

Selecting the most cost-effective remedial technique for large chlorinated solvent plumes

Drs. Ben Keet FRSC, MRSNZ and Royston Gillett M.Sc. (biochem), **Geo & Hydro – K8 Ltd**
correspondence: ben@benkeet.com

ABSTRACT

Laboratory and field-scale pilot testing has been conducted to select the most cost-effective remedial technology to remediate 2 large chlorinated solvent plumes on an industrial property. In area 2 the objective was to remove 500 kg of chlorinated solvents present under a factory hall. The contamination was caused by leakage from a carpet recycling facility operated during the 60 – 70-ies. The groundwater plume containing the contaminants has an area of 25,000m², maximum depth of 12 meters and a volume of 200,000m³. Over the 40 years the solvents have been converted by natural dechlorination. Most of the original solvents, Perchloroethylene (PER) and Trichloroethylene (TRI), have been naturally converted into cis-1,2-Dichloroethylene (CIS) and Vinyl chloride (VC), which are far more toxic than the original solvents. In area 4 the plume is more recent and consist mainly out of Perchloroethylene (PER) and Trichloroethylene (TRI). Perched DNAPL is expected to be present on silt and peat lenses. Due to the multiple entry points of the contaminant the plume is extremely elongated.

In area 2 the remediation is urgent as the plume is migrating past the property boundary, while the factory workers have to be protected from the gaseous and highly toxic Vinyl chloride (VC). In area 4 the focus is more on the unidentified mass of DNAPL which will influence any remedial measure except excavation.

Eight remedial technologies are evaluated: full remediation (excavate and extraction of groundwater), hydraulic control (pump and treat or placement of containment wall), and 5 variations of in-situ remediation (air stripping with vapour extraction, chemical oxidation, pump and treat relying on natural attenuation, diffusion sparging micro sparging and bio-augmentation (bacteria seeding)).

This paper focuses on the effectiveness of the remedial alternatives, their relative costs and the uncertainties. Laboratory and field-scale pilot testing has been carried out and the execution and results will be presented. Full scale pilot implementation of the selected technique will be shown and design complications discussed.

Key words

In-situ remediation, field scale, pilot test, chlorinated solvents, Perchloroethylene (PER), Trichloroethylene (TRI), cis-1,2-Dichloroethylene (CIS), Vinyl chloride (VC), air stripping, vapour extraction, chemical oxidation, pump and treat relying on natural attenuation, diffusion sparging micro sparging and bio-augmentation (bacteria seeding).

INTRODUCTION

A carpet tile manufacturing plant initiated an environmental responsibility project in the 1960-ies, recycling old carpet tiles. In this process the bitumen backing was dissolved using Perchloroethylene (PCE) and the bitumen and fibres recovered for re-use.

However some of the PCE leaked into the ground and made its way to groundwater in area 2. It migrated down to about 15 m bgl where it accumulated on a thick clay layer. The presence of silt and peat lenses caused the downward migration to disperse and contamination has resulted in a large area.

Groundwater flow is very slow and often stagnant during summer. The presence of residual bitumen and some other solvents created anaerobic conditions favourable for natural reductive dechlorination. As a result all PCE degraded into Trichloroethylene (TCE) and further into cis-1,2-Dichloroethylene (CIS) and Vinyl chloride (VC) following:



Dichloroethene (CIS and Trans) : 1,1-DCE + cis-1,2-DCE + trans-1,2-DCE: $\text{C}_2\text{H}_2\text{Cl}_2$
 (on this site the Cis DCE makes up over 95 % of the DCE formed)



The subsequent breakdown of VC following:



progresses very slow under strict anaerobic conditions. Therefore we see a strong accumulation of VC and its precursor CIS on this site. Under aerobic conditions these degradation steps would progress much faster.

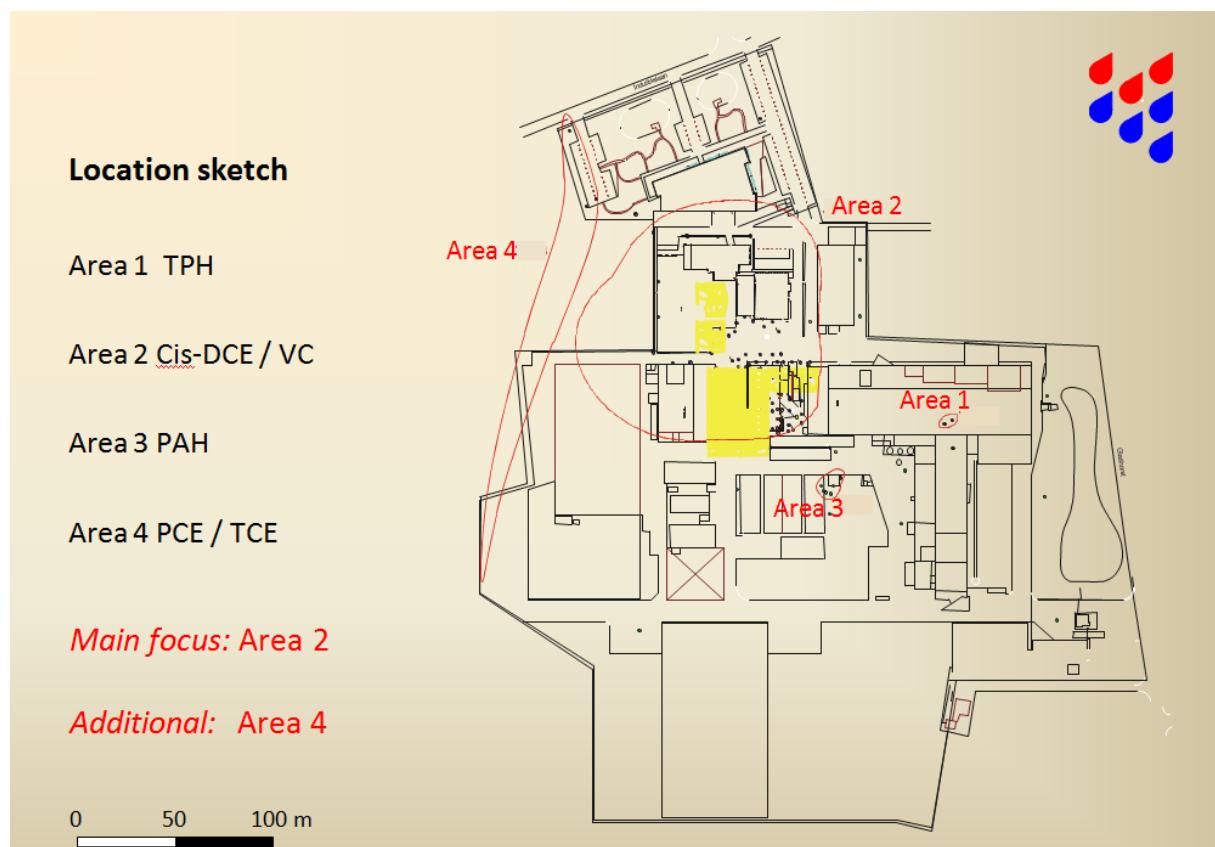
More recently (late 1980-ies) a dry cleaning facility was operated on site using PCE and an activated carbon steam regeneration unit. The condensed water was discharged to sewer. For some time there has been some carry-over of PCE into the sewer. The PCE travels through the sewer under the

water and accumulates in depressions like in the joints. Here it dissolved many of the rubber connection rings and leaked out creating an array of multiple leak points (area 4 below).

Site layout

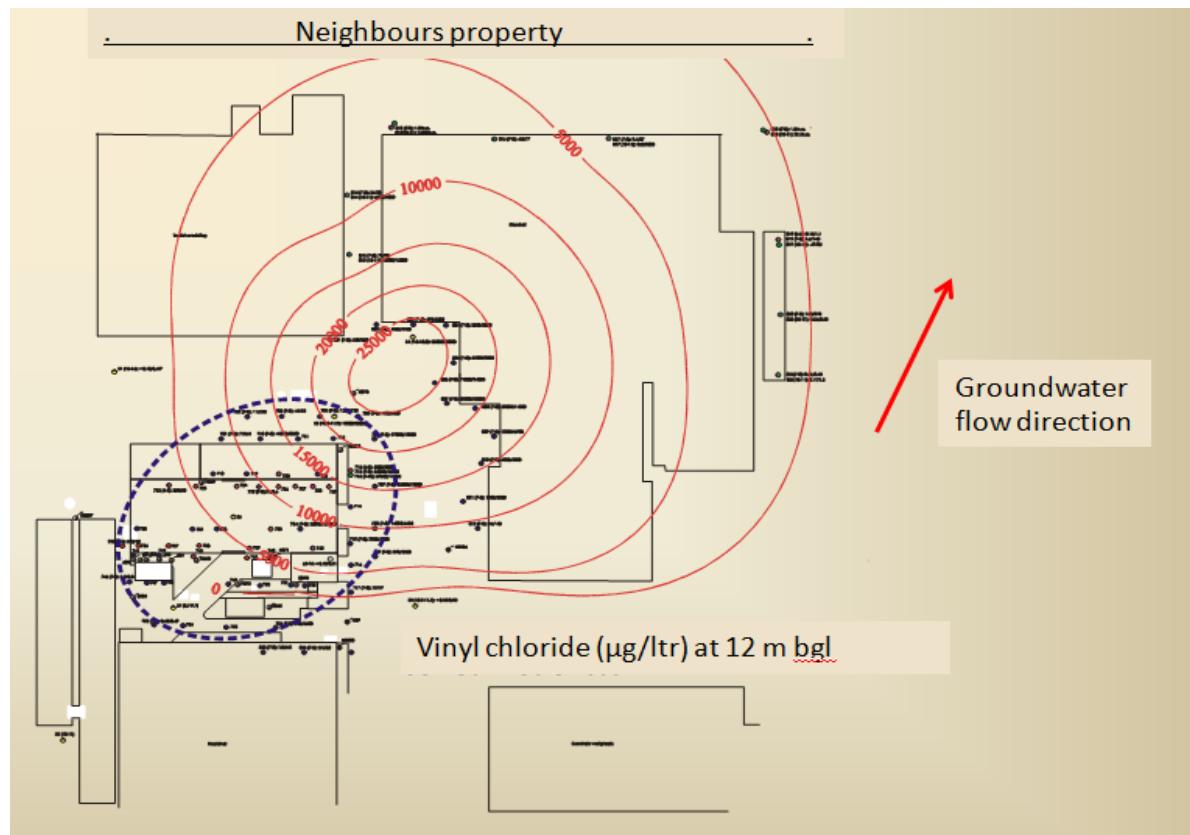
The approximately 14 ha site is located in an industrial area, surrounded by factory buildings and some grass areas (undeveloped lots).

For this paper we focus on the 2 chlorinated solvent contaminated areas: 2 and 4. The main focus will be area 2 with the residual contamination with CIS and VC.

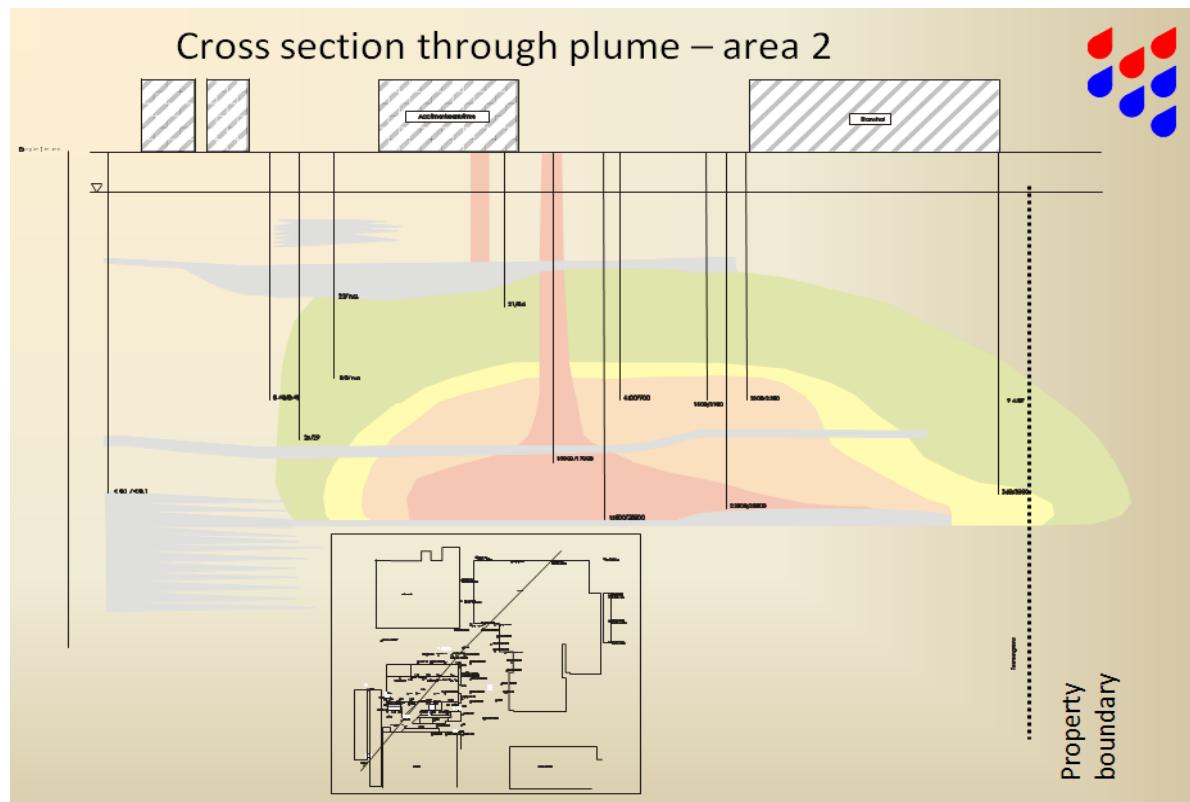


Contamination is mainly present in groundwater. Only traces of adsorbed residual PCE and TCE have been found. Contaminant area and mass in groundwater in area 2 is given in the table below.

Contaminant Mass	Plume area	Plume Volume	Max concentration	Times over guideline level
500 kg	25,000 m ²	200,000 m ³	CIS 4,800 µg/ltr	240
			VC 21,000 µg/ltr	4200



Concentration contours for Vinyl chloride in groundwater at 12 m bgl. For some months of the year there is a minor groundwater flow to the north northeast. The area with the dashed line indicates the source area where traces of adsorbed residual PCE and TCE are encountered in a few of the many boreholes.



Main Remediation Options

Sheet pile and Excavate Costs approx. \$NZ 70,000,000

- Fast remediation
- Requires demolition and rebuild of buildings
- Requires landfill space and water treatment installation
- Cost basis is \$ 300.-/m³ wet soil



Intensive in situ: Costs approx. \$NZ 30,000,000

- Remediation period 2 - 3 years
- Mainly physical removal (air stripping & SVE, see picture below)
- Requires provision of safety measures against intrusion of VC into the factory
- Potential adsorbed fraction gives uncertainty



Extensive in situ: Costs approx. \$NZ 6,000,000

- Remediation period 10 years (rough estimate, technology dependent)
- Apply new, partially proven technology

Crossing off the options

Selecting a remedial technique often follows the ‘negative choice’ method. This involves focussing on the negatives like cost and risks.

For this project de-selected were:

- Sheet-pile and Excavation cost too high
 - Intensive in-situ cost too high and risk VC escape too high

A desk study was carried out considering other techniques. The following were not chosen for the reasons listed:

- Oxidation (Fenton's, Ozone, H₂O₂) too much organic matter in soil (peat lenses)
 - Thermal risk VC escape too high, CIS condensation problems expected due to incomplete access
 - Bio-augmentation hardly any PCE/TCE left – main limiting factor is lack of oxygen

The desk study, complemented by several in-depth discussions with the site owners, their overseas management and the regional authority lead to the following approach:

To control and possibly pull back the contaminant plume in the neighbouring property was given a high priority. A temporary hydraulic control (pump and treat) was seen as cost effective given the low adsorption rates of CIS and VC and ease of treatment using a conventional stripping tower.

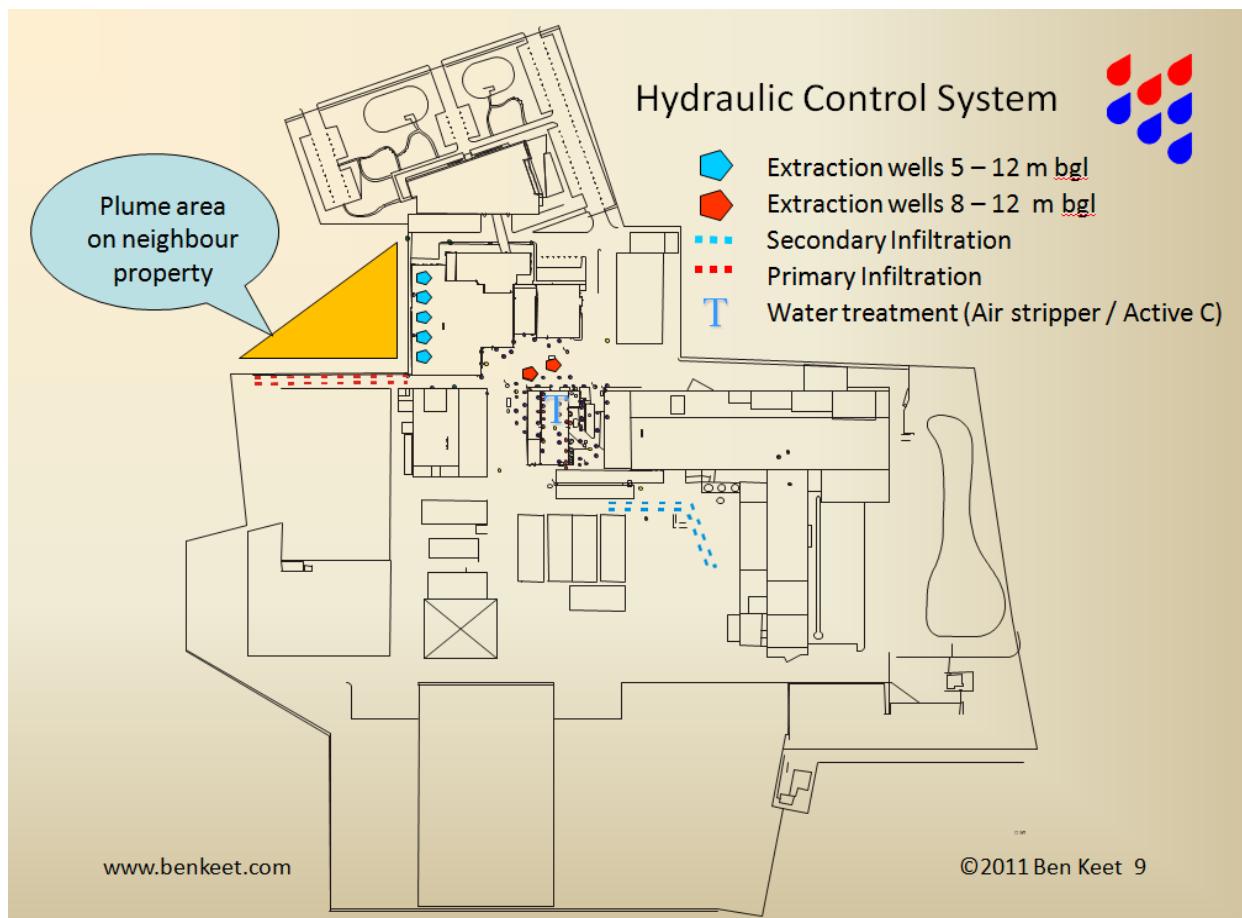
Secondly it was decided to pilot test two extensive remedial techniques and investigate the potential effectiveness of monitored natural attenuation. The in-situ remediation techniques selected were:

- a) Diffusion sparging from horizontal boreholes
 - b) Increase Dissolved Oxygen by direct injection ORC (magnesium peroxide)

To gain useful insight these pilot studies were carried out on 'full scale' basis, however in a limited area of the site.

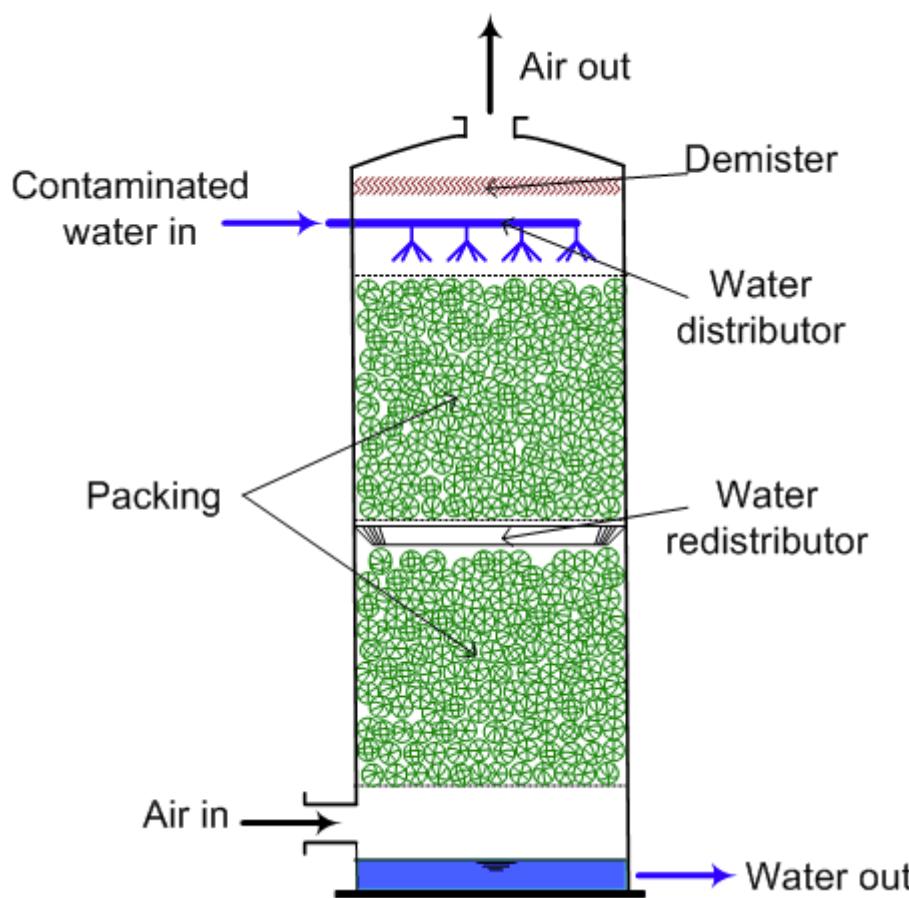
Hydraulic control of VC plume

The basic principle of an hydraulic control system is to counted the natural groundwater gradient to stop the contaminant plume moving. In this case the plume seemed to move only in the winter period. Therefore a continuously operating hydraulic control system, capable of zero migration during the winter months is able to draw back some of the plume towards the extraction wells during summer months. The owners of the neighbouring site were rather hostile and communications were poor. Therefore a system was designed to draw the plume back from that property so that in due course there would be no contamination left to argue about. The tail of the plume contained mainly VC which has a very low adsorption rate, therefore the pump and treat remediation was thought to be effective. On the map below the main extraction wells are indicated in blue, with the related injection drains in red.



As the extracted groundwater needed treatment before re-infiltration a treatment system was installed (at 'T' on the map above). The system was a classic air-stripper (see next page) and activated carbon filter to treat the air. Given the high cost of operating a treatment system the concentration of contaminants was optimised by blending groundwater with a higher level of contaminants into the water pumped into the air-stripper. This was extracted closer to the centre of the plume (red). To allow for this extra water, further infiltration drains were installed (blue) opposite the other infiltration drains.

Water treatment system



Above schematic of air-stripper¹, below dragging the stripping tower into the building.



¹ http://upload.wikimedia.org/wikipedia/commons/4/4e/Air_Stripper_for_Wikipedia.png

The stripping installation was installed inside the building to avoid 'advertising' the site to be contaminated.

The 8 meter high stripping tower just fitted under the roof of one of the factory halls.



Automating the system was important to reduce operator costs. With the groundwater at only 2 meter below the surface and the infiltration drains at 0.8 m, it was important to ensure the drains would not flood the car parks and other area around the factory.

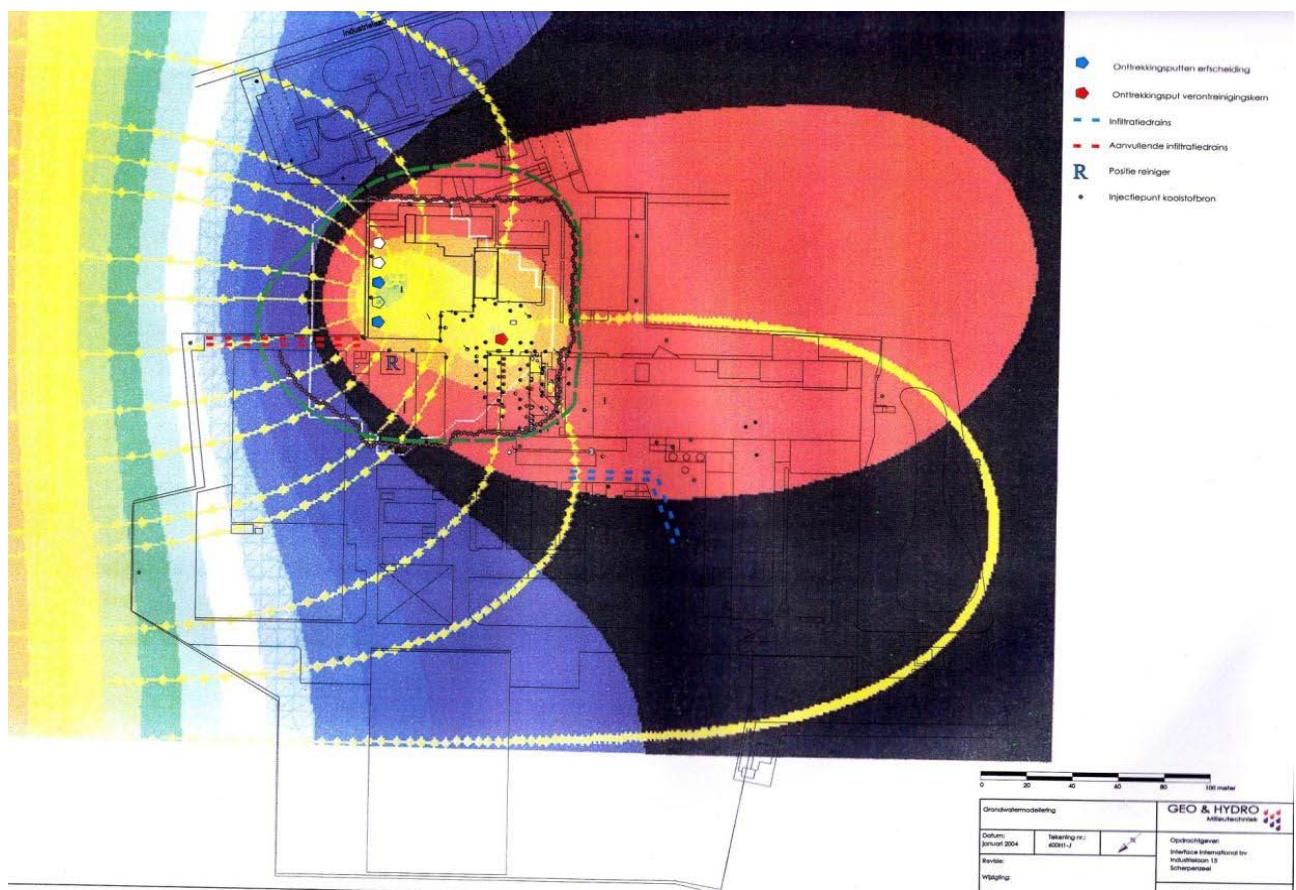


Therefore a number of float controls were added to the drains to allow early cut-out of the infiltration. Levels controls in monitoring wells as well in the extraction wells controlled the flow pattern of the groundwater.



Photo below shows one of the five extraction wells in the factory floor. Due to the level controls and sampling requirement a flush completion was not possible.





MicroFem groundwater model was used to model the flow in the different aquifer layers. Shown above: the flow pattern with 3 main extraction wells operating and 1 auxiliary extraction well near the centre of the plume and infiltration equal over the primary and secondary infiltrations drains.

Area 2 pilot test no. 1 Bio-sparging using horizontal borehole comparison diffusion with normal and micro-sparging

The main aim of bio-sparging is to increase the dissolved oxygen content of the groundwater to allow aerobic biodegradation to take place effectively. With normal and most micro-sparging techniques air is injected creating air bubbles which migrate due to buoyancy forces to the groundwater surface (water table). Even if all oxygen is dissolved during this migration most nitrogen will not dissolve and will migrate to the water table. During its migration vapours of contaminants will enter the air bubble, which is the principle of airtstripping. The vapour concentration in the air bubble will depend on the coefficient of Henry which is a measure of how much vapour will partition from the water phase to the vapour phase. In this project vinyl chloride is the main contaminant and stripping it from the deeper groundwater and migrating it to the vadose zone, just below the buildings, is undesirable.

However the migration process does create agitation and the buoyancy effect assists the dissolution of the oxygen out of the air bubbles. In comparison the diffusion sparging process does not create bubbles and thus the migration of the oxygen through the formation is concentration gradient driven. As pure oxygen is used the concentration close to the diffusion sparger is significantly higher than 100% (saturation level of oxygen in water when aerated with air). The purpose of the pilot study is to see how far from the diffusion spargers the dissolved oxygen levels are increased significantly (i.e. over the 3 mg/ltr under which level micro-biological activity slows down significantly).



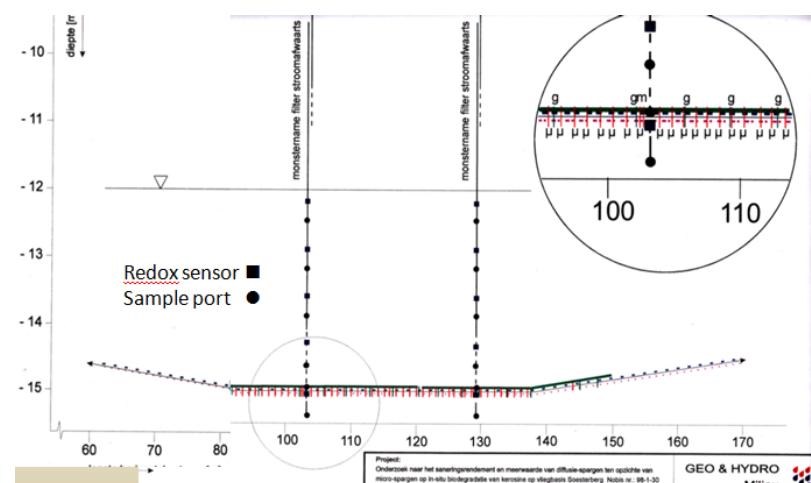
Installed on this site: Horizontal string 170 m with 60 m horizontal section

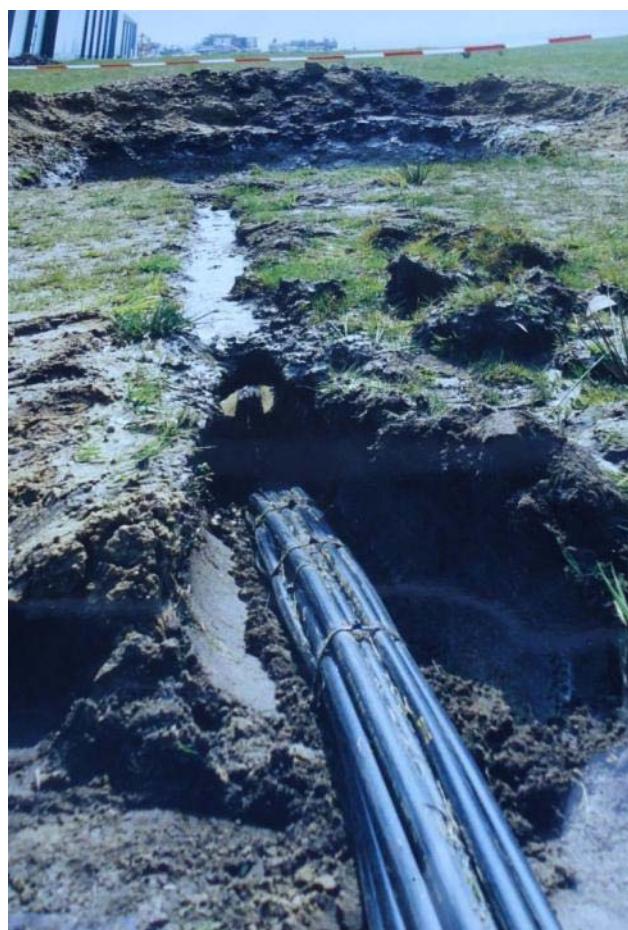
Standard slotted HDPE spargers, 3 meters every 5 meters

Micro-spargers: 300 mm long stainless steel 10 micron every meter

Diffusion spargers: 1 km 3mm silicon tubing coiled up in 25 m perforated tubes (yellow on the picture on the left).

Redox sensors and groundwater sampling ports every 10 meters





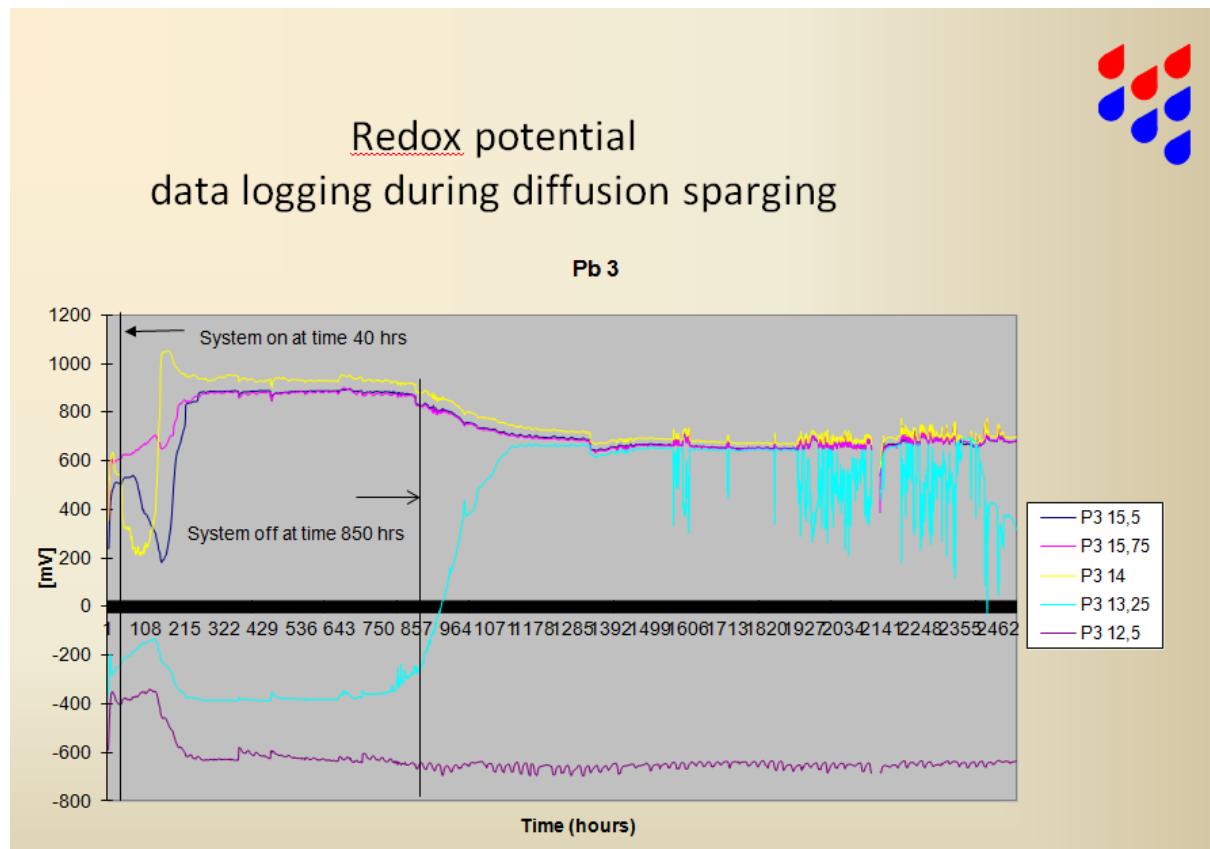
Installing the sparger string

Watch out for: wall smearing and residues of drilling fluid. For example Bariod 'Biobore' is a biodegradable dilling fluid.

The advantage is that he borehole wall will open up when it is fully degraded.

Disadvantage is it consumes all the oxygen injected for quite a significant period of time (months).

Best solution is to clean the borehole thoroughly including jetting the borehole wall just prior, or while pulling in the sparger string.



Redox potential was data logged automatically. Sensors were placed in the sparger sting as well as in monitoring wells at the depth shown in the graph above for monitoring well P3.

Clearly visible is the redox potential change after about 100 hours after turning on the oxygen in the diffusion sparger system. At 850 hours the system was shut off and the redox has taken about 200 hours to get back to what it was before diffusion sparging started.

Conclusions:

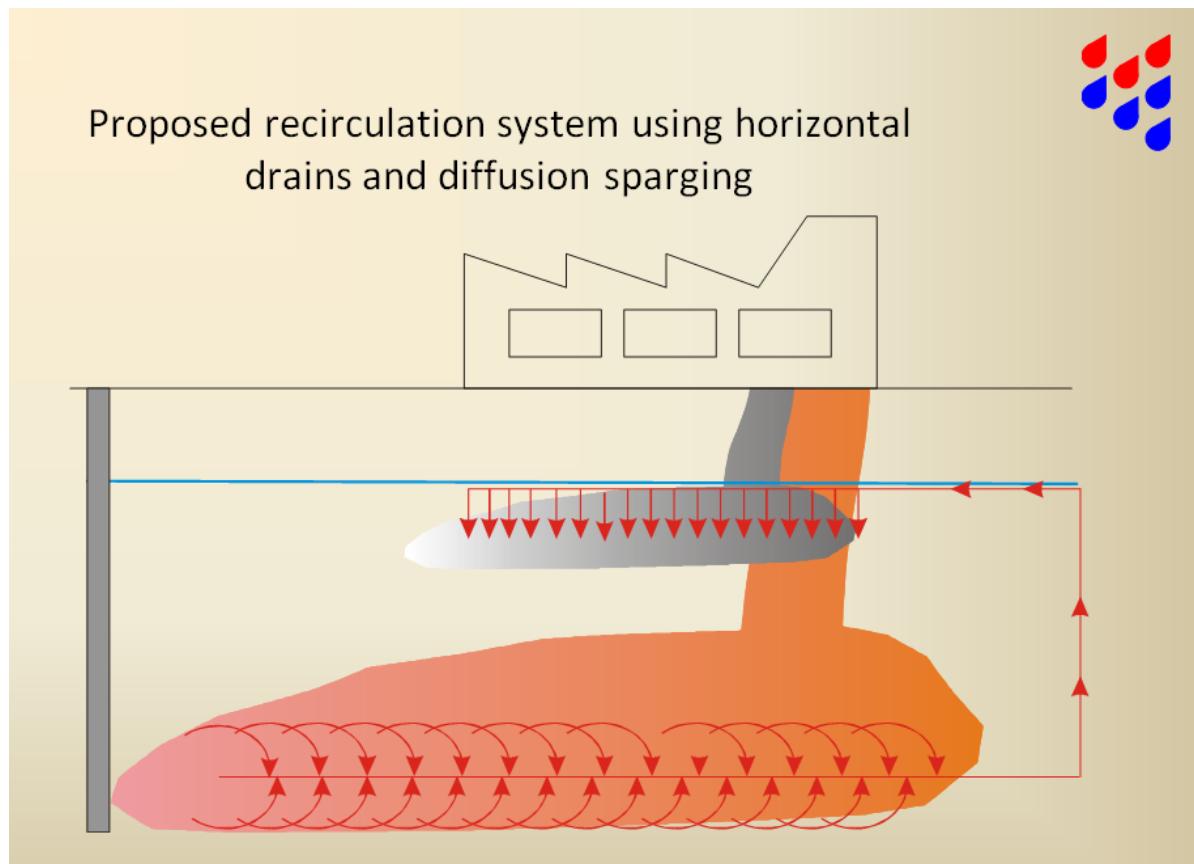
- Initial aerobic degradation delayed due to presence of remnants of the biodegradable drilling fluid
- Increase in DO possible beyond the '100%' due to use of pure oxygen

Advantages

- Bacterial growth is faster
- Cost (capital and maintenance) of surface equipment is lower
- No vapour (VC) transport to surface

Disadvantages:

- Limited radius of influence (expands as contaminant level reduces)
- Will work better with some slow groundwater circulation



Pilot test 2 Direct placement of ORC (magnesium peroxide)

Oxygen release compounds (ORC's) are solid compounds, often applied as powder or as a powder inside a gel which slowly dissolves.

Placement ORC was carried out using a hollow rod with a hot point through which the MgO₂ as fine powder in thin wall filters was pushed down using compressed air



Conclusions:

- Fast acting - DO increases beyond the '100%' close to placement well
- Limited ROI – relies on groundwater flow

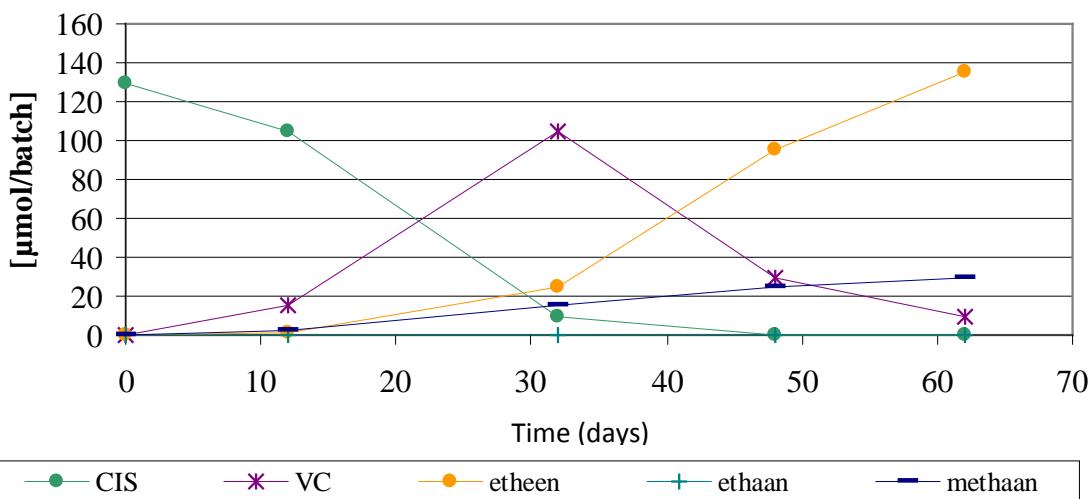
Advantages

- No vapour (VC) transport to surface
- Low capital outlay

Disadvantages:

- Limited radius of influence (expands as contaminant level reduces)
- Will work better with some slow groundwater circulation
- Requires dense network of injection points
- Repeat application required – long term costs

Pilot (Lab) test 3: Natural attenuation of CIS



Anaerobic samples were taken and in a nitrogen box spiked with a carbon source, simulating natural influx of DOC through groundwater transport or with magnesium peroxide simulating influx of dissolved oxygen by groundwater from outside the plume area.

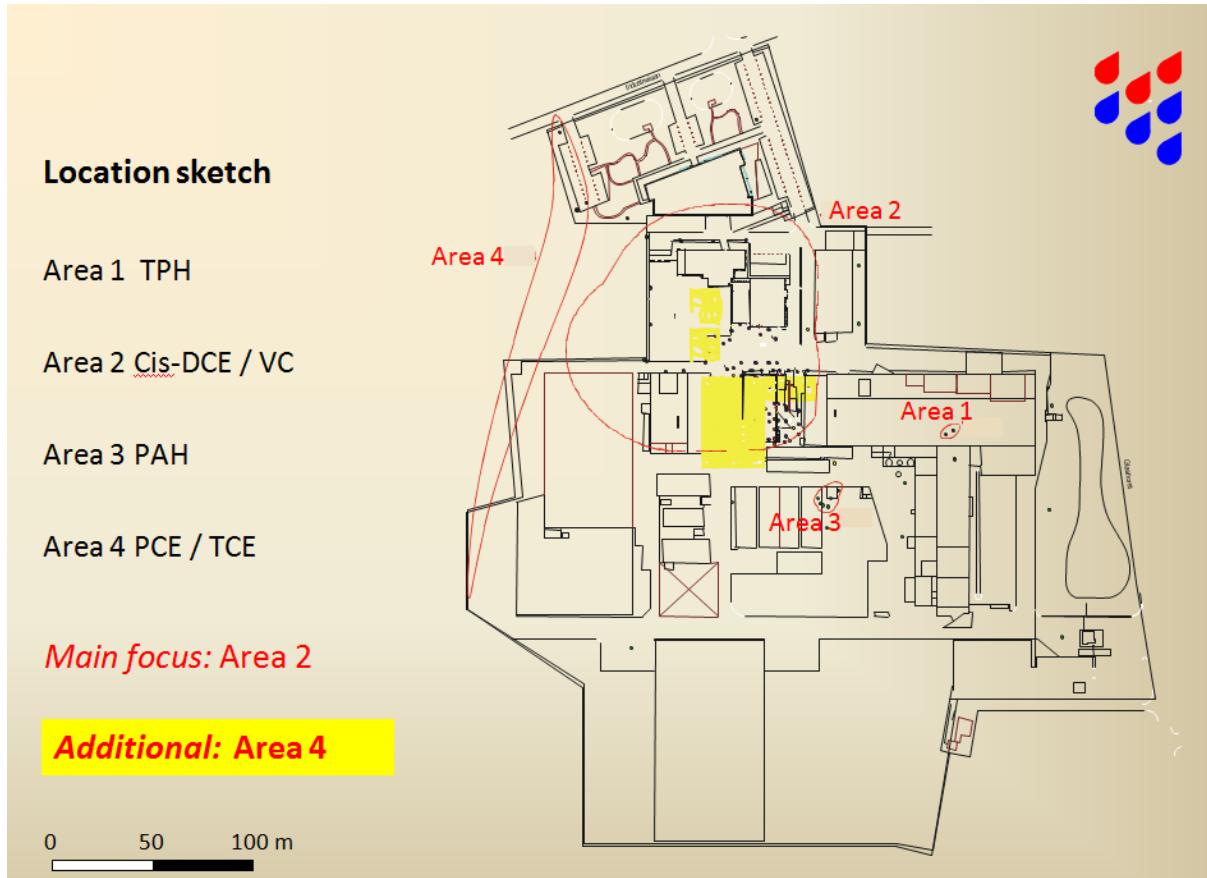
Conclusion Area 2

- Diffusion sparging showed most promise
- Estimated cost for 14 diffusion sparger strings is \$NZ 1,200,000.- which is 20 % of initial estimate of extensive in-situ with prognosed project time of 4 years.

However ...

- Client opted for MNA with longer use of the hydraulic control measure.
- MNA will rely on influx of DOC initially and oxygen, later, with groundwater stimulated by the groundwater extraction
- Duration expected : 20 – 30 years
- Operating cost \$ 150,000.- per year

Area 4



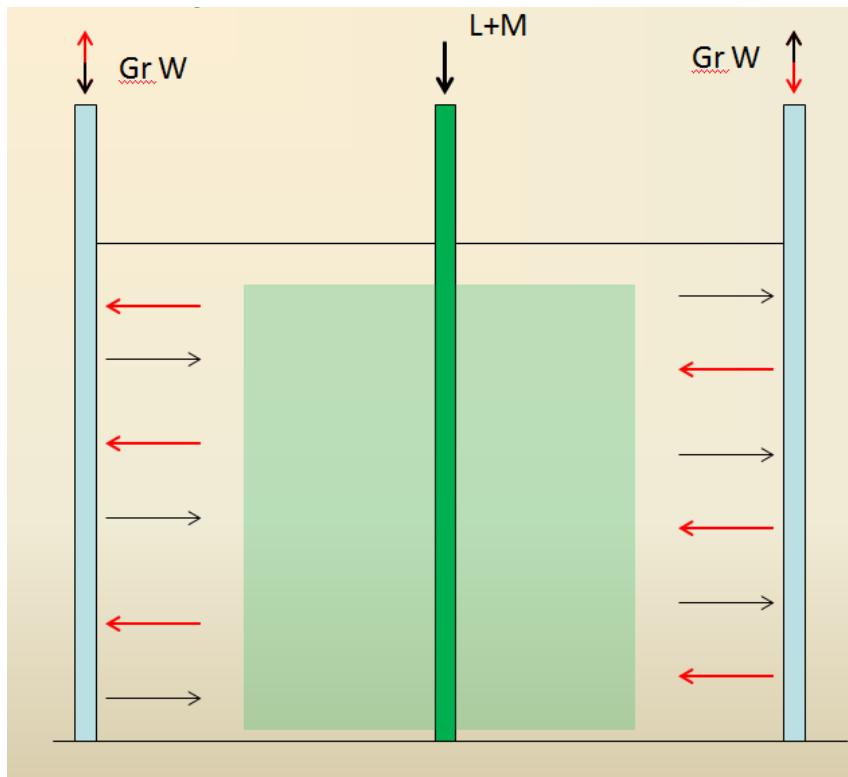
Area 4 Characteristics

- > Main contaminant: PCE / TCE
- > Result of leaking sewer line
- > Expected DNAPL on / in peat lenses
- > Main contaminant position 7 – 12 m bgl

Pilot test extensive remedial techniques

- a. Dechlorination using reciprocating lactate/methanol flushing
 - b. Dechlorination using direct injection molasses
 - c. Bio-augmentation (one-step dechlorination:
seeding Dehalococcoidetes Ethanogenensis 195)
- a. and b. stimulate the natural step-wise dechlorination as is active in Area 2
- c. one step dechlorination, however requires introduction of new species

Area 4 a. Reciprocal groundwater flushing – Lactate + Methanol injection



Experience with substrate injection in previous project had shown injection well fouling requiring frequent cleaning with high pressure jetting or using sodium hypochlorite to kill the bacterial growth around the well screen. Both procedures are cumbersome and the reciprocal groundwater flushing was trialled as a means to avoid the bio-fouling of the wells.

In this procedure the groundwater is removed from the first row of wells and injected in the third row to move the groundwater towards the first row of wells. After a certain time this is reversed, moving the groundwater in the opposite direction.

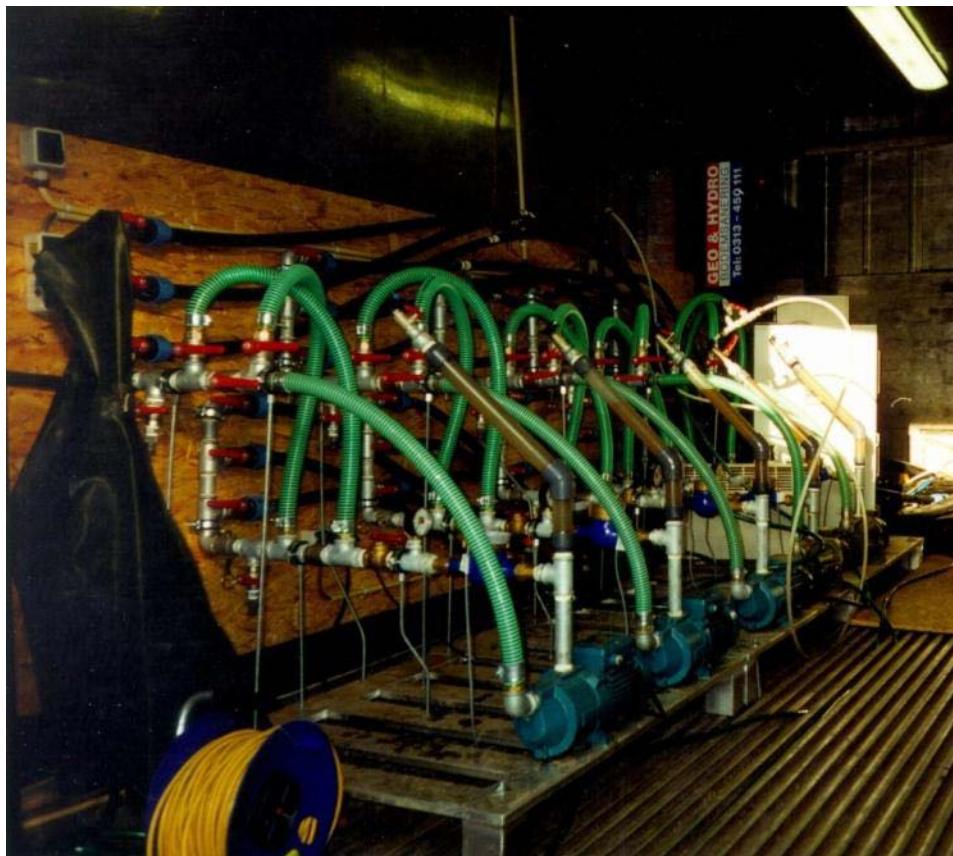
In between these rows a row of substrate injection wells is placed. By keeping the concentration of the substrate above the biocidal level, there is no bio-fouling in the injection wells and as the alternating groundwater injection and extraction wells are spaced at a fair distance from the treatment zone, they are outside the substrate zone and therefore remain free from bio-fouling as well.

Lactate – Methanol Substrate injection



Substrate blending (above)

Sensor controlled reciprocating groundwater flushing units (below),



Area 4 Pilot b. Direct injection of Molasses

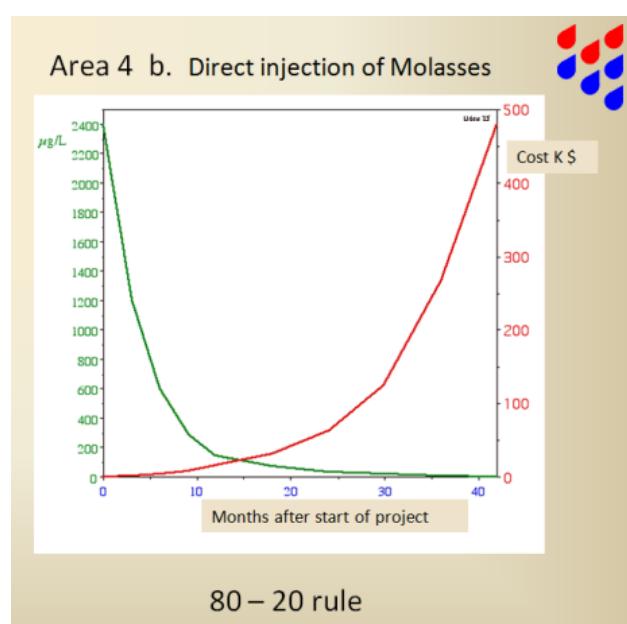


For the molasses injection the same rig was used as for the ORC injection. However this time the point was retractable as a side port opened when the drill rod is retracted. The molasses was injected diluted 1 : 1 with water to allow penetration in the formation. The injection was continuous while pulling the rods back to the surface.

Repeat application is needed to supply all the molasses needed without creating biocidal conditions at the start of the project (by over application).

This leads to a increase in cost for each kg of contaminants removed, as the lower the residual concentration the higher the cost for a injection round will be in relation to the expected breakdown of the contaminants.

This leads to the well know 80 – 20 rule; 80% of the contamination can be removed for 20% of the cost.



Area 4, pilot c. Bio-augmentation: Bacteria seeding pilot

On this site no Dehalococcoidetes Ethanogenis 195 is found however at a other remediation site located only 20 km from this site Dehalococcoidetes Ethanogenis 195 was available naturally. Initial tests involving the transportation of 200 liters of Dehalococcoidetes Ethanogenis 195 containing groundwater and infiltrating this in wells on this site while maintaining anaerobic conditions resulted in one step full dechlorination of PCE to ethane.

However the Dehalococcoidetes were short lived and to overcome this a breading reactor (blue on picture below) was build from which each time only half of the volume was injected and by adding PCE and substrate the number of bacteria was rapidly increased to allow frequent injections.



Main findings:

- Need to grow bacteria under controlled anaerobic conditions
- Follow each injection with substrate at biocidal concentration to avoid well plugging

Main drawback:

- Establishment of bacteria is very slow (too much in-soil competition)
- Well plugging does occur and regeneration is required

Conclusions Pilot testing in Area 4

- Reciprocal groundwater flushing with substrate injection provides lowest residual contaminant levels
- Agitation essential in presence of 'hanging DNAPL'
- Costs can be controlled by automation
- Direct injection molasses provides cost effective solution for bulk removal. Cost / kg removed rise exponentially at lower concentrations
- Bacteria seeding is difficult (maintaining aerobic conditions, incubating new batches, operator intensive) and therefore expensive.

For area 4 Reciprocal groundwater flushing was chosen, however with molasses as substrate which was direct injected in some areas where frequent access was possible and infiltrated through a series of injection wells in less accessible areas.



Sensor and micro-processor controlled intelligent remediation systems

IHRIS Systems

Intelligent
High-efficient
Remediation
In
Situ

[http://www.benkeet.com/
gallery/fh068.html](http://www.benkeet.com/gallery/fh068.html)



Overall conclusions

The series of pilot tests were run over a 3 year period. Given the very significant costs of a full scale short duration remediation provided the incentive to look at alternative technologies. Frequent meetings with presentations to the client, their overseas management and the local and regional authorities have been instrumental in maintaining support for the project.

By collaborating with other consultants, specialist laboratories and universities during various steps during these pilot tests ensured that the best people worked on the project. This way it was avoided that one pilot was carried out by one consultant and the next by another. This often leads to the quality of execution becoming the deciding factor when choosing a certain technology, rather than the effectiveness of the technology.

