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Evaluation of Iron Sulfide Soil Formation Following Coastal Marsh Restoration – Observations from Three Case Studies

Jacob F. Berkowitz and Christine M. VanZomeren

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Evaluation of Iron Sulfide Soil Formation Following Coastal Marsh Restoration – Observations from Three Case Studies

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Abstract

Wetland restoration activities utilizing sediments, including dredged material, may induce formation of solid phase iron sulfide (FeS) materials. Under certain conditions subsequent oxidation of FeS materials can negatively impact soil pH, posing a risk to restoration success. As a result, procedures have been developed to document the presence of FeS using both field and laboratory techniques. This technical report evaluated conditions at three restoration sites, identifying FeS materials at a subset of sample locations. Guidance for evaluating FeS materials in a restoration context and associated management strategies are also discussed.

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Preface

Project funding was provided by the Dredging Operations Technical Support (DOTS) Program, the Ecosystem Management Restoration Research Program (EMRRP), and the U. S. Army Corps of Engineers (USACE) Philadelphia and New England Districts under 3121-18/XX-2460 “Restoring and Sustaining Ecological Function in Coastal Marshes Affected by Sea Level Rise.” The Technical Director was Dr. Al Cofrancesco.

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Mr. Steven Currie, Ms. Monica Chasten, Mr. Bobby McComas, Mr. Larry Oliver, and Ms. Genevieve Rybicki assisted with field data collection. Ms. Nicole Fresard aided in the collection of laboratory data. Dr. Jeff King and Dr. Damarys Acevedo-Mackey provided comments a draft version of this report.

COL Teresa A. Schlosser was Commander of ERDC, and Dr. David W. Pittman was the Director.

Unit Conversion Factors

Multiply	By	To Obtain
acres	4,046.873	square meters
acre-feet	1,233.5	cubic meters
cubic feet	0.02831685	cubic meters
cubic inches	1.6387064 E-05	cubic meters
cubic yards	0.7645549	cubic meters
feet	0.3048	meters
hectares	1.0 E+04	square meters
yards	0.9144	meters

Acronyms and Abbreviations

Acronym	Meaning
AVS	Acid Volatile Sulfides
cm	Centimeters
DI	Deionized
DoD	Department of Defense
DOTS	Dredging Operations Technical Support
EL	Environmental Laboratory
EMRRP	Ecosystem Management Restoration Research Program
ERDC	Engineer Research and Development Center
Fe ²⁺	Ferrous iron
FeS	Solid phase iron sulfide
IRIS	Indicator of Reduction In Soils
MHa	Million hectare
NRCS	Natural Resources Conservation Service
S ⁻	Sulfur sulfides
TR	Technical Report
USACE	U.S. Army Corps of Engineers
USDA	U.S. Department of Agriculture
USFWS	U.S. Fish and Wildlife Service

1 Introduction

1.1 Background

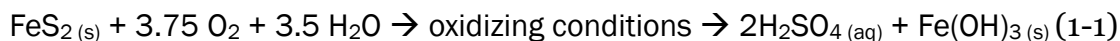
The U.S. Army Corps of Engineers (USACE) conducts a variety of ecosystem restoration activities, including the enhancement of wetlands (Berkowitz and White 2013; Berkowitz et al. 2017). Recent interest has focused on restoring coastal marshes in order to provide habitat, improve resiliency, and maximize ecological services that benefit society (Berkowitz et al. 2016). Coastal marsh restoration projects often include removing invasive species, reestablishing natural patterns of hydrology and sedimentation, and improving habitat for species of concern. The projects examined in this technical report (TR) include activities designed to (1) remove previously placed fill materials to reestablish historic marsh elevations, and (2) convey sediments onto degrading marshes to increase sediment retention, stabilize the marsh platform, and increase resiliency by maintaining marsh elevation with respect to anticipated relative sea level rise. While solid phase iron sulfide (FeS) soils such as acid volatile sulfides and pyrite are common in salt marshes (Tobias and Neubauer 2009), in some instances, the disturbance of coastal marine sediments may lead to enhanced development and/or activation of acid forming soil materials commonly referred to as acid sulfate soils.

Soils containing FeS occur naturally in many coastal environments throughout the United States and the world covering an estimated 12–15 million hectare (MHa) of land area (Fanning 2002; Andriessse 2001). These soils, first reported in the literature as early as the 18th century and historically referred to as cat clay soils or poison earth soils, have the potential to negatively impact the growth of agricultural and native plant communities when coastal areas undergo management activities that alter iron and sulfur cycling pathways (e.g., drainage, movement of dredged materials; Rabenhorst and Fanning 2002). As a result, the presence of FeS can lead to substantial land use limitations via the formation of acidic conditions (i.e., acid sulfate soils). As the name suggests, acid sulfate soils exhibit the capacity to produce sulfuric acid under certain circumstances. Soil Taxonomy defines acid sulfate soils as follows (USDA-NRCS 1999):

Sulfidic materials contain oxidizable sulfur compounds.
They are mineral or organic soil materials that have a pH

value of more than 3.5 and that, if incubated as a layer 1 cm thick under moist aerobic conditions (field capacity) at room temperature, show a drop in pH of 0.5 or more units to a pH value of 4.0 or less (1:1 by weight in water or in a minimum of water to permit measurement) within 8 weeks.

Notably, FeS materials form under saturated and anaerobic conditions common in coastal wetlands and submerged environments, where chemically reduced forms of sulfur (sulfides; S⁻) react with soluble cations (mostly ferrous iron; Fe²⁺) to form insoluble pyritic precipitates dominated by FeS and FeS₂ (FeS herein) (Rabenhorst et al. 1990). These FeS_x compounds remain stable under saturated, anaerobic environments and as a result are labeled *potential* acid sulfate soils. If FeS materials are exposed to aerobic conditions (i.e., drained or excavated) acid production may occur and the materials are labeled *active* acid sulfate materials due the production of sulfuric acid (Rabenhorst et al. 2002).



The formation of sulfuric acid (a strong acid) results in a rapid decrease in soil pH if sufficient buffering capacity (e.g., CaCO₃) is not present. The subsequent hydrolysis of ferric (Fe³⁺) species under aerobic conditions may produce additional acidity. The oxidization of FeS often drives soil pH values below 3.5 or 4.0, severely limiting vegetative establishment and growth. In some cases soil pH values can decrease below 2.0. The presence and drainage of acids can have substantial negative impacts in the surrounding terrestrial and aquatic environment, with potential impacts to benthic organisms, fish, and other ecological components (Melville and White 2002). Acidic conditions were associated with a drought-induced marsh dieback in Louisiana and in simulated drought conditions utilizing marsh sediments in laboratory experiments (McKee et al. 2004; Palomo et al. 2013). This TR examines three case studies in which restoration activities may have contributed to the formation of FeS yielding materials.

1.2 Objectives

Several recent salt marsh restoration projects located in the New England and mid-Atlantic regions reported the potential formation of FeS materials following restoration activities. This study reports the results of incubation experiments and field data collection efforts designed to identify the presence of FeS and potential acid forming materials utilizing standard

field and laboratory protocols. Guidance on avoidance and remediation strategies are also discussed.

1.3 Study locations

Potential development of FeS soil materials were reported to the Engineer Research and Development Center (ERDC) staff in 2016–2017 at restoration sites in Narrow River, Rhode Island, Avalon, New Jersey, and Broad Meadows, Massachusetts. Although each of these study locations are unique, they each share the following traits: (1) each location underwent sediment placement or removal to reach a desirable elevation for establishment or enhancement of coastal salt marsh habitat, (2) the material placed on site or removed consisted of dredged materials or materials from offsite locations, and (3) evidence of potential FeS formation was reported based upon the lack of vegetative establishment, poor vegetative growth, or vegetative die-off. The following provides more specific data regarding each study location.

1.3.1 Narrow River, Rhode Island

The Narrow River restoration site located on the John H. Chafee National Wildlife Refuge is owned and operated by the U.S. Fish and Wildlife Service (USFWS). The USFWS sought to increase marsh elevation in order to improve resiliency in the face of storm surge and relative sea level rise. Prior to initiation of the restoration project, a pilot project was implemented to evaluate the impact of sediment application on marsh vegetation; a local upland sand quarry provided the source material for the pilot project. A layer of sand approximately 10–15 centimeters (cm) thick was placed in two test plots. A year after placement, ERDC was requested to investigate the test plots due to observed dieback of vegetation and the presence of dark red and black soil materials developing on the marsh surface (Figure 1). A navigation channel adjacent to the study location was selected as source material for the full scale restoration effort and sediment from the channel was also evaluated.

Figure 1. The Narrow River, Rhode Island study site.



1.3.2 Avalon, New Jersey

The Avalon restoration site is owned by the state of New Jersey Department of Environmental Protection Division of Fish and Wildlife who, with USACE, including the ERDC and a number of interagency and non-profit partners, sought to increase marsh elevation in order to promote vegetation establishment in recently degraded open water areas and supplement elevation in low-lying vegetated areas. The project utilized dredged sediments from a federal navigation channel funded through post Hurricane Sandy recovery funds. Sediment placement occurred during the winter of 2015–2016. After a year and half, ERDC was requested to investigate the location due to observed dieback of vegetation and the presence of dark red and black soil materials developing on the marsh surface (Figure 2).

Figure 2. The Avalon, New Jersey study site.



1.3.3 Broad Meadows, Massachusetts

Owned by the local municipality, the Broad Meadows restoration objective was to reestablish a coastal marsh community in an area that had been utilized as a dredged material disposal area during 1938 and 1956 as part of the Town River Federal Navigation Project. Unlike the other two study sites, the dredged material at Broad Meadows was mounded to supratidal elevations minimizing tidal flushing and maximizing aerobic conditions. In 2011, approximately 35 acres were restored to elevations suitable for the development of low and high marsh vegetation. Dredged material removed from the site was deposited in adjacent areas for the creation of coastal grassland habitat. Following several years of efforts to establish vegetation and preliminary investigation of soil conditions, ERDC staff visited the study location in 2017 to further evaluate site conditions, including the potential presence of FeS (Figure 3).

Figure 3. The Broad Meadow, Massachusetts study site.



1.4 Approach

At each study location multiple study areas were evaluated for the presence of FeS using established field techniques. A number of laboratory samples were also collected for further investigation at the ERDC facilities utilizing the U.S. Department of Agriculture (USDA)-Natural Resources Conservation Service (NRCS) incubation method outlined above.

1.4.1 Field evaluations

Sample sites were selected at each study location, including areas suspected of containing FeS soils and (where possible) areas lacking FeS

(Figures 4–7). Table 1 provides a description of parameters evaluated to document iron sulfide presence or absence utilizing field techniques. Individual parameters can result in false positives under certain conditions; evaluation of multiple parameters prevents false identification of iron sulfide materials.

Table 1. Field evaluation tools to identify the presence FeS soils.

Parameter	Diagnostic	Example
Soil Descriptions	FeS forms dark black coatings on soil particles and within soil pores	Figure 4
Application of hydrogen peroxide (3%)	FeS materials oxidize instantaneously in the presence of strong oxidizing agents, resulting in removal of dark soil coating and revealing the underlying grey soil matrix color	Figure 5
Application of hydrochloric acid (10%)	FeS materials rapidly liberate hydrogen sulfate gas in the presence of acid, resulting in formation of a strong rotten egg odor	NA
Installation of indicator of reduction in soils (IRIS) tubes (one hour)	When present, FeS will rapidly precipitate on the surface of IRIS tubes, resulting in the formation of a black coating on the IRIS tube surface	Figure 6
α -dipyridyl dye	Diagnostic test for the presence of ferrous iron, a key component in the formation of FeS; verifies that the soil is chemically reduced with respect to iron.	Figure 7

Figure 4. Narrow River (left) soil sample displaying black iron sulfide materials at the contact point between placed upland sands and the underlying marsh soils; Avalon (right) soil sample displaying extensive iron sulfides coating with recently placed dredged materials.



Figure 5. Dark soil coatings (soil on left) from iron sulfide soil materials at Avalon, then oxidized with 3% hydrogen peroxide (soil on right) resulting in removal of dark soil coating and revealing of the underlying grey soil matrix color.



Figure 6. When present, free sulfides precipitate on the surface of Indicator of Reduction in Soils (IRIS) tubes within one hour of installation, resulting in the formation of a black coating (left). Removal of black coating on the IRIS tube by hydrogen peroxide oxidation (right).



Figure 7. Reaction of reduced iron to α -dipyridyl dye, seen as the development of a pink color, in the upland sands placed at Narrow River.



1.4.2 Laboratory evaluations

When possible, filtered soil pore water samples were collected from soil pits for analysis of sulfides and ferrous iron. Additionally, soil samples were collected in each soil horizon within the upper 30 cm (including the dredged material layer where present) for analysis of acid volatile sulfide, total iron, aluminum, and a subset of metals. In the laboratory, a bench-top aerobic incubation study was conducted to document the presence of FeS as described by USDA-NRCS (1999), and to estimate the acid forming potential of collected samples. During the laboratory incubation, soils were placed in open beakers with continuous exposure to atmosphere to ensure aerobic conditions and induce drying over time. Soil pH (minimum amount of deionized (DI) water added to permit measurement) was monitored weekly for a period of 8–16 weeks under aerobic conditions. It should be noted that the aerobic soil incubations are designed to identify potential acid forming conditions and that laboratory results do not reflect in-situ conditions. As a result, the pH values presented herein reflect a worst case scenario, and less extreme changes in pH are anticipated under field real-world conditions, where tidal flushing, buffering capacity, and other factors would decrease the impact of FeS oxidation.

2 Results

Each of the study locations exhibited the presence of FeS materials and *potential* acid sulfate soil conditions within a subset of samples based upon both field and laboratory data. The following sections outline findings from each study locations.

2.1 Narrow River

Field results documented the presence of FeS materials at four of the five locations examined. Based on visual observations, black FeS coated portions of the soil profile within areas receiving sediment applications (Figure 4). Additionally, FeS was documented using hydrogen peroxide (Figure 5), hydrochloric acid, Indicator of Reduction in Soils (IRIS) tubes (Figure 6), and α -dipyridyl dye (Figure 7). A positive reaction with α -dipyridyl dye documented the presence of ferrous iron. Laboratory testing of soil pore water samples confirmed the presence of free sulfides in solution (0.1–13 mg/L). As a result, the constituents to form FeS were present within the pore water of the native marsh reference areas and within the pilot study placement areas. Additionally, acid volatile sulfides (AVS) were detected within the dredged material source (32 mg/kg), the black FeS soil layer (10–126 mg/kg) and the native marsh soil (4.5 mg/kg). The upland sand material used in the pilot study contained very limited (<1.0 mg/kg) AVS.

Laboratory incubation further verified the presence of FeS, with pH decreases occurring in a subset of both the placed sand material and the underlying native marsh soil (Figure 8). Notably, FeS materials were also observed in native marsh soils (10–20 cm below the surface) in reference areas that received no sediment additions. This demonstrates that FeS naturally occurs in the marsh; however, the extent of FeS was more pronounced in sediment placement locations. The source materials for sediment placement, upland sand used in the pilot study and dredged materials from adjacent navigation channel, displayed no acid forming capacity prior to placement within the marsh (Figure 9). As a result, the FeS observed with the soil test plots formed following placement activities. The rapid formation of FeS within sediment placement areas could negatively affect restoration outcomes with the potential for acid formation under certain scenarios, although more monitoring and research is required to characterize the range of possible effects and the conditions that may induce them.

Figure 8. Incubation results demonstrating the presence of FeS materials within sand material placed on top of native marsh soils (left) and underlying native marsh soils (right) at Narrow River. Note that laboratory incubation results represent a worst case scenario and do not reflect in-situ conditions where tidal flushing, buffering, and other factors influence soil pH.

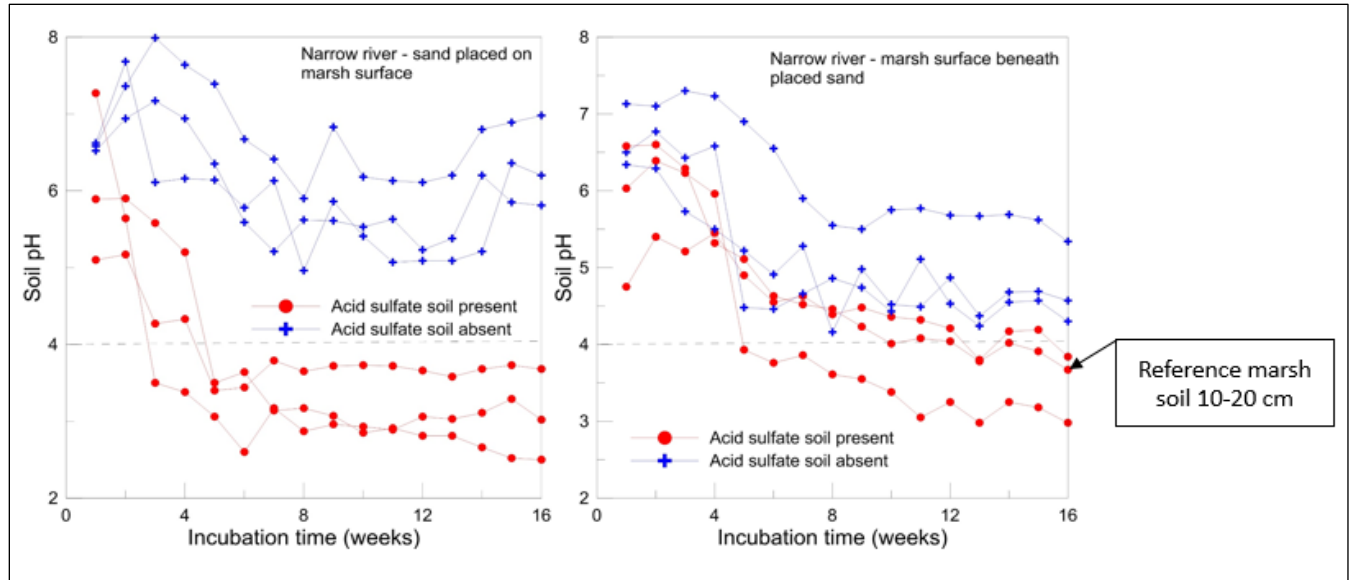
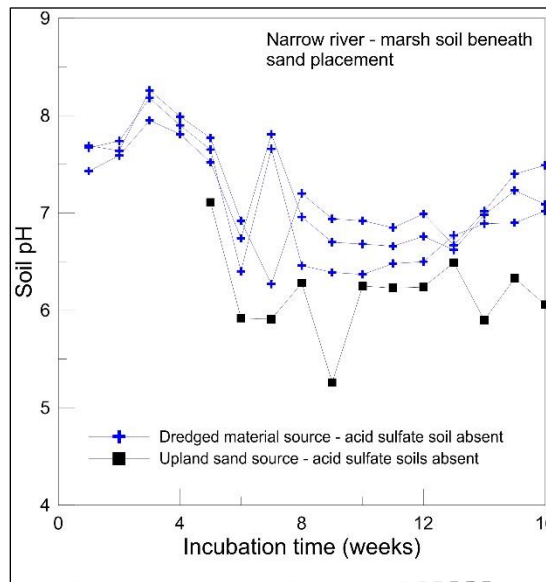


Figure 9. Source materials utilized at Narrow River. Note that in the absence of marsh soil, the source materials displayed no acid forming capacity.



2.2 Avalon

Field results documented the presence of FeS at each of the sample locations examined, including reference areas and areas in which dredged material was placed. Notably, in areas receiving dredged materials the formation of FeS occurred rapidly since the previous sampling event (a

period of approximately one year) resulting in development of a nearly continuous coating of FeS in near surface soils at some sample locations (Figure 4). Additionally, FeS was documented using IRIS tubes, hydrogen peroxide, hydrochloric acid, pore water samples, and α -dipyridyl dye as described in section 1.4.

Laboratory incubation further verified the presence of FeS, with pH decreases occurring in a subset of both the placed dredged material and the underlying native marsh soil (Figure 10). Notably, FeS was also observed in native marsh soils (2–4 cm below the surface) in reference areas that received no sediment additions. This demonstrates that FeS naturally occurs in the marsh. However, the rapid formation of FeS within the placement areas could negatively impact restoration outcomes with the potential for acid formation under certain conditions. For example, plant die off was observed at two locations, both of which yielded potential acid generating capacity capable of decreasing soil pH to ~2.0 (Figure 11). Soil pH was not measured in the field so plant die cannot be attributed to soil acid production; however, this may represent a contributing factor operating in combination with climate (i.e., recent drought), increased salinity following sediment placement, alterations in site hydrology caused by remnant containment structure, rafting of vegetation, and other factors. Additional field research is required to link laboratory studies, which may represent a worst case scenario, with in-situ conditions. Many factors other than soil properties influence marsh restoration trajectories including the presence of invasive species, herbivory, inappropriate hydrologic design or species selection, and adverse environmental conditions after construction. As a result, presence of FeS soils alone, or in combination with other factors, can lead to substantial land use limitations if oxidation occurs, potentially adversely impacting marsh restoration outcomes.

Figure 10. Incubation results demonstrating the presence of FeS within dredged material placed on top of native marsh soils (left) and native marsh soils (right) at Avalon. Note that laboratory incubation results represent a worst case scenario and do not reflect in-situ conditions where tidal flushing, buffering and other factors influence soil pH.

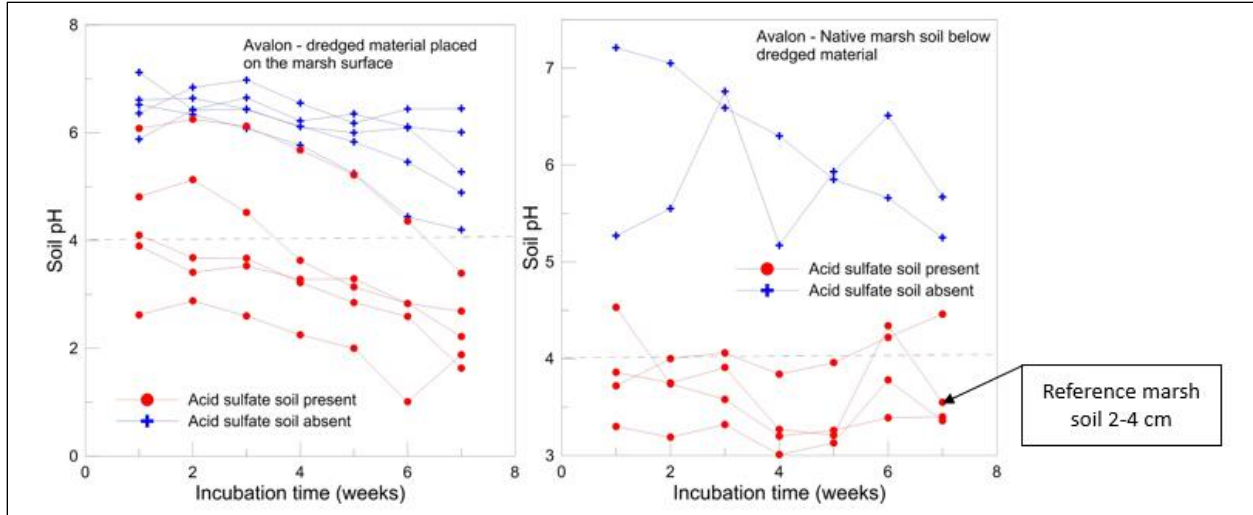
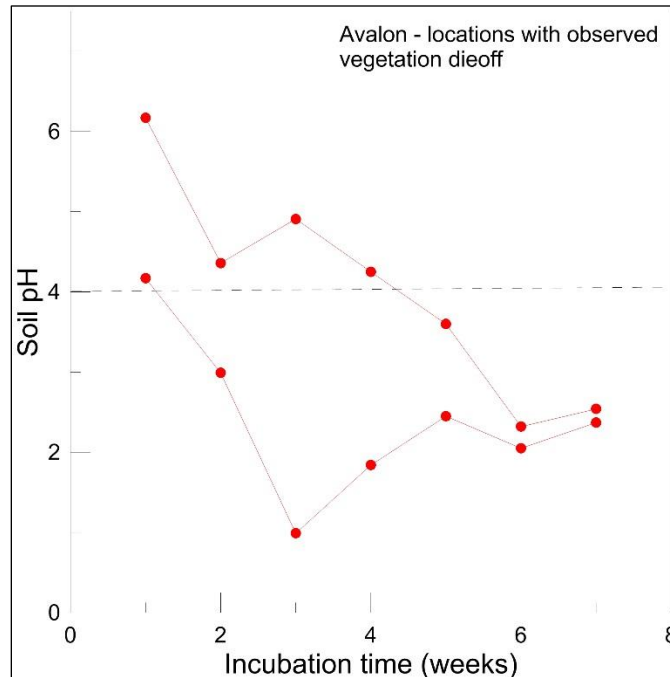


Figure 11. Soil pH decreases in two areas of the Avalon marsh in which vegetative die off was observed. Note that laboratory incubation results represent a worst case scenario and do not reflect in-situ conditions where tidal flushing, buffering and other factors influence soil pH.



2.3 Broad Meadows

Field results documented the presence of FeS at a subset of low marsh, high marsh, and disposal area samples. Black FeS materials coated portions of the soil profile and were documented using the field techniques described above. Laboratory incubation further verified the presence of FeS, with pH decreases occurring in a subset of both high and low marsh soils (Figure 12). Notably, acid sulfate conditions were not observed in reference areas. Acidic soil conditions persisted within unvegetated portions of the dredged material disposal areas adjacent to the marsh, where the soil pH remains <3.8 (Figure 13). Additional monitoring is required to determine how long acidic conditions will persist following the reestablishment of marsh elevations.

Figure 12. Incubation results demonstrating the presence of FeS within low marsh (left) and high marsh (right) soils at Broad Meadows. Note that laboratory incubation results represent a worst case scenario and do not reflect in-situ conditions where tidal flushing, buffering, and other factors influence soil pH.

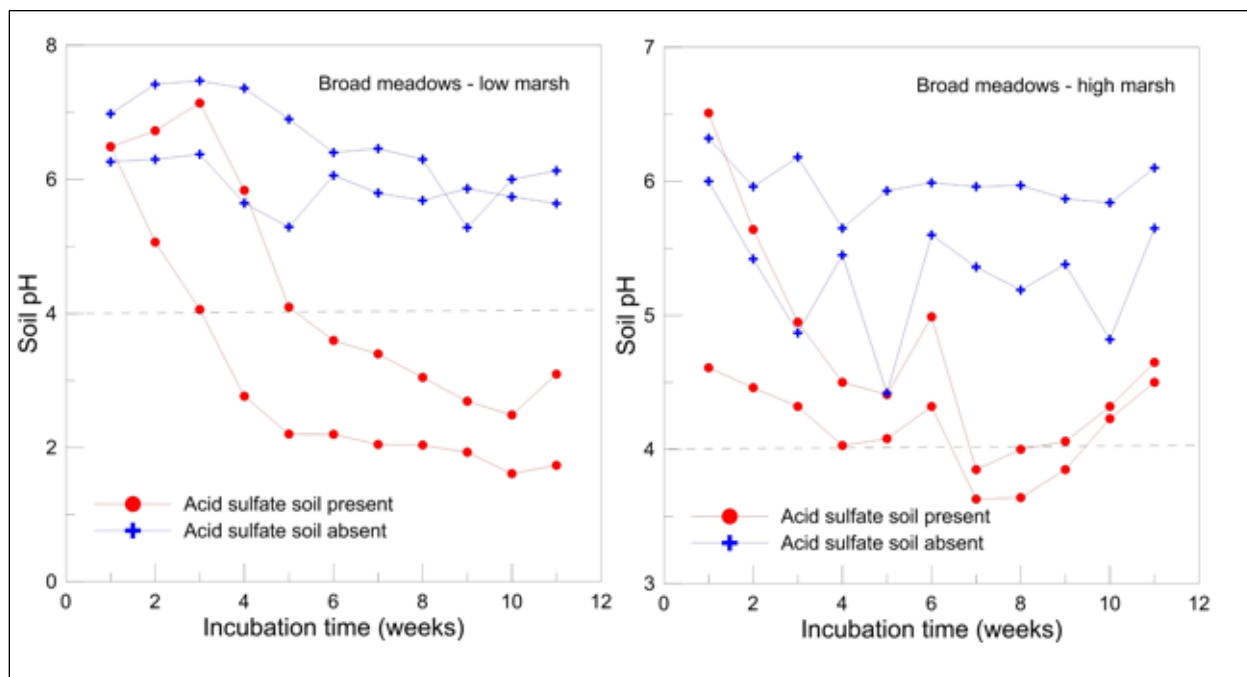
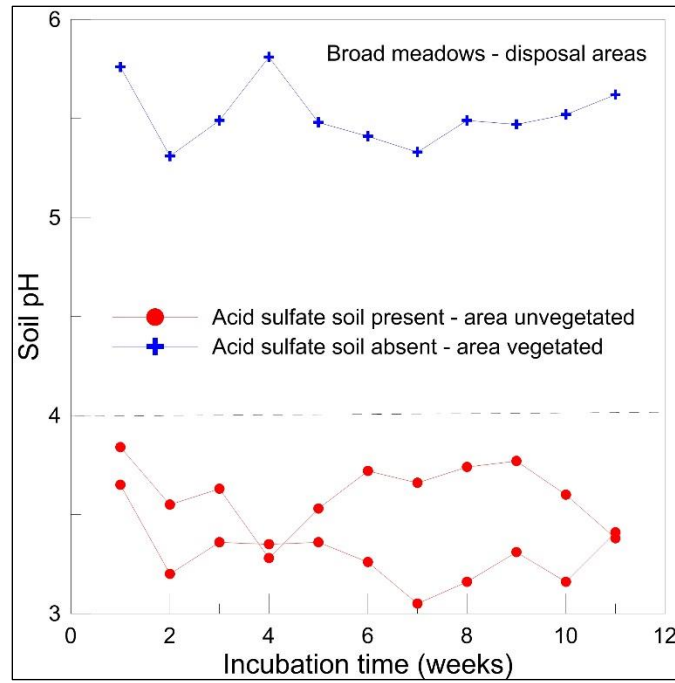


Figure 13. Soil pH conditions remain problematic in unvegetated areas within the dredged material disposal areas at Broad Meadows. Note that laboratory incubation results represent a worst case scenario and do not reflect in-situ conditions where tidal flushing, buffering, and other factors influence soil pH.



3 Discussion

The potential for FeS oxidation and generation of soil acidity following dredged material management is not new. For example, several projects seeking to build land or utilize dredged material for restoration activities in Baltimore and Chesapeake Bay resulted in active soil acidity during the 1980s and 1990s (Rabenhorst and Fanning 2002). The *Engineering and Design Beneficial Use of Dredged Material*, EM 1110-2-5026, (1987) lists the creation of acidic conditions as a potential problem associated with marsh construction (USACE 1987). In those instances, dredged material sources containing FeS were removed from submerged environments and placed at the land surface, where oxidation occurred resulting in soil pH values <2.5, lack of vegetative growth, and potential water quality and fisheries impacts (Demas et al. 2004). Each of the ecosystem restoration study locations examined herein displayed the capacity to produce significant acidity if FeS oxidation were to occur, which may impact restoration success, yet, display distinctive characteristics requiring additional investigation.

The conditions observed at Narrow River and Avalon are unique due to the fact that FeS materials were not observed within the sediment sources (i.e., Narrow River - upland sand; Avalon - navigation channel sediments) prior to placement, but formed *in situ* following sediment placement at the marsh surface. The apparent rapid (e.g., 6–12 month) formation of FeS materials following thin layer sediment deposition is of particular interest, as several similar projects are under development in the region and elsewhere. The first mention of acidic conditions developing in response to sediment placement on marsh substrate was made in passing as early as the 1970s as part of a controlled study on *Spartina alterniflora* smothering (Reimold et al. 1978) but no follow up was conducted to determine if the conditions were a result of the sediment or the marsh substrate. This condition has not been previously documented in detail, requiring additional investigation. As an initial response, a laboratory experiment has been completed to evaluate and document the rapid formation of FeS under simulated dredged material placement scenarios. Incorporating field studies in which soils are exposed to natural patterns of tidal flushing, buffering, and bioturbation is recommended.

The situation at Broad Meadows is also unique, as it involves the removal of dredged materials placed within a coastal wetland marsh prior to 1960.

As a result of the study location history, it is unclear if FeS was present in the dredged material source materials or if they formed in-situ. However, the presence of acidic soil conditions is likely contributing to the limited vegetative establishment within the marsh and in portions of the dredged material disposal area.

Regardless of the origin of FeS, and in order to properly manage the risks associated with acid sulfate soils, the following three management objectives should be considered (adapted from Melville and White 2002):

- Objective 1: Prevent or minimize oxidation of the FeS materials – this will prevent the expression of active acidity and limit any potential damage to plants and organisms. The most practical approach to prevent oxidation is to maintain saturated soil conditions which occur naturally in most intertidal marsh environments.
- Objective 2: Neutralize acidity – if the acidification process is underway, the active acidity and potential acidity can be neutralized via soil amendments and other approaches.
- Objective 3: Mitigate potential impacts of acid formation – Minimizing potential impacts requires determinations of active and potential acidity as well as soil and receiving water buffering capacity. In some instances, capping acidic materials or neutralization of drainage waters may be effective.

The conditions at Narrow River, Avalon, and the low marsh sample locations at Broad Meadows suggest that the soils remains regularly saturated by normal tidal fluctuations, limiting the potential for active acid production at those locations. As a result, site management should focus on Objective 1 and efforts should be made to ensure that FeS materials are not exposed to oxidizing conditions. However, monitoring of soil pH, moisture, water table elevation, oxidation-reduction potentials, and other factors is recommended. Additionally, the rapid development of FeS following sediment placement requires further investigation to avoid potential acid sulfate formation and prevent potential soil pH problems associated with restoration initiatives.

The Broad Meadows high marsh is intermittently inundated by tidal fluctuations, suggesting the potential for aerobic soil conditions capable of inducing active acidity, especially during neap tide periods when tides are lower. On-site monitoring of water table, oxidation-reduction potentials

(using IRIS tubes) and other measurements to evaluate the stability of anaerobic conditions, and FeS in this zone are recommended coupled with future local sea level rise projections which may eventually reduce the time periods over which aerobic soil conditions persist. Based upon those monitoring results, a determination can be made regarding the need for management via Objective 1 or 2 above. The unvegetated areas within the dredged material disposal areas at Broad Meadows currently display pH values <3.8 as a result of active FeS oxidation. Neutralization via soil amendment may be required as described in Objective 2; however, additional analysis will be required to determine the amount of potential or reserved acidity. Notably, liming application rates associated with acid sulfate soils can be high (up to 62–185 tons ha⁻¹ in extreme cases; Rabenhorst and Fanning 2002) and may prove cost prohibitive.

4 Summary

Wetland restoration activities utilizing sediments, including dredged material, may induce formation of FeS materials and in some cases acid sulfate soil conditions. As a result, procedures have been developed to document the presence of FeS using both field and laboratory techniques. This TR evaluated conditions at three restoration sites, identifying FeS materials at a subset of sample locations with potential soil pH decreases <2.0 detected in some instances under worst case scenario laboratory incubation conditions. The rapid development of FeS following sediment applications for restoration activities requires further research to establish formation mechanisms and fate. Additional studies should evaluate the influence of hydrologic regime (e.g., water levels, inundation durations, hydraulic flushing etc.), sediment Fe concentration, in-situ neutralization capacity, the persistence of acidic conditions if oxidation occurs, and other factors under real world conditions. Management options include maintaining saturated soil conditions and neutralization of active and potential acidity. Future work will develop specific guidance regarding FeS within an ecological restoration and dredged material management context.

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