

# Implementation of CLM Below-Ground Biogeochemistry in PFLOTRAN

August 27, 2013

## Abstract

## 1 CLM-CN

### 1.1 Reactions

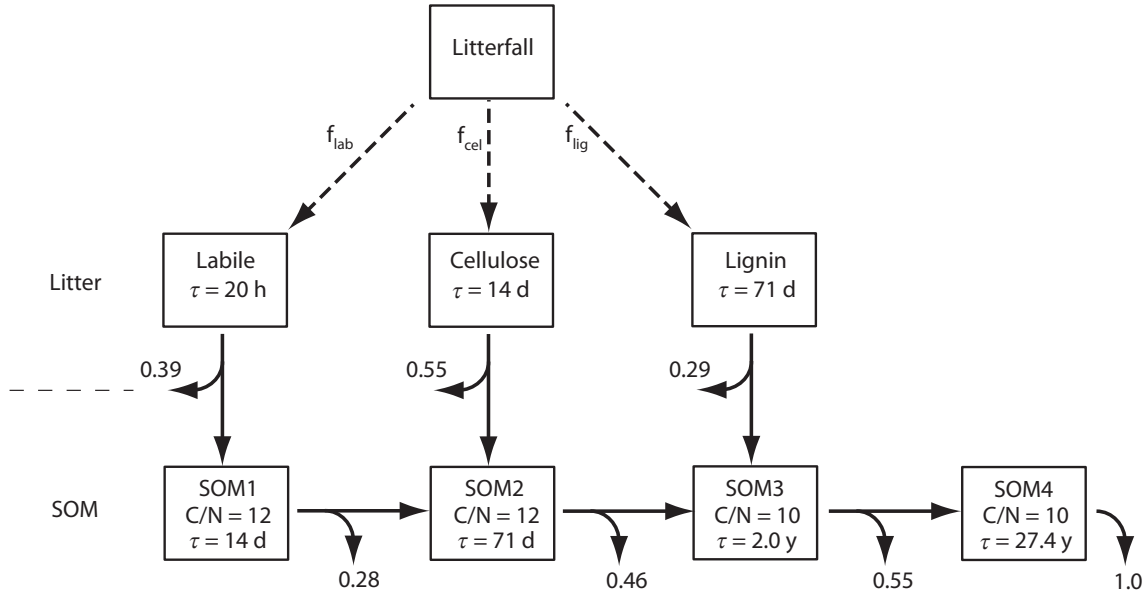


Figure 1: CLM-CN litter and soil organic pools and C and N flows Bonan et al. [2012]

#### 1.1.1 General Reaction

The general decomposition reaction is

$$CN_u = (1 - f)CN_d + fCO_2 + nN_{\text{mineral}} \quad (1)$$

$CN_u$	=	upstream pool [mol/m <sup>3</sup> ]
$CN_d$	=	downstream pool [mol/m <sup>3</sup> ]
$CO_2$	=	[mol/m <sup>3</sup> ]
$N_{\text{mineral}}$	=	mineral nitrogen [mol/m <sup>3</sup> ]
$u$	=	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

SOM1	=	0.72 SOM2 + 0.28 CO <sub>2</sub> + 0.020000 N <sub>mineral</sub>
SOM2	=	0.54 SOM3 + 0.46 CO <sub>2</sub> + 0.025143 N <sub>mineral</sub>
SOM3	=	0.45 SOM4 + 0.55 CO <sub>2</sub> + 0.047143 N <sub>mineral</sub>
SOM4	=	CO <sub>2</sub> + 0.085714 N <sub>mineral</sub>

### 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

Lit1C + 0.027481 Lit1N + 0.016090 N <sub>mineral</sub>	=	0.61 SOM1 + 0.39 CO <sub>2</sub>
Lit2C + 0.027481 Lit2N + 0.004662 N <sub>mineral</sub>	=	0.45 SOM2 + 0.55 CO <sub>2</sub>
Lit3C + 0.027481 Lit3N + 0.033376 N <sub>mineral</sub>	=	0.71 SOM3 + 0.29 CO <sub>2</sub>

### 1.1.4 Summary

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

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

## 1.2 Rate

### 1.2.1 General

$$R = f_T f_\Psi f_N k \text{CN}_u \quad (2)$$

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

For the general reaction 1,

$$\begin{aligned}\frac{\partial \text{CN}_u}{\partial t} &= -R \\ \frac{\partial \text{CN}_d}{\partial t} &= (1 - f) R \\ \frac{\partial \text{CO}_2}{\partial t} &= fR \\ \frac{\partial \text{N}_{\text{mineral}}}{\partial t} &= nR\end{aligned}$$

### 1.2.2 Rates

$$\begin{aligned}R_1 &= f_T f_\theta f_N k_1 \text{Lit1C} \\ R_2 &= f_T f_\theta f_N k_2 \text{Lit2C} \\ R_3 &= f_T f_\theta f_N k_3 \text{Lit3C} \\ R_4 &= f_T f_\theta f_N k_4 \text{SOM1} \\ R_5 &= f_T f_\theta f_N k_5 \text{SOM2} \\ R_6 &= f_T f_\theta f_N k_6 \text{SOM3} \\ R_7 &= f_T f_\theta f_N k_7 \text{SOM4}\end{aligned}$$

### 1.2.3 Mass Conservation

$$\begin{aligned}
\frac{\partial}{\partial t} (\text{Lit1C}) &= -R_1 \\
\frac{\partial}{\partial t} (\text{Lit1N}) &= -u_1 R_1 \\
\frac{\partial}{\partial t} (\text{Lit2C}) &= -R_2 \\
\frac{\partial}{\partial t} (\text{Lit3N}) &= -u_2 R_2 \\
\frac{\partial}{\partial t} (\text{Lit3C}) &= -R_3 \\
\frac{\partial}{\partial t} (\text{Lit3N}) &= -u_3 R_3 \\
\frac{\partial}{\partial t} (\text{SOM1}) &= (1 - f_1) R_1 - R_4 \\
\frac{\partial}{\partial t} (\text{SOM2}) &= (1 - f_2) R_2 + (1 - f_4) R_4 - R_5 \\
\frac{\partial}{\partial t} (\text{SOM3}) &= (1 - f_3) R_3 + (1 - f_5) R_5 - R_6 \\
\frac{\partial}{\partial t} (\text{SOM4}) &= (1 - f_6) R_6 - R_7 \\
\frac{\partial}{\partial t} (\text{CO}_2) &= f_1 R_1 + f_2 R_2 + f_3 R_3 + f_4 R_4 + f_5 R_5 + f_6 R_6 + f_7 R_7 \\
\frac{\partial}{\partial t} (\text{N}_{\text{mineral}}) &= n_1 R_1 + n_2 R_2 + n_3 R_3 + n_4 R_4 + n_5 R_5 + n_6 R_6 + n_7 R_7
\end{aligned}$$

## 1.3 Implementation in PFLOTTRAN

### 1.3.1 Numerical Methods

Applying finite-volume spatial discretization:

$$\int \frac{\partial x}{\partial t} dV = \int - \sum R_j dV \quad (3)$$

$$\frac{\partial x}{\partial t} \Delta V = - \sum R_j \Delta V \quad (4)$$

Implicit time discretization:

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

Residual:

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

Jacobian:

$$\mathcal{J} = \frac{\partial \mathcal{R}}{\partial x} \quad (7)$$

Newton-Raphson Method:

$$\mathcal{J}\delta x = -\mathcal{R} \quad (8)$$

$$x^{k+1,i+1} = x^{k+1,i} + \delta x \quad (9)$$

Table 3: Units for residuals and Jacobian

	aqueous species	immobile species	mixed
$x$	mol/L	mol/m <sup>3</sup>	
$\Delta V$	L	m <sup>3</sup>	L
$R$	mol/Ls	mol/m <sup>3</sup> s	mol/Ls
$\mathcal{R}$	mol/s	mol/s	mol/s
$\mathcal{J}$	L/s	m <sup>3</sup> /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:

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

For Lit1 decomposition, the rate is

$$R_1 = f_T f_\Psi f_N k_1 \text{Lit1C} \quad (10)$$

the derivatives are:

$$\frac{\partial R_1}{\partial \text{Lit1C}} = f_T f_\Psi f_N k_1 = R'_{1, \text{Lit1C}} \quad (11)$$

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



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

Table 4: Jacobian for Litter Pools

	LitiC	LitiN	SOMi	CO <sub>2</sub>	N <sub>mineral</sub>
LitiC	$R'_{i,\text{LitiC}}$	0	0	0	$R'_{i,N}$
LitiN	$-R_i \frac{\text{Lit1N}}{\text{Lit1C}^2} + u_i R'_{i,\text{LitiC}}$	$R_i \frac{1}{\text{Lit1C}}$	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 <sub>2</sub>	$-f_i R'_{i,\text{LitiC}}$	0	0	0	$-f_i R'_{i,N}$
N <sub>mineral</sub>	$R_i \frac{\text{Lit1N}}{\text{Lit1C}^2} - n_i R'_{i,\text{LitiC}}$	$-R_1 \frac{1}{\text{Lit1C}}$	0	0	$-n_i R'_{i,N}$

Table 5: Jacobian for SOM Pools

	SOM1	SOM2	SOM3	SOM4	CO <sub>2</sub>	N <sub>mineral</sub>
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 <sub>2</sub>	$-f_4 R'_4$	$-f_5 R'_5$	$-f_6 R'_6$	$-R'_7$	0	0
N <sub>mineral</sub>	$-n_4 R'_4$	$-n_5 R'_5$	$-n_6 R'_6$	$-n_7 R'_7$	0	0

## 1.4 Applications

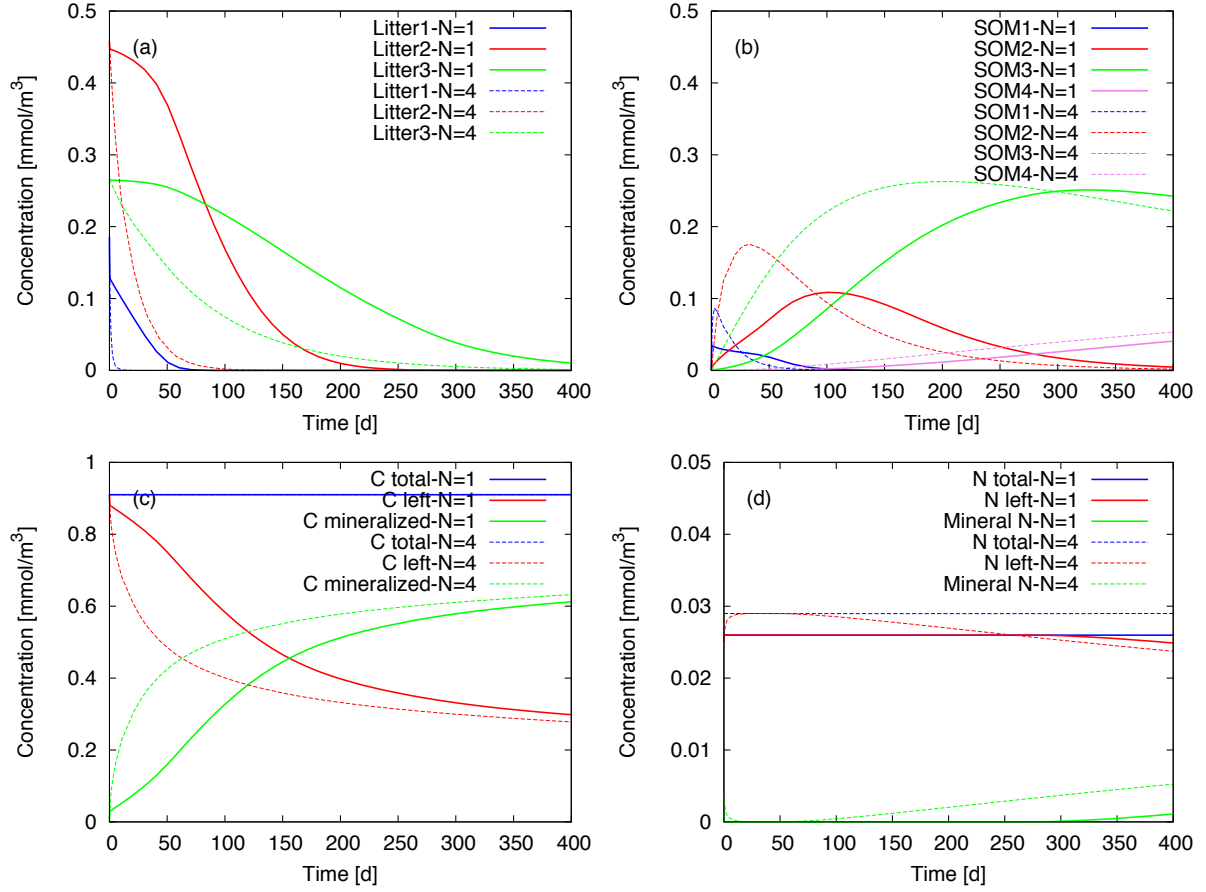


Figure 2: Demonstrating N limiting on C decomposition (initial mineral N=1 and 4  $\mu\text{mol/m}^3$ )

## 2 CLM4.5 CH<sub>4</sub> Oxidation

### 2.1 Reaction



### 2.2 Rate

$$R = k \frac{\text{CH}_4}{k_{\text{CH}_4} + \text{CH}_4} \frac{\text{O}_2}{k_{\text{O}_2} + \text{O}_2} f_T f_\Psi \quad (14)$$

### 2.3 Residuals

$$\begin{aligned} \mathcal{R}_{\text{CH}_4} &= \frac{\Delta V}{\Delta t} (\text{CH}_4^{k+1} - \text{CH}_4^k) + R^{k+1} \Delta V \\ \mathcal{R}_{\text{O}_2} &= \frac{\Delta V}{\Delta t} (\text{O}_2^{k+1} - \text{O}_2^k) + 2R^{k+1} \Delta V \\ \mathcal{R}_{\text{CO}_2} &= \frac{\Delta V}{\Delta t} (\text{CO}_2^{k+1} - \text{CO}_2^k) - R^{k+1} \Delta V \end{aligned}$$

### 2.4 Jacobian

$$\begin{aligned} \frac{\partial R}{\partial \text{CH}_4} &= k \frac{k_{\text{CH}_4}}{(k_{\text{CH}_4} + \text{CH}_4)^2} \frac{\text{O}_2}{k_{\text{O}_2} + \text{O}_2} f_T f_\Psi = R'_{\text{CH}_4} \\ \frac{\partial R}{\partial \text{O}_2} &= k \frac{\text{CH}_4}{k_{\text{CH}_4} + \text{CH}_4} \frac{k_{\text{O}_2}}{(k_{\text{O}_2} + \text{O}_2)^2} f_T f_\Psi = R'_{\text{O}_2} \end{aligned}$$

Table 6: Jacobian for methane oxidation

	CH <sub>4</sub>	O <sub>2</sub>	CO <sub>2</sub>
CH <sub>4</sub>	$R'_{\text{CH}_4}$	$R'_{\text{O}_2}$	0
O <sub>2</sub>	$2R'_{\text{CH}_4}$	$2R'_{\text{O}_2}$	0
CO <sub>2</sub>	$-R'_{\text{CH}_4}$	$-R'_{\text{O}_2}$	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_O2 - 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

```

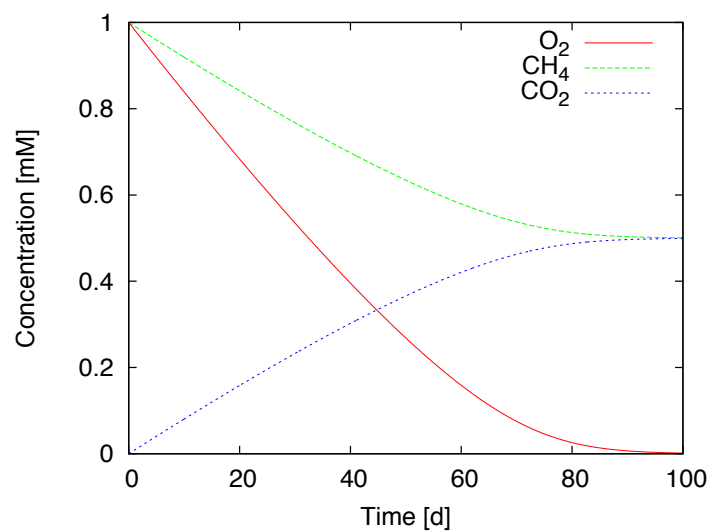


Figure 3: Example calculation for methane oxidation)

### 3 Acetoclastic Methanogenesis

#### 3.1 Reaction



#### 3.2 Rate

$$R = k\text{C}_{\text{bio}} \frac{\text{Ac}^-}{k_{\text{Ac}} + \text{Ac}^-} f_T f_\Psi \quad (17)$$

#### 3.3 Mass Conservation

$$\begin{aligned} \frac{\partial \text{Ac}^-}{\partial t} &= -(1 + \frac{y}{2})R \\ \frac{\partial \text{H}^+}{\partial t} &= -\frac{y}{2}R \\ \frac{\partial \text{CH}_4}{\partial t} &= R \\ \frac{\partial \text{HCO}_3^-}{\partial t} &= R \\ \frac{\partial \text{C}_{\text{bio}}}{\partial t} &= 1000\theta yR \end{aligned}$$

Note: for the last equation, PFLOTTRAN accounts for the  $1000\theta$  internally.

#### 3.4 Residuals

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

### 3.5 Jacobian

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

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

Table 7: Jacobian for methane oxidation

	$\text{Ac}^-$	$\text{CH}_4$	$C_{\text{bio}}$	$\text{HCO}_3^-$	$\text{H}^+$
$\text{Ac}^-$	$(1 + y/2)R'_a$	0	$(1 + y/2)R'_b$	0	0
$\text{CH}_4$	$-R'_a$	0	$-R'_b$	0	0
$C_{\text{bio}}$	$-yR'_a$	0	$-yR'_b$	0	0
$\text{HCO}_3^-$	$-R'_a$	0	$-R'_b$	0	0
$\text{H}^+$	$0.5yR'_a$	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

! always 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  $k_{Ac} = 0$ ,

$$\frac{\partial Ac}{\partial t} = -(1 + 0.5y)kC_{bio}$$

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

$$C_{bio} = C_{bio,0} \text{EXP}(1000\theta y k t)$$

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

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

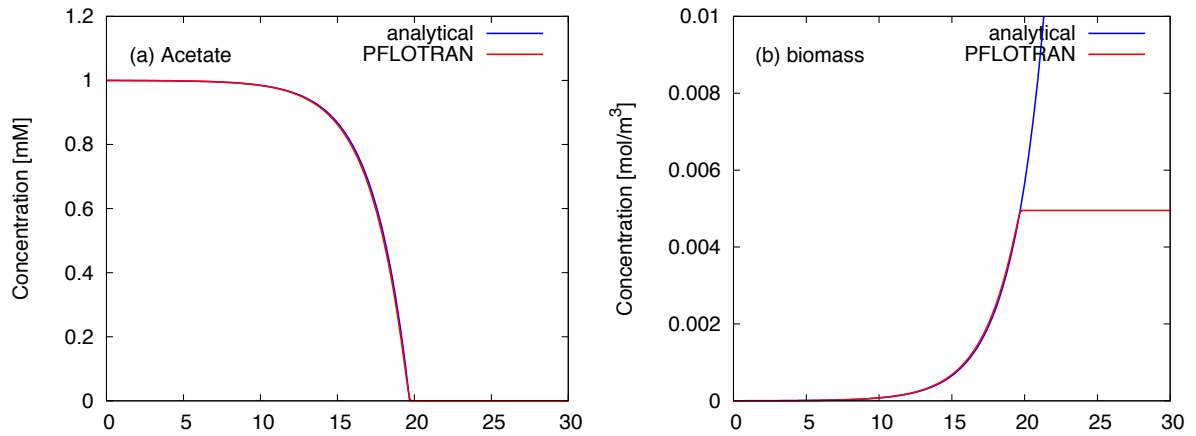
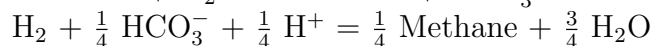
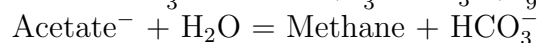
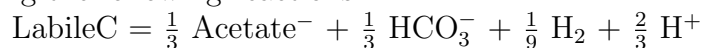


Figure 4: Example calculation for acetoclastic methanogenesis:

## 4 A General Example

If we implement a number of general reactions and rate formulae in PFLOTTRAN, 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 each specific case. For example, if we consider decomposition of LabileC as a first order decay to produce acetate and H<sub>2</sub>, which are used by methanogens to produce methane using the following reactions:



We can use the GENERAL\_REACTION and MICROBIAL\_REACTION functions in PFLOTTRAN 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.

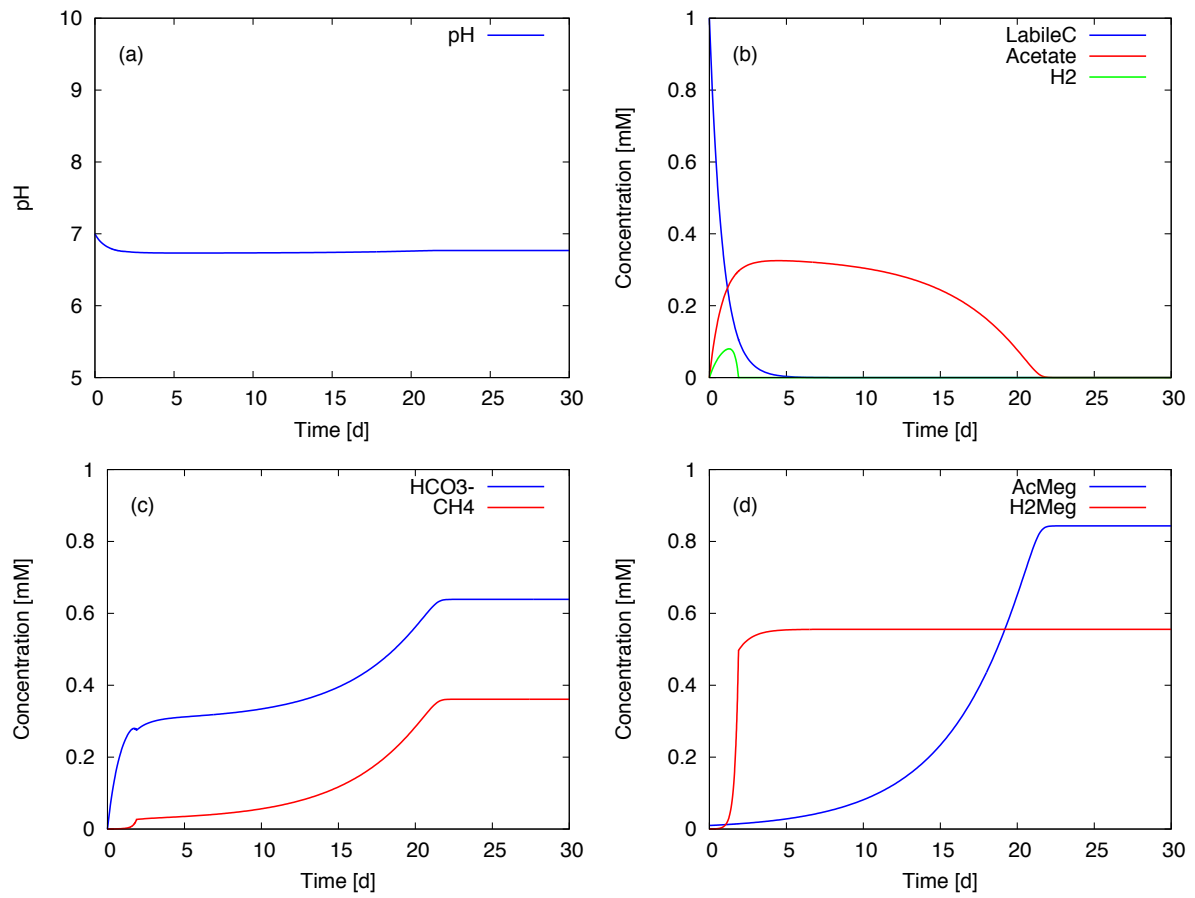


Figure 5: Example calculation for multiple microbial reactions

## 5 CLM-CNP

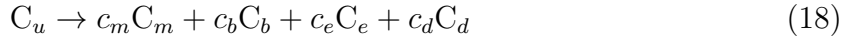
Starting from CLM-CN, CLM-CNP provides options to

1. add microbial, enzyme, and DOC pools
2. allow variable C:N:P ratios in all of the pools
3. use Monod, Machielis-Menten and other rate models
4. specify immobile or mobile pools/species

through an input file. It reduces to CLM-CN if none of the additional features is specified in the input file. These added features can be added incrementally. Sorption, and other geochemical processes can be added separately (outside of the CLM-CNP `reaction_sandbox`).

### 5.1 C

#### 5.1.1 Reaction



or

$$C_u \rightarrow \sum c_i C_i \quad (19)$$

The subscript  $u$ ,  $m$ ,  $b$ ,  $e$ , and  $d$  denote upstream, mineral, bacterial, enzyme, and downstream pools. To balance the reaction,  $c_m + c_b + c_e + c_d = 1$ .  $c_b$  and  $c_e$  can be variable in the future.

For CLM-CN,  $c_m$  is the respiration fraction  $f$ ,  $c_d = 1 - f$ , and  $c_b = c_e = 0$ .

To incorporate microbial pools with Monod rate,  $c_b \neq 0$ .

To use Michaelis-Menten rate,  $c_e \neq 0$

#### 5.1.2 Rate

$$\frac{d[C_u]}{dt} = -R = -k \prod f([C_i])f(pH)f(\psi)f(T) \quad (20)$$

$[C_i]$  is the concentration of  $C_i$ .  $k$  is the rate coefficient. function  $f([C_i])$ ,  $f(pH)$ ,  $f(\psi)$ , and  $f(T)$  account for influence of  $C_i$ , pH, moisture, and temperature on the reaction rate.  $C_i$  can be any component in or not in Eq. (18). We consider four options for  $f([C_i])$ :

$f([C_i]) = 1$	default
$f([C_i]) = [C_i]$	first order
$f([C_i]) = [C_i]/(K_{Ci} + [C_i])$	substrate/electron donor or electron acceptor limitation
$f([C_i]) = I_{Ci}/(I_{Ci} + [C_i])$	inhibition

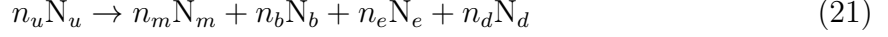
For CLM-CN,  $f([C_u]) = [C_u]$ ,  $f([C_m]) = f([C_b]) = f([C_d]) = 1$ .

To incorporate microbial pools without Monod rate,  $f([C_u]) = [C_u]/(K_{Cu} + [C_u])$ ,  $f([C_b]) = [C_b]$ ,  $f([C_m]) = f([C_d]) = 1$ .

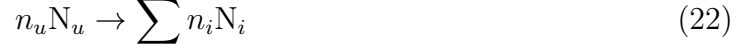
To use Michaelis-Menten rate,  $f([C_u]) = [C_u]/(K_{Cu} + [C_u])$ ,  $f([C_e]) = [C_e]$ ,  $f([C_m]) = f([C_d]) = f([C_b]) = 1$ .

## 5.2 N

### 5.2.1 Reaction



or



$$n_m + n_b + n_e + n_d = n_u \quad (23)$$

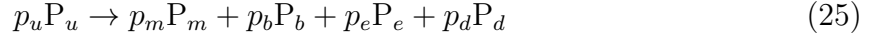
$n_u = [N_u]/[C_u]$ ,  $n_b = [N_b]/[C_b]$ ,  $n_e = [N_e]/[C_e]$ , and  $n_d = [N_d]/[C_d]$ . These stoichiometric coefficient can be fixed or variable. If  $n_m > 0$ , this decomposition reaction produces mineral N (mineralization). Otherwise, the reaction takes up mineral N (immobilization). In the late case, a  $f([N_m]) = [N_m]/(K_{Nm} + [N_m])$  term is added to the decomposition rate in Eq. (20).

### 5.2.2 Rate

$$-\frac{1}{n_u} \frac{\partial [N_u]}{\partial t} = \frac{1}{n_m} \frac{\partial [N_m]}{\partial t} = \frac{1}{n_b} \frac{\partial [N_b]}{\partial t} = \frac{1}{n_e} \frac{\partial [N_e]}{\partial t} = \frac{1}{n_d} \frac{\partial [N_d]}{\partial t} \quad (24)$$

## 5.3 P

### 5.3.1 Reaction



$$p_m + p_b + p_e + p_d = p_u \quad (27)$$

$p_u = [P_u]/[C_u]$ ,  $p_b = [P_b]/[C_b]$ ,  $p_e = [P_e]/[C_e]$ , and  $p_d = [P_d]/[C_d]$ . These stoichiometric coefficient can be fixed or variable. If  $p_m > 0$ , this decomposition reaction produces mineral P (mineralization). Otherwise, the reaction takes up mineral P (immobilization). In the late case, a  $f([P_m]) = [P_m]/(K_{Pm} + [P_m])$  term is added to the decomposition rate in Eq. (20).

### 5.3.2 Rate

$$-\frac{1}{p_u} \frac{\partial [P_u]}{\partial t} = \frac{1}{p_m} \frac{\partial [P_m]}{\partial t} = \frac{1}{p_b} \frac{\partial [P_b]}{\partial t} = \frac{1}{p_e} \frac{\partial [P_e]}{\partial t} = \frac{1}{p_d} \frac{\partial [P_d]}{\partial t} \quad (28)$$

## 5.4 Residuals

$$\begin{aligned}
R_{Cu} &= -R \\
R_{Cdi} &= d_i R \\
R_{Cm} &= (1 - d_i) R \\
R_{Nu} &= -\frac{[N_u]}{[C_u]} R \\
R_{Ndi} &= \frac{[N_{di}]}{[C_{di}]} R \\
R_{Nm} &= \left( \frac{[N_u]}{[C_u]} - \frac{[N_{di}]}{[C_{di}]} \right) R
\end{aligned}$$

## 5.5 Jacobians

Table 8: Jacobian for general decomposition

	$C_u$	$C_{di}$	$C_m$	$N_u$	$N_{di}$	$N_m$
$C_u$	$-\frac{\partial R}{\partial C_u}$	$-\frac{\partial R}{\partial C_{di}}$	0	0	0	$-\frac{\partial R}{\partial N_m}$
$C_{di}$	$d_i \frac{\partial R}{\partial C_u}$	$d_i \frac{\partial R}{\partial C_{di}}$	0	0	0	$d_i \frac{\partial R}{\partial N_m}$
$C_m$	$(1 - d_i) \frac{\partial R}{\partial C_u}$	$(1 - d_i) \frac{\partial R}{\partial C_{di}}$	0	0	0	$(1 - d_i) \frac{\partial R}{\partial N_m}$
$N_u$	$-\frac{[N_u]}{[C_u]} \frac{\partial R}{\partial C_u} + \frac{[N_u]}{[C_u]^2} R$	$-\frac{[N_u]}{[C_u]} \frac{\partial R}{\partial C_{di}}$	0	$-\frac{1}{[C_u]} R$	0	$-\frac{[N_u]}{[C_u]} \frac{\partial R}{\partial N_m}$
$N_{di}$	$\frac{[N_{di}]}{[C_{di}]} \frac{\partial R}{\partial C_u}$	$\frac{[N_{di}]}{[C_{di}]} \frac{\partial R}{\partial C_{di}} - \frac{[N_{di}]}{[C_{di}]^2} R$	0	0	$\frac{1}{[C_{di}]} R$	$\frac{[N_{di}]}{[C_{di}]} \frac{\partial R}{\partial N_m}$
$N_m$	$\left( \frac{[N_u]}{[C_u]} - \frac{[N_{di}]}{[C_{di}]} \right) \frac{\partial R}{\partial C_u} - \frac{[N_u]}{[C_u]^2} R$	$\left( \frac{[N_u]}{[C_u]} - \frac{[N_{di}]}{[C_{di}]} \right) \frac{\partial R}{\partial C_{di}} + \frac{[N_{di}]}{[C_{di}]^2} R$	0	$\frac{1}{[C_u]} R$	$-\frac{1}{[C_{di}]} R$	$\left( \frac{[N_u]}{[C_u]} - \frac{[N_{di}]}{[C_{di}]} \right) \frac{\partial R}{\partial N_m}$

To use  $N_m/(K_N + N_m)$  term for N-limiting cases ( $\frac{[N_u]}{[C_u]} - \frac{[N_{di}]}{[C_{di}]} < 0$ ),

$$\frac{\partial R}{\partial N_m} = R \frac{K_N}{(K_N + N_m)N_m} \quad (29)$$

because

$$\frac{\partial \frac{x}{k+x}}{\partial x} = \frac{k}{(k+x)^2} \quad (30)$$

For the first order rate term,

$$\frac{\partial R}{\partial C_x} = \frac{R}{[C_x]} \quad (31)$$

For the Monod rate term,

$$\frac{\partial R}{\partial C_x} = R \frac{K_x}{(K_x + [C_x])[C_x]} \quad (32)$$

For the inhibition term,

$$\frac{\partial R}{\partial C_x} = -R \frac{K_x}{(K_x + [C_x])[C_x]} \quad (33)$$

because

$$\frac{\partial \frac{k}{k+x}}{\partial x} = -\frac{k}{(k+x)^2} \quad (34)$$

Table 9: Jacobian for general decomposition (add for each rate term)

	$C_u$	$C_{di}$	$C_m$	$N_u$	$N_{di}$	$N_m$
$C_u$	$-\frac{\partial R}{\partial C_u}$	$-\frac{\partial R}{\partial C_{di}}$	0	0	0	$-\frac{\partial R}{\partial N_m}$
$C_{di}$	$d_i \frac{\partial R}{\partial C_u}$	$d_i \frac{\partial R}{\partial C_{di}}$	0	0	0	$d_i \frac{\partial R}{\partial N_m}$
$C_m$	$(1 - d_i) \frac{\partial R}{\partial C_u}$	$(1 - d_i) \frac{\partial R}{\partial C_{di}}$	0	0	0	$(1 - d_i) \frac{\partial R}{\partial N_m}$
$N_u$	$-\frac{[N_u]}{[C_u]} \frac{\partial R}{\partial C_u}$	$-\frac{[N_u]}{[C_u]} \frac{\partial R}{\partial C_{di}}$	0	0	0	$-\frac{[N_u]}{[C_u]} \frac{\partial R}{\partial N_m}$
$N_{di}$	$\frac{[N_{di}]}{[C_{di}]} \frac{\partial R}{\partial C_u}$	$\frac{[N_{di}]}{[C_{di}]} \frac{\partial R}{\partial C_{di}}$	0	0	0	$\frac{[N_{di}]}{[C_{di}]} \frac{\partial R}{\partial N_m}$
$N_m$	$\left( \frac{[N_u]}{[C_u]} - \frac{[N_{di}]}{[C_{di}]} \right) \frac{\partial R}{\partial C_u}$	$\left( \frac{[N_u]}{[C_u]} - \frac{[N_{di}]}{[C_{di}]} \right) \frac{\partial R}{\partial C_{di}}$	0	0	0	$\left( \frac{[N_u]}{[C_u]} - \frac{[N_{di}]}{[C_{di}]} \right) \frac{\partial R}{\partial N_m}$

Table 10: Jacobian for general decomposition (add only once)

	$C_u$	$C_{di}$	$C_m$	$N_u$	$N_{di}$	$N_m$
$C_u$	0	0	0	0	0	0
$C_{di}$	0	0	0	0	0	0
$C_m$	0	0	0	0	0	0
$N_u$	$\frac{[N_u]}{[C_u]^2} R$	0	0	$-\frac{1}{[C_u]} R$	0	0
$N_{di}$	0	$-\frac{[N_{di}]}{[C_{di}]^2} R$	0	0	$\frac{1}{[C_{di}]} R$	0
$N_m$	$-\frac{[N_u]}{[C_u]^2} R$	$\frac{[N_{di}]}{[C_{di}]^2} R$	0	$\frac{1}{[C_u]} R$	$-\frac{1}{[C_{di}]} R$	0



## 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>.