Dissolution and mass transfer of multiple chlorinated hydrocarbons under field conditions

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Abstract The time taken for a residual source of chlorinated hydrocarbons in an aquifer to dissolve without active intervention is controlled by the process that transfers the dissolved phase from the source to the flowing groundwater. Although various equilibrium and kinetic models have been proposed, the nature of this mass transfer process in the field is not yet well understood. To investigate mass transfer under field conditions, a three-dimensional multicomponent kinetic mass transfer model is calibrated against detailed field measurements of dissolved-phase concentrations at an emplaced DNAPL source at the Canadian Forces Base Borden, Ontario. The results show that, at least for the three year observation period, the mass transfer process is clearly equilibrium, and that observed early tailing is due to the declining mole fraction rather than to mass transfer kinetics.

INTRODUCTION

Chlorinated hydrocarbons can be persistent sources of serious groundwater contamination. Various methods for the remediation of such sources have been proposed, but costs can be high and results uncertain (Pankow & Cherry, 1996). As a result, there is an increasing interest in passive remediation. This option requires a sound understanding of the controlling processes involved in the dissolution of a hydrocarbon source.

Our focus here is on the processes that transfer a dissolved hydrocarbon from a residual source in an aquifer to the flowing groundwater. Because the organic liquid will occupy the larger pores in the medium, reducing the hydraulic conductivity of the residual zone, flow will be partly redirected around the source and diffusion could play a role in transferring the dissolved phase to the zone of flowing groundwater. The time required to reduce the effluent below drinking water levels will depend to a large extent on whether the mass transfer process from the source to the flowing groundwater is an equilibrium process (i.e. the concentration of the dissolved phase in the flowing groundwater is at the solubility limit of the hydrocarbon), or a kinetic process driven by diffusion where the concentration in the groundwater is below the solubility limit. Under a kinetic process, the effluent concentration is subject to tailing which will extend the time taken for passive remediation.

A large body of recent literature is devoted to the study of this mass transfer process (see for example Mayer & Miller, 1992; Geller & Hunt, 1993; Powers et al., 1994; Imhoff et al., 1994). Most of this work is based on the interpretation of laboratory column experiments using some form of diffusion layer model (Sherwood et al., 1975), and various kinetic or equilibrium mass transfer relationships have
been proposed. For example, Powers et al. (1994) found that in their experiments, the mass transfer process is equilibrium at early times and kinetic at later times. Mayer & Miller (1996) found that a homogeneous source will tend toward equilibrium mass transfer while a heterogeneous source will tend toward kinetic mass transfer. However, none of these models have as yet been tested under actual field conditions.

Under field conditions, DNAPL equilibrium concentrations have rarely been observed (Feenstra & Cherry, 1988). As a result, there is some reason to believe that mass transfer under field conditions might be kinetic. On the other hand, recent work by McWhorter and Sale (1998) shows that under homogeneous conditions in the field, mass transfer kinetics are relatively unimportant compared to the process of carrying the dissolved NAPL away in the aquifer. Similarly Grathwohl (1997) calculates that equilibrium concentrations should be reached in the groundwater relatively quickly. The objective of the present work is to test these theories by simulating the mass transfer process at a well-documented field site, using a kinetic model.

THE BORDEN EMPLACED SOURCE

This source (Fig. 1) consists of a mixture of three chlorinated hydrocarbons (TCM, TCE, and PCE) that was emplaced into a sandy aquifer at the Canadian Forces Base Borden, Ontario, in the late 1980s (Rivett et al., 1992). For placement, the source area was isolated by sheetpiles, the sand removed and mixed above ground with the DNAPL and a quantity of gypsum powder. The characteristics of the source are summarized in Table 1, and the hydraulic parameters are provided in Table 2. The plume of dissolved DNAPL was monitored for about three years by a three-dimensional monitoring network of 2300 multilevel sampling points arranged in several fences located at various distances along the axis of the plume. Of these samplers, 173 are located at the 1-m fence (Fig. 1). Analyses of cores taken from the source in 1994 and 1996 showed a negligible amount of TCM residual in the source, but high amounts of TCE and PCE.

The peak concentrations, observed at the 1-m fence up to 1000 days for the three organics, are shown in Fig. 2. In the transverse section (not shown), the observed plumes are very narrow and sharply peaked, concentrating most of the mass flux over an area of only one-quarter the width of the source area. The figure also shows the solubility limit of each DNAPL calculated on the basis of the initial mole fractions.

Fig. 1 Site layout of the Borden emplaced source showing 1-m fence.
Table 1 Emplaced source DNAPL properties.

<table>
<thead>
<tr>
<th></th>
<th>TCM</th>
<th>TCE</th>
<th>PCE</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial volume (l)</td>
<td>0.97</td>
<td>6.11</td>
<td>7.63</td>
<td>14.71</td>
</tr>
<tr>
<td>Density (kg l⁻¹)</td>
<td>1.49</td>
<td>1.46</td>
<td>1.63</td>
<td></td>
</tr>
<tr>
<td>Initial mass (kg)</td>
<td>1.44</td>
<td>8.92</td>
<td>12.44</td>
<td>22.8</td>
</tr>
<tr>
<td>Molecular weight (kg mol⁻¹)</td>
<td>0.119</td>
<td>0.131</td>
<td>0.166</td>
<td></td>
</tr>
<tr>
<td>Moles</td>
<td>12.10</td>
<td>68.09</td>
<td>74.94</td>
<td></td>
</tr>
<tr>
<td>Initial mole fraction, X₀</td>
<td>0.078</td>
<td>0.439</td>
<td>0.483</td>
<td>1.000</td>
</tr>
<tr>
<td>Pure phase solubility, C₀ (mg l⁻¹)</td>
<td>8670</td>
<td>1270</td>
<td>242</td>
<td></td>
</tr>
<tr>
<td>Initial effective solubility (mg l⁻¹)</td>
<td>676.3</td>
<td>557.5</td>
<td>116.9</td>
<td></td>
</tr>
<tr>
<td>Diffusion coefficient, Dᵦ (m² s⁻¹)</td>
<td>9.0 x 10⁻⁹</td>
<td>7.0 x 10⁻¹⁰</td>
<td>6.0 x 10⁻¹⁰</td>
<td></td>
</tr>
<tr>
<td>Initial NAPL saturation, S₀</td>
<td>1.1</td>
<td>1.5</td>
<td>1.1</td>
<td>0.05</td>
</tr>
<tr>
<td>Retardation coefficient, R</td>
<td>1.1</td>
<td>1.5</td>
<td>1.1</td>
<td></td>
</tr>
</tbody>
</table>

Table 2 Physical properties.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Aquifer hydraulic conductivity, K (m s⁻¹)</td>
<td>0.5 x 10⁴ – 1.0 x 10⁴</td>
</tr>
<tr>
<td>Porosity, θ</td>
<td>0.33</td>
</tr>
<tr>
<td>Hydraulic gradient</td>
<td>0.0065 (spring)–0.0034 (summer)</td>
</tr>
<tr>
<td>Median grain size, d₅₀ (mm)</td>
<td>0.15</td>
</tr>
<tr>
<td>Residual water saturation, Sᵥ</td>
<td>0.07</td>
</tr>
<tr>
<td>Specific storage, Sₛ</td>
<td>0.001</td>
</tr>
</tbody>
</table>

present in the source. Most of the measured peak concentrations for TCE and PCE are at or just below the solubility limit, while those for TCM decline below this initial solubility limit after 400 days. The scatter in the measurements is most likely due to the plume peak passing between the sampler points, which are spaced at 25–50 cm intervals, as the flow gradient changed seasonally. Thus it is likely that TCE and PCE dissolve at equilibrium rates during the period of measurement. A kinetic process is possible for TCM, or for TCE and PCE at later times. To obtain insight into the mass transfer process at this site, we will calibrate a three-dimensional (3-D) kinetic mass transfer model to the concentration data at the 1-m fence.

MASS TRANSFER MODEL

The model is designed to handle the spatially and temporally variable mass transfer of multiple DNAPL components in 3-D saturated groundwater systems. It is based on the well-known diffusion layer concept where a mass flux of dissolved component

![Fig. 2 Peak concentrations observed at the 1-m fence, showing initial solubility limits.](image-url)
from the residual zone to the zone of flowing groundwater at point $i$ is expressed by:

$$J_i^m = \lambda_i^m (C_i^m - C_w^m)$$

(1)

where $C_i^m = C_0X_i^m$ is the effective solubility of component $m$ as calculated by Raoult’s law (Mackay et al., 1991), with $C_0$ being the pure-phase solubility and $X_i^m$ being the mole fraction, and $C_w^m$ is the concentration of component $m$ in the flowing water at the source. The mass transfer rate coefficient of component $m$ at point $i$ is expressed as:

$$\lambda_i^m = Sh \frac{D_i^m}{(d_{30})^2} \left( \frac{f_i^m S_{ni}}{S_{n0}} \right)^{\beta^m}$$

(2)

where $Sh$ is the Sherwood number, $D_i^m$ is the aqueous diffusion coefficient of component $m$, $S_{ni}$ is the NAPL degree of saturation at point $i$, with $S_{n0}$ being the initial value, and $f_i^m$ is the local volume fraction of NAPL $m$. $Sh$ and $\beta^m$ are empirical parameters whose values are to be determined by calibration. $Sh$ represents the effects of the porous medium within the source area, including the surface area of the NAPL blobs and the thickness of the conceptual diffusion layer; these geometric factors are the same for each component in the source. The component volume fraction $f_i^m S_{ni}/S_{n0}$ serves to represent a possible time dependence of the mass transfer process. The exponent $\beta^m$ can be component-specific.

This mass transfer mechanism is built into a 3-D finite element model that handles variably saturated flow coupled with multicomponent transport. The solution is iterative and time-marching. The discretization varies from 0.05 m within the source area to 0.1 m elsewhere in each coordinate direction, and the time step is 2.0 days. The model was validated by applying it to the column experiments conducted by Powers et al. (1994).

MODEL CALIBRATION

Because most measurements of dissolved TCE and PCE at the 1-m fence are at or near equilibrium concentrations (Fig. 2), the source concentrations must be essentially at equilibrium at least part of the time. Furthermore, the observed behaviour suggests that dispersion between the source and the fence must be small. In order to reduce transverse and upstream dispersion, we use dispersivity values of $\alpha_L = 0.025$ m and $\alpha_{TH} = 0.001$ m, which are well below the range of dispersivity values used previously in a large-scale transport simulation of the Borden aquifer (Frind & Hokkanen, 1987). These values are reasonable because of the small spatial scale (1 m) of the transport process observed here. The DNAPL properties are listed in Table 1 and the physical properties of the medium and the flow system are listed in Table 2. The source is assumed to be isotropic with respect to hydraulic conductivity.

The mass transfer parameters that can be adjusted in the calibration are $Sh$ (constant for the three components) and $\beta^m$. In addition, the source hydraulic conductivity $K_{source}$ and the source porosity $\theta_{source}$ are unknown due to the presence of gypsum. To minimize the number of fitting parameters, we assume a constant
porosity of 0.33, and take $K_{\text{source}}$ as the additional calibration parameter. The source is assumed to be isotropic with respect to hydraulic conductivity. The calibration was carried out by fitting the calculated effluent concentrations to the observed peak concentrations at the 1-m fence. Because some of the peak values might have been missed in the sampling, the high data values are considered to have the greatest credibility. As a check on the calibration, we use the total mass remaining in the source, obtained from the average mass flux passing through the fence.

We first obtain an initial estimate of $Sh$ by utilizing a plot of the Sherwood number versus the Reynolds number obtained for a number of 1D column experiments (Imhoff et al., 1994). With a value of the Reynolds number characteristic of the source area ($Re = 1.46 \times 10^5$) we obtain a value of $Sh = 0.002$ from this plot. The model was first calibrated with respect to the source hydraulic conductivity, and the best fit for all three components was obtained with a value of $K_{\text{source}} = 4 \times 10^{-6} \text{ m s}^{-1}$.

The exponent affects the tail of the breakthrough curve, and Powers et al. (1994) found values of $\beta$ ranging between 0.75 and 0.96, depending on the porous material, in simulations of a column experiment with a single component. In the Borden case, only the TCM effluent curve shows enough tailing during the 1000 day observation period to allow $\beta$ to be fitted. Figure 3 shows the peak concentrations at the 1-m fence obtained with $\beta = 0.5, 0.5, 0.5$, as well as the effective solubility limit for each DNAPL, valid for the downstream edge of the source closest to the fence. Favouring the higher-valued observations, the fit is good for all three DNAPLs. The aqueous concentrations lie about 3 mg l$^{-1}$ below the corresponding solubility limits throughout the observation period, accounting for the diffusion gradient across the stagnant layer and for transverse dispersion between the source and the 1-m fence. The slight undulation in the TCM curve is due to the seasonal variation of the hydraulic gradient. The mass remaining in the source is also fitted well. The results suggest that dissolution within the source takes place essentially at equilibrium.

![Figure 3 Peak concentrations at the 1-m fence and mass remaining in the source](image-url)

**Fig. 3** Peak concentrations at the 1-m fence and mass remaining in the source to 1000 days, fitted with $K_{\text{source}} = 4 \times 10^{-6} \text{ m s}^{-1}$, $Sh = 0.002$, $\beta = 0.5, 0.5, 0.5$; also showing effective solubility limits $C_0 X^\alpha$. 
concentrations throughout the observation period, and that the drop in the TCM values is due to the changing mole fraction and source depletion, and not due to mass transfer kinetics. This agrees with the results of McWhorter & Sale (1998) to the effect that for homogeneous sources, kinetics is not a controlling process.

A value of $Sh = 0.00005$ (40 times lower than the initial value) was found to give, after a suitable adjustment of $K_{source}^s$, a fit almost as good as with the original $Sh$ value. Evidently, the model is quite insensitive with respect to $Sh$. We tested other possible $Sh$ values and found that a range of approximately $10^{-5} < Sh < 10^{-2}$ will produce acceptable fits, provided $K_{source}^s$ is adjusted accordingly. The model, therefore, converges to an equilibrium or near-equilibrium mass transfer process for any value of the mass transfer rate coefficient within the above range.

**EVOLUTION OF THE DISSOLUTION PROCESS**

The evolution of source dissolution is illustrated in Fig. 4 for the case of TCM, showing the flownet, the mole fraction remaining in the source, and the aqueous concentration at 20, 100, and 400 days. Much of the flow is diverted around the source, while some passes through the source and is focused in a narrow streamtube downstream of the source. At 100 days, TCM dissolution has progressed almost halfway through the source, while at 400 days, most of the TCM has dissolved. However, flow continues to be diverted around the source zone because the low source conductivity is maintained on account of the TCE, PCE and gypsum that are still present. The aqueous concentrations show a plume developing which has reached the 1-m fence at 20 days. At 100 days, the plume is narrowly focused along its centre, where it reaches close to the effective solubility limit, while at 400 days

![Fig. 4 Flow system, source dissolution, and plume evolution for TCM.](image)
the plume has dispersed to very low values. These results show that although solubility limit concentrations are approached throughout the source, they are observed downstream only at the very centre of the plume, consistent with field observations. When monitoring the plume, these high concentrations could be easily missed.

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REFERENCES


