

The effectiveness of natural attenuation to remediate BTEX contamination in unconfined sand/gravel aquifers: An investigation of two sites

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Abstract

The effectiveness of natural attenuation as a remedial approach for managing contaminated groundwater caused by two leaking underground storage tanks was evaluated. The primary indicators used to evaluate attenuation included plume characteristics and migration. Statistical analyses of the plumes of dissolved benzene, toluene, ethylbenzene and xylenes (BTEX), using a Mann-Kendall test, indicated decreasing contaminant concentrations. Natural attenuation rates were estimated and changes in groundwater chemistry as a result of intrinsic bioremediation of the fuel hydrocarbons were evaluated. Analysis of the data indicates that the dissolved hydrocarbons have been attenuating naturally at both sites, limiting the migration of the dissolved benzene, toluene, ethylbenzene and xylenes.

Introduction

In January 1996, a review of stock reconciliation information indicated that up to 10,400 L of unleaded petrol may have been lost over a short time period from a former retail service station in Hororata, a small town about 60 km due west of Christchurch in the South Island of New Zealand.

Similarly, during September 1997, the loss of approximately 10,000 L of unleaded (96) motor spirit over 3 months was discovered at an underground storage tank at a former retail service station at Otorohanga in the North Island.

At both sites, following discovery of the leaks, the storage tanks were removed. At the same time all visibly contaminated soil and recoverable free product were also removed from the sites. A groundwater quality monitoring programme was begun immediately at both sites.

Site geology and hydrogeology

Both sites are located on unconsolidated alluvial deposits of Quaternary age: sandy-gravel at Hororata and gravely-sand at Otorohanga. These alluvial deposits form shallow unconfined aquifers. Based on the aquifer lithology and observed hydraulic gradients, groundwater flow velocities were estimated to be approximately 4m/day at Hororata and 2m/day at Otorohanga. These velocity estimates are based on the parameters in Table 1.

The depth to the water-table at Hororata varied seasonally. During the four-year monitoring period, groundwater levels fluctuated by more than two metres (1.1 m bgl in August 1996; 3.5 m bgl in January 1999). At Otorohanga the groundwater throughout the site remained between 3.0 and 4.5 m bgl for the duration of the study. Groundwater elevation contours for the two sites are given in Figures 1 and 2.

Table 1 – Parameters used to estimate the groundwater flow velocities at the two study sites

Site	Hydraulic conductivity (m/day)	Hydraulic gradient (m/m)	Effective porosity
Hororata	100	0.007	0.20
Otorohanga	150	0.003	0.25

Contamination conditions

Following the discovery of the loss of petroleum product, groundwater quality monitoring began at both sites: existing wells were identified, new wells were installed, and groundwater sample collection began. Samples were analysed for BTEX constituents (Benzene, Toluene, Ethylbenzene, and Xylenes) to quantify the level of contamination and compare the results with guideline values (New Zealand Ministry for the Environment, 1999).

Groundwater quality results and assessment

Hororata site

A total of 19 wells were monitored for separate-phase hydrocarbons, sampled, and analysed for BTEX constituents. Since January 1996, a hydrocarbon film has been observed only in the on-site monitoring wells.

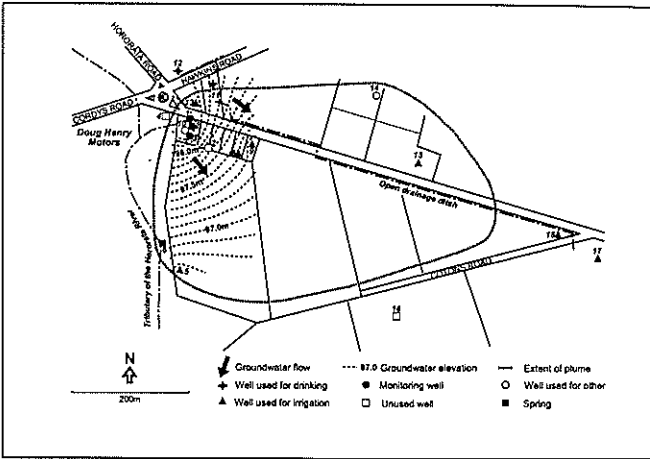


Figure 1 – Hororata site layout and groundwater elevation contours measured during June 1996.

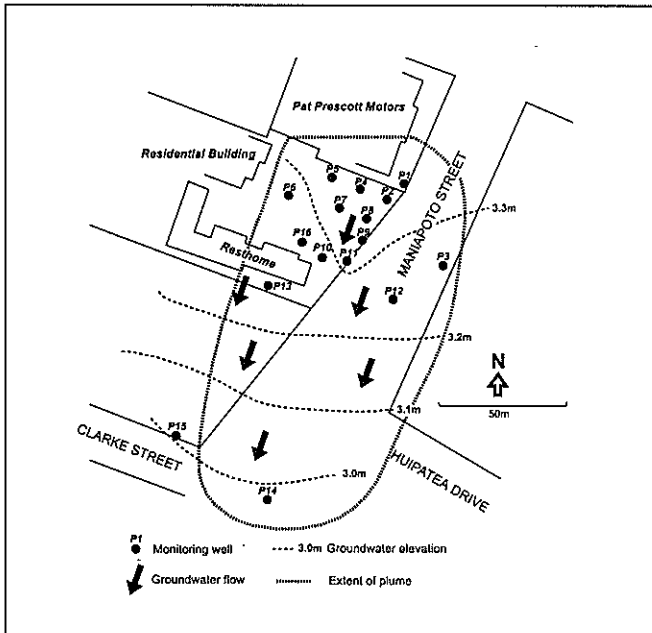


Figure 2 – Otorohanga site layout and groundwater elevation contours measured during October 1997.

Dissolved BTEX constituents were detected in both the on-site wells and those up to 450 m down-gradient. However, of the off-site wells, significant concentrations were detected only in samples collected from wells 7, 8, and 9, which are within 150 m of the source. The highest benzene concentrations reported were from wells 8 and 9, which are about 100 and 120 m respectively from the site of the former underground storage tank. Samples collected from these wells exceeded the irrigation guideline value for benzene (0.8 mg/L, New Zealand Ministry for the Environment, 1999), and in December 1996 the owners were provided with an alternate water supply to irrigate their vegetable garden.

Otorohanga site

The programme to assess groundwater quality at this site involved the staged installation of 16 monitoring wells. Groundwater contamination was found to extend southwards from the site boundary, with a layer of separate-phase hydrocarbons extending up to 30 m from the site of the old underground storage tank. Dissolved BTEX contamination was found to extend 140 m south of this contamination source.

Since January 1998 the thicknesses of separate-phase hydrocarbons within all monitoring wells have declined steadily and no product films been detected since September 1999. Dissolved-phase BTEX concentrations were highest at well P8, approximately 20 m from the source. Here they reached a maximum concentration of 226 mg/l of benzene in September 1997. Significant concentrations of BTEX were also detected in monitoring wells P7 and P11, approximately 30 and 40 m respectively from the source.

Because of the relatively limited impact of contamination on groundwater quality, and the decrease in contaminant concentration over time, active remediation measures were not considered necessary. It is believed that contaminant concentrations will continue to decrease over time through natural attenuation processes. To confirm this assumption, a long-term programme for monitoring groundwater quality was established.

Evaluation of natural attenuation

Natural attenuation results from naturally occurring processes that reduce the mass, toxicity, mobility, or bioavailability of contaminants. They include physical (dilution, dispersion and volatilisation), chemical (chemical (abiotic) reaction and sorption), and biological (biodegradation) processes. For petroleum hydrocarbons, biodegradation is the most important mechanism

for natural attenuation: it is the only natural process that actually reduces the petroleum constituent mass. It should be noted however that, particularly in sand and gravel aquifers, dispersion would reduce contaminant concentrations away from the source.

During biodegradation organic compounds (such as gasoline) are transformed to carbon dioxide, water, inorganic compounds, and cell protein; or to other organic compounds.

Biodegradation can occur under both aerobic and anaerobic conditions. Aerobic biodegradation of BTEX by naturally occurring micro-organisms is, however, more rapid and efficient than anaerobic biodegradation. Oxygen depletion in the subsurface is a characteristic of the biodegradation of petroleum hydrocarbons, as the rate of metabolic oxygen utilisation exceeds the natural capacity for oxygen replenishment. When oxygen is not available an alternative electron acceptor, such as nitrate, sulphate, ferric iron, or manganese, and a micro-organism capable of using the alternative electron acceptor, must be available for biodegradation to occur.

The core of a contaminant plume is typically under anaerobic conditions and only the margins are aerobic. Therefore, even though the rate of anaerobic biodegradation is much slower than aerobic biodegradation (often by a factor of ten to several hundred), anaerobic processes may still dominate the degradation of hydrocarbon contaminants.

A number of methods can be used to evaluate the effectiveness of natural attenuation. At these two sites, both primary and secondary indicators were used: these were based on either readily available, or easily obtainable, field data.

Primary indicators

The primary indicators used to evaluate natural attenuation included plume characteristics and migration. These were analysed using both visual and statistical methods.

To evaluate plume stability, the trends at specific monitoring wells were analysed by plotting contaminant concentration (for example Benzene, Tables 2 and 3) against time (Figs. 3 and 4). At both sites the dissolved BTEX concentrations appear to have decreased since sampling began, although there is considerable scatter in the data.

To identify any trends, the plume data were analysed statistically using the Mann-Kendall test. This is a non-parametric test that can be used to define the stability of a solute plume i.e., whether it is stable, diminishing, or expanding, based on the trends in contaminant concentration at individual wells. The results of the Mann-Kendall test (a diminishing plume) confirmed that contaminant concentrations were decreasing at both sites.

Table 2 – Benzene concentrations throughout the sampling period for wells 8 and 9 at Hororata

Sampling date	Time (days)	Well 8 Benzene (mg/l)	Well 9 Benzene (mg/l)
15 Apr 96	0	10	16
4 Jun 96	50	80	
21 Jun 96	67		
24 Jun 96	70	4.7	
12 Jul 96	88	4.8	6
15 Aug 96	122	1	1.1
13 Sep 96	150	0.15	0.14
21 Oct 96	188	0.53	0.51
14 Nov 96	212	0.66	0.86
28 Nov 96	226	0.71	1.1
16 Dec 96	244	0.59	1.6
10 Jan 97	269	1.37	2.4
6 Feb 97	296		
9 May 97	357	0.004	1.78
2 Jun 97	381		
19 Aug 97	459	1.11	1.57
17 Oct 97	518	0.59	0.967
7 Jan 98	600		0.638
8 Oct 98	874		0.432
23 Oct 98	889		
13 Dec 98	940		
14 Jan 99	972		0.0305
13 Oct 99	1244	0.003	0.004
17 Jan 00	1340	0.017	0.038

Table 3 – Benzene concentrations throughout the sampling period for wells P7, P8, P10, P11 and P14 at Otorohanga

Sampling Date	Time (days)	P7 Benzene (mg/l)	P8 Benzene (mg/l)	P9 Benzene (mg/l)	P10 Benzene (mg/l)	P11 Benzene (mg/l)
2 Oct 97	0	2.22	226	3.46	4.18	0.0141
13 Oct 97	11	26	64	15	34	
20 Oct 97	18	37.1	56.6	7.3	38.5	0.0004
5 Nov 97	33	12.1	67.4	9.79	32.3	
5 Jan 98	94	1.04	46.6	0.456	5.5	
19 Feb 98	138	0.6		0.0004	0.999	
13 May 98	221			4.1	4.36	
12 Aug 98	312			10.7	11.7	
19 Nov 98	409			8.9	1.69	
10 Feb 99	494			0.0492	1.18	
31 Mar 99	543	0.029	3.48			
30 Sep 99	726			0.0151	1.18	
13 Mar 00	891	0.0004	0.14	0.001	0.0149	0.0004

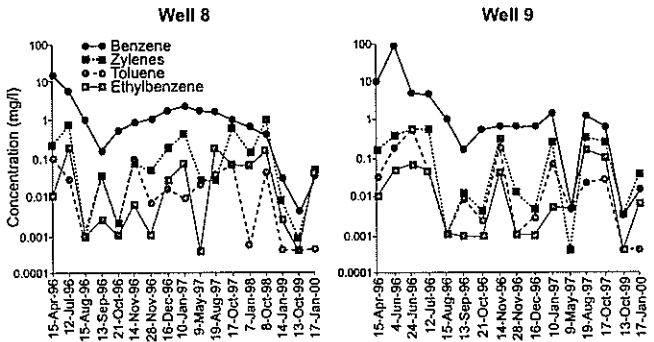


Figure 3 – Variation in contaminant concentration over the sampling period for selected monitoring wells at Hororata.

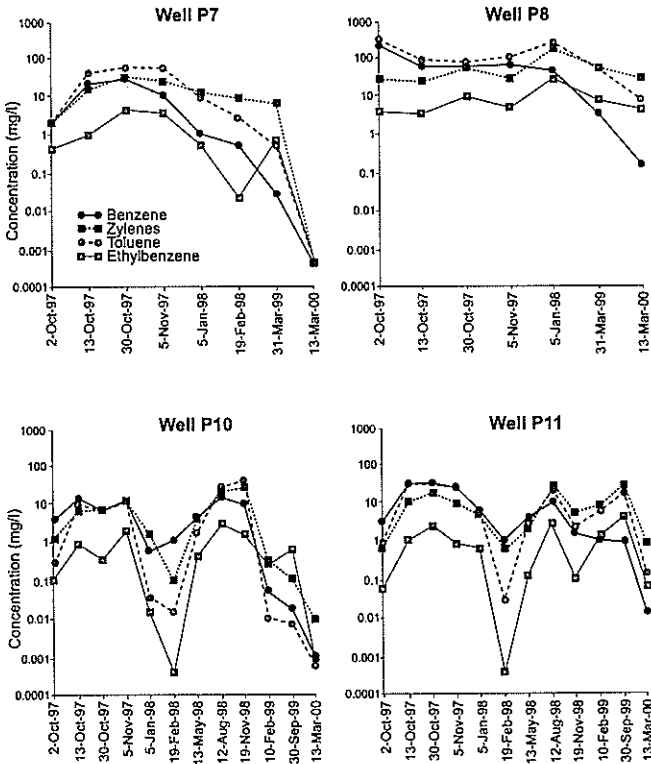


Figure 4 – Variation in contaminant concentration over the sampling period for selected monitoring wells at Otorohanga.

Using the contaminant concentrations measured in the various wells, the actual rate of plume migration was compared to that expected from the age of the spills and groundwater velocities at the sites. The equations used for this were:

$$\Delta L = (V * T) - L_a \quad (1)$$

$$V_p = L_a/T \quad (2)$$

$$NAF = V/V_p \quad (3)$$

- where: L_a - recorded plume edge (m)
 T - age of plume (days)
 V - groundwater seepage velocity (m/day)
 DL - plume migration reduction because of natural attenuation (m)
 V_p - estimated average plume migration velocity as a result of natural attenuation (m/day)
 NAF - a natural attenuation factor; represents the reduction of the actual plume migration velocity relative to the local groundwater velocity

This analysis showed that the actual plume migration rates have been reduced as a result of natural attenuation by factors of 10 and 12.5 at Hororata and Otorohanga respectively. This was assuming a conservative groundwater seepage velocity of 2.0 m/day. If the seepage velocity is greater than this, the effect of natural attenuation on retarding plume migration at these sites is even more significant.

Secondary indicators

Secondary indicators used to assess the effect of natural attenuation at these sites included a 'theoretical' estimate of natural attenuation rates, and an evaluation of the changes in groundwater chemistry caused by the intrinsic bioremediation of the fuel hydrocarbons.

Estimation of natural attenuation rates

There are several methods available to estimate 'theoretical' natural attenuation rates. The method used is usually based on the availability of monitoring data. If the plume is diminishing, a graph of contaminant concentration against time can be used to interpret whether natural attenuation is occurring. One or more wells containing measurable concentrations of BTEX are needed. These wells should be located along the line of the plume and not contain any hydrocarbon films. The data from each well is plotted as the log of contaminant concentration against time. The slope of the line is the first-order decay constant.

This technique was used to evaluate the natural attenuation rates at both sites, with the temporal variation of benzene concentration, (a constituent of major concern) being analysed. The results indicated first-order kinetics for benzene attenuation at both sites:

$$k_1 = -\ln [C_t / C_0] / t \quad (4)$$

where: k_1 - the first order rate constant,
 C_0 - the concentration at time zero in a well, and
 C_t - the concentration at time t at the same well.

Plots of $-\ln[C_t/C_0]$ as a function of time, for selected monitoring wells at the two sites, are presented in Figures 5 and 6.

The first order rate constant is often expressed in terms of a half-life for the chemical where:

$$t_{1/2} = 0.693/k_1 \quad (5)$$

The calculated values of the first-order rate constant (k_1) and half-life ($t_{1/2}$) for the two sites are summarised in Table 4.

Table 4 - Calculated values of the first-order rate constant (k_1) and half-life ($t_{1/2}$) for the two sites

Well	Hororata		Otorohanga			
	8	9	P7	P8	P10	P11
First-order rate constant k_1 (1/day)	0.0047	0.0045	0.0097	0.0083	0.0091	0.0063
Half life for the chemical (days)	146	153	72	84	76	110

A number of laboratory and field studies have reported rates for aerobic and anaerobic biodegradation of BTEX. Rifai *et al.* (1995) indicate total rates (aerobic and anaerobic) from field and microcosm studies ranging between 0.0002 and 0.21 l/day. The values determined in this study are consistent with their data.

The time required for a specific contaminant concentration to reach a treatment objective level was also estimated:

$$t = -\ln (C_t/C_p) / k_1 \quad (6)$$

where: C_t - the concentration at, or below, the target level (0.005 mg/l), and
 C_p - the concentration at present time.

The time required for benzene concentrations to reach target levels, estimated using Equation (6), are summarised in Table 5.

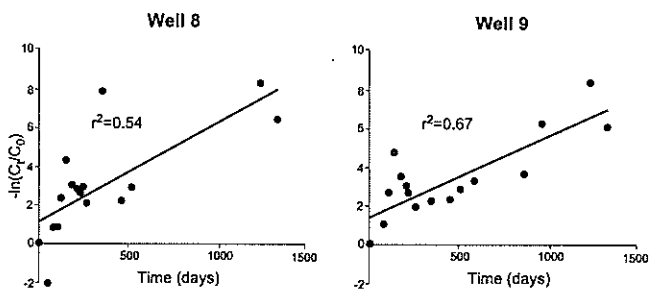


Figure 5 – Change in benzene concentration through time at monitoring wells 8 and 9 at Hororata, using first-order kinetics.

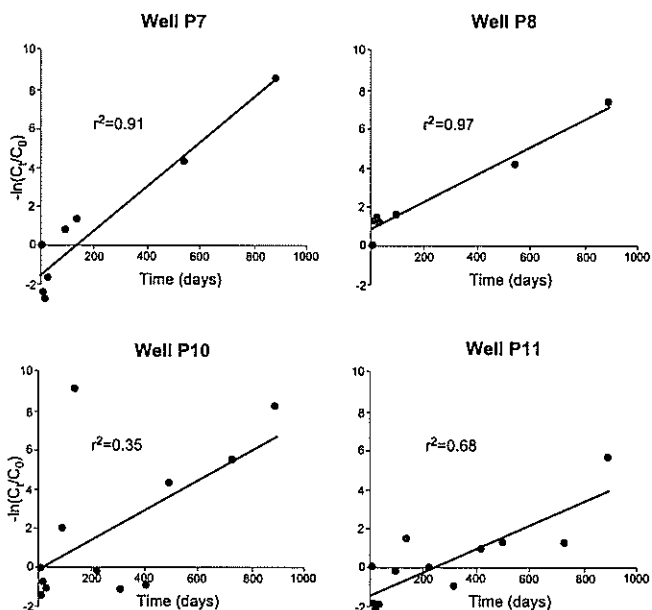


Figure 6 – Change in benzene concentration through time at monitoring wells P7, P8, P10, and P11 at Otorohanga, using first-order kinetics.

Table 5 – Estimated time required (based on approximated average conditions) for benzene concentrations to reach target levels

Well	Hororata		Otorohanga			
	8	9	P7	P8	P10	P11
Estimated time (days)	262	450	-	402	-	173
Reference to sampling event	January 2000			March 2000		

NB: (-) indicates that the criterion was already met

Chemical indicators of biodegradation

Chemical indicators specific to biodegradation were not measured as part of the regular monitoring programme at the two sites. However, to evaluate changes in groundwater chemistry, electron acceptors and metabolic by-products in the groundwater were measured at selected monitoring wells.

In situ analysis of groundwater at both sites indicated significant levels of dissolved oxygen throughout the aquifer. This implies that aerobic respiration probably accounts for the majority of the reduction in the mass of BTEX. However, the variability in nitrate, sulphate and dissolved iron concentrations, both inside and outside the contaminant plume, suggest that natural attenuation is also occurring through anaerobic processes (Table 6). In addition, contaminant dispersion through a sand/gravel aquifer is also likely to contribute to some of the observed reduction in contaminant concentration at the sites.

Table 6 - Electron acceptor concentrations in the groundwater at various wells within the study sites (see Figures 1 and 2 for the location of the wells within plumes). *m* – middle of plume, *e* - edge of plume)

Well	Dissolved oxygen (mg/l)	Nitrate-N (mg/l)	Nitrite-N (mg/l)	Dissolved Iron (mg/l)	Sulfate (mg/l)
2 <i>m</i>	4.2	0.85	0.1	0.012	2
8 <i>m</i>	2.7	0.98	<0.02	0.029	9
9 <i>m</i>	1.9	2.39	<0.02	0.013	15
11 <i>e</i>	-	5.27	<0.02	<0.002	10
13 <i>e</i>	4.0	6.38	<0.02	<0.002	9
P7 <i>m</i>	2.03	4.03	0.009	<0.01	23
P8 <i>m</i>	0.6	<0.002	0.003	0.11	2
P10 <i>m</i>	2.24	0.069	0.009	0.01	10
P11 <i>m</i>	1.29	0.178	0.017	<0.01	13
P14 <i>e</i>	0.31	<0.002	0.350	29.7	3

Conclusions

Despite some uncertainties, dissolved hydrocarbons appear to be attenuating naturally at both sites, limiting the migration of the dissolved BTEX plumes. Natural attenuation therefore appears to be an appropriate remedial option, given the assessed level of risk.

Although several bio-parameters could be used to demonstrate that biodegradation is occurring at the sites, trends in the concentration of the BTEX compounds themselves provide a very good indicator of the effectiveness of natural attenuation. The Mann-Kendall test was useful in analysing plume stability, particularly for data with considerable scatter.

Although natural attenuation has been shown to be an appropriate option for managing these two sites, groundwater quality monitoring should be continued. Future monitoring should be aimed at better understanding and characterising the intrinsic biodegradation processes. This, coupled with a risk assessment demonstrating that the attenuating mechanisms are adequately protecting human health and the environment, should provide a sound basis to negotiate an agreement with the regulators as to when to terminate remediation strategies.

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