

# REMOVAL AND RETENTION OF COPPER AND ZINC IN A CONSTRUCTED WETLAND OVER 20 YEARS

**Anna Sophia Knox, Nathaniel A. Losey, and John J. Mayer**

*14<sup>th</sup> International Symposium on Biogeochemistry of Wetlands and Aquatic Systems*

June 1-5, 2025, Baton Rouge

SRNL-STI-2025-00243

# Removal and retention of contaminants in wetlands

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## Abiotic processes

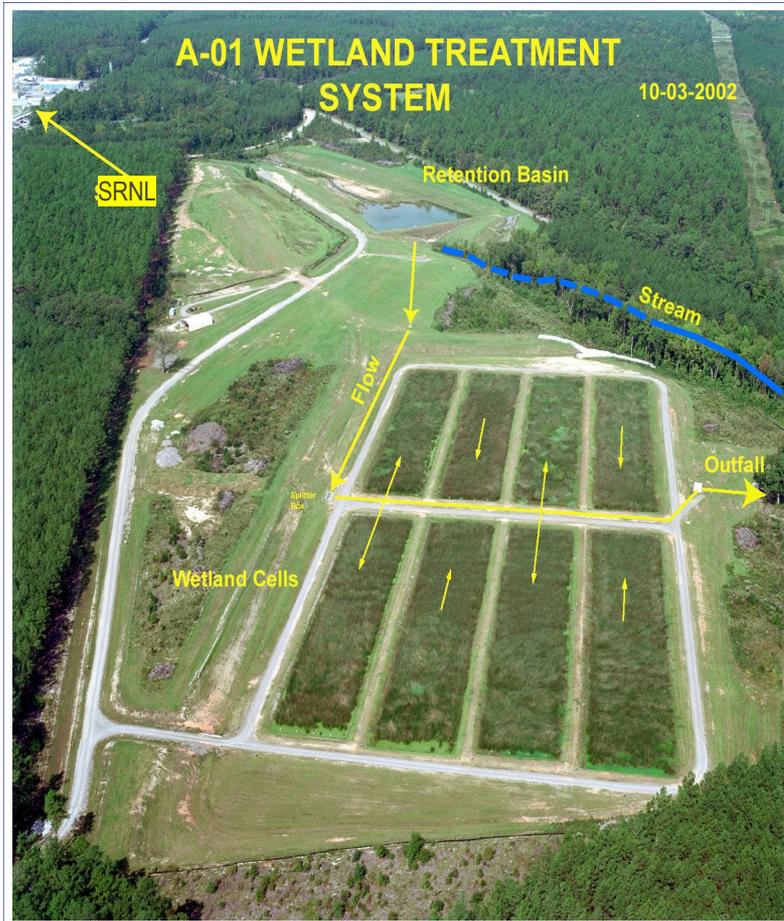
- Settling
- Sedimentation
- Sorption onto organic matter or mineral phases
- Binding to iron and manganese oxides
- Oxidation and hydrolysis
- Formation of carbonates
- Formation of insoluble mineral phases (e.g., sulfides)

## Biotic processes (microbial/phytological)

- Biodegradation
- Phytoaccumulation
- Phytostabilization
- Phytodegradation
- Rhizodegradation



# Background information



Studied area - cells 4A and 4B

- Designed and constructed in 2000 to remove metals, especially copper, from the A-01 effluent.
- Consists of a stormwater retention basin, a splitter box, and four sets of two sequential treatment cells planted with giant bulrush (*Schoenoplectus californicus*)



# Objective

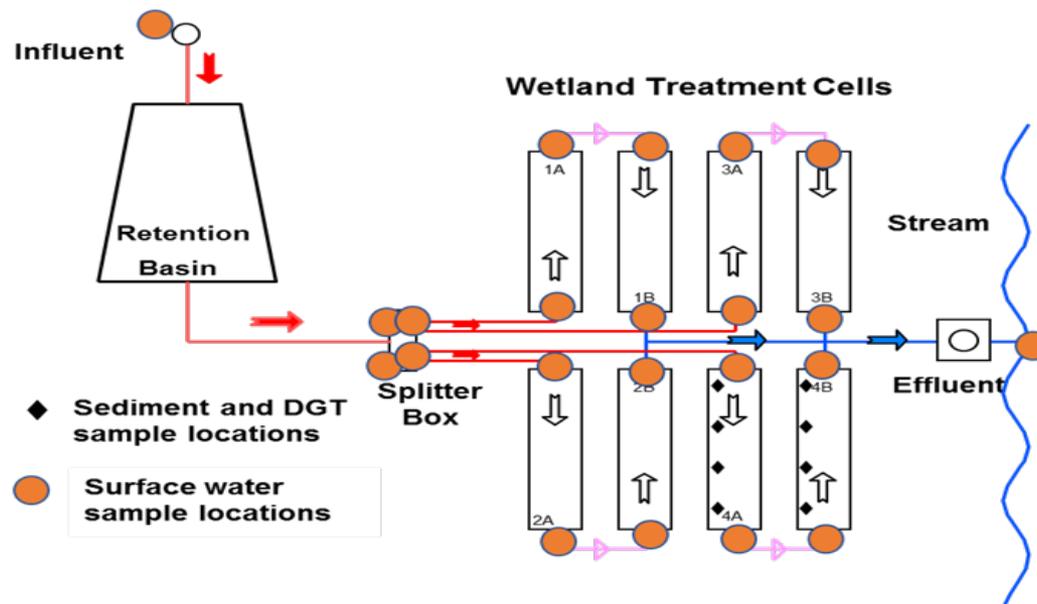
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- **The main objective of this study was to investigate metal removal and binding in the A-01 Constructed Wetlands at Savannah River Site using a unique long-term data set. This objective was addressed in the following tasks:**
  1. Confirmation of contaminant removal from the A-01 wetland after 20 years
  2. Evaluation of metal distribution in wetland sediment profile after 20 years
  3. Assessment of metal bioavailability in the wetland sediment using Diffusive Gradients in Thin Films (DGT) probes
  4. Determination of the Influence of organic matter generation (floc) on metal bioavailability and retention
  5. Synthesize of new data with previously collected data to assess changes in processes that affect long-term wetland performance (samples collected in 2000, 2004/2005, 2016, and 2020).



# Materials and Methods

- Surface water sampling – 2000-2004, 2005, 2016, and 2020; metals were analyzed by ICP-MS, EPA Method 6020B Sediment sample collection – 2000; 2004, 2016, 2020
- DGT probes - 2016 and 2020
- DGT water and sediment probes were placed at intervals in two treatment cells and compared with water and sediment samples collected at the same locations.



- Water samples –surface water grab samples
- Sediment cores – 2.5 cm diameter cores to a depth of 20 cm
- DGT water probes (Cu, Zn) suspended in water for 24 hrs
- DGT sediment probes embedded in sediments for 24 hrs

The flow path of the A-01 effluent is from the retention basin to the splitter box, through the four A-cells, through the four B-cells, to the wetland outfall, and into the receiving stream.

# Surface water properties

- Mean (standard deviation) of surface water dissolved oxygen (DO), electrical conductivity (EC), redox potential (ORP), pH, temperature (Temp), and turbidity for surface water samples collected from the A-01 WTS in 2020, (n =22).

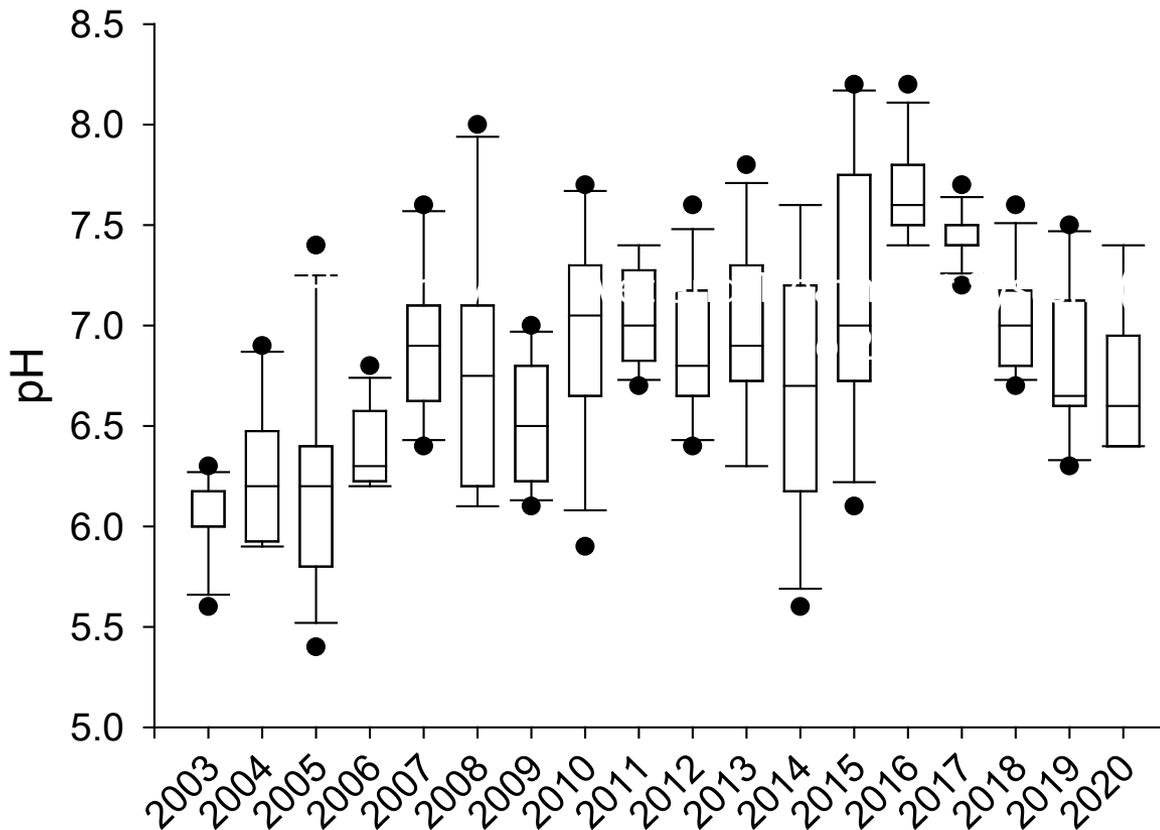
Variable	January	February	March	June	July
DO (%)	95.0 (11.9)	90.6 (8.6)	75.7 (22.9)	64.5 (31.7)	64.1 (23.6)
EC ( $\mu\text{S cm}^{-1}$ )	32.6 (4.3)	28.0 (6.0)	38.0 (2.5)	35.6 (3.3)	28.5 (6.0)
ORP (mV)	-	-	-	-	53.7 (9.0)
pH	7.0 (0.2)	6.7 (0.2)	6.8 (0.2)	6.1 (0.2)	5.8 (0.2)
Temp ( $^{\circ}\text{C}$ )	13.2 (1.4)	9.0 (1.1)	16.5 (1.6)	24.1 (0.6)	24.3 (0.5)
Turbidity (NTU)	3.5 (2.4)	7.9 (2.2)	5.1 (3.0)	5.5 (4.9)	7.5 (4.6)

Decreased pH during the summer was associated with decreased dissolved oxygen concentrations. Both were likely related to temperature driven increases in bacterial respiration and the resulting uptake of oxygen and release of carbon dioxide.



# Surface water pH

- Surface water pH at the A-01 Wetland Treatment System (WTS) discharge point from 2003 to 2020.



- From approximately 2003 to 2016, median annual pH increased irregularly from about 6.0 to about 7.5, then progressively declined to about 6.5 in 2020
- This decline may be related to the increasing prevalence of decomposition processes in the maturing wetland

# Confirmation of contaminant removal from the A-01 wetland after 20 years

- Cu, Pb, and Zn concentrations ( $\mu\text{g L}^{-1}$ ) in surface water from influent to discharge in the A-01 WTS.

Year	Influent*	Splitter Box**	A cell***	B cell***	Discharge (Effluent)*	Avg % removal
Cu						
2001	45.3 (45.8)	25.1 (10.5)	10.9 (6.1)	7.7 (3.6)	8.2 (4.3)	82.0
2002	36 (19.2)	33.6 (19.2)	11.9 (8.9)	7.0 (5.3)	8.4 (6.9)	76.5
2004/2005	25.8 (11.8)	23.4 (14.1)	9.8 (3.1)	4.7 (2.5)	4.4 (1.6)	83.0
2016			6.5 (1.3)	5.6 (1.3)		
2020	20.9 (11.2)	7.4 (3.4)	5.6 (2.5)	3.6 (1.2)	3.0 (0.9)	85.8
Pb						
2004/2005	1.2 (1.0)	1.2 (1.7)	1.1 (1.5)	0.6 (0.6)	0.4 (0.6)	66.6
2016			0.1 (0.1)	0.1(0.1)		
2020	0.65 (0.4)	0.4 (0.2)	0.3 (0.1)	0.2 (0.1)	0.2 (0.1)	74.3
Zn						
2004/2005	18.4 (7.5)	30.7 (14.2)	14.4 (6.7)	9.1 (7.5)	8.8 (6.4)	52.1
2016			42.5 (5.6)	39.8 (6.7)		
2020	27.8 (14.0)	24.8 (14.5)	18.1 (10.9)	11.6 (5.3)	9.8 (4.4)	64.8

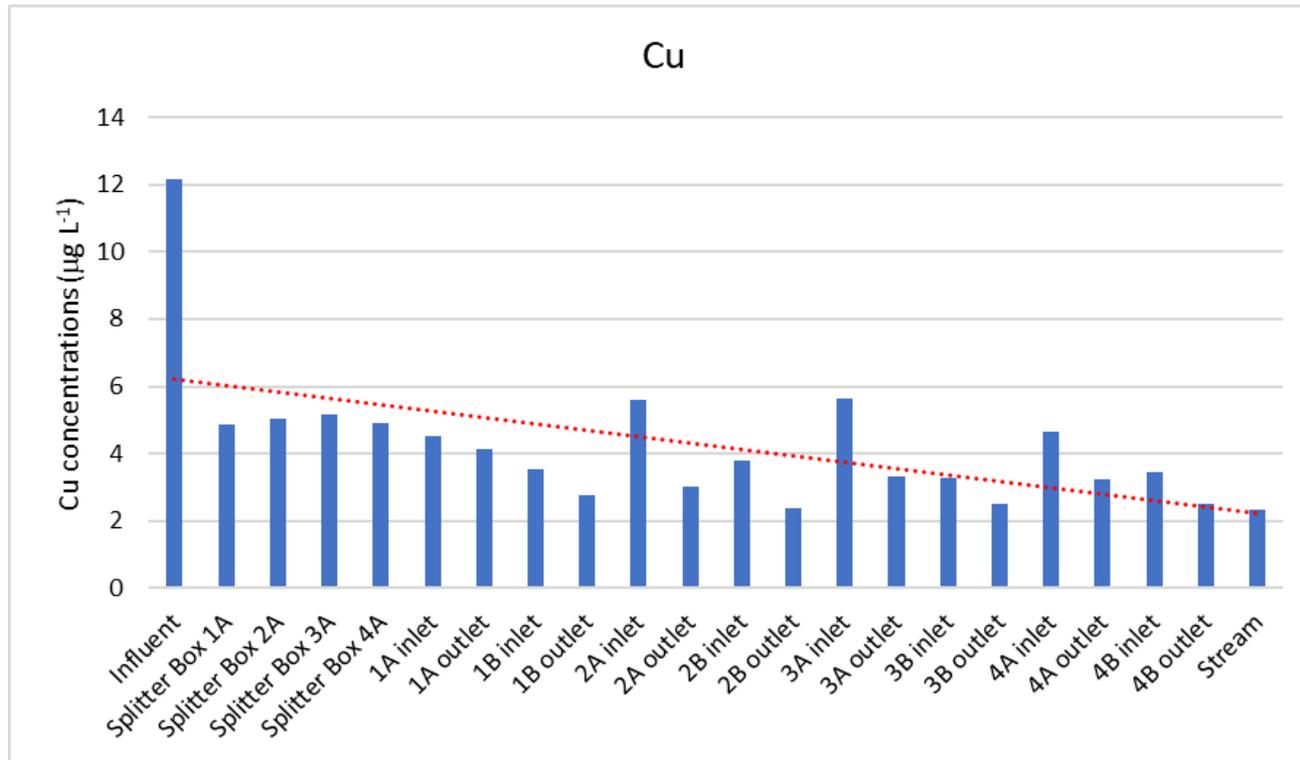
\* n=12 in 2001 and 2002, 9 in 2004/2005, and 5 in 2020.

\*\* n=12 in 2001 and 2002, 36 in 2004/2005, and 20 in 2020.

\*\*\* n=48 n 2001 and 2002, 36 in 2004/2005, and 40 in 2020.

# Cu removal from water column

- Cu removal from water column after passage through the A-01 WTS on January 27, 2020.

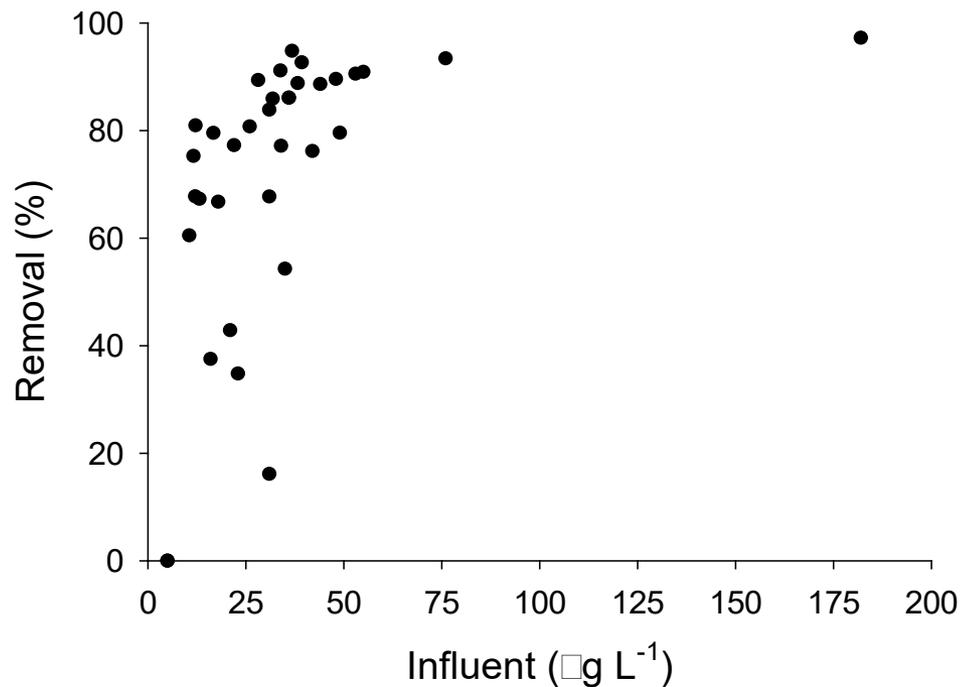


Cu removal occurred rapidly in the wetland system, with most occurring before the water exited the A cells. After passage through the B cells, Cu concentrations were often near the detection limit.



# Cu removal from water column

- Relationship between influent Cu concentrations and percentage removal of Cu following passage through the A-01 WTS.



When influent concentrations were higher, removal of the metals was higher. This is illustrated by the Cu data: influent concentrations above about  $40 \mu\text{g L}^{-1}$  were associated with 85% or greater removal while removal was often less at lower influent concentrations.



# Bioavailability

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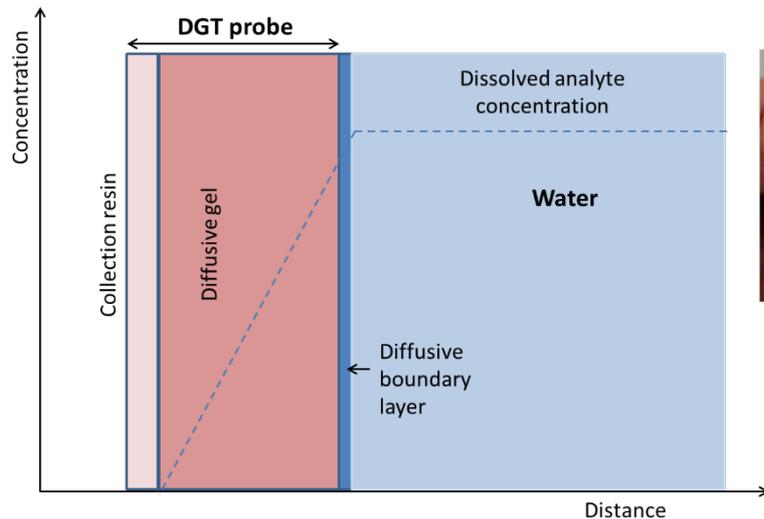
- Bioavailability – degree to which chemicals (e.g., metals) are absorbed or metabolized by human or ecological receptors or are available for biological interactions
- Metals exist in different forms in the environment. These forms differ in toxicity because of differences in bioavailability
- Metals strongly bound to organic molecules and metal sulfides are typically unavailable (Di Toro et al. 2001)\*
- DGT theoretically measures bioavailable dissolved and labile metal species that readily pass through the diffusion gel but excludes relatively unavailable metals, such as those bound to large organic molecules

\* Di Toro DM, Allen HE, Bergman HL, Meyer JS, Paquin PR, Santore RC. 2001. Biotic Ligand Model of the Acute Toxicity of Metals. I. Technical Basis. *Environmental Toxicology and Chemistry* 20: 2383–2396.



# Diffusive Gradients in Thin Films (DGT) Technology

- Diffusive Gradients in Thin Films (DGT) probes consist of an adsorbent layer with a medium that selectively binds to the contaminant of interest and a diffusion gel that selectively admits analyte molecules
- DGT relies on the unassisted molecular diffusion of analytes through the diffusion gel onto the adsorbent layer. After sampling, adsorbed analytes are desorbed off the adsorbent and analyzed (e.g., by mass spectrometry)
- Environmental concentrations of elements are calculated from the concentration of the element in the adsorbent gel, device configuration, analyte diffusion coefficients, deployment time, and other factors

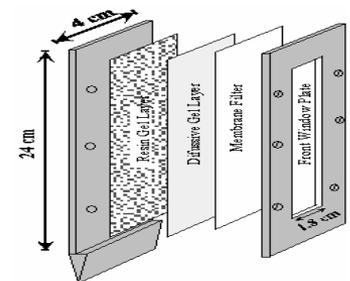


Schematic cross-section through a DGT probe showing a steady state concentration gradient between an analyte in solution and a collection resin.

Water probe



Sediment probe



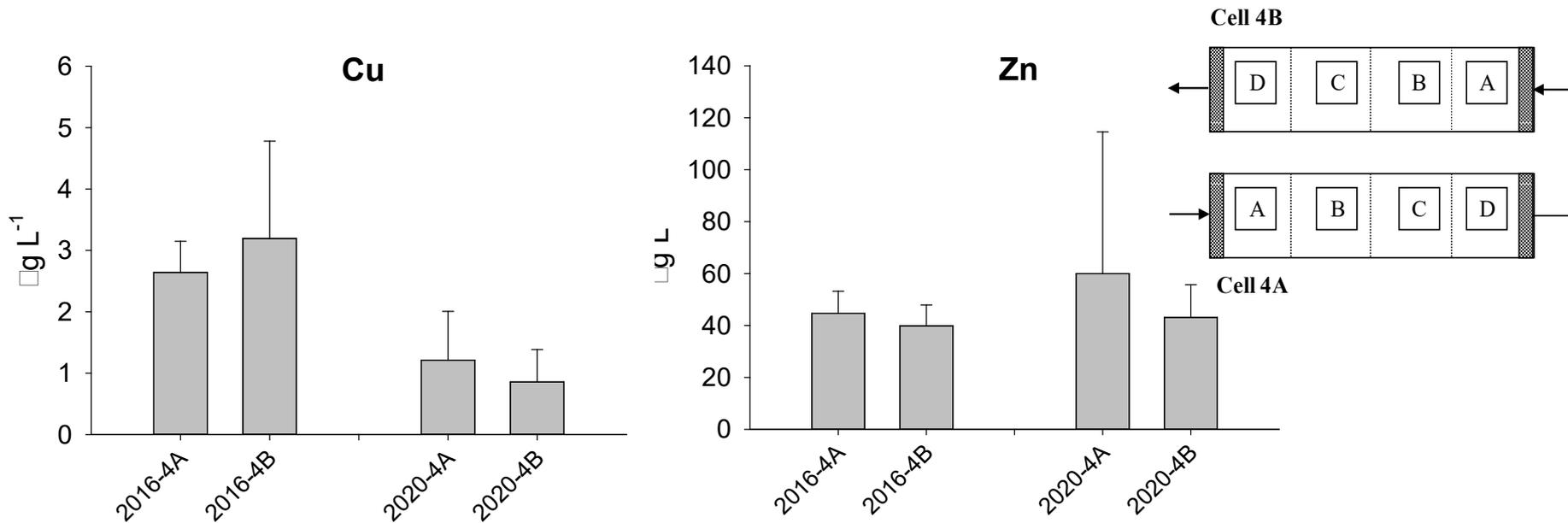
$$M = \frac{C_e^* (V_{NO_3} + V_{gel})}{f_e}$$

$$C_{dgt} = \frac{M^* \Delta g}{D^* t^* A}$$

**Davison, W., H. Zhang. 1994.** In situ speciation measurements of trace components in natural waters using thin-film gels. *Nature*. 367, 546 - 548 (10 February 1994)

# Bioavailability of metals in surface water

- Concentrations of Cu and Zn measured in surface water by DGT in cells 4A and 4B of the A-01 WTS in 2016 and 2020 (n = 8 for each cell). Error bars are standard deviations.

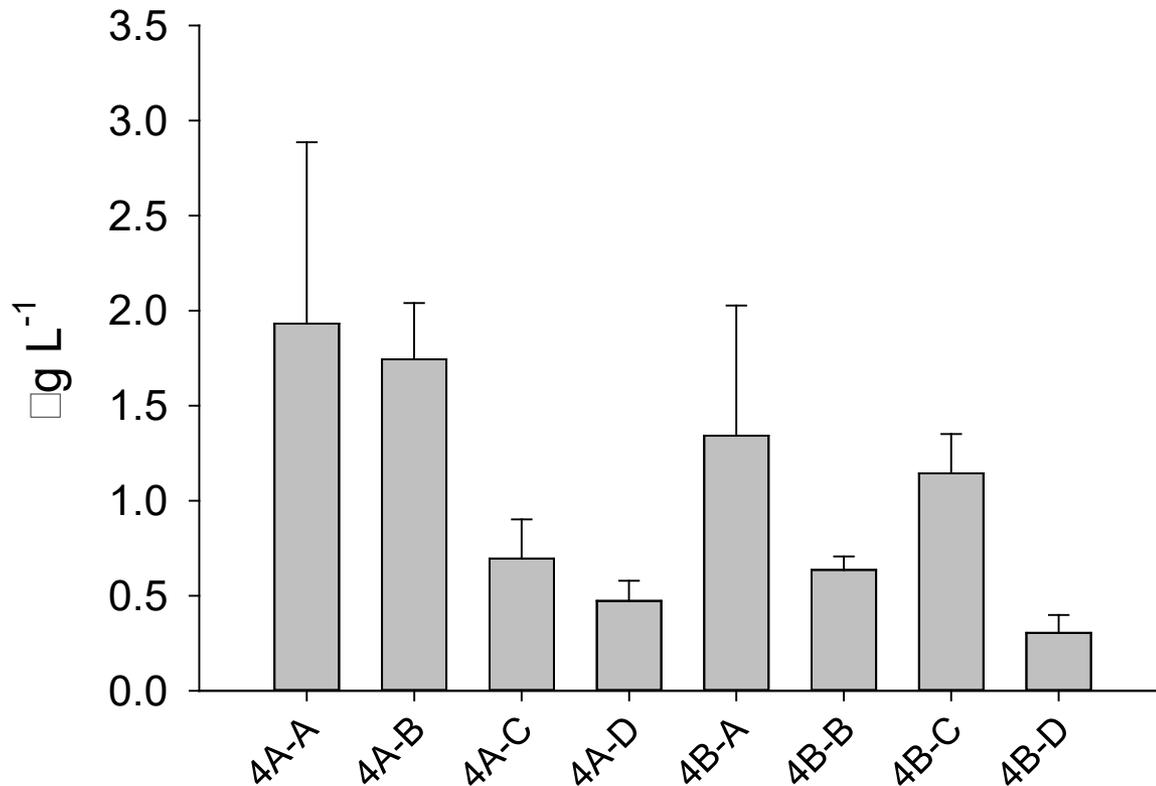


- Average DGT Cu concentrations in surface waters were about 50-75% lower than total Cu concentrations suggesting that half or more of the Cu in the A-01 WTS surface waters was not bioavailable
- In contrast, DGT Zn concentrations were comparable to or higher than total Zn concentrations in the surface waters. Humic acids form strong organic-Cu complexes that are inaccessible for biological uptake and excluded by DGT. In contrast, such complexes are not formed to the same degree with Zn



# Bioavailability of metals in surface water

- Surface water Cu concentrations measured by DGT at sample sites within cells 4A and 4B of the A-01 WTS during 2020, n = 2 for each location, error bars are standard deviations



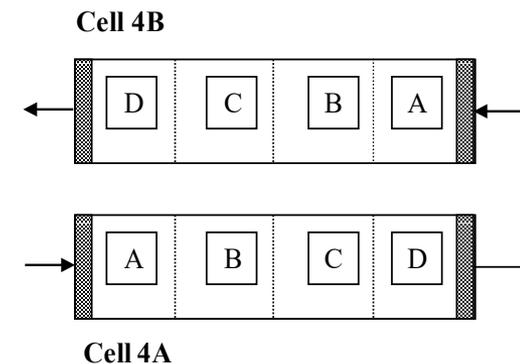
- DGT Cu concentrations in surface waters decreased along the flow path in the 4A and 4B treatment cells from the water entry at location 4A-A to the exit at 4B-D paralleling the pattern observed with total Cu concentrations in water
- DGT Cu concentrations near the exit of cell 4B (i.e., 4B-D) were over 80% lower than DGT Cu concentrations near the entrance of cell 4A



# Sediment properties and analysis

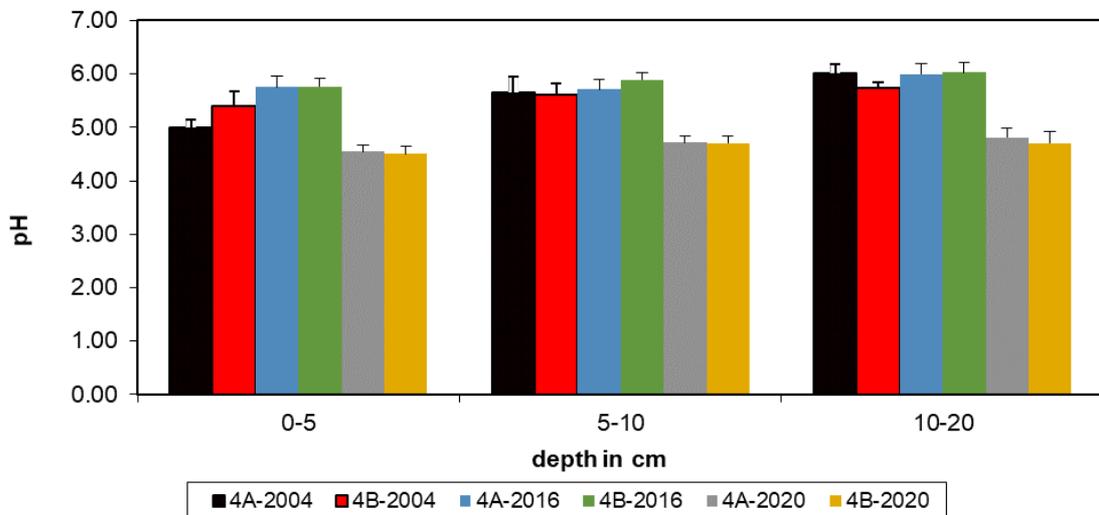
- When the wetland treatment cells were constructed, the hydrosol was amended with organic matter (primarily coarse wood chips), fertilizer (Osmo-coat, 14-13-14 formula) at the rate of 3920 kg/hectare, and gypsum at the rate of 2240 kg/hectare. The treatment system was constructed during the winter/spring of 2000 and began receiving A-01 effluent in July 2000.

Initial Sediment (hydrosol) properties in 2000	
Particle distribution (%)	
Sand	90
Silt/Clay	10
Organic matter content (%)	1-2
CEC (meq/100g)	1.4
pH	5.7
Cu (mg kg <sup>-1</sup> )	3.8
Pb (mg kg <sup>-1</sup> )	5.9
Zn (mg kg <sup>-1</sup> )	10.2
Fe (mg kg <sup>-1</sup> )	4094
Mn (mg kg <sup>-1</sup> )	68.9



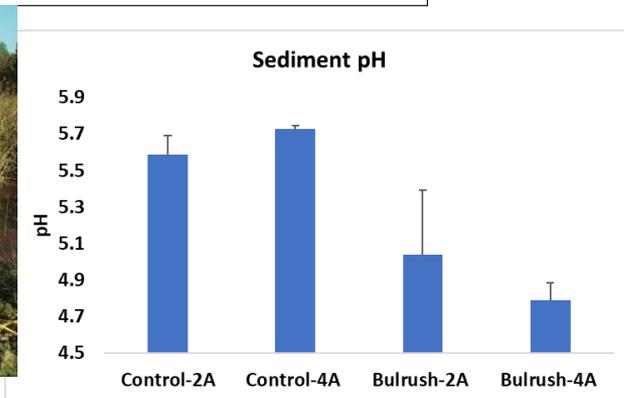
# Sediment pH

- Sediment pH (cells: 4A and 4B) as a function of depth after 20 years of operation of the A-01 WTS (n = 8 for each cell and each sediment layer).



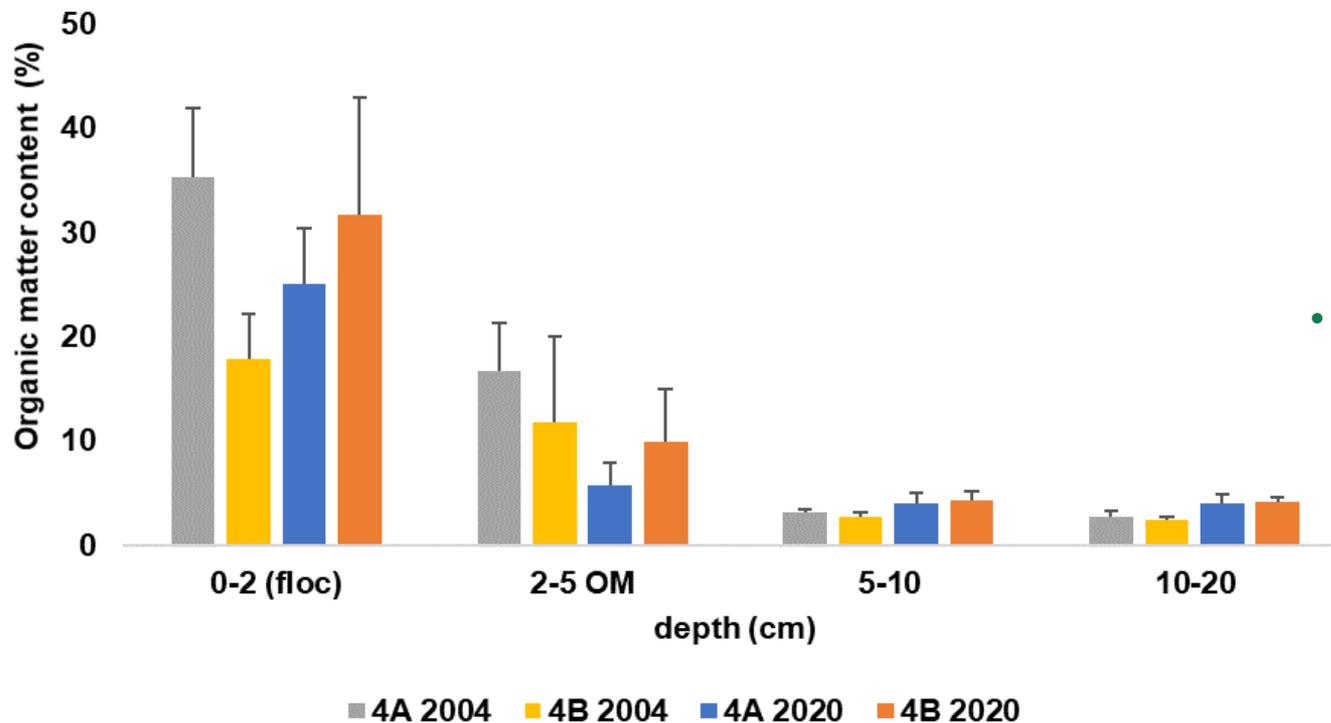
- The 2020 data showed that pH decreased in the sediments of both cells 4A and 4B compared with earlier years, very likely due to the build-up of organic matter around the dense root system of wetland plants that developed over time in the A-01 WTS

- The pH values in sediment at the periphery of cells 4A and 4B, where vegetation was minimal (referred to as control sediment), averaged 5.7 compared with 4.9 in sediments with dense growth of bulrush



# Sediment organic matter

- Sediment organic matter (OM) content as a function of depth after 20 years of operation of the A-01 WTS (n = 8 for each cell and sediment layer).



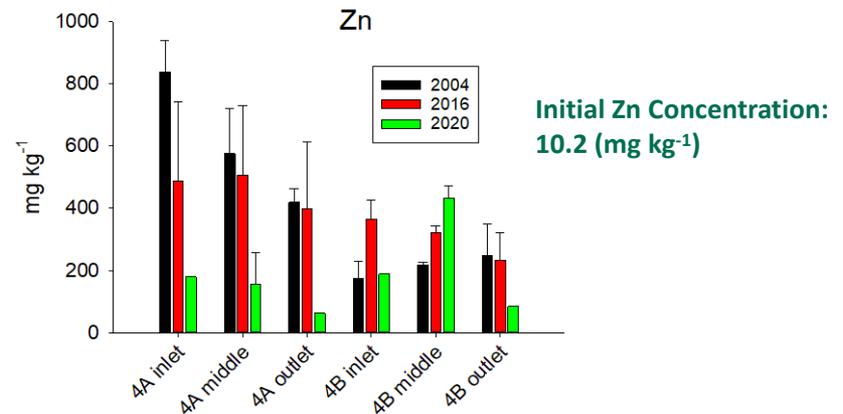
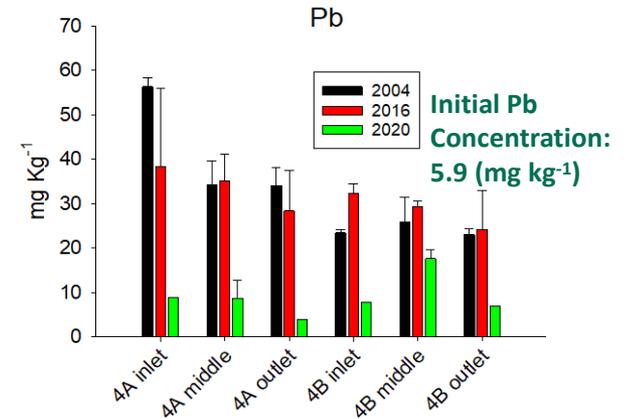
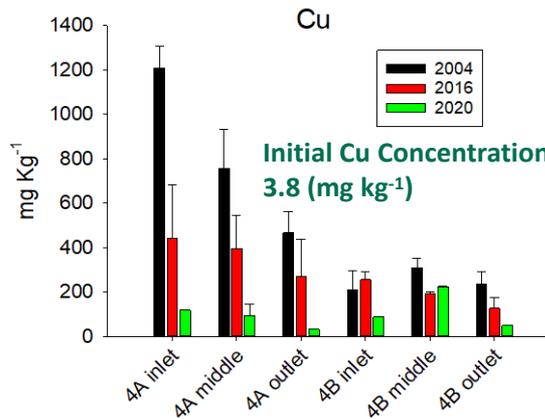
- The role of organic matter in wetlands is to provide a carbon source for sulfate reducing bacteria as well as to provide organic ligands for binding Cu and other metals
- The organic matter data collected in 2004 and 2020 indicated that organic matter was significantly higher in surface sediment. However, there was more organic matter (more than 4%) in the deeper sediment profile (5 to 20 cm) in 2020 than in 2004



# Spatial distribution of metals

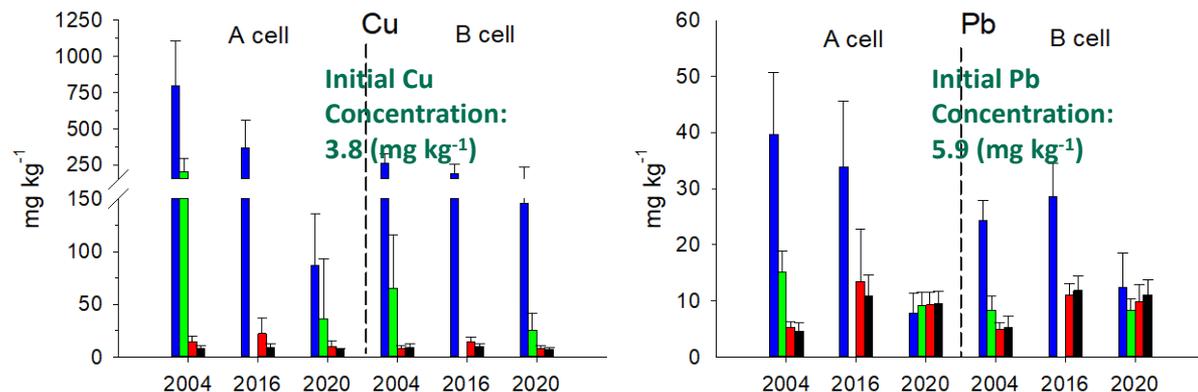
- Spatial distribution of metals ( $\text{mg kg}^{-1}$ ) in the floc layer of sediment (0-2 cm) in cells 4A and 4B of the A-01 WTS in 2004, 2016, and 2020 ( $n = 1-4$  for each location). Error bars are standard deviations.

- Cu concentrations in 2004 decreased from over  $1200 \text{ mg kg}^{-1}$  at the 4A inlet to about  $460 \text{ mg kg}^{-1}$  at the outlet
- Concentrations in cell 4B were lower ( $210 - 308 \text{ mg kg}^{-1}$ ) and without clear spatial trends
- Patterns in 2016 were similar, except that Cu concentrations were lower.
- By 2020, floc Cu concentrations in cell 4A had decreased markedly because of source reductions and, in some locations, were lower than in floc from cell 4B

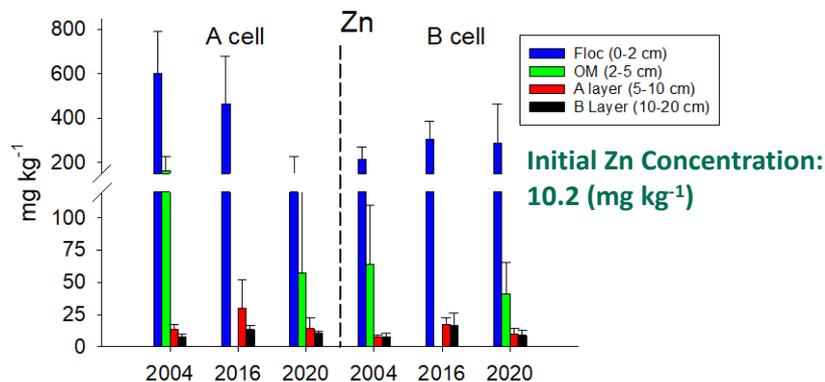


# Sediment metal distribution

Metal distribution ( $\text{mg kg}^{-1}$ ) in the sediment profile of cells 4A and 4B in the A-01 WTS in 2004, 2016, and 2020 ( $n = 8$  for each location). Sediment layers represented in the profile included floc, organic matter (OM), inorganic sediment layer A, and inorganic sediment layer B. Error bars are standard deviations. The OM layer was not sampled in 2016.

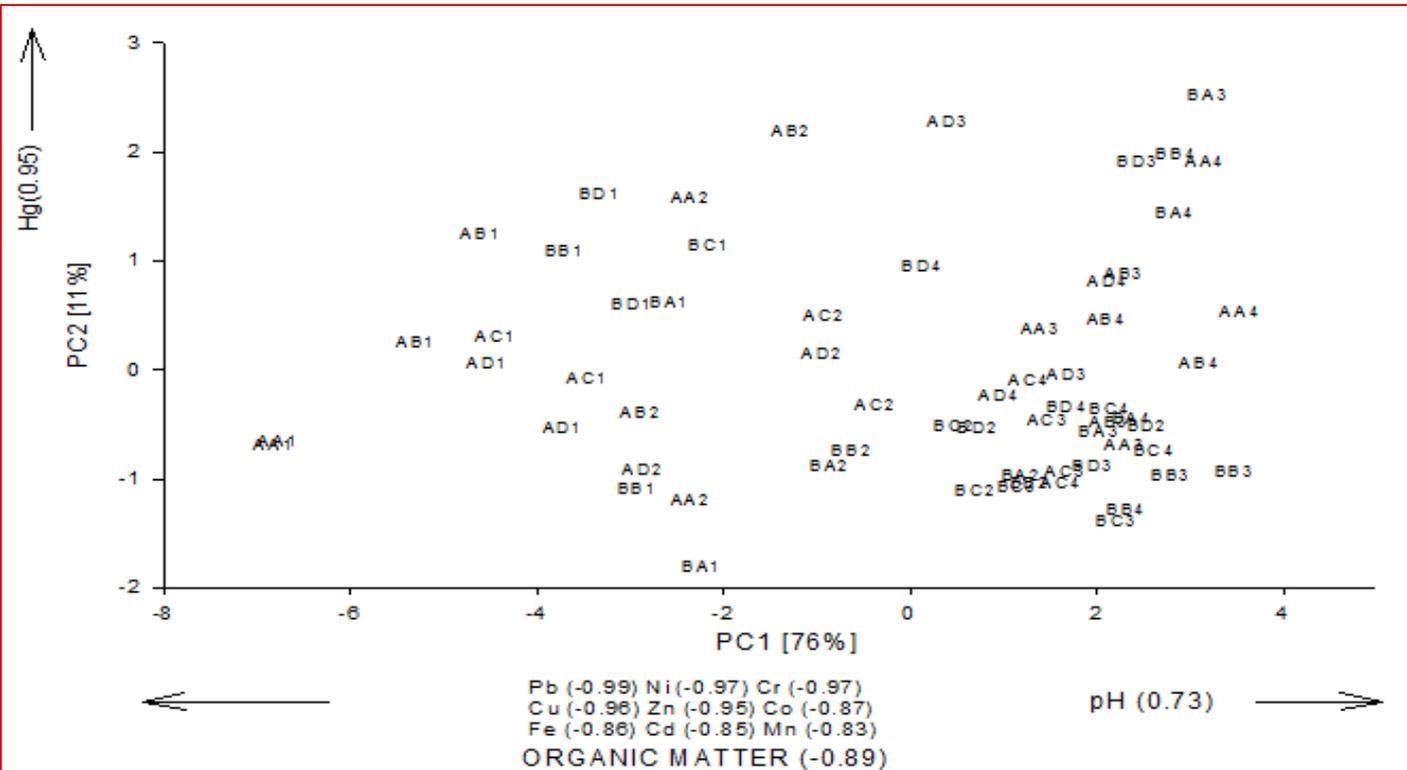


- Much of the metal removed from the water column was captured in the mixture of floc, organic detritus, and fine sediment at the sediment surface
- However, gradual increases in metal concentrations in deeper sediment layers indicated the downward migration of metals as a likely consequence of diffusion and showed that deeper sediments will likely be the final repository of metals removed from the wetland influent



# Sediment metal distribution

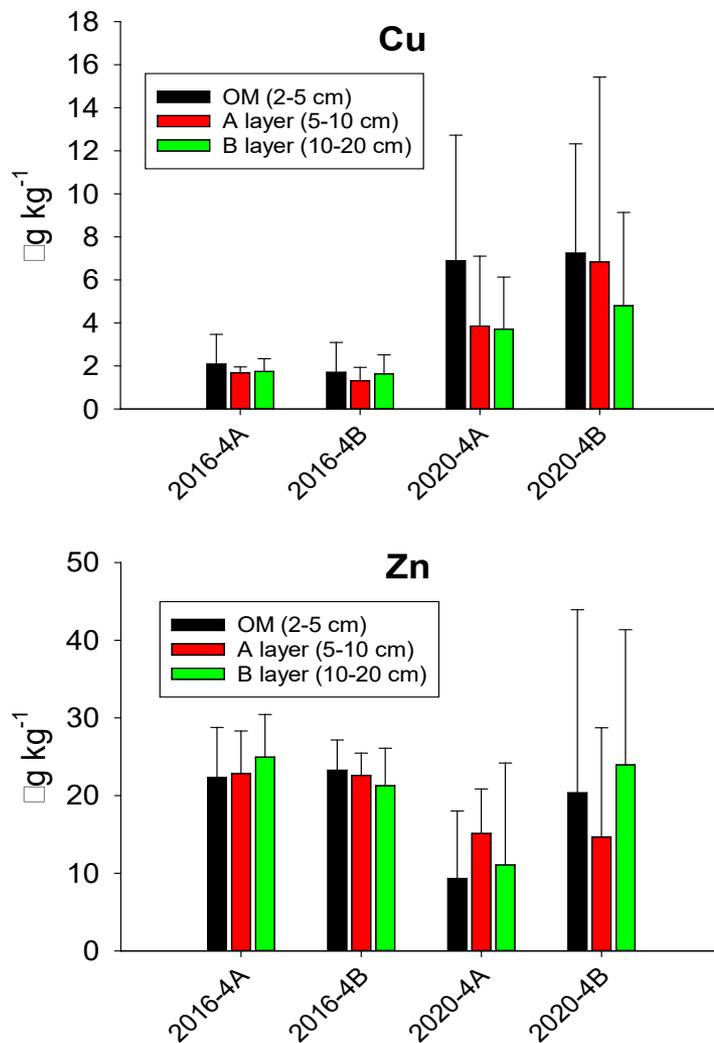
- Principal Components Analysis (PCA) of the total concentration Digestion Data from the A-01 Constructed Wetland



The first letter of each symbol represents the cell (A or B), the second letter represents the cell quarter (A, B, C, or D), and the number represents the depth (1=floc layer, 2=organic matter layer, 3=5-10 cm inorganic layer, 4=10-20 cm inorganic layer). Also shown are the variables correlated with each axis, the Pearson correlation (in parentheses) and the direction of increase (shown by the arrows). The proportion of the variance accounted for by each principal component score is shown in brackets.

- Most of the metal removed by the wetland cells was accumulated in the two top layers. PCA revealed a strong spatial gradient which was strongly correlated with percent organic matter, pH, and the concentration of all metals except mercury
- These results showed that most metals in the A-01 wetland sediments behaved similarly: their concentrations decreased as sediment depth increased

# Metal bioavailability in sediments



Concentrations of Cu and Zn measured by DGT in sediment layers in cells 4A and 4B of the A-01 WTS. The sediment profile was represented by the organic matter (OM) layer (2-5 cm), inorganic A layer (5-10 cm), and inorganic B layer (10-20 cm). There were eight replicates for each layer in each cell. Error bars are standard deviations.

- On average, DGT measurements for Cu (DGT Cu) and Zn (DGT Zn) in the sediments were much lower than bulk sediment concentrations during both years
- These results suggest that most of the Cu and Zn in the A-01 WTS sediments was not bioavailable as a likely consequence of adsorption to sediment particles and complexation with organic and inorganic substances

# Conclusions

