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R.G. McLaughlan, N.P. Merrick and G.B. Davis



CRC for Contamination Assessment and Remediation of the Environment

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Natural attenuation: a scoping review

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Executive summary

‘Natural attenuation’ refers to naturally occurring physical, chemical and biological processes, or any combination of those processes, that reduce the concentration or mass of polluting substances in groundwater. It has been recognised that natural attenuation processes can form the basis of a viable remediation strategy for contaminated sites. Monitored natural attenuation has the potential to reduce contaminant clean-up costs while avoiding exposures to humans and sensitive environmental receptors. Whilst the benefit of using monitored natural attenuation on a site can be significant compared with active remediation, there are also risks associated with this strategy that need to be managed.

CRC CARE commissioned this review of natural attenuation processes as part of its priority scopes of work related to the environmental fate of petroleum hydrocarbons. The goal of the scoping report was to review international, national and industry information about the natural attenuation of petroleum hydrocarbons with a focus on Australian studies. This project seeks to identify scientific knowledge gaps which are relevant to the application of monitored natural attenuation in Australia.

The following are the major observations arising from this review:

1. A risk-based approach using lines of evidence is widely used as a framework for monitored natural attenuation (MNA) guidance.
2. Six years ago, MNA was recognised as a well-established remediation approach for only a few types of contaminants, but importantly these included the petroleum compounds benzene, toluene, ethylbenzene and the xylene isomers (BTEX), and some oxygenated hydrocarbons. For the other classes of petroleum hydrocarbons and oxygenated hydrocarbons, there was either not a complete understanding of biodegradation processes or its confidence of success in an MNA-based remediation strategy. Since then greater knowledge has been gained particularly about methyl tertiary-butyl ether (MTBE) and polycyclic aromatic hydrocarbons (PAH).
3. Biodegradation is recognised as the key natural attenuation mechanism for fuel hydrocarbons. To support the application of MNA, extensive compilations and reviews of BTEX biodegradation rates for laboratory and field sites are available, primarily based on studies from the United States.
4. Australian data that might help define the scope of impact arising from the use of fuel additives (MTBE, ethanol and biodiesel) are scarce. The Australian experience of groundwater contamination from MTBE is likely to differ from the United States, as MTBE is potentially only present in fuels imported from overseas.
5. Approaches for implementing MNA at sites contaminated with PAH are poorly developed compared with BTEX or chlorinated solvent sites. Knowledge about PAH degradation in the field and sorption/desorption processes is reasonably limited.
6. There have been relatively few studies that have addressed the natural weathering of residual and mobile non-aqueous phase liquid (NAPL) fuels compared with studies into the processes affecting dissolved phase contaminants resulting from NAPL. This knowledge gap will be important where MNA is linked as a remedial strategy with NAPL clean-up.

7. Groundwater recharge has recently been recognised as an important attenuation mechanism near the contaminant source. High-resolution multi-level sampling and scenario modeling are increasing our understanding in this area.
8. Whether the assimilative capacity of an aquifer can be sustained over the multi-year life of a MNA remedial strategy is an area of knowledge that is poorly understood. One area of uncertainty relates to the longevity of cycling of redox-active elements (Fe, S) between the dissolved and mineral phases. Another is the prediction of changes in electron acceptors in response to changes in environmental conditions (e.g. recharge).
9. Further knowledge about the expected value of particular biogeochemical indicator data to effectively discriminate contaminant degradation mechanisms at a fuel-impacted site is needed. This knowledge is needed to cost-effectively set up monitoring regimes capable of validating attenuation processes long-term.
10. Published literature on natural attenuation processes at Australian sites for petroleum hydrocarbons is patchy and lacks a degree of specificity about site location, degradation rate and contaminant data, which therefore limits the usefulness of the literature for contributing to a generalised understanding of contaminant behaviour across those specific subsurface environments.
11. In Australia, there have only been two published studies on petroleum hydrocarbon plume characteristics at multiple MNA sites. There is not enough data to conclude whether the generalised behaviour of petroleum hydrocarbon plumes under Australian conditions is similar to that reported from overseas. Therefore the general applicability of overseas data (e.g. degradation rates) to Australian sites is a knowledge gap.
12. Published Australian natural attenuation literature has focused on shallow sand aquifer systems. These include the Quaternary aquifer around Perth and the Botany aquifer near Sydney. Studies on these sites could provide the fundamental data for scenario modelling at those locations. Generally, there were few papers which described contaminant behaviour in fractured rock and clay sites.

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1. Introduction

Within the last 20 years, active remedial strategies (e.g. pump and treat, air sparging) have been widely used technologies for groundwater remediation. Overseas there is a growing regulator and industry acceptance of the role that passive treatment technologies involving natural attenuation can play in groundwater remediation. Natural attenuation (NA) refers to naturally occurring physical, chemical and biological processes or any combination of those processes that reduce the concentration or mass of polluting substances in groundwater (DEC 2004). It has been recognised that NA processes can form the basis of a viable remediation strategy for contaminated sites. Monitored natural attenuation (MNA) is ongoing groundwater monitoring and associated field and laboratory work to confirm whether natural attenuation processes are acting at a sufficient rate to protect environmental values, and to demonstrate that remedial objectives will be achieved within either a specified time period or a site-specific reasonable time period.

MNA has the potential to reduce contaminant clean-up costs while avoiding exposures to humans and sensitive environmental receptors. Whilst the benefit of using monitored natural attenuation on a site can be significant compared with active remediation, there are also risks associated with this strategy that need to be managed. This project seeks to identify scientific knowledge gaps and provide the basis for the ongoing CRC CARE project relating to NA. It is expected that improved support for decision-makers will result from undertaking this project.

1.1 Purpose and scope of this paper

CRC CARE commissioned this review of the natural attenuation of petroleum hydrocarbons as part of its priority scopes of work related to the environmental fate of petroleum hydrocarbons. Within the natural attenuation research program several stages of work were presented to the Policy Advisory Committee of CRC CARE on 20 October 2005. These stages included:

1. Appointment of a single point of accountability – Project Manager.
2. Establish a Project Advisory Group (PAG) (regulator, industry, researcher, project leader, single point of accountability).
3. Hold a workshop to distil issues (e.g. key contaminants of concern, representative groundwater environments).
4. Review international, national and industry information with a focus on Australian studies.
5. Identify knowledge gaps by reviewing 3 and 4. Critique NA protocols and NA assessment needs (e.g. stable plumes, microbiology, geochemistry, isotopes, modelling, LNAPL).
6. Scope field work at demonstration sites, possibly with laboratory study support (e.g. gasoline, diesel sites).
7. Evaluate the potential of NA to consume the flux from residual LNAPL for longevity of impact.

8. Model development (e.g. fractures, density, reactive pathways, geochemistry) and scenario modelling (for plume lengths and longevity).
9. Develop a protocol for NA assessment.
10. Training/workshops.

The current document was intended to address only Stage 4 of the proposed project. It was designed to provide background information and guidance to later stages of the project. The primary goal therefore was to provide a review of natural attenuation at a plume scale suitable to inform policy and high level decision-making and aquifer scale scenario modelling. Detailed reviews of site-specific data such as biodegradation pathways for specific classes of compounds under particular redox environments have not been undertaken in this document, however the reader has been referred to other sources for that information.

While Stage 3 (workshop) did not occur formally, a Petroleum Project Advisory Group (PAG) meeting on 12 September 2006 was convened and commented on a summary document describing work undertaken on the project. At the meeting several issues were raised relevant to the direction of the scoping study:

- consideration needs to be given to biodiesel and ethanol
- ways to enhance natural attenuation need to be considered
- a survey of the policy and technical guidance used to make decisions about monitored natural attenuation in each of the states represented on the PAG should be undertaken. Their views on the Western Australia monitored natural attenuation (MNA) guideline should also be sought.

These issues have subsequently been addressed in this document.

1.2 The review team

This document has been prepared by the University of Technology, Sydney (UTS) team with CSIRO providing input and reviewing the document. The support of Ke Ye undertaking the survey of Australian natural attenuation literature is gratefully acknowledged. Funding for this project was provided by CRC CARE and the organisations of the review team.

2. Petroleum hydrocarbons and fuel characteristics

Crude oil is refined through distillation to create a number of petroleum end-products. These refined products can be classified according to their predominant carbon-atom ranges (ASTM 1995):

- gasoline – C₄ to C₁₂ hydrocarbons
- kerosene and jet fuels – C₁₁ to C₁₃ hydrocarbons
- diesel fuel and light fuel oils – C₁₀ to C₂₀ hydrocarbons
- heavy fuel oils – C₁₉ to C₂₅ hydrocarbons
- motor oils and other lubricating oils – C₂₀ to C₄₅ hydrocarbons.

Within these refined products the functional characteristics are related to the chemical structure of the petroleum hydrocarbons. These include:

- aliphatic hydrocarbons – this comprises straight (paraffins) or branched (isoparaffins) chains of carbon and hydrogen atoms
- monocyclic aromatic hydrocarbons (e.g. BTEX, which consists of benzene, toluene, ethylbenzene and the xylene isomers), and
- Polycyclic aromatic hydrocarbons (PAH) – this refers to hydrocarbons containing two or more fused benzene rings.

The specific composition of gasoline and other refined products can be estimated from composition studies on fresh fuels. The specific composition of gasoline fuel and oil will vary depending on the source of the petroleum, the production method, the end-use location and the season of the year (Cline et al. 1991). Further information on the range of BTEX concentrations within a range of refined fuels is provided in Parsons (2003).

2.1 Fuel additives

Petroleum fuels may contain oxygenated fuel additives which can boost gasoline's octane quality, enhance combustion, and reduce exhaust emissions. Australian data that may define the scope of contamination issues arising from these fuel additives are scarce. This can be attributed to the proprietary nature of many of the additives used, the number of suppliers in the fuels market with individual additives, the use of fuel imported directly to Australia and the ease with which fuel from different sources may be mixed at any one location (EPCSC 2006).

2.1.1 Ethanol

In Australia, ethanol has been blended with gasoline since at least 1992. A limit of up to 10% ethanol (ethyl alcohol) was approved for blending with gasoline (E10 blend) in 2003.

2.1.2 MTBE

In Australia, MTBE (methyl tertiary-butyl ether) has never been used by any Australian refinery, but may be present in fuels imported from overseas (around 30% of fuel used in Australia) (EPCSC 2005). In 2004 MTBE was restricted to 1% or less by volume in

Australia (DEH 2004). MTBE is a volatile organic compound that has two roles as a gasoline additive: to boost octane levels and to reduce emissions. In the US it was approved for use in 1979. Oxygenated gasoline must contain at least 2.7% oxygen by weight, which equals about 15% MTBE by weight. Generally the MTBE concentrations vary from 15 to 30% (Squillace et al. 1997). In Europe it was approved for use in 1988 and concentrations of MTBE vary from 1.5 to 15% (Sinke & Hecho 1999). In Europe the maximum MTBE concentrations are generally below 5% weight per weight (w/w) and often around 1% w/w (Noble & Morgan 2002a).

2.1.3 Biodiesel

Biodiesel can be used as a pure fuel or blended with petroleum in any percentage. Biodiesel is a generic name for fuels obtained by esterification of a vegetable oil. The esterification can be done either by methanol or by ethanol. The Fuel Standard (Biodiesel) Determination 2003 sets a fuel quality standard in Australia for biodiesel (Anon 2006).

2.2 Subsurface hydrocarbons

After petroleum hydrocarbons are released in the subsurface they distribute themselves among the various media (soil, water and soil vapour) and exist in different phases (non-aqueous, aqueous, solid and gas). The persistence and distribution of these hydrocarbons in the subsurface environment (i.e. NA) is controlled by contaminant fate and transport processes.

The focus of this report is on natural attenuation of petroleum hydrocarbons in groundwater. For this situation there are three basic release scenarios:

1. Aqueous release to groundwater. Dissolved hydrocarbon contaminants are directly introduced to the groundwater from the fuel hydrocarbon source. These then migrate and potentially attenuate within the resultant plume.
2. Aqueous-phase and/or light non-aqueous phase liquid (LNAPL) release to the vadose zone only. Dissolved hydrocarbon contaminants are either directly introduced to the vadose zone, or occur through percolating water dissolving contaminants from LNAPL that was released to the vadose zone. These dissolved contaminants are then transported to the water table and potentially attenuate within the resultant plume.
3. LNAPL release to groundwater. LNAPLs are sometimes referred to as phase separated hydrocarbon (PSH). These can be directly introduced to groundwater where they can pool and spread at the upper fringe of the water table. The LNAPL may be either mobile or somewhat immobile (often termed residual NAPL). A NAPL fuel can be smeared over the zone of water level changes – resulting in a distribution of immobile or residual NAPL that is above and below the water table interface. Components in LNAPL will dissolve into groundwater creating a plume of soluble hydrocarbons, which potentially attenuate as they move in the groundwater.

3. Monitored natural attenuation assessment

There are several approaches to MNA and its assessment. A generic approach to monitored natural attenuation developed in the US (NRC 2000; Rittman 2004) comprises three inter-related steps:

1. Development of a site conceptual model. This relies on site characterisation (Section 3.1) and developing biogeochemical footprints (Section 3.2) for contaminants of concern.
2. Analysis of site measurements to establish loss of contaminants, and then establishing a cause-and-effect relationship for specific destruction of contaminant species or strong immobilisation reactions. This step is commonly approached through using lines of evidence (Section 3.3) and may involve determining aquifer assimilative capacity (Section 3.4).
3. Monitor the site over the long-term to ensure that the natural attenuation processes continue to work. This step is underpinned by performance monitoring (Section 3.5) and evaluation (Section 3.6).

3.1 Site characterisation

Site characterisation is an investigative process for developing an understanding of the extent and environmental impacts of contamination sufficient to assess the risk to humans and the environment. Natural attenuation processes impact contaminant fate and transport, and refer to naturally occurring physical, chemical and biological processes, or any combination of those processes, that reduce the concentration and mass of polluting substances in groundwater. These natural attenuation processes are affected by the physical and chemical characteristics of the contaminants, the nature of the subsurface media and the site hydrology/hydrogeology. For petroleum hydrocarbons the key processes are shown graphically in Figure 1. A review of general site characterisation techniques and guidance is given in Davis et al. (2006).

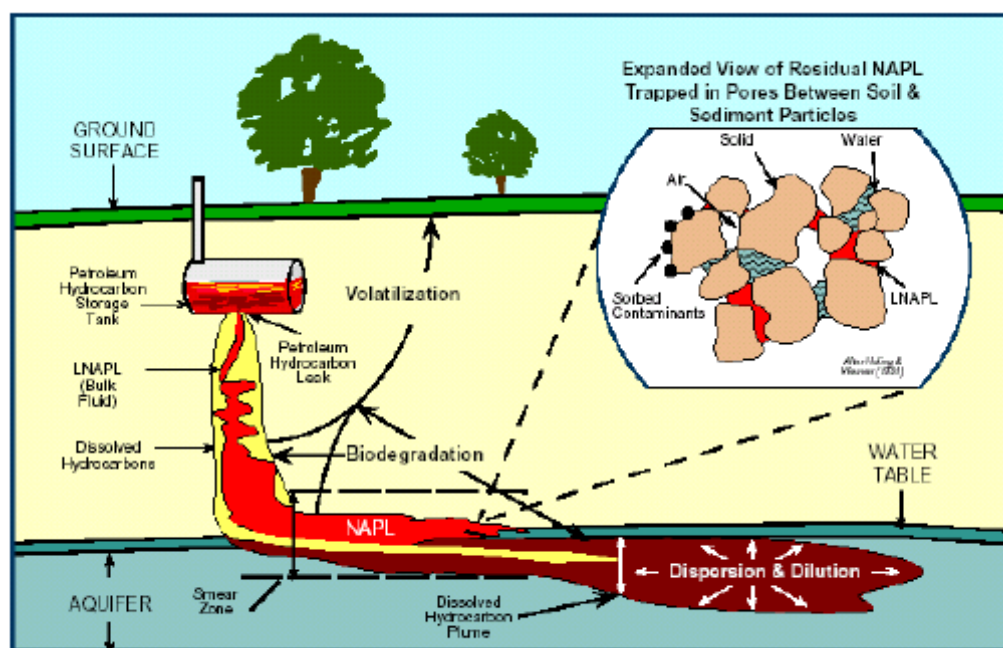


Figure 1. Natural attenuation processes at a petroleum hydrocarbon spill site (after DEP 2004)

3.2 Footprint and plume characteristics

The National Research Council (USA) recommends the use of biogeochemical footprints to distinguish clean water that has never been impacted by petroleum hydrocarbons from contaminants in groundwater which has been impacted by a fuel spill (NRC 2000). A biogeochemical footprint is a concentration change in one or more chemical species (in addition to the contaminants) and products of the reaction process that may be transforming or immobilising the contaminant (NRC 2000). Different fuel hydrocarbon constituents can have different biogeochemical footprints due to their differing physical and chemical properties.

The biogeochemical footprint expected for BTEX in groundwater is a depletion of electron acceptors in groundwater and production of other soluble chemicals and compounds. This may be manifested as decreased concentrations in some or all of dissolved oxygen, nitrate and sulfate, while concentrations would increase for the products of electron acceptor consumption such as manganese, iron, alkalinity and methane (Figure 2). To directly attribute these changes in groundwater biogeochemistry to the depletion of BTEX as the electron donor rather than existing dissolved organic carbon in the aquifer requires good site characterisation and a good conceptual site model.

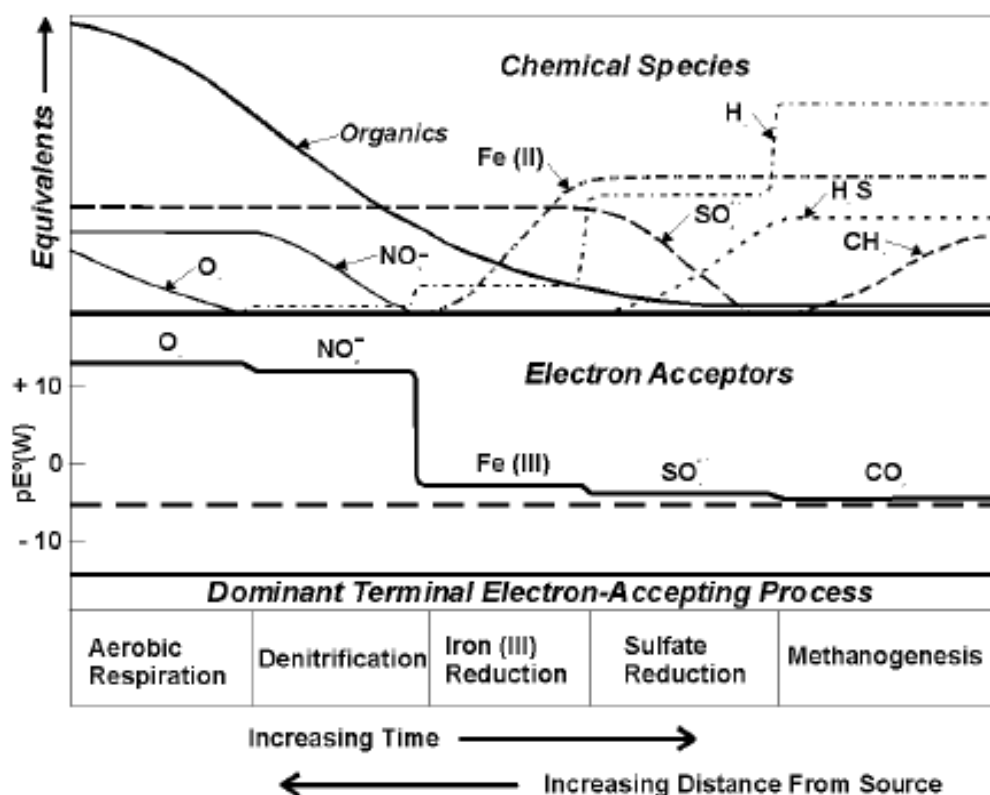


Figure 2. Schematic of electron acceptor usage and organics degradation (after Bouwer & McCarty 1984)

The biogeochemical footprint expected for ethanol within a fuel hydrocarbon plume may be similar to BTEX alone since ethanol is degraded through oxidative mechanisms by a similar range of electron acceptors. Indeed, ethanol may degrade in preference to benzene, in which case for a plume with both ethanol and benzene the ethanol plume length may be shorter than for benzene in the same plume (Mackay et al. 2006).

Evaluating the biogeochemical footprint and plume characteristics for MTBE is more complex than for other BTEX fuel components. MTBE can be degraded under oxidation-reduction conditions that are common in contaminated groundwater at gasoline spill sites. Electron acceptor usage similar to other hydrocarbon degradation is expected, since degradation can occur through oxidative mechanisms. However, the stoichiometric linkage between electron acceptor usage and degradation of MTBE is not as straightforward as for some fuel hydrocarbons. Degradation of MTBE may occur through bacterial metabolism as a sole carbon source for energy and growth, or through cometabolism where it is not utilised for growth or energy, but nevertheless transformed to another product by micro-organisms. Therefore, the challenge is to uniquely identify any changes in aquifer biogeochemistry directly associated with MTBE degradation. Due to its higher solubility, lower sorption (Table 1) and lower apparent biodegradability in some circumstances, MTBE can be more mobile within an aquifer than the BTEX compounds.

Table 1. Petroleum hydrocarbon properties

Chemical name	Organic carbon partitioning coefficient (log (K _{oc}) @20-25 C) (log (1/kg))	Solubility (@20-25 C) (mg/L)
Benzene	1.58	1.75E+03
Ethylbenzene	1.98	6.00E+02
Methyl t-butyl ether	1.08	4.80 E+04
Xylene (mixed isomers)	2.38	1.98 E+02
Xylene, m-	3.20	1.58 E+02
Xylene, o-	2.11	1.75 E+02

Values obtained from Wiedemeier et al. 1999a, Appendix B.

As a result, an MTBE plume may have a greater extent, and where the potential for 'plume diving' (Nichols & Roth 2006) is present, the more recalcitrant fuel components (e.g. MTBE) in older plumes could be found deeper in the aquifer than other fuel components. Therefore the footprint and characteristics of the MTBE plume may differ from any associated BTEX plume.

The biogeochemical footprint for polycyclic aromatic hydrocarbons (PAH) is more complex due to the limited bioavailability and preferred biodegradation pathway which can involve PAH either metabolised as a primary substrate or co-metabolised. Therefore, like MTBE, there may not always be a direct link between expressed assimilation capacity and the mass of PAH degraded.

3.3 Lines of evidence

There is broad scale acceptance of the concept of using lines of evidence to evaluate natural attenuation processes (ASTM 2004; DEP 2004; UK Environmental Agency 2000; US EPA 1997). Three lines of evidence are commonly used:

Primary lines of evidence are provided by observed reductions in plume geometry and observed reductions in concentrations of the constituents of concern at the site. To establish whether there is a clear and meaningful reduction of contaminant concentrations, various types of statistical tests (e.g. Mann-Whitney U Test, Mann-Kendall) can be used.

Secondary lines of evidence are provided by geochemical indicators of naturally occurring degradation and site-specific estimates of attenuation rates. This evidence provides a cause for the primary evidence and therefore must be capable of being clearly linked to the biogeochemical footprint for that class of contaminant. For fuel hydrocarbons, evidence for degradation (primary line of evidence) can be shown by:

- The depletion of electron donors and acceptors, and/or the production of reaction by-products. These changes in subsurface biogeochemistry are inter-linked and used to demonstrate that contaminant mass is removed rather than diluted or sorbed. Typically for BTEX, evidence could include the decreasing concentrations

of dissolved oxygen, nitrate, and sulfate and the increasing concentrations of manganese, iron, alkalinity and methane.

- Conservative tracers may also be used to help distinguish between dilution and degradation processes in analysing plume data. Some fuel components may act as a suitable tracer (e.g. trimethylbenzene, or benzene) where they are recalcitrant.
- New techniques using molecular tools and isotopes are emerging to provide direct evidence of biodegradation (Scow & Hicks 2005; Smets & Pritchard 2003). Stable isotopes for demonstrating MTBE degradation may be a viable approach (Wilson et al. 2005).
- Volatile fatty acids and dissolved hydrogen may also be used as reaction by-products or intermediaries. Phospholipid fatty acids have sometimes been used to determine microbial population changes that may be indicative of particular biodegradation processes. For other components such as MTBE, reaction intermediaries such as TBA may not be reliable indicators of degradation (Wilson et al., 2005).

Additional optional lines of evidence can be provided by microbiological information and further analysis of primary and secondary lines of evidence, such as through solute transport modelling or estimates of assimilative capacity. Microcosm studies can only show that micro-organisms capable of degrading the contaminants were present under the conditions that pertained at the time of sampling and during the experimental period. They do not provide direct evidence of *in situ* microbial activity which would show the contaminant was biologically degraded in the aquifer.

3.4 Assimilative capacity of aquifer

The assimilative capacity of an aquifer reflects the capacity of the groundwater and aquifer matrix to degrade the contaminant of concern. For petroleum hydrocarbons that are degraded by oxidative processes, the assimilative capacity will reflect the terminal electron accepting processes (TEAP). For the BTEX compounds, these processes are aerobic respiration, denitrification, manganese reduction, Fe (III) reduction, sulfate reduction and methanogenesis (Figure 2). The assimilative capacity can be linked to changes in the groundwater chemistry to give the expressed assimilative capacity (EAC) as indicated earlier.

The EAC measures the observed electron acceptor utilisation within an aquifer. This is evaluated from the concentrations of various electron acceptors and by-products from wells within the contaminant plume, compared with those species in background wells outside the plume. From the difference in chemistry between these waters the assimilative capacity of the aquifer that has been utilised during hydrocarbon degradation can be calculated (Brauner et al. 2004; Wiedemeier et al. 1999a, 1999b). The results are given in terms of the equivalent mass of hydrocarbon that would be degraded to give the water chemistry changes occurring within the contaminant plume.

Within an aquifer the total EAC would be comprised of the expressed capacity (in mass of hydrocarbon degraded) for each of the electron acceptor reduction reactions that occurred, and can be written as:

$$EAC_{TOTAL} = EAC_{O_2} + EAC_{Fe(II)} + EAC_{NO_3} + EAC_{Mn(II)} + EAC_{SO_4} + EAC_{CH_4}$$

The EAC is a convenient biogeochemical indicator since only the concentrations of the aqueous phase electron acceptors or metabolic by-products are measured. This considerably simplifies the sample collection and analysis required. However, for iron(II) and manganese(IV) the dissolved concentration may not reflect the total amount of that species that has been produced since these species can react with other ions (e.g. sulfide, carbonate) in the water and precipitate, making them unavailable for measurement in the groundwater. The EAC_{TOTAL} will therefore be a conservative estimate of electron acceptor consumption.

It is important to realise that while the assimilative capacity can be expressed in units of a particular compound (e.g. toluene), which is useful for comparative purposes between wells or through time, it does not mean that the aquifer will degrade that amount of that compound. The effect of multi-component solute mixtures, biodegradative kinetics and the biodegradability of a particular contaminant under different electron acceptor environments may need to be considered.

3.5 Performance monitoring

Monitoring is an essential component of an MNA strategy, which may be of even greater importance for MNA than for other types of remediation strategies due to the potentially longer remediation timeframes, potential for ongoing contaminant migration, and other uncertainties associated with using MNA. Specific objectives that should be met by a monitoring program for an MNA remedy include (US EPA 2004):

1. demonstrate that natural attenuation is occurring according to expectations
2. detect changes in environmental conditions (e.g. hydrogeology, geochemical, microbiological, land use or other changes) that may reduce the efficacy of any of the natural attenuation processes
3. identify any potentially toxic and/or mobile transformation products
4. verify that the plume(s) is not expanding down gradient, laterally or vertically
5. verify no unacceptable impact to down gradient receptors
6. detect new releases of contaminants to the environment that could impact the effectiveness of the natural attenuation remedy
7. demonstrate the efficacy of institutional controls that were put in place to protect potential receptors, and
8. verify attainment of remediation objectives.

Given the strong focus on using biogeochemical indicators to provide evidence for MNA, they are of critical importance in defining an effective monitoring program. Whilst there has been some discussion about the value of particular biogeochemical indicators at different sites (Brauner et al. 2004; Wilson et al. 2005), further knowledge is needed if long-term monitoring regimes are to be set up using these indicators, particularly since they will impact the cost-effectiveness of MNA as a remedial strategy.

The linkage between changes in environmental conditions (point 2 above) and biogeochemical indicators is also not well represented in the published literature, but is a critical aspect of designing an effective performance-oriented monitoring program.

3.6 Evaluating MNA

Monitored natural attenuation uses a weight of evidence based upon all lines of evidence. Lines of evidence are specific to a given site and therefore the amount of evidence/information to establish the efficacy of natural attenuation will vary.

A number of factors which influence the viability of MNA at a site have been identified and embedded within guidelines (see DEP 2004). Guidance documents on site characterisation also identify areas of uncertainty when developing conceptual site models (CSM). When trying to evaluate the CSM model and MNA at a field scale, a number of challenges arise (Alvarez & Illman 2006):

- establishment of credible background concentrations
- seasonal effects in groundwater flow and contaminant concentrations
- recognition of directional effects in mechanical dispersion
- development of preferential channels
- monitoring scale
- monitoring locations
- transformation into alternate compounds
- limits to sorption and reversible sorption.

In general, more information (e.g. more wells, more samples, and more lines of evidence) could be required for MNA demonstrations at sites which have greater uncertainty due to highly variable or heterogeneous conditions. However, the level of acceptable uncertainty may be dependant upon the risk of an impact upon a resource or receptor given that a risk-based approach to management is used.

4. Natural attenuation processes

Natural attenuation (NA) refers to naturally-occurring physical, chemical and biological processes, or any combination of those processes, which reduce the concentration and mass of polluting substances in groundwater (DEC 2004). The NA processes relevant to petroleum hydrocarbons are summarised in Table 2.

Table 2. Summary of important processes affecting solute fate and transport (modified Brauner et al. 2004; Weidemeier et al. 1999a)

Process	Description	Dependencies	Possible effect
Advection	Movement of solute by bulk groundwater movement.	Dependent on aquifer properties, mainly hydraulic conductivity, effective porosity, and hydraulic gradient; independent of contaminant properties.	At most sites, provides the main mechanism for contaminant movement in the subsurface.
Dispersion	Fluid mixing due to variable groundwater velocities and movement – which is accentuated by aquifer heterogeneities.	Dependent on aquifer properties and scale of observation; independent of contaminant.	Causes longitudinal, transverse, and vertical spreading of the plume; reduces solute concentration and can induce greater contact between the hydrocarbon contaminant and electron acceptors.
Diffusion	Spreading and dilution of contaminant due to molecular diffusion.	Dependent on the diffusion coefficient of the contaminant and concentration gradients; described by Fick's Law.	Diffusion of contaminant from areas of relatively high concentration to areas of relatively low concentration; generally unimportant relative to dispersion at most groundwater flow velocities.
Sorption	Reaction between the aquifer matrix and solute whereby the relatively hydrophobic compounds become sorbed to organic carbon or clay minerals.	Dependent on aquifer matrix properties (organic carbon and clay mineral content, specific surface area) and contaminant properties (magnitude of sorption is often related to solubility, hydrophobicity, octanol-water partitioning coefficient).	Tends to reduce solute transport rate relative to the groundwater flow rate and removes solutes from the groundwater via sorption to the aquifer matrix. It may be less important for old (steady state) plumes and in aquifers with significant flow rates.

Process	Description	Dependencies	Possible effect
Recharge	Movement of water through the capillary fringe of the water table into the saturated zone.	Dependent on aquifer matrix properties, depth to groundwater, surface water interactions and climate.	May replenish electron acceptor concentrations. Sorbed compounds may also desorb into infiltrating water.
Biodegradation	Microbially mediated oxidation-reduction reactions that degrade contaminants.	Dependent on groundwater geochemistry, microbial population, and contaminant properties.	Typically the most important process for contaminant mass reduction.
NAPL dissolution and weathering	Partitioning of soluble compounds from NAPL into groundwater. NAPL – whether mobile or residual – can act as a continuing source of groundwater contamination.	Dependent on aquifer matrix (relative permeability, capillary pressure, and residual saturation) and NAPL and NAPL component contaminant properties (magnitude reliant on solubility, mass fraction, volatility, density, interfacial tension).	Dissolution of contaminants from NAPL represents the primary source of dissolved contamination in groundwater.

These processes have been extensively described elsewhere (Brauner et al. 2004; Weidemeier et al. 1999a, 1999b). Within this study the focus is on reviewing current knowledge about these processes with a view to establishing the adequacy of that knowledge to support evaluation of monitored natural attenuation as a remedial strategy at Australian sites impacted by petroleum hydrocarbons.

4.1 NAPL weathering

The primary mechanisms that create LNAPL weathering and subsequent contaminant mass loss from an LNAPL source are dissolution and volatilisation. It is noted that biodegradation will primarily occur in the aqueous phase. Weathering rates or compound-specific depletion rates are a complex combination of the flux of infiltration or groundwater that comes into contact and flows past the NAPL. Subsequently, chemical, biological and other physical processes lead to concentration and mass reductions. There have been relatively few studies which have addressed the natural weathering of residual and mobile LNAPL compared with studies into processes affecting dissolved phase contaminants resulting from LNAPL sources. Davis et al. (1999) show NAPL compositional profiles indicating benzene depletion relative to other components of the gasoline NAPL – these are related to plume concentrations. CSIRO (Bastow et al., unpublished) is furthering studies for diesel and gasoline NAPLs to determine mass removal rates.

A major study was undertaken by Parsons (2003) to improve the estimation of natural LNAPL weathering rates and source term reduction rates which are incorporated into natural attenuation models. It was found that the BTEX weathering rates from mobile LNAPL vary from site to site, and are influenced by factors such as age of spill, aquifer

substrate, relative solubility of individual compounds, free-product geometry and the rate at which groundwater and precipitation contacts mobile LNAPL. Dissolution of components from a NAPL to a water phase is usually described by Raoult's Law. Parsons (2003) believed that dissolution was generally rate-limiting for mobile LNAPL weathering. Benzene and toluene were more rapidly depleted from a NAPL source (i.e. had higher weathering rates) than ethyl-benzene and xylene due to their higher solubilities. As expected, at sites with lower groundwater flows there were significantly lower weathering rates due to lower BTEX fluxes from the LNAPL to groundwater. Recent research (Bastow et al., CSIRO unpublished manuscript) has indicated that additional altered compounds are formed during NAPL aging which may be more soluble in groundwater. The biodegradation and fate of such compounds are yet to be determined.

A compilation of source area wells at 366 petroleum (predominately gasoline) sites by Farhat et al. (2002) has been used to estimate first order BTEX decay rates in NAPL. The decay rates at the 180 most contaminated sites are most likely to represent sites with mobile LNAPL. The data from both of these studies is reproduced in Table 3 and forms the database for the Source-DK model (GSI 2002) which could be used to estimate LNAPL weathering rates.

Table 3. Summary of BTEX and total BTEX first order LNAPL weathering rates

Parameter	Total BTEX	Benzene	Toluene	Ethyl-benzene	Xylene
	(% reduction /year)	(% reduction /year)	(% reduction /year)	(% reduction /year)	(% reduction /year)
JP-4 Mobile LNAPL ^{&}					
Average of six sites	15.1	23.3	-	-	-
Range excluding outlier	4 to 28	11 to 39	-	-	-
Conservative estimate	12.8	12.8	-	-	-
JP-8 Mobile LNAPL ^{&}					
Range at one site	10 to 35	6 to 53	-	-	-
Conservative estimate	21.4	25.1	-	-	-
Petroleum (mostly gasoline) [#]					
Average at 359 sites	-	22	41	18	25
Average at 180 most contaminated	-	16	-	-	-

[&] Data from Parsons (2003)

[#] Data from Farhat et al. (2002)

Predictive modelling of natural attenuation at seven fuel-contaminated sites was found to be generally conservative compared with monitoring data after 3–7 years had elapsed (Jeong et al. 2005; Parsons 2001). Most of the calibrated models over-estimated plume distance, source persistence and time for attenuation to regulatory compliance. Uncertainty regarding source weathering rates was identified as a potentially significant source of error in the modelling and that realistic rates at the study sites were between 8–23% per year. Natural source reduction using the OILENS module of HSSM (Weaver et al. 1994) did not exceed 4.9% per year (geometric rate) and the authors suggest that the rates obtained from this model of less than 5% per year may be overly conservative and should be used with caution.

4.2 Biodegradation

A significant number of studies have identified biodegradation as the key attenuation process for fuel hydrocarbons which causes mass loss of contaminants from groundwater. The degradation or attenuation rate is a key factor in MNA studies. Calculation and use of the field-based first-order attenuation rate constant is discussed in Newell et al. (2002) and various protocol documents. Extensive laboratory data is also available. However, to appropriately apply any rate constant requires an appreciation of the limitations of current understanding about the underlying biodegradation processes for particular classes of hydrocarbons. The current status was reviewed by the National Research Council (Table 4) in 2000.

Table 4. Overview of categories relevant to MNA (modified from NRC 2000)

Chemical class	Current level of understanding ^a	Likelihood of success given current level of understanding ^b	Susceptibility to microbial transformation ^c	
			Aerobic	Anaerobic
Hydrocarbon				
BTEX	High	High	1	2
Gasoline, fuel oil	Moderate	Moderate	1	2
Non-volatile aliphatic compounds	Moderate	Low	1, 2	2, 4
Polycyclic aromatic hydrocarbons	Moderate	Low	1, 2	2, 4
Creosote	Moderate	Low	1, 2	2, 4
Oxygenated hydrocarbons				
Low molecular weight alcohols, ketones, esters	High	High	1, 2	2
MTBE	Moderate	Low	2–5	4, 5

^a Level of understanding: 'high' means there is good scientific understanding of the processes involved and field evidence confirms attenuation processes can protect human health and the environment. 'Moderate' means studies confirm that the dominant attenuation process occurs, but the process is not well understood scientifically. 'Low' means scientific understanding is inadequate to judge if and when the dominant process will occur and whether it will meet regulatory standards.

^b 'Likelihood of success' relates to the probability that at any given site, natural attenuation of a given contaminant is likely to protect human health and the environment. 'High' means scientific knowledge and field evidence are sufficient to expect that natural attenuation will protect human health and the environment at more than 75% of contaminated sites. 'Moderate' means natural attenuation can be expected to meet regulatory standards at about half the sites. 'Low' means natural attenuation is expected to be protective at less than 25% of contaminated sites. A 'low' rating can result from a poor level of scientific understanding.

^c The numeric entries for each chemical class provide a rating of susceptibility to microbial transformation under aerobic and anaerobic conditions: 1 = readily transformed or mineralised; 2 = degraded or transformed under a narrow range of conditions; 3 = metabolised partially when second substrate is present (co-metabolism); 4 = resistant; 5 = insufficient information.

The high level of understanding and high likelihood of success of remediating a site by MNA led the NRC to conclude that at that time natural attenuation was well established as a remediation approach for only a few types of contaminants, primarily BTEX. Each of the other classes of hydrocarbon had various levels of uncertainty. Knowledge about specific classes of hydrocarbon compounds is presented in the following sections.

4.2.1 BTEX data

To support the application of MNA there are extensive compilations available and reviews of BTEX biodegradation rates for laboratory and field sites, primarily based on studies from the United States. Thierrin et al. (1993; 1995) and Davis et al. (1999) provided the first direct *in situ* measures of natural biodegradation rates of the BTEX compounds in groundwater using deuterium-labelled benzene, toluene, o-xylene and naphthalene. These rates were compared to rates inferred from modelling and from detailed depth profiling and cross-sectional investigations of a BTEX plume in urban Perth.

In general, the biodegradation rates are compound-specific and reflect biogeochemical conditions. The compilations have variously been categorised into rates (Monod, zero-order, first-order), field/laboratory studies and biogeochemical (electron acceptor) conditions. These studies include Suarez and Rifai (1999) which incorporated 133 BTEX studies (field and laboratory) and Aronson and Howard (1997).

Biodegradation rates from laboratory experiments are reported to be generally higher than field rates. This result may occur because laboratory studies maintain favourable ambient conditions for biodegradation, including higher temperatures, or perhaps because well mixed conditions are maintained. The difference in median values for fuel hydrocarbons were less than an order of magnitude (Suarez & Rafai 1999), with the exception of toluene and ethyl benzene which were impacted by high rates from one laboratory study. In a review of the literature about the scale-up of laboratory assessments of biodegradation to field scale studies, Noble and Morgan (2002b) conclude that aerobic BTEX and MTBE rates were 2–5 times slower in the field and anaerobic rates for benzene were 10–100 times and for TEX 5–10 times slower in the field. These factors were determined after corrections for ambient temperature conditions had been made. They recommend that site-specific field data be employed where possible and laboratory data only applied where necessary to achieve an appropriate level of confidence in the overall assessment. Johnson et al. (2003) reviewed the potential for benzene degradation under a range of anaerobic groundwater conditions.

As indicated earlier, predictive modelling of natural attenuation at seven fuel-contaminated sites was found to be generally conservative compared with monitoring data after 3–7 years had elapsed (Jeong et al. 2005). The first-order decay rates for dissolved BTEX (0.001–0.007 per day) were greater than or similar to those reported by Suarez and Rifai (1999) for field studies of combined aerobic/anaerobic sites (0.001–0.002 per day).

Recent studies with high resolution multi-level sampling wells through plume fringes and scenario modelling have established that readily biodegraded compounds with fast reaction kinetics may occur in narrow (1–2 m) fringe zones. These studies have indicated that such fringe processes may be the dominant contribution to natural attenuation processes and eventual plume extent (Davis et al. 1999; Ham et al. 2006; Maier & Grathwohl 2006; Wilson et al. 2004). This demonstrates the need to appreciate the spatial variability of key biodegradation processes when designing performance-based monitoring systems.

4.2.2 PAH data

The polycyclic aromatic hydrocarbon (PAH) groups of compounds found in fuels are complex mixtures with the constituent compounds having a wide range of chemical, physical and toxicological properties. Generally, volatilisation and hydrolysis of PAH are not important mechanisms for PAH attenuation in subsurface environments, although naphthalene can be at significant concentrations in soil gas and in groundwater. Primarily, PAHs are drivers of risk in hydrocarbon-contaminated soils rather than groundwater. Due to their low solubility and high partition co-efficient, sorption and consequentially bioavailability for biodegradation are of prime importance.

Numerous studies on biodegradation of PAHs have been performed (Juhasz & Naidu 2000; Rogers et al. 2002), but the knowledge on biodegradation behaviour in the field is very limited. It has been reported that biodegradation rates in the field are primarily governed by bioavailability which differs between PAHs. This was established from a laboratory study which reported that experimental biodegradation rates for 10 PAHs showed much less variation than rates reported for field studies (Knights & Peters 2002).

Approaches for implementing MNA at PAH-impacted sites are poorly developed compared with BTEX or chlorinated solvent sites, although MNA has been reported as being accepted at a former coal tar site in Germany (Blum et al. 2005). Davis et al. (1999) considered naphthalene biodegradation under sulfate-reducing conditions.

4.2.3 Fuel additives data

The presence of fuel oxygenates within a gasoline release increases the level of uncertainty about monitored natural attenuation as a remedial strategy due to the different chemical and physical properties of the additives compared with BTEX. An extensive number of micro-organisms are thought to biodegrade fuel oxygenates but most of them have long acclimation times and slow growth rates (Daugherty et al. 2004).

There is an emerging body of knowledge about MTBE degradation (Fiorenza & Rifai 2003; Schmidt et al. 2004; Squillace et al. 1997), with an excellent review by Wilson et al. (2005). Studies show that MTBE can be degraded under oxidation-reduction conditions that are common in contaminated groundwater at gasoline spill sites (Wilson et al. 2005). For degradation under aerobic conditions it can involve an organism using MTBE as a primary substrate or co-metabolising MTBE. Most of the laboratory studies conducted to date have failed to associate anaerobic MTBE biodegradation with a specific electron-accepting process (Schmidt et al. 2004). The anaerobic biodegradation of TBA (a biodegradation product of MTBE) at gasoline spill sites has not been well documented (Wilson et al. 2005). The growth rate for degraders of MTBE is from one-tenth to one-hundredth of the growth rate of bacteria that degrade conventional petroleum hydrocarbons, and acclimation to MTBE may take several years (Wilson et al. 2005). Therefore, a plume that has stabilised for BTEX components may not have stabilised for MTBE. It is clear from the literature that it is necessary to have a more complete understanding of aquifer biogeochemistry and to use more sophisticated approaches to evaluating degradation for MTBE compared with many other fuel components.

There is a high level of understanding about the biodegradation of ethanol, and knowledge about the impact of ethanol within a gasoline plume is accumulating (Niven 2005; Powers et al. 2001). Ethanol can impact BTEX transport in two ways. Through co-solvency it can increase the concentration of BTEX compounds, although this impact is generally thought to be minor (Rixey et al. 2005) at most sites. It can inhibit BTEX degradation by preferentially consuming electron acceptors and nutrients. The median plume length for benzene in ethanol containing plumes was greater than for plumes without ethanol (Ruiz-Aguilar et al. 2003).

Biodiesel may be used as a replacement or supplement to petroleum diesel. The impact of biodiesel on petroleum fuel degradation has not been widely published.

Zhang et al. (1998) studied blends of biodiesel/petroleum diesel at different volumetric ratios including 80/20, 50/50, and 20/80 and found that all the tested biodiesel fuels were 'readily biodegradable' and in the presence of biodiesel the degradation rate of petroleum diesel increased to twice that of petroleum diesel alone. Lapinskiene et al. (2006) found that biodiesel is easily biotransformed compared with the more resistant diesel fuel. The diesel fuel was found to have toxic properties at concentrations above 3% (w/w), while the biodiesel fuel was shown to have none up to a concentration of 12% (w/w).

4.2.4 Sustainability of degradation rates

For biodegradation to occur, certain requirements must be fulfilled: the presence of micro-organisms capable of degrading the specific compound; a carbon source (the organic compound in this case); the presence of electron acceptors; adequate amounts of nutrients (nitrogen, phosphorus, calcium, magnesium and iron); and appropriate environmental conditions such as ambient temperature, and the absence of toxic materials (Suarez & Rafai 1999). To sustain biodegradation would require maintenance of these conditions.

The longevity of the assimilative capacity of an aquifer over the life of a MNA remedial strategy is poorly understood. For sustainability to occur, the mass flux of contaminants needs to be balanced with the assimilative capacity of the aquifer. Changes to either of these may make MNA unsustainable at a given site.

Recharge is being recognised as playing an important role in electron acceptor supply and revitalisation at some sites. Some groundwater-based electron acceptors (e.g. oxygen, nitrate, sulphate, carbon dioxide) can be replenished by groundwater flow and recharge processes. Other electron acceptors which occur in the solid phase, such as Fe(III), have a finite capacity and are generally not renewable. Expansion of hydrocarbon plumes has been linked to the depletion of Fe(III) oxides in contaminated aquifers (Bekins et al. 2005; Cozzarelli et al. 2001). Field observations at several sites suggest that once bioavailable Fe(III) is depleted, methanogenic conditions occur and the degradation of benzene and ethylbenzene may be limited compared with degradation under iron reducing conditions (Bekins et al. 2005). Recent research in Perth has indicated that benzene was readily degraded under methanogenic conditions, whereas ethylbenzene was somewhat persistent (Davis & King, personal communication). At MNA sites where electron acceptor sustainability is influenced by recharge processes, long-term site management plans would need to accommodate this. Large scale changes to the hydrological cycle such as climate change may therefore impact the replenishment of ground-based electron acceptors and MNA management at these sites.

4.3 Sorption

Sorption may be described as the partitioning of a dissolved contaminant from out of a water phase to a solid phase. The mechanisms responsible may include adsorption onto the surface of the solid, absorption into the crystalline structure of the solid or organic matter, as well as the precipitation as a molecular coating onto the surface of the solid. Sorption can be an important mechanism for the natural attenuation of

dissolved hydrocarbon compounds – at least in retarding the rate of movement of the compounds in groundwater. Sorption is not a MNA mechanism for mass reduction if a plume is considered to be steady state – since it will have reached its maximum extent. Desorption of contaminants during MNA can contribute to pore water contaminant concentrations.

Currently, very simplistic modelling approaches such as linear isotherms are widely adopted in modelling. A more sophisticated approach to understanding desorption and representing it within models is necessary if bio-attenuation of hydrophobic compounds is to be accurately predicted (Allen-King et al. 2002; Haws et al. 2006).

4.4 Recharge – influencing flow paths and electron acceptors

Recharge is a major hydraulic factor which can induce downward vertical migration of a dissolved phase contaminant plume (plume diving). Other hydraulic, biochemical and geological factors also contribute to diving plumes (Nichols & Roth 2006). Plume diving is often discussed in relation to MTBE plumes and is more evident in longer, older plumes with more recalcitrant compounds.

Studies from detailed sampling near the water table surface have shown the importance of recharge infiltration on electron acceptor availability. Scholl et al. (2006) found that recharge infiltration supplies sulfate and nitrate to a depth of 1.75 m. Recharge and seasonal water level fluctuations drive a cycle of sulfide oxidation and sulfate input followed by sulfate reduction. They found that where sulfate reduction occurs, the process may account for significant transformation of organic compounds.

Scenario modelling has shown that the relation between recharge and plume length is non-linear, with a small recharge value causing a significant initial drop in the plume length (Rolle et al. 2005).

Mace et al. (1997) calculated the standard deviation of the direction of groundwater flow at 132 gasoline stations in Texas. For roughly one-third of the sites in Texas, the direction in groundwater flow was highly variable, and the concept of a single flow direction was not the best representation of the behaviour of the plume. Davis et al. (1999) have also reported variability in flow direction which can impact inferences from sampling data.

4.5 Volatilisation

The partitioning of contaminants between the vapour phase and groundwater is dependent on the concentration of the contaminant in groundwater and the Henry's Law constant for the contaminant. Chiang et al. (1989) have demonstrated that 10% of the mass of dissolved BTEX in groundwater is lost to volatilisation. Barber et al. (1990) also showed that only limited exchange between a plume in groundwater and soil gas would occur. Generally the impact of volatilisation on petroleum hydrocarbon contaminant reduction is assumed to be negligible. However, vapour loss from NAPL in the unsaturated zone can be significant.

4.6 Plume behaviour

There have been a number of investigations that have analysed data from multiple sites to establish petroleum hydrocarbon plume behaviour. These have primarily been in California (Happel et al. 1998; Rice et al. 1995; Shih et al. 2004), Texas (Mace et al. 1997), Florida (GSI 1997), Alberta (CAPP 2002) and elsewhere (Newell et al. 1990). It should be recognised that the conclusions from these studies are representative of specific hydrogeological environments, dominant natural attenuation mechanisms, and release scenarios (leaking underground storage tank, upstream facilities) in only those locations that were studied. Therefore the relevance of that data to other locations depends on whether the conditions are broadly similar. These types of studies may have value in that they set broad boundaries for hydrocarbon plume behaviour in different contexts.

4.6.1 Plume stability

Groundwater plumes emanating from petroleum releases were categorised based on calculated plume area from historical data on contaminant concentrations. This can also be equated to stages in the plume life cycle:

- 'Expanding' or 'growth' phase: increase in plume area, mass flux of contaminants exceeds the assimilative capacity of the aquifer.
- 'Stable' or 'steady state' phase: insignificant change in plume area, mass flux of contaminants equals assimilative capacity of aquifer.
- 'Shrinking' or 'decay' phase: decrease in plume area, mass flux of contaminants less than assimilative capacity of aquifer.
- 'Exhausted': plume concentrations very low and unchanging over time.

It is generally accepted that the distribution of contamination at a site needs to be stable or contracting for MNA to be considered a viable component of a remedial strategy (Daugherty et al. 2004). A number of multi-site studies have been analysed for plume stability (Table 5).

Table 5. Plume stability trends

	Plume concentration		
	Expanding	Stable or exhausted	Shrinking
Rice et al. 1995	8%	33%	59%
Mace et al. 1997	14%	38%	47%
CAPP 2002	6%	47%	25%
Buscheck et al. 1996	-	91%	
	Plume length		
	Expanding	Stable or exhausted	Shrinking
Rice et al. 1995	8%	59%	33%
Mace et al. 1997	3%	70%	26%
Buscheck et al. 1996	-	67%	

These studies showed that the concentration of contaminants within the plume were predominantly stable or decreasing at most sites (72–92%) with a relatively small number growing. The plume studies also show that the number of plumes that were stable/shrinking in length were less than the number of plumes that were stable/shrinking in terms of contaminant concentration.

Since releases of petroleum products may contain compounds with significantly different functional characteristics, there may be plumes in different stages of plume stability present at a site. For example, at a site with a BTEX/MTBE release, the MTBE plume may be longer and in an expanding stage due to its greater mobility compared with BTEX components which may be at steady state (i.e. stable) or shrinking.

4.6.2 Plume length

If the remediation objective for MNA is to minimise exposure or to prevent further migration of petroleum hydrocarbons off-site then plume length is an important consideration. The plume length data for a number of multi-site studies has been compiled (Table 6).

The data from the studies is generally comparable; there is some variability between studies particularly due to the different plume delineation limits. While the median length of the plumes only varied from 27–75 m across the studies, there was significant variation between the studies for plume lengths at the 75th and 90th percentile.

Studies that had a greater range of hydrogeological conditions represented had a greater variability in plume length. Mace et al. (1997) found in the karst terrain that some plumes exceeded 2300 m. The CAPP (2002) study found that the median plume length varied from 40 m in low permeability bedrock (e.g. shale, mudstone) to 125 m in high permeability bedrock (e.g. sandstone), while plume length in unconsolidated sediments only ranged from 50 m to 58 m across the low and high permeability sediments.

The Australian study had a limited range of hydrogeology from clays to sand. Recent modelling efforts have determined the impact of lateral diffusivities on the ultimate length of plumes undergoing NA (e.g. Ham et al. 2004).

Table 6. Plume length data for BTEX and TPH

Location of Sites	California	California	Texas	Florida	Alberta	Entire USA	Australia
Study	Rice et al. 1995	Shih et al. 2004	Mace et al. 1997	GSI 1997	CAPP 2002	Newell et al. 1990	Wright et al. 1999
No. sites	271	95	217	74	33	42	10
Plume constituent	Benzene	Benzene	Benzene	Benzene, BTEX	BTEX constituents, Total Purgeable Hydrocarbon, Total Extractable Hydrocarbon	Mostly benzene, BTEX constituents	BTEX, TPH
Maximum length (m)	522	168	493	183	900	920	100
90th percentile (m)	78		116	64	390	288	
75th percentile (m)	45		76	48	140	122	
Median length (m)	31	51	55	27	75	65	30
25th percentile (m)	20		42	18	50	26	
Minimum length (m)	2	7	16	4	25	5	10
Plume delineation limit	10 µg/L	5 µg/L	10 µg/L	1-50 µg/L	Analytical detection limit	Not reported, probably analytical detection limit	10-300 µg/L

Fuel additives

In the US and Europe the production and use of fuel oxygenates has increased dramatically over the last couple of decades in response to requirements to improve petroleum product performance and improve air quality. Several studies have tried to gauge the impact of fuel additives on plume length (Table 7).

Table 7. Plume length data for fuel oxygenates

	Median benzene plume length in plume without oxygenate (m)	Median MTBE plume length in MTBE containing plume (m)	Median benzene plume length in ethanol containing plume (m)
Reid et al. 1999	35	43	
Shih et al. 2004	51	84	
Ruiz-Aguilar et al. 2003	48		80

Generally the plume length of benzene was increased by a factor of less than 2 when realistic concentrations of fuel additives were present in the gasoline. Shih et al. (2004) found that plumes with fuel and oxygenates were significantly longer (20–30%) than TPH and benzene plumes without oxygenates. While MTBE is known to be more mobile than BTEX, it was recognised in the study that there may have been a difference in the age of the plumes which could impact that result. Australian data in defining the scope of the problem arising from these additives are scarce (EPCSC 2006), however due to the apparent limited use of MTBE in Australia it may not be a high priority knowledge gap.

The impact of ethanol on the environment has been reviewed by Niven (2005). While ethanol is readily biodegradable it can compete for electron acceptors with BTEX and therefore may reduce the biodegradation rate of these compounds (Mackay et al. 2006). Ruiz-Aguilar et al. (2003) found the plume length for benzene increased in ethanol containing plumes. Simulations by Molson et al. (2002) have shown that under some conditions a 10% ethanol component in gasoline can extend the travel distance of a benzene plume by up to 150% relative to that from an equivalent ethanol-free gasoline spill.

4.7 Modelling natural attenuation processes

Mathematical modelling of contaminant fate and transport in groundwater can have an important role to play in decision-making at contaminated sites. Natural attenuation screening models have simplifying assumptions which enable judgements to be made about natural attenuation with limited data. They can be applied at early stages of the site investigation process to help develop site conceptual models and data collection strategies. At later stages of the site investigation process they can be used to explore data uncertainty. More sophisticated, fully deterministic numerical models are available to provide a higher level of predictive capacity when the more intensive data and time requirements for their implementation can be met. They are typically required where complex biodegradation, sorption and transport processes occur at a site. In addition, where fringing reactions on the edges of plumes are thought to be important, simple models that assume uniform degradation throughout a plume will be inaccurate.

The goal of this section is to identify various approaches used in a screening level assessment of natural attenuation of petroleum hydrocarbons at a site. A detailed review of contaminant fate and transport modelling is beyond the scope of this report. An excellent review of modelling the fate of petroleum hydrocarbons in groundwater is presented by Prommer et al. (2003b). There are a number of critical reviews about the approaches and mathematical formulations used to represent biogeochemical processes in groundwater (Crawford, 1999; Islam et al. 2001) and the adequacy of these in representing BTEX biodegradation processes (Maurer & Rittman 2004) and bioavailability (Haws et al. 2006).

Some typical outcomes that can be desired from natural attenuation modelling at a screening level include:

- prediction of plume length or contaminant concentrations at some point along the plume
- prediction of time to achieve plume length
- identification of uncertainty associated with the predictions.

There are several different modelling approaches that can be used to generate these outcomes:

- **Degradation rate approach**

Models which use a first-order degradation rate can be used to evaluate spatial data concentrations along plume centre-line. They are based on an analytical or numerical solution to the advective-dispersive reactive transport equation based on simplifying assumptions for the contaminant source. Uncertainties in a number of parameters (e.g. dispersion, sorption, biodegradation) are therefore lumped together in the fitted first-order degradation rate. This is a more empirical approach to modelling natural attenuation involving some theory and empirical fitting of parameters. Further guidance on determining first-order rate constants for monitored natural attenuation studies is provided in Newell et al. (2002). Caution is however required where fringing reactions dominate, or where plumes have multiple redox zones.

- **Electron mass balance approach**

This approach uses an instantaneous reaction rate where petroleum hydrocarbon (electron donor) removal is directly linked to the consumption of electron acceptors based on stoichiometric relationships. This is a more process-oriented approach.

- **Simplified geochemical reaction models**

This approach uses a simplified source zone configuration with a geochemical reaction code coupled to a transport code. This approach can be extended to more complex scenarios using the geochemical code PHREEQC (Parkhurst & Appelo 1999) with its integrated 1D transport code or a 3D transport code (Parkhurst et al. 2004; Prommer et al. 2003a).

There are a number of widely disseminated and well documented codes that are used for screening level assessment of natural attenuation. These codes may use one or several of the modelling approaches described, and some can handle NAPL dissolution. Codes such as Natural Attenuation Software (Chapelle et al. 2003; Mendez et al. 2004), BioScreen (Newell et al. 1996) and SourceDK (GSI 2002) are widely utilised. From a recent European Union project (Wilson et al., 2005) a suite of tools (CoronaScreen) were developed. These include an Analytical model (Gutierrez-Neri et al. 2005), Electron Balance model (Thornton & Hüttmann 2005) and the Travelling 1D model (Watson & Wilson 2005). The CoronaScreen approach recognises that each of the model codes have fundamentally different underlying assumptions, and that the application of all codes to a site allows the user to assess natural attenuation from different perspectives and therefore explore issues related to the quantification of fringe and core processes.

5. Implementing natural attenuation

5.1 Australian studies into natural attenuation processes

To increase the adoption of innovative groundwater remediation strategies there is a need to build a body of scientific knowledge around the behaviour of petroleum hydrocarbons in the subsurface. The authors are not aware of any previous systematic attempt to compile studies related to petroleum hydrocarbon contamination at Australian sites. For this study a review of major Australian conferences, University libraries, as well as searches in electronic databases was undertaken (see Appendix A for details). The immediate goal of this work was to be able to judge the extent of published knowledge about hydrocarbon contamination in groundwater under Australian hydrogeological conditions, and to provide a database that could be used if further research into aquifer scale studies were undertaken. Therefore, a detailed review of each paper and linking that to information about different regional hydrogeological settings and comparing that with international experiences were beyond the scope of this report, but were originally part of a future stage of work involving scenario modelling. A full listing of the papers is made in Appendix A. Descriptive comments about the body of work are made in this report.

A total of 119 articles, which either had information relevant to natural attenuation processes or were generally related to hydrocarbon contamination at Australian sites, were found. These included some active remediation studies as well as natural attenuation processes. Of these, there were 38 journal articles, 16 higher degree theses and 65 conference papers. However, of these only 26 papers had specific data relating to sorption rates, biodegradation rates, plume hydrochemistry and plume dimensions for petroleum hydrocarbons. Many articles lacked a degree of specificity about site location, degradation rates and contaminant data, which therefore limited the usefulness of the articles for contributing to a generalised understanding of contaminant behaviour in those environments. This may be due to a sensitivity of reporting about groundwater contamination.

It was clear from the review that there is not a well-established, published body of knowledge about the actual behaviour of petroleum hydrocarbons in groundwater at Australian sites. There have been some data intensive, highly detailed studies undertaken at several sites which have been published. In particular, there were 18 articles by CSIRO about hydrocarbon contamination in the shallow sand aquifer system (Quaternary aquifer) around Perth. Another focus of studies was in another sand aquifer (Botany aquifer) in New South Wales. They could provide the fundamental data for scenario modeling at those locations. Generally there were few papers which described contaminant behaviour in fractured rock and clay sites.

There were two multi-site papers that illustrated plume behaviour across at least two sites (Borg 2000; Wright et al. 1999). In total those papers described 12 sites. There was very little published data which could be used to benchmark Australian conditions with those reported from overseas sites. There is a large amount of unpublished data and literature held by the oil industry and state regulatory authorities, which could be used to give a much clearer indication of typical behaviours and process uncertainty for hydrocarbon plumes across a range of hydrogeological settings, should that be considered beneficial to all stakeholders.

Future project stages envisaged as part of the NA project include work on scenario modelling of representative hydrogeological settings. Whether the existing hydrogeological settings which may potentially be exposed to hydrocarbon contamination have been mapped and classified in a form suitable for integration with any available contaminant data has not been assessed as part of this review. Within Melbourne, the recent broad scale mapping of hydrogeology for aquifer storage and recovery would provide useful information (Dudding et al. 2006) for the development of representative hydrogeological systems in that region.

5.2 Enhanced MNA

There is interest in techniques which enhance the natural attenuation processes for petroleum hydrocarbons – in essence these are simply remediation techniques for petroleum hydrocarbons. MNA may need to be enhanced or remediation needed, due to cost-benefit considerations obtained through a shorter remedial lifecycle or as part of a contingency strategy when MNA is not reaching its remediation goals. Alternative technologies can be used to enhance MNA (Table 8).

Table 8. Interactions between remedial technologies and MNA of petroleum hydrocarbons (Wiedemeier & Chapelle 1998)

Technology	Possible benefit to MNA	Possible detriment to MNA
Bioslurping	Volatilisation, enhanced oxygen delivery/aerobic biodegradation	None
Pump and treat	Plume containment, enhanced oxygen delivery/aerobic biodegradation	None
Air sparging	Volatilisation, enhanced oxygen delivery/aerobic biodegradation	None
In-well circulation/stripping	Volatilisation, enhanced oxygen delivery/aerobic biodegradation	None
Landfill caps	Source containment/ isolation	Reduced oxygen delivery/aerobic biodegradation
Phytoremediation	Plant-specific transpiration/enzymatically-mediated degradation, enhanced biodegradation in the rhizosphere, and plume containment	None
Excavation/backfilling	Source removal, enhanced oxygen delivery/aerobic biodegradation	None
Chemical oxidation	Enhanced oxidation	None
Chemical reduction	Unknown	Scavenges inorganic electron acceptors/ decreased oxidation
Oxygen releasing compound	Enhanced oxygen delivery/aerobic biodegradation	None
Carbon substrate addition	None	Competing carbon source
Zero-valent iron barrier wall	Unknown	Unknown
Biological barrier wall	Unknown	Unknown

5.3 Australian regulatory approaches to MNA

A review of MNA protocols was beyond the scope of this project and originally envisaged for the next stage of the project. However, at the CRC CARE Petroleum Project Advisory Group (PAG) meeting on 12 September 2006 it was decided to undertake a survey to better understand Australian regulator approaches to MNA. A survey was emailed out and the responses collated (Table 9).

Table 9. Responses to MNA survey

1	Is monitored natural attenuation (MNA) for petroleum hydrocarbons accepted within your jurisdiction?
WA	Yes
NSW	Yes, but with some limitations as outlined in our draft policy document (Appendix B).
SA	Yes it is, subject to sufficient demonstration that NA is occurring and compliance with the WA guidelines.
Qld	Yes, with qualifications.
ACT	MNA has been used in the ACT as one of the acceptable means of groundwater remediation for many years.

2	What is the policy setting for deciding if MNA is appropriate in your jurisdiction? These settings could include factors related to the presence of NAPL, remediation timeframes, land use and technical impracticality of other methods.
WA	DEC released a guideline in April 2004 entitled <i>The Use of Monitored Natural Attenuation</i> . This document outlines the circumstances when MNA is acceptable
NSW	<p>For details, refer to the draft policy document provided. In summary, MNA can be part of a strategy for managing risks from contaminated groundwater. However, a detailed evaluation of the contamination, the aquifer characteristics and potential risks is necessary to confirm that MNA can be an effective part of the overall management strategy.</p> <p>A proposal for MNA must include clear evidence demonstrating that:</p> <ul style="list-style-type: none"> • significant attenuation of contaminants is occurring • remedial goals are capable of being met in an adequate timeframe • the proposed monitoring program is suitable. <p>For DEC to accept MNA as a suitable approach at a site, natural attenuation processes that reduce the mass of dissolved contaminants (e.g. biodegradation) will generally need to be clearly demonstrated. Non mass reduction processes such as dilution, advection or dispersion are not acceptable. Even where it is not practicable in the short-term, restoring water quality to its natural background state should remain the long-term remedial objective for contaminated groundwater. In this context, the use of monitored natural attenuation should be considered.</p>
SA	The WA guidelines are used as a reference when discussing MNA with those proposing this remediation technique.
Qld	The decision about accepting its use is site-specific. Generally MNA will ensue when PSH and gross TPH contamination has been removed from a site, further remediation is impracticable and there has been sufficient assessment of health and environmental risk to show low levels of concern to any receptors.

ACT	The ACT EPA Contaminated Sites Environment Protection Policy 2000 (CSEPP) is the primary policy document relating to contaminated land assessment, remediation and audit in the ACT. MNA, however, is not specifically addressed in the CSEPP. The ACT's policy position is that all phase separated (PS) material must first be removed from groundwater; MNA can then be considered, along with other methods, for the remediation of dissolved phase contamination. Any remediation strategy must be applied on a site-specific basis and submitted to the EPA for review. Should phase separated material be present, a third party independent auditor must be engaged to audit the assessment and remediation process and provide their professional opinion on the suitability of MNA or other remediation methods. Remediation timeframes become important where there is a proposed change of lessee at a site – the difficulty arises in ensuring MNA will continue and will be reported appropriately. Other remedial measures may be required if it cannot be demonstrated that the requirements for MNA will be met.
Commonwealth	The Commonwealth does not set policy on whether MNA should be used in any particular circumstance.

3	What administrative guidance do you use for making decisions about MNA?
WA	DEC MNA guideline.
NSW	<ul style="list-style-type: none"> The Contaminated Land Management Act – the contamination must be remediated or managed so that it does not pose a significant risk of harm. The (currently still draft) Guidelines for the Assessment and Management of Groundwater Contamination (DEC NSW). The relevant DNR policies on groundwater protection and groundwater dependant ecosystems.
SA	None currently. This will be prepared as part of the package that follows the implementation of the Site Contamination Bill.
Qld	EPA usually relies on internal groundwater assessment professionals where the EPA is assessing the work conducted on a site. In the majority of situations of significant groundwater contamination, the sites are subject to third party review. The EPA expects the appointed TPR to use best available practice that is relevant to the site conditions. This may involve consideration of guidance in other national and international jurisdictions and peer review of outcomes by those most qualified in the TPR's back up team.
ACT	No specific administrative guidance is used – refer to question 2.

4	What technical guidance do you use?
WA	DEC MNA guideline.
NSW	See Appendix C.
SA	The WA Guideline, which is based on the UK Guideline.
Qld	See above.
ACT	No specific technical guidance on MNA, however the ANZECC water quality guidelines and background levels are used for assessing the success of the remedial measures.

5	Is the guidance provided by the Western Australia guidelines (DEP 2004) adequate for your needs? What shortcomings (if any?) are there in this guidance for your jurisdiction?
WA	No response.
NSW	Generally speaking, yes. It is a useful summary of MNA. For the details, other guidance is necessary such as US or UK guidelines. The policy points within the WA guideline would need to be interpreted in the NSW policy context as per our groundwater guidelines. An example of this would be the 30-year timeframe for inter-generational equity. This would be relevant in some contexts, but factors such as community consultation would probably necessitate a shorter timeframe.
SA	It is currently adequate but the SA EPA will consider all guidance when preparing its own guidance.
Qld	See above.
ACT	Yes, provided the guidelines can be applied in the fractured rock environment which is predominant in the ACT's geology. The re-existence of PS material due to changes in the local environment must also be considered.

6	Do you see merit in national guidelines on MNA?
WA	Yes, a national approach to MNA would assist regulation of hydrocarbon contaminated sites.
NSW	Not particularly.
SA	Yes. It would be helpful for all practitioners and regulators to have a common understanding and approach.
Qld	It would probably help to have a reference that covers the issue in the broadest sense, provided it maintained an appropriate site-specific focus.
ACT	Yes.
Commonwealth	The Commonwealth does see benefit in the development of a consistent national standard for MNA as this would be likely to result in significant cost and administration efficiency. The Commonwealth, therefore, does support the objective of improved national consistency in the application of MNA.

7	What other guidance/research do you see as important to support your efforts in implementing MNA?
WA	No response.
NSW	Now that we are about to release our Groundwater Guidelines, there is not much more that is needed with respect to implementing MNA for petroleum hydrocarbon contamination in NSW. The science is well-established. However, we consider there to be some scope for further research into MNA with respect to inorganics, but this is likely to be outside the remit of the current AIP CRC CARE project.
SA	No response

Qld	Many of the assessments of health risk rely on modelling of both groundwater plumes and the capacity for any volatiles to penetrate building spaces and accumulate and expose a long-term building occupant to a cancer risk. The modelling often appears faulty/invalid depending on site conditions and the contaminants of concern. In both cases there can be excessive conservatism and exaggerated claims for some sites. In some cases it may reflect the technical uncertainty and the individual professional's aversion to risk and other commercial issues rather than the actual situation. These issues can lead to costly decisions for the community.
ACT	Further research into the effectiveness of MNA and other remediation strategies in the fractured rock environment.

5.4 Overseas adoption of MNA

During this review, differences in the adoption of MNA between the US, UK and Australia have become evident and some aspects contrasted (Table 10).

Table 10. Comparison of international approaches to MNA

Item	United States	United Kingdom	Australia
Approach	Risk-based, lines of evidence	Risk-based, lines of evidence	Risk-based, lines of evidence
Key players for policy-relevant research	Regulator, federal agencies (ACFEE, DOD, Navy, US EPA), state regulators, National Research Council	University-Regulator-Industry consortia (SIRen, CORONA), National Regulator	University-Regulator-Industry consortia (CRC CARE)
Line of evidence required for BTEX MNA	Contaminant concentration reduction or mass reduction depending on jurisdiction	Contaminant concentration reduction and contaminant mass reduction	Contaminant concentration reduction and contaminant mass reduction
Authors of fuel hydrocarbon relevant MNA protocols/guidance	State regulators and federal agencies	National regulator	State regulators (WA, NSW)
Number of BTEX MNA approved sites by 2000	15,660	<5	?
Number of plumes used in multi-site plume analysis	>600	No published study	14
Number of specialty conferences specifically on hydrocarbon assessment/remediation	At least 20 since 1985. Batelle & NGWA/API		2
Maximum MNA remediation timeframe	Site-specific	30 years	30 years (WA) or reasonable time (NSW)

In the USA, since 1997, there has been extensive regulatory support for MNA, and a considerable body of scientific knowledge about MNA across a range of subsurface environments has been established. A large number of sites (>15,660) had been approved for MNA by the year 2000. However the MNA requirements do vary across the different states and there are apparent differences in the minimum level of evidence needed to demonstrate MNA across jurisdictions in the US. MNA for petroleum hydrocarbons can be approved on the basis of contaminant mass reduction in some US jurisdictions and is advocated in the ASTM (2004). This contrasts with the MNA protocols available for the UK and Australia where there must be demonstrated contaminant degradation, not just concentration reductions.

Since the late 1990s in the UK there has been a focused high-level effort to increase the adoption of MNA. This has included a review of remediation techniques applied in England and Wales (Petts et al. 2000; Rivett et al. 2002). MNA is seen as having an important role in contaminated site remediation: 'the remediation of pollutants already in the ground and groundwater may rely heavily, if not totally, on the natural attenuation processes. MNA will be needed not only to address point sources of industrial pollution but will also be relied on for management of diffuse pollution' (CL:Aire 2006). Initially, concerns were expressed in the UK about applying overseas data to UK MNA studies. A review on natural attenuation of specific contaminants of concern (BTEX, inorganic cyanide and selected PAH, fuel additives, pesticides and chlorinated solvents) was undertaken (Noble & Morgan 2002a), with the following findings:

1. Lack of published degradation data relevant to the contaminant of concern for the major consolidated aquifer systems, particularly the fractured sandstone and chalk systems that represent the major UK systems and very few relevant data to guide the estimation of rates of natural attenuation.
2. Wide variation in degradation rates for shallow sand-gravel aquifers.
3. Temperature in UK aquifers is typically 10°C, while groundwater in the warmer US climates is often 15–22°C. These higher temperatures would be expected to increase degradation rates.
4. A 'lines of evidence' approach for MNA is important to manage uncertainty about natural attenuation processes.

A number of university-regulator-industry consortia have been developed in the UK to address MNA issues. However uptake of MNA has been limited and a number of reasons suggested (CL:Aire, 2006):

1. The potential length of monitoring timeframes and eventual closure compared with the normal timeframes for development and redevelopment of land.
2. Difficulties associated with off-site monitoring (access, third party involvement, public perception).
3. Uncertainty over the long-term sustainability of MNA at a particular site (e.g. electron acceptor sufficiency, changes in groundwater pumping regimes in the vicinity of a site).
4. Perceived difficulties of using MNA in site divestments (e.g. timeframe, liability transfer, uncertainty over robustness).
5. Perception (some stakeholders view monitoring as problem avoidance rather than action).

A striking difference between the evolution of the petroleum hydrocarbon knowledge base in the US and that in the UK and Australia is the use of large scale multi-site studies on plume characteristics. This may in part reflect the difference in the availability of centralised plume databases in the US and regulatory differences. This has however generated an extensive body of knowledge about plume characteristics in different environments.

6. Conclusions

This project seeks to identify scientific knowledge gaps and provide the basis for the ongoing CRC CARE project relating to NA. The following are the major observations arising from this review:

1. A risk-based approach using lines of evidence is widely used as a framework for monitored natural attenuation (MNA) guidance.
2. Six years ago, MNA was recognised as a well-established remediation approach for only a few types of contaminants, but importantly these included the petroleum compounds benzene, toluene, ethylbenzene and the xylene isomers (BTEX) and some oxygenated hydrocarbons. For the other classes of petroleum hydrocarbons and oxygenated hydrocarbons there was either not a complete understanding of biodegradation processes or confidence of success in a MNA-based remediation strategy. Since then greater knowledge has been gained, particularly about MTBE and PAH.
3. Biodegradation is recognised as the key natural attenuation mechanism for fuel hydrocarbons. To support the application of MNA, extensive compilations are available and reviews of BTEX biodegradation rates for laboratory and field sites, primarily based on studies from the United States.
4. Australian data that may help define the scope of any impact arising from the use of fuel additives (MTBE, ethanol and biodiesel) are scarce. The Australian experience of groundwater contamination from MTBE is likely to differ from the United States, as MTBE is potentially only present in fuels imported from overseas.
5. Approaches for implementing MNA at sites contaminated with polycyclic aromatic hydrocarbons (PAH) are poorly developed compared with BTEX or chlorinated solvent sites. Knowledge about PAH degradation in the field and sorption/desorption processes is reasonably limited.
6. There have been relatively few studies which have addressed the natural weathering of residual and mobile LNAPL compared with studies into the processes affecting dissolved phase contaminants resulting from LNAPL. This knowledge gap will be important where MNA is linked as a remedial strategy with the practicability of NAPL clean-up.
7. Groundwater recharge has recently been recognised as an important attenuation mechanism near the contaminant source. High-resolution multi-level sampling and scenario modeling are increasing our understanding in this area.
8. Whether the assimilative capacity of an aquifer can be sustained over the multi-year life of a MNA remedial strategy is an area of knowledge that is poorly understood. One area of uncertainty relates to the longevity of cycling of redox-active elements (Fe, S) between the dissolved and mineral phases. Another is the prediction of changes in electron acceptors in response to changes in environmental conditions (e.g. recharge).

9. Further knowledge about the expected value of particular biogeochemical indicator data to effectively discriminate contaminant degradation mechanisms at a fuel-impacted site is needed. This knowledge is needed to cost-effectively set up monitoring regimes capable of validating attenuation processes long-term.
10. Published literature on natural attenuation processes at Australian sites for petroleum hydrocarbons is patchy and lacks a degree of specificity about site location, degradation rate and contaminant data, which therefore limits the usefulness of the literature for contributing to a generalised understanding of contaminant behaviour across those specific subsurface environments.
11. In Australia, there have only been two published studies on petroleum hydrocarbon plume characteristics at multiple MNA sites. There is not enough data to conclude whether the generalised behaviour of petroleum hydrocarbon plumes under Australian conditions is similar to that reported from overseas. Therefore, the general applicability of overseas data (e.g. degradation rates) to Australian sites is a knowledge gap.
12. Published Australian natural attenuation literature has focused on shallow sand aquifer systems. These include the Quaternary aquifer around Perth and the Botany aquifer near Sydney. Studies on these sites could provide the fundamental data for scenario modelling at those locations. Generally there were few papers which described contaminant behaviour in fractured rock and clay sites.

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APPENDIX A.

Survey of Australian literature on natural attenuation processes on Australian sites

The objective of this review was to identify data from the published literature about the behaviour of petroleum hydrocarbons in groundwater at Australian sites. The goal was to identify data that could be used to support a better understanding of natural attenuation processes at an aquifer scale. In particular, the review was seeking data on sorption rates, biodegradation rates, plume hydrochemistry and plume dimensions. The review obtained information from the following sources:

1. Major environmental, groundwater and specialty conferences that were held in Australia and some from overseas. This was searched manually from hardcopies of the Conference Proceedings, Tables of Contents held in libraries and elsewhere. There were 17 in total and these are listed below (Section A1).
2. ISI Proceedings, which cover major international conferences. This was searched electronically by keywords and authors identified from Australian conferences.
3. ISI Web of Science, which covers many Australian and International journals. This was searched electronically by keywords and authors identified from Australian conferences.
4. Selected university library catalogues for higher research degree studies. These were searched electronically by keywords.

Some studies related to chlorinated hydrocarbons rather than just petroleum hydrocarbons were included as these had relevant information on properties of aquifer materials. The results list of publications is listed in Section A2.

Section A1 List of conferences

1. Hazardous and Solid Waste Conference (1994, 1996, 1998).
2. Enviro Conference (2000, 2002, 2004).
3. 1999 Contaminated Site Remediation Conference: Challenges Posed by Urban Industrial Contaminants, Fremantle, WA, CGS.
4. 2000 Contaminated Site Remediation Conference: From source zones to ecosystems, Melbourne, Victoria, Australia, 4-8 December 2000.
5. Water Down Under '94, Adelaide, Australia, 21-25 November 1994.
6. Groundwater in the urban environment: proceedings of the XXVII IAH Congress on Groundwater in the Urban Environment, Nottingham UK, 21-27 September 1997.
7. International Groundwater Conference 1998, Proceedings Groundwater: Sustainable Solutions, Melbourne Australia, 8-13 February, 1998.
8. Groundwater: past achievements and future challenges: Proceedings of the XXX IAH Congress Cape Town, South Africa, 26 November-1 December, 2000.

9. New approaches characterizing groundwater flow: Proceedings of the XXXI International Association of Hydrogeologists Congress, Munich, Germany, 10-14 September, 2001.
10. Contaminated Soil '95: Proceedings of the Fifth International FZK/TNO Conference on Contaminated Soil, Maastricht, the Netherlands, 30 October – 3 November 1995.
11. First International Conference on Contaminants and the Soil Environment in the Australian-Pacific Region, Adelaide, South Australia, 18-23 February 1996.
12. 4th International In Situ and On-Site Bioremediation Symposium, New Orleans, USA, 28 April – 1 May 1997.
13. Geoenvironmental Engineering, Contaminated Ground: Fate of Pollutants and Remediation, Cardiff, UK, 16-18 September, 1997
14. Contaminated Soil '98: Proceedings of the Sixth International FZK/TNO Conference on Contaminated Soil, Edinburgh, UK, 17-21 May 1998
15. The Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, California, USA, 22-25 May, 2000
16. Proceedings of the NATO Advanced Research Workshop on the Utilization of Bioremediation to Reduce Soil Contamination: Problems and Solutions, Prague, Czech Republic, 14-19 June 2000.
17. Proceedings of the 2nd Australia and New Zealand Conference on Environmental Geotechnics, Newcastle NSW, Australia, 28-30 November 2001.

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APPENDIX B.

Monitored natural attenuation in NSW draft guidelines for the assessment and management of groundwater contamination

Appendix 5

Monitored Natural Attenuation

Introduction

Natural attenuation of contaminated groundwater is defined as:

‘The effect of naturally occurring physical, chemical and biological processes to reduce the load, concentration, flux or toxicity of polluting substances in groundwater’ (UK Environment Agency, 2000).

These in-situ processes include biodegradation, dispersion, diffusion, sorption, volatilisation, and chemical or biological stabilisation, transformation or destruction. Although natural attenuation is sometimes referred to as intrinsic bioremediation, non-biological processes may also be important.

The natural attenuation processes may reduce the potential risk posed by site contaminants, for instance, through:

- Reductions of toxicity due to transformation of contaminant(s)¹ through destructive processes such as biodegradation or abiotic chemical transformations.
- Reduction of contaminant mobility and bioavailability through sorption onto the soil or rock matrix.
- Reduction of dissolved contaminant concentrations and consequently the reduction of potential exposure concentrations.

Note that dilution within a receptor, such as a surface water body or groundwater abstraction system, is not considered to be natural attenuation.

The term *monitored natural attenuation* or *MNA* refers to reliance on natural attenuation processes – as part of a planned, controlled and monitored remedial approach – to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods. It emphasises that monitoring to demonstrate and document the progress of MNA must be an integral part of a natural attenuation strategy for any site.

Research over the last twenty years has resulted in a sound technical understanding of natural attenuation processes for many groundwater contaminants and knowledge of the specific conditions under which these contaminants may be degraded. On this basis, MNA is accepted as one of the range of remedial strategies that should be considered in the appraisal of clean-up options for sites where groundwater is contaminated. MNA may be particularly useful in areas of a plume where contaminant concentrations are low. Based on this, MNA may often be applied where more aggressive clean-up has already reduced contaminant concentrations in the core of the plume.

Advantages of MNA

Used alone or in combination with other strategies, such as secondary source removal, MNA may be a non-intrusive, safe and cost-effective strategy to remediate groundwater contamination. It does not require the use of fossil fuels. In some circumstances, it may be the only strategy that is practicable.

¹ Note that contaminant transformation will not always reduce the risk. Some contaminants, for example, some chlorinated organic compounds, may transform to more toxic contaminants as they degrade in the environment. A proposal for MNA must therefore evaluate the impacts of all degradation pathways and their effect on the suitability of MNA at a site.

Disadvantages of MNA

The environmental conditions necessary for effective natural attenuation of a particular contaminant may not exist at the location of concern. Natural processes may work slowly in the subsurface environment, where reaction rates may be restricted by low temperatures and limited availability of the necessary microorganisms, electron acceptors or electron donors, co-metabolites, and nutrients. Natural attenuation may not achieve the remediation goals within adequate timeframes in those cases. Sometimes intervention, or enhancement, may be attempted to change the conditions to allow natural processes to work more effectively, but in other cases this will not be possible, and MNA must be discounted as an option. Also, sometimes the concentration of a contaminant is so great, or the risks to human or ecological health so severe, that other strategies with a shorter effective time frame must be used.

Demonstrating whether MNA is applicable

Remediation by natural attenuation is not considered to be a presumptive remedy. A determination of whether remediation by monitored natural attenuation is appropriate for a particular site (relative to site-specific remedial goals) requires site characterisation, assessment of potential risks, evaluation of the need for primary and secondary source removal or control, and evaluation of potential effectiveness.

Application and implementation of remediation by natural attenuation requires demonstration of progress towards attainment of the remedial goals. This is achieved by using converging *lines of evidence*, which are obtained through monitoring and evaluation of the resulting data. Monitoring should continue until it has been demonstrated that the remedial goals have been met.

The *primary* line of evidence for remediation by natural attenuation is provided by observed constriction in the lateral and vertical extent of the plume, together with observed reductions in concentrations of the contaminants of concern within the plume.

Secondary lines of evidence for remediation by natural attenuation may be provided by geochemical indicators of naturally occurring degradation and estimates of attenuation rates.

Additional optional lines of evidence can be provided by microbiological information, including field and laboratory microcosm studies, where this information directly demonstrates the occurrence of a particular biodegradation process at a site. Further analysis may also be required of primary and secondary lines of evidence using, for example, solute transport modelling or estimates of assimilative capacity.

Any application of MNA at a site requires extensive hydrogeological and geochemical site characterisation, which may often need to be supported by appropriate modelling. It is not sufficient to simply indicate that, for example, groundwater conditions beneath the site are reducing, and therefore reductive dechlorination of chlorinated aliphatic hydrocarbons will occur.

When is MNA appropriate?

Generally, monitored natural attenuation should only be considered as a remediation methodology where the following conditions are met:

- The source of the contamination including contamination “hot spots” have been removed as far as practicable.
- The three-dimensional extent of the contamination has been defined.
- The site and hydrogeology have been adequately characterised and there is clear evidence that attenuation rates are sufficient to achieve the remedial goals within an adequate timeframe.
- The natural attenuation processes include processes which reduce the mass of dissolved contaminants.
- The effects of degradation products have been considered.

As with other remedial approaches, it is expected that where monitored natural attenuation is proposed as part of a remedial strategy for a site, the feasibility and appropriateness of monitored natural attenuation at that site would be demonstrated in a remedial action plan (RAP). The RAP should draw upon site characterisation and risk assessment data acquired during previous investigation of the site. It is expected that within the RAP the proponent will demonstrate an understanding of the particular attenuation processes relevant to the contaminant(s) of concern under the conditions at that specific site.

The RAP should define remedial goals and set out the scope, frequency and expected duration of the monitoring required to demonstrate that natural attenuation has been effective and the goals have been met. Monitoring frequency should be sufficient to allow the progress of natural attenuation to be tracked, and to provide early warning if expectations are not being met, or if adverse impacts on sensitive receptors become possible. The RAP should also address the integration of monitored natural attenuation with other remedial technologies that may be proposed for source removal or reduction, and any potential interactions or interferences. The long-term sustainability of MNA during and following any proposed redevelopment of the site must be considered. Where reference is made to experiences from other sites, an understanding of the potential impacts of differences in, for instance, hydrogeological conditions between the sites must be demonstrated.

The RAP and ongoing monitoring and validation reports should set out the lines of evidence for the progress and success of natural attenuation. Unless the primary line of evidence is conclusive, it will be necessary to evaluate secondary and additional lines of evidence. A checklist has been provided below to assist in undertaking a review of the suitability of MNA at a particular site.

Considering the effect of contaminant degradation on toxicity and mobility

Some contaminants degrade to a more toxic. Vinyl chloride, from the reductive dechlorination of TCE, is a well-known example. Therefore, the potential effects of degradation products on the toxicity and mobility of the contamination need to be carefully considered when evaluating the appropriateness of MNA.

In some cases, and in the right hydrogeological conditions, the more toxic degradation products may breakdown further to form less toxic compounds. In such instances, MNA may be deemed acceptable if it can be demonstrated that the more toxic compounds will not represent a threat to human or ecological health.

Checklist for assessing the applicability of monitored natural attenuation

- ☐ Has the site been adequately characterised in relation to stratigraphy, lithology, structure, water-bearing zones, groundwater flows, solute transport, lateral and vertical hydraulic gradients, hydraulic conductivities and porosities?
- ☐ Has the site been adequately characterised in relation to geochemical conditions, including salinity, temperature, pH, redox potential, organic carbon sources, nutrient availability, sorption capacity and the availability of electron donors and acceptors?
- ☐ Have all contaminants of potential concern been identified?
- ☐ Has the toxicity of the contaminants of concern been adequately assessed?
- ☐ Has the plume been fully delineated for all contaminants of concern?
- ☐ Have all potential receptors been identified?
- ☐ Have all potential beneficial uses and environmental values of the groundwater been identified?
- ☐ Are proposals to remove or control primary sources (leaking infrastructure) and secondary sources (NAPL, adsorbed phase) adequate and feasible?
- ☐ Is the proposed attenuation mechanism feasible for all the contaminants of concern under the conditions prevailing at the site?

- ☐ Do the natural attenuation processes include processes that reduce the dissolved mass of the contaminants of concern?
- ☐ Are there condition conflicts among multiple contaminants of concern?
- ☐ Have the toxicity and fate of all potential daughter products been considered?
- ☐ Will attenuation to acceptable concentrations be achieved well before potential human or ecological receptors could be impacted?
- ☐ Have all feasible alternative remedial options been considered?
- ☐ Will the remediation goals be reached within a time frame that is reasonable compared with other remedial options, and community expectations?
- ☐ Is monitored natural attenuation sustainable, considering proposed source control measures and redevelopment of the site and surrounding area?
- ☐ Are there financial mechanisms in place to ensure that monitoring can be continued for the required period?
- ☐ Have adequate contingency measures been proposed?

APPENDIX C.

Technical Guidance documents used by NSW EPA in MNA decisions

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