Interim Final – December 2008

This interim final document takes effect immediately and is to be used as guidance when conducting response activities under Part 201 and Part 213. The MDEQ will take comments via email and postal mail on this interim final document through June 30, 2009. After comments have been reviewed, the document will be revised in response to those comments and issued as final.

RRD OPERATIONAL MEMORANDUM NO. 4

SITE CHARACTERIZATION AND REMEDIATION VERIFICATION

ATTACHMENT 8 – MONITORED NATURAL ATTENUATION

Acronyms and key definitions for terms used in this document:

NREPA:	The Natural Resources and Environmental Protection Act, 1994 PA 451, as amended
Part 201:	Part 201, Environmental Remediation, of NREPA
Part 213:	Part 213, Leaking Underground Storage Tanks, of NREPA
MDEQ:	Michigan Department of Environmental Quality
RRD:	Remediation and Redevelopment Division
C_{sat} Soils:	Soils where the concentration of a single contaminant has reached the solubility limits of the soil pore water, the vapor phase limits of the soil pore air, and the absorptive limits of the soil particles
CoC:	Contaminants of concern are hazardous substance(s) that were released into the environment and any hazardous substance that has resulted from the release, including breakdown products of the initial hazardous substance(s) that were released, and naturally occurring hazardous substances that have been mobilized as a result of a reaction with the released hazardous substance(s), in concentrations that exceed applicable criteria
Contamination:	Includes both “environmental contamination” as defined in Part 201, and “contamination” as defined in Part 213
Criteria or Criterion:	Includes the cleanup criteria for Part 201 of NREPA and the Risk Based Screening Levels as defined in Part 213 of NREPA and R 299.5706a(4)
Facility:	Includes “facility” as defined in Part 201 of NREPA and “site” as defined in Part 213 of NREPA
MNA:	Monitored natural attenuation is the reliance on natural biological, chemical, or physical processes documented to occur at a facility that result in a reduction in mass, toxicity, volume, mobility, or concentration of the contaminants identified in soil or groundwater
NAPL:	Non-aqueous phase liquids
Op Memo:	Operational Memorandum
Release:	Includes “release” as defined in Part 201 and Part 213 of NREPA
Response Action:	Includes “response activities” as defined in Part 201 of NREPA, and “corrective action” as defined in Part 213 of NREPA

Source Removal or Control:	Removal, treatment, or containment measures to address hazardous substances in concentrated source areas, including but not limited to NAPL, saturated soils, waste, and other highly concentrated areas of hazardous substances

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ACKNOWLEDGEMENTS

Although specific references are cited at the end of this document, the RRD wishes to formally acknowledge the excellent work of staff from the Wisconsin Department of Natural Resources and the United States Environmental Protection Agency (U.S. EPA) in publishing their respective guidance on MNA. The work they have done on the subject of MNA is so thorough that we borrowed heavily from these sources in preparing this document, and they deserve much credit.

1.0 PURPOSE

This document is provided to describe the requirements for an acceptable evaluation of whether MNA is a feasible and effective method of remediation consistent with the requirements of Part 201 or Part 213 of NREPA. This document provides acceptable approaches and ranges of appropriate assumptions that are intended to support a consistent exercise of professional judgment in a manner that produces satisfactory outcomes. Alternative approaches may be used if the person proposing the alternative demonstrates that the approach meets all the requirements of the statute and rules.

To determine if MNA is an appropriate remedy for a facility, there must be adequate data to evaluate the feasibility and effectiveness of the attenuation process. This document provides the MDEQ's evaluation of what data is necessary to support selection of a MNA remedy. The implementation of MNA will generally include extensive facility characterization, risk evaluation, long-term monitoring, and modeling. The MDEQ expects that source removal or control will be a fundamental component of any MNA remedy, unless approved by the MDEQ to be not feasible.

The MDEQ emphasizes that MNA is not to be interpreted as a "no further action alternative." Within the parameters and conditions outlined in this attachment, the MDEQ accepts MNA as a potential remedy only if its use will be protective of public health, safety, and the environment and it will be capable of achieving facility-specific remediation objectives within a time frame that is reasonable compared to other remedial alternatives.

This document is intended solely as guidance to foster consistent application of Part 201 and Part 213 of NREPA and the associated Administrative Rules. This document does not contain any mandatory requirements, except where requirements found in statute or administrative rule are referenced. This guidance does not establish or affect legal rights or obligations for any of the issues addressed. This guidance does not create any rights enforceable by any party in litigation with the MDEQ. Any regulatory decisions made by the MDEQ in any matter addressed by this guidance will be made by applying the governing statutes and Administrative Rules to the relevant facts.

This guidance is based upon the requirements found in Part 201, Part 213, and Part 31, Water Resources Protection, of NREPA and the rules promulgated thereunder.

2.0 INTRODUCTION

MNA is a knowledge-based remedy. Rather than imposing active controls, as in engineered remedies, scientific and engineering knowledge is relied upon to understand and document naturally occurring processes to achieve facility-specific remediation objectives. These natural processes include a variety of physical, chemical, or biological processes, including but not limited to, biodegradation, dispersion, dilution, sorption, volatilization, and chemical transformation. The MDEQ prefers processes that degrade or destroy hazardous substances when natural attenuation is relied on for remediation (Section 20118(4), Section 21311a of NREPA).

The MDEQ anticipates that MNA will almost always be used in conjunction with other remedial measures to address contaminated soils and groundwater (e.g., source removal or control, hydraulic containment, reliable resource use restrictions). Factors to be evaluated in determining whether MNA is a suitable part of a remedial strategy include the time it will take to achieve the selected land use based cleanup when compared to other remedial alternatives, the proximity of the contaminants to the nearest receptor(s), the stability of the groundwater plume (e.g., potential for migration), the presence of NAPL or free product, and the overall protectiveness of public health and the environment. When NAPL (or synonymously free-phase contamination), free product and/or C_{sat} soils are present, they must be removed or treated prior to MNA being considered, unless determined not practical. If removal of the NAPL, free product, or C_{sat} soils is determined to be impractical, then the source may need to be contained with engineering controls.

Source removal or control will be a major component of any MNA remedy regardless of whether the contaminants at a facility are petroleum related, chlorinated solvents, inorganics, or others. Source removal or control must include measures to reduce the toxicity, mobility, and volume of hazardous substances that act as an ongoing source of contamination.

The use of predictive tools such as statistical trends, bench-scale testing of aquifer media, and/or fate and transport modeling are also important components that may be required in MNA implementation. If groundwater modeling is to be used to predict the fate and transport of contaminants, it is important to remember that these predictions alone cannot be used to demonstrate compliance with criteria or the effectiveness of the response action. A model can provide an estimate of the effectiveness of a remediation system; however, verification of actual performance must be demonstrated by the measurement of appropriate field parameters. A detailed discussion of what constitutes appropriate field parameters for petroleum and chlorinated solvents is included in Appendices A and B. Additional guidance on groundwater modeling is included in RRD Op Memo No. 4, Attachment 7, Groundwater Modeling.

Generic cleanup criteria for groundwater have been developed pursuant to Sections 20120a(1) and 21304a of NREPA (RRD Op Memo No. 1)[1]. These criteria are the risk based values the MDEQ has determined to be protective of the public health, safety, and welfare and the environment. The determination that the criteria are protective includes the requirements that the horizontal and vertical extent of hazardous substance concentrations above criteria in an aquifer must not increase after initiation of remediation; and that remediation of an aquifer provides for the removal of the hazardous substances from the aquifer through either active remediation or as a result of naturally occurring biological or chemical processes which have been documented to occur at the facility (R 299.5705(5) to (6)).

A proposal that does not attain a degree of cleanup of hazardous substances that complies with the provisions of R 299.5705(5) and R 299.5705(6) may be approved by the MDEQ, if the MDEQ finds that the response action is protective of the public health, safety, and welfare and the environment. The MDEQ must base its findings on one or more of the following conditions:

[1] For a Part 213 corrective action to attain a degree of cleanup and control of hazardous substances that complies with all applicable or relevant and appropriate requirements, the Part 201 Administrative Rules Part 7 – Cleanup Criteria Requirements for Remedial Action and Interim Response Activities Designed to Meet Criteria are considered applicable requirements because they are the basis for the Part 213 Risk Based Screening Levels R 299.5706a(4).

- It is determined to be technically impractical to comply with the provisions.
- It is determined that the remediation will, within a reasonable period of time, attain a standard of performance that is equivalent to that required by the provisions.
- It is determined that the adverse environmental impact of implementing remediation would exceed the environmental benefit of the remediation.
- It is demonstrated that the remediation provides for the reduction of hazardous substance concentrations in the aquifer through a naturally occurring process that is documented to occur at the facility and both of the following conditions are met:

  (i) There will be no adverse impact on the environment as the result of migration of the hazardous substances during the response action, except for that part of the aquifer specified in the proposal and approved by the MDEQ.
  (ii) Enforceable land use restrictions or other institutional controls necessary to prevent unacceptable risk from exposure to the hazardous substances, as defined by the cleanup criteria, are in place.

In order for the MDEQ to accept a proposal that relies upon MNA for remediation of groundwater, the proposal must document that the remediation is protective of the public health, safety, and welfare and the environment by demonstrating all of the following conditions (Sections 20118, 21309a, 21311a, 21315 of NREPA, R 299.5705(6), R 299.5601, R 299.5603):

- Relevant aquifer characteristics, including but not limited to: porosity, hydraulic conductivity, hydraulic gradient, etc., are determined.
- The plume is fully defined both vertically and horizontally to the most restrictive cleanup criteria.
- All receptors have been identified and are not immediately threatened (R 299.5520).
- The plume has been demonstrated to be stable or shrinking through direct measurements, or a combination of direct measurements and appropriate modeling to predict plume migration. It is recognized that there may be a temporary increase in the breakdown products of the chemicals of concern (e.g., reductive dechlorination of chlorinated volatiles). MNA may also be appropriate if it is shown that the plume will become stable within delineated boundaries based on modeling that utilizes site-specific parameters. Any predictions produced by modeling must be supported by subsequent direct measurements. The horizontal and vertical extent of the contamination above criteria may not increase after initiation of the remediation unless approved by the MDEQ pursuant to Sections 324.20118(5) and (6). If the plume has migrated off the property where the release occurred, appropriate notice must be provided to those affected property owners (Section 21309a(3), R 299.5522(2)) and the potential for unacceptable exposure mitigated.
- All contaminants are capable of undergoing biodegradation or chemical transformation to less mobile or toxic forms (note: metals and some organic compounds do not readily biodegrade), otherwise a waiver to R 299.5705(6) will be required.
- Source removal or control has been completed. When NAPL or C_{sat} soils are present, the NAPL or C_{sat} soils must be removed or treated prior to MNA being considered for the residual contaminants unless it is determined not practical.

- The transfer of contaminants from one medium to another (e.g., from soil to groundwater, from groundwater to soil vapors, and from groundwater to surface water) has been evaluated and determined to be unlikely to result in unacceptable levels of risk.
- Geochemical indicators (e.g., dissolved oxygen (DO), dissolved iron, nitrates, sulfates, pH) document a naturally occurring biological process is sustainable prior to initiating MNA when biodegradation is the primary mechanism for the decline in contaminant levels, otherwise a waiver to R 299.5705(6) will be required.
- An analysis has been completed of alternatives that permanently and significantly reduce the volume, toxicity, and mobility of hazardous substances in accordance with the provisions of Sections 20114(1), 20118(8), 20118(4), 21307(2), and 21311a of NREPA.
- The projected time frame to achieve closure is acceptable when compared to that offered by other remedial alternatives.
- A detailed contingency plan has been prepared and can be implemented in the event that MNA proves ineffective.
- A financial assurance mechanism is in place as provided in Section 20120b(3), Section 21309a(20)(f), R 29.2161 to R 29.2169, and R 299.5532(11)(m) in an amount to pay for monitoring, operation and maintenance, oversight, and other costs (if required) to assure the effectiveness and integrity of the remediation.

3.0 CHARACTERIZATION

A thorough understanding of the variability in the subsurface (which controls physical, chemical, and biological processes) combined with the expected natural degradation processes is necessary to properly apply MNA as a remedy. The results of a remedial investigation or site assessment should provide an initial understanding of the plume behavior, subsurface heterogeneity, likely attenuation processes, the extent of the plume in three dimensions, hydrogeological control, and an initial estimate of contaminant decay rates.

The importance of accurately characterizing the vertical and horizontal extent of groundwater contamination is critical for any remedial decision. When applying a MNA groundwater remedy, adequate characterization takes on additional meaning and significance. Simply understanding the concentrations of all hazardous substances in the aquifer(s) at various points is not enough. When determining the appropriate analytical parameters, the evaluation must include whether potentially toxic and/or mobile by-products may be, or are being formed (i.e., analysis of more than the initial contaminants of concern is necessary).

Groundwater geochemistry in the vicinity of the facility, including upgradient of the contamination plume(s), within the plume(s), and downgradient of the plume(s) also must be characterized with respect to background concentrations of certain metals, nitrates, DO, and other geochemical parameters as outlined in the attached appendices. Many factors must be considered in determining whether groundwater is adequately characterized for a MNA remedy such as: the type(s) of hazardous substances released (e.g., gasoline or diesel fuel vs. chlorinated solvents or soluble solvents (e.g., 1,4-dioxane, methyl-tert-butyl ether)); the horizontal and vertical distribution of contaminants including the assessment of the potential for contaminants to vertically migrate; and the aquifer conditions (e.g., aerobic vs. anaerobic, fraction of organic carbon, sorption coefficients).

3.1 Feasibility Demonstration Requirements

The demonstration for the feasibility of a MNA remedy should, in most cases, include both primary and secondary lines of evidence that demonstrate remediation is occurring through natural attenuation and may include optional lines of evidence. For facilities that have extensive historical monitoring data, the primary lines of evidence alone may (on a case-by-case basis) be adequate to demonstrate remediation by natural attenuation.

Primary lines of evidence: Include chemical data that demonstrate a clear and convincing trend of decreasing contaminant mass, concentration, and/or toxicity over time as demonstrated by the direct laboratory analysis and measurement of the extent of the contaminant plume, the concentration of the CoCs, and possible daughter or breakdown products. The sampling and analytical methodology must be consistent with those as outlined in RRD Op Memo No. 2, Sampling and Analysis Guidance.

Secondary lines of evidence: Include the geochemical indicators of naturally occurring biodegradation and estimates of natural attenuation rates. These secondary parameters may include the pre-determined dominant electron acceptors or donors (e.g., oxygen, nitrates, sulfate, carbon dioxide) and their metabolic by-products (e.g., carbon dioxide, nitrogen, ferrous iron, methane); the daughter products resulting from degradation of the product(s), as well as pH, oxidation reduction potential (ORP or “redox”), specific conductivity, and temperature. The actual secondary lines of evidence required will vary depending on the characteristics of the CoCs and the identified potential receptors. These indicators should be obtained both from within the contaminant plume and at the perimeter (upgradient, sidegradient, and downgradient) of the contaminant plume that represents the type of degradation reactions that dominate at the facility (aerobic vs. anaerobic).

The DO measurements must be obtained in situ using an appropriate instrument or through a flow-through cell to minimize false readings that are not indicative of actual aquifer conditions (see Low Flow Sampling Techniques in RRD Op Memo No. 2, Attachment 5). Bailing or the open cup method is not acceptable to collect DO measurements.

Optional lines of evidence: May be used to more rigorously interpret data collected as secondary lines of evidence, particularly if the primary and secondary lines of evidence are inconclusive to demonstrate remediation by natural attenuation. Optional lines of evidence may include solute transport modeling, estimates of assimilative capacity (to estimate the mass of benzene, toluene, ethyl benzene, xylene, and other CoCs degraded), and microbiological studies. Optional lines of evidence, however, must not be used to override specific criteria developed that require the implementation of the contingency plan (i.e., if those “triggers” are activated, the contingency must be implemented).

3.2 Conceptual Model

Development of a conceptual model is an important part of the facility characterization process. The conceptual model for natural attenuation is the facility-specific qualitative and quantitative description of the migration and fate of contaminants with respect to possible receptors and the geologic, hydrologic, biologic, geochemical, and anthropogenic factors that control contaminant distribution. Essentially, the conceptual model expresses an understanding of the facility structure, processes, and factors that affect plume development and behavior. It is built upon assumptions and hypotheses that have been evaluated using facility-specific data, and is continually re-evaluated as new data are developed throughout the facility lifetime.

A three dimensional conceptual model that incorporates temporal changes is often needed to provide a framework for interpreting the facility data, judging the significance of changes in facility conditions, and predicting future behavior of the source and plume. Understanding plume formation and behavior is the basis for predicting future plume behavior, and therefore, predicting whether the MNA remedy will be able to achieve facility remedial goals within specified time frames. Conceptual models are expressed tangibly in text, facility maps (e.g., contaminant isoconcentration maps and potentiometric surface maps), cross sections (e.g., hydrogeologic and chemical distributions), and other graphical presentations, and in terms of mathematical calculations describing the plume and facility.

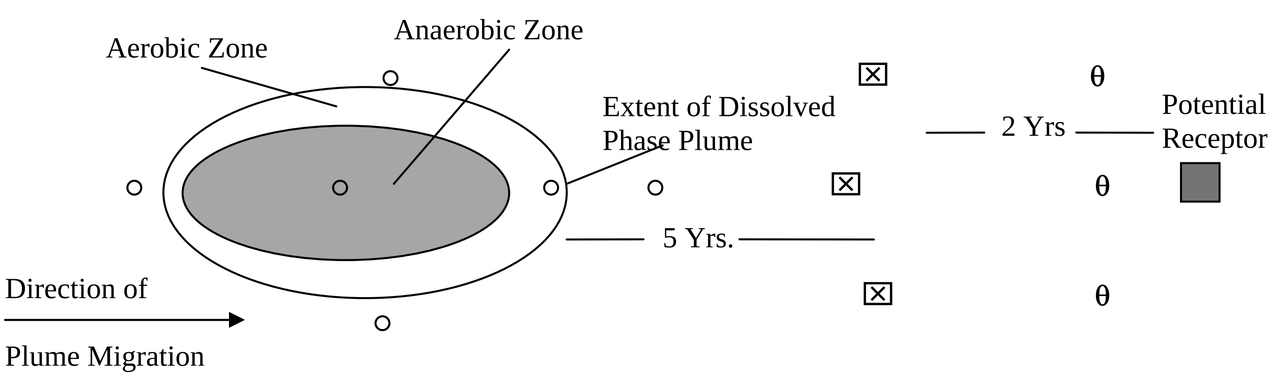
4.0 PERFORMANCE MONITORING

As implied in the name monitored natural attenuation, monitoring is critical to the application of this remedy. Once a facility is adequately characterized and a determination is made that MNA is an appropriate remedy, the ongoing monitoring of the performance of the remedy must be sufficient both to ensure that the remediation is proceeding as expected, and to detect any unexpected condition that may arise. At a minimum, the Performance Monitoring Plan must specify the data quality objectives, the goals of monitoring, the monitoring wells or soils to be monitored, sample locations, the frequency of monitoring, the parameters to be measured, the sampling and analytical methodology, and the generation of monitoring reports.

Proper monitoring is essential for the acceptance of natural attenuation as a response action. Monitoring must demonstrate that natural attenuation is effective and is protective of the public health, safety, and welfare and the environment. Figure 1 is an example of a hypothetical performance monitoring sampling strategy.

Figure 1

HYPOTHETICAL PERFORMANCE MONITORING STRATEGY



LEGEND
☒- Sentinel Monitoring Well
θ - Point of Compliance Well
○ - Performance Monitoring Wells (Not To Scale)

The monitoring layout in Figure 1 assumes that sufficient information has been gathered to define the contaminant plume both vertically and horizontally, to adequately predict contaminant transport, and that all potential receptors have been identified. The long-term performance monitoring wells are placed hydraulically upgradient, sidegradient, and immediately down-gradient of the contaminant plume. The purpose of these wells is to monitor the effectiveness of natural attenuation in reducing the total mass of contaminants within the plume and the aerobic and anaerobic indicators associated with the natural biodegradation process. The actual number of wells required at a facility depends upon facility conditions. A minimum of six performance monitoring wells (not including any necessary point of compliance wells) are required. Wells should be located as follows: at least one hydraulically upgradient of the contaminant plume, at least two sidegradient wells, and at least three in a line along the axis of the plume perpendicular to the groundwater flow direction; one within the anaerobic zone, one in the aerobic zone, and one immediately downgradient (within 100 feet if feasible) of the contaminant plume. When the point of compliance is further downgradient of the performance monitoring well network, point of compliance wells must be installed to verify compliance with applicable criteria (e.g., groundwater surface water interface wells). The monitoring plan must allow adequate travel time from the edge of the contaminant plume to the nearest receptor so that alternative means of remediation may be employed, if necessary. Additional nested monitoring wells should be included in the monitoring network if the plume has a vertical migration component.

In addition to the minimum of six performance monitoring wells and the point of compliance wells, sentinel monitoring wells may be required at locations downgradient of the contaminant plume and upgradient of potential receptors. The sentinel monitoring wells are generally installed either along a downgradient property boundary, at a location to verify the model predictions given the groundwater velocity, or one to two years upgradient of the nearest down-gradient receptor, whichever is most protective.

4.1 Goals of Monitoring

Each facility should establish specific goals to be achieved by monitoring. The list below contains goals expected at all facilities. Specific facilities may have additional goals beyond those listed here. Monitoring reports should contain information to show whether or not the monitoring goals for the facility are being met and assess whether the monitoring program is adequate to achieve the monitoring goals. At a minimum, the goals of monitoring should establish that:

- *MNA is effectively protecting receptors*. The monitoring well network and frequency of monitoring must verify whether existing receptors are protected. Monitoring schedules and well networks may need to be adjusted if new receptors are established (such as private water supply wells or high capacity irrigation wells) near the contaminant plume.
- *Sentinel wells remain free of unexpected concentrations of contaminants.* Sentinel wells provide the ability to determine whether a plume has expanded beyond predictions for the MNA remedy. They must be located to allow sufficient time for additional response actions to be implemented to prevent unacceptable exposures to a receptor. Confirmation of contaminants reaching a sentinel well at unexpected concentrations should trigger the implementation of contingency plan response actions to control contaminant movement. For some extremely small sites, performance monitoring wells or point of compliance wells may also serve as sentinel wells. Point of compliance wells

may only be used as sentinel wells if the contingent response actions are required to be implemented prior to concentrations exceeding applicable criteria at the wells.

- *Point of compliance well concentrations do not exceed applicable criteria.* Concentrations that exceed applicable criteria indicate a failure of the remedy and require immediate additional response actions.
- *There have been no new sources or releases of contamination*. Monitoring wells should be located such that new spills or releases are detected quickly. This includes operating facilities as well as releases caused by hydrogeologic changes that mobilize previously unsaturated or immobile contaminants. New sources can result in an increased contaminant mass that moves through the plume and may cause the plume to expand.
- *The contaminant plume is stable and receding or will become stable within delineated boundaries*. The acceptability of MNA is based on control of the contaminant plume in three dimensions. Changes in factors such as groundwater velocity, geochemical conditions, degradation patterns, and groundwater use can cause a previously stable plume to advance. Monitoring well networks must be located to verify that the plume is contained or will be contained within delineated boundaries.
- *The remedy is performing as predicted to reduce contaminant concentrations*. The monitoring well network and sampling program should be designed to allow assessment of contaminant concentrations in the subsurface. Predictions of contaminant concentrations at specific points in time and space should be documented during the remedial investigation and remedy selection. These predictions reflect assumptions made in the conceptual model. Monitoring will determine the accuracy of the conceptual model and lead to refinement of that model. Assessing contaminant reductions over time will also determine whether the remedy is on track to meet facility cleanup goals.
- *Contaminant mass in the subsurface is being reduced*. Cleanup of the aquifer is based upon contaminant mass loss through degradation. The monitoring well network and sampling program should be designed to allow assessment of contaminant mass in the subsurface and calculation of mass loss of all contaminants in the plume over time.
- *The conditions necessary for MNA continue to be present at the facility*. Degradation of chlorinated and petroleum compounds relies upon specific geochemical and oxidation-reduction capacity conditions. Those conditions, such as carbon content or competing electron acceptors or donors, can change over time. Even when contaminant concentrations are reducing as predicted, it cannot be assumed that natural attenuation conditions will continue into the future. Changes in geochemistry or redox conditions can result in a decreased capacity for biodegradation and natural attenuation, which will reduce the amount of mass being removed or destroyed, and may result in plume migration beyond established boundaries and impact to receptors.
- *Cleanup goals will be achieved within a reasonable period of time when compared to other more active response actions*. The data from monitoring should be evaluated to determine if cleanup standards will be met within a reasonable period of time. Interpretation of reasonable period of time will differ for each contaminated facility based upon risk to receptors and existing and future land use. Predictions of achieving cleanup goals based upon historical data are useful for assessing the conceptual model and for setting performance goals, but should not be relied upon as anything more than just estimates. Monitoring and data assessment should be structured to determine the likelihood that MNA will ultimately achieve cleanup standards. If it is determined that

cleanup cannot be achieved by MNA alone within a reasonable period of time, then additional response actions should supplement or replace MNA.

Due to the uncertainties associated with using MNA and the possible long remediation time frame, it is also imperative that a contingency plan be developed as a component of the remedy. The contingency plan must, at a minimum: list the circumstances that will trigger the plan (e.g., data from performance monitoring wells indicates that attenuation rates are slower than predicted for the MNA remedy, exceedance of a criterion at a sentinel well, unexpected detection of a transformation or degradation product); outline the decision matrix to be used to respond to the situation that triggers the plan; specify the technology(s) that will be utilized; and include a schedule for undertaking contingency measures (this schedule must account for and be able to respond to the potential human health and environmental consequences of the situation).

4.2 Sampling Schedule

The monitoring plan for a MNA remedy must include the basis for the frequency of the initial sampling period (the initial sampling period generally is a minimum of two years) and any criteria that will be used to justify reducing sampling for ongoing monitoring. The minimum initial sampling schedule for performance monitoring should include sampling and analysis of both primary and secondary lines of evidence quarterly to account for seasonal variations in groundwater levels and/or contaminant concentrations. Sampling frequency and/or scope may be reduced based on the initial data if approved by the MDEQ.

Assuming that natural attenuation is occurring at predicted rates, monitoring schedules may be altered based on the sampling history of the facility, CoCs and other contaminant concentrations, risks to receptors, progress of MNA, or other appropriate factors based on agreement with the MDEQ.

4.3 Reporting Schedule and Requirements

The monitoring plan for a MNA remedy must include the schedule for submission of the monitoring data and any criteria that could require adjusting the submissions schedule. Generally, reports must be submitted to the appropriate district office project manager within 60 days of sampling completion. Prompt reporting of monitoring data is crucial to ensure adequate tracking of the progress of the response action and to ensure timely identification of the need to implement any additional actions necessary to protect the public health and the environment. At some facilities, forwarding the sample data as they are received from the laboratory without interpretation or summary tables may be required (e.g., where fast migration rates result in minimal time to react to potential receptor exposure), at least in the initial stages of monitoring the remedy.

Compilation and presentation of monitoring data in an easily usable format that facilitates interpretation requires significant effort. The report should make extensive use of maps, cross sections, and figures to convey the results of monitoring efforts.

The elements of a monitoring report that should be included, at a minimum, are as follows:

- Summary of data interpretations and recommendations.
- Background and facility description.

- Monitoring network and schedule description.
- Evaluation of new data and comparisons with previous data and established performance criteria.
- Interpretation of new data with respect to the conceptual model for natural attenuation.
- Recommendations for action including proposed future activities and the estimated date of the next sampling event and report submittal.
- Groundwater gauging data table including the monitoring well screened intervals, top-of-casing survey data, depth to water, elevation of groundwater, and total depth of the monitoring well.
- Groundwater analytical data table including the date of sampling, analytical parameters, historical and current analytical data, method detection limits, and methods of sampling.
- Geochemical (secondary lines of evidence) data table providing the results, date, and method of collection.
- Scaled figures presenting groundwater elevation contours, contaminant plume extent, isoconcentration map(s) presenting the concentrations and distribution of the electron acceptors or donors driving the biodegradation process (i.e., oxygen, iron, nitrates, carbon dioxide, etc.).
- Graphs relating the groundwater elevation to the contaminant data over time may be beneficial.
- Any other information that may be pertinent to the MDEQ regarding the facility.

5.0 REMEDIATION VERIFICATION

The monitoring plan for a MNA remedy must include verification sampling. Once MNA is believed to have attained the remedial goal(s) for groundwater at a facility, verification sampling is necessary to demonstrate that these goals have been achieved throughout the contaminant plume and are maintained. There are many facility-specific variables to consider but, in general, samples must be collected from all wells identified in the performance monitoring plan and analyzed for all the contaminants originally identified above criteria in the groundwater for which the remedy was implemented, as well as additional parameters such as degradation products, metals that may have been mobilized via attenuation processes, etc. In some instances, particularly in areas of minimal well coverage, it may be necessary to install additional monitoring wells. A minimum of four consecutive sampling events that account for seasonal variations in groundwater levels and/or contaminant concentrations, in which no contaminants are detected above relevant cleanup criteria in any of the monitor wells identified in the performance monitoring plan, is necessary to verify that the remediation of that plume has been successful. The timing of the four (or more) sample events must be based on the facility-specific data such as flow rates, seasonal fluctuations in groundwater flow direction, water levels, and well spacing.

If reliable land use restrictions are part of a MDEQ approved Corrective Action Plan, Remedial Action Plan, or Interim Response Designed to Meet Criteria, the verification of remediation requirements may be different than above.

The following document is rescinded with the issuance of this attachment:

- Storage Tank Division Op Memo No. 13, Monitored Natural Attenuation Guidance for Groundwater Corrective Action Activities at Petroleum Release Sites, dated August 25, 1997.

This memorandum is intended to provide guidance to foster consistent application of Part 201 and Part 213 of NREPA and the associated Administrative Rules. This document is not intended to convey any rights to any person nor itself create any duties or responsibilities under law. This document and subject matters addressed herein are subject to revision.

6.0 REFERENCES

U.S. EPA, 1999. EPA OSWER Directive 9200.4-17P.

U.S. EPA, 2004. "How to Evaluate Alternative Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers," EPA510-R-04-002, Solid Waste and Emergency Response 5401G, May 2004 (www.epa.gov/oust/pubs/tums.htm).

Wisconsin Department of Natural Resources, April 2003. RR-699, Understanding Chlorinated Hydrocarbon Behavior in Groundwater: Investigation, Assessment and Limitations of Monitored Natural Attenuation.

Wisconsin Department of Natural Resources, March 2003. RR-614, Guidance on Natural Attenuation for Petroleum Releases.

APPENDIX A

PETROLEUM

1.0 PURPOSE

This appendix is intended to assist in determining whether MNA is a feasible and effective method of remediation at a petroleum release consistent with the requirements of Part 201 and/or Part 213. The implementation of MNA will generally include extensive facility characterization, risk evaluation, long-term monitoring, and modeling. MNA alone is usually not sufficient to remediate petroleum releases due to the non-degradable by-products that are left behind after degradation of the volatile portions of the released substances, the presence of heavier hydrocarbons that have relatively low solubility that may continue to pose a threat to public health or the environment, and because petroleum plumes generally contain substances other than the principal CoCs, such as gasoline additives (e.g., lead and trimethylbenzenes) that are resistant to biodegradation.

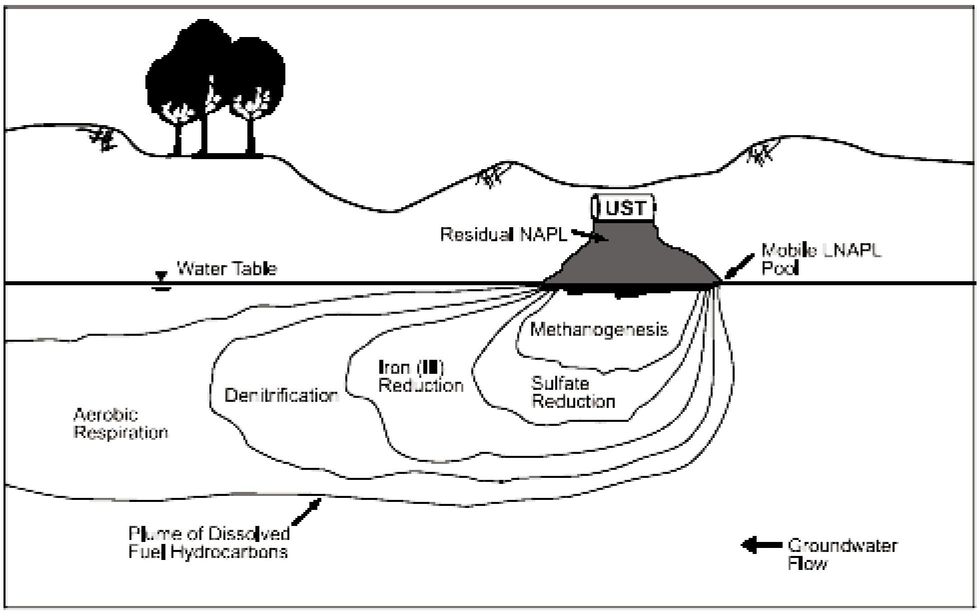
The MDEQ expects that source removal or control will be a fundamental component of any MNA remedy, unless approved by the MDEQ to be not feasible. The MDEQ encourages the consideration of innovative technologies for source control when source removal has been approved to be not feasible. The use of innovative technologies often provides reduced remediation time frames at modest additional cost. The MDEQ emphasizes that MNA is not to be interpreted as a "no further action alternative." Within the parameters and conditions outlined in this appendix, the MDEQ accepts MNA as a potential remedy only if its use will be protective of public health, safety, and the environment and it will be capable of achieving facility-specific remediation objectives within a time frame that is acceptable when compared to other remedial alternatives.

2.0 INTRODUCTION

The two key factors that control the persistence of a petroleum contaminant plume are source mass and biodegradability. These two factors are directly proportional: the greater the source mass, the longer biodegradation may take to realize significant source reduction, thereby increasing the potential for the formation of a significant plume. If the volume of the release results in NAPL accumulating on the water table, MNA is not an appropriate remediation alternative.

Petroleum contaminants can be naturally attenuated by physical, chemical, and biological processes that, under favorable conditions, have the potential to reduce the mass, toxicity, mobility, volume, and/or concentration of contaminants in the subsurface. Nondestructive processes such as dispersion, sorption, and volatilization only reduce the concentration of a contaminant, whereas destructive processes such as biodegradation result in an actual reduction in the mass of the contaminants. Therefore, biodegradation is the most preferred natural attenuation process. Aerobic biodegradation utilizes the available oxygen which generally results in anaerobic conditions in the core of the plume and a zone of oxygen depletion along the outer margins. For both the aerobic and anaerobic processes, the rate of contaminant degradation is limited by the rate of supply of the electron acceptor. As illustrated in the figure below, the anaerobic zone is typically more extensive than the aerobic zone due to the rapid consumption of oxygen, low rate of oxygen replacement, and the abundance of anaerobic electron acceptors (nitrate, ferric iron, manganese, sulfate, and carbon dioxide).

Conceptualization of Electron Acceptor Zones In the Subsurface



Source: U.S. EPA, 2004, "How to Evaluate Alternative Technologies for Underground Storage Tank Sites: A Guide for Corrective Action Plan Reviewers." (Note: Due to the presence of mobile NAPL, the facility depicted in this figure would not be an appropriate candidate for MNA.)

Electron acceptors are reduced through coupled oxidation and reduction reactions during microbial respiration to yield energy to the microorganisms for growth. The DO is generally the first electron acceptor to be utilized during the biodegradation of petroleum hydrocarbons. As a result, the concentration of oxygen will decrease to below background levels indicating aerobic biodegradation is occurring. Once DO concentrations within the aquifer decrease to below 0.5 milligrams per liter (0.5 parts per million), anaerobic processes (initially denitrification) will begin if sufficient anaerobic electron acceptors are available.

Accurate groundwater DO measurements are important since the difference between background concentrations and concentrations within the contaminant plume can be utilized to estimate the mass of contaminants that are aerobically biodegraded. It is difficult to obtain accurate measurements of DO concentrations from conventionally collected samples due to changes in conditions between the aquifer and the surface, temperature, instrument design and calibration, and sample collection technique. Therefore, DO measurements must be obtained in situ using an appropriately calibrated instrument or through a flow-through cell (low flow sampling techniques) to minimize false readings that are not indicative of actual aquifer conditions. Bailing or open cup methods are not acceptable to collect these measurements.

Once the DO has been depleted, biodegradation shifts from aerobic to anaerobic. At some facilities, an electron acceptor may not be naturally occurring resulting in the absence of that process. The order of thermodynamic electron acceptor processes in the absence of oxygen is: 1) nitrates (denitrification); 2) manganese, ferric iron, and sulfates; and 3) methanogenesis, which utilizes carbon dioxide or simple hydrocarbons as the electron acceptor. As with oxygen, the difference between background concentrations and concentrations within the contaminant plume of these electron acceptors can be used to estimate the mass of contaminants that are being degraded by each process. Additionally, the sum of the estimated mass of degraded contaminants from all processes (anaerobic and aerobic) should be used to estimate the biodegradable capacity of the subsurface system. It is important to collect electron acceptor samples each time groundwater samples are collected, since the natural attenuation processes are dynamic, and even subtle changes can affect the rate and completeness of biodegradation. These changes, if caught in time, will allow for contingency measures to be implemented should MNA prove not to be meeting the remediation objectives.

3.0 REQUIREMENTS

3.1 <u>Characterization and Source Removal or Control</u>

Before choosing MNA as the remedial alternative for a facility, it must be determined that the facility has the appropriate characteristics that are conducive for the use of MNA and that the source area is being dealt with appropriately. The minimum facility characterization and source removal or control requirements for considering MNA are as follows:

- The extent of contamination in all affected media must be fully defined (both vertically and horizontally) to the most restrictive relevant and applicable cleanup criteria (RRD Op Memo No. 1). Permanent monitoring points must be established both within the source area(s) and in both hydraulically sidegradient and downgradient locations that define the plume boundaries to provide monitoring of the contaminant concentrations, potential plume migration, and monitoring of the geochemical parameters that indicate natural attenuation is occurring.
- The source area contaminants must be addressed in accordance with Section 21307(2)(d), Section 20114(1)(d), or Section 20118(8) of NREPA. Source removal or control must be completed prior to initiating remediation for soil and/or groundwater contamination. If NAPL, free product, C_{sat} soils, or other highly contaminated media are present, MNA is not by itself an acceptable remedial alternative. If free product is present, an active NAPL recovery or removal program must be implemented. The MDEQ does not support the injection of oxidants or other in situ treatment technologies to enhance biological or chemical degradation into areas containing free product. Additional guidance regarding NAPL is included in RRD Op Memo No. 4, Attachment 6, Non-Aqueous Phase Liquids. Additional guidance regarding in situ injections is included in RRD Op Memo No. 4, Attachment 9, Utilizing In Situ Treatments.
- The extent of the CoCs must be properly characterized. At some facilities, the same geochemical conditions and processes that lead to the biodegradation of petroleum hydrocarbons can chemically transform naturally occurring manganese, arsenic, and other metals in the aquifer matrix to forms that are more mobile and/or more toxic than the original materials. In addition, metal species associated with metal complexes in the aquifer matrix may be released as the ferric iron is used as an electron acceptor. A

comprehensive assessment of a MNA remedial option should include evaluation of whether naturally occurring metals will become CoCs.

- Since electron acceptors/donors for both aerobic and anaerobic processes (DO, iron, nitrates, sulfates, and carbon dioxide) are necessary to the biodegradation of petroleum constituents, they must be characterized and initially sampled as frequently as the CoCs at the facility. Samples must be collected within the contaminant plume as well as upgradient and sidegradient of the plume. Sampling frequency of the electron acceptors/donors may be reduced based on the initial data if approved by the MDEQ.
- As a result of the biodegradation of petroleum contaminants, carbon dioxide, methane, and other gases may accumulate or migrate in the subsurface as soil gas (often referred to as off-gas). The soil gas should be monitored and documented due to the potential for soil gas to accumulate to explosive levels. This is of particular concern if there is a potential for it to migrate to basements. If methane is identified in a concentration that exceeds criteria (1.25 percent or greater by volume in soil gas), measures must be taken to characterize and respond to these levels of methane as outlined in RRD Op Memo No. 4, Attachment 5, Methane.
- The monitored geochemical parameters should include pH, redox, alkalinity, specific conductivity, and temperature to characterize aquifer conditions and suitability to bioremediation processes. These indicators must be compared to background concentrations upgradient and sidegradient of the contamination.
- Modeling may be required to estimate the CoCs travel time and to assist in well placement for monitoring purposes. When groundwater modeling is used to predict the fate and transport of contaminants, it is important to remember that these predictions alone cannot be used to demonstrate compliance with criteria. At best, a model can only provide an estimate of the effectiveness of a remediation system; verification of actual performance must be demonstrated by the measurement of appropriate field parameters. Information on the appropriate use of models is available in RRD Op Memo No. 4, Attachment 7, Groundwater Modeling.
- The contaminant plume should be stable or shrinking. In rare cases, MNA may be appropriate if the plume is still expanding but it can be shown, based on computer modeling, that the plume will become stable within acceptable boundaries. Any computer modeling must be based on site-specific parameters and an intensive performance monitoring program will be needed. The MDEQ will evaluate such proposals on a case-by-case basis.
- All potential receptors must be identified. All current unacceptable exposure pathways must be eliminated.
- The contaminants must be capable of undergoing biodegradation. MNA is not an appropriate remedial alternative for recalcitrant contaminants. If contaminants are present which do not readily degrade, such as metals or trimethylbenzenes, MNA may not be suitable as a remedial alternative or may need to be supplemented with other remediation technologies.
- The results of the facility characterization must demonstrate the potential for MNA.
- The projected time frame to achieve closure must be comparable with that of other remedial methods.

3.2 Contingency Plan

A contingency plan must be included as part of the Corrective Action Plan, Remedial Action Plan, or Interim Response Designed to Meet Criteria for a MNA remedy. The contingency plan must address response to potential failure of the MNA remedy. The contingency plan may specify a technology(s) that may be different from the selected remedy should MNA not be successful, or may address how the existing remedy may be modified and/or enhanced. The contingency plan must, at a minimum: list the circumstances that will require additional actions, outline the decision matrix to be used to respond to the situation that triggers the plan, specify the technology(s) that will be utilized, and include a schedule for undertaking contingency measures (this schedule must account for and be able to respond to the potential public health and environmental consequences of the situation). Criteria "triggers" must be established that require the implementation of the contingency plan. Such criteria must consider the following:

- Impacts to receptors are identified such that MNA is no longer protective.
- Contaminant concentrations in groundwater exhibit an increasing trend or the appearance of free product in monitoring wells.
- Near-source wells exhibit large concentration increases indicative of a new or renewed release.
- Contaminants are identified in sentinel wells located outside of the original plume boundary.
- Contaminant concentrations are not decreasing at rates sufficient to meet the remediation objectives.
- Concentrations of geochemical parameters are changing such that they indicate a declining capacity to support biodegradation of contaminants.
- Changes in land and/or groundwater use will adversely affect the protectiveness of the MNA remedy.

In establishing triggers or contingency remedies, seasonal fluctuations must be evaluated.

APPENDIX B

CHLORINATED HYDROCARBONS

1.0 INTRODUCTION

This appendix is intended to assist in determining whether MNA is a feasible and effective method of remediation for chlorinated hydrocarbons in the groundwater. MNA should only be selected when a cause-and-effect relationship is established between the loss of contaminant mass and the destruction or immobilization processes. When uncertainty is high, those considering MNA must expend more resources to gather and interpret information that documents whether or not the destruction or immobilization processes are effective at the facility.

MNA alone is usually not sufficient to remediate chlorinated hydrocarbons in a timely manner. The MDEQ expects that source removal or control will be fundamental components of any MNA remedy. The MDEQ emphasizes that MNA is not to be interpreted as a “no further action alternative.” Within the parameters and conditions outlined in this appendix, the MDEQ accepts MNA as a potential remedial alternative only if its use will be protective of public health and the environment and it will be capable of achieving facility-specific remediation objectives within a time frame that is acceptable when compared to other remedial alternatives.

2.0 REQUIREMENTS

2.1 Facility Characterization

Before choosing MNA as the remedial alternative for a facility, the appropriate characteristics of the facility must be determined. The minimum facility characterization requirements for considering MNA are as follows:

- The extent of contamination in all affected media must be fully defined (both vertically and horizontally) to the most restrictive relevant and applicable cleanup criteria (RRD Op Memo No. 1).
- The source area contaminants must be addressed in accordance with Section 21307(2)(d), Section 20114(1)(d), or Section 20118(8) of NREPA. Source removal or control must be completed prior to initiating remediation for soil and/or groundwater contamination. If NAPL, C_{sat} soils, or other highly contaminated media are present, MNA is not by itself an acceptable remedial alternative.
- The extent of the CoCs must be properly characterized. At some facilities, the same geochemical conditions and processes that lead to the biodegradation of chlorinated hydrocarbons can chemically transform naturally occurring manganese, arsenic, and other metals in the aquifer matrix to forms that are more mobile and/or more toxic than the original materials. In addition, metal species associated with iron complexes in the aquifer matrix may be released as the ferric iron is used as an electron acceptor. A

comprehensive assessment of a MNA remedial option should include evaluation of whether naturally occurring metals will become CoCs.

- Geochemical indicators should include, at a minimum: DO, ferrous iron, dissolved manganese, nitrate, pH, ethane, ethene, methane, redox, specific conductance, sulfate (in some cases sulfide), dissolved organic carbon, chloride, and temperature. These indicators in and downgradient from the plume must be compared to background concentrations upgradient from the contamination. If there is a presumption during the initial phase of facility characterization that MNA will be the preferred remedy, the additional sampling and analysis for geochemical parameters, and appropriate location of monitoring wells during the characterization phase, will facilitate collection of the necessary documentation that MNA is responsible for contaminant reductions.
- Modeling should be conducted to estimate the CoCs travel time and to assist in well placement for monitoring purposes. When groundwater modeling is used to predict the fate and transport of contaminants, it is important to remember that these predictions alone cannot be used to demonstrate compliance with applicable criteria or the effectiveness of response actions. At best, a model can only provide an estimate of the effectiveness of a remediation system; verification of actual performance must be demonstrated by the measurement of appropriate field parameters.
- The dissolved phase contaminant plume should be stable or shrinking. In rare cases, MNA may be appropriate if the plume is still expanding but it can be shown, based on computer modeling, that the plume will become stable within acceptable boundaries. Any computer modeling must be based on site-specific parameters. The MDEQ will evaluate such proposals on a case-by-case basis.
- All potential receptors must be identified. All current unacceptable exposure pathways must be eliminated.
- The contaminants must be capable of undergoing biodegradation, otherwise a waiver to R 299.5705(6) will be required. MNA is generally not an appropriate remedial alternative for recalcitrant contaminants. If contaminants are present which do not readily degrade, such as metals or 1,4-dioxane (frequently used as a stabilizer for chlorinated solvents), MNA may not be suitable as a remedial alternative or may need to be supplemented with other remediation technologies.
- The results of the facility characterization must demonstrate the potential for MNA.

2.2 Remedial Investigation

Since MNA is a “knowledge-based” remedy, it is critical that an adequate remedial investigation be conducted. Typically, MNA facilities will require more thorough investigations than facilities where only active remedies are applied. A thorough understanding of the variability in the subsurface (which controls physical, chemical, and biological processes) combined with the expected natural degradation processes is necessary to properly apply MNA as a remedy.

The results of the remedial investigation should provide an initial understanding of the plume behavior, subsurface heterogeneity, likely attenuation processes, the extent of the plume in three dimensions, hydrogeological control, and an initial estimate of contaminant decay rates. These results will assist determining where MNA may be a viable remedy and where and how to apply other remediation technologies to achieve facility cleanup goals. In almost all cases where MNA is proposed, long-term monitoring to confirm plume behavior, attenuation processes, decay rates, and cleanup predictions will follow remedial investigation and interim remedial measures.

Data from the remedial investigation should be used to quantify the mass of contamination in the soil and saturated material. Redox conditions of the soil and groundwater should be determined. Groundwater should be sampled and analyzed for contaminants, their degradation products, terminal electron acceptors, and other parameters that identify conditions of plume development.

It is frequently useful to sample the aquifer and confining matrix material because chlorinated solvents may exist as dense non-aqueous phase liquids (DNAPLs) which behave differently in the subsurface depending on the aquifer and confining matrix. The DNAPL migration may be lateral when the DNAPL encounters a fine sand layer (even though the sand is hydraulically transmissive), resuming downward migration when it encounters a pathway through the fine sand. In addition, when chlorinated solvents encounter clay or clay/silt confining layers, they can integrate themselves into that matrix, as well as move laterally, and become a long-term source of contamination to the aquifer.

The contaminated facility should be tied into the regional hydrogeologic setting to determine the overall risk the facility poses to receptors and the likely paths of contaminant movement if contaminants enter the regional flow system.

The MNA remedial investigation must also determine whether there is any actual (versus potential) threat to public health or the environment present for all exposure pathways. All existing unacceptable exposure pathways must be eliminated, and it must be established that receptors are not likely to be affected in the future before MNA can be considered as a remedy for a facility.

For complicated facilities with chlorinated contaminants (highly heterogeneous hydrogeology, facilities exhibiting strong transient flow, or facilities with high contaminant levels), it is recommended that a fate and transport model be developed after the remedial investigation. A fate and transport model can be very useful in assessing alternative conceptual models for the facility and for understanding complex flow or complex contaminant characteristics. Information on the appropriate use of models is available in RRD Op Memo No. 4, Attachment 7, Groundwater Modeling.

For less complicated facilities, statistical, graphical, and mass budget analysis may suffice for assessing facility data. Whatever methods are used to assess data, the results must be verified by long-term monitoring.

3.0 ASSESSMENT OF NATURAL ATTENUATION

3.1 Tools

The primary evidence for the effectiveness of MNA is loss of contaminant mass or decreasing mass flux across control planes in the plumes. Loss of contaminant mass often is assessed indirectly through documenting decreases in contaminant concentration and concomitant changes in geochemistry. Effectively assessing MNA requires information on: decreasing contaminant concentrations, decay rates and their variation with changes in the hydrologic system, contaminant degradation patterns, the extent to which natural processes control plume movement, and an assessment of the likelihood that these processes will continue until cleanup standards are met. An adequate long-term assessment is highly dependent upon the density of monitoring points that define the plume. The environmental conditions necessary for the degradation of chlorinated hydrocarbons are as follows:

Microorganisms capable of degrading contaminants: Natural degradation of contaminants relies on microorganisms that produce enzymes that degrade the contaminants. Usually, the microorganisms are benefited in some way by the degradation process (the organism gains energy to carry on life processes). Generally, if products of complete dechlorination are evident at a contaminated facility, microcosm studies are not needed. There are situations where microcosm studies or gene assays are warranted, such as the accumulation of intermediate dechlorination products or an inability to determine whether dechlorination is occurring.

Redox capacity of groundwater: The oxidation state or redox condition of the aquifer determines the energetics of the microbial system and the likely degradation processes. The most common method of assessing redox conditions in groundwater is through monitoring native terminal electron acceptors such as oxygen, nitrate, manganese, iron, sulfate, hydrogen, and methane.

Availability of a carbon source (electron donors): The main driving force that determines aquifer redox condition is the presence of a degradable carbon source. The subsurface of some contaminated facilities contains naturally occurring carbon that can result in anaerobic conditions and produce hydrogen to support reductive dechlorination. Without a carbon source, or when a carbon source becomes exhausted, reductive dechlorination will not occur and highly chlorinated compounds will not become dechlorinated (biodegrade).

When reductive dechlorination is the primary natural attenuation process at a facility, investigators should attempt to identify the source and mass of carbon that is sustaining MNA, particularly if the carbon is anthropogenic. It is difficult to predict the long-term viability of MNA if the source of the carbon is unknown.

Absence of competing electron acceptors: In reductive dechlorination, chlorinated contaminants serve as electron acceptors, which means that the native geochemical compounds (e.g., nitrate and ferric iron) become competitors in electron transfer processes that generate energy for microorganisms. Reductive dechlorination will not occur in the presence of oxygen, nitrate, or readily reducible iron.

3.2 Assessing Patterns in Groundwater

Natural attenuation processes can be reduced through studying the patterns of contaminant degradation and geochemical changes throughout the source area and plume. Patterns are likely to vary throughout the plume. Often the most strongly reducing conditions occur near the source zone and the plume encounters less reducing conditions as it moves downgradient. The degradation and geochemical patterns must be assessed at each monitoring point to determine the likely degradation conditions at specific points in the aquifer. Inferences can then be drawn as to the likely conditions prevailing through various segments of the plume.

As chlorinated contaminants are degraded, the mechanisms that control the degradation produce or consume materials resulting in geochemical signatures that are identifiable in the groundwater. These geochemical signatures are referred to as “footprints” or “geochemical footprints.” Changes in groundwater geochemistry along with loss of groundwater contaminants help establish a “cause and effect” relationship that is critical to documenting natural attenuation processes at a facility.

Geochemical footprints: The primary reason for assessing geochemical parameters is to establish a footprint of the plume. Geochemical parameters help identify where the plume is and where it is not. With a proper monitoring well network, geochemical parameters can identify “treated” groundwater, that is, formerly contaminated groundwater that contains the geochemical signatures of degradative activity. Geochemical parameters also establish the likely degradative mechanisms occurring within the plume.

Evidence of specific natural attenuation mechanisms: Footprints of reductive dechlorination show loss of the parent compound and production of daughter products, acids, gases such as methane, ethane, ethene, carbon dioxide, and chlorine. Monitoring groundwater quality for these compounds and assessing changes in these compounds over time and distance within the plume, aids in determining microbial processes likely taking place within the plume.

If the geochemical and redox environment indicates that reductive dechlorination is unlikely, aerobic or oxidative degradation of lower chlorinated compounds can still occur. Examples of geochemical footprints for oxidative remediation of chlorinated hydrocarbons include loss of electron acceptors and production of alkalinity and chlorine. Vinyl chloride, methylene chloride (dichloromethane), and methyl chloride (chloromethane) are degraded through aerobic, oxidative, or abiotic processes much more readily than through reductive dechlorination.

Establish effectiveness of the groundwater monitoring networks: Geochemical footprints can also be used to establish a hydrologic connection between source area and downgradient monitoring wells. If the geochemical footprint in a source well is similar to that in a downgradient well, then the downgradient well is in the flow path of the plume. If the geochemical footprints are significantly different, then the down-gradient well is not in the contaminant flow path. This principle can be used to determine which downgradient wells are most useful for assessing natural attenuation. Assessment of natural attenuation decay rates should include only those wells that intersect the plume in order to draw proper conclusions about plume behavior.

Ideally, sentinel wells beyond the downgradient edge of the plume should exhibit geochemical parameters without the presence of the contaminant.

Patterns of contaminant degradation: Contaminant degradation patterns can give clues as to the nature of the original release as well as to the microbial processes occurring at a facility.

Contaminant degradation patterns can be assessed graphically. One example is the construction of isoconcentration maps of individual and total chlorinated compounds. Geochemical and contaminant footprints can be constructed from isoconcentration maps. These maps should be constructed and evaluated after each sampling round.

One of the most difficult issues in assessing MNA of chlorinated plumes is that degradative processes may not be complete or may overlap. In some plumes, reductive dechlorination can stop after the formation of cis-1,2-dichloroethylene, causing the accumulation of this contaminant. In other plumes, dichloroethylene and vinyl chloride may not be detected because aerobic or anaerobic microbes oxidize them. Neither of these situations produces the expected end products of ethane or ethene.

3.3 Determining Attenuation Rates

Unlike petroleum hydrocarbons where benzene degradation can be tracked separately from toluene, ethylbenzene, and xylenes, the degradation of chlorinated hydrocarbons is linked together. A decrease in concentration of a more chlorinated hydrocarbon (e.g., tetrachloroethylene) results in an increase in concentrations of less chlorinated compounds such as trichloroethylene or dichloroethylene. However, this is complicated by the fact that the less chlorinated compounds are usually more soluble, and hence more mobile in the environment. To establish a trend in the behavior of chlorinated hydrocarbons, a system of linear equations is needed to produce a coherent set of trends for contaminants.

Natural attenuation decay rates should be estimated for each monitoring well that intersects the plume through analysis of contaminant concentration data with time and distance. For MNA to be an effective remedy, the decay rates of the source zone and the plume must indicate that contaminant concentrations will reach cleanup goals within a time frame that is acceptable when compared to other remedial alternatives. Most methods for calculating decay rate constants assume that the plume is at a steady state (i.e., the plume has reached its maximum length and is expected to recede back toward the source). In addition, the decay rate in the plume should be faster than the decay rate in the source. If the decay rate in the plume is substantially slower than the source decay rate, then the plume may be expanding, even if concentrations over time are decreasing at all the monitoring wells.

In most instances, monitoring wells are placed at a facility some time after the contaminant release has occurred. The area of contaminated groundwater identified in the remedial investigation can be expected to decline due strictly to advection/dispersion processes even if degradation is not occurring. Monitoring over a relatively short period of time will, in most cases, disclose declining contaminant trends unless there is a continuing release. This is why properly placed sentinel wells and long-term monitoring are so important to MNA. Monitoring must be conducted over a long enough period of time to assess the behavior of the entire plume and each contaminant within the plume. The monitoring program must confirm that the plume is not expanding, or not expanding beyond delineated boundaries, and establish that the rates of degradation will allow cleanup goals to be realized within a reasonable period of time.

Establishing a steady state: A plume must have reached a steady state before MNA can effectively serve as a facility remedy. At a steady state, a plume has reached its maximum extent and the concentrations within the plume are constant. Decreasing concentrations and a reduction in plume extent occur in post steady state plumes.

Plots of monitoring data: All monitoring wells and piezometers within a groundwater plume and sentinel wells outside the plume must be monitored to establish that the plume is not expanding beyond delineated boundaries and that contaminant concentrations within the plume are declining. Observed contaminant concentration vs. time for each well should be graphed using linear or semi-log plots. Concentration vs. distance data should be graphed in a similar fashion.

Non-parametric statistics: Non-parametric statistics (such as the Mann-Kendall or Mann-Whitney tests) can help assess qualitatively (but not quantitatively) whether contaminant concentrations are decreasing at any given monitoring well. Non-parametric statistics cannot be used to estimate time to cleanup or determine decay rates. However, non-parametric tests may be useful to screen for declining concentration trends. Declining trends, along with clean sentinel wells (monitored over a significant period of time), may help establish whether the assumption that the plume is at a steady state is conservative or not. Conclusions from Mann-Kendall, Mann-Whitney, or other non-parametric tests must not be used alone as evidence of MNA at facilities contaminated with chlorinated compounds.

Estimating decay rates: First order decay models provide a parametric estimate of how fast degradation is occurring at given monitoring points. Almost all degradation constants quoted in the literature are first order degradation constants, because calculation of first order rate constants is straightforward and the collected data often appear to fit a first order decay model.

When adequate data exist, decay rates should be estimated. Spatial and temporal analysis of the data should indicate that the plume has stable boundaries.

Extracting first order rate information from field data is prone to error due to uncertainties in monitoring well placement, variations in groundwater flow, and fluctuations in plume movement. Use of first order rate models assumes:

- A steady state plume.
- A uniform groundwater flow field.
- Contaminant concentration data are collected along the plume centerline.
- A constant source strength with time (i.e., dissolution from the source is not a function of time).
- Volatilization is negligible.

If these assumptions are violated, then a first order decay model would likely result in erroneous degradation rates. All decay rates must be verified in the field by monitoring to determine if contaminant loss reflects the calculated rates. In addition, there must be enough monitoring wells along the centerline of the plume to determine that the calculated rates are not artifacts of dispersion.

Rate constants should be calculated using several methods and the results compared. Long-term monitoring data should be used to verify or modify the decay rates. If the rate constants vary with location along the plume, then that variation needs to be considered when predicting groundwater fate and transport for the facility. The goodness of fit of the first order decay model with actual facility data should be evaluated. In addition, sensitivity analyses should be conducted on the input data. Facility-specific data always should be used to determine decay rate constants. Using literature values to estimate cleanup time of a source area and plume is not acceptable.

3.4 Time Frame and Contingency Plans

The projected time frame to achieve closure must be comparable with that of other remedial methods.

A contingency plan must be included as part of the Corrective Action Plan, Remedial Action Plan, or Interim Response Designed to Meet Criteria. The contingency plan must address response to potential failure of the MNA remedy. The contingency plan may specify a technology(s) that may be different from the selected remedy should MNA not be successful, or the existing remedy may be modified and/or enhanced. The contingency plan must, at a minimum: list the circumstances that will require additional actions, outline the decision matrix to be used to respond to the situation that triggers the plan, specify the technology(s) that will be utilized, and include a schedule for undertaking contingency measures (this schedule must account for and be able to respond to the potential public health and environmental consequences of the situation). Criteria "triggers" must be established that require the implementation of the contingency plan. Such criteria must consider the following:

- Contaminant concentrations in monitoring wells exhibit an increasing trend.
- Near-source wells exhibit large concentration increases indicative of a new or renewed release.
- Contaminants are identified in sentinel wells located outside of the original plume boundary.
- Contaminant concentrations are not decreasing at rates sufficient to meet the remediation objectives.
- Changes in land and/or groundwater use will adversely affect the protectiveness of the MNA remedy.

In establishing triggers or contingency remedies, seasonal fluctuations must be evaluated.