Example Problem W-5

Transport, Kinetic Biodegradation, Cell Growth and Sorption

Abstract: *This example problem was developed and published by Parkhurst and Appelo (1999), from an advective-dispersive-reactive transport problem, developed by Tebes-Steven and Valocchi (1998). The transport involves mobile and immobile species; where the immobile species are either bacterial cells or sorbed metals. The chemistry involves speciation, bacterially mediated degradation of an organic substrate, bacterial growth and decay, and kinetic metal sorption, including metal-ligand complexation. In brief the problem involves the steady-flow of an aqueous solution through a 10-m column, initially containing biomass. A pulse of dissolved nitrylotriacetate (Nta) and cobalt (Co) are introduced at the inlet of the column. Nta is defined to degrade in the presence of biomass and oxygen, yielding biomass growth. The equilibrium chemistry in this problem assumes activity coefficients of 1.0. To solve the chemical reactions in this problem, STOMP-W-R is used.*

Problem Description

This problem involves the steady flow of an aqueous solution through a 10-m column with a pore-water velocity of 1.0 m/hr. Hydrological and mechanical properties for the system are given in Table 1. The aqueous solution initially within the column comprises biomass, oxygen, and carbon, at a pH of 6, but is void of Nta and Co. This problem involves 25 species, whose formula and mobility are shown in Table 2. The initial concentrations of species in the column, expressed in terms of aqueous molar concentrations are given in Table 3. The reaction network for this problem is given in Table 4, where the equilibrium constant is defined for equilibrium type reactions and the activity of water is assumed to be 1.0.

Table 1. Hydrological and Mechanical Properties

Property	Value
Porosity	0.4
Grain Density	2500 kg/m³
Hydraulic Conductivity	100 Darcy
Darcy Velocity	0.4 m/hr
Longitudinal Dispersivity	0.05 m

Table 2. Species and Mobility

Species	Mobility	Species	Mobility
CO_2	Dissolved Aqueous	HCO_3^-	Dissolved Aqueous
CO_3^{--}	Dissolved Aqueous	$HNta^{--}$	Dissolved Aqueous
Cl^-	Dissolved Aqueous	NH_3	Dissolved Aqueous
$Co(OH)_2$	Dissolved Aqueous	NH_4^+	Dissolved Aqueous
$Co(OH)_3^-$	Dissolved Aqueous	Nta^{---}	Dissolved Aqueous
Co^{++}	Dissolved Aqueous	Na^+	Dissolved Aqueous
$CoNta^-$	Dissolved Aqueous	O_2	Dissolved Aqueous
$Co(Nta)_2^{----}$	Dissolved Aqueous	OH^-	Dissolved Aqueous
$CoOH^+$	Dissolved Aqueous	$Co^{++}(ads)$	Immobile Sorbed
$CoOHNta^{--}$	Dissolved Aqueous	$CoNta^-(ads)$	Immobile Sorbed
H^+	Dissolved Aqueous	$C_5H_7O_2N$	Immobile
H_2Nta^-	Dissolved Aqueous	Biomass	Immobile
H_3Nta	Dissolved Aqueous		

Table 3. Initial and Pulse Species Concentrations

Species	Initial Concentration	Pulse Concentration
pH	6	6
CO_2	4.9 x 10⁻⁷ mol/L	4.9 x 10⁻⁷ mol/L
O_2	3.125 x 10⁻⁵ mol/L	3.125 x 10⁻⁵ mol/L
Nta^{---}	0.0	5.23 x 10⁻⁶ mol/L
Co^{++}	0.0	5.23 x 10⁻⁶ mol/L
Na^+	1.0 x 10⁻³ mol/L	1.0 x 10⁻³ mol/L
Cl^-	1.0 x 10⁻³ mol/L	1.0 x 10⁻³ mol/L
Biomass	1.36 x 10⁻⁴ mol/L	0.0

Table 4. Reaction Network

Reaction	Equilibrium Constant
$Nta^{---} + 3\,H^+ = H_3Nta$	$\log K_{eq} = 14.9$
$Nta^{---} + 2\,H^+ = H_2Nta^-$	$\log K_{eq} = 13.3$
$Nta^{---} + H^+ = HNta^{--}$	$\log K_{eq} = 10.3$
$Nta^{---} + Co^{++} = CoNta^-$	$\log K_{eq} = 11.7$
$2\,Nta^{---} + Co^{++} = CoNta_2^{----}$	$\log K_{eq} = 14.5$
$Nta^{---} + Co^{++} + H_2O = CoOHNta^{--} + H^+$	$\log K_{eq} = 0.5$
$Co^{++} + H_2O = CoOH^- + H^+$	$\log K_{eq} = -9.7$
$Co^{++} + 2\,H_2O = Co(OH)_2 + 2\,H^+$	$\log K_{eq} = -22.9$
$Co^{++} + 3\,H_2O = Co(OH)_3^- + 3\,H^+$	$\log K_{eq} = -31.5$
$CO_2 + H_2O = HCO_3^- + H^+$	$\log K_{eq} = -6.35$
$CO_2 + H_2O = CO_3^{--} + 2\,H^+$	$\log K_{eq} = -16.68$
$NH_4^+ = NH_3 + H^+$	$\log K_{eq} = -9.3$
$H_2O = OH^- + H^+$	$\log K_{eq} = -14.0$
$HNta^{--} + 1.62\,O_2 + 1.272\,H_2O + 2.424\,H^+ =$ $0.576\,C_5H_7O_2N + 3.12\,H_2CO_3 + 0.424\,NH_4^+$	kinetic
$Co^{++} = Co^{++}(ads)$	kinetic
$CoNta^- = CoNta^-(ads)$	kinetic
Biomass	kinetic

As shown in Table 4, the reaction network involves 13 equilibrium reactions and 4 kinetic reactions. The reaction rates for the kinetic reactions are defined using a variety of forms. A multiplicative Monod rate expression is used to describe the rate of $HNta^{2-}$ degradation:

$$R_{HNta^{--}} = -q_m \, C_{Biomass} \left(\frac{C^M_{HNta^{--}}}{K_s + C^M_{HNta^{--}}} \right) \left(\frac{C^M_{O_2}}{K_a + C^M_{O_2}} \right) \qquad (1)$$

where, $R_{HNta^{--}}$ is the rate of $HNta^{--}$ degradation ($mol_{HNta}/L_{aqu}/hr$), q_m is the maximum specific rate of substrate utilization ($mol_{HNta}/mol_{Biomass}/hr$), $C_{Biomass}$ is the biomass concentration ($mol_{Biomass}/L_{aqu}$), $C^M_{HNta^{--}}$ is the molality of $HNta^{--}$ (mol_{HNta}/kg_{water}), K_s is the half-saturation constant for the donor (mol_{HNta}/kg_{water}), $C^M_{O_2}$ is the molality of O_2 (mol_{O2}/kg_{water}), and K_a is the half-saturation constant for the acceptor (mol_{O2}/kg_{water}).

The rate of biomass production is defined using the Valocci Biomass rate formulation and depends on the rate of $HNta^{--}$ degradation and the first-order decay rate for biomass:

$$R_{Biomass} = -Y \, R_{HNta^{--}} - b \, C_{Biomass} \qquad (2)$$

where, $R_{Biomass}$ is the rate of biomass generation ($mol_{Biomass}/L_{aqu}/hr$), Y is the microbial yield coefficient ($mol_{Biomass}/mol_{HNta}$), and b is the first-order microbial decay coefficient.

Kinetic sorption reactions of $Co^{2+}(ads)$ and $CoNta^-(ads)$ are described by the following rate equations:

$$R_{Co^{++}(ads)} = k_m \left(C_{Co^{++}} - \frac{C^S_{Co^{++}(ads)}}{K_d} \right) \qquad (3)$$

$$R_{CoNta^-(ads)} = k_m \left(C_{CoNta^-} - \frac{C^S_{CoNta^-(ads)}}{K_d} \right) \tag{4}$$

where, $R_{Co^{++}(ads)}$ is the rate of Co^{2+}(ads) sorption ($mol_{Co2}/L_{aqu}/hr$), k_m is the mass transfer coefficient (1/hr), $C_{Co^{++}}$ is the concentration of Co^{2+} (mol_{Co}/L_{aqu}),

$C^S_{Co^{++}(ads)}$ is the concentration of sorbed Co^{2+}(ads) ($mol_{Co}/g_{sediment}$), K_d is the distribution coefficient ($L_{aqu}/g_{sediment}$), $R_{CoNta^-(ads)}$ is the rate of CoNta⁻(ads) sorption ($mol_{CoNta}/L_{aqu}/hr$), C_{CoNta^-} is the concentration of CoNta⁻ (mol_{CoNta}/L_{aqu}),

$C^S_{CoNta^-(ads)}$ is the concentration of sorbed CoNta⁻(ads) ($mol_{CoNta}/g_{sediment}$).

Parameter values for the kinetic rate shown in Equations (1) through (4) are given in Table 5. The problem description (Parkhurst and Appelo, 1999) states that $HNta^{2-}$ is converted to $C_5H_7O_2N$, "where the latter is chemically inert so that its concentration can be discarded." In developing the species set and reaction network, this statement was interpreted to mean that the biomass and $C_5H_7O_2N$ were separate species, instead of the typical interpretation that the $C_5H_7O_2N$ notation indicates biomass.

Table 5. Kinetic Reaction Parameters

Parameter (Species)	Value
q_m	1.407 x 10⁻³ ($mol_{HNta}/mol_{Biomass}/hr$)
K_s	7.64 x 10⁻⁷ (mol_{HNta}/kg_{water})
K_a	6.25 x 10⁻⁶ (mol_{O2}/kg_{water})
Y	65.14 ($mol_{Biomass}/mol_{HNta}$)
b	2.08 x 10⁻³ (1/hr)
k_m (Co^{++})	1.0 (1/hr)

k_m $(CoNta^-)$	1.0 (1/hr)
K_d (Co^{++})	5.07 x 10^{-3} ($L_{aqu}/g_{sediment}$)
K_d $(CoNta^-)$	5.33 x 10^{-4} ($L_{aqu}/g_{sediment}$)

References

Parkhurst, D. L. and C. A. J. Appelo. 1999. User's Guide to PHREEQC (Version 2) – A Computer Program for Speciation, Batch Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations, *Water-Resources Investigation Report* 99-4259, U.S. Geological Survey.

Tebes-Steven, C. and A. J. Valocchi, J. M. van Briesen, and B. E. Rittmann. 1998. "Multicomponent transport with coupled geochemical and microbiological reactions - model description and example simulations." *Journal of Hydrology*, 209:8-26.

Exercises

Tip: save a backup copy of your original input file before making any of these modifications.

1. (Basic) Run the base case input file and plot the aqueous species concentrations for Co^{2+}, $CoNta^-$, and $HNta^{2-}$ as shown versus time in Figure 1 at three locations along the column (i.e., 0.5 m, 4.5 m, and 9.5 m from the column inlet) and compare the results.

2. (Basic) Plot the immobile species concentrations for Co^{2+}(ads), $CoNta^-$(ads), and Biomass as shown versus time in Figure 2 at three locations along the column (i.e., 0.5 m, 4.5 m, and 9.5 m from the column inlet).

3. (Basic) Plot dissolved CO_2 concentrations and pH as shown versus time in Figure 3 at three locations along the column (i.e., 0.5 m, 4.5 m, and 9.5 m from the column inlet).

4. (Moderate) The rate of biomass production depends on the rate of $HNta^{2-}$ degradation and the first-order decay rate for biomass, as shown in Equation (2). Increase both of these parameters by a factor of 10. Does the amount of biomass with time increase or decrease?

5. (Moderate) Restore the rate of $HNta^{2-}$ degradation and the first-order decay rate for biomass to their original values. Decrease the initial and boundary dissolved oxygen concentration by a factor of 100. What is the impact on $HNta^{2-}$ concentration, the amount of biomass with time, and the CO_2 concentration? Explain.

Input File

Two STOMP input files are used for this problem and are shown below. The flow solution is run to steady-state and then the reactive transport is simulated with the initital flow solution being initialized from the flow simulation through a restart file. The steady-flow problem description is described by inputs in the *Solution Control Card*, *Grid Card*, *Rock/Soil Zonation Card*, *Mechanical Properties Card*, *Hydraulic Properties Card*, *Saturation Function Card*, *Aqueous Relative Permeability Card*, *Initial Conditions Card* and *Boundary Conditions Card* inputs. The simulation executes for 75 hrs, using a fixed 0.1-hr time step, where the 10-m column is divided into 10 grid cells of uniform length (i.e., 1 m). Although not necessary, the 2.5×10^{-3} m^2 cross section was used to match the 1 L pore volume for each grid cell used in the PHREEQC solution. Because the flow system is fully saturated, saturation function and aqueous relative permeability functions are not required for the problem solution, but are required inputs for the simulator. Since the aqueous pressure always exceeds the default gas pressure in the simulator the aqueous saturation and aqueous relative permeability remain fixed at 1.0 throughout the problem. The steady-flow boundary conditions used to create the pressure distribution in the restart file are repeated as boundary conditions to maintain steady-flow across the column.

The reactive transport problem description is contained in the *Solution Control Card, Grid Card, Rock/Soil Zonation Card, Mechanical Properties Card, Solute/Porous Media Interactions Card, Aqueous Species Card, Solid Species Card, Conservation Equations Card, Equilibrium Reactions Card, Equilibrium Equations Card, Kinetic Reactions Card,*

Kinetic Equations Card, and *Boundary Conditions Card*. Initial flow conditions are read from the restart file as indicated in the *Solution Control Card*. In developing the reactive transport input, the user must identify mobile and immobile species using the *Aqueous Species Card* (i.e., mobile species) and *Solid Species Card* (i.e., immobile) inputs. The *Conservation Equations Card* contains information about the conservation component species that are identified with the prefix "Total_" in the species name. The *Equilibrium Reactions Card* for this problem simply identifies equilibrium constants with reaction names, where the reactions are given the name "EqRc-x." The *Equilibrium Equations Card* links the equilibrium equations to the equilibrium constant through equilibrium reaction names (e.g., EqRc-4).

This problem uses three kinetic reaction types described in Equations (1) through (4) and the inputs for these reactions are entered through the *Kinetic Reactions Card,* where the reactions are named "KnRc-x." The *Kinetic Equations Card* links the kinetic reactions to the kinetic equations through the Kinetic Reaction names (e.g., KnRc-1). Initial species concentrations are defined through the *Initial Conditions Card*, using the keyword "Overwrite," which instructs STOMP to replace the stored species concentrations contained in the restart file (i.e., zero concentrations) with those specified. The pulse boundary condition at the column inlet is created by specifying species concentrations at four times: 0 hr, 20 hr, 20 hr, and 75 hr. The repeated 20-hr time is used to create the sharp pulse change, which occurs at 20 hrs. Species concentrations are entered in the *Boundary Conditions Card.* However, internally in STOMP these concentrations are converted to mobile conservation-component and kinetic-component species.

Flow Simulation Input File

~Simulation Title Card
3.2,
STOMP Example Problem W-5 Flow,
M.D. White,
Pacific Northwest Laboratory,
13 September 2005,
16:06 AM PDT,
2,

PHREEQC Example 15
1D transport: kinetic biodegradation, cell growth, and sorption

~Solution Control Card
Normal,
STOMP-W,
1,
0,yr,75,hr,0.1,hr,0.1,hr,1.25,8,1.e-06,
1000,
0,

~Grid Card
Uniform Cartesian,
10,1,1,
1,m,
0.05,m,
0.05,m,

~Rock/Soil Zonation Card
1,
Column,1,10,1,1,1,1,

~Mechanical Properties Card
Column,2.5,g/cm^3,0.4,0.4,1.e-5,1/m,Millington and Quirk,

~Hydraulic Properties Card
Column,100.0,Darcy,100.0,Darcy,100.0,Darcy,

~Saturation Function Card
Column,van Genuchten,6.83,1/m,2.08,0.1213,,

~Aqueous Relative Permeability Card
Column,Mualem,,

~Initial Conditions Card
Aqueous Pressure,Gas Pressure,
2,
Aqueous Pressure,102064.81,Pa,,,,,,1,10,1,1,1,1,
Gas Pressure,102064.81,Pa,,,,,,1,10,1,1,1,1,

~Boundary Conditions Card
2,
West,Aqueous Neumann,
1,1,1,1,1,1,1,
0,hr,0.4,m/hr,
East,Aqueous Dirichlet,
10,10,1,1,1,1,1,
0,day,102064.81,Pa,

~Output Options Card
3,
1,1,1,
5,1,1,
10,1,1,
1,1,hr,m,6,6,6,

9

1,
Aqueous pressure,Pa,
0,
0,

Transport Simulation Input File

~Simulation Title Card
3.2,
STOMP Example Problem W-5 Transport,
M.D. White,
Pacific Northwest Laboratory,
13 September 2005,
16:06 AM PDT,
2,
PHREEQC Example 15
1D transport: kinetic biodegradation, cell growth, and sorption

~Solution Control Card
Restart,
STOMP-W w/ ECKEChem w/ Transport,
1,
0,yr,75,hr,0.1,hr,0.1,hr,1.25,8,1.e-06,
1000,
0,

~Grid Card
Uniform Cartesian,
10,1,1,
1,m,
0.05,m,
0.05,m,

~Rock/Soil Zonation Card
1,
Column,1,10,1,1,1,1,
~Mechanical Properties Card
Column,2.5,g/cm^3,0.4,0.4,1.e-5,1/m,Millington and Quirk,

~Hydraulic Properties Card
Column,100.0,Darcy,100.0,Darcy,100.0,Darcy,

~Saturation Function Card
Column,van Genuchten,6.83,1/m,2.08,0.1213,,

~Aqueous Relative Permeability Card
Column,Mualem,,

~Solute/Fluid Interactions Card
1,
tracer,conventional,0.0,m^2/s,continuous,1.e+12,yr,
0,

~Solute/Porous Media Interactions Card
Column,0.05,m,,,
tracer,0.,,

~Aqueous Species Card
21,0.e-9,cm^2/s,Bdot Activity,1.0,
CO2,0.,3.0,A,44.0098,kg/kmol,
CO3--,-2.,4.5,A,60.0092,kg/kmol,
Cl-,-1.,3.0,A,35.4527,kg/kmol,
Co(OH)2,0.,3.0,A,92.9479,kg/kmol,
Co(OH)3-,-1.,0.0,A,0.0,kg/kmol,
Co++,2.,6.0,A,58.9332,kg/kmol,
CoNta-,-1.,0.0,A,247.0638,kg/kmol,
CoNta2----,-4.,0.0,A,435.1944,kg/kmol,
CoOH+,1.,0.0,A,75.9405,kg/kmol,
CoOHNta--,-2.,0.0,A,264.0711,kg/kmol,
H+,1.,9.0,A,1.0079,kg/kmol,
H2Nta-,-1.,0.0,A,190.146,kg/kmol,
H3Nta,0.,0.0,A,191.1543,kg/kmol,
HCO3-,-1.,4.0,A,61.0171,kg/kmol,
HNta--,-2.,0.0,A,189.1385,kg/kmol,
NH3,0.,3.0,A,17.0306,kg/kmol,
NH4+,1.,2.5,A,18.0385,kg/kmol,
Nta---,-3.,0.0,A,188.1306,kg/kmol,
Na+,1.,4.0,A,22.9898,kg/kmol,
O2,0.,3.0,A,31.99880,kg/kmol,
OH-,-1.,3.5,A,17.0073,kg/kmol,

~Solid Species Card
4,
Co(ads),,,58.9332,kg/kmol,
CoNta(ads),,,247.0638,kg/kmol,
C5H7O2N,,,113.09,kg/kmol,
Biomass,,,1.0,kg/kmol,

~Conservation Equations Card
8,
Total_CO2,4,CO2,1.00000E+00,C5H7O2N,-5.41667E+00,CO3--,1.00000E+00,HCO3-,1.00000E+00,
Total_Cl-,1,Cl-,1.00000E+00,
Total_Co++,9,Co++,1.00000E+00,Co(ads),1.00000E+00,CoNTA(ads),1.00000E+00,Co(OH)2,1.00000E+00,Co(OH)3-,1.00000E+00,CoNTA-,1.00000E+00,CoNTA2----,1.00000E+00,CoOH+,1.00000E+00,CoOHNTA--,1.00000E+00,
Total_H+,13,H+,1.00000E+00,C5H7O2N,5.93750E+00,CO3--,-2.00000E+00,Co(OH)2,-2.00000E+00,Co(OH)3-,-3.00000E+00,CoOH+,-1.00000E+00,CoOHNTA--,-1.00000E+00,H2NTA-,2.00000E+00,H3NTA,3.00000E+00,HCO3-,-1.00000E+00,HNTA--,1.00000E+00,NH3,-1.00000E+00,OH-,-1.00000E+00,
Total_NH4+,3,NH4+,1.00000E+00,C5H7O2N,-7.36111E-01,NH3,1.00000E+00,
Total_NTA---,9,NTA---,1.00000E+00,CoNTA(ads),1.00000E+00,C5H7O2N,1.73611E+00,CoNTA-,1.00000E+00,CoNTA2----,2.00000E+00,CoOHNTA--,1.00000E+00,H2NTA-,1.00000E+00,H3NTA,1.00000E+00,HNTA--,1.00000E+00,
Total_Na+,1,Na+,1.00000E+00,
Total_O2,2,O2,1.00000E+00,C5H7O2N,2.81250E+00,

~Equilibrium Reactions Card
13,
EqRc-1,0.0,14.900,0.0,0.0,0.0,1/mol,
EqRc-2,0.0,13.300,0.0,0.0,0.0,1/mol,
EqRc-3,0.0,10.300,0.0,0.0,0.0,1/mol,
EqRc-4,0.0,11.700,0.0,0.0,0.0,1/mol,
EqRc-5,0.0,14.500,0.0,0.0,0.0,1/mol,
EqRc-6,0.0,0.500,0.0,0.0,0.0,1/mol,
EqRc-7,0.0,-9.700,0.0,0.0,0.0,1/mol,
EqRc-8,0.0,-22.900,0.0,0.0,0.0,1/mol,
EqRc-9,0.0,-31.500,0.0,0.0,0.0,1/mol,
EqRc-10,0.0,-6.350,0.0,0.0,0.0,1/mol,
EqRc-11,0.0,-16.680,0.0,0.0,0.0,1/mol,
EqRc-12,0.0,-9.300,0.0,0.0,0.0,1/mol,
EqRc-13,0.0,-14.000,0.0,0.0,0.0,1/mol,

~Equilibrium Equations Card
13,
3,H3NTA,H+,3.00000E+00,NTA---,1.00000E+00,EqRc-1,1.0,
3,H2NTA-,H+,2.00000E+00,NTA---,1.00000E+00,EqRc-2,1.0,
3,HNTA--,H+,1.00000E+00,NTA---,1.00000E+00,EqRc-3,1.0,
3,CoNTA-,Co++,1.00000E+00,NTA---,1.00000E+00,EqRc-4,1.0,
3,CoNTA2----,Co++,1.00000E+00,NTA---,2.00000E+00,EqRc-5,1.0,
4,CoOHNTA--,Co++,1.00000E+00,H+,-1.00000E+00,NTA---,1.00000E+00,EqRc-6,1.0,
3,CoOH+,Co++,1.00000E+00,H+,-1.00000E+00,EqRc-7,1.0,
3,Co(OH)2,Co++,1.00000E+00,H+,-2.00000E+00,EqRc-8,1.0,
3,Co(OH)3-,Co++,1.00000E+00,H+,-3.00000E+00,EqRc-9,1.0,
3,HCO3-,CO2,1.00000E+00,H+,-1.00000E+00,EqRc-10,1.0,
3,CO3--,CO2,1.00000E+00,H+,-2.00000E+00,EqRc-11,1.0,
3,NH3,H+,-1.00000E+00,NH4+,1.00000E+00,EqRc-12,1.0,
2,OH-,H+,-1.00000E+00,EqRc-13,1.0,

~Kinetic Reactions Card
4,
KnRc-14,Valocchi Monod,3,HNTA--,1.0,O2,1.0,Biomass,1.0,0,
7.64e-7,mol/kg,6.25e-6,mol/kg,1.407e-3,1/hr,
KnRc-15,Valocchi Sorption,1,Co++,1.0,1,Co(ads),1.0,
1.0,1/hr,5.07e-3,L/gm,
KnRc-16,Valocchi Sorption,1,CoNta-,1.0,1,CoNta(ads),1.0,
1.0,1/hr,5.33e-4,L/gm,
KnRc-17,Valocchi Biomass,3,HNta--,1.0,O2,1.0,Biomass,1.0,0,
7.64e-7,mol/kg,6.25e-6,mol/kg,1.407e-3,1/hr,65.14,0.00208,1/hr,

~Kinetic Equations Card
4,
Kinetic_C5H7O2N,1,C5H7O2N,1.00000e+00,
1,KnRc-14,5.76000e-01,
Kinetic_Co(ads),1,Co(ads),1.00000e+00,
1,KnRc-15,1.00000e+00,
Kinetic_CoNTA(ads),1,CoNTA(ads),1.00000e+00,
1,KnRc-16,1.00000e+00,
Kinetic_Biomass,1,Biomass,1.00000e+00,
1,KnRc-17,1.00000e+00,

~Initial Conditions Card
Aqueous Pressure,Gas Pressure,
6,
Overwrite Species Aqueous Volumetric,H+,0.83889e-6,mol/liter,,,,,,,1,10,1,1,1,1,
Overwrite Species Aqueous Volumetric,O2,3.125e-5,mol/liter,,,,,,,1,10,1,1,1,1,
Overwrite Species Aqueous Volumetric,Na+,1.0e-3,mol/liter,,,,,,,1,10,1,1,1,1,
Overwrite Species Aqueous Volumetric,Cl-,1.0e-3,mol/liter,,,,,,,1,10,1,1,1,1,
Overwrite Species Aqueous Volumetric,Biomass,1.36e-4,mol/liter,,,,,,,1,10,1,1,1,1,
Overwrite Species Aqueous Volumetric,CO2,4.9e-7,mol/liter,,,,,,,1,10,1,1,1,1,

~Boundary Conditions Card
2,
West,Aqueous Neumann,Tracer Aqueous Conc.,Species Aqueous Conc.,
7,CO2,Na+,Nta---,H+,Co++,Cl-,O2,
1,1,1,1,1,1,4,
0,hr,0.4,m/hr,1.0E-06,1/liter,
4.9e-7,mol/liter,1.0e-3,mol/liter,5.23e-6,mol/liter,1.277095e-6,mol/liter,
5.23e-6,mol/liter,1.0e-3,mol/liter,3.125e-5,mol/liter,
20,hr,0.4,m/hr,1.0E-06,1/liter,
4.9e-7,mol/liter,1.0e-3,mol/liter,5.23e-6,mol/liter,1.277095e-6,mol/liter,
5.23e-6,mol/liter,1.0e-3,mol/liter,3.125e-5,mol/liter,
20,hr,0.4,m/hr,0.0,1/liter,
4.9e-7,mol/liter,,,,0.83889e-6,mol/liter,
,,1.0e-3,mol/liter,3.125e-5,mol/liter,
75,hr,0.4,m/hr,0.0,1/liter,
4.9e-7,mol/liter,,,,0.83889e-6,mol/liter,
,,1.0e-3,mol/liter,3.125e-5,mol/liter,
East,Aqueous Dirichlet,Tracer Outflow,Species Outflow,
0,
10,10,1,1,1,1,1,
0,day,102064.81,Pa,,,

~Output Options Card
3,
1,1,1,
5,1,1,
10,1,1,
1,1,hr,m,6,6,6,
26,
Species Aqueous Concentration,CO2,mol/L,
Species Aqueous Concentration,CO3--,mol/L,
Species Aqueous Concentration,Cl-,mol/L,
Species Aqueous Concentration,Co(OH)2,mol/L,
Species Aqueous Concentration,Co(OH)3-,mol/L,
Species Aqueous Concentration,Co++,mol/L,
Species Aqueous Concentration,CoNta-,mol/L,
Species Aqueous Concentration,CoNta2----,mol/L,
Species Aqueous Concentration,CoOH+,mol/L,
Species Aqueous Concentration,CoOHNta--,mol/L,
Species Aqueous Concentration,H+,mol/L,
Species Aqueous Concentration,H2Nta-,mol/L,
Species Aqueous Concentration,H3Nta,mol/L,
Species Aqueous Concentration,HCO3-,mol/L,
Species Aqueous Concentration,HNta--,mol/L,
Species Aqueous Concentration,NH3,mol/L,

Species Aqueous Concentration,NH4+,mol/L,
Species Aqueous Concentration,Nta---,mol/L,
Species Aqueous Concentration,Na+,mol/L,
Species Aqueous Concentration,O2,mol/L,
Species Aqueous Concentration,OH-,mol/L,
Species Aqueous Concentration,Co(ads),mol/L,
Species Aqueous Concentration,CoNta(ads),mol/L,
Species Aqueous Concentration,C5H7O2N,mol/L,
Species Aqueous Concentration,Biomass,mol/L,
Solute Aqueous Concentration,tracer,1/L,
5,
1,s,
1,hr,
10,hr,
20,hr,
30,hr,
30,
Aqueous Saturation,,
Diffusive Porosity,,
Aqueous Density,kg/m^3,
xnc Aqueous Volumetric Flux,m/s,
Species Aqueous Concentration,CO2,mol/L,
Species Aqueous Concentration,CO3--,mol/L,
Species Aqueous Concentration,Cl-,mol/L,
Species Aqueous Concentration,Co(OH)2,mol/L,
Species Aqueous Concentration,Co(OH)3-,mol/L,
Species Aqueous Concentration,Co++,mol/L,
Species Aqueous Concentration,CoNta-,mol/L,
Species Aqueous Concentration,CoNta2----,mol/L,
Species Aqueous Concentration,CoOH+,mol/L,
Species Aqueous Concentration,CoOHNta--,mol/L,
Species Aqueous Concentration,H+,mol/L,
Species Aqueous Concentration,H2Nta-,mol/L,
Species Aqueous Concentration,H3Nta,mol/L,
Species Aqueous Concentration,HCO3-,mol/L,
Species Aqueous Concentration,HNta--,mol/L,
Species Aqueous Concentration,NH3,mol/L,
Species Aqueous Concentration,NH4+,mol/L,
Species Aqueous Concentration,Nta---,mol/L,
Species Aqueous Concentration,Na+,mol/L,
Species Aqueous Concentration,O2,mol/L,
Species Aqueous Concentration,OH-,mol/L,
Species Aqueous Concentration,Co(ads),mol/L,
Species Aqueous Concentration,CoNta(ads),mol/L,
Species Aqueous Concentration,C5H7O2N,mol/L,
Species Aqueous Concentration,Biomass,mol/L,
Solute Aqueous Concentration,tracer,1/L,

14

Results

Species concentrations for Co^{2+}, $CoNta^-$, and $HNta^{2-}$ are shown versus time in Figure 1 at three locations along the column (i.e., 0.5 m, 4.5 m, and 9.5 m from the column inlet). By 10 hrs, the $HNta^{2-}$, which entered the column inlet as Nta^{3-} appears as a peak near the column outlet. Both Nta and Co complexes are retarded through the sorption reactions with $Co^{2+}(ads)$ and $CoNta^-(ads)$. The peaks in the Nta and Co concentrations at 9.5-m from the column inlet occur in the $CoNta^-$ complex at roughly 33 hours, which is in agreement with the results predicted by PHREEQC (Parkhurst and Appelo, 1999). The peak in Co^{2+} is more retarded because of its higher sorption coefficient compared with that of $CoNta^-$. For reference, a conservative tracer is shown at 9.5-m from the column inlet. Without hydrodynamic dispersion and numerical diffusion the tracer time trace would appear as a square pulse, between 9.5 hrs 28.5 hrs.
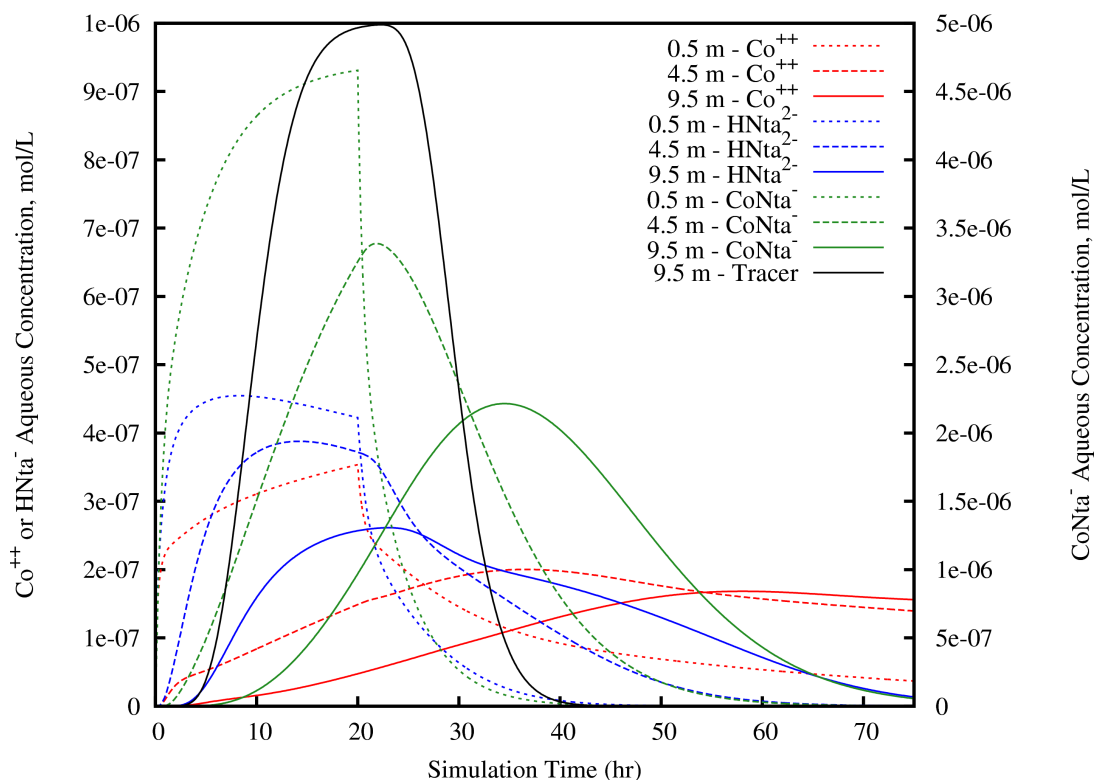

Figure 1. Co^{2+}, $CoNta^-$, and $HNta^{2-}$ Aqueous Concentrations

Immobile species concentrations for $Co^{2+}(ads)$, $CoNta^-(ads)$, and Biomass are shown versus time in Figure 2 at three locations along the column (i.e., 0.5 m, 4.5 m, and 9.5 m from the column inlet). The greater retardation coefficient for Co^{2+} compared with that for $CoNta^-$ yields a more retarded peak in the $Co^{2+}(ads)$ compared with the dissolved peak for Co^{2+} in Figure 1 than a similar comparison for the sorbed and dissolved forms of $CoNta^-$. The sorbed profiles for $Co^{2+}(ads)$ and $CoNta^-(ads)$ at 9.5 m from the inlet compare with those reported by Parkhurst and Appelo (1999) at the column outlet. The Biomass profiles reflect the combined generation and decay terms that comprise the Biomass kinetic reaction rate. At early time, Nta^{3-} enters the column at the inlet yielding Biomass generation near the column inlet. However, the lack of Nta^{-3} substrate near the column end at early times, yields decreasing Biomass concentrations because of decay. Once the Nta complexes have passed through the column, Biomass concentrations across the column decrease over time, because of decay.
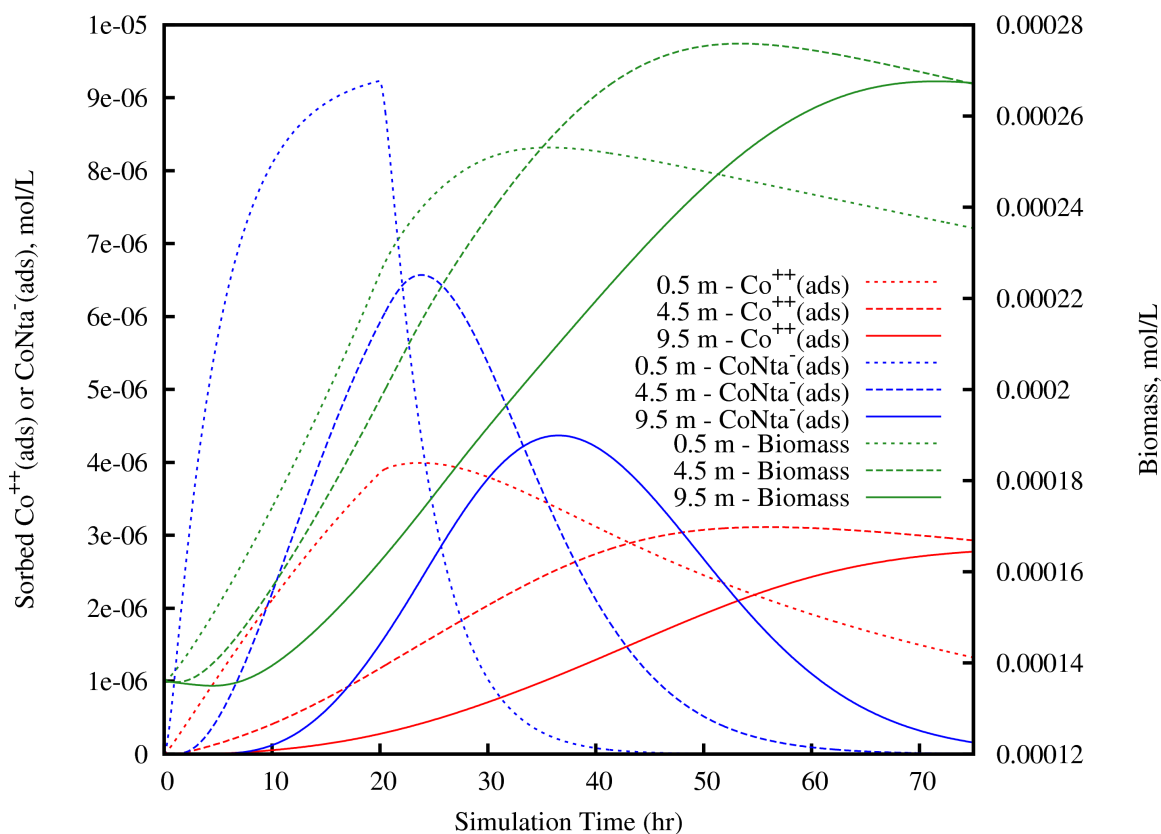

Figure 2. $Co^{2+}(ads)$, $CoNta^-(ads)$, and Biomass Concentrations

16

Dissolved CO_2 concentrations and pH are shown versus time in Figure 3 at three locations along the column (i.e., 0.5 m, 4.5 m, and 9.5 m from the column inlet). Carbon dioxide is initialized and enters the column via a constant dissolved concentration. Carbon dioxide is generated in the column through the degradation reaction of $HNta^{2-}$. The increase in pH from the initial and boundary condition pH of 6.0 coincides with the introduction of Nta^{3-} and Co^{2+}, and the degradation reaction of $HNta^{2-}$. Sharp increases in pH from the degradation reaction are tempered by the evolution of carbon dioxide, which dissociates to carbonic acid through an equilibrium reaction.
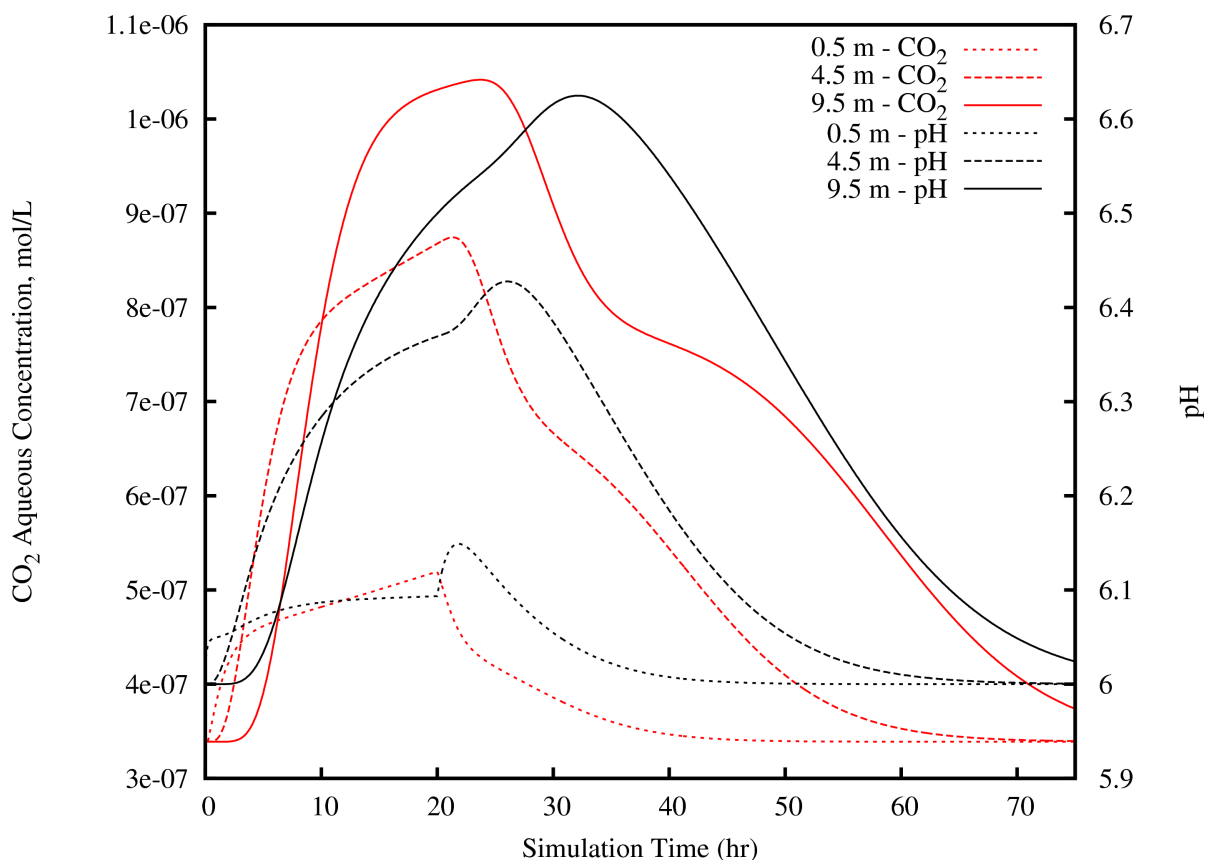

Figure 3. CO_2 Concentration and pH

Solutions to Selected Exercises

Exercise 1

Once the simulation completes, run outputTo.pl. Select "csv" as the plotting package. Specify a name, such as output1.csv, for the plotting-package input file name. Select all reference nodes, and just the species shown in Figure 1 (variables 5, 6, 14 and 25). Plot the species vs simulation time using IgorPro or Excel and compare the results to Figure 1.

Exercise 2

Run outputTo.pl. Select "csv" as the plotting package. Specify a name, such as output2.csv, for the plotting-package input file name. Select all reference nodes, and just the species shown in Figure 2 (variables 21, 22 and 24). Plot the species vs simulation time using IgorPro or Excel and compare the results to Figure 2.

Exercise 3

Run outputTo.pl. Select "csv" as the plotting package. Specify a name, such as output3.csv, for the plotting-package input file name. Select all reference nodes, and just the species CO_2 and H+ (variables 0 and 10). To plot pH you must convert H+ to pH using the equation

$$pH = -log_{10}H^+$$

Plot the species vs simulation time using IgorPro or Excel and compare the results to Figure 3.

Exercise 4

The rate of $HNta^{2-}$ degradation and the first-order decay rate for biomass from Equation 2 are found in kinetic reaction equation KnRc-17 in the *Kinetic Reactions Card* as shown below.

~Kinetic Reactions Card
4,
KnRc-14,Valocchi Monod,3,HNTA--,1.0,O2,1.0,Biomass,1.0,0,

7.64e-7,mol/kg,6.25e-6,mol/kg,1.407e-3,1/hr,
KnRc-15,Valocchi Sorption,1,Co++,1.0,1,Co(ads),1.0,
1.0,1/hr,5.07e-3,L/gm,
KnRc-16,Valocchi Sorption,1,CoNta-,1.0,1,CoNta(ads),1.0,
1.0,1/hr,5.33e-4,L/gm,
KnRc-17,Valocchi Biomass,3,HNta--,1.0,O2,1.0,Biomass,1.0,0,
7.64e-7,mol/kg,6.25e-6,mol/kg,1.407e-3,1/hr,65.14,0.00208,1/hr,

By changing 1.407e-3 to 1.407e-2 and 0.00208 to 0.0208 the rates are increased by a factor of 10. As shown in Figure 4, the amount of biomass with time increases significantly, indicating that the growth of biomass is not limited by the availability of nutrients.
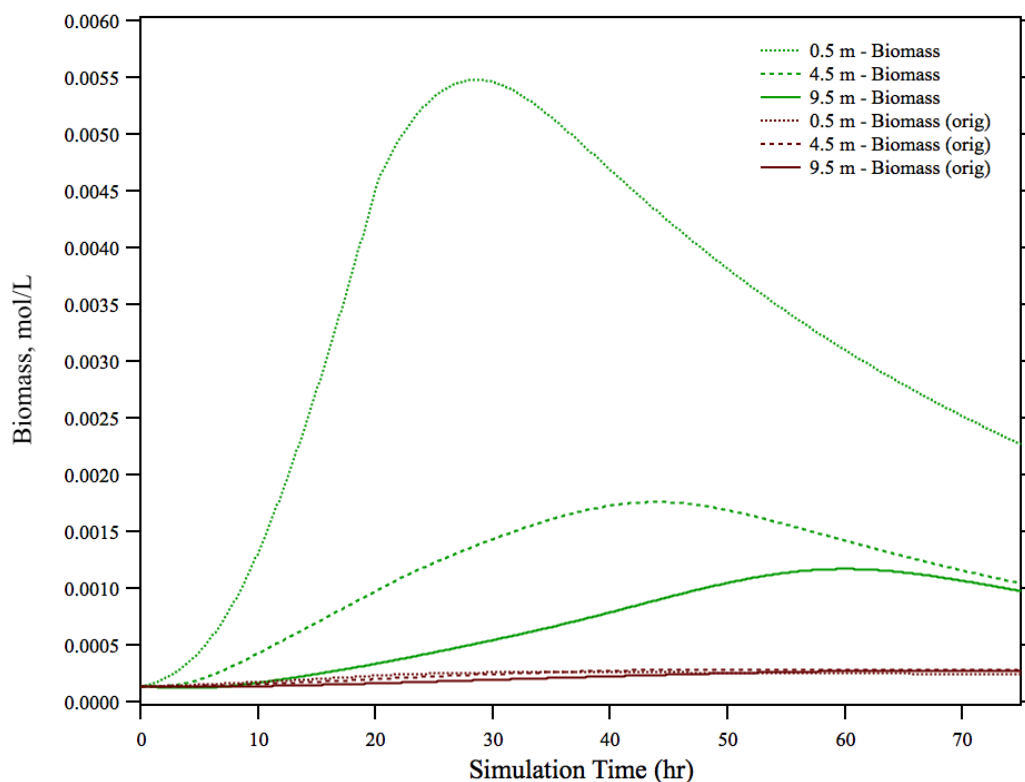

Figure 4. Effect of Increasing Both the Rate of HNta^{2-} Degradation and the First-Order Decay Rate for Biomass by a Factor of 10

Exercise 5

Decreasing the initial and boundary dissolved oxygen concentration by a factor of 100 is done by altering the *Initial Conditions Card* and the *Boundary Conditions Card* as shown below:

~Initial Conditions Card
Aqueous Pressure,Gas Pressure,
6,
Overwrite Species Aqueous Volumetric,H+,0.83889e-6,mol/liter,,,,,,,1,10,1,1,1,1,
Overwrite Species Aqueous Volumetric,O2,3.125e-7,mol/liter,,,,,,,1,10,1,1,1,1,
Overwrite Species Aqueous Volumetric,Na+,1.0e-3,mol/liter,,,,,,,1,10,1,1,1,1,
Overwrite Species Aqueous Volumetric,Cl-,1.0e-3,mol/liter,,,,,,,1,10,1,1,1,1,
Overwrite Species Aqueous Volumetric,Biomass,1.36e-4,mol/liter,,,,,,,1,10,1,1,1,1,
Overwrite Species Aqueous Volumetric,CO2,4.9e-7,mol/liter,,,,,,,1,10,1,1,1,1,

~Boundary Conditions Card
2,
West,Aqueous Neumann,Tracer Aqueous Conc.,Species Aqueous Conc.,
7,CO2,Na+,Nta---,H+,Co++,Cl-,O2,
1,1,1,1,1,1,4,
0,hr,0.4,m/hr,1.0E-06,1/liter,
4.9e-7,mol/liter,1.0e-3,mol/liter,5.23e-6,mol/liter,1.277095e-6,mol/liter,
5.23e-6,mol/liter,1.0e-3,mol/liter,3.125e-7,mol/liter,
20,hr,0.4,m/hr,1.0E-06,1/liter,
4.9e-7,mol/liter,1.0e-3,mol/liter,5.23e-6,mol/liter,1.277095e-6,mol/liter,
5.23e-6,mol/liter,1.0e-3,mol/liter,3.125e-7,mol/liter,
20,hr,0.4,m/hr,0.0,1/liter,
4.9e-7,mol/liter,,,,0.83889e-6,mol/liter,
,,1.0e-3,mol/liter,3.125e-7,mol/liter,
75,hr,0.4,m/hr,0.0,1/liter,
4.9e-7,mol/liter,,,,0.83889e-6,mol/liter,
,,1.0e-3,mol/liter,3.125e-7,mol/liter,
East,Aqueous Dirichlet,Tracer Outflow,Species Outflow,
0,
10,10,1,1,1,1,1,
0,day,102064.81,Pa,,,

This limits the growth of biomass, causing the amount of biomass at each depth to decrease with time as shown in Figure 5. Dissolved CO_2 remains relatively constant with time, due to the lack of biomass respiration. $HNta^{2-}$ concentrations are considerably higher than originally, due to lack of degradation of $HNta^{2-}$.
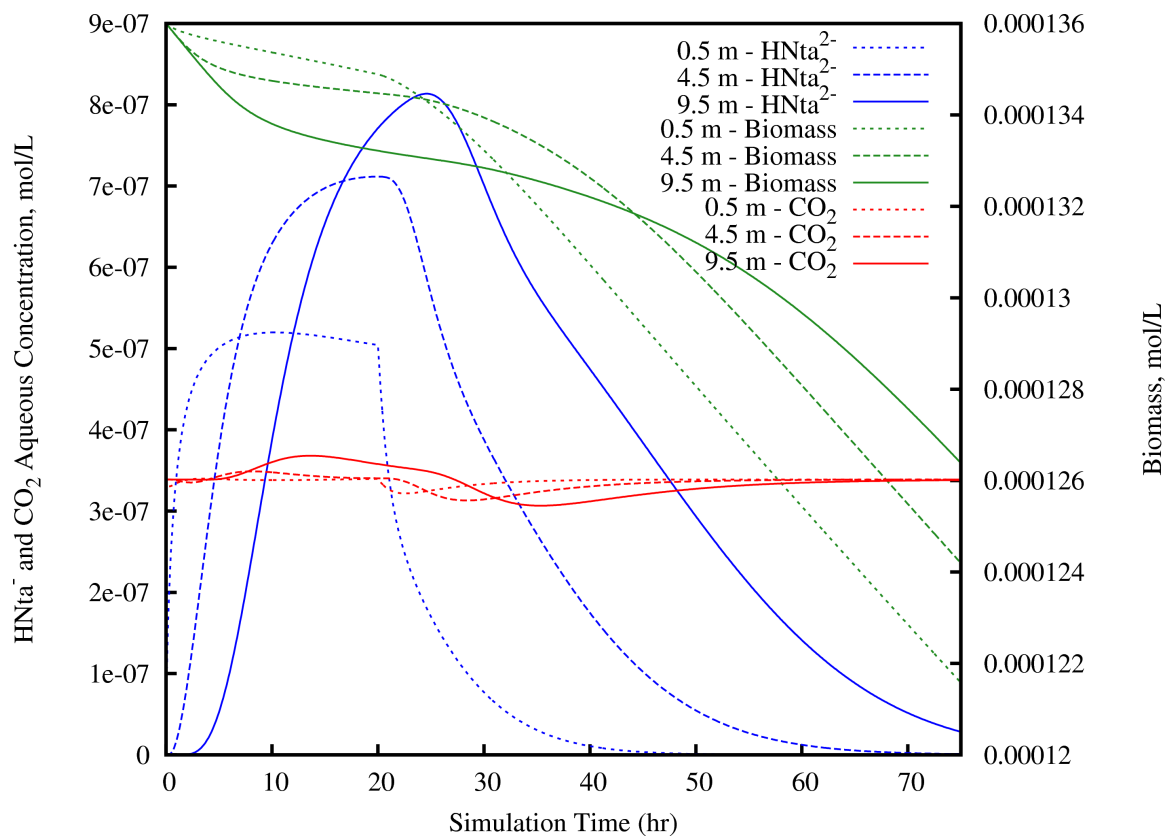
Figure 5. Effect of Decreasing Dissolved Oxygen by a Factor of 100