

## TEMPERATURE EFFECTS ON IRON REDUCTION IN A HYDRIC SOIL

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For soils to be considered hydric, they must demonstrate both saturation and anaerobic conditions in the upper part of the soil. Although several technologies are available for monitoring of soil water tables, documentation of reducing conditions is more problematic. This has led to recent interest in the use of IRIS (indicator of reduction in soils) tubes. IRIS tubes are lengths of PVC pipe coated with ferrihydrite paint, which are inserted into the soil to document reducing conditions. Observations from preliminary studies led us to postulate soil temperature will affect the degree and rate of reduction and removal of ferrihydrite from the IRIS tubes. To quantify the impact of soil temperature on ferrihydrite reduction and removal from IRIS tubes, a time series experiment was designed such that IRIS tubes were placed into a hydric soil for time periods ranging from 7 to 28 days, between February and June, 2004. Water tables were monitored daily, Eh was measured at depths of 10, 20, 30, 40 and 50, cm on a weekly basis, and soil temperature was recorded every 4 hours. Removal of ferrihydrite from IRIS tubes was not constant during periods of anaerobiosis and was related to soil temperature. At temperatures below 2 °C, there was essentially no measurable ferrihydrite reduction, even though soil redox potentials fell within the Fe(II) stability field. As soil temperatures increased between 2 and 8 °C, the quantity of ferrihydrite reduction increased with time. At soil temperatures between 8 and 20 °C, substantial (35% to 45%) ferrihydrite paint was reduced and removed from IRIS tubes within 7 days. For a given temperature, there was greater reduction of ferrihydrite in zones closer to the soil surface, presumably due to higher amounts of oxidizable organic matter in near surface horizons. (Soil Science 2005;170:734-742)

**Key words:** Wetlands, anaerobic soils, biologic zero, IRIS (Index of Reduction in Soils).

**I**N wetland science or the study of wetland soils, there are numerous instances in which reducing conditions in soils need to be documented. For example, in the construction and restoration of wetlands during mitigation projects, there may be requirements to demonstrate that the wetlands are functioning as such and are developing reduced conditions in soils. A second example in which reducing conditions must be documented is in the identification or delineation of wetlands where hydric soils must be observed. Commonly, hydric soils are identified by using approved morphological field

indicators (USDA-NRCS, 2003), but some hydric soils lack field indicators. In cases in which field indicators are lacking, the soil must be shown to meet the definition of a hydric soil by conforming to the specifications spelled out in the Technical Standard for Hydric Soils (TS) (National Technical Committee for Hydric Soils, 2000). In its essence, the TS requires that a soil be both saturated and reducing. A third instance in which reducing conditions in soils must be documented is in cases in which Field Indicators for Hydric Soils are being evaluated or where new indicators are being developed. These also require that those conditions specified in the TS be met.

Two commonly used approaches to documenting reducing conditions in soils are (1) to measure Eh and pH using Pt electrodes and to

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TABLE 1  
Abbreviated morphological description of the soil located at the study site

Horizon	Depth cm	Textural Class	Color	Redox Concentrations	Redox Depletions
A	0–10	Silty clay loam	10YR 4/3	10% 2.5YR 3/6	25% 2.5Y 4/1
Bg1	10–25	Silt loam	2.5Y 5/2	18% 7.5YR 5/8	
Bg2	25–79	Silt loam	2.5Y 5/2	10% 2.5YR 3/6	
Agb1	79–94	Silty clay loam	2.5Y 3/1	8% 2.5YR 3/6	
Agb2	94–114	Loam	N 2/	5% 5YR 4/4	
2Agb3	114–140	Fine sandy loam	N 2/	1% 2.5Y 6/4	
2Agb4	140–161	Fine sandy loam	N 2/		
2Cg	161–178	Loamy fine sand	40% N 5/ 60% 10YR 5/1		

show that these plots below the line for the equation  $Eh = -60 \cdot pH + 595$  or (2) to obtain a positive test when alpha, alpha dipyrindyl dye is applied to the soil (National Technical Committee for Hydric Soils, 2000). Both approaches have certain limitations or difficulties (Faulkner et al., 1989). Measurement of redox potential in the field requires equipment often not available to wetland science practitioners, and lack of familiarity with the methodology may make it unappealing. Alpha, alpha dipyrindyl dye, which tests for the presence of ferrous iron in solution, involves the use of hazardous chemicals not readily available to field scientists. Both tests are also limited in that they provide only a documentation of conditions at the time of sampling. These difficulties and limitations have led to an interest in simpler alternatives.

One simpler approach is the use of steel rods inserted into the soil (Owens, 2001). The theory behind this approach was that the rods would become coated with Fe oxides within the oxidizing portion of the soil but would remain uncoated or “clean” in the reducing portion. Uncertainties associated with the dynamics of

both oxidation and reduction of iron from the rods has led to uncertainties in interpreting data from the rods. Recently, an alternative approach has been proposed by Jenkinson (2002) in which PVC tubes coated with ferrihydrite paint are inserted into the soil to document reducing conditions. Where the soil is saturated and microbes are actively oxidizing soil organic matter, causing reducing conditions, the ferrihydrite is removed from the tube. These have been called IRIS (indicator of reduction in soils) tubes. Initial testing of the tubes appears promising (Castenson, 2004; Jenkinson, 2002), although observations have led to further questions in correctly interpreting the data. Our operating hypothesis is that those factors that affect the development of anaerobic conditions in soils also will affect the degree and rate of Fe oxide removal from the IRIS tubes. During a previous study, it was anecdotally observed that there were greater amounts of the ferrihydrite paint removed from IRIS tubes later rather than earlier in the spring (Castenson, 2004). Therefore, one factor that we postulated would affect iron removal from IRIS tubes is soil temperature.

TABLE 2  
Selected laboratory data\* for the soil located at the study site

Horizon	Sand %	Silt %	Clay %	pH	C <sub>T</sub> g/kg	Fe <sub>d</sub> g/kg	Fe <sub>o</sub> g/kg	CEC NH <sub>4</sub> OAc cmol/kg	BS NH <sub>4</sub> OAc %
A	4.5	68.2	27.3	5.4	42.9	28	15.1	17.9	39
Bg1	3.0	71.1	25.9	4.7	17.2	28	12.1	11.1	28
Bg2	3.0	71.4	25.6	5.1	15.0	21	9.2	10.4	23
Agb1	11.7	58.9	29.4	4.8	48.1	11	5.7	19.2	19
Agb2	42.9	32.1	25.0	4.9	99.4	4	4.4	30.8	29
2Agb3	55.2	26.4	18.4	5.4	54.6	2	1.4	18.8	40
2Agb4	56.9	24.7	18.4	5.7	39.0	1	0.8	14.7	47
2Cg	77.9	15.4	6.7	5.9	4.2	tr	0.2	3.2	47

C<sub>T</sub> = Total C; Fe<sub>d</sub> = Dithionite, citrate, buffer extractable Fe; Fe<sub>o</sub> = acid ammonium oxalate extractable Fe; CEC NH<sub>4</sub>OAc = CEC by ammonium acetate plus extractable acidity; BS NH<sub>4</sub>OAc = Base Saturation based on the ammonium acetate CEC.

\*- Analyses for these data were conducted by the USDA-NRCS National Soil Survey Laboratory, Lincoln, NE.

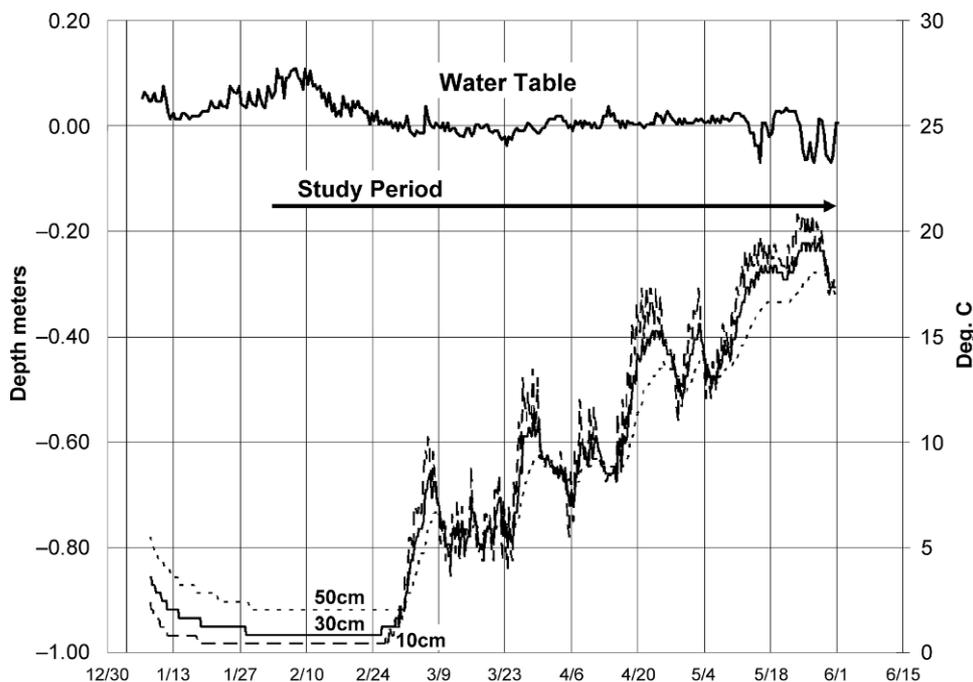


Fig. 1. Water table level and soil temperature measurements made at the study site during the winter and spring of 2004. The study period ran from February 3 through May 31.

The objective of this study was to determine the effect of soil temperature on the removal of ferrihydrite paint from IRIS tubes in a hydric soil.

#### METHODS

We sought a site that would be both saturated and reducing over a time period of several months, during which time the soil temperature

might vary. This would allow the study of temperature effects with minimum complications from other factors. The site selected was a discharge slope wetland on the edge of the flood plain of the North Branch of Rock Creek in Montgomery County, Maryland. This site has been studied during previous investigations (Castenson, 2004), and the soil has been sampled and characterized by the National Soil Survey

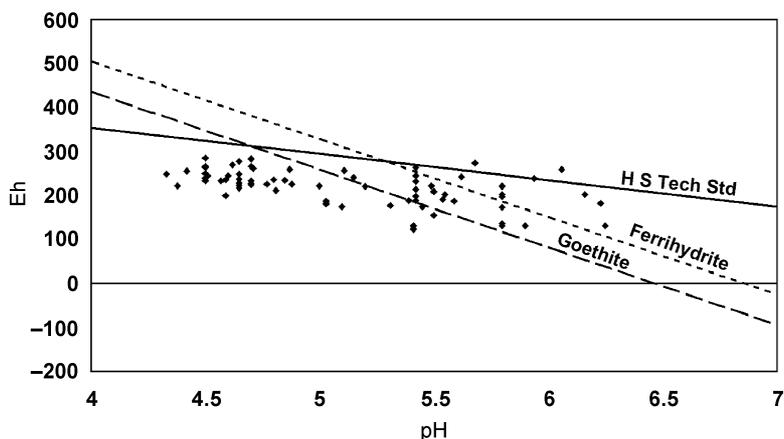


Fig. 2. Redox data measured during the study are plotted on an Eh-pH stability diagram on which have been plotted lines for the Hydric Soil Technical Standard and for ferrihydrite and goethite (assumed Fe(II) activity  $10^{-6}M$ ). Note that only two data points plot above the technical standard line.

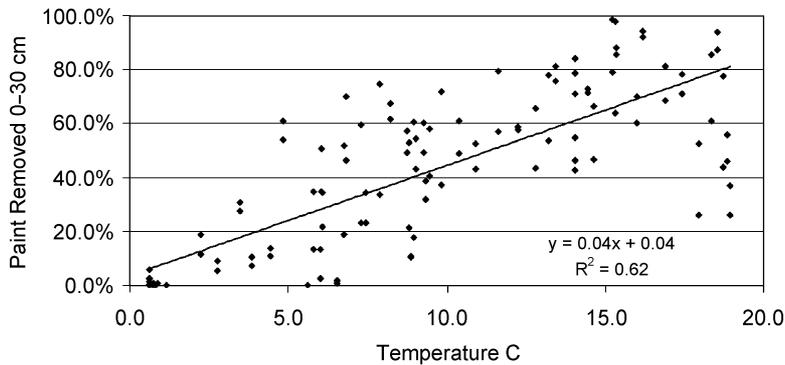


Fig. 3. Percentage of ferrihydrite paint removed from the upper 30 cm of the IRIS tubes as a function of average temperature during times when redox measurements showed that the soil was reducing.

Lab in Lincoln, Nebraska (Soil Survey Staff, 1996). The soil is a fine-silty mixed mesic Typic Fluvaquent and fits within the range of characteristics for the Hatboro soil series. An abbreviated soil description and selected soil characterization data are presented in Tables 1 and 2. The site was instrumented to measure the water table twice daily, using an automated recording well. Temperature loggers were installed at depths of 10, 30, and 50 cm, and soil temperatures were measured 6 times per day. Soil temperatures at 20 and 40 cm were estimated by interpolation. Redox measurements were made weekly at the site by using 6 replicate Pt electrodes installed at depths of 10, 20, 30, 40, and 50 cm. Soil pH was measured at the same time and at the same depths where Eh was measured. The pH was measured with the use of a portable meter with a combination electrode on samples collected by extracting a small (2 cm) core.

IRIS tubes were prepared in a manner similar to the approach of Jenkinson (2002), as de-

scribed below. One-half-inch schedule No. 40 PVC pipe (actual outside diameter, 0.84 inch or 21.3 mm) was cut into 60-cm lengths. The tubes were cleaned and lightly sanded using a very fine (No. 400) grit sandpaper to improve adhesion of the paint to the tubes. Ferrihydrite paint was prepared according to Jenkinson (2002) by adding 1M KOH to a 0.5M solution of  $\text{FeCl}_3$  to precipitate the iron oxyhydroxide. Salts were removed by centrifugation and dialysis, and the paint was then evaporated to the proper consistency (similar to that of oil paint). The lower 52 cm (approximately) of each tube was covered with a single coat of ferrihydrite paint. A reference line was drawn on each tube 50 cm from the bottom to indicate the depth to which the tubes were to be inserted.

Beginning on February 3, 2004, each week, 4 pairs of IRIS tubes (8 tubes per week) were inserted into pilot holes made in the soil, using a 1-inch push probe. Pairs of tubes were removed after they had been in the soil for 7, 14, 21, and 28 days. The experiment was concluded

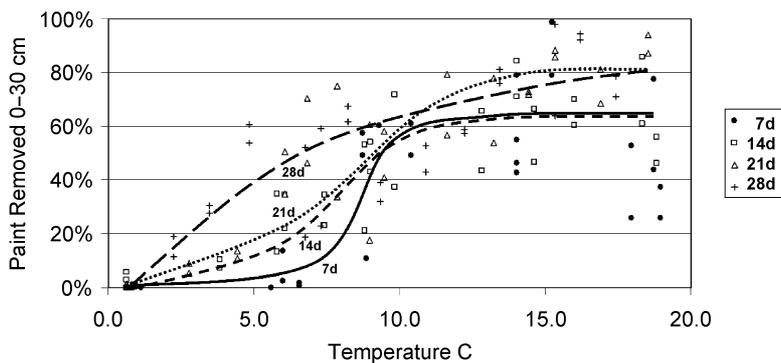


Fig. 4. Removal of ferrihydrite paint from the upper 30 cm of the IRIS tubes as a function of average temperature and time.

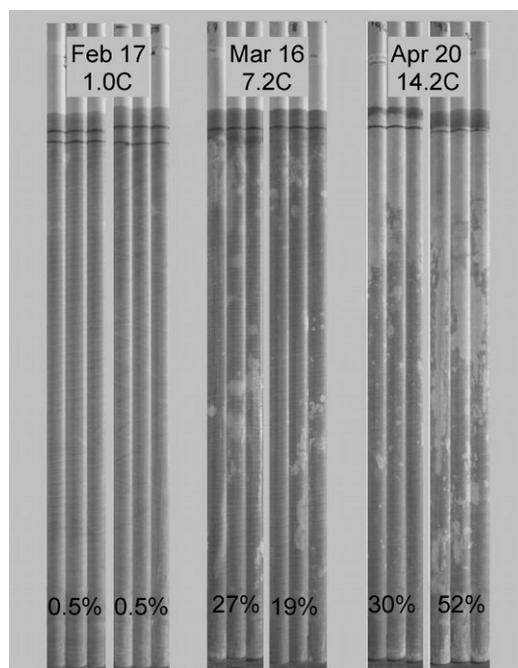


Fig. 5. Scanned images of pairs of IRIS tubes that had been in the soil for 14 days. Average soil temperatures at 30 cm for tubes installed on February 17, 2004, March 16, 2004, and April 20, 2004 were 1.0, 7.2, and 14.2 °C, respectively. Values printed at the bottom represent the percentage of ferrihydrite paint removed, indicating that removal becomes more pronounced as soil temperatures become warmer.

on June 1, 2004, after 17 weeks. After extraction, each tube was gently rinsed to remove adhering soil and was then photographed 3 times, with the tube rotated 120° between photos. The three photos were then cropped and combined into a single digital image of each tube. Digital images of the tube were imported into a freeware image analysis package in which the area of iron paint removal was calculated. For the purpose of analysis, the image of each tube was subdivided into five 10-cm sections that corresponded to the five depths where Eh and pH were measured (0 to 10, 10 to 20, 20 to 30, 30 to 40, and 40 to 50 cm).

## RESULTS AND DISCUSSION

According to the TS, for a loamy soil to be hydric, it must be both saturated and reducing within the upper 25 cm for a period of 14 consecutive days (National Technical Committee for Hydric Soils, 2000). Saturation is documented by the presence of the water table. During the study period, the water table at the

site ranged from +10 cm to -7 cm of the soil surface (Fig. 1); therefore, from the standpoint of the TS, the soil was saturated in the upper part. For a soil to be reducing, redox measurements must plot below the line defined by the equation  $Eh = -60 \text{ pH} + 595$ . This is an empirically derived line that corresponds to positive tests to the presence of Fe(II) in solution using alpha, alpha dipyridyl dye. This line corresponds closely with the ferrihydrite-Fe(II) stability line in the vicinity of pH 5 to 5.5, although the slope is one-half that of the ferrihydrite and goethite lines. Of all the redox measurements made during the study, there were only two points (30 and 40 cm on February 10) where the data plotted above the Eh/pH line defined in the TS (Fig. 2). Thus, with the exception of these two depths on that single date, the soil was considered to be reducing throughout the duration of the study. Therefore, those few data that included these two points when the soil was not reducing were removed from the analyses.

Because the zone of primary interest in identifying loamy hydric soils is the upper 30 cm (USDA-NRCS, 2003), some analyses focused on this zone. When all data from the study were included, the magnitude of the removal of ferrihydrite paint from the upper 30 cm of the IRIS tubes increased steadily with increasing temperature within the range of 1 to 19 °C (Fig. 3). Some of the scatter in the data in Fig. 3 is related to soil variability but some is related to differences in the length of time that the IRIS tubes were in the soil. At temperatures below 6 or 7 °C, there was very little removal of ferrihydrite from the tubes during a 7-day period (Fig. 4), but even at these low temperatures, paint was increasingly removed over periods of 14, 21, and 28 days. At temperatures above 8 °C, the percent removal of ferrihydrite paint is mostly more than 40% to 50%, and the effects of time are less pronounced. Fig. 5 shows scanned images of three pairs of IRIS tubes that had been placed in the soil for 14 days. The average soil temperatures at 30 cm for the 14-day period after installation of the IRIS tubes on February 17, 2004, March 16, 2004, and April 20, 2004, were 1.0, 7.2, and 14.2 °C, respectively. It is evident from examining the tubes that ferrihydrite paint removal becomes more pronounced as soil temperatures become warmer.

Ferrihydrite paint removal from the tubes during a 7-day period is illustrated in Fig. 6. During the first 7 days, there is very little

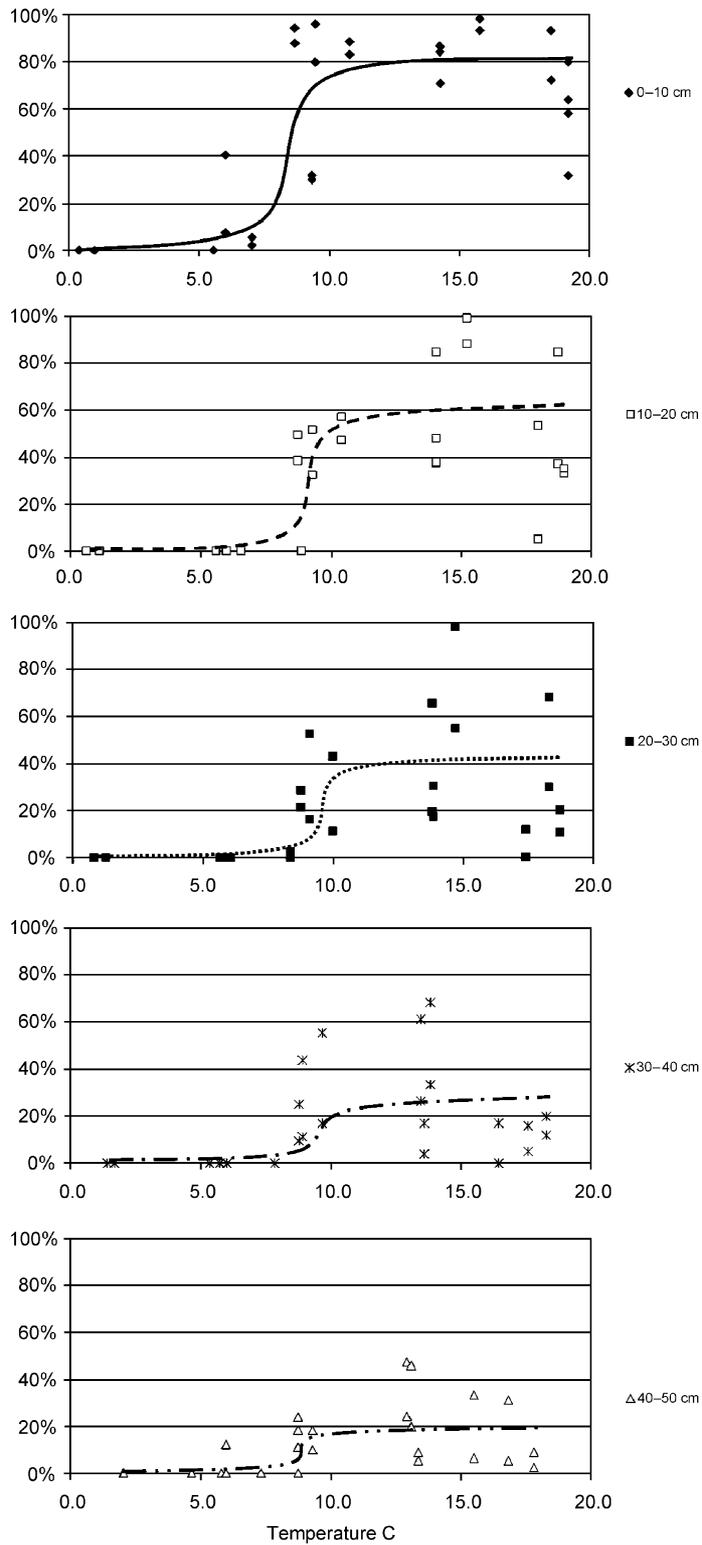


Fig. 6. Ferrihydrite paint removed from IRIS tubes as a function of average temperature and depth from the soil surface during a 7-day period.

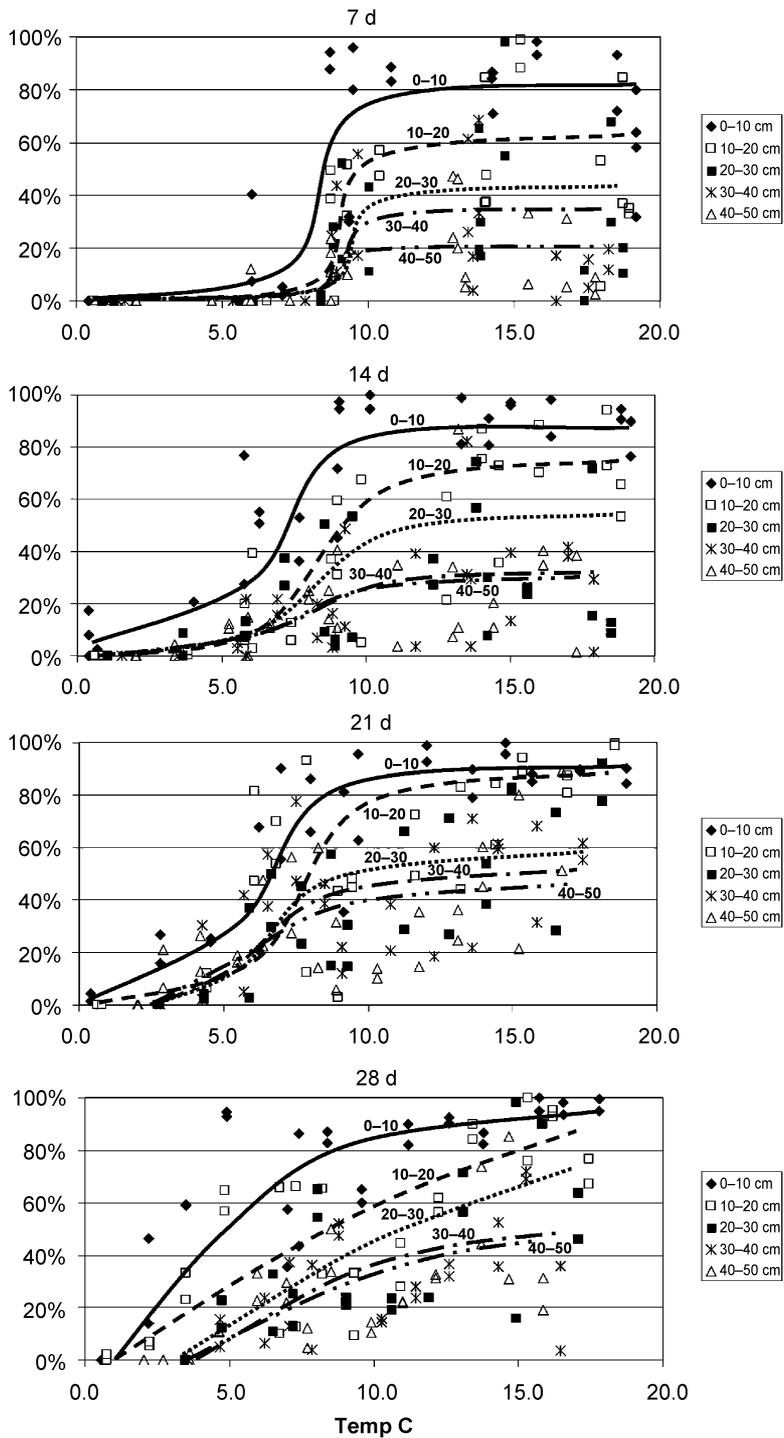


Fig. 7. Ferrihydrite paint removed from IRIS tubes as a function of average temperature and depth from the soil surface after installation periods of 7, 14, 21, and 28 days.

removal of paint at temperatures below approximately 8 °C. At temperatures warmer than this, removal of the paint becomes evident, although

there is considerable variability in the quantity of paint removed. Nevertheless, at a given temperature, there is greater reduction of the

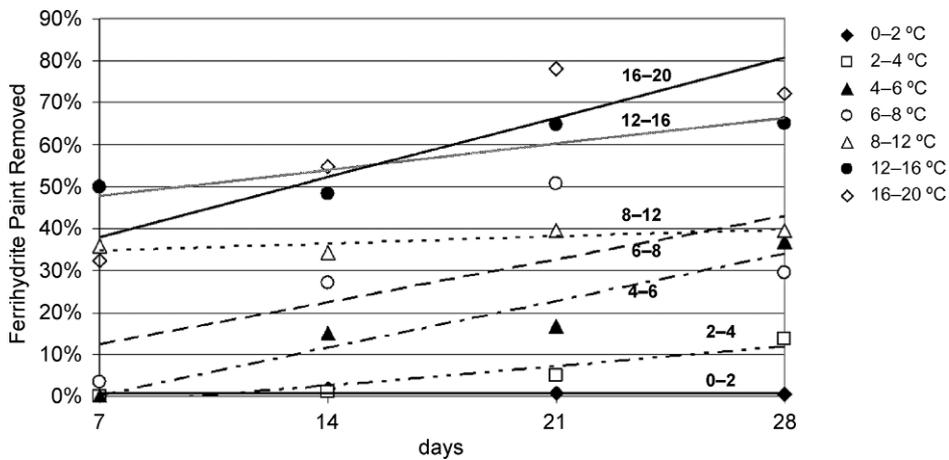


Fig. 8. Average ferrihydrite removed over time from IRIS tube sections grouped by soil temperature. Effect of time on ferrihydrite removal is most pronounced when the soil temperature is between 2 and 8 °C.

ferrihydrite (removal of paint) in zones closer to the soil surface. Because the reduction of Fe oxihydroxides is mediated by heterotrophic microbes as they oxidize soil organic matter, the higher quantities of total organic C nearer to the surface, and that decrease regularly through the Bg horizons (Table 2), may explain why there is greater reduction nearer to the soil surface at a given temperature.

The increased reduction of ferrihydrite paint over longer periods of time (14 to 28 days) becomes most evident at temperatures below 8 °C (Figs. 7 and 8). At temperatures <2 °C, there was almost no paint removed, even after 28 days. However, at temperatures between 2 and 8 °C, reduction and removal of paint increased regularly both with temperature and with time. This suggests that in this temperature range, reduction of the ferrihydrite paint is limited by temperature that controls rates of microbial metabolic activity. It has been suggested that mesophilic microbes become inactive at temperatures below 5 °C, sometimes referred to as biological zero (Rabenhorst, 2005). These data show that ferrihydrite reduction occurs at temperatures lower than 5 °C (down to 2 °C), but at a slower rate than at warmer soil temperatures. When soil temperatures were >8 °C, the effect of time (beyond 7 days) was less pronounced on reduction of the ferrihydrite paint. This suggests that under warmer conditions, there are factors other than temperature that limit the reduction of ferrihydrite paint, such as the abundance of easily oxidizable (active) soil C. In addition, there are probably some physical

constraints associated with this particular experimental arrangement leading to diminishing removal of paint as it is reduced and stripped from the tubes.

## CONCLUSIONS

During periods of reducing conditions in soils, ferrihydrite painted on IRIS tubes is removed, presumably through reduction and dissolution caused by heterotrophic microbes using Fe(III) as an electron acceptor while oxidizing soil organic matter. The reduction of the ferrihydrite is dependent on soil temperature, with faster rates occurring under warmer conditions. At temperatures below 2 °C, there was no measurable ferrihydrite reduction, even though the soil data fell within the Fe(II) stability field based on Eh-pH diagrams. At soil temperatures between 2 and 8 °C, the amount of ferrihydrite reduced increased steadily during the period from 7 to 28 days. Also within this same temperature range, the quantity of ferrihydrite that was reduced increased steadily as the soil temperature warmed. When soil temperatures were >8 °C, substantial (35% to 45%) ferrihydrite paint was reduced and removed from IRIS tubes within the first 7 days, and relatively little additional was removed during the succeeding 21 days. For a given temperature, the rate of Fe paint removal is greater near to the soil surface than at depth, presumably due to higher amounts of oxidizable organic matter in near surface horizons. Further analysis and testing, particularly in other pedological settings,

will be needed before a detailed protocol for IRIS tube use can be prescribed.

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