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MODELING THE BIODEGRADATION OF ORGANIC CONTAMINANTS WITH TMVOCBIO

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ABSTRACT

The contamination of soil and groundwater by organic contaminants, such as hydrocarbons and solvents, represents a potential risk for human health and for the environment. It has been observed in natural systems and verified by laboratory experiences that organic contaminants are actively degraded by naturally occurring micro-organisms living in the subsurface, which can use them as substrates for their metabolic processes and growth. Thus, the modeling of biodegradation reactions can represent a useful tool for the interpretation of coupled processes that govern the migration and degradation of organic contaminants in the subsurface. The existing TMVOC numerical reservoir simulator, developed to model the migration of organic mixtures in the subsurface, was improved by adding capabilities for the modeling of aerobic and anaerobic biodegradation reactions of hydrocarbons and chlorinated solvents. Reactive transport is coupled with the multiphase non-isothermal flow of multicomponent fluid mixtures containing water, and sets of user-defined non-condensible gases (NCG), volatile organic compounds (VOC) and dissolved solids. The mathematical formulation of biodegradation reactions, a modified version of that developed at USGS for the BIOMOC computer code (Essaid and Bekins, 1997), is presented together with underlying assumptions. It allows the modeling of simultaneously occurring aerobic and anaerobic degradation processes involving multiple organic substrates, electron acceptors (EA) and nutrients, accounting for the inhibition phenomena conventionally considered by other analytical and numerical codes. Then, the implemented numerical solution of biodegradation reactions is discussed. It is an extension to multiple degradation processes of the T2LBM EOS module formulation developed to model the aerobic/anaerobic biodegradation of organic matter in municipal landfills (Oldenburg, 2001). Examples of code verification against accurate numerical solutions and code validation against published experimental results are also presented.

THE TMVOC RESERVOIR SIMULATOR

TMVOC V.1.0 (Pruess and Battistelli, 2002) is a numerical simulator for three-phase non-isothermal flow of water, a user-defined set of NCGs, and a mixture of VOCs in 3D heterogeneous porous media. An extension of the TOUGH2 general-purpose simulation program (Pruess et al., 1999), TMVOC is designed for application to contamination problems that involve hydrocarbon fuel or organic solvent spills in saturated and unsaturated zones. It can model contaminants behavior under "natural" environmental conditions, as well as for engineered systems, such as soil vapor extraction, groundwater pumping, or steam-assisted source remediation. TMVOC V.1.0 is available through ESTSC since May 2002.

The mass components tracked by TMVOC are: water, NCG user-defined gases (O_2, N_2, CO_2, CH_4, ethane, ethylene, acetylene, and pseudo-component air) and NHC user-defined VOCs (hydrocarbons or organic solvents). These mass components are distributed under local thermodynamic equilibrium conditions in any of the three possible flowing phases: gas, aqueous, and NAPL. Any combination of the three phases and related possible phase transitions are modeled by TMVOC as shown in Fig. 1. A detailed description of the thermodynamic and numerical formulations of TMVOC V.1.0, is given by Pruess and Battistelli (2002).

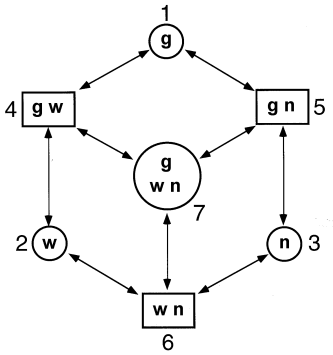

Figure 1. Phase combinations and phase transitions modeled by TMVOC. g , w and n stand for gas, aqueous, and NAPL, respectively.

TMVOC V.1.0 implements a simple representation of biodegradation reactions assuming that VOCs dissolved in the aqueous phase may decay according to the standard exponential decay law.

BIODEGRADATION REACTIONS

Biologically mediated degradation reactions are oxidation/reduction (redox) reactions, involving the transfer of electrons from the organic contaminant compound (the substrate) to an EA (the oxygen in

aerobic conditions). The reactions are catalyzed by enzymes produced by micro-organisms living in the subsurface. In the reaction, the electron donor is oxidized and transfers its electrons to the electron acceptor, generating energy for microbial growth. Organic contaminants can be transformed by biodegradation reactions in two different ways: 1) as a primary substrate, or 2) as a cometabolite (Semprini and McCarty, 1992). A compound is biodegraded as a primary substrate when biodegradation of the compound provides the micro-organism with carbon for synthesis of new biomass and energy for the synthesis function. Most organic subsurface contaminants are degraded as primary substrates.

Biomass growth is made possible by the presence of other important elements needed for the synthesis of cellular material, such as proteins, DNA, RNA, and ATP. Carbon is the most abundant component of cellular material, making up approximately 50% of the cell's dry weight. Other important elements are oxygen (20%), nitrogen (14%), hydrogen (8%) and phosphorous (3%). The remaining 5% consists of trace elements such as sulfur, potassium, and a variety of metals. The uptake of cellular precursors for synthesis of biomass is not related by any stoichiometric reaction. Instead, these nutrients are related by their respective fraction of cell weight. The organic carbon, the EA and the nutrients are all limiting components to microbial growth. The rate of substrate degradation is conventionally expressed in mathematical terms using the Michaelis-Menten rate expression for enzyme kinetics.

An organic compound is biodegraded as a cometabolite when it is transformed fortuitously by enzymes or cofactors produced by a micro-organism for other purposes. Most halogenated aliphatic hydrocarbons are biodegraded through cometabolism (Semprini and McCarty, 1992). In a cometabolic reaction, the transformation of the cometabolite provides neither growth nor energy to the micro-organism. Biodegradation reactions can be classified as either fermentative or respiratory. In fermentation, substrates are only partially oxidized. Electrons are internally recycled, generally yielding at least one by-product that is more oxidized and one that is more reduced than the original substrate. An example of fermentation is that of toluene under methanogenic conditions which generates CO_2 and CH_4. In respiration reactions, an external EA is utilized as a terminal EA in the biodegradation reaction. Respiration reactions are either aerobic or anaerobic. Oxygen is the terminal EA in aerobic reactions, while an EA other than oxygen is the EA in anaerobic reactions. The occurrence of these reactions in the subsurface depends on the availability of different EA and on redox conditions, which can vary substantially as a result of contaminant bio-degradation or other natural conditions.

In the presence of organic substrates and dissolved oxygen, micro-organisms capable of aerobic metabolism will predominate over anaerobic forms. However, dissolved oxygen is rapidly consumed in the interior of contaminant plumes, converting these areas into anoxic zones. Under these conditions, anaerobic bacteria begin to utilize other EA to metabolize dissolved organic contaminants. The principal factors influencing the utilization of the various EA include: 1) the relative biochemical energy provided by the reaction; 2) the availability of individual or specific EA; and 3) the kinetics of the microbial reactions associated with the different EA.

THE TMVOCBIO CODE

The uptake of organic contaminants due to degradation reactions mediated by micro-organisms living in the subsurface is dependent on many coupled processes, including multiphase flow and transport of solutes, biodegradation reactions involving primary and cometabolic substrates, EA and nutrients availability, as well as chemical equilibria in the aqueous phase. The complexity of these phenomena led to the development of many different mathematical models for the simulation of biodegradation reactions in porous media. These models differ in many respects, starting with the way the micro-organisms present in the subsurface are conceptualized and treated, either as biofilms, as microcolonies, or according to the so-called macroscopic approach.

Modified forms of the Michaelis-Menten equation used to express the uptake rate of substrate accounting for the limitation by either the substrate, the EA and nutrients have been proposed to model the kinetics of biodegradation reactions in subsurface porous media. A general consensus on a specific mathematical formulation is not readily available, so that different approaches can be found in presently available numerical models. In particular two approaches are usually followed: 1) it is assumed that all the limiting factors are acting simultaneously to control the substrate uptake rate; this approach is conventionally known as 'multiplicative Monod' or 'multiple Monod' model (Borden and Bedient, 1986); 2) it is assumed that the substrate uptake rate is controlled by the most limiting factor among those acting for the specific substrate; this latter approach is known as the 'minimum Monod' model. Whereas in all models both the primary substrate and EA are considered in the substrate degradation rate equation, the nutrients availability is either considered to limit directly the substrate degradation rate (Waddill and Widdowson, 1998), or to limit biomass growth rate, without explicitly affecting the substrate degradation rate (Essaid and Bekins, 1997).
In order to improve the TMVOC V.1.0 numerical simulator, a literature survey was conducted with the

purpose of reviewing the most widely used mathematical formulations employed to model biodegradation reactions in the subsurface. The final goal of the review was to identify a mathematical formulation suitable to be implemented within the multiphase TMVOC code. Criteria considered for this choice were:

- the generality of the formulation;
- the phenomena taken into consideration, such as inhibitory effects;
- the simplicity of the formulation, based on parameters which can be determined with existing field and laboratory methodologies.

Assumptions

For the implementation of biodegradation reactions in TMVOC, a number of simplifying assumptions have been considered, in analogy to those used by several authors in the field of numerical modeling of biodegradation reactions in the subsurface:

- The microbial populations are conceptualized as multiple independent heterotrophic groups present as scattered colonies attached on the rock grain surfaces.
- Bacteria transport is assumed to be negligible: thus, biomass concentrations are not included among the TMVOCBio primary variables.
- All the biomass is considered active in the biodegradation process.
- Diffusion processes into and out of the biophase are neglected, following the macroscopic approach assumption. Degradation rates depend directly on aqueous phase solute concentrations.
- It is assumed that bioreactions are not affected by chemical equilibria. Inhibition functions of temperature (Oldenburg, 2001) and aqueous phase saturation are included.
- Each microbial population can be involved in several degradation processes, each one involving a single organic substrate.
- The substrate degradation rate for each process can be described using either the 'multiplicative Monod' or the 'minimum Monod' model accounting for substrate, EA and nutrients availability (Waddill and Widdowson, 1998).
- Biomass growth inhibition, toxicity effects, as well as competitive and non-competitive inhibition are described according to commonly used formulations (Essaid and Bekins, 1997).
- It is assumed that the time needed for acclimation of microbial populations to new substrate and EA concentration levels (lag-time) is negligible.
- Predation of microbes by other microorganisms is neglected.
- Changes of porous medium porosity due to biomass growth is neglected as well as related effects on medium permeability (clogging).
- A minimum user-specified biomass concentration is maintained in the absence of any contaminants degradation, assuming that bacteria can grow on natural occurring organic carbon.

Mathematical Formulation of Biodegradation Reactions

The degradation rate of the organic substrate for the generic biodegradation process is expressed using a multiplicative Monod kinetic rate equation (Borden and Bedient, 1986; Waddill and Widdowson, 1998). The following equations are referred to a single process acting on a primary substrate. Extension to multiple processes is given afterwards. For the sake of simplicity, only the limitation due to substrate and EA availability is considered, even though limitations due to any other solute dissolved in the aqueous phase can be modeled by adding the appropriate Monod term. The degradation rate is:

$$\frac{dS}{dt} = -\mu_{0B} B \qquad (1)$$

where

$$\mu_{0B} = \frac{\mu_{\max,B}}{I_{NC}} f_T f_{SW} \frac{S}{K_S I_C + S + I_H} \frac{E}{K_{EA} I_C + E + I_H} \frac{1}{I_B} \qquad (2)$$

and

B, biomass conc. (kg biomass/ kg aqueous phase).

f_T, f_{SW}, inhibitive functions of temperature and aqueous phase saturation (dimensionless).

I_B, biomass growth inhibition factor (dimensionless).

I_C, competitive inhibition factor (dimensionless).

I_H, Haldane inhibition factor due to toxicity effects (kg solute / kg aqueous phase).

I_{NC}, non-competitive inhibition factor, dimensionless.

K_{EA}, the EA half saturation constant (kg EA / kg aqueous phase).

K_S, the substrate half saturation constant (kg substrate/ kg aqueous phase).

E, the EA concentration (kg EA / kg aqueous phase).

S, substrate conc. (kg substrate / kg aqueous phase).

t, time (s).

$\mu_{max,B}$, maximum specific substrate utilization rate by biomass (kg substrate / (kg biomass s)).

$\mu_{0,B}$, specific substrate utilization rate by biomass (kg substrate / (kg biomass s)).

The biomass inhibition is an empirical means to limit excessive biomass growth which could occur near spill areas where a continuous supply of organic substrates can act for extended periods of time:

$$I_B = \frac{K_{Bio} + B}{K_{Bio}} \qquad (3)$$

where K_{Bio} is the biomass inhibition constant (kg biomass/ kg aqueous phase). This is a form of non-

competitive inhibition in which an excessive biomass concentration reduces the growth rate of micro-organisms. The excessive concentration of any solute S_j can inhibit the degradation process due to toxic inactivation. This effect can be modeled using the classic enzyme Haldane equation

$$I_H = \frac{(S_j)^2}{K_{Hj}} \quad (4)$$

where K_H is the Haldane inhibition constant, (kg substrate/ kg aqueous phase).
I_C and I_{NC} are the competitive and non-competitive inhibition factors, respectively, due to any solute (Essaid and Bekins, 1997). For a single solute S_j having inhibitory effects, the inhibition factors are as follows:

$$I_C = \frac{K_{Cj} + S_j}{K_{Cj}} \quad (5)$$

$$I_{NC} = \frac{K_{NCj} + S_j}{K_{NCj}} \quad (6)$$

where K_C and K_{NC} are the competitive and non-competitive half saturation constants (kg substrate/ kg aqueous phase). A different formulation of competitive and Haldane inhibition effects is optionally available in TMVOCBio by applying them only to the substrate Monod term. The form is the conventional one used to model cometabolic degradation processes. The minimum Monod model is implemented in TMVOCBio as an alternative to the multiplicative Monod model, following the formulation proposed by Essaid and Bekins (1997)

$$f_{Monod} = \min\left(\frac{S}{K_S I_C + S + I_H}; \frac{E}{K_{EA} I_C + E + I_H}\right) \quad (7)$$

$$\mu_{0B} = \frac{\mu_{\max,B}}{I_{NC}} f_T f_{SW} f_{Monod} \frac{1}{I_B} \quad (8)$$

The rate of biomass change including the effects of biomass death rate is

$$\frac{dB}{dt} = \left(Y \mu_{0,B} B - \delta B\right) \quad (9)$$

where:
Y, is the yield coefficient (kg biomass/ kg substrate).
δ, is the first order biomass death rate constant; s^{-1}.

Numerical Solution of Biodegradation Reactions

Biodegradation reactions are assembled and solved within subroutine BIOREACT, called by subroutine MULTI in analogy to subroutine QU which computes the contribution of conventional sink/ sources. The biomass growth can be expressed in terms of substrate degradation rate. At the end of the time step the biomass concentration can be evaluated as (Oldenburg, 2001):

$$B = B_0 - Y \left.\frac{dS}{dt}\right|_{S^*} \Delta t - \delta B_0 \, \Delta t \quad (10)$$

where:
Δt, is the time step length (s);
B_o, is biomass concentration at the beginning of the time step, (kg biomass / kg aqueous phase).

The substrate uptake rate is computed at S=S*. S* is evaluated by interpolation between the substrate concentration at the beginning (S_1) and that evaluated at the end of the time step (S_2) according to

$$S^* = S_1(1-w) + S_2 \, w \quad (11)$$

where the weight factor w is chosen between 0 and 1, with $w > 0$. By substituting eq. 10 into 1, and rearranging we obtain:

$$\left.\frac{dS}{dt}\right|_{S^*} = \frac{-\mu_{o,B} \, B_o (1 - \delta \, \Delta t)}{\left(1 - Y \, \mu_{o,B} \, \Delta t\right)} \quad (12)$$

which can then be expanded using eq. 1 and 2.
The substrate degradation rate is discretized as a first-order reaction in time, as in the T2LBM module (Oldenburg, 2001)

$$\Delta S = S_2 - S_1 = \frac{dS}{dt} \Delta t \quad (13)$$

The changes of other mass components ΔX deriving by the substrate degradation are calculated according to the uptake coeffcients β^k,(k=1,NK), for the specific degradation process (Essaid and Bekins, 1997)

$$\Delta X^k = \beta^k \, \Delta S \quad (14)$$

Eq. 13 can be solved for the new substrate concentration, S_2, by Newton-Raphson iteration, by finding the root S_2 of the $f(S_2)$ function below

$$f(S_2) = \left.\frac{dS}{dt}\right|_{S^*} \Delta t + S_1 - S_2 = 0 \quad (15)$$

The iterative N-R equation is:

$$S_2^{\,p+1} = S_2^{\,p} - \frac{f(S_2^{\,p})}{f'(S_2^{\,p})} \quad (16)$$

Convergence is achieved by satisfying the following condition within the user-defined accuracy ε :

$$\left| \, S_2^{\,p+1} - S_2^{\,p} \, \right| = \left| \, \frac{f(S_2^{\,p})}{df(S_2^{\,p}) \big/ dS} \, \right| \le \varepsilon \quad (17)$$

Upon convergence of the time step, assuming there are no changes of the amount of aqueous phase stored in the grid element, the microbial mass fraction in the aqueous phase would be updated according to

$$B(t + \Delta t) = B(t) \left(1 - \delta \Delta t\right) - Y \Delta S \quad (18)$$

In multiphase conditions, the microbial mass fraction in the aqueous phase is updated considering both the microbial mass growth and death, as well as the

change in the aqueous phase mass stored in the porous medium, due to variations of aqueous phase saturation and density. Mass balances of microbial populations are performed without including the biomass among conventional mass components.

Extension to Multiple Simultaneous Processes

Following the BIOMOC approach, the above numerical formulation is extended to model the occurrence of multiple degradation processes simultaneously acting on the same organic substrate but mediated by different microbial populations or based on different redox reactions, thus involving different EA. Let's assume the generic substrate *S(i)* is degraded in *Nproc(i)* simultaneous degradation processes. Each process is mediated by a single bacterial population *B(ip)*, *ip*=1, *Nproc(i)*, whereas the same population can degrade different substrates in different degradation processes. The total degradation rate for the substrate *S(i)* is:

$$\frac{dS(i)}{dt} = \sum_{ip=1}^{Nproc(i)} [\frac{dS(i)}{dt}](ip) = \sum_{ip=1}^{Nproc(i)} [-\mu_{0B}(ip)\, B(ip)] \quad (19)$$

Eq. 2 to 15 can be rewritten with reference to the *ip* generic process, extending it to the occurrence of *Nproc(i)* simultaneous processes:

$$\frac{dS(i)}{dt} = \sum_{ip=1}^{Nproc(i)} [\frac{-\mu_{o,B}(ip)\, B_o(ip)(1-\delta(ip)\,\Delta t)}{(1-Y(ip)\,\mu_{o,B}(ip)\,\Delta t)}] \quad (20)$$

The previous development of N-R iteration can be modified by considering the *Nproc(i)* processes occurring for substrate *S(i)*. Eq. 15 becomes:

$$f(S_2(i)) = [\sum_{ip=1}^{Nproc(i)} [\frac{dS(i)}{dt}\Big|_{S^*}](ip)\,]\;\Delta t + S_1(i) - S_2(i) = 0 \quad (21)$$

Function $f(S_2(i))$ is derived numerically for the N-R iteration process within subroutine BIOREACT to find the substrate concentration at the end of the time step. The substrate changes due to the contribution of each degradation process are tracked to compute the related EA consumption and by-products generation. The concentration of microbial populations is updated at the end of a converged time step considering the different processes in which the microbial populations are active, following the procedure delineated for single substrate degradation.

CODE VERIFICATION

Numerical results of contaminants degradation in batch models can be easily compared to numerical solutions calculated with a spreadsheet using a fully explicit Euler method with very small time steps. Batch modeling was used to verify the proper implementation of the numerical solution of biodegradation equations into TMVOCBio. As an example, the simulation of the degradation of two primary substrates mediated by a single microbial population and limited by oxygen availability is presented. Different maximum time steps of 0.05 and 0.025 days were used to test the sensitivity to time discretization. Substrates concentrations were accurately reproduced for both maximum time steps and w_{VOC} weighting factor in the range 0.5 to 1. On the other hand, the oxygen and biomass concentrations were affected both by time step length and the weighting factor w_{EA} chosen to interpolate the oxygen concentration value. Fig. 2 shows the TMVOCBio results compared with the spreadsheet calculations. These results were obtained using a maximum time step of 0.05 days, and weighting factors w_{VOC}=0.9 and w_{EA}=0.5.

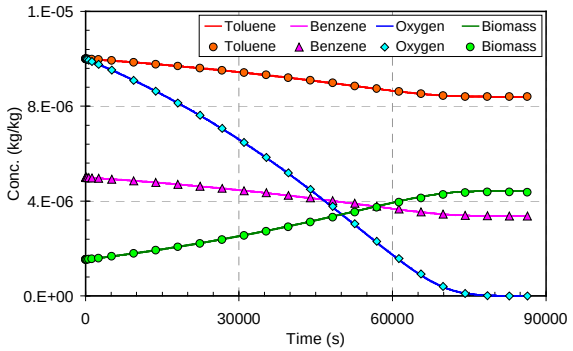

Figure 2. Batch test simulation: biodegradation of two primary substrates by a single microbial population limited by oxygen availability. (TMVOCBio: symbols; spreadsheet calculations: lines).

CODE VALIDATION

The TMVOCBio formulation was validated using published laboratory and field experimental results to check the actual code ability to simulate the biodegradation processes observed in real systems. McQuarry et al. (1990) presented the results of a laboratory experiment of toluene degradation under aerobic conditions in a sand-packed column. They simulated the experiment with a flow and transport computer code incorporating biodegradation reactions following a multiplicative Monod model. Water was injected at one side of the column for 53 days with variable oxygen and toluene concentrations and samples were taken at the column outlet to determine the composition of effluent water. Average toluene and oxygen concentrations were 0.4 mg/L and 6 mg/L, respectively. Water flow rate was also increased after the first 44 days of injection.

McQuarry and coworkers performed a best fit analysis to determine the unknown values of maximum specific degradation rate of toluene, the biomass yield, the half saturation constant of toluene

and the biomass death rate. The same values were used for the TMVOCBio simulation without attempting to better reproduce the experimental results. As concentrations in the injected water were changed several times during the experiment, a smoothed concentration history was used for the TMVOCBio simulation. Maximum time steps of 0.05 days and weighting factor w_{EA}=0.5 and w_{VOC}=0.5 were used. Fig. 3 shows measured toluene concentration at column outlet (dots), the simulated results of McQuarry et al., 1990, and those obtained with TMVOCBio (lines).

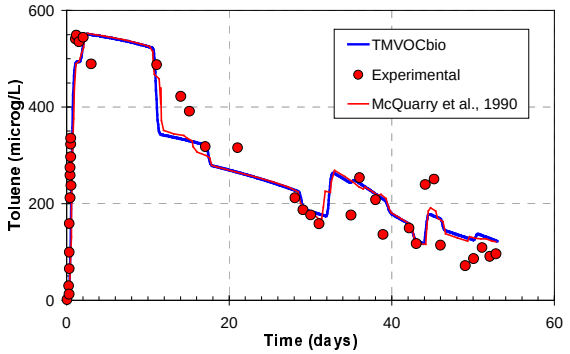

Figure 3. TMVOCBio simulated concentration of toluene at column outlet compared to the experimental data (dots) and simulated results (line) of McQuarry et al., 1990.

The experimental data and simulated results for oxygen are shown in Fig. 4. Considering the smoothed concentration history used and the differences in the numerical formulations, it can be concluded that TMVOCBio is able to reproduce the experimental data with the same accuracy of the McQuarry et al. (1990) model.

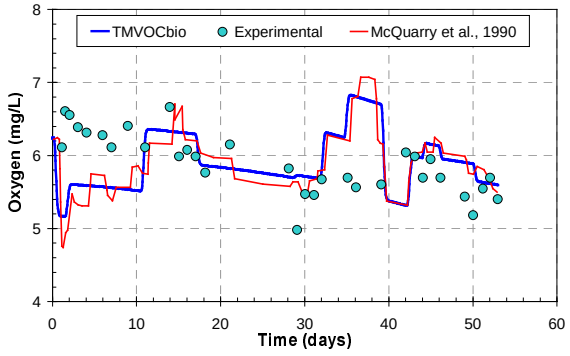

Figure 4. TMVOCBio simulated concentration of oxygen at column outlet compared to the experimental data (dots) and simulated results (line) of McQuarry et al., 1990.

Another validation test of TMVOCBio was performed by simulating the degradation of chlorinated solvents and hydrocarbons within a contaminated groundwater plume monitored at the Dover AFB (USA). Essaid and Bekins (1997) used the BIOMOC code to model the reductive dehalogenation of chlorinated halifatics under anaerobic conditions (PCE→TCE→DCE→ VC), as well as the aerobic degradation of DCE and VC together with benzene and methane dissolved in the groundwater.

The complete problem specifications are given by Essaid and Bekins (1997) and reference to their work is made for detailed information. Essaid and Bekins simulated 1D flow and reactive transport along a 457 m long streamline, by specifying the groundwater flow velocity and the recharge of dissolved oxygen (DO) rich surface water taking place in the first 198 m of the streamline. Initial conditions were zero concentrations for all the solutes, whereas constant solute concentrations at the inlet boundary were specified during the 8-year simulation. Steady state conditions were reached at the end of the simulated period.

Seven different degradation processes are simulated: 3 anaerobic processes representing the dechlorination chain PCE→TCE→DCE→VC; 4 aerobic processes involving DCE, VC, benzene and methane. Including DO, 7 reactive solutes are modeled. Two non-growing microbial populations are simulated, one anaerobic and one aerobic. Fig. 5 and 6 show the TMVOCBio simulated results, compared with the field data reported by Essaid and Bekins. The TMVOCBio simulated results reproduce the field data with an accuracy which is comparable to that obtained by BIOMOC. There is however, a visible difference in the concentration of DO, DCE, VC and benzene in the first 100 m.

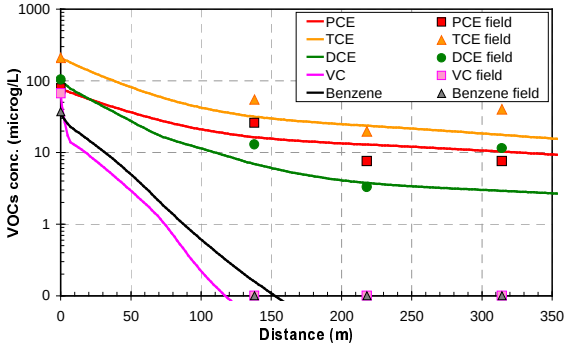

Figure 5. Dover AFB problem: TMVOCBio simulated (lines) and measured (symbols) concentrations of PCE, TCE, DCE, VC and benzene.

Due to the initial low content of DO in inflowing groundwater, anaerobic degradation of PCE, TCE and DCE occurs. The oxygen added through surface water recharge is consumed for the aerobic degradation of CH_4, primarily, and to a lesser extent, of DCE, benzene and VC. After the first 70 m, the

CH_4 concentration is reduced to levels that slow down the DO consumption, so that its concentration in groundwater starts to increase to about 150 m from the inlet. DO concentration becomes almost constant up to about 200 m, where water recharge stops, and then decreases in the final section due to aerobic degradation reactions.

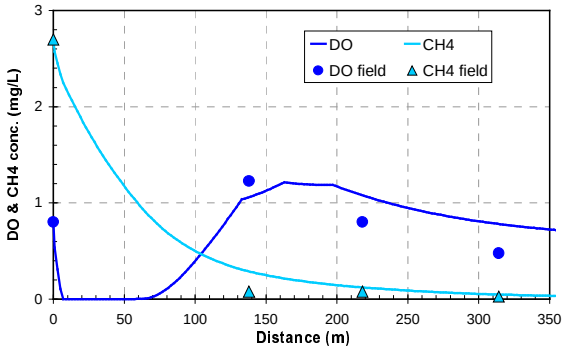

Figure 6. Dover AFB problem: TMVOCBio simulated (lines) and measured (symbols) concentrations of DO and methane.

Anaerobic reactions are simulated with a first order decay rate using the Monod model. They are inhibited by the presence of DO using a non-competitive inhibition approach to slow down the reductive dehalogenation of solvents in aerobic conditions. The aerobic reactions are limited by the DO availability as well, using a multiple Monod approach with a fairly low half saturation concentration of DO, equal to 0.1 μg/L: this low concentration allows the aerobic reactions to occur at a relatively high rate even at low oxygen concentrations.

The Dover AFB simulation results obtained with BIOMOC are shown in Fig. 7. They were produced by running BIOMOC using the original input file kindly supplied by Barbara Bekins. BIOMOC simulates a constant DO concentration of 52.6 μg/L in the first 70 m, whereas TMVOCBio gives a much lower concentration. The lower DO concentration modeled by TMVOCBio still allows the degradation of CH_4, which is present at high concentrations, but results in a lower degradation of VC and benzene compared to that simulated by BIOMOC.

The different handling of disappearing solutes in the two codes is mainly responsible for the different values of DO concentration in the first 70 m. Whereas in BIOMOC a control is performed on all solutes involved in simulated degradation processes, in TMVOCBio the algorithm implemented avoids negative concentrations of the substrates only. If substrate concentration becomes negative at the end of a time step, then the degradation rates of all the processes involving that substrate are recomputed, in order to have a (numerically) small but positive substrate concentration.

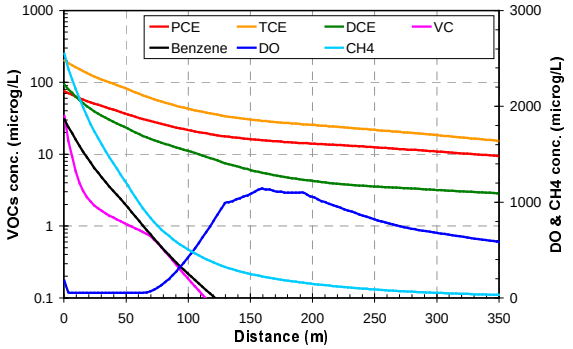

Figure 7. Dover AFB problem: BIOMOC simulated results (Essaid and Bekins, 1997).

Negative concentrations of EA or nutrients are not explicitly treated in TMVOCBio with a dedicated algorithm: they are just reset to numerically small positive values within the EOS subroutine. If a negative concentration of an EA is the result of an excessively high degradation rate, then TMVOCBio is not able to find a solution within the maximum number of allowed iterations and the time step is reduced. Tests showed that this approach usually solves the problem of negative concentrations with a slight increase in computation time. Tests performed by inhibiting the handling of negative concentrations within BIOMOC showed that the code produces results closer to those of TMVOCBio even in the first 150 m, with oxygen concentration going almost to zero in the first 70 m as shown in Fig. 6.

The application of TMVOCBio to the Dover AFB field problem shows that the simulator is able to reproduce the degradation processes taking place at the field, with an accuracy comparable to that of BIOMOC. Differences in the results produced by the two codes are mainly due to the algorithm used by BIOMOC to handle negative solutes concentrations, which might be calculated during the iteration process for compounds totally consumed by the biodegradation processes.

CONCLUSIONS

A model for the simulation of aerobic and anaerobic biodegradation of multiple VOCs in multi-phase non-isothermal porous media was implemented in a new version, called TMVOCBio, of the existing TMVOC V.1.0 numerical reservoir simulator (Pruess and Battistelli, 2002). Verification and validation tests provided satisfactory results in testing the implementation of the numerical formulation and the code's capability to actually reproduce the coupled transport and reactive processes occurring in subsurface media contaminated by organic compounds. A condition for successful application is

that the relevant parameters necessary to describe the biodegradation reactions can be reliably estimated from field and laboratory analysis.

Preserving the original capabilities of TMVOC V.1.0, TMVOCBio allows to model the occurrence of aerobic and anaerobic degradation reactions of multiple organic compounds in the subsurface under multiphase flow conditions. TMVOCBio uses a general formulation of degradation reactions which is a modified version of that developed for the BIOMOC simulator by Essaid and Bekins (1997). It allows to define a number of simultaneous degradation processes mediated by different microbial populations. Through the specification of uptake coefficients for all the simulated solutes for each degradation process, TMVOCBio can simulate the consumption of primary substrates, EA and nutrients, as well as the generation of reaction by-products. Reaction rates are computed using either the multiplicative or minimun Monod model, accounting for the availability of primary substrates, EA and nutrients. Inhibitive effects including competitive, non-competitive and Haldane inhibitions can be simulated, as well as the biomass growth inhibition. Compared to the BIOMOC code, TMVOCBio does not yet simulate the electron acceptors occurring as solid phases, such as ferric iron and oxydized manganese. The inclusion of an additional class of mass components occurring as solid phases will be the purpose of further code versions.

TMVOCBio can be used to simulate both the degradation of primary organic substrates and the cometabolic degradation of chlorinated solvents. The reductive dechlorination chain of organic solvents can also be simulated. TMVOCBio can be used to model both natural-occurring and stimulated biodegradation reactions taking place in aquifers as well as in the unsaturated zone. Thus, both the contaminant distribution in the unsaturated zone beneath spill areas and the evolution of groundwater contaminated plumes can be modeled. When the modeling of degradation reactions is not invoked, TMVOCBio is fully compatible with TMVOC V.1.0 and produces the same results, with no negative effects on numerical code performances.

As possible further improvements of TMVOCBio, the modeling of the effects of solutes concentration on the aqueous phase properties (density, dynamic viscosity, enthalpy, vapor pressure) has already been taken into consideration. Simulation of density dependent flow is important for the modeling of coastal contaminated aquifers, where sea water intrusion can substantially affect the contaminant plumes close to the coastline.

Additional efforts must be directed to study time discretization strategy and its effects on the accuracy of numerical solution. The need for a limitation of time step length depending on the maximum substrate degradation rate has been already pointed out.

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