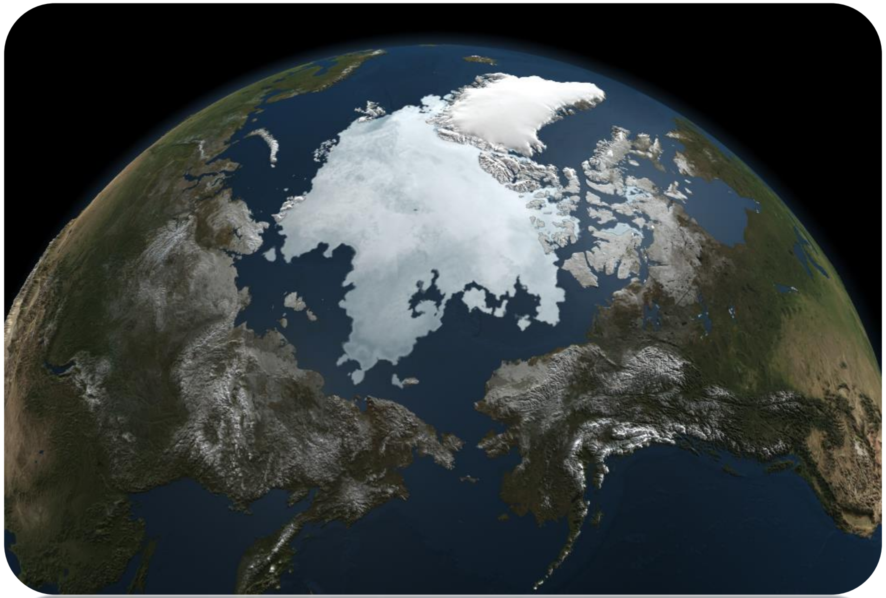
Dissolved Organic Carbon In Arctic Rivers : Reduced Model with Functional Groups

Amadini M Jayasinghe
New Mexico Tech, LANL
6-19-2020

Arctic Ocean



- Arctic Ocean, strong seasons
- Arctic Ocean, climate sensitive area

- Sea ice, albedo

Arctic Permafrost

Arctic permafrost is thawing and that affects biogeochemistry esp. C cycle.

As the frozen ground warms much faster than expected, it's reshaping the landscape—e.g. releasing carbon gases that fuel global warming.

Arctic Rivers

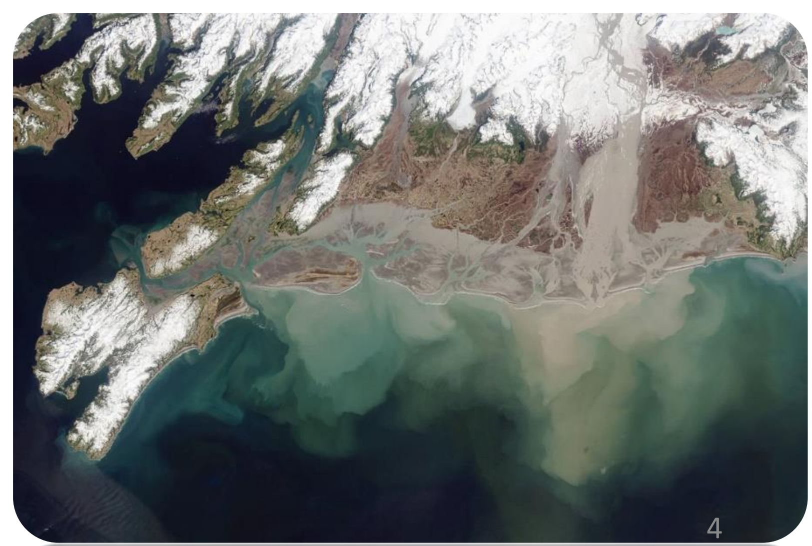
Arctic rivers constitute:

- A large source of DOC to Arctic Ocean
- Major inputs: Yenisey, Lena, Ob, etc.

DOC can influence physics in coastal plumes:

- Light penetration
- Mineral discharge and turbidity
- Surface activity
- Ligands
- Block brine channels, antifreeze?

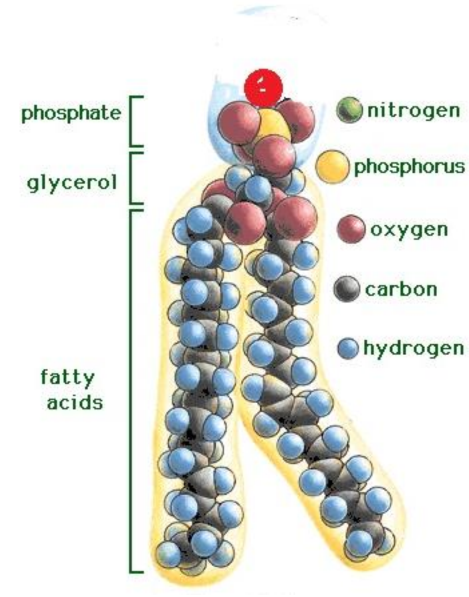
(Dittmar & Kattner, 2003)

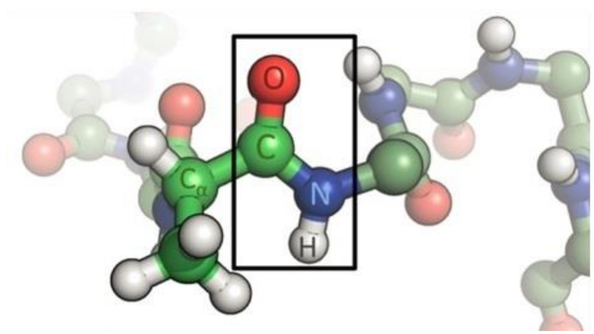


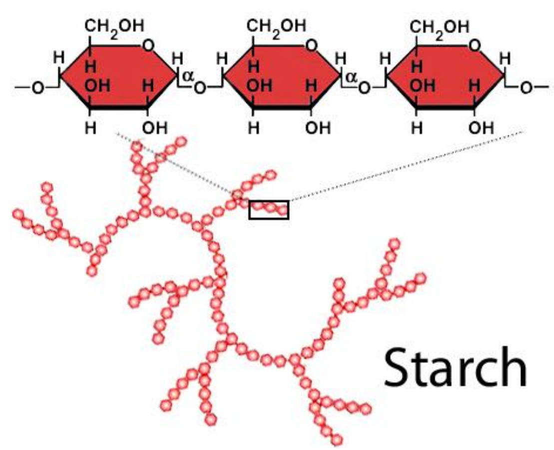
River Organics

Subdivide organic matter into macromolecular classes

- Proteins and derivatives
- Lipids and lignin
- Carbohydrates and derivatives
- Colored materials
- Heteropolycondensates (humics)

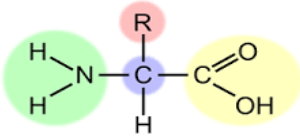




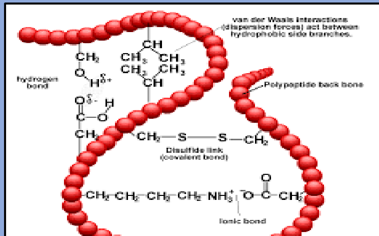


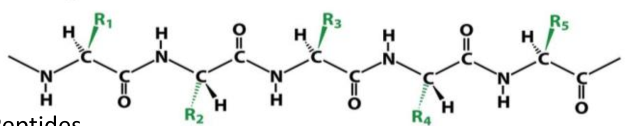
Portraits of organic molecules: structures

Proteins and derivatives



Amino acid


Protein

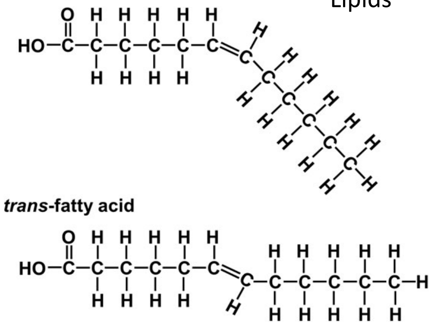

Peptides

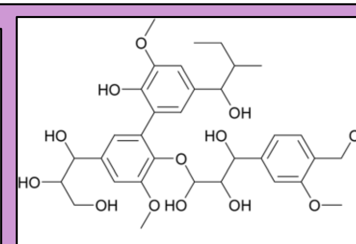
Lipids and lignin

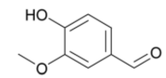
Lipids

cis-fatty acid

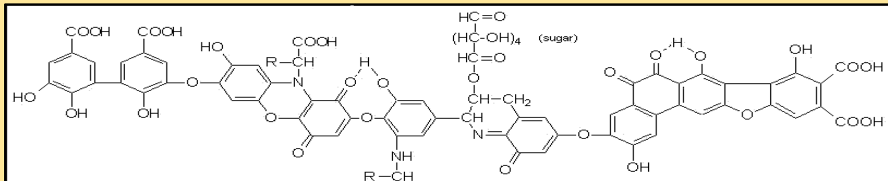
trans-fatty acid




Lignin


Vanillin

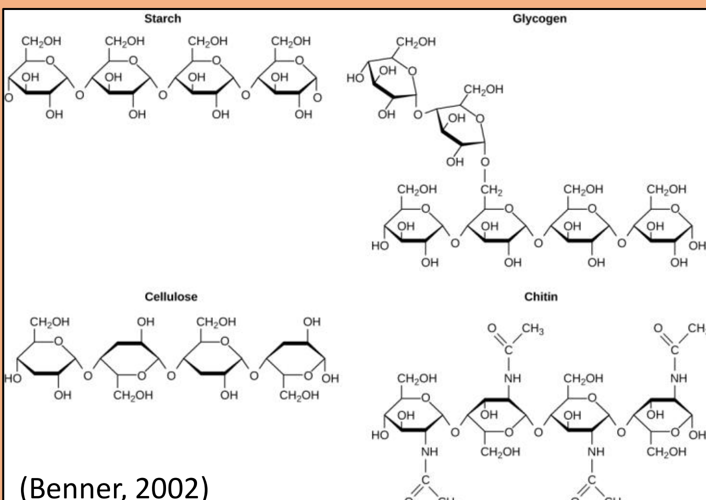
Heteropolycondensates(Humics)



Humic

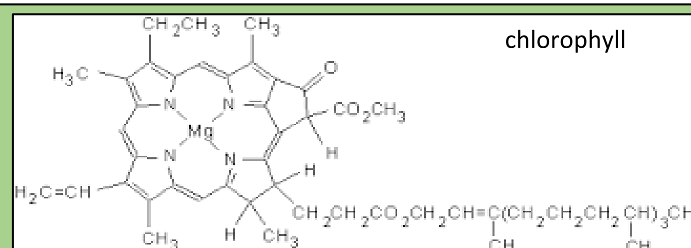
Model structure of humic acid (Stevenson 1982)

Carbohydrates and derivatives



(Benner, 2002)

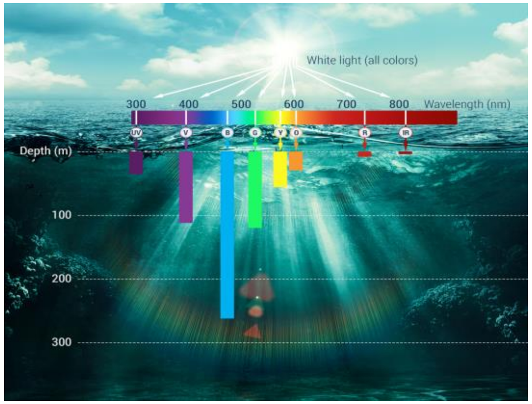
Colored materials

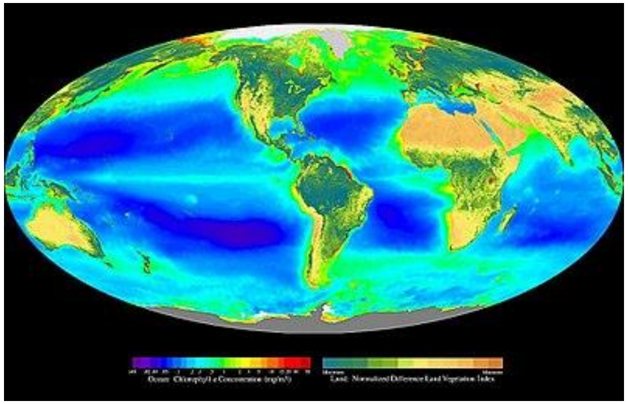

chlorophyll

River Organics……

Macromolecular classes influence coastal physical properties

- Absorption and light attenuation
- Primary production is reduced
- Surface activity -wind stress , mass/energy transfer, POA
- We also consider blocking colloids, protein antifreeze





(S Elliott et al., 2014; Scott Elliott et al., 2019; Krembs et al., 2011; Mungall et al., 2017; Stedmon et al., 2011)

Method

We model an idealized Arctic river, accounting for the **evolution of biogeochemically active forms**

Our idealized arctic river (nominally the Lena…)

Pre-processes

- With the **boreal soil**, with special attention to the differences between the major **sub-ecologies** of tundra/taiga/woodland/peatland/mountains.

Floodplain

- Inserted mixing parameterization for a “**node**” -a location at which tributaries feed together.
- A **dilution algorithm** applied at this point as a placeholder for real channel simulation.
- Along the course, factored in the possibilities of **bacterial degradation and photochemistry**

Post-processing

- Simple representation of delta post-hoc to act as a counterpoint to soil initialization

Idealized arctic river model

Our idealized Arctic river: trajectory

Idealized arctic river chemistry boxes follow **Lagrangian** trajectories

Our idealized Arctic river: parameters

Preprocesses

- ***Initial concentration***, based on the soil water composition of sub-ecological systems
- ***Turnover rates***, coastal marine lifetimes with sensitivity tests
- ***Transport velocity***, simple representation of soil preprocessing

Floodplain

- ***Node*****,** representing the linkage of tributaries
- ***Dilution factor,*** applies where there is channel mixing
- ***Chemical kinetics,*** bacterial and photochemical degradation time constants
- ***Chemical mechanism,*** decay of major biomolecular class molecules into small molecules
- ***Chemical mechanism,*** but include recombination toward heterogenous polymers
- ***Transport velocity***, numerical values represent kinetics of the reaction vessel

Deltaic processes

- ***Transport velocity,*** simple delta post-processing to act as counterpoint to soil initialization

Idealized arctic river model

Solutions : QSSA

- As Lagrangian integrations proceed, the functionally resolved species are treated as independent over any one time step in an exponential-form Euler, embodied by the Quasi-Steady State Approximation or QSSA

$$\frac{dC_i}{dt_{QSSA}} = P_i(C_j, C_k, ..) - L_i(C_j, C_k, ..)C_i \qquad \textbf{(1)}$$

$$C_{i,t+\delta t} = \frac{P_i}{L_i}\left(1 - e^{-L_i \delta t}\right) + C_{i,t}e^{-L_i \delta t} \qquad \textbf{(2)}$$

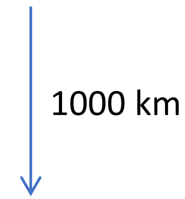
$$P_i, L_i \; fixed \; for \; \delta t$$

- C_i are concentrations for some biomacromolecule of interest while
- $C_{j(k)}$ are those of others in the table (lying elsewhere in the kinetic network),
- P and L represent the production term and loss constant respectively

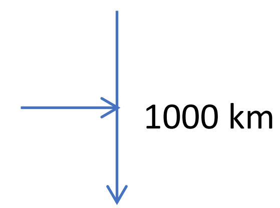
(Hesstvedt et al., 1978)

Idealized Arctic River Model…

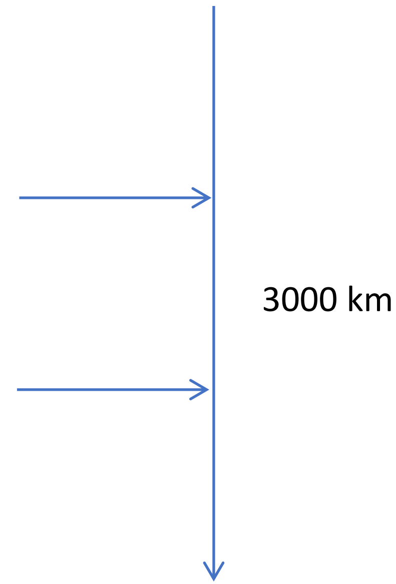
Idealized 1000 km river, only:



- Primary taiga flow
- Primary tundra flow
- Taiga river network with tundra: one node
- Tundra river network with taiga: one node

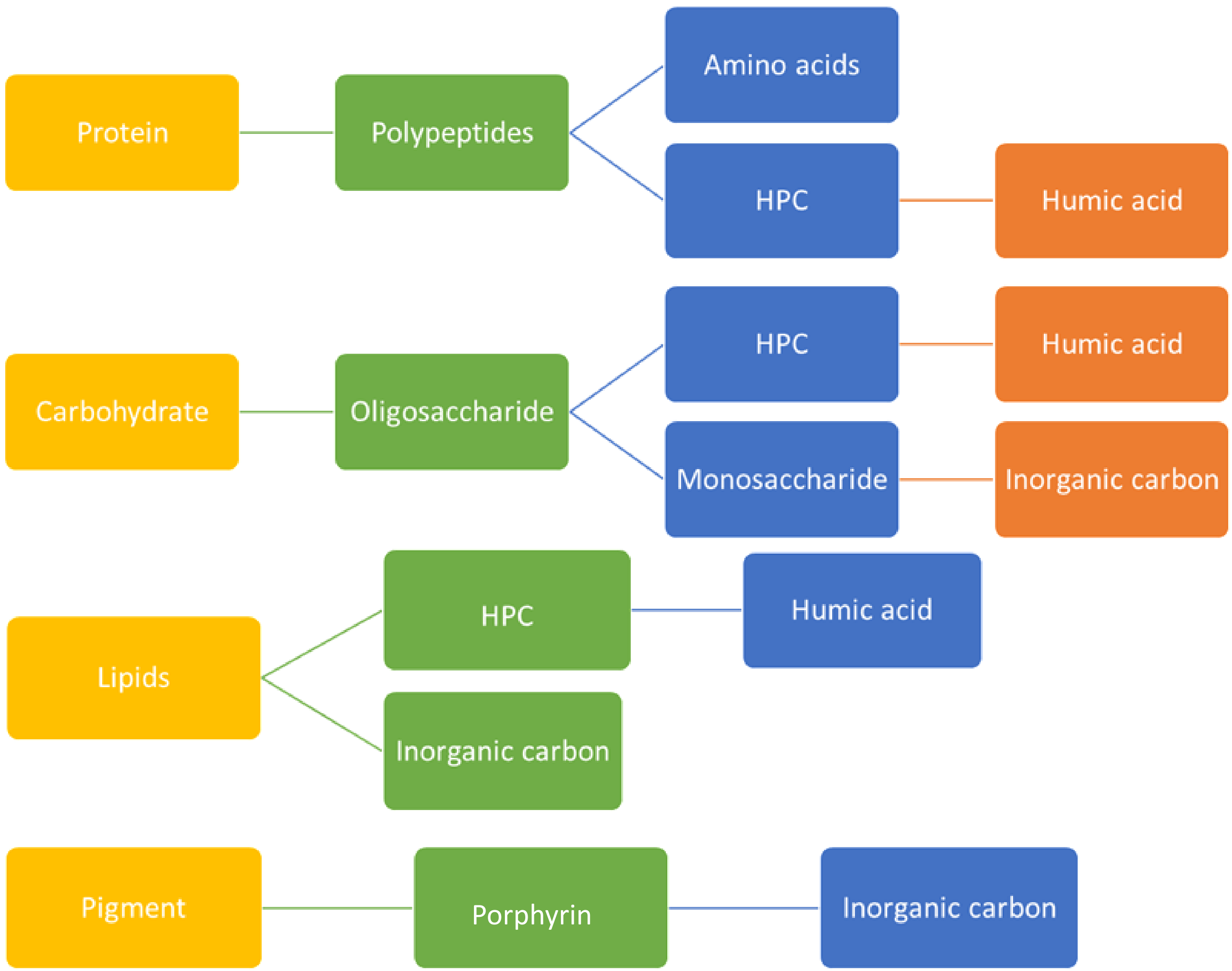


Idealized 3000 km river, more detail:



- Mountain, woodland/peat, taiga/tundra
- River networks: two nodes
- Fast/slow kinetics within network
- Low/high initial concentrations

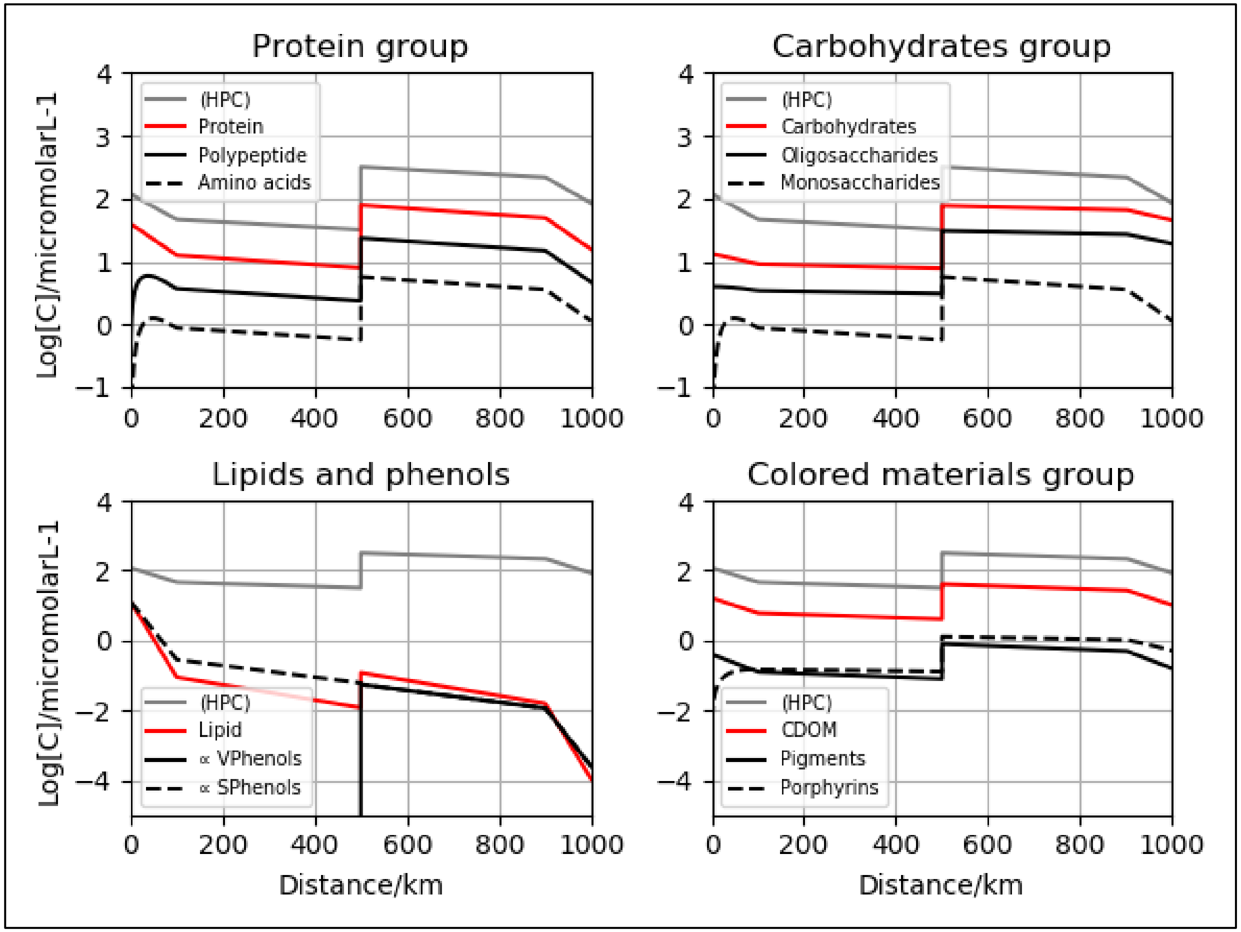
Schematic Mechanism…



(Stumm & Morgan, 1981)

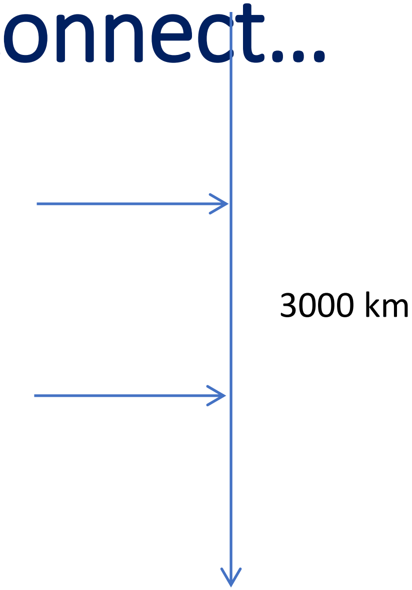
Results: Idealized Arctic Single Link…

Closer to measurements: tundra + taiga one node



Results: Idealized Arctic double connect…

Idealized 3000km river only

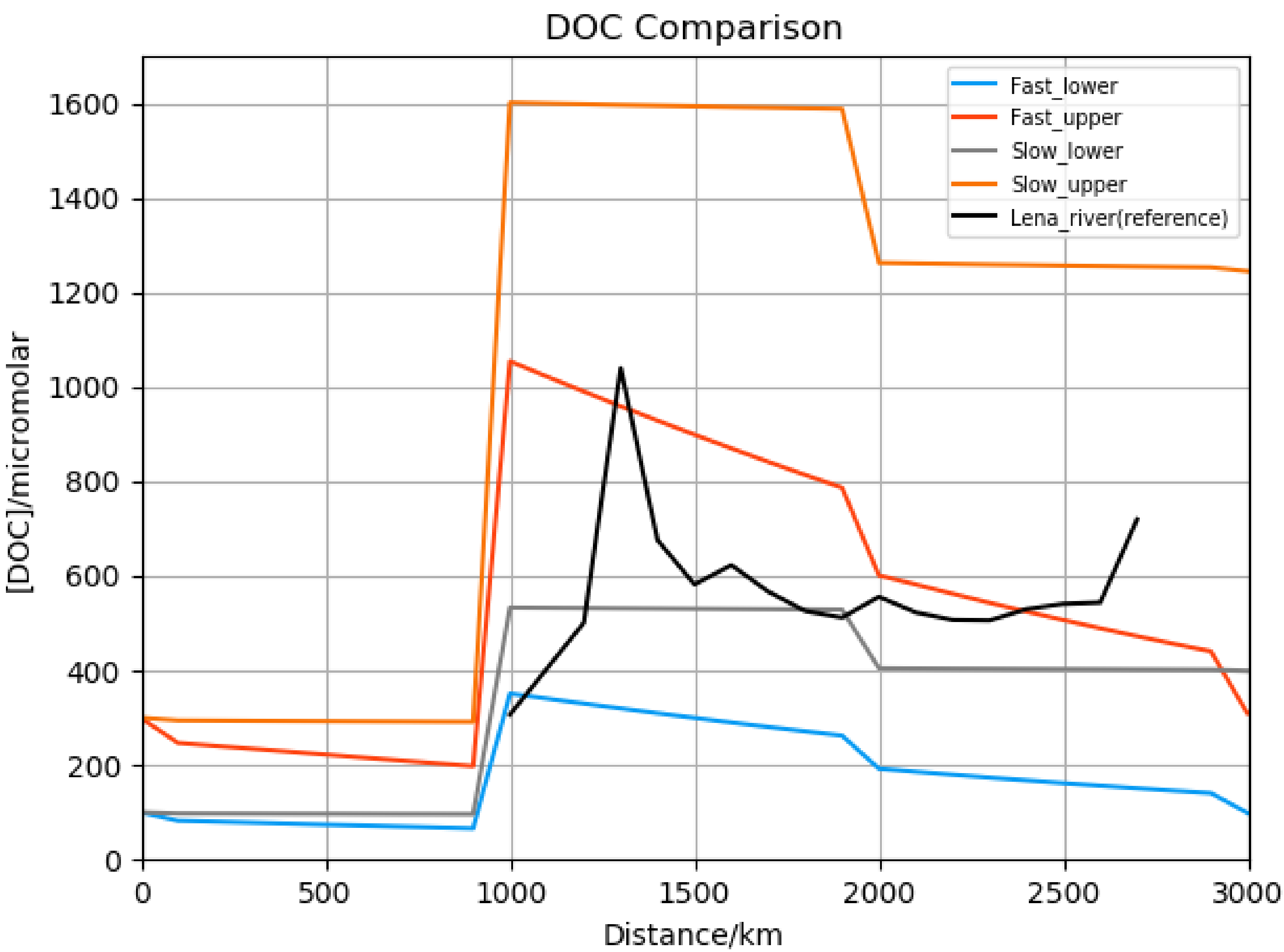


- Mountain, woodland/peat, taiga/tundra
- River networks: two nodes
- Fast/slow kinetics within network
- Low/high concentrations

DOC	Lower /micromolar	Upper /micromolar	Reference value /micromolar	
Primary	100	300	100-300	Shogren et al.,2019
Node_01	1000	3000	500-6000	Frey and McClelland., 2009
Node_02	300	1000	100-1000	Shogren et al.,2019

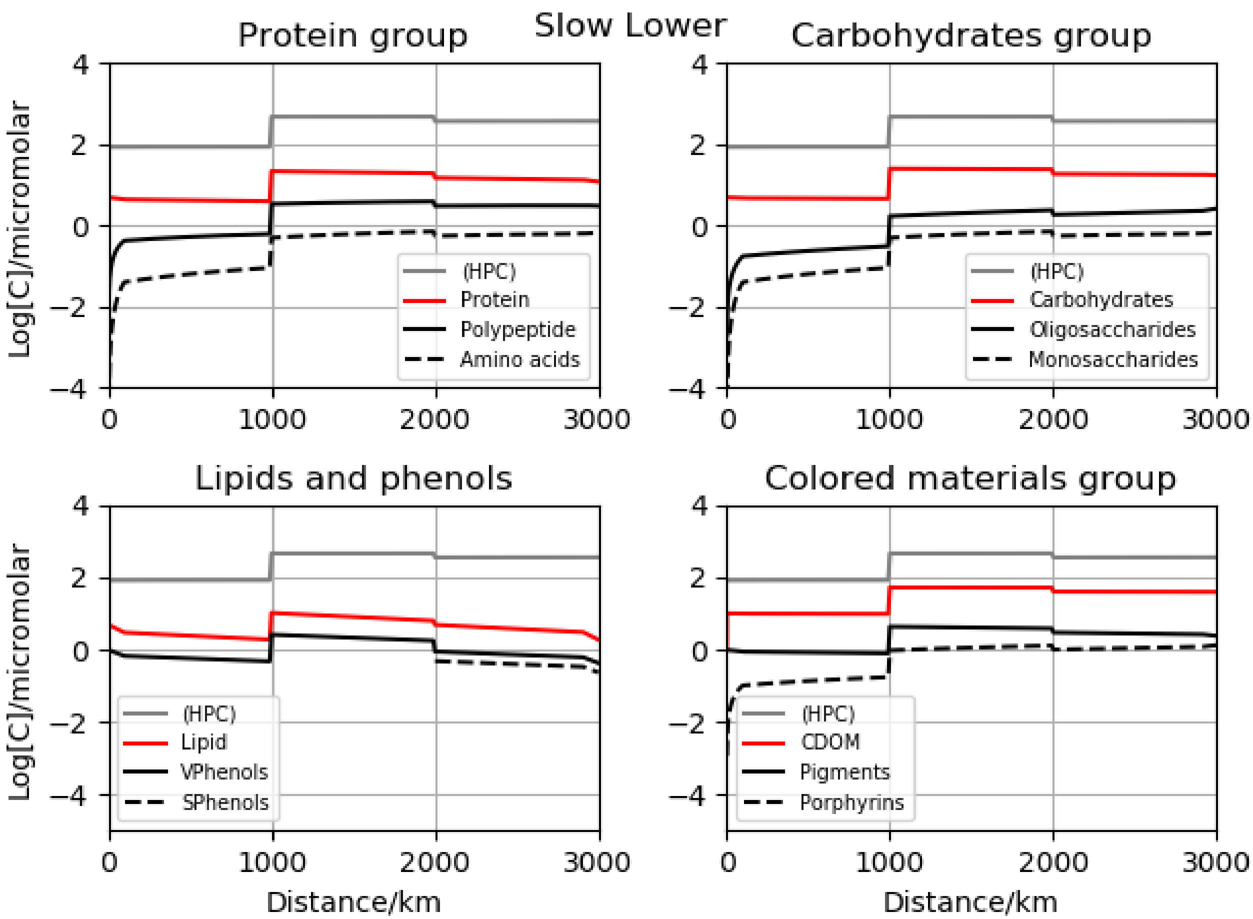
Results: Idealized arctic river model…

Idealized 3000 km double node



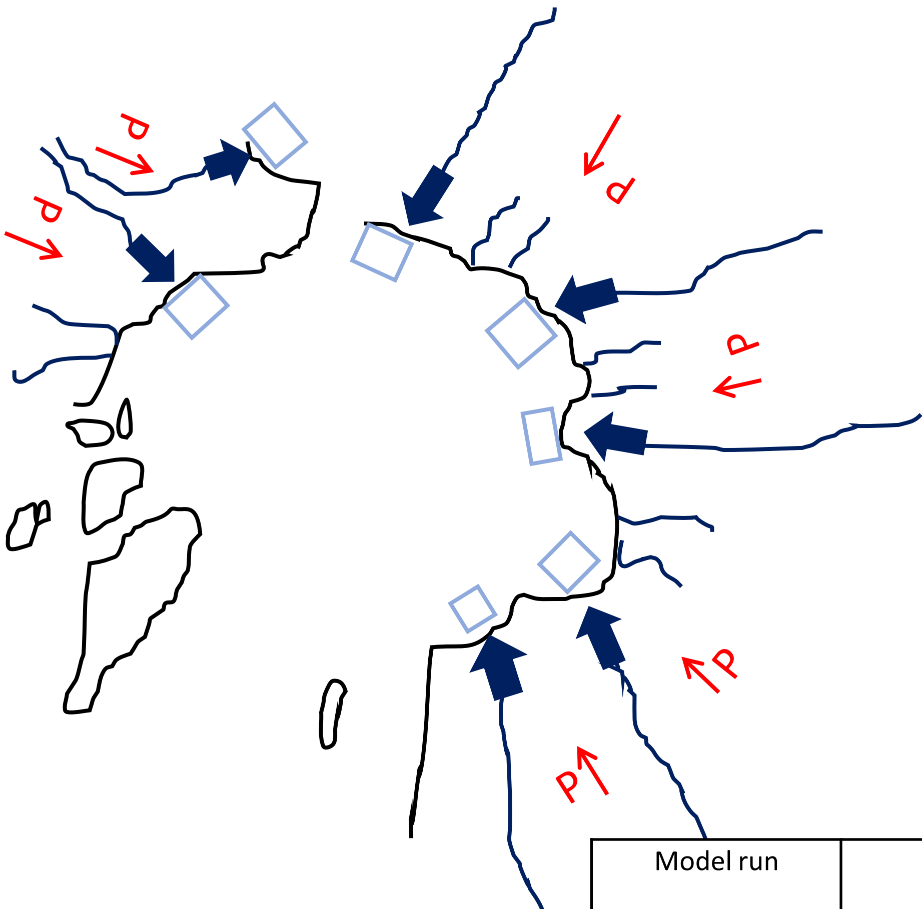
Results: Idealized Arctic river model…

Idealized 3000 km species on broad, log scale



Results: Idealized Arctic river model…

Idealized 3000 km double tributary



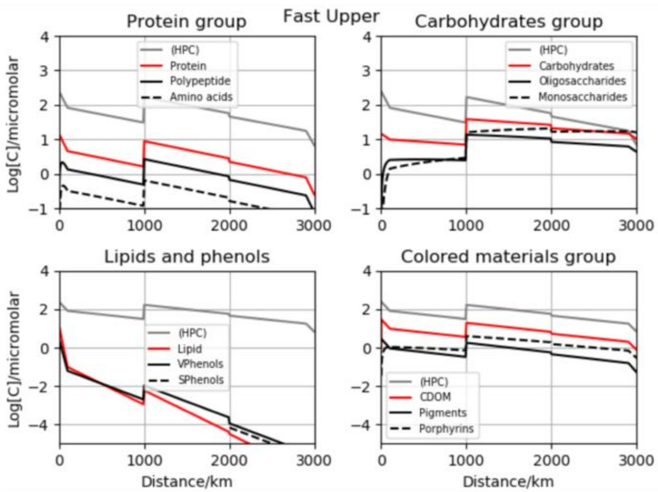
- Dilution, CDOM and more
  - tool for examine the distribution
  - salinity and DOC relationship
- Statistics

$$RMS = \sqrt{\frac{\sum_{i=1}^{N}\left(x_{i,model} - x_{i,ref}\right)^2}{N}} \quad (3)$$

Model run	RMS	Group	Average	Standard deviation
Fast_low	370	TDOC	550	250
Fast_upper	280	Proteins	11.5	3.5
Slow_low	180	Carbohydrates	25.2	10.6
Slow_upper	890	CDOM	8.6 (1/m)	4.1 (1/m)

Results: Other facts

- Major Bio macromolecular and Tracer Groups



- Biomarker phenols (lower left image)
- V-phenol -present in high altitude litter
  -react either photochemically or microbially
- S-phenol -form enters the main flow only later
  -tundra marker

- Aqueous Volatile Organics

- Biopolymers and macromolecules- can operate as the intra- or extracellular source for organic gases (isoprene)
- Organic gases trapped in soil are volatile, equilibration of the aqueous medium comprised by the river is rapid.
- Ventilation into pristine air masses and equilibration with forest haze plumes were both shown to be extremely rapid.
- Similar –mountain, high solute and tundra

Conclusion

- Relatively slow transformation rates along the water course.
- Channel combinations and mixing play the dominant role.
- Microbial and photochemical losses help determine final coastal concentrations for most species.
- Chemical evolution is distinct for the various functionalities tracked, with special contributions from pre- and post reactivity in soil waters and the delta.
- Portions of several organic groups are combined to represent the collective colored or chromophoric dissolved organic matter, characterized by its absorption properties.
- Outlet concentrations of individual species such as protein and adsorbers lie well above threshold values for biophysical influence on adsorption

Future Work

- From idealized river to true major systems: Lena , multimode system
- Particles to study interactions with condensed organics and minerals –flocculation
- Size distribution will include minerals

Thank you