Multiphase flow and enhanced biodegradation of dense non-aqueous phase liquids: experimental design

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Abstract Simulation of biodegradation of dense non-aqueous phase liquids (DNAPLs) in the subsurface is often done by means of solute transport models that focus on biodegradation of a contaminant plume. Most models neglect the possibility of the presence of mobile DNAPL while biodegradation processes occur. However, during prolonged leakage of DNAPL from an underground storage tank, mobile DNAPL is present in the subsurface, and biodegradation in this area of multiphase flow may be important. Biodegradation of perchloroethylene (PCE), a common DNAPL, is possible at concentrations near the solubility limit. Large-scale sand box experiments are planned to study the interaction between two-phase flow and biodegradation of dissolved PCE close to the source area. The design of these experiments is presented and preliminary calculations for the optimum length of the sand box are carried out. It is found that the length must be 0.4 to 2.1 m, given a water velocity of 0.1 m day\(^{-1}\).

Key words biodegradation; DNAPL; multiphase flow; PCE; remediation; sand box experiments; UTCHEM

INTRODUCTION AND OBJECTIVES

It is known that the remediation of soil and groundwater contaminated by dense non-aqueous phase liquids (DNAPLs) is often very difficult. Major reasons are: (a) DNAPL can reach great depths in the subsurface due to its high density; (b) the solubility is low when considering the time needed for dissolution and flushing; on the other hand, (c) the solubility is too high when considering drinking water standards; (d) natural attenuation is often slow, i.e. DNAPLs are considered to be recalcitrant; and (e) if biodegradation occurs, it often leads to high concentrations of vinyl chloride, a very toxic metabolite.

A common method for DNAPL remediation is pump-and-treat, which has disadvantages such as the long time needed for flushing and the disappointing results when a low end-concentration must be achieved, as stated in a report by the US National Research Council (1994). Pump-and-treat relies on dissolution, diffusion and dilution processes, which are often very slow and limited by soil heterogeneities.

Bioremediation is a promising alternative, because the contaminant undergoes actual in situ degradation, instead of solute displacement and removal, and even low
end-concentrations can be achieved. The most widely used industrial DNAPLs are chlorinated ethylenes, such as perchloroethylene (PCE) and trichloroethylene (TCE). These compounds, which can serve as electron-acceptors under anaerobic conditions, are known to be degradable by soil microorganisms, provided that essential nutrients and a substrate are available. A substrate is defined here as the chemical compound that serves as an electron-donor and/or carbon source for microbial metabolism. In the case of DNAPL degradation, a substrate can be, for example, acetate or proprionate. In the case of oil degradation, the contaminant itself serves as a substrate for microbial metabolism.

When biodegradation of DNAPLs is studied, it is often assumed that only the contaminant plume needs to be considered. Degradation in the vicinity of the pure phase is considered not to be possible, because high concentrations of contaminant are thought to be toxic to microorganisms. Recent experiments by Nielsen & Keasling (1999), however, have shown that both PCE and TCE can be degraded under anaerobic conditions at their solubility concentrations, 200 mg l\(^{-1}\) and 1100 mg l\(^{-1}\), respectively. Therefore, we believe that degradation of PCE and TCE is not only possible near a source, but may also be significant in the case of a prolonged DNAPL spill. Moreover, their results show that at higher PCE or TCE concentrations, methanogenesis is inhibited, vinyl chloride (VC) gas production is much lower, while ethene production is much higher. The rate of VC gas production is very important, because VC has a much higher human toxicity compared to its parent compounds. The rate of both methane and VC production is also important because of the possible negative effect of gas production on the water relative permeability of the soil.

The above considerations show that biodegradation near a DNAPL source zone is most likely possible, and may also have important advantages. Although highly relevant for remediation actions, the combined processes of flow and biodegradation near a DNAPL source have so far not received much attention. As this subject deserves to be studied, we plan to analyse it using both numerical modelling and laboratory experiments. We have designed a large-scale sand box experiment to study biodegradation of DNAPLs under two-phase flow conditions.

The objectives of our study are: (a) to evaluate the significance and rate of biodegradation of dissolved contaminants during the two-phase flow stage, i.e. when DNAPL is mobile; (b) to study the form of microbial population (free bacteria, microcolony, biofilm) under such conditions; (c) to study the influence of microbial growth and population form on the two-phase flow properties; and (d) to study enhanced biodegradation—with the least possible interference—in a realistic system.

In this paper we present our experimental design, preliminary calculations, and our plans for modelling work with the multiphase flow-biodegradation simulator UTCHEM. Equations used in UTCHEM are documented in Delshad et al. (1996) and De Blanc et al. (1996).

**MATERIAL AND METHODS**

A set of large-scale, long term sand box experiments were designed to study the coupled biomass growth, biodegradation, and DNAPL flow processes. In designing these experiments, we had the following requirements in mind: (a) the experiments
must be mass-balanced, i.e. all mass flows must be accounted for; (b) temperature can be controlled; (c) both water flow and DNAPL flow can be controlled; (d) biodegradation can be controlled by adjusting the added amount of nutrient and substrate; (e) the degree of soil homogeneity and permeability should be high; (f) the contaminant must be known to be biodegradable at concentrations near the solubility limit; (g) the microbial culture must be able to completely degrade PCE to ethene; (h) excessive growth of contaminant non-specific bacteria must be inhibited; and (i) the experiments must be comparable to a natural system.

The experimental set up is shown in Fig. 1 (not to scale), and is described in the following section. Two containers with dimensions $2 \times 1 \times 1$ m will be placed in a temperature-controlled room. One of the containers will serve as the control system (not shown in Fig. 1). All flow and transport processes will be the same in the two containers except that biodegradation will be suppressed in the control container, by withholding nutrients and addition of a biocide to the water. As a result we can separate the effects of natural attenuation processes such as adsorption, from biodegradation.

The containers will be filled with pre-washed natural sand with a low organic carbon content. The filling procedure will be such that the packing will be as homogeneous as possible. Various measuring instruments will be installed and embedded before or during packing. In particular, we will install water sampling ports, soil sampling ports, manometers, TDR sensors, temperature and EC sensors, as indicated in Fig. 1. The front will be made of glass so that visual observation of the DNAPL spreading and microbial growth will be possible. After filling, the containers will be flushed with CO$_2$ from below, then saturated with water and sealed. The containers will then be flushed with anaerobic water and the achievement of anaerobic conditions will be tested.

Horizontal saturated water flow will be established in the containers. The inflow water will be pre-treated to make it anaerobic. DNAPL will be introduced at the top boundary at a very small constant flow rate for several months, in order to simulate a long-term leaking underground storage tank. The DNAPL spill is situated in the top 10 cm of the container, at about 1/3 of the horizontal length away from the upstream boundary, next to the front glass wall. In total, about 10 l of DNAPL will be introduced over a period of several months to a year. DNAPL will be collected at the bottom if necessary to avoid excessive pooling.

A microbial culture, capable of completely degrading PCE to ethene (as tested at concentrations near the solubility limit), will be added to the water of one of the containers. Nutrients and a substrate, which are both essential for microbial growth, must also be added to the water. Regular microbial analyses of soil and water samples will allow for control of contaminant non-specific bacteria. Since biodegradation is a slow process, the duration of the experiments is expected to be several months to a maximum of two years, with weekly monitoring of parameters. All materials that are used for the experimental set up, must be unaffected by DNAPL, i.e. made of either glass, steel or teflon.

The following factors can be varied to study the effects of coupled biomass growth, biodegradation and two-phase flow processes: (a) water flow rate, (b) DNAPL flow rate, (c) substrate concentration, (d) type of substrate (for example acetate or
propionate), and (e) amount of bio-augmentation. At a later stage, the type of DNAPL may be varied to study the effects of DNAPL properties such as density, solubility and DNAPL-water interfacial tension.

PRELIMINARY CALCULATION OF DIMENSIONS

In this section, some simple calculations are presented for estimating the dimensions of the experimental set up and flow rate. We used a one-dimensional solute transport
equation with a Monod sink term for biodegradation, assuming that substrate and nutrients are available in excess:

\[
\frac{\partial C}{\partial t} + v \frac{\partial C}{\partial x} - D \frac{\partial^2 C}{\partial x^2} = \frac{\mu_{\text{max}}}{Y} \frac{C}{(K + C)} X
\]

where \( C \) is concentration of contaminant [mg l\(^{-1}\)], \( t \) is time [day], \( v \) is groundwater velocity [m day\(^{-1}\)], \( D \) is dispersion coefficient [m\(^2\) day\(^{-1}\)], \( x \) is horizontal distance [m], \( \mu_{\text{max}} \) is maximum growth rate for microorganisms [day\(^{-1}\)], \( Y \) is yield coefficient (biomass produced divided by contaminant consumed, unitless), \( K \) is half-saturation constant [mg l\(^{-1}\)], and \( X \) is biomass concentration [mg l\(^{-1}\)].

Equation (1) can be made dimensionless by choosing a reference length \( L \) and a reference time \( Lt/v \). \( L \) should be considered as the length from the DNAPL spill location to the downstream boundary. Assuming that \( K \) is much smaller than \( C \), we obtain:

\[
\frac{\partial C^*}{\partial t^*} + \frac{\partial C^*}{\partial x^*} - \frac{1}{Pe} \frac{\partial^2 C^*}{\partial x^{*2}} = \frac{\mu_{\text{max}} X}{Y} \frac{L}{vC_0}
\]

where \( C_0 \) is the maximum solute concentration [mg l\(^{-1}\)], expected to be present next to the DNAPL source, and \( Pe = vL/D \) is the Peclet number. Dimensionless variables are designated by an asterisk. For our experimental work, a concentration decrease of about 95% is desirable to get a large concentration gradient and an outflow concentration that is still easily detectable. Therefore, when we assume steady state and neglect dispersion, the order of magnitude of the group on the right-hand side of equation (2) should be 0.95. This results in the following equation for \( L \):

\[
L = \frac{0.95vC_0 Y}{\mu_{\text{max}} X}
\]

If \( Y\mu_{\text{max}}^{-1}X^{-1} \) is assumed to be a known constant, we can estimate the length \( L \) for a fixed velocity \( v \). Note that the assumption of a constant \( X \) is not valid for long-term experiments, however, we can assume constant \( X \) if we choose a conservative (low) value for \( X \). We assume that \( \mu_{\text{max}}/Y \) for anaerobic biodegradation of PCE is equal to 4.58 mg PCE mg\(^{-1}\) day\(^{-1}\), after Nielsen & Keasling (1999). We assume that \( X \) is equal to 2–10 mg biomass per litre of pore water. This assumption is based on the work of Cirpka et al. (1999), who experimentally determined biomass concentration for anaerobic PCE degradation at 10°C in a sand box. Cirpka et al. (1999) found values for \( X \) of between 1.1 and 24.2 mg l\(^{-1}\). \( C_0 \) is set equal to the solubility of PCE: 200 mg l\(^{-1}\). In Table 1, the calculated values of length \( L \) for different values of groundwater velocity and biomass concentration are given.

<table>
<thead>
<tr>
<th>Groundwater velocity (m day(^{-1}))</th>
<th>Length (m) for ( X = 2 ) mg l(^{-1})</th>
<th>Length (m) for ( X = 10 ) mg l(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>0.4</td>
<td>1.1</td>
</tr>
<tr>
<td>0.05</td>
<td>1.0</td>
<td>0.2</td>
</tr>
<tr>
<td>0.10</td>
<td>2.1</td>
<td>0.4</td>
</tr>
<tr>
<td>0.20</td>
<td>4.1</td>
<td>0.8</td>
</tr>
</tbody>
</table>
We shall design our experiments to have a groundwater velocity of 0.1 m day$^{-1}$. Then with a value of $L$ between 0.4 and 2.1 m, according to Table 1, we should use a container length of 2 m.

**FUTURE WORK**

The experiments need to be analysed with a numerical model to get insight as to the sensitivity of parameters. Numerical model analysis can be used to determine the desired flow rates, the appropriate size of reservoirs and container, boundary effects, expected time scale, appropriate locations of measurement points, the necessary frequency of measurements and the expected fluxes and pressures. We plan to use UTCHEM, documented by the Reservoir Engineering Research Program (2000), and an extended version of the multiphase simulator STOMP, documented by White & Oostrom (2000), for numerical analysis of the experimental set up. Subsequently, the experimental results will be used to calibrate and test the numerical models.

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**REFERENCES**


