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Mn-Coated IRIS to Document Reducing Soil Conditions

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ABSTRACT

Iron-coated Indicator of Reduction In Soils (IRIS) devices have been utilized 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 Mn-coated IRIS devices has increased because Mn oxides are reduced under more moderately reducing conditions than 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 two year period from 40 plots at 18 study sites among eight states were utilized to compare the performance of Mn-coated IRIS with Fe-coated IRIS and to assess the impact 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 $^{\circ}$ C). In contrast, Mn-coated devices are particularly

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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.

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

INTRODUCTION

For nearly 30 years now, 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). Practitioners of wetland science, therefore, utilize or need to provide 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 has generally been more involved. The NTCHS has approved the use of indicator dyes (Berkowitz, et al. 2017) or the measurement of Eh and pH (Rabenhorst et al., 2009), but 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 (Fe or Mn) that demonstrate reducing (anaerobic) conditions in soils as the oxide coatings are solubilized and stripped. Typically, IRIS technology is utilized 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 about 15 years (Castenson and Rabenhorst, 2006; Jenkinson and 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 lose (be stripped of) some of the oxide coating due to biogeochemical reduction (Fig. 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 utilize organic carbon compounds (e.g., organic matter, dead organisms) as an energy source during metabolism. Under saturated conditions dissolved oxygen (O₂), when available, is used as an electron acceptor. This results in depletion of dissolved O₂ from the saturated soil zone, leading to anaerobic conditions. In addition, saturation slows the further diffusion of additional O₂ into the saturated soil layer maintaining anaerobic conditions. Under such anaerobic conditions, soil microbes seek an alternate (to O₂) electron acceptor, such as nitrate (NO3⁻), 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. The resulting stripped zones can be quantified to demonstrate that reducing soil conditions are present (Castenson and Rabenhorst, 2006). Quantifiation can be done by visual estimation (Rabenhorst 2010) which is less accurate, through a manual grid counting approach (Rabenhorst 2012), or using a more accurate digital approach for processing the IRIS images (Rabenhorst 2018). IRIS devices are typically deployed for approxiamtely 1 month (4 weeks) for normal use, although in the case of reconnaissance investigations, they could be deployed for longer periods (perhaps up to 6 months) (Rabenhorst 2008).

The first IRIS devices that were developed were coated with an Fe oxide paint composed of ferrihydrite and goethite (Rabenhorst and Burch, 2006). Following the development of Fecoated 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 and 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 turned out to be 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 and Persing, 2017).

In the early use of IRIS, the oxide coating was applied to polyvinyl chloride (PVC) pipes (½ inch schedule 40), 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/tapes made from 10 mil (0.25 mm) rigid PVC sheets. The IRIS films are approximately the same

dimensions as earlier IRIS tubes (Fig. S1). However, the flat shape allows for easy scanning; 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 National Technical Committee for Hydric Soils (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 Pt 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% to 25% of the Fe coating within a 10-cm zone represented 90% to 100% likelihood of reducing conditions based on Eh and pH measurements. Currently, the NTCHS has provided guidance saying that if at least 3 out of 5 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 are: 1) to evaluate the performance of Mn-coated IRIS in reference to soil saturation and temperature; 2) to compare the performance of Mn-coated IRIS in relation to Fe-coated IRIS; and 3) to develop a recommendation regarding the interpretation of data collected using Mn-coated IRIS.

MATERIALS AND METHODS

Study sites

Included in this study are 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 and were located in VA, MD, DE, WV, PA, MA, RI and WY. There were also three additional sites in MD. At each of these 11 sites, three plots were set up along a transect that included a wetland, a non-wetland and a transitional plot (which in some cases was, and other cases was not, a wetland). In 2019 four study sites were used in MD and six in VA. 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 two year period at these 40 plots, IRIS were deployed twice, or three times sequentially, for one month periods during the spring of the year (see Table 1 - Supplementary Information).

Instrumentation

At each study plot, automated recording wells were installed and water table levels were recorded at least once daily (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.

IRIS

IRIS films were deployed for one month periods at each location. During each deployment, five Fe-coated films and five Mn-coated IRIS films were installed following the guidance of Rabenhorst (2018). At the end of each one month deployment (28 to 31 days), 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., Sunnyvale, CA, USA) and saved as a JPEG image.

Scanned JPEG images (300 dpi) of the films were processed using Adobe Photoshop[™] software (Adobe Photoshop Inc., San Jose, CA, USA). 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 the areas where oxide coatings were stripped as black pixels. Binary images were quantified using a routine in MATLAB (© 1994-2020 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). Analysis of variance was conducted using JMP software (JMP[®], Version 14.1.0. SAS Institute Inc., Cary, NC, 1989-2021.) and least significant differences were further elucidated by using Student's T.

RESULTS AND DISCUSSION

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 and Persing, 2017), which is predicted from thermodynamics (i.e. the locations of Fe oxide and Mn oxide stability lines on Eh-pH diagrams (Takeno 2005)).

Table 1. Analysis of variance including all study plots evaluating the median (of 5 replicate films) maximum 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). Percent of time saturated, average soil temperature and coating type were all highly significant[†] factors.

| Source | DF | Sum of Squares | F Ratio | Prob > F | | |
|------------------------|----|----------------|---------|--------------------------------|--|--|
| Pct. of time saturated | 1 | 15.274 | 210.303 | <0.0001 [†] | | |
| Avg. temperature | 1 | 1.471 | 20.260 | <0.0001 [†] | | |
| Coating type | 1 | 3.234 | 44.533 | <0.0001 [†] | | |
| Pct. saturated*coating | 1 | 0.067 | 0.924 | 0.338 | | |
| Avg. temp*coating | 1 | 0.016 | 0.218 | 0.641 | | |

To further examine the effects of temperature, we analyzed the results from the IRIS deployment study plots/dates that met the hydrological criteria of the NTCHS TS (14 days continually saturated above 25 cm) (Table 2). Preliminary examination of data suggested that there was a general change in responses around 11 °C and this was confirmed upon closer analysis (Fig. S2 supplemental materials). 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 (2013) showed a temperature effect on the release of soluble forms of Mn (presumed to be due to reduction) under saturated soil conditions within 1 to 2 weeks, with little release at temperatures below 10 °C and substantially greater amounts at temperatures of 20 °C and above. Therefore, data were classified into two temperature groups that corresponded to early growing season conditions (average soil temperatures between 5 and 11 °C) and later growing season conditions (average soil temperatures between 11 and 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 these plots/dates meeting the TS hydrological requirements, there was a significant difference caused by the effect of soil temperature. There was also (again) a significant effect from the IRIS oxide coating type.

Table 2. Analysis of variance that included only those study plots/dates where the hydrology requirement of the NTCHS TS was met (14 days continuous saturation within 25 cm of the soil surface) and which evaluated the effect of IRIS coating type (Fe vs Mn) and soil temperature group (5-11 °C vs 11-19 °C). Both soil temperature grouping and IRIS coating type were significant⁺ factors.

| Source | DF | Sum of Squares | F Ratio | Prob > F |
|--------------------------------|----|----------------|---------|------------------------------|
| Temperature group | 1 | 0.898 | 10.006 | 0.0020 † |
| Coating type | 1 | 2.739 | 30.512 | < 0.0001 [†] |
| Temperature group*coating type | 1 | 0.163 | 1.814 | 0.181 |

These differences were further elucidated by using Student's T to distinguish significant differences between specific groups, which are shown in Figure 1. Regardless of whether the soil temperatures were cool (<11 $^{\circ}$ C) or warm (>11 $^{\circ}$ 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 and Persing, 2017). Under cool conditions (corresponding to early in the growing season), there is significantly less Fe coating removed from the IRIS than those deployed under warmer soil conditions (i.e., later in the growing season). In the case of Mn oxide IRIS coatings, although there was greater removal under warmer conditions, this effect was not statistically significant, probably owing largely 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 (i.e. documenting how much coating had been removed after 1, 2, 3 and 4 weeks) it is expected that temperature effects would have been significant for the Mn oxide coatings also, as laboratory studies have demonstrated that Mn coatings can be removed quite rapidly under saturated conditions, (Park and Rabenhorst, 2018; Dorau et al.,

These differences the soil terr than Fe coa state that N oxide stabil consistent v cool condit coating rem in the grow removal un owing large which confi included in and 4 week oxide coatin removed qu 2018).



Figure 1. Box and whisker plots for those study plots/dates where the hydrology requirement of the NTCHS TS was met (14 days continuous saturation within 25 cm of the soil surface) and which evaluated the effect of IRIS coating type (Fe vs Mn) and soil temperature group (5-11 °C vs 11-19 °C). Data that do not share the same letter designation are significantly different at the 95% level (based on analysis of Student's T 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 is always significantly more Mn than Fe coating removed. Under cool (i.e. early growing season) conditions, there is significantly less Fe coating removed than later in the growing season when soil temperatures are warmer.

Coating Removal and Implications for Thresholds

Using the recommended metric from the NTCHS for IRIS coating removal (i.e., median of five replicate IRIS 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/date met the hydrological requirement of the TS (14 day continuous saturation at a depth of 25 cm or shallower) (Fig. 2).

When soil temperatures are between 5 and 11 $^{\circ}$ C (i.e. 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 (Fig. 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% or more of the IRIS coating be 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".

Average Soil Temp 5-11 C

Average Soil Temp 11-19 C

20%

40%

60%

% Mn Coating Removed

80%

100%



continuous saturation within 25 cm) when a certain percentage of IRIS 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. Fe coating removal is shown in **a** and **b**; Mn coating removal is shown in c and d. The dashed red line (a and b) represents the current NTCHS requirement of 30% removal of Fe coating.

CCCDIC



Figure 3. Percentage of data sets that did (Wet) or did not (Not Wet) meet the TS 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 IRIS threshold for Fe or Mn coating removal when soil temperatures were cool (5-11 °C) or warm (11-19 °C). Fe coating removal is shown in **a** and **b**; Mn coating removal is shown in **c** and **d**. 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.

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 (Fig. 2b). This is likely because of greater microbial activity under warmer soil conditions. These data show that 90% of the plots with 10% or more removal of the Fe coating met the hydrological

requirement, and 95% of the plots with 30% or more removal of the Fe coating met the hydrological requirement. The current National Technical Committee guidance says 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 quite conservative such 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. Figure 3b, however, also illustrates that using a threshold of 30% optimally reduces assessment errors, especially 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 are between 5 and 11 °C there was significantly greater removal of Mn coatings (Fig. 2c) than Fe coatings (Fig. 2a and Fig. 1). 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% or more removal of the Mn coating met the hydrological requirement, and 100% of the plots with 30% or more 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%¹ removal of Mn-coated IRIS coatings may be an appropriate threshold. This is illustrated in Fig. 3c which demonstrates that using a Mn threshold of 20-30% would generate a very small percentage of cases that might be saturated.

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% or more removal of the Mn coating met the hydrological requirement, and 90% of plots with 90% or more 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.

The Need for Temperature-Adjusted IRIS Standards

¹ 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 Fig. 3c, using 20% would provide 95% confidence and using 30% would provide 100% confidence.

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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 perhaps seems reasonable for conditions when soil temperatures are warmer (average >11 °C), although one could argue that a threshold of 15 or 20% might better minimize errors or inconsistencies (Fig. 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 following 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 that by the time that 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 six years of data from a seasonally saturated wetland in Caroline County, MD, 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 going down while soil temperatures are coming up), 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.



Figure 4. Graphs of soil water table (top) and soil temperature (bottom) derived from six years of data at a site in Caroline county, MD that is representative of Mid-Atlantic seasonally saturated wetlands. The graphs represent generalized means +/- 2 standard deviations 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.

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 O₂ has been consumed, anaerobic conditions occurring in soils can result in the

reduction of NO3⁻ and Mn oxides even when conditions are not sufficient to cause reduction of ferric iron (Patrick and Jugsujinda, 1992). Both Mn oxide-coated IRIS and Fecoated 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, 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. Manganese-coated devices have particular utility early in the growing season when soil temperatures are cooler (<11 °C) but when 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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Table S1. Information on sites used in this study.

| | | | | | | | | | Der | | Deployments | | |
|------------------|-------|---------------------|------------------------|-------------------|----------|------------|--|--------------------------------------|-------|--------|-------------|-------|-----|
| | State | Site-Project Name 1 | Site-Project Name 2 | Relative Position | Latitude | Longitude | Soil Map Unit Name - Web Soil Survey | Nearest Soil Series | 20 | 2018 | | 2019 | |
| | DE | NE1438 | Blackbird | Low | 39.34723 | -75.67894 | Sassafras sandy loam, 5-10 percent slopes | Corsica | March | April | | | |
| | DE | NE1438 | Blackbird | Mid | 39.34723 | -75.67894 | Sassafras sandy loam, 5-10 percent slopes | Fallsington | March | April | | | |
| | DE | NE1438 | Blackbird | High | 39.34723 | -75.67894 | Sassafras sandy loam, 5-10 percent slopes | Woodstown | March | April | | | |
| | MA | NE1438 | | Low | 42.47603 | -72.58558 | Merrimac fine sandy loam, 3-8 percent slopes | | April | May | | | |
| | MA | NE1438 | | Mid | 42.47603 | -72.58558 | Merrimac fine sandy loam, 3-8 percent slopes | | April | May | | | |
| | MA | NE1438 | | High | 42.47603 | -72.58558 | Merrimac fine sandy loam, 3-8 percent slopes | | April | May | | | |
| | MD | AIO | Church View | | 39.0506 | -76.65606 | Shrewsbury loam, 0-2 percent slopes | | | | March | April | May |
| | MD. | NE1438 | Brookshire Woods | Low | 39.05758 | -75.82875 | Woodstown sandy loam, 2-5 percent slopes | Lenni | March | April | | | |
| | MD | NE1438 | Brookshire Woods | Mid | 39.05759 | -75.82858 | Woodstown sandy loam, 2-5 percent slopes | Hurlock | March | April | March | April | May |
| | MD | NE1438 | Brookshire Woods | High | 39.05757 | -75.82841 | Woodstown sandy loam, 2-5 percent slopes | Downer | March | April | | | |
| | MD | UMD Pedology | Forage Farm | Low | 39.26485 | -76.92965 | Hatboro-Codorus silt loams, 0-3 percent slopes | Codorus | March | April | | | |
| | MD | UMD Pedology | Forage Farm | Mid | 39.26483 | -76.92955 | Hatboro-Codorus silt loams, 0-3 percent slopes | Codorus | March | April | | | |
| • | MD | UMD Pedology | Forage Farm | High | 39.26476 | -76.92939 | Hatboro-Codorus silt loams, 0-3 percent slopes | Codorus | March | April | | | |
| - I | MD | UMD Pedology | OPE3 | Low | 39.02856 | -76.84113 | Zekiah and Issue soils, frequently flooded | Widewater | March | April | March | April | May |
| - I | MD | UMD Pedology | OPE3 | Mid | 39.02864 | -76.841 | Russett-Christiana complex, 2-5 percent slopes | Russett | March | April | | | |
| | MD | UMD Pedology | OPE3 | High | 39.02889 | -76.84127 | Downer-Hammonton complex, 5-10 percent slopes | Evesboro | March | April | | | |
| | MD | UMD Pedology | Plant Materials Center | Low | 39.00791 | -76.84713 | Elkton silt loam, 0-2 percent slopes | Elkton | March | April | March | April | May |
| | MD | UMD Pedology | Plant Materials Center | Mid | 39.00814 | -76.8478 | Russett-Christiana complex, 2-5 percent slopes | Elkton | March | April | | | |
| | MD | UMD Pedology | Plant Materials Center | High | 39.0077 | -76.84871 | Russett-Christiana complex, 2-5 percent slopes | Evesboro | March | April | | | |
| | PA | NE1438 | | Low | 40.70533 | -77.9288 | Buchannan extremely stony loam, 0-8 percent slopes | | April | May | | | |
| | PA | NE1438 | | Mid | 40.70533 | -77.9288 | Buchannan extremely stony loam, 0-8 percent slopes | | April | May | | | |
| | PA | NE1438 | | High | 40.70533 | -77.9288 | Buchannan extremely stony loam, 0-8 percent slopes | | April | May | | | |
| | RI | NE1438 | Great Swamp | Low | 41.4695 | -71.5784 | Scarboro mucky fine sandy loam, 0-3 percent slopes | Scarboro | April | May | | | |
| $\boldsymbol{<}$ | RI | NE1438 | Great Swamp | Mid | 41.4695 | -71.5784 | Scarboro mucky fine sandy loam, 0-3 percent slopes | Walpole | April | May | | | |
| | RI | NE1438 | Great Swamp | High | 41.4695 | -71.5784 | Scarboro mucky fine sandy loam, 0-3 percent slopes | Sudbury | April | May | | | |
| | VA | AIO | Grassland WA1 | | 39.06778 | -77.84303 | Scattersville silt loam, 0-7 percent slopes | | | | March | April | May |
| | VA | AIO | Grassland WC3 | | 39.06789 | -77.83998 | Scattersville silt loam, 0-7 percent slopes | | | | March | April | May |
| | VA | COE | BP | | 37.18998 | -76.46048 | Tomotley fine sandy loam | | | | March | April | May |
| | VA | COE | Stumpy | | 36.76381 | -76.17081 | Acredale silt loam | | | | March | April | May |
| | VA | COE | Woodards | | 36.66637 | -76.21198 | Arapahoe mucky fine sandy loam, 0-1 percent slopes | | | | March | April | May |
| | VA | COE | Woodville | | 37.32605 | -76.50052 | Meggett sandy loam | | | | March | April | May |
| · · · · · | VA | NE1438 | Big Pond | Low | 37.35831 | -80.43972 | Calvin very channery loam 15-35 percent slopes | Meckesville, very poorly drained var | April | May | | | |
| | VA | NE1438 | Big Pond | Mid | 37.35829 | -80.44009 | Calvin very channery loam 15-35 percent slopes | Meckesville, poorly drained var | April | May | | | |
| | VA. | NE1438 | Big Pond | High | 37.3583 | -80.44031 | Calvin very channery loam 15-35 percent slopes | Ungers, mod well drained var | April | May | | | |
| | W۷ | NE1438 | | Low | 38.25957 | -80.55817 | Clifftop channery silt loam, 3-15 percent slopes | | April | May | | | |
| | WV | NE1438 | | Mid | 38.25999 | -80.55811 | Clifftop channery silt loam, 3-15 percent slopes | | April | May | | | |
| | WV | NE1438 | | High | 38.25993 | -80.55827 | Clifftop channery silt loam, 3-15 percent slopes | | April | May | | | |
| | WY | NE1438 | | Low | 41.32366 | -106.41274 | NA | | July | August | | | |
| | WY | NE1438 | | Mid | 41.32366 | -106.41274 | NA | | July | August | | | |
| | WY | NE1438 | | High | 41.32366 | -106.41274 | NA | | July | August | | | |



Figure S1. Examples of Fe-coated (top) and Mn-coated (bottom) IRIS films following deployment. Note the light colored areas where the oxide coating has been stripped as a result of reduction and dissolution. The black line represents deployment depth at the soil surface.

rticle CCCC



Figure S2. Temperature (degrees C) evaluations. a - Data from those sites meeting the Technical Standard hydrology requirement, arranged in ascending order and plotted as ten point running averages of mean temperature vs the amount of Fe oxide coating removed from the IRIS films. b - Calculated p values for comparisons of Fe coating removal above and below a particular temperature threshold. The 11 degree threshold seemed to best differentiate colder vs warmer conditions as evidenced by the steep increase in coating removal up to 11 degrees (a) while the p value when comparing samples above and below 11 degrees remained very low (< 0.001) (b).