Formation and Fate of Iron Sulfide Compounds Following Simulated Dredged Sediment Placement in Coastal Wetlands

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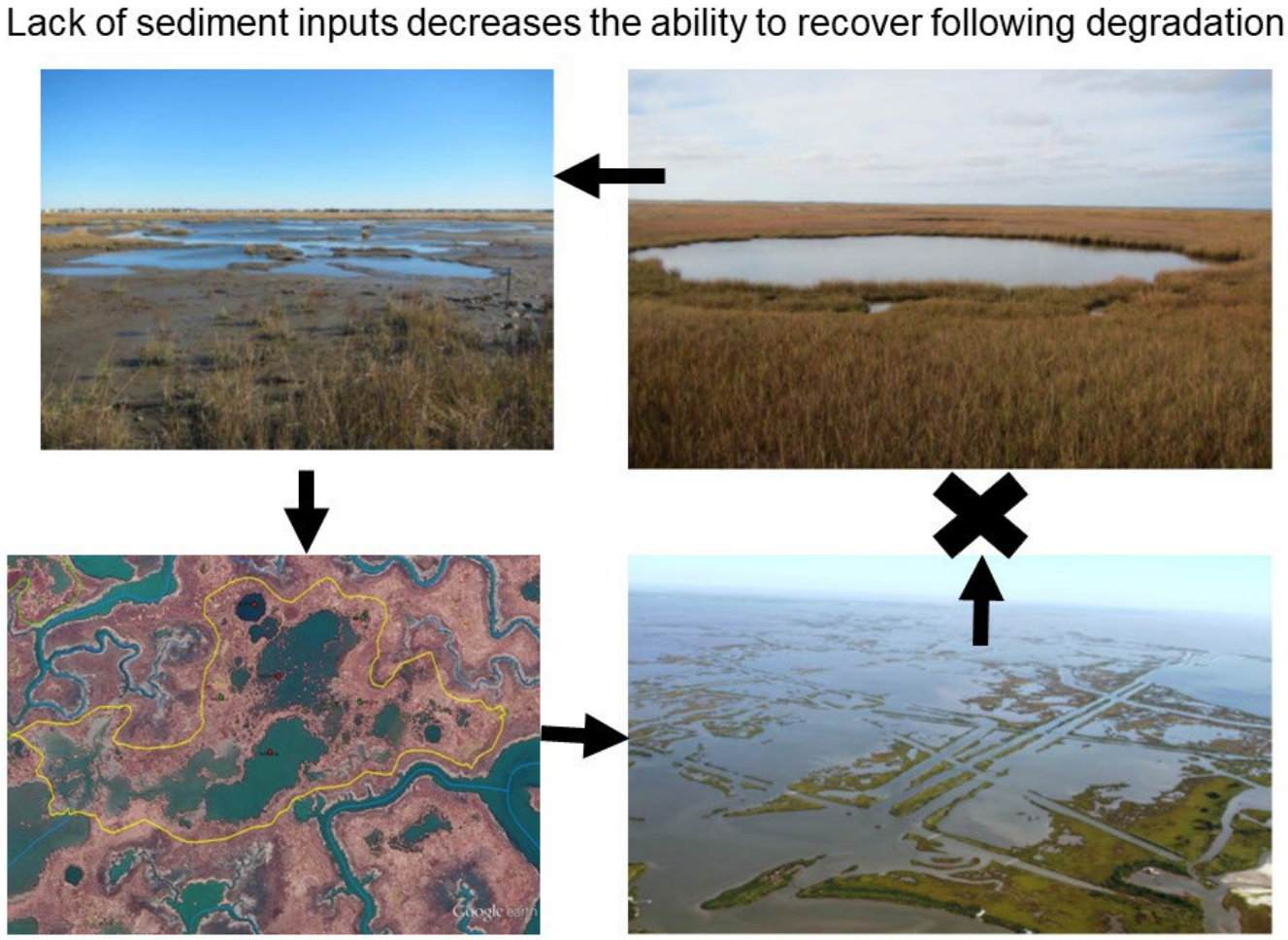
Introduction

- Coastal wetland loss due to erosion, degradation, drowning
- Rising sea levels and subsidence
- Reduced sediment supply as many coastal wetlands disconnected from sediment sources (e.g., riverine sediment detained behind dams)
- Sediment deposition:
  - Restoration (dredging) and/or
  - Natural events (e.g., storms)



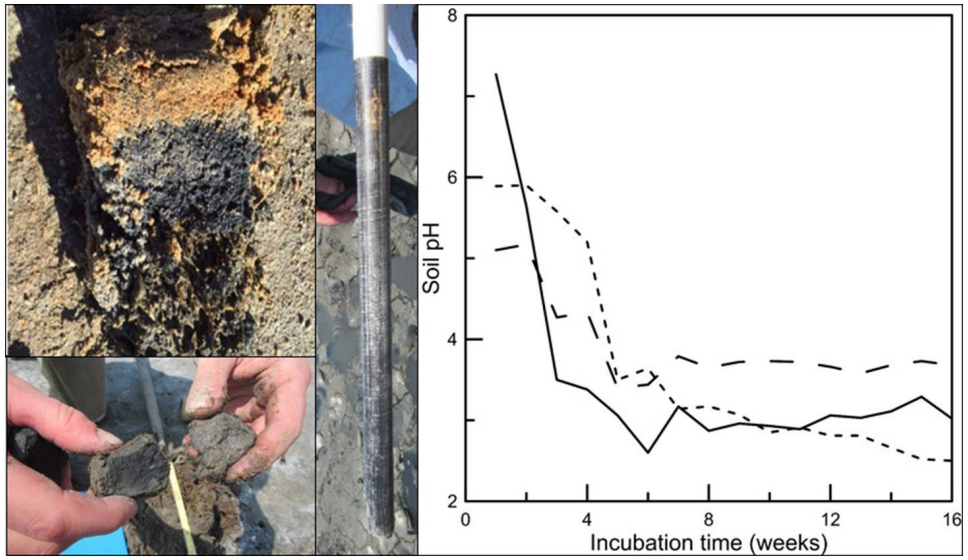
Dredging and wetland restoration

- Many USACE restoration project involve the removal, dredging, placement, or transport of sediments
- Dredging navigation channels (>25,000 miles) and ports (>400)
- Beneficial use of dredged materials to restore historical elevation, stabilize marsh platform, and create new marshes
- These activities alter the biogeochemistry of the sediments and wetlands

USACE, New Orleans

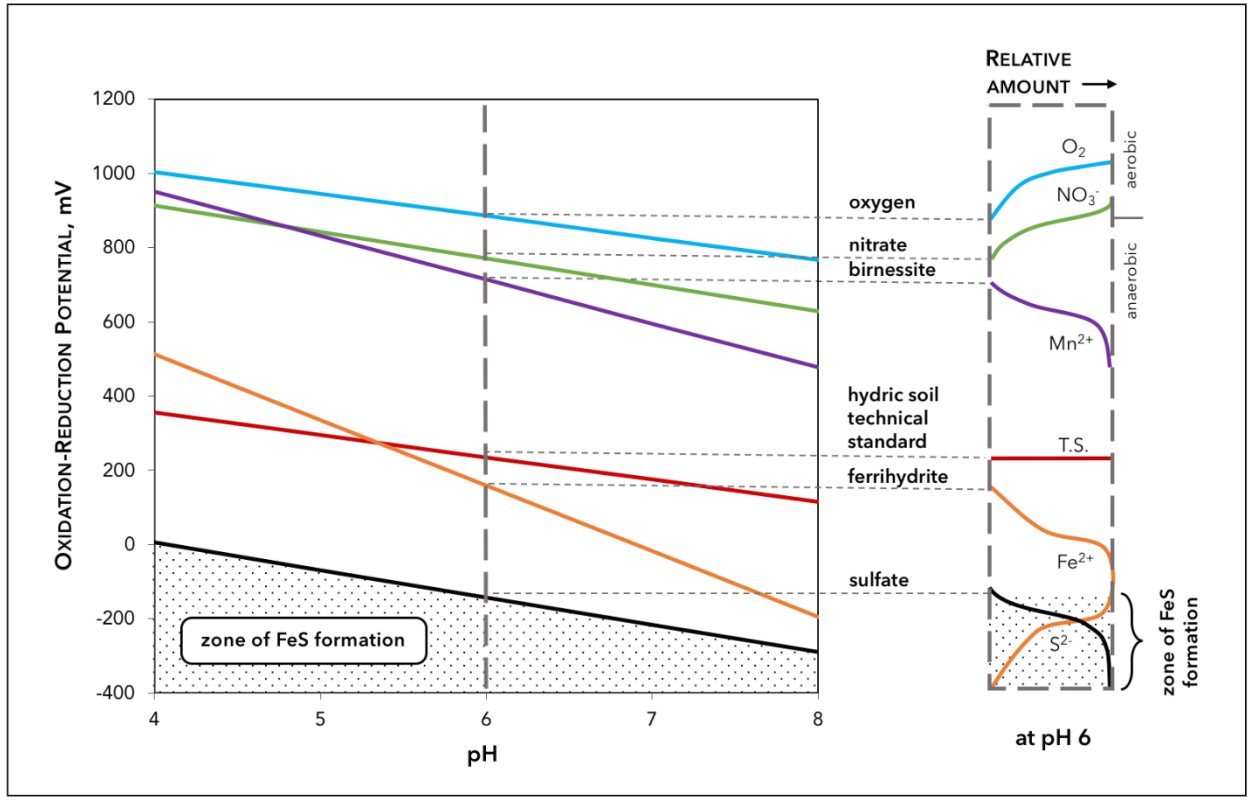
Iron sulfide compounds in restoration sites

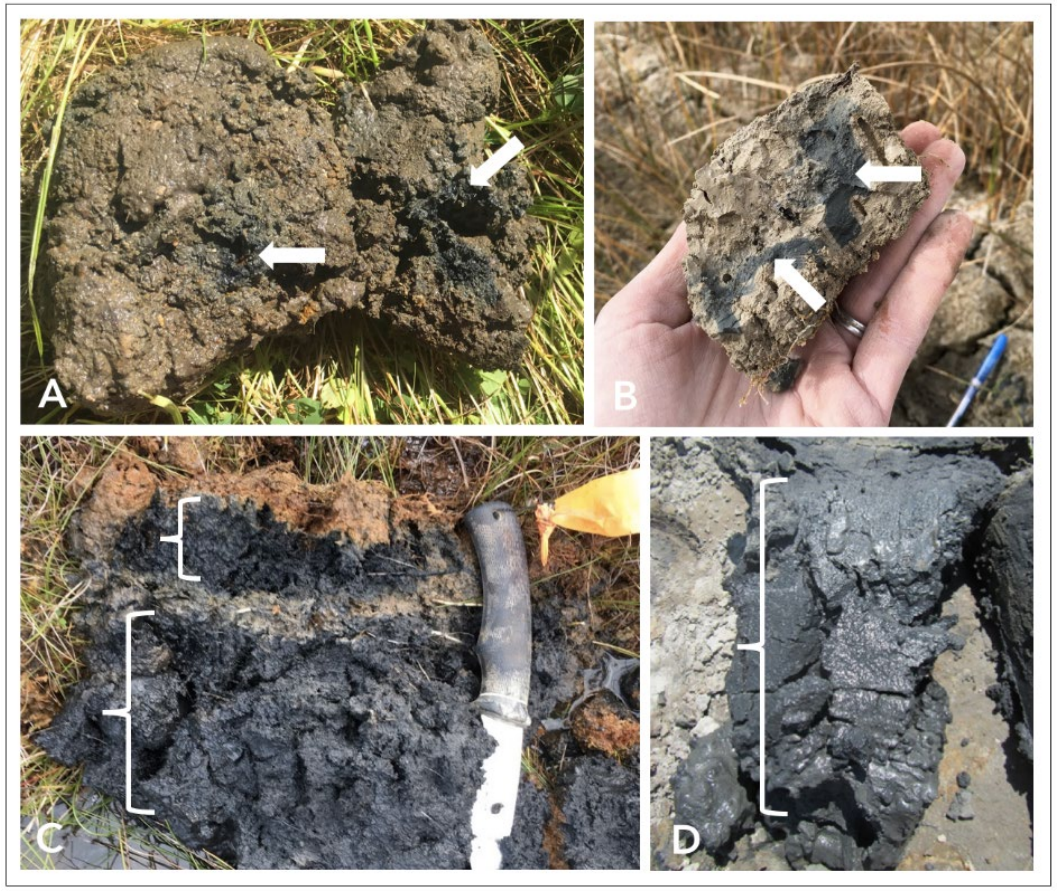
- Lack of vegetation recovery and vegetation death in restored sites
- Recent field observations: dark gray to black colored iron sulfide (FeS)
- Under drought conditions, oxidize to sulfuric acid lowering soil pH



Iron sulfide and wetland restoration

Iron sulfide formation → presence of reduced Fe and S, anaerobic conditions
Wetland restoration has these elements (often pre- AND post-restoration)

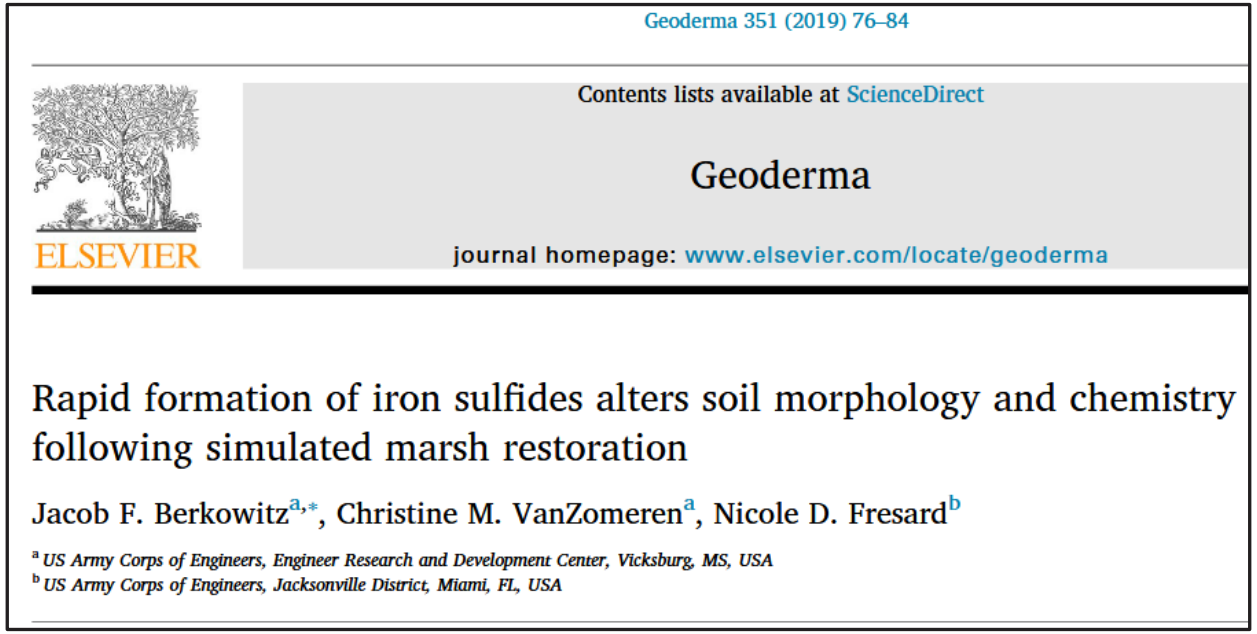




Simulated dredged sediment placements

Two experiments:

1) Dredged sediment did not contain iron sulfide compounds
2) Dredged sediment contained iron sulfide compounds



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Rapid formation of iron sulfides alters soil morphology and chemistry following simulated marsh restoration

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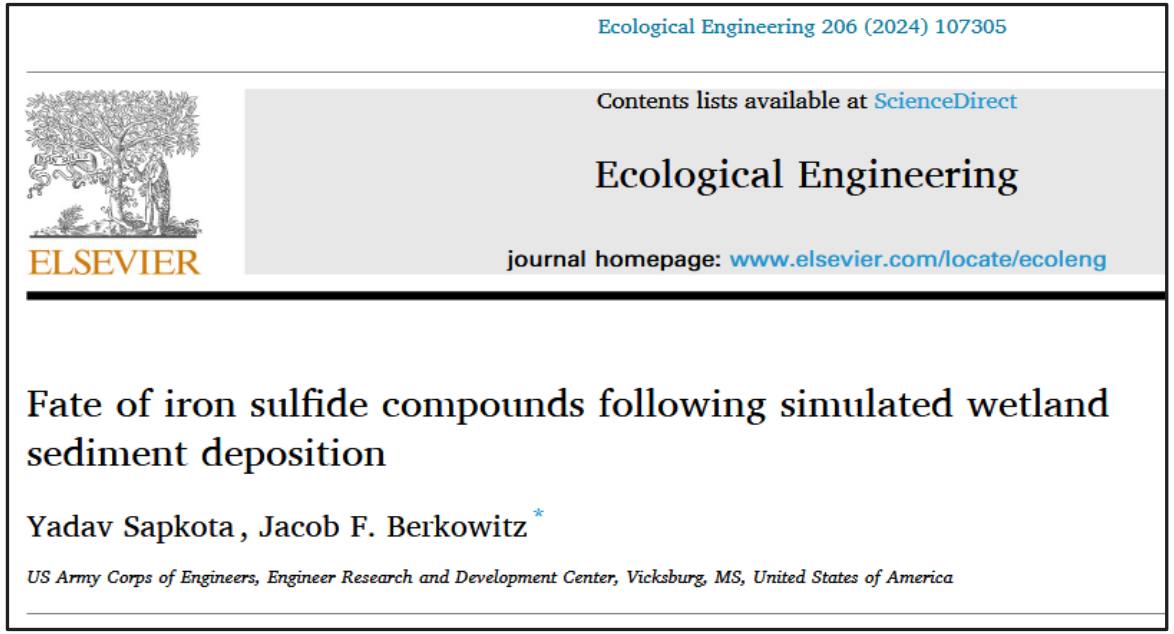

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ELSEVIER

Fate of iron sulfide compounds following simulated wetland sediment deposition

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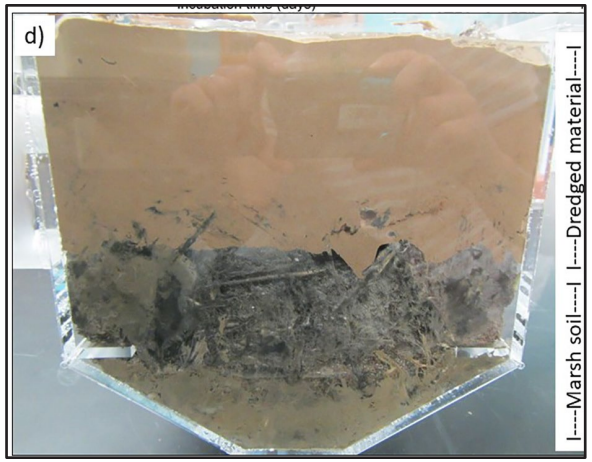
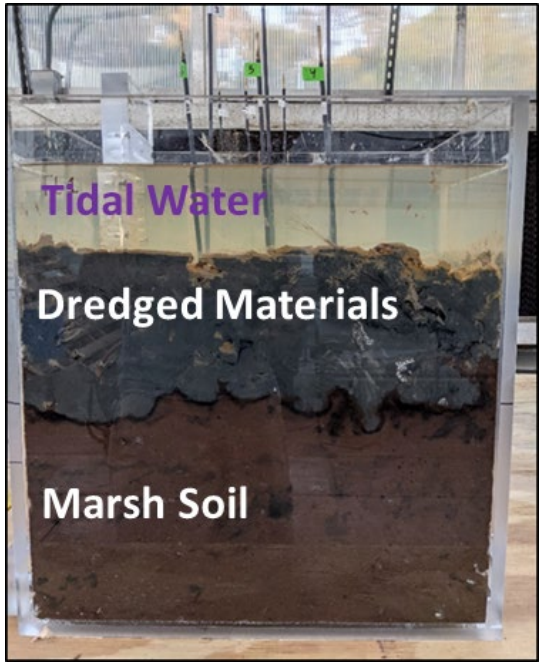
Experimental design

- Dredged sediment topped above marsh soil; duration 120 days
- Treatments: Continuously flooded, tidal, and drought
- Replication: 3 (9 tanks on each experiment)

	Experiment 1	Experiment 2
Dredged sediment	**Did NOT** contain iron sulfide compounds	Contained iron sulfide compounds
Layer thickness	10 cm	15 cm
Tidal water salinity	26.7 psu	5 psu
Morphological changes	Grid technique	Image analysis
Porewater	Sippers	Peepers

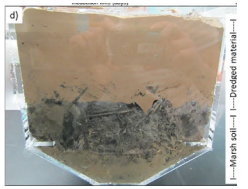


Experiment 1

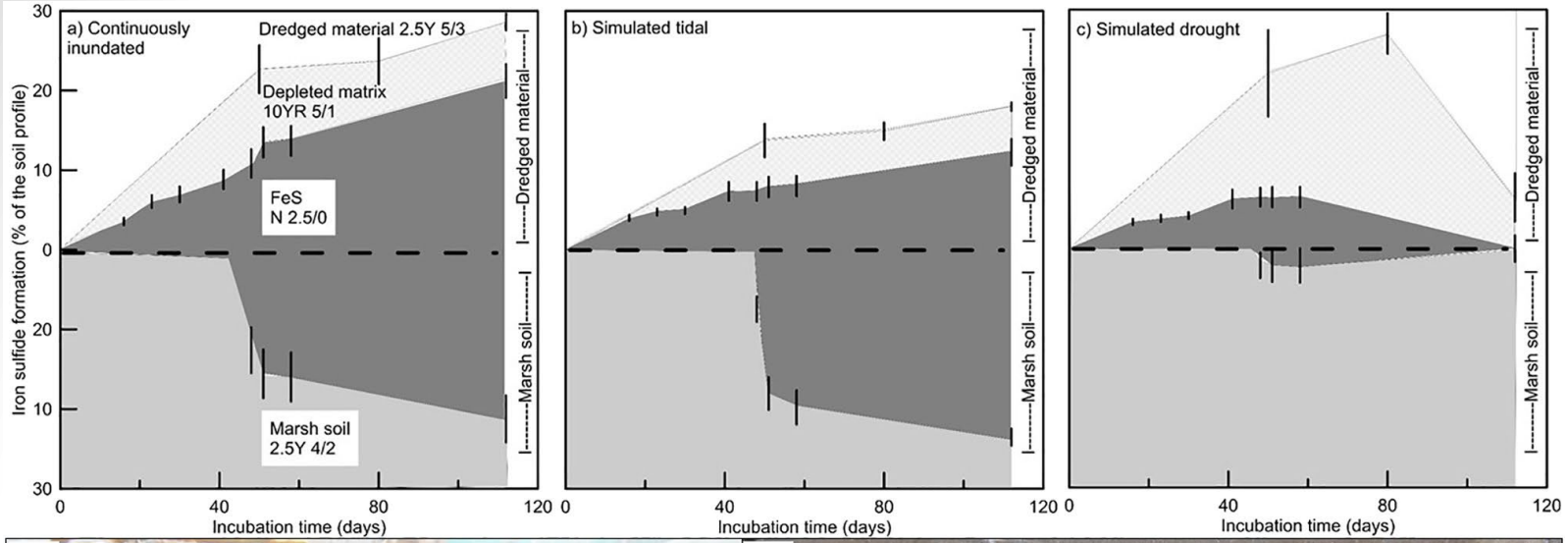


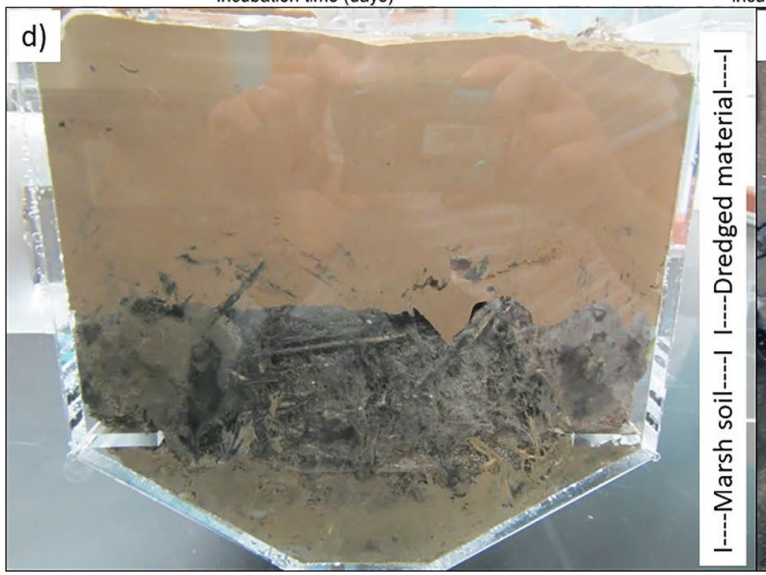
Experiment 2

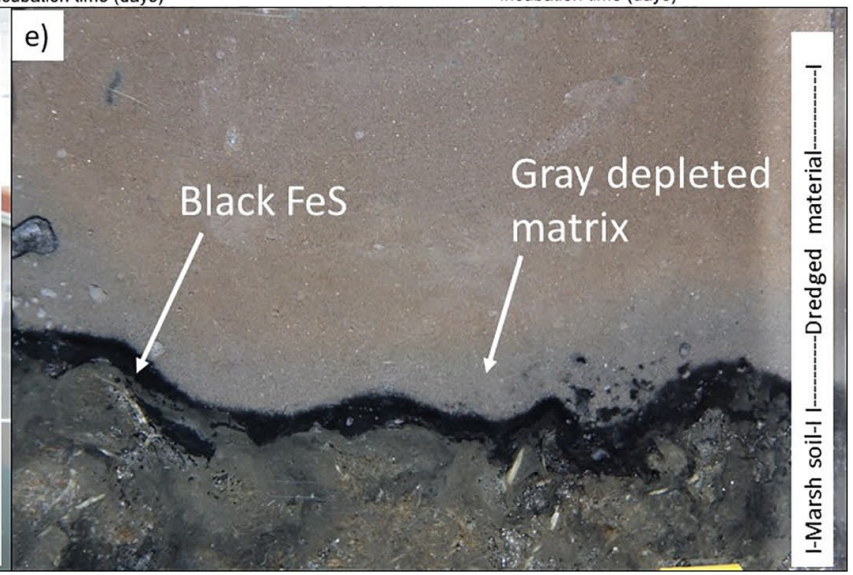
Morphological changes



Experiment 1

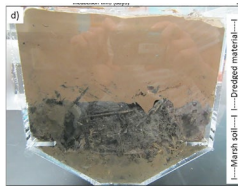






- FeS horizon development initiated within 16 days, covered >30% of the soil profile after 120 days under continuously inundated and tidal conditions
- Continuous inundation had larger extent of FeS horizon compared to other treatments
- Least amounts of FeS formed within the simulated drought treatment followed by subsequent FeS oxidation

Redox status



Experiment 1

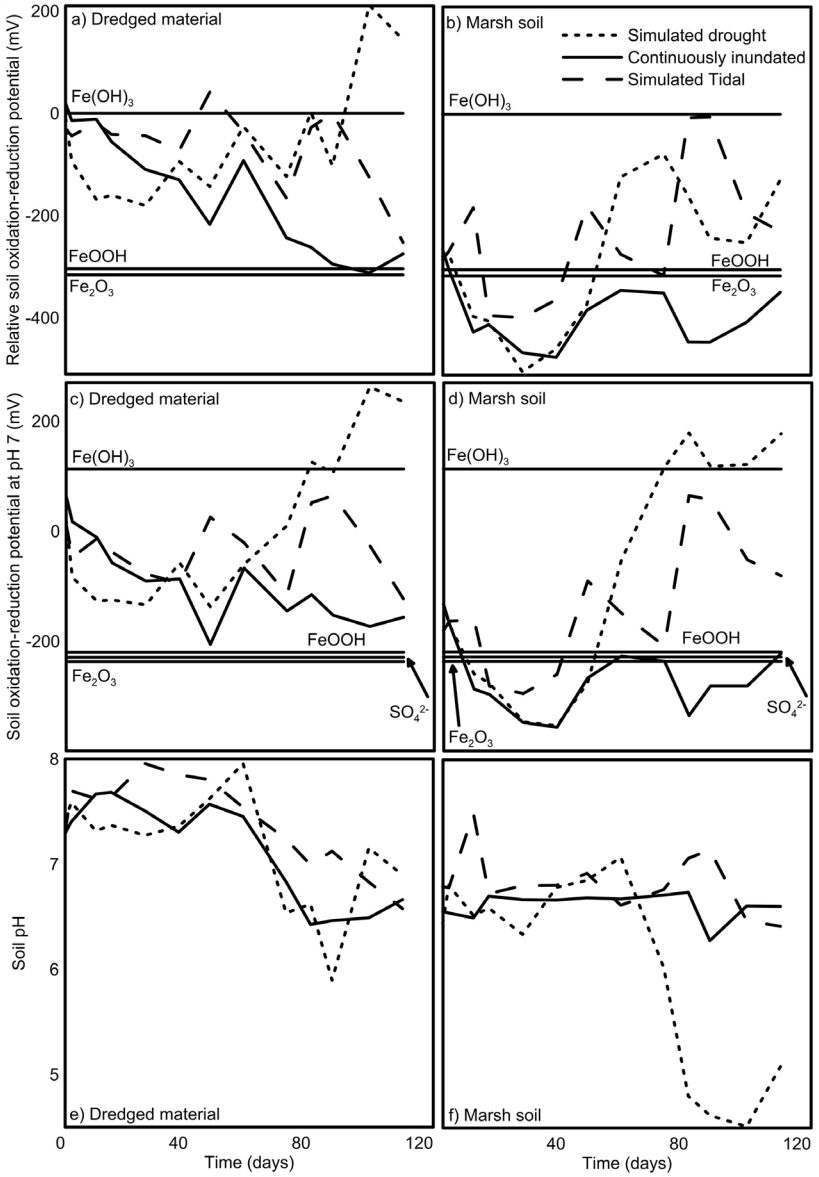
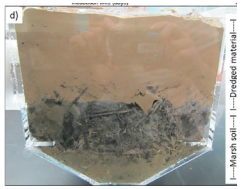


Fig. **Oxidation-reduction** potential data indicating when experimental treatments were reduced with respect to common Fe and S species

- Reduced with respect to $Fe(OH)_3$, suggesting Fe dissolution occurred during the experiment
- The marsh soil also displayed periods of FeOOH and Fe_2O_3 reduction for portions of the study
- The reduction of Fe species in both layers corresponds with the observed development of the gray depleted matrix layer
- pH decreased in drought treatment toward the end of the experiment

Redox and porewater Fe^{2+} and S^{2-}



Experiment 1

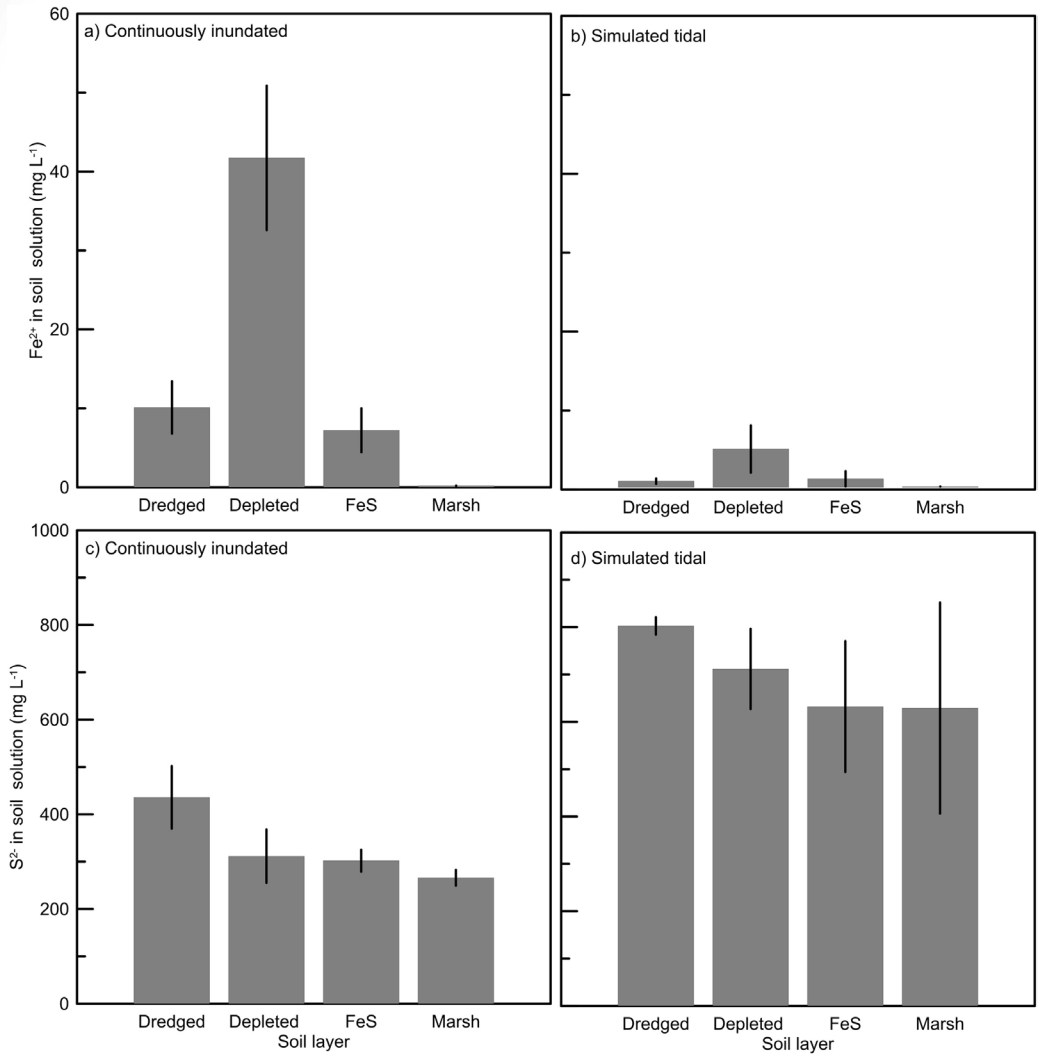
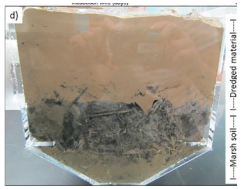


Fig. **Soil pore water** Fe^{2+} (upper panels) and S^{2-} (lower panels) under continuously inundated and simulated tidal treatments following 90 days of incubation.

- Soil pore water Fe^{2+} was significantly higher in the gray layer than in the other horizons
- Further supports the evidence of an Fe^{3+} depleted matrix within the soil profile
- More Fe^{2+} was observed in the FeS and dredged material horizons than within the underlying marsh soils

Total Fe and S



Experiment 1

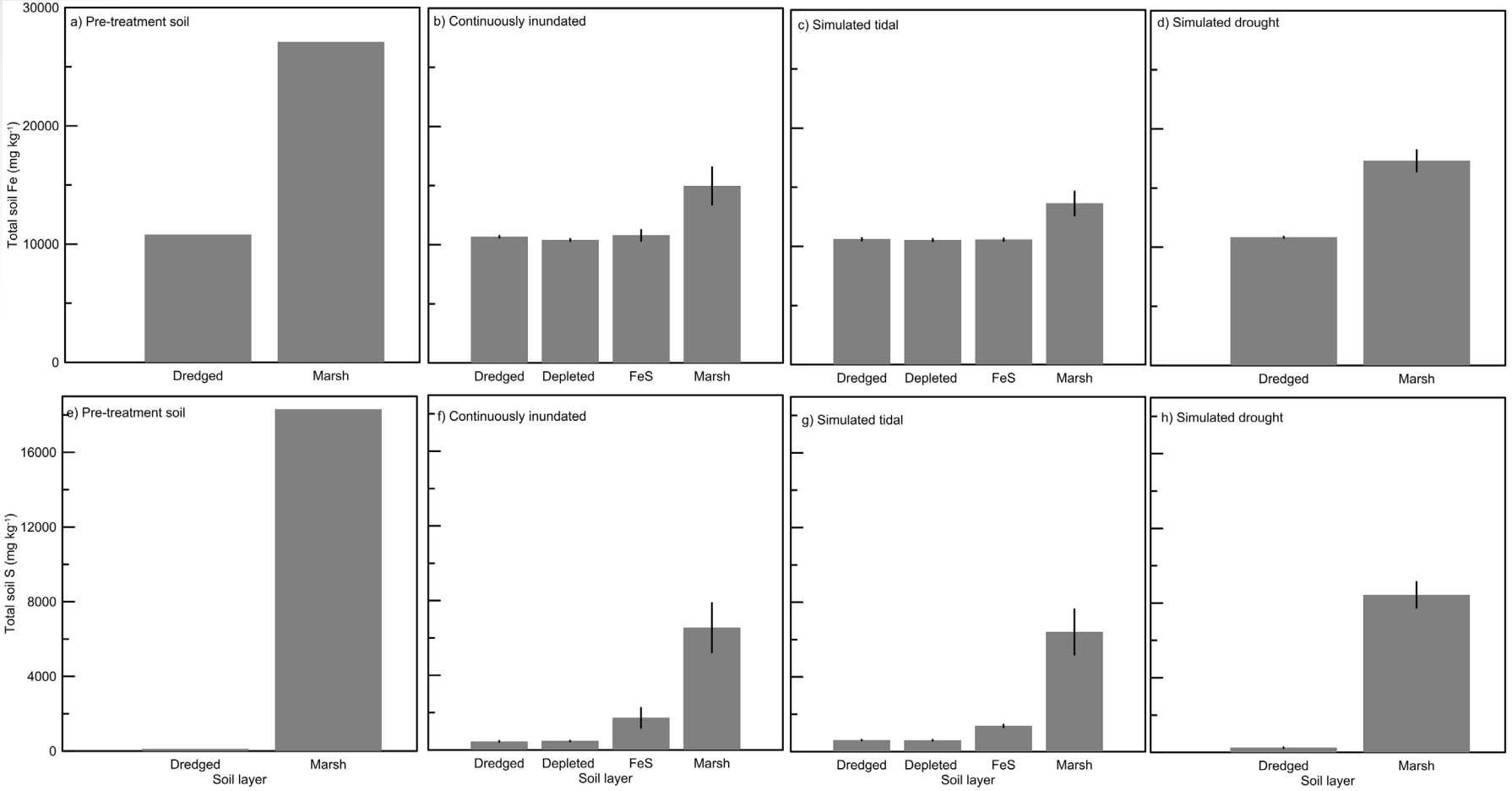
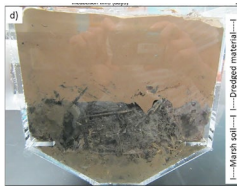


Fig. Total soil Fe and S under pre-treatment and day 90 (all treatments)

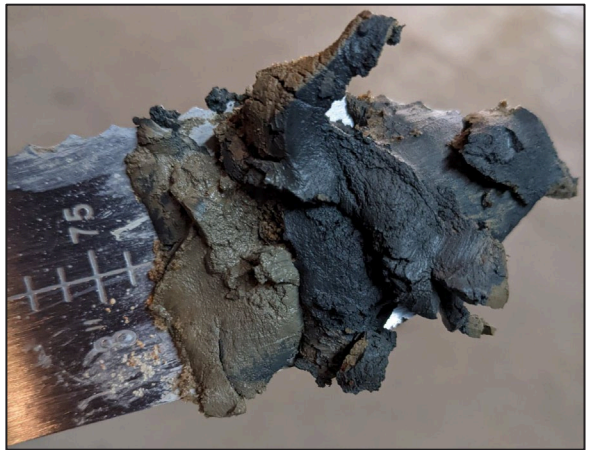
- Total Fe was at pre-treatment level in dredged material layers
- Marsh soil total Fe decreased during the experiment
- Marsh soils may be contributing Fe to the dredged material in the form of Fe^{2+}

Experiment 1 Summary



Experiment 1

- Rapid FeS horizon formation followed simulated marsh restoration
- Continuous inundation increased FeS formation compared to other treatments
- FeS oxidized within 60 days following simulated drought
- Oxidation-reduction potential and diffusion differentials drove FeS formation
- Marsh restoration should consider potential FeS formation during design/monitoring

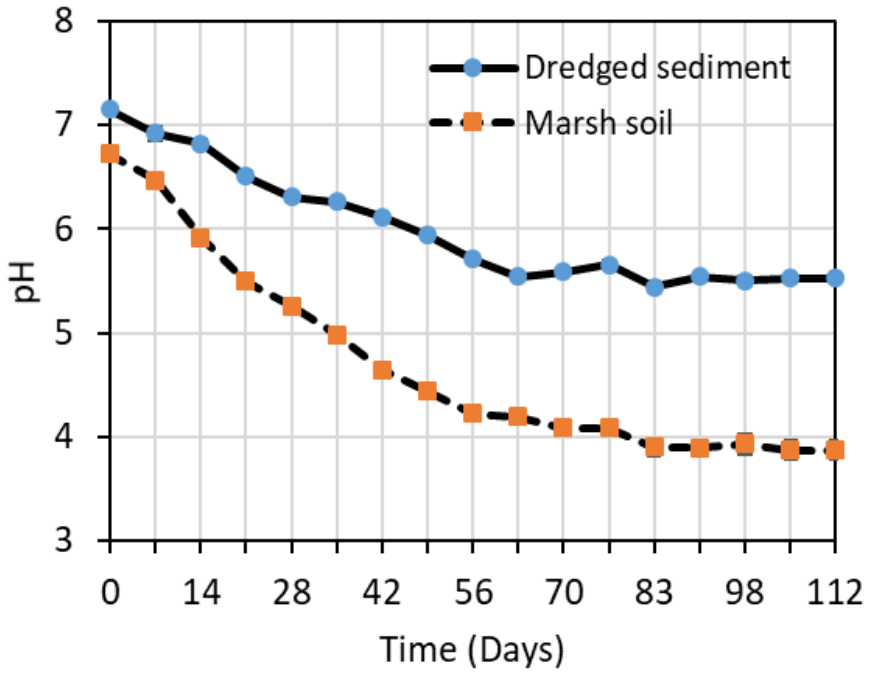


Experiment 2

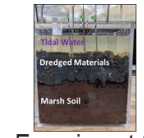
Experiment 2

- Confirmed for the presence of FeS using field test methods
- Incubated for 16 weeks to record pH change

Physiochemical properties	Dredged sediment	Marsh soil
Munsell color	N 2.5/0 (black)	7.5YR 2/2
Texture	Clay	Muck (sapric material)
Soil classification	Hyposulfidic Technosols	Euic, hyperthermic Typic Haplosaprists
Moisture content (%)	47.4	87.3
Conductivity at 25 °C (mS cm^{-1})	22.6	4.7
Salinity (psu)	13.9	2.5
pH	7.1±0.02	6.7±0.02
Alkalinity (mg $CaCO_3$ L^{-1})	376.9	327.3±18.7
Total Fe (gkg^{-1})	31.0±0.9	7.8±0.3
Total S (gkg^{-1})	3.5±0.6	20.6±0.7
Acid Volatile Sulfide ($mgkg^{-1}$)	28.5±7.2	99.5±24.7



Morphological changes



Experiment 2

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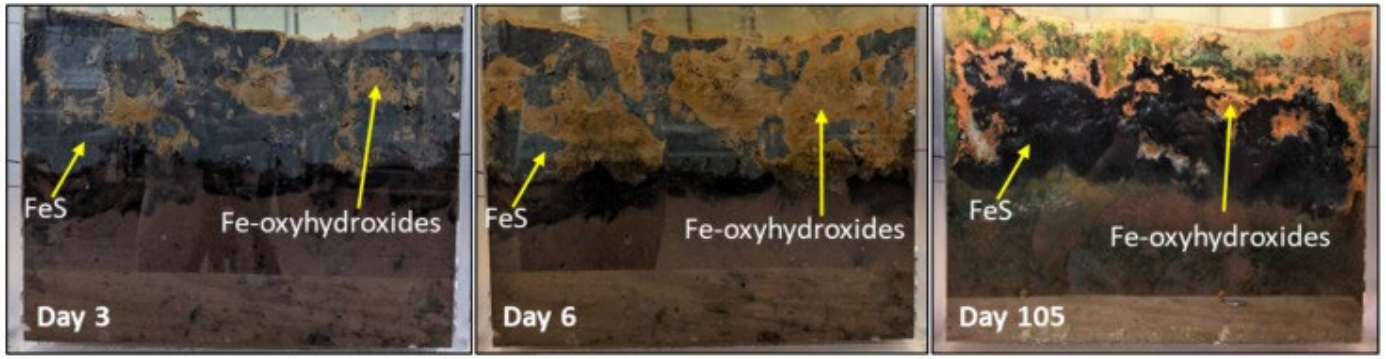
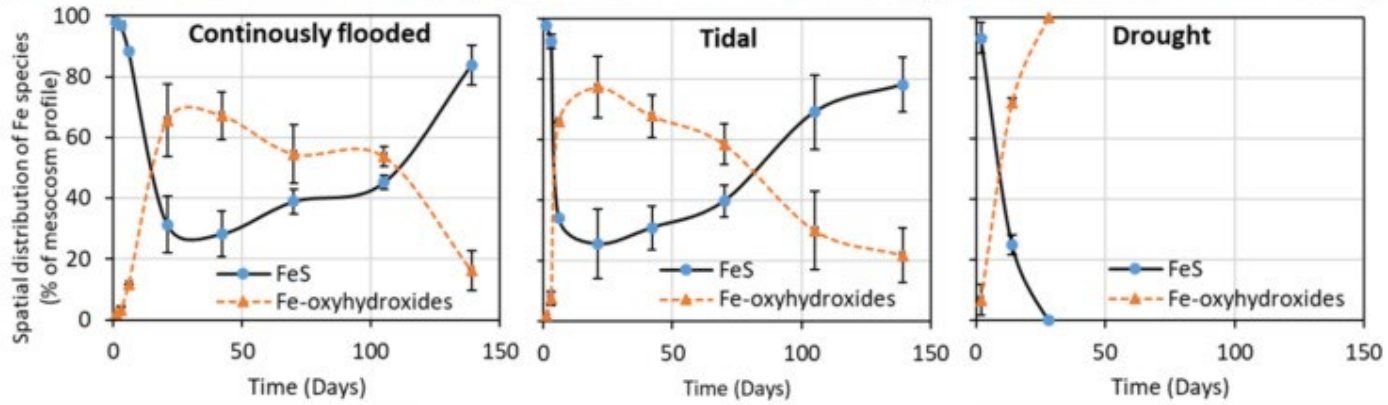
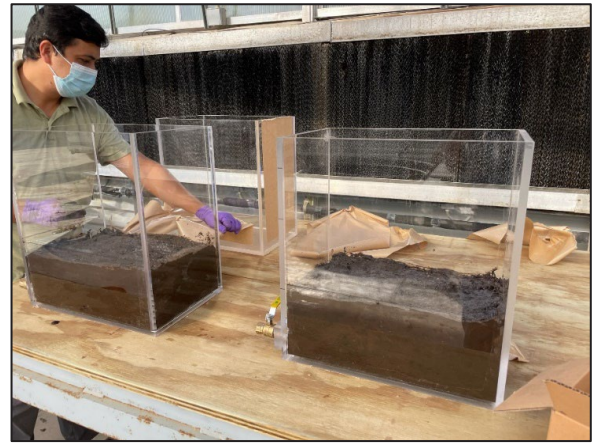
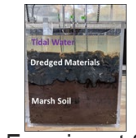
- Readily observable dredged sediment color change (black to yellowish-orange in as little as three days
- 66 to 100% color change within 3 weeks of experiment indicating FeS dissolution and Fe oxidation (O2 introduced during handling)
- Re-precipitation stated by 28 days with up to 84% reprecipitation by 120 days





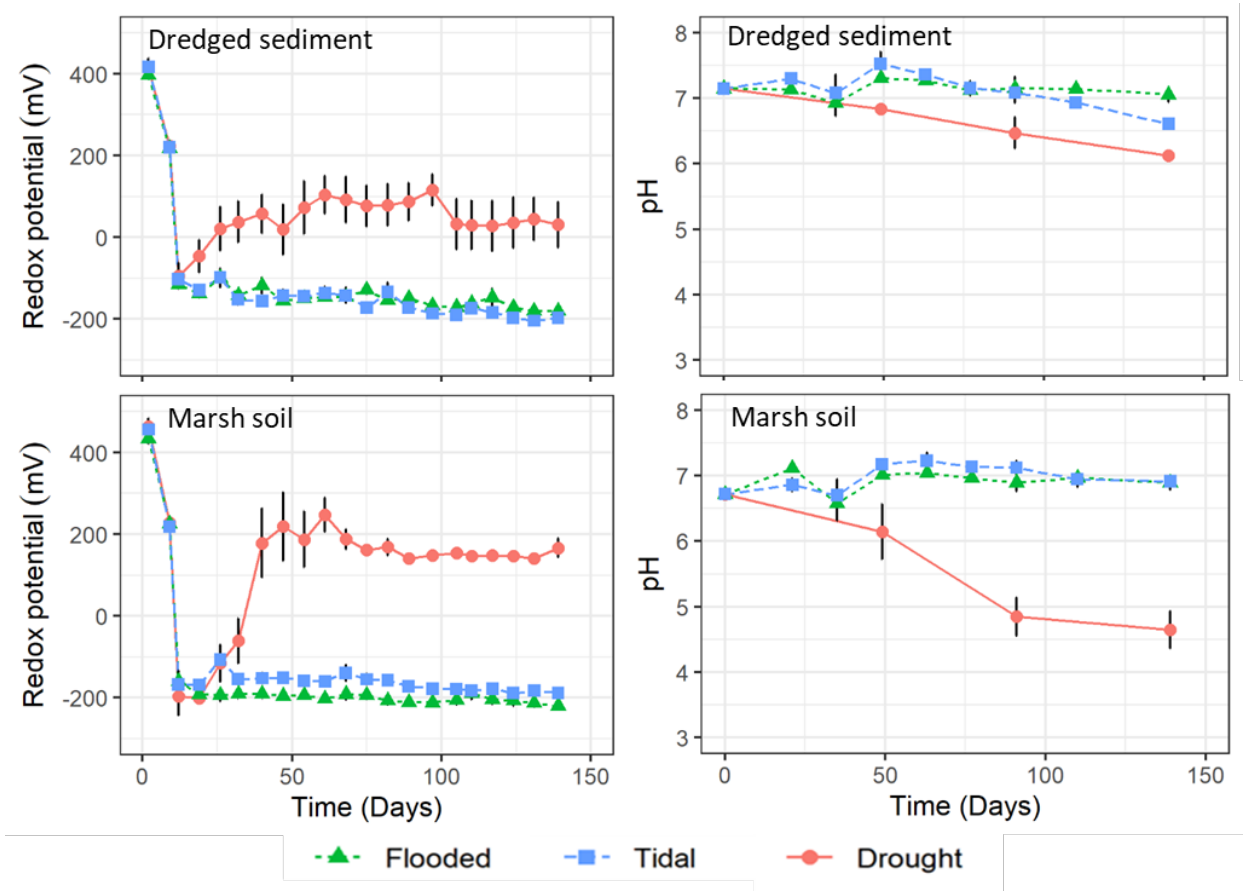


Redox (Eh) and pH

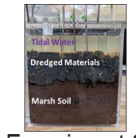


Experiment 2

- Eh rapidly decreased during first two weeks
- Increased from 3rd week in drought treatment
- pH did not change on flooded and tidal treatment
- pH decreased to 6.0 in dredged layer and 4.5 in marsh soil layer of drought treatment in 16 weeks

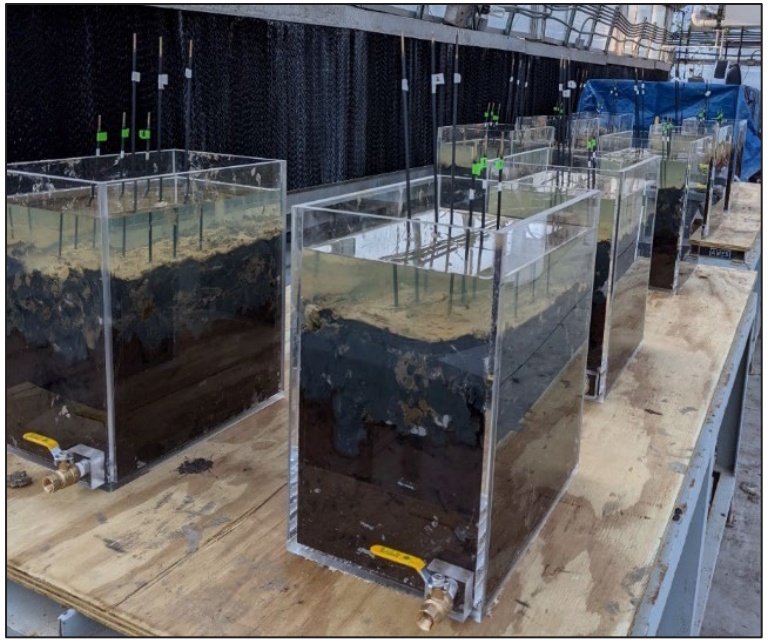


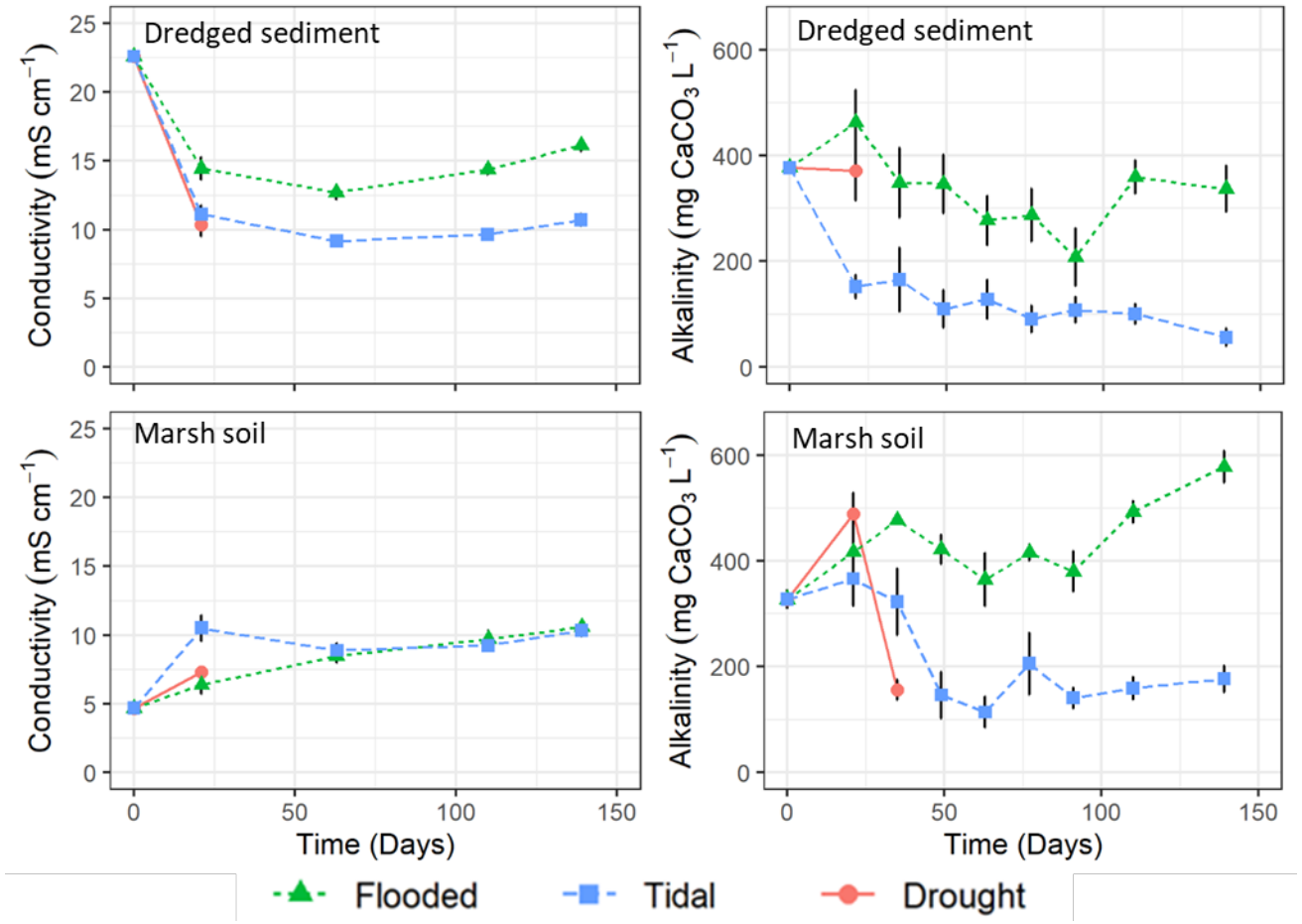
Conductivity and alkalinity



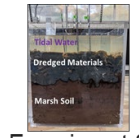
Experiment 2

- Conductivity decreased in dredged layer but increased in marsh layer
- Alkalinity decreased in dredged layer



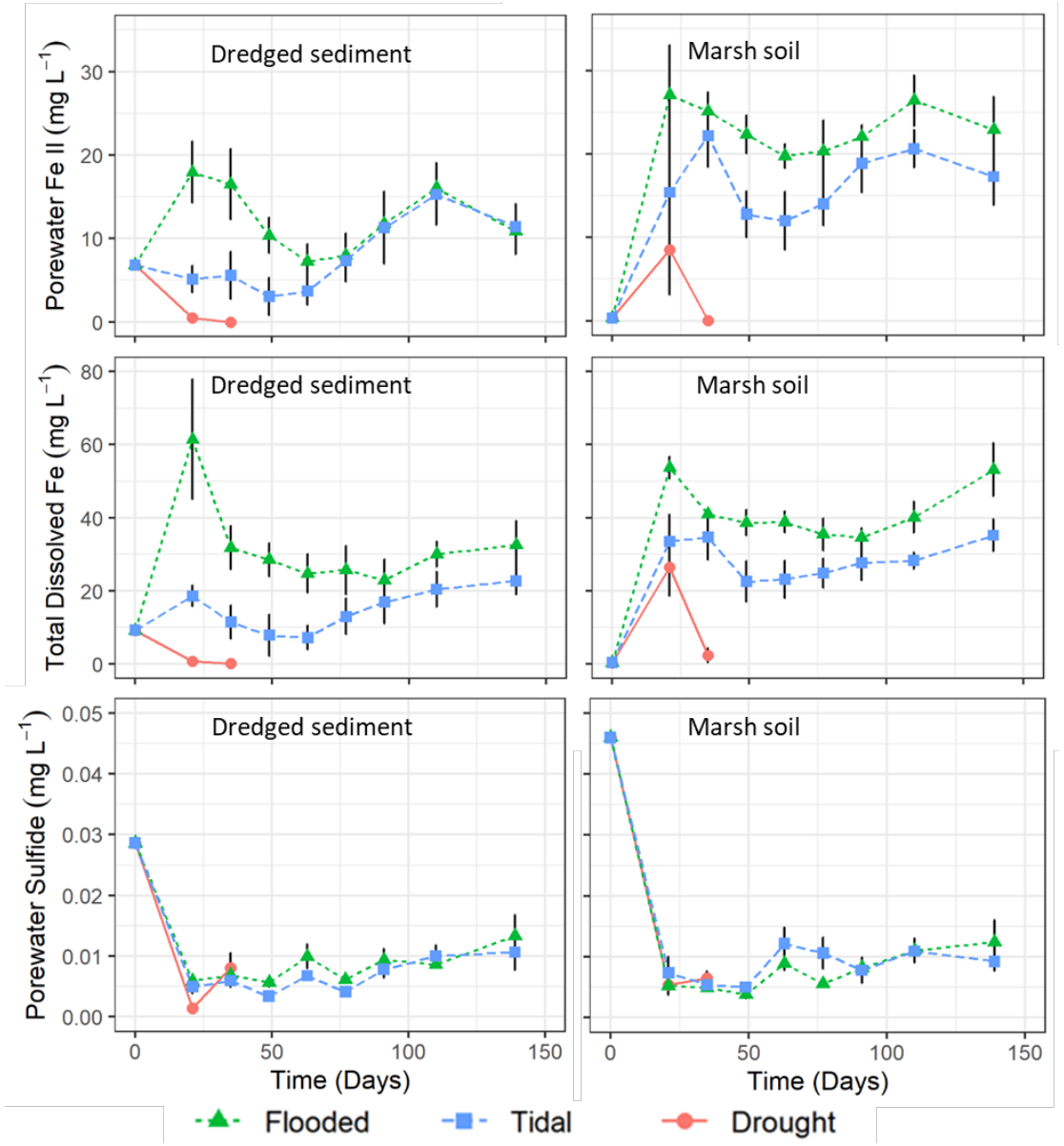


Porewater iron and sulfide

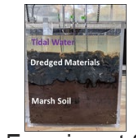


Experiment 2

- Decreasing Fe^{2+} and total dissolved Fe over time in continuously flooded layer- indicating the formation of FeS precipitate
- Tidal loss of ions in tidal treatment
- Low sulfide concentration
- Plenty of free Fe^{2+} that prevents the accumulation of free S^{2-} - combine to produce FeS

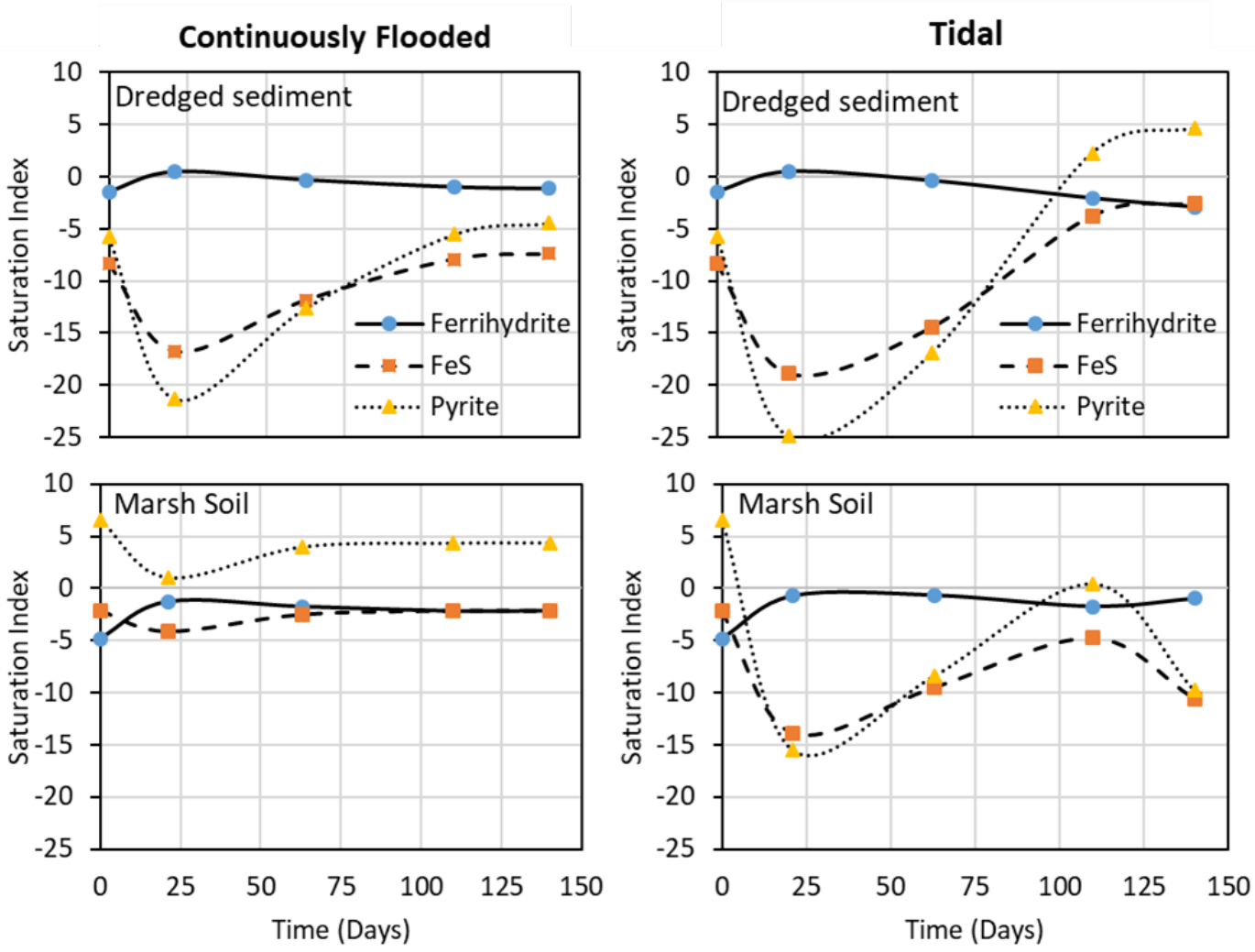


Modeling results- visual MINTEQ

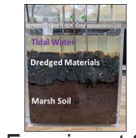


Experiment 2

- Saturation index of FeS and pyrite is increasing over time
  - <0 = Under saturated,
  - 0 = Saturated,
  - >0 = Over saturated
- The FeS and FeS_2 oxidized following initiation of the experiment setup and then reprecipitated as redox potentials decreased
- Consistent with the morphological changes and porewater chemistry results



Summary- Experiment 2



Experiment 2

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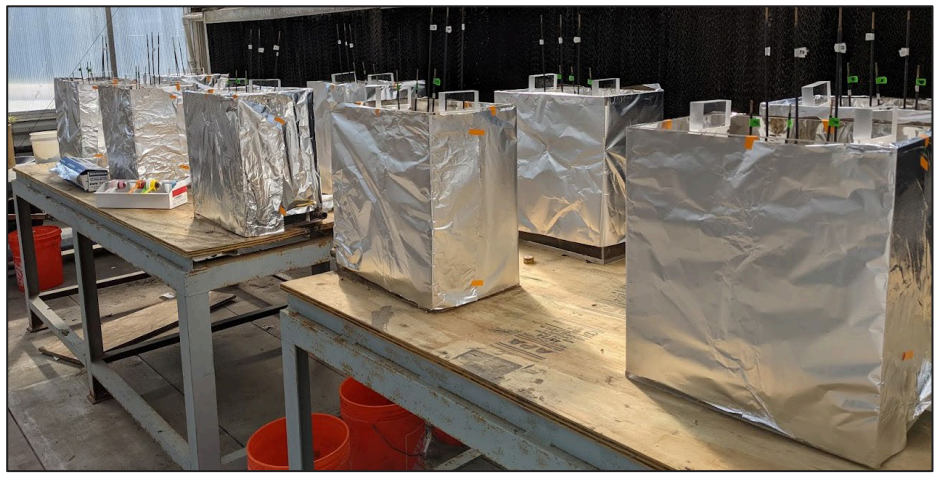
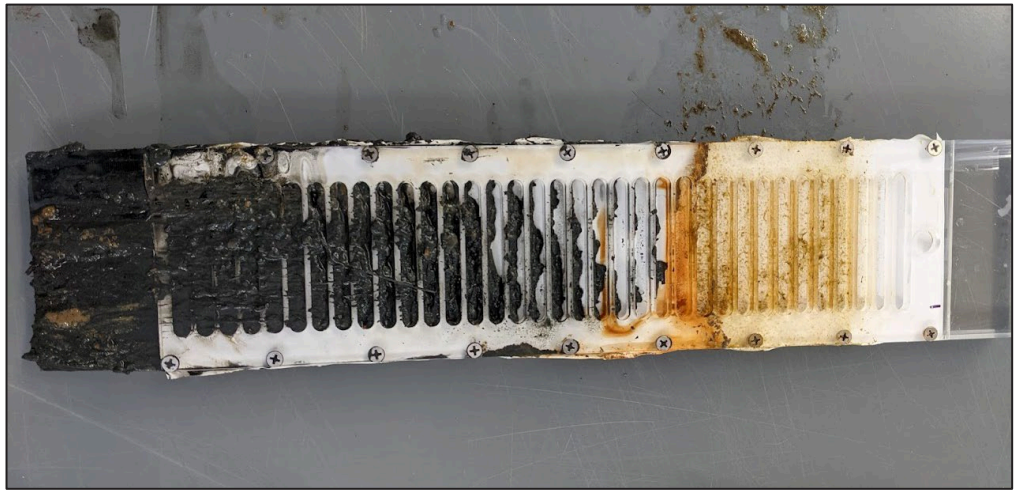
- Additional FeS is forming in both continuously flooded and tidal treatments
- No toxic level of sulfide formed due to the presence of plenty of iron
- No pH change in continuously flooded and tidal treatments indicating no acidity development in the restoration sites under tidal influence
- pH decreased in drought treatment indicating acidity will be developed under drought condition in restoration sites





Conclusions

- Rapid FeS horizon formation occurs in thin layer placement restoration areas that received saline tidal water
- Drying/drought induce acid production in restored sites
- No acidity development in the restoration sites under tidal influence
- Moderate saline tidal water may not accelerate the formation of iron sulfide in restored sites
- FeS-rich fine grained dredged material is suitable for use in coastal restoration when properly screened and managed
- Marsh restoration should consider potential FeS formation during design/monitoring

Acknowledgement

- Ecosystem Management & Restoration Research Program
- Anticipating Threats to Natural Systems (ACTIONS) project
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Nia Hurst
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Questions?

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