Government of **Western Australia**
Department of **Water and Environmental Regulation**

Use of monitored natural attenuation (MNA) for groundwater clean-up

Contaminated sites guidelines

DRAFT

Department of Water and Environmental Regulation

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1   Purpose

The purpose of this guideline is to provide guidance on the application of monitored natural attenuation (MNA) for cleaning up groundwater at contaminated sites in Western Australia. This guidance should be applied within the legislative framework provided by: the *Contaminated Sites Act 2003* (CS Act) and the *Contaminated Sites Regulations 2006* (CS Regulations); and the revised national site assessment framework provided in the *National Environment Protection (Assessment of Site Contamination) Measure 1999* (NEPM).

This guideline has been prepared to assist proponents and environmental practitioners, including environmental consultants and auditors, when planning and implementing a programme of monitored natural attenuation and when preparing a report(s) to be submitted to the Department of Water and Environmental Regulation (DWER) and/or accredited contaminated site auditors under the CS Act and CS Regulations.

This guideline sets out a staged assessment process that DER will require proponents/practitioners to undertake in order to provide evidence that MNA will be an effective management option for contaminated groundwater at a given site.

This document provides guidance on a staged approach to implementing MNA :
• Stage 1 – screening assessment to evaluate feasibility and acceptability • Stage 2 – site characterisation and demonstrating MNA • Stage 3 – predicting the long term viability of MNA • Stage 4 – implementing performance monitoring and achieving closure

International research over recent decades has shown that a variety of natural processes that take place below the ground are capable of removing contaminants from soil and groundwater. These contaminant removal mechanisms are collectively referred to as Natural Attenuation (NA) and, under some circumstances, NA can be used as one of a number of measures for cleaning up contaminated groundwater.

This guideline does not provide a detailed discussion of natural attenuation mechanisms for specific contaminant types or sources of contamination. Practitioners are referred to the references herein for further information on natural attenuation mechanisms.

This guideline may also be useful for other purposes such as due diligence assessments. However, it may also be necessary to discuss site-specific circumstances with DWER, refer directly to the CS Act and CS Regulations and/or seek specific legal advice.

2   Introduction

2.1   General

DWER has prepared this guideline to help land owners, industry, consultants and auditors and other interested parties, understand the requirements for applying monitored natural attenuation to clean up groundwater at contaminated sites in WA.

In WA, contaminated sites are regulated by DWER through the CS Act and CS Regulations (available from Parliamentary Counsel's Office at www.legislation.wa.gov.au). DWER works in consultation with the Department of Health in relation to public health issues at contaminated sites.

The NEPM provides guidance on the assessment of site contamination and is available at http://nepc.gov.au/nepms/assessment-site-contamination. When referring to the NEPM, practitioners should also consult this website for errata and additional information provided in the NEPM toolbox. The *National Environment Protection Council Act 1994* limits the scope of the NEPM to site assessment and therefore it does not include detailed guidance on remediation of contaminated sites.

DWER provides additional guidance specific to WA within the Contaminated Sites Guidelines (CSG), which includes this guideline - available at www.der.wa.gov.au/contaminatedsites.

Practitioners are expected to refer to the NEPM and DWER guidelines when conducting site assessments and remediating contamination. It is essential that practitioners keep up to date with current versions of guidance documents referred to herein and published updates and/or errata.

The Contaminated Sites Guidelines replace the guidelines within the former Contaminated Sites Management Series. Further information is available in DER (2014) and at www.der.wa.gov.au/your-environment/contaminated-sites/61-contaminated-sites-guidelines?showall=&start=1.

2.2   Key terms

2.2.1 Site

Section 3 of the CS Act provides the following definition of a site:

CS Act s 3 - definition of "site"
"site" means an area of land and includes –   (a)   underground water under that land; and   (b)   surface water on that land

A site must be identified by the boundaries identified under the relevant certificate(s) of title. This enables DWER to use the state land administration system to identify and record known and suspected contaminated sites on the Contaminated Sites Register and for lodging memorials under the CS Act.

2.2.2 Source and affected sites

A site may comprise several land parcels or a single land parcel where the contaminating activities occurred. The CS Act differentiates between sites where contamination has originated, and sites that have become contaminated due to the movement or migration of contamination from another site, i.e. the off-site movement of contaminated groundwater, surface water or soil. Section 3 of the CS Act defines these types of sites as source sites and affected sites.

> ### CS Act s 3 - definition of "source site" and "affected site"
>
> **"source site"** means a site –
>
> > (a) on which contamination; or
> >
> > (b) on which a substance
>
> has originated and from which it has migrated to another site (the "**affected site**") causing, or contributing to, contamination on that other site.
>
> **"affected site"** means a site on which contamination is caused, or contributed to –
>
> > (a) by contamination; or
> >
> > (b) by a substance,
>
> which has migrated to that site from another site (the **"source site"**).

2.2.3 Contaminated

Section 4(1) of the CS Act provides the following definition of contamination:

> ### CS Act s 4(1) - definition of "contaminated"
>
> **"contaminated",** in relation to land, water or a site, means having a substance present in or on that land, water or site at above background concentrations that presents, or has the potential to present, a risk of harm to human health, the environment or any environmental value.

Contamination can be present in the soil, groundwater or surface water of a site. It may be present in the solid, liquid or gaseous phases (e.g. soil or groundwater contamination giving rise to contaminant vapours in soil pore spaces). Where substances are present at above background concentrations, further assessment of those substances is required to assess the risk of harm to human health, the environment and environmental values.

Section 4(2) of the CS Act provides for circumstances where sites are not considered contaminated, these are prescribed in regulation 5 of the CS Regulations. Further information is provided in DER (2017).

Further information relevant to the definition of 'contamination' and risk of harm is provided in DER (2014).

2.2.4 Definition of remediation

The CS Act provides the following definition of remediation:

CS Act s 3 - definition of "remediation"
"remediation" in respect of a site that is contaminated includes –   (a) the attempted restoration of the site to the state it was in before the contamination occurred;   (b) the restriction, or prohibition, of access to, or use of, the site;   (c) the removal, destruction, reduction, containment or dispersal of the substance, causing the contamination, or the reduction or mitigation of the effect of the substance;   (d) the protection of human health, the environment or any environmental value from the contamination.

Although the CS Act definition of remediation includes measures to manage contamination such as by restricting access or use of the site, the term 'remediation' is commonly used in the literature to refer to active clean-up measures such as treating, removing or engineered means of containing contamination. The terms 'remediation' and 'management' are also used interchangeably in the literature.

The clean-up and management of contaminated sites are discussed in sections 12 and 13 of DER (2014).

3 Monitored natural attenuation

Natural Attenuation (NA) refers to naturally-occurring physical, chemical and biological processes (or various combinations of these processes) that reduce the mass, toxicity, mobility, volume or concentration of organic or inorganic contaminants in groundwater (Environment Agency, 2000).

Monitored natural attenuation (MNA)
MNA refers to ongoing groundwater quality monitoring and associated field and laboratory based research that is undertaken to demonstrate that NA is taking place at a sufficiently rapid rate over a sufficient extent to protect sensitive environmental receptors from the effects of groundwater contamination.

Organic contaminants

MNA has been widely used as a remedial measure for organic contaminants in groundwater, primarily for managing contamination by petroleum hydrocarbons (Beck and Mann, 2010) and chlorinated solvents. This is because microbial processes in soils and aquifer sediments progressively break down these chemicals into harmless substances, although toxic intermediary by-products such as vinyl chloride may be produced in the case of chlorinated solvents. Under these conditions, there is a high degree of certainty that the parent chemical compounds will be eventually completely removed from soils, aquifer sediments and groundwater over a period of time.

Metals and metalloids

More recent work (US EPA, 2007a,b; US EPA, 2017) has demonstrated that the principles of MNA can also be used for managing groundwater contamination by metals and metalloids, particularly at abandoned or closed mine sites where contamination by these chemical constituents may persist for long periods of time after mining activities have ceased. However, although metals and metalloids may be removed from groundwater by adsorption onto aquifer sediments or by similar NA processes, these chemicals are not actually removed from the system, and could be potentially released back into groundwater if chemical conditions in an aquifer were to change. As a consequence of this, there is typically a higher burden of proof required to demonstrate that MNA will be an effective remedial measure for metals and metalloids than for other chemical constituents in groundwater where mass removal can be demonstrated with confidence.

4 Application and constraints

4.1 MNA processes

Monitored Natural Attenuation is a risk-based approach to managing groundwater contamination which considers the size and characteristics of the source of contamination, the characteristics of the groundwater pathway that transmits the contaminants, and the presence and sensitivity of receptors that may be affected by groundwater contamination (Figure1).
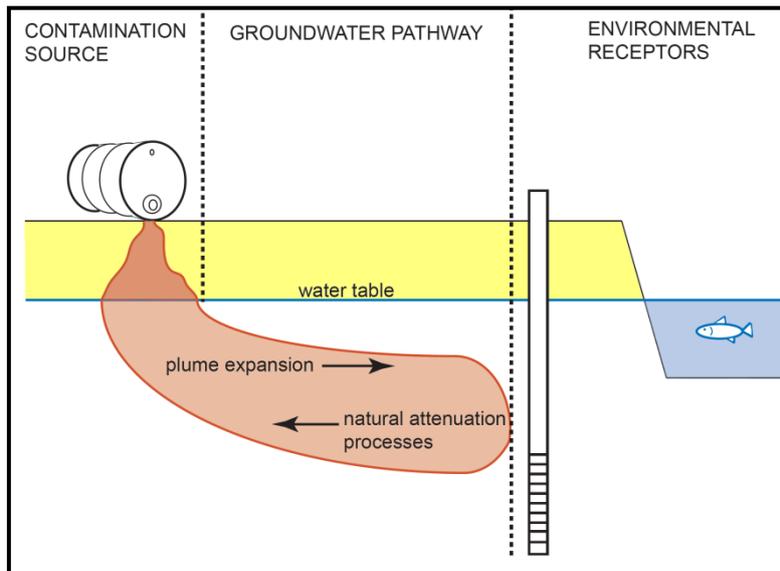
Figure 1. Assessing the environmental effects of groundwater contamination within a source-pathway-receptor risk-assessment framework.

The severity of groundwater contamination at a given site and the ultimate extent of a contamination plume will depend on the degree to which factors that cause the plume to grow (particularly the size of the contamination source and the hydraulic properties of the aquifer) are balanced by NA processes which typically retard the movement of the plume or cause the plume to shrink (Figure 1).

The dominant NA processes that affect key groups of contaminants in groundwater are summarised in Table 2.

Table 2 Dominant NA mechanisms for key groups of contaminants (adapted from Environment Agency, 2004)

Contaminant type	Examples	Meth	Ppt & ion exc	Sorp	Volat	Aer Deg	An Deg	Dehal	Fer	Comet	Redox
Chlorinated solvents (≥3 chlorine atoms)	TCE			✔	✔	✔?	✔	✔✔		✔	✔
Chlorinated solvents (<3 chlorine atoms)	DCE			✔	✔	✔✔	✔	✔	✔	✔	
Petroleum hydrocarbons	BTEX			✔	✔	✔✔	✔		✔	✔	
Fuel oxygenates	MTBE				✔	✔✔				✔	
Metals (cationic)	Hg, Cd, Pb	✔(Hg)	✔	✔✔							✔
Metals (anionic)	CrO4			✔✔							✔
Metalloids	As, Se	✔(Se)		✔✔							✔
Cyanide	CN			✔		✔					✔
PAHs	Naphthalene			✔✔		✔	✔			✔?	
Phenols	Phenol				✔	✔✔	✔✔		✔	✔	
Pesticides	Dieldrin			✔		✔	✔	✔?		✔?	

Meth – Methylation   **Ppt & ion exc** – precipitation and ion exchange   **Sorp** – Sorption and binding
Volat – Volatilisation   **Aer Deg** – Aerobic degradation   **An Deg** – Anaerobic degradation
Dehal- Dehalogenation   **Fer** – Fermentation   **Comet** – Co-metabolism
Redox – oxidation/reduction reactions

✔✔ **- PROCESS IS OF PRIMARY IMPORTANCE**   ✔ - Process is of secondary importance
✔? - Some doubt exists about the importance of the process

The purpose of MNA is to demonstrate, with monitoring and specific field- and laboratory-based research, that NA processes are taking place at a sustainable and sufficient rate to prevent a groundwater contamination plume from affecting sensitive environmental receptors such as water supply bores and aquatic environments that receive groundwater discharge (Figure 1). In general, natural attenuation processes are most likely to be effective in protecting receptors where the contamination source has been removed or has been contained to prevent or minimise contaminant discharge to groundwater.

Dilution and MNA
DWER does not consider dilution of contaminants on discharge of groundwater to an aquatic environment to be an acceptable form of NA as impacts on benthic fauna may take place even if concentrations in the overlying water column are diluted to negligible levels. This is because organisms that live in sediments at the interface between groundwater and a surface water body (the so-called 'hyporheic zone') could be subject to the impacts of the undiluted discharge of contaminants by groundwater.

In situations where groundwater contamination is discharged to a hydraulically-closed surface water environment such as a mine pit-lake, proponents/practitioners should also consider the long-term effects of evaporation and water-rock reactions on water quality and the potential environmental impacts on wildlife when considering whether MNA will be a suitable clean-up option under these circumstances.

4.2   Weight of evidence approach

It is not possible to conclusively prove whether particular NA processes are taking place below the ground. Consequently, demonstrating that natural attenuation is taking place in groundwater relies on a "weight of evidence" approach. DWER will generally require that practitioners provide at least two lines of evidence to demonstrate that MNA will be a suitable clean-up option at a particular site. The required lines of evidence will generally include:

- documented decreases in the concentration and/or mass of contaminants in groundwater over a period of time

- the presence of geochemical and biochemical indicators that indicate the natural attenuation processes are taking place; and

- for most inorganic contaminants - sediments and/or weathered rock materials in aquifers are capable of adsorbing and binding sufficient contaminants on a sustainable basis to minimise their mobility in groundwater to prevent impacts on sensitive human and environmental receptors.

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

4.3 Criteria for acceptance of MNA

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

- natural attenuation can be demonstrated with confidence;

- natural attenuation will protect sensitive receptors from contamination;

- natural attenuation can be effectively monitored;

- remedial objectives will be achieved in a reasonable time frame; and

- a contingency plan has been prepared and can be implemented if necessary.

- ***Natural attenuation can be demonstrated with confidence***
  For biodegradable organic contaminants in simple groundwater systems, this will typically require a minimum of two 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 and results to demonstrate at least two lines of evidence that the natural attenuation processes are taking place in a manner consistent with the conceptual model. Additional data will be required in heterogeneous and/or highly dynamic groundwater systems to demonstrate the performance of NA processes to a sufficient level of confidence.

  The weight of evidence required will typically be higher for inorganic contaminants like metals and metalloids, particularly at mine sites where groundwater contamination may continue to discharge for long periods of time after mine closure. For inorganic contaminants, investigations and modelling should be largely focussed on the ability of the aquifer materials to adsorb and bind contaminants on a sustainable basis (US EPA, 2007a, US EPA, 2015). This work will be necessary before DWER will consider MNA to be a viable clean-up option.

- ***Natural attenuation will protect sensitive receptors***
  Natural attenuation processes should prevent groundwater contamination affecting groundwater dependent ecosystems, or affecting the quality of water pumped from bores. The expansion of the contamination plume into uncontaminated groundwater should be minimised as far as possible, and will only be acceptable if it can be demonstrated that sensitive receptors and environmental values are protected. DWER may accept MNA as a clean-up 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 and other groundwater users from contamination and that these measures are acceptable to stakeholders following community engagement.

- ***Natural attenuation can be effectively monitored***
  The monitoring program must be sufficiently detailed to demonstrate that natural attenuation is occurring according to expectations. This requires that there is an adequate number of suitably constructed and maintained monitoring bores, and that the bores are monitored consistently for a suite of chemical parameters that will provide evidence of natural attenuation. The proponent/responsible person must also ensure that access to all monitoring bores can be guaranteed on a long-

term basis, particularly for bores that may be located on neighbouring properties (including 'affected sites'). The proponent/responsible person should also ensure that sufficient funding is available for implementing the monitoring program (including maintenance of the monitoring bore network) over the entire time period that is predicted to be necessary for the MNA programme to achieve the remediation objectives. Requirements for Site Management Plans are detailed in DER (2014).

- ***Remediation objectives will be achieved in a reasonable time frame***
  DWER will generally require that contamination levels in groundwater will be reduced to background levels or an agreed remedial target concentration or mass flux within a "reasonable" time frame. This should be no longer than 30 years, or a time period of about one generation. The time-scale for MNA to achieve the remedial objectives should also be reasonable when compared with other remedial options.

  - ***A contingency plan has been prepared and can be implemented if necessary***
  DWER requires that proponents/responsible persons who wish to use MNA as a remedial option provide achievable contingency plans for alternative clean-up strategies in the event that natural attenuation is unable to meet the remediation objectives. DWER may also require proponents/responsible persons to demonstrate that sufficient funding is available to implement contingency plans as a condition of approving the use of MNA as a remedial option at specific sites.

5 Structured approach for implementing MNA

5.1 Overview of technical criteria

DWER recommends that practitioners assess and implement an MNA program according to the staged process outlined in Figure 3 which has been adapted from the process developed by the Environment Agency. The stages outlined are comparable with the staged approach presented in Beck and Mann (2010) and includes the appropriate development and application of data quality objectives for MNA. The key steps in the process are summarised below and are described in more detail in subsequent sections of this guideline.

The initial **screening** stage (Section 6) 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 both practitioners and regulators with a quick yes/no assessment based on preliminary data for the site. It is assumed at this stage that sufficient investigations have been undertaken in accordance with the NEPM and DWER guidelines to characterise the spatial distribution of contamination at the site. An initial conceptual model of NA processes is then developed based on these data and on a general understanding of the geochemical behaviour of the contaminants present.

In the **demonstration** and **prediction** stages (Sections 7 and 8) additional field and laboratory data are collected and modelling is undertaken to characterise NA processes in more detail. During these stages, a comprehensive conceptual model is developed of the processes that are taking place at the site to reduce contaminant concentrations or mass in groundwater beneath the site. The aim of these stages is to provide scientifically and legally defensible data to support the use of MNA as a clean-up measure at the site. The level of information required in these stages will depend on both the nature of contamination present at the site, and on the proximity and characteristics of the relevant receptors. These factors will determine the performance criteria (remediation objectives) that are applicable to the successful clean-up of groundwater contamination at the site. Practitioners are also generally required to develop contingency plans during these stages to ensure that alternative management measures are available in the event that monitoring indicates that NA processes are not effectively removing contaminants from groundwater.

The **implementation** stage (Section 9) covers the long-term performance monitoring carried out to determine whether the NA taking place is consistent with modelled predictions. Contingency plans are implemented in the event that MNA does not perform to expectations.

It is important that the conceptual model, based on the hydrogeological and geochemical information from the site, is constantly challenged and revised as more information becomes available. The process of revision progressively reduces uncertainty and conservatism, which provides greater confidence in management decisions.
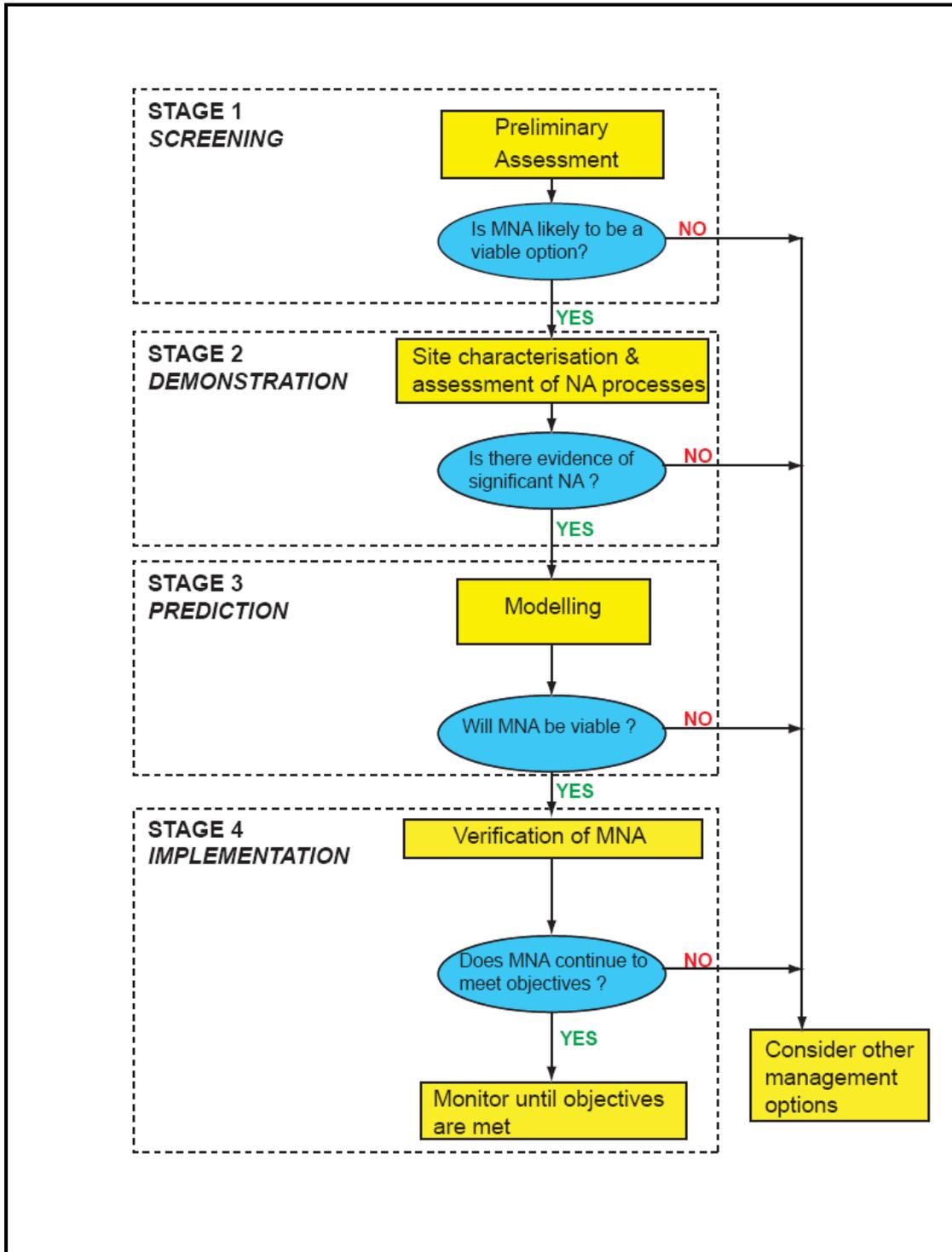
Figure 3: Process for implementing MNA as a clean-up option at a site (adapted from Environment Agency, 2000)

5.2 Overview of socio-economic and administrative considerations

5.2.1 Introduction

In addition to the technical factors outlined in Section 5.1 there are a number of social, financial and administrative issues that should be considered before selecting MNA as a remedial measure at a site. These issues include:

- consultation with relevant stakeholders;

- time scale for clean-up;

- classification under the CS Act; and

- sustainability considerations, including the costs and benefits of MNA compared with active clean-up.

5.2.2 Consultation with relevant stakeholders

The acceptance of MNA as a clean-up measure usually requires the agreement of a wide range of stakeholders including DWER, affected land owners (such as private landowners, local government authority and Main Roads) as well as financiers, insurers, and potentially the prospective purchasers of the site. It is also recommended that relevant indigenous communities are consulted where the site may have a special cultural significance for those communities. Neighbouring land owners and indigenous communities may need to be consulted to secure access for monitoring bores beyond the site boundary, or to discuss the effects of the clean-up program on groundwater resources in the area.

Regular consultation with DWER (and/or the contaminated sites auditor appointed for the site) is recommended during the assessment process to ensure that the information gathered and the proposed monitoring program will meet the regulatory requirements of DWER.

Guidance on community engagement is provided in DER (2014) and the NEPM.

5.2.3 Time-scale for clean-up

The application of MNA at a particular site is likely to take many years to reach a satisfactory outcome. This long time frame for completion potentially makes MNA susceptible to changes in various technical, economic and regulatory conditions. These factors generally require financial provisions to be set aside to manage the long-term monitoring program or the implementation of contingency plans.

5.2.4 Classification under the *Contaminated Sites Act 2003*

The source site is most likely to be classified as *contaminated - remediation required* until the remediation objectives of the site are achieved. At this point, the source site may be classified as *remediated for restricted use* or *decontaminated* depending on the site-specific circumstances and the effectiveness of NA processes. Any associated affected site may also be classified as *contaminated - remediation required* or *contaminated - restricted use* depending on the site-specific circumstances.

For further information on the administration of the CS Act and site classifications refer to DER (2017).

5.2.5 Sustainability considerations

The evaluation of potential remedial options is an important stage in developing the remedial strategy for a site (DER 2014). When deciding on the appropriate remedial approach, the sustainability[1] of the potential options should be considered.

In many cases, the overall cost of implementing MNA will be considerably lower than for active groundwater clean-up measures. However, as a large body of evidence is generally required to demonstrate that natural attenuation processes are taking place at a site, the initial investment in undertaking investigations to obtain specific geochemical information is typically high. The cost of undertaking field and laboratory investigations may be much higher than is generally required to undertake a routine assessment of the nature and extent of contamination at a given site.

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[1] For the purposes of the *Cost Benefit and Sustainability Analysis* guideline being developed as part of the National Remediation Framework (refer section12 in DER 2014), sustainability refers to "the practice of demonstrating, in terms of environmental, economic and social indicators, that an acceptable balance exists between the effects of undertaking remediation activities and the benefits that those activities will deliver."

6 Stage 1 – screening process to assess the viability of MNA

6.1 Introduction

The degree to which MNA is likely to be a viable clean-up option at a given site will depend to a large extent on the chemical and physical properties of the contaminants, the physical properties of the aquifer and on the proximity and sensitivity of human and environmental receptors near the site. As a prerequisite for determining the extent to which these factors will apply at any given site, it is essential that soil and groundwater investigations are carried out at the site in accordance with DWER guidelines and the NEPM.

6.2 Chemical properties of contaminants

In general, MNA is likely to be most successful where contaminants have the following chemical and physical properties:

- **the contaminants are organic compounds**

This is because organic chemical compounds are generally broken down in soil and groundwater by microorganisms (the process of biodegradation) and natural attenuation of these compounds is irreversible. In situations where sources of contamination have been removed, the resulting groundwater contamination plumes will progressively shrink and dissipate (Figure 3), although contamination may persist for long periods if a large contaminant mass is present or if the organic compounds are particularly resistant to biodegradation.

By contrast, many (but not all) inorganic compounds are removed from groundwater by reversible natural attenuation processes such as sorption of metals by clay and iron oxide minerals on aquifer sediments. Although these processes will also cause dissolved contamination plumes to shrink, a halo of residual contamination will remain in the aquifer substrate (Figure 3) which could be released back into groundwater if chemical conditions in the subsurface were to change. This factor does not exclude MNA as a clean-up option for inorganic contaminants such as metals, but does mean that practitioners will need to undertake specific investigations to determine the nature of natural attenuation processes that are removing these contaminants from groundwater. For MNA to be viable, these investigations should indicate that contaminants are unlikely to be released back into groundwater under a wide range of chemical conditions in the aquifer.
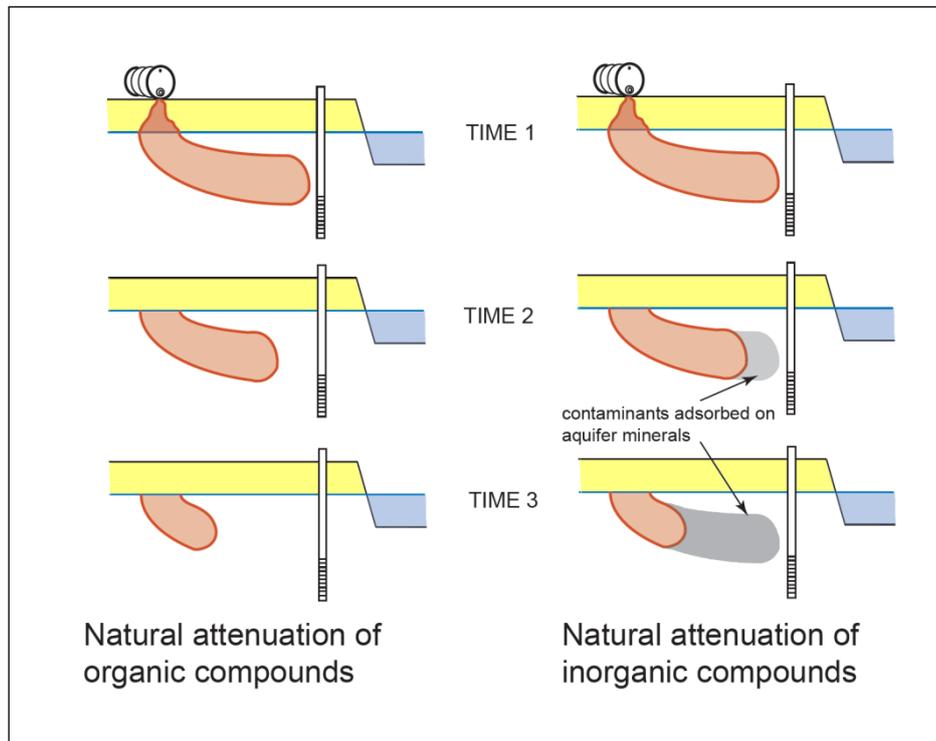
Figure 3: Shrinking of groundwater contamination plumes due to natural attenuation processes for organic (destructive, irreversible NA processes) and inorganic contaminants (generally non-destructive, reversible NA processes).

- *the contaminants have a low toxicity*

Contaminants that have a low toxicity at high concentrations, or that have an extremely low solubility relative to environmental investigation levels, are less likely to reach concentrations that will cause environmental harm in a groundwater contamination plume than more toxic compounds.

- *the contaminants are rapidly broken down by microorganisms*

Contaminants that are rapidly degraded into less toxic by-products are less likely to reach concentrations of environmental concern within a groundwater contamination plume than less readily degraded compounds that may be broken down into more toxic by-products.

Table 2 summarises the applicability of MNA to key groups of groundwater contaminants based on an assessment of their chemical properties and on the current level of understanding about their behaviour in groundwater flow systems.

Table 2. Applicability of MNA to key groups of chemical contaminants (Adapted from US Department of Energy, 2001)

Contaminant type	Level of understanding	Likelihood that MNA will be successful
Hydrocarbons		
BTEX (dissolved hydrocarbons)	High	High
Petrol, diesel (NAPLs present)	Moderate	Moderate
Non-volatile aliphatic compounds	Moderate	Low
PAHs	Moderate	Low
Creosote (phenolics)	Moderate	Moderate
Oxygenated Hydrocarbons		
Low molecular weight alcohols, ketones, esters	High	High
MTBE	Moderate	Low
Halogenated aliphatic compounds		
Trichloroethene (TCE), carbon tetrachloride	Moderate	Low
Trichloroethane (TCA)	Moderate	Low
Methylene chloride	High	High
Halogenated aromatic compounds		
PCBs, pentachlorophenol, multichlorinated benzenes	Moderate	Low
(Mono) chlorobenzene	Moderate	Moderate
Metals		
Ni, Cu, Zn, Pb, Cr	Moderate	Moderate

Cd, Hg, U	Moderate	**Low**
Metalloids		
As, Se	Moderate	**Low**
Nutrients		
Nitrate	High	**Low**
Ammonium	Moderate	**Low**

Likelihood of success:

High – scientific knowledge and field evidence are sufficient to expect that MNA will protect human health and the environment at more than 75% of sites

Moderate – MNA will meet regulatory standards at about 50% of sites

Low – MNA will typically be unsuccessful at 75% of sites

Table 2 indicates that MNA is most readily applicable to low-molecular weight, highly soluble hydrocarbon compounds, and that MNA is likely to be much less successful if hydrocarbon liquids which have a low miscibility with water (Non-Aqueous Phase Liquids or NAPLs) are also present at the site. This can be a problem at many sites where petroleum hydrocarbons have leaked from storage tanks as NAPLs beneath the ground can be an ongoing source of dissolved hydrocarbon contamination that can continue for many years after the surface of the site has been cleaned up. Successful clean-up of such sites may require NAPL contaminated soil to be removed from beneath the site or otherwise contained before clean-up of the groundwater plume by MNA is effective.

Dissolved groundwater contamination plumes produced by spills or leaks of petroleum hydrocarbons are biodegraded in aquifers by microorganisms that utilise a variety of electron accepting chemical reactions for respiration. As there is only a limited amount of dissolved oxygen present in groundwater, microorganisms that use oxygen reduction for respiration (aerobic respiration) are only able to metabolise hydrocarbon compounds on the fringes of contamination plumes. In the absence of oxygen, other electron acceptors are utilised for biodegradation which, in order of declining energy yield and reaction rates, are nitrate reduction, iron (III) reduction, sulfate reduction and carbon dioxide reduction (methane production or methanogenesis) within hydrocarbon plumes. These biochemical reactions take place in a hierarchical manner controlled by the availability of electron acceptors, giving rise to a distinct pattern of zones within plumes where particular electron-accepting reactions dominate (Figure 4).
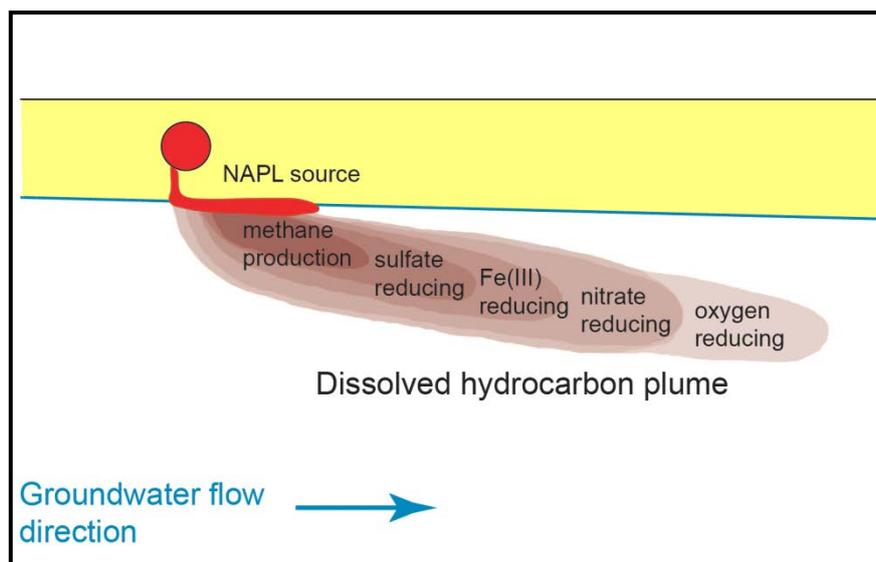
Figure 4. Hierarchy of electron acceptors utilised by microorganisms in the biodegradation of contamination plumes caused by leaks of petroleum hydrocarbons

The same zonation takes place within a wide range of contamination plumes that contain dissolved carbon-based compounds, including plumes associated with landfill sites. These biochemical reactions produce a distinct suite of reaction products that can be used to quantify the extent to which a plume is being biodegraded, but there are a number of chemical conditions that can limit the viability of some biodegradation processes which should be considered when screening whether MNA is likely to be a suitable clean-up option at a site. These conditions can be assessed using preliminary field measurements and include:

Groundwater pH

The optimal pH for microbial degradation of most organic contaminants in groundwater usually lies in the range of about 6.0 to 8.5. Biodegradation may be severely impeded under acidic conditions, particularly where the pH of groundwater is less than about 5.0. Similarly, the ability of aquifer materials to adsorb metals is greatly reduced under acidic conditions.

Dissolved oxygen concentrations

Aerobic degradation of organic compounds is unlikely to take place in groundwater where the dissolved oxygen concentration is less than about 1 mg/L. Conversely, nitrate contamination is unlikely to be degraded by the process of denitrification in well-oxygenated groundwater.

Oxidation-reduction potential

Although field measurements of oxidation-reduction potential (Eh) are generally only an approximation of actual redox conditions in an aquifer, these measurements can give a preliminary indication of the electron acceptor processes that are likely to be taking place in a contamination plume.

Dominant degradation mechanism	Eh conditions (approximation)	comment
Aerobic reduction	more than +150mV	
Nitrate reduction	-150 to +50 mV	Mildly reducing conditions
Iron(III) and sulfate reduction	Less than -200 mV	Arsenic and selenium may be desorbed from aquifer sediments under conditions where iron(III) reduction takes place due to the dissolution of ferruginous coatings which typically contain a high concentration of these elements.

Significant biodegradation of chlorinated hydrocarbon compounds (through the process of reductive dehalogenation) may only take place where measured Eh values are less than about -400 mV, which rarely occurs under natural conditions and generally requires the use of strong reducing agents like zero-valent iron to achieve this condition in an aquifer.

6.3 Aquifer properties

The physical properties of aquifers also have a strong influence on how difficult and costly it is to demonstrate that natural attenuation processes are taking place. These characteristics should be considered during the screening stage.

Typically, it is much easier to demonstrate that natural attenuation is taking place in homogenous, porous-medium aquifers such as unconsolidated sands because groundwater flow directions and rates are more predictable in these aquifers than in fractured rock systems. This means that monitoring bores can be generally sited in suitable locations to determine the extent and severity of a groundwater contamination plume with a high level of confidence.

By contrast, it is more difficult to determine the distribution of contamination in a fractured rock aquifer due to the presence of preferred groundwater flow paths which may be difficult to identify during site investigations. Additionally, high groundwater flow rates in large fractures may limit the contact-time between groundwater and the aquifer matrix, limiting the effectiveness of natural attenuation processes to reduce contaminant concentrations. Although these factors do not necessarily exclude the use of MNA as a remedial measure at sites underlain by fractured rock aquifers, a large number of monitoring bores may be required to adequately determine the distribution and behaviour of groundwater contamination.

As the rate of groundwater flow often exerts a strong control on natural attenuation in aquifers, it is recommended that practitioners make a preliminary estimate of this parameter during the screening process for a site using the equation:

V (m/year) = (hydraulic conductivity (m/day) x hydraulic gradient) / aquifer porosity

If no aquifer testing has been undertaken at the site, values of hydraulic conductivity for sediments from the superficial aquifer on the Swan Coastal Plain can be estimated from site-specific lithological data using values listed in Table 3. Practitioners should seek expert hydrogeological advice regarding estimated hydraulic conductivity values for other aquifers.

Hydraulic gradients should be determined using site-specific water level measurements from appropriately constructed monitoring bores.

Table 3 Typical values of hydraulic conductivity for sediments from the superficial aquifer on the Swan Coastal Plain (adapted from Davidson, 1995)

Lithology	Hydraulic Conductivity (m/day)
Sandy materials	
- *very coarse grained sands to gravels*	250
- *very coarse grained sands*	200
- *coarse grained sands*	75
- *medium to very coarse sands (moderately sorted)*	50
- *fine sands to gravel (poorly sorted)*	10
- *medium grained sand*	15
- *fine to medium grained sand*	8
- *fine grained sand*	4
- *fine to very fine grained sand*	2
- *very fine grained sand*	1
- *silty sand*	4
- *clayey sand*	1
Clay	0.5
Sand and limestone (e.g. Ascot Formation)	8
Limestone and calcarenite (e.g. Tamala Limestone)	500

Aquifer porosities can generally be assumed to lie in the range of 0.25 to 0.35 (i.e. 25 to 35%) in sandy aquifers such as those that occur on the Swan Coastal Plain. The porosity weathered bedrock aquifers (particularly weathered granites) are typically in the range of 0.05 to 0.15 (i.e. 5 to 15%: refer to Navarre-Sitchler et al., 2015).

Monitored natural attenuation may not be an effective management option at sites where groundwater flow rates exceed about 100 m per year (Environment Agency, 2000).

6.4   Regulatory and socio-economic constraints

In addition to the physical factors described above, there are a variety of regulatory and socio-economic issues that should be considered when assessing whether MNA is likely to be a suitable groundwater clean-up option for a site. In particular, DWER

does not consider MNA to be a suitable groundwater clean-up option in areas which are zoned as P1 or P2 public water source protection areas, or within 100 m of Conservation-category or Ramsar wetlands.

> Information about the locations of public water source protection areas is available from the DWER website.
>
> Contact Department of Biodiversity, Conservation and Attractions for advice on the location of Conservation-category and Ramsar wetlands in the state.

As MNA may need to continue for several years for management objectives to be achieved, DWER will typically require a high level of commitment from proponents/responsible persons to fund and maintain the required monitoring program at the screening stage. DWER will also consider whether groundwater contamination plumes extend beyond property boundaries to affect other bore users and environmental values at the screening stage.

It is recommended that practitioners use **Table 4** to determine the likely feasibility of MNA as a groundwater clean-up option at a site based on a number of physical and socio-economic factors. DWER will generally not accept the use of MNA as the sole groundwater clean-up measure at sites where the screening process in Table 4 indicates that there is a "low feasibility" of successful clean-up by this measure. At these sites, DWER will generally require additional active groundwater clean-up measures to be implemented to improve the likelihood of a successful outcome.

Table 4. Summary of screening criteria to assess MNA feasibility

Screening criteria	High feasibility	Medium feasibility	Low feasibility
Technical screening criteria			
Source of groundwater contamination	Removed	Being removed	Continuing or unknown
Extent and severity of groundwater contamination	Well defined		Poorly defined
Nature of contamination plume	Shrinking	Stable	Expanding
Persistence of contamination in groundwater	Readily attenuated (degraded) under site conditions	Not readily degraded under site conditions	Attenuation processes poorly understood
Aquifer heterogeneity	Homogenous, porous medium		Heterogeneous, fractured rock
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 water 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 m of the site	None within 100 m of the site	Conservation-category wetland within 100 m of the site
Level of confidence in monitoring data	High – more than 2 years of representative data	Moderate – 2 years of representative data	Low – single set of representative monitoring data

Screening criteria	High feasibility	Medium feasibility	Low feasibility
Level of confidence in the understanding of the distribution of contamination	High – e.g. dissolved substances in a shallow homogenous aquifer		Low – e.g. 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 (i.e. those in shaded cells)	One or more critically important criteria, or no factors of "High" rating

7 Stage 2 – demonstrating natural attenuation at a site

7.1 Lines of evidence

The purpose of the demonstration stage is to show quantitatively that natural attenuation is taking place at a site at a rate that will achieve the remediation objectives in a time frame that is acceptable to DWER and stakeholders. This requires providing at least two lines of evidence that natural attenuation is occurring in a manner consistent with the conceptual model developed for the site.

7.1.1 Primary lines of evidence

Historical concentration data are used to demonstrate a trend of reducing contaminant _concentrations_ along the groundwater flow path down-gradient of the source. DWER may require that concentration decreases with time are statistically significant using the Mann-Kendall (Appendix A) or similar statistical tests. This form of evidence shows that attenuation is taking place, but does not indicate the mechanisms responsible for reducing contaminant concentrations in groundwater.

7.1.2 Secondary lines of evidence

These involve measuring changes in geochemical data to prove a loss of contaminant _mass_ from groundwater. This can be achieved by using graphs to show that the concentration of the contaminants decrease with distance downgradient of the contaminant source and over time in individual monitoring bores. Similar plots of specific electron acceptors should also show rising or decreasing trends in accordance with the specific biogeochemical processes that are leading to a loss of mass of organic contaminants. Ideally, contour plots of contaminant concentrations over various time periods should indicate that the plume is shrinking over time or is stable.

7.1.3 Tertiary lines of evidence

These apply to biodegradable organic contaminants, and 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. Information on the microbial and isotopic techniques that can be used to provide this line of evidence can be found in NJDEP (2012) and Beck and Mann (2010).

The following sections provide guidance on collecting and interpreting information from field and laboratory studies to demonstrate that MNA will be a viable option for groundwater clean-up at a site.

7.2   Establishing a network of monitoring bores

The establishment of a suitable network of groundwater monitoring bores is a prerequisite for undertaking a successful MNA program. Although monitoring bores may have been drilled and constructed during the initial contaminated site investigations, there may be insufficient bores to adequately characterise the full extent and spatial distribution of contamination in the aquifer for the purposes of MNA. Consequently, additional bores may need to be installed prior to commencing an MNA program.

A number of site-specific factors should be considered when designing the MNA monitoring network, particularly the complexity of the local hydrogeology, the nature and severity of groundwater contamination, and the number and sensitivity of receptors that are at risk of being affected by the contamination. These factors will affect the number and distribution of bores required for any given site, making it impossible to be prescriptive about monitoring requirements. However, as a minimum requirement, an MNA monitoring network should include (Figure 5.1):

- a background bore that is located at a sufficient distance up-gradient of the source of contamination for groundwater monitoring to indicate natural background levels of water quality parameters associated with the contamination source;

- a bore located near the contamination source;

- nests of bores located at least two sites along the central axis of the contamination plume (at each of these locations, bores should be screened at varying depths to determine the vertical distribution of contamination within the aquifer); and

- sentinel bores located beyond the toe and lateral edges of the plume that are screened at suitable depths to detect the expansion of the plume.

In situations where monitoring indicates that contamination has reached existing sentinel bores, DWER will generally require new sentinel bores to be installed further down gradient to ensure that groundwater monitoring continues to determine the full spatial extent of groundwater contamination at the site. At sites where there is a significant risk of contamination affecting environmental receptors, DWER may also require additional bores to be constructed on transects across the contamination plume to develop control planes to monitor changes in the mass-flux of contaminants (refer to section 7.6).
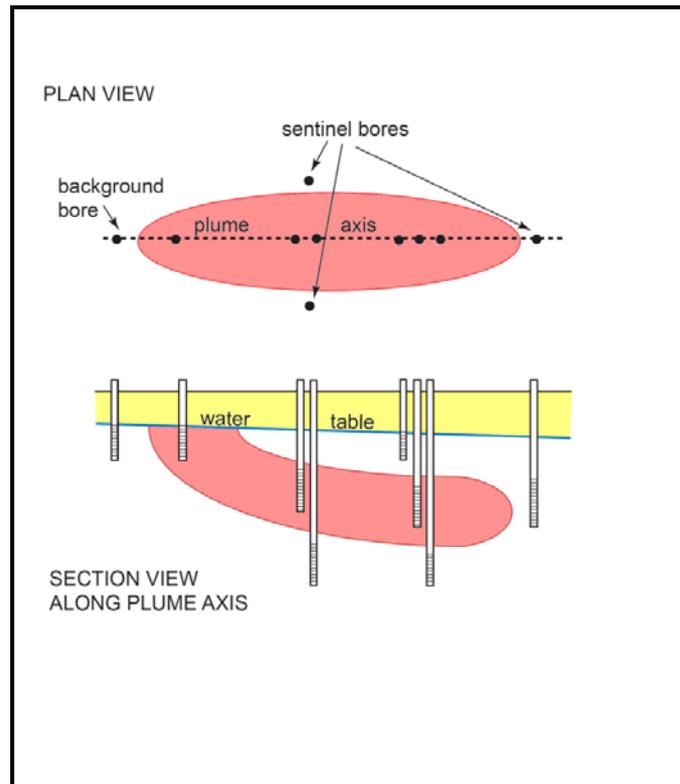
Figure 5.1. Minimum requirements for a groundwater monitoring network for MNA

The construction of monitoring bores should be compatible with the proposed groundwater sampling equipment. Casing materials should be chemically inert in the groundwater conditions present at the site. Monitoring bores are typically constructed with PVC casing with a machine-slotted section over the sampling interval (Figure 5). DWER recommends that monitoring bores are constructed to allow low-flow pumping or passive sampling techniques wherever possible, such as short screened intervals (≤3 m long) and narrow diameter casing (≤ 50 mm diameter) to minimise purging requirements or the risk of vertical mixing in boreholes during sampling.

 For further information on monitoring bore construction refer to NEPM Schedule B2.
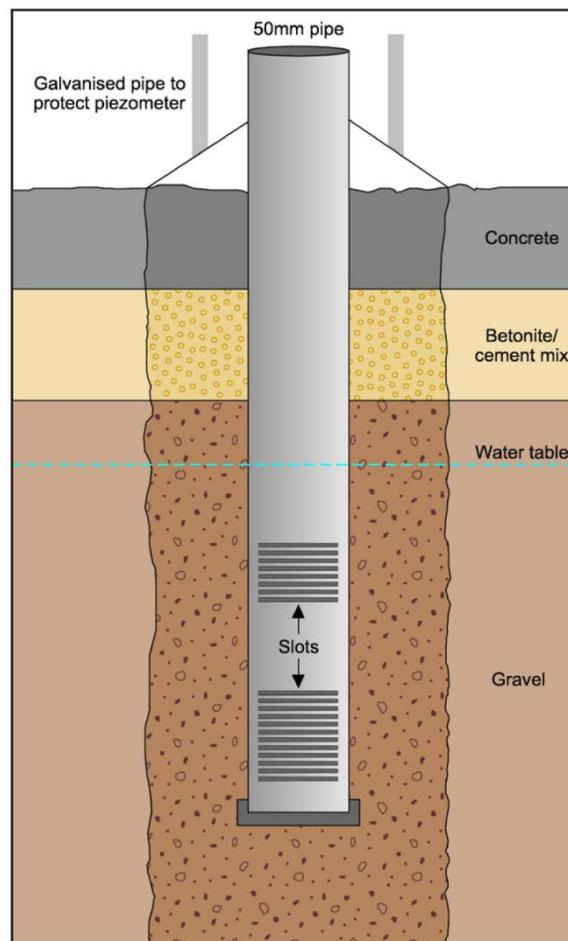
Figure 5. Typical construction of a groundwater monitoring bore (Sundaram et al., 2009)

There are a number of field measurements that can be used to indicate the presence of a range of contaminants during drilling and which can be used to guide the construction of monitoring bores such as the location of screened intervals. Typically, one or more of these tests would be carried out at 25 cm intervals on wet cuttings obtained during the drilling of an investigation borehole. Example field measurements are listed in Table 5.

Table 5. Field indicators that may be used to identify the presence of groundwater contamination during a drilling program

Field Indicator	Method of measurement	Example land uses associated with contamination	Characteristics of field indicator
pH measurements on cuttings or in a cuttings-water slurry	pH meter, pH test-strips	Mine sites, landfill sites	Low pH values typically occur in acidic groundwater from mine sites, pH values within a plume from a landfill site are typically more alkaline than uncontaminated groundwater.
Eh[*] measurements on a cuttings-water slurry	pH and Oxidation-Reduction Potential (ORP) meter	Landfill sites, service stations	Eh values within landfill leachate and dissolved hydrocarbon plumes are typically much lower than in uncontaminated groundwater
Electrical conductivity measurements on a cuttings-water slurry	EC meter	Landfill sites, mine sites, industrial sites	EC values within landfill leachate and inorganic contamination plumes are typically much higher than in uncontaminated groundwater
Ammonium measurements on a cuttings-water slurry	Ammonium test kit	Landfill sites, sewage treatment plants, septage disposal	Contamination plumes from landfills and sewage treatment sites usually contain high concentrations of ammonium, whereas concentrations are usually negligible in uncontaminated groundwater and sediments
Soluble sulfide measurements on a cuttings-water slurry	Sulfide colorimetric test kit	Landfill sites, service stations	Sulfides are produced in plumes containing organic matter and petroleum hydrocarbons as a result of sulfate reduction
Volatile hydrocarbons from cuttings	PID meter	Service stations, fuel depots, workshops, dry cleaners	Soil and groundwater near fuel spills often contains elevated levels of volatile hydrocarbons
Alkalinity in a cuttings-water slurry	Alkalinity test kit	Landfill sites, service stations	Alkalinity values within landfill and dissolved hydrocarbon plumes are typically much higher than in uncontaminated groundwater and sediments

[*] Where ORP measurements have been made with a platinum electrode calibrated with Zobell's solution, Eh is approximately equal to (ORP + 244) mV

7.3 Groundwater sampling procedures

Sampling for the purposes of MNA should be as non-intrusive as possible to ensure that redox-sensitive or volatile chemical constituents are not lost from solution during the sampling event. As a consequence, DWER will generally require that sampling in an MNA program is carried out using low-flow pumping or passive sampling techniques.

Although most sampling in water resource investigations is carried out using submersible pumps pumping at high rates to displace at least three casing-volumes of water (see e.g. Sundaram *et al.*, 2009), this sampling technique may cause problems when sampling contaminated groundwater. Excessive drawdown caused by high-rate pumping (Figure 7a) may mobilise contaminants in LNAPL smear zones in aquifers; may lead to the loss of volatiles from solution; and may cause the oxidation of dissolved iron and the loss of dissolved metals by sorption on iron oxyhydroxide colloids that are typically formed under these pumping conditions. These factors can lead to misleading chemical analysis results for contaminated groundwater. This form of sampling may also generate a large volume of contaminated effluent which will require appropriate disposal arrangements to prevent adverse environmental impacts.

Similarly, surging associated with the use of bailers (Figure 7b) or inertial pumps with a foot-valve ("jiggle" pumps) can increase the level of turbidity and oxygen within sampled water, affecting the concentration of volatile and redox-sensitive chemical constituents in groundwater samples collected using these sampling techniques.
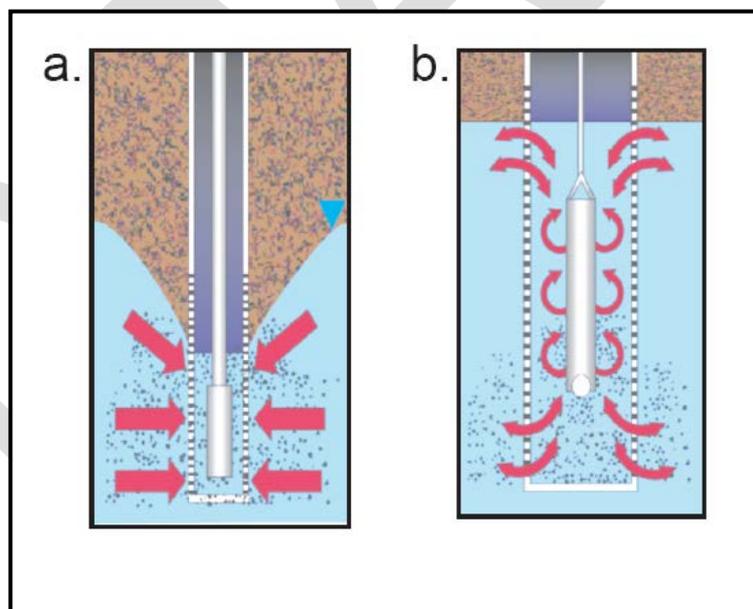
Figure 7. Sampling problems associated with the use of (a) high flow -rate pumps and (b) bailers or inertial pumps with a foot-valve ("jiggle" pumps).

By contrast, low-flow groundwater sampling (Figure 8) minimises the drawdown of the water table and vertical mixing within the borehole. Samples collected by this technique are less likely to suffer from the loss of volatiles, and the low level of turbidity in pumped water means that metal loss by sorption on colloids is greatly reduced. Pumping rates in low-flow sampling are typically of the order of 0.1 – 0.5 litres per minute to ensure that water is sampled directly from the aquifer with minimal mixing within the water column in the monitoring bore (Puls and Barcelona, 1996). For a detailed description of the procedures used in low-flow groundwater sampling, refer to Puls and Barcelona (1996).
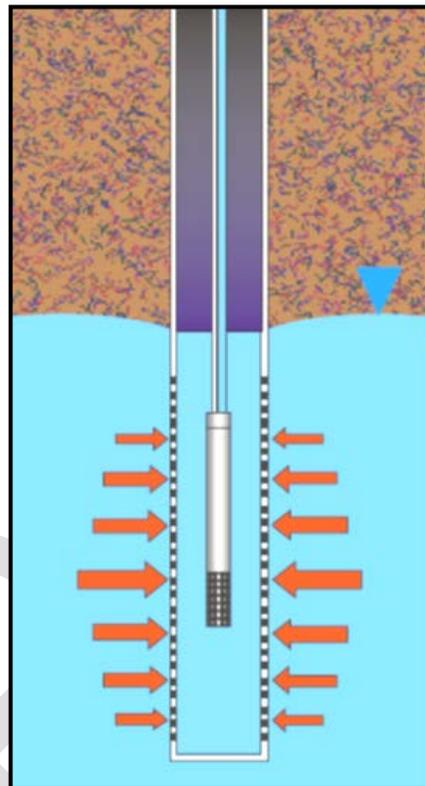
Figure 8. Low-flow groundwater sampling showing laminar groundwater flow to the sampling pump and minimal drawdown of the water table

DWER may also accept the use of some passive (no-purge) sampling techniques in MNA programs. These are devices that use the natural groundwater flow to obtain a sample without disturbing the water column in a monitoring bore by pumping (ITRC, 2006). Six passive sampling systems have been approved for use by State and Federal government regulatory agencies in the USA (USGS, 2001; ITRC, 2007), and these will also be accepted for use by DWER. The six passive sampler technologies fall into three categories on the basis of sampler mechanism and on the method of sample collection. These are:

- **Devices that rely on diffusion and sorption to accumulate analytes in a sorptive matrix**

  Samples are a time-integrated representation of conditions at the sampling point over the period of deployment of the device. The accumulated mass and

duration of deployment are used to calculate analyte concentrations in groundwater. The **GORE® Module** is an example of this type of sampler.

- *Devices that recover a grab-sample of water within a monitoring bore*

    Samples are an instantaneous representation of conditions in the monitoring bore at the time of sample collection. The two devices of this type which have been approved for use are the **HydraSleeve™** and **Snap Sampler™**.

- **Devices that rely on diffusion of analytes across a membrane into high-purity water**

    Samples are a time-integrated representation of conditions over the period of deployment (generally over a 2-4 week period). The approved samplers of this type are the regenerated-cellulose dialysis membrane (**Dialysis**) sampler, the rigid, porous polyethylene (**RPP**) sampler, and the polyethylene-based passive diffusion bag (**PDB**) sampler.

For further information about passive samplers, refer to USGS (2001) and ITRC (2006; 2007) and Schedule B2 of the NEPM.

7.4 Groundwater sampling and analysis

Samples collected in groundwater sampling programs are typically analysed for a range of chemical parameters that provide evidence that natural attenuation processes are taking place in the aquifer (Table 6). Additionally, DWER will require that measurements of temperature, conductivity, pH and Eh (oxidation-reduction potential) are made on samples in the field using appropriately calibrated equipment. If passive sampling techniques are being used, field measurements should be made using meters equipped with downhole electrodes, otherwise in-flow meters should be used.

Contaminated groundwater may react with sediments or rock materials in aquifers to release a wide range of toxic constituents into groundwater and DWER may require additional chemical analyses to be carried out to assess the risks of this taking place at a given site. In particular, acidic groundwater may release potentially harmful metals including aluminium, cadmium, copper, chromium, lead, nickel, thallium, uranium and zinc into groundwater. Alkaline groundwater contamination plumes may cause metalloids, including arsenic and selenium, to be leached from the aquifer matrix, together with some metals including aluminium, cadmium, chromium, molybdenum, vanadium, uranium and zinc. Highly reducing conditions in plumes undergoing biodegradation may cause arsenic to be released into groundwater as a result of the reductive dissolution of ferruginous coatings from aquifer sediments (Cozzarelli et al 2015).

DWER will generally require groundwater samples to be collected and analysed on at least a three-monthly basis during the demonstration phase of an MNA program. DWER may allow the sampling frequency to be reduced in situations where sufficient representative sampling has occurred to demonstrate statistically significant

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decreases in contaminant concentrations over at least a two-year period and where there is a negligible risk of adverse impacts on sensitive environmental receptors and environmental values.

Detailed guidance on assessing the statistical significance of concentration trends can be found in Idaho Department of Environmental Quality (2014).

Table 6. Chemical parameters measured by field tests and laboratory analysis to provide evidence of natural attenuation (adapted from Environment Agency, 2000).

| Chemical parameter | Contaminant applicability | | Line of evidence | Comments |
	organics	inorganics		
Contaminant concentration	✓	✓	Primary	Provides a measure of the distribution of contamination in groundwater and of concentration changes with time
Contaminant degradation products	✓		Primary	Provides a measure of the degradation rate of contaminants in groundwater
Naturally occurring toxic constituents mobilised by the reaction of contaminated groundwater with aquifer materials	✓	✓	--------	Metals may be mobilised under acidic conditions. Arsenic may be mobilised by the reductive dissolution of ferruginous coatings on aquifer sediments under iron reducing conditions. Arsenic and selenium may accumulate in mine pits receiving contaminated groundwater discharge
Dissolved oxygen	✓		Secondary	Highest energy yielding electron acceptor for the biodegradation of organic contaminants. Concentrations below 0.5 mg/L generally indicate anaerobic degradation
Nitrate	✓		Secondary	In the absence of oxygen, the highest energy yielding electron acceptor for the biodegradation of organic contaminants
Dissolved manganese	✓		Secondary	Indication of Mn(IV) reduction during the biodegradation of organic compounds

Chemical parameter	Contaminant applicability		Line of evidence	Comments
	organics	inorganics		
Dissolved iron (mostly Fe^{2+})	✓	✓	Secondary	Indication of Fe(III) reduction during the biodegradation of organic compounds. Indicator of iron mobility under acidic conditions
Sulfate	✓	✓	Secondary	Used as an electron acceptor in the biodegradation of organic compounds. Produced by the oxidation of sulfide minerals
Dissolved sulfides	✓		Secondary	Produced by sulfate reduction during the biodegradation of organic compounds
Methane	✓		Secondary	Produced from the reduction of carbon dioxide during the biodegradation of organic compounds
Ethane and ethene	✓		Secondary	Indicators of the biodegradation of chlorinated solvents
Dissolved hydrogen	✓		Secondary	Indicator of the biodegradation of organic compounds
Total organic carbon	✓	✓	Secondary	A measure of the amount of carbon available to assist with the degradation of chlorinated solvents. Also an indicator of the ability of aquifer materials to trap and contain metals
pH	✓	✓	Secondary	Indicator of metal mobility and of bacterial activity for biodegradation
Alkalinity	✓	✓	Secondary	Produced by the biodegradation of organic compounds. Indicator of aquifer buffering capacity
Eh (oxidation-reduction potential)	✓	✓	Secondary	A measure of the capacity of the aquifer to sustain a range of attenuation processes
Chloride	✓	✓	Secondary	Indicator of evaporative concentration

| Chemical parameter | Contaminant applicability | | Line of evidence | Comments |
	organics	inorganics		
Microbial counts/ biomass	✓		Tertiary	Indicator of the ability of indigenous bacteria to degrade contaminants
RNA probes	✓		Tertiary	Used to detect specific bacteria that degrade contaminants

7.5 Sampling of aquifer solids

Groundwater contamination plumes containing elevated concentrations of metals and metalloids are largely attenuated by reactions with minerals in the aquifer matrix. Therefore, it is important to sample and characterise sediments or rock materials in the aquifer if it is proposed to use MNA as a clean-up option for groundwater contamination plumes containing elevated concentrations of metals or metalloids.

It is recommended that cores of the aquifer matrix are collected both from within the current contaminant plume and from uncontaminated areas near existing groundwater monitoring sites to allow a direct comparison between groundwater concentrations of contaminants and levels present in aquifer solids (Figure 9). Aquifer solids should be sampled and preserved in a manner that will prevent oxidation and changes to their chemical characteristics.
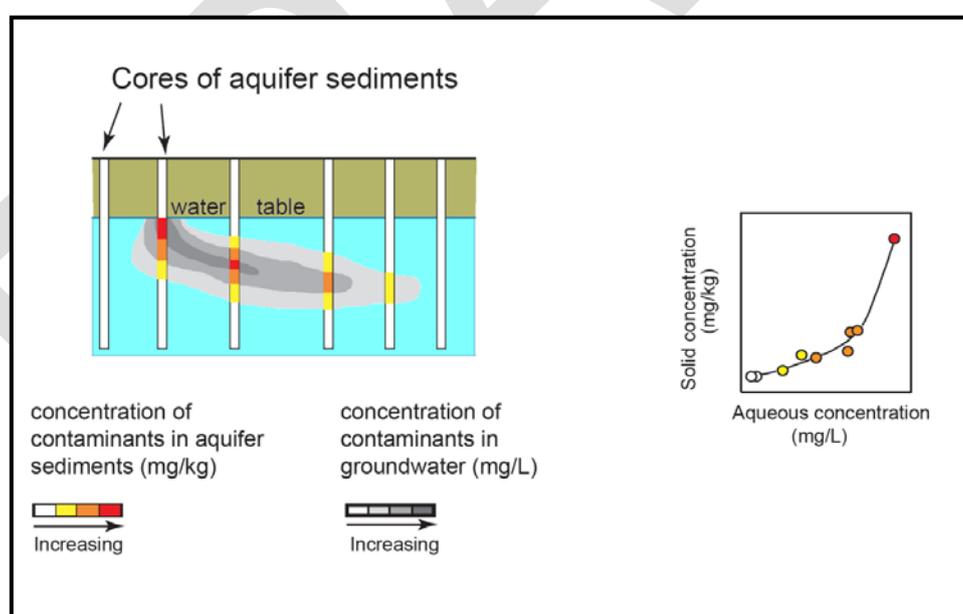
Figure 9. Sampling of aquifer solids within a groundwater contamination plume to demonstrate a relationship between contaminant levels dissolved in groundwater and levels adsorbed or co-precipitated in minerals in the solid matrix (adapted from US EPA, 2007a).

The main aims of sampling aquifer solids are to:

- demonstrate that there is a relationship between the aqueous and solid concentrations of a particular contaminant (i.e. there is indirect evidence that natural attenuation is taking place);

- determine the chemical process(es) responsible for immobilising contaminants from the groundwater contamination plume;

- determine the capacity of un-reacted aquifer solids for immobilising contaminants from groundwater; and

- determine the extent to which natural attenuation by aquifer solids is reversible at a given site, and the chemical conditions where release of contaminants back into groundwater could take place.

A variety of mineralogical and geochemical techniques can be used to achieve these aims. These include the use of x-ray diffraction (XRD) and electron microscopy techniques (particularly electron microprobe analysis and energy dispersive spectroscopy) to identify minerals in the aquifer matrix that are likely to be controlling the natural attenuation of metals and metalloids in groundwater.

Sequential chemical extraction techniques (Tessier et al., 1979; Clark et al., 2000; Filgueiras et al., 2002) can be used to determine the degree to which metals and metalloids will be susceptible to leaching under a range of geochemical conditions, and can be used to infer the dominant processes controlling natural attenuation.

Metals and metalloids are immobilised within aquifer solids in three main ways (US EPA, 2007a; US EPA, 2015):

- precipitation of insoluble minerals (principally as oxyhydroxide, carbonate and sulfide phases);

- co-precipitation with other metals in insoluble minerals, and/or

- adsorption onto iron or manganese oxides or clay minerals.

Many organic compounds are also immobilised by adsorption onto organic carbon present in aquifer solids.

As these solid phases are all susceptible to changes in pH and Eh conditions, chemical testing is required to determine the extent to which the aquifer is able to resist changes in these conditions and prevent the release of metals and metalloids back into groundwater (back diffusion).

Key parameters that should be considered when assessing aquifer vulnerability to changing Eh and pH conditions are provided in Table 7 together with information regarding conditions which may indicate that natural attenuation of metals, metalloids and some organic compounds by the aquifer matrix is not sustainable.

Table 7. Chemical parameters measured by the analysis of aquifer solids to assess the ability of the aquifer matrix to attenuate contaminants in groundwater.

Chemical parameter	Indicator	Level of concern / Comments
Total Organic Carbon (TOC) (%)	Measure of the reduction potential of aquifer solids, and their potential to adsorb organic compounds	TOC levels <0.2% may indicate that sediments have a low capacity to resist oxidation and adsorb organic compounds (Smith and Lerner, 2007)
Cation Exchange Capacity (CEC) (meq/ 100 g)	Measure of the ability of metals to be adsorbed by the aquifer matrix	CEC values < 5 meq/100 g usually indicate that aquifer sediments have a limited capacity to adsorb metals (Smith and Lerner, 2007)
Anion Exchange Capacity (AEC) (meq/ 100g)	Measure of the ability of metals and metalloids that are present in solution in anionic form (e.g. arsenates, chromates, calcium-uranium-carbonate complexes) to be absorbed by the aquifer matrix	AEC values <5 meq/100 g usually indicate that aquifer sediments have a limited adsorption capacity for anions
Total Inorganic Carbon (TIC) (%)	Measure of the carbonate content and acid buffering capacity of aquifer solids	TIC levels <0.2% have a low acid buffering capacity (Smith and Lerner, 2007). Conversely, high TIC values (≥2%) may indicate metals are bound in carbonate phases with a low risk of being released by acidification.
Chromium Reducible Sulfur (S_{Cr}) (%)	Measure of pyrite content and the ability of aquifer sediments to produce acidity on oxidation	In poorly buffered aquifers, S_{Cr} levels as low as 0.01% can produce acidity and cause metal release if allowed to oxidise through a falling water table. The risk of acidification is low when TIC and TOC levels are high and the water table is stable

Chemical parameter	Indicator	Level of concern / Comments
Acid Volatile Sulfides (AVS) (%)	Measure of active sulfate reduction and the formation of new sulfide minerals	The presence of AVS typically indicates that metals are being co-precipitated in sulfide phases, and are susceptible to being redissolved if Eh or pH conditions were to change
Metal and metalloid concentrations by sequential extraction techniques (mg/kg)	Measure of the extent to which contaminants are being removed from groundwater, or are being released to groundwater from aquifer solids within the contamination plume	Sequential extraction techniques (Filgueiras et al., 2002) can indicate which phases are likely to be storing metals and metalloids in aquifer solids

7.6 Assessing and presenting monitoring data

The decision to accept MNA as a remedial strategy will be based to a large extent on results obtained from the laboratory and field studies carried out during the demonstration stage. DWER will generally require evidence that two or more of the following criteria have been met to demonstrate that MNA will be a suitable clean-up option at a site:

- **The dominant natural attenuation process has been 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 has been demonstrated.**

    That is, there are sufficient representative data to determine 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); by showing decreases in the mass-flux of contaminants with time (high 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 or mass-fluxes show a consistent pattern of decline with no major fluctuations and seasonal trends in groundwater elevation and flow direction have been characterised.

- **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.

- **The geochemical conditions in groundwater are consistent with proposed attenuation mechanisms.** For example, Eh conditions in

groundwater need to be consistent with the presence of proposed electron acceptors/donors.

- **Sensitive parameters have been adequately 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.

Data obtained from field and laboratory studies may be analysed and presented in a number of ways to achieve these objectives. Methods of presentation include distribution and contour maps of contaminants and reaction products, time series graphs (see e.g. Figures. 10 and 11), and cross-sections showing the vertical distribution of contamination.

All raw data (laboratory and field data) should be provided in the report and included in summary tables and appropriate graphs. The rationale for excluding any data must be documented and justified.
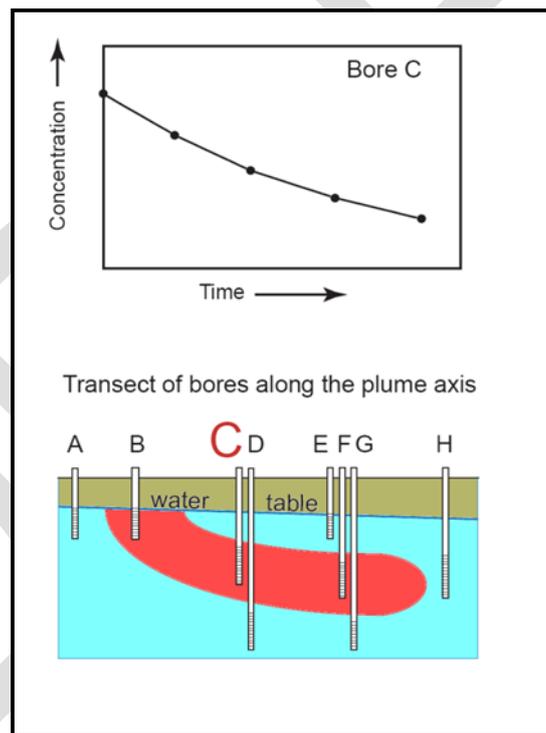
Figure 10. **Graph of concentration versus time showing a progressive decline in contaminant concentrations over time in bores within a groundwater contamination plume near the plume axis** *(adapted from Wiedemeier, 2000).*
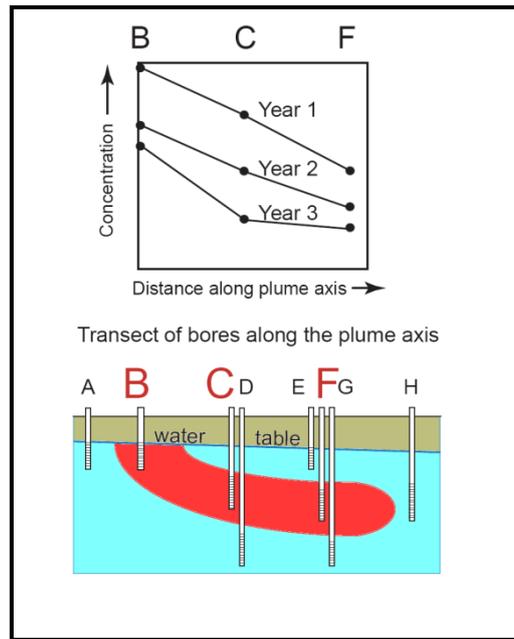
Figure 11. Graph of contaminant concentrations versus distance along the plume axis showing the progressive decrease of the severity of contamination over a three-year period (adapted from Wiedemeier, 2000)

The method of presentation is likely to vary, however, DWER expects that all information will be considered and appropriate graphical displays and tables will be included in reports to support the use of MNA as a clean-up measure at a given site. Table 8 provides guidance on ways in which information may be presented to support the continued use of MNA as a groundwater remedial measure.

Table 8. Presentation of information to demonstrate natural attenuation (adapted from Environment Agency, 2000).

Information	Presentation method	Purpose
Groundwater levels	Maps showing contours of equal groundwater elevation	To show the direction of groundwater flow in comparison with the distribution of contamination. Contour maps should be presented for different times to determine whether there are any seasonal or long-term changes in flow direction
	Hydrographs for monitoring bores	To illustrate seasonal and long term changes in water level. This should be compared with variations in contaminant concentrations and NAPL thicknesses with time. Long-term decreases in water table

Information	Presentation method	Purpose
		increase the risk of sulfide oxidation and metal release
	Sections showing variations of potentiometric heads with depth	To illustrate whether variations in vertical heads are present. These should be compared with the observed vertical distribution of contamination
Contaminant concentrations	Maps showing contoured contaminant concentrations	Maps should be produced for various sampling events to show how the distribution of contamination varies over time
	Concentration-time plots for individual monitoring bores	To indicate how rapidly contaminant concentrations are changing over time, and with distance from the source
	Concentration-distance plots	
Degradation products	Maps showing contoured concentrations of contaminant degradation products	To provide secondary evidence of biodegradation and that the process is proceeding as anticipated.
	Concentration – time and -distance plots	
Electron acceptors (dissolved oxygen, nitrate, iron, sulfate)	Maps showing contoured concentrations of electron acceptors	To provide secondary evidence that biodegradation or other oxidation-reduction reactions are taking place in the aquifer
	Plot of vertical distribution of electron acceptors along plume axis	
	Concentration – time and – distance plots	
Alkalinity	Maps showing contoured concentrations of alkalinity	Increases in alkalinity provide indirect evidence of biodegradation of organic compounds. Decreases in alkalinity may indicate sulfide oxidation due to a falling water table
	Concentration – time and – distance plots	
Aquifer solids	Plots of concentrations in groundwater versus concentrations in aquifer solids by sequential chemical extraction	To provide evidence of NA by aquifer solids

Mass flux

At sites where there is a significant risk of contamination affecting groundwater users or groundwater dependent ecosystems, DWER may also require additional bores to be installed on transects across the plume to demonstrate that the mass flux of contaminants is decreasing with time and distance from a contamination source.

At least two transects across the plume are required with sufficient monitoring bores screened at various depths to characterise the spatial distribution of contamination (Figure 12). A rectangular cross-sectional measurement area is then defined for each monitoring interval with boundaries mid-way to adjacent monitoring intervals (Figure 12).

Contaminant mass-fluxes can also be measured directly by deploying passive sampling devices in each monitoring interval for a fixed time interval and then determining the accumulated mass in each sampler by chemical analysis (ITRC, 2010).

A more detailed discussion of measuring mass-fluxes in groundwater contamination plumes can be found in ITRC (2010) and CRC CARE (2016).
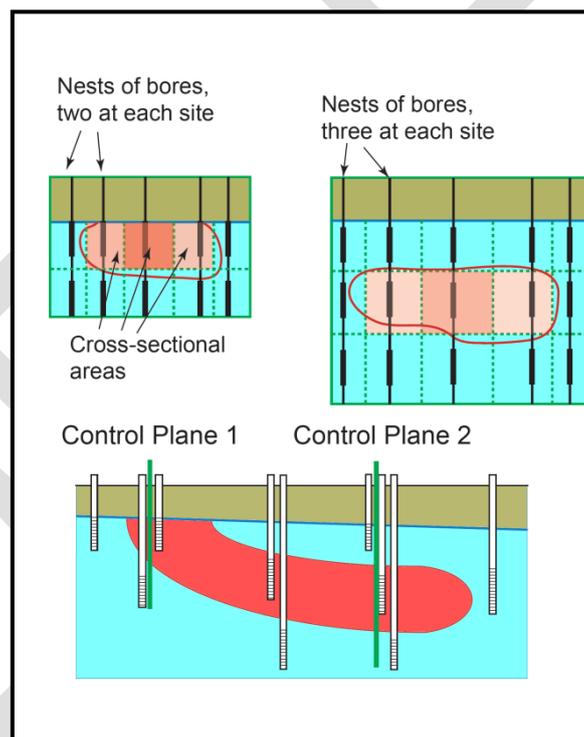
Figure 12. Establishing control-planes with transects of monitoring bores across a plume to measure changes in the mass-flux of contaminants with time and distance from a contamination source.

8 Stage 3 – predicting the long term viability of natural attenuation

Work undertaken during the screening- and demonstration-stage MNA investigations will indicate whether natural attenuation processes are taking place at a site, but may not indicate whether these processes will continue to protect sensitive environmental receptors from harm. Additional geochemical evidence and calculations are generally required to enable practitioners and DWER to make a decision about the long-term viability of MNA at a site. The information required will depend on the nature and severity of contamination and on the environmental sensitivity of a site, but may include:

- evidence that the mass-flux of contaminants from a source is decreasing with time and that the contamination source has been removed or contained;

- mass-balance calculations or geochemical modelling to indicate that sufficient electron acceptors are available in an aquifer to allow the continual biodegradation of organic contaminants at a sufficiently rapid rate to prevent adverse impacts on relevant (human health and ecological) receptors;

- geochemical and mineralogical evidence that the aquifer matrix will continue to assimilate metals and metalloids and that contaminants will remain trapped in the aquifer matrix;

- geochemical modelling to demonstrate that the continual discharge of contaminants by groundwater into mine pit-lakes or other closed water bodies will not cause concentration increases to levels that may cause environmental harm due to evaporative concentration and water-rock reactions.

A range of geochemical methods and public-domain software tools are available to help practitioners demonstrate the viability of MNA as a clean-up option for biodegradable organic contaminants, particularly for petroleum hydrocarbons (Table 9).

First-order rate constants for the degradation of organic compounds can be derived from concentration-time and -distance plots (see Appendix F in Washington State Department of Ecology, 2005) and used to predict the future behaviour of the plume through the use of models that simulate biodegradation processes and solute transport (Table 9).

Table 9. Examples of public-domain software tools for predicting the natural attenuation of organic compounds in groundwater.

Software package	Description	Source
BIOSCREEN	An EXCEL spreadsheet-based model that simulates biodegradation of dissolved hydrocarbons at petroleum release sites. The model uses an analytical solution to simulate contaminant transport	Software and user's manual are available for download from the US EPA at web site https://www.epa.gov/water-research/bioscreen-natural-attenuation-decision-support-system
Natural attenuation spreadsheet tools	EXCEL spreadsheet tools for data assessment of petroleum hydrocarbon attenuation	Software and user's manual are available for download from web site www.ecy.wa.gov/programs/tcp/policies/pol_main.html
BIOPLUME III	A 2-D finite difference model based on the solute transport code MOC that simulates biodegradation and transport of organic contaminants	Software and user's manual are available for download from the US EPA at web site https://www.epa.gov/water-research/bioplume-iii
NAS (Natural Attenuation Software)	A software tool to estimate clean-up time frames for MNA. Produced jointly by Virginia Technical University, USGS and the US Navy	Software and user's manual are available for download at web site http://toxics.usgs.gov/highlights/nas_2.2.0/
BIOCHLOR	An EXCEL spreadsheet software tool that simulates the biodegradation of chlorinated solvents in groundwater and which uses an analytical solution for solute transport	Software and user's manual are available for download at web site https://www.epa.gov/water-research/biochlor-natural-attenuation-decision-support-system

A number of software packages are also available for predicting the natural attenuation of inorganic contaminants in groundwater (Table 10). These include geochemical speciation and reaction models like Phreeq-C which are capable of simulating the chemical reactions between dissolved constituents in groundwater, adsorption reactions onto solid surfaces, precipitation and dissolution reactions, and gas exchange reactions in solution. Many geochemical speciation models (like

Phreeq-C) are also capable of undertaking 1-D reactive transport modelling of inorganic constituents in groundwater, but some 2-D and 3-D reactive transport models are also available (Table 10).

Table 10. Examples of software tools for predicting the natural attenuation of inorganic constituents in groundwater.

Software Package	Description	Source
Mineql+	Commercial geochemical speciation software	Environmental Research Software, available from web site www.mineql.com
MinteqA2	Public domain geochemical speciation software	US EPA, software and manual available for download from web site https://www.epa.gov/exposure-assessment-models/minteqa2
Phreeq-C	Public domain geochemical speciation software and 1-D reactive transport model	USGS, software and manual available for download from web site wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/
Geochemist's workbench®	Commercial geochemical speciation software	Developed by the University of Illinois and available from web site https://www.gwb.com/
Visual Minteq	Public domain geochemical speciation software	Developed by KTH (Sweden) and available for download from web site https://vminteq.lwr.kth.se/download/
CrunchFlow	Public domain 3-D reactive transport model	Software and manual are available for download from web site http://www.csteefel.com/CrunchFlowIntroduction.html
Phast	Public domain 3-D reactive transport model	Software and manual are available for download from web site wwwbrr.cr.usgs.gov/projects/GWC_coupled/phast/
MT3DMS	Public domain 3-D reactive transport model	Software and manual are available for download from web site https://hydro.geo.ua.edu/mt3d/index.htm
PHT3D	Public domain 3-D reactive transport model	Software and manual available for download from web site www.pht3d.org/

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 (refer NEPM Schedule B2). 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.

Additional guidance on utilising and interpreting the results of contaminant transport models can be obtained from the Environment Agency document "*Guidance on the Assessment and Interrogation of Subsurface Analytical Contaminant Fate and Transport Models*" which is available from the UK government web site www.gov.uk/government/organisations/environment-agency.

Where data from the site shows clear evidence of a shrinking plume (refer Appendix A) and the mechanisms resulting in the observed attenuation are well understood (and this can be demonstrated), this may be sufficient to demonstrate MNA as a viable clean-up 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.

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; and

- the range of parameter values used is well defined in the literature, and that a conservative value is being used in the modelling assessment.

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 effective clean-up option in the longer term.

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 site-specific investigations; or

- consider using active clean-up strategies for the site in combination with MNA. This may require further modelling to take into account the effect of additional clean-up measures.

9 Stage 4 – implementing a performance monitoring program

9.1 Introduction

The final decision to implement an MNA (performance monitoring) program at a site should be made in consultation with DWER (and/or the contaminated sites auditor as relevant for the site), and will be based on the submission of a report (comparable to a Remediation Action Plan (RAP) described in DER 2014) to the auditor/DWER as relevant. This report should detail the results of Stages 1 to 3, or a summary of these Stages if the information has been provided in previous reports that meet the standards set out in this guideline, and include:

- results of all site investigations and monitoring results;

- the presentation of a clear conceptual model of the natural attenuation processes operating at the site;

- the identification of all human and ecological receptors and environmental values that could be affected by groundwater contamination, and information on how these will be protected during the program;

- evidence that the proponent/responsible person has the financial capacity and the resources to undertake the MNA programme;

- confirmation that the proponent/responsible person will continue to have access to monitoring bores during the entire MNA programme;

- lines of evidence supporting natural attenuation details and justification of the modelling methods used to assess the fate and transport of groundwater contaminants;

- description and justification of values for parameters used in modelling the fate and transport of groundwater contaminants;

- results of model predictions and a discussion of uncertainties in the analysis;

- the basis for proposing MNA as the preferred remedial option;

- an outline of the proposed monitoring strategy to confirm whether natural attenuation will continue to be effective; and

- details of one or more contingency plans (to include SAQP, action criteria for contingencies and required remedial objectives) that would be implemented in the event that natural attenuation proves to be inadequate to protect receptors and environmental values.

The report prepared for DWER and/or the contaminated sites auditor should, therefore, contain both a well-argued case for the use of MNA for clean-up based on information collected during initial site investigations, and a comprehensive SAQP with data quality objectives for ongoing performance monitoring at the site. Issues that should be considered when preparing the SAQP are discussed below.

9.2 Reviewing the existing network of monitoring bores

Although monitoring bores will have already been constructed at a site, practitioners should consider whether the existing network is adequate to determine the full extent of groundwater contamination and to adequately protect sensitive receptors.

Typically, drilling carried out during the demonstration phase of an MNA investigation program will reveal new information about the hydrogeology of a site which may require revisions to the conceptual model that has been developed to describe the behaviour of contaminants in groundwater in the area. Additionally, existing monitoring bores are often lost or destroyed during the redevelopment of a site, and may need to be replaced before the SAQP is finalised. These factors often require additional monitoring bores to be constructed in the following areas (US EPA, 2004):

- ***Sites adjacent to remediated source areas*** – in circumstances where the contamination source has been contained, increasing levels of contamination could indicate problems with the containment system. These new contaminant increases could exceed the local capacity of the subsurface to attenuate concentrations in groundwater without significant plume expansion. Additional bores may therefore be required immediately down-gradient of source areas to detect new releases of contaminants.

- ***Highly transmissive zones (preferential pathways) in the underlying aquifer*** – at many sites, most of the contaminant mass is transported in narrow zones in the aquifer where the hydraulic conductivity is especially high (preferential pathways). These zones may not have been recognised during preliminary site investigations, and additional bores with short screened intervals (less than 1 m) may be required to ensure that these groundwater pathways are adequately monitored.

- ***Near plume boundaries*** – these are areas where concentrations of contaminants change most rapidly and where the expansion or contraction of the groundwater contamination plume or changes in the contamination flow direction due to seasonal changes in groundwater flow direction can be most readily detected.

- ***Zones in the aquifer where contaminant concentrations show a low or negligible rate of decline*** – these are areas where attaining clean-up targets may be impeded due to specific site conditions (e.g. due to the presence of previously undetected source materials or a low availability of electron acceptors). Such zones are often detected during the evaluation of data collected during performance monitoring, and may require additional investigations to be carried out to determine whether additional remedial actions are required to ameliorate the contamination.

- ***Monitoring sites up-gradient of the contamination source*** – often insufficient monitoring bores are constructed during initial site investigations to adequately characterise geochemical conditions in groundwater and aquifer solids that are unaffected by contamination. As the natural attenuation of contamination may depend on a flux of electron acceptors being delivered by groundwater flow to contaminated zones in the aquifer, additional monitoring bores may be required up-gradient of the contamination source to determine how this flux may vary spatially and with time.

The screen length of bores that are constructed to monitor these zones should be as short as possible while ensuring that sufficient water can be pumped from the monitoring interval to obtain a representative groundwater sample. Depending on the hydraulic properties of the aquifer and vertical distribution of contamination, screen lengths to monitor discrete vertical intervals in an aquifer will typically vary between 0.3 and 2 m.

9.3 Groundwater sampling and frequency of monitoring

The performance monitoring SAQP should be prepared in accordance with guidance in Schedule B2 of the NEPM and include information about:

- the chemical parameters that will be measured;

- the frequency of analysis for each parameter;

- the method of sampling;

- how samples will be preserved and stored prior to chemical analysis -- the laboratory methods to be used and their levels of detection and reporting; and

- the quality control and assurance methods that will be used to ensure the integrity of the analyses.

Water level measurements should also be carried out routinely during performance monitoring together with, where appropriate, measurements of the thickness of free product (NAPL). The range of chemical parameters measured will depend on the nature of contamination at a given site and on the level of risk to nearby environmental and human health receptors, but will typically include the contaminant(s), one or more of its/their degradation products, and one or more critical electron acceptors. At sites that have been well-characterised and where there are clear declining trends of contaminant concentrations with time, DWER may agree to a reduced suite of chemical parameters being measured during performance monitoring compared with the analysis suite for the earlier site investigation phases (see section 7.4 and Table 6).

The sampling frequency required to adequately characterise changes of contaminants concentrations with time will depend on the rate of groundwater flow; the magnitude of seasonal variations in groundwater flow direction at a site; the rate of attenuation of contaminants in groundwater; and on the proximity and level of threat to receptors and environmental values. The relative importance of these factors will vary from site-to-site and with time at a given site, therefore, the sampling frequency should be determined through consideration of the site-specific conditions.

At sites which have been well characterised by drilling investigations, and where there is a negligible risk of contamination affecting nearby environmental receptors, DWER will generally accept the sampling schedule outlined in Table 11 for performance monitoring carried out in Stage 4 of the MNA evaluation process unless site-specific factors indicate that more extensive monitoring is required.

Table 11. Performance monitoring schedule for well-characterised sites with a negligible risk of adverse impacts on environmental receptors and environmental values (adapted from Washington State Department of Ecology, 2005)

Measured parameter	Year of monitoring	Monitoring frequency
Water table elevation, contaminant concentrations, concentrations of primary geochemical indicators	1st year	Quarterly
	2nd & 3rd years	Semi-annually (if the plume is stable or is shrinking)
	Subsequent years	Annually (if the plume continues to be stable or is shrinking)
Secondary geochemical indicators	1st & 2nd years	Semi-annually
	Subsequent years	Annually

9.4   Contingency measures and triggers

In situations where monitoring indicates that natural attenuation of contaminants is not proceeding as expected, DWER will typically require that additional management measures are implemented to ensure that a groundwater contamination plume does not expand and threaten nearby environmental receptors and environmental values. Depending on the nature of the contamination and on the level of threat, the contingency measures could include:

- increasing the frequency of groundwater monitoring for a larger suite of chemical parameters to better define the performance of natural attenuation processes in the aquifer;

- installing additional monitoring bores to improve understanding of the source and distribution of contamination in groundwater;

- implementing additional site works to remove or contain contamination sources; and

- implementing additional groundwater treatment measures (such as air sparging or in-situ chemical oxidation or reduction) to reduce concentrations of contaminants in groundwater and increase the effectiveness of MNA as a clean-up measure.

Contingency measures are usually implemented in a hierarchical manner depending on the level of threat posed by contamination to receptors. The performance monitoring SAQP should include the site-specific criteria that will be used to trigger the implementation of contingency measures. These might include (US EPA, 1999):

- contaminant concentrations in specific monitoring bores showing trends of increasing concentrations that were not predicted to take place;

- bores near the contamination source showing large increases in concentrations of contaminants, possibly indicating a renewed release of contamination to groundwater in this area;

- contaminants detected in monitoring bores located outside of the original plume boundary (sentinel bores) or other specified compliance boundary (such as the property boundary);

- changes in groundwater and land uses near the site are adversely affecting the ability of MNA to protect receptors; and

- contaminants detected in locations that pose an unacceptable risk of affecting human health or the environment.

9.5 Attainment of remediation objectives

The performance monitoring SAQP should indicate the criteria (consistent with the remediation objectives) that will be used to determine when MNA has been successfully completed. DWER will generally require that concentrations of contaminants in groundwater meet the appropriate groundwater environmental value (beneficial use criteria) at the property boundary or other agreed compliance point down-gradient of the contamination source.

Groundwater modelling can be carried out to determine the appropriate contaminant target concentrations for other bores in the monitoring network to achieve the required clean-up concentration at the compliance point. Details of how to carry out such an assessment using simple spreadsheet models can be found in Environment Agency (2006). Alternatively, at small sites with biodegradable organic contaminants and a uniform hydrogeological setting, simple analytical solutions can be used to determine the appropriate target concentrations for contaminants in monitoring bores to indicate that MNA has been successfully completed (see e.g. Chappelle and Bradley, 1998).

In some situations (particularly where groundwater contains elevated concentrations of metals or metalloids) , DWER may require clean-up criteria to be set on the basis of groundwater flux rather than concentration measurements to protect aquatic ecosystems that may be affected by groundwater discharge.

DWER will generally require monitoring to continue for at least one year after the required clean-up concentration criteria are met in groundwater at the compliance point to demonstrate that there are no significant seasonal variations in contaminant concentrations measured at this point. Monitoring may need to continue for more than one year in complex hydrogeological settings to provide confidence that the remediation objectives have been met.

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Appendix A
Mann-Kendall test for assessing the statistical significance of contaminant concentration declines

The Mann-Kendall test 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 in the same month each year.

Further guidance on assessing concentrations trends where there are significant seasonal variations can be found in Idaho Department of Environmental Quality (2014). A minimum of 4 years data is required to use this technique.

A high degree of variability in the data can cause the test results to be misinterpreted, therefore the coefficient of variation (explained at the end of this section) for the data set should be assessed.

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.

A software tool to undertake Mann-Kendall tests is available for download from the following web site: http://www.gsi-net.com/en/software/free-software/gsi-mann-kendall-toolkit.html. The tests can also be carried out manually in the following way:

- contaminant concentration data for each bore are assembled 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.

- a matrix of sample concentration versus sampling event is set up in the manner shown in Table A.1. If the concentration of a contaminant collected in a particular sampling event is lower than the concentration at the previous sampling, 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.

Table A.1. Concentration – sampling time matrix for a Mann-Kendall test

	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)	**S = -5**

- results for each row are added and the sum is entered at the end of the row. The row-totals are summed 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 0.1 is generally required.

Table A.2 gives the maximum value of the S statistic (S_{max}) to accept an alternative hypothesis for α=0.1 (i.e. 90% confidence level) for *n* concentration measurements.

Table A.2. Mann-Kendall look-up table for α=0.1 (90% confidence level)

S Value	No. of sampling events						
	4	5	6	7	8	9	10
0	Red	Red	Red	Red	Red	Red	Red
±1	Red	Red	Red	Red	Red	Red	Red
±2	Red	Red	Red	Red	Red	Red	Red
±3	Red	Red	Red (NO TREND)	Red (INDICATED)	Red	Red	Red
±4	Red	Red	Red	Red	Red	Red	Red
±5	Green	Red	Red	Red	Red	Red	Red
±6	Green	Red	Red	Red	Red	Red	Red
±7	Green	Green	Red	Red	Red	Red	Red
±8	Green	Green	Green	Red	Red	Red	Red
±9	Green	Green	Green	Red	Red	Red	Red
±10	Green	Green	Green	Green	Red	Red	Red
±11	Green	Green	Green	Green	Red	Red	Red
±12	Green	Green	Green	Green	Green	Red	Red
±13	Green	Green (TREND)	Green (LIKELY)	Green	Green	Red	Red
±14	Green	Green (≥ 90 %)	Green (CONFIDENCE)	Green	Green	Green	Red
±15	Green	Green	Green	Green	Green	Green	Red
±16	Green	Green	Green	Green	Green	Green	Green
±17	Green	Green	Green	Green	Green	Green	Green
±18	Green	Green	Green	Green	Green	Green	Green
±19	Green	Green	Green	Green	Green	Green	Green
±20	Green	Green	Green	Green	Green	Green	Green

(Adapted from Wiedemeier et al., 2000)

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 result 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 (CV) can be calculated in the following way to assess the scatter in the data:

$$CV = (standard\ deviation) \div (arithmetic\ mean)$$

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 B
EXAMPLE OF A CONTAMINANT DEGRADATION MASS BALANCE CALCULATION

Field data

A petrol spill has caused a NAPL layer (i.e. 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 m from the source. BTEX concentrations in the plume are up to 10 mg/L. Up-gradient measurements indicate that O_2, NO_3^- and SO_4^{2-} are present in groundwater, whereas in the most distant down-gradient 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 m wide and is 2 m thick. Table B.1 summarises the up-gradient and down-gradient concentration values.

Table B.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

To simplify the calculation process, it is usually assumed that all of the NAPL phase is comprised of one chemical compound, typically toluene which is often the most abundant constituent. The relevant reactions for the biodegradation of toluene in groundwater are shown in Table B.2.

Table B.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	____	$C_7H_8 + 5H_2O \rightarrow 7CO_2 + 4.5CH_4$

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

Table B.3 Stoichiometric ratios for the biodegradation of toluene

Reaction acceptor	g C_7H_8 /g acceptor	gCO_2-C/g acceptor	g alkalinity (as $CaCO_3$)/g
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:
$$CO_2 + H_2O \rightarrow CO_3^{2-} + 2H^+$$
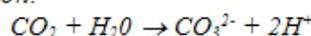
Combining the stoichiometric ratios with the observed concentration changes of electron acceptors allows concentrations of CO_2 and alkalinity to be calculated, and the amount of BTEX (as toluene) that has been degraded to be determined.

Table B.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 = 2550 g/year

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

GLOSSARY

Adsorption	The attachment of a chemical to the surface of a solid.
Anaerobic groundwater	Groundwater that 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.
Assimilative capacity	The potential for a specific volume of an aquifer to reduce concentrations of contaminants in groundwater.
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.
BTEX	Benzene, toluene, ethyl-benzene and xylenes.
Cometabolism	A process in which a chemical compound is fortuitously degraded by enzymes during the biodegradation of another chemical compound.
Coprecipitation	The entrapment of metals or metalloids in the crystal lattice during the precipitation of insoluble minerals which generally do not contain those elements. For example, nickel may be co-precipitated in the iron sulfide mineral, pyrite (FeS_2).
Compliance point	Specified location where the remedial target concentration must be achieved.
Degradation product	A chemical compound that results from the (bio)degradation of another chemical compound.
Denitrification	A chemical reaction where electrons produced by the microbial oxidation of carbon compounds are used to convert nitrate ions in solution to nitrogen oxide and nitrogen gases which are lost from solution.

Dispersion	An attenuation process that causes concentrations of contaminants to be reduced due to the lateral and vertical expansion of a plume and mixing with uncontaminated groundwater.
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.
Eh	A measure of the ability of chemical constituents to exchange electrons and their oxidation state in solution.
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.
Hydraulic conductivity	A coefficient of proportionality describing the rate at which groundwater moves through a porous medium.
Iron reduction	A chemical reaction where electrons provided by the microbial oxidation of carbon compounds are used to convert iron from its ferric state (iron III) to its ferrous form (iron II). This usually causes iron oxide coatings on aquifer solids to dissolve and form soluble ferrous compounds.
LNAPL	Light Non-Aqueous Phase Liquid. A chemical immiscible with and lighter than water. The liquid floats on a water column.
Methanogenesis	A chemical reaction where electrons produced by the microbial oxidation of carbon compounds react with dissolved bicarbonate ions, carbon dioxide and water to form methane gas which is released from solution.

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 (i.e. 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.
pH	Measure of the concentration of hydrogen ions in solution.
Precipitation	The formation of a new mineral when the concentrations of its constituents in solution exceed the solubility of that mineral.
Plume	Body of groundwater containing concentrations of contaminants above natural background levels.
Reactive transport model	A model that that simulates both groundwater flow and geochemical processes in aquifers.
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 other media.
Reductive dechlorination	Reduction of a chlorine-containing organic compound via the replacement of a chlorine atom by hydrogen.
Remedial target	The objective 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.

Sulfate reduction

A chemical reaction where electrons from the microbial oxidation of carbon compounds are used to convert dissolved sulfate ions to hydrogen sulfide gas or sulfide ions which then generally react with iron to form insoluble iron sulfide minerals.

Target concentration

Desired chemical concentration at a compliance point to indicate that clean-up of groundwater has been successful.