Use of monitored natural attenuation in management of risk form petroleum hydrocarbons to human and environmental receptors

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Abstract
Monitored Natural Attenuation has potential for passive remediation of dissolved phase petroleum hydrocarbon impacts in groundwater. The successful application to any groundwater contamination situation is dependent on a number of factors. Soil conditions affect both the physical and chemical aspects of natural attenuation processes. Key soil related aspects include retention of hydrocarbon mass, groundwater flow regime and hydrocarbon degradation rate. Risk is another element that needs to be considered, particularly in relation to volatile vapours that could affect human health. Therefore the risk aspects, both present and future need to be understood. Finally the nature and character of the source is a critical aspect that establishes whether monitored natural attenuation can be utilised to manage or remediate dissolved phase hydrocarbons in groundwater. While from a technical standpoint monitored natural attenuation would revolve around the collection of primary, secondary and tertiary lines of evidence to demonstrate natural attenuation is occurring, soil properties, risk and source aspects also need to be considered in decision making.

Introduction
Monitored natural attenuation (MNA) has been utilised for passive remediation of petroleum hydrocarbon impacted soil and groundwater for over two decades. Most application has occurred in situations where primary and secondary source zones have been remediated and natural attenuation was used to deal with the residual soil and groundwater impacts. Over the last decade a number of guidance documents have been developed to guide the process and demonstrate the applicability of MNA (Sinke and le Hencho, 1999; WSDE, 2005), including the recent guidance prepared by CRC CARE on the technical aspects of implementing MNA strategies.
Technical consideration for implementation of MNA projects for Petroleum Hydrocarbons (TPH, BTEX, PAH) include their properties and behaviour in the environment, as well as natural attenuation processes (ASTM, 1998; Blum *et al.* 2007; McAllister *et al.* 1994). Following consideration of the contaminants and the environment in which they occur, collection and interpretation of the primary, secondary and tertiary lines of evidence are required to demonstrate that natural attenuation is capable of limiting the spread of hydrocarbons to within an acceptable extent (DEP, 2004; EA, 2000). Limitations and uncertainties associated with implementation of an MNA project include affects of primary, secondary and tertiary source activity and presence of Light Non-Aqueous Phase Liquid (LNAPL) with associated effects on MNA performance (Rice and McNab, 199; Chapelle *et al.* 2003; Wiedemeier *et al.* 1995; Wiedemeier and Haas, 1999). Effects of heterogeneous and dynamic geological, hydrogeological and hydrogeochemical conditions also need to be considered. This paper focuses on two technical aspects of implementing an MNA strategy that are often not directly considered in the technical evaluation of the approach.

Importance of Soil Condition
Soil conditions can have a critical influence on the performance of and the duration over which an MNA strategy needs to be implemented (Chapelle *et al.* 2003; Wiedemeier *et al.* 1995). Implementing MNA in homogenous isotropic soils results in limited uncertainty in regards to performance. When dealing with heterogeneous anisotropic conditions however, the uncertainty can be significant and may result in stakeholders being reluctant to accept MNA (USEPA, 1994; WSDE, 2005). The key areas where soil conditions can have a significant effect on the performance of MNA are:

- Retention of residual trapped free phase hydrocarbons that act as a long term source. This trapped phase usually occurs as discrete globules of product within the soil pore space. As a consequence a high surface area is available for the dissolution of the hydrocarbons into the groundwater leading to increased mass loading and longer plumes. Therefore understanding the thickness of the residual phase is important when estimating timeframes for remediation, mass loading characteristics and the size and scale of the plume that may develop;
- Groundwater flow is strongly influenced by the properties of the soil. The nature and interconnectivity between pore spaces through which groundwater travels have a fundamental influence on the velocity of

flow as well as the dispersion of the contaminant (Figure 2). Differences in flow velocity result in differential travel within portions of the plume causing differential concentration distribution due to advection. Dispersion is also affected and generally assists in biodegradation as many constituents in petroleum products become less toxic as concentrations decrease, allowing biodegradation to occur; and

– Degradation of hydrocarbons occurs through oxidation – reduction reactions that are facilitated by micro-organisms. These organisms live in biofilms on the surface of soil grains and their survival is dependent on the presence of carbon and nutrients that facilitate the biological cycle. Therefore variability in the presence of these within the soil matrix causes differential rates of biodegradation;

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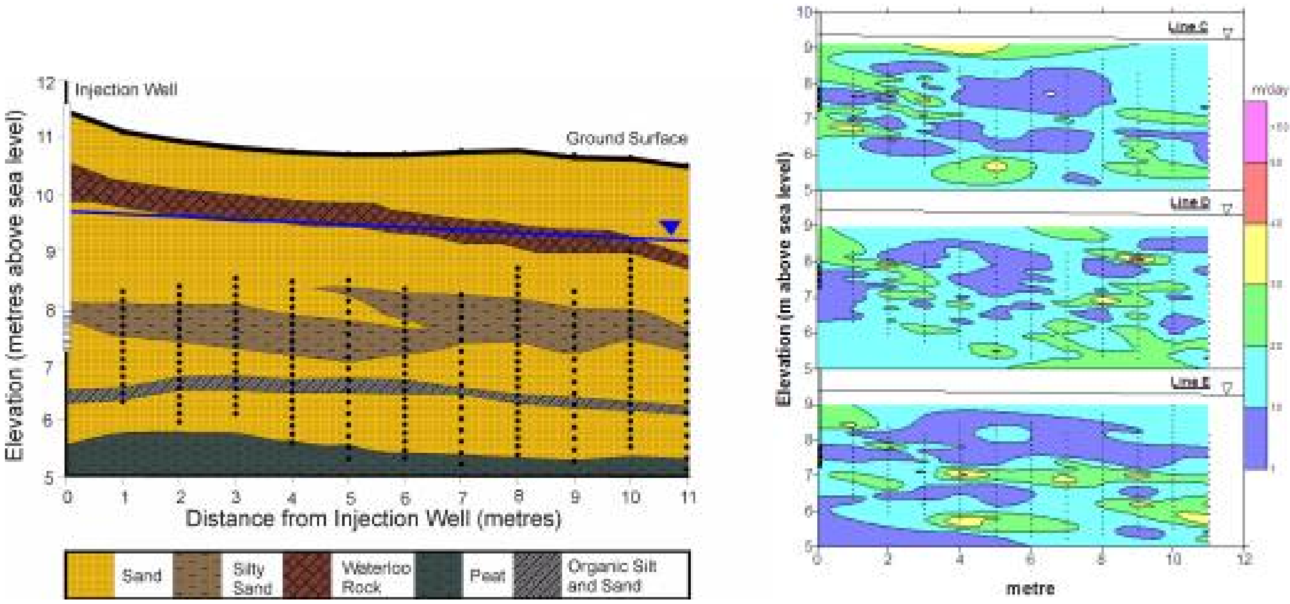

Figure 2. Effect of small heterogeneity on hydraulic conductivity in the Botany Sand Aquifer (Beck and Jankoski 1998).

These soil related aspects can often affect the performance of MNA strategies but are not commonly included in site characterisation investigations which focus largely on groundwater sample analysis and plume delineation. In most situations they may not need to be extensively considered in the initial stages of MNA if progress is anticipated but may require consideration, should there be unanticipated performance characteristics.

Understanding Risk

Another aspect often not included in the early stages of assessment for MNA viability is consideration of risk from volatile emissions by free, residual and dissolved phase product, particularly in relation to land use or land use changes in the area overlying the plume. The risk is often highly dependent on the nature of the soils that overlie the impacted zone and hence have a significant influence on the risk posed.
Understanding the potential risk due to vapour migration into buildings overlying the plume is an important pre-requisite when considering implementation of a MNA strategy to deal with dissolved phase hydrocarbon impacts, particularly considering that the timeframe involved may be extensive. Therefore considering the risk in terms of the conceptual site model such as the example shown on Figure 3 is important to the development of a clear understanding of the applicability and uncertainty associated with any MNA strategy.

Management versus Remediation using MNA

A third element that must be considered in any MNA strategy is whether the objective is to remediate the impacts or manage them until remediation can be undertaken. Groundwater impact by dissolved phase hydrocarbons occurs as a consequence of mass loading from primary (fuel storage and dispensing infrastructure) and secondary sources (impacted soils with free and sorbed phase hydrocarbon impact). The presence of free phase LNAPL further complicates the source and mass loading mechanism. In most situations removal of primary and most of the secondary sources is practicable. However, the presence of LNAPL on the water table and the associated formation of a smeared zone with trapped hydrocarbons in the soil pore space due to hydraulic head fluctuations is more difficult to remediate, particularly if they occur at depth (USEPA, 1994; USEPA, 1997; USDN, 1998). Therefore an ongoing source remains and is subject to degradation over time. The rate of degradation of the source is highly dependent on the environment and can lead to long-term (decades) mass loading of dissolved phase to the groundwater (Chapelle *et al.* 2003; Wiedemeier *et al.* 1995; Wiedemeier and Haas, 1999).

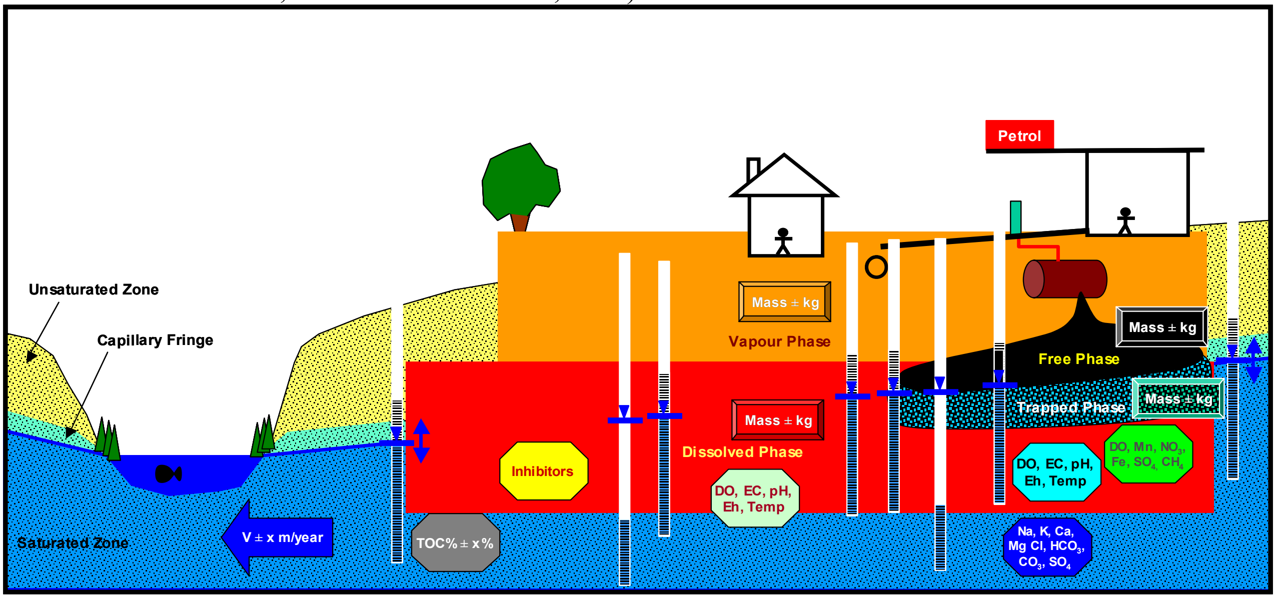

Figure 3. Example of a conceptual site model that includes consideration of the source, pathway and receptor linkage (CRC CARE unpublished draft).

Clearly in situations where an ongoing long term source remains, implementation of an MNA strategy would lead to the requirement for monitoring over an extended period and clean up would only be achieved once the source mass loading ceased (WSDE, 2005). Clearly these extended timeframes to reach clean up may not be acceptable to some stakeholders and therefore more active remediation may be required. However complete removal of all sources may not be practicable, for example at facilities with ongoing hydrocarbon storage and dispensing infrastructure in source zones limiting access. In these situations, MNA may be used to manage the resultant dissolved phase plume until such time when remediation can be accomplished. Therefore MNA may be applied as either a remediation technology if the timeframe to meet clean up goals are acceptable to stakeholders or alternatively if long timeframes are required or source clean up is not pragmatic then MNA may be used as a management strategy until more active clean up becomes feasible.

Conclusion

Therefore MNA is a strategy that can be applied to remediation or management of dissolved phase hydrocarbons. While the technical aspects and lines of evidence for demonstrating the occurrence of natural attenuation processes are extensively documented, there are a number of important considerations that can affect the applicability, effectiveness and duration of an MNA strategy. Soil properties affect retention of residual phase, groundwater flow and biodegradation, while the volatility affects risk that may limit the applicability of an MNA strategy. The character of the source also affects the duration over which an MNA strategy needs to be applied. CRC CARE identified the need to develop a nationally consistent approach to the implementation of MNA strategies that outlines the key technical requirements to demonstrate MNA as well as note factors that affect the applicability, efficiency and duration of MNA strategies, such as those outlined in this paper. In response a national technical guidance document on implementation of MNA strategies was developed, incorporating technical requirements, as well as aspects that result in limitations and uncertainties and minimum data requirements.

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