Pyrite Oxidation and Formation During Dredged Material Wetland Creation: Poplar Island, Maryland, USA

- Character of dredged materials
- Sediment to soils
- Pyrite oxidation and formation
- Formation of marsh iron sulfides and consequences

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EMRRP
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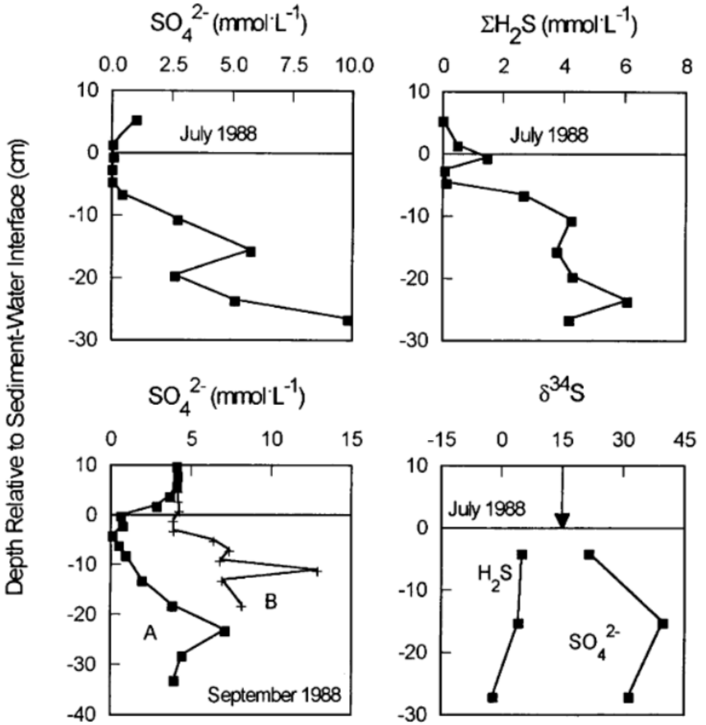
Sulfur was on my mind in the 1st Wetland Biogeochemical Symposium – Baton Rouge

Fig. 1. Vertical profiles of pore water sulfur sulfate, sulfide, and $\delta^{34}S$ in experimental impoundments at the Delta Marsh Ecology Research Complex. Metaphyton-dominated site A (■) was 50 cm deep and was sampled in July and September. Site B, located in a cattail stand with 10 cm of overlying water, was sampled only in September (+). The $\delta^{34}S$ of overlying water sulfate is indicated by an arrow.



Biogeochemical origin of $\delta^{34}S$ isotopic signatures in a prairie marsh

Jeffrey C. Cornwell, C. Neill, and J.C. Stevenson

WETLANDS, Vol. 21, No. 4, December 2001, pp. 629–638

NITROGEN, PHOSPHORUS, AND SULFUR DYNAMICS IN A LOW SALINITY MARSH SYSTEM DOMINATED BY *SPARTINA ALTERNIFLORA*

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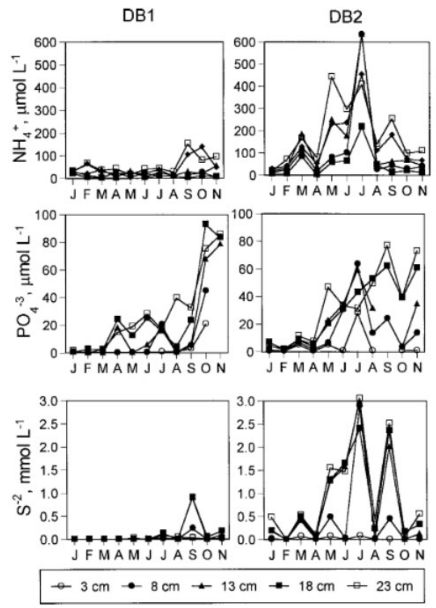

Figure 4. Porewater ammonium, phosphate, and sulfide concentrations at DB1 and DB2 for all sampling months. Plant roots were concentrated at 8-, 13-, and 18-cm depths (solid symbols).

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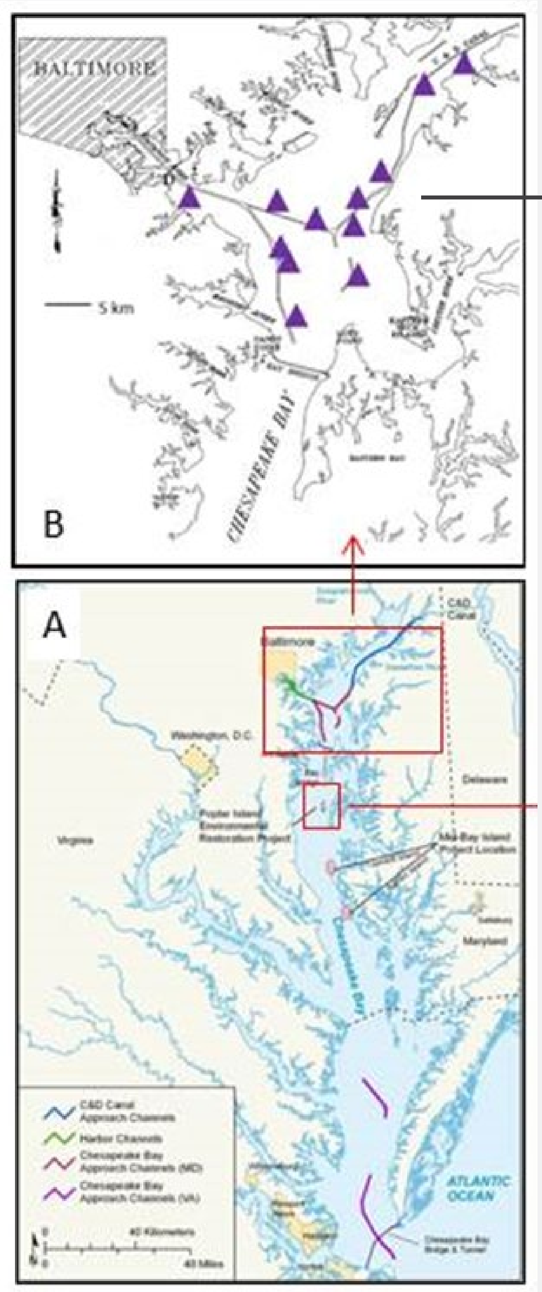
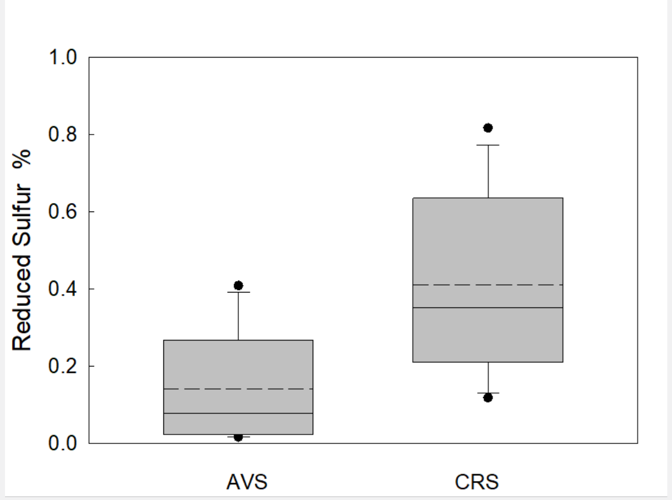
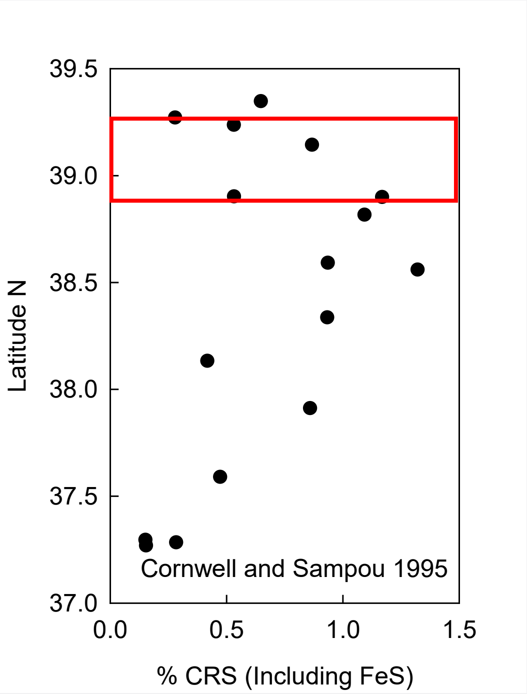
The Trajectory of Iron Sulfide Oxidation and Production in Marshes Created from Dredged Sediments at Poplar Island: Implications for Wetland Plant Establishment

By Jeffrey Cornwell, Lorie Staver, Safra Altman, Elizabeth Murray

PURPOSE: The following technical note (TN) provides a summary of the effects of iron sulfide dynamics (e.g., oxidation and formation) on the establishment of plant communities in wetlands created from fine-grained dredged sediments at Poplar Island, in Maryland's mid Chesapeake Bay. The challenges associated with handling sulfide-rich sediments are discussed using examples from dredged channels and subsequent placement in a created wetland setting in the upper Chesapeake Bay. This TN synthesizes information from multiple previous peer-reviewed publications as well as unpublished studies all conducted by the Cornwell lab (University of Maryland, Center for Environmental Science) on the trajectory of sulfur constituents in Poplar Island created wetlands and discusses the implications for vegetation trajectories, building on the knowledge base of sulfide mineral biogeochemistry in managed coastal wetland systems (Berkowitz and VanZomeren 2022).





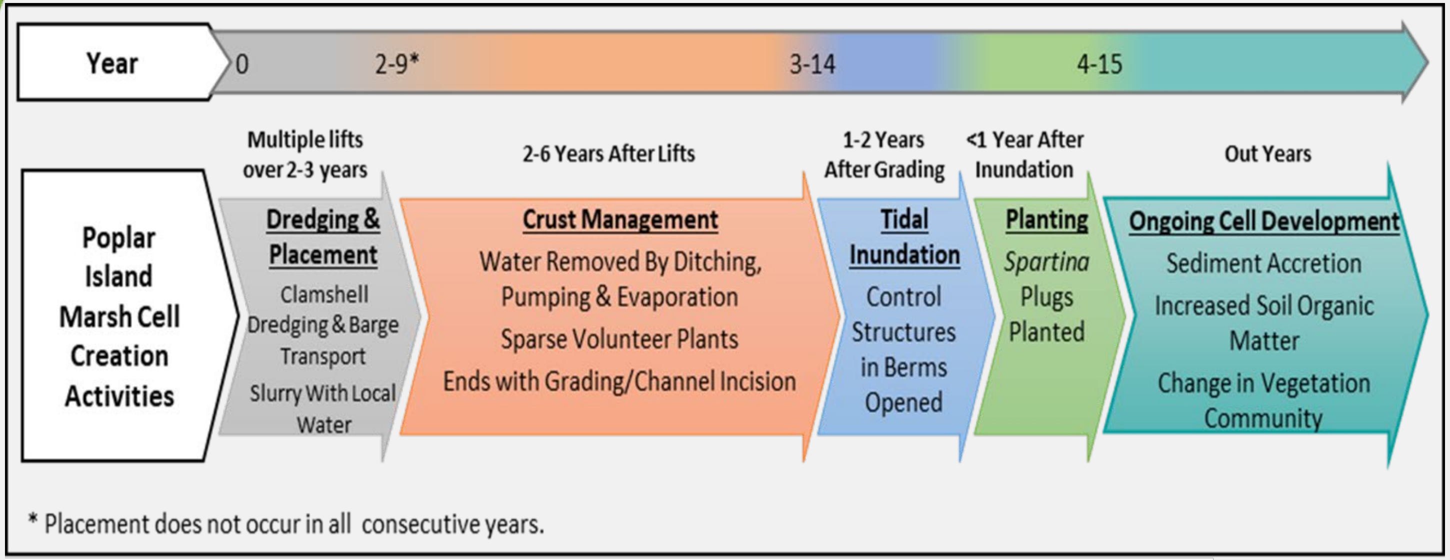


- Sediments settling into upper Chesapeake Bay navigation channels are generally fine-grained and entrain algal-derived organic matter into them.
- In channels, regeneration of nitrogen promotes high concentrations of ammonium (Cornwell and Owens 2011).
- Hydrogen sulfide reacts with sediment iron to from iron sulfide minerals, predominantly pyrite (FeS)
- A key concern with beneficial use of upper Chesapeake Bay dredged materials is pyrite oxidation leading to low pH's that can inhibit plant growth and release metals.

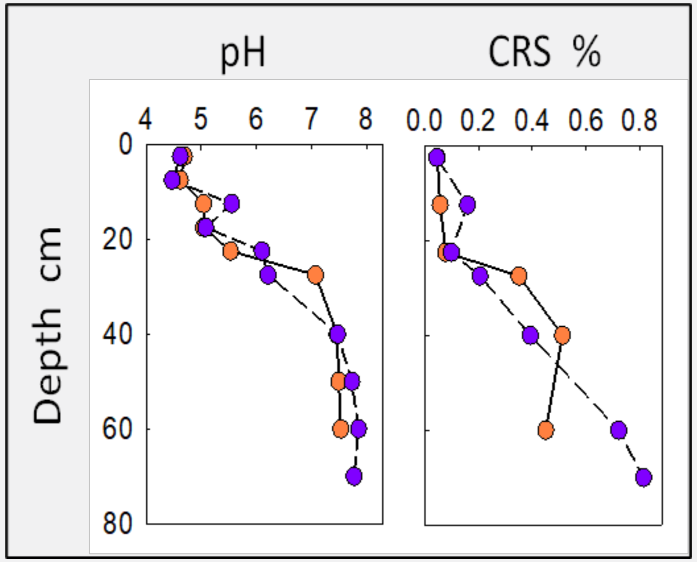
- 44/68 million cu yds added
- 776 acres tidal wetlands
- Last inflow in ~2029
- Restoration complete ~2041
- Cost ~ $1.4 billion or about ¼ of 1 yr of port economic activity

Program Elements

- Characterization of channel deposits from a previous project: ammonium, pyrite sulfur, iron and phosphorus
- Initial characterization of solid phase (C, N, P, Fe, S) and dissolved(N, P, Fe, S, sulfate, chloride) composition at time of planting.
- Solids and pore water were characterized to determine trajectories
- Biogeochemical rate processes included nutrient exchange, oxygen exchange/edaphic algal photosynthesis, and denitrification

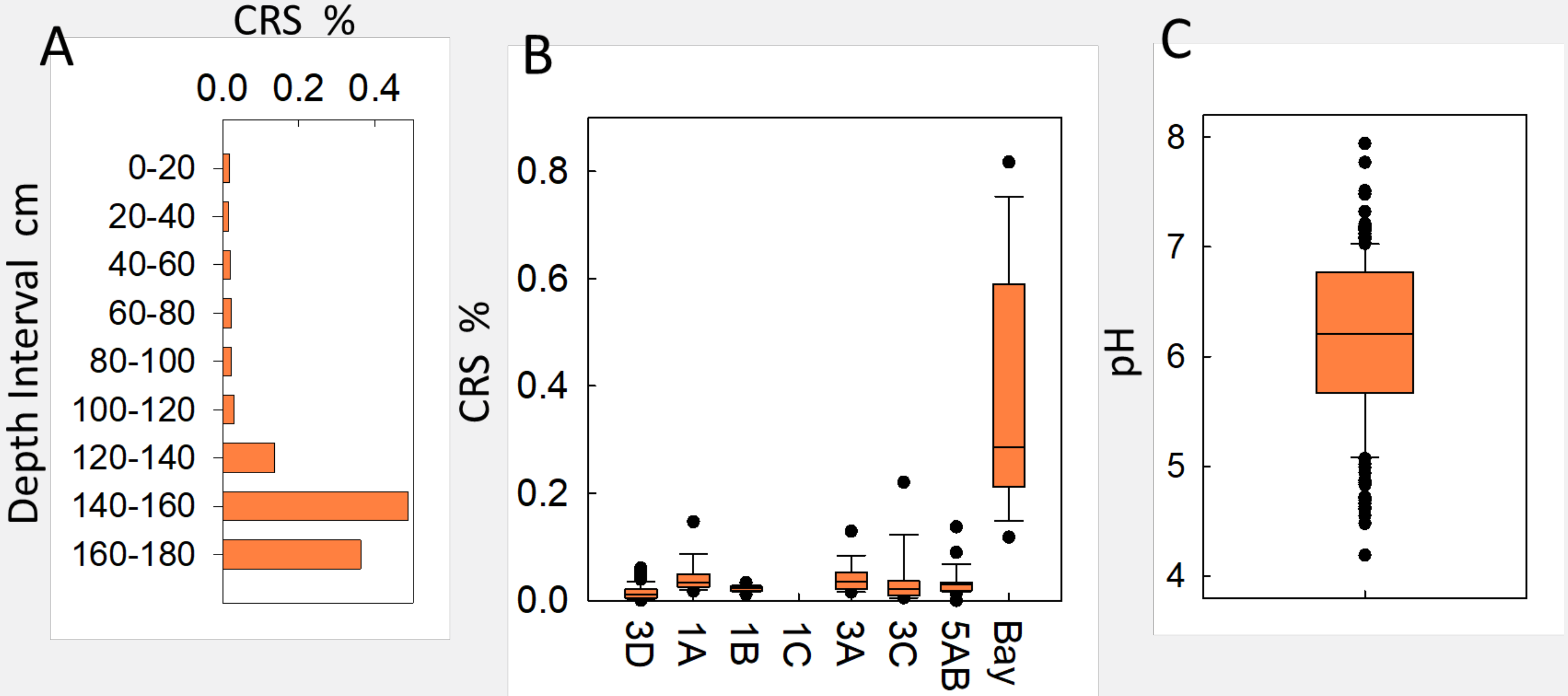


Cornwell et al., ERDC Technical Note 2026.



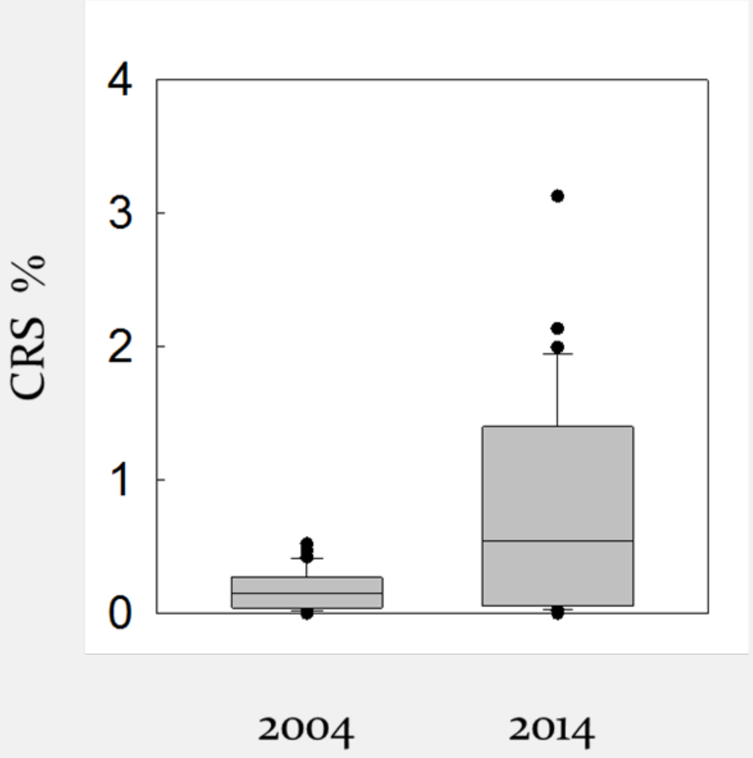
1 year of crust management

- Crust management results in a relatively dry, compacted soil prior to marsh planting.
- Drying oxidizes pyrite resulting in low pH's.
- Ammonium concentrations are high
- With tidal inundation, pH's in the soil surface support growth of marsh vegetation.



Upon exposure to oxygen during drying and "crust management", low pH arises because of pyrite oxidation :

$$4FeS_2 + 15O_2 + 8H_2O \rightarrow 2Fe_2O_3 + 8\,H_2SO_4$$

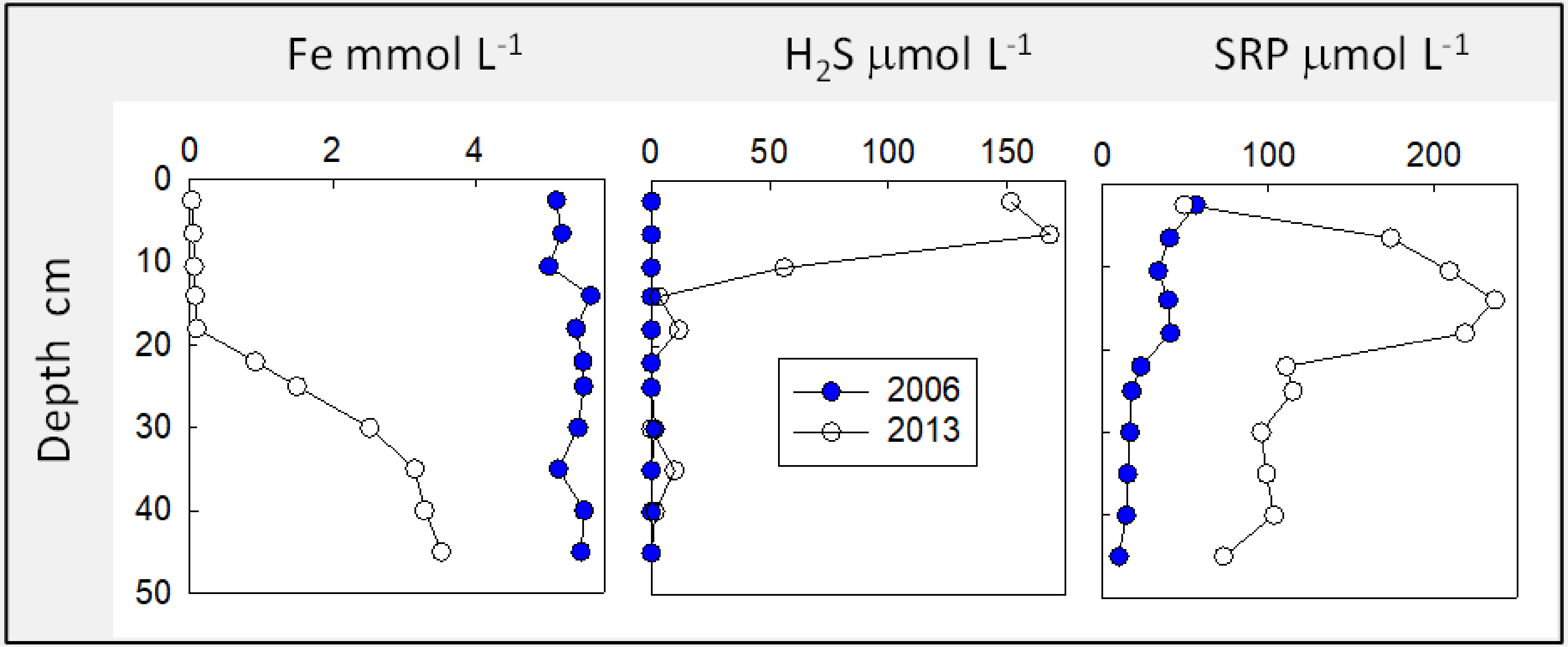


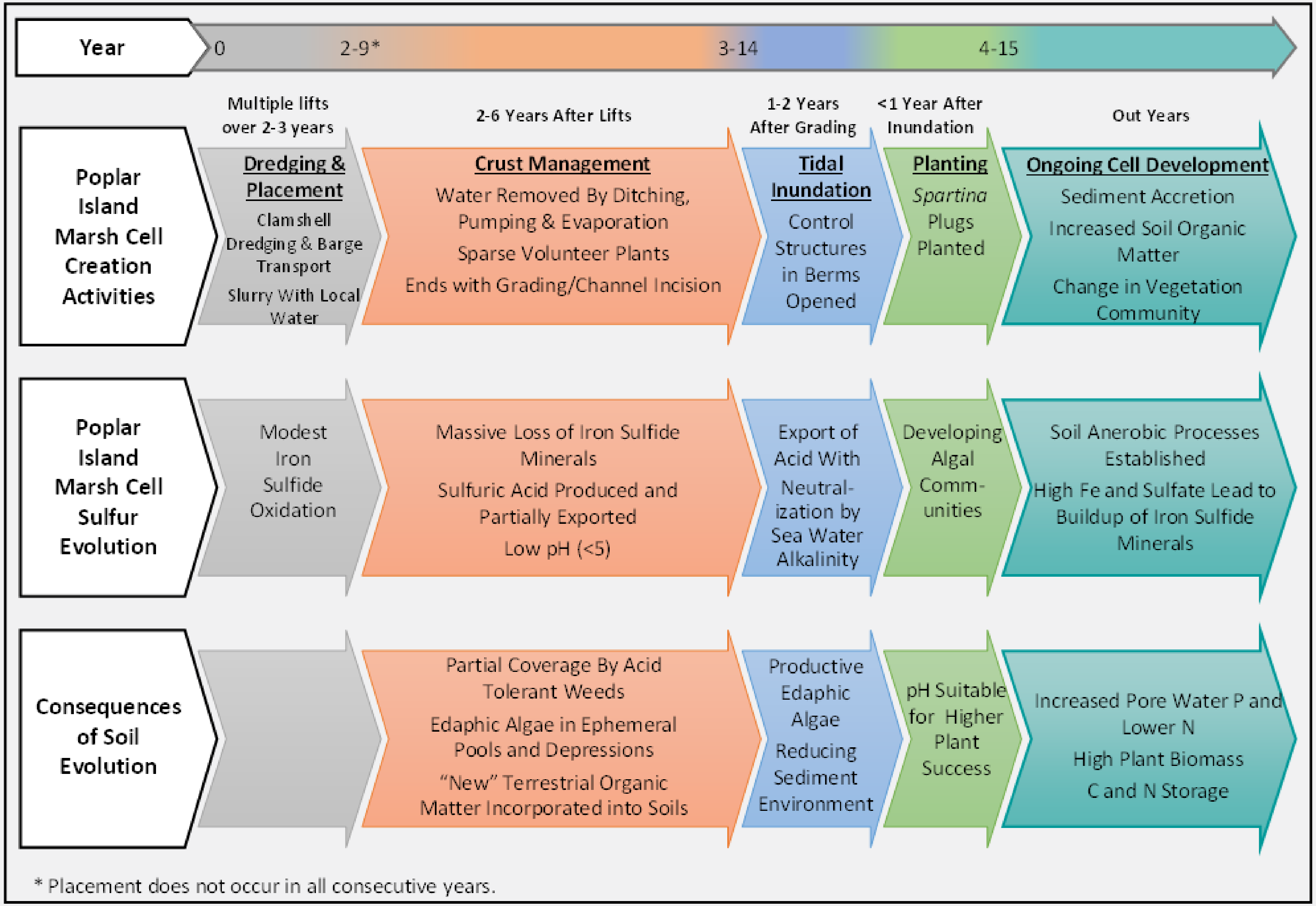
Edaphic algal production occurs at the outset of wetland cell development and FeS is evident below the algae. This labile organic matter input is a "jump start" to soil respiration and is reflected in almost immediate near-surface sulfate reduction and other anaerobic processes such as denitrification
(Cornwell 2025 submitted)

Anerobic conditions result in pyrite formation

Bottom Line: pyrite oxidation/ pH was not a major issue for marsh success

With time, conversion of Fe oxides to sulfides release Fe-bound inorganic P





Year
0
2-9*
3-14
4-15
Multiple lifts over 2-3 years
2-6 Years After Lifts
1-2 Years After Grading
<1 Year After Inundation
Out Years
Poplar Island Marsh Cell Creation Activities
Dredging & Placement
Clamshell Dredging & Barge Transport
Slurry With Local Water
Crust Management
Water Removed By Ditching, Pumping & Evaporation
Sparse Volunteer Plants
Ends with Grading/Channel Incision
Tidal Inundation
Control Structures in Berms Opened
Planting
Spartina Plugs Planted
Ongoing Cell Development
Sediment Accretion
Increased Soil Organic Matter
Change in Vegetation Community
Poplar Island Marsh Cell Sulfur Evolution
Modest Iron Sulfide Oxidation
Massive Loss of Iron Sulfide Minerals
Sulfuric Acid Produced and Partially Exported
Low pH (<5)
Export of Acid With Neutral-ization by Sea Water Alkalinity
Developing Algal Comm-unities
Soil Anerobic Processes Established
High Fe and Sulfate Lead to Buildup of Iron Sulfide Minerals
Consequences of Soil Evolution
Partial Coverage By Acid Tolerant Weeds
Edaphic Algae in Ephemeral Pools and Depressions
"New" Terrestrial Organic Matter Incorporated into Soils
Productive Edaphic Algae
Reducing Sediment Environment
pH Suitable for Higher Plant Success
Increased Pore Water P and Lower N
High Plant Biomass
C and N Storage
* Placement does not occur in all consecutive years.

Why Such Rapid Development of Wetland Soil Processes?

- Fine-grained sediments: because of the compacted soils, ammonium transport was diffusion limited, unlike a sandy or coarse-grained soil.
- Considerable edaphic algal production and respiration, with diffusive conditions in the soil, led to reducing conditions close to the soil surface
- The soils, after crust management, had high remaining ammonium concentrations and high adsorbed phosphorus, leading to high plant biomass from the outset

Lessons Beyond Poplar Island?

- Poplar Island wetlands are somewhat unusual due to the fine-grained dredged materials, physical separation from the bay via sand/stone dikes, and high degree of substrate drying. The ensuing connection to the bay is through culverts.
- This biogeochemical assessment approach would translate well to other projects.
- Development was enhanced by 1) proper elevation, 2) high nutrient concentrations, 3) modest infiltration into the soil.
- Commitment of assessment resources beyond planting is essential for informing future design. To keep the Port of Baltimore open, this use of dredged materials is likely to last in perpetuity.

What Could Go Wrong?

Hart-Miller Island Observations

- Without tidal exchange as in wetlands, soil pH can remain low
- The soils at HMI were mostly dried when the system was flooded with rainwater, bringing H_2SO_4 from soil horizons
- The north cell had ~ 400 acres of water that was pH 3-4
- Despite the low pH, we observed SAV and Phragmites, benthic and water column algal production, and benthic animals
- Water was removed from cell after running through creeks with added $CaCO_3$

Biogeochemical Summary

Observations

- Pyrite oxidation did not limit project success
- Edaphic algae were highly productive and help induce reducing conditions
- Formation of iron sulfide minerals with cell development lead to P release

Recommendations

- Characterizing sediment and initial soil conditions can help predict marsh success trajectory
- Establishment of long-term characterization sites within the project
- Rapid turn around of results can help adaptive management of long-term projects