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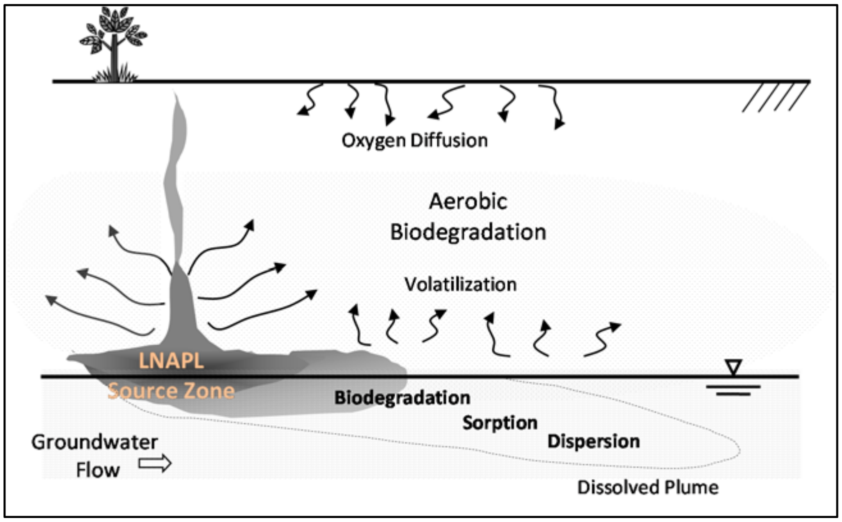
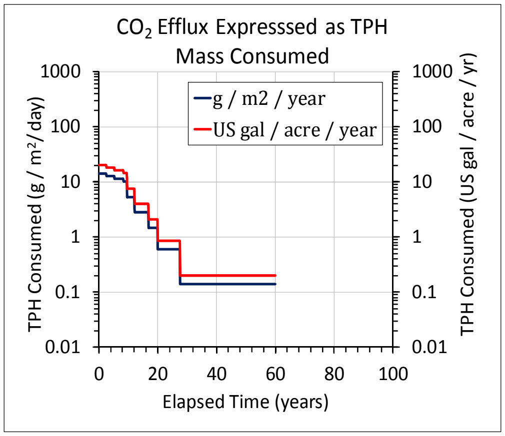
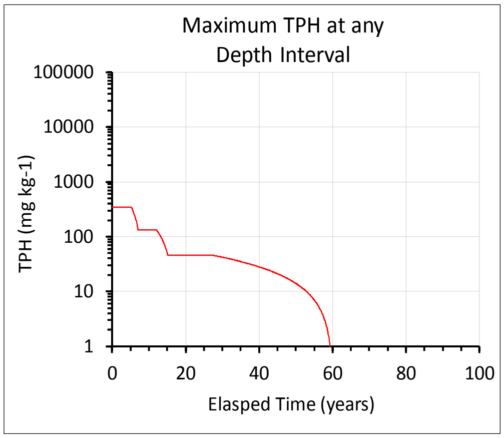
Toolkits for Evaluation of Monitored Natural Attenuation and Natural Source Zone Depletion







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REPORT

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SUMMARY

Introduction to Toolkits

Monitored natural attenuation (MNA) is a well-established remediation technology for petroleum hydrocarbon groundwater plumes and monitored natural source zone depletion (NSZD) is an emerging remedial approach involving the natural weathering of petroleum hydrocarbon (Light Non-Aqueous Phase Liquid – LNAPL) sources, which may be enhanced by partial removal of contamination or *in-situ* treatment. While processes for natural attenuation and depletion are well understood, less well known or documented are timelines for these processes or the effectiveness of remediation on source zone longevity, contaminant concentrations and plume lengths.

This knowledge is important in the current regulatory context in British Columbia, where new guidance is being considered to guide groundwater remediation requirements, which may include timelines for monitored natural attenuation or enhanced attenuation. Draft BC MoE Technical Guidance (TG) 22 on Monitored Natural Attenuation (MNA) and Enhanced Attenuation (EA) provides an overview of methods and information sources for evaluation of natural attenuation processes and remedial technologies that may be used to enhance source depletion.

More broadly, there are common questions on the science underlying MNA and NSZD that these toolkits address. Data and information gaps that currently exist include the time for source zones and plumes to attenuate to groundwater standards, which may have policy implications depending on the regulatory jurisdiction, available tools to assess MNA and NSZD, and the effectiveness of available remedial technologies to enhance concentration attenuation at petroleum hydrocarbon impacted sites. Available studies, such as the U.S. National Research Council (2013) report, indicate current remediation technologies are not expected to achieve maximum contaminant level (MCL) clean-up goals at many sites, and hence MNA and monitoring are important components of the site management paradigm.

While there is new science and tools under development, there is limited guidance that brings together the current understanding of natural and enhanced attenuation for petroleum hydrocarbon impacted sites. To address these gaps, this guidance has been developed following a toolkit approach to summarize current knowledge and provide practical tools for practitioners evaluating sites using these technologies. The guidance is intended to support remedial decision-making to address LNAPL source zones and associated plumes typically after mobile LNAPL has been initially remediated to the extent practicable and after determining there is no current unacceptable risk to human or ecological receptors. Four toolkits have been developed or are in-progress, as follows:

- Toolkit #1: Conceptual Site Model and Case Study Toolkit.
- Toolkit #2: Monitoring and Prediction Toolkit.
- Toolkit #3: Remediation Technology Toolkit (in-progress).
- Toolkit #4: Sustainability Toolkit (in-progress).

The approaches and methods in these toolkits are designed to answer the following key questions:

1) Is the hydrocarbon groundwater plume expanding, stable or shrinking and what attenuation processes are occurring?
2) Approximately how long will it take for source depletion?
3) Approximately how far is the hydrocarbon groundwater plume expected to migrate?
4) What are the options for petroleum hydrocarbon remediation and enhanced attenuation and potentially how effective and sustainable are these measures?
5) What are appropriate monitoring strategies to support prediction and verification of natural and enhanced attenuation?

The above questions are broadly addressed through a review of available data from multiple sites and model simulations based on generalized conditions as well as analyses where site-specific conditions and factors are considered. Available tools and methods are described in the toolkits with respect to their use, uncertainty in prediction and potential advantages and disadvantages, and new tools for predictive modeling purposes have been developed for this project. As part of a toolkit approach, multiple options and tiers of evaluations have been identified to provide flexibility in assessment and to promote cost effective site assessment and closure. The toolkits address petroleum hydrocarbon contamination, but some methods described also apply to other types of contaminants.

Toolkit #1 provides the regulatory context for this project, describes the conceptual site model, followed by learnings from multi-site database evaluation and detailed case studies. Toolkit #2 describes the framework and methods for evaluation of MNA of dissolved plumes, screening models and measurement methods for estimation of NSZD and multi-process models for evaluation of source depletion and dissolved plumes under a MNA and EA approach. Toolkit #3 will provide an overview of *in-situ* remediation approaches followed by available technologies and key site factors that control remediation success with an emphasis on understanding the effect of mass removal and change in petroleum hydrocarbon composition on attenuation timelines. Toolkit #4 will address sustainability of remediation technologies and will include comparison on available tools for sustainability evaluations.

Toolkit #1 – Conceptual Site Models and Case Studies

The site management and regulatory context, the conceptual site model for natural attenuation and source depletion, and empirical data from US and British Columbia documenting natural attenuation and the effectiveness of remediation for reducing source zone longevity and dissolved plumes are described in Toolkit #1.

Site Management and Regulatory Context

Sites where *in-situ* management of petroleum hydrocarbon contamination is evaluated require assessment of the potential risks to human and ecological health. There are specific issues that relate to petroleum hydrocarbon LNAPL that should be considered as shown in the framework in Figure A, beginning with an evaluation of LNAPL mobility and recovery, followed by appropriate and necessary actions for mobile LNAPL remediation, which will depend on site-specific conditions, regulatory policy and other factors. The final step in the LNAPL management paradigm is assessment of remediation requirements for residual LNAPL or contaminated soil source zones, which should begin with an assessment of current potential risk to human or ecological receptors, with appropriate actions taken. Depending on regulatory policy and site factors, long-term clean-up of source zones may be warranted or desired to promote restoration of contaminated groundwater to enable future use of water as a resource. This is an emerging science and policy issue that requires consideration of:

- Timelines for restoration under natural and enhanced remediation conditions;
- The commonly observed impracticability of full source remediation; and
- Potential benefit and limitations of partial source remediation.

Draft BC MoE Technical Guidance 22 describes conditions under which MNA or EA can be carried out as remediation measures at a site. Notable conditions are that it will not result in any unacceptable risks to human health or the environment and the groundwater contaminant plume is stable or shrinking. Lines of evidence for the confirmation of MNA/EA operating at a site are as follows:

1) Observed reduction in contaminant mass (required).

2) Geochemical and biochemical indicators (required).

3) Microbiological laboratory data (only if the first and second are inconclusive).

We recognize that establishing timelines for MNA or EA is an emerging policy issue that regulatory agencies, including BC MoE, are beginning to evaluate. MoE Technical Guidance 22 indicates remediation concentration goals under a MNA or EA approach should be met within 20 years (this timeline is under review). The ITRC Integrated DNAPL Strategy Guidance recommends that functional goals for clean-up, such as specific goals relating to progress, phases or locations for clean-up, should have relatively short time frames – years to less than one generation (or about 20 years), even though absolute objectives may require management and even subsequent active remediation well beyond such durations (decades to centuries).[1] The focus of this Toolkit is to provide insight on timelines for natural attenuation, but where appropriate there are references to the progress of attenuation observed or predicted at sites relative to a 20-year or similar timeline (*i.e.*, few decades) based on the context for this project, recognizing that such timelines may change.

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[1] http://www.itrcweb.org/GuidanceDocuments/IntegratedDNAPLStrategy_IDSSDoc/IDSS-1.pdf

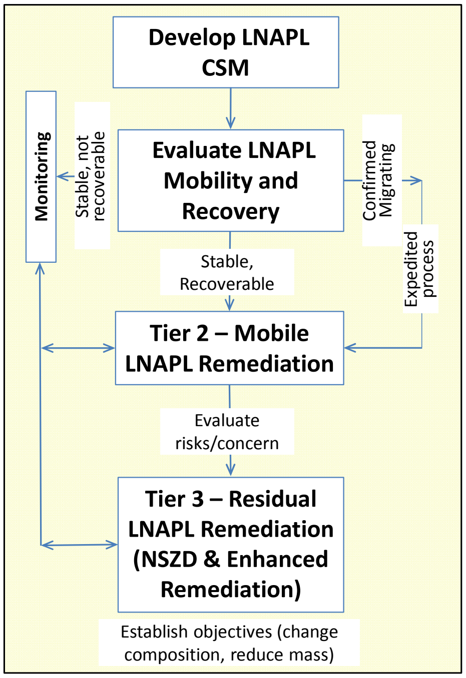

Figure A: LNAPL remediation framework.

Conceptual Site Model

The conceptual site model addressed in this guidance describes petroleum hydrocarbon source zones and dissolved plumes, natural attenuation processes, site specific factors that affect plume characteristics and conceptually how remediation measures may affect hydrocarbon concentrations and longevity. Figure B shows the conceptual model of processes related to the release, fate, transport, and groundwater plume formation of petroleum hydrocarbon contamination.

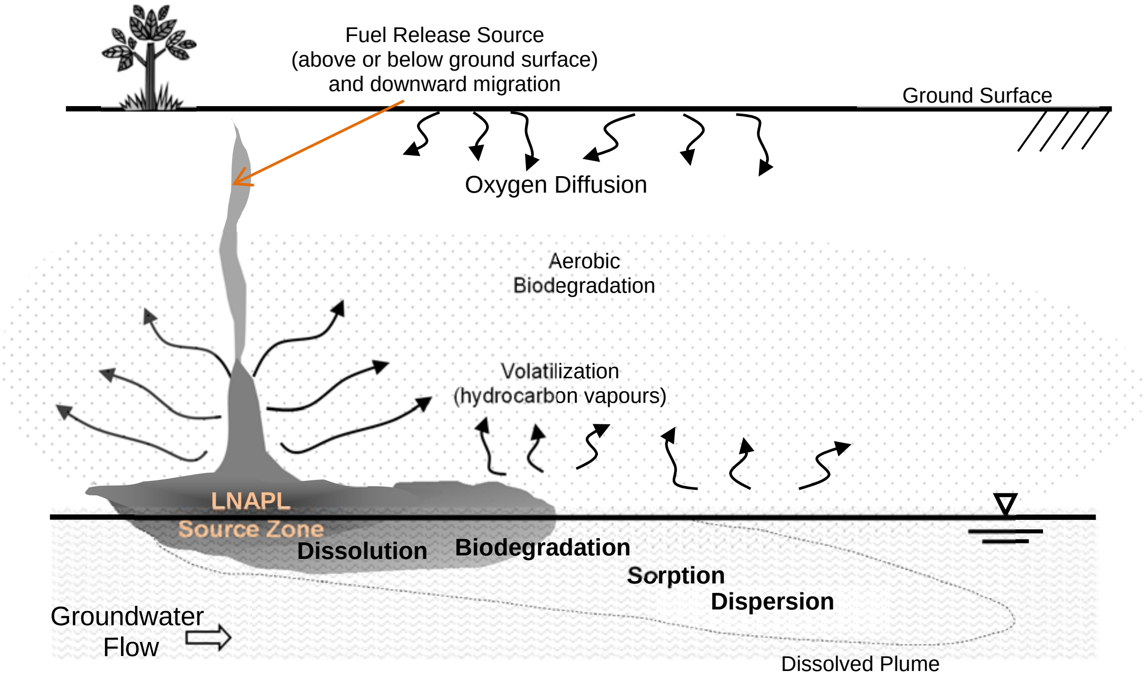

Figure B: Processes related to LNAPL source zone and groundwater plume formation.

When LNAPL is released in the vadose zone, the LNAPL moves predominantly downward as a separate immiscible phase under the influence of gravity, until it encounters the water table, where buoyancy forces and capillary forces due to higher water contents result in vertical accumulation and lateral spreading of the LNAPL. Residual LNAPL remains within the vadose zone in the path of LNAPL migration. At the water table, the repeated rising and falling of the water table often results in the formation of a LNAPL smear zone.

The processes for NSZD include dissolution of petroleum hydrocarbon compounds from flowing groundwater below the water table and infiltrating water in the vadose zone, biodegradation of hydrocarbons, and volatilization of hydrocarbons in the vadose zone. Volatilization can occur above the water table from LNAPL and dissolved constituents, while biodegradation occurs in the aqueous phase both in the water-filled portion of the pore space in the unsaturated zone and the saturated zone below the water table. Biodegradation reactions can occur under aerobic and anaerobic conditions, and are controlled by the availability of the terminal electron acceptors (TEAs) and substrate (petroleum hydrocarbon) availability. The fate and transport of dissolved hydrocarbons in groundwater are primarily controlled by advective-dispersive transport, biodegradation reactions and sorption of petroleum hydrocarbon compounds on native organic matter and/or minerals present in the aquifer.

There is significant complexity of hydrocarbon attenuation based on the above processes due to the LNAPL distribution (whether above or below the water table), mass transfer limitations within the LNAPL zone (in geologically complex environments), and the potential for groundwater to bypass the LNAPL zone. The biodegradation kinetics will also vary depending on location and will tend to be slower in the LNAPL source area compared to the dissolved downgradient plume.

Review of Petroleum Hydrocarbon Plume Studies

Six petroleum hydrocarbon groundwater plume studies that include discussions of relevant processes on a conceptual basis, interpretation of field data and observations, and predictive modeling for the evaluation of remedial technologies were reviewed. The results include model predictions and/or monitoring data indicating remediation timelines to achieve drinking water guidelines of greater than 100 years for sites with relatively large releases. These studies also provide insight on the LNAPL conceptual site model.

Schirmer *et al.* (2004) found that dissolution of NAPL components into groundwater can be described by Raoult's Law, which states that the saturated concentration in groundwater at equilibrium reflects the molar fraction of a substance in a mixture. More soluble NAPL components will be preferentially removed from the source into the groundwater and therefore decrease the mole fraction and thus concentration.

Huntley and Beckett (2002) using the American Petroleum Institute (API) LNAST model predicted that LNAPL recovery would not be effective in reducing the longevity of a dissolved-phase gasoline plume except in medium to coarse-grained soils. The maximum downgradient plume extent was not affected by remediation through recovery. Instead, remediation such as air sparging or soil vapour extraction (SVE) that reduces the mole fractions of hydrocarbon constituents (*e.g.*, benzene) are predicted to be more effective in decreasing the downgradient plume extent and maximum concentrations.

Multi-Site "Big-data" Studies from United States

Several multi-site studies of petroleum hydrocarbon groundwater plumes have recently been completed in the United States (Table A). These "big-data" studies enable longer-term trends to be evaluated with respect to source concentrations, plume lengths and the effectiveness of remediation to be quantified. The multi-site studies are summarized in Table A below.

Table A: Summary of US Multi-Site Data

Conner *et al.* (2015) 13 multiple-site studies of mostly gasoline releases at retail service station sites.	Median and 90th percentile benzene plume lengths based on 5 µg/L were 55 and 130 m, respectively, for sites with range of remediation completed. The proportion of sites with stable, shrinking or exhausted plumes was 94%.
McHugh *et al.* (2014) 12,000 sites in the California GeoTracker database.	Estimated median benzene attenuation rate at source zone wells for sites with range of remediation types (including 3% of sites with just MNA implemented) was 0.18/year. When data was separately analyzed for remediation type (sparging, SVE, groundwater pump-and-treat), the attenuation rates increased 17-53% depending on technology. A 20-year timeframe for benzene remediation assuming an initial source concentration of 10 mg/L is predicted to be met for 14 of 72 sites (19%), where MNA was reported to be the only remediation technology.
Kamath *et al*. (2012) Data from 48 gasoline retail sites mostly in California and New Jersey	Timelines for benzene remediation to the drinking water guideline were 12-52 years. The effect of active remediation and LNAPL recovery on estimated attenuation rates were found not to be statistically significant compared to rates for sites with no active remediation or recovery. The 90th percentile benzene plume length was 110 m.

Conner *et al.* (2015) 13 multiple-site studies of mostly gasoline releases at retail service station sites.	Median and 90th percentile benzene plume lengths based on 5 µg/L were 55 and 130 m, respectively, for sites with range of remediation completed. The proportion of sites with stable, shrinking or exhausted plumes was 94%.
Shih *et al*. (2004) 500 UST sites in the Los Angeles, CA area	Statistical analysis of benzene plume length based on a 5 µg/L threshold indicated geometric mean, 90th percentile and maximum plume lengths of 51 m, 100 m and 168 m, respectively.
Kulkarni *et al*. (2015) 3,523 LUFT sites in the California GeoTracker database	While benzene source concentrations decreased at the majority of sites, an analysis of source attenuation rates did not identify an improvement towards remediation time for sites with physical LNAPL recovery. The median benzene attenuation rate was 0.09/year for sites with LNAPL recovery and 0.19/year for sites without LNAPL recovery.

Lessons learned from the multi-site studies include:

1) Almost all (94%) dissolved benzene plumes were stable or shrinking.
2) Dissolved benzene plumes were relatively short, for example, the 90th percentile length was 130 m in the review study (Connor *et al.*, 2015).
3) Statistical analysis of site data where no active remediation or only free LNAPL recovery was implemented indicate significant decreases in benzene concentrations in source wells signifying that natural weathering of hydrocarbons is an important process.
4) There were variable results with respect to the effect of remediation on benzene concentrations at source zone wells. Two studies found that remediation did not result in an increase in the benzene attenuation rate at source wells, in another study there was a significant increase in the attenuation rate depending on remediation technology.

Low-Threat Groundwater Plumes

The clean-up of sites to protect groundwater resources is a challenging policy issue as there are knowledge gaps with respect to how sources and plumes change over time and effectiveness of remediation, and there are few regulatory frameworks that address this issue. The above studies are valuable in that they provide monitoring data on longer-term trends and through plume studies provide a technical basis for an improved and more sustainable site management approach particularly for low risk or threat sites, including the California policy described below.

The policy developed by the state of California, the Low-Threat UST Closure Policy (California State Water Resources Control Board, CSWRCB, 2012), is based on multi-site data studies completed in California including Shih *et al.* (2014) and Kamath *et al.* (2012). The Policy is designed to address low-threat releases of petroleum hydrocarbon fuels from USTs. The Low-Threat UST Closure Policy defines four classes of low threat groundwater plumes, applied in areas that include aquifers used for drinking water, based on the following indicators:

groundwater plume lengths, indicator constituents and buffer or separation distances to receptors. Sites with stable LNAPL bodies where LNAPL has been removed to the extent practicable, and where dissolved plumes are demonstrated to be stable based on five years of data, or where concentrations of indicator constituents are below safe thresholds may be closed when there is an acceptable separation distance between the edge of the dissolved plume and receptor (drinking water well or surface water body). The separation distances from the edge of the defined plume range from 250 to 1,000 ft and incorporate safety factors of 1 to 4 depending on the class.

British Columbia and Yukon Case Studies

Groundwater monitoring data from five sites in British Columbia (BC) and one site in the Yukon representing a range of site and climatic conditions were reviewed (see Appendix B in Toolkit #1). Site remediation through excavation of most of the contamination source or SVE was implemented at four sites.

The key results are:

1) The BC drinking water (DW) groundwater standards were not achieved at all six sites; the data indicate at some sites DW standards will not be met for many decades even if additional remediation is implemented.

2) For BC sites, the benzene concentrations decreased or were predicted to decrease to below the DW standard (5 µg/L) within approximately 20 years at all five sites evaluated, but concentrations of ethylbenzene (2.4 µg/L), xylenes (300 µg/L) and benzo(a)pyrene (0.01 µg/L) remained above the DW standards, depending on the site. The data suggest ethylbenzene and xylenes may currently be the regulatory drivers at many BC sites.[2]

3) For BC sites, the dissolved plumes were stable or shrinking and plume lengths were short, estimated to range from a few metres at one site to 50 to 70 m at a site with a large gasoline release.

The case study data indicated that DW standards for benzene were met in a relatively short time frame (few decades) but that for ethylbenzene and xylenes DW standards will not be met for many decades at some sites, consistent with the results of modeling presented in Toolkit #2. The geometric mean of the attenuation rates (first-order decay constants) for benzene and ethylbenzene were 0.55/year and 0.29/year, respectively. For a starting benzene and ethylbenzene concentration of 10 mg/L, these decay rates predict attenuation to below the drinking water standards in 14 and 29 years, respectively. The attenuation rates indicate significant reductions in benzene and ethylbenzene concentrations are occurring at the sites and that natural weathering of hydrocarbons is an important process. Moreover, the geometric mean of the attenuation rates for benzene and ethylbenzene estimated for the BC case studies are higher than the median or average rates for multi-site US studies, although it is recognized that the BC dataset is small. Similar timelines observed for the multi-site studies in the United States have been the impetus for low-threat closure policies.

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[2] It is noted that groundwater standards in British Columbia are currently under review as part of the Omnibus updating process.

Summary of Toolkit #1

In summary, the data reviewed for Toolkit #1 suggest NSZD of petroleum hydrocarbons is a viable process over longer time frames (generally decades); that it occurs in a predictable manner; and that associated dissolved plumes are relatively short and stable. Contaminant (benzene) plumes were largely stable or decreasing and less than 130 m in length. The US studies also indicated variable results with respect to the effect of remediation on benzene concentrations at source zone wells. Two studies found that remediation did not result in an increase in the benzene attenuation rate at source wells, in another study there was a significant increase in the attenuation rate depending on remediation technology. One study indicated that LNAPL recovery did not result in faster attenuation rates of benzene in the source zone.

Longer timelines for remediation to groundwater standards are expected for large releases, although hydrogeologic factors such as groundwater velocity may also be important, while shorter timelines are expected for sites with smaller releases, or where the majority of the source is removed. Complete removal or treatment of sources is often not feasible because of infrastructure at sites (*e.g.*, roads, sidewalks, buildings).

Data gaps in the BC case study include the relatively limited dataset and absence of well characterized sites with longer-term data that would enable source zone depletion and dissolved plume attenuation (for a range of compounds) to be accurately quantified.

Toolkit #2 – Monitoring and Prediction

Toolkit #2 describes the framework and methods for evaluation of MNA of dissolved plumes. It includes a review of screening models and measurement methods for estimation of NSZD, as well as a review of multi-process models for evaluation of source depletion times and dissolved plume lengths under a MNA and EA approach. The contents of this toolkit are designed to answer the following key questions:

1) Is the hydrocarbon groundwater plume stable and what attenuation processes are occurring?
2) Approximately how long will it take for source depletion?
3) Approximately how far is the hydrocarbon groundwater plume expected to migrate?

Three evaluation steps for answering these questions are:

Step 1: Monitored Natural Attenuation Evaluation of Dissolved Plumes

Step 2: Use of Screening Models and Measurements for Estimation of NSZD

Step 3: Use of Multi-Process Models for Evaluation of Natural Depletion and Plume Attenuation

This monitoring and prediction toolkit describes a range of screening to more complex methods for evaluation of MNA and NSZD and brings together information that is not currently available in a single document. The purpose of the toolkit is to provide practitioners with multiple options for assessment and prediction of MNA or EA based on site data.

Under Step 1, the basic principles followed by methods for evaluation of MNA and plume stability are described. Where concentration trends indicate a significant decreasing trend, methods for prediction of timelines to reach a remediation goal are described.

Under Step 2, screening models and measurement methods that may be used to evaluate NSZD are described including a range of practical tools and new innovative technologies. The available published data on NSZD are summarized for different measurement methods.

Under Step 3, multi-process models for evaluation of depletion times and plume lengths are described and compared through example site scenarios. Multi-process models are demonstrated for two scenarios where there is natural depletion of a petroleum hydrocarbon source and EA through source mass removal.

Step One – Monitored Natural Attenuation Evaluation of Plumes

The US EPA defines natural attenuation to include a variety of physical, chemical, or biological processes that, under favourable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater (US EPA, 1999). The processes that act to attenuate contaminants include dispersion, dilution, sorption, volatilization, biodegradation or biotransformation, chemical transformation, chemical or biological stabilization, radioactive decay, and destruction of substances.

The common approach for evaluation of MNA consists of three inter-related steps (NRC, 2000; NJDEP, 2012):

1) Site characterization and development of a site conceptual model.

2) Analysis of field data, supported by laboratory data and modeling, as necessary to establish that there is mass loss of contaminants as a result of biodegradation, typically conducted through a line of evidence evaluation.

3) Long-term monitoring of natural attenuation to demonstrate that remedial objectives continue to be met.

Site Characterization and CSM Development

Site characterization and CSM development requires data on site geology and hydrogeology, contamination characteristics (source and dissolved plume), aquifer properties and geochemistry. Comprehensive guidance on groundwater investigation is provided in BC MoE Technical Guidance 8 (TG 8). Of importance is the spatial and temporal distribution of contamination and how contamination may vary seasonally including changes in groundwater flow direction. To meet this objective, initially monitoring on a quarterly to twice yearly basis is typically required to establish an appropriate dataset, with subsequent longer-term monitoring conducted at a reduced frequency.

Two spreadsheet tools that can improve investigations are:

1) **US EPA 3PE Tool**, a three-point solution method for estimating gradients and groundwater flow direction; and

2) **US EPA Optimal Well Locator (OWL) Tool**, a method for selecting new well locations based on hydrogeologic data.

Site characterization and CSM development also require the demonstration of natural attenuation.

Lines of Evidence Evaluation

The common approach for the demonstration of natural attenuation (BC MoE Draft TG 22, 2014; US EPA, 2009; AFCEE, 2000; ASTM, 2010) is described in detail in Toolkit #2 and in general involves a lines of evidence evaluation of the following:

1) *Primary line of evidence*: Field data that demonstrate trends of decreasing contaminant mass and/or concentration over time at appropriately located monitoring points. Practically, the goal of the primary line of evidence evaluation is to determine whether there is an expanding, stable or shrinking plume.

   A number of tools are presented in Toolkit #2. For example, dissolved plume extent over time and point concentration trend analyses are typically conducted either by regression analysis (**Regression Analysis Tool** developed by Dr. John Wilson (RegressionMNA.xlsx)) or non-parametric analysis such as Mann-Kendall or other statistical techniques described. Software packages such as **MAROS** (US Air Force Centre for Engineering and the Environment, AFCEE) or **ProUCL** (US EPA) are available for Mann-Kendall analysis.

   Average-based methods (Ricker, 2008), as opposed to point-concentration methods, are a powerful technique because they integrate concentration data across the plume as part of plume stability evaluation. The API **Groundwater Spatio-Temporal Data Analysis Tool** (GWSDAT) includes the average-based concentration analysis method, and enables the time-series tracking of the centre of hydrocarbon mass.

2) *Secondary line of evidence*: Hydrogeologic and geochemical data that demonstrate the types of natural attenuation processes at the site and that show mass loss through analysis of terminal electron acceptors and degradation products.

   Data on geochemical indicators obtained from wells up-gradient of the source, within the source area and downgradient of the source are compared and qualitatively evaluated with respect to spatial trends and changes over time. Assimilative or biodegradation capacity calculations can be performed using the **Assimilative Capacity Tool** (BioCapacity.xlsx) or more advanced models such as the US EPA **BIOSCREEN** model.

3) *Tertiary line of evidence*: Data from microcosm studies or other biological monitoring tools to evaluate or demonstrate specific biological processes and ability of microorganisms to degrade specified contaminants.

Long-term Monitoring

The US Department of Defense Environmental Security Technology Certification Program (ESTCP) recently published a Frequently Asked Questions (FAQs) document for MNA (Adamson and Newell, 2014) that provides a useful framework for long-term monitoring (Figure 2-5 of Toolkit #2). This framework considers plume stability and distance to receptor and recommends a range of monitoring frequencies depending on site conditions.

Step Two – Use of Screening Models and Measurements for Estimation of NSZD

There are a range of screening models and measurements that may be used to assess the applicability of MNA at a contaminated site based on source longevity or source depletion times. The estimation of the source depletion time requires two types of data: 1) the starting petroleum hydrocarbon mass and 2) rate of hydrocarbon mass removal or degradation.

Natural processes that can lead to source zone depletion include:

- Biodegradation of hydrocarbon above the water table within the unsaturated soil zone;
- Volatilization of hydrocarbon above the water table and upward migration to ground surface;
- Biodegradation of hydrocarbon below the water table; and
- Dissolution of hydrocarbon in flowing groundwater below the water table.

Conceptually, biodegradation and volatilization above the water table are typically combined and a model is applied where the downward oxygen flux is used to estimate the aerobic biodegradation and mass loss rate. Screening models and tools to quantify the above processes are described below.

Screening Models

The ITRC (2009) describes a conceptual model for NSZD, where the constituents that compose the LNAPL may be removed or retained on aquifer materials over time by various mechanisms, such as sorption, volatilization, and dissolution (Figure C). To address at what rate NSZD is occurring, a quantitative model based on a control volume concept and the three depletion processes above is presented consisting of 1) the oxygen gradient method for biodegradation in the unsaturated soil zone, 2) assimilative capacity calculation for estimation of saturated zone biodegradation, and 3) dissolution calculation based on a hydrocarbon mass flux calculation. The **Control Volume Excel Spreadsheet Tool** (CV-NSZD in progress) developed by Golder Associates enables calculations to be readily performed for comparison of depletion times through different mechanisms.

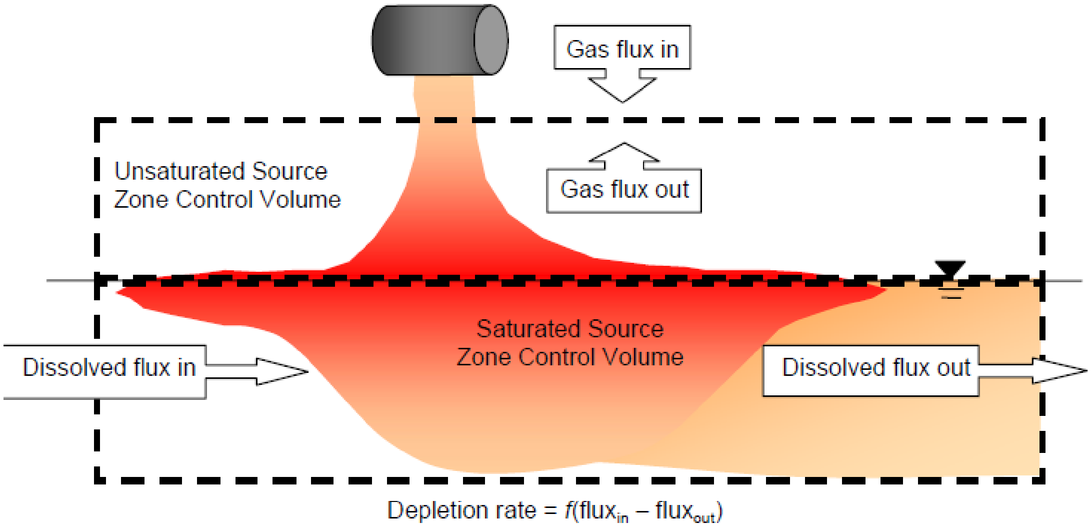

Figure C: Control volume "box" for quantitative assessment of NSZD (from ITRC, 2009).

Estimates of the depletion rates from different mechanisms are used to demonstrate the Control Volume concept in Toolkit #2 with the Golder **NSZD Nomograph Tool** (Figures 3-3 to 3-6 of Toolkit #2). The Nomographs provide a simple and easy to use tool for estimating depletion times through biodegradation in the vadose zone (using rates compiled in this toolkit) and dissolution in the saturated zone, when data on the petroleum hydrocarbon source mass (dimensions and concentration or saturation) are available.

Another tool is the GSI Environmental Inc.'s **Mass Flux Toolkit**[3] developed for the US Environmental Security Technology Certification Program (ESTCP) (GSI Environmental Inc., 2011). The Mass Flux Toolkit is a free Microsoft® Excel Spreadsheet designed to calculate the total mass flux of a contaminant across one or more transects of a groundwater plume in order to evaluate the effects of natural attenuation processes at a site. The Mass Flux Toolkit enables more accurate estimation of the hydrocarbon dissolution rate, but requires relatively detailed groundwater data.

Methods for Estimation of Unsaturated Source Zone Biodegradation

Three methods for estimation of unsaturated zone biodegradation are reviewed (Table 3-1 of Toolkit #2):

- O_2 Gradient method – involves estimation of the oxygen concentration gradient;
- Carbon dioxide (CO_2) efflux method – involves measurement of the surface CO_2 flux; and
- Temperature method – involves measurement of the thermal gradient.

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[3] http://gsi-net.com/en/software/free-software/mass-flux-toolkit.html

There are important questions and gaps in understanding on methods, site factors and spatial and temporal variability of NSZD measurements and significant work has recently been completed or is currently in-progress (*e.g.*, LA LNAPL Workgroup, 2015; Jourabchi *et al*., 2016; Gaito *et al*., 2015).

The O_2 gradient method utilizes data often obtained at sites (TPH concentrations in soil and soil properties) and is recommended as an initial screening method for approximate estimates of NSZD. Carbon dioxide efflux measurement is a newer method with promise as more direct surface-based technique for estimation of biodegradation rates. The temperature method is an emerging method currently being evaluated for NSZD studies.

O_2 Gradient Method

The O_2 Gradient method calculations may be performed using the **Vadose Zone Biodegradation Loss (VZBL)** tool, a free Microsoft® Excel Spreadsheet developed by Dr. John Wilson of Scissortail and Golder Associates. The model estimates the oxygen consumption rate for petroleum hydrocarbons based on the oxygen gradient and the effective oxygen diffusion coefficient, assuming oxygen is depleted at the depth of hydrocarbon in soil, and is thus used to estimate the source depletion rate when TPH soil data are available. The model is easy to use and includes features that provide for more accurate estimates including input of soil properties for multiple soil layers to obtain an overall effective diffusion coefficient, time-dependent vertical depletion of the hydrocarbon source simulated based on a mass balance, and variable position of water table relative to the hydrocarbon source. Novel methods for estimation of soil physical properties are provided in Appendix D of Toolkit #2. Additionally, when nitrogen soil gas data from near to the contamination source are available and anaerobic conditions are resulting in generation of methane through fermentation reactions (as confirmed by elevated methane concentrations), the methane flux is estimated based on the Stefan-Maxwell equations for a binary CH_4 and N_2 system (Thorstenson and Pollock, 1989) to evaluate an anaerobic biodegradation rate of the petroleum hydrocarbon. The available oxygen for aerobic degradation is also adjusted to account for the oxidation of methane.

CO_2 Efflux Method

Two methods have been developed for the estimation of CO_2 flux, a dynamic closed chamber method, primarily developed by researchers at the University of British Columbia (UBC) (Sihota and Mayer, 2012; Sihota *et al.*, 2011) and a static trap method, primarily developed by researchers at Colorado State University (McCoy, 2012). The dynamic chamber involves collection of multiple measurements over relatively short durations (minutes to hour) using an infra-red gas analyzer. The static trap involves measurement of flux over longer time periods (2 to 4 weeks). For both methods, the CO_2 efflux should be corrected for background efflux using radiocarbon (^{14}C) data or other acceptable technique.

Temperature Method

Measurement of subsurface temperature has recently been proposed as a tool to evaluate aerobic biodegradation in hydrocarbon contaminated soil (Sweeney *et al.*, 2014). Aerobic biodegradation generates heat and therefore by measuring the temperature gradient the biodegradation rate can be estimated. The method requires measurement of temperature profiles in and above LNAPL source zones and at un-impacted background locations.

Database of Hydrocarbon Mass Loss Rates

A database of petroleum hydrocarbon mass loss rates are compiled in Table 3-2 of Toolkit #2. The hydrocarbon biodegradation (mass loss) rates are relatively consistent between studies and methods, excluding static trap results reported for two studies. The rates are summarized below for the range of average mass loss rates[4], and average (of the average rates) reported:

- Static Trap: 0.38 to 3.8 (1.8) g-HC/m^2-day or 170 to 1,700 (880) US Gal/acre-year (N = 6 sites);
- Dynamic Closed Chamber: 1.1 to 2.4 (1.7) g-HC/m^2-day or 530 to 1,100 (810) US Gal/acre-year (N = 5 sites); and
- Modeling Studies: 0.5 to 3.0 (1.3) g-HC/m^2-day or 290 to 1,400 (670) US Gal/acre-year (N = 5 sites).

The database values may be used as a first approximation to estimate biodegradation rates when measurement data are not available. An order of magnitude estimate of the biodegradation rate based on the above data is 1 to 3 g/m^2-day or 500 to 1,500 Gal/acre-year.

Step Three – Use of Multi-Process Models for Evaluation of NSZD and Plumes

Three publicly available multi-process models, the LNAST, REMFuel and BIOSCREEN models, are reviewed and evaluated through example applications and comparison to a three-dimensional reactive transport model, the MIN3P-Dusty model in Toolkit #2. These models can be used to answer the following questions:

1) Approximately how long will it take for source depletion?

2) Approximately how far is the hydrocarbon groundwater plume expected to migrate?

3) What is effect of source removal and enhanced remediation on remediation timelines?

Step 3 in Toolkit #2 also describes how multi-process modeling tools can be applied to the evaluation of MNA and EA in accordance with the conditions set in BC MoE TG 22.

The three models LNAST, REMFuel, and BIOSCREEN are based on the Domenico (1987) solution to solute transport and biodegradation in one-dimension for advection with dispersion in three-dimensions but include different processes for hydrocarbon source depletion, as described in Table 4-1 of Toolkit #2, and summarized below:

- LNAST model: Provides the greatest flexibility in terms of number of LNAPL constituents, source depletion processes, and vertical layers of varying soil types. The inclusion of volatilization is advantageous and the factor can be estimated from oxygen gradient method calculations.
- REMFuel model: Simulates biodegradation in multiple zones and source remediation, but does not include volatilization. The gamma term (Γ), which describes how the source concentration term is attenuated over time, is not a well characterized parameter for petroleum hydrocarbon releases. For larger releases,

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[4] Where an average rate was not reported, the average was approximated as (minimum range + maximum range)/2.

conceptually, a gamma term of zero or close to zero is considered reasonable; for smaller releases or sites where matrix diffusion could be important, a gamma term greater than zero may be appropriate (see discussion in Toolkit #2).

- BIOSCREEN model: Simulates biodegradation reactions for dissolved hydrocarbon fate and transport, but is not recommended for evaluation of source depletion.

Source depletion times and plume lengths are predicted using the multi-process models for hypothetical small and large petroleum release scenarios for a BC-specific hydrogeological setting. Large differences in plume lengths and concentrations and source depletion times are predicted indicating models are highly sensitive to source depletion processes and input parameters. Predicted source depletion times are several hundred years for baseline scenarios, but decrease to a few decades when volatilization or partial source removal are considered. The simulations demonstrate the importance of accounting for multiple components and effective solubility for prediction of source depletion. None of the modeling scenarios predicted source depletion and reduction in benzene concentrations to less than the drinking water standard in less than 20 years (timelines were 2X to more than 10X longer than 20 years).

Conclusions and Recommendations

Toolkits #1 and #2 describe the conceptual site model, empirical data, and monitoring approaches for evaluation of the longevity of petroleum hydrocarbon source zones and associated plumes under a MNA and NSZD framework, and evaluation of available modeling tools. The multi-site data summarized in Toolkit #1 and modeling predictions in Toolkit #2 indicate significant source zone attenuation of petroleum hydrocarbon occurs over longer timeframes indicating natural weathering processes are significant, depletion of sources and reduction in concentrations to below standards may take many decades and possibly centuries for large releases. The BC case studies reviewed (mostly partially remediated sites) are instructive in that they indicate a statistically significant decline in concentrations were measured at most sites. When compared to current drinking water standards, ethylbenzene is the regulatory driver at sites evaluated.

Nomographs have been developed to enable rapid screening estimation of source depletion times for hydrocarbon biodegradation in the vadose zone and dissolution of hydrocarbon in the saturated zone. Hydrocarbon biodegradation rates may be estimated from literature values or the methods described below. Two screening spreadsheet models for NSZD have been developed, the CV-NSZD model based on the control volume concept (in-progress), and the VZBL model for depletion estimates based on the O_2 gradient method and additional feature of methane flux estimate if applicable. Biodegradation is shown to be a potential significant process for NSZD; however, predictions are sensitive to soil properties for the O_2 gradient method, and intra-method comparability is somewhat poor for the CO_2 efflux method. The CO_2 efflux method holds significant promise but further method validation is required on the background correction for natural soil respiration. The CO_2 efflux method with appropriate design can be a useful added line of evidence for comparison to the O_2 gradient method estimates.

The recommended process for estimation of NSZD and plume longevity will depend on the site-specific objectives and conditions. For screening purposes, a combination of the screening models developed for this project should be considered, supported by one and if possible, two of the three measurement methods described for estimation of biodegradation losses in the vadose zone. For some projects, use of multi-process models described will be warranted for more detailed assessments. Model selection is dependent on the availability of resources in terms of site-specific data and the time required to construct scenarios of varying complexity.

From a regulatory policy standpoint respecting groundwater resource protection, a limited degradation policy is proposed for petroleum hydrocarbon sites associated with typically small to moderate size releases (*e.g.*, service stations, tank farms) recognizing that natural depletion of petroleum hydrocarbon sources is demonstrated to be a significant process that occurs in a predictable manner and associated dissolved plumes are typically relatively short and stable, and given the impracticality and cost of source remediation at many sites (the benefits of partial remediation are also indicated from multi-site studies to be inconclusive). The recommended framework requires free LNAPL recovery to achieve conditions of a stable LNAPL body and a stable or shrinking dissolved plume based on a minimum of five years of data as supported by trend analysis of plume concentrations. Consideration could also be given to whether there would be added benefit from a framework that would require a statistically significant downward trend in dissolved concentrations at source zone wells based on a minimum of five years of data. As warranted, buffer distances to receptors (drinking water wells or surface water bodies) based on a safety factor approach could be added to the framework.

The review of empirical data and modeling studies for scenarios considered indicate a relatively large range and significant uncertainty in source depletion timelines. Data gaps and recommended future research include additional field studies from British Columbia that include long-term monitoring data. While attenuation to applicable groundwater standards ultimately will occur at sites, better estimates of attenuation timelines are desirable from a long-term resource management perspective. An important data gap that warrants further research is a better understanding of the effect of partial remediation or enhanced remediation on source depletion and plume attenuation. This gap was partially addressed through the multi-site evaluation and modelling, but could be improved by quantifying the mass loss rates associated with different technologies (*e.g.*, bioventing, biosparging and SVE) and comparison to NSZD rates, and through consideration of technology performance with respect to achieving compositional (*i.e.*, change chemistry) versus saturation (*i.e*., reduce mass) objectives. This could be further evaluated through field studies involving measurements of natural and enhanced mass loss rates and composition changes as supported by modeling studies. A potential opportunity is to utilize relatively simple and low cost technologies such as bioventing (possibly passively implemented) to enhance NSZD, which will be addressed in Toolkits #3 and #4.

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TOOLKIT #1: Conceptual Site Model and Case Studies

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1.0 INTRODUCTION

Monitored natural attenuation (MNA) is a well-established remediation technology for petroleum hydrocarbon groundwater plumes. Natural source zone depletion (NSZD) is a remedial approach involving the natural weathering of petroleum hydrocarbon sources, which may be enhanced by partial removal of contamination or *in-situ* treatment. Toolkit #1 begins with a summary of the recent BC Ministry of Environment draft guidance for MNA. The toolkit then describes the conceptual site model for hydrocarbon source zones and dissolved plumes, natural depletion and attenuation processes, site specific factors that affect plume characteristics and conceptually how remediation measures may affect hydrocarbon concentrations and longevity. The main findings of empirical data from multi-site evaluations of MNA and natural and enhanced source zone depletion are described, with a focus on remediation timelines and plume lengths. Case study data from six sites in British Columbia are also summarized.

Monitored NSZD is an emerging remedial approach involving the natural weathering of petroleum hydrocarbon sources, which may be enhanced by partial removal of contamination or *in-situ* treatment. While processes for natural attenuation and depletion are well understood, less well known or documented are timelines for these processes or the effectiveness of remediation on source zone longevity and plume concentrations and plume lengths.

2.0 REGULATORY CONTEXT

The Land Remediation Section of the British Columbia Ministry of Environment provides guidance on the investigation and remediation of contaminated sites in British Columbia under the Environmental Management Act (July 8, 2004) and the Contaminated Sites Regulation (CSR). In this role, the Land Remediation Section provides policies, protocols, procedures and guidance for the interpretation and implementation of the CSR for contaminated site investigations and remediation.

In British Columbia, new regulatory protocol and guidance are being considered to guide groundwater remediation requirements, which may include timelines for monitored natural attenuation or enhanced attenuation. Draft Technical Guidance 22 describes the natural attenuation processes and the primary mechanisms of attenuation, particularly biodegradation of organic contaminants. For sites where natural attenuation is not effective within a reasonable timeframe, the guidance also provides enhanced attenuation (EA) as an alternative remedial strategy through chemical treatment or biological enhancements to the biodegradation processes.

The guidance provides conditions under which MNA or EA can be carried out as remediation measures at a site including there are no unacceptable risks to human health or the environment, groundwater contamination sources are remediated or contained and controlled, the groundwater contaminant plume is stable or shrinking and there is a long-term performance monitoring and validation program. The guidance indicates the remediation concentration goals under a MNA or EA approach should be met within 20 years (this timeline is under review).

The use of EA should result in an increase in the attenuation rate with sufficient longevity to meet remediation standards with minimal applications. Lines of evidence for the confirmation of MNA/EA operating at a site are as follows:

1) Observed reduction in contaminant mass (required).

2) Geochemical and biochemical indicators (required).

3) Microbiological laboratory data (only if the first and second are inconclusive).

TG 22 provides a decision diagram for groundwater remediation using either MNA alone or in conjunction with EA. Use of supplemental guidance, in particular US EPA (1999), and other more recent guidance is allowed and additional references are provided in Appendix 2 of Draft TG 22.

3.0 CONCEPTUAL SITE MODEL

The conceptual site model addressed in this guidance focuses on petroleum hydrocarbon source zones and dissolved plumes, natural attenuation processes, site specific factors that affect plume characteristics and conceptually how remediation measures may affect hydrocarbon concentrations and longevity. Some principles described in this document would also apply to other organic compounds such as those found in coal tar or creosote. The most common types of releases of petroleum hydrocarbon contaminants that impact groundwater are associated with leaking underground fuel tanks that typically occur at gasoline retail or service stations. Figure 1 shows the conceptual model of processes related to the release, fate, transport, and groundwater plume formation of petroleum hydrocarbon contamination. The following sections describe the overview of processes, detailed discussion of contaminant plume characteristics, and review of select studies.

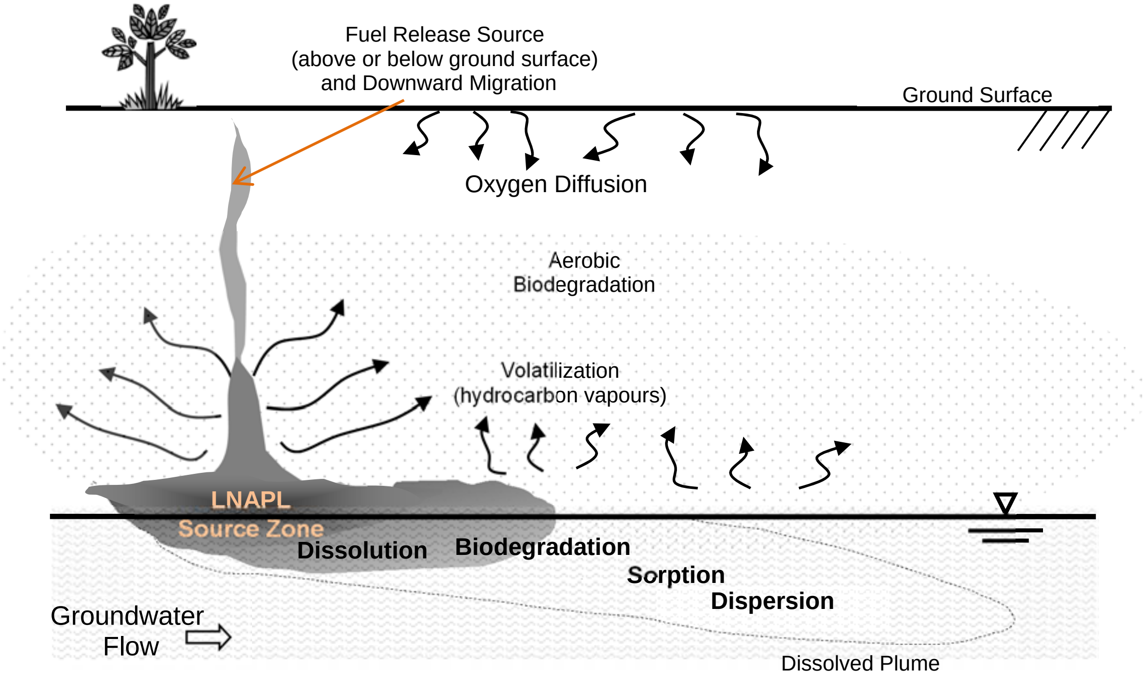

Figure1: Processes related to LNAPL source zone and groundwater plume formation.

3.1 Overview of Processes

The conceptual model begins with a light non-aqueous phase liquid (LNAPL) source consisting of petroleum hydrocarbons. When LNAPL is released in the vadose zone, the LNAPL moves predominantly downward as a separate immiscible phase under the influence of gravity, until it encounters the water table, where buoyancy forces and capillary forces due to higher water contents result in vertical accumulation and lateral spreading of the LNAPL. Residual LNAPL remains within the vadose zone in the zone of LNAPL migration. At the water table, the repeated rising and falling of the water table often results in the formation of a LNAPL smear zone.

For the above conceptual source model, the fate and transport of organic constituents will be controlled by physical, biological, and geochemical processes and reactions involving mineral, petroleum hydrocarbon (immiscible phase), aqueous and gaseous constituents.

Subsurface fate and transport processes may include:

- dissolution of petroleum hydrocarbon compounds in the LNAPL source; in the vadose zone this occurs because of infiltrating water and in the smear zone (below the water table) because of flowing groundwater;
- dissolution and precipitation of inorganic constituents (minerals);
- advective-dispersive transport of solutes in flowing groundwater;
- volatilization of petroleum hydrocarbon compounds from LNAPL and dissolved hydrocarbon;
- gas-exchange at the water table, for example, exchange between gaseous and dissolved oxygen;
- microbial mediated oxidation-reduction reactions;
- re-oxidation of the reduced products such as methane oxidation in the vadose zone or at the outer fringes of the groundwater plume where oxygen is available;
- aqueous and surface complexation reactions;
- adsorption or absorption of petroleum hydrocarbon compounds and inorganic constituents onto or into aquifer materials, for example, absorption of hydrocarbons into organic matter and adsorption of inorganic constituents onto organic matter and/or minerals;
- ion exchange; and
- aqueous and gas-phase diffusion.

The focus of this toolkit is on the formation and evolution of a groundwater contaminant plume due to dissolution and transport of petroleum hydrocarbon constituents in flowing groundwater and related processes. Volatilization and biodegradation of petroleum hydrocarbon are key processes that act to reduce the extent and persistence of the LNAPL source and contaminant plume.

Volatilization can occur above the water table from LNAPL and dissolved constituents, while biodegradation occurs in the aqueous phase both in the water-filled portion of the pore space in the unsaturated zone and the saturated zone below the water table. Biodegradation reactions can occur under aerobic and anaerobic conditions, and are controlled by the availability of the terminal electron acceptors (TEAs) and substrate (petroleum hydrocarbon) availability. The biodegradation reaction rates depend on the hydrocarbon constituents and their physical and chemical properties.

The efficiency of the biodegradation reactions thus depend on the redox conditions, and, in general the microbial degradation of hydrocarbon fuels are favoured in more oxidizing conditions (*e.g.*, ITRC, 2009a; Pope *et al*., 2004; and references therein). The energy gained by microorganisms through oxidation-reduction reactions depends on the electron acceptor. Because aerobic respiration is the most energetically favourable reaction, oxygen is the first electron acceptor utilized in the oxidative process. If dissolved oxygen is depleted, other terminal electron acceptors, such as nitrate, manganese (Mn^{4+}), ferric iron (Fe^{3+}) and sulphate may be used by microorganisms depending on their availability and potential energy yield, or methanogenesis (fermentation) of petroleum hydrocarbons can occur under highly reducing conditions.

Where the dissolved concentrations are relatively high (*i.e.,* in source zones), the reaction kinetics are often best described by a zero-order kinetic reaction. The rate of biodegradation occurring in the dissolved-phase plume beyond the source zone of petroleum hydrocarbon is often described by a first-order reaction rate with respect to the dissolved-phase concentration of the LNAPL constituent, although other kinetic models of biodegradation assuming a zero-order or Monod kinetic model are also used in groundwater fate and transport models (US EPA, 2004 and US EPA REMFuel, 2012). In some cases, the biodegradation rate can be assumed to be “instantaneous” and limited only by the availability of the electron acceptors. In these cases, the biodegradation reaction is assumed to be fast relative to the transport of the electron acceptor (US EPA BIOSCREEN, 1996 and US EPA, 2004).

There is significant complexity of hydrocarbon attenuation based on the above processes due to the LNAPL distribution (whether above or below the water table), mass transfer limitations within the LNAPL zone (in geologic complex environments), and the potential for groundwater to bypass the LNAPL zone. The biodegradation kinetics will also vary depending on location and will tend to be slower in the LNAPL source area compared to the dissolved downgradient plume.

3.2 Contaminant Plume Characteristics

The dissolution and spreading of the LNAPL constituents both vertically and in the groundwater flow pathway lead to the formation of a groundwater contaminant plume. The spreading results from advective-dispersive transport in the direction of the groundwater flow and dispersion in the transverse horizontal and vertical directions that lead to the formation of a plume in three dimensions. Transport through molecular diffusion is generally negligible except at very low groundwater velocities. The horizontal spreading in the direction of the groundwater flow is typically referred to as the plume length. While dissolution and groundwater flow act to increase plume lengths, processes including sorption, volatilization and biodegradation reactions act to decrease plume lengths. The dynamics of these transport and reaction processes determine the plume dimensions at any given time. The stages of plume evolution can include the formation, stabilization, and exhaustion of the plume based on dissolved contaminant concentrations and/or plume lengths.

The plume length depends on the local hydrogeological conditions, the physical-chemical properties of the LNAPL constituent under consideration and its susceptibility to biodegradation. The extent of the plume for a specific chemical contaminant is typically defined by a concentration to which the plume is delineated and which represents a remediation concentration goal. The remediation concentration goals can potentially be the applicable numerical standards for the site, background concentrations, or site-specific risk-based standards.

The stages of a plume can be defined by the temporal trend for either plume length or concentrations and are defined as follows (Connor *et al*., 2015):

- Expanding plume;
- Stable/No Trend plume;
- Shrinking plume; or
- Non-Detect (contaminant concentrations in groundwater of the affected zone are not detectable) or Exhausted (trace concentrations of petroleum hydrocarbons remaining near the source location) plume.

3.3 Site Specific Factors Affecting Plume Characteristics

The overall mass of the LNAPL as a residual phase in the soil or mobile continuous-phase product at the water table are key factors in the formation and persistence of the groundwater plume. Therefore, the distribution of the LNAPL in the subsurface, as determined by estimates of the horizontal and vertical extents of LNAPL saturations defines the source zone of the plume at a given site. The dissolved-phase concentrations of the LNAPL constituents within the source zone can be described by their effective solubility and mole fraction as governed by Raoult's law and form the upgradient zone of the plume.

In addition to the physical-chemical properties of the contaminant forming a groundwater plume, the local hydrogeological conditions at the site can affect the plume length and longevity. Key factors are those affecting the contaminant transport, particularly groundwater velocity, which is a function of the soil hydraulic conductivity, porosity, and hydraulic gradient at the plume location. The soil organic carbon content affects not only the sorption, or the retardation process, but also the availability of the terminal electron acceptors for the biodegradation of the organic contaminant.

While most natural soil conditions contain the microbial communities required for the degradation of petroleum hydrocarbons, the time required for the onset of the biodegradation reactions and nutrient availability can affect the overall degradation rates. Hence, enhanced attenuation (EA) technologies through bio-stimulation may be needed at some sites in conjunction with MNA for the successful remediation of the dissolved contaminant plume. For petroleum hydrocarbon compounds, bio-augmentation is applied in rare cases to enhance anaerobic biodegradation of benzene. It is rarely applied because benzene-degrading microbes are ubiquitous and it is generally easier to supply oxygen to stimulate aerobic biodegradation or anaerobic bioremediation through sulfate amendments rather than introduce and maintain non-native microbes.

Volatilization also affects source zone depletion and the longevity of the dissolved contaminant plume. Factors that affect the volatilization of LNAPL constituents are the properties of the overlying soil, depth to source from the ground surface, and ground cover. Soil and ground surface conditions affect not only the transport of volatile hydrocarbon vapours through the vadose zone, but also affect the downward transport of oxygen, which impacts the extent of aerobic biodegradation of the volatile hydrocarbons that can occur in the unsaturated soil. The respiration of natural organic carbon in the vadose zone can act as a sink for oxygen available for aerobic hydrocarbon biodegradation.

3.4 Overview of the Effects of Remediation

Remediation efforts can be directed at either the source or the plume or both, where the reduction of the source mass can also affect the plume characteristics. Technologies for source mass treatment include hydraulic recovery of free LNAPL, multi-phase extraction (MPE), soil vapour extraction (SVE), air sparging and thermal treatment. *In-situ* chemical oxidation of petroleum may also be an option at some sites. Soil vapour extraction and air sparging, often referred to as bioventing and biosparging, result in bio-stimulation that can result in enhanced rates of source mass treatment. The effect of bio-stimulation or bio-augmentation on source zones will depend on the distribution of LNAPL and size of the release, and timescales for clean-up through bio-stimulation may be relatively long. Other remediation technologies include pump-and-treat systems and permeable reactive barriers for the treatment of the contaminant plume in groundwater.

The Los Angeles LNAPL Workgroup (2015) report describes an evaluation of 20 LNAPL remediation technologies, and results of pilot tests of three technologies, consisting of pulsed oxygen biosparging, surfactant flushing and NSZD. On the basis of this work, a LNAPL management strategy decision tree is presented. For residual LNAPL source zones, the basis for including NSZD as a potentially applicable and effective technology is described if the objective is LNAPL mass removal. If the remedial objective is LNAPL phase change (*i.e.*, to achieve concentration-based criteria) or plume control, air-phase technologies (*e.g.*, SVE, air sparging) or groundwater pumping may be warranted.

4.0 REVIEW OF PETROLEUM HYDROCARBON PLUME STUDIES

Summaries of six petroleum hydrocarbon groundwater plume studies that include discussions of relevant processes on a conceptual basis, interpretation of field data and observations, and predictive modeling for the evaluation of remedial technologies are described below.

4.1 Suarez and Rifai (2004)

Modeling Natural Attenuation of Total BTEX and Benzene Plumes with Different Kinetics

The BioPlume III model was used in this study to compare the natural attenuation of benzene and BTEX at a coastal site based on combination of field data and pertinent literature values. A relatively large BTX-only (not gasoline) release occurred at this site (approximately 30,000 gallons remained in the ground after initial recovery). The conceptual model for the coastal site is a shallow, continuous, unconfined aquifer with variable thickness that is comprised of silty clay and sandy silt soil. A kinetic model based on instantaneous reaction was assumed for BTEX biodegradation, while a first-order biodegradation rate was assumed for benzene.

The study evaluated two alternatives for BTEX and benzene fate at the site; 1) decaying sources using regression line values of field data, and 2) decaying sources assuming 20% annual LNAPL removal. For each alternative, the maximum concentration, average concentration across the site, distance to downgradient plume edge, total dissolved mass, plume length and time to reach the cleanup goal was evaluated. The model was calibrated by altering source concentrations and hydraulic parameters until simulated plume concentrations and heads and plumes approximated observed field conditions.

> The BioPlume III model was used to compare the natural attenuation of benzene and BTEX at a site with a large BTEX-only release. The estimated remediation timeframes based on a target of 5 µg/L for benzene and 5 mg/L for total BTEX were approximately 100 years for benzene, and between 150 to 200 years for BTEX (note that longer timeframes would be predicted for a BTEX-only plume compared to BTEX in gasoline). Removing LNAPL at an annual rate was predicted to shorten the remediation time for BTEX but not for benzene.

The model results were used to estimate remediation timeframes based on a target of 5 µg/L for benzene and 5 mg/L for total BTEX. The estimated timeframes were approximately 100 years for benzene, and between 150 to 200 years for BTEX. Removing LNAPL at an annual rate was predicted to shorten the remediation time for BTEX, but not for benzene. The authors provide the uncertainty for plume characteristics estimated by the model based on variations in input parameters and a 95% confidence interval on the mean. The results indicate mean plume lengths of 485 +/- 132 m and 466 +/- 175 m for benzene and BTEX, respectively.

4.2 Schirmer and Butler (2004)

Transport Behaviour and Natural Attenuation of Organic Contaminants at Spill Sites

Effective remediation strategies require understanding of pathways for mass loss of multiple organic compounds in heterogeneous aquifers under natural conditions. The authors of this paper summarize the five main processes affecting organic contaminants in groundwater: 1) dissolution of the source plume constituents; 2) mass transfer from the residual zone to groundwater zone; 3) transport via diffusion, advection and dispersion in the saturated zone; 4) sorption; and 5) chemical and biological transformation. The key processes are reviewed and discussed through the results of two controlled field experiments.

Dissolution of NAPL components into groundwater can be described by Raoult's Law, which states that the saturated concentration in groundwater at equilibrium reflects the molar fraction of a substance in a mixture. More soluble NAPL components will be preferentially removed from the source into the groundwater and therefore decrease in mole fraction and thus concentration. Conversely, the mole fraction of low solubility components will gradually increase over time, and so will their concentration in the source zone.

Multiple components in NAPL plumes lead to a range in hydrophobicity within the plume. This will yield differences in susceptibility to sorption along the flow path, causing different rates of transport and concentrations for individual constituents within the plume. Ultimately, this means that the exposure of contaminant concentrations changes over time and space, and may affect the microbial populations dependent on the plume as an energy source. The acclimation time of indigenous microbial populations (from minutes to months), their growth and decay dynamics, availability of electron acceptors, capacity to use alternate electron acceptors, and toxic level of one compound that can inhibit the biodegradation of another are all factors that can lead to preferential biodegradation and affect the relative longevity of organic compounds in the groundwater.

Two controlled field experiments carried out at the Canadian Forces Base Borden Research Site (Ontario, Canada) were reviewed: a gasoline mixture with and without added methanol or methyl *tert*-butyl ether (MTBE); and a second experiment with coal tar creosote organics placed in the subsurface. The results of the gasoline mixture experiment resulted in varying retardation within the aquifer. Plume separation occurred due to differences in retardation and contaminant velocity and influenced the biodegradation of the contaminants over time, because of the spatial variation in the hydrocarbon composition. MTBE did not seem to influence BTEX degradation and it is possible that preferential BTEX utilisation inhibited the degradation of MTBE.

Modeling and field studies indicate Raoult's Law is expected to be applicable for most field situations. Variable retardation rates of gasoline constituents cause plume separation, which affects biodegradation rates. The study concludes all relevant contaminant constituents should be considered when evaluating plume behaviour.

Parallel laboratory microcosm studies and numerical modeling were used to interpret the results of the coal tar experiment. The analysis showed that oxygen availability was the limiting factor in the degradation of naphthalene. The results also suggested that Raoult's law would be applicable in many field situations. Overall, the experiments showed that plume behaviours of different compounds from the same source zone can vary significantly because of combined effect of retardation and variable biodegradation. The study authors recommend that all relevant contaminant constituents be considered in the evaluation of MNA at a spill site.

4.3 Huntley and Becket (2002)

Persistence of LNAPL Sources: Relationship Between Risk Reduction and LNAPL Recovery

This study applies a modeling tool (API LNAST Model – refer to Toolkit #2) to various LNAPL spill conditions and evaluates the effectiveness of LNAPL recovery on the downgradient extent of the dissolved-phase plume. The authors define four phases associated with the release and degradation of LNAPL: 1) downward movement through the vadose zone; 2) presence at the water table and formation of dissolved-phase plume; 3) pseudo-steady-state for biodegradable constituents, where biodegradation "keeps pace" with LNAPL source dissolution; and 4) contraction of the dissolved-phase plume following LNAPL source depletion.

The theoretical background for estimation of source zone depletion through dissolution and volatilization are described. Through calculations of mass flux for each constituent of LNAPL considered and Raoult's Law, the source zone concentrations are used as input to the analytical groundwater model (Domenico, 1987) for the prediction of down-gradient dissolved-phase concentrations. The analytical model takes into account the biodegradation, sorption, one-dimensional advective flow and three-dimensional dispersion. The results are presented for benzene as a representative biodegradable constituent and MTBE as a minimally degradable constituent.

The study evaluates the effects of LNAPL thickness and remediation for coarse sand and silty sand deposits. The model predicts that free-product removal significantly decreases the longevity of a benzene plume in coarse sand but not for silty sand. This is because the LNAPL recovery, characterized in the model as the estimated difference in LNAPL saturation before and after remediation, is larger in coarse sand than silty sand. Remediation through recovery is shown to result in a rapid contraction of the groundwater plume although the maximum downgradient extent is not affected for coarse sand, whereas, the effects of remediation are shown to be negligible for silty sand.

> A modeling study using API LNAST indicated LNAPL recovery would not be effective in reducing the longevity of a dissolved-phase gasoline plume except in medium to coarse-grained soils. The maximum downgradient plume extent was not affected by remediation through recovery. Instead, remediation such as air sparging or SVE that reduces the mole fractions of hydrocarbon constituents (*e.g.*, benzene) are predicted to be more effective in decreasing the downgradient plume extent and maximum concentrations.

The study also considers air sparging and soil vapour extraction as alternate remediation approaches to target the more volatile constituents in finer-grained soils. The alternate remediation technologies are implemented in the models as lower source zone mole fractions of the components of concern in the LNAPL. The results indicate lower post-remediation concentrations, although depletion times are not significantly affected due to lower dissolution rates. The lower mole fractions result in a decrease in the downgradient extent and maximum concentrations at a specific receptor distance for both benzene and MTBE.

The authors conclude that free-product recovery is not effective in reducing the longevity of the dissolved-phase plume except in medium to coarse-grained soils. The maximum downgradient extent of the biodegradable constituents is shown to be a function of groundwater velocity and biodegradation rate and not affected by remediation through recovery. Instead, alternate technologies such as air sparging or soil vapour extraction that would result in the reduction of the mole fractions of the constituents of concern (benzene and MTBE) are predicted to be more effective in decreasing the downgradient extent and maximum concentrations at a specific receptor distance, particularly for fine-grained soils and when the initial LNAPL saturation is low.

4.4 Vaezihir *et al*. (2012)

Field-Scale Modeling of Benzene, Toluene, Ethylbenzene, and Xylenes (BTEX) Released from Multiple Source Zones

A three-dimensional reactive transport and flow model (BIONAPL/3D) was used for the simulation of groundwater BTEX plumes resulting from petroleum hydrocarbon LNAPL at an oil refinery site. Field measurements were used to define the source zones and calibrate the flow and transport components of the model. Groundwater chemistry data from monitoring and pumping wells were used to calibrate the degradation rate constant and sorption coefficient of BTEX compounds. The model was subsequently used to evaluate two remediation strategies based on a desired outcome of 1) remediating the site to the applicable drinking water limits for BTEX, and 2) preventing the migration of the plumes to the nearest receptor wells.

The modeling scenarios that assumed the source release had been stopped predicted remediation times to meet the drinking water limit for benzene under natural attenuation conditions that ranged from 77 to 120 years. Three scenarios each assuming 50% source removal of LNAPL and varying *in-situ* treatments to promote EA (air or pure oxygen injection, nitrate and sulphate amendments) were then simulated. The remediation was assumed to occur after plume migration had already started. The predicted decrease in the benzene remediation time for these three scenarios ranged from approximately 20% to 50%.

A numerical modeling study using BIONAPL indicated benzene remediation timelines (to meet a drinking water limit) of 77 to 120 years under natural attenuation conditions. Relatively aggressive source LNAPL remediation and addition of bio-amendments was predicted to result in up to a 50% decrease in the benzene remediation timeline. Greater reductions were predicted for other BTEX constituents for select cases.

4.5 Kim *et al*. (2015)

Comprehensive Environmental Investigation at Former Industrial/Petroleum Underground Storage Tank Sites in Long Beach, CA: A Forensic Perspective

Two petroleum hydrocarbon groundwater plumes at two industrial sites in California were investigated where source control measures were partial remedial excavation of contaminated soil. The extent of source removal was not sufficient to reduce dissolved-phase concentrations to clean-up levels. The soil and groundwater monitoring was carried out for five years at one site and for ten years at the second site. Free product was not detected at either of the two sites.

The effect of weathering was evaluated through a comparison of maximum concentrations of gasoline constituents in groundwater to those of a fresh gasoline release (in equilibrium in groundwater). Age-dating of the contamination with constituent ratios (B+T)/(E+X) indicated a continuously releasing source at one of the sites and release within the last decade at the second site. Localized but high concentrations of BTEX were measured near the source zone with maximum benzene concentration of 3,800 µg/L and maximum plume length of approximately 25 m. The authors recommend *in-situ* remediation of residual sources with MNA as a longer-term remediation approach.

4.6 Overview of the Bemidji Studies

The crude oil spill site near Bemidji, Minnesota has been well characterized through numerous studies (over 200 publications; Essaid *et al.*, 2011). The spill was the result of a 1979 pipeline rupture causing the subsurface infiltration of over 400,000 L of crude oil, which was composed of approximately 60% saturated hydrocarbons and aromatics as much of the remainder of the oil (Bekins *et al.*, 2011 and references therein). The review below summarizes two studies that provide insight on the natural attenuation of chemical constituents associated with the crude oil spill at Bemidji.

Essaid *et al.* (2011) provide a review on long term natural attenuation and monitoring (25 years) at the Bemidji crude oil spill site. The extent and evolution of the hydrocarbon plume is shown to be the result of a complex set of processes including multiphase flow and transport, biogeochemical reactions, and microbial metabolism. The review of field and modelling studies show the significance of anaerobic biodegradation reactions and, in particular, the role of iron reduction and methanogenesis on plume extent and longevity. The significance of the composition of the oil and differences in the evolution of the alkanes and aromatic compounds are discussed. For example, the loss of relatively soluble BTEX compounds is shown to be controlled by dissolution, which is sensitive to concentrations of these parameters in groundwater and flow rates. This review also identifies the redox zones that result from biodegradation processes in sequence of terminal electron acceptors starting from aerobic degradation, to manganese reduction, to iron reduction, and to methanogenesis. The Essaid *et al.* (2011) study also provides a summary of the modelling studies of various complexities applied to the Bemidji site, as well as calibration of model parameters with field data.

Bekins *et al.* (2011) report on changes in the groundwater plume and the LNAPL composition since the release of the crude oil in 1979 in one of the three main areas of the spill, the north pool oil body. In reviewing the benzene concentrations in groundwater near the source zone, they report a drop from 4.6 mg/L to 2.1 mg/L or 55% during a 14-year time period extending from 1993 to 2007. In contrast to the decrease in benzene concentrations, Bekins *et al.* (2011) found the ethylbenzene concentrations were relatively constant. The same relative decrease in benzene concentrations versus ethylbenzene concentrations was observed in the crude oil samples collected from the source zone.

5.0 MULTI-SITE EVALUATION STUDIES

The main findings of case study data from multi-site evaluations of MNA and NSZD from select studies are summarized in this section. This summary includes the comprehensive studies completed by Groundwater Services Incorporated (GSI) for the American Petroleum Institute and the more recent evaluations by GSI of the California GeoTracker Database.

5.1 Connor *et al*. (2015)

Review of Quantitative Surveys of the Length and Stability of MTBE, TBA, and Benzene Plumes in Groundwater at UST Sites

This study compiled datasets from 13 past multiple-site (or multi-plume) studies at sites with primarily gasoline releases from USTs at retail service stations and represents an update to the Newell and Connor (1998) publication. Studies reviewed involved sites in specific states (CA, TX, FL, SC, CT or NH) or nationwide in USA (CA, NJ, AK, OR, NV). Data from 12 of the 13 studies were grouped together and a weighted mean on the ordered statistics from these datasets were used to summarize the data. The data from one study (McHugh *et al.*, 2014), which involved compilation of data from 4,000 sites in CA in the California GeoTracker database, was considered separately. While no specific information is provided, it is expected that a range of remediation was completed at sites evaluated for this study.

Studies selected were based on the following criteria:

- Gasoline fuel from USTs primarily associated with retail or service stations;
- Each study considered multiple plumes of benzene, MTBE, and/or *tert*-butyl alcohol (TBA);
- Studies of plume lengths (number of sites per study ranged from 22 – 289);
- Studies of plume stability (number of sites per study ranged from 34 – 271);
- Minimum of 1 year monitoring and greater than 3 years of monitoring at most sites; and
- Studies based on a minimum of 3 to 8 monitoring points per site; on average there were 4 to 17 points per site.

The assumption for use of a weighted mean to combine results of previous studies is stated as follows: “for sufficiently large datasets, order statistics, such as the median and 90th percentile values, are normally distributed, even if the underlying populations are not normally distributed.” Data from the McHugh CA study were not combined with the other studies. This study considered the maximum annual concentration of each parameter, which was conservatively chosen as the value more likely to represent concentrations near to the source in order to lessen the effects of plume delineation or change in number of monitoring wells with time. The plume characterization focused on two aspects: plume lengths and plume stability conditions.

5.1.1 Plume Lengths

Plume lengths for most sites were defined using a concentration limit or criteria of 10 µg/L for benzene. Data was summarized for three of the studies assuming a limit of 5 µg/L. The methods used for delineating the plume at the concentration limits were:

- hand-contouring concentrations measured at sampling locations, if the plume was delineated; and
- empirical or analytical method to extrapolate concentrations, if monitoring did not delineate the plume.

The weighted means of the 90th percentile benzene plume lengths were 105 m at 10 µg/L and 130 m at 5 µg/L, respectively, for the 12 studies presented in Table 1 and Figure 2. The means of the median plume lengths were 43 m and 55 m, respectively.

Table 1: Summary of compiled plume length data.[1]

Parameter	Number of studies	Total Number of sites	Delineation criteria (µg/L)	Weighted mean on the median (m)	Weighted mean on the 90th percentile (m)
Benzene	3	772-826[2]	10	43	105
Benzene	3	165	5	55	130

1. Median and 90th percentile plume lengths are weighted means of respective values reported in the individual studies.
2. Number of sites used in calculation of median and 90th percentile plume lengths were 826 and 772, respectively.

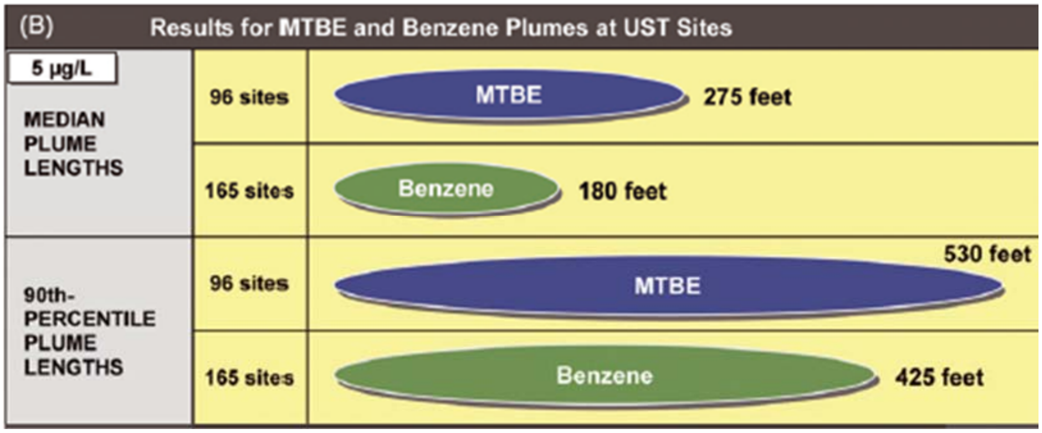

Figure 2: Plume lengths of benzene and MTBE from Connor et al. (2015).

5.1.2 Plume Stability Conditions

The methods for plume stability conditions were based on the trend on either plume length or concentration according to ASTM (2010), with the following categories for stability condition:

- Expanding plume;
- Stable/no trend plume;
- Shrinking plume; and
- Non-detect or exhausted plume.

In this study, the plume contours at different times or statistical trend analyses on concentrations as characterized by weighted means were used to evaluate trends and compiled to determine the number of results for each of the above four categories. For benzene data, the proportion of sites falling in the “non-increasing” concentration categories of plume stability was 92%. The proportion of sites falling in the “non-increasing” concentration categories of plume lengths was 94%.

The authors conclude that the narrow range in the plume lengths from various plume studies with multiple sites suggests that hydrogeologic conditions may be less important than factors such as spill volume and biodegradation rates. Similar biodegradation characteristics for benzene and MTBE are stated as the likely reason for the comparable plume lengths and stability conditions. Conner *et al*. (2015) reference other studies that also indicate hydrogeologic conditions are not key factors in plume characteristics such as Reid *et al*. (1999); Mace *et al*. (1997); Newell and Connor (1998); Shorr and Rifai (2002); and Wilson (2003).

> This compilation study of 13 previous multiple-site studies of primarily gasoline releases at retail service station sites indicates the median and 90th percentile benzene plume lengths (defined by 5 µg/L) were 55 and 130 m, respectively. The proportion of sites with stable, shrinking or exhausted plumes was 94%. The data indicates that hydrogeologic conditions may be less important than factors such as spill volume and biodegradation rates.

5.2 McHugh *et al*. (2014)

Progress in Remediation of Groundwater at Petroleum Sites in California

McHugh *et al.* (2014) use the GeoTracker Database for over 12,000 sites in California from 2001 to 2011 to evaluate the remediation progress at groundwater contaminated sites selected based on continuous monitoring records during a 10-year period. For data analysis, the maximum concentrations of the gasoline constituents for 6-month periods were used. Maximum concentrations were deemed to represent locations near the source. The study results are summarized as follows:

- Analysis of greater than 4,000 sites with at least four years of monitoring data showed decreases of 85%, 96%, and 87%, for benzene, MTBE, and TBA, respectively, over a period of 10 years. These values represent changes in the median of the maximum site concentrations.
- While benzene and MTBE concentrations showed a continuous decreasing trend, the TBA concentrations initially increased over a 3-year period before starting to decline. This difference was attributed to sequential degradation of MTBE to TBA followed by degradation of TBA itself.

- Estimated median attenuation rates at source zone wells for all sites with at least 5-years of monitoring data were 0.18/year for benzene and 0.36/year for MTBE. Less than 3% of sites were identified as having MNA as the only remediation technology; for the remaining 97%, the remediation consisted of a range of measures from LNAPL recovery to *in-situ* remediation.
- Different remediation technologies were compared with respect to the percent increase in the estimated median source attenuation rates (compared to the remaining dataset excluding that technology) that were statistically significant (Table 2).

Statistical (Mann-Whitney U-test) comparisons at 5% significance level ($p < 0.05$) showed sites with SVE or air sparging remediation implemented had significantly higher attenuation rates for benzene and MTBE, and sites with chemical oxidation had significantly higher attenuation rates for benzene.

The authors concluded that while SVE and air sparging are more effective technologies for benzene remediation, groundwater pump-and-treat is more effective for MTBE, consistent with the differences in their chemical properties.

Data from 12,000 sites in the California GeoTracker database were analyzed for the progress of groundwater remediation. The estimated median benzene attenuation rate at source zone wells for sites with a range of remediation types implemented was 0.18/year. Assuming first-order decay and this attenuation rate, and a reasonable initial source concentration for benzene at gasoline sites of 10 mg/L, the remediation timeframe for benzene attenuation to 5 μg/L is approximately 42 years. With a 53% increase in the source attenuation rate (reported for air sparging), the remediation timeframe is reduced to 28 years.

Table 2: Percent increase in the estimated median source attenuation rates.

Technology	Constituent	Increase in Source Attenuation Rate (%)
SVE	benzene	28
	MTBE	11
Air Sparging	benzene	53
	MTBE	22
Chemical Oxidation	benzene	20
Pump & Treat	MTBE	17

5.2.1 Further Evaluation of the McHugh *et al*. (2014) Study on Effect of MNA Remediation

Further analysis of the data compilation from the GeoTracker database conducted by McHugh *et al*. (2014) indicates that the number of sites, where MNA was reported to be the only technology employed, is 72 of the 3,524 sites with at least five years of monitoring of benzene concentrations in groundwater. The median source attenuation rate of benzene was estimated to be 0.21/year for sites with information on the remediation technology, excluding those with MNA as the only remediation (3452 sites) compared to a median rate of 0.13/year for sites with MNA-only remediation (72 sites). Assuming first-order decay at this attenuation rate, and a reasonable initial source concentration for benzene at gasoline sites of 10 mg/L, the remediation timeframe for benzene attenuation to 5 μg/L is approximately 58 years. The source attenuation rate that would be required to reach a 20-year timeframe for remediation is 0.38/year. For this data set, the number of sites that would meet a 20-year timeframe for remediation assuming an initial source concentration of 10 mg/L is 14 out of 72 or approximately 19% of the sites, where MNA was reported to be the only remediation technology.

5.3 Kamath *et al*. (2012)

Use of Long-Term Monitoring Data to Evaluate Benzene, MTBE, and TBA Plume Behavior in Groundwater at Retail Gasoline Sites

This study focuses on analysis of long-term monitoring data from 48 retail gasoline sites across the US. The majority of the sites were in New Jersey and California. Sites were selected based on availability of data over five years or longer from six or more monitoring wells. MNA was the only remediation at 16% of the sites. Product recovery was implemented at 20% of the sites, and some type of active groundwater remediation was implemented at 64% of the sites (in addition to product recovery). These data were used to support the California Low Threat Closure Policy described in Section 7.0.

For each site evaluated, the plume characteristics of benzene, MTBE and TBA were characterized in terms of current (*i.e.*, at time of most recent sampling event at the site) plume length and stability condition. The current plume length was estimated as the distance between the source and downgradiant location that met the remediation goal for well-delineated plumes; or it was estimated based on an observed bulk attenuation rate (Newell *et al*., 2002) for sites that were not well-delineated downgradient of the source; or, the maximum measured or estimated plume lengths for each constituent in the study were assumed.

The current stability condition was assessed through comparison of the maximum historical plume extent to the extent determined from the most recent sampling event; or through long-term concentration trends in wells at the downgradient edge of the plume. The temporal concentration trends were estimated at a single well location and on a site-wide basis using Mann-Kendall analysis. The trend analysis on concentrations was used to estimate attenuation rates and timeframes for achieving applicable remediation goals (drinking water criteria of 5 µg/L).

The effect of active remediation and NAPL recovery on estimated attenuation rates were estimated and found not to be statistically significant compared to MNA only. Total remediation timeframes were defined as the duration of groundwater monitoring period from the first detection of the constituent, plus the maximum estimated additional remediation timeframe from the most recent monitoring event to achieve remediation goals. The total remediation timeframes that were estimated in the study are summarized in Table 3.

Table 3: Total Remediation Timeframes.

Constituent	range (years)	median (years)	# of sites
Benzene	12 – 52	24	36
MTBE	7 – 41	15	31
TBA	9 – 29	17	15

Kamath *et al.* (2012) conclude that the MTBE plume characteristics analysed in the study were similar to that of benzene in terms of diminishing concentrations over time (at point location), current plume lengths, plume stability trend, and timeframe to achieve remediation goals. The conclusion is deemed by the authors to be consistent with the discontinued use of MTBE as a fuel additive. The TBA plume lengths were also similar to benzene and MTBE; however, in terms of plume stability, 68% of sites were found to have plumes that were stable or shrinking for TBA versus greater than 90% for benzene and MTBE. The results were considered consistent with expected build-up of TBA associated with MTBE degradation.

> Data from 48 gasoline retail sites mostly in California and New Jersey indicated benzene remediation timelines of 12 to 52 years. Active remediation and LNAPL recovery had occurred at most sites. The effect of active remediation and LNAPL recovery on estimated attenuation rates were estimated and found not to be statistically significant compared to rates for sites with no remediation or recovery.

5.4 Shih *et al.* (2004)

Evaluation of the Impact of Fuel Hydrocarbons and Oxygenates on Groundwater Resources

This is a multi-site study of leaking underground fuel tanks (LUFT) from the Los Angeles area in California with a focus on groundwater monitoring data where the frequency of detection, maximum concentrations and contaminant plume lengths are reported. Data from 7,200 monitoring wells at 868 LUFT sites were used to assess detection frequency, maximum site concentrations and correlation among the gasoline constituents; and 500 sites were selected randomly from 1,100 active LUFT facilities for assessment of groundwater plume lengths. These data were used to support the California Low Threat Closure Policy described in Section 7.0.

The spatial extents of the groundwater plumes were estimated based on the following factors:

- Average groundwater gradient directions; and
- Extrapolation of the contaminant concentrations in the most downgradient wells to target concentration contours.

Groundwater monitoring data for seven parameters were considered: benzene, total petroleum hydrocarbons for gasoline contamination that includes C4 – C12 (TPH_G), MTBE, diisopropyl ether (DIPE), ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME), and TBA. The results of the plume length analyses indicated that MTBE had the greatest plume length amongst benzene, TPH_G and fuel oxygenates. The statistical significance of differences between the plume lengths was also tested after log-transformation of the data. Table 4 below shows the maximum and geometric mean of plume lengths for benzene, MTBE, and TPH_G from this study.

Table 4: Maximum and geometric mean of plume lengths.

Statistics	Benzene (5 µg/L)	TPH_G (100 µg/L)	MTBE (5 µg/L)
Geometric mean (m)	51	64	83
Maximum (m)	168	259	317

Note: the 90th percentile benzene plume length was 100 m.

The analysis indicated no significant change for plume lengths of MTBE, TPH_G and benzene, while an increasing trend was determined for other fuel oxygenates. In order to evaluate the effect of fuel oxygenates on the plume lengths of benzene and TPH_G, the data set was divided into LUFT sites with and without fuel oxygenates. There was a distinct (statistically significant) difference between the two populations with 20% to 30% longer plumes for the population of sites where fuel oxygenates were present. It was noted that this could be a result of the age of the plume, where more recent releases could be associated with the presence of fuel oxygenates.

A statistical analysis of benzene plume length (based on a 5 µg/L threshold) on data from 500 UST sites in the Los Angeles, California area indicated geometric mean, 90th percentile and maximum plume lengths of 51 m, 100 m and 168 m, respectively. Sites with fuel oxygenates present had 20-30% longer plumes.

5.5 Kulkarni *et al*. (2015)

Evaluation of Source-Zone Attenuation at LUFT Sites with Mobile LNAPL

This study uses the GeoTracker database for a statistical evaluation of 3,523 LUFT sites for the effect of mobile LNAPL on source zone attenuation rates. Source-zone attenuation is defined in the study as “reduction in groundwater concentrations of key constituents”. There were two study objectives: 1) assess the effect of mobile LNAPL on groundwater concentrations and source attenuation rates; and 2) assess the effect of hydraulic LNAPL recovery on observed LNAPL thicknesses, constituent concentrations, and source attenuation rates.

The database accessed contained information for 10,760 LUFT sites from the period of 2001 to 2011 of which 3,523 represented sites with at least five years of monitoring data for benzene and MTBE. Of the total LUFT sites analysed, 972 had reported apparent LNAPL thickness in monitoring wells, while 2,253 reported no apparent LNAPL thickness. Using the ITRC (2009b) definition for “mobile LNAPL” and “residual LNAPL”, an LNAPL site was defined by having at least one well with a minimum of one historical measurement of observed LNAPL thickness (mobile LNAPL), otherwise it was considered a non-LNAPL site, likely to have “residual LNAPL”. In order to evaluate the effectiveness of LNAPL recovery, the change in total LNAPL thickness was estimated. The total LNAPL thickness was defined as the summation of the maximum historical LNAPL thicknesses for all wells at a site.

The maximum benzene and MTBE concentrations for the entire site, assumed to represent dissolved concentrations within the source zone, were used to estimate the source attenuation rates (k_{source}) using least square regression. This procedure differs from the method followed by McHugh *et al*. (2014), in which the attenuation rate (k_{point}) was estimated for each monitoring well in the source zone. The estimated k_{source} values were assumed to represent the combined effects of all attenuation processes including biodegradation, dissolution, volatilization, and active remediation.

The conceptual model for attenuation of the dissolved-phase concentrations in groundwater considered both vadose zone and saturated zone processes, where the saturated zone processes included methanogenesis and ebullition (vertical transport of methane gas bubbles from the saturated zone to the vadose zone). A summary of the historical maximum benzene concentrations and attenuation rates from this study are provided in Table 5. The authors indicate a statistically significant difference ($p = 0.002$) in maximum concentrations using a two-tailed t-test between the LNAPL and non-LNAPL sites.

Table 5: Comparison of maximum benzene concentrations and attenuation rates for "LNAPL" and "Non-LNAPL" sites.

Site Type (# of sites)	Median historical maximum concentration (µg/L)	Median attenuation rate k_{source} (year^{-1})
LNAPL (972)	14,000	0.13
LNAPL with recovery* (327)	12,000	0.09
LNAPL without recovery (444)	18,000	0.19
Non-LNAPL (2,253)	2,300	0.22

*Recovery is defined as free-product removal in GeoTracker and likely includes skimming or bailing but does not include pump-and-treat or dual-phase extraction technologies.

Analysis of the estimated attenuation rates for LNAPL sites with and without recovery (defined as physical product removal through skimming or bailing) indicated lower attenuation for sites with recovery. The authors considered the possibility that this surprising result could be due to the release volumes of sites with and without physical LNAPL recovery. However, further analysis of the data with respect to LNAPL thickness (as indicator of release volume) did not support this hypothesis. The authors thus conclude that, undetermined factors other than release volume are responsible for the difference in estimated attenuation rates for sites with and without physical LNAPL recovery.

A comparison of the maximum historical concentration and attenuation rates did not show a correlation between these two parameters; however, there was a weak correlation between the attenuation rate and the total LNAPL thickness, which was not statistically significant for benzene. Overall, the study results indicated:

1) The majority of sites showed decreasing groundwater source concentrations of benzene (72% for LNAPL and 79% for non-LNAPL sites);

2) Higher maximum concentrations of benzene in groundwater and slower source attenuation rates for sites where mobile LNAPL has historically been identified; and

3) Analysis of maximum concentrations, LNAPL thickness, and source attenuation rates did not identify an improvement towards remediation for sites with physical LNAPL recovery.

6.0 BRITISH COLUMBIA AND YUKON CASE STUDIES

One of the project goals is to better characterize conditions for MNA in British Columbia. To achieve this goal, monitoring data from petroleum hydrocarbon sites in BC was sought. An information request was sent to the Contaminated Sites Approved Professional (CSAP) Society, internally within Golder Associates and organizations represented on the advisory group (Appendix A). The objective was to obtain data from different types of sites, for example, large and small gasoline and diesel releases, and large site (*e.g.*, refinery) mixed releases. Currently six BC and Yukon case studies have been reviewed (Table 6 and Appendix B).

The five sites in British Columbia include four sites in the interior regions and one site in the Vancouver area. Four sites were service stations with gasoline contamination and one site was a rail yard with diesel contamination. Remediation conducted at the sites ranged from LNAPL recovery using skimmers at the diesel site, SVE at a gasoline site with a large release and deep contamination, and excavation at three sites where most contamination was removed excluding contamination below infrastructure such as roadways and sidewalks.

Monitoring data for source zone wells indicate that BC drinking water (DW) groundwater standards were not achieved or likely to be achieved at all six sites (at two sites there are limited data and therefore the determination is uncertain). Benzene concentrations decreased to below the DW standard (5 µg/L) within approximately 20 years at all five BC sites evaluated (it remained above standard only at the Yukon tank farm site), but concentrations of other substances remained above the DW standards, including ethylbenzene (drinking water standard of 2.4 µg/L), xylenes (300 µg/L) and benzo(a)pyrene (0.01 µg/L). In addition, the toluene, extractable petroleum hydrocarbon (C10-19) and volatile hydrocarbon (C6-10) concentrations remained above the DW standards at the Yukon site, where there was a very large gasoline release. However, dissolved plumes were stable or shrinking and plume lengths were short, estimated to range from a few metres at one site to 50 to 70 m at a site in BC with a large gasoline release.

At Case Study #4 site, representing a large gasoline release where vadose zone contamination was largely removed through SVE, the concentration trends were dependent on where the well was located. At wells within the upgradient area of the residual LNAPL (relative to groundwater flow), there were significant decreases in BTEX concentrations (including ethylbenzene) to below DW standards within approximately 20 to 30 years. The inferred depletion time for the downgradient area of the residual LNAPL zone is significantly (decades) longer. The results suggest downgradient depletion of the LNAPL was limited due to the solubility limit being reached in flowing groundwater in the upgradient area.

Attenuation rates were estimated for the sites through fitting a linear regression equation to the log-plot of the concentration data (first-order decay constants). The geometric mean of the attenuation rates for benzene and ethylbenzene were 0.55/year and 0.29/year, respectively. For a starting benzene and ethylbenzene concentration of 10 mg/L, these decay rates predict attenuation to below the drinking water standards in 14 and 29 years, respectively. The geometric mean attenuation rates for benzene and ethylbenzene estimated for the case studies are higher than the median or average rates for multi-site US studies reviewed in this document, although it is recognized that the BC data set is small.

Table 6: Summary of BC and Yukon case studies.

Case Study/ Location	**Site Type**	**Release Size**	**Remediation**	**Remediation to DW within 20 yrs?**	**Substances > DW at 20 yrs**	**Estimated Plume Length (m)**	**Attenuation Rate**	
							k ethyl-benzene (year^{-1})	**k benzene (year^{-1})**
1-BC	G	Small-mod	Partial excavation*	No	Ethylbenzene	Up to 30 m	0.11,0.8, 0.32	0.52, 0.53, 0.31
2- BC	D	Large	LNAPL skimming	No	Ethylbenzene	15-20 m	N/A**	N/A**
3-YT	G	Very Large	Partial excavation	No	BTEX, EPH10-19, VH6-10, benzo(a) pyrene	NC	NC	NC
4-BC	G	Large	SVE	No	Ethylbenzene, xylenes	50-70 m	ug: 0.55, 0.36; dg: 0.03	ug: 0.82, 1.07 dg: 0.35
5-BC	G	Small-mod	Partial excavation*	Uncertain but unlikely	Ethylbenzene	10-15 m	0.28	N/A***
6-BC	G	Small-mod	Partial excavation*	Uncertain but unlikely	Ethylbenzene, benzo(a)pyrene	Negligible	0.45	N/A***
Geomean							0.29	0.55

Notes: G = gasoline; D = diesel; Mod = moderate, * - most of contamination excavated, remaining contamination generally below sidewalks, edge of site, roadways. ** - stable but low concentrations that were just above standard, trend analysis not meaningful. *** - benzene concentrations below DW standard from beginning of monitoring, trend analysis not meaningful.

dg = downgradient in LNAPL source area, ug = upgradient in LNAPL source area, NC = not calculated, BC = British Columbia, YT = Yukon

7.0 ASSESSMENT APPROACHES FOR LOW-THREAT GROUNDWATER PLUMES

In some regulatory jurisdictions in the US, stream-lined assessment approaches have been adopted for sites that pose a low risk or threat to human health and the environment based on defined site characteristics, but that contain low levels of groundwater contamination above applicable regulatory criteria. Several references to guidance and policy regarding low-risk groundwater plumes are provided in the US Department of Defence Environmental Security Technology Certification Program (ESTCP) FAQs (Adamson and Newell, 2014) for the US Air Force and states of California and Colorado.

7.1 California Low-Threat UST Policy

The state of California has a specific policy document related to releases of petroleum hydrocarbon fuels from underground storage tanks (UST), the Low-Threat UST Closure Policy (California State Water Resources Control Board, CSWRCB, 2012) that defines four classes of low threat groundwater plumes, applied in areas that include aquifers used for drinking water. A fifth classification of plumes is a site-specific evaluation. The four classes of low-threat groundwater plumes are based on the following factors:

- Groundwater plume lengths;
- Indicator constituents;
- Concentrations; and
- Buffer or separation distances to receptors.

The receptor or separation distances are defined from the edge of the groundwater plume for each class. The separation distances are based on the plume lengths (from edge of source zone) of benzene, MTBE and total petroleum hydrocarbon as gasoline (TPH_g) including a carbon range of C4 to C12 and that incorporate safety factors ranging from 1 to 4. These constituents are used for deriving the separation distances because of toxicity (benzene) and field evidence from studies that show higher plume lengths for MTBE and common use of TPH_g to represent other components of the hydrocarbon contamination. These are also constituents used in multi-site studies of groundwater plume characteristics (*e.g.*, Shih *et al*., 2004 and Kamath *et al*., 2012). In a BC context, VPH (C6-C10 excluding BTEX) and LEPH (C10 – C19) could be used to represent TPH_g.

The applicable concentrations of plume constituents for defining the plume lengths in these studies are 5 µg/L for benzene and MTBE, and 100 µg/L for TPH_g. The California Low-Threat UST Policy bases the limits for plume lengths on multi-site studies taken as average plume length for benzene and maximum length for MTBE, and adopts safety factors to account for additional expansion of the plume that could potentially be caused by unexpected plume migration, or presence of fuel oxygenates other than MTBE such as ethanol that can result in benzene plume expansion, and for consistency with other policies that require separation or “setback” between water supply wells and sanitary sewers (typically 50 feet) or septic system leach fields (typically 100 feet). The safety factor is also considered to account for the California MCL for benzene that is 1 µg/L rather than 5 µg/L, which was used in the multi-site study of Shih *et al*. (2004). Table 7 provides a summary of conditions and required separation distances from the edge of groundwater plume for the four classes of low-threat groundwater plumes in the state of California.

Table 7: California low-threat groundwater plume classes.

Class / Description	**Conditions**	**Stabilized Plume Length (feet)**	**Safety Factor**	**Receptor or Separation Distance from Edge of Plume (feet)**
Class 1 / short	See plume length	< 100	2.5	250
Class 2 / moderate	Benzene and MTBE concentrations less than 3,000 µg/L, and 1,000 µg/L, respectively	< 250 (average for benzene)	4	1,000
Class 3 / moderate	5 years of monitoring of free product and dissolved concentrations in the plume to validate plume stability and natural attenuation	< 250 (average for benzene)	4	1,000
Class 4 / long	Benzene and MTBE concentrations less than 1,000 µg/L, each; benzene in the source area does not pose a vapour intrusion risk	< 1,000 (maximum MTBE plume length)	1	1,000

The plume lengths used in the “Technical Justification for Groundwater Plume Lengths, Indicator Constituents, Concentrations, and Buffer Distances (Separation Distances) to Receptors” document for the derivation of receptor or separation distances from the edge of plume shown in Table 7 are based on the Shih *et al*. (2004) study. In this study, the authors estimate plume lengths from the analysis of groundwater monitoring data from 500 LUFT sites in the greater Los Angeles, CA region. Factors to consider for how applicable the California approach would be to BC conditions include regional scale differences in soil and hydrogeological conditions. For example, lower average groundwater temperatures in BC could potentially result in lower solubility of LNAPL constituents and lower biodegradation rates, although studies of biodegradation in colder climates indicate biodegradation rates typically decrease by a factor of about 2-3 for 10^{o}C decline in groundwater temperature (Ulrich *et al.,* 2006; Sayles *et al*., 1995). An analysis of long-term groundwater monitoring data from sites in BC with petroleum hydrocarbon contamination could potentially be useful in implementing a similar approach to the estimation of receptor or separation distances.

7.2 US Air Force Low-Risk Site Closure

The US Air Force Center for Engineering and the Environment has a guidance manual for closure of low-risk sites with groundwater contamination (Farhat *et al*., 2012). The manual is a decision support tool for identifying low-risk sites and using multiple lines of evidence in support of closure or reduced monitoring of low-risk sites.

The guidance manual provides a decision logic table and flow chart that are centered on answering three main questions:

1) Is there a complete CSM that reflects key low-risk closure concepts?

2) Are sources controlled?

3) Will residual contamination have no adverse effect on present and future land and water uses?

The manual provides a template for the CSM checklist and an example diagram to aid in answering the first question. To answer the second question, a number of assessment tools regarding the mobility, quantity, size, and stability of the source material are provided. In addition, the model describes the potential for NSZD, the effects of future source remediation, and matrix diffusion. The third question relates to the groundwater plume and tools to evaluate its stability and evidence of on-going natural attenuation. It also involves the assessment of receptors and exposure pathways in the area of the site, as well as the evaluation of potential impacts to current and future water resources. In addition, the manual provides qualitative and quantitative tools and strategies for reducing the long-term monitoring intensity when complete site closure cannot be justified.

8.0 SUMMARY

The processes for natural attenuation and empirical data from US and British Columbia documenting natural attenuation and the effectiveness of remediation for reducing source zone longevity and dissolved plumes are summarized. This knowledge is important in the current regulatory context in British Columbia and other jurisdictions, where the science and policy in relation to groundwater remediation requirements are being developed, and that may include timelines for MNA or enhanced attenuation for remediation of groundwater contamination to numerical standards for applicable water uses.

Processes for NSZD include dissolution of petroleum hydrocarbon compounds from flowing groundwater below the water table and infiltrating water in the vadose zone, biodegradation, and volatilization of hydrocarbons in the vadose zone.

The results of the multi-site studies from the United States are summarized as follows:

- Conner *et al*. (2015): A compilation study of 13 previous multiple-site studies of primarily gasoline releases at retail service station sites (with a range of remediation completed) indicates the median and 90th percentile of benzene plume lengths (based on 5 µg/L) were 55 and 130 m, respectively. The proportion of sites with stable, shrinking or exhausted plumes was 94%.
- McHugh *et al.* (2014): Data from 12,000 sites in the California GeoTracker database were analyzed for the progress of groundwater remediation. The estimated median benzene attenuation rate at source zone wells for sites with a range of remediation types (including 3% of the sites with just MNA implemented) was 0.18/year. When data was separately analyzed for specific remediation types (sparging, SVE, groundwater pump-and-treat), there was a 17 to 53% increase in the attenuation rate depending on the technology. For this data set, a 20-year timeframe for benzene remediation assuming an initial source concentration of 10 mg/L would be met for 14 of 72 sites (19%), where MNA was reported to be the only remediation technology.
- Kamath *et al*. (2012): Data from 48 gasoline retail sites mostly in California and New Jersey indicated timelines for benzene remediation to the drinking water guideline were 12 to 52 years. Active remediation and LNAPL recovery had occurred at most sites. The effect of active remediation and LNAPL recovery on estimated attenuation rates were found not to be statistically significant compared to rates for sites with no remediation or recovery. The 90th percentile of benzene plume length was 110 m.
- Shih *et al*. (2004): A statistical analysis of benzene plume length (based on a 5 µg/L threshold) on data from 500 UST sites in the Los Angeles, California area indicated geometric mean, 90th percentile and maximum plume lengths of 51 m, 100 m and 168 m, respectively.
- Kulkarni *et al*. (2015): Analysis of the California GeoTracker database indicated that while the majority of sites showed decreasing groundwater source concentrations of benzene, an analysis of maximum concentrations, LNAPL thickness and source attenuation rates did not identify an improvement towards remediation for sites with physical LNAPL recovery. The median benzene attenuation rate was 0.09/year for sites with LNAPL recovery and 0.19/year for sites without LNAPL recovery.

The multi-site data indicated variable results with respect to the effect of remediation on benzene concentrations at source zone wells; at two sites remediation did not result in an increase in the concentration attenuation rate at source wells, at one site there was a significant increase in the attenuation rate depending on remediation technology. Overall, groundwater benzene concentrations are indicated to decrease suggesting NSZD is a significant process and the dissolved benzene plume lengths were indicated to be relatively short (90th percentile length of 130 m estimated in the review study of Connor *et al,* 2015).

The multi-site data were used to develop a site management strategy for low-threat sites in California where sites with residual petroleum hydrocarbon contamination, but meeting criteria for LNAPL and plume stability, may be closed based on source concentration data or trends and thresholds for safe distances from sources to drinking water wells.

Groundwater monitoring data from five sites in BC and one site in the Yukon representing a range of site and climatic conditions were reviewed. Site remediation through excavation of most of the contamination source or SVE was implemented at four sites. Monitoring data for source zone wells indicate that BC drinking water (DW) standards were not achieved or likely to be achieved at all six sites (at two sites there are limited data). Benzene concentrations decreased to below the DW standard (5 µg/L) within approximately 20 years at all five BC sites evaluated, but concentrations of other substances remained above the DW standards, including ethylbenzene (drinking water standard of 2.4 µg/L), xylenes (300 µg/L) and benzo(a)pyrene (0.01 µg/L). The case study data indicated that DW standards for benzene were met in a relatively short time frame (few decades) but that for ethylbenzene and xylenes DW standards will not be met for many decades at some sites. The dissolved plumes were stable or shrinking and plume lengths were short, estimated to range from a few metres at one site to 50 to 70 m at a site with a large gasoline release.

The geometric mean of attenuation rates for benzene and ethylbenzene at BC sites were 0.55/year and 0.29/year, respectively. The attenuation rates indicate significant reductions in benzene and ethylbenzene concentrations are occurring at the sites and that natural weathering of hydrocarbons is an important process. The geometric mean of attenuation rates for benzene and ethylbenzene estimated for the case studies are higher than the median or average rates for multi-site US studies reviewed in this document, although it is recognized that the BC dataset is small.

Longer timelines for remediation to groundwater standards are expected for large releases, although hydrogeologic factors such as groundwater velocity may also be important, while shorter timelines are expected for sites with smaller releases or where the majority of the source is removed. Complete removal or treatment of sources is often not feasible because of infrastructure at sites (roads, sidewalks, buildings). The data suggest NSZD of petroleum hydrocarbons is a viable process over longer time frames (generally decades); that it occurs in a predictable manner; and that associated dissolved plumes are relatively short and stable.

Data gaps in the BC case study include the relatively limited dataset and absence of well characterized sites with longer-term data that would enable source zone depletion and dissolved plume attenuation for a range of compounds to be accurately quantified.

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APPENDIX A

Request for Data on Petroleum Hydrocarbon Impacted Sites in BC

Request for Data on Petroleum Hydrocarbon Impacted Sites in BC

Golder Associates Ltd. is conducting a study on monitored natural attenuation and enhanced attenuation of hydrocarbons for the Society of Contaminated Sites Approved Professionals (CSAP) of British Columbia and Shell Global Solutions (US) Inc. The objectives of the study are to provide toolkits that would be practically useful to practitioners and stakeholders in the British Columbia regulatory context. The toolkits are intended to address questions and data gaps on timelines and effectiveness of source remediation as related to the draft BC MoE Protocol 5 on Groundwater Remediation and Technical Guidance on Monitoring Natural Attenuation (MNA) and Enhanced Attenuation (EA).

As a first step, a toolkit on case studies involving sites in BC with monitoring data (longer term) and other jurisdictions that would provide information on source characteristics and contaminant distribution in groundwater is being developed. This request for data is intended to aid in the data compilation component that would be similar to the California GeoTracker database of environmental monitoring data, albeit on a much smaller scale and focused on sites in BC. By participating and providing data you will be assisting in the development of a better understanding as to BC conditions for natural attenuation.

We request that data be provided that includes the following information:

1) Petroleum hydrocarbon source type and release scenario;
2) Number of monitoring well locations (minimum of 4);
3) Number of years of monitoring and number of monitoring events (minimum of 3 years and seasonal data is preferred);
4) Concentration data of key constituents (e.g., BTEX and fuel oxygenate MTBE depending on the source) and preferably natural attenuation indicator parameters (e.g., dissolved oxygen, nitrate, sulfate, methane);
5) Information on remediation technologies implemented at the site if applicable (other than monitored natural attenuation) in terms of type of technology, system operation time and duration;
6) Brief overview of hydrogeology, groundwater temperature and soil type at the site;
7) Client name: optional; and
8) Site location: optional.

We would like to make it as simple as possible to provide information, which could be through an email and attached data figures and tables. Alternately complete electronic reports could be provided. If the report is publicly available, we would appreciate receiving a reference to the site ID to search for the report. Attribution to persons/companies providing data can be provided as requested.

We thank you in advance for participating in this project and thank you for your time.

APPENDIX B

BC Case Studies

1.0 CASE STUDY #1

Location: Confidential, Fraser Valley, BC.

Site Type: Service station.

Release: Gasoline release occurred from leaking underground storage tank (UST).

Remediation: Likely most contaminated soils were removed from site during station upgrade activities in late 1990's or early 2000's.

Site Setting: Floodplain deposits, relatively flat topography, small ditches or streams are few hundred meters away.

Soil Type: Sand and gravel fill to approximately 1.5 m depth underlain by interlayered silty sand to clayey silt deposits.

Hydrogeology: Depth to groundwater ~ 2 m; shallow groundwater flow direction is south to southwest. Hydraulic conductivity is approximately 1.0 x 10^{-5} m/s to 1.1 x 10^{-4} m/s, with a geometric mean of approximately 3.8 x 10^{-5} m/s. Groundwater velocity was not characterized but is expected to be relatively slow. Groundwater temperature ranged from about 9 - 18 ^{o}C.

Contaminant Characterization: The petroleum hydrocarbon concentrations are decreasing relatively quickly and the plume at the site is shrinking (Figure B-1). The maximum historical extent of the dissolved plume beyond the site boundaries is estimated to be about 30 m. Geochemical monitoring indicates evidence for MNA processes. Benzene and ethylbenzene are the primary chemicals of concern relative to the BC Contaminated Sites Regulation (CSR) drinking water (DW) standards. The benzene concentrations at one on-site and one off-site well remain greater than the DW standard based on monitoring in November 2014 (up to 1.5 times the DW standard). It is inferred that there may be localized contaminated soil that may remain in this area.

Commentary: The rate of natural attenuation at this site has likely been accelerated through removal of most contamination present at this site. Because of the shallow water table, contamination was relatively accessible at this site and it appears that there was limited, if any, off site migration of LNAPL. There remained in 2014 exceedances of DW standard for benzene; however, concentration trends suggest that benzene will decrease to below the DW standards within a short period of time (few years). At this site, concentrations of benzene (and other parameters) have generally decreased to below DW standards within 20 years. Site closure and cessation of monitoring is considered a reasonable outcome for this site.

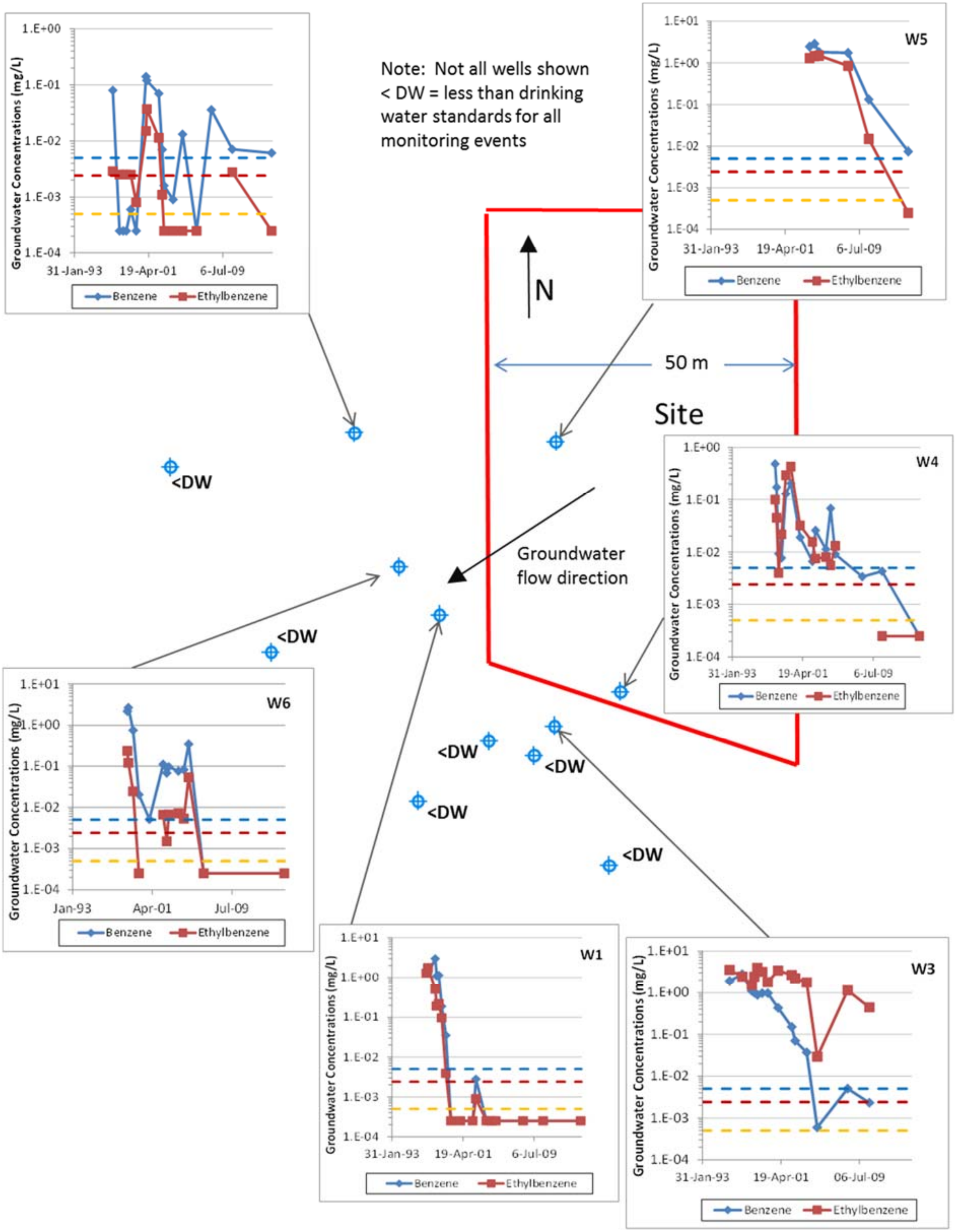


Figure B-1: Case Study #1 Site (note blue and red dashed lines are DW standards, orange dashed line is detection limit)

2.0 CASE STUDY #2

Location: Confidential, Interior BC.

Site Type: Confidential.

Release: A relatively large historical diesel release that ceased in 1988 or earlier. Diesel LNAPL has migrated off-site and is present below buildings and roads, and is deep and inaccessible.

Remediation: Approximately 150 L of LNAPL has been recovered from skimmers.

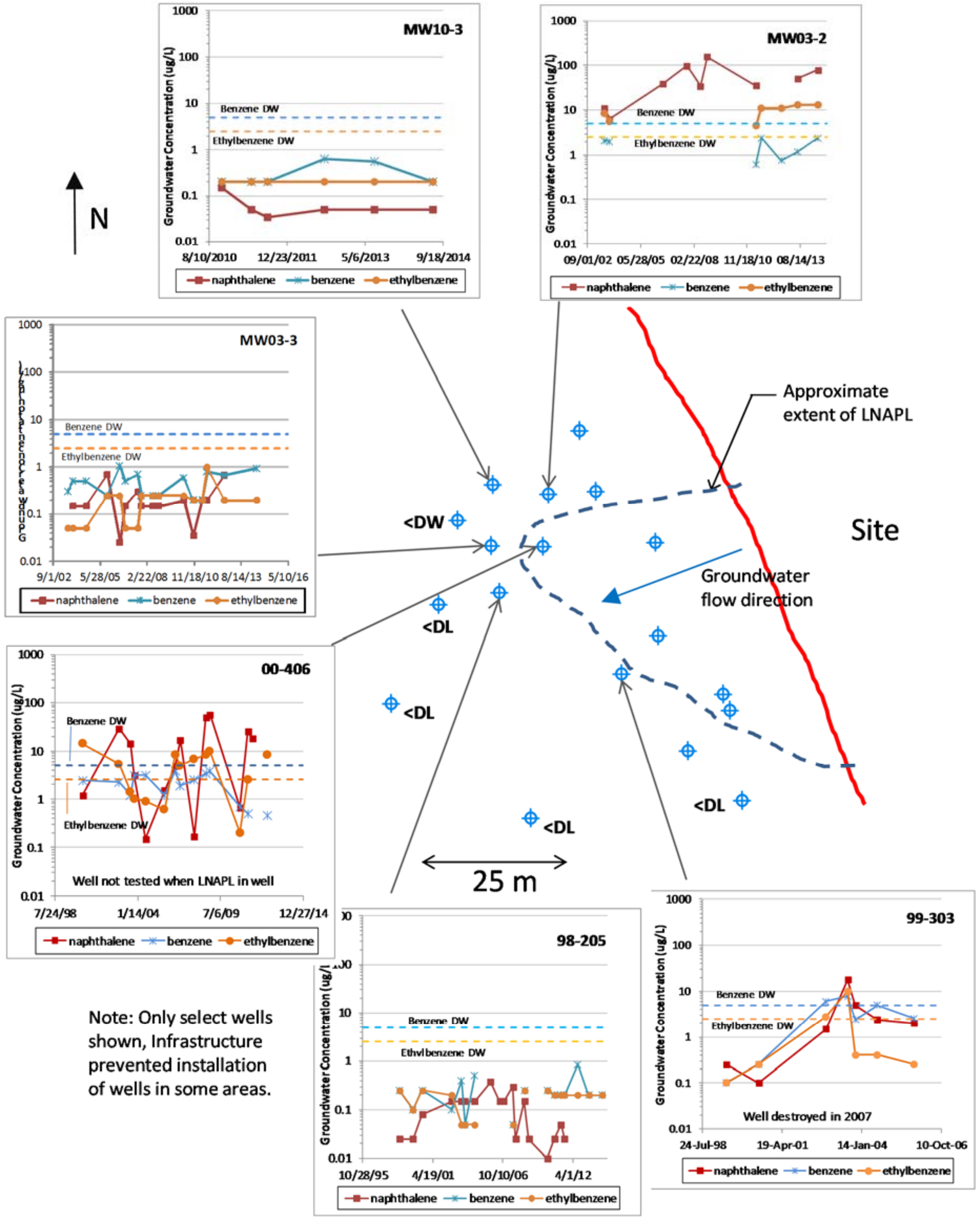
Site Setting: Fluvial and alluvial deposits, relatively flat topography, river is about 500 m away. There are no known drinking water wells within 500 m downgradient of the site.

Soil Type: Mostly sandy gravel to sand, underlain by deeper (below water table) fine-grained unit in some areas.

Hydrogeology: Depth to groundwater was 14-15 m; shallow groundwater flow direction was to the southwest. The hydraulic conductivity in Sandy Gravel unit ranges from 2 x 10^{-5} to 3 x 10^{-4} m/s, in Upper Fine Sand unit ranges from 6 x 10^{-6} to 4 x 10^{-5} m/s and in Lower Fine Sand unit ranges from 8 x 10^{-6} to 6 x 10^{-5} m/s. The lateral hydraulic gradient in the off-site area varied from about 0.0075 to 0.015 m/m. Groundwater temperature ranges from about 7 to 14^{o}C seasonally.

Contaminant Characterization: Monitoring of presence and absence of LNAPL in wells indicates the LNAPL body is stable. Fifteen years of monitoring data indicate the dissolved petroleum hydrocarbon concentrations are stable based on qualitative observation (Figure B-2). Mann Kendall analysis in almost all cases indicates no trend (i.e., no evidence for advancing plume). The dissolved concentrations decrease to below the CSR drinking water standard within approximately 15 to 20 m of the inferred edge of the dissolved plume. Geochemical monitoring indicates evidence for MNA processes.

Commentary: Natural attenuation at this site is resulting in the attenuation of dissolved hydrocarbon concentration to below DW standards and below detection limits over short distances from the LNAPL body. The LNAPL body and dissolved plume are considered to be stable at this site based on the data. Because of the size of the release, elevated concentrations in the immediate area of the release are expected to remain elevated for a relatively long period of time (decades). However, the area of impact is small and risk to groundwater outside of the immediate area of impact is considered negligible. The LNAPL thickness at the site is small and transmissivity is low (cannot be measured because of insufficient LNAPL thickness in wells). Further removal of mobile LNAPL that remains is considered to essentially have no effect on LNAPL stability and plume concentrations and longevity. Site closure with some continued monitored on a reduced frequency is considered a reasonable outcome for this site.



Note: Only select wells shown, Infrastructure prevented installation of wells in some areas.

Figure B-2: Case Study #2 Site. < DW indicates less than the drinking water standards for all monitoring events and < DL indicates less than the detection limit for all monitoring events.

3.0 CASE STUDY #3

Location: Whitehorse, Yukon.

Site Type: Former petroleum hydrocarbon tank farm.

Release: Incidental spills and leaks on a 50-hectare diesel and gasoline storage tank farm in operation from 1944 until 1996 resulted in groundwater contamination. The total mass of residual petroleum hydrocarbon at the Site was estimated at approximately 450,000 kilograms (Hamilton and Patrick, 2008).

Remediation: Partial source removal, where petroleum hydrocarbon contaminated soil was removed to a depth of 3 m to 7 m across the site, although more recently excavation to 11 m depth has been performed in some areas. An assessment of the plume stability and rate of source zone depletion and natural attenuation was completed. As of 2015, there remains soil and groundwater contaminated with petroleum hydrocarbons at deeper depths.

Site Setting: Located on a plateau that is underlain by a permeable sand and gravel aquifer. The regional climate of the site is sub-arctic, where the annual temperatures range from -22 °C in January to 21 °C in July.

Soil Type: The former tank farm is situated on well-drained gravel, and in some areas of the site, contamination travelled vertically through this gravel (which is up to 34 m thick in some areas) before reaching less permeable silt material and encountering the water table.

Hydrogeology: Depth to groundwater is approximately 30 m; groundwater from the site discharges to an off-site drainage feature that flows directly into the Yukon River. The site plan and groundwater level contours are shown on Figure B-3. The average annual groundwater temperature is approximately 5 °C.

Contaminant Characterization: Contamination source is residual petroleum hydrocarbons in soil with total hydrocarbon concentration in the NAPL zone above the capillary fringe of 2,000 mg/kg. The thickness of the residual NAPL above the capillary fringe was estimated at 25 m covering an area of approximately 180 m^2. Patrick and Hamilton (2008) report a maximum concentration of LEPH measured in groundwater of 19.8 mg/L in July 2001 at location 96-02 with concentrations below 10 mg/L on subsequent monitoring events across the site.

Geochemical monitoring indicates evidence for biodegradation in the groundwater plume through five degradation pathways in order of impact: sulfate reduction, aerobic respiration, denitrification, iron & manganese (IV) reduction. The total estimated assimilative capacity was calculated to be as high as 10.6 mg/L based on measurements of geochemical and natural attenuation indicator parameters (Hamilton and Patrick, 2008).

Commentary: Natural attenuation at this site is resulting in the attenuation of dissolved hydrocarbon concentration and the dissolved plume is considered to be stable at this site based on the data.

The natural source zone attenuation rates based on aerobic biodegradation in the vadose zone following the method of Johnson et al. (2006) and site characterization data is estimated to be 0.12 kg-HC/day. Therefore, Hamilton and Patrick (2008) estimate time to deplete the source zone above the capillary fringe to be approximately 350 years. However, the area of impact is small and risk to groundwater outside of the immediate area of impact is delineated and assessed to be stable. As of August 2015, an on-going program for soil characterization and remediation through excavation and groundwater monitoring was in place at the site.

Figure B-3: Site plan with groundwater flow contours (from Hamilton and Patrick, 2008).

4.0 CASE STUDY #4

Location: Confidential, Interior BC.

Site Type: Service station.

Release: A very large historical gasoline release occurred in the 1980s at two adjacent service stations. The release stopped in about 1986. Gasoline LNAPL migrated off-site and is present below roads and adjacent properties.

Remediation: A soil vapour extraction (SVE) system was operated between August 1993 and May 1996. It was estimated that between 6,000 and 7,930 kg of hydrocarbons were removed through SVE. The system was turned off because the hydrocarbon removal rates had reached an asymptotic level and the rates were lower than the estimated mass removal through naturally occurring biodegradation processes in the vadose zone. However, the lower portion of hydrocarbon smear zone was not removed through SVE (estimated to be about 1 m thick on average). The radius of influence of SVE may not have extended to the eastern end of the LNAPL smear zone.

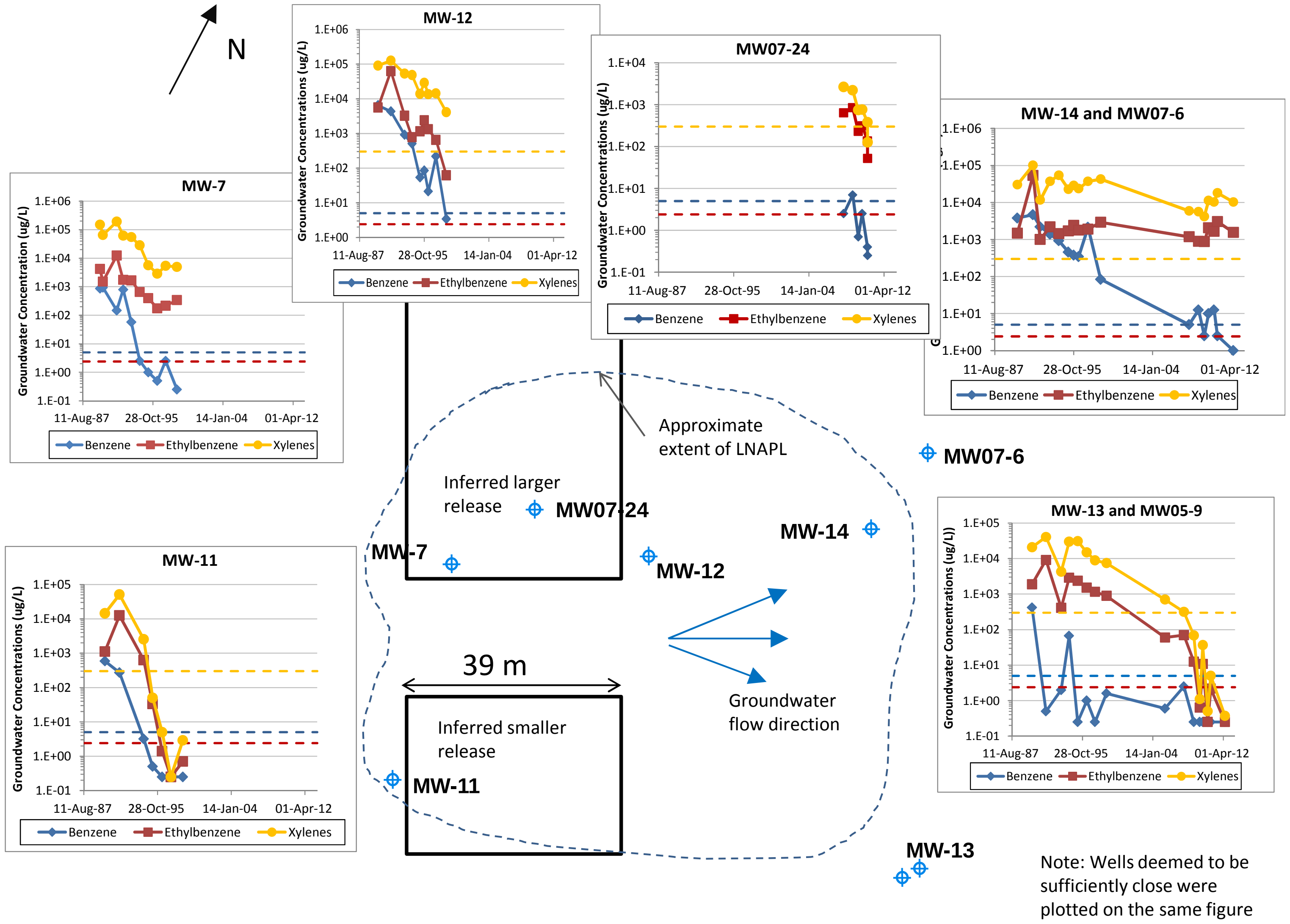
Site Setting: There are alluvial deposits at the site and relatively flat topography. A slough is located about 150 m from the service station site and a river is located 900 m away. A drinking water well was impacted and re-located further from the site. There are currently no known drinking water wells within 500 m downgradient of the site.

Soil Type: Interlayered sand, sand and gravel and gravel.

Hydrogeology: The depth to groundwater was approximately 10 to 12 m below ground surface with a seasonal variation of up to 2 m. The shallow groundwater flow direction was to the northwest to west. Hydraulic conductivity at the site was estimated to be 6×10^{-4} m/s. The lateral hydraulic gradient varied from about 0.0008 to 0.002 m/m. The estimated Darcy velocity is 15 to 38 m/year. The estimated average linear groundwater velocity is 60 to 150 m/year assuming an effective porosity of 0.25. The groundwater temperature ranges from about 10 to 13 ^{o}C seasonally.

Contaminant Characterization: Outside of the immediate release area (where there could be shallower contamination), there is a well-defined hydrocarbon smear zone, which is on the order of 1 m to 4 m thick (i.e., from about 10 m to 14 m below ground surface at the location where the smear zone is thickest). On average, the LNAPL smear zone is approximately 2 m thick. No LNAPL has been measured in wells since early in the monitoring program. The dissolved plume is stable or shrinking based on qualitative observations and Mann-Kendall analysis of trend. Geochemical parameters support the findings of a stable plume.

Commentary: Natural attenuation at this site is resulting in the attenuation of dissolved hydrocarbon concentrations to below CSR DW standards and below analytical reporting limits over a short distance from the residual LNAPL source. The dissolved plume is estimated to extend approximately 50 to 70 m from the edge of LNAPL zone and is stable or shrinking. The dissolved plume data within the source zone indicates the benzene concentrations decreased to less than the DW standard in less than approximately 25 years after the release was stopped; however, the rate in the decrease in ethylbenzene concentrations was significantly less, and concentrations in 2012 exceeded the DW standard at three of five wells shown in Figure B-4 (note that although not shown xylenes, also exceed the DW standard). There is evidence that the upgradient area of the residual LNAPL zone is beginning to be remediated through depletion based on the decrease in both ethylbenzene and xylenes concentrations at wells MW-11, MW-7 and MW-12. Further detailed analysis of this site through a modeling case study is provided in Appendix H of Toolkit #2.



Note: Wells deemed to be sufficiently close were plotted on the same figure

Figure B-4: Case Study #4 Site (dashed lines are the DW standards).

5.0 CASE STUDY #5

Location: Confidential, Northern BC.

Site Type: Former service station.

Release: There is limited information on the release but inferred to be relatively small.

Remediation: Remedial excavations were conducted and contaminated soil was partially removed. It is inferred that some contamination remains in-place.

Site Setting: A creek is located approximately 250 m north and southeast of the site.

Soil Type: Soil at the site consists of silty sand to coarse sand.

Hydrogeology: The depth to groundwater at the site is approximately 6.5 to 7 m below ground surface. The shallow groundwater flow direction is to the south to southeast. The hydraulic conductivity (K) from single-well response tests were 6×10^{-5} m/s, 9×10^{-4} m/s and 9×10^{-5} m/s. The groundwater temperature in October ranged from about 6 to 7 ^{o}C.

Contaminant Characterization: Groundwater monitoring data for two wells downgradient of the contamination source are shown in Figure B-5. At the well within the source zone ethylbenzene and VPHw concentrations were slowly decreasing. At the southeastern downgradient well, groundwater concentrations were below the DW standards and detection limit for all monitoring events. At the southwestern downgradient well, the concentrations were below the DW standards for three of five monitoring events.

Commentary: Natural attenuation within the source zone and downgradient of the source is occurring. The results at one down-gradient well are unusual in that there were low concentrations except for two monitoring events. Although there are no detailed data on groundwater flow direction, one possible reason for the variable groundwater concentrations could be variability in the groundwater flow direction.

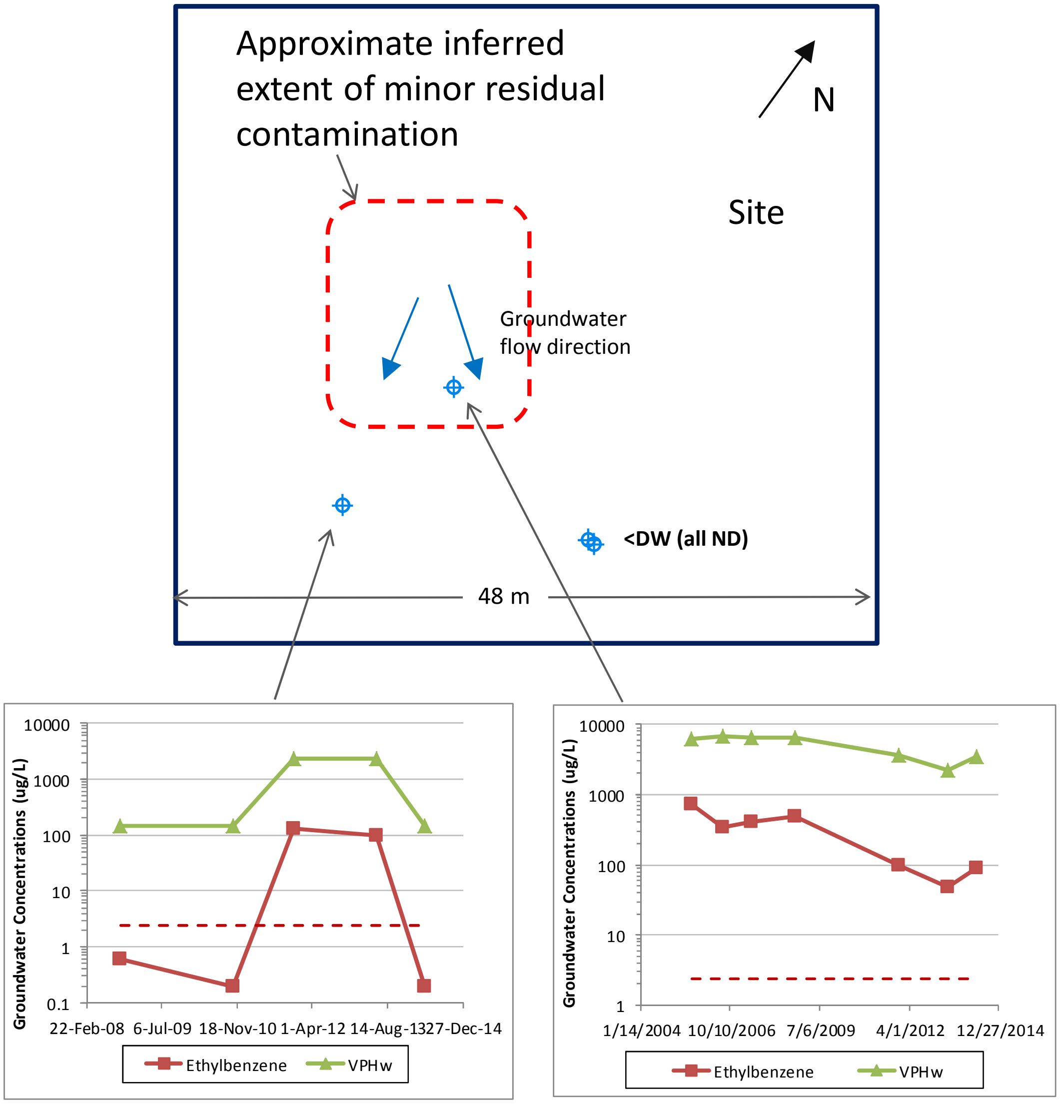


Figure B-5: Case Study #5 Site.

6.0 CASE STUDY #6

Location: Confidential, Vancouver area, BC.

Site Type: Service station.

Release: The service station was developed in the 1950's and was decommissioned in 1999. The release was inferred to have occurred up to the late 1990's. Gasoline LNAPL likely migrated off-site and some residual LNAPL is inferred to be present below a road to the south of the site.

Remediation: Remedial excavations took place on the site between 1999 and 2004. It appears that most if not all contamination on the service station site was remediated but that localized contamination below the road was not removed. A groundwater pump and treat system operated at the site between November 2000 and May 2001.

Site Setting: There are glacial drift deposits at the site and topography at the site slopes slightly downward to the southeast. The closest surface water body is a creek, located approximately 150 to 200 m southwest of the site. One drinking water well was located approximately 1.3 km from the site in the upgradient groundwater flow direction.

Soil Type: Sand and gravel to approximately 7 m below ground surface, underlain by a silt layer that extends to about 7.5 m below ground surface, underlain by a sand layer that extends to about 9.5 m below ground surface, underlain by a sand and gravel layer to over 17 m below ground surface.

Hydrogeology: The depth to groundwater in the deeper aquifer at the site is approximately 10.5 m below ground surface with measured seasonal variation of approximately 0.4 m. There is also a seasonal perched shallow aquifer. The shallow groundwater flow direction is to the south to southeast. The geometric mean hydraulic conductivity (K) from single-well response tests in both the perched aquifer and deeper aquifer was 2 x 10^{-5} m/s. The average linear groundwater velocity in the perched aquifer was estimated as 90 to 130 m/year while in the deeper aquifer the groundwater velocity was estimated as 4 m/year.

Contaminant Characterization: Soil contamination above the CSR commercial land use standard was present in a localized area below the road south of the site (Figure B-6) when the site was characterized in the mid to late 2000's. The concentrations were moderately elevated and suggest a relatively small zone of residual LNAPL. Groundwater monitoring conducted between 2004 and 2010 indicated a few wells where concentrations were still above the DW standards, but a rapid decline in concentrations occurred to below DW standards in two years, with the exception of two wells within the residual source zone. At these wells, the ethylbenzene and benzo(a)pyrene concentrations remained above the DW standards during the most recent monitoring event completed in 2010. Because of the relatively short time period over which groundwater concentrations were monitored, trends cannot be accurately determined, although it appears that concentrations were decreasing at the northern well. Groundwater concentrations at wells outside of the zone of inferred soil contamination in Figure B-6 were below the DW standards.

Commentary: Given the site was mostly remediated through removal of contamination, a relatively rapid decline in groundwater concentrations through flushing and natural attenuation is expected. There remain elevated groundwater concentrations in a localized area with soil contamination but there is essentially no plume and groundwater concentrations attenuate to below the DW standards within a few metres of the residual contamination. The zone of impact and risk of contamination migration at this site is considered negligible.

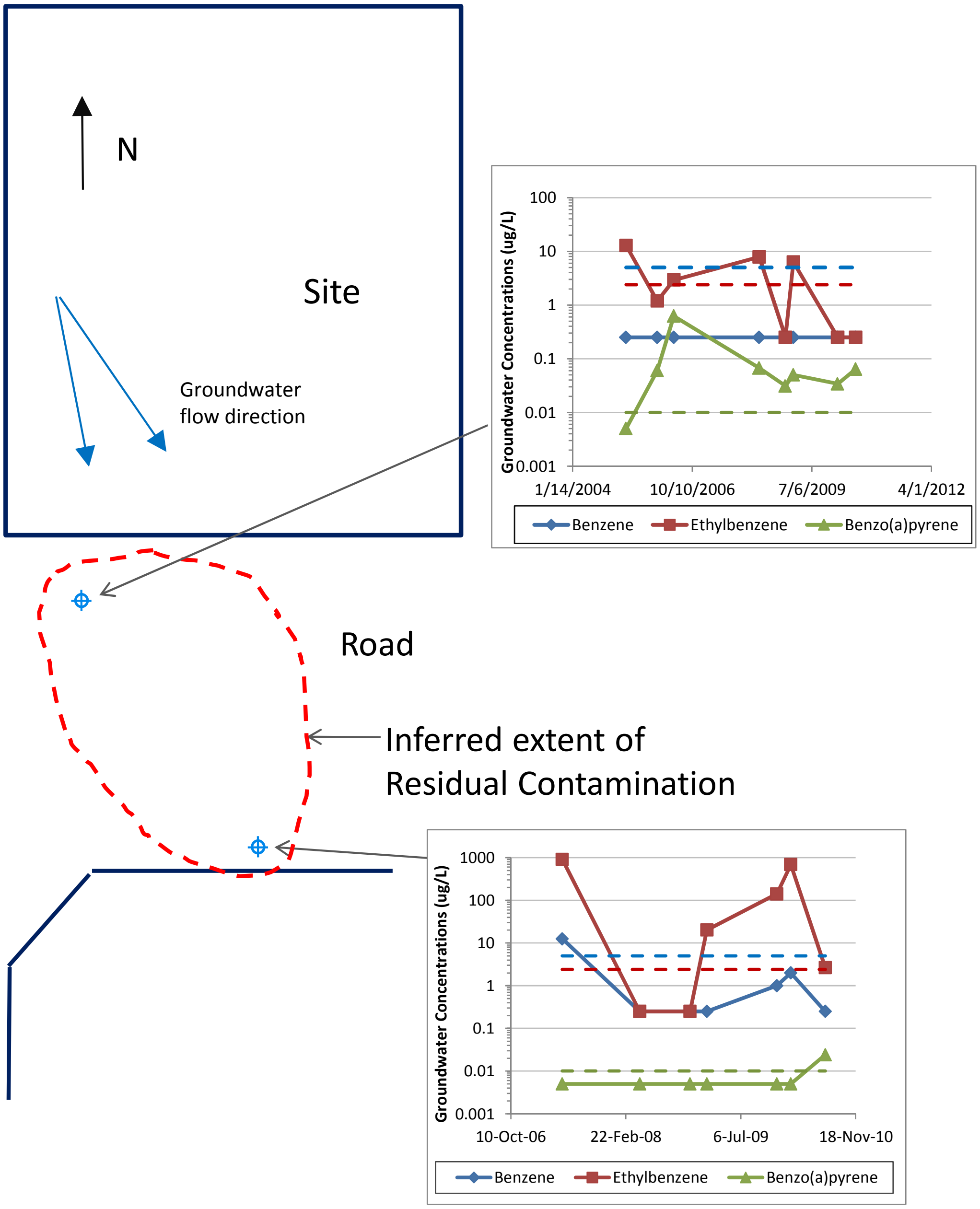


Figure B-6: Case Study #6 Site.

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