Advances in Water Resources 33 (2010) 969–986

Contents lists available at ScienceDirect

Advances in Water Resources

journal homepage: www.elsevier.com/ locate/advwatres

Biological reduction of chlorinated solvents: Batch-scale geochemical modeling

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ARTICLE INFO

Article history:
Received 29 August 2009
Received in revised form 29 April 2010
Accepted 30 April 2010
Available online 7 May 2010

Keywords:
Modeling
Groundwater
Bioremediation
Chlorinated ethenes
Biogeochemical reactions
Sensitivity analysis

ABSTRACT

Simulation of biodegradation of chlorinated solvents in dense non-aqueous phase liquid (DNAPL) source zones requires a model that accounts for the complexity of processes involved and that is consistent with available laboratory studies. This paper describes such a comprehensive modeling framework that includes microbially mediated degradation processes, microbial population growth and decay, geochemical reactions, as well as interphase mass transfer processes such as DNAPL dissolution, gas formation and mineral precipitation/dissolution. All these processes can be in equilibrium or kinetically controlled. A batch modeling example was presented where the degradation of trichloroethene (TCE) and its byproducts and concomitant reactions (e.g., electron donor fermentation, sulfate reduction, pH buffering by calcite dissolution) were simulated. Local and global sensitivity analysis techniques were applied to delineate the dominant model parameters and processes. Sensitivity analysis indicated that accurate values for parameters related to dichloroethene (DCE) and vinyl chloride (VC) degradation (i.e., DCE and VC maximum utilization rates, yield due to DCE utilization, decay rate for DCE/VC dechlorinators) are important for prediction of the overall dechlorination time. These parameters influence the maximum growth rate of the DCE and VC dechlorinating microorganisms and, thus, the time required for a small initial population to reach a sufficient concentration to significantly affect the overall rate of dechlorination. Self-inhibition of chlorinated ethenes at high concentrations and natural buffering provided by the sediment were also shown to significantly influence the dechlorination time. Furthermore, the analysis indicated that the rates of the competing, nonchlorinated electron-accepting processes relative to the dechlorination kinetics also affect the overall dechlorination time. Results demonstrated that the model developed is a flexible research tool that is able to provide valuable insight into the fundamental processes and their complex interactions during bioremediation of chlorinated ethenes in DNAPL source zones.

1. Introduction

Chlorinated ethenes are among the most common organic groundwater contaminants because of their wide use, and uncontrolled disposal and improper management [105]. Often released in substantial quantities, they are frequently present in the subsurface as dense non-aqueous phase liquids (DNAPLs). In a solvent DNAPL source zone, aqueous phase chlorinated ethenes continuously dissolve into groundwater, resulting in an aqueous phase plume emanating downgradient. Such plumes are of concern due to the carcinogenic and mutagenic potential of chlorinated solvents [97,113].

In situ biodegradation is an attractive technique for the treatment of chlorinated ethenes in soil and groundwater [83]. Under anaerobic conditions, tetrachloroethene (PCE) and trichloroethene (TCE) can be degraded by metabolic reductive dechlorination (i.e., dechlororespiration) in a sequential manner to less chlorinated compounds: dichloroethene (DCE), vinyl chloride (VC), and non-toxic ethene (ETH) [59]. The dechlorination process relies on the presence of electrons, whereby the chlorinated compound is used by microbes as the terminal electron acceptor and hydrogen (H_2) as the electron donor (e-donor). Other compounds can potentially serve as direct e-donor (e.g., acetate and formate), however their utilization depends on the microbial species involved and therefore may not occur readily [8,37,92]. Although direct addition of H_2 is possible in the field [1], H_2 is typically added indirectly by the injection of fermentable (primary) organic substrates (e.g., lactate, ethanol, pentanol, glucose, soybean oil) [35,59]. In the absence of external e-donors, biomass decay can slowly release H_2 sufficient to

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doi:10.1016/j.advwatres.2010.04.017

support dechlorination [96,110], referred to as endogenous respiration [66].

Rapid and complete dechlorination may be impeded by alternative terminal electron-accepting processes (TEAPs) competing with reductive dechlorinators for H_2 and short-chain fatty acids [16]. Competing microbial populations include denitrifiers, methanogens, acetogens, sulfate reducers and iron-reducers. Iron and sulfate are the most important alternative electron acceptors due to their ubiquity in aquifer systems and the similarity of the H_2 threshold for their respective TEAPs: ~2 nM for dechlorination [108], 0.1–0.8 nM for iron reduction [55], 1–4 nM for sulfate reduction [17,56].

Reductive dechlorination within DNAPL source zones is of particular interest as recent studies have demonstrated the ability of microbial isolates [4] and mixed dechlorinating consortia [15,34,67,109] to dechlorinate PCE at (or near) saturated aqueous phase concentrations to ETH. Additional benefits of source zone bioremediation include (i) reduced DNAPL longevity due to enhanced DNAPL dissolution [4,18,90,109,111], and (ii) toxic inhibition of microbial communities competing for e-donor (e.g., homoacetogens and methanogens [36,108]). In addition, employing substrates that partition into the DNAPL phase (e.g., emulsified vegetable oil) provides a long-term source of e-donor for biodegradation [111]. 'Enhanced' bioremediation refers to the addition of nutrients and/or dechlorinating microbial cultures to the subsurface to initiate or accelerate the process [59].

Descriptions of biodegradation of chlorinated ethenes in DNAPL source zones have focused on the main reactants, i.e., chlorinated ethenes, (fermentable) e-donor, and competing TEAPs (e.g., [4,19,36,48]). However, geochemical interactions occur also—both in response to biodegradation reactions and independently—and may play a critical role in the dechlorination process (e.g., [9]). Each dechlorination step produces one chloride ion, giving rise to hydrochloric acid (HCl) production. The combination of this strong acid and build-up of short-chain fatty acids formed during e-donor fermentation can result in significant groundwater acidification [2,21,72]. The pH may be partially buffered through the dissolution of calcite and iron oxides (e.g., goethite FeOOH, ferrihydrite $Fe(OH)_3$). However, the natural soil buffering capacity may be limited, and acidic conditions can inhibit microbial activity. Laboratory studies have demonstrated that the optimal pH range for anaerobic microbes is from 6.5 to 7.5 [54] and low pH has been shown to reduce microbial reaction rates [2,27,51,117]. The influence of pH on biodegradation is expected to be of particular importance during the treatment of DNAPL source zones, as opposed to chlorinated ethene plumes, due to the higher total mass of dechlorination and fermentation products generated.

Numerical models of varying sophistication have been developed to simulate the biodegradation of chlorinated ethenes and associated reactions. Table 1 summarizes the characteristics and capabilities of existing models, as well as the model presented here. A number of models assume direct addition of H_2 [4,22,31], while others include the fermentation of typical organic substrates used in field applications [6,19,35,48]. Competition for e-donor with TEAPs is neglected in models simulating systems with high levels of uniform contamination or laboratory studies with pure cultures [4,31]. However, systems with complex microbial ecology and non-uniform contaminant distribution require the simulation of competition for e-donor [6,19,36,48,107]. Some models have included competition between chlorinated ethenes [4,22,31,32], often assuming that the presence of more chlorinated ethenes exclusively inhibits the dechlorination of less chlorinated ethenes [107,115,116]. Self-inhibition (also known as Haldane inhibition) associated with high chlorinated ethene concentrations (up to 1000 μM) has also been considered in some models [4,58,115]. Dechlorination kinetics have been approximated by first order [15,25], Michaelis-Menten [41] and Monod-type rate equations [19,21,31,32]. In Michaelis-Menten and Monod-type formulations the dechlorination rate is limited by e-donor availability [4,6,22,36]. Several models include interphase mass transfer processes such as DNAPL dissolution [4,15,19,20,74,107] or transfer of H_2 from the gas to aqueous phase [22] while two have considered endogenous respiration [36,48]. None of the available dechlorination models have incorporated geochemical processes (e.g., mineral interactions, pH, and alkalinity).

This paper presents a general framework for modeling enhanced DNAPL source zone bioremediation that includes the interaction of key physical, biological and geochemical processes. The main goal is to use the model to assess dechlorination complexity and process feedbacks. As outlined in Table 1, the model accounts for e-donor fermentation, dechlorination of chlorinated ethenes, competing TEAPs (e.g., sulfate and iron reduction), growth and decay of multiple microbial communities, pH and alkalinity, mineral precipitation/dissolution, gas formation, and mass transfer of species between non-aqueous and aqueous phases. Although other complex models with comparable features exist, for example models that integrate the dependency of the reaction kinetics on the concentration of solutes [24,91], explicitly simulate growth and decay of bacteria [79] and account for pH-dependent bacterial growth [11], these complex biogeochemical models were applied in systems such as landfill leachate aquifer plumes and BTEX (benzene, toluene, ethylbenzene and xylene) spills [11,12,77–79,86]. The presented model is the first that accounts explicitly for reductive dechlorination by microbial communities as well as detailed soil–water geochemistry. In addition, it differs to most of the previous biogeochemical models, in which the organic substrate (contaminant) is consumed via a sequence of electron acceptors (redox zonation), since here the fermentation of organic substrate (e-donor) occurs simultaneously with the consumption of competing electron acceptors including the reduced chlorinated ethenes. This work provides an example of the interaction of the biological and geochemical processes in a base case simulation of a hypothetical batch system with high, aqueous phase chlorinated solvent concentrations. Subsequently, sensitivity analyses are performed to determine the dominant model parameters and processes in the system and their influence on the various subsets of reaction complexities.

2. Numerical model

Fig. 1 presents the main processes involved in the anaerobic degradation of chlorinated ethenes. For each process from Fig. 1 included in the model the associated reactions are provided in Table 2 (see corresponding process number). As illustrated in Fig. 1, microbially mediated fermentation and degradation processes are linked in the model by dynamic hydrogen concentrations. In addition, the model accounts for all relevant acid and alkalinity-associated reactions (e.g., aqueous speciation, gas formation, mineral interactions) to track pH and the subsequent effects on microbial populations. In this section, the various processes given in Fig. 1 are described mathematically.

The fermentation of an organic substrate (process 1 in Fig. 1) is generally described by Eq. (1) (Table 2). The stoichiometric yield coefficients for H_2, acetate (CH_3COOH) and CO_2 (x, y, and z, respectively) for commonly used substrates are provided in Table 3. The concentrations of H_2 generated can differ by orders of magnitude depending on H_2-production ceilings of the specific fermentation reaction (i.e., maximum levels of H_2 that can be achieved via fermentation [36]). This is accounted for in the model by an H_2 inhibition term. The intermediate products identified by Eq. (1) refer to the breakdown of complex substrates into compounds with simpler structures (e.g., volatile fatty acids, Table 3).

In the model, fermentation kinetics is expressed as:

$$\frac{dC_{ps}}{dt} = -k_{max}^{ps} X_{FB} \left(\frac{C_{ps}}{K_S^{ps} I_{CI} + C_{ps}} \right) F(pH) \phi(H_2) \left(1 - \frac{C_{H_2S}}{K_1^{H_2S}} \right), \quad (17)$$