Using Indicators of Wetland Condition to Predict Trace Metals Changes in Natural and Treatment Wetlands in the Tar Creek Watershed

Samantha Taylor and Robert Nairn
Center for Restoration of Ecosystems and Watersheds, University of Oklahoma

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GALLOGLY COLLEGE OF ENGINEERING
SCHOOL OF CIVIL ENGINEERING AND ENVIRONMENTAL SCIENCE
The UNIVERSITY of OKLAHOMA

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The University of Oklahoma

Presentation Agenda

- Introduction
- Hypotheses & Objectives
- Methodology
- Results and Discussion
- Conclusions

SBB-WL effluent

Introduction

Introduction – Incidental and Treatment Wetlands

- Ecotone between terrestrial and aquatic ecosystems with many ecosystem benefits
- Incidental wetlands develop naturally
- Treatment wetlands are Nature Based Solutions (NBS)
  - Human-designed
- Physical, chemical, biological, and microbial processes
  - Applications in mine drainage treatment

https://www.mvp.usace.army.mil/Media/Images/igphoto/2000793517/

https://extension.wvu.edu/natural-resources/acid-mine-drainage/passive-treatment/passive-treatment-systems-for-treating-acid-mine-drainage

Introduction – Removal Processes

- Fe in oxidizing conditions, trace metal sorption to particles

$$Fe^{2+} + \frac{1}{4}O_2 + H^+ \rightarrow Fe^{3+} + \frac{1}{2}H_2O$$

$$Fe^{3+} + 2H_2O \rightarrow FeOOH + 3H^+$$

- Metal microbial transformation to sulfides in reducing conditions

$$M_2 + H_2S + 2HCO_3^- \rightarrow MS + 2H_2O + 2CO_2$$

Precipitated iron oxides in mine drainage incidental wetland

Introduction – Hydrology and Water Chemistry

- Water source and time inundated

- Influent water quality affects function
  - Vegetation growth
  - Microbial activity
  - Substrate redox properties

- Pulsing hydrology rereleases metals
  - Chevron treatment wetland (Hansen and Horne 2022)
  - French incidental wetland (Olivie-Lauquet et. al 2001)

S40-WL artesian mine water discharge

Introduction – Vegetation

- Water and substrate affect vegetation
- Mining impacted wetlands
  - No convergence to reference ecosystem (Timoney et al. 2015)
- Contribute organic matter to substrate
  - Organic matter increases microbial activity
  - Trace metal sorption
  - Major removal pathways for metals (Younger et al. 2002)

Sagittaria latifolia at SBB-WL

Introduction – Substrate

- Wetland substrate correlates to wetland health and function

- Mining impacts wetland substrate
  - Low organic matter and nutrients
  - Trace metals impair vegetation growth (Timoney 2015)

Howe-WL substrate sampled

Hypotheses & Objectives

Photo taken by Olivia Mitchell

Research Question

What are the relationships between hydrology, soils, and vegetation with trace metal concentration changes in constructed treatment and incidental wetlands impacted by mine drainage?

Hypotheses

1. Treatment wetlands will decrease trace metal concentrations more effectively than incidental wetlands because continuous inundation promotes sequestration and intermittent inundation promotes remobilization.

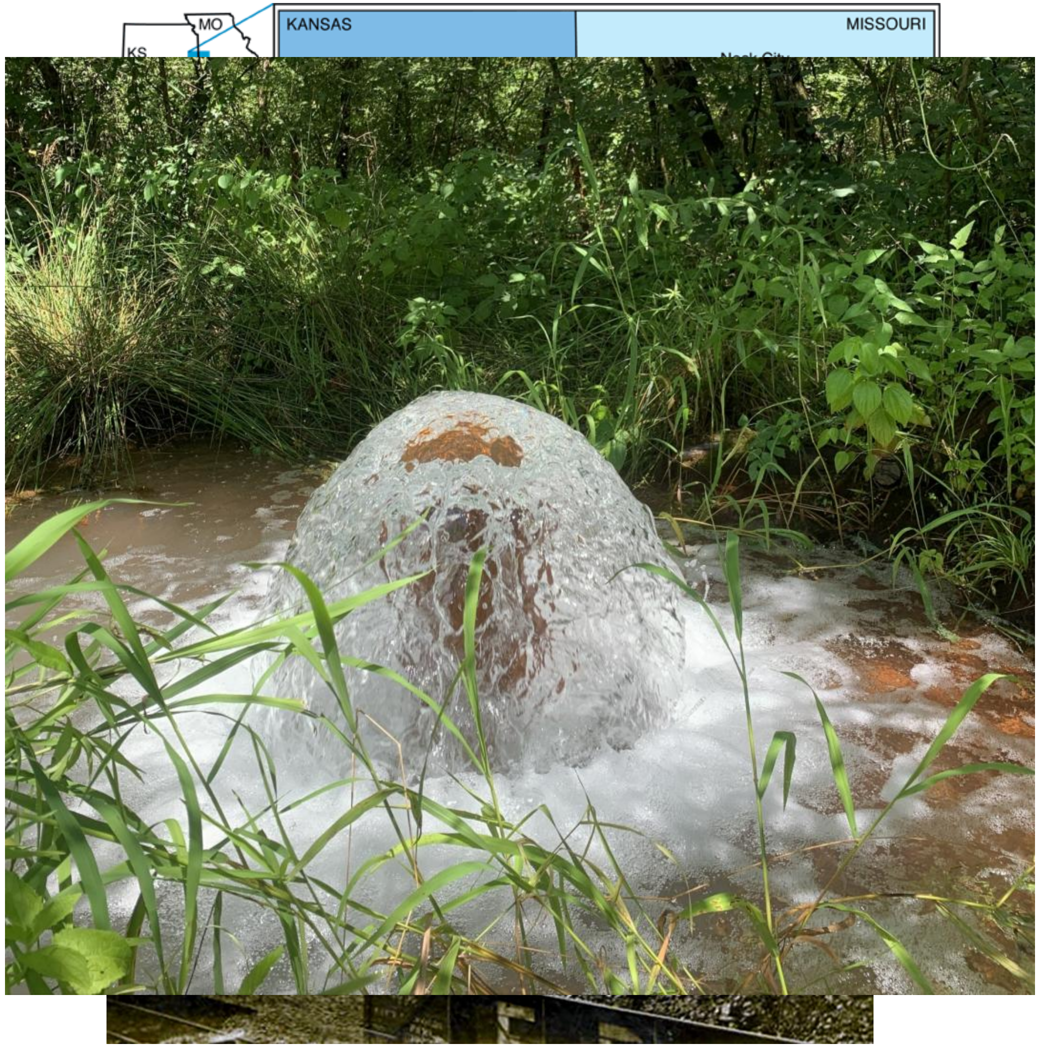
2. Wetland vegetative cover will be a more reliable predictor of trace metal concentration changes than species richness or species diversity because greater biomass leads to greater soil organic matter accumulation.

3. Wetland vegetation species richness and species diversity will be lesser in wetlands on mine waste-impacted soils than native soils because of greater trace metals concentrations and lesser phosphorus and organic matter.

Methodology

Methodology – Tar Creek Watershed

- Tri-State Mining District
  - 1850-1950
  - 9 million tons of Zn ore
  - 2 million tons of Pb ore
- Tar Creek Superfund Site
  - "irreversibly damaged" surface water
  - Fe, Pb, Zn, and Cd
- Reclamation efforts
  - Chat removal
  - Passive water treatment

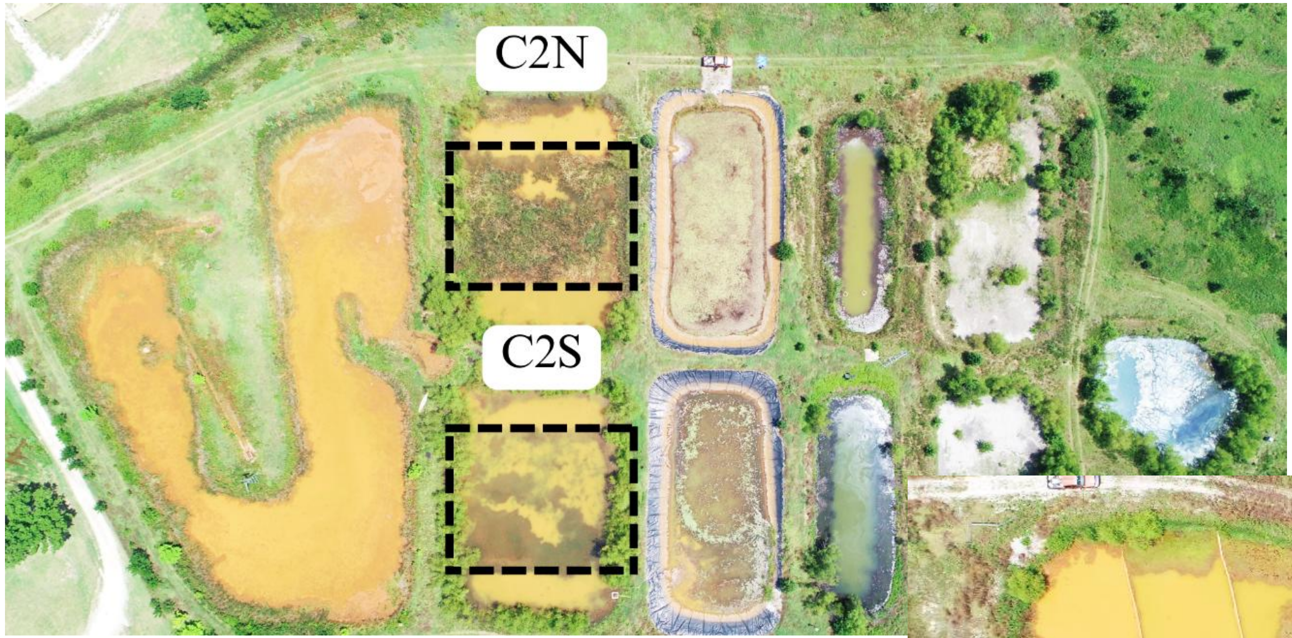


https://en.wikipedia.org/wiki/Tri-State_district

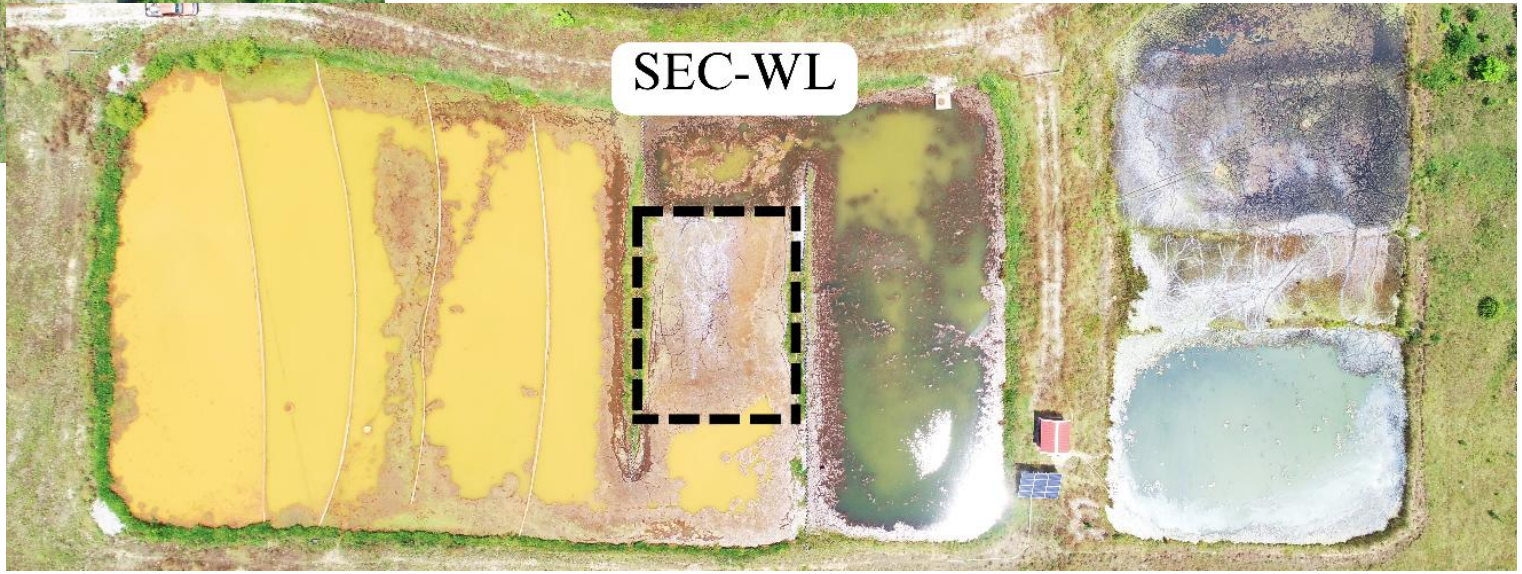
Methodology - Sites

- 10 wetlands sites
  - 6 incidental, 4 constructed
  - Varying hydrology, water quality, vegetation, and substrates

Methodology – PTS Sites



DJI Aerial Photo July 2024



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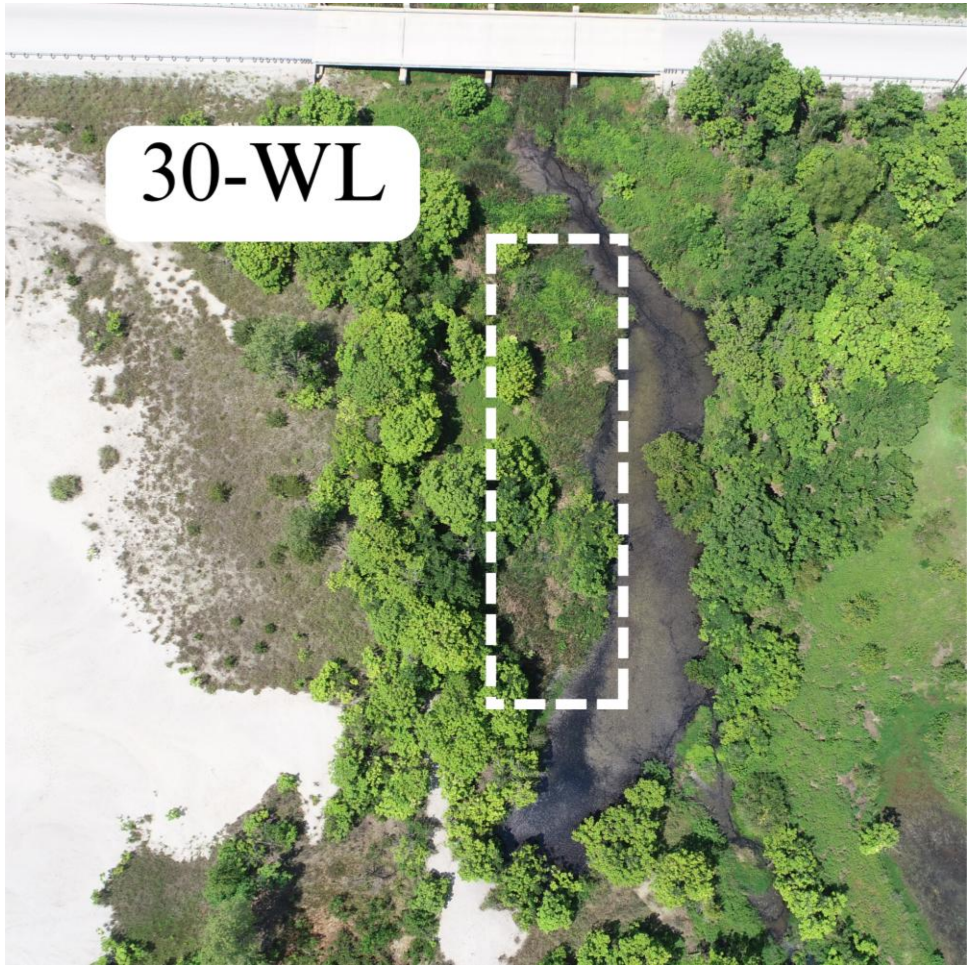
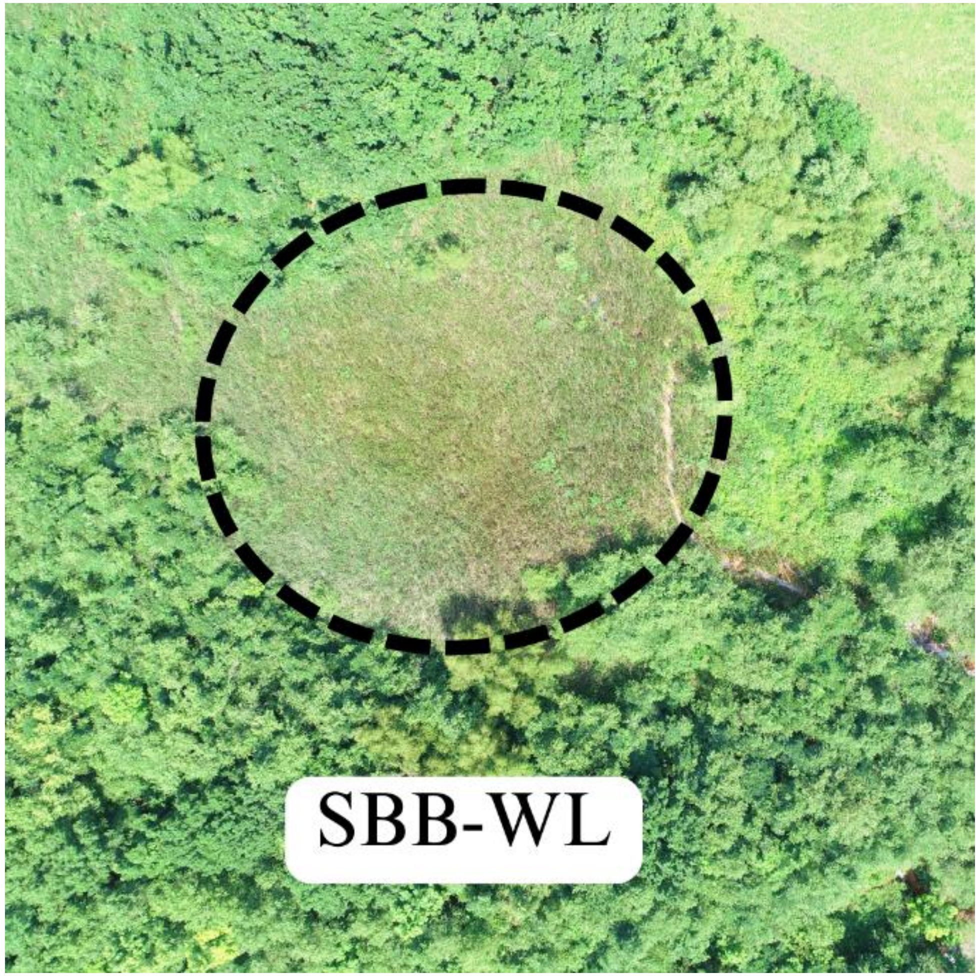
Methodology – Riparian Sites



DJI Aerial Photo July 2024

DJI Aerial Photo July 2024

Methodology – Artesian MD Sites



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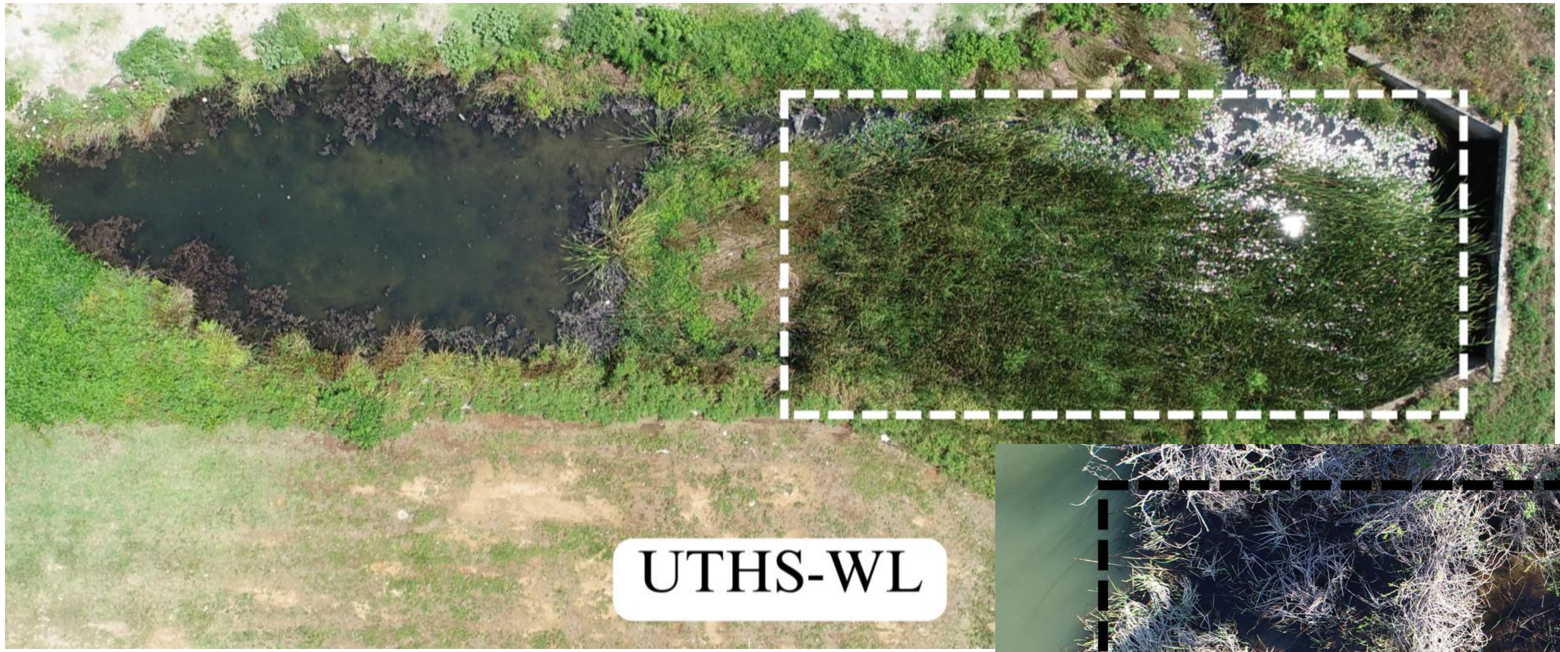
DJI Aerial Photo July 2024

Methodology – Treated MD Sites



DJI Aerial Photo July 2024

DJI Aerial Photo April 2025

Methodology – Interim Measure Site

DJI Aerial Photo July 2024

Methodology – Water Quality

Monthly influent and effluent of each wetland

Field Measurements:

- Alkalinity
- Turbidity
- Physiochemical parameters (dissolved oxygen, pH, temperature, specific conductance)

Laboratory Measurements:

- Total and dissolved trace metals (Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Se, Si, Zn)
- Selected anions (NO_3^-, NO_2^-, PO_4^{3-}, SO_4^{2-}, Cl^-)

Measuring physiochemical parameters with YSI EXO1 datasonde

Methodology – Hydrology

- Water source identification

- Estimated hydroperiod based on presence of surface water during sampling trips

S40-WL artesian mine water discharge

Methodology - Vegetation

- July survey
- Point-intercept method
- Vegetative cover
  - $\frac{\text{\# of vegetated points}}{\text{\# of sampled points}}(100) = \%\ \text{cover}$
- Species richness
  - # of identified species
- Simpson's Index
  - $\frac{1}{\sum p_i^2} = \text{Simpson Index (D)}$

TC-Adams showing approximate transects

Methodology - Soils

Field measurements:

- Wet Munsell soil color
- Plant-root simulator probes (NO_3-N, NH_4-N, P, K, S, Ca, Mg, Fe, Mn, Cu, Zn, B, Al, Pb, Cd)

Laboratory measurements:

- Organic matter content
- Particle size distribution
- Trace metal concentrations (Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Se, Si, Zn)

PRS probes deployed at SEC-WL

Collecting substrate samples at TC-Adams "out"

Results and Discussion

Study 1: Comparisons of Treatment & Incidental Wetlands

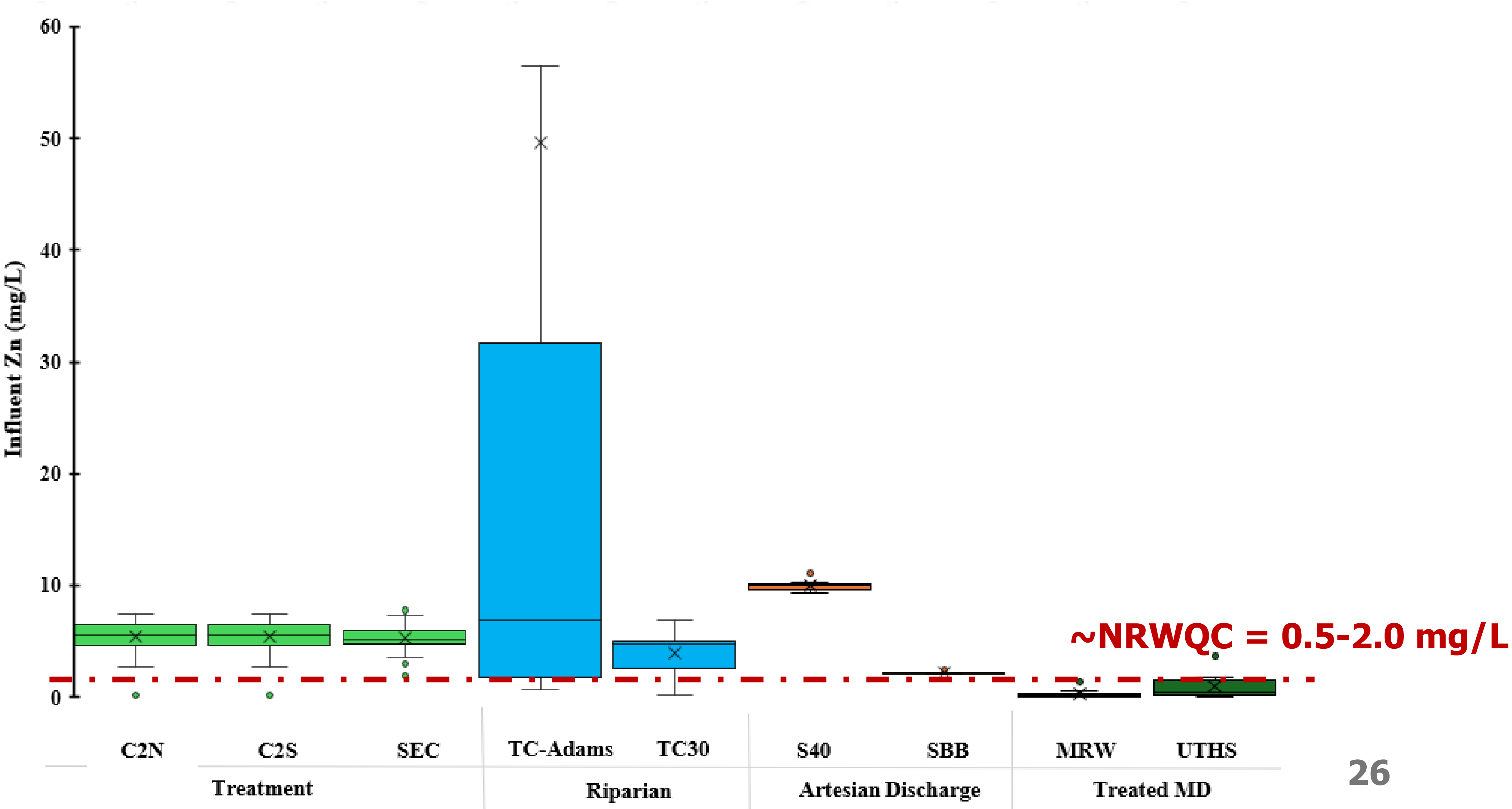
Hypothesis

Treatment wetlands will decrease trace metal concentrations more effectively than incidental wetlands because continuous inundation promotes sequestration and intermittent inundation promotes remobilization.

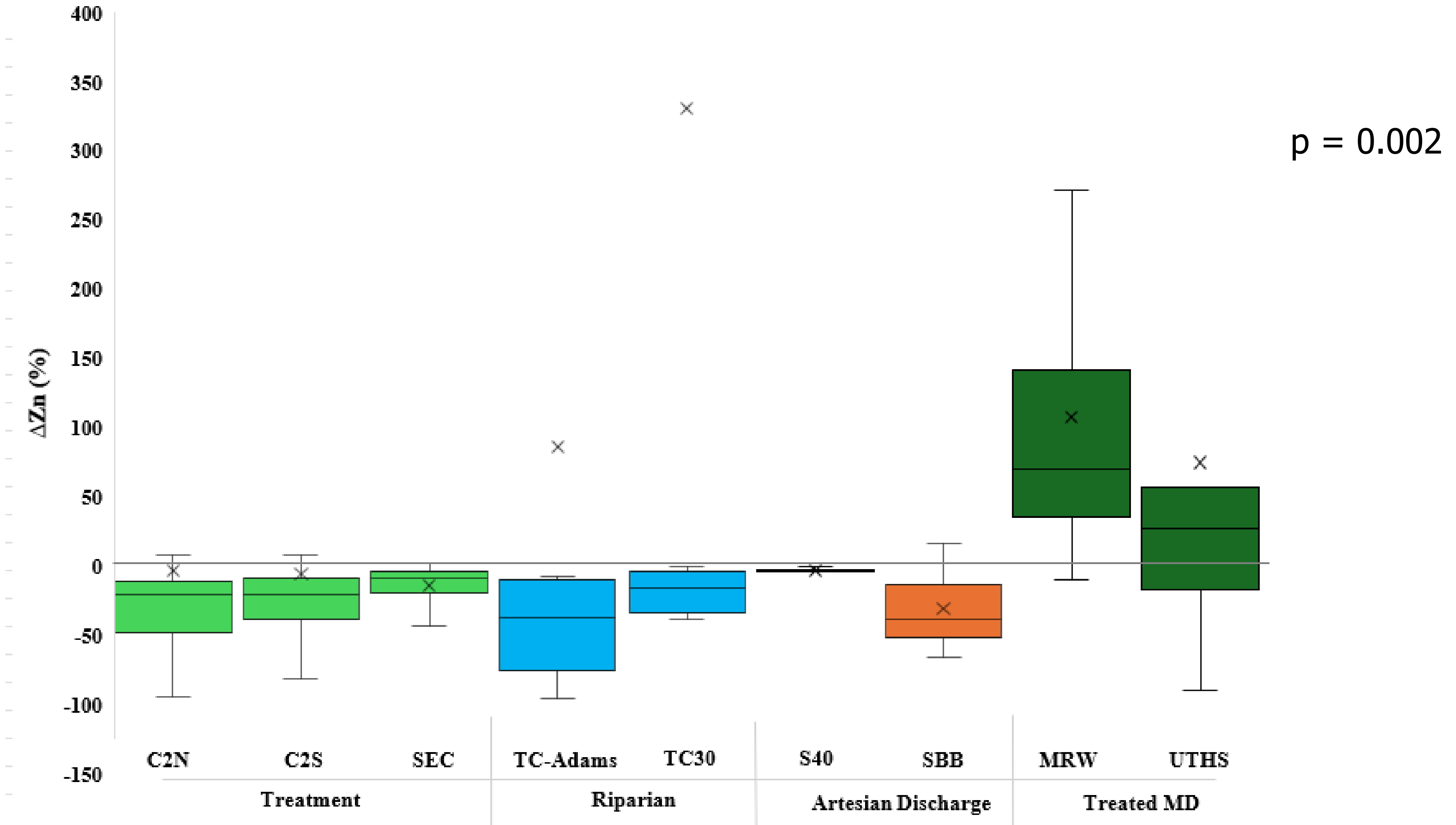
Objective

Compare the effectiveness of treatment wetlands and incidental wetlands in removing trace metals from surface water.

Study 1: Total Zinc Influent Concentrations



Study 1: Total Zinc Concentration Changes



Study 1: Treatment and Incidental Comparisons

Total Metals

	Null Hypothesis	Sig.	Decision
Fe	The distribution of ΔFe (%) is the same between treatment and incidental wetlands	<0.001	**Reject null hypothesis**
Pb	The distribution of ΔPb (%) is the same between treatment and incidental wetlands	<0.001	**Reject null hypothesis**
Zn	The distribution of ΔZn (%) is the same between treatment and incidental wetlands	0.002	**Reject null hypothesis**
Cd	The distribution of ΔCd (%) is the same between treatment and incidental wetlands	0.103	Retain null hypothesis

Dissolved Metals

	Null Hypothesis	Sig.	Decision
Fe	The distribution of dissolved ΔFe (%) is the same between treatment and incidental wetlands	0.001	**Reject null hypothesis**
Pb	The distribution of dissolved ΔPb (%) is the same between treatment and incidental wetlands	0.828	Retain null hypothesis
Zn	The distribution of dissolved ΔZn (%) is the same between treatment and incidental wetlands	<0.001	**Reject null hypothesis**
Cd	The distribution of dissolved ΔCd (%) is the same between treatment and incidental wetlands	0.011	**Reject null hypothesis**

Study 1: Time Inundated and Metal Removal

Parameter	Correlation Coefficient (r_s)	Statistical Significance (p)
Total ΔFe (%, mean) vs Surface Water Presence (%)	-0.546	0.102
Total ΔZn (%, mean) vs Surface Water Presence (%)	-0.257	0.474
Total ΔFe (%, mean) vs Influent Fe (mg/L)	**-0.525**	**<0.001**
Total ΔZn (%, mean) vs Influent Zn (mg/L)	**-0.523**	**<0.001**

Study 1: Discussion

★ Treatment wetlands removed trace metals; incidental wetland concentration changes varied

★ No statistical significance shown between time inundated and trace metal concentration changes

★ Statistical significance shown between influent water quality and trace metal concentration changes

Study 2: Vegetation and Metal Changes

Hypothesis

Wetland vegetative cover will be a more reliable predictor of trace metal concentration changes than species richness or species diversity because greater biomass leads to greater soil organic matter accumulation.

Objective

Determine indicators of vegetative condition which correlate with effective removal of trace metals in mining-impacted wetlands.

Study 2: Vegetation and Organic Matter

Site	Wetland Type	…getative …ver (%)	Species Richness		
		77.46	4		
		88.46	6		
				4.88	8.52 ± 3.23
				2.95	13.30 ± 2.94
UTHS	Incidental – Treated			6.08	14.97 ± 0.39
MRW	Incidental – Treated			3.68	11.51 ± 2.92

Study 2: Results

- Comparison of vegetative cover, species richness, Simpson's Index, and organic matter with the change in total metals

ΔMetal	%	Vegetative Cover (%)		Species Richness		Simpson's Index		Organic Matter	
		r_s	p	r_s	p	r_s	p	r_s	p
Fe	Mean	-0.358	0.310	0.561	0.092	0.576	0.082	-0.067	0.855
	Median	-0.188	0.603	0.390	0.265	0.467	0.174	0.188	0.603
Pb	Mean	-0.200	0.800	0.632	0.368	0.800	0.200	-0.400	0.600
	Median	-0.200	0.800	0.632	0.368	0.800	0.200	-0.400	0.600
Zn	Mean	0.164	0.651	0.335	0.343	**0.733**	**0.016**	0.079	0.829
	Median	**0.648**	**0.043**	0.098	0.789	0.394	0.260	0.333	0.347
Cd	Mean	0.250	0.589	-0.72	0.878	0.679	0.094	-0.143	0.760
	Median	0.107	0.819	-0.144	0.758	0.071	0.879	0.214	0.645

Study 2: Discussion

- As ΔZn increases (and the removal efficiency decreases), the vegetative structure improves
- Spearman's Ranked Correlation Coefficient showed only weak, statistically insignificant correlations between organic matter and trace metal concentration change
- Correlation =/= causation

Study 3: Substrate and Vegetation

Hypothesis

Wetland vegetation species richness and species diversity will be lesser in wetlands on mine waste-impacted soils than native soils because of greater trace metals concentrations and lesser phosphorus and organic matter.

Objective

Determine indicators of substrate condition which correlate with wetland vegetative structure in mining-impacted watersheds.

Study 3: Native and Mine-waste Impacted

Parameter	Null Hypothesis	Sig.	Decision
Vegetative Cover (%)	The distribution of vegetative cover is the same across mine waste impacted and native soils	0.056	Retain the null hypothesis
Species Richness	The distribution of species richness is the same across mine waste impacted and native soils	0.095	Retain the null hypothesis
Simpson's Index	The distribution of Simpson's Index is the same across mine waste impacted and native soils	0.421	Retain the null hypothesis

Substrate Concentrations	Null Hypothesis	Sig.	Decision
Fe	The distribution of Fe is the same between native and mine-waste soils	0.095	Retain the null hypothesis
Pb	The distribution of Pb is the same between native and mine-waste soils	0.056	Retain the null hypothesis
Zn	The distribution of Zn is the same between native and mine-waste soils	1.00	Retain the null hypothesis
Cd	The distribution of Cd is the same between native and mine-waste soils	0.056	Retain the null hypothesis

Study 3: Results

Soil Parameter	Vegetative Cover (%)		Species Richness		Simpson's Index	
	r_s	p	r_s	p	r_s	p
Tot. Fe	0.370	0.293	-0.372	0.290	**-0.685**	**0.029**
Bio. Fe	0.127	0.726	-0.256	0.475	-0.612	0.060
Tot. Pb	-0.442	0.200	0.348	0.325	0.467	0.174
Bio. Pb	-0.600	0.067	0.189	0.601	0.103	0.777
Tot. Zn	0.030	0.934	-0.524	0.120	-0.248	0.489
Bio. Zn	-0.486	0.154	-0.284	0.426	0.103	0.776
Tot. Cd	-0.152	0.676	0.421	0.226	**0.636**	**0.048**
Bio. Cd	-0.647	0.083	0.323	0.435	0.551	0.157
Organic Matter	0.394	0.260	-0.165	0.649	-0.224	0.533
Bio. P	-0.024	0.955	0.491	0.217	0.381	0.352

Study 3: Discussion

- Native and mine-waste impacted soils are statistical similar
- Negative, statistically significant correlations between Simpson's Index and Fe
- Positive, statistically significant correlations between Simpson's Index and Cd

Conclusions

UTHS-WL

Study 1: Treatment Wetlands, Incidental Wetlands, and Hydrology

- Treatment wetlands will decrease trace metal concentrations more effectively than incidental wetlands because continuous inundation promotes sequestration and intermittent inundation promotes remobilization.

- **The hypothesis is partially accepted**
  - Treatment wetlands did decrease trace metal concentrations more effectively than incidental wetlands
  - Time inundated was not a statistically significant factor contributing to the trend

Study 2: Vegetative Structure, Metal Changes, and Organic Matter

- Wetland vegetative cover will be a more reliable predictor of trace metal concentration changes than species richness or species diversity because greater biomass leads to greater soil organic matter accumulation.

- **The hypothesis is not accepted**
  - Vegetative cover did not have stronger correlations with metal removal than other parameters
  - No statistical significance between organic matter and trace metal removal

Study 3: Substrate Quality and Vegetative Structure

- Wetland vegetation species richness and species diversity will be lesser in wetlands on mine waste-impacted soils than native soils because of greater trace metals concentrations and lesser phosphorus and carbon.

- **The hypothesis is not accepted**
  - Vegetative structure were not statistically different between native and mine-waste impacted soils
  - Trace metal concentrations in the soil were not statistically different between native and mine-waste impacted soils
  - Negative correlation between Fe and Simpson's Index; positive correlation between Cd and Simpson's Index

Study Limitations

- Limited sample size of incidental wetlands and water samples of incidental wetlands
- No flows limited ability to compare wetland mass loadings, which could provide a clearer picture
- Correlations do not guarantee causation

Future Work

- Expanding sample size of incidental wetlands and number of sampling events
- Exploring other wetland condition indicators, including the associated microbial communities
- Exploring the statistically significant correlations to determine if the parameters are related
- Comparisons of vegetative structure with hydrology and water quality to explore the ecological impacts of historic mining on wetland habitat

Data and Results Sharing

- Background information for a microbially focused PhD project
- Most robust vegetation survey data of species thriving in this watershed – informing wetland greenhouse plans this summer
- Watershed planning contracted through the EPA might look at water quality data to determine efficacy of wetland/sed trap installations

Thank you! Any questions?

Presentation adapted from master's thesis titled:

"Using Indicators of Wetland Condition to Predict Trace Metals Changes in Natural and Treatment Wetlands in the Tar Creek Watershed"

University of Oklahoma Civil Engineering and Environmental Science
Advisor: Dr. Robert Nairn
Email: samanthataylor@ou.edu

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