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Innovations in Site Characterization

Streamlining Cleanup at Vapor Intrusion and Product Removal Sites Using the Triad Approach:
Hartford Plume Site, Hartford, Illinois

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF SUPERFUND REMEDIATION AND TECHNOLOGY INNOVATION
SUPERFUND TECHNOLOGY SUPPORT CENTER
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Streamlining Cleanup at Vapor Intrusion and Product Removal Sites Using the Triad Approach:

Hartford Plume Site, Hartford, Illinois

Prepared by:

Office of Superfund Remediation and Technology Innovation and Tetra Tech, EMI

In Cooperation with:

U.S. Environmental Protection Agency Region 5

NOTICE

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FOREWORD

This case study is one in a series designed to provide cost and performance information for innovative tools and approaches that support streamlined site characterization and cleanup. These case studies will include reports on new technologies as well as novel applications of familiar tools or processes. They are prepared to offer operational experience and to further disseminate information about ways to improve the cleanup process at hazardous waste sites.

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ACRONYMS AND ABBREVIATIONS

%RE	Percent Fluorescence Intensity
µg	micrograms
µg/kg	Microgram per Kilogram
µg/m^3	Micrograms per Meter Cubed
µm	Micrometer
ADL	Arthur D. Little, Inc.
AOC	Administrative Order of Consent
Apex	Apex Oil Company, Inc.
Apex/Clark	Apex Clark Oil Company, Inc.
API	American Petroleum Institute
ARCO	Atlantic-Richfield Company, Inc.
asl	Above Sea Level
ASTM	American Society for Testing and Materials
bgs	Below Ground Surface
BTEX	Benzene, Toluene, Ethylbenzene, and Xylenes
CAA	Clean Air Act
CC Report	Current Condition Report
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CERCLIS	Comprehensive Environmental Response, Compensation, and Liability Information System
Clayton	Clayton Group Services, Inc.
CLU-IN	Clean-Up Information System
cm/sec	Centimeters per Second
cP	Centipoise
COC	Contaminants of Concern
CPT	Cone Penetrometer Testing
CSM	Conceptual Site Model
D	Deep
DIPE	Diisopropyl Ether
DMA	Demonstration of Methods Applicability
DMDEL	Dimethyl Diethyl Lead
DNAPL	Dense Non-aqueous Phase Liquid
DOE	U.S. Department of Energy
DOJ	U.S. Department of Justice
DPE	Dual Phase Extraction
DPH	Department of Public Health
DPR	Dual Pump Recovery
DRO	Diesel Range Organics
DTI	Dakota Technologies, Inc.
dyn/cm	Dynes per Centimeter
E&I	Environment and Infrastructure
ECD	Electron Capture Detector
EDB	Ethylene Dibromide
EDC	Ethylene Dichloride
ENSR	ENSR Corporation, Inc.
EPA	U.S. Environmental Protection Agency
ERT	Environmental Response Team
E-S	Engineering-Science Record
ES	Executive Summary
ETBE	Ethyl-tert-butyl Ether
EVS	Earth Vision Software
FID	Flame Ionization Detector
FPD	Flame Photometric Detector
FPH	Free-Phase Hydrocarbon
F_R	Friction Ratio
f_s	Sleeve Friction
ft/day	Feet per Day
Fugro	Fugro Geosciences, Inc.
g/cm^3	Grams per Cubic Centimeter
g/gal	Grams per Gallon
g/mL	Grams per Milliliter
GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
GIS	Geographic Information Systems
GM	General Motors Research Corporation, Inc.
GP	GeoProbe® Systems
gpd/ft^2	Gallons per Day per Square Foot
GRO	Gasoline Range Organics
H2A	H2A Environmental, Ltd.
HA	Hand Auger
HF	Hydrofluoric Acid
HROST	Hartford Area Rapid Optical Screening Tool Location
HSA	Hollow Stem Augur
HVR	High Vacuum Recovery
HWG	Hartford Working Group
IAC	Illinois Administrative Code
ID	Inside Diameter
IEPA	Illinois Environmental Protection Agency
ITRC	Interstate Technology Regulatory Council
K	Conductivity
LEL	Lower Explosive Limit
LIF	Laser Induced Fluorescence
LNAPL	Light Non-aqueous Phase Liquid
LUST	Leaking Underground Storage Tank
M	Medium
MCL	Maximum Contaminant Level
mg/kg	Milligram per Kilogram
MMT	Methylcyclopentenadienyl Manganese Tricarbonyl
MP	Monitoring Point
MPE	Multi-Phase Extraction
MS	Mass Spectrometer
msl	Mean Sea Level
MTBE	Methyl-tert Butyl Ether
MTEL	Methyl Tetraethyl Lead

MWH	MWH Americas, Inc.
NAD	North American Datum of 1927
NAPL	Non-aqueous Phase Liquid
NCP	National Contingency Plan
NDSU	North Dakota State University
NGVD	National Geodetic Vertical Datum of 1929
NSCEP	National Service Center for Environmental Publications
O_c	Tip Resistance
OD	Outside Diameter
OSC	On-Scene Coordinator
OSRTI	Office of Superfund Remediation and Technology Integration
PAH	Polycyclic Aromatic Hydrocarbon
PAS	Praxair Points
PESC	Philip Environmental Services Corporation
PHC	Petroleum Hydrocarbon Compound
PIANO	Paraffins, Isoparaffins, Aromatics, Napthemes, and Olefins
PID	Photo Ionization Detector
PMPE	Periodic Multi-Phase Extraction
PMR	Periodic Manual Removal
ppbv	Parts per Billion by Volume
ppm	Parts per Million
PTS	PTS Laboratories, Inc.
PVC	Polyvinyl Chloride
QA/QC	Quality Assurance/Quality Control
RCRA	Resource Conservation and Recovery Act
RL	Reporting Limit
ROI	Radius of Influence
ROST	Rapid Optical Screening Tool
RUST E&I	Rust Environment & Infrastructure
S	Shallow
S	Storativity
SG	Specific Gravity
Site	Village of Hartford Hydrocarbon Plume Site
SPR	Skimmer Pump Recovery
SSMP	Sub-slab Monitoring Point
SVE	Soil Vapor Extraction
SVOC	Semi-Volatile Organic Compound
T	Transmissivity
TAME	Tert Amyl Methyl Ether
TBA	Tert-butyl Alcohol
TCD	Thermal Conductivity Tester
TEKLAB	TEKLAB, Inc.
TEL	Tetraethyl Lead
TMEL	Tetramethylethyl Lead
TML	Tetramethyl Lead
TMP	Trimethylpentanes
Torkelson	Torkelson Geochemistry, Inc.
TPH	Total Petroleum Hydrocarbons
USACE	U.S. Army Corps of Engineers
USCS	United Soil Classification System
USGS	United States Geological Survey
UST	Underground Storage Tank
VCS	Vapor Control System
VES	Vacuum-Enhanced Skimmer
VI	Vapor Intrusion
VMP	Vapor Monitoring Point
VOC	Volatile Organic Compound
VP	Vapor Point
VS	Very Shallow
WRMC	Wood River Manufacturing Complex

CASE STUDY ABSTRACT

HARTFORD PLUME SITE
Hartford, Illinois

Site Name and Location:

Hartford Hydrocarbon Plume Site
Hartford, Illinois

Period of Operation:

1900-present

Site Description:

The property includes about 400 residences in the northern half of the Village of Hartford and includes surrounding refinery and bulk storage facilities.

Project Approaches, Methods and Technologies:

- Systematic planning process
- Conceptual site model (CSM)
- Dynamic work strategies
- Direct push soil and groundwater sampling
- Detection of hydrocarbons in soil using laser induced fluorescence (LIF)
- Cone penetrometer testing (CPT) geologic data
- Product thickness in wells
- Product removal tests from wells
- Physical property testing and core analyses
- Standard methods for soil, groundwater, and soil gas
- Simulated distillations
- On-site laboratory analyses for U.S. Environmental Protection Agency (EPA) Method Modified TO-15
- Vapor screening for lower explosive limit (LEL) and hydrocarbons
- Passive soil gas

Comprehensive Environmental Response, Compensation, and Liability Information System (CERCLIS) #:

None

Current Site Activities:

Optimizing and installing additional soil vapor extraction (SVE) systems and product removal wells.

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Media and Contaminants:

Surface and subsurface soil site-wide:

- Numerous types of petroleum spills on site affect soil.
- Lead additives for gasoline are also present.

Groundwater:

- Groundwater has also been affected by petroleum related constituents including benzene, ethylbenzene, toluene, xylenes (BETX), methyl-tert butyl ether (MTBE) above EPA Maximum Contaminant Levels (MCLs).

Vapors:

- In addition to BTEX compounds, high concentrations of isopentane and hexane are also present and indicate the potential for fire and explosive hazards.

Technology Demonstration:

Cone Penetrometer Testing (CPT) / Rapid Optical Screening Tool (ROST) or CPT/ROST used to map geologic relationships and estimate the nature and extent of hydrocarbons at the site.

Passive soil gas probes and on-site analyses of SUMMA canisters and Tedlar® bag samples were used in combination with field screening detectors.

High-level samples based on screening results were analyzed in the field to expedite risk evaluations and fixed laboratory results were used to confirm the information generated in the field.

Number of Samples Analyzed During the Investigation:

Nearly 300 CPT/ROST pushes were performed beneath Hartford and the Wood River Refinery immediately east of Hartford. Several hundred nested vapor probe analyses, manhole passive soil gas samples, indoor and outdoor air canister samples, and sub-slab canister samples were collected to evaluate the potential for vapor intrusion (VI).

Cost Savings:

A sequential sampling program based on CPT/ROST results was used to optimize soil vapor, groundwater, and soil sampling across the site. An estimated cost savings of more than 30 percent was achieved as a function of reduced mobilizations and fixed-base laboratory analyses. In addition to saving costs, use of the Triad Approach increased the size and quality of the data set used to make decisions about the site.

Results:

The project is being completed. The relatively high data density for the site data is allowing regulators and other stakeholders to make decisions with a high degree of certainty. Members of the project team are satisfied with the time and cost savings achieved following the principles of the Triad Approach. Results are being used to target areas where product removal and extraction of soil vapor is most needed. Results allow the team to estimate risk and target resources to reduce environmental issues at the site.

Description:

In this case study, readers will be introduced to concepts and methods for characterization, mitigation, and cleanup at petroleum refinery sites. Concepts and methods related to VI, tracking dissolved phase contamination, and product removal are discussed in the context of this large refinery site located near St. Louis, Missouri, where petroleum refining, storage, and distribution has been conducted since the early 1940s. Readers will be introduced to effective tools such as the CPT/ROST, and concepts such as apparent product thickness measured in wells. Sub-slab depressurization versus soil vapor extraction, bail-down product tests versus high vacuum extraction, conceptual site models (CSM), field-based methods for vapor analyses, and more will be discussed to provide readers with a basis for understanding simple and complex petroleum sites.

Vapor intrusion from widespread hydrocarbon plumes at the Hartford Plume Site in Hartford, Illinois, resulted in numerous fires and forced residents to move from their homes. The U.S. Environmental Protection Agency (EPA) Region 5, Emergency Response Team, On Scene Coordinators (OSC) worked with a proactive group of oil companies from the area to address the public concerns at the site quickly. The project team used Triad Approach best management practices (BMPs) —including, a well-structured systematic planning process, dynamic “learn as you go” work strategies, and field-based measurement technologies—to expedite the investigation, mitigation, and cleanup processes. The EPA Region 5 OSCs engaged Triad advocates representing EPA’s Office of Superfund Remediation and Technology Innovation (OSRTI) to provide second opinions on critical project design considerations. Through the team’s combined efforts, the extent of contamination was defined in approximately 2 years and an existing mitigation system was augmented and optimized. Further augmentations to the mitigation and remedial/corrective action systems are ongoing. Data collected during the project were shown to withstand legal scrutiny and were helpful to support the general allocation of responsibility for the cleanup.

Evaluations of the results from the multiple investigations conducted at the site were compiled to accomplish the following goals:

- Define the nature and extent of a large free product plume
- Estimate the volume and types of product in the subsurface
- Define pathways and potential exposure points
- Understand the short and long term impacts to soil, groundwater, and soil gas
- Understand the timing of releases and the fate of the plume
- Predict where product removal would be possible
- Evaluate the utility of various soil gas methods for predicting vapor intrusion issues
- Prepare a comprehensive CSM to support cleanup

Environmental professionals will gain valuable insights in this case study into the terminology, practices, and results that can be used to design mitigation and remediation actions at petroleum release sites. Refinement of the mitigation and remedial design at the site is ongoing as of September 2010.

EXECUTIVE SUMMARY

Vapor intrusion (VI) from widespread hydrocarbon plumes at the Hartford Plume Site (Site) in the Village of Hartford (Hartford), Illinois, have resulted in numerous residential housing fires and forced residents to move from their homes. The U.S. Environmental Protection Agency (EPA) Region 5, [Environmental Response Team (ERT), On-Scene Coordinators (OSC)] worked with a proactive group of oil companies (the Hartford Working Group [HWG]) from the area, to address public concerns at the Site. The project team used the best management practices (BMPs) of the EPA's Triad Approach—namely, a well-structured systematic planning process, dynamic "learn as you go" work strategies, and field-based measurement technologies—to expedite the investigation, mitigation, and cleanup processes. The EPA Region 5 OSCs were supported by Triad advocates representing EPA's Office of Superfund Remediation and Technology Innovation (OSRTI) to provide a second opinion on critical project design considerations. Through the combined efforts of the project team, the extent of contamination was defined in approximately 2 years and an existing mitigation system was augmented and optimized.

In this case study, readers will be introduced to the basic terminology and innovative methods used to accomplish the following goals:

- Define the nature and extent of a large free product plume
- Estimate the volume and types of product in the subsurface
- Define pathways and potential exposure points
- Understand the short- and long-term impacts on soil, groundwater and soil gas
- Understand the timing of releases and the fate of a plume
- Predict where product removal would be possible
- Evaluate the utility of various soil gas methods for predicting vapor intrusion issues
- Prepare and evolve a comprehensive conceptual site model (CSM) to support cleanup.

Modifications to the mitigation and remedial/corrective action systems are ongoing at the Site. This case study was written primarily to introduce environmental practitioners to the BMPs that can be used at petroleum hydrocarbon sites.

Introduction

Large refinery sites exist across the U.S. and worldwide. Refineries and the villages that house workers are usually located in close proximity to each other. Refineries are placed in areas where abundant groundwater and transportation corridors like rivers and interstate highways are present. Refineries have been retrofitted over the years as the technology and products they produce have changed. Regulations and waste control practices have also changed. Pipeline technologies have improved to limit the potential for releases to occur. Refineries are complex sites, thus owners and regulators typically need more information to make effective site decisions than is required for less complex sites. New tools and approaches, discussed in this case study, are needed to characterize and solve petroleum-related environmental and human health issues.

At many of the U.S. refining and bulk storage and transfer facilities, similar to the Hartford Plume Site, antiquated data from monitoring wells and boring logs provide an inadequate and poorly-supported vision of contaminant distributions and their potential effects on receptors at a site. Large data gaps and assumptions can drive up insurance policy costs for owners and can foster misunderstandings between responsible parties, regulatory agencies, and among stakeholders. The new tools available today for regulators and refining companies can economically provide the information needed to identify and understand environmental issues at other large refinery sites. In this case study, it is suggested that petroleum sites can be cleaned up more effectively and efficiently by using an evolving CSM as a basis for sequencing investigative and remedial/corrective action measures. Taking an innovative approach to characterization and cleanup can help private companies save on insurance premiums, improve their public image, and result in more efficient site cleanups and long-term site-related cost savings.

Use of the CSM and all available site-related data has enabled stakeholders to reach consensus on the nature and extent of contamination at the Site. Engineering considerations are now driving the need for further refinement of site conditions to support remedial efforts at the Site.

Conceptual Site Model

The Site is located in the northern, industrialized portion of Hartford, along the historical edges of the Mississippi and Missouri Rivers flood plain. Beginning in the early 1900s, infrastructure to refine and store petroleum-related products was developed. Many investigations have been conducted since the 1970s to establish the nature and extent of petroleum (primarily gasoline-diesel range fuels) contamination beneath Hartford.

Releases of hydrocarbons along pipelines and beneath the refineries in the area date back to the Site’s early history, but recorded releases were not reported prior to the early 1980s. Free product was measured in monitoring wells in the early 1970s, which suggests a long history of releases to groundwater beneath Hartford. The hydrocarbons present beneath Hartford are one potential source for explosive vapors that could have contributed to the many fires reported in Hartford since the late 1970s. Product removal efforts were conducted at the Site in the 1980s that resulted in the extraction of several million gallons of gasoline and diesel range hydrocarbons. Fires and odor complaints have been reported periodically since the 1980s and it has been hypothesized that changes in the groundwater elevation or prolonged rain events could have contributed to the episodic nature of the fire events.

The geology in the area of the Site is complex because of its proximity to the Mississippi and Missouri Rivers. Site hydrogeology is also complex, controlled by the inter-fingering of silts and sands. Hydrogeologic conditions are also influenced by large seasonal fluctuations in the water table and localized pumping to support refinery operations. In addition, periods of drought have caused the water table to fluctuate by as much as 20 to 40 feet in elevation throughout the period of record. The nature and extent of the contaminant plume in the subsurface is complex, because of the large number of potential release points from the many pipelines and storage facilities located on and adjacent to the Hartford site.

At present, a regional soil vapor extraction (SVE) program and targeted product removal efforts are underway at the Site. The SVE systems were designed based on the high density of data collected using a combination of nested vapor probes, sub-slab vapor samples, real-time vapor measurements, laser induced fluorescence (LIF) measurements using the Rapid Optical Screening Tool (ROST), cone penetrometer testing (CPT), soil core analyses, and product removal tests. In selected homes, sub-slab depressurization systems have been installed. These systems continue to be evaluated and operationally optimized to assure mitigation of any vapor-related issues. Product removal efforts are at the 90 percent design stage and a full-scale system should be in place in the next several years.

Understanding Hydrocarbon Contamination in the Subsurface

The geology and physical properties of the contaminants at a site have a major influence on the mobility of hydrocarbons and the potential for the migration of vapors. In this section, definitions are provided to describe the basic concepts and terms used to understand and predict the mobility of petroleum product and the potential for VI issues at hydrocarbon sites. A better understanding of the architecture of the product plume in the subsurface environment is essential to predicting mobility and the potential for VI-related issues. Improved insight concerning product mobility is also essential to designing an effective product removal and VI mitigation strategy.

Sampling Methods and Investigations at the Hartford Plume Site

Current understanding of contaminant distributions at petroleum sites indicates subsurface heterogeneity is the largest source of predictive errors. These errors can result in design cost inefficiencies on both a large and small scale. Tools and techniques are now available that can improve investigation process efficiency by enabling the real-time collection of a high-density of data. If deployed using a static approach, however, these new technologies can result in an inefficient allocation of resources and leave unanswered questions. At the Site, the project team added some dynamic elements to their characterization strategy, which accelerated the project toward established milestones. This case study provides valuable lessons concerning the implementation of dynamic methods for addressing VI and product distribution issues at refineries.

Results of Site Investigation and Data Interpretation Efforts

Collaborative data sets were developed by combining high-density data obtained in real time with a smaller set of samples that were analyzed using more rigorous analytical methods. More rigorous sampling and analysis methods were used to address specific uncertainties identified using the high-density data sets. For example, the ROST data in combination the many other forms of information made it possible for technical project goals to be accomplished.

Define the Nature and Extent of a Large Free Product Plume

The LIF tool can be used to estimate the total amount of hydrocarbons present in a subsurface free product plume. It can also be used to estimate when and if saturations are sufficient enough to result in free product moving into a well. (To gain a better understanding of the distribution of product across the Site, LIF data were used to prepare an isopach of total product thickness regardless of the type of product present at a particular location. The silicic nature of the sediments and the range of product types (that is, primarily gasoline and diesel range) made the LIF tool ideal for use at the Hartford site.

Estimate the Volume and Types of Product in the Subsurface

The conservative total estimated volume of product beneath the Site was approximately 8 million gallons as of 2006. Considering the conservative (biased low) nature of the porosity and saturation values used in these calculations, however, volume estimates could be off by a factor of two or more. Oil saturations in the presence of free product in wells are anticipated to be up to 30 or more percent as compared to the values of less than 10 used in this calculation.

Define Pathways and Exposure Points

The main findings of the geological investigation program included, but were not limited to, the following:

- The Main Sand is the principal aquifer at the Site and is comprised of highly-permeable and porous sand.
- The Main Sand approaches the surface near the center of the product plume in the northern portion of Hartford, creating a structural high in this area.
- Less porous units are generally comprised of clayey silts and silty clays that may not be impervious to fluid and/or vapor migration.

- Stratigraphic relationships in shallow saturated units at the Site control the flow within these units and are different than those in underlying units like the Main Sand.

The highest concentrations in vapors for benzene, the main risk-driving chemical at the Site, appear to be clustered within three areas of the Site. These include the Hartford Community Center area (in the northeastern portion of the Site), the area where the depth to the Main Stratum is shallowest (in the center of the Site), and along the eastern boundary of the Site. These findings were used to target VI mitigation efforts.

Understand the Short-Term and Long -Term Impacts on Soil, Groundwater, and Soil Gas

Based on observations made during the investigation using the LIF data, analysts concluded that the majority of contamination at the Site was likely to have been present prior to 1978. Hydrocarbon saturation in soil has also likely decreased over time as more pumping and product removal has occurred. The rise and fall of the water table has also likely decreased the mobility of the product present beneath the Site. Regardless of the efforts to remove product from the Site, it is clear that hydrocarbons in the subsurface will continue to act as a long-term source to groundwater and vapors at levels above potential applicable regulatory criteria.

Understand the Timing of Releases and the Fate of the Plume

The free product plume found beneath Hartford is derived from gasoline manufactured between 1969 and 1980. This observation is based principally on the available forensic data for the Site, which indicates that the product is primarily leaded gasoline with lead levels consistent with available product information. Other chemical ratios indicate that the product contains alkylate from a hydrofluoric acid (HF)-catalyzed process that operated in the area from 1969 to 1988.

Predict where Product Removal is Possible

For purposes of designing a petroleum hydrocarbon recovery system, northern Hartford was divided into three (3) areas, based on recovery and recharge rates, and petroleum product characteristics. The proposed active recovery system(s) may not necessarily be restricted to within these areas. Short-term effectiveness and community impact are also being evaluated during the design of the remedy.

Evaluate the Utility of Various Soil Gas Methods for Predicting Vapor Intrusion Issues

Some innovative technologies proved to be less effective then others at the Site. For example, passive soil gas methods were less effective than active soil gas methods for estimating where to expect VI issues. This ineffectiveness is suspected to be related to the complex chemistry of the vapors at the Site and competition for sorption sites. This suggests that the preferred method for optimizing vapor investigative activities at small or large petroleum sites is ROST used in combination with active soil gas methods.

Prepare a Comprehensive Conceptual Site Model to Support Cleanup

Using data collaboratively at large complex sites like the Hartford Plume Site is essential to streamlining project activities. The project had many positive aspects and resulted in lessons learned about implementing the Triad Approach at a large petroleum site. Data visualization of the CSM was one aspect that could have been more efficient. Hundreds of hand-drawn cross-sections and illustrations were prepared in support of the site activities. These were used effectively to reach stakeholder consensus on site conditions, but the significant volume of work products made their effective use cumbersome and the derivation of a simple picture of the Site difficult.

Conclusions and Summary

The work performed at the Site is an example of the type of approaches and activities that can be highly-effective at the larger refinery sites across the United States that have had a long production history. The project depended heavily on the use of historical information, collaborative data sets that combined real-time analytical tools with rigorous laboratory analyses, dynamic work strategies, and an evolving CSM to expedite reaching project milestones.

A dynamic "learn as you go" work strategy was applied during investigative activities, which improved the efficiency of site characterization, resulting in an estimated 30 percent cost savings, which is significant given the multi-million dollar total cost of the project.

The Hartford Plume Site case study provides a detailed example of the methods that are available to environmental practitioners to use at large and small hydrocarbon sites. Sufficient detail is provided for practitioners to begin to learn the basic elements necessary to design and implement site characterization, mitigation, and remedial efforts at hydrocarbon sites.

1.0 INTRODUCTION

This case study was prepared by the U.S. Environmental Protection Agency (EPA) Office of Superfund Remediation and Technology Integration (OSRTI) in cooperation with the U.S. EPA Region 5. In May 2003, the State of Illinois Environmental Protection Agency (IEPA) requested support from Region 5 to implement a time-critical removal assessment, assess current site conditions, and determine if further removal actions were warranted at the North Hartford Premcor Site located in Hartford, Madison County, Illinois.

The Village of Hartford (Hartford) is a small industrial community located less than 0.5 miles to the east of the Mississippi River. Hartford currently has a population of approximately 1,250 and has a history of refining and petroleum-related activities dating back to the early 20th century. Several petroleum pipeline systems cross Hartford to transport terminals on the Mississippi River. Premcor is one of several companies that owned or operated petroleum pipelines in the Hartford area. In September 2002, Premcor ceased production of petroleum products from crude oil in Hartford.

According to IEPA file information, beginning in 1969, house fires and noxious odors were reported in residential homes in North Hartford. Ensuing investigations identified petroleum products such as gasoline, diesel fuel, light oil, and jet fuel floating atop the groundwater. IEPA reports estimated as much as 3 million gallons of gasoline present on top of the groundwater beneath Hartford before cleanup activities were initiated.

In March 2004, EPA signed an Administrative Order of Consent (AOC) with Atlantic Richfield Company (Subsidiary of BP Amoco), Equilon Enterprises, LLC (Subsidiary of Shell Oil Products), and the Premcor Refining Group, Inc. (Purchased by Valero Energy in 2006) to address issues related to the petroleum contamination concerns. The majority of the work discussed in this case study was performed under this AOC by Clayton Group Services Inc. (Clayton) and ENSR Corporation (ENSR). Clayton was tasked with the majority of the soil and groundwater characterization effort, while ENSR performed the majority of the vapor intrusion (VI) related efforts.

Refineries are essential to the U.S. economy and modern society. Perceptions that the problems can be too massive to address cost effectively have led responsible parties and regulators to engage in extensive and expensive legal battles. At the Hartford Plume Site (the Site) the progressive ideas of the Hartford Working Group (HWG), comprised of those companies named in the AOC, their consultants, and EPA make the Site an excellent example of how large, highly-complex sites such as refineries can be characterized and problems mitigated in an efficient and collaborative manner. This case study presents an example of how new tools and approaches can be used to manage petroleum site cleanup on a basis of shared understanding between stakeholders.

1.1 The Triad Approach

The Triad Approach emphasizes the need for a thorough, upfront systematic project planning (SPP) process to build stakeholder consensus on the best approach for addressing potential issues at a site. Based on a sound conceptual site model (CSM) and a site’s anticipated reuse, SPP effectively supports development of site characterization approaches based on dynamic “learn as you go” work strategies. These strategies are used as the basis for developing streamlined workplans. Real-time measurement technologies support successful implementation of the strategies and refinement of the CSM on a continuing basis. The Triad Approach uses interactive data sharing and a dynamic strategy of sequenced activities to support real-time decision-making. Both conventional and innovative technologies are used collaboratively to increase the validity of site characterization conclusions and cleanup decisions.

The Triad Approach can be used to streamline site characterization and improve cleanup decisions at sites regulated under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), Resource Conservation and Recovery Act (RCRA), Brownfields, and other revitalization programs. More widely-accepted and used by increasing numbers of EPA Regions, states, and local governments, Triad best management practices (BMPs) have been demonstrated to compress schedules and reduce budgets required to reach project milestones at many sites across the country. Partnerships forged by OSRTI—with the U.S. Department of Energy (DOE), the U.S. Army Corps of Engineers (USACE) and a number of other organizations such as the Interstate Technology Regulatory Council (ITRC)—have documented use of the Triad Approach at small and large-scale sites. Project milestones have been achieved more quickly and economically, while the level of confidence in project decisions has increased. Further information about the Triad Approach is available at www.triadcentral.org.

The fundamental building block for refining and communicating any mitigation or cleanup strategy under Triad is preparing a robust Preliminary CSM, which is then revised as more is learned about a site. The CSM acts as an information framework upon which characterization efforts can be focused to more efficiently reach project objectives by putting new data into perspective and identifying data gaps. A frequently used form of CSM is the pathway-receptor network diagram used as a component of a risk assessment. A CSM under Triad is more comprehensive, integrating descriptions of the geology, hydrogeology, geochemistry and infrastructure of a site, together with information on exposure scenarios and proposed future uses. Under Triad, the CSM is used to identify the data needed to characterize, close, and monitor a site's progress as efficiently as possible in the context of the anticipated reuse. By starting with the end goal in mind and considering key economic needs and practical considerations related to potential mitigation and cleanup efforts, data collection and other site activities can be optimized to achieve reuse objectives as quickly and efficiently as possible.

The HWG and the U.S. EPA Region 5 project team effectively used an evolving CSM and the dynamic "learn-as-you-go" work strategies promoted in EPA's Triad Approach. Supported with sound SPP efforts and use of innovative technologies, these strategies are primary reasons for the success of the Hartford Plume Site project.

1.2 Report Content and Organization

In the following sections, readers will be introduced to the history of the Site, terminology used in the case study, methods used at the Site, results of previous investigations and the primary findings of data interpretation efforts. Following a description of the Site CSM, readers will be introduced to basic terminology essential to describing conditions at a refinery or other petroleum sites.

It has been EPA's experience that many parties use terms differently and, thus, it is essential for project teams to establish the use of common terminology before preparing and implementing a characterization and remediation strategy. Readers are then introduced to some of the tools and methods used in relation to petroleum sites. From this point on, the discussion follows the evolution of the project teams' understanding of the plume at the Site and describes the results that are currently being used to design mitigation and remediation strategies. Some of the methods used in forensic evaluation at gasoline sites are also discussed.

2.0 CONCEPTUAL SITE MODEL

The Site is located in the northern portion of Hartford, along the historical edges of the Mississippi and Missouri River floodplain. The area surrounding Hartford has been industrialized, and, since the early 1900s, it has focused on refining and storing petroleum-related products. Many investigations have been conducted since the 1970s to establish the nature and extent of petroleum (primarily gasoline-diesel range fuels) contamination beneath Hartford. However, only recently have state-of-the-science methods such as the use of conceptual site models (CSM) and innovative tools, like the Rapid Optical Screening Tool (ROST), made it possible for stakeholders to reach consensus on cleanup at this large, complex refinery site.

Releases of hydrocarbons along pipelines and beneath the refineries in the area date back to the early site history, but recorded releases were not reported prior to the early 1980s. Free product was measured in monitoring wells in the early 1970s, suggesting a long history of releases beneath Hartford. The hydrocarbons beneath Hartford are one potential source for explosive vapors that could have contributed to the many fires reported in Hartford since the late 1970s. Product removal efforts were conducted at the Site in the 1980s that resulted in the extraction of several million gallons of gasoline and diesel range hydrocarbons. Extraction efforts were performed initially based on free product thicknesses observed in the relatively scant network of wells present on the Site in the late 1980s. Fires and odor complaints have increased sporadically since the 1980s and it has been hypothesized that a general rise in the groundwater elevation coupled with seasonal peaks in groundwater elevation related to river fluctuations could have contributed to the observed increase in fire events during the 1980s. In some cases, fire events were also associated with an increase in rainfall.

The geology in the area of the Site is comprised of heterogeneous alluvium due to the Site's proximity to the Mississippi and Missouri Rivers. The heterogeneity of the alluvium provides an intricate framework for contaminant transport. The hydrogeology is complex, controlled by the inter-fingering of silts and sands. Hydrogeologic conditions are influenced by large, seasonal fluctuations in the water table and localized pumping to support refinery operations. In addition, periods of drought have caused the water table to fluctuate by as much as 20 to 40 feet in elevation throughout the period of record (approximately 1960s to present). The fate and transport of the contaminant plume are further complicated by the large number of potential release points from the many pipelines and storage facilities located on and adjacent to Hartford.

At present, a regional soil vapor extraction (SVE) system and targeted product removal efforts are underway at the Site. The systems were designed based on a high density of data collected using a combination of nested vapor probes, sub-slab vapor samples, real-time vapor measurements, laser induced fluorescence (LIF) measurements, cone penetrometer testing (CPT), soil core analyses, and product removal tests. In selected homes, sub-slab depressurization systems have been installed. These systems continue to be evaluated and operationally optimized to assure mitigation of any VI-related issues. Product removal systems are at the 90 percent design stage and should be implemented in the next several years.

Use of an effective CSM expedited implementation of a regional SVE system and targeted product removals, while full remedial systems were optimized and advanced to 90 percent design stage.

2.1 Site Location and Description

The Site is located at the confluence of the Mississippi and Missouri Rivers near St. Louis, Missouri (Figure 1). The Site includes the Hartford Site and the surrounding refineries, pipeline, and fuel distribution facilities (Figure 2). For the purposes of this case study, the Site primarily includes Hartford and the refineries and terminals surrounding Hartford to the north and east. The geographical region around Hartford and other nearby towns is collectively known as the American Bottoms, which encompasses an area of 175 square miles. The American Bottoms is a shallow valley 30 miles long and11 miles wide at its widest point. The Mississippi and Missouri Rivers merge approximately 1.0 mile south of Hartford, and the enlarged Mississippi River flows south in an alluvial meander belt bordered on both sides by limestone bluffs.

Hartford lies 1,500 feet east of the Mississippi River. The Shell Tannery Property and the Premcor facility are located directly east of Hartford. The BP Amoco (formerly Amoco) facility lies north-northeast of Hartford across Rand Avenue. The ConocoPhillips (formerly Shell) manufacturing complex is located east of the Premcor facility. Figure 2 shows the respective property boundaries of these facilities and their geographical relationship to Hartford.

Hartford is located in western Madison County, Illinois, in the Central Lowland Province of the Interior Plains of North America. The major physiographic features of the county are the upland till plains and bluffs and the Alluvial Mississippi River Valley. Wood River and Cahokia Creeks drain the western portion of the county. The Hartford area is located in the Springfield Tills Plain, which is an extensive, relatively flat area overlying till deposits of continental glacial origin. The major kinds of parent material in the area are loess, glacial till, glacial outwash, and alluvium.

2.2 Site Background information

Background information regarding VI and floating or free product issues in the northern portion of Hartford has been discussed in numerous reports by public and private entities. Two of the most comprehensive reports presenting this background information are the *History of Hydrocarbon Releases in the Village of Hartford, Illinois* prepared for Shell Oil Company by Engineering-Science (*E-S* 1992) and the *Hartford Underground Hydrocarbon Investigation* prepared by the Illinois Environmental Protection Agency (IEPA 1990). Numerous other reports prepared by Clayton, on behalf of the HWG and the Premcor Refining Group, including a *Current Conditions Report* (CC Report) for the Premcor Hartford Refinery and River Dock (Clayton 2003) were used as sources of information during preparation of the following sections of this case study.

2.2.1 Odor Complaints and Fires Documented in Hartford

In 1978, investigations were conducted in Hartford because of a series of residential house fires and documented odor complaints. According to *E-S* (*E-S* 1992), in 1978 the Hartford Police Department compiled a report summarizing complaints. Since 1978, the Hartford Police and Fire Departments have maintained detailed records of odor complaints. Further research as part of this case study revealed 363 odor complaints and 26 fires. Seven odor complaints or observations were identified in the 1960s; 245 in the 1970s; 20 in the 1980s; 77 in the 1990s; and 14 since 2000. This research revealed odor issues dating back to May 1966. No fires are known to have been reported in association with the identified free-phase hydrocarbons (FPH) issue since May 1990, which is shortly before installation of the existing vapor control system (VCS) in Hartford in September 1992.

Twenty-five (25) odor complaints or observations were documented in 1974, with 14 occurring within a 7-day period during March. In 1978, 149 odor complaints or observations were made, all occurring during the months of March, April, and May. A series of house fires occurred during the second week of April 1979, with the majority on April 11, after a 5-inch rainfall. Other significant clustering of odor complaints or observations occurred in 1979 with 49 complaints received in the months of March and April.

A severe drought began in 1988 and ended in 1990, according to *E-S* (*E-S* 1992). No documented complaints were recorded in 1989. However, in 1990, numerous complaints again were recorded as drought conditions receded. Twenty-seven (27) odor complaints were recorded in May 1990 along with five fires. All of the fires occurred within a 4-day period after heavy rain on May 16, 1990. The residents of Hartford contacted the Illinois Department of Public Health (DPH) on May 13, 2002, after several weeks of heavy rain; on this date, the Hartford Fire Department had six odor complaints. The Illinois DPH concluded in an earlier health consultation that residential vapor intrusions during the week of May 13, 2002, were a public health hazard to persons in the affected homes. More recent studies indicate a relationship between heavy rain events and reported fire and odor complaints at the Site, presumably related to localized changes in the depth to free product beneath homes in Hartford.

2.2.2 Refineries and Underground Pipelines near Hartford

As part of the initial activities to identify the sources of the hydrocarbon plume beneath Hartford, the IEPA Report identified three oil refineries in the immediate vicinity: the facility known as the Amoco Oil facility (currently the BP Amoco facility), the Clark Oil facility (currently the Premcor facility), and the Shell Oil facility (currently the ConocoPhillips facility). The locations of these facilities are presented in Figure 2.

Collectively these refineries will be referred to as the Wood River Refinery for the purposes of this case study. The Illinois EPA Report, the *E-S* Report, and the Clayton Reports also identified numerous underground and aboveground petroleum pipelines in Hartford and the immediate vicinity including:

- Ten Shell Oil (now ConocoPhillips) pipelines extend, parallel with sewer and waterlines, from the Shell facility to the Shell barge facility on the Mississippi River. The ten below ground product lines consist of one 12-inch line, one 10-inch line, six 8-inch underground lines, and two 6-inch aboveground lines. The lines generally trend westerly from the refinery parallel with Rand Avenue (Figure 3).
- Two out-of-service, 10-inch Sinclair Oil/Atlantic-Richfield Company (ARCO) pipelines from the Premcor facility to the ARCO pump station north of the Hartford/Wood River Terminal. The line trends northwesterly from the refinery parallel with North Olive Street.
- Three abandoned 8-inch and one abandoned 3-inch pipelines from the Premcor facility to the Premcor river dock barge facility on the Mississippi River and one 14-inch out-of-service line to Olive Street. The lines trend generally west from the refinery parallel with Elm Street with the exception of the 14-inch line. These lines were installed in 1953.
- One 14-inch and two 10-inch pipelines from the Premcor facility to the Premcor River dock barge facility on the Mississippi River. The lines, installed in 1982, generally trend west from the refinery parallel with Elm Street.

2.2.3 Known Releases within Hartford

The *E-S* (*E-S* 1992) and Clayton (2003) CC Reports documented 22 known releases of petroleum hydrocarbons within or immediately adjacent to Hartford. Further research by Clayton revealed 48 known spills within Hartford. These releases included eight in the 1970s; 17 in the 1980s; 18 in the 1990s; and five since 2000. No documented releases have been found prior to 1973. Forensic and monitoring data, however, strongly suggested that much of the contamination beneath Hartford was already present prior to 1973 (IEPA, 1990; Mathes, 1978a and 1979). Releases occurred after 1973 throughout the northern portion of Hartford from a number of sources and identified responsible parties. The total quantity of petroleum identified as released from those incidents with a listed amount was estimated at 324,000 gallons.

In addition to these documented releases, according to the *E-S* Report, there was evidence that some product lines had developed slow, continuous leaks. According to a November 1990 report issued by the IEPA, the 10-inch product line along Olive Street may have been leaking when it was in service. Inventory shortages averaged 360 barrels a week. According to the *E-S* Report, the 10-inch Sinclair/ARCO line had been abandoned since 1985 and initially contained approximately 600 barrels of unleaded gasoline. Only 350 barrels were recovered, resulting in a shortage of approximately 250 barrels (10,500 gallons) of gasoline. Two Sinclair/ARCO pipeline pressure tests conducted in August and September of 1990 failed, likely due to a leak within the pipeline.

In addition, three leaking underground storage tank (LUST) sites were identified in Illinois EPA records. Eleven underground storage tank (UST) sites (representing 48 USTs) were also identified within Hartford. The total capacity of the tanks identified at all 11 sites totaled approximately 323,000 gallons of petroleum hydrocarbon. Of the 48 USTs, the contents of 12 of the USTs were either not identified or contained non-petroleum hydrocarbons and, thus, were not included in this total, although it is likely several of the 12 also contained petroleum.

2.2.4 Pre-1990s Investigations

According to the IEPA Report, the vapor/free product issues were investigated over the years by various parties including the utility companies, adjacent oil refineries, and State of Illinois agencies. These investigations date back to 1966. The following information is an excerpt from the 1978 Mathes Report (1978b), the 1990 IEPA Report, and the 1992 *E-S* Report:

> *"In 1966, air samples from a school basement located at Delmar and Rand Avenue revealed the major component was methane gas. In 1969, an air sample from 16 Hawthorne Place showed no natural gas, but the presence of sewer or marsh gas, liquid propane fuel, and gasoline. Soil gas samples were analyzed in 1966 and in 1970. The results showed carbon dioxide and hydrocarbons ranging from methane through pentane with the notable lack of ethane."*

At the suggestion of the IEPA, Hartford officials invited Amoco, Clark, and Shell to cooperate voluntarily in an investigation. John Mathes & Associates, Inc. (Mathes), an environmental consulting firm, was retained by Amoco, Clark, and Shell to investigate the cause of the presence of hydrocarbons beneath Hartford. The 1978 Mathes report entitled "*Engineering Investigation Report, Phase I Gas Odors & Fired, Hartford, IL*" included a summary of the data collected by the Illinois EPA and Shell Oil Company:

- In 1978, IEPA installed ten monitoring wells (IEPA 1-10), and Shell installed two monitoring wells (Shell 1 and 2) in Hartford.
- On May 2, 1978, Shell inspected the 12 IEPA and Shell wells. The results, which were recorded in Mathes' product thickness map of the Hartford plume (1978a), indicated that three wells contained product, three wells contained a combination of water and odors (product-related and other unidentified odors), and four wells contained water with no odor. Two wells were not tested. Hydrocarbon thicknesses ranging from 3.8 to11.5 feet were measured in Shell 2, IEPA 4, and IEPA 6.

In 1983, Shell conducted a geologic and hydrologic site assessment of the Shell Wood River Manufacturing Complex (WRMC) and reported their findings in a document referred to as the 'Shepard Report'. The Shepard Report estimated there to be one million gallons of product underlying Hartford in an area 500 feet by 2,000 feet. The report indicated a northeast groundwater flow direction with a plume of dissolved phase hydrocarbons in the uppermost aquifer beneath Hartford between Arbor and Watkins Streets migrating northeast beneath Olive Street.

2.2.5 Early 1990s Investigations

A soil gas survey performed by Mathes (Mathes, June 1990) documented elevated vapor concentrations existing near the intersection of North Olive Street and Rand Avenue. The *E-S* October 1990 soil gas survey identified separate-phase product in this area.

2.2.6 Groundwater, Surface Water and Vapor Intrusion

There has been speculation concerning the relationship between vapor intrusion and changes in both groundwater and surface water at the Site. In 1973, Amoco observed a direct relationship between increases in the number of hydrocarbon odor complaints coincident with rises in water table elevation. The 1978 Mathes report stated, “experience has indicated that explosive mixtures are generally present only for a relatively short period of time in a particular area and that gas odor reports usually occur after periods of heavy rain or when the levels of the Mississippi River are rising” (Mathes, 1978b). The Mathes report also summarized the relationship between water table elevations and seasonal rainfall patterns, wherein groundwater elevations beneath Hartford were noted to decrease in late spring when groundwater withdrawal exceeded rainfall recharge. Conversely, groundwater elevations were noted to start recovering in the early winter months, and tending to rise during the wet spring months. Historically, groundwater elevations reach maximum levels in May and lowest levels in December.

The 1990 Mathes report contains a hydrograph that illustrates the correlation between fluctuations of groundwater and the number of hydrocarbon odor complaints documented by Hartford residents. Mathes drew the following conclusions:

- Complaints of gas odors generally occurred when the groundwater level began to rise.
- Occasional complaints were received when the groundwater level was already high but was falling.
- Some complaints would occur immediately after heavy rainfall.
- The upward movement of the groundwater level appears to be closely related to reports of gas odors.

In addition, the following observations documented by Clayton in 2006 support the conclusion that rising water levels primarily noted during spring increase the potential for hydrocarbon vapor emissions and potential house fires in Hartford (Clayton 2006a):

- House fires occurred during the second week of April 1979, after a 5-inch rain.
- A house fire occurred at the home of Mr. Doug Neal on May 16, 1990, after “extremely heavy rains.” Within the next four days, three additional fires occurred in homes located in Hartford.
- All but two of the reported house fires in Hartford occurred during March, April, and May. The remaining two fires occurred during June and July.

2.2.7 Historical Observations Relative to Surface Water

Clayton created a hydrograph presenting Mississippi River stage data from 1960 to 2003 (Clayton 2006a). The stream stage data was obtained from the U.S. Geological Survey (USGS) 07010000 Mississippi River at St. Louis, Missouri, gauging station located at Latitude 38°37'44", Longitude 90°10'47" (North American Datum of 1927 (NAD27)), which is approximately 15 miles downstream from Hartford, Illinois. The gauge datum is 379.94 feet above sea level (asl) (National Geodetic Vertical Datum of 1929 (NGVD29)). These data were downloaded from the USGS Water Resources (Clayton 2006a) internet site.

Clayton plotted documented odor complaints and observations and documented house fires on hydrographs and maps of the Site to qualitatively compare the number of recorded vapor and fire issues with the historical stage heights of the Mississippi River and other site features. The historical USGS gauging data generally were provided on a weekly basis. Therefore, the documented odor complaints, odor observations, and house fires were totaled on a weekly basis. The corresponding total was applied to the closest available date of gauging to support a comparison of documented concerns with Mississippi River stage.

As shown previously by other consultants, specifically Mathes and *E-S*, a general correlation appears to exist between times of higher Mississippi River stage and an elevated number of odor complaints, odor observations and fires. The greatest number of odor complaints, odor observations and fires cluster in the earlier portion of the year when groundwater levels and river stages typically are rising. The documented pattern of rising groundwater levels and river stage corresponded to an increase in house fires and hydrocarbon odor complaints and observations. This relationship indicated that fluctuation in groundwater level and river stage is one of the primary factors controlling hydrocarbon vapor emanation from the subsurface beneath Hartford.

2.2.8 Product Recovery

The following information was obtained, in part, from a Burns & McDonnell Waste Consultants, Inc. (Burns & McDonnell) report entitled *Groundwater Monitoring Plan for the Hartford Refinery*, (Burns & McDonnell, December 2002), and was included in the Clayton CC Report (Clayton 2003). On June 14, 1978, Clark Oil Company (Clark) installed a recovery well (RW-1) east of Delmar Avenue at Forest Street. The recovery well, equipped with a skimmer pump, was installed to a depth of 45 feet. In 1979, Clark installed a second product-skimming recovery well (RW-2) west of Olive Street between Date and Cherry Streets. From 1978 to 1990, Clark and Premcor continued to operate the two recovery wells that removed floating product and reported the monthly recovery amounts to the IEPA, except for a period during 1983–1984 when operations ceased. Odor complaints from village residents prompted an inquiry that resulted in reporting (and operations) being resumed. By June 1982, Clark had reportedly recovered 639,022 gallons of gasoline from beneath Hartford. Monthly product recovery rates from both wells ranged from 1,091 gallons to 28,789 gallons. According to the IEPA, Clark and Premcor recovered 1,161,981 gallons of product from the vicinity of Hartford by 1990. Prior to the work by the HWG, there were three product recovery wells (RW-1 through RW-3) in Hartford as shown in Figure 3. From January 1994 through September 2002, more than 82,700 gallons of product were reported as having been recovered from these same wells by Premcor.

2.2.9 Hartford Working Group Investigations

Between 2003 and 2007 the HWG under an AOC with EPA Region 5, conducted a number of modern investigations into the VI concerns and product present beneath Hartford. The HWG is an agglomeration of potentially responsible parties (PRPs) that includes Shell Oil, Premcor Refining (Valero), Atlantic Richfield, and each company's consultants. In the early part of 2004, Clayton and ENSR conducted the initial HWG site-wide investigations. Clayton's work focused on the delineation of product and the dissolved phase groundwater contamination, while ENSR focused on the evaluation of vapor phase contamination and the VI elements of the project. Premcor also used Clayton to evaluate the presence of product beneath the Wood River Refinery, located immediately east of Hartford and currently operated by Valero and Conoco Phillips.

These recent site investigations created the core information upon which this case study is based. The U.S. EPA and the IEPA both have lead roles on the Site. The U.S. EPA Region 5 is the lead agency for the Superfund Emergency Response Action and ultimate cleanup under Hartford, while the IEPA is the lead agency for cleanup-related activities on the operating refineries in the area, including the Wood River Refinery.

The significance of these recent investigations is that they used innovative methods for site characterization at the Site (Enclosure 1), which provided data of a higher density then was possible to collect during prior years (1970s and 1980s) when a majority of the previous work was performed at the Site. These investigations used a variety of innovative tools such as the ROST, which collects continuous geologic and hydrogeologic data using CPT technology fitted with an LIF tool to detect petroleum constituents in both vadose (unsaturated) and saturated soils. The subsurface investigations also included direct push technology (DPT) groundwater grab sampling, nested vapor probes, passive soil gas methods, mobile laboratory analytical services, as well as traditional methods for data collection and analysis such as monitoring wells and soil core analyses. Applying these methods and using the data in a collaborative fashion made this site approach unique. The data from the various tools were used collaboratively to refine a series of CSMs for various portions of the Site and residential properties. In turn, the CSMs were used to define the next sampling locations and sequence of grouped activities to advance the project as efficiently as possible.

A broad suite of real-time measurement technologies and traditional investigation methods were used collaboratively in a dynamic work strategy framework to characterize the Site.

For example, the project was initiated by doing a site-wide ROST investigation to delineate the extent of product (Clayton, 2004a and b). Figure 3 shows the ROST push point locations at Hartford and the Wood River Refinery. Figure 4 shows the approximate extent of the product plume identified during Clayton's initial product investigation beneath Hartford for the HWG (EPA, 2004).

After completing the site-wide ROST investigation site investigators executed subsequent field work based on a Triad Approach dynamic work strategy (DWS) using vapor probes, monitoring wells, sewer vapor samples, drain lines, soil samples, additional ROST borings, soil core analyses, groundwater samples, monitoring well bail-down tests, high vacuum extraction tests and other forms of data collection to progressively fill identified data gaps in the CSM (Clayton 2005a-c, ENSR 2004a-e, ENSR 2005). The "learn-as-you-go" nature of a Triad DWS improves data collection efficiency and reduces project costs. Enclosure 2 is an example of how the project team articulated initial data needs for specific grab groundwater sampling locations during the dissolved phase groundwater investigation (Clayton 2006a). Based on these initial results and the identified state standards for groundwater, the project team performed additional delineation using a step-out approach as necessary within the boundary of the Site. The need for step-out sampling was discussed at weekly project team meetings and conference calls, but no set logic was applied or documented for the dissolved phase groundwater plume investigation.

After conducting the product investigation, the HWG used the reported results to guide the installation of vapor monitoring devices (ENSR 2004 a through e, 2005) and began to plan for the dissolved phase groundwater plume investigation to delineate the extent of dissolved phase hydrocarbons (Clayton 2006a). Additional ROST profiles were also performed where data gaps were identified in the revised CSM products for the Site (Clayton 2005c).

The HWG developed CSMs for VI and product removal during these investigations and used these models to optimize DWS work plans for VI sampling and the evaluation of the potential for product removal. The HWG used the collaborative data obtained during these investigations to achieve project objectives.

These essential questions need to be answered at most hydrocarbon sites. It is important that practitioners understand the basic ways that this data can be collected and the limitations on the methods that can be used to obtain the information. Understanding available techniques and challenges associated with collecting and evaluating this type of data was a critical objective for this case study. Many other more theoretical documents are available that can provide readers with the basis for evaluating petroleum site-related issues, such as the American Petroleum Institute's (API) Interactive Light Non-aqueous Phase Liquid (LNAPL) Guide (API 2004) or the API publication, *"Evaluating Hydrocarbon Removal from Source Zones and its Effect on Dissolved Plume Longevity and Magnitude"* Publication 4715 (API 2002). There are, however, only a very few publically available case studies, such as this one, that actually examine the results from the characterization and remediation efforts at large petroleum sites.

Another important investigation conducted by the HWG based on the product and dissolved phase groundwater plume investigations (Clayton 2004b and 2006a) were pilot testing efforts designed to collect data to support product removal system design. Results were summarized in a document entitled *"Proposal for an Active LNAPL Recovery System"* (Clayton 2006c). During these investigations, testing was conducted for physical properties data for geologic units, fluid properties for petroleum products, core testing, monitoring well bail-down testing, product thickness measurements, and vacuum extraction. All of the sampling performed during these field efforts were optimized based on available ROST results. Formalized CSM work products used to optimize this effort were published in a document entitled *"LNAPL Active Recovery System Conceptual Site Model" (*Clayton 2005c). Later, the Active LNAPL Recovery System 90 Percent Design Report (Clayton 2006d) was published identifying areas and technologies to be considered for product removal at the Site.

2.2.10 Premcor Refining Group Site-wide Product Investigation

The Premcor Refining Group Inc. under a consent order with the State of Illinois also performed a site-wide investigation using the ROST tool (Clayton 2006b). During this investigation, more than 180 additional ROST locations were advanced within the confines of the Wood River Refinery. Based on the results of this portion of the investigation, Premcor's consultant also installed an additional 15 nested monitoring well clusters on the refinery and collected physical properties data for soil and contaminants to evaluate the potential for product removal.

2.3 Site and Regional Geology

Contaminant migration away from source areas is predominantly controlled by the hydraulic conductivity (K) of geologic media with respect to petroleum products and groundwater. The framework for contaminant migration is determined by the stratigraphy, of which the most important characteristic is the heterogeneity of its component units. The distribution and interconnection of the more conductive units create preferred pathways for contaminant transport.

The large quantity of existing information available for the Site makes it relatively straightforward to understand how and why contamination from the Wood River Refinery migrated along preferred pathways to areas beneath portions of Hartford. The relationship between more permeable strata beneath Hartford to source locations can also be used to understand where VI is a concern and why changes in water table elevations could significantly affect soil gas generation and behavior, and thus, directly correlate to VI-related issues in Hartford.

Detailed information on the stratigraphy at the Site is provided and briefly described in the EPA report, "*Considerations for Applying Triad Approach at the Hartford Area Hydrocarbon Plume Site*" (EPA 2007, Enclosure 3), as it relates to developing an overall remedial strategy for the Site.

The 2004 EPA report documents the depositional environment beneath the Site, which is similar to a mixed-load fluvial avulsion zone (Reading 1996; EPA 2004). The Site is located in an area where the Mississippi River has shifted its position in recent geologic time through a process referred to as an "avulsion" of the river channel. An avulsion occurs when a river breaches its natural levee and then cuts and flows via a new channel in the adjacent floodplain. The river bed load is called a "mixed load" because sediments of widely-varying grain size—ranging from finer-grained levee deposits to coarse sands—can be deposited across a broad avulsion band, such as is shown in Figures 5 and 6. These fluvial processes create a highly heterogeneous sedimentary stratigraphy.

The typical sedimentary sequence near large river systems includes thick sequences of sheet-like channel sands, lenticular splay sands, fine-grained levee sands, and fine-grained, silty clay floodplain deposits. Figure 5 depicts the heterogeneous sediments and other materials generally associated with fluvial deposits, while Figure 6 depicts the distribution of deposits and the geomorphology associated with a major river avulsion band. Although not site-specific, Figures 5 and 6 schematically show that near-surface fine-grained sediments grade with depth to massive sand units. Beneath Hartford and the Wood River Refinery, these massive sands are particularly porous because they are composed of unconsolidated sands and gravels from massive glacial outwash. Although the geologic cross-section shown in Figure 5 is a theoretical diagram from "*FPH CPT/ROST™ Subsurface Investigation Report and FPH Monitoring Well and Soil Sampling Plan for the Village of Hartford, Illinois*", Clayton's investigation findings (Clayton 2004b) concur with this generalized geologic sequence.

The CSM shown in Figure 7, also modified from the 2004 EPA report, shows stratigraphic relationships in some detail across Hartford and extending into the refinery. A structural high in the permeable glacial outwash sands in the area referred to as the Main Sand Unit can be seen in Blocks A through D and 1, 2 and 4. This figure also shows the extent and nature of the ROST responses (see vertical profiles), ranging between light gasoline-range hydrocarbons (blue), mid-range fuels such as diesels (green), mid-heavy range heating oils (yellow), and heavy hydrocarbons including crude oil (red). It is important to note the proximity of each hydrocarbon type to ground surface and the approximate location of the responses shown on the figure. In many areas, the lack of an obvious surface expression suggests that contamination has migrated in the subsurface some distance to its current location.

The present landscape of the area and the upper 130 feet of the Hartford area were created by processes (alluvial, glacial and fluvial) active during the last 125,000 years. The dominant creator of the landscape locally is the Mississippi River, which changed its course frequently during the Pleistocene Epoch (1.8 million to 10,000 years ago). The old meander loops are bordered by arcuate ridges and swales that were formed as slack water bars in former channels. East of the meander loops are partially-filled, poorly-drained swamps with silt and clay from floodwaters (Clayton 2006a). The northeastern part of the Mississippi Alluvial Valley in Madison County contains terraces of sand and gravel that stand above the present flood plain. These are outliers of former glacier valley fill sand and gravel. The communities of Wood River and Roxana are built on one of these terraces. The front of the terrace has a sharp rise of 12 to 15 feet, such as along Highway 111 between the Premcor Facility and the ConocoPhillips refinery. This is called the Roxana Terrace and is known as the Henry Formation Mackinaw Member (Clayton 2006a) in the local stratigraphic sequence.

The fluvial and glacial sediments, deposited in relatively recent geologic time, are underlain by consolidated sedimentary rocks more than 3,800 feet thick. These bedrock formations dip gently northeastward from the Ozark Highlands toward the Illinois Basin and predominantly consist of limestone and dolomite with subordinate amounts of sandstone and shale. Mississippian rocks underlie the sediments in the western part of Madison County, and Pennsylvanian rocks underlie the eastern part. The Mississippian bedrock below the Premcor Facility is believed to be Renault Limestone, which consists of relatively pure limestone and an upper sandy limestone (Clayton 2006a). Commonly, bedrock now occurs between 110 and 170 feet below land surface in the valley area. During the Pleistocene Epoch, the valley was filled with sandy glacial outwash as part of the Mackinaw Member of the Henry Formation. The sands of the Mackinaw range from 60 to 150 feet in thickness and comprise what is known as the Main Sand (Main Aquifer). This large, continuous sand body underlies the entire area beginning at depths ranging from approximately 20 to 45 feet below ground surface (bgs).

The uppermost geologic unit is the Cahokia Alluvium of Holocene Age (i.e., the present geological era) which consists of sands, silts, and clays of floodplain, channel, and modern river origin. In recent times, the Mississippi River has reworked the upper part of the valley-fill while migrating across the broad bottomlands, spreading floodwaters that deposited silt and clay along the sides of the channel and in backwater areas. The channel migration, cut-and-fill, and flooding have produced complex heterogeneous deposits. Beneath the northeast section of Hartford are two sand intervals (locally known as the EPA Sand and the Rand Sand; (Mathes 1990)) interbedded with low permeability clay and silty clays. The upper, seasonally saturated Rand Sand is encountered approximately 20 feet bgs. The EPA Sand underlies the Rand Sand and is separated from the Rand Sand by a clay layer that ranges in thickness from 3 to 11.5 feet. The regional and site specific stratigraphy of the area under investigation is illustrated by the geologic cross-sections shown in Figures 8 and 9, respectively.

Site heterogeneity had a significant impact on hydrocarbon plume configuration, contaminant fate and transport, and the location of vapor intrusion concerns.

2.4 Hydrogeology

Based on the collective investigations conducted to date, the hydrogeology in the vicinity of the Hartford Site consists of three aquifers, or hydrostratigraphic units, that vary from unconfined to confined hydraulic conditions. The aquifers generally consist of coarse- to fine-grained permeable sands, i.e. the Rand Sand, the EPA Sand, and the Main Sand (Mathes 1990), separated by interbedded, low permeability clayey silts and silty clays.

Under natural flow conditions before the extraction of groundwater for industrial activities, the flow of groundwater in the Main Sand aquifer and other aquifers was probably southwest, toward the river, or parallel to the direction of flow of the Mississippi River (south) during periods of high runoff. However, massive pumping of water from the former Shell refinery to the east of the Wood River Refinery (Figure 2), and other operations in the vicinity have periodically resulted in a northern and even an easterly trend to flow direction.

The massive pumping of the refineries in the area is the primary control on local groundwater flow directions. Active pumping of large amounts of water for use in various stages of the refining process has been controlling regional flow directions since the early 1940s, when the first data on regional flow directions were recorded. Records are sparse across the area early in the history of refining in the region.

Multiple flow directions have been observed locally in the shallow, less permeable, strata at the Site in response to stratigraphic controls and localized pumping. Shallow water-bearing zones are generally discontinuous and do not appear to have an affect on the regional flow direction in the Main Sand. However, flow directions in the Main Sand appear to be locally influenced in areas of high recharge from shallower water-bearing units, where large sources of artificial recharge are present.

Variable groundwater flow directions are controlled by stratigraphy, adjacent river stage level, and proximity to industrial groundwater extraction systems.

Piezometric (groundwater elevation) contour maps from Clayton (2004a) show flow directions beneath the refinery to be west to northwest toward Hartford. The 2004 Clayton report, "*Investigation Plan to Define the Extent of Free Phase and Dissolved Phase Hydrocarbons in Hartford, Illinois*," shows this general relationship of westerly to northwesterly groundwater flow from beneath the refinery for September, October, November, and December 2003.

Piezometric contour maps from the 2006 Clayton report show pumping stations on the refinery that had not previously been depicted, which change the localized flow direction back eastward toward the facility (Clayton 2006c). On a more regional scale, the groundwater flow directions beneath Hartford are north to northwest toward Hartford and away from the refinery. These two relationships are depicted in maps of piezometric contours for November 2004; February 2005; August 2005; May 2005; and October 2005; as well as in the "*Generalized Ground Water Flow Direction Map of the Main Sand Stratum for October 2004 through October 2005*" (Clayton 2006c).

A review of the hydrographs from the various wells, which have existed in the area for some time (Figure 10), shows a trend of increasing water table elevations, from low in the 1960s and to a relative maximum height above sea level by the late 1980s. This trend in regional groundwater elevations has had a significant effect on the nature and extent of contamination beneath portions of the refinery and Hartford.

The Mississippi River, located approximately 1.0 mile west of the village, is believed to be hydraulically connected to all three of the primary sand units (Mathes 1990). Water level fluctuations in all three sand units correspond to changes in the Mississippi River stage. Since the river stage varies up to 20 feet during a year, the sand units can vary from unconfined to confined conditions during the year. The three primary hydrostratigraphic units are discussed in more detail below.

2.4.1 The Main Sand

The Main Sand is the primary source for large-quantity water production in the area. Natural groundwater movement beneath the American Bottoms is westerly, draining from the limestone bluffs—at the east wall of the valley—to the Mississippi River. For the past 70 years, however, the natural movement of groundwater has been altered in the Hartford vicinity by large-scale water pumpage. Known cones of depression flank Hartford to the north (Amoco) and northeast (Shell; now ConocoPhillips). The net effect of this drawdown has influenced regional groundwater movement generally toward the northeast.

The Main Sand, which underlies the EPA Sand, has been identified at an average depth of 39 feet bgs (Mathes 1990). The Main Sand is coarser than the overlying units and includes gravel. The groundwater flows in a northeasterly direction at a gradient of 0.0018 feet per foot. In 1991, in the area of the Main property of Shell, the K values of the Main Sand ranged from 255.2 to 467.7 gallons per day per square foot (gpd/ft^2) according to the Shell Report (*E-S* 1990).

2.4.2 The EPA Sand

The EPA Sand underlies the Rand Sand and overlies the Main Sand. The unit has been found at an average depth of 28 feet bgs (Mathes 1990). The EPA Sand is approximately 7 feet thick and is in apparent hydraulic communication with the Main Sand in the area where the separating clay pinches out. The unit is coarser than the overlying Rand Sand but also contains silt.

2.4.3 The Rand Sand

The Rand Sand is the uppermost sand unit and has been found at an average depth of approximately 18 feet bgs (Mathes 1990). Groundwater flow in the Rand Sand mimics the direction of groundwater flow of the Main Sand. The groundwater flow is influenced by the cones of depression maintained by Shell/ConocoPhillips at the Main Plant property and at the Rand Avenue site.

The Rand Sand is unconfined during low river stages and becomes a confined unit during times of high river stage (Mathes 1990). An indication that the EPA and Main Sands are hydraulically connected is provided by the similar potentiometric surface of both units. These units also vary with river stage from unconfined to locally confined conditions. During May 1990, *E-S* completed an aquifer performance test at the Rand Avenue site for the Shell Oil Company. According to the document prepared for this testing effort, *E-S* reported that a hydraulic connection appears to exist between the Rand and EPA aquifers (*E-S* 1990). However, according to a later *E-S* report, a preponderance of evidence and subsequent reevaluation of the test results indicate that the EPA and the Rand Sands do not appear to be in hydraulic communication (*E-S* 1992). The average K value for the Rand Sand was determined to be 92.6 gpd/ft^2 (52 x 10-3 cm/sec). In addition, the average values of transmissivity (T) and storativity (S) were determined to be 280 gpd/ft^2 and 0.0033 gpd/ft^2, respectively. The value of storativity indicates semi-confined aquifer conditions.

Differences in the hydraulic heads and flow directions reported for the Rand and the EPA sands, published in recent studies conducted beneath the western portion of the refinery and north beneath the former location of the Shell Tannery property, confirm that the two units have different groundwater flow patterns (Clayton 2006a). The silty nature of the units between the Rand and EPA Sands do, however, suggest that leakage could be occurring and that some limited fluid loss from the Rand into the EPA could be occurring. The fact that hydrocarbons have migrated from the surface through the Rand Sand and into the EPA Sand beneath the refinery confirms that fluids migrate from the Rand Sand into the EPA Sand. Where the Rand Sand is saturated, it is possible that free product could have accumulated in significant quantities after a release. However, because of the generally less porous and permeable nature of the Rand Sand, it is not anticipated that large quantities of mobile phase hydrocarbons would accumulate within it.

Site stratigraphy is conducive to horizontal and vertical migration of hydrocarbons.

2.5 Contaminants of Concern

The contaminants of concern at the Site are those related to the production, storage, and distribution of petroleum hydrocarbons, particularly leaded gasoline. From a VI standpoint, the explosive nature of hydrocarbon mixtures and the concentrations in vapors of highly carcinogenic contaminants such as benzene are some of the primary concerns at the Site. As with any type of hydrocarbon refining and storage facility, some degree of risk is present because of the potential for direct contact with semi-volatile organic compounds (SVOCs) such as polynuclear aromatic hydrocarbons (PAHs) or lighter end fraction components. However, because the majority of Hartford is paved or otherwise covered with structures and access is restricted to workers at the refineries, the primary risk drivers at the Site are volatile organic compounds (VOCs) in vapors and free product on the water table that might prolong or exacerbate the VI-related issues at the Site.

Enclosure 4 contains examples of target analytes for some of the various methods applied at the Site to collect both analytical and physical property data for fluids and solids. Investigation design at this Site, like most applications of the Triad Approach, must consider not only the need for risk estimation data, but also data on which to base remedy design and implementation. This proactive approach to developing the remedy is an essential element to streamlining a project.

The project team used an understanding of the chemistry of fuels present at the Site and their respective levels of concern to modify the analyte lists and analytical procedures to ensure that the data were of sufficient quality for their intended end use. For example, petroleum-specific compounds such as pentanes (particularly isopentane) and octanes were added to the target list to understand when volatile hydrocarbons were present and could create an explosive hazard. Benzene results were reanalyzed to achieve lower reporting limits (RLs). Hydrogen sulfide was also added to list of analytes early during characterization efforts to ensure that a physical hazard to residences was not overlooked. Carbon dioxide and methane were also added to the vapor analysis lists to identify oxygen deprivation conditions and natural gas leaks.

Note that many analytes were specifically selected to serve as indicators of: (1) the presence of hydrocarbons at high, potentially explosive levels; and (2) hydrocarbons that could drive risks associated with vapors. Selecting limited indicator compounds helped save time and money at the Site, while not significantly diminishing the level of information available from sampling and analyses that were conducted. The size of the project and the need for a high level of confidence related to understanding Site-related risks warranted using project resources cost-effectively. Previous experience at the Site was also used to reduce the number of target analytes.

Indicator analytes were selected to ensure that site mitigation activities were appropriate to manage chemical and physical site hazards and to lower project costs.

3.0 UNDERSTANDING HYDROCARBON CONTAMINATION IN THE SUBSURFACE

Site geology and the physical properties of fluids have a major influence on the mobility of hydrocarbons and the potential for the migration of vapors. It is essential that practitioners understand the fundamental physical processes of hydrocarbons and their behavior in the geologic environment and use appropriate terminology when implementing site investigations and designing remedial systems.

A better understanding of the architecture of the product plume in the subsurface environment is essential to predicting mobility and the potential for VI- related issues. Improved understanding of product mobility is essential to designing an effective product removal and VI mitigation strategy.

3.1 Basic Terminology and Concepts for Hydrocarbons at Petroleum Sites

In this section, some of the basic concepts and terms used to describe hydrocarbons and contaminated sediments at petroleum sites are examined. In the literature, terms are often used that can have very different meanings. Some of the basic preconceptions about hydrocarbon behavior in the subsurface have also changed and practitioners need to be aware of these new ways of viewing hydrocarbons in the subsurface because it will increase understanding of observations they may make in the field. Understanding why and how terms are used differently can also help practitioners avoid miscommunication with other stakeholders.

3.1.1 Light Non-Aqueous Phase Liquids

A non-aqueous phase liquid (NAPL) is a liquid whose physical and chemical properties differ from water such that a physical interface will exist between the two liquids in contact. Hence, NAPLs act as a distinct fluid within the subsurface. Practitioners sometimes refer to NAPLs of any type as free-phase or free product, but the general use of these terms is not recommended because they imply a freedom for the product to move, which may or may not occur under given hydrogeologic conditions and the nature of the specific NAPL compound. Non-specific use of terms can cause significant confusion and miscommunication among stakeholders and should be avoided wherever possible. Thus, the term “free” product in this case study will be reserved to describe product that is mobile, as opposed to residual, or immobile, product. In this case study, references to product in the subsurface is meant to indicate ‘total product’. Total product in soil is composed of both residual or immobile product as well as free or mobile phase product.

NAPLs are typically divided into two general categories, light and dense. These terms describe the specific gravity or the density of the NAPL with respect to water. LNAPLs have a specific gravity less than water and dense non-aqueous phase liquids (DNAPLs) have a specific gravity greater than water. Examples of LNAPL include most hydrocarbon fuels (for example, gasoline, diesel, jet A, heating oil) and lubricants. DNAPLs include chlorinated solvent compounds, creosote-based wood-treating oils, coal tar wastes, and pesticides. The focus of this case study is on LNAPL since these compounds, like those present at the Site, comprise the most common type of contaminants associated with petroleum retail, storage, distribution, and refining sites.

3.1.2 Capillary Forces

When liquids (water, NAPLs, or both) and air are both contained within soil, suction—a measure of the capillary forces acting to retain these fluids within pore spaces between sedimentary grains—becomes an important factor in their movement through the soil (Figure 11). “Suction” is a dynamic property of the soil and is related to the grain size, nature of fluid in the pore space, and moisture content of the soil. Where fluids occupy the entire pore space of the soil, the capillary force is negligible and fluid movement is primarily a function of hydraulic gradients. Where fluids only occupy a small portion of the pore space, capillary forces become the dominant force, as greater energy is needed to withdraw fluids retained in smaller and smaller pores. The “capillary fringe” is the transition zone between the fully-saturated zone (groundwater) and the unsaturated zone (vadose soil). The capillary fringe varies in thickness because of the pore size of the soil. In coarse-grained soil (sands and gravels), the thickness of the capillary fringe may be on the order of inches, but in finer soils (silts and clays) the capillary fringe may exceed several feet.

3.1.3 Capillary Fringe and the Water Table

The **capillary fringe** is the zone of soil immediately above the water table where interconnected soil pores act like capillary tubes, drawing water up from the underlying water table and retaining the water as a function of fluid surface tension. The pores within a soil matrix typically are composed of numerous pore sizes. At the base of the capillary fringe most, if not all, of the soil pores are completely filled with water. At the top of the capillary fringe, only the smallest soil pores are filled with water. Therefore, the water content of the capillary fringe generally decreases with increasing height above the water table.

The size of the soil pore defines the capillary rise of the water column. The smaller the soil pores; the greater the rise of water within the capillary fringe zone. Soil is usually fully-saturated with water some height above the water table. The **water table** is defined by that point in the soil column where water is prone to movement because the hydraulic gradient is stronger than the surface tension within the pores. The water table is physically determined by the level to which groundwater flows into a porous pipe or well (www.EarthDRx.org 2009) and can vary based on well diameter.

The water table and capillary fringe, which are controlled by geology and have significant influence on contaminant distribution, should be considered interrelated scientific measurements versus separate physical states of groundwater. The oil-water barrier in the capillary fringe is the location where 100 percent saturation of water is achieved through capillary action (Figure 12). Water does not move freely in the formation at this location, but it does act to retard oil saturation during a release and it is at this level above the water table where hydrocarbons are expected to accumulate with the highest degree of pore saturation. At this point or above, hydrocarbons are most likely to accumulate in the highest percentage of the available pore space and are more likely to be mobile.

The degree of water saturation in the capillary fringe and the force with which a spill is introduced into the subsurface will control the amount of hydrocarbons that can displace water in the soil pore space (Figure 12). The size of the capillary fringe, and thus the oil-water barrier, will fluctuate with changes in barometric pressure and differing water levels creating what is often referred to as the “**smear zone**.” The smear zone may extend above or below the current water table, depending on the history of water table elevation fluctuation from the time a release has occurred. The smear zone is significant when dealing with LNAPL sites because it is in this region—above the water table—that the majority of the mobile phase of free-phase hydrocarbons are usually found. The mobility of hydrocarbons in the smear zone is driven by several factors, including product saturation and thickness, fluid properties, geologic properties, and the thickness of the zone of highest oil saturation.

The height of the capillary fringe above the water table is controlled by the grain size of a geologic formation. The capillary fringe will control the height of the contaminant smear zone above the water table where hydrocarbons tend to accumulate.

3.1.4 Oil Saturation

Oil saturation is the relative fraction of total pore space containing hydrocarbons such as an NAPL (Figure 13). The oil saturation varies between different soil textures and is also influenced by the composition and properties of the NAPL. The saturation level where the oil phase becomes discontinuous and is trapped by capillary forces within the soil is termed the **residual saturation** or irreducible saturation (Figure 12). For a given soil type, the residual saturation is generally lower in the unsaturated zone than in the saturated zone. Residual oil saturation is typically less than 10 percent in the vadose zone and ranges from approximately 10 to 30 percent in the saturated zone (API 2004). This phenomena results because gravity continually causes NAPL to flow downward in the unsaturated zone. In the saturated zone, NAPL is typically trapped by the increased water-induced pore pressure. Because of the increased pore pressures in the saturated zone, oil tends to accumulate as isolated and disconnected blobs further limiting its ability to move freely. LNAPL compounds, being lighter than water, tend to accumulate, migrate and partition into solution at and below the water table surface, thus they are often referred to as “floater” compounds. Conversely, DNAPL compounds tend to accumulate, migrate and partition into solution throughout the depth of the saturated zone due to being heavier than water, thus they are often referred to as “sinker” compounds. A more detailed discussion of LNAPL behavior in the subsurface is presented in Section 3.4

Oil saturation can be calculated by utilizing total petroleum hydrocarbon (TPH) analytical values from soil samples in conjunction with soil porosity, soil bulk density, and hydrocarbon specific gravity (density) measurements. The calculation simply converts the mass of hydrocarbon and soil into volumes and the ratio of the total oil volume relative to the total pore space for the appropriate volume of soil. Note that because of difficulties obtaining representative TPH measurements in fine-grained soils, this methodology is more applicable to coarser and less heterogeneous soil types.

When the oil saturation increases above the residual oil saturation, a petroleum product is capable of moving. For the purposes of this case study, when hydrocarbon saturations are above the irreducible saturation they are referred to as **mobile** or **free-phase** hydrocarbons. It is important to distinguish between free-phase and residual product for several reasons. Primarily it is the free-phase or mobile hydrocarbons that may be amenable to removal using extraction methods, such as product skimming or dual phase extraction. Conversely, residual or immobile hydrocarbons cannot be readily removed without applying more aggressive methods using heat or high vacuum pressures.

In formations with similar porosity and permeability the mobility or ease of product removal is primarily controlled by the degree of oil saturation.

Oil saturation is a dynamic process and changes with time and the influx of new releases. In a static plume without the influx of new releases, the saturations will be greatest near the center of a plume and decrease near the edges (Figure 14). This will have a substantial affect on the potential for product to be mobile. Changes in water level elevations and other factors will also influence the mobility of product in pore spaces. The API Interactive guide provides a good summary of the methods available for estimating oil saturation in soil. It also provides details concerning many other methods used to measure fluid and geologic properties in core samples (API 2004).

3.1.5 Apparent Product Thickness

The **apparent product thickness** is the amount of free-phase petroleum product present in a monitoring well (Figure 12) as measured from the upper exposed surface of the product to the product/water interface. As a function of well hydraulics and the differing specific gravities of product(s) and groundwater, the apparent product thickness will generally be greater than the actual free product thickness in the surrounding soil. This is due to the tendency of the free product in a monitoring well to locally depress the water in the well where the product is being measured. Accordingly, practitioners need to take the product thickness in a well into consideration and correct the water level measurements in a well containing measurable product before mapping piezometric conditions at hydrocarbon sites (Figure 12).

The actual free product thickness in a monitoring well can be more accurately approximated via bail-down tests or high-vacuum extraction tests. These tests, however, do not account for residual phase product present in a formation. At sites like Hartford, where water levels have fluctuated over the history of the Site, a significant mass of residual product can be trapped in small pore spaces above or below the water table and can act as a long term source of aqueous and or gaseous phase petroleum contamination. The **total product** present in a formation—that is, the combination of free product and residual product that are present in a formation—can be effectively estimated using downhole, direct sensing technologies which are not dependent on, or impacted by, hydraulic forces when measuring the presence of hydrocarbons.

At sites with predominantly fine-grained soil, a thin, free product layer may exist near the upper extent of a thick capillary fringe. A monitoring well screened across the capillary fringe and water table provides a capillary break that may allow the product to drain to the well, filling the entire interval between the free water surface observed in the well and the free product surface as it exists in the subsurface, exaggerating the true thickness of free product.

For all these reasons, the apparent product thickness is rarely an accurate reflection of the amount of free-phase product (which it generally overestimates) or residual phase product (which it generally underestimates). Apparent product thickness measurements, however, may be a valuable source of information, particularly when repeated measurements are made on a quarterly or more frequent basis and compared with data representing water table fluctuations. However, the effects of spatially and temporally varying conditions on apparent product thickness measurements must be taken under consideration.

The apparent product thickness in a well is an inaccurate measurement of the actual amount of free phase or residual phase product present in the formation adjacent to the well. Bail-down or high-vacuum extraction tests should be used to estimate the total amount of free product present. Water table elevations need to be corrected in wells containing free phase product.

This case study discusses how apparent product thicknesses in wells from similar locations can vary with simple changes in the geologic and hydrogeologic environment. Changes in apparent product thickness can also be realized in response to pumping pressure, loss of head pressure, infiltration, the proximity to a spill, and active pumping of product. Residual or sorbed product is not readily influenced by these factors, and residual product usually makes up the largest percentage of hydrocarbons that remain in the environment regardless of removal efforts.

3.2 Geologic Data and Terms

The critical geologic information that needs to be considered when investigating a petroleum site generally includes, but may not be limited to, the following:

- Grain size and bulk density,
- Porosity, and
- Permeability and hydraulic conductivity.

These parameters may be estimated based on available descriptive information and reference materials. However, it is also important to verify estimates to make sure that proposed remedial designs are appropriately sized and not over-built or under-designed for a specific application. The API Interactive guide provides details concerning available and preferred methods for specific applications (API 2004).

It is also often desirable to find alternative, cost-effective methods to improve the project team's understanding of a site. For example, using innovative tools like the ROST in conjunction with geologic and fluid property data, it may be possible to predict the behavior of fluids or vapors in the subsurface without necessarily conducting more expensive product removal tests at every well on a site. Several types of physical property data can be used together with innovative tools to expand predictions concerning the ability for product removal and vapor transport. These data types and techniques are described in the following section.

Predicting the relative permeability of oil and vapor in a geologic unit is the ultimate goal of most projects as it can be used to design a product removal or SVE system for a site. Collecting the information described below is, therefore, extremely important to the design of a remedial strategy for VI mitigation and product removal.

3.2.1 Grain Size and Bulk Density

The size, configuration, and physical composition of soil grains determine the connectivity of pores in aquifers and control the movement of fluids. The pore geometry of a geologic unit is primarily controlled by the grain size of the particles. Post deposition diagenesis or infilling of pore spaces can also influence pore connectivity and the ease with which fluids or vapors can move through or out of a formation. Soil type, which is based on the relative percentage of clay, silt, sand, and gravel-size particles, can be easily determined as a basic start to understanding and predicting petroleum product mobility in a contaminated geologic unit.

In general, the greater the percentage of larger grain size soil (such as sands and gravels), the larger and greater the connectivity of pore spaces, the more easily petroleum products can move through or out of a formation. In contrast, the smaller the grain size and the wider the distribution in particle size (that is, poorly sorted), such as is representative of clayey soil, the smaller the pores and the lower the permeability. Figure 15 shows the grain size distribution for the Main Sand Aquifer at the Hartford Site and the grain size distribution of the fine-grained sediments from the Site. The tri-linear plots demonstrate why the Main Sand aquifer is capable of producing thousands of gallons of cooling water to the refineries in the area. They also confirm that the supposed clay units at the Site are primarily silts and not impervious clays and, thus, why they do not form a complete barrier to vapor or fluid migration at the Site.

Soil bulk density is the ratio of the mass of soil to the volume of soil particles and pore spaces in a soil or aquifer material. Since most common minerals have similar densities, soil bulk density reflects the packing or the structural arrangement of the grains. Bulk density is a widely-used parameter for calculating hydrocarbon saturations from TPH concentrations in soil, porosity, and the retardation of dissolved hydrocarbons.

3.2.2 Porosity

The percentage of soil or rock comprised of void space is termed total porosity. Mathematically, total porosity is simply expressed as the ratio of the volume of void space to the total volume of the soil or rock. Under field conditions, the available void space is never equivalent to the porosity as water or other fluids are retained due to capillary forces. Thus, the "effective porosity" is the true volume that fluids are able to flow within the soil or rock. Although total porosity generally increases with decreasing grain size, the effective porosity generally decreases with decreasing grain size. Hence, the volume capable of transmitting fluids decreases with decreasing grain size. The difference between the total porosity and the effective porosity is described by the term, the specific yield, which is the drainable porosity. American Society for Testing and Materials (ASTM) method D 4404-84 (http://www.astm.org/Standards/D4404.htm) is a standard approach to measuring the porosity of soils. While it may be useful to have several soil samples analyzed for porosity for key formations, reasonable estimates of porosity can usually be derived from existing literature.

3.2.3 Permeability and Hydraulic Conductivity

Intrinsic permeability is a measure of the ability of geologic media to transmit fluids and is independent of the nature of the fluid flowing through the media. It is one of the most important properties to be determined in understanding the hydrologic conditions at a site and the potential for LNAPL migration and recoverability. Permeability is defined by units of length (for example, 1 square centimeter [cm^2] or 1 square foot [ft^2]). Hydraulic conductivity differs from permeability in that it is a measure of the ability of the aquifer material to transmit water, expressed as a rate of flow. It is a function of the properties of both the geologic formation and the fluid. Hydraulic conductivity is defined by units of length per time (for example, centimeters per second [cm/sec] or feet per day [ft/day]). Aquifer materials with high hydraulic conductivities, such as sands and gravels, are highly permeable and may readily transmit free product. In contrast, clays and silts have low permeability and do not readily transfer free product. The permeability of fractured media is dependent upon the size and degree of interconnectivity of the distinct fractures.

3.3 Physical Properties of Hydrocarbons

The physical properties, nature, and distributions of fluids that fill the pore spaces at contaminated sites, along with the properties of geologic media and hydrologic conditions, control, to a large degree, the observed nature and extent of contamination. These properties also have a large affect on the ability of environmental practitioners to remediate or mitigate environmental issues. Water plays a key role as the primary wetting fluid at most hydrocarbon sites.

The general properties and terminology discussed in this section include, but are not limited to, the following:

- Specific gravity and density
- Viscosity
- Boiling point
- Relative permeability
- LNAPL distribution and mobility
- Weathering

3.3.1 Specific Gravity and Density

Specific gravity (SG) and density are parameters that describe the relationship of mass to volume of a substance. Fluid density is defined as the mass of fluid per unit volume (grams per cubic centimeter [g/cm3] or grams per milliliter [g/mL]). It should be recognized that density is influenced by temperature; as temperatures increase, density decreases. Specific gravity is defined as the ratio of the weight of a given volume of a substance at a specified temperature to the weight of the same volume of water at the same temperature. The specific gravity is the critical indicator that determines whether the NAPL will float above ($SG < 1.0$) or sink below the water table ($SG > 1.0$).

3.3.2 Viscosity

The viscosity of a fluid is a measure of its resistance to flow and is an important parameter in understanding the capability of product to be recovered. Viscosity results from molecular attraction. NAPL with lower viscosity will flow more easily and be conducted through a porous media more readily. In general, as temperature increases in a liquid, the cohesive forces decrease and the absolute viscosity decreases. Viscosity is commonly defined in two general forms: dynamic viscosity (shear stress over shear rate) and kinematic viscosity (dynamic viscosity over density). The viscosity of gasoline is less than water, which indicates faster flow potential, whereas diesel fuel, jet fuel, and crude oil have higher viscosities, which indicates slower movement than water. Note that the viscosity of a product may change over time because of the leaching of the more soluble of its components and volatilization of its more unstable compounds. As a result, the viscosity of most products increases with age, which lowers their mobility.

The mobility of hydrocarbons is controlled by its viscosity and both generally decrease over time as a result of weathering, particularly near the edges of large hydrocarbon plumes.

3.3.3 Boiling Point

A liquid boils when its vapor pressure is equal to the atmospheric pressure. Since petroleum products are not pure substances but a mixture of compounds, they are characterized by a range, versus a single, boiling point. The distribution ranges of boiling point for a product sample can be useful as an indicator of hydrocarbon component composition and volatility. The boiling point for hydrocarbon compounds increases as molecular size increases. Therefore, products with smaller hydrocarbon molecules will have lower boiling point ranges. Typical boiling point range for gasoline is 40-160°C in comparison to lubricating oils, which typically have boiling points greater than 350°C. ASTM D-2887, *Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography* (www.astm.org/Standards/D2887.htm), and ASTM D-3710, *Standard Test Method for Determination of Gasoline and Gasoline Fractions by Gas Chromatography* (www.astm.org/Standards/D3710.htm), are common methods for determining boiling range distributions. Figure 16 shows the general range in boiling points for product samples collected at the Hartford Site.

3.3.4 Relative Permeability

Relative permeability is a factor that reflects the ability of fluid to move through the pore space when it is partially occupied by other fluids. Relative permeability is the ratio of the permeability of a fluid at a given saturation relative to the permeability of the fluid at 100 percent saturation. When a fluid completely fills the pore space, the relative permeability for the phase is one, and when no mobile phase is present, the relative permeability is zero.

When saturations are less than 100 percent, the permeability of the fluid in the soil decreases, and since LNAPL hydrocarbon is generally not the wetting fluid, the permeability of the oil phase in the soil is always less than at complete saturation. Note that the relative permeability of product varies primarily with the oil saturation.

3.4 LNAPL Distribution and Movement in the Subsurface

When an LNAPL is accidentally released at the surface or from an underground pipeline or storage tank, it migrates vertically downward under the force of gravity. When the volume of the release is sufficient, the free product component of LNAPL will migrate through the unsaturated zone to the capillary fringe and may even penetrate into the water table if the size of the spill is large. The increasing water content in the capillary fringe and the effects of buoyancy will impede the vertical movement of the LNAPL near the water table. As a result, the less dense oil will begin to migrate laterally along the capillary fringe and water table. In general, the lateral oil migration will preferentially flow with groundwater. If the rate of downward vertical free product movement from the surface is greater than the lateral migration, the oil will begin to mound vertically and oil flow may become radial (Figure 17). In addition, downward migration into the aquifer will displace increasing amounts of water from the aquifer pore space.

In the aquifer, LNAPL coexists with water in the soil pores. The percentage of LNAPL filling the total pore space is the product saturation, or oil saturation index. Due to the presence of water in the soil, LNAPL saturations are never 100 percent but may range from as little as 5 percent to more than 70 percent. The percent saturation and distribution of LNAPL within the pore network will change over time as oil initially displaces water and is then subsequently displaced as water refills pore spaces when water levels rise. The percent saturation will also change based on proximity to a spill (Figure 14).

When a well penetrates LNAPL-saturated soil, oil and water will migrate into the well casing and reach equilibrium relative to the atmospheric conditions. As a result, a distinct layer of oil will develop in the well above the water. The thickness of oil in the well is related to, but does not accurately reflect, the thickness of free (that is, mobile) product in the aquifer.

Because of capillary forces, some LNAPL is always retained in the soil pores as residual or immobile LNAPL. The remaining “untrapped” LNAPL (i.e. free product) is mobile and may continue to migrate. As LNAPL moves within the subsurface, the volume of mobile or “free” product continually decreases as LNAPL becomes trapped as isolated droplets within the soil pore network (Figure 14). In particular, it becomes difficult for the oil to coalesce into a consistent plume of any significant thickness. Hence, LNAPL plumes, unless continually supplied from an on-going release, are “spatially self-limiting.” This important concept distinguishes LNAPLs from dissolved and vapor plumes that may migrate significant distances.

Unless continuously supplied by an on-going source, LNAPL plumes are spatially self-limiting because of the effects of capillary forces. Dissolved and vapor phase components of plumes are not subject to these forces and, therefore, may migrate beyond LNAPL plume boundaries.

3.4.1 Product Mobility

The most common methods of estimating petroleum product plume mobility revolve around Darcy’s Law. The mathematical product of oil conductivity and gradient is equal to the Darcy Flux, and when divided by the effective oil-filled porosity, results in the average linear velocity known as **oil seepage velocity**. Oil conductivity (sometimes referred to as effective LNAPL conductivity) is a function of permeability, relative permeability, saturation, and fluid properties.

Unlike hydraulic conductivity, product conductivity is only partially a function of the aquifer permeability and porosity, given similar aquifer characteristics, oil saturation will primarily control product mobility. Because LNAPL conditions change when the water table or plume moves, and those conditions either create a new 3-phase state (air-water-LNAPL) or submerge the vadose zone portion (reverts to 2-phase water-LNAPL), the LNAPL conductivity is not a constant, but rather a variable factor. In general, the more disperse an LNAPL plume becomes vertically and laterally, the smaller the transmissivity and conductivity. LNAPL mobility is primarily controlled by the degree of product saturation. Mobility increases with increasing product saturation, product saturated thickness, formation permeability, and fluid viscosity.

The inherent oil mobility was defined by Parker and others (1996) as the ratio of free oil transmissivity to specific oil volume at a given location. These two parameters can be measured with core analyses or with bail-down tests and high vacuum extraction tests.

3.5 Weathering

Gasoline consists of a mixture of lower molecular weight hydrocarbons and non-hydrocarbon chemical additives, such as ethers (for example, methyl tertiary-butyl ether [MTBE]) and alcohols (for example, ethanol). Gasoline hydrocarbons compose 10 to 40 percent of crude oil and yields may increase to over 70 percent through polymerization, cracking, and other chemical processes. Generally, n-alkanes and isoalkanes are the dominant hydrocarbon molecules in gasoline, followed by cycloalkanes and aromatics (Figure 18). During distillation, light aromatics are preferentially partitioned, resulting in high concentrations of benzene, toluene, ethylbenzene, and xylenes (BTEX). Approximately 20 percent of gasoline by weight consists of BTEX molecules, with toluene composing the majority of the fraction. Because PAH compounds are high molecular weight, high boiling point molecules, they do not occur or are present in very small quantities in gasoline. The exception to this is naphthalene, which may be present at concentrations of approximately 0.5 weight percent.

Gasoline is composed of hydrocarbon molecules ranging from C4 to C10. As a result, gasoline is more mobile, volatile, and generally more soluble than other petroleum products. The typical density and dynamic viscosity of gasoline are 0.73 g/cm3 and 0.62 centipoise (cP), respectively.

The relatively high concentrations of aromatic compounds in fresh gasoline, such as BTEX, produce a volatile and soluble product. As a result, a release of gasoline to the subsurface may produce significant dissolved plumes and vapor problems. Over time, these compounds can be leached, and “weathered” gasoline may contain less than 5 percent BTEX (API 2004). The rate of weathering of hydrocarbons is dependant on several factors including the concentration of the product and the suitability of geochemical conditions for anaerobic digestion of the chemical constituents. In general, the more product there is in the subsurface in a particular spill, the less likely it is for degradation to occur. Degradation is generally the greatest near the edges of a plume where the mass of contamination is lower and the toxicity to biological anaerobes from the contaminants is reduced (Figure 14). This explains why gasoline that has been in the ground for several decades can still appear to be relatively fresh and unweathered, as exhibited by many of the product samples collected from the Site.

Figure 18 shows the effects of weathering on gasoline near the edges of a plume as measured by a mass spectrometer (MS). Notice the shift in the peaks shown on the weathered product chromatogram. The largest peaks shift to the right in the lower image indicating the boiling point of the constituents is relatively higher than in the fresh product chromatogram. Lower viscosity and higher mobility is associated with the less-weathered gasoline. Understanding the chemistry of gasoline is also important when evaluating the age of the material present in a plume. An increase in the relative concentration of recalcitrant trace level additives and chemicals compared to volatile and biodegradable components such as BTEX can be indicative of the weathering of petroleum products. The approximate timing of a release can be estimated by mapping the chemistry of gasoline at the source (see Section 5.4).

4.0 SAMPLING METHODS AND INVESTIGATIONS AT THE HARTFORD HYDROCARBON PLUME SITE

Several very powerful tools and many different sampling methods were used at the Site to understand geologic relationships and contaminant distributions. In the past, low-density data, collected with then state-of-the-art investigation tools, was used to characterize most large refinery sites. While those methods provided data of high quality from an analytical standpoint, their relatively high costs frequently impeded the collection of data at the density needed to effectively characterize sites and design remedial strategies. Current understanding of contaminant distributions at petroleum sites indicates subsurface heterogeneity is the largest source of predictive errors. These errors can result in design cost inefficiencies on both a large and small scale.

Beginning in the 1990s, new tools and methods began to emerge that could be integrated with historically used methods to streamline site characterization. Methods for integrating the data streams created by innovative and prior data collection techniques have lagged behind the development of the new technologies themselves. These new technologies, however, if deployed using a non-dynamic approach, can result in an inefficient allocation of resources and leave unanswered questions. At the Hartford Plume Site, the HWG added some dynamic elements to their characterization strategy, which accelerated the project schedule toward established milestones. Because of the growing awareness concerning VI-related issues in the United States, the Site case study provides valuable lessons about utilizing dynamic methods to address VI issues at refineries.

A complete introduction to all of the available tools to support delineation and subsequent design efforts at petroleum sites is beyond the scope of this case study. However, the mix of tools used at the Site and the sequence of application can be considered as a template for similar sites. For example, the CPT\ROST, a key investigative technology, is one of a number of multi-component tools that can increase the density of information to improve real-time decision making.

At the Site, ROST data was combined with other types of real-time and screening methods, including mobile laboratory services, passive soil gas, and head space analyses using a photo ionization detector (PID) and flame ionization detector (FID) in an effort to optimize sampling and analyses using fixed-base laboratory methods. ROST data was used to direct groundwater grab sampling in DPT-advanced boreholes. Groundwater sample results were then used to optimize locations for monitoring wells and nested vapor probes. Sewers and other utility corridors were screened using PID, FID, and passive soil gas. Gas samples were collected using Tedlar® bags as well as Summa® canisters. Passive soil gas methods were compared to headspace analyses for use as screening tools to identify potential vapor issues, with mixed results.

The use of these tools and techniques was guided by a continuously-evolving CSM, which was used to facilitate project planning, and to compile and communicate essential site data; including suspected contaminant sources, types of contaminants, potential receptors and exposure points, potential migration pathways, and project constraints. These data were needed to understand site characteristics and processes that influence chemical fate and transport and plan a strategy for attaining objectives. Project objectives were clearly stated at the beginning of the project and then translated into site-specific decisions and data collection activities designed to answer the questions raised by the existing data. As the model was refined, it became less conceptual and more fact-based. The project team developed the preliminary CSM based on data that was available at the time the investigation was being planned. These data were evaluated to assure that the data collected would be of sufficient quality and quantity to meet the project objectives.

Modifications to the project approach were made as more was learned about the Site and the data needs were refined. A DWS and real-time data evaluation and assessment facilitated continual CSM updates as more data became available. Continual revision of the CSM was a key element to limiting project costs while improving decision certainty.

In the following sections, technologies and approaches are discussed in the sequence they were applied at the Site. Data collection activities were designed to create collaborative data sets used to develop a more complete understanding of a particular site condition. Investigations, therefore, often included a variety of sampling techniques and mediums in combination to assure the robust nature of the data set collected. For example, during the VI investigation, several different types of soil gas sampling methods and media were used, soil physical properties were tested, and soil chemical analyses were performed. Readers should note how these tools were used in the context of the DWS work plan and how they were used to continually evolve the CSM. Enclosure 1 provides additional information concerning the ROST and soil gas tools used at the Site.

4.1 Evaluating the Nature and Extent of Product using the ROST

The ROST combines a CPT with a LIF device and is deployed via a data acquisition vehicle (Figure 19). Few tools offer the diversity of information and density of data that can be obtained using the ROST. Table 1 summarizes the types of optical screening tools available in the market today. The CPT tool has the ability to detect changes in lithology by measuring both resistive and frictional forces with pressure sensors positioned on the tip and sleeve of the penetrating cone, as shown on Figure 20. The tip resistance (Qc) is plotted against the friction ratio (FR, which is the sleeve friction [fs] divided by the tip resistance) and evaluated by an algorithm to assign a soil classification. A plot showing one such classification scheme is provided on Figure 21.

The tool also includes a permeable ring and pressure transducer that can be used to detect slight differences in pore pressures in sediment beneath the water table. The pressure transducer allows it to record excess pore pressure as the cone is pushed. Large excess pore pressures are usually generated in fine-grained sediments, as they cannot transmit water away from the contact zone as readily as granular sediments. This provides a crude, qualitative log of the permeability of the sediments. If penetration is halted, the pore pressure decay curve is recorded; this can be processed by various algorithms to generate a semi-quantitative estimate of K at the point where penetration was stopped.

Figure 22 shows a typical multiple sensor readout from a CPT. Soil classifications obtained using the CPT algorithm are generally representative of a sample of core collected from the same approximate depth.

The ROST uses a wavelength-tunable ultraviolet laser source coupled with an optical detector to measure fluorescence (Figure 23). The measurement is made through a sapphire window on a probe that is pushed into the ground with a truck-mounted CPT. The response is transmitted to instruments on the truck through optical fibers that are strung, along with CPT sensor wires, through the center of the CPT rods. For this reason, groundwater grab sample collection, even if conducted from the same DPT platform, requires a separate, offset push.

The ROST method provides data on the in-situ distribution of total product from the fluorescence response induced in PAH compounds that are components of the petroleum hydrocarbon. The method detects PAHs in the bulk soil matrix throughout the vadose, capillary fringe, and saturated zones. The methods can provide vital information relative to the potential for vapors and free product when used collaboratively with standard soil core analyses.

Kram et al. (2001) states that a concentration of only 1 percent PAH or other fluorescing compound in a NAPL is sufficient to produce a measureable response. Quantitation is approximate, since the strength of fluorescence depends on the concentration of PAHs in the particular petroleum mixture under investigation. Calibration using site-specific contaminants, if available, is required to achieve quantitation. The fluorescence intensity also depends on the nature of the soil matrix. Fine-grained sediments can smear the sapphire window leading to poor response measurements. Moreover, NAPLs present in the subsurface are usually dispersed as blobs and ganglia; since the sensor will measure only the fluorescence of materials immediately adjacent to the sapphire window, it will not detect the presence of contaminants that are not in direct contact with the window.

Many LIF and multiple-sensor tools like the ROST are available from a variety of vendors and service providers. Each unit shown in Table 1 has different capabilities and potential interferences. The ROST cannot distinguish between free product and sorbed or residual-phase hydrocarbons. It can detect only the mixed wavelengths of emitted light read by a light sensor while a contaminated soil sample is irradiated with a beam of ultraviolet light. Tool performance is also related to the chemical nature of the product in the ground and the wavelength of light emitted by the laser unit. An abundance of heavier boiling point hydrocarbons can result in false negatives because of energy adsorption by the product surrounding the tool. Practitioners should always consult with an experienced fluorescence technology vendor before selecting to use a tool at a particular site.

Optical screening tools are prone to false positives when naturally fluorescing minerals, like calcite or gypsum, are present in the subsurface. The siliceous makeup of the strata at Hartford does not exhibit any fluorescent characteristics identified as potentially interfering. However, practitioners should consider the mineralogy and geochemistry of the subsurface media before selecting a tool.

The ROST tool can indicate product type by evaluating fluorescence intensity and wavelength (Figure 24). Strip charts are color-coded based on the predominant wavelength of light that is received during a scan of product in the subsurface. Spectral information is available for all depths on a strip chart from the ROST as shown in Figure 25. No attempt is made in this case study to identify product distributions specifically by product type, although both Clayton and EPA have done so in many site-related evaluations (Clayton 2004b and EPA 2007). Product type has a strong influence on the mobility of product in the subsurface and must be considered early in designing an extraction system at a site The distinction between lighter and heavier carbon range hydrocarbons is used in this case study to explain the general nature of the material where a ROST signature has been obtained.

The reliability of the ROST in estimating the distribution of hydrocarbons in the subsurface is influenced by the presence of carbonates that can create false positives and clayey material that can mask positive responses resulting in false negatives.

4.1.1 ROST at the Hartford Site

Three separate ROST investigations performed at the Site were used in preparing this case study. The initial ROST investigation was performed by Clayton on behalf of the HWG, and was named the "*Free Phase Hydrocarbon (FPH) CPT/ROST Subsurface Investigation of the Village of Hartford, Illinois*". The second investigation plan, entitled the "*Investigation Plan, Village of Hartford, Illinois*" (Plan), was prepared by Clayton on behalf of the HWG and is dated January 7, 2004 (Clayton 2004a). Clayton also completed the last investigation and submitted it to EPA on behalf of the HWG on January 27, 2004. The results report, *CPT/ROST™ Investigation Memorandum*, was dated April 8, 2004.

The first investigation consisted of applying the ROST assessment technology at multiple locations within Hartford to collect data regarding the extent of the petroleum hydrocarbons (Figure 4). This investigation included 66 CPT/ROST borings continuously logged to termination depths ranging from approximately 31 to 76 feet bgs. Fugro Geosciences, Inc. (Fugro) of Santa Fe Springs, California, conducted the CPT borings from January 29 to February 23, 2004; Clayton followed with six DPT soil borings adjacent to the CPT/ROST locations. The DPT borings were conducted at approximately 15 percent of the CPT/ROST locations. The intent of these soil borings was to help evaluate both the subsurface stratigraphy and petroleum hydrocarbon findings from the CPT/ROST.

The second investigation consisted of additional DPT borings and vapor probes installed at the Site as part of a dissolved phase groundwater plume investigation. The CPT/ROST borings were completed in combination with multi-level, direct push groundwater sampling and analyses, to fill data gaps identified during the initial ROST and associated soil and groundwater investigations. Samples were taken from thirty-five (35) DPT multi-level groundwater locations to determine the magnitude and extent of the dissolved phase hydrocarbon plume, within and surrounding the previously-identified plume extents.

A proprietary petroleum hydrocarbon compound (PHC)-containing reference solution was used for ROST calibration purposes. Fluorescence was measured simultaneously at each of four monitoring wavelengths that cover the range of fluorescence produced, from light-range (shorter wavelength) to heavy-range (longer wavelength) petroleum hydrocarbons. The relative percentage of fluorescence at each of the four wavelengths was continuously measured. The results from the monitored wavelengths were combined, based on the relative fluorescence intensity percentages of each of the four wavelengths, and plotted on the ROST log. The emitted fluorescence of the four wavelengths was totaled and recorded as the fluorescence intensity (%RE).

The third ROST investigation was also conducted by Clayton in 2005. Subsurface investigation methods utilized during the implementation of the Site Wide Free Product Investigation Work Plan included CPT\ROST pushes, nested monitoring well installation, and groundwater sampling. There were 95 CPT\ROST locations originally proposed in the Work Plan. The IEPA requested additional locations in their June 22, 2005, approval letter. During the course of the CPT\ROST investigation, more locations were added in consultation with the IEPA based on the results of completed CPT\ROST locations. Clayton retained Fugro to conduct the CPT/ROST borings. Sampling at 183 CPT\ROST locations was completed from June 7 through September 30, 2005. Push locations from each of the three investigations are shown in Figure 3.

4.1.2 ROST Dynamic Work Strategy

A DWS was used for two of the three ROST sampling efforts conducted at the Site. An initial grid was established for the first 50 of the proposed sampling push points. The investigation progressed from the initial grid in the center of the plume outward to delineate the edges of the plume (that is, an inside-out approach). As data were received in real-time it was transmitted to stakeholders in the form of Adobe® PDF files that contained maps of the CPT/ROST results, as well as the logs themselves. These data were used to select the next round of sample locations after consulting with the key stakeholder group. Because the ROST tool responds primarily to the presence of a separate product phase, a ROST response above the baseline “noise” was used as the criterion to determine when additional locations (step-outs) were deemed necessary to continue the delineation effort.

Because of the large volume of data and the difficulty in interpreting both geologic, hydrogeologic, and contaminant information, it was not possible to delineate all the specific areas of interest fully in a single mobilization. However, the propensity of the total undifferentiated product plume was delineated during the first and third ROST sampling events conducted beneath the refinery and Hartford.

After the project team evaluated all of the information derived during the initial investigation, additional ROST push locations were selected for the second investigation to target suspected shallow release points along the Elm Street pipeline corridor (Clayton 2005a). These push points were useful in identifying near surface sources near the River Pipelines beneath the Site. (See Section 5.1).

The project team was urged by EPA to use a 3-dimensional visualization program to help guide the ROST and other sampling efforts and some initial work was performed to prepare a model for the Site using C Tech Development Corporation's Environmental Visualization System (EVS). These images were used in a limited capacity to support the vapor investigation work, but a fully-populated database and 3-D visualization effort for the Site was not pursued by the HWG.

A dynamic work strategy was used to delineate the extent of the free product plume and geologic conditions that would be favorable to vapor migration. Results were used to optimize the locations and limit the number of mobilizations required to install monitoring and extraction wells and vapor probes.

4.2 Vapor Phase Contaminant Plume Delineation

ENSR installed and sampled initial soil vapor monitoring points (VMPs) at the Site in March, July and August 2004. The July and August investigation locations were optimized using the initial ROST sampling event results obtained by Clayton in April 2004. Based on EPA suggestions and a revised CSM, ENSR planned a fourth round of sampling in December 2004. The 2005 mobilization was designed to meet a series of objectives stated in the ENSR CSM Investigation Work Plan (ENSR 2004e). These objectives included the following:

- Further delineating soil vapor plume in the Buffer Zone surrounding the product plume
- Defining the soil vapor plume at the eastern and northern boundaries of the Site
- Developing a dense network of VMP locations within Site boundaries
- Investigating the potential for VI issues in areas where the Main Sand formation is shallow with respect to overburden thickness
- Installing VMPs at off-site locations to investigate potential effects north of Rand Avenue, east of the Site boundary, and west of the Site along Illinois State Route 3.

The potential effect of contaminant VI on the indoor air of residences in Hartford was evaluated by placing vapor monitoring probes and similar instruments at specific locations; selected based on access, geologic conditions indicated by ROST data, and contaminant distribution favorable for the presence of VI issues. Field-based methods included hand-held screening devices such as PID and FID to obtain real-time results from soil where probes or sensors were to be placed. A mobile laboratory stationed onsite provided both screening level and definitive analyses of Tedlar® bag, vapor probe and sub-slab samples. Gore-Sorbers® passive diffusion samplers were installed into utility corridor manholes to screen for the potential for vapor to enter homes through this potential pathway. Gore-Sorbers® and EMFlux® passive soil gas methods were evaluated in a demonstration of methods applicability (DMA) to determine their utility for identifying the potential for contaminant vapors to be present. The following sections describe the basic approaches used during the most recent of the VI sampling efforts conducted at the Site. Details concerning the VI network results are presented in Section 5.2.

ROST data was used collaboratively with other direct vapor measurements tools to understand the distribution of vapors beneath the Site and the potential areas where vapor mitigation was needed.

4.2.1 Vapor Related Dynamic Work Plan Sampling and Analyses

A DWS work plan for vapor sampling and analysis was used to accomplish the following: (1) identify areas where VI issues were expected to be present; and (2) quantify the effect on soil gas at various levels in the unsaturated zone beneath Hartford. The initial portions of the VI program included several different sampling efforts. A complete description of all of the VI sampling efforts is beyond the scope of this case study. However, the last of the major efforts conducted in 2005 by ENSR provides a good example of how a DWS can be applied during a VI delineation program.

Figure 26 is a site map from the Clayton Utility and Pipeline Investigation (Clayton 2004c) used by ENSR in their CSM Investigation Work Plan (ENSR 2004e) showing where ROST results indicated the first encounter with measurable total product in subsurface soil.

Vapor sampling was optimized by using headspace analyses of soil samples in the field, followed by installing nested vapor probes (Figure 27). These probes were then sampled using active soil gas methods and Summa® canisters. Summa® canister samples were paired with Tedlar® bag samples at many locations to screen for the presence of contaminants of potential concern. The project team sampled as many existing vapor probes as possible to augment the network of sub-slab probes and confirm the potential for VI at specific residential properties.

Prior to the fourth active soil gas sampling effort across the area beneath Hartford, ENSR also evaluated the passive soil gas results to identify VI concerns. Figure 28 is a logic diagram that was used to select vapor sampling technologies and locations during the 2005 sampling event. The results of these efforts indicated that passive soil gas methods might not be appropriate for the intended application. Passive soil gas results are discussed in more detail in Section 5.2 of this case study for readers who might be considering the use of passive soil gas on similar efforts. The full results of this study are provided in the ENSR passive soil gas sampler report (Enclosure 6).

4.2.1.1 Collaborative Soil Sampling and Logging Program

During the initial 2004 ENSR efforts, the majority of the new VMP locations were located on Hartford streets and required the use of a diamond bit corer to advance through paved surfaces. Once completed, hand auguring, using either a single or dual 4-inch outside diameter (OD) hand auger advanced 10 feet bgs, was conducted to verify that utilities or other obstructions were not present. Grab soil samples were collected from the hand auger from 0 to 10 feet bgs. Soil borings advanced greater than 10 feet bgs were completed with a hollow-stem auger (HSA) drill rig (Central Mine Equipment Company Model CME 45 or similar). Soil samples were continuously collected from a depth of 10 feet bgs to boring termination using a split-spoon sampler. Split-spoons used for the sampling were typically 5-feet long with a 3.75-inch inside diameter (ID). ENSR personnel observed, described, and classified soil samples following the Unified Soil Classification System (USCS). Field classification included noting, if present, petroleum-impacted soils, discoloration, or odors. The team noted other physical properties, including moisture, color, grain size, and relative density and consistency of each sample. Sample recovery was measured with respect to the sampled interval and the recovered interval noted on the field boring logs.

Soil samples were field-screened utilizing a Thermo Environmental TVA-1000 dual PID and FID. Prior to the start of work each field day, the PID/FID was calibrated in accordance with manufacturer instructions. At a minimum, at least one headspace reading was collected from each soil sample interval, and in some of the borings, two or more readings were collected from a sample interval. The selected soil sample was placed in a sealable bag, sealed, and allowed to equilibrate for a minimum of 5 minutes before the PID/FID measurements were made of the air within the bag.

4.2.1.2 Soil Sample Analyses

Soil samples from vapor point (VP) and VMP locations were collected for petroleum hydrocarbon analyses based on ROST and field screening results and other field observations during drilling and sampling. Seventy-six (76) soil samples were collected and delivered under chain-of-custody to TEKLAB, Inc. (TEKLAB) located in Collinsville, Illinois. Soil samples were analyzed by TEKLAB for BTEX, MTBE and TPH gasoline range organics (GRO) by EPA Method 5035/8260B; TPH diesel range organics (DRO) by EPA Method 8270C; and percent moisture and total solids using ASTM Methods D2974 and 2540G, respectively.

Quality control samples collected included duplicate samples (1 in 20), rinsate samples, and trip blanks. Selected soil samples were collected, packaged, and shipped under chain-of-custody for geotechnical and chemical analyses. Seventeen (17*)* geotechnical samples were obtained from 14 soil borings and were relinquished under chain-of-custody to TEKLAB, which contracted Shively Geotechnical, Inc., located in Fairview Heights, Illinois, for analysis. Analyses included particle size analysis by ASTM D-422, moisture content by ASTM 0-221 6, unit weight by ASTM D-2937 (bulk density), specific gravity by ASTM D-854, and porosity. Porosity was calculated using soil-mass relationships.

4.2.1.3 Permanent Vapor Monitoring Probes

Permanent probes were installed at locations where vapors were most likely to be present, based on geologic conditions (as described in the CSM) and the ROST results (Figure 26). In general, the probes at the Site were nested at depths that corresponded to the permeable strata. Probe locations and installation protocols were performed in a manner consistent with the API draft procedures (API 2005) as follows:

- Short individual sampling intervals were used (for example, 6 to 12 inches).
- Color codes, tag tubing or probes at the surface were used to ensure that the sampling depth was easily identifiable for future sampling events.
- Quick-connect fittings were used to provide easy vapor-tight connections to the sampling equipment.
- Permanent probes were sealed at the ground surface (using road boxes or locked caps, for example).
- When multiple sampling intervals were installed as nested probes, groundwater sampling probes were also considered, especially if a groundwater or product plume was suspected to be present as a source for vapors.
- When using augured borings for installing soil-gas-sampling probes, the following were considered:
  - Sand-pack intervals about 1 foot in size.
  - Each sampling interval sealed with bentonite or grouted above and below the sand pack in the annulus of the boring.

4.2.1.4 Field Activities during Soil Gas Sampling

The following general activities were conducted before selecting permanent probe and monitoring locations:

- A vapor survey was conducted with a field instrument (for example, PID or FID) of all underground utilities to determine if the utilities are preferential vapor-migration pathways. Passive soil gas Gore-Sorber® samplers were also hung in areas where PID and FID readings indicated the potential for VI issues.

- Current weather conditions were recorded (for example, temperature, barometric pressure, humidity, sunny/cloudy).
- The date of the last precipitation event and the approximate rainfall depth were recorded.
- If permanent probes were installed, a photo record was made of the soil core, if collected, and several soil samples were collected for moisture content analysis.
- If the vapor or soil source was not well-defined, then soil samples were collected while installing the soil gas sampling probes at sampling intervals that corresponded to the more permeable geologic units. Samples were analyzed at the fixed-base laboratory for chemicals of concern (COCs). At select locations, samples from finer-grained units (which were of interest because they could dampen or retard upward vapor transport) were submitted to laboratories for physical properties and chemical analyses.
- Field screening was also conducted using headspace analyses of the soil samples, and qualitative indicators of contamination were noted (for example, odors and staining).
- Groundwater samples for laboratory analyses of COCs were collected at similar locations as the soil-gas-sampling locations.

4.2.1.5 Soil Vapor Monitoring Point Installation

Permanent VMPs were constructed within the soil borings following completion to total depth. Forty-two (42) borings were drilled during the third mobilization. One hundred twenty-three (123) ports were installed, with many of these nested within a single boring. A typical schematic of a nested soil vapor monitoring port installation is shown in Figure 27. The VMPs were constructed using a 6-inch long DPT system with a 0.5-inch OD and stainless steel screens connected to a 0.125-inch ID stainless steel riser tubing that extended to ground surface. At ground surface, the riser tubing was completed with a sampling cap. Annular space between the open borehole and the stainless steel screen was backfilled with a sand pack that extended from 6 inches below to 6 inches above the sample port. Bentonite pellets were placed over the sand pack and hydrated in place to act as a seal between individual nested sample ports. Hydrated grout was used close to ground surface as part of the vapor port construction. VMPs were finished at ground surface with a flush-mounted 6-inch diameter protective steel cover and grouted in place.

Vapor port screens were placed at various depths based on the CSM to sample soil vapors within the more permeable unconsolidated deposits and fill materials encountered. As many as four vapor port screens were nested within a single boring. The vertical placement of vapor ports was primarily based on geologic conditions observed while drilling, with the majority of ports constructed in unsaturated portions of the North Olive and Rand Stratums, where present, as well as in the Main Sand above the water table.

Most of the very shallow (VS) ports were installed from approximately 4.5–6 feet bgs in the VMPs completed for this mobilization. The purpose of these ports was to assess the distribution of hydrocarbons in soils at an equivalent depth and formation as typical building foundation depths within Hartford. Vapor ports were assigned a suffix abbreviation of VS for ports typically installed less than 10 feet from the ground surface, which generally consisted of either clayey overburden soils or fill materials. The S (shallow) designation was assigned to those ports generally placed between 8 feet and 19 feet of the ground surface and concentrated near or within the North Olive Stratum when present. The M (medium) designation includes those ports generally greater than 12.5 feet but less than 23.5 feet bgs and situated either in the Rand Stratum, when present, or the upper Main Sand. The D (deep) vapor ports generally extended greater than 25 feet bgs and were in almost all cases set in the unsaturated Main Sand above the water table. Color coding of tubing caps was used to differentiate VS, S, M, and D ports in the field.

4.2.1.6 Active Soil Vapor Sampling to Update the CSM

A comprehensive round of vapor sampling was conducted to update the CSM for VI after the vapor monitoring network had been augmented and the ROST efforts completed beneath Hartford. ENSR collected soil vapor samples from sampling points installed by ENSR (VPs and VMPs), Clayton (MPs), and Premcor (Praxair points [PAS]), during January and February 2005 (2005, Quarter 1). Because sample port construction differed, sample collection methods varied slightly based on sample port construction. The Praxair points were previously installed by a Premcor contractor along their pipelines located on East and West Elm streets and not as part of the HWG investigations.

Active soil vapor samples were collected from sampling points using Summa® canisters. Summa® canisters were provided by the contracted laboratory (Air Toxics, Ltd.) and were batch certified. Each canister had an initial negative pressure of approximately 30-inches of mercury. In order to collect time-integrated samples, each Summa® canister was fitted with a flow-controller and internal particulate filter assembly that allowed for collection of an approximate 30-minute sample. The sample-train assembly consisted of the Summa® media, a miniature three-way purge valve, and a short section of Teflon® sample line. After attaching the sample-train assembly to the vapor point, three well-volumes of air were removed using a 60-ml plastic syringe (for VP, VMP, and Praxair locations) or a manually operated stainless steel hand pump (for MP locations). After purging and immediately prior to sampling, each member of the two-person sampling team verified that the sample trains were configured correctly and that the purge valve was correctly set to the sampling configuration. After verification, the main valve on the Summa® canister was opened and the initial canister vacuum and sample start time was documented. Because the canister was at negative pressure, soil vapor was sampled through the flow-controller assembly and associated sample line directly into the Summa® canister at a constant rate. The actual sample flow rate was dependent upon the flow controller calibration setting and the permeability of the soils adjacent to the vapor well. At the conclusion of the sampling, a final vacuum reading was recorded. The difference between the initial and final vacuum pressure on the canister allowed the laboratory to determine the sample volume and calculate the sample dilution factor needed as part of the analytical method.

The sampling lines and associated purge valves were disposed of after each use in order to minimize the potential for cross-contamination between samples. Weather conditions were also noted during sample collection activities.

4.2.1.7 Field Screening of Soil Vapor Samples

The majority of the vapors collected from the vapor wells were also field-screened using real-time, direct readout instruments immediately following the collection of the Summa® canister sample. A battery operated or manually operated stainless steel hand pump (dependent on the permeability of the soils) was utilized to collect a sample directly from the vapor well into a 1-liter Tedlar® bag. The bag samples were screened at the ENSR site trailer for VOCs—using PID/FID—and lower explosive limit (LEL) and oxygen and the results recorded on the field data sheets.

4.2.1.8 Sub-slab Monitoring Point Installation

Sub-slab monitoring points (SSMPs) have been installed in 29 homes within Hartford in order to collect sub-slab soil vapor samples. A typical sub-slab monitoring point construction detail is shown in Figure 29. Because there is a potential for vapor release during installation, health and safety guidelines were followed. After assessing satisfactory indoor air quality in the area adjacent to the monitoring point installation, a rotary hammer drill used in conjunction with a 1.5-inch diameter bit was used to bore a hole through the sub-slab foundation. Immediately after drilling, the borehole was screened using a direct readout LEL and VOC monitor.

After determining that installation was non-hazardous, the SSMP was assembled and placed into the borehole at the desired depth (depending on thickness of the concrete). The top of the point was located at floor grade or slightly below. Filter sand was then used to fill the space surrounding the screened section of the point to at least 0.5-inches above the top of the screen. A layer of bentonite pellets was then applied immediately above the point-screen filter pack in order to provide a barrier to vertical flow of vapor in the annular space between the borehole and the monitoring point assembly. A small amount of water was used to hydrate the bentonite. A quick-drying cement was then used to seal the borehole assembly from the top of the bentonite plug to approximately half-way up the cap compression fitting. After the cement seal had solidified, a quick drying epoxy mixture was applied for the final seal.

4.2.1.9 Sub-slab Monitoring Point Vapor Sampling

ENSR collected soil vapor samples from the sub-slab monitoring points using either 1-liter or 6-liter Summa® canisters, depending on the location of the monitoring point and expected target compound concentrations. Purging the sub-slab monitoring points prior to sample collection was monitored using real-time, direct readout instruments. The instruments are connected directly to a barbed fitting that was previously attached to the monitoring point and allowed to monitor the vapor point until a stable reading was recorded. This procedure allowed for both the vapor well purging and screening to be conducted concurrently. After purging, the Summa® media was connected to the barbed fitting using a short section of dedicated Teflon® tubing. The main canister valve was then opened and the initial canister vacuum and sample start time documented on the sample data sheet. Each Summa® canister was fitted with a dedicated 30-minute or 24-hour flow controller (dependent on site accessibility) in order to allow a flow rate of no greater than 200 ml/minute.

4.2.2 Passive Soil Vapor Sampling

Shallow passive soil vapor surveys were conducted in two areas to measure the effectiveness of the passive samplers as a soil vapor screening tool. The following sections describe the passive sampling media used and the areas where they were deployed.

4.2.2.1 Passive Sample Media and Procedure

Both Gore-Sorber® and EMFlux® passive soil vapor sampling media were deployed to compare their effectiveness. Gore-Sorber® and EMFlux® Samplers were installed in either HA (hand auger) or DPT (referenced as “GP” (GeoProbe® Systems)) borings.

The Gore-Sorber® sampler consists of a chemically-inert, vapor-permeable, waterproof GORE-TEX® membrane that houses a series of engineered adsorbents. The module is approximately 6 inches long, looped on one end and coded with a unique module number. The modules are packaged in glass vials for shipment and coded with the same unique module number. The number and locations of the modules to be used along with the time and date of deployment are noted on the sample log. The module is removed from its individual glass storage vial and string or wire is affixed to the looped end of the module. The vial is kept to store the Gore-Sorber® upon retrieval. The module is lowered into a previously prepared borehole (mini-well, for example) at a set depth until the unit is in the screened interval of a mini-well. The end of the wire or string is fastened to an expandable well plug or end cap and the cap or plug is then secured on top of the mini-well. Upon retrieval, typically after two weeks, the cap is removed and the module is retrieved from the mini-well. The string or wire is removed from the module and discarded and the module is returned to its individually labeled storage vial.

The EMFlux® sampler consists of an approximately 2-inch-long glass vial with a plastic cap that is interchangeable with a screened cap for deployment. Inside each vial are four hydrophobic adsorbent cartridges and the outside of each vial is pre-wound with approximately 6 inches of steel wire. The samplers are packaged in a sampling kit that includes a container of screened sampling caps, an empty container to hold the solid storage caps during sampling, an empty container to hold the used mesh caps, and a wooden tray to hold and secure the vials and trip blanks, which are double wrapped in air tight storage bags. A similar tracking procedure is used for EMFlux® samplers as previously described for Gore-Sorber®. The date and time is first noted on the sampling log, then an EMFlux® sampler is selected and the solid storage cap is replaced with a mesh sampling cap from the sampling cap storage container. The solid cap is placed in the storage cap container to be used again upon retrieval. The sampler is inverted, and sampler and wire are lowered down the well. The unit is set at the top of the screened portion. Excess wire is affixed to the top of the mini-well.

The EMFlux® manufacturer, Beacon Environmental, recommends that aluminum foil, rolled into a ball and forced into the opening of the mini-well, be used to create a seal. Typically, the sampler is extracted from the well after approximately 48 hours. After sample extraction, the mesh sampling cap is removed, the threads are cleaned with gauze to ensure a tight seal and a solid storage cap is screwed on the vial. The mesh sampling cap is placed in the sampling cap storage container to be returned with the samples. The wire is removed and discarded. The vial is placed back in the sample tray. The location of the sample is noted on the top of the storage cap and the vial is replaced in the sampling kit.

Passive Soil Sampler Installation

ENSR performed passive sampling in Area 2 in January 2005. Because of wet field conditions, ENSR elected to postpone the Area 1 passive sampling until conditions improved; sampling was completed in February 2005. Figures 30 and 31 show the location of these two sampling areas, and the location of mini-wells for probe deployment in each area.

The shallow passive soil vapor surveys were completed to (1) measure soil vapor concentrations along profiles within residential neighborhoods where VI was a potential concern; (2) compare with active vapor sampling data collected contemporaneously with passive soil data; (3) correlate with PID/FlD response; and (4) determine if passive soil data results coincide with limits of the residual free-phase hydrocarbon plume defined in the ROST investigation.

Area 1

Area 1 passive soil samplers were deployed in mini-wells at depths of 5.5-6 feet bgs. The mini-wells were constructed using a typical hand auguring system to roughly 6 feet bgs. Mini-well construction consisted of approximately 5 feet of solid 1-inch diameter polyvinyl chloride (PVC) riser, a 12–18-inch-long PVC screen and an end cap. A sand filter pack was placed around the annulus of the mini-well from the bottom of the well to approximately 6 inches above the screened interval. Bentonite was placed around the well to prevent surface water and seepage from entering the well. This plug was approximately 2 feet thick. The remainder of the annulus was filled with filter sand to surface. The mini-wells were completed as stick-ups approximately 1.0 foot above grade. Hand auguring was completed by GRP Mechanical using a two-man crew. Soil cuttings were containerized and properly disposed. Thirteen (13) locations were completed with pairs of mini-wells for each sampler (EMFlux® and Gore-Sorber®). EMFlux® samplers were deployed on February 18 and retrieved on February 21, 2005. Gore-Sorber® samplers were deployed on February 18 and retrieved on February 25, 2005. Passive samplers were deployed for the length of time recommended by the manufacturer.

The Area 1 sampling procedures were modified after it was determined that cross-contamination was possible because a vial that had been exposed to vapors was placed into the storage container with unused vials. The procedure changes consisted of placing the sample media in a clean empty vial after retrieval. The vial used for sampling and the mesh sampling cap were both discarded. An expandable well plug was utilized to seal the mini-well instead of aluminum foil for ease of use.

Area 2

Area 2 mini-wells were constructed similar to Area 1 mini-wells, except that the mini-wells were flush-mounted at Area 2. Installation of the mini-wells was completed the weeks of January 3 and January 10. Twenty-eight (28) locations were completed. Each location consisted of two mini-wells, one for the Gore-Sorber® the other for the EMFlux® sampler. The first mini-well at each location was drilled to a depth of 12–15 feet bgs for soil classification and field screening purposes. The boring was backfilled with bentonite to a depth of 6 feet and the mini-well was constructed. The second mini-well was blind-drilled adjacent to the first to a depth of 6 feet bgs.

4.2.2.2 Passive Sewer Vapor Sampling

Passive sewer vapor sampling was conducted to assess the spatial and temporal variability of hydrocarbon vapor constituents in sanitary sewers within Hartford. Objectives for this effort were to collect data to compare to shallow passive soil vapor samplers and to evaluate potential sources and pathways for vapors in the sewers. Gore-Sorber® samplers were selected for this investigation because they could be deployed for extended periods.

Sample Media and Procedure

The module to be deployed was removed from a glass vial container. The glass vial with module number was saved for future sampler retrieval. A nylon string was affixed to the looped portion of the module. The module was lowered into the open manhole to a predetermined depth, ranging from 2 to 6 feet. The depth selection was based on the depth to the laterals tied into the sewer. The modules were hung above these laterals. The string was affixed to the inside of the manhole and the module was allowed to hang freely. The manhole cover was then replaced.

Prior to retrieval, the date and time was noted on the sampling summary. The string was removed from the inside of the open manhole and the module extracted. The string was removed from the module and discarded, and the module was repacked into its original individual glass vial. The manhole cover was then replaced.

Sample Collection

The passive sewer vapor sampling network consisted of twenty-eight (28) sewer manhole locations where passive samplers were deployed from January 2005 to May 2005. As shown on Figure 32**,** the passive sewer vapor sampling was focused on two areas within Hartford. The first area was Cherry Street north to Rand Avenue. The second area extended from East Elm Street south to East Maple Street.

A sampling event consisted of one Gore-Sorber® module deployed for an approximate 2-week period at a sewer manhole location and replaced with a new one for the next 2-week period. The first event started on January 13, 2005 with the final retrieval occurring on May 1, 2005.

A demonstration of method applicability (DMA) study was performed to identify vapor sampling technologies that would provide the most reliable analytical results given the site conditions. Head space and vapor probe measurements proved to be the most reliable. Passive soil gas methods were found to be less reliable, presumably because the large volume of hydrocarbons present in vapors tend to fill sorption sites in the samplers resulting in the underestimation of target analyte concentrations.

4.3 Dissolved Phase Plume Delineation using Direct Push Grab Groundwater Sampling

The Dissolved Phase Groundwater Investigation addressed the dissolved phase hydrocarbon constituents associated with the identified LNAPL located in the northern portion of Hartford, Illinois (Clayton 2006a). Direct push groundwater grab sampling data was collected by Clayton from 2003 through October 2005. The objectives of the investigation were to: (1) delineate the dissolved phase hydrocarbon plume adjacent to the LNAPL; (2) define areas where VI from dissolved phase hydrocarbon constituents could potentially affect residential homes or other buildings; (3) delineate the dissolved phase hydrocarbon plume in the direction of the Hartford municipal water supply wells; and (4) collect data to verify the understanding of groundwater flow near the active Hartford municipal wells.

The investigation report (Clayton 2003) proposed a network for continued groundwater monitoring to verify the understanding of groundwater flow and to enhance the understanding of the dissolved phase groundwater plume. The continuing groundwater monitoring program included the following:

- Installing a nest of piezometers south of the LNAPL plume to assess groundwater flow in the deep Main Sand and potential vertical flow gradients in the relative vicinity of the Hartford municipal wells.
- Installing nested monitoring wells at selected areas bounding the LNAPL plume to further assess groundwater quality and flow, both horizontally and vertically, in northern Hartford. These activities will also enhance the Hartford geologic and hydrogeologic databases.
- Gauging selected piezometers and monitoring wells on a quarterly basis, including the new nested piezometers and wells, to monitor groundwater flow in the more permeable units (Rand, EPA and Main Sand strata).
- Sampling and analyzing groundwater from selected monitoring wells (without LNAPL) on a quarterly basis, including the new nested wells, to monitor the dissolved phase hydrocarbon plume in Hartford.

The investigation also included in situ hydraulic conductivity testing, and investigating the previous detection of lead in the sentinel wells. Description of sentinel well program and results data is beyond the scope of this case study.

4.3.1 Direct Push Multi-level Groundwater Investigation

The groundwater investigation consisted of DPT borings advanced at select locations and was based primarily on the findings presented in Clayton (2004b). The groundwater investigation locations are presented in Figure 33. Locations were adjusted based on accessibility, clearances for utilities, and other field conditions. As shown on Figure 33, several of the borings were within the identified area of LNAPL in the Main Sand. The primary purpose of these points was to obtain data on the nature of the LNAPL at these areas using the ROST technology. However, shallow strata above the Main Sand were also sampled at these locations if groundwater was present. No groundwater samples were collected within the Main Sand at LNAPL-containing boring locations to avoid potential cross-contamination from the overlying LNAPL during advancement of sampling equipment.

Thirty-five (35) DPT multi-level groundwater sample locations were completed to determine the magnitude and extent of the dissolved phase hydrocarbons. Locations were selected within the identified dissolved phase hydrocarbon plume as they were within the previously identified dissolved phase plume extents (Clayton 2005a); these locations were intended to fill in data gaps by providing vertical delineation data. Additional DPT locations were intended to provide the magnitude and extent of the dissolved phase hydrocarbons in areas where they had not been delineated.

The type of samples collected by the multi-level sampling network depended on the findings of the subsurface investigation. Specifically, if saturated, permeable units (the North Olive, the Rand, the EPA and the Main Sand strata) were encountered but did not have a ROST response indicative of the presence of LNAPL, samples were obtained to identify dissolved phase hydrocarbons. In addition, sampling was conducted at multiple discrete depths within the Main Sand to evaluate the vertical concentration gradient of dissolved phase hydrocarbon contamination within this stratum. The initial sampling depth within the Main Sand was at the surface of the saturated zone, which was encountered at approximately 30 feet bgs. Deeper Main Sand samples were typically collected between 40 to 50 feet bgs, 50 to 60 feet bgs, and at the maximum depth achievable by the equipment. Within these general intervals, samples were collected from the more permeable or coarser-grained zones.

Sealed-screen samplers were used to collect multi-level groundwater samples. A typical sealed-screen unit consists of a short (for example, 6-inch to 3-foot) screen nested within a sealed, water-tight tool body, or can be as simple as a disposable PVC screen and casing assembly inserted into an outer casing with an expendable tip. To collect the sample, the sealed-screen sampler was advanced to the target sampling depth and the protective outer rod was retracted, exposing the screen to groundwater. Groundwater flowed through the screen under the hydraulic head conditions that existed at that depth and into the drive rods or sample chamber. O-ring seals placed between the drive tip and the tool body helped ensure that the sampler was water tight as it was driven to the target sampling interval. The integrity of the seal could often be checked by lowering an electronic water level indicator into the sampler prior to retracting the protective outer rod.

Because the screen is not exposed to the formation as the sampler is advanced into the subsurface, the screen does not become plugged or damaged. In addition, the potential for cross contamination is greatly reduced and a true depth-discrete sample that is representative of the target sampling zone can be collected.

Sample collection times in formations with low K may exceed several hours for some tools, compared to several minutes or tens of minutes in formations of high to moderate hydraulic conductivity. However, to avoid downtime, the samplers can be left in the borehole to recharge while the installing rig moves off the hole to another sampling location. To decrease sample collection time, samples can be collected from samplers with longer, 30- to 42-inch screens (for example, Geoprobe® Systems Screen Point 15) while the tool is downhole. A bailer or pump is needed to collect the sample from the target zone.

Sealed-screen samplers generally are limited to collecting one sample per advance of the sampler. Alternatively, multi-level sampling in a single borehole can be accomplished with sealed-screen samplers by retrieving the sampler and decontaminating it or replacing it with a clean sampler before reentering the hole to collect another sample. Some open-screen DPT sampling systems are designed to enable collection of multiple vertical samples in a single, continuous push. These are generally only effective for dissolved phase plume investigations, however, and are not recommended for use in media known to be contaminated with product due to decontamination challenges.

Vertical groundwater profiling was used effectively at the Site to delineate the nature and extent of the dissolved phase contamination given the high degree of geologic heterogeneity.

4.3.2 In situ Hydraulic Conductivity Testing

In situ hydraulic conductivity testing was conducted within the shallower strata overlying the Main Sand as proposed in (Clayton 2004a). The testing was conducted to estimate the K values of the formations near the well and thereby provide K ranges for the saturated units. This consisted of instantaneous head aquifer testing (slug testing) wells within the Rand and EPA Strata using a PVC slug of known volume. No conductivity testing was performed in the North Olive Stratum because groundwater in this stratum only occurs as isolated areas of perched water, often consisting of less than 1.0 linear foot of water, on the surface of the underlying B Clay Stratum. The selected wells in the Rand Stratum were chosen from areas that (1) were historically free of LNAPL, (2) typically contained sufficient water to conduct the test and (3) were within the continuously saturated portion of the stratum. Available wells in the EPA Stratum, which were limited in number, were chosen from areas that (1) also historically have been free of LNAPL and (2) were of recent construction.

The Rand Stratum slug testing was conducted on July 27 and July 28, 2005. The boring logs and well construction reports indicate the water-bearing unit screened by the wells in the Rand Stratum is confined at these locations as evidenced by the presence of the potentiometric surface at a level above the bottom of the overlying B Clay Stratum. The saturated zone is confined at the two wells screened in the EPA Stratum as indicated by the presence of the potentiometric surface at a level above the bottom of the overlying confining C Clay Stratum.

The data obtained from the hydraulic conductivity tests was downloaded into an electronic database to allow regression techniques to be applied to compute K values. The data analysis and graphic interpretations were conducted using the AquiferWIN32® software package developed by Environmental Simulations, Inc.

4.4 Analytical Methods for Soil, Air, and Groundwater

Analytical methods of many types were used during the investigation and the lists of target analytes were refined as more was learned about the site contaminants. A complete review of the analytical methods used at the Site is beyond the scope of this case study; standard EPA methods (such as those in *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* [SW-846]) were used, along with ASTM, API, and other industry sanctioned methods, in compliance with the requirements of the National Contingency Plan (NCP).

Most available analytical methods for VOC and SVOCs in soil, groundwater, and vapors use gas chromatography (GC) to separate analytes and then use a detector to identify individual compounds. Detectors for a GC include FID, flame photometric detector (FPD), PID, electron capture detector (ECD), thermal conductivity detector (TCD) and MS.

A mass spectrometer (MS) coupled with gas chromatograph (GC/MS) generally provides better identification of individual analytes in complex mixtures than other detectors that are commonly used in environmental analysis (for example, PID and FID). The specific detector or a combination of detectors used is determined by the required specificity (for example, analytes identified) and sensitivity (for example, detection limit) of the application. Enclosure 4 provides examples of the analytical reports provided for investigative activities conducted during the dissolved phase investigation and other investigations used in preparing this case study.

Air Toxics set up an on-site laboratory to provide expedited analytical results with fixed-base laboratory quality, primarily for indoor air samples expected to have high concentrations of VOCs based on screening results. The on-site laboratory was limited to conducting modified EPA Method TO-15 analysis with a shortened petroleum constituent compound list that included the following constituents: 1,3-butadiene; isopentane; hexane; benzene; toluene; ethylbenzene; m,pxylenes; o-xylene; 1,3,5-trimethylbenzene; and 1,2,4-trimethylbenzene. Some soil vapor samples were sent to the Air Toxics fixed-based laboratory in Folsom, California, to be analyzed with more definitive methods, including a GC/MS full scan, modified EPA Method TO-14A GC/FID, and for methane, oxygen, and carbon dioxide by ASTM D-1946.

The QA/QC components performed on samples analyzed at the on-site laboratory were the same as those performed at the fixed-base laboratory. Regardless of which laboratory analyzed the sample, the results were subjected to the same review and QA/QC prior to being finalized. Field duplicate soil gas samples were collected by ENSR and analyzed for QA/QC purposes. Laboratory blanks were also analyzed on an as-needed basis as determined by Air Toxics Ltd.

The lists of target analytes for the methods and sampling events were modified as the project progressed to target only those critical parameters identified as being essential to characterizing the nature and extent of contamination at the Site, to evaluate potential health risks, and to limit calibration times for instrumental analyses. Major constituents of the specific fuels at the Site, such as isopentane and other hydrocarbons, were added to the lists of target analytes as indicator compounds for explosive hazards when BTEX compounds were found in lesser amounts.

The evolution of the lists of target analytes for a site are part of a natural progression or dynamic approach that can be used to focus efforts and reduce project costs, while maintaining the critical level of information needed at a site. A complete description of the evolution of the lists of target analytes for the Site is beyond the scope of this case study, but it is important to note that the project team worked closely with regulators to agree upon reducing specific analyte lists to assure that no critical information was bypassed because of target analyte reductions. Table 2 shows the final revised list of target analytes in air that the project team is currently using for monitoring vapors at the Site.

The refinement of target analyte lists focuses project resources while assuring the reliability of results to define potential risks associated with a complex site.

4.5 Hydrocarbon Testing

The 2006 Clayton document titled "*Proposal for an Active LNAPL Recovery System*" summarized the results from a number of pilot tests conducted across the Site (Clayton 2006c). Tests were conducted to evaluate various technologies designed to remove free product from the subsurface and identify areas where free product might be amenable to removal.

The product characterization program at the Site included the following types of activities to identify areas where free product might be present and available for removal:

- Sampling and analysis for characterizing the product itself (including gasoline and diesel range organic evaluation), density, viscosity and interfacial tension.

- Product recharge evaluation via bail-down testing and recovery measurements collected as part of High Vacuum Recovery (HVR) pilot testing at the Site.
- Soil core sampling, photography and analysis for product saturation, capillary pressure, soil grain size distribution and product mobility.

This data, along with other site-specific information, was used in an API product recovery model to determine the comparative effectiveness of various product recovery techniques.

4.5.1 Product Sampling and Analysis

Clayton collected product samples from twenty-nine (29) monitoring and recovery wells at the Site in August and September 2005. Product sampling was conducted from distinct ROST signature areas and geological settings in order to identify the range of product types across the mobile product plume. Underlying groundwater samples were also obtained to evaluate interfacial tension between the groundwater and product.

The product samples were collected from wells using a clean, sealed, and dedicated PVC bailer. After collection, samples were immediately placed into new laboratory-supplied containers, labeled, placed in appropriate shipping containers, and delivered under chain-of-custody procedures to Torkelson Geochemistry, Inc. (Torkelson). The water samples were kept on ice after collection and during shipping. Torkelson completed the hydrocarbon characterization (including gasoline and diesel range evaluation) using capillary gas chromatography. Torkelson also analyzed the LNAPL samples for density and viscosity by ASTM Method D445 and API Method RP-40, and interfacial tension by DuNouy ring tensiometer using ASTM Method D971. The test results and information from these samples were used to provide input parameters for the API model.

Physical properties testing of product samples using industry accepted practices is a critical element of product removal system design.

4.5.2 Free Product Recharge Evaluation Testing

Two different types of recharge tests were used during the LNAPL characterization effort; bail-down tests and HVR testing. Bail-down tests are less expensive and easier to perform, but may have results that only are representative of conditions within or immediately adjacent to the borehole because of the slow rate of removal. HVR tests on the other hand are more costly, but they can yield results that are representative of soil conditions further away from the borehole because of the higher removal rates, particularly in very porous media. Both methods are accepted by API for evaluating free product recharge rates. The objective of the HVR and bail-down tests was to generate data to determine LNAPL production and free product recharge potential at locations throughout the plume.

4.5.2.1 Bail-down Testing Procedures

Field procedures utilized for the bail-down tests included gauging the depth to product and depth to water prior to each event, removing multiple “slugs” of product utilizing a hand bailer, and subsequently gauging the depth to product and water to measure free product recharge into each well. In general, minimal quantities of water were produced through this procedure.

4.5.2.2 High Vacuum Recovery Testing

HVR testing was used to extract LNAPL from various wells by applying a vacuum to a well via a stinger pipe set at or near the product surface. This method has advantages over other techniques. It can be operated using different configurations depending on conditions, and the well's sand pack is drained of LNAPL faster than the surrounding formation, which yields data that can be more representative of sustainable conditions. The HVR events may also reach closer to a "steady-state" condition of free product recharge into the wells than the bail-down tests (that is, the relatively longer events with larger extraction volumes minimize concern of filter pack recharge effects).

Field procedures for the HVR events involve initially gauging the depth to product and water, installing a downhole stinger into a well positioned within the LNAPL zone, sealing the well, and applying a vacuum (airflow) to extract LNAPL and vapor simultaneously. Approximately 95 percent of the HVR events exhibited some water production. The HVR events typically ran for about 8 hours, and were followed with depth-to-product and water measurements for approximately 4 to 8 hours to monitor free product recharge into the wells.

Bail-down and high vacuum product removal tests should be used to evaluate the potential productivity of product removal efforts.

4.5.3 Core Analyses

Based on the results of the LNAPL sampling, bail-down testing, and other site data evaluation, soil core locations were selected and samples were collected and analyzed to evaluate LNAPL recoverability within differing geologic and hydrogeologic settings. Soil borings were advanced at five (5) locations across the Site and soil cores were collected for LNAPL testing. Soil borings were advanced using a conventional drill rig equipped with 4.25-inch HSA and operated by Philip Environmental Services Corporation (PESC) of Columbia, Illinois. For borings where there was an adjacent ROST response at specific intervals, an attempt was made to collect soil samples at the interval of the ROST response. Samples were collected by pushing a 3-inch diameter Shelby tube. At depths where the soil borings encountered saturated sands, a piston-driven attachment was placed on the end of the Shelby tube to enhance recovery. The Shelby tubes were placed on dry ice upon completion and delivered under chain-of-custody procedures for analysis to PTS Laboratories Inc. (PTS) of Santa Fe Springs, California. As part of their analysis, PTS cut the frozen Shelby tubes, allowed them to thaw to just above 0 degrees Celsius and photographed the soil cores. The five cores were photographed under natural light to identify changes in soil lithology (color and texture) and again under ultraviolet light, which will cause petroleum hydrocarbons to fluoresce.

After review of the photographs, specific sample intervals were identified for various laboratory tests. The tests were conducted on plug samples drilled out of the core by PTS. The 1-inch diameter by 2-inch long plugs were contained and frozen after collection using liquid nitrogen. The plugs were analyzed for soil properties including density and porosity by the API Publication Method RP-40. Soil grain size particles larger than 75 micrometers (µm) (retained by the No. 200 sieve) were evaluated by sieving following the ASTM Method D422. The grain-size particles finer than 75 µm (passing the No. 200 sieve) were evaluated using a Laser Method (ASTM method D4464M) for grain size analysis.

Special core analyses consisted of soil-fluid interaction properties. Plugs from each sample were selected for special core analysis and were analyzed for water and LNAPL saturations by ASTM D2216/API Method RP-40. Air/water drainage capillary pressure curves were measured following the centrifugal technique ASTM Method D425M.

Soil cores were also analyzed for free product mobility by comparing water and LNAPL saturations before, and after, a plug was centrifuged at 1,000 times the force of gravity. This method, known as the Dean-Stark analysis (ASTM D425M), is a distillation extraction method of determining fluid saturations. The sample is weighed and the water fraction is vaporized by boiling solvent. The water is condensed and collected in a calibrated receiver. Vaporized solvent also condenses, soaks the sample, and extracts the LNAPL. The sample is oven-dried and weighed. The LNAPL content is then determined by gravimetric difference.

Initial ROST responses, in conjunction with collocated soil core analyses, can be used to develop a relationship whereby ROST responses alone can then be used to estimate oil saturation and the potential for product removal.

5.0 RESULTS OF SITE INVESTIGATIONS AND DATA INTERPRETATION EFFORTS

This section describes the results from each of the site characterization efforts and subsequent independent expert evaluations of the data. The purpose of this section is to describe how a better understanding of petroleum sites can be gained by using collaborative data sets.

The results presented in this section represent an independent interpretation of the available information for the Site. Expert witness observations provided are strictly those of the authors and in no way reflect the position of the EPA, HWG, the U.S. Department of Justice (DOJ) or any other stakeholders involved with the work being performed at the Site. To the maximum degree possible, the focus of the discussions put forth in this section are based on a compilation of existing results into a factual format.

The results presented in this section of the case study are divided into logically-related topics that environmental practitioners may find useful when dealing with similar site conditions to those found at the Site. The main subjects covered in this section include the following:

- Defining the nature and extent of a large free product plume
- Estimating the volume and types of product in the subsurface
- Defining pathways and potential exposure points
- Understanding the short- and long-term effects on soil, groundwater, and soil gas
- Understanding the timing of releases and the fate of a plume
- Predicting where product removal would be possible
- Evaluating the utility of various soil gas methods for predicting vapor intrusion issues
- Preparing a comprehensive CSM to support cleanup

Each of these elements can be important during the life cycle of an environmental project at a petroleum site. A good characterization not only improves the estimation of risk, but also the design of a streamlined remedy. Specialized analyses, such as forensic chemical analyses, can improve understanding of a site where unknown releases have occurred over time.

5.1 Product Plume Investigations and Dissolved Phase Investigation Results

The product plume and dissolved phase investigations conducted at the Site depended primarily on ROST, DPT groundwater grab sampling, and other traditional forms of data collection. The resulting data were combined with existing information to define the nature of the geologic framework and the nature and extent of petroleum contamination at the Site. The CPT data obtained concurrently with the LIF portion of the ROST create a much clearer picture of the complex stratigraphy at the Site and its effects on the distribution of hydrocarbon contamination. Physical property data from geotechnical samples also set the stage for beginning to design a remedy while exposure points where identified and immediate risks mitigated. Bail-down and HVR tests provided data on the conductivity of the product phase while aquifer pump tests and water level elevation measurements were also used to gain insight on hydraulic properties that govern the movement of the dissolved phase plume. Finally, an extensive vapor air sampling program that measured petroleum contaminants in soil gas in unsaturated geologic formations, storm sewers and immediately below the buildings themselves was critical to evolving the CSM to support cleanup efforts.

Innovative and conventional technologies were used to evolve the CSM in real-time and optimize remedial efforts such that immediate and long-term risks associated with the Site could be mitigated as quickly and efficiently as possible.

5.1.1 CPT and Soil Boring Results

The geology of the north Hartford area consists of alluvial deposits of clayey silts overlying the aerially extensive course-grained Main Sand unit. These units are interfingered in complex patterns across the Site as described in detail in the maps presented in EPA's Publication, "*Considerations for Application of the Triad at the Hartford Plume Site*" (EPA 2007, Enclosure 3) and in the many subsequent cross-sections developed by Clayton and presented in the three main ROST investigation reports mentioned earlier in this case study (Clayton 2004a, 2004b, 2005c and 2006a). The interpreted CPT results are also shown along with other information on Figures 7, 8, and 9 of this case study in the form of geologic cross-sections. The geology at the Site has a strong influence on all facets of contaminant migration; the lithologic information that can be compiled using a CPT is of a much higher density and consistency then can be generated through manual logging procedures in the field.

Detailed geologic relationships based on the CPT results are now being used to design product removal, vapor extraction, and vapor containment systems. The volume of data and the specificity of the results make a complete discussion of the results beyond the scope of this case study. Aspects of the CSM that pertain to site geology and its effect on contaminant transport are discussed in Section 5.4.3. The characterization of the geology was primarily limited by the depth of refusal, which ranged from approximately 50 to 86 feet bgs.

Some representative CPT logs and ROST printouts from the area of the Elm Street pipeline or what will be referred to as the "River Pipelines" are provided in Enclosure 5. These examples are included because they are located along a critical area of the Site where product is near the surface because of a thinning of the silty clays and the presence of a structural high in the Main Sand, which is discussed in more detail in Section 5.4. A careful review of the ROST profiles found in Enclosure 5 also suggests that the River Pipeline could have been a source of contamination because fluorescence was found to a depth near the base of the buried pipelines in at least one location (HROST-115).

The main findings of the CPT and geotechnical program discussed in the case study include, but are not limited to, the following:

- The Main Sand is highly permeable and porous.
- The Main Sand approaches the surface near the center of the product plume in the northern portion of Hartford creating a structural high in this area.
- Less porous units are generally comprised of clayey silts and silty clays that may not be impervious to fluid and vapor migration.
- Stratigraphic relationships in shallow saturated units (that is, EPA stratum) at the Site control the flow within these units and are different than those in underlying units such as the Main Sand.

These findings are essential to understand both product migration and the potential for VI at the Site.

5.1.2 ROST Results

The LIF tool portion of the ROST system can be used to estimate the total amount of LNAPL present in the subsurface. It can even be used to estimate when and if saturations are sufficient to allow the product to move freely into a well (that is, free product). Figure 33 shows the approximate extent of the undifferentiated product and dissolved phase plume across the portion of the Site beneath the northern portion of Hartford. To gain a better understanding of the distribution of product across the Site, the ROST data was used to prepare an isopach of total product thickness regardless of the type of petroleum product present at a particular location (see Figure 34).

Figure 35 was created to demonstrate how ROST responses can be used in both the saturated and unsaturated zones to delineate the relative saturation or concentrations of product in the subsurface. This figure also shows how ROST signatures can help environmental practitioners unravel the history of spills and changes in water levels at a site. A low percent response of fluorescence intensity (%RE) from the ROST indicates lower saturation in the soil matrix in either the saturated or the unsaturated zone. The ROST can be used to identify affected media below the capillary fringe where saturations are expected to be the highest. In general, the %RE is directly related to hydrocarbon saturation, provided readings are from a consistent product type and lithologic unit.

Because of the relationship between ROST response and hydrocarbon saturation, spills that have occurred when the water table was lower can be identified. The high %RE shown on Figure 34 (indicated in yellow) below the water table is a depiction of subsurface conditions that indicate that the capillary fringe was once well below where it is shown on Figure 35. A rise in the water table causes free product to migrate upward as water displaces LNAPL from the pore space. The oil saturation may increase in the zone immediately above the rising water table, but a portion of the LNAPL will remain submerged below the water table, trapped in small pore spaces (see Section 3.1.3) as residual phase LNAPL. When hydrocarbons are found 10 to 20 feet below a water table it may also suggest that the hydraulic head on the spill itself was either very large and/or the spill took place when the water table was below current levels as illustrated in Figure 35.

Historic changes in water table elevations and associated capillary fringe, as indicated by high ROST responses, were used to provide insight into the timing of prior LNAPL releases. An evaluation of historic water level measurements and evidence of LNAPL releases served as collaborative data that supported the ROST findings.

The ROST tool responses can also be used to predict when and where apparent product thickness or free product can be expected to be present. At the Hartford Site, Clayton developed qualitative %RE values for various product types that they then could correlate to the potential for free product to be present.

As shown on Figure 34, apparent product thicknesses (measured in wells screened across the water table and capillary fringe) are likely to be greater in a fine-grained unit then in a coarser-grained unit because the increase in capillary pressures between grains in the finer-grained material creates a thicker capillary fringe, resulting in greater vertical offset between the free-water surface (in a well) and the product layer that is concentrated on top of the capillary fringe (see Section 3.1.3). The ROST %RE is expected to be greatest above the top of the capillary fringe where it would be expected that hydrocarbon saturation would be the highest and there would be the highest likelihood for free product to accumulate in a well (apparent product thickness). These correlations helped the project team understand the long history of petroleum releases at the Site as is discussed in greater detail in Section 5.4.

To augment the project team's understanding of the Site, a map was created showing the composite thickness of the product smear zone using all of the available ROST %RE data. The thickness of the %RE data from available ROST push points above background was used to prepare an isopach map of product thickness at the Site (Figure 34). This map was prepared without differentiating between product types and assumed that any ROST %RE value greater then background was representative of the presence of some type of product in the subsurface at a particular location. The changes in %RE above background were not considered during this mapping exercise; values were either above or below background. The positive responses were summed and a total thickness value was calculated and plotted adjacent to that point on the site map. Isopach lines were created to show the relative thickness of ROST response across the Site.

The data plotted on Figure 34 correspond closely with historical apparent product thickness data and was very useful in understanding the history of releases at the Site and identifying potential source areas that might be amenable to product removal. ROST responses show that the thickness of the smear zone ranges up to more than 50 feet in total thickness beneath the refinery and that the plume extends from portions of the refinery to areas beneath Hartford. The portion of the plume that extends beneath Hartford appears to be thickest immediately to the northwest of the refinery property. The undifferentiated plume then extends west along Elm Street beneath the River Pipelines. Other thick portions of the plume are present beneath the main refining areas and near the terminal that connects the tank farms and the River Pipelines (see Section 5.4).

The majority of the LNAPL resides in the Main Sand underneath the northern portion of Hartford, but extends up to near the surface directly beneath the River Pipelines as can be seen through a close inspection of the ROST logs provided in Enclosure 5. LNAPL also resides to a lesser degree in the more permeable strata above the Main Sand, including the North Olive, Rand and EPA Strata.

The majority of the LNAPL in the Main Sand beneath the northern portion of Hartford has been identified as GROs. The northern and easternmost portions of the Site contain mixtures of GROs and DROs. The LNAPL in both the EPA and Rand Strata consists predominantly of DROs, though there are mixtures containing smaller amounts of GROs in the EPA Stratum. The distribution of estimated product types based on the ROST logs was mapped across the Site as part of the EPA support effort and can be found in Enclosure 3, Figure 17.

5.1.3 Dissolved Phase Groundwater Sampling Analytical Results

Clayton collected 133 groundwater samples (including 14 duplicate samples) from 39 locations at and adjacent to the Site during the dissolved phase investigation. Most of the samples were collected within the Main Sand. The groundwater analytical results varied widely beneath the product plume and in the dissolved phase portion of the plume. Examples of some of the typical concentrations of BTEX compounds beneath the product plume are shown in Table 3. The locations of these wells are shown in Figure 3. Each of these recovery wells is located in the area of the plume where significant product is present in the subsurface based on the ROST response.

Groundwater results for benzene were measured against Illinois Class I Groundwater Quality Standards (35 IAC 620) or, where not available for other BTEX compounds, Illinois Groundwater Remediation Objectives for Class I Groundwater (35 IAC 742) for comparison purposes. The dissolved phase plume does not generally extend very far beyond the estimated extent of ROST response contour (Figure 33). Presumably, the limited extent of the dissolved phase plume is because of the north to northeast groundwater flow direction within the Main Sand stratum. These generalized flow directions are the result of pumping associated with the refinery supply wells and they are regionally consistent except where interrupted by localized geologic features discussed in Section 5.4. The extent of benzene concentrations above relevant regulatory criteria was not completely defined to the northwest of the Site. If flow directions were to reverse to historical northwest flow, the extent of the dissolved phase plume could extend farther away from the current outline for the ROST response.

5.1.3.1 In situ Hydraulic Testing

The average K for the Rand Stratum wells was 4.2E-03 cm/s with a geometric mean of 1.9E-03 cm/sec. The average K and geometric mean for the EPA Stratum wells was 2.0E-04 cm/sec and 7.6E-05 cm/sec, respectively.

The K values for the North Olive Stratum ranged from 1.4E-06 to 2.9E-04 cm/sec (8.9E-05 cm/sec average) in the area of the Hartford Community Center. At this same location, K values for the clay strata ranged from 1.7E-04 to 6.0E-09 cm/sec (5.7E-05 cm/sec average). The Rand Stratum K values ranged from 5.5E-05 to 7.9E-03 cm/sec (2.8E-03 cm/sec average). In the northeastern portion of Hartford, the K values of the EPA Stratum ranged from 1.5E-05 to 3.8E-04 cm/sec (2.0E-04 cm/sec average).

The K values for the unconfined Main Sand in the central portion of Hartford ranged from 1.6E-02 to 3.1E-02 cm/sec (2.2E-02 cm/sec average). Pump tests performed at the Premcor Facility suggests K for the Main Sand is approximately 1.0E-01 to 1.0E-02 cm/sec.

Based on permeability testing and slug tests, the average K values differ by two orders of magnitude between the North Olive and Rand Strata, though there appears to be no significant difference between the North Olive Stratum and the clay strata. However, K values derived from slug testing provided results for a single stratum that can vary more than one order of magnitude. Furthermore, the analyses of these strata are limited in both number and extent. As expected, there is a significant difference between the Main Sand average K testing results and those of the overlying strata. The difference between the Main Sand and the overlying alluvial silts and clays ranges from one to three orders of magnitude. The proximity of the Main Sand to the groundwater table and its relatively high conductivities substantiates why it is the formation with the highest potential for free product removal.

5.2 Vapor Phase Investigation Results

The results of the field investigation activities related to vapors are summarized in the following sections. Results show that vapors are most prevalent in near surface soil gas beneath Hartford where the Main Sand nears the surface and the silty clay layer (that is, the "A" Clay) thins. Obviously, the presence of hydrocarbon contamination in the subsurface also plays a role in the pervasiveness of high vapor concentrations in a particular area of the Site. Tests of the capability of screening technologies like passive soil gas indicate that they are inappropriate for application at the Site primarily because of their tendency to underestimate concentration in soil. Headspace methods, on the other hand, tend to correlate well with soil gas and soil sampling results.

Soil samples collected during installation of the VMPs were field screened using a PID and an FID. Results of headspace readings were categorized based on readings less than 100 ppm, 100 to 1,000 ppm, and greater than 1,000 ppm.

The results were consistent with previous investigations conducted by ENSR and Clayton, including the distribution of affected soils defined by the ROST Investigations (Clayton 2004b). Screening results for soil samples proved to be more useful then other forms of field analyses like passive soil gas probes as is discussed in more detail in Section 5.2.5.

5.2.1 Chemical Analyses

ENSR collected 76 soil samples for fixed-base laboratory analysis during the VMP drilling. The following is a brief summary of the soil analytical results. For these results, estimated values (indicated by "J") were provided when compounds were detected below method quantitation or reporting limits.

- Benzene was detected in 69 of 76 samples at concentrations ranging from 1.0J to 245,000 micrograms per kilogram (µg/kg).
- Ethylbenzene was detected in 59 of 76 samples at concentrations ranging from 5.1J to 823,000 µg/kg.

- Toluene was detected in 68 of 76 samples at concentrations ranging from 4.8J to 1,320,000 µg/kg.
- Xylenes were detected in 67 of 76 samples at concentrations ranging from 5.1J to 1,750,000 µg/kg.
- MTBE was detected in 2 of 76 samples at concentrations of 2.2J µg/kg and 2.8J µg/kg.
- TPH-DRO was detected in 56 of 76 samples at concentrations ranging from 12.7J to 9,870 milligrams per kilogram (mg/kg).
- TPH-GRO was detected in 55 of 76 samples at concentrations ranging from 1.11J to 29,700 mg/kg.

Consistent with previous investigations, these concentration ranges in soil were indicative of the presence of LNAPL in soil pores at many locations across the Site. The concentrations in soil for compounds such as benzene are elevated well-above applicable regulatory criteria. Based on the data presented in this section, high-concentration soil source areas have affected dissolved phase groundwater and soil gas and will likely continue to affect these media indefinitely unless some type of remedy can be implemented.

5.2.2 Geotechnical Analyses

Seventeen (17) soil samples were analyzed for grain-size distribution using wet sieve analysis. Five of these samples were also analyzed for moisture content and porosity. Percent moisture in these generally fine-grained sediments ranged from 17 to 28 percent. Bulk Density ranged from 1.37 to 1.55 g/cm^3 and specific gravity ranged from 2.6 to 2.7 (ENSR 2005). Porosities were high at 41 to 49 percent and silt content was greater then 50 percent in all but one of the samples analyzed. These results are consistent with the known geologic make-up of the sediments at the Site and confirm that the migration of vapors through site soil is very likely even at good distances away from a source area.

5.2.3 Active Soil Vapor Sampling Results

Four hundred forty-six (446) active soil vapor samples were collected in January, February, and March 2005. VOC constituents were detected in the samples collected from the various strata.

Thirty-one (31) sample field duplicates were collected for QA/QC purposes, representing approximately 7 percent of the total number of samples collected. Seventeen (17) VMPs could not be sampled because they were saturated with water. At one location (VMP-76D), a sampling port was saturated with petroleum product (gasoline) (ENSR 2005, Figure 26).

5.2.3.1 Praxair Point Vapor Sampling Results

Vapor samples were collected from four Praxair vapor points located along West Elm Street. The Praxair vapor points are installed to a depth of approximately 2.0 feet bgs. Several VOC constituents were detected in samples collected from the vapor points. Benzene was detected at concentrations ranging from 0.62 parts per billion by volume (ppbv) to 260 ppbv. Isopentane was detected at concentrations ranging from less than 0.62 ppbv to 770,000 ppbv, and methane was detected at concentrations ranging from 0.0002 percent to 0.021 percent. These results demonstrated that elevated concentrations of known carcinogenic compounds like benzene were present in soil gas at the Site in concentrations above applicable regulatory threshold screening criteria. Isopentane was also identified as a primary indicator for the presence of hydrocarbons in vapors even when trace level constituents like benzene were not found at appreciable concentrations.

5.2.4 Sub-slab Soil Vapor Sampling Results

Two hundred seventy-five (275) samples were collected from SSMPs installed in homes throughout Hartford and at the Hartford Community Center. Several VOC constituents were detected in the samples collected from the SSMPs, as follows:

- Benzene was detected at concentrations ranging from less than 0.65 to 200,000 ppbv.
- Isopentane was detected at concentrations ranging from less than 2.6 to 30,000,000 ppbv.
- Methane was detected at concentrations ranging from less than 0.00013 percent to 70 percent.

The highest concentrations were predominantly observed at the Hartford Community Center. Once again, these results demonstrated that high levels of hydrocarbons and risk driving chemicals like benzene are present in vapor directly in contact with homes in Hartford.

5.2.5 Passive Soil Vapor Sampling Results

The results of the passive soil vapor sampling using EMflux® and Gore-Sorber® samplers are summarized in the ENSR technical memoranda provided in Enclosure 6, which provides a detailed analysis of the passive sampler results from the Hartford Community Center (Area 1) and their potential application to the Site. A similar memorandum for passive vapor sampling from another area located near the River Pipeline corridor (Area 2) is also presented in Enclosure 6.

Analytical results for the passive samplers are reported in units of mass as function of sorbing a known mass of contaminants from an unknown volume of soil vapor. Therefore, the contours depicted on the figures provided in Enclosure 6 of the technical memoranda do not indicate actual soil vapor concentrations. Rather, the contours provide a general indication of areas where petroleum constituents were detected in soil vapor and how those detections qualitatively relate to detections from nearby portions of the survey.

Many of the passive soil vapor samplers submitted to the fixed-base laboratory had very high concentrations of target compounds present. Because high-concentration samples often require multiple dilutions in order to quantify a particular target compound concentration accurately, it is often necessary to re-analyze (rerun) the sample at a lower dilution using a bypass apparatus. The bypass apparatus removes the lighter, high-concentration compounds from the analysis to avoid the potential for these compounds to interfere with later-eluting compounds. This procedure allows the analyses to achieve lower detection limits for the low-concentration compounds present in the samples and to report their concentration accurately.

5.2.5.1 Area 1 Results

Soil samples were collected from the soil borings that were hand-augured to install passive soil samplers in Area 1. The following sections present the field screening (headspace) and laboratory analytical results for 22 soil samples.

Soil samples collected during the hand auguring of the sampling locations were field-screened using a PID/FID. Headspace values were measured for samples collected at the 5–6 feet depth interval. PID/FID readings greater than 1,000 ppm were observed in five of 22 soil samples.

PID readings greater than 1,000 ppm were not observed in any of the hand-augured borings. PID/FID readings between 100 ppm and 1,000 ppm were observed in seven soil samples. No readings greater than 100 ppm for both the PID and FID were observed for the 22 samples collected during the Area 1 investigation (Figure 30). ENSR collected 14 subsurface soil samples during the hand auguring. A brief summary of ENSR's results include the following:

- Benzene was detected in 3 of 14 samples at concentrations ranging from 1.2 to 2,480 µg/kg.
- Ethylbenzene was detected in 4 of 14 samples at concentrations ranging from 5.5 to 485 µg/kg.
- Toluene was detected in 2 of 14 samples at concentrations ranging from 5.9 to 15 µg/kg.
- Xylenes were detected in 6 of 14 samples at concentrations ranging from 4 to 1,060 µg/kg.
- MTBE was not detected in the 14 samples collected.
- TPH-GRO was detected in 10 of 14 samples at concentrations ranging from 0.883 to 6.35 mg/kg.

The reported results for the PID/FID were consistent with those expected at the Site, confirming the utility of the PID/FID when used as a screening a tool at the Site.

Area 1 Gore-Sorber® Passive Vapor Results

ENSR collected 14 Gore-Sorber® passive soil vapor samples in Area 1. A brief summary of Gore-Sorber® analytical results follows:

- TPH was detected in the 14 samples at values ranging from 0.19 to 142.17 µg.
- Benzene was detected in 6 of 14 samples at values ranging from 0.03 to 5.92 µg.
- Ethylbenzene was detected in 4 of 14 samples at values ranging from 0.12 to 1.23 µg.
- Toluene was detected in 3 of 14 samples at values ranging from 0.03 to 0.09 µg.
- Total xylenes were detected in 6 of 14 samples at values ranging from 0.02 to 1.47 µg.
- MTBE was detected in 1 of 14 samples at a value of 0.04 µg.
- Isopentane was detected in 10 of 14 samples at values ranging from 0.02 to 29.80 µg.

Regardless of the air flux estimated in the formation, the generally low values reported from the Gore-Sorber® suggests the technology is being affected by site-specific conditions and may not be a reliable indicator of site condition.

Area 1 EMFlux® Passive Vapor Results

ENSR collected 21 EMflux® passive soil vapor samples in Area 1. A brief summary of EMFlux® analytical results follows:

- Total aliphatic hydrocarbons were detected in 10 of 21 samples at values ranging from 1.60 to 534.26 µg.
- Benzene was detected in the 21 samples at values ranging from 0.02 to 58.44 µg.
- Ethylbenzene was detected in 5 of 21 samples at values ranging from 0.02 to 1.87 µg.
- Toluene was detected in the 21 samples at values ranging from 0.02 to 2.04 µg.
- Total xylenes were detected in 10 of 21 samples at values ranging from 0.02 to 1.85 µg
- MTBE was detected in 2 of 21 samples at an equivalent value of 0.02 µg.

These reported results are also biased low relative to expected soil gas concentrations as will be discussed in more detail in the following sections.

5.2.5.2 Area 2 Results

Soil samples were collected from DPT soil borings in Area 2 for passive soil sampler installation. The following sections present the field-screening and fixed-base laboratory analytical results for 26 soil samples collected.

Headspace Screening Results

Soil samples were collected at four or five depth intervals at 26 DPT soil boring locations and screened using a PID/FID. The following paragraphs summarize these results.

PID/FID readings greater than 1,000 ppm were observed for soil samples obtained from soil boring locations GP-1 through GP-7, GP-24 and GP-26. Nine of 26 borings had PID or FID readings greater than 1,000 ppm.

Readings greater than 100 ppm for both the PID and FID were observed for soil samples obtained from boring locations GP-1, GP-2; GP-5 through GP-7, GP-24, GP-26; and GP-34.

Lower level readings (less than 100 ppm) were observed for soil samples obtained from boring locations GP-3, GP-8 through GP-11, GP-13 through GP-22 and GP-25 (Figure 31).

Chemical Analyses

ENSR collected 29 subsurface soil samples during installation of the passive soil vapor samplers in Area 2. A brief summary of sample analytical results follows:

- Benzene was detected in 21 of 29 samples at concentrations ranging from 0.8 to 55,900 µg/kg.
- Ethylbenzene was detected in 11 of 29 samples at concentrations ranging from 15.5 to 125,000 µg/kg.
- Toluene was detected in 14 of 29 samples at concentrations ranging from 3.7 to 364,000 µg/kg.
- Xylenes were detected in 20 of 29 samples at concentrations ranging from 3.9 to 535,000 µg/kg.
- MTBE was not detected in the 29 samples collected.
- TPH-GRO was detected in 11 of 29 samples at concentrations ranging from 2.32 to 8,420 mg/kg.
- TPH-DRO was detected in 7 of 29 samples at concentrations ranging from 25.4 to 4,390 mg/kg.

Area 2 Gore-Sorber® Passive Soil Vapor Results

ENSR collected 25 Gore-Sorber® passive soil vapor samples in Area 2. Analytical results for Gore-Sorber® passive vapor samples collected in Area 2 are summarized below:

- TPH was detected in 25 samples at values ranging from 0.02 to 2,967.45 µg.
- Benzene was detected in 16 of 25 samples at values ranging from 0.03 to 138.02 µg.
- Ethylbenzene was detected in 17 of 25 samples at values ranging from 0.03 to 65.25 µg.
- Toluene was detected in 14 of 25 samples at values ranging from 0.03 to 200.15 µg.
- Total xylenes were detected in 20 of 25 samples at values ranging from 0.02 to 21 7.79 µg.
- MTBE was not detected in the 25 samples collected.

Area 2 EMFlux® Passive Soil Vapor Results

ENSR collected 23 EMFlux® passive soil vapor samples in Area 2. Analytical results for EMFlux® passive vapor samples collected in Area 2 are summarized below:

- Total aliphatic hydrocarbons were detected in 22 of the 23 samples at values ranging from 1.02 to 350.76 µg.
- Benzene was detected in 11 of the 23 samples at values ranging from 0.03 to 0.71 µg.
- Ethylbenzene was detected in 20 of the 23 samples at values ranging from 0.02 to 13.49 µg.
- Toluene was detected in 22 of the 23 samples at values ranging from 0.05 to 6.70 µg.
- Total xylenes were detected in 10 of the 23 samples at values ranging from 0.03 to 140.30 µg.
- MTBE was not detected in the 23 samples.
- Isopentane was detected in 16 of the 23 samples at values ranging from 0.02 to 0.50 µg.

The disparity between the passive soil gas and the soil sampling results from Area 2 demonstrate that a significant negative bias is observed in the passive soil gas results.

5.2.6 Passive Sewer Vapor Sampling Results

Passive Gore-Sorber® samplers were installed in 28 sewer manholes within Hartford beginning in January 2005. They were retrieved and replaced at approximately 2 week intervals through April 2005. Concentrations were relatively low during this sampling effort and did not exceed the site screening criteria for any chemical constituents except TPH, which had reported concentration of less then 10 µg in all cases.

5.2.7 Soil Vapor Plume

The following sections provide further discussion and conclusions regarding the soil vapor sampling results. These sections include discussion of the distribution of soil vapors, statistical evaluations of the soil vapor analytical data set, and use of passive soil vapor samplers.

5.2.7.1 Soil Vapor Distribution

Soil vapor samples were collected by ENSR from monitoring points located throughout north Hartford during the January and February 2005 (2005, Quarter 1) sampling event. ENSR subsequently prepared maps that show the distribution of benzene, isopentane, and methane vapors within the Shallow Overburden (A Clay), North Olive Stratum, and the Main Stratum (ENSR 2005). In addition to soil vapor data, SSMP data collected from individual homes were used to develop vapor distribution maps for the shallow overburden ("A" Clay, Figure 36). Labeled sample point locations illustrated on the maps include the number of samples (shown in parentheses) for a particular location. Multiple samples at a single location are the result of nested sample points being located within the same stratum, samples being collected on multiple dates, or multiple SSMPs present in buildings. The average concentration was used if there were multiple sampling points located in the same stratum or multiple sampling dates for the same sample location. For mapping purposes, non-detect values were used at one-half the detection limit if the reported detection limit was less than 1,000 micrograms per meter cubed (µg/m^3). If the reported detection limit was greater than 1,000 µg/m^3, then the data point was not utilized to create the vapor distribution maps. The following sections discuss the distribution maps by stratum.

Shallow Overburden (“A” Clay)

Figure 36 presents the vapor distribution map for benzene in the “A” Clay, which generally occurs within the upper 10 feet across the entire Site (ENSR 2005). The depths of the 332 sampling points in this stratum ranged from 4.5 to 14.5 feet bgs. Vapor analytical results for SSMPs were also used to generate the distribution maps for the “A” Clay. SSMPs are installed at the interface of the base of the basement floor (typically a concrete slab) and the subsurface. Most range in depth from approximately 5 to 6 feet bgs and, therefore, are considered representative of vapors within the Shallow Overburden ("A” Clay).

Approximately two-thirds of the investigation area is dominated by generally low benzene concentrations (less than 100 $\mu g/m^3$). The highest benzene concentrations (approximately 1,000,000 $\mu g/m^3$) appear to be clustered within three areas of the Site. These include the Hartford Community Center area (in the northeastern portion of the Site), the area where the depth to the Main Stratum is shallowest (in the center of the Site), and along the eastern boundary of the Site (Figure 36). These data, in addition to geologic information, indicate stratigraphy controls soil vapor distribution at the Site.

The distribution of isopentane mimics that for benzene, but the concentrations are significantly higher with values ranging into the 100,000,000 $\mu g/m^3$. As with the benzene distribution, lower isopentane concentrations appear to be present around vapor extractions wells.

Methane distribution within the “A” Clay is more localized than benzene and isopentane. Soil vapor containing up to 70 percent methane was present at only a few locations that follow no apparent pattern (ENSR 2005).

North Olive Stratum

Vapor distribution maps were prepared by ENSR for benzene, isopentane and methane within the North Olive Stratum (ENSR 2005). The North Olive Stratum is a silt unit that is capped by the shallow overburden (“A” Clay). The North Olive Stratum does not occur site-wide. The results, therefore, are of less interest and are not discussed in more detail in this case study.

Main Sand

Figure 37 presents the vapor distribution maps for benzene within the Main Sand. The Main Sand occurs site-wide, is lower in stratigraphic section than the North Olive Stratum and separated from the North Olive Stratum by various clay layers. The North Olive Stratum is comprised of silt and sand that is saturated at depths of approximately 30 to 35 feet bgs across the Site. The Main Sand is limited in extent in the northern area of the Site where it is confined by greater thicknesses of overlying clay strata and is fully saturated.

Considerable unsaturated thicknesses (up to 15 feet) of the Main Sand are present within the central areas of the Site. The depth of the sampling points ranged from 12 to 34 feet bgs.

One-hundred thirty-four (134) data points were used to create the map shown on Figure 37. The data indicate that benzene concentrations within the Main Sand are very low (less than 10 µg/m3) within the “Buffer Zone” area located in the southern and southwestern portion of the Site. A sharp transition to higher benzene concentrations occurs to the north and northeast. This sharp transition closely aligns with the extent of the previously-defined, residual free-phase hydrocarbon plume (Clayton 2004b). Benzene concentrations appear to be lower in proximity to SVE wells. Isopentane distribution within the Main Sand mimics that for benzene, but with concentration sometimes several orders of magnitude higher.

The majority of the Main Sand is not affected with methane, with the exception of the eastern and northeastern Site boundaries, where methane concentrations reach levels of up to 65 percent.

Overall, the vapor investigations show that there is some attenuation from silt layers overlying the Main Sand to vapor concentrations found in the near-surface "A" Clay horizon. Concentrations are much higher at the structural high of the Main Sand near the center of the Site, where the North Olive Stratum pinches out and the overlying fine-grained layers are relatively thin. The project team will focus their efforts to augment the existing SVE system in this central area.

Using an evolving Design Stage CSM, existing SVE systems are being optimized based on integration of geologic and soil vapor distribution data.

Passive soil gas methods had limited success at the Site, as summarized in ENSR's Soil Vapor Investigation Report (2005). It is not known exactly why the performance of the passive soil gas methods was so poor compared with the active methods. It may be that relatively high concentrations of chemicals like isopentane and other petroleum constituents compete for sorption sites making it difficult for trace constituents like benzene to sorb to the passive sampler.

5.3 Product Removal Investigation Results

An API liquid product recovery model was used to determine the relative effectiveness of various mobile product recovery techniques. Input to the model included data from the CSM for product (*LNAPL Active Recovery System Conceptual Site Model Report*, (Clayton 2005c)) and the following product characterization:

- Product sampling and analysis for identifying product type (including GRO and DRO evaluation), density, viscosity and interfacial tension.
- Product recharge evaluation via bail-down testing and recovery measurements collected as part of pilot testing at the Site.
- Soil core sampling, photography and analysis for product saturation, capillary pressure, soil grain size distribution and product mobility.
- Multi-phase extraction (MPE) pilot testing by H2A Environmental, Ltd. (H2A) using an HVR system to extract product from wells.

Based on interpretation of the chromatographs, the majority of the mobile product underlying the Site consists of GRO. The northern and eastern portions of the Site also contain varying percentages of DRO. LNAPL density values ranged from 0.7335 (GRO) to 0.8528 g/mL (DRO). LNAPL viscosity ranged from 0.47 to 3.39 centipoise, with the higher viscosity values generally associated with samples containing a higher percentage of DRO. Surface tension represents the strength of the film separating two immiscible fluids or a liquid and its own vapor. The air/water surface tensions ranged from 51.0 to 68.8 dynes per centimeter (dyn/cm). The air/LNAPL surface tensions ranged from 16.0 to 24.1 dyn/cm. The LNAPL/water surface tensions ranged from 19.2 to 26.4 dyn/cm; with higher surface tensions associated with samples containing a higher percentage of DRO.

The LNAPL distribution in permeable strata is described in detail in the CSM (Clayton 2005c). Clayton has defined the lateral and vertical extent of the LNAPL at the Site using ROST methodology and observing product in monitoring wells. Residual phase LNAPL is found in all of the permeable strata covering much of northern Hartford. However, free-phase LNAPL (sufficient saturation and volume to flow into a well) is primarily limited to the Main Sand over a portion of northern Hartford.

An important concept used in interpreting LNAPL characterization data is that of soil permeability with respect to oil. In general, permeability to oil (LNAPL) is not only a function of the properties of the strata, but of the LNAPL saturation in the strata. If LNAPL is present below a minimum saturation, called the irreducible oil saturation, it is trapped as globules or droplets in the larger pores, and it will not readily move. If LNAPL saturations, therefore, are at or below the irreducible limit, permeability to oil is zero and there will be no flow of free-phase LNAPL. If LNAPL saturations exceed the irreducible limit, the permeability to oil increases. This was demonstrated at individual wells where bail-down tests were conducted and it was observed that the time of recovery was progressively slower after LNAPL had been removed from the wells multiple times, indicating lower permeability as LNAPL saturation decreased. This information is important, because it affects how recovery systems are designed; it indicates that systems and expectations need to be adjusted over time, as the limits to the recovery of free product are approached.

Different types of free-phase LNAPL recovery technology pilot tests were performed in Hartford, Illinois, during 2004 and 2005. The technologies tested included the following:

- Dual Phase Extraction (DPE)
- Dual Pump Recovery (DPR)
- Multi-Phase Extraction (MPE)
- Skimmer Pump Recovery (SPR)
- Vacuum-Enhanced Skimmer (VES) Pump Recovery
- Soil Vapor Extraction (SVE)
- Periodic Manual Removal (PMR)
- Periodic Multi-Phase Extraction (PMPE)

For purposes of designing free-phase LNAPL recovery system(s), northern Hartford was divided into three (3) areas (areas A-C), based on recovery/recharge rates and LNAPL characterization (Figure 38). The proposed active recovery system(s) will not necessarily be restricted to within these areas. The eight free-phase LNAPL remediation technologies were evaluated separately for different areas. In summary:

- The area surrounding well HMW-44 exhibited high free-phase LNAPL recovery and recharge rates relative to other areas and was designated “Area A.”
- Localized areas outside Area A exhibiting moderate liquid recovery and recharge rates were designated “Area B.” Area B was then divided into subsections B1 through B4 based on further consideration of product type or recovery rates.
- The remaining area of northern Hartford where LNAPL has exhibited poor free product recovery and recharge rates, and higher vapor than LNAPL production, was designated “Area C.”

The technologies were evaluated based on the criteria identified in the AOC (Section VI. Paragraph 53), which are protectiveness, long-term effectiveness, implementability and cost. Short-term effectiveness and effect on the community were also evaluated. MPE was chosen as the recovery technology for Area A, based on the high free-phase LNAPL recovery observed during pilot testing and the additional evaluation criteria.

MPE was also chosen as the primary recovery technology for Areas B1, B2 and B4. It was determined that MPE would more effectively remove LNAPL than SVE, because it has the capability to be optimized to varying fluid level elevations at different times and in different areas. In addition, for Area B4, MPE was chosen because a substantial portion of the LNAPL in this area is composed of DRO, which is not amenable to removal via SVE.

Area B3 is unique, because it is a relatively small area where MPE pilot testing showed moderate free-phase LNAPL recovery, but limited potential for sustained recovery for any period. Based on these considerations, only the mobile technologies were considered for Area B3. PMPE was selected as the recovery technology for Area B3 over PMR based on long-term effectiveness considerations (for example, flexibility, potentially greater radius of influence [ROI], and ability to address all phases of LNAPL).

Periodic mobile technologies were eliminated from consideration for Area C, because of the lack of long-term effectiveness over such a large area. DPE and DPR were also eliminated from consideration for Area C for implementability and other reasons. Of the remaining technologies (SVE, MPE, SPR and VES), SVE is the most efficient technology to implement since the non-sustainable free-phase LNAPL production in Area C minimizes the advantages of any of the fluid withdrawal technologies. This is supported by MPE pilot testing that indicated the majority of LNAPL is removed in the vapor-phase throughout Area C.

In summary, the conceptual design of the proposed active recovery system for Areas A, B-1, B-2 and B-4 is a stationary MPE system with a series of extraction wells spaced at approximately 60 to 100 feet. Wells will be equipped with a stinger pipe intended to withdraw primarily free-phase LNAPL. The MPE system will be designed to transfer LNAPL, water and vapors to a treatment area, where the LNAPL recovery, blower and vapor destruction systems will be located.

The proposed free-phase LNAPL recovery technology for B-3 consists of a mobile MPE unit operated periodically on a series of recovery wells located near well MP-79C.

The conceptual design for the SVE recovery technology in Area C will include the existing and expanded system, with additional SVE wells, as necessary, to provide coverage of the LNAPL plume in northern Hartford.

Identifying areas with thick zones of high oil saturation near the HMW-44 and Area A were important findings during this study that also helped the project team understand the mechanisms that controlled product distributions at the Site. As described in Section 5.4, the presence of a saturation corridor adjacent to and beneath the former refinery, coupled with regional flows in the shallow saturated EPA Sand aquifer, may explain why hydrocarbons preferentially moved from the refinery toward Hartford.

5.4 Source Areas, Pathways and Product Type

Recent activities at the Site involved developing expert opinions about the evolution of the contaminant related issues in Hartford. EPA was interested in identifying historical information concerning past use and evidence of the nature and extent of contamination through time at the Site. Professional opinions in the matter of *United States v. Apex Oil Company* were considered when preparing the basis for the following discussion. The information provided has been modified and in no way reflects the opinion of the U.S. Government. Information presented in this section was also collected for U.S. EPA Region 5 and the EPA OSRTI in support of their efforts to develop more innovative remedial strategies at sites.

The objectives in developing the expert opinions concerning the Site included, but were not limited to, the following:

- Identifying potential sources
- Delineating preferential flow pathways
- Estimating the volume of the plume
- Understanding the approximate timing of releases

In order to reach these objectives, the project team relied heavily on making maximum use of historical observations and results for wells and soil borings compared to ROST results to identify potential sources, pathways, and understanding timing of releases. The team also maximized the use of collaborative data to understand the temporal variations that could influence site conditions. The project team calculated the volume of contamination beneath the Site using the ROST information. Information concerning chemical make up of the contaminants (that is, forensics) was specifically used to estimate the period when products were released.

5.4.1 Product Type Information

During initial investigations at the Site, soil borings and chemical analysis were among the only tools available to examine the physical and chemical nature and extent of the contamination. Hydrocarbon probes were used to measure the apparent thickness of free product in wells at the Site. Data for samples from wells provided important, but limited, information on the extent of free product beneath Hartford. Likewise, these data provided only limited information on geologic conditions and the nature and extent of the amount of total petroleum hydrocarbons released during the history of operations of the refinery.

The Wood River Refinery is located directly east of Hartford and was built in 1941 by the Wood River Oil and Refining Company. It was purchased by Sinclair Oil Company in 1950 and by Clark Oil and Refining Corporation in 1967. Clark was acquired by the Apex Oil Corporation (Apex) in 1981. It was operated by Apex until 1988. The refinery assets are currently owned by the Premcor Refining Group, which was recently acquired by Valero.

The Wood River Refinery produced leaded and unleaded gasoline. Only the leaded gasoline samples from the refinery contained tetraethyl lead (TEL) (IEPA 1990). During the Apex/Clark era, the refinery used an alkylation process catalyzed by hydrofluoric acid (HF) (IEPA1990).

The Shell refinery was constructed in 1918. This facility was located east-northeast of Hartford and northeast of the Wood River Refinery site. This refinery is now owned by ConocoPhillips. The refinery has produced leaded and unleaded gasoline. The February 10, 1981 affidavit by Mr. C.R. Woodford from Shell states that during the interval of May 1977 to late 1978, Shell added tetramethyl lead (TML) to gasoline (*E-S* 1992).

The Shell refinery has historically used a sulfuric acid alkylation process to produce reformate used in its gasoline blending streams (IEPA 1990). In addition, Shell owns a former tannery facility, which is immediately east of Hartford and directly north of the Apex/Clark Refinery. The Amoco refinery was located northeast of Hartford, west of the Shell refinery. The property was operated as a refinery from 1906 to 1981 and has been used as a petroleum storage facility since then. It is now owned by BP Amoco (formerly British Petroleum). Gasoline produced at this facility was formulated using alkylate produced from a sulfuric acid catalyzed alkylation process (IEPA 1990).

The nature of refining processes used at the site was essential to documenting relative contributions to contamination from refineries surrounding the Site.

5.4.1.1 Pipelines

The Wood River Refinery and other surrounding refineries used multiple underground pipelines with routes that pass through Hartford to transport finished products, including two 10-inch pipelines that supplied the north product terminal and three 8-inch pipelines and one 3-inch pipeline used for barge loading (Figure 39). Numerous leaks occurred on these lines during the period from October 1967 to October 1988 CC Report (Clayton 2003).

The three 8-inch pipelines and one 3-inch pipeline, installed in 1944, extended from the refinery underground along Olive Street from a point 855 feet north of Watkins Street in a northerly direction to Elm Street. The lines then ran westward along the south side of Elm Street from the east side of Olive Street and continued through Hartford to the barge dock on the Mississippi River.

The two 10-inch pipelines, installed in 1952, extended underground westward from the refinery, then turned toward the northwest. The lines then ran along the east side of Olive Street from a point approximately 50 feet south of the center of Forest Street through Hartford to the south side of Rand Street. From there, the lines ran westward along the south side of Rand Street for a distance of 125 feet, where the lines then turned northward underneath Rand Street and continued to the north product terminal.

5.4.1.2 Contaminants

In a 1979 report, Mathes estimated the presence of approximately 10 million gallons of hydrocarbon product confined in sands beneath the refinery, based on apparent product thicknesses from piezometer readings at a depth of 40 to 50 feet bgs. The thickest part of this product layer was estimated as slightly northeast of the current wastewater treatment plant (Figure 40). The layer was found to encompass the northeastern corner of the wastewater treatment plant area and most of the southwestern portion of the Bulk Storage Tanks North Area. In a similar report for wells under Hartford, Mathes reported large areas with apparent product in wells ranging up to 6 feet in thickness.

A July 1987 presentation by Arthur D. Little, Inc. (ADL), identified major areas of concern at the refinery. ADL recommended correcting the surface soil contamination, which would require removing and disposing of 30 million cubic yards of soil and replacing it with compacted clay. ADL also noted that the Wood River Refinery showed losses of petroleum stock in the range of 1.4 to 1.9 percent during the years 1985 through 1987. The observation of stock losses during this period may be related to surface soil contamination observed at the refinery.

Stock losses and evidence of soil contamination are sometimes the only evidence of releases at sites that predate the implementation of a formal regulatory framework. The Resource Conservation and Recovery Act that required formalized spill recording was not implemented until the early 1980's.

A January 1988 RCRA Facility Assessment Sampling Report conducted for EPA by Jacobs Engineering Group Inc. found evidence of oil contamination in surface soil at the Apex/Clark refinery. Two on-site soil samples collected near tanks 10-6 and R-16 on November 17, 1987, were described as soil "saturated with oil" (Jacobs 1988).

Between October 2003 and May 2004, ConocoPhillips conducted a due diligence investigation that included the Wood River Refinery property. Based on visual observations documented with photography, this investigation indicated that soils across the property were contaminated with hydrocarbons at that time (MWH Americas, Inc. [MWH] 2005).

These observations indicate the presence of hydrocarbon-contaminated soils at the refinery date back to the late 1970s, if not before. The presence of contaminated soil indicates a potential source for the large plume of hydrocarbons beneath the refinery.

5.4.1.3 The Recent ROST Plume and the Plume Identified in the 1980s

Based on the information available from the several ROST investigations beneath Hartford and the Wood River Refinery, the extent of the undifferentiated hydrocarbon product plume has been estimated, as shown on Figure 34 and again on Figure 40 (Clayton 2004b, 2006a, 2006b). ROST responses are thickest beneath the refinery and range up to more than 50 feet in total thickness in the area of the wastewater treatment plant and surrounding the main refinery workings (Figure 39).

In the CC Report (Clayton 2003), apparent product thickness measurements from beneath Hartford from the Mathes 1978a investigation were provided. Historical records for the Wood River Refinery also contained apparent product thickness data from beneath the refinery (Mathes 1979). The data from both of these Mathes investigations was combined and then plotted on Figure 40. Based on this map, it appears a majority of the contamination that registered during the ROST investigation was also present during the late 1970s.

In 1978 and 1979, Apex/Clark installed two product recovery wells in Hartford. The first well (RW-1) is located east of Delmar Avenue at Forest Street. The second well (RW-2) is located west of Olive Street, between Date and Cherry Streets. Clayton asserts that these wells were operated from 1978 to 1990, removing more than 1.1 million gallons of product. Between 1994 and 2002, Clayton asserts that an additional 82,700 gallons of product had been recovered from these wells and from a third well (RW-3) located south of Birch Street (Figure 39) between Market and Olive Streets (Clayton 2004a). Since these early efforts, some additional product removal efforts have been conducted across Hartford and in the refinery resulting in the removal of an additional million or more gallons of product as detailed in Section 2.2.7 of this case study.

Figure 41 shows a similar plot with a recent map showing apparent product thicknesses that were present at the Site in February 2005. The map shows the extent of the apparent product thicknesses across the Site, which had diminished, but a distinct area still existed at this point in time between the refinery and Hartford. This area of higher hydrocarbon saturations, and thus apparent product thickness, is significant in that it demonstrates that a "hydrocarbon conductivity corridor" appears to exist, defined by greater hydrocarbon saturations. This corridor begins near the refinery's treatment ponds and extends northwest toward Hartford. The corridor appears to have existed from the 1970s to present day, providing a pathway for persistent hydrocarbon contaminant migration between the refinery and Hartford.

The potential for hydrocarbon mobility and the presence of preferential pathways is influenced by the degree and thickness of oil saturation.

Based on these observations, it can be concluded that the majority of contamination observed at the Site using the ROST data was likely to have been present prior to 1978. Hydrocarbon saturation in soil has also likely decreased over time as more pumping and product removal has occurred. The rise and fall of groundwater beneath the Site has also likely decreased the mobility of the product present beneath the Site (API 2004).

Figure 42 shows the hydrocarbon conductivity corridor that was mapped by Clayton and described in the LNAPL CSM report (Clayton 2005c). On top of this colored corridor, historical groundwater piezometric data collected by *E-S* (1992) were plotted. This data were used to demonstrate the potential for groundwater to enhance movement of spills between Hartford and the refinery. As more detailed information was obtained, it became obvious that the data collected by *E-S* could be in error because of the way in which wells were completed across the Main and the EPA stratums.

Figure 43, however, confirms that the uppermost part of the water table, which is present in the EPA stratum beneath the refinery, does indeed flow from the refinery toward Hartford. Regardless of the problems discovered with the *E-S* data from the 1992 report, flow in the EPA stratum beneath the refinery has likely almost always enhanced movement of spills toward Hartford.

As can be seen in Figure 43, a structural feature or hydrogeologic divide is present in the EPA stratum with flow going to the west and east. The groundwater divide parallels the river in the EPA stratum and runs north south above the wastewater treatment plant on the Shell tannery property. Water on the west side of this structural feature has likely flowed in the direction of Hartford ever since the EPA stratum became saturated. Spills on the west side of this divide would tend to move west toward Hartford following the flow direction of first water encountered.

5.4.2 Estimation of Volume of Petroleum Product from ROST Data

As mentioned in Section 5.4.1.2, early estimates by Mathes suggested that at least 10 million gallons of product was present beneath the refinery. Using core data, geologic information, and the ROST data, it is possible to check these estimates with some degree of certainty. The following section describes how such an estimate was developed for the Site. The estimation technique is based on logs generated from ROST responses, in combination with physical analyses of soil cores. As an example of part of this process, data for five core holes (HCSB-1 through HCSB-5) recently drilled as part of the LNAPL removal study (Clayton 2006c) were used to estimate physical quantities.

The first part of estimating the volume of hydrocarbon present is to review the ROST logs and measure the thickness of all intervals on each log where percent fluorescence exceeded 5 percent, based on a review of the site-specific available ROST data logs. The thicknesses were then plotted on a map and isopleths lines drawn, as shown on Figure 34. The ROST cannot detect the relatively low concentrations of dissolved-phase hydrocarbons and therefore measures only free product and residual phase hydrocarbons.

The volume estimation process requires estimates of porosity and percent LNAPL saturation (percentage of pore space filled with LNAPL). The physical analyses of core hole samples (Appendix C: Clayton 2006c) contain information on parameters such as total porosity, air-filled porosity, percent water saturation, and percent LNAPL saturation, which could be used to select parameters to estimate volumes of hydrocarbon in the subsurface. These samples were analyzed using API Method RP-40. Core plugs were also submitted to a laboratory for LNAPL saturation as determined by the Dean-Stark analysis. The Dean-Stark analysis generally yielded higher values of LNAPL saturation than did API RP-40. However, Dean-Stark analyses were conducted only on samples from two of the five boreholes. Therefore, the average values of porosity and saturation used in the calculations shown in Table 4 were from the API RP-40 results. Enclosure 7 provides additional calculations used during this estimation process.

Table 4 provides average values for porosity and LNAPL saturation developed from the API RP-40 data provided in Enclosure 7. The Main Sand and the EPA Sand exhibited a marked decrease in porosity from the geologic units above them, so the total porosity was calculated for these two units separately from the upper formations to better characterize the geology in the plume area. However, all values were averaged together to develop an “undifferentiated” number that could be used in a volume calculation. In the same manner, average saturation values were developed separately for the vadose zone and the saturated zone, and values from both zones were averaged together to get a single undifferentiated value that could be used in a volume calculation. Undifferentiated values are easier to use in the calculation and bias results low.

The thickness of hydrocarbon total product was measured through the review of individual ROST logs and the data used to prepare the contour intervals shown on Figure 34. These were digitized using geographic information system (GIS) software, and the area within each interval calculated. The area within each contour interval was then multiplied by (1) the average thickness of the interval, (2) the estimated total porosity of the interval, and (3) the estimated LNAPL saturation to calculate the estimated volume of product within each contour interval. The sum of the volumes for each contour interval was then used to estimate of the total volume of hydrocarbon product for the given subsurface region (beneath Hartford or beneath the Wood River Refinery).

The conservative totals for the estimated volume of product beneath the Site were less than 8 million gallons as of 2006. Considering the conservative (biased low) nature of the porosity and saturation values used in these calculations, volume estimates could be off by a factor of two or more. Oil saturations in the presence of free product in wells are anticipated to be up to 30 or more percent compared to the values of less then 10 used in this calculation.

Data from direct sensing tools such as ROST can be used to estimate the total volume (free-phase and residual) of hydrocarbons at a site.

5.4.3 Geologic and Hydrogeologic Pathways

This section examines the preferential geologic, hydrogeologic, and oil saturation induced pathways that have contributed to migration of portions of the hydrocarbon plume beneath the Wood River Refinery to beneath portions of Hartford. These pathways have existed through time; the likelihood of migration through these pathways has been enhanced by a long history of releases that occurred during operation of the refinery. The subsequent rise in water levels during the later portions of the 1980s may have further enhanced the tendency of free product to move from portions of the refinery to portions of Hartford. Flow directions in the EPA Sand that trend from the refinery to Hartford may also influence the movement of hydrocarbons from the refinery toward Hartford.

Examining the boring logs from the Clayton refinery investigation (Clayton 2006b) indicates that minor amounts of gravel fill at the surface overlay native silty clay (the “A” clay, as it is referred to by Clayton). The “A” Clay grades to clayey silt at approximately 10 feet bgs, commonly referred to as the North Olive Stratum. Beneath this clayey silt is another silty clay that Clayton termed the “B/C” clay. At 25 feet, a fine sand unit with a trace of silt is encountered. Clayton has termed this unit the EPA Sand. The EPA Sand is separated from the top of the Main Sand by a very thin clay termed the “D” clay (Figure 44). Cross-sections shown on Figure 44 were drawn along an approximately east to northwest section line. These cross-sections show the Site stratigraphy and the hypothesized effects of changes in water levels at the site between 1960 and 1990 on the subsurface migration of free product.

The Main Sand is characterized by the presence of gravel and coarse sand, indicating that it consists mostly of sand deposited during the end of the Pleistocene glacial extension. As the glaciers melted and large volumes of water filled the Mississippi River flood plain, blanket sands such as the Main Sand were created because of the tremendous flows of the river.

Based on this review of the stratigraphy, it is apparent that there are limited barriers to the downward migration of hydrocarbons in the area of the wastewater treatment plant (Figure 44). Silty clays found in the geologic sequence beneath the Site, while less permeable, have insufficient density to act as a complete barrier to downward migration of product. The coarse sand and gravel at the base of the sequence are ideal conduits for the transmission of contaminants from the refinery to beneath Hartford.

The cross-sections shown in Figure 44 were developed by combining the information from the Clayton 2004 ROST investigation report with the information from the ROST Site Wide Investigation (Clayton 2006b). These cross-sections show the stratigraphy across the boundary between the refinery and Hartford, starting from the wastewater treatment plant and running northwest under Hartford up along the hydrocarbon conductivity corridor beneath Hartford identified by Clayton (Clayton 2005c).

Examination of cross section A-A’ on Figure 44 shows how the EPA Sand intersects the Main Sand beneath Hartford. A structural high in this area, extending across Hartford in the combined Main and EPA sands, represents a structural trap—the highest elevation of the sand body. This feature becomes a trap when the rising water table forces the mobile and potentially-mobile product into a smaller and smaller volume of permeable sand.

In many ways, it can be thought of as the “freeboard” in a tank, the empty volume above the fluid surface. Except in this case, the freeboard may be exceeded, exerting pressure on the hydrocarbon-rich upper surface of the saturated zone. This pressure can have two important effects. First, it can drive rapid lateral movement of free-phase LNAPL in the permeable formation’s up-structure direction. The up-structure direction of the combined Main/EPA Sand is to the northwest, under Hartford. Second, the hydraulic pressure can cause LNAPL that is immobile under hydrostatic pressures to become mobile; in other words, it can overcome capillary forces that keep small ganglia separate and re-form larger hydrocarbon stringers that are more mobile. Together, these phenomena act to squeeze the free-phase LNAPL upward and forward along the formation contact, at least until it reaches the maximum elevation of the formation—the stratigraphic trap. This process is likely to result in a net northeastward movement of free-phase LNAPL toward the stratigraphic trap, where it may provide an increased source of hydrocarbon vapors in a very localized area, primarily during high water stands, when the “freeboard” in the Main Sand is squeezed.

This phenomenon may be expressed as areas of high LNAPL saturation, particularly if the highest concentrations follow the uppermost contact of the combined EPA/Main Sand (in plan view) and are concentrated along the contact between the sand and overlying clay. In fact, a suite of physical parameters collected at five borings in Hartford, which included air-filled porosity, water saturation, LNAPL saturation and total saturation, indicated product was likely concentrated between 31 and 32 feet at four of the borings. The significance of this depth interval is that it is immediately above the water table (in 2004) and within a few feet of the upper contact of the Main/EPA Sand at the four locations. Thus, a one- to two-foot rise in the water table at these four locations will likely squeeze the LNAPL-saturated layer. Potential consequences include enhanced lateral mobility as ganglia become connected and driven along the clay contact, and possibly enhanced vapor transport as the small portion of the unsaturated zone (within the permeable deposit) begins to close.

This structural high can be seen on Figure 42 and can be seen on maps provided in the 1992 *E-S* and 2004 EPA reports. This structural high extends from the refinery beneath the wastewater treatment area to beneath the central portion of Elm Street, where it crosses through the center of Hartford. Hydrocarbons naturally migrate upward into structural high spots (traps) because they are less dense than water. Sometimes they can even migrate in the opposite direction of groundwater flow or cross-gradient because of the strength of the gravitational forces at work.

The Rand Stratum merges with the Main Sand along this structural high as shown in Figures 3 and 10 of the 2006 EPA report (Enclosure 3). This stratigraphic relationship beneath Hartford, shown in block diagram areas 3 and 4 in Figure 4, taken from the 2006 EPA report, allows free product and vapors from beneath Hartford to migrate into the near surface where they affect vapors in the “A” clay as shown in Figure 36. From high in the stratigraphic column, vapors have the highest probability of creating indoor air or VI issues.

5.4.3.1 Hydrogeologic Pathways

Piezometric surface maps created by the USGS and Illinois State Geological Survey from the 1950s through the 1970s are regional in scale and do not differentiate piezometric gradients for either the deep aquifer or shallow aquifers. Nonetheless, the majority of the maps show the prevailing general piezometric surface gradient to be oriented east-northeast through Hartford toward a piezometric surface low located almost due east of Hartford (Mathes 1978a). A noticeable variation occurs on the 1971 piezometric surface map from Mathes (1978a), where piezometric gradients in the Hartford region are directed almost due north through Hartford toward a piezometric low located due north of Hartford. This change in piezometric flow gradients from 1966 to 1971 was most likely caused by the installation and continued pumping of water wells on the Shell or Amoco Oil refinery property located north of Hartford (Mathes 1978a).

Only one piezometric surface map is available for the years 1972 to 1990. It shows the localized flow directions beneath Hartford in May 1978 to be northeasterly, toward the Shell and Amoco water production facility (Mathes 1978a). The lack of piezometric surface maps during the 1980s is significant, because groundwater and contaminant extraction wells were installed in the northeastern corner of Hartford, changing the localized piezometric gradients beneath Hartford. Three general piezometric flow directions are apparent from the piezometric flow gradient map of Geraghty & Miller for July 16–20, 1990 (*E-S* 1992) for the Main Sand:

- From the south to the north and northeast
- General flow directions from the west to the northeast through Hartford
- Localized flow directions from the east (under the Apex/Clark refinery) are directed west and northwest under Hartford

The seven figures showing piezometric surface contours under the Wood River Refinery prepared by Rust Environment and Infrastructure (RUST E&I) (from Clayton 2004a) for 1995 and 1996 show a piezometric low on the refinery property for June 1995, October 1995, February 1996, January 1996, and June 1996, which is probably associated with refinery on-site pumping and groundwater removal. During the same time, figures from RUST E&I show piezometric contours from October 1995 and November 1995 that indicate flow beneath the refinery toward the west and northwest under Hartford. Recent maps produced by Clayton of the hydraulic gradient in the EPA stratum (Figure 43) confirm that flow direction in this stratum is from the refinery toward Hartford.

The flow in the EPA stratum, along with the preferential oil saturation corridors described in the previous section, has promoted the movement of hydrocarbons from the refinery to beneath Hartford. From there, increases in the water table elevation may have resulted in continued migration of contamination up-structure and cross-gradient to beneath the central portions of Hartford.

The piezometric surface was relatively low during the early years of operation of the Wood River Refinery, a condition that persisted into the late 1970s, as depicted in the cross section from the early Apex/Clark era in Figure 44. As groundwater levels rose in the area, contamination was driven from the refinery up along geologic flow paths, the structural high in the Main stratum. The hydrograph on Figure 10 shows a trend of drought conditions for the period January 1961 to November 1978. During this time, the average elevation of the water table was between 385 and 390 feet above mean sea level (msl). The relief from drought in the Hartford area during the late 1970s increased the water table for the period of 1978 to 1991 to an average of 400 feet above msl.

The low stand in groundwater is well-documented over the Apex/Clark era and has played a significant role in the vertical movement of contamination to depth beneath the refinery; specifically, a large volume of LNAPL was able to penetrate to the Main Sand because the water table was down in the Main Sand. Once the contamination reached the Main Sand, the subsequent rise in water level has driven contamination up the structural high to the top of the Main Sand. Changes of water levels over the long history of spills at the Site have continued to spread the contamination in a smear zone, exacerbating VI issues across Hartford.

5.4.4 Product Type

As part of on-going evaluations of the nature and extent of contamination, available chemistry data and forensics information was compiled for the Site to corroborate the hypothesis about when most of the product releases occurred. The following sections present the basic chemistry, forensic information and techniques used to draw conclusions about the Site.

5.4.4.1 Historical Information

In 1978, the IEPA conducted a characterization of the alkyl lead compounds in gasoline samples from the Wood River (Apex/Clark), Amoco and Shell refineries and in product samples from the then existing monitoring wells (EPA 1-10 and Shell 1 and 2) in and near Hartford. Three of these wells, which contained free product, had only TEL as an additive (Mathes 1978a). Gasoline samples from Clark Oil contained TEL; samples from Shell and Amoco contained mixed alkyl leads.

Early in 1979, Clark Oil and Refining retained a professor at Purdue University to determine whether traces of unique compounds produced from H_2S0_4-catalyzed alkylation were present in the Shell-2 monitoring well. The gasoline sample from Shell-2 was composed exclusively of compounds indicative of HF alkylation, further indicative of the Clark Oil refining process (Nicholson 2006). The IEPA conducted additional product characterizations in 1990. Free product was collected and analyzed from three wells under Hartford, a well at Shell's 1989 spill site at Rand Avenue, a well on Shell's tannery property east of Hartford, and an out of service portion of the ARCO/Sinclair pipeline. The three samples from under Hartford were determined to be regular leaded gasoline with TEL as the only lead additive. The sample from Shell's 1989 spill site was determined to be unleaded gasoline. The sample from Shell's Tannery property was determined to be leaded gasoline, but dissimilar from the leaded gasoline found under Hartford. The sample from ARCO/Sinclair's pipeline was also unleaded gasoline but different from the sample from Shell's spill site. In addition, evidence was found that the gasoline under Hartford had a signature compatible with the HF alkylation process used at the Wood River Refinery when operated by Apex/Clark (IEPA 1990).

5.4.4.2 Description of Forensic Tools and Site Data

Several forensic tools were used in hydrocarbon forensic investigations conducted at the Hartford Site in this report, including the following:

- Gas chromatography
- PIANO (paraffins, isoparaffins, aromatics, napthenes, and olefins) analyses
- Gasoline additives
- Alkylate ratios

The principles behind applying each parameter are briefly described below.

Gas Chromatography

Gas chromatograms depict compounds in the order in which they elute from the chromatographic column, which depends on the molecular weight of the compound. The first compounds that elute from the column are predominantly gasoline range (C4 to C12), and later peaks are characteristic of diesel (C9 to C22) and heavy products (C14 to C36) such as bunker fuel, lube and furnace oils. Gas chromatography is commonly used to identify different types of products (for example, gasoline or diesel) by their hydrocarbon composition, but can also be used as a tracer of a particular release.

The general shape of gas chromatograms are used here to determine the general composition of hydrocarbons underneath Hartford and as a diagnostic tool in distinguishing between hydrocarbon products. Detailed analysis and comparison to standards by analytical laboratories allows them to determine specific concentrations of compounds contained in free product.

PIANO Analyses

Analyses of PIANO constituents can differentiate unprocessed materials and different refined products from each other and those from different sources. PIANO constituents comprise the major hydrocarbon classes within the gasoline range, generally from C3 to C12. The natural distribution of these components differs in crude oils from different sources and is also altered during refining. Gasolines can have different octane ratings, which are dependent on composition. In general, the higher the relative content of isooctane and aromatics, the higher the octane rating of the fuel. Olefins are diagnostic of cracked refined products. PIANO analyses were used to delineate the general composition of free product in Hartford area.

Alkylate Ratios

The alkylation process was developed in the late 1930s to improve the octane content of aviation gasoline. In this process, olefinic compounds are joined with iso-butane to produce higher molecular weight compounds with higher octane ratings. Propylene, butylenes and pentanes are the olefinic feedstock. Butylene is preferred, because it produces the highest percentage of high octane compounds. The product of the alkylation reaction consists mostly of a mix of trimethylpentanes (TMP) and dimethylhexanes.

In the refining industry, the alkylation reaction is catalyzed by either HF or H_2S0_4. The type of acid used results in different ratios of TMP isomers in the alkylate product. Therefore, the relative distribution of TMP ratios is indicative of the source of the product that contains alkylate where there are different alkylation processes being used.

Gasoline Additives

Identifying gasoline additives is a useful forensic tool, because several different additives have been used, often for specific time intervals. Gasoline additives can thus be used to distinguish between different sources and for the age dating of releases. Gasoline additives have been used commercially in the United States since 1923 to enhance performance or to solve engine operation problems. The most useful for forensics include the organic lead compounds—for example, TEL, methyl tetraethyl lead (MTEL) and lead scavengers, methylcyclopentenadienyl manganese tricarbonyl (MMT), tert-butyl alcohol (TBA) and the oxygenates MTBE, ethyl-tert-butyl ether (ETBE), and tert amyl methyl ether (TAME).

TEL was the first widely-accepted gasoline additive for reducing noisy combustion in automobile engines, commonly referred to as "knocking." TEL, developed as an anti-knock agent in December 1921 by General Motors Research Corporation (GM), was first marketed by GM in 1923 in Dayton, Ohio (EPA 1985). The Ethyl Corporation, then a subsidiary of General Motors, was formed in 1924 to bring TEL to the mass market (Kovarik 1999) TEL remained the only lead additive widely used in the U.S. until 1960, when Standard Oil Company (later Chevron) introduced TML. TEL and TML were used in combination with each other and with other lead alkyls including tetramethylethyl lead (TMEL), dimethyl diethyl lead (DMDEL), and MTEL. After 1980, TEL was again the only typical alkyl lead additive (Morrison 2000). TEL was blended with gasoline at concentrations of 1.5 to 1.8 grams per gallon (g/gal) prior to 1985 (Morrison 2000).

Because alkyl leads cause lead oxide to form in automobile engines, and lead oxide erodes spark plugs and burn exhaust valves, the lead scavengers ethylene dibromide (EDB) and ethylene dichloride (EDC) were added to gasoline beginning in 1928 (Zymax 2006). Health concerns related to lead emissions from gasoline engine resulted in a gradual phase out of leaded gasolines. Up to 1959, the maximum lead concentration was 3.17 g/gal; in 1959, the maximum was increased to 4.23 g/gal (Gibbs 1990).

In 1973, EPA issued a requirement that lead concentrations in "leaded" gasoline be reduced from 2-3 g/gal to 0.1 g/gal by 1986. Initially, on January 1978 the average lead concentration for leaded and unleaded gasoline combined was set at 0.8 g/gal for large refiners and 2.65 g/gal for independent small refiners with a production capacity of less than 50,000 barrels per day. Average limits of 0.8 g/gal became effective October 1, 1979, and then lowered to 0.5 g/gal on October 1, 1980 (Gibbs 1990). An average maximum for leaded gasolines of 1.1 g/gal came into effect November 1, 1982 (Gibbs 1990).

On July 1, 1983, a maximum average limit for leaded and unleaded gasolines combined became effective for all refineries, regardless of size. This limit phased down to 0.5 g/gal on July 1, 1985 and finally to 0.1 g/gal on January 1, 1986. The 0.1 limit was not reached until 1988, because refiners could buy and sell lead credits from November 1 to January 1, 1985, and bank, buy and sell lead credits from January 1, 1985 to January 1, 1986 (Gibbs 1990). Lead additives in motor vehicle gasoline were not completely prohibited until January 1, 1996 (EPA 1996). The use of EDB and EDC in gasoline decreased in tandem with that of leaded gasoline.

Unleaded gasolines appeared on a large scale in the early 1970s, hastened by the introduction of catalytic converters in late 1974. Catalytic converters contain platinum group metals that are inactivated by lead.

Until recently, MTBE was the most commonly used oxygenate in the United States as an octane booster for unleaded gasolines. ARCO obtained EPA approval to add up to 7 percent MTBE to unleaded gasoline in 1979, increasing to 11 percent in 1981 and then to 15 percent in 1988 (Gibbs 1990). Between 1979 and the mid-1980s, MTBE was most commonly used in the eastern states.

The use of MTBE further increased due to the 1990 Clean Air Act (CAA) amendments, which required the use of oxygenated fuels (also known as reformulated gasoline) to attain clean air standards. As a result of the amendments, the use of MTBE increased in areas where carbon monoxide or ozone standards were not met. These requirements became effective in November 1992 for carbon monoxide non-attainment areas, and in January 1995 for ozone non-attainment areas. Although MTBE is by far the most commonly used oxygenate in the United States, several other chemicals have also been used. Other oxygenates that are useful for forensic characterization include ETBE, TAME, and disisopropyl ether (DIPE). MTBE and other oxygenates have also been used to enhance octane in gasoline.

5.4.4.3 Forensic Data Evaluated

This report considers the historic forensic data for free product samples as well as more recent data. The data were obtained from various sources as described below. The historic data used in this report are taken from the 1990 IEPA report (IEPA 1990), a report by Perry Polss of DuPont (Polss 1978) and various notes and memos originating from Clark Oil personnel with product formulation analyses results. Newer data consist of data in a due-diligence study by ConocoPhillips in 2004, and data collected by Premcor in 2003 and 2005. The data from Premcor include analyses for product under Hartford as well as under the Wood River Refinery site.

5.4.4.4 Results of Forensic Analyses

The product present beneath Hartford was determined to be primarily leaded gasoline because it has an octane rating of greater the 80 (Mathes 1978a, Unknown 1983), and the product contained approximately 1 g/gal of lead (Nicholson 2006). Gas chromatographs of product from under Hartford are similar to gas chromatographs of gasoline (Figure 45), with the highest concentrations of compounds in the C_5 to C_8 carbon range, and a distinct compositional cutoff at approximately C_{12} (Premcor 2003 and 2005). The PIANO analyses of product from Hartford resemble those of reference gasolines (Figure 46) with elevated levels of aromatics and paraffin compounds and lower levels of olefin and naphtha compounds (Premcor 2003and 2005).

The total lead concentration of the product under Hartford is consistent with the gasoline formulation history at the Wood River Refinery during the period from 1960 to 1988. Total lead in free product floating on groundwater within Hartford is 1 g/gal, with many samples being higher (up to 2 g/gal) Temporal data suggests that free product lead concentrations have remained relatively constant within Hartford from 1978 to 2005 (Premcor 2003 and 2005).

The average lead concentration of gasoline produced by the Wood River Refinery between 1976 and October 1979 was between 1 and 2.6 g/gal lead. During 1980 and through 1981, the average lead concentration of gasoline produced dropped to levels averaging less than 0.6 g/gal, and never rising above 1 g/gal. Lead in gasoline likely fell further until 1986, when it was phased out.

The organo-lead additive speciation of the product under Hartford is consistent with the gasoline formulation history at the Wood River Refinery during the period from 1960 to 1988. The primary form of lead in free product is TEL, with TEL comprising more than 90 percent of all organo-lead forms in free product within Hartford (Premcor 2003 and 2005). No significant amounts of TML were detected in free product from Hartford. Product samples collected on the Wood River Refinery site are composed of at least 90 percent TEL. TML was only detected in two samples at levels less than 0.1 percent.

The alkylate concentration of the product under Hartford is consistent with the gasoline formulation history at the Wood River Refinery. Product samples from under Hartford contain alkylate with a TMP composition characteristic of an HF catalyzed process, which was used at the Wood River Refinery.

Free product found in Hartford is in part derived from gasoline manufactured at the Wood River Refinery. This observation is based on all of the before-mentioned information, but principally the fact that the product is primarily leaded gasoline with lead levels consistent with available product information. TMP ratios indicate that the product contains alkylate from an HF-catalyzed process.

Product fingerprinting techniques, used in conjunction with an understanding of the history and variability in fuel formulations, processes and additives, can be used to establish the timing of releases.

6.0 CONCLUSIONS AND SUMMARY

The work performed at the Site is an example of the types of activities and approaches that are needed at the larger refinery sites across the United States that have had a long history of product generation. The project depended heavily on the use of historical information, collaborative data sets that combined real-time analytical tools with rigorous laboratory analyses, dynamic work strategies, and an evolving CSM to expedite reaching project milestones.

Innovative technologies such as the ROST and other standard methods (Enclosure 4) and practices were used collaboratively in order to create a consensus model upon which the SVE system and product removal systems could be designed. Fortunately, because of the siliceous nature of the sediments beneath Hartford, very few interferences where encountered while applying the ROST tool at the Site. Detailed definition of the extensive plume was used to optimize many sampling and analyses efforts conducted to support the VI evaluations throughout Hartford.

A dynamic "learn as you go" work strategy was applied during the many investigative activities, which improved the efficiency of the site characterization, resulting in an estimated 30 percent cost avoidance at the time of this research.

The ROST data in combination the many other forms of information made it possible for the project team to achieve the following goals:

- Define the nature and extent of a large free product plume
- Estimate the volume and types of product in the subsurface
- Define pathways and potential exposure points
- Understand the short- and long-term effects on soil, groundwater, and soil gas
- Understand the timing of releases and the fate of the plume
- Predict where product removal would be possible
- Evaluate the utility of various soil gas methods for predicting vapor intrusion issues
- Prepare a comprehensive CSM to support cleanup.

Innovative technologies used to collect high-density, collaborative data enabled expedited optimization of the existing SVE system and design of product removal systems, resulting in an estimated 30 percent cost avoidance.

Define the Nature and Extent of a Large Free Product Plume

The LIF tool portion of the ROST system can be used to estimate the total amount of hydrocarbons present in the subsurface. It can even be used to estimate when and if saturations are sufficient to allow the product to move freely into a well (that is, free product). Figure 33 shows the approximate extent of the undifferentiated product and dissolved phase plume across the portion of the Site beneath the northern portion of Hartford. To gain a better understanding of the distribution of product across the Site the ROST data was used to prepare an isopach of total product thickness regardless of the type of product present at a particular location. The silicic nature of the sediments and the range of product types (that is, primarily GRO and DRO) made the ROST tool ideal for application at the Hartford Site.

The LIF tool can be used to estimate the total amount of hydrocarbons present in the subsurface free product plume. It can also be used to estimate when and if saturations are sufficient enough to result in free product moving into a well.

Estimate the Volume and Types of Product in the Subsurface

The conservative total for the estimated volume of product beneath the Site was less then 8 million gallons as of 2006. Considering the conservative (biased low) nature of the porosity and saturation values used in these calculations volume estimates could be off by a factor of two or more. Oil saturations in the presence of free product in wells is anticipated to be up to 30 or more percent as compared to the values of less than 10 used in this calculation.

The product present beneath Hartford was determined to be primarily leaded gasoline because it has an octane rating of greater the 80 (Mathes 1978a, Unknown 1983) and the product contained approximately 1 g/gal of lead (Nicholson 2006). Gas chromatographs of product from under Hartford are similar to gas chromatographs of gasoline (Figure 45), with the highest concentrations of compounds in the C_5 to C_8 carbon range, and a distinct compositional cutoff at approximately C_{12} (Premcor 2003 and 2005). The PIANO analyses of product from Hartford resemble those of reference gasoline's (Figure 46) with elevated levels of aromatics and paraffin compounds and lower levels of olefin and naphtha compounds (Premcor 2003and 2005).

The total lead concentration of the product under Hartford is consistent with the gasoline formulation history at the Wood River Refinery during the period from 1960 to 1988. Total lead in free product floating on groundwater within Hartford is 1 g/gal, with many samples being higher (up to 2 g/gal) Temporal data suggests that free product lead concentrations have remained relatively constant within Hartford from 1978 to 2005 (Premcor 2003 and 2005).

Defining Pathways and Exposure Points

The main findings of the CPT and geotechnical program included, but were not limited to, the following:

- The Main Sand is highly permeable and porous.
- The Main Sand approaches the surface near the center of the product plume in the northern portion of Hartford creating a structural high in this area.
- Less porous units are generally comprised of clayey silts and silty clays that may not be impervious to fluid and vapor migration.
- Stratigraphic relationships in shallow saturated units (that is, EPA stratum) at the Site control the flow within these units and are different than those in underlying units like the Main Sand.

These findings were essential to the understanding of both product migration and the potential for VI at the Site as is discussed in Sections 5.2 and 5.4. Results show that vapors are most prevalent in near surface soil gas beneath Hartford where the Main Sand nears the surface and the silty clay layer (that is, the “A” Clay) thins. Obviously, the presence of hydrocarbon contamination in the subsurface also plays a role in the pervasiveness of high vapor concentrations in a particular area of the Site.

Figure 26 is a site map from the Clayton (Clayton, 2004c) Utility and Pipeline Investigation used by ENSR in their CSM Investigation Work Plan (ENSR 2004e) showing where ROST results indicated the first encounter with measurable total product in subsurface soil. Approximately two-thirds of the investigation area is dominated by generally low benzene vapor concentrations (less than 100 $\mu g/m^3$). The highest benzene concentrations (on the order of 1,000,000 $\mu g/m^3$) appear to be clustered within three areas of the Site. These include the Hartford Community Center area (in the northeastern portion of the Site), the area where the depth to the Main Stratum is shallowest (in the center of the Site) and along the eastern boundary of the Site (Figure 36). These findings were used to target VI mitigation efforts.

Understand the Short Term and Long Term Affects on Soil, Groundwater, and Soil Gas

In the CC Report (Clayton 2003), apparent product thickness results from beneath Hartford from the Mathes 1978a investigation were provided. Historical records for the Wood River Refinery also contained apparent product thickness data from beneath the refinery (Mathes 1979). The data from both of these Mathes investigations was combined and then plotted on Figure 40. Based on this map, it appears as though a majority of the contamination that registered during the ROST investigation was also present during the late 1970s.

Based on these observations, it can be concluded that the majority of contamination observed at the Site using the ROST data was likely to have been present prior to 1978. Hydrocarbon saturation in soil has also likely decreased over time as more pumping and product removal has occurred. The rise and fall of groundwater beneath the Site has also likely decreased the mobility of the product present beneath the Site (API 2004). Regardless of the efforts to remove product from the Site, it is clear that hydrocarbons in the subsurface at the Site will continue to act as a source to groundwater and vapors at levels above potential applicable regulatory criteria.

Understand the Timing of Releases and the Fate of the Plume

The organo-lead additive speciation of the product under Hartford is consistent with the gasoline formulation history at the Wood River Refinery. The primary form of lead in free product found in the samples collected was TEL. At the Wood River Refinery during this time, the operator used TEL as their primary alkyl lead additive (Clark Oil 1981, IEPA 1990). Product samples collected on the Wood River Refinery site contain significant amounts of TEL. TML was only detected in two Wood River Refinery samples at levels less than 0.1 percent.

Free product found in Hartford is in part derived from gasoline manufactured between 1969 and 1980. This observation is based on all of the before-mentioned information, but principally the fact that the product is primarily leaded gasoline with lead levels consistent with available product information. TMP ratios indicate that the product contains alkylate from an HF-catalyzed process and a HF-alkylation process that was used at the Wood River facility from 1969 to 1988.

Predict where Product Removal is Possible

For purposes of designing product recovery system(s), northern Hartford was divided into three (3) areas, based on recovery/recharge rates and product characteristics (Figure 38). The proposed active recovery system(s) will not necessarily be restricted to within these areas. The eight product remediation technologies were evaluated separately for different areas. In summary:

- The area surrounding well HMW-44 exhibited high product recovery and recharge rates relative to other areas and was designated “Area A.”
- Localized areas outside Area A exhibiting moderate product recovery and recharge rates were designated “Area B.” Area B was then divided into subsections B1 through B4 based on further consideration of product type or recovery rates.
- The remaining area of northern Hartford, where poor product recoveries, slow recharge rates and high vapor recovery rates have been recorded, was designated “Area C.”

The technologies were evaluated based on the criteria identified in the AOC (Section VI. Paragraph 53), which are protectiveness, long-term effectiveness, implementability, and cost. Short-term effectiveness and effect on the community were also evaluated. MPE was chosen as the recovery technology for Area

A, based on the high product recovery observed during pilot testing and the additional evaluation criteria. MPE was chosen as the primary recovery technology for Areas B1, B2 and B4.

Evaluate the Utility of Various Soil Gas Methods for Predicting Vapor Intrusion Issues

Some innovative investigation technologies proved to be less effective then others at the Site. For example, passive soil gas methods were less effective then active soil gas methods for estimating where to expect VI issues. The ineffectiveness is suspected to be related to the complex chemistry of the vapors at the Site and competition for sorption sites. This suggests that an effective method for optimizing VI investigative activities at small or large petroleum sites is ROST used in combination with active soil gas methods.

Prepare a Comprehensive Conceptual Site Model to Support Cleanup

Using data collaboratively at large complex sites like the Hartford Plume Site is essential to streamlining project activities. The project had many positive aspects and resulted in lessons learned about implementing the Triad Approach at a large petroleum site. Data visualization was one aspect that could have been more efficient. Hundreds of hand-drawn cross-sections and illustrations were prepared in support of the Site activities. These were used effectively to build a consensus vision of site conditions, but the sheer volume of work products made their effective use cumbersome and difficult to develop a simplified rendition of the Site.

Using a 3-D visualization program could have reduced the effort spent preparing these illustrations manually. Visualizations and data management schemes can form the basis for adding additional data to mature the CSM and optimize the remedial systems as clean-up progresses. Recent support projects conducted by OSRTI technical teams highlight the extensive value derived when project teams capture historical and existing data and display them using new and innovative visualization software. These tools have become increasingly effective for estimating contaminant mass, targeting source areas, identifying areas of uncertainty, placing remedial systems, placing flux-based monitoring systems, and communicating with stakeholders.

Summary

The Hartford Plume Site case study provides a detailed example of some methods that are available to environmental practitioners to use at large and small hydrocarbon sites. Sufficient detail is provided for practitioners to begin to learn the basic elements necessary to design and implement site characterization, mitigation, and remedial efforts at hydrocarbon sites.

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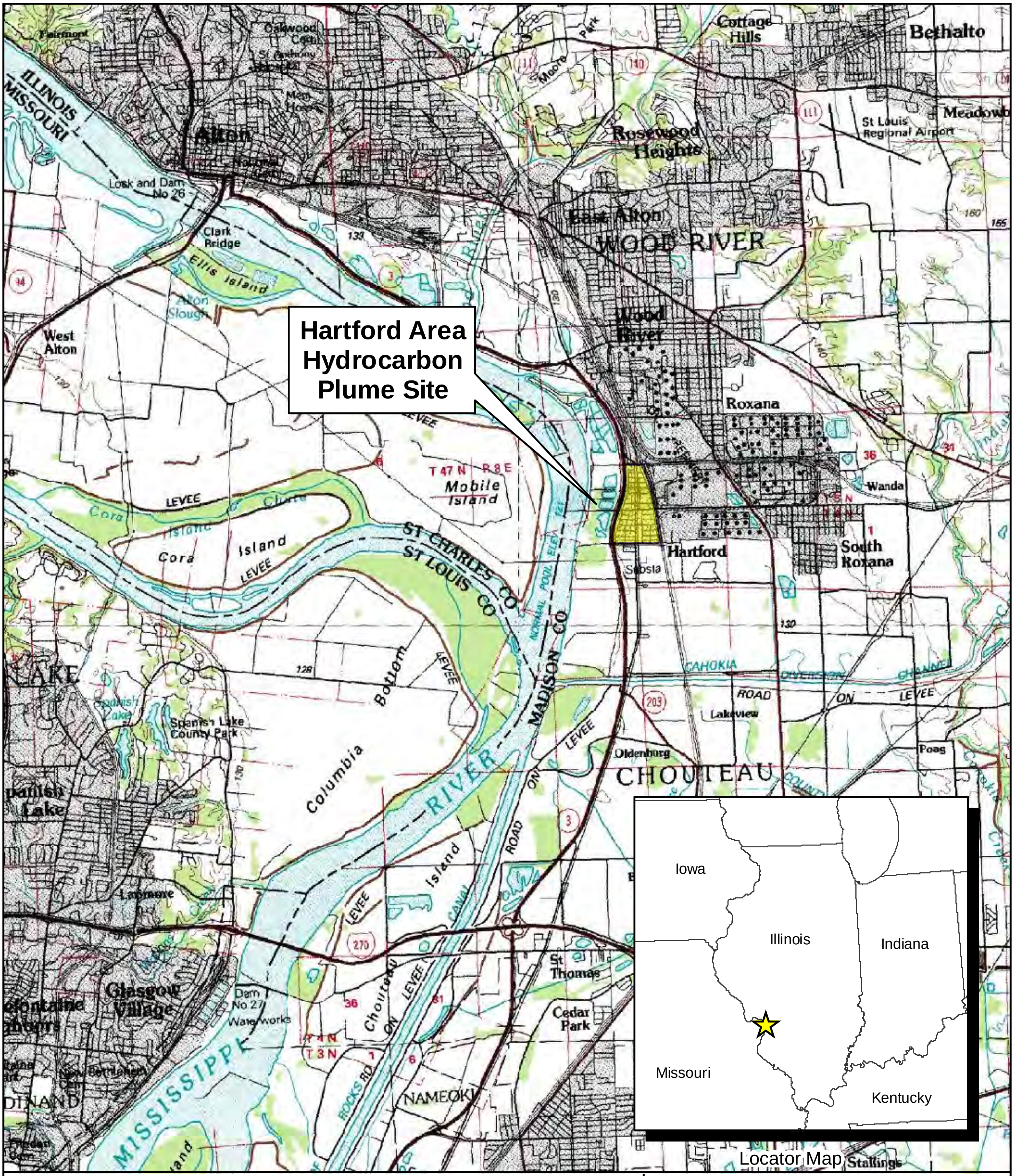


Legend

🟨 Site Boundary

N W E S

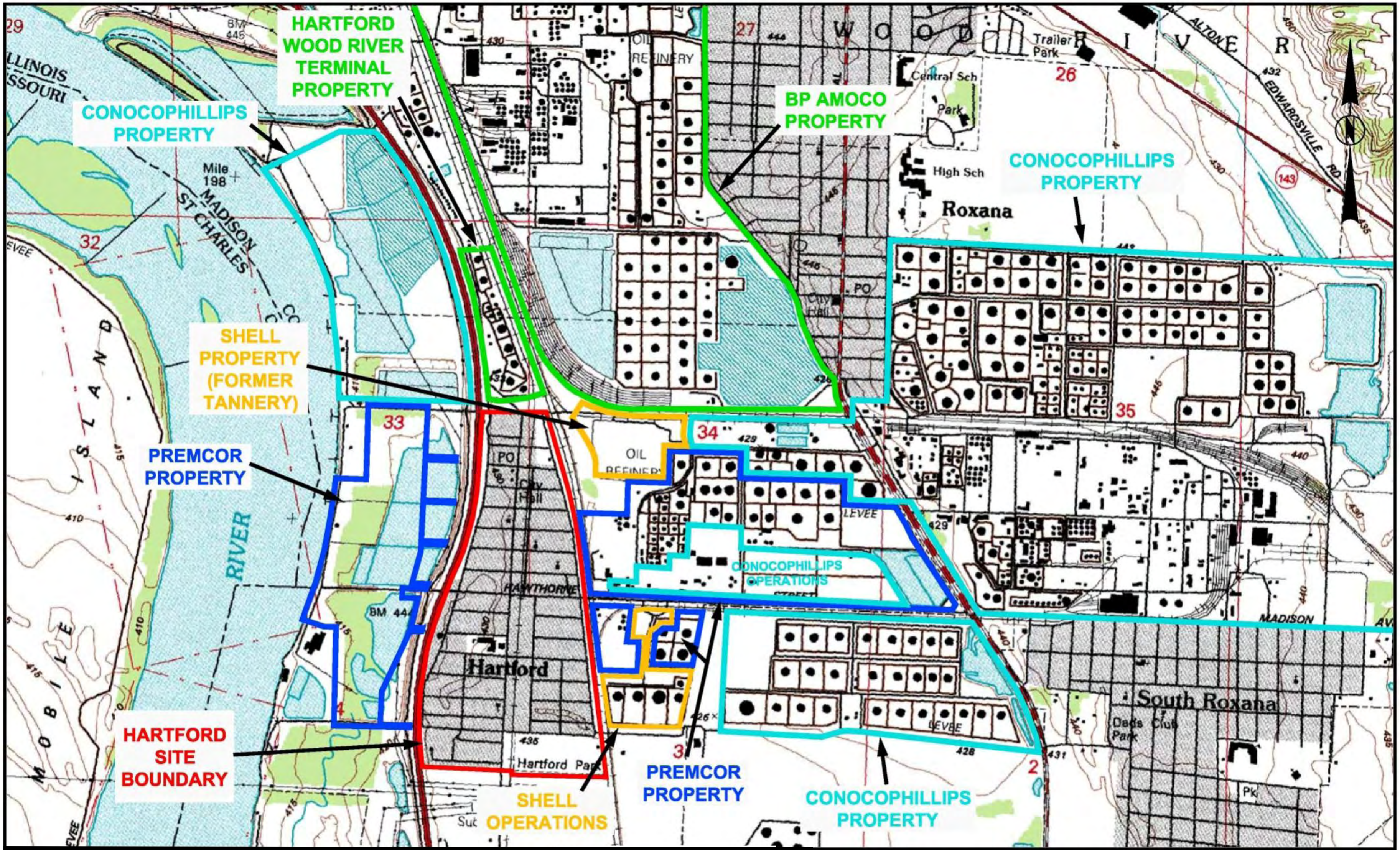
0 1.5
Miles

HARTFORD AREA HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

FIGURE 1
LOCATION MAP

TETRA TECH EM INC.

2007/07/23 O:\DOJ\Fig1_Location_Map1.mxd TtEMI-DN Kurt.Cholak



SCALE IN FEET

0 1000 2000 4000

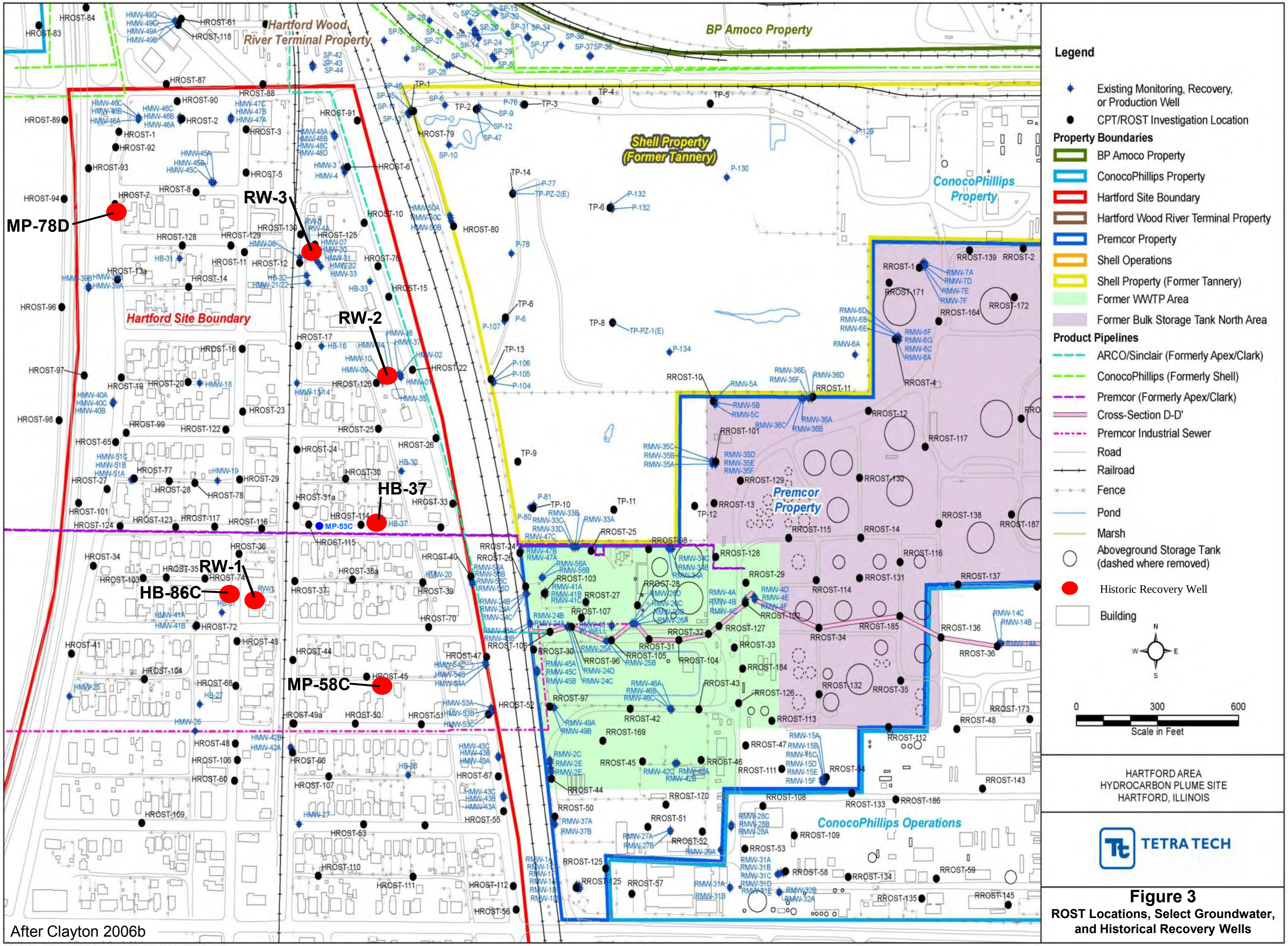
SOURCE:
USGS 7.5 MINUTE SERIES TOPOGRAPHIC MAP
(WOOD RIVER, ILL.–MO. – rev.1994)

VILLAGE OF HARTFORD AND
SURROUNDING AREA MAP

THE HARTFORD WORKING GROUP
HARTFORD, ILLINOIS

TETRA TECH

Figure 2



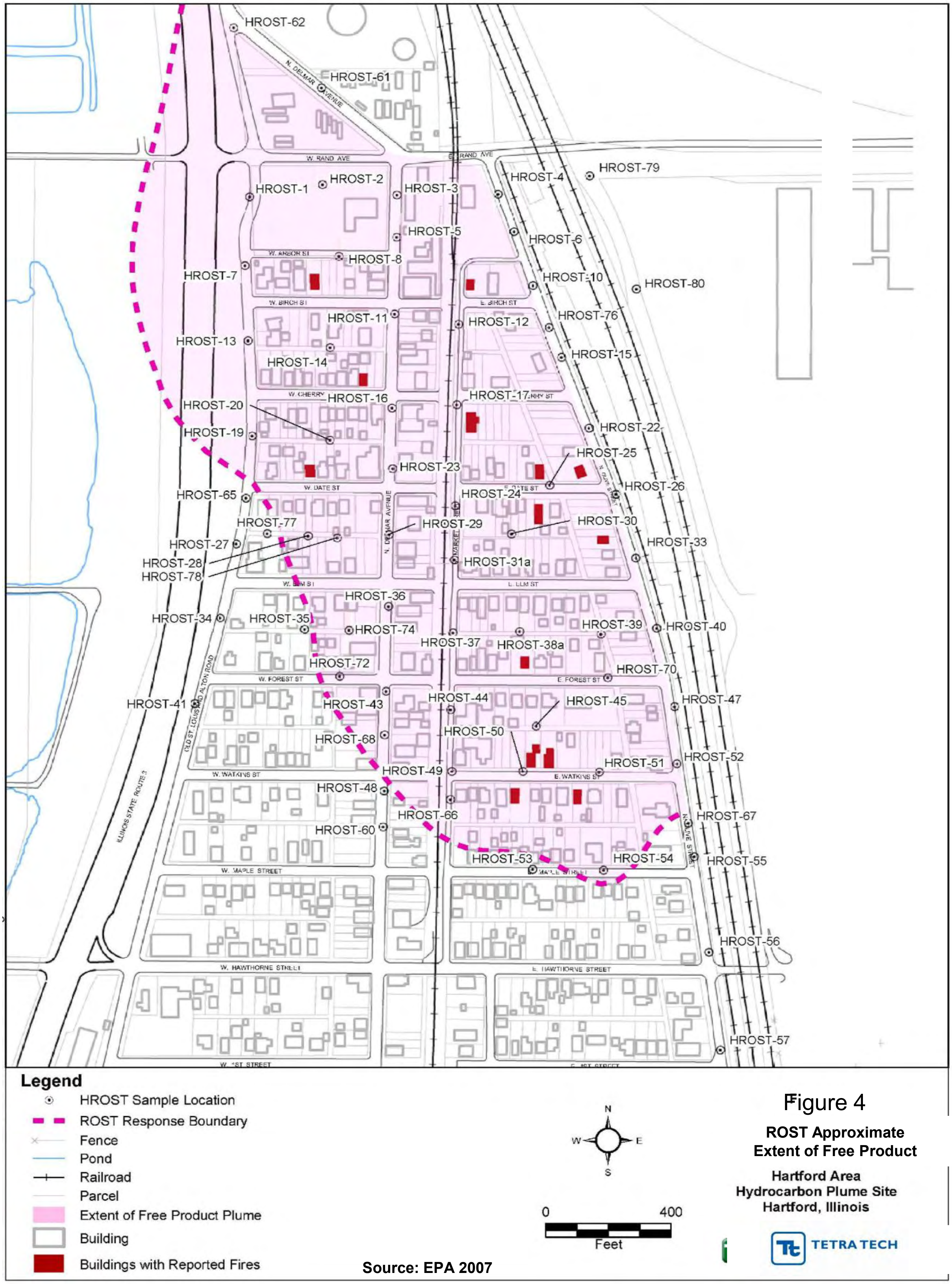
After Clayton 2006b

HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

TETRA TECH

Figure 3
ROST Locations, Select Groundwater, and Historical Recovery Wells

2006-04-04 O:\DOJ\Fig2_Refinery_Property.mxd TtEMI-DN Kurt.Cholak



Source: EPA 2007

Figure 4

ROST Approximate Extent of Free Product

Hartford Area Hydrocarbon Plume Site
Hartford, Illinois

TETRA TECH

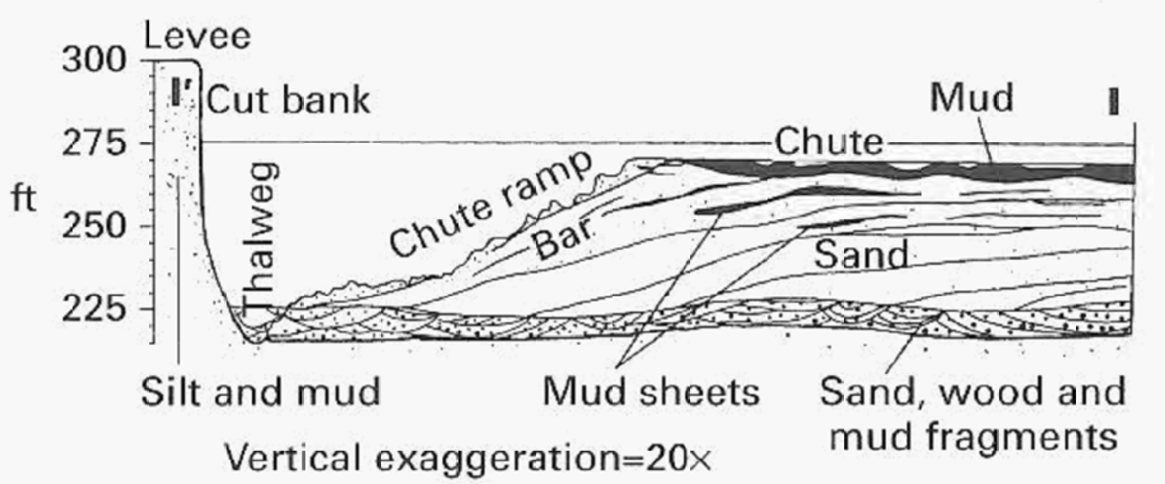


Figure 5: Cross-section of a Mixed Load River
(From Reading, 1998, "Sedimentary Environments")

Note I - I' Cross-Section

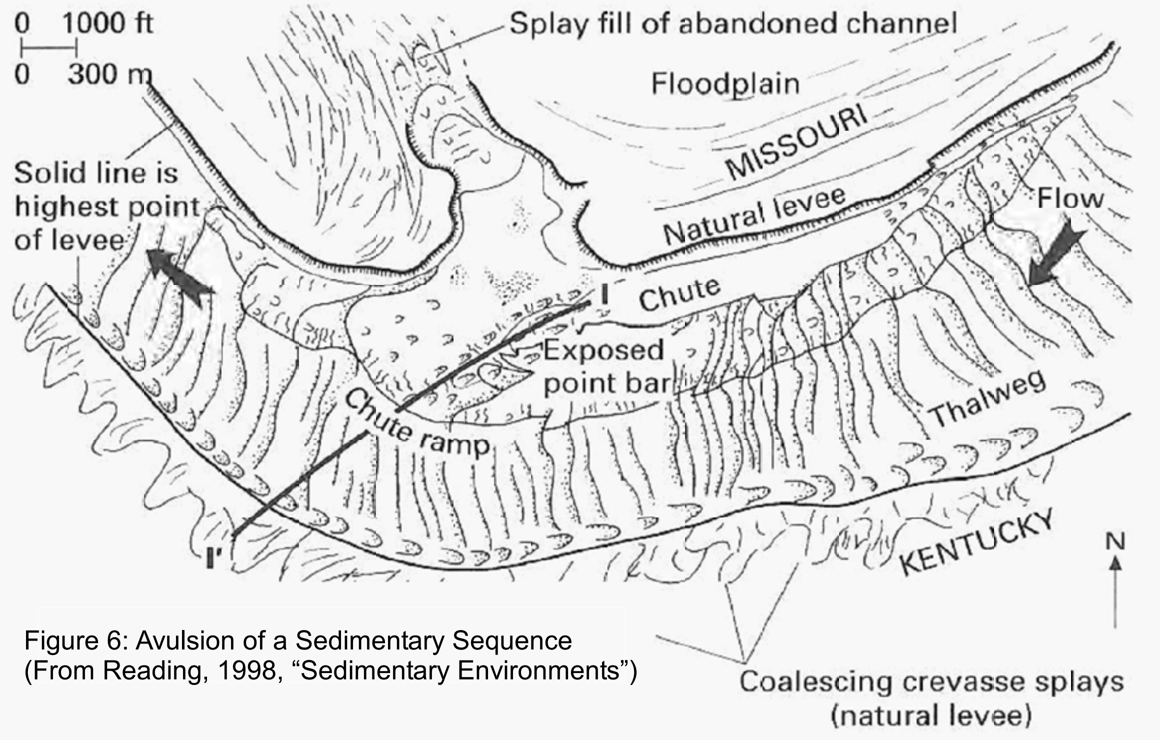
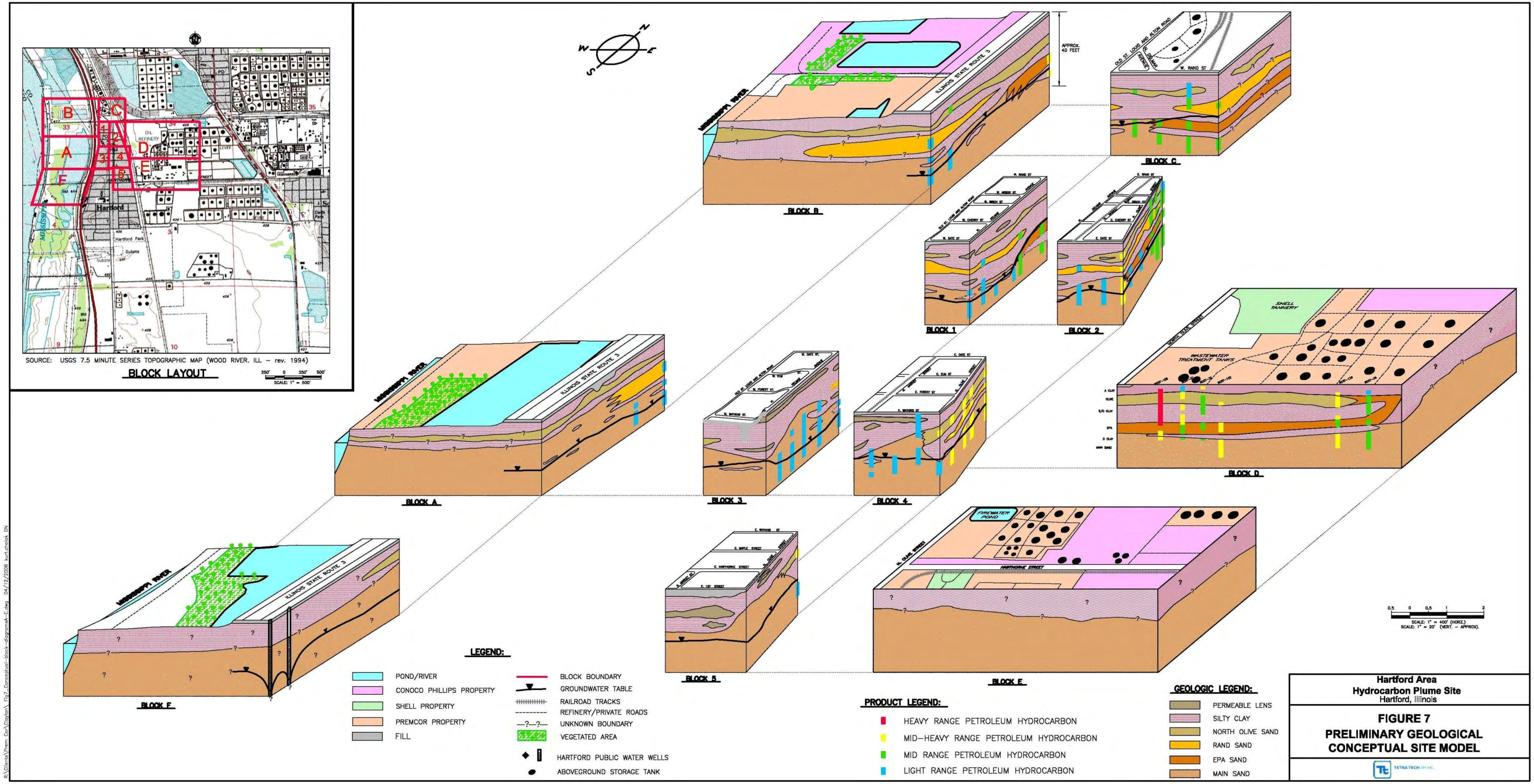


Figure 6: Avulsion of a Sedimentary Sequence
(From Reading, 1998, "Sedimentary Environments")

FIGURES 5 AND 6

TYPICAL RIVER RELATED
SEDIMENT PACKAGES

TETRA TECH EM INC



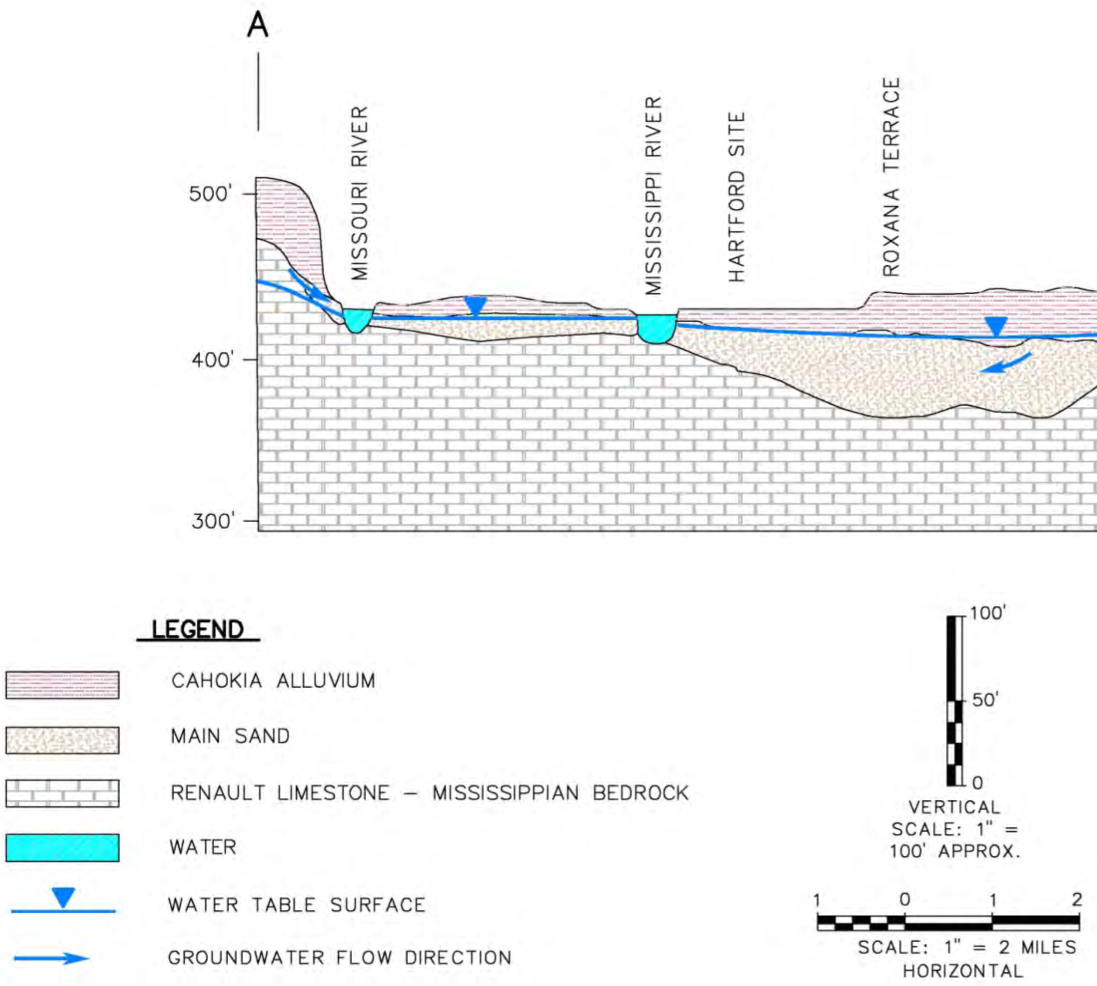
Hartford Area
Hydrocarbon Plume Site
Hartford, Illinois

FIGURE 7
PRELIMINARY GEOLOGICAL
CONCEPTUAL SITE MODEL

Source: EPA 2007

R:\Clients\Prem Cor\Clayton\ Fig7_Conceptual-block-diagramsA-E.dwg 04/12/2006 kurt.cholak DN

R:\Clients\Prem Cor\Clayton\ PREMCOR-GEO_X-SECTION.dwg 06/12/2006 paul.ragalla DN



HARTFORD AREA HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

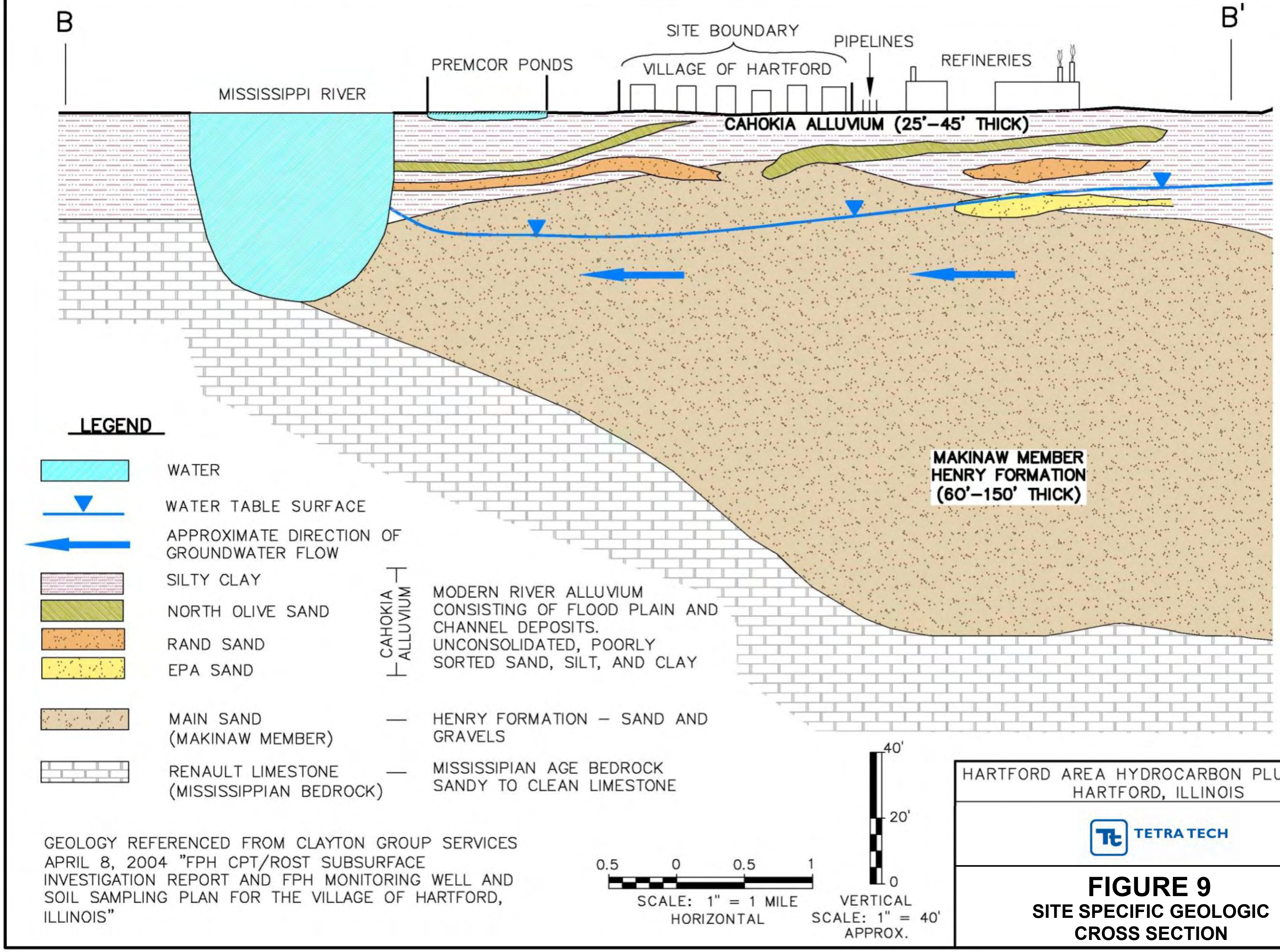
TETRA TECH

FIGURE 8

REGIONAL GEOLOGIC CROSS SECTION

Source: EPA 2007

R:\Clients\Prem Cor\Clayton\ Local-cross-section.dwg 06/12/2006 paul.rogalla DN



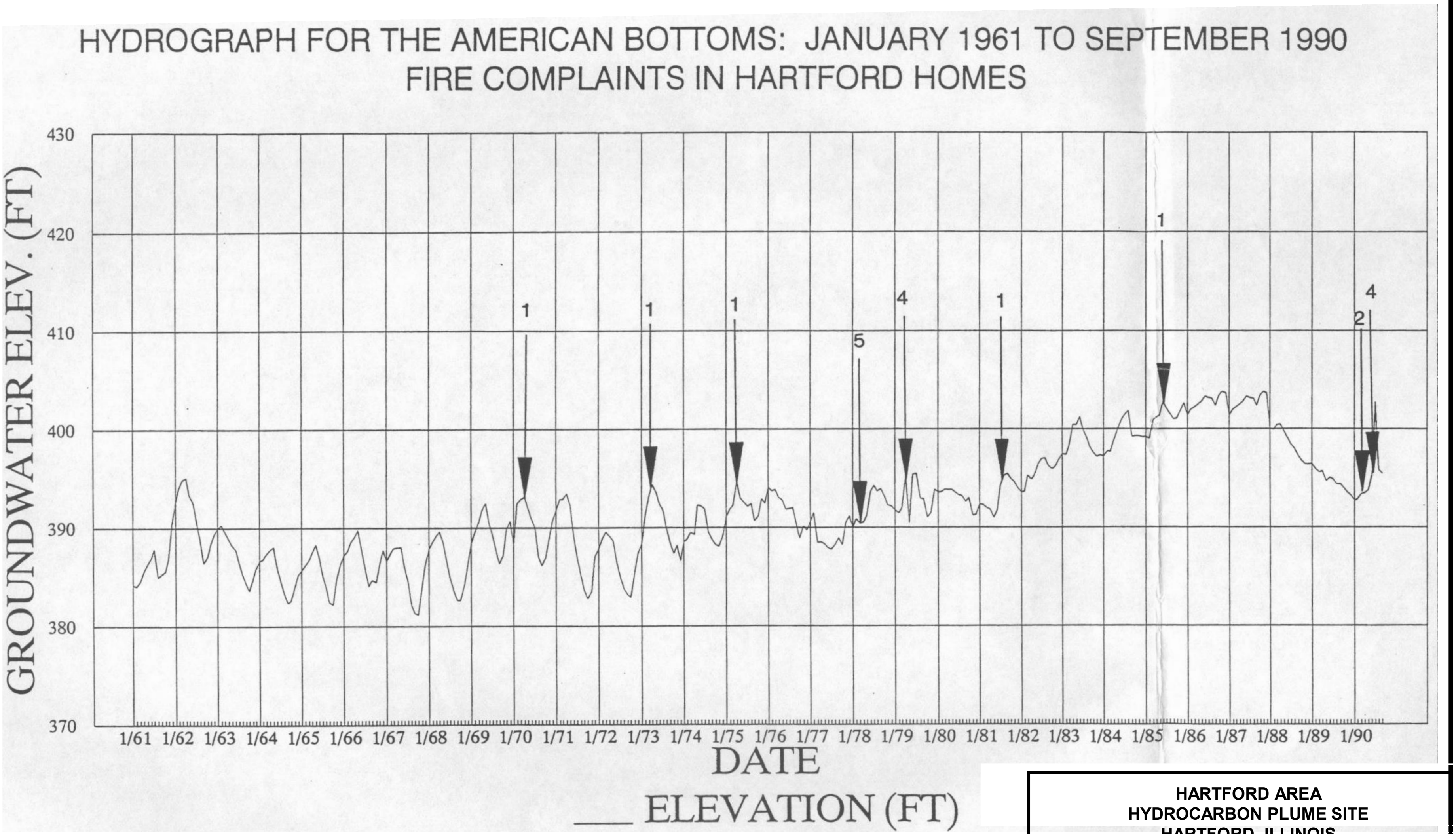
GEOLOGY REFERENCED FROM CLAYTON GROUP SERVICES APRIL 8, 2004 "FPH CPT/ROST SUBSURFACE INVESTIGATION REPORT AND FPH MONITORING WELL AND SOIL SAMPLING PLAN FOR THE VILLAGE OF HARTFORD, ILLINOIS"

HARTFORD AREA HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

TETRA TECH

FIGURE 9
SITE SPECIFIC GEOLOGIC CROSS SECTION

Source: EPA 2007

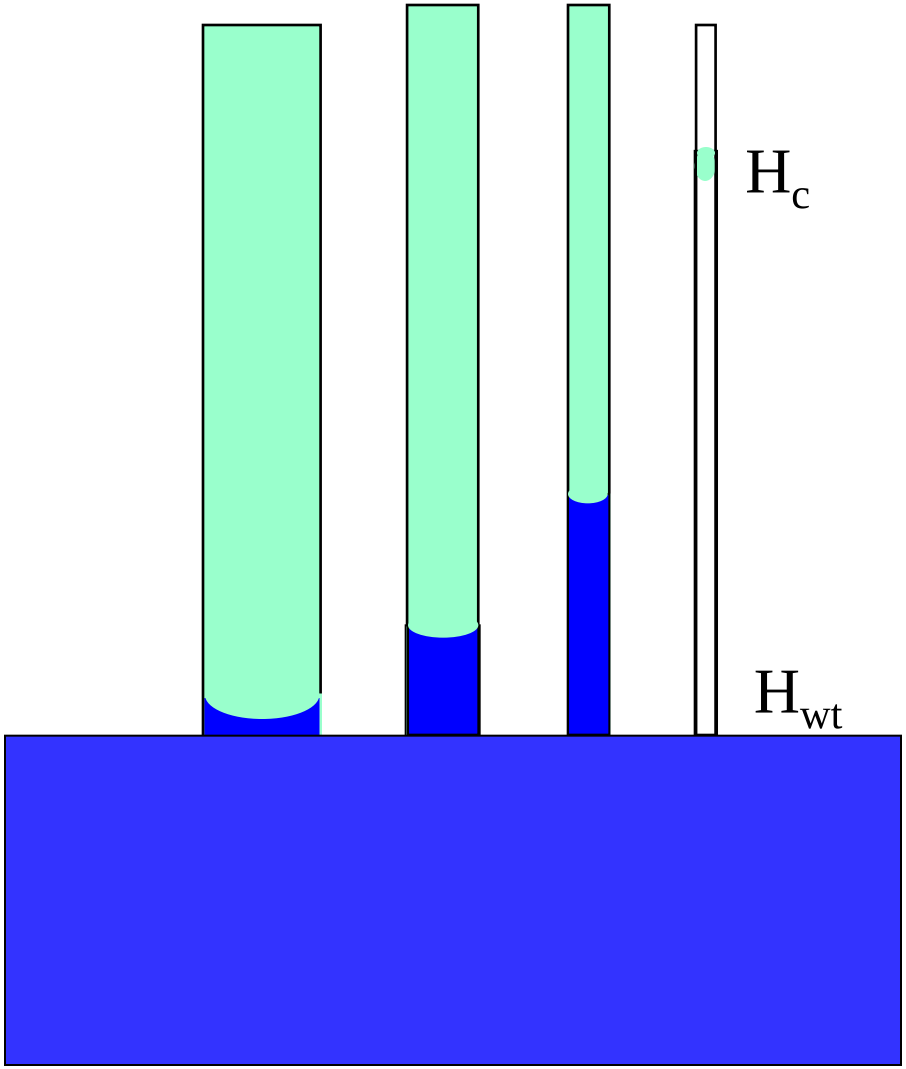


SOURCE: E-S, 1992

HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

FIGURE 10
GROUNDWATER ELEVATION
1961 - 1990

TETRA TECH



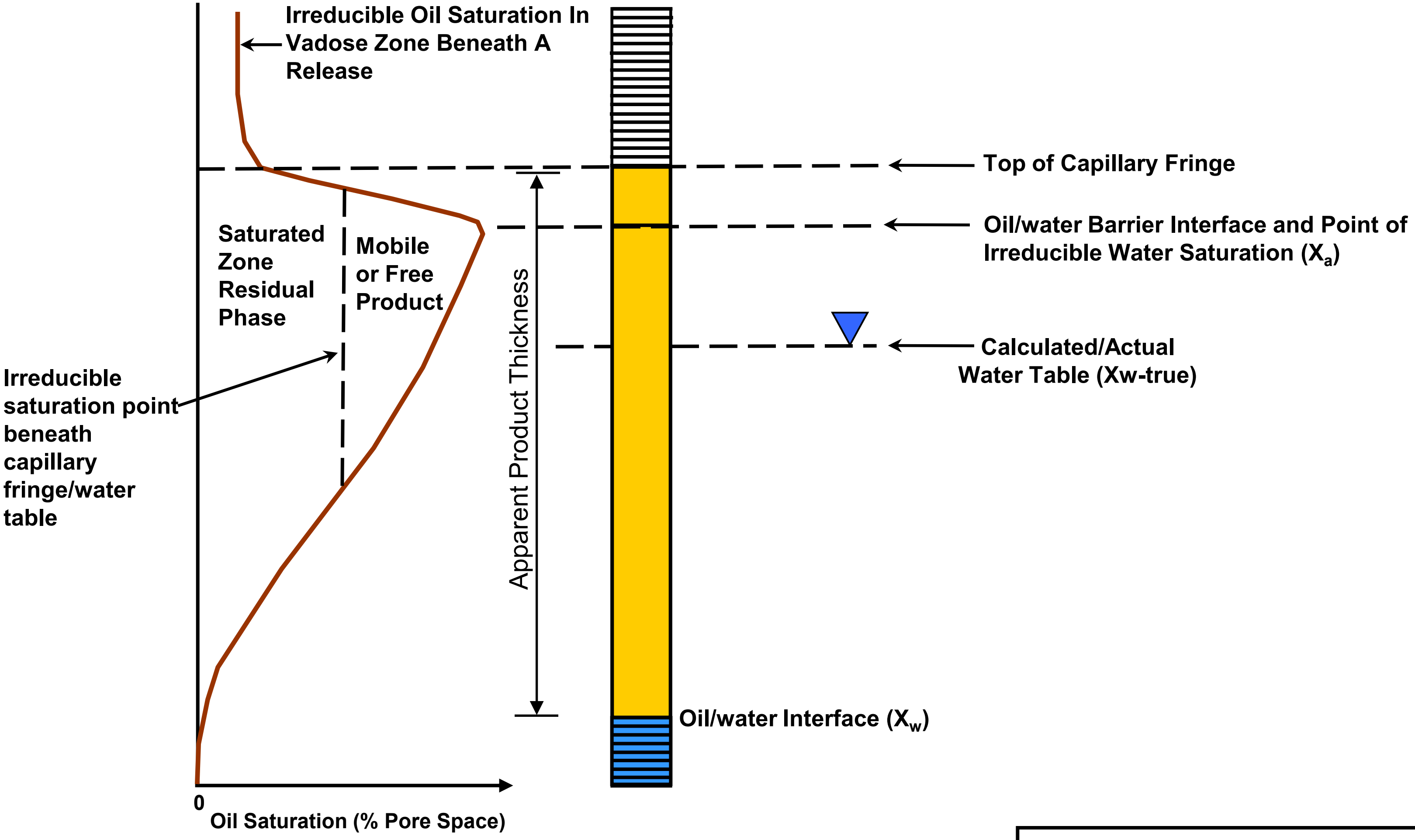
- •As pore sizes get smaller, capillary rise gets bigger.
- •Apparent product thicknesses in wells are driven in part by capillary forces.

SOURCE: Premeseck 2004

HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

FIGURE 11
Capillary Pressure and Apparent Product Thickness (Thickness Measured in a Well)

TETRA TECH



True water table elevation ($X_{w\text{-true}}$) = $X_a - X_w (SG_{LNAPL}) + X_w$

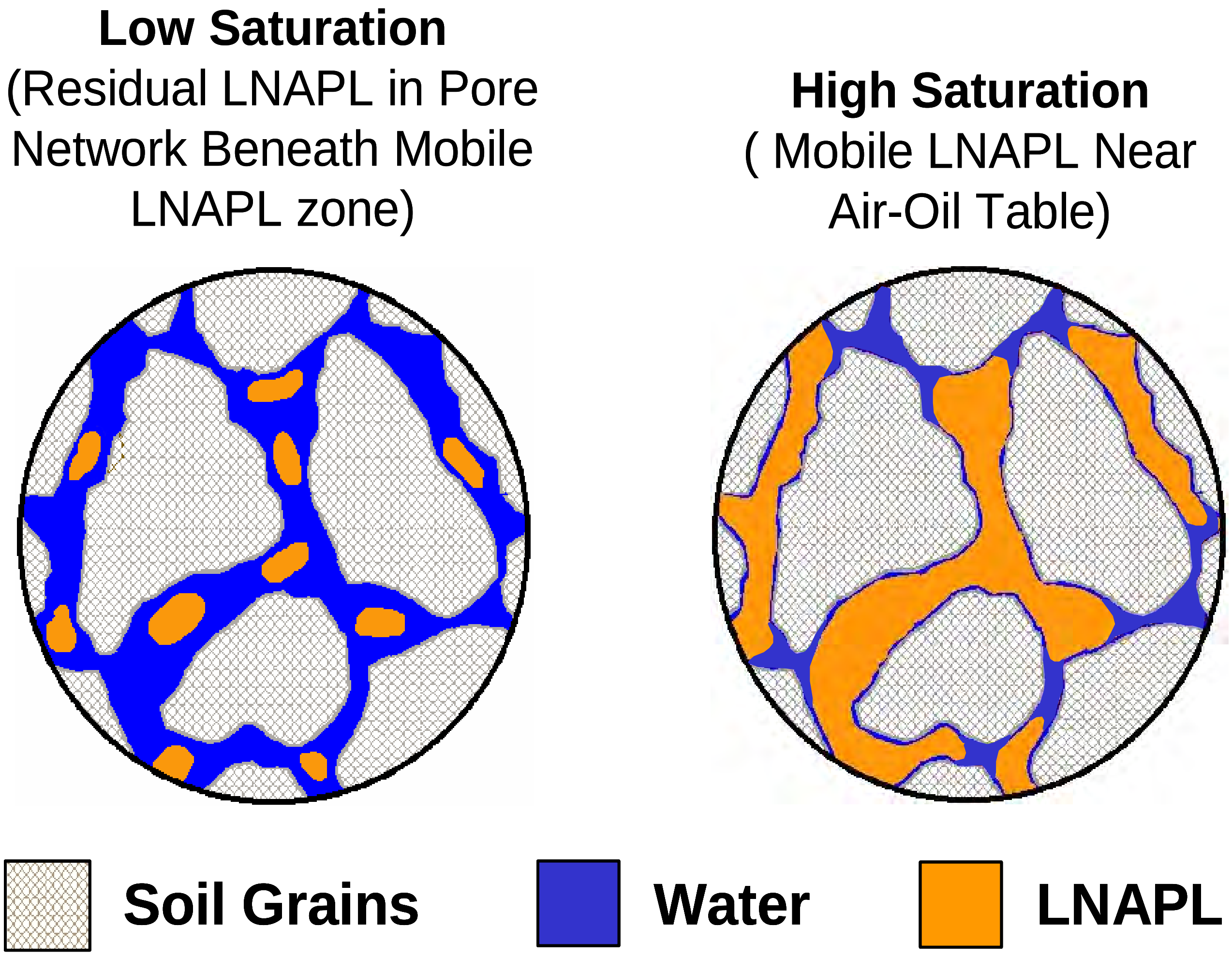
Where: SG_{LNAPL} = LNAPL specific gravity

Adapted from: API Interactive LNAPL Guide 2004

HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

FIGURE 12
Capillary Fringe and Oil
Saturation Curve

TETRA TECH



Low Saturation
(Residual LNAPL in Pore Network Beneath Mobile LNAPL zone)

High Saturation
(Mobile LNAPL Near Air-Oil Table)

▨ **Soil Grains**

🟦 **Water**

🟧 **LNAPL**

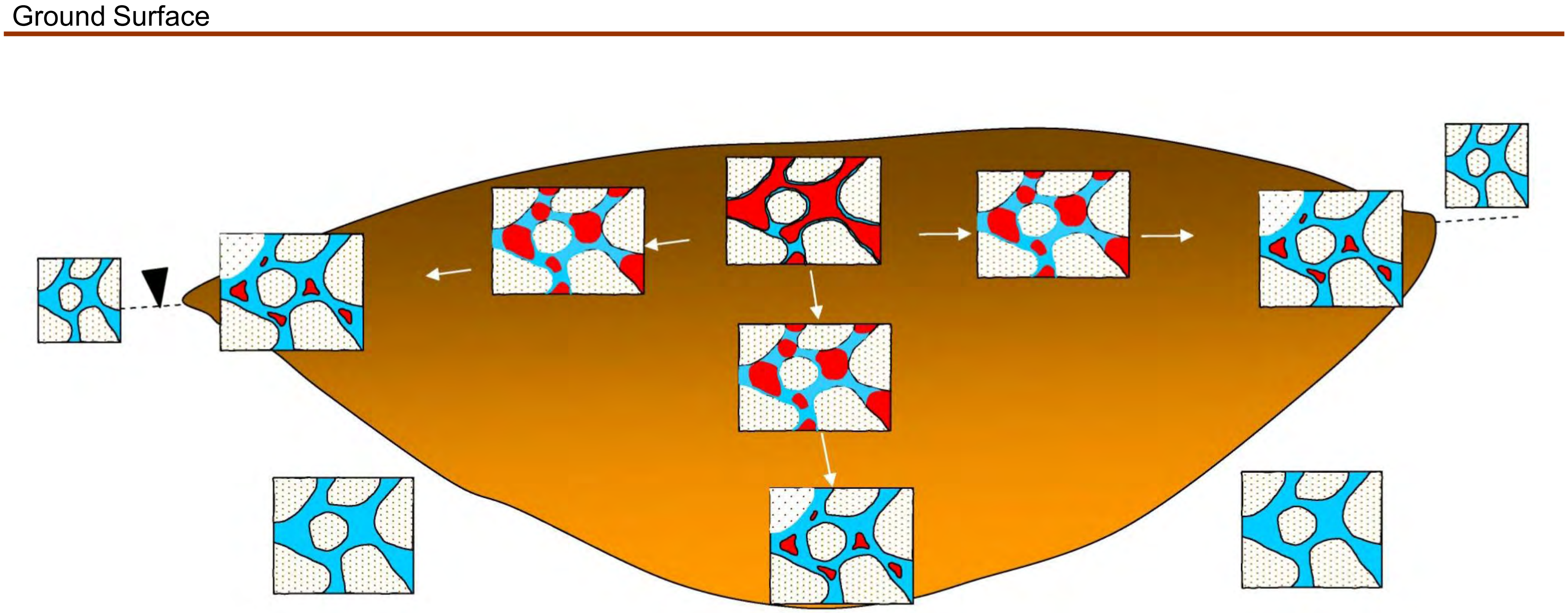
HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

FIGURE 13

Oil Saturation Diagram

TETRA TECH

Source: Lyverse, M. 2008



Notes:

- **LNAPL saturation, and therefore relative permeability/mobility, will vary throughout the plume**
- **The relative permeability at the edges of a stable LNAPL plume will be lower than in the core**

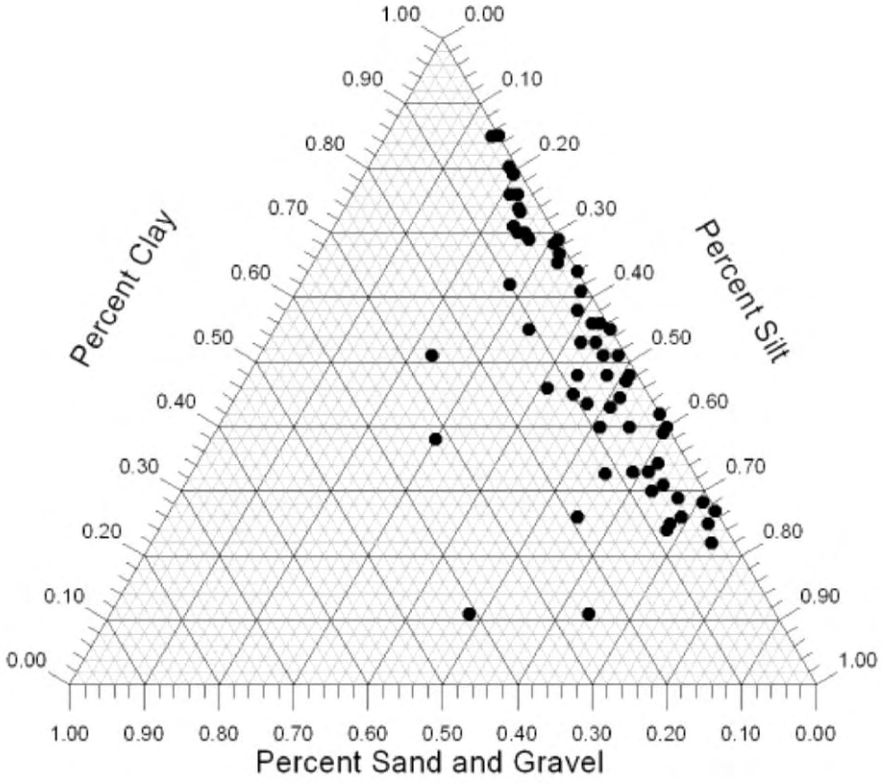
Source: Lyverse, M. 2008

HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

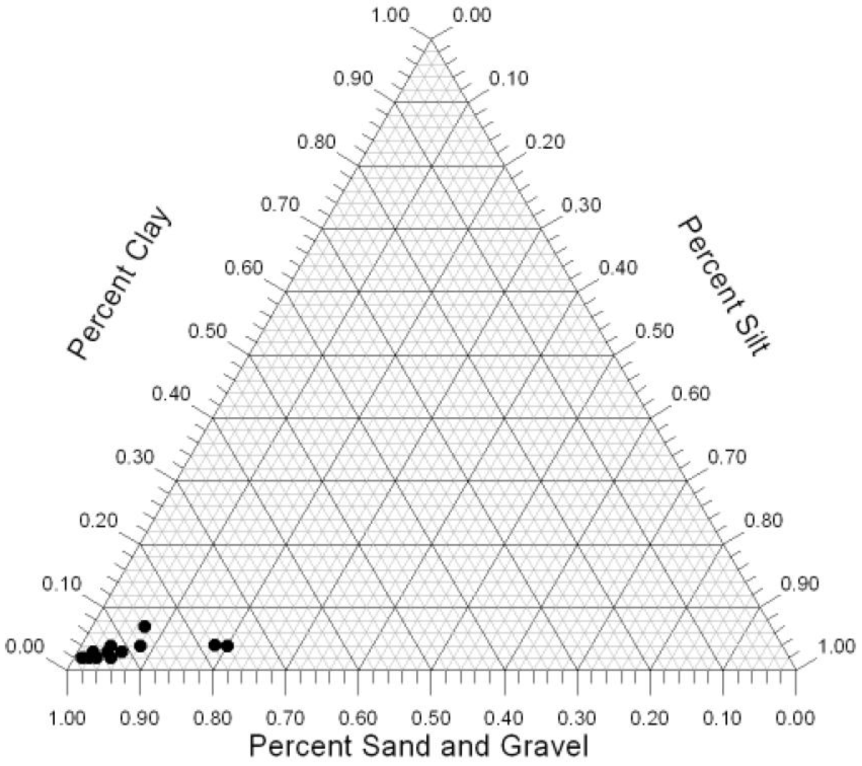
FIGURE 14
Schematic of Oil Saturation
Across a Plume

TETRA TECH

Composition of Clay Strata Geotechnical Samples
Village of Hartford



Composition of Main Sand Geotechnical Samples
Village of Hartford



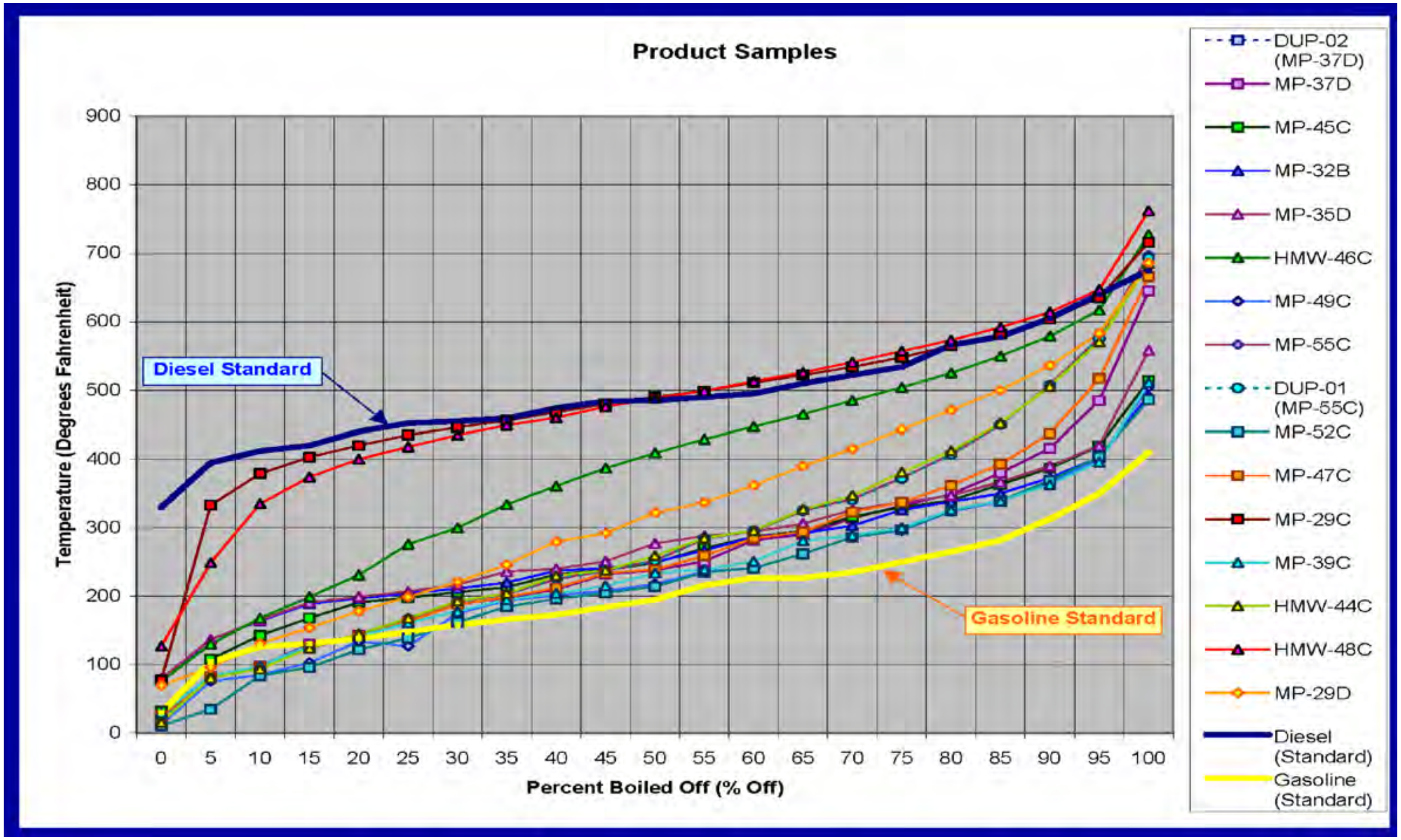
HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

FIGURE 15

Geotechnical Tri-linear Plots

TETRA TECH

Source: Clayton. 2005c



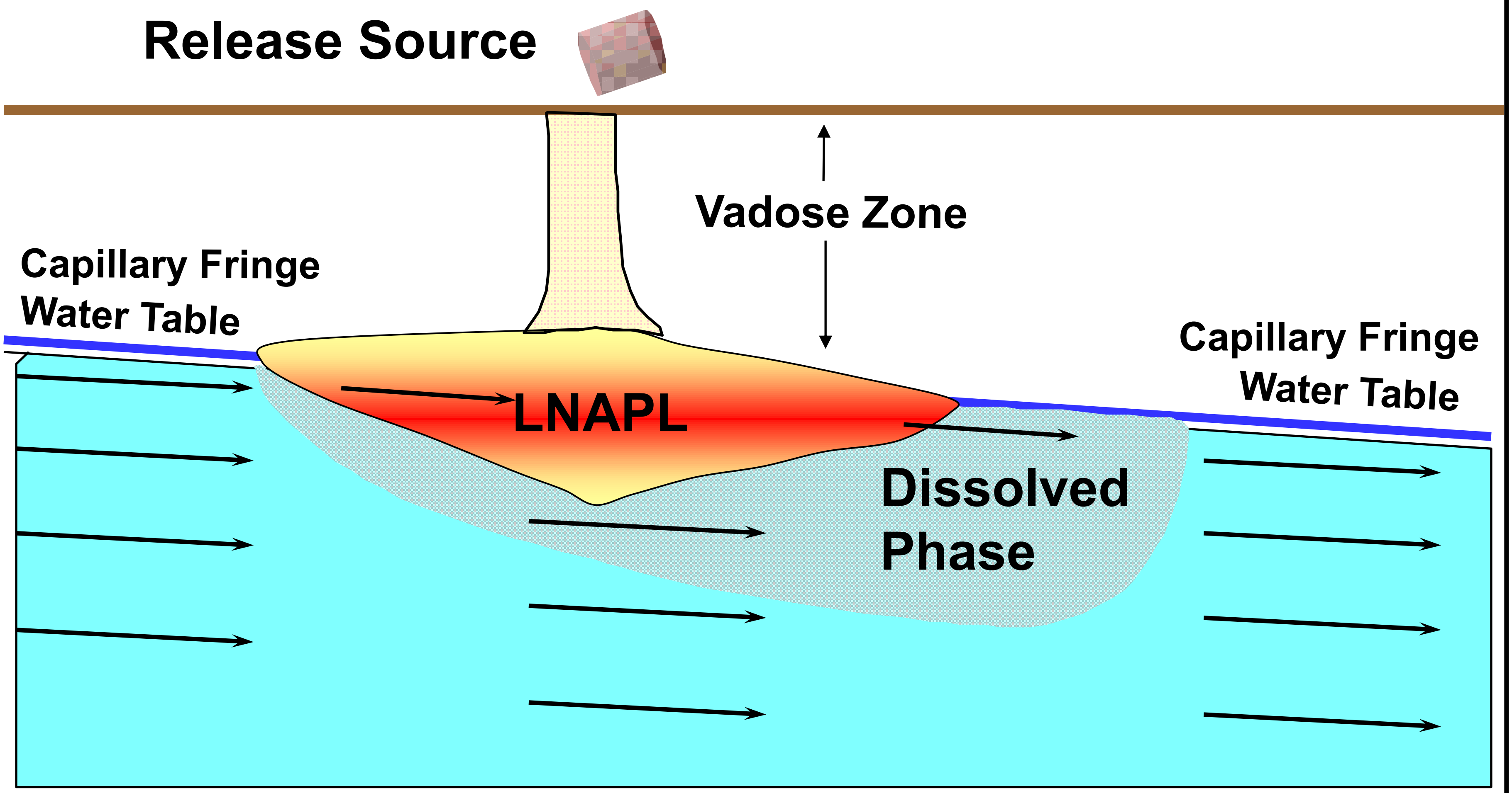
Source: Premeseck 2004

HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

FIGURE 16

Boiling Points

TETRA TECH



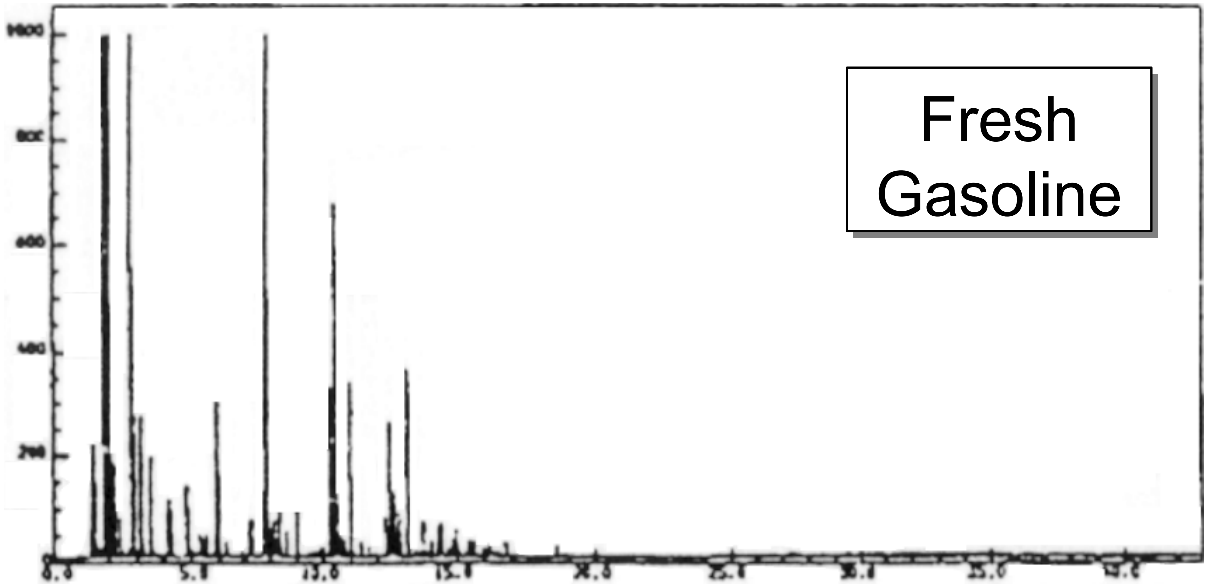
HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

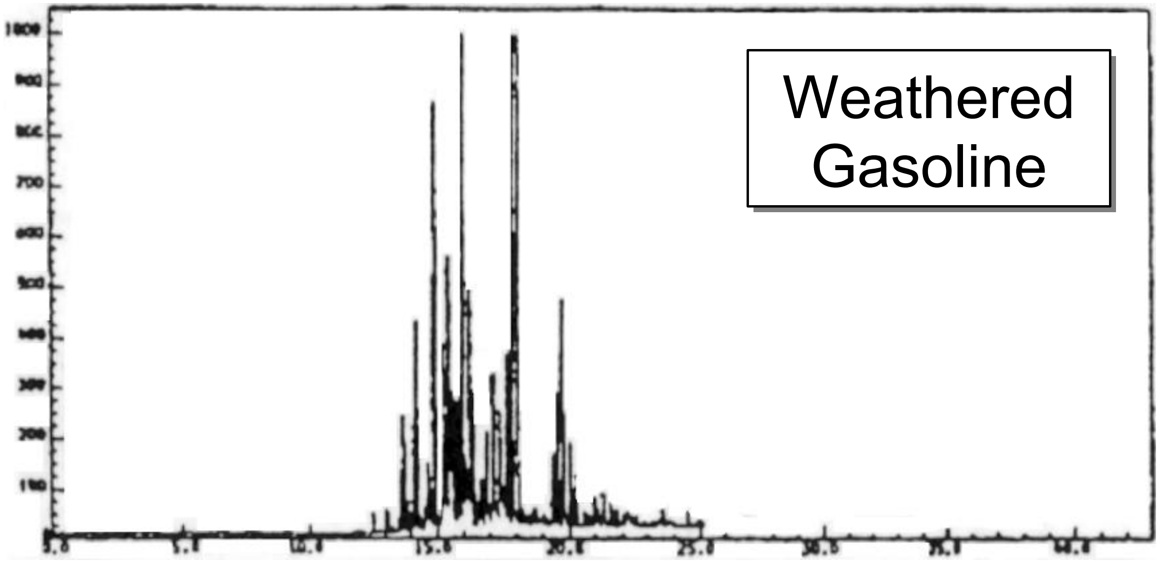
FIGURE 17

Typical LNAPL Plume

TETRA TECH

Source: Premeseck 2004





Source: API Interactive LNAPL Guide 2004

**HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS**

**FIGURE 18
Gas Chromatograph Curves Showing
Weathered and Unweathered Gasoline**

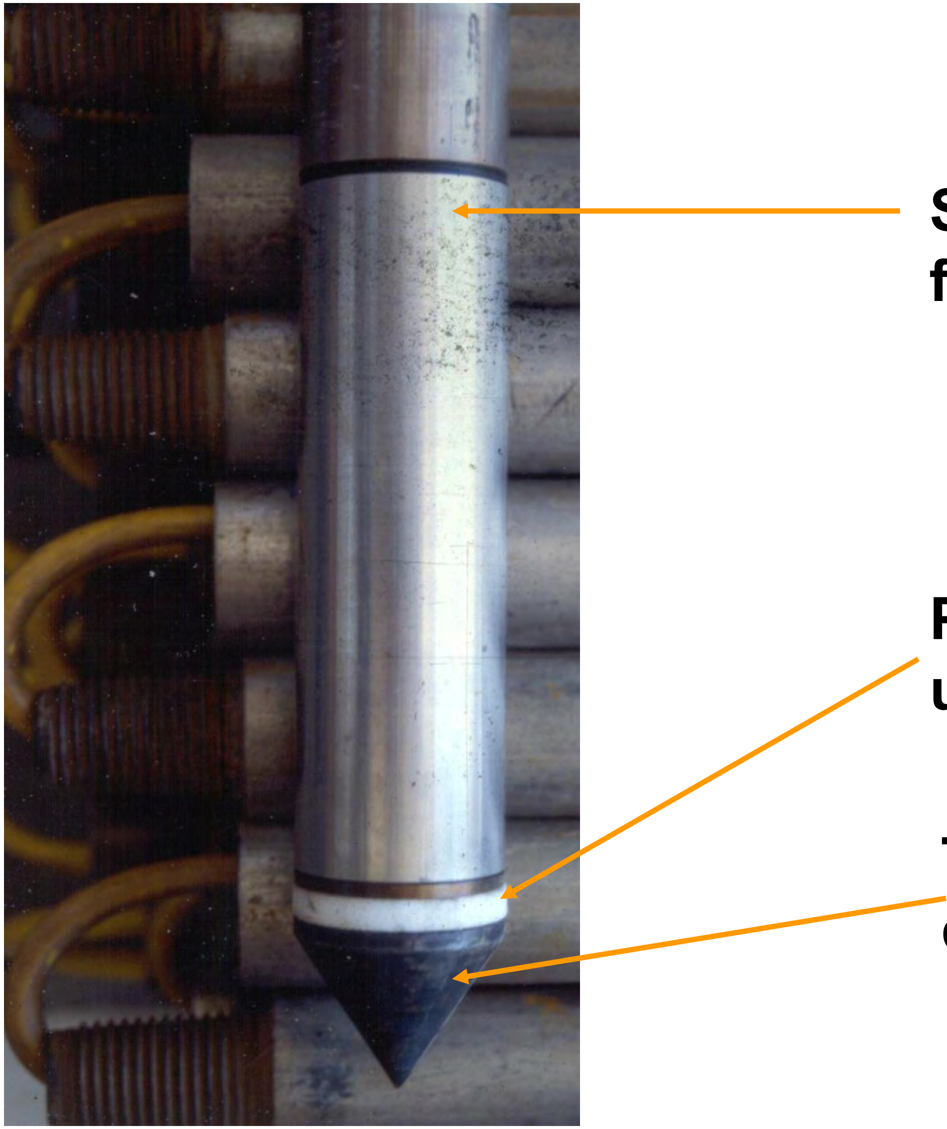
TETRA TECH

HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

FIGURE 19

CPT ROST Rig

TETRA TECH



Sleeve Friction

$f_s \text{ (tsf)} = {}^{\text{load}}/_{2\pi rh}$

Pore Pressure

$u_2 \text{ (psi)}$

Tip Resistance

$q_c \text{ (tsf)} = {}^{\text{load}}/_{\pi r^2}$

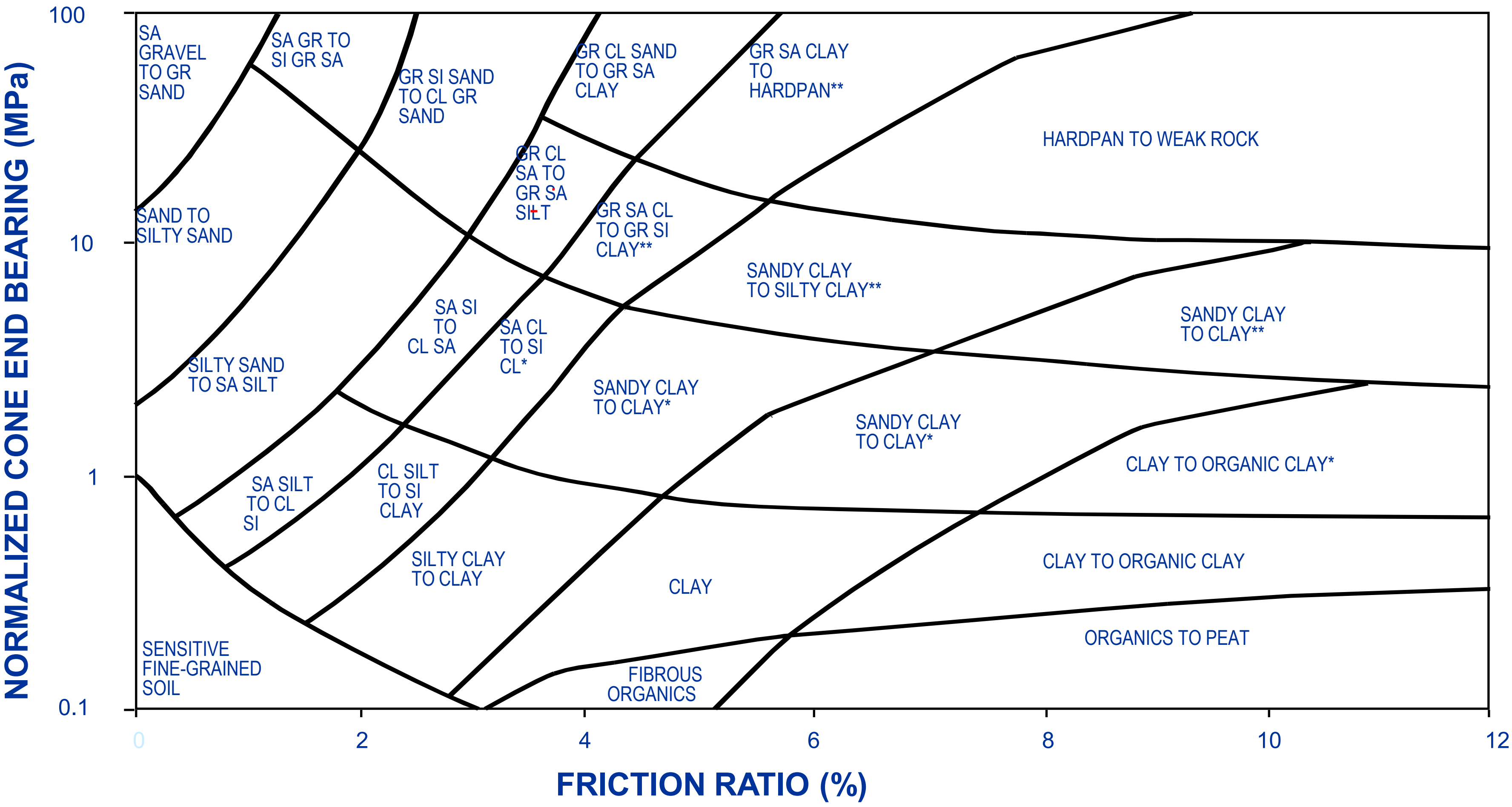
HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

FIGURE 20

Cone Penetrometer Components

TETRA TECH

Source: Gregg Drilling & Testing, Inc. 2006



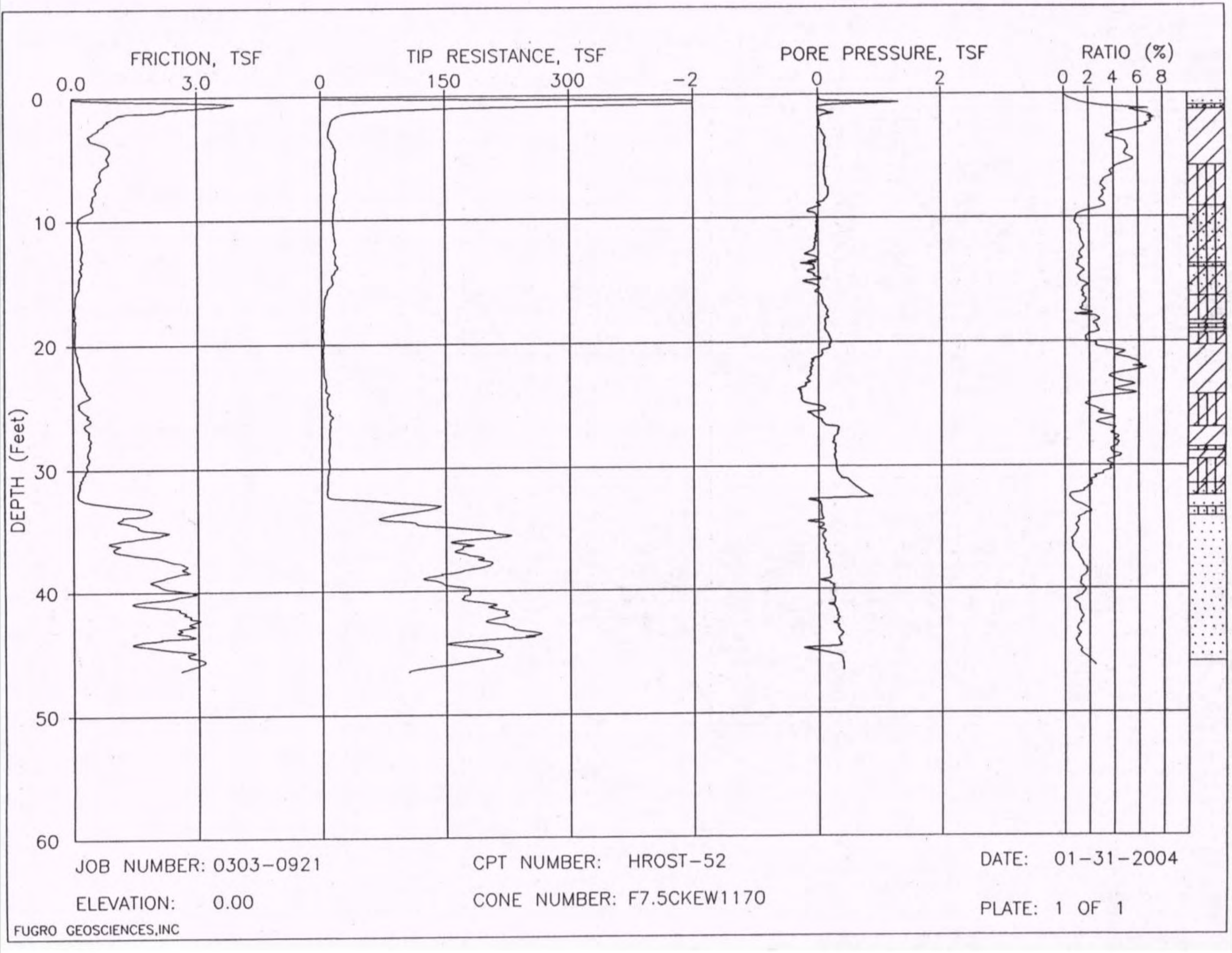
*** Overconsolidated**
**** Heavily overconsolidated or cemented**

HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

FIGURE 21
CPT Data Interpretation Algorithm

TETRA TECH

Source: Gregg Drilling & Testing, Inc. 2006



▦ Sand and Sandy Soil

▨ Clay and Clayey Soil

▥ Silt and Silty Soil

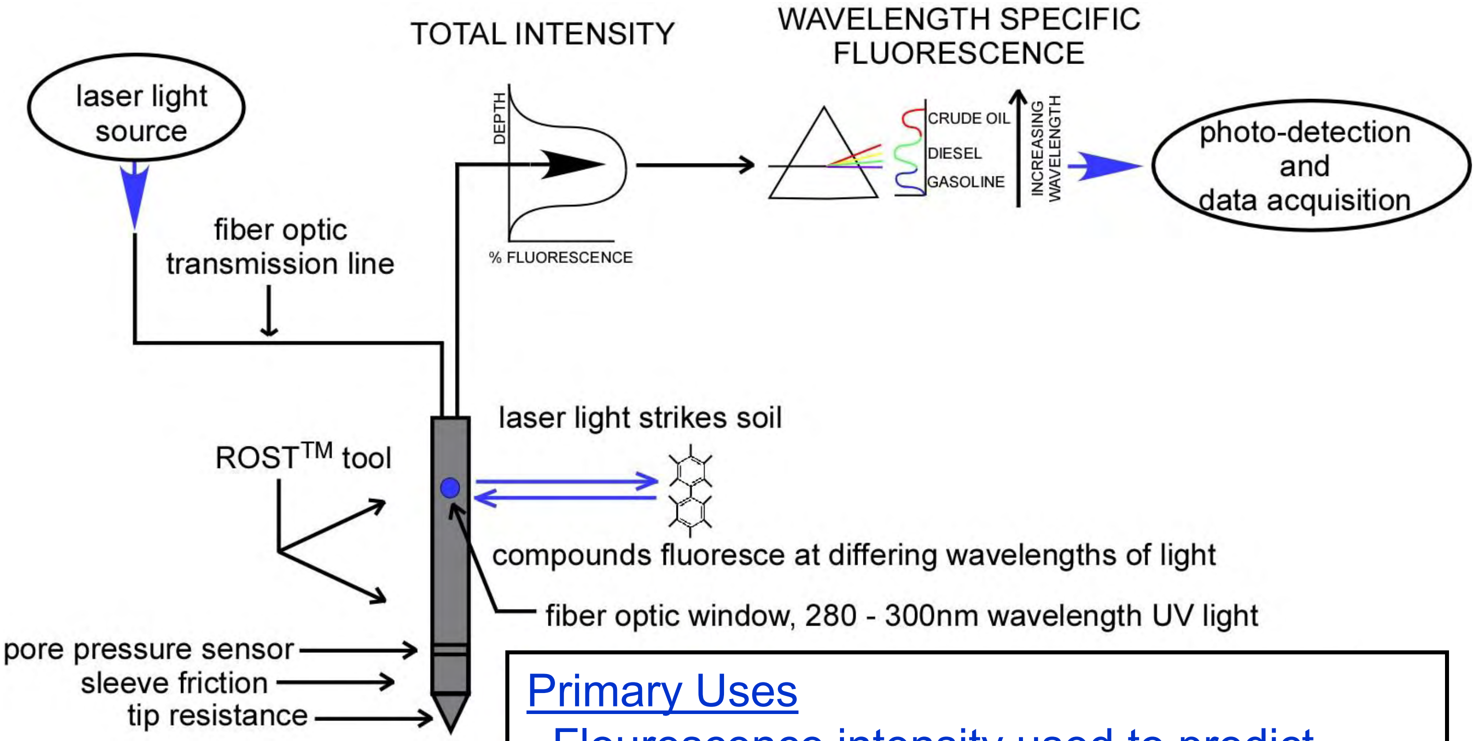
Source: Clayton, 2004b.

HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

FIGURE 22
EXAMPLE CONE
PENETROMETER LOG

TETRA TECH EM INC.

2006-03-15 O:\DOJ\Fig3_Cone_Penetrometer.mxd TtEMI-DN Kurt.Cholak



Primary Uses

–Flourescence intensity used to predict present of free product

–Wavelength specific intensity used to estimate product type

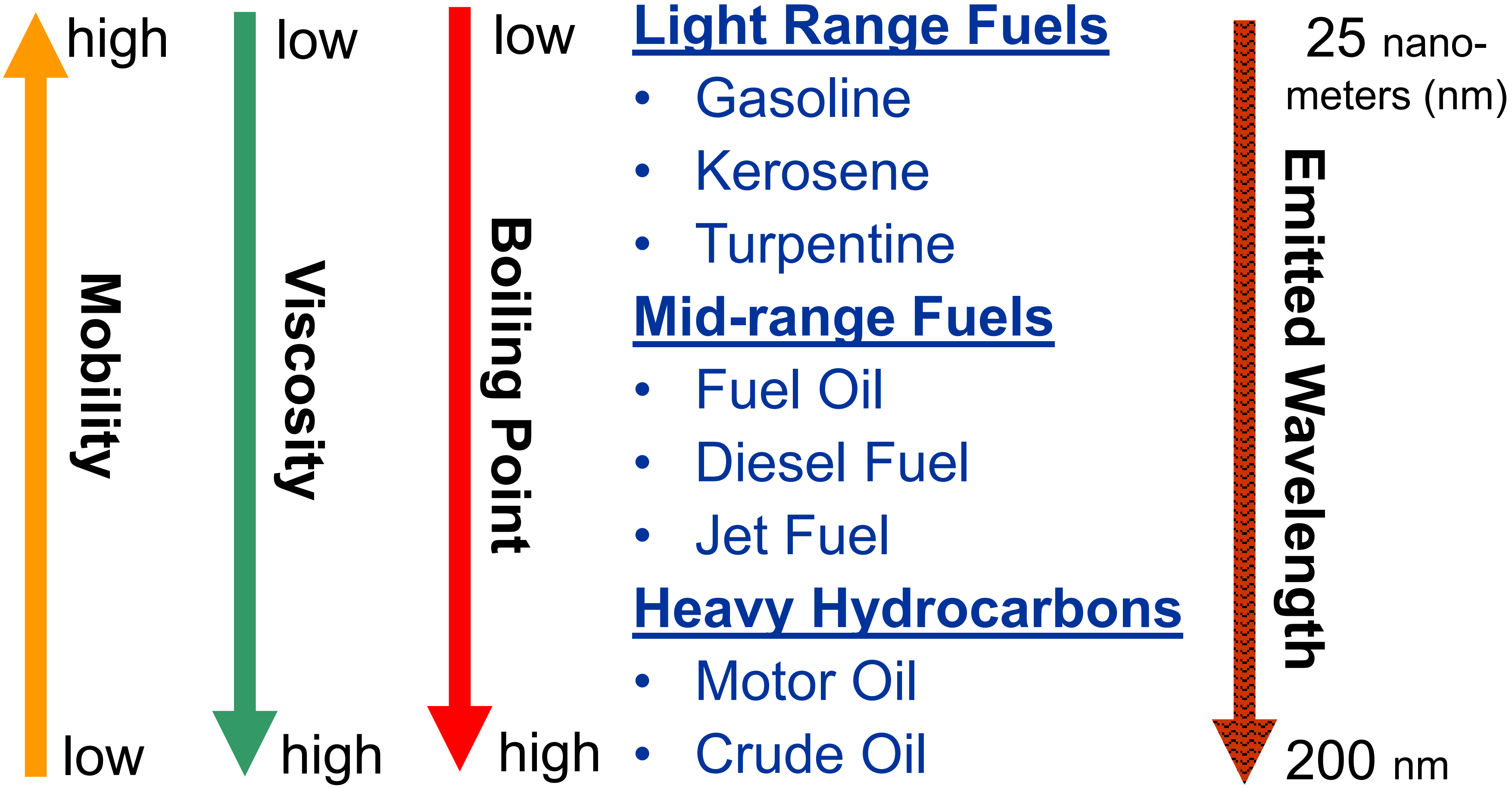
–Understand geology and hydrogeology

HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

FIGURE 23

How ROST Works

TETRA TECH



high

Mobility

low

low

Viscosity

high

low

Boiling Point

high

Light Range Fuels

- Gasoline
- Kerosene
- Turpentine

Mid-range Fuels

- Fuel Oil
- Diesel Fuel
- Jet Fuel

Heavy Hydrocarbons

- Motor Oil
- Crude Oil

25 nano-meters (nm)

Emitted Wavelength

200 nm

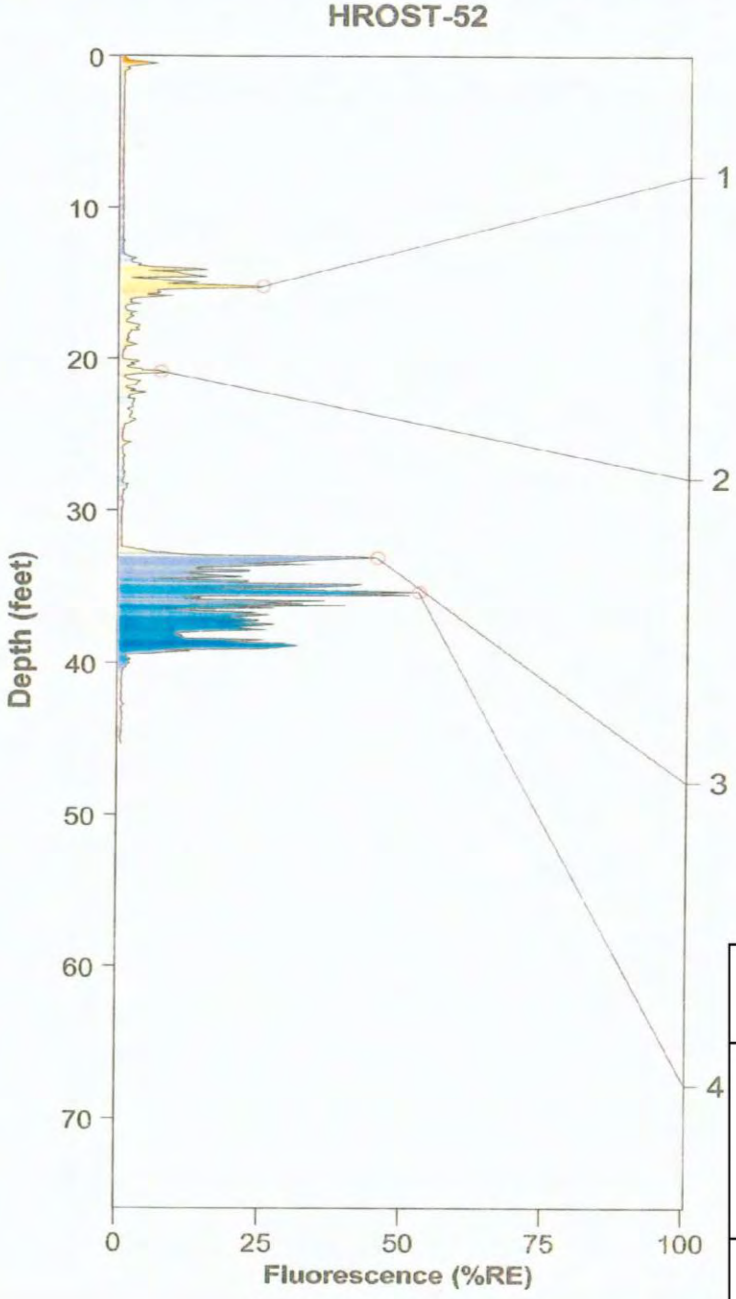
HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

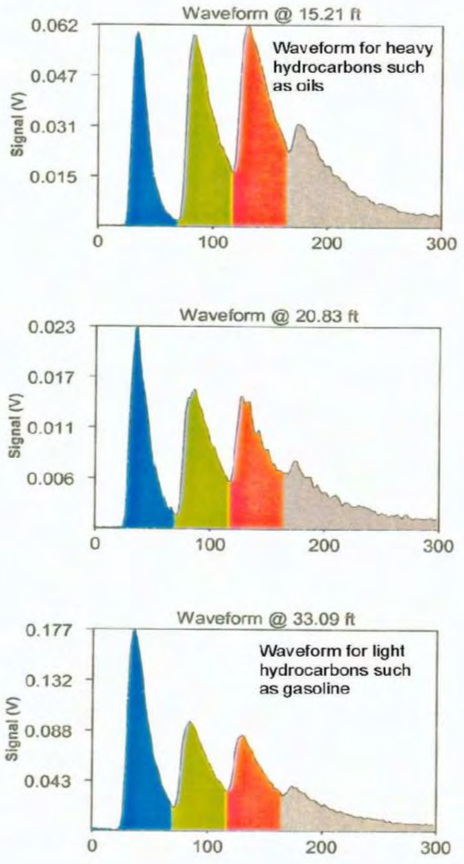
FIGURE 24
Hydrocarbons Detected Using Fluorescence Techniques

TETRA TECH

ROST Fluorescence Response Data

Site: Village of Hartford	Operator: ddeleon
Client: Clayton Group Services	Fugro Job #: 0303-0921
Date/Time: 1/31/2004 @ 9:25:28 AM	Max fluorescence: 52.41% @ 35.35 ft
ROST Unit: 1	Final depth BGS: 45.31 ft



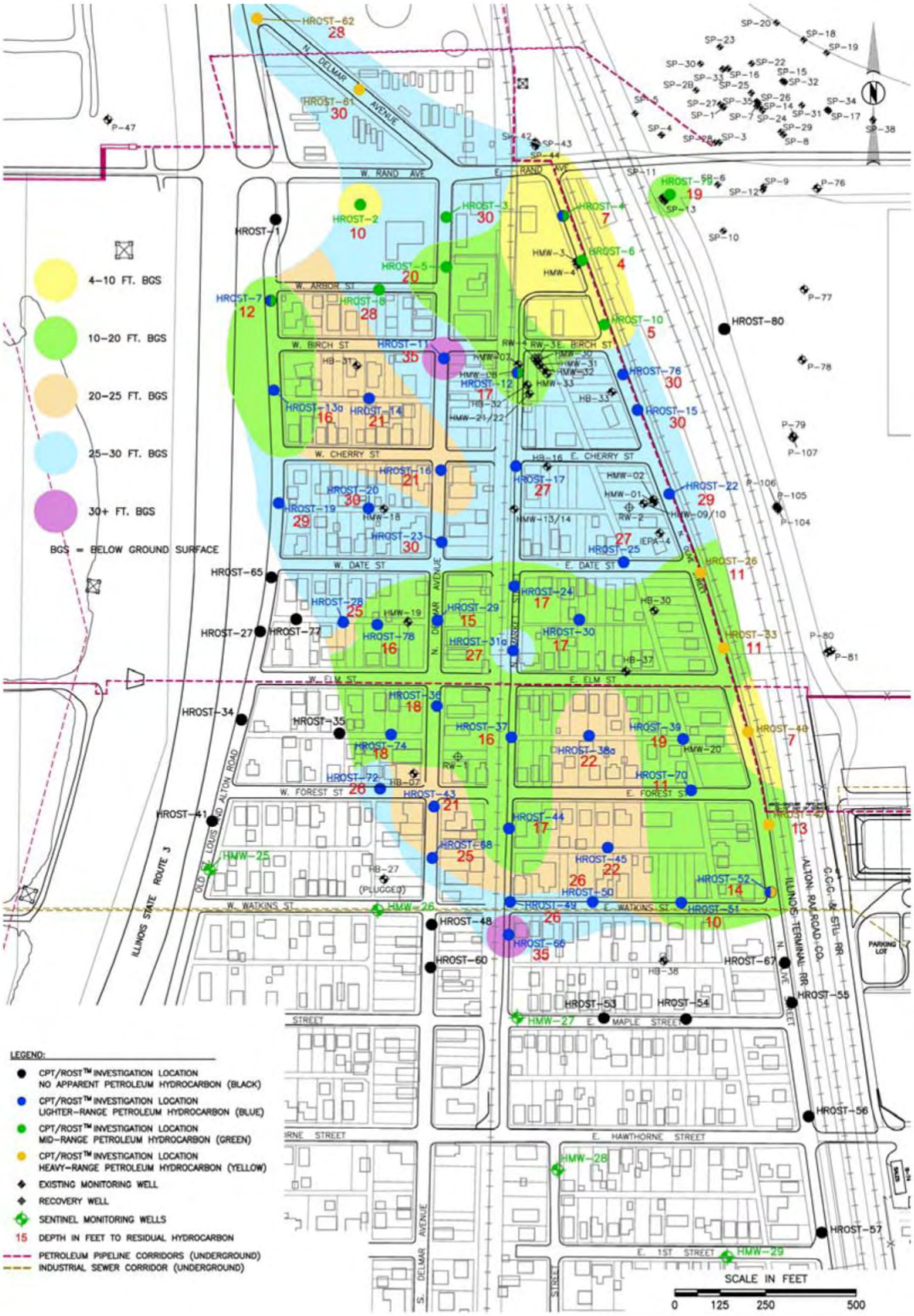


Source: Clayton 2004b.

HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

FIGURE 25
EXAMPLE ROST FLUORESCENCE RESPONSE DATA

TETRA TECH EM INC.

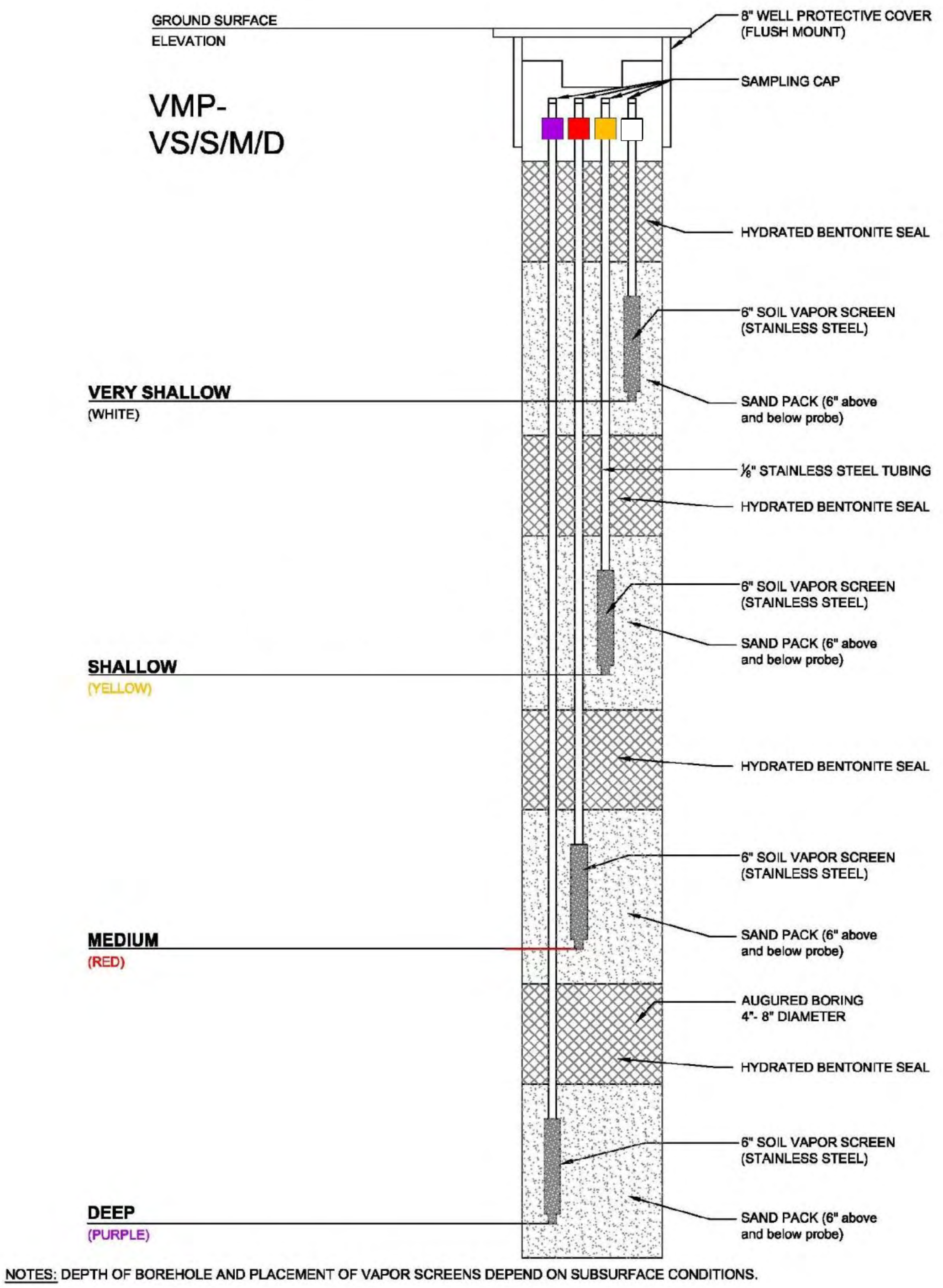


HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

FIGURE 26
Inferred Depth to First Encountered Residual Petroleum Hydrocarbon

TETRA TECH

Source: ENSR 2005



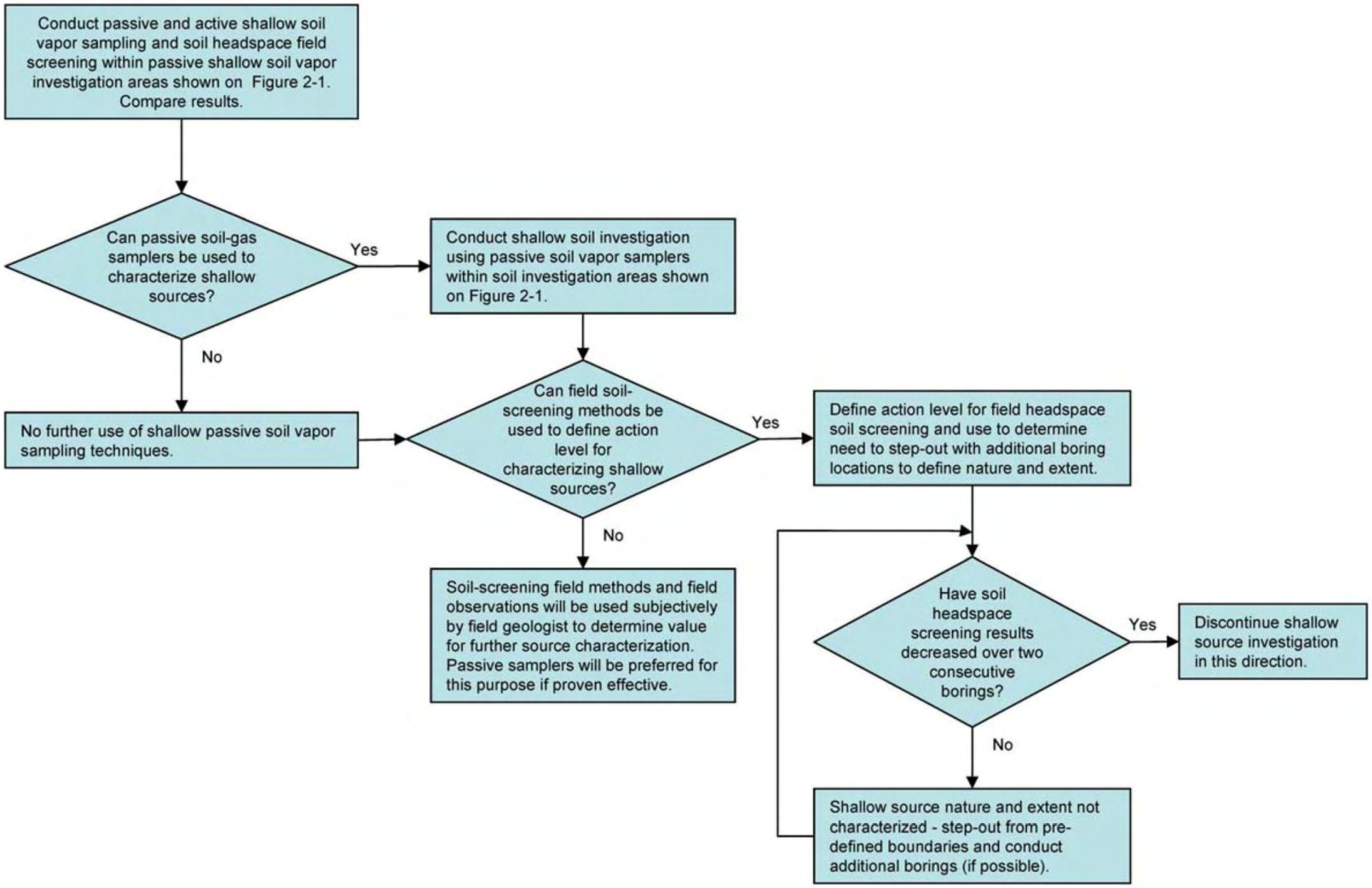
NOTES: DEPTH OF BOREHOLE AND PLACEMENT OF VAPOR SCREENS DEPEND ON SUBSURFACE CONDITIONS.

HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

FIGURE 27
Typical Nested Soil Vapor Monitoring Port Construction

TETRA TECH

Source: ENSR 2005

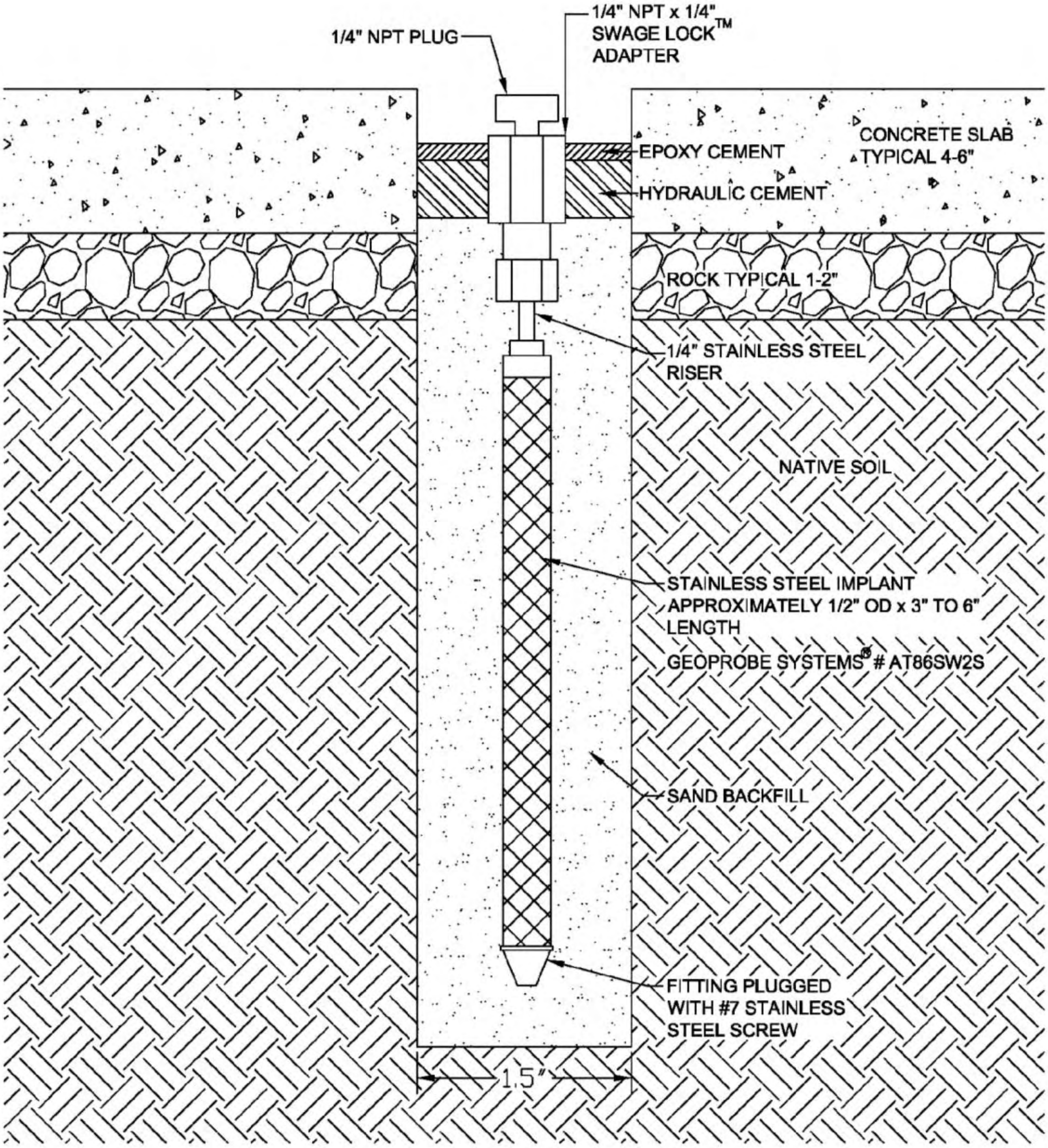


HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

FIGURE 28
Decision Tree for Passive Soil Vapor Survey and Shallow Soil Investigation

TETRA TECH

Source: ENSR 2005



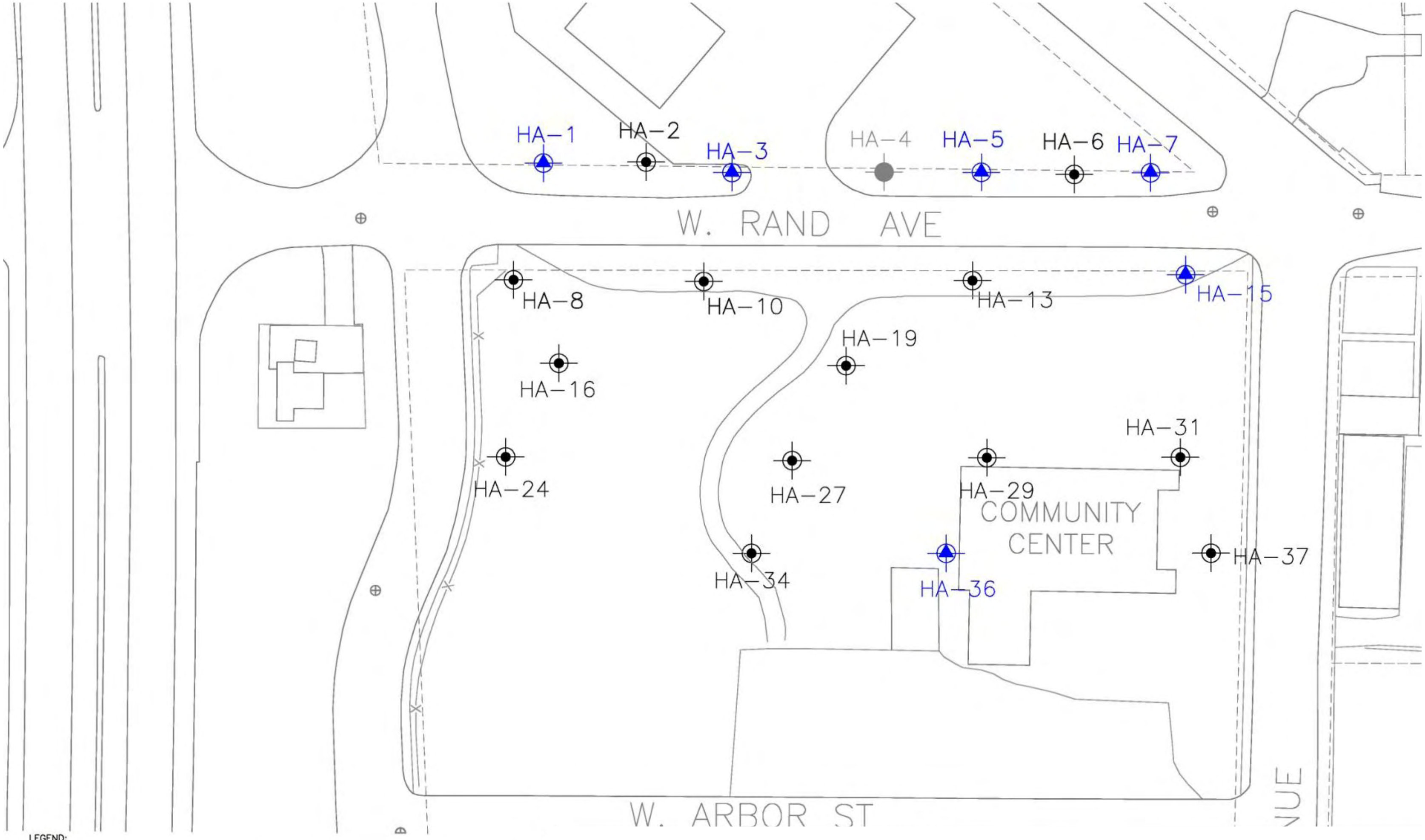
NOT TO SCALE

HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

FIGURE 29
Sub-Slab Monitoring Point

TETRA TECH

Source: ENSR 2005



Source: ENSR 2005

HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

FIGURE 30
Area 1 – Passive Shallow Soil Vapor Sampling Locations

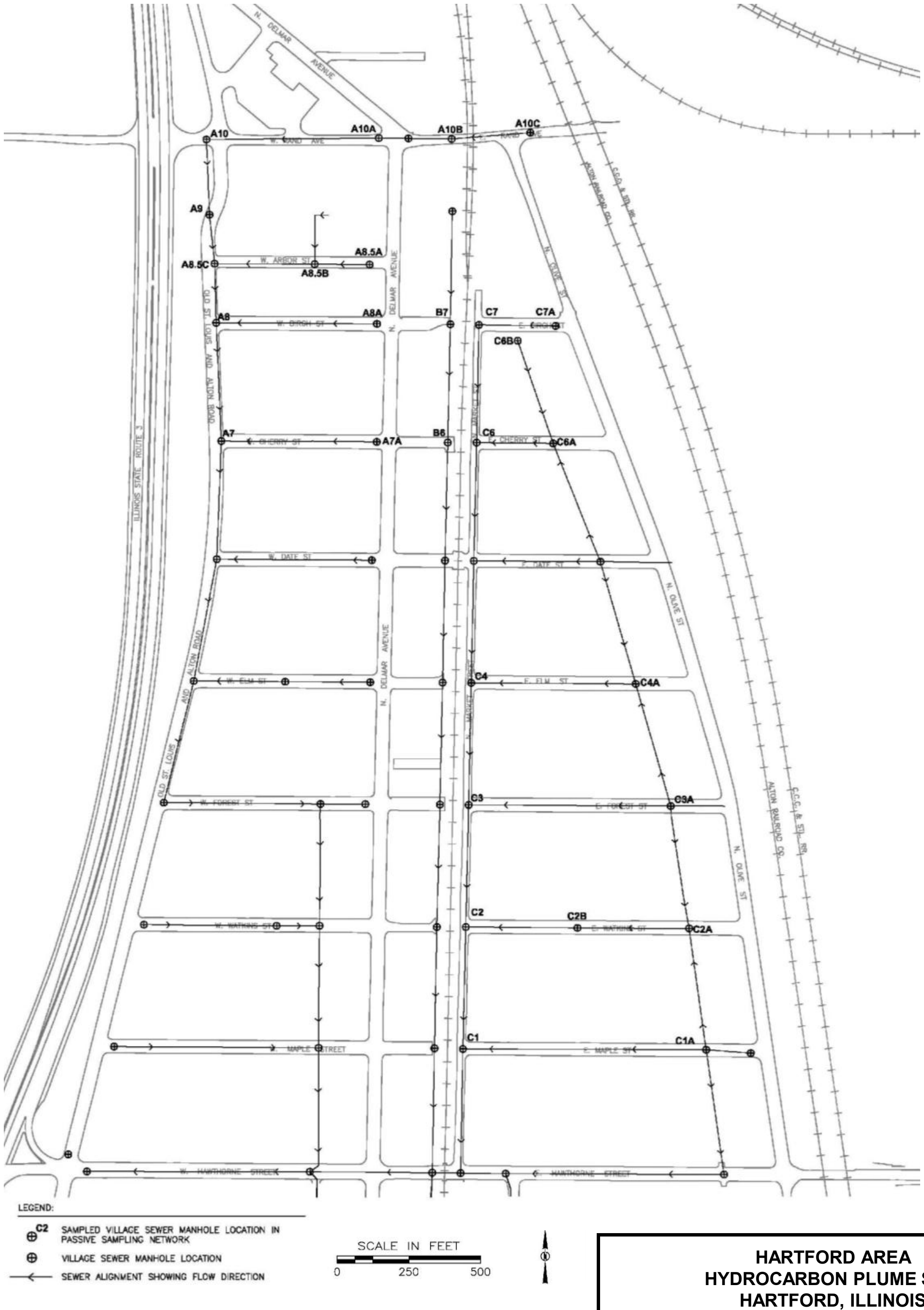
TETRA TECH

HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

FIGURE 31
Area 2 – Passive Soil Gas Vapor Sampling Locations

TETRA TECH

Source: ENSR 2005

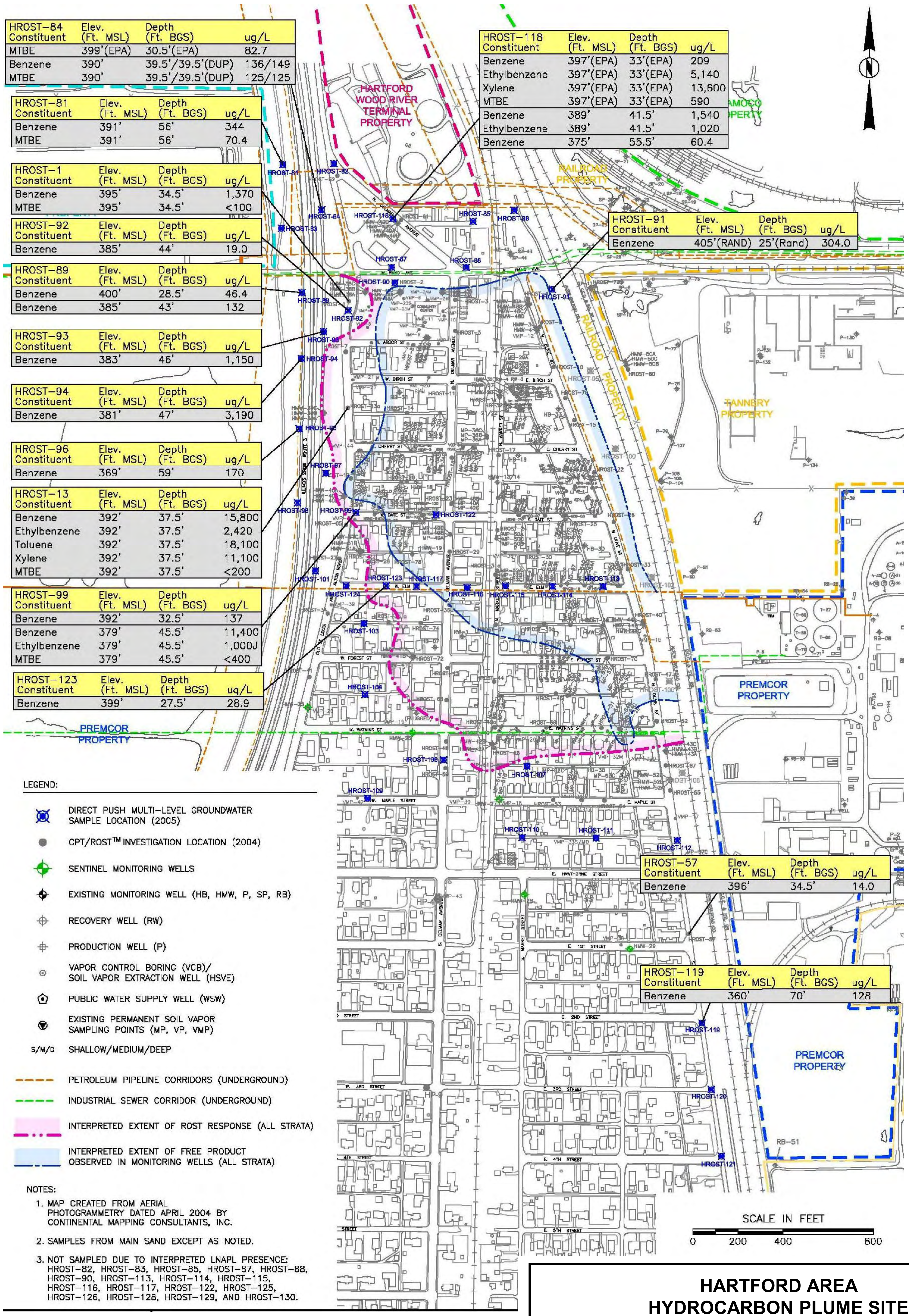


Source: ENSR 2005

HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

FIGURE 32
Passive Soil Gas Sewer Sampling Location Map

TETRA TECH



HROST-84 Constituent	Elev. (Ft. MSL)	Depth (Ft. BGS)	ug/L
MTBE	399'(EPA)	30.5'(EPA)	82.7
Benzene	390'	39.5'/39.5'(DUP)	136/149
MTBE	390'	39.5'/39.5'(DUP)	125/125

HROST-118 Constituent	Elev. (Ft. MSL)	Depth (Ft. BGS)	ug/L
Benzene	397'(EPA)	33'(EPA)	209
Ethylbenzene	397'(EPA)	33'(EPA)	5,140
Xylene	397'(EPA)	33'(EPA)	13,600
MTBE	397'(EPA)	33'(EPA)	590
Benzene	389'	41.5'	1,540
Ethylbenzene	389'	41.5'	1,020
Benzene	375'	55.5'	60.4

HROST-81 Constituent	Elev. (Ft. MSL)	Depth (Ft. BGS)	ug/L
Benzene	391'	56'	344
MTBE	391'	56'	70.4

HROST-1 Constituent	Elev. (Ft. MSL)	Depth (Ft. BGS)	ug/L
Benzene	395'	34.5'	1,370
MTBE	395'	34.5'	<100

HROST-91 Constituent	Elev. (Ft. MSL)	Depth (Ft. BGS)	ug/L
Benzene	405'(RAND)	25'(Rand)	304.0

HROST-92 Constituent	Elev. (Ft. MSL)	Depth (Ft. BGS)	ug/L
Benzene	385'	44'	19.0

HROST-89 Constituent	Elev. (Ft. MSL)	Depth (Ft. BGS)	ug/L
Benzene	400'	28.5'	46.4
Benzene	385'	43'	132

HROST-93 Constituent	Elev. (Ft. MSL)	Depth (Ft. BGS)	ug/L
Benzene	383'	46'	1,150

HROST-94 Constituent	Elev. (Ft. MSL)	Depth (Ft. BGS)	ug/L
Benzene	381'	47'	3,190

HROST-96 Constituent	Elev. (Ft. MSL)	Depth (Ft. BGS)	ug/L
Benzene	369'	59'	170

HROST-13 Constituent	Elev. (Ft. MSL)	Depth (Ft. BGS)	ug/L
Benzene	392'	37.5'	15,800
Ethylbenzene	392'	37.5'	2,420
Toluene	392'	37.5'	18,100
Xylene	392'	37.5'	11,100
MTBE	392'	37.5'	<200

HROST-99 Constituent	Elev. (Ft. MSL)	Depth (Ft. BGS)	ug/L
Benzene	392'	32.5'	137
Benzene	379'	45.5'	11,400
Ethylbenzene	379'	45.5'	1,000J
MTBE	379'	45.5'	<400

HROST-123 Constituent	Elev. (Ft. MSL)	Depth (Ft. BGS)	ug/L
Benzene	399'	27.5'	28.9

HROST-57 Constituent	Elev. (Ft. MSL)	Depth (Ft. BGS)	ug/L
Benzene	396'	34.5'	14.0

HROST-119 Constituent	Elev. (Ft. MSL)	Depth (Ft. BGS)	ug/L
Benzene	360'	70'	128

LEGEND:

⊠	DIRECT PUSH MULTI-LEVEL GROUNDWATER SAMPLE LOCATION (2005)
●	CPT/ROST™ INVESTIGATION LOCATION (2004)
⊕	SENTINEL MONITORING WELLS
⊕	EXISTING MONITORING WELL (HB, HMW, P, SP, RB)
⊕	RECOVERY WELL (RW)
⊕	PRODUCTION WELL (P)
⊙	VAPOR CONTROL BORING (VCB)/ SOIL VAPOR EXTRACTION WELL (HSVE)
⊙	PUBLIC WATER SUPPLY WELL (WSW)
▼	EXISTING PERMANENT SOIL VAPOR SAMPLING POINTS (MP, VP, VMP)
S/M/D	SHALLOW/MEDIUM/DEEP
- - - -	PETROLEUM PIPELINE CORRIDORS (UNDERGROUND)
- - - -	INDUSTRIAL SEWER CORRIDOR (UNDERGROUND)
🟪	INTERPRETED EXTENT OF ROST RESPONSE (ALL STRATA)
🟦	INTERPRETED EXTENT OF FREE PRODUCT OBSERVED IN MONITORING WELLS (ALL STRATA)

NOTES:

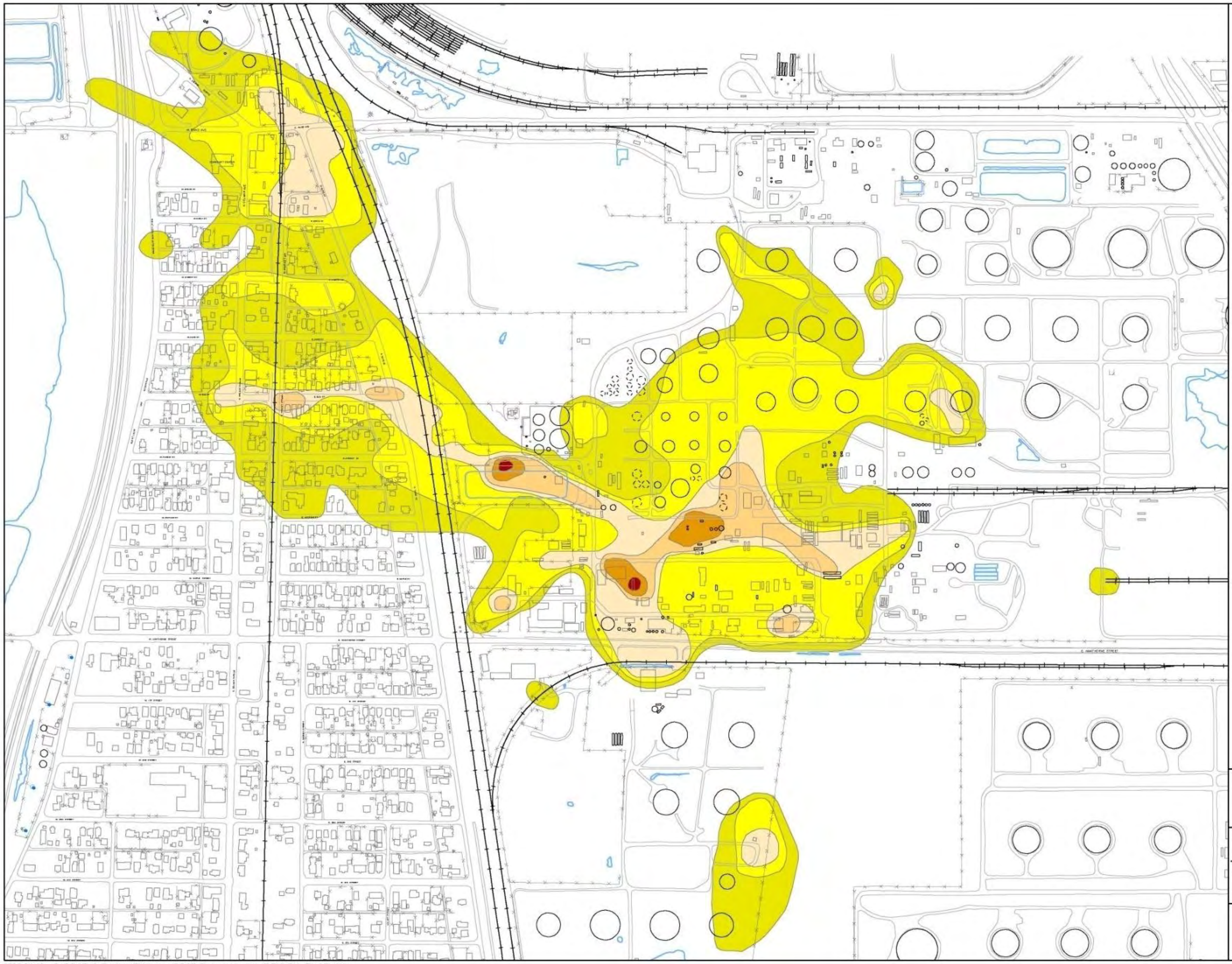
1. MAP CREATED FROM AERIAL PHOTOGRAMMETRY DATED APRIL 2004 BY CONTINENTAL MAPPING CONSULTANTS, INC.
2. SAMPLES FROM MAIN SAND EXCEPT AS NOTED.
3. NOT SAMPLED DUE TO INTERPRETED LNAPL PRESENCE: HROST-82, HROST-83, HROST-85, HROST-87, HROST-88, HROST-90, HROST-113, HROST-114, HROST-115, HROST-116, HROST-117, HROST-122, HROST-125, HROST-126, HROST-128, HROST-129, AND HROST-130.

HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

FIGURE 33
Dissolved Phase and ROST Free-Product Extents

TETRA TECH

Source: Clayton 2006c



Sources: Clayton Group Services, Inc. 2006a.,
Clayton Group Services, Inc. 2004b.,
Clayton Group Services, Inc. 2006c.
Howe 2006

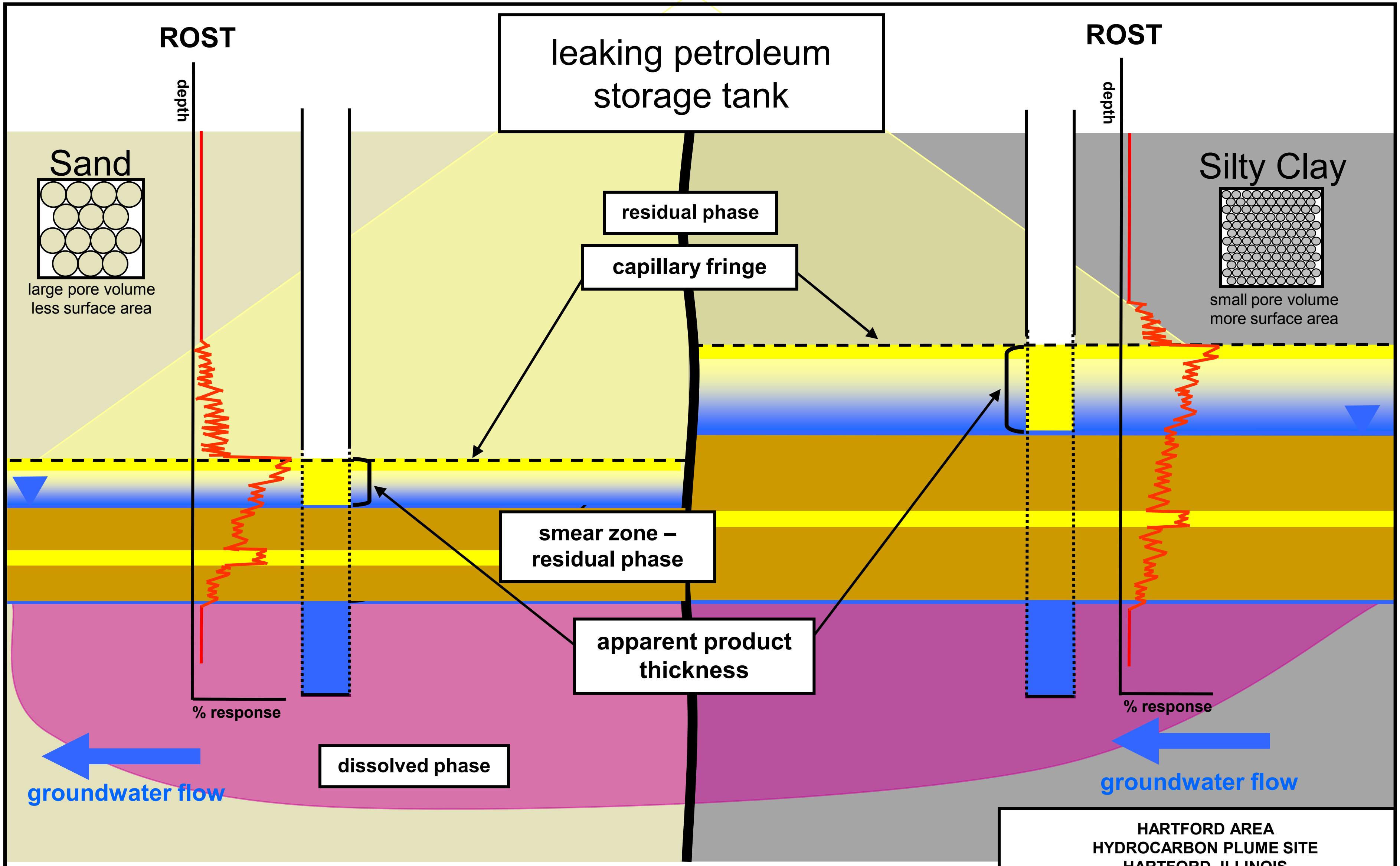
HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

Figure 34

TOTAL PETROLEUM HYDROCARBON ROST RESPONSE THICKNESS

TETRA TECH EM INC.

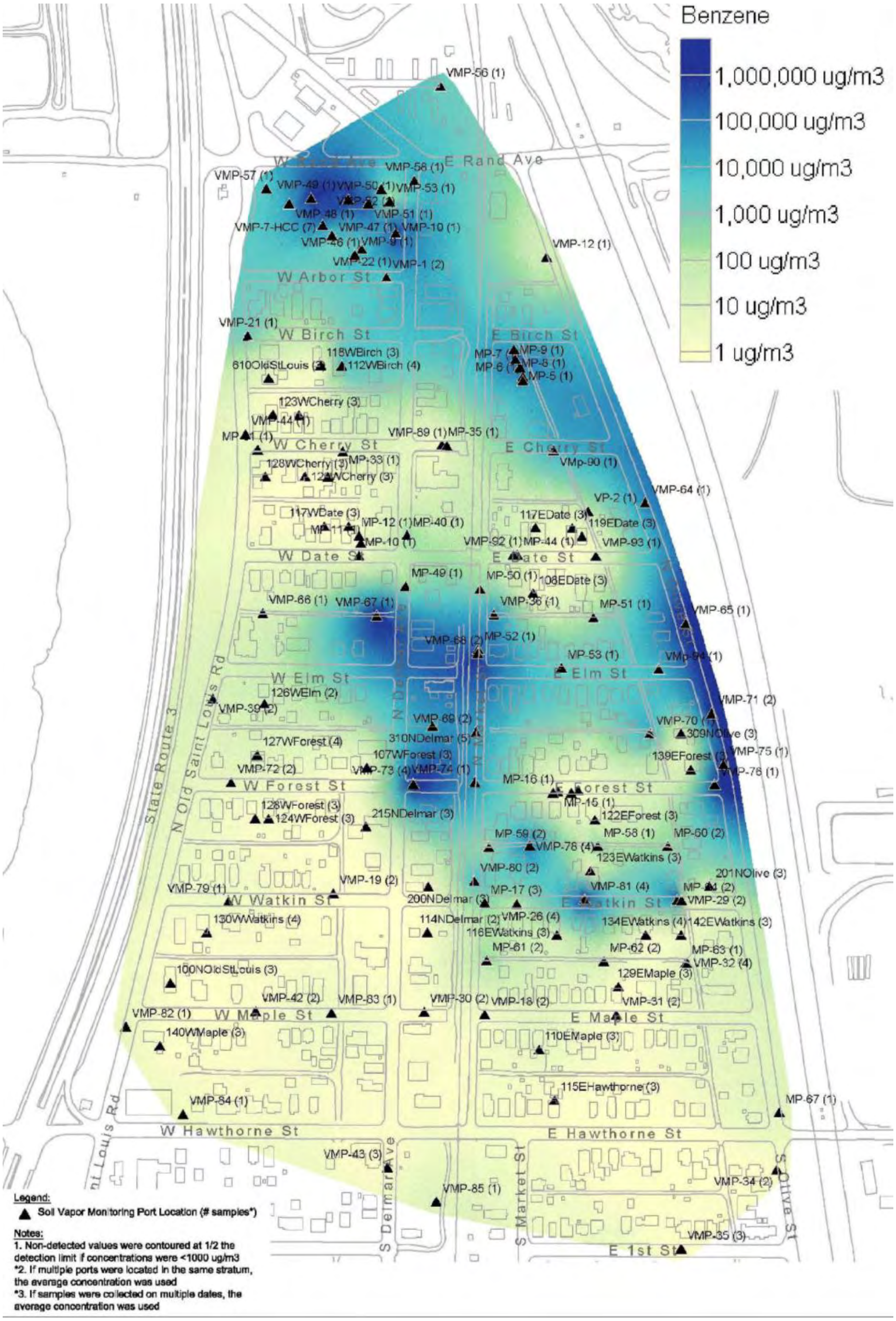
2006-04-12 O:\DOJ\Fig9_Product_Thickness_ROST_Responses.mxd TtEMI-DN Paul.Rogalla



HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

FIGURE 35
Apparent Product Thickness, and ROST Response

TETRA TECH



Legend:

▲ Soil Vapor Monitoring Port Location (# samples*)

Notes:

1. Non-detected values were contoured at 1/2 the detection limit if concentrations were <1000 ug/m3

*2. If multiple ports were located in the same stratum, the average concentration was used

*3. If samples were collected on multiple dates, the average concentration was used

SCALE IN FEET

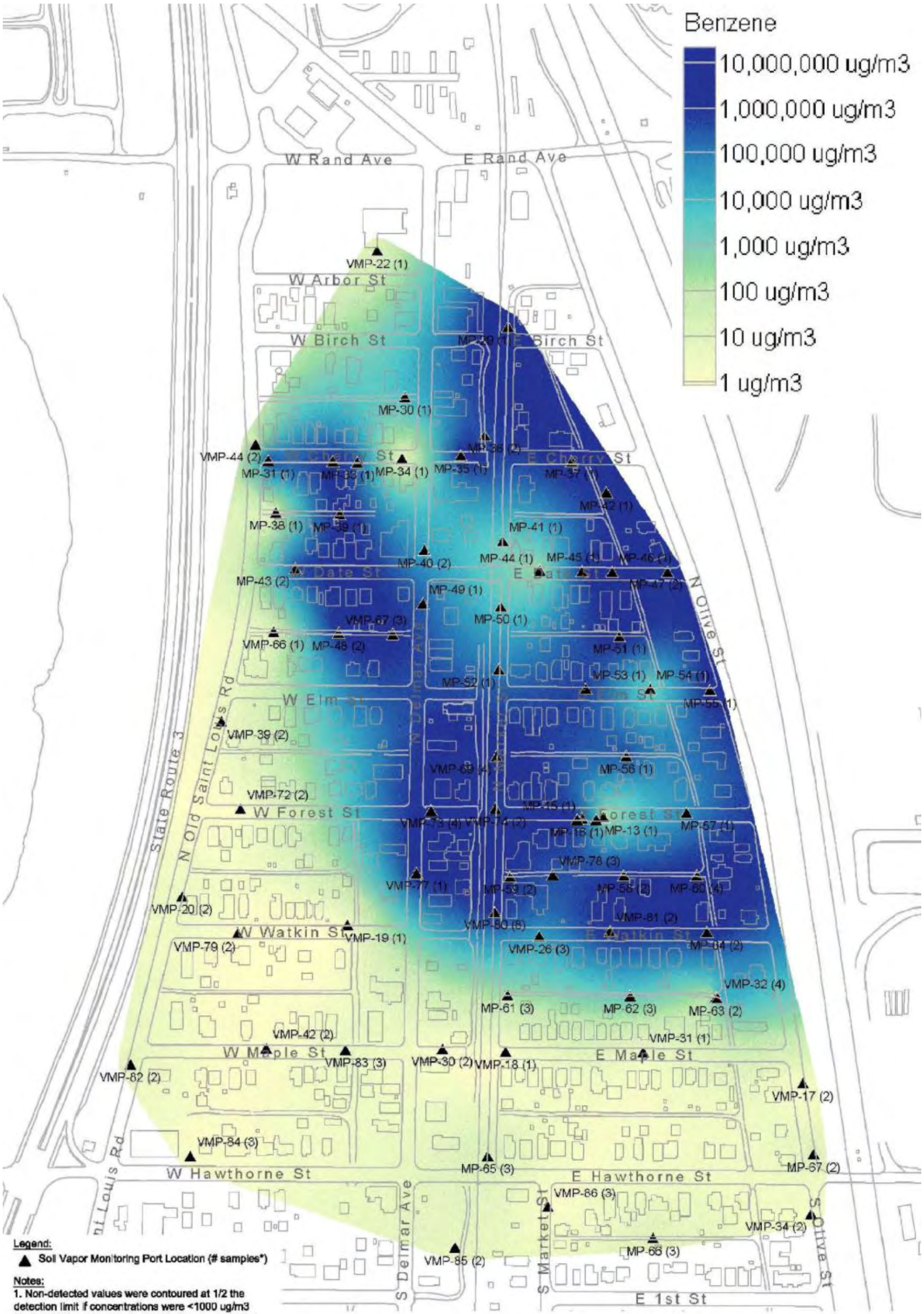
0 250 500

Source: ENSR 2005

HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

FIGURE 36
Benzene Soil Gas Distribution in A-Clay Stratum

TETRA TECH



Legend:

▲ Soil Vapor Monitoring Port Location (# samples*)

Notes:

1. Non-detected values were contoured at 1/2 the detection limit if concentrations were <1000 ug/m3

*2. If multiple ports were located in the same stratum, the average concentration was used

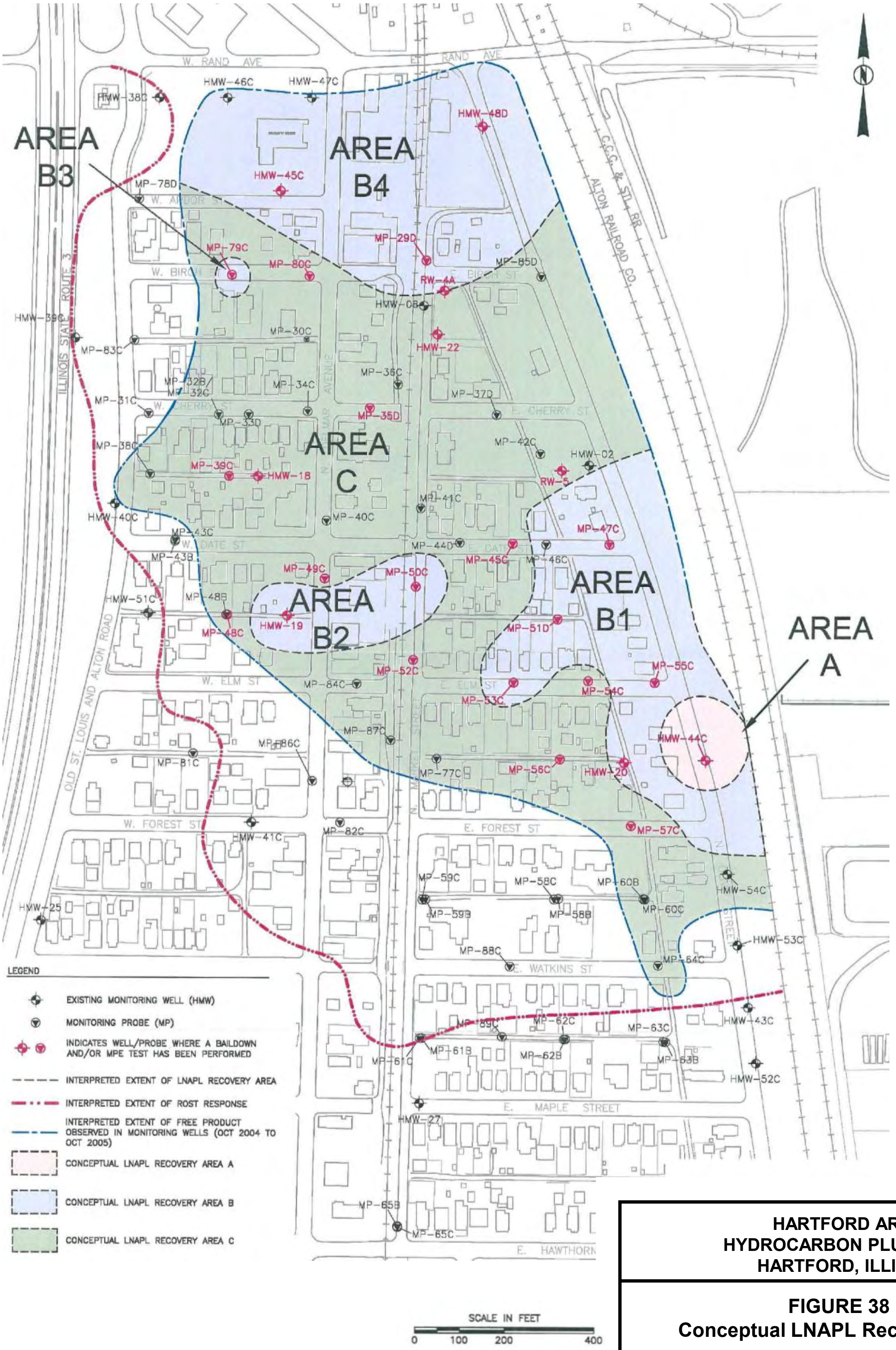
*3. If samples were collected on multiple dates, the average concentration was used

Source: ENSR 2005

HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

FIGURE 37
Benzene Soil Gas Distribution in Main Sand Stratum

TETRA TECH

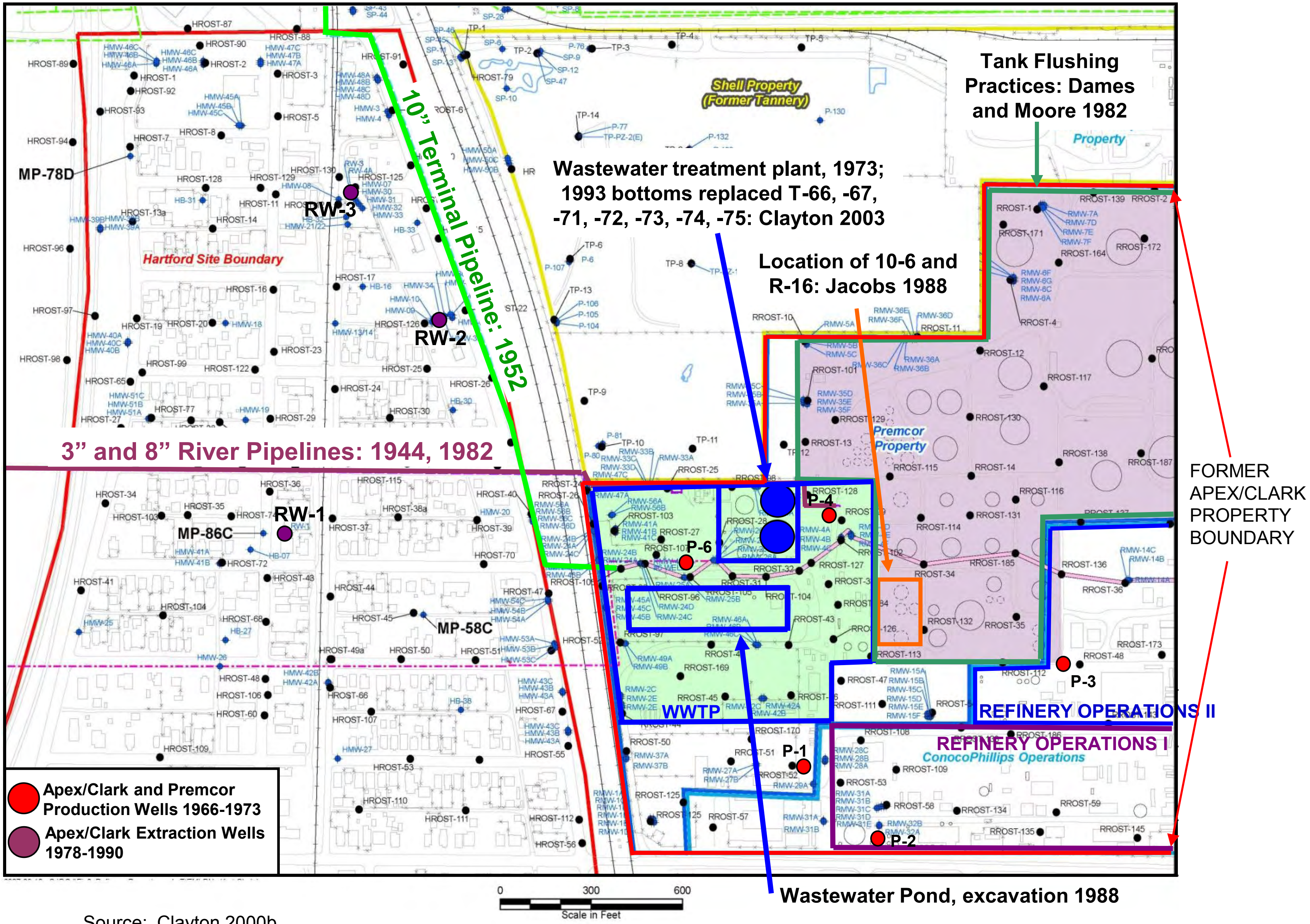


HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

FIGURE 38
Conceptual LNAPL Recover Areas

TETRA TECH

Source: Clayton 2006c



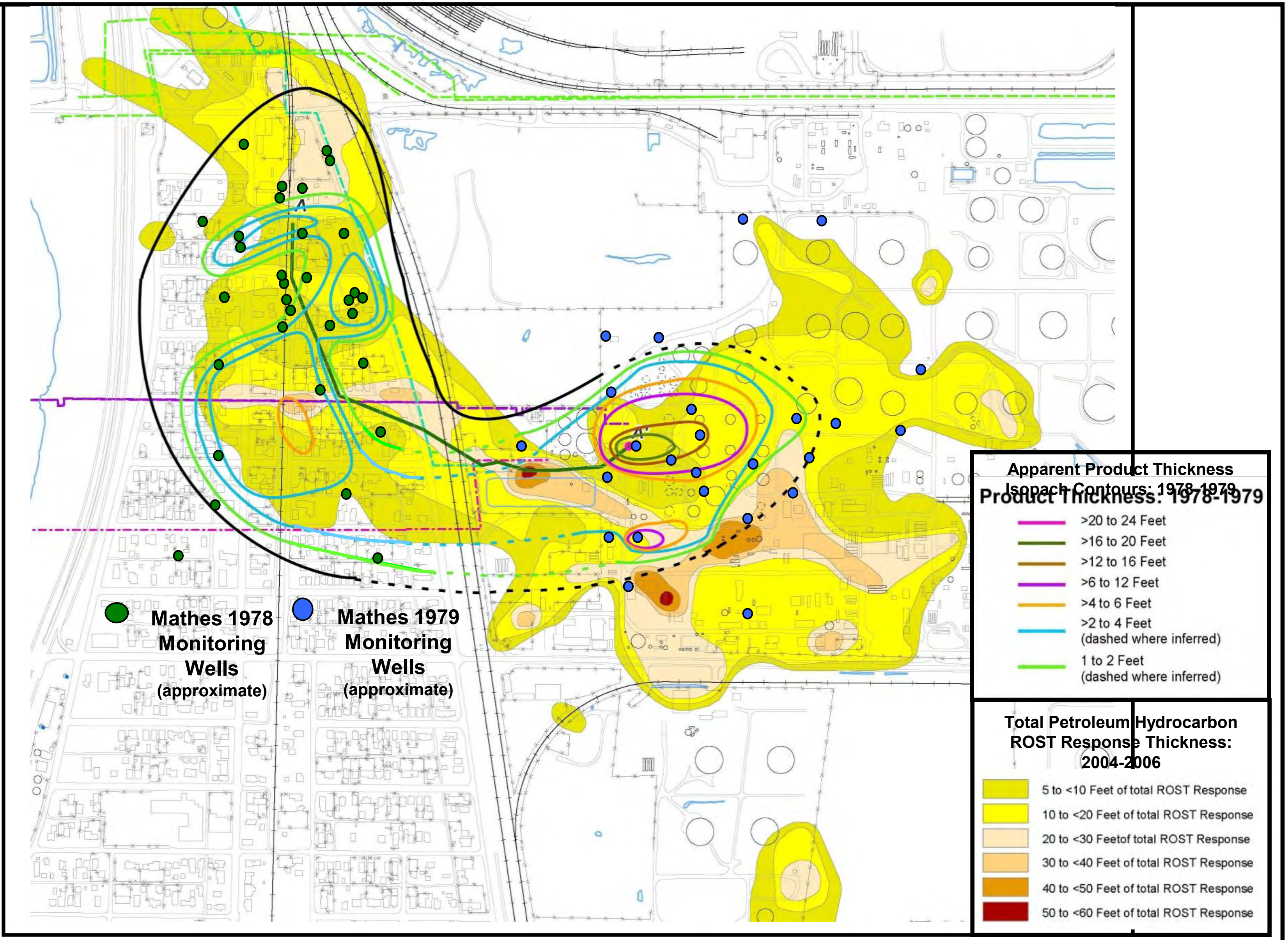
Source: Clayton 2000b

HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

FIGURE 39

Site Salient Features

TETRA TECH

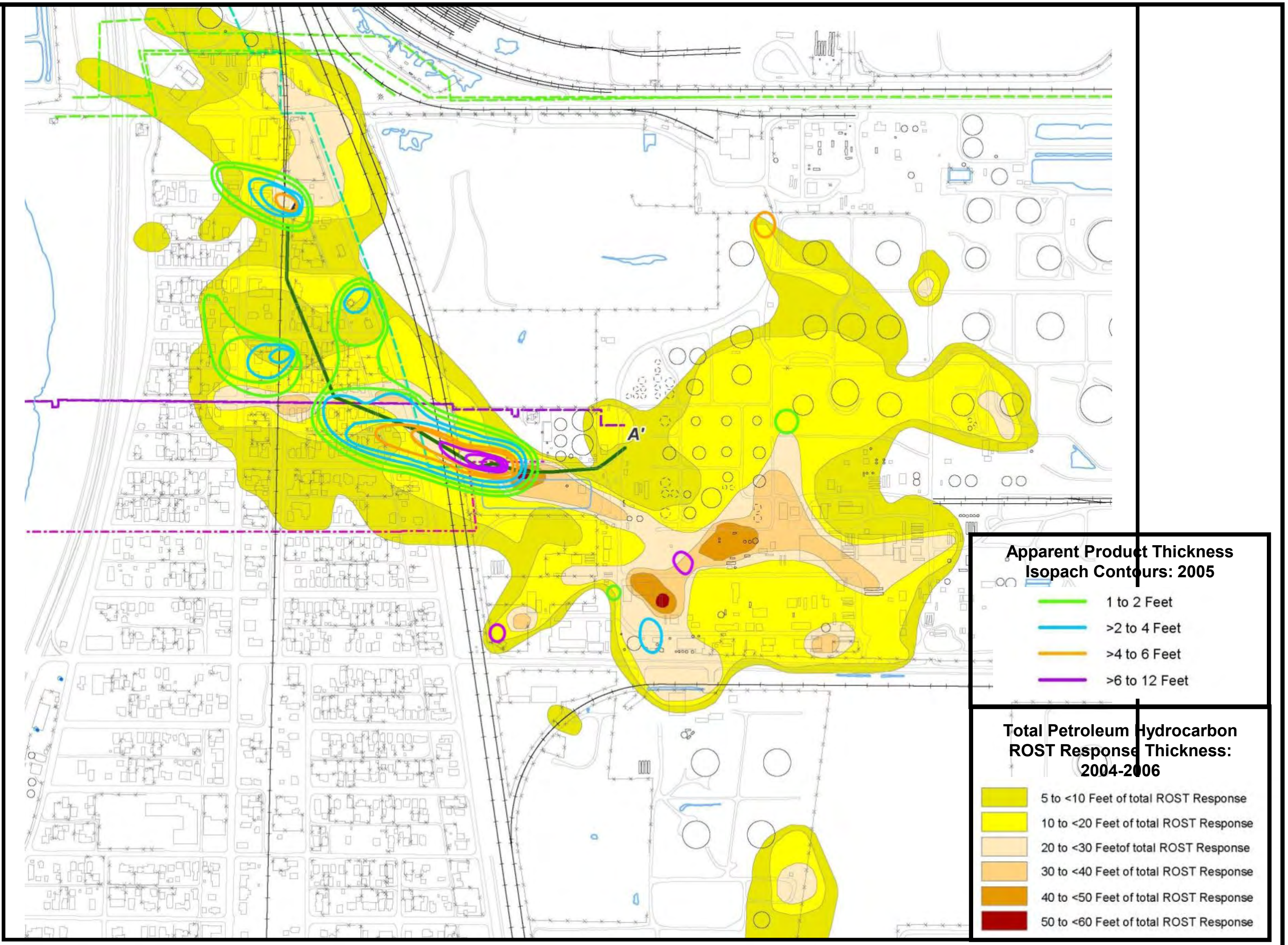


Source: Howe 2006; Clayton 2004, 2006a,c

HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

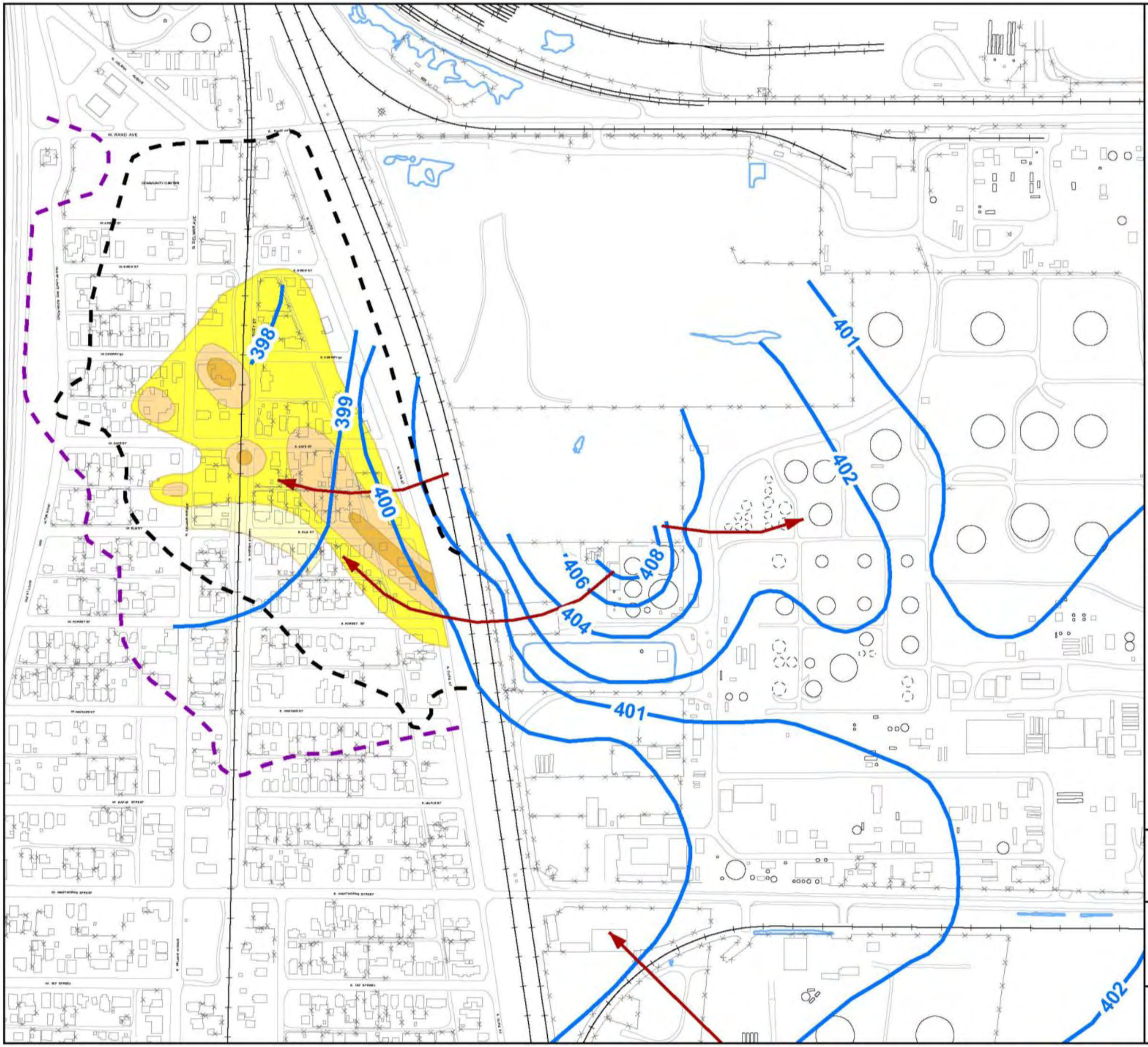
FIGURE 40
Historic Apparent Product Thickness
Versus Modern ROST Plume

TETRA TECH



Source: Howe 2006; Clayton 2004, 2006a,c

HARTFORD AREA HYDROCARBON PLUME SITE HARTFORD, ILLINOIS	FIGURE 41 Modern Apparent Product Thickness Versus Modern ROST Plume	TETRA TECH

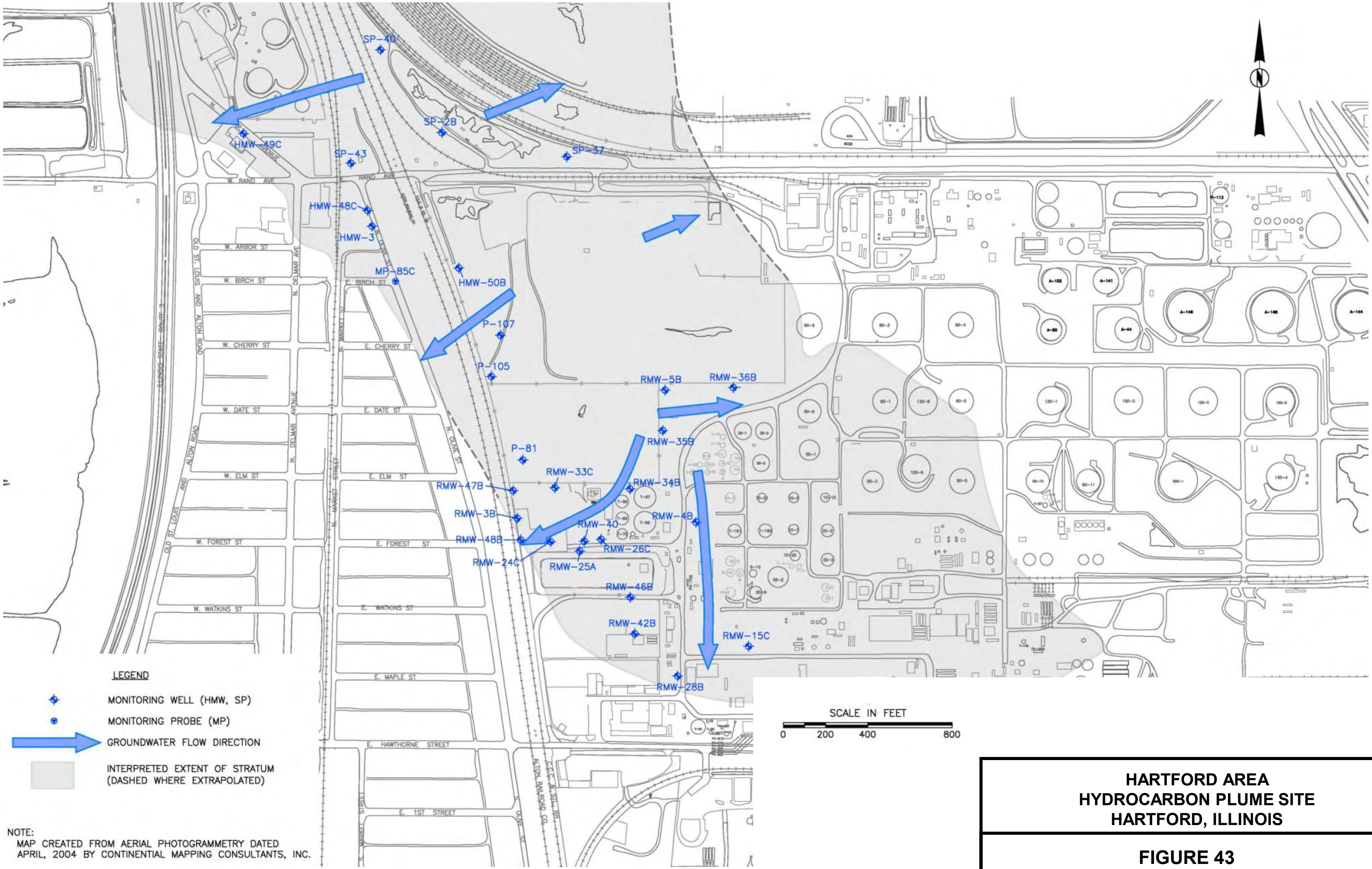


Adapted from Clayton 2006
Active LNAPL Recovery
System Proposal, Section 5.0
Expert Opinion Paper

HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

Figure 42
PIEZOMETRIC SURFACE AND LNAPL CONDUCTIVITY ISOPLETH

TETRA TECH EM INC



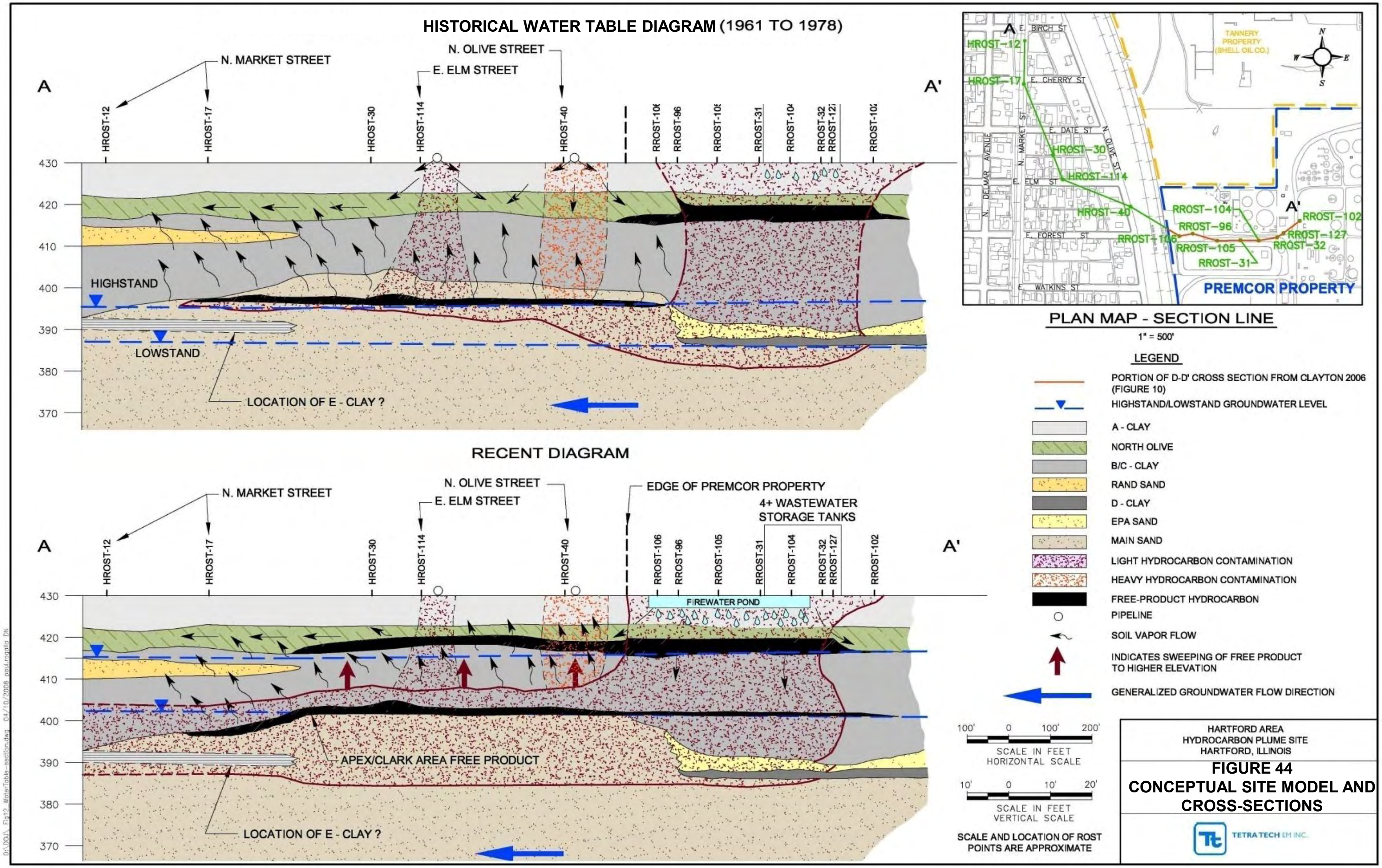
NOTE:
MAP CREATED FROM AERIAL PHOTOGRAMMETRY DATED APRIL, 2004 BY CONTINENTAL MAPPING CONSULTANTS, INC.

HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

FIGURE 43
Generalized Groundwater Flow Direction
EPA Stratum, Oct 2004 – Oct 2005

TETRA TECH

Source: Clayton 2006c

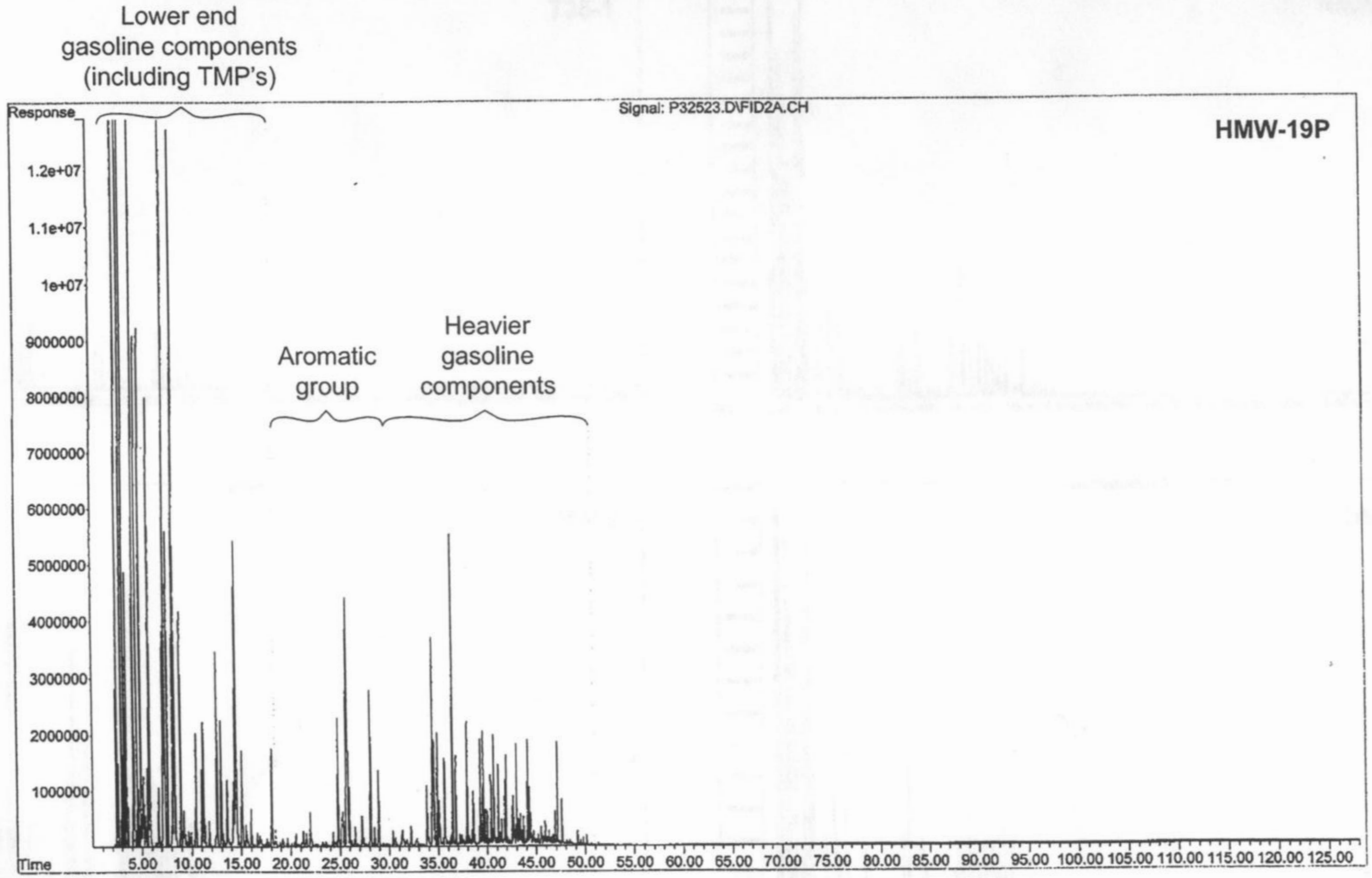


HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

FIGURE 44
CONCEPTUAL SITE MODEL AND CROSS-SECTIONS

TETRA TECH EM INC.

Source: Howe 2006

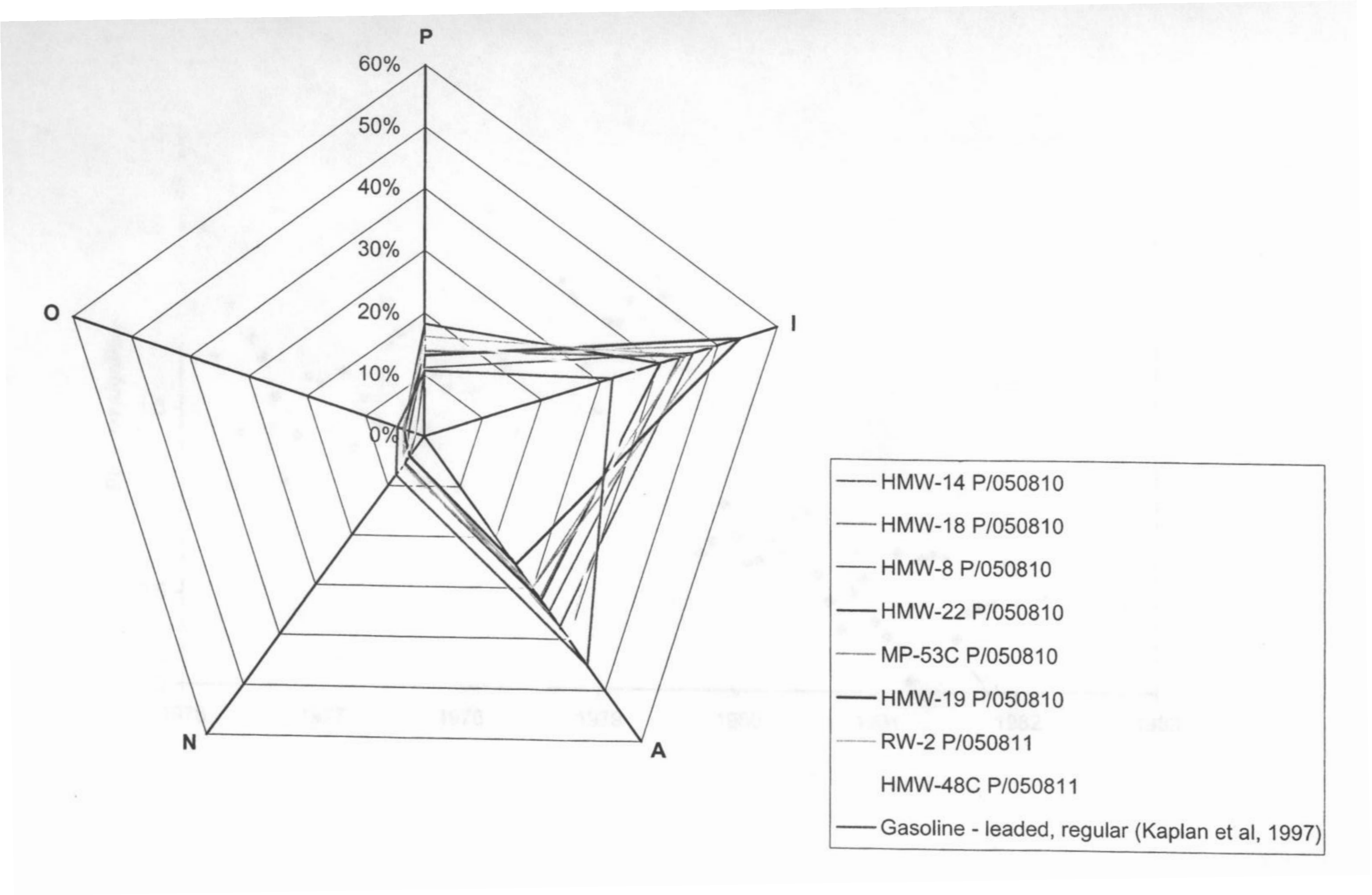


Source: Nicholson 2006

HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

FIGURE 45
Typical Gas Chromatogram of Refinery Derived Free Product

TETRA TECH



HARTFORD AREA
HYDROCARBON PLUME SITE
HARTFORD, ILLINOIS

FIGURE 46
PIANO Distribution of Free Product from the Village of Hartford, Illinois

TETRA TECH

Source: Nicholson 2006

Table 1: Optical Screening Tools

Model	Manufacturer / Providers	Technology / Deployment	Target
Not Applicable	Site Characterization and Analysis Penetrometer System (SCAPS) (Army/Navy AF) government use	nitrogen laser-337 nm OMA detector, Cone Penetrometer (CPT) only	fuels/oils (poor jet fuel response)
FFD - Fuel Florescence Detector	Vertek Corporation manufactured offered by numerous field service vendors	CW Hg Lamp - 254.7 nm PMT CPT only	fuels/oils containing low to moderate PAH
ROST - Rapid Optical Screening Tool	Dakota Technologies Fugro exclusively	dye laser - 290 nm spectral/temporal Percussion & CPT	fuels/oils containing low to moderate PAH
UVOST - Ultra-Violet Optical Screening Tool	Dakota Technologies offered by numerous field service providers	XeCL laser - 308 nm spectral/temporal Percussion & CPT	fuels/oils containing low to moderate PAH
TarGOST - Tar-specific Green Optical Screening Tool	Dakota Technologies Dakota exclusively	ND:YAG laser - 532 nm spectral/temporal Percussion & CPT	coal tars/creosotes containing moderate to heavy PAH
Soil Color (late stage development)	Dakota Technologies manufactured to be offered by field service providers	broadband white light reflectance Percussion & CPT	Munsell soil color, soil class

Source: Dakota Technologies 2008

Table 2: Indoor Air and Sub-Slab Analysis Analyte Lists
Village of Hartford, Illinois

INDOOR AIR

Compound	Revised Comparison Value (1)	Units
1,3-BUTADIENE	2	ug/m3
HEXANE	200	ug/m3
BENZENE	10 / 29 (2)	ug/m3
METHYLCYCLOHEXANE	3000	ug/m3
TOLUENE	300	ug/m3
M,P-XYLENE	217	ug/m3
O-XYLENE	217	ug/m3
1,2,4-TRIMETHYLBENZENE	6	ug/m3
1,3,5-TRIMETHYLBENZENE	6	ug/m3
ISOPENTANE	115	ug/m3
BUTANE	115	ug/m3
OXYGEN	NA	%
METHANE	NA	%
CARBON DIOXIDE	NA	%

(1) Comparison Values as defined in EMP, 7/12/07

(2) Benzene Chronic / Benzene Acute.

ug/m3 - micrograms per cubic meter

NA - not applicable

NR - not recorded

U - compound was analyzed for but not detected above the reporting limit

J - estimated value

E - exceeds instrument calibration range

UJ - non-detected compound associated with low bias in the CCV

-- compound was not analyzed

PID/FID readings taken in breathing zone of sample collection area

PID/FID readings obtained with a TVA 1000

PID/FID readings in parts per million (ppm)

SUB-SLAB

Compound	Revised Comparison Value (1)	Units
1,3-BUTADIENE	20	ug/m3
HEXANE	2000	ug/m3
BENZENE	100 / 290 (2)	ug/m3
METHYLCYCLOHEXANE	30000	ug/m3
TOLUENE	3000	ug/m3
M,P-XYLENE	2170	ug/m3
O-XYLENE	2170	ug/m3
1,2,4-TRIMETHYLBENZENE	60	ug/m3
1,3,5-TRIMETHYLBENZENE	60	ug/m3
ISOPENTANE	1150	ug/m3
BUTANE	1150	ug/m3
OXYGEN	NA	%
METHANE	NA	%
CARBON DIOXIDE	NA	%

(1) Comparison Values as defined in EMP, 7/12/07

(2) Benzene Chronic / Benzene Acute.

ug/m3 - micrograms per cubic meter

NA - not applicable

NR - not recorded

U - compound was analyzed for but not detected above the reporting limit

J - estimated value

E - exceeds instrument calibration range

UJ - non-detected compound associated with low bias in the CCV

-- compound was not analyzed

PID/FID readings obtained with a TVA 1000

PID/FID readings in parts per million (ppm)

Pressure readings are recorded as inches of water

Table 3: Tabulated BTEX Values and Maximum Contaminant Levels

Monitoring Well ID	**Sample Date**	**Concentration (µg/L)**			
		Benzene	**Ethylbenzene**	**Toluene**	**Xylenes (total)**
MP-86C	7/12/2005	34,300	2,320	29,900	10,900
	10/13/2005	29,200	2,230	26,800	10,600
MP-58C	7/14/2005	33,800	1,790	27,500	8,530
	10/13/2005	15,200	1,000	12,300	5,130
	10/13/2005 (Duplicate)	35,700	2,310	29,200	12,300
HB-37	2/3/2005	32,800	2,930	28,000	13,200
	4/18/2005	30,500	2,770	30,500	12,500
	10/12/2005	31,200	2,470	23,100	11,000
MP-78D	7/13/2005	15,400	1,590	24,300	7,680
	10/7/2005	20,300	2,550	29,000	11,500
MCL:		**5 µg/L**	**700 µg/L**	**1,000 µg/L**	**10,000 µg/L**

Table 4: Estimation of Total Product Volume

Core Hole	**Well**	**ROST**		**ROST**		**Total Porosity of:**		**Percent Total Product Saturation In:**	
			USCS code for saturated interval	**Fluorescence interval (feet)**	**Response type**	**Upper formations**	**Main and EPA Sands**	**Vadose Zone**	**Saturated Zone**
HCSB-1	HMW-44C	HROST-40	SW	12.0	yellow	51.4	41.0	2.5	4.6
HCSB-2	RW-5	HROST-126	unknown	12.5	blue	51.7	44.2	1.1	4.6
HCSB-3	MP-50C	HROST-24	SP	1.0	blue	N/A	42.7	4.6	5.9
HCSB-4	MP-39C	HROST-20	SW	1.0	blue	48.3	45.7	1.5	7.8
HCSB-5	MP-29D	HROST-130	SP	17.0	green	48.2	42.9	7.3	5.6
Overall						50.5	43.0	3.4	5.5
Undifferentiated						**45.2**		**4.8**	