Development of a Rapid, Stable and Inexpensive Monitoring Technique for Porewater Sulfide in the Intertidal Zone

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Introduction

At temperate latitudes, ***Spartina*-dominated salt marshes** exist as a dynamic balance between the rate of sea level rise; the availability of sediment for vertical marsh accretion; and the growth and predominance of specific **botanical forms with varying tolerances for salt exposure and rootzone saturation**. For these coastal marshes, a limiting condition for healthy growth and sustained function may lie in the **frequency, depth and duration of tidal inundation**. Specifically, prolonged soil saturation following inundation results in water logging; biogeochemically, **water logging In the presence of sulfate (SO_4^{2-}))** results in shallowing (shoaling) of the depth of microbial sulfate reduction and resultant **accumulation of sulfide** with potential impacts on seed germination, plant root development and rhizome propagation.

Monitoring sulfide within the root zone of marsh soils is challenging for reasons including analytical costs, specificity of materials and sample stabilization requirements and temporal limitations on the duration of field deployments. Our research is focused on **developing a rapid, stable, and inexpensive method for monitoring sulfide in marsh soils** over a concentration range (~ 0.5 – 50 mg/L) relevant for **assessing botanical toxicity**.

Based on the high affinity of silver (Ag) for free sulfide (S) ($K_{sp} \approx 10^{-50}$), the method employs strips of **field-deployed photographic paper** ("silver gelatin prints") as the monitoring medium. Utilizing this approach and applying free software to quantify and chemically characterize the results of **stabilized (fixed) and subsequently digitally scanned test strips**, short (< ½ hr) field deployments are possible for fine-scale determination of ecologically relevant concentrations of porewater sulfide. Results are presented here for deployment series in **salt marsh pools (5 min. deployment period)** and on the **salt marsh platform** during flood and ebbing of a tidal cycle (**20 min. deployment period**).

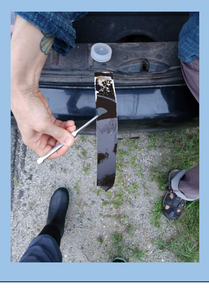
Materials and Methods

Q1: Can we use photo paper as an inexpensive, rapid, and stable alternative to other methods of porewater sulfide determination? **(A1: Yes!)**

- $25 for 10 sheets of paper (= 110 test strips)
- $20 for a gallon of fixer
- $10 for 60 craft sticks
- headlamp with red light
- bathroom / dark space for preparing light-sensitive paper

Q2: How long to deploy the test strips?

A2: **Start testing**; reaction of photo emulsion with available sulfide is a kinetic phenomenon so deployment time is a function of porewater concentration. Deployment time too short and color intensity doesn't develop; Deployment time too long and photo paper saturates with no useful color gradient evident.



Materials and Methods

Q3: How can the results be quantified?

A3: Take it to the lab! Strategy is to test for deployment duration in a specific environment, confirm color intensity coverage and then create Na_2S standards for that same deployment duration.

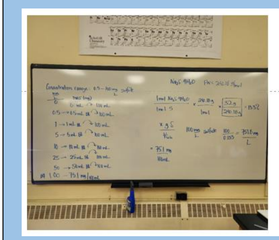
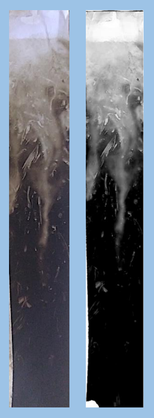


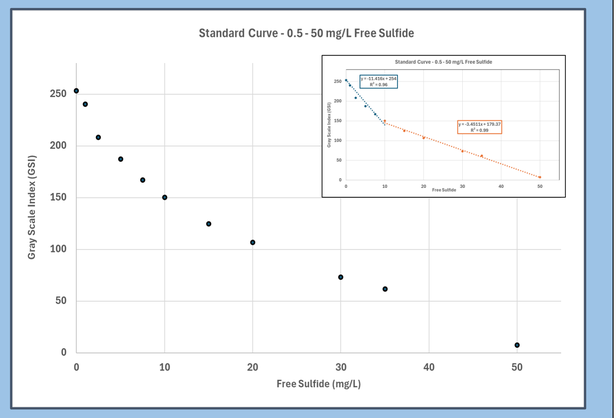
Photo paper is light-sensitive, but once a test strip is stabilized in fixer and allowed to dry, the strip is durable.

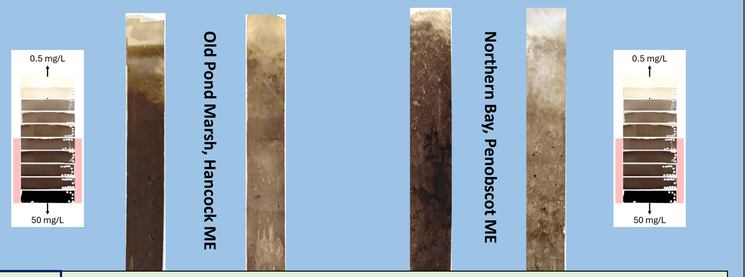
With matching deployment durations in the field and in the lab, the free sulfide concentration can be quantified.

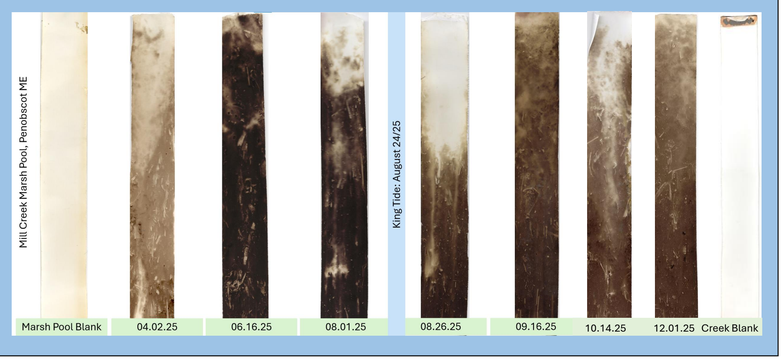
Quantification:

- Scan stabilized (fixed) photo strips and convert scan to gray scale
- Gray scale provides a 255-point range
- Use free ImageJ software (https://imagej.net/ij/index.html) to quantify gray scale value by pixel
- Create a gray scale index curve
- Determine relevant spatial scale and resolution (cm-scale in the field)





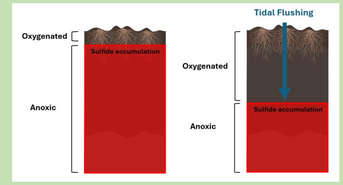




Field Research – CMES Capstone Project

Hypothesis: Tidal flushing prevents sulfide from accumulating to toxic levels in the root zone of saltmarsh plants

Deployments: The marsh platform had significantly lower sulfide concentrations compared to marsh pools which required a new set of 20 min. standards

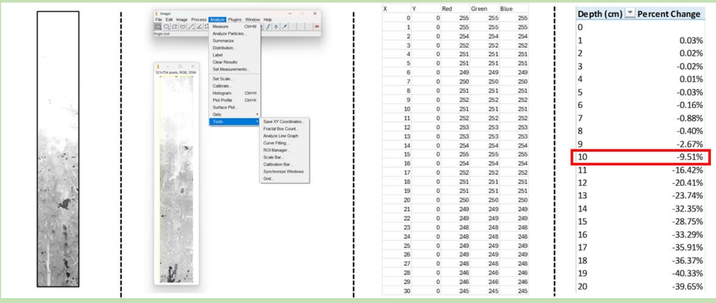


Concentration Range: With 20 min. deployments, free sulfide concentration range that can be characterized on the 0-255 Gray Scale Intensity (GSI) index is 0.5 – 13 mg/L.

Field Study Site: Sulfide test strips were deployed multiple times on the Mill Creek Marsh platform in Penobscot, Maine. Deployment locations include high marsh dominated by *Spartina patens* and low marsh dominated by *Spartina alterniflora*.

Experimental Design: Test strips were deployed in triplicate at four (4) time intervals over a tidal cycles to evaluate the stability and depth of the sulfide redox boundary prior to, during, and following tidal inundation.

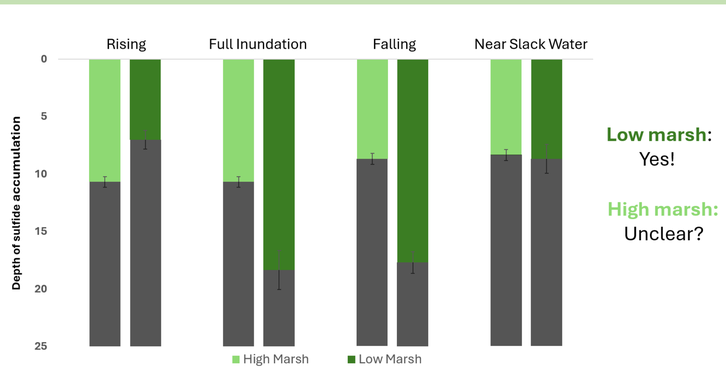
Image Process Recovered and Stabilized (Fixed) Test Strips:



Depth (cm)	Percent Change
0	
1	0.03%
2	0.02%
3	-0.02%
4	0.01%
5	-0.03%
6	-0.16%
7	-0.88%
8	-0.40%
9	-2.67%
10	-9.51%
11	-16.42%
12	-20.41%
13	-23.74%
14	-32.35%
15	-28.75%
16	-33.29%
17	-35.91%
18	-36.37%
19	-40.33%
20	-39.65%

Sulfide accumulation depth is the depth at which there is a cumulative percent change of 5% in GSI over a 1-cm depth increment following digital scanning and scan evaluation using ImageJ software.

Results: Inundation resulted in a statistically significant shift in the sulfide accumulation depth in the low marsh platform during a high spring tide.



Acknowledgements

Thank you to the **Corning School of Ocean Studies** and to the Administration at Maine Maritime Academy for supporting this research project and to **Maine Coast Heritage Trust** for inviting us to tromp around on Old Pond Marsh. Thanks, Tatia Bauer! Thank you also to **Dr. Lourdes Vera @ SUNY Buffalo** for the seed from which this DIY idea has grown.