

Practitioner Guidance for Managing Iron Sulfur Compounds During Wetland Restoration

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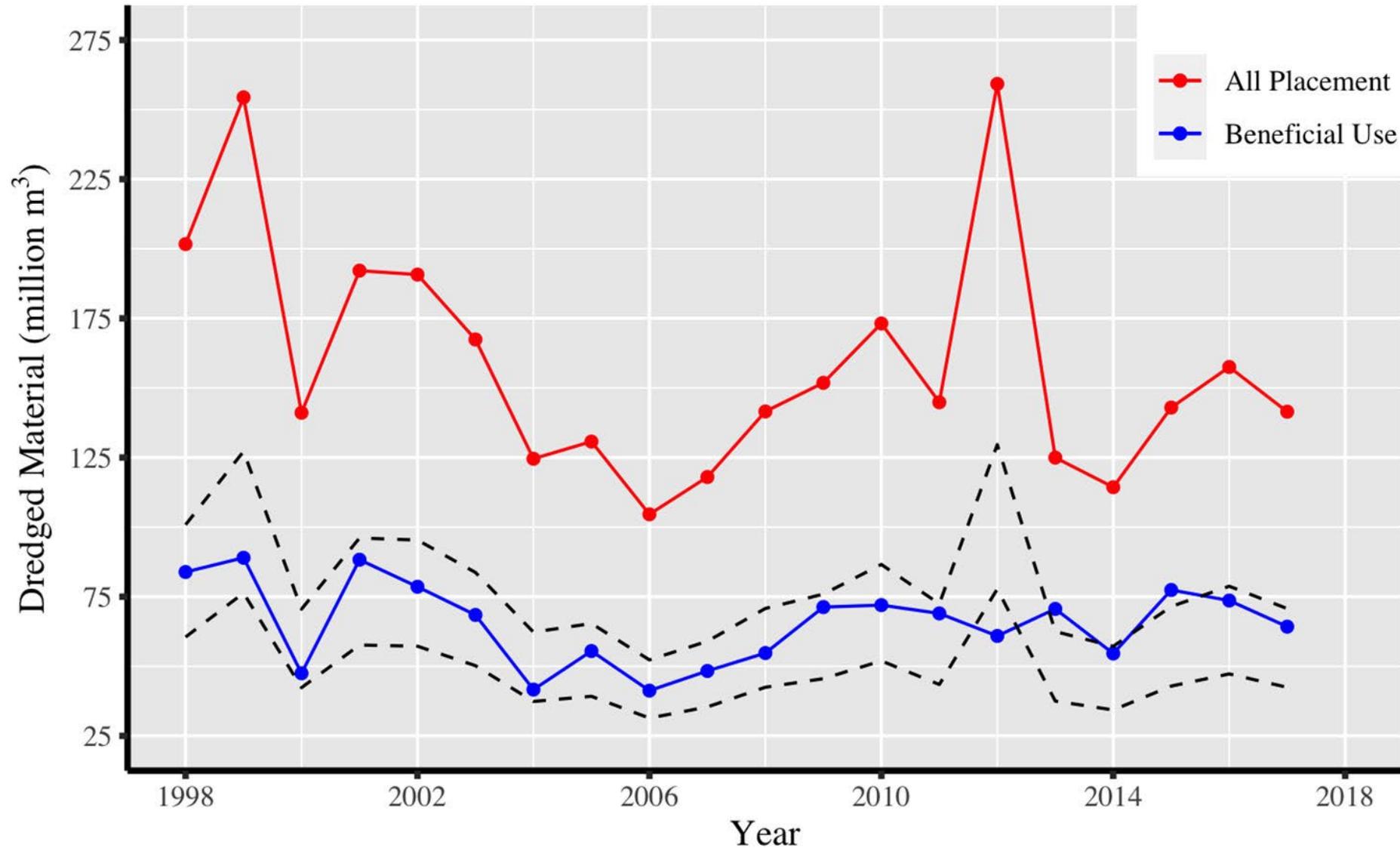
Introduction



- Statement of Need: Addressing the Effects of Acid Sulfides on Salt Marsh Restoration Success
- Problem:
 - Coastal marsh restoration projects lack vegetation recovery in conjunction with observations of black iron sulfidic (FeS) at the soil surface.
 - FeS has the potential to produce acidity impacting project success.
 - Impacted projects include restoration of tidal flooding, excavation to restore historic elevations, and thin layer placement of dredged sediments.
- Purpose: Address FeS concerns within the Corps and partner agencies in an ecological restoration context for **practitioners**.

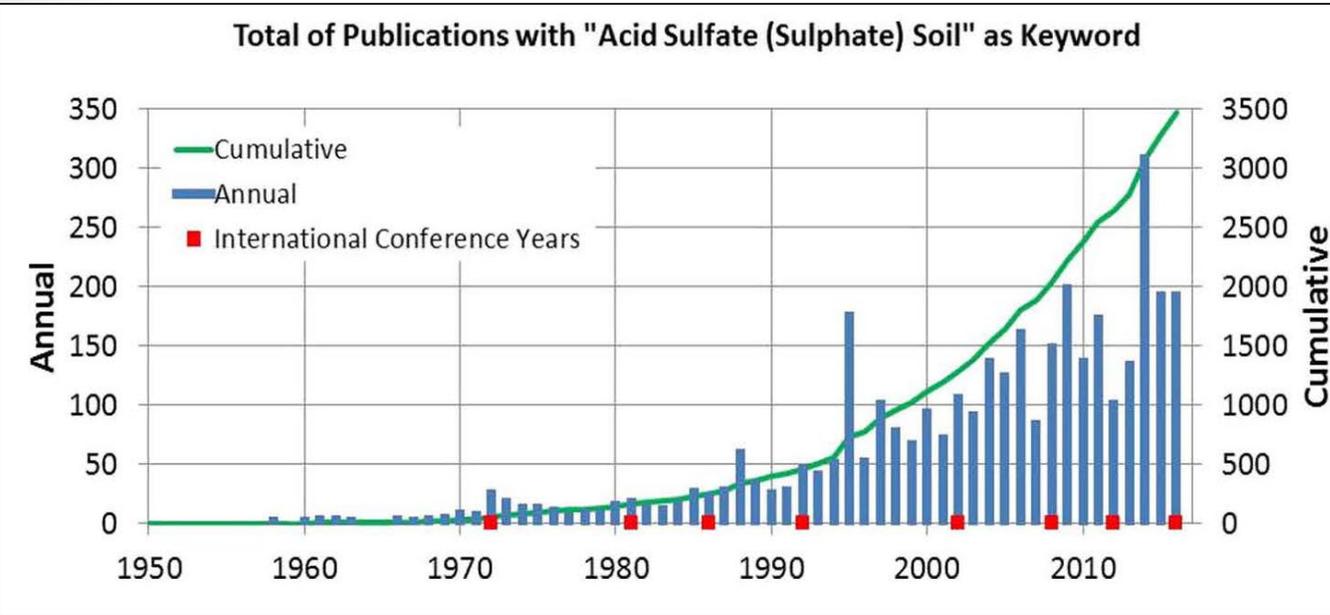


GOAL → 70% BENEFICIAL USE BY 2030





Research vs practitioner guidance



International Acid Sulfate Soils Conference



USACE, New Orleans



Focus on practitioners



ERDC/EL TR-25-8

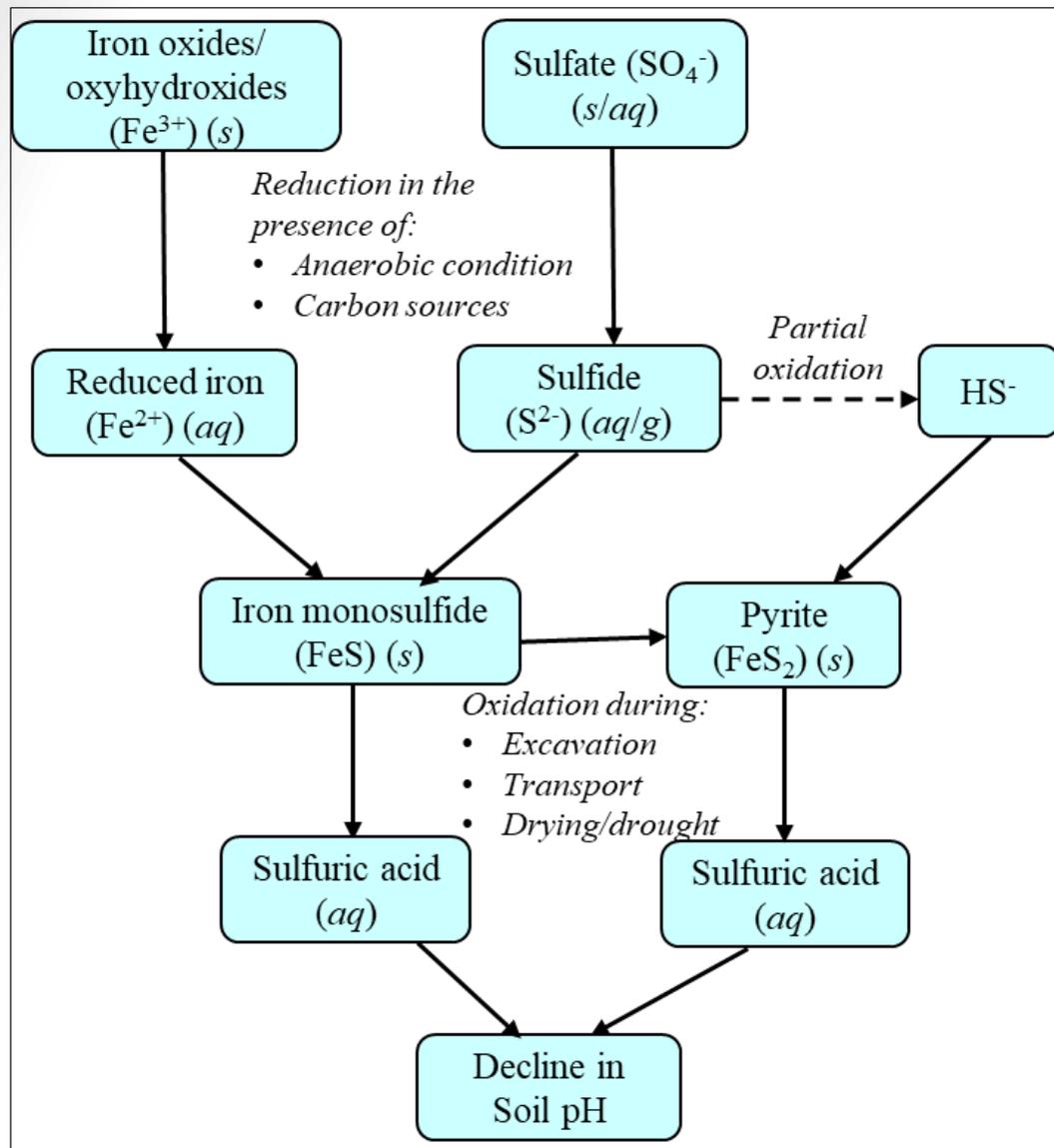
Environmental Laboratory



- Introduction to FeS
- FeS primer for end users
- FeS identification
 - Field techniques
 - Laboratory techniques
- Management recommendations
- Summary

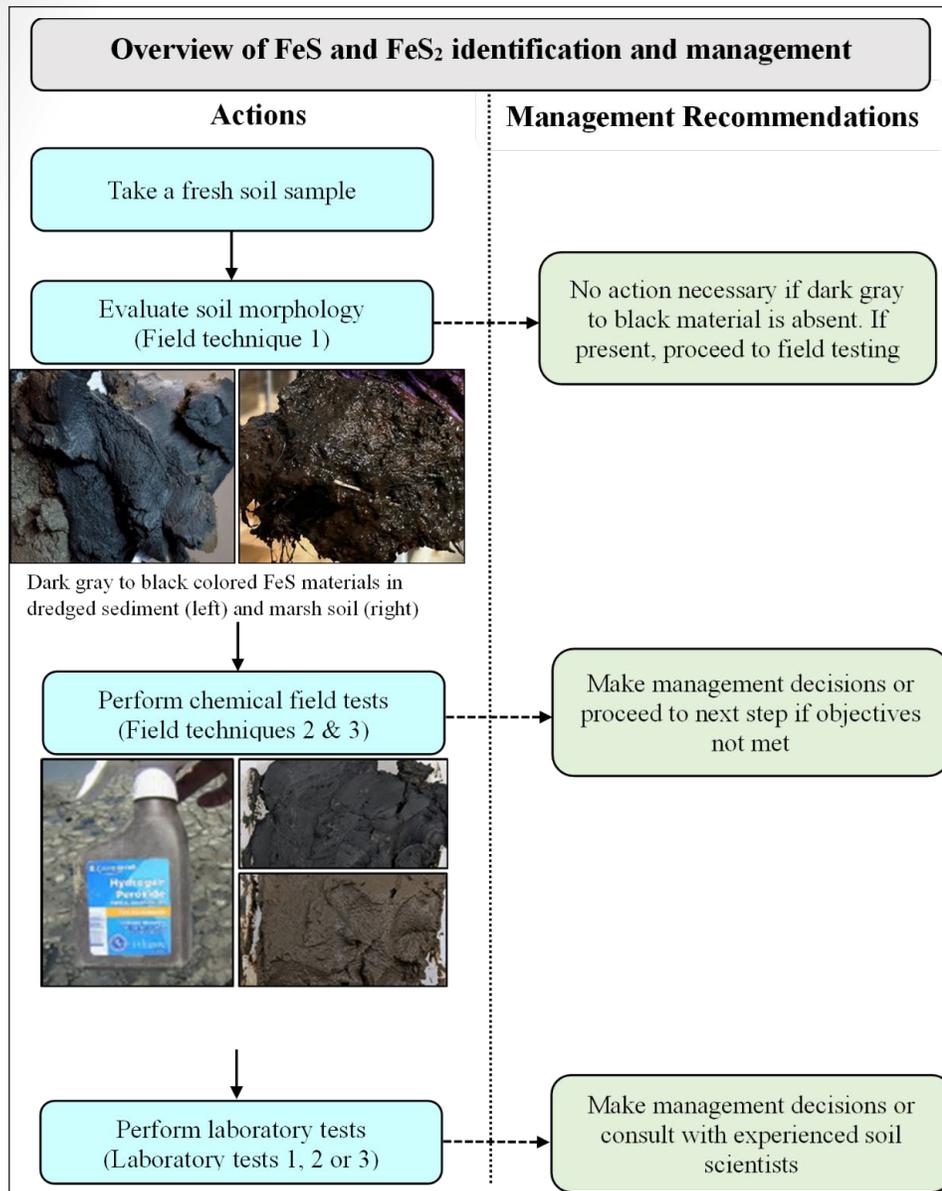


Iron sulfide science for practitioners





Iron sulfide identification overview



1) Look

2) Test

3) Manage



Common management decisions

- A. If FeS is confirmed absent** by evaluating soil morphology and/or field test, use the material without additional actions/considerations
- B. If FeS confirmed present,**
1. Use the material, but maintain saturated conditions OR
 2. Use the material if adequate flushing is incorporated into the project design to prevent negative project impacts OR
 3. Use the material, but monitor for site hydrology, soil moisture content, or changes in pH OR
 4. Use the material after curing or addition of acid neutralizing compounds (Calcium Carbonate) OR
 5. Do not use the material

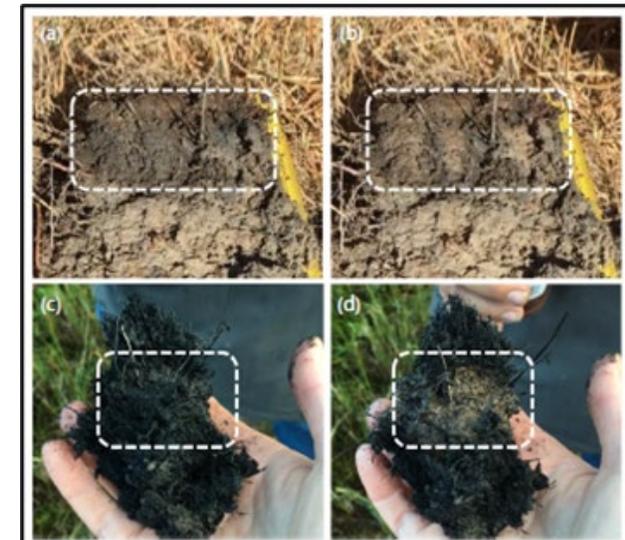
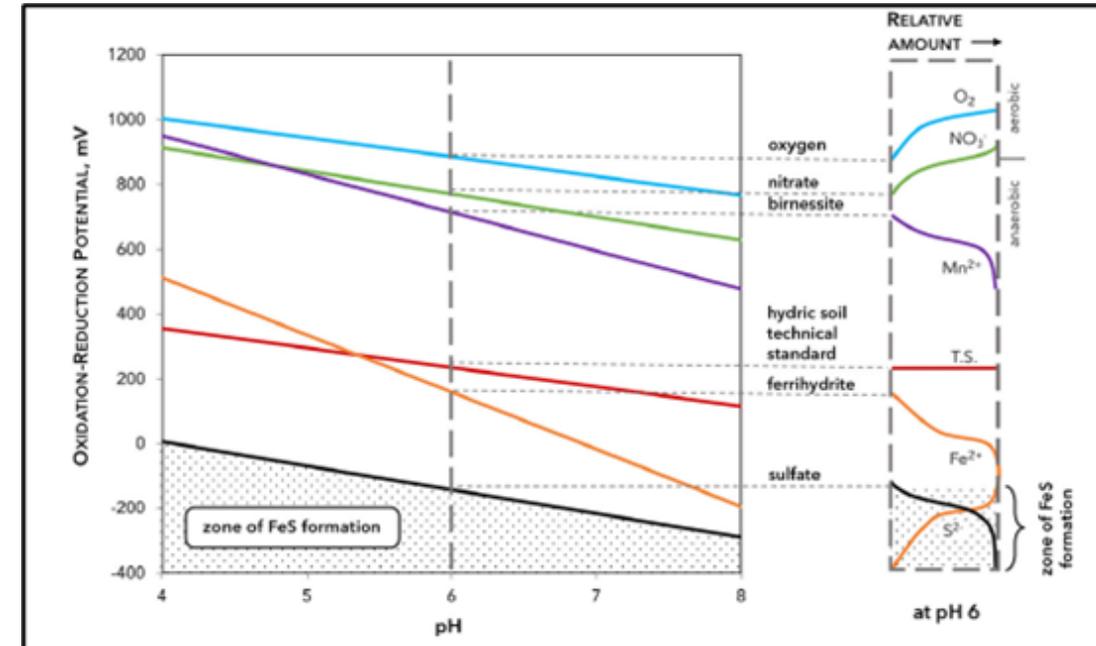


Field Techniques

1. Soil morphology
2. Induce oxidation – color change
3. Add HCL – generate H_2S gas
4. Supplemental information

α α dipyridyl dye

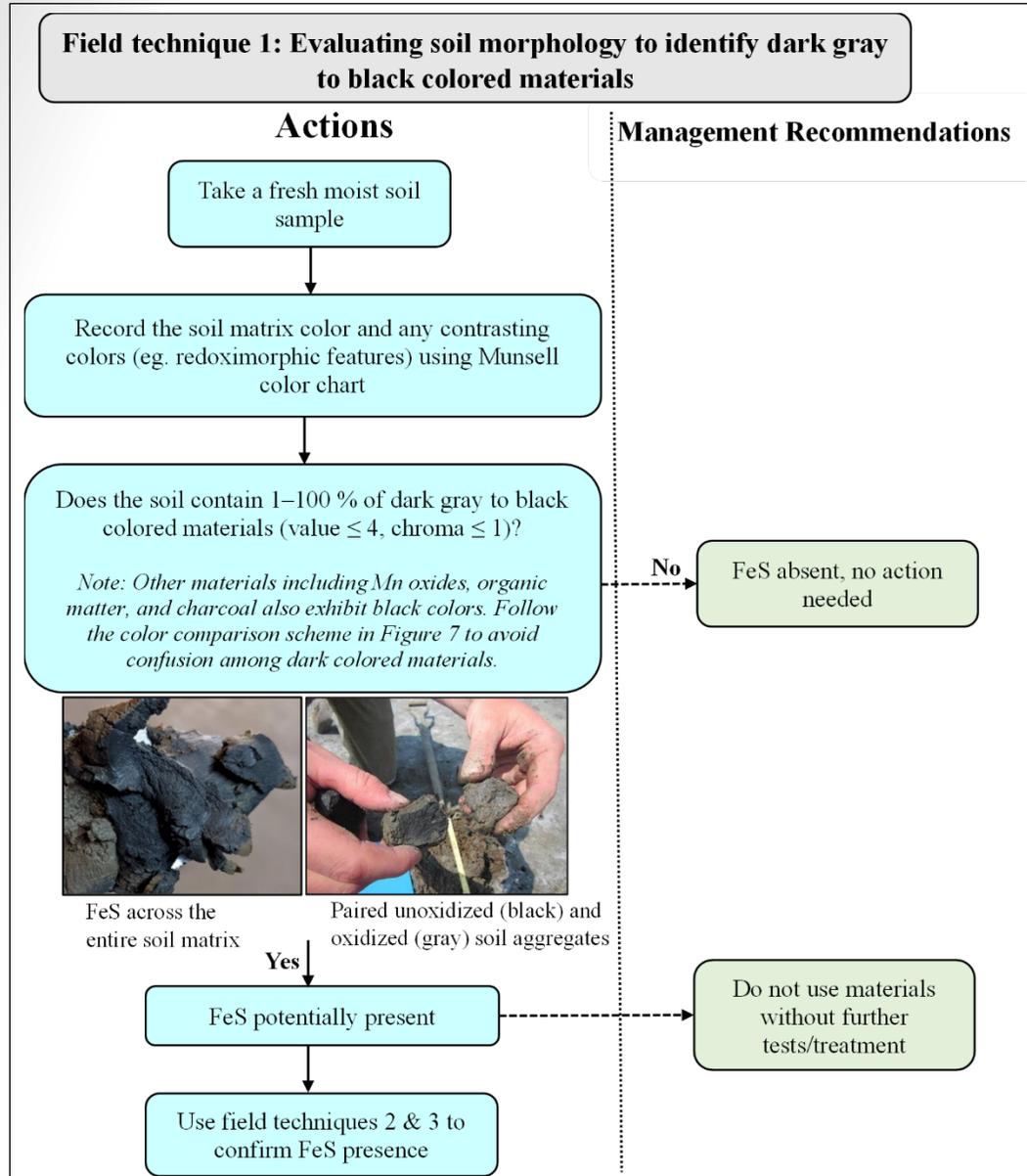
Indicator of Reduction In Soil devices



Duball et al. 2020



Field Technique 1: Evaluating Soil Morphology



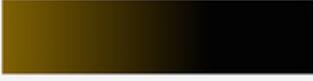
Duball et al 2020



FIELD TECHNIQUE 1: EVALUATING SOIL MORPHOLOGY

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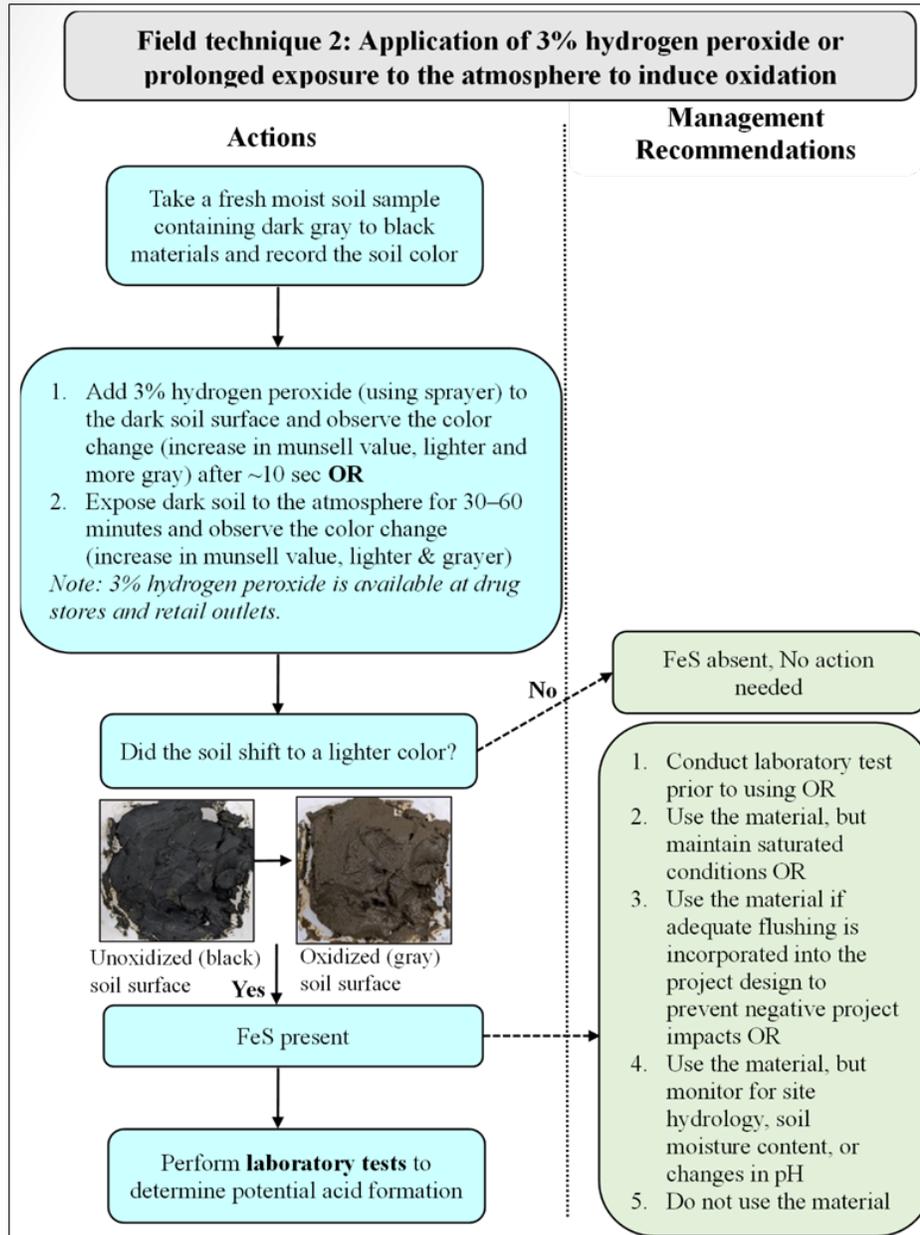
	Appearance and morphology	Reaction to 3% H ₂ O ₂	Reaction to 1 M HCl
FeS 	dark gray to black; coatings, soft masses, pore linings	immediate color change, increase in value	production of H ₂ S, rotten egg odor
Mn oxides 	purple to black; coatings, soft masses, pore linings	effervescence, no color change	no observable change
Organic matter 	brown to black; stains, organic bodies, & coatings with slippery or greasy feel	no immediate change	no observable change
Charcoal 	black; stains, streaks, brittle	no immediate change	no observable change

Duball et al. 2020

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Field Technique 2: Induce Oxidation





Field Technique 3: Application of HCl

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Field technique 3: Application of 1 M hydrochloric acid to induce the evolution of hydrogen sulfide gas

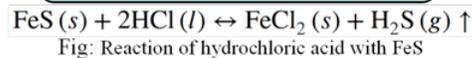
Actions

Take a fresh moist soil sample containing dark gray to black materials

1. Place a golf ball size soil in a sealable container (eg. zip lock bag, bottle or jar with tight fitting lid, etc.)
2. Add 3–5 drops of 1 M Hydrochloric acid to the dark soil surface and seal the container
3. Observe the odor after ~ 1 min

Note: Hydrochloric acid is available in a laboratory supply stores. Caution should be used during acid handling, despite 1 M hydrochloric acid is not considered as concentrated acid it will damage clothing, skin, and eyes.

Was the rotten egg odor (hydrogen sulfide gas) observed?



Yes

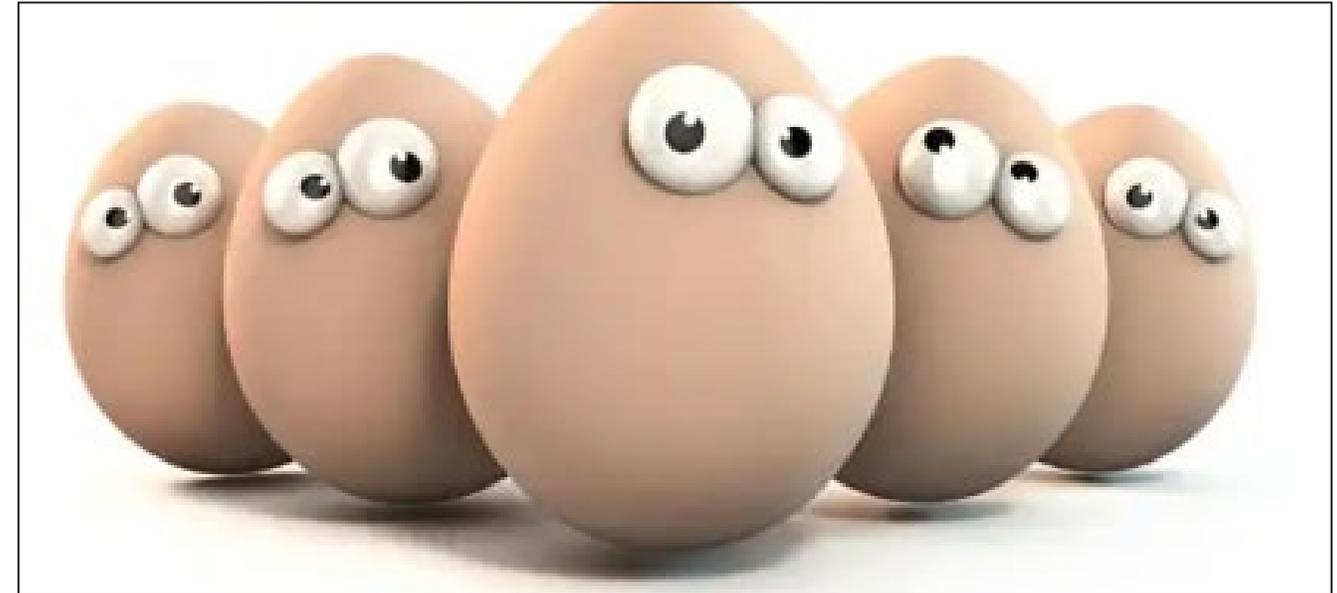
FeS present

Perform **laboratory tests** to determine acid formation potential

Management Recommendations

FeS absent, no action needed

1. Conduct laboratory test prior to using the material OR
2. Use the material, but maintain saturated conditions OR
3. Use the material if adequate flushing is incorporated into the project design to prevent negative project impacts OR
4. Use the material, but monitor for site hydrology, soil moisture content, or changes in pH OR
5. Do not use the material



‘The vessels used should be properly disposed of since they can impart a rotten-egg odor to vehicles, backpacks, coat pockets, or other items if left unattended’.

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Field Technique 4: Gather Supplemental Information: α α dipyridyl dye and IRIS devices





Laboratory Techniques



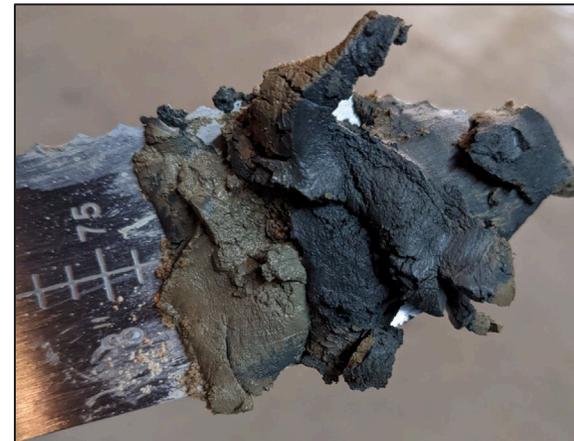
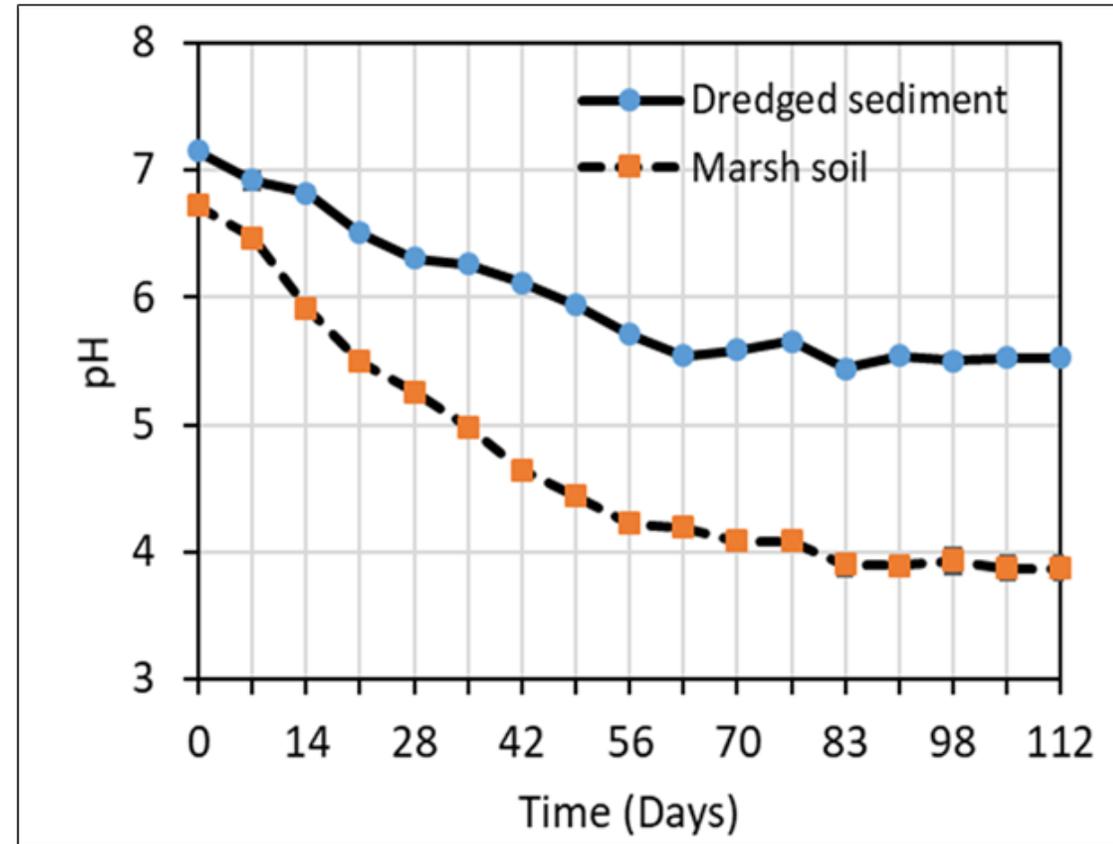
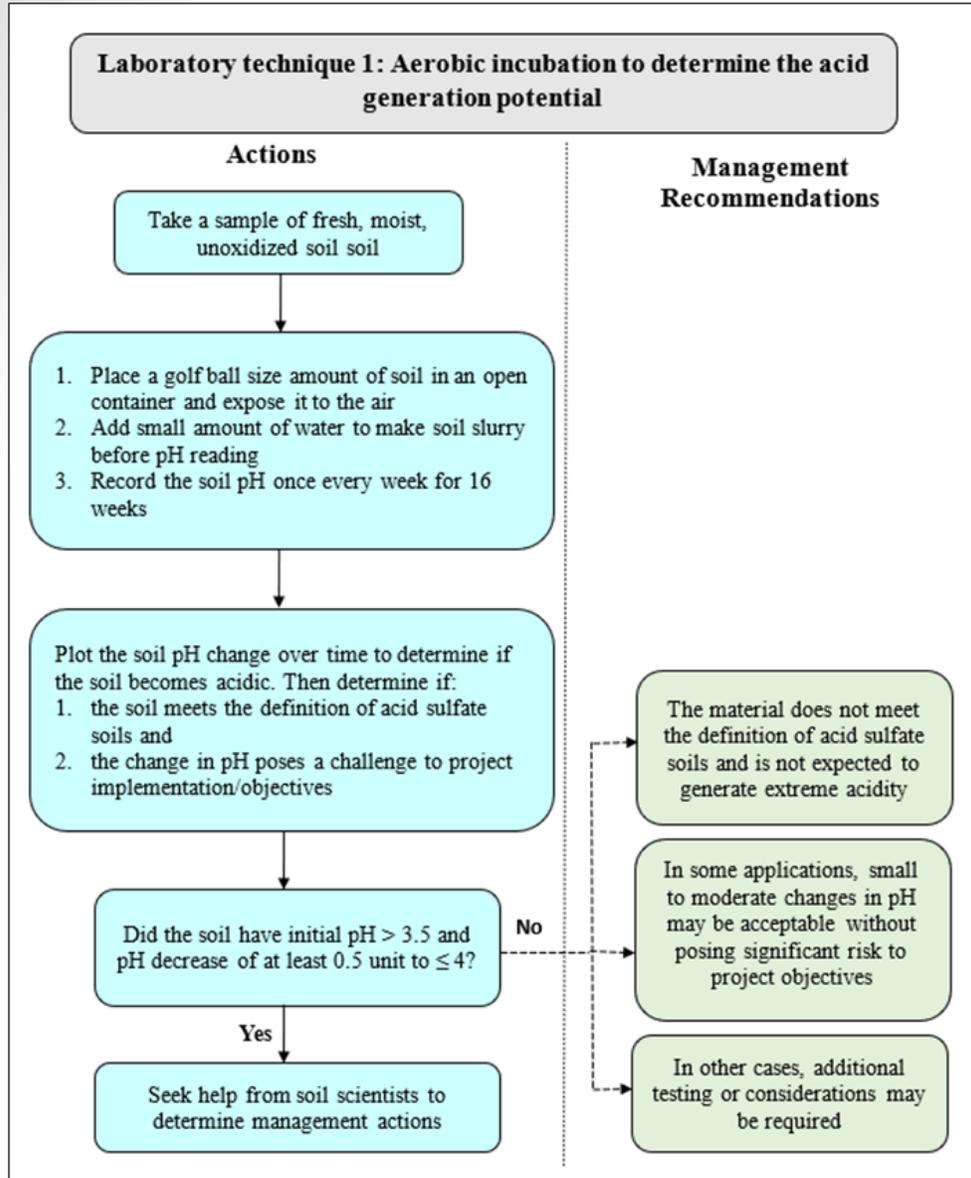
1. Aerobic incubation
2. Acid base accounting
3. Acid Volatile Sulfide (AVS) and Chromium Reducible Sulfide (CRS) Testing





Aerobic incubation

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Aerobic incubation – context matters!



Table 1. Optimum pH requirement for growth of some common wetland plants (USDA-NRCS 2024).

Common Wetland Plants	Wetland Type	Optimal pH Range for Growth
<i>Spartina alterniflora</i> (Smooth cordgrass)	Salt and brackish marshes	5.4–7.0
<i>Spartina patens</i> (Saltmeadow cordgrass)	Fresh to saline marshes	5.5–7.5
<i>Juncus roemerianus</i> (Black needlerush)	Brackish marshes	4.0–7.0
<i>Juncus effusus</i> (Common rush)	Fresh to brackish marshes	5.5–8.8
<i>Pontederia cordata</i> (Pickerelweed)	Fresh marshes	4.9–8.7
<i>Sagittaria latifolia</i> (Duck potato)	Fresh to lightly brackish marshes and swamps	4.7–8.9
<i>Distichlis spicata</i> (Salt grass)	Salt marshes	6.4–10.0
<i>Sagittaria lancifolia</i> (Bulltongue arrowhead)	Fresh marshes	6.0–7.2
<i>Typha latifolia</i> (Broadleaf cattail)	Fresh marshes	5.5–8.7



Table 2. Soil pH threshold or range inducing stress or mortality in dominant wetland plant species. Note that the soil pH effect on plant stress or mortality depends on environmental conditions.

Dominant Plant Species	Soil pH Threshold or Range Inducing Stress or Mortality	Location	Notes	Citation
<i>Spartina alterniflora</i>	<4.0 and >8.0	North Carolina, US	Greenhouse experiment	Linthurst and Blum 1981
<i>Spartina patens</i>	<3.7 and >8.8	Mississippi, US	–	Martin and Sparks 2019
<i>Juncus roemerianus</i>	<4.0 and >7.2	Louisiana, Mississippi, North Carolina, US	–	Martin and Sparks 2019; Stalter and Lonard 2023
<i>Juncus effusus</i>	<4.0 and >8.8	United States	–	Martin and Sparks 2019; USDA-NRCS 2024
<i>Pontederia cordata</i>	<4.0	Nanjing, China	Greenhouse experiment	Li et al. 2023
<i>Typha latifolia</i>	≤3.5	Lake Barband, Denmark	Growth chamber experiment	Dyhr-Jensen and Brix 1996

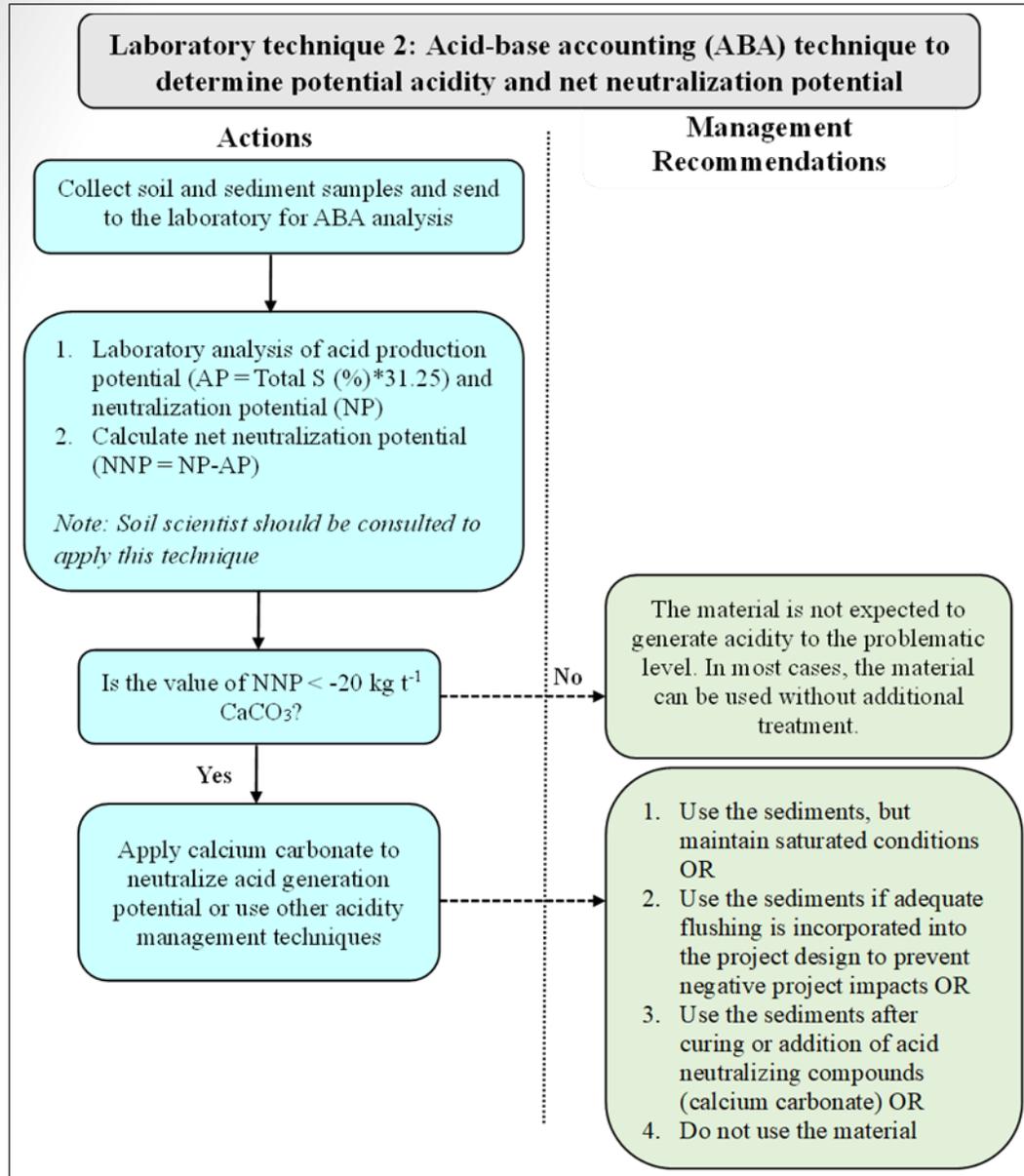




Laboratory Technique 2: Acid-Base Accounting



Technique to Determine Potential Acidity and Net Neutralization Potential



Field tests positive for:

Morphology: Black color observed

Application of 3% hydrogen peroxide: Color changes from black to light gray observed

Application of 1 M hydrochloric acid: Hydrogen sulfide gas observed

Acid-base accounting:

Total sulfur (S) (determined at the laboratory) = 0.35%

Potential acidity (PA) = Total S (%) \times 31.25

PA = 0.35 \times 31.25 = 10.94

NP (calculated from titration) = 9.7

NNP = NP - PA

NNP = 9.7 - 9.94 = $-0.24 \text{ kg t}^{-1} \text{ CaCO}_3$

The NNP value ($-0.24 \text{ kg t}^{-1} \text{ CaCO}_3$) indicates that this dredged sediment is rich in FeS and FeS₂ minerals, yet poses little risk of producing excessive acidity so neutralization (e.g., lime addition) is not essential. During aerobic incubation (Laboratory technique 1) the pH of these dredged materials decreased from 7.1 to 5.5 (see Figure 14). This drop of pH by 1.6 units is not a major concern for plant growth in this case, because the pH after acidification (5.5) is within the growth/tolerance range of most wetland plants (see Table 1). However, if the initial pH was 5.0, a decrease of 1.6 units to 3.4 due to oxidation of iron sulfide compounds would be problematic and may require management interventions. Therefore, both the initial pH of the soil and sediment and pH drop due to acidification should be considered to determine if problematic levels of soil acidification due to oxidation of iron sulfide compounds is likely to occur.

Laboratory Technique 3: AVS and CRS



Laboratory technique 3: Acid volatile sulfide (AVS) and chromium reducible sulfide (CRS) testing to determine potential acidity

Actions

AVS and CRS

To determine FeS and FeS₂ concentration

- Collect soil samples, seal in zip lock bags or containers and send to the laboratory immediately
- Whenever possible keep the sample bags in a cooler and cover with ice to keep them cold

Note: Soil scientist should be consulted for this technique to apply

Is AVS and CRS greater than the threshold to generate acidity?

No

The material is not expected to generate excessive acidity. In most cases, the material can be used without additional treatment.

Yes

Manage potential acidity

1. Use the sediments, but maintain saturated conditions OR
2. Use the sediments if adequate flushing is incorporated into the project design to prevent negative project impacts OR
3. Use the sediments after curing or addition of acid neutralizing compounds (calcium carbonate) OR
4. Do not use the material

Management Recommendations

Testing to Determine Iron Monosulfide (FeS) and Pyrite (FeS₂) Concentrations

Sample 1: Fine-grained dredged sediments confirmed for the presence of FeS using the field techniques describe in Section 4. The pH of this sediment decreased from 7.1 to 5.5 during 16 weeks of aerobic incubation (see Figure 14). The AVS of this sample was 28.5 mg kg⁻¹ dry soil.

Sample 2: Marsh soil confirmed for the presence of FeS using the field techniques described in Section 4. During 16 weeks of aerobic incubation at the laboratory, pH decreased from 6.8 to 3.9 (see Figure 14). The AVS of this sample was 99.5 mg kg⁻¹ dry soil.



Management/Remediation Considerations



Approach: (1) avoid or minimize oxidation of FeS and FeS₂ minerals, (2) neutralize acidity, and (3) mitigate potential impacts of acid formation (step-wise regression)

Prescreening of Potential Dredged Sediment Sources and Restoration Project Areas
NRCS soil maps – sulfhemists

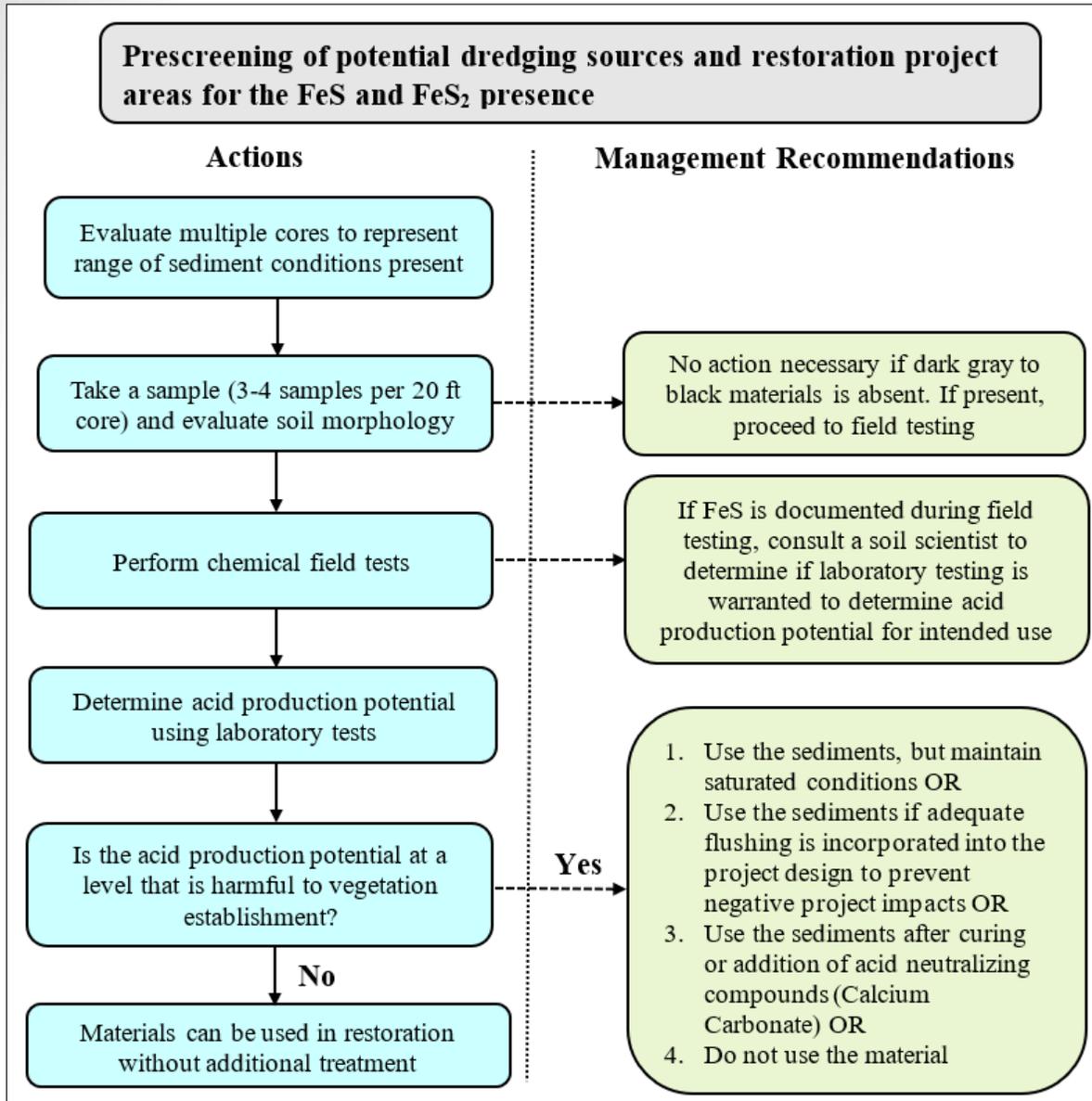
Screening and Curation of Dredged Sediments Before Field Application (e.g., Poplar Island)

Addition of Soil Amendments – during or after application

Risk and cost evaluation

Management of Iron Sulfide Compounds in Restored Wetlands

Prescreening and curation



Studies in Poplar Island, Maryland, have shown that the proper dewatering and curation for 1–2 years before marsh application has been shown to decrease sulfide levels in fine-grained dredged sediments (Cornwell et al. 2020).



Addition of Soil Amendments



The total amount of sediment should be calculated based on the bulk density and volume of the sediment.

The lime requirement = NNP = -30 kg CaCO_3 per metric ton dry sediment.

Restoration area = $4,046 \text{ m}^2$ (1 acre)

Sediment depth = 0.25 m

Bulk density = 1.3 g cm^{-3} ($1,300 \text{ kg m}^{-3}$)

Volume of total sediment = Area \times Depth = $4,046 \times 0.25 = 1,011 \text{ m}^3$

Amount of sediment = Volume \times Bulk density = $1,011 \times 1,300 = 283,280$ metric ton

Quantity of lime required = Application rate \times Amount of sediment
= $30 \times 1,314 = 39$ ton

Average price of lime = \$170 per metric ton (IndexBox 2022)

Cost of lime per acre = $\$170 \times 39 = \$6,630$

Transportation and application cost = \$3,000 (This is an example cost and actual cost depends on various factors)

Total estimated cost of liming per acre = \$9,630

This is the estimated liming cost (\$9,630) per acre of wetlands if the potential acid sulfate soils with acid-generating potential of $-30 \text{ kg t}^{-1} \text{ CaCO}_3$ (i.e., NNP) are deposited at the thickness of 0.25 m . This cost of lime application varies depending on the acid-generating potential of the materials used, the thickness of the materials placed, the market price of the lime, the location of the restoration sites for transportation, and the lime application techniques.

*Must address both active and potential acidity

Approaches:

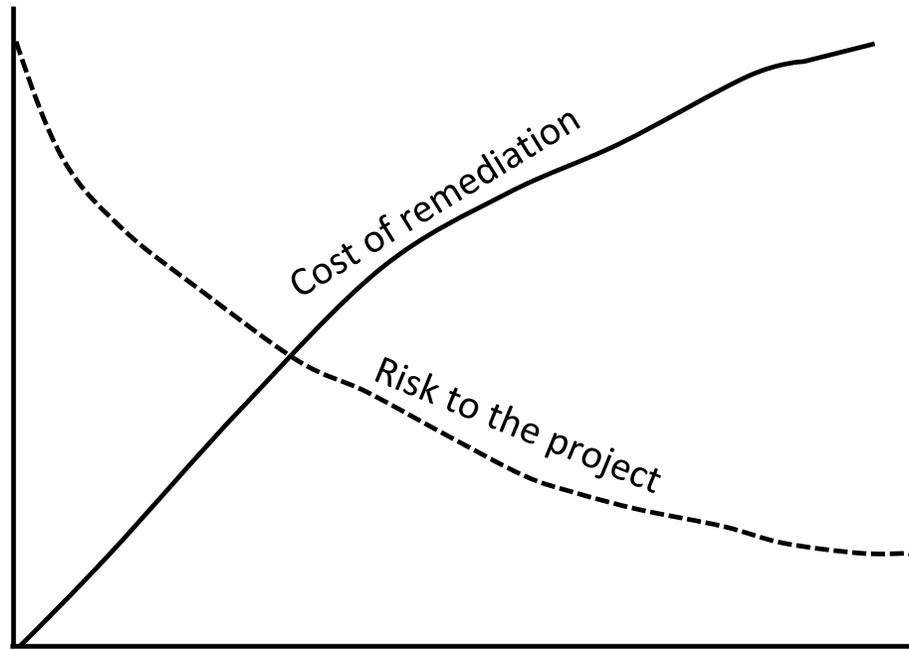
- pumping a slurry of lime along with the dredged sediments into the marsh platform,
- bulk blending of lime with the dredged sediments,
- layered liming with the layers of dredged sediments, or
- mixing lime with dredged sediments.



Risk-cost register and monitoring



Cost of remediation/Risk to the project



Time

FeS and FeS₂ management recommendations in the restored wetlands

Collect multiple soil cores from dredged sediment sources and restoration areas

Evaluate soil samples for the presence of FeS materials using field techniques 1, 2, & 3

If FeS identified

Determine acid production potential using laboratory tests

1. Maintain saturated conditions via continuous flooding or tidal connections
2. Apply lime if potential acidity is high and the wetlands are subject to oxygen
3. Monitor changes in soil pH and site hydrology regularly

If FeS not identified

Evaluate conditions of FeS formation using IRIS devices and alpha-alpha dipyridyl dye techniques

1. If conditions of FeS formation is absent, no action necessary
2. If conditions for FeS formation identified, maintain saturated soil conditions
3. Monitor changes in soil pH and site hydrology regularly

Acknowledgements

Connect for questions and discussion: Scan for pubs →

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