Indicator of Reduction in Soil (IRIS): Evaluation of a New Approach for Assessing Reduced Conditions in Soil

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ABSTRACT

Research and management of wetlands often requires the documentation of reducing soil conditions. Documentation of reduction in soils by measuring oxidation–reduction (redox) potentials using Pt electrodes is often difficult because of the time and cost involved in employing these techniques. This study evaluated a new procedure called Indicator of Reduction in Soil (IRIS) that has been recently developed to assist in the detection of reduced soil conditions. Polyvinyl-chloride (PVC) tubes coated with a ferrihydrite paint were inserted into the upper 50 cm of the soil for periods of 12 to 32 d. Soil redox potentials, water table height, and soil temperature were measured concurrently. Upon removal, the tubes were analyzed to assess the loss of ferrihydrite paint from the tube surface. When ferrihydrite paint was substantially depleted from 20% of the area of the IRIS tube, 87% of the observations at the corresponding depth indicated the soil was reduced. When ferrihydrite paint was substantially depleted from 30% of the area of the IRIS tube, essentially all of the soil observations at corresponding depths showed that the soil was reduced. Although not without complications, IRIS tubes appear to be a promising new alternative to traditional methods used to identify reducing conditions in soil.

H YDRIC SOILS are defined as those that "…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). Anaerobic conditions exist when oxygen has been depleted from the soil, causing heterotrophic microbes to act on electron acceptors other than oxygen to oxidize organic material.

Field indicators of hydric soil are used widely throughout the USA as a method of identifying hydric soils (USDA-NRCS, 2002). These indicators describe morphological features in soil that suggest saturation for sufficient time to maintain reduced conditions. Soil morphological features are a relatively permanent element in wetlands; however, there are particular settings where the soil and/or hydrology have been altered. In such cases where redoximorphic features indicative of the water table may not have had sufficient time to form, it is more difficult to determine whether or not a soil is hydric.

The National Technical Committee for Hydric Soils (NTCHS) established a technical standard to assist in adopting, modifying, or eliminating field indicators of hydric soils. In problematic soil settings, where field indicators may not be applicable, the technical standard can also be used in lieu of field indicators to identify hydric soils in the field. This technical standard includes requirements for saturation and redox potential (NTCHS, 2000). Soil redox potential measurements can be used to determine the electrochemical status of the soil and to predict which mineral species will be stable. For this method, according to the technical standard, at least five platinum (Pt) electrodes must be installed at a depth of 25 cm (12.5 cm for sands) (NTCHS, 2000). Measurements of soil redox potential, in combination with pH measurements, can be used to infer reduced conditions in hydric soils. The disadvantages of this method are the time and equipment necessary to make these measurements. Multiple redox potential measurements must be made throughout the year to document that the soil is reduced for 14 or more consecutive days.

An alternate method, using α, α'dipyridyl dye, can be employed to detect the presence of reduced iron [Fe(II)] in the soil and thus infer that the soil is reduced (USDA-NRCS, 2002). A positive reaction to α, α'dipyridyl dye is indicated by a pinkish-red color that appears in the presence of ferrous iron. To meet this criterion of the technical standard, there must be a positive reaction in 10 cm of the upper 30 cm for loamy soils (15 cm for sandy soils) in two out of three samples tested. In addition, a positive reaction must be observed at regular intervals within a 14-d period to conclude that this soil has been reduced for at least 14 consecutive days.

A new procedure was developed to monitor wet soil environments and document soil reduction. Jenkinson and Franzmeier (2006) introduced the use of IRIS devices that consist of PVC tubes coated with ferrihydrite paint. These tubes were installed in saturated and unsaturated soils in Indiana, North Dakota, and Minnesota. A significant correlation was found between depth to water table and removal of Fe(III) from the IRIS tubes. Iron(III) was removed from the tubes in locations where the soil was saturated by the seasonally high water table. The Fe(III) coating was left undisturbed in locations where the soil was unsaturated. The assumption was that the iron paint was removed or translocated in soluble form [Fe(II)] from the tube surface due to reducing conditions in the soil.

In this study, IRIS tubes were tested to evaluate their suitability for identifying reduced conditions in soils in the Mid-Atlantic region. It was postulated that the IRIS tubes might indicate where Fe was being reduced in the profile providing a simpler, more robust, and less time-

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Abbreviations: DCB, dithionite-citrate-bicarbonate; IRIS, Indicator of Reduction in Soil; MP, Middle Patuxent River; NTCHS, National Technical Committee for Hydric Soils; PVC, poly-vinyl chloride; RC, North Branch of Rock Creek; redox, oxidation–reduction; WCC, White Clay Creek; XRD, x-ray diffraction.

consuming approach than measuring redox potential. The objective of this study was to compare Fe oxide removal from IRIS tubes with soil redox potential measurements to assess the usefulness of IRIS tubes for confirming reduced soil conditions.

MATERIALS AND METHODS

Study Area

Three floodplains in the Piedmont physiographic region of Maryland and Delaware were selected as part of a larger study examining soil hydromorphology in these settings (Castenson, 2004). Two sites were located in Maryland on the Middle Patuxent River (MP) and the North Branch of Rock Creek (RC), and one site was located in Delaware on White Clay Creek (WCC). The sites were set up along transects from a ground water discharge wetland, across the floodplain toward drier soil nearer the natural levee of the river. The sites at the MP and RC contained three monitoring stations located in the wet, backswamp area (low), intermediate area (middle), and the drier area (high) of the floodplain. White Clay Creek contained an additional fourth monitoring station (low/mid) in the wet, backswamp area.

Field Procedures

Water table measurements were made twice daily using automated monitoring wells. Soil temperature was measured six times daily using soil temperature loggers installed 30 cm below the soil surface.

Soil redox potential was measured at all well locations every 2 to 3 wk. These measurements were made using six Pt electrodes inserted at five depths, 10, 20, 30, 40, and 50 cm below the surface. A pilot hole was made with a thin steel rod to ensure the Pt tip was not damaged when inserted into the soil.

The Pt tip was inserted into the hole and pressed to make solid contact with the soil. The electrodes were placed in a semicircle around the calomel reference electrodes maintaining <30 cm between the Pt and reference electrodes. Redox potentials were measured with digital multi-meters and calomel reference electrodes. Raw voltage measurements were converted to E_H by adding 244 mV.

To accurately compare soil conditions with E_H/pH stability diagrams, soil pH measurements were also made at the same intervals and depths as redox measurements. pH was measured in the field on a 1:1 soil/water slurry using a pH meter. Figure 1 shows E_H/pH stability diagram for selected Fe species (assumed Fe activity of 10^{-6} M). The solid line shows the line prescribed by the technical standard for hydric soils and is an empirically derived line. Points that plot below this line are considered to be reducing with respect to Fe.

Soil pits were excavated at each site near the well location, and soil profiles were described and sampled by horizon (Soil Survey Staff, 1996). Soil organic C was determined for each horizon via dry combustion with a LECO CHN-600 analyzer (LECO, St. Joseph, MI).

Preparation of IRIS Tubes

IRIS tubes were constructed based on the procedure established by Jenkinson (2002). A brief synopsis of the procedure follows with modifications from the original method discussed by Jenkinson.

Ferrihydrite paint was prepared by dissolving ferric chloride salt ($FeCl_3$) in distilled water. One molar KOH was added to raise the pH and precipitate the ferrihydrite. This solution was centrifuged and then placed in dialysis tubing to remove the salts. The viscosity of the paint suspension was adjusted by evaporation to that of oil paint. It was stored in an opaque plastic container at room temperature.
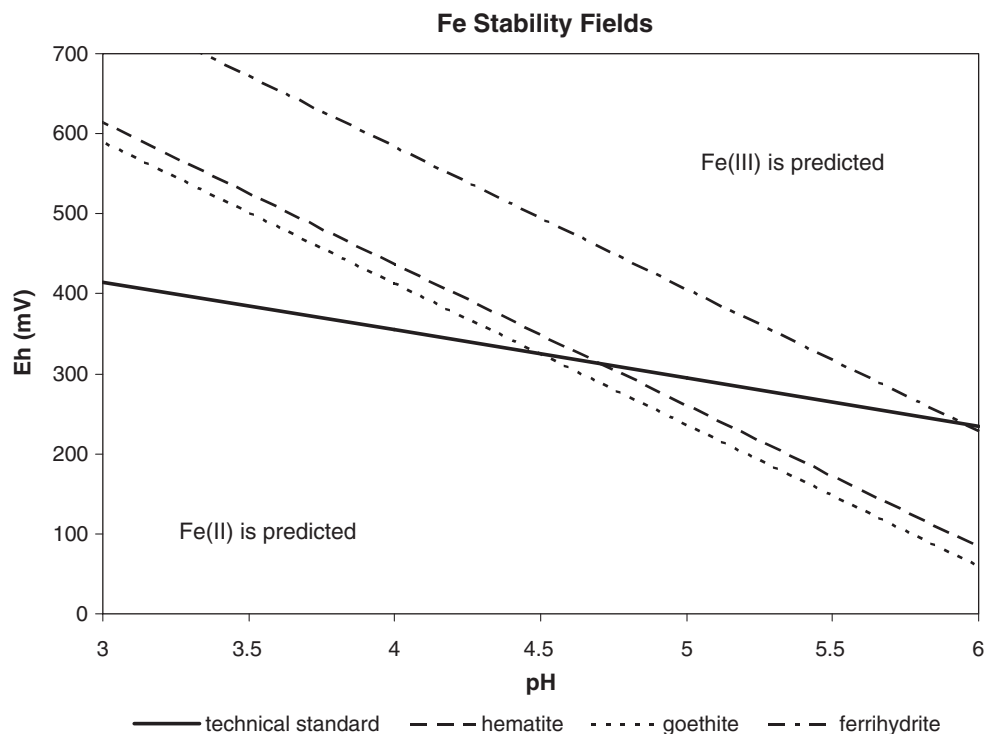
Fe Stability Fields

Fe(III) is predicted

Fe(II) is predicted

— technical standard   – – – hematite   · · · · goethite   – · – ferrihydrite

Fig. 1. E_H-pH diagram showing the stability fields for hematite (α Fe$_2$O$_3$), goethite (α FeOOH), and ferrihydrite (~Fe(OH)$_3$) [assumed Fe(II) activity 10^{-6}M] (Lindsay, 1979; Schwertmann and Cornell, 2000). Also plotted is the line adopted as part of the technical standard for hydric soils (National Technical Committee for Hydric Soils, 2000).
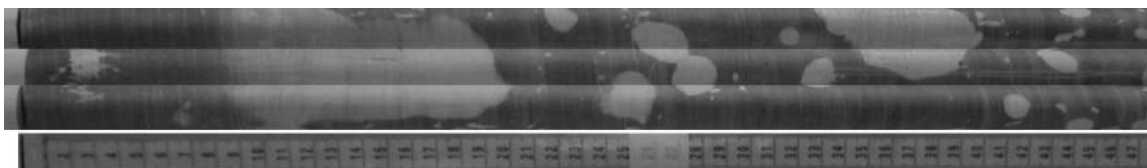
Fig. 2. Image displaying the removal of ferrihydrite paint from an IRIS tube from White Clay Creek (middle well) removed 23 June 2003. The top of tube is on the left; the scale is in centimeters.

The paint was analyzed to determine the mineralogy of the iron oxides present. Samples of the paint were dried and ground for analysis using x-ray diffraction (XRD)(Cu Kα). The XRD pattern indicated that goethite and another poorly crystalline iron mineral was present. Two broad peaks, typical of ferrihydrite, were identified (d-spacings around 0.254 and 0.149 nm). Samples of the paint were also extracted using dithionite-citrate-bicarbonate (DCB) (Loeppert and Inskeep, 1996) and acid ammonium oxalate (Schwertmann, 1964) to determine the dominant iron species (Soil Survey Staff, 1996). The DCB extracts essentially all the secondary Fe oxides while ammonium oxalate extracts the poorly crystalline Fe oxides, particularly ferrihydrite. The ratio of oxalate extractable Fe to DCB Fe was 0.7, suggesting that most (approximately 70%) of the total iron oxyhydroxide was in a poorly crystalline form, assumed to be ferrihydrite.

Polyvinyl chloride tubes, 2.1 cm o.d. (one-half inch schedule 40 PVC tubing), were cut into 60 cm lengths. Fifty centimeters of the tube were cleaned with acetone and lightly sanded using fine grit sand paper. Tubes were set on lathe type device and the ferrihydrite paint was applied to the sanded portion of the tube. Jenkinson (2002) suggested two coats of paint should be applied to each tube.

Preliminary data were collected before the beginning of this study. Tubes with two coats of paint were installed in backswamp areas while soil temperatures were low. Upon the removal of these tubes, the amount of Fe removed from the tube was not substantial. Therefore, it was decided that the remainder of the study be conducted using tubes painted with a single coat. Thus approximately 25 of the initial tubes were given two coats and the remainder of the 150 tubes received one coat. In hindsight, low soil temperature appeared to be the reason for the lower percentage of Fe removal from the initial tubes with two coats of paint, and it is expected that tubes with either one or two coats would have produced similar results.

IRIS Tube Procedures

Beginning in March 2003, duplicate IRIS tubes were installed at each well location. A 22-mm (0.875 in.) diam. push probe was used to make a pilot hole so the tube could be inserted into the soil with minimal abrasion while ensuring soil contact. Tubes remained in the field for between 12 and 32 d before removal (mean 20 d; median 22 d). The redox potential was measured on the dates the tubes were installed and removed. Upon removing a set of tubes, another set was immediately inserted into new holes. The removed tubes were partially cleaned of soil in the field and returned to the lab for additional cleaning.

All IRIS tubes removed from the soil were labeled and gently rinsed with tap water to remove any adhering soil material. Three digital photos were taken of each tube following 120° rotation. These photos were then cropped and joined with a photo of a tape measure (cm) to form a single image of the whole surface of the tube. Figure 2 shows an image of an IRIS tube removed on June 23 from the middle well at White Clay Creek.

For analysis, tubes were divided into five 10-cm sections corresponding to the five depths at which redox potential and pH were measured. Using published figures designed for esti-mating percentage of aerial coverage for comparison (Stoops, 2003), visual estimates were made of the percentage of tube area from which substantial ferrihydrite paint had been depleted. It should be noted that sometimes the zones where the Fe paint was reduced and stripped were nearly clean of Fe oxide and in some cases the zones retained a thin coating of Fe oxide but were distinctly contrasting from the original reddish brown color. When the zones where the paint had been stripped or depleted constituted <5% of the area, estimates were made to the nearest 1%. When the zones where the paint had been stripped or depleted constituted more than 5% of the area, estimates were made to the nearest 5%.

RESULTS AND DISCUSSION

The technical standard equation for E_H-pH was used to determine if the soil was reduced or oxidized (National Technical Committee for Hydric Soils, 2000) in each 10-cm zone. Each 10-cm soil section was placed into one of four groups based on the soil E_H and pH when the tubes were installed and removed. These groups were: (1) reduced at installation, reduced on removal; (2) oxidized at installation, oxidized on removal; (3) reduced at installation, oxidized on removal; and (4) oxidized at installation, reduced on removal.

Table 1 shows the total number of 10-cm sections that were observed in each of the four groups. The sections in

Table 1. Number of IRIS tube sections (10 cm) observed in each of four groups based on whether the soil was oxidizing or reducing at the times when the tubes were inserted and removed.

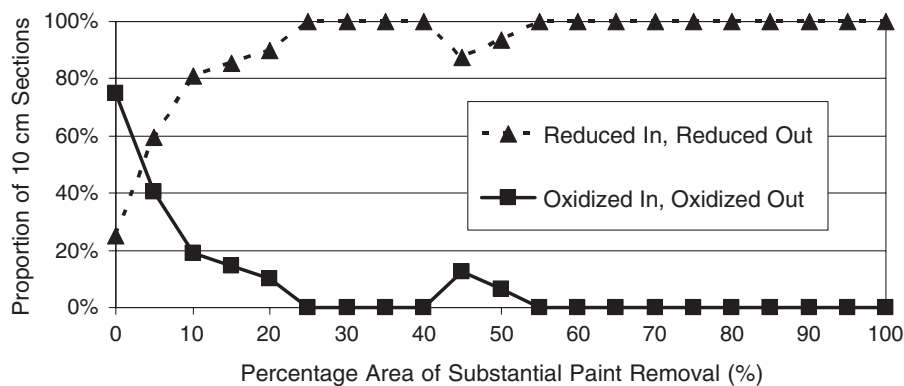| % of area from which substantial removal of ferrihydrite paint occurred	IRIS tube sections			
	Group 1	Group 2	Group 3	Group 4
	reduced in, reduced out	oxidized in, oxidized out	reduced in, oxidized out	oxidized in, reduced out
	number of observations			
0	32	95	1	0
5	71	48	5	3
10	43	10	4	2
15	29	5	0	2
20	18	2	2	2
25	8	0	0	1
30	21	0	2	3
35	7	0	2	0
40	15	0	0	2
45	7	1	1	0
50	14	1	0	1
55	12	0	0	0
60	8	0	0	1
65	18	0	2	0
70	10	0	0	0
75	11	0	1	0
80	8	0	0	0
85	13	0	0	0
90	25	0	1	1
95	52	0	1	0
100	11	0	0	0
Total	433	162	22	18

Fig. 3. Proportion of 10-cm sections of IRIS tubes observed in soils that were reducing (dashed) or oxidizing (solid) versus the percentage of the IRIS tube area from which substantial iron oxide paint has been removed.

Groups 3 and 4 were difficult to interpret since reducing conditions were observed on only one of the two dates. These data show that there are relatively few instances (40 of 635) when the soil zones were oxidizing on one date and reducing on the other. Because we could not be assured that these soil zones were either reduced or oxidized during the period that the tubes were in the soil, these ambiguous data were removed from further analyses. If the soil zone was either reducing or oxidizing on both dates, it was considered to be reducing or oxidizing respectively during the period that the tubes were in the soil.

The data from Groups 1 and 2 are presented in Fig. 3 as a percentage of number of observations made when a given portion of the ferrihydrite paint was removed. Seventy five percent of the instances where no ferrihydrite paint was removed from the IRIS tubes occurred in soils that were oxidizing.

When as little as 2% of the ferrihydrite was removed, the soil conditions were reducing 50% of the time. Figure 3 demonstrates that as more of the ferrihydrite paint was removed, the observation of reducing soil conditions increased so that when 10% of the ferrihydrite was removed, the soil was reducing more than 80% of the time. Utilizing the data in Fig. 3, one could predict whether reducing soil conditions occur. Using a threshold of 10, 20, or 30% ferrihydrite removal to predict the occurrence of reducing soil conditions would result in an error (the soil being oxidizing rather than reducing) in 19, 13, and 0% of the time, respectively.

Somewhat surprisingly, there were 32 observations (25%) where there was no ferrihydrite removed from the tubes although the soils were reducing with respect to the Technical Standard (Table 1). Figure 4 presents the soil organic C distributions for the upper meter in the sites studied. The median value for organic C in the upper 50 cm was 14.6 g kg^{-1} and the minimum value observed was 4.0 g kg^{-1}. Therefore, it would appear that organic C was not a particularly limiting factor in these soils. Rather, cool soil temperatures and the length of time the tubes were in the soil may have been the cause for this occurrence. Figure 5 shows that the soil temperatures during the beginning of the study period were low and were even below 5°C, which some have referred

to as biological zero (Rabenhorst, 2005). In general, less ferrihydrite paint was removed earlier in the season when the soil temperatures were lower and more was removed later when the soil temperatures were warmer. If the soil was not warm enough for microbes to actively reduce the ferrihydrite, or if the tubes were not in the soil for a long enough period of time, the paint would not be removed from the tube (Rabenhorst and Castenson, 2005).
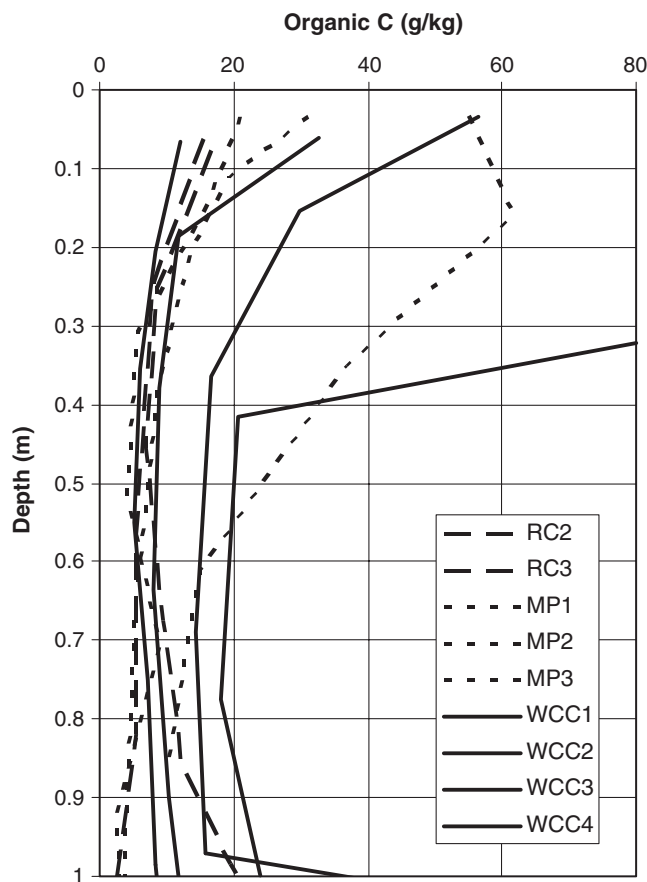

Fig. 4. Soil organic C content in the upper meter of the study sites. Within the zone where IRIS tubes were installed (0–50 cm), the median organic C content is 14.6 g kg^{-1} and the minimum value is 4.0 g kg^{-1}.

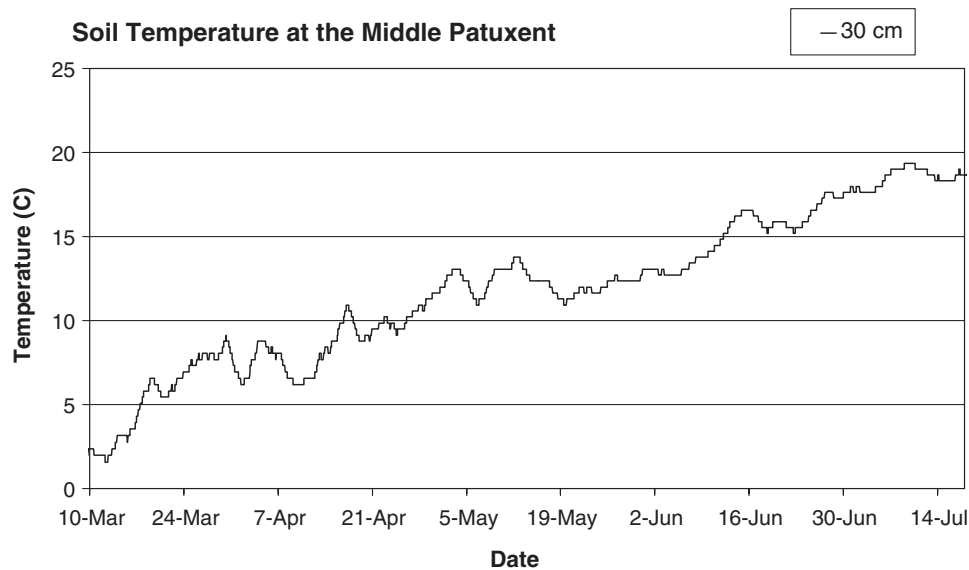**Soil Temperature at the Middle Patuxent**

Fig. 5. **Soil temperature at the Middle Patuxent River site over the period of study. Data at the other two sites were very similar to these data. Soil temperatures range between 2 and 20°C.**

In contrast to the instances where the redox potentials were low but no ferrihydrite was removed, there were observations where the soil was determined to be oxidizing but there were substantial zones where the iron oxide paint was removed from a section. One possible explanation for this may be microsite variability in the soil. Because a Pt redox electrode measures the potential in only a small area of soil, the tube surface may have intercepted a more reducing zone. Alternatively, reducing conditions of short duration may have occurred in the soils but were not recorded on the dates that the E_H was measured. Also, some of the variability observed in this study is likely due to not using a standard time period for deploying the tubes in the soil.

CONCLUSIONS

Indicator of reduction in soil tubes appears to be a useful tool in the identification of reduced soil conditions. A relationship exists between soil redox potential and the amount of iron oxide paint removed from the tubes. If after a tube is installed in the soil for a period of approximately 3 wk, 20% of the ferrihydrite paint is removed within a 10-cm section of the tube, one can conclude that that the soil is reducing (according to the redox potential criteria for the technical standard for hydric soils) with a high level of confidence (87% of observations). If 30% of the ferrihydrite is removed, then one can be even more confident that the soil is reducing (essentially 100% of observations). Removal of lesser amounts of ferrihydrite paint under reducing conditions, and removal of small amounts of paint in soils deemed to be oxidizing, suggests that some complications remain unresolved. Among other possible issues, future work should focus on understanding temperature and temporal effects on rates of ferrihydrite removal.

REFERENCES

Castenson, K.L. 2004. Hydromorphology of piedmont floodplain soils. M.S. thesis. Univ. of Maryland, College Park, MD.

Federal Register. 1994. Vol. 59. No. 133. July 13. p. 35680.

Jenkinson, B. 2002. Indicators of reduction in soils (IRIS): A visual method for the identification of hydric soils. Ph.D. dis. Purdue Univ., West Lafayette, IN.

Jenkinson, B.J., and D.P. Franzmeier. 2006. Development and evaluation of Fe-coated tubes that indicate reduction in soils. Soil Sci. Soc. Am. J. 70:183–191.

Lindsay, A.L. 1979. Chemical equilibria in soils. John Wiley & Sons, New York.

Loeppert, R.H., and W.P. Inskeep. 1996. Iron. p. 639–664. *In* D.L. Sparks et al (ed.) Methods of soil analysis. Part 3. SSSA Book Ser. 5. SSSA and ASA, Madison, WI.

National Technical Committee for Hydric Soils. 2000. Technical note 11: Technical standards for hydric soils. Available online at: http://soils.usda.gov/use/hydric/ntchs/tech_notes/ (verified, 28 Feb. 2006).

Rabenhorst, M.C. 2005. Biologic zero: A soil temperature concept. Wetlands 25:616–621.

Rabenhorst, M.C., and K.L. Castenson. 2005. Temperature effects on iron reduction in a hydric soil. Soil Sci. 170:734–744.

Schwertmann, U. 1964. The differentiation of iron oxide in soils by a photochemical extraction with acid ammonium oxalate. Z. Pflanzenernaehr. Dueng. Bodenkund. 105:194–201.

Schwertmann, U., and R.M. Cornell. 2000. Iron oxides in the laboratory: Preparation and characterization. 2nd ed. Wiley-VCH, New York.

Soil Survey Staff. 1996. Soil survey laboratory methods manual. Soil survey investigations report No. 42 (version 3.0). USDA-NRCS. U.S. Gov. Print. Office, Washington, DC.

Stoops, G. 2003. Guidelines for analysis and description of soil and regolith thin sections. Soil SSSA, Madison, WI.

USDA-NRCS. 2002. Field Indicators of Hydric Soil in the United States. Ver. 5.0. G.W. Hurt et al. (ed.) USDA, NRCS, Fort Worth, TX.