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Manganese-coated IRIS to document reducing soil conditions

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Abstract

Iron-coated indicatorof reduction in soils (IRIS) devices have been used for nearly two decades to help assess and document reducing conditions in soils, and official guidance has been approved for interpreting these data. Interest in manganese (Mn)-coated IRIS devices has increased because Mn oxides are reduced under more moderately reducing conditions than iron (Fe) oxides (which require strongly reducing conditions), such that they are expected to be better proxies for some important ecosystem services like denitrification. However, only recently has the necessary technology become available to produce Mn-coated IRIS, and the need is now emerging for guidance in interpreting data derived from Mn IRIS. Ninety-six data sets collected over a 2-yr period from 40 plots at 18 study sites among eight states were used to compare the performance of Mn-coated IRIS with Fe-coated IRIS and to assess the effect of duration of saturation and soil temperature as environmental drivers on the reduction and removal of the oxide coating. It appears that the current threshold prescribed by the National Technical Committee for Hydric Soils for Fe-coated IRIS is appropriate for periods when soil temperatures are warmer (>11 ˚C), but is unnecessarily conservative when soil temperatures are cooler (5–11 ˚C). In contrast, Mn-coated devices are particularly useful early in the growing season when soil temperatures are cool. Our data show that when using a threshold of 30% removal of Mn oxide coatings there is essentially 100% confidence of the presence of reducing soil conditions under cool (<11 ˚C) conditions.

Abbreviations: Eh, oxidation–reduction potential; IRIS, indicator of reduction in soils; NTCHS, National Technical Committee on Hydric Soils; PVC, polyvinyl chloride; TS, technical standard.

1 | INTRODUCTION

For ~30 yr, hydric soils have been understood to "have formed under conditions of saturation, flooding or ponding, long enough during the growing season to develop anaerobic conditions in the upper part" (Federal Register, 1994). Therefore, practitioners of wetland science require evidence that these specific provisions (hydrology and reducing conditions) are met. Often, this can be done by recognizing diagnostic soil morphological characteristics (field indicators) (USDA-NRCS, 2018). In some cases, hydrological and chemical evidence is required. Hydrological conditions can be documented using any number of manual or automatic recording devices, but demonstration of reducing conditions generally is more involved. The National Technical Committee for Hydric Soils (NTCHS) has approved the use of indicator dyes (Berkowitz, et al., 2017) or the measurement of oxidation–reduction potential (Eh) and pH (Rabenhorst et al., 2009); however, these present specific challenges and require multiple observations over time. The NTCHS has also approved the use of indicator of reduction in soils (IRIS) technology (Berkowitz et al., 2021). These are devices coated with metal oxides (iron [Fe] or manganese [Mn]) that demonstrate reducing (anaerobic) conditions in soils as the oxide coatings are solubilized and stripped. Typically, IRIS technology is used in wetlands research and site assessment where it is important to recognize and document reducing soil conditions. The IRIS approach was developed by Jenkinson (2002) and has been in use by both researchers and consultants for ~15 yr (Castenson & Rabenhorst, 2006; Jenkinson & Franzmeier, 2006). The basic premise behind IRIS technology is that a polyvinyl chloride (PVC) device coated with an Fe or Mn oxide paint, when exposed to reducing soil conditions, will be stripped of some of the oxide coating due to biogeochemical reduction (Supplemental Figure S1), and this removal can be quantified.

In general, soils must be both saturated and reduced for the Fe or Mn oxide paint on the IRIS devices to be removed. In the saturated soil, heterotrophic microbes use organic carbon compounds (e.g., organic matter, dead organisms) as an energy source during metabolism. Under saturated conditions, dissolved oxygen (O_2), when available, is used as an electron acceptor. This results in depletion of dissolved O_2 from the saturated soil zone, leading to anaerobic conditions. In addition, saturation slows the further diffusion of additional O_2 into the saturated soil layer, maintaining anaerobic conditions. Under such anaerobic conditions, soil microbes seek an alternative to the O_2 electron acceptor, such as nitrate (NO_3^-), Mn^{+4}, or Fe^{+3}, to facilitate respiration (Ponnamperuma, 1972). During this process, electrons are transferred to the oxide coatings causing them to become reduced and solubilized. The dissolution of Mn or Fe oxides leaves zones on the IRIS devices stripped of Fe or Mn paint.

Core Ideas

- Reduction of Fe and Mn oxides in soils is temperature dependent.
- Mn oxides are reduced faster and more easily than Fe oxides.
- At temperatures between 5–11 ˚C, removal of Fe oxides from IRIS is slow.
- The 30% threshold for Fe oxide removal from IRIS is appropriate when soil temperatures are >11 ˚C.
- A threshold of 30% removal for Mn coated IRIS is appropriate when soil temperatures are <11 ˚C.

The resulting stripped zones can be quantified to demonstrate that reducing soil conditions are present (Castenson & Rabenhorst, 2006). Quantification can be done by visual estimation (Rabenhorst, 2010) through a manual grid-counting approach (Rabenhorst, 2012), which is less accurate, or by using a more accurate digital approach for processing the IRIS images (Rabenhorst, 2018). The IRIS devices are typically deployed for ~1 mo (4 wk) for normal use, although in the case of reconnaissance investigations, they could be deployed for longer periods (up to 6 mo) (Rabenhorst, 2008).

The first IRIS devices developed were coated with an Fe oxide paint composed of ferrihydrite and goethite (Rabenhorst & Burch, 2006). After the development of Fe-coated IRIS, there was interest in exploring the use of Mn oxide-coated IRIS. According to thermodynamics, Mn oxides are reduced under less strongly reducing conditions than those required to reduce Fe, and closer to the redox conditions where important environmental reactions, like denitrification, occur (Megonigal & Rabenhorst, 2013). However, for many years, there were difficulties encountered in finding a way to ensure the Mn oxide coating adhered to the PVC (Stiles et al., 2010; Coffin, 2012). Successful adherence was finally demonstrated by Dorau and Mansfeldt (2015), who reported a method to make Mn-coated devices, but their approach was tedious and time consuming. More recently, Rabenhorst and Persing (2017) reported a simple approach to synthesizing a birnessite (Mn oxide) mineral that is easy to apply to PVC and resists damage from handling. Using this synthesized birnessite, Mn-coated IRIS can be easily produced, much like the Fe-coated IRIS. During preliminary experimental efforts, workers have reported that, as expected, the coatings on Mn-coated IRIS are more easily (and more rapidly) reduced than the coatings on Fe-coated IRIS (Dorau et al., 2016; Rabenhorst & Persing, 2017).

In the early use of IRIS, the oxide coating was applied to PVC pipes (half inch, schedule 40; 21.3-mm o.d.), but over time, it became clear that these devices had certain limitations. Rabenhorst (2018) introduced a new approach to IRIS technology by using IRIS films or tapes made from 10 mil (0.25-mm) rigid PVC sheets. The IRIS films are approximately the same dimensions as earlier IRIS tubes (Supplemental Figure S1). However, the flat shape allows for easy scanning. Also, reusable polycarbonate tubes are used to protect the coated surface during transport and deployment, and the new design uses only a small fraction (12%) of the amount of PVC as IRIS tubes and reduces storage volume to 4–5% of the space occupied by an equal quantity of tubes (Rabenhorst, 2018).

Since 2008, Fe-coated IRIS devices have been endorsed by the NTCHS as one way of demonstrating that soils meet the technical standard (TS) requirement for reducing soil conditions (other options being the use of redox measurements with platinum electrodes or the reaction of the soil to alpha-alpha′-dipyridyl dye) (Berkowitz et al., 2021). Based on work in flood plain seep wetlands in the Maryland Piedmont, Castenson and Rabenhorst (2006) reported that stripping of 20–25% of the Fe coating within a 10-cm zone represented 90–100% likelihood of reducing conditions based on Eh and pH measurements. Currently, the NTCHS has provided guidance indicating that if at least three out of five IRIS devices show at least 30% stripping of Fe oxide coating from a contiguous 15-cm zone anywhere within the upper 30 cm of the soil, then the soil is considered to have reducing conditions present (NTCHS, 2015; Berkowitz et al., 2021). At present, no similar guidance has been developed regarding the use and interpretation of Mn-coated IRIS devices for understanding reducing conditions in soils. The objectives of this study were as follows: (a) to evaluate the performance of Mn-coated IRIS in reference to soil saturation and temperature; (b) to compare the performance of Mn-coated IRIS in relation to Fe-coated IRIS; and (c) to develop a recommendation regarding the interpretation of data collected using Mn-coated IRIS.

2 | MATERIALS AND METHODS

2.1 | Study sites

Included in this study were 96 data sets from 40 plots collected at 18 study sites across eight states. In 2018, 11 study sites were used; eight of these were associated with the NE-1938 multistate research project (NIMSS, 2019) and were located in Virginia, Maryland, Delaware, West Virginia, Pennsylvania, Massachusetts, Rhode Island, and Wyoming. There were also three additional sites in Maryland. At each of these 11 sites, three plots were set up along a transect that included a wetland, a nonwetland, and a transitional plot (which, in some cases was, and in other cases was not, a wetland). In 2019, four study sites were used in Maryland and six in Virginia. Seven of these 10 were new sites not previously used in 2018. A single plot was established at each of these 10 sites, which mostly were understood to be wetlands. Over the 2-yr period at these 40 plots, IRIS was deployed twice, or three times sequentially, for 1-mo periods during the spring of that year (see Supplemental Table S1).

2.2 | Instrumentation

At each study plot, automated recording wells were installed, and water table levels were recorded at least once daily, and often twice daily. Also at each plot, recording temperature probes were installed at a depth of 25 or 30 cm below the surface, and temperatures were recorded multiple times per day and averaged to give a daily soil temperature. Depths of water tables were extracted for the specific periods when IRIS devices were installed, and cumulative frequency curves were calculated to determine what portion of the IRIS deployment time a given plot was saturated at specified depths.

2.3 | IRIS

The IRIS films were deployed for 1-mo periods at each location. During each deployment, five Fe-coated films and five Mn-coated films were installed following the guidance of Rabenhorst (2018). At the end of each 1-mo deployment (28–31 d), films were extracted and, if additional films were being deployed, they were installed at that time in newly made pilot holes. Films were rinsed to remove any adhering soil and after drying were scanned using a Fujitsu ix1500 document scanner (Fujitsu Inc.) and saved as a JPEG image.

Scanned JPEG images (300 dots per inch) of the films were processed using Adobe Photoshop software (Adobe Photoshop Inc.). After cropping images to include only the portion of the film installed below ground, the Photoshop color selection tool was used to produce binary images of the films that showed as black pixels the areas where oxide coatings were stripped. Binary images were quantified using a routine in MATLAB (The MathWorks, Inc.) that was written to calculate the percentage of black pixels within each 1-cm vertical section along the 50-cm film. These data were imported into a spreadsheet where the maximum paint stripped from a contiguous 15-cm zone entirely within the upper 30 cm could be calculated for each film as specified by the NTCHS TS. The median value among five replicate films was also calculated, which represented the value at which a majority of the films had as much, or more, coating removed as recommended by the NTCHS. An ANOVA was conducted using JMP software (Version 14.1.0) (SAS Institute Inc.), and LSDs were further clarified by using the Student *t* test.

TABLE 1 An ANOVA including all study plots evaluating the median (of 5 replicate films) maximum indicator of reduction in soils (IRIS) coating removal from a 15-cm contiguous zone within the upper 30 cm of the soil as a function of the percentage of time of the deployment month that the soil was saturated at or above 25 cm, the average soil temperature during the month of deployment, and the type of IRIS coating (Fe or Mn)

Source	df	Sum of squares	F ratio	Probability > *F*
Percentage of time saturated	1	15.274	210.303	<.0001[a]
Avg. temperature	1	1.471	20.260	<.0001[a]
Coating type	1	3.234	44.533	<.0001[a]
Percentage of saturated × coating	1	0.067	0.924	.338
Avg. temp. × coating	1	0.016	0.218	.641

[a]Percentage of time saturated, average soil temperature, and coating type were all highly significant factors.

TABLE 2 An ANOVA that included only those study plots and dates where the hydrology requirement of the National Technical Committee on Hydric Soils technical standard was met (14 d continuous saturation within 25 cm of the soil surface), and which evaluated the effect of indicator of reduction in soils (IRIS) coating type (Fe vs Mn) and soil temperature group (5–11 vs. 11–19 ˚C)

Source	df	Sum of squares	*F* ratio	Probability > *F*
Temperature group	1	0.898	10.006	.0020[a]
Coating type	1	2.739	30.512	<.0001[a]
Temperature group × coating type	1	0.163	1.814	.181

[a]Both soil temperature grouping and IRIS coating type were significant factors.

3 | RESULTS AND DISCUSSION

3.1 | General effects of saturation, temperature, and coating type

Our studies confirmed that saturation and soil temperature were important environmental drivers for the process of IRIS oxide coating removal, with greater oxide coating removal associated with longer duration of saturation and with warmer soil temperatures (Table 1). These data and analyses also confirmed earlier perceptions that Mn oxides are removed more easily and more rapidly than Fe oxide coatings (Dorau et al., 2016; Dorau et al, 2018; Rabenhorst & Persing, 2017), which is predicted from thermodynamics (i.e., the locations of Fe and Mn oxide stability lines on Eh–pH diagrams [Takeno, 2005]).

To further examine the effects of temperature, we analyzed the results from the IRIS deployment study plots and dates that met the hydrological criteria of the NTCHS TS (14 d continually saturated above 25 cm) (Table 2). Preliminary examination of data suggested a general change in responses around 11 ˚C that was confirmed upon closer analysis (Supplemental Figure S2). This temperature threshold is close to the 10 ˚C value reported by Rabenhorst and Castenson (2005) using a much smaller and geographically restricted data set. In a laboratory study, Sparrow and Uren (2014) showed a temperature effect on the release of soluble forms of Mn (presumably because of reduction) under saturated soil conditions within 1 to 2 wk, with little release at temperatures <10 ˚C and substantially greater amounts at temperatures ≥20 ˚C. Therefore, data were classified into two temperature groups that corresponded to early growing season conditions (average soil temperatures 5–11 ˚C) and later growing season conditions (average soil temperatures 11–19 ˚C). Of the 96 data sets, 43% were in the cooler group, and 57% were in the warmer group. The analysis confirmed that for the plots and dates that meet the TS hydrological requirements, a significant difference was caused by the effect of soil temperature. The IRIS oxide coating type also caused a significant effect.

These differences were further clarified by using the Student *t* test to distinguish significant differences between specific groups, which are shown in Figure 1. Regardless of whether the soil temperatures were cool (<11 ˚C) or warm (>11 ˚C), there is significantly more Mn than Fe coating removed. This corresponds with expectations from thermodynamics, which state that Mn oxides are reduced more easily and more rapidly than Fe oxides because Mn oxide stability lines plot higher than Fe oxide stability lines on Eh–pH diagrams, and is consistent with previous reports (Dorau et al., 2018; Rabenhorst & Persing, 2017). Under cool conditions, which correspond to early in the growing season, there is significantly less Fe coating removed from the IRIS than those deployed under warmer soil conditions, which are later in the growing season. Although Mn oxide IRIS coatings had greater removal under warmer conditions, this effect was not statistically significant, due to the fact that the data were distributed strongly toward 100% removal, which confines the distribution on the high end. Had the rate of coating removal been included in the analysis by documenting how much coating had been removed after 1, 2, 3, and 4 wk, it is expected that temperature effects also would have been significant for the Mn oxide coatings because laboratory studies have demonstrated that Mn coatings can be removed quite rapidly under saturated conditions (Park & Rabenhorst, 2018; Dorau et al., 2018).

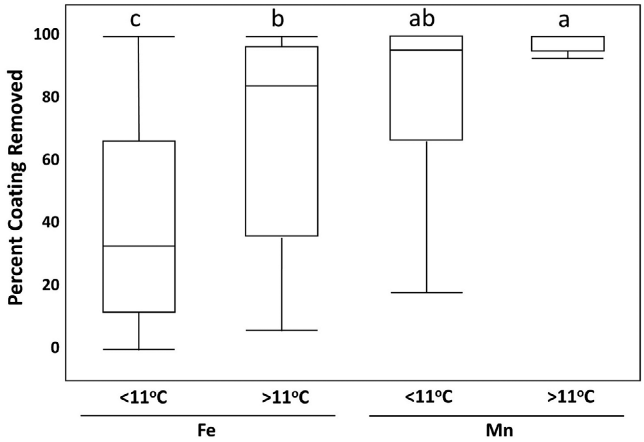

FIGURE 1 Box and whisker plots for those study plots and dates for which the hydrology requirement of the National Technical Committee for Hydric Soils technical standard was met (14 d continuous saturation within 25 cm of the soil surface), and which evaluated the effect of indicator of reduction in soils coating type (Fe vs. Mn) and soil temperature group (5–11 vs. 11–19 ˚C). Data that do not share the same letter designation are significantly different at the 95% level (based on analysis of the Student *t* test for LSD). Boxes represent the 25th and 75th percentiles, and the whiskers represent the 10th and 90th percentiles. Under both cooler (<11 ˚C) and warmer (>11 ˚C) conditions, there was significantly more Mn than Fe coating removed. Under cool (i.e., early growing season) conditions, there was significantly less Fe coating removed than later in the growing season when soil temperatures are warmer

3.2 | Coating removal and implications for thresholds

Using the recommended metric from the NTCHS for IRIS coating removal (i.e., median of five replicate IRISs of the maximum removal from a contiguous 15-cm zone within the upper 30 cm of the soil) the magnitude of IRIS coating removal was compared with whether or not that plot and date met the hydrological requirement of the TS (14 d continuous saturation at a depth of 25 cm or shallower) (Figure 2).

When soil temperatures are between 5 and 11 ˚C (early in the growing season) it is clear that there is relatively little removal of the Fe coating even when the soils meet the hydrological requirement for the TS (Figure 2a). All of the plots showing as little as 5% or more removal of the Fe coating met the hydrological requirement. Figure 3a demonstrates that under cool conditions (5–11 ˚C), the assessment error for soils that are wet but not reducing is minimized using a threshold of 5% Fe coating removal. The current requirement for a site to be considered reducing is that ≥30% of the IRIS coating is removed. These data suggest that maintaining this current requirement for 30% removal during the early part of the growing season would likely result in many sites being missed as not reducing.

When soil temperatures are between 11 and 19 ˚C, there is substantially more removal of the IRIS coating in soils that meet the hydrological requirement for the TS (Figure 2b). This is likely because of greater microbial activity under warmer soil conditions. These data show that 90% of the plots with ≥10% removal of the Fe coating met the hydrological requirement, and 95% of the plots with ≥30% removal of the Fe coating met the hydrological requirement. The current NTCHS guidance indicates that 30% stripping of the Fe oxide coating demonstrates that a soil is reducing (NTCHS, 2015). This suggests that the current threshold of 30% Fe coating removal is so conservative that, even under warmer (>11 ˚C) conditions, using a threshold of 30% would ensure that in 95% of the cases, these sites would also meet the hydrological requirement for the TS. However, Figure 3b also illustrates that using a threshold of 30% optimally reduces assessment errors, minimizing those cases where the soils are not sufficiently saturated to meet the TS hydrology requirement but meet the requirement for reducing conditions.

When soil temperatures were between 5 and 11 ˚C, Mn coatings had significantly greater removal (Figure 2c) than Fe coatings (Figures 1 and 2a). Generally speaking, the Mn-coated IRIS during the cool early season behaved much like the Fe-coated IRIS during the warmer period. These data show that, during this cooler early period, roughly 90% of the plots with ≥10% removal of the Mn coating met the hydrological requirement, and 100% of the plots with ≥30% removal of the Mn coating met the hydrological requirement. This suggests that early in the growing season, while a 30% requirement for Fe coating removal is unrealistically high, 20–30% removal of Mn-coated IRIS may be an appropriate threshold. This is illustrated in Figure 3c, which demonstrates that using a Mn threshold of 20–30% would generate a very small percentage of cases that might be saturated but not reducing, while having no instances of the site being reducing but not saturated. Based on our data, a case could be made for 20 or 30%, but we have no data that fell within this narrow range. According to Figure 3c, using 20% would provide 95% confidence and using 30% would provide 100% confidence.

The Mn coating data for warmer soil conditions are presented in Figure 2d. When soil temperatures are between 11 and 19 ˚C, there is substantially more removal of IRIS coatings in soils that meet the hydrological requirement for the TS. These data show that approximately 80% of plots with ≥60% removal of the Mn coating met the hydrological requirement, and 90% of plots with ≥90% removal of the Mn coating met the hydrological requirement. Figure 3d demonstrates that under warmer conditions (11–19 ˚C), erroneous assessments are minimized when a minimum threshold of 50% coating removal is used, but that in order to minimize instances where the site is considered reducing but not wet, a threshold of 90% would be required.

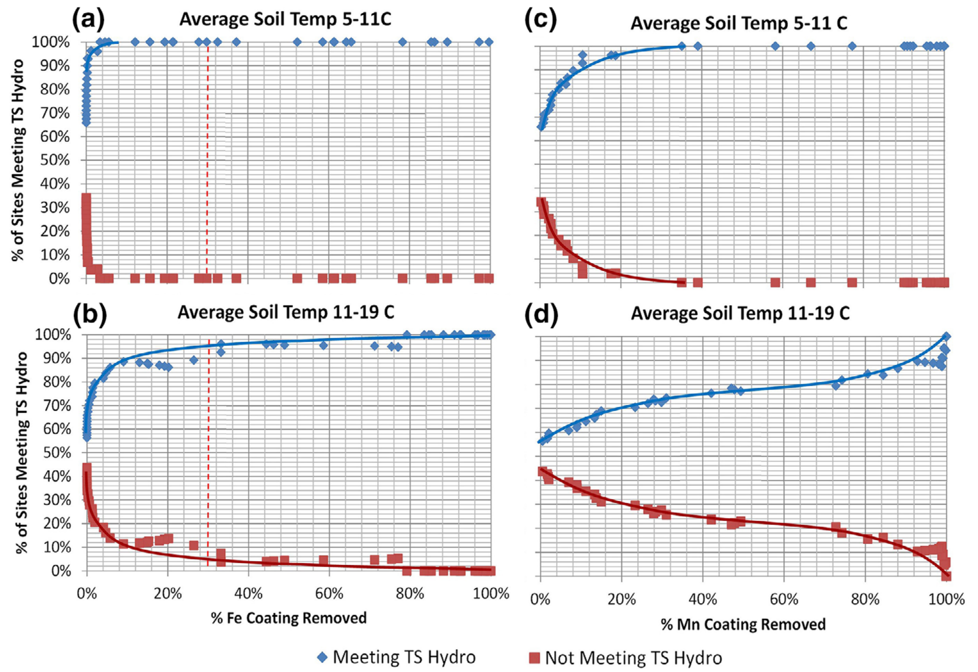

FIGURE 2 Proportion of data sets meeting (or not meeting) the National Technical Committee for Hydric Soils (NTCHS) technical standard (TS) hydrology requirement (14 d continuous saturation within 25 cm) when a certain percentage of indicator of reduction in soils coating (Fe or Mn) was removed (median maximum of 5 replicates from a 15-cm contiguous zone within the upper 30 cm) under cool (5–11 ˚C) or warm (11–19 ˚C) conditions. (a and b) Fe coating removal. The dashed red line represents the current NTCHS requirement of 30% removal of Fe coating. (c and d) Mn coating removal

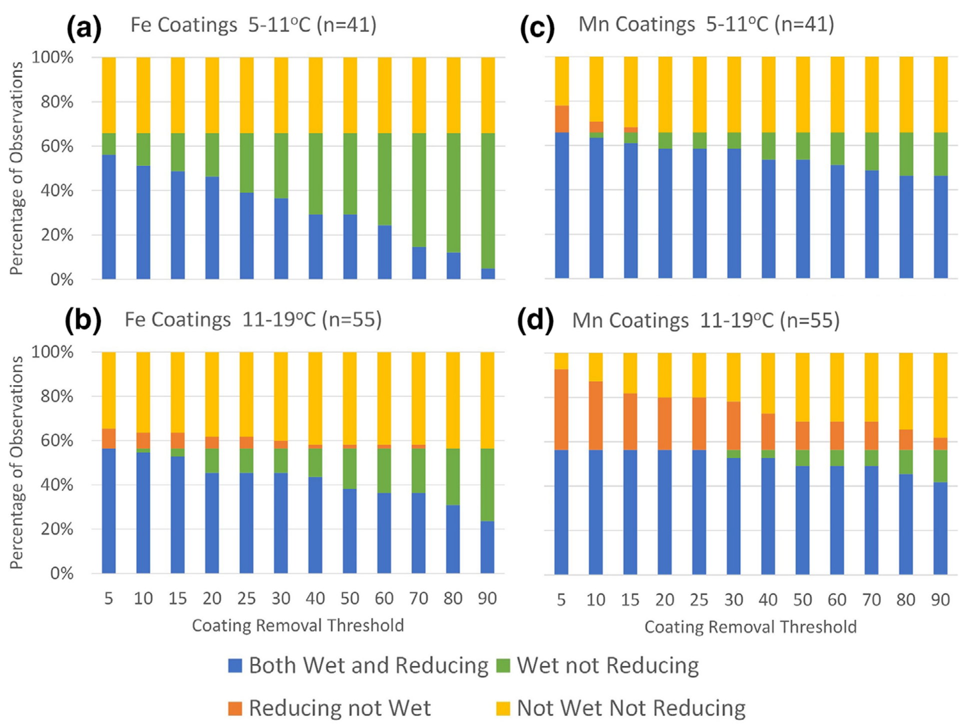

FIGURE 3 Percentage of data sets that did (wet) or did not (not wet) meet the technical standard hydrology requirement (14 d continuous saturation within 25 cm) shown in conjunction with those that would or would not be considered reducing based on a given indicator of reduction in soils threshold for Fe or Mn coating removal when soil temperatures were cool (5–11 ˚C) or warm (11–19 ˚C). (a and b) Fe coating removal. (c and d) Mn coating removal. Those that either were both not wet and not reducing or were both wet and reducing would be the expected and consistent condition. Those that were only one or the other (wet or reducing but not both) would be considered to be problematic

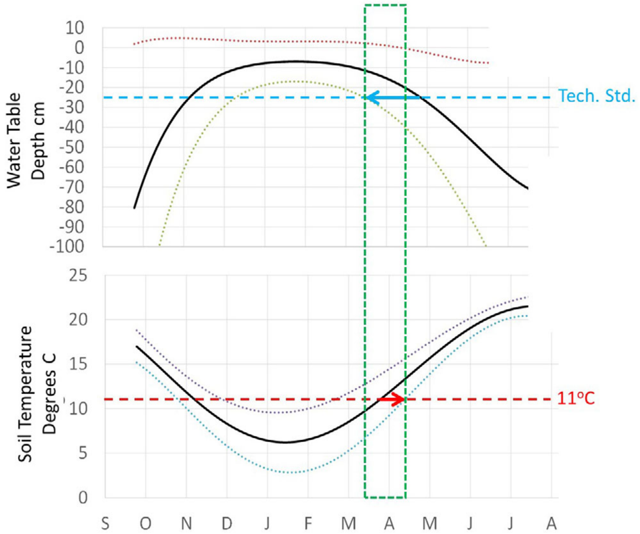

FIGURE 4 Graphs of soil water table (top) and soil temperature (bottom) derived from 6 yr of data at a site in Caroline County, Maryland, that is representative of Mid-Atlantic seasonally saturated wetlands. The graphs represent generalized means ±2 SD to show where approximately 95% of the data are expected to occur. The green box illustrates that there is a time period in some years when water tables could drop below 25 cm as soon as early March while soil temperatures might not get above 11 ˚C until as late as mid-April

3.3 | The need for temperature-adjusted IRIS standards

It is clear that the removal of oxide coatings from IRIS devices demonstrates biogeochemical reduction. The question at hand is what degree of oxide coating removal is required to adequately demonstrate that reducing soil conditions are present. The current NTCHS threshold requirement for 30% removal of Fe IRIS coating seems reasonable for conditions when soil temperatures are warmer (average >11 ˚C), although a threshold of 15 or 20% might better minimize errors or inconsistencies (Figure 3b). However, for those conditions earlier in the growing season when soil temperatures are below 11 ˚C, this threshold seems unreasonably high. This could be especially important because there are many seasonally saturated wetlands that are at their wettest during the late winter and early spring and then begin to dry out as water tables drop after leaf out in the early spring. Thus, at the same time that soil temperatures are slowly warming during the early growing season, water tables in those wetlands are very often beginning to draw down. This means that there could be common instances where seasonally saturated wetlands are saturated in the early growing season when soil temperatures are between 5 and 11 ˚C, but by the time soil temperatures begin to approach 11 ˚C or higher, the water tables are beginning to drop beneath the upper part of the soil.

By way of example, Figure 4 shows a summary of 6 yr of data from a seasonally saturated wetland in Caroline County, Maryland, where the growing season typically begins in early March. These data demonstrate that 80% of the time that the soil is saturated at or above 25 cm, the soil temperature is <11 ˚C. It also shows that, in some years, soil temperatures might not approach 11 ˚C until mid-April, whereas water tables begin to drop in early March and might drop to below 25 cm in some years by mid-March. Because of this phenomenon (water tables decreasing while soil temperatures are increasing), practitioners working in delineation or restoration typically seek to document hydric soil conditions early in the growing season when water tables are most likely to be nearer the soil surface, but this is also at a time when soil temperatures are typically cooler than 11 ˚C.

4 | SUMMARY AND CONCLUSIONS

Although evidence of Fe oxide reduction is commonly used in soil science as a morphological indicator of reducing conditions, Fe oxide reduction represents a very strongly reducing condition, much more strongly reducing than that required for important environmental processes like denitrification (Ponnamperuma, 1972). Provided that dissolved O_2 has been consumed, anaerobic conditions occurring in soils can result in the reduction of NO_3^- and Mn oxides even when conditions are not sufficient to cause reduction of ferric iron (Patrick & Jugsujinda, 1992). Both Mn oxide- and Fe-coated IRIS devices demonstrate biogeochemical reduction in the soil, and because the reduction of both Fe and Mn oxides is microbially mediated, there is greater reduction under warmer soil temperatures. The reduction of Fe coatings requires more strongly reducing conditions than Mn. Analyses of data in this study that were collected from a wide geographic area and range in soil conditions demonstrate that the current threshold prescribed by the NTCHS for Fe-coated IRIS may be appropriate for periods later in the growing season when soil temperatures are above 11 ˚C, but are unnecessarily conservative for periods early in the growing season when soil temperatures are between 5 and 11 ˚C. The data also confirm that, following thermodynamic predictions, the removal of IRIS coatings from Mn-coated devices occurs faster and to a greater degree than Fe-coated IRIS. The Mn-coated devices have particular utility early in the growing season when soil temperatures are cooler (<11 ˚C), and water tables in seasonally saturated wetlands are typically higher. Under cooler (early growing season, <11 ˚C) conditions, a threshold of 30% removal of Mn oxide coatings can be used to confirm the presence of reducing soil conditions with >95% accuracy. Our results suggest that the NTCHS should consider developing temperature dependent standards for documenting reducing conditions in hydric soils based on Mn IRIS devices.

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AUTHOR CONTRIBUTIONS

Martin C. Rabenhorst: Conceptualization; Data curation; Formal analysis; Investigation; Methodology; Resources; Software; Writing-original draft; Writing-review & editing. Patrick J. Drohan: Conceptualization; Investigation; Methodology; Resources; Writing-review & editing John M. Galbraith: Conceptualization; Investigation; Methodology; Resources; Writing-review & editing. Colby Moorberg: Writing-review & editing. Lesley Spokas: Conceptualization; Investigation; Methodology; Resources; Writing-review & editing. Mark H. Stolt: Conceptualization; Investigation; Methodology; Project administration; Resources; Writing-review & editing. James A. Thompson: Conceptualization; Investigation; Methodology; Project administration; Resources; Writing-review & editing. Judith Turk: Writing-review & editing. Bruce L. Vasilas: Conceptualization, Investigation, Methodology, Project administration, Resources, Writing-review & editing. Karen L. Vaughan: Conceptualization, Investigation, Methodology, Project administration, Resources, Writing-review & editing.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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REFERENCES

Berkowitz, J. F., VanZomeren, C. M., Currie, S. J., & Vasilas, L. (2017). Application of α,α'-dipyridyl dye for hydric soil identification. *Soil Science Society of America Journal*, *81*, 654–658. https://doi.org/10.2136/sssaj2016.12.0431

Berkowitz, J. F., Vepraskas, M. J., Vaughan, K. L., & Vasilas, L. M. (2021). Development and application of the Hydric Soil Technical Standard. *Soil Science Society of America Journal*, *85*, 469–487. https://doi.org/10.1002/saj2.20202

Castenson, K. L., & Rabenhorst, M. C. (2006). Indicator of reduction in soil (IRIS): Evaluation of a new approach for assessing reduced conditions in soil. *Soil Science Society of America Journal*, *70*, 1222–1226. https://acsess.onlinelibrary.wiley.com/doi/abs/10.2136/sssaj2005.0130

Coffin, C. A. (2012). *Indicators of Reduction in Soils (IRIS) in various conditions of saturation in south Florida marl* [Master's thesis, University of Florida]. University of Florida Digital Collections. https://ufdc.ufl.edu/UFE0044806/00001

Dorau, K., Eickmeier, M., & Mansfeldt, T. (2016). Comparison of manganese and iron oxide-coated redox bars for characterization of the redox status in wetland soils. *Wetlands*, *36*, 133–141. https://link.springer.com/article/10.1007/s13157-015-0724-5

Dorau, K., & Mansfeldt, T. (2015). Manganese-oxide-coated redox bars as an indicator of reducing conditions in soils. *Journal of Environment Quality*, *44*, 696–703. https://acsess.onlinelibrary.wiley.com/doi/10.2134/jeq2014.03.0140

Dorau, K., Papenfuß, S., & Mansfeldt, T. (2018). Temperature-dependent oxide removal from manganese- and iron oxide-coated soil redox bars. *Journal of Soils and Sediments*, *18*, 680–687. https://doi.org/10.1007/s11368-017-1812-3

Federal Register (1994). *Changes in hydric soils of the United States, July 13, 1994*. U.S. Department of Agriculture Soil Conservation Service.

Jenkinson, B. (2002). *Indicators of Reduction in Soils (IRIS): A visual method for the identification of hydric soils* [Doctoral dissertation]. Purdue University.

Jenkinson, B. J., & Franzmeier, D. P. (2006). Development and evaluation of Fe coated tubes that indicate reduction in soils. *Soil Science Society of America Journal*, *70*, 183–191. https://acsess.onlinelibrary.wiley.com/doi/abs/10.2136/sssaj2004.0323

Megonigal, J. P., & Rabenhorst, M. (2013). Reduction–oxidation potential and oxygen. pp. 71–86. In R. DeLaune, R. Reddy, C. R. Richardson, & J. P. Megonigal (Eds.), *Methods in biogeochemistry of wetlands*. SSSA.

National Information Management & Support System (NIMSS). (2019). NE1938: Carbon dynamics and hydromorphology in depressional wetland systems. NIMSS. https://www.nimss.org/projects/view/mrp/outline/18634

National Technical Committee for Hydric Soils (NTCHS). (2015). Technical note 11: Hydric soils technical standard and data submission requirements for field indicators of hydric soils. USDA-NRCS. https://www.nrcs.usda.gov/Internet/FSE_DOCUMENTS/nrcs142p2_051608.pdf.

Park, E., & Rabenhorst, M. (2018). Assessing new developments in IRIS technology. *Wetland Science and Practice*, *35*, 324–327.

Patrick, W. H., & Jugsujinda, A. (1992). Sequential reduction and oxidation of inorganic nitrogen, manganese, and iron in flooded soil. *Soil Science Society of America Journal*, *56*, 1071–1073. https://doi.org/10.2136/sssaj1992.03615995005600040011x

Ponnamperuma, F. N. (1972). The chemistry of submerged soils. *Advances in Agronomy*, *24*, 29–96. https://doi.org/10.1016/S0065-2113(08)60633-1

Rabenhorst, M. C. (2008). Protocol for using and interpreting IRIS tubes. *Soil Survey Horizons*, *49*, 74–77. https://doi.org/10.2136/sh2008.3.0074

Rabenhorst, M. C. (2010). Visual assessment of IRIS tubes in field testing for soil reduction. *Wetlands*, *30*(5), 847–852. https://doi.org/10.1007/s13157-010-0098-7

Rabenhorst, M. C. (2012). Simple and reliable approach for quantifying IRIS tube data. *Soil Science Society of America Journal*, *76*, 307–308. https://doi.org/10.2136/sssaj2011.0267n

Rabenhorst, M. C. (2018). A system for making and deploying oxide-coated plastic films for environmental assessment of soils. *Soil Science Society of America Journal*, *82*, 1301–1307. https://acsess.onlinelibrary.wiley.com/doi/full/10.2136/sssaj2018.05.0178

Rabenhorst, M. C., & Burch, S. N. (2006). Synthetic iron oxides as an indicator of reduction in soils (IRIS). *Soil Science Society of America Journal*, *70*, 1227–1236. https://doi.org/10.2136/sssaj2005.0354

Rabenhorst, M. C., & Castenson, K. L. (2005). Temperature effects on iron reduction in a hydric soil. *Soil Science*, *170*, 734–742. https://doi.org/10.1097/01.ss.0000185908.26083.53

Rabenhorst, M. C., Hively, W. D., & James, B. R. (2009). Measurements of soil redox potential. *Soil Science Society of America Journal*, *73*(2), 668–674. https://doi.org/10.2136/sssaj2007.0443

Rabenhorst, M. C., & Persing, K. A. (2017). A synthesized manganese oxide for easily making durable Mn-coated IRIS tubes. *Soil Science Society of America Journal*, *81*, 233–239. https://acsess.onlinelibrary.wiley.com/doi/abs/10.2136/sssaj2016.10.0348n

Sparrow, L. A., & Uren, N. C. (2014). Manganese oxidation and reduction in soils: Effects of temperature, water potential, pH and their interactions. *Soil Research*, *52*, 483–494. https://doi.org/10.1071/SR13159

Stiles, C. A., Dunkinson, E. T., Ping, C. L., & Kidd, J. (2010). Initial field installation of manganese indicators of reduction in soils, Brooks Range, Alaska. *Soil Survey Horizons*, *51*, 102–107. https://acsess.onlinelibrary.wiley.com/doi/abs/10.2136/sh2010.4.0102

Takeno, N. (2005). Atlas of Eh–pH diagrams: Intercomparison of thermodynamic databases. National Institute of Advanced Industrial Science and Technology, Research Center for Deep Geological Environments. https://www.nrc.gov/docs/ML1808/ML18089A638.pdf

USDA-NRCS (2018). Field indicators of hydric soil in the United States. USDA-NRCS. https://www.nrcs.usda.gov/Internet/FSE_DOCUMENTS/nrcs142p2_053171.pdf

SUPPORTING INFORMATION

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