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TOOLKITS FOR EVALUATION OF MONITORED NATURAL ATTENUATION AND NATURAL SOURCE ZONE DEPLETION

Toolkit #2 - Monitoring and Prediction

Submitted to:
Contaminated Sites Approved Professional Society and
Shell Global Solutions

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REPORT

Golder Associates

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1.0 INTRODUCTION

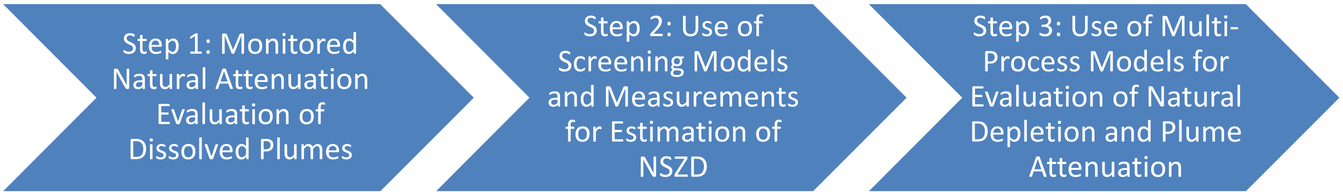
Toolkit #2 describes the framework and methods for evaluation of monitored natural attenuation (MNA) of dissolved plumes, screening models and measurement methods for estimation of natural source zone depletion (NSZD) and multi-process models for evaluation of source depletion and dissolved plumes under a MNA and enhanced attenuation (EA) approach. The methods in this toolkit are designed to help 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:



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 monitored natural attenuation 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 including new innovative technologies. The available published data on NSZD are summarized for different measurement methods.

Under Step 3, multi-process models for evaluation of natural depletion and plume attenuation are described and compared for 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. A detailed modeling case study is also provided for Case Study #4 site described in Toolkit #1 (Appendix H).

2.0 STEP 1: MONITORED NATURAL ATTENUATION EVALUATION OF DISSOLVED PLUMES

Step 1 of the evaluation process begins with a description of processes for MNA and overall assessment framework. Next, the lines of evidence approach for MNA evaluation and monitoring strategies are described.

2.1 Definitions

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 BC Ministry of Environment has adopted a similar definition in Procedure 8 – Acronyms and Definitions. In a regulatory context, monitored natural attenuation may be defined as reliance on the above processes to achieve a remedial objective and where attenuation is carefully monitored.

2.2 Biodegradation Processes

Natural attenuation processes may be separated into processes that result in the reduction of the concentration and/or mobility of a contaminant, but not the total mass, referred to as “non-destructive” mechanisms and those that result in the reduction in total mass, referred to as “destructive” mechanisms (ASTM, 2010). For petroleum hydrocarbons, biodegradation is an important attenuation mechanism because it results in the reduction in total hydrocarbon mass (ASTM, 2010).

Aerobic biodegradation occurs along the outer margins of the plume, but oxygen consumption typically results in anaerobic conditions in the core of the plume. The anaerobic zone is typically more extensive than the aerobic zone due to the depletion of oxygen, and assimilative capacity calculations (the sum of all the electron acceptor mass utilized in the biodegradation of contaminant mass) show that anaerobic processes typically result in much greater mass destruction than aerobic processes in the saturated zone (Wiedemeier *et al.*, 1995). Terminal electron acceptors that facilitate anaerobic biodegradation include nitrate, sulfate, ferric iron, manganese, and carbon dioxide. For aerobic respiration, the electron acceptor is oxygen. Another way to understand these processes and sustainability of natural attenuation is as an energy balance, where sufficient electron acceptors must be available to facilitate energy flow for biodegradation of petroleum hydrocarbons (USGS, 2007).

2.3 MNA Evaluation Approach

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.

There are several precluding conditions for implementing an MNA strategy for groundwater plume management. These include clear data indicating an expanding groundwater plume that is spatially significant, geological conditions (*e.g.*, karst) where it is not possible to reliably demonstrate natural attenuation conditions or where biodegradation may be negligible, and data indicating that contamination has impacted human and/or ecological receptors (*e.g.,* discharge to surface water, contamination of potable water, soil vapour impacts).

2.4 Site Characterization and Conceptual Site Model

The site conceptual model 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), and key points relating to natural attenuation studies are summarized here. Before developing a remediation plan including a plan for MNA or EA, a detailed site investigation as outlined in TG 8 is required. Because the spatial and temporal distribution of contamination is important to understand, it is important to collect sufficient data to develop a 3-D representation of contamination and an understanding of how contamination may vary seasonally. To meet this objective, initially monitoring on a quarterly to twice yearly basis will typically be required to establish an appropriate dataset, with subsequent longer-term monitoring conducted at a reduced frequency. During the site characterization stage, TG 8 states that quarterly or more frequent sampling should be performed over at least one year, where seasonal or other factors (*e.g.*, tidal fluctuations or changes in river stage during spring freshet) could have a significant effect on contaminant concentrations and/or hydrogeologic conditions.

Chemical parameters are typically regulated substances in groundwater but may include other parameters that may serve as markers such as trimethylbenzenes, which are potentially more recalcitrant to biodegradation compared to BTEX compounds. Geochemical parameters provide data on biodegradation reactions and are an important part of a lines of evidence evaluation. Hydrogeological tests such as single-well response tests and aquifer properties such as grain size and organic carbon content are routine data required for site investigation purposes. Less common are more in-depth tests to determine contaminant sorption onto aquifer materials, such as collection of aquifer cores and groundwater samples from the same zone and analysis of contaminant concentrations both in the aquifer solids and groundwater, or tests of mineralogy to better understand specific sorption mechanisms.

For development of the conceptual site model, it is important to understand how changes in water table elevation and anisotropy can affect contaminant concentrations and to avoid making erroneous inferences as to plume concentration trends. Seasonal changes in groundwater elevations and anisotropy is reported to change groundwater flow directions by 10 to 40 degrees (NJDEP, 2012). For this reason, an adequate well network is required to monitor changes and to compare data obtained for similar groundwater conditions.

A useful tool for estimating groundwater flow vectors is the US EPA spreadsheet model 3PE (US EPA, 2014)[1] that is based on the three-point solution method. This is an interactive Excel© spreadsheet, which can be used for capturing transient hydrogeologic conditions specific to a site, visualization of hydraulic gradients and groundwater velocity vectors and assessment of measurement uncertainties to inform monitoring network design. Another useful tool is the US EPA Optimal Well Locator (OWL) Excel© spreadsheet (US EPA, 2004a)[2] for selection of new monitoring well locations based on groundwater elevation measurements of existing wells to evaluate variations in groundwater flow magnitude and direction over time.

Tools for Estimating Groundwater Flow Direction and Locating Wells

Seasonal changes in groundwater flow direction can be significant due to anisotropy. Such changes can affect the dissolved plume distribution. 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.

Changes in water table elevations relative to sources can cause changes in concentrations where concentrations may either increase or decrease depending on screen length and locations of sources. To help interpret time-series data, possible causes for changes in concentrations due to seasonal fluctuations are identified in Table 2-1.

Table 2-1: Possible causes of seasonal conditions observed at source water table monitoring wells (adapted from NJDEP, 2012)

Observed Condition	Dry Season	Wet Season
High Concentration	Low well screen dilution	Potential new source Water table rises into/above zone of residual contamination
Low Concentration	Water table falls below “smear zone” of residual contamination	High well screen dilution

2.5 Lines of Evidence Assessment of MNA

The common approach for the demonstration of natural attenuation (BC MoE Draft TG 22, 2014; US EPA, 2009; Air Force Center for Environmental Excellence (AFCEE), 2000; ASTM, 2010) 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.

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 electron acceptors/donors and degradation products.

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.

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[1] http://cfpub.epa.gov/si/si_public_record_report.cfm?dirEntryId=287064

[2] http://www.epa.gov/water-research/optimal-well-locator-owl

Typically, the primary and secondary lines of evidence are evaluated, while demonstration of the tertiary line of evidence is optional depending on project and site requirements.

The goal of the primary line of evidence evaluation is to determine whether there is an expanding, stable or shrinking plume (Figure 2-1). For an expanding plume, the rate of mass loading of contaminants to groundwater exceeds the natural attenuation rate. For a stable plume, the rate of mass loading is approximately equal to attenuation rate. For a shrinking plume, the rate of mass loading of contaminants to groundwater is less than the attenuation rate.

As part of the primary and secondary lines of evidence evaluation, biodegradation rates may be estimated from plume data. In addition, through the use of a predictive model, the rate at which natural attenuation is reducing contaminant mass may be predicted and the time for contaminant concentrations to reach a remediation goal may be estimated.

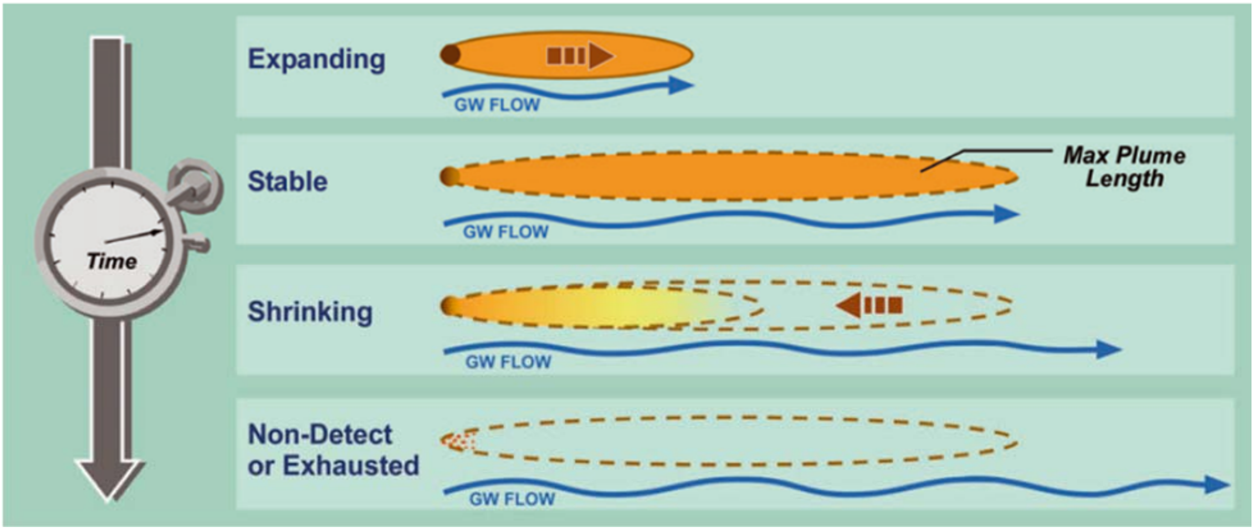


Figure 2-1: Plume stability conditions from Conner et al. (2015).

2.5.1 Primary Line of Evidence

2.5.1.1 Monitoring Design

An evaluation of MNA involves collection of initial concentration data to identify trends and to help establish whether MNA is a viable approach, followed by additional data collection to confirm trends. A typical frequency for the initial phase is quarterly monitoring, for minimum of one year, of petroleum hydrocarbon concentrations, geochemical indicators (see Section 2.5.2 for details) and hydrogeologic data (*e.g.*, water table levels) (Washington Department of Ecology (DEC), 2005; NJDEP, 2012). If the trend analysis is favourable, monitoring frequency can transition to less frequent monitoring as described under the longer-term monitoring approach in Section 2.6.

A generalized design for a monitoring well network is shown in Figure 2-2. For idealized conditions (uniform geology and groundwater flow), Washington DEC (2005) indicate a minimum design consists of one well in upgradient background area, one well within the source, two wells near the contaminated plume centre-line, and one down-gradient sentinel well.

Monitoring well networks for more complex hydrogeological conditions are described by Pope *et al.* (2004). As part of the well design under more complex conditions, it is important to match the well screen interval to the hydrostratigraphic unit of concern. To enable consistent interpretation of results, wells should be completed in the same hydrostratigraphic unit.

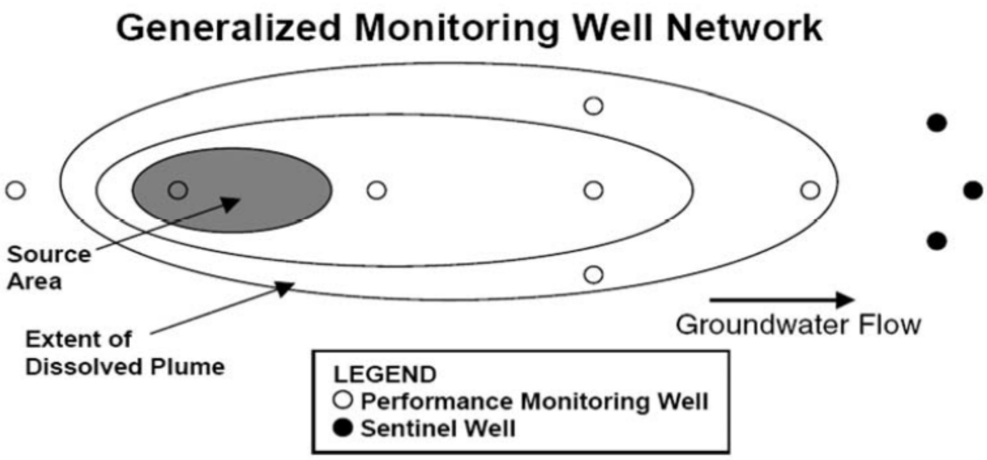


Figure 2-2: Generalized monitoring well network for evaluation of MNA from Missouri DNR (2007).

2.5.1.2 Point Concentration Data Analysis Methods

Common approaches for evaluation of data for analyses of plume stability are:

- Concentration versus time graphs for individual wells;
- Concentration versus distance data along the groundwater flow axis; and
- Maps showing plume iso-concentrations over time.

For the above analyses, there should be a sufficient network of wells such that concentrations are characterized vertically and horizontally and the frequency of sampling should be such that short-term temporal trends caused by water table fluctuations, infiltration along the groundwater flow path, changes in primary groundwater flow direction or other hydrogeological factors can be evaluated and distinguished from natural attenuation processes (Pope *et al.*, 2004). If remediation other than MNA is occurring or has occurred, its potential effect on plume behaviour should be considered.

The data analysis methods for plume concentration trends require sufficient temporal data and often analysis may be initially performed with a smaller data set, and then updated when additional data is obtained. Linear regression analysis may be conducted to evaluate the significance of concentration trends. The 100(1-α)% confidence intervals for the slope can be readily calculated in EXCEL or other statistical software. If a confidence interval of the slope includes zero, then the regression parameter cannot be considered different from zero at the 100(1-α)% confidence level. Washington Department of Ecology (2005) recommends a 85% or higher level of confidence as a guide for evaluation of the feasibility of natural attenuation, where applicable.

Regression Analysis Tool for Prediction of Attenuation Timelines

Concentration attenuation can be evaluated using an EXCEL spreadsheet **Regression Analysis Tool** developed by **Dr. John Wilson** (RegressionMNA.xlsx). A case study of how this tool can be used to evaluate whether MNA or EA is sufficient to reach a remediation goal is presented in Appendix A.

Wilson (2011) provides an approach based on regression analysis to evaluate whether or not MNA is sufficient to reach remediation goals within a specified time interval (*e.g.*, 20 years). For moderate to large petroleum hydrocarbon releases, data reviewed in Toolkit #1 indicates at many sites petroleum hydrocarbon concentrations will remain elevated over relatively long time periods until a significant portion of the LNAPL source is removed. Regression analysis will be more applicable for sites with smaller releases or where a significant portion of the mass has been removed. Wilson (2011) also indicates a slow tailing of concentrations (often following an approximate first-order rate law) is observed at older chlorinated solvent release sites where there may be longer-term back diffusion of contaminants from lower permeability zones, or where mass is reduced through remediation. At such sites a statistical approach based on a first-order rate law may be appropriate to extrapolate long-term monitoring data and make a forecast of concentrations in the future. Linear regression is a parametric analysis, and while it is easy to compute with available tools, it can be biased by outliers and does not take non-detect values into account (US EPA, 2009). Bulk attenuation rates may also be estimated from concentration versus time data as described below.

There are several non-parametric statistical analysis methods that may be used to evaluate plume stability including Mann-Kendall, Mann-Whitney U and Spearman rho's tests. Mann-Kendall and Spearman rho's are non-parametric tests that can be performed in a spreadsheet with similar results (Yue *et al.*, 2002). Software packages such as MAROS (US Air Force Centre for Engineering and the Environment, AFCEE) or ProUCL (US EPA) are also available for the Mann-Kendall analysis.

The above tests may be used to infer concentration trends but cannot be used to estimate rates or time for concentrations to decrease to below a certain threshold. When there is a monotonic trend in concentration that is increasing or decreasing (as shown by a Mann-Kendall test) and the slope of the observed values appears to be linear, the Theil-Sen non-parametric method may be used to estimate the slope of the trend (Helsel and Hirsch 2002). Most statistical tests assume independence of sample data. Possible autocorrelation or non-independent data as a result of seasonal variability or other factors should be assessed because of the potential for biased results. Where there are sufficient seasonal data, a seasonal Mann-Kendall trend test may be a more appropriate method to evaluate concentration trends. Additional information on trend analysis is provided in ITRC (2010) and US EPA (2009).

When interpreting trend analysis results, the totality of the results should be considered. For example, while concentration trends at the majority of wells may indicate stable conditions, there may be one or two wells (or individual substances) that suggest the plume is advancing. Washington DEC (2005) suggest a 80% threshold (*i.e.*, number of results suggesting a certain trend) is sufficient to draw inferences as to plume stability. The average-based analysis methods described below are another option to address between well variability. Monitoring frequency and duration for trend analysis of longer-term monitoring data is described in Section 2.6.

2.5.1.3 Average-based Concentration Analysis Methods

The above point concentration-based techniques are limited in that they do not integrate to the overall plume characteristics with respect to potential for an expanding, stable or shrinking plume. Ricker (2008) presents relatively simple but innovative techniques to calculate and assess time-series trends with respect to the 1) average area of the plume (relative to a defined threshold), 2) the average concentration, 3) the contaminant mass, and 4) centre of contaminant mass. The first three techniques can be conducted using the SURFER software, while the last technique can be conducted using EXCEL by combining spatial coordinate and concentration data to calculate the centre of mass. By comparing the analysis results for different monitoring events, the plume behaviour can be assessed.

Another useful and publicly available tool for visualizing the trend in groundwater monitoring data is the API Groundwater Spatio-Temporal Data Analysis Tool (GWSDAT Version 2.1). The GWSDAT can be used to plot time-series of concentration, groundwater elevation and/or LNAPL thickness, or it can be used for contour plots of spatial data based on the data input of well coordinates and/or imported GIS shape files.

Average-based Concentration Methods

Average-based methods integrate concentration data (Ricker, 2008) across the plume as part of plume stability evaluation, and are a powerful technique when there are sufficient data. The **API Groundwater Spatio-Temporal Data Analysis Tool** (GWSDAT) includes the average-based concentration analysis method.

The spatial plots may include:

- Concentration contours in various output formats using the spatiotemporal smoother (using a non parametric regression technique known as Penalised Splines (P-Splines));
- NAPL thicknesses for wells where data are available;
- Groundwater flow direction and relative flow velocity; and
- Plume diagnostics calculated based on the concentration smoother such as:
  - Delineated plume boundary at a given threshold concentration;
  - Plume mass and location of plume's centre of mass, where the assumptions made for calculation are similar to those presented by Ricker (2008); and
  - Plume area.

The well trend plots include time-series concentration and groundwater elevation data and an option to conduct statistical analyses on concentration trend including 1) a non-parametric smoother of the mean trend and the associated 95% confidence interval; 2) linear trend line to the logarithm of concentration data (equivalent to exponential decay/growth fit) and display of the half-life concentration, and 3) Mann-Kendall trend analysis.

2.5.1.4 Estimation and Use of First-order Decay Constants

First-order decay constants are useful to evaluate natural attenuation processes and support modeling studies where plume lengths and concentrations are predicted. Where there is sufficient confidence in data and model, the time to achieve remediation goals can be estimated. Two types of first-order decay constants can be estimated, the first is a bulk attenuation rate constant (k) that incorporates biodegradation, dispersion and sorption, and the second is a biodegradation rate constant, which may be used in solute transport models such as BIOSCREEN (Newell *et al.*, 2002).

Bulk attenuation rates may be estimated from concentration versus distance or concentration (single point) versus time plots (Figure 2-3) and may be used for estimating if a plume is expanding, showing relatively little change, or shrinking due to the combined effects of dispersion, biodegradation, and other attenuation processes. The bulk attenuation rate from a concentration versus time plot for well located in the LNAPL source zone can provide input data for models described in Section 4. Bulk attenuation rates may also be estimated from data on mass flux versus distance where there are multiple transects of concentration data perpendicular to groundwater flow as a function of distance from the source (Newell *et al.*, 2002), although such analyses would not be practical based on data obtained as part of typical investigations at petroleum hydrocarbon impacted sites.

Biodegradation rates may be obtained several different ways: 1) by calibrating a solute transport model that includes dispersion, sorption and biodegradation, 2) using the method of Buscheck and Alcantar (1995) for 1-D contaminant transport and first-order biodecay, or 3) comparing contaminant concentrations along the groundwater flow path to a conservative tracer such as chloride or trimethylbenzenes (Wiedemeier *et al.*, 1999). The method of Buscheck and Alcantar (1995) enables calculation of the biodegradation rate using an analytical equation and the slope of the concentration attenuation along the groundwater flow path but assumes steady state conditions and only includes longitudinal dispersion (and not transverse dispersion) and therefore may overestimate the biodegradation rate.

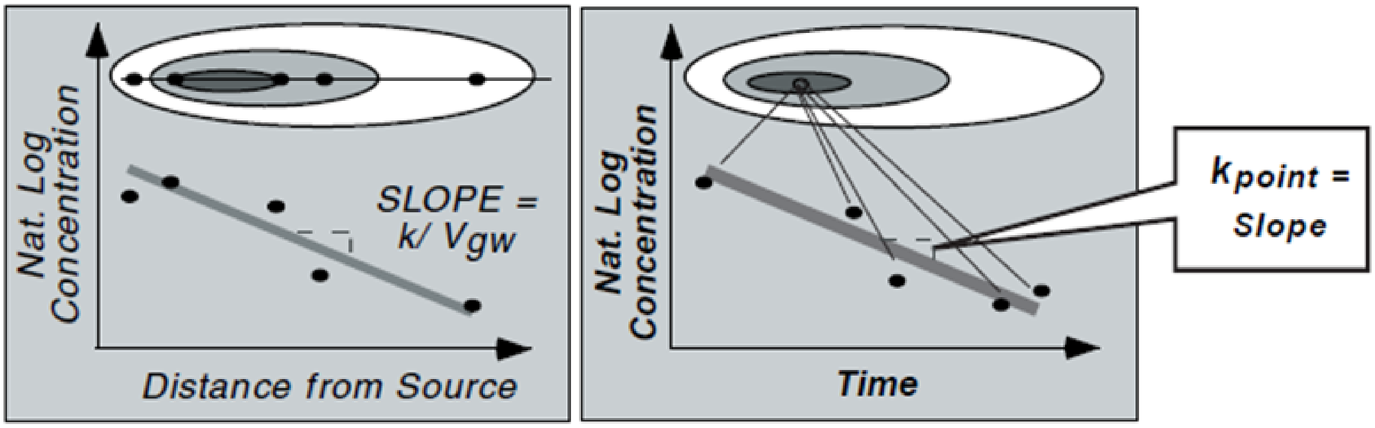


Figure 2-3: Methods for estimation of the bulk attenuation rate (from Newell et al., 2002).

2.5.2 Secondary Line of Evidence

The secondary line of evidence are hydrogeologic and geochemical data on natural attenuation processes occurring at the site and mass loss through analysis of terminal electron acceptors and degradation products (Table 2-2). Geochemical indicators include dissolved oxygen (DO), reduced iron (Fe^{2+}) and manganese (Mn^{2+}) for evaluating the redox conditions. Low DO concentrations and presence of Fe^{2+} and Mn^{2+} would imply anaerobic degradation through reductive dissolution of iron (oxy)hydroxides and/or manganese oxide minerals that are naturally present in most soils. It is expected that the biodegradation of the petroleum hydrocarbons will proceed in order of terminal electron acceptor availability (Christensen *et al.,* 2000). Data on geochemical indicators (Table 2-2) from wells upgradient 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.

Table 2-2: Geochemical indicators of redox conditions.

Terminal electron acceptor (TEA)	Reduced product
Oxygen	Water
Nitrate	Nitrogen (N_2); and intermediate compounds N_2O (dissolved gas) and nitrite (NO_2^-)
Manganese oxide minerals	Divalent manganese (Mn^{2+})
Iron (oxy)hydroxide minerals (*e.g.,* goethite; ferrihydrite; hematite)	Ferrous iron (Fe^{2+})
Sulphate	Hydrogen sulfides (HS^- and H_2S)
Carbon dioxide	Methane (CH_4)

Measurements of the change in the concentrations of terminal electron acceptors (TEA) in the dissolved phase (*e.g.*, O_2, NO_3^-, and SO_4^{2-}), or the product of the biodegradation reaction (reduced form of the TEA, *e.g.*, Fe^{2+}, Mn^{2+} and CH_4) can provide an indication of the occurrence and pathway of petroleum hydrocarbon degradation.

Assimilative capacity is the potential capacity of groundwater systems to biodegrade petroleum hydrocarbon contaminants into other compounds or elements. Expressed assimilative capacity is often defined as the capacity for biodegradation based on the difference in electron acceptor and metabolic by-products concentrations or mass between upgradient and downgradient wells. The expressed assimilative capacity can be estimated by dividing this difference by a utilization factor, which for purposes here is the stoichiometric ratio of the mass of electron acceptor utilized (or metabolically produced) to mass of contaminants potentially biodegraded (Table 2-3).

Assimilative capacity calculations can be a quick screening method for estimating the capacity for biodegradation in a groundwater system in that the biodegradation capacity should be similar to or exceed the total petroleum hydrocarbon concentration. The assimilative capacity calculation does not provide any information on the rate of reactions and plume extent as biodegradation is assumed to occur quickly (almost instantaneously) relative to the hydraulic residence time in the source area and plume. Aerobic and anaerobic biodegradation reactions and consideration of assimilative capacity is included in the BIOSCREEN model as discussed in Section 4.

Assimilative Capacity Tool

An EXCEL spreadsheet (BioCapacity.xlsx) calculates the Biodegradation Capacity (BC). A low BC is considered less than 20 mg/L, moderate BC is 20 to 50 mg/L and high BC is greater than 50 mg/L.

Table 2-3: Calculation procedure for biodegradation capacity (from BIOSCREEN manual version 1.3, 1996)

Biodegradation Capacity (mg/L) =
{ (Average Upgradient Oxygen Conc.) - (Minimum Source Zone Oxygen Conc) } / 3.14
+ { (Average Upgradient Nitrate Conc.) - (Minimum Source Zone Nitrate Conc) } /4.9
+ { (Average Upgradient Sulfate Conc.) - (Minimum Source Zone Sulfate Conc) } / 4.7
+ { Average Observed Ferrous Iron Conc. in Source Area} / 21.8
+ { Average Observed Methane Conc. in Source Area } / 0.78

Note: Some technical protocols (*e.g.*, Air Force Intrinsic Remediation Technical Protocol (Wiedemeier *et al.*, 1995)) use the maximum ferrous iron and methane concentration in the source zone as opposed to average concentration.

Calculated biodegradation capacities (from Groundwater Services sites) and expressed assimilative capacities (from Parsons Engineering-Science sites) at different US Air Force RNA research sites have ranged from 7 to 70 mg/L (see Table 1 in BIOSCREEN manual version 1.3, 1996). The median capacity for 28 AFCEE sites is 28.5 mg/L.

Measurements of MNA parameters

Measurement of redox sensitive parameters can be challenging, because exposure of the water sample to atmospheric (*i.e.*, oxygen rich) conditions increases DO and results in the oxidation of the reduced iron and manganese and their precipitation out of solution. Therefore, parameters measured in the field can better represent the true aquifer conditions. In general, the same steps followed for measurement of volatiles would apply in sample collection and handling. For example, using a low flow pump and purging water until there are no air bubbles and field parameter readings are stable.

Parameters that can potentially be measured in the field include:

- Dissolved oxygen, electrical conductivity, pH, water temperature and redox potential (Eh) using hand-held field meters installed in a flow-through cell;
- Nitrate, ferrous iron (Fe^{2+}) and divalent manganese (Mn^{2+}) using colourmetry kits; and
- Total alkalinity using a field titration kit.

Parameters for laboratory analysis include:

- Dissolved metals (including major cations);
- Major anions;
- Hydrogen sulphides;
- Total and dissolved organic carbon;
- Speciated alkalinity (includes total alkalinity, bicarbonate, carbonate and hydroxide);

- Dissolved methane (could be limited to samples with low dissolved oxygen to reduce costs); and
- Kjeldahl nitrogen, orthophosphate, phosphorus, nitrate and nitrite.

To test the validity of the measurements, more than one method can be used. For example, DO ampules can be used for a colorimetric measurement of the oxygen concentration. The methane and hydrogen sulfide vapour concentrations of the well headspace can be measured and compared to the laboratory results of the same parameters in the dissolved phase.

2.5.3 Tertiary Line of Evidence

The tertiary line of evidence can include microcosm studies, to evaluate biodegradation processes and rates under controlled conditions, or Compound Specific Isotope Analysis (CSIA) or Molecular Biological Tools (MBT). CSIA can be used to assess and potentially demonstrate that biodegradation is occurring (Adamson and Newell, 2014; ITRC, 2011).

CSIA is a recent development that for targeted compounds can be used to demonstrate biodegradation is occurring through analysis of the ratio of stable isotopes of carbon (^{12}C and ^{13}C) and understanding of fractionation that occurs through preferential biodegradation of the lighter stable isotope. MBT can be used to identify the presence of specific microorganisms and functional genes active in the biodegradation process. While tertiary tools are relatively uncommon (and generally not warranted) as a line of evidence at petroleum hydrocarbon sites, CSIA and MBT have been successfully used to demonstrate that MTBE has been degraded and incorporated into biomass (Adamson and Newell, 2014).

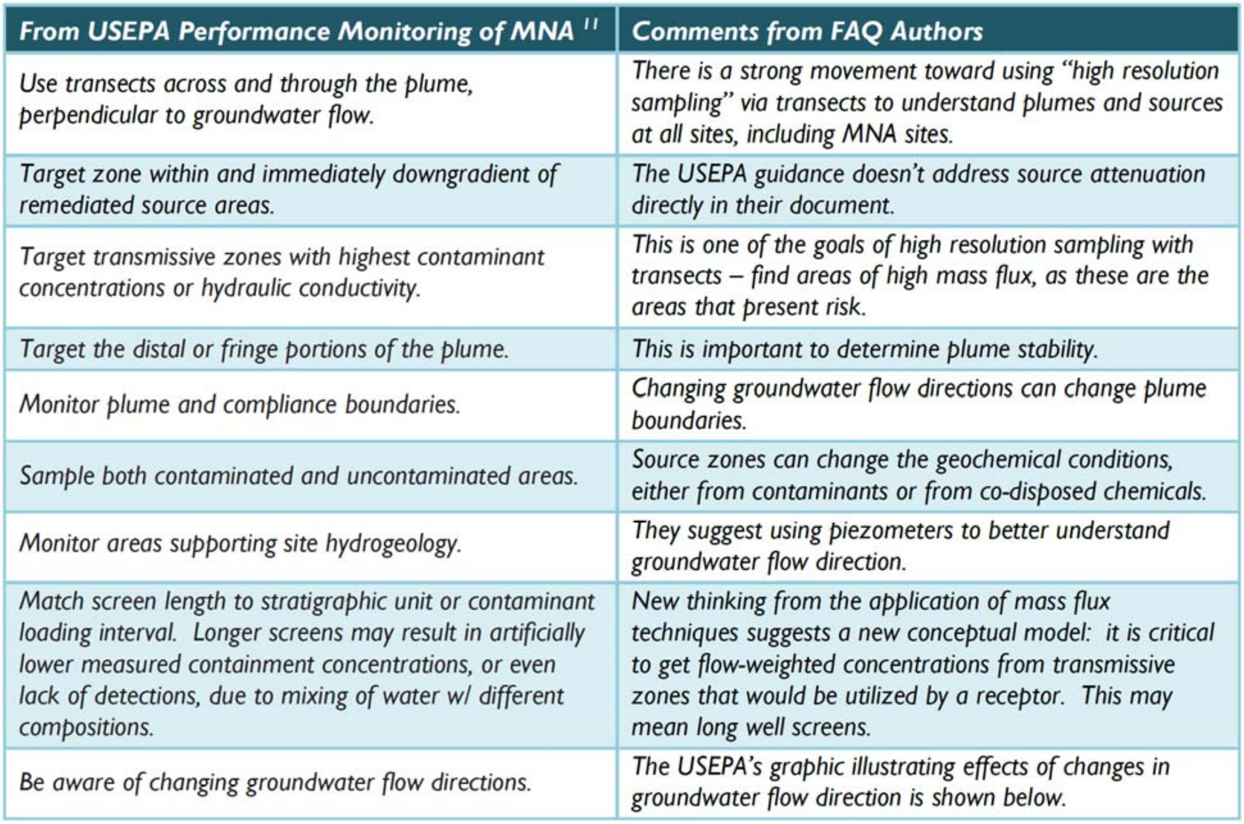
2.6 Long-term Monitoring

The US Department of Defense Environmental Security Technology Certification Program (ESTCP) has recently provided a Frequently Asked Questions (FAQs) document for MNA (Adamson and Newell, 2014). For MNA monitoring, this document recommends following the US EPA MNA guidance on performance monitoring (Pope *et al.*, 2004) and provides a table of key concepts presented in Figure 2-4. MNA monitoring is divided into two distinct phases of Site Characterization and Long-term Monitoring. During the Site Characterization phase, efforts are made to define the hydrogeological and geochemical conditions at the site, which include seasonal effect on groundwater and changes in flow direction (see Section 2.4 for available tools). For the Long-term Monitoring phase, methods for determining the monitoring frequency are presented along with measurements of flow-weighted average concentration (*e.g.*, through longer screens or passive flux meters).

Monitoring frequency is recommended based on large dataset research study with over 3,090 monitoring wells across the United States (from Utah, Georgia, and across US) and an average of 10 years of data from each (McHugh *et al.*, 2011):

- Less frequent monitoring at sites with high short-term variability and slow source attenuation rates; and
- More frequent monitoring at sites with low short-term variability and faster source attenuation rates.

This study concludes that monitoring more frequently than once a year would show more time independent variability rather than long-term trends in concentrations. Often, the objective of long term monitoring is for the estimation of attenuation rates in concentrations of contaminants in individual monitoring wells. McHugh *et al.* (2016) describe the trade-off between monitoring frequency and monitoring duration on the accuracy and confidence on the estimated attenuation rates. McHugh *et al.* (2016) present methods for estimating the relative accuracy in estimated attenuation rates as a function of monitoring duration and frequency and demonstrate that the estimated accuracy is independent of site-specific data.



From USEPA Performance Monitoring of MNA [11]	Comments from FAQ Authors
Use transects across and through the plume, perpendicular to groundwater flow.	*There is a strong movement toward using "high resolution sampling" via transects to understand plumes and sources at all sites, including MNA sites.*
Target zone within and immediately downgradient of remediated source areas.	*The USEPA guidance doesn't address source attenuation directly in their document.*
Target transmissive zones with highest contaminant concentrations or hydraulic conductivity.	*This is one of the goals of high resolution sampling with transects – find areas of high mass flux, as these are the areas that present risk.*
Target the distal or fringe portions of the plume.	*This is important to determine plume stability.*
Monitor plume and compliance boundaries.	*Changing groundwater flow directions can change plume boundaries.*
Sample both contaminated and uncontaminated areas.	*Source zones can change the geochemical conditions, either from contaminants or from co-disposed chemicals.*
Monitor areas supporting site hydrogeology.	*They suggest using piezometers to better understand groundwater flow direction.*
Match screen length to stratigraphic unit or contaminant loading interval. Longer screens may result in artificially lower measured containment concentrations, or even lack of detections, due to mixing of water w/ different compositions.	*New thinking from the application of mass flux techniques suggests a new conceptual model: it is critical to get flow-weighted concentrations from transmissive zones that would be utilized by a receptor. This may mean long well screens.*
Be aware of changing groundwater flow directions.	*The USEPA's graphic illustrating effects of changes in groundwater flow direction is shown below.*

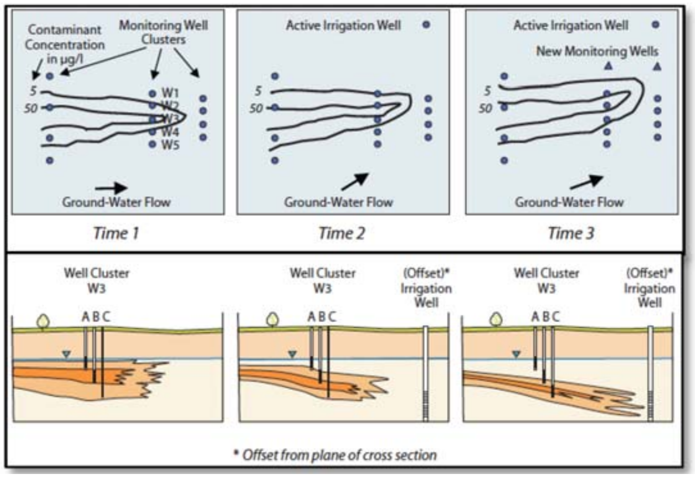
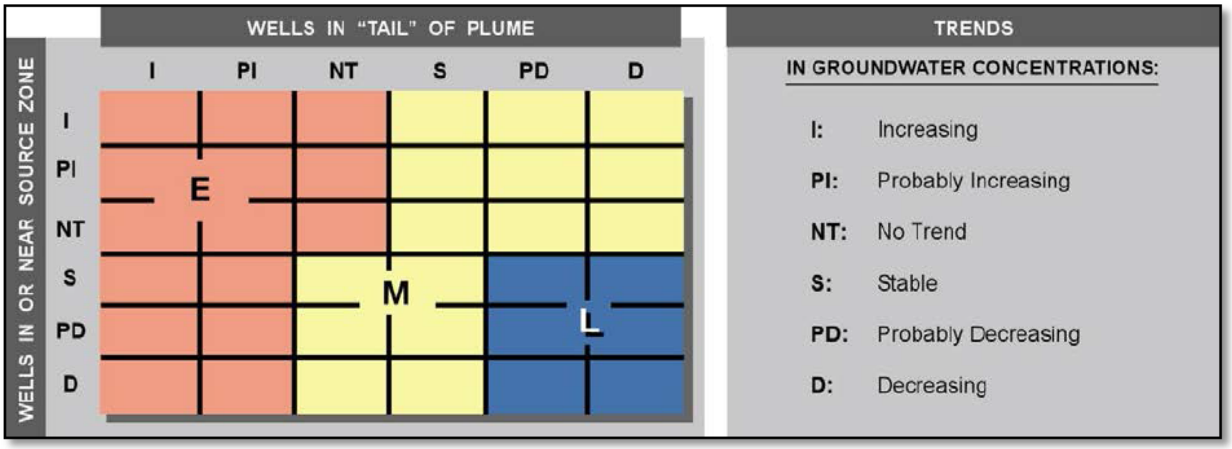
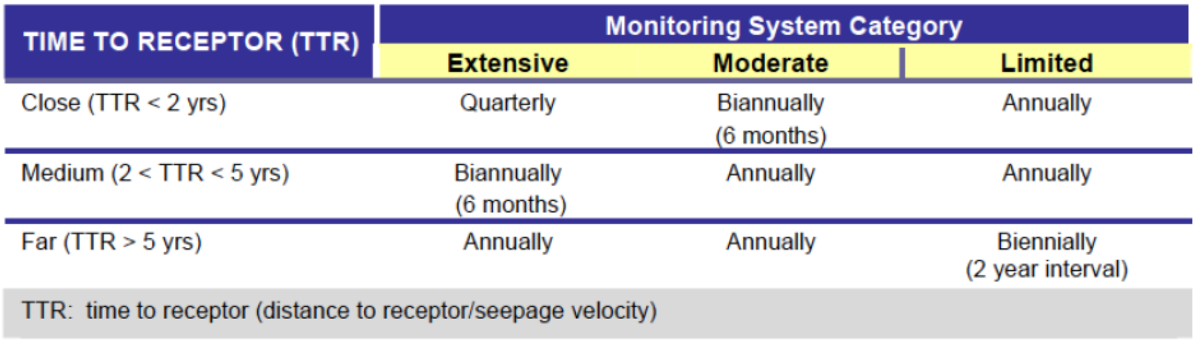


Figure 2-4: Graphics from ESTCP FAQs document on key concepts of MNA monitoring system (Adamson and Newell, 2014).

> **MAROS Tool**
>
> The **Monitoring and Remediation Optimization System (MAROS)** tool developed by the US Air Force Centre for Engineering and the Environment is a data management and evaluation tool intended to improve long-term groundwater management. The tool analyzes concentration trends, assesses appropriate sampling frequencies for well networks, identifies redundant monitoring locations and identifies area of higher uncertainty that may require more monitoring locations.

The MAROS tool enables statistical trend analysis of temporal concentration data and provides a useful framework for identifying an appropriate monitoring frequency. The first step is to define the level of monitoring warranted (Extensive (E), Moderate (M) or Limited (L) based on an assessment of plume stability for wells in the source and tail of the plume (Figure 2-5). The second step is to estimate the groundwater travel time to the receptor, which is the distance from the leading edge of the plume to the receptor divided by the seepage velocity. Wilson *et al*. (2011) in evaluating monitoring frequency suggest in some cases a frequency of one monitoring event per five years may be appropriate, and McHugh *et al.* (2016) provide a method for estimating the accuracy in the predicted attenuation rates based on monitoring frequency and duration.





TIME TO RECEPTOR (TTR)	Monitoring System Category		
	Extensive	Moderate	Limited
Close (TTR < 2 yrs)	Quarterly	Biannually (6 months)	Annually
Medium (2 < TTR < 5 yrs)	Biannually (6 months)	Annually	Annually
Far (TTR > 5 yrs)	Annually	Annually	Biennially (2 year interval)

TTR: time to receptor (distance to receptor/seepage velocity)

Figure 2-5: Graphics from ESTCP FAQs document on Monitoring Frequency from MAROS (Adamson and Newell, 2014).

2.7 Summary and Recommendations

A common framework for evaluation of MNA consists of three steps: 1) site characterization and development of a conceptual site model, 2) evaluation of lines of evidence for natural attenuation, and 3) long-term monitoring to verify that natural attenuation processes continue to occur.

The primary line of evidence, field data that demonstrate trends of decreasing contaminant mass and/or concentration over time at appropriately located monitoring points, and secondary line of evidence, geochemical data that demonstrate the types of natural attenuation processes at the site and that show mass loss through analysis of electron acceptors/donors and degradation products, should be evaluated at all sites. The tertiary line of evidence, microcosm studies or other biological monitoring tools, is optional but may be considered if demonstration of specific biological processes is warranted.

Under a primary line of evidence evaluation, both a qualitative evaluation of dissolved plume extent over time and point concentration trend analyses (*e.g.*, Mann-Kendall or other suitable statistical technique) test should be conducted for wells close to the hydrocarbon and further downgradient in the tail of the plume. Where there are sufficient data available, average-based methods for evaluation of plume trends should be considered. Assimilative or biodegradation capacity calculations presented here can be used as a simple technique for broadly assessing whether there are sufficient electron acceptors to support biodegradation of hydrocarbon present, or more advanced models under Step 3 can be considered.

New thinking with respect to long-term monitoring is presented including a flexible framework where monitoring frequency is based on the plume stability and time for groundwater transport from a source to receptor.

3.0 STEP 2: 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: the starting petroleum hydrocarbon mass and rate of hydrocarbon mass removal or degradation. More generally, estimates of hydrocarbon source depletion also provide valuable insight on LNAPL stability (higher depletion rates correspond to lower potential for migration) and relative importance of weathering mechanisms.

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, in subsequent discussion in this section, biodegradation and volatilization above the water table are combined and a model is applied where the downward oxygen flux is used to estimate the aerobic biodegradation and mass loss rate. This model assumes hydrocarbon (including methane) is degraded to carbon dioxide before reaching the ground surface. For conceptual simplification, three processes are addressed in the subsequent discussion of available models and methods that characterize one or more natural attenuation processes:

1) Biodegradation in the unsaturated zone.
2) Biodegradation in the saturated zone.
3) Dissolution in the saturated zone.

The discussion below covers the following screening models and tools:

- The ITRC (2009) model based on control volume concept, which describes all three processes above.
- The Golder NSZD Nomographs for vadose zone biodegradation and dissolution in the saturated zone.
- The GSI Mass Flux Toolkit (2012), a tool for estimation of mass flux and potentially loss through dissolution in the saturated zone.
- Three methods for mass loss through estimation of the biodegradation rate in the unsaturated soil zone:
  - Oxygen gradient method – involves estimation of the oxygen concentration gradient.
  - Carbon dioxide (CO_2) efflux method – involves measurement of the surface CO_2 flux.
  - Temperature method – involves measurement of the thermal gradient.

For estimation of mass loss through biodegradation in the unsaturated zone, the oxygen gradient method is recommended as a relatively simple method for order of magnitude estimation using typically readily available data. The other two methods are reviewed to provide a range of options and complexity for input into a multiple lines of evidence assessment of NSZD.

Biodegradation of hydrocarbon in the saturated zone may occur under anaerobic conditions and result in the generation of methane through fermentation reactions. Methane that evolves to the oxic portions of the saturated or the unsaturated zone is oxidized to form carbon dioxide. This toolkit also describes a new model developed for this project, the Vadose Zone Biological Loss (VZBL) model. This model incorporate both anaerobic processes (prediction of methane flux) and aerobic processes (oxidation of methane and petroleum hydrocarbon vapours) for prediction of petroleum hydrocarbon source depletion.

3.1 Screening Models

3.1.1 Control Volume Concept Model for Estimation of Depletion Rates

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. 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 (Figure 3-1).

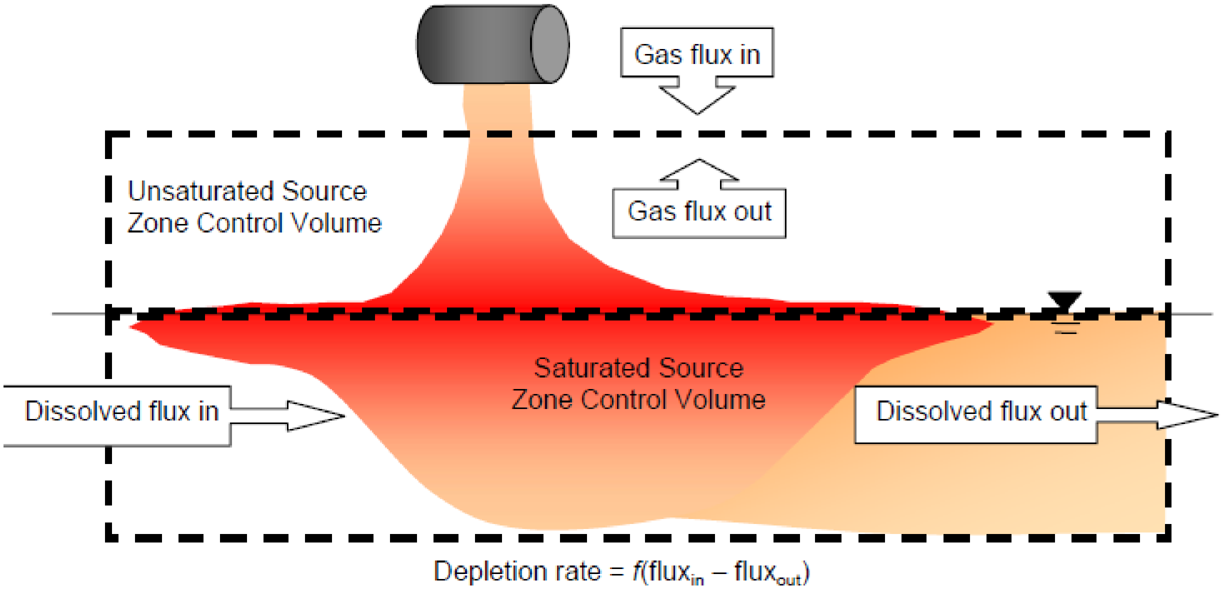


Figure 3-1: Control volume "box" for quantitative assessment of NSZD (from ITRC, 2009).

When there are data on hydrocarbon source mass, the dissolution and biodegradation rates in the saturated source zone can be used to estimate the source depletion time for the saturated portion of the source; likewise, the volatilization and biodegradation rate in the vadose zone can be used to estimate the source depletion time in the unsaturated portion of the source.

An estimate of the dissolution flux ($R_{Dissoln}$, mass/time*)* may be calculated for submerged LNAPL, as shown conceptually in Figure 3-2 and mathematically below (ITRC, 2009).

$$R_{Dissoln} \approx q_d HW \langle C_d \rangle \qquad \text{Eq. 3-1}$$

Where q_d is the groundwater specific discharge (length/time), H is the height of the submerged source zone (length), W is the width of the submerged source zone (length) and $\langle C_d \rangle$ is the area-averaged dissolved NAPL concentration downgradient of the source zone (mass per length cubed).

An estimate of biodegradation mass loss rate ($R_{BioSat,}$ mass/time*)* may be calculated for submerged LNAPL, shown conceptually in Figure 3-2, with the detailed mathematical equation provided in ITRC (2009). Thus, the saturated source depletion rate is approximated by the sum of $R_{Dissoln}$ and R_{BioSat}.

An estimate of the hydrocarbon volatilization and biodegradation loss ($R_{Bio\text{-}Unsat,}$ mass/time) may be calculated for the exposed LNAPL, as shown conceptually in Figure 3-2 (simplified from ITRC, 2009) and mathematically below.

$$R_{BioUnsat} \approx WL \left\{ S_{O_2} D_{O_2} \left. \frac{\mathrm{d}[C_{O_2}]}{dz} \right|_{z=L} \right\} \qquad \text{Eq. 3-2}$$

Where L is the length of the submerged source zone (length); S_{O2} is the stoichiometric coefficient for aerobic biodegradation of hydrocarbon (unit mass of hydrocarbon degraded per unit mass of O_2 consumed); D_{O2} is the effective diffusion coefficient for oxygen (length squared per time); and $\frac{\mathrm{d}[C_{O_2}]}{dz}$ is the concentration gradient between the ground surface and source (mass per length cubed per time).

The equation for mass loss is based on the oxygen consumption rate estimated using Fick's Law and a linear model for oxygen concentrations (atmospheric at ground surface and zero at the source). Assumptions incorporated in the calculation include fast aerobic biodegradation reaction relative to O_2 transport in the vadose zone and that all hydrocarbons are degraded before reaching the ground surface. The stoichiometric coefficient is based on the primary hydrocarbon components in soil vapour undergoing aerobic degradation.

We recommend that the control volume model ITRC (2009) be considered for evaluation of multiple depletion processes. The mass loss through biodegradation in the unsaturated zone can be relatively large and at some sites is expected to be the primary process for source zone depletion, although there are few case studies where the relative contributions of different depletion processes are quantified. The key data requirements for this model are concentration data, hydrogeological data (hydraulic conductivity and gradient) to estimate groundwater flow, detailed data on electron acceptors upgradient and downgradient of the source, and data on unsaturated zone soil properties. A potential advantage of the control volume method is a more accurate estimate of natural source depletion; however, a relatively dense well network is required adding to investigation cost. In addition, there is currently no commercially available computer code for this model, although such a code is in development as part of this project.

Control Volume Model Tool

The control volume model can be a useful screening method for accounting for natural source zone depletion reactions when there are groundwater and soil vapour geochemistry data. The **Control Volume CV-NSZD Tool** (EXCEL spreadsheet) enables calculations to be readily performed and comparison of depletion through different mechanisms.

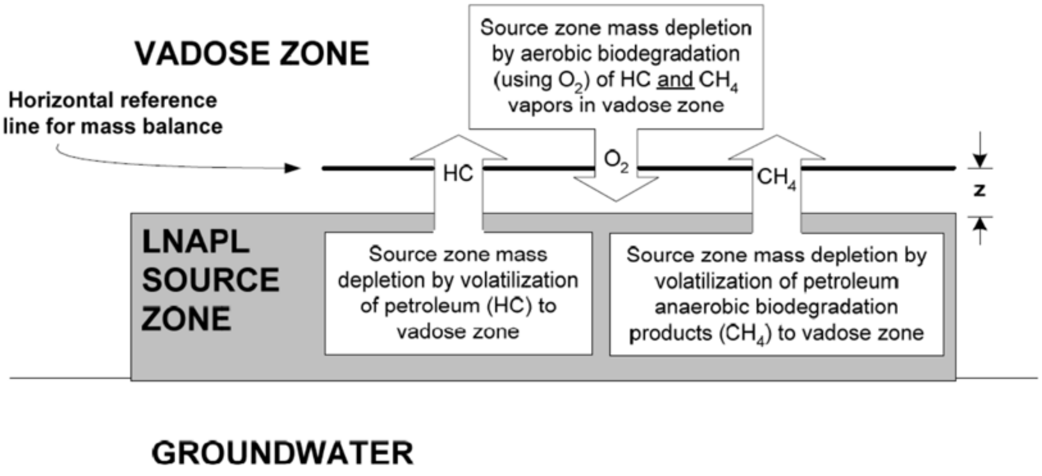


Figure 3-2: Conceptual model of processes in the vadose zone (ITRC, 2009).

3.1.2 Nomograph Method for Estimation of Source Depletion Times

This section presents a simple nomograph method for screening estimates of LNAPL source mass depletion times. The nomographs can be used for estimating hydrocarbon mass depletion times resulting from biodegradation (mass loss rate) in the vadose zone and dissolution (mass loss rate) in the saturated zone. Example nomographs are provided for biodegradation (mass loss) rate for petroleum hydrocarbons, presented in Figures 3-3 and 3-4, and dissolution mass loss rates, presented in Figures 3-5 and 3-6.

Golder NSZD Nomograph Tool

A simple nomograph tool can be used to estimate approximate depletion times when there are data on TPH concentrations or LNAPL saturation in soil and biodegradation (mass) loss rates.

The hydrocarbon mass (M_{HC}) can be estimated one of three ways: Method 1 - the average hydrocarbon concentration in soil (Figures 3-3 and 3-5); Method 2 - the average LNAPL (oil) saturation (Figures 3-4 and 3-6), which can be estimated from laboratory tests or literature values, and Method 3 - the LNAPL (oil) specific volume estimated using a model and the in-well LNAPL thickness, for example, the API LDRM model. It is recommended to choose a method based on available data and literature values. Where possible, more than one method can be used to estimate a range of hydrocarbon mass depletion times. An example calculation, based on Method 2 and assumed input parameters, is provided below:

- Soil type: Medium to coarse sand;
- Product type: Gasoline;
- LNAPL is at residual saturation;
- LNAPL (oil) saturation = 0.15 (from laboratory test results of core samples or literature values, *e.g.*, Brost and DeVaull (2000));
- LNAPL thickness = 1.0 m (from API LDRM model or laboratory test results of core samples); and
- Hydrocarbon (LNAPL) mass loss rate = 1 g/m^2-day (estimated based on methods described in this document).

The LNAPL saturation multiplied by thickness is 0.15 m. From the nomograph (Figure 3-4), the estimated source depletion time from biodegradation in the vadose zone is approximately 90 years. If the LNAPL density or porosity differs significantly from the assumptions, the calculations shown in Figures 3-3 and 3-4 may be used.

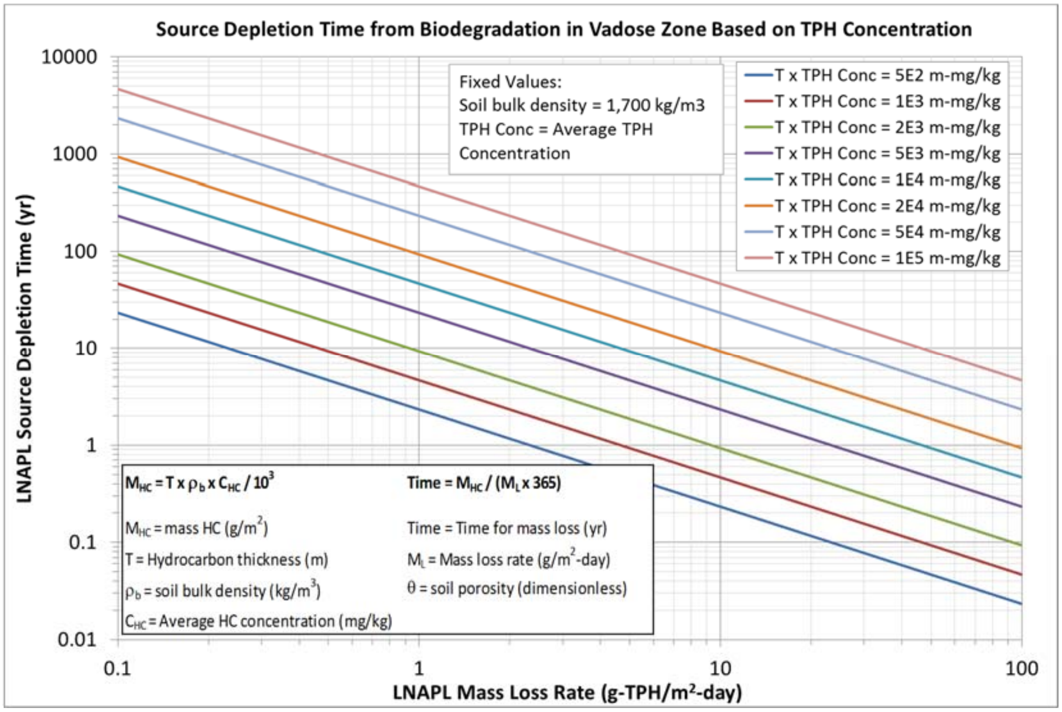


Figure 3-3: Nomograph for source depletion from biodegradation in the vadose zone based on hydrocarbon concentration.

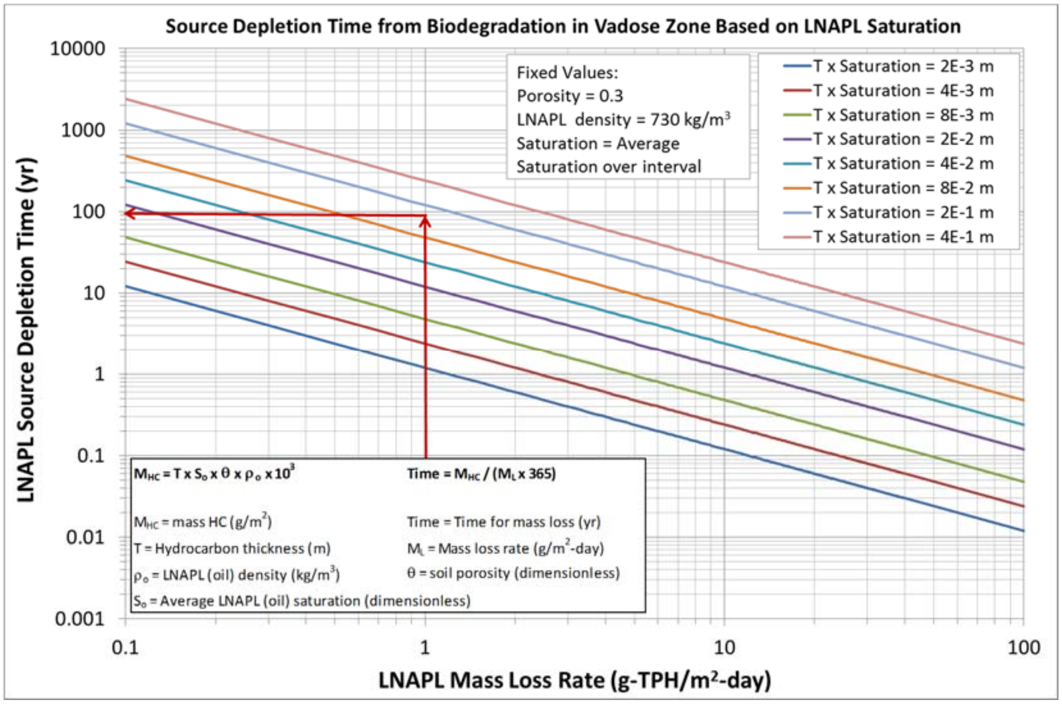


Figure 3-4: Nomograph for source depletion from biodegradation in the vadose zone based on LNAPL saturation.

The source depletion time from dissolution should be considered when there is residual LNAPL below the water. An example calculation, based on Method 2 and assumed input parameters, is provided below:

- Soil type: Medium to coarse sand;
- Product type: Gasoline;
- LNAPL is at residual saturation;
- LNAPL (oil) saturation = 0.1 (from laboratory test results of core samples or literature values, *e.g.*, Brost and DeVaull (2000));
- LNAPL length in the direction of groundwater flow = 10 m;
- Darcy velocity of 0.04 m/day (from measured hydraulic conductivity and groundwater levels); and
- Dissolved phase concentration of 75 mg/L in the source zone (from laboratory analysis of groundwater samples).

From the nomograph (Figure 3-6), the estimated source depletion time from dissolution in the saturated zone is approximately 200 years.

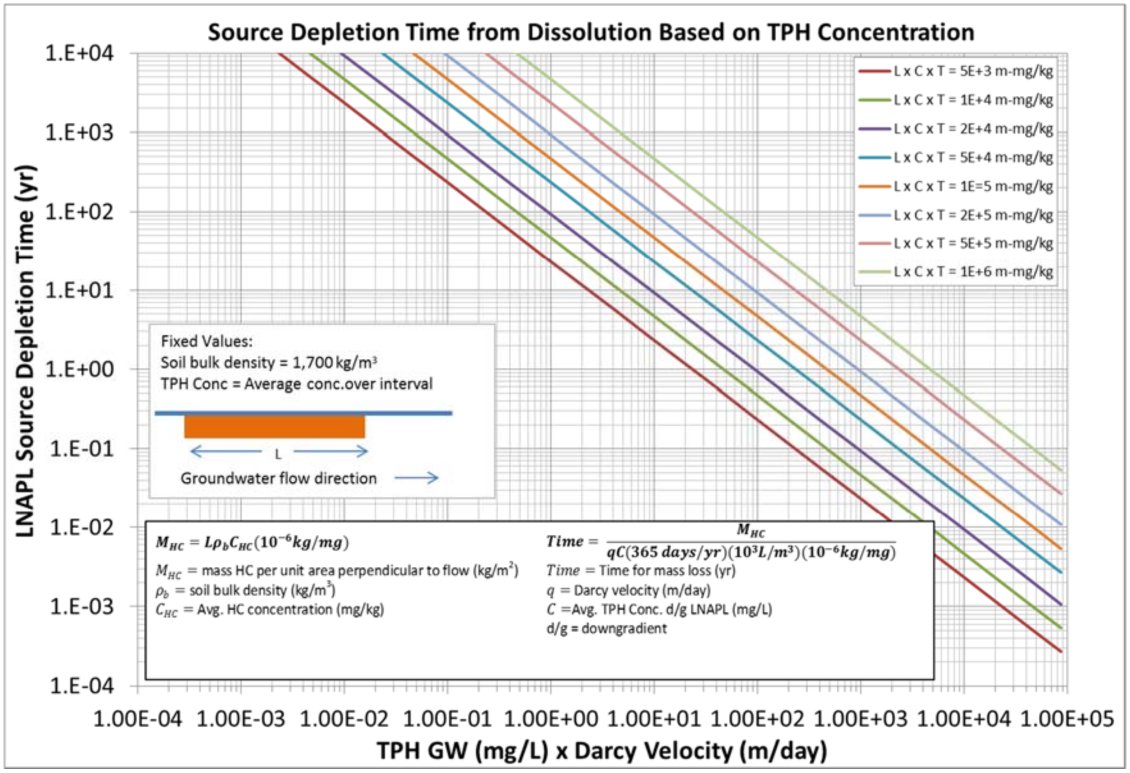


Figure 3-5: Nomograph for source depletion from dissolution in the saturated zone based on hydrocarbon concentration.

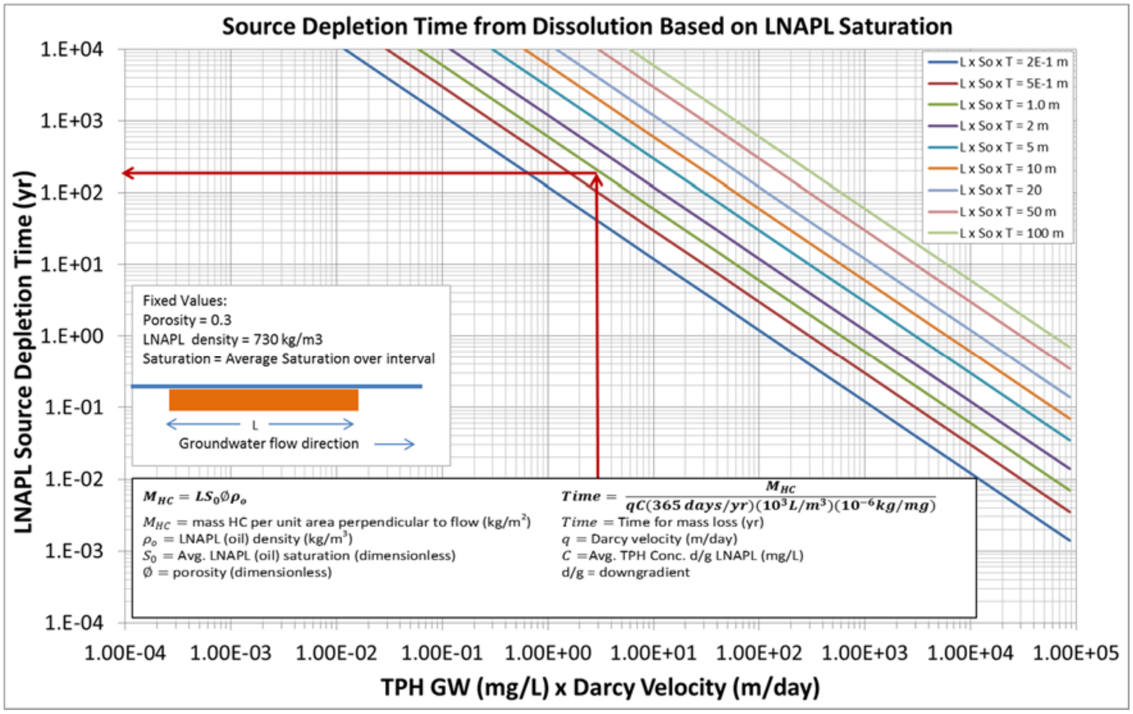


Figure 3-6: Nomograph for source depletion from dissolution in the saturated zone based on LNAPL saturation

3.1.3 GSI Groundwater Mass Flux Toolkit

GSI Environmental Inc. developed the Mass Flux Toolkit[3] 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 and other remediation technologies implemented at a site.

The Mass Flux Toolkit, in essence, is the dissolution method described for the ITRC (2009) control volume method. Potential advantages are the tool enables calculation of a spatially integrated flux based on multiple data points, enables uncertainty in the calculations to be quantified and identifies gaps where the greatest benefit is derived in reducing uncertainty. If multiple transects are available, the Toolkit enables estimation of mass loss between transects, which may be useful to support a MNA assessment of a dissolved plume. A useful feature of the tool is the calculation of the capture zone of a water supply well that could potentially be impacted by the groundwater contaminant plume.

The GSI Toolkit is recommended when a more in-depth analysis of dissolution mass loss is warranted. The key data requirements for this model are concentration data and hydrogeological data (hydraulic conductivity and gradient) to estimate groundwater flow. A potential advantage is a more accurate estimate of dissolution mass loss; however, detailed concentration data (vertically and horizontally) are required, which adds to investigation cost. The model is useful in identifying uncertainty in dissolution estimates.

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

Estimates of mass discharge and flux estimates can also be obtained through well capture and pumping test methods (in some cases referred to as integral pumping tests or IPT), which rely on extracting groundwater and measuring the flow and mass discharge from the wells, and by a passive flux meter (PFM), which is a recently developed device to estimate mass flux directly in wells. The IPT method involves measurement of concentration and discharge during a pumping test together with estimates of the well capture zone to calculate the contaminant flux in groundwater (ITRC, 2010). The PFM consists of a permeable sorbent that is infused with soluble tracers, which is placed in a well for a known period of time. The measurements of contaminants sorbing into the PFM and tracer out of the PFM is used to estimate the groundwater and contaminant fluxes (Annable *et al.* 2005; ITRC, 2010).

3.2 Methods for Estimation of Unsaturated Source Zone Biodegradation

The O_2 gradient, CO_2 efflux and temperature methods for estimation of source zone biodegradation are described below and compared in Table 3-1. The O_2 gradient method is considered a first-tier method and can be readily implemented, often with existing data. The CO_2 efflux and temperature methods are considered second tier methods. Measurement of CO_2 efflux is an emerging method under rapid development and is anticipated to more commonly be implemented at sites where an additional line of evidence is required for NSZD estimates. Additional details on the first-tier and second-tier methods are provided in Appendices B and C, respectively.

Table 3-1: Comparison of methods for estimation of unsaturated zone biodegradation.

Method	Method Status	Key Data Required	Advantages	Disadvantages
O_2 Gradient	Well developed	O_2 concentration, soil porosity, moisture content, depth to source and water table, native organic carbon	Simple method, uses readily available data	Highly sensitive to soil moisture and water table
CO_2 Efflux	Emerging but rapidly developing	Surface CO_2 efflux above LNAPL and background sites, ^{14}C of CO_2, $\delta^{13}C$ of CO_2 (optional)	Direct measurement, avoids estimation of diffusion	Sensitive to natural soil respiration, methods are variable
Temperature	New	Temperature profile above LNAPL and background sites, soil thermal conductivity	Direct measurement, potentially lower cost, possible to collect a large data set to assess spatial variability	Requires estimate of thermal conductivity, further research needed

The conceptual understanding of unsaturated zone biodegradation kinetics measured by the above NSZD measurement methods as represented by the rates in Section 3.2.5 continues to evolve. For LNAPL source zones, bulk TPH biodegradation or depletion rates will tend to be zero-order related to the rate of oxygen diffusion through the vadose zone. At some point, bulk attenuation will slow as the LNAPL becomes highly weathered (because dissolution is limiting) and thus degradation becomes first-order. Compound specific attenuation rates published in the literature are generally first-order. The degradation of specific hydrocarbons will occur sequentially as some hydrocarbons will attenuate faster than others depending on factors including biodegradation pathway (*e.g.*, aerobic vs. anaerobic), compound (*e.g.*, straight chain vs. branched/cyclic), and physical/chemical properties.

3.2.1 Oxygen Gradient Method

Overview

The source biodegradation rate and mass loss is estimated from the oxygen consumption rate in the unsaturated zone and stoichiometric consideration of oxygen required for aerobic biodegradation of hydrocarbons. The oxygen consumption rate is estimated from a diffusion model and oxygen gradient.

Conceptual Model

LNAPL is present within the unsaturated zone or near the water table as a smear zone. The top of the LNAPL is located above the water table. There is aerobic biodegradation of hydrocarbons from the LNAPL that is assumed to be limited by the downward diffusion of oxygen. Oxygen consumption is due to aerobic biodegradation of fuel hydrocarbon and native organic matter, if present. Hydrocarbon is assumed to be fully degraded within the vadose zone and the estimate of oxygen gradient is based on the assumption of oxygen depletion at the hydrocarbon source depth.

Methods for Estimation of Unsaturated Zone Biodegradation

Three methods for estimation of unsaturated zone biodegradation are reviewed: 1) O_2 gradient, 2) CO_2 efflux and 3) temperature. The gradient method utilizes data often obtained at sites (oxygen, soil properties, TPH concentration) and can be used to estimate the NSZD rate. Carbon dioxide efflux measurements are a newer method with promise as a more direct surface-based technique for estimation of biodegradation rates. The temperature method is an emerging method currently being evaluated for NSZD studies.

Mass Loss Calculation

From an approximate linear oxygen profile, constant soil properties can be inferred, and the oxygen consumption rate may be estimated from Fick's first law equation for diffusion of oxygen and spatially-averaged soil properties (Equation 3-2 above). Appendix B describes models for heterogeneous soil deposits and more complex behaviour. Roggemans *et al*. (2002) includes a conceptual overview of different soil gas behaviours and expected oxygen profiles.

Modeling Tool

The Vadose Zone Biodegradation Loss (VZBL) model, a free Microsoft® Excel Spreadsheet, is a new model developed by Dr. John Wilson of Scissortail and Golder Associates. The model estimates the hydrocarbon source depletion rate based on the oxygen gradient and the estimated effective oxygen diffusion coefficient. 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. When the influence of methane is included, the VZBL model goes beyond the simple oxygen gradient method described above.

The model is easy to use and has the following features that provide for more accurate estimates:

- Properties for multiple soil layers can be entered to obtain an overall effective diffusion coefficient;
- Time-dependent vertical depletion of the hydrocarbon source is simulated based on a mass balance;
- The potential influence of water table fluctuations is accounted for in that mass loss is turned on if the water table is below the top of the LNAPL source, but turned off when the water table is above the top of the source;
- The water table depth varies based on a probability function for a given average depth and standard deviation of the depth; and
- The hydrocarbon biodegradation rate may be reduced to account for baseline oxygen respiration of native organic carbon.

Vadose Zone Biodegradation Loss (VZBL) Tool

The Vadose Zone Biodegradation Loss (VZBL) model is an Excel spreadsheet that estimates the oxygen consumption rate and biodegradation loss rate for petroleum hydrocarbons based on site data. When data on TPH concentrations in soil are available, the source depletion time can be estimated.

The data inputs for the VZBL model are as follows:

1) Water-filled and total porosity for depth-discrete layers.
2) Depth-discrete profile of TPH concentrations in soil.
3) The stoichiometric coefficient for aerobic biodegradation.
4) Baseline respiration rate for native organic carbon (OC) (optional). The default rate is 1.69 x 10^{-2} mg O_2/ g-OC day (DeVaull, 2007).
5) Average soil OC content between the source and ground surface (optional).
6) Depth to the water table measurements.
7) Nitrogen concentrations in soil gas near to the hydrocarbon source (optional).
8) The stoichiometric coefficient for methane produced per mole of hydrocarbon degraded through fermentation and methanogenesis (optional if N_2 concentration data in soil gas are available and methane is present).

Appendix D provides recommendations for geotechnical and total petroleum hydrocarbon soil testing. A novel approach is described where initially vertical profiles of electrical conductivity measurements by direct push technology are obtained. These data could be used to distinguish soil layers with high fines (clay) and water content and thus low air-filled porosity, which are targeted for soil sampling to obtain air-filled porosity estimates through measurements of soil bulk density. In addition, recommendations from Wilson *et al.* (2012) for collection and screening of core samples for TPH analyses are included.

US EPA OUST guidance (US EPA, 2004b) provides additional insight on natural source zone depletion timelines based on application of the gradient method as summarized in Appendix E.

Equivalent Zero-Order Rate and Check on Gradient Method

Given an oxygen flux or consumption rate in the vadose zone, a hydrocarbon degradation rate can be estimated in terms of an equivalent "zero-order" rate (R_{equiv}, kg-hydrocarbon (HC))[4]/kg-soil-day) for an estimated or assumed smear zone thickness (S_m) and soil bulk density (ρ_b),

$$R_{equiv} = \frac{S_{o2} O_r}{S_m \rho_b}, \qquad \text{Eq. 3-3}$$

where O_r is the oxygen consumption rate or flux (kg/m^2-day) and S_{o2} is the stoichiometric coefficient for kg of hydrocarbon degraded per kg of oxygen consumed.

Equivalent zero-order aerobic biodegradation rates published in the literature on *in-situ* bioventing respiration tests from fuel release sites indicate that the majority of calculated rates are between 1 and 10 mg/kg-soil-day (USEPA, 1995). A passive loss rate from a fuel release through volatilization and biodegradation would be expected to be less than the published bioventing rates above, where oxygen is in excess from an engineered delivery system.

Passive zero-order aerobic biodegradation rates have also been estimated from laboratory studies or carefully controlled field research studies. Franzmann *et al.* (1999) conducted benzene mineralization experiments on samples obtained at a sandy site in Perth and estimated a hydrocarbon degradation rate of 6.6 mg-hexane/kg-soil-day (Davis *et al.*, 2005). Hers *et al.* (2000) estimated BTX zero-order mineralization rates of 0.6 to 1.4 mg-BTX/L-aqueous phase per hour based on model calibration to detailed soil gas profiles. Fischer *et al.* (1996) estimated rates from field soil gas data of 0.5 to 40 mg/kg-soil-day for a gasoline release in sandy soils.

It is recommended that caution be used when R_{equiv} is greater than 1 mg/kg-soil-day and in all cases if the estimated R_{equiv} is greater than 5 mg/kg-soil-day, the use of the gradient should be re-evaluated.

Case Study

The VZBL model is used to estimate mass loss rates based on reported vertical profiles of porosity (water-filled and total) and TPH concentration data for the Traverse City site (Ostendorf and Kampbell, 1991). A large release of jet fuel (100,000 kg) occurred at this site. The depth to the water table is approximately 5 m and there are sandy soils. A detailed description of the modeling results for the Traverse City case study is provided in Appendix F.

The VZBL model estimated hydrocarbon biodegradation rates with baseline respiration off range from 0.18 to 0.86 g-HC/m^2-day (with baseline respiration on, the rates are approximately 10 percent lower). The corresponding source depletion times range from 6.5 to 141 years. Possible reasons for the large range in predicted source depletion times are the variable soil moisture and effective diffusion coefficient profiles and underestimation of the source mass (the high concentration portion of the TPH layer was only 0.2 m thick). Given that the spill occurred in 1969 and latest available data for the Traverse City site was 27 years later, the depletion time must be significantly greater than 27 years considering that other processes such as dissolution and saturated zone biodegradation will occur. For the Traverse City case study, the equivalent zero-order biodegradation rate for the site-specific LNAPL thickness is about 2.5 mg/kg-day for the fast depletion case and 0.5 mg/kg-day for the slow depletion case. These rates are not implausible based on the procedure to check rates described above.

Ostendorf and Kampbell (1991) used a coupled one-dimensional model for diffusion and aerobic biodegradation to analyze the same data set from the Traverse City, Michigan site. Their model was calibrated based on best estimate of the effective diffusion coefficient and best fit to measured soil gas profiles (*i.e.*, an advanced application of the simple gradient method above). From the estimated biodegradation rate, an equation for hydrocarbon flux

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[4] Unless noted otherwise HC refers to total petroleum hydrocarbon

(mass loss) directly above the source zone was developed. The estimated mass loss rates at four soil gas profile locations were approximately 0.6 to 1 g-HC/m^2-day. The model calibrated zero-order degradation rate for hydrocarbon is approximately 0.3 to 0.6 mg-HC/kg-soil-day. The gradient method biodegradation rate is less than that estimated by Ostendorf and Kampbell (1991), which are relatively high rates given the depletion times estimated.

Summary

The O_2 gradient method is recommended as a relatively simple method for estimation of source depletion times using TPH and porosity (total and water-filled) profile data. Appropriate field methods should be utilized including continuous sampling of LNAPL zones and collection of soil property (geotechnical) data. The primary disadvantage with this method is that the oxygen consumption rate and mass loss is highly sensitive to the soil moisture. Predictions are less accurate when the unsaturated soil profile is variable and there are thin fine-grained soil units that are close to saturation.

3.2.2 CO_2 Surface Efflux Method

Overview

An emerging approach for quantification of MNA of source zones is measurement of surface CO_2 efflux. The CO_2 efflux attributable to contaminant-related soil respiration (CSR) can be used to estimate the biodegradation or mass loss rate.

Conceptual Model

Petroleum hydrocarbons are degraded (respired) by microbes in the presence of terminal electron acceptors (TEAs) including O_2, NO_3^-, manganese oxides, iron oxides, and SO_4^{2-} (Sihota *et al*., 2013). These biodegradation reactions result in contaminant decomposition and production of CO_2 (Figure 3-7). Depending on the type of petroleum spilled, hydrocarbon-contaminated source zones may become highly reducing leading to methanogenic conditions with production of CH_4 in addition to CO_2.

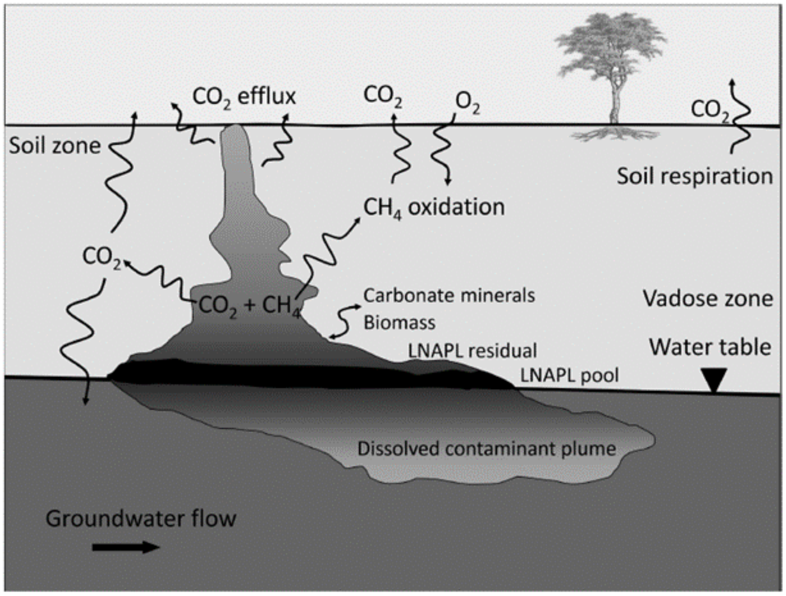

Figure 3-7: Conceptual model of processes affecting source zone natural attenuation and CO_2 migration at petroleum hydrocarbon contaminated sites (from Sihota et al., 2011).

When present in soil gas, CO_2 and CH_4 will migrate away from source zones toward ground surface by diffusive and advective gas transport processes. At most sites, atmospheric O_2 ingress results in CH_4 oxidation, and thus carbon loss across the ground surface is dominated by the efflux of CO_2, and CH_4 emissions are insignificant (Sihota *et al.*, 2013). However, if CH_4 efflux and/or carbon sequestration by biomass are significant, the CO_2 efflux will under predict mineralization. If there is natural soil respiration occurring, the CO_2 efflux will over predict mineralization. For these reasons, the method includes measurements in background areas with similar soil conditions. In addition, measurement of carbon's radioisotope (^{14}C) may be used to identify carbon sources, and distinguish CO_2 produced from petroleum respiration from that attributable to natural respiration of soil organic matter (Conrad *et al*., 1997; Aelion *et al*., 2010, Sihota and Mayer, 2012). The use of ^{14}C as a CSR tracer relies on the relatively short half-life of this species (5,730 ± 40 year) (Aelion *et al*., 2010) in relation to the age of the petroleum hydrocarbons. The CO_2 derived from petroleum hydrocarbon oxidation contains no modern carbon in contrast with respiration of recently created soil organic matter in bioactive near surface soils where living organisms continually exchange ^{14}C with the atmosphere. The ^{14}C in recent organic carbon is approximately 105% modern carbon (pMC) (Hua *et al.,* 2013).

Stable carbon isotope testing may also be used to assess biodegradation processes. The stable isotope $\delta^{13}C$ of CO_2 is expected to be more negative in areas of aerobic respiration of petroleum hydrocarbon compared to natural organic matter (Sihota and Mayer, 2012). McCoy *et al.* (2014) also found highly negative $\delta^{13}C$ values in carbon dioxide traps above LNAPL source zones compared to background locations, although possible fractionation effects in the soil column are not well understood (*i.e*., the process of soil vapour transport may change the isotopic composition).

Methods

Two methods have been developed for the estimation of CO_2 efflux, 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 *et al*., 2012). The dynamic chamber involves collection of multiple measurements over relatively short durations (minutes to hour) using an infra-red gas analyzer. The static chamber involves measurement of flux over longer time periods (2 to 4 weeks). While recent research indicates CO_2 efflux measurements are potentially affected by several factors related to the testing protocol and environmental conditions, of significant importance is the correction for natural respiration rate. Jourabchi *et al.* (2016) compare different methods for background correction of dynamic chamber tests including a new mass balance method based on location-specific measurements of CO_2 and ^{14}C. Each method is discussed in greater detail in Appendix C.

Case Studies

Dynamic Chamber: Sihota *et al.* (2011) report the results of dynamic chamber testing at the Bemidji oil spill site. The average estimated efflux attributed to contamination respiration was 2.6 μmol-CO_2/m^2-sec corresponding to 3.3 g-HC/m^2-day based on n-alkane $C_{10}H_{22}$. For comparison, the model predicted effluxes for the Bemidji site range from 1.6 to 4.4 g-HC/m^2-day (Sihota *et al*., 2011). These fluxes coincide well with previous biodegradation estimates at the site based on integrated modeling studies and biodegradation rates derived from various field investigations. Sihota *et al.* (2016) report the results of two-years of CO_2 efflux monitoring at the Bemidji site to estimate seasonal changes in natural attenuation processes. Surficial CO_2 effluxes varied seasonally, with peak values of total soil respiration (TSR) occurring in the late spring and summer; however, the contaminant soil respiration efflux was highest in the fall. The annual average efflux was 1.1 μmol-CO_2/m^2-s, while the seasonal minimum (spring) and maximum (fall) values were 0.5 and 1.7 μmol-CO_2/m^2-s, respectively.

Dr. Uli Mayer and co-workers at UBC have conducted carbon dioxide efflux measurements at other sites in Minnesota. Results indicate CO_2 effluxes about 2.5 times higher for the Cass Lake site, a site with similar oil contamination and depth to water table to Bemidji, and CO_2 effluxes about 10 times higher for the Balaton and Cambria sites, which are sites with shallow denatured ethanol (E95) releases. These results are confirmed by the more weathered nature of the oil at the Cass Lake site and the highly labile nature of ethanol, which leads to the high observed biodegradation rates.

Porter (2014) present the results of dynamic chamber testing at 6 sites, involving 21 rounds of efflux monitoring at 163 locations and 1,529 measurements in Canada (Yukon and Alberta). Site conditions range from active gas plants to remote maintenance yards containing several types of hydrocarbons (crude oil, waste oil, natural gas liquids and diesel). For grass-covered sites, the reported range in corrected CO_2 effluxes was 0.23 to 3.5 μmol/m^2-s, which is 0.24 to 4.3 g-HC/m^2-day based on C_8H_{10} degradation. For gravel-covered sites, the reported range in corrected CO_2 effluxes was 0.23 to 2 μmol/m^2-s or 0.29 to 2.5 g-HC/m^2-day.

Static Trap: The results of CO_2 trap testing at a refinery with LNAPL contamination indicated CO_2 measurements could be resolved from background at 14 of 20 locations (McCoy *et al.*, 2014). The vadose zone soil consists of sandy alluvium (no depth to LNAPL source is provided). The measured mass loss rates in fall, considered likely concurrent with higher soil temperatures and consequently higher degradation rates, ranged from 2.18 to 21.2 μmol/m^2-s, or 2.7 to 26 g-HC/m^2-day based on decane, or 13,400 to 130,000 liters LNAPL per hectare per year (L/Ha-year). A set of field triplicates at one location indicated a coefficient of variation of 18% resulting from local spatial variations and issues with measurement accuracy. A weak correlation between mass loss rates and temperature was observed with higher rates at higher temperatures.

McCoy (2012) presents the results of testing at six sites (N = 75). The CO_2 efflux could not be resolved from background (0.8 to 9.0 μmol/m^2-s) in 28 of 75 samples. For samples where the flux was greater than background, the CO_2 efflux ranged from 3.3 to 36 μmol/m^2-s (mean = 9.5 μmol/m^2-s), which corresponds to 3.7 to 40 g-HC/m^2-day.

The LA LNAPL Workgroup in collaboration with Colorado State University have conducted pilot test studies for measurements of NSZD rates at two sites in the LA Basin, the Shell Carson and Tesoro Hynes facilities, using the static trap method with ^{14}C correction for natural soil respiration (Los Angeles LNAPL Workgroup, 2015). The study provides estimated NSZD rates that vary with measurement location from 415 to 4,000 gal/acre/year at the Shell Carson facility and from 120 to 2,660 gal/acre/year at the Tesoro Hynes facility.

Comparison of Dynamic Chamber and Static Traps: Gaito *et al.* (2015) report results of comparisons of dynamic chamber and static traps (N = 2 for each method) where the background corrected CO_2 efflux ranged between 0.25 and 1.5 μmol/m^2-s (about 0.3 to 1.9 g-HC/m^2-day). The difference between the two methods was up to a factor of 1.5. The variability in natural shallow respiration and rainfall were indicated to be important factors that affect measurement accuracy and variability. Dynamic chamber and static trap results are further compared and discussed in Section 3.2.5 below.

Summary

The CO_2 efflux method is an emerging second-tier method that should be considered as another line of evidence for natural attenuation studies. The method has shown significant promise for evaluation of natural depletion at LNAPL sites and does not require estimation of soil properties. The static trap has potential advantages with respect to simplicity of installation and time-integrated flux, and the dynamic chamber has potential advantages with respect to obtaining greater density of higher accuracy test results.

3.2.3 Temperature Method

Overview

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; by measuring the temperature gradient the biodegradation rate can be estimated. Appendix C describes the theoretical basis for this method.

Conceptual Model

Atmospheric temperature changes will affect subsurface soil temperature with the magnitude of the effect decreasing with increasing depth. Without a heat source in the soil column, the soil temperature varies but on average is approximately equal to the mean annual temperature of the atmosphere. If there is a subsurface heat source from aerobic biodegradation, a thermal gradient will develop, with the magnitude of the gradient dependent on the source heat flux and rate of heat transport away from the source due to thermal conductance through the soil. The source heat flux is dependent on the rate at which oxygen is consumed in the biodegradation of petroleum hydrocarbon (Sweeney *et al*., 2014).

Method

The temperatures may be estimated through the use of downhole temperature probes that are installed in wells screened within the unsaturated zone at multiple depths above a source. Temperature measurements should also be made in background wells in a similar hydrogeologic environment for comparison purposes. In addition, depending on the depth to the hydrocarbon-impacted soil zone, the influence of ambient temperatures and heating of near-surface soils may need to be taken into account when designing monitoring programs and interpreting data. When surface heating is potentially significant, longer-term seasonal monitoring and/or modelling of temperatures may be warranted.

Case Study

Sweeney *et al.* (2014) present data from one site where the temperature increase above residual LNAPL relative to background was approximately 2 to 2.5 ºC, and where the reported minimum oxygen flux was approximately 1.7 g/m^2-day. Based on the stoichiometry for hydrocarbon degradation, the mass loss rate is approximately 0.5 g/m^2-day.

Summary

The temperature monitoring technique is a relatively new method and holds promise as a relatively low cost method for estimation of hydrocarbon biodegradation rates and as a another line of evidence for natural attenuation studies. Disadvantages of this method include that it may be difficult to resolve the temperature gradient from aerobic biodegradation relative to background gradients from surface heating and the calculation requires an estimate of the soil thermal conductivity, an uncertain parameter. Data from additional sites are required to validate this method.

3.2.4 Biodegradation Rates from Numerical Modeling Studies

Numerical models have been used in several research studies to estimate hydrocarbon biodegradation rates and are useful for comparison of biodegradation rates to methods previously described (*e.g.*, Molins *et al.*, 2010, Sihota and Mayer, 2012, Hers *et al.*, 2014). Depending on the numerical model, processes such as non-equimolar diffusion and advection caused by biodegradation reactions can be incorporated, potentially resulting in more accurate estimates of biodegradation rates and mass loss compared to simpler models.

Hers *et al.* (2014) present results of simulations using the MIN3P-Dusty numerical model to assess vapour fate and transport above a gasoline LNAPL source in North Battleford, Saskatchewan. At this site, there were glacial till soils and the depth to LNAPL was approximately 3 m. Using the model calibrated to soil gas profile data, the predicted total hydrocarbon (HC) flux (mass loss rate) directly above the residual LNAPL source was 0.7 to 1.3 g-HC/m^2-day. Assuming a 1 m thick LNAPL smear zone and bulk density of 1,700 kg/m^3, the approximate average equivalent zero-order degradation rate is 0.6 mg HC/kg-soil-day.

Lahvis *et al.* (1999) present results of numerical model simulations to analyze vapour fate and transport in the unsaturated zone at a gasoline spill site in Beaufort, South Carolina. The depth to the source was approximately 3.3 m and soils consisted of relatively uniform silts and fine sands. Based on a calibrated model for diffusion, advection and aerobic biodegradation, the hydrocarbon mass loss near the water table above the source were highest for toluene (0.20 to 0.84 g/m^2-day), followed by xylenes (0.12 to 0.69 g/m^{2-}day). The estimated total petroleum hydrocarbon mass loss was 0.66 to 2.4 g-HC/m^2-day. Assuming a 1 m thick LNAPL smear zone and bulk density of 1,700 kg/m^3, the average approximate equivalent zero-order degradation rate is 0.9 mg-HC/kg-soil-day. These rates were reported to exceed predicted rates of solubilisation to groundwater, demonstrating the effectiveness of aerobic biodegradation and volatilization as a combined natural attenuation pathway.

Molins *et al.* (2010) present model simulations using the MIN3P-Dusty model of petroleum hydrocarbon fate and transport at the Bemidji site. In 1979, the rupture of an underground pipeline near Bemidji, Minnesota spilled 1,700 m^3 of crude oil over a 6,500 m^2 area of a glacial outwash aquifer (Essaid *et al.*, 1995). The depth to the water table and source is approximately 6 to 7 m. At this site, anaerobic biodegradation of oil and methane generation is a significant process. Based on calibration of MIN3P-Dusty model to measured data, the maximum methane flux from the smear zone is 0.13 mol-CH_4/m^2-day or 2.1 g-CH_4/m^2-day based on 1:1 stoichiometric relationship for carbon dioxide production from methane oxidation (Molins *et al.*, 2010). The methane was oxidized prior to reaching ground surface at the Bemidji site. Sihota and Mayer (2012) used stable carbon isotope testing to further assess processes occurring at Bemidji and found that the isotopic signature indicated that in aerobic degradation zones, the stable isotope δ^{13}C of CO_2 was more negative than in surrounding regions, consistent with oxidation of CH_4 and addition of light (^{12}C) isotope to CO_2.

3.2.5 Database of Petroleum Hydrocarbon Biodegradation Rates

A database of petroleum hydrocarbon mass loss rates through volatilization and biodegradation are compiled in Table 3-2. The hydrocarbon biodegradation (mass loss) rates are relatively consistent between studies and methods, excluding static trap results reported by McCoy (2012) and McCoy *et al.* (2014). The hydrocarbon biodegradation rates for the McCoy *et al.* studies range from 1.3 to 37 g-HC/m^2-day, but for other studies evaluated, the maximum rate for either static trap or dynamic chamber tests (maximum at a single site) was 8.9 g-HC/m^2-day. For the upper range of published static trap rates, complete depletion of hydrocarbon in short time-frames is predicted (few years to decades).

The reason for the higher biodegradation reported in the McCoy *et al.* studies is not known but may be associated with conditions conducive to biodegradation (*e.g.*, temperature, soil type or moisture). We note that there continue to be refinement in methods for static trap and dynamic chamber measurements. The installation of traps and chambers require excavation of soil, placement of the trap, and backfilling, which may affect natural diffusive gas migration patterns. In addition, static traps cover the ground surface and avoid wetting of the soil during precipitation events. Recently, static trap methods have been refined such that the trap is a lower height above ground and therefore less prone to wind effects, which were found to be significant. Further research is warranted including side-by-side comparison of static trap and dynamic chamber methods and comparison to model simulations. The effects of deployment method, precipitation, soil properties, temperature and natural respiration on results need to be better understood.

The results are summarized with respect to the range of average rates[5], and average (of the average rates)[6]:

- 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 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).
- 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 = 6 sites).

There are insufficient data to draw conclusions on the influence of depth to contamination or soil type, but conceptually, lower rates are expected for deeper contamination and wetter soils. Given the potential factors that can affect biodegradation, the consistency in results is considered good. 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 based on the above data is 1 to 3 g/m^2-day or 500 to 1,500 Gal/acre-year.

Table 3-2: Compilation of vadose zone biodegradation rates estimated from natural source zone depletion studies.

Site and Reference	Method	Contami-nant Type	Soil Type	Depth to Water Table or Contamination (m)	Biodegradation Mass Loss Rate (g-HC/m^2-d)	Biodegradation Mass Loss Rate (L/hectare-year)	Biodegradation Mass Loss Rate (US Gal/acre-year)
Former Refinery, Vancouver, BC (Golder, 2015)	CO_2 – Dynamic Chamber	Weathered middle distillate	Silty Sand & Silt	0.6 to 2.2 (highly variable)	**0.4 to 8.9** Average = **2.4** (37 locations)	**1,700** to **37,000** **Average = 10,100**	**180** to **4,000** **Average = 1,100**
Former Refinery, Vancouver, BC (Golder, 2015)	CO_2 – Static Trap	Weathered middle distillate	Silty Sand & Silt	0.6 to 2.2 (highly variable)	**0.1 to 5.2** Average = **1.9** (7 locations)	**420 to 22,000** **Average = 8,000**	**54** to **2,300** **Average = 870**
Traverse City, this report[7]	Gradient Method	Aviation Fuel	Sandy	5	**0.18** to **0.86** (2 locations)	**900** to **4,300**	**100** to **470**
Traverse City: Ostendorf and Kampbell (1991)	Numerical Model and Soil Gas Profile	Aviation Fuel	Sandy	5	**0.6** to **1.0** (4 locations)	**3,000** to **5,100**	**320** to **550**
Bemidji Site; Sihota *et al.* (2016)	CO_2 – Dynamic Chamber	Oil	Glacial outwash	6 to 7	**1.4** (average)	**6,000**	**660**
Bemidji Site; Sihota *et al.* (2011)	Numerical Model and Soil Gas Profile	Oil	Glacial outwash	6 to 7	**1.6 to 4.4**	**7,300** to **21,000**	**780** to **2,100**

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

[6] The results exclude the two McCoy *et al.* studies and deep data from Site 1 in McDonald et a. (2015) in Table 3-2

[7] Based on data in Ostendorf and Kampbell (1991)

Site and Reference	Method	Contami-nant Type	Soil Type	Depth to Water Table or Contamination (m)	Biodegradation Mass Loss Rate (g-HC/m^2-d)	Biodegradation Mass Loss Rate (L/hectare-year)	Biodegradation Mass Loss Rate (US Gal/acre-year)
Six Sites in Yukon and Alberta; Porter (2014)	CO_2 Efflux – Dynamic Chamber	Crude oil, waste oil, natural gas liquids and diesel	N/A	N/A	**0.24** to **4.3** (grass) **0.29** to **2.5** (gravel) (163 locations, 1,529 measurements)	**1,100** to **20,000** **(grass)** **1,300** to **11,000** (gravel)	**120** to **2,100** (grass) **140** to **1,200** (gravel)
Refinery US Site; McCoy *et al.* (2014)	CO_2 Efflux – Static Trap	Fuels	Sandy Alluvium	N/A	**2.7** to **26** (20 locations)	**12,000** to **120,000**	**1,300** to **13,000**
Six US Sites; McCoy *et al.* (2012)	CO_2 Efflux – Static Trap	Fuels	N/A	N/A	**1.3** to **37** (75 locations)	**6,100** to **170,000**	**660** to **18,000**
US Site Gaito *et al.* (2015)	CO_2 Efflux – Static Trap	N/A	N/A	~ 5	**0.53** to **1.9** (2 locations)	**2,400** to **8,500**	**260** to **910**
US Site Gaito *et al.* (2015)	CO_2 Efflux – Dynamic Chamber	N/A	N/A	~ 5	**0.31** to **1.8** (2 locations)	**1,400** to **8,400**	**150** to **900**
Victoria, Australia Site McDonald *et al.*(2015) – Site 1	CO_2 Efflux – Static Trap	Gasoline	Clay with Sand Lenses	Shallow (average of 2) Deep (~ 4)	Shallow = **1.8** Deep = **0.1**	Shallow = **7,800** Deep **= 430**	Shallow = **830** Deep **= 46**
Victoria, Australia Site McDonald *et al.*(2015) – Site 2	CO_2 Efflux – Static Trap	Gasoline	Bedrock	8 - 10	**0.38**	**1,600**	**171**
Sweeney *et al.* (2014)	Temperature	Gasoline	N/A	N/A	~ **0.5**	N/A	N/A
North Battleford, Saskatchewan; Hers *et al.* (2014)	Numerical Model and Soil Gas Profiles	Gasoline	Glacial Till	3.0	**0.7** to **1.3**	**3,500** to **6,400**	**370** to **700**
Beaufort, South Carolina; Lahvis *et al.* (1999)	Numerical Model and Soil Gas Profiles	Gasoline	Silts and Fine Sands	3.3	**0.66** to **2.36**	**330** to **12,000**	**350** to **1,200**
Shell Carson Facility, CA: LA LNAPL Workgroup (2015)	CO_2 Static Trap	Gasoline	Clay with sandy layers	Not reported	**0.92** to **8.9** **Average = 2.8** **(8 locations)**	**3,900** to **37,000** **Average = 16,000**	**415** to **4,000**
Tesoro Hynes Facility, CA: LA LNAPL Workgroup (2015)	CO_2 Static Trap	Gasoline	Sand to Silty Sand	Not reported	**0.27** to **5.9** **Average = 2.4** **(7 locations)**	**1,100** to **25,000** **Average = 16,000**	**120** to **2,660**
Galloway Township, New Jersey; Lahvis and Baehr (1996)	Numerical Model and Soil Gas Profiles	Gasoline	Sand / Silts	3.3	**1.1**	**5,400**	**570**

HC = Total petroleum hydrocarbon

3.3 Summary and Recommendations

Processes for natural depletion of the hydrocarbon source are described relative to the position of source zone: volatilization and biodegradation in the vadose zone for the exposed part of the source above the water table; and biodegradation and dissolution along the groundwater path for the submerged part of the source. Screening level models for estimation of source mass loss rate based on the above processes are described and data requirements for models and methods are summarized in Table 3-3.

Screening level (order of magnitude) estimates of the source depletion time can be made knowing the source petroleum hydrocarbon mass and distribution and mass loss rate. As a first-tier estimate, the O_2 gradient method is recommended as a relatively simple method for estimation of oxygen consumption rate and corresponding biodegradation losses of a hydrocarbon source above the water table. The method requires data that is often available or can be readily obtained, but requires detailed continuous distribution of total petroleum hydrocarbon within the source zone (in BC context, the sum of volatile and extractable petroleum hydrocarbons) and geotechnical data to estimate soil moisture and porosity. A limitation of the O_2 gradient method is that it is highly sensitive to soil moisture content in the vadose zone and near the water table. Literature values of the mass loss rate are also available from studies or sites summarized in this toolkit.

The CO_2 efflux method for estimation of the biodegradation rate should be considered when a second line of evidence for NSZD is warranted. The advantage of this method is that it only involves surface flux measurements and can be relatively cost effective, but further research on methods for measuring flux is warranted. At some sites, it is difficult to distinguish the biodegradation flux from natural respiration occurring in near surface soils. The temperature method holds promise for estimation of biodegradation rate but is considered in the research and development stage.

The above methods for estimation of mass loss do not include processes for hydrocarbon depletion below the water table (excluding the VZBL model, which provides option to account for the influence of methane under anaerobic conditions). Typically, when there is hydrocarbon contamination in the vadose zone, aerobic biodegradation is the most significant process for mass loss. However, methanogenesis may also be important, although additional research is needed on anaerobic biodegradation processes and measurement and modeling methods. While dissolution is typically a less important process, the Golder Nomograph model and/or the GSI Mass Flux Tool can be used to model groundwater dissolution where warranted. There are additional data requirements for dissolution estimates including hydrogeological data on groundwater flow (hydraulic conductivity and gradient) and a detailed transect of concentration data downgradient of the source (Table 3-3). For the ITRC control volume model, additional geochemical data on electron acceptors is required. While these data are typically obtained as part of a detailed site investigation for purposes of a NSZD assessment a greater sampling density (*e.g.*, multi-depth wells or geoprobe sampling) may be warranted.

Table 3-3: Recommended data for screening models of NSZD.

Purpose	Application	Data
Qualitative assessment of NSZD processes.	Justification for use of screening models based on NSZD processes.	Methane, oxygen and/or hydrocarbon vapour concentrations in soil gas to qualitatively assess biodegradation processes (not needed for oxygen gradient estimates). Groundwater concentrations of geochemical indicators of biodegradation up-gradient and down-gradient of the source.
Delineate source zones: in the vadose zone and the saturated zone.	Estimate total mass and volume of source – used in all models.	Hydrocarbon concentrations in soil including vertical profile data.
Estimate of water-filled and total porosities for effective diffusion coefficient calculations. Depth to the water table (average and standard deviation).	Oxygen Gradient Method (incorporated in VZBL model)	Vertical profiles in the vadose zone above source and the capillary fringe: • Soil properties (moisture, density, f_{oc}) • Electrical conductivity (optional) Depth to water table.
Estimate petroleum hydrocarbon biodegradation rate Account for background respiration of native organic matter.	CO_2 Surface Efflux Method	CO_2 efflux at ground surface and data to assess background respiration • ^{14}C of CO_2 • $\delta^{13}C$ of CO_2
Calculate oxygen consumption rate for estimating hydrocarbon loss rate through biodegradation.	Temperature Method	Vertical profiles of temperature and oxygen above source Soil thermal conductivity
Groundwater flow and mass flux (dissolution) calculations	GSI Mass Flux Toolkit	Groundwater flow direction Hydraulic conductivity Hydraulic gradient Vertical extent of groundwater plume Hydrocarbon constituent concentration in groundwater along transect perpendicular to flow

4.0 STEP 3: USE OF MULTI-PROCESS MODELS FOR EVALUATION OF NATURAL DEPLETION AND PLUME ATTENUATION

While site characterization data along with the screening models described in Section 3 can be used for order of magnitude estimates of source depletion times, a more comprehensive evaluation of the natural attenuation processes involving the entire source zone and the groundwater plume are best achieved through the use of multi-process models.

Three publicly available multi-process models, the REMFuel, BIOSCREEN and LNAST models, are reviewed and evaluated in this section through example applications and comparison to a three-dimensional reactive transport model, the MIN3P-Dusty model. These models can be used to help 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?

This section 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 Technical Guidance 22 by approximating plume lengths and source longevity. While REMFuel, BIOSCREEN and LNAST models are publicly available and relatively easy to use, MIN3P-Dusty is far more complex and is used here for comparison purposes.

The purpose and rationale of the model applications are primarily two-fold: 1) compare attributes of available models for prediction of groundwater plume lengths and source longevity, and 2) gain insight on estimated source depletion times for hypothetical small and large petroleum release scenarios for inputs representative of a BC-specific hydrogeological setting. A detailed example presenting comparison of multi-process modeling results to monitoring data is shown for one of the BC case studies in Appendix H. Through this work, guidance on selection of models and input parameters is provided. We also show how modeling could be used to evaluate the potential effect of enhanced remediation (EA) or source remediation on groundwater plume length and source depletion times. We are not aware of a similar published study of this type in the literature.

We note caution should be exercised when using models, which are generally not considered stand-alone tools because of the often significant uncertainty in estimation of LNAPL source zone mass and extent of dissolved plumes. Instead models are rather intended to support and guide monitoring efforts.

4.1 Background

4.1.1 Conceptual Site Model

The conceptual model of natural attenuation processes in the source zone have been presented in Toolkit #1 and described in detail in Section 3. The processes are generally divided into those affecting the submerged portion of the source in the saturated zone; and those affecting the exposed portion of the source in the vadose zone. All models evaluated in this section consider dissolution in the saturated zone and transport along the groundwater flow path. The source zone represents the boundary condition for contaminant concentrations in groundwater that undergo sorption and biodegradation reactions and are transported through advection and dispersion. Plume characteristics of stability, longevity, and extent are thus tied to source zone concentrations. In turn, reaction and transport processes in the groundwater plume as well as volatilization and biodegradation in the vadose zone determine source depletion times.

4.1.2 Examples of Similar Modeling Studies in Literature

There are limited published applications of multi-process models for evaluation of natural attenuation and source depletion.

Huntley and Becket (2002) describe use of the American Petroleum Institute (API) LNAST model to predict groundwater plume lengths and source zone depletion times for a variety of LNAPL spill conditions (see Toolkit #1). Hypothetical scenarios were considered for different soil types and remediation scenarios involving LNAPL removal and removal of the more volatile constituents (*e.g.*, through air sparging or SVE).

Vaezihir *et al.* (2012) describe application of a three-dimensional reactive transport model (BIONAPL/3D) to simulate evolution of a groundwater BTEX plume that was calibrated using data from a petroleum hydrocarbon LNAPL source at an oil refinery site. The model results in terms of predicted plume stabilization times and plume lengths were used to evaluate two remediation strategies. This model is not commercially available.

4.2 Description of Models

Available analytical and numerical models for the prediction of natural attenuation are described together with data needed for comparison or calibration purposes. Two models have been developed by US EPA: REMFuel, which may be used to simulate the transient effects of groundwater source and plume remediation for fuel hydrocarbons (and chlorinated solvents) and BIOSCREEN, which may be used to simulate hydrocarbon plume evolution subject to natural attenuation processes. A third model, the API LNAST model is also evaluated, which includes volatilization of the source. The numerical model reviewed, MIN3P-Dusty, is a three-dimensional model for coupled flow and reactive transport and is a highly useful model for simulation of source depletion and natural attenuation reactions.

4.2.1 REMFUEL Model

The US EPA REMFuel (2012) model includes a LNAPL source model and a dissolved hydrocarbon fate and transport model. The LNAPL source model includes dissolution and biodegradation. A key assumption is that the concentrations in the source zone will decrease in proportion to the mass of hydrocarbon remaining. The source mass to source discharge (analogous to a source decay term) and concentration relationship is based on a power function represented by a gamma term (Γ).

$$\frac{dM(t)}{dt} = \left(\frac{dC_s(t)}{dt}\right)^{\Gamma}, \qquad \text{Eq. 4-1}$$

where $M(t)$ is the time (t) varying source mass and $C_s(t)$ is the source concentration.

The simplest model of LNAPL source behavior is one in which $\Gamma = 0$ and source decay (λ) = 0, which leads to a constant source discharge (concentration) until the source is fully depleted. This is also known as a “step function” model, and the source mass declines at a constant rate with respect to time. When $\Gamma = 0$, the dissolution model is the same as for LNAST. When Γ is greater than zero, the source concentrations will decrease over time. When $\Gamma = 1$ the decrease in source concentration is proportional to decrease in mass.

The plume model is based on an advection-dispersion-biodegradation equation, where the biodegradation or decay term can be specified as a zero order, first order, or Monod kinetic formulation for each of the fuel constituents considered. A constant porewater velocity is assumed in the x- direction with longitudinal, transverse, and vertical dispersion.

REMFuel has the added feature of allowing the user to specify biodegradation rate parameters that vary over space and time. Different biodegradation parameters for each constituent can be specified for three spatial zones along the flow direction, as well as three time intervals for a total of nine spatio-temporal zones that can be used to simulate enhanced attenuation in distinct zones and time intervals. In addition, source removal can be simulated by indicating the fraction of mass removed over a specified time interval.

4.2.2 BIOSCREEN Model

The US EPA BIOSCREEN Natural Attenuation Decision Support System (Version 1.4, July 1997) is a screening model that simulates the formation and natural attenuation processes of a groundwater plume of dissolved hydrocarbons resulting from petroleum fuel releases. BIOSCREEN is an EXCEL spreadsheet model based on the analytical solution to the Domenico solute transport model. The processes included are advection, dispersion, linear adsorption, and biodegradation. The model provides two options for specifying biodegradation reactions:

1) First-order biodegradation of BTEX compounds, where the degradation rate constant accounts for aerobic and anaerobic biodegradation; and

2) Fast occurring (“instantaneous”) biodegradation reactions relative to the transport processes that are limited by the availability of terminal electron acceptors (TEA). The user inputs the TEAs consisting of oxygen, nitrate, and sulphate. For biodegradation through iron reduction and methanogenesis, it is the reaction by-products, dissolved ferrous iron and methane, respectively that are input by the user.

The version 1.3 User Manual provides examples and case studies for the selection of options depending on site conditions. There are two options for specifying the source discharge concentration: one is based on the assumption of an infinite source mass; and the other is based on an assumption of first-order (exponential) decay of the source mass with time. The latter option is equivalent to a Γ term equal to one as described in the previous section on REMFuel.

4.2.3 LNAST Model

The API LNAST model simulates the depletion of a LNAPL source zone coupled with the downgradient fate and transport of dissolved hydrocarbon constituents. Depletion of the LNAPL is estimated through a mass flux model consisting of three components:

1) Solubilisation of the LNAPL zone in laterally migrating groundwater according to Raoult's law and transport away from the source zone in migrating groundwater.
2) Diffusion vertically downward below the LNAPL zone and transport away from the source in migrating groundwater.
3) Volatilization of components and migration through the vadose zone.

Solubilisation is proportional to the mole fraction of components in the LNAPL assuming equilibrium conditions. This is a reasonable assumption when there is sufficient contact time between flowing groundwater and LNAPL. For each time step, the mole fractions of the components are updated based on a mass balance concept. The LNAPL profile can vary vertically and groundwater flow velocity in the model is adjusted based on the LNAPL saturation.

The volatilization flux is calculated using a diffusion model for hydrocarbon vapour transport between the source and ground surface, where the effective diffusion is calculated using the Millington Quirck (1961) relationship. Constant water-filled porosity and total porosity are assumed for the unsaturated soil zone. The diffusive flux is multiplied by the vapour diffusion efficiency (VDE) coefficient, a unitless factor between 0 and 1, when there are conditions where a lower flux is expected, for example, sites with wet soil layers or ground cover such as pavement or buildings (for paved ground cover the User Manual recommends a factor of 0.01). If there are layered soil deposits and site-specific measurements, the VDE parameter could be estimated (*i.e.*, VDE = D^{eff}_{site} / D^{eff}_{LNAST} where D^{eff}_{site} is the site effective diffusion coefficient divided by D^{eff}_{LNAST} calculated for uniform soil layer in LNAST model).

The longevity of the LNAPL source is predicted to be primarily controlled by the length of LNAPL zone parallel to the direction of groundwater flow and LNAPL saturation, although example simulations in the LNAST User's Manual suggest volatilization may be important under certain conditions (*e.g.*, coarse-grained soils).

The LNAST model also includes a module to incorporate site remediation measures that reduce mobile LNAPL such as a skimmer well, single/dual pump recovery and vacuum enhanced skimmer well (these features were not evaluated for this study).

4.2.4 MIN3P-Dusty Model

The MIN3P-Dusty model is a multicomponent reactive transport model coupled to an aqueous phase flow model that can be used to simulate contaminant attenuation processes in a variably saturated porous media (Mayer *et al.*, 2002; Molins and Mayer, 2007). The MIN3P-Dusty model allows for the simulation of geochemical reactions involving aqueous, gaseous and the solid phases and includes transport processes for the gas phase and the aqueous phase including gas advection and multicomponent gas diffusion.

LNAPL dissolution can be modeled as a fast reversible reaction between an immobile LNAPL in the source zone and the dissolved phase concentration to represent equilibrium conditions according to the specified solubility of each constituent. The aqueous and gas phases are in equilibrium according to Henry's law, thus allowing for volatilization and vapour transport through diffusion and advection in the vadose zone. Biodegradation reactions are assumed to occur in the aqueous phase with several options available for specifying the rate law and dependence on multiple components (*e.g.*, dependence on oxygen concentration).

Examples of its application to LNAPL attenuation include the modeling of a crude oil spill at Bemidji, MN (Molins *et al.*, 2010) and more recently a Golder research project for the Contaminated Sites Approved Professional (CSAP) Society in British Columbia, where the MIN3P-Dusty was used to evaluate iron and manganese fate and transport in groundwater from a petroleum hydrocarbon source where different scenarios for LNAPL source mass and depletion were considered (Golder, 2013).

4.2.5 BIONAPL/3D MODEL

BIONAPL/3D is a three-dimensional numerical model for simulating multi-component NAPL dissolution and biodegradation in a porous or discretely fractured porous aquifer (Molson and Frind, 2010). The model includes a transient, groundwater flow model coupled with an advective dispersive multi-component transport model that includes sorption and biodegradation according to a Monod kinetic model. The NAPL dissolution can either be simulated as an instantaneous process according to Raoult's Law or by a kinetic rate equation (Frind *et al*., 1999).

A challenge with the kinetic rate equation is that it is difficult to parameterize and typically instantaneous dissolution is assumed. The BIONAPL model does not include volatilization, which can be an important process as shown below. The BIONAPL model is not commercially available and is not further reviewed in this report.

4.2.6 Summary of Model Features: Source Zone Processes

The source zone processes included in each of the models are summarized in Table 4-1. The three models BIOSCREEN, LNAST, and REMFuel are based on the Domenico (1987) solution to solute transport and biodegradation in one-dimension for advection with dispersion in three-dimensions. These modelling platforms provide easy to setup problem formulations and results are calculated quickly and presented in the form of easy to interpret tables and graphs. The limitations and differences amongst these models pertain to processes included for natural attenuation of the source as well as in the assumptions regarding the uniformity in source zone and soil type.

Amongst these models, LNAST 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 (only MIN3P-Dusty also includes this process), but it can be difficult to accurately estimate the volatilization factor (VDE), and it is not based on oxygen consumption and biodegradation (gradient method in Section 3.2.1).

The REMFuel model includes user-friendly features for rapid evaluation of source removal/decay and biodegradation rates to represent enhanced groundwater plume remediation. The source decay is represented by the gamma term (Γ), which when greater than zero results in a time-dependent decrease in the source concentration that is linked to the remaining source mass. Conceptually, this may be appropriate to use for complex layered deposits where LNAPL is trapped in low flow zones resulting in non-equilibrium conditions for LNAPL dissolution in the latter stages of the natural depletion process. A drawback is that Γ is not necessarily physically based (*i.e.*, the rate of discharge out of the source can be different than the rate of mass depletion). In materials reviewed (five-part training course by Ron Falta and Chuck Newell), there appears to be little data to support selection of Γ. One study that is cited (Chen *et al.*, 2002) presents a bi-phasic partitioning model, although it is not apparent how this model relates to selection of Γ.

The US EPA's BIOSCREEN model provides for flexibility in prediction of groundwater transport and includes options of first-order decay or instantaneous biodegradation reactions that are limited by the availability (transport) of terminal electron acceptors. Source depletion is based on an exponentially decaying source concentration (equivalent to Γ = 1), which cannot be easily justified and that leads to overestimation of the source depletion times.

The MIN3P-Dusty provides a flexible platform for defining a process-based model that can accommodate heterogeneities in soil, volatilization and effects of source and plume remediation. A challenge of using MIN3P-Dusty is its complexity and limited user interface.

Table 4-1: Model source zone processes.

Model	Processes in LNAPL Source Zone			Vertical Diffusion from LNAPL	Volatilization from LNAPL
	Dissolution	Biodegradation	Source Mass-Discharge Term (Γ)		
BIOSCREEN	Yes	Yes	No	No	No
LNAST	Yes	No	No	Yes	Yes
REMFuel	Yes	Yes	Yes	No	No
MIN3P-Dusty	Yes	Yes	No	Yes	Yes

4.3 Modeling Study

Predictions of groundwater plume migration and source depletion are compared for multi-process models of varying complexity, consisting of three analytical models, the LNAST, BIOSCREEN and REMFuel models, and the MIN3P-Dusty numerical model. The primary purpose of the study is to compare models and understand how different factors affect the results; however, realistic input parameters were chosen for a petroleum hydrocarbon source and representative soil and hydrogeological conditions for a generic site near the Lower Fraser River (near Vancouver, BC) to facilitate appropriate conclusions on generally expected source depletion times.

All models consider the dissolution of an LNAPL source and transport of the dissolved plume through advection, dispersion, linear sorption, and decay through biodegradation. Hydrocarbon components biodegrade under aerobic and anaerobic conditions both in the saturated zone (all models) and unsaturated zone (MIN3P-Dusty only). Volatilization of hydrocarbons is assumed to occur at the top of the capillary fringe (MIN3P-Dusty and LNAST).

The outputs of the model results below are plume lengths at 5 years and 20 years. The plume lengths are based on a benzene drinking water standard of 5 µg/L. The time for source depletion is based on benzene concentration decreasing to below 5 µg/L.

4.3.1 Modeling Scenarios

The modeling scenarios are baseline scenarios for a hypothetical small and large gasoline release, and three special modeling cases to assess the effect of volatilization, partial source remediation and multicomponent fate and transport (Figure 4-1). The conceptual model is a LNAPL smear zone at the water table at 10% saturation (S_o = 10%, or 10% of soil pores are filled with LNAPL) based on reported residual saturation data for medium sand in Brost and Devaull (2000). The small-size source at the water table is 10 m wide, 10 m long (in direction of groundwater flow) and one metre thick and the large-size source is 50 m wide, 50 m long, and two metres thick.

For purposes of describing physical-chemical properties, the gasoline contamination is assumed to be solely comprised of benzene. This approximation is considered reasonable because dissolved plumes in groundwater at gasoline release sites are comprised primarily of aromatic hydrocarbons with similar properties to benzene. The hydrocarbon contamination is present in an otherwise pristine (oxic conditions) background soil.

The properties of Fraser River sand are selected as a representative soil type. For the MIN3P-Dusty model that also considers processes in the vadose zone, an approximately 3 m layer of silty sand is selected as overlying the Fraser River Sand. The input parameters for the source, hydrogeologic and geochemical conditions are summarized in Appendix G.

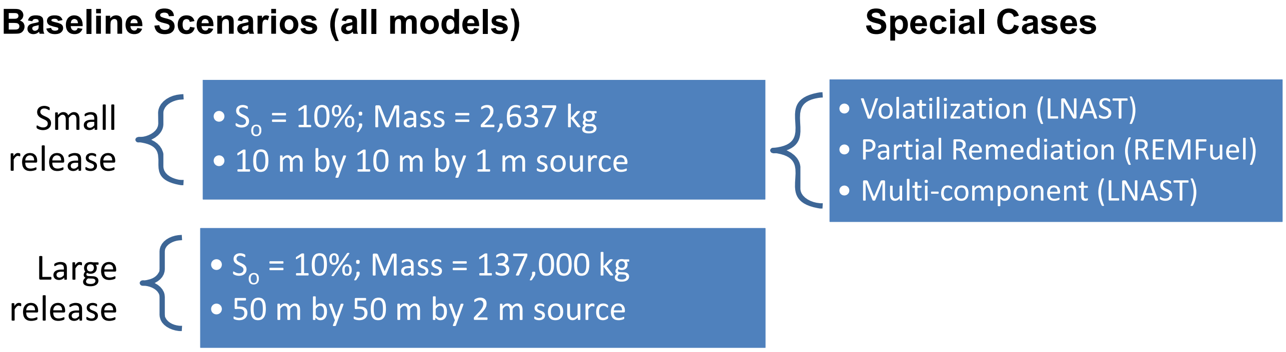

Figure 4-1: Baseline and special cases modelling scenarios.

4.3.2 Baseline Modeling Results

The results of the baseline modeling results for small and large sources are presented in Figure 4-2. The input parameters and results of the short-term (5 years) results are provided in Appendix G.

Plume Length

There is a reasonable agreement between the MIN3P-Dusty, LNAST and REMFuel models for the predicted plume length at 20 years, for which a length of approximately 400 m is predicted, with the exception of the BIOSCREEN result (lower by approximately a factor of two).

Based on the groundwater velocity of 51 m/year in these scenarios, the plume is expected to migrate 1,020 m in 20 years in the absence of biodegradation and sorption. The results highlight the significance of biodegradation in limiting the plume extents. Even though biodegradation reduces the plume length, the prediction of plume length is conservative because benzene is modelled as the sole constituent

Key Results

Large differences in plume lengths/ concentrations and source depletion times are predicted indicating models are highly sensitive to source depletion processes and input parameters (even though to the extent possible similar inputs were used). Predicted source depletion times are several hundred years (a high source concentration and only limited volatilization was considered).

of the LNAPL and the source concentration (100 mg/L) is much higher than typical benzene source concentrations. The statistical analyses of average plume lengths of benzene from multi-site studies involving petroleum hydrocarbon contamination indicate lower extents of plume migration (Toolkit #1). For example, the 90th percentile benzene plume lengths from three multi-site studies were 210 m at 36 sites in Texas (Rifai and Rixey, 2004), 100 m at 96 sites in California (Shih *et al.*, 2004) and 110 m at 34 US sites (Kamath *et al.*, 2012).

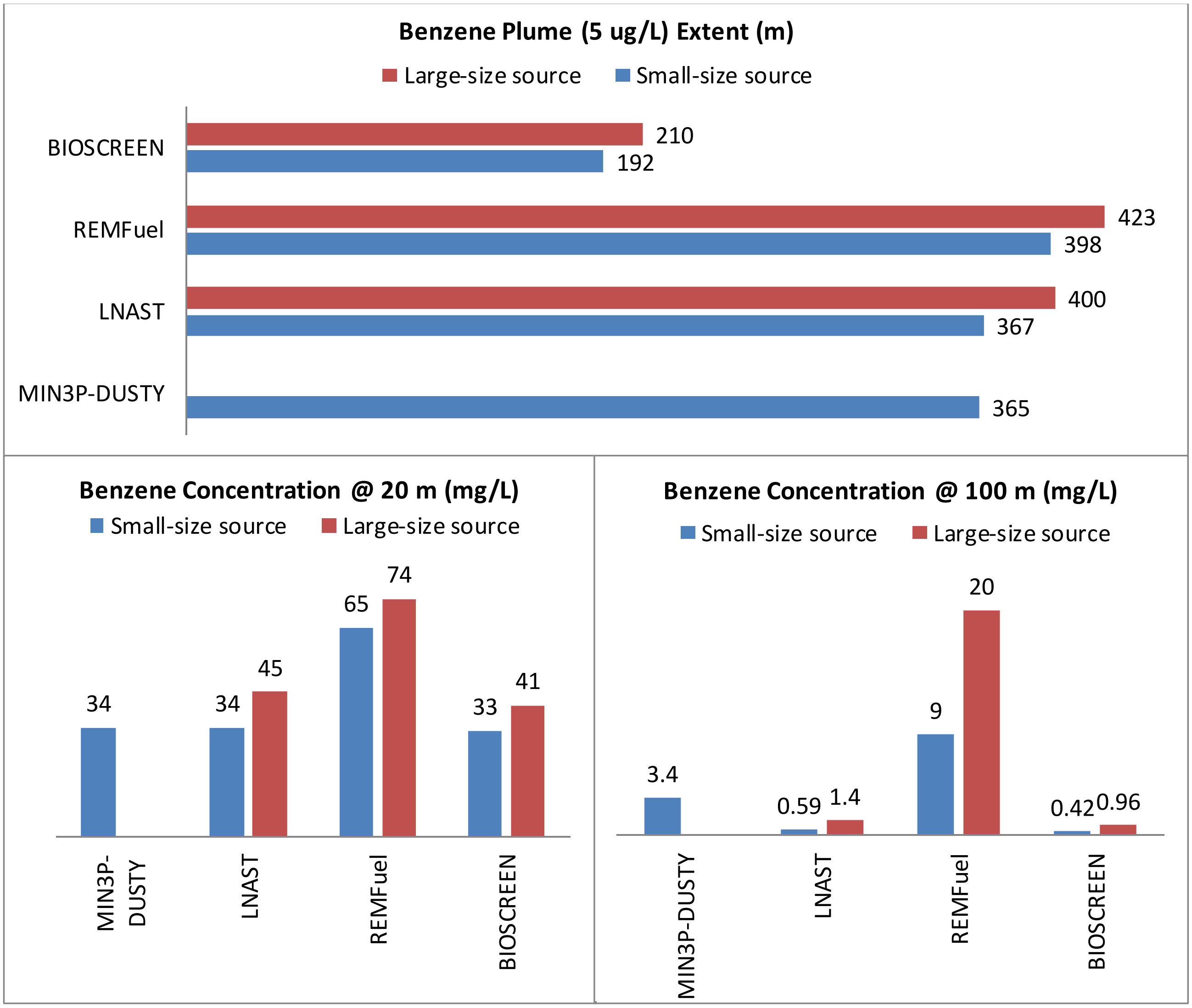

Figure 4-2: Predicted benzene plume extent and concentrations for baseline scenarios (MIN3P-Dusty was not run for large source scenario).

Concentration

There is relatively good agreement at short (20 m) distance between the models except for REMFuel, which predicts higher concentrations. This may be due to the scale-dependent longitudinal dispersivity that is used in REMFuel, in which the applied dispersivity value would be lower closer to the source. There is greater variability in the predicted concentrations at 100 m distance, although excluding REMFuel the concentrations predicted by the other three models are within a factor of eight.

Source Depletion Times

The estimated source depletion times for a small source range from 167 to 1,650 years depending on the model (Table 4-2). There is significant variability in the estimated source depletion times due to the differences in natural attenuation processes considered between the different models (see Table 4-1). For these simulations, the gamma term was zero for REMFuel model, and source decay rate was set to zero for the BIOSCREEN model (Appendix G). For the LNAST model, there is negligible mass loss through volatilization based on the VDE factor chosen (0.001).

Table 4-2: Estimated source depletion times in years.

Scenario	MIN3P-Dusty	LNAST	REMFuel*	BIOSCREEN*
Small-size	340	235	167	1,650
Large-size	NA	1200	830	8,300

*Assumptions and equations used in the derivation of the source depletion times for these models are described in Appendix G (Eq. G-3 and Eq. G-7).

Similar to LNAST, the source depletion time predicted by MIN3P-Dusty also depends on volatilization and biodegradation in the source zone. In this baseline simulation for a small-size source, the same biodegradation rate is assumed in the vadose zone as in the groundwater plume. However, the aerobic biodegradation rate in the vadose zone is expected to be faster and dependent on oxygen availability. This alternate scenario is considered in Appendix G.

4.3.3 Special Cases Model Results

4.3.3.1 Volatilization

The effect of the vapour diffusion efficiency (VDE) in LNAST is evaluated for values ranging from 0.01 to 1 (Table 4-3). For comparison to estimated biodegradation rates reported in Section 3.2.5, the scenario with VDE = 0.1 best approximates this condition (approximately 1.2 g/m^2-day). The source depletion time for a small source decreases from 235 years for a VDE of 0.001 (negligible volatilization loss) to 46 years for a VDE of 0.1.

Key Results

Volatilization is a potentially important process for mass loss and models that incorporate volatilization (LNAST or MIN3P) should be used when warranted. The LNAPL VDE parameter can be estimated from site-specific soil property data and from results of the O_2 Gradient Method.

Table 4-3: LNAST and vapour diffusion efficiency (VDE).

Scenario	Years	VDE = 1	VDE = 0.1	VDE = 0.04	VDE = 0.01
Vapour mass loss (kg/day)					
Small-size Source		1.2	0.12	0.048	0.012
Large-size Source		38	3.8	1.5	0.38
Source depletion time (years)					
Small-size Source		7.4	46	95	200
Large-size Source		11	95	200	590

The LNAST modelling results indicate that volatilization and vadose zone processes of diffusion and biodegradation have a large effect on the predicted source depletion times. Therefore, it is recommended to use models that account for this process, where the input data can be calibrated with field data. These estimates can also be used to support other statistical methods described in Section 2.

4.3.3.2 Partial Remediation

The effects of source removal and source decay in the REMFuel model are evaluated in terms of predicted source depletion times (Table 4-4). Two cases for source removal are considered, one where 30% of initial LNAPL mass is removed, which may be representative of a site where mobile LNAPL is removed, and a second where 80% of the mass is removed, which may be representative of LNAPL removed through a more aggressive treatment technology. Removal is assumed to take place over the initial five years. The gamma (Γ) term that relates total source mass (*M*) to dissolved phase source concentration (C_s) is varied from 0 to 1, the expected range for contaminant sources located in higher permeability soils (Falta, 2008). The source decay rate of 0.1/year selected here is based on calibration with data from an MTBE plume in Port Huememe, California provided in the REMFuel User's Manual.

Key Results

Source depletion times predicted with the REMFuel model are reduced almost proportionally to the percent mass removed with $\Gamma = 0$. With $\Gamma > 0$ concentrations slowly decrease over time but source depletion times are much longer. Even with aggressive remediation (80% removal) and source decay, it still takes 38 years for the small release to be depleted.

The source depletion times are greatly reduced from the baseline scenario (almost proportionally to the percent mass removed) with Γ and source decay rates equal to zero. Much greater source depletion times are estimated when the source concentration is assumed to decrease linearly with time ($\Gamma = 0.5$), or exponentially ($\Gamma = 1$). The source decay rate of 0.1/year, however, has a relatively minor effect on the depletion times. While the percent removal and source decay do not affect the predicted plume lengths, they do affect the time at which groundwater plumes become stable (Table 4-4). The predicted benzene concentrations at various times during and following source mass removal are shown in Figure 4-3 for scenario with Γ and source decay equal to zero. The predicted plume length continues to extend five years after partial source removal, and the dissolved phase concentrations rapidly drop following source depletion.

What Gamma Term to Use

Gamma is not based on a physical model but $\Gamma = 0$, where the source concentration is constant and in equilibrium with LNAPL, may best describe physical conditions for some sites. The REMFuel modeling study in Appendix H indicated a Γ of 0.5-1 provided a qualitative best fit to the observed trends in concentration for a large release site, however, the longevity of the LNAPL source and concentrations were significantly overpredicted. A possible reason for the difference in model results and data is that source zone biodegradation and volatilization may not have been fully accounted for. In addition, the measured "source" concentration may have been diluted due to placement of the monitoring well screen interval in relation to the LNAPL source zone, recognizing that the vertical dimension of the source is also likely to be changing with time. Practically, $\Gamma > 0$ may be needed to account for this effect. The study highlights the challenges in selection of gamma for the REMFuel model. Our preliminary recommendation is Γ of zero or close to zero for larger releases and $\Gamma > 0$ for smaller releases or where matrix diffusion or dilution is significant.

Table 4-4: Effect of natural source decay and remediation on source depletion times for the small source scenario (years).

Percent removal of source	Predicted Source Depletion Time (years)	Γ	Source Decay (per year)
0	167	0	0
30	122	0	0
	120	0	0.1
	285	0.5	0
	1,670	1	0
	1,640	1	0.1
80	39	0	0
	38	0	0.1
	160	0.5	0
	1,455	1	0
	1,430	1	0.1

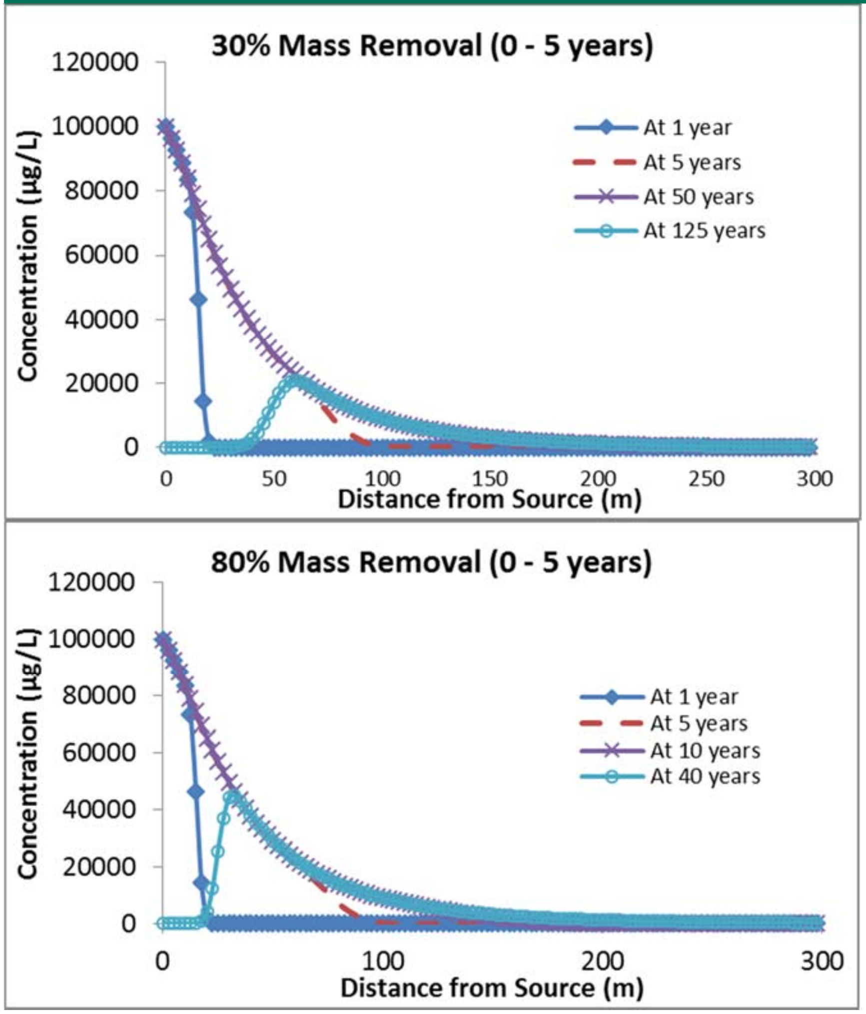

Figure 4-3: REMFuel predicted benzene concentrations versus distance from source for scenarios with source mass removal from 0 to 5 years.

The effect of remediation on plume lengths was evaluated by considering higher degradation rates by an order of magnitude for either the entire plume, or up to 50 m distance from the source (Table 4-5). Two remediation timeframes of 0 – 5 years and 5 – 10 years were considered. The REMFuel results suggest that maximum impact on plume length from plume remediation may be achieved when the plume has expanded, which in this example is at least 100 m from the source at five years for both the small and large size sources.

Table 4-5: Effect of plume remediation on predicted plume lengths at 20 years

Remediation Zone	Remediation Timeframe (years)	Predicted Plume Length (m)
Small-Size Source		
No remediation	NA	398
0 to 50 m from source	0 – 5	328
	5 – 10	398
Entire plume	0 – 5	328
	5 – 10	238
Large-Size Source		
No remediation	NA	423
0 to 50 m from source	0 – 5	345
	5 – 10	423
Entire plume	0 – 5	343
	5 – 10	248

4.3.3.3 Multiple Source Zone Contaminants

The baseline scenario was based on a LNAPL comprised of a single constituent, benzene for simplicity. In this section, the effect of a multi-component source is evaluated through simulations with LNAST. This feature is also available in MIN3P-Dusty and REMFuel, but not presented here. The components considered in LNAST are shown in Appendix G. All other input parameters were those specified for a small-size source. The plume characteristics and source depletion time of benzene for this scenario are compared with the baseline scenario representative of small-size source in Table 4-6. The initial benzene source concentration in this scenario is 32 mg/L.

Key Results

Source depletion times for benzene for multi-component mixture predicted with the LNAST model decrease from 235 to 90 years for a decrease in source benzene concentration from 100 mg/L to 32 mg/L but there is only a small change in the plume extent. The simulations demonstrate that it is important to account for effective solubility for prediction of source depletion.

Table 4-6: Comparison of benzene plume characteristics for single and multiple component gasoline source.

Time (years)	Single Component	Multiple Components
plume extent (m)		
5	114	112
20	367	331
concentration at 20 m distance from the source (mg/L)		
5	34	9.4
20	34	2.7
concentration at 100 m distance from the source (mg/L)		
5	0.28	0.07
20	0.59	0.07
Vapour mass loss (kg/day):	1.2×10^{-3}	2.1×10^{-5}
Source depletion time (years):	235	90

The plume lengths predicted at 5 years and 20 years are similar for the single and multiple component simulations. However, much shorter source depletion times are predicted when benzene corresponds to a small fraction of the LNAPL mass and where the effective benzene solubility is lower than assumed in the baseline scenario. The faster source depletion also yields lower predicted concentrations at 20 m and 100 m distance from the source at 5 years and 20 years. The downgradient extent of the benzene plume reaches a maximum and begins to drop at 24 years indicating a shrinking benzene plume, and the source zone concentration begins to decline at 0.6 years for the scenario with multiple LNAPL components.

4.3.4 Summary and Conclusions

The multi-process models reviewed have strengths and limitations, summarized as follows:

- 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 O_2 gradient method calculations. Source remediation during the project life-cycle cannot be simulated.
- 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, 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. As gamma increases, the REMFuel model predicts increased plume longevity and tailing and potentially long source depletion times.
- BIOSCREEN model: Simulates biodegradation reactions for dissolved hydrocarbon fate and transport, but is not recommended for evaluation of source depletion times.

The data requirements for models are provided in Table 4-7. Most basic data listed are readily available from detailed site investigation, except parameters such as dispersivity and first-order decay constant. In this regards, the BIOSCREEN and REMFuel User's Manual provide useful guidance and recommended parameter ranges. Typically, there is significant uncertainty in the LNAPL source mass and extent. The approach and methods presented in Step 2 of this Toolkit can reduce this uncertainty, but practically, estimates of mass and source depletion will be order of magnitude predictions.

While the model comparisons for multi-process models are order of magnitude predictions and are specific to the input parameters chosen, they provide valuable insight on source and plume longevity. When compared to a benzene drinking water standard of 5 μg/L, for a smaller gasoline (benzene) release (approximately 2,700 kg), the REMFuel model with 30% source reduction (*e.g.*, a hypothetical scenario for removal of most mobile LNAPL) predicts attenuation within about 122 years (gamma equal to zero), while for 80% source reduction (a scenario for aggressive LNAPL remediation), predicts attenuation within about 38 years. The LNAST model predicted attenuation within about 46 years when a relatively high volatilization efficiency of 0.1 was assumed and much longer time frames when lower volatilization rates were assumed.

We conclude from the modeling simulations that timelines for natural and enhanced depletion of source and reduction in benzene concentrations to less than 5 μg/L will be decades to hundreds of years for many typical sites. The results are limited to the specific scenarios and input parameters considered for the model simulations, and additional research on model validation through field data is recommended. While not specifically considered in the modeling, source depletion timelines could be shorter for sites with very high volatilization rates (*e.g.*, gravel deposits), fast flowing groundwater systems, and small releases (few hundred litres or kilograms). We note that the size of impact of such sites is also smaller and could be readily addressed through low-threat closure approaches described in Toolkit #1.

Table 4-7: Recommended model use and data requirements for NSZD estimates.

Model	**When to use**	**Overview of Key Data requirements**	
		Basic	**Additional, Specific to Model**
LNAST	When volatilization is potentially important	Hydraulic conductivity Hydraulic gradient Porosity (total or effective) Dispersivity Fraction organic carbon LNAPL source properties (dimensions, saturation or concentration *i.e.* mass) First-order decay rate dissolved plume Physical-chemical properties	Vapour Diffusion Efficiency (VDE) factor – obtain from site-specific soil (geotechnical) tests or calibrate from gradient method results LNAPL properties – lab tests Soil capillary properties – estimate from soil type or lab tests
REMFuel	For evaluation of remediation effectiveness (source removal/source decay or variable biodegradation rates)		Gamma term – recommend Γ=0 for short estimate source depletion, Γ>0 if layered deposits or where matrix diffusion could be significant
BIOSCREEN	For groundwater fate and transport predictions, not recommended for source depletion estimates		Electron acceptor and metabolic product concentrations – site data
MIN3P-Dusty	When volatilization and biodegradation in vadose zone is important, for sites with complex geology, variable conditions		Soil capillary properties – estimate from soil type or lab tests Vadose zone biodegradation rates – literature values

5.0 CONCLUSIONS AND RECOMMENDATIONS

This toolkit describes measurement and modeling 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 for the prediction of groundwater plumes. Where longer-term monitoring data exists, concentration trends may be evaluated using statistical tools developed for this project to estimate timeframes for concentrations to attenuate to below defined thresholds. The estimation of timelines should be supported by an appropriate well network and the conceptual site model should be well understood.

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 methods described below. Two screening computer models for NSZD have been developed, the CV-NSZD model based on the control volume concept (in-progress), and the VZBL model. A significant challenge is the limited detailed validation studies of measurement methods and models for estimation of NSZD. Biodegradation is shown to be a potential significant process for NSZD; however, predictions are sensitive to soil properties for the gradient method, and intra-method comparability is somewhat poor for the CO_2 efflux method.

Three different methods are evaluated for estimation of NSZD through biodegradation consisting of the O_2 gradient method, surface CO_2 efflux measurement method, and the temperature gradient method. Because of the sensitivity in the gradient method to soil properties, detailed site-specific data will typically be warranted. The CO_2 efflux method holds significant promise but further method validation is required on the background correction for natural soil respiration. The use of the CO_2 efflux method is encouraged and with appropriate design can be a useful added line of evidence. In particular, gradient method calculations can be used to estimate CO_2 efflux, which can be compared to direct measurements using chamber methods.

In summary, 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 volatilization and biodegradation losses. The available modeling tools can be helpful in decision-making at sites with petroleum hydrocarbon contamination if appropriately used and where site-specific data is available. An advantage of using multi-process models is in assessing relative scenarios and as an additional line of evidence when best estimates of input parameters are used for the prediction of plume lengths and source depletion times. 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.

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7.0 USEFUL LINKS

Table 7-1: Links to available tools mentioned in the Toolkit.

Tool Name	Description	Link
BioCapacity.xlsx	Calculation of assimilative biodegradation capacity in groundwater system	In-progress
BIOSCREEN	Natural Attenuation Decision Support System	https://www.epa.gov/water-research/bioscreen-natural-attenuation-decision-support-system
CV-NSZD	Control Volume Based NSZD Tool	In-progress
GWSDAT	Visualisation and interpretation of groundwater monitoring data.	http://www.api.org/oil-and-natural-gas/environment/clean-water/ground-water/gwsdat
LDRM	LNAPL Distribution and Recovery Model	http://www.api.org/oil-and-natural-gas/environment/clean-water/ground-water/lnapl/ldrm
LNAST	API Interactive LNAPL Guide	http://www.api.org/oil-and-natural-gas/environment/clean-water/ground-water/lnapl/interactive-guide
MAROS	Monitoring and Remediation Optimization System	http://www.gsi-net.com/en/software/free-software/monitoring-and-remediation-optimization-systems-maros-version-3-0.html
Mass Flux Toolkit	Mass flux calculations from transect groundwater data	http://www.gsi-net.com/en/software/free-software/mass-flux-toolkit.html
NSZD Nomograph	Depletion time estimates from NSZD processes	In-progress
OWL	Optimal Well Locator	https://www.epa.gov/water-research/optimal-well-locator-owl
ProUCL	Statistical Software for Environmental Applications	https://www.epa.gov/land-research/proucl-software
RegressionMNA.xlsx	Regression Analysis Tool	In-progress
REMFuel	Remediation Evaluation Model for Fuel hydrocarbons	https://www.epa.gov/water-research/remediation-evaluation-model-fuel-hydrocarbons-remfuel
VZBL	Vadose Zone Biodegradation Loss Model	In-progress

APPENDIX A

Regression Analysis Tool for the Prediction of Attenuation Timelines

Regression Analysis Tool for the Prediction of Attenuation Timelines

A case study is presented in this appendix where an EXCEL spreadsheet regression analysis tool developed by Dr. John Wilson (RegressionMNA.xlsx) is used to assess MTBE attenuation (note this technique could be used for any hydrocarbon compound that is attenuating). The case study presenting this approach is for a site contaminated with gasoline in Port Hueneme, California. Figure A-1 presents data from a spill of automobile gasoline at the gasoline filling station of the Navy Exchange at the Naval Construction Battalion Center at this site. Approximately 11,000 gallons of automobile gasoline containing MTBE was lost from an underground storage tank and the associated piping. The release occurred between September 1984 and March 1985. Within a few months of time, free product extended over an area approximately 500 feet long and 300 feet wide. Well CBC-10 in Figure A-1 was the most contaminated well. Well CBC-25 was screened further down gradient and was out of the area that exhibited free product. Panel B of Figure A-1 is redrafted from Figure 3-26 of Wilson (2003).

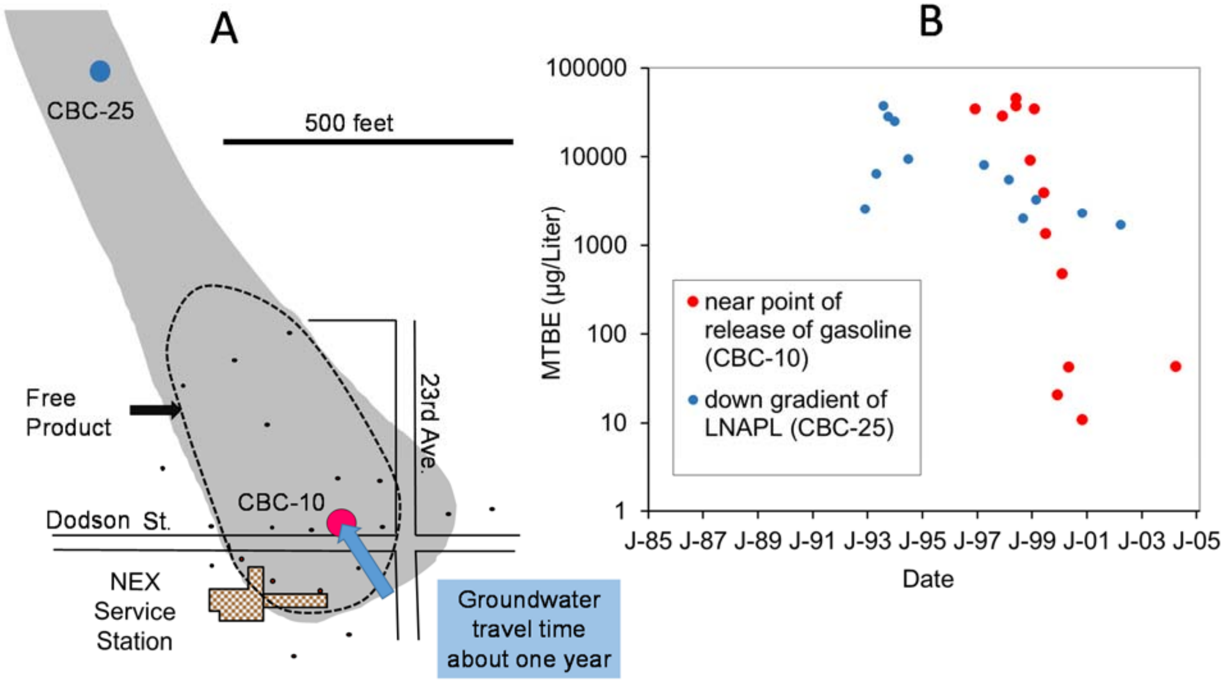

Figure A-1: Comparison of the natural attenuation of MTBE in a well screened in LNAPL at the source of plume, to a well down gradient of the LNAPL source area. Plume of automobile gasoline released at Port Hueneme, Naval Base Ventura County, California, USA.

The concentration of MTBE in well CBC-25 increased overtime to a maximum, and then declined at a steady rate. The natural attenuation of MTBE in well CBC-10 behaved very differently. The concentrations of MTBE stayed near the maximum for an additional six or seven years, and then the concentrations decreased one thousand fold in only three years, and then were steady for an additional four years.

If natural attenuation follows a first order rate law over time, a plot of the logarithm of concentration on time will be a straight line. Starting at the time when the maximum concentration was reached, the trend in the logarithm of concentrations in well CBC-25 was a straight line (Figure A-2). It would be appropriate to apply the US EPA guidance (Wilson, 2011) to the data from well CBC-25. The data from well CBC-25 may have fit a first order rate law because the well was a sufficient distance down-gradient of the source. Flow paths to well CBC-25 include flow lines from the margin of the LNAPL area where the LNAPL is thin and is weathering rapidly, and flow lines from the center of the LNAPL area where the LNAPL is thicker and the weathering is slower.

Figure A-2 organizes the data in Figure A-1 as is discussed in Section 2.1 of Wilson (2011). The natural logarithm of the concentration of MTBE is plotted on the date of sampling expressed in decimal years. The chart was created in Excel 2013®. A trendline was fit to the data and the equation of the line is presented on the chart.

$$y = -0.3466x + 701.03$$

The natural logarithm of 5 is 1.609. Substituting 1.608 for y and solving for x, the concentration of MTBE could be expected to reach the standard in the year 2018.

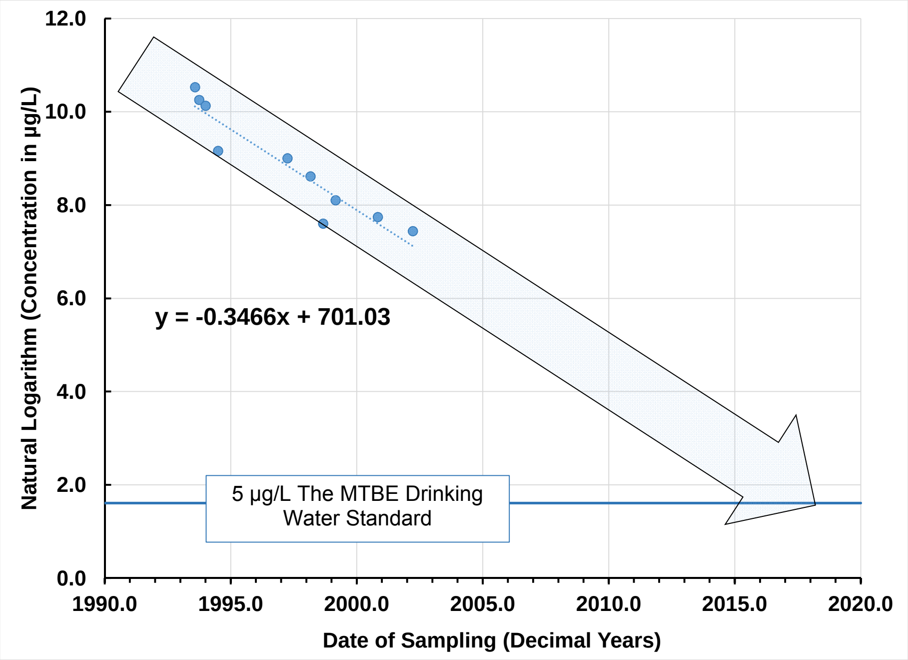

Figure A-2: Extrapolation of the trend in concentrations of MTBE in well CBC-25 to estimate the time required to attain the drinking water standard.

The data are scattered around the trend line, and there is uncertainty in the estimate. Wilson (2011) provided as an approach to evaluate that uncertainty. The approach is illustrated in Figure A-3.

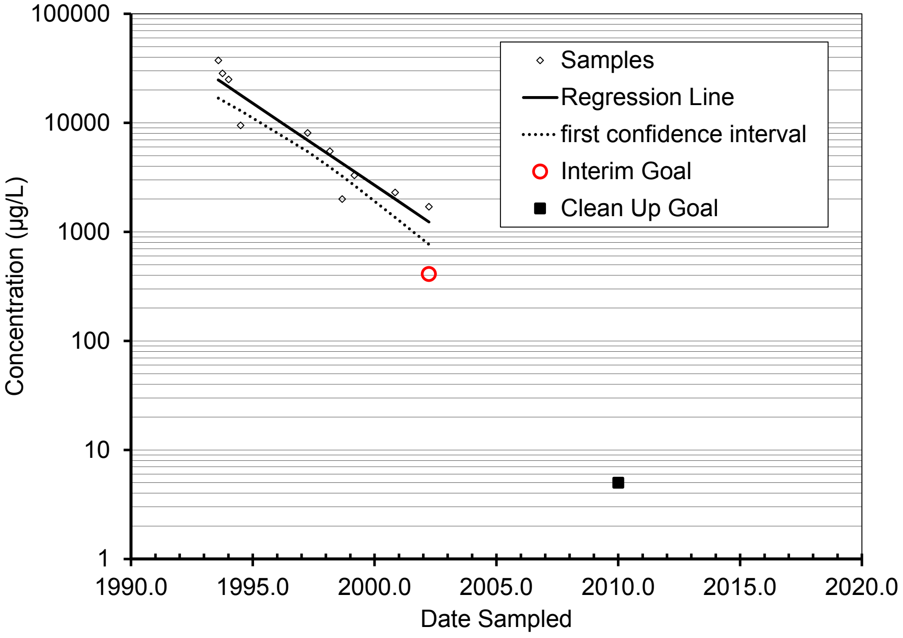

Figure A-3: Evaluating the uncertainty in the extrapolation of the trend in concentrations of MTBE in well CBC-25.

Wilson (2011) provides an Excel spreadsheet titled ***RegressionMNA.xlsx*** that supports the evaluation. The user provides (1) the monitoring data, (2) the clean-up goal, (3) the date by which the goal is to be attained, and (4) the date at which the rate of attenuation will be evaluated to see if there is evidence that attenuation is not adequate to attain the goal at the specified time. For purposes of illustration in Figure A-3, the date to evaluate the data was set at the date that the last data were obtained, and the clean-up goal of 5 µg/L was to be attained by 2010.

RegressionMNA.xlsx uses a first order rate law to calculate an interim goal. If the trendline is below the interim goal, concentrations in the past have attenuated more rapidly than is necessary to meet the concentration based goal at the specified time. If the trendline is above the interim goal, then the rate of attenuation is not adequate to reach the concentration goal by the specified time. ***RegressionMNA.xlsx*** also calculates a confidence interval on the line. The level of confidence can be set by the user. In Figure A-3, α was set to 0.05, corresponding to 95% confidence. If the confidence interval is above the interim goal, then the rate of attenuation is not adequate to reach the concentration goal by the specified time at the selected level of confidence. In this example, analysis with ***RegressionMNA.xlsx*** indicates that that the rate of natural attenuation of MTBE in well CBC-25 is not adequate to meet a clean-up goal of 5 µg/L by 2010, and we can assert that conclusion with 95% confidence.

As described in Wilson (2011), the process carried out in Figure A-2 can easily be carried out for every monitoring well at a site. The wells that will require the longest to attain the clean-up goal are the wells that will most likely delay or prevent closure at the site. In some of the wells, the concentrations may increase over time. These wells identify the areas of the aquifer that are the best candidates for focused active remediation.

In Figure A-3, the trend in concentrations of MTBE at well CBC-25 provided evidence at 95% confidence that concentrations would not reach the standards before the year 2010. The U.S. Navy went through a similar process for data analysis and decided not to wait on natural attenuation. In 2000 they installed an aerobic biobarrier to treat MTBE contamination in the aquifer (Johnson et al., 2003; Lesser et al., 2008).

The power of the approach illustrated in Figure A-3 depends on the number of data points. If the interim goal is far above the regression line, and the decision for a particular well is particularly clear with the current level of monitoring, it should be possible to cut back on the frequency for monitoring that well, although it is advised to continue monitoring at a reduced frequency. If the interim goal is near the confidence interval on the line, the decision for that particular well could change during subsequent monitoring. It would not be wise to cut back on the frequency of monitoring for that well. If the interim goal is between the regression line and the confidence interval, it may be worthwhile to increase the frequency of monitoring and better understand the distribution of the regression line. More monitoring point will draw the confidence interval on the regression line closer to the line.

Well CBC-10 was in the most contaminated portion of the LNAPL release (Figure A-1). In contrast to well CBC-25, the concentrations of MTBE in well CBC-10 were stable over time in the first part of the monitoring record. As the groundwater moved through the region with LNAPL, the concentrations of MTBE in groundwater came to equilibrium with MTBE in un-weathered NAPL gasoline in the portion of the aquifer that was up-gradient of the well (Figure A-1). Starting approximately fifteen years after the release, and extending forward in time, the gasoline up-gradient of well CBC-10 had much less effect on the concentrations of MTBE. It appeared as if a weathering front had started at the leading edge of the LNAL, and moved with groundwater flow into the region with LNAPL. Over time the front moved further and further into the region with LNAPL and after fifteen years the front moved past well CBC-10. A useful forecast of the type of behavior that was exhibited by well CBC-10 can be developed using the conceptual model discussed in Section 3.1.

In the year 2000, the weathering front was well past the location of well CBC-10. Figure A-4 presents the relationship between the vertical extent of TPH and MTBE in core material at the location of well CBC-10 in the year 2000 and the vertical extent of hydraulic conductivity. Concentrations of TPH and MTBE were determined on continuous core samples. Sub-cores were extracted and analyzed every four inches. Hydraulic conductivity was determined by preforming a miniature pumping test using push tools. The vertical interval of the screened section in the push tool was 18 inches.

The conductive portion of the aquifer extended from 130 to 280 inches below the land surface. High concentrations of TPH remained in the interval between 100 and 140 inches. The TPH in the upper portion of the aquifer that was less conductive had as much as 1% MTBE. The TPH lower in the aquifer that was in contact with more conductive aquifer material was depleted of MTBE. Apparently the MTBE that was originally present in the gasoline in the more conductive aquifer material had dissolved in the groundwater and washed away.

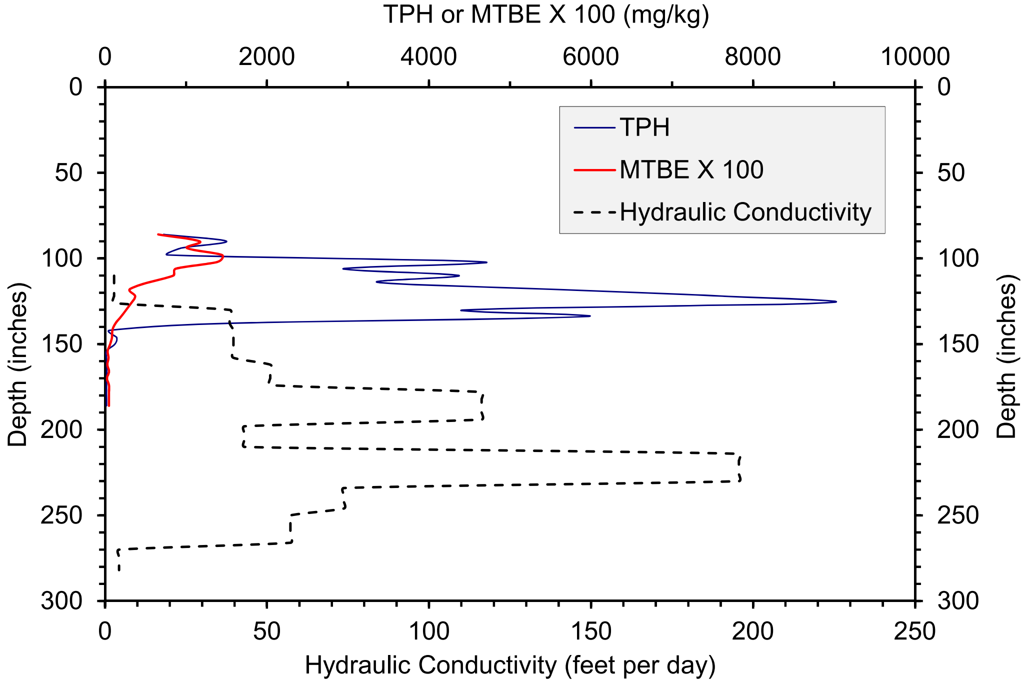

Figure A-4: Vertical distribution of MTBE in the TPH at well CBC-10 after the weathering front had passed.

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APPENDIX B

Gradient Method Theoretical Considerations

Gradient Method Theoretical Considerations

This appendix discusses theoretical considerations relating to the gradient method including approaches for non-linear oxygen profiles.

Linear Oxygen Depth Profiles

The simplest model is where there is rapid aerobic biodegradation near to the hydrocarbon source and a linear vertical profile of oxygen concentrations from surface to the biodegradation zone. From a linear oxygen profile, constant soil properties can be inferred, and the oxygen consumption rate may be estimated from Fick's first law equation for diffusion of oxygen and spatially averaged soil properties. The model assumes oxygen consumption occurs at the depth where the oxygen concentration is zero (or a low concentration that does not further decrease) (Ritchie, 1977; Patterson et al., 1999; Davis et al., 2005). The model can further include source depletion by assuming that the biodegradation zone moves progressively downward in soil as petroleum hydrocarbon vapours and oxygen are consumed by microbes and where a sufficient source of hydrocarbon is assumed. The oxygen consumption rate (O_r, kg/m^2-day) may be estimated by fitting the following equation to field data:

$$O_r = D_{eff}\frac{(C_0 - C_{o2}(d))}{d} \qquad \text{Eq. B-1}$$

Where *d* is the depth below ground surface (m) where the oxygen concentration $C_{o2}(d)$ is zero (or low), C_0 is the oxygen concentration at ground surface (kg-O_2/m^3-vapour) and O_r is the oxygen consumption rate (kg-O_2/m^2 day^{-1}) and D_{eff} is the effective diffusion coefficient (m^2/day). For a linear profile, the oxygen consumption rate represents a rate to the reaction front over the soil column from source to ground surface. The equation assumes the biodegradation reaction occurs fast relative to oxygen transport. The effective diffusion coefficient may be estimated from the Millington-Quirk (1961) equation.

The hydrocarbon degradation rate (R_{vapour}, kg/day) is obtained by multiplying the oxygen consumption rate by the stoichiometric coefficient for kg of hydrocarbon degraded per kg of oxygen consumed (S_{o2}) and multiplying by the cross-sectional area (width,W x length,L of the source) over which the reaction occurs:

$$R_{vapour} = WLS_{o2}O_r. \qquad \text{Eq. B-2}$$

A limitation of this model is that the effective diffusion coefficient is highly sensitive to the water-filled porosity. An average water-filled porosity, estimated from moisture content profile data, will overestimate the effective diffusion coefficient, potentially by orders of magnitude when there are thin fine-grained soil units that are close to saturation. This model also does not consider the potential for localized higher moisture content within and near to the source zone because of water generated during biodegradation and formation of biomass (Hers et al., 2000). The models described below are better able to handle variability within the unsaturated soil zone.

Non-Linear Oxygen Profiles and Non-Constant Soil Properties

For most sites, the oxygen profile is non-linear and soil properties, most importantly soil moisture, are not constant. There are two ways in which screening models can be improved.

The first approach is where an equation is fit to a non-uniform oxygen profile to obtain the oxygen consumption rate as described by Davis *et al.* (2005). The model assumes a steady-state oxygen distribution profile and a constant effective diffusion coefficient, a constant atmospheric oxygen concentration at ground surface and zero oxygen concentration at depth. The equation for the oxygen concentration as a function of depth is:

$$C(z) = C_0 - (C_0 A L^2)\frac{z}{L} + Az^2 \qquad \text{Eq. B-3}$$

where $C(z)$ is the oxygen concentration (atm) at depth z, L is the distance from ground surface to the source, A = $O_r / 2D_{o2}$, D_{o2} is the effective oxygen and where other terms are previously defined. The equation can be solved through curve-fitting or matched to a single oxygen concentration at the depth z_0, where the oxygen concentration drops to half of the atmospheric concentration ($C(Z_o) = C_o/2$), as follows:

$$O_r = \frac{2D_{o2}C_0}{z_0 L}\frac{(0.5 - z_0/L)}{(1 - z_0/L)} \qquad \text{Eq. B-4}$$

The second approach involves either estimation of an overall effective diffusion coefficient for the vadose zone profile or use of a numerical model as described below. The overall effective diffusion coefficient for oxygen may also be estimated using the equation below.

$$\frac{D_{O2}^{r}}{d} = \left[\sum_{i=1}^{n}\frac{d_i}{D_{o2,i}}\right]^{-1}; d = \sum_{i=1}^{n} d_i, \qquad \text{Eq. B-5}$$

where n is the number of soil layers of thickness d_i, and D_{O2}^{r} is the overall effective diffusion coefficient at depth, d.

Hinlein and Kelly (1999) described a similar model to the above for curve-fitting an oxygen profile for non-constant air-filled porosity and thus diffusion coefficient.

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APPENDIX C

Second Tier Methods

1.0 REVIEW OF METHODS FOR CARBON DIOXIDE EFFLUX MEASUREMENTS

Dynamic Chamber

The dynamic closed chamber method involves measuring the increase in CO_2 concentrations using an infra-red CO_2 gas analyzer coupled to a closed chamber placed on ground surface (Hanson et al. 2000; Jassal et al. 2012). (Figure C-1). The increase in the CO_2 concentration within the chamber headspace is typically recorded over a time period of one to two minutes to avoid feedback mechanisms due to concentration build-up in the chamber. When the water vapour mole fraction, initial air temperature, initial pressure inside the chamber and the total system volume are measured, changes in gas composition within the chamber headspace can be equated to a gas flux (Jassal et al. 2012). The LiCor systems LI-8100A (or similar) is often used for automated CO_2 measurements, and is an off-the shelf unit with an extensive track record of use. The advantage of this method is that it has been rigorously tested and documented in peer-reviewed literature and that multiple measurements (either repeat measurements or at different locations) per day can be readily made. The sampling strategy could include a single or a few tests at many locations, or repeat testing over days to weeks at select locations.

Figure C-1. LiCor System Flux Chamber and Infrared Gas Detector.

The dynamic chamber method is relatively straightforward and multiple measurements (up to 100 measurements per day, assuming soil collars are set) can be made per day. If ^{14}C analysis is required, a separate static ^{14}C chamber is recommended[1]. The dynamic chamber method also enables analysis of CH_4 concentrations or effluxes, if interfaced with a greenhouse gas analyzer (e.g laser-based field portable instruments from Picarro or LGR). This technique has been successfully used on carbon capture and storage (CCS) monitoring projects.

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[1] For ^{14}C analysis, there are few commercial laboratories that provide these capabilities.

Static Trap

The static trap method consists of small chamber inserted into soil with bottom and top sorbent media (sodalime) traps to measure soil and atmospheric CO_2, respectively (Zimbron *et al*., 2013) (Figure C-2). The CO_2 is estimated from total carbonate analysis of the sorbent material. The static trap is typically left in-place for 2-4 weeks. Quality control samples include a trip blank to correct for CO_2 originally present in the media and sorption of CO_2 at times other than trap deployment. Potential advantages of CO_2 traps include simplicity of use and time-composite sample, which averages short-term temporal variability that may exist due to barometric pressure or diurnal (temperature) changes.

CO_2 fluxes are calculated by dividing the field sorbed CO_2 mass by the cross-sectional area of the trap and the period that the trap was deployed. Following the method described in Johnson *et al.* (2006), CO_2 fluxes are converted to equivalent volumetric fluxes of LNAPL (L/Ha/year) using a reference hydrocarbon as an analog for all constituents in the LNAPL. For references reviewed, the reference hydrocarbon was decane for a refinery site, where 10 mol of CO_2 per mole of decane is degraded, the decane density is 0.73 g/mL and 1 $\mu mol/m^2/s$ equals 6138 L/Ha/year (McCoy *et al*., 2014), and benzene for gasoline sites (McCoy, 2012).

The static trap is marketed through E-Flux Environmental Services Company, a spin-off company from Colorado State University. The number of samples needed to sufficiently characterize a site will depend on size of release and other site-specific factors and is an area of on-going research.

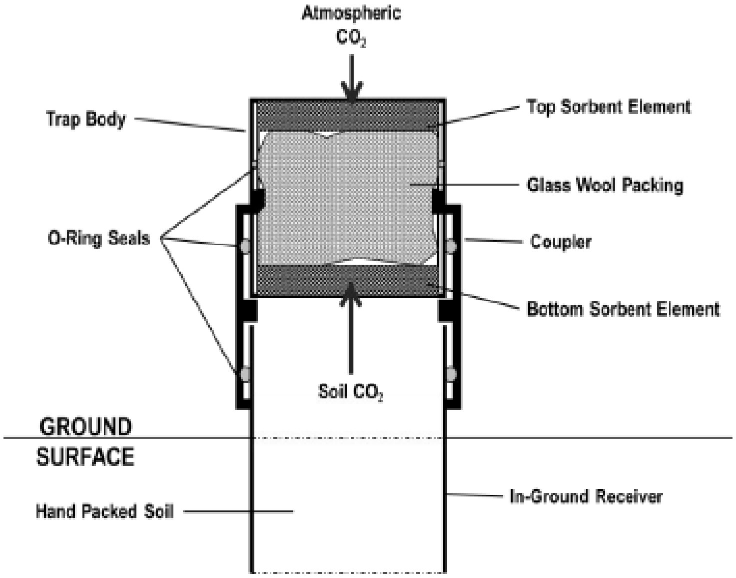

Figure C-2. Static CO2 Trap (McCoy et al., 2014)

2.0 SUBSURFACE TEMPERATURE PROFILES FOR EVALUATING AEROBIC BIODEGRADATION

For hydrocarbons, the general oxidation equation below can be used to calculate heat released from individual molecules:

$$C_xH_y + \left(x + \frac{1}{4}y\right)O_2 = xCO_2 + \frac{1}{2}yH_2O, \qquad \text{Eq. C-1}$$

where x = number of carbon and y = number of hydrogen atoms in the molecule. Based on the standard heat of formation of molecules, benzene oxidation releases 47.4 kJ/g, whereas octane oxidation releases 52.0 kJ/g. Sweeney *et al.* (2014) reports that a reasonable value for oxidation of petroleum products is assumed to be 48 kJ/g-hydrocarbon ($H_{hydrocarbon}$) or 15 kJ/g-oxygen (H_{oxygen}) used in the reaction.

The theory below is from Sweeney *et al.* (2014). From Fick's first law the flux of oxygen through the soil F_{O2} can be calculated according to:

$$F_{O2} = D_e \frac{dC}{dz}, \qquad \text{Eq. C-2}$$

where D_e is the effective diffusion coefficient (m^2/s), C is the oxygen concentration (g/m^3), and z is depth (m) below ground surface. The heat released from petroleum biodegradation are:

$$G_{bio} = F_{O2}H_{oxygen} \qquad \text{Eq. C-3}$$

and

$$H_{bio} = \frac{G_{bio}}{H_{hydrocarbon}}, \qquad \text{Eq. C-4}$$

where G_{bio} is the heat released from petroleum biodegradation (kJ/m^2-s), H_{oxygen} is the heat released during oxygen consumption (15 kJ/g-oxygen), H_{bio} is the rate of petroleum depletion (g/m^2-s) and $H_{hydrocarbon}$ is the heat released during petroleum depletion (48 kJ/g-hydrocarbon).

The conceptual model for heat transport is that highest heat flux would be at boundary between the aerobic and anaerobic zone (A/A boundary). Heat flux will occur upward to ground surface and downward toward groundwater from this boundary. The heat transport equation above and below the A/A boundary is

$$G_{bio} = k_u \frac{dT_u}{dz_u} + k_d \frac{dT_d}{dz_d} \qquad \text{Eq. C-5}$$

where G_{bio} is the rate of heat generation (J/m^2-s), $\frac{dT_u}{dz_u}$ is the thermal gradient between A/A and atmosphere, $\frac{dT_d}{dz_d}$ is the thermal gradient below the A/A; ΔT is the temperature difference between the A/A boundary and the ground surface, and k_u and k_d (J/m-s-K) are the thermal conductivities of soil above and below the biodegradation layer, respectively.

Re-arranging the above equations and introducing SF, a factor to address proportion of heat flux to ground surface above the A/A boundary to total heat flux, the following equation is obtained for the effective diffusivity,

$$D_e = \frac{G_{bio}}{H_{oxygen}\frac{dC}{dz}} = \frac{\Delta T k_u}{H_{oxygen} \times \Delta C \times SF}, \qquad \text{Eq. C-6}$$

where

$$SF = \frac{k_u \frac{dT_u}{dz_u}}{G_{bio}} \quad \text{Eq. C-7}$$

The hydrocarbon degradation rate may be estimated from:

$$H_{bio} = \frac{F_{O2} H_{oxygen}}{H_{hydrocarbon}} \; and \; F_{O2} = D_e \frac{dC}{dz}. \quad \text{Eq. C-8}$$

Sweeney *et al.* (2014) provide thermal conductivity values for soil, k, that is estimated as between 1.2 and 2.5 J/m-s-K for water content that would be typical of the vadose zone, citing the study by Smitts *et al.* (2009). In addition, if the thermal diffusivity of a soil is known, then the thermal conductivity can be calculated from the heat capacity of the soil. The effective diffusion coefficient could also potentially be estimated from soil properties.

3.0 REFERENCES

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APPENDIX D

Data Needed for VZBL Model

Preliminary Evaluation of the Vadose Zone

At most sites, the texture of the soil or sediment in the profile varies with depth from the land surface to the water table. Depth intervals with tight texture, high water content, and low air-filled porosity will not transmit oxygen from the surface as rapidly as intervals with light texture, low water content, and high air filled porosity. It is important to know the particular depth intervals represented by materials with tight texture, high water content, and potentially low air-filled porosity. These intervals in particular should be sampled for bulk density, and the vertical distribution of these intervals should be accurately represented in setting up the Vadose Zone Biodegradation Loss (VZBL) model.

Material with tight texture and associated high water content usually have an important component of clay sized material. The exchangeable bases on the clays make this material more conductive to electricity. As a result, the depth interval with clay will have a higher electrical conductivity than depth intervals without clay. Butler et al. (2000) associated electrical conductivity of sediment with the texture of the sediments at sites in Kansas, USA (Figure D-1). Wilson et al. (2005) associated electrical conductivity of sediment with texture of the sediments at a site in Illinois, USA.

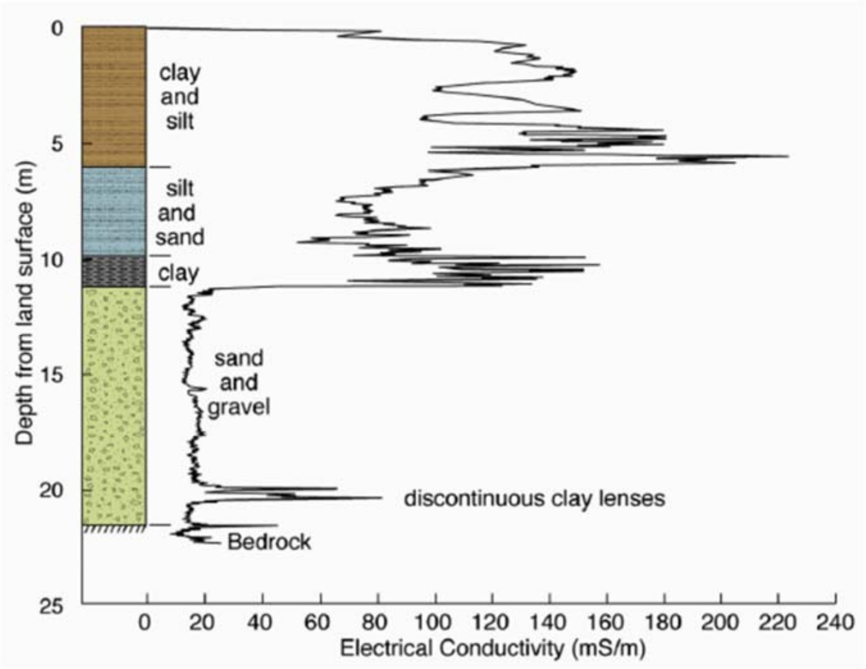

Figure D-1: Association of electrical conductivity with texture in a sediment profile.

The device to measure electrical conductivity can be advanced by push technology (Figure D-2). The device is commercially available for GeoProbe Systems®, Salina Kansas.

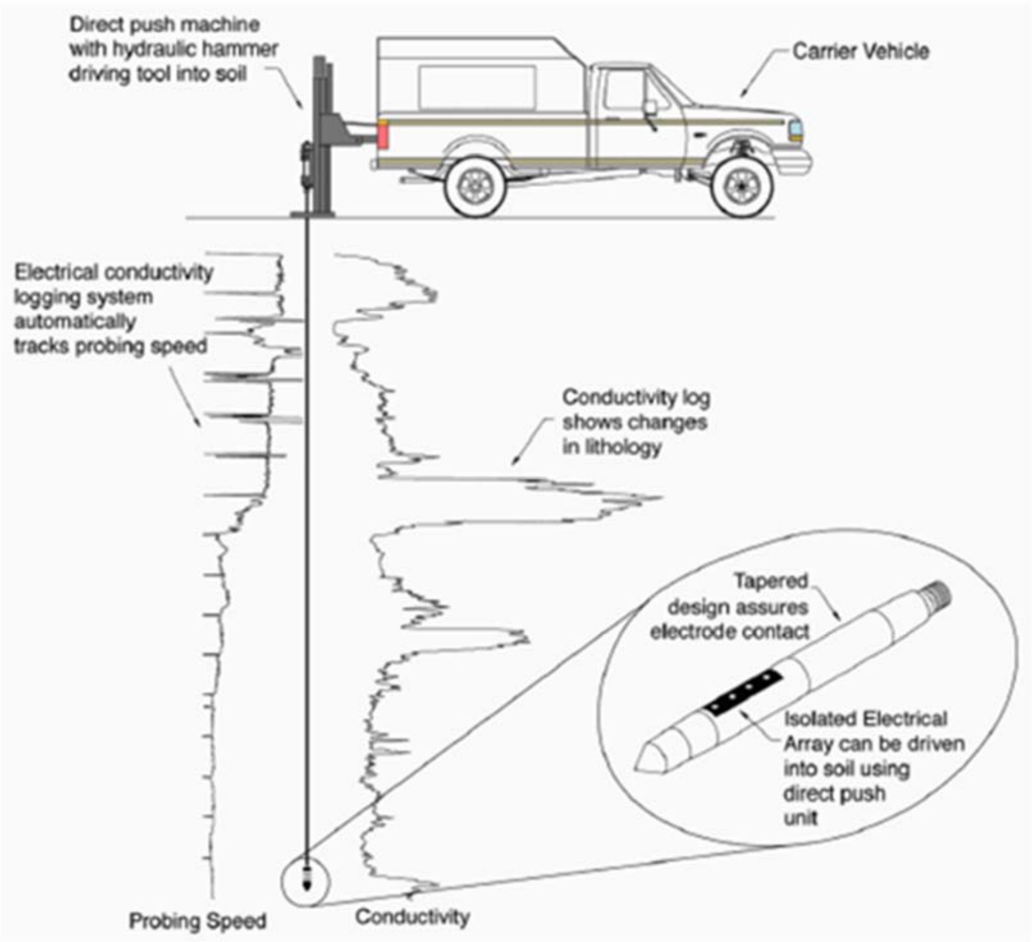

Figure D-2: A device to log electrical conductivity profiles.

A preliminary electrical conductivity profile can be useful to identify the depth intervals that might impede the diffusion of oxygen in soil gas. This information can guide the selection of the depth intervals that should be sampled for a determination of bulk density.

Calculations of Air-Filled Porosity from Bulk Density Measurements

Material from the unsaturated zone includes solids, water and soil air or soil gas. The Vadose Zone Biodegradation Loss (VZBL) model is very sensitive to the air filled porosity of the vadose zone. This parameter (θ_{air}) is defined as the volume of air in the material divided by the total volume of air, solids and water. The porosity filled with water (θ_{water}) is defined as the volume of water divided by the total volume.

Data on θ_{air} is not routinely available at fuel spill sites. The usefulness of the model will depend on the data used to calibrate it. The following suggestions are offered.

The value of θ_{air} is not directly measured. It is calculated from the bulk density of the vadose zone material, and the water content of the vadose zone material.

The wet bulk density of a sample of vadose zone material is the mass of a sample divided by the volume the sample occupies. Imagine that a sample with a volume of 0.6 L of sample weights 1316 g. The wet bulk density (D_{wet}) is

$$D_{wet}=(1316/1000)*0.6=2.193\ \mathrm{kg/L} \qquad \text{Eq. D-1}$$

Imagined that the sample is dried to remove the water, and the weight of the sample is reduced from 1316 grams to 1252 grams. There was 64 gm of water in the 0.6 L of sample. The value of θ_{water} is

$$\theta_{water}=(64/1000)/0.6=0.107 \qquad \text{Eq. D-2}$$

The dry bulk density (D_{dry}) of the sediment is

$$D_{dry}=(1252/1000)*0.6=2.087\ \mathrm{kg/L} \qquad \text{Eq. D-3}$$

If the organic matter content of the sediment is low, below a few percent, then the density of the solids can be estimated from the particle density of quartz (D_{quartz}), which is 2.65 kg/L.

Usually the contribution of organic matter in the soil is ignored. If the fraction of organic matter is known, the density of the solids (D_{solids}) can be corrected. Assume the fraction organic matter (f_{oc}) is 0.05, and the density of soil organic matter is 1.1 kg/L.

$$D_{solids} = f_{oc} * D_{organic\ matter} + (1-f) * D_{quartz} = 0.05 * 1.1 + (1-0.05) * 2.65 = 2.56\ kg/L \qquad \text{Eq. D-4}$$

The proportion of the space in the sample occupied by solids is

$$\frac{Volume_{solids}}{Volume\ _{total}} = \frac{D_{dry}}{D_{solids}} \qquad \text{Eq. D-5}$$

The porosity of the sample that is filled with air and water is

$$\frac{Volume_{air\ and\ water}}{Volume\ _{total}} = 1 - \frac{Volume_{solids}}{Volume\ _{total}} = 1 - \frac{D_{dry}}{D_{solids}} \qquad \text{Eq. D-6}$$

The porosity of air in the sample is the porosity of air and water minus the porosity of water.

$$\theta_{air} = 1 - \frac{D_{dry}}{D_{solids}} - \theta_{water} \qquad \text{Eq. D-7}$$

In this illustration θ_{air} is

$$\theta_{air} = 1 - \frac{2.087}{2.56} - 0.107 = 0.078 \qquad \text{Eq. D-7}$$

The value of the fraction organic matter used in the illustration is common for surface soils. Deeper vadose zone materials would be expected to have from ten to one-hundred fold less organic matter. Unless the vadose zone is noticeably rich in organic matter, the correction for organic matter can be ignored.

Measuring Soil Bulk Density

Tools such as the GeoProbe® Macro-Core system that are commonly used to acquire core samples for analysis of contaminant parameters such as total petroleum hydrocarbons, or for logging the profile, may not be appropriate for a measurement of the soil bulk density. Contractors that do soil or sediment sampling in support of hazardous waste management or remediation of fuel spills may not have the appropriate tools or experience.

There are a variety of devices that are available to collect soil samples for the determination of wet bulk density. Richardson and Clayton (2013) compared the performance of the modified Madera sampler, the Eijkelkamp sampler, and the Drive Cylinder sampler on soils in California. Of the three options, they found that the Eijkelkamp sampler was easier to use, and was less likely to compress the sample, and thus compromise the sample during sample collection. Richardson and Clayton (2013) provide the following conclusions:

> *“The Eijkelkamp soil sampler has an open-ended sampling cylinder. This provides for less risk of soil compaction during sampling and for inspection of the soil core for completeness prior to its extraction from the sampling cylinder. The sampler uses interchangeable stainless steel cylinders that can be sealed with a cap for safe containment of the soil sample during transportation and storage prior to analysis for bulk density.*
>
> *Advantages:*
>
> - *Easiest to use to obtain an accurate sample*
> - *It is convenient for collecting soil samples at specific depths.*
> - *The soil sampling cylinder is of an open-end design reducing potential for soil compaction during sampling.*
> - *The soil sample can be inspected prior to its removal from the sampling cylinder.*
> - *It is commercially available with readily available replacement parts.*
>
> *Disadvantages:*
>
> - *Extensions for deep soil coring required pipe-thread coupling unions that are not compatible with standard U.S. pipe-thread sizes. This would require ordering of sampler-specific extensions or custom fabrication of specialized parts.”*

Vertical Distribution of Total Petroleum Hydrocarbons

The Vadose Zone Biodegradation Loss (VZBL) model requires detailed information on the vertical distribution of Total Petroleum Hydrocarbons (TPH). Section 3 of Wilson et al. (2012) provide recommendations for screening core samples for TPH and collecting samples for analysis of TPH. These recommendations are reprinted below.

> *“To avoid missing a depth interval that might be contaminated, it is necessary to recover a complete profile of core samples from the land surface to the water table. If possible, it is better to recover core samples to a depth equal to the lowest elevation of the water table over time.*

> *To assure that the core profile is complete, compare the length of the core that is recovered (including material in the core retainer and the cutting shoe) to the depth interval that the core barrel was driven into the earth. In some subsurface materials, core samplers driven two or three feet will recover an equivalent length of core sample, but core samplers driven four or five feet will not. Adjust the depth interval driven in each core if necessary to recover a complete core sample.*
>
> *On occasion, material with a high concentration of TPH will literally be well lubricated, and will fall out of the core sampler as it is being recovered. Do not ignore the missing sample. Attempt to collect core samples in an adjacent bore hole, starting just above the elevation that would correspond to the missing sample, and drive the core sampler the maximum interval that will acquire a complete core sample.*
>
> *…To minimize the chance of missing a contaminated depth interval, it is good practice to screen the core samples with an Organic Vapor Monitor (OVM) every 0.5 foot starting at 1.0 foot below land surface or 1.0 foot below the bottom of the structure of concern. Continue screening until the depth of the core samples exceeds the lowest possible position of the water table. If the OVM meter reading exceeds 100 ppm, a sample should be analyzed in the laboratory for benzene and total petroleum hydrocarbons (TPH). Detailed recommendations for extracting and analyzing core samples are provided in Appendix A."*

It is tempting to collect core samples and send them back to the laboratory for analysis. It is easy to lose volatile hydrocarbons during shipping and storage. Appendix A of Wilson et al. (2012) provides recommendations for extracting the hydrocarbons in the field.

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APPENDIX E

US EPA Source Depletion Times

US EPA Office of Underground Storage Tanks (OUST) Source Depletion Estimates

Expected timelines for natural source zone depletion based on the application of the gradient model can vary significantly as discussed in Section 3 of the report. To provide additional insight on depletion timelines, this appendix provides the scoping calculations of natural depletion times for petroleum hydrocarbon sources presented in US EPA OUST guidance (US EPA, 2004)[1]. These calculations for source depletion times are based on an oxygen consumption model where the diffusive oxygen flux, and corresponding mass loss and biodegradation rate, is estimated for LNAPL residual saturations and porosities representative of different soil types. The model and calculations do not consider potential limitations with respect to biodegradation rates, which is a potential concern for an un-calibrated model where the oxygen flux is high (*i.e.*, scenarios where the contamination is shallow and soils have a high effective diffusion coefficient).

The scoping calculations first provide the equivalent rate of aerobic biodegradation of hydrocarbons that could be supported based on oxygen diffusion for a 1 m thick LNAPL smear zone, as shown in Table E-1. As shown, the rates are higher than those estimated for detailed modeling studies described in Section 3.2.4, and suggest that the rates may be unrealistically high particularly for coarse sand scenarios. The scoping calculations also do not consider potential limitations in biodegradation rates

Table E-1: Rate of aerobic biodegradation of hydrocarbons (mg/kg/day) that can be sustained by diffusion of oxygen through the vadose zone - assuming a one metre thick smear zone. (from US EPA OUST guidance, US EPA, 2004[1]; Exhibit IX-7)

Depth to Top of Contaminated Soil (m)	Silty Clay	Sandy Silt	Coarse Sand
1	5	12	22
2	2	6	11
3	2	4	7
4	1	3	6

Based on the above model, the time required to consume hydrocarbons is shown in Table E-2. The depletion times are expected to be longer if the biodegradation rates at a site is slow compared to the supply of oxygen through diffusion, which is particularly relevant for coarser deposits and shallow depths. Also shown are the depletion times calculated for a 1 m thick smear zone assuming the biodegradation rate estimated for the Traverse City site ("biodegradation-limited"). The biodegradation rate at the Traverse City site is described to be relatively slow compared to other petroleum hydrocarbon sites because of properties of fuel and soil. This is reflected in the hydrocarbon vapour profiles where hydrocarbon concentrations decrease relatively slowly with decreasing depth, compared to much faster exponential declines in concentrations observed at many other sites.

The BIOSCREEN version 1.3 user manual provides a good discussion of cases where microbial kinetics are the limiting factor in the biodegradation process and implications for modeling of solute transport.

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[1] US EPA. 2004. How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites, A Guide for Corrective Action Plan Reviewers. Chapter IX: Monitored Natural Attenuation. EPA 510-R-04-002, May, 2004.

Table E-2: Time in days required to consume hydrocarbons present at residual saturation. (from US EPA OUST guidance, US EPA, 2004[1]; Exhibit IX-8).

Soil Type	**TPH at Residual Saturation (mg/kg)**	**Oxygen Diffusion-Limited Depth (m) to Top of Contaminated Soil in the Vadose Zone**				**Biodegradation Limited**
		1	2	3	4	0.41 mg/kg per day
Silty Clay	10,000 to 49,000	6 to 28 days	11 to 56 days	17 to 84 days	23 to 113 days	67 to 326 days
Sandy Silt	5,000 to 36,000	1 to 9 days	2 to 17 days	4 to 26 days	5 to 34 days	33 to 240 days
Coarse Sand	2,000 to 17,000	<1 to 2 days	<1 to 4 days	1 to 6 days	1 to 8 days	13 to 113 days

APPENDIX F

Traverse City Case Study

Traverse City Case Study

The VZBL model was used to estimate mass loss rates based on reported vertical profiles of porosity (water-filled and total) and TPH concentration data for the Traverse City site (Ostendorf and Kampbell, 1991). A large release of jet fuel (100,000 kg) occurred at this site. The depth to the water table is approximately 5 m to 6 m and there are sandy soils. The VZBL model estimated hydrocarbon biodegradation rates with baseline respiration off range from **0.18 to 0.86** g/m^2-day at 5 m depth. The corresponding source depletion times range from **6.5 to 141** years. The detailed inputs to the modeling are provided in Table F-1 as well as the estimated source depletion times for the two Traverse City sites.

Table F-1: Summary of Input Parameters for the VZBL model for the two Traverse City sites

Parameter	**Site 1** Porosity Values: 50AN Soil TPH Concentrations: 50AC Soil Gas Profile: PT4 Depth to Water Table: 50BS	**Site 2** Porosity Values: 50AS Soil TPH Concentrations: 50AS Soil Gas Profile: M30 Depth to Water Table: 50BT
Range of Saturation Values (unitless)[1]	0.25-0.49	0.16-0.83
TPH Concentrations[2]	Depth (m) — TPH (mg/kg) 4.7 — 11 4.8 — 39 4.9 — 2370 5.0 — 8400 5.1 — 624 5.2 — 624 5.3 — 13	Depth (m) — TPH (mg/kg) 5 — 20500 5.1 — 24600
Average Depth to Water Table, and Standard Deviation (m)[3]	5.8, 0.35	5.5, 0.35
Assumed bulk soil density (kg/m^3)	1,700 kg/m^3	1,700 kg/m^3
Stoichiometric coefficient (g-O_2 required to degrade 1 g-HC)	3.5	3.5
Fraction Organic Carbon (unitless)	0.0008	0.0008
Free Diffusion Coefficient of O_2 in Air (cm^2/s)	0.175	0.175
Baseline Respiration Rate (mg O_2/g-OC day)	1.69×10^{-2}	1.69×10^{-2}
Hydrocarbon Biodegradation Rate with Baseline Respiration Off (g/m^2-day) at 5 m depth	0.86	0.18
Hydrocarbon Biodegradation Rate with Baseline Respiration On: (g/m^2-day) at 5 m depth	0.81	0.15
Ostendorf Kampbell (1991) Model-Predicted Hydrocarbon Flux (g/m^2-day)[1]	0.6	0.7
TPH Source Depletion Time with Baseline Respiration Off (years)	6.5	141
TPH Source Depletion Time with Baseline Respiration On (years)	6.8	179
Equivalent Zero-Order Biodegradation Rate with Baseline Respiration Off Based on Site-specific LNAPL thickness (mg/kg-day)	2.5	0.5

Notes:
1. Ostendorf and Kampbell (1991)
2. Wilson et al. (1994) for Site 1 and unpublished data for Site 2
3. Ostenforf et al. (1993)

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APPENDIX G

Multi-Process Models

1.0 MODEL DOMAIN AND SOURCE ZONE CHARACTERISTICS

For the analytical models LNAST, REMFuel, and BIOSCREEN the model domain is specified by the user for display of the model results and/or to estimate the initial source mass. For the MIN3P-DUSTY numerical model, which is based on a finite-volume approximation, the model is set up in three-dimensions (*x, y,* and *z*) with the LNAPL source zone located near one end of a 600 m long (x) by 35 m (y) in half-space assuming symmetry about the x-z plane, and 15 m elevation (z) solution domain (Figure G-1). Only the small-size gasoline source scenario is simulated using the MIN3P-DUSTY model. Variable grid spacing for higher resolution in proximity of the source zone is used.

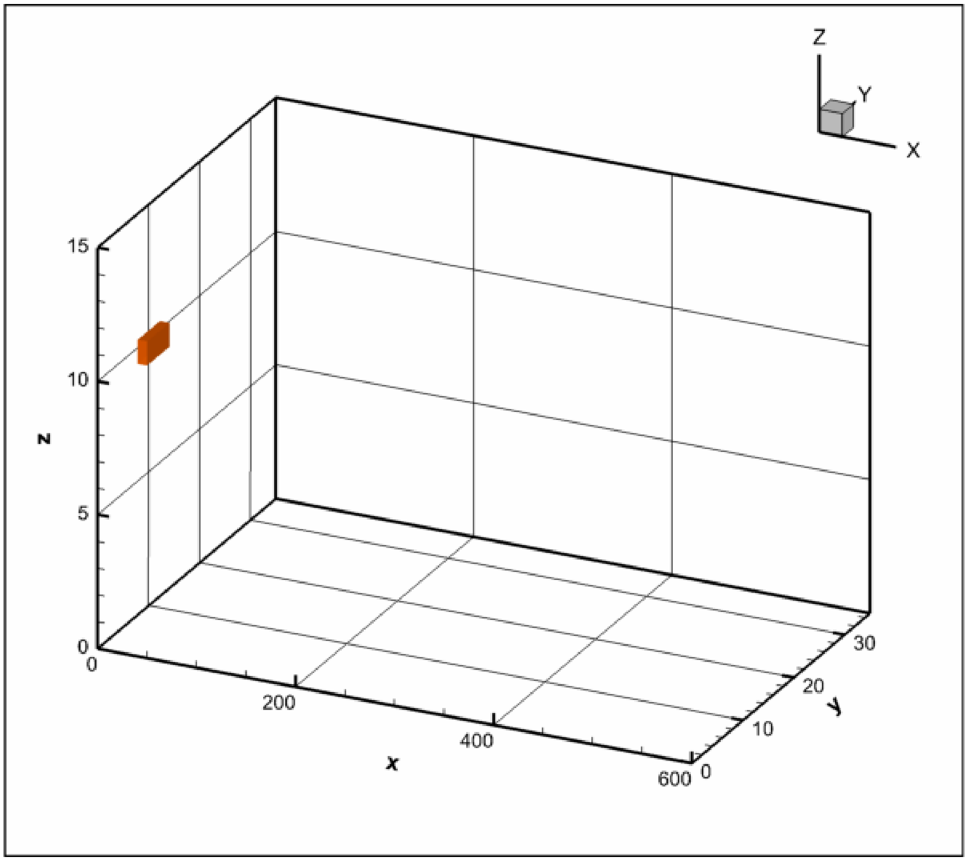

Figure G-1: MIN3P-DUSTY model domain and source zone location defined as a rectangular box defined by x = 40 – 50 m; y = 0 – 5 m; and z = 10.9 – 11.9 m.

Table G-1 defines the input parameters that define the source zone characteristics used in each of the four models considered. The applicable model for each input parameter is indicated by L (LNAST), M (MIN3P-DUSTY), R (REMFuel), and B (BIOSCREEN). Tables G-2 and G-3 define the LNAPL and benzene properties, respectively. The source zone as defined in the MIN3P-DUSTY and LNAST models straddle the water table based on the density of the LNAPL, while the source is assumed to be entirely in the saturated zone in the REMFuel and BIOSCREEN models. For the LNAST model and baseline simulations, the vapour diffusion efficiency coefficient is set to 0.001, which is a low value and results in essentially no loss through volatilization. Table G-4 defines the properties used for modeling of multicomponent LNAPL fate and transport (special case scenario).

Table G-1: Source Zone Characteristics

Parameter	Unit	Small-Source / Value	Large-Source / Value	Applicable Models[1]
LNAPL saturation	%	10	10	L, M
LNAPL constituents	-	benzene	benzene	L, R, M
Source thickness	M	1	2	L, R, M, B
LNAPL source length (in direction of groundwater flow)	m	10	50	L, R, M
LNAPL source width	m	10	50	L, R, B
Average depth to top of LNAPL	m	3	3	L, M
Vapour diffusion efficiency[3]	-	0.001	0.001	L
Gamma	-	0	0	R
Source remediation time period	years	NA	NA	R
Source fraction removed	-	0	0	R
Source decay rate constant	per year	0	0	R, B[2]
Initial source mass	kg	2,740	136,900	R, B[2]

[1] MIN3P-DUSTY simulation run for the small source scenario only.
[2] BIOSCREEN model calculates a half-life for the given source mass based on a first order decay approximation of mass removal through dissolution and groundwater flow. The user also has the option of specifying infinite source.
[3] Defines the fraction of vapour removed through the vadose zone. See text for details.
NA = not applicable.

Table G-2: LNAPL Properties (LNAST)

Parameter	Unit	Gasoline	Applicable Models
Density	g/cm^3	0.73	L
Oil/water interfacial tension	dynes/cm	52.0	L
Oil/air interfacial tension	dynes/cm	24.0	L
Viscosity	Cp	0.62	L

Table G-3: LNAPL Constituent (benzene) Properties

Constituent	unit	Value	Applicable Models
Pure Phase Solubility	mg/L	100	L
Pure Phase Vapour Concentration	mg/L	324	L
Mass Fraction of LNAPL	-	1	L
Log Koc		1.77	L, B
Source Concentration	mg/L	100	M, R, B
Target Concentration	µg/L	5 (DW)	L
First-Order Biodegradation Rate[1]	per day	0.002	M, R, B
Half-life[*]	days	347	L
Source Mass	kg	2740	R, B
Retardation Factor	-	3.2	R, B
Effective distribution coefficient	-	2.2	M

[*] Equivalent to the first-order biodegradation rate of 0.002 per day as specified for other models.

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[1] The first-order biodegradation rate constant for benzene was selected based on the aerobic and anaerobic values compiled from review of field studies in Table 3 of Suarez and Rifai (1999). The reported arithmetic and geometric means of the rate constants are 0.001 per day and 0.01 per day, respectively. For comparison, the default value in REMFuel is 1.1 per year (equivalent to 0.003 perday). The default value in LNAST is a half-life of 90 days (equivalent to 0.008 per day).

Table G-4: LNAPL constituents and properties used in the multi-component scenario in the LNAST model. Note that the target concentrations in this snapshot of input screen are to be specified in units of mg/L

Dissolved Phase Constituent	Pure Phase Solubility (mg/L)	Pure Phase Vapour Concentration (mg/L)	Mass Fraction of LNAPL	Log(Koc)	Biodegradation Half-Life (days)	Target Concentration (mg/L)
MTBE	48,000	1,204	0.11	1	9,000	0.015
Benzene	1,780	324	0.018	1.77	347	0.005
Ethylbenzene	135	57	0.018	3	65	0.0024
Toluene	515	111	0.079	2.06	60	0.024
Xylene	175	38	0.075	2.6	150	0.3

2.0 SOIL AND HYDROGEOLOGICAL PARAMETERS

The soil properties and hydrogeological conditions are selected based on a literature search to obtain parameter values representative of “typical” conditions in the Lower Mainland region of British Columbia (near Vancouver). The model domain is assumed to represent isotropic and homogeneous soil conditions. For the MIN3P-DUSTY simulation only, two layers of isotropic and homogeneous soil types are considered: Fraser River sand that is overlain by silty sand in the top 3 m of the soil. Table G-5 summarizes the soil and hydrogeological parameters input to the models.

Table G-5: Soil and Hydrogeological Parameters.

Parameter	Unit	Fraser River Sand	Silty Sand (MIN3P-DUSTY only)	Applicable Models
Porosity, ϕ	-	0.375	0.39	L, M
Effective porosity	-	0.3225	NA	L, R, B
Soil hydraulic function (Van Genuchten) parameters: α	1/m	3.5	2.7	L, M
N	-	3.2	1.4	L, M
Residual water saturation, S_r	-	0.14	0.10	L, M
Temperature	°C	10	10	M
Specific storage coefficient	1/m	1.8×10^{-4}	1.0×10^{-4}	M
Saturated hydraulic conductivity: $K_{xx} = K_{zz}$	m/s	5.2×10^{-4}	6.0×10^{-5}	L, M, B
Hydraulic head gradient	m/m	1.0×10^{-3}	-	L, M, B
Longitudinal dispersivity	M	1.0	0	L, M, B
Sigma v (width of normal velocity distribution)*	-	0.14	NA	R
Vmin*	-	0.5	NA	R
Vmax*	-	1.5	NA	R
Number of stream tubes*	-	100	NA	R
Horizontal Transverse dispersivity	M	0.1	NA	L, R, B
Vertical Transverse dispersivity	m	0.01	0	L, R, M, B
Recharge rate	m/yr	-	0	M
Darcy velocity	m/yr	16	NA	R
Seepage velocity	m/yr	50.8	NA	B
Fraction organic carbon	-	0.006	0.006	L, R, M, B
Retardation Factor	-	3.2	NA	R, B
Effective distribution coefficient	-	2.2	2.0	M

*Parameters used in REMFuel to define longitudinal dispersivity by assuming a normally distributed velocity field through individual “stream tubes”. The values selected here result in a longitudinal dispersivity of 1.0 m at a distance of 100 m from source.

The porosity and soil hydraulic function parameters are based on generic values for sand and sandy loam, which is assumed to approximate the silty sand (Tillman and Weaver, 2007). The specific storage coefficient and hydraulic conductivity of the silty sand layer are taken from the study of Neilson-Welch and Smith (2001) for similar soil (Unit 2 in that study). The temperature in the soil is assumed to be the average air temperature of the region and is the average recorded temperature at the Environment Canada Vancouver International Airport weather station from 1971-2000. The longitudinal and transverse dispersivity are assumed to be 1.0 m and 0.01 m, respectively (Neilson-Welch and Smith, 2001; Schulze-Makuch, 2005) for the Fraser River sand layer.

Constant values in time and space for dispersivity are specified in all of the models except the REMFuel model. In the REMFuel model, the longitudinal dispersivity (along the flow direction) is scale dependent; transverse and vertical dispersivities can be specified as constants. The longitudinal dispersivity in the REMFuel model is based on the assumption of a normally distributed velocity field through individual “stream tubes”. The user specifies the coefficient of variation for the velocity field, the minimum and maximum normalized streamtube velocities, and number of streamtubes (REMFuel, 2012). The values selected here result in a longitudinal dispersivity of 1.0 m at a distance of 100 m from source.

The specific storage coefficient, hydraulic conductivity and the hydraulic head gradient for the Fraser River sand layer are based on the Zawadzki *et al.* (2002) study at a site on the north side of the Fraser River estuary and approximately 20 km upstream from the Pacific Ocean. These selected values for Fraser River sand are similar to those obtained in other studies. For example, Neilson-Welch and Smith (2001) estimate hydraulic conductivity of 4 x 10^{-4} m/s for the sand layers at a site in Richmond, BC, and Jackson *et al.* (2006) select values of 2.1 x 10^{-4} m/s for the sand aquifer at a site along the lower Fraser River near Vancouver, BC.

3.0 BASELINE MODELING RESULTS

Table G-6 shows the predicted concentrations at 20 m and 100 m distance from the source zone in addition to predicted plume lengths. There is good agreement at short distance between the models except for REMFuel, which predicts higher concentrations. This could be due to the scale dependent longitudinal dispersivity that is used in REMFuel, in which the applied the dispersivity value would be lower closer to the source There is greater variability in the predicted concentrations at a 100 m distance, but benzene concentrations predicted by all models are less than 1 mg/L. At 100 m distance from the source, the REMFuel predicted concentrations are greater for both the small and large source zone scenarios.

TableG-6: Summary of Plume Characteristics at 5 years and 20 years.

Scenario	Years	MIN3P-DUSTY	LNAST	REMFuel	BIOSCREEN
plume extent (m)					
Small-size Source	5	175	114	115	114
	20	365	367	398	192
Large-size Source	5	NA	115	118	115
	20	NA	400	423	210
concentration at 20 m distance from the source (mg/L)					
Small-size Source	5	35	34	65	33
	20	34	34	65	33
Large-size Source	5	NA	45	74	41
	20	NA	45	74	41

Scenario	Years	MIN3P-DUSTY	LNAST	REMFuel	BIOSCREEN
concentration at 100 m distance from the source (mg/L)					
Small-size Source	5	0.91	0.28	0.36	0.059
	20	3.4	0.59	9.0	0.42
Large-size Source	5	NA	0.66	0.79	0.12
	20	NA	1.4	20	0.96

Source Depletion Time Estimates: REMFuel and BIOSCREEN

This section compares the estimated source depletion times for simulations in REMFuel and BIOSCREEN based on the equations and assumptions used in each model.

The source depletion time estimated for the small and large size source scenarios using REMFuel are the shortest amongst the models considered. The depletion times are estimated based on:

$$\frac{dM(t)}{dt} = -Q(t)C_s(t) = -QC_0 \; for \; \Gamma = 0 \; and \; \lambda_s = 0, \qquad \text{Eq. G-1}$$

where $M(t)$ is the total mass of source at time, t; $Q(t)$ is the volumetric groundwater flow through the source zone; $C_s(t)$ is the dissolved phase concentration in the source zone with $C_s(0) = C_0$; and λ_s is the source decay rate.

Integrating Eq. G-1 results in:

$$M(t) = M_0 - QC_0 t, \qquad \text{Eq. G-2}$$

such that the source depletion time ($M(t) = 0$) corresponds to

$$t_{depletion} = \frac{M_0}{QC_0} = \begin{cases} \dfrac{2{,}740kg}{16.4m/yr \times 10m \times 1m \times 0.1kg/m^3} = 170 \; years \; (small \; source) \\ \dfrac{136{,}900kg}{16.4m/yr \times 50m \times 2m \times 0.1kg/m^3} = 830 \; years \; (large \; source) \end{cases} \qquad \text{Eq. G-3}$$

The depletion times thus represent instantaneous dissolution and removal from a point source. The longest depletion times are predicted by the BIOSCREEN model, it is assumed that the source zone concentration decays exponentially based on the assumption that the dissolution process can be represented by first-order decay. In this sense, it is similar to REMFuel, where $\Gamma = 1$:

$$\frac{dM(t)}{dt} = -Q(t)C_s(t) = -Q\frac{C_0}{M_0}M(t) \; for \; \Gamma = 1 \; and \; \lambda_s = 0 \qquad \text{Eq. G-4}$$

Integrating the above equation with respect to time, yields the exponentially decaying source mass

$$M(t) = M_0 e^{\frac{-QC_0}{M_0}t} \qquad \text{Eq. G-5}$$

and the flow averaged source concentration

$$C_s(t) = C_0 e^{\frac{-QC_0}{M_0}t} \qquad \text{Eq. G-6}$$

Since neither the source mass nor concentration reach zero with time, one can use the remediation goal concentration to estimate a depletion time. For example, the time to reach $C_s(t) = 5\ \mu g/L$ would be

$$t_{depletion} = \frac{\ln\left(\frac{100{,}000\ \mu g/L}{5\ \mu g/L}\right) M_0}{Q C_0} = \begin{cases} \dfrac{9.9 \times 2{,}740kg}{16.4m/yr \times 10m \times 1m \times 0.1kg/m^3} = 1{,}700\ years\ (small\ source) \\ \dfrac{9.9\ \times 136{,}900kg}{16.4m/yr \times 50m \times 2m \times 0.1kg/m^3} = 8{,}300\ years\ (large\ source) \end{cases} \qquad \text{Eq. G-7}$$

The estimated depletion times in equations Eq. G-3 and Eq. G-7 are as shown in Table 4-2 of the report for REMFuel and BIOSCREEN, respectively.

4.0 EVALUATION OF FASTER VADOSE ZONE BIODEGRADATION RATE FOR MIN3P-DUSTY

For simplicity and comparison to the other models, the MIN3P-DUSTY model inputs defined in the baseline scenario assumed that biodegradation occurs at the same rate throughout the model domain as a first-order reaction with respect to the hydrocarbon concentration. A more realistic scenario is considered here in which a faster biodegradation rate R_{bio} is specified for the vadose zone, but with added oxygen limitation (represented by a Monod term):

$$R_{bio} = -k_{o2}[C_6H_6]\frac{[O_2]}{[O_2] + K_{O2}}, \qquad \text{Eq. G-8}$$

where k_{o2} is the first-order biodegradation rate (0.79 per hour)[2] and $K_{O2}$is the oxygen half-saturation constant (3.4 µM or 0.25% in soil gas). The results summarized in Table G-7 indicate a vapour mass loss that is double that predicted in the baseline scenario and which corresponds to 0.4 g/m^2/day at 5 years simulations time. The predicted source depletion time is however only 7% lower than the baseline scenario.

Table G-7: MIN3P-DUSTY Results for Vadose Zone Biodegradation.

Scenario	Years	Fast biodegradation in Vadose Zone	Baseline
plume extent (m)			
Small-size Source	5	170	175
	20	355	365
concentration at 20 m distance from the source (mg/L)			
Small-size Source	5	26	35
	20	24	34
concentration at 100 m distance from the source (mg/L)			
Small-size Source	5	0.62	0.91
	20	2.0	3.4
Vapour mass loss (kg/day)		**0.04 (at 5 years)**	**0.02 (at 5 years)**
Source depletion time (years)		**315**	**340**

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[2] DeVaull, G.E. (2011) Biodegradation rates for petroleum hydrocarbons in aerobic soils: A summary of measured data. Presented at International Symposium on Bioremediation and Sustainable Environmental Technologies, Reno, NV. June 27-30.

5.0 REFERENCES

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APPENDIX H

Model Applications for Case Study #4

1.0 MODEL APPLICATION FOR CASE STUDY #4

A modeling case study is conducted for the site conditions described in Case Study #4 (large release at service station site) to enable comparison of estimated concentrations and source depletion times for different models. Case Study #4 is a very large release of gasoline where the hydrocarbon contamination in the unsaturated soil zone was partially remediated through soil vapour extraction. The four models used are:

- Regression analysis on concentrations
- NAPL dissolution nomograph
- LNAST model
- REMFuel model

The modeling objectives are to illustrate how source depletion rates can be obtained and to compare model predictions to measured data. For REMFuel, the model is used to back calculate the gamma term.

2.0 REGRESSION ANALYSIS ON CONCENTRATIONS

The time-series data for benzene, ethylbenzene and xylenes are shown on Figure H-1. The trend analysis below focuses on ethylbenzene because times to meet the CSR DW standards are longest for this substance in this case study.

For monitoring wells MW-7 and MW-12, an analysis of concentration trend suggests ethylbenzene concentrations would decrease to below the DW standard in approximately 20 years from the onset of monitoring in about 1990, as shown on Figure H-2. While there are no recent data for MW-7 and MW-12, there are for MW07-24, which is located nearby, where the ethylbenzene concentrations are decreasing at a slower rate, and where the trend analysis in Figure H-2 predicts concentrations will decrease to below the standard in about 2020, or roughly 30 years. The reason for the difference in concentration trends for MW-7 and MW-12 compared to MW07-24 may be due to variability in the LNAPL source distribution and well screen position.

Further downgradient at well MW-14 and MW07-6 there are significant decreases in the benzene concentrations, but not the ethylbenzene and xylenes concentrations. This could be due to a combination of the radius of influence of the SVE system not extending to this area and the reduction in mass through dissolution not extending to this area (i.e., dissolution occurs first in the upgradient LNAPL zone).

The trend analysis for wells near to the release location indicate a significant reduction in ethylbenzene concentrations to below DW standards, and inferred substantial depletion of the LNAPL source, within approximately 20 to 30 years. The inferred depletion time for the downgradient edge of the residual LNAPL zone is significantly (decades) longer. It is noted that a very large release occurred at this site; typical releases at service stations are smaller. The results show the influence of the solubility on relative depletion rates of the BTEX compounds.

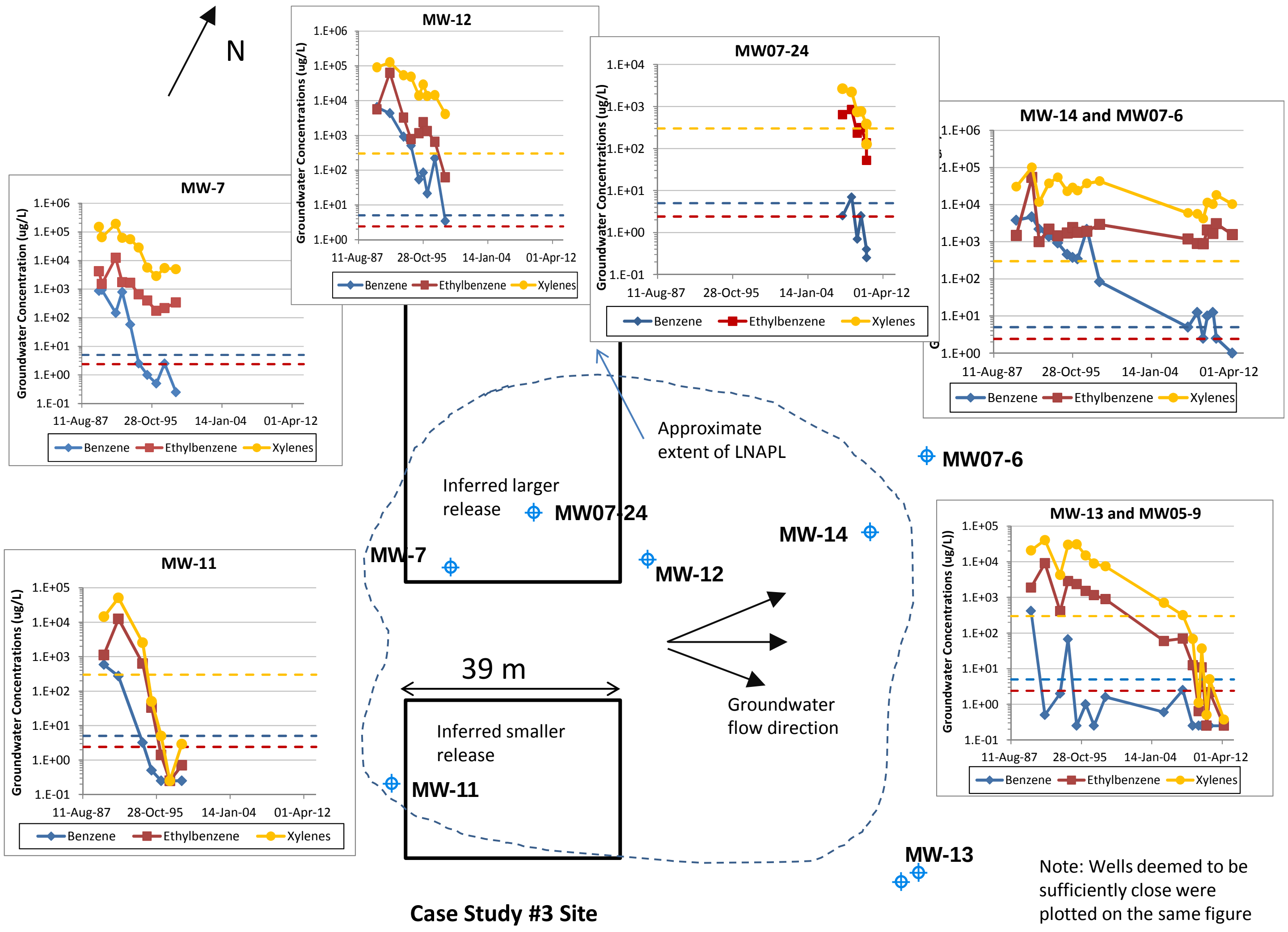


Figure H-1: LNAPL source depletion nomograph from NAPL dissolution model.

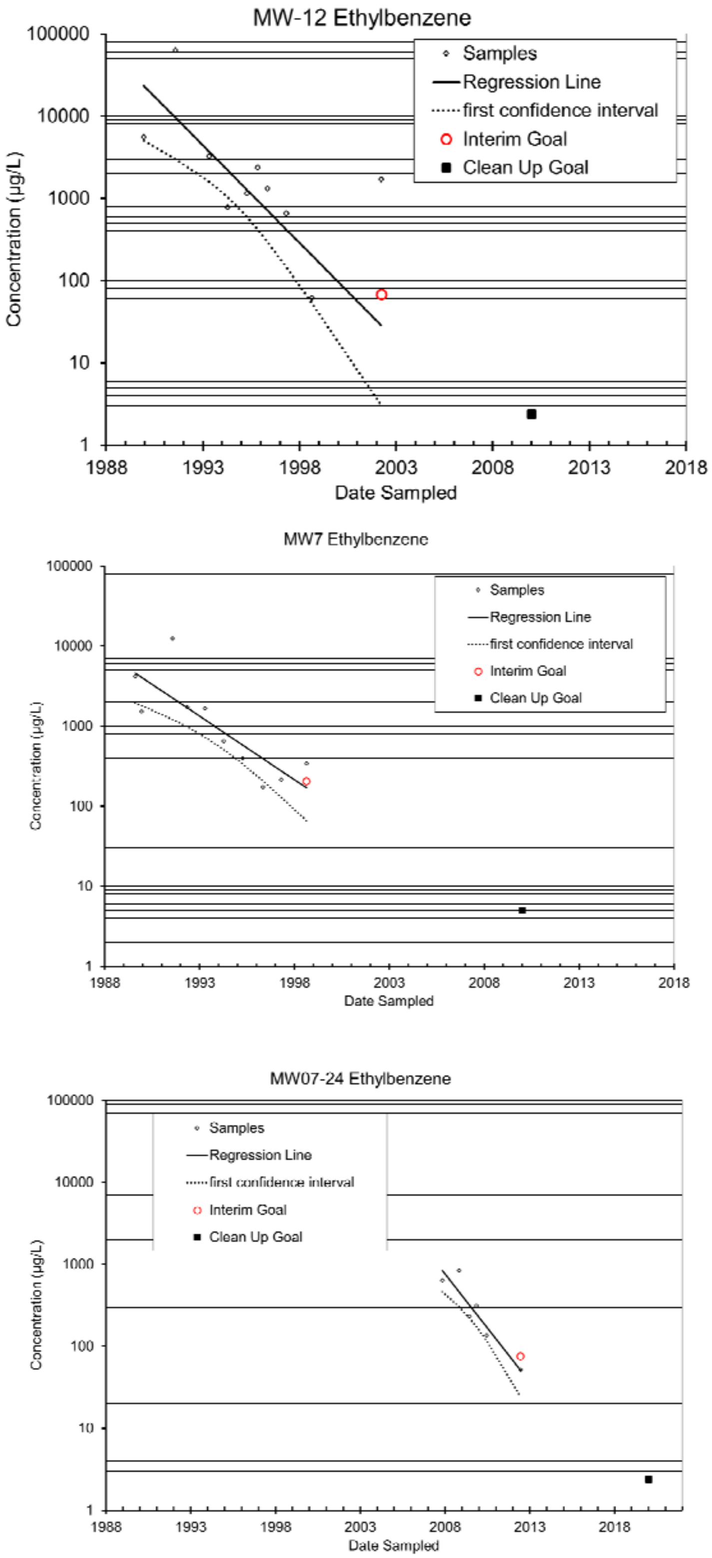


Figure H-2: Regression analysis of ethylbenzene concentrations in groundwater.

3.0 LNAPL DISSOLUTION NOMOGRAPH

The LNAPL dissolution model is a simple mass balance model for the reduction in the hydrocarbon mass based on the estimated concentration in flowing groundwater exiting the downgradient LNAPL smear zone. The model input parameters are as follows:

- Darcy velocity = 15 to 38 m/year (estimated)
- TPH concentration in groundwater = 100 mg/L (estimated from groundwater chemistry results)
- LNAPL thickness = 1 m (measured)
- Length of LNAPL in direction of groundwater flow = 90 m (measured)
- LNAPL (oil) saturation = 0.02 (50th percentile value from Brost and DeVaull (2000) for coarse sand)

The estimated time for source depletion is 100 to 300 years based on the above values (Figure H-3). A single value estimate for both the LNAPL saturation and TPH concentration in groundwater was used. Had these parameters been varied, there would have been greater variation in the predicted depletion times.

Based on a simple progressive LNAPL dissolution model and 90 m long source, for the 100 year estimate, depletion would take place at a rate of approximately 1.1 m per year. From the trend analysis described above, the LNAPL at wells within approximately 30 m to 40 m of the upgradient edge of the LNAPL source zone appears to be depleting within about 30 years. Therefore, the lower estimate of depletion time, which corresponds to a higher Darcy velocity, appears to be more representative for the site.

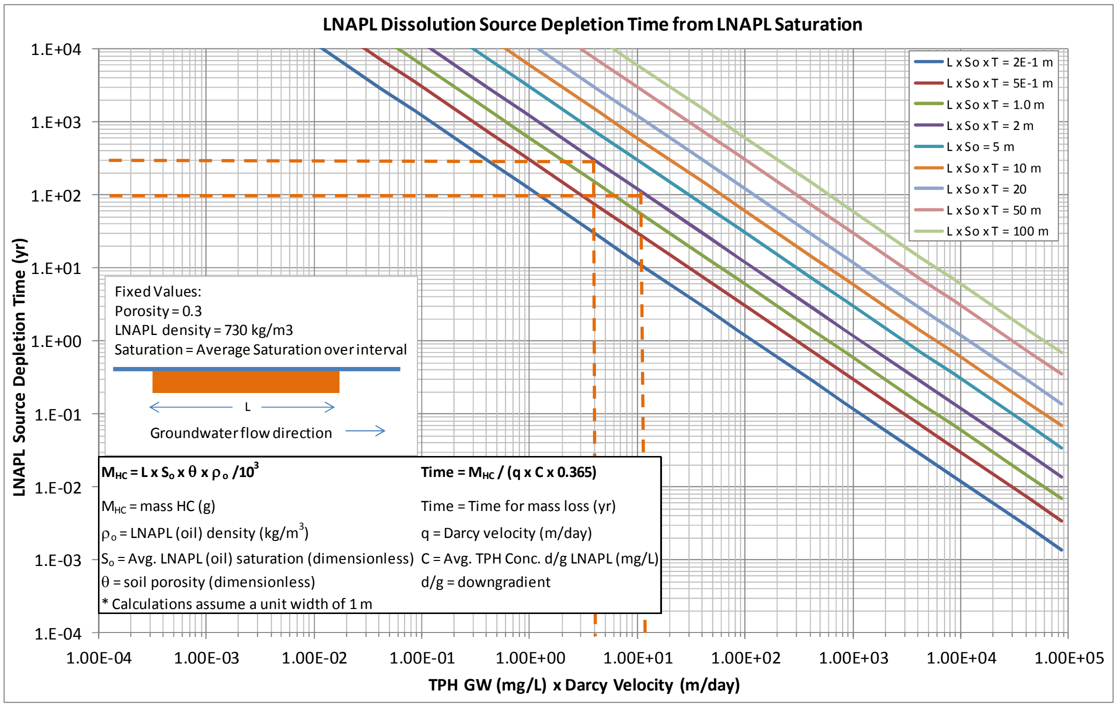


Figure H-3: LNAPL source depletion nomograph from NAPL dissolution model.

4.0 LNAST MODEL

The LNAST model was used to predict groundwater concentrations at the downgradient edge of the LNAPL source zone. The input parameters are provided in Table H-1. The initial source concentrations and mole fractions in the model were based on the average measured concentrations in source zone wells for the first two years of monitoring. Because the screening model using the nomograph method suggested a higher Darcy velocity (38 m/yr) is more appropriate for the site, this estimate was used for the LNAST model simulations. Two different source lengths (in the direction of groundwater flow) were used consisting of 30 m and 90 m with results presented in Figure H-4. The 30 m length simulation was intended to enable comparison to wells in the source area located roughly 30 m from the inferred upgradient edge of the LNAPL smear zone.

The model predictions for a 90 m source indicate that reductions in concentrations are highly dependent on the BTEX compound. For ethylbenzene and xylenes, the timeline for significant reduction to low (<10 µg/L) concentrations is 200 to 300 years (compared to about 100 years for the nomograph method). For a 30 m source, the timeline for these compounds is roughly 100 to 120 years. Compared to the trend analyses, the LNAST model appears to overpredict source depletion times for these compounds based on site data.

5.0 REMFUEL MODEL

The REMFuel model was used to predict groundwater concentrations at the downgradient edge of the LNAPL source zone. The input parameters are provided in Table H-1 and to the extent possible, similar input parameters were used as for the LNAST model. A single source length (in the direction of groundwater flow) of 30 m was used in the simulations with results presented in Figure H-5. The 30 m length simulation was intended to enable comparison to wells in the source area located roughly 30 m from the inferred upgradient edge of the LNAPL smear zone.

The REMFuel model was run with gamma terms of 0, 0.5 and 1.0 For gamma equal to 0, the BTEX concentrations are constant until the source is depleted, which ranges from approximately 3.5 years for benzene to 55 years for ethylbenzene. For gamma equal to 1, the BTEX concentrations decrease exponentially (linear trend on log-plot) but for ethylbenzene and xylenes the model predicts it would take several hundred years for concentrations to decrease to low levels (less than 10 µg/L).

For the REMFuel model using best estimate input parameters, a gamma term of 0.5 to 1 appears to provide for a qualitative best fit to the trend in the concentration attenuation observed; however, the longevity of the LNAPL source and concentrations are significantly overpredicted. It is hypothesized that a possible reason for the difference in model results and data is that certain processes may not be accounted for such as source zone biodegradation and volatilization, or that monitoring well data may not represent source concentrations depending on screen location with respect to the source zone.

6.0 SUMMARY

The trend analysis for wells near to the release location (within about 30 to 40 m of the inferred upgradient edge of the LNAPL smear zone) indicate a significant reduction in BTEX concentrations (i.e., to below DW standards) within about 30 years. It is inferred that based on the significant decrease in concentrations that most of the LNAPL is depleted within this area. Comparison of BTEX concentration results show the influence of the solubility on relative depletion rate of BTEX compounds.

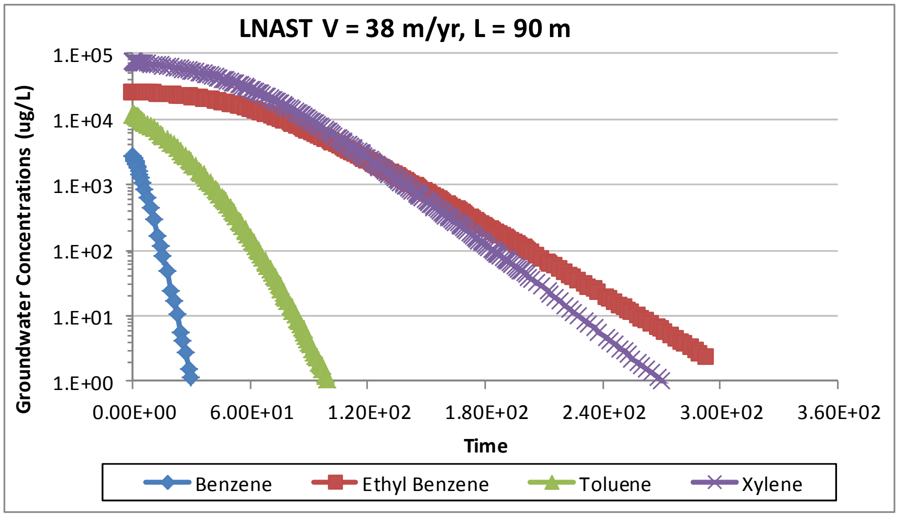
The predicted timelines for LNAPL dissolution from the nomograph method and simple mixing model is 100 to 300 years. It is noted that a very large release occurred at the case study site; typical releases at service stations are smaller.

The LNAST model has the added benefit of simulation of chemical-specific concentrations and results were generally consistent with observed data with respect to much faster depletion of benzene compared to ethylbenzene and xylenes; however, longer timelines for concentration reduction and hence LNAPL dissolution are predicted than indicated by the measured decline in concentrations. The REMFuel model likewise overpredicts the longevity of the source for gamma values greater than zero.

Table H-1: Input Parameter for LNAST and REMFuel Models for Case Study Site #4.

Parameter	Unit	Value	Applicable Models	Comments
Saturated hydraulic conductivity	m/s	6×10^{-4}	L, R	Measured geometric mean
Groundwater hydraulic gradient	-	0.002	L, R	High end of range
Darcy velocity	m/yr	38	L, R	Measured
Total porosity	-	0.3	L, R	Best estimate
Van Genuchten alpha	1/m	25	L	Default coarse sand
Van Genuchten n	-	0.04	L	Default coarse sand
Residual saturation of water	-	0.04	L	Default coarse sand
Field residual saturation of LNAPL	-	0.04	L, R	Best estimate
Method used to calculate LNAPL saturation	-	From residual Saturation	L, R	
Initial thickness of LNAPL	m	1	L, R	Measured
Length of LNAPL zone	m	90, 30	L, R	Measured
Width of LNAPL zone	m	80	L, R	Measured
Oil/water interfacial tension	dynes/cm	52	L	Default
Oil/air interfacial tension	dynes/cm	24	L	Default
Viscosity	cp	0.62	L	Default
Density	g/cm^3	0.73	L	Default
Effective porosity	-	0.25	L	Estimate
Longitudinal dispersivity	m	1.0	L, R	Estimate
Horizontal transverse dispersivity	m	0.1	L, R	Estimate
Vertical Transverse dispersivity	m	0.01	L, R	Estimate
Fraction organic carbon content	-	0.005	L	Estimate
Sigma v	-	0.14	R	Estimate
Vmin	-	0.5	R	Estimate
Vmax	-	1.5	R	Estimate
Number of stream tubes	-	100	R	Estimate

Parameter	Unit	Value	Applicable Models	Comments
Vapour diffusion efficiency	-	0.0001	L	Estimate
Half-life				
Benzene	days	347	L, R	Default
Ethylbenzene	days	65	L, R	Default
Toluene	days	60	L, R	Default
Xylenes	days	150	L, R	Default
Log(Koc)				
Benzene	-	1.77	L	Default
Ethylbenzene	-	3.0	L	Default
Toluene	-	2.06	L	Default
Xylenes	-	2.6	L	Default
Source Concentrations				
Benzene	mg/L	2.78	L, R	Average initial concentrations source zone
Ethylbenzene	mg/L	25.2	L, R	
Toluene	mg/L	11.6	L, R	
Xylenes	mg/L	73.9	L, R	
Mole Fraction				
Benzene	-	0.00156	L	Calculated from above and effective solubility
Ethylbenzene	-	0.186	L	
Toluene	-	0.022	L	
Xylenes	-	0.422	L	
Mass				
Benzene	Kg	25.6	R	Calculated from above
Ethylbenzene	Kg	4153	R	
Toluene	Kg	426	R	
Xylenes	Kg	9419	R	
Retardation Factor				
Benzene	-	2.57	R	Calculated from above
Ethylbenzene	-	27.7	R	
Toluene	-	4.06	R	
Xylenes	-	11.62	R	



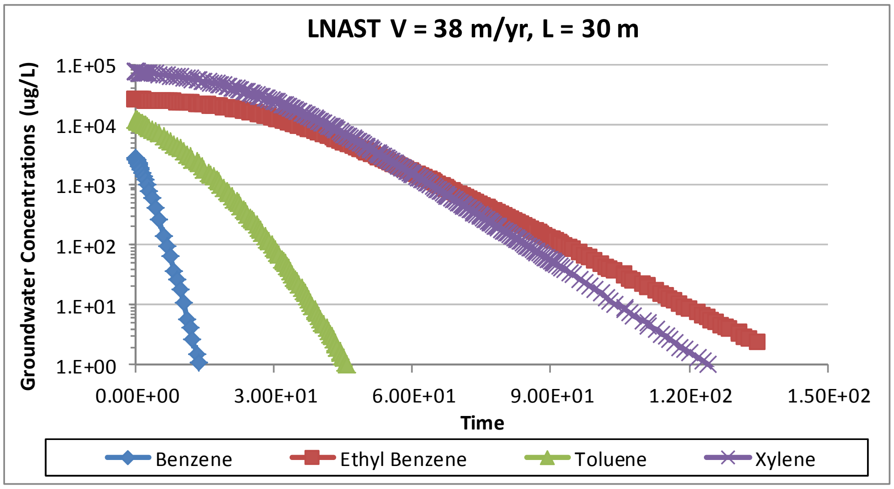
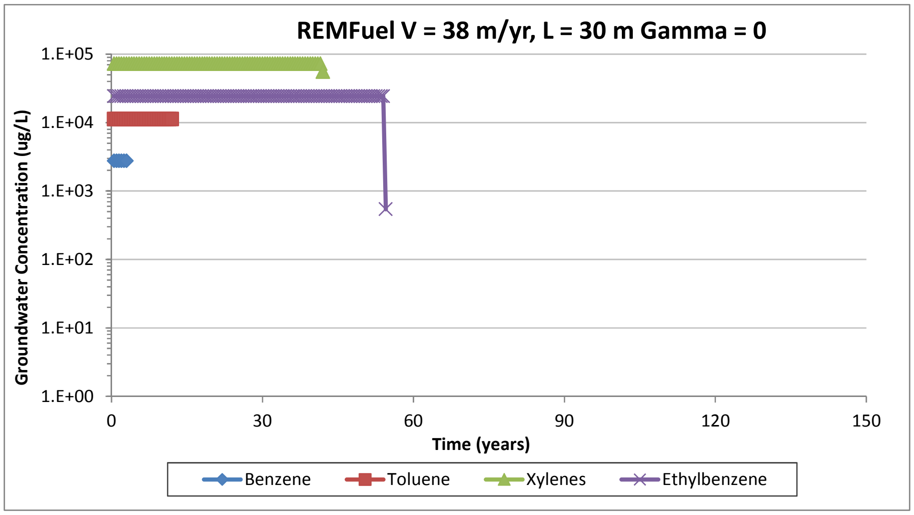
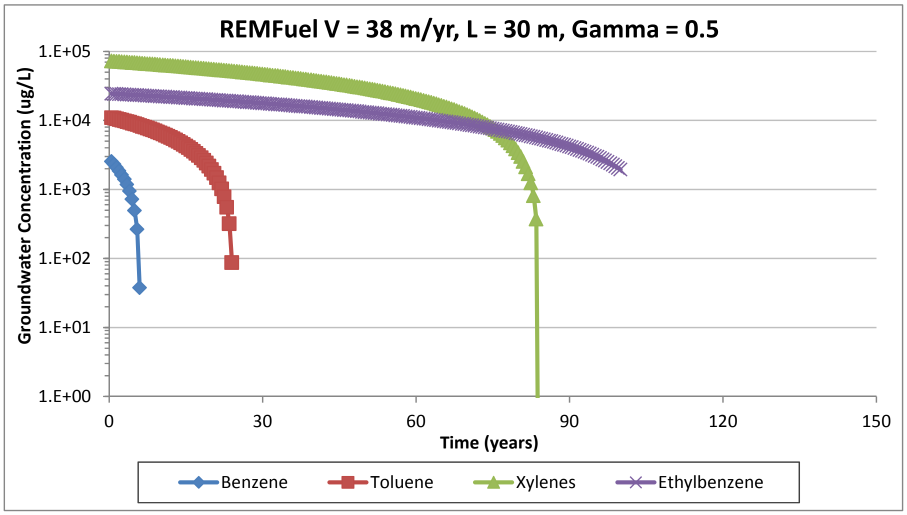


Figure H-4: LNAST model simulations.





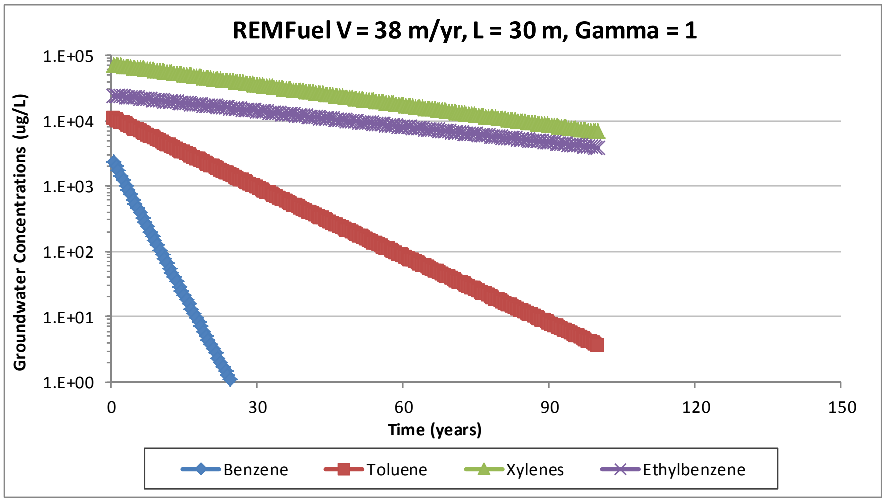


Figure H-5: REMFuel model simulations.

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