

Temperature dependent sulfate transport and reaction in sediment

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Wild Rice Standards Study mid-project review

February 28-March 1, 2013

Outline

1. Conceptual study design
2. Methods description
 - Sediment collection
 - Microcosm preparation/maintenance
 - Experimental phases and sampling plan
3. Theoretical model of temperature effects

1. Sulfate transport and transformation
 - Sulfate is relatively non-reactive in waters containing oxygen
 - Sulfate transported into anoxic sediments from the overlying water via passive (molecular) or active (biologically enhanced) diffusion
 - Sulfate biologically transformed to sulfide in environments lacking oxygen
2. Effect of temperature
 - Sulfate diffusion depends on temperature ($\sim 1.35x$ per 10°C)
 - Sulfate reaction depends on temperature ($\sim 2-4x$ per 10°C)
3. Sulfide chemistry
 - Sulfide participates in several types of reactions
 - pH defines distribution between $\text{H}_2\text{S}_{(\text{gas})}$ and HS^-
 - Presence of iron and other metals form relatively insoluble solids ($\text{FeS}_{(\text{solid})}$, etc.)
 - Sulfide can be re-oxidized back to sulfate in the presence of a favorable electron acceptor (O_2 , Fe^{3+} , NO_3^-)

- Ongoing and historic mining on Mesabi Iron Range has led to some water bodies with elevated sulfate (>500 mg/L)
- Sulfate standard includes language related to the timing of sulfate release (limits imposed when harmful to rice)
- Key question:
 - What would happen to sulfate released to a surface water body during cold winter months when rice is not growing?

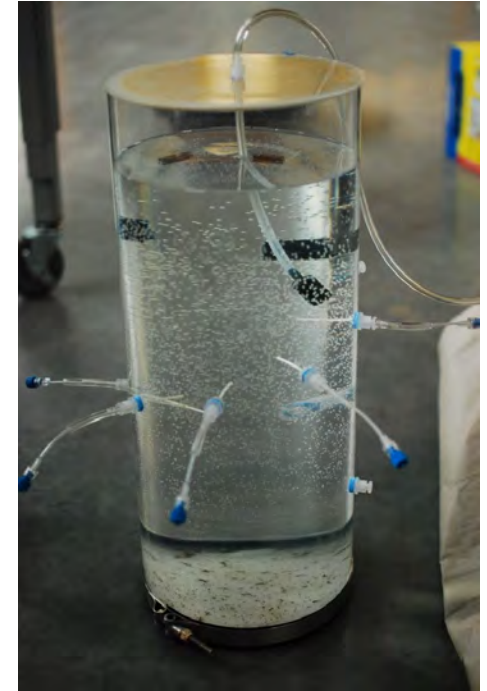
Objectives

1. Measure the flux of sulfate into and out of sediment at temperatures relevant for summer and winter in MN
 - Two contrasting types of sediment used in the lab to investigate quantity/type of organic matter
 - Two contrasting temperatures to simulate summer and winter
 - Initial phase, loading phase, recovery phase.
2. Develop a model the flux of sulfate into and out of sediment at different temperatures to predict depth of penetration, rates of diffusion out, and rates of sulfate reduction.
 - Include temperature dependence of diffusion rate
 - Include temperature dependence of reaction rates
 - Calibrate model to observations made in lab

Methods

Microcosm fabrication

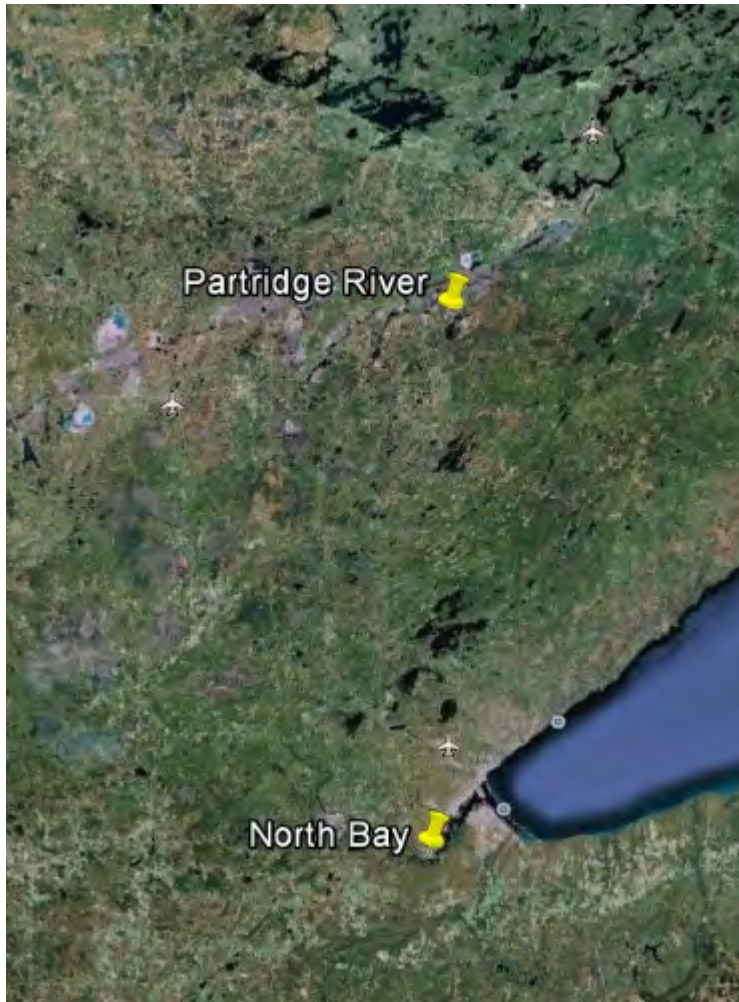
- Polycarbonate/Acrylic 8" diameter tubing (1/8" wall thickness)
- Buna and silicone O-rings
- 100% Silicone Caulk around base
- Teflon tubing used for air bubbling
- Custom fitting to insert Rhizon filters (0.2 μm pores) at 2 cm depth spacing in sediment



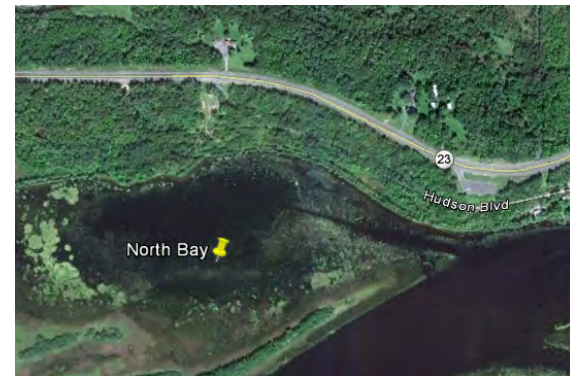
Methods

Site selection

- Two riverine sites with contrasting levels of organic matter



- Partridge River
- ~75 mg/L SO_4 in overlying water
- 16% OC



- North Bay (St. Louis River, near Duluth)
- ~15-25 mg/L SO_4 in overlying water
- 6% OC

Methods

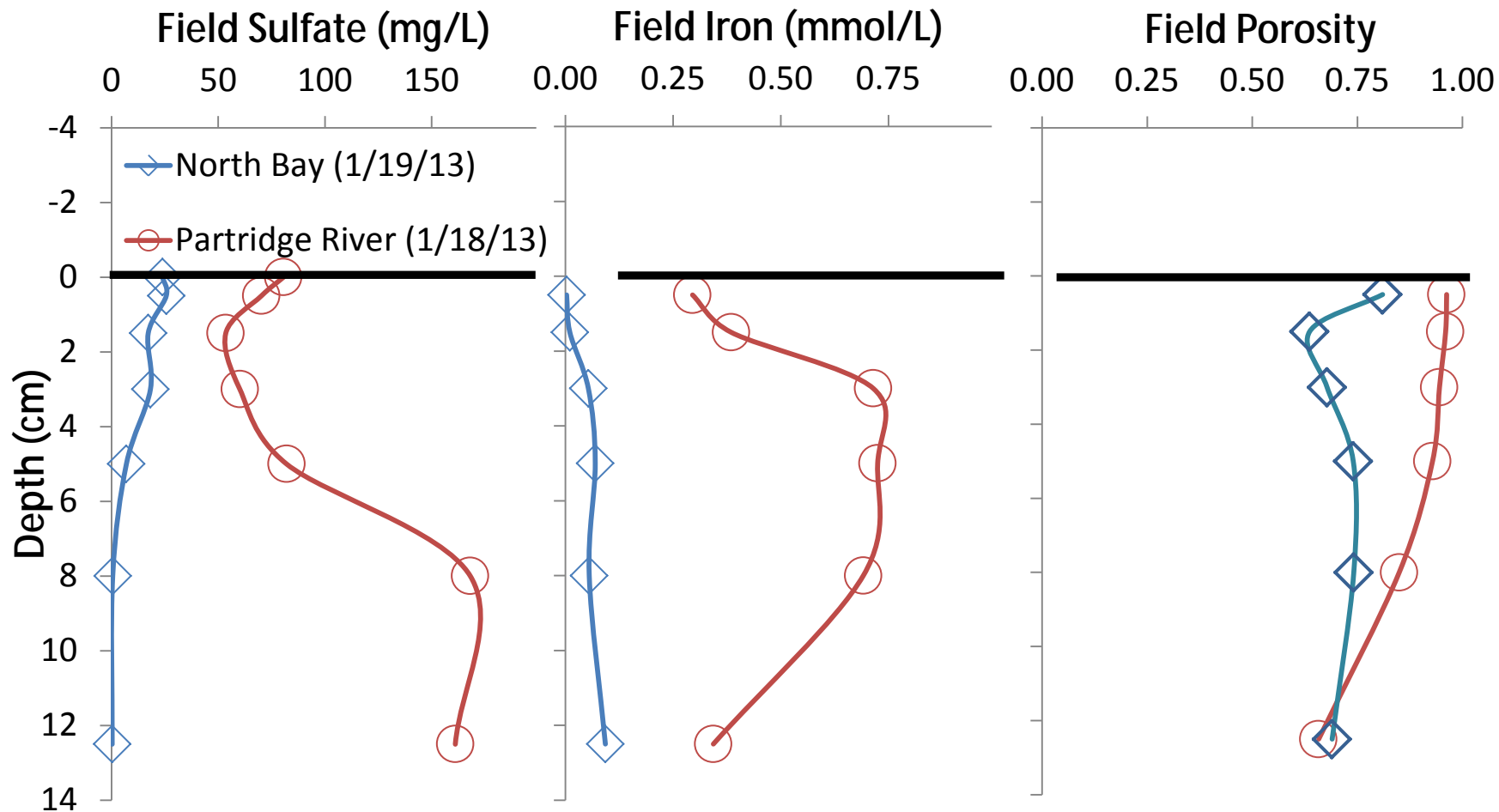
Sample collection

- Site water collected for producing overlying water amendments
- Bulk sediment from the approximately top 10 cm collected through the ice
- Small diameter (~2.5") cores also collected for characterization of in-situ sediment density and chemistry
- Sediment and water samples stored at 4 °C until the initiation of experiments (~4 weeks)



In-situ measurements

sulfate, iron, porosity



Note that this slide contains preliminary information, which the MPCA is using to guide the collection of additional study data. It is not appropriate to draw conclusions from the information prior to study completion.

Sediment Homogenization

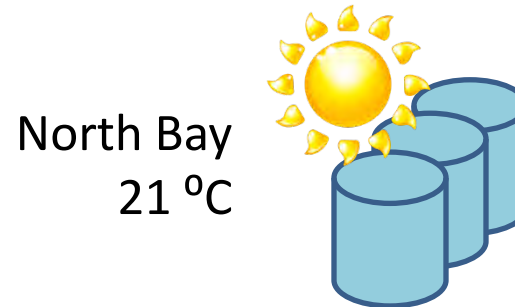
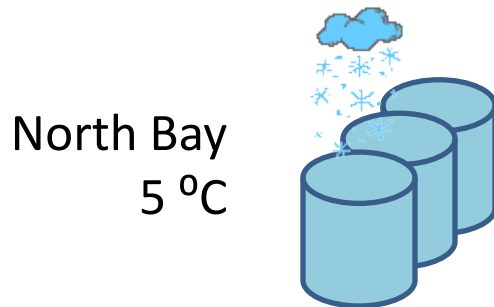
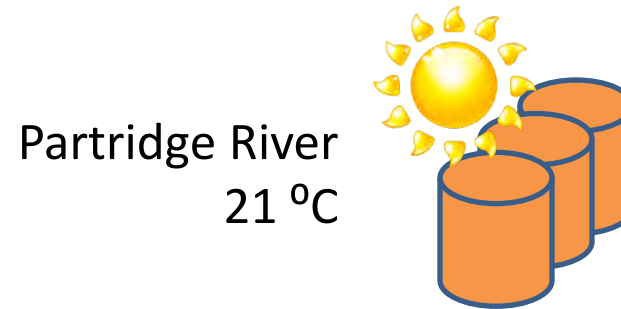
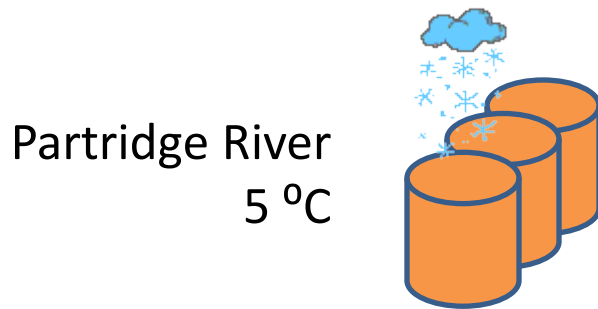


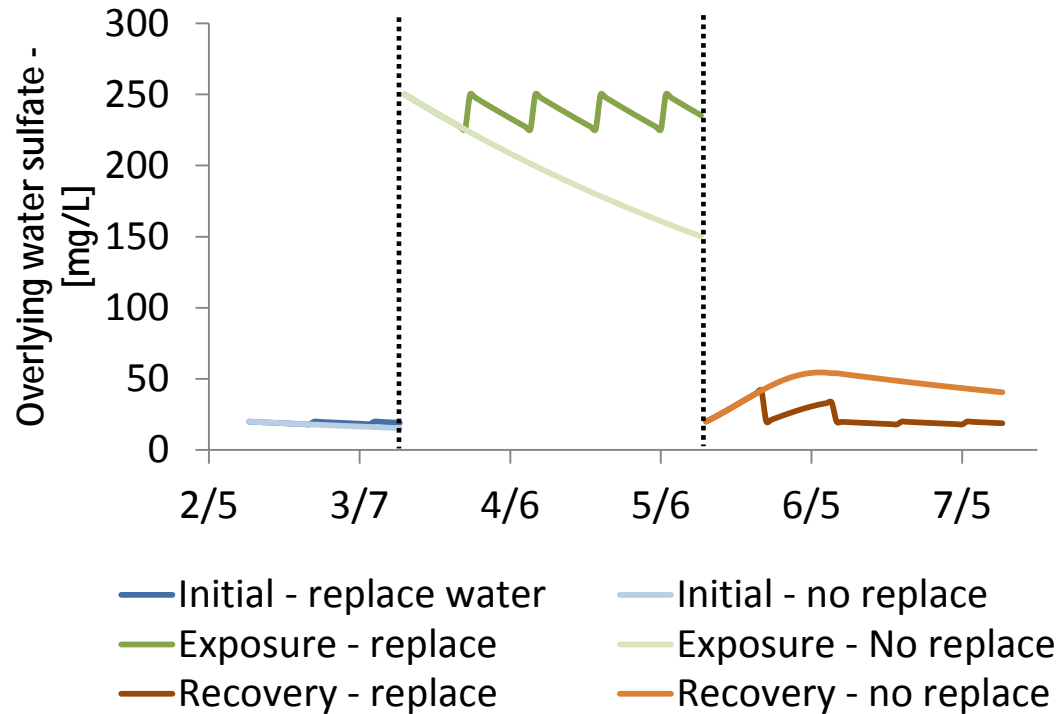
- Sediment from each site was mechanically mixed in a 35 gallon drum with a low R.P.M drill and a mudding paddle
- The sediment in the microcosm was then shaken using a consolidation table to remove voids

Methods

experimental design

- Triplicate microcosms from each site incubated (in the dark) at two different temperatures





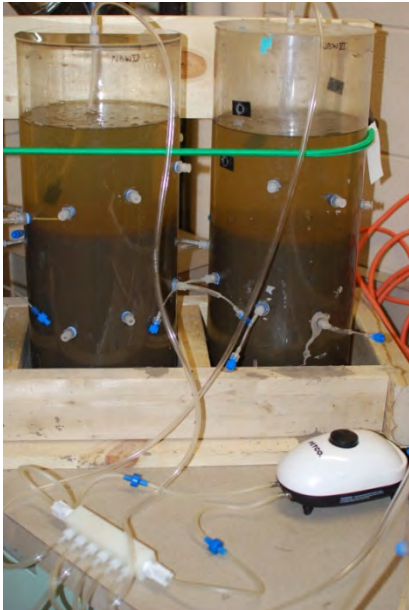
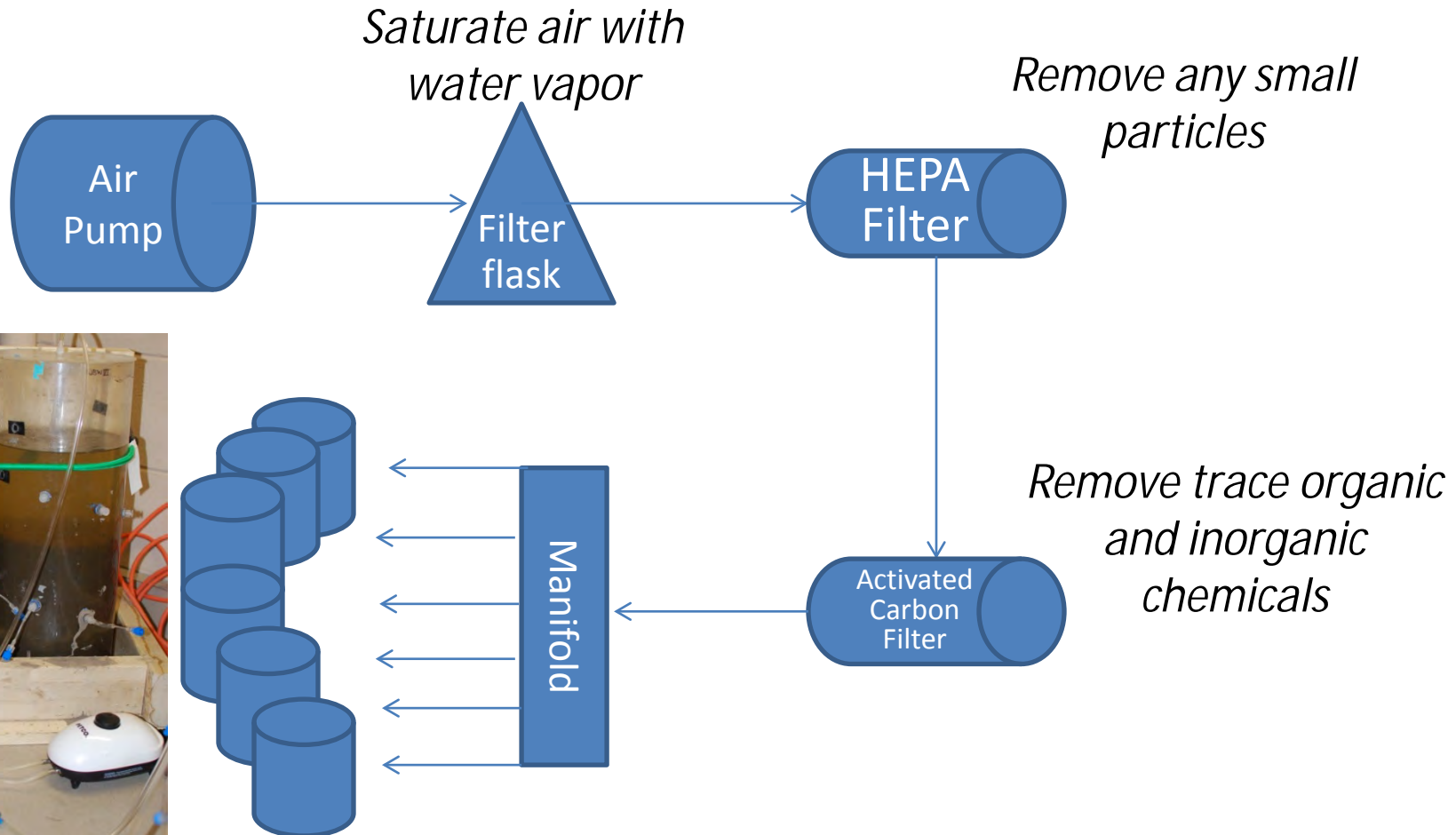
- Three experimental phases (for both temps) including:
 1. Initial equilibration (in-situ sulfate in overlying water)
 2. Sulfate loading (250 mg/L sulfate)
 3. Recovery phase (in-situ sulfate)

- Sulfate amended overlying water will consist of site water with added sulfate (mixture of Calcium / Magnesium / Sodium salt)
- Relevant overlying water sulfate concentration determined by permitting considerations
- Inert tracer also added to overlying water to quantify diffusion in the absence of reaction
 1. Initial equilibration (in-situ sulfate in overlying water + chloride)
 2. Sulfate loading (250 mg/L sulfate + bromide)
 3. Recovery phase (in-situ sulfate + fluoride)

Methods

maintaining overlying water

Oxygenating/mixing the overlying water



- Microcosm water samples collected...
 - From overlying water, weekly
 - Purpose: maintain overlying water sulfate/tracer and calculate flux to/from sediment; change water when necessary
 - From porewater at beginning / end of each phase
 - Purpose: quantify depth of sulfate/tracer diffusion, potentially measure reduced species (iron/sulfide)

Modeling

effect of temperature

Modeling procedures:

- Time dependent reactive-transport model will be calibrated to observations

PDE:
$$\frac{dC}{dt} = D \frac{d^2 C}{dx^2} - u \frac{dC}{dx} - kC$$

$$C_{ss}(x) = C_0 e^{-\frac{u}{D}x - \frac{k}{D}x^2}$$

$$C(x=0) = C_0$$

$$D_w \Big|_T = D_w \Big|_0 + 0.2125 \times 10^{-6} * T$$

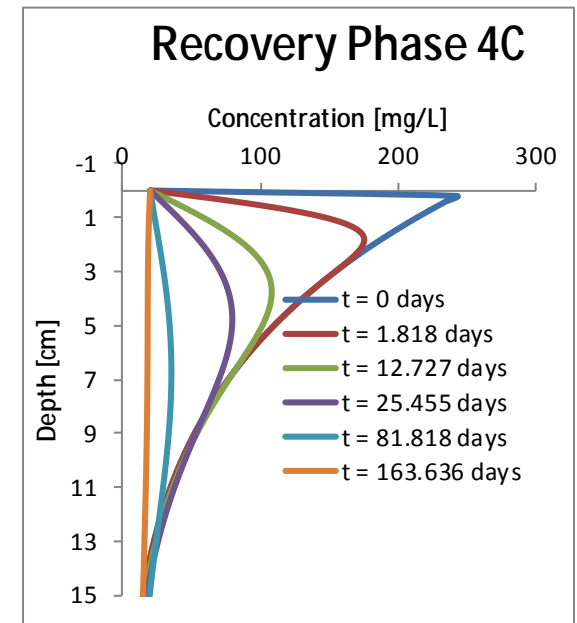
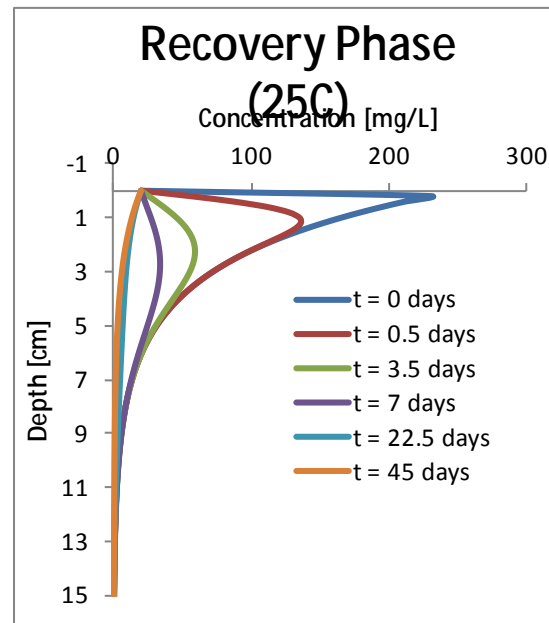
$$k \Big|_T = k \Big|_{25} Q_{10}^{\frac{T-25}{10}}$$

BC & IC:
$$\frac{dC(x=L)}{dx} = 0$$

$$C(t=0) = f(x)$$

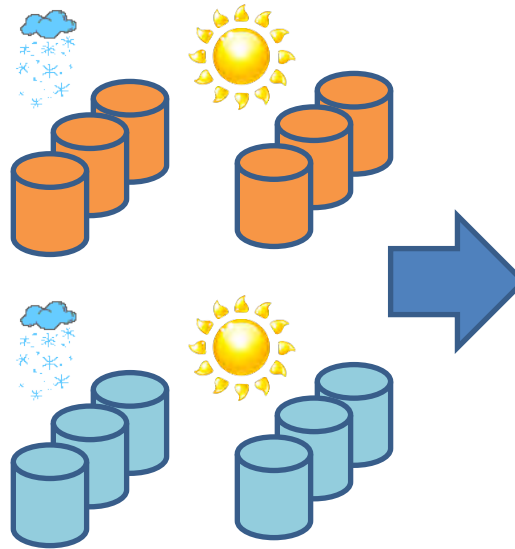
Preliminary Modeling: Theoretical effect of temperature (hypothesis to be tested)

Theoretical time for diffusion / reaction to remove sulfate considerably (5-10x) longer at 5 °C than 21 °C



Related / future work

- Measure effective diffusion in field to enhance model's utility
- Test preliminary porewater geochemistry lab results in field conditions
- Understand when (in spring) sediment warms and significant sulfate reduction begins



Questions / comments

