B31B-0419 Exploring the controls of soil biogeochemistry in a restored coastal wetland using object-oriented computer simulations of uptake kinetics and thermodynamic optimization in batch reactors

Payn, R. A.[1,2] (rpayn@montana.edu), A. M. Helton[3], G. C. Poole[1,2,4], C. Izurieta[2,4], E. S. Bernhardt[3], and A. J. Burgin[5]
1. Department of Land Resources and Environmental Sciences, Montana State University; 2. Institute on Ecosystems, Montana University System;
3. Biology Department, Duke University; 4. Computer Science Department, Montana State University; 5. School of Natural Resources, University of Nebraska – Lincoln

Acknowledgements: This work is funded by NSF grant DEB-1021001. Thanks to the NEO team for their support, especially Isaac Griffith and Ryan Nix. Thanks to the Timberlake Research team (past and present) for their support, especially Marcelo Ardon, Medora Burke—Scoll, and Anna Fedders.

1. Motivation

- We are studying the biogeochemical response of the soils from (a) Timberlake Wetland in North Carolina, USA, to restoration from agricultural land use (re-flooding) and surface water intrusion of seawater (via wind tides)
- Thermodynamic theory is frequently invoked to explain biogeochemical patterns in wetland soils.
- Most thermochemical models are too detailed to be practical for comparisons with typical (b) field and (c) lab measurements
- Therefore, we have few tools for testing thermodynamic theory against typical observations of solute dynamics

2. Objective

Build a thermodynamic model of microbial growth and metabolism with sufficient generality for comparison to measurements of solute dynamics in wetland soils

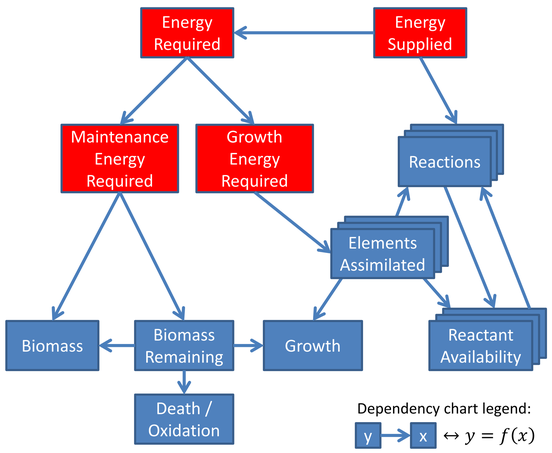
a 

b 

c 

3. Thermodynamic theory

Each time step is an optimization that maximizes the biomass remaining at the end of the time step, subject to linear constraints on variables defined by the energy and mass balance of the system. The following is an abstract dependency chart of the variables used for optimization.



The generalized energy balance constraint

$$\sum_{i=1}^{n} m_{S,i} E_{S,i} = m_M \frac{B_t + B_{t+\Delta t}}{2} + \sum_{j=1}^{n_G} m_{G,j} G_j$$

Sum of energy from reactions | Energy needed to maintain biomass | Energy needed to produce biomass

The generalized mass balance constraint for each compound

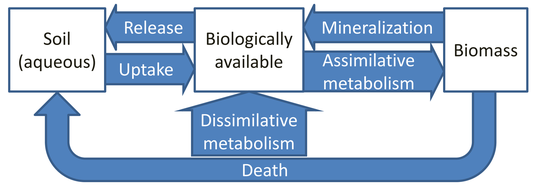
$$X_{t+\Delta t} = X_t + \sum_{i=1}^{n} f_{XP,i} m_{S,i} - \sum_{i=1}^{n} f_{XR,i} m_{S,i} - \sum_{j=1}^{n_G} f_{XG,i} G$$

Change in availability of the compound | Amount of compound produced or consumed in reactions | Assimilation of compound for growth

$m_{S,i}$	number of reactions for reaction i
$E_{S,i}$	standard free energy yield of reaction i
m_M	energy needed to maintain biomass, per carbon atom
B_t	biomass at time t
$m_{G,j}$	energy needed to assimilate compound j for growth
G_j	amount of compound j assimilated for growth
X_t	amount of a compound available at time t
$f_{XP,i}$	stoichiometric factor for a compound as a product in reaction i
$f_{XR,i}$	stoichiometric factor for a compound as a reactant in reaction i
$f_{XG,i}$	stoichiometric factor for an assimilated compound relative to each carbon atom assimilated for growth
n	total number of potential reactions that may occur
n_G	total number of compounds that are potentially assimilated

4. Model structure and algorithm

Metabolism rates are calculated through time as sequential optimizations, and resulting changes in amounts of compounds in aqueous, biologically available, and living biomass forms are tracked using Network Exchange Objects (NEO). NEO is an object-oriented modeling framework for simulation of distributed flux networks.



- Uptake is based on Monod kinetics, providing the capability to simulate asymptotic rate limitation

$$U_X = \frac{C_X U_{XB,max}}{C_X + C_{X,half}} B_t$$

U_X	uptake rate of compound X
C_X	concentration of compound X in aqueous form
$U_{XB,max}$	maximum uptake rate per mole C in biomass
$C_{X,half}$	concentration at which half the maximum uptake occurs

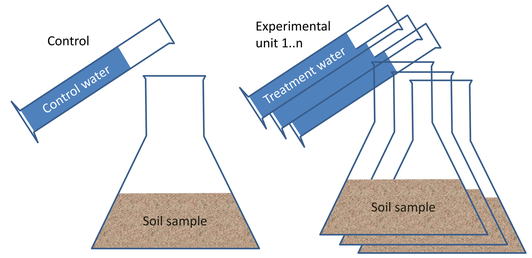
- Metabolism and mineralization rates are all determined by the linear optimization (see panel 3)
- Death is based on a constant mortality rate plus any death from a lack of available energy needed for maintenance
- Each time step is calculated as a sequence of uptake, optimization, release, and death
- At the end of each time step, the mass balance of the calculated and optimized fluxes are used to determine the change in aqueous phase, biologically available, and biomass compounds.

Reactions implemented in current model

Metabolic process	Reaction	$E_S = -\Delta G_r^0$ (kJ mol^{-1})
Aerobic organic carbon oxidation	$CH_2O + O_2 \leftrightarrow CO_2 + H_2O$	502
Denitrification - Nitrate reduction	$CH_2O + 2NO_3^- \leftrightarrow CO_2 + 2NO_2^- + H_2O$	354
Denitrification - Nitrite reduction	$CH_2O + 2NO_2^- + 2H^+ \leftrightarrow CO_2 + N_2O + 2H_2O$	481
Denitrification - Nitrous oxide reduction	$CH_2O + 2N_2O \leftrightarrow CO_2 + 2N_2 + H_2O$	710
Nitrification - Ammonium oxidation	$O_2 + 2/3NH_4^+ \leftrightarrow 2/3NO_2^- + 4/3H^+ + 2/3H_2O$	183
Nitrification - Nitrite oxidation	$O_2 + 2NO_2^- \leftrightarrow 2NO_3^-$	148
Methanogenesis	$CH_2O \leftrightarrow 1/2CO_2 + 1/2CH_4$	93
Methane oxidation	$O_2 + 1/2CH_4 \leftrightarrow 1/2CO_2 + H_2O$	409
Sulfate reduction	$CH_2O + 1/2SO_4^{-2} + 1/2H^+ \leftrightarrow 1/2HS^- + CO_2 + H_2O$	104

5. Batch reactor model implementation and simulations

- We are collecting solute processing data from soil slurry batch reactors, with soil samples taken from the Timberlake Wetland.
- Ultimately we will be using these batch reactor data to help parameterize the model, currently we are using the concept of a batch reactor environment to evaluate model behavior
- A batch reactor is a closed system, so the aqueous compartment for each reactor was assumed to be isolated and contain a constant volume of water
- The initial concentrations for simulations can be arbitrarily set at application run time, to allow for numerical experimentation and sensitivity analysis
- Application runs a default "control" reactor, and multiple additional reactors configured to vary the experimental treatments



Autotrophy

Stimulate simulated nitrification with high ammonium and oxygen concentrations.

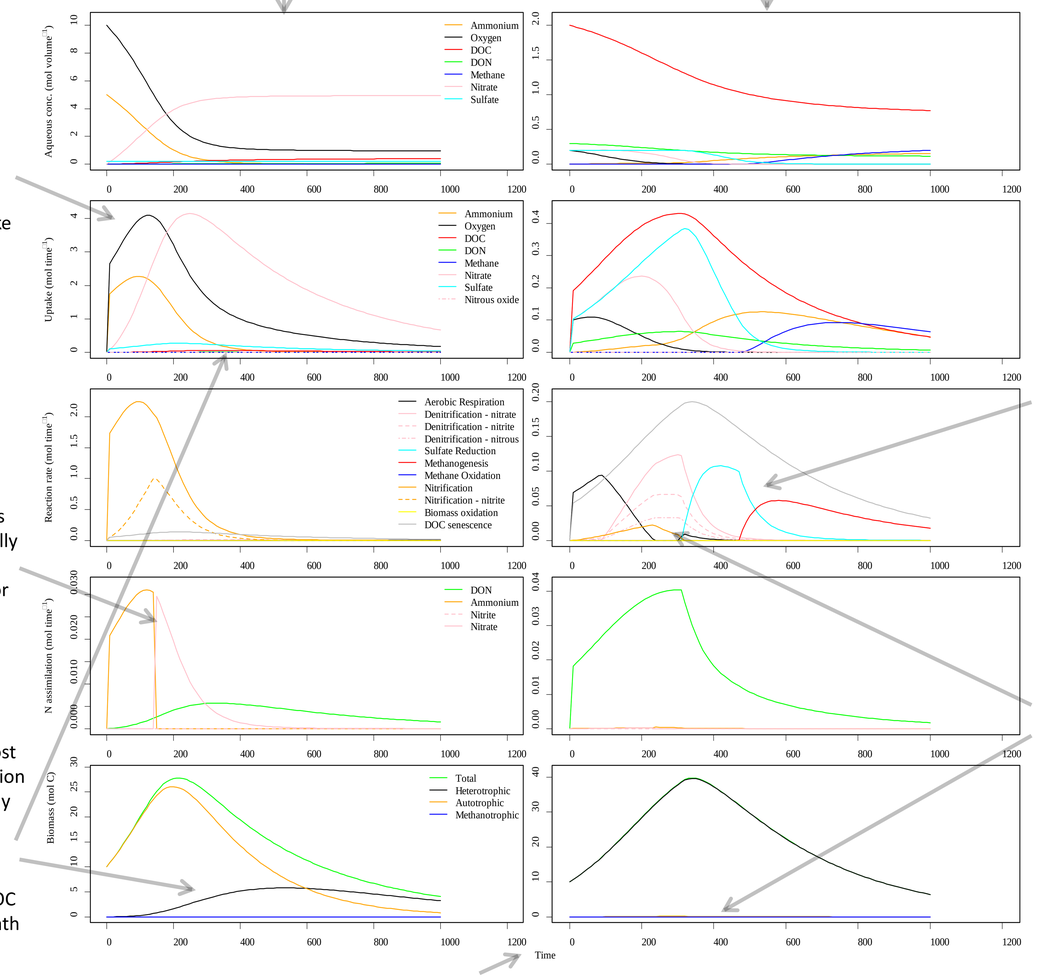
Heterotrophy

Stimulate simulated aerobic respiration, denitrification, sulfate reduction, and methanogenesis with high concentrations of DOC and terminal electron acceptors (TEAs)

Availability of compounds for the iterated optimizations is proportional to the rate of uptake

Transition of N uptake occurs when it becomes more energetically favorable to reduce nitrate for growth

Relatively low cost of DOC assimilation allows a relatively substantial heterotrophic assemblage to develop from DOC produced by death of autotrophs



Metabolic processes progress in a sequence observed frequently in TEA limited aquatic systems, consistent with thermodynamic theory

Autotrophic nitrification occurs due to production of ammonium mineralized by heterotrophs, but the relatively high cost of autotrophy prevents substantial autotrophic growth

We are currently working to parameterize the model such that time-scales are appropriate for comparison with laboratory batch reactor experiments. For these initial model evaluations, the time scale is conceptual.

6. Conclusions and implications

- **Simulations consistent with thermodynamic theory can be produced by optimization of a relatively parsimonious and generalized collection of linear constraints on energy and mass balance**
- **This model is unlikely to be accurate when compared to field and lab data, however interpretation of residual errors will allow a better understanding of how emergent properties of complex microbial systems are important to biogeochemical behavior**
- **We suggest that models such as this serve as useful heuristic tools; in particular ,this model will provides a mechanistic "benchmark in parsimony" useful for evaluating new hypotheses arising from the more enigmatic observed biogeochemical behaviors**