

Monitored natural attenuation of a long-term petroleum hydrocarbon contaminated sites: a case study

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Abstract This study evaluated the potential of monitored natural attenuation (MNA) as a remedial option for groundwater at a long-term petroleum hydrocarbon contaminated site in Australia. Source characterization revealed that total petroleum hydrocarbons (TPH) as the major contaminant of concern in the smear zone and groundwater. Multiple lines of evidence involving the geochemical parameters, microbiological analysis, data modelling and compound-specific stable carbon isotope analysis all demonstrated natural attenuation of hydrocarbons occurring in the groundwater via intrinsic biodegradation. Groundwater monitoring data by Mann–Kendall trend analysis using properly designed and installed

groundwater monitoring wells shows the plume is stable and neither expanding nor shrinking. The reason for stable plume is due to the presence of both active source and natural attenuation on the edge of the plume. Assuming no retardation and no degradation the contaminated plume would have travelled a distance of 1,096 m (best case) to 11,496 m (worst case) in 30 years. However, the plume was extended only up to about 170 m from its source. The results of these investigations provide strong scientific evidence for natural attenuation of TPH in this contaminated aquifer. Therefore, MNA can be applied as a defensible management option for this site following significant reduction of TPH in the source zone.

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Introduction

Soil and groundwater contamination with petroleum released from leaking underground or above ground fuel storage tanks and accidental spillages are serious problems worldwide. Due to the presence of toxic and carcinogenic chemicals such as benzene, toluene, ethyl benzene, xylene (BTEX) and naphthalene petroleum contamination presents a significant risk to human and ecological health. The conventional methods of remediation involve land-filling, incineration and pump and

treat which are not only expensive but environmentally unfriendly compared to bioremediation and natural attenuation. Natural attenuation (NA) is the reduction in concentration and mass of the contaminant due to naturally occurring processes in the environment. The process is monitored for regulatory purposes to demonstrate continuing attenuation of the contaminant reaching the site-specific regulatory goals within reasonable time and space, hence, the use of the term monitored natural attenuation (MNA). MNA has been widely accepted as a suitable management option for petroleum hydrocarbon contaminated soil and groundwater in USA (American Society for Testing and Materials 2004). Despite significant opposition to the use of MNA in some countries, the process has rapidly become an acceptable tool for risk based management of groundwater contaminant plumes containing petroleum hydrocarbons and their derivatives (Cho et al. 1997; Kao and Wang 2000; Khan and Husain 2003; Rugner et al. 2006; Suarez and Rifai 2002; Wiedemeier et al. 1996).

Natural attenuation includes a combination of biological, chemical and physical processes that occur naturally (Sanchez et al. 2000). Physical processes include dispersion, diffusion, dilution by recharge and volatilization. The physical and chemical processes such as sorption result in the reduction in concentration and mobility of petroleum hydrocarbons in groundwater but not in the total mass and are “non-destructive” mechanisms. However, chemical or abiotic reactions together with biological reactions result in the reduction of total contaminant mass in the system and are “destructive” mechanisms. The most important process for contaminated site remediation is biodegradation because it is an irreversible destructive process, unlike sorption, dilution and volatilisation (Wiedemeier et al. 1996).

Natural attenuation, if effective, provides significant benefits in terms of cost saving and effort (Sanchez et al. 2000) and often equally protective of human health and the environment on most sites. Demonstration of NA of petroleum hydrocarbons in groundwater requires multiple lines of evidence (American Society for Testing and Materials 2004; USEPA 2009). Regulatory approval requires demonstration of both primary and secondary lines of evidence at the contaminated sites (American Society for Testing and Materials 2004). Primary lines of evidence are demonstration of a shrinking or stable

plume while secondary lines of evidence include indicator parameters for intrinsic bioremediation and estimates of attenuation rate.

Implementation of MNA as a remediation strategy for the contaminated site requires evaluation and quantification of the potential for successful NA (Lee and Lee 2003). Various types of methods are used for evaluating NA (American Society for Testing and Materials 2004; Clement et al. 2000, 2002; Lu et al. 1999; National Research Council (NRC) 1993; Nyer and Boettcher 2001; Wiedemeier et al. 1999). Lee and Lee (2003) and Suarez and Rifai (2002) quantitatively evaluated the NA of BTEX in which Mann–Kendall trend analyses of contaminant concentrations were included. Using this tool, they successfully demonstrated NA of BTEX.

Groundwater contamination with petroleum hydrocarbons requiring very high clean up costs has been reported at many sites in Australia. Although MNA has generally been widely accepted in the United States and Europe, its acceptance as a remedial option by regulators in Australia is limited. Often the major limitation for the application of MNA is the lack of demonstration of scientific basis for attenuation of contaminants. The objective of this investigation is to demonstrate scientific basis for NA at a long-term petroleum hydrocarbon contaminated site.

Materials and methods

Site description

The site, former fuel farm area 1 (FFA1) was a shallow unconfined aquifer located within Royal Australian Air Force (RAAF) Base Williamtown (Australia). Underground tanks were used to store fuel at the site. This area is underlain by extensive quartzose sand deposits of the Newcastle Bight Embayment inner barrier dune system, known as the Tomago Sandbeds. The Stockton Sandbeds extends to the south from the outer barrier of the Bight. The general groundwater flow direction in the aquifer is towards south-east. The saturated hydraulic conductivities in the Tomago Sandbeds range from between 10 to 100 m day⁻¹, with an average of 10 to 20 m day⁻¹ (ERM 2002). Transmissivity values of up to 900 m² day⁻¹ have been reported (Egis Consulting Australia 2001). The hydraulic gradients at the RAAF Base range between

0.0035 and 0.007 and effective porosities range between 20 and 35 %. The depth of groundwater in FFA1 varies between 1.7 and 2.8 m from the ground surface due to seasonal fluctuation (ERM 2003). The annual rainfall is around 1,120 mm.

Source history

The fuel facility was in operation between 1963 and 1984 (Douglas and Partners 1995). There were two above ground and two below ground aviation turbine fuel tanks with a combined volume of 181,160 l. Storage tanks were contained within concrete bunded areas with adjoining gravel ground surface. Exact date of leakage from the fuel tanks is unknown. The maximum potential time for active leaching to the aquifer is 42 years, assuming leaching since operation. However, an approximate age of 30 years was considered for the groundwater plume. Investigation and risk assessment of potentially contaminated sites depends on the past, current and future activities at the site. The site in this study is classified as commercial/industrial. Sensitive receptors (drinking water extraction wells) at the site are 675 m away from the source.

Contaminant source characterisation

Soil and ground water sampling

Contamination in the soil and ground water was delineated following detailed sampling of surface (0–50 cm) and subsurface (50–100 cm, 100–200 cm and 200–300 cm) soils. The site had a shallow ground water table at a depth of 3 m. For this reason soil sampling was limited to 3 m depth. Fourteen cores were drilled in 2004 (Fig. 1) near the source area to estimate the mass of hydrocarbon contaminants. Three cores were used to install bore wells for monitoring ground water contaminants. Additional 13 cores were drilled which were converted to bore wells in 2005 to assist delineation of the groundwater plume. Soil sampling procedures were in accordance with Australian Standard 4482-1 (Standards Australia 2005). At the investigation site, the approximate area with potential for soil and groundwater contamination was initially identified from previous reports (ERM 2002, 2003). Grid sampling across this area was used with sufficient sampling density to identify a 10 m radius hot spot in accordance with the Australian

Standard 4482-1 (Standards Australia 2005). The final sampling density was altered slightly following locations of electrical and fibre optic cables that prevented drilling at some of the pre-selected sampling locations. Where possible these sampling locations were relocated within a few metres of the original planned locations.

Groundwater sampling was carried out from three installed wells in 2004 and 13 newly installed wells in 2005 in accordance with Australian Standard AS 5667.11 (Standards Australia AS 1998). In addition to wells installed by the project team there were a number of previously installed wells and data from these monitoring wells demonstrate appreciable concentrations of TPH in ground water. Two days were given for each monitoring well to settle after well construction as the material is silty sand with high porosity and permeability and no fill materials and drilling fluids were used for well construction. Prior to sampling (2 days after well construction), the monitoring wells were purged using a submersible pump by removing at least five bore-volumes of water until the water was clear as part of well development process. During purging, water quality parameters of the monitoring wells were measured using a TPS multimeter until the values stabilized.

In order to assess the stability of TPH plumes we designed and installed groundwater monitoring wells at appropriate locations (RISC 2001; USEPA 2000). This requires two messenger wells, three perimeter of compliance (POC) wells and one background well. Wells B123 and W19 are close to the source area and considered as messenger wells. Well W18, W25 and W22 are located down gradient and considered as POC wells. Well W17 located up gradient was used as a background well.

Volatile and semi-volatile organic compounds

Samples for volatile organic compounds (VOC) analysis were collected in 40 ml head-space gas chromatography (GC) Purge and Trap glass vials fitted with a screw cap and Teflon coated rubber septa. and extracted on site with methanolic water. Samples for semi-volatile organic compounds (SVOC) and heavy metal analyses were collected in 1 l amber glass jars with airtight metal caps containing inner Teflon covers. All the samples were placed immediately on ice soon after collection and transported to the

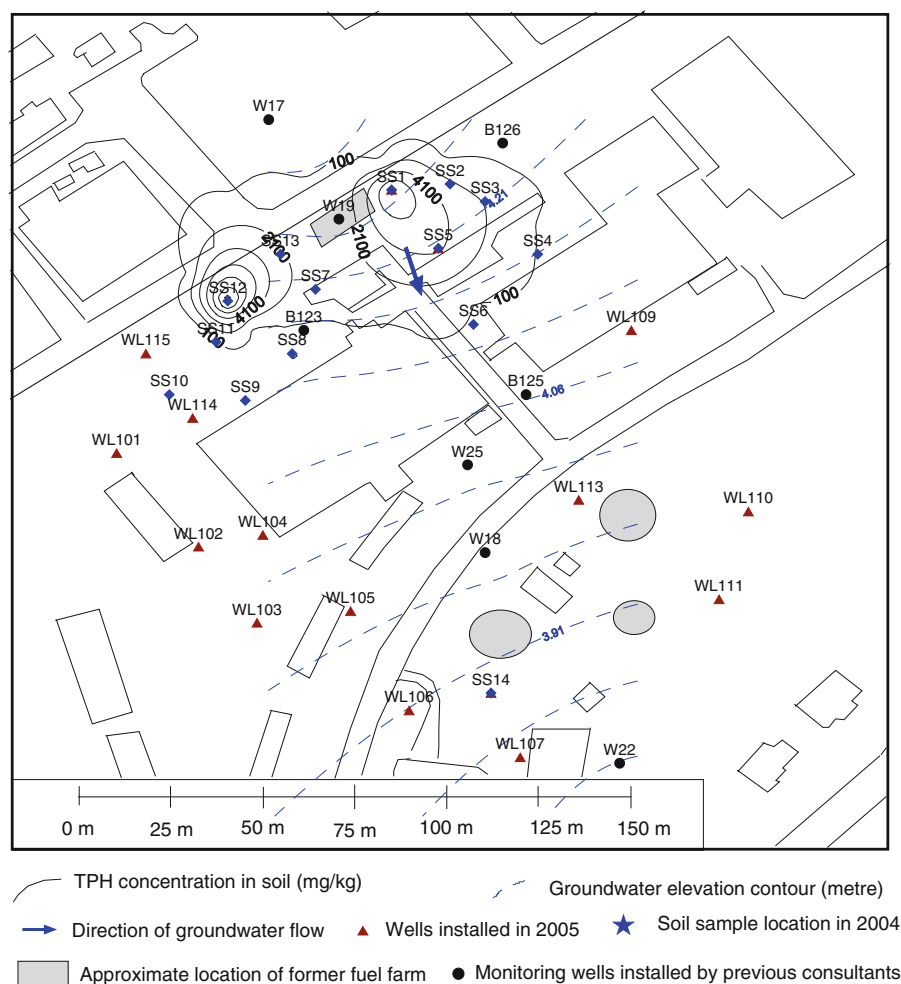


Fig. 1 Sampling locations of soil and groundwater

laboratory for chemical analyses. All sampling bottles were appropriately labelled prior to sampling.

Analytical methods

All analyses were conducted following the United States Environmental Protection Agency (USEPA 2005) protocols except where otherwise noted. Quality assurance and quality control (QA/QC) procedures were maintained throughout the analysis. These include (a) collection of all environmental samples by a set of uniform methods including blank samples, (b) implementation of decontamination procedures, (c) sample identification/labelling procedures, (d) chain of custody information, (e) sample duplication frequency, (f) field equipment calibration, (g) split

duplicates and field blanks and (h) appropriate controls and spike-recoveries.

Chemical analysis

The extraction and analysis of VOC from soils followed the USEPA method 5035 while the USEPA method 5030B was used for groundwater (USEPA 2005). Both methods used gas chromatography/mass spectrometry (GC/MS; Agilent Technologies 6890 N GC with 5973 Mass selective detector) with a purge and trap (Tekmar–Dohrmann) for quantification against known standards.

The extraction of SVOC from soils used microwave assisted extraction according to the USEPA method 3546 (USEPA 2005). Groundwater extractions were

carried out using separator funnel liquid–liquid extraction according to the USEPA method 3510C (USEPA 2005). SVOCs in soil and groundwater samples were analysed by GC/MS (Agilent Technologies, 6,890 N GC with 5973 Mass Selective Detector) following the USEPA method 8270B (USEPA 2005) while TPH were analysed by GC/FID (Agilent Technologies 7890A) with DB-5 column (30 m length \times 0.25 mm ID \times 0.25 μ m film thickness) using the USEPA method 8015 (USEPA 2005).

Microbiological analysis

Microbial enumeration is used as a screening tool to assess the presence of micro-organisms and their bioremediation potential for hydrocarbons in soil or groundwater. Selected groundwater samples from wells (SS1 from the source area and SS14 from the downgradient) were assessed for the presence of bacteria which is able to degrade TPH following the most probable number (MPN) method. Aliquots from serial dilutions (10-fold) prepared from the groundwater were inoculated into Bushnell–Haas mineral medium with gasoline as a carbon source and incubated at 20 ± 2 °C in the dark for 3 weeks. At the end of incubation period, the number of positive and negative wells were scored and population density was estimated using the standard MPN tables. Iodonitro-tetrazolium violet (INT) was used to identify the positive wells (Haines et al. 1996). A few bacterial colonies able to utilise gasoline as sole carbon source were isolated by plating the bacterial suspension from the above positive wells onto M9 mineral agar medium supplemented with gasoline as carbon source in gas phase (Megharaj et al. 1997). Five of these bacterial colonies picked randomly were tested for their ability to utilise gasoline as sole carbon source in liquid M9 mineral medium (5 ml M9 medium in 16 ml sterile glass culture tube supplemented with 5 μ l gasoline as carbon source).

Laboratory microcosm study

In order to evaluate the role of microorganisms in the NA of petroleum hydrocarbons in the contaminated aquifer, the groundwater collected from the source area was tested for hydrocarbon degradation in microcosms under laboratory conditions. The microcosm consisted of sterile 40 ml glass Purge and Trap

GC vial fitted with screw cap containing Teflon lined butyl rubber septa and groundwater (20 ml for aerobic and completely filled for anaerobic). Filter sterilized groundwater (0.22 μ m) served as abiotic controls. The microcosms were incubated at 20 °C in the dark for 60 days on an orbital shaker set at 90 rpm. The groundwater had 6,401 mg l⁻¹ TPH, 41 μ g l⁻¹ ethyl benzene, 432 μ g l⁻¹ xylenes and 261 μ g l⁻¹ naphthalene. Triplicate microcosms were sacrificed at 15 days intervals for hydrocarbons analysis using GC/MS.

Stable isotope fractionation analysis (SIFA)

Carbon isotope fractionation is useful to assess the in situ biodegradation of contaminants in the aquifer. Although benzene and toluene were not detected at significant levels in the contaminated aquifer, ethylbenzene and xylene were found in the groundwater from source area and along the centreline of the plume. Groundwater samples collected from the wells in the source area and down gradient along the centreline of the plume were assessed for compound specific carbon isotope fractionation. The groundwater samples were adjusted to pH 10 by using sodium hydroxide pellets to inhibit microbial activity and stored at 4 °C until extraction with *n*-pentane. The stable carbon isotope composition was determined by gas chromatography-combustion-isotope-ratio mass spectrometry (Richnow et al. 2003). ¹³C/¹²C ratios were measured for specific compounds (toluene, ethyl benzene, xylene and naphthalene). The results of the analysis were examined for their ¹³C/¹²C enrichment in the source and down gradient areas. The isotope values are reported as $\delta^{13}\text{C}$ in units per mill (‰); $\delta^{13}\text{C}[\text{‰}] = (\text{R}_{\text{sample}} - \text{R}_{\text{standard}}) / \text{R}_{\text{standard}} \times 1000$, where R is the ratio of heavy to light isotope (¹³C/¹²C) of the sample and the international standard (Vienna Pee Dee Belemnite), respectively.

Results

Contaminants in the unsaturated zone

TPH and BTEX were recorded in soil samples at a depth of 1–3 m in the smear zone (Table 1). The top metre of the soil was relatively devoid of any major contamination in all of the six cores sampled including

Table 1 Total petroleum hydrocarbons (TPH) concentrations (mg kg^{-1} soil) in source soil samples

Soil bore ID	0–1 m depth	1–2 m depth	2–3 m depth	Total mass of TPH
FFISS1	nd (nd)	8,767 (0.536)	5,989 (1.221)	14,756 (1.757)
FFISS3	86 (nd)	2,028 (0.06)	15,300 (1.649)	17,414 (1.709)
FFISS4	22 (nd)	33 (nd)	10,801 (1.581)	10,856 (1.581)
FFISS5	281 (nd)	4,410 (0.260)	5,346 (0.337)	10,037 (0.597)
FFISS6	30 (nd)	25 (nd)	<10 (nd)	55 (nd)
FFISS7	36 (nd)	1,014 (nd)	11,811 (4.996)	12,861 (4.996)
FFISS12	<10 (nd)	13,782 (2.633)	24,106 (4.817)	37,888 (7.450)
FFISS13	28 (nd)	2,256 (0.042)	6,916 (0.159)	9,200 (0.201)
NSW guideline value ($\text{C}_{10}\text{--C}_{36}$) ^a				1,000
NSW guideline value ($\text{C}_6\text{--C}_9$) ^a				65

Data in parenthesis represent total BTEX concentrations; *nd* not detected

^a New South Wales EPA (1994) guidelines for assessing service station sites

the cores that exhibited elevated levels of TPH in the subsurface. Comparison of the soil data with the New South Wales Environment Protection Authority (NSW EPA 1994) Guidelines for Assessing Service Station Sites and Australian National Environmental Protection Measure (NEPM) (1999) reveals considerable exceedance of the TPH industrial threshold limit of $1,000 \text{ mg kg}^{-1}$ for $\text{C}_{10}\text{--C}_{36}$ fraction in the majority of samples taken from 1 to 2 and 2 to 3 m depth soil cores.

The total BTEX concentrations in soils from 1 to 2 and 2 to 3 m depths showed trends similar to TPH distribution although individual BTEX components did not exceed the NSW EPA (1994) threshold limit. Naphthalene was detected in soil samples in the source area with the concentration varying from 0.2 to 22 mg kg^{-1} soil. Samples from SS7 located close to the source zone showed the highest concentration of naphthalene that slightly exceeded the environment investigation limit (EIL) of 20 mg kg^{-1} (NEPC

1999). Similar to most contaminated sites, the distribution of contaminants was heterogeneous both spatially and with depth.

Contaminant mass in the unsaturated source zone

The presence of TPH in the smear zone and groundwater were monitored over a period of 5 years using both bore wells installed in 2005 and those installed by consulting companies prior to 1995. Total volume and mass of the contaminant in the source zone were estimated using three possible scenarios (Table 2);

- best case (lowest concentration of TPH in 2005 ($10,000 \text{ mg kg}^{-1}$) with a thickness of 1 m);
- likely case (based on mean concentration of the highest and lowest);
- worst case (highest concentration of TPH ($24,106 \text{ mg kg}^{-1}$) with a possible thickness of 2 m.

Table 2 Mass calculation of TPH and BTEX in the source area

	Concentration of TPH in soil (mg kg^{-1})	Thickness of the source (m)	Volume of the source (m^3)	Total mass of the soil at source (using density of sand 1.6 g cm^{-3}) kg	Total mass of TPH in source (kg)
Best case	10,000	1.0	3,168	5,068,800	50,688
Likely case	17,000	1.5	4,752	7,603,200	129,254
Worst case	24,106	2.0	6,336	10,137,600	244,376
	Concentration of BTEX in soil ($\mu\text{g kg}^{-1}$)	Thickness of the source (m)	Volume of the source (m^3)	Total mass of the soil at source (using density of sand 1.6 g cm^{-3}) (kg)	Total mass of BTEX in source (kg)
Best case	500	1.0	3,168	5,068,800	2.53
Likely case	1,000	1.5	4,752	7,603,200	7.60
Worst case	4,000	2	8,485.6	10,137,600	40.55

Mass of TPH was estimated using 1.6 mg cm^{-3} as the bulk density of soil total mass of contaminants in 2005 was likely to be as high as $2.44 \times 10^5 \text{ kg}$ (the worst case) and the mass of contaminants was $5.07 \times 10^4 \text{ kg}$ for the best case (Table 2). Similarly, the total BTEX in soil could be as low as 2.53 kg or as high as 40.55 kg (Table 2). Table 1 presents the mass of TPH in soils sampled in the source area.

Contaminants in groundwater

Petroleum hydrocarbons were detected in groundwater over an area approximating $14,100 \text{ m}^2$. Groundwater sampling and analysis revealed that TPH, naphthalene and amongst BTEX, xylene are the main contaminants of concern. Groundwater monitoring data from existing wells prior to the current study showed high concentrations of TPH particularly in wells W19 and B123 and xylene in well B123. The contour maps plotted for TPH, BTEX and naphthalene (Fig. 2) for all wells shows a narrow groundwater plume with the concentrations of TPH, BTEX and naphthalene in wells located away from the centreline of the plume being extremely low.

The TPH value exceeds the threshold limit set by the Clean Water Act 1970 (CWA 1972) Schedule 2 regulations for restricted substances discharge to clean water ($10,000 \mu\text{g l}^{-1}$ equivalent to oil and grease) in well B123. Amongst BTEX only xylene exceeded the guideline values in well B123. Other constituents of BTEX did not exceed any guideline value. Naphthalene exceeded its guideline values ($3 \mu\text{g l}^{-1}$) in most of the contaminated area (NEPC 1999). The concentration of phenols exceeded threshold concentrations in wells B123, W25 and W18, but they degrade very fast. Monitoring of dissolved TPH in ground water at the site during 2003–2010 demonstrates a fairly stable plume that neither shrinks nor expands although a significant seasonal fluctuation in the concentration is observed. The average groundwater velocities at the contaminated site was estimated to be 36 m year^{-1} . Assuming no retardation, no degradation and using hydrogeological parameters from the ERM (2002) report, the contaminated plumes would have travelled a distance of 1,096 m in 30 years when the site was first contaminated. However, the plume in its present form has extended up to only about 170 m from its source with this being stable since 2005. This was attributed to NA via biodegradation as confirmed by

the presence of micro-organisms able to degrade hydrocarbon contaminants in the selected wells.

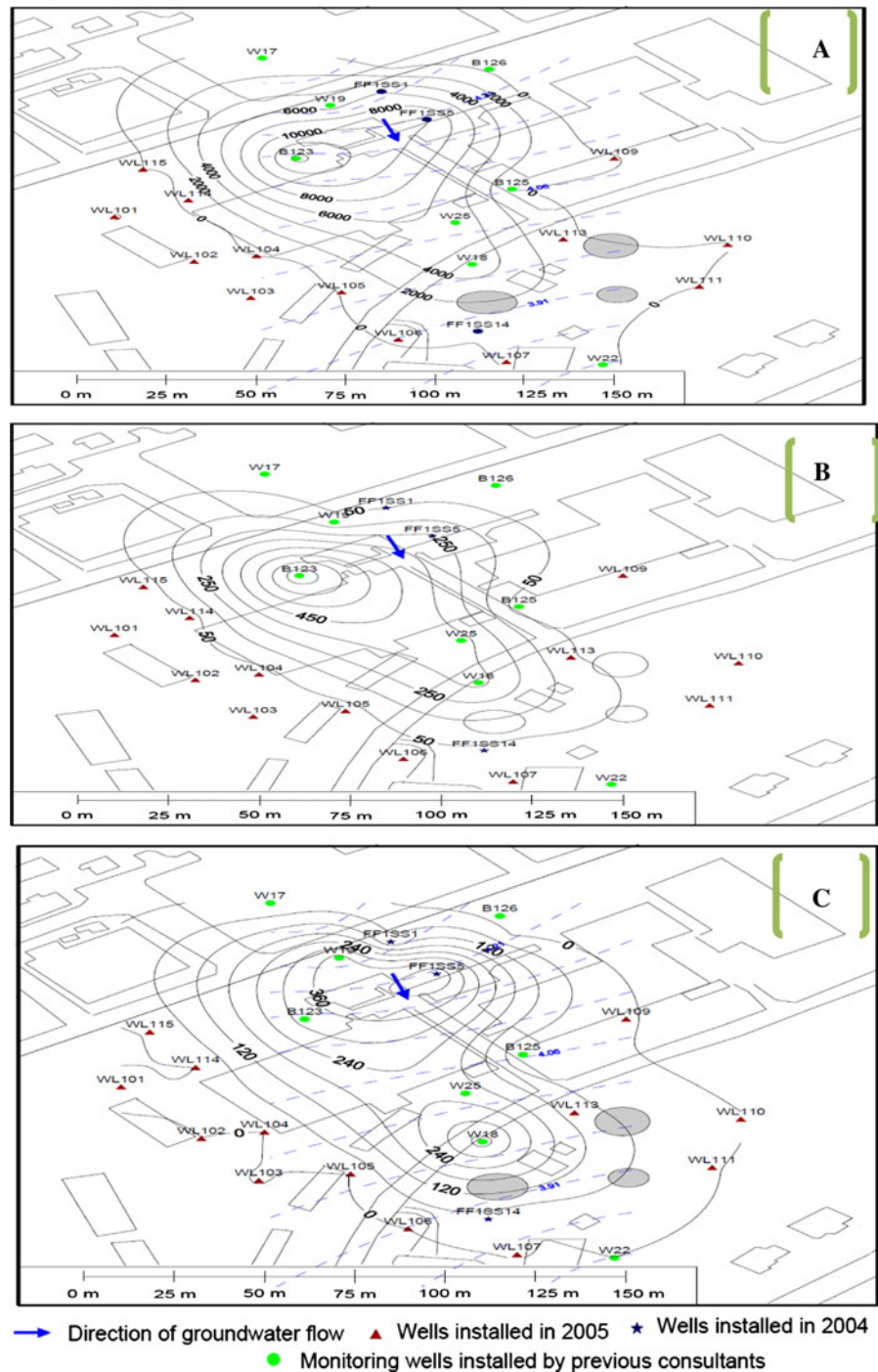
Geochemical parameters

Depending on the location of the well, sulfate concentrations at this site varied from 1 to 41 mg l^{-1} (Table 3). The lowest concentration of sulfate was detected near the fuel tank area with the background sulfate concentrations ranging from 25 to 40 mg l^{-1} . The distribution of sulfate concentrations in this site indicates anaerobic degradation via sulfate reduction in the source zone. The background nitrate concentration at the RAAF Base is generally low ($1.5\text{--}2.0 \text{ mg l}^{-1}$). The concentration of nitrate increases from below quantification limit ($<0.05 \text{ mg l}^{-1}$) in the contaminated area to 25 mg l^{-1} in the uncontaminated area. The low concentration of nitrate in ground water may limit the capacity for biodegradation by denitrification. These results suggest that the capacity of nitrate reduction to contribute to TPH degradation is not as significant as sulphate reduction.

Dissolved oxygen concentrations in the groundwater ranged from 0.02 to 2.07 mg l^{-1} . Dissolved oxygen (DO) shows low DO in the source zone which increases towards the edge of the plume. Further, the DO concentrations in all the wells showed both an increase and decrease depending on the sampling season. Also, the groundwater from the source area showed the production of methane (data not shown). This suggests both aerobic and anaerobic degradation of petroleum hydrocarbons was occurring in the source area. While the concentration of methane was not measured in all of the installed wells, those measured in the wells lying along the centreline of the plume shows significant levels of methane (as high as 5.89 mg l^{-1}) near the fuel tank area, but below detection level away from the source area (data not shown). However, along the centreline of the plume methane was detected at W18 (5.1 mg l^{-1}) 84 m down gradient from the source. In contrast, methane was not detected in W22, which is 162 m down gradient from the source. The presence of methane and concurrent depletion of dissolved oxygen near the source zone are indicative of anaerobic degradation of petroleum hydrocarbons.

A high concentration (10.4 mg l^{-1}) of ferrous iron (Fe^{2+}) was detected in groundwater from the storage tank area. Once the available oxygen and

Fig. 2 TPH (a), BTEX (b) and naphthalene (c) concentrations ($\mu\text{g l}^{-1}$) in groundwater



nitrate are depleted, subsurface micro-organisms may use oxidised iron (Fe^{3+}) mineral as an electron acceptor (Lovley 1991). The background concentration of ferrous iron was below detection level ($<0.05 \text{ mg l}^{-1}$), probably anaerobic degradation of

hydrocarbons is occurring simultaneously with iron reduction.

Analysis of the TPH data with rainfall pattern during the monitoring period demonstrates an inverse relationship ($R^2 = 0.637$) between these parameters

Table 3 Geochemical data for selected wells

Well Id	2006		2007		2008		2009
	February	August	February	August	April	September	April
<i>DO (mg l⁻¹)</i>							
W18	0.63	1.19	1.81	0.8	0.82	0.02	0.71
W22	1.03	1.5	1.01	0.42	1	0.03	0.36
W25	0.34	2.07	0.36	0.56	0.62	0.01	0.68
B123	0.7	1.1	0.4	0.9	0.4	0.16	0.31
FF1SS5	0.77	1.22	0.37	0.93	0.79	0.02	0.24
<i>Nitrate (mg l⁻¹)</i>							
W18	0.072	bd	bd	2.51	0.76	16.26	< bd
W22	0.608	3.51	bd	1.05	bd	18.39	1.84
W25	0.076	7.31	bd	4.52	bd	12.09	2.44
B123	0.057	bd	bd	bd	1.61	25.13	bd
FF1SS5	bd	bd	<bd	bd	bd	23.05	bd
<i>Ferrous iron (mg l⁻¹)</i>							
W18	0.009	bd	0.29	1.67	1.47	1.69	1.173
W22	bd	bd	0.17	0.08	0.05	<bd	0.087
W25	bd	bd	0.07	0.22	0.06	<bd	0.14
B123	0.07	bd	10.39	6.13	4.63	2.91	3.725
FF1SS5	bd	bd	0.67	6.42	1.47	1.94	1.908
<i>Sulphate (mg l⁻¹)</i>							
W18	6.62	10.15	7.32	17.74	9.73	40.37	8.1
W22	20.014	28.06	16.26	13.38	7.93	13.64	15.35
W25	4.364	21.87	13.73	27.49	18.26	12.88	14
B123	1.405	6.31	6.3	4.95	1.82	1.72	1.41
FF1SS5	4.167	9.63	7.3	4.74	bd	0.09	8.13

Bd below detection limit

with the TPH concentration decreasing with an increase in rainfall (Fig. 3). The inverse relationship is observed in all the listed monitoring wells however the significance of relationship is dependent on the monitoring well. The effect of increased rainfall on ground water is also evident from the rise in groundwater table showing enhanced recharging of the aquifer during wet summer months.

Microbiological analysis of groundwater and microcosm study

The population of TPH degrading bacteria from wells within FFA1 ranged from between 13×10^5 (SS1) and 4.9×10^2 ml (SS14). The TPH degrading bacterial densities within these wells were related to their TPH concentration with higher population densities found in groundwater containing higher TPH concentrations

(5.87 mg TPH l⁻¹ in SS1) compared to lower TPH concentrations (0.061 mg TPH l⁻¹ in SS14). All the five bacteria isolated from the groundwater were able to grow on gasoline as sole carbon source. All these bacteria were putatively identified as *Burkholderia cepacia* by 16S rRNA gene sequencing.

The groundwater microcosm study revealed complete degradation of BTEX in 30 days and TPH in 60 days incubation in both aerobic and anaerobic treatments. The abiotic controls (filter-sterilized groundwater) did not show any degradation of hydrocarbons during the same period.

Compound specific stable carbon isotope analysis

In order to investigate the in situ biodegradation of petroleum hydrocarbons in the contaminated aquifer, groundwater collected from source area and down

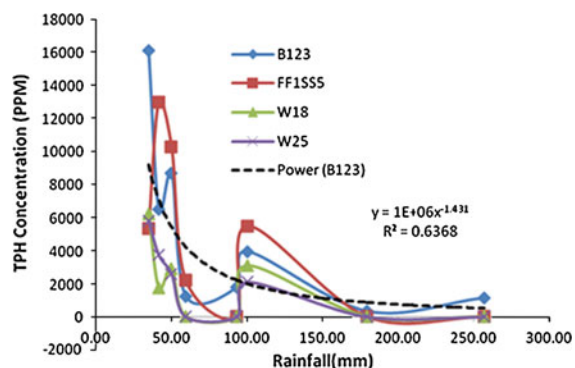


Fig. 3 Variation of TPH concentration with rainfall at different wells

gradient along the plume were assessed for concentration and isotope composition of xylene and naphthalene. Five wells (W9, SS5, B123, W25 and W18) were chosen for this investigation. Compound specific stable isotope analysis (CSIA) was conducted only for xylene and naphthalene since other chemicals such as benzene or toluene were either not present or below the detection limit for CSIA. CSIA of water showed enrichment of $\delta^{13}\text{C} \text{ ‰}$ in *m, p*-xylene and naphthalene along the flowpath in this contaminated aquifer (Fig. 4).

Discussion

The ASTM Standard for Remediation by NA (American Society for Testing and Materials 2004) suggests that NA may include primary, secondary and optional lines of evidence. The primary lines of evidence include plume stability reflected by changes in its size with the plume either remaining stable, shrinking or expanding while secondary lines of evidence include geochemical indicators of intrinsic bioremediation. Optional lines of evidence include modelling, estimates of assimilative capacity, and microbiological studies. In this study, we used multiple lines of evidence including geochemical data, modelling, microbiological analysis and stable carbon isotope fractionation to evaluate natural attenuation. The plume was assessed for its stability- whether it was shrinking or stable based on plume length, statistical analyses using Mann–Kendall test (Suarez and Rifai 2002) and the analysis of time series data and also mass reduction as evident from the secondary lines of evidence. The stable plume together with the

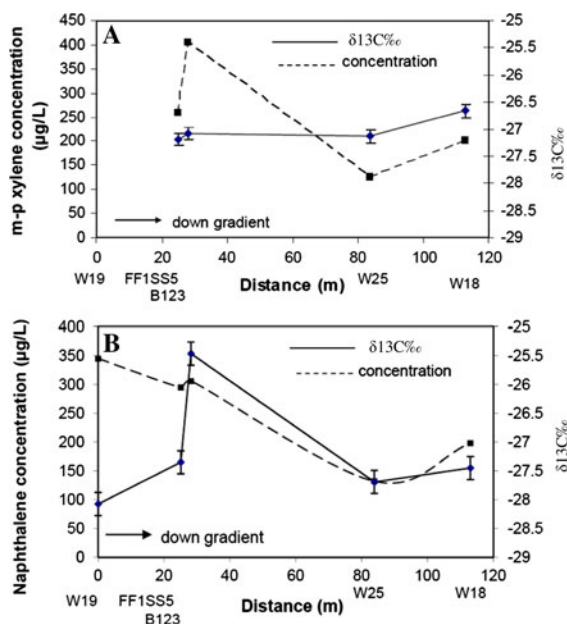


Fig. 4 Concentration and isotope composition of **a** *m, p*-xylene and **b** naphthalene in the down gradient of the contaminant source

presence of geochemical indicators demonstrate both primary and secondary evidence for natural attenuation. During the monitoring period, the concentration of TPH decreased with increasing rainfall which was coupled with a decrease in depth to ground water table demonstrating enhanced recharging of the aquifer. The reasons for NA of petroleum hydrocarbons at the site are discussed below.

Primary lines of evidence

Plume stability monitoring evaluates screening data to determine concentration trend for contaminants of concern at each monitoring well (RISC 2001; USEPA 2000). Numerical changes in contaminant concentration levels can often appear insignificant from one quarterly monitoring event to another. To analyse the stability of the TPH plume, we analysed the ground-water monitoring data using the Mann–Kendall test, a non parametric statistical test (Suarez and Rifai 2002). Mann–Kendall test enables prediction of plume stability as decreasing, stable/no trend and increasing at given confidence levels (Lee and Lee 2003).

Twelve sets of data for monitoring wells B123, W19, W25, W18, W22 and W17 from January 2002 to

March 2009 were used for Mann–Kendall trend. The Mann Kendal test involves computing a statistics S which is the difference between the number of pairwise slopes that are positive minus the number that are negative. Standard error of S (SE_S) is calculated using the formulae:

$$SE_S =$$

$$\sqrt{\frac{1}{18} [n(n-1)(2n+5) - \sum_{p=1}^g w_p(w_p-1)(2w_p+5)]}$$

where n represents the total observation/data points, g represents the number of tied groups and w_p represents the number of data points in the p th group.

The TPH and BTEX data for B123, W19, W25 and W22 from January 2002 to March 2009 were considered for analysis. The TPH trend analysis (Table 4) showed that B123, W19, W25 and W22 are stable with a 95 % confidence level. Wells W18 and W17 demonstrate a decreasing trend. BTEX trend analysis (Table 4) showed that the wells B123, W19, W25, W18 and W22 are stable with a 95 % confidence level. W17 was found to be free from BTEX contamination throughout the monitoring period. The upgradient well W17 exhibited TPH contamination but showed a decreasing trend. The contaminant concentration appears to depend highly on the ground water seasonal fluctuation. With high rainfall, the contaminant concentration decreases and it increases during periods of low or no rainfall (Fig. 3).

Attenuation rate constant

The groundwater plume was found to be stable from the Mann–Kendall trend analysis. The bulk

attenuation rate constant (k) is calculated based on the centreline approach (Bockelmann et al. 2003) using the following formula:

$$C_x = C_0 \exp \left[\left\{ v - \sqrt{v^2 + 4kD} \right\} \frac{x}{2D} \right]$$

where, C_x represents the concentrations (M/L^3) as a function of the distance travelled x (L), C_0 (M/L^3) is the concentration at the source, v is the groundwater velocity (L/T) and D (L^2/T) is the dispersion coefficient ($D = \alpha v$; where α is the longitudinal dispersivity that can be approximated to be equal to $0.1 L_D$ where L_D is the total domain length. It is assumed that the plume is stable.

The Wells B123, W25, SS14 and WL22 which are lying approximately along the plume centreline were selected and the TPH, BTEX, naphthalene concentrations in February 2004 and April 2005 of these wells were used for estimation of bulk attenuation rate constant (k), with a groundwater velocity of 36.5 m year^{-1} and a total domain length of 162 m. The natural log concentration-distance plot is shown in (Fig. 5) as an example for April 2005 TPH data.

The half-lives of TPH were calculated using the formula:

$$t_{1/2} = 0.693/k$$

where $t_{1/2}$ is half-life. The half-lives of BTEX, TPH, total xylene, ethyl benzene and naphthalene were estimated (Table 5).

The carcinogenic benzene was not detected in groundwater suggesting its rapid degradation. Toluene was detected only at well B123 and W25. There was no toluene in down gradient wells SS4 or W22 and hence it may have a half-life less than ethyl benzene and xylene.

Table 4 Trend analysis for TPH and BTEX

Well no	TPH		BTEX	
	Trend of contaminants	Confidence level (%)	Trend of contaminants	Confidence level (%)
W19	Stable	95	Stable	95
B123	Stable	95	Stable	95
W25	Stable	95	Stable	95
W18	Decreasing	95	Stable	95
W22	Stable	95	Stable	95
B126	Decreasing	99.3	Decreasing	99.3
W17	Decreasing	95	Not available	Not available

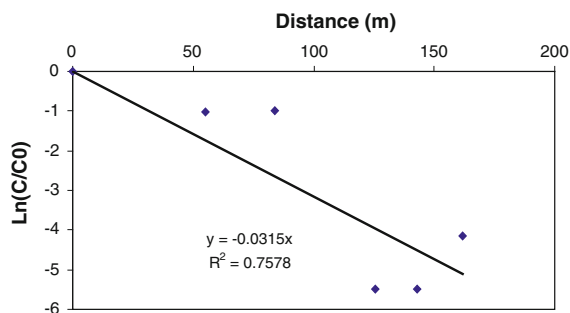


Fig. 5 Natural log of TPH concentration ratio of individual wells (C) to source wells (C_0) versus distance plot

The highest concentration of TPH in groundwater was $14,725 \mu\text{g l}^{-1}$. In order to meet the remediation goal, the time (t) required for decay of these dissolved contaminants as these move down gradient was calculated using the formula:

$$t = -\ln\left(\frac{C_{\text{goal}}}{C_{\text{start}}}\right)/k$$

where k is bulk attenuation rate constant and t is time, C_{goal} is concentration of the remediation goal and C_{start} is concentration at the starting point. Using C_{start} as $14,725 \mu\text{g l}^{-1}$ (highest TPH concentration in groundwater at FFA2), C_{goal} as $600 \mu\text{g l}^{-1}$ (DIL limit) and k as 1.216, t is estimated as 2.63 years. The distance L that the TPH will travel as they are decaying can be calculated by:

$$L = v \frac{t}{R}$$

where R is retardation factor and v is groundwater velocity. Using v as 36.5 m year^{-1} and R as 1 (the same as advection), the TPH will travel a distance of 96 m before the remediation goal is reached. Hence, the levels of TPH in groundwater should decline to below the drinking water guideline values before the

water reaches to the sensitive receptors which are 675 m away from the source.

From the plot and trend analysis it was found that for TPH, only W18, B126, and W17 show a decreasing trend, while other wells are stable. W17 did not have BTEX. BTEX at W18 did not show any decreasing trend. Point attenuation rate was calculated from the slope of time vs log concentration plot for TPH at well W18 and W17 (Table 6). Both W18 and W17 show a very weak correlation coefficient. The well W18 was slightly offset from the centreline of the plume and also showed evidence of point attenuation. This also indicates that at the periphery the rate of attenuation is high.

Secondary lines of evidence

Most dissolved petroleum hydrocarbons are biodegradable under aerobic conditions (Kao et al. 2005). The relative concentrations of electron acceptors (DO, nitrate and sulphate) and ferrous iron are useful geochemical indicators for biodegradation. Typically, the concentration of DO in ground water (wells W25, W123 and SS5) are generally quite low ($<1 \text{ mg l}^{-1}$ and lower than the background concentrations that ranged from 1.5 to 2 mg l^{-1}) especially within the contaminant plume with high concentrations of TPH and TEX. Analyses of geochemical parameters with TPH in groundwater demonstrates that no single parameter is solely responsible for the degradation of TPH. These results are however, supported by Buscheck et al. (1993) who found that the average DO concentrations in wells with hydrocarbon BTEX exceeding $1,000 \mu\text{g l}^{-1}$ was 0.56 mg l^{-1} compared to 1.43 mg l^{-1} in wells with non-detectable BTEX. For the part of the year when DO concentrations are not adequate for aerobic conditions, anaerobic degradation may be more important.

Table 5 Regression data for bulk attenuation rate for February 2004 and April 2005

Contaminants	Regression slope		R^2		Attenuation rate constant		Half Life (months)	
	2004	2005	2004	2005	2004	2005	2004	2005
BTEX	-0.0359	-0.0216	0.903	0.978	2.072	1.064	4.01	7.81
TPH	-0.024	-0.0207	0.988	0.997	1.216	1.008	6.83	8.25
Total xylene	-0.0374	-0.0212	0.847	0.985	2.192	1.039	3.79	8.00
Ethyl benzene	-0.022	-0.0213	0.872	0.884	1.089	1.045	7.63	7.95
Naphthalene	-0.0179	-0.0211	0.869	0.916	0.842	1.033	9.87	8.29

Table 6 Point attenuation rate data

Contaminants	Well no.	R^2	Point attenuation rate (per day)
TPH	B126	0.8133	0.004
TPH	W18	0.426	0.007
TPH	W17	0.203	0.002

Depletion of dissolved oxygen, nitrate and sulphate and elevated concentrations of ferrous iron and methane suggest that contaminant degradation is occurring through the microbially mediated processes of anaerobic degradation via iron reduction, nitrate reduction and sulfate reduction. Based on the stoichiometric relationship, electron acceptors in groundwater can degrade 13.96 mg l^{-1} of BTEX mass. The highest BTEX concentration in monitoring wells during February 2004 period was $842 \text{ } \mu\text{g l}^{-1}$. This is less than the total amount of electron acceptors available in the groundwater. This provides a preliminary comparison of available electron acceptors and BTEX compounds based upon the stoichiometric relationship of BTEX oxidation. This ratio may change depending on chemical and microbial conditions in groundwater. Vroblesky and Chapelle (1994) showed that the dominant terminal electron accepting processes can vary temporally and spatially. Table 3 clearly shows the temporal variation in some geochemical parameters in selected wells during 2006–2009 period. For e.g. one of the wells in source area, SS5 showed great temporal variation in its O_2 concentration which varied between 0.02 and 1.22 mg l^{-1} during 2006–2009 sampling period. This suggests the occurrence of microaerophilic conditions in the source area and not necessarily the absolute anaerobic conditions.

Microbiological analysis of groundwater from source area and the down gradient in the plume confirmed the presence of TPH degrading bacteria and their population density was related to the TPH content in the wells. Thus, the source area contained higher number of TPH degrading bacteria compared to the down gradient well that contained lower TPH content. The groundwater microcosm study showed the complete degradation of hydrocarbons in 60 days without any external nutrient supplementation compared to abiotic control that did not show TPH degradation. This clearly supports the observed loss of TPH in this aquifer is due to microbial degradation

rather than abiotic losses. Further, the presence of aerobic bacteria able to grow on gasoline as carbon source from the source area as demonstrated by the MPN counts and isolation of an aerobic bacterium *Burkholderia cepacia* able to utilise gasoline aerobically confirms the presence and activity of aerobic bacteria even in the source area where low oxygen concentrations were recorded. For e.g. Aburto et al. (2009) has enriched the typical aerobic bacteria able to utilize benzene from contaminated groundwaters with very low in situ O_2 conditions. Also, the compound specific carbon isotope analysis of xylene and naphthalene revealed a clear enrichment of heavy carbon ($\delta^{13}\text{C} \text{ } \text{‰}$) isotope along the flowpath in the plume which confirms the intrinsic biodegradation petroleum hydrocarbons in this contaminated aquifer. These results show that carbon isotope fractionation provides additional line of evidence for in situ biodegradation of hydrocarbons in contaminated aquifers and thus can be used as a valuable tool in evaluation of NA of petroleum hydrocarbon contaminants.

Conclusion

The multiple lines of evidence such as biogeochemical indicators, microbiological analysis, compound specific stable carbon isotope analysis and modelling demonstrated that NA of petroleum hydrocarbons is occurring in the aquifer. Assuming no retardation and no degradation the contaminated plume would have travelled a distance of 1,096 m (the best case) to 11,496 m (the worst case) in 30 years. However, the plume in its present form at this site is found to extend up to about 170 m from its source indicating attenuation is occurring. The Mann–Kendall analysis of TPH and BTEX indicate that the groundwater plume is stable. The contaminants in wells located along the centreline of the plume do not decrease with time since large amount of contaminant still present in the source area with continuous leaching into the groundwater. The amount of contaminant leaching is in equilibrium with hydrocarbon degradation with variation in seasonal fluctuation. The identified sensitive receptors (drinking water extraction wells) are 675 m away from the source and the stable plume boundary is 200 m away from the source. Hence, there is no immediate threat to the sensitive receptors. However, the plume at this site will shrink once the TPH in the

source zone is significantly reduced. Thus, this study clearly demonstrates the applicability of MNA as a cost effective remedial strategy for this site.

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