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A remediation performance model for enhanced metabolic reductive dechlorination of chloroethenes in fractured clay till

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ABSTRACT

A numerical model of metabolic reductive dechlorination is used to describe the performance of enhanced bioremediation in fractured clay till. The model is developed to simulate field observations of a full scale bioremediation scheme in a fractured clay till and thereby to assess remediation efficiency and timeframe. A relatively simple approach is used to link the fermentation of the electron donor soybean oil to the sequential dechlorination of trichloroethene (TCE) while considering redox conditions and the heterogeneous clay till system (clay till matrix, fractures and sand stringers). The model is tested on lab batch experiments and applied to describe sediment core samples from a TCE-contaminated site. Model simulations compare favorably to field observations and demonstrate that dechlorination may be limited to narrow bioactive zones in the clay matrix around fractures and sand stringers. Field scale simulations show that the injected donor is expected to be depleted after 5 years, and that without donor re-injection contaminant rebound will occur in the high permeability zones and the mass removal will stall at 18%. Long remediation timeframes, if dechlorination is limited to narrow bioactive zones, and the need for additional donor injections to maintain dechlorination activity may limit the efficiency of ERD in low-permeability media. Future work should address the dynamics of the bioactive zones, which is essential to understand for predictions of long term mass removal.

1. Introduction

Chlorinated solvents are widespread subsurface contaminants and may pose a threat to groundwater. In many places in North America and Northern Europe, contaminant sources are located in fractured low permeability deposits such as glacial clay tills. In these geological settings, contaminants slowly diffuse from fractures and sand stringers into the clay matrix and become a long-term source of contamination. These sources can impact an underlying aquifer for hundreds of years because of slow back-diffusion and leaching (Chambon et al., 2010; Hønning et al., 2007b; Reynolds and Kueper, 2002). Remediation of such sites is challenging because of the mass transfer limitations due to negligible advection and slow diffusion process in the low-permeability clay matrix (Parker et al., 1997).

Enhanced Reductive Dechlorination (ERD) has been successfully applied to sandy aquifers for in-situ remediation of dissolved phase chlorinated solvents (Lee et al., 2008; Loffler and Edwards, 2006; Major et al., 2002; Scheutz et al., 2008), but the performance of the technology has not yet been fully investigated in fractured clay tills (Scheutz et al., 2010). ERD of chlorinated ethenes is generally achieved by bioaugmentation and/or biostimulation where biomass and/or substrate are injected to stimulate degradation (Loffler and Edwards, 2006; Major et al., 2002; Scheutz et al., 2008). Efficient mixing and contact between contaminants, substrate and specific degraders (bacteria of the genus *Dehalococcoides*, MaymoGatell et al., 1997) are necessary for

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complete dechlorination to ethene and efficient cleanup. In low permeability formations bioremediation is limited by diffusion-controlled transport in the clay matrix so that complete mass removal of contaminants is difficult and post-treatment rebound can occur (Chambon et al., 2010; Mundle et al., 2007).

A significant amount of work has been done in the last decade to model low permeability settings and the metabolic reactions involved in the reductive dechlorination process (see Table S1 in the SI [Supporting Information]). In order to evaluate ERD as a remediation technology in clay tills, it is necessary to understand and be able to predict the fate of contaminants and applied donor in a heterogeneous clay–sand system. Recent studies have addressed the issue of modeling ERD in fractured clay tills (Chambon et al., 2010; Scheutz et al., 2010), demonstrating the fundamental role of heterogeneities (fractures and sand stringers) in determining remediation performance. Chambon et al. (2010) simulated transport and sequential dechlorination of trichloroethene (TCE) in a single fracture–clay matrix system using modified Monod kinetics. Lemming et al. (2010) extended this to a system with horizontal injection zones where the need for a close spacing between injections points was demonstrated. Scheutz et al. (2010) showed the development of bioactive zones extending approximately 5 cm in the clay matrix at the fracture–matrix interface by comparing field observations with a diffusive first-order biodegradation model. However, none of these models includes the electron donor limitation that is crucial for bioremediation design. More recently Takeuchi et al. (2011) showed that microbial dechlorination of TCE to VC was taking place in a clay aquitard, despite the small pore size of the clay layer.

To simulate the performance of ERD it is necessary to couple the dechlorination processes to the substrate added. Existing studies consider a direct addition of H_2 (Clapp et al., 2004; Cupples et al., 2004b) or simulate the fermentation of simple primary substrates such as lactate (Fennell and Gossett, 1998), glucose (Lee et al., 2004) or pentanol (Christ and Abriola, 2007). However, commercial soybean oil donors such as EOS® emulsion (EOS Remediation, LLC, North Carolina, U.S.) and Newman Zone® (RNAS Inc., Minnesota, U.S.) are more complex, consisting of a mixture of long-term electron donors. For these donors a new modeling approach is necessary.

The chemistry of dechlorination is quite complex. The presence of H_2 is necessary for dechlorination and is produced by substrate fermentation (Fennell and Gossett, 1998). In the degradation reaction, thermodynamic inhibition of donor fermentation is a controlling factor (Fennell and Gossett, 1998; Lee et al., 2004), but most studies neglect the process (Christ and Abriola, 2007). Most existing models account for methanogenesis (Christ and Abriola, 2007; Clapp et al., 2004; Fennell and Gossett, 1998; Lee et al., 2004), but other terminal electron-accepting processes (TEAPs) have often been ignored. A simplified model capable of linking the fate of injected substrate to the transformation of contaminants while considering redox conditions, transport, and geological heterogeneities, is developed here and is an innovative tool for engineers designing ERD systems.

Currently available models describing the reductive dechlorination processes observed in laboratory experiments generally neglect the redox processes occurring in aquifers (Cupples et al., 2004a, 2004b; Fennell and Gossett, 1998; Lee et al., 2004; Yu and Semprini, 2004). Under field conditions, nitrate, $Mn(s)^{3+/4+}$, $Fe^{3+}(s)$ and sulfate can act as terminal electron acceptors thus limiting the amount of hydrogen available for dechlorination (Watson et al., 2003). In Kouznetsova et al. (2010) a detailed laboratory scale geochemical batch model is presented, but simulation results are not compared with experimental data. In general, the existing metabolic models have been developed and applied at the laboratory-scale and have not been compared with field observations from a full scale bioremediation (see Table S1 in the SI). In this paper such a laboratory and field model is presented.

The objectives of this study are (1) to present a model of ERD in clay till (2) apply the model to simulate laboratory and field scale data at a full scale ERD and (3) use the model for process understanding and long term evaluation of donor consumption and remediation performance. The aim is to combine modeling with monitoring at different scales for system understanding and practical ERD design. Model calibration and uncertainty evaluation are beyond the scope of this study.

A conceptual and numerical model of metabolic ERD is presented in this paper. The model is coupled to a 1-D transport model to describe field observations from sediment core samples (heterogeneous clay with interspersed fractures and sand stringers). The metabolic ERD model includes a simplified fermentation step, inhibition of fermentation by H_2, modified Monod kinetics of dechlorination, and competition by methanogenesis, iron, and sulfate reduction. The model is tested on laboratory experiments and is then applied to sediment core samples from a contaminated site undergoing ERD. Multiple 1-D simulations are used to assess the remediation timeframe and donor lifetime for the entire source at the site. The paper is the first to compare a model of transport and metabolic ERD in fractured clay till with laboratory and field observations. The model is particularly relevant for field applications of ERD in clay tills which are common subsurface deposits in for instance Canada, parts of USA and Northern-Europe.

2. Field and laboratory case study

2.1. Field case study

The model is benchmarked on data from a TCE-contaminated site located at Sortebrovej 26, Tommerup, Denmark. The site is characterized by two fractured clay layers, which are two lodgement tills (Haldorsen and Kruger 1990), divided by a hummocky sandy layer and overlying the regional aquifer located around 40 m below surface (mbs). The site was contaminated by approximately 25 kg of TCE located in the upper fractured clay till between 13 and 22 mbs. The contamination originated from a workshop active over a period of 13 years in the 1970's, however, very poor historical records exist. It is assumed that TCE was released as DNAPL, migrated downwards through the preferential pathways formed by vertical fractures and rapidly dissolved and diffused from the fractures into the low-permeability matrix. Analysis of sediment cores before implementation of bioremediation indicated TCE concentrations of up to 10 mg/kg in the source zone. The redox