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### **REVIEWER JKS**

### DISSOLVED PHASE INVESTIGATION WORK PLAN

#### HARTFORD PETROLEUM RELEASE SITE

RECEIVED

#### HARTFORD, ILLINOIS

FINAL

AUG 2 0 2013

IEPA/BOL

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Project #: 24S-005-001

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## **1.0 INTRODUCTION**

Apex Oil Company, Inc. (Apex) has prepared this work plan detailing the dissolved phase investigation activities to be implemented at the Village of Hartford Petroleum Release Site (Hartford Site). Figure 1 presents the location of the Hartford Site. This work plan has been prepared in accordance with the April 26, 2013 letter issued by the United States Environmental Protection Agency (USEPA), which set "forth an initial assignment of work amongst the responsible parties" at the Hartford Site (Assignments Letter). The dissolved phase investigation will be conducted pursuant to Paragraph 5 of the July 28, 2008 Order (Docket Number 05-CV-242-DRH). As part of this work plan, Apex will identify data gaps within the conceptual site model (CSM) for dissolved phase petroleum hydrocarbons beneath the Hartford Site, describe proposed methods for resolving these data gaps, and provide an implementation schedule.

#### 1.1 PURPOSE

The primary objective of the additional dissolved phase investigation is to provide data to support updates to the portions of the CSM related to dissolved phase petroleum hydrocarbons beneath the Hartford Site. These updates will also be incorporated into the Comprehensive CSM.<sup>1</sup> Specifically, the additional data will be evaluated to better understand: (1) changes in the distribution of light non-aqueous phase liquids (LNAPL) within the smear zone that act as the source for dissolved phase constituents, (2) the rates of depletion of dissolved phase constituents of concern in response to engineered remedial efforts and natural smear zone depletion (NSZD), and (3) natural attenuation processes acting to reduce petroleum hydrocarbon mass within the saturated zone. The same processes acting to deplete hydrocarbons within the saturated zone are also reducing the mass, source strength, and longevity of LNAPL present in the smear zone. Defining the rates and processes that are depleting dissolved phase constituents in response to either engineered or natural processes provides evidence of the rates of partitioning and subsequent losses from the LNAPL source, as well as information regarding the overall longevity of constituents of concern partitioning from the LNAPL. An updated CSM, including data from an additional dissolved phase investigation, will be a critical input for design of the final remedy for the Hartford Site. Data collected as part of the investigation described herein will provide a baseline for future dissolved phase monitoring and development of final remedial goals that will be protective of both current and future receptors. It is anticipated that the final remedy will be designed in such a manner as to contemplate,

<sup>&</sup>lt;sup>1</sup> The schedule for preparing updates to the dissolved phase portion of the CSM and the Comprehensive CSM was provided to the USEPA within a memo describing the CSM Framework submitted on June 21, 2013, in accordance with the Assignments Letter. Hereafter, the term "CSM" will be used to refer to both the dissolved phase CSM and/or the Comprehensive CSM.



among other inputs, changes in land use, hydraulic conditions, and processes acting to deplete LNAPL in the smear zone.

### 1.2 BACKGROUND

The lithology beneath the Hartford Site consists of alternating alluvial deposits of clay and silt overlying the regionally extensive Main Sand. The Main Sand consists of alluvial sands and coarse grained glacial outwash that ranges from 60 to 150 feet in thickness. The permeable zones of alluvial deposits overlying the Main Sand are locally known (in descending order) as the North Olive, the Rand, and the EPA hydrostratigraphic units. These permeable zones are bounded by discontinuous clay deposits identified as (in descending order) the A, B, C, and D Clay Strata.

The North Olive and Rand units laterally grade into and are hydraulically connected with the Main Sand, where the B and C Clay Strata pinch out south of Date Street. The EPA hydrostratigraphic unit grades laterally into the Main Sand to the south of a southwesterly trending line extending from the Old St. Louis Road and Delmar Avenue intersection to just north of the East Date Street and North Olive Street intersection. Along this boundary, the EPA and Main Sand are hydraulically connected. A more detailed description of the hydrogeology underlying the Hartford Site is provided in the December 15, 2005 LNAPL Active Recovery System Conceptual Site Model (Clayton 2005b).

Petroleum hydrocarbons were released from the former refineries and related facilities located to the north and east of the Village of Hartford, as well as pipelines connecting these refineries and facilities with terminal operations on the Mississippi River (Figure 1). Released hydrocarbons (LNAPL) migrated down through the subsurface under the influence of gravity until encountering the water table. Due to capillary forces, some fraction of the LNAPL was retained in soil pore space in the unsaturated zone, whereas some fraction of the LNAPL reached the capillary fringe where it displaced water present in soil pore space. As the volume of LNAPL became sufficient to overcome hydrostatic forces, further lateral and vertical migration occurred. The distribution of LNAPL stabilized as gravity and capillary forces approached equilibrium.

Vertical smearing of the LNAPL occurred over time as a result of fluctuation of the groundwater elevations within the hydrostratigraphic units beneath the Hartford Site, leaving some LNAPL within the soil pore spaces below and above the water table. The bottom of the "smear zone" is roughly coincident with the historical low groundwater elevation in the Main Sand. The thickness of the smear zone is variable measuring only a few inches at the plume periphery, to tens of feet in locations near historical releases. The vertical and lateral distribution of the smear zone also varies due to heterogeneities in the lithology. The LNAPL and dissolved phase plume boundaries are generally coincident at the up-



gradient and lateral edges of the smear zone. Whereas, in the primary flow direction, a dissolved phase plume extends down-gradient from the LNAPL smear zone boundary.

The smear zone is the three-dimensional feature describing the horizontal and vertical extent of LNAPL (including residual and mobile) beneath the Hartford Site. The nature and extent of the LNAPL smear zone and dissolved phase petroleum hydrocarbons has been previously defined, at least in part, across the various water bearing units using laser induced fluorescence, soil core analyses, multi-level groundwater sampling, and routine monitoring of the nested well network (Clayton 2004, 2005, 2006a, 2006b). Based on these studies, the majority of the remaining LNAPL is present in the Main Sand and consists of weathered gasoline, except in the northern and easternmost smear zone limits, which contain mixtures of gasoline and diesel (Clayton 2006b). LNAPL is also present to a lesser degree in the units above the Main Sand, including the North Olive, Rand, and EPA consisting primarily of diesel (Clayton 2006b).

Based on the previous laser induced fluorescence investigations and more recent routine monitoring activities, dissolved phase hydrocarbons (as defined by the limits of benzene, ethylbenzene, toluene, xylenes, and methyl-tertbutyl ether [MTBE]) extend as a "narrow halo" around the southern and the majority of the western portions of the LNAPL smear zone. As shown on Figure 2, the dissolved phase plume in the Main Sand (based on semiannual monitoring performed over the past two years) extends approximately ½-block south of Watkins Street and no further west than Illinois State Route 3. Dissolved phase hydrocarbons are contiguous with releases present on the former Premcor, Shell, British Petroleum, Buckeye, and ConocoPhillips properties to the east and north of the Hartford Site (Figure 1). The highest concentrations of MTBE have typically been measured in nested monitoring well HMW-049, which is located approximately 200 feet north of Rand Avenue, between a service station and the Hartford Wood River Terminal (Figure 2). These elevated concentrations of MTBE are believed to be attributable to an alternate source north of Rand Avenue.

Based on routine groundwater monitoring conducted in the sentinel monitoring network (wells HMW-25 through HMW-29) located between the smear zone and the municipal well field, LNAPL and dissolved phase hydrocarbons have not been observed within the reported recharge zone for the Hartford Municipal well field. Groundwater flow in the Main Sand, in which the municipal wells are screened, primarily flows to the north and east away from the well field, as a result of hydraulic controls and groundwater production performed on the refinery and terminal properties. Pumping from the municipal wells has not influenced groundwater flow near the southern limits of the dissolved phase plume in the Main Sand, and based on current pumping protocols (i.e., intermittent operations of the municipal wells), no future influence is anticipated. So long as the dissolved phase and fluid level monitoring results from the sentinel network continue to indicate that groundwater flow or dissolved constituent flux are not in a southwesterly direction, it is anticipated that additional evaluation of the municipal well field, beyond the current monitoring program, will not be



necessary. Routine monitoring of the sentinel well network will be performed by the Hartford Working Group (HWG) starting in July 2013 per the Assignments Letter, but the results of the monitoring performed by HWG will nevertheless continue to be evaluated as part of the overall dissolved phase monitoring program.

### 1.3 DATA GAPS AND WORK PLAN ORGANIZATION

Based upon review of the previous investigations and the results of routine monitoring conducted since 2004, the following data gaps have been identified in the CSM with respect to dissolved phase constituents:

- 1. Previous investigations performed in 2004 and 2005 using laser induced fluorescence and soil cores have defined the horizontal and vertical distribution of LNAPL beneath the Hartford Site. However, there is uncertainty in the distribution of LNAPL in response to engineered recovery and NSZD within the smear zone since these investigations were performed. Additional laser induced fluorescence borings will be installed using a Rapid Optical Screening Tool (ROST) or Ultraviolet Optical Screening Tool (UVOST) in select locations that have been previously assessed along the western and southern limits of the smear zone, as well as within the core of the smear zone, in order to define changes in the vertical distribution of LNAPL and lateral extent of the smear zone since investigations first performed in 2004 and 2005.
- 2. Routine monitoring in recent years has been focused primarily on wells located beyond the extent of the dissolved phase plume to the south and west of the Hartford Site in order to demonstrate LNAPL and dissolved phase hydrocarbon stability. In order to allow for evaluation of the rates of depletion of dissolved phase constituents in response to engineered recovery and NSZD processes, future routine monitoring will focus on collection of groundwater samples within wells located within the smear zone in the Main Sand and other water bearing units.
- 3. Many of the processes attenuating hydrocarbons in the smear zone cannot be measured directly (e.g., biological transformation of constituents); however, the influence of these processes may cause observable geochemical changes in groundwater. These changes are influenced by oxidation-reduction (redox) processes in which naturally occurring inorganic geochemical species serve as electron acceptors and are reduced during microbial degradation of petroleum hydrocarbons. Monitoring redox indicators (such as dissolved oxygen, nitrate, nitrite, manganese, iron, sulfate, sulfide, and methane) provide additional lines of confirmation that intrinsic biodegradation is occurring in the saturated zone. Future monitoring will include analysis of groundwater samples for these geochemical indicators within selected wells to qualitatively and quantitatively evaluate natural attenuation processes acting to deplete petroleum hydrocarbons across the smear zone.



The remainder of this work plan is organized into the following sections:

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- Section 2.0 Describes the scope of work including sample locations and analyses that will be performed to
  resolve the data gaps within the CSM.
- Section 3.0 Provides a summary of the analyses and associated deliverables that will be provided to the USEPA and the Illinois Environmental Protection Agency (Illinois EPA) as part of the dissolved phase investigation.
- Section 4.0 Provides a summary of the implementation schedule for the dissolved phase investigation and future monitoring activities.



## 2.0 SCOPE OF WORK

This section describes the field activities that will be performed to address the data gaps in the CSM for the dissolved phase hydrocarbons beneath the Hartford Site. Fluid level gauging, water quality sampling, and laboratory analyses will be conducted in general accordance with the draft Quality Assurance Project Plan (QAPP) dated March 24, 2009 (RAM 2009). Additional description of the methods and alternate monitoring procedures are provided for reference and will be noted in the routine and non-routine deliverables described herein.

#### 2.1 LASER INDUCED FLUORESCENCE

In 2004, 80 laser induced fluorescence borings (HROST-1 through HROST-80) were installed using ROST beneath the Village of Hartford to define the lateral and vertical extent of LNAPL. In 2005, an additional 50 laser induced fluorescence borings (HROST-81 through HROST-130) were installed using ROST to further refine the vertical and horizontal distribution of petroleum hydrocarbons beneath the Hartford Site. Figure 3 shows the location of the laser induced fluorescence borings installed in 2004 and 2005. The results of these investigations were summarized in the *FPH CPT/ROST*<sup>TM</sup> Subsurface Investigation Report (Clayton 2004) and the LNAPL Active Recovery System Conceptual Site Model (Clayton 2005).

Fluorescence is a property of polycyclic aromatic hydrocarbons (PAHs) that make up a portion of the petroleum hydrocarbons present as LNAPL beneath the Village. PAHs will absorb ultraviolet light and then release this stored energy as photons (aka, light) of a longer wavelength. This fluorescence response of PAHs can be used to detect small amounts of LNAPL within the vadose zone, capillary fringe, and saturated zones.

Laser induced fluorescence techniques (e.g., ROST and UVOST) make use of a wavelength-tunable laser source with an optical detector to measure fluorescence by transmitting ultraviolet light through a fiber optic cable strung within direct push probe rods. The ultraviolet light is reflected by a parabolic mirror and then exits through a sapphire window on the side of the probe. As the direct push probe is advanced, the soil is exposed to the light and if LNAPL is present, the PAHs will fluoresce. A second fiber optic line captures the fluorescent response and returns this light to the equipment at the ground surface. The data are continuously recorded and averaged to create a real-time graph of fluorescence response versus depth.

The laser induced fluorescence system is calibrated daily using a reference standard containing the spectrum of petroleum hydrocarbons that can be detected by the system. The fluorescence response measured by the system is consistently normalized as a percentage of the intensities measured within the reference standard. The power output of the laser can change due to environmental conditions over time (e.g., temperature and humidity) and aging of the



components of the system. Use of the standard normalizes the data collected during each event. While the laser induced fluorescence results are not directly comparable between events, the data that is collected during a given event across the depth profile are semi-quantitative in nature, as the fluorescence results have been referenced against a known standard. Therefore, the laser induced fluorescence results can be used to evaluate changes in the type and distribution of petroleum hydrocarbons between investigative events. It should be noted that the calibration of the system is not to a known concentration or LNAPL saturation, but instead to a known fluorescence signature.

The laser induced fluorescence system will be used in a multi-wavelength mode to screen for petroleum hydrocarbons in the subsurface. In the multi-wavelength mode, several characteristics of the emitted fluorescence are measured and recorded simultaneously at four specific wavelengths (340, 390, 440, and 490 nanometers), representing the range of fluorescence typically produced by PAHs present in various petroleum products ranging from light fuels to heavier hydrocarbons. The recorded data from the four wavelengths are combined on the fluorescence intensity versus depth graph and the color represents the proportional fluorescence intensity of each individual wavelength. Similar colors on the fluorescence intensity versus depth graph represent similar product types regardless of fluorescence intensity; a change in the color of the fluorescence intensity typically indicates a change in the LNAPL type.

### 2.1.1 ADDITIONAL LASER INDUCED FLUORESCENCE MONITORING

A minimum of 25 laser induced fluorescence borings will be installed using ROST or UVOST across the Hartford Site. Fourteen borings will be installed at previous monitoring locations within the six remediation areas (Areas A, B1, B2, B3, B4, and C) described in the *LNAPL Active Recovery System 90% Design Report* (Clayton 2006a). Eleven additional borings will be installed at locations previously completed in 2004 and 2005 to assess changes in the lateral and vertical distribution of LNAPL along the western and southern limits of the smear zone. If the laser induced fluorescence results indicate an increase in the vertical distribution of LNAPL within the smear zone coupled with significantly higher fluorescence response (compared to the 2004 and 2005 events), then step out borings may be completed further to the south and west. Laser induced fluorescence boring locations will be approved by the Village of Hartford, avoiding any recently placed asphaltic concrete within the roadways, where possible. Confirmation of subs<sup>2</sup>urface utility and remedial system component locations will be performed using ground penetrating radar.

The borings within the six remediation areas will be installed first to compare the fluorescence response to results from the historical borings. Following installation of these fourteen borings, laser induced fluorescence borings will be completed at the eleven locations along the southern and western limits of the smear zone. Each boring will be installed to a minimum of five feet below the vertical smear zone limits previously identified in the Main Sand unit, as summarized on Table 1. Based on the bottom of the smear zone reported in the historical laser induced fluorescence



borings, it is anticipated that the borings will not extend deeper than 65 feet below ground surface (ft-bgs). The borings may be extended deeper if there is evidence that the smear zone extends deeper than 60 ft-bgs.

Figure 3 shows the locations where additional laser induced fluorescence borings will be installed. Table 1 provides a summary of the historical thickness of the LNAPL smear zone, maximum fluorescence, and elevation of the smear zone relative to mean sea level, as measured at these locations between 2004 and 2005. Appendix A includes a copy of the historical laser induced fluorescence logs for the locations listed on Table 1.

### 2.2 GROUNDWATER INVESTIGATION ACTIVITIES

The monitoring network necessary for evaluating dissolved phase constituent trends and geochemical indicators is already well established at the Hartford Site. Previous dissolved phase investigation work plans (Clayton 2006b, URS 2009) indicated the need for additional monitoring nests beyond the western limits of the smear zone near groundwater monitoring nests HMW-039 and HMW-040. Dissolved phase concentrations for benzene, ethylbenzene, toluene, xylenes, and MTBE have been reported below the comparison values (Illinois Class 1 Groundwater Remediation Objectives) in samples collected from nests HMW-039 and HMW-040 since 2004, with the exception of a single detection in the groundwater sample collected from well HMW-040C in April 2013.<sup>2</sup> As shown on Figure 3, HMW-040 is located within the limits of the smear zone while HMW-039 is located beyond the smear zone limits.

Dissolved phase benzene trends for monitoring wells HMW-041B, HMW-042B, and MP-078D, located within the western limits of the smear zone (based on 2004 and 2005 laser induced fluorescence results reported in Clayton 2006a), are shown on Figures 4 through 6. As shown on these figures, benzene concentrations within the smear zone measured at these three wells are either stable or decreasing over time, providing evidence that the western extent of the dissolved phase plume has been defined and installation of additional groundwater monitoring wells further west of the smear zone boundary are not necessary.

#### 2.2.1 HIGHER FREQUENCY FLUID LEVEL GAUGING

Current quarterly gauging of the monitoring network does not capture groundwater elevation response to precipitation events or changes in river stage, as well as LNAPL occurrence over a range of hydraulic conditions. Therefore, fluid levels will be measured using manual and automated methods on a more frequent basis across the Hartford Site.

<sup>&</sup>lt;sup>2</sup> The comparison values referenced herein provide a point of reference for evaluating dissolved phase concentrations over time, and have not been stated here as remedial goals for dissolved phase constituents. Remedial goals for groundwater and other pathways will be developed as part of defining the remedy for the Hartford Site.



Manual fluid level gauging will be performed monthly within the monitoring network listed on Table 2 and shown on Figure 7 to provide additional information regarding changes in LNAPL thickness over a range of water level conditions and to determine when groundwater elevations are within the screen interval of a monitoring well so that sampling can be performed. For reference, historic fluid levels for these wells are provided as Appendix B. Fluid levels within each of the monitoring wells will be measured within a 24-hour period. Fluid level measurements will be conducted using an interface probe accurate to 0.01-feet in accordance with SOP No. 220 included in the draft QAPP. The measurements will be made from the pre-marked (surveyed) measuring point on the well casing. The exposed portion of the tape and the probe will be decontaminated before performing measurements at each monitoring well in accordance with SOP No. 5 included in the draft QAPP.

Pressure transducers will also be deployed in two transects of groundwater monitoring nests from the west to east across the Hartford Site as shown on Figure 7. Transducers will be programmed to record groundwater elevations on an 8-hour basis in general accordance with SOP No. 220 provided in the draft QAPP. The data will be downloaded from the transducers at least once each quarter. Each transducer has a memory capacity of at least one megabyte, and the download frequency will be sufficient so as not to exceed storage capacity. The pressure transducer monitoring results will be used to assess changes in groundwater elevations in response to seasonal variations in precipitation rates and river stage.

#### 2.2.2 DISSOLVED PHASE CONCENTRATION TRENDS

Groundwater samples will be collected from the monitoring wells installed within each of the hydrostratigraphic units beneath the Hartford Site, i.e., North Olive, Rand, EPA, and Main Sand units in order to: (1) continue to demonstrate that dissolved phase petroleum-related constituents are stable along the southern and western limits of the smear zone, and (2) evaluate concentration trends in wells located across the smear zone. Groundwater samples will be collected annually from the wells identified on Table 2 and shown on Figures 8 through 10. For reference, historic analytical results for benzene, toluene, ethylbenzene, total xylenes, and MTBE for these wells are provided as Appendix C.

Sampling will be performed when the groundwater elevation is gauged to be within the screened interval of the monitoring well, which will be determined via monthly manual gauging measurements. Samples will not be collected if LNAPL is measured within a well or if a LNAPL sheen is observed on the groundwater during purging activities. LNAPL recovery operations using skimming pumps will continue to be performed as groundwater samples will not be collected in wells with appreciable LNAPL.

Groundwater will be purged and sampled using a low flow methodology to prevent potential disturbance of the water conditions within the formation, as described in SOP No. 18 provided in the draft QAPP. Portable pneumatic pumps,



or similar types of pumps, will be installed so that the pump intake height is located in the middle of the water column within the screen interval of the groundwater monitoring well. The flow rate will be maintained between 0.1 and 0.5 liters per minute to minimize drawdown, undue pressure, temperature, or physical disturbances to the water over the sampling interval. The water level and field parameters will be recorded over successive time intervals. The following stabilization criteria shall be met over three successive readings before collecting groundwater samples:

• pH ± 0.1

- Specific conductivity ± 3%
- Temperature +/-3%
- Turbidity ± 10% or <10 nephelometric turbidity units</li>

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- DO+/-0.3 milligrams per liter
- ORP +/-10 millivolts

Physical characteristics of the water will be noted and recorded during sampling (e.g., sediment, color, evidence of sheening, and odor). Decontamination of the pumps will be performed in accordance with SOP No. 5 prior to purging and sampling each well. Groundwater samples will be analyzed for benzene, ethylbenzene, toluene, xylenes, and MTBE.

#### 2.2.3 GEOCHEMICAL INDICATORS OF NATURAL ATTENUATION

Natural source zone depletion will reduce the mobility, toxicity, and/or bioavailability of petroleum hydrocarbons beneath the Hartford Site over time. These processes tend to be more active on the margins of the smear zone and result in an outside-in weathering towards release areas within the smear zone. These intrinsic processes will become more dominant as additional mass is removed via engineered remedial efforts.

Intrinsic biodegradation occurs in the saturated zone as petroleum-related constituents partition from the LNAPL smear zone. Aerobic biodegradation is expected to be an important process at the periphery of the smear zone. Anaerobic biodegradation is expected to be the dominant process within the smear zone. This trend of aerobic to anaerobic biodegradation occurs in both the lateral and vertical dimensions.

Groundwater samples will be analyzed for geochemical indicators of natural attenuation from those wells identified in Table 2 and depicted on Figures 8 through 10. Samples will be collected to qualitatively and quantitatively define the redox conditions across the smear zone, including electron acceptor flux into the smear zone. Groundwater samples will be analyzed for ferric iron, ferrous iron, dissolved and total manganese, methane, nitrate, nitrite, sulfate, and



sulfide. Revisions to this analyte list or wells sampled may be proposed based on future monitoring results and evaluations. The intent of the natural attenuation monitoring is to collect data to define baseline conditions for incorporation into the CSM. Adjustments to the monitoring location, frequency, and/or requested analyses may be proposed based on the baseline monitoring results.



## 3.0 DATA EVALUATION AND REPORTING

Results from the dissolved phase investigation activities described herein will be used to: (1) evaluate changes in the vertical and horizontal distribution of the LNAPL smear zone that is the source of the dissolved phase petroleum hydrocarbons, (2) confirm the stability of the plume beyond the smear zone limits, (3) quantify depletion rates within the smear zone due to engineered recovery and NSZD, and (4) evaluate those natural attenuation processes acting to deplete the source within the saturated zone. Data collected as part of this investigation will provide a baseline for future dissolved phase monitoring performed as part of the final remedy. It is expected that monitoring performed as part of the final remedy will be designed to confirm the stability of dissolved phase hydrocarbons and demonstrate protectiveness of potential receptors. It is also anticipated that the final remedy will be designed in such a manner as to contemplate, among other inputs, changes in land use, hydraulic conditions, and processes acting to deplete LNAPL in the smear zone. This section describes how data collected as part of this dissolved phase investigation will be evaluated and reported to the USEPA and Illinois EPA.

### 3.1 LASER INDUCED FLUORESCENCE MONITORING

Graphical logs from additional laser induced fluorescence borings will be evaluated to assess the current vertical and horizontal distribution of LNAPL within the subsurface. As previously indicated, the percent fluorescence response cannot be quantitatively correlated to petroleum-related constituent concentrations or hydrocarbon saturations. However, a semi-quantitative comparison of the logs from newly installed borings, showing percent fluorescence versus depth, can be compared to collocated logs from the previous ROST borings installed between 2004 and 2005. This comparison will include tabulating the new and historic laser induced fluorescence results based on (1) the vertical extent of LNAPL, (2) the depth and degree of maximum fluorescence response, and (3) the individual wavelength peaks and/or overall color of the fluorescence response. Temporal changes in the vertical extent of the LNAPL and maximum fluorescence response within a location may indicate if there is preferential depletion of the smear zone (e.g., depletion at the upper portions versus lower portions of the smear zone). Changes in individual wavelength peaks or overall color of the fluorescence response may indicate a shift in LNAPL composition. Laser induced fluorescence logs will be provided to the USEPA daily. Results of the additional laser induced fluorescence investigation and comparison with previous data will be provided in the CSM, and specifically addressed within updates to the LNAPL source.



#### 3.2 GROUNDWATER MONITORING

The results of the fluid level monitoring and groundwater sampling activities will be provided within the routine groundwater monitoring reports submitted for the Hartford Site. In addition, gauging and dissolved phase analytical results will be incorporated into the CSM.

### 3.2.1 FLUID LEVEL MONITORING

Monthly fluid level gauging and more frequent measurements recorded with the pressure transducers will be tabulated on a quarterly basis for the network of monitoring wells and monitoring points listed on Table 2. Graphs of the fluid level trends in response to precipitation rates and river stage will be prepared to evaluate fluctuations in hydraulic conditions and LNAPL thicknesses.

#### 3.2.2 DISSOLVED PHASE CONSTITUENT TRENDS

Dissolved phase monitoring results will be used to demonstrate the stability of dissolved phase petroleum hydrocarbons along the western and southern portions of the smear zone and to evaluate dissolved phase depletion rates in response to engineered remediation and natural attenuation processes within the saturated portions of the smear zone.

### 3.2.2.1 MONITORING OUTSIDE OF THE SMEAR ZONE LIMITS

The analytical results from the groundwater samples collected beyond the southern and western limits of the smear zone will be tabulated and compared to comparison values (Illinois Class 1 Groundwater Remediation Objectives). The results of these monitoring activities performed beyond the smear zone limits will be used to evaluate the stability of the dissolved phase plume under the range of hydraulic conditions observed at the Hartford Site.

#### 3.2.2.2 MONITORING WITHIN THE SMEAR ZONE

Results from the groundwater monitoring conducted within the limits of the smear zone in the North Olive, Rand, EPA, and Main Sand units (as listed in Table 2 and shown on Figures 8 through 10) will be used to assess the baseline dissolved phase constituent trends in response to current engineered recovery and NSZD processes. It is expected that the groundwater data collected over the course of remedial activities will show a meaningful trend of decreasing hydrocarbon mass and/or constituent concentrations over time, compared to baseline conditions. 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 inside and at the edges of the LNAPL



smear zone, to identify areas that are not behaving as predicted. Trend analyses will be conducted in monitoring locations situated throughout the distribution of petroleum hydrocarbons to assess the range of processes acting on the smear zone. Temporal trends in individual wells may also be affected by conditions unrelated to engineered recovery or NSZD processes (e.g., climate, hydrogeochemistry, surface activity, land use, regional pumping, alternate petroleum hydrocarbon release) and will need to be evaluated in the context of other lines of evidence, such as geochemical indicator concentrations or fluid level trends.

Second, groundwater quality trends can be averaged within areas of the smear zone or hydrostratigraphic unit 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.

Historically, groundwater samples may not have been collected from many of the monitoring nests located within the smear zone limits due to the presence of LNAPL during sampling or due to lack of groundwater within the well. Trend analyses will only be performed for wells for which samples were collected when groundwater was present within the screened interval during at least three monitoring events spanning three separate years.

#### 3.2.3 NATURAL DEPLETION PROCESSES

During microbial degradation of petroleum impacts, dissolved oxygen concentrations steadily decrease until anaerobic conditions prevail. Once anaerobic conditions exist and multiple potential electron acceptors (i.e., oxidizers) are available, microorganisms preferentially use the electron acceptor that is thermodynamically most favorable. In other words, petrophyllic bacteria that utilize the electron acceptor that offers the most energy during consumption of the petroleum hydrocarbon source will proliferate over other bacteria until that electron acceptor is exhausted and then other bacteria that use the next most favorable electron acceptor (based on availability in groundwater) thrives. The general order of preference for anaerobic hydrocarbon biodegradation based on the Gibb's energy of the reaction is:

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



These microbial processes generally segregate into distinct zones dominated by oxygen, nitrate, ferric iron, sulfate, and carbon dioxide reduction. Furthermore, given the different electron acceptors consumed and final by-products, it is theoretically possible to differentiate the "zones" of microbial processes across the smear zone, although due to the heterogeneity in the release history and lithology, these processes may be variable within each hydrostratigraphic unit. When applied at a field scale, this differentiation of microbial zones must be framed in general terms, which accommodate uncertainties, because several of the by-products of microbial metabolism (such as ferric iron, hydrogen sulfide, and methane) are readily transported down-gradient.

The monitoring results for the geochemical indicators will be tabulated and spatially analyzed to assess the baseline redox processes acting to deplete the smear zone in the North Olive, Rand, and Main Sand hydrostratigraphic units. These analyses will be performed in those wells listed in Table 2 and shown on Figures 8 through 10. Geochemical processes in the EPA unit will be inferred based on the results from the other hydrostratigrahic units. The EPA unit is limited to the northeasterly limits of the Hartford Site. First, the distribution of the electron acceptors and by-products will be plotted with comparison to the dissolved phase petroleum hydrocarbon concentrations. Second, the electron acceptor and by-product concentrations will be plotted versus distance from the up-gradient edge of the smear zone to evaluate redox conditions through the "centerline" of each hydrostratigraphic unit. Finally, the dissolved phase hydrocarbon and geochemical indicator analytical results may be integrated with transport rates (e.g., hydraulic conductivities, hydraulic gradients) within the saturated zone to estimate NSZD rates across various portions of the smear zone. This method is described in detail in the 2009 Interstate Technology & Regulatory Council (ITRC) document titled, *Evaluating Natural Source Zone Depletion at Sites with LNAPL*, and is based largely on the methodology described in Johnson et al. (2006a, 2006b). This analysis will allow for estimation of NSZD rates in the saturated zone that is attributable to specific redox processes.

Transient recharge and discharge of groundwater into the perched hydrostratigraphic units will complicate conventional analyses and may require additional assessment of electron acceptor and by-product flux into and out of the smear zone. Additional data regarding electron acceptor flux (e.g. rainwater infiltrate or rapid rise of the groundwater table into the perched zones), as well as microbial degradation by-product efflux out of the perched units (e.g., vertical drainage as the water table recedes) may be necessary to fully evaluate natural depletion processes in the perched units.



## 4.0 IMPLEMENTATION SCHEDULE

The dissolved phase investigation will commence following final approval by the USEPA and Illinois EPA (Agencies) and will adhere to the implementation schedule described below. Field activities are subject to modification due to inclement weather conditions, subcontractor availability, or access limitations. Written notification will be provided to the Agencies and the Village of Hartford before initiating any intrusive field activities, such as installation of the laser induced fluorescence borings. Field activities will be planned with the Village of Hartford in order to coordinate with repaving and pilot test preparation activities that are being planned for the coming months. In the event that the field schedule requires modification for any reason, notification will be given to the Agencies and Village of Hartford.

Activity	Schedule and Frequency of Activities		
Installation of pressure transducers	Within 30 days of receiving Agency approval of this work		
	plan. Data will be collected and evaluated from the		
	transducers on a quarterly basis. Monitoring results will be		
	provided in routine quarterly and semiannual groundwater		
	monitoring reports prepared by Apex and also incorporated		
	into the CSM.		
Monthly gauging of fluid levels within select	Within 30 days of receiving Agency approval of this work		
monitoring wells (includes monitoring wells with	plan. Data will be tabulated and evaluated on a quarterly		
pressure transducers)	basis. Gauging results will be provided in routine quarterly		
	and semiannual groundwater monitoring reports prepared by		
	Apex and also incorporated into the CSM.		
Field preparation, siting laser induced fluorescence	Within 60 days of receiving Agency approval of this work		
borings, and location of subsurface utilities	plan.		
Laser induced fluorescence investigation	Within 30 days of siting the boring locations and approval by		
	the Village of Hartford. Boring logs will be provided daily		
	to the Agency and evaluated as part of the CSM.		
Groundwater sampling for dissolved phase	Annually, following Agency approval of this work plan		
petroleum hydrocarbons and geochemical indicators	Analytical results will be evaluated on a semiannual basis.		
	Monitoring results will be provided in routine quarterly and		
	semiannual groundwater monitoring reports prepared by		
	Apex and also incorporated into the CSM.		



## 5.0 REFERENCES

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# TABLE 1. LASER INDUCED FLUORESCENCE MONITORING RESULTS HARTFORD PETROLEUM RELEASE SITE, HARTFORD, ILLINOIS

Laser Induced Fluorescence Boring ID	Installation Date	Vertical Extent of Fluorescence Response (ft-bgs)	Maximum Fluorescence Response (%)	Depth of Maximum Fluorescence Response (ft-bgs)	Ground Surface Elevation (ft-msl)	Top of Smear Zone Elevation (ft-mst)	Bottom of Smear Zone Elevation (ft-msl)
HROST-002	2/16/04	31-42	135.94	35.61	430.95	399.95	388.95
HROST-004	2/16/04	6-53	120.82	33.58	429.34	423.34	376.34
HROST-005	2/18/04	20-46	242.12	39.73	430.50	410.50	384.50
HROST-007	2/17/04	30-40	11.60	39.31	429.75	399.75	389.75
HROST-013	2/16/04	16-39	58.76	32.87	427.00	411.00	388.00
HROST-019	2/16/04	28-36	43.20	32.15	426.00	398.00	390.00
HROST-025	2/19/04	26.5-40.5	39.92	32.79	430.00	403.50	389.50
HROST-028	2/21/04	25-37	50.66	32.46	426.80	401.80	389.80
HROST-029	2/18/04	15-43	197.50	29.68	431.75	416.75	388.75
HROST-030	1/31/04	17-43	123.55	40.68	431.75	414.75	388.75
HROST-039	1/30/04	19.5-44.5	121.64	47.70	430.75	411.25	386.25
HROST-040	1/30/04	7-46	202.64	31.92	429.85	422.85	383.85
HROST-049	1/29/04	6-40	147.44	7.25	431.75	425.75	391.75
HROST-052	1/31/04	13-39	52.41	35.35	429.00	416.00	390.00
HROST-066	2/20/04	35-36.5	9.14	35.60	432.00	397.00	395.50
HROST-068	2/20/04	29-39	15.83	33.32	431.25	402.25	392.25
HROST-072	2/23/04	25.5-32	9.30	26.09	426.00	400.50	394.00
HROST-078	2/21/04	17-52	50.90	40.66	431.50	414.50	379.50
HROST-090	6/22/05	12-47	348.87	38.84	430.34	418.34	383.34
HROST-099	6/5/05	30-59	31.57	31.69	424.88	394.88	365.88
HROST-113	6/20/05	9-73	714.92	29.72	429.88	420.88	356.88
HROST-123	6/27/05	26-48	166.42	32.35	426.12	400.12	378.12
HROST-128	8/29/05	32-47	445.61	38.58	429.81	397.81	382.81
HROST-129	8/30/05	33-47	775.84	34.31	430.27	397.27	383.27
HROST-130	9/16/05	16-50	300.85	40.81	429.74	413.74	379.74

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#### TABLE 2. PROPOSED GROUNDWATER MONITORING NETWORK AND ACTIVITIES HARTFORD PETROLEUM RELEASE SITE, HARTFORD, ILLINOIS

1

Location	Hydrostratigraphic Unit	Transducer	Monthly Gauging	Dissolved Petroleum Hydrocarbon	Geochemical Indicators		
Wells Beyond the Limit of the Smear Zone							
MP-132S	N. Olive		х	x	x		
MP-132M	Rand		x	x	x		
HMW-039A	Main Sand	-	X X		-		
HMW-039B HMW-039C	Main Sand Main Sand	×	x	-	~		
HMW-042B	Main Sand		â	X X	X X		
HMW-052B	Main Sand	_	x	x	~		
HMW-052C	Main Sand		x	x			
MP-063C	Main Sand	-	x	x	×		
MP-065C	Main Sand		x	x	x		
MP-092D	Multiple Strata	X2	X				
Total				8	6		
	N 01	Well Within the Limit					
HMW-038A	N. Olive		x	-	-		
HMW-048A	N. Olive		x	X	-		
HMW-049A	N. Olive		x	X	X		
MP-034A	N. Olive	-	x	x	X		
MP-042A MP-056A	N. Olive		x	X	X		
MP-036A MP-078B	N. Olive N. Olive	-	X X	Х	x		
MP-083A	N. Olive	-	x	×	-		
MP-085A	N. Olive	-	x	x	×		
				^	-		
HMW-048B	Rand	<b></b>	X	-	-		
MP-029C	Rand	х	X				
MP-034B	Rand	-	X	X	X		
MP-042B	Rand	-	X	X	X		
MP-049B	Rand	-	x	X	х		
MP-056B	Rand		x	х	-		
MP-078C	Rand	-	X	-	-		
MP-083B MP-085B	Rand Rand	-	X X	x	х		
		-	^	x	-		
HMW-048C	EPA		Х	х	-		
HMW-049C	EPA		Х	х			
MP-085C	EPA	-	x	х			
HMW-038C	Main Sand	-	х	х			
HMW-040B	Main Sand		X	x			
HMW-040C	Main Sand		X	x	x		
HMW-041A	Main Sand	-	х	x	-		
HMW-041B	Main Sand	-	X	X	x		
HMW-041C	Main Sand	-	X	X			
HMW-048D	Main Sand	-	x	x	x		
HMW-049D	Main Sand	-	X	x	-		
MP-034C MP-042C	Main Sand Main Sand		X	x	х		
MP-042C	Main Sand	-	x x	X	-		
MP-049C	Main Sand	 Y	x	× -			
MP-055C	Main Sand	×	x				
MP-056C	Main Sand	<u> </u>	â	×			
MP-078D	Main Sand	_	x	Â.	×		
MP-079D	Main Sand	×	x	<u>^</u> .	^		
MP-080C	Main Sand	x	x	_	-		
MP-083C	Main Sand	-	x	×	x		
MP-085D	Main Sand	x	x	x	Â		
MP-084C	Multiple Strata	x	x				
MP-090C	Multiple Strata	x	x	-	-		
Total		8	42	31	16		
1							

Notes:

"X" indicates the activity to be performed; "--" indicates activity will not be performed

Groundwater samples will only be collected if groundwater is within the screened interval of the indicated well and LNAPL is not present

### FIGURES

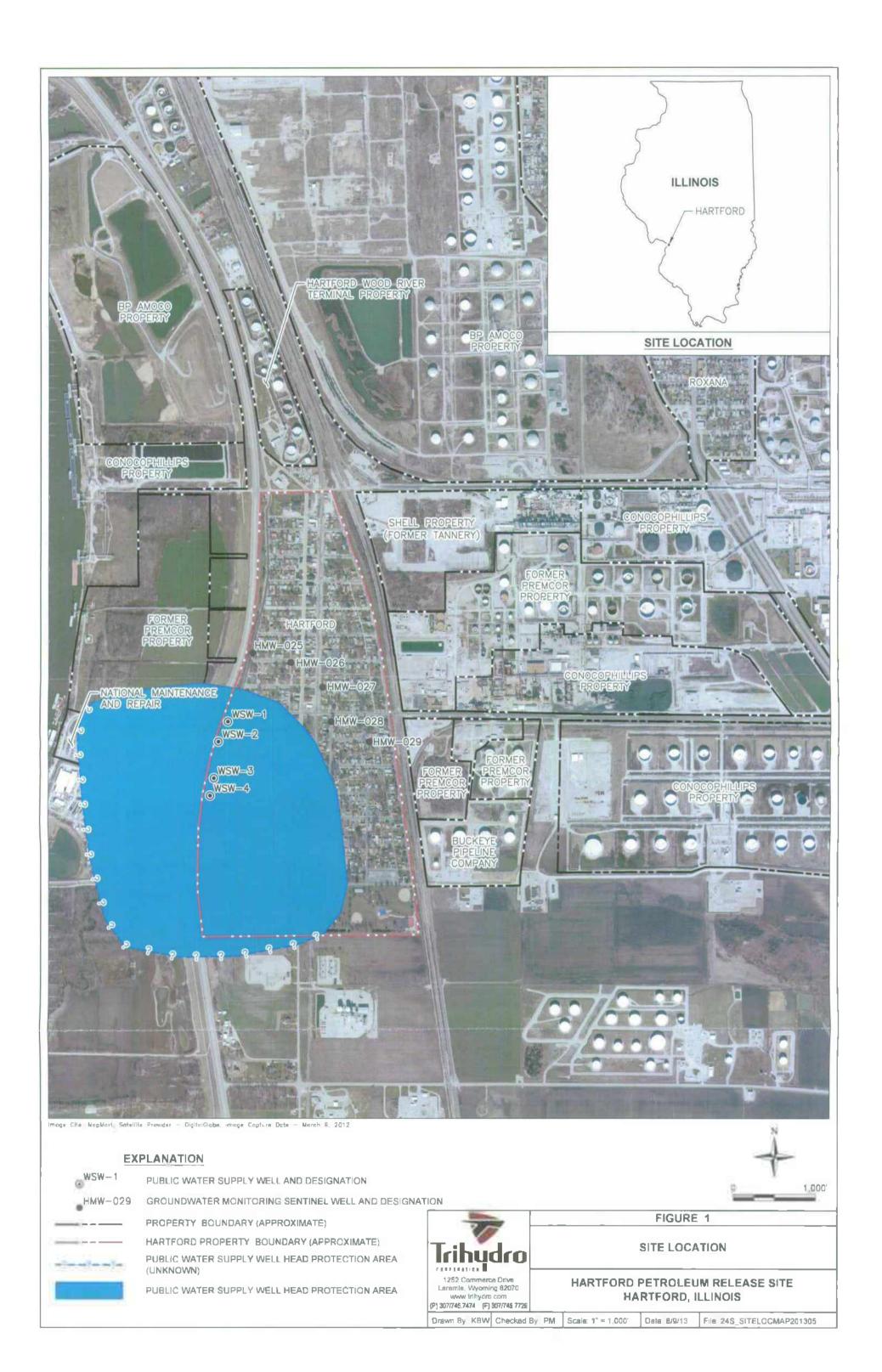
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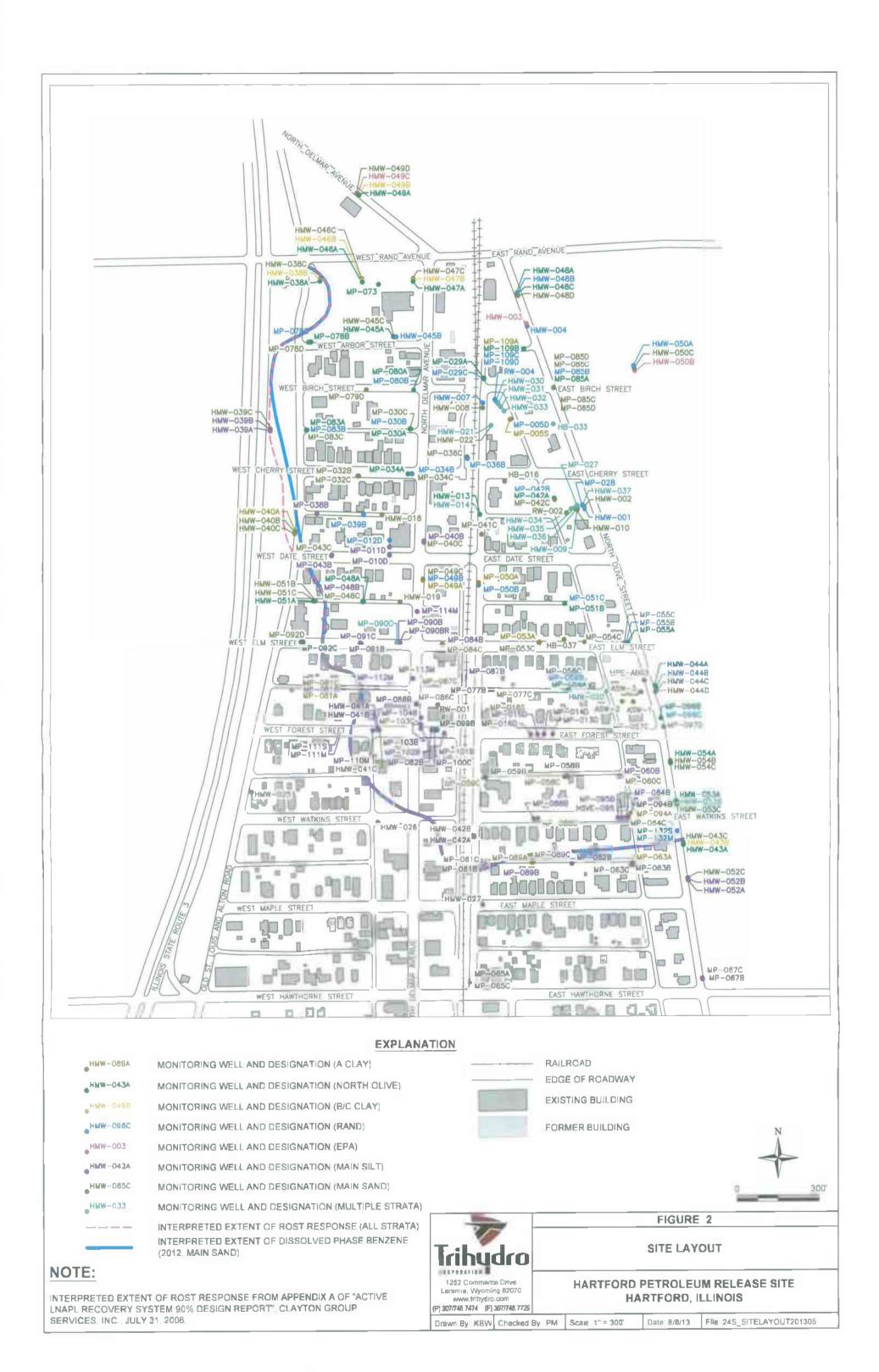
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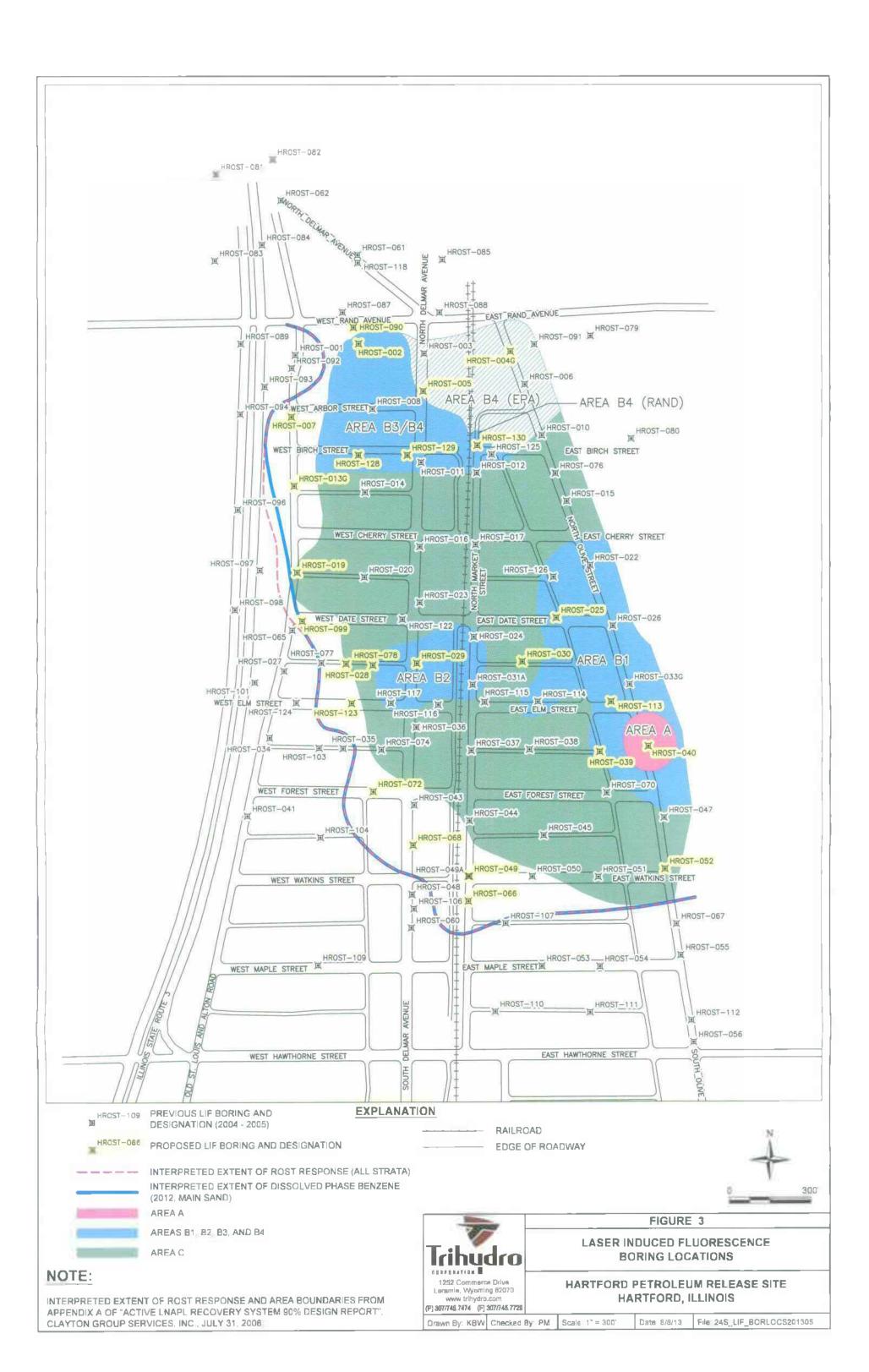
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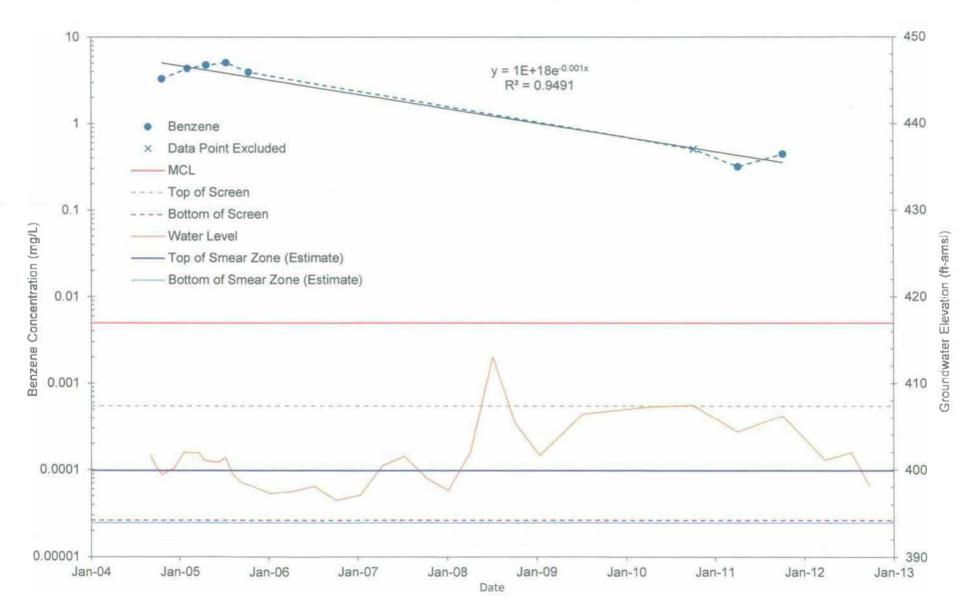


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#### FIGURE 4. DISSOLVED PHASE BENZENE CONCENTRATION TREND FOR MONITORING WELL HMW-041B HARTFORD PETROLEUM RELEASE SITE, HARTFORD, ILLINOIS

Note: Data point excluded if groundwater table outside of monitoring well screened interval.

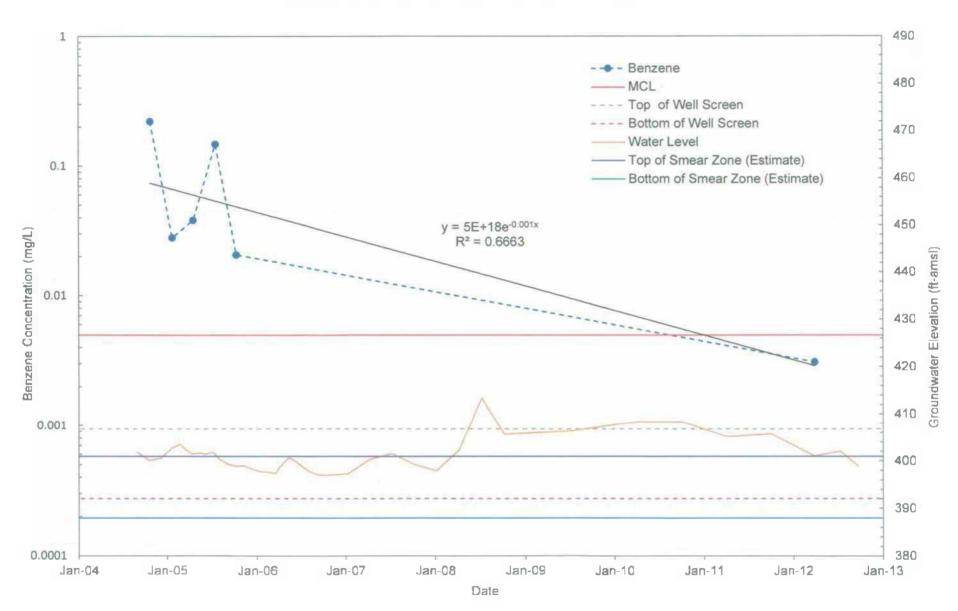
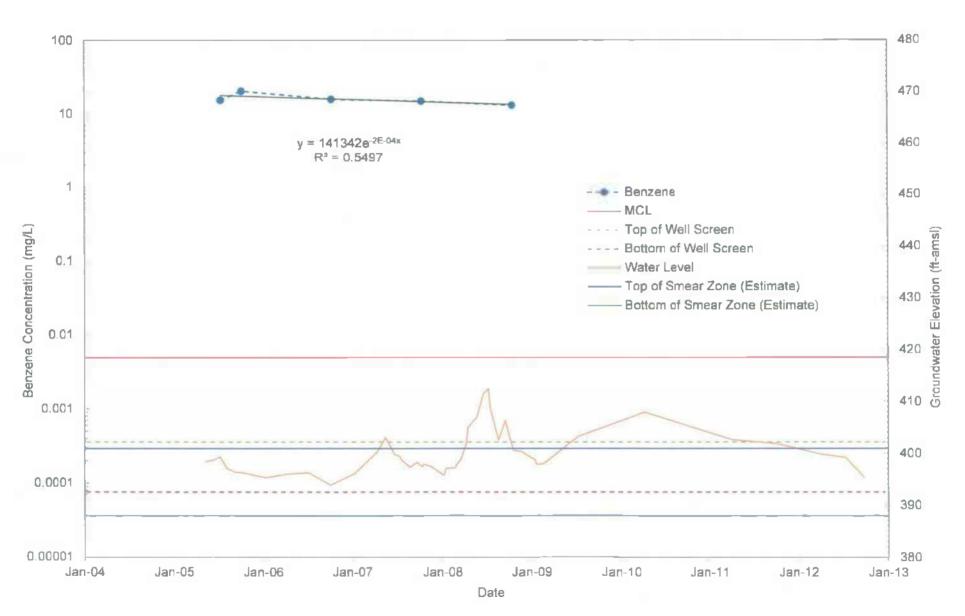
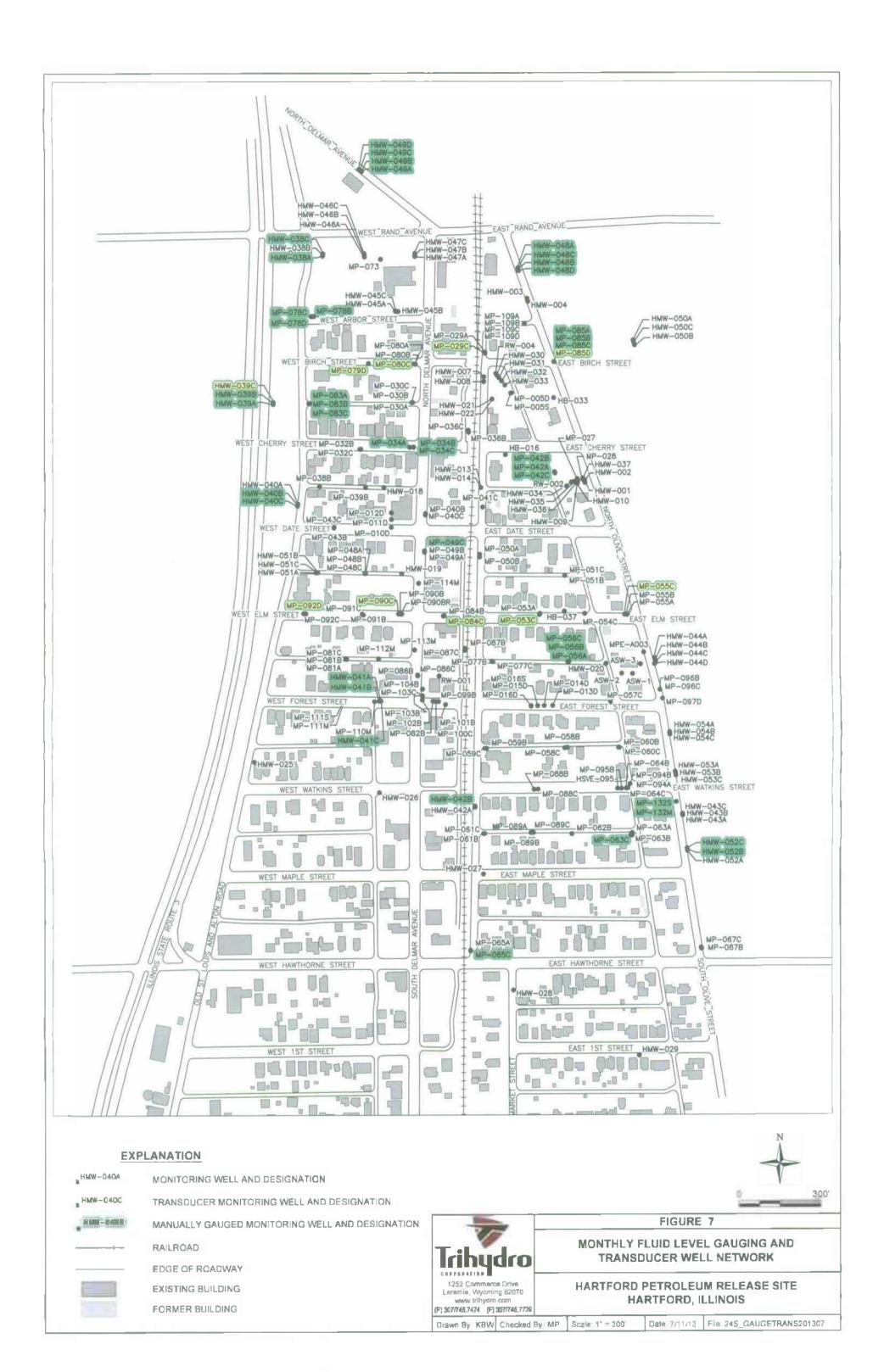
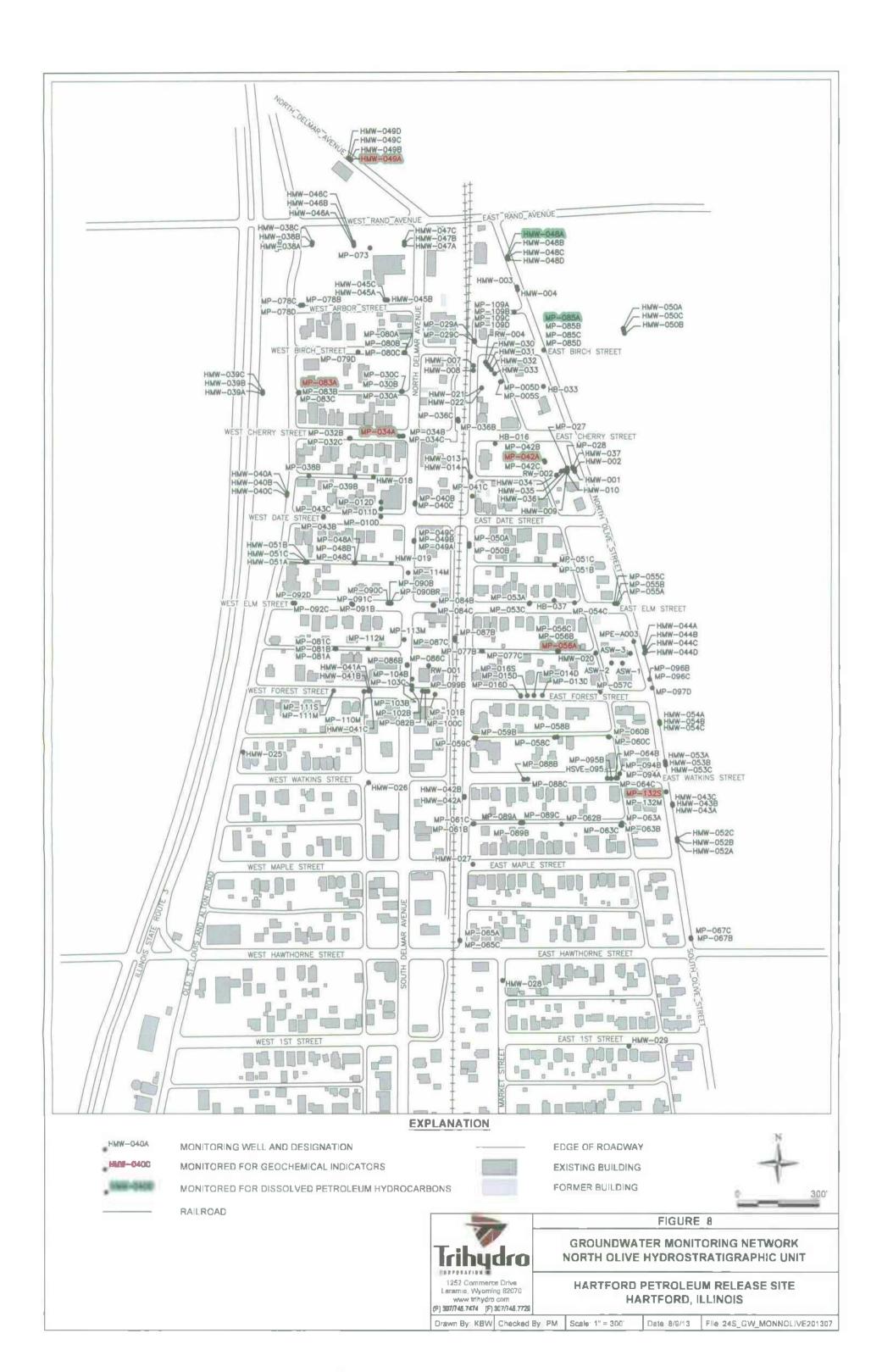


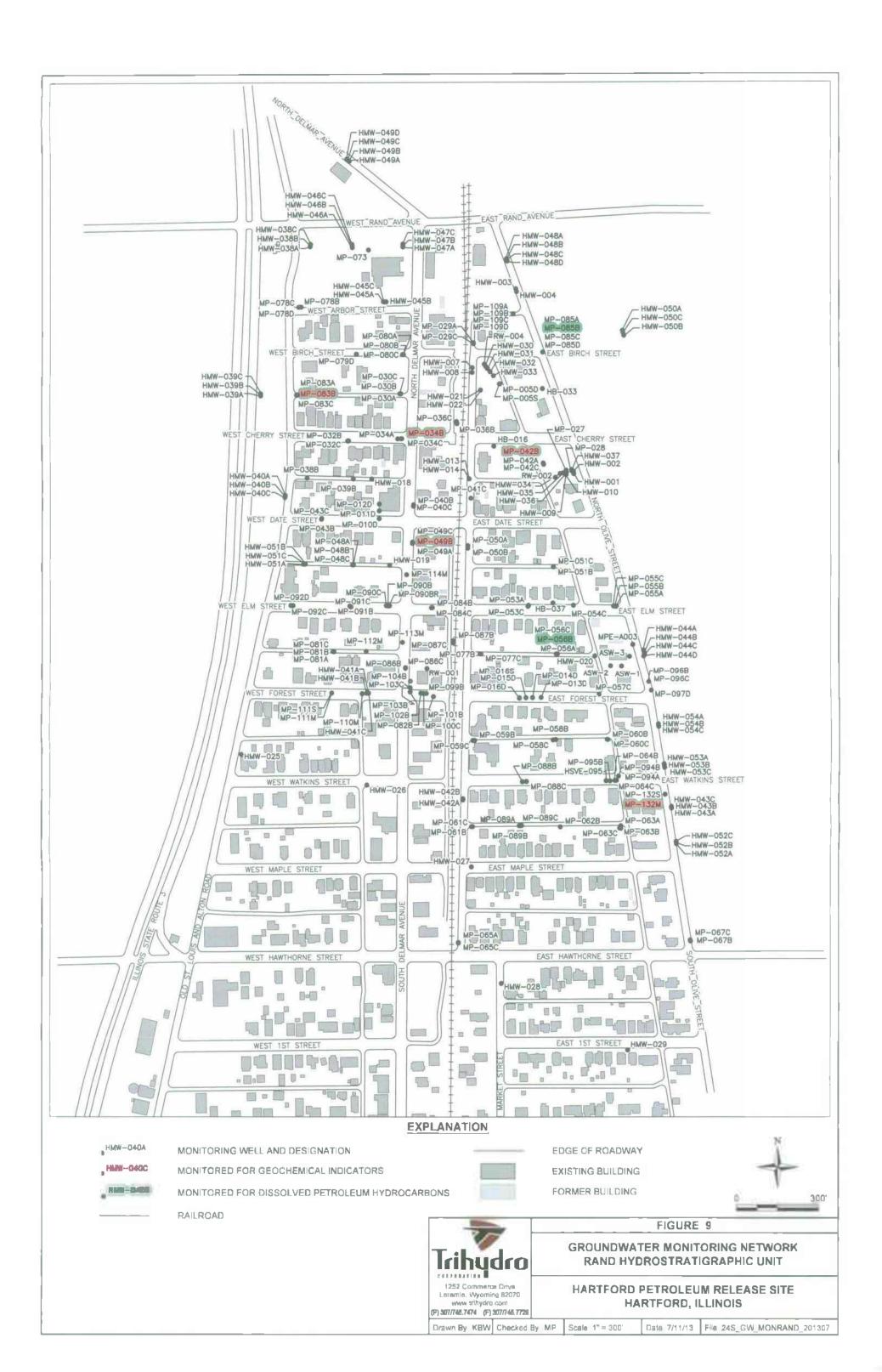
FIGURE 5. DISSOLVED PHASE BENZENE CONCENTRATION TREND FOR MONITORING WELL HMW-042B HARTFORD PETROLEUM RELEASE SITE, HARTFORD, ILLINOIS

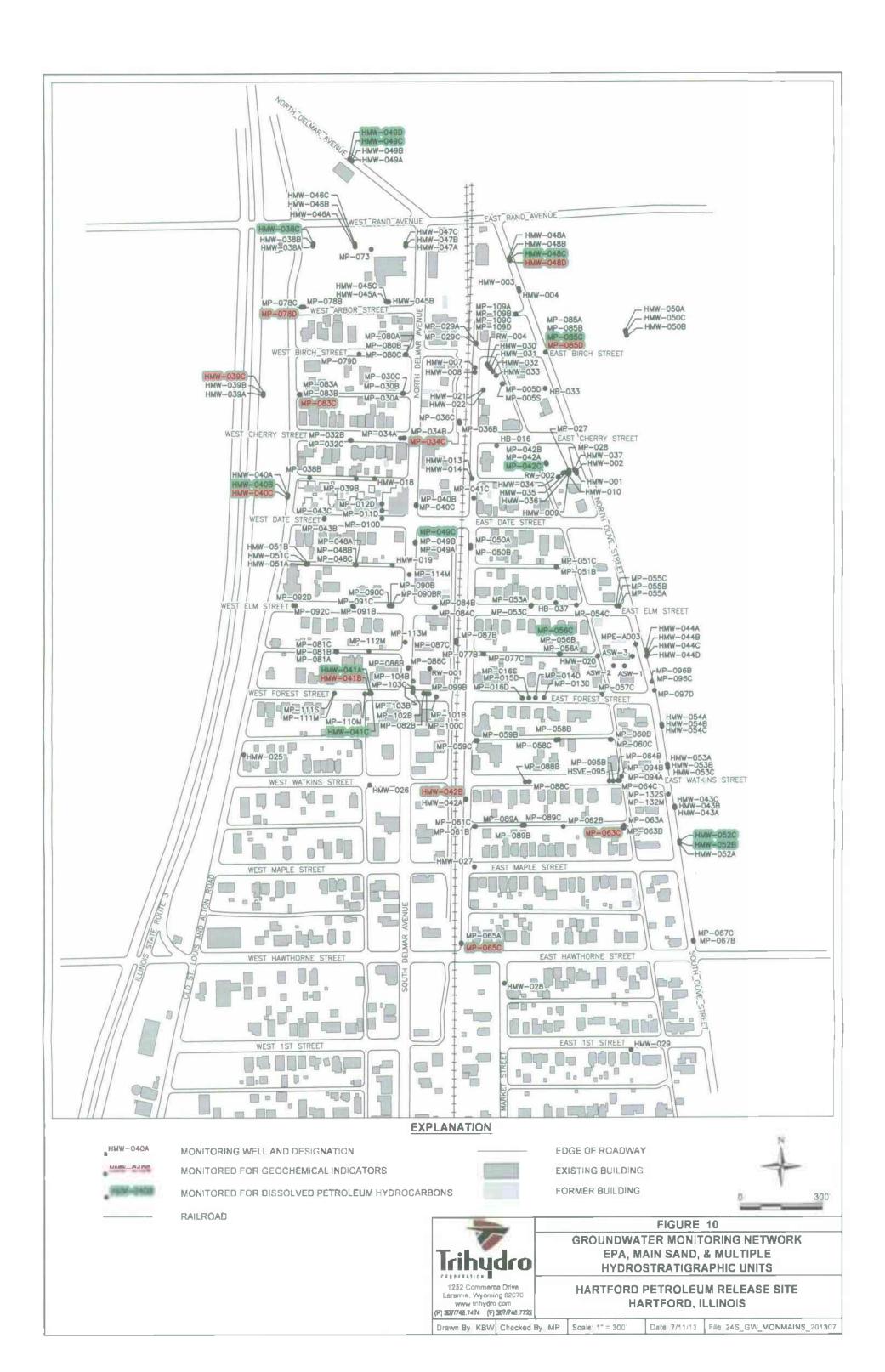


#### FIGURE 6. DISSOLVED PHASE BENZENE CONCENTRATION TREND FOR MONITORING WELL MP-078D HARTFORD PETROLEUM RELEASE SITE, HARTFORD, ILLINOIS









### **APPENDICES A THROUGH C**

### (PLEASE SEE ATTACHED CD)



#### BOL REFERENCE SHEET --- SAME FACILITY

Facility Number:			
Facility Name:	Hartford Free Hyd	rocarbon	Pool
USEPA Number:		•	
File Category:	19C - SF Te	h	
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FOR ADDITIONAL INFORMATION ON THIS, SEE CATEGORY  $\underline{19c-SFTech}$ UNDER THIS SAME FILE HEADING. (One CD)

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