# Monitored natural attenuation (MNA) as a cost effective sustainable remediation technology for petroleum hydrocarbon contaminated sites: Demonstration of scientific evidence

Ravi Naidu[A,B], Mallavarapu Megharaj[A,B], Seidu Malik[A,B], Praveen Kumar Rachakonda[A,B], Sreenivasulu Chadalawada[B], Fiona Perso[A,B], Natalie Watkin[A,B], Zuliang Chen[A,B] and Mark Bowman[C]

[A]Centre for Environmental Risk Assessment and Remediation (CERAR), University of South Australia, Mawson Lakes, Adelaide, South Australia, Australia – 5095.
[B]CRC for Contamination Assessment and Remediation of the Environment (CRC CARE), University of South Australia, Mawson Lakes, Adelaide, South Australia, Australia – 5095.
[C]Department of Defence, Canberra, ACT 2600, Australia.

**Abstract**
Recently, monitored natural attenuation (MNA) is recognized as a cost effective and sustainable remediation technology alternative to other engineered technologies for hydrocarbon contaminated sites. However, MNA to be accepted as an appropriate remedy for a contaminated site by the regulators requires demonstration of scientific evidence. This study has evaluated the feasibility of MNA for petroleum hydrocarbons in a long term (>40 years old) contaminated site (soil and groundwater) using a combination of contamination monitoring, biogeochemical indicators, modeling, compound specific stable carbon isotope analysis and molecular microbial techniques. Results demonstrate convincing scientific evidence for natural attenuation of petroleum hydrocarbons by biodegradation rather than dilution or dispersion at this site. Further, this study demonstrates MNA as a defensible remediation technology for petroleum hydrocarbon contaminated sites besides offering suitable methods for evaluation of MNA.

**Key Words**
Monitored natural attenuation, MNA, petroleum hydrocarbons, contamination.

## Introduction

The flagship project site is RAAF Base Williamtown situated on a flat coastal plain 30 km north of New Castle. This site was chosen because of its representativeness to the potentially contaminated Defence sites elsewhere in Australia. The aquifer in the RAAF Base is unconfined (Tomago Sandbeds) and the general groundwater flow direction is towards south-east with an average hydraulic conductivity of 10 to 20 m/day. Historically, hydrocarbon contamination at the investigation sites at the RAAF Base Williamtown occurred primarily as a result of their former use as fuel storage facilities. The Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE) in collaboration with Centre for Environmental Risk Assessment and Remediation (CERAR), University of South Australia and Department of Defence (DoD) has conducted source characterisation of hydrocarbon contamination and the extent of the groundwater plume at Fuel Farm Area 1 (FFA1) and Fuel Farm Area 2 (FFA2) at RAAF Base Williamtown. This investigation demonstrated that the light non aqueous phase liquid (LNAPL) hydrocarbon contamination source is in the 'smear zone / capillary fringe', mostly concentrated at one metre to three metres depth in both areas, within the likely seasonal variations in the depth to water table. Toxicological analysis using algal and plant bioassays indicated that the TPH in the source zone is bioavailable in both areas. Preliminary calculations of the TPH mass in the soil in FFA1 and FFA2 indicated large amounts, 244376 kg in FFA1 and 342302 kg in FFA2 for the worst case scenario. At these TPH levels, it is likely the source will need active remediation. These investigations were limited to characterization of source and groundwater plume followed by bioavailability testing as required by Risk Based Land Management (RBLM) practice.

## MNA – Scientific evidence

Natural attenuation has been used as an option for remediation of groundwater contaminated with hydrocarbons in USA and Europe. However, there is no consensus in Australia among the regulators with regard to the acceptability of natural attenuation as a remediation method. Nevertheless, natural attenuation is being considered an option for remediation of the groundwater plumes at FFA1 & 2. For this, the scientific basis for natural attenuation processes (provision of scientific evidence that the hydrocarbons are really attenuating) in groundwater needs to be documented and the process characterised to gain acceptance by the

regulatory agencies. Regulatory authorities like EPA Victoria attach a high priority to ensure that natural attenuation can be demonstrated through multiple lines of evidence that degradation of the contaminant is occurring (*e.g.* biodegradation). These lines of evidence include documentation of (a) contaminant loss at field scale, (b) presence of biogeochemical indicators of natural attenuation and (c) presence of contaminant degrading microbes. Simple physical processes involving adsorption, dispersion and dilution tend not to be accepted as 'natural attenuation', unless accompanied by biodegradation. A promising development in recent years is to use the stable isotope composition of individual contaminants to detect and quantify the extent of biodegradation in contaminated aquifers and the use of advanced molecular microbiological techniques to detect the catabolic genes.

Hence, CERAR and CRC CARE conducted further studies to demonstrate natural attenuation as a potential option for remediation of hydrocarbon contaminated groundwater at these sites. This study involved (a) characterisation of hydrogeology of the sites, (b) contaminant delineation in soil and groundwater, (c) determining geochemical indicators of natural attenuation (oxygen, methane, iron, sulphate, nitrate etc.), (d) contaminant modelling and plume stability, (e) molecular microbiological techniques to document the presence of catabolic genes/microbes and (f) compound specific stable isotope fractionation of carbon for BTEX in groundwater.
The major findings of this study are:

- Hydrocarbon degrading genes and bacteria are present in the groundwater and soil.
- Bacteria able to utilise petroleum hydrocarbons as sole source of carbon have been isolated and genes characterised.
- Contaminated soil from source area contained hydrocarbon degrading bacteria but at a very low numbers which is due to lack of nutrients.
- Nutrient amendment enhanced the degradation of TPH in contaminated soils from source area while no significant degradation of TPH was observed in nutrient unamended soils.
- Irrespective of nutrient addition TPH was degraded in contaminated groundwater but at a slightly slower rate compared to nutrient amended. This indicates that natural attenuation of TPH occurring in groundwater.
- BTEX was degraded rapidly in both soil and groundwater with nutrient amendment.
- Compound specific stable isotope analysis (CSIA) of water from FFFA1 shows enrichment of $\partial$13C‰ in m-p xylene and naphthalene at the down gradient wells indicating biodegradation is occurring at FFA1.
- Similarly CSIA of water from FFFA2 shows enrichment of $\partial$13C‰ in toluene, ethyl benzene, m-p xylene and naphthalene at the down gradient wells indicating biodegradation is taking place at FFFA2.
- Also stable isotope fractionation indicated the presence of 2 separate spills of hydrocarbons in FFA2.
- Groundwater monitoring data indicate that plume is stable and not expanding.
- Treatability studies suggest nutrient amendment could be a cost effective remediation option for contaminated soil.
- These studies provide multiple lines of scientific evidence that natural attenuation of hydrocarbons is occurring in both the aquifers from FFA1 and FFA2.

In summary, the results of this investigation demonstrate that MNA is a potential remediation option for hydrocarbon contaminated sites at Williamtown RAAF Base. Further, the 'lines of evidence' used in this investigation can serve as a useful approach for demonstration of 'MNA' at other hydrocarbon contaminated sites in Australia.

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