Lower Coeur d'Alene River Basin Sediment Research Overview

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Summary of Studies

Studies included in overview:

- FY20 Superfund Technical Liaison Research (STLR) Grant: *Metal bioavailability in sediments experiencing wetting and drying cycles—the impact of sulfur and iron chemistry*

  Study time frame: field: 2021; mesocosm: 2023-2024

- CH2MHill: *Incremental Thin-Layer Capping Pilot Study*

  Study time frame: 2017 to 2019

- FY18 Regional Applied Research (RARE) grant: *Soil amendments to reduce bioavailability of toxic metals in contaminated soils and sediments*

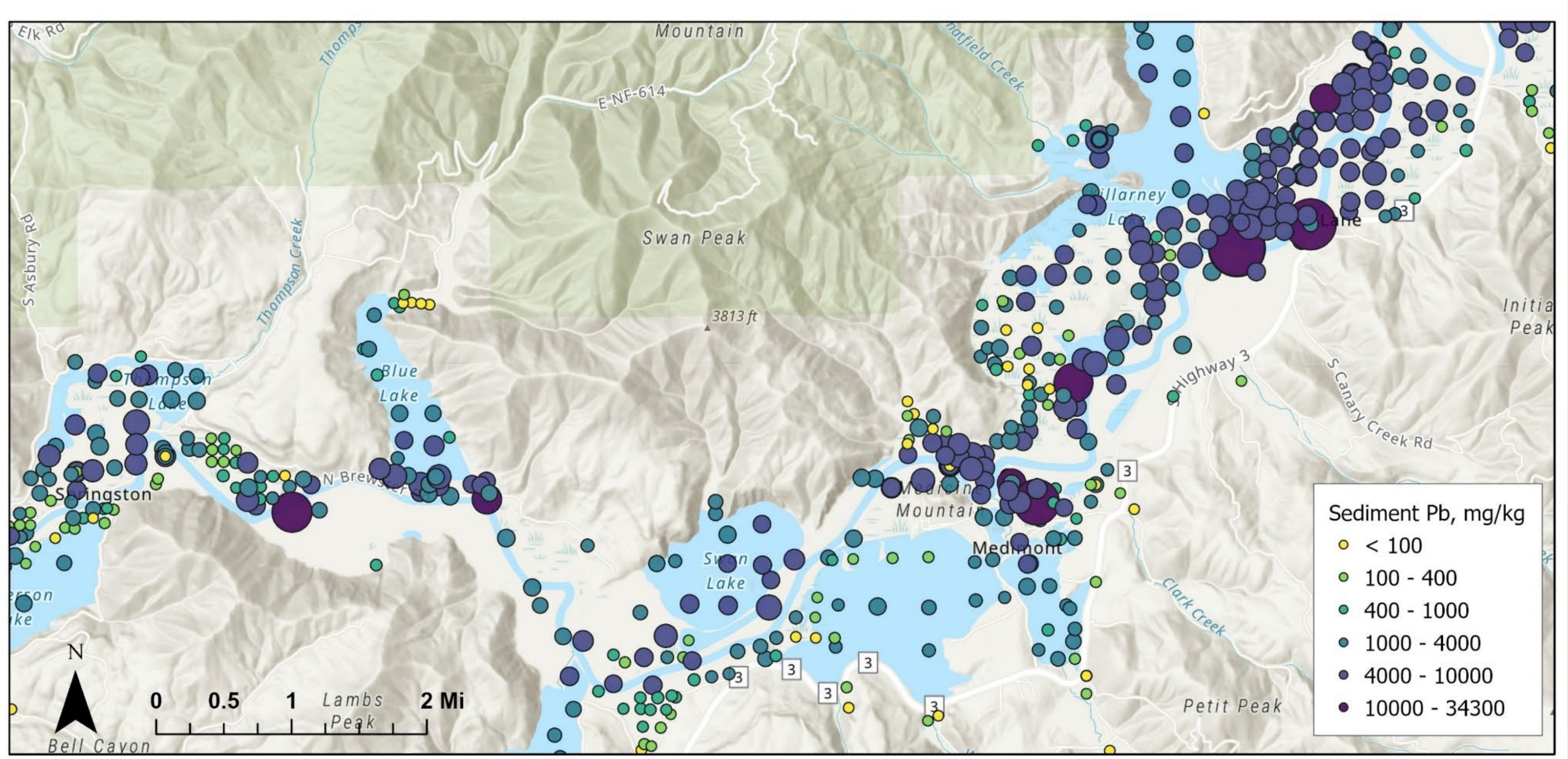
  Study time frame: field: 2019; laboratory: 2020

- FY22 Regional-ORD Applied Research Program (ROAR) grant: *Application of jarosite-based remediation technologies to significantly decrease lead (Pb) bioavailability in contaminated soils*

  Study time frame: 2023-ongoing

Context for sediment studies

- Lead (Pb) contaminated sediments (≥ 1,000 ppm Pb) cover the Coeur d'Alene Lower Basin in lateral wetlands/marshes along river channel.

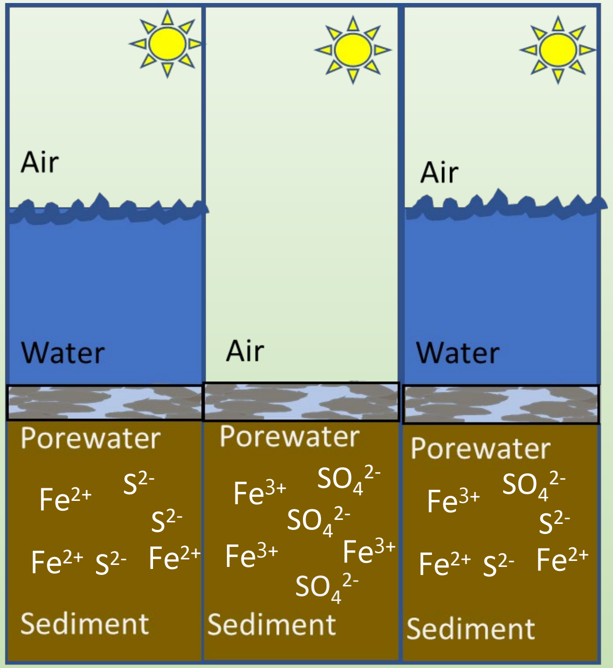


Data source: https://www.waterqualitydata.us/

Pic: Coeur d'Alene Tribe

Introduction: *Metal bioavailability in sediments experiencing wetting and drying cycles—the impact of sulfur and iron chemistry*

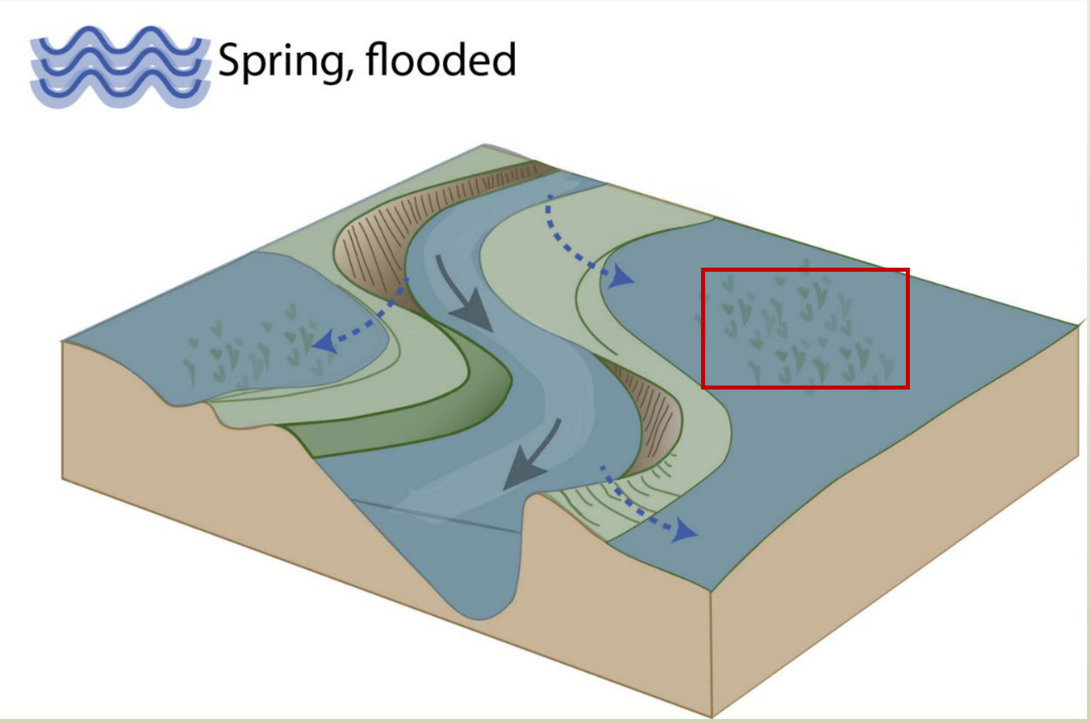
- Metal mobility & toxicity varies depending on its form and speciation
- Sediment constituents like iron (Fe) and sulfur (S) can impact Metal cycling by binding—which can be influenced by oxidation-reduction (redox) conditions.
- Sediment Fe/S redox conditions are dynamic when subjected to wetting/drying cycles.

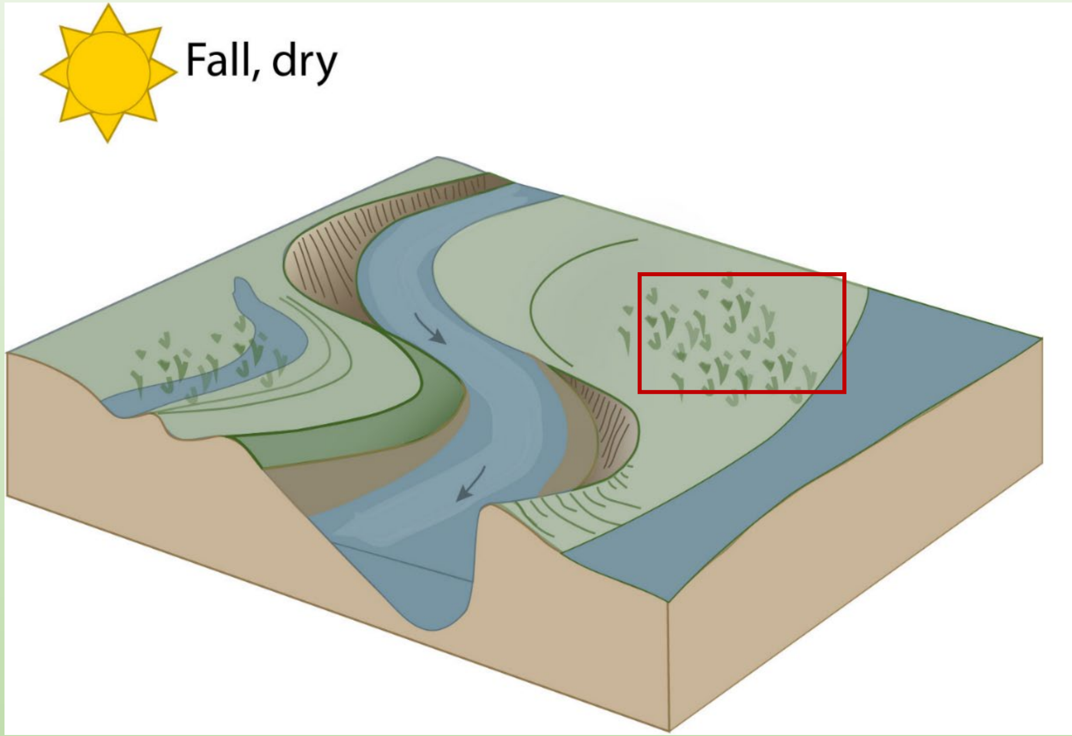


Study Objective:

Hydrological Conditions (sediment wetting/drying) → **Sediment Redox** (Fe & S chemistry) → **Metal Availability** (Porewater partitioning)

Introduction: *Metal bioavailability in sediments experiencing wetting and drying cycles—the impact of sulfur and iron chemistry*



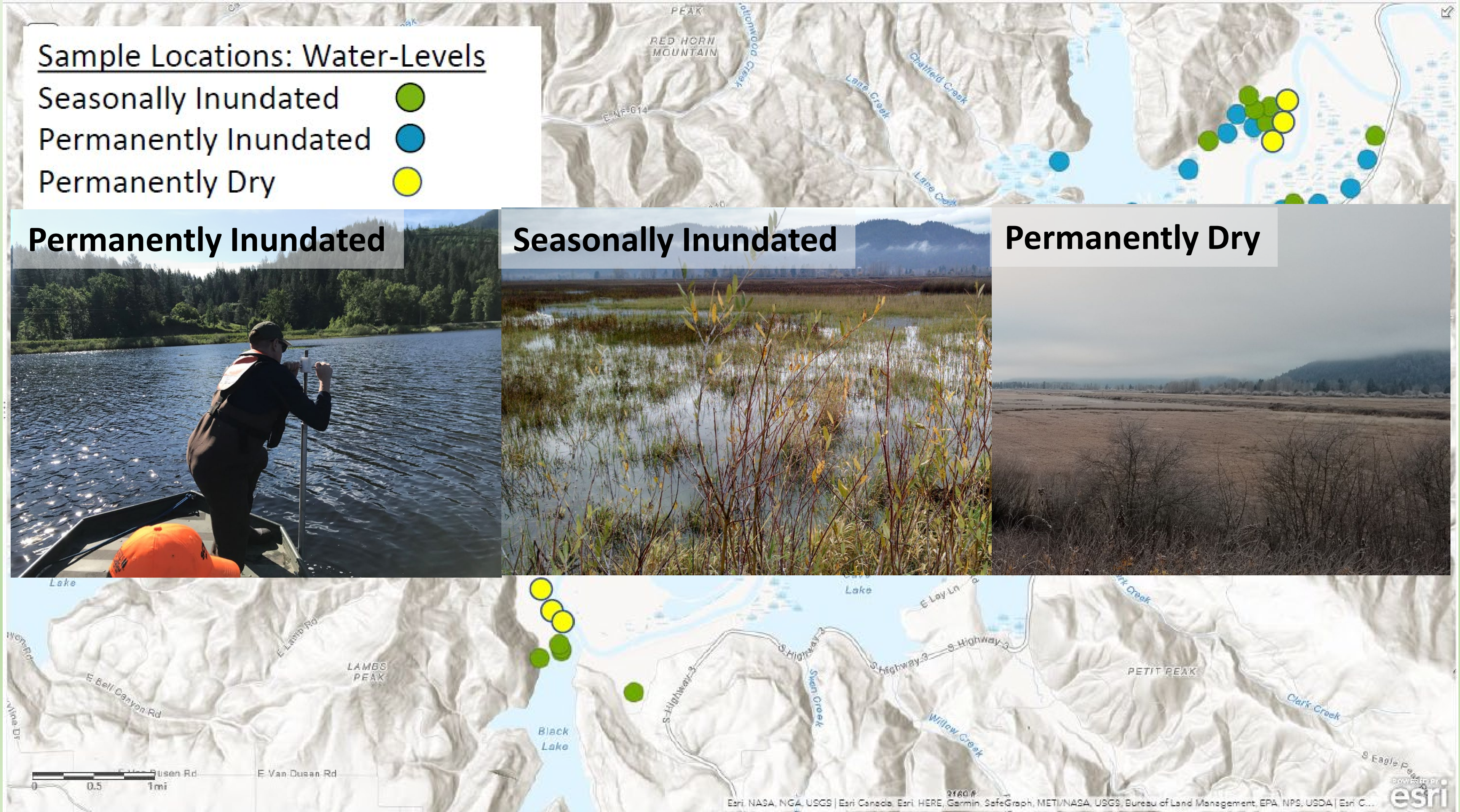


- Snow melt → annual spring floods
- Seasonal flooding in wetlands/marshes
- Mobilization of river sediment load

- Drop in water levels during fall months
- Seasonal drying in wetlands/marshes

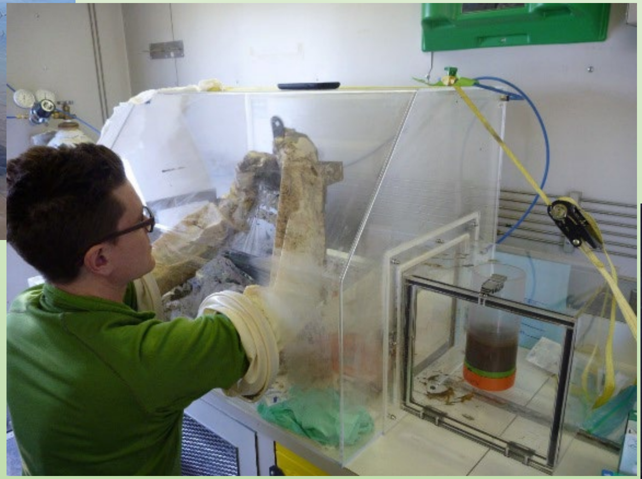
Study Location: *Metal bioavailability in sediments experiencing wetting and drying cycles—the impact of sulfur and iron chemistry*

Study Location: The Lower Coeur d’ Alene River Basin includes lateral lakes and wetlands that experience seasonal flooding and water-level fluctuations.



Field Study Methods: *Metal bioavailability in sediments experiencing wetting and drying cycles—the impact of sulfur and iron chemistry*

Step 1) Collect Sediment Cores



Step 2) Section cores (0-4 cm)

Step 3) Centrifuge

Step 4) Filter porewater

Porewater Samples

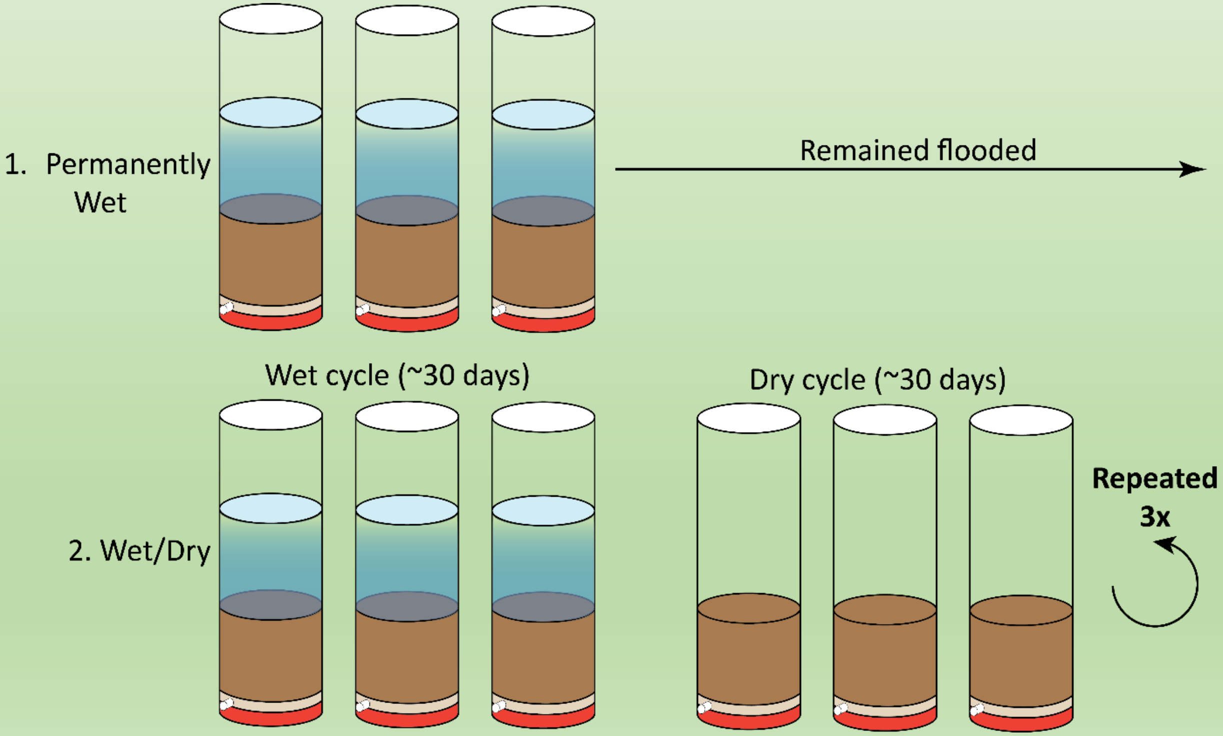
Controlled Lab Study Methods: *Metal bioavailability in sediments experiencing wetting and drying cycles—the impact of sulfur and iron chemistry*

- Quantify rate of Pb mobilization over repeated wetting/drying cycles

Sampling site

- Wetland sediment (dried)
- Lake sediment (kept anoxic)

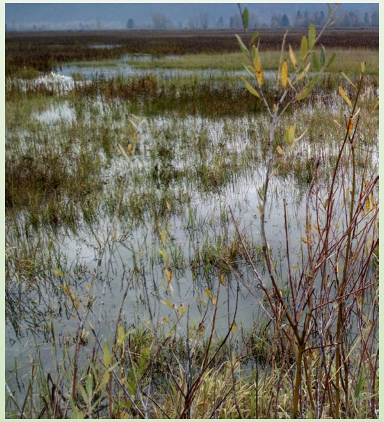
- Treatment

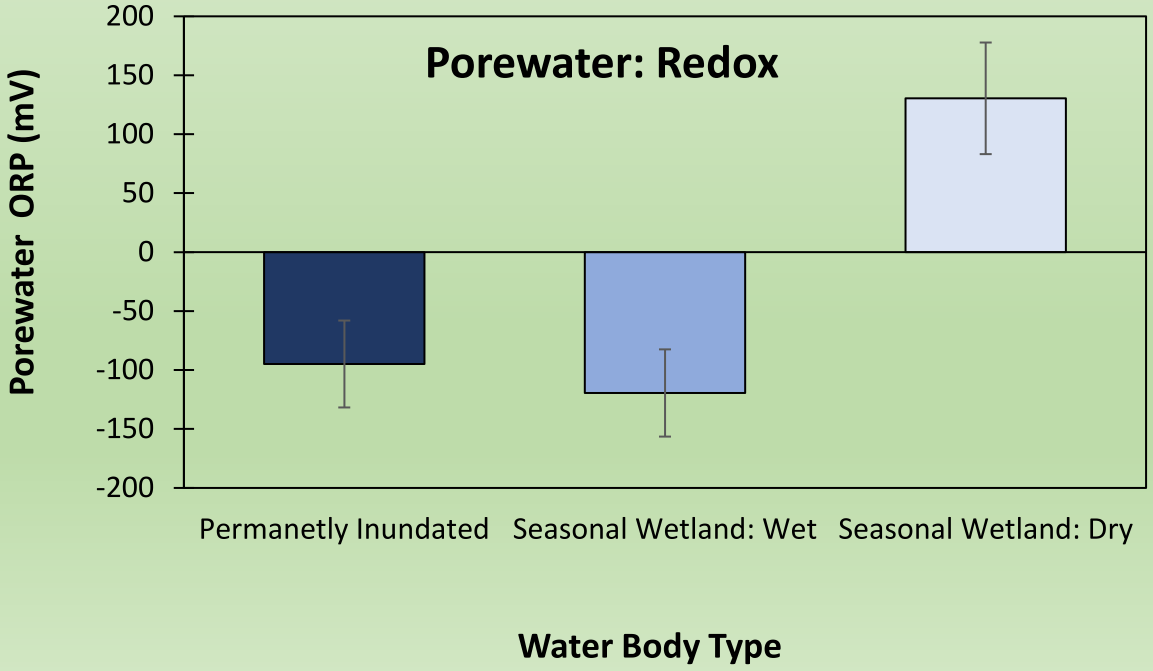


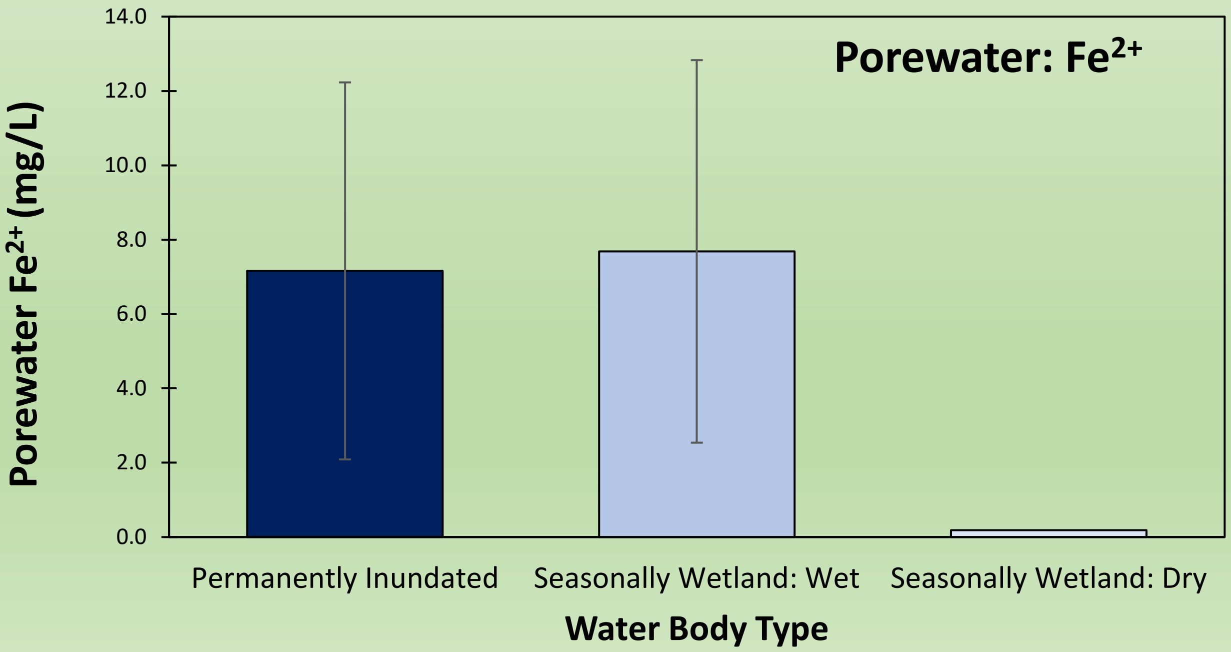
Field Results: *Sediment/Porewater Chemistry*

Permanently Inundated

Seasonally Inundated



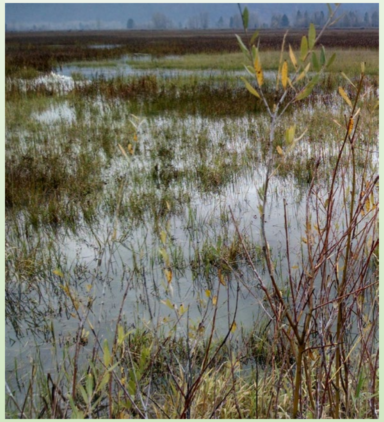


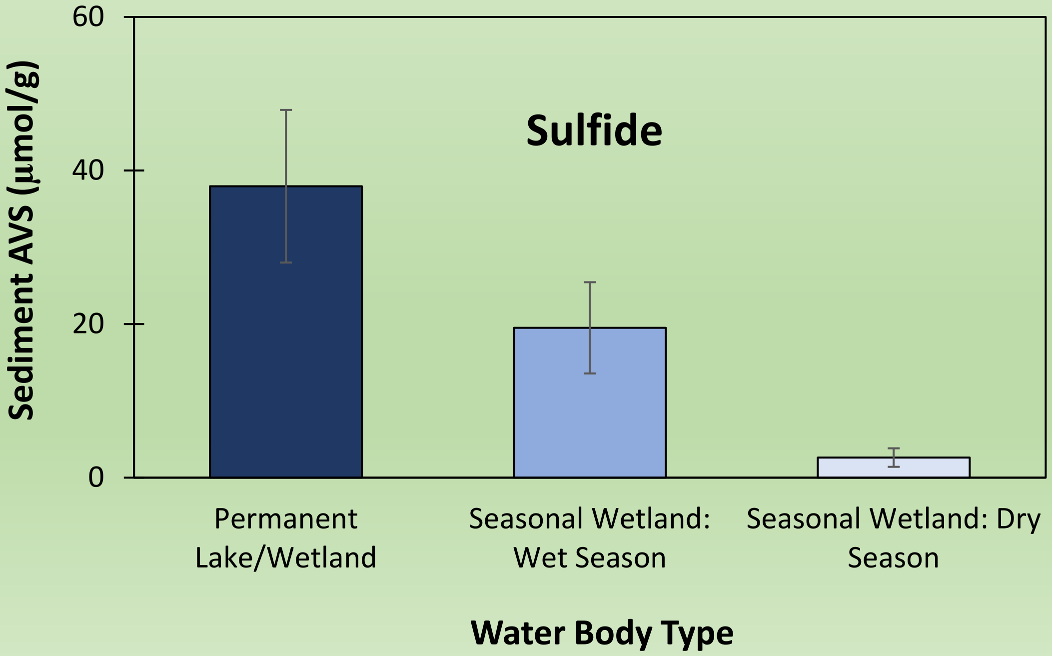


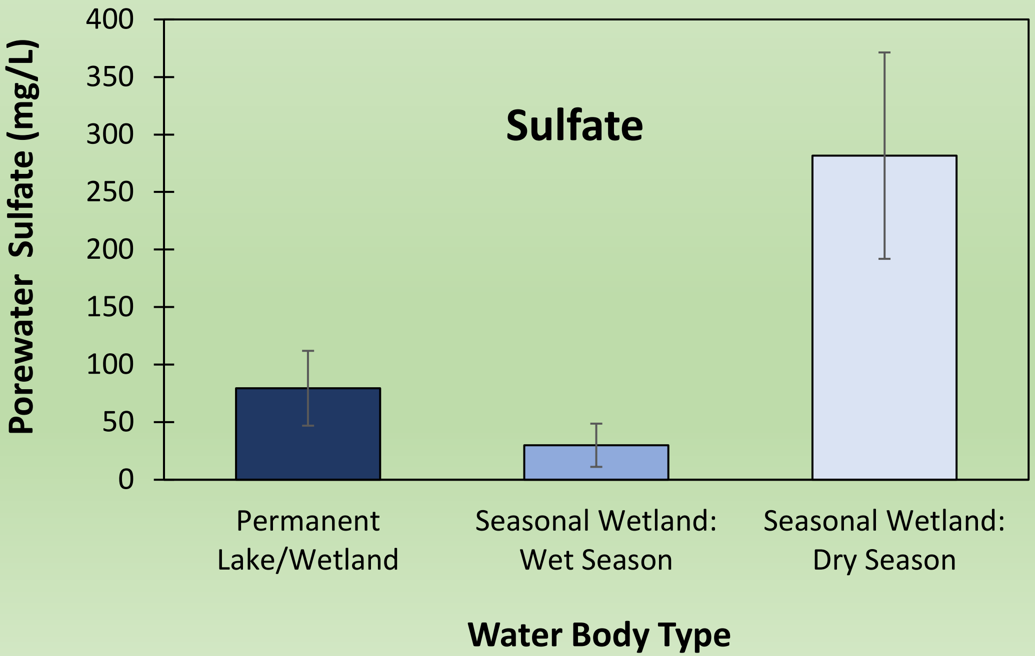
Field Results: *Sediment/Porewater Chemistry*

Permanently Inundated

Seasonally Inundated



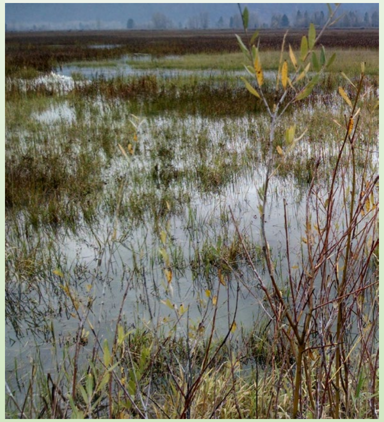


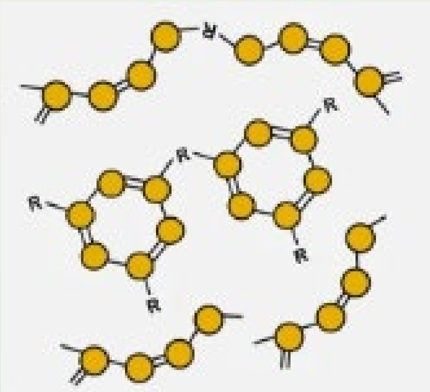


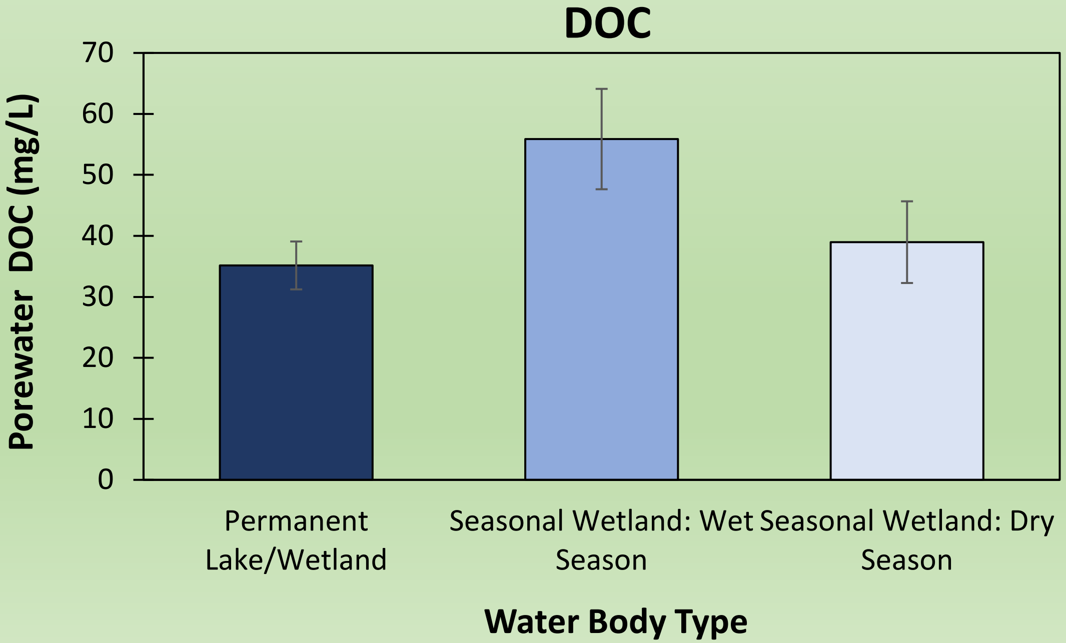
Results: *Sediment/Pore Water Chemistry*

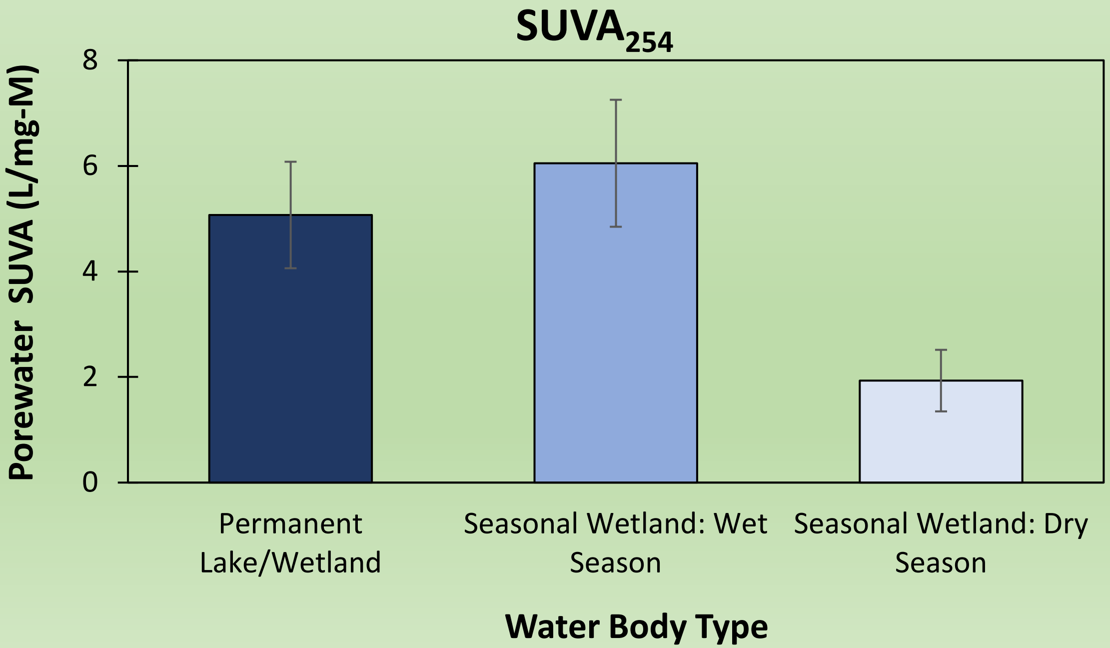
Permanently Inundated

Seasonally Inundated





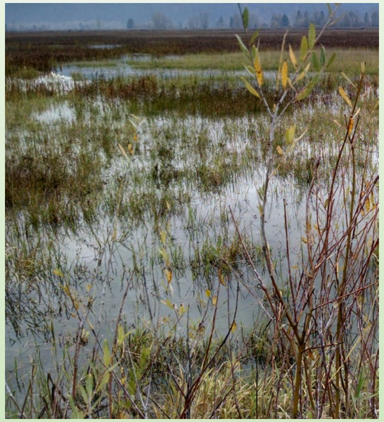


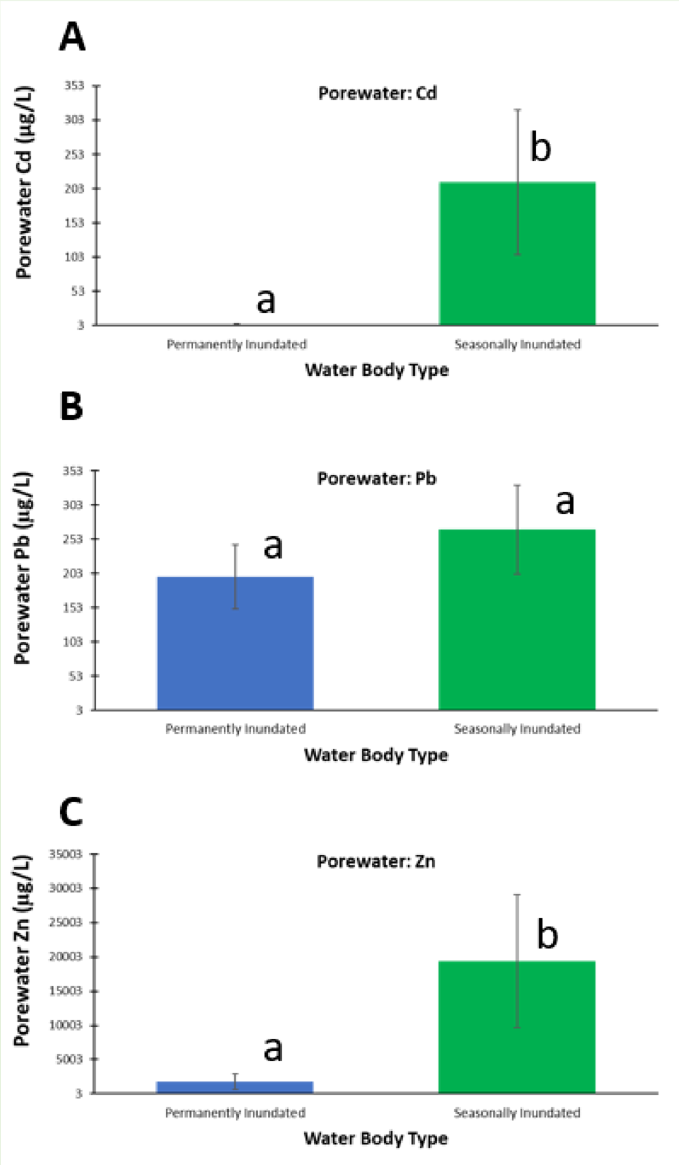


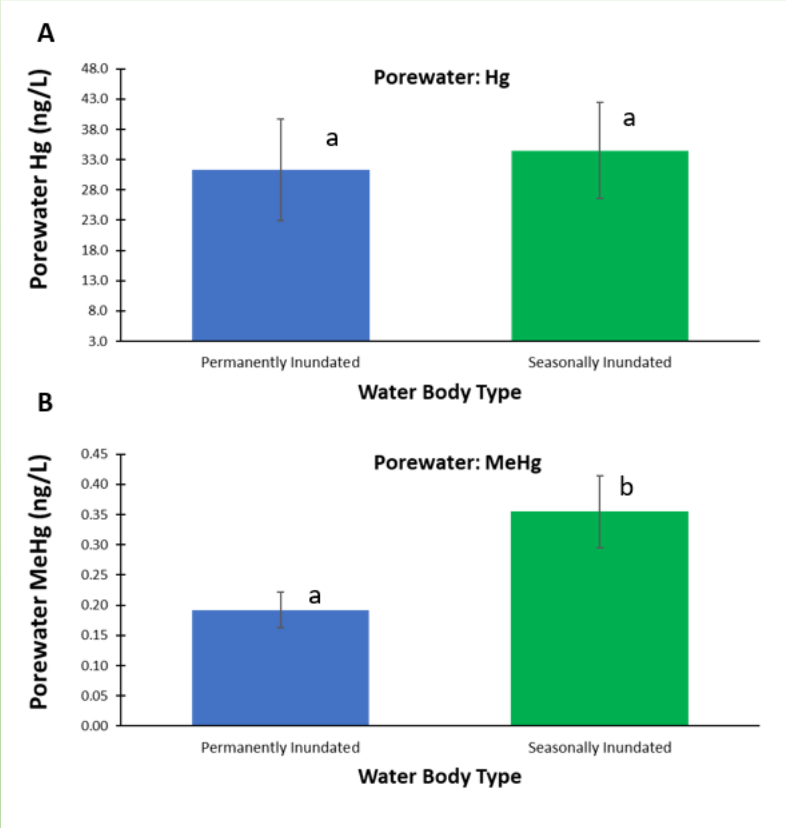
Field Results: *Sediment Metals*

Permanently Inundated

Seasonally Inundated

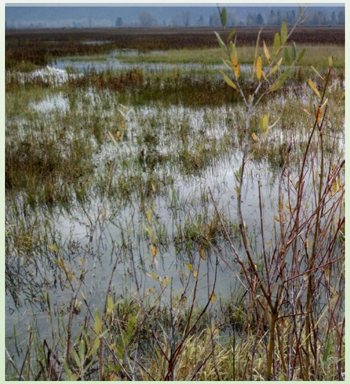




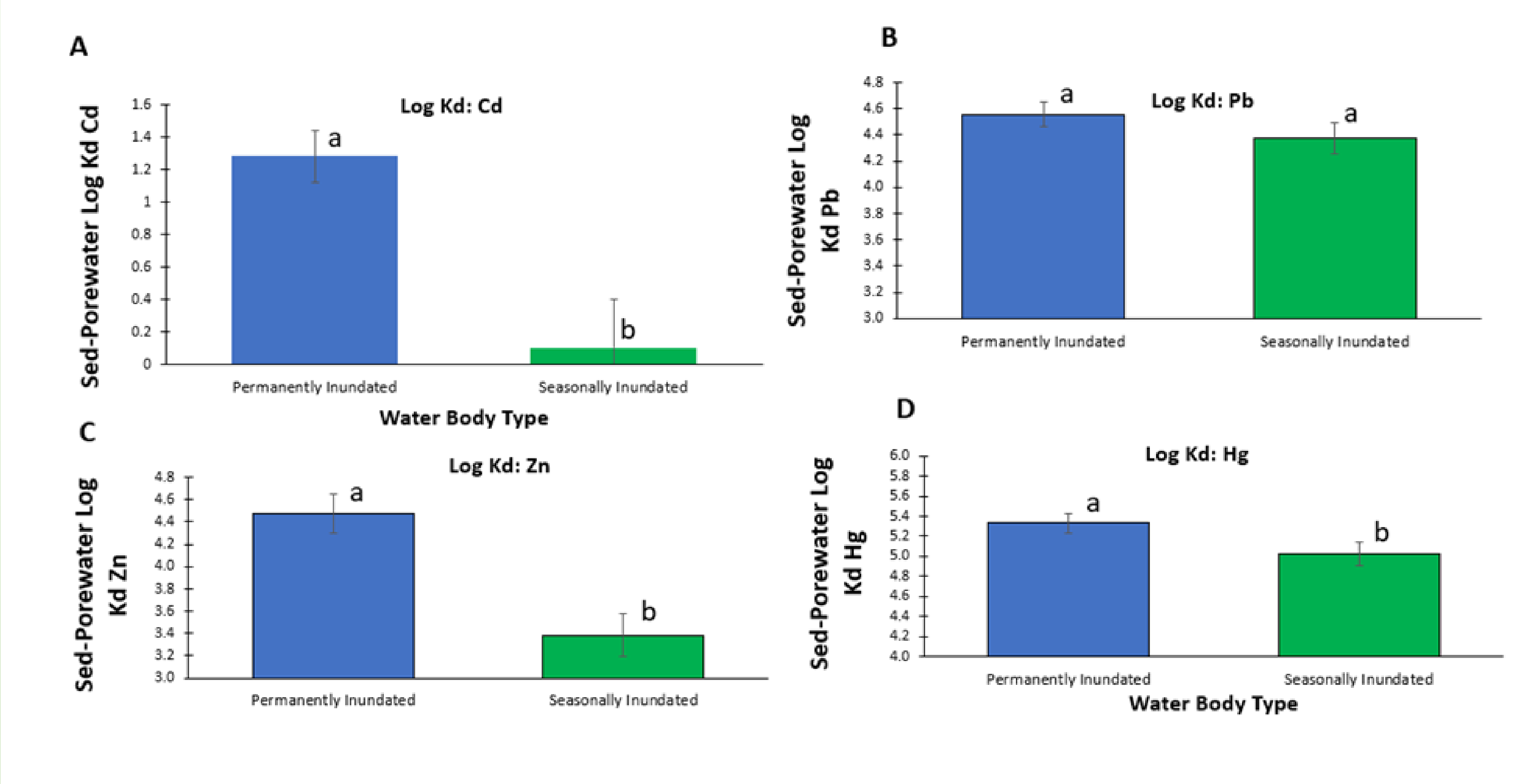


Field Results: *Sediment-Porewater Partitioning*

Permanently Inundated **Seasonally Inundated**



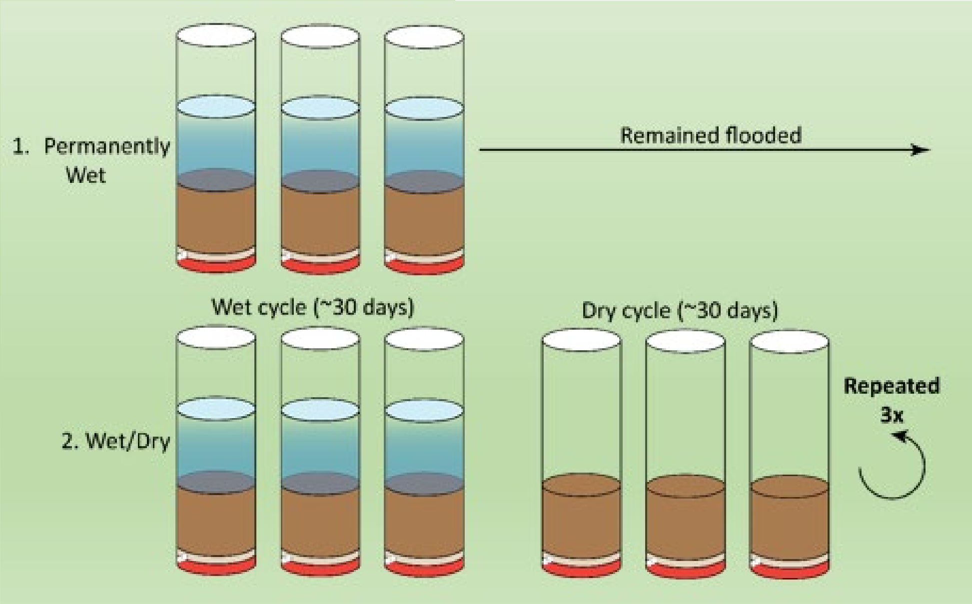
$$Kd = \frac{[Sediment]}{[Porewater]}$$

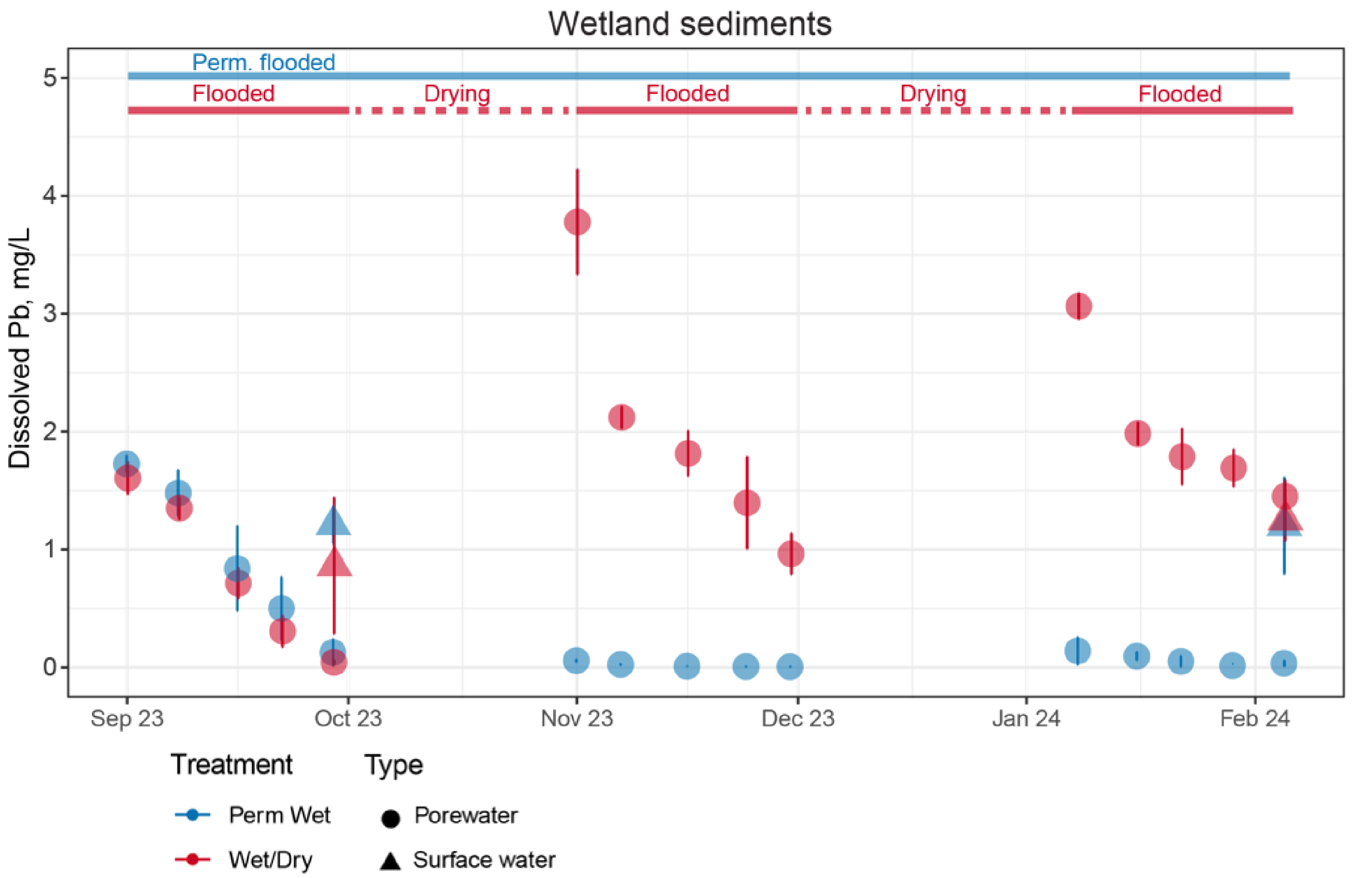


Laboratory Results: *Porewater*

Pb mobilization higher in Wet/Dry sites (red)

- Repeated wetting/drying cycles appear to mobilize more Pb over time

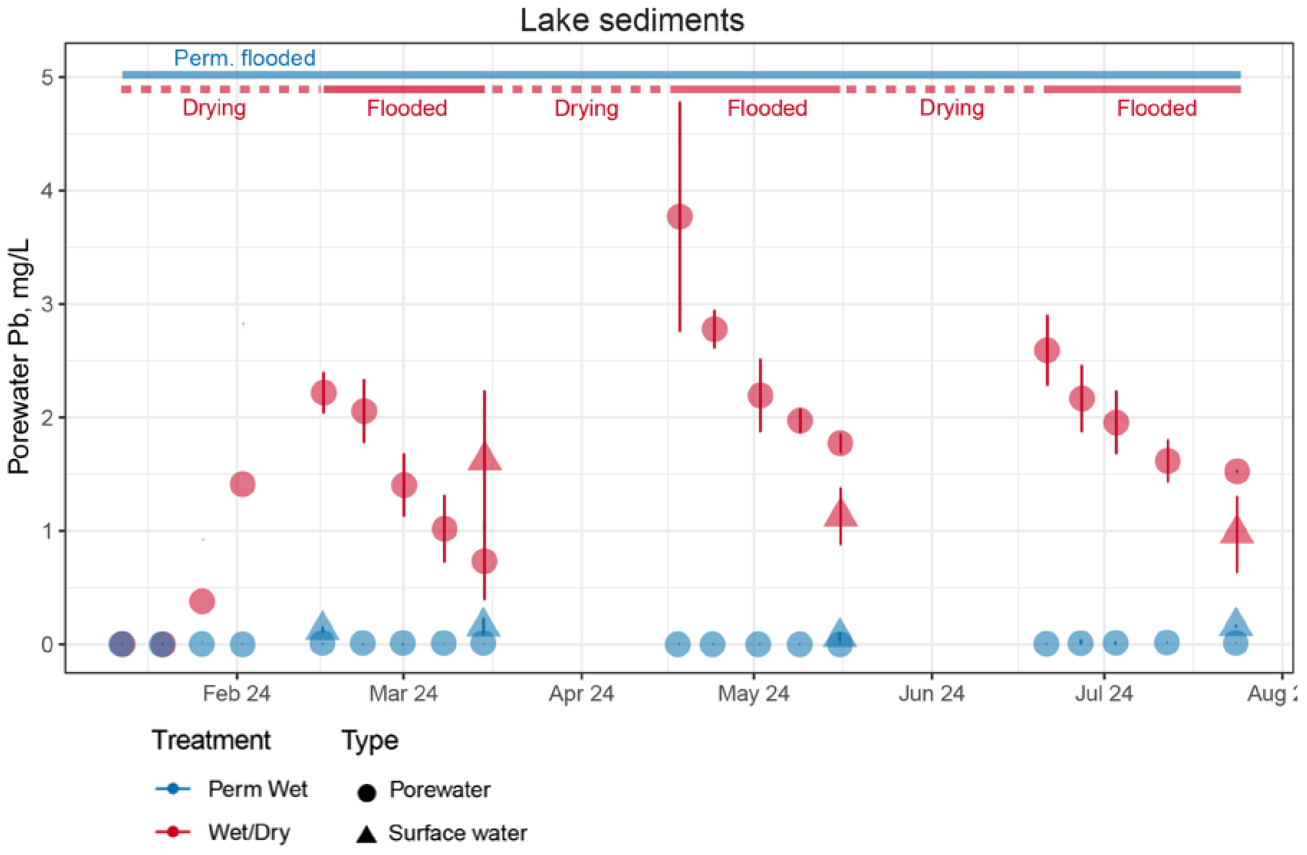


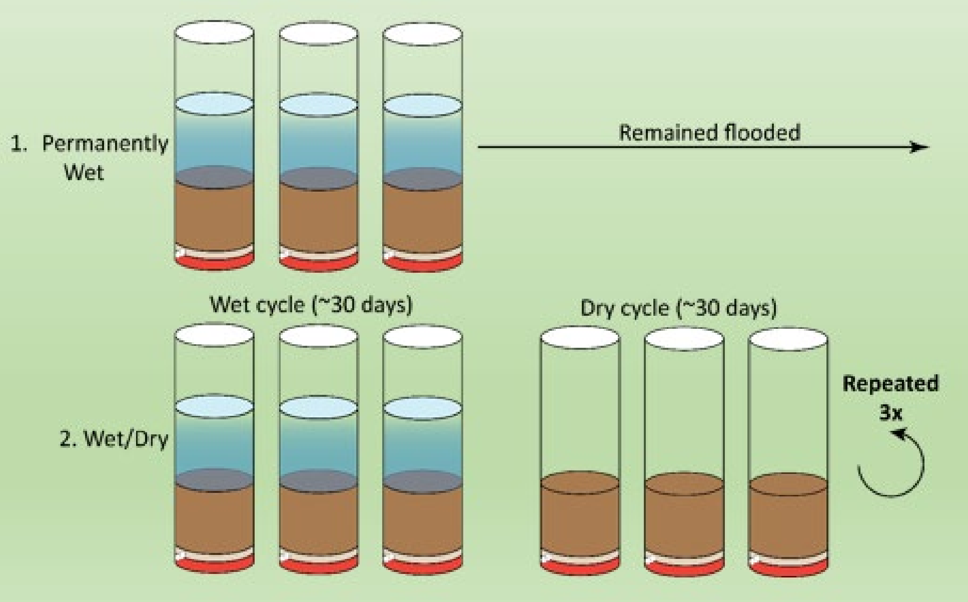


Laboratory Results: *Porewater*

Similar findings in lake sediment

- Longer time under reducing conditions did not provide protective measure after drying
- No soluble Pb in sediments kept submerged (blue)





Conclusions: *Metal bioavailability in sediments experiencing wetting and drying cycles—the impact of sulfur and iron chemistry*

Seasonal water level fluctuations influence sediment metal cycling:

- Changes in water levels impact redox conditions such as iron and sulfate cycling
- Increased partitioning of metals into the porewater
- Enhanced MeHg production
- Provide a remediation tool that may reduce Hg availability on a landscape-scale
- Help predict the impacts of changing climatic/hydrological conditions on metal mobility

Introduction: *Incremental Thin-Layer Capping Pilot Study*

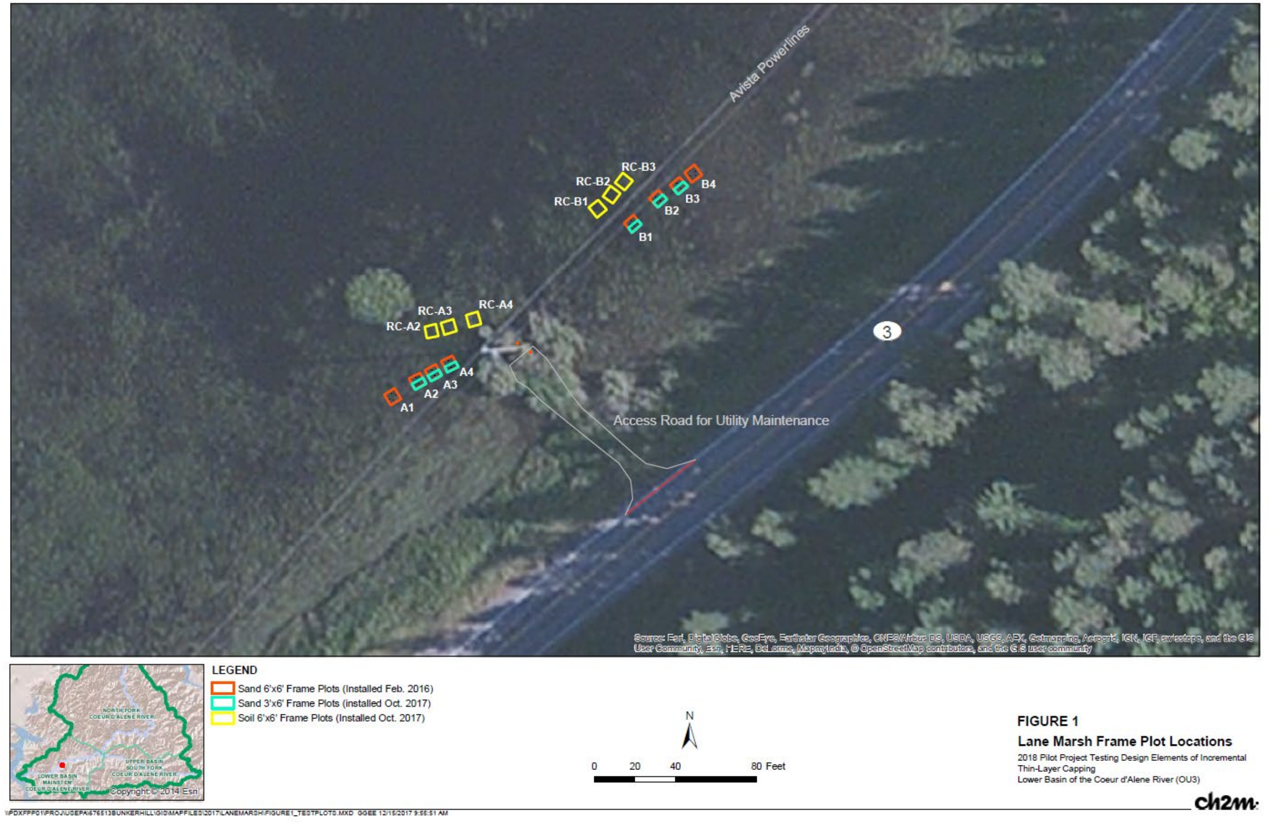
- Incremental thin-layer capping (ITLC) is a remediation approach involving the incremental placement of clean material over time, simulating natural sedimentation processes and allowing native vegetation to recover after each application

Study Location:
Lane Marsh

Methods: *Incremental Thin-Layer Capping Pilot Study*

Small-Scale Test Plots established in 2017 and monitored to 2019

Test plots included capping with sand and clean soil (2, 4 and 6 inch treatments)



Photograph 3A. Arrowhead 4-inch sand frame plot LM A3, second 4-inch cap application (total = 8 inches) in foreground, with single 4-inch cap immediately behind it (October 4, 2017).

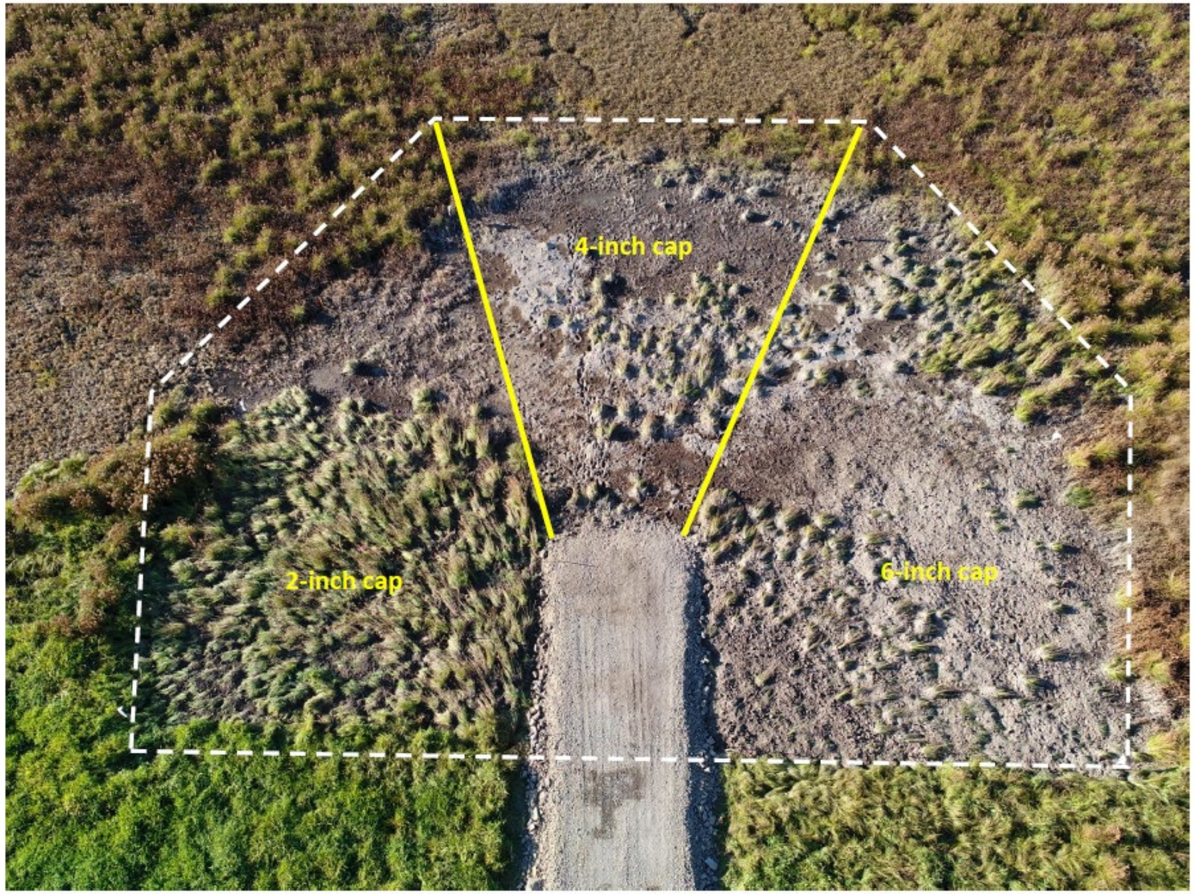
Photograph 3B. Arrowhead 4-inch sand frame plot LM A3, second 4-inch cap application (total = 8 inches) in foreground (two closest grid cells), with single 4-inch cap immediately behind it (two furthest grid cells) (July 17, 2018).

Photograph 3C. Arrowhead 4-inch sand frame plot LM A3, second 4-inch cap application (total = 8 inches) in foreground (two closest grid cells), with single 4-inch cap immediately behind it (two furthest grid cells) (July 23, 2019).

Methods: *Incremental Thin-Layer Capping Pilot Study*

Expanded (O.4 acre) Test Area Incremental Thin-Layer Capping Pilot (2017 to 2019). Soil was applied in 2-, 4-,and 6-inch lifts.

EXPANDED TEST AREA (ETA1) YEAR 2 (2019) MONITORING, INCREMENTAL THIN-LAYER CAPPING DESIGN ELEMENTS FOR THE LANE MARSH PILOT PROJECT



Photograph 4. As-applied conditions at ETA1 on October 5, 2017, immediately after ITLC application. Capping thickness increases from approximately 2 inches on the left, to approximately 4 inches above, and approximately 6 inches on the right.

EXPANDED TEST AREA (ETA1) YEAR 2 (2019) MONITORING, INCREMENTAL THIN-LAYER CAPPING DESIGN ELEMENTS FOR THE LANE MARSH PILOT PROJECT

Photograph 1. Year 2 site conditions at ETA1 (July 24, 2019), showing vegetation recovery 2 years after cap applications.

Results & Conclusions: *Incremental Thin-Layer Capping Pilot Study*

- Vegetation regrowth was robust after applying up to 6 inches of capping material
- Colonization of capped areas by noxious weeds was barely observed.
- Benthic monitoring showed macroinvertebrate recolonization in the soil cap test areas
- The thin layer cap may be effective in decreasing lead (Pb) concentrations; however, they are susceptible to recontamination either through bioturbation or fresh sedimentation

EXPANDED TEST AREA (ETA1) YEAR 2 (2019) MONITORING, INCREMENTAL THIN-LAYER CAPPING DESIGN ELEMENTS FOR THE LANE MARSH PILOT PROJECT

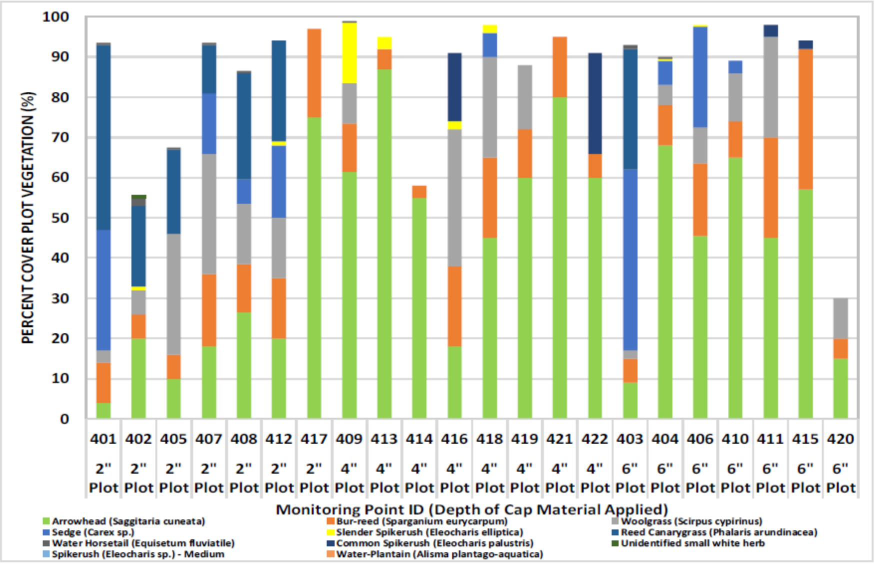


Figure 2. Year 2 Vegetation Percent Cover in ETA1 at Lane Marsh during the Second Growing Season after Application of the Soil Cap (July 2019)

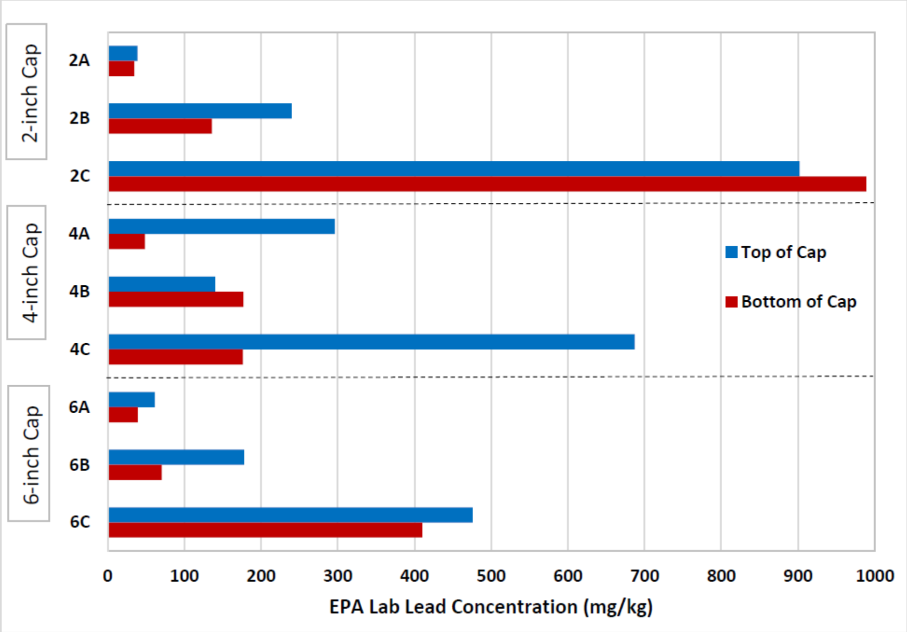


Figure 2. October 2020 Lead Concentration using EPA Laboratory results for Top and Bottom 1 inch of Cap Layer in Each Test Plot (2-, 4-, and 6-inch caps) at the Expanded Test Area at Lane Marsh

Introduction: *Soil amendments to reduce bioavailability of toxic metals in contaminated soils and sediments*

- Soil and sediment amendments are a type of in situ remediation option that can reduce the solubility of contaminants and decrease their uptake into biota following ingestion.

- The benefit of amendments is that they can be applied over large areas with minimal landscape disturbance.

- Biochar is a commonly used soil/sediment amendment that can absorb contaminants and promote soil health.

- Biochar is created through pyrolysis (i.e., heating) of organic matter in low or no oxygen environments. Differences in feedstocks and pyrolysis temperatures impact the characteristics of the resulting biochar (e.g., pH, surface area, functional group density, total and water-soluble phosphorus content) and subsequent interaction with soil/sediment contaminants

Methods: *Soil amendments to reduce bioavailability of toxic metals in contaminated soils and sediments*

Project Objective:
Determine the effectiveness of different types of biochar amendments at reducing lead (Pb) bioaccessibility in Pb-contaminated soils/sediments with differences in soil/sediment type and contaminant source.

Methods:
Biochars tested: blends of 30% manure (poultry litter or dairy manure) and 70% lignocellulosic material (wheat straw or grand fir shavings) and pyrolyzed at 300, 500, 700, and 900 °C.

Soils were amended with 2% biochar and incubated for 6 months.

A suite of standard (e.g., EPA Method 1340) and experimental soil Pb bioaccessibility assays were used to assess the impact of the treatments.

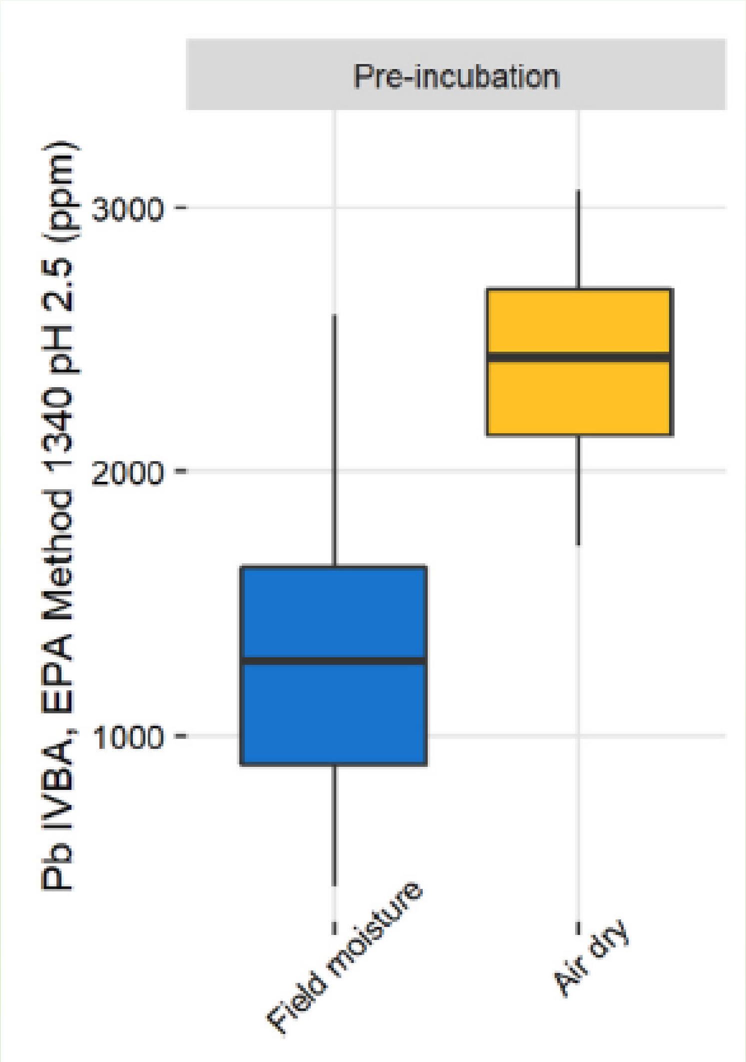
Results: *Soil amendments to reduce bioavailability of toxic metals in contaminated soils and sediments*

Differences in the analytical methods can have a large impact on the assessment of Pb bioaccessibility.

- In unamended sediments using a pH 1.5 extraction showed that 85 to 92% of the Pb was bioaccessible; but a pH 2.5 solution was used bioaccessible Pb decreased to 54 to 74%.

- There was a larger difference observed when the anoxic sediment samples were air-dried prior to analysis, which resulted in a 4-fold increase in Pb bioaccessibility.

- Using the Avian Ohio State University Gastrointestinal Method which is designed to reflect an avian digestive system where soil is ingested along with food there was a 6-fold decrease in bioaccessibility, likely due to enhanced Pb sorption in the presence of food (e.g., protein, phosphorous, calcium, etc).

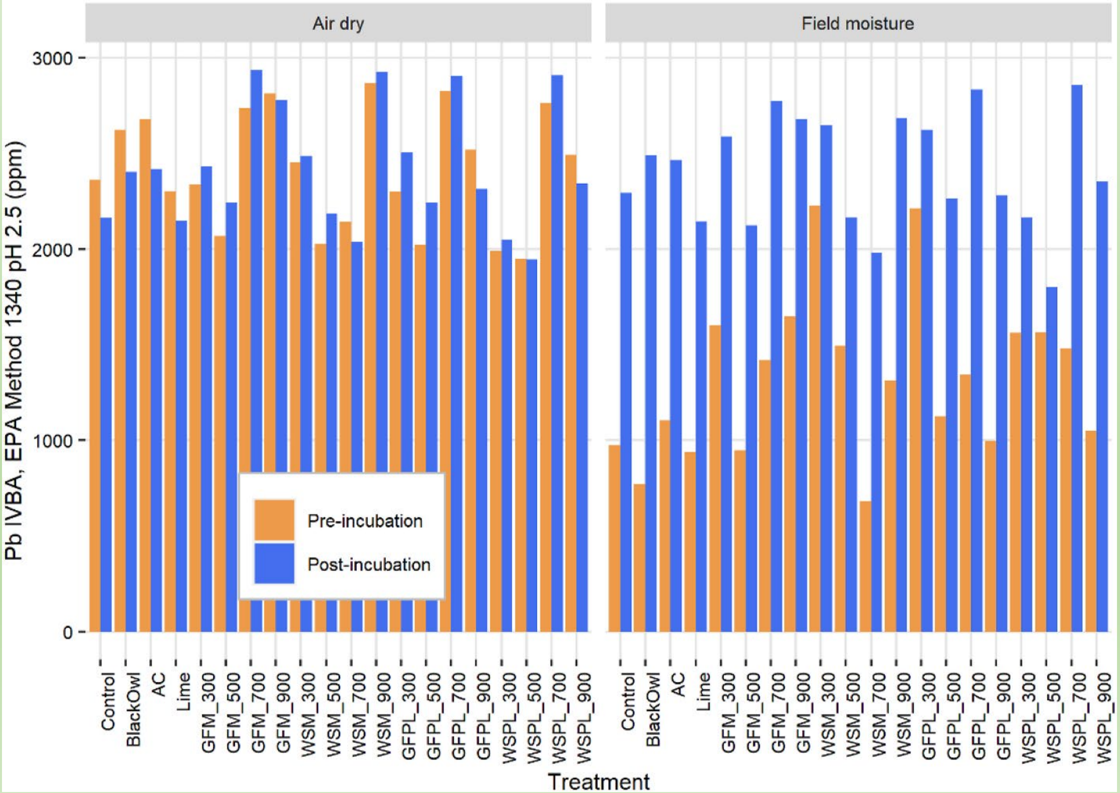


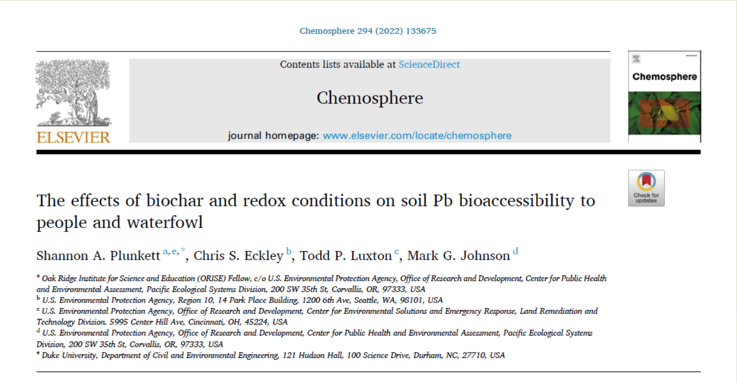
Results: *Soil amendments to reduce bioavailability of toxic metals in contaminated soils and sediments*

- Sediments were amended with 17 different types of biochar; with roughly half of them resulting in significant decreases in Pb bioaccessibility.

- The magnitude of the decrease in bioaccessibility was relatively low, with none of the biochar additions deceasing bioaccessibility by more than 10% at any of the contaminated soils/sediments in this study.

- There did not appear to be any significant differences in effectiveness based on feedstock material (i.e., wheat straw, grand fir, manure); however, it was observed that biochars that were pyrolyzed at 700 °C were more effective than those pyrolyzed at the other temperatures (300, 500 and 900 °C).





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The effects of biochar and redox conditions on soil Pb bioaccessibility to people and waterfowl

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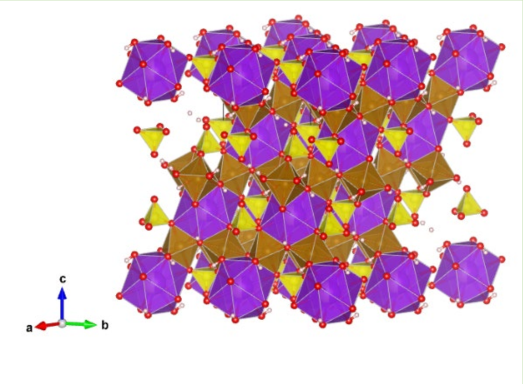
Introduction: *Application of jarosite-based remediation technologies to significantly decrease lead (Pb) bioavailability in contaminated soils*

Chemical remediation techniques may allow for in situ conversion of soil contaminants to phases that are not easily mobilized upon ingestion

Jarosite is a mineral that is a combination of potassium, ferric iron, and sulfate

Study Goal: develop a remediation strategy induce jarosite formation in Pb contaminated soils to reduce lead bioavailability



Fe
Pb/K
SO_4
O

$$Pb^{2+}_{0.5}Fe^{3+}_{3}(OH)_6(SO_4)_2$$

Methods: *Application of jarosite-based remediation technologies to significantly decrease lead (Pb) bioavailability in contaminated soils*

34 soils in the study from EPA Regions 4, 7, 8, and 10 (2 from Bunker Hill)

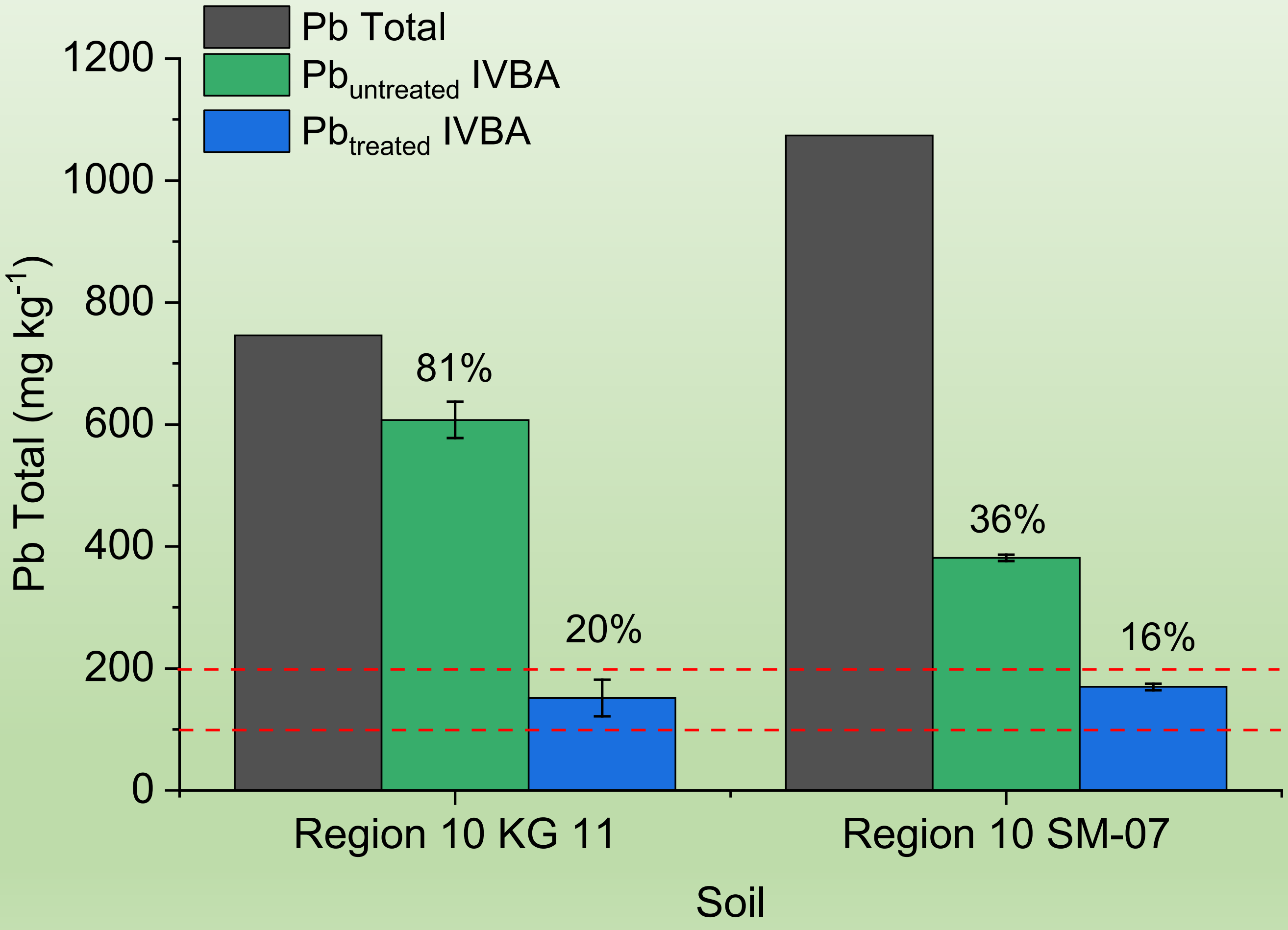
The process involves:

- Soil hydration
- Mixing with Potassium Jarosite
- Addition of Ferric Sulfate with H_2SO_4
- Moderate Heating (22 and 40 °C)

Soils pre- and post-treatment were analyzed for total Pb concentration and extracted via EPA Method 1340 in vitro lead bioaccessibility.

Results: *Application of jarosite-based remediation technologies to significantly decrease lead (Pb) bioavailability in contaminated soils*

- Two soil samples were collected from Bunker Hill for the Jarosite Treatment.
- Initial total lead in the soils was 746 and 1073 mg kg^{-1}
- After treatment the amount of lead extracted (IVBA) from each soil was less than 200 mg kg^{-1}
- 55 to 75% reduction in bioaccessibility of Pb after treatment.
- Difference in the initial IVBA and the reduced IVBA post remedy related to the initial lead chemical speciation



Percent values indicate the percentage of lead total lead extracted during an IVBA analysis

Results/Conclulsions: *Application of jarosite-based remediation technologies to significantly decrease lead (Pb) bioavailability in contaminated soils*

For the entire study (multi-Region samples):

Room temperature treatments resulted in average Pb %IVBA decreases of 58%

Heated conditions (≥40°C), resulted in average decrease of 74%.

Table 1. Current IVBA results for combined Regions 4, 7, 8, and 10 soils.

Summary Statistics			**Untreated**	**Treated**	**Decrease**
				%IVBA	
All conditions	n =34; n = 24 for untreated	Average	71.6%	23.8%	68.5%
		Median	70.0%	15.8%	75.3%
22°C: Room temperature	n =16	Average	76.4%	32.4%	58.0%
		Median	62.5%	21.9%	70.3%
≥40°C	n =18	Average	70.8%	17.6%	73.6%
		Median	70.0%	15.5%	76.4%


Questions/Comments?