Modeling the Dynamics of Fermentation and Respiratory Processes in a Groundwater Plume of Phenolic Contaminants Interpreted from Laboratory- to Field-Scale

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A biodegradation model with consecutive fermentation and respiration processes, developed from microcosm experiments and simulated mathematically with microbial growth kinetics, has been implemented into a field-scale reactive transport model of a groundwater plume of phenolic contaminants. Simulation of the anaerobic plume core with H2 and acetate as intermediate products of biodegradation allows the rates and parameter values for fermentation processes and individual respiratory terminal electron accepting processes (TEAPs) to be estimated using detailed, spatially discrete, hydrochemical field data. The modeling of field-scale plume development includes consideration of microbial acclimatization, substrate toxicity toward degradation, bioavailability of mineral oxides, and adsorption of biogenic Fe(II) species in the aquifer, identified from complementary laboratory process studies. The results suggest that plume core processes, particularly fermentation and Fe(III)-reduction, are more important for degradation than previously thought, possibly with a greater impact than plume fringe processes (aerobic degradation processes considered). (3) Bioavailability of Fe(III)- and Mn(III,-IV)-minerals as TEAs appeared to be higher initially and decreasing with time indicating, at least qualitatively, a more and a less bioavailable form to be present. (4.) Aqueous Fe2+ behavior could be understood through inclusion of surface complexation equilibria and solubility equilibria with secondary mineral phases.

The aim of the present study is to implement this additional process understanding in field-scale simulations of the associated contaminant plume. The main objectives

Introduction

Biodegradation is often the most important process contributing to the natural attenuation (NA), or engineered in situ bioremediation, of organic contaminants in groundwater (1). Reactive transport modeling can be used to assess the potential for NA by quantifying biodegradation rates and contributions of other relevant processes (e.g., dispersion, sorption, precipitation, and dissolution reactions) for predictions of plume development. A recent review of current biogeochemical transport modeling approaches shows that biodegradation processes are usually modeled as either a single-step or a two-step process (2). Single-step biodegradation is often used to conceptualize aerobic respiration or denitrification where a single strain of organism is capable of degrading a contaminant to inorganic carbon. The two-step approach addresses strongly anaerobic degradation and comprises fermentation of the organic substrate by one group of organisms to intermediate species, e.g., H2(aq) or acetate, followed by respiration by other groups of organisms where fermentation products are consumed by reaction with terminal electron acceptors (TEAs). The fermentation is overall rate limiting, and is thus described with kinetic rate expressions. The respiration, or terminal electron accepting processes (TEAPs) are considered to occur much faster. A partial equilibrium approach is therefore often used to describe TEAPs, whereby they approach thermodynamic equilibrium with the H2(aq) produced by fermentation (2−5).

Alternatively, the TEAP step can be treated as kinetically controlled, which notably assumes that the microbial TEAPs are irreversible chemical processes; i.e., far from thermodynamic equilibrium (6, 7). It is desirable that biogeochemical transport models can account for secondary inorganic reactions (e.g., aqueous complexation, sorption, and mineral precipitation and dissolution) in addition to the primary biodegradation reactions (e.g., 2, 7, 8). These processes affect the concentrations of many solute species involved in biodegradation reactions, and measured in hydrochemical field samples to assess mass and electron balances (9).

Laboratory-scale biodegradation experiments provide important results that demonstrate the potential for NA at field sites (e.g., 10, 11−13) and provide parameter values for biodegradation process models that constrain field-scale modeling. A recently published microcosm study (14), of processes relevant to a field-scale contaminant plume of phenolic compounds (subsequently referred to as phenolics), identified the following four factors that are not routinely considered in field-scale biodegradation modeling studies. (1) Consideration of the temporal evolution of H2(aq) and acetate concentrations, with a two-step, fully kinetic description of biodegradation, allowed parameter values for rate expressions and the relative rates of fermentation and individual TEAPs to be determined. (2) To describe the chemical dynamics of organic contaminants and biodegradation products it was necessary to simulate the dynamics of individual microbial populations that represent unique functional activity with respect to the biodegradation processes considered. (3) Bioavailability of Fe(III)- and Mn(III,-IV)-minerals as TEAs appeared to be higher initially and decreasing with time indicating, at least qualitatively, a more and a less bioavailable form to be present. (4.) Aqueous Fe2+ and Mn2+ behavior could be understood through inclusion of surface complexation equilibria and solubility equilibria with secondary mineral phases.

The aim of the present study is to implement this additional process understanding in field-scale simulations of the associated contaminant plume. The main objectives
of this study are as follows: (1) to build upon an existing reactive transport model of the specific field site by incorporating additional reactive processes combined with advanced computational techniques; (2) to assess the ability of the new model to describe the hydrochemical data for H2-(aq) and acetate as fermentation products which have not been previously simulated; (3) to consider the bioavailability of higher valent mineral Fe and Mn as TEAs and adsorption reactions on aquifer mineral surfaces as a sink for biogenic Fe2+ and Mn2+, instead of the often postulated process of precipitation of carbonate minerals, which presents difficulties for plausibly closing carbon mass and electron balances (discussed in ref 8, 15); and (4) to reassess the plume carbon and electron balance and extent of biodegradation over the plume history in light of the new reaction processes that are considered.

Broader aims in extending this model were to address general weakness in current approaches to reactive transport modeling of plumes (e.g., ref 16), that is by considering (1) more accurate 2-D modeling of the steep chemical gradients at the plume fringe where mass transport of dissolved oxidants from outside the plume can limit aerobic respiration and denitrification processes, but are poorly quantified for this field site (17); (2) more complex biodegradation processes such as combined fermentation and respiration that control carbon turnover within the plume core; and (3) complexity of heterogeneous flow fields and complex source terms that often characterize contaminant plumes.

**Modeling Methods**

Figure 1 illustrates the main features of the phenolics plume located at the field site, as identified from groundwater quality surveys (8, 18, 19). The schematic includes the location of multilevel groundwater samplers (MLS) installed at 130 m (BH59) and 350 m (BH60) along the plume flowpath, and the key degradation pathways identified from the conceptual model. Although substantial amounts of contaminant are degraded, this has resulted in only a few weight percent (~5%) loss of phenols during the site history. Though phenolics themselves seem almost like a nondegrading tracer, the occurring biodegradation processes produce major changes in aquifer hydrochemistry due to loss of TEAs and accumulation of biodegradation products. Previous laboratory studies using rock core from the field site (Figures 2–4, 8, and 9 in ref 20; 14) demonstrated no significant abiotic mass loss of phenol from aqueous solution under similar pH conditions thus suggesting that phenol also approximates the behavior of an inert solute with respect to adsorption at site conditions.

This work extends previous reactive transport modeling of the site (8), performed with the code MIN3P (21). That work focused on 1-D transport along 2 flowlines in a homogeneous aquifer, one approximately along the center of the plume and the other located within the top half of the plume. The current model adopted key features of the previous model including the flow domain and hydraulic boundary conditions, the calibrated source terms in the saturated zone, the representation of total phenolics (phenol, cresol, and xylene) by phenol only, the general form of the kinetic rate laws, the stoichiometry of aerobic respiration and denitrification (Table 1, nos. 1 and 2), inclusion of aqueous speciation and mineral solubility equilibria (Table S2 in the Supporting Information), and parameter values in specific rate equations (Table S3). The same data set (17), used to test the previous model (8, 22), was used for calibration of the current model. Key changes to the previous model included increased model complexity in terms of (1)
TABLE 2. Rate Parameters, $k_{\text{max}}$ (mol/L$-S$), for This Study Compared to Those of Previous Studies

<table>
<thead>
<tr>
<th>substrate, $S$</th>
<th>values of $k_{\text{max}}$ used in this paper</th>
<th>ratio back/front</th>
<th>$k_{\text{max}}$ in other modeling studies based on this field site</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1^a$ C$<em>\text{6}$H$</em>\text{5}$OH</td>
<td>$4.0 \times 10^{-10}$</td>
<td>$1$</td>
<td>4.0 $\times 10^{-10}$</td>
</tr>
<tr>
<td>$2$ C$<em>\text{6}$H$</em>\text{5}$OH</td>
<td>$4.0 \times 10^{-11}$</td>
<td>1</td>
<td>4.0 $\times 10^{-11}$</td>
</tr>
<tr>
<td>$3$ C$<em>\text{6}$H$</em>\text{5}$OH</td>
<td>$8.4 \times 10^{-13}$</td>
<td>3.2</td>
<td>3.8 $\times 10^{-11}$</td>
</tr>
<tr>
<td>$4$ C$<em>\text{6}$H$</em>\text{5}$OH</td>
<td>$2.1 \times 10^{-13}$</td>
<td>1.2</td>
<td>1.1 $\times 10^{-8}$</td>
</tr>
<tr>
<td>$5$ H$_\text{2}$</td>
<td>$9.8 \times 10^{-12}$</td>
<td>0.43</td>
<td>5.0 $\times 10^{-10}$</td>
</tr>
<tr>
<td>$6$ H$_\text{2}$</td>
<td>$2.2 \times 10^{-11}$</td>
<td>0.84</td>
<td>9.0 $\times 10^{-8}$</td>
</tr>
<tr>
<td>$7$ H$_\text{2}$</td>
<td>$8.0 \times 10^{-12}$</td>
<td>20</td>
<td>1.0 $\times 10^{-7}$</td>
</tr>
<tr>
<td>$8$ H$_\text{2}$</td>
<td>$2.8 \times 10^{-12}$</td>
<td>30</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Same as in Mayer et al. $^b$ Calibrated. $^c$ Converted from microcosm simulation parameters: (rate constant $3.8 \times 10^{-3}$ mol/(L.s)). $^d$ Fermenter biomass in microcosm $1 \times 10^{-3}$ mol/L (14). $^e$ Calculated by converting stated $k_{\text{max}}$ in terms of phenol degradation to $H_2$ degradation and correcting for different Monod and inhibition terms using typical values: $H_2 1 \times 10^{-7}$ mol/L, phenol $5 \times 10^{-2}$ mol/L. $^f$ Reaction numbers are the same as those in Table 1.

CONCEPTUALIZATION AND MATHEMATICAL REPRESENTATION OF THE PHYSICAL HETEROGENEITY OF THE PERMEABILITY FIELD. (2) FULL 2-D SIMULATION OF REACTIVE TRANSPORT, ALSO INCLUDING MICROBIAL ACCLIMATIZATION IN SIMPLE FORM, (3) INCLUSION OF FERMENTATION CONCEPTUALIZATION AND MATHEMATICAL REPRESENTATION OF THE

Biodegradation Chemistry. The four key biogeochemical factors identified in the microcosm study were implemented directly in the new field model, but a few specific adaptations from the laboratory model were introduced where field-scale conditions imposed them (Table 1 for stoichiometry, Figure 1 for pathways). These modifications were the following. (i) In the plume there is a mixture of phenolics (phenol, cresols, and xyleneols) rather than a single contaminant. Nevertheless, by accounting for their difference in electron acceptor demand to oxidize phenolics-derived carbon it is possible to represent total phenolics as phenol, C$_\text{6}$H$_\text{5}$OH (8). (ii) The fermentation of phenol was represented as two parallel reactions degrading phenol to acetate (reaction 3, Table 1) or to inorganic carbon (TIC) (reaction 4). (iii) Phenol concentrations in the plume are substantially higher than those in the simulated microcosm. Results from other microcosm and field studies show that these high phenol concentrations will exhibit substrate toxicity effects on microbial activity (25–27). These were accounted for as discussed below.

Kinetic Reactions. Fermentation and respiration process rates are modeled using the Monod rate expression (eq 1) as formulated in the previous models (8, 14).

$$r_S = \frac{dS}{dt} = -k_{\text{max}} \frac{S}{(K_{M,S} + S)} \frac{TEA}{(K_{M,TEA} + TEA)} \frac{K_I}{(K_I + I)}$$

The variable $r_S$ is the rate of consumption of substrate S, [mol/L/s]; $S$ is the substrate concentration [mol/L]; $k_{\text{max}}$ is the maximum substrate utilization rate [mol/L/s]; $K_{M,S}$ is the Monod half saturation constant with respect to substrate $S$ [mol/L]; $TEA$ is the concentration of the particular TEA [mol/L]; $K_{M,TEA}$ is the Monod half saturation constant with respect to the TEA [mol/L]; $K_I$ is the inhibition constant [mol/L], which may represent inhibition of one process by another (through microbial competition (8, 14)) or toxic effects due to a chemical substance (e.g., phenol) (8), and $I$ is the concentration of the inhibiting substance [mol/L].

Fermentation reactions are more robust to toxic inhibition by phenols than respiration reactions (26). Hence, H$_2$(aq) and acetate accumulate as intermediate species in this plume to higher concentrations than are generally observed in plumes (14, 17), and preliminary modeling in this study showed that acetate respiration even is negligible. Consequently, the model is formulated to allow different $k_I$ values for the inhibition of fermentation and respiration processes that respectively produce and consume H$_2$(aq) (cf. Table S3).

In the absence of historical data on the temporal evolution of biomass, but having samples representing aquifer zones that had been in contact with contaminated groundwater for approximately 34 years (BH559) and 12 years (BH60), respectively, the simplest possible approach was applied. Microbial biomass is not explicitly modeled in our formulation (eq 1), and microbial biodegradation activity, proportional to microbial biomass, is included only intrinsically in the $k_{\text{max}}$ term. However, microbial acclimatization is accounted for by using two values for $k_{\text{max}}$, a smaller $k_{\text{max}}$ value for the front of the plume, where the indigenous microbial populations were exposed over a shorter time scale to contamination, and a higher $k_{\text{max}}$ near the plume source, where there was more time for microbial acclimatization during plume development (Table 2). Mathematically this was represented by a moving interface indicating the step change of $k_{\text{max}}$

$$X_{\text{interface}} = \frac{(velocity) \times (time - time_{\text{change}})}{time_{\text{change}}}$$

where $X$ is measured longitudinally from the plume source, and the interface enters the aquifer at $time_{\text{change}}$ travelling at groundwater flow velocity. Table 3 shows the spatial and temporal distribution of source concentrations used, in addition to the background
### TABLE 3. Background and Source Concentrations

<table>
<thead>
<tr>
<th>species</th>
<th>background (mol/L)</th>
<th>source, 0 to 25 years</th>
<th>source, 25 to 47 years</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Z range(a)(m):</td>
<td>C range(b)(mol/L)</td>
<td>Z range(a)(m):</td>
</tr>
<tr>
<td>(\text{C}<em>{6}\text{H}</em>{4}\text{O})</td>
<td>(3.4 \times 10^{-10})</td>
<td>10(\rightarrow)20m: 3.4 (\times 10^{-10}) (\rightarrow)1.11 (\times 10^{-1})</td>
<td>10(\rightarrow)19m: 3.4 (\times 10^{-10}) (\rightarrow)8.3 (\times 10^{-2})</td>
</tr>
<tr>
<td>(\text{SO}_{2}^{2-})</td>
<td>(6.7 \times 10^{-4})</td>
<td>20(\rightarrow)30m: 4.8 (\times 10^{-10}) (\rightarrow)3.4 (\times 10^{-10})</td>
<td>19(\rightarrow)30m: 3.2 (\times 10^{-2}) (\rightarrow)3.4 (\times 10^{-10})</td>
</tr>
<tr>
<td>(\text{TiC}^c)</td>
<td>(2.3 \times 10^{-3})</td>
<td>24(\rightarrow)30m: 7.0 (\times 10^{-3})</td>
<td>26(\rightarrow)30m: 2.5 (\times 10^{-3}) (\rightarrow)6.7 (\times 10^{-4})</td>
</tr>
<tr>
<td>pH</td>
<td>6.9</td>
<td>10(\rightarrow)30m: 1.3 (\times 10^{-2}) (\rightarrow)2.1 (\times 10^{-2})</td>
<td>10(\rightarrow)30m: 1.1 (\times 10^{-2}) (\rightarrow)3.6 (\times 10^{-2})</td>
</tr>
</tbody>
</table>

#### Other Mobile Aqueous Species

<table>
<thead>
<tr>
<th>species</th>
<th>background (mol/L)</th>
<th>mineral</th>
<th>surface species</th>
<th>mol/kg-solid</th>
<th>mol/L-H(_2)O</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{O}_2)</td>
<td>(2.9 \times 10^{-4})</td>
<td>(\text{FeOOH})</td>
<td>(\text{TOTXFeOH}^f)</td>
<td>9.8 (\times 10^{-2})</td>
<td>(1.39 \times 10^{-2})</td>
</tr>
<tr>
<td>(\text{NO}_3^-)</td>
<td>(1.7 \times 10^{-3})</td>
<td>(\text{MnO}_2)</td>
<td>(\text{XFeOH}_2^+)</td>
<td>8.7 (\times 10^{-4})</td>
<td>equil</td>
</tr>
<tr>
<td>(\text{H}_2)</td>
<td>(1.0 \times 10^{-10})</td>
<td>(\text{FeS})</td>
<td>(\text{XFeO}^+)</td>
<td>6, equil</td>
<td>equil</td>
</tr>
<tr>
<td>(\text{CH}_3\text{COOH})</td>
<td>(1.0 \times 10^{-10})</td>
<td></td>
<td>(\text{XFeOF}_2^-)</td>
<td></td>
<td>equil</td>
</tr>
<tr>
<td>(\text{Fe}^{2+}\text{aq})</td>
<td>(8.9 \times 10^{-7})</td>
<td></td>
<td>(\text{XFeOMn}^+)</td>
<td></td>
<td>equil</td>
</tr>
<tr>
<td>(\text{Mn}^{2+}\text{aq})</td>
<td>(1.2 \times 10^{-7})</td>
<td></td>
<td>(\text{XfEOFeOH})</td>
<td></td>
<td>equil</td>
</tr>
<tr>
<td>(\text{HS}^-)</td>
<td>(3.0 \times 10^{-10})</td>
<td></td>
<td></td>
<td></td>
<td>equil</td>
</tr>
<tr>
<td>(\text{CH}_4)</td>
<td>(6.2 \times 10^{-10})</td>
<td></td>
<td></td>
<td></td>
<td>equil</td>
</tr>
<tr>
<td>(\text{O}^{18}\text{H}_2)</td>
<td>equil</td>
<td></td>
<td></td>
<td></td>
<td>equil</td>
</tr>
<tr>
<td>(\text{CO}_3^{2-})</td>
<td>equil</td>
<td></td>
<td></td>
<td></td>
<td>equil</td>
</tr>
<tr>
<td>(\text{H}_2\text{CO}_3)</td>
<td>equil</td>
<td></td>
<td></td>
<td></td>
<td>equil</td>
</tr>
</tbody>
</table>

\(^a\) Z range represents height in domain (0\(\rightarrow\)40m), not depth. The Dirichlet type concentration boundary is applied along the specified segments of the inflow boundary. Unspecified Z ranges use the background concentration. \(^b\) C range specifies the source concentration values at the ends of each boundary segment, with intermediate points being linearly interpolated. Segments are discontinuous, rather than smoothly changing, to reflect sharp gradients observed in downstream borehole profiles. \(^c\) Surface adsorption capacity same as that used in microcosm modeling (14). \(^d\) Equil = Equilibrium species whose concentration is computed by the program. The thermodynamic equilibrium constants used are the same as those used in the microcosm work (14). \(^e\) TIC = total inorganic carbon, equivalent to TOTAL(HCO\(_3\)) or sum of CO\(_3^{2-}\), H\(_2\)CO\(_3\), HCO\(_3\). \(^f\) TOTXFeOH represents surface complexation capacity, i.e., sum of all XFeO\(_{...}\) type species.
suggesting that the source zone parameters, also affecting
the simulated phenolics profiles, were reasonably well-
constrained. Other solutes of the source zone, particularly
TIC and SO$_4^{2-}$, as well as acetate, H$_2$(aq), and TEAs and their
reduced forms, were also sensitive to values for $k_{\text{max}}$ which
were thus well-constrained. The profiles were relatively
insensitive to parameter values for $K_D$ and $K_s$, which as a
result could be taken from laboratory studies without
calibration.

Fe- and Mn-reduction processes were difficult to calibrate
when the adsorption processes were included. Inclusion of
Fe$^{2+}$ and Mn$^{2+}$ adsorption was necessary in order to
reproduce the profiles for these ions as well as H$^+$ and TIC
and to provide a sink for these ions from solution that did
not require sequestration of inorganic carbon as for formation
of carbonate minerals. In addition, values for $k_{\text{max}}$ for Fe-
and Mn-reduction were required to be higher at the front of
the plume in order to reproduce the profiles. Finally, all the
considered biodegradation processes proved necessary to
explain the loss or appearance of the respective solutes
downstream of the source area, confirming that these
processes actually occur at the site.

**Results and Discussion**

Figures 2 and 3 show the concentration profiles for 2-D
simulations compared with observed data at the MLS
locations. The plume fringe is defined by the vertical location
along the profile where solute concentrations approach

![FIGURE 2. BH59 concentration profiles (x = 130 m) showing one set of observed data, and simulation results from heterogeneous flow
model with both reactive and nonreactive cases after 47 years (data set of 1998).](image)
background values for the aquifer. The model results are shown for the final version of the model where all of the additional reactive processes and the heterogeneous flow field are considered simultaneously. Results for a homogeneous case did not differ dramatically and are compared in the Supporting Information. Phenolics concentration profiles for both boreholes are reproduced relatively well by the model. Consistent with the low relative mass loss of phenolics identified in other studies of the plume (8, 17, 19), the calculated profiles for nonreactive and reactive transport are very similar. The overestimation of phenolics concentration in the upper half of the plume at BH59, and underestimation at BH60, result from uncertainty in the source term and precisely how it changes over time.

**Biodegradation Results.** Predicted TIC results agree very well with the concentration profiles (Figures 2b and 3b). There is a significant contribution of TIC from biodegradation processes considered in the model. The dominant TIC input to the plume is from the source area, probably arising from more significant biodegradation in the unsaturated zone (8). For both boreholes, the highest phenolics concentrations coincide with the lowest TIC concentration, providing indirect evidence of substrate toxicity by the phenolics. This appears to occur within the source zone, as the greatest contribution to the concentrations profiles from the model is the vertical distribution of the source terms.

**Assessment of TEAPs.** Concentrations of $O_2$, $NO_3^-$, and $SO_4^{2-}$ decrease significantly, and $Fe^{2+}$, $Mn^{2+}$, and $CH_4$ increase substantially, within the plume compared with the uncontaminated aquifer. This indicates the dominant role of six TEAPs in controlling these solute profiles during the plume evolution. The $O_2(aq)$, $NO_3^-$, and $CH_4(aq)$ results agree very well with the concentration profiles (Figures 2b and 3b). There is a significant contribution of TIC from biodegradation processes considered in the model. The dominant TIC input to the plume is from the source area, probably arising from more significant biodegradation in the unsaturated zone (8). For both boreholes, the highest phenolics concentrations coincide with the lowest TIC concentration, providing indirect evidence of substrate toxicity by the phenolics. This appears to occur within the source zone, as the greatest contribution to the concentrations profiles from the model is the vertical distribution of the source terms.

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TABLE 4. Mass Balance Comparison among Field Models\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>Total mass degraded (mol phenol)</th>
<th>2D with homogeneous flow field, 25 years</th>
<th>2D with homogeneous flow field, 47 years</th>
<th>2D with heterogeneous flow field</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total mass degraded per m plume width (mol phenol)</td>
<td>5.18 \times 10^2</td>
<td>1.47 \times 10^3</td>
<td>1.66 \times 10^3</td>
</tr>
<tr>
<td>Total mass degraded relative to total added (wt. %)</td>
<td>2.3</td>
<td>4.2</td>
<td>5.1</td>
</tr>
<tr>
<td>Balance of carbon in products (% of mol C degraded)</td>
<td>TIC: 62.6</td>
<td>Acetate: 36.7</td>
<td>CH\textsubscript{4}: 0.7</td>
</tr>
<tr>
<td>Relative contribution of each TEA to total degradation (%)</td>
<td>O\textsubscript{2}: 6.7</td>
<td>NO\textsubscript{3}\textsuperscript{--}: 47.4</td>
<td>FeOOH: 26.7</td>
</tr>
<tr>
<td></td>
<td>Mn\textsubscript{O}\textsubscript{2}: 12.1</td>
<td>SO\textsubscript{4}\textsuperscript{2--}: 3.2</td>
<td>CH\textsubscript{4}: 3.9</td>
</tr>
<tr>
<td></td>
<td>CH\textsubscript{4}: 54.1</td>
<td>CH\textsubscript{4}: 33.0</td>
<td>CH\textsubscript{4}: 45.9</td>
</tr>
</tbody>
</table>

\textsuperscript{a} All figures based on global masses cumulatively reacted in 47 years unless stated otherwise. \textsuperscript{b} Plume width 65 m.

well with the data for the upper half of the plume. For the lower half, the vertical sampling has not fully captured the data for these three solutes at the plume fringe to allow a quantitative comparison between the model and field data.

The profiles of Fe\textsuperscript{2+} and Mn\textsuperscript{2+} concentration are reproduced well. Temporally variable degradation kinetics and surface complexation, accounting for Fe(II)(aq) species in the mass and electron balance within the plume, are included in the simulation of the Fe\textsuperscript{2+} and Mn\textsuperscript{2+} distribution. The corresponding TEAPs required higher rates of mineral oxidant utilization in the front of the plume (Table 2). This is an important result and is interpreted to arise from initially higher bioavailability of mineral oxidants, which decreases with time, fully consistent with findings from the laboratory microcosm study (14). The plume mass balance (Table 4) shows that Fe-reduction is the most important TEAP, suggesting that it is necessary to understand the geochemical processes that influence Fe\textsuperscript{2+} species, including oxidant bioavailability, precipitation, and sorption processes, to correctly interpret the Fe dynamics and thus the electron balance in the system.

This raises a generally important feature of closing Fe and C mass and electron balances when considering Fe biogeochemistry. Inspection of Table 1 shows that production of Fe\textsuperscript{2+} via respiration of H\textsubscript{2}, produced from organic carbon fermentation, yields a stoichiometric ratio for Fe/C of 28:6. The mass balance for TIC usually indicates much higher concentrations of Fe\textsuperscript{2+} should be produced than are observed in solution: thus indicating a sink for Fe\textsuperscript{2+} such as neogenic mineral formation (15). If formation of carbonate minerals is invoked as a sink for Fe\textsuperscript{2+}, then a much larger source of TIC is required for the 1:1 stoichiometry to form the mineral. Sinks for Fe\textsuperscript{2+} other than carbonate mineral formation thus circumvent this limitation from the carbon mass balance. This has previously been resolved by postulating formation of Fe(II)-bearing clay mineral phases (15). Here this is resolved by considering adsorption of Fe\textsuperscript{2+} to aquifer minerals. The adsorption capacity estimated for the aquifer, and the pH dependence of Fe\textsuperscript{2+} adsorption represented by the surface complexation equilibria considered here, is consistent with the observed aqueous concentrations of Fe\textsuperscript{2+} (and likewise for Mn\textsuperscript{2+}).

The simulated pH is generally within half a pH unit of field values, and at BH59 is largely controlled by the source term (Figure 2k). At BH60 groundwater pH is influenced most strongly by surface complexation reactions (Figure 3k). This results directly from the rate of biogenic Fe\textsuperscript{2+} generation and the adsorption equilibria which limits Fe\textsuperscript{2+} concentrations. Many stoichiometric reactions that remove Fe\textsuperscript{2+} from aqueous solution, be it carbonate-, silicate-, or oxide (or other) mineral precipitation, or adsorption onto aquifer minerals, require proton transfers to solution in order to maintain charge balance as Fe\textsuperscript{2+} cations are removed. A consequence is that downstream of the source zone, particularly at the plume front where Fe\textsuperscript{2+} production is higher, the proton balance is affected strongly by the Fe\textsuperscript{2+} sink. In these simulations this is described by the surface complexation equilibria (Table S2).

Simulation of SO\textsubscript{4}2-- posed particular problems (Figures 2i and 3i). The model results and data profile agree very well at BH60 at the front of the plume. This is because the simulated SO\textsubscript{4}2-- profile is dominated by the source term due to substrate toxicity, rather than biodegradation. This profile is thus particularly important as a constraint on reconstruction of the vertical distribution of the source term for this solute. At BH59 the profiles do not agree well for the data plotted, as obtained in 1998 at the site (17), while the model calibration used the full data set obtained between 1998 and 2002 (cf. Figure S2). This arises due to the significant uncertainty in the temporal evolution of the source term for SO\textsubscript{4}2--. This uncertainty makes it difficult to conclude from modeling alone that significant SO\textsubscript{4}2-- loss occurs by biodegradation within the plume core. Crucially, 34S isotopic data throughout the profile combined with major element hydrochemistry previously confirmed that biological SO\textsubscript{4}2-- reduction does occur and this permitted independent quantification of SO\textsubscript{4}2-- mass loss due to biodegradation alone (27).

Assessment of Fermentation. Acetate and dissolved H\textsubscript{2} concentrations are elevated significantly within the plume, but are absent in the aquifer outside the plume. This strongly supports the conceptual model of syntrophic biodegradation used to describe biodegradation within the plume. The simulated acetate profile agrees very well with the field data for BH59. Here the impact of phenolics substrate toxicity is evident, because the peak in phenolics concentration near 25-m depth coincides with suppressed concentrations of acetate. This results from the high phenolics concentrations suppressing acetate production by fermentation. Also, for BH60 the model captures the plume width and acetate peak concentration, but the model results show a wider suppression of acetate concentration for this borehole, which is not so pronounced in the field data.
H$_2$(aq) accumulates to higher levels than reported in other studies of organic contaminant plumes (3, 28–33); e.g., in most hydrocarbon plumes TEAPs, and thus H$_2$(aq) consumption, are not inhibited. These significantly elevated H$_2$ concentrations are reproduced by the model, as are the top and bottom fringes of the H$_2$ plume. For both boreholes, the field data show spikes of H$_2$(aq), which coincide with the peak phenol concentration. This is also seen in the model results. However, the calculated H$_2$(aq) peaks are broader than seen for the field data and they do not exhibit as high a concentration spike; underestimating the measured H$_2$-(aq) concentrations at the depth of the phenolics peak, but overestimating H$_2$(aq) concentrations at the plume fringe.

The spatial relationship between phenolics, acetate, and H$_2$(aq) provided by the detailed vertical profiles has been reproduced in the simulations by including the inhibition terms in eq 1, which describes the relative phenol toxicity to fermentation and TEAPs within a fully kinetic handling of biodegradation processes. In an earlier study the partial equilibrium concept was applied to this set of field data (17), but this approach was inconclusive due to the unknown threshold in free energy required for methanogenesis and the very broad range in free energy values for possible higher valent iron oxide mineral phases in the aquifer.

**Interpretation of Two-Dimensional Concentration Distributions.** Figure 4 shows contour plots for simulated reactive species in the heterogeneous flow-field, visualizing the plume in a vertical plane. There is significant spatial variability in the simulated plume species. This is largely due to the spatially and temporally varying source term (Table 3), the coupled fermentation and respiration processes, and the relative toxicity variation with phenol concentration. The source term species, C$_6$H$_6$O, TIC, SO$_4^{2-}$, and H$^+$ (shown as pH), in Figure 4a, b, g, and q, respectively, are anchored to the source plane at the left boundary, while the remaining species are produced by reactions that occur downstream of the source. The O$_2$ and NO$_3^-$ concentrations clearly illustrate the outer limit of the plume fringe. Note that the computational grid (Figure 4) was adaptively refined to improve computational effectiveness, by targeting computation resources on resolution of the steep gradient of these species across the plume fringe while utilizing a relatively coarser grid within the plume core and in the aquifer outside the plume (22). The smaller-scale features, such as fingering at the leading edges of the plume (Figure 4a–q) are due to consideration of a heterogeneous flow field (Figure 4r and s).

Dissolved H$_2$(aq) concentrations in the plume are relatively high, yet the total mass of H$_2$(aq) is very small and evolves rapidly downstream of the source. This explains why H$_2$(aq), which is typically turned over in minutes (28), responds rapidly to the step change of rate $k_{max}$ imposed at 25 years. The rate data in Table 2 yield a characteristic reaction time for H$_2$(aq) of between 2 min and 5 days. Therefore a sharp increase in H$_2$(aq) concentration appears at 200 m downgradient of the source. This is unrealistic, but is a consequence of the simplest possible rate transition chosen for the model (cf. eq 2)— and that is very clearly constrained by the different solute profiles observed at travel times of 13 years (BH59) and 35 years (BH60) from the source area. Acetate and CH$_3$(aq) concentrations in the plume build up and reach the highest concentrations inside the plume fringes, whereas...
they are lower within the plume core, where phenol concentrations and resulting substrate toxicity effects are greatest. Nevertheless, over 50% of the degraded carbon is present as acetate (Table 4).

The mineral TEAs MnO$_{2}$ and FeOOH$_{(s)}$ are consumed more extensively in the outer region of the plume core where the phenol concentration is lower, due to decreased phenol toxicity. Simulating the resulting distribution of Fe(II)(aq) and Mn(II)(aq) requires inclusion of transport, mineral precipitation, and sorption in the model. The fast, reversible surface complexation reactions cause greater retardation of Fe(II)(aq) than Mn(II)(aq), because a greater proportion of the total Fe(II)(aq) is present as an adsorbed species on the aquifer sediment.

Consideration of temporal changes in biodegradation rate results in increased degradation near the plume source, that approximately doubles the relative amount of degraded phenol mass. This can be deduced in Table 4 where 4.2% of the total dissolved phenol that has entered the aquifer has been degraded after 47 years compared with 2.3% after 25 years. In addition to the presumed impact of microbial acclimatization, this in part reflects a lower contaminant flux from the source zone in later years, characterized by lower phenolics concentration and thus less inhibition of degradation in the plume, and in part results from the increasing size of the plume. However, Table 4 shows that the relative contribution of the plume fringe to the total biodegradation of phenol decreases with time. This shows that the plume fringe size and thus mixing increases not as much as does the plume area, the latter favoring core processes as long as TEAs are present there in sufficient quantities. At the latest stage, degradation in the plume core accounts for approximately 65% of the total contaminant mass loss, whereas degradation at the plume fringe is 35%.

Implications for Natural Attenuation. Consideration of the additional reaction processes and aquifer heterogeneity has a significant impact on the estimated mass loss of phenolics. Inspection of Table 4 indicates that consideration of Fe(II) and Mn(II) production (and adsorption) alone would almost double the mass loss of phenol over the plume history, compared to a simulation that neglects their contribution to NA. This point, together with fermentation and the accumulated mass of acetate within the plume, produces a comparative 5-fold increase in phenol mass loss. Finally, considering these processes while quantifying the effect of aquifer heterogeneity ultimately increases the estimated phenol mass loss 6-fold. When compared to results from the previous model (8), the current estimate (5.1%) is more than double the earlier estimate (2.2%). There is an enormous phenol load to the aquifer at this site, making the relative differences in simulated residual phenol concentrations small for these additional processes. However, the relative increase in mass loss (6-fold within the current set of results) would be very significant for sites with weaker source terms or without toxicity effects.

The main advances demonstrated by the new modeling approach are as follows. (1) Simulating 2-D transport with calibration against a complete vertical profile of hydrochemical data has improved estimation of biodegradation by plume fringe processes. (2) Considering fermentation with H$_{2}$ respiration provides rate estimates of fermentation as well as individual TEAPs within the plume core. (3) Describing biogenic Fe(II) and Mn(II) retardation by adsorption reactions resolves difficulties in closing the electron balance and iron and carbon mass balances for the plume. It can be noted that the spatial discretization of the numerical model required in the simulations was only possible from the improved resolution of solute and TEAP distributions in the plume and particularly across the plume fringe using the MLS data. It is also important to ensure that data collection efforts for NA assessment include information on concentrations of relevant chemical species which can be the fermentation included in this analysis. A further conclusion from this study is that that reactive transport models should consider factors that influence temporal and spatial changes in biodegradation rates, to be able to understand the distribution of contaminants and TEAPs, and quantify NA over the plume history.

For the field case considered here, the FeOOH$_{(s)}$ TEAP is very important and should be considered with regard to surface complexation of ferrous species and formation of secondary mineral phases. Failure to consider processes that remove dissolved Fe(II) could underestimate the importance of the FeOOH$_{(s)}$ TEAP in plume-scale electron and carbon mass balances. Often, dissolved Fe(II) concentrations used to estimate Fe mineral oxide consumption in plumes are limited by rates of SO$_{4}$-reduction. However, in this study, low dissolved Fe(II) concentrations in the plume are not related to attenuation by metal sulfide precipitation, but by increased sorption to the aquifer matrix through surface complexation reactions. Thus, not considering surface complexation leads to a four times lower rate of FeOOH$_{(s)}$ reduction to close the plume mass and electron balance. In contrast, if the limitation of FeOOH$_{(s)}$ bioavailability is not accounted for, then the importance of the FeOOH$_{(s)}$ reduction may be overestimated, particularly if estimates are based on measurements of aquifer oxidation capacity attributable to mineral oxide content. These observations and the relatively significant role of Fe(III)-reduction in the global mass balance for the system is an important and novel discrimination achieved with the new modeling approach.

Conceptual process models for contaminant plumes are typically developed from an idealized evolution of redox conditions, based on the sequential consumption of TEAs which produces a distribution of TEAPs related to the dominance of respiration over fermentation (29, 30, 34). Central to this concept is the use of models invoking either control by microbial physiology or partial chemical equilibrium for the syntrophic degradation of H$_{2}$ in respiration reactions (3, 28–32) and explanation of TEAP distributions according to threshold levels of H$_{2}$ required for the dominant redox process (28–31, 33, 34). However, this approach is not a particularly useful diagnostic tool for determining dominant TEAPs, as it proposes the occurrence of individual processes rather than their reaction rates. It is also limited by uncertainty in the threshold H$_{2}$ concentrations for individual processes (e.g., Fe(III)-reduction and methanogenesis) (3, 31, 32, 35). In our study, the evolution of H$_{2}$ concentrations and distribution of TEAPs could be satisfactorily described using a fully kinetic description of biodegradation, which allowed parameter values for rate expressions and the relative rates of fermentation and individual TEAPs to be determined. This means the process rates for fermentation and respiration can be individually constrained at field-scale from the relevant hydrochemical data. This is an important advance in deducing the significance of TEAPs and parametrization of reactive transport models in NA assessments.

Implications for Upscaling from Laboratory to Field. The main lessons learned from our modeling exercise with respect to transferring lab results to field scale are that (i) a detailed conceptual model of the reactive processes derived at laboratory scale (14, 36) can be successfully applied at a field site. This is provided that the laboratory experiments have been performed in close connection with the field site conditions, e.g., including inoculation by material from the field site. (ii) While there are studies that have been able to keep all the degradation parameters during this transfer, e.g. ref 37 for a BTEX plume, in cases of high contaminant loading such as the Four Ashes site at least the degradation rates will in general have to be decreased in the field-scale model.
some of the several reasons are the toxicity of contaminants, lower fraction of active biomass, the variation of enzyme activity within a population, and a slower enrichment of the degrading microorganisms inside the community structure. However, the half saturation and inhibition coefficients, which influence the sequence of redox reactions, should preferably not be subject to calibration at the field scale. (iii) A fully kinetic 2-step approach allows distinction between the kinetic limitations of the degradation of the organic substrate and the consumption of electron acceptors, as reviewed in ref 2. Furthermore, it enables use of the valuable information provided by concentrations of fermentation products, but requires their measurement at the field site. (iv) The computational software capabilities are available now to describe NA plume processes at the field scale with a relatively complete set of biogeochemical reactions and components that originated from lab-scale experiments. These processes can be described for time scales of decades, in two and three dimensions, and including a stochastically generated permeability field. The lack of such computational capabilities, particularly the use of adaptive grids, has been pointed out very recently as a major current limitation for these factors, here particularly quantifying rates of fermentation and individual TEAPs, and Fe(II)(aq) sorption, should be more generally considered at sites for NA applications in the future.

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Supporting Information Available

Four sections of additional experimental and modeling details, two figures, and three tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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