GUIDELINES FOR THE ACCEPTANCE OF MONITORED NATURAL ATTENUATION PROCESSES IN SOUTH AFRICA

Report to the Water Research Commission

by

B.H. Usher, J.A. Pretorius and R.A. Gebrekristos

Institute for Groundwater Studies
University of the Free State
Bloemfontein 9300

Report to the Water Research Commission

Project Leader: B.H. Usher

WRC 1501/4/08
ISBN 978-1-77005-666-4
Set 978-1-77005-657-2

January 2008

The publication of this report emanates from a project entitled**:** *Field investigations to study the fate and transport of dense non-aqueous phase liquids (DNAPLs) in groundwater* (WRC Project No K5/1501)

Guidelines for the acceptance of Monitored Natural Attenuation processes in South Africa

Monitored Natural Attenuation (MNA) has been discussed as a promising, cost-effective additional or alternative remediation option for DNAPL plumes. Though these economic considerations argue for MNA and the regulatory acceptance of MNA in general is increasing, MNA with respect to DNAPLs and especially chlorinated solvents (Grandel & Dahmke, 2004) is still a controversial topic. Despite the fact that knowledge about their degradation pathways has improved, large plume dimensions and complex degradation mechanisms complicate demonstration of MNA in the field. However, independent of the remediation technology chosen, site investigation and remediation of most DNAPLs will, in general, be hampered by the difficulty of locating source and/or DNAPL and by characterising long plumes in heterogeneous aquifers. Natural attenuation is not expected to remediate the NAPL phase and therefore MNA is often applied together with source remediation actions.

In South Africa there is very little proven expertise regarding the remedial techniques currently employed in the US and Europe at DNAPL sites. One of the aims of this project is to evaluate MNA as an acceptable remediation option at DNAPL sites under typical South African aquifer conditions.

The following aspects are dealt with in this report:

- To give an overview of the physical, chemical and biological processes involved during MNA
- To provide an overview of international methodologies in dealing with the regulation of MNA
- To provide an overview of existing legislative frameworks within South Africa where MNA can be incorporated
- To evaluate acceptable protocols and standards for regulation
- To recommend practically implementable protocols in a local context.

Based on the above, the overall aim of this research is therefore to provide a guideline document containing these findings, which can be used by regulators, site owners and site investigators.

This document forms part of a series of documents, produced by Water Research Commission project K5/1501 "*Field investigations to study the fate and transport of dense non-aqueous phase liquids (DNAPLs) in groundwater*".

The documents in this series include:

- Executive Summary of the Project
- Manual for Site Assessment at DNAPL Contaminated Sites in South Africa
- Groundwater monitoring guidelines for DNAPLs in South African Aquifers
- *Guidelines for the acceptance of Monitored Natural Attenuation processes in South Africa*
- Handbook for DNAPL Contaminated Sites in South Africa
- An Introduction to DNAPLs in South Africa: A Community Guide
- Field and laboratory investigations to study the fate and transport of DNAPLs in groundwater

All these documents are contained on the CD included with this report.

Contents

Tables

Figures

1. INTRODUCTION

1.1 Aims of the Report

Clean-up of both the NAPL and dissolved contamination in soils and groundwater at DNAPL contaminated sites is often expensive and slow. Often active approaches such as pump-and-treat (P&T) indicate that the cleanup process is lengthy, expensive and even ineffective. According to the US, EPA (1992 and 2002) P&T operations generally last between 5 and 10 years and median annual operating costs were estimated at 260,000 US$ for a treated groundwater volume of 115,500 m^3 year. Evaluation of P&T efficiency (NRC 1994; EPA 1992) showed that though in 23 of 34 cases containment was achieved, clean-up goals have failed in 90% of the cases. Removal of the contaminants from the aquifer is slowed by, for example, matrix diffusion in porous fractured media, thereby increasing both the time required to achieve clean-up and the total volume of water that must be extracted to flush the contaminated zone. Thus, pumping is often ceased before all of the contaminant is removed from the porous matrix system and back diffusion causes continued groundwater contamination (Pankow and Cherry, 1996).

For this reason, Monitored Natural Attenuation (MNA) has been discussed as a promising, cost-effective additional or alternative remediation option for DNAPL plumes. Though these economic considerations argue for MNA and the regulatory acceptance of MNA in general is increasing, MNA with respect to DNAPLs and especially chlorinated solvents (Grandel & Dahmke, 2004) is still a controversially discussed topic. Despite the fact that knowledge about their degradation pathways has improved, large plume dimensions and complex degradation mechanisms complicate demonstration of MNA in the field. However, independent of the remediation technology chosen, site investigation and remediation of most DNAPLs will, in general, be hampered by the difficulty of locating source and/or DNAPL and by characterising long plumes in heterogeneous aquifers. Natural attenuation is not expected to remediate the NAPL phase and therefore MNA is often applied together with source remediation actions.

In South Africa there is very little proven expertise regarding the remedial techniques currently employed in the US and Europe at DNAPL sites. One of the aims of this project is to evaluate MNA as an acceptable remediation option at DNAPL sites under typical South African aquifer conditions.

The following aspects are dealt with in this report:

- To give an overview of the physical, chemical and biological processes involved during MNA
- To provide an overview of international methodologies in dealing with the regulation of MNA
- To provide an overview of existing legislative frameworks within South Africa where MNA can be incorporated
- To evaluate acceptable protocols and standards for regulation
- To recommend practically implementable protocols in a local context.

Based on the above, the overall aim of this research is therefore to provide a guideline document containing these findings which can be used by regulators, site owners and site investigators.

1.2 Research methodology

The research methodology is as follows:

1. Obtain relevant literature related to MNA internationally.

2. Use the literature to describe natural attenuation processes.
3. Consult with key persons associated with industry and regulators in South Africa to gain an understanding of current South African regulations and guidelines currently in place.
4. Compare international methodologies to local methodologies.

The following sections will describe some of these techniques and methods listed above, in more detail.

- Overview of MNA processes
- Overview of MNA protocols and guidelines
- Assess viability of MNA for DNAPL contamination

2. WHAT IS MONITORED NATURAL ATTENUATION?

2.1 Introduction

Natural attenuation (NA) processes such as biodegradation, dispersion, sorption, and volatilisation affect the fate and transport of NAPLs in all hydrologic systems. When these processes are shown to be capable of attaining site-specific remediation objectives in a time period that is reasonable compared to other alternatives, they may be selected alone or in combination with other more active remedies as the preferred remedial alternative. Monitored Natural Attenuation (MNA) is a term that refers specifically to the use of natural attenuation processes as part of overall site remediation. The United States Environmental Protection Agency (U.S. EPA) defines monitored natural attenuation as (OSWER Directive 9200.4-17, 1999):

"The term 'monitored natural attenuation', refers to the reliance on natural attenuation processes (within the context of a carefully controlled and monitored clean-up approach) to achieve site-specific remedial objectives within a time frame that is reasonable compared to other more active methods. The 'natural attenuation processes' that are at work in such a remediation approach include a variety of physical, chemical, or biological processes that, under favourable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil and groundwater. These in-situ processes include biodegradation, dispersion, dilution, sorption, volatilisation, and chemical or biological stabilisation, transformation, or destruction of contaminants. When relying on natural attenuation processes for site remediation, EPA prefers those processes that degrade or destroy contaminants. Also, EPA generally expects that MNA will only be appropriate for sites that have a low potential for contaminant migration."

Natural attenuation processes typically occur at all contamination sites, but to varying degrees of effectiveness, depending on the types and concentrations of contaminants present and the physical, chemical, and biological characteristics of the soil and groundwater.

Where conditions are favourable, natural attenuation processes may reduce contaminant mass or concentration at sufficiently rapid rates and therefore achieve remediation objectives at some sites without the aid of other (active) remedial measures. The EPA however, encourages MNA to be used in conjunction with active remediation measures, which may offer greater confidence and reduced remediation time frames at modest additional cost. While MNA is often dubbed "passive" remediation because natural attenuation processes occur without human intervention, its use at a site does not preclude the use of "active" remediation or the application of enhancers of biological activity. However, by definition, a remedy that includes the introduction of an enhancer of any type is no longer considered to be "natural" attenuation. The use of MNA does not imply that activities (and costs) associated with investigating the site or selecting the remedy (e.g. site characterisation, risk assessment, comparison of remedial alternatives, performance monitoring and

contingency measures) has been eliminated. These elements of the investigation and clean-up must still be addressed, regardless of the remedial approach selected (EPA, 1999).

There is no European definition for NA, although several European countries have published guidelines on the implementation of MNA. According to Rügner and Teutsch (2001) a future European definition may differ from the US definition with respect to the following:

1. In Europe groundwater is considered as a receptor. This implies that risk- based methodologies need to take cognisance of the source as a receptor.
2. Mixing by dispersion and dilution will not be referred to as NA processes. NA processes are only considered if (bio)degradation or immobilisation of contaminants takes place.

In 2000 a guidance document was published by the UK Environment Agency (UK EA) with the purpose of promoting the use of "appropriately monitored natural attenuation where it is effective and appropriate" (Carey *et al.,* 2000). 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'. In developing this guidance, the Environment Agency has made a clear distinction between natural attenuation (NA) and monitored natural attenuation (MNA).

The definition of Natural Attenuation (NA) in groundwater is:

"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."

The definition of Monitored Natural Attenuation (MNA) is:

"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."

The lines-of-evidence approach set out in other protocols has been adopted in the UK EA'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 UK 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 Department of Environment and Conservation (New South Wales) in Australia (DEC NSW, 2005) has also adopted the definition given by the UK EA for MNA. On these principals and a sound technical understanding

of NA processes, some jurisdictions in Australia have accepted MNA as a possible remediation strategy for groundwater contaminated sites.

All of these popularly accepted international definitions of MNA are based on similar principals. It may be assumed that natural attenuation occurs to some degree at every site; however, depending on site conditions, there can be definite limits to its effectiveness as an interim or long-term solution, because natural attenuation does not necessarily imply that contaminants are removed. Furthermore, the site-specific conditions that often limit the effectiveness of natural attenuation as a contaminant removal/destruction process are rarely properly evaluated. It is vital that there be a distinction made between destructive processes and dilution.

Before an acceptable definition of MNA can be defined for South Africa, the unique properties of aquifer systems and groundwater contamination locally need to be considered. The following chapters will highlight some of the general issues regarding MNA, as well as the specific issues related to South African aquifer conditions.

2.1.1 What is not MNA?

In the previous section popular definitions of monitored natural attenuation are listed. However, often these popular definitions go on to mention that the 'in-situ' processes of NA include biodegradation, dispersion, dilution, adsorption, volatilisation and chemical or biological stabilisation or destruction of contaminants, meaning that natural attenuation is composed of numerous contributing factors of which biodegradation is only one. In practice unfortunately, the term 'natural attenuation' is often used synonymously with such terms as intrinsic bioremediation, self-remediation, natural restoration, passive bioremediation or intrinsic remediation (Odencrantz *et al.*, 2002).

The negative result of this is that it is increasingly common to interchange 'natural attenuation' with 'remediation,' when in fact they are not synonymous. Natural attenuation occurs to some degree at every site; however, depending on site conditions, there may be definite limits to its effectiveness as an interim or long-term solution, because natural attenuation does not necessarily imply that contaminants are removed. Furthermore, the site-specific conditions that often limit the effectiveness of natural attenuation as a contaminant removal/destruction process are rarely properly evaluated. It is vital that we distinguish between *destructive processes and dilution*.

It is very important to note that MNA IS NOT A 'DO NOTHING' APPROACH.

Indeed, the lines of evidence to select it as a mitigation strategy and to prove that it occurs to the required degree, shifts the onus squarely onto the site owner to show that the risks associated with allowing natural attenuation to occur are acceptable.

In Section 3.1, the specific mechanisms that play a role in these 'destructive processes' will be discussed in more detail.

3. MECHANISMS OF (MONITORED) NATURAL ATTENUATION

Natural attenuation processes include a variety of physical, chemical or biological processes that, under favourable conditions, act 'without human intervention' to reduce the mass, toxicity, mobility, volume or concentration of contaminants in soil or groundwater. Biological degradation of DNAPL in source zones is based on the ability of microorganisms to transform chemical constituents within close proximity to the DNAPL surfaces (the order of 100 µm), thereby resulting in enhanced rate of dissolution of the DNAPL constituents (EPA, 2003).

The processes that affect solute contaminant transport may be divided into three groups: physical (dispersion, diffusion, dilution and volatisation), 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).

It should be noted that in the NAPL form, rather than dissolved in water or sorbed on soil particles, organic contaminants are not readily degraded biotically or abiotically. Additionally, dispersion, dilution and sorption of the NAPL are slow. Therefore, it is important to determine where this NAPL may be at a polluted site, in order to remove or contain as much of it as possible, because the processes of natural attenuation would not effectively remediate most of this material in a reasonable time (US EPA, 1998).

The transport processes may be divided into non-degradative attenuation mechanisms and degradative attenuation mechanisms.

Table 2 gives the dominant attenuation mechanisms for principal groundwater contaminant groups. Contaminant types include more than DNAPL contaminants; other contaminants listed are often associated with DNAPL contaminated sites.

Table 1: Dominant attenuation mechanisms for principal contaminant groups

(Modified from Carey et al., 2000)

		Non-degradative attenuation mechanisms						**Degradative attenuation mechanisms**					
Contaminant type	**Examples**	*Methylation*	*Precipitation& cation exchange*	*Sorption and binding*	*Dispersion*	*Diffusion*	*Volatilisation*	*Aerobic degradation (contaminant as electron donor)*	*Anaerobic degradation (contaminant as electron acceptor)*	*Reductive dehalogenation (contaminant as electron acceptor)*	*Fermentation*	*Co-metabolism*	*Oxidastion/reduction*
*Chlorinated Solvents**													
≥ 3 chlorine atoms	PCE, TCE, TCA, TCM			x	x	x	x	x?	x	xx		x	x
≤ 3 chlorine atoms	DCM, VC, DCE			x	x	x	x	xx	x	x	x	x	
Petroleum hydrocarbons	BTEX, middle distillates			x	x	x	x	x	x		x	x	
Oxygenates	MBTE, EBTE,				x	x	x	Xx				x	
Heavy metals (cationic)	Hg, Cd, Zn, Pb, Ni, Sr, Co	x	x	xx	x	x							
Heavy metals (anionic)	CrO_4, AsO_4, AsO_3			xx	x	x							
Inorganics	Ca, Mg, Si		xx		x	x							
Anions	PO_4, BO_3		xx	xx	x	x							
Ammonia	NH_3, NH_4^+		xx	x	x	x		X					
Cyanide	CN			x	x	x		X			x		x
Nitrate	NO_3^-				x	x			x				x
PAHs*	Naphthalene			xx	x	x		X	x			x?	
Creosote*	Phenols and phenolics				x	x	x	Xx	xx		x	x	
Pesticides*	Chlorinated; organophosphate; pyrethroid; triazine; phenyl urea; phenoxyacid; cationic			x	x	x		X	x	x?		x?	

Xx; xx = primary importance; **X; x** = secondary importance; **x?** = some doubt exists over the process*
Contaminant groups are classified mainly as DNAPL contaminants

Certain contaminant characteristics can favour NA processes. These are typically:

- 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; and
- Rapid degradation (for example, low half-life) relative to groundwater velocity to reduce the risk that the contaminant may "break through" at a receptor;

The physical properties of an aquifer that have the greatest impact on the application of NA are the flow rate and flow mechanism present and the hydraulic conductivity. Preferential groundwater pathways, including fractures, joints and solution channels result in higher contaminant velocities, which in turn, may 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.

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 NA 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 fractured/fissured aquifers is complicated by the highly heterogeneous nature of the system. Long-term predictions in the performance of NA are, therefore, likely to be inherently uncertain.

The properties of selected South African aquifers are shown in Table 2 and Table 3, related to the dominant flow mechanisms, flow characteristics and the implications for MNA.

Table 2: Flow mechanisms of main aquifer systems in South Africa.

Dominant flow mechanism	Porosity type	Hydrogeological domains	Examples	Rock type
Intergranular	Primary	Quaternary and Tertiary deposits	Alluvium, Cape Flats, Kalahari Sands	Unconsolidated sands
Intergranular and fractured	Dual	Sedimentary rock and composite rock regions	Table Mountain Group, Karoo Group	Sandstones, shales, arenites
Fracture flow	Fracture	Crystalline metamorphic and igneous regions, Intrusive and extrusive rock regions	West Rand Group, Basement	Granites
Karst	Karstic	Sedimentary rock regions and composite rock regions	Karst Belt, Ghaap plateau	Dolomite

Table 3: Properties of selected South African aquifers, and their implications for MNA

Aquifer	Issues	Implications
Sandstones, shales, arenites	▪ Intergranular flow ▪ High fracture porosity, low matrix porosity ▪ Fracture/pore water interaction ▪ Multi-layered aquifer due to presence of hydraulic variance in horizons ▪ Horizontal and vertical flow important ▪ Generally "deep" aquifer ▪ Mineralogy: Fe (II) Oxide	▪ 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
Dolomite	▪ Fracture and Karst flow ▪ Preferential pathways ▪ Rapid flow ▪ Low matrix porosity ▪ Fracture/pore water interaction ▪ Significant variation in vertical and horizontal permeability ▪ Large seasonal water table variation ▪ Regional variations in behaviour of the aquifer (e.g. solution features)	▪ 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
Granite	▪ Fracture flow ▪ Preferential pathways ▪ Rapid flow ▪ Low matrix porosity ▪ Significant variation in vertical and horizontal permeability	▪ Borehole location in relation to preferential pathways ▪ Difficult to be confident about representative nature of monitoring results
Unconsolidated Sand/ gravel	▪ Thin aquifer ▪ Shallow water table ▪ High porosity ▪ High organic and clay content ▪ Nutrient availability ▪ Variable lithology and permeability	▪ Range of investigation techniques ▪ Thin unsaturated zone ▪ Easiest translation of US and other international experience to SA hydrogeology ▪ Little buffering

The following sections are a summary of the main processes affecting contaminant transport and therefore, cause natural attenuation. Emphasis is placed on the degradation pathways of chlorinated hydrocarbons (CAHs), as examples of common DNAPLs.

3.1 Non-degradative attenuation mechanisms

The non-degradative mechanisms discussed in this section may reduce the concentration of a contaminant, but do not necessarily affect its mass, toxicity or mobility. These physical/chemical processes include: dilution, dispersion, diffusion, solution/precipitation, sorption, cation exchange, methylation, and volatilisation.

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 may occur through:

- Recharge from uncontaminated infiltration of precipitation away from the source area.
- Contaminated groundwater discharging to a clean surface water resource or mixing with clean water at an abstraction point.
- Infiltration may be an important mechanism in introducing electron acceptors (dissolved oxygen, nitrate, sulphate) where contaminants are being microbiologically degraded.

According to Carey et al. (2000), only the first type of dilution is accepted by the UK EA as a natural attenuation process.

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

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, as often found in South Africa e.g. Karoo aquifers, diffusion of contaminants from the mobile 'fracture' water to the less mobile 'pore' water may be an important mechanism in retarding contaminant movement. Reverse diffusion from the pore water may act as a persistent secondary source of contamination.

Solution/precipitation of contaminants out of solution may occur, when physiochemical conditions change; for example, precipitation as insoluble sulphides and carbonates. However, the contaminant may be dissolved back into solution.

Sorption describes the interaction of a contaminant between water and soil/rock matrix. 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 will retard the rate at which contaminants move through the system. Sorption may 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 and redox reactions are the dominant mechanisms for reducing the mobility, toxicity or bioavailability of 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; for example, sorption to iron hydroxides, carbonate minerals and clay matrices (Carey et al., 2000).

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 may represent a longer-lasting source.

The extent of contaminant sorption may 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 or non-conservative)
- the contaminant concentration in solution
- the nature and concentration of other contaminants (competition with other contaminants may reduce the number of sites for sorption or some organic contaminants may provide additional sites for further sorption)
- the nature of the soil/rock matrix, including available surface area
- the presence of clay, organics and oxyhydroxides which may provide ideal sites for sorption
- the pH and redox potential of the system may influence sorption
- the flow rate may influence the time available 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. Measurement of f_{oc} (fraction of organic carbon) is therefore an important task when assessing the sorption potential of an aquifer system. (For more on sorption mechanisms of DNAPLs refer to Progress Report 1 of this project, Usher et al., 2004).

Methylation involves attaching methyl groups to inorganic forms of metal ions to form organometallic compounds. Methylation reactions may be microbially mediated. Organometallic compounds are more volatile than inorganic metals and this process may be used to remove metals through volatilisation and the subsequent removal from the gas stream. However, organometallics are also more toxic and mobile than other metal forms and may potentially contaminate surrounding groundwater and/or surface water (Means and Hinchee, 1994).

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. It occurs primarily in the unsaturated zone and is therefore 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 water table. Volatilisation may lead to a reduction in the soluble mass if some of the gases escape the groundwater system.

Table 4: Overview of non-degradative attenuation mechanisms and their effects.

Process	Description	Dependencies	Effect
Volatilisation	Volatilisation of contaminants dissolved in groundwater into the vapour phase	Dependent on the chemicals' vapour pressure and Henry's Law constant	Removes contaminants from groundwater and transfers them to soil gas
Sorption	Reaction between aquifer matrix and solute in which 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

3.2 Degradative attenuation mechanisms

From the above discussion, it is clear that not all the mechanisms actually remove mass from the plume. The mechanisms that do remove mass are provided with their effects and significance.

Table 5: Overview of Degradative attenuation mechanisms and their effects.

Process	Description	Dependencies	Effect
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	May result in partial or complete degradation of contaminants. Rates typically much slower than for biodegradation

It is often difficult or impossible to determine in the field the exact mechanisms functioning to transform the contaminants. However, an understanding of the geochemical environment and the patterns of contaminant degradation are essential to discerning the likely degradative processes at a site. Knowledge of the degradative mechanisms will help the investigator determine the effectiveness of a natural attenuation remedy, the need for supplemental remediation and to design a long-term monitoring programme.

Unlike metals which cannot be destroyed, the mass of organic and inorganic compounds (such as ammonia) may 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 (Carey et al., 2000).

3.2.1 Abiotic reactions

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 may vary from days to hundreds of years, but this process is generally slower than biodegradation. Generally, the rates of abiotic processes are slow compared to biologically-mediated degradative mechanisms.

The most common abiotic reactions are hydrolysis (the halogen is replaced with a hydroxyl (OH-) group) and dehydrohalogenation (an elimination reaction that removes a halogen and a hydrogen from adjacent carbon atoms in an alkane and produces an alkene). Substitution and abiotic oxidation reactions also occur. Abiotic degradation primarily affects chlorinated and brominated methanes and ethanes. The kinetics of abiotic reactions varies greatly with each contaminant, such that intermediates tend to accumulate. Often, biotic processes (which change pH and redox potential) are necessary to stimulate abiotic reactions (Wiedemeier et al., 1998).

The most well-documented abiotic degradation reactions involve carbon tetrachloride, chloroform, chloromethane, trichloroethane (TCA) and chloroethane. McCarty (1997) states that TCA is abiotically converted under almost all likely groundwater conditions. The products of this abiotic transformation are acetic acid (approximately 80%) with the remaining 20 percent converting to 1,1-DCE. Chloroethane readily hydrolyses to ethanol with a half-life of approximately 44 days (Wiedemeier et al., 1998).

Temperature plays a significant role in biotic and abiotic reaction rates. For polychlorinated ethanes and methanes, abiotic half-lives are likely to be in the order of hundreds to thousands of years at ambient groundwater temperatures, while monochlorinated compounds have much lower half-lives (Wiedemeier et al., 1998).

3.2.2 Biotic reactions

Biotic (Biological) degradation is the dominant process controlling the fate and transport of many organic contaminants. 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. Depending on groundwater geochemistry, microbial population and contaminant properties, biodegradation may occur under aerobic and/or anaerobic conditions. 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. This may be represented by the following generalised equation:

Micro-organisms + electron donor + electron acceptor + nutrients

↓

metabolic by-products + energy + micro-organisms

All degradative mechanisms involve the transfer of electrons to or from the contaminant molecule. Micro-organisms often mediate this transfer of electrons. The oxidative state of the environment as well as the contaminant determines the direction of the electron transfer and whether a particular transfer is likely to occur.

Biodegradation of chlorinated compounds in groundwater occurs via three basic mechanisms (Wisconsin DNR, 2003):

a) As a primary growth substrate (i.e. micro-organisms use the contaminant as food for energy and growth),
b) As an electron acceptor (i.e. micro-organism 'breathes' the contaminant),
c) Through co-metabolism (i.e. the contaminant is fortuitously degraded without producing energy for the micro-organism).

Microbial degradation requirements include: electron donors (availability of a carbon source), electron acceptors (e.g. oxygen, nitrate, iron (III), manganese (IV), sulphate, carbon dioxide), essential nutrients and proper environmental conditions (proper range of pH, temperature, salinity, redox potential).

With regard to this discussion, enzymes are responsible for the degradation of organic carbon, which is used by the bacterial cell to produce both the building blocks of life and energy. The degradation of any organic molecule, including contaminants, requires the production and efficient utilisation of enzymes. In most instances, degradation is merely a complex oxidation/reduction reaction. The electrons or reducing equivalents (hydrogen or electron-transferring molecules) produced must be transferred to a terminal electron acceptor (TEA). During the transfer process, energy is produced which is utilised by the cell.

With regard to TEAs, bacteria are generally grouped into three categories:

1. Aerobic bacteria — bacteria which can only utilise molecular oxygen as a TEA. Without molecular oxygen, these bacteria are not capable of degradation.
2. Facultative aerobes/anaerobes — bacteria, which can utilise molecular oxygen or when oxygen concentrations are low or non-existent, may switch to nitrate, manganese oxides or iron oxides as electron acceptors.
3. Anaerobes — bacteria which cannot utilise oxygen as an electron acceptor and for which oxygen is toxic.

Though reactions may utilise nitrate or other electron acceptors, it may be said that they generally utilise sulphate or carbon dioxide as electron acceptors.

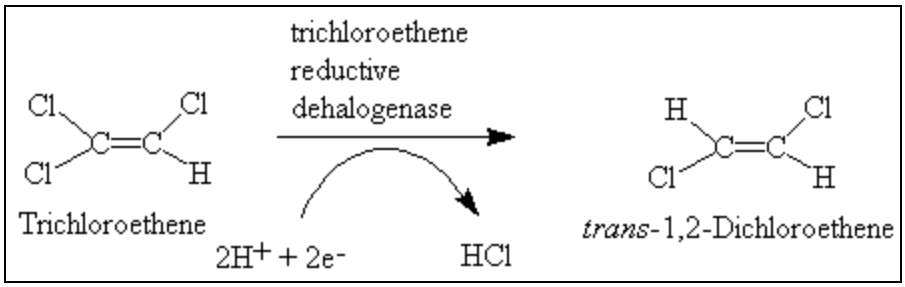

Figure 1: Reductive dechlorination of trichloroethene (Available from http://umbbd.ahc.umn.edu)

In general, all 'types' of bacteria (e.g. aerobic, anaerobic) are present at all sites. However, all bacteria involved in all of the potential biodegradation pathways for chlorinated solvents are not necessarily present at every site. For example, it is believed that all of the bacteria needed for the reductive dechlorination of PCE or TCE to DCE are present at approximately 90% of all sites and all of the bacteria needed for the reductive dechlorination of PCE or TCE to ethene are present at approximately 75% of all sites (Weidemeier et al.,1999).

McCarty (1997) provides a general review of the redox-dependent biodegradability of chlorinated ethenes. In summary, the complete transformation from PCE and TCE to ethene will occur only under methanogenic conditions. Under less reducing conditions, PCE and TCE may be transformed to DCE, but will not be transformed further to vinyl chloride or ethene. Reductive dechlorination of these chlorinated ethenes will not occur in the nitrate reducing zone.

Table 6: Common degradation processes for different CAHs

Degradation Process		**PCE**	**TCE**	**DCE**	**VC**	**TCA**	**CT**	**CF**	**DCM**
Aerobic Biodegradation	Primary Substrate	N	N	Y	N	N	N	N	Y
	Methane/Alkanes	N	Y	Y	Y	Y	N	Y	Y
Cometabolism supported by:	*Aromatics*	N	Y	Y	Y	N	N	N	N
	Ammonia	N	Y	Y	Y	Y	N	Y	Y
Anaerobic Biodegradation	Primary Substrate	N	N	N	Y	N	N	N	Y
	Denitrification	Y	Y	Y	Y	N	Y	Y	Y
Cometabolism supported by:	*Iron Reduction*	Y	Y	Y	Y	Y	Y	Y	Y
	Sulphate reduction	Y	Y	Y	Y	Y	Y	Y	Y
	Methanogenesis	Y	Y	Y	Y	Y	Y	Y	Y
Chemical Degradation		N	N	N	N	Y	Y	N	N

The parameters for chlorinated solvents may include: temperature, redox potential, DO, sulphide, Fe(II), methane, ethane/ethene, alkalinity, pH, sulphate, nitrate, chloride, dissolved organic carbon and hydrogen.

3.2.2.1 Aerobic degradation

Aerobic degradation is a 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.

The three modes of contaminant degradation have already been referred to. The aerobic case occurs when the contaminants, for example, petroleum hydrocarbons, are utilised by bacteria as a sole source of carbon. Petroleum hydrocarbons are degraded through a series of enzymatic reactions to produce needed cellular constituents. While this may seem incidental to DNAPL MNA processes, many of the sites are not 'pure DNAPL' sites and as part of the cocktail of contaminants that may occur, petroleum hydrocarbons and diesel may occur in many cases. Electrons or reducing equivalents must be regenerated. If a contaminant serves as a sole source of carbon and energy, conditions must be within acceptable pH, Eh and temperature limits and the appropriate TEA must be present. In this case, the rate of degradation will be determined by the rate of dissolution of toxic end products away from the microbial population and the rate at which the TEA is replenished. Some of the lesser chlorinated solvents, such as dichloroethene (DCE), may also serve as sole sources of carbon; however, tetrachloroethene (PCE) and trichloroethene (TCE) are not thought to serve as sole sources of carbon. In the case of TCE (and lesser chlorinated solvents), degradation may occur through co-metabolic processes. Under aerobic conditions, the enzymes necessary for the degradation, however, must be induced. Inducible enzymes are those that are not produced unless an inducer compound is present within the bacterial cell. Pertinent to this discussion are the inducers for methane mono-oxygenase and various mono- and dioxygenase enzymes produced by aromatic degrading bacteria.

In the presence of oxygen and methane, methanotrophic bacteria are known to produce the enzyme methane mono-oxygenase (Hanson and Hanson, 1996; Patel et al., 1982). The substrate for this enzyme is methane, but it has been shown to have a broad substrate specificity including chlorinated solvents (Mayer et al., 1988).

Methanotrophs downgradient from a chlorinated solvent event may feed on methane produced within the anaerobic portion of the plume and co-metabolically degrade some chlorinated solvents. This is of potential significance to the Test Site 1 where methane and oxygen values from the soil vapour survey may suggest that this process is occurring. Oxygenase enzymes produced by bacteria capable of degrading aromatic hydrocarbons are capable of degrading chlorinated solvents. Aromatic compounds, such as toluene and phenol, have been shown to induce the responsible enzymes. In contaminated aquifers which contain both aromatic hydrocarbons and chlorinated solvents, degradation of both may occur.

Of the chlorinated ethenes, vinyl chloride is the most susceptible to aerobic oxidation under natural groundwater conditions. While laboratory studies have shown TCE may degrade oxidatively, there is no field evidence to support this. Cis-1,2-dichloroethene (cis-DCE), and 1,2-dichloroethane (1,2-DCA) may be subject to aerobic biodegradation. Chloroethane tends to hydrolyse (an abiotic reaction) preferentially over aerobic or anaerobic biodegradation. Vinyl chloride rapidly degrades aerobically, particularly in comparison to reductive dechlorination. Chloromethane (CM) and dichloromethane (DCM) are degraded aerobically (Leisinger et al., 1994). Chlorobenzene and polychlorinated benzene (up to tetrachlorobenzene) are degraded aerobically, similar to benzene (Wiedemeier et al., 1998).

3.2.2.2 Anaerobic degradation

Anaerobic degradation is a transformation and/or elimination of an organic compound by micro-organisms in the absence of oxygen. Compounds other than oxygen act as electron acceptors. The processes include, denitrification, Fe(III) reduction, sulphate reduction, methanogenesis i.e. NO_3, Fe, SO_4 and CO_2 (in that order), plus chlorinated solvents acting as electron acceptors. VC and DCM are the only known examples of chlorinated solvents that undergo anaerobic degradation as electron donors. Highly chlorinated solvents do not degrade aerobically. Decreases in the concentration of electron acceptors and the corresponding increase in the concentration of metabolic by-products provide indirect evidence for degradation.

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

- fermentation - oxidation and reduction reactions involving the transfer of electrons between organic compounds;
- cometabolism - for example, anaerobic cometabolism ('reductive dechlorination') is a common degradation route for highly chlorinated aliphatic compounds such as PCE and TCE.

Aerobic degradation - oxygen acts as the electron acceptor. Co-metabolism of chlorinated ethenes is generally of little significance, unless a suitable electron donor (e.g. methane, ammonia, or phenol) is present (McCarty, 1997). Thus, it is important to consider that, in the absence of a suitable electron donor, TCE and (to a lesser extent) DCE, appear to be relatively recalcitrant under aerobic conditions.

3.2.2.2.1 Chlorinated Ethenes

The transformation requires consortia of many microorganisms which then ferment these products to alcohols and fatty acids for energy. Secondly, other microbes oxidise the alcohols and organic acids, producing acetate and molecular hydrogen (H_2). Thirdly, another set of microbes oxidises the acetate and hydrogen as electron donors, using either the contaminant or naturally available chemicals. Dehalococcoides ethenogenes is the only anaerobic microorganism that is known to completely dechlorinate chlorinated ethenes in the laboratory. Other species of Dehalococcoides working together with a group of microorganisms called a 'consortium' may also dechlorinate chlorinated ethenes. Hendrickson et al., 2002, has shown that Dehalococcoides species were found in 21 of 24 soil and groundwater samples contaminated with chlorinated ethenes collected in North

America and Europe. At the sites where Dehalococcoides was not found, chlorinated degradation proceeded only to 1,2-DCE that then accumulated in the groundwater.

Reductive dechlorination of the contaminants competes with other electron acceptors for the electrons from hydrogen and acetate (Smatlak et al., 1996; Yang and McCarty, 1998). When reductive dechlorination is not highly successful in this competition, it gains only a small share of the available electrons. Then, the microorganisms oxidise a large amount of H2 or acetate to reduce only a small amount of the chlorinated contaminant. Theoretically, a minimum of 0.04 mole of H2 is required to reduce 0.01 mole of PCE (1.7 g) to ethene. This amount of hydrogen may be produced biologically under suitable anaerobic conditions from decomposition of 1.0 to 1.5 g of organic matter. However, because of competition, as little as 1 to 10 percent of the hydrogen intermediate be produced may be used for dehalogenation. Thus, if 0.10 mg/litre were present, from 1.0 to 10.0 mg/litre of organic matter might be needed to achieve complete dehalogenation. Such a large amount of organic matter generally is not present in aquifers. An insufficient concentration of electron donors is a primary reason that the dechlorination of chlorinated aliphatic hydrocarbons is often incomplete.

However, it is possible for vinyl chloride to be oxidised under aerobic conditions or under anaerobic conditions where iron (III) is the electron acceptor (Bradley and Chapelle, 1996). Vinyl chloride is also readily and very efficiently co-metabolised aerobically by methane, phenol, or BTEX oxidisers (McCarty, 1997). Similarly, rapid methanotrophic mineralisation of TCE and DCE under aerobic conditions has also been observed. Chlorinated solvents are not utilised as a carbon source, but rather as an acceptor for electrons produced during the metabolism of other oxidisable carbon (electron donor). Thus, this process cannot be termed cometabolism. Electrons or reducing equivalents formed during metabolism are accepted by the chlorinated solvent. As an example, PCE will accept electrons or reducing equivalents formed during metabolism. This results in the reduction of PCE, the concomitant release of a chloride ion and the formation of TCE. While almost any degradable carbon appears capable of driving reductive dechlorination, in most instances, a low percentage of the electrons or reducing equivalents are utilised in the reductive process. This is a function of other metabolic requirements for reducing equivalents (substrate specific) and the presence or absence of more suitable terminal electron acceptors (Bouwer, 1994).

The behaviour of the chlorinated solvent plumes may be classified into three types based on their primary substrate source (U.S. EPA, 1998).

- ***Type 1 Behaviour —*** Primary substrate is the adequate amount of anthropogenic organic carbon, solvent plume degrades
- ***Type 2 Behaviour —*** Primary substrate is the adequate amount of native organic carbon, solvent plume degrades
- ***Type 3 Behaviour —*** Low native organic carbon concentrations or low anthropogenic organic carbon concentrations, PCE, TCE, and DCE do not degrade

The transformation requires consortia of many microorganisms which then ferment these products to alcohols and fatty acids for energy. Secondly, other microbes oxidise the alcohols and organic acids, producing acetate and molecular hydrogen (H_2). Thirdly, another set of microbes oxidises the acetate and hydrogen as electron donors, using either the contaminant or naturally available chemicals

For complete detoxification, the parent chlorinated solvent must be dechlorinated in a stepwise fashion to the environmentally benign ethene. This is illustrated in Figure 2.

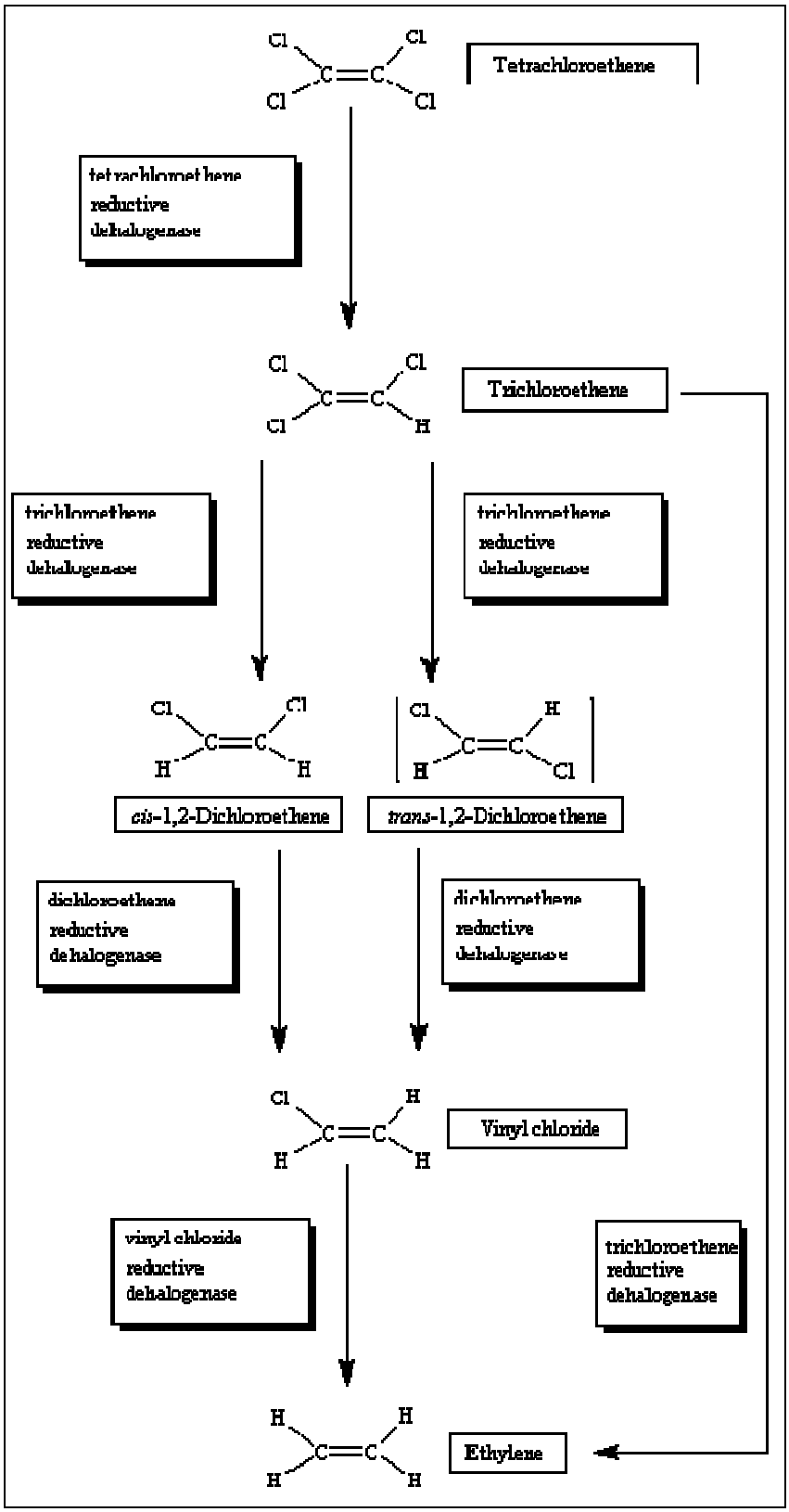

Figure 2: Step-wise dechlorination of PCE (Available from http://umbbd.ahc.umn.edu)

PCE and TCE are readily reduced as a result of their oxidative states; the more reduced daughter products (DCE and VC) are less prone to reductive processes. These intermediates tend to accumulate in anaerobic aquifers where contaminants are allowed to naturally attenuate (Lesage et al., 1990). This may also be a function of the concentration of degradable organic matter within the contaminated system. Co-metabolism of TCE by autotrophic bacterial populations, obtained from soil and groundwater, has been demonstrated; this route of removal is limited only to low concentrations of TCE. The co-metabolism of TCE proceeds in the presence of methane ammonia or toluene as co-substrate. Due to the inherent toxicity of TCE to microorganisms responsible for degradative process and because of the competitive inhibition between a co-substrate and the secondary substrate for oxygenase enzymes, special attention to concentrations of TCE and its co-substrate is warranted (McCarty, 1997).

The process can be summarised by the figure below:

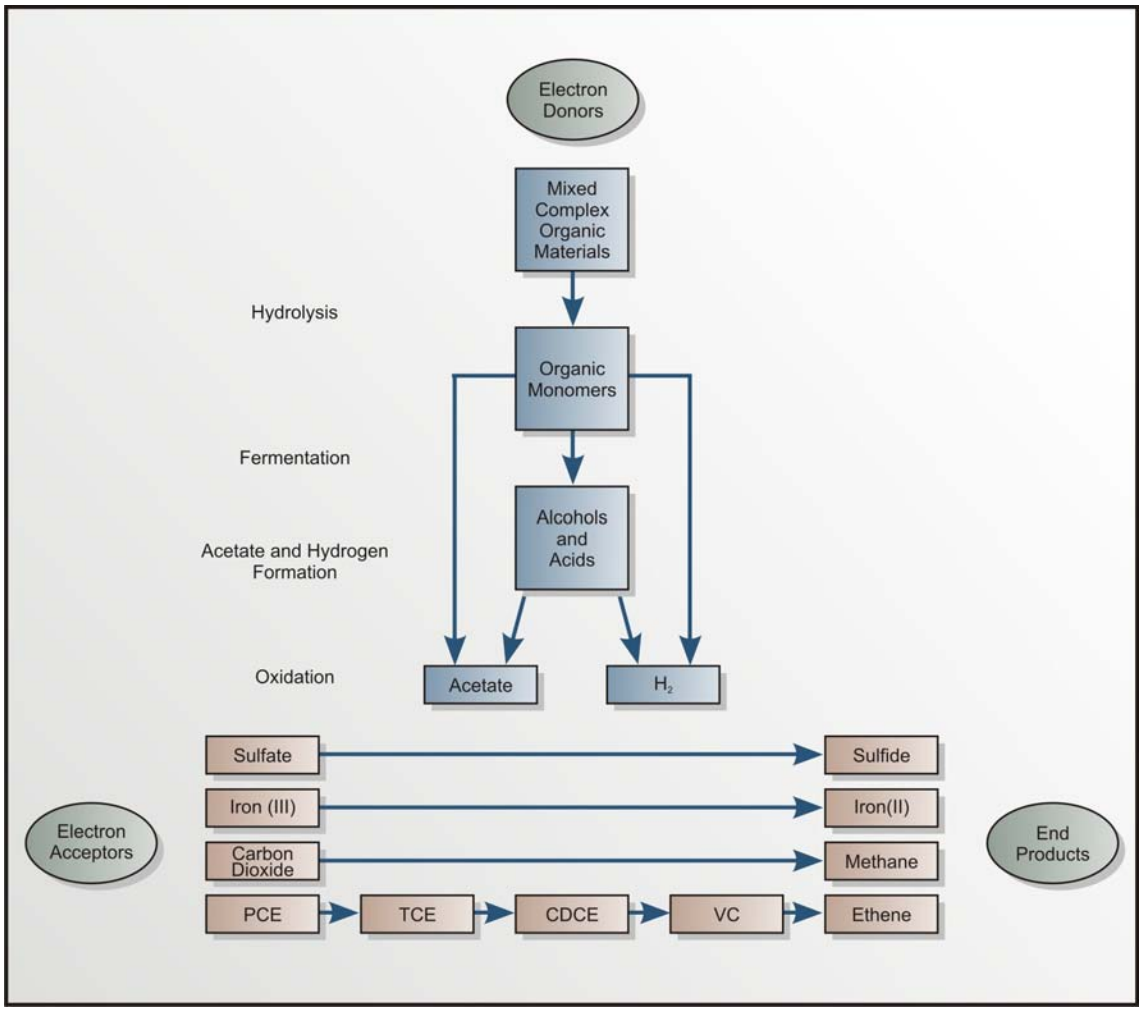

Figure 3: Steps in the process of biodegradation of PCE by reductive dechlorination. As shown, biodegradable organic matter is required as an electron donor to initiate the process.

(After McCarty, 1997.)

Different types of microbes are involved at each stage.

The bottom step shows that PCE must compete for electrons with sulphate, iron and carbon dioxide, meaning that a large amount of organic electron donors may be needed to supply enough electrons.

3.2.2.2.2 PAHs

PAHs biodegrade very slowly. The fate of PAHs in subsurface systems is governed largely by their hydrophobic nature (the reason for their low solubility and tendency to attach to surfaces). PAH molecules held within NAPLs or adsorbed to surfaces cannot be biodegraded. Consequently, understanding dissolution (Ghoshal et al., 1996) and the sorption processes (Luthy et al., 1994) for PAHs is often the key to understanding biodegradation and natural attenuation potential.

4. EXISTING PROTOCOLS AND GUIDELINES

4.1 US EPA Protocols and guidelines

In 1997 the OSWER Directive was first published with the purpose to clarify EPA's policy regarding the use of monitored natural attenuation (MNA) for the clean-up of contaminated soil and groundwater in the "*Superfund, RCRA Corrective Action, and Underground Storage Tank programs*". The Directive was accepted in April 1999 as Directive number 9200.4-17P. These programmes are administered by EPA's Office of Solid Waste and Emergency Response (OSWER) which include the Office of Emergency and Remedial Response (OERR), the Office of Solid Waste (OSW), the Office of Underground Storage Tanks (OUST) and the Federal Facilities Restoration and Reuse Office (FFRRO).

Statutory authority for these remediation programmes is provided under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the Resource Conservation and Recovery Act (RCRA).

The US EPA is committed to the goals of "*protecting human health and the environment by remediating contaminated soils, restoring contaminated groundwaters to their beneficial uses, preventing migration of contaminant plumes, and protecting groundwaters and other environmental resources."* The EPA advocates using the most appropriate technology for a given site and does not consider MNA to be a 'presumptive' or 'default' remedy; it is merely one option that should be evaluated with other applicable remedies. The effectiveness of MNA in both short-term and long-term timeframes should be demonstrated to the EPA (or other overseeing regulatory authority) through:

1) sound technical analyses which provide confidence in natural attenuation's ability to achieve remediation objectives;
2) performance monitoring; and
3) contingency (or backup) remedies where appropriate.

Therefore, MNA is not viewed as a 'no action' or 'walk-away' approach by the EPA, but rather as an alternative means of achieving remediation objectives that may be appropriate for specific, well-documented site circumstances where its use meets the applicable statutory and regulatory requirements. In the majority of cases where MNA is proposed as a remedy, its use may be appropriate as one component of the total remedy; that is, either in conjunction with active remediation or as a follow-up measure. MNA should be used very cautiously as the sole remedy at contaminated sites.

4.1.1 Role of MNA in OSWER Remediation Programmes

Under the OSWER programmes, remedies selected for contaminated media may achieve the required level of protection using a variety of methods, including treatment, containment, engineering controls and other means identified during the remedy selection process.

The regulatory and policy frameworks for corrective actions under the UST, RCRA and Superfund programmes have been established to implement their respective statutory mandates and to promote the selection of technically defensible, nationally consistent and cost effective solutions for the clean-up of contaminated media. Although there are differences among these programmes, they share several key principles that should generally be considered during the selection of remedial measures, including (US EPA, 1999):

- **Source control measures** should use treatment to address 'principal threat' wastes (or products) wherever practicable and engineering controls such as containment for waste (or products) that pose a relatively low long-term threat or where treatment is impracticable.
- Contaminated groundwater should be returned to "its beneficial uses wherever practicable, within a timeframe that is reasonable given the particular circumstances of the site." When the **restoration of groundwater** is not practicable, EPA "expects to prevent further migration of the plume, prevent exposure to the contaminated groundwater, and evaluate further risk reduction."
- Contaminated **soil should be remediated** to achieve an acceptable level of risk to human and environmental receptors and to prevent any transfer of contaminants to other media (e.g. surface or groundwater, air, sediments) that would result in an unacceptable risk or exceed required clean-up levels.
- Ample opportunities should exist during any remedial action for **public involvement** that serves to both educate interested parties and to solicit feedback concerning the decision-making process.

Therefore, the EPA does not consider the selection of MNA as a substitute for other remedies. It should also be emphasised that the selection of MNA as a remedy does not imply that active remediation measures are not feasible or are 'technically impracticable' from an engineering perspective. Technical impracticability (TI) determinations may be used to justify a departure from clean-up levels that would otherwise be required at a Superfund site or RCRA facility based on the inability to achieve such clean-up levels using available remedial technologies (US EPA, 1993).

TI determination indicates that the clean-up levels and objectives which would otherwise be required cannot practicably be attained using available remediation technologies. In such cases, an alternative clean-up strategy must be identified. Such an alternative strategy may still include engineered remediation components, such as recovery of free phase NAPLs and containment of residual contaminants, in addition to approaches intended to restore some portion of the contaminated groundwater to beneficial use. Several remedial approaches could be appropriate to address the dissolved plume, one of which could be MNA under suitable conditions. However, the evaluation of natural attenuation processes and the decision to rely upon MNA for the dissolved plume should be distinct from the recognition that restoration of a portion of the plume is technically impracticable (i.e. MNA should not be viewed as a direct or presumptive outcome of a technical impracticability determination.)

4.1.2 Demonstration of Efficacy of NA through Site Characterisation

The US EPA requires that a decision to employ MNA as a remedy or a remedy component should be supported with "*site-specific characterization data and analysis*".

It is stated very clearly in the OSWER Directive that the level of site characterisation necessary to support a comprehensive evaluation of MNA is "more detailed" than that needed to support active remediation.

Site characterisations for NA as required should include collecting data to define (in three spatial dimensions over time) the nature and distribution of contaminants of concern and contaminant sources, as well as potential impacts on receptors. Such a characterisation would typically include the following elements:

- quantitative understanding of source mass;
- groundwater flow (including preferential pathways);
- contaminant phase distribution and partitioning between soil, groundwater and soil gas;
- rates of biological and non-biological transformation; and
- an understanding of how all of these factors are likely to vary with time.

To demonstrate the efficacy of MNA, an analytical or numerical simulation of complex attenuation processes may be required. Such analyses, which are critical to demonstrate natural attenuation's ability to meet remediation objectives, generally require a detailed conceptual site model as a foundation. Therefore, the EPA recommends the use of conceptual site models to integrate data and guide both investigative and remedial actions. However, warning is given to the application of a wrong conceptual model, in the context of evaluating an MNA (or any other) remedy, as this can result in a deficient site and the inappropriate selection of an MNA remedy where long-term sources (e.g. NAPL source zones) were not identified nor considered during remedy selection. (Specific site characterisation methods are described in Section 4.3.)

4.1.2.1 Lines of Evidence

Once site characterisation data have been collected and a conceptual model developed, the next step is to evaluate the potential efficacy of MNA as a remedial alternative. A three-tiered approach (EPA, 1999) is prescribed, where successively more detailed information is collected as necessary, to provide a specified level of confidence on the estimates of attenuation rates and remediation timeframe. These three tiers of site-specific information are often referred to as "lines of evidence" and are:

1) ***Historical groundwater and/or soil chemistry data*** that demonstrate a clear and meaningful trend of decreasing contaminant mass and/or concentration over time at appropriate monitoring or sampling points. In the case of a groundwater plume, the decreasing concentrations should not be solely the result of plume migration. In the case of inorganic contaminants, the primary attenuating mechanism should also be understood.
2) ***Hydrogeological and geochemical data*** that may be used to demonstrate indirectly the ***types of NA processes*** active at the site and the rate at which such processes will reduce contaminant concentrations to required levels. For example, characterisation data may be used to quantify the rates of contaminant sorption, dilution or volatilisation or to demonstrate and quantify the rates of biological degradation processes occurring at the site.
3) ***Data from field or microbial studies*** (conducted in or with actual contaminated site media) which directly demonstrate the occurrence of a particular NA process at the site and its ability to degrade the contaminants of concern.

Unless the EPA or the overseeing regulatory authority determines that historical data (1) are of sufficient quality and duration to support a decision to use MNA, data characterising the nature and rates of natural attenuation processes at the site (2) should be provided. Where the latter are also inadequate or inconclusive, data from microcosm studies (3) may also be necessary.

The first line of evidence does not prove that contaminants are being destroyed. Reduction in contaminant concentration could be the result of non-degradative mechanisms (Section 3.1). However, this line of evidence is critical for determining if any exposure pathways exist for current or potential future receptors (Wiedemeier *et al.*, 1998).

In order to evaluate remediation by natural attenuation at most sites, the investigator will have to determine whether contaminant mass is being *destroyed*. This is done using either or both, of the second or third lines of evidence. The second line of evidence relies on chemical and physical data to show that contaminant mass is being destroyed and not just being diluted or sorbed to the aquifer matrix.

For many contaminants, biodegradation is the most important process, but for certain contaminants non-biological reactions are also important. The second line of evidence is divided into two components (Wiedemeier *et al.*, 1998):

1) Using chemical analytical data in mass balance, calculations to show that decreases in contaminant and electron acceptor/donor concentrations may be directly correlated to increases in metabolic end products/daughter compounds. This evidence may be used to show that electron acceptor/donor concentrations in groundwater are sufficient to facilitate degradation of dissolved contaminants. Solute fate and transport models may be used to aid mass balance calculations and to collate and present information on degradation.
2) Using measured concentrations of contaminants and/or biologically recalcitrant tracers in conjunction with aquifer hydrogeologic parameters such as seepage velocity and dilution to show that a reduction in contaminant mass is occurring at the site and to calculate biodegradation rate constants.

The biodegradation rate constants are used in conjunction with the other fate and transport parameters to predict contaminant concentrations and to assess risk at down-gradient performance evaluation boreholes and within the area of the dissolved plume.

Microcosm studies (third line of evidence) may be necessary to demonstrate physically that natural attenuation is occurring. Microcosm studies may also be used to show that indigenous biota are capable of degrading site contaminants at a particular rate. Microcosm studies for the purpose of developing rate constants should only be undertaken when they are the only means available of obtaining biodegradation rate estimates (Wiedemeier *et al.*, 1998).

In the UK, the following approach to lines of evidence provides a succinct summary:

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. (Carey et al., 2000).

Table 7: Summary of the lines of evidence used to evaluate natural attenuation (EPA, 1998).

Line of Evidence	Data Requirements	Comments
Plume Stabilisation and/or Loss of Contaminant Mass over Time	Historical Contaminant Data	Can be evaluated using visual techniques or statistical techniques such as those presented by the EPA or the Mann-Whitney U Test or the Mann-Kendall Test. Historical database must be 'statistically significant.'
Analytical Data Confirming Intrinsic Bioremediation	Data Presented in Tables 7.1 and 7.3 (EPA, 1998)	One, two, and three dimensional plots of contaminants, electron acceptors and metabolic by-products in time and space. Things to look for include: - depletion of electron acceptors and donors - increasing metabolic by-product concentrations - decreasing parent compound concentrations - increasing daughter compound concentrations
Microbiological Laboratory Data	Microcosm Studies, microbial cell counts, etc.	Should be used only to evaluate the conditions under which biodegradation processes occur or do not occur or when biodegradation rates constants cannot be obtained using other lines of evidence.
Modelling*	Model-specific	Useful for examining the relative importance of the processes influencing the transport of organic compounds.

**Not a line of evidence but helpful in documenting natural attenuation*

4.1.3 Sites Where Monitored Natural Attenuation May Be Appropriate

The EPA (1999) views MNA as an appropriate remedial approach where it can be demonstrated that it is capable of "*achieving a site's remediation objectives within a timeframe that is reasonable compared to that offered by other methods and where it meets the applicable remedy selection criteria for the particular OSWER program."*

The EPA expects that MNA will be most appropriate when used in conjunction with other remediation measures (e.g. source control, groundwater extraction) or as a follow-up to active remediation measures that have already been implemented. The following factors are considered by the EPA (or other regulatory authorities) in determining the appropriateness of MNA as a remedy:

- Whether the contaminants present can be effectively remediated by natural attenuation processes;
- Whether or not the contaminant plume is stable and the potential for the environmental conditions that influence plume stability to change over time;
- Whether *any* receptors could be adversely impacted as a consequence of selecting MNA as the remediation option;
- Current and projected demand/use for the affected resource over the time period that the remedy will remain in effect;
- Whether the contamination, either by itself or as an accumulation with other nearby sources, will exert a long-term detrimental impact on available water supplies or other environmental resources;
- Whether the estimated timeframe of remediation is reasonable compared to timeframes required for other more active methods;
- The nature and distribution of sources of contamination and whether these sources have been or can be, adequately controlled;

- Whether the resulting transformation products present a greater risk, due to increased toxicity and/or mobility, than do the parent contaminants;
- The impact of existing and proposed active remediation measures upon the MNA component of the remedy or the impact of remediation measures or other operations/activities in close proximity to the site; and
- Whether reliable site-specific mechanisms for implementing institutional controls are available and if an institution responsible for their monitoring and enforcement can be identified.

Of the above factors, the most important considerations regarding the suitability of MNA as a remedy include: whether the contaminants are likely to be effectively addressed by natural attenuation processes, the stability of the groundwater contaminant plume and its potential for migration and the potential for unacceptable risks to human health or environmental resources by the contamination.

Therefore, sites where the contaminant plumes are no longer increasing in extent or are shrinking, are considered to be the most appropriate candidates for MNA remedies.

4.1.4 Reasonable Timeframe for Remediation

EPA recognises that determination of what timeframe is 'reasonable' for attaining remediation objectives is a site-specific determination (US EPA, 1999). A reasonable timeframe is obtained through comparison of approximate ranges of time periods needed to attain groundwater clean-up levels with other restoration alternatives from most aggressive to most passive methods.

It is required that the advantages and disadvantages of each remedy alternative, including the timeframe, should be evaluated in accordance with the remedy selection criteria used by each OSWER programme. Whether a particular remediation timeframe is appropriate and reasonable for a given site is determined by balancing tradeoffs among many factors, which include:

- Classification and value of the affected groundwater resource;
- Relative timeframe in which the affected portions of the aquifer might be needed for future water supply (including the availability of alternate supplies);
- Subsurface conditions and plume stability which may change over an extended timeframe;
- Whether the contamination, either by itself or as an accumulation with other nearby sources, will exert a long-term detrimental impact on available water or other environmental resources;
- Uncertainties regarding the mass of contaminants in the subsurface and predictive;
- Reliability of monitoring and of institutional controls over long time periods;
- Public acceptance of the timeframe required to reach remediation objectives; and
- Provisions by the responsible party for adequate funding of monitoring and performance evaluation over the time period required for remediation.

It should be noted that the timeframe required for MNA remedies is often longer than that required for more active remedies. As a consequence, the uncertainty associated with the above factors increases dramatically. Adequate performance monitoring and contingency remedies are required to be utilised because of this higher level of uncertainty.

Time-based estimates are used to predict the time required for MNA to achieve remediation objectives and distance-based estimates provide an evaluation of whether a plume will expand, remain stable or shrink. For environmental decision-making, EPA requires that the data used be of "adequate quality and usability for their intended purpose" (US EPA, 1999).

The EPA or other regulatory authorities thus considers a number of factors when evaluating reasonable timeframes for MNA at a given site. These factors, on the whole, should allow the overseeing regulatory authority to determine whether a natural attenuation remedy will fully protect potential human and environmental receptors and whether the site remediation objectives and the time needed to meet them are consistent with the regulatory expectation that contaminated groundwater will be restored to beneficial uses within a reasonable timeframe. When these conditions cannot be met using MNA, a remedial alternative more likely to meet these expectations is recommended.

4.1.5 Guidelines and Technical Protocols for implementation of MNA in the US

From the above, it is clear that although most of the legislation on contaminated land management is enacted by the federal government, the US EPA has delegated authority to many states to implement their own programmes. Therefore many of the states have their own guidelines on the implementation of remediation programmes. Examples of these guidelines and technical protocols will be discussed in the following sections.

Often these state requirements are even more stringent than the requirements established by the EPA (Rügner and Teutsch, 2002). In a survey in 1997 performed on partners in the RBCA-programme, it was revealed that of the 21 States which responded, 15 accepted NA as a remedy, 3 did with some restrictions and 3 did not accept NA as a remedial strategy. Wiedemeier et al. (1999) gives a complete overview on programmes for implementation of NA in the individual states.

4.1.5.1 US Air Force/ EPA Technical Protocols for evaluating NA

The first protocols for the implementation of NA were published by the US Air Force together with the US EPA (Rügner and Teutsch 2002). These included a technical protocol for the implementation of NA at Fuel contaminated sites (Wiedemeier *et al.*, 1994) and a technical protocol for the implementation of NA at Chlorinated Solvent contaminated sites (Wiedemeier *et al.*, 1998).

The protocols provided precise guidance for data acquisition and evaluation with respect to NA as a remedial option. From previous experience, the US Air Force and EPA have concluded that the level of site investigation was often not sufficient to prove that NA processes take place on site. The protocols are therefore very clear on the additional data which should be collected in order to prove scientifically, that NA takes place at a site.

The OSWER directive (US EPA, 1999) and US Air Force protocols are closely related, but with some differences. The OSWER Directive requires that there is a decrease in the contaminant mass "over time" (which can only be achieved for shrinking plumes), whereas the protocol only requires a decrease along the flow path downgradient of a contaminant source, which can be observed also for stable plumes. The OSWER Directive further requires "clean-up of contaminant zones" as a prerequisite.

The protocol presents a technical course of action to be taken in order to scientifically document and quantify NA processes at a site. It does however, not replace the OSWER Directive or state-specific guidance on conducting remediation investigations. The approach set out in the protocol includes the following nine steps:

1. Review available site data and develop a preliminary conceptual site model.

2. Perform a site screening and assess the potential for NA. (If evidence exists that NA can be successfully used as a remedy, then proceed to step 3; if not, then collect more data for site screening.)
3. Performance of additional site characterisation to support NA.
4. Refinement of site conceptual model.
5. Simulation of NA with use of a numerical (with exception, an analytical) model.
6. Identification of potential receptors and performance of an exposure pathways analysis.
7. Evaluation of additional measures for source remediation.
8. Preparation of long-term monitoring programme.
9. Presentation of all results to regulatory agencies.

4.1.5.2 Report of the National Research Council

In May 2000, a report was published by the National Research Council's (NRC's) Committee on Intrinsic Remediation. The purpose of this report was to examine public concerns about NA, the scientific bases for NA and the criteria for evaluating the potential success or failure of NA.

The NRC appointed a committee in 1997 in response to concerns from some scientists that the use of natural attenuation may be outpacing scientific understanding and from others, that unwarranted doubts about natural attenuation are preventing its wider use. The committee included members with expertise in all of the scientific disciplines needed to understand natural subsurface processes, the effects of these processes on contaminants and sociopolitical factors that influence the selection of remedies for contaminated sites. The findings were based on the expertise of committee members, a careful review of numerous documents and protocols concerning NA, interviews with other experts and community leaders involved at contaminated sites and four public information gathering meetings.

The principal findings of the report were:

- That NA is an established remedy for only a few types of contaminants;
- Rigorous protocols are needed to ensure that NA potential is analysed properly;
- NA should be accepted as a formal remedy for contamination only when the processes are documented to be working and are sustainable; and
- Where communities are affected by contamination, community members must be provided with documentation of these processes and an opportunity to participate in decision making.

Several recommendations are made in the report. One of the important recommendations was with regard to the establishment of suitable protocols for NA as a remedy and the requirements for such protocols.

4.1.5.3 Wisconsin Department of Natural Resources – Guidance document for implementation of NA at chlorinated hydrocarbon contaminated sites

This guidance document is an example of a state specific guideline. Principals are based on the OSWER Directive and other EPA endorsed guidelines/protocols. The intent of the document is to provide guidance on characterising and monitoring sites where MNA of chlorinated hydrocarbons is being considered as part of a clean-up remedy (Carey et al., 2003).

The guidelines require that all sites with chlorinated hydrocarbon contamination of soil or groundwater should identify the:

1. Degree and extent of contamination, including the presence of residual or mobile non-aqueous phase liquid (NAPL).
2. Geological and hydrogeological controls on contaminant migration.
3. Degradation patterns for contaminants and changes in geochemical species.
4. Factors driving degradation of the chlorinated contaminants and to determine whether those factors will continue to function until clean-up standards are met.
5. Rate of mass loss of contaminants and an estimate of a clean-up time frame.
6. Long-term monitoring programme that will be implemented to verify that clean-up goals will be met.
7. Contingency plan(s) if MNA fails or land use changes.

This guidance document is for responsible parties, consultants or other interested parties and Department of Natural Resources (DNR) staff. It is recommended that the document should not be used as the sole reference for understanding or evaluating NA processes. Rather, it is to be used along with published references, state of the practice research and development, information from training courses and current journals.

4.2 Other International Protocols and Guidelines

4.2.1 Guidance on the Assessment and Monitoring of Natural Attenuation of Contaminants in Groundwater - UK Environment Agency

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'. MNA is a valid risk management approach for polluted groundwater in England and Wales. However, approaches to demonstrate the effectiveness of natural processes at remediating groundwater in England and Wales have varied widely.

The Environment Agency has made a clear distinction between natural attenuation (NA) and monitored natural attenuation (MNA) in the development of their guidance (Carey *et al.*, 2000). 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.

In verifying the performance of MNA, the main criteria for acceptance by the UK Environment Agency are (Carey et al., 2000):

- 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.

4.2.2 Other European guidance/protocols

Rügner and Teutsch (2001) summarise other guidelines which are available in Member Countries of the EU. These include guidelines for remediation of contaminated sites in Denmark and the Decision Support System (DSS) developed in the Netherlands (the DeMonA tool forms part of this DSS). The Danish approach is similar to other risk-based methodologies. The DSS is a simple tool for use by site owners and regulators for evaluating the chances of use of MNA as a remedy for a site. Four steps are considered:

1. Analysis of data (screening of historical and other site data).
2. Use of a solute and transport model (proof that NA is occurring and/or predicting plume behaviour).
3. Discussion with regulators.
4. Implementation of NA as remedy.

Several other pilot studies and projects have been initiated by European partners (Nicole, Nobis, FP6, etc.) and from all of these, it is expected that clearer and more uniform guidelines will soon be available for implementation of MNA in these countries.

4.3 Risk-Based Corrective Action

The European and UK approaches rely strongly on the risk associated with the contaminant and the effect of NA on this risk to regulate MNA. Such an approach protects the end user and ensures that MNA is the most appropriate mitigation option to be followed.

Risk-based decision making is a key to cost effective and appropriate implementation of MNA in South Africa. As such a short overview of the most well-known risk assessment procedure, RBCA is given as a discussion of some the main issues. While RCBA in the traditional sense is petroleum specific, the concepts have wider application to contaminant hydrogeology, including DNAPLs.

4.3.1 Overview of Risk-Based Corrective Action

Risk-based Corrective Action (RBCA) is a decision-making process for assessment and response to subsurface contamination associated with petroleum hydrocarbon releases. The guidelines for RBCA are published in the American Society for Testing Materials (ASTM E-1739-95). RBCA integrates EPA risk assessment practices with traditional site investigation and remedy selection activities in order to determine cost-effective measures for the protection of human health and environmental resources.

Under this integrated approach, sites are characterised in terms of sources, transport mechanisms and receptors. Remedial measures are then applied as needed to prevent human health or environmental exposure to harmful levels of site constituent. Risk-based Corrective Action may be used by addressing any step in the exposure process such as (Connor et al., 1995):

- Removing or treating the source
- Interrupting contaminant transport mechanisms or
- Controlling activities at the point of exposure.

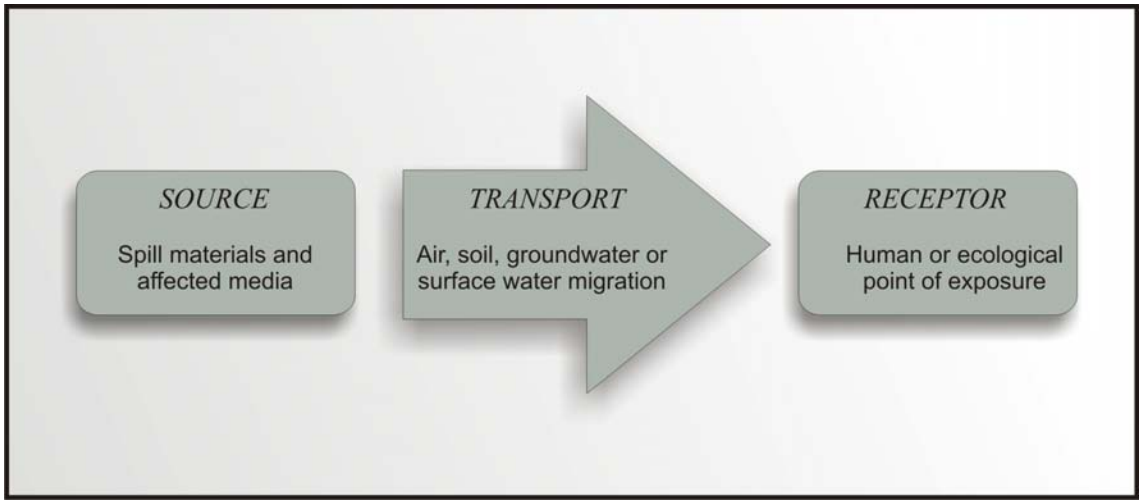

Figure 4: Conceptual Exposure Model

Under RBCA, risk management strategies are developed and implemented in accordance with the process flowchart as shown below (Figure 5). Based on the available site information, a site classification step is completed to characterise the relative magnitude and immediacy of site risks and to prescribe immediate response actions (Step 2). After any acute or near-term hazards have been properly addressed, risk-based clean-up standards are developed to protect against potential chronic health or environmental impacts associated with long-term exposure to low levels of contaminants (Steps 3 -7). To achieve the final risk management goals, the remedial action programme may involve:

- Source removal/treatment
- Containment measures
- Institutional controls and
- Some combination thereof.

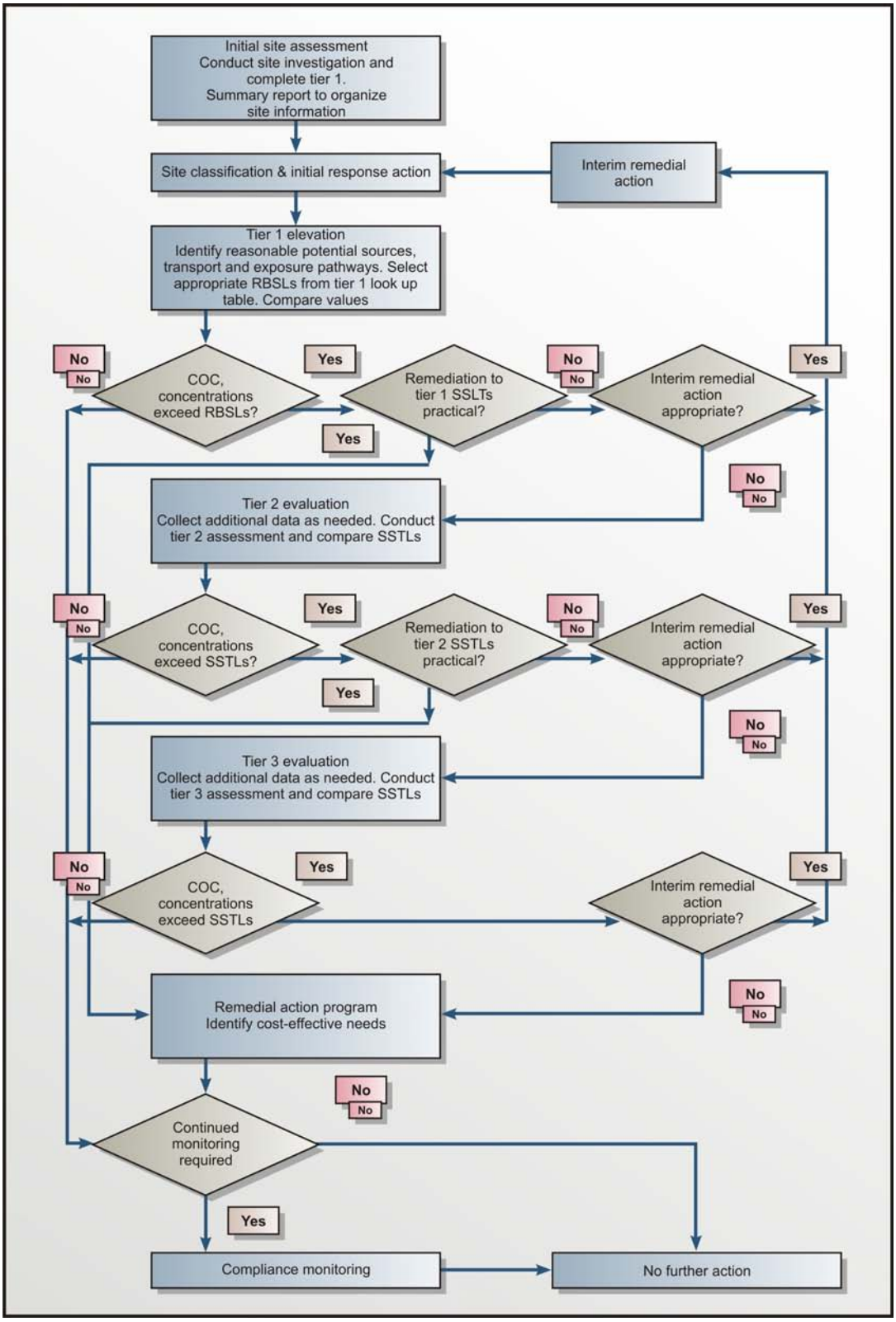

Figure 5: RBCA Process flowchart

4.3.2 Significance and use

RBCA is commonly used by the petroleum industry. It represents a consistent, streamlined decision process for selecting corrective actions at petroleum sites. Since risk assessment is a developing science, the risk-based screening levels (RBSLs) and the site-specific target levels (SSTLs) may vary by user, depending on the regulatory requirements and the use of other methods. The advantages of the approach are (ASTM, 1995):

- Decisions are based on reducing the risk of adverse human or environmental impacts
- Site assessments activities are focused on collecting only information that is required for risk-based corrective actions
- Resources are focused on sites that pose the greatest risk
- Remedial action achieves an acceptable level of exposure and risk reduction
- Compliance may be evaluated relative to site-specific standards applied at site-specific points of compliance

4.3.3 RBCA site Classification

Under the RBCA planning process, sites are first classified with regard to the current magnitude and immediacy of human health and environmental risks. Appropriate emergency actions are then implemented without delay to address acute hazards or near-term impacts. Under the classification scheme outlined in ASTM E-1739, applicable exposure scenarios are reviewed to match the site with one of the four qualitative risk categories indicated in Table 8 below. For each classification, an appropriate response action is prescribed to effectively manage the potential site hazards as the site evaluation and remediation process. As shown in Table 8, remedial actions are expected at near-term high-risk sites, while an interim monitoring system is required for long-term, low-risk sites. This site classification represents a 'snapshot' in time, addressing hazards associated with current site conditions and land use.

Table 8: RBCA site classification and response actions (Connor et al., 1995)

Current Hazard	Site Classification	Initial Response Action
Acute	Class1: Immediate Threat	Abate release
Chronic	Class 2: Near-Term Threat (0-2 years) Class 3: Future Threat (>2 years)	Monitor/Remediation Monitor/Investigate
Aesthetic	Class 4: No Current Demonstrable Risk	Monitor only

4.3.4 Tiered Evaluation of Risk-Based Standards

To address chronic human health or environmental hazards, site remediation requirements are evaluated on the basis of risk-based soil and groundwater clean-up goals, developed in accordance with US EPA risk assessment guidelines. To provide for economical use at both small and large facilities, the RBCA process has been designed to match the site evaluation effort to the relative risk or complexity of each site. For this purpose, a tiered approach is employed for the determination of risk- based clean-up goals, involving increasingly sophisticated levels of data collection and analysis. Upon completion of each sequential tier, the user reviews the results to determine whether further data collection and evaluation are warranted. For the purpose of efficiency, the site investigation steps and decisions involved in this process are indicated on the RBCA flowchart. The scope of Tiers 1, 2, and 3 are as follows (Connor et al., 1995):

4.3.4.1 Tier 1: Generic Screening-Level Corrective Action Goals

Tier 1 of the RBCA process involves comparison of site constituent concentration to generic Risk-Based Screening Levels (RBSLs), to determine whether further evaluation is required. RBSL values are derived from standard exposure equations and reasonable maximum exposure (RME) estimates per US EPA guidelines. As shown RBSL concentration limits are designed to be protective of human health even if exposure occurs directly within the on-site area of affected soil or groundwater (i.e. the 'source zone').

If Tier 1 limits are not exceeded, the user may proceed directly to compliance monitoring and/or no further action. However, if these generic levels are exceeded, the affected media may be addressed by:

- Remediating to the generic Tier 1 limits, if practicable,
- Conducting a Tier 2 evaluation to develop site-specific remediation goals, or
- Implementing an interim action to abate risk 'hot spots'.

In general, the Tier 1 evaluation serves to identify sites requiring no further action. For most sites exceeding Tier 1 limits, a Tier 2 analysis will provide a more cost-efficient basis for evaluation of appropriate remedial measures.

4.3.4.2 Tier 2: Site-Specific Corrective Action Goals

Under Tier 2, Site-Specific Target Levels (SSTLs) for soil and groundwater clean-up, goals are determined on the basis of site-specific information and/or points of exposure. Simple analytical models are employed in conjunction with additional site data to calculate Tier 2 SSTL values in a manner consistent with EPA recommended practices. Modelling and calculation procedures are streamlined so as to represent a minor incremental effort relative to Tier 1. Both the Tier 1 RBSL and Tier 2 SSTL values represent concentration limits for constituents within the source zone. However, SSTLs differ from RBSLs in three significant ways:

- Site-specific data are used to calculate risk-based clean-up goals
- Human exposure to affected media may be assumed to occur not at the source zone, but at a separate 'point of exposure' (POE) and
- The effects of natural attenuation of constituent concentration during lateral transport from the source to an off-site POE may be considered in the SSTL calculation

If site constituent concentrations exceed SSTL values, subsequent actions may involve the following:

- Remediation to site specific Tier 2 clean-up goals
- Further evaluation per Tier 3 of the RBCA process
- Interim response measures targeted at principal risk sources

4.3.4.3 Tier 3: Site-Specific Corrective Goals

If Tier 2 results are judged inappropriate or impracticable, a Tier 3 evaluation may be conducted to refine Tier 2 corrective action goals on the basis of a more complex risk and exposure assessment, involving more detailed site information, probabilistic data analysis, and/or numerical fate and transport modelling. Such Tier 3 evaluation will typically entail significant additional data and expense relative to Tiers 1 and 2 and should therefore be **reserved for highly complex, cost-significant sites**. Tier analysis may be warranted at sites for

which Tier 2 modelling methods are non-conservative or where detailed ecological impact assessment is required.

Similar to Tier 2, the Tier 3 evaluation provides source zone clean-up levels designed to protect against health or environmental impacts at a site-specific point of exposure (POE). The tiered evaluation process concludes upon derivation of applicable and remediation standards.

It should be noted that the soil and groundwater standards developed under Tier 1, 2, and 3 are equally protective of human health and the environment, based on applicable target risks and exposure criteria. However, with each tier upgrade, the degree of uncertainty and conservation involved in the clean-up standard calculation is reduced, based upon a more detailed characterisation of actual site condition. As indicated on the RBCA process flowchart, the user reviews the results of each tier to determine if further evaluation is necessary (Connor et al., 1995).

For DNAPL contaminated sites in South Africa Tier 3 level risk assessment will be needed for MNA acceptance.

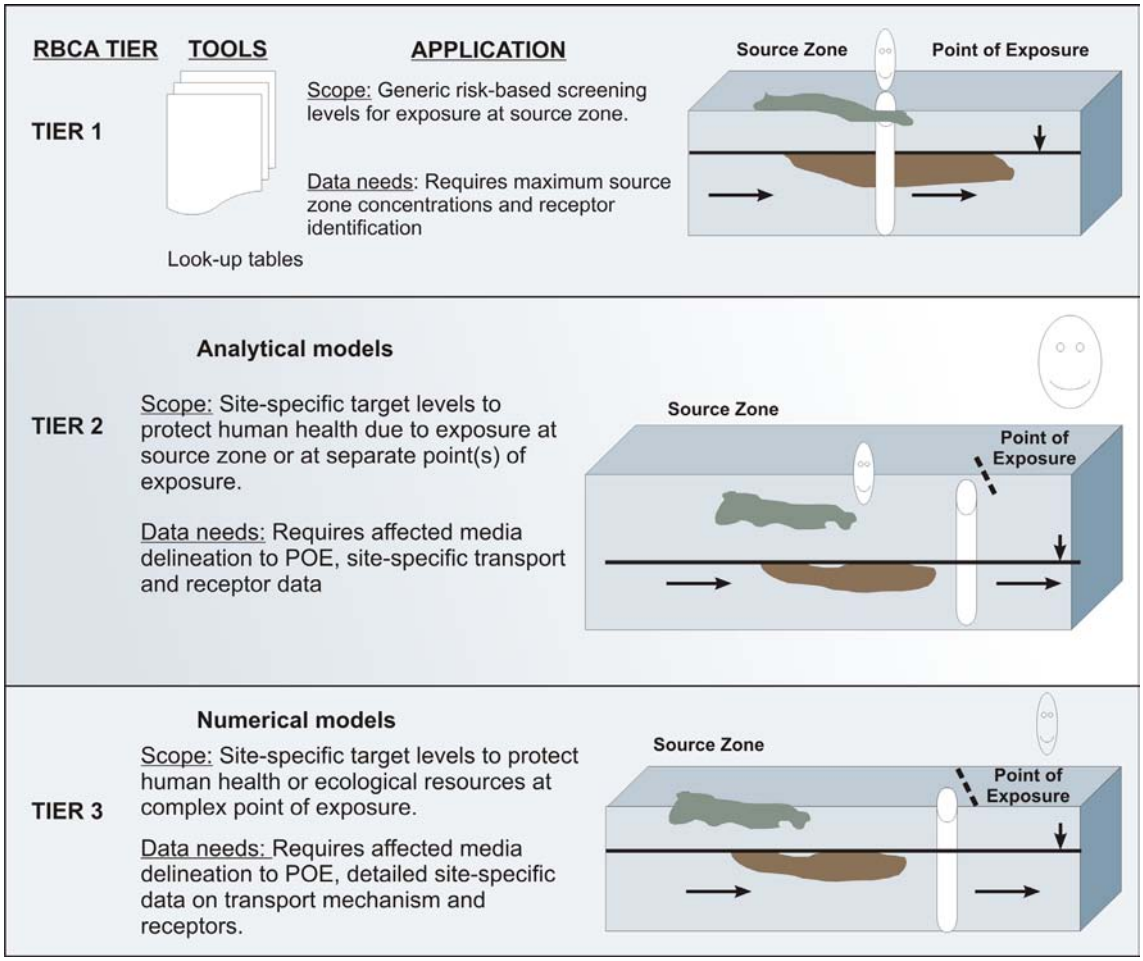

Figure 6: Overview of Tiered Process for Cleanup Goal Calculation

5. SITE CHARACTERISATION METHODS FOR MNA

Because MNA is a knowledge-based remedy, it is critical that an adequate site investigation be conducted. Typically, MNA sites will require more thorough site investigation than sites where only active remedies are applied. Investigators need a better understanding of the variability in the subsurface (which controls physical, chemical and biological processes) combined with the expected natural degradation processes if they are properly to apply MNA as a remedy. Sound data collection during the site investigation will improve the reliability of the site conceptual model and site analytical or numerical models. A single effort at site investigation will rarely result in the complete assessment of a contaminant source and groundwater plume. An iterative site investigation is recommended to delineate successfully the source and plume (Carey et al., 2003).

This section provides the reader with a framework for a contaminated site that may be used to review data to evaluate whether the NA of contaminants is occurring, to identify and collect additional data to support the three lines of evidence (Section 4.1.2.1) and to integrate NA into a long-term site remediation/management strategy.

Most of the guidelines and protocols described in previous chapters (Wiedemeier et al., 1994; Wiedemeier et al., 1998; Carey et al., 2003; Sara, 2003) place great emphasis on the site investigation/characterisation of contaminated sites, because the decision to support MNA as a remedy is obviously based on the outcome of these investigations. It is recommended that the investigations are performed in a step-wise manner with a review of data after the completion of each step.

Wiedemeier et al., 1998 gives the following steps for evaluating natural attenuation:

1. Review available site data and develop a preliminary conceptual model.
2. If sufficient existing data of appropriate quality exist, apply the screening process to assess the potential for natural attenuation.
3. If preliminary site data suggest natural attenuation is potentially appropriate, perform additional site characterisation to further evaluate natural attenuation.
4. Refine conceptual model based on site characterisation data, complete pre-modelling calculations and document indicators of natural attenuation.
5. Simulate, if necessary, natural attenuation using analytical or numerical solute fate and transport models that allow incorporation of a biodegradation term.
6. Identify potential receptors and exposure points and conduct an exposure pathways analysis.
7. Evaluate the need for supplemental source control measures.
8. Prepare a long-term monitoring and verification plan for the selected alternative. In some cases, this includes monitored natural attenuation alone or in other cases, in concert with supplemental remediation systems.
9. Present findings of natural attenuation studies in an appropriate document for regulators.

5.1 Review of Available Site Data and Development of Preliminary Conceptual Model

The first step in evaluating NA is to review available site data. If there have been previous investigations or on-going monitoring of groundwater contamination on a site, these data are now collected and reviewed. A thorough review of these data also allows development of a preliminary conceptual model. The preliminary conceptual model should help identify any shortcomings in the data and will facilitate placement of additional data collection points in the most scientifically advantageous and cost-effective manner possible.

The following site information should be obtained during the review of available data. If information is not available for this initial review, it should be collected during subsequent site investigations when refining the site conceptual model.

- The nature, extent and magnitude of the contamination. This includes the type of release and the 3-D distribution of dissolved contaminants and mobile and residual NAPLs.
- Groundwater and soil chemical data.
- Historical water quality data showing variations in contaminant concentrations both vertically and horizontally.
- Chemical and physical characteristics of the contaminants.
- Potential for biodegradation of the contaminants.
- Potential for natural attenuation to increase toxicity and/or mobility of natural occurring metals.
- Geologic and hydrogeological data in three dimensions
    - Lithology and stratigraphic relationships.
    - Grain-size distribution
    - Aquifer hydraulic conductivity
    - Groundwater flow gradients and potentiometric or water table surface maps (over several seasons, if possible).
    - Preferential flow paths.
    - Interactions between groundwater and surface water and rates of infiltration/recharge.
- Locations of potential receptor exposure points: Groundwater production and supply boreholes and areas that may be deemed a potential source of drinking water. Additionally, down-gradient and cross-gradient discharge points including any discharges to surface waters or other ecosystems.

In some cases, site-specific data will be limited. In such a case, all future site characterisation activities should include collecting the data necessary to screen the site for the use of monitored natural attenuation as a potential site remedy. Much of the data required to evaluate natural attenuation may be used to design and evaluate other remedial measures.

This available site characterisation data should now be used to develop a conceptual model for the site. This conceptual model is a three-dimensional representation of the source area as a NAPL or region of highly contaminated groundwater, of the surrounding uncontaminated area, of groundwater flow properties and of the solute transport system based on available geological, biological, geochemical, hydrological, climatological and analytical data for the site. A successful conceptual model development thus involves the clear definition of the problem to be solved (generally the three-dimensional nature, magnitude and extent of existing and future contamination) and the geologic and hydrogeological setting in which the problem exists.

5.2 Site Screening for Assessment of potential for NA

After reviewing available site data and developing a preliminary conceptual model, an assessment of the potential for natural attenuation must be made. As stated previously, existing data can be useful to determine if natural attenuation is capable of attaining site-specific remediation objectives in a time period that is reasonable compared to other alternatives. This is achieved by first determining whether the plume is currently stable or migrating and the future extent of the plume based on (1) contaminant properties, including volatility, sorptive properties and biodegradability; (2) aquifer properties, including hydraulic gradient, hydraulic conductivity, porosity and concentrations of native organic material in the sediment and (3) the location of the plume and contaminant source relative to potential receptor exposure points. These parameters (estimated or actual) are

used in this section to make a preliminary assessment of the effectiveness of natural attenuation in reducing contaminant concentrations.

This screening process may be approached in several ways. Sara (2003) lists five questions related to the 'lines of evidence' in the OSWER directive and recommends further action depending on the answers. Other protocols (Wiedemeier et al., 1998, Carey et al., 2004) have tables with specific screening values which, according to a scoring system, dictate the successive steps to be followed. An example of such screening criteria may be seen in Table 9.

Samples should be analysed for the parameters listed in such tables and the data used to determine if biodegradation is occurring. Some tables contain scoring values that can be used as a test to assess the likelihood that biodegradation. This method relies on the fact that biodegradation will cause predictable changes in groundwater chemistry (Wiedemeier, provides the range of redox conditions under which different dominant transformations will occur.

After it has been shown that biodegradation is occurring, it is important to quantify groundwater flow and solute transport parameters. This will make it possible to use a solute transport model to estimate quantitatively the concentration of the plume and its direction and rate of travel. To use an analytical model, it is necessary to know the hydraulic gradient and hydraulic conductivity for the site and to have estimates of porosity and dispersivity. To determine the groundwater flow and solute transport direction, it is necessary to have at least three accurately surveyed boreholes in each hydrogeological unit of interest at the site. The porosity and dispersivity are generally estimated using accepted literature values for the aquifer matrix materials containing the plume at the site. If the investigator has the total organic carbon data for soil, it is possible to estimate the coefficient of retardation; otherwise, it is conservative to assume that the solute transport and groundwater velocities are the same.

Further data that need to be collected during the screening process as model input parameters include the distance between the source of contamination and any potential down-gradient or cross-gradient receptor exposure and the biodegradation rate of the contaminants. If it is not possible to determine site-specific biodegradation rates, then the literature values may be used in a sensitivity analysis. A useful approach is to start with average values and then to vary the model input to predict 'best-case' and 'worst-case' scenarios. However, estimated biodegradation rates may be used only after it has been shown that biodegradation is occurring.

At this early stage in the natural attenuation demonstration, comparison of the rate of solute transport to the rate of attenuation may be accomplished using an analytical model. Several models are available (BIOSCREEN, BIOPLUME, BIOCHLOR, etc.). It is suggested that the decay option be first in order of use in any of the models.

Table 9: Parameters for Preliminary Screening for Anaerobic Biodegradation Processes

(Wiedemeier et al., 1998)

Analysis	Concentration in Most Contaminated Zone	Interpretation
Oxygen*	<0.5 mg/L	Tolerated, suppresses the reductive pathway at higher concentrations
Oxygen*	>5 mg/L	VC may be oxidised aerobically
Nitrate*	<1 mg/L	At higher concentrations may compete with reductive pathway
Iron II*	>1 mg/L	Reductive pathway possible; VC may be oxidised under Fe(III)-reducing conditions
Sulphate*	<20 mg/L	At higher concentrations may compete with reductive pathway
Sulphide*	>1 mg/L	Reductive pathway possible
Methane*	<0.5 mg/L >0.5 mg/L	VC oxidises Ultimate reductive daughter product, VC Accumulates
ORP	<50 (mV) <-100mV	Reductive pathway possible Reductive pathway likely
pH*	5 < pH < 9 5 > pH >9	Optimal range for reductive pathway Outside optimal range for reductive pathway
TOC	> 20 mg/L	Carbon & energy source; drives decolourisation; natural/ anthropogenic
Temperature*	> 20°C	At T >20°C biochemical process is accelerated
Alkalinity	>2x background	Results from interaction between CO_2 and aquifer minerals
Chloride*	>2x background	Daughter product of organic chlorine
Hydrogen	>1 nM	Reductive pathway possible, VC may accumulate
Hydrogen	<1 nM	VC oxidised
Volatile Fatty Acids	> 0.1 mg/L	Intermediates resulting from biodegradation of aromatic compounds; carbon and energy source
BTEX*	> 0.1 mg/L	Carbon and energy source; drives dechlorination
PCE		Material released
TCE		Material released Daughter product of PCE
DCE*		Material released Daughter product of TCE. If cis is > 80% of total DCE it is likely a daughter product 1,1-DCE can be chemical reaction product of TCA
VC*		Material released Daughter product of DCE
1,1,1-TCA		Material released
DCA		Daughter product of TCA under reduction conditions
CCl4		Material released
Chloroethane*		Daughter product of DCA or VC under reduction conditions
Ethene/Ethane	>0.01/>0.1 mg/L	Daughter product of VC/ethane
Chloroform		Material released Daughter Product of Carbon Tetrachloride
DCM		Material released Daughter Product of Chloroform

* Required analysis. a/ Points awarded only if it can be shown that the compound is a daughter product (i.e. not a constituent of the processes on site)

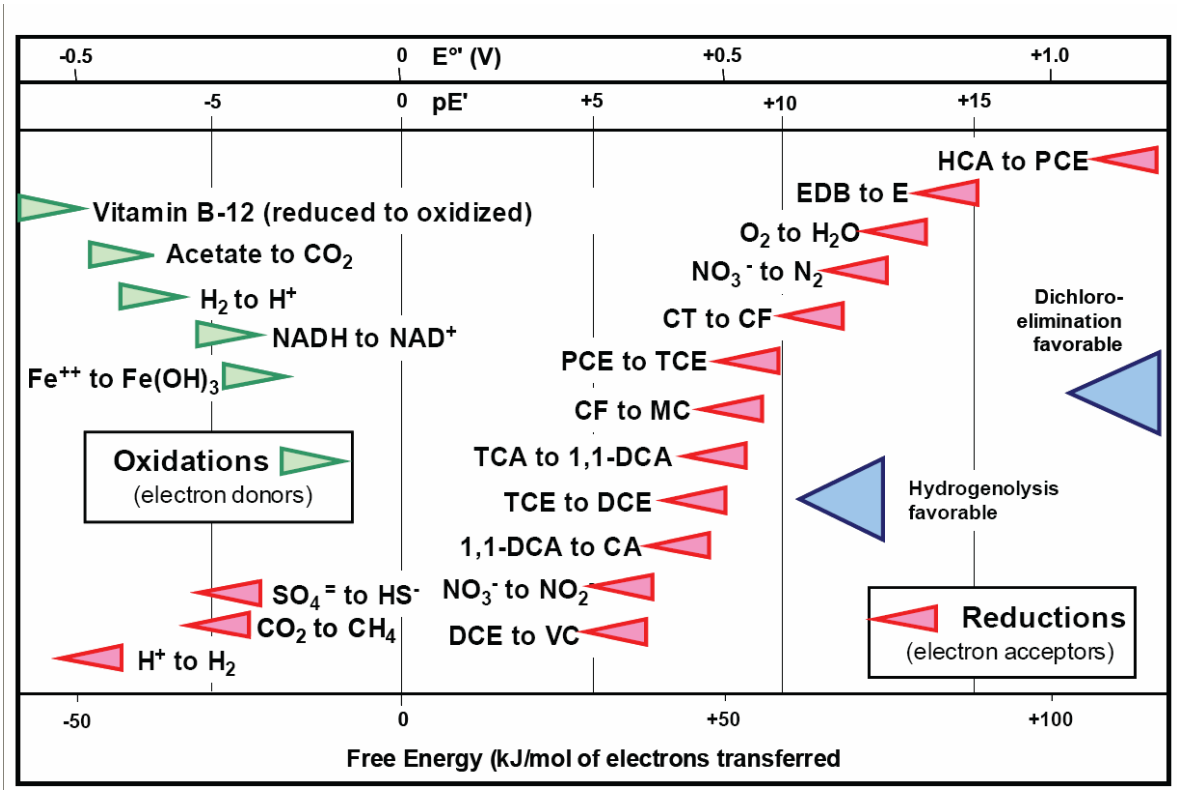

Figure 7: Half-reaction potentials of environmentally relevant redox reactions (ITRC, 2005)

The primary purpose of comparing the rate of transport to the rate of natural attenuation is to determine if natural attenuation processes will be capable of attaining site-specific remediation objectives in a time period that is reasonable compared to other alternatives. For the purposes of the screening effort, if modelling shows that the screening criteria are met, the investigator can proceed with the natural attenuation evaluation.

5.3 *Additional site characterisation to support NA*

Once the site investigator has proved through the preliminary conceptual model, the screening process and predictive modelling that NA is a viable option as a remedy at a contaminated site, a critical review of all data is required. This will allow for identification of data gaps and guide the most effective placement of additional data collection points.

The goals of the site investigation from here on are to determine if natural mechanisms of contaminant attenuation are occurring at rates sufficient to attain site-specific remediation objectives in a time period that is reasonable, compared to other alternatives and to provide sufficient site-specific data to allow prediction of the future extent and concentrations of a contaminant plume through solute fate and transport modelling. Table 10 gives a summary of data collection which will be required during this phase of the site characterisation. Due to the often complex nature of contaminated sites, the site investigator should always sample and evaluate the *three-dimensional character* of the site with respect to (1) interaction of contaminant releases with the aquifer matrix material, (2) local hydrological features that control development and migration of plumes and (3) the geochemical interactions that favour bio-attenuation of contaminants.

Table 10: Data Collection required for Evaluation and Implementation of Natural Attenuation

(Adapted from Sara, 2003)

Parameter	Data Type	Ideal Use, Value, Status and Comments	Method
Geological			
Area geology	Topography/soil type/surface water/climate	Provides information of groundwater flow systems, recharge/discharge areas, infiltration rates, evaluation of geological deposits with regard to aquifer/aquitard properties	Geological/soil/topographic maps, aerial photographs and field geological mapping.
Hydrogeological			
Subsurface geology	Lithology/stratigraphy/structure	Identify water-bearing units, thickness, confined/ unconfined aquifers, effect on groundwater flow and direction (anisotropy)	Hydrogeologic surveys/maps
			Review soil boring and borehole logs
			Surface and subsurface geophysics
Velocity	Hydraulic conductivity/ permeability	Saturated hydraulic conductivity of geological matrix. Calculate specific discharge and if site is complex vertical and horizontal conductivity	Estimate range base on geology
			Pump or slug tests
			Grain size analyses
			Permeability testing
			Downhole flowmeter
			Tracer and dilution tests
	Gradient	Measure potential of fluid to move (hydraulic gradient)	Water table and piezometric surface measurements
	Porosity	Measures the soil/matrix pore space. Specific discharge divided by porosity gives average groundwater velocity	Estimate range base on geology
			Measure bulk and particle mass density
Direction	Flow field	Estimate direction of groundwater flow	Water and piezometric contour maps
			Downhole flowmeter
Dispersion/sorption	f_{oc}	Fraction of organic carbon is used to estimate the retardation of chemical migration relative to the average groundwater velocity	Measure from soil/rock samples, estimate from published values or use reactive and non-reactive tracers in groundwater
	Dispersion	Longitudinal and horizontal dispersion spreads out the chemical(s)along the flow path	Estimate based on the distribution of chemicals or use tracer testing

Parameter	Data Type	Ideal Use, Value, Status and Comments	Method
Chemistry			
Organic chemistry	VOCs	Identify parent chemicals and degradation products, and assess distribution. Certain isomers/degradation products provide direct evidence of biodegradation while others are formed due to abiotic degradation. Some aromatic hydrocarbons and ketones can support biodegradation of cVOCs	Purge and trap GC-MS analyses (Based on US EPA method 8260)
	Semi-VOCs	Selected SVOCs can support biodegradation of cVOCs	GC-MS analyses (Based on US EPA method 8270)
	Volatile Fatty Acids	Some organic chemicals (e.g. acetic acid) can provide insight into microbial activity	Standard analytical methods, published modified methods using ion chromatography
	Methane, ethane, ethene, propane and propene	Provides evidence of dechlorination of chlorinated methanes, ethenes and ethanes. Methane also indicates activity of methanogenic bacteria. Isotope analysis of methane can b e used to determine its origin.	Modified analytical methods, GC-FID
	TOC/BOD/COD/TPH	Potential availability of general growth substrates.	Analytical method depended on parameter and laboratory
Inorganic Chemistry	Alkalinity	Increased levels is indicative of carbon dioxide production	Analytical method depended on parameter and laboratory
	Chloride	Provides evidence of dechlorination. Possible use in mass balancing and as conservative tracer. Care should be taken when interpreting chloride data.	Analytical method depended on parameter and laboratory
	Conductivity	Assess overall water quality of water samples and indicate possible flow patterns across the well depth.	Field electrode measurement and downhole probe measurement.
	Dissolved Oxygen	Indicator of aerobic environments, electron acceptor.	Preferable to take field measurement/ downhole probe or through flow cell.
	Iron	Nutrient, ferrous indicates activity of iron reducing bacteria. Ferric is used as electron acceptor.	Analytical method depended on parameter and laboratory
	Manganese	Nutrient, indicator of iron and manganese reducing conditions.	Analytical method depended on parameter and laboratory
	Nitrate	Used as electron acceptor by denitrifying bacteria, or is converted to ammonia for assimilation.	Analytical method depended on parameter and laboratory
	Nitrite	Produced from nitrate under anaerobic conditions.	Analytical method depended on parameter and laboratory
	Phosphorous	Limiting nutrient	Analytical method depended on parameter and laboratory

Parameter	Data Type	Ideal Use, Value, Status and Comments	Method
	Sulphate	Used as electron acceptor. Changes in its concentration may provide evidence of activities of sulphate reducing bacteria.	Analytical method depended on parameter and laboratory
	Sulphide	May provide evidence of sulphate reduction. May not be detected because it may react with various oxygenated chemical species and metals.	Analytical method depended on parameter and laboratory
	Toxic metals	Presence of these metals may reduce microbial activity.	Analytical method depended on parameter and laboratory
Physical/ inorganic	pH	Measurement of suitability of environment to support range of microbial species. Activity tends to be reduced in pH range outside of 5 – 9. Anaerobic organisms more sensitive to pH extremes.	pH can change rapidly and measurements are best taken on site with pH probe immediately after sample is taken or through a flow cell.
	Redox Potential	Measure of oxidation-reduction potential of the environment. Site and species specific and gives indication of aerobic or anaerobic conditions.	Field measurements with redox electrode. Flowcell or downhole measurements.
	Temperature	Help to correct temperature sensitive parameters and measuring devices.	
Microbiology			
Biomass	Micro-organisms Per Unit Soil or Groundwater	Microbial population density between impacted and non-impacted/treated areas can be compared to assess whether microbial populations are responsible for observed degradation. The value of biomass measurements is still being explored for cVOC biodegradation.	There are three general techniques available: culturing (plate counts, BioLog, MPN enumerations); direct counts (microscopy); and indirect measurement of cellular components (ATP, phospholipid fatty acids).
	Biodegradation Rate and Extent	Demonstrate the indigenous micro-organisms are capable of performing the predicted transformations. Determine nutrient requirements and limitations. Measure degradation rates and extent.	Varied. Shake flasks, batch, column, bioreactors designs.
	Species/Genera/ Functional Group	The presence of certain microbial species of functional groups (e.g. methanogenic bacteria) that have been correlated with cVOC biodegradation may be assessed. Research is being conducted to identify patterns of microbial composition that are predictive of successful cVOC biodegradation.	There are three general techniques available: culturing and direct counts; indirect measurement of cellular components; and molecular techniques (16s RNA, DNA probes, RFLP).

5.4 Refine the conceptual model

Conceptual model refinement involves integrating newly gathered site characterisation data to refine the preliminary conceptual model that was developed on the basis of previously collected site-specific data. During conceptual model refinement, all available site-specific data should be integrated to develop an accurate three-dimensional representation of the hydrogeological and contaminant transport system. This refined conceptual model may then be used for contaminant fate and transport modelling. Conceptual model refinement consists of several steps, including preparation of geologic logs, hydrogeologic sections, potentiometric surface/water table maps, contaminant and daughter product contour maps and electron acceptor and metabolic by-product contour maps.

The construction of conceptual models for DNAPL contaminated sites in South Africa will be discussed in detail in a subsequent deliverable report.

The first few steps are common practice during contaminant site characterisation and will not be discussed in more detail. The contaminant and daughter product maps are discussed in the following section.

5.4.1 Contaminant and Daughter Product Contour Maps

Contaminant and daughter product contour maps should be prepared for all contaminants present at the site for each discrete sampling event. Such maps allow for the interpretation of data on the distribution and the relative transport and degradation rates of contaminants in the subsurface (Wiedemeier et al., 1998). In addition, contaminant contour maps are necessary so that contaminant concentrations can be gridded and used for input into a numerical model. Detection of daughter products not present in the released NAPL (e.g. cis-1,2-DCE, VC, or ethene) provides evidence of reductive dechlorination.

If mobile and residual NAPLs are present at the site, a contour map showing the thickness and vertical and horizontal distribution of each should be prepared. These maps will allow interpretation of the distribution and the relative transport rate of NAPLs in the subsurface. In addition, these maps will aid in partitioning calculations and solute fate and transport model development. It is important to note that, because of the differences between the magnitude of capillary suction in the aquifer matrix and the different surface tension properties of NAPL and water, NAPL thickness observations made at monitoring points may not provide an accurate estimate of the actual volume of mobile and residual NAPL in the aquifer and values should be corrected to reflect the true thickness of NAPL phase.

5.4.2 Electron Acceptor, Metabolic By-product, and Alkalinity Contour Maps

Contour maps should also be prepared for electron acceptors consumed (dissolved oxygen, nitrate, and sulphate) and metabolic by-products produced [iron (II), chloride, and methane] during biodegradation. In addition, a contour map should be prepared for alkalinity and ORP. The electron acceptor, metabolic by-product, alkalinity and ORP contour maps provide evidence of the occurrence of biodegradation at a site. If hydrogen data are available, they should also be contoured.

During aerobic biodegradation, dissolved oxygen concentrations will decrease to levels below background concentrations. Similarly, during anaerobic degradation, the concentrations of nitrate and sulphate will be seen to decrease to levels below background. The electron acceptor contour maps allow the interpretation of data on the distribution of the electron acceptors and the relative transport and degradation rates of contaminants in

the subsurface. Thus, electron acceptor contour maps provide visual evidence of biodegradation and a visual indication of the relationship between the contaminant plume and the various electron acceptors.

Contour maps for iron (II), chloride, and methane allow interpretation of data on the distribution of metabolic by-products, resulting from the microbial degradation of fuel hydrocarbons and the relative transport and degradation rates of contaminants in the subsurface. During anaerobic degradation, the concentrations of these parameters will be seen to increase to levels above background.

Similarly, a contour map for total alkalinity (as $CaCO_3$) will allow visual interpretation of alkalinity data. Respiration of dissolved oxygen, nitrate, iron (III), and sulphate tends to increase the total alkalinity of groundwater. Thus, the total alkalinity inside the contaminant plume generally increases to levels above background.

5.4.3 Pre-Modelling Calculations

Several calculations must be made prior to implementation of the solute fate and transport model. These calculations include sorption and retardation calculations, NAPL/water partitioning calculations, groundwater flow velocity calculations and biodegradation rate-constant calculations. Examples of these calculations are found in various publications such as Carey et al., 2000, Weidemeier et al., 1998, etc.

5.5 Simulation of NA using a transport model

Simulating natural attenuation allows for the prediction of the migration and attenuation of the contaminant plume through time. Natural attenuation modelling is a tool that allows site-specific data to be used to predict the fate and transport of solutes under governing physical, chemical and biological processes. Hence, the results of the modelling effort are not in themselves sufficient proof that natural attenuation is occurring at a given site. The results of the modelling effort are only as good as the original data input into the model; therefore, an investment in thorough site characterisation will improve the validity of the modelling results. In some cases, straightforward analytical models of solute transport are adequate to simulate natural attenuation.

Several well-documented and widely accepted solute fate and transport models are available for simulating the fate and transport of contaminants under the influence of advection, dispersion, sorption, and biodegradation.

5.6 Identification of potential receptors and exposure pathway analysis

After the rates of natural attenuation have been documented and predictions from appropriate fate and transport models indicate that MNA is a viable remedy, the proponent of natural attenuation should combine all available data and information to provide support for this remedial option.

Supporting the natural attenuation option, generally will involve performing a receptor exposure pathways analysis. This analysis includes identifying potential human and ecological receptors and points of exposure under current and future land and groundwater use scenarios. The results of solute fate and transport modelling are central to the exposure pathways analysis. If conservative model input parameters are used, the solute fate and transport model should give conservative estimates of contaminant plume migration. From this information, the potential for impacts on human health and the environment from contamination present at the site may be assessed.

5.7 Evaluation of additional measures for source remediation

Additional source removal, treatment or containment measures, beyond those previously implemented, may be necessary for MNA to be a viable remedial option or to decrease the time needed for natural processes to attain site-specific remedial objectives.

If a solute fate and transport model has been prepared for a site, the impact of source removal can readily be evaluated by modifying the contaminant source term; this will allow for a re-evaluation of the exposure pathways analysis and it may also be used to forecast the benefits of source control by predicting the time required to restore the aquifer to drinking water quality and the reduction in contaminant loadings to sensitive ecosystems.

5.8 Preparation of long-term Monitoring plan

A long-term monitoring plan can be developed based on site characterisation data, analysis of potential exposure pathways and the results of solute fate and transport modelling. This plan is used to monitor the plume over time and to verify that natural attenuation is occurring at rates sufficient to attain site-specific remediation objectives and within the time frame predicted at the time of remedy selection. In addition, the long-term monitoring plan should be designed to evaluate long-term behaviour of the plume, verify that exposure to contaminants does not occur, verify that natural attenuation breakdown products do not pose additional risks, determine actual (rather than predicted) attenuation rates for refining predictions of the remediation time frame and to document when site-specific remediation objectives have been attained (Wiedemeier et al., 1998).

The design of such a monitoring plan is discussed in the following chapter. It should be noted that it is important that the long-term monitoring plan includes two types of monitoring boreholes. The boreholes should be designed with the purpose of determining if the behaviour of the plume is changing and performance evaluation boreholes are intended to confirm that contaminant concentrations meet regulatory acceptance levels and to trigger an action to manage potential expansion of the plume.

5.9 Presentation of findings

Upon completion of the previous eight steps, all findings should be presented to the regulatory agencies in a suitable format. The format of presentation will be dictated by the agency involved. However, this presentation must provide scientific documentation that allows an objective evaluation of whether MNA is the most appropriate remedial option for a given site.

All available site-specific data and information developed during the site characterisation, conceptual model development, pre-modelling calculations, biodegradation rate calculation, groundwater modelling, model documentation and long-term monitoring plan preparation phases of the natural attenuation investigation, should be presented in a consistent and complementary manner in the feasibility study or similar document. Of particular interest to the site decision makers, will be evidence that natural attenuation is occurring at rates sufficient to attain site-specific remediation objectives in a time period that is reasonable compared to other alternatives and that human health and the environment will be protected over time. Since a weight-of-evidence argument will be presented to support an MNA remedy, all model assumptions should be conservative and all available evidence in support of MNA should be presented (Wiedemeier et al., 1998).

6. MONITORING NETWORK DESIGN

6.1 Introduction

One of the final steps in ensuring that NA is an effective remedy at a contaminated site is the establishment of a long-term monitoring plan. If the results from the conceptual model and data analysis lead to the decision that natural attenuation is protective, long-term monitoring must then provide assurance that the site's protective processes continue to operate over time (NRC, 2000). Monitoring within the plume is necessary to ensure that reactions that destroy the contaminants continue to be active. Monitoring the down-gradient from the plume is necessary to ensure that contaminants are not migrating beyond the zone in which NA is supposed to take place. Monitoring frequency, intensity and duration will vary with the complexity of the site, groundwater flow direction and velocity and plume transport speed.

However, regardless of the site conditions, the monitoring will have to continue until it demonstrates that NA has succeeded in achieving the required clean-up goals or that NA has failed in achieving clean-up standards and a contingency plan has to be implemented. Sites at which NA is a formal remedy should have an exit strategy specifying when long-term monitoring of NA can stop (NRC, 2000).

Because the media of primary concern will be groundwater at many sites, it should be the focus of the monitoring network design. However, monitoring of other media (e.g. indoor air, soil gas, soils, surface water and sediments) may be necessary to determine possible impacts to receptors and other measures of remedial effectiveness. Interactions of groundwater and surface water should also be considered when designing a monitoring network. The focus of the following discussion is primarily on the monitoring of groundwater, as this is often an exposure pathway of significant concern.

A monitoring system designed for evaluating the performance of an MNA with respect to specific site clean-up objectives may be very different from the network established during earlier phases of site characterisation, feasibility studies or interim actions (Pope et al., 2004). Existing boreholes are often incrementally installed for different purposes, such as defining the extent of contamination during the remedial investigation or evaluating an engineered remedy during a feasibility study. The location and number of these boreholes may not be well suited for MNA performance monitoring. The network should be designed to provide data to demonstrate attainment of all the remedial action objectives for an MNA remedy.

Because a plume is a dynamic, three-dimensional distribution of contaminants in the subsurface that generally necessitates three-dimensional monitoring, plume shape is influenced by many factors, including original source distribution, geology, hydrology and biological processes. The resulting spatial and temporal variability significantly impact the choice of monitoring locations and frequencies and necessitate continual re-evaluation of the performance monitoring network. The density of sampling points in a monitoring network will depend on the geology and hydrology, the spatial scales at which contaminant distribution varies horizontally, vertically and temporally and the desired level of confidence in the evaluation. Plumes often vary significantly in concentration in transverse and vertical cross sections (e.g. Pankow and Cherry, 1996), making evaluation of contaminant distribution and remedy performance difficult. In these cases, a dense network of monitoring points will often be needed to support many of the performance monitoring evaluations described below.

Although the final number and placement of long-term monitoring wells and performance evaluation boreholes should be determined through regulatory negotiation (Wiedemeier, 1998), the locations of long-term monitoring boreholes should be based on the behaviour of the plume as revealed during the site characterisation and on

regulatory considerations. The final number and location of performance evaluation wells will also depend on regulatory considerations.
The basic elements of the design of a monitoring network should include the following (Carey et al., 2000):

1. The *type, number, location* of monitoring points (borehole, surface water, spring);
2. 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. 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;
3. The *methodology* needed to obtain representative samples;
4. The *number and type* of samples;
5. *Range of determinants* for analysis, including the key contaminants identified, appropriate analytical methods and their limits of detection and breakdown products, where appropriate;
6. *Frequency and duration* of monitoring;
7. *Methods of analysis* in assessing the monitoring results (for example, statistical techniques);
8. *Reporting requirements*, including presentation of data;
9. *Basis for ceasing monitoring* or the trigger for implementing contingency measures.

The aims of such a system should include the following (UK Environmental Agency):

- to demonstrate that natural attenuation occurs according to expectations;
- to identify any toxic breakdown products resulting from degradation;
- to detect new releases of contaminants;
- to demonstrate that receptors are protected;
- to confirm compliance with remedial targets/objectives;
- to provide a basis for implementing contingency measures, if they are required.

6.2 Monitoring Locations

Generally, each distinct zone of contaminant migration and geochemical regime within the contaminated area should be monitored to assess its impact on remediation. For instance, if part of a plume of tetrachloroethene is anaerobic with high levels of electron donors available and another part of the plume is aerobic with few electron donors available, degradation of the tetrachloroethene may be very active in the anaerobic zone but nonexistent in the aerobic zone (Pope et al., 2004). For each zone with distinctly different conditions or controls on contaminant migration and fate, the following locations would be monitored: areas hydraulically up-gradient and adjacent to the plume, source area, main body of the plume and distal portions and boundaries of the plume.

Up-gradient and adjacent boreholes are used to determine 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. Boreholes in the contaminant source area monitor changes in source strength over time. Boreholes located down-gradient of the source area, but within the contaminant plume, monitor plume behaviour and changing concentrations over time. These will normally be located along the centre line of the plume. Boreholes located immediately down-gradient from the contaminant plume should 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). Sentinel boreholes located between the plume and the identified receptor should be monitored for exceedence of the remedial target which will require implementation of the contingency plan.

Figure 8 and Figure 9 are a schematic outlay of a typical monitoring network for the purpose of monitoring NA at a contaminated site.

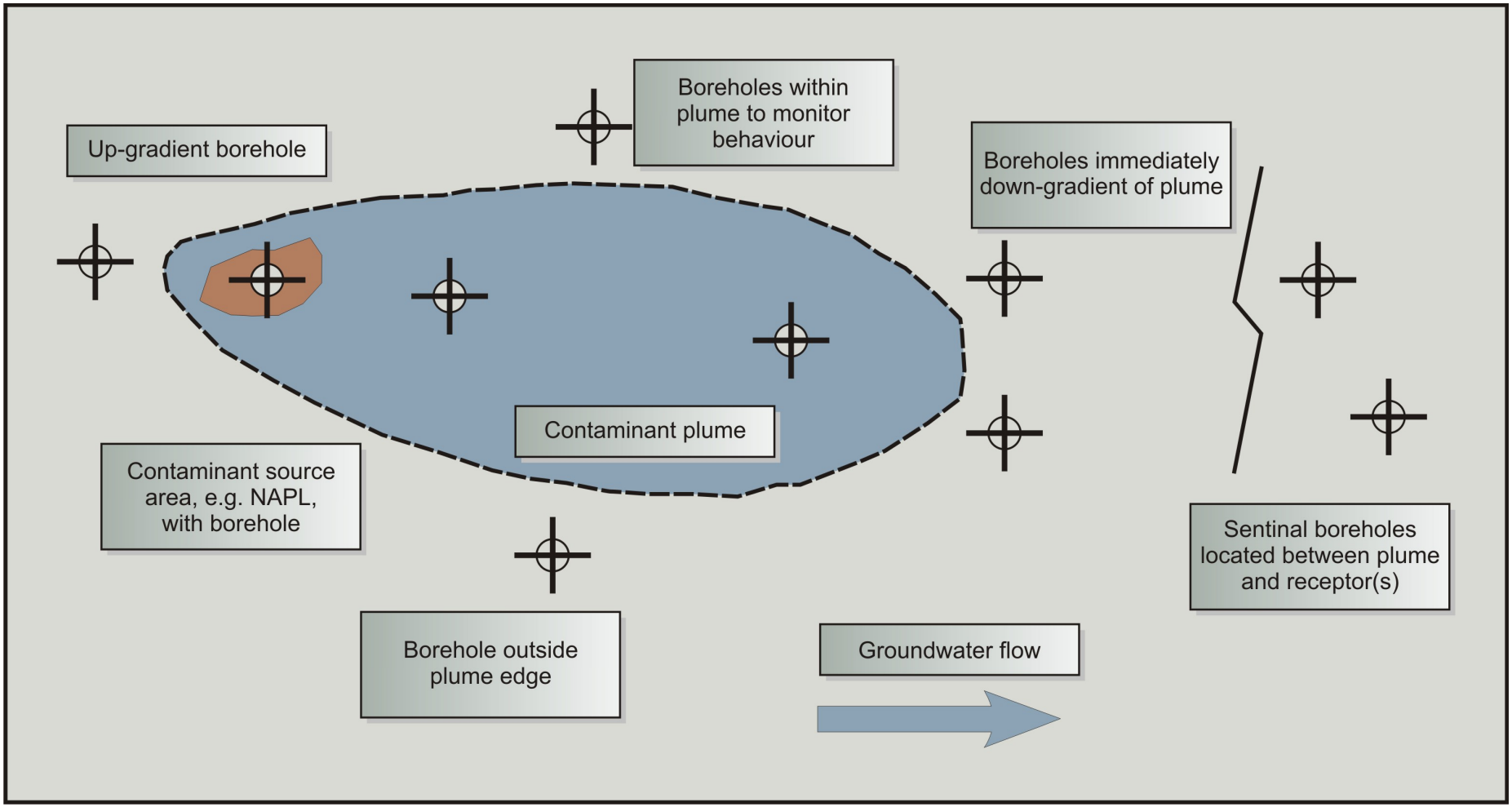

Figure 8: Plan view of schematic location of monitoring boreholes around a plume (From Carey et al., 2000)

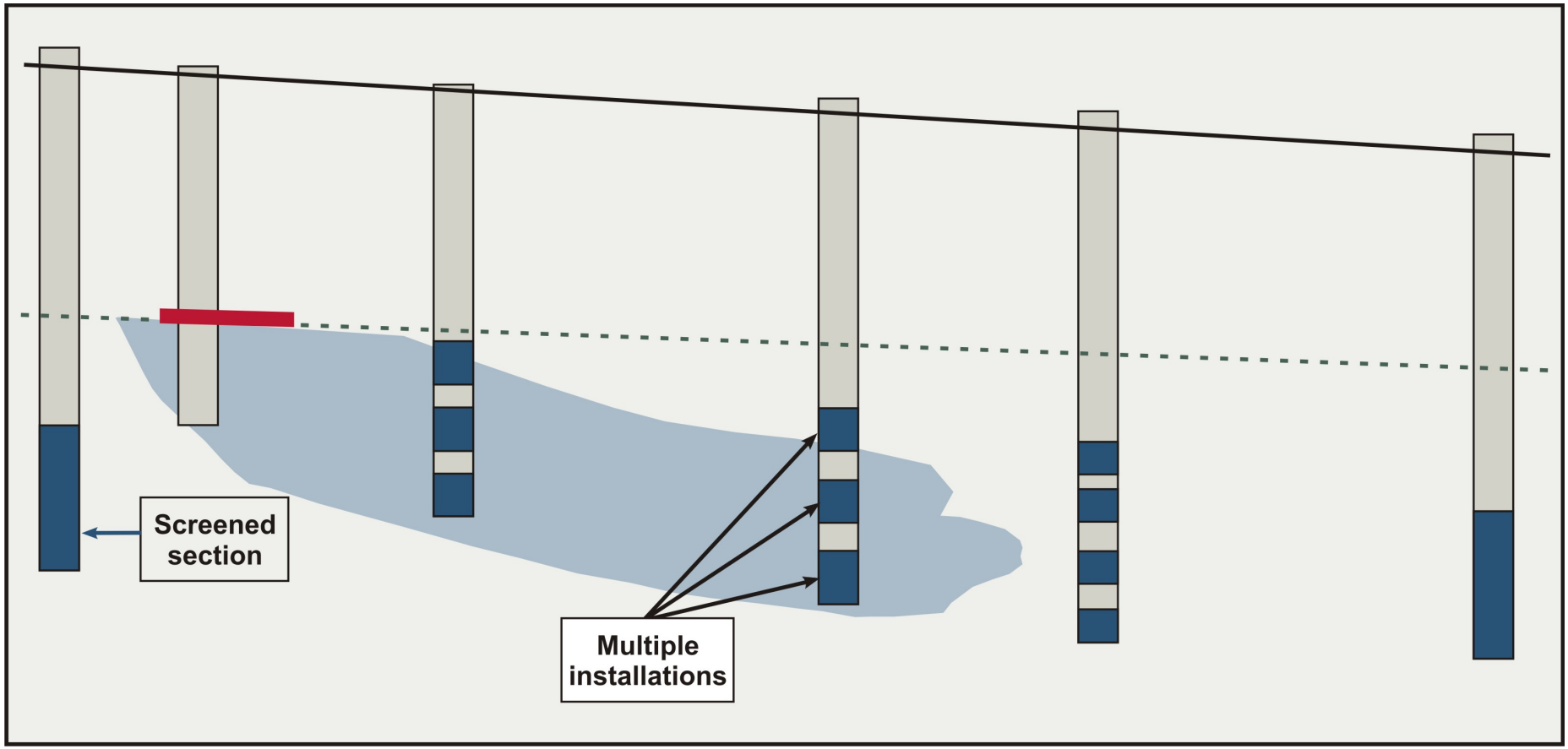

Figure 9: Cross-section of schematic location of monitoring boreholes around a plume (From Carey et al., 2000)

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 should be located at sufficient distance up-gradient of the receptor to provide adequate warning/protection. The UK Environment Agency recommends a minimum travel-time of 400 days. If the site falls within a 400-day travel-time for conservative species (this is known as the Outer Source Protection Zone, in the UK), then very strong evidence will need to be presented to demonstrate that NA will provide protection to the receptor (Carey et al., 2000). The distance to down-gradient boreholes will also influence the duration of monitoring. 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 therefore recommended for determining borehole locations.

6.3 Monitoring Parameters

The primary classes of parameters to be monitored during these evaluations generally will be the *contaminants of concern* (COCs), *geochemical indicators of transformation processes and hydrogeologic parameters* (Pope et al., 2004).

Contaminants of concern are those chemicals identified during site investigations that pose a risk according to the risk assessment protocol followed. Contaminants of concern may be identified from: groundwater and soil monitoring data; contaminant source histories; and evaluation of contaminants that potentially may be formed or mobilised as a result of biotransformation processes or changes in the geochemical environment. (e.g. toxic products such as dichloroethene and vinyl chloride would be measured at sites contaminated with chlorinated solvents where they might be expected to be present.)

The purposes for long-term monitoring of geochemical parameters, in addition to groundwater contaminants include: confirmation of dominant biotransformation processes; evaluation of the potential for continued transformation; and identification of the zones of contaminant migration (e.g. where geochemistry indicates contaminant degradation has taken place). The specific parameters useful at a given site depend on site contaminants, natural geochemical settings and dominant biotransformation processes. In most cases, a select group of parameters that indicate the geochemical environment (e.g. oxidation-reduction potential, dissolved oxygen, pH), identify geochemical regimes affecting contaminant degradation (e.g. nitrate, iron (II), sulphate, methane) or are products of contaminant degradation (e.g. ethane, ethene) will be measured in most samples.

The primary hydrologic parameter of interest is the elevation of groundwater in monitoring boreholes. Estimates of hydraulic gradients and changes in the elevation of the water table with respect to locations of residual source materials, are fundamental to all evaluations conducted during performance monitoring (Pope et al., 2004). The boreholes used in these evaluations should be discretely screened in individual hydrogeologic units within and adjacent to the contaminant plume. Additional data that are often essential in assessing groundwater flow include surface water elevations, local rates and schedules of irrigation, local precipitation data and pumping rates and schedules for nearby boreholes. The challenge of NA assessment monitoring is to resolve these discrete TEAP zones adequately, since the information gained provides the chemical framework to quantify attenuation processes. In the case of plumes with very large areal extent, it could be argued that since the top and bottom represent the majority of plume surface area, processes occurring there may dominate natural attenuation. Even plumes emanating from modest spills will have surface areas dominated by the top and bottom fringes. TEAPs may be characterised by using fine-resolution vertical multi-level wells. If such data is coupled with a general understanding of plume spatial variability and estimates of total mass flux obtained from modest transect instrumentation, only a few of these wells might be necessary. This is especially appealing where contamination occurs deep in rock aquifers that are expensive to instrument.

6.4 Monitoring Frequency

The frequency of monitoring will be a function of the plume behaviour; the rate of contaminant migration; the sensitivity of receptors; and the natural variability of groundwater flow regime and contaminant concentrations. For example, 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 (see Table 3), a higher frequency of monitoring would be required (Carey et al., 2000).

A higher frequency of sampling would typically 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 a Regulator. An annual monitoring frequency may be appropriate for some sites, once baseline conditions and trends in plume behaviour have been established. However, increases and decreases in monitoring frequency may occur several times over the life of the remedy in response to changes in site conditions and monitoring needs (Pope et al., 2004). The monitoring frequency may be adjusted to capture information regarding trends of interest while eliminating unnecessary redundancy. Monitoring frequency determinations should take into account that apparently stable site parameters may sometimes change due to natural or anthropogenic causes. For example, contaminant releases or remediation activities on adjacent properties may cause chemical or hydrologic changes in plume properties at the site. Increased rainfall may change recharge rates, groundwater extraction may cause changes in groundwater flow and air sparging for volatiles stripping or hydrogen peroxide injection for contaminant oxidation could change the geochemical regime, possibly changing biodegradation rates.

6.5 Review and Assessment of Data

The presentation of good data is an important component in setting out the evidence to support NA. Methods of presentation include tabulation of data, distribution and contour maps, time-series graphs and cross-sections (Carey et al., 2000). The method for presentation is likely to vary from site to site, but the clear illustration of information is critical to the acceptance and monitoring of NA. To assist in the review and assessment of the monitoring results, the data could be presented as time-series graphs to identify any trends and compliance, where appropriate, with remedial targets and as contour plots to identify any changes in the plume geometry.

The monitoring information will need to be reviewed routinely to:

- discover whether NA 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).

The regular review/assessment of monitoring data will therefore determine whether monitoring should continue as is, be changed according to change in the hydrogeological system, whether a contingency plan needs to be implemented and/or the conceptual model needs to be revised.

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

- errors in sampling and laboratory practice;
- seasonal variations in water quality;
- insufficient data set to allow meaningful trends to be determined; and
- 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. The methods of analysis and basis for accepting compliance with remedial targets (objectives) should therefore form part of the monitoring plan.

7. MNA RECOMMENDATIONS FOR SOUTH AFRICA

7.1 Introduction

As interest in using natural attenuation to manage contaminated sites has surged, an increasing number of protocols have been developed internationally to guide evaluations of the potential for natural attenuation to occur. As part of this project the aims were set to provide an overview of existing legislative frameworks within South Africa where MNA can be incorporated and to evaluate acceptable protocols and standards for regulation. In the following sections MNA will be discussed in terms of the existing legislative framework within South Africa and suggestions towards protocols will be made.

7.2 Regulatory Framework

Environmental law is a new, distinct branch of law. This body of law is extremely wide, and the scope imprecise (Rabie, as cited by Glazewski, 2000). This is a cause for concern for most environmental law practitioners and implementers of the law (government bodies) in South Africa.

Several acts exist in South Africa pertaining to waste management, actions to be taken against potential polluters, as well as remedial action. The NWA requires site remediation, but very little regulatory guidelines exist on how this is to be attained. Little guidance exists on the processes that must be followed to get from the stage where the problem is identified up to the point of remediation. The task is made more difficult by the fact that all the laws of the different departments must be harmonised in such a way that all the legal implications of a decision are considered so as to prevent illegal processes from occurring. Regulations should drive clean-ups and hence site characterisation at polluted sites and hazardous waste sites. It is thus imperative that South Africa develops guidelines for site characterisation for different types of pollution.

When applying legislation, it must be determined which legislation has the authority to overrule the other. A distinction must be made between original (primary) legislation and subordinate legislation. Original (primary) legislation pertains to Acts of Parliament, as well as laws made by any of the nine Provinces (DWAF, 2001). Subordinate legislation derives its authority from primary legislation. This includes regulations, ordinances, proclamations and authorisations such as licences, general authorisations, permits and even policy (DWAF, 2001).

Listings of the legislation in South Africa in their relative statutory importance are given as follows:

1) Constitution
2) Parliamentary or National Legislation (Acts of Parliament) – (National Environmental Management Act - NEMA, National Water Act - NWA, Water Services Act - WSA)

   i. Provincial Legislation
   ii. Laws from 1994
   iii. Proclamations between 1986-1994
3) Ordinances before 1986
4) Local authority bylaws

This implies that the Constitution is the only legislation that has the authority over the NEMA and NWA and these Acts have authority over provincial laws.

The following sections highlight the applicable sections of these various legislations and the possible importance to groundwater contamination and remediation.

7.3 Protocols for Documenting Natural Attenuation

The NRC (2000) defines the term "protocol" very broadly to include any policy statement, state regulation or technical document on how decision-making and the implementation of natural attenuation should be carried out. As defined here, a protocol is an outline of a strategy and methodology to be followed. It is an assessment and planning tool. A protocol is not necessarily a 'how-to' manual, although some existing protocol documents (such as those prepared by the U.S. Air Force), have extensive appendices that provide considerable information on field sampling techniques, analytical methods and data interpretation.

However, standardising the steps in data gathering, analysis, and decision making should be the most important use of a protocol.

In the review document of the NRC (2000), a list of important subject areas and subtopics that protocols should address with regard to natural attenuation, is given. These are:

1. **Community Concerns:**
   1.1 Community Involvement - early community involvement is especially important in order to gain public acceptance and confidence in decisions regarding natural attenuation and a comprehensive natural attenuation protocol needs to identify critical decision points at which community involvement is necessary.
   1.2 Institutional Controls - Natural attenuation processes may operate for many years, during which time, land re-use may have to be restricted. A comprehensive protocol has to describe the criteria for deciding whether institutional controls are necessary and how to ensure the long-term viability of these controls. Having clear institutional controls also helps to assure the affected community that natural attenuation is more than a walk-away solution.
   1.3 Contingency Plans - A comprehensive protocol has to provide guidance on contingency plans in the event that natural attenuation does not perform as predicted.

The community surrounding a contaminated site includes the people who live close to the site, local business owners, elected officials, local government agency representatives, workers at the site and others who live further away from the site. However, those who live close to the site bear the brunt of the health and environmental risk and the most significant potential economic losses. Although members of affected communities have concerns about all remedies for contaminated sites, they may have special questions about natural attenuation, because of the lack of visible, active steps to remove the contamination. All these aspects need to be addressed in a South African context for the acceptance of MNA.

2. Scientific and Technical Issues:

2.1 Cause-and-effect determination - A comprehensive protocol has to explain clearly what scientific evidence is needed to establish that specific natural attenuation processes are responsible for observed decreases in contaminant concentrations. It should describe the class of contaminants it addresses and the general hydrogeological setting in which natural attenuation is applicable for these contaminants.

2.2 Site Assessment - A comprehensive protocol has to provide guidance on what information is needed to understand important hydrogeological factors affecting contaminant transport and fate at the site.

2.3 Long-term viability - The long-term viability of natural attenuation has to be understood because a considerable period of time may be required to achieve clean-up goals. A comprehensive protocol should provide criteria for assessing the capacity of the natural attenuation processes at work on the site, whether the processes are likely to be constant and the length of time required to reach clean-up goals. It also has to provide strategies for determining the rates of the processes, whether these are variable over space and time and whether they are sufficient to prevent migration of contaminants to undesired locations.

2.4 Peer Review - Peer review is important for ensuring scientific credibility and completeness of natural attenuation protocols. All protocols should be independently peer reviewed prior to publication. Because a successful natural attenuation evaluation embraces various engineering and scientific disciplines, as well as public policy and management, the peer review process likewise, has to involve participation from various disciplines.

3. Implementation Issues

3.1 Usability and User Qualifications - A comprehensive protocol has to be easily understood and implemented by individuals responsible for managing operations in the field, as well as by regulators. Detail must be sufficient to allow the protocol to serve as an effective tool for assessing natural attenuation implementation. The comprehensive protocol should describe the qualifications (such as disciplinary expertise, practical field experience and specific training) needed to carry out the various analyses it recommends.

4. **Decision-making tools –** Most protocols make use of 'decision-making tools' such as flow charts, check lists, scoring systems or interactive software. It should be recognised that **such tools have very limited ability to recognise adequately the differences between sites based on size, composition or geological complexity and *should therefore be used with care.***

4.1 Flow Charts - can be very useful for organising data needs and the decision process.

4.2 Check Lists – can be very useful for maintaining consistency, ensuring thoroughness and serving as a reminder of what sort of information may have to be gathered. However, rigid use of check lists could impede the decision-making process and it should be clear on any checklist what information is mandatory and what is optional.

4.3 Scoring Systems – a scoring system assigns positive or negative numeric scores to various geochemical indicators, contaminant mixtures and key biodegradation products. **A high positive numeric score is intended to mean that a site should be evaluated further for natural attenuation and does not imply that attenuation is proven.** Unfortunately, scoring systems are often widely adopted for uses that the authors never intended.

The issues surrounding protocols and guidelines for natural attenuation have been clearly debated and addressed in the US and in Europe. Lessons learned from these experiences should therefore be incorporated when addressing the way forward for South Africa in this regard. The last section of this document provides suggestions for a suitable way forward in setting up suitable protocols for dealing with MNA at groundwater

contaminated sites. It was attempted to take cognisance of all factors listed in this section, as well as the unique South African aquifer conditions.

8. SUGGESTED PROCESS TO BE FOLLOWED

It is recommended that the approach for assessing and implementing monitored natural attenuation in South Africa be risk-based management strategy. The methodology should be 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.

The screening stage, should consider 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, must 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 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/protocol must be the conceptual model that describes hydrogeological, biochemical and geochemical characteristics at a site. The model should be continually challenged and revised as additional data are collected during successive stages of the assessment.

The following figure provides a simplified overview of the process to be followed when MNA is considered as a remedy at a groundwater contaminated site. The principles are based on guidance by the UK Environment Agency (Carey et al., 2000) and the Government of Western Australia, Department of Environmental Protection (2004).

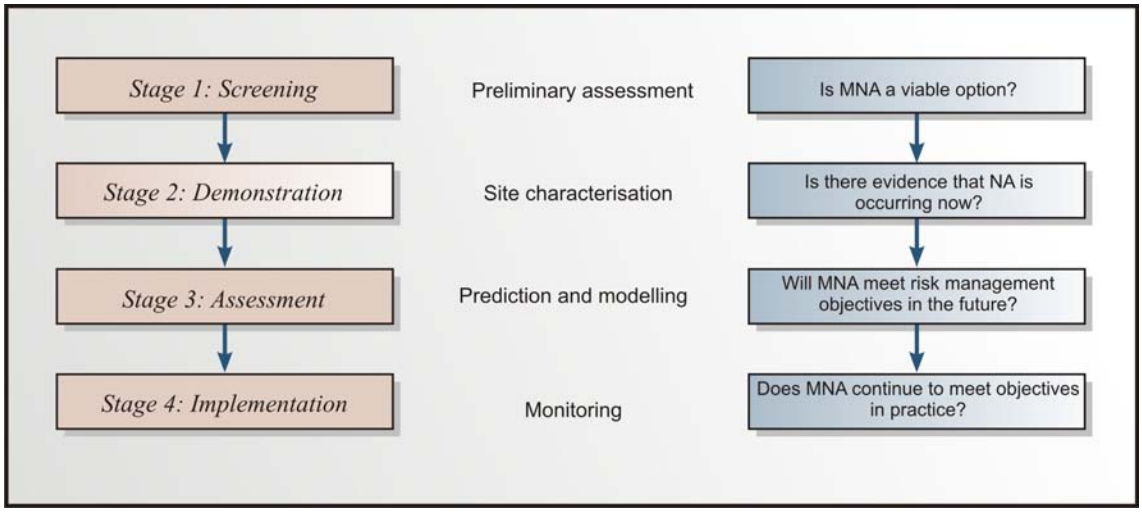

Figure 10: Overall procedure for the assessment of natural attenuation

8.1 Screening

Based on the principles outlined in the Environment Agency's protocol, the government of Western Australia has suggested generic screening criteria to be considered in the pre-feasibility stage of MNA implementation. For each aspect, a rating of high, medium or low feasibility is assigned and this is combined to give an overall conceptual rating regarding the potential feasibility of MNA on a site.

Table 11: Summary of screening criteria to assess the feasibility of using MNA as a remedial option

(Adapted from WA DEP, 2004)

Screening criteria	High feasibility	Medium feasibility	Low feasibility
Technical screening criteria			
Source of groundwater contamination	Removed	Being removed	Continuing/ Unknown
Extent and severity of groundwater contamination	Well defined		Poorly defined
Nature of contamination plume	Shrinking	Stable	Growing
Persistence of contamination in groundwater	Readily attenuated (degraded) under site conditions	Not readily degraded under site conditions	Attenuation processes poorly understood
Dominant attenuating processes	Irreversible/ destructive		Reversible/ non-destructive
Aquifer Classification	Non-aquifer	Minor, Poor, Major	Sole source, Special
Aquifer heterogeneity	Homogenous and isotropic		Heterogeneous and anisotropic
	Intergranular	Fractured, Intergranular and Fractured	Karst, Fractured, Intergranular and Fractured
Rate of groundwater flow	Slow (less than 10 m/year)	Medium (10-100 m/year)	Rapid (more than 100 m/year)
Groundwater usage near the site	None, or boreholes mainly used for industrial supply	Boreholes mainly used for domestic gardens	Boreholes used for drinking supply within 300 m of the site
Surface water bodies	None within 300 metres of the site	None within 100 metres of the site	Present within 100 metres of the site
Level of confidence in monitoring data	High – more than 2 years of comprehensive data		Low-single set of monitoring data
Practical screening criteria			
Objectives of land owner	Long-term interest in the site (>10 years)	Medium-term interest in the site (3-10 years)	Short-term interest in the site (<3 years)
Financial provisions for monitoring and implementation of a contingency plan	Long-term, legally binding budget provisions secured	Long-term, non-legally binding provisions secured	No long-term budget provisions

Screening criteria	High feasibility	Medium feasibility	Low feasibility
Access to off-site monitoring locations	Long-term access secured		
Overall assessment of feasibility			
	All Highs or Intermediates, no Lows	No critically important criteria (i.e. those in bold type and underlined)	One or more critically important criteria, or no factors of High Rating

This type of screening is very generic and should be combined with tools such as DeMONA, the MNA Toolbox and others to point to a consistent result. Additional to the above table as a minimum, the site-specific information detailed in Table 11 should be collected on site, to screen for the suitability of a site for natural attenuation.

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.

Table 12: Minimum data requirements for screening stage

A. Contaminant properties
▪ 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)
B. Aquifer characteristics
▪ Major / Minor / Non-aquifer ▪ Source Protection Zone ▪ Flow mechanism, e.g. fracture/intergranular flow ▪ Direction of groundwater flow ▪ Groundwater velocity (hydraulic conductivity, hydraulic ▪ gradient, porosity
C. Receptors/compliance points
▪ Location of receptors, e.g. extent of aquifer, location of abstractions, springs, rivers and estuaries and their proximity to site

If, after reviewing information relating to the screening factors outlined in this section and it is concluded that MNA is a viable option, detailed site characterisation should be performed as part of the next stage. If the process fails according to the screening, a conservative risk assessment process may be undertaken and this may lead to MNA still being considered to be viable.

8.2 Demonstration

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. Demonstrating the effectiveness of NA involves obtaining data to test and calibrate the conceptual model. The process is iterative, in which 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 to MNA demonstration in South Africa has to be according to a 'lines of evidence' approach.

The key steps involved in acquiring and analysing data in order to demonstrate natural attenuation are described below.

8.2.1 Lines of Evidence

Most of the protocols/guidance used as background for this document, make use of 'lines of evidence' 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*.

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.

It was found by the research in this project (WRC project No K5/1501) that determination of the microbial population can illustrate why certain daughter products are present at a particular site and others are not found.

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.

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

Table 11 presents a description of physical, chemical, biological and geochemical parameters and their use in demonstrating natural attenuating mechanisms, with the methods of collecting this data given in Section 5. The

process of selecting appropriate determinants from this list will depend upon the nature of contamination, the biogeochemical environment at a site and the dominant attenuation processes under consideration.

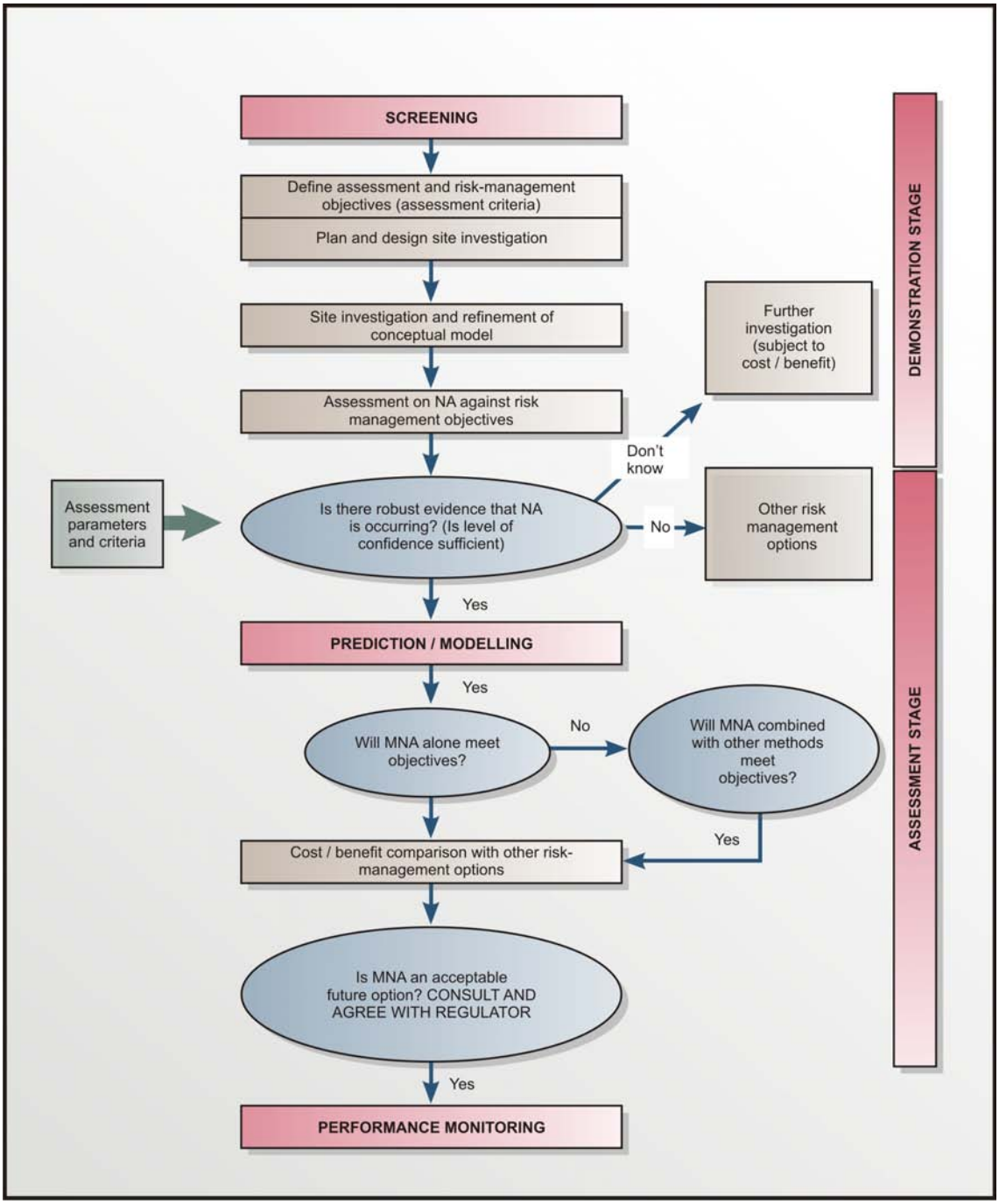

Figure 11: Flow chart for demonstration & assessment of natural attenuation (From Carey et al., 2000)

8.2.2 Assessment

When the assessment stage of the investigation is reached, it is assumed that adequate information has been obtained to define the site and to demonstrate that natural attenuation is occurring and by what processes. Acceptance of MNA as a remedial option should be dependent on demonstrating that:

1) Natural attenuation processes are protecting receptors and will continue to do so;
2) Any further migration of the contaminant plume will not result in significant additional pollution of groundwater; and
3) The period over which contaminant concentrations are reduced by natural attenuation is reasonable.

The following steps are required to assess these factors:

8.2.2.1 Define objectives for the assessment

This will include identifying the receptors that need to be protected, determining appropriate remediation targets to ensure the protection of the receptors and determining the time frame over which natural attenuation is acceptable.

8.2.2.2 Selection of appropriate model

The purpose and benefits of using numerical or analytical models to predict the transport and fate of contaminants should be clearly defined before any modelling is carried out.

A model should not be used to replace data from field investigations, but should rather be used as a tool to complement field data to assist in the assessment and decision-making process.

The choice of the model used is dependent on:

- The objectives of the modelling exercise;
- The conceptual model (complexity of the hydrogeology of the site);
- The chemical and physical behaviour of the contaminants in groundwater and the natural attenuation processes that occur at the site,
- The quality and quantity of field data available for the site; and
- The limitations of the fate and transport model.

8.2.2.3 Define parameter values for the 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;
- model predictions are insensitive to this; or
- the range in parameter values is well defined from the literature and a conservative value has been used in the assessment.

8.2.2.4 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.

8.2.2.5 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; and
- location of monitoring points (particularly in relation to the front of the plume) for performance monitoring.

Because it is recommended that MNA be implemented together with some method of source control/removal, it would be expected that the source term will decrease over 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 may 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. Most analytical models assume a constant source term and therefore, are likely to provide a conservative estimate.

8.2.2.6 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.

8.2.2.7 Review of model predictions

The significance of the model predictions will need to be assessed taking into account the sensitivity of the identified receptors and should consider: the uncertainties in the conceptual model and the significance of preferential pathways for contaminant transport; the uncertainties in parameter values and their influence on model results; and the applicability and limitations of the model for predicting contaminant concentrations at a specific site, particularly if receptors are considered to have a high risk of being affected by contamination.
If the review of the modelling results indicates that there is insufficient certainty, then a decision should be made to either obtain further data from specific site investigations or consider using active remediation strategies for the site in combination with MNA. This may require further modelling to take into account the effect of additional remediation measures.

8.2.3 Implementation

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

1. The number of monitoring boreholes required, their location and construction details;
2. The sampling methodology;
3. The sampling frequency and duration of monitoring;
4. Quality assurance (QA) procedures for sampling;
5. Methods of chemical analysis;
6. Reporting requirements to the Regulator; and
7. The basis for ceasing monitoring or to trigger the implementation of contingency measures.

Section 6 gives more detail with regard to the design of a monitoring network for the implementation of MNA as a remedy.

It is important that the criteria for ceasing monitoring should be defined as part of the monitoring plan. Typically, monitoring will continue until: contaminant concentrations in the plume have reached background levels; remedial objectives accepted by the Regulator have been met and natural attenuation can be relied on to further reduce contaminant levels; or remedial objectives have been substantially met and declines in contaminant concentrations have been defined to the extent that there is a high degree of confidence that the remedial objectives will be achieved within a time-frame acceptable to the Regulator or that the ***proven*** risks are acceptable.

8.2.3.1 Contingency plan

The monitoring plan should include a contingency plan, in case 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 during 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;
- contaminant concentrations do not decrease at a sufficient rate to meet remedial objectives;
- changes in groundwater or land use adversely influencing the effectiveness of NA;
- increases in contaminant concentrations that indicate continued release of contaminants to groundwater.

9. PRACTICAL IMPLEMENTATION IN A SOUTH AFRICAN CONTEXT

The sections outlined above (particularly Section 8) provide a clear overview of the approaches that need to be followed for MNA to be successfully applied to South African sites that have been impacted on by DNAPLs.

Implicit in these methodologies are the four basic steps outlined in Figure of screening for suitability, detailed site characterisation of the impacted site, assessment of natural attenuation processes and then monitoring to ensure that these processes will continue to meet the set criteria.

There are some key areas that need to be addressed for this to occur and several have been verified in nationwide symposia with many of the role players (site owners, environmental and geohydrological practitioners and regulators). Several of the recommendations from this range of multi-sectoral stakeholders included the following points (based on Message to Decision-Makers from 130 participants):

- There is a lack of specific regulations addressing aspects such as site characterisation and monitoring and remediation policies to deal with dissolved organic contaminants and NAPLs in groundwater in this country.
- There is a very urgent need to establish South African water quality guidelines/standards for these types of contaminants. Several international guidelines exist but standardisation in South Africa for consistent decision-making and management is needed.
- The South African regulatory framework allows for risk-based decision-making to be applied in the management of groundwater contamination. Consensus on the acceptance of this approach and the application thereof is required, as is guidance for regulators, site owners and environmental specialists to apply this consistently in South Africa.
- There is very little specific guidance and policy on the remediation of these contaminants in groundwater in South Africa. Aspects such as site clean-up levels, monitored natural attenuation and Best Practice for these technologies should receive attention.

The application of MNA in this country will not succeed without the acceptance of risk-based approaches and the standardisation of the requirements for site assessment, monitoring and remediation. Under the correct conditions, MNA along with source remediation, long-term monitoring and conservative risk determination might be more appropriate than other conventional technologies, provided there is clear understanding that it is not a 'do nothing' alternative. There will be sites where monitored attenuation will not be acceptable due to the conditions on site or the receptors affected.

10. REFERENCES

ASTM. (1995) Emergency Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites: ASTM E-1739, Philadelphia, PA.

Bradley, P.M., and Chapelle, F.H. (1997) Kinetics of DCE and VC mineralization under methanogenic and Fe(III)-reducing conditions: Environ. Sci. Technol., 31:2692-2696.

Bouwer, E.J. (1994) Bioremediation of chlorinated solvents using alternate electron acceptors, In Handbook of Bioremediation: (Norris, R.D., Hinchee, R.E., Brown, R., McCarty, P.L, Semprini, L., Wilson, J.T., Kampbell, D.H., Reinhard, M., Bouwer, E.J., Borden, R.C., Vogel, T.M., Thomas, J.M., and Ward, C.H., Eds.), Lewis Publishers, Boca Raton, FL, p.149 -175.

Carey, M.A., Finnamore, J.R., Morrey, M.J. & Marsland, P.A. (2000) Guidance on the Assessment and Monitoring of Natural Attenuation of Contaminants in Groundwater. Report completed for the office of National Groundwater & Contaminated Land Centre, UK Environment Agency under R&D Project P2-158. ISBN: 1 85705 263 2

Connor, J.A., Malander, M., and. Guiseppi-Elie A. (1995). RBCA State Risk Policy/Strategy Issues Workbook. ASTM RBCA Task Group. Philadelphia, PA.

DWAF (Department of Water Affairs and Forestry), 2001, Water Quality Management Orientation Course: Legal Tools

DWAF (2000) Policy and Strategy for Groundwater Quality Management in South Africa. Number W.1.0: First Edition 2000. ISBN 0-620-23789-9

Department of Environment and Conservation, New South Wales. (2005) Contaminated Sites: Draft Guidelines for the Assessment and Management of Groundwater Contamination. ISBN41371058.

Glazewski, J., 2000, *Environmental Law in South Africa*, Butterworths

Grandel, S. and Dahmke, A. (2004) Monitored natural attenuation of chlorinated solvents: assessment of potential and limitations. Published in Biodegradation 15: 371–386, 2004. Kluwer Academic Publishers. Printed in the Netherlands.

Hanson, R. S. and Hanson, T. E. (1996) Methanotrophic bacteria. Microbiol. Rev. 60: 439-471.

Hendrickson, E.R et al*.,* 2002. Molecular analysis of Dehalococcoides 16S ribosomal DNA from chloroethene-contaminated sites throughout North America and Europe. Applied and Environmental Microbiology. 68(2) 485-495.

ITRC, 1999 Natural Attenuation of Chlorinated Solvents in Groundwater: Principles and Practices Technical/Regulatory Guidelines Interstate Technology and Regulatory Cooperation Work Group In Situ Bioremediation Work Team and Industrial Members of the Remediation Technologies Development Forum (RTDF).

Leisinger, T., Bader, R., Hermann, R., Schmid-Appert, M. & Vuilleumier, S. (1994). Microbes, enzymes and genes involved in dichloromethane utilization. Biodegradation 5, 237-248

Lesage, S., R.E. Jackson, M.W. Priddle, and P.G. Riemann. (1990). Occurrence and fate of organic solvent residences in anoxic groundwater at the Gloucester landfill. Canada Environ. Sci. Technol. 24(4):559-566.

Mayer, K.P., Grbi.-Gali., D., Semprini, L., and McCarty, P.L., 1988, Degradation of trichloroethylene by methanotrophic bacteria in a laboratory column of saturated aquifer material: Water Sci. Technol. (Great Britain), 20(11/12):75-178.

McCarty, P.L. (1997) Biotic and abiotic transformations of chlorinated solvents in groundwater. In Proceedings of the symposium on natural attenuation of chlorinated organics in groundwater. EPA-540-R-97-504. http://www.epa.gov/ordntrnt/ORD/WebPubs/natural/natural.pdf

Means, J.L. and Hinchee, R.E. (1994) Emerging Technology for Bioremediation of Metals, Lewis Publishers, Boca Raton, FL.

NRC (1994) Alternatives for Groundwater Cleanup. Committee on Groundwater Cleanup Alternatives. National Academy of Sciences, p. 111/112

NRC (2000) Natural Attenuation for Groundwater Remediation. Published by the Committee on Intrinsic Remediation, Water Science and Technology Board, Board on Radioactive Waste Management, National Research Council. ISBN: 0-309-51645-5, 292 pages, 6 x 9, (2000) This PDF is available from the National Academies Press at: http://www.nap.edu/catalog/9792.html

Odencrantz, J. E., Varljen, M.D. and Vogl, R.A., (2002) "Natural Attenuation: Is Dilution the Solution?" Article published in LUSTLine Bulletin 40, March 2002. Available online at: www.epa.gov/swerust1/cat/LL40Wander LUST.pdf

Office of Environmental Restoration. (1999) Technical Guidance for the Long-Term Monitoring of Natural Attenuation Remedies at Department of Energy Sites. USA Department of Energy, October 18, 1999.

Pankow, J.F. and Cherry, J.A. 1996. Dense Chlorinated Solvents and other DNAPLs in Groundwater. Waterloo Press, Ontario, Canada.

Patel, R.N., Hou, C.T., Laskin, A. I., and Felix A. (1982) Microbial Oxidation of Hydrocarbons: Properties of a Soluble Methane Monooxygenase from a Facultative Methane-Utilizing Organism, Methylobacterium sp. Strain CRL-26 Appl Environ Microbiol. 1982 November; 44(5): 1130–1137.

Pope, D.F., Acree S.D., Levine, H., Mangion, S., Van Ee, J., Hurt, K., and Wilson, B. (2004). Performance Monitoring of MNA Remedies for VOCs in Groundwater. Document prepared under contract for the National Risk Management Research Laboratory, Office of Research and Development US EPA, April 2004

Rügner, H and Teutsch, G. (2002) Literature Study "Natural Attenuation of Organic Pollutants in Groundwater". Final report completed by the Centre for Geosciences, University of Tübingen for the Integrated Concept for Groundwater Remediation (INCORE) (WP6A) Project. 30 April 2001

Sara, M.N. (2003) Site Assessment and Remediation Handbook, Second Edition. Printed by CRC Press LLC, Boca Raton, Florida. ISBN 1-56670-577-0

Smatlak, C.R., Gossett, J.M., and Zinder, S.H. (1996) Comparative kinetics of hydrogen utilization for reductive dechlorination of tetrachloroethene and methanogenesis in an anaerobic enrichment culture: Environ. Sci. Technol., 30:2850-2858.

US EPA (1991) Seminar Publication - Site Characterization for subsurface remediation. Published - EPA/625/4-91/026; 1991.

US EPA (1993) Guidance for evaluating the technical impracticability of groundwater restoration, OSWER Directive 9234.2-25, EPA/540-R-93-080, Office of Solid Waste and Emergency Response. Washington, D.C.

US EPA (1998) Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater. Office of Research and Development, Washington DC, September 1998. EPA/600/R-98/128.US EPA (1992) Evaluation of Groundwater Extraction Remedies: Phase II, February 1992. OSWER Publication 9355.4-05, Vol. 1: NTIS Order Number PB92-963346, 27p.; Vol. 2: NTIS Order Number PB92-963347. Available at http://www.epa.gov/.

The University of Minnesota Biocatalysis/Biodegradation Database, http://umbbd.ahc.umn.edu/index.html