

Natural attenuation processes and site monitoring

M. J Dale

PPK Environment and Infrastructure, Australia

Abstract: It is recognised that the remediation of groundwater may have physical and chemical limits, which will result in any cleanup not attaining the environmental objectives. Natural attenuation of the contaminants, treatment at the end user or institutional controls may therefore be the only feasible remedies for these sites. A number of key questions need to focus the data collection process, to assess whether the use of natural attenuation (or other controls) will be protective of human health and the environment and will ultimately result in the degradation of the chemical of concern to below environmental objectives. This paper provides an overview of the technical aspects of natural attenuation of organic compounds and looks at its role in the remedial decision process. Site monitoring is also an integral part of the process in determining that the biological, chemical and hydraulic conditions are conducive to natural attenuation and that it is appropriate for the site specific land use or beneficial use of the groundwater or surface water.

Keywords: Groundwater, remediation, natural attenuation, site monitoring.

1. INTRODUCTION

Groundwater remediation is a complex process relying on the implementation of a variety of technologies to effectively degrade or remove the contamination of concern. Remediation relies on the knowledge of the physical, chemical and hydrogeological properties of the subsurface. It is acknowledged, however, that it may not be practicable or feasible to fully restore the contaminated groundwater (US EPA, 1988). Active remediation may not be effective or feasible at widespread plumes, or because of hydrogeological constraints (eg fractured rock or karst geology), contaminant properties or the physical/chemical interaction of the contaminants in the subsurface. In these instances natural attenuation, end-user (wellhead) treatment with monitoring or institutional controls may be the only feasible solutions for these sites.

In general natural attenuation should not be considered “a natural remedy” or “do nothing” option at any site. The appropriateness of natural attenuation must be determined, as is any other remedial technology or option, to be protective of human health and the environment. The attention to natural attenuation and the available information has increased significantly in the late 1990s.

This paper provides an overview of the natural attenuation process of organic compounds in groundwater and site monitoring required to determine its effectiveness to protect against impacts to human health and the environment. Comment on the regulatory framework for its use is also provided.

2. NATURAL ATTENUATION PROCESS

2.1 Overview

“Natural attenuation” is currently the favoured term applied to a multitude of *in situ* processes including decay (radioactive), biodegradation, chemical or biological stabilisation, destruction, dilution, dispersion, sorption, transformation or volatilisation. Other terms describing natural attenuation include “intrinsic remediation”, “intrinsic bioremediation” “passive bioremediation” and “natural assimilation”. Many of these latter terms were more commonly used in the early 1990s. Other terms used for this process are “Remediation by Natural Attenuation” (RNA) or “Monitored Natural Attenuation” (MNA). The US EPA (1999) prefer to use MNA as a directive as they believe long-term monitoring is an integral part of the process.

Natural attenuation processes typically occur at most contaminated sites but its effectiveness is controlled by the contaminants of concern, and the physical, chemical, biological and hydrogeological properties of the soil and groundwater. Natural attenuation processes are largely complex oxidation and reduction processes and under favourable conditions, reduce the risks to human health and the environment by:

- Transformation of the contaminants by destruction, degradation and abiotic transformation to less toxic forms;
- Reduction of contaminant concentrations, and;
- Reduction of contaminant mobility or bioavailability.

2.2 *Contaminants of Concern*

This document is largely concerned with hydrocarbons in groundwater, however there is a large amount of information available on a multitude of potential groundwater contaminants. The study of the use of natural attenuation has particularly concentrated on petroleum hydrocarbons and chlorinated solvents in recent times.

Ultimately the transformation or immobilisation process should reduce the compound to its less toxic or mobile form, which in many instances is carbon dioxide and water. Some of the natural attenuation processes may however, result in transformation products, which may be more toxic or mobile than the parent compound. The classic example is the degradation of trichloroethylene to vinyl chloride. The creation of more toxic compounds is less likely however with petroleum releases. While the degradation products may be less toxic, some consideration may also need to be given to the by-products of natural attenuation, namely the greenhouse gases carbon dioxide and methane.

The dominant natural attenuation process for organic and inorganic compounds, the level of understanding of the process and the likelihood of the success of degradation given the level of understanding of the compounds in nature are summarised in Table 1.

2.3 *Processes*

At impacted sites, contaminants partition into the four phases (vapour, dissolved, liquid phase or sorbed to the soil) and are present within the soil pores. As the groundwater migrates through the pores, the contaminants may migrate as liquid phase, be desorbed from the soil profile or dissolve from the free phase liquids. The basis of natural attenuation is that the concentration of the contaminants of concern in the aqueous phase reaches equilibrium with the biological transformation at an acceptable rate and distance from the source. This transformation is essentially an electron transfer process in the production of cell mass. Microbial activity in natural attenuation is a progression from aerobic to anaerobic conditions. A typical plan view of a hydrocarbon plume undergoing natural attenuation is shown in Figure 1.

During natural attenuation, the various aerobic, cometabolising or anaerobic bacteria, in the presence of the contaminant, organic carbon and sufficient micronutrients (particularly nitrogen and phosphorous), will degrade or dechlorinate the contaminant, provided the contaminant is not toxic to the microcosm. If the contaminant is the only source of organic carbon (as is the case in many Australian soils), the availability of carbon may be the limiting factor in the efficiency or continuation of the natural attenuation process.

Table 1 Likelihood of Natural Attenuation (CGER,2000)

Chemical Class	Dominant Attenuation Process	Level of Understanding	Likelihood of Success
<i>Organics</i>			
<i>Hydrocarbons:</i>			
BTEX	Biotransformation	High	High
Non-volatile aliphatics	Biotransformation Immobilisation	Moderate	Low
Gasoline, Fuel Oils	Biotransformation	Moderate	Moderate
PAHs, Creosote	Biotransformation Immobilisation	Moderate	Low
<i>Oxygenated Hydrocarbons</i>			
Low molecular weight alcohols, ketones, esters	Biotransformation	High	High
MTBE	Biotransformation	Moderate	Low
<i>Halogenated Aliphatics</i>			
Tetrachloroethene	Biotransformation	Moderate	Low
Trichloroethene			
Carbon Tetrachloride			
Trichloroethane	Biotransformation Abiotic transformation	Moderate	Low
Methylene chloride	Biotransformation	High	High
Vinyl Chloride	Biotransformation	Moderate	Low
Dichloroethene			
<i>Halogenated Aromatics</i>			
Highly chlorinated PCBs, pentachlorophenol	Biotransformation Immobilisation	Moderate	Low
Tetrachlorodibenzofuran			
Multchlorinated benzenes			
Less chlorinated PCBs, dioxins,	Biotransformation	Moderate	Low
Monochlorobenzene	Biotransformation	Moderate	Moderate
<i>Nitroaromatics</i>			
TNT, RDX	Biotransformation Abiotic transformation Immobilisation	Moderate	Low
<i>Inorganic</i>			
<i>Metals</i>			
Ni, Cu, Zn	Immobilisation	Moderate	Moderate
Cd		Moderate	Low
Pb		Moderate	Moderate
Cr	Biotransformation Immobilisation	Moderate	Low to Moderate
Hg	Biotransformation Immobilisation	Moderate	Low
<i>Non-metals</i>			
As, Se	Biotransformation Immobilisation	Moderate	Low
<i>Oxyanions</i>			
Nitrate	Biotransformation	High	Low
Perchlorate	Biotransformation	Moderate	Low
<i>Radionuclides</i>			
Various	Decay, immobilisation, biotransformation	Low to High	Low to Moderate

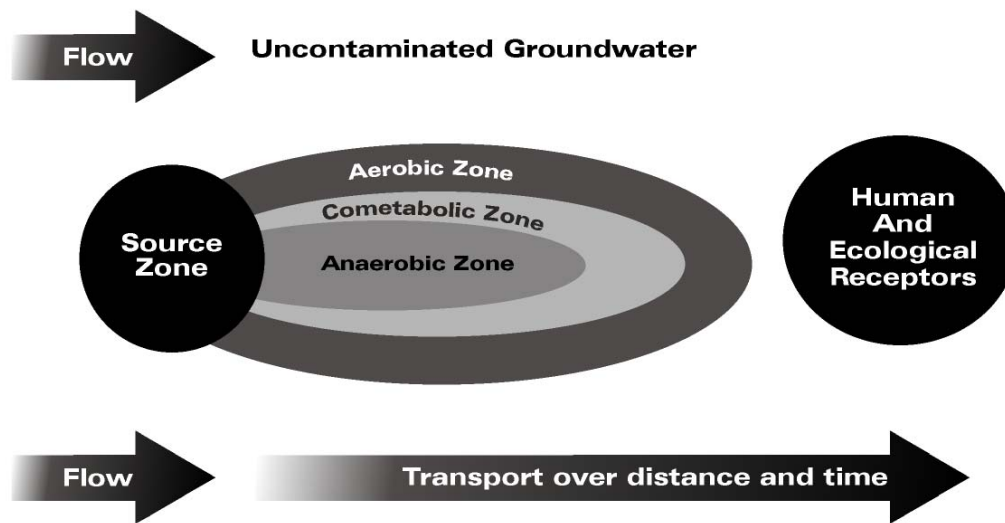


Figure 1 Typical Natural Attenuation Model

The rate, type of microbial population and the level of activity is controlled by the concentration of the electron receptors, substrates that can be used by the bacteria and the specific indigenous bacterial population. The following scenarios (Azadpour-Keeley et al, 2001) summarise the progression from aerobic to anaerobic conditions:

Oxygen to Nitrate Reduction: As available oxygen is consumed, the active aerobic bacteria shift to nitrate respiration. The denitrification will continue until the nitrate or useable carbon is depleted;

Nitrate to Manganese Reduction: As the nitrate is depleted manganese-reducing bacteria will become active until the concentrations of manganese oxide become limiting;

Manganese to Iron Reduction: Iron reduction becomes predominant once all the manganese oxides are depleted. Bacterial Mn(IV) respiration also appears to be limited to areas where sulfate is virtually absent;

Iron to Sulfate Reduction: Iron reduction continues until it is limited by the substrate or carbon availability. Sulfate reduction then becomes dominant;

Sulfate Reduction to Methanogenesis: Once sulfate or useable carbon is depleted methanogenic bacteria become dominant.

The redox condition is important when determining the contribution of microbial degradation to natural attenuation. Data available from many sites shows that benzene, toluene, ethyl benzene and xylene (BTEX) degradation proceeds at higher rates under aerobic compared to anaerobic condition.

Biodegradation of chlorinated solvents is fundamentally different from petroleum hydrocarbons and other oxidising compounds in that the preferred redox conditions for effective degradation is anaerobic. Effective degradation of these compounds occurs when the redox reactions are less than nitrate reducing (Azadpour-Keeley et al, 2001). The oxidation-reduction potential is therefore a relatively simple and inexpensive indicator of the redox state of the aquifer and a comparison of the different processes that are likely to be occurring within the plume. However these can be misleading (eg highly reduced waters due to presence of natural organic matter and pyrite containing sediments) and should be measured in conjunction with other sensitive electron species such as oxygen, Fe(II) and methane.

Detailed descriptions of the reductive or transformation processes are given in numerous publications including the Commission on Geosciences, Environment and Resources (2000) and Azadpour-Keeley et al (2001).

2.4 *Role of Natural Attenuation in Remediation*

Rice et al (1995) undertook an 18 month review of contaminated bores for the Leaking Underground Fuel Tank (LUFT) program in California. In the review, only 48 wells were reported to have measurable benzene concentrations out of 12,151 public water-supply wells tested statewide. A review of the California's database of 28,051 leaking underground fuel tank cases also showed that only 136 sites had affected drinking water wells and that these were mostly shallow private domestic wells in close proximity to the release site. Rice et al (1995), found that groundwater cleanup requirements were found to be consistently applied statewide due to the presence of numerical standards and that remedial efforts did not permit the considerations of technical and economic feasibility with respect to protection of human health, the environment, and beneficial water use as required by the regulators.

In studying the database, they found that once the source is removed, passive bioremediation processes act to naturally reduce the plume mass and that benzene plume lengths tended to stabilise at relatively short distances from the release site. The report sparked wide spread attention and the group subsequently prepared a response to the US EPA (Rice et al, 1997) addressing issues such as the appropriateness of the data set, fractured rock scenarios, other contaminants such as MTBE and that "passive remediation" means "do nothing". The group maintained that their recommended use of risk-based corrective action and passive bioremediation was an appropriate low cost strategy for sites identified as having low exposure risks or impact to beneficial use.

The implications of this study and others (US EPA, 1999) is that the use of natural attenuation, as with any other remedial technology, must consider several key principles to ensure that the risks are managed or that the remedial objectives are achieved, including:

- *Control of source zones.* Engineering or hydrogeological remedial measures should be used to address source zones (eg phase separated hydrocarbons) wherever practicable. This may include containment for wastes (or by-products) where treatment is impracticable;
- *Restoration of Contaminated Groundwater.* Contaminated groundwater should be remediated to its "beneficial use" wherever practicable, within a reasonable site specific timeframe. Where the remediation of the groundwater is not practicable, it is expected that engineering or hydrogeological control or treatment will be instituted to prevent further migration of the plume and exposure to the contaminated groundwater. A risk assessment may also be required to further evaluate the risk reduction measures.
- *Mitigating Media Transfer of Contaminants.* Contaminated soil should be remediated to achieve an acceptable level of risk to human and environmental receptors, and to prevent any transfer of contaminants to other media (eg. to surface water, groundwater, air, or sediments) that would present an unacceptable risk.
- *Risk communication/Public Consultation.* Remedial actions in general should include opportunities for public involvement in the decision making process. This would serve to educate the interested parties, solicit feedback concerning the remedial process and provide greater confidence in remedial strategy in the protection of human and environmental health.

In considering natural attenuation as the primary remedial action or as a component of the overall remedial process, it does not alter the remedy selection principles particularly in relation to say removal of separate phase. Further, the use of natural attenuation does not diminish the

regulators or polluters responsibility to manage or reduce the risk or protect the beneficial uses of the groundwater or to satisfy long-term site remediation objectives. To this end, the US EPA (1999) expects that natural attenuation will only be selected as an appropriate remediation method where its use will be protective of human health and the environment and it will be capable of achieving site-specific remediation objectives within a timeframe that is reasonable compared to other alternatives.

The US EPA in commenting on the Rice et al (1995) study (Rice et al, 1997), supported the use of alternate technologies for contaminated soils and ground water, particularly as it recognised the limitations inherent in pumping and treating ground water. Contaminant removal rates often flatten out to asymptotic levels resulting in contaminant concentrations never achieving the remediation goals. When this occurs, the remedial systems operating costs continue, but the site does not become cleaner. Further, the EPA did not support extensive over-excavation, because this approach tends to lead to large volumes of soil being transported to another location without treatment and cross-media transfer of contaminants.

2.5 Advantages

Natural attenuation has a number of advantages and disadvantages. Each of these will need to be considered with respect to impact to various receptors and the sustainability and efficiency of the remedial efforts. Potential advantages for natural attenuation (and other *in situ* remediation alternatives) include:

- The generation of lower volumes of waste (eg excavated soil);
- Reduced potential for cross-media transfer or remobilisation of contaminants (eg liquid free phase hydrocarbons impacting greater volumes of soil during excavation or additional contamination caused by pumping);
- Reduced risk of exposure to contaminants, contaminated media (soil, air, liquid) and other safety hazards (eg drowning hazards in excavations filled with water);
- Reduced disturbance to ecological receptors;
- *In situ* destruction of some contaminants;
- Less intrusive remedial works (eg remediation under buildings);
- Can be used as a broader application to treat more extensive plumes;
- Can be used with other remedial technologies;
- Monitoring can allow low cost enhancement of natural remedial process (eg replacement of depleted micronutrients or oxygen in the groundwater)
- Potential lower remediation costs compared to active remediation and particularly in some instances where there is little or no energy input, and
- May be appropriate when considering sustainable development principles.

2.6 Limitations

The disadvantages to the use of natural attenuation often result from a lack of understanding of the transformation process or the subsurface conditions and may include:

- Sites which have unfavourable subsurface conditions to promote natural attenuation;
- Compounds which do not degrade naturally;
- Longer time frames to achieve remedial objectives;
- Site characterisation may be more expensive;
- Toxicity or mobility of daughter compounds or transformation products may exceed the parent compound;
- Knowledge of transformation or immobilisation reactions is low to moderate for some compounds;
- Longer-term performance monitoring will be generally more extensive and costly;

- Institutional controls may be necessary to ensure long term protection to human health and the environment;
- Potential exists for continued contamination migration, and/or cross-media transfer of contaminants;
- Hydrologic and geochemical conditions amenable to natural attenuation may change over time and could result in renewed mobility of previously stabilised contaminants (or naturally occurring metals), adversely impacting remedial effectiveness;
- More extensive education may be required to gain public acceptance of natural attenuation.
- Institutional controls may be required particularly with the continued focus on monitoring programs with changes of land ownership, staff or corporate “core” business.

Finally a major concern/limitation is the transfer of ownership of a monitoring program within the corporate or regulatory bodies to ensure that there is continued protection of human health and the environment and that the natural attenuation process does not become the “Do Nothing option”.

3. SITE MONITORING

3.1 Objectives

The primary challenge of monitoring natural attenuation is not that biodegradation is occurring but whether the transformations are taking place at a rate that is protective of human health and the environment. It is also expected that the natural attenuation rate will occur over an acceptable period to both the regulators and the community at large.

The monitoring program needs to establish the dynamics of the plume not just the distribution of the contaminants. There may also be need to forecast the distribution and set performance goals to measure the expected behaviour of the contaminant migration and degradation rate. Wilson (1999) indicates that there are three monitoring stages for natural attenuation including:

- Distribution of the contaminants;
- Characterisation of the plume to design remedial works (source removal etc), and;
- Performance monitoring to provide contingencies for expected versus unexpected plume behaviour and to close out longer term monitoring requirements.

In all cases sampling locations need to be sufficient to characterise the expected and unexpected behaviour.

3.2 Primary and Secondary Evidence

In order to evaluate the appropriateness of natural attenuation, evidence is collected to assess primary, secondary and optional lines of evidence (ASTM, 1998).

For a dissolved plume, primary evidence is generally based on measured analyte concentrations and distribution over time which may demonstrate “expanding”, “shrinking” or “stable” plume dynamics. A shrinking or stable plume is evidence of natural attenuation where the rate of natural attenuation either exceeds or equals the mass loading rate of constituents of concern to groundwater.

Secondary lines of evidence may be required to demonstrate that remediation by natural attenuation is taking place where there is insufficient historical monitoring data to determine the status of a plume, or the existing monitoring data is inconclusive. Secondary lines of evidence may include estimation of the natural attenuation rate (based on measured analyte concentration data) and/or measurement of geochemical indicators of the natural biodegradation processes. The degradation process involves oxidation-reduction reactions that produce electrons. Initially the degradation process will be aerobic with oxygen used as the electron receptor. As the dissolved oxygen (DO) levels become depleted (or where DO is not present), nitrate, manganese, ferric iron

(FeIII), sulfate or carbon dioxide may serve as the electron receptors and the organics are degraded under anaerobic conditions.

Direct qualitative correlation between observed spatial distribution of constituent of concern and reduced levels of electron acceptors or increased levels of their reaction products (manganese, methane, carbon dioxide and ferrous iron), provides a secondary line of evidence for natural attenuation (ASTM, 1998).

Optional lines of evidence may include solute transport modelling and validation, microbiological studies, assessment of nutrient levels and/or estimates of assimilative capacity (based on the measured biodegradation indicators).

3.3 Monitoring Requirements

Firstly, to state the obvious “all sites are different”, therefore it is important to keep in mind, both the level and extent of monitoring to determine whether natural attenuation is appropriate, protective of the receptors and complies with regulatory requirements (eg protection of beneficial use). In cases where there is no plan for future beneficial use of groundwater, alternative cleanup levels may be appropriate on a case-by-case basis. However, time frames and therefore the monitoring of neutralisation or degradation of contaminants must be considered within the context of possible future use. The requirements for monitored natural attenuation are documented in many publications but they are summarised by Nyer and Boettcher (2001) to include:

- Delineation of the areal and vertical extent of groundwater impacts (is it a wide diffuse multi-source plume or a narrow point source plume);
- Determination of the detailed hydrogeological model and properties including potentiometric surface, hydraulic conductivity and gradient and the historical water level trends;
- Measurement of the concentrations of indicator parameters;
- Determination of the distribution of oxidation-reduction processes;
- Determination of (if possible) the likely degradation or transformation process and estimate the biodegradation rates;
- Evaluation of the capacity of the aquifer to degrade the contaminants of concern and their mass flux;
- Comparison of the transportation rate to the biodegradation rate to ensure that the identified receptors are not or not likely to be impacted;
- Determination of the variability and efficiency of natural attenuation, and;
- Design a site specific monitoring system (length of time, frequency, sampling & analysis protocols, environmental objectives and contingency plan) to measure the expected or unexpected dynamics of the plume behaviour.

The monitoring program must have sufficient wells over the areal extent of the plume to understand the inputs to the natural attenuation process from the incoming waters (can they sustain the attenuation process) and to monitor the potential impact to the human and environmental receptors. To monitor this program, there are an increasing number of software programs, which can assist with the presentation and analysis of natural attenuation and identify the inherent deficiencies or limiting factors within the degradation process (eg limited concentration of oxygen in the recharge waters or organic carbon in the substrate).

3.4 Performances and Expectations

Monitoring of the natural attenuation process should be developed specifically for each site to determine whether the strategy is performing as expected and is capable of achieving the remedial objectives within the stated timeframe. Performance monitoring (US EPA, 1999) should therefore designed to:

- Demonstrate that natural attenuation is occurring to expectations;
- Detect changes in environmental conditions that may reduce the efficiency of the process;
- Identify any potential toxic or more mobile transformation products (eg vinyl chloride);
- Confirm that the plume is not expanding laterally or vertically;
- Confirm that there is no impact to downgradient receptors;
- Monitor the dynamics of the plume including potential new releases or remobilisation of contaminants to the environment;
- Demonstrate the effectiveness or workability of the institutional controls to protect the local receptors, and;
- To verify the achievement of the remedial objectives (where feasible).

Performance monitoring should continue until the remedial objectives have been achieved and longer to ensure that there is no rebound or remobilisation of contaminants that may pose a risk to human health or the environment. Contingency remedial actions are an important component of natural attenuation. This is the remedial works or strategy that will be required as a “backup” should natural attenuation fail to perform as expected. These measures are particularly important where natural attenuation is primarily based on predictive analysis, fate and transport modelling or risk assessment.

3.5 Asymptotic Conditions and Site Closure

Remediation of organic contaminated groundwater to asymptotic levels is widely recognised by groundwater practitioners and regulators (US EPA, 1988). Over time, contaminant concentrations will approach constant levels (the asymptote) which may or may not be below the environmental objectives. Once constant levels are being achieved, continued groundwater remediation using the integrated groundwater treatment will provide negligible improvement in the groundwater quality. This observed trend is considered an asymptotic condition and is defined as three consecutive analyses falling on a regression line of best fit where the slope of the regression line is close to zero.

If natural attenuation or monitoring of a remedial system reaches a technological concentration limit or asymptote, the average asymptotic concentration can be considered the final clean-up level for the particular technology used. If best available (economically and technically viable) technology is used, no further active clean up will occur, although natural attenuation will continue at various rates depending on the compound of concern and the hydrogeological inputs.

The use of natural attenuation should be monitored against asymptotic conditions to assess the variability in the concentration with respect to time and the attainment of the environmental objectives. The variability in the plume dynamics may indicate unknown sources or that the best available technology has not achieved the desirable risk based environmental outcomes.

The achievement of the clean up goals will lead directly to the termination of remediation and closure of the remediation project can occur. If the target remediation goals are not reached, asymptotic conditions may apply and the continuation of the groundwater remediation system will not achieve any significant improvement in water quality. At this stage, the longer term monitoring program should focus on the risk to human and environmental health and in particular future beneficial uses or environmental value of the groundwater and be agreed with the regulators and the local community in general.

3.6 Documentation of Case Histories

One of the earlier concerns regarding natural attenuation was that there was little operating history to judge its appropriateness. In many instances, natural attenuation was used at low priority sites, which may not have been monitored sufficiently to determine whether the approach was actually effective or was protective of human health and environment. Further at many sites, the approach to monitoring appears to be simply that natural attenuation is occurring and that the plumes were not investigated with regard to the inputs (recharge waters), the plume dynamics (both spatially and with time) and the protection of the human and ecological receptors. On a positive note, however,

there is now extensive research on particular contaminant plumes that show the complexities and the uncertainties in the use and understanding of natural attenuation. The documentation of site case histories also provides further education to the consulting community, the regulators and the public. One just has to look at the numbers of examples presented in both the professional journals and at conferences to show the increased awareness of the use of natural attenuation.

One site being routinely monitored for natural attenuation in country NSW (Dale et al, 1999), has over 60 monitoring wells to assess the distribution of the contaminant plume, its response during source removal works, the performance of the works and the attenuation process against various human health and ecological receptors. The monitoring has shown a typical natural attenuation model with both aerobic and anaerobic parts of the plume as summarised in Table 2 below and depicted in Figure 1. While continued source removal works are being undertaken to reduce the potential risks to human and environmental health, natural attenuation has been protective of the local downgradient ecosystem. Further the monitoring has identified the hydrogeological limitations associated with the shallow perched aquifer (namely the limited recharge of the incoming waters) and has allowed enhancement of the groundwater quality to replace the depleted oxygen and micronutrients. The monitoring presented in Table 2 shows the classic attenuation parameters (changes in redox potential, depletion of oxygen, nitrate, sulfate and the generation of Fe (II) ions and methane).

Table 2: Summary of Natural Attenuation Indicators (Dale et al, 1999)

Well	TPH mg/L	BTEX mg/L	pH	Redox EV	DO mg/L	Nitrate mg/L	Sulfate mg/L	Fe(II) mg/L	Methane mg/L
Wells previously containing free product									
MW1	24.5	0.031	7.9	-112	3.2	0.02	<1	10.2	5900
MW5	5	0.529	7.6	-109	4.1	-	<1	0.24	2400
MW12	275.9	1.019	7.2	-143	3.2	<0.01	<1	20.8	4500
MW17	1415	0.077	6.8	-108	3.4	<0.01	<1	8.6	2800
MW18	33.7	2.175	7.1	-124	4.6	<0.01	<1	13.5	2200
RW5	48.25	0.082	7.6	-192	2.7	0.01	6	0.79	1900
Downgradient & Upgradient Wells									
MW14	33.4	1.575	6.9	-104	4.3	0.25	15	10.2	420
MW31	1.25	0.001	7	-101	2.1	0.03	23	2.3	990
MW38	1.26	0.667	6.3	-25	0.5	0.08	25	1.9	380
MW40	182.8	4.149	6.4	-17	2.7	0.03	4	5.2	980
MW19	0.536	0.010	7.4	68	5.3	291	170	<0.05	2
MW41	0.295	0.004	7	99	3.9	6.6	73	<0.05	4
No detectable Hydrocarbons									
MW9	ND	ND	7	-162	2.5	0.16	15	<0.05	14
MW10	ND	ND	6.3	92	1.7	0.96	58	<0.05	6
MW13	ND	ND	7.1	-41	4.8	0.63	19	<0.05	110
MW21	ND	ND	7	37	3.3	0.04	91	<0.05	9
MW24	ND	ND	6.6	167	4.8	4.5	104	<0.05	<1
MW37	ND	ND	5.6	141	0.6	2.6	93	<0.05	2
MW43	ND	ND	6.9	-29	1.7	0.01	90	<0.05	3

ND – Not Detected, <1 – Not Detected above the Practical Quantitation Limit

The plume lengths at the former country fuel depot show that the process of natural attenuation is occurring at a rate to be protective of the local surface waters downgradient from the contamination. Elsewhere at other petroleum sites within Australia (Wright et al, 1999), monitoring has shown that contaminant plumes have attenuated to similar length observed by Rice et al (1995 & 1997) as the result of natural attenuation process.

While there are many examples which generally fall within the expected behaviour of a naturally attenuating plume there are always the extremely long dissolved solvent or hydrocarbon plumes that are probably due to subsurface conditions that are either not suited to natural attenuation or are not fully understood. As an example to these concerns, the work done by the

CSIRO on a hydrocarbon plume in the anaerobic sulfate rich groundwater in Western Australia (eg Davis et al, 1999) provides valuable understanding of the natural attenuation process and all its uncertainties.

4. REGULATORY FRAMEWORK

The use of natural attenuation is likely be subject to institutional limitations. Further regulators, environmental groups and the public at large may be unwilling to accept this approach which they may perceive as equivalent to doing nothing.

4.1 *Australian Perspective*

The many regulatory bodies within Australia do not provide guidance on the use of natural attenuation as a remedial tool and while the National Water Quality Management Strategy (Department of Land & Water Conservation, 1998) considers that not all groundwater systems are of equal value, it indicates that the level of protection should always be commensurate with the “environmental value” or “beneficial use” of the groundwater aquifer. Beneficial uses are listed as ecosystem protection, recreation and aesthetics, raw water for drinking water supplies, agricultural water and industrial water by the Strategy.

While the governments encourage ecologically sustainable management of the groundwater resources, the use of the “precautionary principle” often means that remediation is driven by the endorsed environmental numerical standards rather than a risk based sustainable management solution (ie the use of natural attenuation in appropriate situations). The “precautionary principle” is further enhanced by the use of numerical standards in risk of harm legislation (eg NSW EPA, 1997).

4.2 *International Perspective*

Internationally, there is a wide disparity in the use and acceptance of natural attenuation. Some countries are reluctant to consider its use, others are considering its use in limited applications while others are instituting formal technical guidance and policies.

The US EPA (1999) directive indicates that the use of monitored natural attenuation does not change the remedial objectives which includes the control of source materials, prevention of plume migration and restoration of the contaminated groundwater (where appropriate). They also consider that natural attenuation is appropriate commensurate with the uncertainties of any particular site but expects sources control and long-term performance monitoring to be fundamental components. The US EPA however does publish its “record of decisions” or RODs on the use of innovative or established remedial technologies. These are widely available in documents published by the US EPA or available on their internet sites.

In Europe many studies are focusing on the technical approaches of treating contaminated land and groundwater (NATO, 1999). The issues of concern to the application of natural attenuation include sustainability, environmental merit and cost effectiveness. This focus is considered to be well behind other jurisdictions. While natural attenuation is not prohibited by say Netherlands or Germany legislation, their legislative controls such as the soil protection acts are designed around engineered solutions to contamination issues. The discussion now in technical reviews is to ensure that the regulators and policymakers find the right balance between cleanup and sustainable protection of the soil and groundwater resources.

5. CONCLUSION

The use of natural attenuation as a remedial strategy is not the same as “no action” but is perceived as such by many environmental groups, regulators and the public. Some regulators, however, are now seeing natural attenuation as viable alternative on a case by case basis. The advantages of natural attenuation are many particularly in relation to sustainable cost.

Natural attenuation does not, however, remediate all contaminants of concern and in many instances the site's physical, chemical, hydrogeological and biological conditions do not allow natural attenuation to proceed at an acceptable rate (over distance and time) or it is not protective of the human and environmental receptors.

Further the use of natural attenuation does not abrogate the responsibility to control the source of the contamination (particularly phase separated non-aqueous liquid petroleum hydrocarbons or solvents), to prevent the migration of the plume or restoration of the contaminated groundwater to appropriate beneficial use (where feasible). Long-term performance monitoring is also a fundamental component of natural attenuation.

With appropriate site monitoring the contaminant plume can be characterised to demonstrate that the plume is stable or shrinking as a result of natural attenuation and these are expected behaviour of the groundwater contamination. A contingency plan may also be required to deal with unexpected plume behaviour, particularly if this is based on predictive modelling.

As natural attenuation is not appropriate for every situation because of landuse, natural limitations or the location of receptors, it is considered important that each regulatory jurisdiction has appropriate published technical guidelines or policies in place. It is also considered appropriate that a "Record of Decision" process is implemented to provide consistency of approach to protect human health and the environment and to continue the education process of both the technical community and the public at large. With this communication process, the use of natural attenuation can be confidently used to protect human health and the environment.

REFERENCES

- American Society for Testing and Materials (1998) Standard Guide for remediation of Ground water by Natural Attenuation at Petroleum Release Sites, *ASTM E: 1943 – 98*, 42p.
- Azadpour-Keeley, A., Keeley, J.W. Russell H.H. & Sewell G.W. (2001) Monitored Natural Attenuation of Contaminants in the Subsurface: Processes, *Ground Water Monitoring & Remediation*, Spring 2001, Vol 21, No 2, pp97-107
- Commission on Geosciences, Environment and Resources (2000). *Natural Attenuation for Groundwater Remediation*. Washington. National Academy Press. 211p.
- Dale, M.J, Blount, A. & Brideson D. (1999) Source Removal and Natural Attenuation of Petroleum Hydrocarbons – A Case Study, *Proceedings of Contaminated Waste Industry – Future Directions Conference*, Melbourne, 11- 19 November 1999, pp1-14.
- Davis, G.B, Power T.R, Briegel, D & Patterson, B.M, (1999). Natural Attenuation of BTEX Compounds in Groundwater and Soil Environments: Evidence and Uncertainties, *Proceedings Contaminated Site Remediation Conference "Challenges Posed by Urban and Industrial Contaminants*, Fremantle WA March 1999, pp343-350.
- Department of Land & Water Conservation (1998) *The NSW State Groundwater Quality Protection Policy*, NSW Government, 32p
- Rice, D.W, Doohar, B.P., Cullen, S.J, Everett, L.G., Kastenberg, W.E. & Ragaini, R.C. (1997) Response to US EPA Comments on LLNL/UC LUFT Cleanup Recommendations and Californian Historical Case Analysis, Environment Protection Department, Lawrence Livermore National Laboratory, California, p45 (Report UCRL-AR-125912)
- Rice, D. W, Doohar, B.P, Cullen, S.J, Everett, L.E, Kastenberg, W.E, Grose, R.D, and Marino, M.A (1995), Recommendations to Improve the Cleanup Process for California's Leaking Underground Fuel Tanks (LUFTs), Lawrence Livermore National Laboratory, California, p38, (Report UCRL-AR-121762).
- North Atlantic Treat Organisation (1999) NATO/CCMS Pilot Study Evaluation of Demonstrated and Emerging Technologies for the Treatment and Clean Up of Contaminated Land and Groundwater (Phase III), Special Session, Monitored Natural Attenuation, *EPA/542/R-99/008*, 76p.
- NSW EPA (1997) Contaminated Land Management Act No 140, Government Information Service.
- Nyer, E and K and Boettcher, G (2001) Seven Easy Steps and Three Difficult Steps to Natural Attenuation, *Ground Water Monitoring and Remediation*, Winter 2001, pp42-47
- US EPA (1988) Guidance on Remedial Actions for Contaminated Groundwater at Superfund Sites,

- Office of Solid Waste and Emergency Response Directive 9283.1-2*, 110p.
- US EPA (1999) Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action and Underground Storage Tank Sites, *Office of Solid Waste and Emergency Response Directive 9200.4-17P*, 32p.
- Wilson, J.T. (1999) Performance Monitoring for Natural Attenuation of Contaminants in Aquifers, *Proceedings Contaminated Site Remediation Conference "Challenges Posed by Urban and Industrial Contaminants"*, Fremantle WA March 1999, pp283-296.
- Wright, D.S, Fridell, P. and Adams, D. (1999) Implementation of Natural Attenuation Techniques for Remediation of Australian Sites, *Proceedings Contaminated Site Remediation Conference "Challenges Posed by Urban and Industrial Contaminants"*, Fremantle WA, March 1999, p335 - 342.