

Guidance on the Assessment and Monitoring of Natural Attenuation of Contaminants in Groundwater

R&D Publication 95

M. A. Carey¹, J. R. Finnamore², M. J. Morrey¹ & P.A. Marsland¹

Research Contractor:
Enviros Aspinwall¹
LGC²

Further copies of this report are available from:
Environment Agency R&D Dissemination Centre, c/o
WRc, Frankland Road, Swindon, Wilts SN5 8YF



tel: 01793-865000 fax: 01793-514562 e-mail: publications@wrplc.co.uk

Publishing Organisation:

Environment Agency
Rio House
Waterside Drive
Aztec West
Almondsbury
Bristol BS32 4UD

Tel: 01454 624400

Fax: 01454 624409

ISBN: 1 85705 263 2

© Environment Agency 2000

All rights reserved. No part of this document may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise without the prior permission of the Environment Agency.

The views expressed in this document do not necessarily reflect those of the Environment Agency. Its officers, servant or agents accept no liability whatsoever for any loss or damage arising from the interpretation or use of the information, or reliance upon views contained herein.

Dissemination status

Internal: Released to Regions
External: Released to the Public Domain

Statement of use

This technical report presents generic guidance on the assessment and monitoring of natural attenuation of contaminants in groundwater. It has been prepared for Agency staff who assess third party proposals for the use of monitored natural attenuation as part of a remedial strategy, and for problem holders and their consultants who are considering or developing monitored natural attenuation strategies for managing the risks associated with polluted groundwaters. It is intended that this report will form the foundation for the Agency's technical appraisal of monitored natural attenuation schemes on a site-specific basis.

Research contractor

This document was produced under R&D Project P2-158 by:

Enviros Aspinwall
Walford Manor
Baschurch
Shrewsbury
SY4 2HH

in conjunction with

LGC plc
Queens Road
Teddington
Middlesex
TW11 0LY

The Environment Agency's Project Manager

Jonathan Smith, National Groundwater & Contaminated Land Centre

Guidance on the Assessment and Monitoring of Natural Attenuation of Contaminants in Groundwater

R&D Publication 95

M. A. Carey¹, J. R. Finnamore², M. J. Morrey¹ & P. A. Marsland¹

Research Contractor:
Enviros Aspinwall¹
LGC²

Further copies of this report are available from:
Environment Agency R&D Dissemination Centre, c/o
WRc, Frankland Road, Swindon, Wilts SN5 8YF



tel: 01793-865000 fax: 01793-514562 e-mail: publications@wrcplc.co.uk

Publishing Organisation

Environment Agency
Rio House
Waterside Drive
Aztec West
Almondsbury
Bristol BS32 4UD

Tel: 01454 624400

Fax: 01454 624409

ISBN: 1 85705 263 2

© Environment Agency, 2000

All rights reserved. No part of this document may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise without the prior permission of the Environment Agency.

The views expressed in this document are not necessarily those of the Environment Agency. Its officers, services or agents accept no liability whatsoever for any loss or damage arising from the interpretation or use of the information, or reliance on views contained herein.

Dissemination status

Internal: Released to Regions

External: Released to Public Domain

Statement of use

This technical report presents generic guidance on the assessment and monitoring of natural attenuation of contaminants in groundwater. It has been prepared for Agency staff who assess third party proposals for the use of monitored natural attenuation as part of a remedial strategy, and for problem holders and their consultants who are considering or developing monitored natural attenuation strategies for managing the risks associated with polluted groundwaters. It is intended that this report will form the foundation for the Agency's technical appraisal of monitored natural attenuation schemes on a site-specific basis.

Research contractor

This report has been produced under R&D Project P2-158 by:

Enviros Aspinwall,
Walford Manor
Baschurch
Shrewsbury
SY4 2HH

in conjunction with

LGC plc
Queens Road
Teddington
Middlesex
TW11 0LY

The Environment Agency's Project Manager

Jonathan Smith, National Groundwater & Contaminated Land Centre

FOREWORD

The UK has a long history of industrial activity and its legacy is evident within the groundwater environment, where a range of pollutants is found, particularly in urban areas. Legislation introduced in 1999 (Anti-pollution Works Notice Regulations 1999) and 2000 (Part IIA, EPA 1990) provides a new regulatory regime for the identification and remediation of contaminated land and groundwater, which supplements existing planning controls on land redevelopment. The UK approach is based on the principles of risk-assessment and risk-management, such that unacceptable risks to human health and the environment are managed and land is made 'suitable for use'. Monitored natural attenuation is a valid risk management approach for polluted groundwaters in the England and Wales. However, approaches to demonstrate the effectiveness of natural processes at remediating groundwater in England and Wales have varied widely.

In developing this guidance, the Environment Agency has made a clear distinction between natural attenuation (NA) and monitored natural attenuation (MNA). The term NA is used when referring to the naturally occurring physical, chemical and biological processes that act within an aquifer to reduce contaminant mass, concentration, flux or toxicity (i.e. the mechanism), while MNA is used to refer to the remedial technique, which is by definition a monitored activity.

The acceptance of MNA, either in isolation or in combination with other treatments, for remediating historically contaminated groundwater has increased in recent years. To further encourage the robust and transparent application of MNA, technical guidance has been developed that specifically considers the hydrogeological conditions encountered in the UK, and the range of pollutants that are most frequently found. This document provides: stakeholders with a clear framework to assist in the design, evaluation and implementation of MNA strategies; regulators with guidance on the amount and quality of data that are required to verify that MNA is effective; and third parties with information that it is hoped will increase awareness and confidence in natural attenuation.

It is hoped that this document will help to promote the use of appropriately monitored natural attenuation where it is effective and appropriate, as one of the techniques in the remediation toolbox. It is also hoped that improved standards of monitoring of the processes, together with a continuing research programme, will improve the Agency's, and society's, confidence in the effectiveness of MNA for the remediation of pollution.



Dr Jan Pentreath
Chief Scientist and Director of Environmental Strategy

Acknowledgements

This report has been produced by EnviroS Aspinwall and LGC for the Environment Agency under R&D contract P2-158. The project benefited from advice given by selected external experts and the Agency is particularly grateful for the contributions from:

Dr P Morgan, Eutech Ltd

Dr S Thornton, University of Sheffield

Dr M Lambson, BP Amoco

CONTENTS

Chapter	Page No.
Summary	i
1. Introduction	1
2. Overall Approach	13
3. Screening	21
4. Demonstration of Natural Attenuation	39
5. Assessment of Natural Attenuation	47
6. Implementation (Performance Monitoring)	53
7. Final Review	63
8. References	65
Glossary	73
APPENDICES	79
Appendix 1	80
Appendix 2	89
Appendix 3	92
Appendix 4	94
Appendix 5	101
Appendix 6	111
Appendix 7	113

SUMMARY

Executive Summary

Whilst the science base for understanding many of the biological and physico-chemical processes that contribute to natural attenuation is still in its infancy, relative to alternative remedial solutions, there must still be regulatory rigour placed upon the assessment of monitored natural attenuation in any given situation. The lines-of-evidence approach set out in other protocols has been adopted in the Agency's guidance, taking account of the UK's hydrogeology that includes many deep, fractured, indurated aquifers.

In verifying the performance of MNA, the main criteria for acceptance by the Environment Agency are:

- that the Agency has confidence that it will be effective in protecting receptors throughout the duration of the monitoring period (and beyond), and that there will not be significant expansion of the plume into uncontaminated groundwater;
- that the attenuation processes can be monitored (the monitoring network must be adequate to demonstrate that natural attenuation is occurring according to expectations) and;
- that remedial objectives will be achieved within a reasonable time frame, which will typically be no more than one generation or 30 years, and will not be excessively long when compared with other viable remedial options.

The guidance document sets out a four-stage assessment process that should be followed to provide evidence of MNA performance. Essentially this comprises:

Stage 1: screening procedures to assess the viability of natural attenuation;

Stage 2: procedures to demonstrate current attenuation properties;

Stage 3: procedures to evaluate longer-term attenuation capability;

Stage 4: procedures to verify attainment of the agreed remedial objectives

The precise criteria that will determine the acceptability of MNA will vary on a site-specific basis and in particular on the combined impact of contaminant chemistry, hydrogeological and biogeochemical factors.

- NA has to be demonstrated with an acceptable level of confidence and its effectiveness confidently predicted into the future. There must also be sufficient time for MNA to be effective in meeting the defined remedial objectives and the effects of hydrogeological conditions and contaminant chemistry must be assessed. The value of the aquifer resource is an important consideration, and when combined with the lithology, provides a useful screening mechanism.
- It must be shown that intended land uses will not adversely affect MNA in the longer term. Access to the plume has to be obtained and security guaranteed for monitoring borehole locations. In particular, third party agreement has to be obtained for monitoring the contaminant plume beyond the site boundary and the long-term liability of landowners/polluter must have been resolved.

- It will need to be shown that identified receptors will be protected in both the short and long-term and that there will be minimal expansion of the plume into uncontaminated groundwater resources. The remedial objectives must be achieved within a reasonable time-frame, consistent with the Agency's duty to pursue the objective of sustainable development. Adequate institutional control and financial provision must be in place since monitoring is likely to continue over an extended period. In addition, contingency plans have to be developed, which will be implemented if MNA proves to be ineffective. All relevant legislation will need to be complied with and health and safety obligations met.

Key words: groundwater, pollution, remediation, risk-management, monitored natural attenuation.

Key to Parameters and Units

A	=	area of contaminant source (m ²)
ax,ay,az	=	dispersion coefficient in three dimensions (m)
C	=	concentration of contaminant at point x (mg/l)
C _s	=	soil concentration (mg/kg)
C ₀	=	initial concentration of contaminant (mg/l)
C _u	=	background concentration of contaminant (mg/l)
da	=	aquifer thickness (m)
Eh	=	redox potential (mV)
f _{oc}	=	fraction of organic carbon (fraction)
i	=	hydraulic gradient
Inf	=	infiltration (m/d)
K	=	hydraulic conductivity (m/d)
K _d	=	soil water partition coefficient (l/kg)
K _{oc}	=	organic carbon partition coefficient (l/kg)
K _{oc,n}	=	sorption coefficient for related species (l/kg)
K _{oc,i}	=	sorption coefficient for ionised species (l/kg)
L	=	length of site in direction of groundwater flow (m)
Mz	=	mixing zone thickness (m)
n	=	effective porosity (as a fraction)
pH	=	pH value
pKa	=	acid dissociation constant
Q	=	abstraction rate (m ³ /d)
Rc	=	retardation factor
Sz, Sy	=	width and thickness of contaminant plume in groundwater at source (m)
t	=	time (days)
w	=	width of site (metres)
ρ	=	bulk density(g/cm ³)
λ	=	decay constant (0.693/half life of contaminant in days) (d ⁻¹)
ks	=	source decay rate (d ⁻¹)
BC	=	biodegradation capacity
UF	=	utilisation factor

1. INTRODUCTION

1.1 General

Monitored natural attenuation (MNA) is becoming increasingly accepted as a viable, cost-effective option for managing the risks posed by contaminated groundwater in certain situations. This is mostly due to a growing body of evidence which shows that, under certain environmental conditions, naturally occurring processes in the subsurface can reduce the mass, toxicity, mobility, volume or concentration of organic and inorganic contaminants. These effects are due to the following mechanisms acting alone or in combination on contaminants:

- destructive mechanisms, including biodegradation, abiotic oxidation and hydrolysis;
- non-destructive mechanisms such as sorption, dispersion and chemical or biological stabilisation, and volatilisation.

This document describes a framework that sets out the Environment Agency's expectations for the assessment and monitoring of MNA at sites in England and Wales. The Agency recognises that environmental risks and regulatory control mechanisms will vary between sites, so the guidance takes the form of a generic framework, rather than prescriptive requirements. In developing MNA schemes, assessors should always consider the requirements and constraints of the applicable regulatory framework(s).

The Environment Agency adopts the following definitions of natural attenuation and monitored natural attenuation of contaminants, with respect to groundwater.

Definition of Natural Attenuation (NA) in groundwater

“The effect of naturally occurring physical, chemical and biological processes, or any combination of those processes to reduce the load, concentration, flux or toxicity of polluting substances in groundwater. For natural attenuation to be effective as a remedial action, the rate at which those processes occur must be sufficient to prevent polluting substances entering identified receptors and to minimise expansion of pollutant plumes into currently unpolluted groundwater. Dilution within a receptor, such as in a river or borehole, is not natural attenuation.”

Definition of Monitored Natural Attenuation (MNA)

“Monitoring of groundwater to confirm whether NA processes are acting at a sufficient rate to ensure that the wider environment is unaffected and that remedial objectives will be achieved within a reasonable timescale; this will typically be less than one generation or 30 years.”

Application of natural attenuation requires demonstration that natural processes are occurring at a rate that a) protects the wider environment and b) achieves remedial objectives within a reasonable time-frame. Demonstration is achieved by monitoring the system to confirm the attenuation processes. The Environment Agency makes a clear distinction between natural attenuation (NA) and monitored natural attenuation (MNA). NA is used when referring to the naturally occurring physical, chemical and biological processes that act within an aquifer to

reduce contaminant load, concentration, flux or toxicity (i.e. the mechanism), while MNA is used to refer to the remedial technique, which is by definition a monitored activity.

The requirement that MNA achieves remedial objectives within a reasonable time-frame is important in the context of ensuring that the Agency complies with its duty to pursue the objectives of sustainable development. The maximum duration of thirty years for substantial completion of remediation is derived from the aim not to hand-down current pollution to future generations.

MNA may also form a component of an integrated treatment approach incorporating active remedial measures (such as source removal), containment systems, treatment systems (such as funnel and gate), enhanced NA (such as the supply of slow-release nutrients and oxygen and addition of organic substances to promote contaminant degradation).

The principal advantages and disadvantages of MNA can be summarised as:

Advantages	Disadvantages
<ul style="list-style-type: none">• relatively non-intrusive• lower overall costs may be achievable• utilises inherent natural processes• may reduce use of energy, and creation of emissions from active processes	<ul style="list-style-type: none">• longer time-frames may be required to achieve remediation objectives• long-term monitoring will normally be necessary• site characterisation will normally be more complex and costly• toxicity of transformation products may increase the risk

To date, natural attenuation has been accepted as an agreed remedial strategy at only a few sites in the UK. This technical guidance has been designed to provide a framework to assist best and consistent practice in the design, evaluation and implementation of natural attenuation strategies within a risk-based context in the UK. Specifically, this document provides generic guidance on:

- screening procedures to assess the viability of natural attenuation;
- procedures to demonstrate that natural attenuation is occurring;
- procedures to evaluate longer-term attenuation capability;
- procedures to verify attainment of the agreed remedial objectives.

This document deals only with the evaluation of natural attenuation for contaminated groundwater and its use as a remedial solution to protect groundwater and surface water receptors. The attenuation of contaminants within the unsaturated zone is not addressed in this document, although it may be an important process to consider, particularly where groundwater is currently unaffected by land contamination. Assessors must also consider the risks to other receptors, such as humans, property and plants in deriving appropriate risk-management strategies on a “whole-site” basis.

This technical guidance is intended for use by specialists, often consultants acting on behalf of problem holders to develop a strategy to manage risks associated with contaminated groundwater, as well as by Environment Agency staff assessing the acceptability of submitted proposals and designing remedial action for 'orphan sites'. It may also be of use to environmental bodies, academics and other interested parties.

In producing this document, the following protocols have been consulted and are duly acknowledged as valuable sources of information:

AFCEE (1995). Technical protocol for implementing intrinsic remediation with long-term monitoring for natural attenuation of fuel contamination in groundwater (Ref 1).

ASTM (1998). Standard guide for remediation of groundwater by natural attenuation at petroleum release sites (Ref 2).

RTDF (1997). Natural attenuation of chlorinated solvents in groundwater: principles and practices (Ref 3).

Sinke et al (1998). A decision support system for acceptance of natural attenuation as remediation strategy (NOBIS) (Ref 4).

USDON (1998). Technical protocol for factuating natural attenuation of chlorinated solvents in groundwater (Ref 5).

Weidemeier et al (1999). Designing monitoring programs to evaluate the performance of natural attenuation (Ref 6)

1.2 The basis of monitored natural attenuation

In evaluating monitored natural attenuation as a remedial option, three contaminant plume cases can be considered – shrinking, stable or expanding plumes. In general, reliance on natural attenuation processes will be acceptable where it can be shown that the plume is shrinking or stable and where there is no unacceptable impact or risk to receptors. The time-frame within which remedial objectives must be met will be a further factor. For an expanding plume, MNA may be acceptable where it can be demonstrated that there will only be minimal expansion before the plume stabilises and shrinks.

Validating the effectiveness of NA processes will often require the demonstration of several lines of evidence, both direct and indirect, as follows:

- documented loss of contaminant mass in the field (such as historic data showing a reduction in contaminant concentrations with time);
- geochemical and biochemical indicators which demonstrate the natural attenuation process that is resulting in the reduction in contaminant concentration;
- microbiological data to support the occurrence of biodegradation.

Evaluation of these lines of evidence will typically require an understanding of the biogeochemistry and hydrogeology of the site. Specifically, this may involve:

- specialist and detailed hydrogeological investigations to define the flow regime and contaminant transport processes;
- detailed understanding of the flow regime and the processes that influence contaminant transport;
- microbiological testing;
- extended periods of monitoring to collect adequate and representative data.

1.3 Relationship to other guidance

This document provides technical guidance on the evaluation of monitored natural attenuation as a remedial solution to protect groundwater and surface water receptors. The risk to other receptors, such as human health, needs to be considered separately, though the results from assessments of separate receptors must be integrated in any final programme of remedial actions. This guidance is one of the working tools that can be used in the overall process of managing the health and environmental risks that contaminated soil and groundwater represents. Reference should be made to Environment Agency R&D Publication 20, *Methodology for the Derivation of Remedial Targets for Soil and Groundwater to Protect Water Resources* (Ref 7). R&D Publication 20 provides a tiered framework for the derivation of remedial targets to protect identified groundwater and surface water receptors. If natural attenuation is the accepted remedial measure, it will be necessary to demonstrate that either existing groundwater contamination will not exceed these remedial targets in the future, or that contaminant concentrations will be reduced to below these targets. This document is also relevant to the derivation of Tier 3 remedial targets that take account of natural attenuation.

Further guidance on the principles associated with assessing and managing risks from land contamination can be found in *Contaminated Land Research Report CLR11: Model Procedures for the Management of Contaminated Land* (8), which should be read before undertaking any detailed risk assessment on a potentially contaminated site. The Model Procedures detail the principles and processes that may be adopted for assessment and management of risks associated with land contamination. The Model Procedures set out overarching evaluation criteria for the assessment of remedial options including risk management, site conditions, cost benefit, environmental factors, regulatory requirements, time-scale and funding.

1.4 Applicability and constraints in the UK

The main criteria for the acceptance of NA are that:

- 1) NA can be demonstrated with confidence (this will typically require a minimum of two to three years of time-series monitoring data). In view of this requirement, it will also be important to demonstrate that receptors are not at risk during this evaluation period. This is distinct from long-term or performance monitoring, which will be required to demonstrate the continued effectiveness of NA;
- 2) NA will be effective in protecting identified receptors throughout the duration of the monitoring period (and beyond);

- 3) NA can be monitored - the monitoring network must be adequate to demonstrate that NA is occurring according to expectations;
- 4) the remedial objectives for MNA will be achieved within a reasonable time-frame - this will typically be no more than one generation or 30 years. The time-scale for MNA to achieve the remedial objectives should also be reasonable when compared with other remedial options.

The precise criteria that will determine the acceptability of NA will vary on a site-specific basis and will be described in detail in subsequent chapters, but examples of the main technical, practical and regulatory criteria for decision making that may apply are given below:

Technical:

- NA has been demonstrated with an acceptable level of confidence;
- the effectiveness of NA has been shown to continue in the future;
- there is sufficient time for NA to go to completion and it is effective in meeting the environmental objectives in a reasonable time-frame.

Practical:

- access can be obtained and security can be guaranteed for monitoring boreholes;
- there are sufficient budget provisions to investigate and monitor NA;
- NA will work alone or in combination with other techniques;
- future land uses will not adversely affect NA;
- other remedial techniques will not adversely affect NA;
- there is a sufficient time period for monitoring;
- third-party agreement has been obtained for monitoring the contaminant plume beyond the site boundary;
- the long-term liability of landowners/polluters has been resolved.

Regulatory:

- all relevant legislation can be complied with and health and safety obligations met;
- NA will protect identified receptors in both the short-term and long-term;
- expansion of the plume into uncontaminated groundwater should be minimised as far as possible, taking account of the sensitivity of the environment, the impact of any pollution and the likely costs and benefits of preventing plume expansion. This will need to be determined on a site-specific basis, although a general rule should be that the front of the plume should not expand by more than 10 percent of the distance to the nearest specific receptor, which can be either a defined receptor or other compliance point where the groundwater resource must be protected, or by 100 metres (whichever is the lesser);
- remedial objectives can be achieved in a reasonable time frame;
- contingency plan has been developed and can be implemented if NA proves to be ineffective;

- sufficient financial provision for long-term monitoring and contingency plan;
- sufficient (institutional) controls over MNA (for example, section 106 agreement) if undertaken through the planning system.

The Environment Agency considers that the decision to adopt MNA should be based on a judgement that it represents the best overall risk-management option. It should be neither a 'do-nothing' approach nor a mechanism to dilute contaminants throughout the environment.

1.5 Legislation

This section describes the relevant legislation in relation to:

- the control of the activity that caused the pollution of controlled waters;
- the control or removal of residual contamination resulting from activities or releases that have ceased;
- the control of natural attenuation as a remedial option.

The Environment Agency has duties under the Water Resources Act, 1991 (WRA, 1991) to monitor and protect controlled waters (Reference 9). Section 85 of WRA provides powers of prosecution should pollution of controlled waters be caused or knowingly permitted. Within the legislative framework in England and Wales, there is a distinction between statutory controls on activities that are causing or may lead to pollution of controlled waters and legislative instruments that seek to control or remove residual contamination resulting from activities or releases that have ceased. The general relationship between the main legislative instruments, as implemented in England as of May 2000, are set out in Figures 1.1a and 1.1b.

The legal frameworks in Scotland and Northern Ireland are different from those in England and Wales - assessors should consult the Scottish Environment Protection Agency (SEPA) or the Northern Ireland Environment and Heritage Service to ascertain their requirements for MNA proposals.

Control of contamination from existing activities

Figure 1.1a describes the legislation relating to the prevention of water pollution from current activities.

Under the EC Groundwater Directive (80/68/EEC) member states are obliged to take specific measures to prevent List I substances from entering groundwater and to restrict the entry of List II substances so as to prevent pollution. It is important to note that the main focus of the Groundwater Directive is to prevent or restrict discharges from continuing (current) activities, which includes actions undertaken as part of remediation works.

This is enforced primarily via the Groundwater Regulations, 1998 and the Waste Management Licensing Regulations, 1994. Prior to acceptance of MNA as a remedial option, the Environment Agency will require that the activities that caused the pollution have ceased releasing contaminants. In addition, the Environment Agency may also require

works to be undertaken to deal with continuing sources of contamination within the ground, such as non-aqueous phase liquids (NAPLs). That is to say, the Agency expects source control to proceed or accompany MNA proposals.

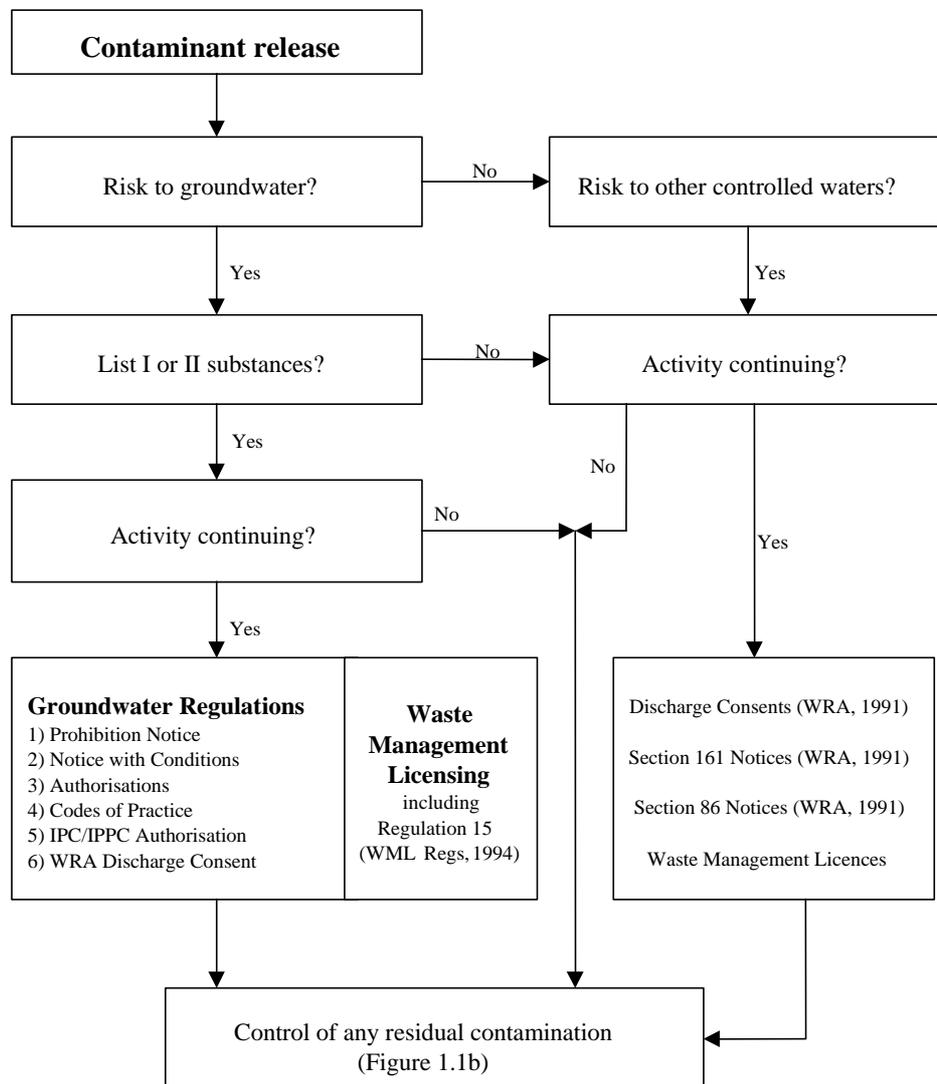
Contaminant releases from current activities normally fall within the following licensing/permitting regimes:

- Discharge consents under the Water Resources Act 1991;
- IPC authorisations under Part I, EPA, 1990 and PPC authorisations in the future;
- Authorisations under Groundwater Regulations, 1998;
- Waste Management Licences under Part II of the Environmental Protection Act 1990.

Where a permit is not automatically required, or where there is an unintentional release, there are also provisions under a variety of legislation to serve notices. These are served at the discretion of the responsible body (normally the Environment Agency, where groundwater is involved) where it is necessary to prevent future pollution or to undertake works to mitigate the immediate effects of polluting activities. Examples of such notices include:

- Groundwater Regulations Notices;
- s86, Water Resources Act Notices;
- s59, Environmental Protection Act, 1990 (removal of unlawfully deposited waste);
- Works Notices (s161A, Water Resources Act).

Figure 1.1a : Legislation associated with releases from current activities



Control of Residual Contamination

The focus of this document is primarily on the use of monitored natural attenuation in the control or remediation of historic contamination. The legislation relating to this, as far as it relates to the pollution of controlled waters, is given in Figure 1.1b.

Until recent years there has been little legislation that has specifically dealt with soil and groundwater contamination arising from historic activities.

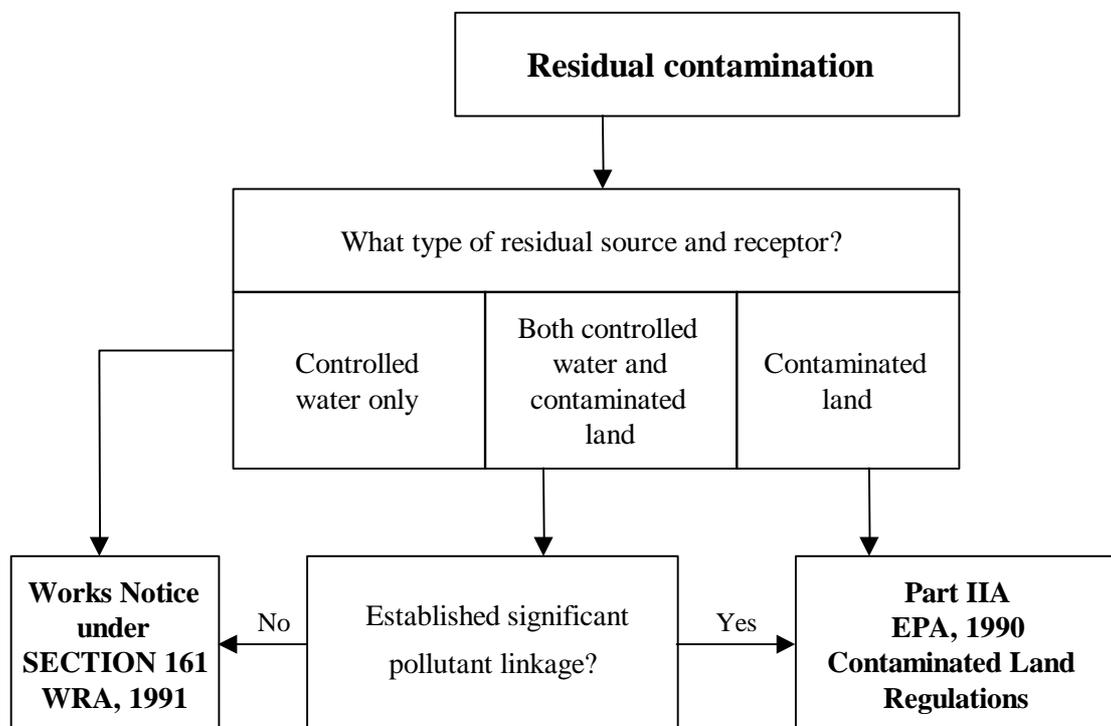
An exception is section 161 of the WRA, 1991 which gives the Environment Agency powers to remedy or forestall pollution of controlled waters and reclaim the costs of so doing from the person(s) causing or knowingly permitting the pollution to occur. Thus the Environment Agency may enter any land or carry out remedial works where it is deemed necessary and appropriate.

Section 57 of the Environment Act, 1995 (which inserts Part IIA into the Environmental Protection Act 1990) introduced specific legislation into the UK to deal with contaminated land that poses unacceptable risks in its current state, and to deal with contaminated groundwater where a significant pollutant linkage to the source of contamination in, on or under land can be demonstrated.

Part IIA of the Environmental Protection Act, 1990, implemented on 1 April 2000, requires local authorities to identify land within their boundaries that falls within the statutory definition of contaminated land, and gives them powers to serve Remediation Notices on “appropriate persons” (that is, those who caused or permitted the pollution and/or the owner or occupier of the site identified as contaminated land). Land may be classed as contaminated land by virtue of actual or likely pollution of controlled waters caused by materials in, on or under the land. Where pollution of controlled waters is an issue, then the Agency must be consulted and its views taken into account. For particular categories of sites, known as “Special Sites”, the Agency takes over regulatory responsibilities. Special Sites include: those where ground waters in certain aquifers (as specified in the Contaminated Land (England) Regulations, 2000) are contaminated by compounds defined in List I of the EC Groundwater Directive; where potable groundwater abstractions are affected and need a change in treatment, or; where watercourses would fail criteria for classification under regulations made under the WRA, 1991.

In other situations, where there is no existing pollutant linkage (because of natural circumstances or human intervention to remove the source or cut the pathway), a modification to Section 161 of the Water Resources Act, 1991 can be used which allows Works Notices to be served on the person or persons who caused or knowingly permitted the pollution to arise, in order that it can be remedied or forestalled. This legislation was implemented in England and Wales in April 1999. Therefore, rather than undertake the work itself and face the difficulties of reclaiming the costs, the Agency can require those responsible for the pollution to undertake the requisite work. If such a person is unable to be found or identified, and if remediation is required, the Environment Agency may decide to undertake the work itself.

Figure 1.1b: Legislation associated with releases from historic contamination



Remedial Activity

Where the Agency considers that it is necessary to require remediation (including MNA) to remedy existing pollution, it will normally enforce such action. Where MNA is being considered as a remediation option, the relevant legislation will be either section 161A of the Water Resources Act, 1991 (implemented via the Anti-Pollution Works Notice Regulations, 1999) or Part IIA of the EPA, 1990 (implemented via the Contaminated Land (England) Regulations, 2000). The relationship between this legislation is described in Figure 1.1b. Where appropriate, powers under s59 of EPA, 1990 in respect of unlawful deposit of waste, or under Part I of EPA 1990 (for IPC-authorized sites) may also be invoked.

Some of the activities that are associated with MNA may themselves be subject to regulatory control. These activities may include drilling and construction of monitoring boreholes, borehole pumping tests, and waste management licensing of complementary remediation techniques.

In some cases, the site owner may voluntarily implement a remediation measure such as MNA. In this case, the Environment Agency may not invoke any powers to control the remediation, although planning controls (such as a Town and Country Planning Act Section

106 Agreement) could be used, if it is subject to planning permission, to provide institutional control to the monitoring process, particularly as this monitoring may occur over several years or decades before the remedial targets are achieved.

The construction and monitoring of off-site boreholes may be a requirement in the assessment and performance monitoring for MNA. Section 161A of the WRA, 1991 gives the Environment Agency the powers to require the construction and monitoring of such boreholes when third party (that is, the landowner) agreement cannot be obtained. The same powers allow the third party to be granted compensation, subject to arbitration. The Environment Agency will not generally undertake the work itself, but require the operator to do so.

1.6 How to use this document

The overall approach for the assessment and monitoring of the effectiveness of natural attenuation as a remedial solution is set out in Chapter 2. Details of each stage of the assessment are described in Chapters 3 to 6 as follows (refer to Figure 2.1):

Initial screening of whether MNA is a viable option	Chapter 3
Procedure for demonstrating that NA processes are occurring	Chapter 4
Procedure for assessing the long-term effectiveness of MNA	Chapter 5
Procedures for monitoring NA to verify that it continues to meet the remedial objectives	Chapter 6

The main text describes the generic approach that should be adopted. The contaminants that are considered in this document include petroleum hydrocarbons, chlorinated solvents, methyl tertiary butyl ether (MTBE) and other fuel oxygenates, phenol, polynuclear aromatic hydrocarbons (PAH), pesticides, herbicides, metals, ammonia and cyanide. The documented procedures may apply to other contaminants, but users will need to collect additional information to that presented here.

The appendices to this document provide technical details in support of the procedures described:

Description of natural attenuation processes	Appendix 1
Data requirements for lines of evidence in demonstration of NA	Appendix 2
Sources of information and analytical techniques	Appendix 3
Fate and transport models	Appendix 4
Methods for assessment of NA	Appendix 5
Presentation of data relevant to NA	Appendix 6
Case histories	Appendix 7

This document does not provide specific information on contaminant properties or degradation rates. Instead references to relevant sources of information are provided, and guidance is given, in Chapter 4, as to the use of literature values in the assessment of natural attenuation.

2. OVERALL APPROACH

2.1 Framework

2.1.1 Structure

The following chapters set out a recommended approach for assessing and implementing monitored natural attenuation as a risk-management strategy for groundwater contamination. The methodology is based on a multi-stage process involving structured decision-making and iterative data collection and analysis. The key steps are described below and summarised in the flow chart in Figure 2.1.

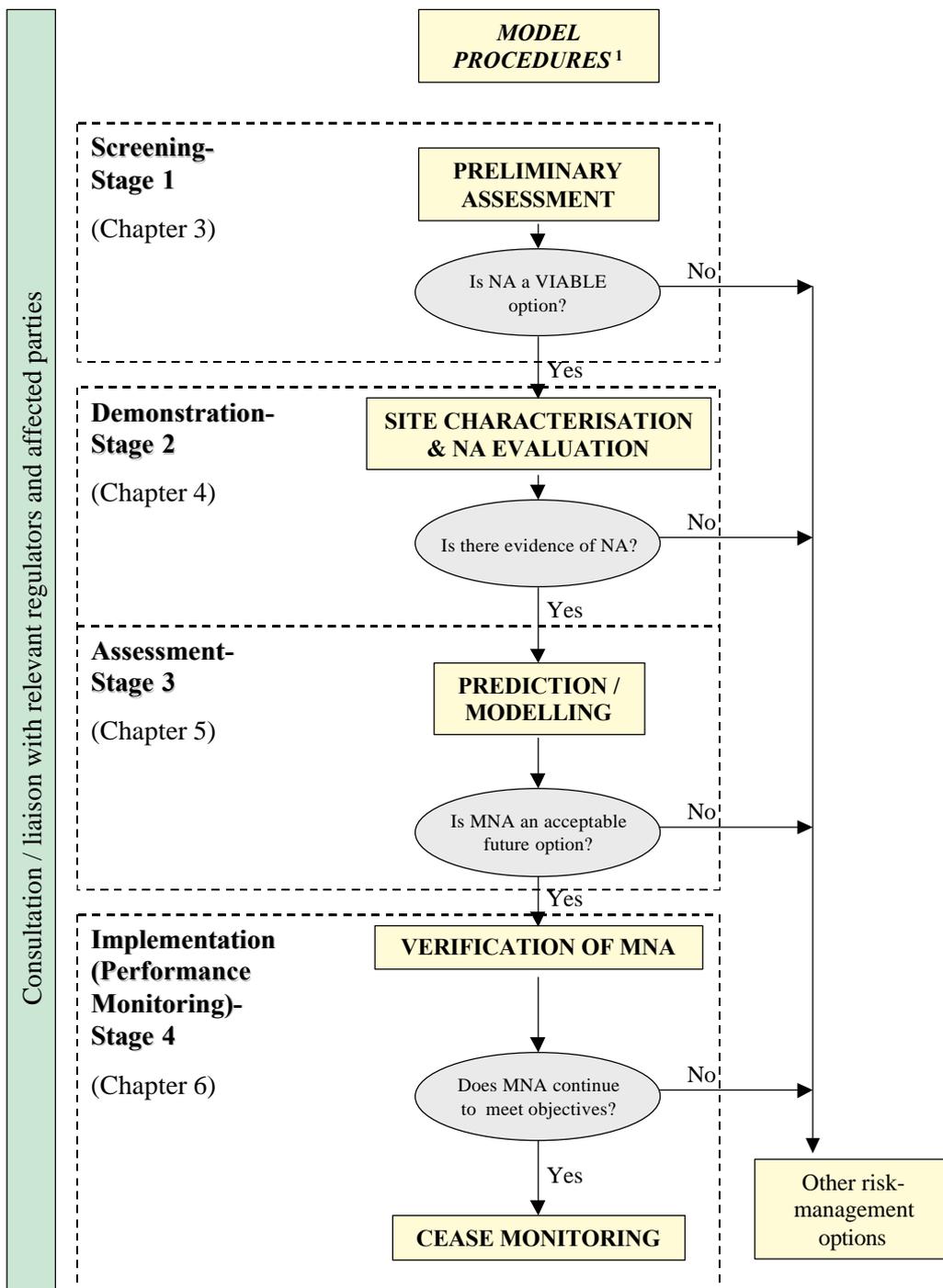
The **screening** stage, described in Chapter 3, considers the *viability* of natural attenuation based on a preliminary assessment of technical, practical, legal and economic constraints. The process is designed for use with limited data where only an indication of the potential for natural attenuation is sought. Typically, this will be at the feasibility stage where alternative active remedial options are also under consideration.

The **demonstration** and **assessment** stages, described in Chapters 4 and 5, address attenuation in greater detail with the aim of providing scientifically defensible evidence to support its subsequent implementation as part of a remediation strategy. The assessment relies on a combination of comprehensive site characterisation and evaluation of natural attenuation to confirm its current effectiveness, followed by predictive modelling to estimate future contaminant fate and transport in groundwater.

The **implementation** stage, described in Chapter 6, covers the long-term monitoring requirements to demonstrate that the remedial objectives are achieved, in line with the predictions made during the assessment. Contingency plans are put into action in the event that performance-monitoring criteria are not met.

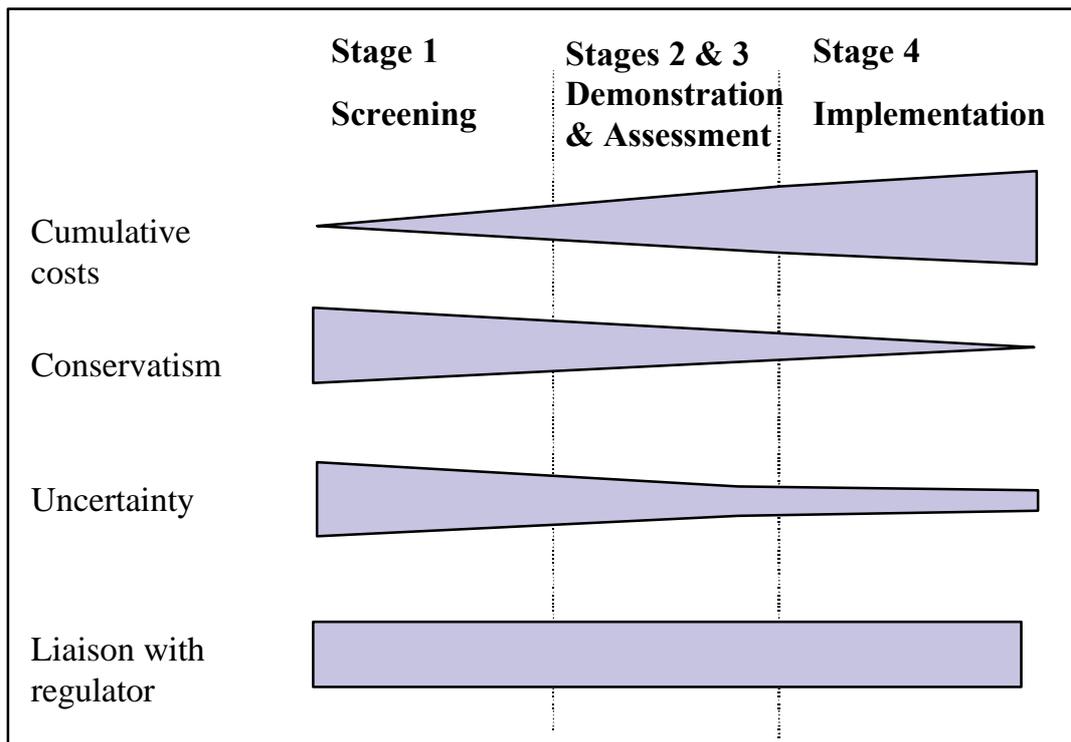
A central focus of this guidance is the conceptual model that describes hydrogeological, biochemical and geochemical characteristics at a site. The model is continually challenged and revised as additional data are collected during successive stages of the assessment. This process entails increased costs as the levels of uncertainty and conservatism in the assessment are reduced - see Figure 2.2.

Figure 2.1: Overall procedure for the assessment of natural attenuation



¹ CLR 11: Model procedures for the management of contaminated land

Figure 2.2 Evolutionary stages of MNA



2.1.2 Key considerations

The following factors should be considered before contemplating a remedial strategy based on MNA.

Liaison and negotiation. Acceptance of MNA for groundwater pollution requires liaison and agreement with various stakeholders, including the relevant regulators (Environment Agency or relevant local authority in England and Wales), landowners, insurers, financiers and prospective purchasers. In the case of the regulator, regular consultation is recommended throughout the screening, demonstration, assessment and implementation stages. Table 2.1 presents the critical decision steps where the regulator’s acceptance of factual data and the problem holder’s interpretation of that data will be needed. Neighbouring landowners may need to be consulted for the purposes of securing access for monitoring wells beyond the site boundary, or highlighting the effects of the remedial programme on groundwater resources in the area.

Time-scale. The application of MNA may take several decades to arrive at a satisfactory outcome. This potentially long time-frame makes MNA susceptible to changes in various technical, economic and regulatory conditions, including groundwater geochemistry, land-use and legislative changes. These factors need to be considered in the design and application of MNA as a long-term remedial strategy. This may mean setting aside financial provisions, such as escrows, to manage the long-term monitoring programme or the contingency plan, as well as accepting institutional controls such as planning restrictions for the land-use.

The determination of what constitutes a reasonable time-frame to attain remedial targets should be made on a site-specific basis, considering factors such as the resource value of the

groundwater (currently and in the future) and the risks to other water bodies and receptors. The Environment Agency seeks to ensure that remediation of contaminated groundwater is achieved effectively and rapidly, while taking account of the likely costs and benefits. In the context of sustainable development, the Agency would expect that, where technically feasible, pollution should not be inherited by future generations and remediation should be substantially complete within a 30-year period.

Contingency plan. In the event that the remedial programme fails to perform as predicted (either as a result of changes to the environment or undefined and unforeseen aspects of the conceptual model) there must be a contingency plan on which to fall back. The proposer will be expected to establish criteria, such as *statistically significant* trends in data, to trigger the contingency plan – see Chapter 6.

Costs and benefits. In many cases, the overall cost of implementing monitored natural attenuation will be considerably lower than for active remedial solutions. However, the initial investment on site investigation is normally greater due to more comprehensive data requirements. Apart from the potential for overall cost savings, natural attenuation solutions offer additional benefits that derive mainly from the relatively non-intrusive, in-situ nature of the process. There are, however, technical and practical limitations. For more guidance on assessing likely costs and benefits for the remediation of contaminated groundwater see References 11 and 12.

Uncertainty and the burden of proof. Considerable technical, legal and economic uncertainties surround natural attenuation. A weight-of-evidence approach can remove some of the uncertainty of the complex biogeochemical processes that govern natural attenuation. This approach is based on providing multiple, independent and converging lines of evidence, including:

- documented loss of contaminants at the field scale;
- presence and distribution of geochemical/biochemical indicators of natural attenuation;
- direct microbiological test data, although this line of evidence should only be used when the first two are inconclusive.

The onus is on the proposer to provide sufficient evidence to show the potential for NA to achieve the remedial objectives within a reasonable time-frame. The level of required confidence increases at successive stages in the evaluation process as more data are acquired.

Legislation uncertainties are managed most effectively by continued negotiation with the regulator, whilst various mechanisms are available to manage the financial risk and uncertainty (Ref 13).

Data requirements. The need for a body of evidence to support NA requires significant data collection and analysis. The types of parameters that are typically measured include (see Appendix 2):

- chemical parameters including concentrations of parent and daughter contaminants and metabolic by-products;
- geochemical parameters including redox potential, electron acceptors (for example, dissolved oxygen, nitrate, sulphate, carbon dioxide) and general water quality parameters such as pH, conductivity and alkalinity;

- physical parameters such as, mineralogy; hydraulic conductivity, hydraulic gradient and temperature;
- biological parameters such as, biodegradation rates.

Third parties. The importance of the agreement/acceptance by third parties for MNA should not be overlooked. The actions or omissions of third parties may, for example, affect the remedial programme, whilst the remediation programme may in turn impact on these parties. A possible concern lies in the potential civil liabilities associated with migration of contamination beneath neighbouring properties in the event that pollutants migrate beyond the boundary. Stakeholders should always consult and liaise with neighbours and the Environment Agency will seek to make factual information about groundwater pollution available where off-site migration is anticipated. Useful guidance on communicating information about risks from contaminated land is provided in Reference 14.

2.1.3 Application

This guidance is sufficiently generic for application to groundwater contaminated by organic and inorganic substances under a wide range of UK hydrogeological conditions. The specificity lies in the actual data requirements that will be needed to demonstrate attenuation of contaminants under different environmental conditions.

This guidance is designed to follow on from risk assessment conducted in accordance with the Model Procedures (Reference 8). MNA may be used independently or as part of an integrated treatment train approach incorporating active remedial measures. Examples of situations where MNA and active remedial technologies can be integrated include:

- periphery of a plume is left to attenuate whilst active remedial measures treat the areas around the source zone;
- natural attenuation is used to manage residual contamination after active remediation has achieved its objectives;
- nutrients, oxygen-releasing compounds or hydrogen-releasing compounds are applied to enhance natural processes (in-situ bioremediation);
- active remedial measures form the basis of a contingency plan should MNA fail to meet its objectives.

Professional judgement will be required throughout the application of MNA, and a thorough understanding of hydrogeology and geochemistry is considered essential. Other disciplines, including microbiology and chemistry, may also be required.

2.2 Regulatory consultation and criteria for acceptance

Key decision points where the Agency will seek to be consulted are presented in Table 2.1, below. Typically the problem holder will present the results and conclusions to the regulator at the end of each stage, before reaching a consensus and commencing to the next. However, it is

recommended that lines of communication are kept open throughout and that regular updates are provided in order to minimise the duration of the ‘formal’ consultation. Consultation must also reflect any additional requirements of the legislation under which works are performed.

Table 2.1. Key decision points requiring Agency consultation

Stage	Decision	Likely outputs
Screening	Are there sufficient site data available to support an initial view that MNA is a viable remedial option?	Initial conceptual model Qualitative predictions that NA will protect identified receptors, if any, and meet all other remedial objectives Judgement that there is no immediate risk to receptors, and that there is sufficient time to undertake a more detailed assessment
Demonstration and Assessment	Do the site characterisation data and results of the modelling demonstrate that NA is occurring and can achieve the risk-management objectives?	Report detailing: <ul style="list-style-type: none"> • lines of evidence • predictions based on modelling of contaminant fate and behaviour • uncertainties and assumptions • identification of monitoring and contingency plan
Implementation	Is the monitoring programme sufficiently robust? Do the results of monitoring demonstrate that the remedial goals have been attained and monitoring can cease?	Proposal detailing planned monitoring strategy, including sampling, performance criteria, quality assurance and contingency plan Report detailing monitoring results, data analysis and justification for ceasing monitoring

The Agency will assess each case on its own merits, according to the specific risks associated with the site and its surroundings. The onus is on the proposer to put forward a case to demonstrate the effectiveness of NA both now and in the future. This requires providing scientifically defensible, independent and objective lines of evidence to demonstrate that MNA will meet the remedial objectives. Uncertainties in the attenuation processes, coupled with the long time-scales typically associated with NA, mean that detailed characterisation, long-term monitoring and the provision of a contingency plan are invariably a prerequisite.

Generally, the weight of evidence required by the regulator will be influenced by the level of actual or perceived risk, which will in turn be influenced by:

- the sensitivity of the site, in terms of the strategic resource value of groundwater and the presence and proximity of vulnerable receptors;
- the hazardous properties of the contamination in terms of its mobility, persistence and toxicity, and the potential to degrade to other substances with those properties;
- the seriousness of the pollution, for example, severe pollution by List I and II substances under the EC Groundwater Directive;

- the nature of the dominant attenuation mechanisms, particularly the reversibility of processes;
- the level of uncertainty in the definition of the conceptual model and in the assessment/monitoring data available.

3. SCREENING

3.1 Introduction

This chapter describes a screening methodology to establish whether monitored natural attenuation is a *viable* remedial option for polluted groundwater at a site. The process is designed to highlight at an early stage, and with minimum information, any practical, technical, legal or economic constraints that, individually or collectively, may preclude its application. Eliminating sites in this manner avoids investing in unnecessarily detailed characterisation where MNA is not viable. Conversely, the process provides a sound basis on which to assess attenuation in greater detail in cases where it is considered a viable option.

The screening stage assumes that the site has been investigated and the risks assessed in accordance with the process described in the *Model Procedures for the Management of Contaminated Land* (Ref 8).

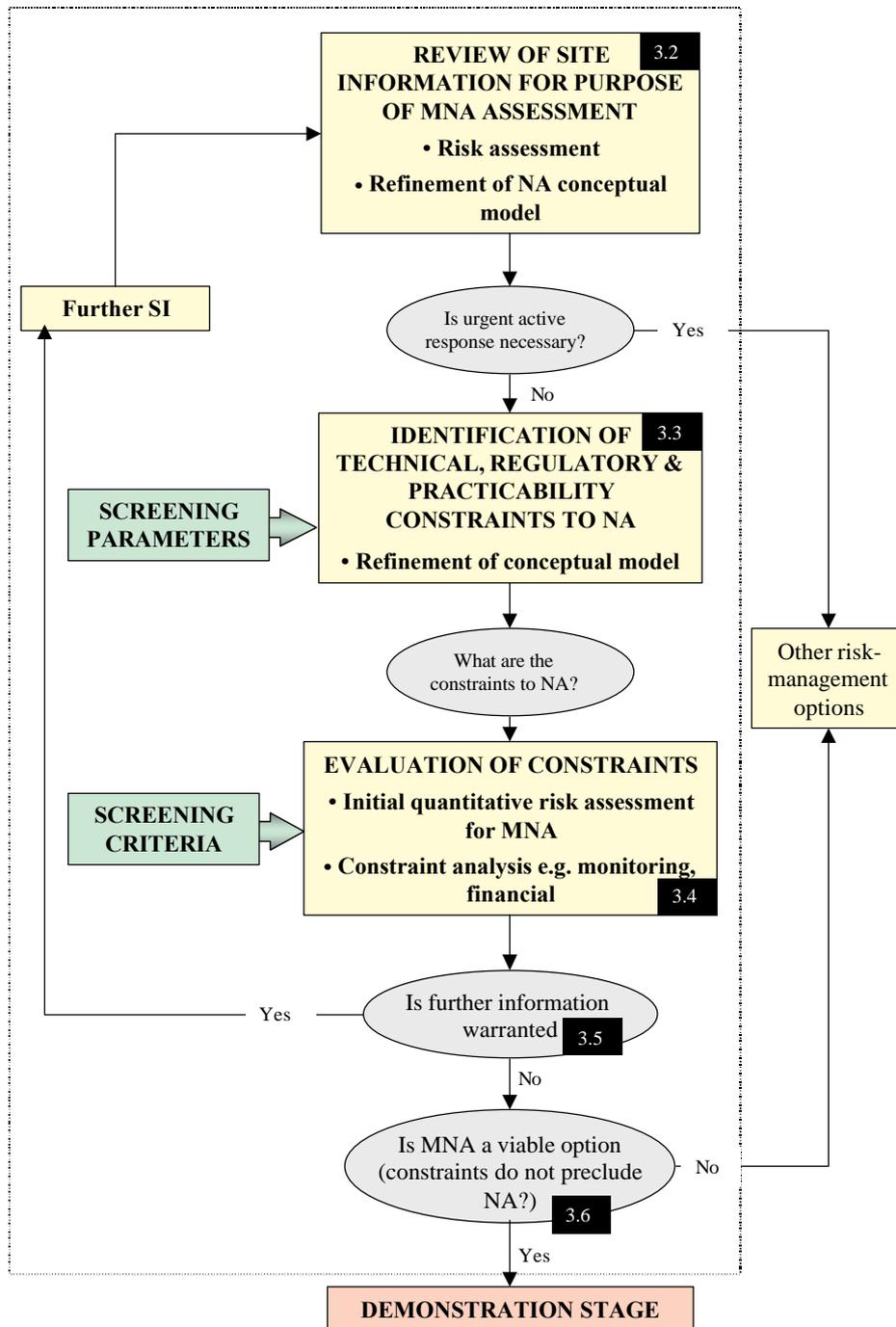
3.2 Methodology

Figure 3.1 outlines the steps involved in the screening of MNA viability. The boundary that defines this stage is not fixed, and more comprehensive data analysis may be conducted using the procedures described in the subsequent assessment stage. This may be warranted where remedial options are limited and/or where there is a strong commitment on the part of the proposer to apply monitored natural attenuation.

3.2.1 Data requirements

As a minimum, the site-specific information detailed in Table 3.1 will be needed to screen the suitability of a site for natural attenuation. Appendices 2 and 3 present a summary of methods for collating data for the purposes of evaluating MNA.

Figure 3.1: Overview of screening stage



3.6 Denotes the section number where explanation can be found

Table 3.1. Minimum data requirements for screening stage

Information	Site-specific data essential	Site-specific data preferable ¹
<u>A. Contaminant properties</u>		
Indication of concentration and location of contaminants, and approximate delineation (vertical and lateral) of plume	✓	
Identification of contaminant source, such as history of contaminant release	✓	
Background contaminant concentrations in locality including, where possible, contribution of other contaminant sources		✓
Nature of contamination, including phase (adsorbed, dissolved, liquid, gaseous)	✓	
<u>B. Aquifer characteristics</u>		
Aquifer status		
• Major / Minor / Non-aquifer	✓	
• Source Protection Zone (SPZ I, II or III, non-modelled abstraction ² , or no abstractions)	✓	
Aquifer properties:		
• Flow mechanism, e.g. fissure/intergranular flow		✓
• Direction of groundwater flow	✓	
• Groundwater velocity (hydraulic conductivity, hydraulic gradient, porosity ³)	✓	
<u>C. Receptors/compliance points</u>		
Location of receptors, e.g. extent of aquifer, location of abstractions, springs, rivers and estuaries and their proximity to site	✓	

1. For more details of the use of data for MNA purposes, see Appendix 2.
2. No modelled SPZ, as in the case of many private potable abstractions.
3. Literature values may be acceptable.

NB. Where no site-specific data are available, References 15 to 19 inclusive are preferred.

3.2.2 Initial review of data

Information acquired during the initial site characterisation is used to construct a preliminary conceptual model that describes the following elements:

- contamination – nature (elements/compounds, liquid (NAPL), dissolved, adsorbed, gaseous phase), location, status (historical or ongoing source), extent (vertical and lateral) and concentration;
- pathways – direction of groundwater flow, flow mechanism (intergranular/fracture, consistent/preferential) and flow rate;
- receptors – type (abstractions, watercourses, springs and groundwater resources) and distance/direction from site.

The conceptual model is used to visualise and assess the plausibility of contaminant - pathway - receptor linkages and, thereby, potential risks, including:

- impact to discrete off-site receptors; and
- expansion of the plume into uncontaminated groundwater.

A priority of this review is to identify any imminent risks that warrant urgent action ahead of, or in place of, natural attenuation. Circumstances where this may be the case include incidents where impact to a receptor has already been detected, or there is a significant likelihood of imminent impact occurring. Where the initial assessment indicates that no active or urgent remedial response is necessary, the viability of natural attenuation is assessed in greater detail during the screening process as described below.

3.3 Screening process

The following aspects need to be considered when assessing the viability of MNA:

- **Technical reliability** of natural attenuation (section 3.3.1) based on:
 - contaminant factors (e.g. chemistry, solubility, toxicity, density, volatility)
 - environmental factors (geochemical conditions and hydrogeological characteristics of aquifer such as heterogeneity, isotropy, conductivity)
- **Practicability** (section 3.3.2);
- **Economics** (section 3.3.3);
- **Regulatory acceptability** and **institutional controls** (section 3.3.4).

Each of these aspects is discussed in sections 3.3.1 to 3.3.4. The level of uncertainty in these factors is also important in determining the viability of natural attenuation. Uncertainty is, therefore, discussed throughout the screening process. Table 3.6 summarises the screening criteria and process.

3.3.1 Technical screening considerations

Technical screening factors can be subdivided into two categories - **contaminant properties** and **environmental characteristics**. Collectively, these factors determine the fate and behaviour of contaminants in aquifer systems. In turn, the fate and behaviour of

contamination, together with the toxicological properties, influence the suitability of MNA in terms of:

- ensuring protection of an identified receptor
 - the relative rates of contaminant migration and degradation/ attenuation will, amongst other factors, greatly influence the risk of impact on a receptor;
 - degradative, non-reversible processes provide greater assurance that MNA will ensure long-term protection of a receptor;
 - degradative mechanisms may, however, increase the risk to a receptor in the shorter term, where contaminants degrade to harmful daughter products (for example trichloroethene degrading to vinyl chloride). Subsequent degradation of the daughter products to ethene means that the increased risk is often temporary.
- avoiding significant pollution
 - contaminant concentrations, compared to environmental quality standards, will determine the severity of pollution and, therefore, the suitability of MNA.

Contaminant factors

The effect of contaminant properties on natural attenuation processes (and the reliability of MNA) are summarised in Table 3.2. The dominant attenuation mechanisms for various contaminant groups are presented in Table 3.3.

Table 3.2. Contaminant properties and their effect on the viability of MNA

Contaminant property	Issues	Implication
Chemistry (elements, compounds and phases)	<ul style="list-style-type: none"> • Reversibility of attenuation (see also Table 3.3) • Rates of degradation • Formation of more harmful daughter products 	<ul style="list-style-type: none"> • The mass of organic and some inorganic <i>compounds</i> (such as ammonia) can be reduced by destructive mechanisms - (bio)chemical reactions, biodegradation, and oxidation (reaction with oxygen) and reduction/elimination reactions – which are irreversible. In contrast, metals (<i>elements</i>) cannot be destroyed and the dominant attenuation mechanisms – sorption and redox reactions – are reversible. Depending upon geochemical conditions, stable metal contaminants may be released into more mobile forms. For this reason, MNA is less suitable for metals than it is for organics and some inorganics. • The rates of contaminant degradation, measured in terms of half-life, vary considerably (orders of magnitude differences) according to site-specific conditions. Even relatively recalcitrant compounds such as MTBE, PAHs and PCBs will undergo degradation under suitable environmental conditions, while compounds generally regarded as biodegradable (such as benzene) may not degrade in environments that appear amenable for degradation. The wide variability and fluctuation in degradation rates make long-term prediction of MNA particularly difficult. • In general, biodegradation rates decrease as the molecular weight and/or number of aromatic rings increase. However, dechlorination by halorespiration is more rapid for highly chlorinated compounds than for compounds that are less chlorinated. Significant degradation only occurs for dissolved phase or sorbed organic compounds, with negligible rates observed for degradation of non-aqueous phase liquids (NAPLs). Generally, aerobic degradative mechanisms are more rapid than anaerobic, although anaerobic reactions are often critical for contaminants. • Degradation may lead to the generation of intermediate ‘daughter products’ with greater toxicity/mobility than the parent compound.
Solubility and toxicity	<ul style="list-style-type: none"> • Potential rate of plume expansion • Contaminant loading/flux • Rate of removal of source term • Inhibitory effects on degradation • Exceedance of environmental quality standards 	<ul style="list-style-type: none"> • High solubility compounds, such as MTBE and phenol, dissolve readily in groundwater, potentially forming rapidly expanding and mobile plumes (depending upon groundwater flow regime). Under these conditions, the contaminant loading within the aquifer will be relatively high. Where groundwater flow rates are slow, inhibitory effects, such as toxicity, may develop or depletion of essential nutrients may occur. This may then reduce the rate of contaminant degradation. Contaminants with lower solubility form plumes which develop over longer periods, thereby extending the time-frame over which attenuation mechanisms must act. However, the contaminant loading within an aquifer will be relatively low, reducing the risk that severe pollution of groundwater will occur. • Compounds with relatively high solubility compared to their environmental standard or background quality have the potential to exceed acceptable concentrations in groundwater. The solubility of benzene, MTBE and many chlorinated solvents exceed the maximum allowable concentrations under drinking water guidelines by many orders of magnitude, as shown below:

		Relative solubility	Compound (and standard)	Solubility in water at 20°C (mg/l)	Solubility/drinking water standard ratio
		High	Trichloromethane ⁽¹⁾	8,000	2.7 x 10 ⁶
			MTBE ⁽³⁾	43,000	8.6 x 10 ⁵
			TCE ⁽¹⁾	1,100	3.7 x 10 ⁴
			Benzene ⁽²⁾	1,780	1.8 x 10 ⁵
			PCE ⁽¹⁾	150	1.5 x 10 ⁴
		Medium	Toluene ⁽²⁾	500	700
			Vinyl chloride ⁽²⁾	1.1	550
			Ethyl benzene ⁽²⁾	150	500
		Low	Benzo-a-pyrene ⁽²⁾	0.0038	5.4
		Drinking water standards: 1= Water Supply (Water Quality) Regulations 1989; 2= World Health Organisation Guidelines for Drinking Water Quality, 2 nd Edition; 3 = Florida State Drinking Water Standard.			
Density	Ability to define, with accuracy, contaminant location, and predict its fate and behaviour	<ul style="list-style-type: none"> Dense non-aqueous phase liquids (DNAPLs) have a complex distribution pattern, sinking below the water table until they reach a confining layer (for example, clay lens, aquitard), or are unable to enter pore throats due to capillary forces. The contamination may not necessarily move in the direction of groundwater, and may move into small fractures and pore spaces. This makes it difficult to locate and delineate DNAPL contamination. The converse applies to light non-aqueous phase liquids (LNAPLs) which are located at the water table and form plumes that follow the direction of groundwater flow, although not necessarily at the same rate. 			
Volatility	Contaminant loading Increased (alternative) risks	<ul style="list-style-type: none"> Volatilisation may contribute to natural attenuation through the transfer of volatile organic compounds (VOCs) from the liquid phase in the subsurface to vapours in the unsaturated zone or to the atmosphere. The rate of volatilisation is a function of the chemical characteristics of the contaminant (for example, Henry's Law constant) and the volumetric air content of the soil. Volatilisation can present additional health and safety risks, for example by migration of vapour through the vadose zone into buildings. These risks should be assessed and taken into account in the design of the remedial strategy. 			

The favoured contaminant characteristics for natural attenuation are:

- low toxicity (or low solubility relative to toxicity-based environmental standard) – this minimises the risk of exceeding an environmental quality standard;
- moderate solubility – this reduces the risk of a high contaminant loading developing which, depending upon the groundwater velocity and dispersion, may present a risk to receptors and inhibit degradation;
- non-reversible (destructive) mechanisms are preferred to (non-destructive) reversible processes;
- rapid degradation (for example, low half-life) relative to groundwater velocity to reduce the risk that the contaminant may “break through” at a receptor;

Table 3.3. Dominant attenuation mechanisms for principal contaminant groups

Contaminant type	Examples	Non-degradative attenuation mechanisms ¹				Degradative attenuation mechanisms ²						
		Methylation	Precipitation ³ & Cation exchange	Sorption & binding ⁴	Volatilisation ⁵	Aerobic degradation ⁶ (contaminant as electron donor)	Anaerobic degradation ⁷ (contaminant as electron donor)	Reductive dehalogenation (contaminants as electron acceptor)	Fermentation	Co-metabolism	Oxidation/reduction	
Chlorinated solvents ^{8,9} ≥ 3 chlorine atoms	PCE; TCE; TCA; TCM			✓	✓	✓?	✓	✓✓			✓	✓
< 3 chlorine atoms	DCM; VC; DCE			✓	✓	✓✓	✓	✓	✓ ¹⁰	✓		
Petroleum hydrocarbons	BTEX; middle distillates			✓	✓	✓✓	✓		✓	✓		
Oxygenates	MTBE, TAME, EBTE				✓	✓✓				✓		
Heavy metals (cationic)	Hg, Cd, Zn, Pb, Ni, Sr, Co	✓ ¹¹	✓	✓✓								
Heavy metals (anionic)	CrO ₄ , AsO ₄ , AsO ₃ , TcO ₄			✓✓								
Inorganics	Ca, Mg, Si		✓✓									
Anions	PO ₄ , BO ₃		✓✓	✓✓								
Ammonia	NH ₃ , NH ₄ ⁺		✓✓	✓		✓						
Cyanide	CN			✓		✓						✓
Nitrate	NO ₃ ⁻						✓		✓			✓✓
PAHs	Naphthalene			✓✓		✓	✓				✓?	
Creosote	Phenols and phenolics				✓	✓✓	✓✓		✓	✓		
Pesticides	See overleaf ¹²			✓		✓	✓	✓?		✓?		

✓✓ = primary importance; ✓ = secondary importance ? = some doubt exists over the process

NB. Dispersion and diffusion are applicable to all contaminants and have, therefore, been excluded.

- Sorption and redox reactions are the dominant mechanisms for reducing the mobility, toxicity or bioavailability of inorganic contaminants. Precipitation reactions and absorption into the solid matrix of a soil (via occlusion, diffusion into dead-end pores, or structural collapse of the mineral around the sorbed species) are generally stable, whereas surface adsorption and organic partitioning (complexation) are more reversible. Contaminant concentrations, pH, redox potential and chemical speciation may release a previously stable contaminant.
- Unlike metals which cannot be destroyed, the mass of organic and inorganic compounds (such as ammonia) can be reduced by (bio)chemical reactions comprising hydrolysis (reaction with water, acids and bases), photolysis (reaction with sunlight, or with reactive radicals produced by light energy), biodegradation (reaction with enzymes or other biogenic compounds) and oxidation (reaction with oxygen) and reduction/elimination reactions. Generally, the rates of abiotic processes are slow compared to biologically-mediated degradative mechanisms, a notable exception being the breakdown of 1,1,1-TCA. Biological degradation is the dominant process controlling the fate and transport of many organic contaminants. Through a series of oxidation-reduction reactions, dissolved contaminants such as trichloromethane are transformed into innocuous by-products such as carbon dioxide, chloride, methane and water. However, intermediates may be generated which are more toxic and mobile than the original compounds. Transient degradation occurs by the following mechanisms:
 - aerobic degradation – transformation and/or elimination of an organic compound by micro-organisms in the presence of oxygen. This is often the most thermodynamically favoured reaction, providing the greatest energy to the micro-organism;

- anaerobic degradation – transformation and/or elimination of an organic compound by micro-organisms in the absence of oxygen. Compounds other than oxygen act as electron acceptors for example, nitrate, manganese IV, iron III, sulphate and carbon dioxide;
 - halorespiration - the contaminant acts as an electron acceptor and hydrogen from fermentation of organic compounds acts as the electron donor;
 - fermentation - oxidation and reduction reactions involving the transfer of electrons between organic compounds;
 - cometabolism - an enzyme or cofactor produced by a micro-organism fortuitously degrades an organic contaminant. For example, anaerobic cometabolism (“reductive dechlorination”) is a common degradation route for highly chlorinated aliphatic compounds such as PCE and TCE.
3. For example, precipitation as insoluble sulphides and carbonates.
 4. For example, sorption to iron hydroxides, carbonate minerals, clay matrices.
 5. Primarily in the unsaturated zone.
 6. Aerobic degradation - oxygen acts as the electron acceptor.
 7. Anaerobic degradation – denitrification, Fe(III) reduction, sulphate reduction, methanogenesis i.e. NO₃, Fe, SO₄ and CO₂ (in that order) plus chlorinated solvents act as electron acceptors. VC and DCM are the only known examples of chlorinated solvents that undergo anaerobic degradation as electron donors.
 8. PCE = tetrachloroethene; TCE = trichloroethene; TCA = 1,1,1-trichloroethane; TCM = trichloromethane; DCM = dichloromethane; VC = vinyl chloride; DCE = dichloroethene.
 9. Highly chlorinated solvents do not degrade aerobically.
 10. DCM is susceptible to degradation by fermentation.
 11. Mercury may undergo methylation and subsequent volatilisation.
 12. Chlorinated (lindane), organophosphate (malathion, diazinon); pyrethroid (cypermethrin); triazine (simazine); phenyl urea (isoproturon, diuron), phenoxyacid (mecoprop); cationic (paraquat).

Environmental factors

On the basis of field trials and case studies, general observations have been made regarding the effects of various biogeochemical factors on attenuation processes. For example, in extreme circumstances the presence or absence of a compound can prevent an attenuation process from working. This has led to the development of “operating windows” which provide an indication of the likelihood that NA will work, all other factors being favourable. Examples of operating windows are provided in Table 3.4.

Table 3.4. Selected environmental, chemical and geochemical screening factors

Screening factor	Example of optimal operating ranges	Examples of operating windows and indicators
<i>Geochemical conditions</i>		
<ul style="list-style-type: none"> pH 	Optimal pH range for microbial degradation lies between approximately 6 and 8.5.	
<ul style="list-style-type: none"> Anoxic conditions 		Anaerobic degradation is unlikely to occur at DO concentrations greater than 0.5mg/l, and does not occur at concentrations greater than 1mg/l.
<ul style="list-style-type: none"> Oxic conditions 		Aerobic degradation unlikely to occur where dissolved oxygen concentrations are below 1mg/l.
<i>Chemical conditions</i>		
<ul style="list-style-type: none"> Concentration of contaminants (in relation to inhibitory concentrations) 		Monohydric phenols: degradation unlikely where concentrations exceed 500mg/l and probable where concentrations less than 50mg/l.

The operating windows do not take into account interrelationships between various factors, such as simultaneous reactions of degradation by-products.

Hydrogeological factors

The physical properties of an aquifer that have the greatest impact on the application of NA comprise the flow rate and flow mechanism present, and the hydraulic conductivity.

Flow rate and mechanism

Preferential groundwater pathways, including fractures, joints and solution channels result in higher contaminant velocities, which in turn can lead to rapidly expanding contaminant plumes where attenuation is limited. Groundwater flow under these conditions is highly unpredictable, making plume characterisation difficult. Intergranular flow is more predictable and the travel rates are lower, providing greater time for degradation to occur, and longer exposure of contaminants to active biodegradative/mineral sites.

Hydraulic conductivity

The hydraulic conductivity of an aquifer depends upon a number of physical factors including porosity and particle size distribution. The favoured aquifer characteristics for the assessment of natural attenuation are isotropic, intergranular flow mechanisms, as these provide the opportunity to predict groundwater flow patterns and attenuation processes with the greatest confidence. By contrast, characterisation of the hydraulic regime in fissured aquifers, such as the Chalk, is complicated by the highly heterogeneous nature of the system. Long-term predictions in the performance of natural attenuation are, therefore, likely to be inherently uncertain.

The properties of selected UK aquifers are shown in Figure 3.2, related to the dominant flow mechanism and strategic resource value, and are further summarised in Table 3.5.

Redox geochemistry

Redox measurements (Eh) may be used to provide an insight into the mechanisms of biodegradation that may be occurring within a groundwater pollution plume. The redox potential of groundwater typically varies between -400mV and $+800\text{mV}$ and different (bio)chemical reaction will only occur under specific redox conditions. Aerobic biodegradation of organic contaminants generally occurs under a redox potential greater than $+150\text{mV}$. Mildly reducing conditions (Eh of $+50\text{mV}$ to -150mV) are normally associated with manganese reduction and nitrate reduction. As the environment becomes increasingly reducing ($<-200\text{mV}$), biological degradation is on the basis of iron reduction, sulphate reduction and CO_2 reduction (methanogenesis) sequentially.

If redox potential is assessed, it should be considered only on field samples collected under suitable (airtight) conditions.

Figure 3.2. Classification of selected geologic formations (based on Ref 9)

Dominant flow mechanism	Intergranular flow	Oxford Clay; Blue Lias; Peat; Lacustrine deposits	Alluvium; Fluvio-Glacial Sands & Gravels	Thames Gravels; Greensands
	Intergranular and fracture flow	Jurassic Lower Lias; Mercia Mudstone	Coal Measures; Devonian (Old Red) Sandstone	Permo-Triassic Sherwood Sandstone; Pleistocene Norwich Crag; Triassic Penarth Group
	Fracture flow	Silurian Shales	Millstone Grit	Magnesian Limestone; Carboniferous Limestone; Chalk; Lower Permian Basal Breccias, Conglomerates and Sandstones; Middle Jurassic Limestones.
		Non-aquifer	Minor Aquifer	Major Aquifer
		Strategic groundwater resource value		

Table 3.5. Properties of selected UK aquifers, and their implications for MNA

Aquifer	Issues	Implications
<i>Chalk</i>	<ul style="list-style-type: none"> • Fissure flow • Preferential pathways • Rapid flow • Low fissure porosity, high matrix porosity • Fissure/pore water interaction • Significant variation in vertical and horizontal permeability • Large seasonal water table variation • Large dispersion • Regional variations in behaviour of the chalk aquifer (e.g. solution features are characteristic of south east England) 	<ul style="list-style-type: none"> • Borehole location in relation to preferential pathways • Variable and rapid travel times need to be taken into account in assessing viability of attenuation and frequency of monitoring • Short-circuiting of normal flow regime at times of high water table • Thick aquifers and deep unsaturated zones may result in high cost of investigation • Alkaline groundwater – metals not generally mobile unless low pH source
<i>Triassic Sandstone</i>	<ul style="list-style-type: none"> • Intergranular flow, although fissure flow can be locally associated with faults, subsidence over coal workings • High porosity • Multi-layered aquifer due to presence of marl horizons • Horizontal and vertical flow important • Deep aquifer • Mineralogy: Fe (II) Oxide 	<ul style="list-style-type: none"> • Construction of boreholes due to multilayered system and potential for diving plume • Slow groundwater velocities • Vertical hydraulic gradients • High cost of investigation in thick aquifers/ deep unsaturated zones • Layering may limit vertical dispersion
<i>Inferior Oolite</i>	<ul style="list-style-type: none"> • Fissured aquifer • Low porosity • Preferential pathways • Rapid flow • Variable permeability 	<ul style="list-style-type: none"> • Borehole location in relation to preferential pathways • Difficult to be confident about representative nature of monitoring results • Well buffered
<i>Lower Greensand</i>	<ul style="list-style-type: none"> • Fissure and intergranular flow • Moderate porosity • Mineralogy (glauconite) 	<ul style="list-style-type: none"> • Potentially good attenuation
<i>Carboniferous Limestone</i>	<ul style="list-style-type: none"> • Fissure flow/Karst • Low matrix porosity • Large seasonal watertable fluctuation • Deep aquifer 	<ul style="list-style-type: none"> • Borehole location • Connectivity of fissures • Rapid flow possible • Alkaline – buffering capacity
<i>Sand & Gravel</i>	<ul style="list-style-type: none"> • Thin aquifer • Shallow water table • High porosity • High organic and clay content • Nutrient availability • Variable lithology and permeability 	<ul style="list-style-type: none"> • Range of investigation techniques • Thin unsaturated zone • Easiest translation of US experience to UK hydrogeology • Little buffering

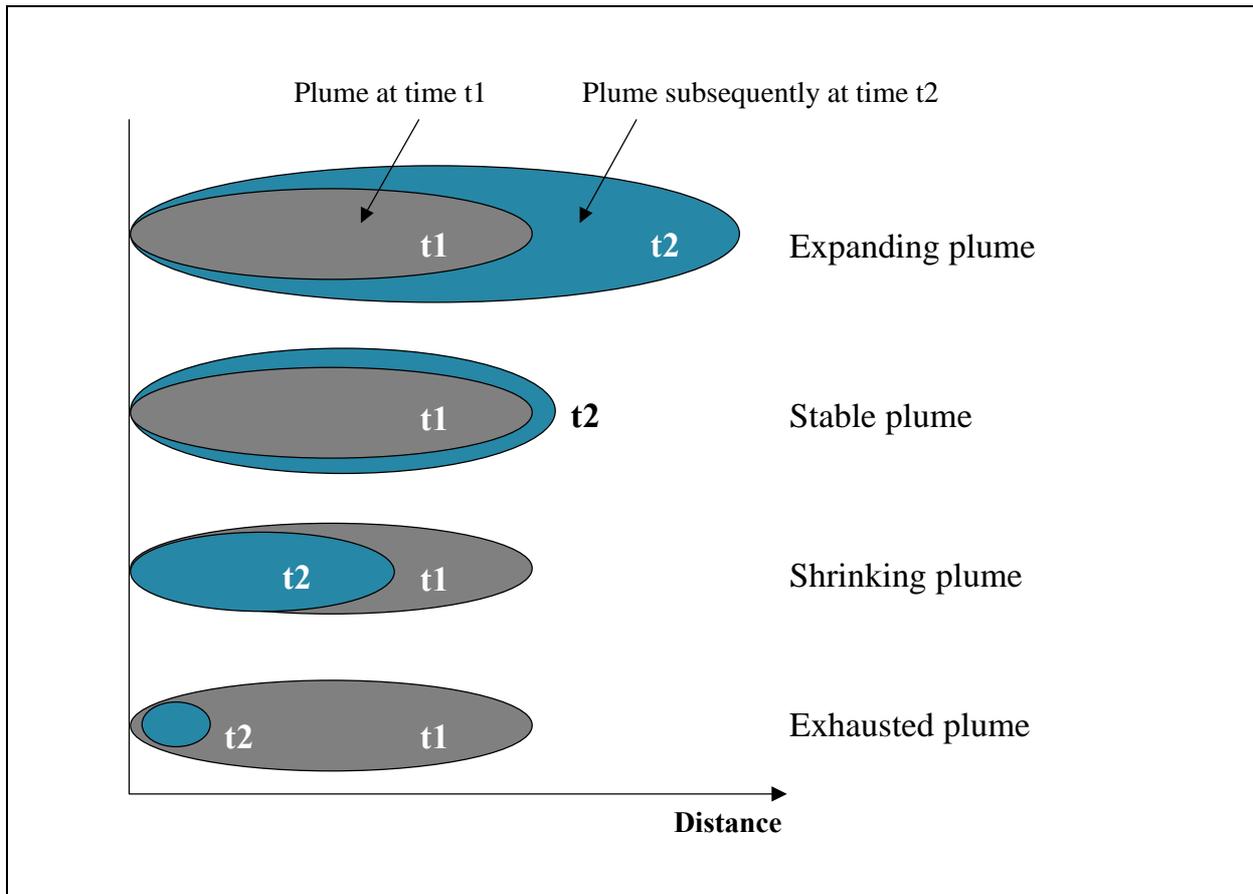
Other technical factors

A number of technical issues need to be considered during the screening of MNA. These include the following:

- multiple contaminant sources and plumes may make it difficult to isolate individual plumes and demonstrate mass reduction;
- the interaction of different types of contaminants may alter NA capability;
- changes in geochemistry may alter the natural attenuation processes during the implementation phase;
- geochemical conditions may mobilise toxic contaminants, especially metals, through chemical transformation of natural minerals;
- naturally reducing conditions may be present within the aquifer;
- concentrations of nitrate and other electron sources may alter the rate of attenuation;
- urban development may affect the hydrogeological regime, for example by causing rising groundwater levels, providing artificial pathways, multiple contaminant sources, as well as an altered baseline chemistry.

Collectively, the contaminant properties and environmental factors described above determine the fate and behaviour of substances in an aquifer. The fate and behaviour, in turn, defines the spatial distribution of contaminant concentrations within a plume over time. Plumes can take on a variety of forms that may be categorised as expanding, stable, shrinking or exhausted, as illustrated in Figure 3.3.

Figure 3.3. Types of naturally attenuating plumes (after Wiedemeier et al, 1999)



Extent of plume at time, t_1 , compared to extent of plume at a later time, t_2 .

3.3.2 Practicability screening considerations

Various issues may influence whether NA is practicable under the site-specific circumstances. These may include the following:

- for small sites, there is a greater likelihood that a contaminant plume may migrate off-site. If access to off-site monitoring wells cannot be secured, it will be difficult to demonstrate natural attenuation;
- time-frame - NA may take several years to complete, and institutional controls may be necessary to ensure the long-term commitment to the necessary monitoring requirements. **MNA may therefore not be suitable if imminent divestment or redevelopment is proposed;**
- alternative active remedial options may not be available.

3.3.3 Economic screening considerations

Economic considerations that may need to be addressed when evaluating MNA include the following:

- long-term monitoring will require significant financial provision;
- the need for detailed site characterisation will increase the initial investment costs, although these may be lower overall than active remedial measures;
- other remedial options may provide a more favourable cost-to-benefit ratio;
- there is a risk that data may confirm that active remediation is required after all;
- the cost of developing contingency plans may be prohibitive.

3.3.4 Regulatory and institutional screening considerations

Regulatory and institutional pressures may be important in determining the acceptability of MNA as a remedial measure. Examples may include the following.

- where there is continuing threat of pollution of controlled waters, and/or a breach of statutory water quality objectives, (such as from a soil, NAPL or above ground source), unless simultaneous action is taken to stop the source;
- groundwater contaminants may present unacceptable risks to human health or ecosystems, and may require urgent remediation to be undertaken under regulatory control. MNA may therefore only be acceptable if undertaken in combination with active remedial methods.

3.4 Summary of screening criteria

Under most circumstances, the criteria highlighted in bold in Table 3.6 will, on their own, automatically preclude the use of MNA. For the remaining criteria, professional judgement should be used to assess the feasibility of monitored natural attenuation.

The decision process will be influenced by the relative weightings that a problem holder attaches to the screening criteria. These weightings will depend upon the particular role and motivations of a problem holder. For example, the time-frame to achieve remedial goals is likely to be a principal decision factor for a company with a short-term interest in a site. In

certain cases, collection of additional data may be warranted to ensure a more informed decision-making process. The benefits of undertaking this work must be balanced against the corresponding additional cost of data retrieval.

Table 3.6. Summary of screening criteria to assess the feasibility of natural attenuation

Screening criteria	Feasibility		
	High	Intermediate	Low
<i>A. Technical screening factors (section 3.3.1)</i>			
Source of groundwater contamination ¹	Removed or being removed	Under removal/exhausted	Continuing
Plume definition	Well defined		Poorly defined
Contaminant plume status	Shrinking	Stable	Expanding
Operating windows (see Table 3.1)	Within	On the boundary	Outside
Persistence of contaminant in environment	Readily attenuated (degraded) under conditions present on site	Not readily degraded under conditions present on site	Attenuation processes poorly understood
Dominant attenuating mechanisms	Irreversible/destructive		Reversible/ non-destructive
Mobility of contaminant ²	Medium	Low	High
Pollution potential ³ of daughter products	Less polluting than parent	Equally polluting	More polluting than parent
Combined effects of multiple contaminants	No effect - attenuation occurs independently		Act as co-contaminants
Aquifer heterogeneity and isotropy	Homogeneous and isotropic		Heterogeneous and anisotropic
Rate of groundwater migration	Slow	Medium	Rapid
Receptor	No external receptors identified	Receptors present (low risk)	Receptors present (high risk)
Groundwater Source Protection Zones (SPZ)	Lies outside SPZ	Lies within SPZ III	Lies in SPZ I or SPZ II⁴
Current and foreseeable groundwater usage ⁵	Low	Medium	High

Table 3.6 continued

Screening criteria	Feasibility		
	High	Intermediate	Low
Level of confidence in:			
Monitoring data	High- comprehensive monitoring data spanning greater than 2 years.		Low- single set of monitoring data
Confidence and understanding of contaminant distribution	High e.g. Dissolved substances in shallow homogeneous aquifer		Low e.g. DNAPLs in deep heterogeneous aquifer
B. Regulatory screening factors (section 3.3.4)			
Acceptability to regulator	No policy objection. Technical support provided.	No policy objection. Technical concerns.	Policy objections in principle. Major technical concerns.
C. Practicability and economic constraints (section 3.3.2 and 3.3.3)			
Off-site monitoring locations	Access available	Access possible	Limited /no access
Financial provisions	Long-term, legally-binding budget provisions secured	Long-term, non-legally binding budget provision secured	No long-term budget provisions
Objectives of landowner	Long-term interest in site (>10 years)	Medium-term interest (3-10 years)	Short-term ownership (<3 years)
OVERALL	All high/ intermediates No lows	High, medium and lows, but no show-stoppers ⁶	One or more show-stopping criteria present, or No factors of high feasibility rating

NB. Criteria highlighted in bold would normally preclude natural attenuation as a sole remedial option

- 1 Definition of contaminant source, i.e. contamination in the unsaturated zone, or liquid phase in the saturated zone.
- 2 Medium mobility enables degradation products to be removed, thus driving degradation reactions.
- 3 Pollution potential is a function of the mobility, toxicity and persistence of the contaminant.
- 4 For SPZ II which have been defined using the 25 percent of total of SPZ III (i.e. low velocity aquifers), then site-specific factors may increase the feasibility of natural attenuation.
- 5 Groundwater uses that should be considered include: baseflow to surface water, abstractions (licensed and others)
- 6 Show-stoppers are conditions indicated in bold type in this table, which are considered to indicate circumstances at the screening stage that will severely limit the potential for effective NA and regulatory acceptance of MNA.

3.5 Information management

The judgement of whether MNA is a viable remedial option involves making a number of key decisions, based on evidence gathered during the screening process. In the event that MNA is implemented, information gathered during the screening process will form the basis of monitoring undertaken to verify the performance of MNA. In addition, the decision to implement MNA may require the support of third parties and will be subject to regulatory control. It is therefore important to ensure that an audit trail is maintained throughout the screening process, with robust quality-control procedures that are open to regulatory and other independent verification.

3.6 Decision to proceed

The decision to proceed to a more detailed assessment of natural attenuation will be determined by:

- an absence of fundamental constraints to the acceptance of natural attenuation, as shown by the screening process;
- an initial indication that MNA may be effective at achieving the remedial objectives;
- a favourable cost-to-benefit ratio compared with alternative remedial options;
- the level of uncertainty associated with the findings.

If, after reviewing information relating to the screening factors outlined in this section, it is concluded that MNA is a viable option, detailed site characterisation should be performed as part of the demonstration stage in Chapter 4.

4. DEMONSTRATION OF NATURAL ATTENUATION

4.1 Objectives

The purpose of the demonstration stage is to show quantitatively that natural attenuation is occurring at a rate that will achieve the remediation objectives in a reasonable time-frame.

4.2 Methodology

Demonstrating the effectiveness of NA involves obtaining data to test and calibrate the conceptual model. The process is iterative, whereby data are used to refine the model that in turn guides any necessary additional site characterisation.

Very rarely will all the necessary information be available at the outset. Instead, additional data relating to source mass, contaminant phase distribution and aquifer hydrogeochemical properties will be required. The key steps involved in acquiring and analysing data in order to demonstrate natural attenuation are described below, and summarised in Figure 4.1.

4.2.1 Lines of evidence

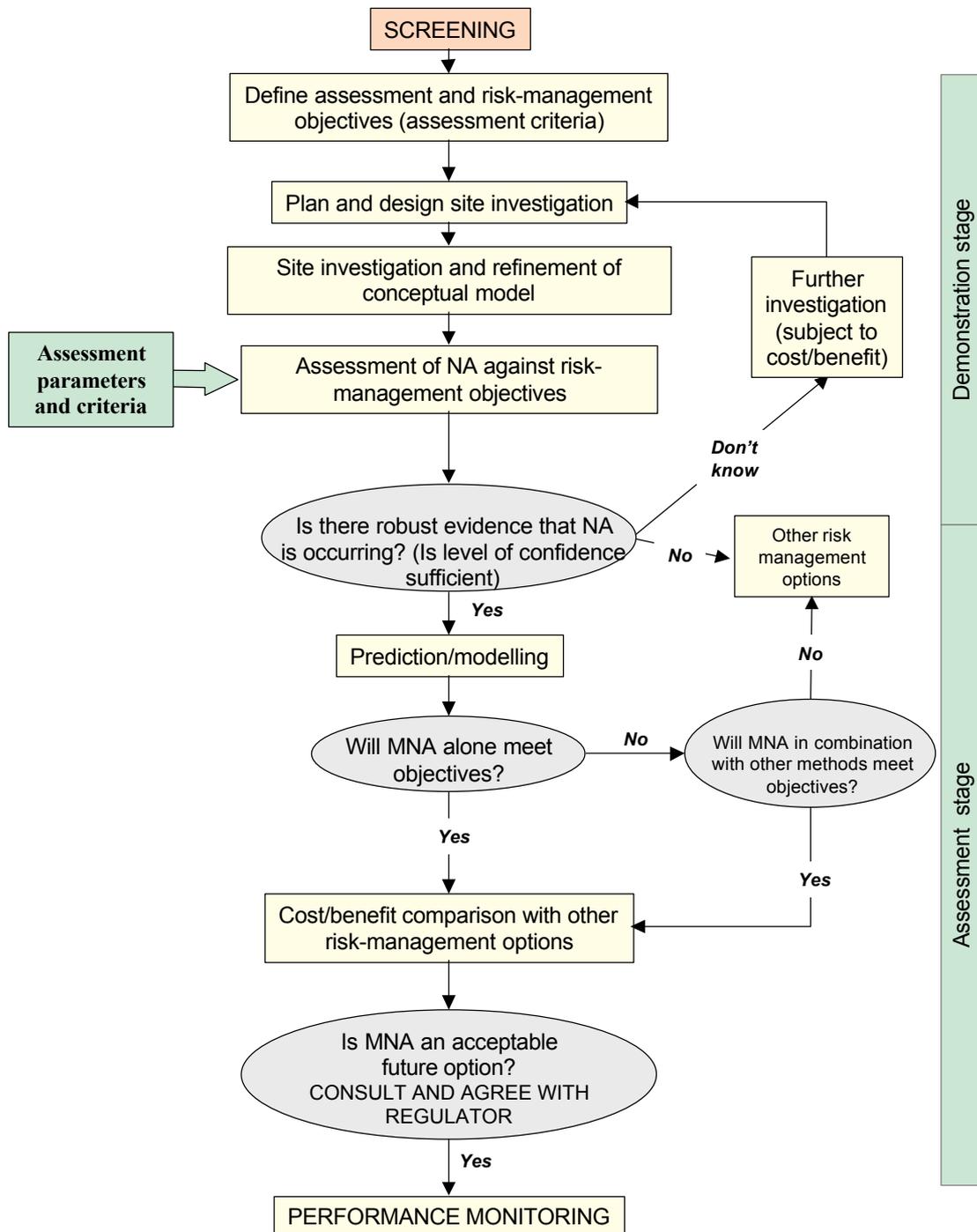
Three lines of evidence are available to demonstrate that natural attenuation is occurring at a site. **Primary** lines of evidence involve the use of historical contaminant data to demonstrate a trend of reduced pollutant *concentrations* down-gradient of the source, along the groundwater flow path. This form of evidence shows that attenuation is taking place, but fails to establish if contaminant mass is being destroyed by biological or non-biological degradative mechanisms.

Secondary lines of evidence involve measuring changes in chemical and geochemical analytical data to prove a loss of contaminant *mass*. Two approaches are available:

- using chemical and geochemical analytical data in mass balance calculations to show that decreases in parent contaminant and/or electron acceptor/donor concentrations can be directly correlated to increases in metabolic by-products and/or daughter compounds;
- using historical chemical data, complemented, if necessary, by biologically recalcitrant tracer testing, to demonstrate that the plume is shrinking, stable or expanding at a rate slower than predicted by conservative groundwater velocity calculations.

The loss of contaminant mass or the stabilisation of a plume can be tested visually, and by statistical techniques such as the Mann-Whitney and Mann-Kendall tests (Refs. 20 and 21).

Figure 4.1: Demonstration & assessment of natural attenuation



Tertiary lines of evidence use data from laboratory microbiological testing to show that indigenous bacteria are capable of degrading site contaminants. This line of evidence should be used when the first two are inconclusive.

Analytical and numerical solute fate and transport models (see Appendix 4) may complement the lines of evidence approach by:

- highlighting differences between observed and predicted contaminant concentrations, which it may be inferred is attributable to attenuation;
- estimating the relative importance of various attenuation mechanisms;
- testing the accuracy of model input data by comparing observed concentrations against those predicted by transport and fate modelling.

Evidence for natural attenuation is often circumstantial, so it is often necessary to seek multiple lines of evidence, particularly where the level of uncertainty is high and the sensitivity of the site is significant. However, where the weight of evidence from a primary line of evidence is overwhelming, then it may be judged unnecessary to collect secondary and tertiary data.

4.2.2 Design of site investigation

The objectives of the site characterisation are twofold:

- to provide data to demonstrate and quantify NA along the lines of evidence approach;
- to provide sufficient site-specific input data to forecast the future behaviour of contamination using solute fate and transport models.

In designing an investigation to meet these objectives, consideration needs to be given to the following issues:

Data requirements

Table A2.1 in Appendix 2 presents a description of physical, chemical, biological and geochemical parameters and their use in demonstrating natural attenuating mechanisms. The process of selecting appropriate determinands from this list will depend upon the nature of contamination and the biogeochemical environment at a site, and the dominant attenuation processes under consideration. In the case of the latter, the recommended data requirements are outlined in Table 4.1, *right*:

Table 4.1. Selection of parameters to demonstrate NA processes

Dominant attenuation mechanism	Aquifer hydraulics	Chemical properties	Concentration of parent contaminant	Concentrations of co-contaminants ¹	Concentration of daughter products	Dissolved oxygen	Total organic carbon (TOC)	Concentrations of electron acceptors ²	Redox	pH	Alkalinity	Temperature	Chloride	Iron hydroxide availability	Hydrogen
Dilution, dispersion and diffusion	✓✓	✓✓	✓✓										✓		
Sorption and precipitation	✓✓	✓✓	✓✓			✓	✓✓		✓✓	✓✓		✓		✓✓	
Volatilisation			✓✓								✓	✓			
Aerobic degradation (contaminant as electron donor)	✓✓	✓✓	✓✓		✓	✓	✓	✓	✓	✓	✓	✓	✓		
Anaerobic degradation (contaminant as electron donor)	✓✓	✓✓	✓✓		✓	✓	✓	✓	✓	✓	✓	✓	✓		✓
Reductive dehalogenation (contaminant as electron acceptor)	✓✓	✓✓	✓✓	✓✓	✓✓	✓✓	✓✓	✓✓	✓✓	✓✓	✓	✓	✓		✓

✓✓ = considered essential; ✓ = recommended

NB 1 for example, petroleum hydrocarbons or chlorinated solvents.
 2 for example, Fe³⁺, Mn⁴⁺, NO³⁻, SO₄²⁻ CO₂ (electron acceptors) and Fe²⁺, Mn²⁺, NO²⁻ & N₂, H₂S, CH₄ (metabolic by-products of redox reactions).

The preferred strategy is to collect, wherever possible, site-specific data for determinands, particularly those that are most relevant to the assessment and that exhibit the greatest levels of uncertainty. Default data are used for the remaining parameters, ensuring that the data are applicable to the particular circumstances under consideration. It is equally important, therefore, that the reasons and assumptions behind the selection of a literature value are highlighted.

The amount of data is another important consideration, which will depend largely upon:

- the level of confidence that is required in the assessment. This will in turn be influenced by the sensitivity and risks associated with a site. The view of the regulator is particularly important in this respect;

- the level of uncertainty associated with the parameters under investigation. For example, highly unpredictable contaminant fate and behaviour will require considerable data retrieval;
- the costs of obtaining additional data balanced against the associated benefits of reducing uncertainty.

Data collection strategies should consider the following aspects:

- sampling points including the number, location and construction of monitoring points. Each of these elements should be factored into the design of a sampling network that aims to (a) obtain representative samples and (b) delineate the contaminant plume both laterally and vertically. The location of sampling points will depend upon the nature of the contamination, the extent of the plume and the hydrogeological setting.
- sampling frequency and analytical suite;
- sampling methods, including sources of error;
- analytical methods including appropriateness, accuracy, precision and limits of detection. The site characterisation process for natural attenuation is relatively unique in the wide range of physical, chemical, geochemical and biological parameters that are measured. Table A3.1 in Appendix 3 presents a summary of standard sources of chemical and geochemical parameters.

It is critical that measurement errors, occurring either through sampling, analysis or transit, are kept to a minimum for natural attenuation. Table 4.2 describes the sources, causes and effects of errors that are particularly relevant to NA, along with good practice guidance to minimise these errors.

Table 4.2. Sources of measurement error critical to assessment of NA

Potential source of error	Effect	Occurrence	Mitigating measure
Introduction of oxygen into samples	Non-representative anaerobic conditions	of Sampling	Use flow through cells
Penetrating (breaching) impermeable horizon or lens	Creation of new pathway for DNAPL to move downwards	Drilling	Use well casing and appropriate borehole seals
Inappropriate well construction, e.g. screened section too long screened section too short	Non-representative water sample collected: contamination is diluted misses contamination	Site characterisation Performance monitoring	Multiple wells

Data retrieval procedures

Table 4.3 presents sources of further information on good practice relating to collection of data for site characterisation and other purposes.

Table 4.3. Further sources of information for site characterisation

Topic	Reference
Design of investigation	22
Design of borehole-monitoring networks and borehole construction	23, 24, 25
Design of monitoring programmes	6, 26
Groundwater sampling	6, 23, 26
Field testing (permeability tests)	27
Laboratory analysis (analytical techniques, limits of detection)	22
Interpretation of monitoring data	23
Statistical analysis of monitoring data	28
Cost-benefit assessment for monitoring schemes	12, 29
Health and safety	22
Setting remedial targets	7

Monitoring

Demonstration of NA will typically require repeat monitoring to show that:

- the plume is stable or shrinking; and/or
- attenuation is occurring over time, not just an instantaneous snap-shot

Typically, the minimum monitoring period will be two years to obtain meaningful and statistically valid trends. The period may need to be extended where the trends are inconclusive, provided that the risk to receptors does not change. Factors that may influence the validity of trends include seasonal changes in groundwater chemistry and flow, and consequently the monitoring frequency should be adequate to define seasonal and long-term trends (see Chapter 6).

Data analysis

The results of the site characterisation are used, together with literature values, to demonstrate natural attenuation by providing evidence on:

- mass balance for parent and daughter products, including metabolic intermediates;
- flux of parent and daughter products, plus electron donors/acceptors and co-metabolites;
- biodegradation kinetics such as half life or degradation constants;
- long term attenuation capacity of the aquifer (for example, supply and availability of electron donors/acceptors);
- rates of non-degradative attenuation mechanisms, such as sorption.

Presentation of data

The presentation of data should be based on the revised conceptual model, and may include:

- potentiometric surface maps;
- hydrogeological cross-sections showing profiles parallel and perpendicular to the groundwater flow path;
- isopleth contour maps for key contaminant and geochemical parameters (including degradation products, redox parameters, electron donors/acceptors, tracers);
- plots of chemical concentrations versus distance and/or time.

Appendix 6 provides further guidance on presentation of data as part of the assessment stage.

4.3 Data evaluation

The decision to accept MNA as an appropriate remedial strategy will be based on the findings of the assessment and monitoring programme. In demonstrating that MNA is a viable and acceptable strategy, one or more of the following criteria will need to have been satisfied. **The more criteria that are satisfied, the greater the level of confidence in MNA.**

- Natural attenuation process is defined, for example,
 - mass destruction shown by one line of evidence plus mechanism identified through second line of evidence.
- Plume status is demonstrated (that is, stable, shrinking or expanding), by data which show:
 - a downward trend in a single parameter (medium confidence);
 - two correlating trends in concentrations of contaminants and metabolic by-products, contaminants and electron donors or contaminants and electron acceptors (high confidence).
- Monitoring trends, as part of line of evidence, show a consistent pattern that is, no significant fluctuations.
- Observed conditions are reproduced / simulated using fate and transport models.
- Microbiological studies provide supporting evidence for biodegradation, although this is not considered to be a key line of evidence.
- Geochemical environment is consistent with attenuation mechanism for example, redox conditions mirror degradation processes.
- There are no inconsistencies between observed conditions and the conceptual model, unless these can be clearly explained and justified.
- Sensitive parameters are sufficiently well defined, for example, field testing confirms a limited range in the value of hydraulic conductivity.
- Uncertainty is reduced in terms of defining pathways, plume and source.

5. ASSESSMENT OF NATURAL ATTENUATION

5.1 Introduction

This section describes the methodology to be adopted in assessing whether MNA will be an effective mitigation measure. Acceptance of MNA as a remedial option will be dependent on demonstrating that:

- NA processes are, and will continue to, protect receptors;
- any future migration of the contaminant plume will not result in significant additional pollution of groundwater;
- the period over which contaminant concentrations are reduced (by natural attenuation) is reasonable.

In undertaking the assessment, reference should be made to the Environment Agency R&D Publication 20 *Methodology for the Derivation of Remedial Targets for Soil and Groundwater to Protect Water Resources* (Ref 7). This document gives guidance on the derivation of remedial targets to protect identified groundwater and surface water receptors. If natural attenuation is the accepted remedial measure, it will be necessary to demonstrate that either existing groundwater contamination will not exceed these remedial targets in the future, or that contaminant concentrations will be reduced to below these targets. If natural attenuation processes have been considered when deriving a remedial target, that is to say at tiers 3 or 4, the degradation rates must be fully justified (see section 5.3).

5.2 Methodology

The basic steps in assessing the natural attenuation potential are summarised in Figure 4.1. The objectives and methodology should be agreed with the Agency. It is assumed at this stage that adequate information has been obtained to define the site and to demonstrate that NA is occurring (and by what process).

Each step in the assessment is described below:

1. Define Objectives for the Assessment. This will include:

- identification of receptors to be protected;
- determination of remedial targets to protect receptors;
- determination of the time-frame over which natural attenuation is acceptable.

2. *Select appropriate model/methodology to predict long-term effectiveness of NA.*

The following sections (2 to 7) are aimed at the use of analytical or numerical solutions to predict the effectiveness of MNA into the future. In certain situations it may not be worthwhile or appropriate to use such models, such as:

- the attenuation process can be adequately demonstrated from field observations;
- the attenuation processes can not be adequately represented by the model;
- insufficient data has been obtained to adequately define the system behaviour;
- too many simplifying assumptions are required to apply the model to the conceptual model with rigour;
- insufficient monitoring data are available to validate the model results.

Further guidance on selection and use of models is given in Reference 30. Before undertaking any modelling exercise, the purpose and benefits of using a model should be clearly defined. A model should not be used in preference to field investigation and monitoring but rather used as a tool to assist in the assessment and decision-making process. Where field monitoring has shown clear evidence of a shrinking plume, then this may be sufficient to demonstrate MNA as a viable approach, although the assessment will need to take account of the points described under Section 8.

In many cases, this model will be the same as that used in the site assessment.

The choice of model or method will be dependent on:

- the objectives of the exercise;
- the conceptual model (complexity of the geology and hydrogeology of the site);
- the contaminant type and natural attenuation process;
- the quality of the available information;
- the limitations of the fate and transport model.

It will be essential that the selected model should be able to represent the system, and that any limitations of the fate and transport model should be fully understood. Appendix 4 provides guidance on the selection and application of models. The basis for selection of the fate and transport model should be fully documented.

A probabilistic approach is recommended at this stage of the assessment, in order to take account of any intrinsic variability of a parameter and any uncertainties in the measurement of parameter values (refer to Appendix 4, Reference 30).

- ## 3. *Define parameter values for model.*
- In general, site-specific values should be used, particularly where degradation is the main attenuation process. The choice of parameter value should be fully documented, including the source of information, method of analysis, range in parameter values and uncertainties. Ideally sufficient information

should be available to describe the range in parameter values by a probability distribution function. If non-site-specific data are used, then it will be necessary to demonstrate that:

- the data are relevant to the site (that is, they are from a similar and relevant setting);
- model predictions are insensitive to this parameter (sensitivity analysis can also assist in the design of a site investigation in determining which are the key parameters to be defined);
- the range in parameter values is well defined from the literature, and a conservative value has been used in the assessment. For example, literature values for the porosity of a sand typically vary from 10 to 40 percent. Since lower values of porosity will result in a calculated increased rate of contaminant movement, the use of a value of 10 percent would, in this case, indicate a conservative assessment. However, care should be taken that unrealistic combinations of conservative assumptions/estimates are not made (for example, high hydraulic conductivity combined with high hydraulic gradients).

For key parameters, such as degradation rates, then non-site specific data are unlikely to be acceptable unless a very strong case can be presented for its acceptance. In such cases, a more stringent performance-monitoring scheme would be required.

4. Model validation. The model should be validated against field observations. Unless the model can provide an acceptable simulation of the observed contaminant concentrations, the model cannot be used reliably to determine whether NA is an acceptable remedial measure in the longer term.

5. Model prediction. The model should be used to determine:

- changes in contaminant concentrations with time;
- volume of aquifer affected (particularly if the plume is likely to migrate);
- rate of contaminant migration and travel time to potential receptors;
- impact, if any, on the identified receptor;
- time-scale for remedial targets to be achieved;
- location of monitoring points (particularly in relation to the front of the plume) for performance monitoring.

Measures should have been implemented to prevent further contamination of groundwater (to comply with legislative obligations such as the Groundwater Directive). It would be expected, therefore, that the source term will decrease through time (via its removal, containment or by controlled dissolution into groundwater or degradation). To be effective, natural processes within the aquifer must remove or retard a greater mass of contaminant than enters the system, in which case the plume will be stable or shrink. In some cases, the source can be sufficiently large or the rates of contaminant release sufficiently low that it will continue for several hundreds of years. The behaviour of the source term with time will be important to the prediction of contaminant concentrations.

Some analytical models and most numerical models allow a declining or variable source term to be represented (refer to Appendix 4). Most analytical models assume a constant source term and, therefore, are likely to provide a conservative estimate in this aspect of the calculation.

6. ***Sensitivity analysis.*** A sensitivity analysis should be undertaken to determine which parameters have the most significant influence on the assessment. This information should be used to determine whether the given parameter(s) have been defined with sufficient confidence.
7. ***Assessment of model predictions.*** The results of the assessment should be reviewed in relation to the:
 - predicted impact on identified receptors;
 - uncertainties in the conceptual model, and in particular the significance of any preferential pathways;
 - uncertainties in parameter definition and influence on the model results;
 - applicability and any limitations of the model.

The significance of the model predictions will need to be assessed in terms of the sensitivity of the identified receptor(s). This may include consideration of the level of risk, for example by undertaking a probabilistic simulation of the impact. Further guidance on the use of groundwater contaminant fate and transport models is given in Reference 30.

If the assessment indicates that there is insufficient certainty, then a decision should be made to:

- obtain further site investigation data; or
 - consider alternative options, including other mitigation measures in combination with natural attenuation. This may require the model predictions to be repeated to take account of the effect of other mitigation measures (for example, groundwater abstraction to remove the contaminant).
8. ***Other factors.*** The assessment will also need to consider the following factors.
 - *Changes in land use or site conditions that may influence natural attenuation.* For example, the implementation of air sparging to remove volatile contaminants (such as, petroleum spirit), will introduce oxygen into the system and change the aquifer environment from anaerobic to aerobic. The latter may be significant where chlorinated solvents are also present, some of which may only degrade under anaerobic conditions.
 - *Breakdown products from degradation.* The assessment will need to identify any breakdown products and whether these will represent a hazard, for example a breakdown product from the reductive dechlorination of PCE/TCE/DCE is vinyl chloride. The assessment will also need to demonstrate that natural attenuation will also be effective for any breakdown products.
 - *Assimilative capacity of the aquifer.* The assessment will need to demonstrate that the assimilative capacity of the aquifer is sufficient to protect the identified receptors in the future. For example, the degradation of fuel oil is dependent on a sufficient

source of electron receptors (oxygen, nitrate, sulphate) being available. An example of how the assimilative capacity of the aquifer system can be evaluated is given in Appendix 5, although the calculation of assimilative capacity needs to be interpreted with care.

- *Remobilisation of contaminants.* For contaminants where the natural attenuation process is non-destructive such as sorption or precipitation, the assessment will need to demonstrate that these contaminants will not be remobilised or that the rate of remobilisation is insufficient to affect the identified receptors. For example, hexavalent chromium (Cr^{6+}) is relatively mobile and very toxic. Under certain conditions, hexavalent chromium can be reduced to less toxic trivalent chromium (Cr^{3+}), which is less soluble and likely to be precipitated from solution. A subsequent change in the chemical environment may result in trivalent chromium being oxidised to hexavalent chromium and remobilised back into solution.

5.3 Remedial Targets

Natural attenuation processes are taken into account in the Environment Agency's *Methodology for the derivation of remedial targets for soil and groundwater to protect water resources*, at Tiers 3 and 4. The methodology described in Sections 3 to 5 of this document sets out the procedure for determining site-specific rates for natural attenuation. The Agency expects that degradation will be assumed to be nil when calculating remedial targets unless relevant and adequate evidence is collected and presented, as described here.

5.4 Acceptance of MNA and regulatory consultation

Agreement will need to be obtained from the relevant regulator (either the Agency or the local authority depending on the legislative context) that:

- MNA is an effective remedial solution in protecting the identified receptor(s); this may include uncontaminated groundwater, particularly where it is an actual or potential resource. In general, the front of the plume should not expand by more than 10 percent of the distance to the nearest specific receptor or by 100 metres (whichever is the lesser). In most cases this will mean ensuring no impact at the identified receptor(s). (Exceptions to this may be where cost-benefit assessment (Refs 11, 12) or practical considerations indicate that limited plume expansion may be a part of the best overall option);
- the time period for MNA to meet the remedial objectives is acceptable (for some sites natural attenuation may take tens of years before contaminant concentrations are reduced to acceptable levels);
- a monitoring strategy for demonstrating that NA is occurring according to expectations;
- an appropriate contingency plan in the event that MNA proves to be ineffective;
- adequate controls (financial, institutional s106 agreement) are available to ensure long-term operation of the scheme;
- any predicted expansion of the plume is acceptable.

5.5 Reporting

The results of the evaluation will need to be fully documented. This must include:

- site investigation and monitoring results (including all data collected as part of the investigation);
- conceptual model;
- lines of evidence and supporting data in support of natural attenuation;
- description and justification of parameter values used in the assessment;
- details and justification of methods used in the assessment;
- results of model predictions and discussion of uncertainties in the analysis;
- basis for proposing MNA as the remedial solution (this will need to be linked to the Model Procedures);
- outline of proposed monitoring strategy to confirm that NA is effective (refer to Chapter 6);
- details of (an agreed) contingency plan in the event that MNA proves to be ineffective;
- proposed regulatory, financial and institutional framework.

6. IMPLEMENTATION (PERFORMANCE MONITORING)

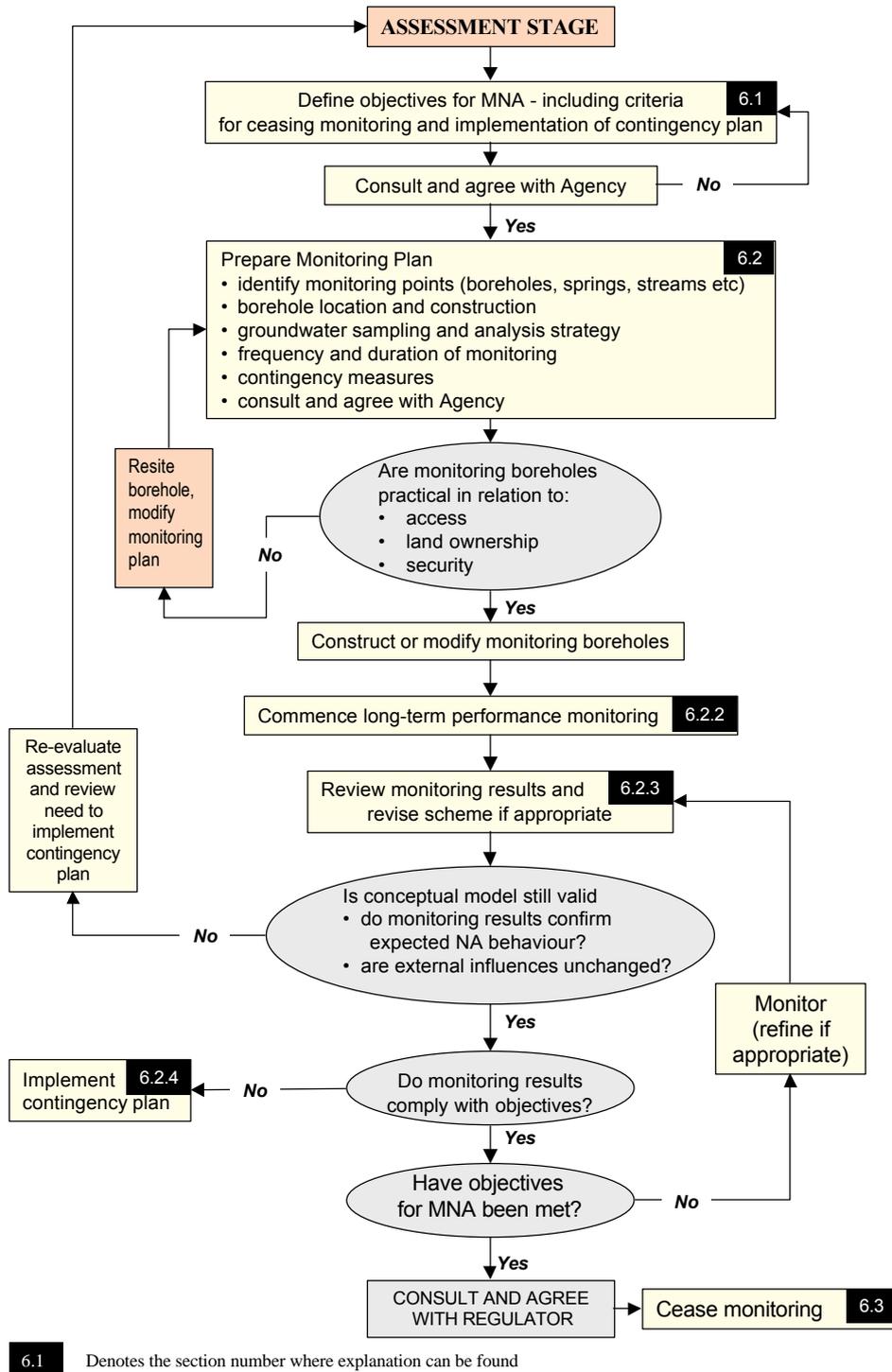
6.1 Objectives

The purpose of performance monitoring is to demonstrate that natural attenuation is effective as a remedial strategy in protecting the water environment. The objectives of long-term monitoring are to:

- demonstrate that natural attenuation is occurring according to expectations;
- determine the plume status (shrinking, stable, expanding);
- identify changes in the groundwater flow pattern;
- identify any toxic breakdown products resulting from degradation;
- detect new releases of contaminants;
- define long-term, baseline/background hydrochemical conditions in the groundwater body/receptor;
- identify changes in geochemical/biochemical conditions that could influence natural attenuation;
- demonstrate that there is no impact to downgradient receptors;
- confirm compliance with remedial targets/objectives. For some sites, observed contaminant levels may already fall within remedial targets, and monitoring may be undertaken only to provide confirmation;
- provide a basis for implementing contingency measures, if required;
- provide a basis for ceasing MNA, that is to say, the site no longer represents a risk to groundwater, surface water or other receptors.

Figure 6.1 summarises the main steps in performance monitoring. The acceptability of natural attenuation will be dependent on whether the required monitoring regime can be implemented.

Figure 6.1: MNA implementation (performance monitoring)



6.2 Design

6.2.1 Monitoring locations

The design of a monitoring programme will need to be site-specific (based on the conceptual model), and should be agreed with the regulator. The basic elements of the design should include:

- the type, number, location of monitoring points (borehole, surface water, spring);
- the design of monitoring points (including borehole construction and depth of screen). The locations and screened intervals of long-term monitoring boreholes should be based on the conceptual model, taking account of the site geology, seasonal variations in groundwater levels or flow direction, and the plume geometry. It will be important to ensure the correct horizons are monitored (particularly important for multi-layered aquifers) and that the borehole does not provide a contaminant pathway;
- the methodology needed to obtain representative samples;
- the number and type of samples;
- range of determinands for analysis, including the key contaminants identified, appropriate analytical methods and their limits of detection, and breakdown products, where appropriate;
- frequency and duration of monitoring;
- methods of analysis in assessing the monitoring results (for example, statistical techniques);
- reporting requirements, including presentation of data;
- basis for ceasing monitoring or the trigger for implementing contingency measures.

For some sites, it may be appropriate to use non-intrusive techniques (geophysical surveys) to map the extent of the plume or to assist in identifying appropriate borehole locations.

In designing the monitoring programme, the following will also need to be taken into account:

- sensitivity of the receptor;
- long-term access for monitoring boreholes, including presence of existing buildings and services, together with land ownership and security of installation;
- cost of long-term monitoring and the cost-effectiveness of the sampling/analytical strategy;
- regulatory requirements;
- type of contaminant (for example, if there is LNAPL, then monitoring should include sampling at the watertable, but may require separate installation for monitoring/sampling groundwater); and geochemical/biochemical environment;
- size and geometry of the plume;
- rate of groundwater flow;

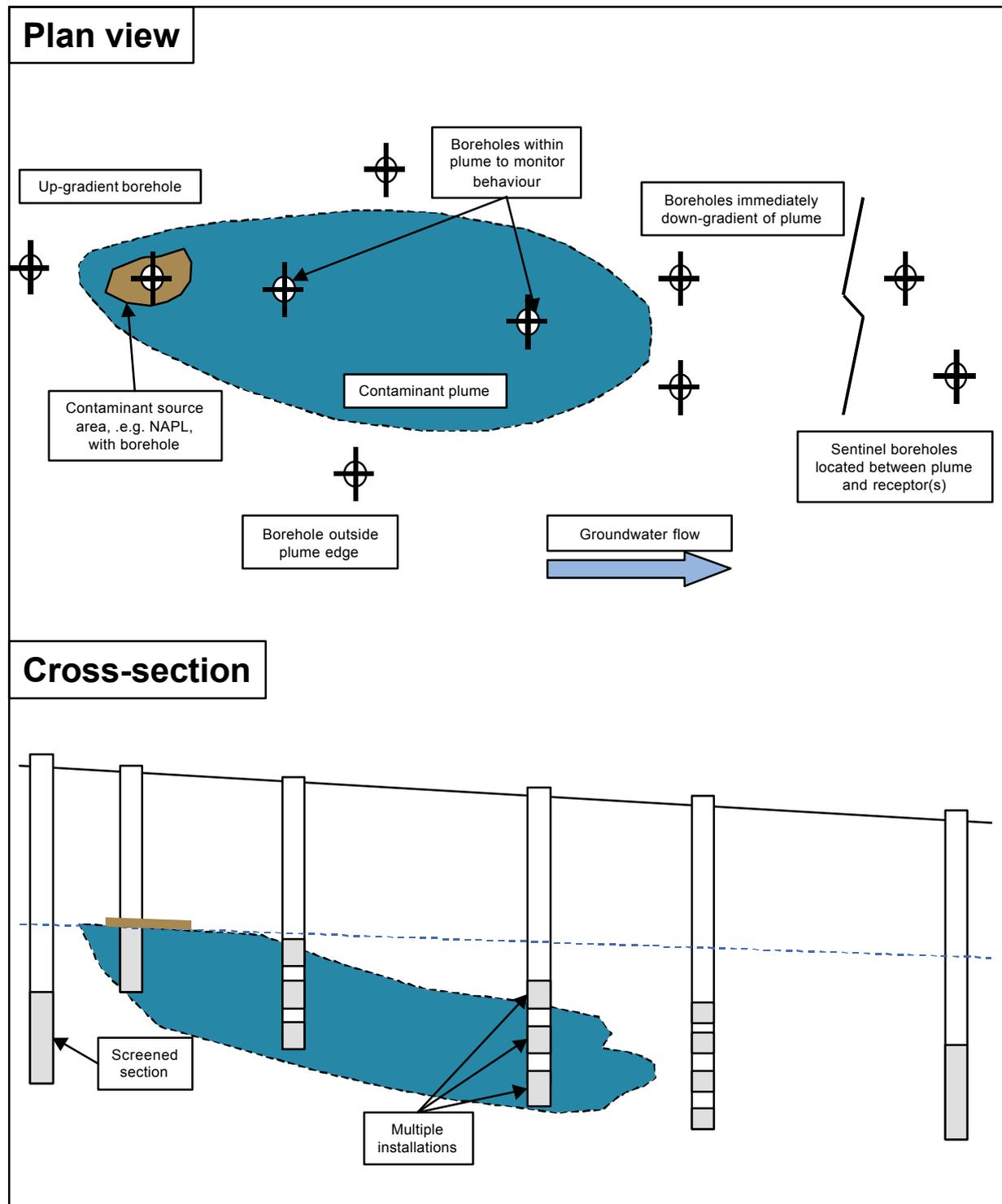
- complexity of the hydrogeological regime and contaminant pathways;
- aquifer type (fissured/intergranular and presence of preferential pathways). For fissured aquifers, consideration will need to be given to the likelihood that the contaminant may by-pass the monitoring locations. (However, in such situations MNA may not be a viable option).

A typical monitoring network (Figure 6.2) will include:

1. Up-gradient borehole(s) to determine changes in background water quality;
2. Side-gradient borehole(s) to monitor changes in background water quality. These boreholes would also provide confirmation of the plume geometry and the absence of seasonal changes in groundwater or plume flow direction;
3. Borehole(s) in the contaminant source area to monitor changes in source strength with time;
4. Borehole(s) located down-gradient of the source area, but within the contaminant plume to monitor plume behaviour and changing concentrations with time. These will normally be located along the centre line of the plume;
5. Borehole(s) located immediately down-gradient from the contaminant plume to provide early warning of any migration of the contaminant plume. Ideally these boreholes will also provide supporting evidence for NA, for example, evidence of an absence of contaminants but the depletion of electron acceptors, (for instance, decrease in nitrate and dissolved oxygen concentrations as advanced evidence of hydrocarbon pollution);
6. Sentinel borehole(s) located between the plume and the identified receptor, for which exceedence of the remedial target will require implementation of the contingency plan.

Boreholes defined under points 4, 5 or 6 may be used as compliance boreholes.

Figure 6.2 Schematic location of monitoring boreholes around a plume



Generally, the **absolute minimum requirement** for monitoring boreholes will be:

- One up-hydraulic gradient borehole;
- At least two boreholes located down-gradient of the contaminant plume. A single down-gradient borehole is not considered satisfactory due to the uncertainty in ensuring that this borehole is in the line of contaminant movement;
- At least one borehole located directly on the flow path between the source and each identified receptor to act as a sentinel or early warning borehole.

Most natural attenuation schemes will require a much denser monitoring network than the minimum requirements presented above. It will be necessary to demonstrate to the Agency that there are an adequate number of appropriately sited and constructed boreholes to define groundwater hydraulic and changes in the plume generally and chemically. This will particularly be the case for fissured and multi-layered aquifers and for aquifers with complex flow fields.

The location of sentinel boreholes down-gradient of the source/contaminant plume will need to be determined based on the rate of groundwater/contaminant movement and the distance to potential receptors. The boreholes will need to be located at sufficient distance up-gradient of the receptor to provide adequate warning/protection. The minimum travel-time should, in general, be 400 days. If the site falls within a 400-day travel-time (Outer Source Protection Zone), then very strong evidence will need to be presented to demonstrate that NA will provide protection to the receptor. The distance to down-gradient boreholes will also influence the duration of monitoring. For example, if the average groundwater velocity is 10m/year and a sentinel borehole is located 50m from the edge of the plume, then more than five years monitoring data will be required to demonstrate that the plume is not expanding. (This simple calculation ignores the effects of dispersion or contaminant retardation). The monitoring strategy will, therefore, need to take account of/demonstrate that the borehole locations, and the period of monitoring, are appropriate to the expected behaviour of the plume. The use of a fate and transport model is recommended for determining borehole locations.

6.2.2 Groundwater sampling and analysis

The monitoring plan should include:

- parameters for analysis;
- frequency of analysis for each parameter;
- method of sampling (refer to Table 4.3);
- transport and storage of sample prior to analysis;
- laboratory technique and level of detection (refer to Table 4.3).

Routine monitoring should also include water level measurement and where appropriate measurement of the thickness of free product. The analytical suite and the frequency of monitoring will be site-specific (it may also vary from borehole to borehole) and depend on the type of contaminant, geochemical environment and background quality. Table 6.1 gives

suggested monitoring suites for different contaminant types, although this is indicative only. Where a site or problem is well defined, then analysis could be limited to the contaminant.

The monitoring strategy should represent a balance between providing sufficient data to confirm that natural attenuation is behaving according to expectations, and cost. For example, assessment of the NA of chlorinated solvents analysis would routinely be made for the solvent and its breakdown products, plus less frequent sampling for electron acceptors/donors (refer to Table 6.1). Reference 29 provides guidance on selecting a cost-efficient monitoring strategy.

The frequency of monitoring will be a function of:

- plume behaviour;
- rate of contaminant migration. For intergranular aquifers such as sand and gravel, and sandstone, where flow velocities are of the order of tens of metres per year, then the frequency of monitoring would typically be quarterly. For more variable systems (such as the Chalk), a higher frequency of monitoring (perhaps, monthly) would be required;
- sensitivity of receptor(s);
- natural variability of groundwater flow regime and contaminant concentrations.

A higher frequency of sampling would be required during the first year of monitoring to confirm the conceptual model and to establish trends. Thereafter, the frequency could be reduced, subject to agreement with the regulator. An annual (or even less frequent for particularly slow-moving groundwater) monitoring frequency may be appropriate for some sites, once baseline conditions and trends in plume behaviour have been established.

6.2.3 Review of data

To assist in the review and assessment of the monitoring results (see Appendix 6), the data should be presented as:

- time-series graphs to identify any trends and compliance, where appropriate, with remedial targets;
- contour plots to identify any changes in the plume geometry.

The monitoring information will need to be reviewed routinely to:

- discover whether natural attenuation is occurring according to expectations, thus confirming the conceptual model;
- ensure changes in contaminant concentrations with time are consistent with predictions;
- demonstrate the remedial/compliance targets are not exceeded;
- identify any change in the contaminant source, such as, new releases of contaminant to the groundwater system;
- note changes in the hydraulic and geochemical environments that could influence NA;
- identify and locate the presence of breakdown products that could present a risk;

- identify changes in the hydrogeological regime (such as rising or falling water levels, change in the direction of groundwater flow).

This review will determine whether:

- monitoring can cease, since the contamination no longer poses a risk or trends are sufficiently well established (see Section 6.3);
- monitoring continues according to the defined programme or that it needs to be revised, including change in the frequency of sampling, boreholes monitored and analytical suite. For example, if field measurement of dissolved oxygen shows a change with time, then additional measurements of other electron acceptors/donors may be appropriate to provide additional information on the geochemical environment. Alternatively, if monitoring confirms expected behaviour, then a reduction in the scale of the monitoring programme might be justified;
- the contingency plan needs to be implemented (because NA is not occurring according to expectations);
- the conceptual model needs to be revised.

The main difficulties in the assessment of the monitoring data are:

- errors due to sampling and laboratory practice;
- seasonal variations in water quality;
- insufficient data set to allow meaningful trends to be determined;
- uncertainty in the hydraulic environment.

Statistical analysis of the data provides the most robust method to determine trends and to check compliance with remedial targets. References 21 and 29 describe appropriate methods for the analysis of data. The methods of analysis and basis for accepting compliance with remedial targets (objectives) should form part of the monitoring plan.

6.2.4 Contingency plan

The monitoring plan should include a contingency plan, to govern additional measures to be implemented if natural attenuation proves to be ineffective or insufficient on its own as a remedial technique. This plan should include:

- the basis for implementing the contingency plan;
- the measures that will be implemented and the time-scale over which these measures will be implemented.

Criteria for implementing the contingency plan or for reviewing the MNA conceptual model may include the following:

- contaminant concentrations in monitoring boreholes exceed remedial targets. Criteria should be set that will determine non-compliance. For example a prescribed statistical

threshold (for example, 95 percentile), to account for likely variation in water quality as a function of sampling and analytical procedures;

- contaminant concentrations are not decreasing at a sufficient rate to meet remedial objectives;
- changes in groundwater or land use adversely influence the effectiveness of NA;
- increases in contaminant concentrations that indicate continued release of contaminants to groundwater.

6.3 When to cease monitoring

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

- 1) Contaminant concentrations in the plume have reached background levels; *or*
- 2) Remedial objectives have been met, and natural attenuation can be relied on to further reduce contaminant levels; *or*
- 3) Remedial objectives have been substantially met and falling trends in contaminant concentrations have been defined to the extent that there is a high degree of confidence that the remedial objectives will be achieved in the near future.

The duration of performance monitoring will be site-specific. For many sites, contaminant concentrations may take tens of years to reach background levels. Contaminant fate and transport modelling should provide an indication of this time-scale. For some sites, a period for performance monitoring of one to two years will be adequate, although more typically over five year's monitoring data will be required.

Table 6.1. Example of analytical suites

Contaminant	Initial Sampling Rounds	Subsequent Sampling Rounds ¹
<i>BTEX, Phenol</i>		
<i>Within plume</i>	BTEX/phenol, DO, NO ₃ , Fe (II), SO ₄ , CH ₄ , CO ₂ , alkalinity, water level, NAPL thickness	BTEX/phenol, water level
<i>Outside plume³</i>	BTEX/phenol, DO, NO ₃ , Fe (II), SO ₄ , CH ₄ , CO ₂ , alkalinity, water level ²	BTEX/phenol, water level
<i>Chlorinated solvents</i>		
<i>Within plume</i>	Chlorinated compound + breakdown products, TOC, DO, NO ₃ , Fe (II), SO ₄ , CH ₄ , Cl, water level, NAPL presence	Chlorinated compound + breakdown products, Cl, water level
<i>Outside plume³</i>	Chlorinated compound + breakdown products, TOC, DO, NO ₃ , Fe (II), SO ₄ , CH ₄ , Cl, water level	Chlorinated compound + breakdown products, Cl, water level
<i>Metals</i>		
<i>Within plume</i>	Metal, redox, DO, water level	Metal, water level
<i>Outside plume³</i>	Metal, redox, DO, water level	Metal, water level
<i>Ammonia</i>		
<i>Within plume</i>	Ammonia, nitrate, water level, pH	Ammonia, water level
<i>Outside plume³</i>	Ammonia, nitrate, water level, pH	Ammonia, water level
<i>MTBE</i>		
<i>Within plume</i>	MTBE + breakdown products, DO, NO ₃ , Fe (II), SO ₄ , CH ₄ , CO ₂ , alkalinity, water level	MTBE, water level
<i>Outside plume³</i>	MTBE + breakdown products, DO, NO ₃ , Fe (II), SO ₄ , CH ₄ , CO ₂ , alkalinity, water level	MTBE, water level

1. Estimate: Source pollutants and water levels are two examples of parameters that may be monitored on a regular basis, however there will be times when other parameters (e.g. DO, NO₃, SO₄) will need to be monitored also.
2. The precise biogeochemical parameters will need to be determined based on the biodegradation process.
3. Outside of plume, including up-gradient monitoring point(s).

7. FINAL REVIEW

Monitored natural attenuation can be a viable, cost-effective remedial option within an overall strategy for managing the risks posed by contaminated groundwater. Naturally occurring processes in the subsurface can reduce the mass, toxicity, mobility, volume or concentration of contaminants in groundwater. Such effects are the result of destructive mechanisms, including biodegradation, abiotic oxidation and hydrolysis, and non-destructive mechanisms such as sorption, dispersion and volatilisation, acting on contaminants.

The adoption of MNA as part of a risk-management strategy requires a comprehensive understanding of the hydrogeological, geochemical and microbiological characteristics of the site to ensure that remediation will occur at a rate sufficient to:

- a) protect the wider environment; and
- b) achieve remedial targets in an acceptable time-frame.

The complexities associated with MNA are such that it is important to adopt a consistent approach. This guidance has been developed to provide industry, regulators and other stakeholders with a clear framework to assist in the design, evaluation and implementation of monitored natural attenuation strategies within a risk-based context. Specifically, this involves following a four-stage assessment process comprising:

Stage 1: screening procedures to assess the viability of natural attenuation

Stage 2: procedures to demonstrate current attenuation properties

Stage 3: procedures to evaluate longer-term attenuation capability

Stage 4: procedures to verify attainment of the agreed remedial objectives

The assessment is centred on the development of a conceptual model that describes the hydrogeological and biogeochemical characteristics at a site. The conceptual model is continually challenged and revised as additional data are collected during progressive stages of the assessment. Stages 1 to 3 will occur over a time-period probably exceeding two years to provide sufficient information for MNA to be confirmed as a suitable remedial option. The cost implications of this are considerable.

This document provides guidance on the information required to support MNA as a remedial option, and the criteria that will be used to support or reject it. The approach is sufficiently generic to enable its application to inorganic and organic contamination and to the range of hydrogeological conditions encountered in the UK. This includes single and multi-layered aquifers where groundwater flows via fissures and/or intergranular pathways.

The document has also been designed to take into account the regulatory, practical and economic issues governing uptake of MNA in the England and Wales. For example, issues that are considered include the constraints that are presented by installing monitoring wells beyond a site boundary and the commitment to long periods of monitoring. Similarly, the guidance highlights cases where legislation may preclude the use of natural attenuation as the sole remedial action.

8. REFERENCES

- 1 Air Force Centre for Environmental Excellence, 1995. *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater, Volumes 1 and 2.*
- 2 American Society for Testing and Materials, 1998. *Standard Guide for Remediation of Ground Water by Natural Attenuation at Petroleum Release Sites.* ASTM Standard Guide E1943-98.
- 3 RTDF Bioremediation Consortium, 1997. *Natural Attenuation of Chlorinated Solvents in Groundwater, Principles and Practices (V3.0)*
- 4 Sinke, A.J.C., Heimoiraara T., Tonnaer H. & Van Been S., 1998. *A decision support system for acceptance of natural attenuation as remediation strategy.* NOBIS.
- 5 US Department of the Navy, 1998. *Technical Guidelines for Evaluating Monitored Natural Attenuation of Petroleum Hydrocarbons and Chlorinated Solvents in Ground Water at Naval and Marine Corps Facilities.*
- 6 Wiedemeier, T.H. & Haas, P., 1999. *Designing Monitoring Programs to Evaluate the Performance of Natural Attenuation.* In *Natural Attenuation of Chlorinated Solvents, Petroleum Hydrocarbons, and Other Organic Compounds 5(1)*, Battelle, pp313-323.
- 7 Environment Agency, 1999. *Methodology for the Derivation of Remedial Targets for Soil and Groundwater to Protect Water Resources.* R&D Publication 20. Prepared by Aspinwall & Company.
- 8 DETR/Environment Agency, in preparation. *Contaminated Land Research Report CLR11. Model Procedures for the Management of Contaminated Land.*
- 9 Environment Agency, 1998. *Policy and Practice for the Protection of Groundwater.* (Second Edition). TSO, London.
- 10 SEPA, 1997 *Groundwater Protection Policy for Scotland (08/97).*
- 11 Environment Agency, 1999. *Costs and Benefits Associated with Remediation of Contaminated Groundwater: A Review of the Issues.* R&D Technical Report P278, Prepared by Komex Clarke Bond Ltd & EFTEC Ltd.
- 12 Environment Agency, 1999. *Costs and Benefits Associated with Remediation of Contaminated Groundwater: A Framework for Assessment.* R&D Technical Report P279. Prepared by Komex and EFTEC Ltd.
- 13 Fynamore, J.R., Denton, B. & Nathanail, P., in preparation. *Contaminated Land: Financial Risk Management.* Construction Industries Research and Information Association, London.
- 14 Scotland & Northern Ireland Forum for Environmental Research (SNIFFER)/Environment Agency, 1999. *Communicating understanding of contaminated land risks.* SNIFFER project SR97(11)F. Environment Agency R&D Technical Report P142.

- 15 Allen D.J. et al 1997. *The physical properties of major aquifers in England and Wales*. BGS Technical Report WD/97/34. Environment Agency R&D Publication 8.
- 16 Morris B., Jones H. & Robinson V. (Eds), in preparation. *The physical properties of minor aquifers in England and Wales*. BGS/EA Publication.
- 17 Allen D.J. et al, 1998. *Fracturing and Hydrogeology of the Permo-Triassic Sandstone in England and Wales*. BGS report WD/98/1. Environment Agency R&D Technical Report W164.
- 18 Environment Agency, 1999. *The Natural (Baseline) Quality of Groundwater in England and Wales*. R&D Project Records W6/i722/1 – 7. EA, Bristol.
- 19 Edmunds W.M. et al., 1989. *Trace Element Occurrence in British Groundwater*. BGS Report SD89/3.
- 20 Gilbert, R.O., 1987. *Statistical Methods for Environmental Pollution Monitoring*. Van-Nostrand Reinhold, New York
- 21 Mann, H.B., & Whitney, D.R., 1947. *On a test of whether one or more random variables is stochastically larger than in the other*. Ann. Math. Sci., vol. 18, pp52-54.
- 22 CIRIA, 1995, *Remedial Treatment for Contaminated Land, Volume III – Site Investigation and Assessment*. Special Publication 103.
- 23 Environment Agency, in preparation. *Monitoring of Landfill Sites, Guidance on Monitoring of Landfill Leachate, Groundwater and Surface Water*. R&D Project HOCO_232. Prepared by Peter Dumble Associates.
- 24 American Society for Testing and Materials, 1990. *Standard Practice for Design and Installation of Ground Water Monitoring Wells in Aquifers*. ASTM Designation D5092-90.
- 25 Nielsen, D.M., 1991. *Practical Handbook of Ground-Water Monitoring*. Lewis Publishers.
- 26 International Standards Organisation, 1999. *Water Quality - Sampling - Part 18: Guidance on the Sampling of Groundwater at Contaminated Sites*. Draft ISO Standard ISO/DIS 5667-18.
- 27 British Standards Institution, 1999. *Code of Practice for Site Investigations*. BS 5930:1999.
- 28 Environment Agency, 1999. *Verification of Remedial Techniques for Contaminated Land*. Draft R&D Technical Report P333, Prepared by WRc plc.
- 29 Reed, P., Minsker, B. & Valocchi, A., 1999. *Cost-Effective Long-Term Monitoring Design for Intrinsic Bioremediation*. In Natural Attenuation of Chlorinated Solvents, Petroleum Hydrocarbons, and Other Organic Compounds 5(1), Battelle, pp301-306.

- 30 Environment Agency, 2000. *Guide to Good Practice for the Development of Conceptual Models and the Selection of Analytical and Numerical Models of Contaminant Transport Processes in the Subsurface*. National Groundwater & Contaminated Land Centre Report, Solihull, UK
- 31 Spitz, K.H. & Moreno, J.L., 1996. *A Practical Guide to Groundwater and Solute Transport Modelling*. J Wiley. 461 pp.
- 32 Bear, J and Verruijt, A, 1987. *Modelling Groundwater Flow and Pollution*. D Riedel, Dordrecht. 414 pp.
- 33 Zheng, C. & Bennett, G.D., 1995. *Applied Contaminant Transport Modelling*.
- 34 Wiedemeier, T. & Rifai, H., 1999. *Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface*. John Wiley and Sons Ltd.
- 35 Thornton, S.F., Davison, R.M., Lerner, D.N. & Banwart, S.A., 1998. *Electron Balances in Field Studies of Intrinsic Bioremediation*. In: GQ98: Groundwater Quality: Remediation and Protection, Tübingen, Germany, Sept 1998. IAHS Publication No 250, 273 – 282.
- 36 Environment Agency, 1999. *Recommendations for the processing and presentation of groundwater quality data*. R&D Technical Report P241. EA, Bristol.
- 37 Cash, H.A., Krupa, A.S., Vance, I. & Johnson B.V., 1992. *Laboratory Testing of Biocides Against Sessile Oilfield Bacteria*. Inst. Gas Technol. Gas, Oil & Environ. Biotechnol. Symp. Chicago, 21-23 September 1992.
- 38 Wiedemeier, T.H., Swanson, M.A., Wilson, J.T., Kampbell, D.H., Miller, R.N. & Hansen, J.E., 1996. *Approximation of Biodegradation Rate Constants for Monoaromatic Hydrocarbons (BTEX) in Ground Water*. GWMR Summer 1996 pp186-194
- 39 Verschueren, K., 1983. *Handbook of Environmental Data on Organic Chemicals*. Van Nostrand Reinhold, New York.
- 40 Lovley, D.R., Coates, J.D., Woodward, J.C., Phillips, E.J.P., 1995. *Benzene Oxidation Coupled to Sulfate Reduction*. Applied and Environmental Microbiology, Vol 61, No 3, pp953-958.
- 41 Suarez, M.P. & Rifai, H.S., 1999. *Biodegradation Rates for Fuel Hydrocarbons and Chlorinated Solvents in Groundwater*. Bioremediation Journal 3(4) pp337-362.
- 42 Edwards, E.A. & Grbic-Galic.D., 1992. *Complete Mineralization of Benzene by Aquifer Microorganisms under Strictly Anaerobic Conditions*. Applied and Environmental Microbiology, Vol. 58 , No. 8, pp2663-2666.
- 43 Hiebert, F.K, Sherrill, R.L. & Naim, T., 1996. *Environmental Compliance and Cutting Costs: Intrinsic Biodegradation of Benzene in a Fresh Water Aquifer*. National Petroleum Refiners Association Environmental Conference, September 15-17 1996, ENV-96-158.
- 44 Jørgensen, B.B., 1978. *A Comparison of Methods for the Quantification of Bacterial Sulfate Reduction in Coastal Marine Sediments I. Measurement with Radiotracer Techniques*. Geomicrobiology Journal, Vol. 1, No.1 pp11 – 27.

Further Reading

- American Petroleum Institute, 1997. *Methods For Measuring Indicators of Intrinsic Bioremediation: Guidance Manual*.
- American Petroleum Institute, 1997. *Effects of Sampling and Analytical Procedures on the Measurement of Geochemical Indicators of Intrinsic Bioremediation: Laboratory and Field Studies*. Prepared by CH2M-HILL, November 1997.
- American Society for Testing and Materials, 1998. *Standard Provisional Guide for Risk Based Corrective Action*. ASTM Designation: PS104-98.
- Anderson, M.D. and Alhajjar, B.J., 1995. *National Bioremediation and Fate/Transport Modelling Enable Closure of Diesel Contaminated Soil in San Diego County, California*. Proceedings of the Ninth National Outdoor Action Conference and Exposition, 2-3 May 1995, pp259-275.
- Anderson, W.C., Loehr, R.C. & Smith, B.P., 1999. *Environmental Availability of Chlorinated Organics, Explosives and Metals in Soils*. American Academy of Environmental Engineers, Chapter 6.
- Anthony, J.W., Henry, B.B., Wiedemeier, T.H., Gordon, E.G & Bidgood, J.B., 1999. *Methodology to Evaluate Natural Attenuation of Methyl Tertiary-Butyl Ether*. In Natural Attenuation of Chlorinated Solvents, Petroleum Hydrocarbons, and Other Organic Compounds 5(1), Battelle, pp121-133.
- Bjerg, P.L., Ruge, K., Corsten, J., Nielsen, P.H. & Christensen, T.H., 1999. *Degradation of Aromatic and Chlorinated Aliphatic hydrocarbons in the Anaerobic Part of the Grinsted Landfill Leachate Plume: In Situ Microsocm and Laboratory Batch Experiments*. Groundwater, Vol 37, No 1, January – February 1999.
- Borden R.C., Daniel, R.A., LeBrun, L.E. IV & Davis, C.W., 1997. *Intrinsic biodegradation of MTBE and BTEX in a gasoline-contaminated aquifer*. Water Resources Research, Vol 33, No 5, pp1105 – 1115.
- Brady, P.V., & Borns, D.J., 1988. *Natural Attenuation (CERCLA, RBCSs and the Future of Environmental Remediation)*. Lewis (CRC Press Inc).
- Burger, E.D., Vance, I., Gammack, G.F. & Duncan, S.E., 1995. *Control of Microbially Generated Hydrogen Sulfide in Produced Waters*. The Fifth International Conference on Microbial Enhanced Oil Recovery and Related Biotechnology for Solving Environmental Problems. Conference Proceedings, pp339-352.
- Buscheck, T.E and Alcantar, C.M., 1995. *Regression Techniques and Analytical Solutions to Demonstrate Intrinsic Bioremediation*. Third International Insitue and On site Bioremediation Symposium in San Diego, California.
- Chappelle, F.H., 1999. *Bioremediation of Petroleum Hydrocarbon Contaminated Groundwater: The Perspectives of History and Hydrology*. Groundwater, Vol 37, No 1, January – February 1999.

- Christensen, T.H., Bjerg P.L. & Kjeldsen, P., 1999. *Natural Attenuation : A Feasible Approach to Remediation of Groundwater Pollution at Landfills*. Technical University of Denmark.
- Christensen, T.H., Kjeldsen, P., Bjerg, P.L., Jensen, D.L., Christensen, J.B., Baun, A., Albrechtsen, H.J., & Heron, G., 1999. *Biochemistry of Landfill Leachate Plumes*.
- CIRIA, 1998. *Hydraulic Measures for the control and treatment of groundwater pollution*. CIRIA Report 186.
- Domenico, P.A and Schwartz, F.W. 1990. *Physical and Chemical Hydrogeology*. J. Wiley & Sons.
- Domenico, P.A., 1987. *An analytical model for multidimensional transport of a decaying contaminant species*: J Hydrology, Vol 91, p 49-58.
- Environment Agency, 1999. *National Sampling Procedures Manual, Volume 25, Quality Management System for Environmental Sampling*. ES 006.
- Environment Agency, 1999. *ConSim: Contamination Impacts on Groundwater: Simulation by Monte-Carlo Method*. (Prepared by Golder Associates (UK) Ltd).
- Environment Agency. *Sustainable Development Series: Taking Account of Costs and Benefits*. EA Bristol.
- Environment Agency, 1999. *Natural Attenuation of Petroleum Hydrocarbons and Chlorinated Solvents in Groundwater*. R&D Technical Report P305. Prepared by Golder Associates (UK) Ltd.
- Environment Agency, 2000. *CEC and Kd determination in landfill performance evaluation: a review of methodologies and preparation of standard materials for laboratory analysis*. R&D Technical Report P340. EA, Bristol.
- Holder, T., Teutsch, G., Ptak, T. & Schwarz R, 1998. *A New Approach for Source Zone Characterisation: The Neckar Valley Study*. In Groundwater Quality: Remediation and Protection (Proceedings of the GQ '98 Conference held at Tubingen, Germany, September 1998) IAHS Publication No. 250.
- International Standards Organisation, 1985. *Water Quality Sampling: Guidance on the Design of Sampling Programmes*. ISO Standard ISO 5667-3.
- International Standards Organisation, 1993. *Water Quality Sampling: Guidance on Sampling Groundwaters*. ISO Standard ISO 5667-11.
- Landmeyer, J.E., Chapelle, F.H., Bradley, P.M., Pankow, J.F., Church, C.D. & Tratnyek, P.G., 1998. *Fate of MTBE Relative to Benzene in a Gasoline-Contaminated Aquifer (1993-98)*. Ground Water Monitoring and Remediation, Fall 1998.
- Lee, M.D., Sehayek, L., Sleep B.E. & Vandell, T.D., 1999. *Investigation and Remediation of a 1,2-Dichloroethane Spill, Part II: Documentation of Natural Attenuation*. Ground Water Monitoring and Remediation, Summer 1999, pp82-88.
- McNab, W.W., Rice, D.W., Bear, J., Ragaini, R., Tuckfield, C. & Oldenburg, C., 1999. *Historical Case Analysis of Chlorinated Volatile Organic Compound Plumes*. Lawrence Livermore National Laboratory, UCRL-AR-133361.

- McNab, W.W. & Dooher, B.P., 1998. *A Critique of a Steady-State Analytical Method for Estimating Contaminant Degradation Rates*. Ground Water, Vol 36, No 6, November-December 1998.
- National Research Council. 2000. *Natural Attenuation for Groundwater Remediation*. National Academy Press, Washington.
- Norris, R.D. & Wilson, D.J., 1999. *Benefits and Concerns with Application of the USEPA Protocol for Monitored Natural Attenuation*. In *Natural Attenuation of Chlorinated Solvents, Petroleum Hydrocarbons, and Other Organic Compounds 5(1)*, Battelle, pp53-58.
- Nyer, E., Mayfield, P. & Hughes, J., 1998. *Beyond the AFCEE Protocol for Natural Attenuation*. GWMR, Summer 1998, pp70-77.
- Oderman, J.R., 1999. *Remediation by Natural Attenuation*. Ground Water Monitoring and Remediation, Summer 1999, pp58-60.
- Piotrowski, M.R., Lovingood, D.A. & Sutch, R., 1999. *Monitored Natural Attenuation, Improving Field Measurements*. Soil & Groundwater Cleanup, April/May 1999, pp22-25.
- Ratz, J.W., Downey, D.C. & Childs, J.E., 1993. *Bioventing, Air Sparging, and Natural Attenuation Modeling: an Integrated Approach to the Remediation of a Petroleum-Contaminated Site*. Seventh National Outdoor Action Conference on Aquifer Restoration, 25-27 May 1993.
- Rice, D.W. & McNab, W.W., 1998. *Natural Biodegradation of Organic Contaminants in Groundwater*. Lawrence Livermore National Laboratory, UCRL-JC-131848.
- Salanitro, J.P., Wisniewski, H.L., Byers, D.L., Neaville, C.C., & Schroder, R.A., 1997. *Use of Aerobic and Anaerobic Microcosms to Assess BTEX Biodegradation in Aquifers*. Groundwater Monitoring and Remediation, Summer 1997.
- Schwarz, R., Ptak, T., Holder, T. & Teutsch, G., 1998. *Groundwater Risk Assessment at Contaminated Sites : A New Investigation Approach*. In *Groundwater Quality : Remediation and Protection (Proceedings of the GW '98 Conference held at Tubingen, Germany, September 1998)* IAHS Publication No 250.
- Sinke, A. & Le Hencho, I., 1999. *Natural Attenuation: Guidelines for Acceptance*. TNO-MEP.
- Testa, S.M., 1996. *Considerations and Methodology in Using Natural Attenuation as a Remedial Strategy*. Proceedings of the Tenth National Outdoor Action Conference and Exposition, 13 –15 May 1996, pp283 – 302.
- United States Environmental Protection Agency, 1992. McLean, J.E., and Bledsoe, B.E. *EPA Groundwater Issue, Behaviour of Metals in Soils*. EPA/540/S-92/018.
- United States Environmental Protection Agency, 1994. *Symposium on Natural Attenuation of Groundwater*. EPA/600/R-94/162.
- United States Environmental Protection Agency, 1994. *Natural Attenuation of Hexavalent Chromium in Groundwater and Soils*. EPA/540/5-94/505.
- United States Environmental Protection Agency, 1997. *Proceedings of the Symposium on Natural Attenuation of Chlorinated Organics in Ground Water*. EPA/540/R-97/504.

- United States Environmental Protection Agency, 1997. *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites*, Directive 9200.4-17.
- United States Environmental Protection Agency, 1998. *Monitored Natural Attenuation of Chlorinated Solvents, Remedial Technology Fact Sheet*. EPA/600/F-98/022.
- United States Environmental Protection Agency, 1998. *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water*. EPA/600/R-98/128.
- United States Environmental Protection Agency, 1999. *Monitored Natural Attenuation of Petroleum Hydrocarbons, Technology Fact Sheet*. EPA/600/F-98/021.
- Wiedemeier, T.H., et al, 1994. *Intrinsic Remediation with Long Term Monitoring Options for Natural Attenuation of Fuel Contamination on Groundwater*.
- Wiedemeier, T.H., Swanson, M.A., Moutoux, D.E., Wilson, J.T., Kampbell, D.H., Hansen, J.E. & Haas, P., 1996. *Overview of the Technical Protocol for Natural Attenuation of Chlorinated Aliphatic Hydrocarbons in Groundwater Under Development for the Air Force Center for Environmental Excellence*. EPA/540/R-96/509, USEPA, Washington, pp 35-59.
- Wiedemeier, T.H., Wilson, J.T. & Kampbell, D.H., 1996. *Natural Attenuation of Chlorinated Aliphatic Hydrocarbons at Plattsburgh AFB New York*. Symposium on Natural Attenuation of Chlorinated Organics in Groundwater, 11-13 September 1996. EPA/540/R-96/509
- Wiedemeier, T.H., Wilson, J.T., Kampbell, D., Hansen, J.E. & Haas, P. *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Ethenes in Groundwater*. pp 425-439.
- Wiedemeier, T.H., Wilson, J.T., Kampbell, D.H. & Miller, R.N., 1994. *Proposed Air Force Guidelines For Successfully Supporting the Intrinsic Remediation (Natural Attenuation) Option at Fuel Hydrocarbon Contaminated Sites*. Eighth National Outdoor Action Conference, 23 May 1994.
- Yang, X., et al. Natural Attenuation Study in Wisconsin and Illinois.

GLOSSARY

Absorption	The incorporation of a chemical within a solid or liquid.
Adsorption	The attachment of a chemical to the surface of a solid or liquid.
Advection	Mass transport caused by the bulk movement of flowing groundwater.
Anaerobic/anoxic groundwater	Groundwater that contains oxygen in concentrations less than about 0.5 mg/l.
Aquifer	A permeable geological stratum or formation that is capable of both storing and transmitting water in significant amounts.
Attenuation	Reduction in contaminant concentration through biological, chemical and physical processes as it passes through a medium.
Biodegradation	The transformation of a substance or chemical by micro-organisms, resulting in a change in chemical structure mass within the environment.
Cometabolism	A process in which a compound is fortuitously degraded by an enzyme or co-factor produced during microbial metabolism of another compound.
Compliance point	Negotiated location where the remedial target concentration must be achieved.
Conservative pollutants	Pollutants that can move readily through the aquifer with little reaction with the rock matrix and which are unaffected by biodegradation (for example, chloride).
Controlled waters	Defined by Water Resources Act 1991, Part III, Section 104. All rivers, canals, lakes, groundwaters, estuaries and coastal waters to three nautical miles from the shore.
Daughter product	A compound that results directly from the degradation of another. For example, <i>cis</i> -1,2-dichloroethene (<i>cis</i> -1,2-DCE) is a daughter product of the biodegradation of trichloroethene (TCE).
Dense non-aqueous phase liquid (DNAPL)	A liquid immiscible with water that has a density greater than water and so sinks in water.
Diffusion	Migration of substances by natural movement of their particles.
Dilution	Reduction in concentration brought about by the addition of water.

Dispersion	Irregular spreading of solutes due to aquifer heterogeneities at pore-grain scale (mechanical dispersion) or at field scale (macroscopic dispersion).
Dispersivity	A property that quantifies the physical dispersion of a solute being transported in a porous medium.
Electron acceptor	A compound capable of accepting electrons during oxidation-reduction reactions. Microorganisms obtain energy by transferring electrons from electron donors such as organic compounds (or sometimes reduced inorganic compounds such as sulphide) to an electron acceptor. Electron acceptors are compounds that are relatively oxidised and include oxygen, nitrate, Fe (III), Mn (IV), sulphate, carbon dioxide, or in some cases the chlorinated aliphatic hydrocarbons such as perchloroethene (PCE), TCE, DCE and vinyl chloride.
Electron donor	A compound capable of supplying (giving up) electrons during oxidation-reduction reactions. Microorganisms obtain energy by transferring electrons from electron donors such as organic compounds (or sometimes reduced inorganic compounds such as sulphide) to an electron acceptor. Electron donors are compounds that are relatively reduced and include fuel hydrocarbons and native organic carbon.
Escrow	A written legal engagement to do something, kept in a third person's custody until some condition has been fulfilled. A financial escrow in this instance is normally a sum of money held in reserve in case some system fails or requires long-term monitoring.
Fermentation	Microbial metabolism, in which a particular compound is used both as an electron donor and an electron acceptor resulting in the production of oxidised and reduced daughter products.
Free phase contamination	Product (e.g. gasoline, diesel) which is present in its original state and at a high saturation. May also include coal tars.
Groundwater	(Regulation 1(2) EC Groundwater Directive.) All water that is below the surface of the ground in the saturation zone and in direct contact with the ground or subsoil.
Ground waters	Any waters contained in underground strata. (<i>s104, WRA, 1991</i>)
Groundwater Protection Zone (GPZ)	An area designated around a groundwater source, the maximum extent of which is the catchment area for the source and within which there are limits to the processes and activities that can occur.

Henry's Law Constant	Coefficient that represents the equilibrium partitioning factor between a solute in the water and vapour phases.
Hydraulic conductivity	A coefficient of proportionality describing the rate at which water can move through a permeable medium. The density and kinematic viscosity of the water must be considered in determining hydraulic conductivity.
Hydraulic gradient	The change in total head with a change in distance in a given direction. The direction is that which yields a maximum rate of decrease in head.
Hydraulic head	The sum of the elevation head, the pressure head, and the velocity head at a given point in the aquifer.
Intergranular	Occurring between the grains of a rock or soil.
Light non-aqueous phase liquid (LNAPL)	A liquid immiscible with water that has a density less than water and so floats on water.
Metabolic by-product	A product of the biologically mediated reaction between an electron donor and an electron acceptor. Metabolic by-products include volatile fatty acids, daughter products of chlorinated aliphatic hydrocarbons, methane and chloride.
MNA	Monitored Natural Attenuation. Monitoring of groundwater to confirm whether NA processes are acting at a sufficient rate to ensure that the wider environment is unaffected and that the remedial objectives will be achieved within a reasonable time-scale; typically less than one generation or 30 years.
NA	Natural Attenuation. The effect of naturally occurring physical, chemical and biological processes, or any combination of those processes to reduce the mass, toxicity, mobility, volume or concentration of polluting substances in groundwater. For natural attenuation to be effective as a remedial action, the rate at which those processes occur must be sufficient to prevent polluting substances entering identified receptors and to minimise expansion of pollutant plumes into currently unpolluted groundwater. Dilution within a receptor (such as a river or borehole) is not natural attenuation.
Non-aqueous phase liquid (NAPL)	Liquids that are immiscible with water.
Oxic/aerobic	Groundwater that contains oxygen in concentrations greater than about 0.5 milligrams per litre (mg/l).
Partition coefficient	In a heterogeneous system of two or more phases in equilibrium, the ratio of the activities (or less accurately the concentrations) of the same molecular species in the phases is a constant at

	constant temperature. This constant is termed the partition coefficient.
Pathway	A route along which a particle of water, substance or contaminant moves through the environment and comes into contact with, or otherwise affects, a receptor.
Permeability	Measure of the ability (of rocks) to transmit water. Defined as the volume of water passing through 1m^2 of aquifer under unit hydraulic gradient; $\text{m}^3/\text{m}^2 \text{ d}$ or md^{-1} .
Pollution of groundwater	The discharge by man, directly or indirectly, of substances or energy into groundwater, the results of which are such as to endanger human health or water supplies, harm living resources and the aquatic ecosystem or interface with other legitimate uses of water (Groundwater Directive 80/68/EEC)
Pollution (EPA, 1990)	Pollution of the environment due to the release (into any environmental medium) from any process of substances that are capable of causing harm to man or any other living organism supported by the environment.
Porosity	The ratio of the volume of void spaces in a rock or sediment to the total volume of the rock or sediment.
Receptor	An entity, such as a human, animal, controlled waters, plant, building or the atmosphere, which is vulnerable to the adverse effects of a hazardous substance or agent.
Recharge	The amount of water that reaches an aquifer, which is calculated as rainfall less runoff, evapotranspiration and soil storage.
Reductive dechlorination	Reduction of a chlorine-containing organic compound via the replacement of chlorine with hydrogen.
Remedial target	The goal of remedial activity set at the compliance point, in the form of a desired concentration in the soil or groundwater.
Retardation	A measure of the reduction in solute velocity relative to the velocity of the advecting groundwater caused by processes such as adsorption.
Saturated zone	The zone in which the voids of the rock or soil are filled with water at a pressure greater than atmospheric. The water table is the top of the saturated zone in an unconfined aquifer.
Sentinel borehole	A monitoring borehole up-gradient of a receptor.
Source	A hazardous substance or agent (e.g. a contaminant that is capable of causing harm).

Sorption	Absorption and adsorption considered jointly.
Target concentration	Derived chemical concentration at compliance point.
Unsaturated zone	The zone between the land surface and the water table. It includes the root zone, intermediate zone and capillary fringe. The pore spaces contain water at less than atmospheric pressure, as well as air and other gases. Saturated bodies, such as perched groundwater, may exist within the unsaturated zone. Also called zone of aeration and vadose zone.

APPENDICES

APPENDIX	CONTENT
APPENDIX 1	Processes involved in natural attenuation
APPENDIX 2	Data requirements for lines of evidence
APPENDIX 3	Data acquisition
APPENDIX 4	Fate and transport models
APPENDIX 5	Methods of assessment
APPENDIX 6	Presentation of information supporting NA
APPENDIX 7	Case studies

APPENDIX 1

Processes involved in natural attenuation

Introduction

The processes that affect contaminant transport can be divided into three groups: physical (dispersion, diffusion, dilution and volatilisation), geochemical (sorption and chemical or abiotic reactions) and biochemical (biodegradation) processes. Some of these processes result in a loss in contaminant mass (destructive, such as degradation); some transfer contaminant from the mobile phase to an immobile phase (retardation) and some may simply redistribute contaminant within the mobile phase (dispersion). Table A1.1 gives a summary of the main processes affecting contaminant transport.

Advection is the main process in the migration of contaminants. It describes the transport of dissolved substances (solutes) by groundwater under a hydraulic gradient. Non-reactive (conservative) substances travel at the same rate as water. Reactive solvents may be retarded by other processes, and travel more slowly than water. Figure A1.1 illustrates the different contaminant profiles that would be expected for advection, dispersion, sorption and degradation.

Figure A1.1. Idealised section along a contaminant flow path to illustrate influence of advection, dispersion, sorption and degradation, after a given duration of time.

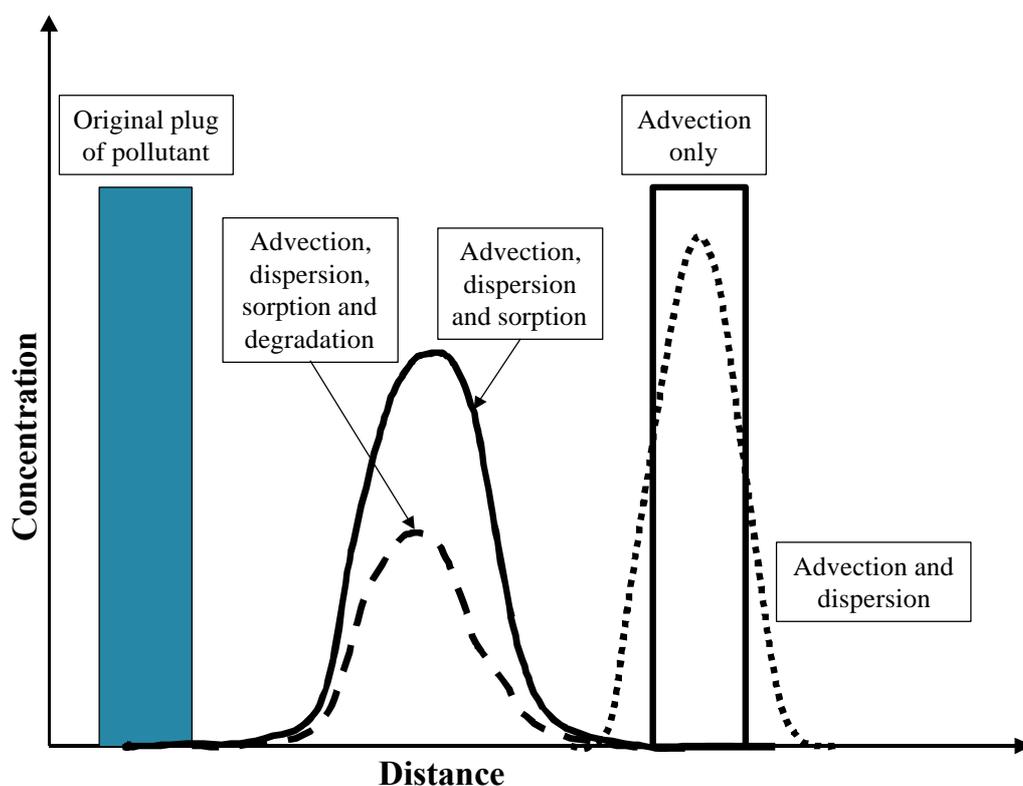


Table A1.1. Summary of important processes affecting solute fate and transport (modified from Wiedemeier, 1999)

Process	Description	Dependencies	Effect
Advection	Movement of solute by bulk groundwater movement	Dependent on aquifer properties, mainly hydraulic conductivity and effective porosity, and hydraulic gradient. Independent of contaminant properties	Main mechanism driving contaminant movement in the subsurface
Dispersion	Fluid mixing due to groundwater movement and aquifer heterogeneities	Dependent on aquifer properties and scale of observation. Independent of contaminant properties	Causes longitudinal, transverse, and vertical spreading of the plume. Reduces solute concentration
Diffusion	Spreading and dilution of contaminant due to molecular diffusion	Dependent on contaminant properties and concentration gradients. Described by Fick's Laws	Diffusion of contaminant from areas of relatively high concentration to areas of relatively low concentration. Generally unimportant relative to dispersion at most groundwater flow velocities
Sorption	Reaction between aquifer matrix and solute whereby contaminants become sorbed or organic carbon or clay minerals	Dependent on aquifer matrix properties (organic carbon and clay mineral content, bulk density, specific surface area, and porosity) and contaminant properties (solubility, hydrophobicity, octanol-water partitioning coefficient)	Tends to reduce apparent solute transport velocity and remove solutes from the groundwater via sorption to the aquifer matrix
Recharge (simple dilution)	Movement of water across the water table into the saturated zone	Dependent on aquifer matrix properties, depth to groundwater, surface water interactions, and climate	Causes dilution of the contaminant plume and may replenish electron acceptor concentrations, especially dissolved oxygen
Volatilization	Volatilization of contaminants dissolved in groundwater into the vapour phase (soil gas)	Dependent on the chemicals' vapour pressure and Henry's Law constant	Removes contaminants from groundwater and transfers them to soil gas
Biodegradation	Microbially mediated oxidation-reduction reactions that degrade contaminants	Dependent on groundwater geochemistry, microbial population and contaminant properties. Biodegradation can occur under aerobic and/or anaerobic conditions	May ultimately result in complete degradation of contaminants. Typically the most important process acting to truly reduce contaminant mass
Abiotic degradation	Chemical transformations that degrade contaminants without microbial facilitation, such as hydrolysis	Dependent on contaminant properties and groundwater geochemistry	Can result in partial or complete degradation of contaminants. Rates typically much slower than for biodegradation
Partitioning from NAPL	Partitioning from NAPL into groundwater. NAPL plumes, whether mobile or residual, tend to act as a continuing source of groundwater contamination	Dependent on aquifer matrix and contaminant properties, as well as groundwater mass flux through or past NAPL plume	Dissolution of contaminants from NAPL represents the primary source of dissolved contamination in groundwater

Dilution, dispersion and diffusion

Dilution, dispersion and diffusion are physical processes that reduce the concentration of a contaminant, but do not affect its mass, toxicity or mobility.

Dilution describes the mixing of contaminated water by clean groundwater. It is likely to be an important mechanism in reducing concentrations, wherever small quantities of contaminant reach the aquifer with a comparatively large groundwater flow or throughput. Further dilution can occur by:

- uncontaminated infiltration (recharge of precipitation) away from the source area (this is the only mechanism of dilution that is strictly applicable to natural attenuation);
- contaminated groundwater discharging to a clean surface water body or mixing with clean water at an abstraction point. Dilution within a receptor (such as a river or borehole) is not considered to constitute natural attenuation by the Environment Agency.

Infiltration can be an important mechanism in introducing electron acceptors (dissolved oxygen, nitrate, sulphate) where contaminants are being microbiologically degraded.

Dispersion will reduce contaminant concentrations by spreading the contaminant (in a longitudinal, transverse and vertical direction) as groundwater flows through the aquifer. Dispersion can facilitate biodegradation by reducing contaminant concentrations below toxic thresholds and spreading the plume into areas with electron acceptors.

Dispersion occurs due to mechanical dispersion and molecular diffusion and can be represented by the following equation:

$$D = D^d + D^* \quad (1)$$

and

$$D = \infty D_w + \alpha.v \quad (2)$$

where

D = hydrodynamic dispersion (m^2/s)
 D^* = mechanical dispersion (m^2/s)
 D^d = molecular diffusion coefficient through medium (m^2/s)
 $\alpha.$ = dispersivity (m)
 v = groundwater velocity (m/s)
 ∞ = tortuosity of medium
 D_w = molecular diffusion coefficient in water (m^2/s)

For many groundwater systems, diffusion is small or negligible compared to mechanical dispersion and equation (2) reduces to $D = \alpha.v$

Mechanical dispersion is the main process in spreading contaminants and is a result of variation in the velocity of water movement through pores of different size, tortuosity (flow path length), and frictional variations within the pore space. Dispersion has a longitudinal (parallel to the flow direction) and transverse (perpendicular to the flow direction) component. As the scale of the plume or system increases, dispersion will also increase, i.e. it is scale dependent. The value of dispersion will directly reflect the heterogeneity of the system.

Diffusion is observed as the movement of contaminants from regions of higher concentration to lower concentration, but occurs due to random atomic scale movement of atoms and molecules. Diffusion is slow in comparison to mechanical dispersion, and only becomes significant in no-flow or very low-flow systems, or over very long time-scales. For dual porosity systems, such as the chalk diffusion of contaminants from the mobile fissure water to the less mobile pore water can be an important mechanism in retarding contaminant

movement. Reverse diffusion from the pore water can act as a persistent secondary source of contamination.

Volatilisation of volatile contaminants to soil gas results in removal of contaminant mass, but is not destructive. Volatilisation is dependent on the physico-chemical characteristics of the contaminant, and is dependent on site-specific conditions including temperature, depth to water and porosity. This is generally not a significant mechanism due to the area of contaminated groundwater exposed to soil gas. The exception may be fresh spills of petroleum hydrocarbons, due to the loss of the more volatile components from free product at the watertable. The partitioning of volatile substances from the dissolved phase into the vapour phase is described by its Henry's Law constant:

$C_v = H \times C \quad (3)$ <p>where</p> $C_v = \text{concentration in vapour phase (mg/l)}$ $H = \text{Henry's Law constant (dimensionless)}$ $C = \text{concentration in aqueous phase (mg/l)}$
--

Sorption describes the interaction of a contaminant between water and soil. This process will reduce contaminant concentrations by their removal from solution due to interaction with the matrix of the aquifer through which groundwater is moving. There is no mass reduction of contaminant. Sorption can occur as a result of:

- adsorption, the attachment of a solute to a solid surface;
- absorption, the movement of a solute (diffusion) into the structure of a porous particle where it sorbs onto an internal surface;
- ion exchange, the replacement of a sorbed ion by the contaminant.

Sorption will retard the rate at which contaminants move through the system. The retardation of a contaminant can be defined as:

$\text{Retardation } (R_c) = \frac{u}{v} \quad (4)$ <p>where,</p> $R_c = \text{retardation factor}$ $u = \text{velocity of contaminant or solute (m/d)}$ $v = \text{velocity of groundwater flow (m/d)}$
--

The contaminant mass is removed from the dissolved phase, but the process is reversible and therefore does not represent a permanent mass reduction. Desorption is generally slower than sorption, such that contaminant concentrations are reduced, although the sorbed contaminant can represent a longer-lasting source.

The extent of contaminant sorption can influence the efficiency of other attenuating mechanisms, such as biodegradation (sorption will retard the rate of contaminant movement and thereby increase the time for other processes to occur). Sorption is a function of:

- the nature of the contaminant (conservative contaminants such as chloride are not sorbed, whereas reactive contaminants, such as metals can be heavily sorbed);
- the contaminant (solute) concentration;
- the nature and concentration of other contaminants (competition with other contaminants can reduce the number of sites for sorption, or some contaminants (organics) can provide additional sites for further sorption);
- nature of the soil/rock matrix, including surface area;
- presence of clay, organics and oxyhydroxides which can provide sites for sorption;
- environment, the pH and redox potential of the system can influence sorption. The sorption of some metals is very sensitive to pH conditions;
- flow rate, in terms of the time for sorption.

For non-polar organic and inorganic contaminants sorption occurs preferentially to soil organic matter or to clay minerals. In most aquifers, sorption to organic matter is the dominant process, except where the organic content is low and then sorption to mineral surfaces is the main process. The partition coefficient for organic contaminants can be calculated as set out in Table A1.2.

Table A1.2: Basic equations for calculation of partition coefficient

Partition coefficient for non-polar organic chemicals (for example, aromatic hydrocarbons such as benzene, toluene):	
$K_d = K_{oc} \times f_{oc}$	
Partition coefficient for ionic organic chemicals (for example, phenol)	
$K_d = K_{oc,n} (1 + 10^{pH-pK_a})^{-1} + K_{oc,i} (1 - (1 + 10^{pH-pK_a})^{-1})$	
K_d	= soil water partition coefficient (l/kg)
K_{oc}	= organic carbon partition coefficient (l/kg)
f_{oc}	= fraction of organic carbon (fraction)
$K_{oc,n}$	= sorption coefficient for related species (l/kg)
$K_{oc,i}$	= sorption coefficient for ionised species (l/kg)
pH	= pH value
pKa	= acid dissociation constant

The partition coefficient (K_d) describes the distribution of a solute between groundwater and the solid and is typically represented by either:

1. Linear isotherm

$$K_d = \frac{C}{C_s} \quad (4)$$

2. Freundlich isotherm

$$K_d = \frac{C^{1/N}}{C_s} \quad (5)$$

3. Langmuir isotherm

$$K_d = \frac{C_s}{C(b - C_s)} \quad (6)$$

K_d = partition coefficient (l/kg)

C = concentration in the aqueous phase (mg/l)

C_s = concentration in the solid phase (mg/kg)

b = maximum amount of contaminant that can be sorbed (g/g)

N = chemical-specific coefficient (values of $1/N$ typically range from 0.7 to 1.1)

Solutes sorbed onto colloids (colloidal sorption) may be transported through the aquifer system.

Complexation. Metal ions in aqueous solution are typically present as complexes. A complex is an ion in a combination of cations with anions or molecules.

Oxidation/reduction. A chemical or biological reaction where an electron is transferred from an electron donor to an electron acceptor and results in a change in the valency state of the ion. In many cases the solubility will also be different, giving rise to precipitation or sorption of the ion. For example, hexavalent chromium (soluble) occurs under oxidising conditions. If conditions become reducing, this is converted to trivalent chromium (insoluble) and this metal is precipitated out of solution.

Solution/precipitation. Contaminants may be precipitated out of solution if physiochemical conditions change. However, the contaminant may be dissolved back into solution.

Chemical or abiotic degradation

Abiotic reactions include the chemical transformation of contaminants. The transformation products may be in a less mobile, less reactive or less toxic form. This process results in a loss of mass (destructive). Examples of abiotic reactions are hydrolysis, (reaction with either water or a hydroxide ion to produce an alcohol), substitution (reaction with another anion as the nucleophilic agent), elimination (two adjacent groups within the molecule are lost resulting in the formation of a double bond) and oxidation/reduction (transfer of electrons from one compound to another). Rates of abiotic degradation can vary from days to hundreds of years, but this process is generally slower than biodegradation.

Biodegradation

Biodegradation is the main process in the natural attenuation of organic contaminants and results in a mass loss (destructive). Organic compounds are biodegraded via biological oxidation when electron donors, electron acceptors and nutrients are combined by micro-organisms to produce metabolic by products and energy for microbial growth. This can be represented by the following generalised equation.

Micro-organisms + electron donor + electron acceptor + nutrients



metabolic by-products + energy + micro-organisms

Aliphatic and aromatic compounds (e.g. BTEX) serve as the electron donor and are broken down in the process. Electron acceptors, in order of preference for utilisation by microbes, include oxygen, nitrate, manganese (IV), iron (III), sulphate and carbon dioxide. Manganese and iron are typically present in the mineral form. Depending on the electron acceptor used, the metabolic by products include carbon dioxide, water, nitrogen gas, Manganese (II), Fe (II), hydrogen sulphide and methane.

Decreases in the concentration of electron acceptors and corresponding increase in the concentration of metabolic by products provide indirect evidence for degradation. Table A1.3 provides a summary of changes in contaminant, electron acceptor and metabolic byproduct concentrations during biodegradation. Figure A1.2 illustrates the geochemical evolution of a groundwater system contaminated with petroleum hydrocarbons.

The degradation of other organics can be more complex. For example chlorinated solvents can be degraded by reductive dechlorination, and the degradation relies on an organic source (petroleum hydrocarbons, natural organic matter) to provide electron donors; a process known as co-metabolism.

The degradation process can also vary in different parts of the plume, e.g. anaerobic degradation may be occurring at the centre of the plume and aerobic degradation at the margin of the plume.

Cometabolism. Process in which a compound is fortuitously degraded by an enzyme or cofactor produced during microbial degradation of another compound. Chlorinated solvents, PAHs and some pesticides can be degraded by cometabolism.

Fermentation. Microbial metabolism in which a particular compound is used both as an electron donor and an electron acceptor resulting in the production of oxidised and reduced daughter products.

Figure A1.2. Conceptual section of oxidation/reduction (electron acceptor) zones in groundwater

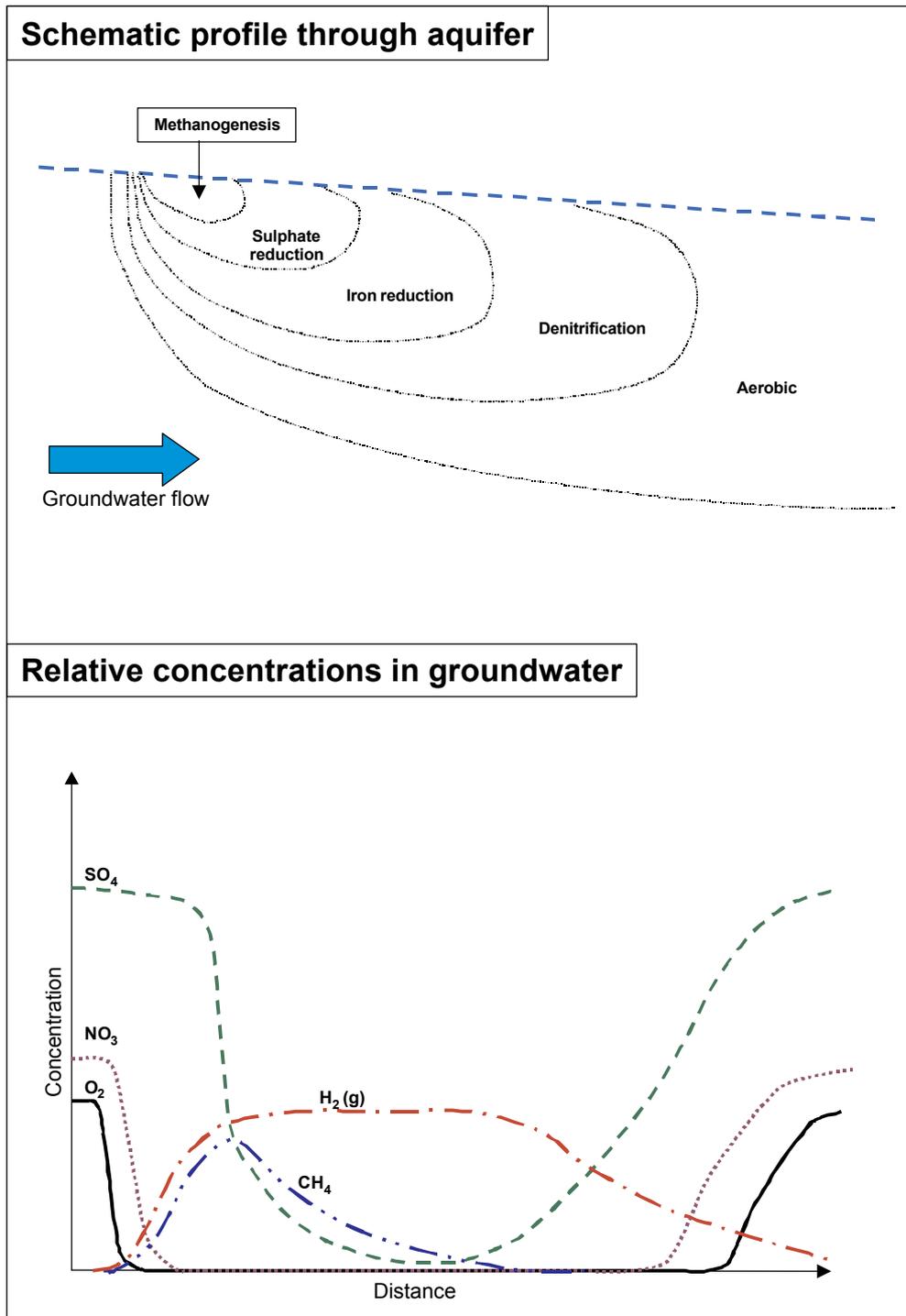


Table A1.3. Trends in contaminant, electron acceptor and metabolic by-product concentrations during biodegradation (modified from Wiedemeier and Chapelle, 1998)

Analyte	Trend in analyte concentrations during biodegradation	Terminal electron accepting processes causing trend ^{2, 3}
Petroleum hydrocarbons	Decrease	Aerobic respiration, denitrification, Mn(IV) reduction, Fe(III) reduction, sulphate reduction, methanogenesis
Highly chlorinated solvents and daughter products	Parent compound concentrations decrease, daughter products increase initially and then may decrease	Reductive dechlorination and cometabolic oxidation
Lightly chlorinated solvents	Decrease	Aerobic respiration and Fe(III) reduction (direct oxidation) and cometabolism (indirect oxidation). Also reductive degradation to ethene, ethane.
Dissolved oxygen	Decrease	Aerobic respiration
Nitrate	Decrease	Denitrification
Mn(II)	Increase (metabolic by-product)	Mn(IV) ¹ reduction
Fe(II)	Increase (metabolic by-product)	Fe(III) ¹ reduction
Sulphate	Decrease	Sulphate reduction
Methane	Increase	Methanogenesis
Chloride	Increase	Reductive dechlorination or direct oxidation of chlorinated compound. In most cases, a significant difference is impossible to measure.
Redox (oxidation/reduction potential)	Decrease	Aerobic respiration, denitrification, Mn(IV) reduction, Fe(III) reduction, sulphate reduction, methanogenesis and halorespiration
Dissolved inorganic carbon	Increase	Aerobic respiration, denitrification, Fe(III) reduction and sulphate reduction

Notes :

1. Mineral phase
2. Oxygen is the most favoured electron acceptor for microbes in the biodegradation of organics. Anaerobic bacteria cannot function if dissolved oxygen concentrations exceed 0.5 mg/l, i.e. if dissolved oxygen levels are greater than this aerobic degradation is the most likely process. The overall process can be completed as multiple processes can occur simultaneously and aerobic degradation.
3. Micro-organisms will generally use electron acceptors in the following order of preference: oxygen, nitrate, iron, sulphate, CO₂.

APPENDIX 2

Data requirements for lines of evidence

Table A2.1. Parameters for site characterisation

Key parameters for assessment	Applicability			Use CM = conceptual model F&T = fate & transport modelling I; II; III = lines of evidence	Potential application to NA evaluation (screening / demonstration / assessment)
	General	Organic	Inorganic		
A. Geologic and hydrogeologic					
Lithology	✓			CM	Indicates isotropic properties of the aquifer, including preferential pathways, water-bearing units, confined/unconfined aquifers. Indicates effects on groundwater flow and direction.
Porosity	✓			CM; F&T	Key factor in groundwater transport.
Aquifer hydraulic conductivity	✓			CM; F&T	Essential for groundwater plume studies.
Seasonal water level fluctuations	✓			CM	Determines extent of smear zone and the whether groundwater velocity and direction varies according to seasons.
Rates of recharge	✓			CM	Factor in groundwater transport.
B. Chemical					
Parent and daughter contaminant concentrations		✓		I	Provides a measure of the type and quantity of parent and biogenic daughter products. Used to estimate biodegradation kinetics such as half-life or degradation rate constants.
Co-contaminant concentrations		✓	✓	I	May indicate that more thermodynamically favourable degradation processes may occur, either by acting as a co-metabolite or as a catalyst.
C. Geochemical					
Dissolved oxygen		✓	✓	II	Highest energy-yielding electron acceptor for biodegradation of organic constituents. Concentrations below ~0.5mg/l generally indicate an anaerobic pathway.
Nitrate		✓		II	Thermodynamically next favourable electron acceptor after oxygen for microbial degradation of organics. Depletion may indicate (denitrification) anaerobic degradation of organics.
Nitrite		✓		II	Product of nitrate reduction. Produced only under anaerobic conditions. Rarely observed.
Iron (III)		✓		II	Biologically available Fe (III) can act as an electron acceptor during anaerobic degradation of organics.
Iron (II)		✓		II	Indication of Fe (III) reduction during microbial degradation of organic compounds in the absence of oxygen, nitrate and manganese (IV).
Manganese (IV)		✓		II	May act as an electron acceptor during anaerobic degradation of contaminants where more thermodynamically favourable electron acceptors are absent.

Key parameters for assessment	Applicability			Use CM = conceptual model F&T = fate & transport modelling I; II; III = lines of evidence	Potential application to NA evaluation (screening / demonstration / assessment)
	General	Organic	Inorganic		
Manganese (II)		✓		II	Indicator of anaerobic degradation of organics, where manganese (IV) acts as an electron acceptor.
Sulphate		✓	✓	II	Used as an electron acceptor in biodegradation of organic constituents. Reduced to form sulphide.
Sulphide				II	Microbially reduced form of sulphate. Indicates reduced conditions.
Methane		✓		II	Indicator of anaerobic conditions and of degradation of organics by methanogenic bacteria. Produced by the microbial reduction of carbon dioxide.
Ethane and ethene		✓			Used to test for biological transformation of chlorinated solvents.
Dissolved hydrogen				II	Provides indicator of redox conditions, since concentrations can be correlated with types of anaerobic activities (methanogenesis, sulphate reduction) in anaerobic environments.
Total organic carbon		✓		II	A measure of the total concentration of organic material (natural and anthropogenic) in water that may act as a primary substrate for biological degradation (reductive dehalogenation).
pH		✓	✓	II	Microbial activity tends to be reduced outside of a pH range of 6 to 8.5, and many anaerobic bacteria are particularly sensitive to pH extremes. Behaviour of metals influenced by pH
Alkalinity/total inorganic carbon		✓	✓	II	Provides an indication of the buffering capacity of the water and the amount of carbon dioxide dissolved in the water. The latter increases due to biodegradation of organic compounds.
Eh (redox potential)		✓	✓	II	A measure of the oxidation/reduction potential of the environment. Typically ranges from +800mV in strongly aerobic conditions to -400mV under methanogenic conditions.
Temperature		✓	✓	II	Affects rates of microbial metabolism. Slower biodegradation occurs at lower temperatures. Also affects solubility of contaminants involved in reduction – oxidation processes.
Chloride	✓			II	Possible indicator of biological dechlorination. Used as a conservative tracer.
Conductivity	✓			II	General water quality parameter used as a marker to verify that site samples are obtained from the same aquifer system.
Phosphorus		✓		II	Essential nutrient for microbial growth and biodegradation.
Ethane/ethene		✓		II	Metabolic end product of reductive dehalogenation of halogenated ethenes and ethane. Provides evidence of complete dechlorination of these compounds. Indicates activity of methanogenic bacteria.
Volatile fatty acids		✓		II	Metabolic by-products of the aerobic degradation of BTEX.
Dehydrogenase		✓		III	Indicator of presence of aerobic bacteria.

Key parameters for assessment	Applicability			Use CM = conceptual model F&T = fate & transport modelling I; II; III = lines of evidence	Potential application to NA evaluation (screening / demonstration / assessment)
	General	Organic	Inorganic		
Carbon dioxide		✓		II	Used as an electron acceptor in methanogenic (anaerobic) degradation of organics. Also a product of the biodegradation of many organics.
D. Biological					
Microbial counts/ biomass		✓		III	Demonstrate the indigenous micro-organisms are capable of degrading contaminants, and to provide indication of rate of degradation. Also used to establish nutrient requirements and limitations.
RNA probes		✓		III	Used to detect specific bacteria that degrade contaminants.

APPENDIX 3

Data acquisition

Table A3.1. Data acquisition

Parameter	Data source	Comments
Porosity	Laboratory measurement, Grain size, Pumping tests Literature	Important to differentiate between total and effective porosity. In soil and unsaturated zone only partial saturation. Water - filled porosity can be estimated from moisture content.
Henry's Law Constant	Literature	Volatile contaminants only.
Bulk Density	Laboratory measurement, Literature	
Clay content	Laboratory measurement Literature	
Fraction of organic carbon	Laboratory measurement, Literature	
Sorption/partition coefficient	Literature, Tracers, Laboratory experiments	Lithology, bulk density, pH-dependent. Competition between different species, chemical reactions, solubility, polarity, changes in media properties.
Hydraulic conductivity	Rising/falling head tests, Packer tests, Pumping tests, Literature, Laboratory tests	Hydraulic conductivity may vary laterally and vertically (anisotropy). Unsaturated zone hydraulic conductivity dependent on saturation.
Groundwater levels Hydraulic gradient	Observation boreholes	Pressure gradient where density is a factor.
Aquifer depth	Boreholes, Geophysical logging, Packer testing	Flow may be in discrete zones such that aquifer depth may differ from the total depth of the formation.
Mixing depth	Monitoring results Geophysical logging Groundwater level variation	Can be estimated using empirical equations.
Direct recharge	Climatological data (rainfall, evaporation), land-use, soil type	Variable recharge through low permeability drift.
Indirect recharge (leakage or discharge to sewers, drains, water mains)	Flow gauging	
Receptors	Environment Agency, SEPA Environmental Health Departments	
Abstraction rates	Environment Agency, SEPA Water Utilities	Actual abstraction may not equal the licensed abstraction rate.

Parameter	Data source	Comments
Dispersion coefficient	Tracer studies, Literature, Laboratory experiments, Empirical values (one tenth of distance plume has migrated)	The value of the dispersion coefficient is scale-dependent. Values reported in field experiments are often several orders of magnitude greater than from laboratory experiments.
Biodegradation	Analysis of observed changes in Contaminant concentrations Microbiological studies Literature	Breakdown products with different properties. Chemical environment. Typical represented as First or Second Order decay kinetic reaction. Alternatively may be linked to available electron acceptors (oxygen, nitrate, sulphate , ferrous iron).
Aquifer geometry	Geological maps, Boreholes, Geophysical survey	
Spring/stream flows	Stream gauging, Topographic maps showing location and elevation of springs and streams Environment Agency, SEPA Institute of Hydrology	
Diffusion coefficient	Literature, Laboratory experiments	Fissure-pore water diffusion in dual porosity media.
Specific gravity of contaminant	Literature Ionic concentration (field investigation)	Temperature, pressure.
Solubility/precipitation	Literature,	Chemical environment (pH, Eh, temperature, pressure, concentration, alkalinity, presence of other contaminants (Raoult's Law)).
Ion exchange	Literature, Tracers, Laboratory experiments	Lithology, pH, Eh, ion concentrations. Chemical reactions, competition between different species, polarity, valency, changes in media properties.
Immiscibility	Literature	Density, viscosity, soil capillarity, surface tension.
Hydrolysis	Literature	Bacterial chemical environment.
Environmental factors (pH, Eh, dissolved oxygen, temperature)	Field measurement	Spatial variation.

APPENDIX 4

Fate and transport models

A groundwater contaminant fate and transport model is a useful tool in the assessment of natural attenuation. The model can be used to:

- simulate the migration of the dissolved contaminant through the groundwater system, taking account of processes that affect its concentration including dispersion, sorption, and degradation;
- predict contaminant concentrations and travel times to receptors;
- predict contaminant movement, including whether the plume is likely to expand, remain stable or shrink;
- predict the size of the plume and hence volume of the aquifer affected by the contaminant;
- improve the understanding of the flow regime and contaminant movement (that is, the conceptual model);
- determine rates of degradation by calibration with observed data;
- derive remedial targets to protect identified receptors;
- determine locations for monitoring boreholes.

A contaminant fate and transport model can be used in two basic ways:

- 1 The prediction of contaminant movement and potential risk to receptors. In many cases this will be based on best or conservative estimates of parameter values, with often no calibration against field data. This is the typical application at the start of an assessment (screening exercise), when limited data may be available, but the likely effectiveness of NA needs to be assessed. Conservative values should be used at this stage of the assessment, such that any decision to proceed in the evaluation of NA will be an element of safety. The model may subsequently be used to predict contaminant concentrations using site specific data to determine whether NA will be an effective remedial option in the long term.
- 2 To evaluate the conceptual model for the site, by determining whether observed contaminant concentrations can be modelled. Here the model is used as a line of evidence in determining the significance and rate of different attenuation processes. This calibrated model could subsequently be used as a predictive tool.

The basic steps in the use of a fate and transport model are summarised in Figure A4.1. Guidance on the selection and use of contaminant transport models is being prepared by the Environment Agency (Ref 30).

The results from any modelling exercise will need to be reviewed in the context of the:

- assumptions made in constructing the model;
- reliability of the data;
- accuracy with which the model represents observed conditions – is it well calibrated with respect to both flow and quality?

Types of model

Two basic types of model are available; analytical and numerical.

Analytical models provide an exact solution to the equations that describe the migration of contaminants subject to advection, dispersion, linear sorption and degradation. Examples of analytical models are given in Tables A4.1 and A4.2. Analytical models are typically applicable to simple flow systems only. In using analytical models a number of assumptions will have been made, normally including:

- the aquifer can be represented by a relatively simple model;
- the aquifer is intergranular, homogeneous and isotropic;
- steady state uniform (normally linear) groundwater flow;
- dispersion is constant;
- the fluid is of constant density and viscosity;
- sorption is linear, instantaneous and reversible;
- decay is governed by first-order kinetics.

Additional assumptions may apply according to the analytical model used. As in practice very few of the above assumptions will be strictly correct, it is important that some form of sensitivity/uncertainty analysis is undertaken. It is important to understand the implications of the model assumptions to the analysis.

The advantages of these models are that they are simple to use and have limited data requirements. The danger in the use of analytical models is their application to complex hydrogeological situations such that the results may be misleading or wrong.

Numerical models provide approximate solutions to the equations governing contaminant transport and allow more complex systems to be represented. The use of numerical models will require technical expertise in groundwater and contaminant movement, together with specialist and detailed investigations to define the flow regime and contaminant transport processes.

The data requirements are significantly greater than for analytical models, and can include spatial variation in aquifer properties plus definition of inflows (recharge) and outflows from the system.

Examples of numerical models that may be appropriate to the assessment of natural attenuation are given in Table A4.3. This list is not comprehensive and other models may be more appropriate, depending on the objectives of the study and the conceptual model.

The decision on what type of model to use will be dependent on:

- the objectives of the study;
- complexity of the site;
- data availability.

It is important to stress that inappropriate use of a model may give rise to erroneous conclusions. It is also important to note that a solution from a model is rarely unique: there may be a number of possible combinations of parameter values that will give the same model result. The range of possible combinations can be reduced through calibration of the model against field data. Further guidance on the use and selection of models is given in References 30, 31, 32 and 33.

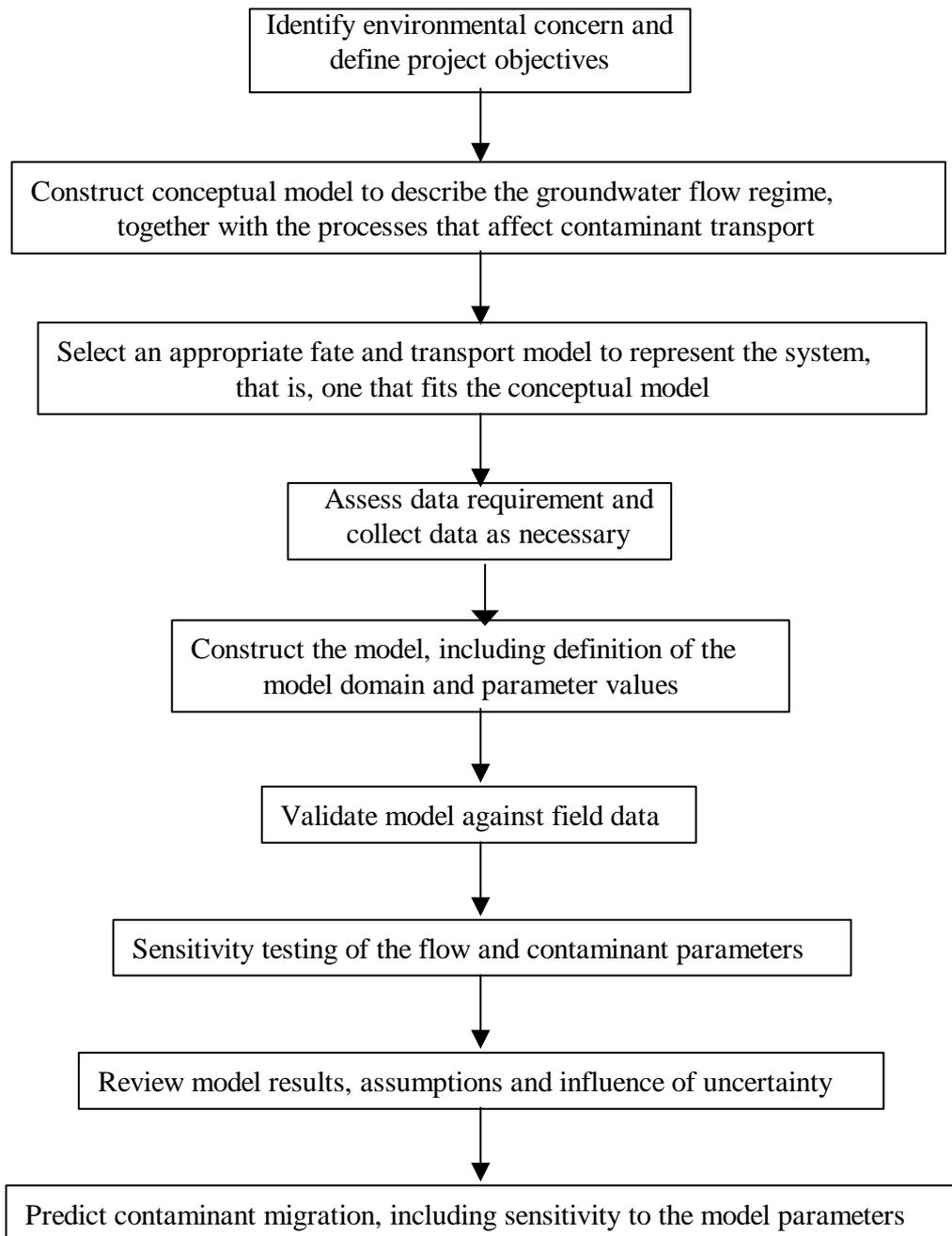
Models may be deterministic or probabilistic. A deterministic model uses a single value to define each model parameter, and the result is a single number. In probabilistic (or stochastic) models, the parameter value is defined by a range or distribution of values, usually referred to as a probability distribution, or density, function (PDF). Consequently, the model output will also be a range of values. Probabilistic models can be used to:

1. represent the intrinsic variability of a parameter (for example, variation of values of hydraulic conductivity in an anisotropic aquifer). In reality, the variability of a parameter cannot be defined precisely and uncertainty will be attached to its definition, particularly as at most sites only a limited data set will be available.
2. represent the uncertainty in defining certain parts of the system. This may be uncertainty in the field measurements, uncertainty in being able to define a parameter (as limited data may be available), or uncertainty in the conceptual model (is the variation in permeability values a function of different aquifer lithologies?). The latter (conceptual uncertainty) cannot be directly represented by a probabilistic model.

The Monte Carlo method is the most widely used probabilistic technique. In general the method involves:

- definition of a probability distribution for each model parameter;
- repeated solution of the model (for example, the Ogata-Banks transport equation) with parameter sets selected from the defined probability distributions;
- analysis of the model results to describe the likelihood of a certain result being obtained.

Figure A4.1 Basic steps in constructing a numerical model



Example of an analytical transport model:

Table A4.1 : Ogata Banks equation (time variant, constant source)

Calculation of concentrations down-gradient of the site (time variant) using the **Ogata Banks equation**

$$C = 0.125.C_o \left[\exp \left(\frac{x}{2ax} \left[1 - \sqrt{1 + \frac{4.\lambda.ax}{u}} \right] \right) \operatorname{erfc} \left(\frac{1}{2\sqrt{ax.u.t}} \left[x - u.t \sqrt{1 + \frac{4.\lambda.ax}{u}} \right] \right) + \right. \\ \left. \exp \left(\frac{x}{2ax} \left[1 + \sqrt{1 + \frac{4.\lambda.ax}{u}} \right] \right) \operatorname{erfc} \left(\frac{1}{2\sqrt{ax.u.t}} \left[x + u.t \sqrt{1 + \frac{4.\lambda.ax}{u}} \right] \right) \right] \\ \left[\operatorname{erf} \left(\frac{y + S_y/2}{2\sqrt{ay.x}} \right) - \operatorname{erf} \left(\frac{y - S_y/2}{2\sqrt{ay.x}} \right) \right] \left[\operatorname{erf} \left(\frac{z + S_z/2}{2\sqrt{az.x}} \right) - \operatorname{erf} \left(\frac{z - S_z/2}{2\sqrt{az.x}} \right) \right]$$

where,

- C = concentration of contaminant at distance x (mg/l)
- C_o = initial contaminant concentration in groundwater (mg/l)
- λ = decay constant (d⁻¹)
= 0.693/half-life for degradation of contaminant in days (d⁻¹)
- a_x, a_y, a_z = dispersion coefficient in three dimensions (m)
- S_z, S_y = width and thickness of plume at source (in the saturated zone) (m)
- u = rate of contaminant movement (m/d)– See Equ. 6, App 5
- x = distance to compliance point (m)
- z = distance (lateral) to compliance point perpendicular to flow direction (m)
- y = distance (depth) to compliance point perpendicular to flow direction (m)
- erf = error function
- exp = exponential
- erfc = complementary error function
- t = time since contaminant entered groundwater (days)

Table A4.2: Example of an analytical transport model: Domenico Equation (time-variant, declining source)

Calculation of concentration down-gradient of site using the **Domenico equation**.

$$C = 0.125.C_0.\exp(-ks(t - x/u)).\exp\left(\frac{x}{2ax}\left[1 - \sqrt{\left(1 + \frac{4.\lambda.ax}{u}\right)}\right]\right)$$

$$\operatorname{erfc}\left(\frac{1}{2\sqrt{ax.ut}}\left[x - ut\sqrt{\left(1 + \frac{4.\lambda.ax}{u}\right)}\right]\right)\left[\operatorname{erf}\left(\frac{y + S_y/2}{2\sqrt{ay.x}}\right) - \operatorname{erf}\left(\frac{y + S_y/2}{2\sqrt{ay.x}}\right)\right]$$

$$\left[\operatorname{erf}\left(\frac{z + S_z/2}{2\sqrt{az.x}}\right) - \operatorname{erf}\left(\frac{z - S_z/2}{2\sqrt{az.x}}\right)\right]$$

where

- C = concentration of contaminant at point x and time t (mg/l)
 C₀ = initial contaminant concentration in groundwater (mg/l)
 λ = decay constant = 0.693/half-life for decay of contaminant in days (d⁻¹)
 ks = first-order decay term for source of contamination (d⁻¹)
 ax, ay, az = dispersion coefficient in three dimensions (m)
 Sz, Sy = width and thickness of plume at source (in saturated zone) (m)
 Rc = retardation factor – See Table A4.4
 Kd = partition coefficient (l/kg)
 v = rate of groundwater flow (m/d) – See Table A4.4
 u = rate of contaminant movement due to retardation (m/d) – See Table A4.4
 x = distance to compliance point (m)
 erfc = complementary error function
 erf = error function
 exp = exponential
 t = time since contaminant entered groundwater (days)

Table A4.3: Analytical and numerical models with application to MNA studies

Model	Description	Reference or Source
AT123D	Based on analytical solution for transient one, two or three-dimensional transport in a homogeneous isotropic aquifer with uniform regional flow. Allows retardation, dispersion, first-order decay, differing source configurations and boundary conditions.	IGWMC
BIOSCREEN	Based on the Domenico analytical solute transport model, simulates natural attenuation of hydrocarbons. Allows advection, dispersion, adsorption, both aerobic decay and anaerobic reactions.	AFCEE
BIOPLUME II & III	BIOPLUME II is a two-dimensional model for simulating transport of a single dissolved hydrocarbon species under the influence of oxygen-limited biodegradation, first order decay, linear sorption, advection and dispersion. Aquifer may be heterogeneous and anisotropic. BIOPLUME III simulates reactive transport of multiple hydrocarbons and allows reactant-limited biodegradation.	IGWMC BIOPLUME III currently under development by AFCEE
FATE 5	Based on the Domenico analytical solute transport model. Used to determine site-specific natural attenuation rates for organics. Allows calibration of the attenuation rate used by Domenico model to match site-specific data	
BioTrans	Two-dimensional finite element transport model for multiple species under the influence of advection, dispersion, sorption, first-order decay and oxygen-limited biodegradation. Requires flow-velocity data from another source.	Environmental Systems and Technologies, Inc.
ConSim	Simulates aqueous phase contaminant mobilisation and transport using a probabilistic (monte carlo) methodology. It includes an assessment of contaminant attenuation through first order biodegradation and retardation.	Golder Associates (UK) Ltd Environment Agency
MODFLOW/MT3D	MT3D is a transport model that is used in conjunction with any block-centered finite-difference flow model such as MODFLOW. MT3D is a three-dimensional transport model for simulation of advection, dispersion, and chemical reactions of dissolved constituents in groundwater systems. It includes linear or non-linear sorption and first-order irreversible decay or biodegradation.	IGWMC S S Papadopoulos & Associates Inc
SUTRA	Simulates fluid movement and transport of either energy or dissolved substances in a variably saturated system. Solute transport is restricted to a single reacting species and accounts for solute sorption (linear, Freundlich or Langmuir equilibrium isotherm), zero and first-order decay and zero-order production, hydrodynamic dispersion (including corrections for anisotropy) and molecular diffusion.	IGWMC USGS
BIOCHLOR	Based on the Domenico analytical solute transport model, simulates 1D advection, 3D dispersion, linear adsorption and reductive dechlorination assuming anaerobic conditions and first order decay. It assumed a homogeneous isotropic aquifer with uniform regional flow.	Groundwater Services Inc
RT3D	RT3D is based on MT3D and is used for simulating three-dimensional, multi-species, reactive transport in groundwater. RT3D can accommodate multiple sorbed and aqueous phase species with user-defined reaction frameworks. Allows instantaneous biodegradation, kinetically limited reaction, non-equilibrium sorption/desorption, NAPL dissolution, dual porosity, anaerobic and aerobic biodegradation.	Pacific Northwest National Laboratory (Source Code) Waterloo Hydrogeologic; Environmental Simulations

This table is not intended to be comprehensive and other models may be more appropriate in particular situations.

APPENDIX 5

Methods of assessment

Estimation of degradation rates

There are a number of methods for determining rates of natural attenuation or degradation. These include:

- mass balance;
- graphical and regression techniques;
- application of fate and transport models (analytical or numerical), to simulate field observations.

Examples of some of the methods that can be applied are described below. Other techniques are described in References 2 and 34. The main difficulty in determining rates of degradation is differentiating the effects of dispersion, sorption and degradation on contaminant concentrations.

Mass balance techniques

The degradation rate can be estimated from the change in the dissolved mass of contaminant within a plume over time. This technique will typically require a relatively dense monitoring network. The mass of contaminant can be estimated as follows:

$$\text{Dissolved Mass (M)} = C_{av} \times b \times n \times A \quad (1)$$

where

- M = dissolved mass
- C_{av} = average plume concentration
- b = aquifer or plume thickness
- n = porosity
- A = plume area

A more exact calculation is to contour contaminant concentrations and to calculate the area between each contour.

An alternative method is to calculate the mass of contaminant flowing across a series of lines drawn perpendicular (normal) to the flow direction, as follows:

$$\text{Contaminant Flux} = L \times b \times v \times n \times C_{av} \quad (2)$$

where

- C_{av} = average concentration between contaminant contours
- b = aquifer or plume thickness
- L = distance between contaminant contours
- n = porosity
- v = groundwater velocity

The calculation is repeated for different lines drawn perpendicular to the flow direction. This information can be used to compare the change in contaminant flux with time and distance from the source. Reference 2, 21 and 34 gives other examples of mass balance techniques.

Graphical techniques

The change in contaminant concentrations with distance or time will typically be a function of dilution, dispersion, sorption and natural degradation. Evidence for natural attenuation can be obtained by plotting:

1. Contaminant concentrations with distance along the centre line of the plume (preferably as a log-linear plot) for a given time period. This technique is only really applicable to stable or shrinking plumes. Degradation typically occurs as a first-order rate reaction and would be expected to plot as a straight line on a log-linear plot (ASTM 1998), Reference 2.
2. Contaminant concentrations with time for a borehole located within the plume. This method is only applicable to shrinking plumes (ASTM 1998), Reference 2.

The slope of a line fitted through the data point will give the rate of attenuation. This rate will be a function of dispersion, sorption and biodegradation. The degradation rate can be determined by comparing the contaminant concentration along the flow path with a conservative contaminant (non-degraded), referred to as a conservative tracer, as described below.

Conservative tracers

For a tracer to be useful, it will need to be biologically recalcitrant and have similar Henry's Law constant and soil sorption coefficients to the contaminant of interest, or be subject to less retardation than the contaminant(s) of concern. The tracer will also normally be associated with the original contaminant spill. Examples of a conservative tracer include:

- chloride, if released within the original spill;
- trimethylbenzene (TMB) and tetramethylbenzene, which are typically present in fuel mixtures, although under certain conditions these organics can be degraded

The concentration of a contaminant at a point down-gradient of the source can be corrected for the effect of dispersion, dilution and sorption using the following equation:

$$C_B C_{\text{corr}} = C_B \left(\frac{T_A}{T_B} \right) \quad (3)$$

where

$C_B C_{\text{corr}}$ = corrected concentration of contaminant at point B (mg/l)

C_B = measured concentration of contaminant at point B (mg/l)

T_A = measured concentration of tracer at point A (mg/l)

T_B = measured concentration of tracer at point B (mg/l)

However, in this approach the following need to be demonstrated:

- the tracer is recalcitrant;
- the tracer behaviour is otherwise similar to the contaminant.

Procedure

Plot corrected contaminant distribution on a log-linear plot of corrected concentration against down-gradient travel time along the flow path. The degradation rate can be calculated as follows:

$$\lambda = -\frac{1}{t} \ln \frac{C_B}{C_A} \quad (4)$$

where

λ = first order degradation rate (d^{-1})

C_B = tracer corrected contaminant concentration at time t at downgradient point B

C_A = measured contaminant concentration at upgradient point A

t = travel time between points A and B

where

$t = x / u$

x = distance between points A and B

u = retarded solute velocity

This method relies on correcting contaminant concentrations for dilution, dispersion and retardation by reference to a conservative tracer.

Comparison of contaminant ratios

Evidence for natural attenuation and degradation can be obtained by comparing contaminant concentrations or ratios along the flow path (as depicted in Figures A5.1a, b and c). This comparison may be aided by normalising contaminant concentrations. Examples of the type of plots include:

- plot of log normalised concentrations of contaminants with distance (Figure A5.1a)
- plot of contaminant concentrations and breakdown product concentrations with distance (Figure A5.1b)
- plot of the ratio of contaminant concentrations with distance (Figure A5.1c).

Examination of these plots may provide evidence for:

- different rates of contaminant migration due to sorption (for recalcitrant) contaminants by comparison with a conservative tracer such as chloride;
- varying rates of degradation for contaminants with similar sorption characteristics;
- degradation, due to a relative increase in the concentration of breakdown products.

In assessing contaminant ratios, the following should be taking into account:

- the breakdown products may be present in the original contaminant source (for example, *tert*-butyl alcohol (TBA) is a breakdown product of methyl-*tert*-butyl ether (MTBE), but this compound is also often a constituent component in fuel oil);
- the breakdown product may have been introduced by other contaminant incidents;
- the analytical technique/sampling method may not be appropriate to identify the breakdown product;
- the sorption characteristics of the contaminants may not be identical;
- the effect of multiple sources or multiple contaminant releases, for example, if the contaminants have a different history of release.

Figure A5.1 Comparison of contaminant ratios

Figure A5.1a: Comparison of contaminant concentrations

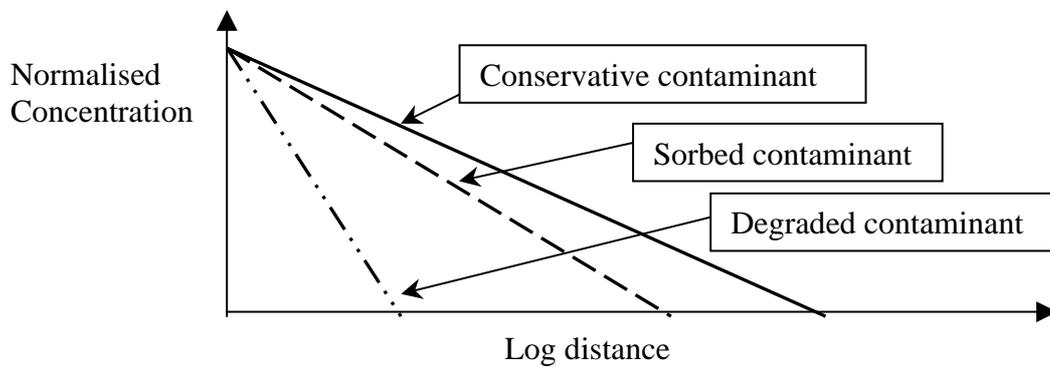


Figure A5.1b: Comparison of breakdown products

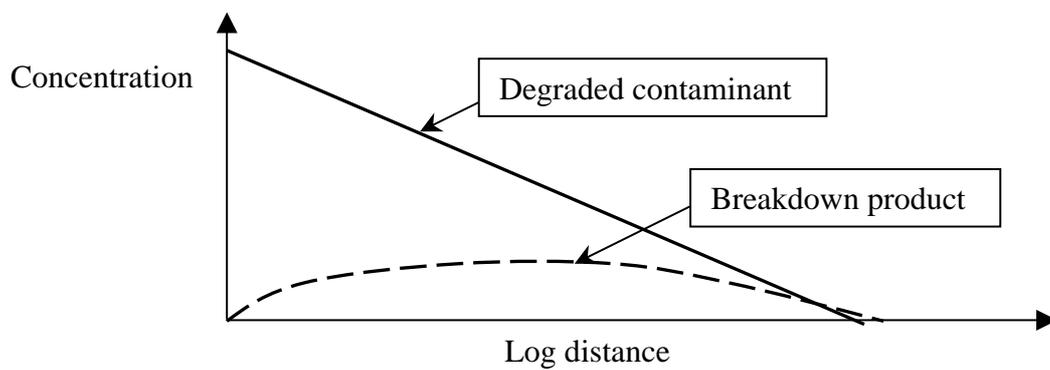
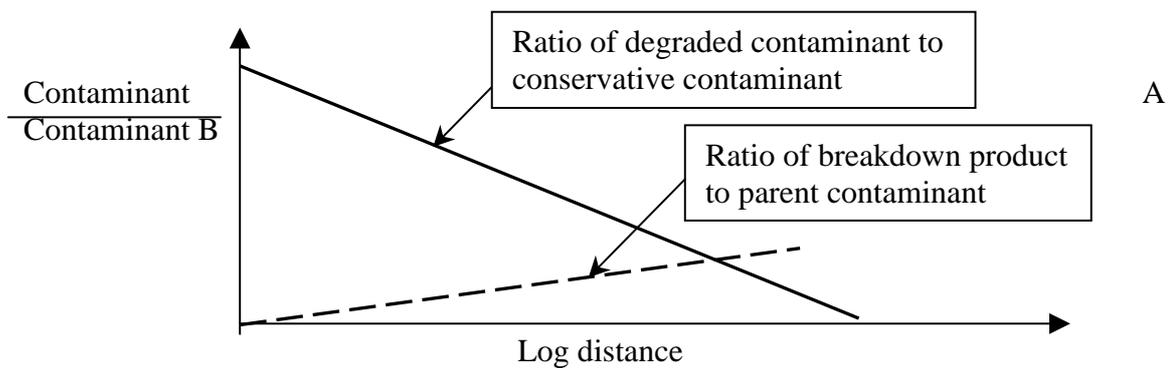


Figure A5.1c: Comparison of contaminant ratios



Determination of degradation rates using fate and transport models

The general use of contaminant fate and transport models is described in Section A5.1. This section describes firstly the application of an analytical transport model to determine degradation rates and, secondly, the use of the Buscheck and Alcantar method to determine degradation rates for stable plumes.

Application of analytical model

Procedure

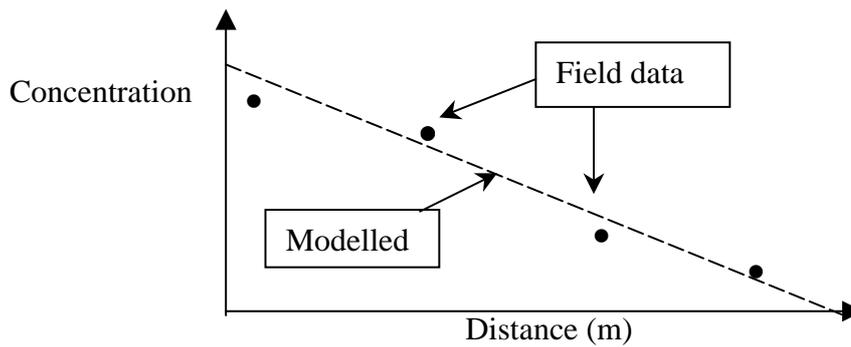
1. Using either a log-linear plot or linear graph, plot contaminant concentration against either time (from start of pollution incident), or distance from contaminant source.
2. Simulate contaminant concentrations with time or distance using fate and transport model, for example the Domenico solution. This will require data values to be assigned for each model parameter (including degradation rate) based on field or literature values.
3. Compare model results with field data (Fig A5.2). Adjust model parameter values to obtain a model fit with the observed data.
4. Assess final model parameter values for reasonableness. For example, if the analysis indicates a degradation rate with a half-life of five days, whilst literature values for similar sites indicate values of 100 to 1000 days are more appropriate, then the assessment should be critically re-evaluated.
5. Undertake sensitivity analyses to determine which parameters have the greatest influence on the model results and assess whether further data are required.

The analysis can be simplified if the model can be calibrated using a conservative contaminant (tracer) to determine values for groundwater velocity and dispersion and/or a recalcitrant contaminant (with the same sorptive properties as the contaminant of concern) to determine the retarded contaminant velocity and dispersion. However, this is reliant on the time and location of the tracer release to be known or coincident with the contaminant release.

The analysis should be reviewed in terms of:

- uncertainty in understanding of the system and in the conceptual model;
- uncertainty in parameter values; some may vary by more than a order of magnitude;
- applicability of the model to the site (including model assumptions);
- use and relevance of literature values to define model parameters;
- whether there is more than one solution, that is, whether different combinations of parameter values can give the same result.

Figure A5.2: Comparison of model prediction with field data



Determination of degradation rate for a steady state plume (Buscheck and Alcantar, 1995)

Procedure

1. Analyse historical data to confirm that the plume is stable (that is, contaminant concentrations are not changing significantly with time).
2. Plot observed contaminant concentrations on a log-linear plot of contaminant concentration versus distance down-gradient of the source.
3. Calculate slope (m) of line fitted through the data points. This could be performed by regression analysis.
4. Substitute values of the slope (m), dispersion coefficient and the retarded contaminant velocity into equation (5) to determine the degradation rate (λ). The value of dispersion coefficient is typically taken as one-tenth of the distance to the x axis intercept. The retarded contaminant velocity can be calculated using equation (6).

$$\lambda = \frac{u}{4 a_x} \left([1 + 2 a_x (m)]^2 - 1 \right) \tag{5}$$

$$u = \frac{K \times i}{n \times R_c} \tag{6}$$

where

- | | |
|-------------------------------------|---------------------------------|
| λ = degradation rate | i = hydraulic gradient |
| m = slope = k/v | n = porosity |
| a_x = dispersion coefficient | K = hydraulic conductivity |
| u = retarded contaminant velocity | R_c = retardation coefficient |

Electron balance calculation

An electron mass balance calculation can be used to give an indication of the capacity of an aquifer to degrade contaminants (its assimilative capacity). The approach relies on the measured changes in groundwater chemistry at a site together with a stoichiometric relationship describing the amount of contaminant degraded through oxidation/ reduction reactions.

The amount of a contaminant, such as benzene, that can be theoretically degraded by a electron accepting process can be estimated from equation 7 as follows:

$$BC = \sum \left(\frac{C_B - C_P}{F} \right) \quad (7)$$

BC = biodegradation capacity (mg/l)

C_B = average background concentration of electron acceptor or metabolic by-product (mg/l)

C_P = lowest measured electron acceptor or metabolic by-product concentration within plume (mg/l)

F = contaminant utilisation factor (mg/mg)

Σ = sum of electron acceptors and metabolic by-products that contribute to degradation

The biodegradation capacity is the amount of contaminant that electron acceptors can assimilate or degrade based on the electron-accepting capacity of the aquifer. This will be a function of:

- groundwater flow below the contaminant source;
- recharge/infiltration over the contaminant source area;

The total biodegradation capacity (TBC) of the system can be estimated as:

$$TBC = 1000 \times Q \times BC$$

Where

TBC = total biodegradation capacity (mg/d)

Q = groundwater flow through plume (m³/d)

BC = biodegradation capacity (mg/l)

This calculation can be used to determine whether the biodegradation capacity of the system is sufficient to have degraded the mass of contaminant. The method can also be used to indicate the relative importance of different electron acceptor/metabolic by products to degradation. **The method should be used only as a qualitative tool in assessing the degradation process, due to uncertainties regarding the cause of the oxidation/reduction reaction.** In some circumstances reducing conditions may be natural and for other sites more than one contaminant may be competing for the electron acceptors.

Examples of electron balance calculations are given in References 34 and 1. A more sophisticated electron balance methodology is described in Reference 35, which shows that dispersion/mixing at the plume margins can be a significant source of electron acceptors.

An example of the oxidation/reduction process is given in Table A5.1 for the degradation of benzene. This table also gives the mass of benzene degraded per unit mass of electron acceptor consumed and metabolic by-product produced.

Table A5.1. Electron acceptors and metabolic by-products involved in the degradation of benzene

Process	Acceptor or metabolic by product	Reaction	Mass of benzene degraded per unit mass of electron acceptor (mg)	Mass of benzene degraded per unit mass of metabolic by-product produced (mg)
Oxidation	Oxygen	$7.5 \text{ O}_2 + \text{C}_6\text{H}_6 \rightarrow 6 \text{ CO}_2 + 3\text{H}_2\text{O}$	0.33	-
Denitrification	Nitrate	$6 \text{ NO}_3 + 6 \text{ H}^+ + \text{C}_6 \text{ H}_6 \rightarrow 6 \text{ CO}_2 + 6 \text{ H}_2\text{O} + 3 \text{ N}_2$	0.21	-
Sulphate reduction	Sulphate	$7.5 \text{ H}^+ + 3.75 \text{ SO}_4^{2-} + \text{C}_6 \text{ H}_6 \rightarrow 6 \text{ CO}_2 + 3.75 \text{ H}_2\text{S} + 3 \text{ H}_2\text{O}$	0.22	-
Manganese reduction	Manganese	$30\text{H}^+ + 15 \text{ Mn O}_2 + \text{C}_6 \text{ H}_6 \rightarrow 6 \text{ CO}_2 + 15 \text{ Mn}^{2+} + 18 \text{ H}_2\text{O}$	0.06	0.09
Iron reduction	Iron	$60\text{H}^+ + 30 \text{ Fe (OH)}_3 + \text{C}_6 \text{ H}_6 \rightarrow 6 \text{ CO}_2 + 30 \text{ Fe}^{2+} + 78 \text{ H}_2\text{O}$	0.024	0.047
Methanogenesis	Methane	$4.5 \text{ H}_2\text{O} + \text{C}_6 \text{ H}_6 \rightarrow 2.25 \text{ CO}_2 + 3.75 \text{ CH}_4$	-	1.3

Similar reactions for toluene, xylene, ethylbenzene and chlorinated solvents are given in References 1 and 34.

Example – Degradation of BTEX

An example of the calculation of the biodegradation capacity for a contaminant plume (with BTEX compounds as the main contaminants of concern) is given in Table A5.2. In this example the measured difference in the concentration of electron acceptors and metabolic by-products would, in theory, be equivalent to the degradation of 13.6mg/l of BTEX. For a groundwater throughput of 100m³/d, then a total of 1.36kg/d of BTEX could be degraded. This amount can be compared with the volume of contaminant lost or the calculated rate of dissolution of BTEX from a NAPL source.

Utilisation factors for the electron acceptors and metabolic by-products that are involved in the degradation of BTEX are given in Table A5.3.

Table A5.2. Example calculation (degradation of BTEX)

Electron acceptor/ metabolic by-product	Up-gradient concentration mg/l	Plume concentration mg/l	Difference mg/l	Biodegradation capacity¹ mg/l
Oxygen	5.2	0.1	5.1	1.6
Nitrate	4.3	0.1	4.2	0.9
Sulphate	34.0	8.0	26	5.5
Manganese	0.01	1.2	1.2	0.2
Iron	0.01	2.4	2.4	0.1
Alkalinity	210	240	30	3.9
Methane	0.01	1.1	1.1	1.4
Biodegradation capacity or quantity of BTEX that could theoretically be degraded				13.6

1. Biodegradation capacity = Difference in concentration of electron acceptors up-hydraulic gradient and within the plume divided by the Utilisation Factor, (see Table 5.3, below)

Table A5.3. Utilisation factors

Electron acceptor/ metabolic by-product	Utilisation Factor¹
Oxygen	3.14
Nitrate	4.87
Sulphate	4.76
Manganese	6.67
Iron	21.8
Alkalinity	7.69
Methane	0.78

1. Mass of BTEX degraded per unit mass of electron acceptor and metabolic by-product produced

APPENDIX 6

Presentation of information supporting NA

The presentation of good data is an important component in setting out the evidence to support natural attenuation. Methods of presentation include tabulation of data, distribution and contour maps, time-series graphs, and cross-sections (Ref 36). The method for presentation is likely to vary from site to site, but the clear illustration of information is critical to the acceptance of natural attenuation. The summary case studies included in Appendix 7 give examples of good data presentation.

Table A6.1 gives guidance on the type of information that will normally be presented, but is not intended to be prescriptive.

Table A6.1. Examples of presentation of data

Information	Presentation method	Purpose
Groundwater levels	Distribution map (contoured)	<ul style="list-style-type: none"> To show direction of groundwater movement. This should be compared with contaminant distribution. Contour maps should be presented for different times to identify whether there are any seasonal or long-term changes in flow direction.
	Hydrographs	<ul style="list-style-type: none"> To illustrate seasonal variation or any long-term change in water level. This should be compared with variations in contaminant concentrations and free product thickness with time.
	Vertical sections (variation in head with depth)	<ul style="list-style-type: none"> To illustrate if vertical hydraulic gradients are present. This should be compared with observed vertical distribution of contaminants (i.e. 3D-plume geometry) and geology.
Contaminant concentrations	Distribution Map (contoured).	<ul style="list-style-type: none"> Relevant plots should be presented for different times to illustrate changes in contaminant concentrations and plume geometry over time. To illustrate plume geometry and whether this is changing with time. To provide primary evidence of plume stability (shrinking, stable, growing).
	Time series plots.	
	Distance concentration graphs.	
	Cross-sections.	
Breakdown products	Distribution Map (contoured).	<ul style="list-style-type: none"> To provide secondary evidence for biodegradation, and that the process has reached or is proceeding to completion. The observation of increasing breakdown product concentrations may indicate that degradation may not be sufficient.
	Time series plots.	
	Distance concentration graphs.	
	Cross-sections.	

Information	Presentation method	Purpose
Electron acceptors/donors including dissolved oxygen, nitrate, iron, manganese, sulphate, methane (as appropriate)	Distribution map (contoured); This information can also be presented using packages such as SEQUENCE™, where contaminant data are presented on multi-axis diagrams. Cross-sections through the plume. Time series plots. Distance-concentration graphs.	<ul style="list-style-type: none"> To provide secondary evidence that biodegradation is occurring. It is important to define conditions uphydraulic gradient of the plume (that is, background conditions). The plots should be compared with contaminant concentrations to determine if these are related to changes in the concentrations of electron acceptors/donors.
Alkalinity, CO ₂ , TOC	Distribution map (contoured). Time series plots. Cross-sections.	<ul style="list-style-type: none"> Increases in Alkalinity or CO₂ concentrations (above background concentrations) provide indirect evidence of microbial activity and degradation.
Free Product	Distribution map (contoured). Time series plots. Cross-section.	<ul style="list-style-type: none"> To illustrate the distribution of free product and whether this is changing with time.
Hydrochemical Indicators such as pH, redox, dissolved oxygen	Distribution map (contoured). Time series plots. Cross-sections.	<ul style="list-style-type: none"> To illustrate the hydrochemical environment, including whether conditions are oxidising or reducing and whether they are changing with time. It is important to define conditions up hydraulic gradient of the plume (i.e. background conditions).

Note. It is assumed that geological maps, geological sections etc will be produced as supporting information to the conceptual model.

Further guidance on the presentation of data is given in References 1, 34, 35 and 36.

APPENDIX 7

Case Studies

Two summary case studies are presented here to highlight the main features of the framework described and experiences encountered in field situations. They are necessarily concise, but it is intended to place more detailed illustrative case studies on the Environment Agency's web site (www.environment-agency.gov.uk) in due course.

Case Study 1

Background

Investigation at a chemical factory identified the presence of contaminated groundwater beneath the site. The main contaminant was phenol, with concentrations in excess of 500mg/l, as illustrated by Figure A7.1. The site is located over the Triassic Sandstone, a Major Aquifer, although the nearest discharge point is a watercourse nearly 2km down hydraulic gradient of the site. The total thickness of the aquifer, as determined from the site investigation, is approximately 40m, and the winter watertable is around 5m below ground level. Groundwater sampling from boreholes around the site provided some evidence of degradation, including low dissolved oxygen concentrations, (<0.5mg/l), and elevated iron (Fe(II)) concentrations, (> 5mg/l) (Figure A7.2). No analyses had been undertaken for other electron acceptors and metabolic by-products, such as nitrate and sulphate. Borehole drilling and monitoring had also been restricted to within the site boundary and as a consequence there was no information on the extent of groundwater contamination down-gradient of the site boundary.

A review of the site history indicated that contamination could have occurred over the 20 years that the site had been operational. In consultation with the Environment Agency, the site operator had implemented a programme of works (including bunding of storage tanks, replacement of pipelines, improvement in site practices, an upgrade of the site drainage system, and source control) to prevent further contamination.

Screening

An initial assessment, using an analytical fate and transport model, was made to determine the possible extent of the plume in the aquifer and to consider if there was any risk to the watercourse. The site investigation had provided information on the hydraulic gradient, the hydraulic conductivity of the aquifer, and the extent and degree of contamination below the site. Information on the porosity of the aquifer was taken from the BGS/Agency Aquifer Properties Manual (Ref 15), and the aquifer dispersivity and rates of contaminant degradation were based on literature values. The input parameters for the risk assessment are summarised in the Table A7.1. The concentration of phenol in groundwater, down hydraulic gradient of the site, was calculated for the range of parameter values given in Table A7.1 and the results summarised in Table A7.2. These calculations indicated that:

1. The contaminant plume should have migrated to a distance of only 100 to 200m beyond the site boundary, assuming degradation was occurring (Figure A7.3).

2. If biodegradation were occurring according to the rates quoted in literature sources, then one might expect the plume to be in steady state. If, however, degradation were occurring at a slower rate, then further expansion of the plume would be expected with a potential risk for contamination of the watercourse.
3. The average rate of groundwater flow in the Triassic Sandstone aquifer at the site is relatively slow, about 5 to 10m/year (this ignores dispersion).

Table A7.1: Parameter values used in the initial (screening) modelling

Parameter	Range of Values	Source
Hydraulic conductivity	0.5 to 1 m/d	Field measurement
Hydraulic gradient	0.004	Groundwater level measurement
Effective porosity	0.12 to 0.15	Aquifer Properties Manual
Fraction of organic carbon	0.001 to 0.002	Laboratory measurement of sandstone cores
Organic carbon coefficient	27 l/kg	Literature value
Aquifer depth	40m	Site investigation boreholes
Width of source	60m	Observed contaminant distribution
Source concentration	550 mg/l	Maximum observed concentration
Degradation rate	0.02 to 0.07 d ⁻¹	Literature value
Longitudinal, lateral and vertical dispersivity	20 m, 0.2 m, 0.02 m	Literature value, assuming 0.1, 0.001 and 0.0001 times distance to watercourse respectively

Table A7.2 Predicted phenol concentrations

Scenario	Phenol concentration (mg/l)		
	50m from source	100m from source	200m from source
No degradation	290 - 490	86 - 380	5 - 130
Degradation rate: 0.07d^{-1}	0.05 - 35	<0.001 - 0.2	<0.001
Degradation rate: 0.02d^{-1}	<0.001 - 0.02	<0.001	<0.001

The range of values is a function of hydraulic conductivity, effective porosity and fraction of organic carbon as given in Table A7.1

In view of the initial field evidence of natural attenuation and the slow rate of groundwater movement, and following consultation with the Environment Agency, further investigation of the plume was considered warranted. The aim of further works was to define the extent of the plume, and to provide information to determine if MNA would be a feasible remedial measure. Additionally, the investigation was designed to provide the necessary information to assist in the design of alternative remediation measures, such as a pump and treat scheme.

Assessment

The investigation comprised drilling nine off-site boreholes, and monitoring groundwater quality over a two-year period, including measuring electron acceptors and metabolic by-products (DO, NO_3 , SO_4 , Fe(II)). The conceptual and contaminant transport models were also refined using information provided by the investigation.

The observed distribution of phenols in groundwater at the end of the two-year monitoring period is shown in Figure A7.4. This figure indicates that the front of the plume is some 150m from the site boundary. Analyses for electron acceptors showed evidence of reduced nitrate and sulphate concentrations.

However, despite the evidence that degradation was occurring, the observed extent of groundwater contamination is inconsistent with that predicted using literature values, which suggested a slower or inhibited rate of biodegradation. An approximate degradation rate was calculated using the Buscheck and Alcantar method (assuming a stable plume). This calculation indicated a degradation rate of the order of 0.005d^{-1} . Model predictions using this degradation rate indicated that the plume would migrate a further 100 to 200m through the aquifer, but would still be unlikely to affect the watercourse.

Summary

Although the investigation had provided indirect evidence for degradation (depleted oxygen, nitrate and sulphate concentrations and elevated iron concentrations), the observed extent of the plume, together with the contaminant transport simulation, have shown that natural attenuation is not occurring at a sufficient rate to prevent continued expansion of the plume into uncontaminated groundwater. It was therefore concluded that monitored natural attenuation, alone, would not be an effective remedial option at this site. The decision, following consultation with the Environment Agency, was to implement a pump and treat scheme to minimise any further expansion of the plume (by hydraulic control) and to reduce contaminant concentrations. Monitoring would continue to determine if monitored natural attenuation might be a viable option once the highest contaminant concentrations have been reduced by pumping.

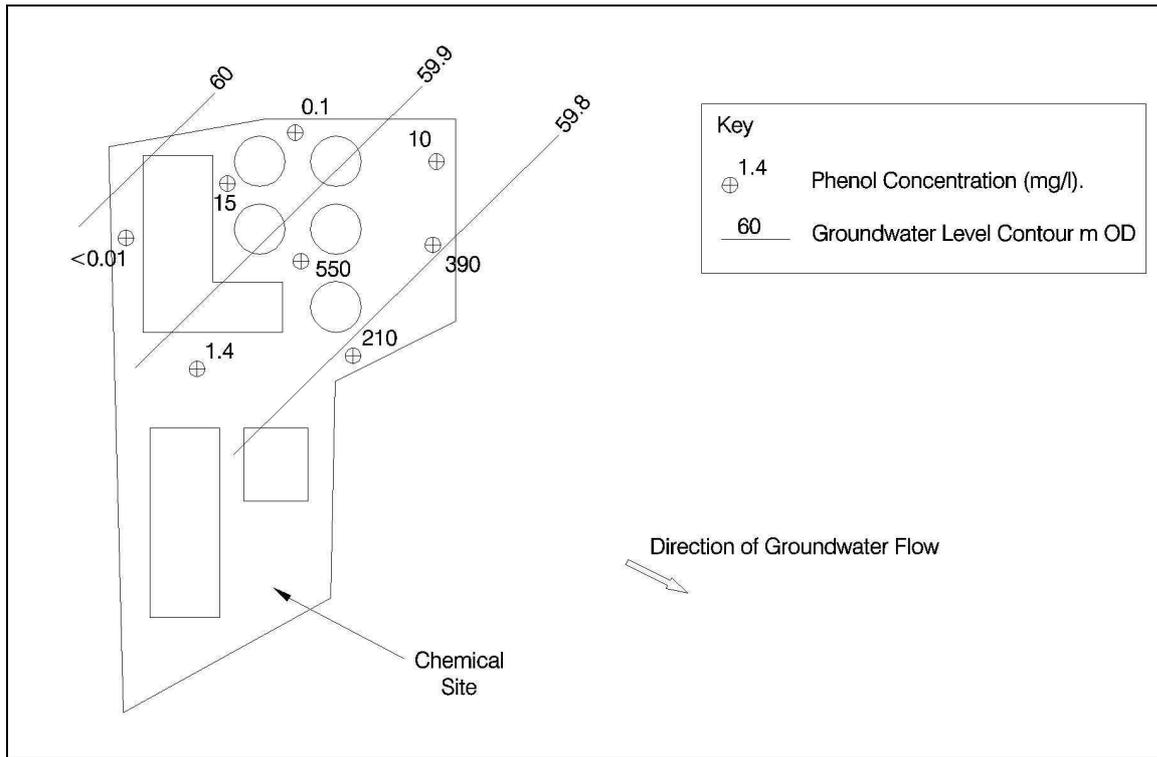


Figure A7.1 Observed Phenol Concentrations in Groundwater

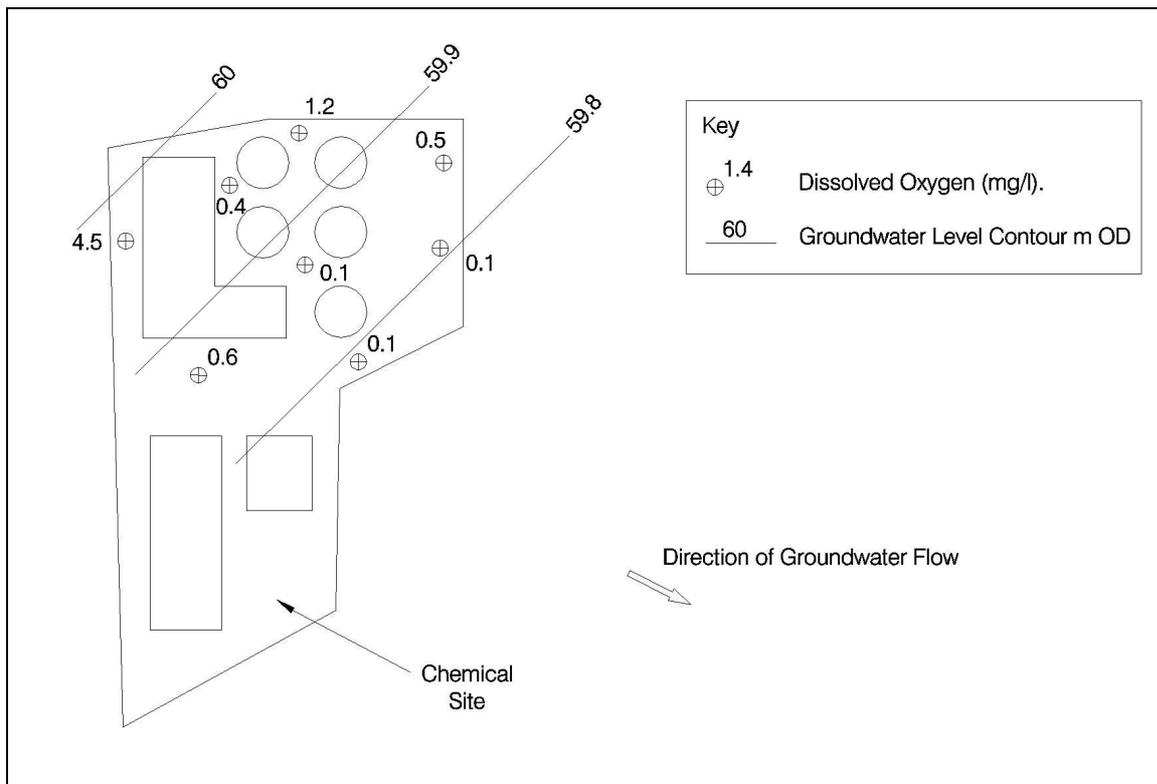


Figure A7.2 Observed Dissolved Oxygen Concentrations in Groundwater

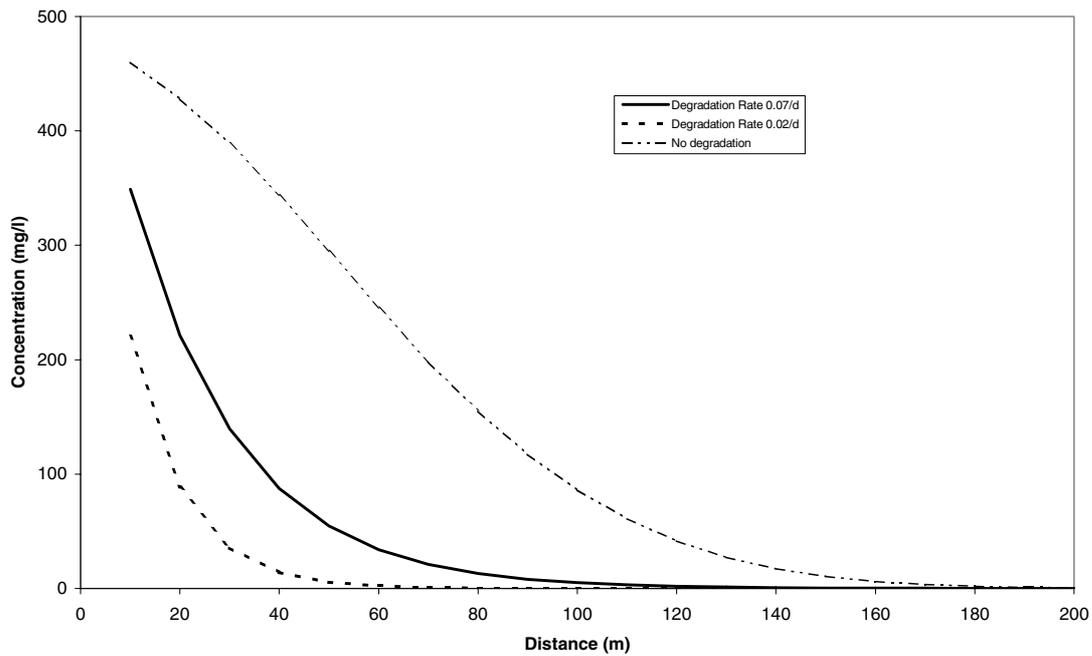


Figure A7.3: Predicted Phenol Concentrations Down-gradient of the Site

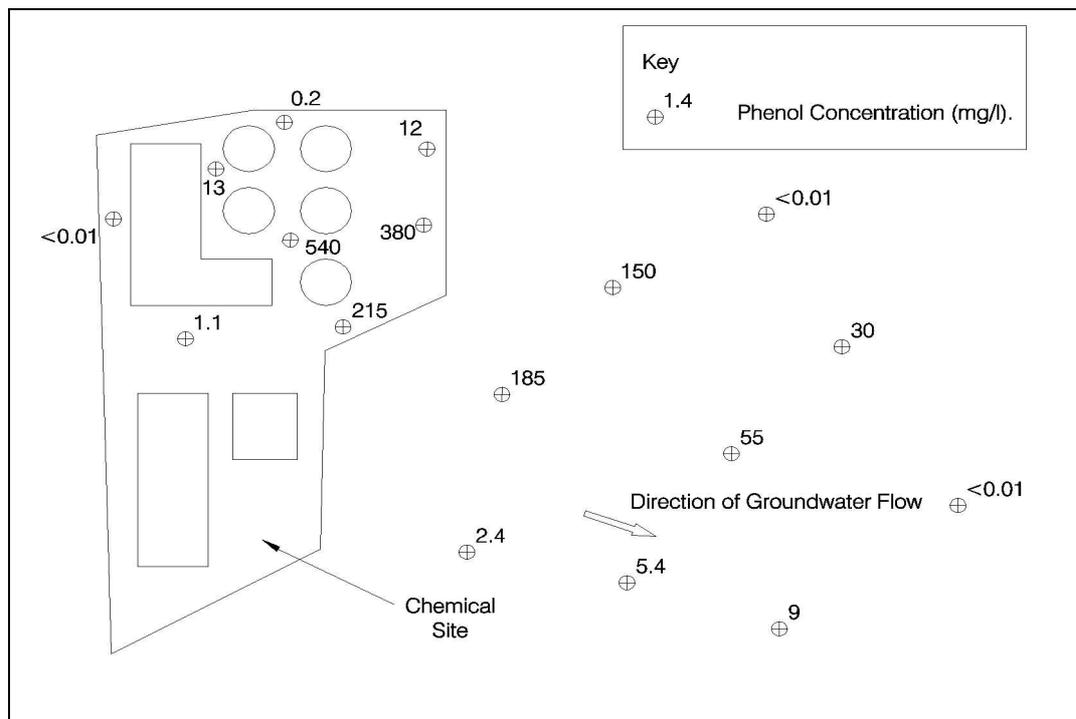


Figure A7.4: Observed Phenol Concentrations in Groundwater

Case Study 2

Background

The site comprises a decommissioned fuel storage and distribution terminal with an area of approximately 5 hectares. It is bounded to the north by residential property, to the east and south by roads and a small industrial estate, and to the west and south-west by open farm land. Figure A7.5 shows the site layout and setting. The site is relatively flat with an elevation of about 73m AOD. No watercourses exist within the site boundary, the nearest being some 500m to the south.

The terminal was constructed in 1958 and closed in 1991. It handled predominantly lighter oils including petrol, diesel and heating oil (white oils) but also provided some storage for heavier oils (black oils). It was a major regional distribution point with a throughput over 100 million litres per year. Product was delivered by rail and distributed by road tanker. During the 1960s additives and octane boosters for premium petrol were handled and blended at the terminal. These additives were stored in two horizontal tanks close to the centre of the white oils tank farm. An accidental release of the additive 'benzole' occurred in the late 1960's. Benzole is essentially a blend of toluene and benzene. The site assessment undertaken upon terminal closure revealed the presence of benzole in soils and groundwater. The remedial approach for the terminal site was agreed with the Environment Agency and involved removal of contaminated soils combined with MNA for dissolved phase hydrocarbons in the groundwater.

Site Conditions

Intrusive site assessment began in 1992 with three further phases of investigation being conducted up to 1995. The objective of these latter investigations was the delineation of the plume and to provide information on the structure of the plume to refine the conceptual model for the site.

The investigations proved the presence of the Gault Clay over about 18m of the Whitchurch Sand formation in the west of the site. Over the eastern part of the site the Gault Clay is absent due to a combination of natural thinning and grading plus levelling for the initial development.

The Whitchurch Sand, which is classed as a Minor Aquifer by the Agency, comprises a multi-layered aquifer system. The upper 3-4m is a red brown colour with strongly cemented horizons which are over a metre thick beneath the northern part of the site. The lower 12-14m of the sands are grey-green in colour indicating a more reduced oxidation state. The sands are fine-medium grained with some thin clays and occasional small well rounded pebbles. The sands are underlain by the Purbeck beds, the thickness of which has not been proven. The geology of the site is illustrated in Figure A7.6.

The groundwater across the site is generally encountered 2.75m to 3.5m below ground level, with a seasonal fluctuation of less than 0.3m. Groundwater flows in a south-westerly direction with the gradient varying across the site from 0.003 m/m to 0.009 m/m. The steeper gradient appears to represent a lower permeability band in the vicinity of BH-2 on the site southern edge (Figure A7.7). Limited tests indicate that the hydraulic conductivity of the Whitchurch Sands aquifer ranges from 7-14m/day.

Twenty groundwater investigation boreholes were installed during the phased investigation to delineate the horizontal extent and concentration variation of the plume. Some of these were dual installations giving separate well screens in the upper (2-7m) and lower (8-14m) parts of the aquifer. They identified that the highest concentrations occurred initially through the upper and lower parts of the aquifer on the site, while off-site the contamination was restricted to the deeper part of the aquifer (Figure A7.6).

The site assessment findings were incorporated into a quantitative health assessment and used to develop remedial targets suitable for future residential redevelopment. These remedial targets were based on BTEXs, hydrocarbon chain groups and metals (lead and arsenic). No active groundwater remediation was undertaken. However, in line with the MNA approach groundwater monitoring continued at no less than 6 monthly intervals.

Screening

The likely success of the MNA approach to reach the groundwater remedial targets was discussed with the Agency during 1995 and early 1996. Although this did not constitute a formal screening approach as set out in this report, it served the same purpose. The screening allowed the groundwater plume to be set in context with reported MNA case studies, primarily from the USA. The discussions with the EA concluded that the application of MNA had a high chance of success at this site, with the situation to be reviewed after a further 18 months of data collection. It was agreed to follow a tiered lines of evidence approach as set out here and elsewhere (Reference 2). The initial conditions were that the soil source zone had been removed and that the groundwater plume was stable or shrinking, and did not pose unacceptable risks to off-site receptors. The primary lines of evidence, addressed the overall plume behaviour and aerobic processes. Secondary lines of evidence were sought to provide geochemical and biochemical evidence to support the confidence in the effectiveness of natural attenuation processes.

It was agreed to monitor at 6 monthly intervals to develop an understanding of the physical behaviour of the plume and groundwater geochemistry. However, to improve the level of knowledge and help future application of MNA it was also agreed to measure a greater number of the potential electron acceptors and to collect data to increase understanding of the biology.

Field Measurements

High quality sampling and analysis of the groundwater using consistent techniques on the site was fundamental in enabling the identification of degradation trends. The early investigations were undertaken by a range of environmental consultants who used different sampling protocols and analytical laboratories. As a consequence the groundwater data from the early investigations were not consistent with the later data. Given the volatile nature of the contaminants, stringent groundwater sampling protocols were followed so that any temporal changes in concentration could be confidently assessed. The field sampling methodology adopted utilised a low flow peristaltic pump with dedicated sampling tubes for each well. Wells were purged of at least three water volumes. The pH, temperature and conductivity were measured during purging to ensure that groundwater conditions had stabilised. Then volatile samples were taken directly from the pump, sealed, labelled and stored at approximately 4°C for transport to the laboratory. As a minimum, one blind duplicate was taken to allow an assessment of the laboratory analytical variability. The analysis of the duplicates indicated a potential laboratory variation of up to 10% between samples.

Field measurements also included dissolved oxygen and redox. Field measurements of oxygen levels were found to be less than 5mg/l and generally less than 1 mg/l (i.e. anaerobic conditions) and, therefore, were not considered to be sufficiently precise for detailed analysis.

Microbiological Assays

During the November 1997 sampling programme, samples of groundwater from all 20 boreholes were analysed for the presence of sulphate-reducing bacteria (SRB) and anaerobic heterotrophic bacteria (AHB).

Detection and enumeration of SRB was carried out using two methods. A commercially available immunoassay test kit was used to quantify the presence of an enzyme (adenosine -5-phosphosulphate reductase) which is present in all sulphate-reducing bacteria. In addition, samples were inoculated into growth medium (Reference 37) which was designed to support the growth of SRB. Population densities were estimated by extinction dilution in a ten-fold dilution series.

Incubation of both inoculated media was carried out at 25°C, in the dark. After 28 days, growth of SRB was assessed by precipitation of iron sulphide and growth of GHB was assessed by increased turbidity.

Lines of Evidence

The assessment of benzene degradation within the aquifer was undertaken using primary and secondary lines of evidence. One primary and two corroborating secondary lines of evidence were judged sufficient to demonstrate MNA.

Primary Lines of Evidence

The primary line of evidence for the occurrence of natural attenuation at the site was the dimensions and behaviour of the plume. Based on the anecdotal information, the release occurred some 25 years previously and given the hydraulic conductivity the plume would be expected to have migrated between 750 and 1,500m from the source area. However, based on the field observations, the leading edge of the plume had only migrated 150m. In addition, the plume showed a number of distinct features, in particular the down-gradient section was restricted to the deeper part of the aquifer. These features were interpreted to show that the down-gradient migration of the plume was being attenuated and that the features observed represent a plume being actively degraded with the plume front being pushed up gradient and downwards to the base of the aquifer as fresh infiltration over the field area enters the aquifer.

Sampling confirmed the changing shape of the plume and decreased overall size during the period of monitoring, as shown in Figure A7.8. This shows a number of key features. Firstly the up-gradient section of the plume moved steadily down-gradient past the remediated source area, while the down-gradient boundary “moved” very slowly up-gradient. There was a slight lateral spreading of the plume, parallel to the low hydraulic conductivity area in the aquifer, before the whole plume decreased to below the remedial target concentration. The apparent concentration increase observed at the centre of the plume is interpreted to be due to a high concentration core in the plume reaching one of the monitoring wells, as shown in Figure A7.9.

(a) Biodegradation rate: Benzene

The maximum concentration of benzene observed (74 mg l^{-1}) is substantially higher than concentrations reported in other aquifers where biodegradation has been reported, for example $<6 \text{ mg l}^{-1}$ (Reference 38) and is likely to be inhibitory for some bacteria. Verschueren (Reference 39), for example, gives 92 mg l^{-1} as the inhibitory concentration of benzene on the growth of *Pseudomonas putida*. In a laboratory study, however, Lovley et al. (Reference 40), demonstrated benzene biodegradation at the expense of sulphate at starting concentrations of approximately 150 mg l^{-1} .

In the plume core, a first order biodegradation rate constant of 0.005 day^{-1} was calculated (Figure A7.10). Similar plots from other boreholes on the periphery of the plume resulted in lower rate constants, with a minimum value of 0.002 day^{-1} . These rates are somewhat lower than the range for benzene ($0.025 - 0.028 \text{ day}^{-1}$) observed by Wiedemeier et al. (Reference 38) at concentrations $<6 \text{ mg l}^{-1}$ and reported by Suarez and Rifai (Reference 41). The rate constants calculated at this site are close to the mean values reported for similar (anaerobic) conditions elsewhere.

(b) Biodegradation rate: Toluene

Knowledge of the benzene contaminant suggested that it originally comprised predominantly toluene with some benzene. Even at the outset of the monitoring programme, the toluene component was only 1% of the total BTEX fraction that, in addition, contained only benzene. This apparent preferential loss of toluene could be explained by the sequential biodegradation of toluene prior to benzene frequently observed in contaminated aquifers under anaerobic conditions (Reference 42). If indeed substantial anaerobic biodegradation of toluene had taken

place before the start of the monitoring programme, there must have been a corresponding consumption of electron acceptor.

Secondary Lines of Evidence

The secondary lines of evidence of natural attenuation were based around the available electron acceptors in the aquifer.

Neglecting results from April 1998, the highest concentrations of potential electron acceptors detected in groundwater samples are shown in Table A7.3. Clearly, sulphate is potentially the most significant electron acceptor for benzene oxidation. The difference between the maximum and minimum concentrations of electron acceptors was used to predict the maximum concentration of benzene that could be oxidised. As shown in Table A7.3, this predicted concentration does not account for oxidation of the maximum concentration of benzene (74 mg l⁻¹) observed from borehole 2-D. This pessimistic prediction argues for a periodic re-charge of electron acceptor in order to account for the observed loss of benzene. Interestingly, analytical results from April 1998 (Table A7.4) showed a dramatic increase in sulphate concentration, up to 610 mg l⁻¹ . The source of sulphate replenishment is presently unresolved.

Low concentrations of methane, up to 0.75 mg l⁻¹ , were observed but since this would account for a loss of less than 1 mg l⁻¹ benzene, methanogenesis was discounted as a significant sink for benzene. Assuming that the observed methane was of recent origin, however, implies that environmental conditions in some zones of the aquifer were sufficiently reducing to allow sulphate-reduction to proceed.

Neglecting results from April 1998, there is a significant negative correlation between benzene concentration and sulphate concentration, as shown in Figure A7.11. These results are interpreted to mean that sulphate is consumed as an electron acceptor in the biodegradation of benzene.

While the main secondary line of evidence was provided by sulphate depletion there are others that relate to different electron acceptors. Iron concentration was inversely proportional to benzene concentration. This is linked to sulphate reduction as the hydrogen sulphide generated reacts with iron in solution to yield iron sulphide precipitate. The aquifer pH was relatively constant in the range 6.5 to 7.1 with no obvious trend with benzene concentration. No other electron acceptors showed a good correlation with benzene concentration. Dissolved oxygen concentration did not show a strong correlation with depth or with benzene concentration. This is due to naturally low oxygen levels in the aquifers, typically <5 mg l⁻¹

Tertiary Lines of Evidence

Detection and Enumeration of SRB

The results of the immunoassay gave a reaction which was above the detection limit of 10^3 SRB ml^{-1} for four of the groundwater samples, as shown in Table A7.5. This is taken as evidence for the potential of bacterial sulphate-reduction to take place in at least some of the groundwater samples.

The fact that 75% of the groundwater samples tested contained viable SRB is further evidence for the possibility of sulphate-reduction taking place in anaerobic regions of the aquifer. With the exception of boreholes 12 and Q, the population densities of SRB recovered in the viable assay (Table A7.5) are consistent with the results of the immunoassay, for the samples where the immunoassay returned levels of $<10^3$ ml^{-1} . The viable counts were lower or the same in samples where $>10^3$ ml^{-1} were predicted by the immunoassay. In general, viable counts are expected to be lower than other methods of estimation since only bacteria which are able to compete successfully for nutrients under the environmental constraints of the selected growth medium and temperature etc., give rise to a positive score. The maximum population densities of SRB and GHB were greater than the highest population density of anaerobes observed by Hiebert et al. in a Texan aquifer where benzene was biodegraded (Reference 43).

By assuming a specific rate of sulphate reduction of 10^{-14} mole per bacterium per day (Reference 44), it follows that the maximum population density of 10^4 SRB ml^{-1} shown in Table A7.5 would be capable of reducing 0.0096 μg sulphate $\text{ml}^{-1} \text{day}^{-1}$. Assuming that all of the sulphate reduction was coupled to the oxidation of benzene, this would account for the complete oxidation of 0.002 μg benzene $\text{ml}^{-1} \text{day}^{-1}$, or 2 μg benzene $\text{litre}^{-1} \text{day}^{-1}$. This is somewhat lower than the average rate of benzene depletion of 78 μg benzene $\text{litre}^{-1} \text{day}^{-1}$ observed at borehole 2-D. The microbiological analysis, however, was only conducted on bulk water phase samples and it is expected that a significant proportion of the SRB population exist as sessile organisms colonising the pore surfaces of the aquifer.

Discussion

MNA of benzene has been successfully demonstrated at this site. There are strong primary lines of evidence for this from the plume physical behaviour and the observed rate of degradation. Migration distances were typically an order of magnitude less than those estimated from the aquifer hydraulic properties and time. Additionally, the mode of plume shrinkage was compatible with the groundwater movement and geochemistry. The plume front receded little with the majority of degradation occurring on the upstream side where groundwater supplies fresh nutrient and electron acceptors. The first order biodegradation rate constants for benzene were calculated in the range 0.005 day^{-1} to 0.002 day^{-1} for the plume centre and edge, respectively. These are in good agreement to the mean values reported by others for benzene degradation at the expense of sulphate. The secondary lines of evidence provided an understanding of the groundwater chemistry for the anaerobic degradation of benzene. Sulphate reduction was the main process with strong chemical and microbiological evidence to support this. Hence both primary and secondary lines of evidence support the MNA approach for benzene at this site.

Consistency of sampling and analysis is important when undertaking MNA since true trends only become apparent over fairly long timescales, typically 2 to 3 years. However, experience

from this and other sites indicates that despite much attention to detail in the implementation of sampling and analysis protocols, including personnel continuity, there is an inherent variability associated with field sampling natural systems.

The screening stage allows an issue to be put in context with past experience and can be used as an early indicator of likely success. Hence it is important to consider the factors upon which judgement can be based. In this instance the benzene and sulphate concentrations in the groundwater are two factors which could be used to establish an 'operating window' within which MNA has a good chance of being successful. There is evidence that under anaerobic conditions the benzene biodegradation rate is dependent upon its concentration and availability of sulphate. There appears an upper threshold of benzene concentration in the range of 100 - 150 mg l⁻¹ above which degradation is inhibited. Below that threshold, dependent upon the available sulphate concentration and other environmental conditions, biodegradation of benzene will occur .

Conclusions

- (1) MNA of benzene has been successfully demonstrated. Application of a tiered, lines of evidence approach provides a useful framework for judgement.
- (2) First order rate constants for benzene biodegradation (0.002 - 0.005 day⁻¹) are of a similar order to mean values reported for benzene biodegradation at the expense of sulphate reported elsewhere.
- (3) Maximum concentration of benzene (74 mg l⁻¹) was considerably higher than values frequently reported in biodegradation studies in aquifers but is within the range of concentrations for which biodegradation at the expense of sulphate has been observed in laboratory studies.
- (4) There is statistically significant evidence for the depletion of sulphate concentrations in groundwater samples with the highest concentration of benzene. This is consistent with the use of sulphate as an electron acceptor for benzene oxidation.
- (5) The greatest depletion of sulphate observed would account for the oxidation of up to 44 mg/l benzene by sulphate-reducing bacteria.
- (6) Evidence for the participation of sulphate reduction as a pathway for the biodegradation of aromatic compounds in the aquifer was provided by the presence of viable SRB and an immunoassay providing positive indications of the presence of a key enzyme of sulphate-reducing bacteria in groundwater samples.

Table A7.3 Potential Electron Acceptors - Prior to April 1998

	Maximum Concentration (mg/l)	Minimum Concentration (mg/l)	Potential Benzene Oxidation (mg/l)	Predicted Benzene Oxidation (mg/l)
Oxygen	5.4	0	1.7	1.7
Nitrate	9.2	0.01	1.9	1.9
Sulphate	220	7	46.2	44.7
Manganese	1	0.01	0.1	0.1
Iron	22.4	0.01	0.5	0.5
		<i>Total</i>	<i>50.5</i>	<i>49.0</i>

Table A7.4 Potential Electron Acceptors - April 1998

	Maximum Concentration (mg/l)	Minimum Concentration (mg/l)	Potential Benzene Oxidation (mg/l)	Implied Benzene Oxidation (mg/l)
Oxygen	5.4	0	1.7	1.7
Nitrate	9.2	0.01	1.9	1.9
Sulphate	610	7	128.1	126.6
Manganese	1	0.01	0.1	0.1
Iron	22.4	0.01	0.5	0.5
		<i>Total</i>	<i>132.4</i>	<i>130.9</i>

Table A7.5 Results of Microbiological Assays

Borehole	RapidChek®II Immunoassay (SRB ml ⁻¹)	Viable Count SRB (bacteria ml ⁻¹)	Viable Count GHB (bacteria ml ⁻¹)
1-D	bdl	<10	<10
1-S	10 ⁴	<10	10 ²
2-D	bdl	10	10 ²
2-S	bdl	10	10 ³
3-D	bdl	10 ²	10 ⁴
3-S	bdl	<10	10 ³
4	bdl	10	10 ²
5	bdl	<10	10 ³
6	10 ³	10 ²	10 ²
7	nt	nt	nt
8	bdl	nt	nt
9	nt	nt	nt
10	10 ³	10 ³	10 ⁴
11	bdl	nt	nt
12	bdl	10 ³	10 ³
F-D	10 ³	10 ²	10 ³
F-S	bdl	10 ²	10 ³
K	bdl	10	10 ³
Q	bdl	10 ⁴	10 ⁵
S	bdl	10 ²	10 ⁴

nt = not tested, bdl = below detection limit (10³ SRB ml⁻¹), detection limit for viable counts = 10 bacteria ml⁻¹

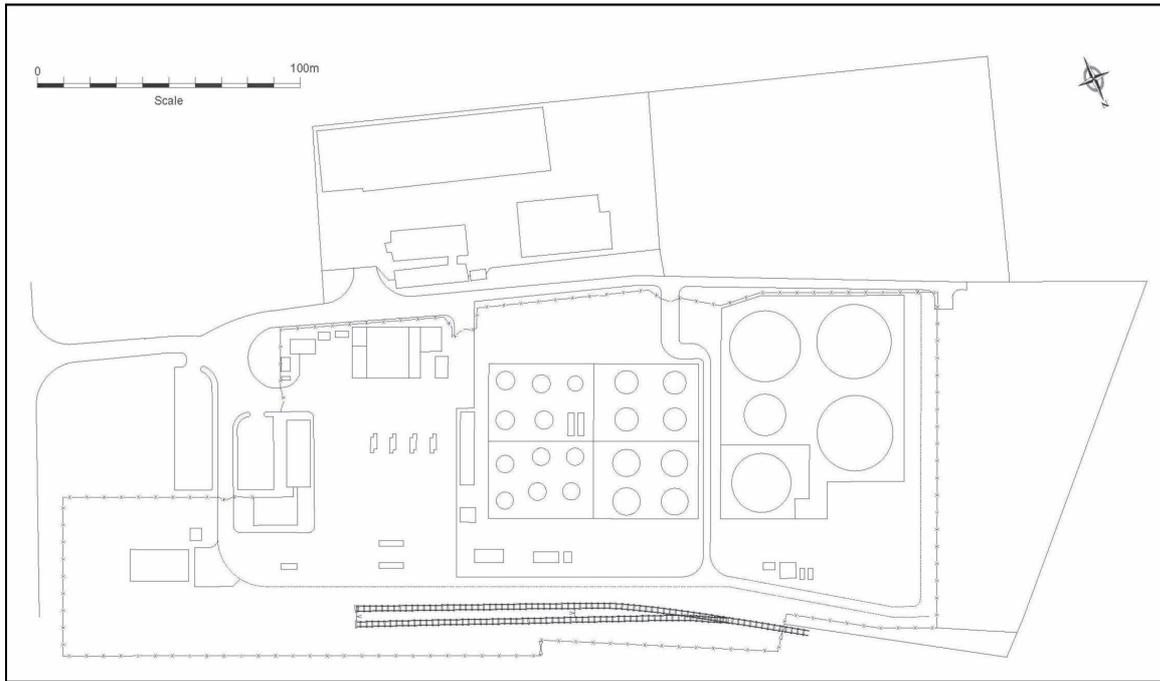


Figure A7.5 Site Layout and Setting

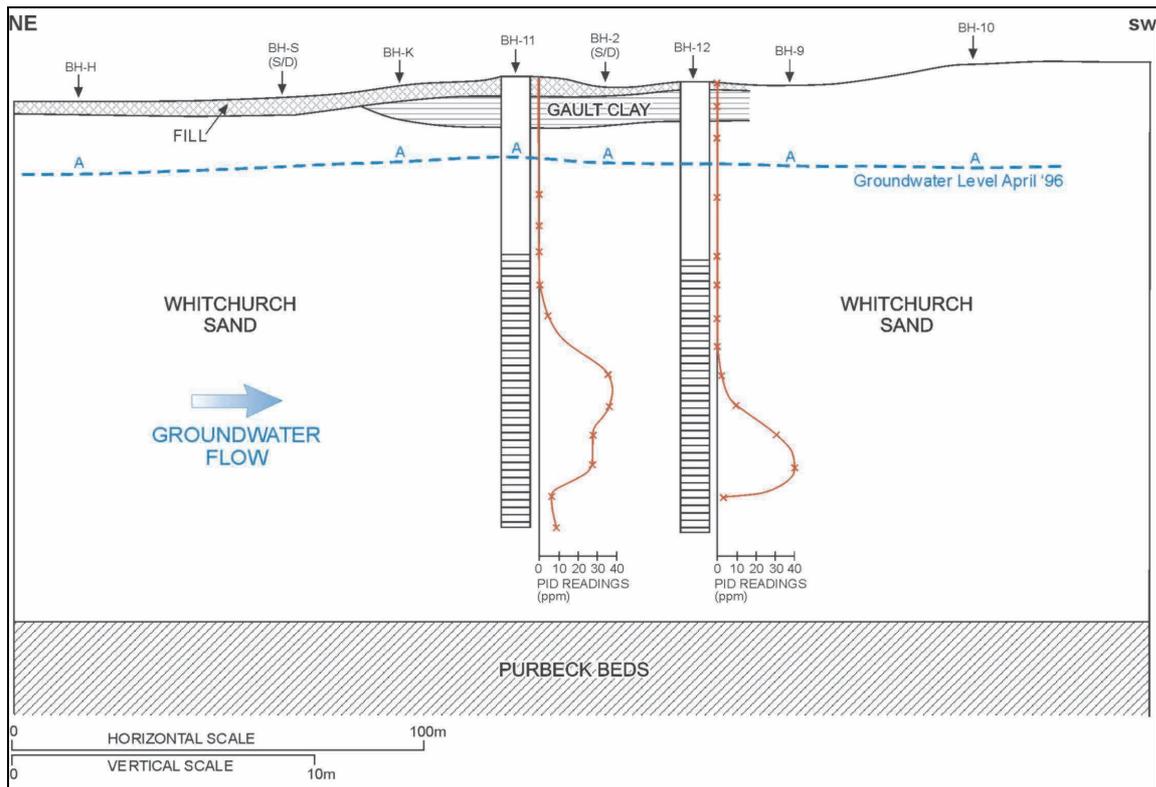


Figure A7.6

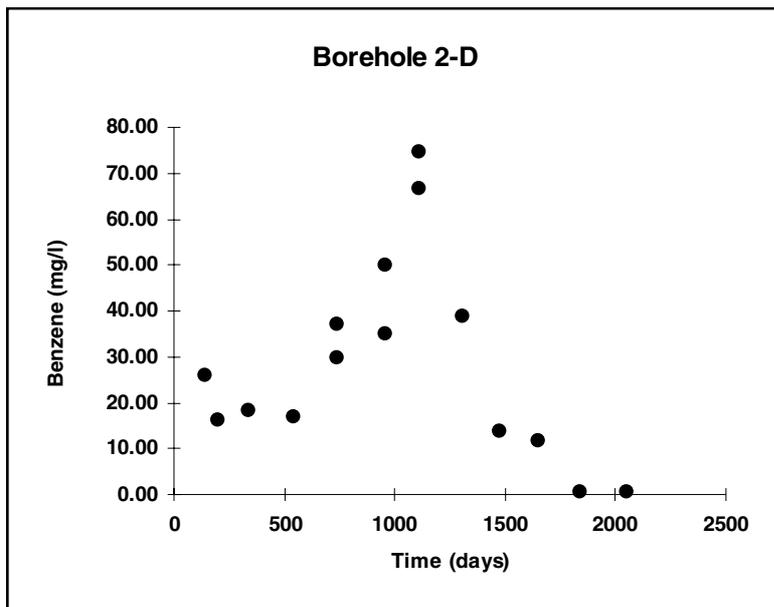


Figure A7.9 Change in concentration of benzene in borehole 2-D. Interpreted as concentrated core of plume reaching, then passing downstream of borehole, with biodegradation.

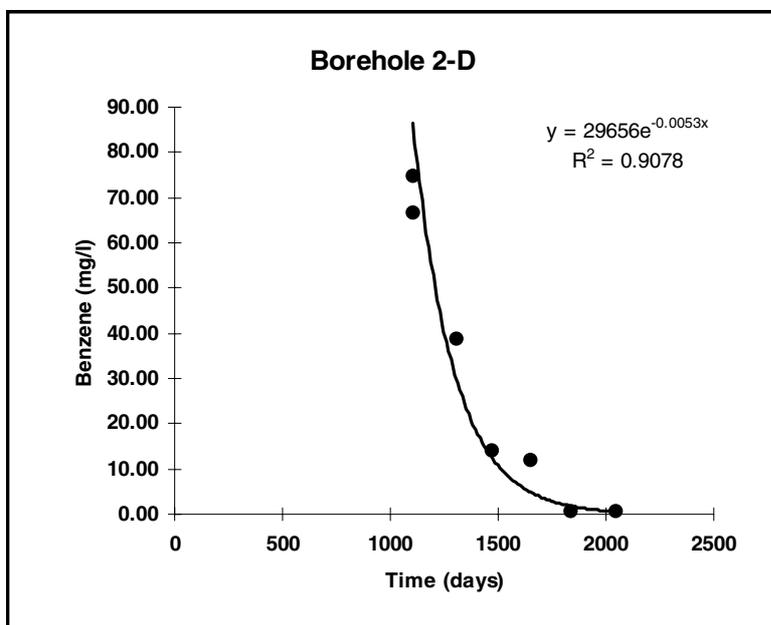


Figure A7.10 First order decay of benzene in borehole 2-D. Degradation rate constant 0.005 day^{-1} , half life 131 days, $n=7$, $r= 0.95$, $p<0.001$

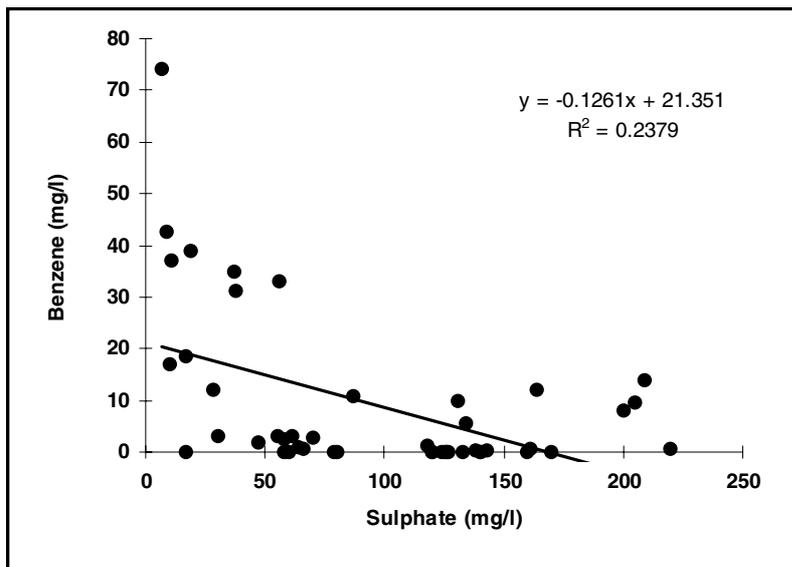


Figure A7.11 Negative correlation between sulphate and benzene concentrations, n=45, r= 0.488, p< 0.001.