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User's Guide for Biodegradation Reactions in TMVOCBio

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Abstract

TMVOCBio is an extended version of the TMVOC numerical reservoir simulator, with the capability of simulating multiple biodegradation reactions mediated by different microbial populations or based on different redox reactions, thus involving different electron acceptors. This modeling feature is implemented within the existing TMVOC module in iTOUGH2. TMVOCBio, originally developed by Battistelli (2003; 2004), uses a general modified form of the Monod kinetic rate equation to simulate biodegradation reactions, which effectively simulates the uptake of a substrate while accounting for various limiting factors (i.e., the limitation by substrate, electron acceptor, or nutrients). Two approaches are included: 1) a multiple Monod kinetic rate equation, which assumes all the limiting factors simultaneously affect the substrate uptake rate, and 2) a minimum Monod model, which assumes that the substrate uptake rate is controlled by the most limiting factor among those acting for the specific substrate. As the limiting factors, biomass growth inhibition, toxicity effects, as well as competitive and non-competitive inhibition effects are included. The temperature and moisture dependence of biodegradation reactions is also considered.

This report provides mathematical formulations and assumptions used for modeling the biodegradation reactions, and describes additional modeling capabilities. Detailed description of input format for biodegradation reactions is presented along with sample problems.

1. Introduction

TMVOC is a numerical simulator developed for multiphase non-isothermal flow of water, gas, and a multicomponent mixture of volatile organic chemicals (VOCs) in variably saturated porous and fractured media (Pruess and Battistelli, 2002). This specialized module of TOUGH2 can be used for applications to subsurface contamination problems involving organic mixtures, such as hydrocarbon solvents or non-aqueous phase liquids (NAPLs). TMVOC includes a simple decay model to represent biodegradation of VOCs, but its application to biodegradation processes of organic contaminants in natural or engineered subsurface environments may be limited.

TMVOCBio, (Aquater, 2002; Battistelli, 2003; 2004), is an extended version of TMVOC with the capabilities of simulating multiple biodegradation reactions mediated by different microbial populations or based on different redox reactions, thus involving different electron acceptors. TMVOCBio uses the modified Monod model to represent biodegradation reactions, and this general form effectively accounts for the substrate uptake as well as various limiting factors. We implemented these modeling capabilities within the existing TMVOC numerical reservoir simulator in iTOUGH2 (Finsterle, 2007a, 2007b, 2007c). The implementation of multiple biodegradation reactions within the TMVOC numerical simulator can provide capabilities to predict the migration and degradation of organic contaminants in groundwater and the evolution of its vapors through the unsaturated zone or toward the atmosphere, etc. With the inversion ability of iTOUGH2, it can also be used for the estimation of site-specific biodegradation parameters, as well as for remediation design and risk assessment/management of contaminated sites.

This report is prepared (1) to provide a brief summary of mathematical formulations and assumptions used for modeling the biodegradation reactions, (2) to describe additional modeling capabilities with respect to TMVOC available in TMVOCBio, and (3) to help users to prepare input files for the handling of biodegradation reactions. Detailed instructions for preparing input data and several sample problems are included. For details of the other modeling capabilities and input formats, users are referred to the original TMVOC manual (Pruess and Battistelli, 2002) and iTOUGH2 documents (Finsterle, 2007a, 2007b, 2007c).

2. Methodology

2.1. Assumptions

To implement biodegradation reactions within the TMVOC numerical simulator, a number of simplifying assumptions have been considered. The assumptions underlying the implementation of biodegradation reactions and the mathematical formulation are fully described in Aquater (2002) and Battistelli (2003, 2004). Here, we summarize the main assumptions.

- Bacteria transport is negligible.
- All the biomass is considered active in the biodegradation process.
- Diffusion processes into and out of the biophase are neglected, so biodegradation rates depend directly on aqueous phase solute concentrations.
- Predation of microbes by other microorganisms is neglected.
- Bioreactions are not affected by chemical equilibria.
- Each microbial population can be involved in several degradation processes, each one acting on a single organic substrate.
- The time needed for acclimation of microbial populations to new substrate and electron acceptors concentration levels is neglected as it is generally much smaller than the overall time scale for biodegradation in subsurface media.
- Changes of porous medium porosity due to biomass growth are neglected as well as the related effects on medium permeability (clogging).
- A minimum biomass concentration, specified by the user, is maintained in the absence of any organic contaminants degradation.

2.2. Implementation of Multiple Biodegradation Reactions

TMVOCBio follows the numerical formulation used by the T2LBM EOS module (Oldenburg, 2001) of the TOUGH2 reservoir simulator (Pruess et al., 2012), developed to model the aerobic/anaerobic biodegradation of solid waste in municipal landfills. The original T2LBM formulation has been modified to model a number of different degradation processes defined by the user, following the BIOMOC general formulation of biodegradation reactions (Essaid and Bekins, 1997), and to take into consideration the changes of aqueous phase density and

saturation in the updating of microbial concentration in the aqueous phase, to account for the changes occurring in unsaturated or multiphase flow conditions.

The degradation rate of substrates and related consumption of electron acceptors and nutrients, as well as the generation rate of by-products and heat, are computed within subroutine BIOREACT, called by subroutine MULTI which assembles the balance equations for the mass components and thermal energy during each simulated time step. This numerical scheme allows solving the multiphase flow and reactive transport of mass components in a coupled way. The total uptake of each substrate within a simulated time step is considered as a sink/source term in the mass balance equation. Since the transport of microorganisms is assumed to be negligible, no mass balance equations for the microbial populations are set up within TMVOCBio. Biomass growth and decay are tracked during the simulation by updating local biomass concentration in the aqueous phase after each converged time step, accounting also for the changes in aqueous phase saturation and density.

This numerical approach of treating biodegradation reactions as internal sink/sources computed for each Newton- Raphson iteration of TMVOCBio introduces an additional source of numerical errors, known as splitting error, generated by the decoupling of governing equations (Valocchi and Malmstead, 1992). This error depends on the time step length and is also related to the magnitude of reaction rates (Kanney et al., 2003; University of Texas, 2000). Thus, the numerical solution of biodegradation reactions is sensitive to time step length, depending on the rate of reactions of the modeled process, and may suffer from numerical instability if the time step is too long to accurately model fast biodegradation rates. To avoid this issue, users may need to properly assign a maximum time step value, reduce the convergence criterion of mass balance solution, or allow time step increase only when convergence is achieved with a small number of iterations, generally less than the standard value of 4.

2.2.1. Mathematical Formulations

The degradation rate is expressed using modified forms of the Monod kinetic rate equation, which can account for various limiting factors, such as the limitation by the substrate, the electron acceptor and nutrients, on the uptake rate of substrate. Two approaches are included: (1)

a multiple Monod kinetic rate equation, which assumes all the limiting factors simultaneously affect the substrate uptake rate (Borden and Bedient, 1986; Waddill and Widdowson, 1998), and (2) a minimum Monod model, which assumes that the substrate uptake rate is controlled by the most limiting factor among those acting for the specific substrate (Kindred and Celia, 1989).

Below the degradation rate *dS/dt* of a primary substrate by a microbial population *B* is shown for the case in which only the limitation of the substrate and the electron acceptor availability is considered, even though limitations due to any other solute dissolved in the aqueous phase, including nutrients, can be modeled by invoking the appropriate Monod term. Note that biomass growth inhibition, toxicity effects, as well as competitive and non-competitive inhibition effects are also included as the limiting factors (see Nomenclature for notation).

$$\frac{dS}{dt} = -\mu_{0B}B \tag{1}$$

where the specific substrate utilization rate μ_{0B} is given by

$$\mu_{0B} = \frac{\mu_{max,B}}{I_{NC}} f_T f_{SW} f_{Monod} \frac{1}{I_B} \tag{2}$$

The Monod kinetic rate term f_{Monod} is

$$f_{Monod} = \begin{cases} \dfrac{S}{K_{S,B}I_C + S + I_H} \dfrac{E}{K_{E,B}I_C + E + I_H} & \text{for the multiple Monod kinetic model} (3\text{-}1) \\[4mm] \min\left(\dfrac{S}{K_{S,B}I_C + S + I_H} ; \dfrac{E}{K_{E,B}I_C + E + I_H} \right) & \text{for the minimum Monod kinetic model} (3\text{-}2) \end{cases}$$

The rate of biomass change with the effect of death rate δ is

$$\frac{dB}{dt} = Y\mu_{0B}B - \delta B = -Y\frac{dS}{dt} - \delta B \tag{4}$$

Following the BIOMOC approach (Essaid and Bekins, 1997), the formulation of the degradation rate is extended for the case where a generic substrate is simultaneously degraded by different microbial populations involving the same or different electron acceptors. When a substrate $S(j)$ is degraded in $N_{proc}(j)$ simultaneous degradation reactions mediated by different microbial populations $B(ip)$, $ip = 1$, $N_{proc}(j)$, the total degradation rate for the substrate $S(j)$ is

$$\frac{dS(j)}{dt} = \sum_{ip=1}^{N_{proc}(j)} -\mu_{0B}(ip)B(ip) \tag{5}$$

The same approach can be extended to simultaneous degradation processes of multiple substrates, providing the capability to model a number of different degradation processes defined by the user, following the general formulation of biodegradation reactions described above.

2.2.2. Numerical Discretization

As in T2LBM (Oldenburg, 2001), the substrate uptake rate is discretized as a first-order reaction in time as

$$\Delta S = S_{k+1} - S_k = \frac{dS}{dt}\Delta t \tag{6}$$

which is solved for the function of the new substrate concentration S_{k+1} using Newton-Raphson iterations within subroutine BIOREACT.

$$f(S_{k+1}) = \frac{dS}{dt}\bigg|_{S*}\Delta t + S_k - S_{k+1} = 0 \tag{7}$$

where $S^* = S_k(1-\omega) + S_{k+1}\omega$

with the weighting factor $0 < \omega \leq 1$. The iterative solution of Eq. (7) is

$$S_{k+1}^{p+1} = S_{k+1}^p - \frac{f(S_{k+1}^p)}{f'(S_{k+1}^p)} \tag{8}$$

The iteration is continued until the following convergence criterion is achieved:

$$\left| S_{k+1}^{p+1} - S_{k+1}^p \right| = \left| \frac{f(S_{k+1}^p)}{df(S_{k+1}^p)/dS} \right| \le \varepsilon \tag{9}$$

The biomass growth rate is discretized as

$$\Delta B = B_{k+1} - B_k = -\left(Y \left. \frac{dS}{dt} \right|_{S^*} + \delta B_k \right) \Delta t \tag{10}$$

The biomass at the end of a time step is evaluated by solving for B_{k+1} at $S = S^*$ in subroutine CONVER. Note that the substrate concentration at the end of a time step is the converged value of the last completed Newton-Raphson iteration in subroutine BIOREACT. The microbial mass concentration is then updated to account for the changes in aqueous phase saturation and density.

2.3. Additional Modeling Capabilities

2.3.1. Inclusion of Dissolved Solids

Microbial degradation often involves electron acceptors that are not volatile. For instance, in subsurface environments, the supply of oxygen may not be sufficient to sustain aerobic biodegradation reactions that use oxygen as the electron acceptor. The complete depletion of oxygen will trigger anaerobic biodegradations that use non-volatile compounds, such as nitrates and sulfates. To model these multi-step reactions involving non-volatile compounds as electron acceptors, nutrients, or even substrates, a new type of mass components, dissolved solids, are included in TMVOC. It is assumed that (1) dissolved solids have no vapor pressure and negligible solubility in the organic liquid phase, and that (2) at their low concentrations commonly encountered in shallow subsurface systems, they do not affect the aqueous phase

properties, such as density, dynamic viscosity, enthalpy, and vapor pressure as well as the solubility of non-condensible gases (NCGs) and VOCs in the aqueous phase. Note that due to the approach used to handle dissolved solids, code applications involving the dissolved solids are limited to the phase conditions that include the aqueous phase (i.e., single-phase aqueous condition and two- and three-phase conditions including the aqueous phase). On the other hand, for problems involving only fully saturated conditions, it is possible to use only dissolved solids to specify substrates, electron acceptors, nutrients, or reaction byproducts.

Dissolved solids are defined in a new data block SOLID; the details of the input format are described in Section 3. Users can specify the adsorption constant and the first-order decay constant for each dissolved solid. The adsorption is modeled in complete analogy with the adsorption of organic compounds onto natural organic carbon present in the subsurface (Pruess and Battistelli, 2002). In the cases including NTR dissolved solids, they are added at the end of the other mass components, which are water, NCG non-condensible gases, and NHC volatile compounds. Therefore, the total number of mass components is $NK = 1 + NCG + NHC + NTR$.

2.3.2. Adsorption and First-Order Decay of NCGs

VOCs that are not condensible at prevailing temperature conditions can be treated as NCGs (e.g., methane). To simulate the adsorption and first-order decay of such NCGs, the water-organic carbon partition constant and the first-order decay constant can be optionally given in the data block NCGAS.

2.3.3. Additional Non-Condensible Gases: H_2S and NH_3

Two additional NCGs are added in the TMVOCBio internal data bank: H_2S, which is a reaction product of anaerobic reactions using sulfates as electron acceptors, and NH_3, which can be a source of nitrogen as a nutrient for biomass synthesis. Molecular weight, critical pressure and temperature, dipole moment, and the parameters for the computation of gas enthalpy and dynamic viscosity have been taken from the property database in Reid et al. (1987).

3. Input Formats

3.1. TMVOCBio Input

This section provides input formats related to model biodegradation reactions with TMVOCBio. Only the new or modified input data blocks from the input formats of TMVOC are shown, and details are given only for the modified input specifications.

NCGAS   is a data block for specifying the number and basic parameters of non-condensible gases to be modeled by TMVOC. The NCGAS block must be included with NCG=0 if non-condensible gases are not modeled.

Record NCGAS.1

        Format (I5)

        NCG

Record NCGAS.2

        Format (A10,2E10.4)

        NCGINP, OCKM, ALAMM

NCGINP   name of non-condensible gas, to be chosen among the 11 NCGs included in the internal data bank. They are: AIR, O2, N2, CO2, CH4, ETHANE, ETHYLENE, ACETYLENE, H2, H2S, and NH3. NCG names are case sensitive and must be entered exactly as stated here, starting in column 1.

OCKM   non-condensible gas organic carbon partition coefficient K_{oc}, m^3/kg.

ALAMM   decay constant for NCG, s^{-1}.

Repeat record NCGAS.2 for as many non-condensible gases as specified in record NCGAS.1.

SOLID   is an optional data block for specifying the number and nature of dissolved solids in the aqueous phase.

Record SOLID.1

> Format (I5)
>
> NTR

NTR   number of dissolved solids

Record SOLID.2

> Format (A10,3E10.4)
>
> NTRINP, AMWTM, OCKM, ALAMM

NTRINP   name of dissolved solid. It can be specified by the user with no constraints other than the length of 10 characters.

AMWTM   dissolved solid molecular weight, g/mole.

OCKM   dissolved solid organic carbon partition coefficient K_{OC}, m^3/kg

ALAMM   decay constant for dissolved solid, s^{-1}.

Repeat record Solid.2 for as many dissolved solids as specified in record SOLID.1.

PARAM   introduces computational parameters, time stepping information, and default initial conditions.

Record PARAM.1

> Format (2I2, 3I4, 24I1, 10X, 2E10.4)
>
> NOITE, KDATA, MCYC, MSEC, MCYPR, (MOP(I), I = 1, 24), TEXP, BE

Record PARAM.2

> Format (4E10.4, A5, 5X,3E10.4)
>
> TSTART, TIMAX, DELTEN, DELTMX, ELST, GF, REDLT, SCALE

Record PARAM.2.1, 2.2, etc.

> Format (8E10.4)
>
> (DLT(I), I = 1, 100)

<u>Record PARAM.3</u>

Format (6E10.4,10X,E10.4)

RE1, RE2, U, WUP, WNR, DFAC, AMRES

<u>Record PARAM.4</u>

Format (I5)

INDICAT0

<u>Record PARAM.5</u>

introduces a set of primary variables which are used as default initial conditions for all grid blocks that are not assigned by means of data blocks INDOM or INCON. Option START is necessary to use default INCON. The primary thermodynamic variables used in TMVOCBio depend on the phase conditions, and are summarized in Table 1, below.

Format (4E20.14)

DEP(I), I=1, NKIN+1

Table 1. Primary thermodynamic variables of TMVOCBio (g=gas phase, w=aqueous phase, n=NAPL). Concentrations are expressed in mole fractions.

Phase Conditions	Phase Index		VOC #1	...	VOC #NHC	NCG #1	...	NCG #NCG	Solid #1	...	Solid #NTR	
		1	2	...	NHC+1	NHC+2	...	NHC+NCG+1	NHC+NCG+2	...	NK	NK+1
gas only	1	P	x_g^{2+NCG}	...	$x_g^{1+NCG+NHC}$	x_g^2	...	x_g^{1+NCG}	--	--	--	T
aqueous only	2	P	x_w^{2+NCG}	...	$x_w^{1+NCG+NHC}$	x_w^2	...	x_w^{1+NCG}	$x_w^{2+NCG+NHC}$	...	x_w^{NK}	T
NAPL only	3	P	x_n^{2+NCG}	...	$x_n^{1+NCG+NHC}$	x_n^2	...	x_n^{1+NCG}	--	--	--	T
gas and aqueous	4	P	x_g^{2+NCG}	...	$x_g^{1+NCG+NHC}$	x_g^2	...	S_w	$x_w^{2+NCG+NHC}$	...	x_w^{NK}	T
gas and NAPL	5	P	x_g^{2+NCG}	...	$x_g^{1+NCG+NHC}$	x_g^2	...	S_n	--	--	--	T
aqueous and NAPL	6	P	x_n^{2+NCG}	...	$x_n^{1+NCG+NHC}$	x_n^2	...	S_w	$x_w^{2+NCG+NHC}$	...	x_w^{NK}	T
three phase	7	P	S_g	...	$x_g^{1+NCG+NHC}$	x_g^2	...	S_w	$x_w^{2+NCG+NHC}$	...	x_w^{NK}	T

The format is identical to Table E.1 in the TMVOC user manual (Pruess and Battistelli, 2002) except that dissolved solids are defined after pressure, VOCs, and non-condensible gases but before temperature. Note that dissolved solids can be simulated only for phase conditions in which the aqueous phase is present. Single-phase gas conditions can be assigned to inactive elements used to model atmospheric boundary conditions.

INDOM   introduces domain-specific initial conditions. These will supersede default initial conditions specified in PARAM.4 and PARAM.5, and can be overwritten by element-specific initial conditions in data block INCON. Option START is needed to use INDOM conditions.

<u>Record INDOM.1</u>

      Format (A5,I5)

      MAT, INDECEIN

<u>Record INDOM.2</u>

      Format (4E20.14)

      (X(I), I=1, NK+1), (B(I), I=1, NPOP)

      A set of NK+1 primary variables assigned to all grid blocks in the domain specified in record INDOM.1. Primary variables can be followed by a set of concentrations of NPOP microbial populations in the aqueous phase.

Repeat records INDOM.1 and INDOM.2 for as many domains as desired. The ordering is arbitrary and need not to be the same as in block ROCKS.

<u>Record INDOM.3</u>

      A blank record closes the INDOM data block.

INCON   introduces element-specific initial conditions.

<u>Record INCON.1</u>

      Format (A3,I2,2I5,E15.9,I2)

      EL, NE, NSEQ, NADD, PORX, INDICEE

<u>Record INCON.2</u>   specifies primary variables and biomass concentrations

      Format (4E20.14)

      (X(I), I=1, NK+1), (B(I), I=1, NPOP)

A set of NK+1 primary variables for the element specified in record INCON.1. Primary variables can be followed by a set of concentrations of NPOP microbial populations in the aqueous phase.

<u>Record INCON.3</u>

A blank record closes the INCON data block. Alternatively, initial condition information may terminate on a record with '+++' typed in the first three columns, followed by time stepping information. This feature is used for a continuation run from a previous TMVOC simulation.

BIODG   an optional input data block introducing parameters needed to simulate the biodegradation processes

<u>Record BIODG.1</u>

Format (I5,I5,E10.4,10X,4E10.4)

IMONOD, ICFLAG, BFAC, SW1, SW2, WEA, WSUB

IMONOD   selects between multiplicative and minimum Monod model for the substrate degradation rate equation.

0 : multiplicative Monod model (default).

>0: minimum Monod model.

ICFLAG   selects how to consider the competitive and Haldane inhibition terms in the Monod model.

0: competitive and Haldane inhibition factors are applied to all Monod terms in the substrate degradation rate equation, including the electron acceptor and nutrients terms as in the BIOMOC code formulation (default).

>0: competitive and Haldane inhibition factors are applied only to the substrate Monod term, as in conventional formulations of cometabolic degradation processes modelled using competitive inhibition effects.

BFAC   reduction factor criterion for local Newton-Raphson iteration in BIOREACT subroutine to reduce substrate residual.

SW1   lower limit of aqueous phase saturation considered in the saturation inhibition function (if =0, the default value is 0.02).

SW2   upper limit of aqueous phase saturation considered in the saturation inhibition function ($SW1 < SW2 \leq 1$).

WEA   weighting factor for the linear interpolation of electron acceptor and nutrients concentrations to be used in the substrate degradation rate equation ($0 < WEA \leq 1$). Default value is $WEA = 0.5$. $WEA = 1$ corresponds to using the concentration evaluated at the end of the time step.

WSUB   weighting factor for the linear interpolation of substrate concentration to be used in the substrate degradation rate equation ($0 < WSUB \leq 1$). Default value is $WSUB = 0.5$. WSUB=1 corresponds to using the concentration evaluated at the end of the time step.

Record BIODG.2

        Format (I5)

        NPROC

NPROC   number of biodegradation processes in the simulation ($NPROC \leq 20$).

Record BIODG.3

        Format (2(5X, I5), 2E10.4, 3(5X, I5), E10.4)

        NSPROC(IP), IBIO(IP), AMUMAX(IP), YIELD(IP), NCOMP(IP), NNC(IP), NHAL(IP), ENTB(IP)

NSPROC(IP)   number of mass components controlling the substrate degradation rate in process IP.

IBIO(IP)   index of microbial population involved in process IP.

AMUMAX(IP) maximum specific substrate degradation rate in process IP (kg substrate/ (s kg biomass)).

YIELD(IP)   yield coefficient for the growth of biomass due to the degradation of unit mass of substrate in process IP (kg biomass / kg substrate).

NCOMP(IP)   number of mass components responsible for competitive inhibition in process IP.

NNC(IP)   number of mass components responsible for non-competitive inhibition in process IP.

NHAL(IP)   number of mass components responsible for Haldane inhibition in process IP.

ENTB(IP)   heat of reaction for the degradation of substrate in process IP (J/kg substrate).

Record BIODG.4

        Format (4(5X, I5, E10.4))

        KSPROC(IP,NC), AKS(IP,NC) ; NC=1, NSPROC(IP)

KSPROC(IP,NC) index of mass component # NC controlling the substrate degradation rate in process IP. By convention, the first (NC=1) must refer to the primary substrate of process IP.

AKS(IP,NC)   half saturation constant of mass component # NC in the Monod term of substrate degradation rate in process IP (kg substrate / kg aqueous phase). If specified, must be >0.

Record BIODG.5

        Format (4(5X, I5, E10.4))

        KSCOMP(IP,NC), AKCOMP(IP,NC) ; NC=1, NCOMP(IP)

KSCOMP(IP,NC) index of mass component # NC responsible for competitive inhibition in process IP.

AKCOMP(IP,NC) competitive inhibition coefficient for mass component # NC in process IP (kg solute / kg aqueous phase).

Record BIODG.6

        Format (4(5X, I5, E10.4))

KSNC(IP,NC), AKNC(IP,NC) ; NC=1, NNC(IP)

KSNC(IP,NC) index of mass component # NC responsible for non-competitive inhibition in process IP.

AKNC(IP,NC) non-competitive inhibition coefficient for mass component # NC in process IP (kg solute / kg aqueous phase).

Record BIODG.7

Format (4(5X, I5, E10.4))

KSHAL(IP,NC), AKHAL(IP,NC) ; NC=1, NHAL(IP)

KSHAL(IP,NC) index of mass component # NC responsible for Haldane inhibition in process IP.

AKHAL(IP,NC) Haldane inhibition coefficient for mass component # NC in process IP (kg solute / kg aqueous phase).

Record BIODG.8

Format (8E10.4)

UPTAKE(IP,L) ; L=1,NK

UPTAKE(IP,L) uptake coefficient of component # L in process IP with respect to 1 mole of degraded primary substrate (mole component / mole substrate).

Repeat records BIODG.3 through BIODG.8 for a total of NPROC (up to 20) different biodegradation processes (IP= 1, NPROC).

Record BIODG.9

Format (2I5)

NPOP, IBFLAG

NPOP   number of microbial populations (NPOP ≤ 20).

IBFLAG   specifies if initial conditions for biomass concentration are supplied through input blocks INDOM, INCON, or through an INCON file.

    0:    constant biomass concentrations are given as initial conditions through block BIODG.10.

>0: variable biomass concentrations are supplied as initial conditions through
blocks INDOM, INCON or through an INCON file.

Record BIODG.10

Format (5E10.4)

BAI(IB), BA0(IB), TMAX(IB), DEATH(IB), AKBIO(IB)

BAI(IB)   initial concentration (valid for the entire simulation grid) in the aqueous phase of
microbial population # IB (kg biomass / kg aqueous phase).

BA0(IB)   minimum concentration in the aqueous phase of microbial population # IB
enforced during the simulation (kg biomass / kg aqueous phase).

TMAX(IB)   maximum temperature for the calculation of temperature inhibition function in the
substrate degradation rate equation (°C).

DEATH(IB) death rate constant, or maintenance constant, for the microbial population # IB
(s^{-1}).

AKBIO(IB) inhibition constant for biomass growth of microbial population # IB (kg biomass
kg aqueous phase).

Repeat record BIODG.10 for a total of NPOP (up to 20) different microbial populations (IB= 1,
NPOP).

3.2. iTOUGH2 commands

Several iTOUGH2 commands related to biodegradation reactions are added, so the reaction constants can be parameterized for the estimation of their values, sensitivity analysis, and uncertainty qualification analysis. In addition, the flexibility of extracting output data of interest can be useful as well. For instance, the biomass concentration in each grid block of interest can be printed out at the time steps specified in the iTOUGH2 input file, generating time series data for elements for plotting. A detailed description of each iTOUGH2 parameter and observation command available for biodegradation reactions is given below, and an example is included for each command. We present the commands in alphabetic order. Here, we assume the reader is familiar with the command syntax of iTOUGH2 commands. The user should refer to the original iTOUGH2 command reference (Finsterle, 2007b) for the basic concepts and formats of the iTOUGH2 input.

Command

```
>> BIODEGRADATION
```

Parent Command

```
> PARAMETER
```

Subcommand

```
>>> MODEL
```

Description

This command selects as a parameter the maximum specific substrate biodegradation rate in process IP (kg substrate/ (s kg biomass)). The process IP is identified by its process number through subcommand $>>>>$ INDEX. The parameter value can be estimated directly (command $>>>>$ VALUE) or its logarithm (command $>>>>$ LOGARITHM),

Example

```
> PARAMETER
  >> BIODEGRADATION
    >>> MODEL
        >>>> ANNOTATION: AMUMAX_1
        >>>> INDEX: 1
        >>>> GUESS: -4.5
        >>>> LOGARITHM
        <<<<
```

Command

```
>> BIOMASS
```

Parent Command

```
> OBSERVATION
```

Subcommand

```
>>> ELEMENT
```

Description

This command selects as an observation type the concentration of microbial population IB in the aqueous phase (kg biomass/kg aqueous phase). The microbial population IB is identified by its population number through subcommand `>>>> INDEX`.

Example

```
> OBSERVATION
  >> BIOMASS
    >>> ELEMENT: A___1
        >>>> INDEX: 1
        >>>> NO DATA
        <<<<
```

Command

```
>> DEATH
```

Parent Command

```
> PARAMETER
```

Subcommand

```
>>> MODEL
```

Description

This command selects as a parameter the death rate constant for microbial population IB (s^{-1}). The microbial population IB is identified by its population number through subcommand >>>> INDEX. The parameter value can be estimated directly (command >>>> VALUE) or its logarithm (command >>>> LOGARITHM),

Example

```
> PARAMETER
    >>> MODEL
        >>>> ANNOTATION: DEATH_RATE_2
        >>>> INDEX: 2
        >>>> GUESS: 1.0E-6
        >>>> VALUE
        <<<<
```

Command

```
>> HALF SATURATION
```

Parent Command

```
> PARAMETER
```

Subcommand

```
>>> MODEL
```

Description

This command selects as a parameter the half saturation constant of mass component NC in the Monod term of substrate degradation rate in process IP (kg substrate / kg aqueous phase). The mass component NC and process IP are identified by a pair of its mass component and process number through subcommand >>>> INDEX. The first one specifies the process number, and the second is the number of the mass component controlling the substrate degradation rate in process IP. The parameter value can be estimated directly (command >>>> VALUE) or its logarithm (command >>>> LOGARITHM).

Example

```
> PARAMETER
  >> HALF SATURATION
    >>> MODEL
      >>>> ANNOTATION: AKS_1
      >>>> INDEX: 1 1
      >>>> GUESS: 1.0E-5
      >>>> VALUE
      <<<<
```

4. Sample Problems

Here we present a number of sample problems, which can serve as a tutorial for TMVOCBio applications and as benchmarks for proper code installation. The first two sample problems are originally presented in Battistelli (2004), and here we include the input data files, which can be used as templates for similar problems.

4.1. Problem No. 1 – Code Verification

To verify the proper implementation of the multiple biodegradation processes, the results of TMVOCBio are compared with numerical solutions of the biodegradation equations in a batch model. The numerical solutions are calculated with a spreadsheet using a fully explicit Euler method with very small time steps. Two substrates (toluene and benzene) are assumed to be degraded by a single microbial population using oxygen as an electron acceptor. The reactions are only limited by substrate and oxygen availability, and the other inhibition effects are not considered here. The TMVOCBio input file prepared for this batch reaction is shown in Figure 1. The two organic compounds are specified as hydrocarbons (NHC = 2) through block CHEMP, and oxygen is specified as the non-condensible gas (NCG = 1) through block NCGAS. Two biodegradation processes (NPROC = 2), i.e., the aerobic degradation of toluene and benzene, are specified in block BIODG using the multiplicative Monod model (IMONOD = 0). The consumption of the substrates and oxygen and the biomass growth are modeled for one day. Since this is a forward problem, we can just provide any dummy, empty file as the iTOUGH2 input file. Here, we use iTOUGH2 to generate a time plot of toluene, benzene, oxygen, and biomass concentrations, and Figure 2 shows the iTOUGH2 input file. In block `> OBSERVATION`, we specify the times at which the calculated concentrations are printed out (`>> TIME`) as well as the output variables of interest (`>> MASS FRACTION` and `>> BIOMASS`). In Figure 3, TMVOCBio results are shown as symbols, whereas the results obtained with the numerical solution are shown as lines of the corresponding colors. They are in good agreement.

```
C-04  Batch test:  2 substrates + oxygen limitation ( 1 biomass pop.).
ROCKS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
SAND1    3    2650.        .300  1.0E-11  1.0E-11  1.0E-11      3.1    1000.
     0.e-8        0.       2.85      0.0              0.000
      6         .200       .05      .010       3.0
     11        0.000      1.84       10.       11.


MULTI----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    4    4    3    6
CHEMP----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    2
toluene
      591.8      41.0     0.263     0.263      0.4
      383.8  -7.28607   1.38091  -2.83433  -2.79168
     92.141-.2435E+020.5125E+00-.2765E-030.4911E-07
       867.    293.00 0.880E-05    303.10      1.41
   -.5878E+010.1287E+040.4575E-02-.4499E-05    316.0
    0.101E-03 0.000E+00 0.000E+00 0.000E+00
    8.8649e-3        0.        0.        0.
BENZENE
      562.2      48.2     0.271     0.212      0.0
      353.2  -6.98273   1.33213  -2.62863  -3.33399
     78.114-.3392E+020.4739E+00-.3017E-030.7130E-07
       885.    289.00 0.770E-05    273.10      1.52
   0.4612E+010.1489E+03-.2544E-010.2222E-04    259.0
    0.411E-03 0.000E+00 0.000E+00 0.000E+00
    0.891E-01    0.000
NCGAS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    1
O2
....*----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
IMon iCflg     bfac                  sw1       sw2       wEA       wSUB
Nproc
NSproc(ip)  ibio(ip)  mumax(ip) yield(ip) Ncomp(ip)   Nnc(ip)   Nhal(ip)   Entb(ip)
 Isp(ip,1)  Ks(ip,1)  Isp(ip,2)  Ks(ip,2)  Isp(ip,3)  Ks(ip,3)  Isp(ip,4)  Ks(ip,4)
 I c(ip,1) Kco(ip,1)  I c(ip,2) Kco(ip,2)  I c(ip,3) Kco(ip,3)  I p(ip,4) Kco(ip,4)
 Inc(ip,1) Knc(ip,1)  Inc(ip,2) Knc(ip,2)  Inc(ip,3) Knc(ip,3)  Inp(ip,4) Knc(ip,4)
 I h(ip,1) Kha(ip,1)  I h(ip,2) Kha(ip,2)  I h(ip,3) Kha(ip,3)  I h(ip,4) Kha(ip,4)
 Upt(ip,1) Upt(ip,2) Upt(ip,3) Upt(ip,4) Upt(ip,5) Upt(ip,6) Upt(ip,7) Upt(ip,8)
 NpopiBflg
   bai(L)    ba0(L)   tmaxa(L)  death(L)   Kbio(L)
BIODG----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    0        1.e-10              .0        .2       0.9       0.9
    2
         2         1 1.2732e-5       1.0         0         0         0        .0
         3      2.e-6         2      1.e-6
         0
         0
         0
        -4.       +9.0        1.        0.
         2         1 1.1574e-5       0.8         0         0         0        .0
         4      1.e-6         2     0.5e-6
         0
         0
         0
        -3.       +7.5        0.        1.
    1
  1.530e-6  1.00e-6       40. 2.3148e-7    0.e-6
SELEC----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    0    0    0
```

Figure 1. TMVOCBio input file for biodegradation of toluene and benzene in a batch reaction.

```
START----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
----*----1 MOP: 123456789*123456789*1234 ---*----5----*----6----*----7----*----8
PARAM----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
   2 100   1 10010005010002200 4 0005001
         8.6400e+4        -1.  2160.E+0                9.8065
     10.0
     1.E-7    1.E-2                                 1.000E-8                1.e4
     2
         10.00000e5             1.9553e-6        1.15319E-06             5.6302e-6
              20.0
RPCAP----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
     6          .150        .05        .01        3.
     8         0.000       1.84       10.       11.
ELEME----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
A   1         SAND1         1.

CONNE----1----*----2----*----3----*----4----*----5----*----6----*----7----*----

ENDCY----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
```

Figure 1 (cont.). TMVOCBio input file for biodegradation of toluene and benzene in a batch reaction.

```
 > OBSERVATION
   >> TIME: 48 EQUALLY [HOURS]
      0.5  24.0

   >> MASS FRACTION
      >>> ELEMENT: A___1
         >>>> ANNOTATION: OXYGEN
         >>>> COMPONENT: 2
         >>>> PHASE : 2
         >>>> NO DATA
         <<<<
      >>> ELEMENT: A___1
         >>>> ANNOTATION: TOLUENE
         >>>> COMPONENT: 3
         >>>> PHASE : 2
         >>>> NO DATA
         <<<<
      >>> ELEMENT: A___1
         >>>> ANNOTATION: BENZENE
         >>>> COMPONENT: 4
         >>>> PHASE : 2
         >>>> NO DATA
         <<<<
      <<<

   >> BIOMASS
      >>> ELEMENT: A___1
          >>>> INDEX: 1
          >>>> NO DATA
          <<<<
      <<<
   <<

 > COMPUTATION
   >> OPTION
      >>> FORWARD
      <<<

   >> OUTPUT
      >>> HOURS
      >>> FORMAT: COLUMNS
      <<<
   <<
 <
```

Figure 2. iTOUGH2 input file for biodegradation of toluene and benzene in a batch reaction.
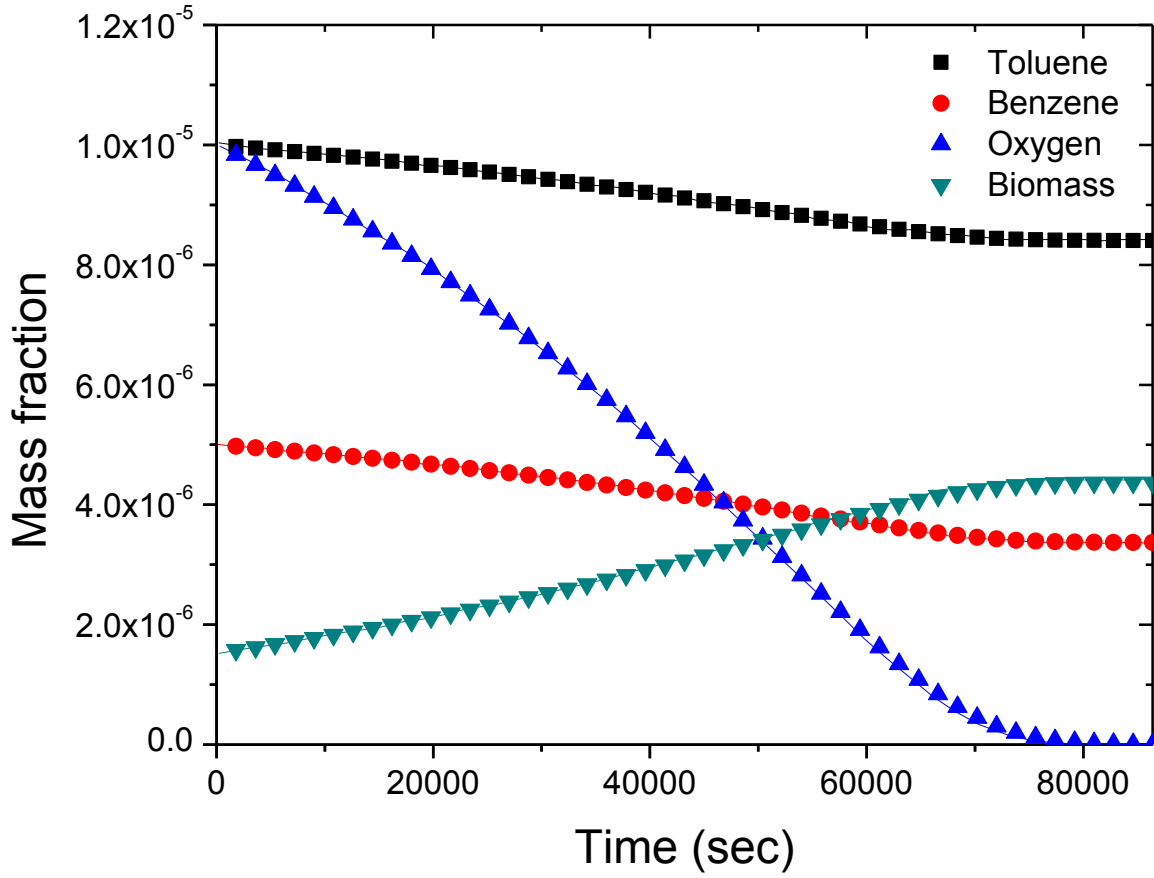
Figure 3. Mass fractions of two substrates (toluene and benzene), oxygen, and biomass in the aqueous phase as a function of time.

4.2. Problem No. 2 – Toluene Degradation in a Laboratory Column

This problem is adapted from MacQuarrie et al. (1990); it models toluene degradation in a laboratory column under aerobic conditions. MacQuarrie et al. (1990) conducted a laboratory column experiment and compared the results with their numerical solution. Water with variable toluene and O_2 concentrations was injected into a 26-cm-long sand-packed column for 53 days, and the composition of the effluent water was analyzed for toluene and O_2. The flow rate was increased after the first 44 days of injection from the average linear velocity of 0.62 m d^{-1} to 0.99 m d^{-1}. The average toluene and O_2 concentrations in the injected fluid were 0.4 and 6 mg L^{-1}, respectively.

     A horizontal 1-D column is generated. Most of the grid blocks are 0.4 cm in length, and the grid blocks near the inlet and outlet of the column are a little smaller than 0.4 cm. The average linear velocity is converted to the mass injection rate for water. For the TMVOCBio simulation, we use the same parameter values as MacQuarrie and coworkers estimated, which include the maximum specific degradation rate and half saturation constant of toluene, the biomass yield, and the death rate, without attempting to better reproduce the experimental results. Maximum time steps of 0.05 days and weighting factors w_{EA}=0.5 and w_{SUB}=0.5 were used. In block GENER, the injection history of water and dissolved toluene and O_2 shown in MacQuarrie et al. (1990) is accurately accounted for. Figure 4 shows the TMVOCBio input file (the iTOUGH2 input file is not shown), and Figure 5 shows the measured toluene and O_2 concentrations at the column outlet, the simulated results of MacQuarrie et al. (1990), and those obtained with TMVOCBio, respectively. The results obtained with TMVOCBio are consistent with those of MacQuarrie et al. (1990), and reproduce the main trends in the experimental data fairly well.

```
MQ_1  MacQuarrie et al.(1990) aerobic biodegradation of toluene in 1D lab column.
ROCKS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
SAND1    1    2650.      .370   1.0E-11   1.0E-11   1.0E-11       3.1     1000.
     0.e-8        0.     2.85      0.0                         0.010
SAND2    1    2650.      .370   1.0E-11   1.0E-11   1.0E-11       3.1     1000.
     0.e-8        0.     2.85      1.E-9                       0.010
BOUD3    1    2650.      .370   1.0E-11   1.0E-11   1.0E-11       3.1    50000.
     0.e-8        0.     2.85      1.E-9                       0.000


MULTI----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
   3    3    3    8
CHEMP----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
   1
toluene
     591.8      41.0     0.263     0.263      0.4
     383.8  -7.28607  1.38091  -2.83433  -2.79168
    92.141-.2435E+020.5125E+00-.2765E-030.4911E-07
      867.    293.00 0.880E-05    303.10      1.41
-.5878E+010.1287E+040.4575E-02-.4499E-05    316.0
 0.101E-03 0.000E+00 0.000E+00 0.000E+00
 8.8649e-3        0.        0.        0.
NCGAS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
   1
O2
BIODG----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
   0       1.e-10                   .0       .2      0.5      0.5
   1
        2        1 5.706e-6     0.426        0        0        0       .0
        3 6.546e-7        2    1.e-7
        0
        0
        0
       -4.    +9.000         1.
   1
  2.300e-7  2.30e-7       40. 8.831e-18    0.e-5
SELEC----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
   0    0    0

START----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
----*----1 MOP: 123456789*123456789*1234 ---*----5----*----6----*----7----*----8
PARAM----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
  31900    1900100030100002200 4 0001001
         4.5792e+6        -1. 4320.E+0              9.8065
    1.00      5.00
    1.E-8     1.E-2                          1.000E-8              1.e4
    2
         1.013000e5              0.0       3.51323e-6              20.0
DIFFU----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    2.e-5 0.0000e-6   6.e-10
    2.e-5 1.7573e-9   6.e-10
    2.e-58.3835e-10   6.e-10
RPCAP----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
   6         .150      .05      .01       3.
   8        0.000     1.84      10.      11.
```

Figure 4. Input file for aerobic biodegradation of toluene in a laboratory column.

```
ELEME
A11 1            10.2000E-020.4000E-02            0.1000E-020.5000E+00-.5000E+00
A11 2            10.2000E-020.4000E-02            0.3000E-020.5000E+00-.5000E+00
A11 3            10.4000E-020.8000E-02            0.6000E-020.5000E+00-.5000E+00
A11 4            10.4000E-020.8000E-02            0.1000E-010.5000E+00-.5000E+00
A11 5            10.4000E-020.8000E-02            0.1400E-010.5000E+00-.5000E+00
…
…
A1165            10.4000E-020.8000E-02            0.2540E+000.5000E+00-.5000E+00
A1166            10.3000E-020.6000E-02            0.2575E+000.5000E+00-.5000E+00
A1167            10.1000E-020.2000E-02            0.2595E+000.5000E+00-.5000E+00
A1168            3-.1000E-050.2000E-05            0.2600E+000.5000E+00-.5000E+00


CONNE
A11 1A11 2               10.1000E-020.1000E-020.1000E+01
A11 2A11 3               10.1000E-020.2000E-020.1000E+01
A11 3A11 4               10.2000E-020.2000E-020.1000E+01
A11 4A11 5               10.2000E-020.2000E-020.1000E+01
…
…
A1165A1166               10.2000E-020.1500E-020.1000E+01
A1166A1167               10.1500E-020.5000E-030.1000E+01
A1167A1168               10.5000E-030.5000E-060.1000E+01

GENER----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
A11 1WAT 1              4    COM11
        0.0     3726432.0    3813696.0     5665600.0
    2.6503E-03    2.6503E-03    4.2319E-03    4.2319E-03
       84.E+03       84.E+03       84.E+03       84.E+03
A11 1TOL 3             28    COM31
        0.0      16903.6      32132.0       85190.4
    127872.0     871776.0     959040.0     1221696.0
   1310688.0    1481760.0    2434752.0    2518560.0
   2610144.0    2690496.0    2779488.0    3119040.0
   3294432.0    3381696.0    3642624.0    3726432.0
   3813696.0    3896640.0    3982176.0    4237920.0
   4323456.0    4409856.0    4497120.0    5665600.0
   1.0071E-09    1.3046E-09    1.3619E-09    1.4148E-09
   1.5272E-09    1.3663E-09    1.0512E-09    1.0357E-09
   9.6742E-10    9.0571E-10    8.0432E-10    7.7787E-10
   7.4041E-10    9.7183E-10    1.1658E-09    1.1944E-09
   1.2187E-09    1.1041E-09    9.2334E-10    9.3656E-10
   1.6116E-09    1.4884E-09    1.3125E-09    1.4075E-09
   1.4392E-09    1.4884E-09    1.5060E-09    1.5060E-09
      84.E+03       84.E+03       84.E+03       84.E+03
     …
     …
      84.E+03       84.E+03       84.E+03       84.E+03
A11 1O2  2             35    COM21
        0.0      36941.2      85190.4      127872.0
    165192.5     261380.7     341538.3     521089.6
    604453.5     780798.5     871776.0     959040.0
   1221696.0    1310688.0    1481760.0    1826046.7
   2434752.0    2518560.0    2610144.0    2690496.0
   2779488.0    3036096.0    3119040.0    3294432.0
   3381696.0    3642624.0    3726432.0    3813696.0
   3896640.0    3982176.0    4237920.0    4323456.0
   4409856.0    4497120.0    5665600.0
```

Figure 4 (cont.). Input file for aerobic biodegradation of toluene in a laboratory column.

```
     1.6818E-08     1.2909E-08     1.3499E-08     1.4925E-08
     1.4507E-08     1.4433E-08     1.5638E-08     1.4753E-08
     1.5244E-08     1.6056E-08     1.5785E-08     1.6818E-08
     1.8243E-08     1.7014E-08     1.6523E-08     1.5785E-08
     1.5933E-08     1.5638E-08     1.6080E-08     1.6523E-08
     1.8120E-08     1.9718E-08     2.0628E-08     1.8415E-08
     1.6277E-08     1.7580E-08     1.7997E-08     2.8031E-08
     2.8855E-08     2.7796E-08     2.6972E-08     2.7403E-08
     2.7246E-08     2.6422E-08     2.6461E-08
        84.E+03        84.E+03        84.E+03        84.E+03
       …
       …
        84.E+03        84.E+03        84.E+03        84.E+03
        84.E+03        84.E+03        84.E+03

FOFT ----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
A1167

ENDCY----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
```

Figure 4 (cont.). Input file for aerobic biodegradation of toluene in a laboratory column.
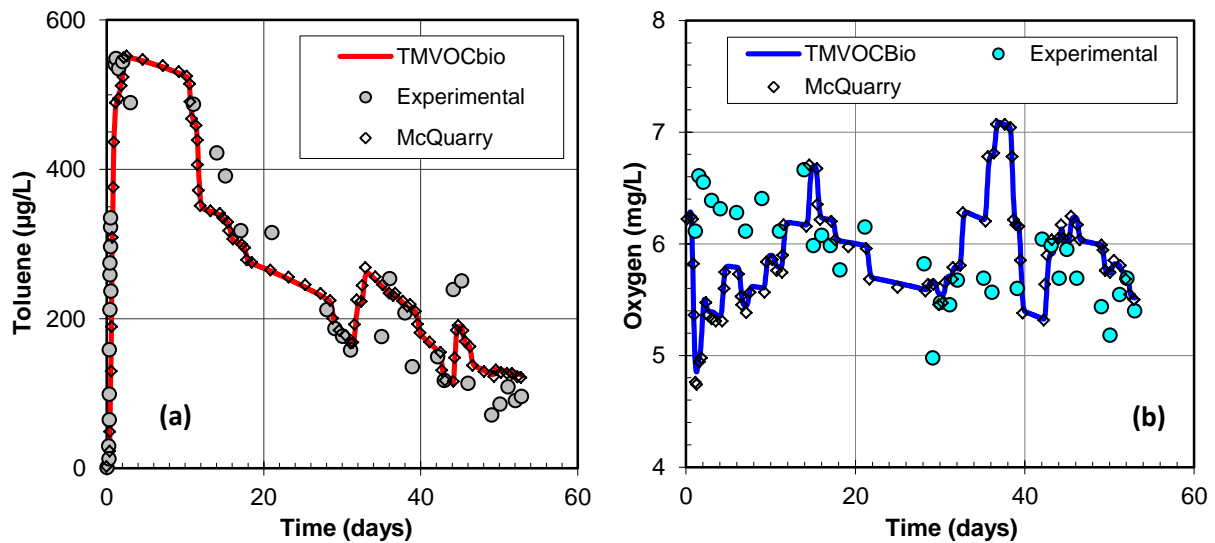

Figure 5. TMVOCBio simulated concentration of (1) toluene and (2) oxygen at column outlet compared with experimental data (circles) and simulated results (diamonds) of MacQuarrie et al. (1990).

4.3. Problem No. 3 – Calibration of Biodegradation Model

Synthetic data are generated from a forward TMVOCBio run, and random noise is added to simulate measurement errors. The forward simulation conditions, including the parameters related to biodegradation, are adapted from Chen et al. (1992). Benzene, toluene, and O_2 dissolved in water are injected at constant rate into a 56-cm-long one-dimensional, horizontal column, and their concentrations are monitored at the column outlet for 10 days.

Here, the maximum specific degradation rate and half saturation of benzene and toluene and the death rate constant of two different microbial populations are estimated, which are specified in the iTOUGH2 input file as `>> BIODEGRADATION`, `>> HALF SATURATION`, and `>> DEATH`, respectively, in block `> PARAMETER`. Figures 6 and 7 show the forward TMVOCBio input file and the iTOUGH2 input file for the model calibration. All of these parameters can be estimated either in their values or in their logarithms. For instance, as shown in Figure 7, the logarithms of the maximum specific degradation rates are estimated instead of their values. Figure 8 shows the synthetic breakthrough data of benzene and toluene and the simulated results with the initial and final parameter sets, and Table 2 summarizes the estimated and true parameter values. The simulated results are in good agreement with the synthetic data, and the estimated parameter set is also almost identical with the true parameter set.

Table 2. True and estimated parameter values of Problem No. 3.

Parameter	Type	True value	Estimated value	Marginal standard deviation
$\mu_{max,toluene}$	LOG	-3.941E+00	-3.98E+00	3.5E-02
$\mu_{max,benzene}$	LOG	-4.017E+00	-4.02E+00	2.3E-02
$K_{S,toluene}$	VALUE	1.74E-05	1.50E-05	1.9E-06
$K_{S,benzene}$	VALUE	1.22E-05	1.21E-05	1.5E-06
$\delta_{toluene}$	VALUE	1.157E-06	1.42E-06	3.4E-07
$\delta_{benzene}$	VALUE	1.157E-06	1.13E-06	8.0E-07

```
Chen-5 BENZENE & TOLUENE DEGRADATION IN A COLUMN (Chen et al.,1992)
ROCKS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
SAND1    1     2645.      .380  1.0E-12  1.0E-12  1.0E-12      3.1     1000.
     0.e-8       0.      2.85      0.0              .0100
BOUN3    1     2645.      .380  1.0E-12  1.0E-12  1.0E-12      3.1    50000.
     0.e-8       0.      2.85      0.0              .0100


MULTI----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    4    4    3    8    0
CHEMP----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    2
toluene
     591.8      41.0     0.263     0.263      0.4
     383.8  -7.28607   1.38091  -2.83433  -2.79168
    92.141-.2435E+020.5125E+00-.2765E-030.4911E-07
      867.     293.00 0.880E-05    303.10      1.41
-.5878E+010.1287E+040.4575E-02-.4499E-05    316.0
 0.101E-03 0.000E+00 0.000E+00 0.000E+00
 0.139E-01 0.000E+00 0.000E+00 0.000E+00
benzene
     562.2      48.2     0.271     0.212      0.0
     353.2  -6.98273   1.33213  -2.62863  -3.33399
    78.114-.3392E+020.4739E+00-.3017E-030.7130E-07
      885.     289.00 0.770E-05    273.10      1.52
0.4612E+010.1489E+03-.2544E-010.2222E-04    259.0
 0.411E-03 0.000E+00 0.000E+00 0.000E+00
 0.093E-01 0.000E+00 0.000E+00 0.000E+00
NCGAS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    1
O2
BIODG----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    0       1.e-10                 .0       .2      0.9      0.9
    2
        2       11.14583e-4      0.5        0        0        0       .0
        3   17.4e-6         2    1.e-7
        0
        0
        0
      -4.     +6.306        1.        0.
        2       29.60648e-5      0.5        0        0        0       .0
        4   12.2e-6         2    1.0e-7
        0
        0
        0
      -3.     +5.248        0.        1.
    2
  0.820e-6   0.82e-6      40. 1.1574e-6     0.e-6
  0.210e-6   0.21e-7      40. 1.1574e-6     0.e-6
SELEC----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    0    1    0


START----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
----*----1 MOP: 123456789*123456789*1234 ---*----5----*----6----*----7----*----8
PARAM----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
   35000    1000100030000000000 4 0005001
              8.64E5       -1.   864.E1          9.8065
     1.e+0      10.
     1.E-6     1.E+0                            1.000E-8          1.e4
     2
         4.008148e5             0.0           0.00              0.
              20.0
```

Figure 6. TMVOCBio input file for toluene and benzene degradation in a column.

```
DIFFU----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    2.e-6    0.e-10    6.e-10
    2.e-6 2.153e-09    6.e-10
    2.e-6 8.495e-10    6.e-10
    2.e-6 9.537e-10    6.e-10
RPCAP----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    6          .150       .05       .01        3.
    8          0.000      1.84      10.        11.
ELEME
A11 2              10.1000E-010.2000E-01         0.5001E-020.5000E+00-.5000E+00
A11 3              10.1000E-010.2000E-01         0.1500E-010.5000E+00-.5000E+00
A11 4              10.1000E-010.2000E-01         0.2500E-010.5000E+00-.5000E+00
…
…
A1156              10.1000E-010.2000E-01         0.5450E+000.5000E+00-.5000E+00
A1157              10.1000E-010.2000E-01         0.5550E+000.5000E+00-.5000E+00
A11 1              2-.1000E-050.2000E-05         0.5000E-060.5000E+00-.5000E+00

CONNE
A11 1A11 2                    10.5000E-060.5000E-020.1000E+01
A11 2A11 3                    10.5000E-020.5000E-020.1000E+01
A11 3A11 4                    10.5000E-020.5000E-020.1000E+01
…
…
A1156A1157                    10.5000E-020.5000E-020.1000E+01

GENER----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
A1157OUT 1                        MASS -1.4488E-3

ENDCY----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
```

Figure 6 (cont.). TMVOCBio input file for toluene and benzene degradation in a column.

```
 > PARAMETER
   >> BIODEGRADATION

     >>> MODEL
         >>>> ANNOTATION: AMUMAX_1
         >>>> INDEX: 1
         >>>> GUESS: -4.5
         >>>> LOGARITHM
         <<<<

      >>> MODEL
         >>>> ANNOTATION: AMUMAX_2
         >>>> INDEX: 2
         >>>> GUESS: -4.5
         >>>> LOGARITHM
         <<<<
      <<<

   >> HALF SATURATION
      >>> MODEL
         >>>> ANNOTATION: AKS_1
         >>>> INDEX: 1 1
         >>>> GUESS: 1.0E-5
         >>>> VALUE
         <<<<

      >>> MODEL
         >>>> ANNOTATION: AKS_2
         >>>> INDEX: 2 1
         >>>> GUESS: 1.0E-5
         >>>> VALUE
         <<<<
      <<<

   >> DEATH
      >>> MODEL
         >>>> ANNOTATION: DEATH_RATE_1
         >>>> INDEX: 1
         >>>> GUESS: 1.0E-6
         >>>> VALUE
         <<<<

      >>> MODEL
         >>>> ANNOTATION: DEATH_RATE_2
         >>>> INDEX: 2
         >>>> GUESS: 1.0E-6
         >>>> VALUE
         <<<<
      <<<
   <<

 > OBSERVATION
   >> TIME: 100 EQUALLY [DAYS]
      0.1  10.0
```

Figure 7. iTOUGH2 input file to estimate the reaction parameters for toluene and benzene degradation in a column.

```
   >> CONCENTRATION

     >>> ELEMENT: A1157
        >>>> ANNOTATION: TOLUENE
        >>>> HEADER: 1
        >>>> COMPONENT: 3
        >>>> PHASE : 2
        >>>> FACTOR: 2.171E-1
        >>>> DATA read from FILE: toluene.dat [HOURS]
        >>>> DEVIATION: 0.01
        <<<<

     >>> ELEMENT: A1157
        >>>> ANNOTATION: BENZENE
        >>>> HEADER: 1
        >>>> COMPONENT: 4
        >>>> PHASE : 2
        >>>> FACTOR: 2.561E-1
        >>>> DATA read from FILE: benzene.dat [HOURS]
        >>>> DEVIATION: 0.02
        <<<<
     <<<
   <<

 > COMPUTATION

   >> CONVERGENCE
     >>> ITERATION: 20
     <<<

   >> OUTPUT
     >>> HOURS
     >>> FORMAT: COLUMNS
     <<<
   <<
 <
```

Figure 7 (cont.). iTOUGH2 input file to estimate the reaction parameters for toluene and benzene degradation in a column.
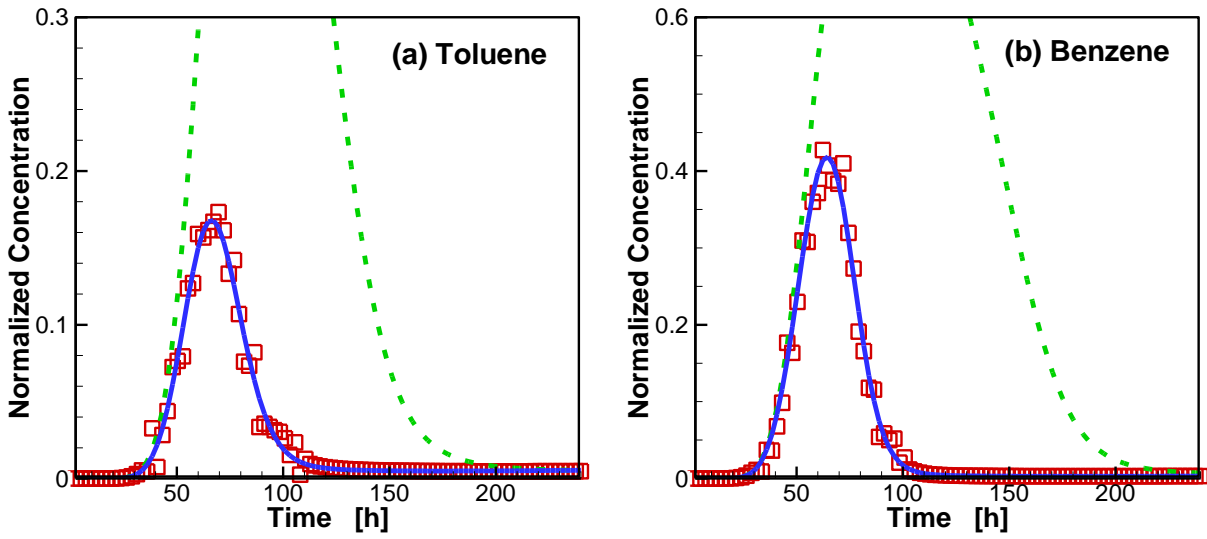
Figure 8. Effluent concentrations of (a) toluene and (b) benzene calculated with initial parameter set (dashed line) and after optimization (solid line). Synthetic data are shown as squares.

5. Concluding Remarks

TMVOCBio, an extended version of the TMVOC numerical simulator, is capable of simulating aerobic and anaerobic biodegradation reactions of multiple organic substances mediated by different microbial populations or based on different redox reactions, thus involving different electron acceptors. This modeling feature is implemented within the existing TMVOC numerical reservoir simulator in iTOUGH2. TMVOCBio uses the modified forms of the Monod kinetic rate equation to express biodegradation reactions, and this general form effectively simulates the uptake rate of substrate accounting for various limiting factors (i.e., the limitation by substrate, electron acceptor, or nutrients). Two approaches are included: (1) a multiple Monod kinetic rate equation, which assumes all the limiting factors simultaneously affect the substrate uptake rate, and (2) a minimum Monod model, which assumes that the substrate uptake rate is controlled by the most limiting factor among those acting for the specific substrate. As the limiting factors, biomass growth inhibition, toxicity effects, as well as competitive and non-competitive inhibition effects are included. The temperature and moisture dependence of biodegradation reactions is also considered.

This report provides mathematical formulations and assumptions used for modeling the biodegradation reactions, and describes additional modeling capabilities. Detailed description of input format for biodegradation reactions is presented along with sample problems. By including a new mass component type—dissolved solids—various biodegradation reactions involving non-volatile compounds can be modeled as well. With the aid of the functionality of iTOUGH2, TMVOCBio can be used for diverse applications related to natural attenuation or engineered remediation of organic contaminants by biodegradation in variously saturated near-surface and subsurface environments.

Notation

Nomenclature

B biomass concentration, kg biomass/kg aqueous phase

E electron acceptor concentration, kg electron acceptor/kg aqueous phase

f_{SW} inhibitive function of water saturation (El-Kadi, 2001), dimensionless,

$f_{SW} = -(S_{W2} - S_W)^2 /(S_{W2} - S_{W1}) + 1$ with $0 < S_{W1} < S_{W2} \leq 1$

if $S_W > S_{W2}$ then $f_{SW}(S_W) = 1$

if $S_W < S_{W1}$ then $f_{SW}(S_W) = 0$

f_T inhibitive function of temperature (Oldenburg, 2001), dimensionless,

$f_T = T(T_{\max,B} - T)/(T_{\max,B}/2)^2$

I_B biomass inhibition factor, dimensionless, $I_B = (K_{Bio} + B)/K_{Bio}$

I_C competitive inhibition factor, dimensionless, $I_C = (K_{C,j} + S_j)/K_{C,j}$

I_H Haldane inhibition factor due to toxicity, kg solute/kg aqueous phase,

$I_H = (S_j)^2 / K_{H,j}$

I_{NC} non-competitive inhibition factor, dimensionless, $I_{NC} = (K_{NC,j} + S_j)/K_{NC,j}$

K_{Bio} biomass inhibition constant, kg biomass/kg aqueous phase

$K_{C,j}$ competitive half saturation constant of solute S_j, kg substrate/kg aqueous phase

$K_{E,B}$ electron acceptor half saturation constant, kg electron acceptor/kg aqueous phase

$K_{H,j}$ Haldane inhibition constant of solute S_j, kg substrate/kg aqueous phase

$K_{NC,j}$ non-competitive half saturation constant of solute S_j, kg substrate/kg aqueous phase

$K_{S,B}$ substrate half saturation constant, kg substrate/kg aqueous phase

S substrate concentration, kg substrate/kg aqueous phase

S_j concentration of solute j, kg substrate/kg aqueous phase

t time, s

T	temperature, °C
$T_{max,B}$	maximum temperature for biodegradation reaction, °C
Y	biomass yield coefficient, kg biomass/kg substrate
δ	first-order death rate constant of biomass, s^{-1}
$\mu_{0,B}$	specific substrate utilization rate by biomass, kg substrate/(kg biomass·s)
$\mu_{max,B}$	maximum specific substrate utilization rate by biomass, kg substrate/(kg biomass·s)

Acknowledgement

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