

Approaches and Examples for Modeling Microbially-Mediated Reactions

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Abstract

This document summarizes approaches and provides examples for modeling microbially-mediated reactions for the implementation of functions in PFLOTRAN for NGEE-Arctic fine/intermediate scale models. The kinetic rate is generally modeled by the Monod equation with various factors to account for thermodynamics, temperature, etc. In some applications (e.g., Wang et al. [2003], Fang et al. [2009], Yabusaki et al. [2007], Riley et al. [2011]), the biomass is not tracked. When the biomass is tracked, the biomass synthesis reaction is either included (anabolic reaction, e.g., Luo et al. [2007], Istok et al. [2010], Rittmann and McCarty [2001]) or not include (catabolic reaction, e.g., Jin and Roden [2011], Li et al. [2009], Bethke [2007], Gu and Riley [2010]) in the redox reactions. The decay of the biomass is generally modeled with a first order decay, but without explicitly model the reactions. To complete the carbon cycle, the carbon incorporated into and decomposed from biomass may need to be explicitly included.

1 Biomass Not Tracked

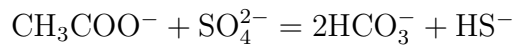
When the biomass is not tracked (e.g., Wang et al. [2003], Fang et al. [2009], Yabusaki et al. [2007], Riley et al. [2011]), the reaction rate is

$$r = k_{max} \frac{m_D}{k_D + m_D} \frac{m_A}{k_A + m_A} \frac{k_I}{k_I + m_I} \quad (1)$$

r	reaction rate for the redox reaction [ML ⁻³ T ⁻¹]
k_{max}	maximum rate coefficient [ML ⁻³ T ⁻¹]
m_A	electron acceptor concentration [ML ⁻³]
m_D	electron donor concentration [ML ⁻³]
m_I	inhibitor concentration [ML ⁻³]
k_A	electron acceptor half saturation concentration [ML ⁻³]
k_D	electron donor half saturation concentration [ML ⁻³]
k_I	inhibitor half saturation concentration [ML ⁻³]

Example 1. Sulfate reduction with acetate as the electron donor

The sulfate reduction reaction is



The parameters are: $k_{max} = 1 \times 10^{-10}$ M/s, $k_A = 3.9 \times 10^{-5}$ M, $k_D = 5 \times 10^{-6}$ M, initial acetate = 1 mM, sulfate = 1.5 mM. The simulation results are shown in Figure 1 using PHREEQC.

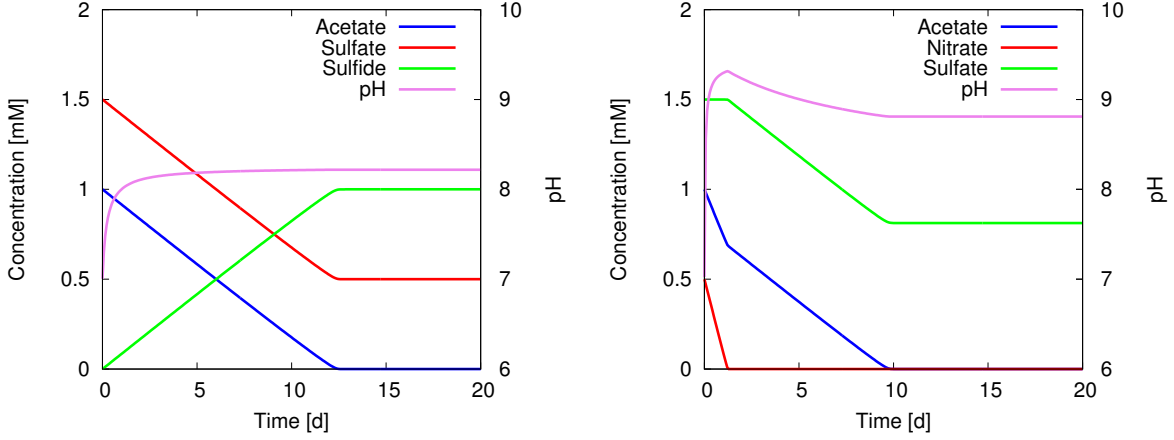
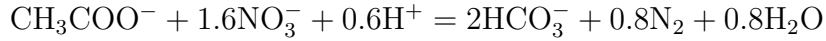


Figure 1: PHREEQC results for Example 1 (left) and 2 (right)

Example 2. Sulfate reduction with acetate as the electron donor and with nitrate inhibition

The nitrate reduction reaction is

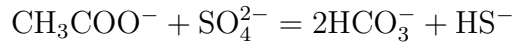


The parameters for nitrate reduction are: $k_{max} = 3 \times 10^{-9}$ M/s, $k_A = 2.3 \times 10^{-6}$ M, $k_D = 1 \times 10^{-6}$ M, $k_I = 1 \times 10^{-6}$ M, the initial nitrate concentration = 0.5 mM. The parameters for sulfate reduction are identical to Example 1. The simulation results are shown in Figure 1

2 Catabolic Reaction with Monod Growth

This approach includes a redox reaction, a cell synthesis reaction, and a decay reaction. However, the cell synthesis, and decay reactions are often not explicitly accounted for (Jin and Roden [2011], Li et al. [2009], Bethke [2007], Gu and Riley [2010]). As the growth and decay of biomass are part of the carbon and nitrogen cycle, we need to consider explicitly including these reactions. However, the representation of biomass, growth and decay reactions are not widely used. A treatment was included in Wang et al. [2012] for a microbial-enzyme-mediated carbon decomposition model.

The reaction rate for the redox reaction, for example,



is

$$r = \mu_{max} x \frac{m_D}{k_D + m_D} \frac{m_A}{k_A + m_A} \frac{k_I}{k_I + m_I} F_T F_\theta F_{pH} \quad (2)$$

with
 μ_{max} maximum rate coefficient [$ML^{-3}T^{-1}$]
 x biomass [ML^{-3}]
 F_T thermodynamic factor

$$F_T = 1 - \exp\left(-\frac{\Delta G_A - \Delta G_C}{\chi RT}\right) \quad (3)$$

ΔG_A energy available from the redox reaction
 ΔG_C energy saved by the functional group
 χ average stoichiometric number
 R gas constant
 T absolute temperature

$$\Delta G_A = -\Delta G_T^0 - RT \ln \prod a_i^{\nu_i} \quad (4)$$

$$\Delta G_C = m_{ATP} \Delta G_P \quad (5)$$

ΔG_T^0 standard Gibbs free energy change
 a_i activity of reactants
 ν_i stoichiometric coefficient
 m_{ATP} ATP yield
 ΔG_P the phosphorylation energy
The growth rate is

$$dx/dt = -Yr \quad (6)$$

Y yield coefficient
The first order decay rate is

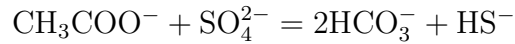
$$dx/dt = Dx \quad (7)$$

D first order decay rate coefficient

Example 3. Sulfate reduction with acetate as the electron donor

This example is extended from Bethke [2007]. A solution, initially sterile, contains 500 mM NaCl, 20 mM CaSO₄, 2 mM FeCO₃, and 1 mM NaCH₃COO. Its pH is buffered to 7.2. At $t = 0$, the solution is inoculated with enough of the sulfate reducers to bring the initial biomass, expressed in terms of the dry weight of the cells, to 0.1 mg/L. The solution is incubated for three weeks.

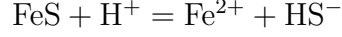
The reaction is



$\chi = 5$, $\Delta G_P = 45$ kJ/mol, $m = 1$, therefore,

$$F_T = 1 - \left(\frac{Q}{K}\right)^{1/5} \exp\left(\frac{9}{RT}\right) \quad (8)$$

Sulfide produced from sulfate reduction is expected to precipitate with ferrous iron to form mackinawite (FeS), a precursor to pyrite (FeS), with reaction.



with $\log K = -3.6$ at 25 °C. The yield coefficient Y is 4.3 g/mol.

We consider four simulation cases:

Case 1: no acetate for biomass synthesis, no biomass decay

Case 2: first order decay at rate coefficient $D = 10^{-7}$ 1/s

Case 3: biomass synthesis from acetate

For each mole of sulfate reduction $\text{CH}_3\text{COO}^- + \text{SO}_4^{2-} = 2\text{HCO}_3^- + \text{HS}^-$, Y mole biomass is synthesized following $2.5\text{CH}_3\text{COO}^- + 2.5\text{H}^+ \rightarrow \text{C}_5\text{H}_7\text{O}_2\text{N}$. $\text{C}_5\text{H}_7\text{O}_2\text{N}$ is used to represent the biomass.

Case 4: biomass synthesis from acetate, and decay to produce CO_2 following $\text{C}_5\text{H}_7\text{O}_2\text{N} \rightarrow 5\text{CO}_2$. The simulation results are shown in Figure 2.

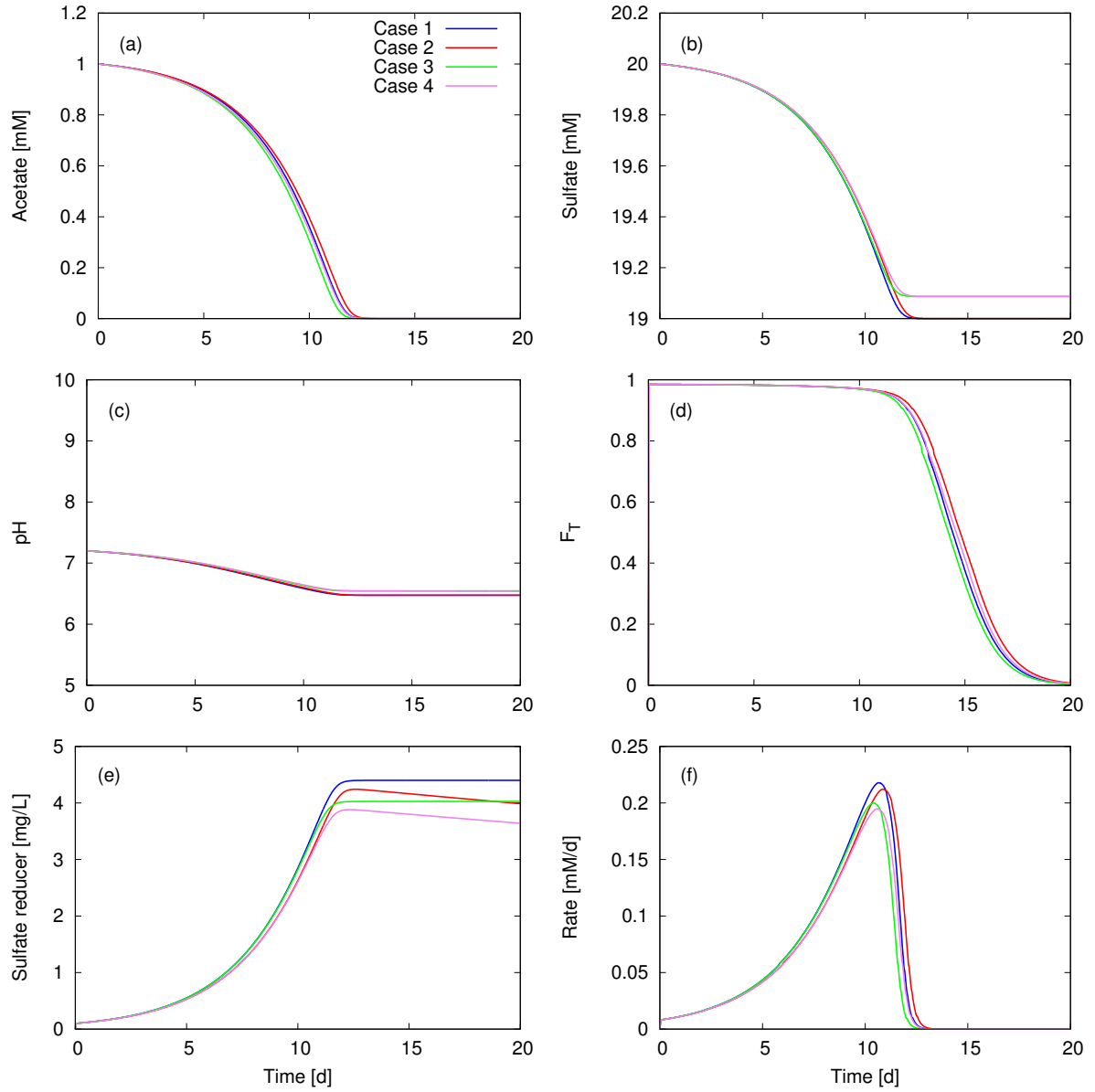
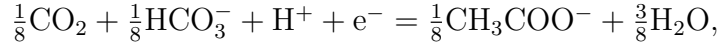


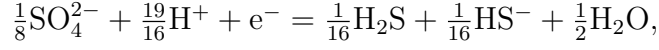
Figure 2: PHREEQC results for Example 3

3 Anabolic Reaction with Monod Growth

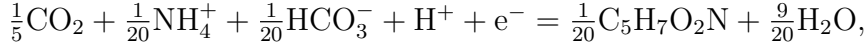
An anabolic reaction often combines an electron donor (reduction) half reaction, e.g.,



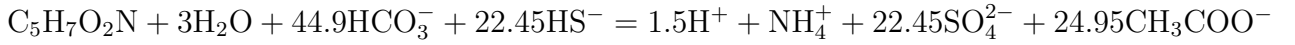
an electron acceptor (oxidation) half reaction, e.g.,



and a cell synthesis reaction, e.g.,

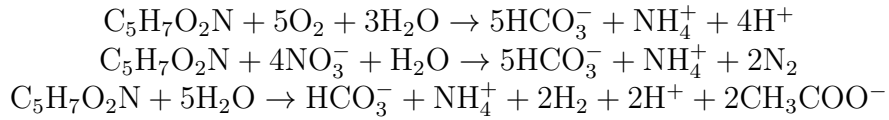


by partitioning the electron transfer (Rittmann and McCarty [2001]). For example, the anabolic reaction for the microbially-mediated sulfate reduction with acetate as the electron donor can be written as (Istok et al. [2010])



with $\log k = -137.87$. The yield coefficient (4.5 g/mol) is slightly greater than that used in Example 3 (4.3 g/mol).

The decomposition of the decayed biomass can be linked to aerobic respiration, denitrification, or fermentation following the reactions (Jin and Roden [2011])



Example 4. Sulfate reduction using anabolic reaction

We replace the redox and cell synthesis reaction in Example 3 Case 4 with anabolic reaction. The results are compared with the catabolic reaction results in Figure 3.

4 Complex Reaction Network

Multiple redox reactions may contribute to one group of microbes, i.e., one species can use various electron donors, e.g., denitrifiers can use ethanol, acetate, and H_2 in the Fig. 1. in Jin and Roden [2011].

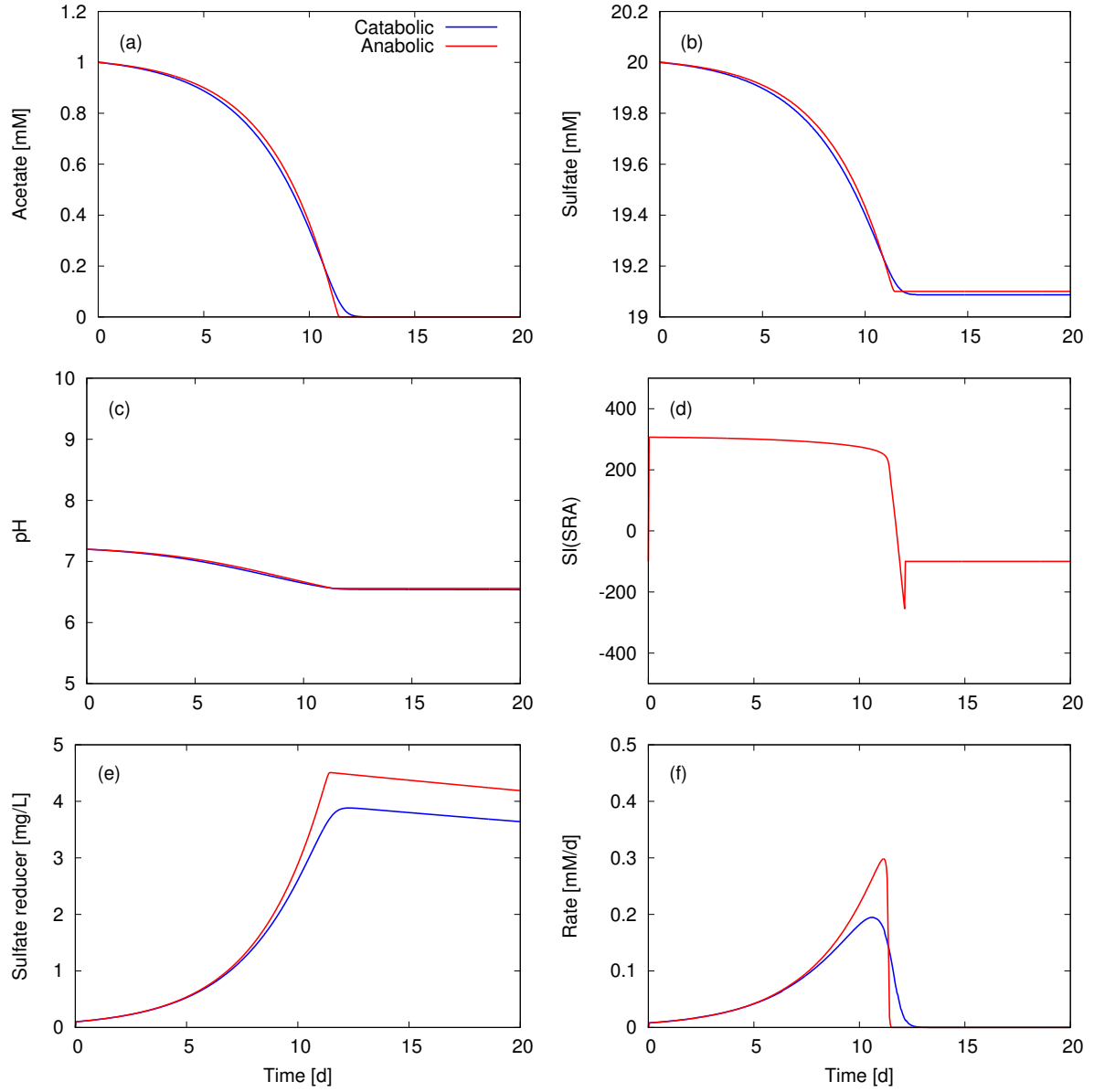


Figure 3: PHREEQC results for Example 4. Comparison of simulation results with anabolic vs. catabolic reactions.

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