

Consequences of Different Kinetic Approaches for Simulation of Microbial Degradation on Contaminant Plume Development

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Abstract

This study investigates the consequences of assuming different kinetic approaches for calculation of microbial degradation on plume development in a simple case of natural attenuation on field scale. If the required parameters are properly chosen, all approaches can simulate similar plumes for a particular given time step. The differences of contaminant concentrations in the plumes are small and would not attract attention in a natural aquifer. On long term prognoses the kinetics result in very different plumes: A complex Monod approach considering microbial growth prognoses a further spreading of the plume, compared to a first order rate law, which results in a short and early stationary plume. Other approaches show plumes between these two extremes. On the other hand, the forecasts for plumes assuming Monod kinetics are similar, even if different values for parameterization are chosen. The reason for this insensibility is, that degradation is not limited by microbial kinetics in the simulation, but by dispersive mixing. Simplifying approaches may have few and well determinable parameters, but they are not suited for proper prognoses if they neglect the prerequisite, that contaminant and electron acceptor have to be present for a reaction.

Keywords

bioremediation; modeling; microbial kinetics; prognosis; reliability

Introduction

For natural attenuation (NA) of organic pollutants in aquifers microbial degradation has to be considered as the most important destructive process (Wiedemeier et al. 1999). Biological degradation is based on a complex system of enzymatic reactions in cell organelles and transfer processes through membranes, but most of these processes are not yet completely understood (Alexander 1994, Chapelle 1993). Hence, various simplifying mathematical approaches exist to simulate microbial degradation (Koch 1998, Schmidt et al. 1985, Simkins and Alexander 1984).

Monod-kinetics is one of the most complex approaches, it considers changes in microbial population density, maximum uptake rates and non-linear dependency of turnover on substrate concentrations. This approach is quite sophisticated, but it is rarely used to simulate natural attenuation (Schäfer 2001), because it is numerically extensive and because it requires a large number of hardly determinable parameters. Michaelis-Menten kinetics (Borden and Bedient 1986) is a simplification of Monod-kinetics, since it neglects changes of microbial population and therefore spatial and temporal variation of maximum turnover rate. It is annoying, that these two approaches are often not distinguished in literature, e.g. Borden and Bedient (1986) investigate “Monod-kinetics”, but assume a constant concentration of microorganisms, i.e. in fact it is a Michaelis-Menten kinetics. In order to reduce numerical effort and parameter demand other simplifying approaches are used, like first-order (McNab Jr. and Narasimhan 1994) and zero-order rate laws (Nielsen and Christensen 1994) or kinetics are completely neglected by assuming instantaneous chemical equilibrium (Borden and Bedient 1986).

The simplification of complex kinetics yields the risk of erroneous results and misinterpretations. From direct comparison of mathematical functions it is known, that first-order as well as zero-order rate laws can overestimate the degradation rate up to several thousand percent compared to Michaelis-Menten kinetics (Bekins et al. 1998). This overestimation has been confirmed in 1D biofilm reactor models (Bonomo et al. 2000). Simkins and Alexander (1984) investigate the application range of 6 different kinetic approaches for interpretation of measured benzoate degradation in batch experiments. These and other investigations (Kelly et al. 1996, Schmidt et al. 1985) were performed in batch or column studies, where short timescales are chosen intending to observe microbial kinetics. Additionally in batch experiments electron acceptors required for contaminant degradation are often available in surplus and do never limit degradation. These conditions are not transferable to natural attenuation on site scale,

where long timescales are investigated and where the presence of electron donor as well as electron acceptor can inhibit degradation.

On larger scales (tank experiment ~1m) Michaelis-Menten kinetics have found to be more accurate than first order degradation to simulating aerobic BTX degradation (Jean et al. 2002). On site scale instantaneous chemical equilibrium has shown to be a good approximation of Michaelis-Menten kinetics (Rifai and Bedient 1990) or Monod kinetics (Koussis et al. 2003) for “fast” reactions or “long” time scales (i.e. high Damköhler number), but it causes erroneous results, if the reaction is slower than expected. Instantaneous equilibrium is also a better approach to simulating intrinsic remediation in field applications than a first order decay model (Newell et al. 1995).

These individual comparisons on different scales demonstrate, that the approach chosen to calculate microbial degradation will influence the simulation of plume development and possibly the decision, if NA is applicable. This study will compare all the different approaches discussed above and apply them to a simple scenario of aerobic toluene degradation in a homogeneous aquifer with stationary flow. These simplified conditions make sure, that all concentration changes are attributed to kinetic effects and not to heterogeneity or complex boundary conditions, allowing a direct comparison of different approaches. The spreading of the contaminant plume is simulated assuming the diverse kinetic approaches and differences of the generated plumes and in forecast plume evolution are discussed. The following questions will be attributed: How severe are the differences of simulated plumes on field scale, if diverse kinetics or chemical equilibrium are assumed? Is it possible to identify the underlying kinetics from measured concentrations? Which consequences has the assumption of a kinetic approach on the prognosis of future plume development? How different are ill parameterized complex Monod kinetics compared to a well parameterized approach with simplified kinetics?

Methods

The numerical model TBC (Schäfer et al. 1998) is able to simulate all the approaches discussed above. This ensures, that flow- and transport conditions are exactly the same for all simulations.

The simulated aquifer with dimensions of 120m x 40m x 4m (XYZ) is discretized in cells of 1m x 1m x 1m. The homogeneous conductivity is 2 m·d⁻¹ in horizontal and 0.2 m·d⁻¹ in vertical direction. A gradient of 2.5‰ in X-direction and an effective porosity of 33% result in a flow velocity of

$1.5 \text{ cm}\cdot\text{d}^{-1}$. In the beginning of the simulation the aquifer is aerobic with an oxygen concentration of $0.3 \text{ mmol}\cdot\text{l}^{-1}$, which is also found in the inflow boundary. An immobile toluene NAPL phase of $3\text{m} \times 10\text{m}$ is assumed on the groundwater table, dissolving into the mobile pore water via a gradient law

$$\frac{\partial C_{\text{mobile}}}{\partial t} = k \cdot (C_{\text{equilibrium}} - C_{\text{mobile}}) \quad (1)$$

with a maximum solubility $C_{\text{equilibrium}}$ of $5.6 \text{ mmol}\cdot\text{l}^{-1}$ and a constant dissolution velocity k of 0.001 d^{-1} . For transport of toluene and oxygen a longitudinal dispersivity α_L of 0.90 m , transversal dispersivities in horizontal and vertical direction of $\alpha_{\text{Th}}=0.09 \text{ m}$ and $\alpha_{\text{Tv}}=0.009 \text{ m}$, respectively, and a molecular diffusion of $7.4\text{E-}5 \text{ m}^2\cdot\text{d}^{-1}$ are assumed.

The first numerical approach to describe degradation considers microbial growth via Monod-kinetics. It is used to calculate concentrations after 2000, 4000 and 6000 days ($\sim 16 \text{ y}$) simulation time. The other approaches require kinetic parameters, which can not be derived from the Monod-parameters. Hence, these unknown parameters and degradation rates are chosen such that they reproduce the concentration distribution after 2000 d. Main focus was set to obtain the same plume lengths. With the parameterized kinetics the future behavior of the plume is calculated for 4000d and 6000d simulation time. The prognostic capabilities of the approaches are evaluated by comparing the simulated plumes.

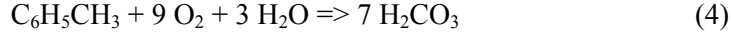
For application of Monod-kinetics a group of immobile toluene oxidizing aerobic microbes is ubiquitarily present in low concentrations ($5\text{E-}4 \text{ mmolC}\cdot\text{kg}^{-1}$). Growth of this microbial group X follows a “double Monod-kinetics” (Bae and Rittmann 1996) with two multiplied Monod-terms for toluene and oxygen, allowing a microbial growth and degradation only if toluene and oxygen are present. A constant rate simulates biomass decay e.g. due to endogenous respiration. Net growth rate is growth minus decay, resulting in a permanent consumption of substrates even if biomass is constant.

$$\frac{\partial X}{\partial t} = v_{\text{max}} \cdot X \cdot \frac{C_{\text{toluene}}}{MC_{\text{toluene}} + C_{\text{toluene}}} \cdot \frac{C_{\text{O}_2}}{MC_{\text{O}_2} + C_{\text{O}_2}} - v_{\text{dec}} \cdot X \quad (2)$$

The values for maximum growth velocity v_{max} , half velocity concentrations MC for toluene and oxygen, and decay rate v_{dec} assumed for this reaction are summarized in table 1. The consumption of toluene is coupled to microbial growth by a Yield-coefficient Y_{toluene} .

$$\frac{\partial C_{\text{toluene}}}{\partial t} = -\frac{1}{Y_{\text{toluene}}} \cdot v_{\text{max}} \cdot X \cdot \frac{C_{\text{toluene}}}{MC_{\text{toluene}} + C_{\text{toluene}}} \cdot \frac{C_{\text{O}_2}}{MC_{\text{O}_2} + C_{\text{O}_2}} \quad (3)$$

An analogous formulation is used to calculate oxygen consumption, the Yield-coefficient is calculated from the stoichiometric oxygen demand.



Assuming a constant microbial activity over time and space and the presence of a sufficiently large amount of oxygen, Eq. 3 can be transformed to:

$$\frac{\partial C_{\text{toluene}}}{\partial t} = -k_M \cdot \frac{C_{\text{toluene}}}{MC_{\text{toluene}} + C_{\text{toluene}}} \quad (5)$$

This equation is a Michaelis-Menten kinetics with respect to toluene concentration. The main difference is the assumption of a spatially and temporally constant microbial population. The half-velocity concentration for toluene MC_{toluene} is taken from table 1, the lumped maximum degradation rate k_M is chosen such that the length of the toluene plume after 2000d simulation time is equal to the previous plume calculated with Monod-kinetics.

For small toluene concentrations the denominator of the Monod-term is approximately MC_{toluene} and Eq. 5 can be transformed to a first order rate law:

$$\frac{\partial C_{\text{toluene}}}{\partial t} = -k_1 \cdot C_{\text{toluene}} \quad (6)$$

For high toluene concentrations the Monod-term is nearly one and Eq. 5 can be substituted by a zero order rate law:

$$\frac{\partial C_{\text{toluene}}}{\partial t} = -k_0 \quad (7)$$

If the reaction is fast compared to the transport velocity (high Damköhler number), equilibrium is achieved and kinetics of the reaction can be neglected. A law of mass action is formulated according to the stoichiometric equation for toluene oxidation (Eq. 4):

$$\frac{C_{\text{H}_2\text{CO}_3}^7}{C_{\text{toluene}} \cdot C_{\text{O}_2}^9} = K \quad (8)$$

Equilibrium is far on product side, causing a reaction of toluene and oxygen until one reaction partner is nearly completely consumed. The approach requires no fitting of kinetic parameters.

In order to test the relevance of accurate parameterization of Monod-kinetics, two parameter sets deviating from the values in table 1 are chosen. The first set of parameters generally overestimates microbial degrada-

tion by a factor of 2 in all parameters, while the second scenario underestimates degradation (table 2).

The simulated plumes are displayed and analyzed with Surfer[®]. In addition to simple optical comparison the following more objective criteria are used to compare the simulated plumes.

1. Contaminant mass in the plume at simulated time steps (measure for contaminant degradation)
2. Plume volume with contaminant concentrations $>0.02 \text{ mmol}\cdot\text{l}^{-1}$ (measure for total plume volume)
3. Plume volume with contaminant concentrations $>0.40 \text{ mmol}\cdot\text{l}^{-1}$ (measure for high contaminated areas)
4. Plume length

Contaminant mass in the plume is calculated by the simulation program TBC. Surfer[®] determines the areas of high concentrations ($>0.40 \text{ mmol}\cdot\text{l}^{-1}$) and total plume area ($>0.02 \text{ mmol}\cdot\text{l}^{-1}$) in every simulated aquifer layer. Multiplication with the layer thicknesses results in plume volumes. The limiting values for “high” and “low” concentrations were chosen arbitrarily. Plume length is defined as the distance between downstream boundary of the NAPL source zone and the forefront of the plume defined by the concentration isoline of $0.02 \text{ mmol}\cdot\text{l}^{-1}$.

Table 1. Parameters of Monod-kinetics

v_{\max}	1.0 d^{-1}	MC_{toluene}	$1\text{E-}5 \text{ mmol}\cdot\text{l}^{-1}$	Y_{toluene}	$0.100 \text{ mol}\cdot\text{mol}^{-1}$
v_{dec}	0.1 d^{-1}	MC_{O_2}	$1\text{E-}5 \text{ mmol}\cdot\text{l}^{-1}$	Y_{O_2}	$0.086 \text{ mol}\cdot\text{mol}^{-1}$

Table 2. Monod-parameters for over- or underestimation of microbial degradation

overestimation of microbial degradation					
v_{\max}	2.0 d^{-1}	MC_{toluene}	$0.5\text{E-}5 \text{ mmol}\cdot\text{l}^{-1}$	Y_{toluene}	$0.200 \text{ mol}\cdot\text{mol}^{-1}$
v_{dec}	0.1 d^{-1}	MC_{O_2}	$0.5\text{E-}5 \text{ mmol}\cdot\text{l}^{-1}$	Y_{O_2}	$0.172 \text{ mol}\cdot\text{mol}^{-1}$
underestimation of microbial degradation					
v_{\max}	0.5 d^{-1}	MC_{toluene}	$2\text{E-}5 \text{ mmol}\cdot\text{l}^{-1}$	Y_{toluene}	$0.050 \text{ mol}\cdot\text{mol}^{-1}$
v_{dec}	0.1 d^{-1}	MC_{O_2}	$2\text{E-}5 \text{ mmol}\cdot\text{l}^{-1}$	Y_{O_2}	$0.043 \text{ mol}\cdot\text{mol}^{-1}$

Results and discussion

If Monod kinetics is considered, the highest bacteria population and therefore main degradation potential evolves at the upstream boundary of the NAPL contamination, where toluene and oxygen are mixed advectively

(no figure). Downstream of the source degradation is only found in the dispersive mixing zone of the plume fringe. Outside of the plume no degradation occurs due to a lack of toluene, inside of the plume oxygen is depleted.

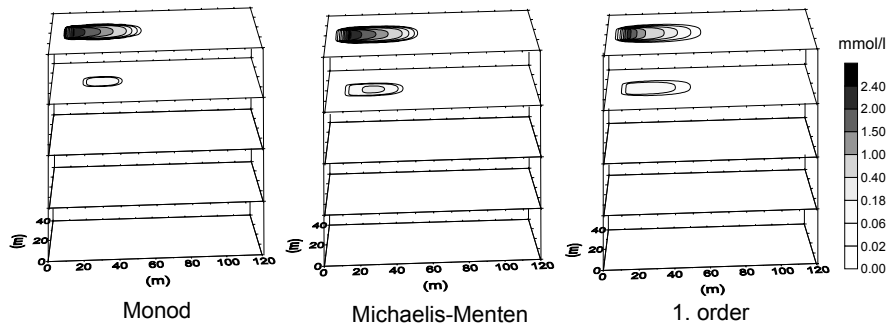


Fig. 1. Toluene concentrations in the simulated 5 aquifer layers after 2000d of simulation time for three different approaches for microbial degradation

Only toluene concentrations are considered for comparison of different simulation approaches. The unknown parameters of the approaches are chosen such that the toluene plumes after 2000d are similar to the plume calculated with the Monod approach. No simplifying approach was able to reproduce this plume exactly in all details (Fig. 1). Hence, we decided to choose the parameters such that the plume lengths after 2000d are the same. This means, that other criteria like contaminant masses of the plumes (see Fig. 4) are different already at $t=2000d$. Figure 1 shows the toluene concentrations after 2000d for Monod-kinetics (Eq. 3), Michaelis-Menten kinetics (Eq. 5), and first order degradation (Eq. 6). Difference plots allow a more detailed comparison of the simulated toluene concentrations after 2000d (Fig. 2). Positive values indicate, that the appropriate approach overestimates contaminant concentrations compared to the Monod approach.

Michaelis-Menten kinetics satisfactorily reproduce the plume simulated with Monod-kinetics. Upstream of the contaminant source toluene concentrations are overestimated with respect to the Monod approach (up to +8.2% C_{max}), due to neglecting a high bacteria population and increased uptake rates. The same is found for first order degradation, though in predominant part of the plume concentrations are underestimated (up to -37.3% C_{max}). Zero order degradation generally overestimates concentrations (up to +9.4% C_{max}) in the whole plume regarding the Monod ap-

proach. Toluene concentrations calculated assuming chemical equilibrium agree well with the Monod kinetics, only in the plume front concentrations are underestimated (up to $-1.0\% C_{\max}$) due to neglecting the lag-time of bacteria.

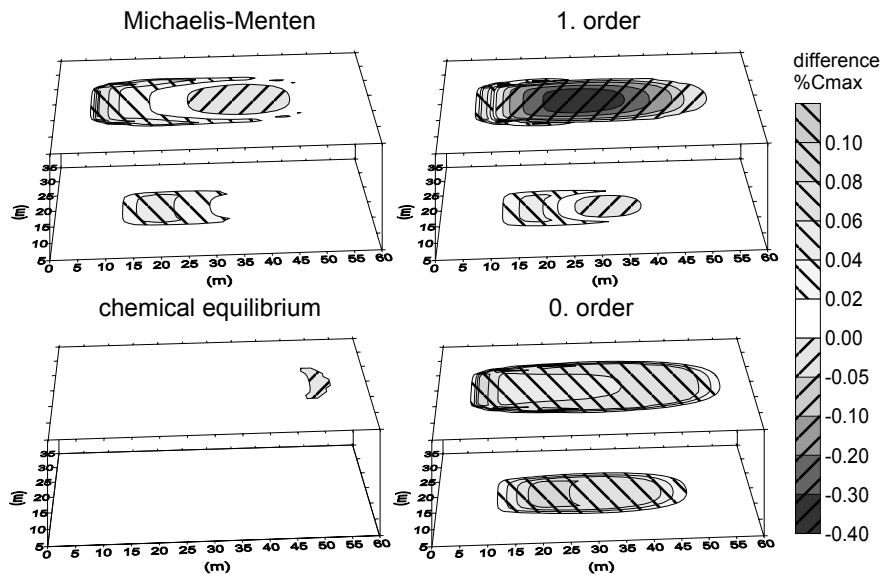


Fig. 2. Difference plots toluene concentrations “appropriate approach – Monod-approach”, detail of the upper two aquifer layers after 2000d simulation time

While plume shapes agree quite well after a simulation time of 2000d, the prognosis of the future plume development shows increasing deviations. Figure 3 shows the toluene concentrations after 6000d for the approaches discussed above. The plume simulated assuming a Michaelis-Menten kinetic is shorter and not as wide (horizontally and vertically) as the plume simulated for Monod-kinetics. The first order degradation approach overestimates degradation in high contaminated areas resulting in a short and already stationary plume.

The prognoses of all kinetic approaches are evaluated by calculated plume lengths, contaminant masses and plume volumes with toluene concentrations $>0.40 \text{ mmol}\cdot\text{l}^{-1}$ or $>0.02 \text{ mmol}\cdot\text{l}^{-1}$ (Fig. 4). Compared to Monod-kinetics all other approaches generally underestimate the plume length. The plume simulated with first order degradation reaches steady state after 4000d. The other approaches show increasing plume lengths, but slower than under consideration of microbial growth.

The mass of toluene in the plume is different already after 2000d of simulation time (Fig. 3), because the distributions of contaminant concentrations in the plumes are different for most approaches. With spreading of the plume contaminant mass increases, but to a different degree for each approach. Due to varying toluene distributions the volumes of the plume containing toluene concentrations $>0.40 \text{ mmol}\cdot\text{l}^{-1}$ or $>0.02 \text{ mmol}\cdot\text{l}^{-1}$ vary and develop differently over time (Fig. 4).

The chosen over- and underestimation of microbial degradation assuming Monod-kinetics has only negligible consequences on plume spreading. Plume lengths, masses and volumes are nearly identical to the calculation with the original Monod parameters (Fig. 4).

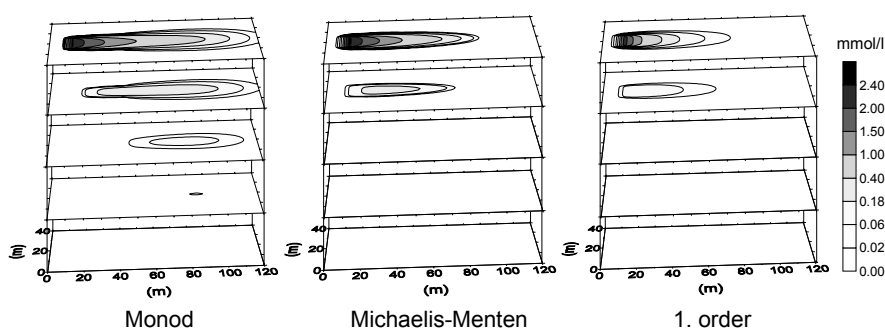


Fig. 3. Prognosed toluene concentrations in the simulated 5 aquifer layers after 6000d simulation time for three approaches for microbial degradation

Conclusions

As expected the numerical approaches for calculation of microbial degradation result in similar, but not identical plumes after 2000d simulation time. Due to sparse observational networks, measuring errors, mixing in full screened observation wells or in heterogeneous flow fields it is unlikely that concentration differences in the range of $\pm 20\%$ can be detected. Hence, most of the kinetics investigated can sufficiently reproduce a single snapshot of measured contaminant concentrations and it seems to be impossible to identify the underlying kinetics from one concentration distribution only. The only exception is first order degradation with significant concentration differences compared to the other approaches. Since this approach is quite often used, either degradation in real applications

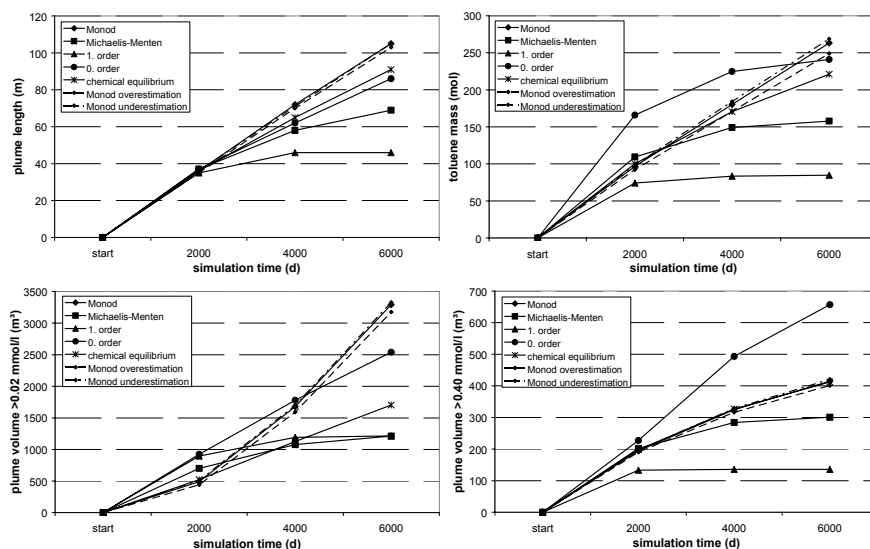


Fig. 4. Plume development over time for the assumed numerical approaches

follows first order kinetics (in contrast to our simulation) or even these larger concentration differences are not detectable in real sites.

With increasing time the simulated plumes behave different, hence measured concentration time series may increase the chance to detect the underlying kinetics. If the assumed kinetic is not appropriate, it may be able to reproduce the plume at a specific time, but the long term prognosis will fail. All investigated simplifying approaches overestimate degradation compared to Monod kinetics and forecast shorter or early stationary plumes, what is an alarming result with regard to risk assessment.

The main argument against the more complex Monod approach is the large number of unknown parameters, which are often not well-definable. The systematic over- and underestimation of microbial degradation by changing all parameter values by a factor of 2 has no relevant consequences on contaminant plume behavior, that is the simulation results are not very sensitive to these parameter changes. The plumes calculated with ill parameterized Monod-kinetics agree better with the original plume than the approaches with simplifying kinetics.

The reason for this insensibility is, that in the simulation aerobic degradation is not limited by microbial kinetics, but by the dispersive mixing of aerobic water in the aquifer and toluene contaminated water inside of the plume, what is a well known phenomenon for dissolved contaminants and electron acceptors (Cirpka et al. 1999, Klenk and Grathwohl 2002). Monod

kinetics take care, that microbial degradation occurs only if toluene and oxygen are present at the same time and at the same place. The same applies to the assumption of chemical equilibrium. Hence, Monod kinetics and chemical equilibrium show very similar plumes as expected from Koussis et al. (2003), Borden and Bedient (1986) or Rifai and Bedient (1990), though the concentration distribution inside of the plumes is not exactly the same (Fig. 3).

Simplifying kinetic approaches do not consider, that contaminant and electron acceptor have to be present. A first order rate law, for example, calculates degradation like radioactive decay, depending on contaminant concentrations only, and simulates degradation even in the centre of the plume, where no oxygen is present (Jean et al. 2002; Newell et al. 1995). But the same applies for simple Michaelis-Menten kinetics or zero order degradation. All these approaches overestimate degradation, causing non-conservative prognoses, because the rate limiting step (dispersion) is neglected. Simplifying approaches can only be successful, if they represent the kinetics of the degradation limiting step, e.g. if microbial consumption of Fe(III)-minerals follows a (pseudo) zero order rate law, the whole process of Fe(III)-reduction and contaminant oxidation should be zero order.

The presented results are based on the simple case of one non-sorbing contaminant and a single electron acceptor. For more complex (i.e. most natural) systems the assumption of a single degradation rate or the equilibrium approach are hardly applicable. If several electron acceptors are present, degradation rates will change depending on the redox reaction. In chemical equilibrium exclusively the thermodynamically most favorable oxidant is consumed, what does not correspond to the observation, that more than one degradation reaction can occur at the same time (Lovley and Phillips 1987, Lyngkilde and Christensen 1992). Microbial degradation can be inhibited by the presence of toxic substances, what is not considered in simplifying approaches, and some thermodynamically favorable reactions simply do not occur, if the catalyzing microorganisms are not present. Kinetic effects also have to be considered, if competitive reactions occur, e.g. if oxygen is consumed by aerobic bacteria and pyrite oxidation or if organic contaminants are adsorbed or degraded simultaneously.

Hence, simplifying approaches should only be assumed for prognoses, if the assumptions required to drive them are in fact fulfilled. E.g. if electron acceptors are never limiting degradation, at small contaminant concentrations and sufficient amounts of active microorganisms catalyzing the reaction, the assumption of a first order rate law may be successful. If degradation is limited by slow mixing of electron acceptor and –donor, the simulation approach has to make sure that a reaction only occurs, if both reactants are present – what is a trivial but often neglected demand. In aq-

uifers with one electron acceptor, one donor and high Damköhler numbers chemical equilibrium can be an adequate simplifying approach. For more complex systems Monod kinetics are recommended. Though we cannot conclude from the simulations, that Monod-kinetics simulate the “real” degradation processes and plume spreading, it definitely considers many of the processes known from extensive laboratory studies. The problem, that the Monod parameters cannot be exactly identified, has no significant consequences on the simulated plume at least on the simple system investigated.

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