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sabre bulletin

CL:AIRE SABRE bulletins describe specific, practical aspects of research from the LINK Bioremediation Project SABRE, which aimed to develop and demonstrate the effectiveness of *in situ* enhanced anaerobic bioremediation for the treatment of chlorinated solvent DNAPL source areas. This bulletin describes modelling tools developed to support remediation scheme design and provide insights for future application of the technology.

Insights and Modelling Tools for Designing and Improving Chlorinated Solvent Bioremediation Applications

1. INTRODUCTION

The chlorinated solvents tetrachloroethene (PCE) and trichloroethene (TCE) have been used extensively in industry and are now amongst the most common and hazardous groundwater contaminants (National Research Council, 2004). These solvents are typically present as dense, non-aqueous phase liquids (DNAPLs) and represent long-term source zones that produce persistent contamination plumes in aquifers (Johnson and Pankow, 1992). Under anaerobic conditions, chlorinated ethenes may be biodegraded via reductive dechlorination (the biologically mediated, step-wise removal of chlorine) to form ethene, a relatively innocuous end-product. The rate of reductive dechlorination can be enhanced by stimulating the activity of dechlorinating bacteria by injection of an electron donor (typically an organic substrate that generates hydrogen upon fermentation), nutrients and, in some cases, microbial communities known to dechlorinate effectively to ethene (i.e., bioaugmentation). Reductive dechlorination has been shown to be a viable technology for *in situ* treatment of dissolved chlorinated solvent plumes (e.g., Ellis et al., 2000; Major et al., 2002), and recent laboratory studies have suggested that this strategy may also be effective for chlorinated solvent DNAPL (Yang and McCarty, 2000). Here, the source zone is targeted directly, with the aim of reducing its lifespan by enhancing dissolution from the DNAPL and sorbed phases and coupling this with effective and sustained dechlorination near the DNAPL-water interface and within the plume (Aulenta et al., 2006).

The five-year SABRE project aimed to develop and demonstrate the effectiveness of *in situ* enhanced reductive dechlorination for DNAPL source areas (CL:AIRE SABRE Bulletin 1). It consisted of three main components: (i) microcosm and column laboratory studies to determine appropriate process conditions for effective DNAPL bioremediation; (ii) a field pilot-scale treatment test at a contaminated site in the United Kingdom to demonstrate and optimise the effectiveness of this bioremediation technique; and (iii) modelling studies to assist in the design of experiments and to provide insights and tools for future successful application of the technology. This bulletin focuses on the modelling component and is number 4 in a series of CL:AIRE Bulletins reporting the findings of the SABRE project. In Section 2, the modelling tools developed are summarised. In Section 3, insights gained from the models into factors controlling the rates and extent of enhanced source zone DNAPL bioremediation are discussed. Finally, Section 4 presents a summary of how the modelling tools can be used to assist future applications of this technology.

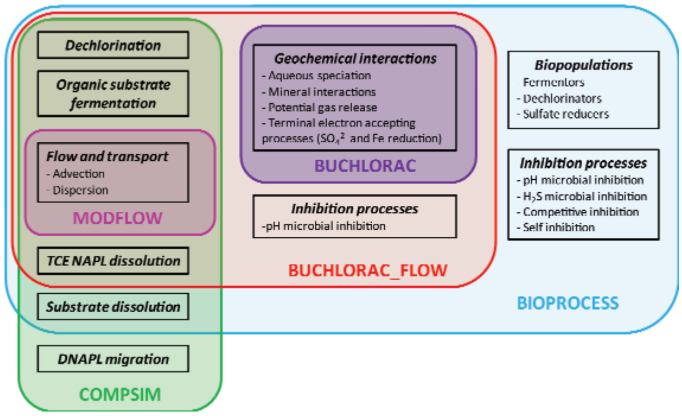

Figure 1. Overview of bioremediation relevant processes considered in the family of models used for the SABRE project.

2. MODELLING TOOLS

Reductive dechlorination of chlorinated solvents in groundwater involves complex interactions between physical, biological and geochemical processes. Key biological processes include microbially mediated dechlorination, sulphate reduction and iron reduction, electron donor fermentation, competition for electron donor, microbial inhibition from excessive chlorinated ethene and hydrogen sulphide concentrations, and microbial inhibition from non-neutral pH conditions. Key geochemical processes include kinetic mineral dissolution (e.g., calcite) and precipitation (e.g., iron sulphides), aqueous speciation reactions, sorption and the production of gases (e.g., CO_2). Key physical phenomena include advection, dispersion, diffusion, and interphase mass transfer. Four modelling tools were employed for the SABRE project, each with a distinct level of complexity as appropriate for addressing a specific set of research questions. Illustration of the processes considered by each of the models is shown in Figure 1; each is described in turn below. In general, the modelling successfully (i) assisted in the design and analysis of the SABRE laboratory and field experiments, (ii) validated the simulation methodologies via comparison with laboratory and field data, (iii) probed the feedbacks between the biological, geochemical, and physical processes, and (iv) provided tools to assist in future remediation scheme design.

2.1 MODFLOW (field-scale groundwater flow model)

A groundwater flow model was developed in MODFLOW (McDonald and Harbaugh, 1988) to analyse the hydraulic conditions in the SABRE field test cell and to evaluate different electron donor injection strategies.

MODFLOW is a simple, widely used and verified groundwater flow package. A model of the field test cell was set-up in MODFLOW based on preliminary geophysical investigations (Cheney et al., 2005). The model consisted of seven isotropic horizontal layers, each with different hydraulic properties. The model parameters were first calibrated using hydraulic data obtained during the baseline experimental period. The hydraulic conductivity of the most conductive geologic layers was found to control strongly the groundwater flow patterns in the test cell. Following calibration, the model was verified against measured water levels and was found to be able to represent successfully the average hydraulic conditions of the test cell. The model was then used as a tool to investigate physical factors influencing the performance of the test cell such as precipitation and clogging effects. The design of electron donor injection strategies was also investigated (number and location of injection wells, rates, etc.), with the objective of maximising the substrate distribution while minimising the cost of the on-site application.

2.2 COMPSIM (comprehensive simulator for field-scale bioremediation)

COMPSIM is a comprehensive numerical groundwater fate and transport model capable of simulating multi-phase, multi-dimensional and multi-component systems (Sleep and Sykes, 1993). COMPSIM has been validated and previously been used as an evaluation tool for a range of contamination and remediation scenarios (McClure and Sleep, 1996). COMPSIM includes the key processes controlling source zone dechlorination whilst also being computationally efficient. As a result it provides a practical platform for conducting field-scale simulations in terms of data requirements and execution time. The processes considered for the simulation of the SABRE experiments with COMPSIM include multi-phase advective and dispersive flow and transport, inter-phase partitioning (e.g., sorption, dissolution) and reaction. The sequential dechlorination from TCE to ethene is simulated using first-order reaction kinetics whereby the chlorinated ethene reaction rates vary linearly with the chlorinated ethene concentrations. Using this approach, the effects of electron donor and microbial concentration and other biogeochemical processes are lumped into a single rate constant for each dechlorination step.

The model was first validated against an analytical solution for one-dimensional contaminant transport with first-order sequential dechlorination (Beranger et al., 2005). COMPSIM was then used to simulate the column experiments conducted by the SABRE laboratory team (CL:AIRE SABRE Bulletin 3). For these simulations, the soil was assumed to be homogeneous and first-order dechlorination rates were assumed to be spatially uniform and constant within each time step. The flow and concentration boundary conditions adopted, including flow rate changes and variations in inlet TCE concentration, were based on the column set-up and data. The model was first calibrated against column tracer tests to determine values for soil properties such as porosity and dispersivity. Following this, the dechlorination column experiments were simulated and first-order dechlorination rates were fitted for sub-periods during the experiments. The agreement between the simulated and experimental data indicates that changes in chlorinated ethene concentrations were captured adequately (Figure 2). The calibrated dechlorination reaction rate constants over time followed a sigmoid function which suggests a Monod-type bacterial growth pattern. Prediction of these sigmoid functions is difficult as they depend on specific environmental conditions and, therefore, the results suggest

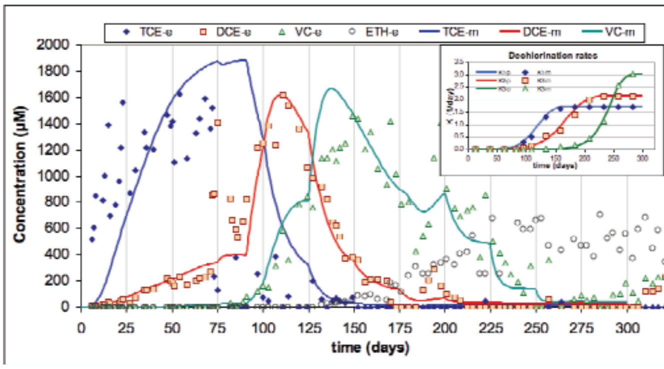

Figure 2. Comparison of experimental (symbols) and modelled (COMPSIM, solid lines) TCE and daughter product concentrations in the effluent of the SABRE column experiments (GE, Table 1 in CL:AIRE SABRE Bulletin 3). The subplot shows calibrated rate constants for sequential dechlorination steps (symbols) and the Weibull function producing the best fit (solid lines).

that electron donor and bacterial concentrations also need to be considered for predictive modelling. For future simulation of the SABRE field scale experiment, the first-order decay approach will be replaced by a Monod formulation which incorporates the controlling variables as identified by the more comprehensive bio-geo-process model, BIOPROCESS.

2.3 BIOPROCESS (comprehensive bio-geo-process research model)

BIOPROCESS is a numerical model developed to simulate the complex suite of biological and geochemical processes governing anaerobic bioremediation. The purpose of this model was to (i) assist in the design and interpretation of the SABRE microcosm and column experiments (CL:AIRE Research Bulletin 6 and SABRE Bulletin 3), and (ii) provide insight into the feedbacks between processes controlling effective anaerobic source zone bioremediation design. For these reasons, it included the most comprehensive set of processes (Figure 1) with the consequence that it exhibits the highest computational demand in the SABRE family of models. The model was implemented through the modelling platform PHREEQC (Parkhurst and Appelo, 1999) for batch simulations and through PHAST (Parkhurst et al., 2004) for simulations including flow and reactive transport. The strength of this approach is the inclusion of well-accepted and comprehensive geochemical databases (e.g., minteq.v4, Allison et al., 1990). The model developed includes microbially mediated fermentation and degradation processes linked by dynamic hydrogen concentrations, growth and decay of multiple microbial populations, aqueous speciation, gas formation, mineral interactions and interphase mass transfer processes (Kouznetsova et al., 2010a). Monod-kinetic rate expressions linked to toxic and competitive inhibition are used to simulate the microbially mediated processes. In addition, the model accounts for all relevant acid and alkalinity-associated reactions to track pH and the subsequent effects on microbial populations.

BIOPROCESS was validated by comparing simulation results with the SABRE microcosm and column studies. The model kinetic rates adopted were first calibrated to results from the SABRE microcosm experiments (CL:AIRE Research Bulletin 6). This provided a database of key parameters controlling TCE dechlorination for batch conditions (e.g., nutrient addition, organic substrate type, bioaugmentation, TCE concentration) (Mao et al., 2010). An example of the good agreement between simulated and experimental results for six organic substrates is shown in Figure 3. The full version of BIOPROCESS was then validated

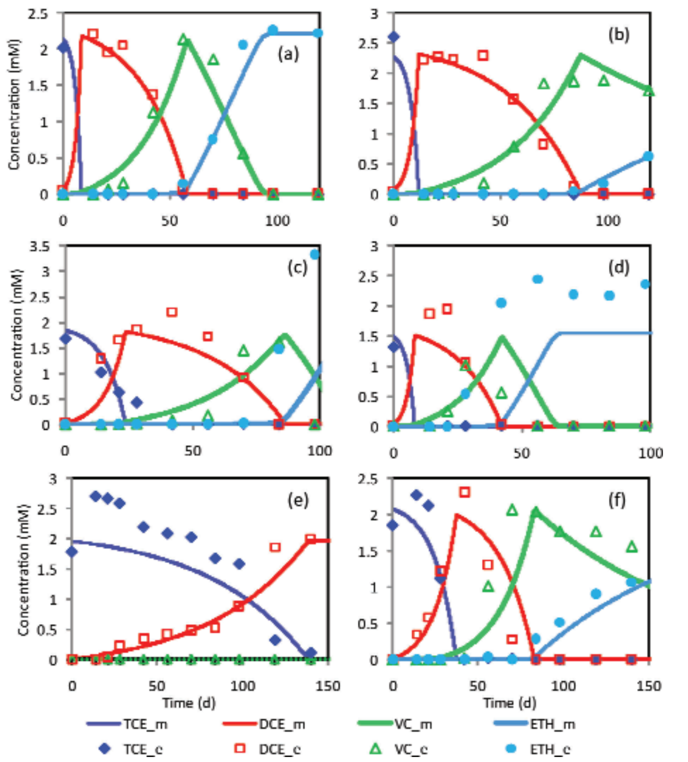

Figure 3. Comparison of experimental (symbols) and modelled (BIOPROCESS, solid lines) TCE and daughter product concentrations for the organic substrates (a) lactate, (b) acetate, (c) methanol, (d) SRS, (e) hexanol and (f) butyl acetate, in high TCE and bioaugmented microcosms. In all microcosms H_2 limitation was significant.

by simulating the GE column experiments in which 250 mg/l TCE was delivered to native soil in a 60 cm column for over one year (CL:AIRE SABRE Bulletin 3). The model results were consistent with the spatial and temporal column data, showing that (i) TCE concentrations rapidly decreased and vinyl chloride (VC) was observed close to the inlet, (ii) dichloroethene (DCE) was the main chlorinated ethene throughout the column and (iii) sulphate was observed throughout the column (Kouznetsova et al., 2010b). This comparison with experimental results provided confidence in the model processes incorporated and their interactions, particularly in the presence of injected electron donor. Ongoing work is now focused on improving simulation of the continued dechlorination that was observed in the column experiment following exhaustion of the organic substrate and also on extending the model to include the aqueous transport of (typically film-bound) microbial populations downgradient.

2.4 BUCHLORAC and BUCHLORAC_FLOW (pH buffer models)

SABRE laboratory and field experiments revealed that the development of acidic groundwater conditions associated with the extensive dechlorination occurring in source zones can significantly reduce the effectiveness of source zone remediation. To investigate this key issue and to assist in future remediation scheme design, BUCHLORAC (BUffering of deCHLORination ACidity) and BUCHLORAC_FLOW were developed to explore the geochemical processes influencing the acidity as dechlorination proceeds. The models simulate batch (microcosm) and flowing (*in situ*) conditions, respectively (Robinson et al., 2009; Brovelli et al., 2010a). In cases where the soils' natural buffering capacity may be insufficient and acidic conditions may develop, BUCHLORAC predicts the amount of external buffer (e.g., $NaHCO_3$) that needs to be added to maintain the groundwater pH at a level suitable for dechlorination. The model, developed in PHREEQC, accounts for the amount of chlorinated solvent degraded, site water chemistry, specific electron donor used, sulphate and iron reduction, gas production and soil mineralogy. Very good agreement was found between the model results and the significant pH decreases observed in the GE SABRE column experiment (CL:AIRE SABRE Bulletin 3). The model was then used to determine the buffer addition needed to prevent acidic conditions developing in the column experiments and, also, in the field test cell (CL:AIRE SABRE Bulletin 5). As buffer dosage systems may be a critical element to remediation system design, a version of BUCHLORAC with a Windows Graphical Interface was developed as an easy-to-use tool for engineers (Figure 4). The programme is available as free supplementary material with Robinson and Barry (2009) or from http://infoscience.epfl.ch/record/135054.

BUCHLORAC_FLOW was developed to further understand how the acidity build up in the DNAPL source zone is influenced by the complex interactions between the flow system, and *in situ* heterogeneity of physical, geochemical, and biological processes. This model is an extension of BUCHLORAC (Robinson et al., 2009) and includes flow and reactive transport, rate-controlled NAPL dissolution and sorption, and pH inhibition for dechlorination (Brovelli et al., 2010a). Confidence in BUCHLORAC_FLOW was achieved by simulating a well-documented field application in which pH decrease due to acid accumulation was observed (Brovelli et al., 2010a).

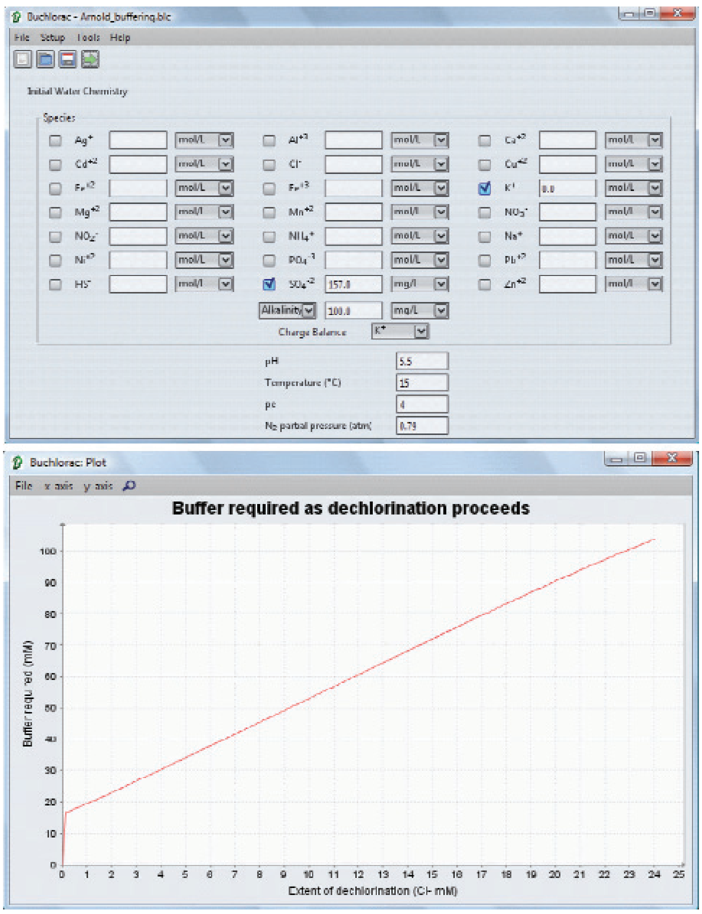

Figure 4. Screenshot of the graphical user interface BUCHLORAC. The upper window shows the form used to input the initial composition of the groundwater and the lower window is a generated plot of the amount of buffer required as dechlorination proceeds for a specific case study (Robinson and Barry, 2009).

3. INSIGHTS FROM MODELLING: FACTORS CONTROLLING THE RATE AND EXTENT OF DECHLORINATION

Modelling of the SABRE column experiments showed that significant variability should be expected in the rate and extent of dechlorination under different operating conditions. While first-order dechlorination rates calibrated using COMPSIM were consistent with values reported in the literature (Suarez and Rifai, 1999), comparison between simulations of the different SABRE column experiments revealed that dechlorination rates varied over two orders of magnitude. These variations were largely related to the organic saturation, TCE concentrations, presence of organic substrate and geochemical conditions (e.g., pH, sulphate concentrations). Therefore, to maximise dechlorination rates it is essential that the DNAPL saturation, organic substrate distribution and groundwater chemistry are carefully accounted for in the system design. Numerous processes compete for the hydrogen produced from fermentation of the injected organic substrate. Typically, a portion (sometimes a substantial portion) of the hydrogen produced is consumed by competing processes such as sulphate reduction, iron reduction, and methanogenesis. Results from BIOPROCESS simulations of the extensive SABRE microcosm dataset (CL:AIRE Research Bulletin 6) indicate that the fermentation rate of the injected organic substrate can be the rate-limiting step in the overall degradation of TCE to ethene, particularly in bioaugmented systems with high (e.g., > 200 mg/l) TCE concentrations. Lactate and SRS™ (a commercial soya oil emulsion provided by Terra Systems Inc.) were found to be the best performing substrates for the SABRE site conditions (CL:AIRE Research Bulletin 6), primarily because they are slowly fermented and the hydrogen produced is efficiently used by the dechlorinators. Modelling also showed the key role that competitive inhibition (i.e., the inhibition of daughter chlorinated ethenes by parent compounds) and toxic inhibition (i.e., microbial inhibition due to high chlorinated ethene concentrations) have in these systems. One benefit of modelling is that these inhibition terms can be isolated from the influence of other processes and quantified. Sensitivity analysis using the GE SABRE column conditions as the base case suggests that competitive inhibition becomes noticeable above TCE concentrations of 200 mg/l, and at 500 mg/l causes a 200% increase in the time required to achieve complete conversion to ethene. Independent from this, toxic inhibition causes an additional 300% slowdown of dechlorination at 500 mg/l TCE. It should be noted that for the GE column conditions, although relatively slow, BIOPROCESS predicted that continued dechlorination will occur up to 750 mg/l TCE (Kouznetsova et al., 2010a). This conclusion is supported by the SABRE microcosm (CL:AIRE Research Bulletin 6) and column experiments (CL:AIRE SABRE Bulletin 3).

Hydrochloric acid produced directly from dechlorination and organic acids generated from organic substrate fermentation both may contribute to significant groundwater acidification. Acidification from organic acids is greater when concentrations of dissolved sulphates are high in the groundwater as fermentation rates increase to meet the additional electron donor demand. Modelling for conditions at the SABRE field site indicates that the extent of acidification likely to occur depends on a number of factors including (i) the extent of dechlorination, (ii) the pH-sensitivity of dechlorinating bacteria, and (iii) the natural buffering capacity of the water and soil (Figure 5). This buffering capacity depends on the availability of buffering minerals such as calcite and the groundwater chemistry (e.g., alkalinity, sulphate and iron availability) (Robinson et al., 2009; Brovelli et al., 2010a). The substantial mass of solvents available for dechlorination when treating DNAPL source zones means that these applications are particularly

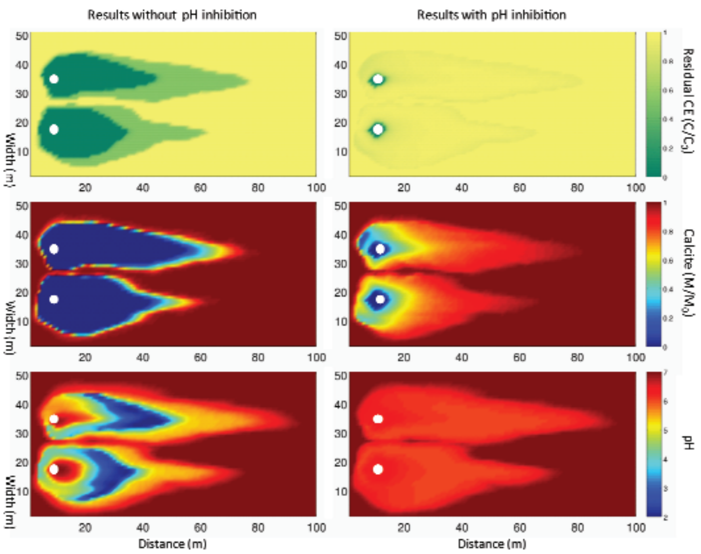

Figure 5. BUCHLORAC_FLOW simulation results showing the influence of pH-inhibition of microbial processes on dechlorination success at the field scale. Plots are shown in plan view and the simulations used a heterogeneous hydraulic conductivity distribution. The white circles indicate the wells where organic substrate (emulsified vegetable oil) was injected. The three panels on the left illustrate the residual chlorinated ethene (CE), residual calcite and the pH assuming microbial activity is not inhibited by non-neutral groundwater conditions. The panels on the right illustrate a more realistic case in which pH-inhibition is considered.

susceptible to acidification. In such cases, the addition of a buffering solution can help maintain pH at a level sufficient to ensure maximum microbial dechlorination efficiency (see CL:AIRE SABRE Bulletin 5). As the buffer dosage requirement is site-dependent, an easy-to-use Windows interface version of the program BUCHLORAC is available to assist with this calculation for specific operating and design conditions (Robinson and Barry, 2010).

Sensitivity simulations performed using BIOPROCESS showed that the mineral composition of the soil has further important consequences for the behaviour of the system in addition to the buffering requirement. For example, iron and sulphate minerals can supply dissolved species that compete for electron donor. These species also combine to precipitate significant quantities of iron-sulphide minerals; this was observed both in the modelling and in the column studies. The modelling, examining the situation of iron-poor soils, shows that such precipitation may not occur leading to the build up of dissolved hydrogen sulphide, whose toxicity to microorganisms may reduce dechlorination rates (Kouznetsova et al., 2010b). Thus, measuring the soil mineralogy at a site, and properly accounting for the interactions of those minerals with the site-specific water chemistry and biological processes should be considered in the optimisation of a bioremediation application.

BIOPROCESS simulations with conditions similar to the SABRE columns emphasise that the rate at which the microbial populations conduct fermentation and dechlorination is a controlling factor. Each microbial consortium evolves with time and therefore exhibits time-dependent dechlorination kinetics that impact significantly both the rate and the extent of dechlorination (Figure 6, Kouznetsova et al., 2010a). The growth rate of each population strongly affects the overall rate of TCE conversion, particularly in the start-up/acclimation phase. For these reasons, bioaugmentation with a suitable culture (particularly one with rapid dechlorination kinetics and containing members of the *Dehalococcoides* genus, which are key to converting VC to ethene (Duhamel et al., 2004)), is predicted to significantly accelerate clean-up times. This conclusion corroborates with the finding from the SABRE microcosm, column, and field studies.

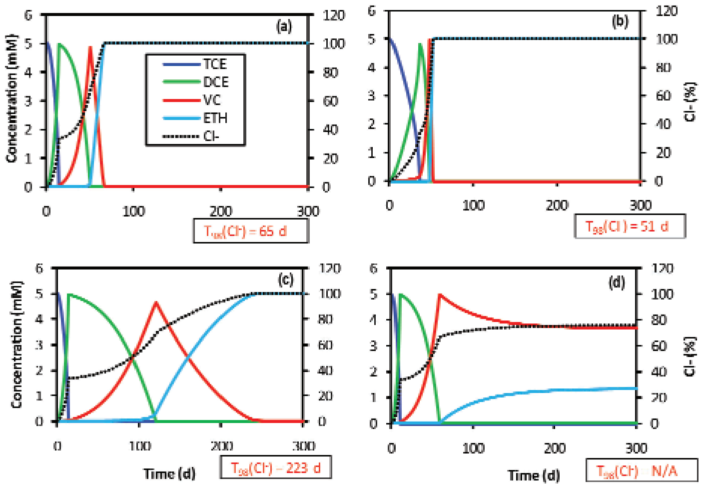

Figure 6. BIOPROCESS simulation results showing the influence of the dechlorination kinetics of different microbial cultures. The figures present chlorinated ethene concentration profiles over time for four microbial cultures in otherwise identical microcosm conditions (a) KB-1, (b) mixed cultures (Fennell and Gossett (1998)), (c) EV Culture (Yu 2003), and (d) PM culture (Yu 2003). In the lower right corner of each plot is the time (days) required for 98% conversion of TCE to ethene except for (d) where only 78% was converted after 300 d.

Groundwater flow rate (i.e., residence time in the active treatment zone) was observed to be an important factor in both column (Kouznetsova et al., 2010b) and field scale simulations (Brovelli et al., 2010b). BUCHLORAC_FLOW demonstrated that where substantial acid production occurs, higher flow rates may be beneficial by minimising acidity accumulation in the reaction zone and therefore reducing potential pH inhibition of dechlorination (Brovelli et al., 2010a). On the other hand, a lower flow rate can also be beneficial by reducing the overall time to reach complete conversion of TCE to ethene by providing the fixed-film microorganisms increased contact time for dechlorination. For specific site conditions, these competing effects should be considered in order to optimise the groundwater flow rate through the treatment zone.

Field scale SABRE modelling underscores another well known but important result: field site heterogeneity - of hydraulic conductivity, of DNAPL saturations, of solvent concentrations, and of mineral compositions - will result in irregular spatial distributions of (i) the injected electron donor, (ii) the injected buffer solution, (iii) chlorinated ethene daughter products, (iv) microbial density, and (v) acidity build-up (Brovelli et al., 2010b). High velocity flow paths through a system may limit residence/reaction time in high conductivity regions while also restricting access of injected fluids/nutrients to lower conductivity regions in which chlorinated solvents may be sequestered. This modelling result from a synthesised field scenario was corroborated by evidence at the field SABRE site of solvent and electron donor mass transport being dominated by a region of high hydraulic conductivity (CL:AIRE SABRE Bulletin 2). MODFLOW modelling of the hydraulics of the SABRE flow cell only included spatially varying layers each having homogeneous hydraulic parameters representative of the geological units observed at the site. However, by not accounting for the region of high hydraulic conductivity, this approach may have overestimated the residence time for bioremediation (CL:AIRE SABRE Bulletin 6). Future field scale modelling is exploring engineering approaches that may be employed to improve bioremediation success in physically and chemically heterogeneous systems.

4. USE OF MODELLING TOOLS

This project has developed and utilised models ranging from practical modelling tools for engineering design to research codes. These numerical models have proved valuable in interpreting and understanding laboratory and field data by providing insight into processes (and their interactions) that are difficult to observe directly. In addition, they have supported the design and optimisation of the SABRE field pilot-scale treatment test. At all scales and degrees of complexity, models are particularly valuable for evaluating what-if scenarios and examining the sensitivity of bioremediation performance to the natural and engineered site conditions. A summary of the modelling tools developed, including their potential to support and optimise future remediation scheme design, are outlined below (also see Figure 1).

- MODFLOW - This widely-used and simply applied groundwater flow code was useful for understanding the field scale hydraulics and in predicting and optimising basic field hydraulic design and amendment delivery (e.g., injection well placement, number of wells, organic substrate dosage rates). This model is freely available from the website of the United States Geological Survey (USGS) and numerous commercial vendors provide user-friendly interfaces for processing the input and output.

- BUCHLORAC - This model was developed as a practical and easy-to-use software tool that can provide detailed buffer dosage estimates for field dechlorination projects. With many remediation sites prone to groundwater acidification as dechlorination proceeds, implementation of pH control strategies may be crucial to the design of successful treatment schemes. The programme is available as free supplementary material with Robinson and Barry (2009) or from http://infoscience.epfl.ch/record/135054 (or contact Prof. C. Robinson, crobinson@eng.uwo.ca).

- BUCHLORAC_FLOW, an extension of BUCHLORAC that includes flow and reactive transport in multiple dimensions, was able to demonstrate how the acidity build up is influenced by field scale flow system, including *in situ* heterogeneity. This model is primarily a research tool, but could be readily applied to field sites by the developers on behalf of interested parties (contact Prof. D. A. Barry, andrew.barry@epfl.ch).

- COMPSIM - Incorporating the key processes that control source zone development and dechlorination, this model provides a practical and computationally efficient modelling platform for simulating bioremediation at the field scale. Once calibrated for specific field conditions, this model may be a useful design engineering tool that can most effectively be applied by the developers for interested parties (contact Prof. Brent Sleep, sleep@ecf.utoronto.ca). This model is also being used extensively in research on various groundwater remediation technologies.

- BIOPROCESS - Simulating the complex suite of processes, this numerical model was able to provide significant insight into the feedbacks between processes controlling effective bioremediation design, including sensitivity to potential inhibition factors. BIOPROCESS was also useful for analysis of the SABRE column experimental data. The understanding gained from this model will help direct future remediation scheme design. Due to the model's complexity, high computational demand and input requirements, its primary use is for research.

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