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Publication date:
2012

Document Version
Publisher's PDF, also known as Version of record

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Feasibility and Performance of Full-Scale In-situ Remediation of TCE by ERD in Clay Tills.

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ABSTRACT: The feasibility and performance of full-scale applications of ERD in clay tills were investigated in a research project including 2 sites in Denmark, which have been undergoing remediation since 2006. At both sites organic substrates and bioaugmentation cultures have been injected in TCE-contaminated clay till. An integrated investigative approach consisting of water and clay core sample analysis, including stable isotopes and specific degraders, as well as analysis for chlorinated solvents, degradation products, donor fermentation products and redox-sensitive parameters combined with modelling has been applied. The results showed that the chlorinated solvent TCE was converted into its daughter products (cDCE, VC and ethene) but complete conversion of contaminants to ethene (as expected) was not achieved within a timeframe of 4 years. Large variation in the effect of ERD in the clay matrix between sites, boreholes and even between cores was observed. Four years post ERD initiation, the mass removal at the 2 sites varied between <5% and 50% within the treated zones. Low mass removal was associated with degradation being restricted to narrow bioactive zones (few cm) around high permeability features in some parts of the clay tills. The bioactive zones may expand in zones where both donor and chlorinated compounds are present. In some cores TCE was depleted (degraded to DCE) in zones up to 1.8 m thick – an extent which could not be explained by diffusive loss to narrow bioactive zones. Hence, biomass migration in the clay matrix appears to play an important role in terms of contaminant mass reduction.

INTRODUCTION

Remediation of trichloroethene (TCE) in clay and other low-permeability geologic media, where groundwater flow occurs preferentially in higher permeability sand lenses or fractures, is a significant challenge (Chambon et al., 2010, Scheutz et al., 2010, Hønning et al., 2007). At older sites, much of the contaminant mass is present as a sorbed phase in the matrix due to matrix diffusion. The principal challenge for in situ remediation in clay is to achieve effective contact between contaminant and bioremediation additives (e.g., substrates and bioaugmentation cultures).

Sequential dechlorination of TCE via dichloroethylene (DCE, predominantly cis-DCE) and vinylchloride (VC) to the harmless ethene requires anaerobic conditions, a hydrogen donor and dehalorespiring bacteria. Complete dechlorination requires specific dehalorespiring bacteria *Dehalococcoides* (*Dhc*) with vinylchloride reductase genes (*vcrA* or *bvcA*). Enhanced reductive dechlorination (ERD) aims to stimulate/enhance this degradation process by supplying a fermentable organic substrate (to provide anaerobic conditions and hydrogen) and a mixed bioaugmentation culture with *Dhc* with *vcrA* and/or *bvcA*. ERD has proven successful for TCE remediation in sand aquifers, but experience with ERD in low-permeability media such as clay tills is limited.

The feasibility and performance of full-scale applications of ERD in clay tills were investigated in a research project including 2 sites in Denmark, which have been undergoing remediation since 2006. An integrated investigative approach was applied.

Scope. The scope of the investigations at the 2 sites was to gain insight in the diffusion and degradation processes in the low-permeability clay till matrix of significance for ERD and to evaluate the feasibility and performance of ERD in clay till contaminated by chlorinated solvents.

SITE DESCRIPTION AND REMEDIATION APPROACH

The 2 sites (referred to as “Gl. Kongevej” and “Sortebrovej”) located in Denmark are both contaminated with TCE from industrial solvent use. In both cases the TCE contamination is predominantly found in clay till aquitards overlying groundwater aquifers. Remediation of TCE by ERD in the clay till was initiated by injection of substrate and bioaugmentation culture in 2006 at both sites.

Sortebrovej, Tommerup. The TCE contamination is located 10-20 m bgs. in a basal clay till deposit with imbedded sand stringers (mm thick). An emulsified oil substrate (EOS) and a bioaugmentation culture (KB1®) with specific degraders *Dhc* were injected in a network of wells screened at 2 depth intervals (10-13 and 15-18 m bgs.). The locations of TCE-contamination and injection wells are illustrated in Figure 1. The substrate and culture spread in the natural sand stringers embedded in the clay till. Further site and remediation description is given in Manoli et al. (2012).

FIGURE 1. Sortebrovej site. TCE-contamination and network of injection wells for substrate and bioaugmentation culture injection in clay till.

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Gl. Kongevej, Copenhagen. The TCE-contamination is found in a fractured basal clay till unit 2-8 m bgs. A source zone and a downgradient plume area, outlined in Figure 2, were treated. The TCE concentration level is very high in the source zone suggesting the occurrence of dense non-aqueous phase liquid TCE at the site. Organic molasses donor and Bioclear Dechlorinating bioaugmentation culture with specific degraders *Dhc* were injected with a drive-point probe (Geoprobe) in 25-cm-spaced vertical intervals over the depth interval 2-7 m bgs. in the clay till in a closely spaced network. The injection method was tested in a clay till by Christiansen et al. (2012) and found suitable for enhanced reactant injections in clay till for in-situ treatment compared to other enhanced injection methods (pneumatic and hydraulic fracturing) by Christiansen et al. (2010). Further site and remediation description is given in Damgaard (2012) and Damgaard et al. (2012). The underlying chalk aquifer is affected by the contamination (also outlined in Figure 2) and remediation. For further information on the effects on the primary aquifer, see Damgaard et al. (2012) and Chambon et al. (2010).

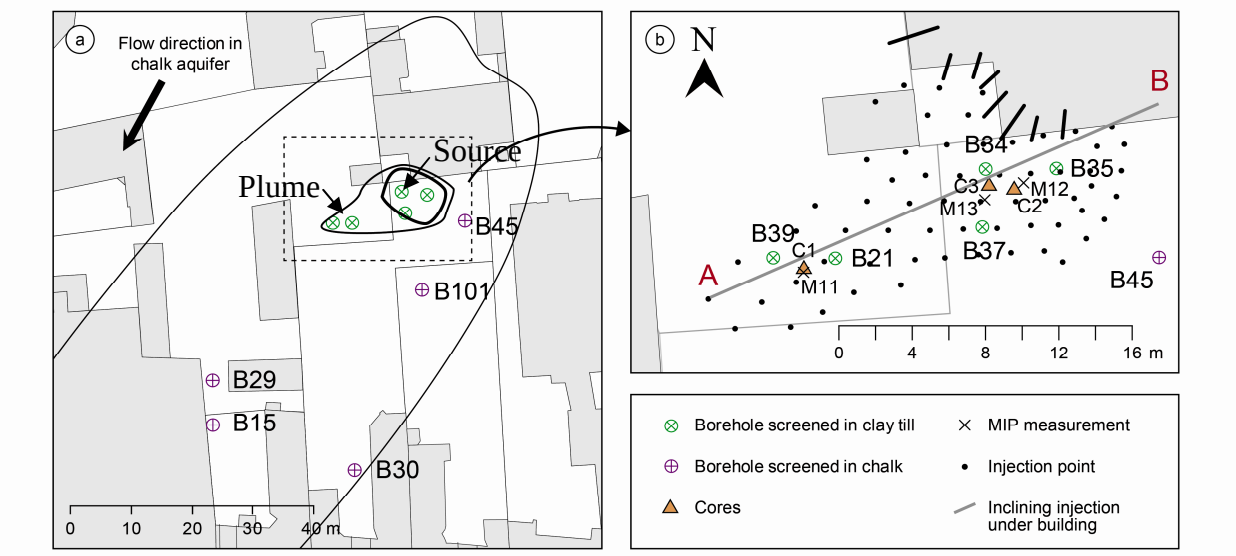

FIGURE 2. Gl. Kongevej site. TCE-contamination and network of injection points for substrate and bioaugmentation culture in source and plume areas in clay till. Modified from Damgaard et al. (2012).

INVESTIGATIVE ACTIVITIES

An integrated investigative approach consisting of water and clay core sample analysis, including stable isotopes and specific degraders, as well as analysis for chlorinated solvents, degradation products, donor fermentation products and redox-sensitive parameters combined with modelling was applied.

Groundwater monitoring of selected wells for chlorinated solvents, degradation products, donor fermentation products, redox-sensitive parameters and specific degraders was performed 2-3 times per year. Water sample chemical analyses were conducted by certified laboratories. For Sortebrovej, analysis for *Dhc* and the vinylchloride reductase gene *vcrA* were conducted by GEUS. For Gl. Kongevej, analysis for Dhc was conducted by Bioclear. In a separate sampling round at Gl. Kongevej, 4-5 years after initiation of ERD, sampling and analysis for *Dhc*, dehalobacter (*Dhb*), the vinylchloride reductase genes *vcrA* and *bvcA* and activity of *vcrA* and *bvcA* were conducted by GEUS. In the same sampling round, samples for stable carbon isotope analysis by University of Neuchatel were also collected. These microbial analyses and stable isotope analyses are described in detail in Damgaard et al. (2012).

Coring and detailed profile subsampling. Clay till cores were collected from the treated areas at Sortebrovej after 2 and 4 years after initiation of ERD. At Gl. Kongevej cores were collected after 4 years. The location of cored boreholes at the sites is shown in Figures 1 (Sortebrovej) and 2 (Gl. Kongevej). Very detailed subsampling (on 0.25-5 cm scale) of the intact clay cores for matrix profile analysis was performed. Only the 4-year data is presented in this paper. Analysis for chlorinated solvents, degradation products, donor fermentation products and redox-sensitive parameters in clay till samples were conducted as described earlier by Scheutz et al. (2010). Selected clay core subsamples from Sortebrovej were analysed for *Dhc* and *vcrA* by GEUS. For Gl. Kongevej, selected core subsamples were analysed for stable carbon isotopes by University of Neuchatel and selected core subsamples were analysed for *Dhc*, *Dhb*, *vcrA*, *bvcA*, and *vcrA* and *bvcA* activity by GEUS. These microbial analyses and stable isotope analyses are described in detail in Damgaard et al. (2012).

Modelling. The transport including matrix diffusion and degradation in fractures/sand stringers and in bioactive zones in the clay till adjacent to the fractures/sand stringers was modelled to gain insight on remediation efficiency and timeframes. Further description of the modelling was given in Chambon et al. (2010) and Manoli et al. (2012).

RESULTS

Selected results for each site representing the variation in ERD development over 4 years are presented below. In general, groundwater monitoring results represent the development in sand stringers, fractures and/or other high permeability features in the clay till. In contrast, the low-permeability matrix can only be evaluated from clay till samples and requires relatively detailed sampling.

Sortebrovej site. The groundwater monitoring for most monitoring wells in the treated zone showed fast degradation of TCE to cis-DCE corresponding to an increase in degree of dechlorination (DoD) to 33% (few months) and slower further degradation of cis-DCE via VC to ethene approaching a DoD of about 50% (mix of cDCE, VC and ethene), where it leveled off. However, in some wells practically complete dechlorination with DoD >95% was observed.

Large variation was likewise observed in the development of ERD in the clay till matrix. Profiles of TCE and degradation products for cored boreholes representing an area where DoD in groundwater leveled off at about 50% (B370) and an area where DoD reached >95% (B371, located ~20 m from B370) are illustrated in Figure 3. No difference in clay till type or texture for the 2 locations was recorded. In the upper part of B370, relatively narrow zones with TCE degradation to cis-DCE and VC with little apparent ethene production are observed mostly in relation to imbedded sand stringers. Microbial analysis confirmed the presence of *Dhc* and *vcrA* in the narrow zone with TCE degradation in the matrix surrounding a sand stringer. In the deeper part of the clay till, no significant dechlorination appears to be taking place. This is likely a result of inadequate substrate injection and distribution.

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In B371 much more significant degradation is occurring. Practically complete degradation is seen in some parts and degradation to cis-DCE with minor further dechlorination is seen in other parts. The total concentration level appears to have decreased significantly and even where complete dechlorination appears to have taken place, the ethene and ethane concentrations are low. This indicates loss or further degradation of ethene and ethane. It is also noteworthy that VC concentrations are low compared to cis-DCE and ethene, suggesting cis-DCE to be the time-limiting step in the sequential dechlorination.

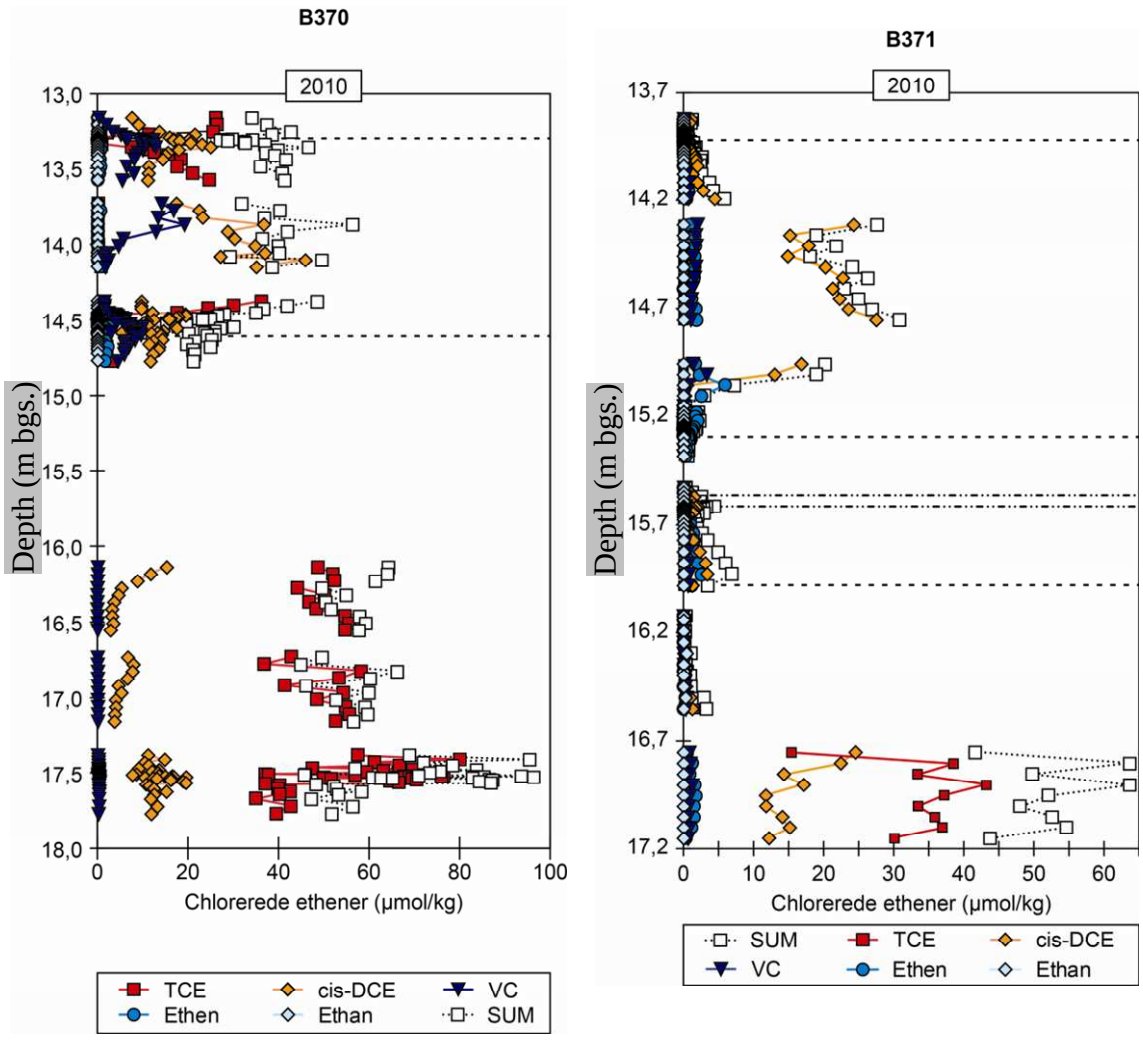

FIGURE 3. Sortebrovej Site. Detailed concentration profiles for TCE and degradation products in clay till for 2 cored boreholes representing different ERD developments.

Gl. Kongevej site. In the source zone, where TCE concentrations were very high, degradation to cis-DCE and subsequently via VC to ethene and ethane progressed relatively slowly in the groundwater and has reached a DoD of 50-90% in 4 years. In the plume (in clay till), degradation was initially much faster but leveled off at DoD ~70% (mix of cis-DCE, VC and ethene/ethane). Then TCE and cis-DCE re-bounded, resulting in a DoD-decrease to about 50%. The rebound was apparently due to donor limitation in the high-permeability features in the plume area. High numbers of *Dhc* and *vcrA* were observed in the groundwater in both the source zone and plume, and activity of the degraders was documented in both plume and source zone. However, a lower activity was found in the plume than the source, which suggests a decreasing activity in response to donor depletion in the plume.

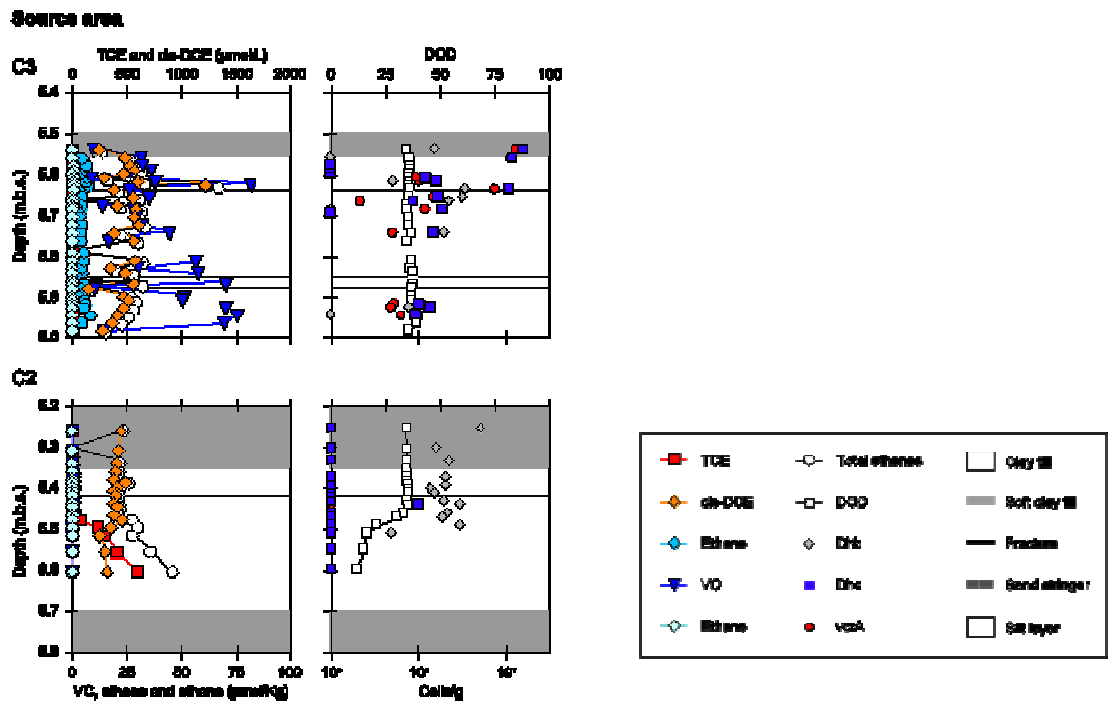

FIGURE 4. Gl. Kongevej site. Example core sections from the source zone illustrating sequential dechlorination and microbial composition. Modified from Damgaard (2012).

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The analysis of core subsamples from the source zone revealed a 1.8 m long zone where TCE had been degraded to cis-DCE in the upper part of the clay till (in C3). In part of this zone, further degradation to VC and ethene had started to take place, see Figure 4 core C3. In this part of the zone, microbial analysis revealed high numbers of *Dhc* and *vcrA* and less frequently *Dhb*. In the deeper and much firmer clay till, the analysis revealed narrow zones with degradation of TCE to cis-DCE, but without significant further dechlorination to VC and ethane. One such narrow zone is illustrated in Figure 4 core C2. In this zone only single samples near fractures had a measurable content of *Dhc*, whereas *Dhb* were abundant. Hence, it appears that *Dhb* rather than *Dhc* were responsible for TCE-degradation to cis-DCE. Stable carbon isotope analysis suggested that kinetic desorption of TCE is limiting the further sequential dechlorination of cis-DCE. This, in turn, suggests that the dynamic change in microbial population composition (from *Dhb* to *Dhc* with *vcrA*) in the matrix may be controlled by kinetic TCE desorption.

In the treated plume VC and/or cis-DCE were the dominant compounds in the clay till matrix and *Dhc* with *vcrA* completely dominated over *Dhb*. The rebound in the groundwater was not reflected in the core, but was likely caused by flow in permeable features from other areas with less degradation in the matrix. A more thorough analysis of the results from Gl. Kongevej is given in Damgaard et al. (2012).

LESSONS LEARNED

The chlorinated solvent TCE was converted into its daughter products (DCE, VC and ethene) but complete conversion of contaminants to ethene (as expected) was not achieved within a timeframe of 4 years. Large variation in the effect of ERD in the clay matrix between sites, boreholes and even between cores was observed. After 4 years, the mass removal at the 2 sites varied between <5% and 50% within the treated zones. The limited efficiency of the bioremediation in terms of mass removal is due to the limited spatial extent of dechlorination. If degradation is restricted to narrow bioactive zones of a few cm developing around fractures and sand stringers, contaminants in the remaining part of the matrix are not degraded and remediation efficiency is low due to the mass transfer limitations. However, the bioactive zones may expand in zones where both donor and chlorinated compounds are present. And in some cores TCE was depleted (degraded to DCE) in zones up to 1.8 m thick – an extent which could not be explained by diffusive loss to narrow bioactive zones. Hence, biomass migration in the clay matrix appears to play an important role in terms of contaminant mass reduction.

ACKNOWLEDGEMENTS

The site investigations,sample and data analysis were funded by the Region of Southern Danmark and the Capital Region of Denmark and the Danish Council for Strategic Research funded research project REMTEC, Innovative REMediation and assessment TEChnologies for contaminated soil and groundwater, contract 2104-07-0009.

Technical staff at DTU Environment assisted with field and laboratory work and graphics. Stable isotope analysis were performed by University of Neuchatel. Microbial analysis were conducted by the Geological survey for Denmark and Greenland (GEUS).

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