Development of a standard for visual S reduction to identify hydric soils

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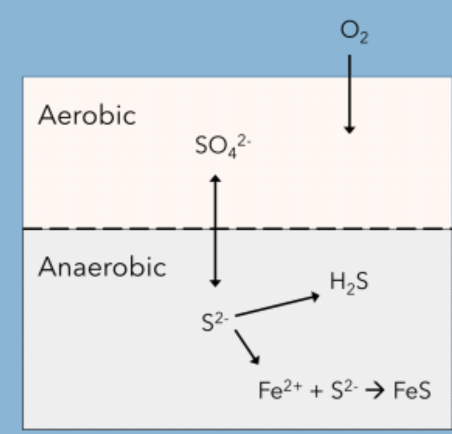


Abstract

Hydric soils present a unique set of problems associated with their identification, including morphological features not reflective of current hydrology and masked redoximorphic features. A novel tool to identify reduced soil environments is Indicator of Reduction in Soil (IRIS) tubes. This concept was developed to demonstrate whether or not Fe is oxidized (colored and solid) or reduced (colorless and soluble) and therefore anaerobic in the soil environment. Another commonly observed phenomenon in soils is the reduction of S to form black monosulfides (FeS) under anaerobic conditions. The objective of this experiment was to document and develop a visual standard for S reduction on PVC surfaces coated in Fe oxide paint in order to simplify the identification of hydric soils in some settings. IRIS panels were installed in soil mesocosms containing varying concentrations of sulfate and saturated for 11 weeks. Throughout the duration of the study, oxidation-reduction potential and pH were measured weekly. When the experiment concluded the IRIS plates were removed and analyzed quantitatively for percent of oxidized iron (Fe^{3+}), percent of reduced iron (Fe^{2+}), and percent of reduced S (FeS). When at least 30% Fe was reduced from the IRIS plates, more than 2% prominent black FeS stains were observed. The strong visual observation of monosulfides is a simple, quick determination of highly reduced conditions. Wetlands are a valuable natural resource that can be challenging to delineate; the incorporation of a visual S reduction standard on IRIS surfaces will be beneficial for timely and accurate identification of hydric soils.

Objectives

- To identify the minimum percentage of black FeS staining indicative of reduction as measured using Eh/pH diagrams and Indicator of Reduction in Soil (IRIS) paint removal.
- To propose a new technical standard to the National Technical Committee for Hydric Soils (NTCHS) concerning the presence of iron mono-sulfide staining on IRIS tubes.

Hypotheses

1. Increasing amounts of added S will lead to higher amounts of FeS staining on IRIS panels.
2. Higher amounts of FeS staining will correspond to more reducing conditions as measured using Pt-tipped electrodes and pH.
3. A small percentage of FeS staining will qualify a soil as hydric.

Methodology

Soil preparation and S addition

- Silty clay loam-textured soil was collected from the A horizon of an upland soil (Cropley series). The soil was sieved to remove coarse fragments greater than 2 mm.
- Bulk soil (14 kg) and gypsum ($CaSO_4$) powder at 0, 1, 2.5, and 5% concentrations corresponding to the treatment group were mixed while dry.

Indicator of Reduction in Soil (IRIS) panel development

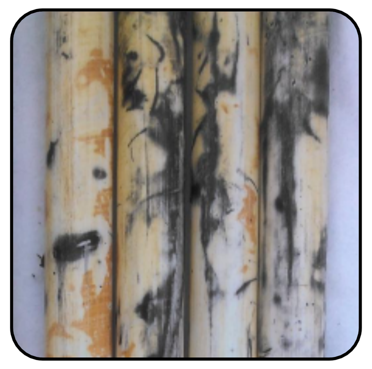
- Opaque, white polyvinyl-chloride plates (12" x 12' x 0.125") were lightly sanded then painted with a single coat of standard IRIS paint (composed of ferrihydrite and goethite) on each side.
- Four panels were installed in each mesocosm prior to adding soil. A jig was used to hold the panels in place for the duration of the experiment.
- IRIS panels were analyzed quantitatively using image analysis software (Abobe Photoshop CS6) using the pixel counting feature to quantify the amount of Fe^{3+} (orange), Fe^{2+} (white), and FeS (black).
- Both sides of the IRIS panels were analyzed resulting in 8 sides of panels per 3 replicate mesocosms = 24 surfaces per treatment.

Monitoring of mesocosms

- Soil mesocosms were constructed in clear, solid plastic tubs.
- Triplicate treatments were constructed for S concentrations (0, 1, 2.5, and 5%).
- Soil was added after IRIS panels were installed. Mesocosms were saturated with water for the duration of the 11-week study. Soil temperature was measured throughout the study.
- Oxidation-reduction potential was measured weekly at 10 cm below the soil surface using 5 replicate Pt-tipped electrodes and reference electrode. Soil pH was measured in situ at the same time intervals.

To find out why this research was conducted – START HERE

- Prior field observation of black FeS staining on IRIS tubes provided the impetus to further examine the phenomenon.
- Students observed FeS on IRIS tubes removed from soils with varying concentrations of added S and organic matter.
- Quantification could help develop a new criteria to identify hydric soils via FeS staining on IRIS tubes by updating the Technical Standard for Hydric Soils (USDA NRCS, 2010).



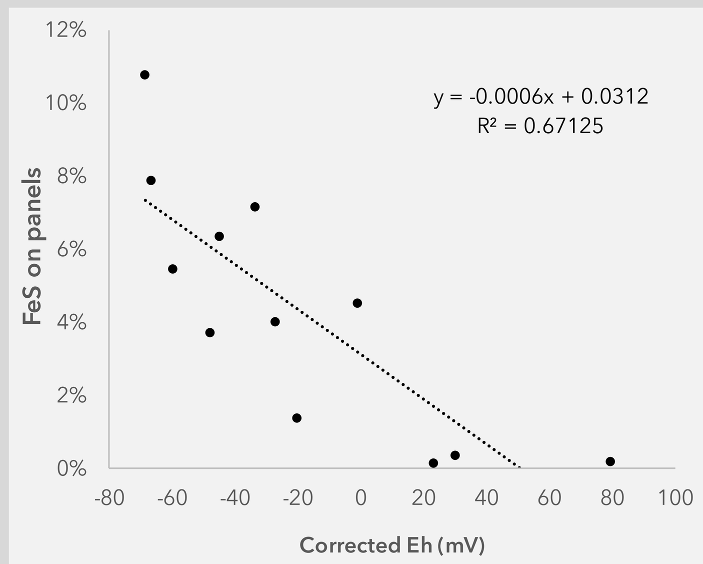
If you only have a couple of minutes – READ THIS

- When black, iron monosulfides (FeS) appear on iron coated panels installed in saturated soil – it means that the environment is highly reduced and certainly anaerobic (as is the requirement for HYDRIC SOILS) – *see figure 1.*
- The greater the S concentration in the soil → the greater the FeS presence on the plates (to a point) – *see figure 2.*
- We propose that when there is 2% FeS visible on IRIS tubes or plates, the soil is reduced with respect to S and therefore ANAEROBIC – *see figure 3.*

Results and Discussion

Figure 1. FeS formation vs. redox potential

At the pH values measured, the soils were reduced with respect to Fe below 100 mV.



- FeS staining was compared to oxidation-reduction potential (redox, Eh) after 11 weeks of incubation. Analysis revealed a negative correlation between FeS staining and Eh values (p=0.001).
- Since S is a less energetically favorable electron acceptor used by microbes, it is reasonable that higher amounts of S reduction correspond to lower Eh values. This suggests that increasing FeS staining on IRIS panels is indicative of more reducing conditions.

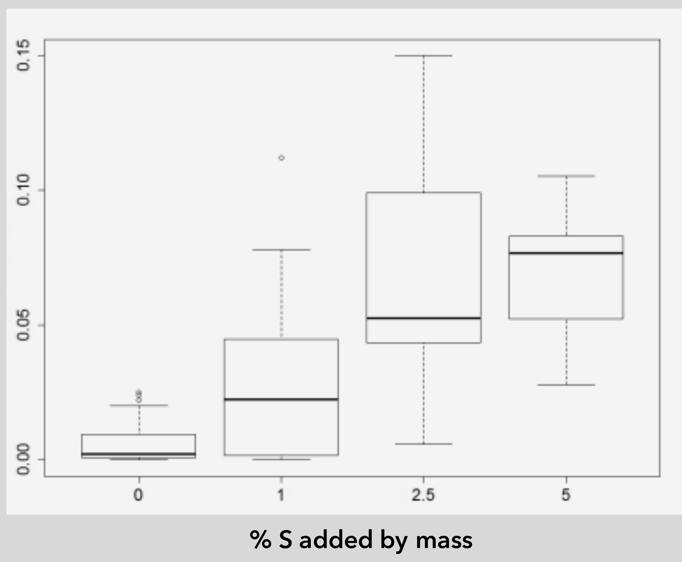


Figure 2. FeS formation vs. treatment

- Percent FeS staining increased as S concentration increased (median values shown with solid line).
- Concentration of S may have reached a high enough level and led to the maximum FeS formation in this system with mean FeS on panels being 6.95 and 6.82 % in the 2.5 and 5.0 treatment groups respectively.
- Future examination of greater S concentrations would improve our understanding of the mechanisms behind FeS formation at these higher concentrations.

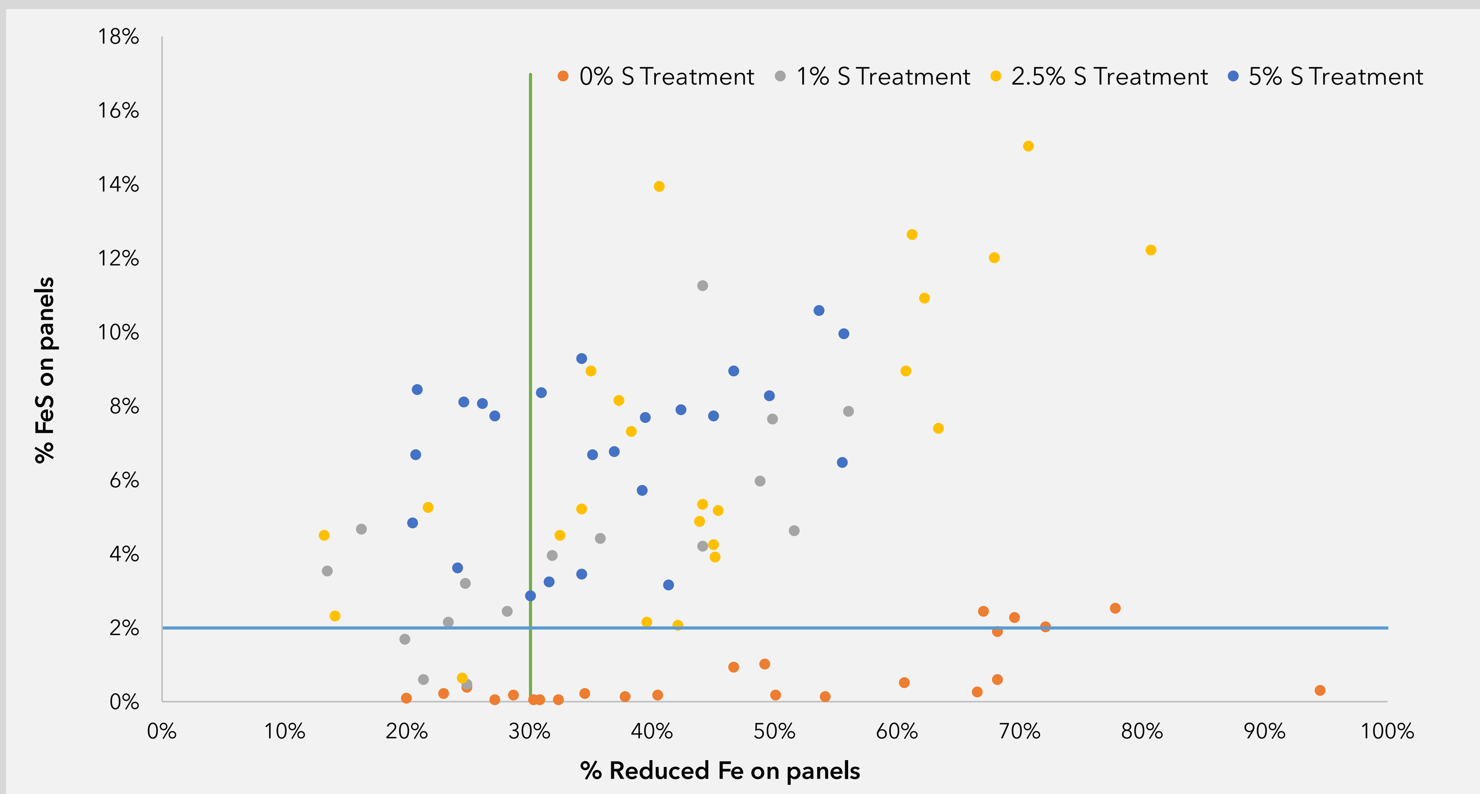
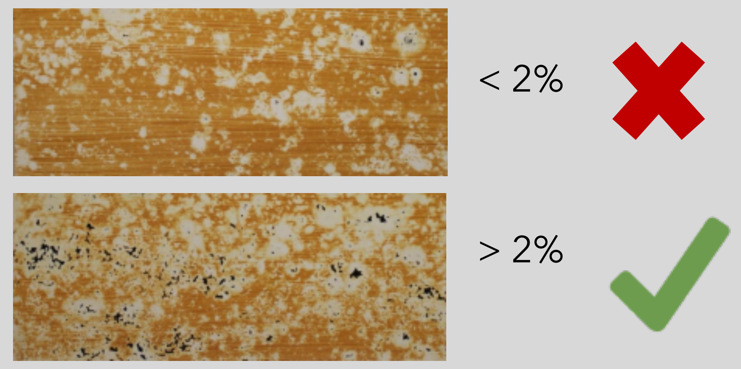


Figure 3. FeS formation vs. Fe reduction

- Percentage of FeS staining was compared to the % reduced Fe^{2+} stripped from the IRIS panels. For photographic analysis both reduced Fe^{2+} and FeS were included in the percentage of total Fe reduction. This was because of the $^{2+}$ oxidation state of Fe in FeS.
- In the majority of cases >2% FeS staining (blue horizontal line) corresponded with >30% total reduced Fe^{2+} (green vertical line). Given the strong visual presence of FeS staining on IRIS plates, it is proposed that 2% or greater of FeS staining should supplement the technical standard for identifying anaerobic conditions in soils.

Suggested addition to the National Technical Committee for Hydric Soils Technical Standard

Observation of 2% FeS on IRIS tube or plate in a zone 15-cm thick starting within 15 cm of the soil surface meets the criteria for anaerobic conditions.



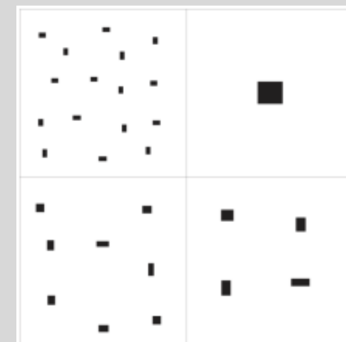
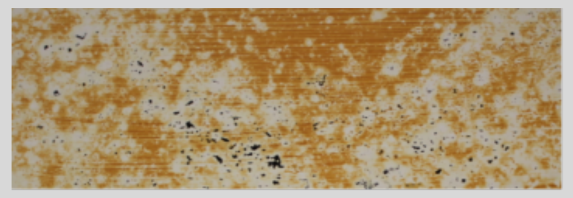


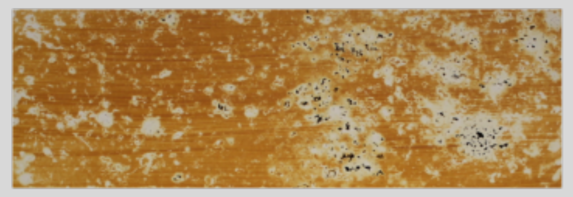
Figure 4. Percent of area covered shown is 2% (Schoeneberger et al., 2012)

Can you differentiate between < 2 and > 2% S reduction?

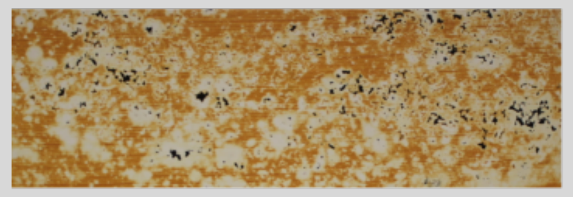
What percentage FeS do you see on the following IRIS panels? Use Figure 4 as a guide. Percentage oxidized iron (orange, Fe^{+3}), reduced iron (colorless/white, Fe^{2+}), and reduced sulfur (black, FeS) are shown under the flaps.



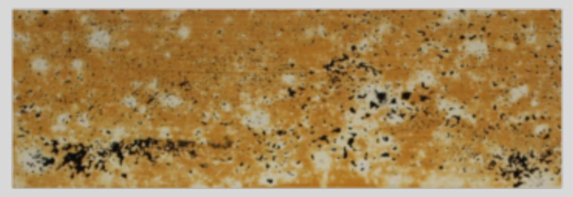
	%
Fe^{+3}	31.8
Fe^{+2}	67.7
FeS	0.5



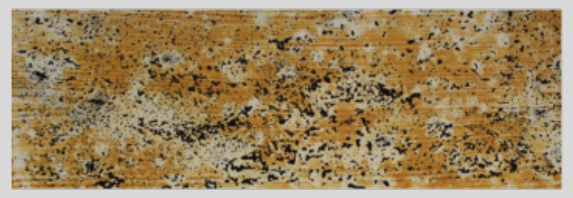
	%
Fe^{+3}	50.7
Fe^{+2}	48.3
FeS	1.0



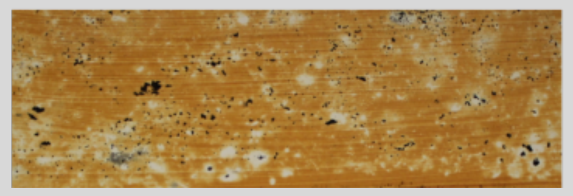
	%
Fe^{+3}	32.9
Fe^{+2}	64.7
FeS	2.4



	%
Fe^{+3}	51.2
Fe^{+2}	42.9
FeS	5.9



	%
Fe^{+3}	38.7
Fe^{+2}	48.7
FeS	12.6



	%
Fe^{+3}	76.6
Fe^{+2}	22.3
FeS	2.1

Percent coverage values were quantified using Adobe Photoshop CS6.

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Partial funding for this project has been provided by the California State University Agricultural Research Institute (ARI).