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Site characterization and in-situ remediation in fractured geologic media contaminated by chlorinated solvents.

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Characterization of dense non-aqueous phase liquid (DNAPL) source zone architecture is essential to develop accurate site specific conceptual models, delineate and quantify contaminant mass, perform risk assessment, and select and design remediation alternatives. The activities of a distribution facility for perchloroethene (PCE) and trichloroethene (TCE) at the Naverland site near Copenhagen, Denmark, has resulted in PCE and TCE DNAPL impacts to a fractured clay till and an underlying fractured limestone aquifer/bedrock. The scope of the investigations was to evaluate innovative investigation methods and characterize the source zone hydrogeology and contamination to obtain an improved conceptual understanding of DNAPL source zone architecture in clay till and bryozoan limestone bedrock.

A wide range of innovative and current site investigative tools for direct and indirect documentation and/or evaluation of DNAPL presence were combined in a multiple lines of evidence approach. Though no single technique was sufficient for characterization of DNAPL source zone architecture, the combined use of membrane interphase probing (MIP); coring with quantitative subsample analysis, SudanIV test, and PID; and NAPL FACT FLUTe gave good insight in the source zone architecture in the clayey till. Surface geophysics with ground penetrating radar (GPR) and seismic reflection and refraction combined with geologic information supplemented the conceptual understanding of transport and distribution of DNAPL in the fill and clayey till and the interface to the limestone. Core loss in the limestone, particulary from soft zones in contact with flint beds, was caused by the water flush applied during drilling and likely also resulted in loss of DNAPL from high permeability features. Hence, coring and subsampling for quantitative analysis and SudanIV tests continues to be an unresolved challenge in limestone. The coring may also have impacted DNAPL in high permeability zones near the borehole, thereby, potentially affecting the use of the NAPL FLUTe. Water-FLUTe multilevel groundwater monitoring and sampling (under two flow conditions) and FACT-FLUTe sampling and analysis provided important information regarding potential presence of DNAPL versus dissolved and sorbed phase contamination in the limestone

matrix. These combined methods provided an improved conceptual understanding of DNAPL source zone architecture in fractured limestone. The DNAPL source zone architecture in the clay till was consistent with conceptual expectations. In contrast the documentation for and quantification of DNAPL in the limestone aquifer was limited and demands refinement of techniques and further characterization.

Contamination with chlorinated solvents, constituting a threat to groundwater resources, often occurs in low permeability sediments such as clayey tills overlying aquifers. Clayey tills are mostly fractured, and solvent migrating through the fractures has spread to the low permeability matrix by diffusion. This results in a long term source of contamination due to back-diffusion. The challenge in remediation of the low permeability matrix by biological in-situ technologies is to bring the donor and bacteria and the contaminant in contact. Remediation of the matrix is diffusion limited, as contaminants has to diffuse through the matrix to natural or induced fractures and/or sand stringers or lenses, where donor and specific degraders can be supplied, or donor has to diffuse into the matrix. The principal challenge for in situ remediation in clay is to achieve effective contact between contaminant and bioremediation additives (e.g., organic electron donors and bioaugmentation cultures).

Stimulated reductive dechlorination (SRD) in some cases including bioaugmentation with specific degraders has proven to be very efficient for remediation of sandy aquifers, but knowledge regarding the effectiveness for remediation of low permeability sediments such as clayey till is lacking. SRD is currently being tested/applied at a number of Danish sites with chlorinated ethene contamination in clayey till. Model calculations reveal that the treatment period for significant solvent concentration reduction in a clayey till matrix (0.3 m to 1 m between fractures) will likely be 10 to >100 years, if biodegradation is restricted to the fractures.

Enhancement techniques, such as environmental fracturing offers assistance to remediation efforts at contaminated, low-permeability sites via creation of active fracture networks, and hence, reduction of mass transport limitations set by diffusion in low-permeability matrices. Pilot studies of pneumatic fracturing, hydraulic fracturing and direct push injections, focusing on direct documentation of fracture propagation patterns and spacing and tracer distribution, were performed at a typical basal clay till site. Direct push injection (3 point cluster, 25 cm spaced injections) was most successful in distributing tracer in the clayey till (2-10 m bgs.). Enhancement techniques providing a sufficiently close spacing between reaction zones are essential for obtaining sufficient remediation of the clayey till matrix. Direct push injection was found promising with respect to enhancement of SRD in clayey till.

At Rugårdsvej a slow release donor (Newman Zone) and specific degraders (KB-1 culture) was applied by injection in a hydraulic induced sand-filled fracture. Groundwater monitoring showed complete degradation of c-DCE and VC to ethene in the induced fractures was obtained within 5 months. After 5 months the effect of the stimulated degradation in the clayey till matrix was documented through detailed profiles of sediment samples from intact cores of the clayey till. These profiles revealed a reaction zone in the clayey till in contact with the induced fracture, where biodegradation of c-DCE and VC in the low permeability matrix was documented. The development of a reaction zone in the matrix greatly increases the potential for SRD in the clayey till.

The feasibility and performance of full-scale applications of ERD in clay tills were investigated in a research project including 2 sites in Denmark undergoing remediation since 2006. At the Sortebrovej site an emulsified oil donor (EOS) and a bio-augmentation culture (KB1®) with specific degraders Dehalococcoides were injected in a net-work of screened wells and spread in natural sand stringers embedded in the clay till. At the Gl. Kongevej site organic molasses donor and Bioclear Dechlorinating bioaugmentation culture with specific degraders Dehalococcoides were injected with a drive-point probe (Geoprobe) at 25 cm spaced vertical intervals in the clay till in a closely spaced network.

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 was performed 2-3 times per year, and very detailed subsampling (on 0.25-5 cm scale) of the intact clay cores for matrix profile analysis was performed after 2 and 4 years. 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 the effects of sand stringer/fracture /injection spacing, thickness of bioactive zones, density/numbers of specific degraders, donor longevity, etc., on remediation efficiency and timeframes.

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.

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Our new focus area with respect to chlorinated solvent contamination, transport, fate and remediation is on limestone aquifers. It involves both hydrogeological and chemical characterization of the aquifers and contamination and natural and stimulated bioremediation including enhancement methods such as electrokineticly facilitated transport.

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