Implementation of CLM Below-Ground Biogeochemistry in PFLOTRAN

August 13, 2013

Abstract

1 CLM-CN

1.1 Reactions

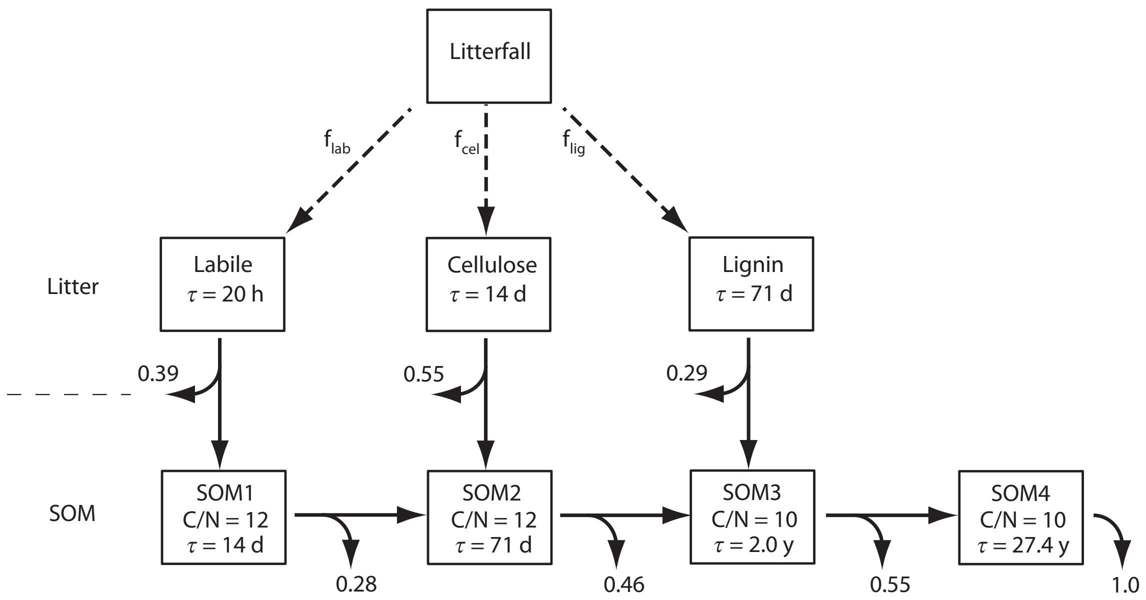

Figure 1: CLM-CN litter and soil organic pools and C and N flows **?**

1.1.1 General Reaction

The general decomposition reaction is

$$\mathrm{CN}_u = (1-f)\mathrm{CN}_d + f\mathrm{CO}_2 + n\mathrm{N}_{\mathrm{mineral}} \tag{1}$$

CN_u	$=$	upstream pool [mol/m^3]
CN_d	$=$	downstream pool [mol/m^3]
CO_2	$=$	[mol/m^3]
N_{mineral}	$=$	mineral nitrogen [mol/m^3]
u	$=$	molecular weight ratio of C and N divided by upstream pool C/N [-]
d	$=$	molecular weight ratio of C and N divided by downstream pool C/N [-]
f	$=$	respiration fraction [-]
n	$=$	$[u-(1-f)d]$

1.1.2 Soil Organic Matter Pools

The C/N ratio is fixed in soil organic matter pools. The reactions are

Table 1: Reactions for the soil organic matter pools

$$\begin{aligned}
\mathrm{SOM1} &= 0.72\ \mathrm{SOM2} + 0.28\ \mathrm{CO_2} + 0.020000\ \mathrm{N_{mineral}} \\
\mathrm{SOM2} &= 0.54\ \mathrm{SOM3} + 0.46\ \mathrm{CO_2} + 0.025143\ \mathrm{N_{mineral}} \\
\mathrm{SOM3} &= 0.45\ \mathrm{SOM4} + 0.55\ \mathrm{CO_2} + 0.047143\ \mathrm{N_{mineral}} \\
\mathrm{SOM4} &= \mathrm{CO_2} + 0.085714\ \mathrm{N_{mineral}}
\end{aligned}$$

1.1.3 Litter Pools

The C/N ratio is dependent on the input from plant function groups. As the C/N ratio is generally greater in the litter pools than in the soil organic pools **?**, mineral N is needed to decompose the litter pools. Namely, litter decomposition involves N immobilization through microbial mass synthesis. For example, one observation indicates a C/N ratio of 31.19 for yellow birch **?**. The reactions are

Table 2: Reactions for the litter pools

$$\begin{aligned}
\mathrm{Lit1C} + 0.027481\ \mathrm{Lit1N} + 0.016090\ \mathrm{N_{mineral}} &= 0.61\ \mathrm{SOM1} + 0.39\ \mathrm{CO_2} \\
\mathrm{Lit2C} + 0.027481\ \mathrm{Lit2N} + 0.004662\ \mathrm{N_{mineral}} &= 0.45\ \mathrm{SOM2} + 0.55\ \mathrm{CO_2} \\
\mathrm{Lit3C} + 0.027481\ \mathrm{Lit3N} + 0.033376\ \mathrm{N_{mineral}} &= 0.71\ \mathrm{SOM3} + 0.29\ \mathrm{CO_2}
\end{aligned}$$

1.1.4 Summary

$$
\begin{aligned}
\mathrm{Lit1C} + u_1\mathrm{Lit1N} &= (1-f_1)\,\mathrm{SOM1} + f_1\mathrm{CO_2} + n_1\mathrm{N_{mineral}} \\
\mathrm{Lit2C} + u_2\mathrm{Lit2N} &= (1-f_2)\,\mathrm{SOM2} + f_2\mathrm{CO_2} + n_2\mathrm{N_{mineral}} \\
\mathrm{Lit3C} + u_3\mathrm{Lit3N} &= (1-f_3)\,\mathrm{SOM3} + f_3\mathrm{CO_2} + n_3\mathrm{N_{mineral}} \\
\mathrm{SOM1} &= (1-f_4)\,\mathrm{SOM2} + f_4\mathrm{CO_2} + n_4\mathrm{N_{mineral}} \\
\mathrm{SOM2} &= (1-f_5)\,\mathrm{SOM3} + f_5\mathrm{CO_2} + n_5\mathrm{N_{mineral}} \\
\mathrm{SOM3} &= (1-f_6)\,\mathrm{SOM4} + f_6\mathrm{CO_2} + n_6\mathrm{N_{mineral}} \\
\mathrm{SOM4} &= f_7\mathrm{CO_2} + n_7\mathrm{N_{mineral}}
\end{aligned}
$$

$$u_i = \mathrm{LitiN}/\mathrm{LitiC}$$

1.2 Rate

1.2.1 General

$$R = f_T f_\Psi f_\mathrm{N} k \mathrm{CN}_u \tag{2}$$

$$
\begin{aligned}
R &= \text{rate } [\mathrm{mol}/(\mathrm{m}^3\mathrm{s})] \\
f_T &= \exp\left[308.56\left(\frac{1}{71.02} - \frac{1}{T-227.13}\right)\right] \\
f_\Psi &= \frac{\log\left(\Psi_\mathrm{min}/\Psi\right)}{\log\left(\Psi_\mathrm{min}/\Psi_\mathrm{max}\right)} \\
f_\mathrm{N} &= \frac{\mathrm{N_{mineral}}}{\mathrm{N_{mineral}} + k_{\mathrm{N_{mineral}}}}(\text{if u} < 0) \\
k &= \text{kinetic rate constant}[\mathrm{s}^{-1}] \\
T &= \text{temperature [K]} \\
\Psi &= \text{soil water potential[Pa]} \\
\mathrm{CN}_u &= \text{upstream carbon pool } [\mathrm{mol}/\mathrm{m}^3] \\
\mathrm{N_{mineral}} &= \text{nitrogen concentration } [\mathrm{mol}/\mathrm{m}^3] \\
k_\mathrm{N} &= \text{Mineral N half saturation constant } [\mathrm{mol}/\mathrm{m}^3]
\end{aligned}
$$

For the general reaction **??**,

$$\frac{\partial \mathrm{CN}_u}{\partial t} = -R$$
$$\frac{\partial \mathrm{CN}_d}{\partial t} = (1-f)\,R$$
$$\frac{\partial \mathrm{CO}_2}{\partial t} = fR$$
$$\frac{\partial \mathrm{N}_{\mathrm{mineral}}}{\partial t} = nR$$

1.2.2 Rates

$$R_1 = f_T f_\theta f_\mathrm{N} k_1 \mathrm{Lit1C}$$
$$R_2 = f_T f_\theta f_\mathrm{N} k_2 \mathrm{Lit2C}$$
$$R_3 = f_T f_\theta f_\mathrm{N} k_3 \mathrm{Lit3C}$$
$$R_4 = f_T f_\theta f_\mathrm{N} k_4 \mathrm{SOM1}$$
$$R_5 = f_T f_\theta f_\mathrm{N} k_5 \mathrm{SOM2}$$
$$R_6 = f_T f_\theta f_\mathrm{N} k_6 \mathrm{SOM3}$$
$$R_7 = f_T f_\theta f_\mathrm{N} k_7 \mathrm{SOM4}$$

1.2.3 Mass Conservation

$$
\begin{aligned}
\frac{\partial}{\partial t}(\text{Lit1C}) &= -R_1 \\
\frac{\partial}{\partial t}(\text{Lit1N}) &= -u_1 R_1 \\
\frac{\partial}{\partial t}(\text{Lit2C}) &= -R_2 \\
\frac{\partial}{\partial t}(\text{Lit3N}) &= -u_2 R_2 \\
\frac{\partial}{\partial t}(\text{Lit3C}) &= -R_3 \\
\frac{\partial}{\partial t}(\text{Lit3N}) &= -u_3 R_3 \\
\frac{\partial}{\partial t}(\text{SOM1}) &= (1-f_1)R_1 - R_4 \\
\frac{\partial}{\partial t}(\text{SOM2}) &= (1-f_2)R_2 + (1-f_4)R_4 - R_5 \\
\frac{\partial}{\partial t}(\text{SOM3}) &= (1-f_3)R_3 + (1-f_5)R_5 - R_6 \\
\frac{\partial}{\partial t}(\text{SOM4}) &= (1-f_6)R_6 - R_7 \\
\frac{\partial}{\partial t}(\text{CO}_2) &= f_1R_1 + f_2R_2 + f_3R_3 + f_4R_4 + f_5R_5 + f_6R_6 + f_7R_7 \\
\frac{\partial}{\partial t}(\text{N}_{\text{mineral}}) &= n_1R_1 + n_2R_2 + n_3R_3 + n_4R_4 + n_5R_5 + n_6R_6 + n_7R_7
\end{aligned}
$$

1.3 Implementation in PFLOTRAN

1.3.1 Numerical Methods

Applying finite-volume spatial discretization:

$$\int \frac{\partial x}{\partial t} dV = \int -\sum R_j dV \tag{3}$$

$$\frac{\partial x}{\partial t}\Delta V = -\sum R_j \Delta V \tag{4}$$

Implicit time discretization:

$$\frac{\Delta V}{\Delta t}\left(x^{k+1} - x^k\right) = -\sum R_j^{k+1}\Delta V \tag{5}$$

Residual:

$$\mathcal{R} = \frac{\Delta V}{\Delta t}\left(x^{k+1} - x^k\right) + \sum R_i^{k+1}\Delta V \tag{6}$$

Jacobian:

$$\mathcal{J} = \frac{\partial \mathcal{R}}{\partial x} \tag{7}$$

Newton-Raphson Method:

$$\mathcal{J}\delta x = -\mathcal{R} \tag{8}$$

$$x^{k+1,i+1} = x^{k+1,i} + \delta x \tag{9}$$

Table 3: Units for residuals and Jacobian

	aqueous species	immobile species	mixed
x	mol/L	mol/m^3	
ΔV	L	m^3	L
R	mol/Ls	mol/m^{3}s	mol/Ls
$\mathcal{R}$	mol/s	mol/s	mol/s
$\mathcal{J}$	L/s	m^3/s	

1.3.2 Implementation

The source code reaction_sandbox_clm_cn.F90 implements CLM-CN with input file like the following:

```
CHEMISTRY
  ...
  IMMOBILE_SPECIES
    N
    C
    SOM1
    SOM2
    SOM3
    SOM4
    LabileC
    CelluloseC
    LigninC
    LabileN
    CelluloseN
    LigninN
  /
  ...
  REACTION_SANDBOX
    CLM-CN
      POOLS   ! CN ratio
        SOM1  12.d0
        SOM2  12.d0
        SOM3  10.d0
        SOM4  10.d0
        Labile
```

```
    Cellulose
    Lignin
  /
  REACTION
    UPSTREAM_POOL Labile
    DOWNSTREAM_POOL SOM1
    TURNOVER_TIME 20. h
    RESPIRATION_FRACTION 0.39d0
    N_INHIBITION 1.d-10
  /
  REACTION
    UPSTREAM_POOL Cellulose
    DOWNSTREAM_POOL SOM2
    TURNOVER_TIME 14. d
    RESPIRATION_FRACTION 0.55
    N_INHIBITION 1.d-10
  /
  REACTION
    UPSTREAM_POOL Lignin
    DOWNSTREAM_POOL SOM3
    TURNOVER_TIME 71. d
    RESPIRATION_FRACTION 0.29d0
    N_INHIBITION 1.d-10
  /
  REACTION
    UPSTREAM_POOL SOM1
    DOWNSTREAM_POOL SOM2
    TURNOVER_TIME 14. d
    RESPIRATION_FRACTION 0.28d0
    N_INHIBITION 1.d-10
  /
  REACTION
    UPSTREAM_POOL SOM2
    DOWNSTREAM_POOL SOM3
    TURNOVER_TIME 71. d
    RESPIRATION_FRACTION 0.46d0
    N_INHIBITION 1.d-10
  /
  REACTION
    UPSTREAM_POOL SOM3
    DOWNSTREAM_POOL SOM4
    TURNOVER_TIME 2. y
    RESPIRATION_FRACTION 0.55d0
    N_INHIBITION 1.d-10
  /
  REACTION
```

```
        UPSTREAM_POOL SOM4
        TURNOVER_TIME 27.4 y
        RESPIRATION_FRACTION 1.d0
        N_INHIBITION 1.d-10
      /
    /
  /
```

In the source code, the key is to specify the residual and Jacobian. The residuals are:

$$
\begin{aligned}
\mathcal{R}_{\mathrm{Lit1C}} &= \frac{\Delta V}{\Delta t}\left(\mathrm{Lit1C}^{k+1} - \mathrm{Lit1C}^{k}\right) + R_1^{k+1}\Delta V \\
\mathcal{R}_{\mathrm{Lit1N}} &= \frac{\Delta V}{\Delta t}\left(\mathrm{Lit1N}^{k+1} - \mathrm{Lit1N}^{k}\right) + u_1 R_1^{k+1}\Delta V \\
\mathcal{R}_{\mathrm{Lit2C}} &= \frac{\Delta V}{\Delta t}\left(\mathrm{Lit2C}^{k+1} - \mathrm{Lit2C}^{k}\right) + R_2^{k+1}\Delta V \\
\mathcal{R}_{\mathrm{Lit2N}} &= \frac{\Delta V}{\Delta t}\left(\mathrm{Lit2N}^{k+1} - \mathrm{Lit2N}^{k}\right) + u_2 R_2^{k+1}\Delta V \\
\mathcal{R}_{\mathrm{Lit3C}} &= \frac{\Delta V}{\Delta t}\left(\mathrm{Lit3C}^{k+1} - \mathrm{Lit3C}^{k}\right) + R_3^{k+1}\Delta V \\
\mathcal{R}_{\mathrm{Lit3N}} &= \frac{\Delta V}{\Delta t}\left(\mathrm{Lit3N}^{k+1} - \mathrm{Lit3N}^{k}\right) + u_3 R_3^{k+1}\Delta V \\
\mathcal{R}_{\mathrm{SOM1}} &= \frac{\Delta V}{\Delta t}\left(\mathrm{SOM1}^{k+1} - \mathrm{SOM1}^{k}\right) - \left[(1-f_1)R_1^{k+1} - R_4^{k+1}\right]\Delta V \\
\mathcal{R}_{\mathrm{SOM2}} &= \frac{\Delta V}{\Delta t}\left(\mathrm{SOM2}^{k+1} - \mathrm{SOM2}^{k}\right) - \left[(1-f_2)R_2^{k+1} + (1-f_4)R_4^{k+1} - R_5^{k+1}\right]\Delta V \\
\mathcal{R}_{\mathrm{SOM3}} &= \frac{\Delta V}{\Delta t}\left(\mathrm{SOM3}^{k+1} - \mathrm{SOM3}^{k}\right) - \left[(1-f_3)R_3^{k+1} + (1-f_5)R_5^{k+1} - R_6^{k+1}\right]\Delta V \\
\mathcal{R}_{\mathrm{SOM4}} &= \frac{\Delta V}{\Delta t}\left(\mathrm{SOM4}^{k+1} - \mathrm{SOM4}^{k}\right) - \left[(1-f_6)R_6^{k+1} - R_7^{k+1}\right]\Delta V \\
\mathcal{R}_{\mathrm{CO_2}} &= \frac{\Delta V}{\Delta t}\left(\mathrm{CO}_2^{k+1} - \mathrm{CO}_2^{k}\right) \\
&\quad - \left[f_1 R_1^{k+1} + f_2 R_2^{k+1} + f_3 R_3^{k+1} + f_4 R_4^{k+1} + f_5 R_5^{k+1} + f_6 R_6^{k+1} + R_7^{k+1}\right]\Delta V \\
\mathcal{R}_{\mathrm{N_{mineral}}} &= \frac{\Delta V}{\Delta t}\left(\mathrm{N}_{\mathrm{mineral}}^{k+1} - \mathrm{N}_{\mathrm{mineral}}^{k}\right) \\
&\quad - \left[n_1 R_1^{k+1} + n_2 R_2^{k+1} + n_3 R_3^{k+1} + n_4 R_4^{k+1} + n_5 R_5^{k+1} + n_6 R_6^{k+1} + R_7^{k+1}\right]\Delta V
\end{aligned}
$$

For Lit1 decomposition, the rate is

$$R_1 = f_T f_\Psi f_{\mathrm{N}} k_1 \mathrm{Lit1C} \tag{10}$$

the derivatives are:

$$\frac{\partial R_1}{\partial \mathrm{Lit1C}} = f_T f_\Psi f_{\mathrm{N}} k_1 = R'_{1,\mathrm{Lit1C}} \tag{11}$$

$$\frac{\partial R_1}{\partial \mathrm{N}_{\mathrm{mineral}}} = f_T f_\Psi k_1 \mathrm{Lit1C} \frac{k_N}{(k_N + \mathrm{N}_{\mathrm{mineral}})^2} = R'_{1,\mathrm{N}} \tag{12}$$

$$
\begin{aligned}
\frac{\partial R_{\text{Lit1N}}}{\partial \text{Lit1C}} &= \frac{\partial (u_1 R_1)}{\partial \text{Lit1C}} &&= R_1 \frac{\partial u_1}{\partial \text{Lit1C}} + u_1 R_{1,\text{Lit1C}} &&= -R_1 \frac{\text{Lit1N}}{\text{Lit1C}^2} + u_1 R'_{1,\text{Lit1C}} \\
\frac{\partial R_{\text{Lit1N}}}{\partial \text{Lit1N}} &= \frac{\partial (u_1 R_1)}{\partial \text{Lit1N}} &&= R_1 \frac{\partial u_1}{\partial \text{Lit1N}} &&= R_1 \frac{1}{\text{Lit1C}} \\
\frac{\partial R_{\text{Lit1N}}}{\partial \text{Nmineral}} &= \frac{\partial (u_1 R_1)}{\partial \text{Nmineral}} &&= R_1 \frac{\partial u_1}{\partial \text{Nmineral}} + u_1 R'_{1,\text{N}} &&= u_1 R'_{1,\text{N}} \\
\frac{\partial R_{\text{Nmineral}}}{\partial \text{Lit1C}} &= -\frac{\partial (n_1 R_1)}{\partial \text{Lit1C}} &&= -R_1 \frac{\partial n_1}{\partial \text{Lit1C}} - n_1 R'_{1,\text{Lit1C}} &&= R_1 \frac{\text{Lit1N}}{\text{Lit1C}^2} - n_1 R'_{1,\text{Lit1C}} \\
\frac{\partial R_{\text{Nmineral}}}{\partial \text{Lit1N}} &= -\frac{\partial (n_1 R_1)}{\partial \text{Lit1N}} &&= -R_1 \frac{\partial n_1}{\partial \text{Lit1N}} &&= -R_1 \frac{1}{\text{Lit1C}} \\
\frac{\partial R_{\text{Nmineral}}}{\partial \text{N}_{\text{mineral}}} &= -\frac{\partial (n_1 R_1)}{\partial \text{N}_{\text{mineral}}} &&= -R_1 \frac{\partial n_1}{\partial \text{N}_{\text{mineral}}} &&= -n_1 R'_{1,N}
\end{aligned}
$$

Table 4: Jacobian for Litter Pools

	LitiC	LitiN	SOMi	CO_2	$N_{mineral}$
LitiC	$R'_{\text{i,LitiC}}$	0	0	0	$R'_{i,N}$
LitiN	$-R_i \frac{\text{LitiN}}{\text{LitiC}^2} + u_i R'_{\text{i,LitiC}}$	$R_i \frac{1}{\text{LitiC}}$	0	0	$u_i R'_{i,N}$
SOMi	$-(1-f_i) R'_{\text{i,LitiC}}$	0	0	0	$-(1-f_i) R'_{i,N}$
CO_2	$-f_i R'_{\text{i,LitiC}}$	0	0	0	$-f_i R'_{i,N}$
$N_{mineral}$	$R_i \frac{\text{LitiN}}{\text{LitiC}^2} - n_i R'_{\text{i,LitiC}}$	$-R_1 \frac{1}{\text{LitiC}}$	0	0	$-n_i R'_{i,N}$

Table 5: Jacobian for SOM Pools

	SOM1	SOM2	SOM3	SOM4	CO_2	$N_{mineral}$
SOM1	R'_4	0	0	0	0	0
SOM2	$-(1-f_4)R'_4$	R'_5	0	0	0	0
SOM3	0	$-(1-f_5)R'_5$	R'_6	0	0	0
SOM4	0	0	$-(1-f_6)R'_6$	R'_7	0	0
CO_2	$-f_4 R'_4$	$-f_5 R'_5$	$-f_6 R'_6$	$-R'_7$	0	0
$N_{mineral}$	$-n_4 R'_4$	$-n_5 R'_5$	$-n_6 R'_6$	$-n_7 R'_7$	0	0

1.4 Applications

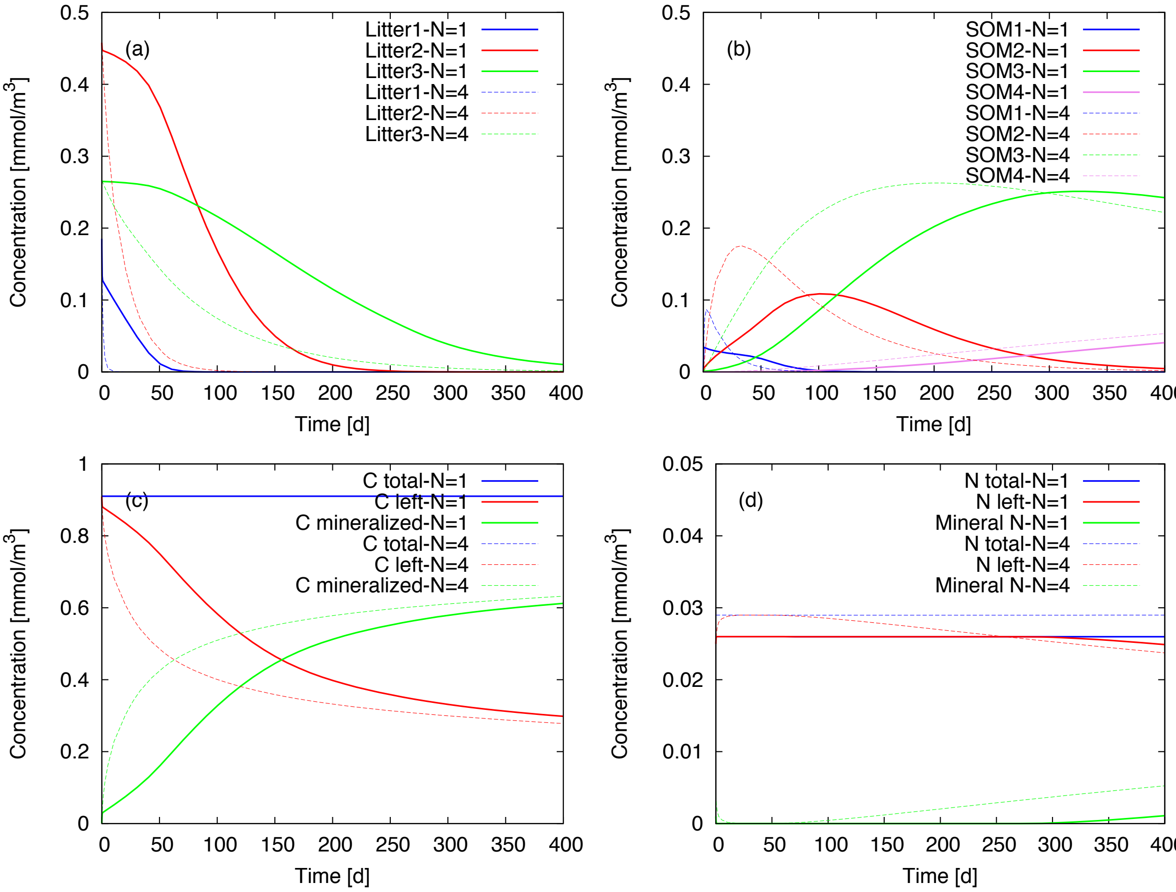

Figure 2: Demonstrating N limiting on C decomposition (initial mineral N=1 and 4 μ mol/m^3)

2 CLM4.5 CH_4 Oxidation

2.1 Reaction

$$CH_4 + 2O_2 = CO_2 + 2H_2O \tag{13}$$

2.2 Rate

$$R = k\frac{CH_4}{k_{CH4} + CH_4}\frac{O_2}{k_{O2} + O_2} f_T f_\Psi \tag{14}$$

2.3 Residuals

$$\begin{aligned}
\mathcal{R}_{CH4} &= \frac{\Delta V}{\Delta t}\left(CH_4^{k+1} - CH_4^k\right) + R^{k+1}\Delta V \\
\mathcal{R}_{O2} &= \frac{\Delta V}{\Delta t}\left(O_2^{k+1} - O_2^k\right) + 2R^{k+1}\Delta V \\
\mathcal{R}_{CO2} &= \frac{\Delta V}{\Delta t}\left(CO_2^{k+1} - CO_2^k\right) - R^{k+1}\Delta V
\end{aligned}$$

2.4 Jacobian

$$\begin{aligned}
\frac{\partial R}{\partial CH_4} &= k\frac{k_{CH4}}{(k_{CH4} + CH_4)^2}\frac{O_2}{k_{O2} + O_2} f_T f_\Psi = R'_{CH4} \\
\frac{\partial R}{\partial O_2} &= k\frac{CH_4}{k_{CH4} + CH_4}\frac{k_{O2}}{(k_{O4} + O_2)^2} f_T f_\Psi = R'_{O2}
\end{aligned}$$

Table 6: Jacobian for methane oxidation

	CH_4	O_2	CO_2
CH_4	R'_{CH4}	R'_{O2}	0
O_2	$2R'_{CH4}$	$2R'_{O2}$	0
CO_2	$-R'_{CH4}$	$-R'_{O2}$	0

2.5 Application

Input file

```
CHEMISTRY
  PRIMARY_SPECIES
    O2(aq)
    Methane(aq)
    CO2(aq)
```

```
  /
  REDOX_SPECIES
    CO2(aq)
    Methane(aq)
    O2(aq)
  /
  REACTION_SANDBOX
    CH4O
      RATE_CONSTANT 1.25d-10 ! mol/m3 s
      HALFSATURATIONCH4 5.0d-6
      HALFSATURATIONO2  2.0d-5
    /
  /
  DATABASE ../../pflotran-clm4me/database/hanford.dati
......
CONSTRAINT initial
  CONCENTRATIONS
    O2(aq)      0.001 T
    Methane(aq) 0.001 T
    CO2(aq)   1.0d-10 T
  /
END
```

Code

```
subroutine CH4OReact(this,Residual,Jacobian,compute_derivative, &
                         rt_auxvar,global_auxvar,porosity,volume,reaction, &
                         option)
  word = "Methane(aq)"
  is_ch4 = GetPrimarySpeciesIDFromName(word,reaction,option)

  word = "CO2(aq)"
  is_co2 = GetPrimarySpeciesIDFromName(word,reaction,option)

  word = "O2(aq)"
  is_o2 = GetPrimarySpeciesIDFromName(word,reaction,option)

  temp_K = global_auxvar%temp(1) + 273.15d0
  F_t = exp(308.56d0*(one_over_71_02 - 1.d0/(temp_K - 227.13d0)))

  F_theta = log(theta_min/global_auxvar%sat(1)) * one_over_log_theta_min

  L_water = porosity*global_auxvar%sat(iphase)*volume*1.d3
  c_ch4 = rt_auxvar%total(is_ch4,iphase)
  c_o2 = rt_auxvar%total(is_o2,iphase)

  rate = this%rate_constant * L_water * &  ! mole/(L sec)
```

```
    c_ch4/(this%kmch4 + c_ch4) * c_o2/(this%kmo2 + c_o2) * F_t * F_theta

  Residual(is_ch4) = Residual(is_ch4) + rate
  Residual(is_o2) = Residual(is_o2) + 2.0 * rate
  Residual(is_co2) = Residual(is_co2) - rate

  if (compute_derivative) then

    ! always add contribution to Jacobian
    ! units = (mol/sec)*(kg water/mol) = kg water/sec

    !dx/(k+x) = k/(k+x)^2

    drate_dch4 = rate * this%kmch4 / c_ch4 / (this%kmch4 + c_ch4)
    drate_do2  = rate * this%kmo2 / c_o2 / (this%kmo2 + c_o2)

    Jacobian(is_ch4,is_ch4) = Jacobian(is_ch4,is_ch4) - drate_dch4
    Jacobian(is_ch4,is_o2) = Jacobian(is_ch4,is_o2) - drate_do2
    Jacobian(is_o2,is_ch4) = Jacobian(is_o2,is_ch4) - 2.0 * drate_dch4
    Jacobian(is_o2,is_o2) = Jacobian(is_o2,is_o2) - 2.0 * drate_do2
    Jacobian(is_co2,is_ch4) = Jacobian(is_co2,is_ch4) + drate_dch4
    Jacobian(is_co2,is_o2) = Jacobian(is_co2,is_o2) + drate_do2

  endif

end subroutine CH4OReact
```

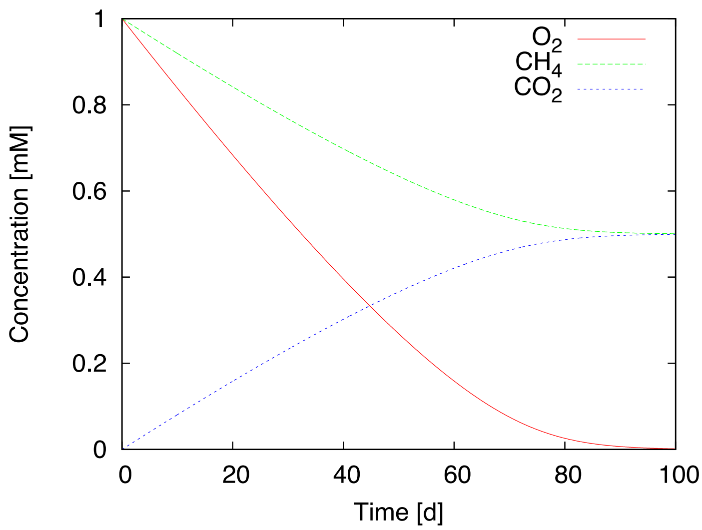

Figure 3: Example calculation for methane oxidation)

3 Acetoclastic Methanogenesis

3.1 Reaction

$$\mathrm{Ac}^- + \mathrm{H_2O} = \mathrm{CH_4} + \mathrm{HCO_3^-} \tag{15}$$

$$(1 + y/2)\mathrm{Ac}^- + 0.5y\mathrm{H}^+ + \mathrm{H_2O} = \mathrm{CH_4} + \mathrm{HCO_3^-} + y\mathrm{C_{bio}} \tag{16}$$

3.2 Rate

$$R = k\mathrm{C_{bio}}\frac{\mathrm{Ac}^-}{k_{\mathrm{Ac}} + \mathrm{Ac}^-} f_T f_\Psi \tag{17}$$

3.3 Mass Conservation

$$\begin{aligned}
\frac{\partial \mathrm{Ac}^-}{\partial t} &= -(1 + \frac{y}{2})R \\
\frac{\partial \mathrm{H}^+}{\partial t} &= -\frac{y}{2}R \\
\frac{\partial \mathrm{CH_4}}{\partial t} &= R \\
\frac{\partial \mathrm{HCO_3^-}}{\partial t} &= R \\
\frac{\partial \mathrm{C_{bio}}}{\partial t} &= 1000\theta y R
\end{aligned}$$

Note: for the last equation, PFLOTRAN accounts for the 1000θ internally.

3.4 Residuals

$$\begin{aligned}
\mathcal{R}_{\text{Ac-}} &= \frac{\Delta V}{\Delta t}\left(\mathrm{Ac}^{-k+1} - \mathrm{Ac}^{-k}\right) + (1 + y/2)R^{k+1}\Delta V \\
\mathcal{R}_{\text{CH4}} &= \frac{\Delta V}{\Delta t}\left(\mathrm{CH}_4^{k+1} - \mathrm{CH}_4^{k}\right) - R^{k+1}\Delta V \\
\mathcal{R}_{\text{Cbio}} &= \frac{\Delta V}{\Delta t}\left(\mathrm{C}_{\mathrm{bio}}^{k+1} - \mathrm{C}_{\mathrm{bio}}^{k}\right) - yR^{k+1}\Delta V \\
\mathcal{R}_{\text{HCO3-}} &= \frac{\Delta V}{\Delta t}\left(\mathrm{HCO}_3^{-k+1} - \mathrm{HCO}_3^{-k}\right) - R^{k+1}\Delta V \\
\mathcal{R}_{\text{H+}} &= \frac{\Delta V}{\Delta t}\left(\mathrm{H}^{+k+1} - \mathrm{H}^{+k}\right) + y/2R^{k+1}\Delta V
\end{aligned}$$

3.5 Jacobian

$$\frac{\partial R}{\partial \mathrm{Ac}} = k\mathrm{C_{bio}}\frac{k_{\mathrm{Ac}}}{(k_{\mathrm{Ac}} + \mathrm{Ac}^-)^2} f_T f_\Psi = R'_a$$
$$\frac{\partial R}{\partial \mathrm{C_{bio}}} = k\frac{\mathrm{Ac}^-}{k_{\mathrm{Ac}} + \mathrm{Ac}^-} f_T f_\Psi = R'_b$$

Table 7: Jacobian for methane oxidation

	Ac^-	$\mathrm{CH_4}$	$\mathrm{C_{bio}}$	$\mathrm{HCO_3^-}$	$\mathrm{H^+}$
Ac^-	$(1+y/2)R'_a$	0	$(1+y/2)R'_b$	0	0
$\mathrm{CH_4}$	$-R'_a$	0	$-R'_b$	0	0
$\mathrm{C_{bio}}$	$-yR'_a$	0	$-yR'_b$	0	0
$\mathrm{HCO_3^-}$	$-R'_a$	0	$-R'_b$	0	0
$\mathrm{H^+}$	$0.5yR'_a$	0	$0.5yR'_b$	0	0

3.6 Application

Input

```
CHEMISTRY
  PRIMARY_SPECIES
    Acetate-
    Methane(aq)
    H+
    HCO3-
  /
  SECONDARY_SPECIES
    OH-
    CO3--
    CO2(aq)
:     Acetic_acid(aq)
  /
  REDOX_SPECIES
    Acetate-
    Methane(aq)
  /
  IMMOBILE_SPECIES
    Acemeg
  /
  REACTION_SANDBOX
     AceMeg
      RATE_CONSTANT      1.0d-6
      HALFSATURATIONAC   1.0d-5
```

```
      YIELDCOEFFICIENT   0.02
     /
  /
  DATABASE ../../pflotran-clm4me/database/hanford.dat
/end{verbatim}

\noindent Code
\begin{verbatim}
  L_water = porosity*global_auxvar%sat(iphase)*volume*1.d3
  c_ac = rt_auxvar%pri_molal(this%is_ac)
  c_bio = rt_auxvar%immobile(this%ispec_id_cbio)

  rate = this%rate_constant * L_water * &
    c_bio * c_ac/(this%kmac + c_ac) * F_t * F_theta

  ! alway subtract contribution from residual (mole/sec)
  Residual(this%is_ac) = Residual(this%is_ac) + (1.0 + 0.5 * this%yield) * rate
  Residual(this%is_ch4) = Residual(this%is_ch4) - rate
  Residual(this%is_cbio) = Residual(this%is_cbio) - this%yield * rate
  Residual(this%is_hco3) = Residual(this%is_hco3) - rate
  Residual(this%is_h) = Residual(this%is_h) + 0.5 * this%yield * rate

  if (compute_derivative) then

! 11. If using an analytical Jacobian, add code for Jacobian evaluation

    ! always add contribution to Jacobian
    ! units = (mol/sec)*(kg water/mol) = kg water/sec

    drate_dac = rate * this%kmac / c_ac / (this%kmac + c_ac)
    drate_dcb = rate / c_bio

    Jacobian(this%is_ac,  this%is_ac)   = Jacobian(this%is_ac,this%is_ac)   &
                                        - (1.0 + 0.5 * this%yield) * drate_dac
    Jacobian(this%is_ch4, this%is_ac)   = Jacobian(this%is_ch4,this%is_ac)  &
                                        + drate_dac
    Jacobian(this%is_cbio,this%is_ac)   = Jacobian(this%is_cbio,this%is_ac) &
                                        + this%yield * drate_dac
    Jacobian(this%is_hco3,this%is_ac)   = Jacobian(this%is_hco3,this%is_ac) &
                                        + 0.5 * this%yield * drate_dac
    Jacobian(this%is_ac,  this%is_cbio) = Jacobian(this%is_ac,this%is_cbio) &
                                        - (1.0 + 0.5 * this%yield) * drate_dcb
    Jacobian(this%is_ch4, this%is_cbio) = Jacobian(this%is_ch4,this%is_cbio) &
                                        + drate_dcb
    Jacobian(this%is_cbio,this%is_cbio) = Jacobian(this%is_cbio,this%is_cbio) &
                                        + this%yield * drate_dcb
```

```
  Jacobian(this%is_hco3,this%is_cbio) = Jacobian(this%is_hco3,this%is_cbio) &
                                         + 0.5 * this%yield * drate_dcb

endif
```

For $k_{Ac} = 0$,

$$\frac{\partial \mathrm{Ac}}{\partial t} = -(1 + 0.5y)k\mathrm{C_{bio}}$$
$$\frac{\partial \mathrm{C_{bio}}}{\partial t} = 1000\theta yk\mathrm{C_{bio}}$$

$$\mathrm{C_{bio}} = \mathrm{C_{bio,0}EXP}(1000\theta ykt)$$
$$\mathrm{Ac} = \mathrm{Ac_0} - \frac{1 + 0.5y}{1000\theta y}\mathrm{C_{bio,0}EXP}(1000\theta ykt)$$

This analytical solution is used in the following figure to check the numerical solution. Note $\mathrm{C_{bio}}$ is supposed to stop increasing when acetate is exhausted.

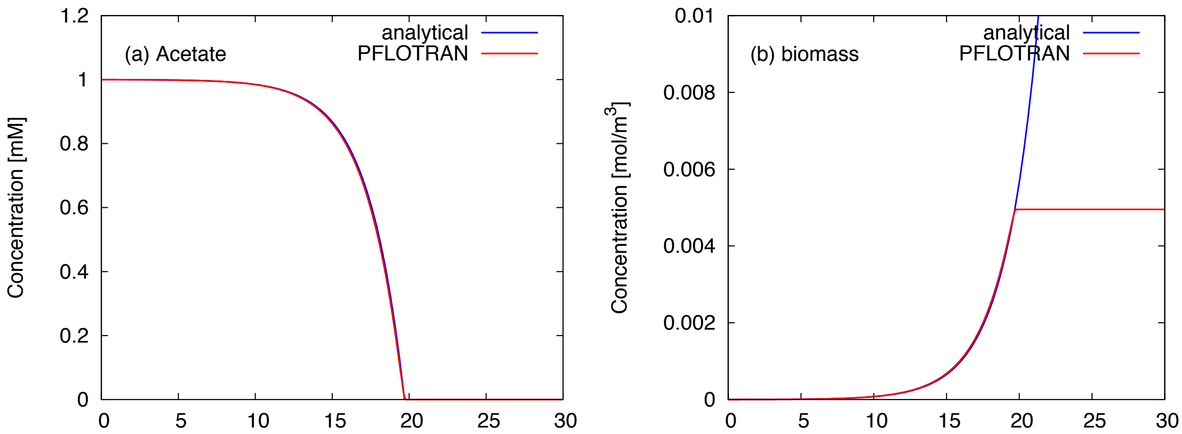

Figure 4: Example calculation for acetoclastic methanogenesis:

4 Generalization

If we implement a number of general reactions and rate formulae in PFLOTRAN, we can add as many specific reactions with specific parameter values in the input file. By doing this, we do not have to change the source code or develop a new reaction_sandbox. For example, if we consider decomposition of LabileC as a first order decay to produce acetate and H_2, which are used by methanogens to produce methane using the following reactions:

LabileC $= \frac{1}{3}$ Acetate$^-$ $+ \frac{1}{3}$ HCO_3^- $+ \frac{1}{9}$ H_2 $+ \frac{2}{3}$ H^+

Acetate$^-$ $+ H_2O =$ Methane $+ HCO_3^-$

$H_2 + \frac{1}{4}$ HCO_3^- $+ \frac{1}{4}$ $H^+ = \frac{1}{4}$ Methane $+ \frac{3}{4}$ H_2O

We can use the GENERAL_REACTION and MICROBIAL_REACTION functions in PFLOTRAN to specify the reactions and parameter values as follow:

```
CHEMISTRY
  PRIMARY_SPECIES
    A(aq)
    Acetate-
    H2(aq)
    H+
    HCO3-
    Methane(aq)
    Na+
  /
  SECONDARY_SPECIES
    OH-
    CO3--
    CO2(aq)
:     Acetic_acid(aq)
  /
  REDOX_SPECIES
    Acetate-
    Methane(aq)
    H2(aq)
    H+
  /
  IMMOBILE_SPECIES
    Acmeg
    H2meg
  /

  GENERAL_REACTION
    REACTION A(aq) <-> 0.3333 Acetate- + 0.3333 HCO3- + 0.1111 H2(aq) + 0.6666 H+
    FORWARD_RATE 1.3889d-5  ! 1/s
    BACKWARD_RATE 0.d0
  /
```

```
  MICROBIAL_REACTION
    REACTION Acetate- + H2O <-> Methane(aq) + HCO3-
    RATE_CONSTANT     1.0d-6
    MONOD Acetate-    1.0d-5
    BIOMASS           Acmeg 0.01
  /

  MICROBIAL_REACTION
    REACTION H2(aq) + 0.25 HCO3- + 0.25 H+ <-> 0.25 Methane(aq) + 0.75 H2O
    RATE_CONSTANT     1.0d-5
    MONOD H2(aq)      1.0d-7
    BIOMASS           H2meg 0.02
  /

  DATABASE ../../pflotran-clm4me/database/hanford.dat
```

With initial conditions as follow,

```
CONSTRAINT initial
  CONCENTRATIONS
    A(aq)          0.001 T
    Acetate-     1.0d-10 T
    H2(aq)       1.0d-10 T
    H+               7.0 pH
    HCO3-         5.0d-3 T
    Methane(aq)  1.0d-10 T
    Na+           5.0d-3 Z
  /
  IMMOBILE
    Acmeg        1.0d-5
    H2meg         1.0d-7
  /
END
```

PFLOTRAN will give results like in the following figure. The point is that we can add many reactions in the input file.

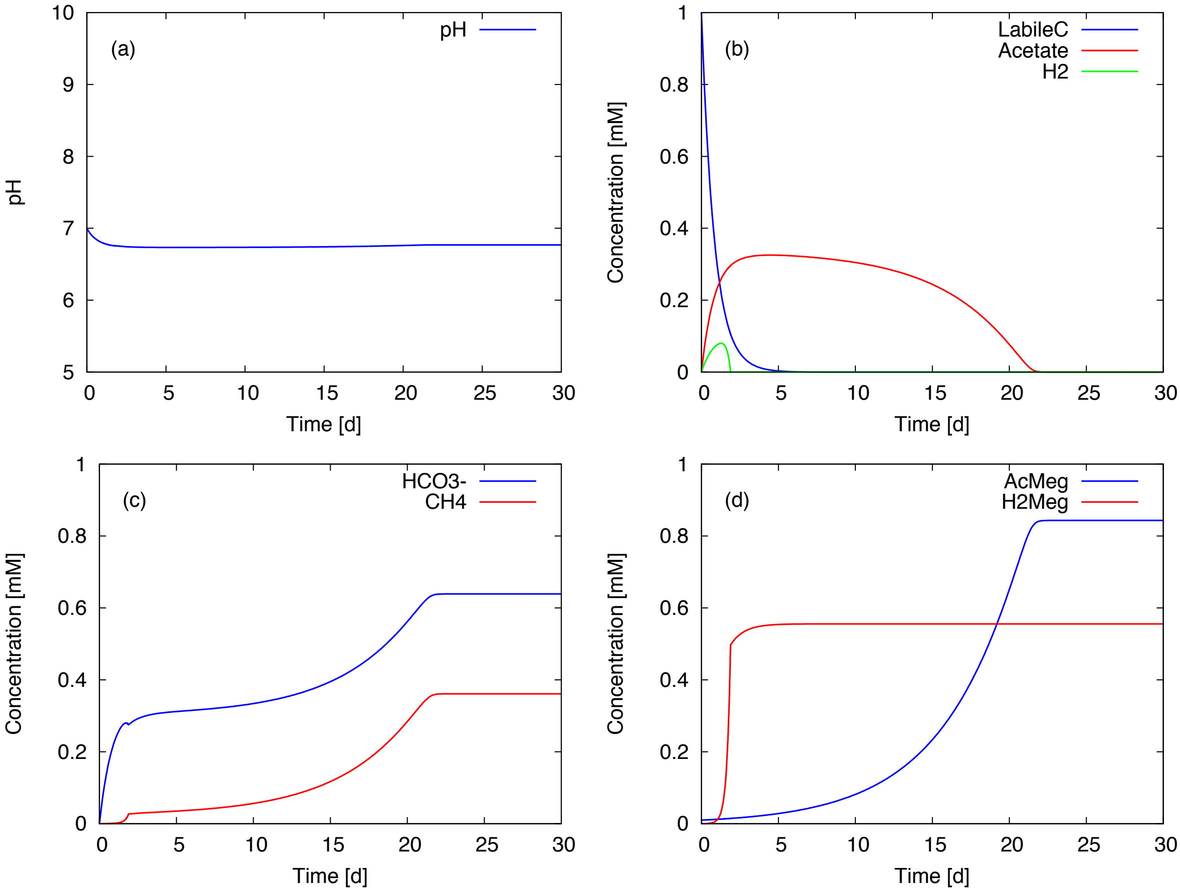

Figure 5: Example calculation for multiple microbial reactions