdown, only minimal LNAPL thicknesses (between 0.01 and 0.02 feet) developed for brief periods in some observation wells. Beginning in early November, there was an increase in the ambient groundwater levels (measured using monitoring well MW-21), located outside of the influence of the production well. The high-grade recovery event was discontinued on November 7, 2011 due to the low rate of LNAPL recovery combined with an increasing ambient water table.

Table 4-3 provides a summary of cumulative and daily LNAPL recovery rates, average groundwater extraction rates, as well as the LNAPL removal efficiency for the primary production wells used during the 2007, 2009, 2010, and 2011 high-grade recovery events. During the 2011 event, LNAPL was recovered at an average rate of 15 gallons per day (gpd) from production well PROD_25, with an average of 3,067,900 gallons of groundwater recovered each day, resulting in a LNAPL recovery efficiency of 4.8 gallons of LNAPL recovered for every million gallons of groundwater removed from the aquifer. For comparison, the LNAPL recovery efficiency for high-grade pumping performed during the extended 2010 high-grade event at PROD_25 was 280 gallons of LNAPL removed per million gallons of groundwater. The substantially lower recovery efficiency observed during the 2011 event can be attributed to increasing ambient water table elevations observed in groundwater monitoring well MW-21 following start-up of the event, as well as the high effectiveness of the previous year's recovery completed in the Central Area, which likely reduced LNAPL saturations within the upper portions of the smear zone.

4.1.2 REVISED TRIGGER ELEVATIONS

LNAPL recovery is undertaken during low water table conditions, based on historical trends and field observations during seasonal dry periods. LNAPL appears in wells and is recoverable as a function of water table elevations (triggers) as they relate to the smear zone. The water table must be low enough to expose the approximate bottom third of the smear zone before LNAPL can be recovered. The goal of high-grade pumping is to use focused groundwater extraction to maximally expose the smear zone and recover LNAPL during low water table conditions. Maximal exposure of the smear zone occurs when the water table is drawn down below the previous minimum groundwater elevation. Thus, the minimum historical groundwater elevation within a well is used to establish targets for initiating high-grade recovery. With each successful high-grade event, the depth of maximum smear zone exposure will be lowered, thereby establishing new, lower triggers for starting high-grade recovery over subsequent events. The trigger for initiating high-grade recovery is determined via the following equation:

$$\text{Pumping Trigger} = PT_i + s_{i,j}$$

Where:

PT_i = Pumping target at monitoring well location i; value is the historical minimum water table elevation in feet above mean sea level (ft-amsl)

$s_{i,j}$ = Expected drawdown at monitoring well location i caused by high-grade pumping at production well j

As noted by the subscripts in the above equation, pumping triggers are specific to the monitoring location and the production well. Prior to each high-grade event, new pumping triggers will be calculated by analyzing the fluid level data from the preceding event. New triggers will be established at locations where the water table was lowered to a new minimum elevation. Otherwise, triggers from the preceding year will be carried forward. The expected drawdown will be based on fluid level monitoring data collected during previous high-grade pumping events.

As the water table was not depressed to a new minimum elevation, trigger elevations for initiating high-grade pumping using production wells PROD_25 were not updated. The next high-grade event will be conducted using the trigger levels established for production well PROD_25 and reported in the *Five-Year Groundwater CMI Review* (Trihydro 2011b).

4.2 BIOLOGICAL ENHANCED GAC SYSTEM OPERATION

The biologically enhanced GAC is designed to remove dissolved phase petroleum hydrocarbons, primarily BTEX from extracted groundwater. Extracted groundwater is transmitted to the GAC for treatment from one or more of the production wells located at the Facility. The GAC treatment process is discussed in further detail in the *OMM Plan* (Trihydro 2007b).

Following treatment in the GAC, groundwater is transmitted to the sedimentation pond and constructed wetlands prior to discharge to the Great Miami River through the wetlands outfall. Groundwater samples are collected weekly at the wetlands outfall to evaluate compliance with National Pollutant Discharge Elimination System (NPDES) discharge limits. A composite groundwater sample was collected each week using an automated sampler, which collects a sample aliquot every 45 minutes over a 24-hour period. Composite samples were analyzed to evaluate compliance with discharge requirements set forth in the Facility’s NPDES permit. Groundwater samples are analyzed for pH, biological oxygen demand, total suspended solids, oil and grease, total lead, as well as dissolved phase BTEX, total phenols, and 1,2-dichloropropane. Monthly and daily concentration and loading limits are established for these constituents. None of the effluent limits were exceeded in the weekly samples collected from the outfall during 2011.

4.3 HSVE SYSTEM OPERATION

Chevron installed the HSVE system as an interim measure for reducing petroleum hydrocarbon mass beneath Hooven (ERM 1999). Pilot testing to determine the effectiveness of soil vapor extraction technology was conducted in June and November 1998. Based upon the results of the pilot testing and completion of a remedial options analysis in June 1999, it was determined that soil vapor extraction presented the best available technology for removing volatile hydrocarbons, while minimizing disruptions to residents in Hooven.

The HSVE system is comprised of three six-inch diameter, Schedule 40 carbon steel pipes that extend from the western edge of the facility beneath State Route 128 continuing under Hooven, coincident with the distribution of refinery related hydrocarbons. Line No. 1 extends westward beneath Hooven Avenue, Line No. 2 is located beneath Brotherhood Avenue curving to the south towards Hooven Elementary School, and Line No. 3 is located beneath Ohio Street. The well screens for each of the lines were installed approximately 5-feet above the 15 year maximum groundwater elevation at the time of installation (478 ft-amsl for Line Nos. 1 and 2 and 475 ft-amsl for Line No. 3).

Pilot test, modeling, tracer test, and performance monitoring results indicate a radius of influence of the HSVE system of at least 125 and likely more than 450 feet from the extraction lines (Chevron 2010b). No structure in Hooven, situated over the distribution of petroleum hydrocarbons associated with releases from the former refinery, is more than 200 feet from one of the HSVE extraction lines, with the exception of a single residence located approximately 250 feet north of Line No. 3. Therefore, operation of the HSVE system affects soil vapor conditions within the deeper portions of the vadose zone throughout portions of Hooven overlying the smear zone.

The system commenced operation in November 1999 following installation of HSVE Line No. 1. Lines No. 2 and No. 3 were installed in 2000 and brought online during the first quarter 2001. Currently, operation of the HSVE occurs in accordance with the USEPA AOC amendment dated June 23, 2010, which states that the system will be operated upon completion of soil vapor monitoring in the 10-, 20-, 30, and 40-foot intervals in nested wells VW-96 and VW-99 once a groundwater elevation of 465 ft-amsl is reached in monitoring well MW-96. Seasonal operation of the HSVE system is terminated once groundwater elevations rebound above the trigger elevation in monitoring well MW-96.

4.3.1 2011 OPERATIONS SUMMARY

As summarized on Table 4-4, during the 2011 high-grade event the HSVE system was operated by cycling two extraction lines: Line No. 2 operated for 37 days and Line No. 3 for 29 days. Approximately 5,600 pounds of volatile constituents was recovered via operation of the HSVE system during the high-grade event. The estimated hydrocarbon mass removed from the system is calculated based upon the concentration of total petroleum hydrocarbons and CH_4 reported in the influent vapor samples, average flow rate recorded at the wellhead, and hours of operation over the reporting period.

Operational data is collected at each of the process lines during operation of the HSVE system including the rate of airflow and vacuum, as well as the fixed gas concentrations including O_2, CO_2, CH_4, total organic vapors, and the lower explosive limit. Table 4-5 presents a summary of the operational monitoring data recorded at each of the extraction lines. In general, during operation of each extraction line, O_2 concentrations would increase over time within the influent, with a corresponding decrease in CO_2, CH_4, total organic vapors, and the lower explosive limit. Combined influent and effluent vapor samples were collected monthly to demonstrate compliance with the Hamilton County Permit to Operate. The compliance monitoring data is compared to permitted operational limits on a quarterly and semiannual basis. Table 4-6 presents a summary of compliance monitoring data collected from the system during operation in the second half of 2011, as well as a summary of the calculated volatile hydrocarbon extraction and emission rates (reported in pounds per hour, pounds per day, and tons per year). Monthly emission rates were below the allowable limits of 6.25 pounds per hour. The average emission rate was approximately 1.4 pounds per hour during operation of the system in late 2011.

Figure 4-2 presents the estimated organic carbon removed beneath Hooven via operation of the HSVE system since November 1999, as well as the benzene and total petroleum hydrocarbon concentrations in the influent. More than 600,300 pounds of petroleum hydrocarbons have been removed from the smear zone beneath Hooven since 1999. The HSVE system was designed to remove volatile petroleum hydrocarbons at a high rate initially, with an expectation that the mass removal rate would gradually diminish as the volatile petroleum hydrocarbons within the smear zone were depleted, at which time the system would be operated intermittently and ultimately shut down. It's anticipated that when the system is ready to be permanently shut down, the remaining hydrocarbon mass within the influence of the system would diminish to a level where continued operation does not result in reduction of soil vapor concentrations beyond those observed via aerobic biodegradation alone, as can be observed in the vapor source concentration trends for nested soil vapor monitoring well VW-93 (Figure 3-2). However, in some portions of Hooven, volatile petroleum hydrocarbon concentrations have persisted in the smear zone, despite operation of the HSVE system. This may be explained by alternate sources of petroleum hydrocarbons identified in the vadose zone near these locations, as discussed in the *Hooven Vapor SCM Update* (Trihydro 2010a). Aerobic biodegradation of these alternate petroleum hydrocarbon sources in the shallower portions of the subsurface preferentially utilizes O_2. As such, O_2 transport to deeper depths where hydrocarbons from the former refinery are present at the water table is limited; therefore decreasing natural attenuation within the smear zone. This can be observed in the vapor source trends for wells VW-96 and VW-99 (Figures 3-3 and 3-4). In portions of Hooven where alternate sources of hydrocarbons are present at shallower depths, the HSVE system not only removes volatile petroleum hydrocarbons, but also advectively transports O_2 to the deepest portions of the vadose zone where it would otherwise not be present. Aerobic biodegradation, and not source removal, may be the primary mechanism degrading the volatile petroleum hydrocarbons present in the smear zone, hence the difference in vapor source concentrations observed in vapor well VW-93 compared to wells VW-96 and VW-99 since 1999.

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. Due to vapor probes being submerged, soil vapor samples were not collected in Gulf Park during the second half of 2011 and therefore evaluation of soil vapor data is not included herein.

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 O_2 to sustain aerobic microbial activity. Airflow is injected at rates designed to maximize O_2 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 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 July 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 2011. As shown, groundwater elevations were generally below the trigger levels within wells GPW-5S and TH-2 from mid-July through mid-November 2011.

The bioventing system at Gulf Park was operated continuously from July 15 through November 15, 2011. 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 performed during the biovent system in the second half of 2011 consisted of:

- Recording operational parameters (pressure, flow rate, and temperature) periodically at the process blower in order to document the blower performance.
- Measuring air flow parameters in each of the biovent wells weekly in order to document the amount of air delivered to the subsurface through each injection well.
- Gauging fluid levels within the system trigger wells (GPW-5S and TH-2) on a weekly basis to determine the schedule for system startup and shutdown.

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; whereas 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 was measured using a digital manometer and injection air temperature measured using a 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 the 2011 operational period, 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 335,569,000 standard cubic feet of process air was injected into the expanded biovent system area. Biovent well performance measurements, including dates and time of operation, are presented in Appendix H.

5.1.2 GROUNDWATER MONITORING RESULTS

Groundwater samples were collected from the shallow monitoring wells (GPW-1S through GPW-5S, TH-1S, TH-2, and TH-3) and intermediate groundwater monitoring wells (GPW-1I, GPW-2I, GPW-3I and TH-1I) in July 2011 for analysis of the dissolved phase constituents of concern. Monitored natural attenuation parameters were also analyzed in groundwater samples collected from each of the shallow monitoring wells. The field forms for groundwater samples collected in Gulf Park are provided in Appendix C. Groundwater analytical and data validation reports for samples collected in the second half of 2011 are included in Appendix D.

Table 5-1 presents a summary of the constituents of concern measured in groundwater samples collected between 2006 and 2011. Concentrations of the volatile constituents of concern were only detected in samples collected from TH-1S and TH-2 in July 2011. Dissolved phase concentrations of benzene and ethylbenzene exceeded the remedial goals (i.e., MCLs) in one or more samples collected from these two wells. Monitoring well TH-2 is situated at the southern limits of the biovent system and well TH-1S is located approximately 100 feet south of the nearest air injection point.

A comparison of total BTEX versus time for groundwater samples collected from shallow monitoring wells GPW-1S through GPW-5S is provided on Figure 5-3. For these GPW wells, the last significant detection (i.e., greater than 0.001 mg/L) of total BTEX in groundwater was reported in November 2005. The overall decrease in total BTEX concentrations observed in these wells installed across Gulf Park is attributable to a combination of intrinsic biodegradation and historic biovent system operations.

The total dissolved phase BTEX concentration compared to the groundwater elevation over time for monitoring wells TH-1S and TH-2 is provided on Figures 5-4 and 5-5, respectively. An overall decreasing trend has been observed in dissolved phase BTEX concentrations measured in well TH-2. This decrease is attributed to both operation of the biovent system and natural attenuation processes within the smear zone beneath this portion of the Park. Concentrations of total BTEX measured in groundwater samples collected from well TH-1S do not exhibit a clear decreasing trend with total BTEX concentrations exhibiting weak correlation with water table fluctuations.

Dissolved phase natural attenuation indicators were analyzed in the shallow wells during the July 2011 monitoring event and are summarized on Table 5-2. In addition, the spatial distribution of oxidizers and attenuation by-products measured during the second 2011 semiannual monitoring period is displayed on Figure 5-6. Electron acceptors including nitrate and sulfate were reported at greater concentrations within the up-gradient monitoring well TH-3 compared to concentrations measured in wells TH-1S and TH-2, situated within the area of residual hydrocarbons beneath the Park. A rebound in the nitrate and sulfate concentrations was observed within the down-gradient monitoring well GPW-2S. In general, the spatial distribution of reduced species including dissolved iron, manganese, and CH_4 show a direct relationship with total BTEX in groundwater beneath Gulf Park, with low concentrations measured in up-gradient well TH-3 and an increase of these attenuation by-products measured across the distribution of petroleum hydrocarbons present beneath the Park. These attenuation by-products generally decrease down-gradient of the smear zone in samples collected from monitoring well GPW-2S.

Figure 5-7 shows the concentration of total BTEX versus distance through the centerline of the smear zone with a comparison to oxidizer (nitrate and sulfate) and attenuation by-product (ferrous iron, manganese, and CH_4) concentrations. It should be noted that only monitoring wells GPW-2S, GPW-5S, TH-1S, TH-2, and TH-3 were utilized for this centerline analysis, with monitoring well TH-1S located approximately 180 feet from the centerline depicted on Figure 5-6. Anaerobic degradation of each of the preferred electron acceptors is occurring across the smear zone with utilization of sulfate and nitrate and generation of reduced species of manganese and CH_4 across the distribution of petroleum hydrocarbons associated with the historic pipeline release. The nitrate and sulfate concentrations rebound, and the ferrous iron and CH_4 concentrations decline down-gradient of the distribution of petroleum hydrocarbons associated with the release.

5.2 BARRIER WALL INSTALLATION AND PERFORMANCE MONITORING

In order to isolate petroleum hydrocarbons present in the smear zone along the east bank of the Great Miami River in Gulf Park, a partially penetrating sheet pile barrier and river bank stabilization measures were installed along the northern portion of the smear zone during the second half of 2009. The sheet pile barrier placement was selected based on smear zone morphology with the objective of eliminating potential petroleum hydrocarbon flux towards the river. A summary of the sheet pile installation and river bank stabilization measures performed along the northern transect were presented in the *Second 2009 Semiannual Monitoring Report, Chevron Cincinnati Facility, Hooven, Ohio* (Trihydro 2010b). A second section of the sheet pile wall and bank stabilization measures were proposed along the southern transect in the Park. Installation and stabilization measures were not completed in 2009 along the southern transect due to refusal of a third-party property owner to allow access to this portion of the river bank. These access issues were resolved and the installation of the southern barrier was performed in the second half of 2011. A summary of the construction activities is provided in Section 5.3, below.

5.2.1 NORTHERN BARRIER WALL GROUNDWATER MONITORING RESULTS

Two groundwater monitoring wells were installed along the northern section of the barrier wall to monitor the effectiveness of the bank stabilization measures. The wells are monitored according to the procedures identified for Gulf Park in the *OMM Plan* (Trihydro 2007b). The two wells were constructed near the center of the barrier wall, with one well on the inboard and one on the outboard side of the wall (Figure 5-1). Groundwater analytical results for the dissolved phase constituents of concern are provided on Table 5-3. No constituents of concern were detected in either the inboard (GPBW-1) or outboard (GPBW-2) monitoring wells installed along the northern barrier. These results indicate that dissolved phase petroleum hydrocarbons present in the smear zone beneath the Park have not encroached upon the northern transect of the barrier wall and there is no dissolved phase flux into the Great Miami River.

5.2.2 SOUTHERN BANK STABILIZATION AND BARRIER CONSTRUCTION

On February 28, 2007, Chevron submitted an evaluation of containment options for petroleum hydrocarbons present near the east bank of the Great Miami River within the *Evaluation of Engineered Options along the East Bank of the Great Miami River, Gulf Park, Cleves, Ohio* (Trihydro 2007c) in fulfillment of Section VI.11.g of the *2006 AOC*. The USEPA provided comments regarding the options analysis on January 24, 2008. The options analysis was subsequently revised and finalized incorporating the USEPA comments. The selected 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 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 Construction and Bank Stabilization along the East Bank of the Great Miami River, Gulf Park, Cleves, Ohio* (Trihydro 2008). Based on comments to the design, Chevron subsequently revised the plans and submitted the final approved design in an updated report dated September 17, 2008.

The bank stabilization and barrier construction activities were completed between September and October 2011 in general accordance with the *Remedial Measures Work Plan for Sheet Pile Barrier Construction and Bank Stabilization along the East Bank of the Great Miami River, Gulf Park, Cleves, Ohio* (Trihydro 2008). An as-built barrier alignment is shown on Figure 5-1. Note that the basemap contours shown on Figure 5-1 are from the Hamilton County GIS Database dated July 2004. Since this time, the east bank of the Great Miami River has been eroded to varying degrees inland along the Park. The portion of the sheet pile barrier alignment parallel to the river approximates the 460 ft-amsl contour as surveyed prior to installation of the barrier in 2011, as this was the lateral alignment design criteria for the wall. While the riverbank has shifted eastward between two to six feet in this area, the alignment shown represents the actual barrier location relative to other stationary site features (e.g., structures, roads, and wells). Basemap contours will be updated on future Gulf Park figures upon availability of such data from Hamilton County. Additional details regarding construction activities are provided below and organized by project component in the general order performed.

5.2.2.1 SITE PREPARATION

On September 8, 2011 construction activities commenced with the installation of temporary perimeter fencing and signage to limit access to the construction area. Preparation activities consisted primarily of the clearing, and removal of trees and miscellaneous vegetation along the riverbank at the proposed sheet pile barrier wall alignment, allowing subsequent access for construction equipment. Where necessary, topsoil was also stripped and stockpiled for reuse as part of the low sloping bench stabilization and seeding activities. In addition to tree clearing and vegetation removal, site preparation activities included preparatory slope and platform excavation and the installation of a silt fence. Maintained throughout construction, the silt fence was placed as appropriate to act as an erosion control before final stabilization of the area. The platform and slope excavation was required to provide an access route for the construction equipment (particularly the track-mounted pile driver used to install the sheet piles). The construction equipment used to complete these activities included excavators, bull dozers, a sheepsfoot roller, smooth drum roller, and off-road trucks.

5.2.2.2 SHEET PILE BARRIER WALL

The sheet pile wall construction commenced on September 13, 2011. The wall was constructed starting at the southern corner (where the main wall and wing wall intersect) and then proceeded north along the main wall parallel to the River. When approximately half of the main wall was completed, the south wing wall was constructed. Construction then progressed north along the remaining main wall and continued up to the terminus of the north wing wall. Sheet pile consisted of 30-foot-long JZ-120 sheet piling with a water-swelling sealant (ADEKA) applied to the interlocking joints prior to driving. Individual piles were driven with the male side leading to prevent accumulation of soil or debris in the interlock. Sheet piles were driven vertically to the specified depth by equipment stationed on the bank. Using a track-mounted pile driver (aka a mobile RAM), sheet piles were driven to the target depth without any noted refusal or other difficulty. The top of the piles were installed to the target elevation of approximately 465 ft-amsl within a tolerance of +/- 4 inches. The mobile RAM accessed the bank via the constructed platform. Sheet pile installation activities were completed on September 20, 2011.

5.2.2.3 RIP RAP REVETMENT SYSTEM

In order to prevent scour, Ohio Department of Transportation (ODOT) Class C rip-rap was placed on the river side of the barrier wall. A 3-foot key trench was excavated and approximately six feet of rip-rap was placed to the angle of repose, or greater, along the length of the sheet pile barrier wall. A track-mounted excavator was used to construct the key trench and then place the rip-rap. Rip-rap revetment construction activities were performed on September 18, 2011.

5.2.2.4 LOW SLOPING BENCH

As sheet pile wall construction progressed, installation of the low sloping bench occurred from the southernmost to the northernmost point of the barrier wall alignment. Soil was placed in approximately 8-inch-thick loose lifts and compacted with at least six passes of a sheepsfoot roller and smooth drum roller. The first 10 to 15 feet of the low sloping bench in-land of the barrier wall was placed at an approximate 12-percent slope (8 feet horizontal to 1 foot vertical, 8:1). The design drawings originally specified a 3-percent slope in these areas, but in order to prevent sediment migration to the river, this area was finished to an elevation below the sheet pile wall. Based on observations over time along the low-sloping bench in-land of the barrier wall at the former refinery and the northern portions of Gulf Park, the low area behind the wall will accumulate sediments following flood events and the designed slope will be achieved. Then, the slope was transitioned from the bench to the existing grade at an approximately 50-percent slope (2:1). A track-mounted excavator, bulldozer, sheepsfoot roller, and smooth drum roller were primarily used to construct the low sloping bench.

Low sloping bench construction activities were primarily performed between September 16 and September 22, 2011. Due to a large amount of rain, construction temporarily halted from September 23 to 30, 2011. After soils had dried, the low sloping bench was re-compacted from October 1 to October 2, 2011.

5.2.2.5 LOW SLOPING BENCH STABILIZATION

Beginning on October 1, 2011 during bench construction, a GeoWeb™ mat was installed to provide stabilization to the area and prevent erosion of the low sloping bench. GeoWeb™ is a 6-inch-thick polyethylene cellular confinement mat system that confines and reinforces the upper soil layer. The GeoWeb™ was placed in accordance with the manufacturer instructions and topsoil was subsequently installed to provide a sub-base for future vegetative growth. The completed areas were seeded with flood-tolerant vegetation and straw was placed to prevent erosion and seed migration. The stabilization activities were conducted before periods of precipitation and some erosion of these areas was noted following substantial completion. Repairs were made to the low sloping bench in March 2012, including the placement of seed and straw matting. Stabilization activities were substantially completed on October 7, 2011, with repairs performed in March 2012. Continued inspection and repair of the low sloping bench will be conducted by Trihydro as part of performance monitoring and maintenance of the wall.

6.0 REFERENCES

Cox-Colvin & Associates, Inc. 1996. Evaluation of Background Metal Concentrations in Ohio Soils.

Chevron Cincinnati Groundwater Task Force. 2005. Update to Site Conceptual Model and Summary of Remedial Decision Basis, Chevron Cincinnati Facility.

Johnson, P.C., Mariush W. Kemblowski, and Richard L. Johnson. 1999. Assessing the Significance of Subsurface Contaminant Vapor Migration to Enclosed Spaces: Site-Specific Alternatives to Generic Estimates. Journal of Soil Contamination, 8(3): 389-421.

National Research Council. 2000. Natural attenuation for groundwater remediation: Washington, D.C., National Academy Press, 274 p.

Ohio Environmental Protection Agency Division of Hazardous Waste Management (OEPA). 2009. Closure Plan Review Guidance for RCRA Facilities. October 2009.

Spieker, and Durrell R. H. 1961. A Guide to Geohydrology of the Mill Creek and Mad River Valleys, Ohio. Guidebook for Field Trips, Cincinnati Meeting, 1961. U.S.G.S. pgs. 215-251.

Speiker, A.M. 1968. Groundwater Hydrology and Geology of the Lower Great Miami River Valley, Ohio. U.S. Geological Survey Professional Paper 605-A. Washington, D.C. Pages A1-A37.

Trihydro Corporation. 2012. First 2011 Semiannual Monitoring Report, Chevron Cincinnati Facility, Hooven, Ohio.

Trihydro Corporation. 2011a. Second 2010 Semiannual Monitoring Report, Chevron Cincinnati Facility, Hooven, Ohio.

Trihydro Corporation. 2011b. Five-Year Groundwater Corrective Measures Implementation Review, Chevron Cincinnati Facility, Hooven, Ohio.

Trihydro Corporation. 2010a. Hooven Vapor Site Conceptual Model Update, Chevron Cincinnati Facility, Hooven, Ohio.

Trihydro Corporation. 2010b. Second 2009 Semiannual Monitoring Report, Chevron Cincinnati Facility, Hooven, Ohio.

Trihydro Corporation. 2009a. First 2008 Semiannual Monitoring Report, Chevron Cincinnati Facility, Hooven, Ohio.

Trihydro Corporation. 2009b. Second 2008 Semiannual Monitoring Report, Chevron Cincinnati Facility, Hooven, Ohio.

Trihydro Corporation. 2009c. Work Plan for Contingency Measures in the Southwest Quad, Chevron Cincinnati Facility, Hooven, Ohio.

Trihydro Corporation. 2009d. First 2009 Semiannual Monitoring Report, Chevron Cincinnati Facility, Hooven, Ohio.

Trihydro Corporation. 2007a. Remedy Implementation Plan for Final Groundwater Remedy, Chevron Cincinnati Facility.

Trihydro Corporation. 2007b. Operations, Maintenance and Monitoring Plan for Final Groundwater Remedy, Chevron Cincinnati Facility.

Trihydro Corporation. 2007c. Performance Monitoring Plan, Sheet Pile Barrier Along Great Miami River, Chevron Cincinnati Facility, Hooven, Ohio.

United States Environmental Protection Agency (USEPA). 2003. Performance Monitoring of MNA Remedies for VOCs in Ground Water.

United States Environmental Protection Agency (USEPA). 1999. Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites.

Watkins, J. S. and Spieker, A. M. 1971. Seismic Refraction Survey of Pleistocene Drainage Channels in the Lower Great Miami River Valley, Ohio. United States Geological Survey, Geological Survey Professional Paper, P605B.

TABLES

FIGURES

APPENDICES A THROUGH H

(PLEASE SEE ATTACHED CD)