Idaho Risk Evaluation Manual for Petroleum Releases

State of Idaho

Department of Environmental Quality

~~July~~January 202~~5~~7

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Abbreviations, Acronyms, and Symbols

AST	aboveground storage tank
ASTM	American Society for Testing and Materials
atm	atmosphere
ATSDR	Agency for Toxic Substances and Disease Registry
AUL	activity and use limitation
BAA	benz(a)anthracene
BBF	benzo(b)fluoranthene
BTEX	benzene, toluene, ethylbenzene, and xylene
CAP	Corrective Action Plan
cc	cubic centimeter
COI	chemical of interest
CSF	cancer slope factor
CSM	Conceptual Site Model
DEQ	Idaho Department of Environmental Quality
EDB	ethylene dibromide
EPA	United States Environmental Protection Agency
EPC	exposure point concentration
EU	exposure unit
g	gram
HI	hazard index
HQ	hazard quotient
IDAPA	Idaho Administrative Procedures Act
IDWR	Idaho Department of Water Resources
IELCR	individual excess lifetime cancer risk
IRIS	Integrated Risk Information System
ISCE	Initial Site Characterization and Evaluation
ITRC	Interstate Technology Regulatory Council
IUR	inhalation unit risk
kg	kilogram
LNAPL	light nonaqueous phase liquid
m^3	cubic meter
MCL	maximum contaminant level
MDL	method detection limit
mg	milligram
MTBE	methyl tert-butyl ether

NA	natural attenuation
NAPL	nonaqueous phase liquid
NCBI	National Center for Biotechnology Information
ND	nondetect
OSWER	Office of Solid Waste and Emergency Response
PAH	polycyclic aromatic hydrocarbon
PEF	potency equivalency factor
POC	point of compliance
POE	point of exposure
PQL	practical quantitation limits
QA	quality assurance
QAPP	Quality Assurance Project Plan
QC	quality control
RCRA	Resource Conservation and Recovery Act
RE	risk evaluation
REDOX	reduction-oxidization
RfC	reference concentration
RfD	reference dose
RNA	remediation by natural attenuation
ROE	route of exposure
RSL	regional screening level
SOP	standard operating procedure
SSL	soil screening level
STATECOMM	State Communications Center
THQ	target hazard quotient
UCL	upper confidence limit
UECA	Uniform Environmental Covenants Act
UST	underground storage tank
VISL	vapor intrusion screening level
VOC	volatile organic compound

Introduction

In July 2025, the Idaho Legislature approved the Idaho Department of Environmental Quality (DEQ) "Rules for Petroleum Release Corrective Action" (IDAPA 58.01.24). This rule requires that substantive revisions to the *Idaho Risk Evaluation for Petroleum Releases Manual* be completed through public participation. This document represents the updated revision~~final version agreed upon through the~~that included public participation involving a series of open meetings and training~~process~~. The manual was developed to supplement the rule in assisting users through the risk evaluation process. Although the manual is guidance and is not enforceable, it does expand upon requirements in the rule that must be followed. Throughout the manual, references to *must* are actions specified in the rule and *should* or *recommended* are optional actions. The manual does not relieve the user from complying with other applicable state or federal laws such as the "Ground Water Quality Rule" (IDAPA 58.01.11), or "Idaho Rules for Public Drinking Water Systems" (IDAPA 58.01.08).

Organization and References

The document begins with a general description of the steps in the risk evaluation (RE) process and is then followed by detailed implementation information for each step. DEQ follows the United States Environmental Protection Agency's (EPA's) risk evaluation process and online risk assessment application. EPA's Risk Assessment website provides the user with numerous documents, a user's guide, tables of applicable screening levels, and access to the online site-specific *Regional Screening Level (RSL) Calculator*. Resources include, but are not limited to, the following:

- *EPA's Regional Screening Levels (RSLs) User's Guide*
- *EPA's Vapor Intrusion Screening Level (VISL) Calculator User's Guide* (EPA 2003)
- *Risk Assessment Guidance for Superfund, Volume I: Human Health Evaluation Manual (Part A) Interim Final* (EPA 1989)
- *Risk Assessment Guidance for Superfund, Volume I: Human Health Evaluation Manual (Part C, Risk Evaluation of Remedial Alternatives) Interim* (EPA 1991)
- Guidance for Data Usability in Risk Assessment (Part A) – Final (section 7.3)
- Office of Solid Waste and Emergency Response (OSWER) *Technical Guide for Assessing and Mitigating the Vapor Intrusion Pathway from Subsurface Vapor Sources to Indoor Air* (EPA 2015a)
- *Technical Guide for Addressing Petroleum Vapor Intrusion at Leaking Underground Storage Tank Sites* (EPA 2015b)

Appendices A-D support the Information in the manual. As dates on the referenced technical documents are subject to change, use the most current versions of the documents.

1 Overview of the Risk Evaluation Process

1.1 Steps in the Risk Evaluation Process

The overall RE process for a site where a petroleum release is discovered and reported to DEQ is illustrated in Figure 1. The process consists of multiple steps and brief descriptions are provided. In some cases, when adequate data are available concerning a release, the owner or operator (as defined in IDAPA 58.01.24.010) of the release site may skip the screening level evaluation and proceed directly to the site-specific RE, which is a more detailed level of evaluation, without formally completing the intermediate steps. In cases where corrective action is known to be required, the owner/operator may proceed with corrective action if they notify DEQ, comply with any conditions imposed by DEQ, and incorporate the corrective action and subsequent risk evaluations into a corrective action plan (CAP) submitted for DEQ's approval (IDAPA 58.01.4.61.06d).

1.1.1 Site Discovery

The RE process begins with the discovery of a petroleum release site. A petroleum release site may be discovered and reported to DEQ under a variety of circumstances. These include, but are not limited to, citizen complaints, investigations conducted as a part of real estate transactions, environmental impacts observed in surface water bodies, and notification of accidents and spills. The owner/operator is responsible for ensuring that DEQ is notified (IDAPA 58.01.24.60).

Upon site discovery, the owner/operator must carefully evaluate the available information to determine whether the site poses any imminent threat to human health or safety, or to the environment. Threats include, but are not limited to, impacts to water wells; vapors or odors in residential and commercial structures; concentrations approaching explosive levels; impacts to a surface water body; and impacts to human health and the environment. If any imminent threats are identified, the owner/operator must call 911, if applicable; take immediate steps to abate the threat; and notify DEQ or Idaho State Communications Center (STATECOMM) immediately (section 2). Documentation of abatement activities and confirmation that imminent threats have been removed should be provided to DEQ. Section 2 provides details for this step.

Upon completing the emergency response action, an initial site characterization and evaluation (ISCE) must be performed. In some cases, when adequate data are available concerning a release, the owner/operator may proceed directly to the site-specific RE. In cases where corrective action is known to be required, the owner/operator may proceed to corrective action if they notify DEQ, comply with any conditions imposed by DEQ, and incorporate the corrective action and subsequent risk evaluations into a CAP submitted for DEQ's approval (IDAPA 58.01.24.61.06d). As a part of the ISCE, media-specific data (for soil, soil vapor, and groundwater media) must be collected to characterize the source. This step is intended to identify the maximum contaminant concentrations for the identified petroleum products in soil and groundwater. Since a site may be a candidate for closure after the completion of the

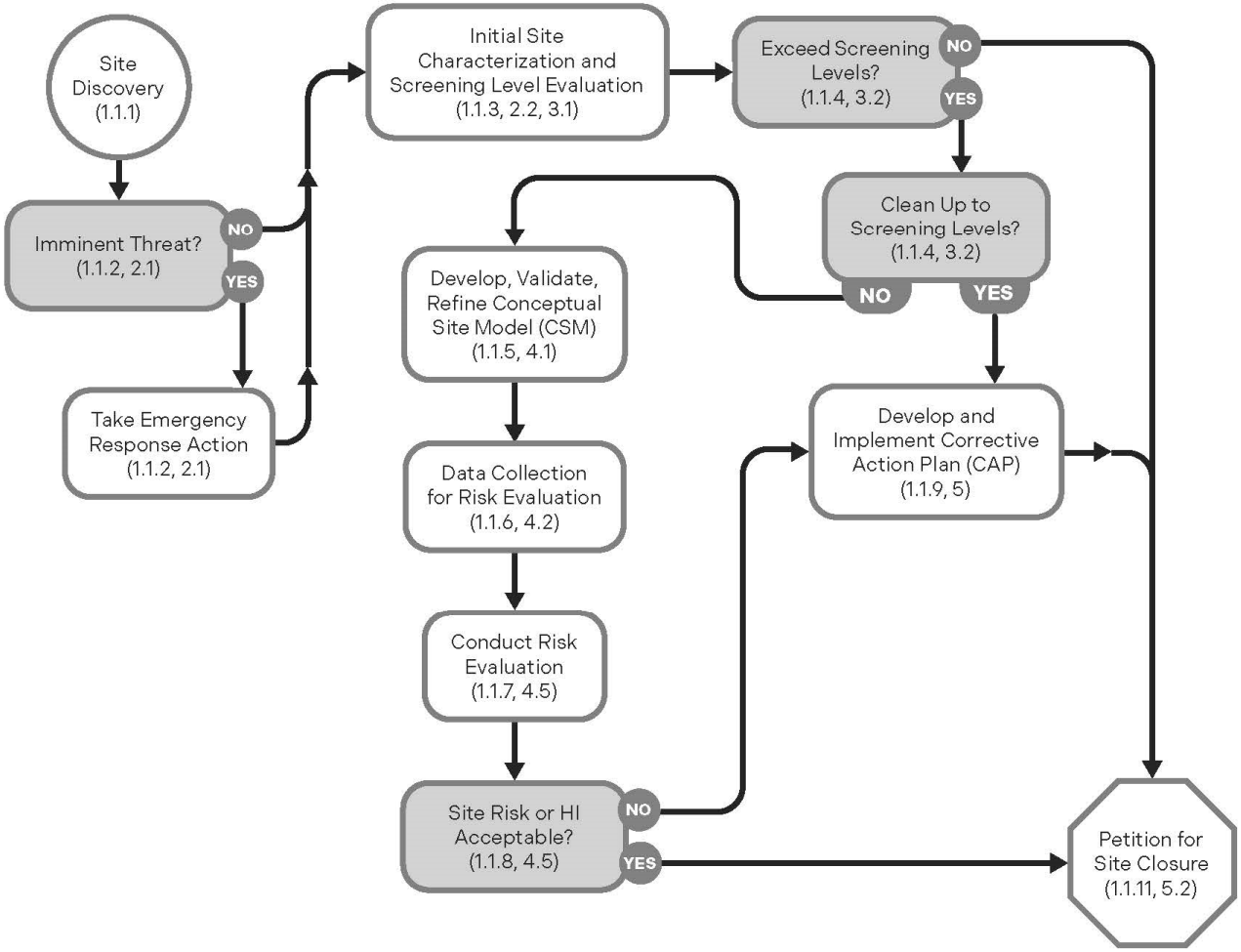


Figure 1. Idaho petroleum release risk evaluation process flowchart. **( ) represent document section.**

screening level evaluation (section 3), it is essential that the data collected at this time identify the maximum media-specific concentrations. Section 2 provides details for this step.

1.1.2 Comparison with Screening Levels

This step involves comparing the maximum media-specific concentration of each contaminant, identified in the ISCE, with EPA's generic regional screening levels. There is a screening level for each contaminant in each media (section 3.1). The screening level is the lowest of the media-specific (soil, soil vapor, and groundwater) risk-based concentrations for the applicable exposure pathways. Screening levels are considered criteria that, if not exceeded (i.e., maximum contaminant concentrations are below the screening levels), will allow unrestricted (residential) use of the property. Since exposure to these low concentrations (below the screening levels) of contaminants does not pose a threat to human health, if the owner/operator meets these criteria, they will not be required to evaluate site-specific exposure pathways and develop a conceptual site model (CSM), and no land use restrictions will be needed on the property.

When DEQ and the owner/operator agree that a petroleum release has been adequately characterized, DEQ will not require any further action of the owner/operator related to the release if the maximum contaminant concentrations in soil, soil vapor, surface water, and groundwater do not exceed the screening levels, subject to other applicable requirements, if any (IDAPA 58.01.24.200). If any of the maximum soil, groundwater, or soil vapor concentrations exceed the screening levels, the owner/operator may either:

- Adopt the screening levels as cleanup criteria and develop a CAP to achieve these levels, or
- Perform a site-specific RE. Sections 3 and 4 provide further details.

1.1.3 Development and Validation of a Conceptual Site Model

If the screening levels are exceeded, and the owner/operator chooses to conduct a more detailed (site-specific) RE, they must first develop and validate a CSM. A CSM provides the framework for the overall management of the site and guides data collection and risk management activities while the RE is performed. The key elements of the CSM include the following:

- Release scenarios
- Source description
- Petroleum chemicals of interest (COI)
- Exposure model that incorporates the appropriate receptors
- Exposure pathways and routes of exposure (ROE)
- Site stratigraphy and hydrogeology
- Spatial and temporal distribution of the petroleum COI

This step validates the CSM based on site-specific data. Section 4.1 provides details for this step.

1.1.4 Identify and Collect Data for Risk Evaluation

Depending on the site-specific conditions, the RE may require collecting additional site-specific data. To prepare for conducting the RE, the owner/operator must review the CSM, identify data gaps, and collect additional data if necessary. This data are used to calculate estimates of site-specific exposure point concentrations (section 4.3.4 and Appendix A~~Appendix B~~) and an estimate of the site-specific cumulative risk (section 4.5) and, potentially, to develop remediation standards using EPA's RSL and VISL calculators. Section 4.2 provides details for this step.

1.1.5 Site-Specific Risk Evaluation

Conducting the RE requires developing site-specific estimates of exposure point concentrations for soil and groundwater, estimating site-specific cumulative risk, comparing these with acceptable target risk levels and, if necessary, developing media-specific remediation standards. Remediation standards are target concentrations developed using EPA's RSL and VISL calculators with a combination of conservative default and site-specific parameters. These concentrations depend on the receptor, media, pathway, and ROE and are developed for each petroleum COI and each media identified in the CSM. This step is discussed in section 4.6.

1.1.6 Comparison with Acceptable Target Risk Levels and Decision Making

Once the site-specific cumulative risk has been estimated, it is compared to acceptable target risk levels, as specified in the rule. If acceptable target risk levels are not exceeded, the site is eligible for closure, subject to other applicable requirements, if any (IDAPA 58.01.24.200). If the site-specific cumulative risk is at or above the acceptable target risk levels, two options are available:

1. Refine the CSM and RE. It is possible that the site-specific cumulative risk is lower than initially estimated and may not pose an unacceptable risk, but this can only be determined with a more refined CSM and RE. Collection of additional data or use of other models may be necessary. Before collecting additional data, DEQ recommends developing a work plan that outlines additional data needs and the overall approach for the refined evaluation. The plan should be submitted to DEQ for review and approval before proceeding with data collection and the evaluation because the DEQ's suggestions may help with completing the required work more efficiently and eliminate the need for resampling. Section 4.7 provides details for this step, including the basic contents of a work plan.
2. Calculate and adopt media-specific remediation standards for each petroleum COI and develop and implement a CAP to achieve these concentrations.

Upon completing the RE, the owner/operator should provide recommendations to DEQ. In most cases, DEQ and the owner/operator will work together to identify the best alternative.

1.1.7 Development and Implementation of a Corrective Action Plan

Based on the results of the RE process, the owner/operator proposes a set of remediation standards and prepares a CAP describing the measures that will be used to achieve the standards, ensuring the long-term protection of human health and the environment. The CAP is submitted to DEQ for approval. The CAP may include a combination of options for active remediation and passive remediation along with limitations on activities and land uses that were assumed in the RE step. Section 5 provides details for this step.

1.1.8 Evaluation and Modification of the Corrective Action Plan

The data collected during CAP implementation must be evaluated by the owner/operator and submitted to DEQ to determine whether the CAP is progressing as anticipated. Modifications to the CAP may be necessary in some circumstances, including (1) identification of significant deviations from the remedial strategy, (2) unacceptable risk levels to receptors, or (3) if data indicate that site cleanup is not progressing at the rate anticipated. In these cases, appropriate modifications to the CAP should be considered and an amended CAP submitted to DEQ for approval.

1.1.9 Site Closure with a Corrective Action Plan

When the regulatory obligations specified in the DEQ-approved CAP have been achieved, the site is eligible for closure. The owner/operator submits a request for closure with documentation that all the work specified in the CAP has been completed and all cleanup criteria have been achieved.

1.1.10 Certification by a Registered Professional

If work is performed that the State of Idaho requires a geologist or professional geologist or professional engineer (Idaho Code § 54-12 and 28) to perform, the owner/operator must employ the use of, and obtain certification from, a geologist or professional geologist or professional engineer registered in Idaho for that work. An example that requires a professional engineer is construction of public works. A professional land surveyor is required for land surveys. Examples that require a geologist or professional geologist review are well design and most assessment, remediation system design, or corrective action that involves the subsurface.

2 Site Discovery and Initial Steps

2.1 Determining Imminent Threats

Once an impacted site has been identified or a release has occurred, the first step is to determine whether contamination poses any imminent threat to human health or the environment. If so, abatement measures must be completed before any other activities. Examples of abatement measures include taking action to prevent further release into the environment, providing an alternate water supply if drinking water supplies are impacted,

evacuating residents/commercial workers if they are or could be exposed to vapors at high concentrations, installing booms on surface water bodies that have a sheen, or ventilating utility facilities where vapors are present. If there is an imminent threat, or uncertainty regarding potential threats, associated with a release, call 911, if applicable, and STATECOMM at 1-800-632-8000 or (208) 846-7610.

Releases that do not pose an imminent threat do not have to be reported to STATECOMM, but do have to be reported to DEQ. Owner/operators must follow the Petroleum Release Reporting, Release Response and Initial Abatement Measures as provided in IDAPA 58.01.24.060 and 061.

2.2 Initial Site Characterization

2.2.1 Site Characterization Introduction

Within the RE process, initial site characterization is performed after any necessary emergency response actions are completed. The overall objective of the initial site characterization is to identify the maximum chemical concentrations on the site in each of the affected media. These maximum concentrations are then compared with screening level criteria to determine the need for any further action.

A brief description of the initial site characterization process is presented below.

2.2.2 Site Description and Adjacent Land Use

The owner/operator must conduct a thorough site reconnaissance and a historical review of site operations to identify sources of contamination on site. Sources may be identified based on knowledge of a known or documented release; location of certain structures that typically represent a contamination source such as petroleum storage tanks, pipes, or pumps; and interviews with current and former site employees who may have knowledge of source areas.

In addition to identifying sources, the owner/operator must collect data related to historic, current, and future land use on and adjacent to the site. A chronology of relevant site activities is often useful.

Based on this information, the owner/operator must identify the type of petroleum that may have been released at the site. Data collected during initial site characterization must follow DEQ's quality management program, quality assurance project plan (QAPP), and standard operating procedures (SOP) or a DEQ-approved QAPP (section 4.2 and section 7.3.

2.2.3 Soil Source Characterization

The owner/operator must collect soil data representative of the release's maximum concentration of petroleum COI. The exact number of samples, the analytical methods used, and the specific technology used to collect data will vary among sites (section 7.3). DEQ

recommends that the owner/operator develop a work plan and have it reviewed and approved by DEQ before beginning the work.

The overall intent of initial site characterization is to identify maximum concentrations of petroleum COI. However, for sites that will likely require further characterization, it may be efficient and cost-effective to collect additional data at this stage of the evaluation. Additional data may be used to identify the nature and extent of contamination and potential for exposure. ~~For example, if contamination is suspected to exist in both surficial and subsurface soil zones, samples representing maximum concentrations in both zones must be collected.~~

2.2.4 Groundwater Source Characterization

In the initial site characterization, if there is evidence of possible groundwater impact from the site release, the owner/operator must collect groundwater samples below or immediately adjacent to the source. For sites that require further characterization, it may be more efficient and cost-effective to install at least three monitoring wells so the magnitude and the direction of groundwater flow can be established.

2.2.5 Documentation of Initial Site Characterization

The owner/operator must document the initial site characterization results in a report submitted to DEQ. The report must include the information outlined in IDAPA 58.01.24.061.03 and DEQ's QAPP and SOP (section 7.3).

3 Screening Level Evaluation

Data collected during the initial site characterization is typically evaluated using screening levels. This evaluation is intended to achieve the following objectives of the screening level evaluation:

- Demonstrate the site or portions of the site do not pose a threat to human health and does not require any further evaluation, and
- Identify areas of the site that need further evaluation.

These objectives are achieved by comparing the maximum site concentrations with the screening level values.

3.1 Screening Levels

The screening levels for the petroleum COIs have been developed by EPA and are found on EPA's website (RSL generic tables and RSL and VISL calculators). The screening levels represent unrestricted use and are risk-based target concentrations developed with the following:

- Assumption that receptors will be residential
- Conservative input parameter values
- Acceptable target risk of 10^{-6}

- Target hazard quotient (THQ) of 0.1

The screening level is the lowest of the media-specific (soil, soil vapor, and groundwater) risk-based concentrations. The screening levels are based on a THQ of 0.1 and assumes multiple COIs with the same toxic endpoint. Most petroleum sites will include multiple COIs with the same toxic endpoint. Each petroleum COI and its associated toxic endpoint is presented in Table 1. The rationale for using a THQ of 0.1 for screening is when multiple contaminants of concern are present at a site or one or more are present in multiple exposure media, the total hazard index (HI) could exceed 1.0 if each were screened at the THQ of 1.0. If screening only one contaminant, a THQ of 1.0 may be used, but consult DEQ (section 4.5).

~~Specific exposure factors and models used to develop screening levels are presented in Appendix A and Appendix D.~~ Screening levels are the lowest target concentrations for the following exposure pathways and ROE for soil, soil vapor, and groundwater.

Specifically, screening levels for soil are the lowest of the following concentrations:

- ~~Surficial and subsurface s~~Soil concentrations protective of exposure via groundwater ingestion at maximum contaminant levels (MCLs) or risk-based concentrations at the downgradient edge of the source (U~~u~~se the Summary Table, Protection of Groundwater soil screening level [SSL]), MCL-based SSL column if an MCL for that COI exists or risk-based SSL column if an MCL does not exist. ~~, but t~~The RSL calculator can also be used.). The RSL calculator uses the dermal, ingestion, and inhalation pathways to derive the risk-based SSL, however, users may independently calculate a risk-based SSL by using the Soil to Groundwater SSL equation on the RSL Calculator website and the lowest of the Ingestion SL TR=1E-06 and Child Ingestion SL THQ=0.1.~~, or~~
- ~~Surficial and subsurface s~~Soil concentrations protective of combined ingestion, dermal contact, and outdoor inhalation exposures for a residential scenario (use the Summary Table, Resident Soil column).

Screening levels for groundwater are the lowest of the following concentrations:

- MCLs for chemicals that have them or calculated values for ingestion of water in a residential scenario (Use the Summary Table (TR=1E-06 THQ=0.1); MCL column if an MCL for that COI exists~~,~~. Where no MCL exists, use the ~~Tap Water column where no MCL exists. However, EPA's tap water screening level is based on dermal, ingestion, and inhalation so the Ingestion column in the~~ Resident Tap Water table (TR=1E-06 THQ=0.1), Carcinogenic Target Risk Ingestion column or Noncancer Ingestion Child column if carcinogenic doesn't exist ~~can also be used~~. The RSL calculator can be used for all scenarios.).~~, or~~
- Groundwater concentrations protective of exposure via indoor inhalation of vapors emanating from groundwater for a residential scenario (use the VISL calculator rather than the EPA Summary Table for Resident Air and Industrial Air). If the Target Groundwater Concentration in the VISL calculator is lower than the chemical's respective MCL, vapor intrusion may pose an unacceptable risk. Consult with DEQ to determine if additional factors may be considered and/or if the MCL may be used.

Screening levels for soil vapor are protective of exposure via indoor inhalation of vapors emitted from contaminated soil or groundwater. There are screening levels for ~~both~~the "Target ~~s~~Sub-~~s~~Slab and N~~n~~ear-source ~~s~~Soil ~~g~~Gas Concentration" ~~using~~in EPA's VISL calculator.

Because of the methods and assumptions used in developing the screening levels and the current limitations of laboratory analytical methods, the calculated screening levels may be lower than the practical quantitation limit reported by a laboratory for selected chemicals. In these situations, site-specific review by DEQ will be required based on the criteria provided in IDAPA 58.01.24.500 and Appendix D. Screening levels for chemicals without an MCL are based on conservative assumptions about the release and transport of contaminants in the subsurface. With justification, many of these parameters can be changed by the user in the calculator's site-specific mode.

Table 1. Soil, groundwater, and soil vapor chemicals of interest, and associated toxic endpoints.

Chemical	Gasoline/ JP-4/ AVGas	Diesel/ Fuel Oil No. 2/ Kerosene/Jet Fuels (Jet A, JP-5, JP-8)	Fuel Oil No.4	Carcinogen	Mutagen	Target Endpoints Chronic Exposure	Source
Benzene	X	X		C	No	Hematologic system, reproductive and developmental	ATSDR
Toluene	X	X		NC	No	Central nervous system	ATSDR
Ethylbenzene	X	X		PC	No	Kidney, ear (irreversible damage inner ear)	ATSDR
Xylenes (mixed)	X	X		NC	No	Nervous system, Lungs, skin	ATSDR
1,2 Dibromoethane (EDB)[a]	X1			PC	No	Reproductive, lung, skin, nervous system	ATSDR
1,2 Dichloroethane (EDC)[a]	X1			NC	No	Nervous system, liver, kidneys	ATSDR
Methyl Tert-Butyl Ether (MTBE)	X			NC	No	Nervous system, liver, and kidneys	ATSDR
Acenaphthene[b]		X	X	PC	No	Kidneys, liver	NCBI 2024
Anthracene[b]		X	X	NC	No	Kidney, breast	NCBI 2024
Benzo(a)pyrene[b]		X	X	PC	Yes	Lungs, liver, stomach, skin	ATSDR
Benzo(b)fluoranthene[b]		X	X	PC	Yes	Skin, lungs	ATSDR
Benzo(k)fluoranthene[b]		X	X	PC	Yes	Skin, lungs	ATSDR

Chemical	Gasoline/ JP-4/ AVGas	Diesel/ Fuel Oil No. 2/ Kerosene/Jet Fuels (Jet A, JP-5, JP-8)	Fuel Oil No.4	Carcinogen	Mutagen	Target Endpoints Chronic Exposure	Source
Benz(a)anthracene		X	X	PC	Yes	Lung, stomach skin, liver, bone	ATSDR
Chrysene[b]		X	X	PC	Yes	Lung, stomach, skin	ATSDR
Fluorene[b]		X	X	NC	No	Lung, stomach, skin	ATSDR
Fluoranthene[b]		X	X	NC	No	Lung, stomach, skin	ATSDR
Naphthalene	X	X	X	PC	No	Lungs, blood, eyes, liver, central nervous system, skin	EPA
Pyrene[b]		X	X	NC	No	Kidney	EPA

a. Leaded only
b. Vapor intrusion is not applicable because there is no inhalation toxicity information and/or the chemical is not sufficiently volatile and toxic to pose an inhalation risk from a soil or groundwater source.
Notes/Sources: Agency for Toxic Substances and Disease Registry (ATSDR 2024); National Center for Biotechnology Information (NCBI 2024a,b); United States Environmental Protection Agency (EPA 1990, 1998)

3.2 Comparison of Site Concentrations with Screening Levels

If the maximum site concentration does not exceed the screening level for any petroleum COI in any media, the site is eligible for closure subject to other regulatory obligations (IDAPA 58.01.24.200) and the owner/operator may request DEQ approval for site closure. If the maximum site concentration for any petroleum COI exceeds the screening level, the owner/operator must select one of the following options:

1. Adopt screening levels as remediation standards and develop a CAP (section 1).
2. Perform a more detailed, site-specific RE.

If option 1 is chosen, the owner/operator must submit a report that includes the information outlined in IDAPA 58.01.24.061.03 and DEQ's QAPP and SOP (section 7.3). The owner must then submit a CAP that includes the information outlined in IDAPA 58.01.24.061.06 and section 5.

If option 2 is chosen, further details on site-specific risk evaluations are in the following sections. The soil to groundwater medium in the RSL Calculator does not have a risk output and the risk option will become disabled when selected.

4 Site-Specific Risk Evaluation

A site-specific RE is needed only if the owner/operator chooses not to use the default screening levels as the remediation standards.

Conducting a site-specific RE requires completing several steps: (1) developing a CSM, (2) identifying the chemicals present in environmental media, (3) assessing exposure and exposure pathways, (4) assessing the toxicity of the petroleum COIs, and (5) characterizing human health and ecological risks. This section describes each of these steps and provides the suggested format for some of the deliverables (mostly reports) that assist in developing and documenting the evaluation.

4.1 Conceptual Site Model

A CSM provides an overall understanding of the site and a CSM report can be a convenient format for compiling all the relevant data associated with a release. The CSM provides a framework for the entire project and identifies specific data needs (correct quality and quantity of data). A CSM is necessary to develop any data collection work plan and is also an important communication tool for regulators, owner/operators, and stakeholders.

In addition to basic site information (section 4.1.1), three key elements must be included in the CSM. Each element will require certain types of data to validate the CSM. The amount of data required is typically based on site-specific considerations. The CSM is a dynamic entity that should be revisited and potentially refined any time additional data is collected for a site. The resulting CSM refinements must be incorporated, if necessary, into the RE:

- **Sources**: Contaminant source areas (nature, magnitude, and extent of release) and COI (section 4.1.2).
- **Exposure Pathways**: Release, fate and transport mechanisms, exposure pathways, and ROE (section 4.1.3).
- **Receptors**: Characteristics of current and reasonably future land uses and receptors (section 4.1.4).

More detailed information on these elements is provided below and in the sections on data requirements (section 4.2) and exposure assessment (section 4.3). The OSWER *Technical Guide for Assessing and Mitigating the Vapor Intrusion Pathway from Subsurface Vapor Sources to Indoor Air* (EPA 2015a) discusses developing a CSM for vapor intrusion.

4.1.1 Site Characteristics

As described below, basic site characteristics must be included in the RE.

4.1.1.1 Site History and Map

The CSM must include a comprehensive chronology of events including remediation projects, tank removal activity, and reported releases. The chronology of events must be clearly and accurately documented.

All maps should be made to scale, with a bar scale and a north arrow. As appropriate, multiple site maps must be prepared to show sample collection points and locations of various site structures. A detailed facility map showing the layout of underground storage tanks (USTs),

aboveground storage tanks (ASTs), pipes, loading and unloading areas, sumps, paved and unpaved areas, and canopy buildings must be prepared. A second facility map must be prepared to show locations of all on-site monitoring wells, water use wells, soil borings, soil vapor extraction wells, and soil excavation areas. All on-site structures must be clearly identified.

4.1.1.2 Ground Surface Conditions

Before conducting an RE, the owner/operator and any other involved parties should make a site visit and walk through. Document areas of the site that are paved, unpaved, landscaped, or covered with buildings and note the type, extent, slope, and general condition of the ground surface and current land uses.

4.1.1.3 Location of Utilities on and Adjacent to the Site

Due to the potential for preferential flow of contaminated groundwater and vapors into underground utility lines and conduits, a thorough documentation of the location of and potential impacts to underground utilities must be performed. Utilities may include phone lines, water lines, sanitary sewers, storm sewers, and natural gas lines. A combination of site observations, knowledge of buried utilities, and discussions with utility representatives and the site owner should reveal the utility locations.

At a minimum, the following activities must be performed:

- Locate all underground utility lines and conduits within the area of known or potential soil and groundwater impact, both on site and off site, where the release may have migrated, or may migrate in the future.
- Determine the direction of flow in the utilities (water, storm water, and sewage).
- Identify utility lines/conduits on a base map that illustrates the extent of soil and groundwater impacts.
- Determine depth of utility lines/conduits relative to the depth of groundwater. Seasonal fluctuations of groundwater levels must be carefully evaluated. As appropriate, a cross-sectional diagram should be provided illustrating the depth to groundwater and the locations and depths of the lines/conduits.
- Determine any past impacts to utilities and any pertinent complaints that may have been previously filed with DEQ.

4.1.1.4 Existing Structures

The location, condition, and construction characteristics of each structure on and adjacent to the site should be described.

4.1.2 Contaminant Source Areas

This element of the CSM must include a discussion of the nature, location, timing, and magnitude of petroleum products spilled at the site. It is important to understand the location and timing of past spills and releases in making decisions regarding assessment needs related to current releases. The petroleum COI must be determined. Any actions performed as a part of

emergency response must be delineated and their impact on the source evaluated. The residual size of the source after any emergency or interim actions must be determined.

Knowledge about the nature, magnitude, and extent of the release is necessary to identify the petroleum source in soil and/or the groundwater at the site as well as to identify the petroleum COIs. The following information regarding a release, if available, is critical:

- Release location
- Release quantity
- Petroleum product released
- Interim corrective action measures performed

Release-related information can be obtained by reviewing inventory records, interviewing current and past employees, and checking any spill incident reports filed with DEQ. Information related to site activities can also identify source location and petroleum COIs.

4.1.2.1 Location of Release

The location of the release defines the source of the petroleum that is in the soil and potentially the groundwater. Release locations include, but are not limited to, corroded or damaged tanks, pipe bends and joints, dispensers, and loading and unloading areas.

The owner/operator must review operational history to determine the location of the source. The assessment should focus on the identified release area; however, the exact location and timing of the spill source area may not be known. In these cases, soil and groundwater sampling must be used to identify the extent (vertical and horizontal) of residual soil and/or groundwater source. The exact number and location of necessary samples must be determined on a site-specific basis using professional judgment and in consult with DEQ. DEQ may have information that can help the owner/operator improve the overall efficiency of sample collection or the entire RE and eliminate or reduce the need for resampling.

4.1.2.2 Quantity of Release

An estimate of the amount released may help evaluate the severity of the impact and extent of contamination, and may help in planning site characterization measures. Estimation of release quantities is typically based on inventory records.

4.1.2.3 Chemicals of Interest and Spatial and Temporal Trends

This section must include a discussion of chemicals detected in each media and their spatial and temporal distribution. Contour maps indicating concentrations of individual petroleum COIs may be useful. Graphs of petroleum COI groundwater concentrations in individual wells and concentration along the flow line (concentration versus distance plots) may also be useful. Based on data collected over time, it should be determined whether the chemical concentrations are stable, declining, or expanding.

When specific petroleum products are spilled or released, the petroleum COIs must be identified. Evaluation of nonpetroleum chemicals in addition to those in IDAPA 58.01.24.800 (Table 1) may be required by DEQ when there is a reasonable basis for site-specific information. DEQ demonstrates a reasonable basis through documentation of releases or suspected releases of other nonpetroleum chemicals. The environmental behavior (mobility, persistence, biodegradation, and intermedia transport) of the petroleum product and its adverse environmental and human health effects depend on chemical properties and their concentrations in the petroleum product.

If a release can be identified as a single petroleum product based on a documented release, free product analysis, or location of impact (e.g., tank bottom of a particular product tank), only the COIs for that petroleum product need to be analyzed. If the product released cannot be conclusively identified, DEQ recommends analyzing monitoring samples for all petroleum COIs associated with the products suspected to have been stored at the site. Additional assessment may be required to identify the source of the release.

If previously collected data did not include all suspected site petroleum COIs, additional sampling may be necessary for petroleum COIs before a RE can be performed.

4.1.3 Exposure Pathways and Transport Mechanisms

This section of the CSM describes site characteristics and mechanisms that influenced or will influence the release, fate, and transport of chemicals of interest and determines which exposure pathways and ROE will be most likely to occur.

4.1.3.1 Site Stratigraphy and Hydrogeology

The owner/operator must conduct a review of published literature and any investigations conducted on adjacent sites to determine regional hydrogeology, soil types, and aquifer characteristics. This evaluation determines the type and depth of aquifers in the area and whether they are confined, semiconfined, or unconfined. Understanding regional characteristics helps the owner/operator to efficiently collect site-specific soil and groundwater information. The CSM must include a detailed discussion of site-specific stratigraphy and hydrogeology. Site stratigraphy can be determined based on boring logs and an adequate number of geologic cross sections.

The hydrogeologic discussion must include estimates of horizontal and vertical hydraulic gradients, seasonal variations in groundwater elevations and flow direction, and hydraulic conductivity of relevant water-bearing zones. How these characteristics may influence the fate and transport of chemicals to potential receptors should be discussed.

The survey should also locate potentially impacted surface water bodies located within one-half mile of the site. If a surface water body is identified, information including the type (perennial or intermittent), water flow rate, flow direction, depth of water, width or surface area of the water body, and water use must be provided. Indicate the location of the water body on an area map.

4.1.3.2 Complete Exposure Pathways and Routes of Exposure

A complete exposure pathway involves a source of petroleum products, release and transport mechanisms, ROE, and potential receptors. The definition of complete exposure pathways starts with knowledge of the release, petroleum COIs, and site physical conditions (section 4.1.3.1), then combines these with assumptions about land use and receptors. Exposure pathways and ROE are described and discussed in more detail in section 4.3.3.

The CSM must identify each of these components in its descriptions of exposure pathways. One example of a common exposure pathway is leaching of petroleum chemicals from a gasoline release in soils (release) to the groundwater with subsequent transport (fate and transport) to a residential well where water is extracted for drinking water and ingested by residents (land use and receptors). Another example is volatilization of petroleum chemical vapors from a soil source with subsequent transport through the soil and into the air in an occupied structure where the vapors are inhaled.

Defining the complete or potentially complete exposure pathways and ROE in a CSM involves identifying the locations where exposure to petroleum chemicals can occur and the media of concern at those locations. These known or potential exposure locations are called exposure units. The exposure unit for each complete pathway and receptor must be described. The exposure unit may consist of a specific location (e.g., well) or an area (e.g., parcel) over which receptors move. For large sites or where impacts of the release have moved off-site, it may be necessary to subdivide the site into multiple exposure units.

Exposure pathways defined in the CSM are subsequently used in the exposure assessment phase of the RE (section 4.3).

4.1.3.3 Protection of Groundwater

During CSM development, it is assumed that groundwater may be used for drinking water. Consequently, if groundwater is not remediated to levels suitable for ingestion, the CAP must also include provisions in the final remedy for implementing limitations on activities and land uses. Such limitations are achieved through environmental covenants (activity and use limitations [AULs]) to prevent exposure via groundwater ingestion throughout the horizontal and vertical extent of the plume that has concentrations exceeding the RSL for groundwater ingestion.

The CSM, as it relates to the use of groundwater, must include characterization and evaluation of the following groundwater aspects.

- The current and historical use of groundwater for drinking water or irrigation. The location and approved use of existing groundwater wells within a one-half mile radius from the release point at the contaminated site.
- The potential for communication between the impacted groundwater and other groundwater-bearing zones or surface water.
- The location of delineated source water protection areas for public drinking water systems.

This information, along with other data collected for the evaluation, will be used to determine if groundwater ingestion is a complete exposure pathway in the CSM, and will guide the selection and use of appropriate remedial target concentrations, measures, time frames, and compliance conditions.

A water well survey must be conducted to identify all water use wells within a one-half mile radius. Information sources include the United States Geological Survey, Idaho Department of Water Resources (IDWR), water system operators, and local residents. Well characteristics including depth, water use, and screened interval must be documented. It is necessary to identify any dewatering wells located within a 1,000-foot radius of the site (or greater if the groundwater plume is extensive).

Land use considerations include, but are not limited to, the following:

- Current zoning and land use. Consultation with local planning and zoning officials regarding future land use planning direction and interpretation of planning and zoning policies.
- Land use development trends. Conversion of agricultural land to residential land uses requires development of drinking water sources. The proximity of these conversions to urban centers and available public drinking water supplies must be taken into account.
- Local ordinances that include agreements with IDWR governing well drilling or state-designated restrictions or specifications for constructing wells into groundwater in a locality for drinking water purposes.
- Existence of source water assessment delineations and source water protection plans and ordinances associated with public drinking water supplies.
- Availability of alternative water supplies.

4.1.4 Land Use and Receptors

This portion of the CSM describes the current and future assumptions about land use as they relate to identifying potential receptors. The identification of land uses includes both the site of the release and adjacent properties that may be impacted by the release.

4.1.4.1 Land Use

Evaluating current and reasonably future land uses at and adjacent to the release site is a critical component when determining potential exposure points, exposure pathways, receptors, and exposure factors during the RE process and when determining cleanup concentrations.

Residential land use generally requires lower target concentrations. Cleanup to residential standards will usually allow unrestricted land use. Whenever assumed land use is other than residential and cleanup is not to residential standards, DEQ will require that an AUL be imposed on the property through the use of an environmental covenant.

Residential land uses include use by sensitive subpopulations (e.g., children, older adults, pregnant women). Examples of land uses with sensitive subpopulations include but are not

limited to hospitals, nursing homes, schools, childcare centers, farms with houses, and any other areas/structures with population groups considered sensitive.

The owner/operator must submit to DEQ illustrated land use maps clearly identifying current land uses at the site and the adjacent properties. One map must clearly show the area within one-half mile of the known or estimated extent of contamination. At sites where there is likelihood that the extent of impacts may be greater, due to the magnitude of the spill or other site-specific conditions, a land use map covering the entire impacted and potentially impacted area is necessary. A walking land use survey should be conducted for the area within a 500-foot radius of the source, with an emphasis on the downgradient direction and potential off-site impacts. The survey should clearly identify the following: schools, hospitals, residences (apartments, single-family homes, and others), day care centers, nursing homes, and types of businesses. In addition to this survey, efforts should be made to identify structures with basements (which may enhance the transport of contamination) in areas in proximity to the source and where site conditions warrant it, including where shallow groundwater or nonaqueous phase liquid (NAPL) is present. The map should also identify groundwater wells, surface water bodies, parks, recreational areas, wildlife sanctuaries, wetlands, and agricultural areas.

Current land use refers to land use as it exists today and can be determined by a site visit. A site visit should identify homes, playgrounds, parks, businesses, industries, or other land uses at, and in proximity to, the release site. As appropriate, state or local zoning boards; the United States Census Bureau; zoning, topographic, land use, housing and other types of maps; and aerial photographs can provide information for determining land use.

Undeveloped land is considered residential unless the owner/operator develops and implements an AUL as a part of a DEQ-approved CAP.

The exposures to be evaluated in a RE can depend upon the activities that could occur under future uses of land and groundwater at the site. For example, consider property that is currently used as farmland. If the impacted farmland includes a residence, the current land use is residential. However, if the owner/operator provides information establishing clear plans to develop the residence into a nonresidential building in the near future, the future use may be evaluated as nonresidential but will still require an AUL on the property.

While evaluating future land use presents uncertainties, DEQ identified certain factors that assist in this evaluation. These factors include, but are not limited to, local zoning ordinances; knowledge of current land use and changing land use patterns; zoning decisions; community master plans; interviews with current property owners; nonresidential appraisal reports; proximity to wetlands, critical habitat, and other environmentally sensitive areas, such as source water protection areas; and the use of remedial action institutional controls at a site.

Site characterization includes a determination of the on-site and off-site areas of impact. These areas are considered in determining the pathway-specific exposure units for each type of receptor. Exposure units are discussed in more detail in section 4.3 and Appendix B.

4.1.4.2 Receptors

The objective of the RE is to quantify the adverse health effects to current and potential future receptors both on site and off site. These terms are defined as follows:

- On Site—The area located within the legal property boundaries where the source of the release is located. Within those boundaries, this includes soil, groundwater, surface water, and air. Adjacent property purchased after the release is considered off site.
- Off Site—The areas of concern located outside the boundaries of the property where the release source is located. Outside of the property boundaries, this includes soil, groundwater, surface water, and air.

Risk is evaluated for various receptors depending on the specific exposure route, and whether the petroleum COI is noncarcinogenic, carcinogenic, or carcinogenic with a mutagenic mode of action. The EPA RSL Calculator User's Guide explains various human receptor types (resident, composite worker, outdoor worker, indoor worker, construction worker, recreator), exposure routes, exposure durations for the receptors, and how some chemicals and exposure route risk calculations incorporate modifications based on exposure occurring at different life stages.

4.1.4.3 Ecological Risk Considerations

In addition to identifying potential impacts to human receptors, the CSM should identify potential exposure pathways where a release may impact sensitive habitats, such as wetlands, surface water bodies, or other ecologically significant environments near the site, and where wildlife may be potential receptors.

Threatened and endangered species that may be exposed to site-specific chemicals should be identified. Note that within the RE process, protection of surface waters and streams is independent of an ecological RE. As appropriate, a walking survey in the vicinity of the site may be necessary to identify ecological receptors.

Contact DEQ to obtain additional guidance on these issues.

4.2 Data Requirements and Evaluation

Once the CSM has been developed, an evaluation of data collection needs, data quality needs, and data collection methodology must be conducted. Depending on the amount and complexity of the proposed data collection effort, a work plan may be needed to guide the data collection process. Section 4.7 discusses suggested content for this work plan.

This section describes general data collection objectives and requirements for the RE process, including quality assurance/quality control (QA/QC) considerations to ensure the data collected is of sufficient quality and quantity to meet desired objectives; the categories of data necessary to meet these objectives; and data collection techniques.

Data collection objectives for RE include, but are not limited to, the following:

- Accurately characterize the magnitude, nature, and extent of contamination, including the characterization of petroleum chemical concentrations for all impacted media, as appropriate.
- Allow the development and/or validation of an accurate CSM.
- Develop estimates of risks posed by the release.

4.2.1 Data Collection Planning

Data collection planning involves a careful review of all available site information and data for its suitability in the RE. This process, in the context of the CSM, must identify any data gaps with the goal of determining the types, locations, quality, and numbers of samples or measurements needed.

Depending on the stage the RE process is in for a given site, the relative importance and specific data requirements of each objective described above will vary. The goal of data collection is to efficiently reduce uncertainty in those areas that contribute the most to potential or actual risk and for which the greatest uncertainty exists.

For example, it may be determined through the CSM that vapor intrusion represents the largest potential source of risk at a site, but little is known about subsurface conditions that may impact exposure point concentrations and only soil or groundwater data are available. To more realistically model this exposure pathway, it may be most effective to better characterize subsurface stratigraphy and properties, document the conditions supporting biodegradation, and collect soil vapor data.

At many impacted sites, data collection efforts may have been conducted multiple times over an extended period of time. For example, interim corrective action measures may have been undertaken before planning for the RE. Soil and groundwater data collected before these activities may not represent current conditions and generally should not be used in the RE. At such sites, collecting additional soil and groundwater concentration data may be needed after completing interim corrective measures.

The exact number of samples required is a site-specific decision based on the balance between cost and representativeness and requires professional judgment and expertise. Numerous tools are available to assist in estimating the number of samples required for statistical analysis, but none provide a definitive number and statistical analysis may not be practical in many cases. These tools include, but are not limited to, data quality objectives and statistical and geostatistical evaluation. Section 7.1 provides references on developing and completing data collection efforts.

4.2.2 Quality Assurance/Quality Control Considerations

The RE process relies on site-specific data to make decisions related to the magnitude of site risk, nature and extent of remedial activity, and site closure. The data must be reliable, representative, complete, and of known quality.

To ensure the data is of appropriate quality, QA/QC activities must be applied to all environmental data collection activities throughout the RE process (site characterization, risk evaluation, remediation implementation, and monitoring).

While the level of QA/QC applied to data collection efforts will vary (depending on factors such as site complexity, size of the release, and the immediacy of the response) all the elements of QA/QC described in DEQ's quality management program, QAPP, and SOP or DEQ-approved QAPP (section 4.2 and section 7.3) must be followed. This process allows adequate review of the quality of the data used in the analysis.

If a work plan is submitted to DEQ for approval, it should include a project-specific QAPP. The QAPP documents the QA/QC procedures applied to various aspects of the project to ensure the data obtained are of the type and quality required for decision-making.

EPA developed guidance for developing QAPPs, and DEQ developed an internal QAPP template that may be restructured for external use (section 7.3).

The QAPP is implemented during the data collection process. Problems can be identified and corrected at this stage. The impact of field and laboratory techniques and sampling and analysis conditions on data quality are determined using field and laboratory QC samples and periodic audits. Oversight and corrective action can prevent improper procedures or techniques from continuing.

Data verification and validation should be performed to validate data quality and usability. Data verification and validation depends on compliance with field and laboratory procedures for sample collection, identification, handling, preservation, chain-of-custody management, shipping, analysis, and reporting. EPA and DEQ provide several guidance documents to assist in performing data verification and validation (section 7.3).

4.2.3 Documentation of the Data Collected

Once data have been collected, a field investigation report must be prepared and follow DEQ's quality management program, QAPP, and SOP or a DEQ-approved QAPP (section 4.2 and section 7.3).

4.2.4 Data Collection Methods

The common categories for collecting data for the RE include the following:

- Vadose zone soil characteristics
- Saturated zone characteristics
- Distribution of petroleum COIs in soil, soil vapor, groundwater, and surface water bodies

EPA developed default values for many of the vadose and saturated zone characteristics that affect the fate and transport of petroleum COIs. These values are presented in the RSL Calculator User's Guide and tables. The default values can be used or site-specific values can be established.

4.2.5 Vadose Zone Soil Characteristics

The vadose zone or unsaturated zone soil is the media through which petroleum COIs can migrate to the groundwater and vapors can move upward to the surface and into an enclosed space. Characteristics of vadose zone soils have considerable impact on risk estimates and target concentration calculations. Relevant vadose zone characteristics include the following:

- Vadose zone thickness and depth to groundwater
- Bulk density
- Porosity
- Water and air content
- Fractional organic carbon content

Additional site-specific, exposure pathway-specific parameters that may be valuable to measure include the following:

- Vapor permeability, effective diffusion coefficient, and building characteristics where indoor inhalation is a potentially complete exposure pathway
- Infiltration rates for developing a detailed evaluation of the potential for leaching to groundwater

4.2.5.1 Thickness of Vadose Zone and Depth to Groundwater

Vadose zone thickness is determined from boring logs. This thickness is the distance from the ground surface to the depth at which the water table is encountered, less capillary fringe thickness.

Depth to groundwater is used in estimating vapor emissions from groundwater. For indoor inhalation, use the depth to groundwater below the *floor* of an existing structure of concern or the most likely location of a future structure.

For sites with considerable seasonal fluctuation in water table level, depending on the data available and the nature of the fluctuations, a yearly average depth or a time-weighted depth may be used. The vadose zone depth that is estimated should also form the basis for selecting soil samples used in the evaluation of subsurface soil vapor emissions to indoor air (*Technical Guide for Addressing Petroleum Vapor Intrusion at Leaking Underground Storage Tank Sites* [EPA 2015b]). Shallower water table depths often result in groundwater target levels set at lower concentrations to be protective of inhalation exposure pathways.

4.2.5.2 Porosity

Porosity is the ratio of the volume of voids to the total undisturbed field volume of soil. Many laboratories use dry bulk density and specific gravity data to determine porosity using Equation 1~~Equation 1~~:

$$n = 1 - \rho_b/\rho_s$$ **Equation 1. Determining porosity.**

Where,

n = porosity (cubic centimeter per cubic centimeter [cc/cc])
ρb = dry bulk density (grams per cubic centimeter [g/cc])
ρs = specific gravity or particle density (g/cc)

Dry bulk density is the dry weight of a soil sample divided by the field volume of the soil sample. An accurate measurement of bulk density requires determining the dry weight and volume of an undisturbed sample. This method involves collecting a core of known volume, using a thin-walled sampler, such as a Shelby tube or similar coring device, to minimize disturbance of the sample, and transporting the core to a laboratory for analysis. This method is described in American Society for Testing and Materials (ASTM 2000a) *Standard Test Method for Density of Soil in Place by the Drive-Cylinder Method, Method D2937*.

The *Standard Test Method for Specific Gravity of Soil Solids by Water Pycnometer, Method D854* (ASTM 2002), may be used to determine specific gravity. If specific gravity is not assessed, then 2.65 g/cc can be assumed as the particle density.

Consideration should be given to collecting multiple samples if multiple lithologies are present that might affect COI transport.

If site-specific values of porosity are not available, it should be estimated based on values provided in an appropriate literature source.

4.2.5.3 Volumetric Water Content/Moisture Content

Volumetric water content is the ratio of water volume to the total soil volume. The *Standard Test Method for Laboratory Determination of Water [Moisture] Content of Soil and Rock by Mass, Method D2216-19* (ASTM 2019) is a gravimetric oven-drying method; however, the water content value used in most models is the volumetric water content.

It may be necessary to use Equation 2 to convert gravimetric water content to a volumetric basis:

$$\theta_{wv} = \theta_{wg} * \frac{\rho_b}{\rho_l}$$

Equation 2. Converting gravimetric water content to volumetric.

Where,

Θwv = volumetric water content (cc water/cc soil)
Θwg = gravimetric water content, typically reported by the laboratory (g of water/g of soil)
ρ_b = dry bulk density (g of dry soil/cc of soil)
ρ_l = density of water (g/cc)

Volumetric water content can also be measured in the field using instruments such as a neutron probe, time domain reflectometer, or gypsum block sensors.

4.2.5.4 Fractional Organic Carbon Content in Soil

Fractional organic carbon content is the organic carbon weight in the soil divided by soil weight and is expressed either as a ratio or as a percent. The Walkley Black Method is a chemical oxidation method (rapid dichromatic oxidation) while the *Standard Methods for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils, Method 2974* (ASTM 2000b) is a furnace method for determining fractional organic carbon content in soil.

Results are usually reported as percent organic carbon content. The reported value can be converted to a fraction by dividing by 100.

If measurements of total organic matter content are available, they should be divided by 1.724 to estimate the fractional organic carbon content. This adjusts for the portion of soil organic matter that is actually carbon. Typically, total organic carbon content is estimated using ASTM (2000b) Method 2974. Organic carbon content should be determined using soil samples not impacted by the release.

4.2.6 Saturated Zone Characteristics

Petroleum COIs that reach the water table typically travel horizontally through the saturated zone. However, if a vertical gradient is present, chemicals may also move vertically in the direction of the gradient. Saturated zone characteristics that determine the travel time and direction for the petroleum COIs include the following:

- Horizontal hydraulic conductivity
- Horizontal and vertical hydraulic gradients (magnitude and direction)
- Saturated zone soil characteristics (fractional organic carbon content and porosity)

4.2.6.1 Hydraulic Conductivity

Hydraulic conductivity is the discharge of water per unit area per unit hydraulic gradient in a subsurface formation. Estimates of site-specific hydraulic conductivity can be obtained by conducting aquifer tests such as slug or pump tests. Data gathered during the tests are then analyzed using appropriate methods. Slug tests are easier to conduct than pump tests, generate no wastewater for treatment, and may be more appropriate for low-permeability formations. The primary disadvantages are the small aquifer volume that is explored, resulting in the need to conduct multiple tests across the site. Properly conducted pump tests will often provide better estimates of hydraulic conductivity. The simplest pump tests are single-well short-duration (2 to 4 hours) tests. The best pump tests employ a pumping well and multiple observation wells and are of longer duration (12 hours or more). These tests identify boundary effects. Regardless of the type of test conducted, different methods of data analysis often yield different estimates of hydraulic conductivity. The *Standard Guide for Selection of Aquifer Test Method in Determining Hydraulic Properties by Well Techniques, Method D4043-96* (ASTM 2017) provides guidance on the selection of aquifer test methods.

In the absence of these tests, estimates of hydraulic conductivity may be obtained from literature, with values corresponding to the type of soil in the saturated zone, using empirical

equations based on the grain size distribution of the porous formation, or they may use specific capacity data from well logs of wells in the vicinity of the site that represent the aquifer being investigated. In either case, adequate references and justification for the value chosen must be provided.

4.2.6.2 Hydraulic Gradient

The magnitude and direction of the hydraulic gradient is estimated by comparing water levels measured in the monitoring wells. Typically, water level contour maps are prepared based on measured data using a computer program or manual calculations along with professional judgment. Calculations done using automated procedures should be spot-checked with hand calculations. Three wells or more are needed to adequately estimate the direction of flow and magnitude of the gradient. When drawing the contour maps, care should be taken to ensure that the measurements used are from monitoring wells that are screened in the same interval or hydrologic unit.

For sites that have seasonal variation in hydraulic gradient, estimate the average hydraulic gradient for each season. Consideration should also be given to determining any vertical gradients. This requires a comparison of adjacent water levels in wells screened in different intervals.

In areas where the shallow aquifer has been impacted and a deeper aquifer is used for drinking water, the vertical gradient must be determined. When drilling deep wells, care should be taken to avoid cross contamination.

4.2.6.3 Saturated Zone Soil Characteristics

In addition to hydraulic conductivity, other important saturated zone soil characteristics include fractional organic carbon content, porosity, and bulk density. These parameters are required to quantify the movement of chemicals within the saturated zone. Section 4.2.5 describes the laboratory methods used to measure these parameters.

4.2.7 Biodegradation Indicators

Biodegradation of petroleum chemicals occurs in all media (soil, soil vapor, groundwater). Depending on the media, different indicators (chemical concentrations, geochemical indicators, microorganisms, oxygen, and carbon dioxide) can be measured at a site to demonstrate the occurrence of biodegradation of these organic substances.

When evaluating the potential for biodegradation in groundwater, these indicators are commonly classified into three groups: primary, secondary, and tertiary lines of evidence. Data collected under each line of evidence can be evaluated qualitatively or quantitatively to determine the occurrence of biodegradation.

The primary line of evidence demonstrates spatial stability or a reduction in chemical concentrations at a site by evaluating measured concentrations within monitoring wells, groundwater velocity, rates of contaminant transport, and time of the release.

The secondary line of evidence refers to measurement of geochemical indicators including reduction-oxidization (REDOX) potential, dissolved oxygen, dissolved nitrates, manganese, ferrous iron, sulfate, and methane. These indicators should be measured in at least three wells located along the flow line, one of which should be located at a background or upgradient location, one within the plume near the source, and one within the plume downgradient from the source.

The tertiary line of evidence involves microbiological studies such as identifying types of subsurface microbial populations and microbe cell counts.

Commonly used methods to estimate biodegradation rates include mass balance analysis for expanding, stable, or shrinking plumes and plots of plume concentration versus distance. Appendix A provides additional details on biodegradation for petroleum COIs in groundwater.

When evaluating the potential for, or presence of, biodegradation in soil or soil vapor, the most common indicators used are soil vapor concentrations, oxygen, and carbon dioxide. These indicators are measured at multiple depths in the subsurface and related to a potential source. More information on evaluating biodegradation of petroleum vapors in relation to the vapor intrusion exposure pathway is provided in the *Technical Guide for Addressing Petroleum Vapor Intrusion at Leaking Underground Storage Tank Sites* (EPA 2015b).

4.2.8 Distribution of Petroleum Chemicals of Interest

Petroleum COI may be distributed between soil, soil vapor, groundwater, surface water, and sediments present at a release location. Knowledge of contaminant distribution entails determining the spatial extent and magnitude of concentrations in each of these media, where they are present.

4.2.8.1 Distribution of Petroleum Chemicals of Interest in Soil

Adequate soil concentration data are necessary to estimate risk to receptors, compare representative concentrations for each complete exposure pathway to target levels, and define the soil source dimensions. Sufficient data must be collected to define horizontal and vertical extent of impacts. The vadose zone investigations must achieve the following:

- Identify the horizontal and vertical extent of soil impacts. Unless otherwise directed by DEQ, the extent of impact is defined as those areas where petroleum COI concentrations exceed screening level concentrations.
- Identify areas of maximum concentration of petroleum COIs.
- Collect samples adequate to estimate exposure point concentrations for the potentially complete exposure pathways that have been defined based on the CSM.

To determine the spatial extent of contamination, soil borings should be drilled starting from the known or suspected source area and drilling outwards until borings with sample concentrations at or below screening levels are reached in all directions. To determine the vertical extent of contamination, soil borings are extended to the base of petroleum impact and samples collected from surface and subsurface soil zones as explained in the following sections.

The soil analytical data should identify the soil source area. If more than one source area is identified at a site, each source area is evaluated separately. Once the soil source is identified, source dimensions can be estimated. These dimensions can be used in the RSL and VISL calculators, with other input parameters, to estimate risk and remediation standards protective of indoor inhalation and to evaluate the soil to groundwater leaching exposure pathway. Depth to ~~subsurface~~ soil source (used to estimate the target concentrations) is the depth, in the source area, from the surface to the zone where concentrations are above quantification limits. Professional judgment should be used in choosing the representative depth.

4.2.8.1.1 ~~Surficial~~ Soil Sampling

~~The RE process distinguishes between surficial soil and subsurface soil zones. Surficial soil is defined as the soil zone from the ground surface to 1 foot below ground surface.~~ Exposure pathways that ~~may~~ apply to ~~the surficial~~ soil ~~zone~~ include direct contact exposure via incidental ingestion, inhalation of vapors and particulates, dermal contact, volatilization from soil to indoor air, and leaching of petroleum COIs to groundwater and surface water.

Evaluation of soil exposure pathways ~~within the surficial soil zone~~ requires collection of an adequate number of soil samples to estimate both maximum and representative concentrations of all potential petroleum COIs. ~~Given the small vertical depth interval of this soil zone, close attention should be given to vertical variations in contamination. The acceptability of vertical depth composite samples versus samples from discrete depth intervals is a site specific decision. Criteria that influence this decision include the type of petroleum COIs, vertical extent of contamination, and areal extent of the contaminated zone. Sampling within the surficial soil zone is typically done from test pits using hand samplers such as trowels or corers.~~

The presence of impervious (paved) surfaces poses difficulties for sampling. In some cases, very permeable material may be located 2 inches below the pavement. Residues from the paved surface may also be present. When sampling beneath impervious surfaces, sampling should begin 2 inches or deeper below the concrete or asphalt pavement. Cracked areas in impervious surfaces may represent conduits for chemical migration or leaching and should be evaluated during the selection of sampling locations.

~~4.2.8.1.2 Subsurface Soil Sampling~~

~~Soil below the surficial soil zone (more than 1 foot below ground surface) and extending to the water table is termed the subsurface soil zone. Exposure pathways evaluated for this zone include volatilization from soil to indoor air and leaching to groundwater and surface water. Most receptors will not have direct exposure to this soil. However, some construction workers may be involved in excavation activities below the surficial soil zone and subsurface soil removed during excavation may be deposited at the surface allowing greater exposure. This possibility must be considered during CSM development.~~

To test for indoor inhalation of vapors from subsurface soils, collect soil vapor samples from areas directly overlying residual soil contamination and adjacent to existing structures. Soil vapor sampling intrusion will delineate the exposure areas so better decisions can be made on

AULs. More information on evaluating the vapor intrusion exposure pathway is provided in the *Technical Guide for Addressing Petroleum Vapor Intrusion at Leaking Underground Storage Tank Sites* (EPA 2015b).

To test for direct contact exposure to soils~~a construction or utility worker during excavation activities~~, soil samples must be collected from both surface and subsurface soil zones~~ to depths where construction-related activities are likely to occur~~.

To test for leaching of petroleum COIs in soil to groundwater, determine the thickness of the contaminated soil zone, the distance from the bottom of the contaminated zone to the water table, if any, and representative concentrations of petroleum COIs within the contaminated zone.

Soil sampling must follow these guidelines and procedures:

- Samples must be collected from the source area(s). Samples must be collected to determine the full horizontal and vertical extent of soil contamination. Sampling must characterize any horizontal or vertical stratigraphic variation at the site that could impact petroleum COI fate and transport. To fully characterize the vertical extent of contamination, borings should be extended to the water table and features such as the capillary fringe and any smear zone, if encountered, must be characterized. Vertical sampling intervals generally should not be greater than 5 feet.
- Soil borings must be logged and samples for laboratory analyses collected according to current industry practice.
- All samples must be adequately preserved according to requirements of the laboratory analyses and analyzed within holding times required by each method. Sample analyses must be conducted according to current, Office of Solid Waste and Emergency Response SW-846 Methods, or other accepted methods.
- Adequate QA/QC procedures must be used to ensure sample quality and integrity. Section 4.2.2 contains additional information on QA/QC considerations.
- All sampling equipment must be decontaminated using current state of industry practice, such the *Practice for Decontamination of Field Equipment Used At Nonradioactive Waste Sites, Method D5088-90* (ASTM 2000).
- Abandonment of boreholes that extend to the water table, which are considered wells by IDWR, must follow IDWR abandonment procedures (IDAPA 37.03.09.16). Appropriate methodology for abandoning other boreholes is described in detail in the *Standard Guide for Decommissioning Ground Water Wells, Vadose Zone Monitoring Devices, Boreholes, and Other Devices for Environmental Activities, Standard Guide* D5299-99 (ASTM 2018).

~~4.2.8.1.3~~4.2.8.1.2 Subsurface Soil Vapor Data

At sites where petroleum COIs in soil or groundwater are volatile and there is concern about potential indoor inhalation of vapors, it is necessary to assess soil vapor concentrations. For details about these samples, refer to the *Technical Guide for Addressing Petroleum Vapor*

Intrusion at Leaking Underground Storage Tank Sites (EPA 2015b) and *EPA Region 4 Soil Gas Sampling Operating Procedure* (EPA 2025).

~~DRAFT LANGUAGE FOR POSSIBLE 2026 INCLUSION:~~
For soil vapor sampling, if the criteria below, from *EPA's Technical Guide For Addressing Petroleum Vapor Intrusion At Leaking Underground Storage Tank Sites* (2015b), for benzene concentration and vertical separation distances are met OR the soil sample results are non-detect or below groundwater protection screening levels, then collecting soil vapor samples and additional investigation into the soil vapor intrusion pathway may be unnecessary if reasonable justification is provided.

Criteria: Residual soil contamination (benzene equal to or less than 10 mg/kg) at a depth greater than 16 ft. (6 ft. standard + 10 ft. depth of typical basement) with clean, biologically active soil between the contamination and the ground surface. The limit for LNAPL (benzene greater than 10 mg/kg) is 25 ft. in depth (15 ft. standard + 10 ft. depth of typical basement).

Residual groundwater contamination (benzene equal to or less than 5 mg/L) at a depth greater than 16 ft. (6 ft. standard + 10 ft. depth of typical basement) with clean, biologically active soil between the contamination and the ground surface. The limit for LNAPL (benzene greater than 5 mg/L) is 25 ft. in depth (15 ft. standard + 10 ft. depth of typical basement).

~~4.2.8.1.4~~4.2.8.1.3 Logging of Soil Boreholes

Each soil boring must be logged to record depths correlating with changes in lithology (with lithologic descriptions), soil vapor (e.g., photo-ionization detector) analyses, occurrence of groundwater, total depth, visual and olfactory observations, and any other pertinent data.

When a monitoring well is installed, as-built diagrams with depth to groundwater and construction details with a continuous soil profile with detailed lithologic descriptions must be submitted for each well. Particular emphasis should be placed on characteristics that control chemical migration and distribution, such as zones of greater or lesser permeability, changes in lithology, correlation between soil vapor concentrations and different lithologic zones, obvious areas of soil discoloration, organic content, fractures, and other lithologic characteristics.

4.2.8.2 Distribution of Petroleum Chemicals of Interest in Groundwater

Adequate groundwater samples must be collected to delineate the extent of free product, dissolved contaminant plumes in all directions, maximum petroleum COI concentrations, and representative concentrations based on the CSM. This sampling should account for the soil source and direction of groundwater flow.

4.2.8.2.1 Groundwater Sampling

If groundwater has been impacted, temporary sampling points may be used to screen levels of groundwater impacts and to assist in determining optimal locations of permanent monitoring wells. A sufficient number of monitoring wells must be installed, designed, and located properly

to delineate the horizontal and the vertical extent of the groundwater plume, estimate the direction of groundwater flow, identify source areas, and to document petroleum COI migration and NAPL. The monitoring wells must be installed according to current IDWR rules (IDAPA 37.03.09) and industry standards such as the *Standard Practice for Design and Installation of Ground Water Monitoring Wells in Aquifers D5092* (ASTM 2024). The EPA (1986, 1992, 2009) Resource Conservation and Recovery Act (RCRA) technical guidance documents for groundwater monitoring are also useful references.

Well casing and screen materials must be properly selected. The screen interval length must be minimized to the extent possible but should be set at least 2 to 3 feet above the expected high water table and encompass the range of expected variation in water table depth. EPA recommends screen interval lengths of 10 to 15 feet except where specific monitoring objectives or site knowledge result in other requirements. Wells must be properly developed and gauged after installation. A site survey must be conducted to establish well casing elevations. Based on the groundwater elevations, groundwater flow direction and gradient must be determined and plotted on a map.

Groundwater samples must be collected according to the following guidelines and procedures:

- Monitoring wells must be purged of an adequate number of well volumes before collecting a sample. Low-flow purging is recommended (EPA 2017).
- Samples must be collected using EPA-approved methods and equipment.
- All samples must be adequately preserved according to the requirements of the laboratory analyses and analyzed within holding times required by each method.
- Sample analyses must be conducted in accordance with Office of Solid Waste and Emergency Response SW-846 Methods, or other accepted methods.
- Adequate QA/QC procedures must be used to ensure sample quality and integrity. Section 4.2.2 provides additional information on QA/QC considerations. All sampling equipment must be decontaminated using current state-of-industry practice, as described in the Practice for Decontamination of Field Equipment Used At Nonradioactive Waste Sites, D5088-90 (ASTM 2000).
- If the plume is not delineated in all directions, locations of new monitoring wells must be chosen based on groundwater flow direction and location of the soil source area.

4.2.8.3 Surface Water and Sediment Sampling

Appropriate samples must be collected when petroleum COI migration is known or suspected to have impacted surface water. Water samples must be collected from upstream and downstream of a groundwater discharge point. Sediment samples must be collected if the CSM indicates a potential for releases to surface water.

In places where a groundwater plume may discharge into a stream, it is necessary to estimate the discharge concentration into the stream. This can be achieved by installing one or more monitoring wells or temporary wells within the plume adjacent to the stream.

4.3 Exposure Assessment

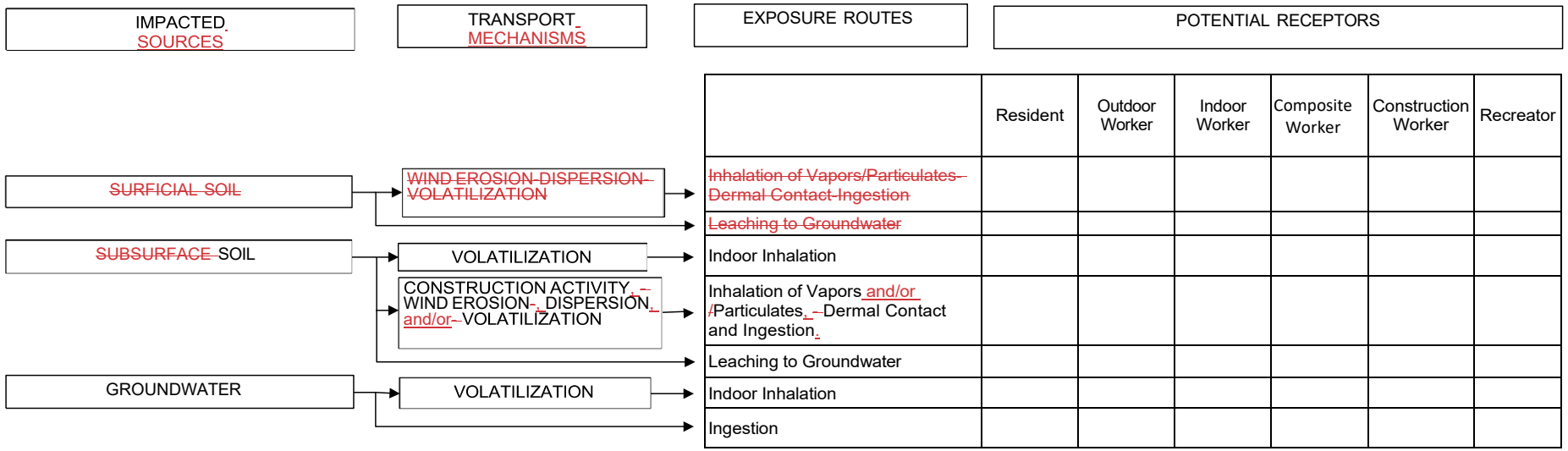
The following are goals for the exposure assessment portion of the RE:

- Characterize the physical setting.
- Identify potentially exposed populations.
- Identify complete or potentially complete exposure pathways.
- Estimate exposure concentrations.
- Estimate petroleum chemical intakes.

The exposure assessment uses much of the data collected in support of and assumptions contained in the CSM (section 4.1). Figure 2 displays an example of the CSM, which is helpful for assessing exposure.

4.3.1 Physical Setting

Characterization of the physical setting for exposure assessment identifies those site factors that may influence the fate and transport of chemicals from the source to a receptor. These factors include climate, meteorology, geologic and hydrogeologic setting, soil types, biodegradation potential, and surface water hydrology. The potential for a chemical to reach a receptor can be assessed when considering the context of the media from which petroleum COIs are released (e.g., ~~surficial~~ soil~~s~~, ~~subsurface soils,~~ groundwater, surface water), the transport mechanisms for the petroleum COIs from each media (e.g., leaching, groundwater transport, volatilization), and the chemical concentrations and distribution of the petroleum COIs in each media. Section 4.1 provides a detailed discussion of the data needs related to the physical setting of a site.



	YES	NO
FREE PRODUCT?		
UTILITIES THREATENED?		
POTENTIAL SURFACE WATER IMPACT?		
ECOLOGICAL RECEPTORS?		

Figure 2. Example of a conceptual site model.

4.3.2 Potentially Exposed Populations/Receptors

Potential exposure populations/receptors must be identified from the information contained in Section 4.1 "Conceptual Site Model."

4.3.3 Exposure Pathways

A receptor comes in contact with petroleum COIs through a complete exposure pathway. For an exposure pathway to be complete, all of the following must be present:

1. Source of petroleum
2. Mechanism that releases the petroleum
3. Transport medium through which petroleum travels from the point of release to the receptor location
4. ROE by which the petroleum chemical enters the receptor's body (ingestion, inhalation, or dermal contact)
5. Potential receptor

If the migration of petroleum chemicals to a receptor or contact by a receptor is not possible (e.g., due to formal engineering controls such as a paved site that will prevent human contact with petroleum-contaminated soil) under current and future land use conditions, the site-specific petroleum COI concentrations may not pose a risk, but limitations may be required on activities and land uses that are allowed on the property.

DEQ identified the most commonly encountered exposure pathways for various environmental media for which an evaluation must be conducted. These exposure pathways are discussed below. At sites where receptors, exposure pathways, or ROE other than those discussed below are important, the owner/operator must identify them and discuss their quantitative evaluation with DEQ. In some cases, it may be determined that one or more of the exposure pathways are incomplete and do not need to be quantitatively evaluated. Adequate justification for exclusion of these exposure pathways must be provided to and approved by DEQ.

4.3.3.1 Pathways ~~for Surficial~~ Soils ~~(0–1 foot below ground surface)~~

~~Surficial soils are defined as soils extending from the surface to 1 foot below ground surface. For construction worker exposure, however, the applicable depth is the depth of excavation.~~ The exposure pathways associated with impacted ~~surficial~~ soils include the following:

- Groundwater protection (leaching of petroleum chemicals from soil to groundwater with subsequent potential ingestion of groundwater)
- Indoor inhalation of vapor emissions from soil
- Surface water protection (leaching of petroleum chemicals from soil to groundwater with subsequent migration to a surface water body)
- Ingestion of soil, outdoor inhalation of vapors and particulate emissions from soil, and dermal contact with soil

~~#### 4.3.3.2 Exposure Pathways for Subsurface Soils (1 foot below ground surface to the water table)~~

~~Subsurface soils are defined as soils extending from 1 foot below the ground surface to the water table. The exposure pathways associated with subsurface soils include the following:~~

- ~~Indoor inhalation of vapor emissions from soil~~
- ~~Groundwater protection (leaching of petroleum chemicals from soil to groundwater with subsequent potential ingestion of groundwater)~~
- ~~Surface water protection (leaching of petroleum chemicals from soil to groundwater with subsequent migration to a surface water body)~~

~~4.3.3.3~~4.3.3.2 Exposure Pathways for Groundwater

Potentially complete exposure pathways for impacted groundwater include the following:

- Indoor inhalation of vapor emissions from groundwater
- Current and/or future ingestion of water on or off site

The *Technical Guide for Addressing Petroleum Vapor Intrusion at Leaking Underground Storage Tank Sites* (EPA 2015b) describes the process used to evaluate potential exposure via indoor inhalation of vapors from soil and groundwater.

~~4.3.3.4~~4.3.3.3 Exposure Pathways for Surface Water and Sediments

Depending on the beneficial use designation of impacted surface waters, complete exposure pathways for surface water include the following:

- Intentional ingestion of surface water and ingestion of fish when surface water is used as a drinking water supply
- Ingestion of fish from surface waters designated for recreational use

~~4.3.3.5~~4.3.3.4 Other Exposure Pathways

Other complete or potentially complete exposure pathways, such as ingestion of produce grown in impacted soils, ingestion of fish, contact with contaminated sediments, or use of groundwater for irrigation purposes, should be evaluated on a case-by-case basis. The owner/operator should contact DEQ for further guidance.

4.3.4 Exposure Point Concentrations

Exposure point concentrations are the average petroleum chemical concentrations to which receptors could be exposed over a specified duration within a specified geographical area. The *exposure unit,* or spatial area over which a given receptor is likely to be exposed to contamination, must be established for on-site receptors and any off-site impacted or potentially impacted receptors and for each exposure pathway or ROE. The same site may have different exposure units for current and future use scenarios.

Appendix B discusses the estimation of exposure point concentrations, use of exposure units, and various methods available to estimate the exposure point concentrations. This appendix describes the sources of uncertainty that affect the estimation of exposure point concentrations, strategies to reduce this uncertainty, and methodologies to evaluate data quality. It also provides guidance on selecting appropriate data for various ROE and statistical methods for analyzing available data.

The RE report should clearly identify specific data and methods used to estimate the exposure point concentrations and provide a rationale for the method and data used. Provide the following information in a table:

- Media
- ROE/exposure pathway
- Receptor
- Data used
- Method of estimation

Table 2 provides an example of how to present specific data and methods for exposure point concentrations.

Table 2. Example table describing derivation of exposure point concentrations.

Media	Route of Exposure	Receptor	Data Obtained From	Method
~~Surficial~~ Soil	Direct Contact	Construction Worker	Unpaved Area	Average
~~Subsurface Soil~~	~~Indoor Inhalation~~	~~Commercial Worker~~	~~Building Footprint~~	~~Maximum~~
Groundwater	Ingestion	Residential	Source Area	Upper Confidence Limit
Soil Vapor	Indoor Inhalation	Commercial Worker	Sub-slab and near soil gas samples	Maximum

As shown in Table 2, an exposure point concentration is estimated for each complete ROE. Appendix B discusses various methods used to estimate the exposure point concentrations. Use of the maximum concentration as the exposure point concentration is most conservative and also the easiest to calculate when compared with other ways of calculating exposure point concentration (average, area-weighted average, upper limit of the confidence interval around the mean). If the risk that is calculated using the maximum concentration is acceptable, considerable computational effort can be avoided.

4.3.4.1 Soil

Exposure point soil concentrations used to evaluate protection of the groundwater exposure pathway should be calculated based on soil data collected within the source area only.

Soil data from the most recent comprehensive investigation must be used. The use of older soil data , while discouraged, may be acceptable if site conditions that would result in an increase in petroleum COI concentrations (such as a new release) have not changed. If a new release has or may have occurred, additional soil assessment activities that adequately characterize current

conditions must be performed. New data collection efforts may be documented in a work plan and submitted for approval by DEQ.

4.3.4.2 Groundwater

Based on the CSM, several exposure point groundwater concentrations at a site may have to be estimated. These could include exposure point concentrations for the source area, at compliance locations, for protection of indoor inhalation on-site and off-site, and for off-site areas.

As discussed in section 4.3.5, estimating these concentrations often requires using fate and transport models.

To account for site-specific conditions, such as source characteristics in relation to the depth to groundwater and the age of the release, it is typically necessary to perform multiple sampling events over time to ensure that the potential for the release to impact groundwater has been accounted for and groundwater concentrations are representative. If these factors can be accounted for, it may be possible to perform an RE using data from one sampling event. If temporal data indicate significant variability, additional sampling events may be required before conducting the RE. Subsequent to RE, DEQ may require additional monitoring data to be collected. If groundwater data less than 12 months old is unavailable, current data will be necessary for the RE. The owner/operator may elect to document data collection objectives in a work plan submitted to DEQ for review and approval.

4.3.4.3 Point of Exposure and Point of Compliance

The point of exposure (POE) is the location where a receptor has or could come in contact with petroleum COIs under current and future conditions. A separate POE is associated with each complete exposure pathway-receptor combination identified in the CSM. For direct exposure pathways, the POE is located at the source of the petroleum COIs. For example, for the ingestion of ~~surface~~ soil, the POE is at the same location as the soil source. For indirect exposure pathways, the POE and the source of petroleum COIs are physically separate. For example, for the case of indoor inhalation of vapors from soil, the POE is inside the building (the breathing space) whereas the source is the soil below and adjacent to the building. Section 4.3.3 discusses the POE location for the protection of the groundwater for groundwater ingestion.

A point of compliance (POC) is a location where concentrations are measured to determine if compliance with cleanup criteria has been achieved. Concentration measurements at the POC may be in any media (e.g., soil, groundwater, soil vapor). The POC location may be identical to the POE or may be located between the source and the POE. In the latter case, the target concentrations at the POC are back-calculated to ensure that the concentrations at the POE do not exceed the target concentration at the POE. For example, to protect the groundwater exposure pathway, the POC well may serve as a sentry well for protecting the POE. The calculated target levels for the POC are then compared to measured concentrations. POC locations may be predetermined based on program-specific requirements. Most sites, particularly those involving groundwater impacts, will have multiple POC locations.

4.3.4.4 Estimating Point of Compliance Well Concentrations

As a part of the RE process, it is necessary to designate and monitor appropriate POCs. The POCs, located on site and/or off site, are used to provide additional assurance that approved concentrations at a selected POE are not exceeded. Monitoring of POC locations is required, and data obtained are compared with approved remediation standards. Monitoring of POC locations must be continued until the concentrations stabilize below approved levels. Concentrations at the POC may also be used to determine the need for additional remedial activities.

4.3.5 Fate and Transport and Exposure Models

Different types of models or equations, uptake equations, risk equations, and fate and transport models, are required to calculate chemical intake, risk, exposure point concentrations, and target concentrations. Fate and transport models simulate the transfer of chemicals from one media (e.g., soil) to another (e.g., air). The models also are used to simulate the movement of chemicals within a given media, such as the transport of chemicals in groundwater from a source area to a POE, which allows estimating concentrations at points distant from the source. EPA's default exposure parameters are on their website in the RSL generic tables section and in the RSL Calculator User's Guide. Alternative models may be used if justified.

4.3.5.1 Fate and Transport Parameters

Fate and transport parameters are necessary in the models used to estimate exposure point concentrations and compliance point concentrations for indirect exposure pathways (e.g., vapor intrusion and groundwater protection). These parameters characterize the physical site properties such as the dilution attenuation factor (DAF), soil porosity, and infiltration rate. For RE, a combination of site-specific and default values for these parameters is typically used. However, the value of each parameter used, whether site-specific or default, must be justified based on site-specific conditions. Where fate and transport models other than those selected by EPA are used, the specific fate and transport parameters required to calculate exposure point concentrations and risk may vary and have specific data collection requirements.

The DAF is one of the most commonly changed fate and transport parameters. EPA's soil to groundwater screening levels are based on a DAF of 1, which assumes no dilution or attenuation. A DAF of 1 should be used for sources over 0.5 acres, fractured rock or karst formations, stagnant groundwater, and potentially other conditions. EPA allows a default DAF of 20 for a source up to 0.5 acres. If parameters needed to calculate a site-specific DAF are known, they may be entered into the RSL calculator to develop a site-specific DAF. Lastly, EPA's RSL calculator DAF equation only accounts for dilution in groundwater and does not address biodegradation. External computer models, including but not limited to SEVIEW, may be used to account for some forms of biodegradation.

4.3.5.2 Physical and Chemical Properties of the Petroleum Chemicals of Interest

The development of target levels requires selecting values for the physical and chemical properties of petroleum COIs. Values of these parameters are listed on EPA's website in the RSL Generic Tables section and in the RSL Calculator User's Guide. To use different values, the owner/operator must provide sufficient justification to DEQ. The use of different values will be allowed only with prior DEQ approval.

4.3.6 Estimation of Chemical Intake

Risk evaluation requires quantifying the magnitude, frequency, and duration of exposure for the receptor populations and exposure pathways selected for analysis. Oral exposures are quantified on a dose per unit body weight basis while inhalation exposure is based on concentration in air.

4.3.6.1 Exposure Factors

To determine receptor and exposure pathway-specific intake estimates, select values for a number of exposure parameters in the equations used to calculate intake. When determining these values, it is often necessary to make assumptions. EPA's default exposure parameters are on their website in the RSL Generic Tables section and in the RSL Calculator User's Guide. Alternative models may be used if justified.

Exposure factors describe the physiological and behavioral characteristics of the receptor:

- Water ingestion rate
- Body weight
- Exposure duration for each ROE
- Exposure frequency
- Soil ingestion rate
- Exposure times for indoor/outdoor inhalation
- Dermal relative absorption factor
- Skin surface area for dermal contact with soil
- Soil-skin adherence factor
- Oral relative absorption factor

4.4 Toxicity Assessment

4.4.1 Chemical-Specific Toxicological Factors

The toxicity of chemicals with carcinogenic adverse health effects is quantified using cancer slope factors (CSF) for oral and dermal ROE, or inhalation unit risk (IUR) for the inhalation route. A CSF is an upper-bound estimate of the probability of a response (developing cancer) per unit intake of a chemical over a lifetime. The IUR is the upper-bound excess cancer risk estimated to result from continuous exposure to a chemical at a concentration of 1 microgram per cubic meter in air.

For chemicals that cause noncarcinogenic health effects, toxicity is typically quantified by reference doses (RfD) for oral and dermal ROE, and reference concentrations (RfC) for the inhalation ROE. The RfD is an estimate of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without risk of adverse health effects during a lifetime. Since RfDs are based on oral exposure, they are modified for use in dermal exposure assessment to account for differences between gastrointestinal and dermal absorption. The RfC is an estimate of a continuous inhalation exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of adverse health effects over a lifetime.

The primary source of information for toxicity factors for the petroleum COI is EPA's RSL Generic Tables.

4.4.2 Carcinogens with a Mutagenic Mode of Action

Current EPA guidance for risk assessment of carcinogens addresses the potential for increased susceptibility to cancer from exposure to carcinogens that occurs early in life (EPA 2005a, 2005b). When information is available to establish the mode of action of a chemical for early-life and adult exposures, it may be appropriate to develop separate risk estimates for childhood exposure and exposure occurring later in life. When the mode of action cannot be established, risk estimates are based on a lifetime daily average exposure without adjustment. Currently, information is sufficient to develop separate risk estimates only for chemicals with a mutagenic mode of action.

When data indicate a mutagenic mode of action for a chemical (i.e., the chemical interacts directly with DNA), available studies indicate higher cancer risk for a given exposure when it occurs early in life compared to a similar exposure in adulthood. Among the petroleum chemicals of interest, the following carcinogenic chemicals are considered mutagens:

- Benz(a)anthracene
- Benzo(a)pyrene
- Benzo(b)fluoranthene
- Benzo(k)fluoranthene
- Chrysene

The EPA RSL Calculator User's Guide and Frequent Questions address how adjustments are made to risk estimates for resident soil, resident tap water, resident air, recreator soil, and recreator surface water.

The effect of the adjustments will be a somewhat higher estimate of risk for a given exposure (and somewhat lower screening levels) compared to risk estimates without an age-specific adjustment. Calculated risk estimates for residential exposure will incorporate these adjustments, but nonresidential risk estimates will not, as they are based on adult exposure.

4.5 Risk Characterization

The process of risk characterization consists of combining the intake estimates developed through the exposure assessment and toxicity information for the petroleum COIs and calculating carcinogenic risk and noncarcinogenic hazard. Calculations are made for each exposure pathway-receptor combination and are summed to calculate a cumulative risk and a HI for each receptor. These risk results are then presented and discussed in a risk summary and are compared to acceptable target risk levels.

Risk and hazard calculations are completed using a standard set of risk equations provided by in EPA's RSL Calculator User's Guide. To minimize rounding errors, estimates made using these equations should be presented using one significant figure, although all digits should be retained for the supporting calculations, such as when summing risks from multiple petroleum chemicals or exposure pathways. For example, calculated cancer risks would be presented as 1×10^{-4} and HQs or HIs would be expressed as 2, 0.7, or 0.03.

This risk-based decision-making process specifies the acceptable risk levels for both carcinogenic and noncarcinogenic health effects. For carcinogenic effects, risk is quantified using the individual excess lifetime cancer risk (IELCR) that represents an increase over background in the probability of an individual developing cancer due to exposure to specific petroleum COI through a specific exposure pathway. Since a receptor may be exposed to multiple petroleum chemicals through multiple ROEs, the acceptable risk level should account for the effect of ~~simultaneous~~cumulative exposure to multiple petroleum chemicals and multiple ROEs. Therefore, combined, or cumulative exposure includes chemicals that are detected and quantified by the laboratory even if those detected chemicals are below applicable screening levels. The concentration measurement that is detected and quantified by the laboratory should be entered into EPA's calculators. See Appendix D for situations where an analyte is reported as non-detect and the practical quantitation limit (PQL) or method detection limit (MDL) exceeds the applicable screening level.

Overall, site carcinogenic risk is calculated as the sum of the individual chemical risk estimates. The probability of a receptor getting cancer is the sum of the probabilities of getting cancer from exposure to each petroleum chemical through each exposure route. In this calculation, there is an assumption of independence of action of the individual chemicals. If the carcinogenic actions of different petroleum chemicals are not independent, there is the possibility of synergistic interaction in which case risk may be underestimated. However, information is generally not available to address this possibility.

For noncarcinogenic effects, risk is quantified using a hazard quotient (HQ) that represents the ratio of the estimated dose of a petroleum chemical for a ROE to the reference or allowable dose. The hazard quotient is calculated in the RSL calculator site-specific mode by the following formula (Equation 3):

$$HQ = (C \times THQ) / RSL$$ **Equation 3. Hazard quotient.**

Where,

HQ = unitless ratio of exposure concentration to reference concentration where a value less than or equal to unity indicates the exposure is not likely to result in adverse health effects
C = concentration entered by the user
THQ = target hazard quotient provided by the user
RSL = regional screening level, determined by the values entered by the user

When a receptor is exposed to multiple chemicals and multiple ROEs, individual HQs are added together to estimate the HI.

For site-specific REs, the following target risk criteria must be satisfied at the POE:

Acceptable Target Risk Level: ~~For combined exposure to all carcinogens and ROE, IELCR must be less than or equal to 1 x 10^{-5} for a receptor at a reasonable maximum exposure.~~ For exposure to individual carcinogens a lifetime excess cancer risk of less than or equal to one per one million (1 E-6) for a receptor at a reasonable maximum exposure. For combined exposure to all carcinogens and routes of exposure, a lifetime excess cancer risk of less than or equal to one per one hundred thousand (1 E-5) for a receptor at a reasonable maximum exposure.

Acceptable HI: ~~The summation of HQs for all petroleum chemicals that have noncarcinogenic health effects and ROE must be less than or equal to 1.~~The summation of the hazard quotients of all chemicals and routes of exposure to which a receptor is exposed and equal to a value of one (1). If the initial value exceeds one (1), further evaluation, including individual organs, can be completed.

The screening level is the lowest of the media-specific (soil, soil vapor, and groundwater) risk-based concentrations. The screening levels are based on a THQ of 0.1 and assumes multiple COIs with the same toxic endpoint. Most petroleum sites will include multiple COIs with the same toxic endpoint. Each petroleum COI and its associated toxic endpoint is presented in Table 1. The rationale for using a THQ of 0.1 for screening is that when multiple contaminants of concern are present at a site or one or more are present in multiple exposure media, the total hazard index could exceed 1.0 if each were screened at the THQ of 1.0. If screening only one contaminant, a THQ of 1.0 may be used but DEQ should be consulted.

The target risk level and HI must be met for each current and potential future receptor at the site. If the initial calculated HI exceeds 1, complete further evaluation by analyzing the mode of action and toxic endpoint (Table 1) for each petroleum chemical. If this analysis indicates sufficient independence of target organs and mode of action for different chemicals, it may be acceptable to present separate HQs, and/or one or more HI for subsets of the chemicals. This kind of analysis should be performed by a toxicologist.

In addition to the target risk levels, DEQ requires meeting the MCLs, or comparable risk-based values for groundwater ingestion, at the POE when the groundwater ingestion pathway is complete. If the groundwater ingestion pathway is incomplete, the leaching to groundwater and/or groundwater vapor intrusion pathways may still be complete. Similarly, for impacts to surface water bodies, calculated target concentrations must be met.

The risk summary should include an analysis and discussion of the sources of uncertainty so that the risk estimates can be placed in perspective. The uncertainty analysis can be qualitative or quantitative in nature. It is more important during the analysis to identify the key site-related parameters and assumptions in the CSM that contribute the most to the uncertainty than to precisely quantify the degree of uncertainty. Typically, there is insufficient information available at a given site to reliably quantify the uncertainty in a given risk estimate, such as conducting a probabilistic risk assessment or sensitivity analysis. The typical sources of uncertainty that are included in the analysis are the (1) petroleum COIs selected and their estimated site concentrations; (2) toxicity values used; (3) fate and transport models used to estimate exposure point concentrations; (4) exposure parameter values used in the exposure assessment; and (5) summing of risks from multiple exposure pathways or petroleum chemicals.

4.6 Risk-Based Target Levels

As described in section 4.5, if the calculated risk or hazard for all petroleum COIs and complete ROE for identified potential receptors exceeds the Acceptable Target Risk or Hazard Levels and corrective action is required, then remediation standards to achieve these targets should be calculated using EPA's RSL and VISL calculators by gathering site-specific data and updating the default parameters, if appropriate. The RSL and VISL calculators will calculate a risk-based screening level that can be used as the remediation standards. Ingestion of water is not included in this calculation (section 4.6.1.1). EPA's calculators will use chemical-specific toxicological factors, receptor-specific exposure factors, fate and transport parameters, physical and chemical properties of the petroleum COIs, and mathematical models to calculate remediation standards but other models may be used with DEQ approval.

Target concentrations should apportion the acceptable target cumulative risk and HI equally among the different chemical-exposure pathway combinations so those petroleum chemicals that contribute the greatest proportion of the total risk have the most stringent remediation standards. The primary goal is to develop target concentrations in all media to ensure the acceptable target risk levels and hazard levels are met. If a petroleum COI has toxicity that is based on both carcinogenic and noncarcinogenic effects, the applicable remediation standards for that chemical should be the lower of the two calculated allowable concentrations.

4.6.1 Developing Remediation Standards Concentrations for Groundwater and Surface Water Protection

For groundwater and surface water protection, target concentrations are calculated using the following procedures.

4.6.1.1 Groundwater Protection

The remediation standards for groundwater ingestion are equivalent to the federal MCLs or a risk-based calculated equivalent. MCLs are health-protective target concentrations promulgated by EPA and adopted by the State of Idaho for protecting drinking water and

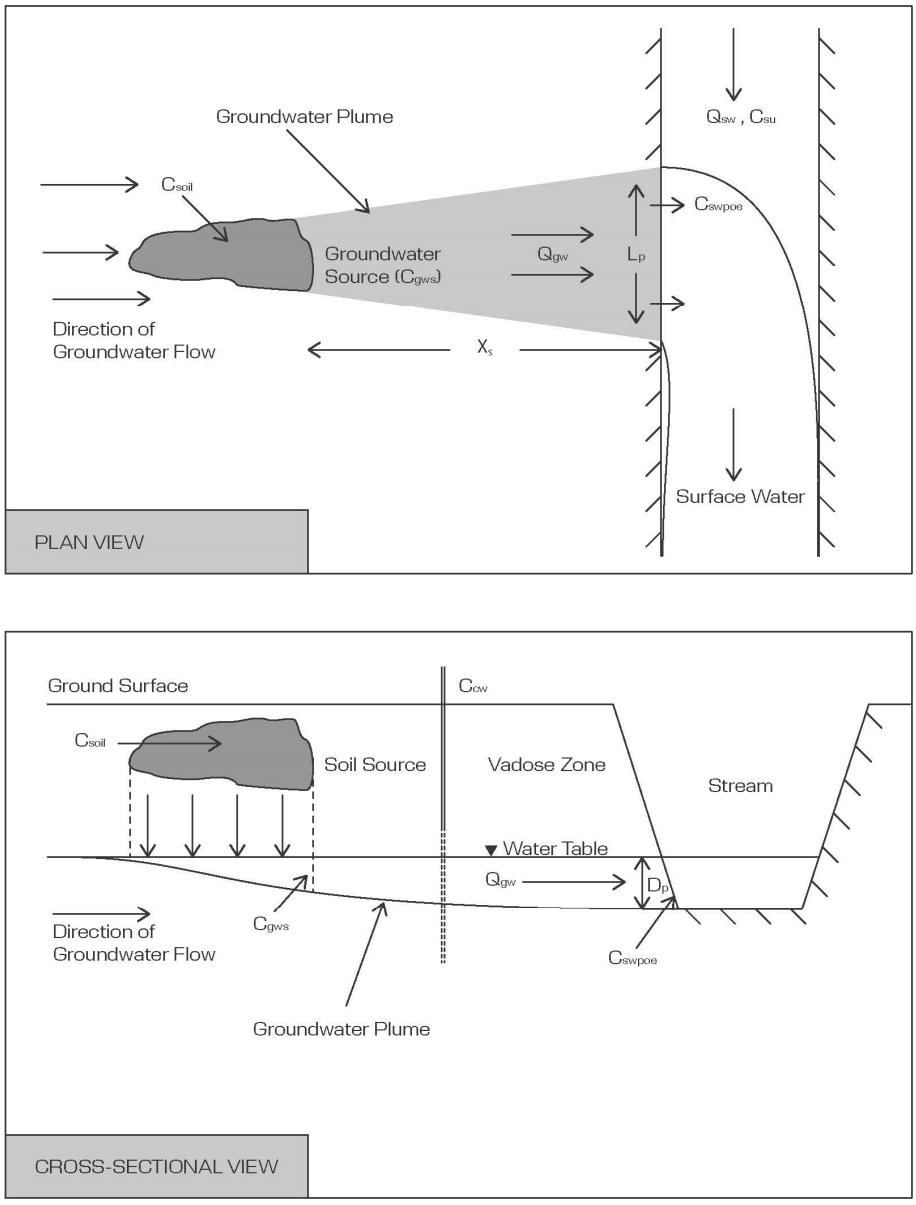
specified groundwater resources. For any petroleum COI that has an MCL, the remediation standards for groundwater ingestion is equal to the MCL. For any petroleum COI that does not have an MCL, the risk-based equivalent level for groundwater ingestion is calculated as residential tap water (section 3.1).

The remediation standards will apply at the POE. The POE will be the downgradient property boundary, as it existed when the release occurred, or the nearest downgradient location where a well exists or could be reasonably placed. Depending on site-specific conditions, it is also possible to have multiple points of exposure.

4.6.1.2 Surface Water Protection

Potential impacts to streams and other surface water bodies from a petroleum release must be evaluated and surface water quality must be protected according to Idaho's "Water Quality Standards"(IDAPA 58.01.02). Section 4.6.1.2 describes the primary receptors and ROE for potentially impacted surface waters evaluated in the RE process. Other ROE, such as contact with contaminated sediments or overland flow discharge, are evaluated on a case-by-case basis.

This section describes the evaluation of potential impacts to surface water via discharge of impacted groundwater to a surface water body. Figure 3 illustrates this exposure pathway, indicating the relevant compliance and exposure locations and associated concentrations. Within the RE process, protection of surface water bodies requires the owner/operator to determine or calculate the applicable surface water standards at the point where groundwater discharges into a surface water body (C_{swpoe}). Once the appropriate surface water standard is determined, compliance with the standard may be achieved in a number of ways. These include measuring surface water concentrations at the point of groundwater discharge, measuring groundwater concentrations at the point of discharge into the surface water body, or



Explanation of Symbols:

Q_{sw} = Streamflow upstream of the point of groundwater discharge
C_{su} = Concentration upstream of the groundwater discharge
Q_{gw} = Impacted groundwater discharge into the stream
C_{sw} = Allowable downstream concentration after uniform mixing
C_{swpoe} = Allowable concentration at the point of groundwater discharge to the stream
C_{gws} = Allowable concentration in the groundwater at the edge of the soil source
C_{soil} = Allowable soil concentration at the source protective of the stream
C_{cw} = Allowable soil concentration in groundwater at different distances between the stream and the source
L_p = Width of groundwater plume discharging to the stream
D_p = Thickness of groundwater plume discharging to the stream
X_s = Distance from the downgradient edge of the groundwater source to the stream

Figure 3. Schematic of leachate migration from the soil source to the stream.

determining appropriate alternate concentrations in other media and at POC locations. Selecting alternate locations may be appropriate for those sites where contamination has not yet reached a surface water body. Alternate concentrations (or remediation standards) and POC locations can include the following:

- Source area soils (C_{soil}), or
- Compliance points in groundwater at different distances between the surface water and the source (C_{cw}) other than the point where groundwater discharges into the surface water body.

4.6.2 Determination of Applicable Risk-Based Levels

The calculated allowable remediation standards for protecting groundwater and/or surface water and those calculated for other potentially complete exposure pathways are compared to determine which media-specific concentrations will guide the cleanup. Typically, the lower of these concentrations will be selected.

Using groundwater as an example, target POE concentrations are based on the most limiting concentrations determined from evaluating the complete or potentially complete exposure pathways in addition to the groundwater ingestion pathway. These exposure pathways may include indoor inhalation of vapors volatilized from groundwater, groundwater impacts to surface water, impacts to deeper groundwater systems with the potential for use as drinking water supplies, and incidental ingestion of and dermal exposure from irrigation water. Potential impairment of other beneficial uses of groundwater such as for agricultural or industrial water supplies is also included.

The applicable POE is based on the location of the plume (on site versus off site) and which exposure pathway(s) and receptors are limiting with respect to risk and allowable groundwater concentration. In many cases, particularly if a plume has migrated off site, multiple POE and exposure pathways must be considered.

For example, a petroleum-sourced volatile organic compound plume may have migrated off site into a residential area and have the potential to discharge to a downgradient stream.

Source area groundwater concentrations on site must be controlled so that concentrations at the POE where groundwater discharges to the stream meet applicable criteria. In addition, unless vapor intrusion has been separately addressed, such as through the use of soil vapor, residential vapor intrusion criteria in groundwater would need to be met at the downgradient boundary of the source property and commercial criteria for on-site POE.

4.7 Deliverables

The primary deliverables associated with conducting a site-specific RE typically include an optional work plan for collecting and evaluating data, a data collection report, and the required RE report. In many cases, the results of a data collection effort are combined with the RE report. Data collected must follow DEQ's quality management program, QAPP, and SOP or a

DEQ-approved QAPP (section 4.2 and section 7.3). If the results of the RE report indicate the need for corrective action, a CAP must also be developed and submitted. The contents of CAPs are discussed in section 5.

4.7.1 Work Plan

A work plan may be desirable where extensive data collection activities or significant departures from default exposure assumptions or modeling are proposed.

As appropriate, a work plan to fill identified data gaps may be prepared and submitted to DEQ for review. The amount of detail to be included in the work plan will vary among sites. At sites where a considerable amount of data has already been collected, the work plan may be a brief letter indicating activities to be performed to fill in the data gaps. For a complex or large site, a very detailed work plan, including the CSM, data collection methodology, analysis methods, a data QAPP, and a health and safety plan may need to be developed.

A RE work plan should address each item discussed in sections 4.7.1.1 through 4.7.1.11 as appropriate to the RE's purpose and goals.

4.7.1.1 Purpose and Goals

The purpose and goals of the work plan should be clearly stated. If the purpose is to fill data gaps, then a listing and description of the data gaps should be provided with an explanation about why they constitute data gaps and how the work proposed will fill those gaps.

If the purpose of the work plan is to propose use of alternative models, exposure factors, physical and chemical properties, toxicity factors, or methods of calculating remedial target concentrations, then a rationale should be provided about why the alternatives proposed are needed. A short description of the scope and nature of the work proposed should be provided.

4.7.1.2 Site Background

This portion of the work plan may refer to documents previously submitted to DEQ; it is not necessary to repeat the entire site background description. Refer to documents that contain a comprehensive chronology of site investigations.

4.7.1.3 Conceptual Site Model

A concise summary of the existing CSM should be provided. If the goal of the work plan is to revise a previously completed RE, then an CSM already exists that can be referenced rather than repeated. If validation or revision of a previous CSM is necessary, those aspects of the current CSM that are the target of the work plan should be described. Refer to section 4.1 for suggestions on CSM content.

4.7.1.4 Exposure Factors

If alternate exposure factors values are proposed in the work plan, these factors must be justified and acceptable to DEQ. The default exposure factor values can be obtained from the RSL and VISL calculators and tables.

4.7.1.5 Physical and Chemical Properties

Owner/operators should use the default physical and chemical properties for the petroleum COIs.

4.7.1.6 Toxicity

Toxicity values can be obtained from the RSL and VISL calculators and tables.

4.7.1.7 Fate and Transport Models

If alternative models are proposed, the work plan should include reasons for using alternative models and demonstrate that the proposed models will better simulate site-specific conditions, and sufficient site-specific data are available or will be collected to justify the use of the proposed model. Alternative models must be approved by DEQ before they are used.

4.7.1.8 Fate and Transport Parameters

Data collection may be proposed to collect site-specific values in lieu of using DEQ default values for fate and transport parameters used in models for the RE. The parameters for which values are to be obtained should be specified and the methodology used to obtain those values described.

DEQ accepts the use of chemical-specific biological decay rates or attenuation factors in the fate and transport models. Use of decay rates in a RE must use values supported by site-specific information. Refer to Appendix B for data necessary to demonstrate occurrence of natural attenuation and methods to calculate decay rates. Examples of this type of information include, but are not limited to, the following:

- Consistent stable or decreasing concentration (above the RSLs) trends in properly located and constructed monitoring wells
- Measurements of natural attenuation parameters that provide evidence of biodegradation

4.7.1.9 Calculating Remediation Standards Concentrations

Section 4.6 describes the process for calculating target concentrations (remediation standards). If a method of apportioning risk and calculating remediation standards different than the DEQ default method is desired, the proposed methodology and rationale for the choice should be described.

4.7.1.10 Methodology and Quality Control

Work plans in support of data collection efforts should describe the methodology that will be used to obtain the data and provide a clear description of the level of data quality required to meet the stated objectives, and how this data quality will be achieved and ensured.

4.7.1.11 Schedule and Deliverables

The optional work plan should include an overall project schedule and deliverables that will be submitted to DEQ. The schedule should include any agency meetings necessary during work plan implementation.

4.7.2 Implementing the Work Plan

Upon receipt of a work plan approval, the owner/operator should implement the work plan according to the schedule in the work plan. If delays occur, the owner/operator's must inform DEQ of the delay and revised schedule. DEQ should be notified of deviations in the work performed from that specified in the approved work plan and their impact on the purpose and goals of the work plan.

Upon completion of work specified in the work plan, the owner/operator should document the results and submit them to DEQ. If the purpose of the work plan included data collection, the data collection results can be summarized in a separate data collection report or incorporated into a revised RE report.

4.7.3 Risk Evaluation Report

The RE for a site must be clearly and concisely documented and submitted to DEQ for review. Appendix C provides an example outline of a RE report. At a minimum, the report must include the items required in IDAPA 58.01.24.200, such as a screening level evaluation and/or site-specific evaluation and the results of the risk evaluation. Within 30 days of receiving a CAP, DEQ must provide an approval, an approval with modifications, or a rejection (specifying reasons for the rejection) in writing. Provisions are made in IDAPA 58.01.24.200.03 for extending this time frame.

5 Developing and Implementing Corrective Action Plans

CAP development and implementation may be necessary if, after the screening level evaluation or site-specific RE, concentrations exceed screening levels or an unacceptable risk is identified. The owner/operator must then develop cleanup criteria (or remediation standards) and create a CAP to achieve those standards or to ensure that the remaining risk is acceptable. The risk management strategy described in the CAP depends on the results of the RE (which exposure pathways, petroleum chemicals, and media are responsible for the unacceptable risk) and other circumstances unique to the site.

5.1 Contents of a Corrective Action Plan

As required in IDAPA 58.01.24, the CAP must include the following:

- Description of remediation standards selected, points of exposure, and points of compliance
- Description of the remedial strategy and actions to take to achieve the remediation standards
- Current and future land use and use of groundwater and surface water both on site and off site
- AULs that will be required as part of the remedial strategy and the associated environmental covenants
- Estimated timeline for completion of remedial actions
- Monitoring plan to gauge effectiveness of the remedial strategy
- Description of practical quantitation limits and background concentrations as they apply to the remediation

Include the following additional elements in the plan:

- Brief site description.
- Brief description of the RE approved by DEQ, including assumptions used for receptors and land use, and a list of approved remediation standards for specific exposure pathways, media, chemicals, and specific areas of the site (if applicable).
- Clear description of reasons a CAP is needed.
- Identification of the areas to be managed under the CAP.
- Description of the strategy selected to achieve cleanup goals, including a comparison and evaluation of remedial alternatives considered in developing the overall strategy. Present a rationale for the strategy selected; include any data collected in support of or used to determine the feasibility of a particular remedial measure such as pilot testing.
- Description of what QA/QC measures will be implemented to ensure that data collected to support remedial decision-making is of adequate quality.
- Description of project closure requirements.
- Reporting schedule to document progress of the corrective action.

5.2 Implementing a Corrective Action Plan

The CAP should not be implemented until approved by DEQ. Within 30 days of receiving a CAP, DEQ must provide an approval, an approval with modifications, or a rejection (specifying reasons for the rejection) in writing. Provisions are made in the IDAPA 58.01.24.200.03 for extending this time frame.

While DEQ is reviewing the CAP, implementation of interim corrective action measures may take place. However, as provided in IDAPA 58.01.24.061.06.d, owner/operators may, in the interest of minimizing environmental contamination and promoting more effective cleanup, begin cleanup of soil, surface water, and groundwater before the CAP is approved if they fulfill certain conditions:

- Notify DEQ of their intention to begin cleanup.
- Comply with any conditions imposed by DEQ, including halting cleanup or mitigating adverse consequences from cleanup activities.
- Incorporate self-initiated cleanup measures in the CAP that is submitted to DEQ for approval.

Typical interim corrective actions include excavating and disposing of contaminated soil, removing free product, extracting soil vapor, and pumping and treating groundwater.

Upon approval of the CAP, the owner/operator must implement the plan according to the proposed schedule. All performance data should be submitted to DEQ in a timely manner. This data should be carefully evaluated by both the owner/operator and DEQ to determine if the CAP is progressing as anticipated. Major deviations in schedule or plan implementation should be reviewed and approved by DEQ, in the form of a CAP addendum, well in advance of proposed implementation. The specific modifications that may be needed will vary from site to site. If screening levels change due to EPA toxicity updates, and the screening level becomes more conservative, it is acceptable to adhere to the original CAP. If the screening level has become less conservative, the owner or operator may submit a CAP addendum for review and approval. An entirely new CAP is required if the proposed remediation method has changed.

When the CAP has been successfully implemented, the owner/operator should document these conditions in a completion report along with a petition to DEQ for site closure.

6 Activity and Use Limitations

An AUL is a restriction or obligation, with respect to real property, created by an Environmental Covenant pursuant to the Uniform Environmental Covenants Act (UECA), Idaho Code § 55-30.

The purpose of AULs is to reduce the potential for exposure to contaminants at a release site. AULs are also commonly referred to as *institutional controls*. AULs are typically proposed to DEQ for approval through the RE process. Nonremedial land use restrictions (e.g., local zoning ordinances) may reinforce the sustainability of AULs; however, they are not considered sufficient by themselves. These types of nonremedial land use restrictions, such as zoning ordinances, may change or be removed without DEQ approval and are not approved by DEQ as part of a CAP. However, nonremedial land use restrictions may be relevant to evaluating current and reasonably likely future use and exposure scenarios at a site.

6.1 Environmental Covenants

Owner/operators may propose an Environmental Covenant as part of the CAP, which will include the AUL language. Any proposed Environmental Covenant must be consistent with UECA. Each proposed Environmental Covenant is reviewed and evaluated on a site-specific basis.

Following is a *nonexclusive* list of the types of activity and use limitations that may be included in an Environmental Covenant:

- Restrictions on Water Use
  - Prohibit use
  - Limit use
  - Monitor use
  - Report use
  - Operation and maintenance procedures for physical controls and devices
  - Prohibit well installation and operation
  - Abandon an existing well
- Restrictions on Land Use
  - Prohibit, or require DEQ approval for, disturbance of soil, cap, or vegetation
  - Limit activities and land use
  - Limit structures and buildings
- Actions Regarding Access
  - Right of access necessary to implement the activity and use limitation
  - Limit or deny public access
- Obligations to perform certain actions to maintain the effectiveness of an approved corrective action. For example, this may involve the need for periodic inspections and maintenance to ensure that a cover or barrier retains its primary function. In this case there might be a specific reference in the Environmental Covenant to an Operations and Maintenance Plan, developed as part of the corrective action.

DEQ has an Environmental Covenant template on its website that lists example restrictions owners/operators can use when proposing activity and use limitations as part of a CAP. The owner/operator can propose an Environmental Covenant consistent with UECA for consideration and approval by DEQ.

6.2 Specific Application of Activity and Use Limitations at Petroleum Release Sites

IDAPA 58.01.24.600 outlines the circumstances under which AULs will be included as part of a CAP:

- Where the assumed on-site land use for the purpose of the RE is not residential and either the maximum media concentrations exceed the screening levels or the calculated risk for a residential receptor is unacceptable
- Where off-site groundwater concentrations exceed screening levels or risk-based concentrations (AUL would be required on off-site properties)
- Where DEQ determines, based on the proposed CAP, that such AULs are required to ensure the continued protection of human health and the environment or the integrity of the cleanup action

On a limited, case-by-case basis, DEQ can determine if closure can be granted at properties that exceed residential soil and/or soil vapor screening levels or risk. DEQ will take into consideration residual soil and/or soil vapor sample results, risk calculations, separation distances, release location, existing contamination sources, previous and future land use, etc. Properties that may meet this criteria are highways, right-of-ways, historically and high future likely industrial sites such as railyards, airports, and manufacturing plants. If DEQ grants closure under these circumstances, the closure letter issued will outline the specific circumstances and why the decision was made. If the closure was based on current land use and likelihood of future land use, the letter will specify that DEQ must be contacted if land use changes because additional assessment or corrective action may be required.

6.3 Use of Activity and Use Limitations at Impacted Neighboring Properties

Implementability and enforceability issues become more complicated when an owner/operator proposes use of AULs on impacted neighboring properties. It is the owner/operator's obligation to negotiate language and reach agreement with both the impacted property owner and DEQ.

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EPA (United States Environmental Protection Agency). 2011. *Exposure Factors Handbook: 2011 Edition*. Washington, DC: Office of Research and Development, National Center for Environmental Assessment. EPA/600/R-090/052F.

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7.3 Additional Resources for Quality Assurance and Quality Control

- DEQ Quality Management: *https://www.deq.idaho.gov/public-information/assistance-and-resources/quality-management/*
- DEQ QAPP Template: *https://www.deq.idaho.gov/public-information/assistance-and-resources/quality-management/*
- Waste Division Sample Collection (QA/QC) Procedures:
  - *How DEQ Evaluates Sample Collection and Data Analysis for Site Assessments and Corrective Actions* (June 2023). *https://www2.deq.idaho.gov/admin/LEIA/api/document/download/4728*

  - *Data Review, Verification, and Validation of External Party Petroleum Data Quality Assurance Project Plan and Standard Operating Procedure* (January 2023). *https://www2.deq.idaho.gov/admin/LEIA/api/document/download/16288*
  - *How DEQ Evaluates Sample Collection and Data Analysis For Used Oil UST Closures and Releases* (November 2024) *https://www2.deq.idaho.gov/admin/LEIA/api/document/download/4726*
  - *Used Oil UST Closure and Release Sampling Standard Operating Procedures* (May 2017) *https://www2.deq.idaho.gov/admin/LEIA/api/document/download/4727*
  - *Standard Operating Procedure for Landfarming Petroleum-Contaminated Soils* (July 2017) *https://www2.deq.idaho.gov/admin/LEIA/api/document/download/4732*
  - *Standard Operating Procedures for Management and Disposal of Petroleum-Contaminated Soil Following a Release from a Non-Underground Storage Petroleum Storage Tank* (February 2014) *https://www2.deq.idaho.gov/admin/LEIA/api/document/download/4731*
- EPA Quality Management: *https://www.epa.gov/quality*
- EPA Quality Assurance: *https://www.epa.gov/fedfac/assuring-quality-federal-cleanups*
- EPA Data Quality: *https://www.epa.gov/fedfac/guidance-systematic-planning-using-data-quality-objectives-process*
- EPA Data Useability: *https://www.epa.gov/risk/guidance-data-useability-risk-assessment-part-1-final-april-1992*

Appendix A. Estimation of Exposure Point Concentrations in Soil and Groundwater

1. Background

Exposure point concentrations (EPC) are the *average* chemical concentrations to which receptors are exposed over a specified duration within a specified geographical area. The geographical area where a receptor moves and contacts contaminated media during the specified exposure duration is the exposure unit (EU). EPCs are also often referred to as representative concentrations.

This appendix describes the concept and methodology used to estimate EPCs. This guidance provides general recommendations on procedures to accurately determine EPCs. These recommendations may not apply to all sites, particularly large, complex sites. Site-specific circumstances may require consultation with the Idaho Department of Environmental Quality (DEQ), the application of professional judgment, and reference to the cited literature. Other useful resources are also included in this appendix.

In the site-specific application of the risk evaluation process, EPCs are used as input parameters in estimating the risk to a specified receptor for each complete route of exposure identified in the conceptual site model (CSM) and each petroleum chemical of interest (COI). Risk management decisions are then made based on a comparison of the estimated risk with the regulatory specified target risk. This comparison is termed a forward-mode calculation. EPCs can also be used in what are termed backward-mode calculations when they are compared with calculated target levels for each complete route of exposure and each petroleum COI. In either mode, the calculation of EPCs is critical in the outcome of the risk evaluation.

Complications in the calculation of the EPCs may arise because the concept of EPC is often mistakenly associated with a site as opposed to an exposure pathway or the source. Since there may be several complete pathways at a site, several EPCs, one for each complete pathway, should be estimated. For example, estimation of the soil EPC for the pathway involving soil leaching and protection of groundwater ingestion typically considers data over the entire soil profile from the source area. ~~At the same site, soil EPC estimates for the direct contact route of exposure involving surficial soil would typically consider only the upper several feet of the soil profile and would focus on the portions of the site where receptors may travel.~~ The accurate estimation of EPCs is complicated by several factors, including the following:

- Spatial variability in the concentrations
- Temporal variability in the concentrations
- Lack of sufficient, appropriately located, site-specific concentration data
- Poor definition or uncertainty in the location, size, or other characteristics of the EU

The uncertainty in the EPC introduced by some of these factors can be reduced by considering them during the development of the CSM and the sampling and analysis plan.

After samples have been collected and analyzed, the results need to be appropriately evaluated to produce sound estimates of EPCs. This evaluation includes assessing the following:

- Data quantity
- Data quality (which data are acceptable for use)
- Statistical methods (which methods to use)
- Which usable data apply to a specific EU

This guidance focuses primarily on the latter two issues.

2. Statistical Considerations for Estimating Exposure Point Concentrations

Numerous statistical methods can be employed to develop estimates of the exposure point (average) chemical concentration to which a receptor will be exposed. These methods include examining the maximum detected concentration, upper confidence limit (UCL) of the mean (for example the 95% UCL), arithmetic average, geometric average, area-weighted average, depth-weighted average, and volume-weighted average concentration (rarely used). Associated with each of these methods are certain advantages, disadvantages, and constraints on their appropriate use. There is no uniformly accepted statistical methodology to estimate the EPC. Implicit in the decision to use any particular method is the need to acknowledge and account for the representativeness of the samples collected, the homogeneity of the defined EU, the statistical distribution of the data, the minimum data requirements of the statistical method used, and the uncertainty in the resultant data used to derive the estimated concentration.

From a practical perspective, several factors common to petroleum release sites may make the use of statistical methods to develop EPCs at a given site unrealistic, particularly for ground water. These factors include the following:

- Small release areas
- Dominantly subsurface releases, often at great depth
- Focus on source areas and not exposure pathways
- Limited sample numbers due to temporal/spatial constraints

2.1 Maximum Detected Concentration

The use of the maximum detected chemical concentration is required for comparison to screening levels during the screening level evaluation (Section 3, “Screening Level Evaluation,” in the main body of the document). Depending on the quality of the site characterization data available, the maximum detected concentration can be used as EPCs in site-specific risk evaluations and will typically represent a conservative estimate of the average concentrations, particularly when sample numbers are low (i.e., four or less).

The effort necessary to calculate EPCs for certain complete pathways can be avoided by using the maximum media-specific concentrations when they do not exceed the target levels or when the cumulative risk, calculated using maximum concentrations, does not exceed the target risk.

2.2 Upper Confidence Limit

The true population mean is a unique value that can be calculated only if the entire population has been sampled (i.e., the entire contaminated media analyzed). Since the entire population is almost never sampled, the true mean is never known. At best, only an estimate of the true population mean concentration is possible.

To account for the uncertainty associated with the estimated mean concentration, a confidence interval about the true but unknown mean is often constructed. The interval estimate includes a range and an associated degree of confidence that the true unknown mean lies within this range. In risk assessment applications, instead of calculating a two-sided confidence interval, a one-sided confidence interval is most often estimated.

For the calculation of EPCs, the United States Environmental Protection Agency (EPA) has recommended, in most cases, using the 95% upper confidence limit (UCL) of the mean. The upper limit for a one-sided 95% confidence interval of the mean is defined as a value that, when calculated repeatedly for randomly drawn subsets of site data, equals or exceeds the true mean 95% of the time. Alternatively, the true mean exceeds the UCL only 5% of the time. Ideally, a minimum of 8 to 10 samples is desirable to generate a 95% UCL. Although the UCL can be determined with fewer samples, doing so tends to results in the 95% UCL estimate being larger (large variances) than the arithmetic average and will sometimes exceed the maximum measured concentration. In these instances, the maximum measured concentration can be substituted for the 95% UCL or the user can decide to collect more samples to reduce the sampling variance.

Several issues commonly arise with environmental data sets that complicate the development of the confidence limit and should be evaluated through the use of an exploratory analysis before performing the calculation. These issues include the following:

- Determination of the distribution of the data chosen to represent the EU (normal, lognormal, or nonparametric [i.e., not conforming to a specific distribution]). This determination includes decisions on what analysis and statistical tests to perform, how to interpret the test results, and how to treat the data once a determination is made.
- How to handle censored data and/or skewed data (typically due to nondetect [ND] values).

Depending on the nature of the underlying distribution of the data (or lack of), the one-sided 95% UCL can be calculated using a number of methodologies. The details about these methodologies are beyond the scope of this guidance.

EPA has developed technical guidance, a user's guide, and computer software (ProUCL) for calculating the UCL based on parametric (normal and lognormal distributions) and nonparametric distributions and when data sets have ND observations. The ProUCL (2022a) technical guidance describes the minimum data set conditions under which the ProUCL software will perform UCL calculations. These guidelines generally involve data set sizes greater than or equal to five with more than one detected value.

For samples collected using a multi-increment sampling approach, data set sizes as small as three may be sufficient to calculate a UCL. The Interstate Technology Regulatory Council (ITRC 2012) has developed a guide for incremental sampling methodology.

2.3 Arithmetic Average

Using the arithmetic average (or mean) is similar to the UCL with the disadvantage that no estimate of the uncertainty, variability of the average, or information regarding the underlying distribution of the population is incorporated into the value generated. For a population that is normally distributed, the estimates generated using the 95% UCL versus the mean tend to converge as the number of samples approaches 20 to 30.

2.4 Geometric Average

The geometric average is sometimes used as an estimate of the mean of lognormally distributed variables. It represents the value in the original scale of the mean of the transformed variable. It is, however, a biased estimate of the mean, and statistical texts caution against its use in environmental applications. Statistical texts or the ProUCL guide should be consulted when attempting to develop an unbiased estimate of the mean of a lognormally distributed variable (EPA 2022a,b). Exploratory data analysis should be conducted to confirm an assumption that the variable is lognormally distributed before calculating an EPC. As with the arithmetic average, no estimate of the uncertainty or variability is incorporated into the value generated by the geometric average and it may not be conservative.

2.5 Area-Weighted Average

Where sampling locations are unevenly spaced, area-weighted averaging methods can be employed to generate an estimate of the average concentration across an area. This calculation is done by generating an area (or Thiessen polygon) associated with each sampling location, assigning a *weight* to each data point based on the area of the polygon associated with that point, and summing the weighted data point values. One advantage of the method is that it is useful in characterizing areas where the number of sample points is low.

The method also has several disadvantages. First, the shape, and consequently the contribution of an area associated with a sample location to the *average*, is totally dependent on the spatial distribution of all data points and may not be reflective of the true distribution of contaminants at a site. Second, since each polygon is associated with one sample point, no estimate of the accuracy or error in the average value is possible. Finally, the method, unlike several other interpolation schemes, does not assume that points that are closer together are more similar than points that are farther apart. The method for calculating an area-weighted average using Thiessen polygons is discussed in section 5.

2.6 Depth-Weighted Average

Depth-weighted averaging methods are used to develop an average or EPC for a specific borehole where multiple samples at varying depth intervals have been obtained. In

characterizing a source area with multiple boreholes, the depth-weighted averages from each borehole can be used in a 95% UCL calculation. The methodology for depth-weighted averaging is described in the *Soil Screening Guidance: User's Guide* (EPA 1996).

2.7 Volume-Weighted Average

Volume-weighted averaging methods are a combination of area- and depth-weighted averaging techniques. They are rarely used in risk assessment evaluations.

3. General Considerations for Estimating Exposure Point Concentrations

Estimating EPCs requires considering several issues. Prior to performing the computations, consider the information in the following sections.

3.1 ~~Surface and Subsurface~~ Soil Concentrations

When evaluating exposure point soil concentrations consider the following:

- The spatial resolution of the data must be sufficient. While the exact number of necessary samples cannot be specified, data should be available from areas of known or likely sources, and the EU should be defined for a given pathway and receptor.
- Historical data should be examined closely before inclusion in the EPC estimate, particularly if the petroleum COIs are susceptible to biodegradation (such as petroleum hydrocarbons), volatilization, or leaching. If sufficient new data are collected, they may be used for risk evaluation and the old data may be disregarded. A new release requires the collection of additional data.
- If there is a *high* density of soil samples (> 30) for a homogeneous EU and sample locations are approximately equally spaced, the arithmetic average may be used instead of the 95% UCL or the area-weighted average. This method is acceptable because the area-weighted average, arithmetic average, and UCL concentrations will tend to converge if the underlying population can be assumed to be normally distributed. The > 30 value mentioned above should also be considered in relation to the size of the EU and may not be appropriate for very large EUs.
- ND soil samples located at the periphery of the EU (e.g., the footprint of a building) should not be used.
- ND samples (also referred to as left-censored data) located within the EU require special treatment. EPA has recently discouraged using replacement methods (such as half the detection limit). The proportion of ND samples in the subject data set and whether multiple detection limits exist will affect the specific methods used to generate summary statistics and the UCL. EPA ProUCL software has several options for handling left-censored data. Consult the technical guidance accompanying the software to determine which method is most appropriate for the specific data set and how to treat the censored data.

- If multiple ~~surficial~~ soil samples ~~and/or multiple subsurface soil samples are~~ available from the same borehole within the EU, the depth-weighted average or arithmetic average concentration of these samples may be used. If the samples are equally spaced, the depth-weighted average concentration will be the same as the arithmetic average concentration.
- An alternative to using discrete soil samples to calculate the UCL is to use incremental sampling methodologies. Incremental sampling is a sampling approach to obtain a pooled sample for analysis that has an analyte concentration representative of the EU. While it is similar to composite sampling, the incremental approach takes into account sample size to reduce variability and also allows for the calculation of a UCL while only requiring a few samples for laboratory analysis. It typically requires greater up-front planning with respect to sampling design, methodology, and defining of data quality objectives than traditional composite sampling.
- If vapor intrusion is a potentially complete pathway, collecting soil vapor data, in lieu of soil samples, for characterizing the potential risk should be considered. Consult the *Technical Guide for Addressing Petroleum Vapor Intrusion at Leaking Underground Storage Tank Sites* (EPA 2015b).

3.2 Groundwater Concentrations

Follow the guidelines listed below to account for the temporal and spatial variation in groundwater concentrations. These recommendations apply primarily to evaluation of groundwater data for estimating EPCs for risk evaluation.

They are not intended for cases where other monitoring objectives, such as determining compliance with cleanup criteria or site closure, are the primary goals.

- For wells with a clear increasing or a decreasing trend, data from the most recent 12 months or the 4 most recent measurements should be averaged (use whichever covers the longer duration). Note that for wells with increasing trends, continued monitoring may be needed until the trend stabilizes or decreases. The need for additional monitoring is a site-specific determination that depends on a number of factors, including the magnitude of measured concentrations in relation to risk-based criteria, the degree to which samples are representative and address site factors such as seasonality, and the estimated travel time of contamination from the release area to groundwater and to potential receptors. For example, four measurements, taken at appropriate intervals over the course of a year, show an increasing trend but are all below applicable risk criteria. Further monitoring to develop an EPC may not be necessary.
- For wells with stable or fluctuating concentrations with no apparent trend, data from either the most recent 24 months or the 8 most recent measurements should be used to develop a 95% UCL.
- If site groundwater analytical data are limited (number of wells or number of sampling events) and prevent adequate statistical analysis, using the maximum concentrations is preferred. Using the average concentration is discouraged, particularly if the plume

stability status (increasing, decreasing, or stable) with respect to the release is unknown or the representativeness of the available data is in question.

- While developing the EPC for wells described by the first two bullets above, the treatment of left-censored data (concentrations below detection limits) deserves special consideration and may require specialized analysis techniques. Replacement techniques (such as using half the detection limit) are currently discouraged by EPA. If the percentage of ND values is a significant percentage of the total number of data points (> 25%), the representativeness of the data set for the EU in question should be evaluated.
- Wells with concentrations consistently below detection limits in the periphery of the EU should not be used.
- For wells that contain free product where it is not possible to obtain a representative dissolved phase sample, the use of the effective solubility of petroleum COIs should be considered as a conservative surrogate for their chemical concentration in estimating EPCs.

Two useful documents that provide guidance on the statistical evaluation of groundwater monitoring data are the *Statistical Analysis of Groundwater Monitoring Data at RCRA Sites Unified Guidance* (EPA 2009) and *Statistical Guidance for Determining Background Ground Water Quality and Degradation* (DEQ 2009).

4. Calculation of Exposure Point Concentrations

An EPC is necessary for each complete exposure pathway at a site. Based on the pathways typically considered in the risk evaluation process, the EPCs listed below are typically needed for each media.

4.1 ~~Surficial~~ Soil ~~(0–1 Foot Below Ground Surface)~~

The risk evaluation process considers two pathways of exposure associated with ~~the surficial~~ soil: (1) ingestion of chemicals in groundwater or exposure to surface water impacted by discharge of contaminated groundwater resulting from ~~due to~~ leaching of ~~residual~~ chemicals ~~present~~ in ~~the surficial~~ soil; (2) indoor inhalation of vapor emissions; and (~~2~~3) accidental ingestion of soil, outdoor inhalation of vapors and particulates from ~~surficial~~ soil emissions~~,~~ and dermal contact ~~with surficial soil~~. These ~~two~~three pathways are referred to as the groundwater protection, vapor intrusion, and direct soil contact pathways, respectively. Three different soil EPCs are required (one for each complete pathway). Additional EPCs may be required if the receptor's EU for current and future conditions is different.~~At most, two different surficial soil EPCs are required, although typically one EPC estimate can be used for both pathways.~~

4.1.1 Exposure Point ~~Surficial~~ Soil Concentration for the Groundwater Protection Pathway

Figure A-1 shows a schematic of the soil leaching to groundwater pathway. ~~The evaluation of this pathway for surficial soil assumes that the contamination does not extend greater than 1 foot below ground surface. If this is not the case, then samples taken in the surficial soil zone~~

~~should be included with those from greater depth and evaluated together.~~ The EPC for this pathway should be based on the soil concentrations measured within the source area.

The conceptual site model for this pathway also assumes that the leachate from the ~~surficial (or subsurface)~~ soil source travels vertically downwards to the water table without any lateral or transverse spreading. The horizontal dimensions of the ~~surficial (or subsurface)~~ soil source and the groundwater source are identical. Estimating the source dimensions requires considerable professional judgment. Factors typically considered in making these estimates include historical knowledge of where a spill or source was located, visual clues such as soil discoloration, and laboratory data (taking care not to include samples with ND results).

Irrespective of the manner in which the source area is identified, it is important to indicate the dimensions of the source on a map. The method used to derive the EPC should typically be either the UCL of the mean (when the quantity and characteristics of the data available allow a statistical analysis) or the values derived from an incremental sampling approach. The exposure point soil source concentration would be the average concentration calculated using the data within the soil source area. If the source area is small (several tens of feet across), typically smaller numbers of soil samples are available. In this case, the 95% UCL should first be calculated if the sample numbers for applicable data are adequate. If the 95% UCL exceeds the maximum concentration, it may be appropriate to use the maximum concentration.~~The exposure point surficial soil source concentration should be estimated using only the surficial soil data collected within the delineated source zone. The method used to derive the EPC should typically be either the UCL of the mean (when the quantity and characteristics of the data available allow a statistical analysis) or the values derived from an incremental sampling approach.~~

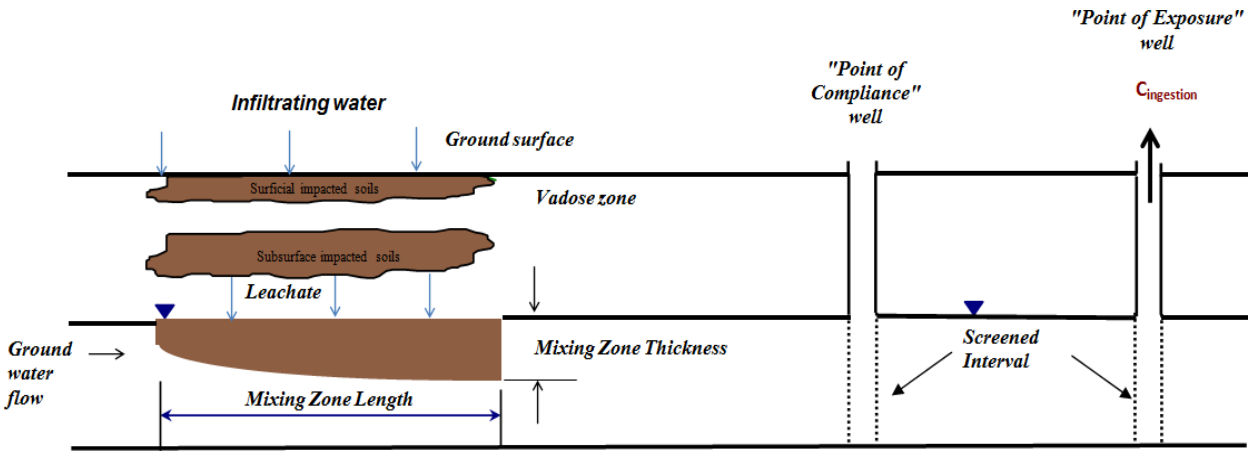


Figure A-1. Schematic of soil leaching to groundwater.

4.1.2 Exposure Point ~~Surficial~~ Soil Concentrations for the Direct Contact Pathway

The direct contact pathway includes: accidental ingestion, dermal contact, and outdoor inhalation of vapors and particulates from soil.

For this pathway, the exposure point ~~surficial~~ soil concentration must be based on the receptor's EU (i.e., the area where the receptor may be exposed to the ~~surficial~~ soil). The exact location of this area is often difficult to estimate because it must represent a period of time equal to the receptor's exposure duration (e.g., up to 30 years for residential land use and about 7 years for nonresidential land use). In most cases, it is reasonable to assume that the receptor will access all portions of the EU in a random manner. ~~Under current conditions, in the absence of specific information about the receptor's activities, the unpaved portion of the site may be considered as the receptor's approximate EU. This guide would not apply when volatile organic compounds (VOCs) are included in the list of potential petroleum COIs and/or the paved portion is in poor condition or consists of a material that does not limit VOC migration. For potential future exposures, if the current condition cannot be assumed to continue, the assumption should be made that the pavement is removed, exposure to surficial soil is possible, and the entire site should be considered as the EU.~~

~~If the possibility exists that, for a future-use residential scenario, contaminated subsurface soil existing under a current nonresidential scenario may be brought to the surface and result in direct contact residential exposures at the surface, the appropriate subsurface data should be included in the estimate of the EPC.~~

To estimate the EPC for this pathway, it would be necessary to estimate the receptor's area of exposure and determine the depth, areal extent, and number of soil samples available within this EU. This information should be used to estimate the 95% UCL or an area-weighted average concentration using the procedures discussed in section 5. The use of an incremental sampling approach for characterizing EPCs for this route of exposure may be particularly well-suited and efficient.

~~4.2 Subsurface Soil (Greater Than 1 Foot Below Ground Surface)~~

~~The risk evaluation process includes two pathways of exposure associated with subsurface soil: (1) ingestion of chemicals in groundwater or exposure to surface water impacted by discharge of contaminated groundwater resulting from leaching of chemicals in subsurface soil and (2) indoor inhalation of vapor emissions. These two pathways are referred to as the groundwater protection and vapor intrusion pathways, respectively. Two different subsurface soil EPCs are required (one for each complete pathway). Additional EPCs may be required if the receptor's EU for current and future conditions is different.~~

~~4.2.1 Exposure Point Subsurface Soil Concentration for Groundwater Protection Pathway~~

~~The leachate from the subsurface soil source is assumed to travel vertically downwards without any lateral or horizontal spreading (Figure A-1). The EPC for this pathway should be based on the subsurface soil concentrations measured within the source area.~~

~~As in the case of the surficial soil concentration protective of groundwater (section 4.1.1), the exposure point subsurface soil source concentration would be the average concentration calculated using the data within the soil source area. If the source area is small (several tens of~~

~~feet across), typically smaller numbers of soil samples are available. In this case, the 95% UCL should first be calculated if the sample numbers for applicable data are adequate. If the 95% UCL exceeds the maximum concentration, it may be appropriate to use the maximum concentration.~~

4.12.23 Exposure Point ~~Subsurface~~ Soil Concentration for Vapor Intrusion Pathway

The use of soil concentration data is not allowable, collect soil vapor data (section 4.5).

~~4.3 Exposure Point Concentration for Protection of a Construction Worker~~

~~The risk evaluation process includes the evaluation of one pathway of exposure for construction workers: accidental ingestion, dermal contact, and outdoor inhalation of vapors and particulates from soil.~~

~~For the construction worker, no distinction is made between the surficial and subsurface soil because subsurface soils may be exposed during construction. To estimate the EPC for the construction worker, identify the depth, areal extent, and number of samples taken within the zone of construction. The potential future depth of construction can be estimated by contacting local construction firms and identifying the typical depth of utilities on and adjacent to the site, contacting local utility companies, or using as-built plans for proposed facilities if they exist. If the areal extent of the construction area is not known, it may be conservatively estimated as the source area. If sample results are available for several depth intervals, these should be averaged using depth weighting. The depth-weighted averaged values from multiple boreholes could then be combined to calculate a 95% UCL or area-weighted average, as appropriate. The EPC would be the depth-weighted average concentration within this zone of construction.~~

4.24 Groundwater

The risk evaluation process requires evaluating two routes of exposure associated with shallow groundwater: (1) ingestion of groundwater and (2) indoor inhalation of vapor emissions from groundwater. Where multiple aquifers are present, the shallowest aquifer is typically the aquifer first considered for both pathways. Site-specific circumstances—such as the disappearance of the shallow aquifer or transport of contamination to the deeper aquifer—may require evaluation of both aquifers. Characterization of petroleum COIs in both aquifers should still be performed. At a minimum, two different groundwater EPCs, one for each complete pathway, are required.

4.24.1 Exposure Point Compliance Well Concentration for Groundwater Protection Pathway

For the ingestion of groundwater pathway, maximum contaminant levels (MCLs) or equivalent concentrations must be met at the point of exposure location. For any petroleum COI that does not have an MCL, the risk-based equivalent level is calculated as residential tap water (section 3.1). Often, the point of exposure well location is hypothetical and data may not be available.

Alternatively, if a point of exposure well is present, an upgradient sentry or compliance well is often used as an early warning monitoring location. In both cases, groundwater transport models are used to calculate the predicted concentrations at the point of exposure based on source area concentrations, the allowable concentrations in the source area, or an alternate point of compliance location concentration that will result in acceptable concentration at the point of exposure. In any case, EPCs must be estimated for the source area or for the alternate point of compliance location. In addition, one or more compliance wells must be identified, and target compliance well concentrations (typically higher than the exposure well concentration) must be calculated at these wells.

To evaluate this pathway, the EPCs in the source area, point of compliance, or point of exposure locations should be calculated based on the measured concentrations as discussed below. In most cases, a rule of thumb is that measurements taken more frequently than quarterly would not be considered statistically independent samples, would not be accepted to meet the specified number of measurements, and should not be used for statistical analysis and hypothesis testing. Methods to evaluate temporal independence are discussed in the EPA (2009) *Statistical Analysis of Groundwater Monitoring Data at RCRA Sites Unified Guidance* and DEQ (2009) *Statistical Guidance for Determining Background Ground Water Quality and Degradation*.

For wells with no clear trend, the EPC should be estimated as the 95% UCL if the data permit. Where the calculated 95% UCL exceeds the maximum concentration or if the data are not suitable for statistical analysis, the maximum concentration should be used as the EPC. For compliance wells with stable, clearly decreasing, or clearly increasing trends, the EPC is estimated as the 95% UCL of the most recent 1 year of data or most recent 4 measurements, whichever represents the longer time duration. For wells with an increasing concentration trend, continued monitoring may be needed until the trend stabilizes. Quarterly data for at least 1 year is recommended. The data should be pooled for source area characterization where multiple wells are available. Wells clearly not part of the source area of contamination should not be included in the calculations.

4.24.2 Exposure Point Groundwater Concentration for Protection of Indoor Inhalation Pathway

Groundwater concentrations protective of indoor inhalation are estimated using EPA's Vapor Intrusion Screening Level (VISL) calculator. The EPCs for this pathway should be based on the groundwater concentration measured within and adjacent to the footprint of the building.

For the indoor inhalation of vapor emissions from groundwater, multiple EPCs may be required if the plume has migrated below several current or potential future buildings. For example, if a plume has migrated or is likely to migrate below two different buildings (e.g., on-site and off-site buildings), separate on-site and off-site EPCs should be estimated.

If the plume has migrated below several buildings with similar receptors (residential or commercial), it may be sufficient to evaluate this pathway only for the building below which the

concentrations are the highest and/or the depth to groundwater is the lowest. If this building is protective of indoor inhalation exposures, it may not be necessary to evaluate other buildings.

The plume may not be in the proximity of current structures. If assumed future land use includes the possibility of building structures in the vicinity of the plume, a similar calculation of EPCs and risk should be made using appropriate assumptions about the location and type of future structures.

While the target groundwater concentrations are based on the assumption of no lateral or transverse spreading of the vapors as they diffuse upwards to the building, site characteristics such as site lithology and preferential pathways may result in lateral migration towards a structure (*Technical Guide for Addressing Petroleum Vapor Intrusion at Leaking Underground Storage Tank Sites* [EPA 2015b]). For this reason, the EPCs should be conservatively based on data gathered adjacent to the structure. After identifying the locations of the building footprints and the appropriate groundwater monitoring data within and adjacent to each footprint, the 95% UCL or area-weighted average concentration within each footprint may be estimated (section 5).

4.~~5~~3. Soil Vapor

Soil vapor is used exclusively to evaluate the risk posed via the vapor intrusion pathway. In most cases, because of the variability commonly observed with vapor measurements and the uncertainty of vapor flow paths from the subsurface into indoor spaces, it is preferable to use the maximum concentrations measured within the defined EU. Where multidepth sampling of soil vapor has demonstrated attenuation of concentrations and the presence of a sufficient thickness of oxygenated soil conditions, the use of lower concentrations may be acceptable. Sufficient sample numbers are more often available where source areas or the buildings under consideration are large. In these situations, the use of area- weighted averaging or other statistical methods may be appropriate.

5 Estimating Area-Weighted Exposure Point Concentrations

Area-weighted EPCs can be estimated using the Thiessen polygon method. If the available data are located on a uniform grid, the area-weighted average would be the same as the arithmetic average. If the dimensions of the source and the receptor's EU are relatively small (several tens of feet across) and very few (one to six) soil samples are available within the soil source, the arithmetic average concentration may be used as an approximation of the area-weighted average concentration.

5.1 Step 1: Identify the Exposure Unit

The first and most critical step is to identify the size and location of the EU over which the area-weighted EPC has to be estimated. The location and size of this EU will often vary depending on the evaluated pathway. Specific guidance on the location of the receptor's area of exposure is discussed in sections 3 and 4. Area-weighted concentrations can only be estimated if multiple samples have been collected within the unit. If several samples are available just outside the

EU, it may be reasonable to extend the size of the unit to include this data. If the values of these samples are ND, they should not be included. This exclusion is technically justified since at most sites the location of the EU is approximate at best.

As part of Step 1, draw a site map of the various EUs for which area-weighted concentrations are desired. Clearly label the location of data points (i.e., soil borings and monitoring wells) on the map.

If the borings or monitoring wells within the EU are located in a regular grid, the calculation of an area-weighted average is unnecessary and the user should proceed with an EPC calculation using a different method, such as the 95% UCL.

5.2 Step 2: Subdivide the Exposure Unit

The EU, identified in Step 1, is discretized into polygonal elements by connecting the sampling points within each EU (identified in Step 1) and drawing perpendicular bisectors to these lines to form polygons. The area of each Thiessen polygon is then estimated.

5.3 Step 3: Estimate Exposure Point Concentrations for Each Thiessen Polygon

The concentration measured at the sampling location within each polygon is considered representative of the area of each polygon. As discussed in section 3, if multiple data are available from a location (either multiple depths or dates), compute the arithmetic average concentration of each petroleum COI measured at that location. The arithmetic concentration is then considered representative of the polygon.

5.4 Step 4: Estimate Area-Weighted Average Concentration for the Exposure Unit

The area-weighted average concentration for the EU is estimated using Equation A-1:

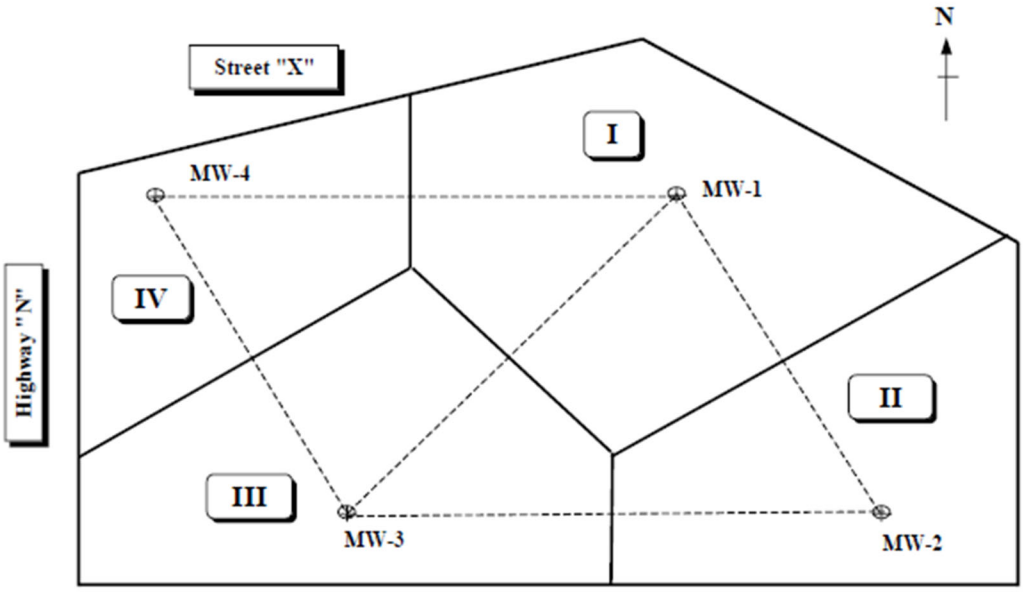
$$C_{area} = \frac{\sum_{i=1}^{i=n} (A_i * C_{avg,i})}{A_{Total}}$$

Equation A-1. Area-weighted average concentration.

Where,

C_{area} = area-weighted average concentration over the EU (mg/kg)
A_i = area of each Thiessen polygon (m^2)
A_{Total} = total area of the polygons (i.e., area of the EU) (m^2)
$C_{avg,i}$ = mean of soil or groundwater concentrations measured within the polygonal element *i* (mg/kg)

An example application of the Thiessen polygon method is schematically shown in Figure A-2.



Polygonal Element	Mean Soil Concentration $C_{avg,i}$ mg/kg	Area of the Element A_i m^2	$A_i * C_{avg,i}$ m^2 - mg/kg	Area Weighted Average Concentration mg/kg
I	2	604	1208	
II	1.8	398	716.4	
III	1.2	578	693.6	
IV	1	234	234	
	TOTAL	**1814**	**2852**	
Area Weighted Average Concentration = $C_{area} = \frac{\sum_{i=1}^{i=n}(A_i * C_{avg,i})}{A_{Total}}$				**1.57**

Figure A-2. Thiessen polygon method.

6 Recommendations

- For most pathways, 95% UCL techniques are recommended for developing EPC estimates of average concentrations. For cases where the number of samples is low (four or fewer) and/or the number of ND values is high, the use of the maximum concentration may be most appropriate. The use of the maximum may also be appropriate when the calculated 95% UCL exceeds the maximum concentration

measured at the site and the collected data are considered representative of site and EU conditions.

- The use of area-weighted average methods is not recommended for most pathways~~, but may be justified in developing EPCs for the surficial soil pathways.~~ . The inclusion of methods that evaluate and incorporate spatial uncertainty into the area-weighted average calculation increases the validity of the estimate derived.

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Appendix B. Application of Natural Attenuation

Introduction

This appendix presents general guidance on the applicability and implementation of remediation by natural attenuation (RNA) at petroleum release sites in Idaho. Its primary focus is on attenuation of groundwater contamination. Attenuation of petroleum hydrocarbons has also been documented in other media such as soil and soil vapor.

Attenuation in soil vapor is addressed in the *Technical Guide for Addressing Petroleum Vapor Intrusion at Leaking Underground Storage Tank Sites* (EPA 2015b), which discusses evaluation of the vapor intrusion pathway. This appendix is divided into three parts:

- Part I presents a brief overview of the science of natural attenuation (NA).
- Part II presents the regulatory requirements for implementing NA as a remedial option.
- Part III discusses the techniques available to support, quantify, and implement NA as a remedial option.

PART I: The Science of Natural Attenuation

Part I presents an overview of the science of NA, including the following topics:

- Brief overview of the processes that constitute NA (section 2)
- Description of how biodegradation operates in attenuating petroleum hydrocarbons (section 3)
- Description of the indicators of NA of hydrocarbon plumes (section 3.5)

1 The Concept of Natural Attenuation

The term natural attenuation refers to the reduction in concentration or mass of chemicals in a media due to the effects of various environmental fate and transport processes. NA occurs without human intervention. Although NA is applicable to a reduction in concentration in any medium (e.g., air, surface water, and groundwater), in this appendix it refers to the reduction in concentration of a dissolved groundwater contaminant plume. For a groundwater plume, environmental fate and transport processes include physical processes (advection, dispersion, dilution, sorption, and volatilization); chemical processes (hydrolysis, oxidation, and reduction); and biodegradation processes (aerobic and anaerobic). Physical processes are nondestructive in that they redistribute the chemicals in the environment without affecting the total mass of the individual chemical. Chemical transformation processes and biodegradation result in the transformation of the parent chemical into other chemicals referred to as daughter products.

The only human action involved in RNA is monitoring to demonstrate that concentration reduction is occurring at a reasonable rate. Depending on site-specific conditions, RNA may be used as a stand-alone corrective action strategy or in combination with other engineered remediation alternatives.

This guidance focuses on using NA on sites contaminated with petroleum products. NA has also been used at sites with other classes of contaminants, such as metals, explosives, and pesticides. The same concepts for evaluation, requirements for site characterization, and demonstrations as to effectiveness are required regardless of the class of contaminant. A general approach to the evaluation of the bioremediation aspects of NA for a range of biotreatable compounds is described in the *A Systematic Approach to In Situ Bioremediation in Groundwater Including Decision Trees on In Situ Bioremediation for Nitrates, Carbon Tetrachloride, and Perchlorate* (ITRC 2002).

2 Overview of Natural Attenuation Processes

Although each contaminated site is unique, for this discussion it is useful to consider a generic site where a petroleum spill has occurred. The soil immediately below and around the point of release becomes contaminated, and the contaminant front moves downward. The downward movement of the contaminant front continues until one of the following three conditions occurs:

1. The soil sorption capacity exceeds the amount of contaminant available.
2. An impermeable barrier is encountered and the contaminant spreads horizontally.
3. The contaminant reaches the water table and, if it is a light nonaqueous phase liquid (LNAPL), spreads horizontally.

The term LNAPL relates to the density of the released contaminant. LNAPLs are chemicals that are liquid at ambient temperature but lighter than water. For example, the density of toluene is 0.866 grams per cubic centimeter (g/cc) compared to a density of 1 g/cc for water.

After the contaminant movement has stopped, the soil through which it traveled is contaminated with residual chemicals that act as a contaminant source for the groundwater plume. Figure B-1 shows a schematic of a LNAPL moving through the soil to the groundwater.

When rainwater infiltrates through the residual contaminated soils, it dissolves and leaches out the soluble components. For petroleum hydrocarbons, the toxic soluble chemicals include, but are not limited to, benzene, toluene, ethylbenzene, and xylene (BTEX); the soluble additives methyl tertiary butyl ether (MTBE) and ethylene dibromide; and smaller fractions of other less-soluble constituents. After undergoing NA processes in the unsaturated zone, these dissolved chemicals reach the water table, mix with groundwater, and move with the groundwater to form a dissolved plume. At sites where the spill is of a sufficient quantity to reach the water table and form an LNAPL layer on the water table, soluble constituents from the LNAPL gradually dissolve in groundwater and form a dissolved groundwater plume.

Additionally, vapors of volatile hydrocarbons (chemicals with a Henry's Law constant greater than 1×10^{-5} atm-m^3/mole) will spread outwards from the contaminated soil and dissolve in soil moisture and groundwater.

As the dissolved plume moves through the unsaturated and the saturated zones, its concentration decreases due to the combined influence of several NA processes. Each of these processes is briefly discussed below.

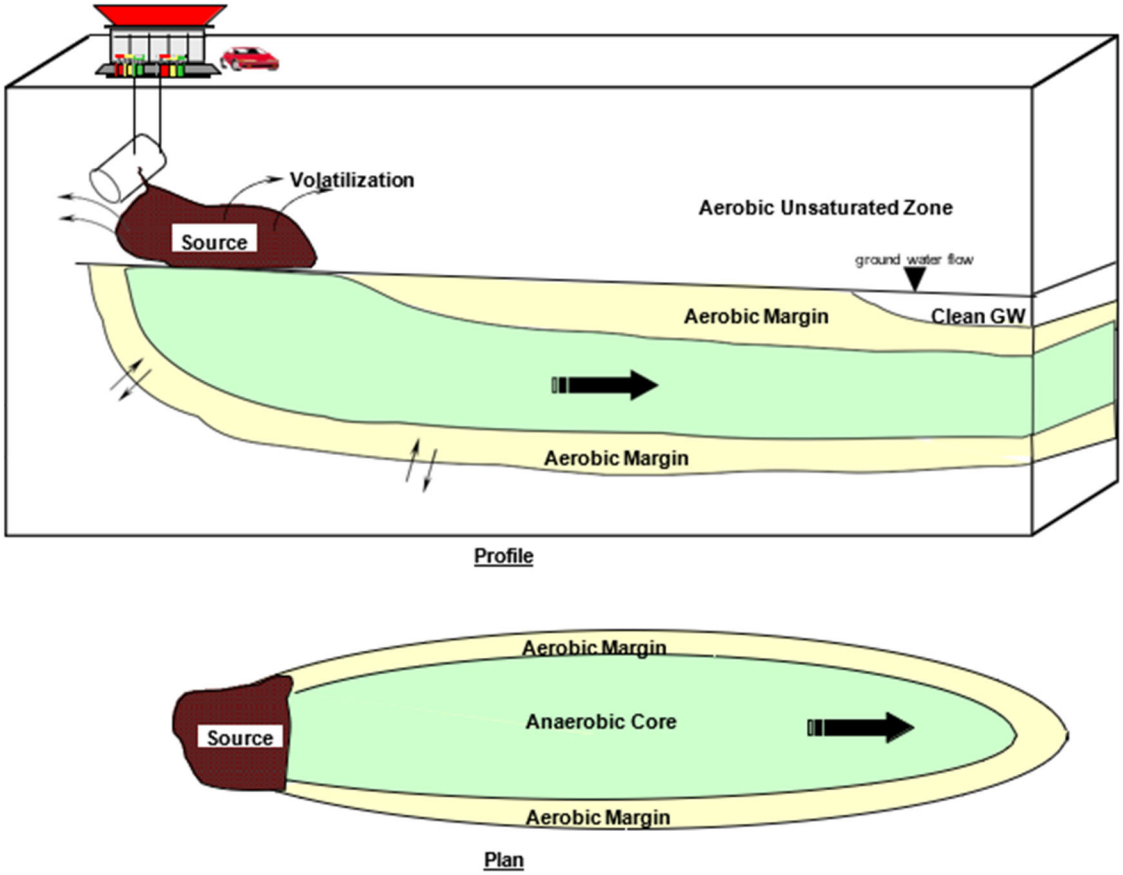


Figure B-1. Schematic of a hydrocarbon release.

2.1 Advection

Advection refers to the bulk movement or flow of water caused by differences in density, temperature, or pressure. In most aquifers, flow occurs predominantly due to hydraulic gradients that may be natural—resulting in regional groundwater movement—or man-made, caused by pumping or artificial recharge. In saturated zones, hydraulic gradients may exist in horizontal and vertical directions, resulting in complex three-dimensional flow patterns. However, at most sites a predominant flow direction exists that results in the migration of most mass.

As water moves in the saturated zone, it carries with dissolved constituents. The process results in the migration of dissolved constituents in the saturated zone without a change in concentration and is termed advection.

Parameters required to estimate the volume of water moving through a saturated zone include the Darcy velocity and the cross-sectional flow area. Darcy velocity is estimated using hydraulic conductivity and hydraulic gradient.

Hydraulic conductivity may be estimated using a variety of methods, including slug tests, pump tests, grain size distribution, and literature values corresponding to the site stratigraphy. For most saturated zones, hydraulic conductivity varies in the horizontal and vertical directions.

Site-specific values of hydraulic gradients are estimated based on water-level measurements in monitoring wells, or piezometers. When estimating horizontal hydraulic gradients, it is important to compare data from wells screened in the same saturated zone. Wells screened in different zones or at different depths (e.g., cluster wells) can be used to estimate the vertical hydraulic gradient between the zones. Site-specific hydraulic gradients may exhibit seasonal and spatial variations (in magnitude and direction) due to a variety of factors such as pumping, seasonal flow in surface water bodies, and seasonal variations in rainfall.

Another related parameter used to estimate the travel time of a chemical due to advection is the seepage velocity, which requires an estimate of the porosity of the media.

Typically, literature values corresponding to the aquifer type (e.g., sand or silt) are used to estimate porosity.

2.2 Molecular Diffusion

Molecular diffusion refers to the transport of chemical mass from a zone of higher concentration to a zone of lower concentration due to the movement of molecules. The effect of diffusion is to spread the chemical mass over a large area and reduce the overall concentration. Diffusion results in a reduction in concentration by dilution. In most groundwater systems where there is advection, the attenuation in concentration or the chemical mass transport due to diffusion is small and often negligible. However, in no-flow or low-flow situations, diffusion can be an important attenuation mechanism.

Molecular diffusion is quantified using Fick's Law, and the parameter required to quantify diffusion is the effective diffusion coefficient of the chemical.

2.3 Mechanical Dispersion

Mechanical dispersion refers to the spreading of the contaminant plume that occurs due to variations in the flow velocity. In the saturated zone, velocity variations occur due to a variety of factors, including interpore and intrapore velocity variations and the tortuosity of the porous media. The net effect of mechanical dispersion is that the chemical spreads both horizontally and vertically, reducing the overall concentration in the plume. Like diffusion, dispersion is a dilution process.

The transport of mass due to mechanical dispersion is quantified using Fick's Law. The key parameters are the dispersivity coefficients in the three cardinal (*x*, *y*, and *z*) directions. Dispersivity values have been measured using tracers at several research sites, based on which

empirical dispersivity relationships have been developed. For most site-specific applications of fate and transport models, these empirical relationships are used. Higher dispersivity values result in larger plumes, which result in increased dilution and lower concentrations.

2.4 Hydrodynamic Dispersion

The term hydrodynamic dispersion refers to the sum of molecular diffusion and mechanical dispersion. In most groundwater systems where there is advection, hydrodynamic dispersion is approximately equal to mechanical dispersion, since the effect of molecular diffusion is negligible.

2.5 Sorption

Sorption refers to the transfer or distribution of mass between the liquid and solid phases. Sorption has the overall effect of reducing the mobility of the chemical, which increases its residence time in the subsurface and the amount of microbial degradation. This distribution is quantified by the soil water partition coefficient. For organic chemicals, the partition coefficient depends on the chemical-specific normalized organic carbon partition coefficient and the organic carbon content in the soil. The partition coefficient is used to estimate the retardation factor for the chemical, which is a measure of the *stickiness* of the chemical to the formation. Parameters required to estimate the retardation factor include porosity, organic carbon content of soil, bulk density of soil, and chemical-specific normalized organic partition coefficient.

2.6 Volatilization

Volatilization refers to the transfer of chemical from the LNAPL or dissolved phase to the vapor phase. Vapors can migrate by diffusion alone (in the absence of a pressure gradient) and by diffusion and advection if a pressure gradient exists in the formation. Chemicals volatilizing from the dissolved plume occupy the pores in the unsaturated zone and migrate outwards due to the combined influences of molecular diffusion and vapor-phase advection if pressure gradients exist. Volatilization can result in a net loss of chemical from the dissolved phase or from the LNAPL.

The chemical-specific factors controlling volatilization from a dilute solution and LNAPL are the Henry's Law constant and saturated vapor pressure, respectively. These factors are sensitive to the temperature of the media where volatilization occurs.

2.7 Biodegradation

Biodegradation refers to the destruction of chemicals by indigenous microorganisms present in the aquifer. For petroleum hydrocarbons, biodegradation is the primary destruction mechanism. Due to the significance of biodegradation within the overall process of NA, biodegradation is discussed at length in section 3. In certain situations, additional compounds (e.g., ozone, oxygen, and peroxide), nutrients, or microorganisms may be added to the contaminant plume to enhance the rate of biodegradation.

2.8 Overall Effect of Natural Attenuation Processes

As explained above, the process of NA refers to a combination of advection, molecular diffusion, dispersion, sorption, volatilization, chemical reactions, and biodegradation.

The combined effect of these processes is to spread or reduce the chemical mass in the dissolved plume. The concentration of the chemical decreases as distance from the source increases. Figure B-2 shows the concentration profiles in actual monitoring wells downgradient of a source and the expected concentrations under ideal conditions.

Although such patterns have been observed at several sites, fluctuations in water levels, flow direction, and climatic conditions often result in nonideal behavior. Additional complications occur due to errors in data collection, analytical measurements, and the existence of multiple sources (in space and time) at a site.

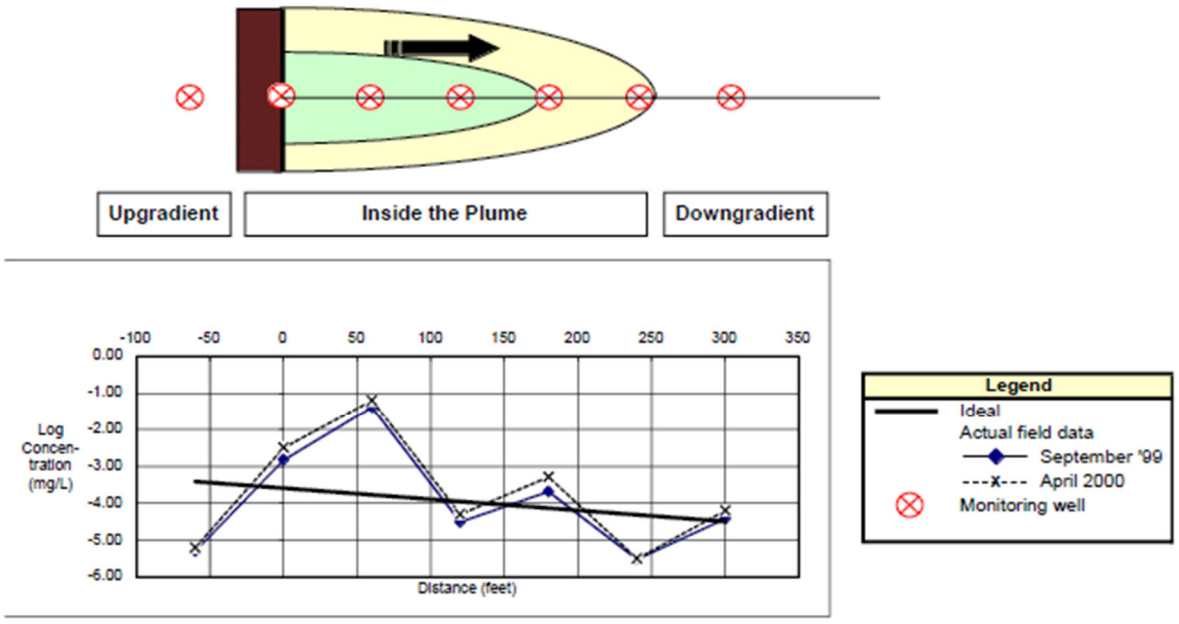


Figure B-2. Concentration profile as a function of distance (ideal behavior and data from an actual site).

Depending on the overall rate of NA and the on-going contribution of chemicals to the groundwater plume from the residual soil source, groundwater plumes may be classified as expanding, stable, or shrinking.

2.8.1 Expanding Plume

An expanding plume is characterized by increasing concentrations within the plume and/or an outward movement of the plume that increases the size of the plume. An expanding plume

occurs when the chemical mass loading to the plume from leaching or dissolution of residual LNAPL exceeds the mass loss due to NA processes.

In an expanding plume, NA processes continue to occur but at a rate too slow to prevent the increase in concentrations or the size of the plume.

2.8.2 Stable Plume

A stable plume is characterized by stable concentrations within the plume and at the periphery of the plume (i.e., the concentrations do not show a decreasing or increasing trend). For a plume to be stable in size or concentration, the rate of chemical mass addition to the plume from the source is equal to the rate of chemical mass loss by NA processes. The source may be the chemicals leaching from adsorbed and residual concentrations in the capillary/water table fluctuation zone or in the vadose zone or the dissolution of chemicals from the LNAPL source.

2.8.3 Shrinking Plume

A shrinking plume is characterized by decreasing groundwater concentrations within the plume, decreasing concentrations at the periphery of the plume, or a decrease in the area of the plume. For a shrinking plume, the addition of chemical mass from the source is less than the mass lost due to NA processes. Unless site-specific conditions change that result in an increase in chemical mass addition to the plume or a decrease in the rate of NA, the plume will eventually disappear.

2.8.4 Lifecycle of a Plume

Initially, when a chemical reaches the groundwater and a plume forms, it is an expanding plume. The plume continues to expand as long as the addition of chemical mass from the source exceeds mass loss by NA processes. As the plume expands and occupies an ever-increasing portion of the aquifer, the loss of mass by NA processes increases. A point is reached when the mass addition equals mass lost, and the plume becomes stable. Because of the phenomenon of NA, most BTEX plumes resulting from service station spills become stable at lengths less than 500 feet, as demonstrated by numerous plume studies. At most sites, the chemical source is finite; in time, the mass loading from the source to the dissolved plume decreases.

Meanwhile, the rate of mass loss due to NA processes increases or stays the same, so eventually the plume begins to shrink.

Under ideal conditions, all dissolved chemical plumes would follow this lifecycle; however, real plumes may not follow this pattern due to a number of confounding factors:

- Variations in groundwater velocities that affect the rate of NA
- Fluctuations in the water table that affect the source mass loading due to the release of chemicals trapped in the capillary fringe
- Variations in climatic conditions that affect the rate of NA
- Variations in rainfall and infiltration that affect mass loading to groundwater
- Additions to the plume from new releases and spills from operating facilities

Because of the above complications, it is important to collect and evaluate all the site data and look at multiple lines of evidence to understand the plume behavior and predict its future behavior (section 3.5).

3 Biodegradation of Petroleum Hydrocarbons

This section discusses the biodegradation of dissolved petroleum hydrocarbons and identifies the various indicators that should be measured to confirm biodegradation.

The biodegradation of hydrocarbons is the process by which naturally occurring subsurface microorganisms biodegrade contaminants. The process of biodegradation, as facilitated by microorganisms, is represented by the general reaction:

Hydrocarbon + Electron Acceptors + Nutrients YIELDS Carbon Dioxide + Water + Microorganisms + Waste Products

This biologically mediated reaction produces energy for cell growth and reproduction of the microbial population. The process of electron transfer results in the oxidation of the donor (hydrocarbon), reduction of the electron acceptor, and the production of usable energy for the organisms. Based on the principles of thermodynamics, biologically mediated reactions that yield the most energy are favored over reactions that yield less usable energy for the organisms. For hydrocarbons, biologically mediated reactions ideally occur in the following order:

1. Dissolved oxygen in the groundwater is used as the electron acceptor.
2. After all oxygen has been depleted and anaerobic conditions exist within the dissolved plume, dissolved nitrate is used as the electron acceptor.
3. After the depletion of dissolved oxygen and nitrate, ferric iron is used as an electron acceptor and is reduced to ferrous iron.
4. After the depletion of oxygen, nitrate, and iron, sulfate is used by sulfate-reducing bacteria to degrade the hydrocarbons.
5. Methanogenesis degrades the hydrocarbons.

While all petroleum hydrocarbons are biodegradable, the rate of biodegradation can differ significantly from site to site depending on the composition and amount of hydrocarbons; type and amount of available electron acceptors; type, number, and characteristics of the microorganisms; and quantity and quality of nutrients.

Site-specific measurements of these factors, comparison of these factors within and outside the plume, and temporal variations in these factors can demonstrate the occurrence of biodegradation. Each factor is discussed below.

3.1 Composition and Amount of Hydrocarbons

Almost all petroleum hydrocarbons are biodegradable under aerobic conditions. The ease of biodegradation depends on the type of hydrocarbon. Low molecular weight hydrocarbons (e.g., C10 to C24 alkenes) and single-ring aromatics are the most easily biodegradable. As molecular

weight increases, resistance to biodegradation also increases. Individual compounds degrade at different rates under aerobic and anaerobic conditions.

For most hydrocarbon-impacted sites, the primary chemicals of interest (from a risk perspective) are BTEX, MTBE, and naphthalene. Naphthalene and BTEX are readily degradable under aerobic conditions. Benzene typically degrades slower than other BTEX hydrocarbons under anaerobic conditions. MTBE degrades under both aerobic and anaerobic conditions. However, the rates of MTBE degradation and controlling factors have not yet been firmly established.

3.2 Available Electron Acceptors

The biodegradation of hydrocarbons is essentially an oxidation-reduction reaction. In this reaction, the hydrocarbon donates the electron (i.e., the hydrocarbon is oxidized) and a second compound (the electron acceptor) is reduced. Of the several electron acceptors available in the subsurface environment, oxygen, because of its high energy yield, is typically used first by microorganisms. Anaerobic bacteria can use other electron acceptors, including the following:

- Nitrate (NO_3^-) that is reduced to nitrogen (N_2)
- Manganese (Mn^{4+}) that is reduced to water soluble Mn^{2+}
- Ferric iron (Fe^{3+}) that is reduced to water soluble Fe^{2+}
- Sulfate (SO_4^{--}) that is reduced to sulfide (S^-)
- Carbon dioxide (CO_2) that may be used by methanogens to yield methane (CH_4)

As the biodegradation of hydrocarbons occurs, the concentration of the electron acceptors decreases and the concentration of the products formed increases. This concept can be used to demonstrate the occurrence of biodegradation (i.e., secondary line of evidence; section 3.5.2). Table B-1 shows the expected relationship between the BTEX concentration, electron acceptors, and products of the oxidation reduction reaction.

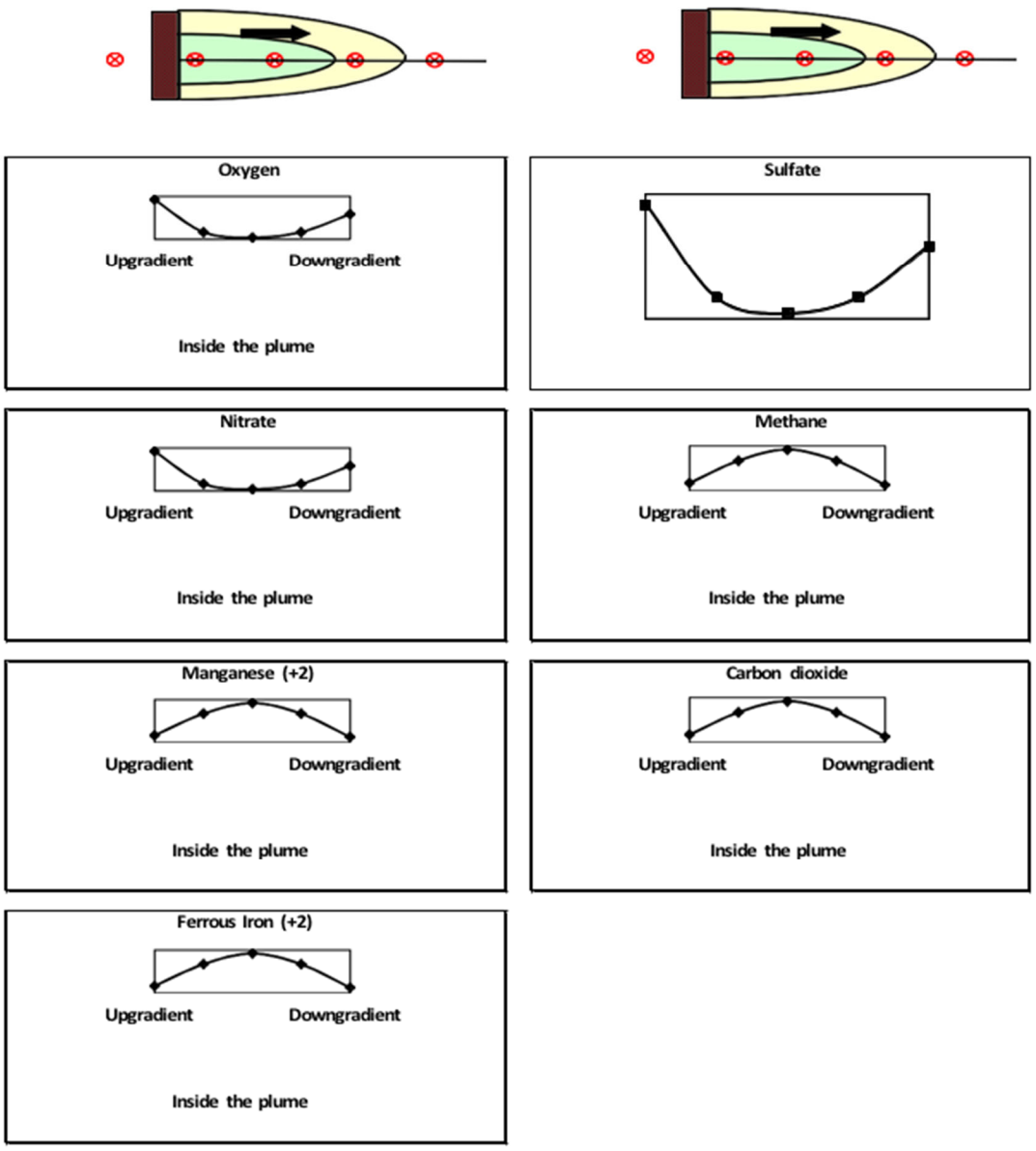


Figure B-3. Expected pattern of natural attenuation indicators (secondary line of evidence).

3.3 Quantity and Quality of Nutrients

In addition to the electron acceptors, microorganisms also require nutrients. These nutrients are incorporated into the biomass and are necessary to form cells. The nutrients nitrogen and phosphorous are required in relatively large amounts. Small amounts of micronutrients (e.g., sulfur, manganese, and magnesium) are also required.

Certain compounds (e.g., nitrates and sulfates), can serve either as nutrients or electron acceptors. Nutrients are rarely a limiting factor in the subsurface biodegradation of petroleum hydrocarbons. A decrease in nutrient levels within the zone of degradation can indicate biodegradation.

3.4 Characteristics of Microorganisms

The ability of microorganisms to degrade a wide variety of petroleum hydrocarbons is well documented. Hydrocarbon-degrading microorganisms are widespread in the environment, as they occur in fresh water, salt water, soil, and groundwater. The number of cells per milliliter of water can also be used as an indicator of biodegradation. As hydrocarbons degrade, the cell count for hydrocarbon-degrading bacteria increases.

3.5 Indicators of Natural Attenuation of Hydrocarbon Plumes

Based on the information presented above, concentrations of several substances (hydrocarbons, electron acceptors, microorganisms, nutrients, and carbon dioxide) can be measured to demonstrate the occurrence of NA.

These measurements are typically divided into three tiers, or *lines of evidence* (i.e., primary, secondary, and tertiary lines of evidence), to demonstrate NA. Data collected under each line of evidence can be evaluated qualitatively or quantitatively.

3.5.1 Primary Line of Evidence

The primary line of evidence for NA demonstrates the loss of chemical mass by evaluating measured petroleum hydrocarbon concentrations. Of all the methods available to demonstrate the occurrence of NA, this is the simplest and most useful to demonstrate site-specific reductions in risk. Site-specific application of the primary line of evidence requires an adequate number of correctly installed sampling points (monitoring wells), an adequate amount of chemical data from these points, and a thorough evaluation of these data. These issues are discussed in Parts II and III.

Although the primary line of evidence can show whether the concentration of a plume is attenuating, it does not show whether the decrease is due to destructive mechanisms or dilution. Secondary lines of evidence are necessary to determine whether the decrease is due to biodegradation.

3.5.2 Secondary Line of Evidence

The secondary evidence for NA refers to measurements of electron acceptors and products of metabolism within the plume and their comparison with concentrations in the unimpacted area of the aquifer, where no biodegradation activity would be expected to occur.

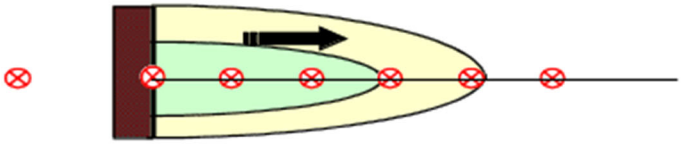
Parameters that are typically measured in the field include dissolved oxygen, REDOX potential, dissolved nitrates, manganese, ferrous iron, sulfate, and methane. These parameters should be measured at upgradient locations, inside the plume near the source, and at downgradient locations. Expected patterns of these parameters indicative of biodegradation are shown in Table B-1 and Figure B-3.

As microorganisms consume chemicals, there is a corresponding consumption of the compounds that serve as electron acceptors. The concentration of these compounds would

decrease in the portion of the plume where biodegradation is occurring. For example, under aerobic biodegradation, the concentration of oxygen would decrease, assuming oxygen is not added to the plume. Similarly, under anaerobic conditions, a depletion of nitrate, ferric (III) iron, and sulfate can be expected.

Biodegradation also results in an increase in the concentration of metabolic byproducts. For example, increased concentrations of nitrite and ferrous (II) iron within the plume would indicate biodegradation.

Table B-1. Expected pattern of natural attenuation indicators (secondary line of evidence).



	Upgradient	Inside the plume		Downgradient
BTEX	ND	High	Low	ND

Type of Reaction	Geochemical Indicator	Geochemical Indicator Concentration		
Aerobic	Oxygen	High	Low	High
Anaerobic	Nitrate	High	Low	High
	Manganese	Low	High	Low
	Ferrous Iron	Low	High	Low
	Sulfate	High	Low	High
	Methane	Low	High	Low
	Carbon dioxide	Low	High	Low

The secondary line of evidence demonstrates the occurrence of biodegradation only. It does not provide any data on the occurrence of other NA processes.

3.5.3 Tertiary (Optional) Line of Evidence

The tertiary (optional) line of evidence involves performing microbiological studies, such as identifying the microorganisms present in the formation and counting their cells, to demonstrate the occurrence of NA. The objectives of secondary and tertiary lines of evidence are similar. In the portion of the plume where NA is occurring, the ratio of petroleum degraders to the total number of bacteria should be higher than in the uncontaminated portion of the plume due to the readily available petroleum energy source. Tertiary lines of evidence are seldom required at petroleum hydrocarbon impacted sites.

PART II: Process for the Implementation of Remediation by Natural Attenuation

Remediation by natural attenuation refers to the achievement of site-specific cleanup goals using NA. As discussed in Part I, NA consists of several processes that occur at all contaminated sites at varying rates. As with any other remedial option, the site-specific applicability of RNA must be carefully evaluated before it is selected as the remedial alternative of choice. RNA should not be considered a presumptive remedy; rather, it is one of several available strategies that should be evaluated to ensure its applicability based on site-specific conditions.

The first step in evaluating NA is the collection of appropriate site characterization data. In general, the data collected must confirm the occurrence of NA, the effectiveness of RNA, and that the receptors are not exposed to unacceptable risk throughout the period when the site is being remediated by NA. The data collected should help answer the following questions and support the activities described in the questions.

- Has the full horizontal and vertical extent of the source and the plume been delineated?
- Is the plume at steady state and is it stable or shrinking in size?
- Can contaminant degradation be demonstrated and quantified?
- Can the long-term behavior of the source and the plume be modeled?
- Can the time frame to achieve remedial cleanup goals be estimated?
- What is the impact of source removal/reduction on the remedial time frame?

Once the site has been characterized to document the feasibility of NA, an evaluation on the site-specific appropriateness of NA as the preferred remedy should be performed. RNA is applicable only at the following types of sites:

- Sites where immediate threats to human health, safety, and the environment do not exist or have been mitigated
- Sites where *active* sources, such as leaking tanks and drums, have been removed
- Sites where the projected time frame to achieve remedial objectives is *reasonable*, as defined in section 7
- Sites where the plume is stable or shrinking and is not likely to impact current receptors or sensitive habitat
- Sites where active remediation has removed the bulk of the contaminants and the role of RNA is to perform the *final touchup*
- Sites where any necessary institutional controls can be reliably implemented

Upon selection of RNA as part or all of the preferred remedy, a corrective action plan will be developed to document the selection process and provide details about implementation of the remedy. The Idaho Department of Environmental Quality (DEQ) must approve this corrective action plan. At all sites, RNA will be accompanied by long-term monitoring to demonstrate that RNA is occurring at the rate anticipated when RNA was selected as the remedial option. Monitoring will continue until the specified cleanup goals have been achieved. If the monitoring data indicate that RNA is not occurring at an acceptable rate, the remedial plan will need to be modified.

4 Risk Management Plan for Remediation by Natural Attenuation

At sites where RNA is part of the preferred remedial option, the responsible party should include a discussion in the corrective action plan that addresses the following elements:

- Summary of site characterization activities that demonstrates a thorough understanding of the nature and extent of the source and the nature and extent of the impacts, provides data supporting the likely effectiveness of RNA, and discusses any source removal/control activities performed at the site
- Discussion of remedial endpoints and points of compliance, and the manner in which these were determined
- Discussion of the time frame over which the endpoints are expected to be achieved
- Demonstration that during this time frame, risks to human health and the environment are acceptable
- Discussion of monitoring locations, the rationale for monitoring location selection, and the type and frequency of data that will be collected to monitor the performance of RNA and the achievement of cleanup criteria
- Description of the tools to be used to evaluate/analyze the monitoring data
- Description of the institutional controls that may be required and documentation of their implementation
- Description of a contingency plan that will be implemented if the monitoring results indicate that RNA is not sufficiently effective or is not proceeding at the expected rate
- Description of the frequency and form of the reports to be submitted to DEQ during the course of implementing RNA

Components critical to the RNA portion of the corrective action plan are presented below.

5 Source Characterization and Control

Characterizing and controlling the source are important aspects of RNA. Sufficient data should be collected during the site investigation phase to delineate the nature and extent of the source and estimate the source lifetime. The term *nature* refers to an evaluation of the chemicals of interest and a determination that the chemicals are amenable to NA. The extent refers to the physical dimensions of the source as well as a determination of the mass of residual chemicals present in the source. An estimate of the lifetime of the source can be made by calculating the mass flux out of the source area (using groundwater flow characteristics and contaminant concentrations in the source area) and comparing this to the total contaminant mass in the source area (including free phase product, soils, and groundwater).

DEQ requires that all active sources (e.g., leaking pipes, tanks, and spills) are stopped and any free phase product in groundwater is removed, to the maximum extent practicable. It is best to reduce the source and remediate soils containing residual product that are significant sources of contamination to groundwater. Such control measures will reduce the time required to achieve remedial objectives. At a minimum, sufficient source material should be removed to

ensure a declining plume. The amount of active remedial activity necessary should be determined on a case-by-cases basis and clearly presented in the risk management plan.

6 Plume Characterization

The goals of collecting data to characterize the plume are to demonstrate the magnitude and direction of contaminant transport and the stability status of the plume, to confirm degradation is occurring, and to estimate the contaminant degradation rate or the ability of the aquifer to assimilate the contamination.

To achieve these goals, the responsible party must construct wells to account for aquifer heterogeneity and dominant zones of contaminant transport, select appropriate monitoring locations, collect samples at an adequate frequency, and collect and evaluate the appropriate analytical data. How to determine the appropriate monitoring locations, sampling frequency, and data is discussed below.

The location and number of groundwater samples collected and analyzed must be determined based on site-specific conditions. At a minimum, sampling points should be used to achieve the following:

- Locate the distribution of contaminants within the plume.
- Locate the plume boundaries.
- Track plume movement and migration.

Sampling points help define the extent of the plume, but at nondetect locations, they provide little useful information for documenting plume characteristics for an NA evaluation. Most sampling points must be located within the plume boundaries for NA evaluation purposes.

Monitoring wells should be located upgradient of the source, within or immediately downgradient of the source area, and within the plume aligned along the plume axis. Data should also be collected from an unimpacted downgradient well. A downgradient clean well can be used to characterize the extent of the plume and may be used to protect downgradient receptors by providing early detection of plume movement. This function is described in section 8. Wells delineating the sides of the plume assist in determining if there are significant seasonal changes in groundwater flow direction.

As discussed in sections 3.5.1 and 3.5.2, data related to the primary and secondary lines of evidence should be collected. In rare cases, it may be necessary to collect data to demonstrate tertiary lines of evidence. Based on the data collected, a determination should be made whether the plume is expanding, stable, or shrinking. The specific analytical tools that may be used to conduct this characterization are discussed in Part III.

Expanding plumes require continued monitoring. Depending on site conditions, such as the risk to current or potential future receptors and the rate at which the plume is expanding, additional assessment of the plume and/or source removal and reduction may be necessary. An expanding plume typically requires active remediation.

Plumes documented to be stable or shrinking are candidates for the use of NA. These plumes will also require continued monitoring but at a lower frequency than expanding plumes. Depending on site conditions and the remediation time frame, a stable plume may require residual source characterization or removal.

The frequency and duration of monitoring during the plume characterization phase should be determined on a site-specific basis and in consultation with DEQ. However, in most cases, 1–2 years of quarterly monitoring data are necessary to evaluate the degree of seasonal variations in water levels and flow directions present at a site. This information is necessary to characterize a plume as expanding, stable, or shrinking and to estimate degradation rates. As clear trends emerge in the data, the monitoring frequency may be modified. The actual duration of sampling will depend on the time it takes to demonstrate a clear trend in the concentrations.

7 Reasonable Time Frame Determination

The determination as to what constitutes a reasonable time frame for RNA is a complex, site-specific determination not amenable to simple rules of thumb or quantification. In making this determination, DEQ will take into account factors that include, but are not limited to, the following:

- Time frame for RNA compared to that for other remedies evaluated
- Time frame in which affected portions of the aquifer might be needed for various uses
- Likelihood that impacted groundwater will be used
- Degree of uncertainty in site characterization and NA estimates
- Reliability of institutional controls over the time frames for which they may be required to function
- Ability of the responsible party to maintain the required monitoring and plume evaluation required when NA is used as a remedy

8 Monitoring to Demonstrate the Effectiveness of Remediation by Natural Attenuation

Due to the uncertainties associated with the site-specific implementation of RNA, long- term monitoring is necessary to demonstrate its effectiveness. Long-term monitoring is used to ensure that the behavior of the plume does not change and that predictions of plume behavior are accurate. The objectives of long-term monitoring are to demonstrate NA is continuing to occur, human health and the environment are protected, and the plume is not expanding.

The specifics of the monitoring plan (e.g., the location, frequency, and type of samples to be collected and the analytical procedures to be used) should be determined on a site-specific basis. The primary factors that should be considered when designing a long-term monitoring program include the following:

- Distance to potential receptor exposure points
- Groundwater seepage velocity and direction

- Types of contaminants
- Aquifer heterogeneity
- Three-dimensional distribution of chemicals of interest
- Areas of unique geochemical conditions
- Surface water impacts
- Effects of active remediation systems

The secondary factors that should be considered include the following:

- Access issues
- Property lines
- Contaminant contributions from off-site sources

Two types of wells are required for any long-term monitoring program: performance monitoring wells and contingency monitoring wells. Performance monitoring wells are used to demonstrate that NA is proceeding according to expectations; document that geochemical conditions continue to be adequate to support NA processes; identify any toxic products resulting from NA processes; determine if plume conditions remain stable or are shrinking; identify changes in groundwater conditions, such as change in flow direction, and recharge; and document that cleanup criteria have been met.

Contingency monitoring wells are placed beyond the predicted downgradient boundary of the plume and upgradient from known or potential receptor exposure points. Their purpose is to provide an *early-warning* if unexpected plume expansion occurs and allow implementation of a contingent remedy if needed. Multiple contingency wells may be needed, particularly if seasonal variations in groundwater flow direction are known to occur.

Sampling frequency should be based on the following factors:

- Natural variability observed in contaminant concentrations
- Distance and travel time from the source to the point of compliance
- Reduction in concentrations needed to meet target levels

9 Contingency Measures

The RNA corrective action plan should include a contingency plan to be implemented if the site data indicate that RNA is not occurring at the expected rate or the exposure conditions at the site have changed, resulting in an unacceptable risk to human health or the environment.

Contingency measures will prevent delays in site remediation and provide a clear roadmap for site remediation. Triggers should be established and included in the plan so the responsible party can implement alternative active strategies to enhance RNA. The triggers should be as objective and quantitative as possible. Examples of triggers include, but are not limited to, the following:

- Consistent increase in concentrations in one or more wells
- Failure of any of the institutional conditions necessary to protect human health and the environment during the period of RNA
- Change in the exposure conditions (e.g., removal of pavement)
- Continued expansion of the plume
- Unacceptably low rates of RNA

PART III: Techniques Available to Demonstrate Natural Attenuation

Several techniques are available to evaluate the data collected to demonstrate NA or to design and implement an RNA program. These techniques are divided into three categories: (1) techniques to demonstrate the occurrence of NA, (2) techniques to estimate the site-specific rate of NA, and (3) techniques to quantify the future behavior of the plume.

10 Techniques to Demonstrate the Occurrence of Natural Attenuation

The occurrence of NA may be demonstrated by using graphical and/or statistical techniques. The specific techniques used will vary depending on site conditions and the specifics of the data. To the extent possible, multiple techniques should be used to provide added insight into the NA process.

10.1 Graphical Techniques

Chemicals-of-interest data collected from strategically located monitoring wells can be used to draw sitewide contour maps of individual constituent concentrations for each monitoring event, create concentration versus time plots for each well with detectable constituent levels and at least four rounds of data, and create concentration versus distance plots along the flow direction for several monitoring events. Depending on the variability in the concentrations, it may be better to plot the natural logarithm of concentration versus time and distance. An example plot is shown in Figure B-4. When creating these plots, ensure that the selected scale clearly demonstrates the trend. Since the concentrations are affected by water level fluctuations, it is important to also plot water levels as a function of time.

These plots can indicate whether the concentration trend is decreasing, stable (no significant trend), increasing, or mixed. The latter refers to a situation where different wells (source wells versus periphery wells) exhibit different trends. Increasing concentrations in the source well and decreasing concentrations in the downgradient wells may occur due to a variety of reasons. For example, the mass loading to the source may cause an increase in the source wells due to an increase in the infiltration rate, or the rate of biodegradation near the source may be reduced due to a depletion of oxygen.

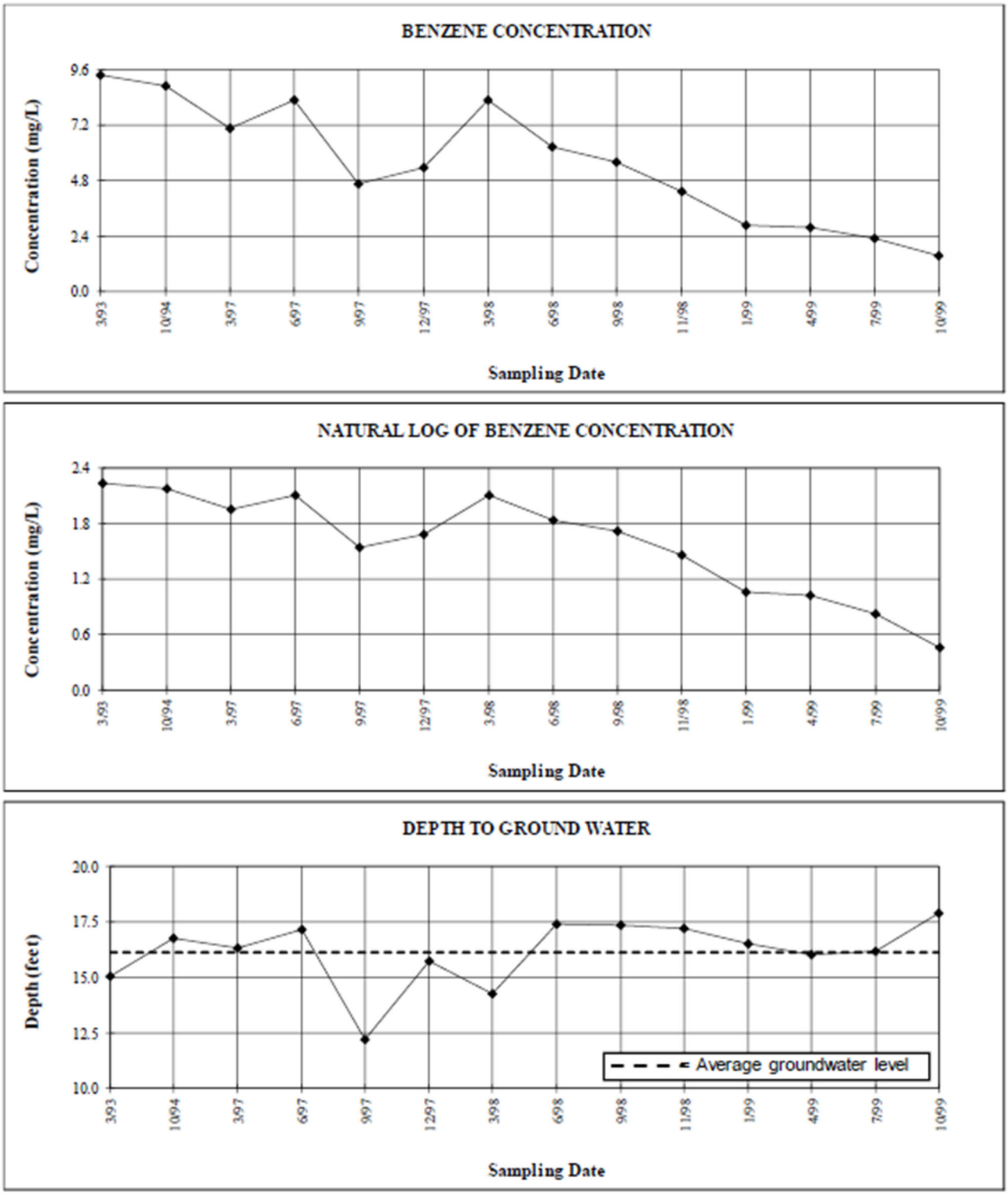


Figure B-4. Benzene concentration versus time plot.

Conversely, increasing concentrations in downgradient wells and decreasing concentrations near the source may indicate that the plume is moving, but the source has depleted. Conclusions related to concentration trends based on visual observations of the data must be supported by statistical analysis.

In addition to the chemical-of-interest concentrations, indicator chemical concentrations should be plotted along the plume axis (in the concentration versus distance plots) along with the hydrocarbon concentrations. The observed pattern of concentrations can be used to demonstrate NA. For example, low dissolved oxygen concentrations within the plume and higher concentrations upgradient and downgradient of the source indicate biodegradation within the plume.

10.2 Statistical Evaluations

Statistical tools may be used to determine and quantify the concentration trend. These tests can be used to test a null hypothesis and an alternative hypothesis. A null hypothesis might be that there is no time trend in the concentrations versus distance or time, and the alternative hypothesis might be that there is a downward trend. Application of the statistical test would then result in accepting or rejecting the null hypothesis at a specified level of significance.

The Mann-Kendall nonparametric test is often used to determine whether a trend exists in the data. This test is particularly useful for environmental data for several reasons:

- Nonparametric test implies it is applicable irrespective of the underlying distribution of the data.
- Test is simple to implement.
- Concentration values below the detection limit can be used.
- Results are not affected by missing data.

The Mann-Kendall test is applicable only when the data do not show any seasonal variations or the data were collected from one season. When data indicate seasonality, the seasonal Kendall test may be used. For details on both of these tests, refer to books on statistical analysis.

DEQ recommends using the Mann-Kendall test to determine the trend in nonseasonal data except in situations where a visual plot of data indicates without any ambiguity that a trend exists in the data.

If the concentration versus time or concentration versus distance data indicate a decreasing trend, a regression analysis may be used to estimate the slope of the best-fit line.

As explained in section 11.2 and 11.3, the slope of the line can be used to estimate the NA or the biodegradation rate. For additional information on regression analysis, refer to any statistics textbook.

11 Techniques to Estimate the Site-Specific Rate of Natural Attenuation

The data collected to demonstrate the primary line of evidence of NA can be used to estimate site-specific NA rates and biodegradation rates. Since NA includes multiple processes in addition to biodegradation, the NA rate would be higher than the biodegradation rate. The latter can be used as an input into a groundwater fate and transport model, such as Domenico's (1987) model, to estimate the future migration of the plume, and to estimate a site-specific dilution attenuation factor. Three methods are available to estimate the NA rate: (1) mass balance analysis for expanding, stable, or shrinking plumes; (2) plume concentration versus time plots; and (3) plume concentration versus distance plots. Descriptions of each of these methods are presented below. The calculation and use of rate constants for NA evaluations is presented in the *Calculation and Use of First-Order Rate Constants for Monitored Natural Attenuation Studies* (EPA 2002). This section also includes a discussion of calculating biodegradation rates using recalcitrant tracers.

11.1 Mass Balance Analysis

This method of estimating the NA rate is based on the concept of mass balance. For a stable plume, the mass entering the groundwater plume must equal the mass lost by NA. If the mass entering the plume can be estimated, it should be possible to estimate the NA rate. A detailed description of the application of mass balance analysis to estimate the NA rate of a petroleum release is described in the *Standard Guide for Remediation of Groundwater by Natural Attenuation at Petroleum Release Sites,* Section X6.1 (ASTM 2004).

11.2 Well Concentration Versus Time Plot

The estimate of the overall attenuation rate for a shrinking plume can be calculated assuming a first-order decay rate and is represented mathematically by Equation B-1:

$$\frac{dC}{dt} = exp^{(-kt)} \qquad \textbf{Equation B-1}$$

Where:

C = concentration
t = time (years)
k = NA rate (1/yr)

The solution to the above differential equation results in the familiar exponential decay equation (Equation B-2):

$$C(t) = C(t = 0)\, exp^{(-kt)} \qquad \textbf{Equation B-2}$$

Where:

C(t) = Concentration at any time *t* (mg/L)

Taking the natural logarithms of both sides of the equation results in Equation B-3:

$$ln\,C(t) - ln\,C(t=0) = -kt$$ **Equation B-3. Concentration versus time.**

A plot of natural log of concentration versus time would be a straight line with a slope equal to *k* (the NA rate).

11.3 Well Concentration-versus-Distance Plot

Advective travel time can be expressed in Equation B-4:

$$t = \frac{x}{v}$$ **Equation B-4. Advective travel time.**

Where:

x = Advective travel distance (cm)
v = Seepage velocity (cm/yr)

Substituting Equation B-4 in Equation B-2 results in Equation B-5:

$$C(t) = C(t=0)\,exp^{(-k\frac{x}{v})}$$ **Equation B-5**

Taking the natural log of both sides of the equation results in Equation B-6:

$$ln[C(t=0)] - ln[C(t)] = -k\frac{x}{v}$$ **Equation B-6**

For a shrinking plume that follows the first-order attenuation rate presented above, a plot of log concentration versus distance would be a straight line with a slope of *k*/*v*. By multiplying the slope with the seepage velocity, the NA rate (*k*) can be estimated.

Buscheck and Alcantar (1995) used the solution of the one-dimensional transport equation with biodegradation to estimate the biodegradation rate based on the slope of the log concentration versus distance plot. Specifically, they derived the following expression (Equation B-7) for the biodegradation rate:

$$\lambda = \frac{v}{4\alpha_x}\left\{\left[1+2\alpha_x\left(\frac{k}{v}\right)\right]^2 - 1\right\}$$ **Equation B-7. Biodegradation rate.**

Where:

λ = Biodegradation rate, assumed to occur at equal rates in the dissolved and sorbed phases
α_x = Longitudinal dispersivity (0.1x)

Zhang and Heathcote (2003) modified this method to account for situations with finite source size and lateral dispersion to improve the estimates of the biodegradation rate.

The following step-by-step description of the biodegradation rate estimation process can be implemented on a site-specific basis.

Step 1: Determine the groundwater flow direction based on the water level measurements for each monitoring event.

Step 2: For each monitoring event, identify the wells located along the direction of flow (i.e., along the plume center line). Since the flow direction may vary seasonally, different wells may be used for different monitoring events.

Step 3: Tabulate the concentrations of the chemicals of interest and calculate the natural log concentrations.

Step 4: Plot the natural log concentrations on the *y*-axis and the distance along the *x*-axis.

Step 5: Calculate the slope of the best-fit line and the confidence in this estimate by examining the 95% confidence limits of the slope.

Step 6: Estimate the groundwater seepage velocity.

Step 7: Multiply the slope of the best-fit line calculated in Step 5 with the seepage velocity. The result will represent the overall NA rate. This NA rate represents the reduction in concentration due to the combined influence of the various NA processes mentioned in section 2. This decay rate should not be confused with the biodegradation rate (λ) that is an input to groundwater models.

Step 8: Estimate the biodegradation rate from Equation B-7.

Steps 1–8 should be completed for each time period for which data are available and the results presented as a range of NA and biodegradation rates. The latter can be used as an input to the Domenico (1987) model to estimate the dilution attenuation factor. Due to confounding factors such as seasonal variations in groundwater velocity, fluctuations in water levels, and errors in sampling and analysis methods, the NA and biodegradation rates may vary significantly (by as much as a factor of 10). It is best to present the range and average rates.

11.4 Evaluation of Plume Behavior with a Recalcitrant Tracer

Physical, chemical, and biological processes act together to decrease contaminant concentrations away from a source. However, monitored NA requires knowledge of accurate biodegradation rates for a site. To estimate accurate biodegradation rates, conservative tracers can be employed. The concentrations of these tracers are not affected by biodegradation processes and can be used to delineate between the effects of biodegradation and other NA

processes such as dilution and sorption. Generally, tracers are biologically recalcitrant and have chemical properties similar to the contaminant of interest. Examples of common tracers include MTBE for petroleum hydrocarbon plumes.

12 Techniques to Quantify the Future Behavior of the Plume

The future behavior of the plume can be estimated by using fate and transport models. A number of analytical and numerical models are available. Commonly used analytical models include the Domenico (1987) model and BIOSCREEN.

These models can be used to estimate plume length, concentrations at downgradient receptor locations, and dilution attenuation factors and can be calibrated to site-specific groundwater data. The correct application of fate and transport models requires experience and specialized knowledge that is beyond the scope of this document.

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Appendix C. Example Table of Contents for a Risk Evaluation Report

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Appendix D. Practical Quantitation Limits

1. Introduction

When collecting media-specific chemical concentration data and establishing remediation standards, situations may arise where practical quantitation limits (PQLs) for specific chemicals and samples may exceed screening levels or site-specific, risk-based concentrations. "Rules for Petroleum Release Corrective Action"(IDAPA 58.01.24.500) delineates the following factors that may be used to allow the use of PQLs as remediation standards:

- Analytical method
- Method detection limit
- Sampling procedures
- Estimated risk levels
- Other

This appendix provides background on the concepts of PQLs, method detection limits (MDLs), and remediation standards and provides guidance on using the above factors when PQLs are proposed as remediation standards.

2. Background—Practical Quantitation Limits, Method Detection Limits and Remediation Standards

2.1 What are PQLs and MDLs?

A PQL is defined in part in IDAPA 58.01.24.010 as "The lowest concentration of a chemical that can be reliably quantified among laboratories within specified limits of precision and accuracy for a specific laboratory analytical method during routine laboratory operating conditions." The ~~method detection limit (~~MDL~~)~~ is defined as "The minimum concentration of a substance that can be reported with 99% confidence is greater than zero."

2.2 How are PQLs and MDLs Derived?

PQL values are derived in a number of ways, and there is no consensus as to the process used to develop them. In some cases, they are derived as a fixed multiplier applied to the MDL value or the standard deviation of samples used to develop the MDL. The multiplier commonly ranges from 3 to 5 and may be as great as 10. In other cases, PQLs may be derived by analysis of data from actual laboratory performance studies. In these cases, PQL values are a function of analytical methods, a given laboratory's equipment, operating protocols, operating conditions, quality assurance/quality control procedures, and sampling and media considerations. Values are sometimes reported by laboratories at levels between the MDL and the PQL and are commonly qualified as estimated quantities. The closer the estimated value is to the PQL, the more confidence in the estimated value.

For the petroleum chemicals of interest (COI) listed in the rule, the common analytical methods at petroleum release sites are established by the United States Environmental Protection

Agency (EPA). These analytical methods include 8011, 8260C, 8270D (SIM), TO-17, and TO-15 SIM. In the method descriptions, EPA lists examples of lower limits of quantitation for individual analytes but indicates that they are instrument-dependent and influenced by sample preparation/introduction technique or highly matrix-dependent and are provided for guidance only.

For a given media, sampling considerations may have an impact on achievable detection limits. For example, when sampling soil vapor or ambient air with certain methods, the achievable quantitation limit can be a function of the amount of vapor or air sampled. Quantitation limits are commonly reduced as the amount of air sampled increases.

Specialized analytical techniques can sometimes provide lower MDL and PQL values. In a comparison of values achieved with the use of standard method 8270D for semivolatile compounds versus employing method 8270D using selective ion monitoring (SIM). PQL values are 6 times lower for soils and 20 times lower for water samples.

Depending on the petroleum product released, levels of contamination, chemicals present, and media in question (soil, water, and vapor), interferences to analytical detection and quantitation may be present. Procedures such as sample dilution may allow quantification of petroleum COI concentrations but will also result in elevated detection and quantitation limits.

3. Remediation Standard

A remediation standard is defined in IDAPA 58.01.24.010 as a “media specific concentration which, when attained, is considered to provide adequate protection of human health and the environment.”

Remediation standards are established at petroleum release sites where corrective action has been determined to be required. The need for corrective action is commonly determined after completing a risk evaluation. Remediation standards are commonly established as part of a risk evaluation or an approved corrective action plan (CAP).

The magnitude of a remediation standard that is established for a given chemical and the potential that it may be exceeded by a PQL depends on a number of factors, including, but not limited to, the following:

- Assumptions about current and future site land use, both on and off site
- What petroleum products were released and the relative distribution of chemicals detected
- Magnitude and distribution of contamination (which media are impacted)
- Routes of exposure determined to pose the greatest threats

The two risk evaluation scenarios where elevated PQL values may require the re-evaluation of initially selected remediation standards are as follows.

3.1 Screening Level Evaluation

The screening level evaluation described in IDAPA 58.01.24 employs the simplest and most straightforward use of remediation standards in the form of screening levels. The screening levels are conservative, calculated, risk-based concentrations determined to be protective of unrestricted use exposures.

Because laboratory analytical technology is continually changing, these media-specific chemical concentrations are established without consideration of the ability of standard laboratory methods to detect and quantify these values. The compounds benz(a)anthracene (BAA) and benzo(b)fluoranthene (BBF) in water and ethylene dibromide (EDB) in soil pose the greatest potential challenges with respect to PQL values meeting screening level concentrations.

For BAA and BBF, common practical quantitation limits in water using EPA (2014) method 8270D with SIM slightly exceed the groundwater screening levels while the method detection limits are slightly below the screening values. At petroleum release sites where these chemicals are COIs and groundwater analytical results for these chemicals are reported either as estimated values (between the quantitation and detection limits) or below the detection limit, the screening levels will be assumed to have been achieved. Additional support for this determination is provided if all other polycyclic aromatic hydrocarbon (PAH) chemicals are also reported at concentrations below screening levels.

The most commonly used analytical method for EDB in soils, EPA (2006) Method 8260C, has typical quantitation and detection limits that exceed the soil screening level concentration. The soil screening level for EDB is based on protection of groundwater. The groundwater quantitation limit for EDB is below groundwater screening level and the soil quantitation limits are low enough to evaluate the other relevant pathways and routes of exposure. At petroleum release sites where EDB is a COI and groundwater is potentially impacted and representative groundwater samples report EDB below the screening level but soil quantitation limits are above the soil screening level, the groundwater results will take precedence.

In the screening level evaluation, the user must compare maximum media-specific concentrations measured during site assessment activities to the screening levels. If the measured concentrations do not exceed the screening levels, the site may be eligible for site closure. If the measured concentrations do exceed screening levels, the user may select screening levels as the remediation standards upon which corrective action is based and develop a CAP. The user may also choose to conduct additional investigation or evaluation and perform a site-specific risk evaluation. Samples may also have results reported as undetected at a concentration that is less than the PQL but higher than the screening level. In this case, a potentially unacceptable risk would be indicated.

3.2 Site-Specific Risk Evaluation

During the site-specific risk evaluation process, media-specific chemical concentration data are collected and used, along with assumptions regarding exposure pathways and receptors, to calculate risk to expected receptors. If the calculated risk is unacceptable, media-specific, risk-

based chemical concentrations are established. These risk-based concentrations become the remediation standards for site corrective action. Samples are then taken during and after corrective action to demonstrate the standards have been attained.

PQLs for selected analytes in a given media sample may exceed one or more of the calculated risk-based remediation standards, making the demonstration that the standard has been attained problematic. It is also problematic when samples with results below a PQL are included in the calculation of exposure point concentrations and risk.

Remediation standards are oftentimes the lowest at sites where:

- Screening levels have been selected as the standards
- Unrestricted use is the desired corrective action land use goal
- Contamination has migrated off site in groundwater
- On-site vapor intrusion risk is determined to exist
- Diesel fuel contamination (and polynuclear aromatic hydrocarbon chemicals) is present in surface soil or in proximity to surface water

Accordingly, PQL-related issues often arise at such sites.

4. Checklist for Proposals to Use PQLs as Remediation Standards

Proposals to DEQ for the use of PQLs as remediation standards at petroleum release sites should include the following:

- Results of any risk evaluation
- Remediation standards developed from that process
- Proposed PQL
- Site-specific issues, with supporting information, that justify the use of the proposed PQLs as remediation standards.

The supporting information that should be provided in the proposal is listed below with a discussion of how DEQ will evaluate that information and potential solutions to various issues, as they may be relevant to the evaluated site. Given the number and variety of factors that may arise with PQLs in relation to remediation standards, both the list and the discussion are not all-inclusive.

4.1 Risk Evaluation

- Describe the conceptual site model.
- Identify the level of risk evaluation, chemicals, media, and pathway or route of exposure at issue.
- State the magnitude of the proposed PQL and MDL versus the remediation standard.

4.1.1 Screening Level Evaluation

For sites where a screening level evaluation has taken place and the proposal is to use PQLs in place of screening levels as remediation standards for specific COI and media, the information provided will be reviewed in a number of ways. The proposed PQLs will first be reviewed relative to the conceptual site model (CSM) and the pathway/routes of exposure, which are the basis of the screening levels for the chemicals under consideration.

- If the PQL for a chemical exceeds a soil screening level based on groundwater protection but the PQL achieves the groundwater screening level (also based on groundwater protection) for the same chemical, the soil PQL may be used as the soil remediation standard for that chemical.
- If the PQL for a chemical exceeds a soil or groundwater screening level for other routes of exposure (groundwater ingestion, vapor inhalation, or direct contact), DEQ will review the magnitude of the difference between the PQL/MDL and the screening level (whether greater than or less than the screening level) for all COI with a common route of exposure to estimate the potential impact on the cumulative risk from that pathway.

If only a screening level evaluation has been done, completion of a site-specific evaluation may revise the remediation standards and still allow unrestricted use of the site, if that is the desired/expected future land use condition.

4.1.2 Site-Specific Evaluation

PQL issues may be related to cleanup criteria from a site-specific risk evaluation. Site-specific evaluations depend on the calculation of cumulative risk to a receptor from all pathways/routes of exposure and chemicals, based on estimated exposure point concentrations. The calculation of exposure point concentrations can be influenced by the number of chemicals with PQL issues, proportion of samples with less than PQL values, the magnitude of the PQL, and how these censored data are treated in the calculation procedure. If the calculations result in unacceptable risks, remediation standards for individual COI are calculated, some of which may be low enough to be exceeded by PQLs. DEQ will evaluate whether and to what extent the less than PQL data were used appropriately in these calculations, if the resultant calculated risks are over or underestimated, the degree to which the less than PQL data contribute to overall risk, and whether the calculated cleanup criteria can be modified to avoid the PQL issue or if use of a PQL will not materially affect the protectiveness of the cleanup.

The assumptions of the CSM and risk evaluation will be reviewed to determine if the land use scenarios, receptors, and input parameter values are appropriate. Exclusion of an inappropriate pathway may eliminate the specific PQL concern. Alternatively, the pathways/routes of exposure may be appropriate, but the receptor/land use scenario may not be.

If the PQL for a COI is above a remediation standard but the MDL is at or below the standard, there may be instances where sample results falling between these limits can be considered to have met the remediation standard. If a sample result is reported as an estimated value and that concentration is at or below the remediation standard, the standard will have been met.

Sample results reported as undetected (less than the detection limit, provided the limit is at or below the standard) will have met the standard.

Additional guidance on the treatment of PQL/MDL data and issues in site-specific risk evaluation are available in the *Guidance for Data Useability in Risk Assessment (Part A)* (EPA 1992), the *Risk Assessment Guidance for Superfund*, *Volume I (Part A)* (EPA 1989), and the EPA ProUCL statistical software technical guide (EPA 2010b).

4.2 Analytical Issues

- Identify the analytical methods used that are the basis of the PQL.
- Provide all relevant quality assurance/quality control (QA/QC) information from the laboratory sheets for the analyses in question, including data quality assessment and summaries provided by the laboratory.

When reviewing the proposal, DEQ will evaluate whether the data quality assessment and QA/QC accompanying the analytical results adequately explain and support the PQLs proposed. Generally, PQL proposals should be based on PQLs derived from undiluted samples. Elevated PQLs resulting from sample dilution are typically the result of an attempt to quantitate all the COIs when the concentrations of one or more chemicals (some of which may not be COI) are highly elevated, often referred to as matrix interference.

Matrix interference can also occur due to the nature of the media (soils in particular) and can impair the quantitation of a COI. The matrix spike and matrix spike duplicate portions of the laboratory QA procedures can sometimes clarify whether there are matrix interferences and whether they are causing over or underestimation of actual concentrations of a COI.

4.3 Sampling

- Provide information on the number of sampling events completed to support the PQL proposal.
- Provide information on the sampling procedures and QA/QC measures implemented during each of the sampling programs undertaken at the release site. Copies of quality assurance project plans and evaluations of adherence to and departure from those plans for the site in question for each event should be included.

The owner/operator may select alternative sampling procedures, which may provide for a lower PQL. The PQLs for analysis of air and vapor samples can be dramatically affected by the volume of air which is sampled.

DEQ will review the proposal for use of a specific PQL as a remediation standard as part of the overall CAP and approve or deny the request along with specifying any conditions of approval or reasons for denial.

5. How to Evaluate Cancer Potency of Polycyclic Aromatic Hydrocarbons in Soil

Benzo(a)pyrene can be used as a surrogate, or index chemical, to estimate the toxicity of other congener PAHs (*https://www.epa.gov/risk/regional-screening-levels-rsls-frequent-questions#FQ47*). They have similar toxicological properties and can be evaluated as a mixture. In 1993, EPA released an interim guidance for the quantitative risk assessment of polycyclic aromatic hydrocarbons; however, EPA is conducting a hazard assessment of PAH mixtures that will be part of the Integrated Risk Information System (IRIS) database. A common approach to screen PAHs is to use potency equivalency factors (PEFs) to express the carcinogenicity of several PAHs as a single value (i.e., benzo(a)pyrene equivalent).

To calculate a benzo(a) equivalent for screening purposes, follow these steps:

1. For each PAH (benzo(a)pyrene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, and chrysene) listed in Table E-1, identify the concentration sampled. For PAHs that have a PQL above the screening level, three options are possible:
   a. If one or more PAHs analyzed have not been detected in any sample at the site, then a value of zero may be assigned for the analytes for the calculation of the toxicity equivalent concentration.
   b. If the analyte has not been detected in the sample but has been detected at the site, calculate toxic equivalent concentrations using one-half of the MDL.
   c. If the analyte has been detected in the sample and has been detected at the site, calculate the toxic equivalent concentration using the full method MDL.
2. Multiply the measured concentration of each PAH by the relative potency factor in Table D-1 to obtain a toxic equivalent concentration for each PAH.

Table D-1. Relative potency factor.

Compound	RPF
Benzo(a)pyrene	1.0
Benz(a)anthracene	0.1
Benzo(b)fluoranthene	0.1
Benzo(k)fluoranthene	0.01
Chrysene	0.001
Dibenz(a,h)anthracene	1.0
Indeno(1,2,3-c,d)pyrene	0.1

3. Sum the congener-specific toxic equivalent concentration to calculate the total toxicity equivalent factor for each sample (Table D-2).

4. Compare the maximum total benzo(a)pyrene equivalent across samples to the screening level for benzo(a)pyrene in soil.
   Example: TEC Calculation for Determining Compliance for Residential Soil

Table D-2. Example toxicity equivalent concentration calculation.

cPAH	Measured Soil Concentration	Toxicity Equivalent factor (unitless)	Toxicity Equivalent Concentration (mg/kg)
Benzo(a)pyrene	0.06	1.0	0.06
Benzo(b)fluoranthene	0.03	0.10	0.003
Benzo(k)fluoranthene	0.15	0.10	0.015
Benzo(a)anthracene	0.09	0.1	0.009
Chrysene	0.05	0.01	0.0005
Sum			0.0875
Benzo(a)pyrene RSL for residential soil		0.1 mg/kg	

The sum of the toxicity equivalent concentrations (0.0875 mg/kg) is lower than the benzo(a)pyrene screening level (0.11 mg/kg). Therefore, no further action is needed. If levels are at or above the screening level, further evaluation would be necessary.

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