Implementation of CLM Below-Ground Biogeochemistry in PFLOTRAN

July 31, 2013

Abstract
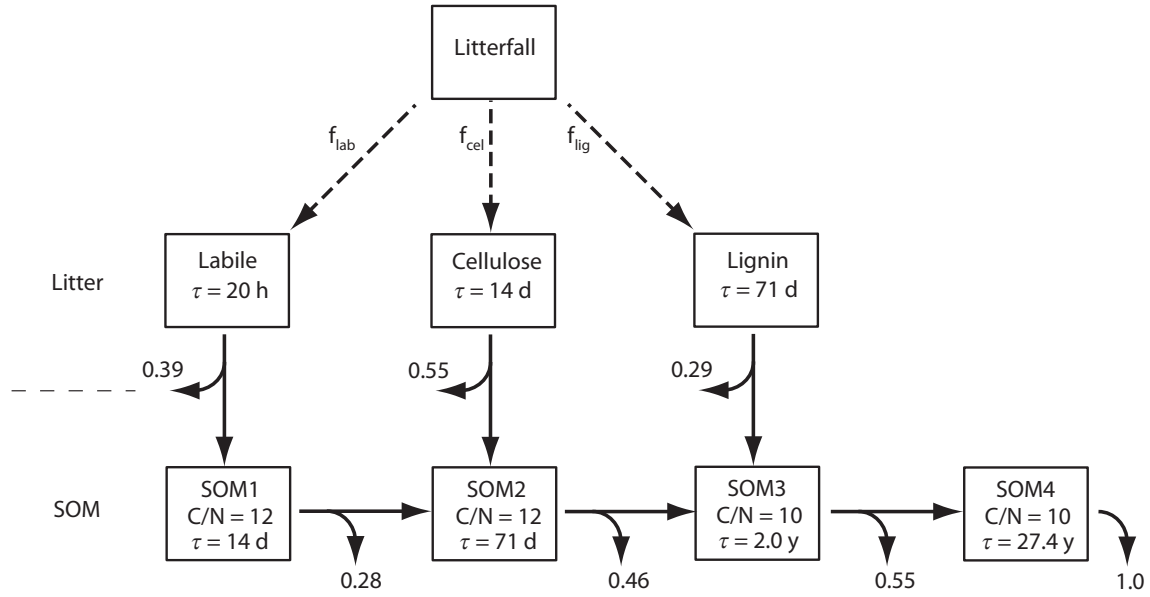
1 CLM-CN

1.1 Reactions

Figure 1: CLM-CN litter and soil organic pools and C and N flows Bonan et al. [2012]

1.1.1 General Reaction

The general decomposition reaction is

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

$$
\begin{aligned}
\mathrm{CN}_u &= \text{upstream pool } [\mathrm{mol/m^3}] \\
\mathrm{CN}_d &= \text{downstream pool } [\mathrm{mol/m^3}] \\
\mathrm{CO_2} &= [\mathrm{mol/m^3}] \\
\mathrm{N_{mineral}} &= \text{mineral nitrogen } [\mathrm{mol/m^3}] \\
u &= \text{molecular weight ratio of C and N divided by upstream pool C/N } [\text{-}] \\
d &= \text{molecular weight ratio of C and N divided by downstream pool C/N } [\text{-}] \\
f &= \text{respiration fraction } [\text{-}] \\
n &= [u - (1-f)d]
\end{aligned}
$$

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 Adair et al. [2008], 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 Adair et al. [2008]. 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

$$\text{Lit1C} + u_1\text{Lit1N} = (1 - f_1)\,\text{SOM1} + f_1\text{CO}_2 + n_1\text{N}_{\text{mineral}}$$
$$\text{Lit2C} + u_2\text{Lit2N} = (1 - f_2)\,\text{SOM2} + f_2\text{CO}_2 + n_2\text{N}_{\text{mineral}}$$
$$\text{Lit3C} + u_3\text{Lit3N} = (1 - f_3)\,\text{SOM3} + f_3\text{CO}_2 + n_3\text{N}_{\text{mineral}}$$
$$\text{SOM1} = (1 - f_4)\,\text{SOM2} + f_4\text{CO}_2 + n_4\text{N}_{\text{mineral}}$$
$$\text{SOM2} = (1 - f_5)\,\text{SOM3} + f_5\text{CO}_2 + n_5\text{N}_{\text{mineral}}$$
$$\text{SOM3} = (1 - f_6)\,\text{SOM4} + f_6\text{CO}_2 + n_6\text{N}_{\text{mineral}}$$
$$\text{SOM4} = f_7\text{CO}_2 + n_7\text{N}_{\text{mineral}}$$

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

1.2 Rate

1.2.1 General

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

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

For the general reaction 1,

$$\frac{\partial \mathrm{CN}_u}{\partial t} = -R$$

$$\frac{\partial \mathrm{CN}_d}{\partial t} = (1 - f) R$$

$$\frac{\partial \mathrm{CO}_2}{\partial t} = fR$$

$$\frac{\partial \mathrm{N_{mineral}}}{\partial t} = nR$$

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

$$\frac{\partial}{\partial t}\left(\text{Lit1C}\right) = -R_1$$

$$\frac{\partial}{\partial t}\left(\text{Lit1N}\right) = -u_1 R_1$$

$$\frac{\partial}{\partial t}\left(\text{Lit2C}\right) = -R_2$$

$$\frac{\partial}{\partial t}\left(\text{Lit3N}\right) = -u_2 R_2$$

$$\frac{\partial}{\partial t}\left(\text{Lit3C}\right) = -R_3$$

$$\frac{\partial}{\partial t}\left(\text{Lit3N}\right) = -u_3 R_3$$

$$\frac{\partial}{\partial t}\left(\text{SOM1}\right) = (1 - f_1)R_1 - R_4$$

$$\frac{\partial}{\partial t}\left(\text{SOM2}\right) = (1 - f_2)R_2 + (1 - f_4)R_4 - R_5$$

$$\frac{\partial}{\partial t}\left(\text{SOM3}\right) = (1 - f_3)R_3 + (1 - f_5)R_5 - R_6$$

$$\frac{\partial}{\partial t}\left(\text{SOM4}\right) = (1 - f_6)R_6 - R_7$$

$$\frac{\partial}{\partial t}\left(\text{CO}_2\right) = f_1 R_1 + f_2 R_2 + f_3 R_3 + f_4 R_4 + f_5 R_5 + f_6 R_6 + f_7 R_7$$

$$\frac{\partial}{\partial t}\left(\text{N}_{\text{mineral}}\right) = n_1 R_1 + n_2 R_2 + n_3 R_3 + n_4 R_4 + n_5 R_5 + n_6 R_6 + n_7 R_7$$

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:

$$\mathcal{R}_{\text{Lit1C}} = \frac{\Delta V}{\Delta t} \left(\text{Lit1C}^{k+1} - \text{Lit1C}^k \right) + R_1^{k+1} \Delta V$$

$$\mathcal{R}_{\text{Lit1N}} = \frac{\Delta V}{\Delta t} \left(\text{Lit1N}^{k+1} - \text{Lit1N}^k \right) + u_1 R_1^{k+1} \Delta V$$

$$\mathcal{R}_{\text{Lit2C}} = \frac{\Delta V}{\Delta t} \left(\text{Lit2C}^{k+1} - \text{Lit2C}^k \right) + R_2^{k+1} \Delta V$$

$$\mathcal{R}_{\text{Lit2N}} = \frac{\Delta V}{\Delta t} \left(\text{Lit2N}^{k+1} - \text{Lit2N}^k \right) + u_2 R_2^{k+1} \Delta V$$

$$\mathcal{R}_{\text{Lit3C}} = \frac{\Delta V}{\Delta t} \left(\text{Lit3C}^{k+1} - \text{Lit3C}^k \right) + R_3^{k+1} \Delta V$$

$$\mathcal{R}_{\text{Lit3N}} = \frac{\Delta V}{\Delta t} \left(\text{Lit3N}^{k+1} - \text{Lit3N}^k \right) + u_3 R_3^{k+1} \Delta V$$

$$\mathcal{R}_{\text{SOM1}} = \frac{\Delta V}{\Delta t} \left(\text{SOM1}^{k+1} - \text{SOM1}^k \right) - \left[(1 - f_1) R_1^{k+1} - R_4^{k+1} \right] \Delta V$$

$$\mathcal{R}_{\text{SOM2}} = \frac{\Delta V}{\Delta t} \left(\text{SOM2}^{k+1} - \text{SOM2}^k \right) - \left[(1 - f_2) R_2^{k+1} + (1 - f_4) R_4^{k+1} - R_5^{k+1} \right] \Delta V$$

$$\mathcal{R}_{\text{SOM3}} = \frac{\Delta V}{\Delta t} \left(\text{SOM3}^{k+1} - \text{SOM3}^k \right) - \left[(1 - f_3) R_3^{k+1} + (1 - f_5) R_5^{k+1} - R_6^{k+1} \right] \Delta V$$

$$\mathcal{R}_{\text{SOM4}} = \frac{\Delta V}{\Delta t} \left(\text{SOM4}^{k+1} - \text{SOM4}^k \right) - \left[(1 - f_6) R_6^{k+1} - R_7^{k+1} \right] \Delta V$$

$$\mathcal{R}_{\text{CO}_2} = \frac{\Delta V}{\Delta t} \left(\text{CO}_2^{k+1} - \text{CO}_2^k \right)$$
$$- \left[f_1 R_1^{k+1} + f_2 R_2^{k+1} + f_3 R_3^{k+1} + f_4 R_4^{k+1} + f_5 R_5^{k+1} + f_6 R_6^{k+1} + R_7^{k+1} \right] \Delta V$$

$$\mathcal{R}_{\text{N}_{\text{mineral}}} = \frac{\Delta V}{\Delta t} \left(\text{N}_{\text{mineral}}^{k+1} - \text{N}_{\text{mineral}}^k \right)$$
$$- \left[n_1 R_1^{k+1} + n_2 R_2^{k+1} + n_3 R_3^{k+1} + n_4 R_4^{k+1} + n_5 R_5^{k+1} + n_6 R_6^{k+1} + R_7^{k+1} \right] \Delta V$$

For Lit1 decomposition, the rate is

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

the derivatives are:

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

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

$$\frac{\partial R_{\text{Lit1N}}}{\partial \text{Lit1C}} = \frac{\partial(u_1 R_1)}{\partial \text{Lit1C}} = R_1 \frac{\partial u_1}{\partial \text{Lit1C}} + u_1 R_{1,\text{Lit1C}} = -R_1 \frac{\text{Lit1N}}{\text{Lit1C}^2} + u_1 R'_{1,\text{Lit1C}}$$

$$\frac{\partial R_{\text{Lit1N}}}{\partial \text{Lit1N}} = \frac{\partial(u_1 R_1)}{\partial \text{Lit1N}} = R_1 \frac{\partial u_1}{\partial \text{Lit1N}} = R_1 \frac{1}{\text{Lit1C}}$$

$$\frac{\partial R_{\text{Lit1N}}}{\partial \text{Nmineral}} = \frac{\partial(u_1 R_1)}{\partial \text{Nmineral}} = R_1 \frac{\partial u_1}{\partial \text{Nmineral}} + u_1 R'_{1,\text{N}} = u_1 R'_{1,\text{N}}$$

$$\frac{\partial R_{\text{Nmineral}}}{\partial \text{Lit1C}} = -\frac{\partial(n_1 R_1)}{\partial \text{Lit1C}} = -R_1 \frac{\partial n_1}{\partial \text{Lit1C}} - n_1 R'_{1,\text{Lit1C}} = R_1 \frac{\text{Lit1N}}{\text{Lit1C}^2} - n_1 R'_{1,\text{Lit1C}}$$

$$\frac{\partial R_{\text{Nmineral}}}{\partial \text{Lit1N}} = -\frac{\partial(n_1 R_1)}{\partial \text{Lit1N}} = -R_1 \frac{\partial n_1}{\partial \text{Lit1N}} = -R_1 \frac{1}{\text{Lit1C}}$$

$$\frac{\partial R_{\text{Nmineral}}}{\partial \text{Nmineral}} = -\frac{\partial(n_1 R_1)}{\partial \text{Nmineral}} = -R_1 \frac{\partial n_1}{\partial \text{Nmineral}} = -n_1 R'_{1,N}$$

Table 4: Jacobian for Litter Pools

	LitiC	LitiN	SOMi	CO_2	N_{mineral}
LitiC	$R'_{i,\text{LitiC}}$	0	0	0	$R'_{i,N}$
LitiN	$-R_i \frac{\text{LitiN}}{\text{LitiC}^2} + u_i R'_{i,\text{LitiC}}$	$R_i \frac{1}{\text{LitiC}}$	0	0	$u_i R'_{i,N}$
SOMi	$-(1-f_i) R'_{i,\text{LitiC}}$	0	0	0	$-(1-f_i) R'_{i,N}$
CO_2	$-f_i R'_{i,\text{LitiC}}$	0	0	0	$-f_i R'_{i,N}$
N_{mineral}	$R_i \frac{\text{LitiN}}{\text{LitiC}^2} - n_i R'_{i,\text{LitiC}}$	$-R_1 \frac{1}{\text{LitiC}}$	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
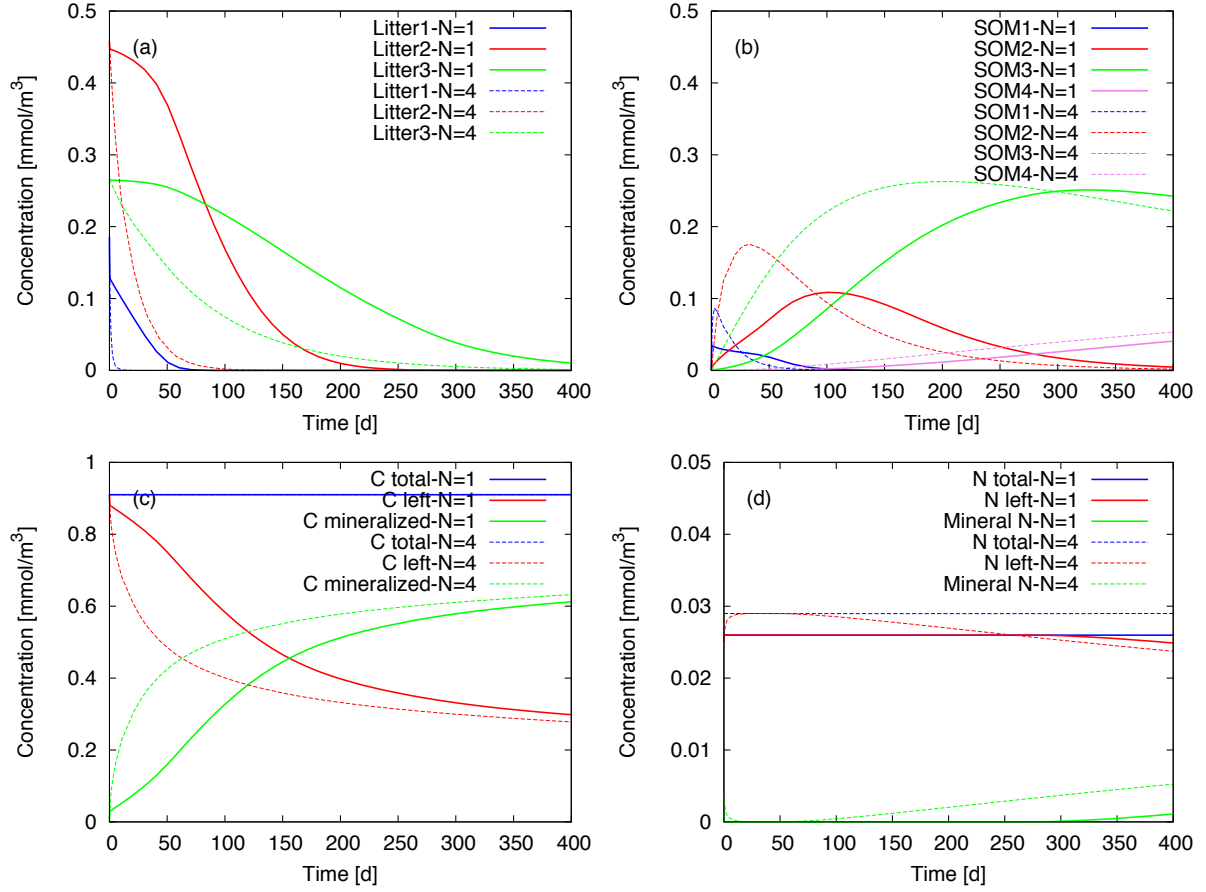
Figure 2: Demonstrating N limiting on C decomposition (initial mineral N=1 and 4 μ mol/m^3)

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

$$\mathcal{R}_{CH4} = \frac{\Delta V}{\Delta t}\left(CH_4^{k+1} - CH_4^k\right) + R^{k+1}\Delta V$$

$$\mathcal{R}_{O2} = \frac{\Delta V}{\Delta t}\left(O_2^{k+1} - O_2^k\right) + 2R^{k+1}\Delta V$$

$$\mathcal{R}_{CO2} = \frac{\Delta V}{\Delta t}\left(CO_2^{k+1} - CO_2^k\right) - R^{k+1}\Delta V$$

2.4   Jacobian

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

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

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
```
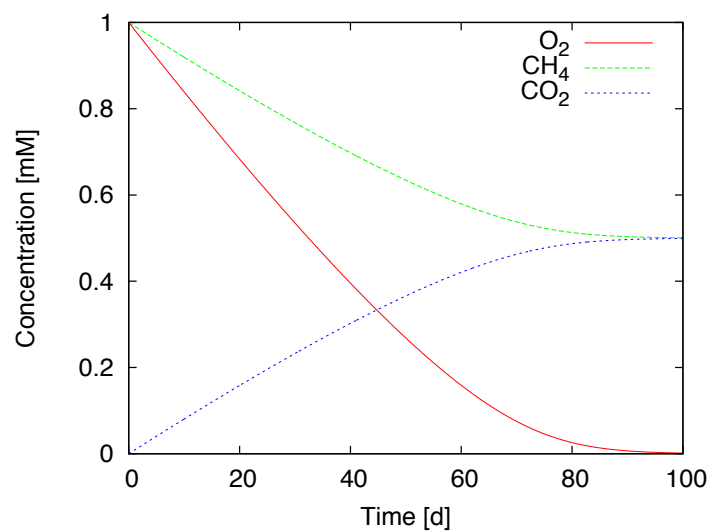

Figure 3: Example calculation for methane oxidation)

3 Acetoclastic Methanogenesis

3.1 Reaction

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

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

3.2 Rate

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

3.3 Mass Conservation

$$\frac{\partial Ac^-}{\partial t} = -(1 + \frac{y}{2})R$$

$$\frac{\partial H^+}{\partial t} = -\frac{y}{2}R$$

$$\frac{\partial CH_4}{\partial t} = R$$

$$\frac{\partial HCO_3^-}{\partial t} = R$$

$$\frac{\partial C_{bio}}{\partial t} = 1000\theta y R$$

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

3.4 Residuals

$$\mathcal{R}_{Ac^-} = \frac{\Delta V}{\Delta t}\left(Ac^{-k+1} - Ac^{-k}\right) + (1 + y/2)R^{k+1}\Delta V$$

$$\mathcal{R}_{CH4} = \frac{\Delta V}{\Delta t}\left(CH_4^{k+1} - CH_4^k\right) - R^{k+1}\Delta V$$

$$\mathcal{R}_{Cbio} = \frac{\Delta V}{\Delta t}\left(C_{bio}^{k+1} - C_{bio}^k\right) - yR^{k+1}\Delta V$$

$$\mathcal{R}_{HCO3^-} = \frac{\Delta V}{\Delta t}\left(HCO_3^{-k+1} - HCO_3^{-k}\right) - R^{k+1}\Delta V$$

$$\mathcal{R}_{H^+} = \frac{\Delta V}{\Delta t}\left(H^{+k+1} - H^{+k}\right) + y/2R^{k+1}\Delta V$$

3.5 Jacobian

$$\frac{\partial R}{\partial \text{Ac}} = k\text{C}_{\text{bio}}\frac{k_{\text{Ac}}}{(k_{\text{Ac}} + \text{Ac}^-)^2}f_T f_\Psi = R'_a$$

$$\frac{\partial R}{\partial \text{C}_{\text{bio}}} = k\frac{\text{Ac}^-}{k_{\text{Ac}} + \text{Ac}^-}f_T f_\Psi = R'_b$$

Table 7: Jacobian for methane oxidation

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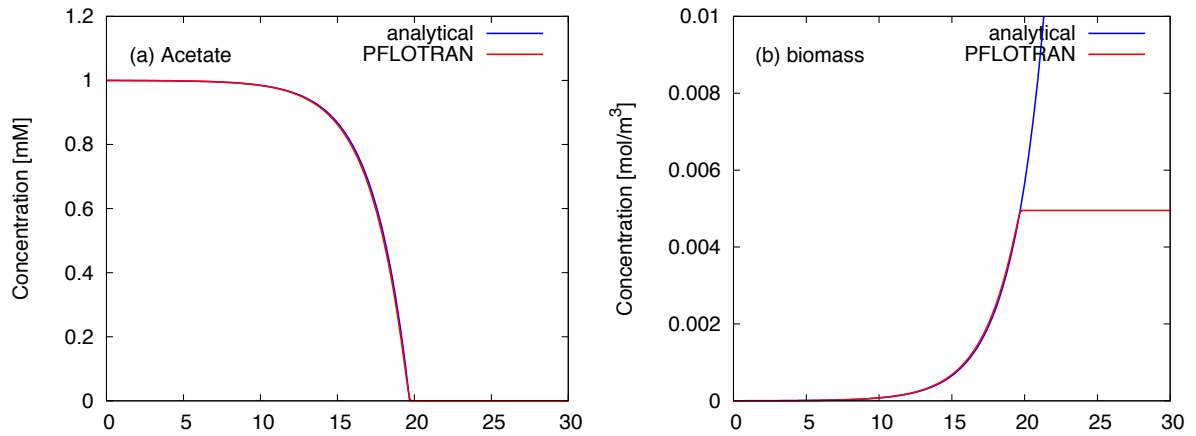

Figure 4: Example calculation for acetoclastic methanogenesis:

References

E. Carol Adair, William J. Parton, Steven J. del Grosso, Whendee L. Silver, Mark E. Harmon, Sonia A. Hall, Ingrid C. Burke, and Stephen C. Hart. Simple three-pool model accurately describes patterns of long-term litter decomposition in diverse climates. *Global Change Biology*, 14(11):2636–2660, 2008. ISSN 1365-2486. doi: 10.1111/j.1365-2486.2008.01674.x. URL `http://dx.doi.org/10.1111/j.1365-2486.2008.01674.x`.

Gordon B. Bonan, Melannie D. Hartman, William J. Parton, and William R. Wieder. Evaluating litter decomposition in earth system models with long-term litterbag experiments: an example using the community land model version 4 (clm4). *Global Change Biology*, pages n/a–n/a, 2012. ISSN 1365-2486. doi: 10.1111/gcb.12031. URL `http://dx.doi.org/10.1111/gcb.12031`.