Theme 1 Dealing with contamination of soil, groundwater and sediment

Session 1c. Remediation technologies and approaches

SUCCESFULLY STIMULATED BIOLOGICAL IN-SITU REMEDIATION OF VOC CONTAMINATED SOURCE ZONES.

M.J.C. Henssen, M.H.A.B. Wagelmans, A.S. Roosma, H.M.T. de Vries (Bioclear b.v., Rozenburglaan 13. PO Box 2262, 9704 CG Groningen, The Netherlands)

Summary

At several sites in the Netherlands Bioclear stimulated biological degradation of volatile organic chlorinated compounds (VOC) in **source zones** is applied successfully. The technique often used is based on direct injection of carbon source and, if needed additional specific dechlorinating bacteria Dehalococcoides spp. (DHC). This technique is, instead of most in situ remediation techniques, very well applicable in poorly permeable soils like clay and peat and at those sites that are more difficult te reach (like urban areas). Direct push injections are typically used to remediate a source zone. Research and field experience have shown that chlorinated ethylenes concentrations close to the maximum solubility can be biologically degraded.

Direct injections are performed with a small injection machine. Protamylasse can be used as carbon source. Protamylasse does not only contain organic carbon but contains also enough nutrients for the growth of dechlorinating bacteria. Protamylasse is an organic waste stream from the potato starch industry. Which is an environmentally friendly (and cheaper) alternative compared to chemically produced carbon sources like lactate, acetate or hydrogen release compound. If injection of dechlorinating bacteria is desired, a culture with a high concentration of dechlorinating bacteria is obtained from a lab.

The biological treatment of source zones in urban areas has proven to be a very interesting method. Although remediation time may take various years, the cost of such a remediation is quite low and hindrance during remediation is minimal. Especially for those source zone that pose no human health risks at the moment but should be remediation in order to prevent flux of contaminants into the groundwater, this approach is very suitable.

Biotreatment of chlorinated solvents in contaminated *plume areas* is a well established technology, showing good results. Biological treatment of high concentrations, encountered in source zones, is supposed to be ineffective and some believe that high concentrations are toxic to the bacteria. This has been shown to be not true in general. Various source zones already show high concentrations of intermediate degradation products (like c-DCE and VC), indicating degradation of very high PCE and/or TCE concentrations under natural, non-stimulated conditions. This already shows that toxicity is not always a problem.

Biological source zone treatment accelerates natural degradation processes of chlorinated ethylenes by injecting carbon source and, if needed, chlorinated ethylene degrading bacteria (Bio-augmentation). The results of the evaluated locations showed that it is possible to biologically remediate DNAPLs with tetrachloroethene (PCE) and trichloroethene (TCE), within timeframes of 5 to 10 years. If mainly intermediate products occur at the site in high concentrations, remediation within 1 to 2 years is possible, even sometimes with only 1 carbon source injection.

Biological source zone treatment effectively removes the contamination but it also prevents migration of chlorinated ethylenes from the source zone to the plume. If natural attenuation occurs in de plume, source zone removal will result in a retreating plume and immediate groundwater quality improvement, which is an important target of the European Groundwater Directive and very important in an regional treatment strategy.

Introduction

Full scale applications have shown that chlorinated ethylene concentrations close to the maximum solubility are biodegradable. The reason that biological DNAPL degradation is possible is the presence of micro niches in the soil matrix. The conditions in these micro niches differ from the overall soil conditions and can be favorable for anaerobic dechlorination. Besides dechlorination, biological activity also accelerated the dissolution of free phase product up to a factor 16 which has a positive effect on the total degradation proces. The accelerated dissolution is a result of the lowered chlorinated ethylene concentration in the groundwater due to biological degradation.

When applied properly biological source zone treatment has several advantages:

- Capital and operational costs are usually lower than those of other DNAPL source zone treatment technologies;
- The overall hindrance due to remediation activities is quite lower than with other techniques (like ISCO, thermal treatment), also since no additional equipment or dosing systems are needed at the site;
- Other contaminants present with the chlorinated ethylenes, specifically other chlorinated organic compounds, may simultaneously be degraded.
- The technique can be used in combination with a number of other treatment technologies as part of a larger overall site treatment strategy.
- By removing contamination mass, the overall treatment time frame at a DNAPL-contaminated site is shortened and natural attenuation of the plume contaminants can be used more effectively (lowered flux from source).

To verify the many promises of the biological source zone treatment technique, five full scale biological treatment projects conducted in The Netherlands have been reviewed.

Biological source zone treatment projects

The first full scale source zone treatment application in The Netherlands was initiated in 2001 in Appingedam. Several other source zone treatment projects have followed.

Biological source zone treatment accelerates natural degradation processes by adding carbon source and, if needed, chlorinated ethylene degrading bacteria to the soil (Bio-augmentation). The added carbon will result in redox conditions and organic carbon concentration favorable for reductive dechlorination. Active bacteria will degrade solvents like tetrachloroethene (PCE) and trichloroethene (TCE) to harmless ethene and ethane without the accumulation of toxic degradation products like dichloroethene (DCE) and vinylchloride (VC). The degradation pathway is visualized in figure 1.

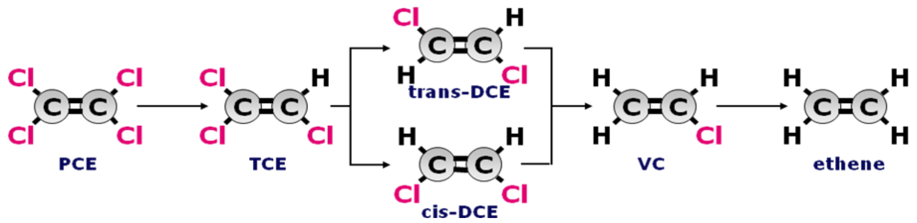


Figure 1. Anaerobic biological dechlorination of tetrachloroethene (PCE)

The monitoring of the remediation processes of the five full scale locations is focused on the applied technique, contaminants, redox parameters, total organic carbon (TOC), microbial populations and formation of methane and sulfide (important safety issues). A typical monitoring consisted of 4 rounds. The results of the monitoring are discussed in the next paragraphs. Table 1 shows an overview of the evaluated treatment projects.

Operational activities for the source zone treatment

In most cases the source zone remediation is executed by injection of carbon sources (and in some cases additional bacteria) using direct injection technology. This technique is quite well applicable for these situations, especially in densely build-on urban areas. The technique may also be applied for injection underneath buildings.

Figure 2. Photos of direct injection of carbon source to stimulate biological degradation.

Due to the low permeability of the soils treated (quite often the case in the Netherlands in the upper soil layers) a grid with a distance of 1 to 2 meter between every injection point is needed and used. In various cases Nutrolase (protamylasses), molasses and/or lactate was used for carbon source. Carbon source is overdosed by a factor ten to ensure a successful treatment. In four of the five location 0.23 to 0.85 kg TOC/m^3 soil volume is added (TOC is a measure for the total amount of carbon). At the location IJlst a carbon source shock load was applied, resulting in an addition of 1.5 kg TOC/m3 soil volume.

Treatment results

Direct injections create a biologically active zone in which the contamination is degraded to harmless degradation products. An important side effect of the biological active zone is that it **prevents migration** of chlorinated ethylenes **from the source zone to the plume**. In other words: the mass flux of contaminants leaking into the plume will decrease in course of time due to the stimulated degradation in the source zone.

If natural attenuation occurs in de plume, source zone removal will result in a retreating plume and immediate groundwater quality improvement. Figure 3 depicts a schematic overview of how direct injection can treat a small heavy contaminated area resulting in a retreating plume. The combination of Natural Attenuation in the plume and bio-source zone treatment therefore results in a cost-effective solution, whereby remediation actions only take place in the relatively small area of the source zone.

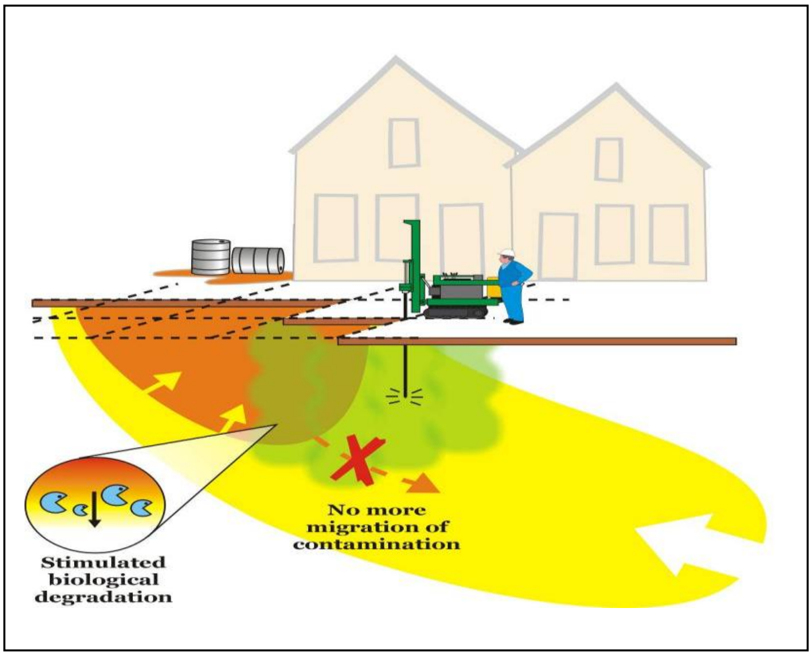


Figure 3, direct injection of carbon source can result in a retreating plume.

The last column of table 1 shows the remediation results of the six sites. On the location Appingedam remains one contaminated well, the locations The Hague and IJlst are completely remediated. Location Haren and a location in the west of the Netherlands show a very active degradation process. The site in Groningen was closed with positive result after 8 years, with only 2 injection rounds. Retreating or stable plumes have been observed in five of the six evaluated locations.

The duration of a biological source zone treatment depends on the type and amount of contaminant present. If the source zone contains high concentrations or free phase product PCE and/or TCE the treatment duration varies between 5 and 10 years. Sites contaminated with DCE and VC can be treated very fast. Location The Hague showed that it was possible to treat the DCE and VC contamination in one year.

Table 1. overview of the evaluated biological source zone treatment projects.

Site	Size of source zone	Maximum conc (µg/l) at t=0	Used carbon source	Longevity carbon source (years)	Injection grid (m)	Duration treatment (years)	Treatment result
Appingedam	65 m^2 520 m^3	PCE 69,000 TCE 69,000 DCE 150,000 VC 14,000	Molasses/ lactate	9.0	1,5	13	Size of source zone is strongly reduced. Complete plume removal
The Hague	90 m^2 1080 m^3	PCE 5,900 TCE 3,100 DCE 19,000 VC 700	Nutrolase (protamylasses)	2.8	1,5	1	Source zone treated in one year. Max. concentration after treatment: 0,005 mg/l VC
Haren	680 m^2 6800 m^3	PCE 100 TCE 53,000 DCE 32,000 VC 300	Nutrolase (protamylasses)	2.6	2	2	Within 2 year all TCE degraded to DCE and VC. Plume size is decreasing
West of The Netherlands	156 m^2 936 m^3	PCE 40 TCE 40 DCE 140,000 VC 80,000	Nutrolase (protamylasses)	1.9	1	2	Source zone has decreased in size. Active degredation process is ongoing
IJlst	250 m^2 3750 m^3	PCE 57,000 TCE 42,000 DCE 34,000 VC 5,700	Nutrolase (protamylasses)	Unknown	2	2	Size source zone strongly reduced. Plume is decreasing in size.
Groningen	4,300 m^3	c-DCE 33,000 VC 22,000	Protamylasses	3-4 years	2	8	Within 2 injection rounds (2006 and 2010) 90% reduction of I-value contour was reached and leakage of contaminants to lower gw-layer was stopped

Carbon source

The feasibility and cost-effectiveness of the presented technique with direct injection of carbons sources is very much dependent on the longevity of the carbons sources. If consumption of the carbon source is taking place too quickly, re-injection may be needed and cost (and hindrance at the site) will increase. Therefore longevity of the carbon source is important.

Based on the monitoring results from the various sites it can be concluded that longevity of the substrates like protamylasse is on average 3 to 4 years and therefore comparable with slow release carbon sources like HRC® and emulsified oils. Re-injections are therefore normally needed within a timeframe of approximately 4 to 5 years. Figure 4 shows a typical TOC concentration development in time as we monitored it at various sites.

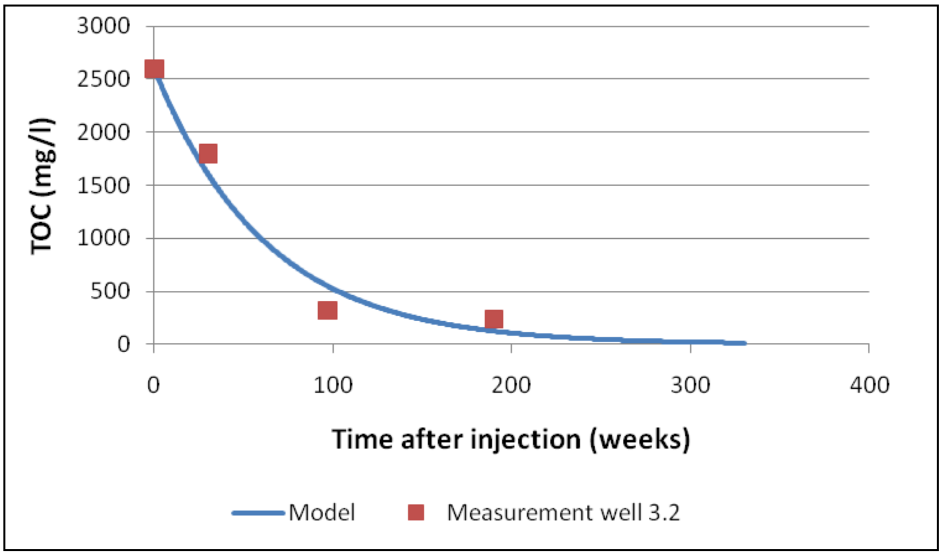


Figure 4, TOC concentration in time of well 3.2 at location Appingedam

The injection of large quantities of carbon source could cause soil acidification. Measurements at the evaluated sites showed a decrease in pH in the first months after the injections. The lowest measured pH was 5.5. Since dechlorinating bacteria can cope with pH 5.5, acidification causes no inhibition of biological treatment processes. Within 1 or 2 years the pH had rebounded on all locations to the original level. A typical pH development after carbon source injections is depicted in figure 5.

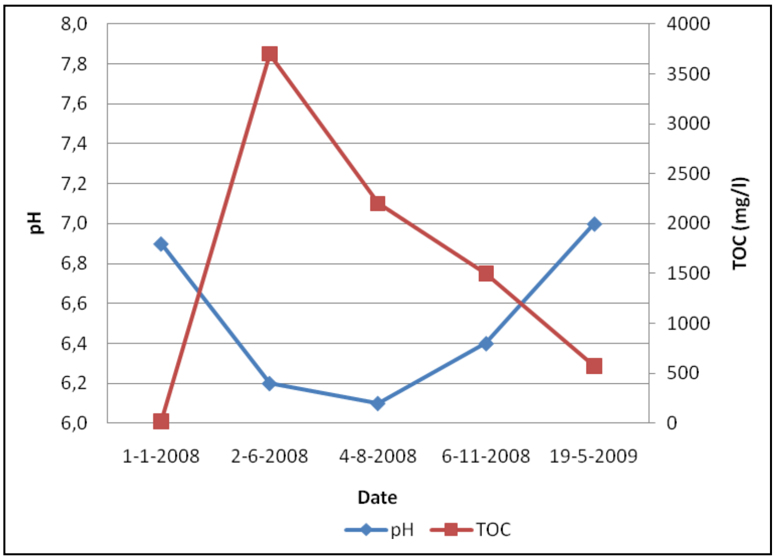


Figure 5. pH development after carbon source injections in well 302 at location The Hague.

The injection of large quantities of carbon source might result in unwanted methane and sulfide gas production. Two sites were investigated but no accumulation of methane and sulfide above critical concentrations were measured. This shows that when designed properly, direct injection of carbon source does not cause any human health or explosion risks.

Costs

The costs of biological source zone treatments is 20 to 30 euro/m3 soil volume, including environmental supervision and monitoring (in source areas with a soil volume > 2,000 m3). The costs are low compared with conventional treatment techniques such as chemical oxidation (average 60 euro/m3) and electroreclamation or thermal treatment systems (170 and > euro/m3).

In the case ‘Haren’ and 'Groningen' biological source zone treatment resulted in a cost reduction of 70% compared to the alternative treatment techniques suggested for this site. The reduced costs made it for the local government possible to raise enough funds to start the treatment process. The specific remediation results for the location Haren are given below.

Biological source zone treatment, case ‘Haren’

Activities of a former dry cleaner in the Dutch village Haren caused a soil and groundwater contamination with chlorinated ethylenes. The total contamination volume was estimated at 450 to 900 kg and had migrated under houses and a parking lot. The contamination was 825 m^2 in size and went to a depth of 10 meter below ground level. The maximum TCE concentration was 53,000 µg/l and there were potentially free phase chlorinated ethylenes present. The soil is composed of low permeable boulder clay.

On site, carbon source as well as dechlorinating bacteria have been injected. Direct injections were chosen is stead of infiltration en extraction because of the low permeability of the soil. The injections have been performed within the area containing 99% of the contamination. A total 200 injections to 9 meter below ground level have been performed. The treatment progress is monitored from 2007.

The total costs of the treatment are €175,000 including extra injections after five years, quality checks and monitoring of the treatment progress for ten years. This is € 26.50 per cubic meter soil. The choice for biological source zone treatment resulted in a cost reduction of 70% compared to alternative treatment techniques. The reduced costs made it for the local government possible to raise enough funds to start the treatment process.

Current status

Complete degradation of chlorinated ethylenes occurs. Derived from the amount of degradation products (VC 130,000 µg/l en ethene 130,000 µg/l) it is concluded that more contamination was present than expected. Within one year the size of the contamination plume has decreased with 30%. Gas sampling in the unsaturated zone showed no vaporization of chlorinated ethylenes like VC. Human health risks were thereby ruled out.

The treatment progress is according plan. The conditions for biological degradation are favorable and an active bacterial population is present. Due to the large amount of chlorinated ethylenes present a re-injection of carbon source is needed in time.

Biological source zone treatment, case ‘Groningen’
Ground and groundwater at a site in Groningen is contaminated with volatile chlorinated ethylene’s (VOCl) as a result of usage of degreasing agent for the polishing of glasses (spectacles). The contamination was mainly present in the poorly permeable clayey soil layer till 6 meter below ground level (m-gl). In 1994 the groundwater at the site was remediated by extraction of groundwater and aboveground treatment before discharging. Because of insufficient remediation results, was in 2002 Bioclear asked to formulate an alternative remediation approach based on in situ stimulated biological degradation. The site was mainly contaminated with the components cis-1,2-dichloroethylene (cis-DCE) and vinyl chloride (VC). The maximum concentrations measured concerned respectively 33.000 µg/l en 22.000 µg/l. The extent of the contamination amounted approximately 4.300 m^3 strongly (> I-value according to the Dutch soil policy) contaminated soil volume.

The in situ biological remediation approach exists of injection of carbon source in the upper clayey soil layer till 6 m-gl and ten-yearly monitoring of the groundwater in de upper soil layer and the underlying aquifer. In 2006 the injections of carbon source were performed and in 2010 local additional carbon source injections were performed.

Since the performance of the carbon source injections, the contamination completely degraded to harmless end products (ethylene and ethane). Within the stimulated area the concentrations of contamination are decreased below the T-value (Dutch soil policy remediation value). The total strongly contaminated (> I-value) soil volume is from the start of the biological in situ remediation decreased with approximately 90%. Furthermore the source of the contamination is removed as a result of the stimulated biological degradation. Therefore leakage of contamination from the source zone in the upper clay layer into the underlying aquifer has stopped. The remediation resulted in a limited volume (< 1.000 m^3) of remaining contamination with concentrations above the I-value. Moreover there are no risks as a result of dispersion of contamination and no environmental protection areas are at risk.

Within eight years a successful remediation of the site was exectuted by in situ stimulated biological degradation using only two carbon source injection rounds.

Sustainability

A biological source zone treatment can be subdivided in an active and passive phase. The active phase is typically a few weeks of direct injections. The passive phase follows the active phase and is the time needed for the bacteria to degrade the chlorinated ethylenes, this phase consist of just monitoring activities. Because the active phase is relatively short the amount of energy needed, compared to techniques like pump and treat, is small. Related to the energy demand is the carbon dioxide emission, which is therefore smaller for biological source zone treatment.

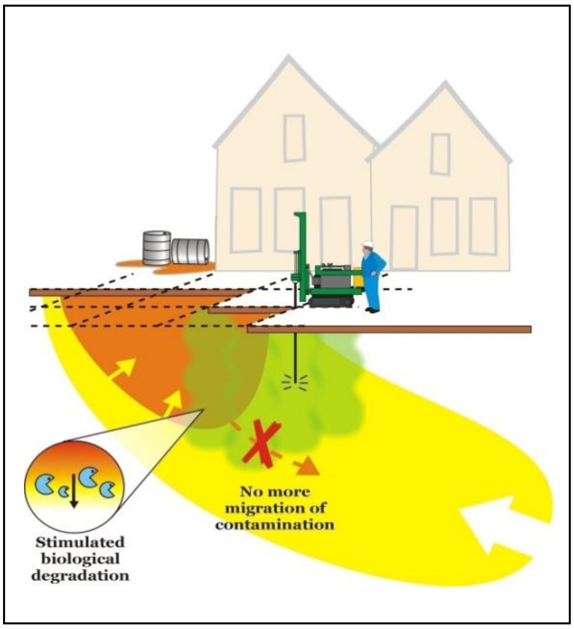
Direct injections are performed with a small vehicle that can be employed in hard to reach areas. If a proper design is applied no dangerous gasses like sulfide and methane are formed. And because no corrosive chemicals or high temperatures are used no specific safety measurements have to be taken. This makes direct injection a very safe technique with minimal hindrance for the surroundings.

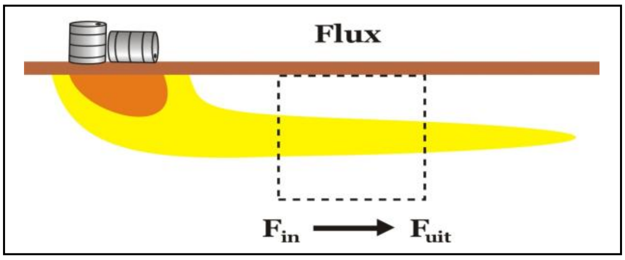
The resources needed for the direct injection consist mainly of carbon source. In four out of five evaluated sites nutrolase (protamylasse) is used. This is a rest product from the potato processing industry. There is no need for chemical oxidizing agents, heat generation or the installation of transport networks for chemical agents or groundwater, which are needed for techniques like chemical oxidation and pump&treat. This makes biological source zone treatment a very sustainable and resource efficient technique.

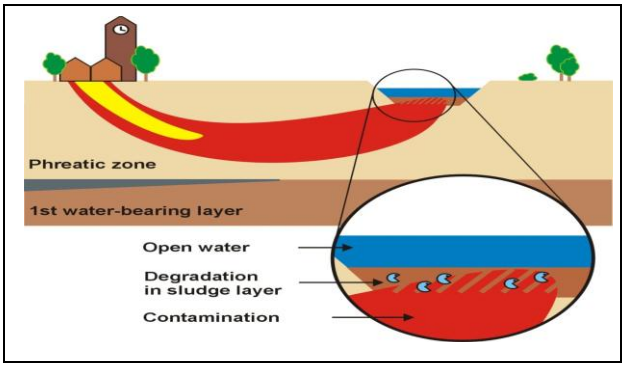
Biological source zone removal and area oriented approach

In the Netherlands focus has shifted in the last decade from cleaning up all contaminated sites as much as possible (both source zone and plume areas) towards more risk-based approaches. This in combination with the urgency to develop solutions in which management of groundwater contamination (mainly plume areas) is combined with societal issues and needs like sustainable energy and climate adaptation. In these situations still source zone removal stays important.

Source treatment can be very effective in the context of an area oriented approach. Lowering the total mass in the source will decrease the mass flux of contaminants entering the groundwater. Due to this lowered mass flux natural attenuation processes in groundwater and sediments may cope more easily with the existing contaminants and the feed from sources. In situ biotreatment of source zones can offer an efficient and sustainable option for this.







Conclusions

Based on the evaluation of various full scale biological source zone treatments it can be concluded that:

- It is possible to remediate chlorinated ethylene concentration close to the maximum solubility in one to ten years.
- Biological source zone treatment prevents migration of chlorinated ethylenes from the source zone to the plume. If natural attenuation occurs in de plume, source zone removal will result in a retreating plume;
- also in an area oriented approach - focusing on removal of the source and decline mass flux entering the groundwater - bioremediation of source zones can be effective;

- Direct injection of carbon source and dechlorinating bacteria can be performed in difficult to reach urban areas, causes little hindrance for the surroundings, are sustainable and resource efficient.
- Biological source zone treatment does not have a negative effect on the soil properties like pH and methane of sulfide gas production, if properly designed.
- Low permeable peat or clay layers in the soil do not have an adverse effect on the treatment process.
- It is cheaper (20-50% of normal cost) compared to alternative source zone treatment techniques and more sustainable.