INFLUENCE OF METHANOGENIC BACTERIAL DEGRADATION OF PETROLEUM HYDROCARBONS ON MOBILE LNAPL

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ABSTRACT

A case study is presented highlighting changes in geochemical conditions induced by the anaerobic degradation of petroleum hydrocarbons (PHCs) that enhanced the coalescence of dissolved phase PHCs into light non-aqueous phase liquid (LNAPL). Forensic analysis detected the presence of weathered light, middle and heavy weight PHCs in groundwater and LNAPL samples that were consistent with straight run gasoline, diesel fuel and crude oil. Dissolved phase concentrations migrated over 1,500 feet through dense silt and clay alluvium and mobile LNAPL was observed in recovery wells bisecting the migration path. The combined concentration of PHCs in soil, groundwater and vapor phases exceeded the Soil Saturation Concentration (C_{sat}) literature values for gasoline and diesel fuel in fine sand and silt, indicating the presence of immobile LNAPL. Combined PHC concentrations, however, were well below the LNAPL Saturation Concentration (C_{res}) literature values for gasoline, diesel fuel and crude oil PHCs in fine sand, silt and clay soil. The ample storage capacity available for PHCs, particularly in soil, suggests that the presence of LNAPL in the central area of the site did not migrate there as a contiguous plume, but rather formed from the enhanced coalescence of dissolved phase PHCs. The findings of subsurface investigations performed to confirm a conceptual site model (CSM) developed for the long range migration of dissolved phase PHCs and the formation of isolated pockets of LNAPL are presented. Also discussed are the results of a pilot test involving the injection of an anionic surfactant and brine solution that simulated similar geochemical conditions associated with the coalescence of PHCs to LNAPL that resulted in the recovery of approximately 80 gallons of LNAPL downgradient of the treatment area.

INTRODUCTION

The recovery of petroleum hydrocarbons (PHCs) from poorly permeable soils continues to be a challenge for the effective remediation of groundwater.[1] A case study is

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[1] Innovations in Groundwater and Soil Cleanup. From Concept to Commercialization (1997) ISBN: 978-0-309-06358-6. Commission on Geosciences, Environment and Resources. Water Science and Technology Board

presented that defines the degree and extent of straight run gasoline, diesel fuel and crude oil PHCs partitioned among soil, groundwater, vapor and LNAPL phases and how the anaerobic biodegradation of PHCs that altered the dynamic equilibrium among these phases influenced the long range migration of dissolved phase PHCs over 1,500 feet and the isolated occurrence of LNAPL.

This paper presents the recent findings of subsurface investigations performed to evaluate a Conceptual Site Model (CSM) that was developed to explain the long range migration of PHCs through seemingly impenetrable silt and clay soil and the appearance of LNAPL in wells that bisected the contaminant flow path. The information obtained was used to design and perform a pilot test that resulted in the recovery of approximately 80 gallons of LNAPL.

Key to the design of effective remedial actions is an understanding of the distinction between immobile and mobile LNAPL, and how changes in the dynamic phase partitioning equilibrium of PHCs in soil, groundwater, vapor and LNAPL phases can enhance PHC migration and LNAPL formation, but also aid in the design and performance of effective remedial actions.

Distinction between Mobile and Immobile LNAPL

Upon the release of petroleum to soil, the migration of the free product phase (i.e. mobile LNAPL) is typically restricted to the immediate vicinity of the release, and is directly related to soil permeability and the type and volume of product released. For small releases, soil pore capillary forces are effective at retaining LNAPL to site soil. For larger releases, gravitational forces create a pressure head that exceeds the capillary retention forces, promoting further migration until the volume of mobile LNAPL diminishes.

In cases where mobile LNAPL reaches the groundwater table, groundwater will be displaced to the extent gravitational head pressure and soil permeability permit. Once the LNAPL plume ceases to be mobile, PHCs comprising this immobile LNAPL will continue to migrate by advection and/or dispersion via groundwater according to their water solubility or volatilize into saturated as well as unsaturated soil pores based on their vapor pressure.

As dissolved phase PHCs continue to migrate, their overall hydrophobic nature drives their coalescence into LNAPL, in accordance with their effective water solubility and vapor pressure. While this LNAPL is not capable of migrating as free product, it serves as a secondary source capable of partitioning into soil, groundwater and vapor phases.[2] It is the recovery of immobile LNAPL that is most central to achieving the required remediation of groundwater and vapor phase PHCs.

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[2] Three and Four Phase Partitioning of Petroleum Hydrocarbons and Human Health Risk Calculations (December 2006) Geosphere, Inc. and CH2MHILL for the Alaska Department of Environmental Conservation, Statement of Cooperation Working Group

Phase Partitioning of PHCs

A prerequisite for the design of effective remedial measures is an awareness of the type of petroleum product(s) present, the PHCs comprising them, and their distribution among soil, groundwater, vapor and LNAPL phases. The partitioning of PHCs among these phases is in dynamic equilibrium where changes in the mass present in one phase affects the distribution among the others.

Henry's Law essentially describes the tendency of a substance to dissolve in groundwater and/or volatilize into soil pores. For example, gasoline related PHCs have a greater propensity to volatilize into soil gas and dissolve into groundwater compared to diesel fuel and crude oil PHCs. As the product weathers or as PHC vapors are actively remediated, the amount of PHCs capable of occupying the vapor phase decreases and the equilibrium shifts towards groundwater, soil or LNAPL phases. Under conditions where decreases in the effective water solubility of PHCs occur as the number and/or mass of dissolved phase constituents increases, the tendency for PHCs to coalesce into LNAPL increases.

Differences in absolute and effective water solubility of benzene is a prime example of how changes in the number of constituents present in a solution can affect the phase partitioning equilibrium. The absolute solubility of benzene (the maximum amount that can be dissolved in pure water) is approximately 1,780,000 ug/l. When present in groundwater the maximum amount of benzene that can dissolve decreases as the number of constituents in groundwater increases. This effective water solubility of benzene when present in groundwater impacted by gasoline is approximately 100 times lower than its absolute water (i.e. 17,000 ug/l), and 2,000 times lower in groundwater impacted by diesel fuel (i.e. 880 ug/l).[3] As will be discussed further, the effective water solubility of benzene proximate to the LNAPL wells is as high as 4,000 ug/l with the highest concentration in soil being 3 mg/kg (restricted target remediation goal (TRG) of 1.36 mg/kg).

The combined concentration of PHCs adsorbed to soil, dissolved in groundwater and volatilized into soil gas provides a measure of the amount of petroleum that can be stored in the subsurface. The maximum storage capacity of soil, groundwater, and soil gas for PHCs is referred to as the Soil Saturation Concentration (C_{sat}), which varies depending upon the types of PHCs and soil present. At concentrations below C_{sat}, the mass of PHCs is insufficient to coalesce into immobile LNAPL and groundwater is not expected to be impacted. At concentrations above C_{sat}, the mass of PHCs is capable of coalescing into immobile LNAPL which serves as a secondary source of PHCs capable of diffusing into groundwater or volatizing into soil gas.

Proximate to the immediate vicinity of a release of mobile LNAPL, the combined PHC concentration is expected to exceed the LNAPL Residual Concentration (C_{res}), which like C_{sat}, is dependent upon the types of petroleum product and soil present.[4]

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[3] Natural attenuation of fuels and chlorinated solvents. Wiedemeier T. H. et al (1999). John Wiley & Sons, Inc. ISBN 0-471-19749-1.

[4] Non-aqueous phase liquid (NAPL) mobility limits in soil. Brost, E.J and DeVaull, G.E. (June 2000) American Petroleum Institute Soil & Groundwater Research Bulletin

Comparing the combined PHC concentrations in soil, groundwater and vapor phases to literature values of C_{sat} and C_{res} for a given petroleum product and soil type provides a measure of the presence of immobile and mobile LNAPL.[3] Literature values for C_{sat} and C_{res} have been developed for various soil types impacted by gasoline, diesel fuel or crude oil. The C_{sat} values for gasoline and diesel fuel PHCs for fine sand and silt soil are 387 mg/kg and 18 mg/kg, respectively. The C_{res} values in fine sand, silt and clay soil for gasoline, diesel fuel and crude oil are 5,000 mg/kg, 10,000 mg/kg and 20,000 mg/kg, respectively.

Case Study

The study area is located at an elevation of approximately 120 feet above mean sea level (amsl) within an agricultural field downgradient and west of a decommissioned asphalt refinery at the eastern limit of the Mississippi River delta. Surface topography gradually descends towards the western limit of the study area rising to approximately 240 feet amsl at the top of a bluff located approximately 2,000 feet east of the former refinery. A site plan showing the former refinery and stormwater impoundment, and groundwater monitoring and recovery wells is presented as **Figure 1**.

Depth to groundwater ranges from approximately 2-8 feet proximate to the former refinery and 15-30 feet in the western limits of the study area. Regional and localized groundwater flow is to the west trending locally to the northwest in the western part of the study area. The average hydraulic gradient is approximately 2.4% in the east and 0.7% in the west, corresponding to an average groundwater transport velocity of approximately 81 feet/year and 23 feet/year, respectively.

The surficial geology of the study area is dominated by relatively dense alluvium of the Mississippi River delta comprised of poorly permeable silt and clay soil. Discontinuous lenses of fine to medium sand and silt exist at varying depths where the depth and frequency of occurrence of these preferential groundwater flow pathways decreases from east to west, as depicted in **Figure 2**.

Petroleum hydrocarbons were initially detected in soil and groundwater samples collected from the former stormwater impoundment. Subsurface investigations confirmed the presence of PHCs in soil and groundwater further downgradient within the agricultural field west of a highway. Assessment and remedial actions involving the installation of 29 monitoring wells and 47 dual phase extraction (DPE) wells were conducted from 2009 to 2013. Quarterly groundwater analysis of BTEX compounds, naphthalene, and 2-methylnaphthalene by EPA Method 8021B and total petroleum hydrocarbon-diesel range organics (TPH-DRO) via EPA Method 8015C detected maximum concentrations of benzene (4,100 ug/l), naphthalene (360 ug/l) and TPH-DRO (4,800 ug/l) above the Mississippi Department of Environmental Quality (MDEQ) target remediation goals (TRGs) of 5 ug/l, 6.2 ug/l and 650 ug/l, respectively. Of the 13 perimeter wells, only PW-10, PW-11 and PW-12 exhibited benzene, naphthalene and TPH-DRO in groundwater samples above minimum reporting limits (RL), with benzene (310 ug/l) exceeding its TRG in PW-12.

Two fixed DPE systems were installed to recover impacted groundwater and LNAPL. Scaling of the transfer piping and equipment resulted in frequent system shut

downs requiring biweekly flushing and cleaning with muriatic acid. The large number of recovery wells and long connection piping runs limited the DPE operations to 4 to 10 wells per fixed system, which constrained the recovery of vapor and groundwater phase PHCs. The highest levels of TOVs reported by PID meter in vapors recovered by the DPE systems positioned in the impoundment and agricultural field were 10 ppmv and 330 ppmv, respectively.

In November 2013, Ramboll Environ was asked to perform a 3rd party review of the effectiveness of the fixed DPE systems. The forensic analysis of samples of LNAPL and impacted groundwater were recommended to identify the type of petroleum product(s) present. Samples were submitted to Alpha Analytical, Inc. of Westborough, MA, a MS certified laboratory, for comprehensive analyses. The results were reviewed by NewFields who identified the petroleum products to be a very weathered mix of light, middle and heavy weight PHCs consistent with straight run gasoline (C_{5-9} carbon fractions), diesel fuel (C_{9-28} carbon fractions) and crude oil (C_{28-44} carbon fractions).

Ramboll Environ presented a comprehensive work plan in 2014 recommending the use of mobile DPE equipment to define the extent of contamination throughout the study area through the recovery of vapor and groundwater phase PHCs. Real time total organic vapors (TOVs) and methane levels were measured via an in-line Foxboro Model 1000A flame ionization detector (FID) and groundwater samples were collected daily from a 15-gallon scrub tank on the mobile DPE units. TOV and methane levels as high as 20,000-25,000 ppmv were detected in the former impoundment area and in areas of the agricultural field proximate to recovery wells A 4-7 and C 1-10, with lower levels detected elsewhere.

Vapor phase PHCs accounted for the majority of the mass of contaminants recovered via DPE, exceeding the recovery of groundwater phase PHCs by 2-3 orders of magnitude. DPE performed at varying depths within the existing recovery wells demonstrated the potential for preferential PHC migration pathways along the A-series recovery wells to the north and C-series recovery wells to the south. The proportion of gasoline and diesel fuel PHCs in groundwater recovered during DPE events was approximately 20% and 80%, respectively, which was the inverse to that detected in well samples. The concentrations of PHCs detected in groundwater recovered during DPE events were considered to be representative of the PHCs comprising immobile LNAPL.

Based on the results of the DPE events conducted at the existing recovery wells, Ramboll Environ oversaw the installation of a total of 29 recovery wells (ERW 1-29). Five recovery wells were installed north of the former impoundment area upgradient of the A-series wells and seven wells were installed upgradient of the C-series wells within the impoundment area east of the highway. The remaining wells were installed across the study area to evaluate soil conditions and analyze PHCs in soil to further characterize potential migration pathways.

The vertical extent of TOVs and PHCs coincided with sand and silt lenses occurring most frequently in the eastern portion of the study area and least to non-existent in the west and northwest areas. The horizontal and vertical extent of TOVs by PID meter, and TPH-GRO and TPH-DRO concentration by laboratory analyses, in soil, are depicted in **Figures 3A, 3B and 3C, respectively**. Soils analyzed for VOCs (full list) exhibited very low concentrations and as such are not presented graphically.

The initial characterization of site conditions demonstrated a correlation between methane levels and wells exhibiting the presence of LNAPL. The detection of methane at levels as high as 25,000 ppmv were indicative of the high rates of anaerobic degradation of PHCs by methanogenic bacteria.

The analysis of groundwater samples collected from wells located throughout the study area at varying depths, taking care to avoid the intake of free phase product, revealed the presence of elevated concentrations of benzene, TPH-GRO and TPH-DRO with the highest concentrations detected proximate to the LNAPL wells. **Figure 4** presents benzene isoconcentration maps based on the analysis of groundwater samples collected in 2010 (collected by others) and 2015/2016 (Ramboll Environ data). **Figure 5** presents TPH-GRO and TPH-DRO isoconcentration maps based on the analysis of groundwater samples collected in 2015/2016. Black triangles represent wells exhibiting measureable LNAPL above 0.01 feet in thickness.

Additional investigations were conducted to evaluate the CSM developed to explain the migration of PHCs over 1,500 feet and the appearance of LNAPL in wells located approximately 700 feet west of the former refinery. The presence of mobile LNAPL was not considered to be the result of the contiguous migration of mobile LNAPL from the refinery due to the low PHC concentrations detected in soil and groundwater upgradient of the LNAPL area. High concentrations of methane that coincided with the wells exhibiting LNAPL suggested that the degradation of PHCs by methanogenic bacteria that created strongly reducing conditions decreased the effective water solubility of PHCs that enhanced the coalescence of dissolved phase PHCs to LNAPL.

METHODS

Naturally Occurring Soil Minerals

Ramboll Environ oversaw the installation of seven (7), 4-inch diameter, recovery wells by Walker Hill Environmental, Inc. of Foxworth, MS using sonic drilling methods in May 2016, to further define the extent of PHCs in soil and groundwater proximate to the northern property boundary of the agricultural field. Soil samples were field screened for TOVs by PID meter, and up to three representative samples per soil boring were analysed by Alpha Analytical, Inc. for VOCs via USEPA Method 8260C (full list), TPH-GRO and TPH-DRO via USEPA Method 8015C(M) and Petroleum Hydrocarbon Identification (PHI) Scan via EPA Method 8015. The PHI scan, which is essentially an extended 80 minute chromatographic run, provides a quantitative analysis of C_{9-44} carbon fractions, that subtracted from TPH-DRO (C_{9-28} carbon fraction) concentrations provide an estimate of the heavier weight C_{28-44} carbon fractions representative of crude oil PHCs.

A total of 9 soil samples were also analyzed for 26 target analyte list (TAL) metals by USEPA Method 6010B to identify the naturally occurring soil minerals most likely to contribute to dissolved phase metal concentrations under the strongly reducing conditions at the site.

Dissolved Phase Soil Minerals

Groundwater samples were collected in June and July 2016 from 35 recovery wells in accordance with USEPA low flow methods[5]. Samples were analysed by Alpha Analytical, Inc. for VOCs (full list), TPH-GRO, TPH-DRO, PHI Scan, dissolved methane and carbon dioxide via US EPA Method RSK SOP-175. Total and dissolved metals previously identified as being most prevalent at the site were analysed by USEPA Method 6010B. Groundwater samples for the analysis of dissolved metals were field filtered using GoPro Inline 0.45u filters prior to nitric acid preservation.

Dual Phase Extraction (DPE) Employing Mobile Equipment

Mobile DPE units provided by Fruits & Associates of Acworth, GA were used to characterize groundwater and vapor phase PHCs throughout the study area. Each unit was capable of performing DPE at up to six recovery wells, achieving groundwater recovery rates of up to 500 gallons/hour, applied vacuums of up to 15 inches of mercury and total air flow rates of up to 400 air cubic feet/minute (acfm). Real time TOV and methane levels were measured via an in-line Foxboro Model 1000A flame ionization detector (FID) calibrated to methane. Daily groundwater samples were collected from a 15-gallon scrub tank for laboratory analysis of PHCs where the results were used to calculate the proportions and mass of PHCs in the groundwater recovered during DPE events.

PHC vapors were combusted by a 95-99% efficient on-board thermal incinerator fueled by propane gas when the thermal BTUs provided from the recovered PHCs were insufficient to sustain effective combustion. Recovered groundwater was stored in a 3,400 gallon on-board tank until transfer to 21,000 gallon frac tank(s) via tanker truck. Groundwater was treated on-site by pumping through two in-line bag filters, two filters containing 1,000 pounds of liquid phase granular activated carbon (LGAC), and one filter containing 1,800 pounds of activated alumina (provided by Carbonair) for the removal of PHCs and naturally occurring arsenic, respectively, before being discharged to a drainage ditch in accordance with a National Pollution Discharge Elimination System (NPDES) permit. The mobile DPE equipment and on site treatment and disposal of recovered groundwater avoided problems associated with the scaling of the fixed DPE systems that required frequent muriatic acid cleaning to maintain limited operational capabilities.

Comparison of Total PHCs in Soil, Groundwater and Soil Gas to Literature Values for C_{sat} and C_{res}

The total mass of PHCs partitioned in soil, groundwater and vapor phases were calculated on a weight to weight basis (i.e. in mg/kg) using the analytical results obtained for gasoline (TPH-GRO), diesel fuel (TPH-DRO) and crude oil (PHI Scan minus TPH-DRO) PHCs in samples collected upgradient, within and downgradient of the LNAPL wells.

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[5] Low Stress (Low Flow) Purging and Sampling Procedure for the Collection of Groundwater Samples from Monitoring Wells. US EPA EQA SOP-GW 001 Revision 3 January 19, 2010

Since PHCs in groundwater were reported by the laboratory on a weight by volume basis (i.e. mg/l), the conversion factor of 0.3 liter/kg soil[6] was used to determine the average mass of PHCs in groundwater present in one kilogram of soil.

Total organic vapors (TOVs) measured in ppmv by FID Analyzer at individual recovery wells were averaged and converted to vapor phase PHC concentrations in mg/m^3 using the linear regression equation of y = 0.263x + 181, where and x equals TOVs minus methane in ppmv and y equals laboratory derived VOCs in mg/m^3 based on the analysis of volatile PHCs by the MADEP air phase petroleum hydrocarbon (APH) Method and USEPA Method 7C(M) in air samples collected from recovery wells C-8, C-9 and B-10 in July 2016. The conversion factor of 0.0003 m^3/kg soil was used to determine the average mass of PHCs in soil gas (i.e. vadose zone) present in one kilogram of soil.[7]

Surfactant Feasibility Study and Pilot Test

Surfactant Enhanced Aquifer Remediation (SEAR) involves the injection of a solution of engineered compounds and minerals designed to reduce the interfacial tension between immobile LNAPL and groundwater within soil pores, thereby making the LNAPL more mobile and recoverable. In general, nonionic surfactants increase the solubility of LNAPL through the formation of an emulsion, whereby a mixture of petroleum and water is recovered via groundwater extraction. Conversely, anionic surfactants enhance the mobilization potential of immobile LNAPL minimizing the formation of emulsions, whereby remedial efforts primarily focus on the recovery of LNAPL. Anionic surfactants are preferred over cationic surfactants due to their net negative charge that repels negatively charged soil so that more surfactant is available to liberate LNAPL. Anionic surfactants are also biodegradable and nontoxic to PHC degrading bacteria, and the LNAPL liberated is less likely to migrate beyond property boundaries as would emulsions formed from non-ionic surfactants.[8]

A treatability study was performed by Surbec, a company comprised of senior researchers at the School of Chemical, Biological and Materials Engineering at the University of Oklahoma, in Norman, OK, in cooperation with Tersus Environmental of Wake Forest, NC. Samples of site soil, groundwater and mobile LNAPL were used in batch testing and column studies to confirm whether or not the use of anionic surfactants was feasible at the site.

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[6] Conversion factor for mg/l of PHCs in groundwater to mg/kg of soil = 0.037 tons soil/ cf = 74 lbs/cf = 33.6 kg/cf; 33.6 kg soil/28.4 liters = 1.18 kg/liter or 0.847 liter/kg soil x 35% = 0.3 liter/kg soil

[7] Conversion factor for mg/m^3 of PHCs in soil gas to mg/kg of soil = 0.037 tons soil/ cf = 74 lbs/cf = 33.6 kg/cf; 33.6 kg/0.028 m3 = 0.00084 m3/kg soil x 35% = 0.0003 m^3/kg soil

[8] Technology Practices Manual for Surfactants and Cosolvents, Chapter 4. Surfactant/Cosolvent Enhanced Recovery of NAPLs. February 1997) CH2MHILL. https://clu-in.org/products/aatdf/toc.htm

RESULTS

Naturally Occurring Minerals in Site Soil and Groundwater

Of the 26 TAL metals analyzed, 14 were detected above minimum laboratory reporting limits (RL), as summarized in **Table 1,** together with maximum TOV levels (ppmv). The sum of TAL metal concentrations (mg/kg) were inversely related to TOV levels where metal concentrations were lowest in soil exhibiting the highest TOV levels. Similar trends were observed when metal concentrations were compared to PHC concentrations. There was no apparent correlation in metal concentrations to soil type, moisture content or sample location. Of the 14 TAL metals detected in soil, iron, calcium, magnesium, aluminum, potassium, manganese and barium were present at concentrations considered to contribute the greatest to dissolved phase metal concentrations under strongly reducing conditions.

Results of the analysis of groundwater samples collected upgradient (ERW6, A4, C4, ERW21), within (A6, B6, C6, C8, ERW20, C9, C11) and downgradient (B10, C14, B14, A14) of the mobile LNAPL for the selected metals and PHCs are summarized in **Table 2**. No significant difference was noted between total and dissolved metal concentrations, and based on their predominance, calcium (56%), magnesium (36%), iron (5%), manganese (2.5%) and barium (0.1%) were used to represent the sum of metals present in groundwater at the site.

Correlation of Dissolved Metals and Methane to Mobile LNAPL

The relationship between soluble metals and methane concentrations in groundwater is presented in **Figure 6**. Solid symbols represent samples collected from recovery wells exhibiting mobile LNAPL.

The wells exhibiting mobile LNAPL coincided with dissolved metal concentrations above approximately 140,000 ug/l and methane concentrations above approximately 5,000 ug/l. Background concentrations of dissolved metals and dissolved methane were (56,000 ug/l) and (<1 ug/l), respectively.

Correlation between Dissolved PHCs and Mobile LNAPL

The relationship between dissolved carbon dioxide, dissolved methane, PHCs and LNAPL thickness is depicted in **Figure 7.** The trends in PHC, dissolved carbon dioxide and methane concentrations were similar in groundwater samples collected between recovery wells ERW-6 and B-6, which are located upgradient of the wells exhibiting the majority of LNAPL. The spike in dissolved methane and gasoline PHC concentrations corresponds to the wells containing LNAPL, where care was taken not to recover any LNAPL during sample collection. The continued decreasing trend in carbon dioxide within the area of LNAPL is consistent with its use as an electron acceptor by methanogenic bacteria. The rise in carbon dioxide concentrations downgradient of LNAPL wells is consistent with its high water solubility despite decreases in the methanogenic degradation of PHCs.

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Petroleum degradation via methanogenic bacteria is unique to other anaerobic catabolic processes in that it does not rely on the availability of exogenous terminal electron acceptors (i.e. nitrate, iron and sulfate). Instead methanogenic bacteria produce their own electron acceptor, carbon dioxide, which like methane, is a byproduct of the anaerobic degradation of PHCs. This process was first demonstrated by Zengler et al (1999) using hexadecane as a petroleum food source per the stoichiometric equation below.

$$4 \; C_{16}H_{34} + 30 \; H_2O \to 15 \; CO_2 + 49 \; CH_4$$
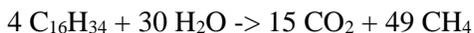
Given that carbon dioxide has an absolute water solubility of approximately 1,450,000 ug/l compared to 23,000 ug/l for methane, much higher concentrations of dissolved phase carbon dioxide can accumulate in groundwater compared to methane, which readily enters the vapor phase. Methane levels as high as 20,000 ppmv (i.e. 20,000,000 parts per billion by volume) were detected by FID Analyzer during DPE events. Air samples collected in July 2016 and analyzed for methane confirmed the detection of methane concentrations comparable to that measured by the FID Analyzer.

The concentration (ug/l) and proportion (%) of gasoline and diesel fuel related PHCs in groundwater samples collected upgradient, within and downgradient of the LNAPL are depicted in **Figure 8.** The wells are arranged from west (B-14) to east (RW-4). Gasoline PHC concentrations exceeded diesel fuel related PHC concentrations in groundwater with the highest concentrations coinciding with wells exhibiting mobile LNAPL and decreasing thereafter. Changes in diesel fuel PHC concentrations were less distinct. An inverse relationship between gasoline and diesel fuel PHCs was demonstrated when the proportion of TPH-GRO and TPH-DRO to their total concentration was determined.

Phase Partitioning of PHCs in Soil, Groundwater and Soil Gas

Gasoline, diesel fuel and crude oil PHC concentrations in soil, groundwater and soil gas are depicted on a weight to weight basis in milligrams per kilogram of soil (mg/kg) in **Table 3**. The total PHC concentrations per petroleum product type are presented separately to permit comparison to their individual C_{sat} and C_{res} literature values. PHI Scan analyses were limited to groundwater and soil samples collected from the former storm water impoundment southeast of US Highway 3 (ERW 23-29) and the north-central portion of the agricultural field (ERW 30-36). The average ratios of crude oil PHC to diesel fuel PHC concentrations in soil from the former impoundment (2.2x) and north-central (0.28x) wells were used to estimate crude oil concentrations for samples located proximate to these locations (see bolded data).

As expected, PHC concentrations were most prevalent in the soil phase, followed by groundwater, and soil gas. Total gasoline PHC concentrations exceeded the C_{sat} literature value of 387 mg/kg in 50% (11 of 22) of the samples evaluated, whereas the C_{sat} value of 18 mg/kg for diesel fuel was exceeded in 77% (17 of 22) of the samples.

Gasoline, diesel fuel and crude oil total PHC concentrations were well below their respective C_{res} literature values of 5,000 mg/kg, 10,000 mg/kg and 20,000 mg/kg, respectively in fine sand, silt and clay, except for the total diesel fuel PHC concentration of 13,001 mg/kg located southeast of US Highway 3 at ERW-29. While this exceedance

of the diesel fuel C_{res} was consistent with the detection of mobile LNAPL at nearby wells RW-2 and RW-3, the sub-C_{res} concentrations proximate to the wells in the center of the study area exhibiting mobile LNAPL were not.

Surfactant Pilot Test

The observation of the enhanced coalescence of dissolved phase PHCs to LNAPL by anaerobic bacteria in poorly permeable soil was explored as a potential groundwater remediation strategy. Surbec recommended a proprietary anionic surfactant formulation comprised of a 1.8% aqueous solution of TASK™ supplemented with 1.3% sodium chloride (NaCl) and 0.05 % calcium chloride ($CaCl_2$). A pre-surfactant flush of a similar aqueous solution limited to NaCl and $CaCl_2$ was recommended to purge mobile LNAPL from the pilot test area where surfactant was injected into ERW-20 and C-8 and groundwater was extracted at nearby recovery wells C-7, C-9, and B-8 and B-9 to enhance surfactant dispersion. The total pore volume in the pilot test area was estimated to be 39,000 gallons based on the presence of sand and silt lenses totaling the vertical depth of 1 foot and a porosity estimate of 35%.

A pilot test was conducted at seven of the LNAPL wells where the injection of brine followed by surfactant solutions resulted in the recovery of approximately 80 gallons of LNAPL at a downgradient well (C-9) located approximately 80 feet from the treatment area (C-8 and ERW-20) during DPE. No LNAPL was recovered downgradient of treatment wells where the brine solution was omitted.

Analysis of product in samples collected from wells exhibiting LNAPL indicated varying proportions of gasoline (16-65%, average of 41%), diesel fuel (24-67%, average of 44%) and crude oil (11-18%, average of 14%). The LNAPL recovered from C-9 following surfactant treatment was comprised of 65% gasoline, 25% diesel fuel and 11% crude oil. Conversely, the proportions of gasoline, diesel fuel and crude oil PHCs in groundwater ranged from 49-76% (average of 62%), 22-44% (average of 30%) and 4-13% (average of 8%), respectively.

DISCUSSION

Importance of Comprehensive Site Characterization

The remediation of soil and groundwater impacted by PHCs in low permeability sites continues to be a challenge, presumably due to the low water solubility and volatility of these compounds. Through the use of innovative assessment tools, like electrical resistivity imaging (ERI), contaminant migration in even the most dense of clays is observed to occur over substantial distances.[9] The case study presented in this paper demonstrates the migration of weathered PHCs consistent with straight run gasoline, diesel fuel and crude oil over 1,500 feet in the silt and clay alluvium of the Mississippi River delta.

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[9] Using electrical resistivity imaging to evaluate permanganate performance during an in situ treatment of an RDX-contamnated aquifer. Halihan et al (2009). Environmental Security Technology Certification Program Final Report ER-0635. Department of Defense.

Earlier investigations limited site characterization to the analysis of BTEX compounds, naphthalene and TPH-DRO in groundwater. Based on these results, a total of 46 recovery wells were installed in a 6 acre area to facilitate DPE operations from two fixed systems. This remedial approach proved to be ineffective at the recovery of vapor, groundwater and LNAPL phase contaminants where frequent system shutdowns, equipment scaling and pump failure, and the inability to perform DPE at more than 10 wells at a time constrained the effectiveness of remedial efforts.

The forensic analysis of groundwater and LNAPL samples revealed the presence of a complex mix of weathered straight run gasoline, diesel fuel and crude oil PHCs. A total of 36 additional recovery wells were installed to characterize soil conditions and define the lateral and vertical extent of PHCs in soil, groundwater, vapor, and LNAPL.

Impacted soil was shown to contain approximately 50% diesel fuel, 34% gasoline, and 16% crude oil, and dissolved phase PHCs contained approximately 30% diesel fuel, 62% gasoline, and 8% crude oil. Groundwater recovered during DPE events contained approximately 80% diesel fuel, 15% crude oil and 5% gasoline, which was considered to be consistent with PHCs comprising immobile LNAPL in soil pores that were recovered during DPE. Conversely, mobile LNAPL collected from recovery wells was comprised of approximately 43% diesel fuel, 44% gasoline, and 14% crude oil.

This comprehensive characterization of site conditions and analysis of the PHCs present at the site was used to enhance the recovery of dissolved and LNAPL phase contaminants and to develop a more accurate CSM for the distribution of contaminants present and preferential migration flow paths across the site.

Phase Partitioning of PHCs and the Shift towards Mobile LNAPL

The isolated occurrence of LNAPL appearing in recovery wells approximately 700 feet from the former refinery is attributed to increases in the coalescence of dissolved phase PHCs resulting from decreases in their effective water solubility. Strongly reducing conditions induced by the anaerobic biodegradation of PHCs increased the effective water solubility of soil minerals thereby shifting the phase partitioning equilibrium of PHCs towards LNAPL.

While the combined concentration of PHCs in soil, groundwater and vapor phases exceeded the C_{sat} literature values for gasoline and diesel fuel in fine sand and silt, indicating the presence of immobile LNAPL, the combined PHC concentrations were well below the C_{res} literature values. This finding suggests the presence of ample PHC storage capacity, particularly in soil, and that the mobile LNAPL in the central recovery wells did not originate as a contiguous plume from the refinery but rather occurred as dissolved phase PHCs coalesced to LNAPL as a result of a shift in the phase partitioning equilibrium primarily from dissolved to LNAPL phase PHCs.

It should be mentioned that, for low permeable sites, the migration of LNAPL into monitoring or recovery wells may not be representative of how LNAPL would migrate through the subsurface in the absence of these artificial pathways. The void spaces created

by such wells reduces the capillary forces in soil pores contributing to the liberation of immobile LNAPL into the annulus and/or well screen of nearby wells.[10]

Conceptual Site Model for the Presence of Mobile LNAPL and Long Range Migration of PHCs in Groundwater

The biodegradation of PHCs substantially altered the geochemical conditions at the site as various microbial populations reduced the complete supply of electron acceptors (i.e. oxygen, nitrate, iron and sulfate) to electron rich byproducts that created the strongly reducing conditions required for the growth of methanogenic bacteria. The presence of LNAPL in recovery wells located approximately 700 feet downgradient of the former refinery coincided with high concentrations of dissolved and vapor phases of carbon dioxide and methane, and high concentrations of dissolved phase soil minerals. Carbon dioxide generated from the oxidation of PHCs by methanogenic bacteria served as an exogenous electron acceptor that was reduced to methane during the anaerobic degradation of PHCs.

The proportions of diesel fuel and crude oil PHCs in groundwater decreased as their proportions increased in LNAPL. Despite their presence in mobile LNAPL, the proportion of dissolved phase gasoline PHCs increased further downgradient. These trends are attributed to increases in the effective water solubility of gasoline PHCs as a result of the diminished concentrations of dissolved phase diesel fuel and crude oil PHC, and soluble soil minerals.

Methanogenic bacteria may also be contributing to the formation of LNAPL and/or long range migration of dissolved phase PHCs through the production of anionic or nonionic biosurfactants released into the groundwater to enhance the bacterial access to and degradation of LNAPL The generation of high concentrations of vapor phase carbon dioxide and methane may also be contributing to the long range migration of PHCs by creating preferential migration pathways formed by the fracturing of poorly permeable silt and clay soil below the groundwater table[11]. This is consistent with the observation of dry silt and clay soil below the groundwater table.

The Design of Feasible Remedial Options

The recovery of immobile LNAPL from soil pores to levels where the dissolution of PHCs into groundwater is controlled is key to preventing the formation and entry of mobile LNAPL into site wells, and the continued migration of dissolved phase PHCs. While methanogenic bacteria can contribute substantially to the formation of LNAPL and the long range migration of PHCs in groundwater, they also play a substantial role in their biodegradation.

While the use of in situ chemical oxidation (ISCO) technology may prove beneficial to limiting the potential for the migration of dissolved phase PHCs beyond property boundaries, its implementation in areas bordering property boundaries needs to

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[10] LNAPL and the MCP: Guidance for Site Assessment and Closure (2014). MASSDEP

[11] Communication with Todd Halihan, associate professor of hydrology at the School of Geology, Oklahoma State University, Stillwater, OK

be carefully evaluated given the likely repercussions on the biodegradation of PHCs and potential precipitation of high concentrations of dissolved phase soil minerals that could plug what limited soil pores exist thereby complicating remedial actions.

The use of anionic surfactants to enhance desorption, liberation and recovery of immobile LNAPL was shown to be an effective remedy that is not expected to impact the biodegradation of PHCs. Accommodations must be made, however, for the treatment and disposal of groundwater containing surfactant materials recovered during the dispersion of surfactant and recovery of liberated LNAPL, as the surfactants have a similar liberating effect on LGAC-based treatment systems.

States where the reinjection of remedial additives is not permitted should reconsider approving the closed loop injection, dispersion, and reinjection of surfactant solutions that would enhance desorption and removal of immobile LNAPL and thereby address complications posed by the treatment and disposal of surfactant containing groundwater. In states like Mississippi, the injection of surfactant, its subsurface dispersion, treatment and/or disposal, and subsequent LNAPL recovery must be treated as separate operations that prolong site cleanup and increase costs substantially.

ACKNOWLEDGEMENTS

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TABLES

Table 1. Summary of Naturally Occurring Soil Minerals (mg/kg) and TOVs (ppmv)

26 TAL Metals	Soil Sample Depth (feet below grade) and Metal Concentration (mg/kg)								
	ERW-30		ERW-31	ERW-33	ERW-35				SB-37
	25-26	31-33	30-31	29-30	22-23	25-26	29-30	35-36	25-26
Al	5900	4400	3400	5800	4300	5500	3000	4500	3800
An	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL
As	8.6	6.8	2.7	7.4	7	8.1	4.5	4.6	6.3
Ba	120	97	56	79	58	91	49	78	51
Be	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL
Cd	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL
Ca	3600	7900	9100	4800	5000	3600	7700	12000	8000
Cr	8.5	7	5.9	8.9	7.5	8	5.6	7.6	6.4
Co	5.2	3.8	3.6	3.3	3.8	4.5	2.6	3.6	2.9
Cu	11	7.8	5.3	9.1	7.2	11	5	7.3	7.4
Fe	11000	8500	5800	9800	8900	11000	6100	7900	8600
Pb	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL
Mg	3200	3900	4400	3900	3600	3200	3800	6000	5300
Mn	430	300	73	190	310	400	150	270	180
Hg	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL
Ni	13	9	9	9.8	8.7	12	7.1	8.2	8.7
K	650	570	460	550	360	580	360	380	320
Se	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL
Ag	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL
Na	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL
Th	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL
Va	15	11	11	13	12	14	9.6	14	13
Zn	38	28	24	33	25	35	20	24	22
Total Metals (mg/kg)	24,999	25,740	23,351	25,204	22,599	24,464	21,213	31,197	26,318
TOV Max (ppmv)	1,870	850	1,200	332	1,300	1,220	2,796	120	6

<RL   below minimum detection limit
SB-37   control soil boring

Table 2. Summary of Dissolved Metal, Methane, and Carbon Dioxide, and TPH-GRO, TPH-DRO and C28-44 Carbon Fraction Concentrations in Groundwater Samples Collected Upgradient, Within and Downgradient of Mobile LNAPL Areas

Parameter	Well and Groundwater Concentration (ug/l) of Parameters														
	ERW6	A4	C4	ERW21	A6	B6	C6	C8	ERW20	C9	B10	C11	C14	B14	A14
Iron	13,000	4,600	22,000	11,000	2,800	1,700	15,000	6,500	6,400	12,000	7,000	3,100	12,000	9,400	<50
Calcium	120,000	120,000	12,000	120,000	8,600	100,000	96,000	84,000	130,000	78,000	140,000	98,000	85,000	100,000	36,000
Aluminum	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100
Magnesium	68,000	72,000	73,000	66,000	48,000	59,000	56,000	48,000	72,000	47,000	80,000	56,000	50,000	57,000	20,000
Potassium	<2500	<2500	<2500	<2500	<2500	<2500	<2500	<2500	<2500	<2500	<2500	<2500	<2500	<2500	<2500
Manganese	3,190	3,900	6,860	4,940	3,100	3,610	3,370	2,130	3,340	2,130	7,160	4,780	6,470	8,780	10
Barium	308	421	361	398	195	261	255	237	685	305	419	231	203	375	86
Dissolved Metals	204,498	200,921	114,221	202,338	62,695	164,571	170,625	140,867	212,425	139,435	234,579	162,111	153,673	175,555	56,096
Dissolved Methane	7,770	7,730	7,600	6,530	5,210	5,450	6,210	6,720	13,000	9,810	8,150	8,930	8,780	2,880	1
Dissolved CO2	118,000	163,000	153,000	139,000	143,000	130,000	105,000	118,000	126,000	110,000	220,000	Plot Area	134,000	228,000	65,400
GRO (C5-9)	4,300	6,100	4,300	5,700	3,400	1,400	6,600	5,500	14,000	7,400	4,200	7,300	2,100	170	25
DRO (C9-28)	1,200	2,290	1,620	1,940	1,760	913	2,070	2,800	3,250	5,690	2,120	3,200	978	494	52
PHI Scan (C28-44)	340	910	310	410	450	87	760	790	700	1,700	930	1,040	182	62	34

Table 3. Total Mass of PHCs in Soil, Groundwater and Vapor Phases (mg/kg)

Recovery Wells		ERW 19	ERW 17	ERW 16	ERW 15	ERW 11	ERW 12	ERW 30	ERW 14	ERW 22	ERW 20	ERW 36	ERW 35	ERW 10	ERW 13	ERW 21	ERW 9	ERW 8	ERW 7	ERW 6	ERW 29	ERW 1	ERW 4
Soil Phase	GRO (mg/kg)	59	<RL	680	590	<RL	620	350	680	410	550	360	900	320	1500	660	220	710	460	400	86	1100	290
	DRO (mg/kg)	<RL	<RL	<RL	86	<RL	88	553	<RL	45	180	381	1170	280	250	130	340	250	100	73	13000	6110	140
	crude oil (mg/kg)	<RL	<RL	<RL	22	<RL	23	127	<RL	524	396	129	250	616	550	286	748	550	220	161	13000	13442	308
Groundwater Phase	GRO (mg/l)	0.53	0.03	2.1	2.8	0.21	9.8	5.8	4.7	9.5	14	3.1	4.7	0.17	2.6	5.7	1	7.7	2.2	4.3	0.13	0.68	1.2
	GRO (mg/kg)	0.16	0.01	0.63	0.84	0.06	2.94	1.74	1.41	2.85	4.2	0.93	1.41	0.05	0.78	1.71	0.3	2.31	0.66	1.29	0.04	0.20	0.36
	DRO (mg/l)	<RL	<RL	<RL	1.5	<RL	<RL	2.44	2.29	2.1	3.25	1.4	2.48	<RL	0.75	1.94	0.82	1.5	0.7	1.2	1.4	1	1.07
	DRO (mg/kg)	<RL	<RL	<RL	0.45	<RL	<RL	0.73	0.69	0.63	0.98	0.42	0.74	<RL	0.23	0.58	0.25	0.45	0.21	0.36	0.42	0.30	0.32
	crude oil (mg/l)	<RL	<RL	<RL	0.41	<RL	<RL	0.70	0.68	0.57	1.28	0.44	0.52	<RL	0.20	0.41	0.22	0.41	0.19	0.34	0.38	0.27	0.16
	Crude Oil (mg/kg)	<RL	<RL	<RL	0.12	<RL	<RL	0.21	0.20	0.17	0.38	0.13	0.16	<RL	0.06	0.12	0.07	0.12	0.06	0.10	0.11	0.08	0.05
Vapor Phase	TOVs (ppmv)							1198	4250	7460	6193	278	60			3311			1320	1315	1027	5347	4991
	CH4 (ppmv)							264	630	2434	2487	60	2			2296			900	1070	70	2666	4207
	TOV-CH4 (ppmv)	276	2677	276	276	5800	5800	934	3620	5026	3706	218	58	3100	3813	1015	3100	3100	420	245	957	2681	784
	PHCs (mg/m3)	254	885	254	254	1706	1706	427	1133	1503	1156	238	196	996	1184	448	996	996	291	245	433	886	387
	PHCs (mg/kg)	0.08	0.27	0.08	0.08	0.51	0.51	0.13	0.34	0.45	0.35	0.07	0.06	0.30	0.36	0.13	0.30	0.30	0.09	0.07	0.13	0.27	0.12
Total Gasoline PHC (mg/kg)		59	0	681	591	0.6	623	352	682	413	555	361	901	320	1501	662	221	713	461	401	86	1100	290
Total Diesel Fuel PHC (mg/kg)		0	0	0	87	0.5	89	554	1	46	181	381	1171	280	251	131	341	251	100	73	13001	6111	140
Total Crude Oil PHC (mg/kg)		0	0	0	22.1	0	23	127.2	0.2	524.2	396.4	129.1	250.2	616	550.1	286.1	748.1	550.1	220.1	161.1	13000	13442	308.1

FIGURES

Figure 1. Site Plan Showing Former Asphalt Refinery and Stormwater Impoundment,
Recovery and Monitoring Wells and Wells Exhibiting Mobile LNAPL

Figure 2. Geological Cross-Section

Figure 3A. Vertical Extent of TOVs in Soil Samples Collected 2014-16
Along the Northern and Southern Flow Paths, Soil Type and
Depth to Groundwater Table on September 21, 2016

Northern Flow Path

Boring Depth (feet)	Westernmost Field (soy crop)				Central Portion of Agricultural Field (grass area)							Hwy West	HWY East					Near PW-13
	ERW 19	ERW 16	ERW 15	ERW 14	ERW 30	ERW 31	ERW 32	ERW 33	ERW 34	ERW 35	ERW 36	ERW 6	ERW 5	ERW 4	ERW 3	ERW 2	ERW 1	SB-37
0-2												0					278	
2-4																		
4-6		7						10				0	0	610		60	905	
6-8	0		0	0								0		810	1173	202		
8-10		0			3	8	4	7	2		3		18	1012		1062		7
10-12		0	5			4	52					60	221	209		302		
12-14								5	5	9	3		220	711		1024		
14-16	0	0	5	1			11					435	370	1084	699	62		3
16-18			74	3							4	599		1274	25	174		
18-20		0		204	98	398	46		9			734	970	980				6
20-22			740	1143		278	125	67				476	384	78	23			
22-24	0	1241	765		114				144	1300		90	27	98		8	5	
24-26	203	38	670	660	1870	821	222	273	185	1220	140		19		2	6		6
26-28	233	28	427								1333	90	3	17		9		
28-30	0	12		83	325	1200	173	332	395	2796			7	18				110
30-32		16		88	850							38	67	1	0			
32-34	0		16				45	64	60	285	238							
34-36	0	10		24	130	17	55	52	41	120	113	3	10			8	20	50
36-38	0	4	0										8	0				22
38-40	0	0		4	13	25	35	7	17	16	6		5					40
40-42							143			51								
42-44						118	145									0		
44-46										3								
46-48						62	105											
48-50																	0	
50-52																		
52-54						95												
54-56																	0	
56-58						24												
58-60																		

Silty Sand — Dense Clay — Groundwater (9/21/16) — TOVs (ppmv) — PID Meter

Southern Flow Path

Boring Depth (feet)	Western Field			South Central Field						SW Hwy			NE Hwy		SE Hwy - Impoundment				
	ERW 18	ERW 17	ERW 11	ERW 12	ERW 22	ERW 20	ERW 10	ERW 13	ERW 21	ERW 9	ERW 8	ERW 7	ERW 2	ERW 1	ERW 28	ERW 23	ERW 29	ERW 25	ERW 24
0-2														278	4		3		7
2-4																			
4-6	0	0				4		36	0	26	48	0	60	905			1017	740	
6-8		0	0	0		0		8	0	777	515	26	1173	202					274
8-10				13				0	0	738	421	17	1062		794		297		
10-12											1118			302	333			2065	1470
12-14	0								128		330	614	1024				650	240	
14-16				23		0	3	0	237	67	421	1047		62		380			
16-18		0	0	599	125	0	0	21	303	303	25	652		174	88	97	12	78	137
18-20				751		0	63	110	442	4	2	358							
20-22			0						973	478	3	85				3			
22-24		2	3	248	1818				157	169	8	76	8	5	115		8	120	75
24-26	0		73	1281		300	771	1197	998	15			6			84	7		5
26-28		0	16	1255	4507	850	444	906	948	3	1	6	9		5				
28-30			32	1288	1628	1124	74	1268	466			8			6	37	6	14	8
30-32	0	0	10	215	2500	981	218	140	391			3							
32-34		0		129		1177	15	70		0	0		8	20	4		3	7	6
34-36	0	0	16	49		1172		85	73		0	1							
36-38		0		19	943	901	3	20							3	3	4	4	3
38-40	0			4		604		2	56	0									
40-42						143			51										
42-44				118		145							0						
44-46									3										
46-48				62		105													
48-50													0						
50-52																			
52-54				95															
54-56													0						
56-58				24															
58-60																			

Clayey silt — Sand Lens — Silty Clay — Dense Clay — Groundwater (9/21/16) — Highest TOVs (ppmv) — PID Meter

Figure 3B. Vertical Extent of TPH-GRO in Soil Samples Collected 2014-16 Along the Northern and Southern Flow Paths, Soil Type and Depth to Groundwater Table on September 21, 2016

Northern Flow Path

Boring Depth (feet)	NW Field ERW 19	ERW 17	ERW 16	ERW 15	ERW 14	NC Field ERW 30	ERW 31	ERW 32	ERW 33	ERW 34	ERW 35	ERW 36	NW Hwy ERW 21	ERW 6	NE Hwy ERW 5	ERW 4	ERW 3	ERW 2
0-2																		
2-4																		
4-6																		
6-8																		690
8-10																		720
10-12																170		
12-14																		540
14-16															97		140	
16-18																290		
18-20					100									400	190			
20-22																	12	
22-24		<2	680	590						32	550			<16				
24-26	55			300	680	350					510		660					
26-28	59		15									360						
28-30							220	13	110	140	900					4		
30-32							8							54	200			
32-34				9		52							66					
34-36		5.7	4.5		8													
36-38																		
38-40								2										
40-42													<2					
42-44																		
44-46																		
46-48																		
48-50																		
50-52																		
52-54																		
54-56																		
56-58																		
58-60																		

Legend: Clayey silt · Sand lens · Silty Sand · Dense Clay · Groundwater (9/21/16) · TPH-GRO (mg/kg) · Above TRG of 350 mg/kg

Southern Flow Path

Boring Depth (feet)	Western ERW 18	ERW 17	ERW 11	SC Field ERW 12	ERW 22	ERW 20	ERW 10	ERW 13	ERW 21	SW Hwy ERW 9	ERW 8	ERW 7	NE Hwy ERW 2	ERW 1	SE Hwy ERW 28	ERW 23	ERW 29	ERW 25	ERW 24
0-2																			
2-4																			
4-6														1100			86		
6-8											690				240				
8-10											720								
10-12											710							310	
12-14											540								640
14-16								220	250	466						54			
16-18				620										56					
18-20																			
20-22										76									
22-24	<2	<2									13				6			4	
24-26			<0.07			410	320	1500	660							110			
26-28							160					4					<2		
28-30			<0.06	290				47											<2
30-32							320					140							
32-34						550	<41			66				32					
34-36	<2	6	0.2	180				<6											
36-38																			
38-40																			
40-42								<2											
42-44																			
44-46																			
46-48					<43														
48-50																			
50-52																			
52-54				<2															
54-56																			
56-58																			
58-60																			

Legend: Clayey silt · Sand Lens · Silty Clay · Dense Clay · Groundwater (9/21/16) · TPH-GRO (mg/kg) · Above TRG of 350 mg/kg

Figure 3C. Vertical Extent of TPH-DRO in Soil Samples Collected 2014-16 Along the Northern and Southern Flow Paths, Soil Type and Depth to Groundwater Table on September 21, 2016

Northern Flow Path

Boring Depth (feet)	ERW 19	ERW 17	ERW 16	ERW 15	ERW 14	ERW 30	ERW 31	ERW 32	ERW 33	ERW 34	ERW 35	ERW 36	ERW 21	ERW 6	ERW 5	ERW 4	ERW 3	ERW 2
	Northwest Field					North Central Field							NW Hwy		NE Hwy			
0-2																		
2-4																		
4-6																		
6-8																		1200
8-10																		660
10-12																140		
12-14																		350
14-16															460		120	
16-18																77		
18-20				<46										73	99			
20-22																		
22-24		<43	<47	86						76	374			<44			<41	
24-26	<44			<44	200	553					573		130					
26-28	<46		<45									381						
28-30							255	75	87	294	1170					<44		
30-32				<42		77	16							<42	120			
32-34														50				
34-36		<41	<41		<42													
36-38	<43																	
38-40							10											
40-42													<43					
42-44																		
44-46																		
46-48																		
48-50																		
50-52																		
52-54																		
54-56																		
56-58																		
58-60																		

Legend: Clayey silt · Sand lens · Silty Sand · Dense Clay · Groundwater (9/21/16) · TPH-DRO (mg/kg) Above 1...

Southern Flow Path

Boring Depth (feet)	ERW 18	ERW 17	ERW 11	ERW 12	ERW 22	ERW 20	ERW 10	ERW 13	ERW 21	ERW 9	ERW 8	ERW 7	ERW 2	ERW 1	ERW 28	ERW 23	ERW 29	ERW 25	ERW 24
	Western Field			South Central Field						SW Hwy			NE Hwy		SE Hwy - Impoundment				
0-2																			
2-4																			
4-6														6110			13,000		
6-8													1200		7500				
8-10													660						
10-12											250							600	
12-14													350						460
14-16										340	110	100				3700			
16-18					45									<43					
18-20																			
20-22										750									
22-24	<43	<43			<48										<43			<41	
24-26			<43				280	250	130							320			
26-28						180						<42					<41		<41
28-30			<45	89				<42											
30-32							47		50			810		82					
32-34						110	7												
34-36	<46	<41	<44	<43				<40											
36-38																			
38-40																			
40-42									<43										
42-44																			
44-46																			
46-48						10													
48-50																			
50-52																			
52-54					<45														
54-56																			
56-58																			
58-60																			

Legend: Clayey silt · Sand Lens · Silty Clay · Dense Clay · Groundwater (9/21/16) · TPH-DRO (mg/kg) Above TRG of 650 mg/kg

Figure 4. Benzene (ug/l) Isoconcentration Maps for Samples Collected
September 2010 and 2015/2016 Including Location of LNAPL Wells

September 2010 (LNAPL depicted by black triangles)
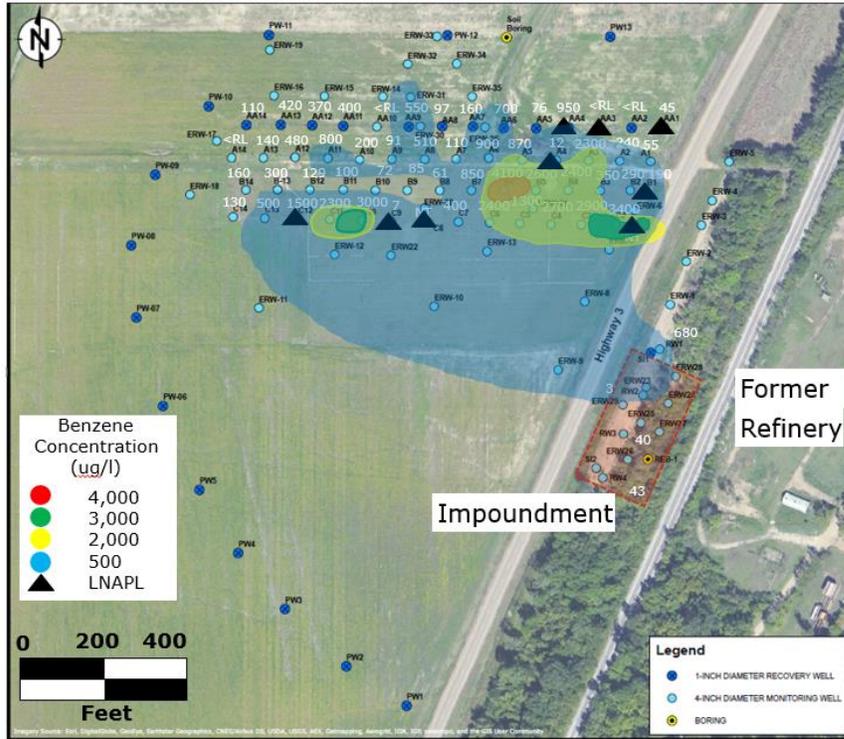
September 2015/2016 (LNAPL depicted by black triangles)
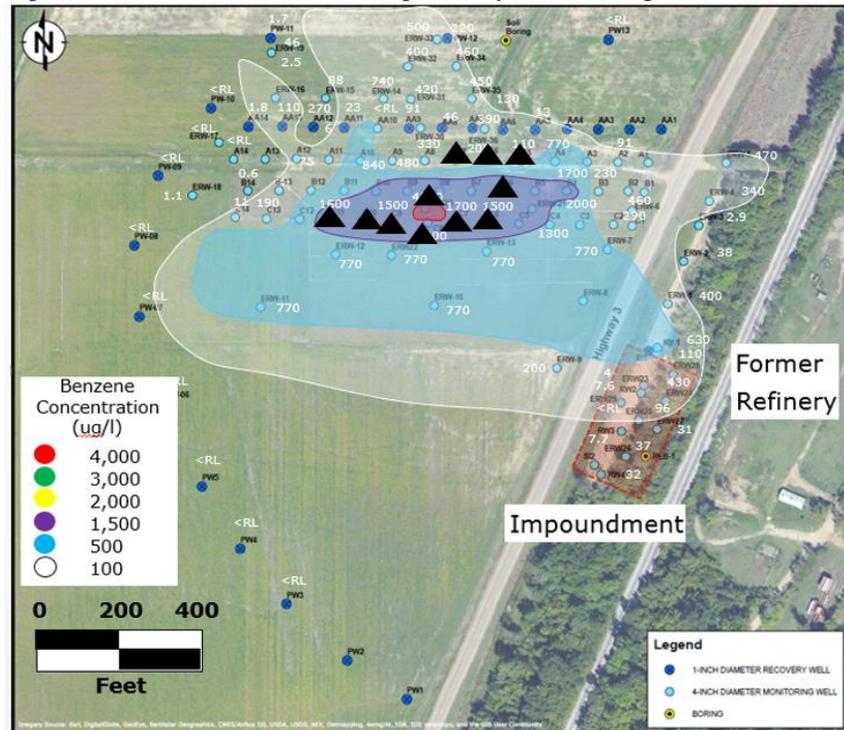
Figure 5. TPH-GRO and TPH-DRO Isoconcentration Maps for
Groundwater Samples Collected in 2016 Including LNAPL Wells

TPH-GRO (LNAPL depicted by black triangles)
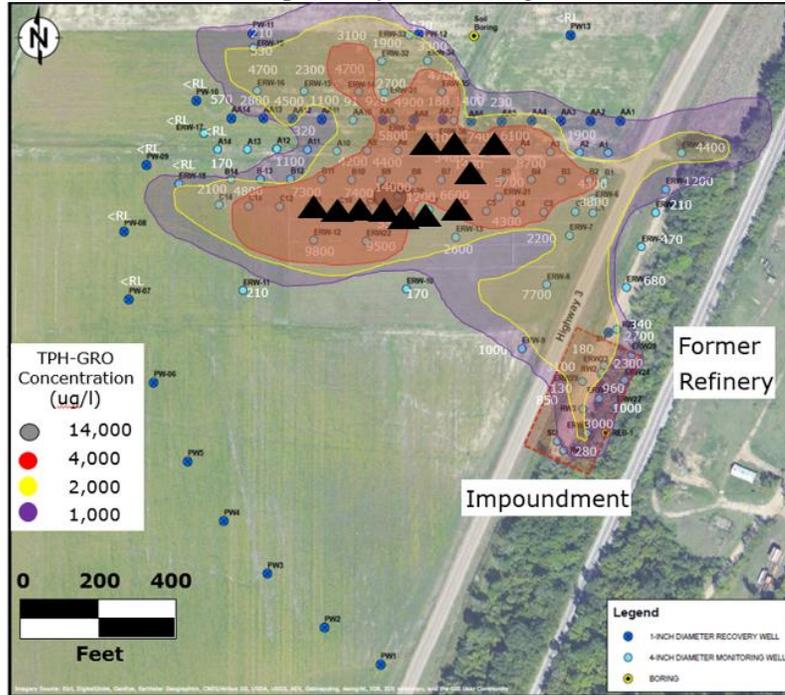
TPH-DRO (LNAPL depicted by black triangles)

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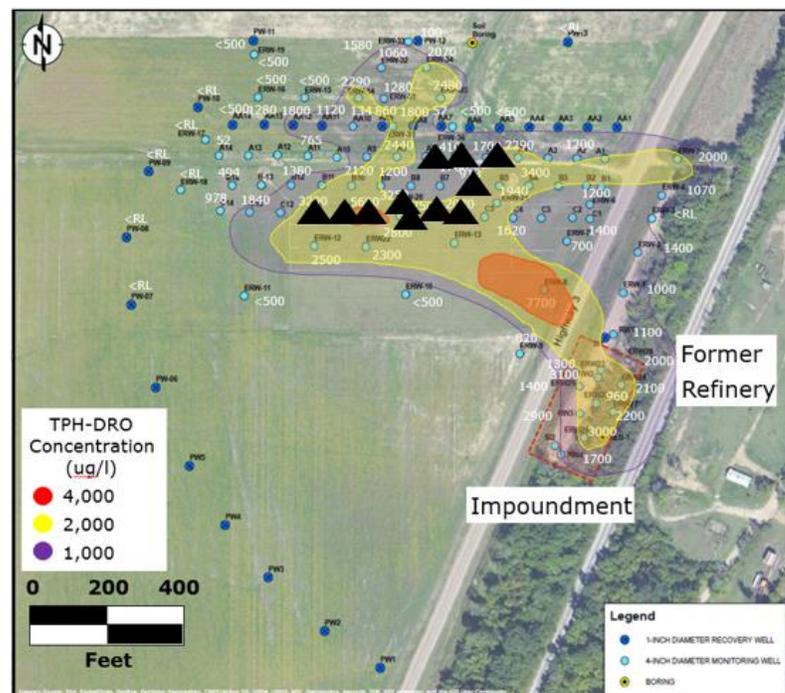
Figure 6. Dissolved Metals and Methane Concentrations in Groundwater
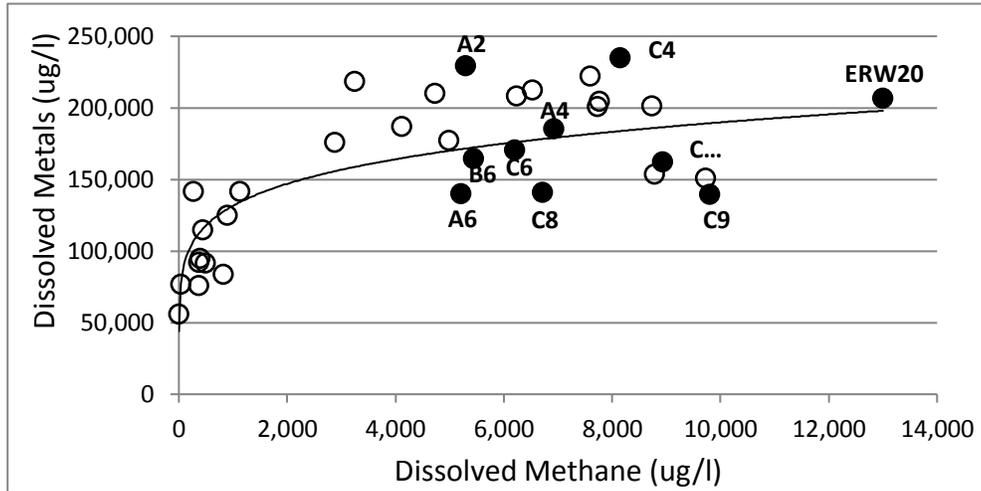
Figure 7. Summary of Dissolved Phase Carbon Dioxide and Methane Concentrations versus LNAPL Thickness in Recovery Wells Upgradient, Within and Downgradient of the LNAPL Plume in June and July 2016
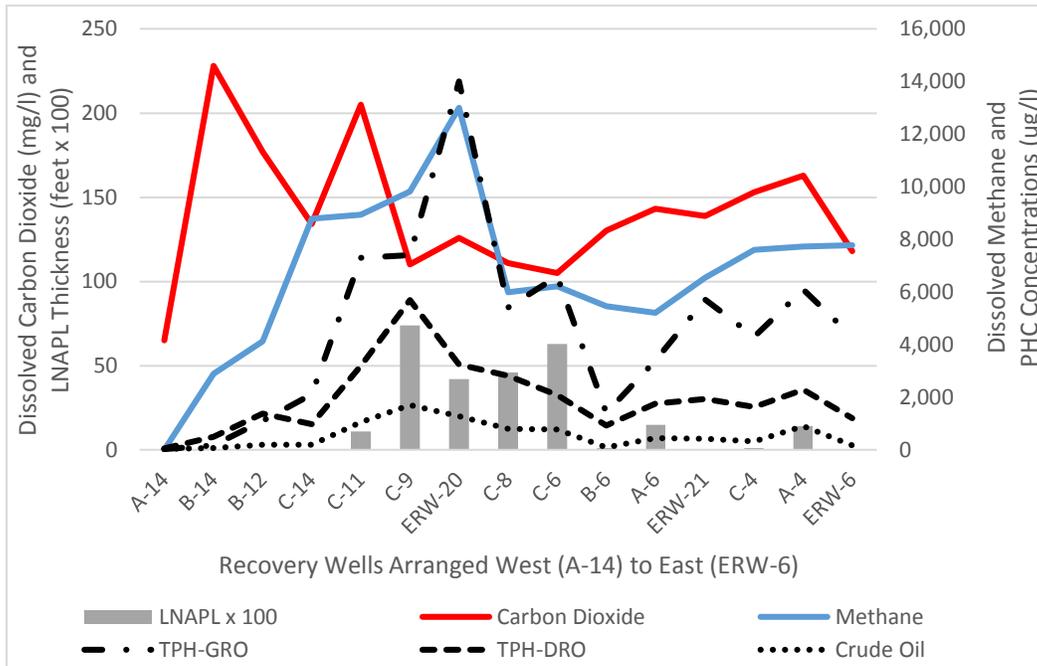
Figure 8. Trends in Gasoline and Diesel Fuel PHCs Proximate to the LNAPL Plume