

# Do Constructed Wetlands Remove Metals or Increase Metal Bioavailability?

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# INTRODUCTION

## Constructed wetland

Engineered systems that utilize natural processes associated with natural functions of vegetation, sediments, organisms, and microbial communities to remove contaminants from wastewaters.

### The H-02 wetland

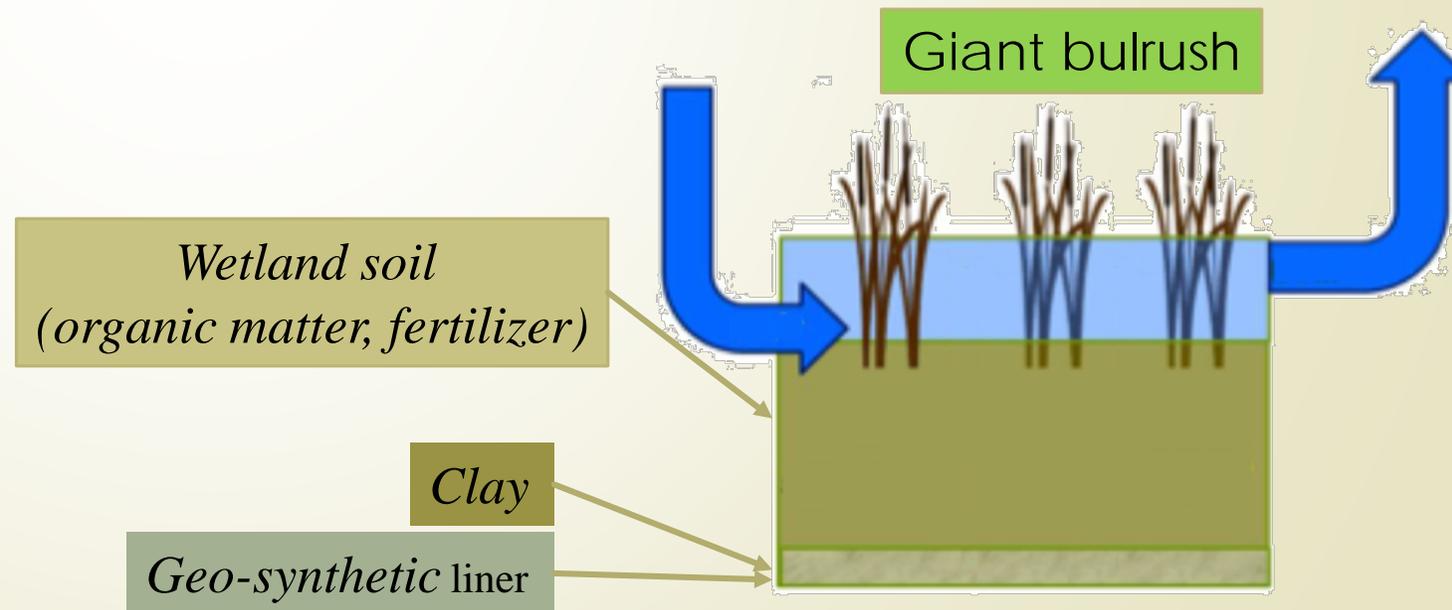
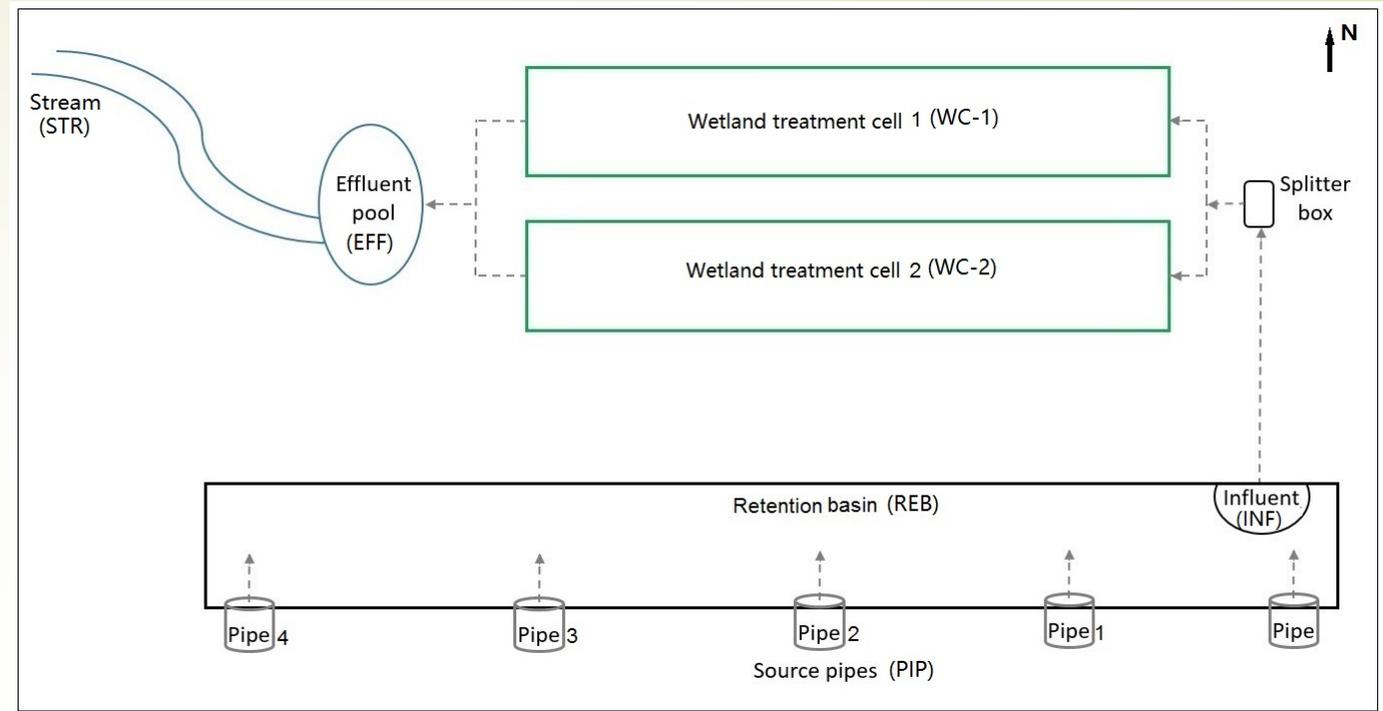
- ▶ Savannah River Site, Aiken, SC
- ▶ A free water surface wetland to treat the process water and some storm runoff water released from the Tritium Processing Facility.
- ▶ Remove heavy metals (Cu and Zn) from the water before it entering the Upper Three Runs Stream.



# INTRODUCTION

## The H-02 wetland

- Source pipes (PIP)
- Retention basin (REB)
- Influent (INF)
- Wetland cells 1, 2 (WC1, WC2)
- Effluent (EFF)
- Stream (STR)
- Water depth: 30 cm
- Residence time: 48 h



# MATERIALS & METHODS

## ➤ Sampling:

- 2014 to 2016: monthly
- pipes, retention basin, influent, wetland cells, effluent, stream

## ➤ Water quality parameters:

- *In situ* : pH, temperature, ORP
- Alkalinity, DOC, chloride, sulfate

## ➤ Metal concentrations:

- Total and dissolved Cu and Zn

## ➤ Metal speciation (WHAM):

- Windermere Humic Aqueous Model



# RESULTS & DISCUSSION - Metal concentrations

- Total concentrations:  
source pipe > retention basin >  
influent > effluent > stream
- Effluent < Influent
- Percentage of dissolved metals:  
60% - 80%
- Removal efficiency:  
66% for Cu and 71% for Zn.
- Effluent concentrations  
< NPDES limit

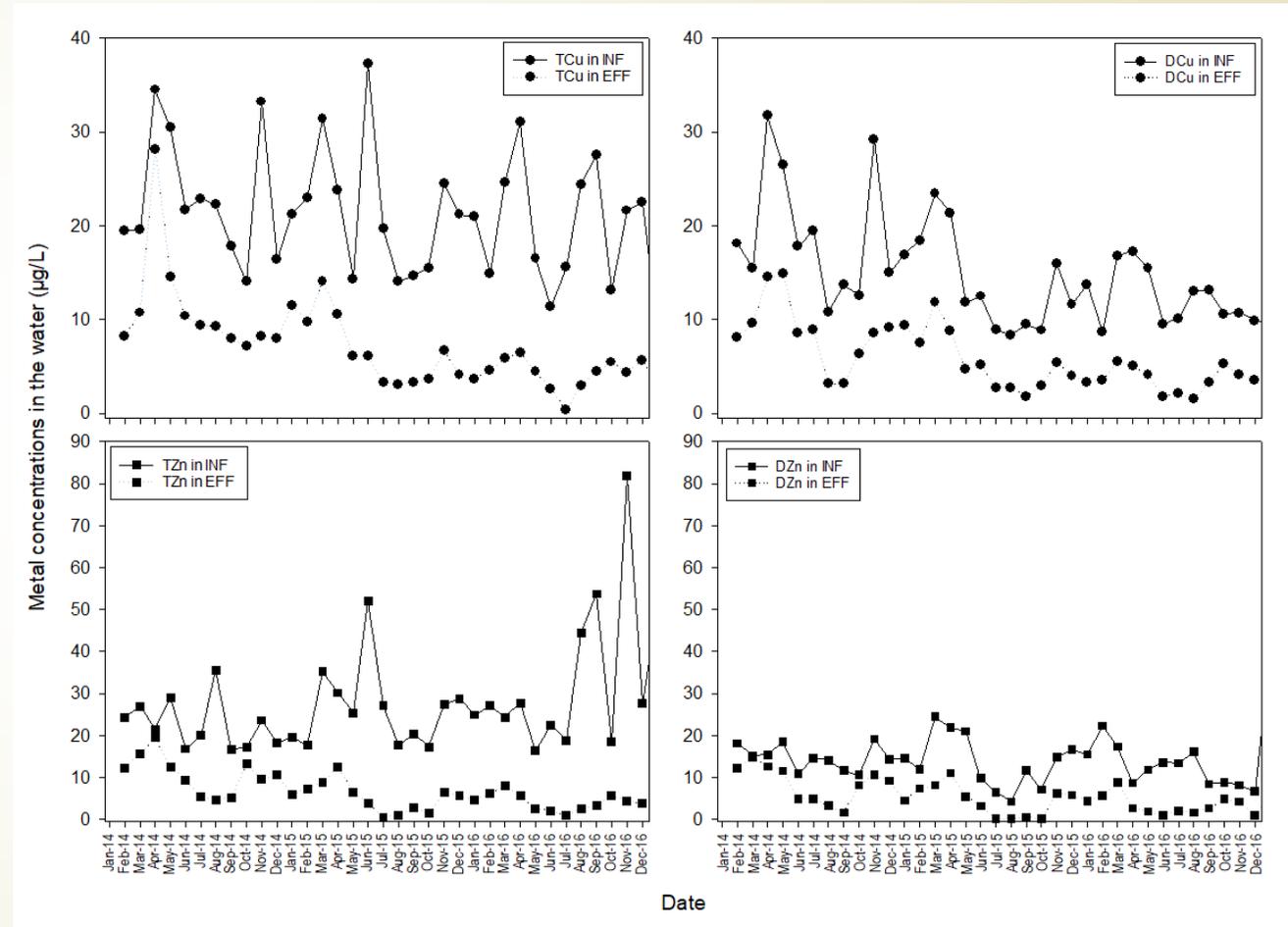


Figure: Total and dissolved concentrations of Cu and Zn in the influent and effluent water samples.

# RESULTS & DISCUSSION - Sulfur cycles

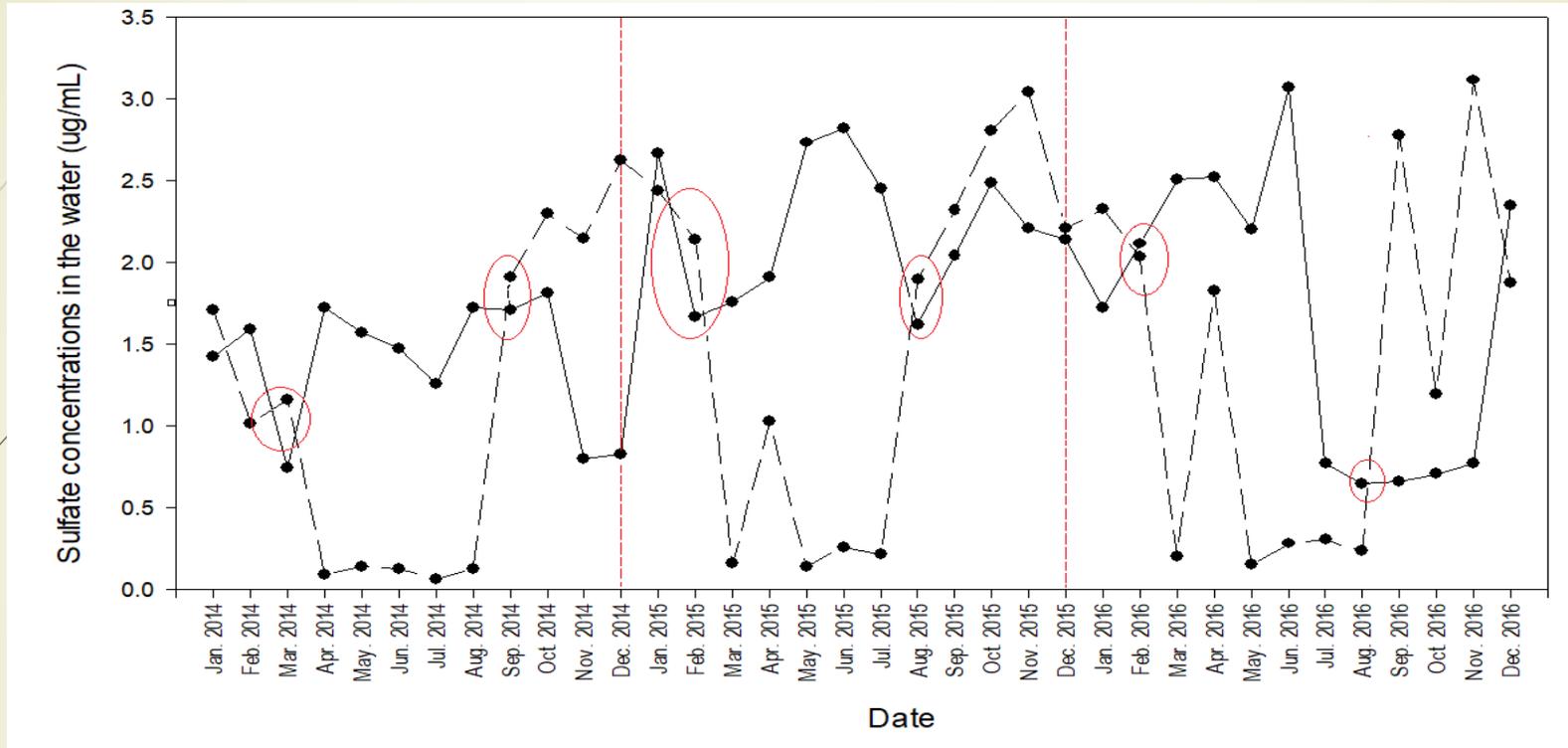


Figure: Sulfate concentrations in the influent and effluent.

- Warm months (February to August)
- Effluent sulfate < influent sulfate
- Sulfate reduction:  $\text{SO}_4^{2-} + 2\text{CH}_2\text{O} \rightarrow \text{H}_2\text{S} + 2\text{HCO}_3^-$
- Sulfate reducing bacteria (SRB)

# RESULTS & DISCUSSION - Sulfur cycles

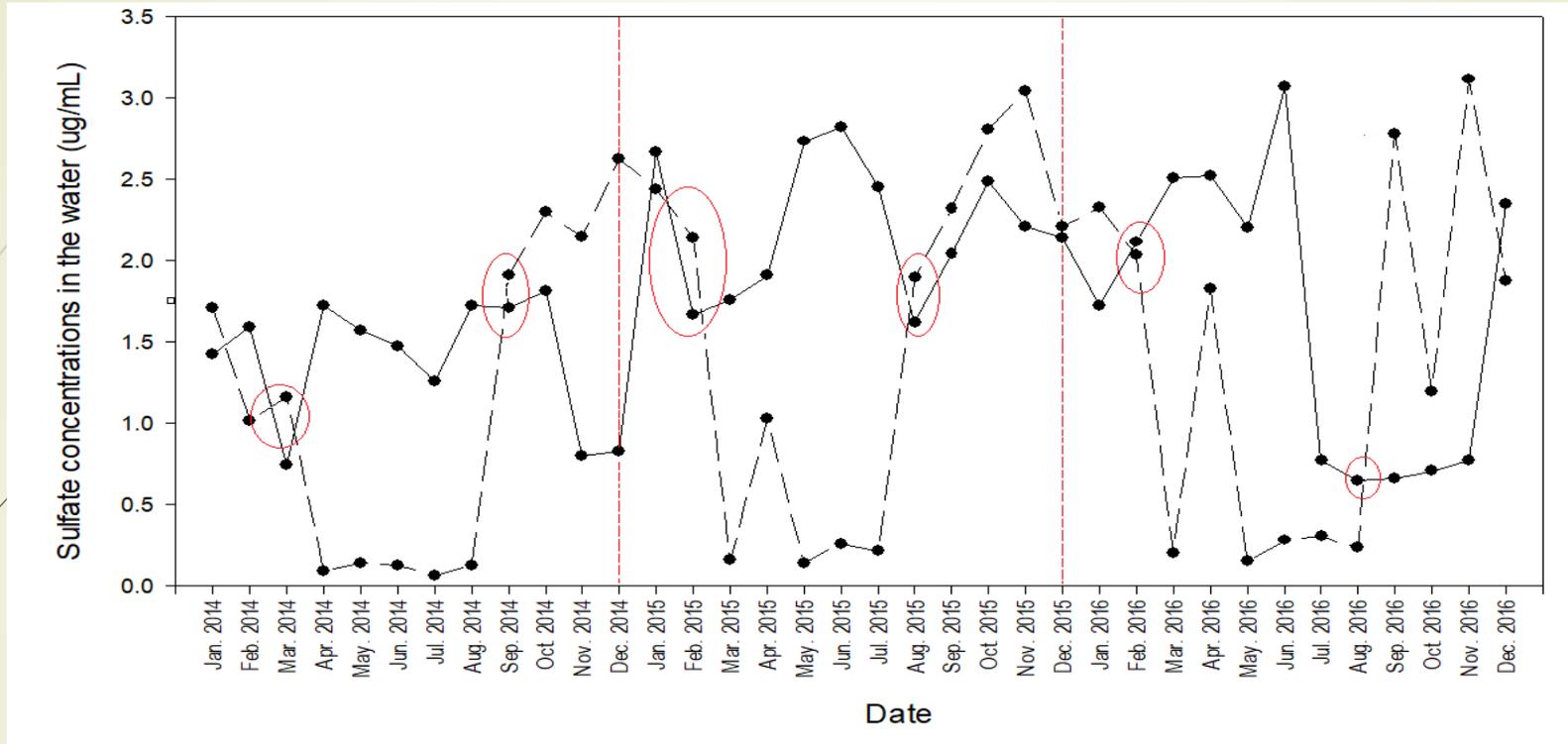


Figure: Sulfate concentrations in the influent and effluent.

## ► Cold months (September to March)

- Effluent concentrations > influent concentrations
- Sulfate oxidation:  $\text{H}_2\text{S} + \text{O}_2 \rightarrow \text{S}_0 + \text{H}_2\text{O} + \text{energy}$ ,  $\text{S}_0 + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \text{H}^+ + \text{energy}$
- Sulfur oxidizing bacteria (SOB)

# RESULTS & DISCUSSION - Sulfur cycles

- ▶ August - September
- Effluent concentrations increased
- Environmental regulators:
  - seasonal temperature changes
  - bacterial population density/activity
  - oxygen levels
  - labile organic content
  - sulfide in pore waters

▶ Next spring

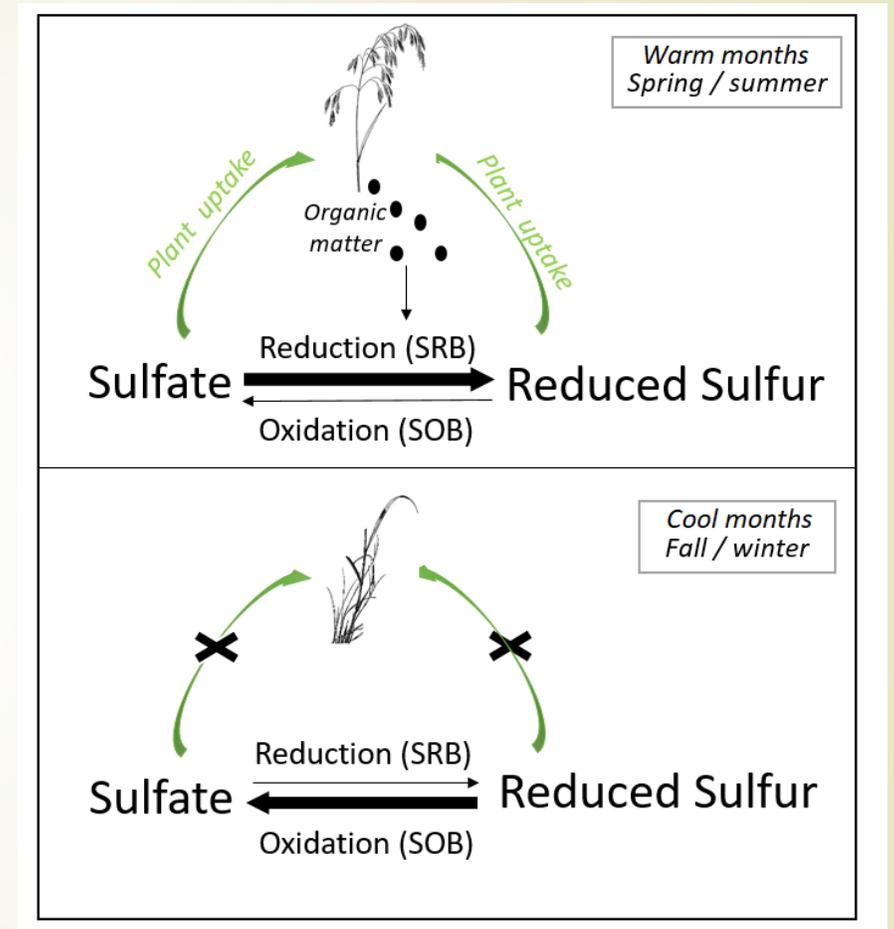
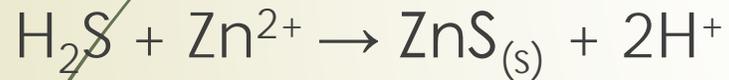
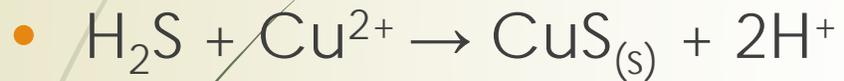


Figure: Schematic diagram of sulfur cycle in the wetland sediments during different seasons.

# RESULTS & DISCUSSION - Removal processes

## ► Warm months (February to August)

- Sulfate reduction



- Metal-sulfide minerals

CuS and ZnS

- Metal precipitation with  $H_2S$

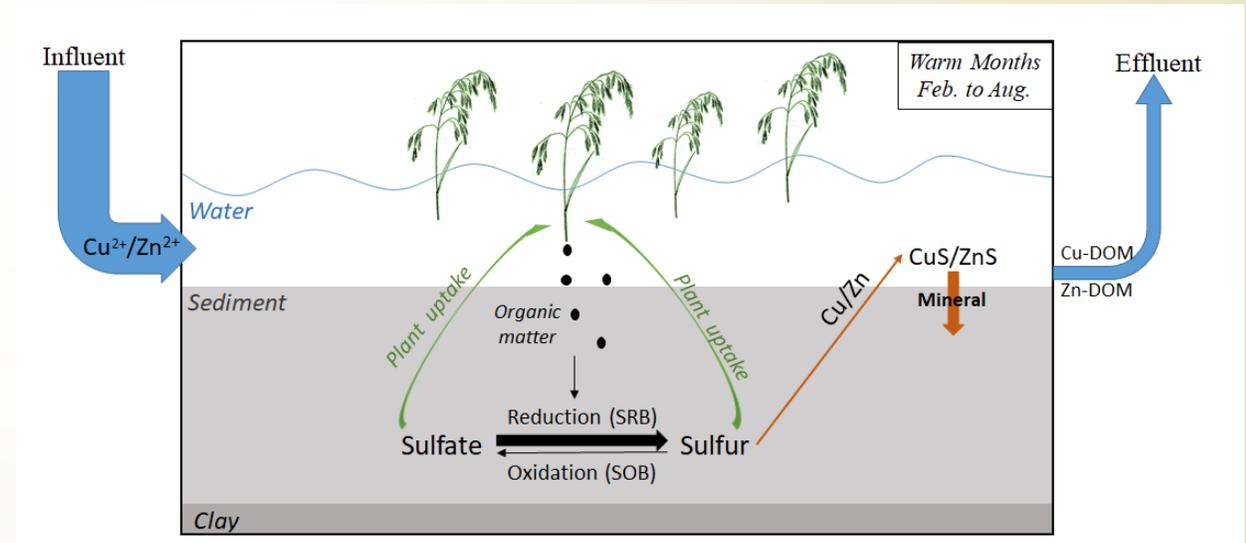


Figure: Schematic diagram of metal removal processes in the wetland.

# RESULTS & DISCUSSION - - Removal processes

## ➤ Cold months (September to March)

- Sulfide oxidation
- Adsorption to organic matter

- Metal speciation

Free metal ion < 0.001%

Inorganic metal < 0.1%

Metal-DOC complexes > 99%  
(metal-HA, metal-FA)

- Colloidal Cu-FA and Zn-FA ↑

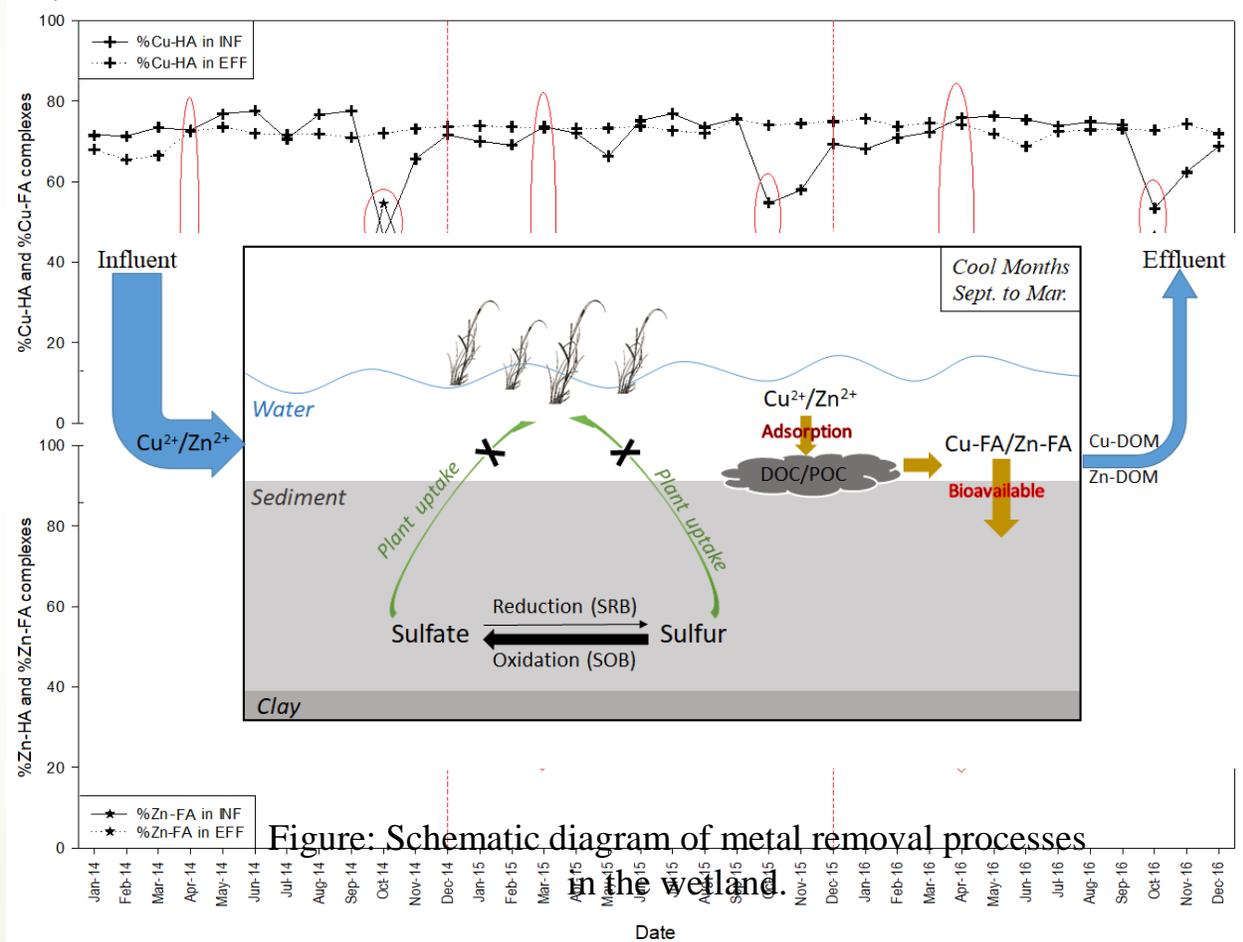


Figure: The percentage of metal-HA (Cu-HA, Zn-HA) and metal-FA (Cu-FA, Zn-FA) complexes in the influent and effluent.

# CONCLUSIONS & IMPLICATIONS

- ▶ Do constructed wetlands remove metals or increase metal bioavailability?

BOTH

- ▶ Metal removal processes?

{ Warm months: precipitation with  $H_2S$   
Cold months: adsorption to organic matter  
*Season-related and regulated by sulfur cycles*

- ▶ Environmental Impacts?

Highly bioavailable colloidal metal-FA

- ▶ Long-term sustainability?



# ACKNOWLEDGEMENT



**THANK YOU !**  
**Questions ?**

## SREL Study catches industrial metals before they reach surface water

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Research assistant Jasmine Parks, Dr. Xiaoyu Xu, and research assistant Kara Norris measure a water sample and record its pH, temperature and oxidation reduction before taking it back to the laboratory for in-depth study.

Since its inception in 1951, the Savannah River Ecology Laboratory at Savannah River Site has advanced studies in biodiversity and ecological impacts of site activities and environmental change. As knowledge advances, so too do capabilities, and the lab now studies man-made wetland systems to isolate and prevent metals from Savannah River Site nuclear activities from reaching outside water systems.

According to study director Dr. Gary Mills, the manmade wetland filtration system is not a new idea.

“Using the wetlands to filter these metals is a novel idea, but the concept isn’t new. It’s been used in agriculture and other industries for years to keep fertilizers or pesticides from running off into water supplies,” he said.



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