

NATURAL ATTENUATION OF CHLORINATED ETHENES IN GROUNDWATER: KEY FINDINGS FROM 8 YEARS OF MONITORING

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Abstract

Chlorinated solvents are present in groundwater within basalt, underlying an Auckland industrial site. Key contaminants of concern include trichloroethylene and vinyl chloride, which potentially present a human health risk due to volatilisation into indoor air or confined spaces. Contaminant concentrations and hydrogeochemical parameters in groundwater at and around the site have been monitored in 51 wells during an 8 year period. The monitoring strategy has been continually updated to focus on key areas and potential risks, as understanding of the system has developed. A polyethylene liner and gas venting system was installed under a building in a key risk area adjacent to the site. Key findings of the groundwater monitoring include that naturally occurring dechlorination bacteria are present, anaerobic conditions exist, and biodegradation of chlorinated ethenes is likely to be occurring.

Introduction

An industrial site in Auckland has been used as a hazardous waste treatment site since 1966. The western part of the site had a number of unlined treatment ponds, as well as unlined areas which were used for drying out sludge from the ponds, prior to disposal. The eastern side of the site was historically used as an ethanol and organic peroxide storage/dispatch area and was partly unsealed prior to 1980. Due to historic operations at the site, contaminants from the former waste treatment areas have migrated to the underlying soil and groundwater. Over the last 15 years, the site has been progressively remediated to minimise the potential for surface runoff to infiltrate through the ground and potentially mobilise contaminants into groundwater.

In November 1999, a detailed investigation programme was initiated at the site. The initial aim of the environmental investigations was to identify the extent of contamination on the site, the nature of the groundwater quality leaving the site, and whether there were any potential off-site effects associated with the discharge. Once a general understanding of the nature of the discharge from the site was established, the subsequent investigations have focussed on monitoring potential off-site effects in order to identify the need for mitigation measures, and gather evidence to establish whether natural attenuation of the contaminants of concern is occurring.

Key contaminants of concern include trichloroethylene and vinyl chloride, which potentially present a human health risk due to volatilisation into indoor air or confined spaces. Numerous other laboratory and field studies undertaken over the last decade have demonstrated that natural attenuation, or biodegradation, of these contaminants can occur.

The purpose of this paper is to present an overview of some key findings of the groundwater monitoring at the site. These results provide evidence that natural attenuation of the contaminants of concern is occurring, and suggest that Monitored Natural Attenuation is a viable remediation strategy for the site.

Natural Attenuation

The United States Environmental Protection Agency (USEPA) (1999) defines natural attenuation as: *“Reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by more active methods. The natural attenuation processes that are at work in such a remediation approach include a variety of physical, chemical, and biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. These in situ processes include biodegradation; dispersion; dilution; sorption; volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants.”*

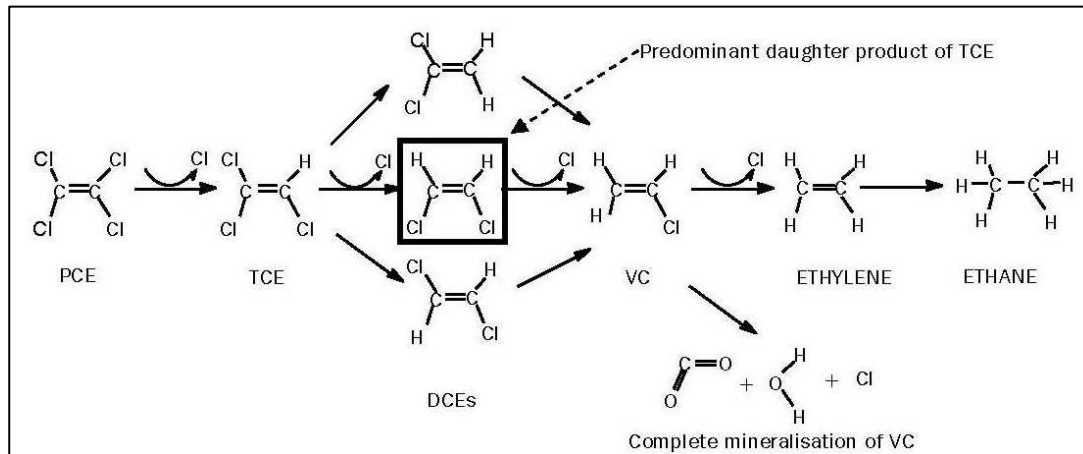
Natural attenuation as a remediation strategy is considered to have several advantages over engineered technologies, as well as some limitations. Key advantages include that the strategy is non-intrusive and allows ongoing use of the site, is less costly than other remediation strategies, and that other engineered remediation activities can pose greater risk to potential receptors if contaminants are released (Wiedemeier *et al.* 1996). Key limitations include the timeframes required, potential for production of intermediate by-products (e.g. vinyl chloride) with higher toxicity than original contaminant, and the ongoing influence on the process of both natural and human influenced changes in site conditions (Wiedemeier *et al.* 1996).

Natural Attenuation of Chlorinated Solvents

In 1998, the USEPA introduced a Technical Protocol for evaluating the natural attenuation of chlorinated solvents in groundwater (USEPA 1998). The Protocol contains an overview of the process of natural attenuation, or biodegradation, of chlorinated solvents, which commonly occurs through the process of reductive dechlorination. Reductive dechlorination is the successive removal of chlorine atoms from the parent compounds (TCE and PCE) leading to formation of daughter compounds (1, 1-DCE, 1, 2-DCE and VC etc) under anaerobic conditions (see Figure 1). This dechlorination is facilitated by micro-organisms and produces an accumulation of daughter products and an increase in concentration of chloride ions.

In this case, the chlorinated solvent is used as an electron acceptor, and not as a carbon source for the micro-organisms. An additional source of carbon in the aquifer is required for this mechanism to occur. If the soil and groundwater contain an adequate supply of organic electron donors, the reductive dechlorination can proceed until all the chlorine atoms are removed and the parent compounds (TCE and PCE) are dechlorinated completely via DCE and VC to ethylene gas, a harmless end-product.

Figure 1: Reductive Dehalogenation of Chlorinated Ethenes (from USEPA 1998).



The Protocol refers to the following three key lines of evidence required to demonstrate that natural attenuation of chlorinated solvents at a site is occurring (USEPA 1998):

1. Historical groundwater and/or soil chemistry data demonstrate a clear and meaningful trend of decreasing contaminant mass and/or concentration over time at appropriate monitoring or sampling points.
2. Hydrogeological and geochemical data that can be used to demonstrate indirectly the type(s) of natural attenuation processes active at the site, and the rate at which such processes will reduce contaminant concentrations to required levels.
3. Data from field or microcosm studies (conducted in or with actual contaminated site media) which directly demonstrate the occurrence of a particular natural attenuation process at the site and its ability to degrade the contaminants of concern.

The biodegradation of chlorinated solvents results in measurable changes in groundwater chemistry, and by measuring these changes the extent of natural attenuation occurring at a site can be evaluated (USEPA 1998). The most relevant parameters for the biodegradation of chlorinated solvents include; dissolved oxygen (DO), oxidation-reduction potential (ORP), pH, nitrate, sulphate, sulphide, alkalinity, free carbon dioxide, chloride, dissolved iron, manganese and methane. Anaerobic conditions and reductive dechlorination in groundwater are generally indicated by the lack of DO, decreased ORP, decreased nitrate and sulphate concentrations, increased dissolved manganese and iron concentrations and increased carbon dioxide and methane production.

In addition to reductive dechlorination, the daughter compounds of reductive dechlorination (e.g. 1, 1-DCE and VC) can be degraded by direct oxidation, while chlorinated ethenes can also be degraded by metabolic processes.

The USEPA (1998) Technical Protocol outlines a scoring system that can be used as a test to assess the likelihood that biodegradation is occurring; the method relies on the fact that biodegradation will cause predictable changes in ground water chemistry as noted above. Scoring values are given to the results obtained for different hydrogeochemical parameters (see USEPA 1998), and the total score obtained relates to the amount of evidence for reductive dechlorination (see Table 1).

Table 1. Interpretation of Points Awarded - Preliminary Screening for Anaerobic Biodegradation Processes (USEPA 1998).

Score	Interpretation
0 to 5	Inadequate evidence for anaerobic biodegradation ¹ of chlorinated organics
6 to 14	Limited evidence for anaerobic biodegradation ¹ of chlorinated organics
15 to 20	Adequate evidence for anaerobic biodegradation ¹ of chlorinated organics
> 20	Strong evidence for anaerobic biodegradation ¹ of chlorinated organics
<i>Notes: 1. Reductive dechlorination.</i>	

Sampling Strategy for the Auckland Industrial Site

Groundwater level monitoring has been undertaken since 2000, a minimum of four times a year, at selected monitoring wells around the site and surrounding area. Groundwater quality monitoring has been carried out on a 6 monthly basis since 2000 at monitoring wells within and around the site. Monitoring has been carried out at a total of 51 wells at various stages throughout the investigations. There has been a progressive reduction over time in the number of wells monitored as the results have been assessed and key monitoring locations have been identified. Currently 18 wells are monitored during the six monthly monitoring rounds. Microbiological testing has also been undertaken to determine whether dechlorination bacteria are present in the groundwater at the site. Dechlorination bacteria are required for natural attenuation of the chlorinated solvents to occur. The samples were sent to DuPont Co Analytical Laboratories in the United States for analysis.

It is important to note that various other risk-based investigations have been undertaken at and around the site (e.g. underground services air sampling, soil gas surveys, stormwater and surface water sampling etc.); however these are not discussed further in this paper.

Site Hydrogeology

The site has some unique hydrogeological features which have made characterisation of the site a reasonably complex process. The site is located on the edge of a basalt lava flow area, which is surrounded by areas of construction fill and underlain by Puketoka Formation sediments. Much of the land around the site has been quarried to extract basalt over the last 15 – 20 years, and back filled with engineered fill suitable for light industrial development. The geology encountered in the drillholes within the site typically comprised between 0.5 and 3.6m of engineered fill (clayey silt with some gravel, and basalt boulders in some areas) underlain by between 2.4 and 6.6m of basalt which is in turn underlain by clay/silt sediments.

The main features established for the base of the basalt contours at the site are:

- Broad pre-basalt valleys trending north and south away from the middle point of the site.
- A pre-basalt valley trending south-west away from the south-west corner of the site.

Groundwater flow directions in basalt beneath the site generally coincide with these valleys down which the basalt lava flowed, namely:

- South-west flow;

- Northerly flow; and
- Southerly flow.

General north-easterly flow also occurs.

Groundwater levels are typically highest in July to September and lowest in January to March. March and September have been identified as the key sampling times as these months coincide approximately with annual low and high groundwater levels respectively. Groundwater levels at the site are typically below the base of the fill, except for rare occurrences.

The following discussion focuses on results for the south-western valley groundwater flow path.

Groundwater Quality Monitoring – Results and Discussion

Chlorinated ethenes and ethanes (CEEs), which are expected to be related to chlorinated solvents, are the most commonly detected contaminants in the groundwater samples. Some of the more volatile of these compounds have been selected as the main contaminants of interest either because of their potential adverse effects on human health, or because they help to characterise the contaminant plumes. The main contaminants of concern at the site are considered to be chlorinated solvents and their daughter products (e.g. PCE, TCE, 1, 1-DCE, 1, 2-DCA and VC), due to their potential to volatilise into indoor air or confined spaces and pose a potential health risk. These contaminants are generally present at low levels in groundwater underlying the site and near to the site boundary, and generally decrease to non-detect levels further off-site. Other contaminants present at the site include hydrocarbons.

Trends in Contaminant Concentrations

Groundwater in the south-western area of the site has typically contained the most elevated levels of PCE/TCE. The long-term monitoring demonstrates a rapid reduction in contaminant concentrations with distance away from the site. The concentrations of CEEs in key on site monitoring wells, while oscillating (generally thought to be related to seasonal groundwater levels), show a generally decreasing trend over the monitoring period (see Figure 2 for examples of time series plots of contaminant levels).

USEPA (1998) Scoring

Figure 3 is a time series plot which shows the scores obtained at the monitoring wells in the south-western valley flow path. The hydrogeochemistry supports the understanding that conditions in key parts of the groundwater system at the site are conducive to reductive dechlorination of the chlorinated solvents and suggest that this degradation is taking place. The graph shows that the level of evidence is consistently "strong" or "adequate" for natural attenuation at these wells.

Figure 2. Time Series Plots of Key Chlorinated Ethenes at Two Monitoring Wells.

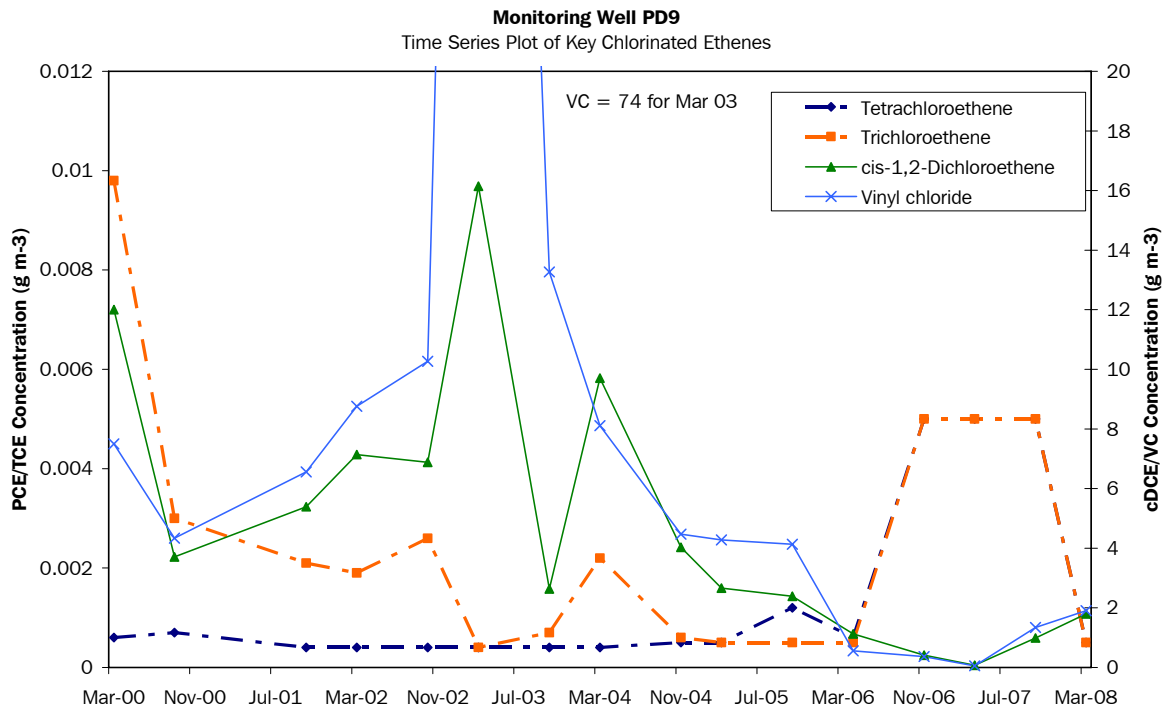
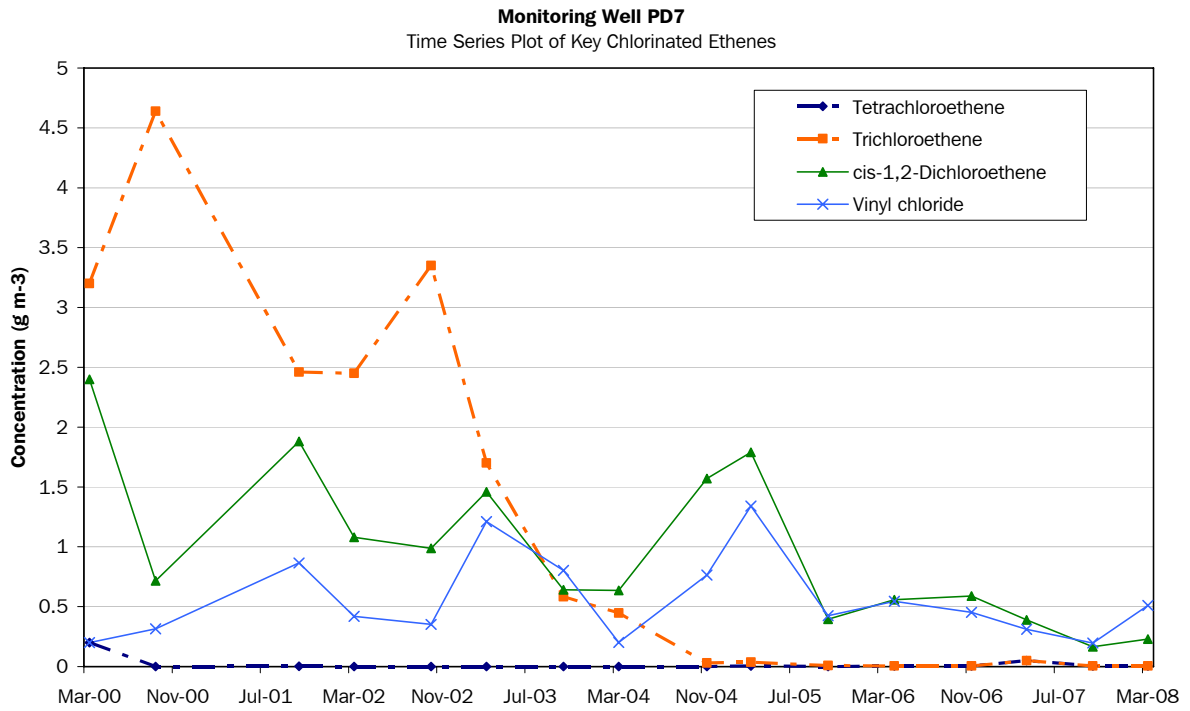
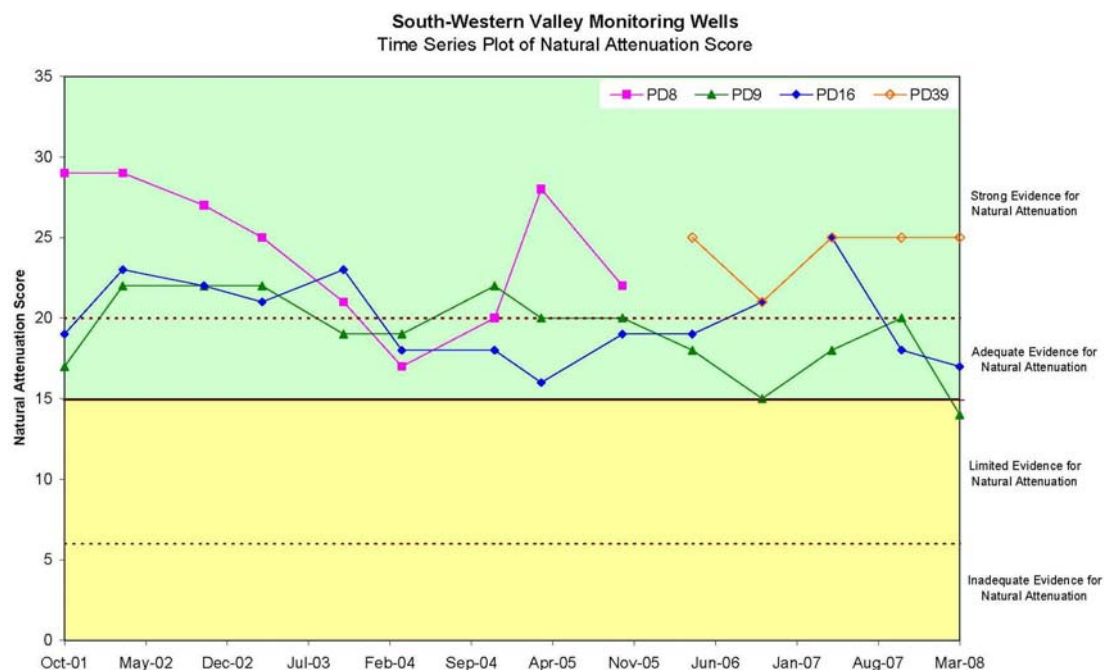


Figure 3. Time Series Plot of Natural Attenuation Score for South-Western Valley.



The hydrogeochemistry at these wells indicates moderately to strongly reducing and anaerobic conditions conducive to the degradation of PCE/TCE. This degradation is supported by the presence of daughter products (DCE and VC) and elevated concentrations of the degradation break-down products methane and chloride.

At least part of the source of organic carbon currently facilitating biodegradation is likely to be petroleum products. Should the organic carbon source diminish or cease (or be used up), degradation of TCE to DCE to VC would be retarded or possibly stop. This could result in “breakthrough” of the plume which causes any plumes of mother products (such as TCE and DCE) to spread further from the site than they currently do.

There is the potential for VC concentrations to increase in the groundwater away from the site as DCE is biodegraded. This potential exists where DCE is present and anaerobic conditions persist in the aquifer for some distance away from the site and there is insufficient carbon to maintain anaerobic biodegradation. Aerobic conditions are required to degrade VC to low levels in the groundwater. It seems unlikely that aerobic conditions would develop in the aquifer close to the site. This is because the presence of compacted fill above the groundwater table is likely to limit entry of oxygen or oxygenated water into the groundwater. Aerobic conditions may develop where the basalt has not been quarried and will develop in areas where the groundwater discharges to surface water however. VC concentrations away from the site are not currently considered to present a human health risk, but will obviously need to be subject to ongoing monitoring and risk assessment.

Specific computer based risk assessment modelling was undertaken in 2001 to determine whether there would be any health risk to future workers within a proposed new building to the southwest of the site. The modelling identified the potential for contaminants (specifically VC) to volatilise off the plume and enter the building. As a result of the modelling, mitigation works were carried out in conjunction with the construction of the building. A high density polyethylene liner and active gas venting system was placed beneath the new part of the warehouse. The system is designed to prevent plume-related gases, and particularly VC, from entering the building. Since the vapour extraction system was installed in 2001, the effectiveness of the system has been monitored via gas sampling ports. Monitoring results within the building have consistently returned non-detectable levels of VC (<0.1 ppm).

Dechlorination Bacteria

Two types of dechlorination bacteria were present in the groundwater samples from the site - *Dehalococcoides ethenogenes* and a newly isolated species at that time tentatively referred to as *Dehalococcoides alameda*. Other laboratory and field studies have confirmed that these types of bacteria are able to completely reduce chlorinated solvents, from PCE or TCE to ethane, via the intermediates cis-dichloroethane and VC (Edwin Hendrickson, pers. comm.; Hendrickson *et al.* 2002). These results provide another line of evidence that chlorinated solvents related to the site are undergoing reductive dechlorination.

Based on the three lines of evidence indicated by USEPA (1998), the fact that an engineered mitigation measure has been installed at a key risk area adjacent to the site, and the results of a full Risk Assessment (not discussed here), Monitored Natural Attenuation is considered to be an appropriate remediation strategy for the site. A long term Monitoring and Management Plan is currently being developed in conjunction with the Auckland Regional Council. This plan includes contingency remediation options should evidence for natural attenuation decrease.

Conclusions

The environmental investigations undertaken at the Auckland industrial site have provided the following evidence to demonstrate that reductive dechlorination is occurring in groundwater at and around the site:

1. Groundwater monitoring has been undertaken, providing 8 years of historic data on groundwater quality and levels. This has identified the main groundwater flows as being to the south-west, north and south of the site. Groundwater in the south-western area of the site has typically contained the most elevated levels of PCE/TCE. Monitoring of groundwater quality indicates decreased concentrations in TCE and DCE away from the site, and the formation of daughter products (1, 1-DCE, VC) away from the site.
2. Geochemical data has been collected during each monitoring round. The hydrogeochemistry supports the understanding that conditions in key parts of the groundwater system at the site are conducive to reductive dechlorination of the chlorinated solvents and suggest that this degradation is taking place. The natural attenuation scores (USEPA 1998) show that the level of evidence is consistently "strong" or "adequate" for natural attenuation at the vast majority of monitoring wells.
3. Microbiological testing undertaken of groundwater from the site has confirmed that reductive dechlorination bacteria are present.

Overall, these factors confirm that the conditions of the aquifer are consistent with the reductive dechlorination indicators and therefore indicate that natural attenuation of the contaminants of concern is occurring at the site. Based on the three lines of evidence indicated by USEPA (1998), the fact that an engineered mitigation measure has been installed at a key risk area adjacent to the site, and the results of a full Risk Assessment (not discussed here), Monitored Natural Attenuation is considered to be an appropriate remediation strategy for the site. A long term Monitoring and Management Plan is currently being developed in conjunction with the Auckland Regional Council. This plan includes contingency remediation options should evidence for natural attenuation decrease.

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