Contaminated Sites Management Series

Use of Monitored Natural Attenuation For Groundwater Remediation

April 2004

Department of Environment

PREFACE

This guideline for the *Use of Monitored Natural Attenuation for Groundwater Remediation* has been prepared by the Department of Environmental Protection (DEP) to provide information to consultants, local government authorities, industry and other interested parties in the use of this groundwater remediation option in Western Australia (WA).

This guideline provides an indication of the methods and work required when developing a monitored natural attenuation groundwater remediation strategy, particularly for sites where groundwater is contaminated with petroleum hydrocarbons.

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- United Kingdom Environment Agency.

LIMITATIONS

This guideline applies to persons investigating and managing contaminated sites. The contents herein provide guidance only and do not purport to provide a methodology for the management of all sites. Competent persons should be engaged to provide specific advice in relation to the management of contaminated sites.

This guideline should be used in conjunction with the texts referenced herein, and any other appropriate references.

This guideline does not contain occupational safety and health procedures and should therefore not be used as a field manual for sampling. WorkSafe Western Australia should be consulted regarding such requirements.

DISCLAIMER

This document has been prepared by the DEP in good faith exercising all due care and attention. No representation or warranty, expressed or implied, is made as to the relevance, accuracy, completeness or fitness for purposes of this document in respect of any particular user's circumstances. Users of this document should satisfy themselves concerning its application to their situation, and where necessary seek expert advice.

CONTAMINATED SITES MANAGEMENT SERIES

This guideline forms part of a management series developed by the DEP to address certain key aspects of contaminated site management in Western Australia.

The management series contains the following guidelines:

- Potentially Contaminating Activities, Industries, and Landuses;
- Development of Sampling and Analysis Programs;
- Assessment Criteria;
- Guidelines for Reporting on Site Assessments;
- Reporting of Known or Suspected Contaminated Sites;
- Community Consultation;
- Disclosure Statements;
- Site Classification Scheme;
- Guidance for Planners;
- Certificate of Contamination Audit Scheme; and
- Contaminated Site Auditor Accreditation Scheme.

Reference to this guideline should ensure that the general requirements of the DEP are satisfied.

Copies of this guidelines are available on the DEP website, www.environ.wa.gov.au.

1. INTRODUCTION TO NATURAL ATTENUATION AND MONITORED NATURAL ATTENUATION

Natural Attenuation (NA) refers to naturally occurring physical, chemical and biological processes, or any combination of those processes, that reduce the concentration and mass of polluting substances in groundwater. For natural attenuation to be effective as a remedial option, the rate at which these processes take place must be sufficiently rapid to prevent polluting substances from entering sensitive receptors, and to minimise the expansion of groundwater contamination plumes into currently unpolluted groundwater. Dilution of contamination within a receptor, such as a river, wetland or water supply bore, is not natural attenuation.

Monitored Natural Attenuation (MNA) is ongoing groundwater monitoring and associated field and laboratory work to confirm whether natural attenuation processes are acting at a sufficient rate to protect environmental values and to demonstrate that remedial objectives will be achieved within one generation, or about 30 years.

The requirement that MNA achieves remedial objectives within 30 years is important because of the DEP's commitment to complying with the principle of inter-generational equity: that is, ensuring current pollution problems are managed now and are not left for future generations to deal with.

This technical guidance has been designed to provide a framework for the design, evaluation and implementation of MNA for groundwater remediation using a structured process developed by the United Kingdom Environment Agency (UK Environment Agency, 2000). Specifically, this document provides generic guidance on:

- screening procedures to assess the viability of MNA as a remedial option at a site;
- procedures to demonstrate that natural attenuation is taking place;
- procedures to evaluate whether natural attenuation will continue to occur; and
- procedures to verify the achievement of agreed remedial goals.

This document updates advice on MNA previously provided by the DEP in contaminated sites guideline document *Development of Sampling and Analysis Programs*.

2. APPLICATION AND CONSTRAINTS ON THE USE OF MNA

Demonstrating that natural attenuation is taking place in groundwater relies on a "weight of evidence" approach, and several lines of evidence are required. These generally include:

- documented decreases in the concentration and mass of contaminants over a period of time;
- the presence of geochemical and biochemical indicators that indicate the natural attenuation processes that are taking place; and
- microbiological data to support the occurrence of biodegradation.

Evaluation of these lines of evidence requires a detailed understanding of the hydrogeology and geochemistry of the site.

The main criteria for the acceptance of MNA as a remedial option by the DEP are:

- ***Natural attenuation can be demonstrated with confidence***
  This will typically require a minimum of two to three years of monitoring data from bores at the site, the development of a conceptual model of the processes that are occurring, and sufficient field and laboratory studies to demonstrate several lines of evidence that the natural attenuation processes are taking place in a manner consistent with the conceptual model. This work will be necessary before the DEP will approve the implementation of MNA an a remediation option.

- ***Natural attenuation will protect sensitive receptors***
  Natural attenuation processes should prevent groundwater contamination affecting surface water bodies receiving groundwater discharge, or affecting the quality of water pumped from bores. The expansion of the contamination plume into unpolluted groundwater should be minimised as far as possible, and will only be acceptable if it can be demonstrated that the receptors are protected. The DEP may accept MNA as a remediation option if some domestic bores are located within a contamination plume, provided that there is a long-term commitment to provide an alternative water supply, or to implement some other management measure to protect residents or other groundwater users from contamination.

- ***Natural attenuation can be monitored***
  The monitoring program must be adequate to demonstrate that natural attenuation is occurring according to expectations. This requires that there is an adequate number of suitable constructed monitoring bores, and that the bores are monitored consistently for a suite of chemical parameters that will provide evidence of natural attenuation. The proponent must also ensure that access to all monitoring bores can be guaranteed on a long-term basis, particularly for bores that may be situated in neighbouring properties.

- ***Remedial objectives will be achieved in a reasonable time-frame***
  The DEP requires that contamination levels in groundwater will be reduced to background levels or an agreed remedial target concentration within a 30 year time-frame. The time-scale for MNA to achieve the remedial objectives should also be reasonable when compared with other remedial options.

- ***Availability of a contingency plan***
  The DEP requires that proponents who wish to use MNA as a remedial option provide an achievable contingency plan for an alternative remediation strategy in the event that natural attenuation is unable to meet remedial objectives.

3. STRUCTURED APPROACH FOR ASSESSING AND IMPLEMENTING MNA

The DEP requires that proponents assess and implement MNA according to a four-stage process outlined in Figure 3.1. The key steps in the process are summarised below, and are described in more detail in the following sections.

The first step in the process, the **screening** stage, described in Section 3.1, considers the *viability* of using MNA at a site based on a preliminary assessment of technical and practical constraints. The aim of this stage is to provide a quick yes/no assessment of the feasibility of this remedial option based on preliminary data for the site.

In the **demonstration** and **assessment** stages described in Sections 3.2 and 3.3, field and laboratory data together with modelling are utilised to investigate natural attenuation processes in more detail. During these stages, a comprehensive conceptual model is developed of the processes that are taking place to reduce contaminant concentrations and mass in the aquifer. The aim is to produce scientifically defensible data to support the use of natural attenuation processes as a remediation strategy.

The **implementation** stage described in Section 3.4 covers the long-term monitoring requirements required to ensure that natural attenuation is taking place in line with predictions made during the assessment stage. A contingency plan is implemented in the event that MNA does not perform to expectations.

3.1 Screening stage

The screening stage assumes that a preliminary soil and groundwater contamination investigation has been carried out in accordance with the requirements of the DEP. As a minimum requirement, the information outlined in Table 3.1 will be needed to assess the viability of MNA as a remedial option.

In addition to the technical information in Table 3.1, there are a number of practical issues that need to be considered when assessing the viability of MNA at a site. These may include the following:

- where groundwater contamination plumes cross site boundaries, it may be difficult to guarantee long-term access to monitoring bores. There is also an increased likelihood that water supply bores will be affected by the contamination;
- MNA usually takes many years to complete and requires a long-term commitment for monitoring. It may not be a suitable option if the site is to be sold or redeveloped in the immediate future;
- the investigations and long-term monitoring required to demonstrate natural attenuation may be more expensive than implementing other active remedial options; and
- the cost of developing contingency remediation plans may also be high.

Table 3.2 uses both technical and practical criteria to assess the viability of using MNA at a sites. These screening criteria should be used in discussions with the DEP to determine whether further work is pursued to demonstrate natural attenuation.

Figure 3.1 Overall process for assessing and implementing MNA remediation

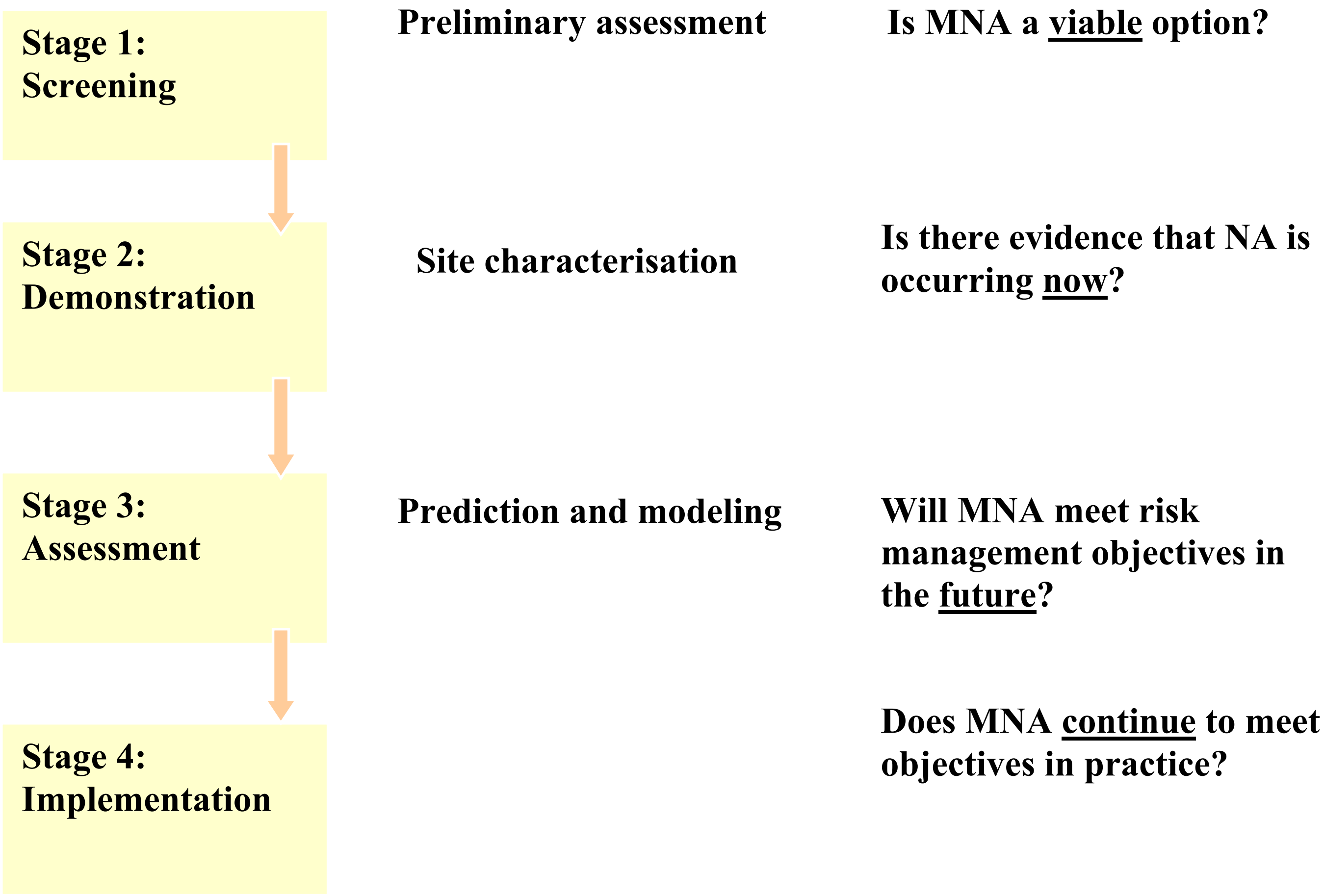


Table 3.1 Minimum technical information required during the screening stage

Information	Site-specific data essential	Site-specific data preferred
Properties of contaminants		
Knowledge of the extent and severity of groundwater contamination	✔	
Identification of the source(s) of contamination and site history	✔	
Background concentrations of contaminants near the site		✔
Chemical composition of the contamination and phase (eg. the presence of phase-separate hydrocarbons)	✔	
Geochemistry of groundwater, including the presence of electron-acceptors, pH and Eh[1]		✔
Aquifer characteristics		
Knowledge of groundwater use near the site	✔	
Knowledge of whether the site is located within a water source protection area	✔	
Direction of groundwater flow and location of discharge areas	✔	
Groundwater velocity		✔
Receptors/compliance points		
Proximity of bores, wetlands, rivers, estuaries or the coast to the site	✔	

Notes:

1. See Appendix A for more information

Table 3.2 Summary of screening criteria to assess the feasibility of using MNA as a remedial option

Screening criteria	**High feasibility**	**Medium feasibility**	**Low feasibility**
Technical screening criteria			
Source of groundwater contamination	Removed	Being removed	**Continuing/ Unknown**
Extent and severity of groundwater contamination	Well defined		Poorly defined
Nature of contamination plume	Shrinking	Stable	Growing
Persistence of contamination in groundwater	Readily attenuated (degraded) under site conditions	Not readily degraded under site conditions	Attenuation processes poorly understood
Dominant attenuating processes	Irreversible/ destructive		Reversible/ non-destructive
Aquifer heterogeneity	Homogenous and isotropic		Heterogenous and anisotropic
Rate of groundwater flow	Slow (less than 10 m/year)	Medium (10-100 m/year)	Rapid (more than 100 m/year)
Water source protection area	Site lies outside of protection areas	Site lies within a P3 protection area	**Site lies within a P1 or P2 protection area**
Groundwater usage near the site	None, or bores mainly used for industrial supply	Bores mainly used for domestic gardens	**Bores used for drinking supply within 300 m of the site**
Surface water bodies	None within 300 metres of the site	None within 100 metres of the site	Present within 100 metres of the site
Level of confidence in monitoring data	High – more than 2 years of comprehensive data		Low- single set of monitoring data
Level of confidence in the understanding of the distribution of contamination	High – eg. dissolved substances in a shallow homogenous aquifer		Low- eg. DNAPLs in a deep heterogeneous aquifer
Practical screening criteria			
Objectives of land owner	Long-term interest in the site (>10 years)	Medium-term interest in the site (3-10 years)	Short-term interest in the site (<3 years)
Financial provisions for monitoring and implementation of a contingency plan	Long-term, legally binding budget provisions secured	Long-term, non-legally binding provisions secured	No long-term budget provisions
Access to off-site monitoring locations	Long-term access secured	Long-term access possible	Limited or no access possible
OVERALL ASSESSMENT OF FEASIBILITY	All Highs or Intermediates, no Lows	No critically important criteria (ie those in bold type and underlined)	One or more critically important criteria, or no factors of High rating

3.2 Demonstration stage

The purpose of the demonstration stage is to show quantitatively that natural attenuation is taking place at a rate that will achieve the remediation objectives in a reasonable time-frame. This requires providing up to three lines of evidence that natural attenuation is occurring in a manner consistent with a conceptual model for a site. These are:

- ***Primary lines of evidence***
  Historical concentration data are used to demonstrate a trend of reducing contaminant **concentrations** along the groundwater flow path downgradient of the source. The DEP may require that concentration decreases with time are statistically significant using the Mann-Kendall (Appendix B) or similar statistical tests. Plots of the logarithm of concentration as a function of time or distance from a source (Appendix C) can be used to determine site-specific degradation rates for contaminants. This form of evidence shows that attenuation is taking place, but does not indicate degradation mechanisms.

- ***Secondary lines of evidence***
  These involve measuring changes in geochemical data to prove a loss of contaminant **mass**. This can be achieved by carrying out mass balance calculations to show that decreases in contaminant and/or electron acceptor/donor concentrations (see Appendix A) can be directly correlated to increases in chemical substances that have been produced by the degradation of the contaminant (see Appendix D). A second approach is to use data from a number of monitoring bores to demonstrate that the contamination plume is shrinking or is stable. The DEP generally requires that both of these secondary lines of evidence are provided.

- ***Tertiary lines of evidence***
  These require data from laboratory testing to show that indigenous bacteria in the aquifer are capable of degrading contaminants at a reasonable rate. This line of evidence is generally only required when both primary and secondary evidence are inconclusive.

Additional site investigations are often required to support the lines of evidence, and to provide information for predicting the future behaviour of the groundwater contamination plume. Table 3.3 indicates the geochemical parameters that are most important for demonstrating various natural attenuation processes.

The demonstration of natural attenuation will generally require ongoing monitoring to show that the contamination plume is stable or shrinking; and/or attenuation is occurring over a period of time. Typically, a minimum of two years monitoring data are required to obtain meaningful and statistically valid trends that take into account seasonal variations in concentrations of contaminants.

Table 3.3 Selection of parameters to demonstrate natural attenuation processes

Attenuation Process	Aquifer Hydraulics	Chemical Properties	Concentration of contaminant	Concentrations of other pollutants	Concentration of reaction products	Dissolved oxygen	Total organic carbon (TOC)	Concentration of electron acceptors	Redox Potential, Eh	pH	Alkalinity	Temperature	Chloride	Availability of iron oxides or hydroxides	Dissolved hydrogen
Dilution & dispersion	✔✔	✔✔	✔✔										✔		
Sorption, precipitation	✔✔	✔✔	✔✔			✔	✔✔		✔✔	✔✔		✔		✔✔	
Volatilisation			✔✔								✔	✔			
Aerobic degradation (contaminant is electron donor)	✔✔	✔✔	✔✔		✔	✔	✔	✔	✔	✔	✔	✔	✔		
Anaerobic degradation (contaminant is electron donor)	✔✔	✔✔	✔✔		✔	✔	✔	✔	✔	✔	✔	✔	✔		✔
Reductive dehalogenation (contaminant is electron acceptor)	✔✔	✔✔	✔✔	✔✔	✔✔	✔✔	✔✔	✔✔	✔✔	✔✔	✔	✔	✔		✔

✔✔ = CONSIDERED ESSENTIAL **✔ = RECOMMENDED**

Data obtained from field and laboratory studies and supplemented with literature values can be used to demonstrate natural attenuation in a number of ways, including:

- carrying out mass balances for contaminants and degradation products (Appendix D);
- determining mass-fluxes of contaminants and degradation products;
- determining the kinetic behaviour of degradation reactions, such as establishing degradation rate constants or contaminant half-lives in groundwater (Appendix C);
- determining the long-term attenuation capacity of the aquifer (for example, determining the supply of electron acceptors or donors involved in degradation reactions); and
- determining the behaviour and rate of non-destructive attenuation mechanisms such as sorption.

The decision to accept MNA as a remedial strategy will be based to a large extent on the laboratory and field studies carried out during the demonstration stage. One or more of the following criteria will need to have been satisfied to assess the acceptability of MNA. **The more criteria that are satisfied, the greater the level of confidence in MNA as a remediation option.**

- ***The dominant natural attenuation process is defined***.
  For example, mass destruction of a contaminant is shown by one line of evidence, and the mechanism is identified by a second line of evidence.

- ***The status of the contamination plume is demonstrated***.
  That is, there are sufficient data to indicate whether the plume is continuing to grow, is stable, or is shrinking. Possible ways of indicating this are by showing a downward trend in the concentration of a contaminant (medium confidence), or; by showing correlating trends between a contaminant, reaction product and/or electron acceptors/donors involved in the reaction (high confidence).

- ***Monitoring trends are consistent***.
  That is, contaminant concentrations show a consistent pattern of decline with no major fluctuations.

- ***Observed trends agree with conceptual model for the site***.
  For example, observed trends can be simulated with fate and transport models based on the conceptual model for natural attenuation at the site.

- ***Microbiological studies support biodegradation***.
  Demonstrating the presence of bacteria in the aquifer that are capable of degrading contaminants is important.

- ***The geochemical conditions in groundwater are consistent with proposed attenuation mechanisms***.
  For example, redox conditions in groundwater need to be consistent with the presence of proposed electron acceptors/donors.

- ***Sensitive parameters are sufficiently well defined***.
  For example, field testing confirms a limited range in the value of hydraulic conductivity.

- ***The distribution and fate of contamination in groundwater is known with a high degree of certainty***.
  That is, the full extent of contamination has been identified.

3.3 Assessment stage

It is assumed at this stage that adequate information has been obtained to define the site and to demonstrate that natural attenuation is occurring and by what process. Acceptance of MNA as a remedial option will be dependent on demonstrating that:

- natural attenuation processes are protecting receptors, and will continue to do so;
- any further migration of the contaminant plume will not result in significant additional pollution of groundwater; and
- the period over which contaminant concentrations are reduced by natural attenuation is reasonable.

The following steps are needed to assess these factors:

- ***Define objectives for the assessment***
  This will include identifying the receptors that need to be protected, determining appropriate remediation targets to ensure the protection of the receptors, and determining the time frame over which natural attenuation is acceptable. This work should be carried out in consultation with DEP.

- ***Select appropriate model to predict the long-term effectiveness of natural attenuation***
  The purpose and benefits of using numerical or analytical models to predict the transport and fate of contaminants should be clearly defined before any modelling is carried out. A model should not be used to replace data from field investigations, but rather should be used as a tool to complement field data to assist in the assessment and decision-making process. The choice of the model used is dependent on:

- the objectives of the modelling exercise;
- the complexity of the hydrogeology of the site;
- the chemical and physical behaviour of the contaminants in groundwater and the natural attenuation processes that occur at the site, and;
- the quality and quantity of field data available for the site.

Where data from the site shows clear evidence of a shrinking plume, this may be sufficient to demonstrate MNA as a viable remediation method. However, the assessment will need to take into account whether future changes in land use may affect natural attenuation, whether the degradation of contaminants produces toxic by-products and whether there is a risk of adsorbed contaminants being remobilised in the future.

- ***Define parameter values for the model***
  Wherever possible, site-specific values for parameters should be used, particularly where biodegradation is the main attenuation process. The choice of parameter values used in modelling should be documented, as should the source of information if literature values are used. If non-site-specific data are used, it will be necessary to demonstrate that:

- the data are relevant to the site;
- model predictions are insensitive to this parameter; or
- the range in parameter values is well defined in the literature, and that a conservative value is being used in the modelling assessment.

The DEP requires that site-specific degradation rates for contaminants are used in modelling.

- ***Model validation***
  The model should be validated against field observations. Unless the model can adequately simulate the observed concentrations of contaminants, it cannot be used with confidence to determine whether MNA is likely to be an acceptable remedial option in the longer term.

- ***Model prediction***
  The model should be used to determine:

- changes in contaminant concentrations with time;
- changes in the extent of contamination with time;

- rate of movement of the contamination from the source and travel time to potential receptors;
- impact (if any) on the receptors;
- time-scale for remedial targets to be achieved; and
- location of monitoring points (particularly at the front of the plume) for long-term performance monitoring.

- ***Sensitivity analysis***
  A sensitivity analysis should be undertaken to determine which parameters have the most significant influence on the assessment. This information should be used to determine whether the given parameter(s) have been defined with sufficient confidence. Assessing the effect of variations of contaminant input from the source is particularly important as this factor may have a large degree of control on the extent and severity of groundwater contamination at a site. The DEP generally requires that the source of contamination is either removed or isolated as a prerequisite to accepting MNA as a remedial option.

- ***Review of model predictions***
  The significance of the model predictions will need to be assessed taking into account the sensitivity of the identified receptors, and should consider:

- uncertainties in the conceptual model and the significance of preferential pathways for contaminant transport;
- uncertainties in parameter values and their influence on model results; and
- the applicability and limitations of the model for predicting contaminant concentrations at a specific site, particularly if receptors are considered to have a high risk of being affected by contamination.

If the review of the modelling results indicates that there is insufficient certainty, then a decision should be made to:

- obtain further data from specific site investigations; or
- consider using active remediation strategies for the site in combination with MNA. This may require further modelling to take into account the effect of additional remediation measures.

- ***Reporting***
  The DEP requires that results of the assessment of the feasibility of using MNA as a remedial option are fully documented. A report on the assessment should include:

- results of all site investigations and monitoring results;
- presentation of a clear conceptual model of the natural attenuation processes operating at the site;
- lines of evidence supporting natural attenuation;
- description and justification of values for parameters used in modelling the fate and transport of groundwater contaminants;
- details and justification of the modelling methods used to assess the fate and transport of groundwater contaminants;
- results of model predictions and a discussion of uncertainties in the analysis;
- basis for proposing MNA as the preferred remedial option;

- outline of the proposed monitoring strategy to confirm whether natural attenuation is effective; and
- details of a contingency plan in the event that natural attenuation proves to be ineffective.

3.4 Implementation stage (performance monitoring)

A decision to implement an MNA monitoring program should be made in consultation with the DEP. The monitoring program will need to be designed on a site-specific basis, and should consider:

- the number of monitoring bores required, their location and construction details;
- the sampling methodology;
- the sampling frequency and duration of monitoring;
- quality assurance (QA) procedures for sampling
- methods of chemical analysis;
- reporting requirements to the DEP; and
- the basis for ceasing monitoring or to trigger the implementation of contingency measures.

The following steps are required to implement an MNA monitoring program:

- ***Design monitoring network***
  The number of monitoring bores required at a site will depend on the complexity of the local hydrogeology and on the sensitivity of the potential receptors for contamination. However, a typical monitoring network (Figure 3.2) will include:

- upgradient monitoring bore(s) to determine changes in background groundwater quality;
- monitoring bores adjacent to the sides of the contamination plume to monitor the lateral expansion of contamination or changes in groundwater flow direction;
- monitoring bore(s) in the contaminant source area to monitor changes in source strength with time;
- monitoring bores located within the contaminant plume downgradient of the source area to monitor changes in contaminant concentrations with time at various distances from the contamination source. These bores are normally located along the centre-line (axis) of the plume; and
- bores located downgradient of the plume to monitor the expansion of groundwater contamination and to provide an early warning of possible effects on receptors.

- ***Develop and implement a groundwater sampling and analysis strategy***
  The DEP requires a sampling and analysis plan to be prepared before an MNA monitoring program is implemented. The plan should include:

- a description of the chemical and physical parameters that will be measured in the monitoring program;
- an indication of the proposed sampling frequency;

- an outline of the proposed method of sampling, sample handling and quality assurance procedures, and;
- a description of laboratory techniques that will be used and their levels of detection and reporting.

Routine monitoring should also include water level measurements and (where appropriate) measurement of the thickness of free product. The analytical suite and the frequency of monitoring will be site specific and depends on the type of contaminant and the geochemical environment in groundwater. Table 3.4 gives suggested monitoring suites for different contaminant types, although this is indicative only and will depend on site-specific conditions.

The frequency of monitoring depends on the hydrogeology of the site and on the sensitivity of the potential receptors. Typically the DEP will require quarterly sampling for the first year of an MNA program, but the sampling frequency may be progressively reduced to a six monthly or annual basis, as may the range of chemical parameters monitored (Table 3.4).

Table 3.4 Typical analytical suites for long-term monitoring of various types of contaminants

Contaminant	First year of sampling	Subsequent sampling
BTEX, Phenols	BTEX and/or phenols, pH, Eh, DO, NO_3^-, Fe^{2+}, SO_4^{2-}, CH_4, CO_2, alkalinity, water level, NAPL thickness	BTEX and/or phenols, pH, Eh, DO, water level, NAPL thickness
Chlorinated solvents	Chlorinated compound & breakdown products, pH, Eh, TOC, DO, NO_3^-, Fe^{2+}, SO_4^{2-}, CH_4, Cl^-, NAPL presence	Chlorinated compound & breakdown products, pH, Eh, DO Cl^-, water level, NAPL presence
Metals	Metals, pH, Eh, DO, water level	Metals, pH, Eh, DO, water level

- ***Develop a contingency plan***
  The DEP requires that the long-term monitoring strategy includes a contingency plan for active remediation measures to be implemented if MNA proves to be an ineffective remedial technique. The plan should include information on:

- the factors that will trigger the implementation of the contingency plan;
- the measures that will be implemented and the time-scale over which these measures will be implemented.

  The DEP will also require evidence that resources are committed both for the long-tem monitoring and to implement the contingency plan if this is required.

  Criteria for implementing the contingency plan may include:

- contaminant concentrations in monitoring bores exceed predetermined “trigger” concentrations accepted by the DEP;
- data that indicate that contaminant concentrations in monitoring bores are not decreasing at a sufficient rate to meet remedial objectives within a time-frame accepted by the DEP;
- changes in groundwater usage or land use near the site that adversely influence the effectiveness of MNA at the site; or
- evidence that concentrations of contaminants in groundwater are increasing, indicating that contaminants are continuing to be released into groundwater.

- ***Report monitoring results to the DEP***

  Monitoring results from an MNA remedial program should be reported to the DEP on at least an annual basis, and within a month if contaminant concentrations exceed values required to implement the remedial contingency plan. Data should be presented in time-series and contour plots wherever possible to help assess trends in contaminant concentrations.

  The monitoring report should:

- indicate whether natural attenuation is occurring according to expectations and in accordance with the conceptual model developed for the site;
- demonstrate that compliance targets are not exceeded;
- identify whether contaminants are continuing to be released into groundwater;
- identify whether there are any changes in groundwater flow or in geochemical conditions in the aquifer that could affect natural attenuation processes; and
- identify whether toxic contaminant degradation products are being produced that could affect sensitive receptors.

  The report should also indicate whether:

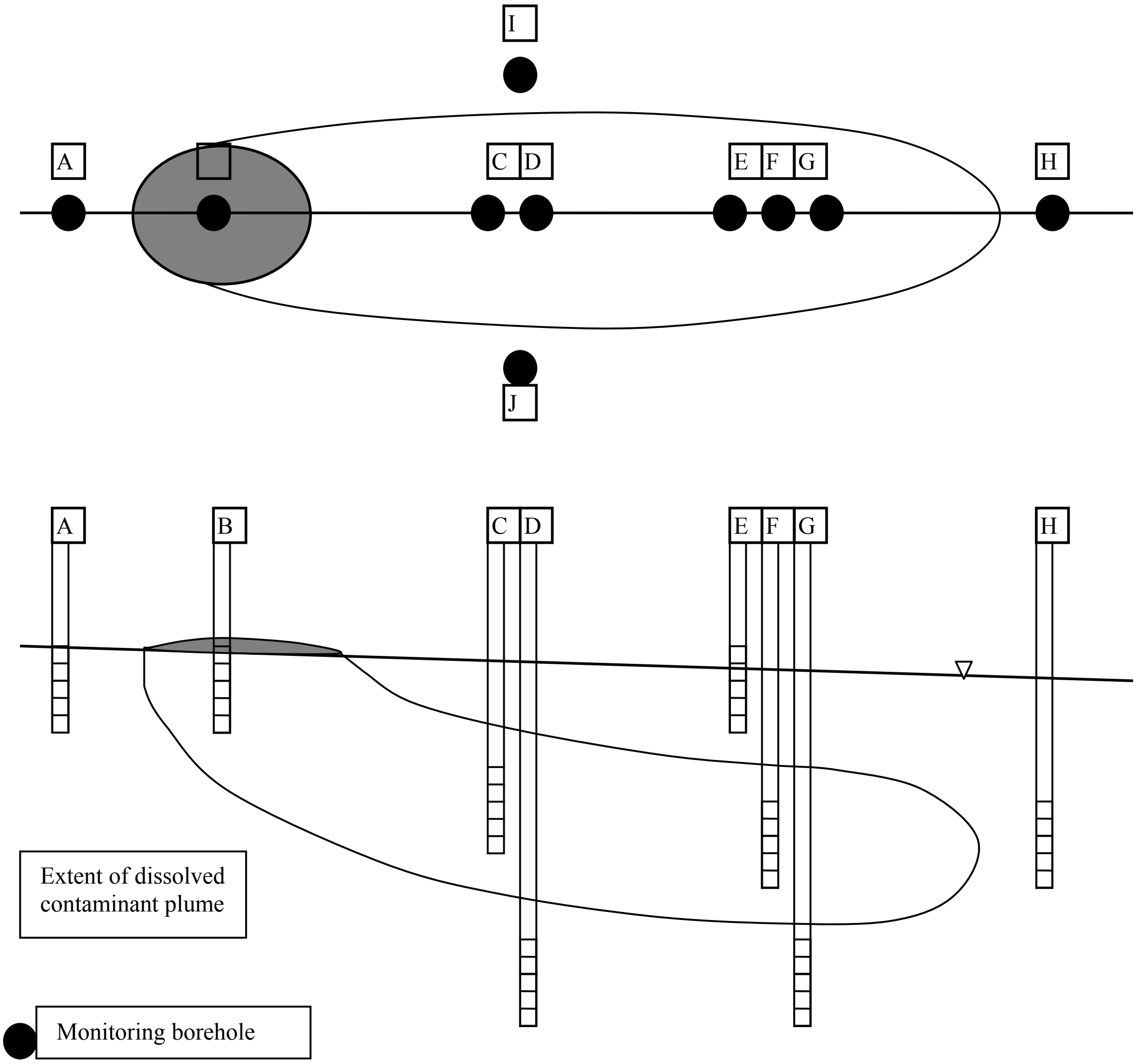
- monitoring can cease as contamination no longer poses a risk to receptors and the decline in contaminant concentrations is statistically significant (Appendix B);
- monitoring should continue according to the defined program;
- the monitoring program needs to be revised;
- the contingency plan needs to be implemented because natural attenuation is not occurring according to expectations; or
- the site conceptual model needs to be revised (this may require additional field investigations).

- ***Cessation of long-term monitoring***

  The criteria for ceasing monitoring should be defined as part of the monitoring plan. Typically, monitoring will continue until:

- contaminant concentrations in the plume have reached background levels; or
- remedial objectives accepted by the DEP have been met, and natural attenuation can be relied on to further reduce contaminant levels; or
- remedial objectives have been substantially met, and declines in contaminant concentrations have been defined to the extent that there is a high degree of confidence that the remedial objectives will be achieved within a time-frame acceptable to the DEP.

FIGURE 3.1 Typical groundwater monitoring network for Monitored Natural Attenuation



Background (A)
Source (B)
Plume (C-G)
Migration (H-J)

4. REFERENCES

United Kingdom Environment Agency, 2000, Guidance on the assessment and monitoring of natural attenuation of contaminants in groundwater. UK Environment Agency R&D Publication No 95, 131pp.

US Navy, 1999, Natural attenuation general data guide. Report No UG-2035-ENG prepared by the Naval Facilities Engineering Service Centre, 37pp.

Wisconsin DNR (Department of Natural Resources), 1999, Interim guidance on natural attenuation for petroleum releases. Wisconsin DNR report PUB-RR-614, 103pp.

5. GLOSSARY

Adsorption	The attachment of a chemical to the surface of a solid.
Anaerobic groundwater	Groundwater than contains less than about 0.5 mg/L of dissolved oxygen.
Aquifer	A permeable geological stratum that is capable of both storing and transmitting groundwater in large amounts.
Attenuation	Reduction of contaminant concentrations through biological, chemical and/or physical processes as contaminated water passes through a porous medium.
Biodegradation	The transformation of a chemical substance by microbial processes into other chemicals.
Cometabolism	A process in which a chemical compound is fortuitously degraded by enzymes during the biodegradation of another chemical compound.
Compliance point	Negotiated location where the remedial target concentration must be achieved.
Conservative pollutants	Pollutants that can move readily through an aquifer with little interaction with aquifer sediments and that are unaffected by biodegradation.
Degradation product	A chemical compound that results from the (bio)degradation of another chemical compound.
DNAPL	Dense Non-Aqueous Phase Liquid. A liquid immiscible with and heavier than water. The liquid sinks in a water column.
Dilution	Reduction in concentration caused by the addition of water.
Electron acceptor	A chemical capable of accepting electrons during oxidation-reduction reactions utilised by microorganisms in groundwater.
Electron donor	A chemical capable of donating electrons during oxidation-reduction reactions utilised by microorganisms in groundwater.
Fermentation	Microbial metabolism in which a particular chemical compound is used both as an electron donor and electron acceptor.
LNAPL	Light Non-Aqueous Phase Liquid. A chemical immiscible with and lighter than water. The liquid floats on a water column.
MNA	Monitored Natural Attenuation. Monitoring of groundwater to confirm that natural attenuation processes are occurring sufficient rapidly to protect sensitive receptors and, to confirm that remedial objectives will be achieved within a reasonable time-frame (ie. within 30 years).
NA	Natural Attenuation. The effect of naturally occurring physical, chemical and biological processes, or any combination of these processes to reduce the mass of contaminants in groundwater. For natural attenuation to be effective as a remedial option, the rate at which these processes occur must be sufficiently high to prevent contaminants affecting sensitive receptors.
NAPL	Non-Aqueous Phase Liquid. Liquid that is immiscible with water.
Receptor	An entity such as a human, animal, plant or an entire aquatic ecosystem that is vulnerable to the effects of contaminants transported by groundwater or though other media.

Reductive dechlorination	Reduction of a chlorine-containing organic compound (typically a solvent) by the replacement of chlorine with hydrogen in the compound.
Remedial target	The goal of remedial activity set at the compliance point, typically set as a desired concentration in soil and groundwater at that point.
Source	The point at which a hazardous chemical compound has been introduced into groundwater by leaks or spills, or through deliberate disposal.
Target concentration	Desired chemical concentration at a compliance point to indicate that remediation of groundwater has been succesful.

APPENDIX A

NATURAL ATTENUATION PROCESSES

APPENDIX A. NATURAL ATTENUATION PROCESSES

The term “natural attenuation” covers a broad range of physical, geochemical and biochemical processes that can reduce the concentration and mass of contaminants in soil and groundwater. Some processes such as sorption or precipitation of insoluble salts can be reversible; that is, contaminants can be re-released into groundwater if there is a change in physical or chemical conditions in an aquifer. Other processes such as the biodegradation of organic compounds are irreversible; that is the original contaminant is broken down into a number of reaction products by biochemical reactions, and the original contaminant can not be constituted even if chemical conditions change in the sub-surface.

Figure A1.1 Natural attenuation processes at a petroleum hydrocarbon spill site

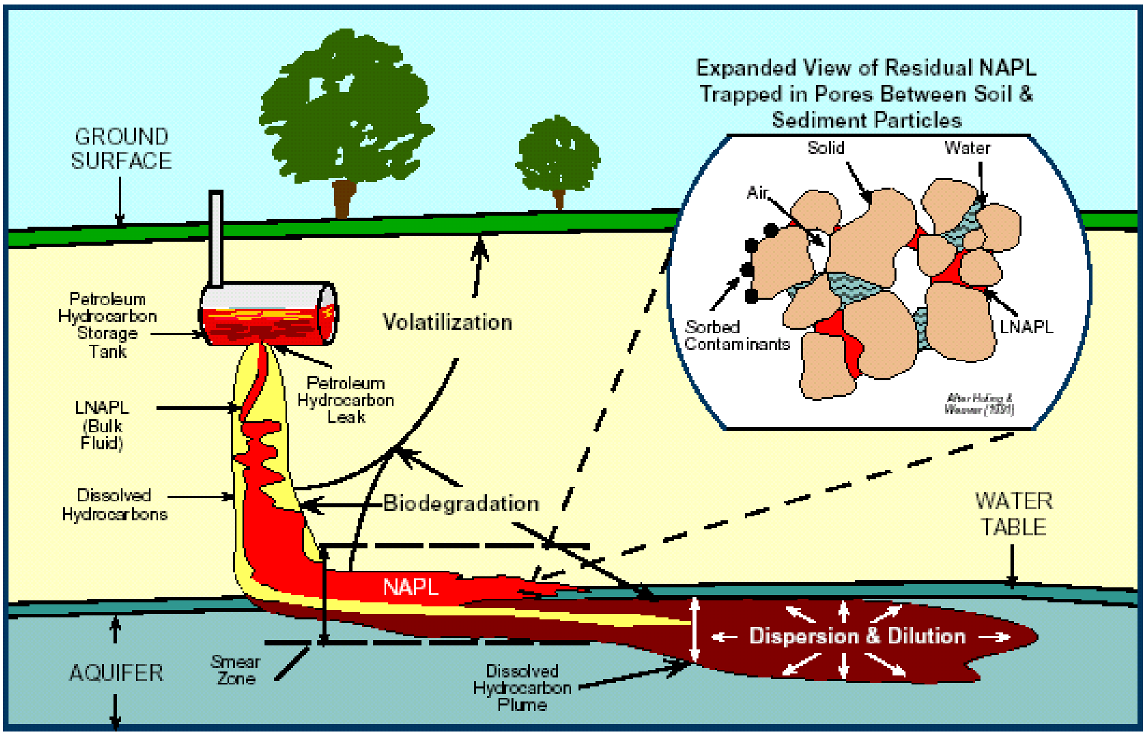


Figure A1.1 shows some of the natural attenuation processes that operate at sites contaminated by petroleum hydrocarbons. Near the source of the hydrocarbon spill, the dominant attenuation process is typically the volatilisation of low molecular-weight compounds. Free-phase hydrocarbons (Non Aqueous Phase Liquid or NAPL) are often trapped sediment pore spaces by capillary forces, but diffusion and dissolution in adjacent aqueous fluid provides an ongoing source of dissolved contamination that can be leached into groundwater.

Concentrations of dissolved contaminants in groundwater contamination plumes that emanate from petroleum hydrocarbon spill sites are reduced by the effects of dispersion and dilution caused by groundwater flow through the porous matrix of the aquifer, but the dominant natural attenuation processes that reduce the mass of contaminants are the biochemical reactions that are collectively known as biodegradation.

Organic contaminants in groundwater are degraded by naturally occurring bacteria that utilise oxidation-reduction reactions between the contaminant and an electron acceptor (or donor) as a source of energy.

Oxidation-Reduction reactions are those chemical reactions that involve the exchange of electrons to change the oxidation state of chemical compounds. In a complete oxidation-reduction reaction, one chemical compound **donates** an electron (ie. the compound is **oxidised**), and another chemical constituent **accepts** an electron (ie. the constituent is **reduced**). These chemical reactions normally take place very slowly if bacteria are absent, but indigenous bacteria in aquifers can produce enzymes that catalyse oxidation-reduction reactions, and increase the rate of reaction by several orders of magnitude.

Biodegradation with the contaminant as an electron donor

Petroleum hydrocarbons and many other organic compounds in aquifers act as **electron donors** in oxidation-reduction reactions. The most important **electron acceptors** involved with the degradation of petroleum hydrocarbons in groundwater are (in order of the energy released as these constituents accept electrons and are reduced):

- dissolved oxygen;
- nitrate;
- ferric iron (ie. iron present in oxidation state Fe(III), usually occurring as iron oxide coatings on sand grains in aquifers);
- sulfate; and
- dissolved carbon dioxide.

Electron acceptors are utilised by bacteria in aquifers in order of the energy released by their reduction. When an electron acceptor is depleted in a contamination plume, the next most energetically favourable acceptor is utilised. Consequently, contamination plumes involving petroleum hydrocarbons are typically zoned, with reactions involving dissolved oxygen and nitrate occurring near the outer fringes of the plume, and reactions involving iron, sulfate and (less typically) carbon dioxide reduction occurring in the core of the plume.

The dominant electron acceptor involved in biodegradation of contaminants can be inferred from field and laboratory measurements of the electron acceptors. Table A.1 summarises typical indicators of the dominant electron acceptors involved with degradation reactions.

Table A.1. Indicators of dominant electron acceptors involved with degradation reactions (adapted from US Navy, 1999)

Dominant electron acceptor	**Indicator**
Dissolved oxygen reduction (ie. groundwater is aerobic)	Dissolved oxygen (DO)> 0.5 mg/L
Nitrate reduction	DO >0.5 mg/L Nitrate > 1mg/L as N
Ferric iron reduction	Ferrous iron (Fe^{2+}) > 0.5 mg/L DO < 0.5 mg/L Nitrate < 0.5 mg/L as N Aquifer sediments may have a "bleached" appearance due to a loss of iron oxides
Sulfate reduction	Sulfate > 1 mg/L DO, nitrate and Fe^{2+} < 0.5 mg/L Sulfides > 0.05 mg/L Groundwater may have a strong "rotten egg" smell due to dissolved hydrogen sulfide

At many sites in Western Australia, most of the mass of contaminants in groundwater is removed by sulfate reduction, largely due to the relatively high concentrations of sulfate in groundwater compared to many other electron acceptors.

Biodegradation with the contaminant as an electron acceptor

Chlorinated solvents can degrade in groundwater under strongly reducing conditions through a process known as reductive dechlorination. During this process, the chlorinated hydrocarbon is used as an electron acceptor, not as a source of carbon, and a chlorine atom is removed and replaced with a hydrogen atom. Other organic contaminants, naturally occurring organic carbon and dissolved hydrogen in the aquifer are used as an electron donors.

Reductive dechlorination of solvents takes place in a series of discrete steps, with a single chlorine atom being removed from the solvent molecule in each step. For example, the solvent tetrachloroethene (perchloroethylene or PCE) is progressively converted to trichloroethylene (trichloroethylene or TCE), dichloroethene (dichloroethylene or DCE), and chloroethene (vinyl chloride), which then further reacts to form carbon dioxide and water. These chemical reactions need to be carefully monitored if this process is being relied on for natural attenuation of solvents, as the reaction product vinyl chloride is highly toxic.

APPENDIX B

MANN-KENDALL TEST FOR ASSESSING THE STATISTICAL SIGNIFICANCE OF CONTAMINANT CONCENTRATION DECLINES

APPENDIX B. MANN-KENDALL TEST FOR ASSESSING THE STATISTICAL SIGNIFICANCE OF CONTAMINANT CONCENTRATION DECLINES

The Mann-Kendall is one of a number of statistical tests that can be used to assess the significance of concentration changes over a period of time. This test should only be used for data that are not affected by seasonal variations in concentration, and therefore it is recommended that trends are only assessed on data that are collected at the same time each year. A high degree of variability in the data can cause the test results to be misinterpreted, so it is recommended that the coefficient of variation (explained at the end of this section) is assessed for the data set.

Because the Mann-Kendall test is a simple test, it can be used to screen data sets prior to performing a regression analysis. If a decreasing contaminant trend is determined by the Mann-Kendall test, the rate of decrease can be further quantified through a regression analysis.

The test is carried out in the following way:

- assemble contaminant concentration data for each bore in the order in which the data were collected. It is recommended data from one or more contaminated bores near the margin of the contaminant plume and a bore near the source of contamination are assessed. All non-detect data values should be assigned a value that is less than the detection limit. If the detection limit varies over time, select a single value to represent all non-detection values.

- set up a matrix of sample concentration versus sampling event in the following manner. If the concentration of a contaminant collected in a particular sampling event is lower than the concentration at the previous sampling event, allocate "–1" in the Table for that event. If the concentration is the same as the previous event, allocate "0" in the Table. It the concentration is higher than the previous event, allocate "+1" in the Table.

	Sampling event 1	Sampling event 2	Sampling event 3	Sampling event 4	Sampling event 5	Sum of Rows
Contaminant concentration	100	50	85	75	50	
Compare to event 1		-1	-1	-1	-1	-4
Compare to event 2			+1	+1	0	+2
Compare to event 3				-1	-1	-2
Compare to event 4					-1	-1
					MANN-KENDALL STATISTIC (SUM OF ROW TOTALS)	**-5**

- sum each row and enter result at the end of the row. Sum all of the row-totals to obtain the Mann-Kendall Statistic (S). If S is positive, then later measurements tend to be bigger than earlier measurements, pointing to an increasing trend in that bore. If S is negative, then a declining trend in that bore may be indicated.

- test the significance of an apparent declining trend in contaminant concentrations. Evaluate the null hypothesis of no trend against the alternative of a decreasing trend. The null hypothesis can be rejected in favour of a decreasing trend if the following conditions are met:
    a. S is a large negative number (see look-up table below for magnitude of S)
    b. the absolute value of S is less than the level of significance, α ,for the test for a given number of concentration measurements, n. A level of significance of 0.2 is generally acceptable.

The following Mann-Kendall look-up table was adapted from the Wisconsin Department of Natural Resources guideline for the assessment of the natural attenuation of petroleum hydrocarbons (Wisconsin DNR, 1999). The table gives the maximum value of the S statistic (S_{max}) to accept an alternative hypothesis at an α level of significance for n concentration measurements. If the computed S is a smaller negative number than S_{max}, then an hypothesis of no-trend or increasing concentration trend must be accepted.

Table B.1. Mann-Kendall look-up table

Number of concentration measurements, n	Range of Mann-Kendall statistic, S	S_{max} for $\alpha = 0.1$	S_{max} for $\alpha = 0.2$
4	-6 to +6	-6	-4
5	-10 to +10	-7	-5
6	-15 to +15	-8	-6
7	-21 to +21	-10	-7
8	-28 to +28	-11	-8
9	-36 to +28	-14	-10
10	-45 to +45	-16	-11

If the hypothesis of declining concentrations is rejected, test for the significance of an apparent trend of increasing contaminant concentrations. An alternative hypothesis of increasing contaminant concentrations in a bore (that is, the plume is growing) is accepted if:
    a. S is positive
    b. S is greater than or equal to the absolute value of S_{max} at a given level of significance, α, and for n concentration measurements.

If the Mann-Kendall test indicates no-trend for concentration variations, additional analysis is required to assess the significance of this assessment as this test does not take into account variations in the scatter of data. A data set with a great deal of scatter may return a Mann-Kendall test indicating there is no trend, when, in fact, no conclusion can be drawn regarding trend because of data variability. In this case, additional data collection may be necessary to determine that the plume is stable, declining or advancing. As a simple test, the coefficient of variation can assess the scatter in the data:

where, the coefficient of variation, CV = (standard deviation of the data)/(arithmetic mean)

The value of CV should be less than or equal to one to indicate that the “no-trend” hypothesis also indicates that the groundwater contamination plume is stable.

APPENDIX C

USE OF LOGARITHMIC PLOTS TO DETERMINE SITE-SPECIFIC DEGRADATION RATES FOR CONTAMINANTS

APPENDIX C. USE OF LOGARITHMIC PLOTS TO DETERMINE SITE-SPECIFIC DEGRADATION RATES FOR CONTAMINANTS

Information that supports the view that contaminants in groundwater are breaking down at a rate consistent with that expected from biodegradation reactions is an important line of evidence in Monitored Natural Attenuation.

Most organic compounds that are consumed by biodegradation reactions in groundwater follow, or at least approximate, first-order kinetic behaviour as they degrade. That is, the rate at which the chemical compound decays is proportional to the concentration of the chemical in water, or:

$$-dc/dt = k.c$$

where c = concentration, t = time and k = the degradation rate constant (units of $time^{-1}$).

Integration gives:

$$-\int dc/c = k\int dt$$

that is:

$$-\ln c/c_0 = \ln c_0/c = k.t$$

or more usefully if you are using logarithmic graph paper to plot data:

$$\log c = -k/2.303.t + \log c_0$$

Another useful concept in first-order decay processes is that of **half life**, that is the time for half of the original contaminant mass to disappear. It can be determined from the following relationship:

$$t_{0.5} = 0.693/k$$

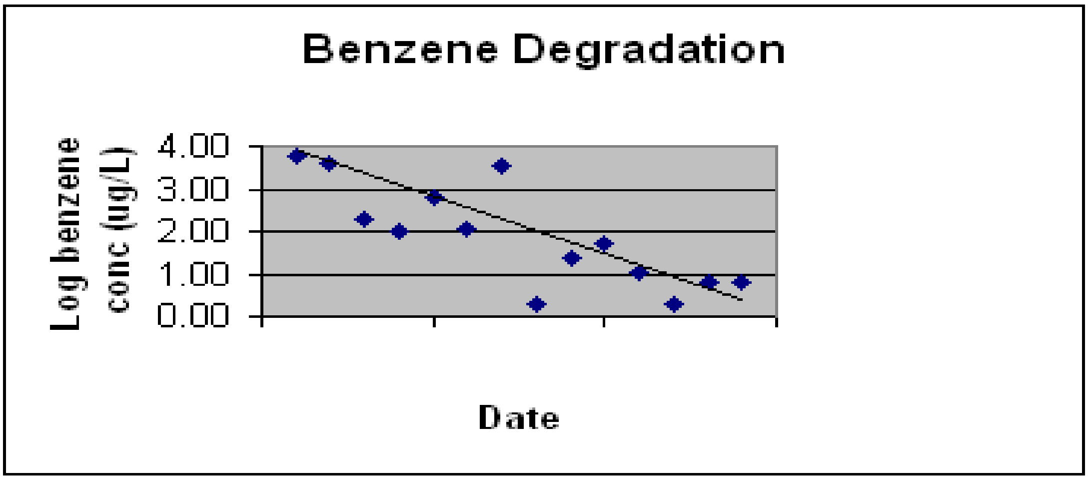
These relationships can be used to determine whether concentration and time data from a single monitoring bore follows first-order decay behaviour and to determine site-specific decay constants and half lives. Data from a number of monitoring bores can also be used. The following examples from the Wisconsin Department of Natural Resources (Wisconsin DNR, 1999) indicate how this can be done.

EXAMPLE 1 – ASSESSING DEGRADATION RATES FROM CONCENTRATION-TIME DATA FROM A SINGLE BORE

The concentration of benzene in a bore varies with time according to the following table (data from the Wisconsin Department of Natural Resources):

Date	Benzene (μg/L)	log benzene (μg/L)
26/1/94	5600	3.75
12/4/94	3900	3.59
20/7/94	200	2.30
18/10/94	100	2.00
18/1/95	610	2.79
18/4/95	110	2.04
12/7/95	3500	3.54
26/10/95	2	0.30
9/1/96	25	1.40
11/4/96	50	1.70
28/8/96	11	1.04
3/12/96	2	0.30
5/3/97	6	0.78
18/6/97	6	0.78

A graph of log benzene concentration versus time gives a good linear fit with an R^2 of 0.65 (i.e. 65% of the variance in the benzene concentrations can be attributed to the passing of time).



The slope of the line of best fit is 0.0024/day. Therefore the apparent decay rate for benzene is 2.303 x (0.0024/day) or 0.0055/day, which is relatively fast for benzene degradation. Note that this degradation rate includes all degradation pathways, not just biodegradation.

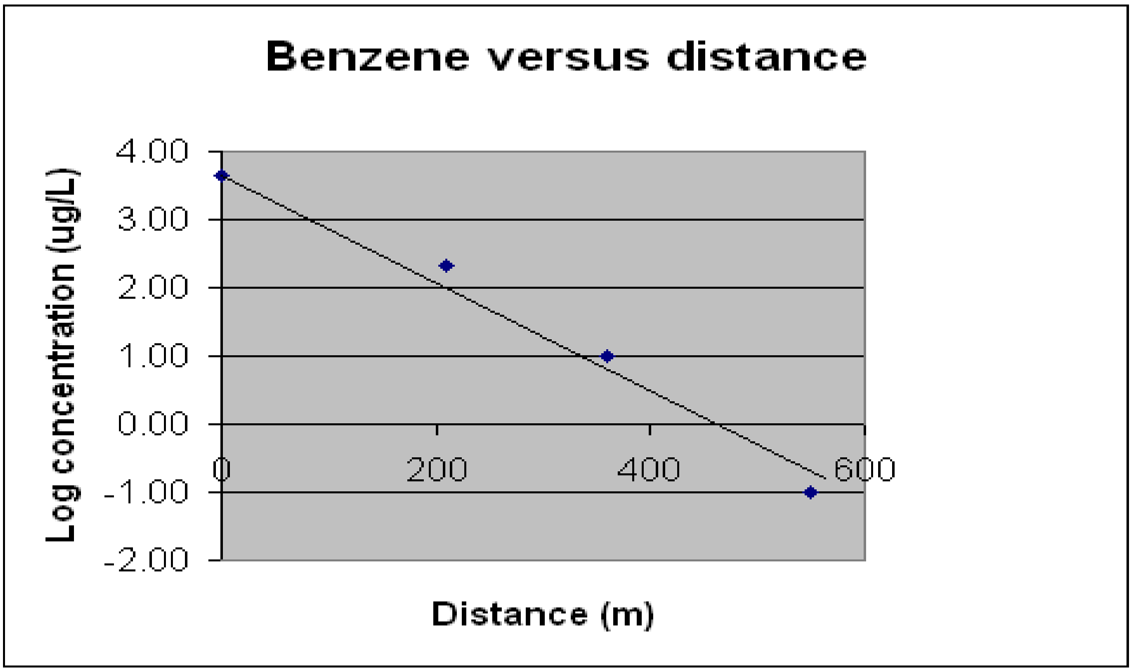
N.B.

The significance of linear regressions depends greatly on the number of data points that you have. For example, to achieve a 99% level of significance with only 5 data points, the R^2 value needs to at least 0.92. To achieve the same level of significance with 10 data points, an R^2 value of 0.58 would be acceptable.

EXAMPLE 2 – ASSESSING DEGRADATION RATES FROM CONCENTRATION-DISTANCE DATA FROM SEVERAL BORES

If a contamination plume is at steady-state, decay rates for contaminants of concern can be obtained from data from bores along the axis of the plume. Prepare plots of log concentration versus distance from source for each of the contaminants of concern, as for the following example (data from the Wisconsin Department of Natural Resources).

Distance (m)	Benzene (µg/L)	log Benzene (µg/L)
0	4411	3.64
210	207	2.32
360	10	1.00
550	0.1	-1.00



The line of best fit has a slope of 0.008/metre and an R^2 of 0.992

The decay rate, k, is equal to (2.303x slope x groundwater flow rate). The calculated flow rate for this example was 0.4 metres/day. The decay rate is therefore:

k = (2.303 x 0.008/metre)x(0.4metres/day) = 0.007/day.

This decay rate is likely to be due to the combined effects of biodegradation, dispersion and sorption. This is the decay rate of benzene in groundwater, not in the source area.

Using this decay rate, the site-specific half-life of benzene in groundwater is given by:

$$\begin{aligned} t_{0.5} &= 0.693/k \\ &= 0.692/0.007 \\ &= \underline{99 \text{ days}} \end{aligned}$$

That is, the benzene mass in groundwater should halve every 99 days.

Again, it is useful to look at the number of data points and the magnitude of the R^2 value to determine the significance of the trends calculated.

APPENDIX D

EXAMPLE OF A CONTAMINANT DEGRADATION MASS BALANCE CALCULATION

APPENDIX D. EXAMPLE OF A CONTAMINANT DEGRADATION MASS BALANCE CALCULATION

Field data

A petrol spill has caused a NAPL layer (ie. a layer of free-phase hydrocarbons) at the top of the water table. BTEX dissolves into the groundwater at an unknown rate, but a series of groundwater monitoring bores indicates that a dissolved BTEX plume extends about 45 meters from the source. BTEX concentrations in the plume are up to 10 mg/L. Upgradient measurements indicate that O_2, NO_3^- and SO_4^{2-} are present in groundwater, whereas in the most distant downgradient bore, BTEX, O_2, NO_3^- and SO_4^{2-} are virtually absent, but Fe^{2+} and CH_4 are present in groundwater. Hydrogeological investigations indicate that the groundwater flow rate is 30m/year and the aquifer porosity is 0.25. The plume is 10 metres wide and is 2 metres thick. Table D.1 summarises the upgradient and downgradient concentration values.

Table D.1 Concentration data

Constituent	Upgradient	Downgradient	Change
BTEX (mg/L)	0	0	0
O_2 (mg/L)	8	0.2	-7.8
NO_3^- (mg/L as N)	7	0.1	-6.9
SO_4^{2-} (mg/L as S)	9	1	-8.0
Fe^{2+} (mg/L)	0	40	40
CH_4 (mg/L)	0	1	1
Alkalinity (mg/L as $CaCO_3$)	10	130	120
pH	4.7	6.1	1.4
Total CO_2 (mg/L as C)	29	44	15

Mass-balance approach

Assume all of the NAPL consists of toluene. The relevant reactions for the biodegradation of toluene in groundwater are shown in Table D.2.

Table D.2 Chemical processes involved in the biodegradation of toluene in groundwater

Process	Electron Acceptor	Chemical Reaction
Aerobic	O_2	$C_7H_8 + 9O_2 \rightarrow 7CO_2 + 4H_2O$
Denitrification	NO_3^-	$C_7H_8 + 7.2NO_3^- + 7.2H^+ \rightarrow 7CO_2 + 3.6N_2 + 7.6H_2O$
Sulfate reduction	SO_4^{2-}	$C_7H_8 + 4.5\ SO_4^{2-} + 9H^+ \rightarrow 7CO_2 + 4.5H_2S + 4H_2O$
Ferric iron reduction	$Fe(OH)_{3(s)}$	$C_7H_8 + 36Fe(OH)_{3(s} + 72H^+ \rightarrow 7CO_2 + 36Fe^{2+} + 94H_2O$
Methanogenesis	Fermentation to CH_4 and CO_2	$C_7H_8 + 5H_2O \rightarrow 7CO_2 + 4.5CH_4$

Using these reactions, you can derive the following stoichiometric ratios:

Table D.3 Stoichiometric ratios for the biodegradation of toluene

Reaction	g C_7H_8 /g acceptor	gCO_2-C/g acceptor	g alkalinity (as $CaCO_3$)/g acceptor
Aerobic (O_2)	0.319g /g O_2	-0.29g C/g O_2	0
Denitrification (NO_3^- as N)	0.917g /g N	-0.83g C/g N	-3.57 g/g N
Sulfate reduction (SO_4^{2-} as S)	0.637g / g S	-0.53 g C/g S	-3.13 g/g S
Iron reduction (Fe^{2+} generated)	-0.046g /g Fe^{2+}	0.042 g/g Fe^{2+}	1.79 g/g Fe^{2+}
Methanogenesis (CH_4 generated)	-1.28g /g CH_4	0.42 g/ g CH_4	0

Notes for table D.3

1. *Minus sign indicates chemical is consumed during the reaction*
2. *Only reactions that involve protons (H^+) can change the alkalinity (i.e. denitrification, sulfate reduction, iron reduction). The concentration of carbon dioxide, protons and alkalinity are related by the following reaction:*

$$CO_2 + H_20 \rightarrow CO_3^{2-} + 2H^+$$

Combining the stoichiometric ratios with the observed concentration changes of electron acceptors allows concentrations of CO_2 and alkalinity to be calculated, and the amount of BTEX (as toluene) that has been degraded to be determined.

Table D.4. Computed alkalinity and BTEX consumption

Reaction	Observed Changes in acceptor concentration (mg/L)	Computed Total CO_2 (mg/L as C)	Computed alkalinity (mg/L as $CaCO_3$)	Computed BTEX consumption (mg/L as toluene)
Aerobic (O_2)	-7.8	2.3	0	2.5
Denitrification (NO_3^- as N)	-6.9	5.7	24.6	6.3
Sulfate reduction (SO_4^{2-} as S)	-8	4.6	25.0	5.1
Iron reduction (Fe^{2+} generated)	+40	1.7	71.6	1.8
Methanogenesis (CH_4 generated)	+1	0.4	0	1.3
TOTAL		14.7	121.2	17.0

The computed changes in inorganic carbon and alkalinity agree well with the observed concentration changes of 15 and 120 mg/L respectively. These results support the view that biodegradation is responsible for the loss of BTEX.

The total BTEX biodegradation is 17 mg/L (i.e. 17 g/m^3). As the groundwater flow rate is 30 m/year, and the plume has a cross-sectional area of 10 m by 2 m, the BTEX degradation rate is then

17 g/m^3 x 10 m x 2 m x 0.25 x 30 m/year = <u>2550 g/year</u>

It is important to note in the above analysis that the majority of BTEX degradation and inorganic carbon generation come from denitrification and sulfate reduction. The majority of the alkalinity, however, comes from iron reduction (mostly from iron oxide coatings on sand grains). Although there is likely to be a large supply of nitrate and sulfate transported into the plume by groundwater flow, the amount of iron oxides within the plume could become depleted over time.