Guidance on Developing a Monitored Natural Attenuation Remedial Proposal for Chlorinated Organics in Ground Water

North Carolina
Division of Waste Management

Hazardous Waste Section

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Guidance on Developing a Monitored Natural Attenuation (MNA) Remedial Proposal for Chlorinated Organics in Ground Water

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Section 1: Definition of Monitored Natural Attenuation (MNA)

Natural attenuation is defined by the US EPA as the "biodegradation, diffusion, dilution, sorption, volatilization, and/or chemical and biochemical stabilization of contaminants to effectively reduce contaminant toxicity, mobility, or volume to levels that are protective of human health and the environment." Simply stated, natural attenuation occurs when physical, chemical and biological processes act to reduce the mass, toxicity, and mobility of subsurface contamination in a way that risks to human health and the environment are decreased to acceptable levels. The term "monitored natural attenuation" (MNA) refers to the reliance on natural attenuation processes, within the context of a carefully controlled and monitored site cleanup, to achieve site-specific remedial objectives. This guidance document focuses on the natural attenuation of chlorinated organics in ground water.

Section 2: Overview of MNA Requirements

Monitored natural attenuation must be protective of human health and the environment. The North Carolina Hazardous Waste Section (HWS) acknowledges natural attenuation as a remedial alternative but does not consider it a "no action" alternative, default option, or presumptive remedy. Natural attenuation should be evaluated along with, and in a manner similar to, other remedial measures. Natural attenuation must be clearly demonstrated by the proponent on a site-by-site basis. Potential exposure pathways and receptors must be identified and any potential current or future risks to sensitive receptors must be explained. The hydrogeology and the contaminant fate and transport mechanisms at the site must be well understood. Contamination sources must be identified and, in most cases, either removed, appropriately remediated if technically feasible, or stabilized. At some sites, natural attenuation may be sufficiently effective so as to be capable of achieving remedial objectives without the aid of other remedial measures. More typically, MNA will be implemented as a component of a comprehensive remedial strategy that includes source control or source removal.

When relying on natural attenuation processes for the remediation of ground water contaminated with chlorinated organics, the Hazardous Waste Section emphasizes the subsurface processes that degrade contaminants. Dilution, dispersion, and sorption do not involve degradation of constituents. Indeed, the primary objective of the natural attenuation investigation is to show that natural processes of contaminant degradation will reduce contaminant concentrations in ground water to levels below North Carolina’s Subchapter 2L Groundwater Standards. The natural attenuation processes at work at the site must be characterized and determined to be capable of achieving the required cleanup levels or objectives in a reasonable time frame.

A "weight-of-evidence" argument is necessary to support a MNA proposal. Figure 1 (Flow Chart for Developing a MNA Proposal) summarizes the sequence of steps a facility should take to develop the proposal. While the sequence outlined in Figure 1 is designed to guide a facility through the building of a sound case, the flexibility to choose and implement an alternate remedial option is available at each major decision point. Figure 1 also emphasizes that a written MNA proposal must include justification for the selection of the MNA option, a performance monitoring plan, a revised ground water sampling and analysis plan, and a plan for a contingency remedy.

After the points discussed above have been adequately addressed, the MNA proposal will be made available to the public for review and comment. At the end of the comment period, the Hazardous Waste Section will review the comments and then make a final decision on the suitability of the MNA remedial option for the site.

Section 3: Establishing Remedial Objectives

Monitored natural attenuation is recognized by the Hazardous Waste Section as a viable method of ground water remediation. However, MNA should be selected only where it meets all relevant remedy selection criteria, where it fully protects human health and the environment, and where it meets site remediation objectives within a reasonable time frame. Since there are many options available for achieving a site's remedial objectives, natural attenuation must be evaluated and compared to other viable remediation methods. In the majority of cases where monitored natural attenuation is proposed as a remedy, its use may be appropriate as one component of the total remedy, either in conjunction with an active remedy, or as a follow-up measure.

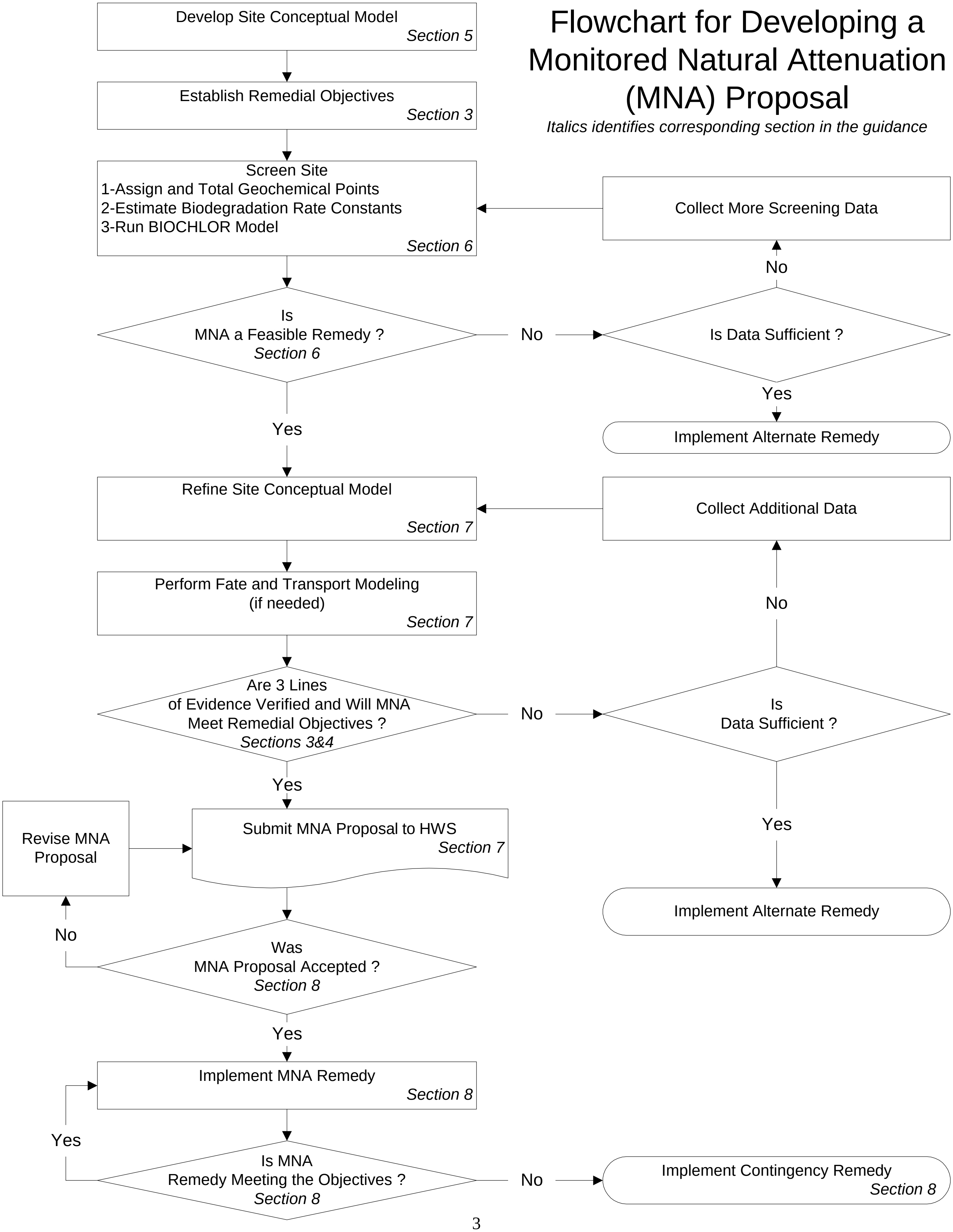
Several key principles must be considered during the selection of monitored natural attenuation, or any other remedial measure, at a site.

- Sources of ground water contamination, including impacted soils, should be controlled to reduce or eliminate further releases of hazardous constituents that may pose threats to human health and the environment. Contaminated soil should be remediated to achieve an acceptable level of risk to human and environmental receptors, and to prevent transfer of contaminants to other media (e.g., surface water, air, sediments) that would result in an unacceptable risk or exceed required cleanup levels. Source controls may not be necessary if the ground water plume will decrease in size at an acceptable rate without

Figure 1

Flowchart for Developing a Monitored Natural Attenuation (MNA) Proposal

Italics identifies corresponding section in the guidance



additional intervention. However, without effective source controls, monitored natural attenuation is unlikely to remediate contaminated ground water in a reasonable time frame. Approval of the MNA option will be contingent upon sources being controlled in a manner that allows remedial objectives to be met in a reasonable time frame.

- Contaminated ground water should be returned to its "beneficial uses wherever practicable, within a time frame that is reasonable given the particular circumstances of the site." In North Carolina, the "beneficial use" of ground water is defined as a drinking water source.

- Remedial actions in general should include opportunities for public involvement. Public involvement should serve to both educate interested parties and to solicit feedback associated with the decision-making process.

Monitored natural attenuation is not a walk away or no action option because adequate site characterization, monitoring, and geochemical analysis must be conducted to determine if it is a viable remedy. Once MNA is in place, continued monitoring is needed to verify that contaminant levels are decreasing as expected, and the remedy is protecting human health and the environment. To ensure there are no human or ecological receptors that are likely to be impacted or potential receptors in the vicinity of the plume, a receptor survey must be conducted. MNA remedies will typically need to include a contingency plan or remedy to be implemented if MNA does not meet remediation goals.

A facility must estimate remediation time frames for all the remedial alternatives proposed for a site. Estimates are more useful for comparison of various cleanup alternatives than for gauging whether a time frame is reasonable. MNA may take longer to achieve site cleanup goals than other methods of remediation and will need to be evaluated on a site-specific basis.

Section 4: Three Lines of Evidence for MNA

The following are three lines of evidence which can be used to demonstrate the natural attenuation of chlorinated organics in ground water:

1. <u>Observed Reduction in Contaminant Mass and Concentration</u>
   Historical ground water data should demonstrate a clear and meaningful trend of decreasing contaminant mass and concentration *over time* at appropriate monitoring or sampling points. These data should also demonstrate a reduction in contaminant mass and concentration *along the flow path* downgradient from the source. In the case of a ground water plume, decreasing concentrations should not be solely the result of the physical processes that are part of plume migration.

2. <u>Identified and Quantified Natural Attenuation Processes</u>
   Hydrogeologic and chemical data should be used to demonstrate indirectly the type(s) of natural attenuation processes active at the site and the rate at which such processes will reduce contaminant concentrations to required levels. This second line of evidence is divided into two components:

   a. Using chemical analytical data in mass balance calculations to show that decreases in contaminant, electron acceptor, and electron donor concentrations can be directly correlated to increases in metabolic end products and daughter compounds. This evidence can be used to show that electron acceptor and electron donor concentrations in ground water are sufficient to facilitate degradation of dissolved contaminants. Solute fate and transport models can be used to aid with the mass balance calculations and to collate and present information on degradation.

   b. Using measured concentrations of contaminants or biologically recalcitrant tracers in conjunction with aquifer hydrogeologic parameters such as seepage velocity and dilution to show that a reduction in contaminant mass is occurring at the site and to calculate biodegradation rate constants.

3. <u>Microcosm Studies</u>
   Data from field or microcosm studies (conducted in or with actual contaminated site media) which directly demonstrate the occurrence of a particular natural attenuation process at the site and its ability to degrade the contaminants of concern (typically used to demonstrate biological degradation processes only). If microcosm studies are undertaken only for the purpose of developing rate constants, they should only be used when they are the sole means available to obtain biodegradation rate estimates.

<u>Applicability of Lines of Evidence</u>

Unless historical data (Item 1 in Section 4) are of sufficient quality and duration to support a decision to use monitored natural attenuation, the Hazardous Waste Section expects that data characterizing the nature and rates of natural attenuation processes at the site (Item 2 in Section 4) should be provided. Where the latter are also inadequate or inconclusive, data from microcosm studies (Item 3 in Section 4) may be acceptable. More supporting information may be required at sites with contaminants which do not readily degrade through biological processes, with contaminants that transform into more toxic and/or mobile forms than the parent contaminant, or where monitoring has been performed for a relatively short period of time. Additional guidance on interpreting the three lines of evidence is given in Appendix A.

Section 5: Initial Site Characterization

A major goal of the Hazardous Waste Section is to protect the ground water quality of the State of North Carolina for its best usage. In most instances, best usage is defined as a source of drinking water which requires little or no treatment. In areas where ground water has been impacted, the HWS's goal is to remediate the ground water to the State's ground water quality standard for each constituent of concern or to each constituent's background concentration. Significant amounts of site characterization data and information are required to prove that natural attenuation processes will meet these remedial goals. Much of this data is required for any proposed remedial option. Additional requirements for data collected specifically to prove that MNA will meet the Section's remedial objectives in a timely manner are discussed in ***Section 6: Screening the Site.***

The data and interpretations listed below are considered part of the initial site characterization. A facility must furnish the Hazardous Waste Section with this information before any remedial option, including monitored natural attenuation, can be accepted by the HWS.

1. Identification of Contaminants
   A remedial proposal should include a description of the contaminants released, an estimate of the volume and concentration of the release, and an attempt to establish the time when the release occurred. Also included in the proposal should be a description of how the contaminants are projected to move in the environment, any by-products that may be formed as a result of degradation or reaction with the environment, and the toxicity and/or carcinogenic potential of contaminants and their by-products. Exposure pathways and potential receptors should be identified.

2. Identification of Sources
   A description of the sources of contamination should be part of the remedial proposal. The horizontal and vertical extent of the source areas and the procedures used to identify the sources also should be submitted.

3. Aquifer Characterization
   The remedial proposal must include a description of the affected aquifer. Characterization of the aquifer should include ground water flow direction(s), porosity, hydraulic conductivity, hydraulic gradient, seasonal and/or tidal variations in ground water flow, and elevation of water table or potentiometric surface. The aquifer characterization should also include a description of the soil or rock types, the orientation of preferential flowpaths, and the lithologic or structural features that may influence ground water movement or contaminant transport.

4. Plume Delineation

The remedial proposal should include a detailed representation of the contaminant plume’s geometry (i.e., the three-dimensional plume boundary and the distribution of the contaminant concentrations within the plume). The plume description should discuss how the contaminants move within the aquifer, the interaction between the contaminants and the aquifer matrix, and any by-products that may be formed by contaminant degradation.

Site characterization includes the development of a site conceptual model. The site conceptual model is a three-dimensional representation of site conditions that communicates what is known or suspected about sources, releases, contaminant fate and transport, exposure pathways and potential receptors, and risks. In other words, the site conceptual model is a synthesis of the information discussed in Items 1 through 4 above. The format for presentation of the site conceptual model may consist of, but is not necessarily limited to, flow nets, diagrams, cross sections, maps, and narrative text. The development and refinement of the site conceptual model should be ongoing until site characterization and remediation are complete.

Section 6: Screening the Site

Several of the chemical and physical processes that may operate on dissolved chlorinated organics in ground water are capable of attenuating the concentrations of these compounds. However, biological activity that results in reductive dechlorination and electron donor reactions is considered a dominant and desirable attenuation process. The types of data collected at a site to prove that biodegradation is operating to degrade hazardous constituents will probably also demonstrate that monitored natural attenuation is a viable remedial option. In other words, if appropriate data are collected and the screening techniques recommended in this section of the guidance document are applied with positive results, then MNA is likely to be a feasible remedial option at a site.

Assignment and Summation of Geochemical Points

The screening process is designed to recognize geochemical environments where anaerobic biodegradation is plausible. The first step in this process is to sample individual locations in and around the contaminant plume and analyze the ground water for a select list of parameters. The parameter values should be compared to the criteria listed in Table 1 and assigned the appropriate number of points. The points are totaled and compared to the interpretations given in Table 2. If the total score for an individual sampling location is 15 or more points, it is likely that anaerobic biodegradation (i.e., reductive dechlorination) is occurring at that location. Table 1 should only be used to evaluate the degradation potential of chlorinated ethenes.

Table 1 Analytical Parameters and Weighting for Preliminary Screening of Anaerobic Biodegradation Processes.

Analysis	Concentration in Most Contaminated Zone	Interpretation	Value
Oxygen*	< 0.5 mg/L > 5 mg/L	Tolerated, suppresses the reductive pathway at higher concentrations Not tolerated; however, VC may be oxidized aerobically	3 -3
Nitrate*	< 1 mg/L	At higher concentrations may compete with reductive pathway	2
Iron (Fe +2)*	> 1 mg/L	Reductive pathway possible; VC may be oxidized under Fe+3 reducing conditions	3
Sulfate*	< 20 mg/L	At higher concentrations may compete with reductive pathway	2
Sulfide*	> 1 mg/L	Reductive pathway possible	3
Methane*	< 0.5 mg/L > 0.5 mg/L	VC oxidizes Ultimate reductive daughter product, VC accumulates	0 3
Oxidation Reduction Potential* (ORP) Against Ag/AgCl Electrode	< 50 millivolts (mV) < -100 mV	Reductive pathway possible Reductive pathway likely	1 2
PH*	5 < pH < 9 5 > pH > 9	Optimal range for reductive pathway Outside optimal range for reductive pathway	0 -2
TOC*	> 20 mg/L	Carbon and energy source; drives dechlorination; can be natural or anthropogenic	2
Temperature*	> 20º C	At T > 20º C biochemical process is accelerated	1
Carbon Dioxide	> 2X background	Ultimate oxidative daughter product	1
Alkalinity	> 2X background	Results from interaction between carbon dioxide and aquifer minerals	1
Chloride*	> 2X background	Daughter product of organic chlorine	2
Hydrogen	> 1 nM < 1 nM	Reductive product possible, VC may accumulate VC oxidized	3 0
Volatile Fatty Acids	> 0.1 mg/L	Intermediates resulting from biodegradation of more complex compounds; carbon and energy source	2
BTEX*	> 0.1 mg/L	Carbon and energy source; drives dechlorination	2
Tetrachloroethene (PCE)		Material released	0
Trichloroethene* (TCE)		Material released Daughter product of PCE	0 **2**
Dichloroethene* (DCE)		Material released Daughter product of TCE (If cis is > 80% of total DCE, it is likely a daughter product. 1,1 DCE can be chemical reaction product of TCA.)	0 **2**
Vinyl Chloride* (VC)		Material released Daughter product of DCE	0 **2**
1,1,1 Trichloroethane*		Material released	0
DCA		Daughter product of TCA under reducing conditions	**2**
Carbon Tetrachloride		Material released	0
Chloroethane*		Daughter product of DCA or VC under reducing conditions	**2**
Ethene/Ethane	> 0.01 mg/L > 0.1 mg/L	Daughter product of VC / ethene Daughter product of VC / ethene	**2** **3**
Chloroform	> 0.1 mg/L	Material released Daughter product of carbon tetrachloride	0 **2**
Dichloromethane		Material released Daughter product of chloroform	0 **2**

* = Required Analysis. Bold number indicates that points are awarded only if it can be shown that the compound is a daughter product (i.e., not a constituent of the source NAPL).

Table 2. Points Awarded to a Sample Location During the Initial Screening for Anaerobic Biodegradation.

Total Points	**Interpretation**
0 to 5 points	Inadequate evidence for anaerobic biodegradation of chlorinated organics.
6 to 14 points	Limited evidence for anaerobic biodegradation of chlorinated organics.
15 to 20 points	Adequate evidence for anaerobic biodegradation of chlorinated organics.
> 20 points	Strong evidence for anaerobic biodegradation of chlorinated organics.

Estimation of Biodegradation Rate Constants

Biodegradation rate constants should be used to simulate the fate and transport of chlorinated organics dissolved in ground water. The Hazardous Waste Section recommends using biodegradation rate constants based upon first-order kinetics. The preferred method of calculating a first-order biodegradation rate constant was proposed by Buscheck and Alcantar (1995). This method is appropriate for plumes that approach steady state conditions (i.e., dynamic equilibrium between plume formation and plume attenuation exists). The method of Buscheck and Alcantar is discussed in greater detail in Appendix B.

A second method of calculating a first-order degradation constant uses a biologically recalcitrant compound as a conservative tracer. The sum of chloride ions and organic chlorine is frequently used as a conservative tracer. The decreasing concentration of the tracer at downgradient sampling points is corrected to account for natural attenuation processes other than biodegradation. The use of a normalized conservative tracer is explained in Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water, EPA/600/R-98/128. This document can be downloaded from the Internet site for the EPA's Subsurface Remediation Information Center (http://www.epa.gov/ada/report.html).

Use of the BIOCHLOR Model

The objective of this step is to estimate the effect natural attenuation is having on the plume. Analytical models such as BIOCHLOR are suitable for this task. BIOCHLOR is relatively easy to use, is in the public domain, and allows for the rapid assessment of a site. BIOCHLOR is available from the EPA's Center for Subsurface Modeling. (It can be downloaded from http://www.epa.gov/ada/csmo.html). By incorporating site-specific values for advection, dispersion, adsorption, biotransformation, information about the source, and plume measurements; the model calculates the distance that ground water contamination is likely to migrate over a given time interval. Model results should be used to address the following questions.

1) Based upon site-specific measurements of hydraulic conductivity and hydraulic gradient and upon site-specific estimates of dispersion, porosity, and contaminant retardation; has the plume migrated less distance than predicted when degradation constants are equal to zero? In other words, compare model simulations with degradation constants equal to zero to those that incorporate site-specific degradation constants and note the difference.

2) Is it likely that site contaminants are attenuating at rates sufficient to meet remedial objectives for the site in a reasonable time period? The BIOCHLOR model allows for a site specific comparison of MNA to a pump-and-treat system.

If the answers to the above two questions are "yes," then the BIOCHLOR model indicates that MNA is a possible remedial option for the site being screened.

Section 7: Refining the Site Conceptual Model

The site conceptual model developed during the initial site characterization should be continuously refined as new data are collected and new interpretations are developed. In addition, there are two suites of maps that should be included in the site conceptual model. A MNA proposal should discuss the likely chemical reactions suggested by these maps. The spatial and temporal trends exhibited in these maps should also be explained.

1. <u>Contaminant and Daughter Product Contour Maps</u>
   After each sampling event, contaminant and daughter product contour maps should be prepared for all contaminants present at the site. Such maps allow interpretation of data on the distribution and relative transport and degradation rates of contaminants in the subsurface. In addition, contaminant contour maps are necessary so that contaminant concentrations can be gridded and used for input into a numerical model. If mobile and residual NAPLs are present at a site, contour maps and cross sections showing the thickness and the vertical and horizontal distribution of each should be prepared.

2. <u>Total Organic Carbon, Electron Acceptor, Metabolic By-product, and Alkalinity Contour Maps</u>
   Contour maps should be prepared for electron acceptors consumed (decrease in the concentration of dissolved oxygen (DO), nitrate, and sulfate) and metabolic by-products produced (increase in the concentration of iron (Fe +2), chloride, and methane) during biodegradation. Under anaerobic conditions, the concentrations of nitrate and sulfate will be seen to decrease to levels below background, and the concentrations of iron (Fe +2), chloride, and methane will increase to levels above background. Dissolved oxygen concentrations will decrease when biodegradation occurs under aerobic conditions.

   Contour maps should also be prepared for total organic carbon, total alkalinity (as calcium carbonate), and oxidation-reduction potential (ORP). Respiration of dissolved oxygen, nitrate, iron (Fe +2), and sulfate tends to increase the total alkalinity of ground water. Knowledge of oxidation-reduction potential in ground water is important because some biological processes operate only within a prescribed range of ORP conditions. If the data is available, contour maps of hydrogen concentration should also be prepared.

Incorporating interpreted chemical reactions, map trends, and results of numerical fate and transport modeling into the site conceptual model should help demonstrate Lines of Evidence 1 and 2 ***(Section 4: Three Lines of Evidence for MNA).***

Execution of Numerical Fate and Transport Simulations

At some sites, hydrogeologic conditions may be complex and/or transient situations (such as pumping wells) could be present. Numerical fate and transport models that allow for the inclusion of biodegradation rates in addition to hydrogeologic and contaminant transport parameters may be needed. Fate and transport modeling at this point in the MNA evaluation should yield a relatively sophisticated site-specific understanding of hydrogeologic and chemical dynamics. The accuracy required of the modeling effort depends to some degree on the relative location of receptors when compared to the effectiveness of the natural attenuation processes. These conditions are highly site-specific and, consequently, numerical fate and transport simulations may not be required at all sites. The BIOPLUME III model is in the public domain and has the capacity to simulate biodegradation, complex hydrogeologic scenarios, and transient conditions. BIOPLUME III can be downloaded from the Internet site for the EPA's Center for Subsurface Modeling Support (http://www.epa.gov.ada.csmo.html).

Section 8: Implementation of MNA Remedial Option

As previously noted, a "weight of evidence" is necessary to show that natural attenuation is an acceptable remedial option for a site. Site-specific sampling provides historical data for indirect evidence of the natural attenuation processes at the site and the rate of reduction of contaminants. Development of the conceptual model shows that the contaminant sources, hydrogeology, and fate and transport mechanisms at the site are understood. Fate and transport modeling provides an affirmation that the potential for contaminant reduction is within reasonable time frames established for a site. When the HWS concurs that compelling evidence has been presented to warrant selection of MNA as the preferred remedial option, then implementation can begin.

Implementing a MNA remedy involves developing and executing a performance monitoring plan. A performance monitoring plan is necessary to ensure that the remedy is meeting the remediation goals as expected (e.g., as predicted by analytical or numerical models). Plan design should be based on the site characterization data, results of solute fate and transport modeling, and results of the exposure pathway analysis.

A performance monitoring plan should describe the monitoring procedures used to evaluate the following:

1. Physical Changes in Aquifer Conditions
   The plan should include monitoring of the hydraulic characteristics (e.g., flow direction, hydraulic gradient, etc) at the site. Changes in the hydraulics of the aquifer may alter the assumptions used in the fate and transport modeling and may necessitate a reevaluation of the site conceptual model. A plausible example would be changes caused by construction activities that alter runoff and/or aquifer recharge.

2. Chemical Changes in Aquifer Conditions
   The plan should include procedures for monitoring the subsurface chemical conditions that allow the natural degradation of contaminants to occur. The site characterization phase should yield information about the existing site-specific conditions such as pH, DO, electron acceptors, etc. Measurements of these parameters are necessary to evaluate the "health" of the subsurface system in which natural attenuation is believed to be working.

3. Physical Changes in Plume Characteristics
   The plan should include procedures for evaluating changes in plume dimensions. This monitoring is necessary to ensure that the plume does not adversely threaten receptors. This is typically accomplished by sampling “sentinel” wells that are placed some distance down-gradient of the plume boundary. If contaminants are detected in the sentinel wells, then the facility may, for example, be required to take action to manage the risk associated with the detected expansion of the plume.

4. Chemical Changes in the Plume
   The plan should include provisions to evaluate the chemical conditions of the plume through time. The protocols described in the plan should allow for the evaluation of the contaminant concentrations throughout the plume. However, there are other important factors that must also be considered when evaluating the chemical changes of a contaminant plume. The detection of new releases and the identification of previously unidentified contaminants that are either more toxic and/or less degradable than the parent compounds must also be taken into account.

Effective Ground Water Monitoring System

A discussion of the design and installation of an effective monitoring system should be included in the performance monitoring plan. The monitoring system should usually consist of permanent wells screened in the same stratigraphic horizon as the contaminant plume being monitored. Generally, monitoring wells should be located so that ground water samples can be collected from 1) the most contaminated portion of the aquifer, 2) downgradient from the source area but still in the dissolved contaminant plume, 3) downgradient from the dissolved contaminant plume, and 4) upgradient and sidegradient of the dissolved plume at locations away from impacted ground water. Several monitoring wells should be screened along the centerline of the dissolved plume. (Since a plume's centerline may not be horizontal, plume orientation must be defined in three-dimensions.) Wells intended as "sentinel" wells should be located a minimum of one year’s travel time upgradient from receptors or facility boundaries. Site conceptual models, analytical models, and numerical fate and transport models developed as part of the justification for the MNA option can help establish optimal monitoring well locations.

Revised Ground Water Sampling and Analysis Plan

A revised ground water sampling and analysis plan should accompany the performance monitoring plan. Ground water analyses should be performed for the contaminants of concern (including degradation products), total organic carbon, dissolved oxygen, nitrate, iron (Fe +2), chloride, sulfate, alkalinity, oxidation-reduction potential, and methane. For monitoring wells located downgradient from the dissolved plume, ground water analyses may be limited to determining the concentrations of volatile organic compounds and dissolved oxygen. Site-specific analytical requirements should also be addressed in the sampling and analysis plan to ensure that all necessary data are collected. Depth to water soundings and determination of the standard field parameters (i.e., temperature, specific conductance, pH, and turbidity) should be conducted during each sampling event. If appropriate for the site, NAPL thickness measurements should also be taken and recorded.

Plan for a Contingency Remedy

A contingency remedy should be proposed at the time MNA is selected as a site remedy. The contingency remedy will function as a "backup" remedy in the event that MNA fails to perform as anticipated. The proposed contingency remedy should be flexible enough to allow for the incorporation of new information about site risks and technologies. Criteria that will define unacceptable performance of the MNA remedial option should be established. Such criteria may include:

- Contaminant concentrations in soil or ground water that exhibit increasing trends not originally predicted during remedy selection. For example, large increases in contaminant concentrations in near-source monitoring wells may signal new or renewed releases. Similarly, contaminants identified in monitoring wells originally located beyond the plume boundary could indicate expansion of the groundwater plume or releases from a separate source area.

- Concentrations of chlorinated compounds cannot be reduced to meet established ground water standards by the process of biodegradation.

- Concentrations of contaminants and/or degradation products are not decreasing at a rate that will meet remedial time frames.

- Changes in land and/or ground water uses that could compromise the protection of human health and the environment.

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Appendix A
Interpreting Lines of Evidence

The following discussion is an excerpt from the September 1998 Technical Protocol for Evaluating Attenuation of Chlorinated Solvents in Ground Water (EPA/600/R-98/128). It can be downloaded from the following Internet site (http://www.epa.gov/ada/reports.html).

OSWER Directive 9200.4-17 (1997) provides the following guidance on interpreting the three lines of evidence discussed in Section 4:

"Unless EPA or the implementing state agency determines that historical data (Item 1-Section 4) are of sufficient quality and duration to support a decision to use monitored natural attenuation, EPA expects that data characterizing the nature and rates of natural attenuation processes at the site (Item 2-Section 4) should be provided. Where the latter are also inadequate or inconclusive, data from microcosm studies (Item 3-Section 4) may also be necessary. In general, more supporting information may be required to demonstrate the efficacy of monitored natural attenuation at those sites with contaminants which do not readily degrade through biological processes (e.g., most non-petroleum compounds, inorganics), at sites with contaminants that transform into more toxic and/or mobile forms than the parent contaminant, or at sites where monitoring has been performed for a relatively short period of time. The amount and type of information needed for such a demonstration will depend upon a number of site-specific factors, such as the size and nature of the contamination problem, the proximity of receptors and the potential risk to those receptors, and other physical characteristics of the environmental setting (e.g., hydrogeology, ground cover, or climatic conditions).

The first line of evidence does not prove that contaminants are being destroyed. Reduction in contaminant concentration could be the result of advection, dispersion, dilution from recharge, sorption, and volatilization (i.e., the majority of apparent contaminant loss could be due to dilution). However, this line of evidence is critical for determining if any exposure pathways exist for current or potential future receptors. In order to evaluate remediation by natural attenuation at most sites, the investigator will have to determine whether contaminant mass is being destroyed. This is done using either, or both, the second or third lines of evidence. The second line of evidence relies on chemical and physical data to show that contaminant mass is being destroyed, not just being diluted or sorbed to the aquifer matrix. For many contaminants, biodegradation is the most important process, but for certain contaminants nonbiological reactions are also important. The second line of evidence is divided into two components:

- Using chemical analytical data in mass balance calculations to show that decreases in contaminant, electron acceptor, and electron donor concentrations can be directly correlated to increases in metabolic end products and daughter compounds. This evidence can be used to show that electron acceptor and electron donor concentrations in ground water are sufficient to facilitate degradation of dissolved contaminants. Solute fate and transport models can be used to aid with the mass balance calculations and to collate and present information on degradation.

- Using measured concentrations of contaminants and/or biologically recalcitrant tracers in conjunction with aquifer hydrogeologic parameters such as seepage velocity and dilution to show that a reduction in contaminant mass is occurring at the site and to calculate biodegradation rate constants.

The biodegradation rate constants are used in conjunction with the other fate and transport parameters to predict contaminant concentrations and to assess risk at downgradient performance evaluation wells and within the area of the dissolved plume. Microcosm studies may be necessary to physically demonstrate that natural attenuation is occurring. Microcosm studies can also be used to show that indigenous biota are capable of degrading site contaminants at a particular rate. Microcosm studies **for the purpose of developing rate constants** should only be undertaken when they are the sole means available to obtain biodegradation rate estimates. There are two important categories of sites where it is difficult or impossible to extract rate constants from concentrations of contaminants in monitoring wells in the field. In some sites, important segments of the flow path to receptors are not accessible to monitoring because of landscape features (such as lakes or rivers) or property boundaries that preclude access to a site for monitoring. In other sites that are influenced by tides, or the stage of major rivers, or ground water extraction wells, the ground water plume trajectory changes so rapidly that it must be described in a statistical manner. A “snapshot” round of sampling cannot be used to infer the plume velocity in calculations of the rate of attenuation.”

The OSWER Directive can be downloaded from http://www.epa.gov/swertio1.index.html.

Appendix B
Biodegradation Rate Constants by the Method of Buscheck and Alcantar

The Hazardous Waste Section recommends using biodegradation rate constants based upon first-order kinetics. The preferred method of calculating a first-order biodegradation rate constant was proposed by Buscheck and Alcantar (1995). This method is appropriate for plumes that approach steady state (i.e., there is dynamic equilibrium between plume formation and plume attenuation). The Buscheck and Alcantar mathematical expression is:

$$\lambda = (v_c/4\alpha_x)\ \{(1 + 2\alpha_x\ [k/v_x]\ )^2 - 1\}$$

λ = first order biodegradation rate constant.
v_c = contaminant transport velocity due to sorption.
α_x = dispersivity in the x direction.
k/v_x = slope of line obtained by plotting natural logarithm of concentration and distance from source (see Step 2 below).

The Buscheck and Alcantar rate constant is site-specific and should be calculated using field data. The individual steps that must be completed to arrive at the biodegradation rate constant are listed below.

Step 1. Confirm that the contaminant plume has reached a steady state configuration.

Step 2. Plot the natural logarithm of a constituent's concentration (y-axis) against the data point's distance downgradient from the source (x-axis). The concentration data should be collected along the center line of the contaminant plume. The slope of the "best-fit" line is equal to the ratio k/v_x.

Step 3. Calculate the velocity of the contaminant (v_c) in the ground water plume. The relationship $v_c = v_x/R$ will give acceptable results. R is the retardation of the chemical constituent and v_x is the average linear velocity (i.e., seepage velocity) of the ground water.

Step 4. Make the appropriate substitutions into the Buscheck and Alcantar equation and calculate the first-order biodegradation rate constant (ë).

Additional details on the use of the method of Buscheck and Alcantar, including example calculations, are given in Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water, EPA/600/R-98/128.