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DIVISION OF OIL AND PUBLIC SAFETY

MONITORED NATURAL ATTENUATION IN GROUNDWATER GUIDANCE DOCUMENT

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1.0 INTRODUCTION

This guidance presents the methodology to be used to determine whether Monitored Natural Attenuation (MNA) may be applied at a site impacted by petroleum hydrocarbons in groundwater. Natural attenuation, as discussed in this guidance, is the reduction in contaminant mass or concentration in groundwater over distance from the source region due to naturally occurring physical, chemical, and biological processes. MNA is a remedial technology that relies on natural attenuation processes to achieve site-specific remedial objectives within an acceptable time frame. MNA is only appropriate if human health and the environment are adequately protected while monitoring occurs and if the cost is less than the cost of other remediation alternatives.

The length of time needed to clean up petroleum contaminants by means of natural attenuation depends on the hydrogeologic properties of the groundwater aquifer, the mass of contaminant in the environment, the availability of electron acceptors, and the ability of the existing microbial population to degrade the contaminants. To achieve site cleanup goals within a reasonable period of time through natural attenuation, source control actions will almost always be required. Source control actions include tank removal, removal of free product to the extent practical, and removal or treatment of highly contaminated soil, which can constitute a long-term contaminant source.

Before proposing MNA as a corrective action alternative, a Site Characterization Report (SCR) must be considered complete by the Division of Oil and Public Safety (OPS) and must provide adequate information necessary to determine if remediation by MNA is a viable option. For further information on site assessment requirements refer to the *Storage Tank Regulations, Colorado Department of Labor and Employment, Oil Inspection Section (7 C.C.R. 1101-14)* and the *Petroleum Storage Tank Owner/Operator Guidance Document.* A complete SCR will include identification of points of exposure (POEs), an updated Site Classification Checklist, land use criteria, identification of completed exposure pathways, determination of full extent of contamination in soil and groundwater, and the hydrogeologic characteristics of the site and the surrounding area.

1.1 Definitions

Additional lines of evidence include conducting microbiological studies, measurement of nutrients concentrations, and specific geochemical indicators not collected as part of the Secondary Lines of Evidence.

Advancing plume describes the configuration where the solute plume margin is continuing to move outward or downgradient from the source area.

Chemicals of concern are specific petroleum constituents that are identified as posing a potential risk to human health or the environment.

Decay (attenuation) rate is the measured reduction in concentration or mass of a compound with time expressed as an amount of reduction per unit time.

Electron acceptors are elements or compounds that are reduced by receiving electrons produced by the oxidation of organic compounds through microbial metabolism or abiotic chemical oxidation processes.

Milestones are projected concentrations over time at in-plume wells. Milestones are used as indicators that degradation of contaminants is occurring at the projected decay rate.

Natural attenuation is the reduction in mass or concentration of a compound in groundwater over time or distance from the source of chemicals of concern due to naturally occurring physical, chemical and biological processes, such as biodegradation, dispersion, dilution, sorption, and volatilization.

Plume refers to a volume of groundwater where chemicals of concern are present.

Point of compliance refers to a location or locations selected between the source area(s) and potential point(s) of exposure where concentrations of chemicals of concern must be at or below the determined groundwater target levels.

Primary Lines of Evidence is the documentation of the change in petroleum hydrocarbon constituent concentrations, measured over four quarters of monitoring, indicating whether or not the plume is shrinking, stable, or advancing. The measurement of dissolved oxygen is also required as part of the primary lines of evidence to demonstrate the presence of appropriate site conditions for biodegradation.

Remediation by natural attenuation describes a remedy where naturally occurring physical, chemical, and biological processes will achieve remedial goals. The use of natural attenuation processes as a remedial action also has been described by a variety of other terms, such as intrinsic remediation, intrinsic bioremediation, passive remediation, natural biodegradation, passive bioremediation, etc. Remediation by natural attenuation does not include remediation methods that require human intervention beyond monitoring.

Secondary Lines of Evidence include the use and evaluation of geochemical indicators of naturally occurring biodegradation, to demonstrate natural attenuation is occurring and to estimate the natural attenuation rates.

Shrinking plume describes a configuration where the solute plume margin is receding over time and the concentrations at points within the plume are decreasing over time.

Source area is the location of free phase liquid hydrocarbons or the location of highest soil and groundwater concentrations of constituents of concern.

Stable plume describes the configuration where the solute plume margin is stationary over time and the concentrations at points within the plume are relatively uniform over time or may decrease over time.

2.0 NATURAL ATTENUATION PROCESSES

This guidance document specifically addresses determining the appropriateness of relying on natural attenuation processes in groundwater to control and remediate petroleum contaminants. These natural processes are physical, chemical, and biological in nature and include dilution, dispersion, sorption, precipitation, volatilization, biodegradation or biotransformation, and abiotic degradation or transformation. Most chemicals found in petroleum fuels are amenable to these processes, and natural attenuation can be expected to occur to some degree at most petroleum contaminated sites. Many site-specific variables affect the rates of natural attenuation processes, including the soil and aquifer physical characteristics, soil and groundwater chemistry, and the types of petroleum products in the soil and groundwater.

2.1 Biological Processes (Aerobic and Anaerobic Biodegradation)

The primary natural attenuation mechanism for reducing the mass and concentration of petroleum contaminants is biodegradation, which is the degradation of the contaminants by microorganisms. To convert (or consume) contaminants, microorganisms require the proper environmental conditions, nutrients and electron acceptors. Nutrients, which include trace levels of phosphorus, potassium, and nitrogen, are usually available within most soil and groundwater systems. The availability of electron acceptors usually controls the extent of contaminant biodegradation. Therefore, it is important to assess electron acceptor distribution and concentration in groundwater.

Microorganisms use electron acceptors (e.g., oxygen, nitrate, iron, and sulfate) to "breathe". Biodegradation generally proceeds at a greater rate in an aerobic (oxygen-rich) environment than under anaerobic (oxygen-depleted) conditions. As long as sufficient oxygen is present, aerobic biodegradation will dominate. Once oxygen has been sufficiently consumed, anaerobic biodegradation, which relies upon electron acceptors other than oxygen to metabolize petroleum contaminants, will dominate. The availability of electron acceptors usually controls the extent of contaminant biodegradation. Therefore, it is important to measure electron acceptor distribution and concentrations in groundwater.

Some petroleum compounds are only slowly degradable by microorganisms, or may not be degradable at all. The chemical structure of the contaminant, the concentration and competition between contaminants, and the ability of the natural microbes to "eat" a contaminant while "breathing" various electron acceptors control the speed and extent of degradation. For instance, benzene is most easily degraded when sufficient oxygen is present. Benzene does degrade when oxygen is depleted, but at a slower rate than if oxygen were abundant. In general, it has been found that toluene and xylenes degrade more readily than benzene and ethylbenzene. Another petroleum contaminant, methyl tertiary butyl ether (MTBE), degrades very slowly, in general, and does not readily sorb (or cling) to soil surfaces. Because of these properties, MTBE moves rapidly and tends to persist in groundwater.

At a typical site with petroleum underground storage tanks (USTs), gasoline may have leaked into the surrounding soils. Microorganisms in the soil will begin to degrade these compounds.

The rate of biodegradation will depend on the amount of contaminant released, the rate of contaminant movement through the soils and the presence of appropriate environmental conditions. Oxygen is usually present in the unsaturated soil to support biodegradation processes. If the release is large enough, contaminants may reach the groundwater, either dissolved in water seeping through the soil, or as pure petroleum product from the spill. Groundwater will transport the contaminants downgradient from the release, and naturally occurring microorganisms in the groundwater will degrade the soluble petroleum contaminants to an extent largely limited by the availability of electron acceptors. Oxygen is readily depleted in groundwater so that aerobic degradation processes are limited to the fringes of a contaminant plume. Anaerobic processes will account for most of the biodegradation that occurs within the contaminant plume.

2.2 Physical Processes

As mentioned above, natural attenuation can involve many other processes besides biological degradation. The processes of dilution, dispersion, sorption, precipitation, volatilization and abiotic degradation/transformation all serve to reduce the concentration of contaminants in groundwater and soils. These processes are particularly important for contaminants that are not subject to biodegradation.

3.0 APPLICABILITY OF MNA

3.1 Requirements for the Application of MNA

The following requirements must be met before MNA will be considered for approval as an appropriate remedial strategy for groundwater:

- There is no threat to any point of exposure (POE), other than the property boundary. Besides the property boundary, POEs include surficial soils, underground utilities, structures not involved with dispensing petroleum products, water wells, surface water bodies, and other sensitive environments.

- Plume status must clearly be shown to be stable or shrinking.

- If mobile free phase product is present, an active free product recovery program must be implemented. Free product must be removed to the fullest extent possible (no more than 0.01 feet remaining).

- If contaminated soil is acting as a continuing source to groundwater, an active soil remediation method must be implemented.

- Contaminants must be capable of undergoing biodegradation.

- Site factors must be conducive to the success of natural attenuation within a reasonable time frame (See Section 7.2).

3.2 Exclusion Criteria

If any of the following conditions are present, MNA cannot be the sole remedy to address groundwater contamination:

- An advancing groundwater plume indicates that the natural attenuation capacity of the system is unable to control the migration of contaminants.
- The contaminated media is difficult to assess as in some bedrock aquifers.
- POEs other than the property boundary are currently impacted.
- Mobile free product is present at the site, and no remedial method addressing the free product removal has been proposed.
- One or more of the other four exposure pathways (Subsurface Soil Leachate to Groundwater, Surficial Soil, Groundwater to Indoor Air Inhalation and Soil Vapor to Indoor Air Inhalation) exists at the site, and no active remediation method has been proposed to eliminate them.
- Contaminants are present which do not readily biodegrade.

3.3 Advantages of MNA

Potential advantages of implementing MNA include the following:

- Petroleum hydrocarbon chemicals of concern (COCs) that undergo biodegradation can be ultimately transformed to non-toxic products, such as carbon dioxide and water, and not simply transferred to another phase or location within the environment.
- Remediation by MNA causes minimal disturbance to site operations, adjacent landowners, and/or the environment and allows continuing use of the site's infrastructure during remediation.
- More conventional remedial technologies may pose greater risks to potential receptors than MNA due to site disruption and/or an inability to properly control these engineered remedial processes (i.e., risk to on-site workers, releases to the atmosphere, etc.).
- Remediation by MNA can be used in conjunction with conventional remedial technologies and can be used at sites where other remedial technologies are not technically feasible for achieving required cleanup goals.
- In many cases, remediation by MNA can be less costly than other available remedial technologies.

- Remediation by MNA can be evaluated by collecting adequate and appropriate geologic and hydrogeologic data during the site characterization phase. Data can be collected using relatively inexpensive field and laboratory analytical methods. If it is shown that remediation by MNA is not solely sufficient to provide adequate protection of POEs, the data collected for the MNA study can be incorporated in the design of other remedial alternatives.

- Remediation by MNA is not subject to the limitations imposed by the use of mechanized remediation equipment (that is, no equipment down time) and can be employed for contaminants below buildings and other areas that are not accessible.

- COCs such as benzene, toluene, ethylbenzene, and xylenes (BTEX) that typically pose the greatest risk are generally most likely to biodegrade.

3.4 Limitations of MNA

Potential limitations associated with the application of remediation by MNA include the following:

- Remediation by MNA may not always achieve the desired cleanup levels within a manageable time frame, particularly with respect to heavier petroleum constituents and at sites with a large source mass.

- The ability of remediation by MNA to achieve remedial goals can be sensitive to natural and human-induced changes in local hydrogeologic conditions and site operations. Potentially important effects include changes in groundwater gradient/velocities, rainfall, temperature, pH, electron acceptor concentrations, exposures not previously anticipated, or potential future releases. Such changes could be brought about by alterations in land use, changes in the local pumping regime, removal of an asphalt cap, third party impacts, or a change in the location of points of exposure.

- Long-term monitoring for remediation by MNA can represent a significant cost and a continued funding commitment.

- In the public perception, remediation by MNA can be viewed as a "do nothing" remedial alternative.

- Remediation by MNA relies on empirical data generated by groundwater monitoring. The inability to place monitoring wells (and to collect groundwater samples) in appropriate locations due to surface obstructions and possible changes in aquifer levels that render monitoring points unusable can preclude appropriate implementation of remediation by MNA.

- Several potential chemical constituents of petroleum products including MTBE and certain polynuclear aromatic hydrocarbons (PAHs), in general, do not readily degrade through natural attenuation processes. However, data from recently published research has shown that, under the right environmental conditions, MTBE will biodegrade. Even so, more active

remedial methods are generally required to reduce concentrations of these chemicals within an acceptable time frame.

4.0 Primary Lines of Evidence

A Primary Lines of Evidence evaluation is required to demonstrate that biodegradation is occurring at a site where MNA is being considered as a remedy for groundwater contamination. The Primary Lines of Evidence evaluation involves demonstrating that the plume is stable or shrinking, measuring dissolved oxygen levels in groundwater (an aerobic geochemical indicator), and measuring physical parameters. In situations where the data does not clearly indicate a decreasing trend, a Secondary Lines of Evidence evaluation may be performed (Section 5.0).

4.1 Plume Status as Defined by Empirical Data

During the Primary Lines of Evidence evaluation, historical groundwater contamination data is used directly to determine if a plume is stable or shrinking. The plume must be defined as stable or shrinking as demonstrated through four consecutive quarters of groundwater sampling of the COCs.

At all sites where MNA is being considered as a remedial option, there are additional requirements including measuring a site-specific hydraulic conductivity value and having correct well placement.

4.1.1 Hydraulic Conductivity

A field measurement of hydraulic conductivity is required at all sites to ensure that MNA will be adequately protective of all POEs, other than the property boundary. *In situ* well tests, such as slug tests, bail-down tests, or pumping tests are required for measuring hydraulic conductivity. The well tests must be performed at a minimum of three monitoring wells, and the geometric mean or average of the three hydraulic conductivity values should be used as the site-specific hydraulic conductivity.

4.1.2 Well Placement

Groundwater monitoring wells must be installed at the site in accordance with Section 5.4 of the *Petroleum Storage Tank Owner/Operator Guidance Document*. These requirements include the installation of monitoring wells upgradient, cross gradient, in-plume and downgradient. Additionally, in order to assess the ability of natural attenuation processes to control and remediate the contaminants, wells are required to be positioned along the center flow line, as determined by hydraulic gradient mapping at a site. The well configuration must meet the following requirements:

- One or more monitoring wells must be located within the source area to determine the highest concentrations of groundwater contamination.

- One or more monitoring wells must be installed within the plume of contamination, between the source well and the leading edge of the plume, along the center flow line.

- One or more point of compliance monitoring wells must be installed beyond the downgradient limits of the contamination along the center flow line.

4.2 Measuring Dissolved Oxygen

Dissolved Oxygen (DO) concentrations are used to indicate that aerobic biodegradation is controlling natural attenuation processes. Biodegradation is the fastest and most efficient degradation process when occurring under aerobic conditions. Methodologies for sample collection are located in Appendix A of this document. At sites where MNA is being considered, samples collected during the two most recent quarterly monitoring events of all wells must be analyzed for DO.

Microorganisms consume organic compounds, such as BTEX, and obtain carbon and energy for survival, growth and reproduction. The microbes metabolize the hydrocarbons and produce carbon dioxide and water through a series of enzyme-catalyzed oxidative-reduction reactions. For these reactions to occur, electron acceptors are required. During aerobic respiration the electron acceptor is DO. Oxygen consumption provides the greatest amount of energy to microbes during metabolism.

An inverse correlation of DO to BTEX concentrations indicates that aerobic biodegradation is occurring. Lower DO concentrations inside the plume, as compared to outside the plume, indicate biodegradation is occurring. At most sites, DO concentrations that are less than one ppm indicate anaerobic conditions. Refer to Section 5.2 for a more detailed description of anaerobic electron acceptors.

4.3 Physical Parameters

The following physical parameters can indicate the presence of appropriate site conditions for natural attenuation and that the samples collected are representative of the aquifer. Additionally, physical parameters may act as indicators of microbial activity. Samples collected during every monitoring event must be analyzed for the following physical parameters:

4.3.1 Temperature

Groundwater temperature affects the rate of many biological and chemical reaction rates, it can indicate biological activity is occurring, and it helps determine if the sample collected is representative of the aquifer being monitored.

- Effective biodegradation can generally occur within a temperature range of 5°C to 45°C; ideally, temperature should be above 15°C for optimal biological activity. Extreme temperatures (either hot or cold) prohibit microbial growth. Additionally, oxygen solubility is dependent on groundwater temperature.

- An increase in biological activity can increase the temperature within the solute plume.

- Temperature can help determine if the samples collected are from the same aquifer.

4.3.2 pH

pH is a measurement of a solution's hydrogen ion (H^+) concentration and is also referred to as a solution's degree of acidity or alkalinity. A pH value of 7.0 is considered neutral. A value lower than 7.0 is acidic and a value higher than 7.0 is basic or alkaline. pH is measured for the following reasons:

- pH can help determine if the sample collected is representative of the aquifer.

- Differences in pH between contaminated and uncontaminated groundwater may indicate bioactivity is occurring.

4.3.3 Specific Conductivity

Specific conductivity is a measurement of an aqueous solution's ability to conduct or carry an electric current. This ability depends on the presence, total concentration, mobility and valence of charged ionic species (e.g., Ca^{+2}, Na^+, Mg^{+2}, HCO_3^-, Cl^-), turbidity, and the solution's temperature.

Specific conductivity can be used as an indicator that samples collected from separate sampling points are from the same aquifer.

Table 4-1. Primary Lines of Evidence for Assessing Natural Attenuation

Analyte	Use	Change with Biological Activity
Dissolved Oxygen (DO)	Terminal electron acceptor.	↓
Temperature	Indicates conducive environment, biological activity, and representative groundwater after purging a well.	↑ or →
pH	Indicates microbial respiration of CO_2 , and representative groundwater after purging a well.	↓ or →
Specific Conductivity	Helps determine representative groundwater when purging a well.	→

Note 1: All sites will not exhibit these parameters or necessarily exhibit the changes indicated.
Note 2: The downward arrow (↓) indicates a reduction with biological activity, the upward arrow (↑) indicates an increase in biological activity, the sideways arrow (→) indicates no change with biological activity.

4.4 Required Map and Table

An isoconcentration map must be prepared for DO concentrations for each and every sampling event. DO data must also be presented in a data table.

5.0 Secondary Lines of Evidence

In situations where four consecutive quarters of monitoring data have not been collected and/or the data proves inconclusive, OPS requires that in addition to the geochemical indicators and physical parameters collected in the Primary Lines of Evidence evaluation, the following data be collected at sites where MNA is being considered.

5.1 Plume Status as Defined by Concentration vs. Travel Time (Distance) Method

If four consecutive monitoring events have not been performed or in situations where a decreasing trend is not indicated, a decay rate must be calculated using the concentration vs. travel time (distance) method (Section 7.1.2). The decay rate obtained using this method must indicate that biodegradation is occurring at the site. Additional data requirements include:

- A minimum of three wells must be installed within the plume of contamination, along the center flow line, when the concentration vs. travel time (distance) method is being used to calculate the decay rate.

- Measurements of fraction of organic carbon (FOC) collected from the same hydrogeologic unit outside of the area of contamination, and bulk density for soil.

5.2 Geochemical Indicators and Metabolic Byproducts

In situations where DO has been consumed, anaerobic processes will dominate. In the absence, or near absence of DO, nitrate (NO_3^-), manganese (Mn^{+4}), ferric iron (Fe^{+3}), sulfate (SO_4^{-2}) or carbon dioxide (CO_2) may serve, if available, as electron acceptors.

The sequential use of electron acceptors as microorganisms consume petroleum contaminants is:

$$DO \rightarrow NO_3^- \rightarrow Mn^{+4} \rightarrow Fe^{+3} \rightarrow SO_4^{-2} \rightarrow CO_2$$

The use of a specific electron acceptor is closely related to the oxidation-reduction potential of the groundwater. The more reducing the groundwater conditions, the greater the depletion of the available electron acceptors. Source zone groundwater usually exhibits the greatest depletion of electron acceptors.

Geochemical indicators monitor electron acceptors directly (e.g., DO, NO_3^- and SO_4^{-2}) or monitor the byproduct of the metabolized electron acceptor (e.g., Mn^{+2}, Fe^{+2}, and methane). Methodologies for sample collection are presented in Appendix A of this document.

5.2.1 Nitrate

Nitrate serves as an electron acceptor through the processes of denitrification and nitrate reduction. Denitrification occurs when nitrate (NO_3^-) is converted to nitrogen (N_2). Nitrate reduction is the process of converting nitrate (NO_3^-) to nitrite (NO_2^-) to ammonium (NH_4^+). In redox reactions, denitrification is favored over nitrate reduction because microorganisms generate more energy through denitrification. Nitrate reduction will occur, as conditions become more reducing.

After dissolved oxygen has been depleted in a given groundwater zone, nitrate, if available, may be used as an electron acceptor. An inverse relationship between BTEX concentrations and nitrate concentration should be expected.

5.2.2 Manganese

The use of manganese (Mn^{+4}) as an electron acceptor by microorganisms yields reduced water-soluble manganese (Mn^{+2}). In anaerobic groundwater zones where BTEX and a source of Mn^{+4} (MnO_2) are present, Mn^{+2} can be used as an indicator of degradation. A direct relationship between BTEX concentrations and Mn^{+2} concentration should be expected.

5.2.3 Iron

The use of ferric (Fe^{+3}) iron as an electron acceptor by microorganisms yields water-soluble ferrous (Fe^{+2}) iron. In anaerobic groundwater zones where BTEX and a source of ferric iron are present, ferrous iron can be used as an indicator of biodegradation. A direct relationship between BTEX concentrations and ferrous iron concentration should be expected.

5.2.4 Sulfate

Under strongly reducing conditions, after available oxygen, nitrate and ferric iron have been depleted sulfate can be used as an electron acceptor. In sulfate reducing zones, an inverse relationship between BTEX concentrations and sulfate concentration should be expected.

Table 5-1. Secondary Lines of Evidence for Assessing Natural Attenuation

Analyte	Use	Change with Biological Activity
Nitrate (NO_3^-)	Terminal electron acceptor when O_2 depleted.	↓
Manganese (Mn^{+2})	Metabolic byproduct of Mn^{+4} reduction.	↑
Ferrous Iron (Fe^{+2})	Metabolic byproduct of Fe^{+3} reduction.	↑
Sulfate (SO_4^{-2})	Terminal electron acceptor.	↓

Note 1: All sites will not exhibit these parameters or necessarily exhibit the changes indicated.
Note 2: The downward arrow (↓) indicates a reduction with biological activity, the upward arrow (↑) indicates an increase in biological activity.

5.3 Required Maps and Tables

In addition to isoconcentration maps of DO (Section 4.4), the following maps will be required during the Secondary Lines of Evidence evaluation:

- Electron Acceptors. Plot isoconcentration maps for nitrate and sulfate for each and every sampling event. During biodegradation, microbes directly utilize these compounds. If biodegradation is occurring, it is expected that oxygen, and perhaps nitrate and/or sulfate will be depleted within the dissolved plume.

- Metabolic Byproducts. Plot isoconcentration maps for dissolved manganese (Mn^{+2}) and dissolved iron (Fe^{+2}) for each and every sampling event. These compounds are byproducts of microbial metabolism and may increase within the dissolved plume.

Current and historic data must also be presented in data tables.

6.0 Additional Lines of Evidence

In unusual situations where data indicating whether or not MNA is occurring is inconclusive, the following data may need to be collected.

6.1 Microbial Studies

Petroleum degrading microorganisms are ubiquitous in soil and groundwater. However, microbes at a given site may not be able to degrade certain petroleum constituents, such as

MTBE. Generally, it is not necessary to perform these evaluations unless the other data collected do not support the use of natural attenuation as a remedy.

Bacterial growth is optimal in soils or groundwater that have a pH between 6 and 8. Microbial activity is generally limited in soils and groundwater with a pH significantly above or below these values.

6.2 Nutrient Concentrations

Nutrients are incorporated into microbial biomass and are necessary for the formation of proteins, DNA, cell membranes and other components of microbial cells. Measuring the concentration of electron acceptors or their reduction products should not be confused with measuring the level of microbial nutrients.

Microbial nutrients are usually divided into two categories:

- Macronutrients (for example, nitrogen and phosphorus), for which microorganisms require relatively large amounts.

- Micronutrients (for example, sulfur, manganese, magnesium and many others), for which only a trace amount is required.

Macronutrient (nitrogen and phosphorus) levels are often assessed in surface and subsurface environments by measuring ammonium (NH_4^+), and nitrate (NO_3^-), organic (Kjeldahl) nitrogen, available phosphorus or phosphate (PO_4^{-3}) and total phosphorus (mostly organic phosphorus compounds + phosphate).

Certain molecules, such as nitrate and sulfate, can serve either as nutrients or electron acceptors. While the availability of electron acceptors in the subsurface is a critical factor in assessing the rate and extent of biodegradation, nutrient levels are generally sufficient to support microbial biodegradation activity in the subsurface.

6.3 Additional Geochemical Indicators

Analyzing for the following geochemical indicators, while not required, may be useful in providing information concerning degradation at a site.

6.3.1 Methane

Methane is produced only under strongly reducing conditions by a group of strict anaerobes. Methanogens either use CO_2 as a terminal electron acceptor, producing methane, or cleave acetate to CO_2 and methane. Because methane is not present in fuels, it can be used as an indicator of biodegradation. Under methanogenic conditions, a positive correlation between BTEX concentrations and methane concentration should be expected.

6.3.2 Carbon Dioxide

Both aerobic and anaerobic biodegradative processes can yield large quantities of CO_2, as the BTEX constituents are completely oxidized. In many circumstances, a negative correlation between BTEX and CO_2 concentrations can be expected and can be used as a qualitative indicator of biodegradation.

6.3.3 Alkalinity

Alkalinity is neither an electron acceptor nor a metabolic byproduct. Alkalinity measures the acid neutralizing capacity of water and primarily includes carbonate (CO_3^{-2}), bicarbonate (HCO_3^-), and hydroxide (OH) ions. Changes in alkalinity are an indication of microbial activity. Alkalinity reflects the buffering capacity of groundwater and is most influenced by CO_2 content. Carbon dioxide originates from dissolution of carbonates in the aquifer, atmospheric CO_2, and the respiration of microbes. As the sequential electron acceptors are utilized, CO_2 is produced at each metabolic step. Therefore, alkalinity can be expected to increase across a site where biological activity is occurring. A zone of increased alkalinity indicates biodegradation is either producing organic acids, which lowers the pH and dissolves carbonate from the soil, or CO_2 is being produced.

6.3.4 Oxidation-Reduction Potential

The Oxidation-Reduction Potential (ORP) of groundwater is a measure of the relative tendency of a solution to accept or donate electrons. Oxidation-Reduction Potential is usually presented in terms of Eh values. Although not always true, a positive Eh value generally indicates that the solution is oxidizing (aerobic) while a negative value indicates that the solution is chemically reducing (anaerobic). If the ORP measurements taken outside the plume are higher than the ORP measurements in the plume, it is an indication that biodegradation may be occurring. Dissolved Oxygen and ORP readings should be in agreement. Dissolved Oxygen should be less than 1 ppm when ORP is negative.

7.0 Estimating Decay Rate and Time to Cleanup

Estimating decay rate and time to cleanup is required for all sites using MNA.

7.1 Decay Rate Calculation

The decay rate can be calculated as a function of concentration vs. time or concentration vs. travel time (distance). The decay rate can only be calculated using these methods when the contaminant plume is in steady state (stable) or decreasing. In addition, it must be understood that the resulting decay rate:

- Applies only to the reduction of contaminant mass in the groundwater, not to the reduction of contaminant mass in the unsaturated or free phase source areas.

- Includes source advection, attenuation, sorption, dispersion, and biodegradation effects, therefore it can not be used as a biodecay term in a fate and transport model.

The typical range for the decay rate of dissolved hydrocarbons is from 0.001 to 0.01 per day.

7.1.1 Concentration vs. Time

The concentration vs. time method involves calculating the decay rate using concentrations over time in a single well. Data from at least four consecutive quarterly sampling events are needed to use this method, and the decay rate must be calculated in at least two wells within the contaminant plume. This method may be preferred at sites where the hydraulic conductivity changes along a flow path. The method involves a four-step process as follows:

Step 1: Collect groundwater monitoring data from four or more consecutive quarterly sampling events in the source well and in a contaminated downgradient well, at a minimum. This information must include concentration and cumulative time (days) since the sampling date of the initial concentration used in the calculation.

Step 2: Prepare a semi-log plot of benzene concentrations (or the COC) for each well as a function of time (see Figures 7-1 and 7-2). This plot should be prepared using computer software such as Microsoft Excel that has the ability to add an exponential trend line and calculate the trend line equation. This plot will determine the following:

- The correlation coefficient (R) of the plotted data corresponds to the linear relationship between data points, and is always between –1 and +1 ($-1 \leq R \leq 1$). The square of R is the coefficient of determination (R^2) and is always a positive number. The R^2 value, calculated by the software, reflects how well the trend line fits the data. Generally, if R^2 is greater than 0.64, the data can easily fit a first order regression (decay) model. R^2 values less than 0.36 indicate that the data is not a good fit for a first order regression analysis. Note that R^2 is always 1 when only two data points are available, so the significance of R^2 is tied to the number of data points. Therefore, if the amount of data is not sufficient to provide a significant R^2 value, or if R^2 value indicates the data is not a good fit, for a first order regression analysis, the data should not be used to calculate the contaminant decay rate.

- The trend line should be sloping downward with the passage of time, which indicates that the contaminant concentrations are decreasing. If the trend line is flat, R^2 will be very small and out of the acceptable range, even if the data is a good fit to the line. If the trend line increases or slopes upward and the data is a good fit, R^2 may still be a value that is acceptable. However, the upward slope indicates an expanding plume and the data cannot be used to determine the decay rate with this method.

- The contaminant decay rate is calculated from the slope of the trend line generated by the computer software and must be displayed on the graph. The line and contaminant regression equations are compared in Step 3.

Step 3: The trend line, or regression line, is calculated by the computer software. The calculated trend line equation must be displayed on the graph and has the following form for a semi-log plot:

$$y = be^{-mx}$$

where: y = y-axis value at unit x
b = y-axis intercept
m = Slope of line
x = x-axis value

The trend line equation is actually the equation for the first-order time decay of a contaminant concentration as follows:

$$C_t = C_o e^{-kt}$$

where: C_t = Concentration calculated from trend line at time t (µg/L)
C_o = Initial concentration calculated from trend line (µg/L)
k = First-order decay rate term (day^{-1})
t = Time after initial concentration (days)

The slope of the trend line is the first-order decay rate (m = k).

Step 4: Compare k values from different sampling points (as available) to define overall plume decay rate. If the decay rates differ, the most conservative decay rate value must be used in time to cleanup calculations.

Example Problem of Concentration vs. Time:

Example Step 1: Given the following groundwater monitoring data in Table 7-1.

Table 7-1. Example Data for Source and Downgradient Wells

Cumulative Days	Source Well Concentration (µg/L)	Downgradient Well Concentration (µg/L)
0	12220	1310
210	11400	102
300	11200	74
510	1540	111
600	1490	125
690	600	69

Example Step 2: Figures 7-1 and 7-2 show graphs of the concentrations versus cumulative time plotted using Excel:

Figure 7-1. Example Plot of Concentration vs. Time at the Source Well

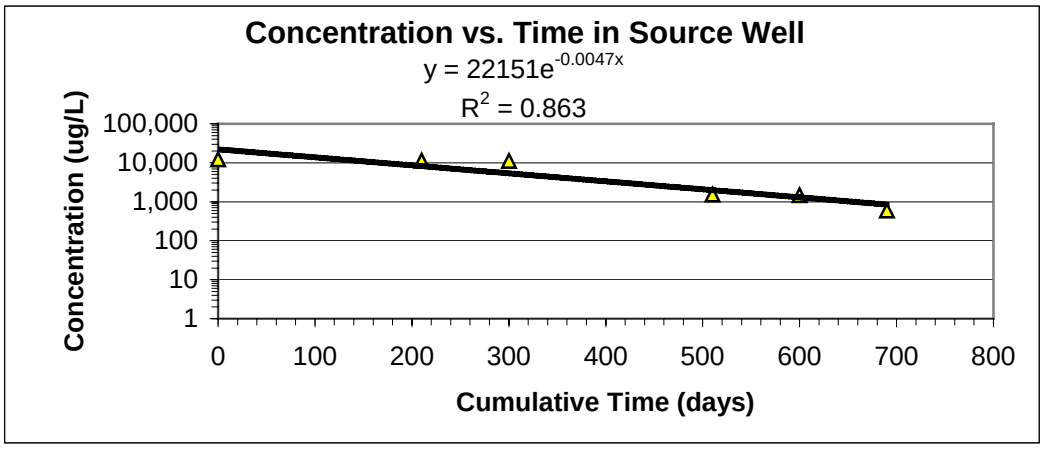
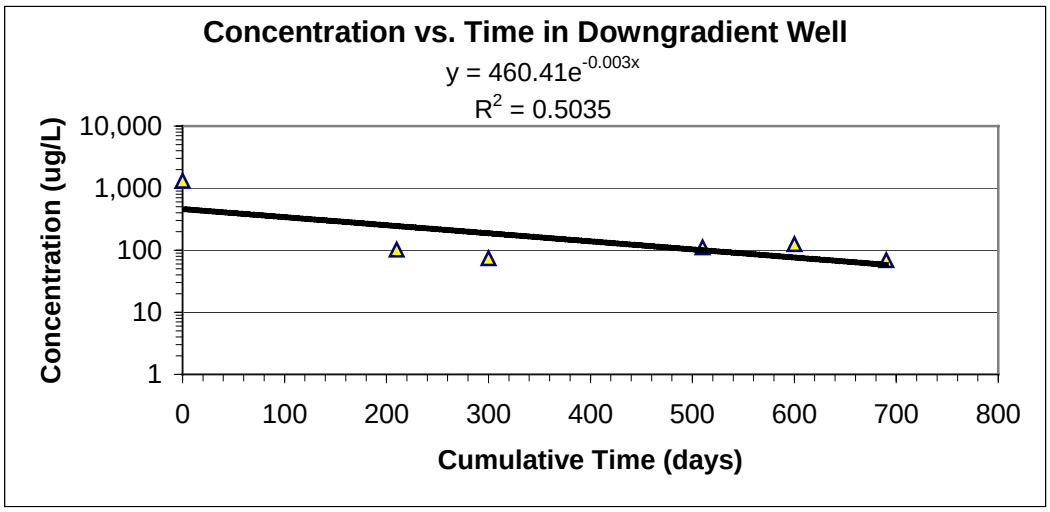


Figure 7-2. Example Plot of Concentration vs. Time at the Downgradient Well



Example Step 3: The line equations, that give the decay rates (k), are as follows:

Source well

$y = 22151e^{-0.0047x}$ (from plot)
therefore k = 0.0047/day
or 0.47 % per day

Downgradient Well

$y = 460.41e^{-0.003x}$ (from plot)
therefore k = 0.003/day
or 0.3 % per day

Example Step 4: The decay rate of 0.003/day is the most conservative of the two decay rates, and therefore will be used in time to cleanup calculations (Section 7.2).

7.1.2 Concentration vs. Travel Time (Distance)

This method can be used when there are limited sampling events. The *concentration vs. time* method described in section 7.1.1 is preferable for calculating the decay rate if at least four quarters of monitoring data have been collected. Therefore, decay rates calculated by the *concentration vs. travel time (distance)* method should be validated by the *concentration vs. time* method once sufficient monitoring data have been collected.

For the *concentration vs. travel time (distance)* method, data are needed from at least two consecutive quarterly monitoring events from at least three contaminated wells along the flow-line (longitudinal axis) of the plume. The travel time of the contaminant from the source well to a contaminated downgradient well is calculated using site-specific parameters. This method involves a six-step process as follows:

Step 1: Collect necessary information, including:

- Groundwater monitoring data from at least three contaminated monitoring wells on the longitudinal axis of the plume, beyond the presence of any free phase product and far enough apart such that the BTEX concentrations differ by several orders of magnitude.
- Geometric or average site-specific hydraulic conductivity calculated from hydraulic conductivities at several points along the flow path.
- Hydraulic gradient.
- Site-specific soil properties for bulk density, fraction of organic carbon (FOC) content and effective porosity. (If a site-specific value for effective porosity cannot be obtained, it can be estimated based on soil type).
- Contaminant-specific organic carbon/water partition coefficient (Koc).

Step 2: Calculate the groundwater seepage velocity and the retardation factor as follows:

$$V = Ki / n_e \text{ and } R = 1 + (\rho_b / n_e)(K_{oc})(FOC)$$

where:
- V = Groundwater seepage velocity (ft/day)
- K = Aquifer hydraulic conductivity (ft/day)
- i = Hydraulic gradient (unitless)
- R = Retardation factor (unitless)
- ρ_b = Soil bulk density of the aquifer material (g/cm^3)
- n_e = Aquifer effective porosity (%)

K_{oc} = Organic carbon/water partition coefficient (ml/g)
FOC = Fraction organic carbon content of aquifer material (unitless)

Step 3: Calculate the contaminant plume velocity as follows:

$$V_p = V / R$$

where: V_p = Contaminant plume velocity (ft/day)
V = Groundwater seepage velocity (ft/day)
R = Retardation factor (unitless)

Step 4: Calculate travel time between the source and each in-plume well along the axis of the plume as follows:

$$t = x / V_p$$

where: t = Travel time (days)
x = Distance between the wells (ft)
V_p = Contaminant plume velocity (ft/day)

Step 5: Prepare a semi-log plot of benzene concentrations for each well identified above (Step 1) as a function of travel time calculated in Step 4 above. Using the built-in spreadsheet function, add an exponential trend line and insert the line equation and R^2 value on the plot. The purpose of this step is described in Section 7.1.1, Step 2.

Step 6: Similar to the *concentration vs. time* method, the decay rate value is calculated from the slope of the trend line or regression line. This decay rate will be used in time to cleanup calculations (Section 7.2).

Example Problem for Concentration versus Travel Time (Distance):

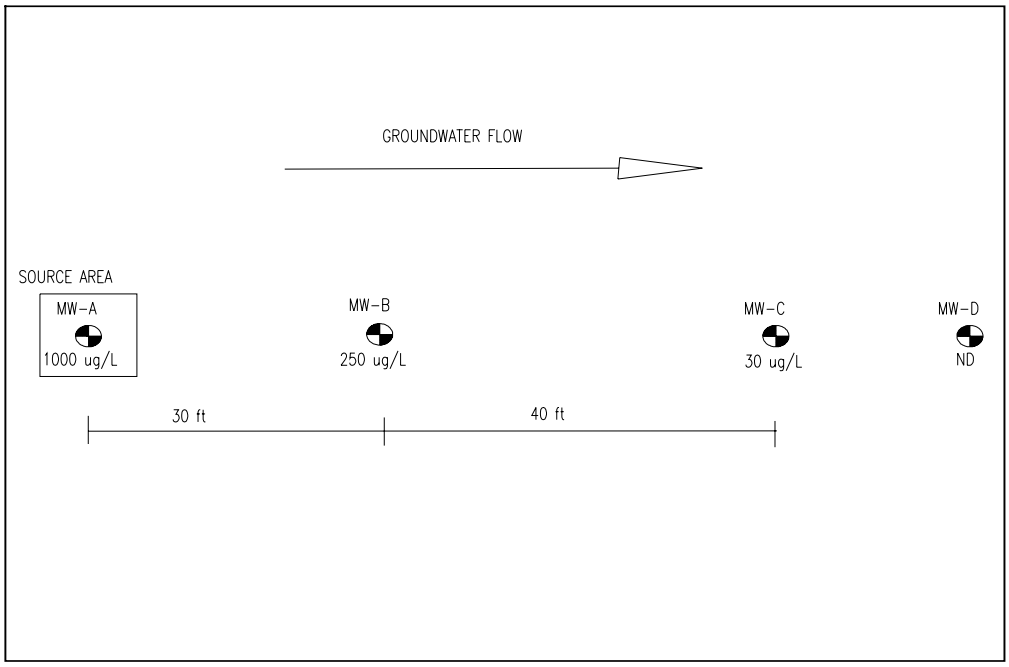
Example Step 1: The following information pertains to the site in Figure 7-3.

average hydraulic conductivity (K) = 1.2 ft/day
hydraulic gradient (i) = 0.05
bulk density (ρ_b) = 1.64 g/cm^3
effective porosity (n_e) = 0.25
FOC = 0.009
K_{oc} = 59 ml/g (benzene; Table 7-2)

Table 7-2. K_{oc} Values for BTEX Compounds

Compound	K_{oc} (ml/g)
Benzene	59
Toluene	182
Ethylbenzene	363
Xylenes	240

Figure 7-3. Example Site Plan with Benzene Concentrations in Groundwater



Example Step 2: Calculate the groundwater seepage velocity and the retardation factor (for benzene) as follows:

$V = Ki / n_e$ and $R = 1 + (\rho_b / n_e)(K_{oc})(FOC)$

$V = (1.2 \text{ ft/day})(0.05) / 0.25 = 0.24 \text{ ft/day}$

$R = 1 + (1.64 \text{ g/cm}^3 / 0.25)(59 \text{ ml/g})(0.009) = 4.48 \text{ ml/cm}^3 = 4.48$

Example Step 3: Calculate the contaminant plume velocity as follows:

$V_p = V / R$

$V_p = 0.24 \text{ ft/day} / 4.48 = 0.054 \text{ ft/day}$

Example Step 4: Travel time is then derived as follows:

$t = x / V_p$

Between MW-A and MW-B

t = 30 ft / 0.054 ft/day = 555.56 days

Between MW-B and MW-C

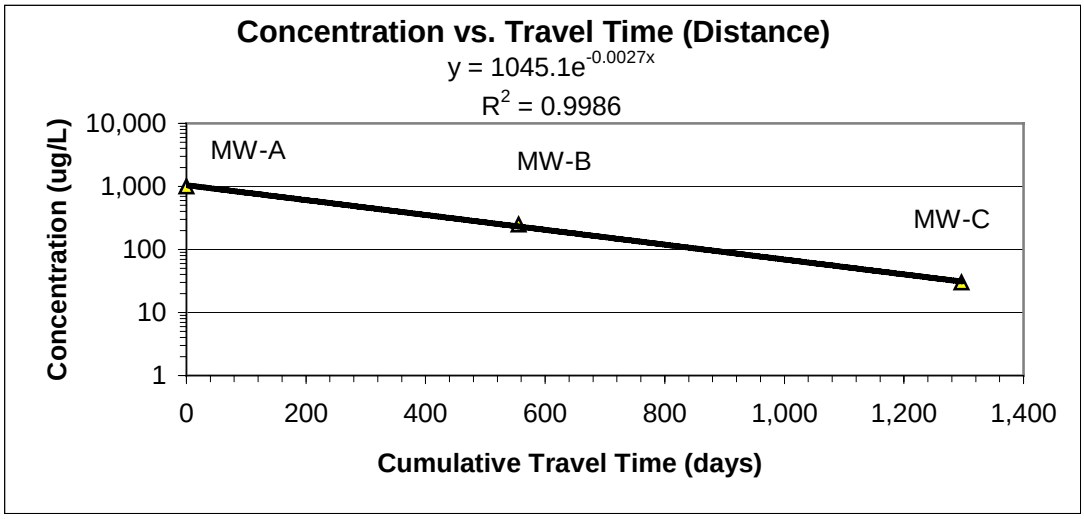
t = 40 ft / 0.054 ft/day = 740.74 days

Example Step 5: Prepare a plot of the benzene concentrations in the wells identified above (Example Step 1) versus the travel times calculated in Step 4 above. Table 7-3 shows the data used for the plot in Figure 7-4.

Table 7-3. Example Travel Times and Concentrations

Well	Cumulative Travel Time from MW-A (days) [Distance (ft) / Plume Velocity (ft/day)]	Benzene Concentration (µg/L)
MW-A	0	1000
MW-B	555.56	250
MW-C	1296.30	30

Figure 7-4. Example Plot of Concentration vs. Travel Time



Example Step 6: As shown in Figure 7-4, the decay rate calculated from the trend line from MW-A to MW-C is 0.0027/day. This decay rate will be used in time to cleanup calculations.

7.2 Estimated Time to Cleanup, Cleanup Levels, and Milestones

This section is designed to determine the estimated time to cleanup, utilizing the calculations that are included. It is necessary to determine the time to cleanup in order to determine if remediation of the site may be completed in a reasonable and acceptable time frame, and what the estimated remediation costs will be. The key components in determining time to cleanup include the site-specific decay rate calculated in Section 7.1, and the known cleanup concentration goal for the site. If no other POEs are located between the source of contamination and the property boundary, the cleanup goal for the site will be the Tier 1 RBSLs for the BTEX constituents at and downgradient of the property boundary. The time to cleanup for the site is the projected time for petroleum contamination at the property boundary to degrade to the Tier 1 RBSLs. If there is not a monitoring well located at the property boundary, the current concentration of contaminants at the property boundary is assumed to be the concentration at the most downgradient, onsite, in-plume well.

Milestones are projected concentrations over time at in-plume wells. Milestones are used as indicators that degradation of contaminants is occurring at the projected decay rate. Projected milestones must be calculated for the most downgradient, onsite, in-plume well for 25%, 50% and 75% contamination reduction towards the goal. Similarly, milestones must also be calculated for all other in-plume wells. In order to calculate milestones for all other in-plume wells, a projected cleanup level is first calculated for each well. The projected cleanup level is calculated using the current contaminant concentration at each well and the estimated time to cleanup calculated for the most downgradient, onsite, in-plume well to reach the site cleanup goal.

The cleanup goal as calculated above is to be used only for estimating the time it will take for a site to cleanup to acceptable levels. If groundwater contamination above RBSLs remains on-site at the time No Further Action is requested, the request must include fate and transport modeling which demonstrates that the concentration at each in-plume well will not impact the property boundary (or any other POE) above RBSLs in the future.

7.2.1 Calculating Estimated Time to Cleanup

The decay rate value (calculated by either method described in Sections 7.1.1 and/or 7.1.2) is used in the calculation of the estimated time to cleanup for the site.

Rearranging the first-order decay equation ($C_G = C_o e^{-kt}$) yields:

$$C_G / C_o = e^{-kt} \quad \text{and} \quad t = [-\ln(C_G / C_o)] / k$$

where:

- C_G = Concentration of cleanup goal (Tier 1RBSL) (µg/L)
- C_o = Current concentration at downgradient, onsite, in-plume well (µg/L)
- k = Decay rate (day^{-1})
- t = Time for C_o to attenuate to C_G or Tier 1 RBSLs (days)

Example #1: Given the decay rate (0.003 day^{-1}) calculated in the example from Section 7.1.1 and the current concentration at the downgradient, onsite, in-plume well (69 µg/L), the time to cleanup at this site is calculated as follows:

$t = [-\ln(C_G / C_o)] / k$

$t = [-\ln(5\ \mu g/L / 69\ \mu g/L)] / 0.003/day = 2.62 / 0.003/day = 873$ days or 2.4 years

Example #2: Given the decay rate (0.0027 day^{-1}) calculated in the example from Section 7.1.2 and the current concentration at well MW-C (30 µg/L), the time to cleanup at this site is calculated as follows:

$t = [-\ln(C_G / C_o)] / k$

$t = [-\ln(5\ \mu g/L / 30\ \mu g/L)] / 0.0027/day = 1.79 / 0.0027/day = 663$ days or 1.8 years

7.2.2 Calculating Estimated Cleanup Levels for Other In-plume Wells

With the time to cleanup and the decay rate values calculated, cleanup levels for all other in-plume wells, including the source well, can now be calculated. Cleanup levels at each in-plume well are calculated as follows:

$$C_L = C_o e^{-kt}$$

where:
- C_L = concentration of cleanup levels (µg/L)
- C_o = current concentration at well (µg/L)
- k = decay rate (day^{-1})
- t = time to cleanup (days)

Example #1: Given the decay rate (0.003 day^{-1}) calculated in the example from Section 7.1.1, the time to cleanup at the downgradient well, and the current concentration at the source well (600 µg/L), the cleanup level at the source well is calculated as follows:

$$C_L = (600\ \mu g/L)\{e^{-[(0.003/day)(873\ days)]}\} = (600\ \mu g/L)(0.073) = 44\ \mu g/L$$

Example #2: Given the decay rate (0.0027 day^{-1}) calculated in the example from Section 7.1.2, the time to cleanup at well MW-C, and the current concentration at MW-A and MW-B, the cleanup goals for wells MW-A and MW-B are calculated as follows:

For MW-A:

$$C_L = (1{,}000\ \mu g/L)\{e^{-[(0.0027/day)(663\ days)]}\} = (1{,}000\ \mu g/L)(0.167) = 167\ \mu g/L$$

And for MW-B:

$$C_L = (250\ \mu g/L)\{e^{-[(0.0027/day)(663\ days)]}\} = (250\ \mu g/L)(0.167) = 42\ \mu g/L$$

7.2.3 Calculating Estimated Milestones

Milestones are represented as the concentration at each in-plume well at 25%, 50%, and 75% reduction in contamination towards the cleanup goal or cleanup level. The time required to reach the milestone is calculated using the milestone concentration, the current concentration, and the decay rate.

The milestone concentrations are calculated using the following equation:

$$C_{L\%} = C_o - [(C_o - C_L)(\% \text{ towards level} / 100)]$$

Where:
- $C_{L\%}$ = Concentration of milestone at selected % towards cleanup level (days)
- C_L = Cleanup level of selected well (µg/L)
- C_o = Current concentration at well (µg/L)

The time required to reach the milestone is calculated by using the first-order regression equation as follows:

$$C_{L\%} = C_o e^{-kt} \quad \text{therefore} \quad t_{L\%} = [-\ln(C_{L\%} / C_o)] / k$$

Where:
- $t_{L\%}$ = Time to reach milestone at selected % towards cleanup goal (days)
- $C_{L\%}$ = Concentration at milestone (µg/L)
- C_o = Current concentration at well (µg/L)
- k = decay rate (day^{-1})

Example #1: From Section 7.1.1, the source well concentration is 600 µg/L, the cleanup level is 44 µg/L, and the decay rate is 0.003 day^{-1}. Therefore the milestones and time to milestones are calculated as follows:

25 percent towards cleanup level of 44 µg/L:

C_{L25} = 600 µg/L – [(600 µg/L – 44 µg/L)(25 / 100)] = 461 µg/L

t_{L25} = [-ln (461 µg/L / 600 µg/L)] / 0.003 day^{-1} = 88 days

50 percent towards cleanup level 44 µg/L:

C_{L50} = 600 µg/L – [(600 µg/L – 44 µg/L)(50 / 100)] = 322 µg/L

t_{L50} = [-ln (322 µg/L / 600 µg/L)] / 0.003 day^{-1} = 207 days

And so on for further milestones.

Example #2: From Section 7.1.2, the source well (MW-A) concentration is 1,000 µg/L, the cleanup level (calculated in Section 7.2.2) is 167 µg/L, and the decay rate is 0.027 day^{-1}. Therefore the milestones and time to milestones are calculated as follows:

25 percent towards cleanup level of 167 µg/L:
C_{L25} = 1,000 µg/L – [(1,000 µg/L – 167 µg/L)(25 / 100)] = 792 µg/L
t_{L25} = [-ln (792 µg/L / 1,000 µg/L)] / 0.0027 day^{-1} = 86 days

50 percent towards cleanup goal 167 µg/L:
C_{L50} = 1,000 µg/L – [(1,000 µg/L – 167 µg/L)(50 / 100)] = 584 µg/L
t_{L50} = [-ln (184 µg/L / 1,000 µg/L)] / 0.0027 day^{-1} = 627 days = 199 days

And so on for further milestones.

8.0 MNA Corrective Actions

MNA can be proposed as a corrective action remedy if it has been demonstrated to be technically feasible through an evaluation of the Primary Lines of Evidence (Section 4.0) and the Secondary Lines of Evidence (Section 5.0), as necessary. MNA may be proposed as a remediation method by using one of two OPS approved corrective action report formats:

- Corrective Action Plan – Monitored Natural Attenuation report format (CAP-MNA)
- Corrective Action Plan report format (CAP)

The CAP includes the comparison of three remedial methods to address contamination and is required in most situations. The CAP-MNA does not require this comparison and can be used in lieu of the CAP only as specified below.

8.1 Format Applicability

8.1.1 CAP-MNA Report Format

The criteria for using the CAP-MNA are listed below:

- There cannot be any recoverable free product (no more than 0.01 feet in any well) remaining at the site. The CAP-MNA does not have a mechanism for technically and economically evaluating free product removal plans.
- All of the other four exposure pathways (Subsurface Soil Leachate to Groundwater, Surficial Soil, Groundwater to Indoor Air Inhalation and Soil Vapor to Indoor Air Inhalation) must have been eliminated (Table 7-2 Exposure Pathway Screening Criteria in the *Owner/Operator Guidance Document*). Methods to eliminate the exposure pathways include; site

concentrations of COCs less than Tier 1 RBSLs, or Tier 1A SS-RBSLs or Tier 2 SSTLs. All model results must be reviewed and approved by OPS prior to submission of the CAP-MNA.

- There cannot be any impacted POEs other than the property boundary.

- The estimated time to cleanup included in the CAP-MNA cannot exceed 10 years. Methods for estimating time to cleanup are presented in section 7.2.1 of this document.

If a CAP-MNA is going to be recommended for a site, it must be indicated in the SCR. This is to allow OPS to concur with the recommendation and pre-authorize the use of a CAP-MNA prior to its development. All additional data collected in support of MNA that was not included in the SCR must be submitted on the approved CAP-MNA form.

8.1.2 CAP Report Format

If any of the conditions listed in Section 8.1.1 do occur (with the exception of impacts to POEs) and MNA can be demonstrated to be technically feasible, the CAP may be used to propose MNA as a remedy to address groundwater contamination.

8.2 Requirements for Both CAP-MNA and CAP Formats

8.2.1 POE Evaluation

An evaluation must be performed to identify all POEs impacted or potentially impacted as a result of the release. See Section 7.3 of the *Owner/Operator Guidance Document* for information concerning POEs.

8.2.2 Cleanup Goal

A cleanup goal must be established for every site. The cleanup goal will be equal to Tier 1 RBSLs both onsite and offsite unless a risked based approach to site cleanup is being implemented. Section 7.2 of this document describes the method to calculate a site-specific cleanup goal.

8.2.3 Estimated Time to Cleanup

It is necessary to estimate the time to cleanup. The predicted time frame for reaching the cleanup goal at the site will be used for determining costs and setting milestones. See Section 7.2.1 of this document for methods to calculate estimated time to cleanup.

8.2.4 Remediation Milestones

It is necessary to calculate milestones for each in-plume well to project the reduction in contamination toward the cleanup goal or level. See Section 7.2.3 for the method of calculating remediation milestones. If a milestone is exceeded, the MNA feasibility at the site will be re-evaluated and OPS may require the re-calculation of the decay rate, time to cleanup, cleanup goals, and milestones.

8.2.5 Groundwater Monitoring Plan

A monitoring plan is required describing the wells to be sampled, the frequency of sampling and the parameters to be analyzed.

- At a minimum, the three wells (source, in-plume, downgradient POC) located on the center flow line and an upgradient well must be sampled during every groundwater monitoring event. Depending on site characteristics, additional wells may be required to be included in the monitoring plan.

- Groundwater is required to be sampled for eight consecutive quarters. Note that consecutive quarterly monitoring events performed prior to CAP or CAP-MNA approval may be used to meet this requirement. After the first two years, monitoring should be conducted at a frequency appropriate to detect any changes in the contaminant plume, especially changes in contaminant concentrations over time and distance. Frequency of monitoring should not be less than once per year, during the same season each year. Annual groundwater monitoring should be performed during the season that exhibits the highest contaminant concentrations, based on the results from the first two years of monitoring. Depending on site characteristics, quarterly groundwater monitoring may be required for the duration of the project. Groundwater monitoring must be performed for four consecutive quarters prior to requesting site closure.

  Note: A No Further Action may be requested at any time following four quarterly events where COCs are not detected above the cleanup goal.

- The parameters that must be collected at the selected wells during each groundwater monitoring event are the concentrations of the COCs, DO, temperature, pH, and specific conductivity.

Table 8-1. Monitoring Schedule Guideline

Time Frame	Frequency	Parameters	Wells
First Year	Quarterly	COCs, DO, Temperature, pH, Specific Conductivity	All monitoring wells in the approved CAP or CAP-MNA monitoring schedule
Second Year	Quarterly		
Third Year	Semi-Annually		
Fourth Year Until Cleanup Goal Met	Annually		
Final Year	Quarterly		

Note 1: Sampling performed prior to CAP approval may be included in the eight quarters of sampling.
Note 2: Progressing from quarterly to semi-annual and annual monitoring must receive OPS prior concurrence.
Note 3: The wells listed represent the minimum; additional wells may be required to be sampled depending on site conditions.

In the event that the Secondary Lines of Evidence evaluation is necessary to confirm that MNA would be effective at the site, additional geochemical indicators are required to be analyzed (Section 5.2). These include nitrate, manganese, ferrous iron, and sulfate. The collection of these parameters is in addition to the parameters listed in Table 8-1. The parameters must be analyzed quarterly, until a decreasing groundwater contaminant concentration trend line is established and approved by OPS.

Table 8-2. Secondary Lines of Evidence Monitoring Schedule Guidelines

Parameters	Frequency	Wells
Nitrate, Manganese, Ferrous Iron, Sulfate, and optional parameters (Section 5.3) as required	Quarterly, until a decreasing groundwater contaminant concentration trend line is established	All monitoring wells in the approved CAP or CAP-MNA monitoring schedule

8.3 Additional CAP-MNA Report Requirements

In addition to requirements in Section 8.2, the following are required when a CAP-MNA is being submitted:

8.3.1 Cost Estimate

The cost of implementing MNA must be estimated and reported on the approved OPS CAP-MNA worksheet. The estimated costs must incorporate the number of monitoring events required in Table 8-1 over the time frame for reaching remedial goals previously calculated in Section 7.0. All applicable costs must be in accordance with the Reasonable Cost Guidelines.

8.3.2 Contingency Plan

A contingency plan for active remediation must be included in the CAP-MNA. This plan is required in the event that remediation by MNA is unsuccessful. In the situation that it is necessary to implement the contingency plan, a pilot test, an Economic and Technological Feasibility Summary (ETF) and detailed remedial system design drawings may be required prior to CAP Modification approval.

8.4 Additional CAP Format Requirements

In addition to those requirements listed in Section 8.2, the following are included in situations where the CAP format is used.

8.4.1 Checklist of Remediation Methods Considered

A checklist of the remediation methods to be considered must be completed to identify technical and economic limitations of all listed remedial methods and to evaluate whether or not each method will address the exposure pathways completed at the site.

8.4.2 Economic and Technological Feasibility Summary

An Economic and Technological Feasibility Summary must be completed for the three most technically feasible methods to remediate soil, groundwater and free product, as appropriate.

8.4.3 Remedial Option Selection

A remedial option selection table must be completed identifying the three most technically feasible methods to remediate soil and groundwater, as appropriate, listing their associated costs, and selecting the remediation option(s) proposed.

8.5 Reporting

Monitoring reports are required to be submitted, on the approved OPS format, within 45 days following each groundwater monitoring event.

8.6 Corrective Action Modification

Triggers are conditions that arise at a site indicating that MNA may not be protective or appropriate. Triggers can include but are not limited to the following conditions:

- A point of exposure becomes impacted.
- It is determined that the plume is advancing.
- A POE that was not present at the time of CAP-MNA or CAP approval now exists and is threatened or impacted (i.e. a house is built on the empty lot downgradient of the site).
- The land use designation is changed due to rezoning.
- Free product appears where it did not exist at the time of CAP-MNA or CAP approval.
- Remediation costs exceed the Economic and Technological Feasibility Summary.
- The approved milestone concentrations are exceeded.

If a trigger occurs, the effectiveness of MNA for remediating the site must be reevaluated. If the new evaluation indicates it is not effective, a CAP Modification will be required by the OPS and an active remedial option will be required at the site.

9.0 No Further Action

No Further Action may be requested at MNA sites where the approved site cleanup goal in groundwater has been achieved for at least four consecutive quarters. Since concentrations at other in-plume wells may be significantly greater than Tier 1 RBSLs, the No Further Action request must include fate and transport modeling of the concentrations in each in-plume well. This modeling must demonstrate that the concentration at each well will not impact any POE within the OPS approved time frame.

If soil and/or soil vapor concentrations exceed RBSLs, a Tier 1A and/or a Tier 2 model may be performed to establish alternate site-specific cleanup levels. A No Further Action determination will not be granted at sites where recoverable free product exists.

Appendix A

Sample Methodology for Geochemical Parameters

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1.0 Sample Methodology for Geochemical Parameters

This appendix provides general information on each electron acceptor or parameter and suggests sample collection and monitoring guidelines.

When collecting field generated data, document the field methodology used to generate data. Document the quality control and quality assurance procedures used for the analyses.

1.1 Temperature

Temperature of groundwater should be measured during or immediately after purging a well and should be read to at least the nearest 0.5°C (preferably to an accuracy of ±0°C or ±2°F). Temperature is commonly measured in the field by using one of the following methods:

1.1.1 Lowering a temperature probe into the water column of a well

This method ensures that the temperature values most closely represent the actual groundwater temperature. The probe should be submersed for a couple of minutes to equilibrate to groundwater temperature.

1.1.2 Inserting a temperature probe into a closed flow-through cell

This method can be used if a low-flow purging method is used prior to well sampling. During low-flow purging on a very hot or cold day, the sample will artificially warm up or cool down, which can be minimized by using a short sample tube and shielding or insulating the flow-through cell from heat and cold.

1.1.3 Inserting an accurate thermometer into a sample

For this method to work effectively, measure the temperature from the sample soon after collecting it (e.g., within two minutes) or while purging. During purging, allow the water to overflow the sample container while measuring the temperature.

1.2 pH

Because a sample's pH can change quickly after collection, it is important to collect this measurement down the well, in a flow-through cell, or immediately after sample collection. Before use, a pH instrument and probe must be properly calibrated with fresh pH buffer solutions of 7.0 and 10.0 or 7.0 and 4.0 (depending on anticipated groundwater pH), at temperatures within 5 °C of the groundwater samples. The procedures for measuring pH using the above methods are the same as those described in Section 1.1 of this Appendix.

1.3 Specific Conductivity

Specific conductivity is measured between two chemically inert probes spaced a fixed distance apart, and are usually recorded as micromhos per centimeter (μmhos/cm). The following

conversion may be helpful when using instruments that provide readings in the International System of Units:

1 mS/m (millisiemens/meter) = 10 μmhos/cm

Before use, the conductivity instrument and probe must be calibrated against a standard potassium chloride solution. Because conductivity depends on temperature, the conductivity measurements must be converted to 25 ^{o}C if your instrument doesn't automatically do so. Most problems related to collecting poor conductivity data include fouling of the electrode, improper or no instrument calibration, not allowing the probe to equalize with the sample temperature, and improperly or not converting readings to 25 ^{o}C. The procedures for measuring conductivity using the above methods are the same as those described in Section 1.1 of this Appendix.

1.4 Oxidation-Reduction Potential

Oxidation-Reduction Potential (ORP) can be useful as a qualitative indicator of groundwater geochemistry, however ORP data can be difficult to interpret. The ORP reading reflects many chemical reactions (oxidation-reduction) within the groundwater, so it is not possible to associate the ORP reading with a specific chemical condition in the groundwater. Data comparability is an issue for ORP measurements because different electrodes (platinum, O_2/H_2O, Fe^{+2}, SO_4^{-2}/H_2S, CO_2/CH_4,etc.) show little agreement with each other. Therefore, if ORP measurements are to be comparable, measurements must be made using the same electrode type throughout the monitoring life of the site. In addition, ORP electrodes tend to exhibit "drift" and become "poisoned" (due to accumulation of oxidation products on the electrode). If these limitations are addressed, ORP can be useful as a qualitative indicator of groundwater geochemistry.

ORP measurements must be made in an airtight flow-through cell or down the well. The water must not come into contact with the atmosphere while ORP (Eh) is being measured. Eh meters must read values to ∀10 millivolts (mV). Eh is measured in the field using an inert indicator electrode and a suitable reference electrode (most commonly platinum).

1.5 Alkalinity

Alkalinity titration can be performed in the laboratory or field. It is recommended that alkalinity be measured twice in monitoring wells and at least once a year thereafter. Alkalinity is calculated using measurements from precise sample volumes and acid titration procedures.

1.6 Dissolved Oxygen

Measure dissolved oxygen (DO) before and after purging each well and use the lowest DO reading obtained as being representative of the groundwater conditions. In some cases, purging may not be necessary to obtain accurate DO measurements; however this should be confirmed by comparing non-purged and purged DO readings. Use consistent sampling and analytical methodologies on all monitoring wells to ensure comparability of the data.

Analyze DO in the field with an oxygen probe, field test kit, or other method sensitive to dissolved oxygen concentrations between 0 and 10 ppm. Accurate DO measurements require the

use of purging, sampling, and analytical techniques that do not introduce air to the water column or sample. DO can be measured using the methods described in Section 1.1 of this Appendix, although the method of inserting the probe into a sample following purging may increase the sample's exposure to air.

1.7 Nitrate

Nitrate (NO_3^-) is often analyzed by methods that measure both nitrate (NO_3^-) and nitrite (NO_2^-), often referred to as nitrate+nitrite. It is acceptable to use nitrate+nitrite as a measure of nitrate because nitrite makes up a small percentage of total nitrogen at the vast majority of sites. Nitrite is not stable under most environmental conditions and will quickly convert to ammonia. Nitrate specific analysis is also acceptable. However, because nitrate-only samples are not preserved, it is important that the samples be analyzed within 48 hours. Otherwise, bacterial action will convert the nitrate and bias the sample.

At this time, laboratory measurement of nitrate is preferred over field techniques. Field methods may evolve to provide accurate nitrate data. The use of the brucine sulfate method to measure nitrate is not recommended because of high variability in the sample results.

1.8 Manganese

Dissolved manganese (Mn^{+2}) is very sensitive to oxidation. Therefore, in-line filtering of manganese is recommended with subsequent field or laboratory analysis for total manganese. Field filtering will remove insoluble Mn^{+4}, so that a total manganese analysis should reflect Mn^{+2} in the sample. Field test kits are available for total (not soluble) manganese. However, manganese dioxide, the typical form of Mn^{+4}, is relatively insoluble, therefore the test kits may be fairly accurate for dissolved manganese (Mn^{+2}). Field test kits may be biased high by turbid samples, so in-line filtering or low-flow sampling is important in obtaining an accurate manganese concentration. If turbid samples are analyzed using a colorimetric method, determine how much "color" the turbidity contributes to the sample before determining the manganese concentration.

1.9 Ferrous Iron

Available ferric iron (Fe^{+3}) on soil surfaces can serve as an electron acceptor and be reduced to soluble ferrous iron (Fe^{+2}). Not all ferric iron can be utilized by microbes as an electron acceptor, and measurement of total iron or ferric iron is of little use in understanding subsurface biological processes at a site. Ferrous iron is an indication of reducing conditions and microbial activity, but is very sensitive to the presence of oxygen and readily oxidizes to the ferric form. Therefore, great care must be used in sampling and analyzing ferrous iron if this parameter is to be of any value in assessing biodegradation capacity at a site.

Ferrous iron is generally measured by one of two methods:

- Immediate field filtering of samples for removal of insoluble ferric iron followed by laboratory analysis for total iron measures dissolved iron rather than ferrous iron, with the assumption that soluble ferric iron is negligible in the groundwater. At neutral pH and

with exposure to air, almost all soluble ferrous iron will precipitate out of solution within 1 minute or less. Therefore, filtering of iron samples should be done with cartridge-style filters, in-line filters or other systems that exclude contact with the atmosphere.

- Field test kits can be used to measure for ferrous iron. Field filtering is not necessary using this method. However, the instability of ferrous iron in the presence of oxygen and sunlight can severely limit the usefulness of the test kit data. Samples must be analyzed immediately after collection. If a colorimetric method is used to determine ferrous iron, determine if the sample is turbid. Determine how much "color" the turbidity contributes to the sample before determining the iron concentration.

1.10 Sulfate

During microbial metabolism, sulfate (SO_4^{-2}) is reduced to sulfide (S^{-2}), which subsequently forms metal sulfide precipitates. Sulfate can be readily analyzed by laboratory methods and is not particularly sensitive to oxidation changes in the sample.

Sulfate can be analyzed in the field using a colorimetric method or in a laboratory. However, automated methods of sulfate analysis are preferred to turbidimetric methods.

1.11 Methane

Methane (CH_4) in water is a more difficult and expensive analysis than the other geochemical parameters. There is no standard U.S. EPA laboratory method for measuring methane in water. In addition, because methane is a gas, it is readily lost from groundwater samples. Methane data can be of little value unless extreme caution is exercised in sample handling. It is recommended that sample collection and handling procedures be carefully documented to determine whether data are comparable to previous sampling events. These problems create difficulties for establishing the precision and sensitivity of methane data. Therefore, when determining whether to analyze for methane, the investigator should assess the site data needs and the ability to produce methane data that accurately represent site conditions.

1.12 Quality Control Checks for Field Measurements

Perform the following field checks to ensure that the field measurements are valid and consistent.

- DO and ORP readings should be in agreement. DO should be less than 1 ppm when ORP is negative. If this is not the case, at least one of the measurements is in error.

- Ferrous iron should be present only if DO is less than 1 ppm and ORP is negative.

- Compare DO and ORP values in the well water before and after purging. The DO and ORP of the well water after purging should be equal to or lower than the readings prior to purging. An increase of DO and ORP after purging indicates the well water has been artificially aerated by the purging process.

A water sample may have "incompatible" water chemistry, such as the presence of ferrous iron and DO, because of sampling technique (such as artificial aeration) or because of mixed water chemistry. Mixed water chemistry occurs when a well screen intersects both contaminated and uncontaminated groundwater and the water sample exhibits characteristics of both of these zones. When field measurements are not in agreement, efforts should be made to achieve measurements that are in agreement by repeated sampling and, if necessary, by using alternative techniques for field purging, sampling and analytical methods. If anomalies persist, it may be useful to consult an analytical chemist to help resolve the inconsistencies. If the chemical anomalies cannot be resolved through changes in field technique, the possibility of mixed water chemistry within the well screen should be considered.

1.13 Microbial Assays

If an evaluation of the abundance of hydrocarbon-degrading microbes is deemed necessary to assess the potential for biodegradation at a site, the laboratory chosen to perform this work should be contacted to make sure that their specific requirements for sampling are met. In general, the following guidelines should be considered during sample collection.

Most laboratories will require at least 100 ml of each groundwater sample for microbiological analyses. For anaerobes, care should be taken during sampling so that no additional oxygen is introduced into the sample bottles. The sample bottles should be filled slowly with no mixing of air into the sample until the sample overflows the bottle. The bottles should be capped carefully, ensuring that there is no air space in the sample bottle. The samples should be stored in a cooler (4˚ C) upon sampling, and delivered to the lab within 48-72 hours. Make certain that the samples do not freeze and do not add any preservative.

1.14 Analysis for Nutrients

As for the microbial assays, the laboratory chosen to perform these analyses should be contacted to make sure that their specific requirements for sampling are met. For inorganic nutrient assays, most laboratories will in general require approximately 500 ml of each groundwater sample. Samples must be stored in a cooler at a temperature no greater than 4˚ C. Preservatives should generally not be added to the sample, and samples should be forwarded to the laboratory as soon as possible (ideally, within 24 to 48 hours). Holding times are quite variable (3 to 4 days for nitrate and phosphate and as high as 28 days for sulfate). However, if for some reason the sample cannot be delivered within 48 hours, the laboratory should be contacted to inquire into specific preservative requirements for individual analytes to meet longer holding times.