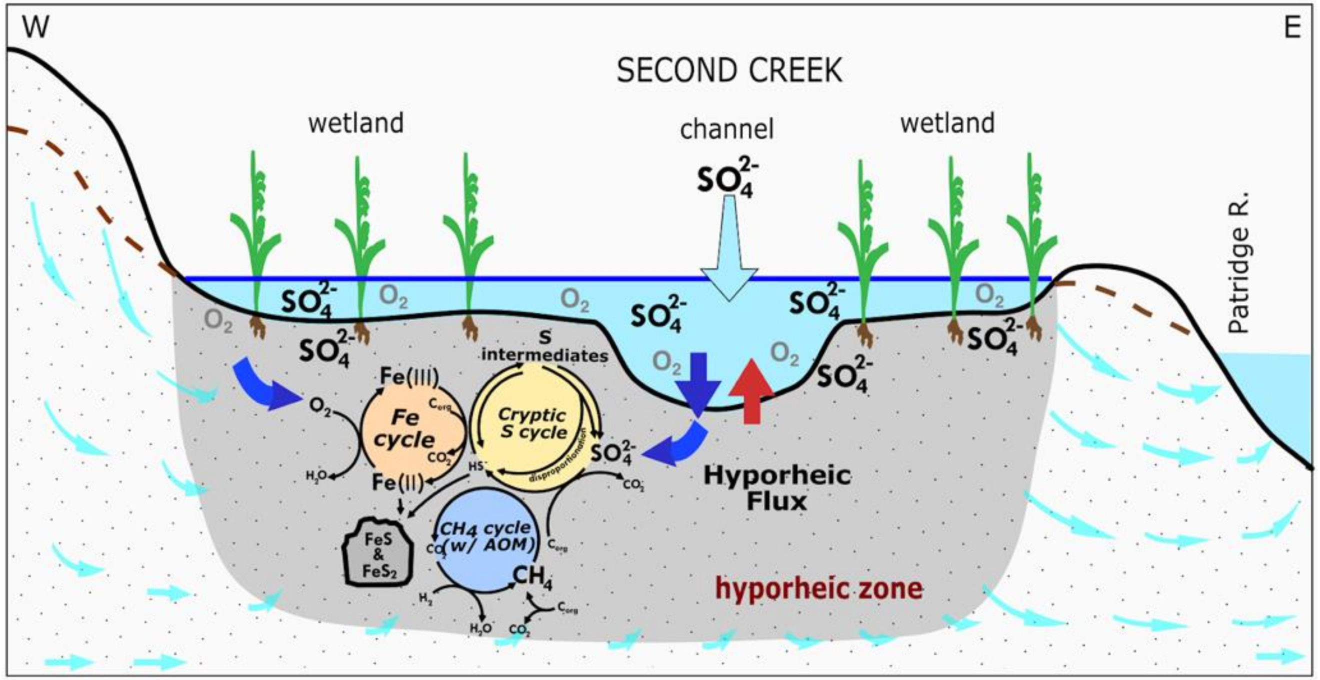
Uncovering hidden sulfur biogeochemical cycles in a sulfate-impacted riparian wetland and stream in northeastern Minnesota



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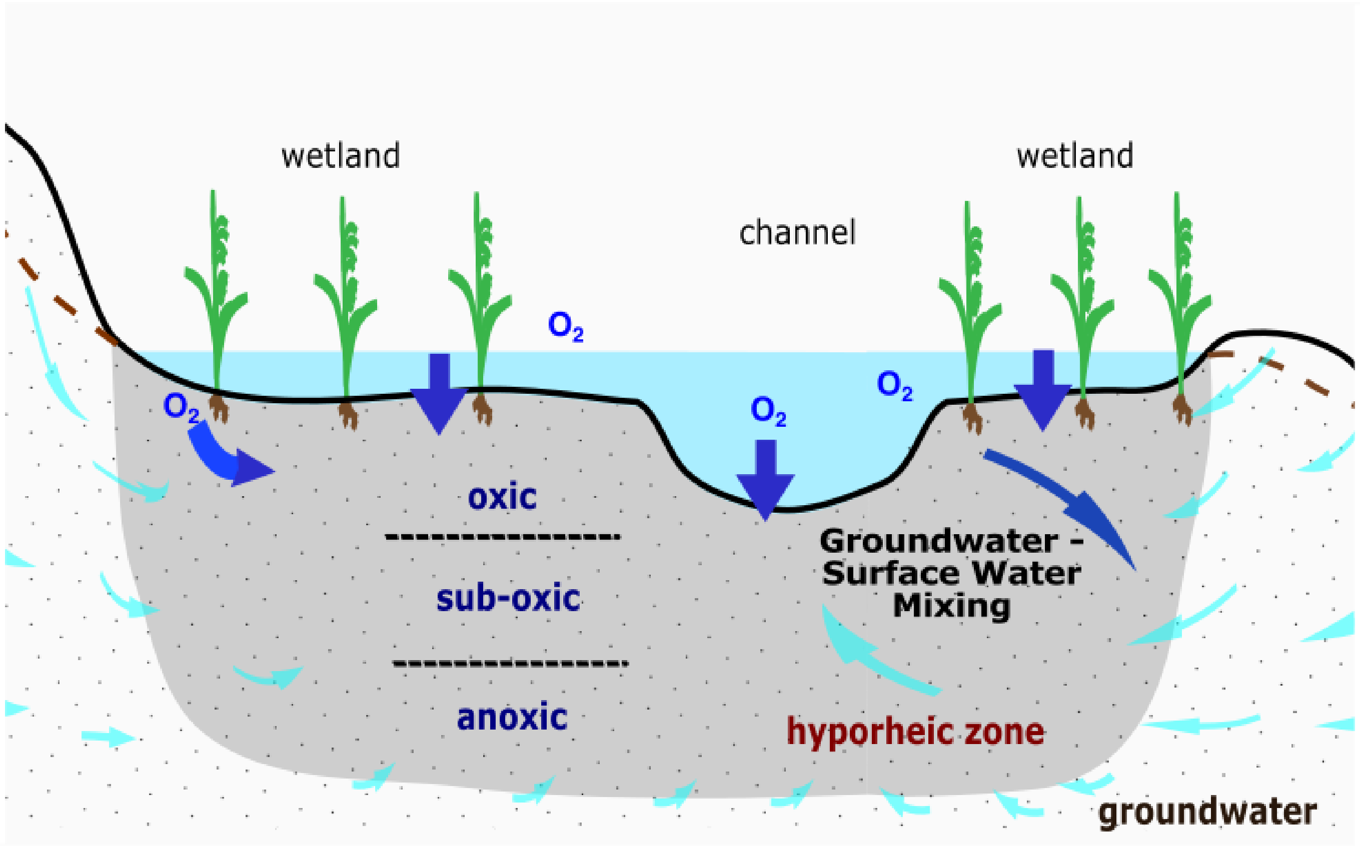
Hyporheic Zone Hydrobiogeochemistry

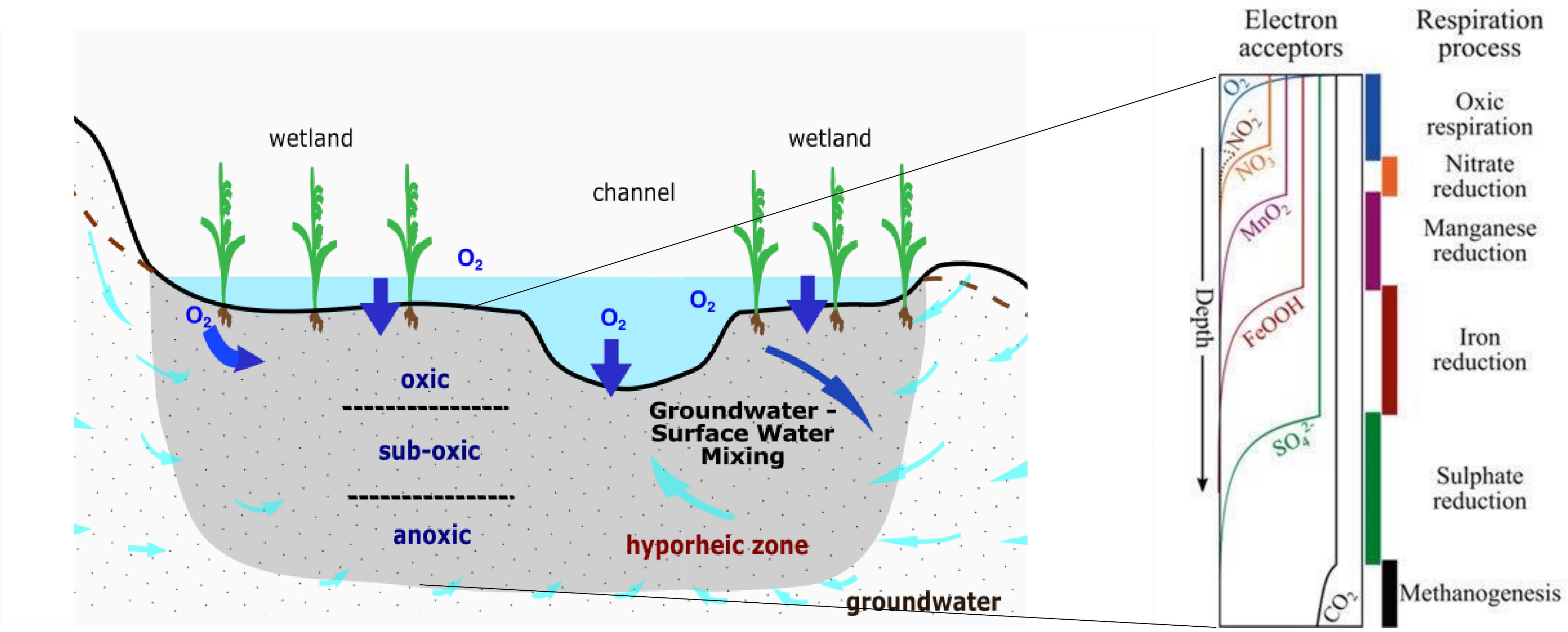
Biogeochemical cycling of nutrients/metals has **important environmental impacts**!



Changes in flux magnitude and direction will impact redox gradients and biogeochemical cycling, and ultimately nutrient/ contaminant fate and transport.

Hyporheic Zone Hydrobiogeochemistry

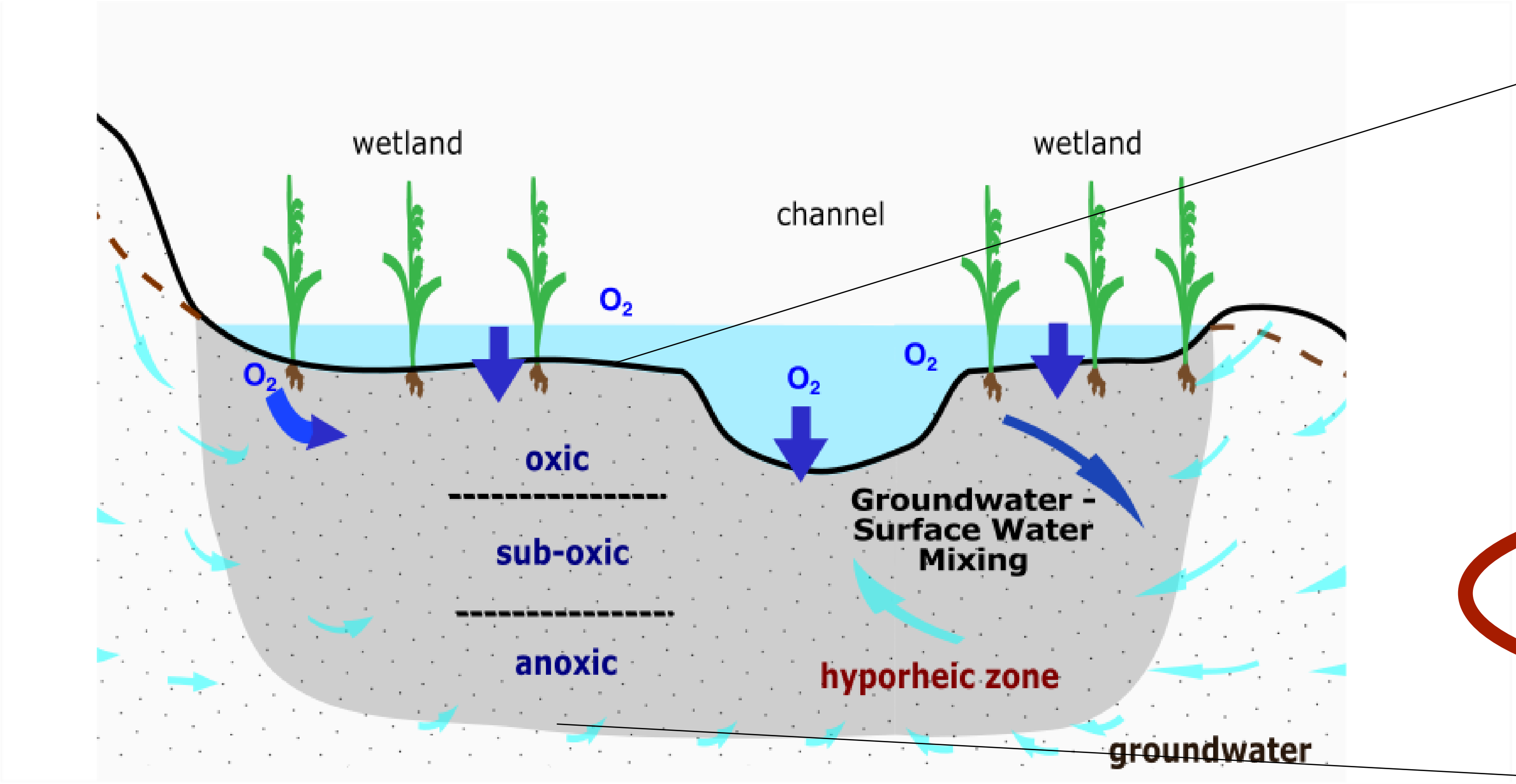
Microbially-driven and abiotic geochemical oxidation-reduction **"redox" reactions occur in a gradient** across this zone. This gradient can be quite dynamic, **influenced by water fluxes**!

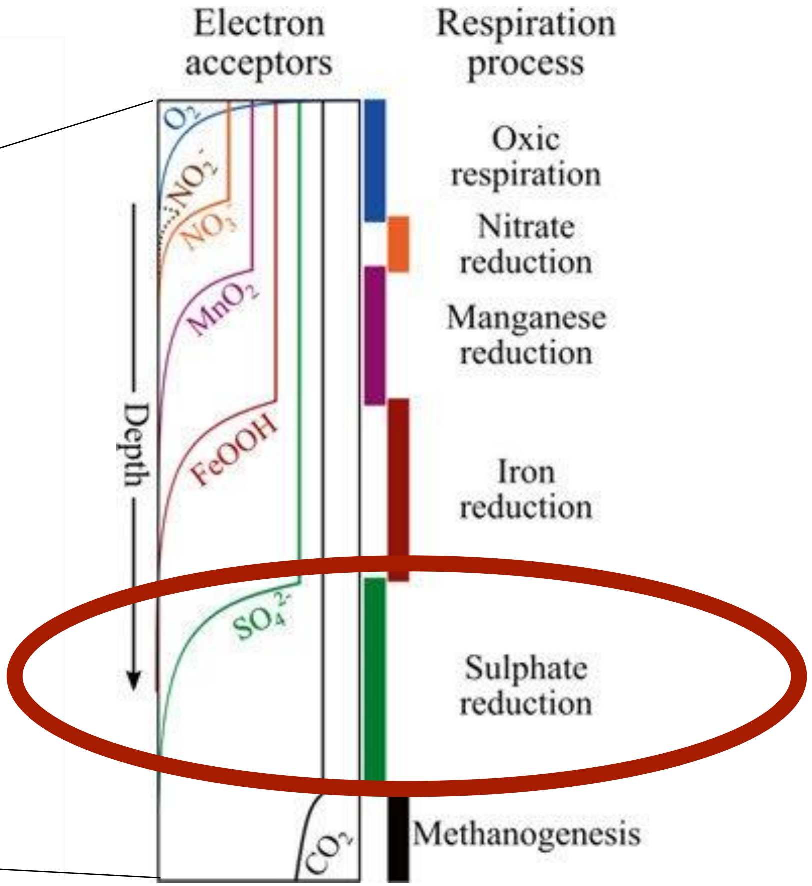


Steffen Weirs, 2020

Why is sulfur overlooked in freshwater environments?

Sulfate concentrations are low in most systems.



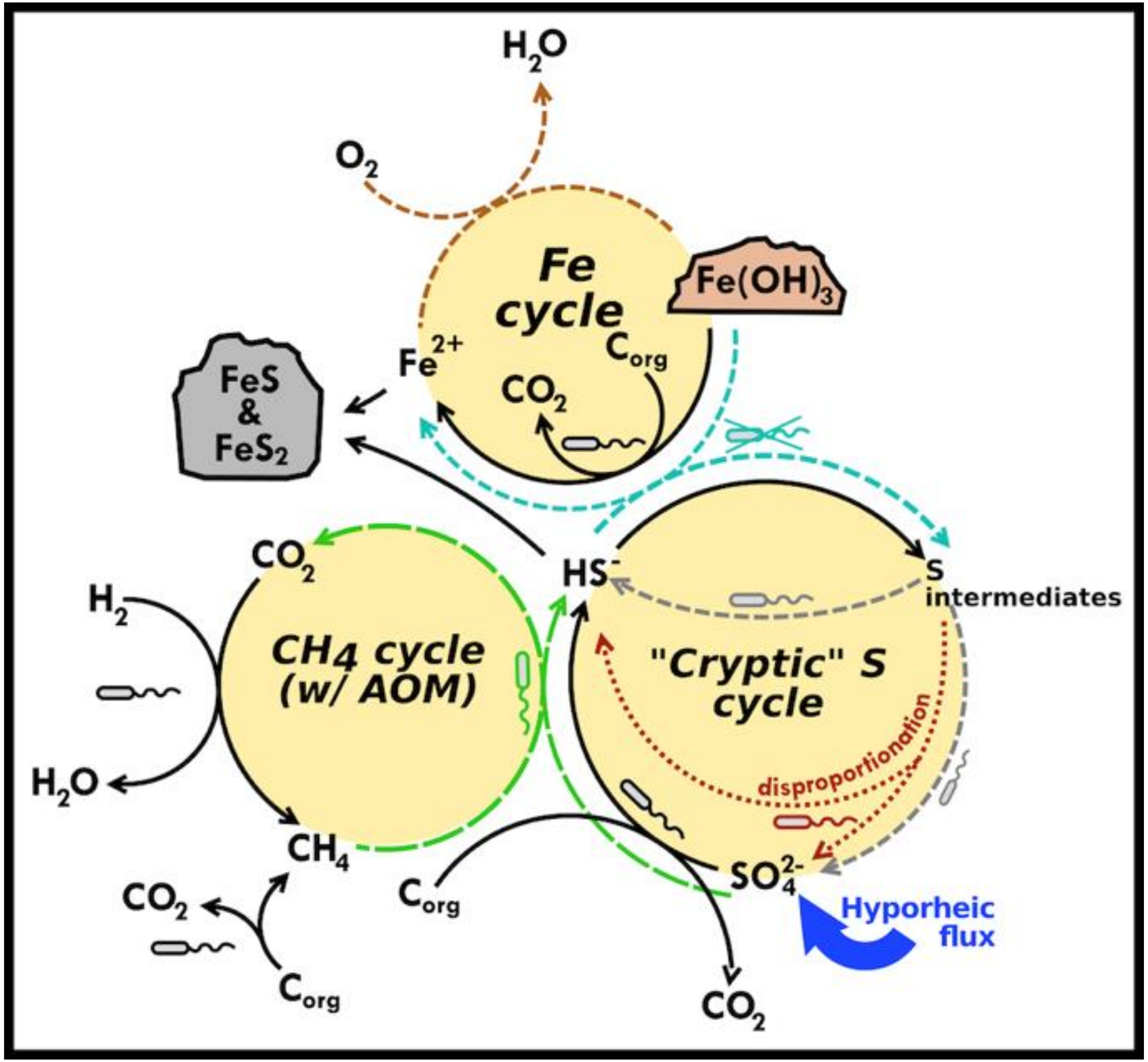


Steffen Weirs, 2020

But S inputs increasing due to agriculture (Hinckley et al., 2020) and industry.

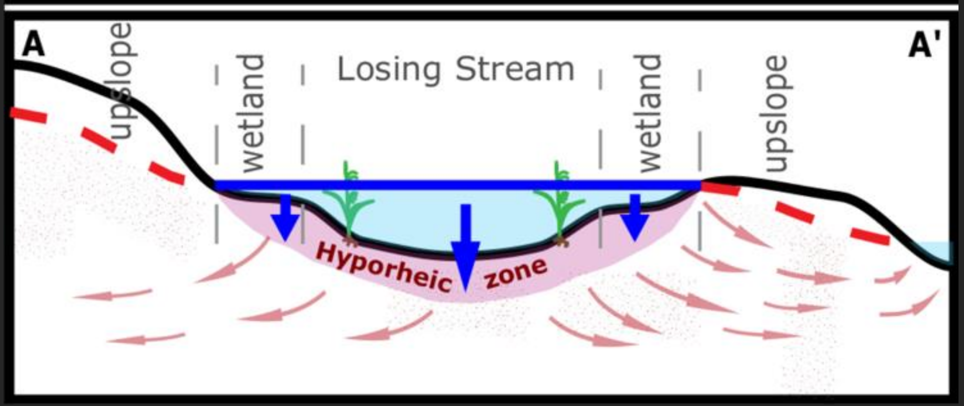
Why care about S cycling in freshwater wetlands and streams?

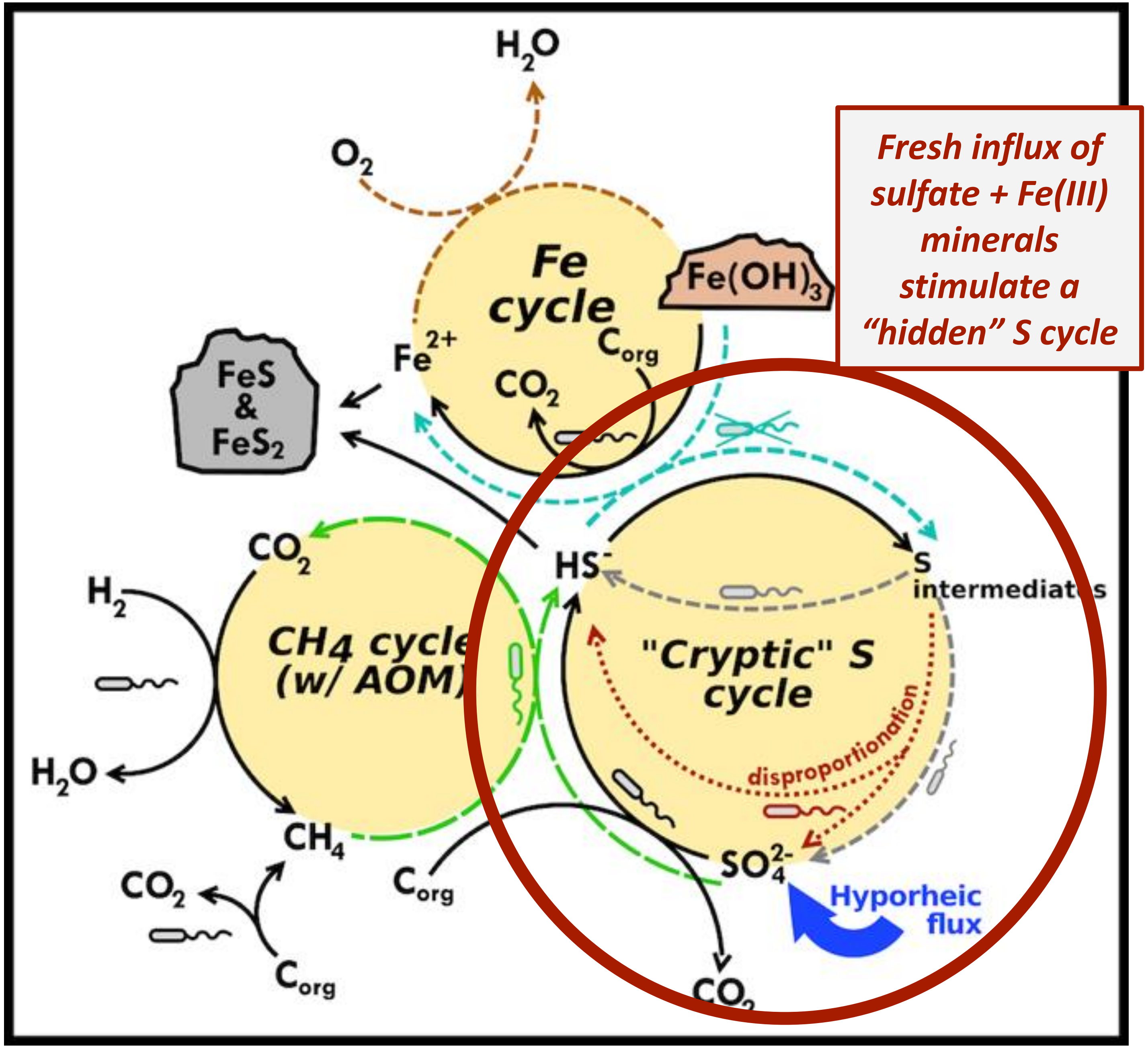
- S high/increasing in industrial (e.g., mining) and agricultural waters
- Coupled to Fe (nutrient) cycling and bioavailability
- Coupled to methane cycling and may impact emissions



Linked Fe-S-C biogeochemical cycling in hyporheic zone stimulated by dynamic hydrologic fluxes

Dynamic hydrologic fluxes can push oxygenated waters into subsurface, altering redox gradients





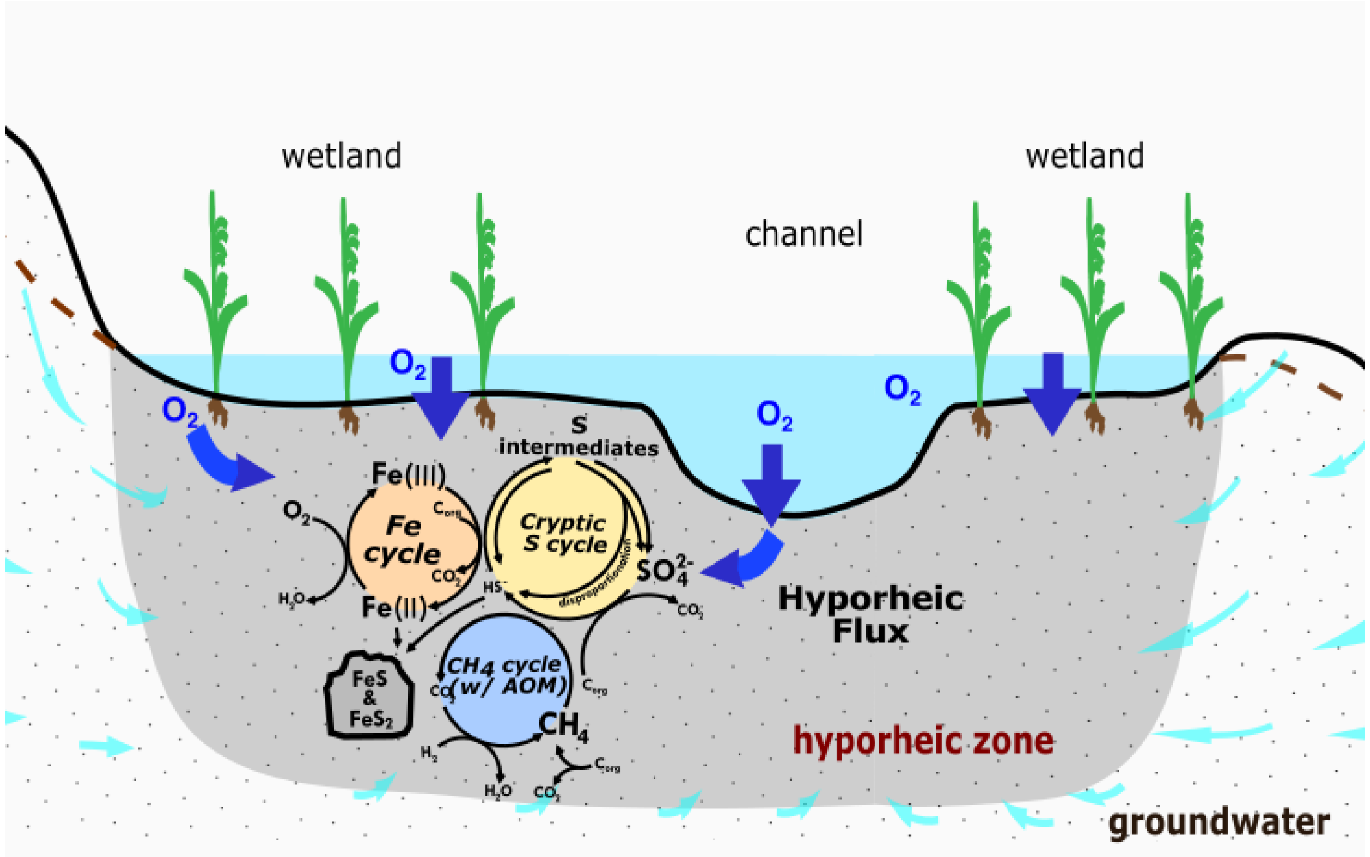
Fresh influx of sulfate + Fe(III) minerals stimulate a "hidden" S cycle

Pester et al., 2012; Hansel et al.,

Objectives

Establish the connection between hyporheic flux and subsurface “cryptic” S cycle coupled to Fe and C redox cycling

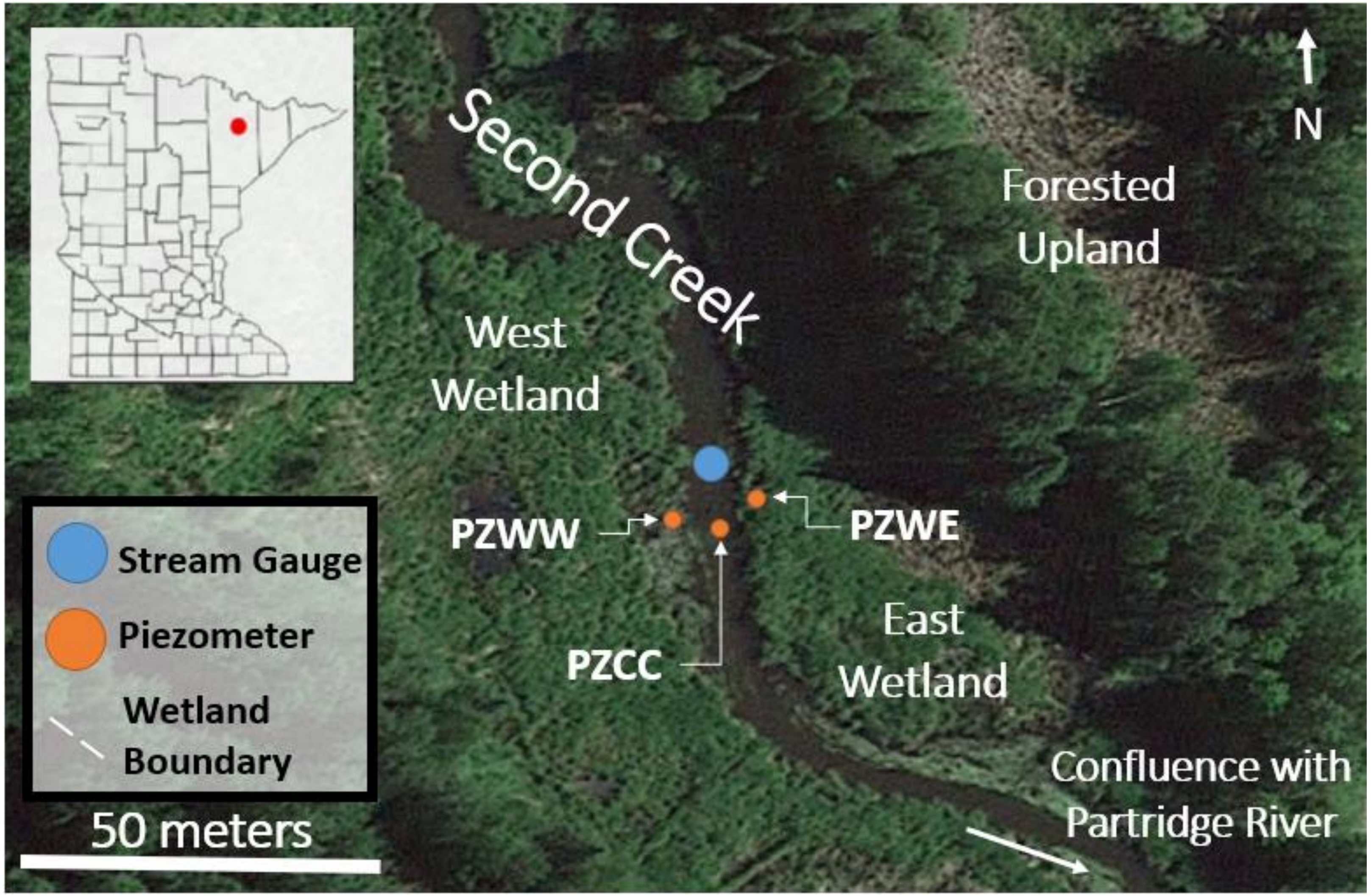
Determine products and impacts of high sulfate water due to cryptic S cycling



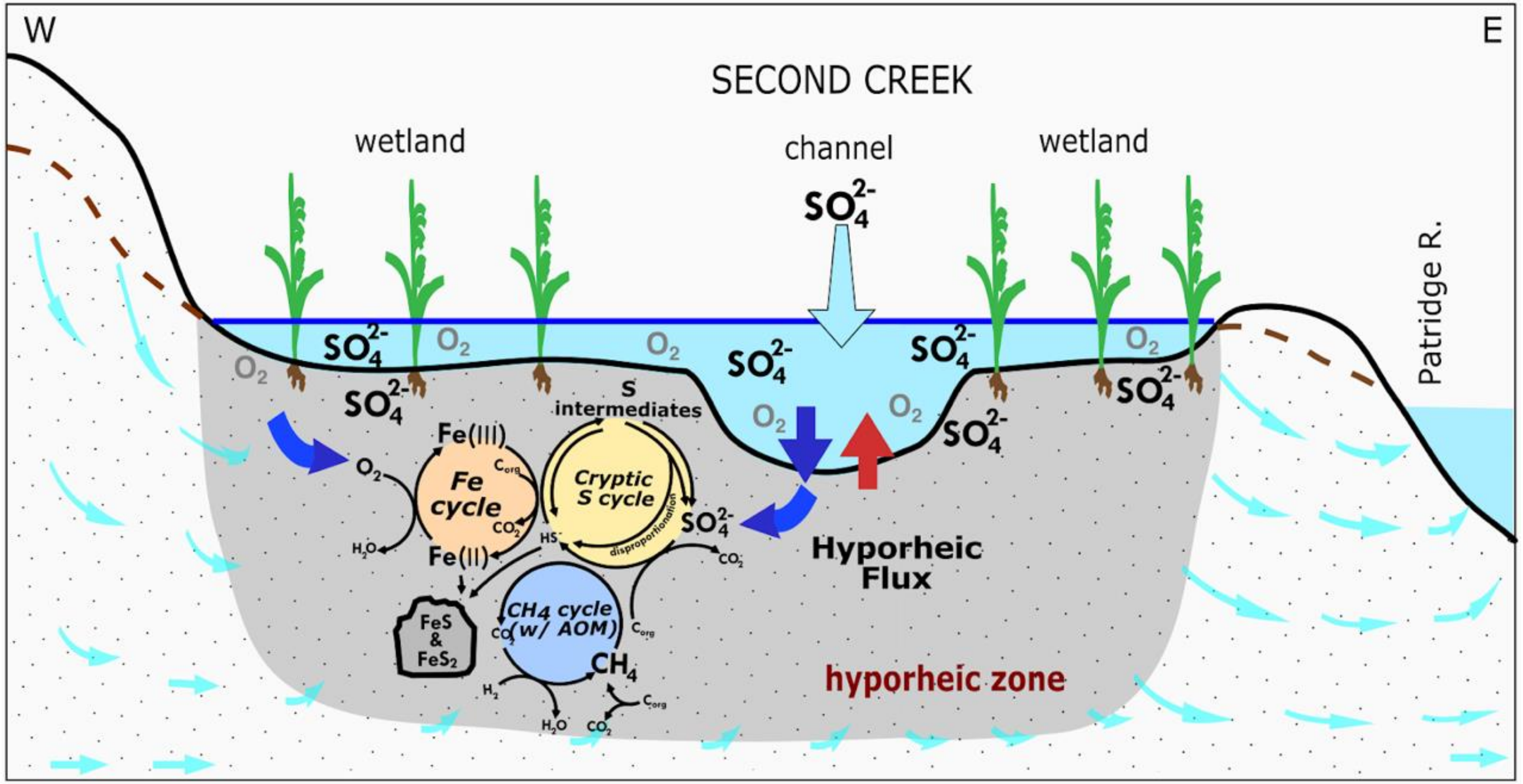
Evidence for cryptic S cycling, influenced by dynamic hyporheic fluxes, in sulfate-impacted stream

Second Creek (Northern MN)

- Mixed boreal-deciduous ecotone
- Second Order stream just downstream of iron ore mining operations
- Fully inundated year round
- High sulfate (1-10 mM) in surface water
- Low nitrate in surface water
- High iron in subsurface
- pH ~7-8



Second Creek riparian wetlands and stream channel



Wetlands
Grasses/Sedges
Organic Carbon rich
Fine particle size

Channel
Sparse plants
Moderate C_{org}
Moderate particle size

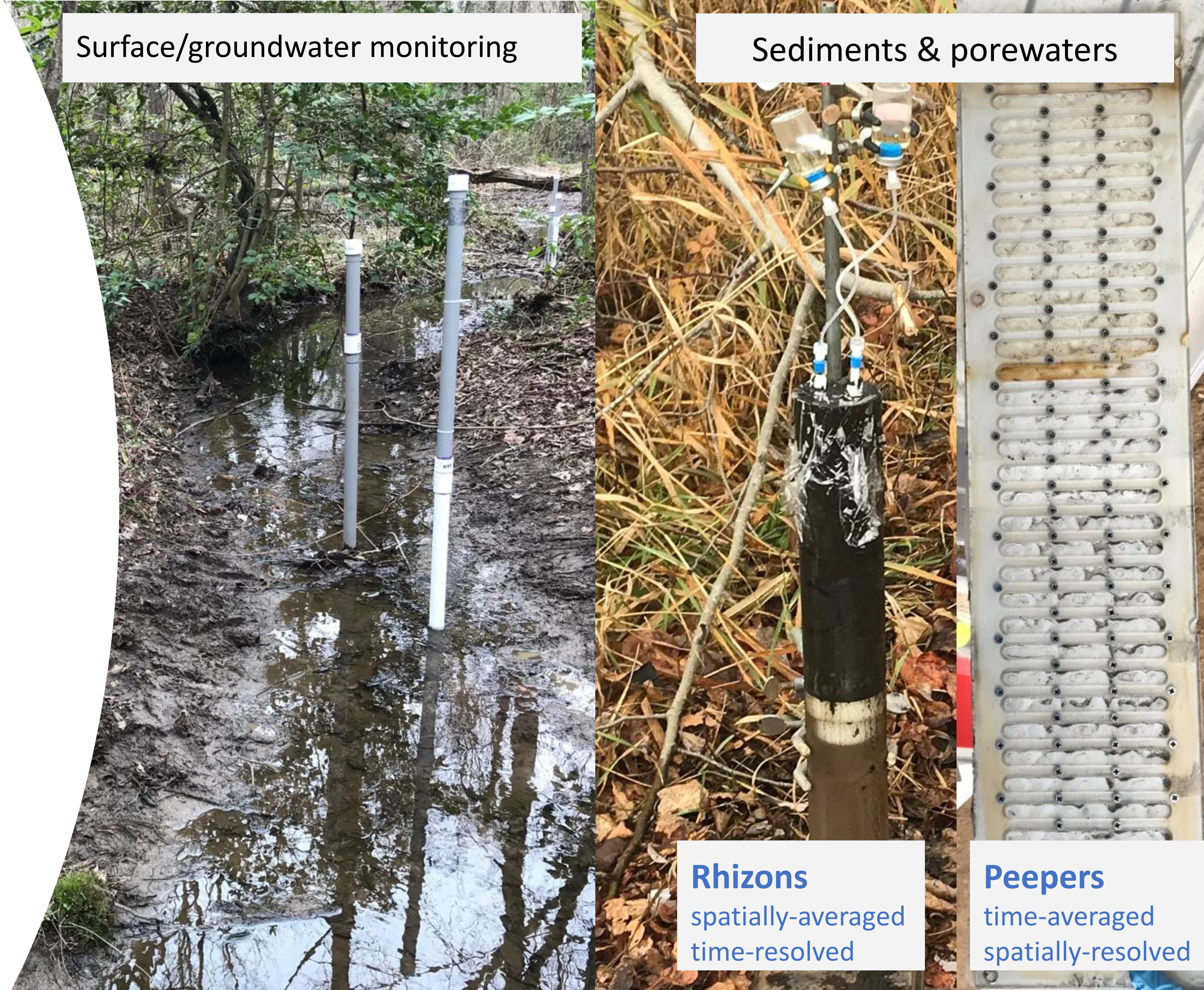
Objective

Establish the connection between hydraulic flux and occurrence of a subsurface “cryptic” S cycle coupled to Fe and C redox cycling

Multi-pronged approach

Field observation:

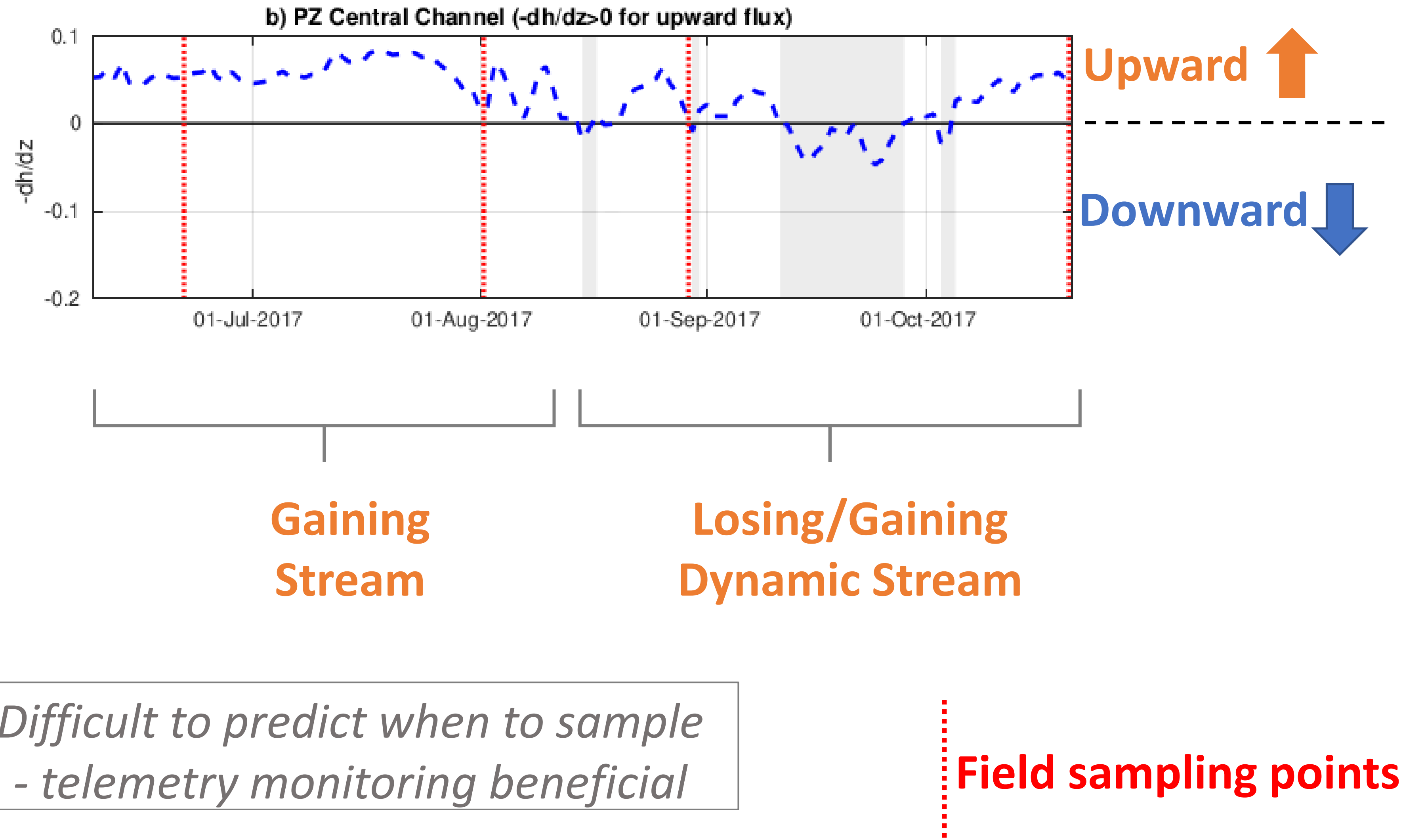
- Hydrologic conditions
- Geochemistry
  - Surface water
  - Porewater
  - sediment



Hyporheic exchange:

Are wetlands and stream gaining or losing? Change with time?

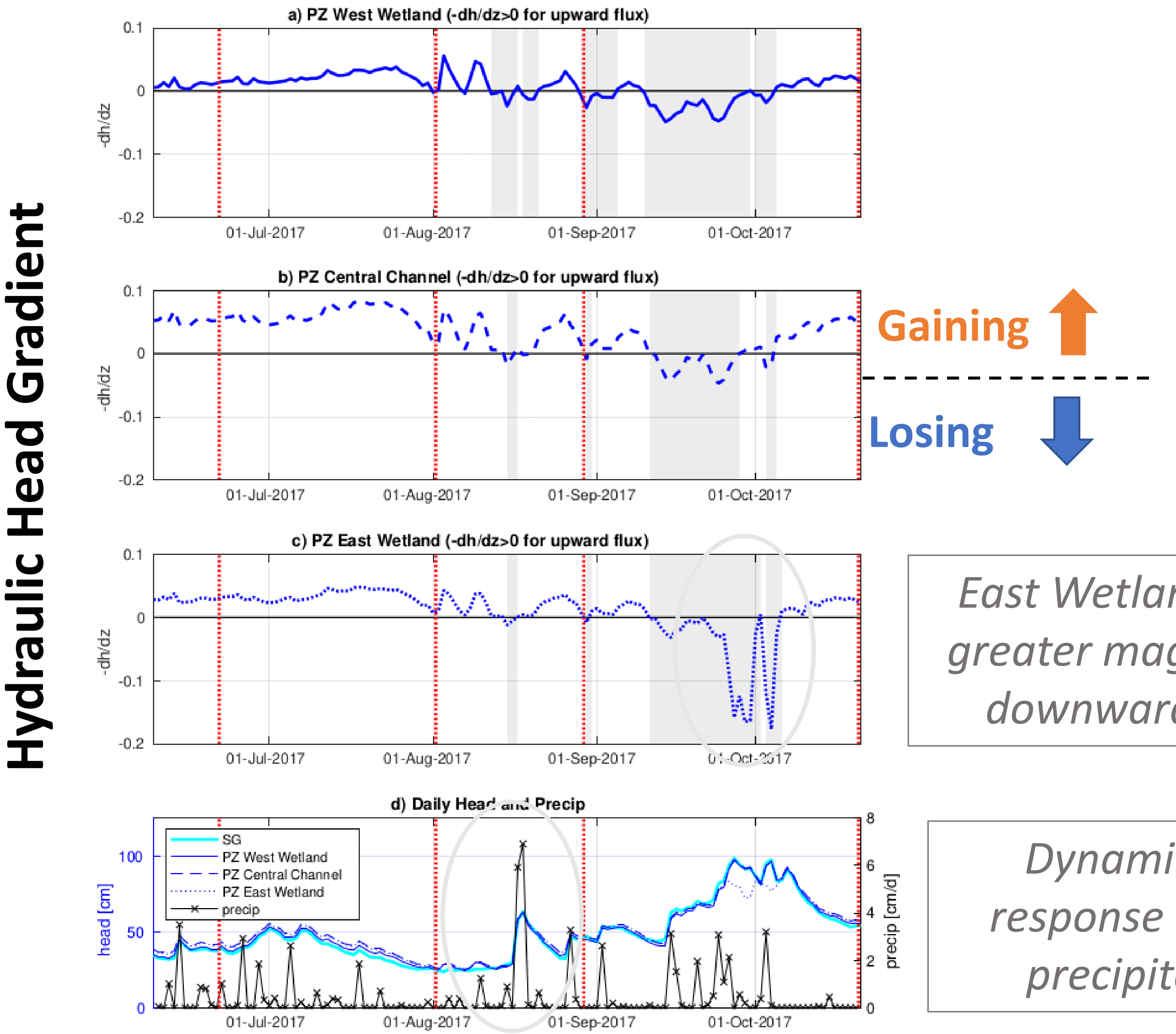
Hydraulic Head Gradient (Central Stream Channel)



Difficult to predict when to sample - telemetry monitoring beneficial

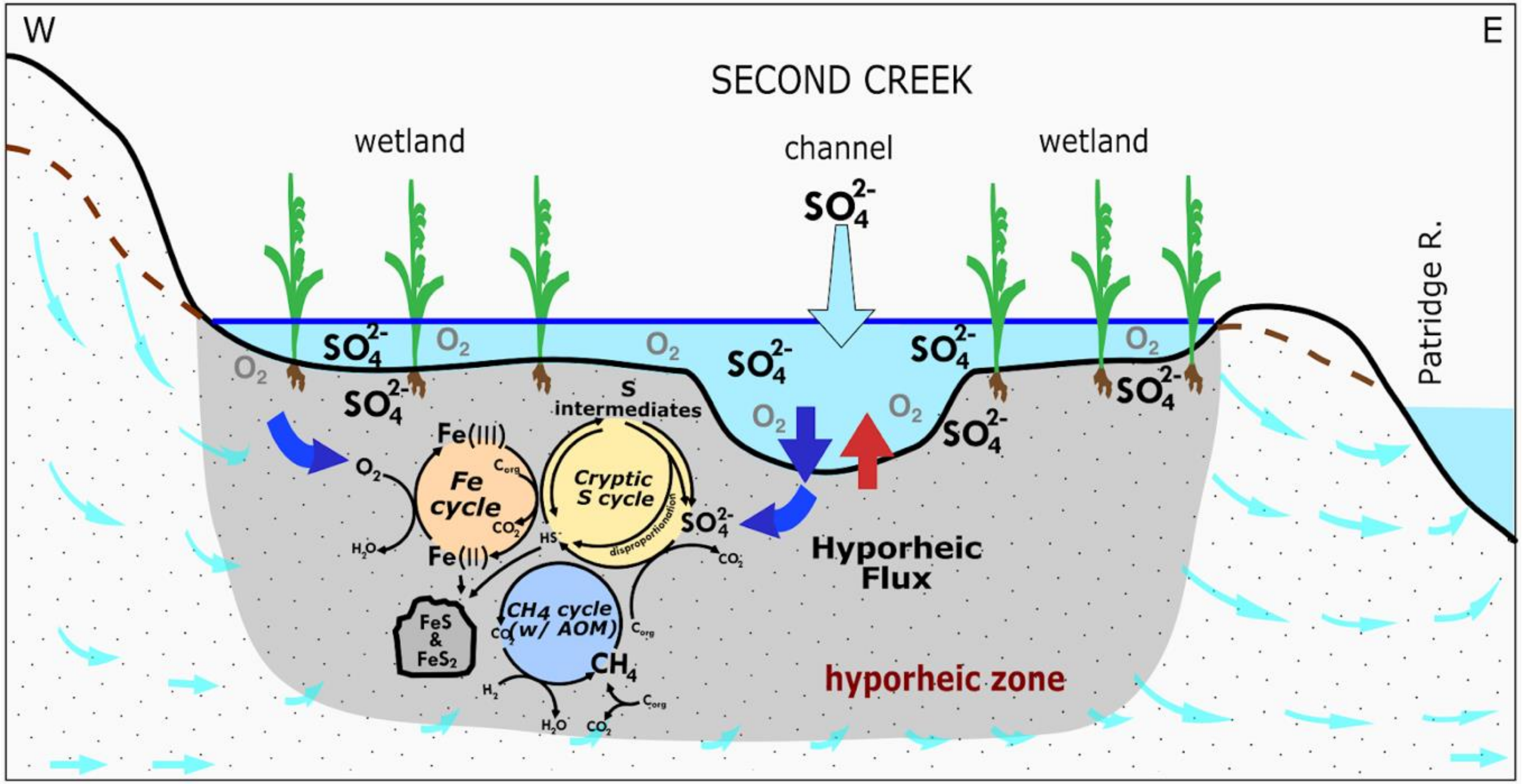
Hyporheic exchange:

Are wetlands and stream gaining or losing?



East Wetland saw greater magnitude downward flux

Dynamic flux response to high precipitation



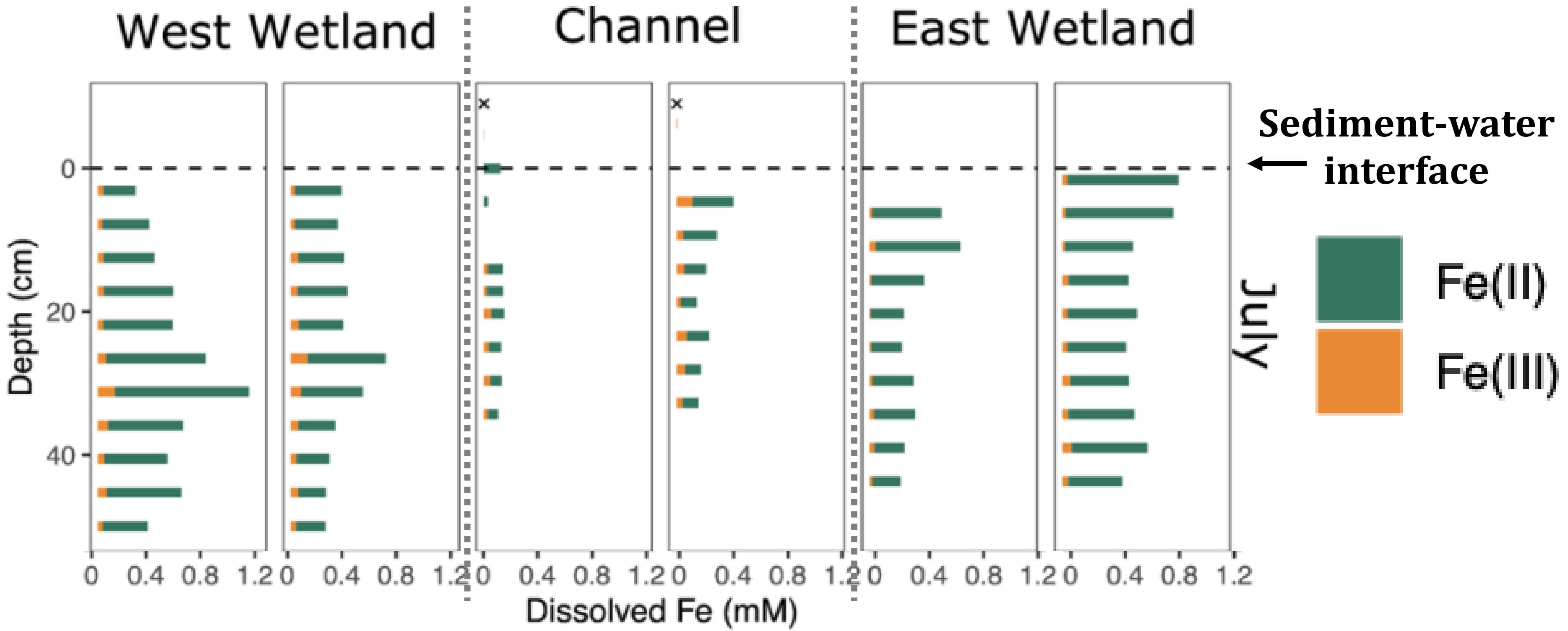
- *How does geochemistry respond to changes in hyporheic flux?*
- *Vary with location (wetlands vs. stream)?*
- *Evidence of Cryptic S cycle?*

Porewater Aqueous Iron

(Fe^{2+} + colloidal Fe^{3+})

High iron in porewater

Aqueous Fe(III) chelated by organics?



Fe(II) dominant

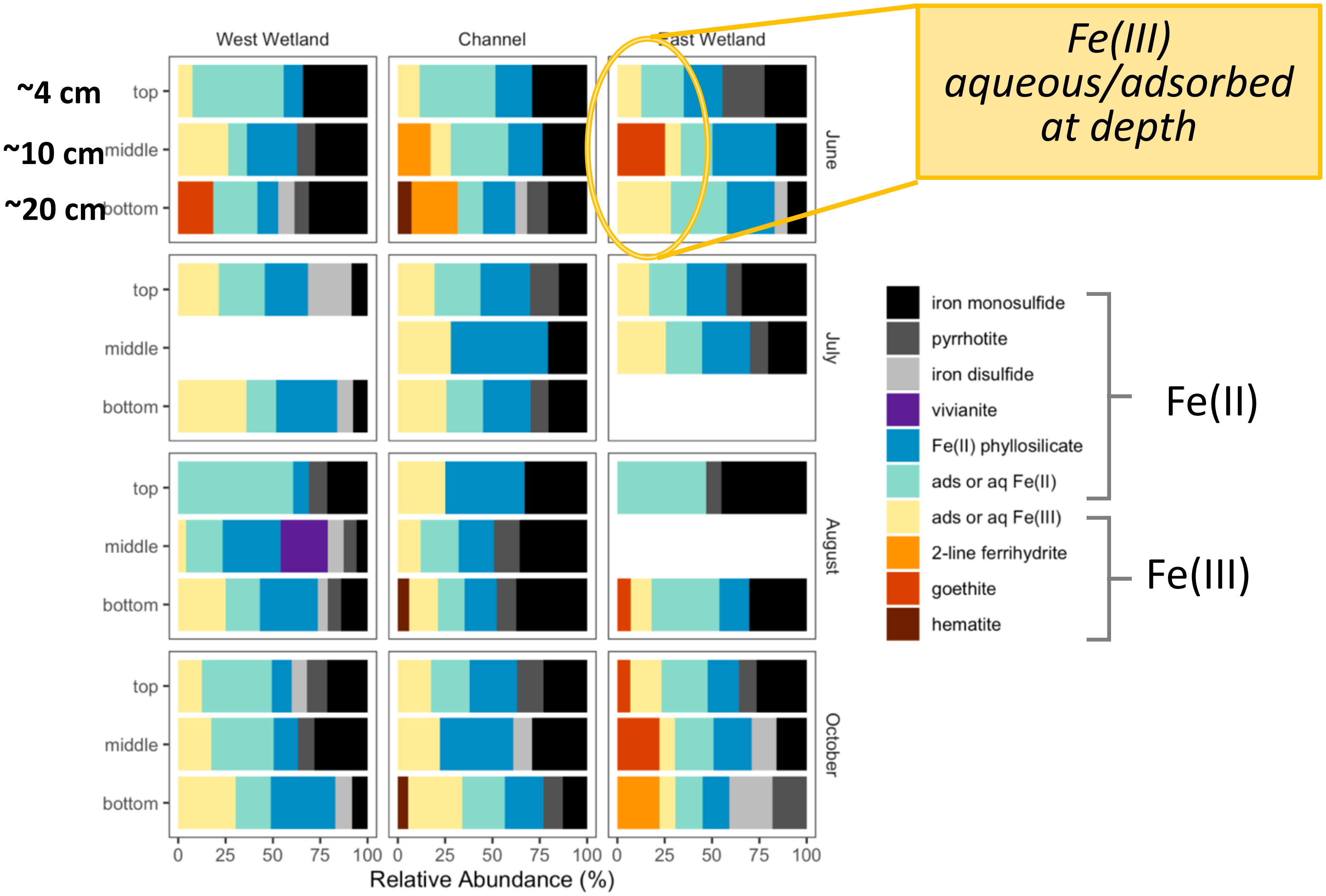
Fe(III) present at depth

Higher Fe_{total} in wetlands

Trends consistent throughout summer/fall

Sediment Iron

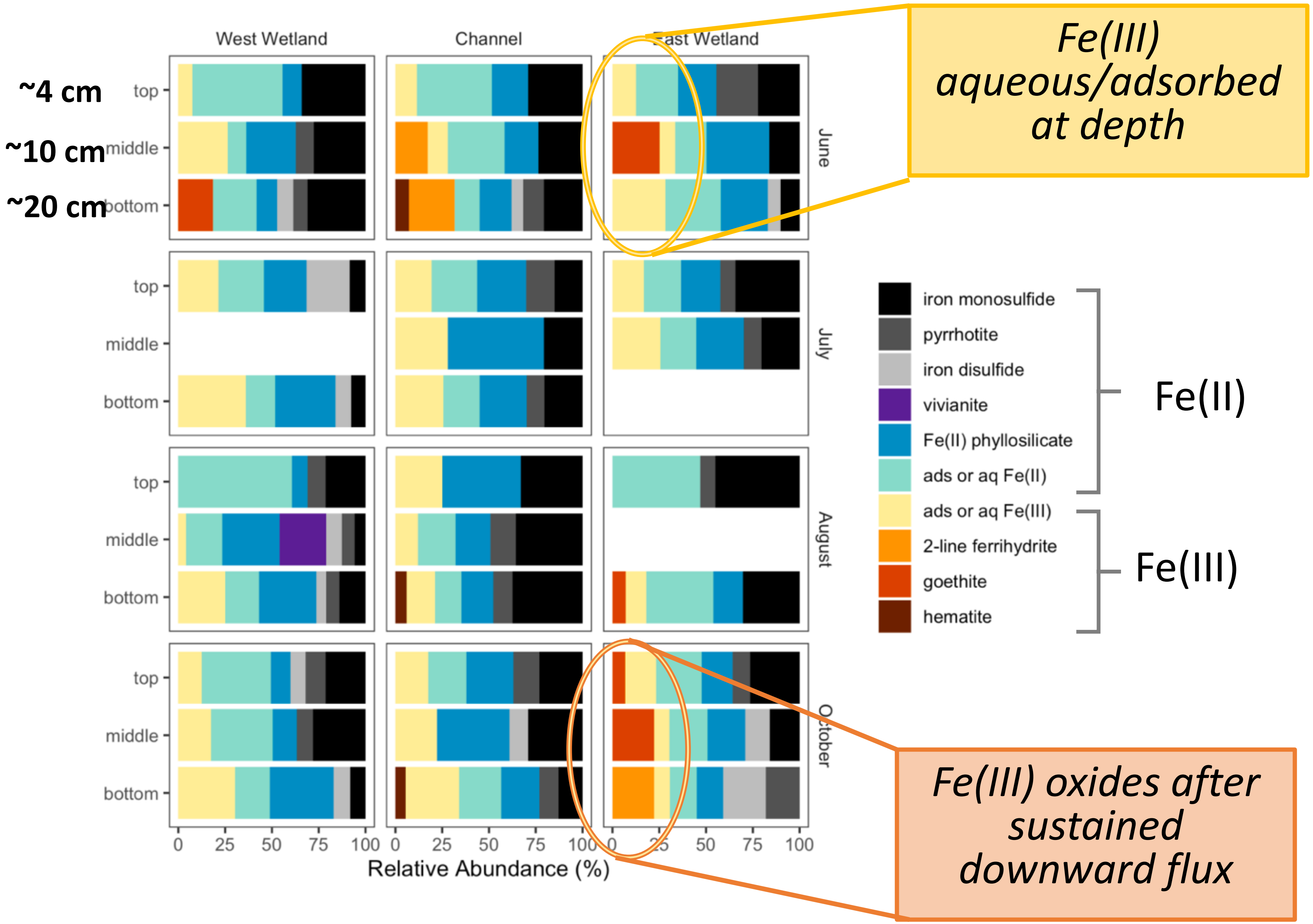
(Fe K-edge EXAFS)



Fe(III) presence can help fueld a

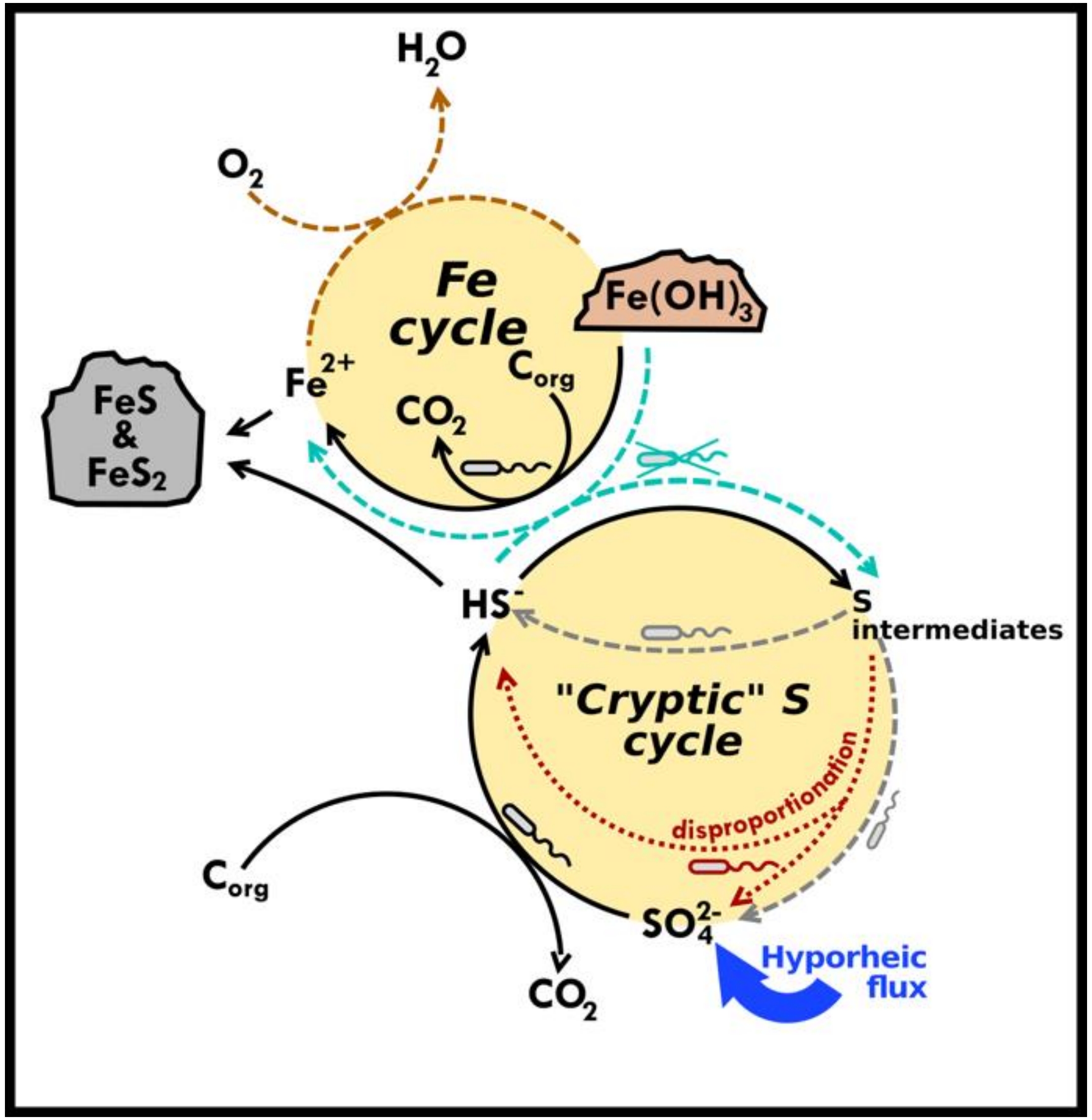
Sediment Iron

(Fe K-edge EXAFS)



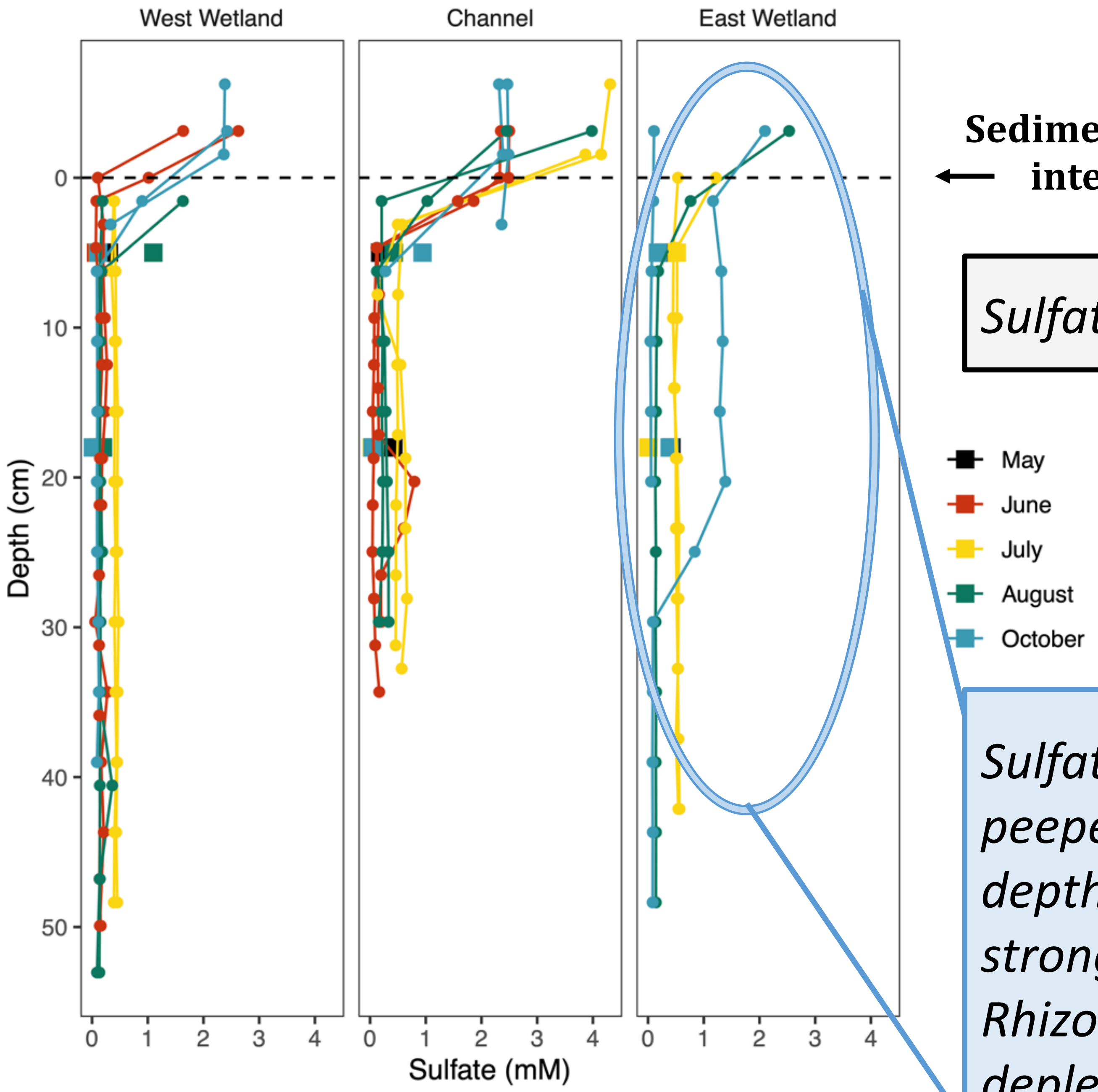
Fe(II) solid/aqueous phases dominate in anoxic sediments

Can "cryptic" S cycle be sustained in anoxic sediments coupled to Fe(III) reduction?



Aqueous sulfate

Sulfate reduced in upper sediments but **levels remain >0 (~200 µM average)**



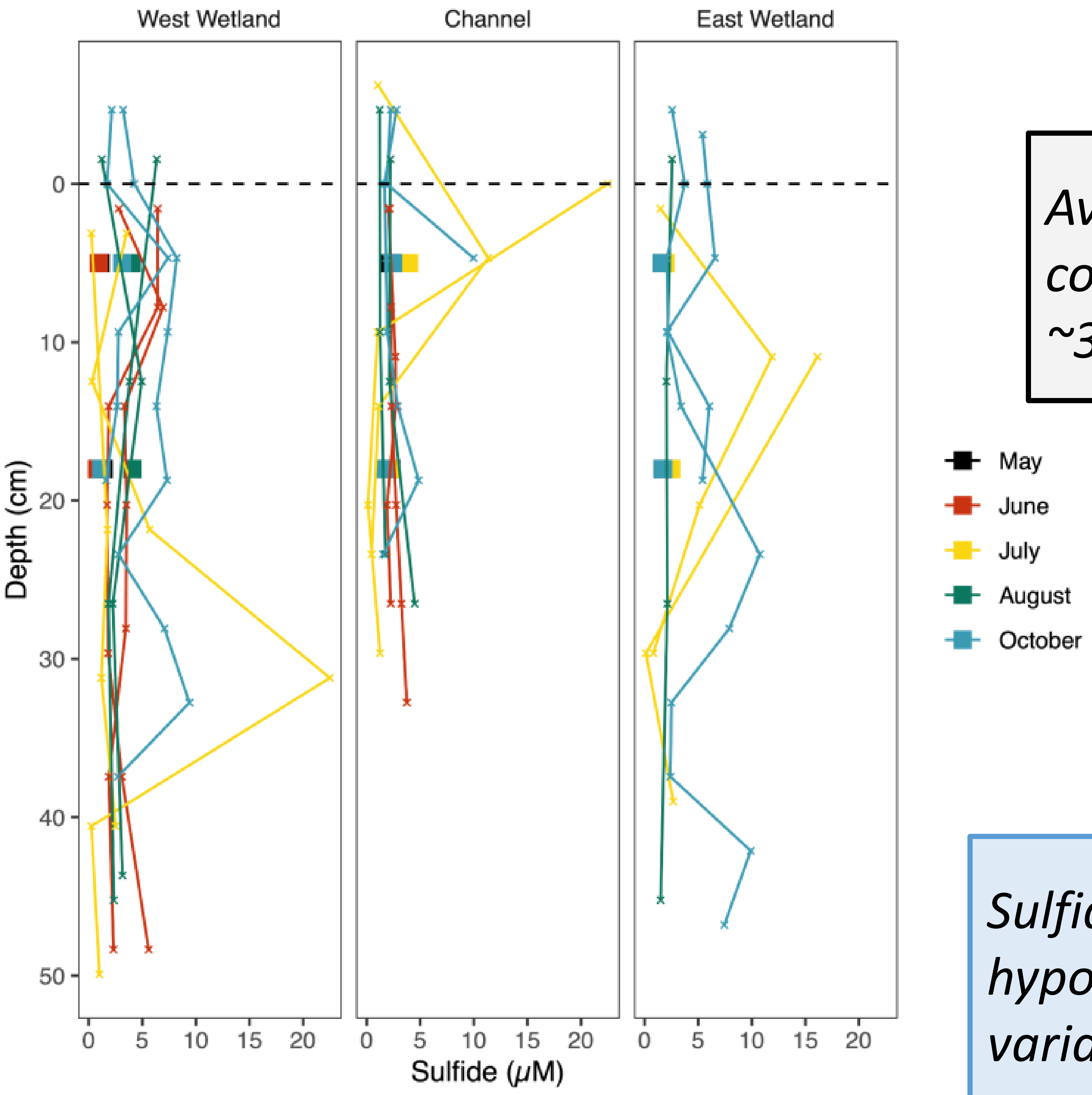
Sulfate depleted ~5 cm

Sulfate elevated in peeper waters (1 only) at depth in October after strong downward flux. Rhizon waters show more depleted sulfate

Aqueous sulfide
(cline method)

Sulfate reduction to sulfide

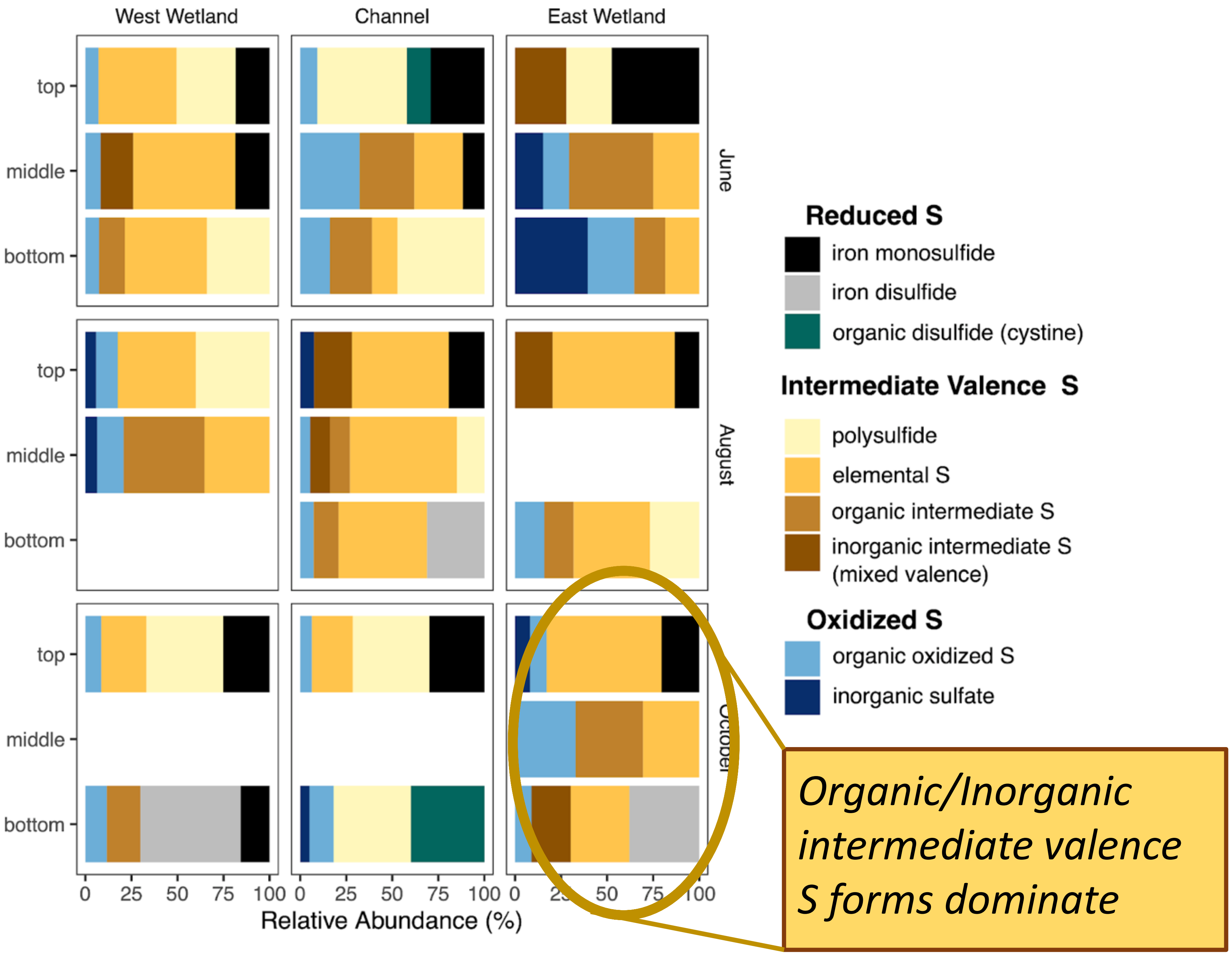
NO major trends observed with depth or season



Average sulfide consistently low ~3 μM

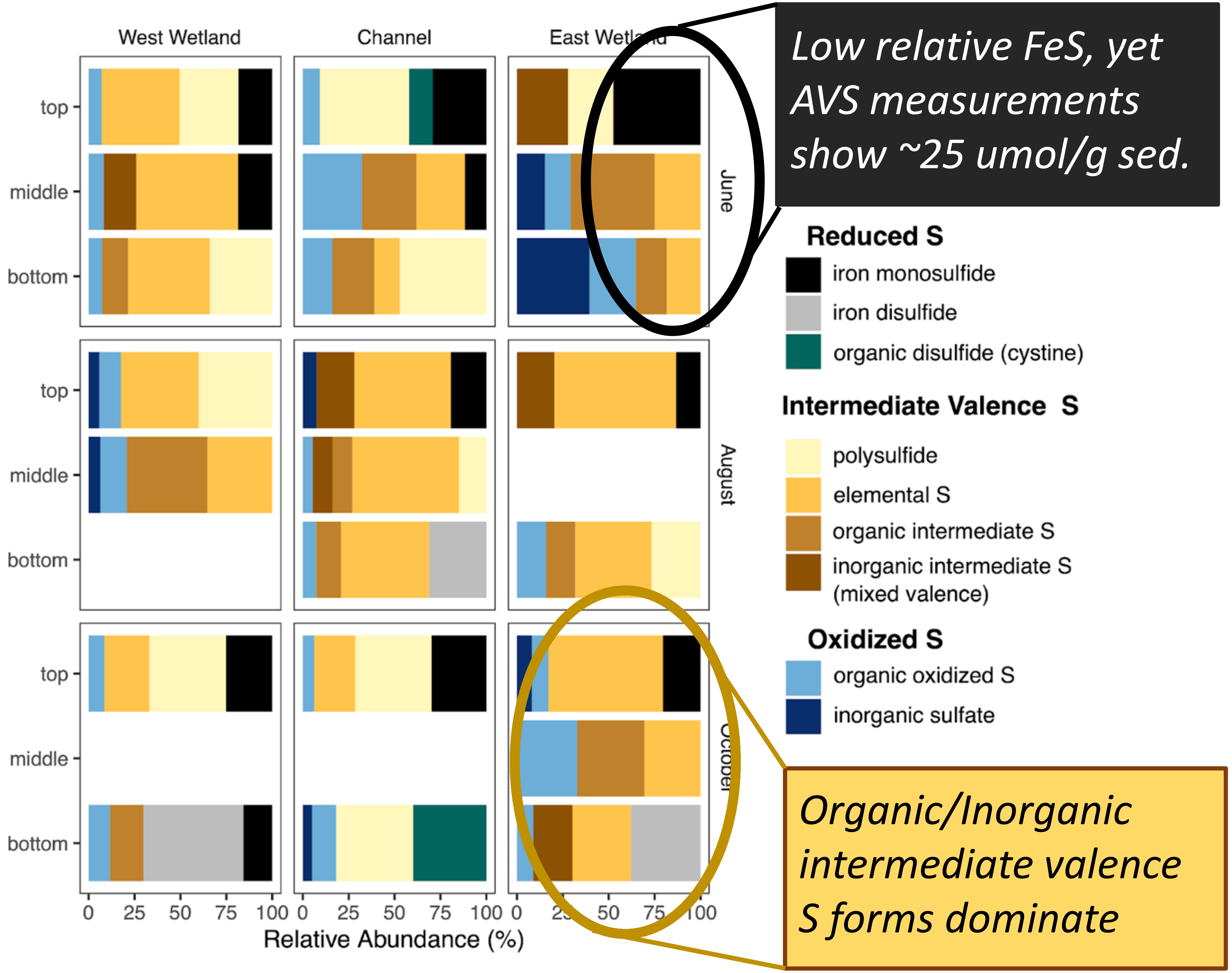
*Sulfide **not impacted** by hyporheic flux variability*

Sediment Sulfur
(S K-edge EXAFS)



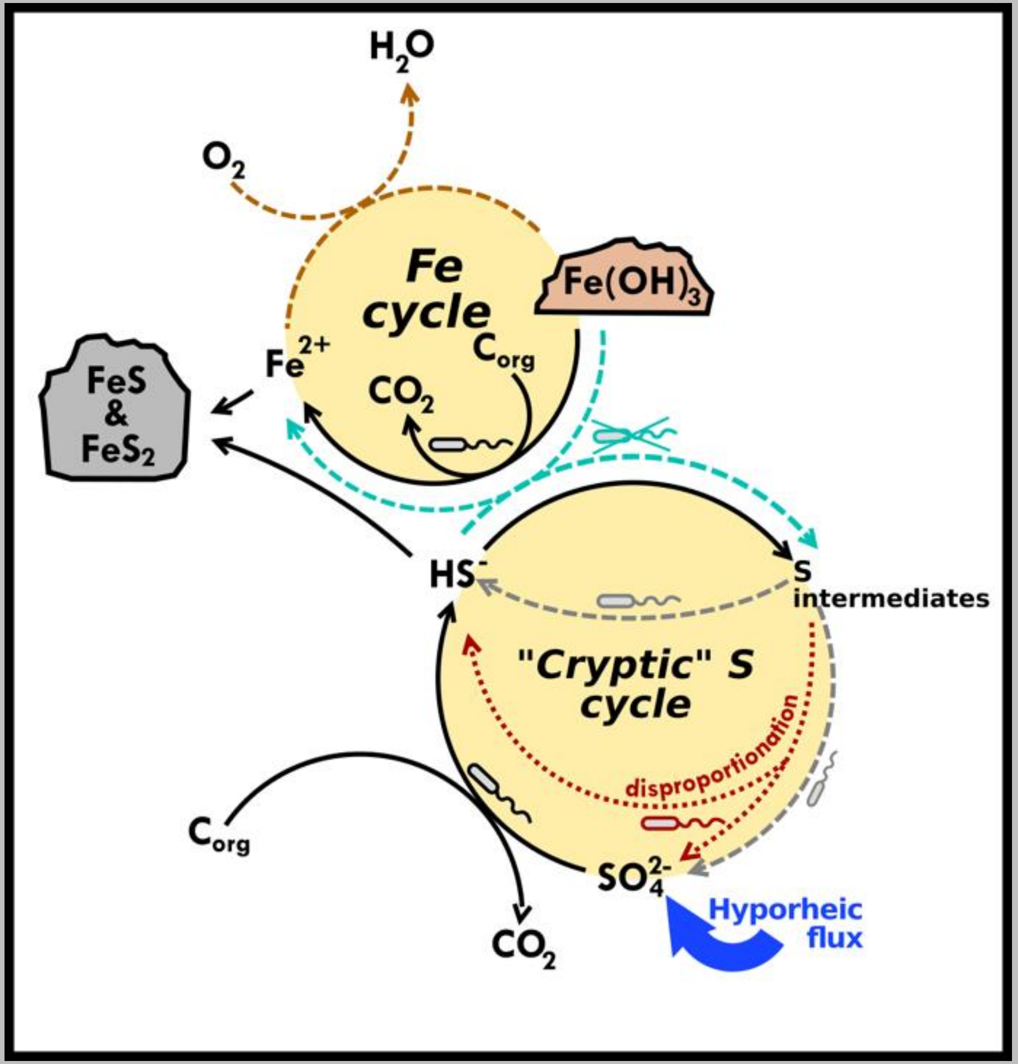
Imtermediate valence S forms (polysulfide, S(0), etc.) dominate total S pool!!!

Sediment Sulfur
(S K-edge EXAFS)



No obvious trends in S composition, but slightly **higher oxidized S in October and June** in East Wetland when Fe(III) oxides more abundant

Abundant S intermediates suggests active cryptic S cycle linked to Fe cycle



Sulfate from hyporheic flux or regeneration at depth from oxidation of S intermediates

What is the fate of all these S intermediates? Are they reactive?

Rates of S cycling and formation/transformation of various products? How does sulfate concentration impact this?

Influence of dynamic hydrologic conditions

- Response and recovery rates still need attention
- Modeling should give us greater insight
- Potential implications for methane fluxes