# Saturation and Temperature Effects on the Development of Reducing Conditions in Soils

**Karen L. Vaughan***
USDA-NRCS
245 Jimmy Doolittle Rd.
Salt Lake City, UT 84116

**Martin C. Rabenhorst**
**Brian A. Needelman**
Dep. Environmental Science and Technology
Univ. of Maryland
1109 H.J. Patterson Hall
College Park, MD 20742

Oxidation-reduction (redox) reactions regulate many chemical processes that occur in soils. Saturation, C availability, microorganisms, and temperature dictate the rate and type of redox reactions that will occur. The measurement of redox potential enables researchers to predict the stability of redox-sensitive species, such as Fe oxides. We determine the amount of time Mid-Atlantic Piedmont floodplain soils must be saturated at a given temperature before becoming reduced with respect to ferrihydrite. Three representative floodplains in Maryland and Delaware were selected for this study. Redox potential, pH, temperature, and depth to water table were measured in six profiles over a 2-yr period. At lower temperatures, longer periods of saturation were required to induce soil reduction with respect to ferrihydrite ($p < 0.0001$). The soils were reduced with respect to ferrihydrite after the soils were saturated for 2 to 20 d depending on the 14-d average soil temperature ranging from 1 to 21°C. When the soil temperature was between 1 and 3.9°C, saturation was required for 20 d before the onset of reducing conditions. At 4 to 6.9°C, 11 d of saturation were required, while at 7 to 8.9°C, 7 d of saturation were required. When the soil temperature was above 9°C, reduction occurred after approximately 2 d. This investigation reveals the importance of considering soil temperature when relating length of saturation to reduction, specifically pertaining to floodplain soils in the Mid-Atlantic Piedmont physiographic province.

S oil redox potential is an estimate of electron activity and is used to predict the electrochemical stability of redox sensitive species. The potential is measured between a Pt-tipped electrode and a reference electrode that are both placed in contact with a soil. Soils with more reducing conditions transfer a relatively negative charge to the Pt electrode, while soils with more oxidizing conditions transfer a relatively positive charge.

Redox potential in soil is influenced by a number of factors including temperature, microbial activity, and the presence of various electron acceptors, such as oxygen, nitrate, Mn oxides, and Fe oxides (Ponnamperuma, 1972). Soils with oxygen present due to either the absence of saturation or oxyaquic conditions have relatively high redox potentials (Soil Survey Staff, 1999). When soil is saturated with stagnant water, oxygen is depleted from the soil environment during microbial decomposition of organic matter and electrons may then be transferred to alternate electron acceptors such as $NO_3^-$, $Mn(IV)$ or $Fe(III)$. These microbially mediated reactions are slower at cooler temperatures (Atlas and Bartha, 1987; Paul and Clark, 1996), while greater C abundance leads to increased microbial activity and therefore more rapid reduction.

The National Technical Committee for Hydric Soils (NTCHS) definition states that a hydric soil is "… a soil that formed under conditions of saturation, ponding, or flooding long enough during the growing season to develop anaerobic conditions in the upper part" (Federal Register, 1994). The initial part of this definition specifies that soil pores are filled with water. The "long enough" portion communicates the length of time necessary for the saturated conditions to persist. This is commonly understood as 5% of the growing season (Environmental Laboratory, 1987). "Growing season" is defined as the portion of the year when soil temperature at 50 cm below the surface is above biologic zero, or the temperature at which the growth and function of locally adapted plants are negligible (Soil Survey Staff, 1975; Soil Survey Staff, 1999; Rabenhorst, 2005). "Anaerobic conditions" occur when oxygen has been depleted from the system, though often the reduction of Fe(III) to Fe(II) is used as an indicator of anaerobic conditions. Finally, "the upper part" refers to the upper 30 cm of a soil for loamy soils, or the upper 15 cm for sandy soils (Vepraskas and Sprecher, 1997).

In an anaerobic environment, microorganisms utilize alternate electron acceptors in the following order: N, Mn, Fe, S, $CO_2$, and H (Ponnamperuma, 1972). The redox potential at which Fe(III) is reduced to Fe(II), the mobile, aqueous phase, is of significant interest in soils. Iron is generally abundant and exists in numerous oxy-oxyhydroxide minerals that act as coloring agents in most soils. Zones where Fe oxides accumulate are termed redox concentrations and appear to stain the soil in various shades of red, orange, and brown. Areas of reduced and depleted Fe are termed redox depletions and are gray in color corresponding to the uncoated mineral grains (Vepraskas, 1992).

Ferrihydrite is among the most common Fe minerals formed in soils with fluctuating groundwater and where there is an abundance of organic material that prohibits more crystalline iron

oxides from forming (e.g., in wetlands) (Bigham et al., 2002). This poorly crystalline Fe oxide is widespread in wetland soils and characteristic of recent iron oxide accumulations. It forms well-aggregated spherical particles that maintain a high specific surface area. Ferrihydrite is a short-range ordered mineral with the bulk formula of $Fe_5HO_8 \cdot 4H_2O$, although several other formulas have been suggested (Schwertmann and Taylor, 1989).

Measured soil redox potential can be compared with the $E_H$–pH phase stability diagrams for minerals to determine which phases are predicted to be thermodynamically stable in the soil environment. When the measured redox potential is above the Fe(II)-thermodynamic equilibrium boundary of ferrihydrite, the soil is oxidized with respect to that couple and ferrihydrite would be expected to be stable. Alternatively, when the redox potential is below the line, the soil is reduced with respect to that couple and ferrihydrite would be expected to become reduced to Fe(II).

Redox potential is a measure of the dynamic and complex soil environment that may contain various phases of redox sensitive species. As a result, both Fe(II) and Fe(III) will likely exist, as well as other species, so that the redox potential is a measure of the overall or mixed voltage in the soil. Iron oxides are generally abundant in soils and most soil redoximorphic features are associated with the segregation (depletion and concentration) of iron oxides. Therefore, reduction of iron is generally linked to the hydric soil concept of "anaerobic." As a result, if the soil redox potential is below the stability line for Fe(II)-ferrihydrite, that soil would be considered anaerobic and meeting that part of the hydric soil definition.

The measurement of soil redox potential is time-consuming, must be taken at least biweekly to document soil reduction, and requires equipment that is often unavailable or too costly for practitioners. It has been suggested that inferences regarding reducing conditions in soils be made from water table measurements alone (He et al., 2003). The depth to water table may be measured using either an automated recording well or a simple open well that, once installed, requires little time and effort to maintain. Past water table data is often available at study sites, whereas redox potential data rarely are. Because microbial processes are affected by temperature, we would expect that soil temperature would also affect the time within which saturated soils become anaerobic. Soil temperature can be estimated from widely available air temperature data (Hillel, 1982; Marshall and Holmes, 1988; Wu and Nofziger, 1999), therefore, soil temperature need not be directly measured. Rather, an improved understanding of the relationship between soil saturation, redox potential, and temperature can elucidate the form of redox sensitive species. The objectives of this research were to document the height and duration of water tables and redox potentials in Mid-Atlantic Piedmont floodplain soils, and to better understand the relationship between length of saturation, soil temperature, and soil redox potentials in these systems. Using these data, we will establish a statistically sound relationship between saturation period and reduction of ferrihydrite as a function of soil temperature.

## MATERIALS AND METHODS
### Study Area

Three representative floodplains were selected on the Mid-Atlantic Piedmont physiographic province in Delaware and Maryland. These sites were chosen based on their low likelihood of human disturbance as well the presence of characteristic floodplain features, including a backswamp wetland and a natural levee. The study sites are situated along the North Branch of the Rock Creek in Montgomery County, Maryland, the Middle Patuxent River in Howard County, Maryland, and the White Clay Creek in New Castle County, Delaware. These are active floodplains with overbank floods occurring in approximately 1 out of 2 yr (Dillow, 1996).

Codorus (Fine-loamy, mixed, active, mesic Fluvaquentic Dystrudepts) and Comus (Coarse-loamy, mixed, active, mesic Fluventic Dystrudepts) soils were identified on the largest portions of these floodplains with Hatboro (Fine-loamy, mixed, active, nonacid, mesic Fluvaquentic Endoaquepts) soils located in the wettest backwater portions of the floodplains near to where the water discharges from the steep upland into the floodplain system (Brown and Dyer, 1995; Matthews and Lavoie, 1970; Matthews and Hershberger, 1968). Soil textures within the upper meter at the three floodplain sites range from silt loam to loam with 8 to 18% clay. The dominant vegetation consists of red maple (*Acer rubrum* L.), pin oak (*Quercus palustris* Münchh.), green ash (*Fraxinus pennsylvanica* Marshall), spicebush (*Lindera benzoin* [L.] Blume), Virginia knotweed (*Polygonum virginianum* L.), and skunk cabbage (*Symplocarpus foetidus* [L.] Salisb. ex W. P. C. Barton).

Two monitoring sites (A and B) were set up on each floodplain to include seasonally saturated soils ranging from hydric soils on the wet margin to better drained non-hydric soils on the drier margin. Figure 1 is a schematic depiction of the site layout. A total of six monitoring sites were established on the three floodplains: three on hydric soils located upgradient of the groundwater discharge wetland toward the natural levee and three on somewhat better drained non-hydric soils located closer to the natural levee of the river (Fig. 1).

### Field Procedures

This study was conducted between November 2001 and November 2003. Depth to water table was logged twice daily using automated recording wells installed to a maximum depth of 1.5 m. The data stored in these wells were offloaded approximately every 3 mo. Simple open bore holes adjacent to the wells were used to confirm accurate readings and to calibrate the automated wells.

Soil redox potential was measured using Pt electrodes adjacent to the wells at depths of 10, 20, 30, 40, and 50 cm at each of the six monitoring stations biweekly during the wet season (February through June) and monthly during the dry season (July through January). Six replicate measurements were made at each depth. To protect the Pt-tipped electrode, pilot holes were made using a 3-mm metal rod inserted to the appropriate depth. The redox electrodes were then inserted into the pilot hole so that the Pt-tip was placed in
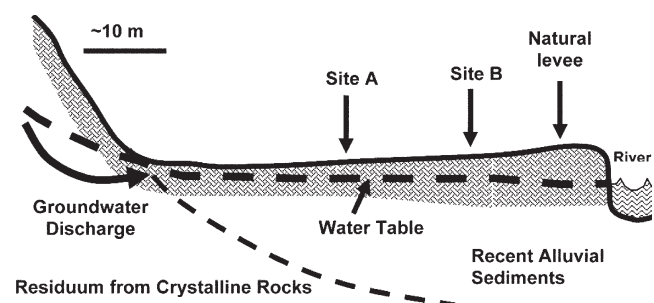


Fig. 1. Schematic of a Piedmont floodplain. Site A is the monitoring station located in a hydric soil upgradient of the groundwater discharge wetland and the natural levee. Site B is the monitoring station in a non-hydric soil closer to the natural levee.

contact with the soil. Calomel reference electrodes were used and a correction of 244 mV was applied to adjust the raw voltage measurements to $E_H$. The equipment was installed before and removed following each measurement of redox potential. Redox electrodes were manufactured and obtained from Jensen Instruments in Tacoma, WA, and were regularly tested for accuracy using a redox standard solution suggested by Light (1972).

Soil pH was measured adjacent to the wells at the same intervals and depths as redox potential. A soil corer with a diameter of 1.6 cm was used to extract a soil sample. This soil was made into 1:1 slurry with deionized water and allowed to equilibrate for 15 min. A pH meter was used to record the pH of this mixture in the field.

Temperature data were collected four times daily using Hobo XTI dataloggers (Onset Computer Corp., Bourne, ME) placed in waterproof polycarbonate containers that were installed at depths of 10, 30, and 50 cm. Soil temperature at 20 and 40 cm was estimated by linear interpolation using the measurements at 10 and 30 cm and 30 and 50 cm, respectively. Soils were sampled by horizon and analyzed for total C by dry combustion using a LECO CHN-600 analyzer (LECO Corp., St. Joesph, MI).

## Data Analysis

To determine whether or not the soil was anaerobic or reducing, the measured redox potential and the pH of the sample were compared with the $E_H$–pH stability line (equilibrium boundary) for ferrihydrite (assumed Fe activity of $10^{-6}$ M) (Lindsay, 1979; Cornell and Schwertmann, 2003). The equation for this equilibrium boundary for ferrihydrite is $E_H = 936.9 - 59\log$ [Fe (II)] $- 177$pH. The difference between each observed datum and the stability line was calculated by subtracting the voltage on the ferrihydrite stability line (in mV) based on the specified pH, from the measured $E_H$ value of each datum. If the computed difference in $E_H$ was >0, the soil datum was above the line and was considered oxidized with respect to ferrihydrite. Conversely, if the computed difference was <0, the datum was below the line and the soil was considered to be reduced with respect to ferrihydrite.

Length of time that a soil zone was saturated was calculated by examining the water table record and determining the number of consecutive days that the water table was at or higher than a particular depth (Fig. 2). If the water table dropped lower than 2 cm below this depth for two consecutive measurements (one full day) the length of saturation was restarted at zero days. Single measurements of unsaturated conditions were excluded to account for capillary action, which can maintain saturated soil conditions several centimeters above the water table (Gillham, 1983). Data were classified by average soil temperature for the 14 d before the date of redox potential measurement using four classes: 1–3.9, 4–6.9, 7–8.9, and greater than 9°C.

The redox potential values relative to the ferrihydrite stability line were plotted against the number of days of continuous saturation, which permitted us to estimate the length of the saturation period before the onset of anaerobic conditions with respect to ferrihydrite.

A multiple regression was performed to determine the statistical significance of temperature, saturation period, and the interaction between temperature and saturation period for the prediction $E_H$ values relative to the ferrihydrite stability line.

## RESULTS AND DISSCUSION

Greater than 90% of the six-replicate redox measurements had a standard error of <40 mV, while greater than 80% had a
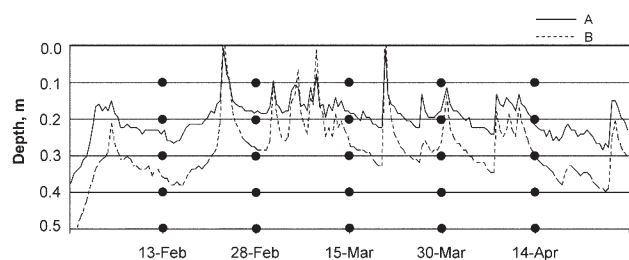
Number of days saturated at the Middle Patuxent River site on select dates in 2003.

| Depth | 13-Feb | | 28-Feb | | 15-Mar | | 30-Mar | | 14-Apr | |
|---|---|---|---|---|---|---|---|---|---|---|
| (cm) | A | B | A | B | A | B | A | B | A | B |
| 10 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 20 | 0 | 0 | 12 | 0 | 27 | 0 | 4 | 0 | 7 | 0 |
| 30 | 13 | 0 | 28 | 8 | 43 | 23 | 58 | 4 | 73 | 7 |
| 40 | 125 | 12.5 | 140 | 27.5 | 155 | 42.5 | 170 | 57.5 | 185 | 72.5 |
| 50 | 126 | 14.5 | 141 | 29.5 | 156 | 44.5 | 171 | 59.5 | 186 | 74.5 |

Fig. 2. Explanation of how saturation time was determined using water table data. Black points on the graph represent the location of redox measurements in the soil. The solid and dotted lines are the water table height at Site A and B respectively along the Middle Patuxent River in 2003. The tabular data shows the number of days the soil was saturated at the various depths and sites for explanation purposes. Soil saturated for longer durations than displayed on the graph (125–186 d) were calculated using continuous water table data collected before January 29 and cannot be discerned directly from this graph.

standard error of <30 mV. The median standard error was 14 mV with many of the higher standard errors being recorded from redox potentials that were measured in soils in the transition zone between reduced and oxidized conditions. Redox potential followed a general trend inversely related to water table height.

Soil pH showed minor fluctuations of <0.5 pH units between periods of reduction and oxidation. When the soils were reducing, the pH increased slightly. When the soils were oxidized, the pH generally decreased by less than a half pH unit. Soil pH ranged from as low as 3.5 in organic rich surface horizons to 5.7 in all samples measured with a median of 4.7.

Saturation period, temperature, and redox potential were significant at $p < 0.0001$. Measured redox potentials were affected by saturation period and temperature and the effect of saturation period was different as soil temperature fluctuated. Temperature and saturation period both significantly effected $E_H$ values relative to the ferrihydrite stability line ($p < 0.0001$). In addition, the effect of saturation period was different at different temperatures ($p < 0.0001$). Soil temperature varied between 1 and 21°C during the period of study (Fig. 3). Previous
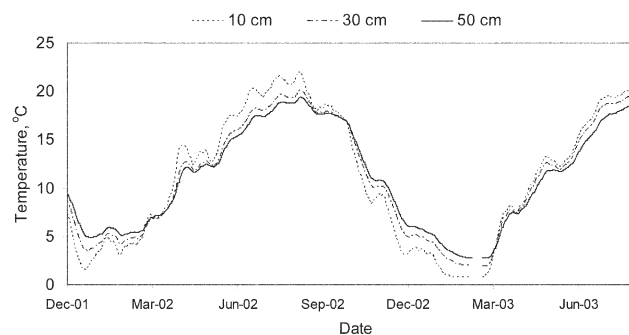
Fig. 3. Typical soil temperature profile shown by data collected at the Middle Patuxent River site. Soil temperature profiles at the North Branch of Rock Creek and White Clay Creek sites were similar to this profile.
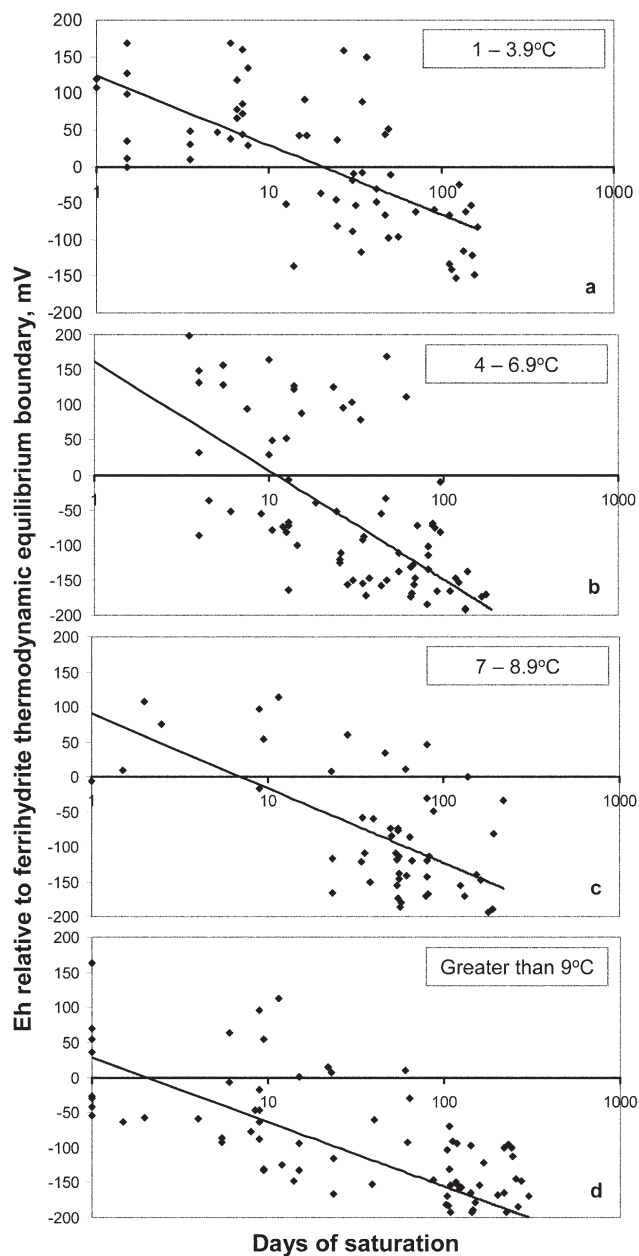
**Fig. 4. Redox measurements of soils with an average temperature of (a) 1 to 3.9°C (mean 3.0°C), (b) 4 to 6.9°C (mean 5.1°C), (c) 7 to 8.9°C (mean 8.0°C), and (d) >9°C (mean 13.5°C) as a function of the length of time the soil had been saturated when the redox measurement was made. For each redox measurement made, its Y position was calculated in reference to the thermodynamic equilibrium boundary of ferrihydrite $\{E_H = 936.9 - 59\log [Fe (II)] - 177pH\}$, based on the measured soil pH. The magnitude in the difference between each observed datum and the equilibrium boundary was calculated by subtracting the equivalent point on the ferrihydrite line (in mV) from the measured $E_H$ value of each datum. The data less than 0 mV are considered reduced with respect to ferrihydrite.**

work by Rabenhorst and Castenson (2005) demonstrated that at temperatures below approximately 9°C, microbial reduction of Fe in wetland soils was positively related to soil temperature, but at temperatures above approximately 9°C, there was no additional increase in microbial reduction with increased temperature. Data in this study were analyzed after grouping into four temperature classes: 1 to 3.9, 4 to 6.9, 7 to 8.9, and >9°C.

When the soil temperature was 1 to 3.9°C (average temperature for all points measured was 3.0°C), approximately 20 d of saturation were required for the redox potentials to drop below the ferrihydrite stability line (Fig. 4a) based on where the best fit least squares line crosses the x-axis at 0 mV. The variability observed in the data was likely related to variation in temperature and also to soil C content. The levels of soil organic C (within the upper 50 cm of the six soils studied among three sites) ranged from 4 to 33 g kg$^{-1}$, and this variability likely affected rates of microbially mediated reduction. The data set, however, was not large enough to also assess the specific effect of soil carbon on the rates at which reducing conditions developed. When the soil temperature was 4 to 6.9°C (average temperature for all points measured was 5.1°C), approximately 11 d of saturation were required for the soils to be reduced with respect to ferrihydrite (Fig. 4b) (again based on the best fit least squares line). Less time was required for reduction in this temperature class than in the 1 to 3.9°C class likely due to increased microbial activity at warmer temperatures. When the soil temperature was 7 to 8.9°C (average temperature for all points measured was 8.0°C), approximately 7 d of saturation were required before ferrihydrite reduction was predicted (Fig. 4c). Lastly, when the soil temperature was >9°C (average temperature for all points measured was 13.5°C), only approximately 2 d of saturation were necessary before the onset of reduction with respect to ferrihydrite (Fig. 4d).

Similar studies have shown that soil influenced by saturation events lasting 18 to 21 d developed considerable redoximorphic features as well as reduction with respect to Fe (Vepraskas et al., 2004; He et al., 2003). The period of saturation required to reduce Fe, is referred to as the lag time. At 15-cm below the soil surface with soil temperatures of 10°C, a lag time of 18 d was required to develop Fe-reducing conditions in soils in North Carolina. At 30- and 60-cm depths, with soil temperatures of 10 and 9°C respectively, 13 d of saturation were required to develop Fe-reducing conditions. This study did not specifically attempt to determine the influence of soil temperature, rather their approach involved using historic precipitation data to model the periods of saturation that lead to the development of redoximorphic features (Vepraskas et al., 2004). Alternatively, our research attempts to determine the saturation time required for Fe reduction while the soil temperature fluctuates throughout the year.

Although there was considerable scatter among the plots owing to variations in soil C content, range in temperatures included in each class, variation in soil temperatures contributing to each 14-d average, and inherent natural soil heterogeneity in $E_H$ measurements; a general trend was observed where under warmer conditions saturated soils become reducing more quickly than when soil temperatures are cooler. This is illustrated in Fig. 5 where values of x-intercepts from Fig. 4 are compiled and fit with an exponential equation. This figure demonstrates the relationship between soil temperature and the number days the soils were saturated before they became reducing. At temperatures of approximately 9 or 10°C and below, there is a strong inverse relationship between soil temperature and the length of time necessary for a saturated soil to become anaerobic. As soil temperatures increased above approximately 9 or 10°C, the effect of temperature is less dra-

matic with soils requiring only a few days of saturation before becoming reduced with respect to ferrihydrite. These trends agree with observations in similar soils where IRIS tubes were used to assess the effect of temperature on the development of reducing soil conditions (Rabenhorst and Castenson, 2005).

## CONCLUSIONS

Based on the observations of this study, measurements of water tables and soil temperature can be used to estimate the likelihood of reducing conditions in soils located on Mid-Atlantic Piedmont floodplains. At temperatures of approximately 9 or 10°C or greater, the onset of reducing conditions generally proceeds rapidly (within a few days) and the lag time between soil saturation and the onset of reducing conditions is minimal. These conditions typically occur between the first of April and the end of October, for the Maryland Piedmont region. During periods of cooler soil temperatures, from November through March, saturated soils take longer to become reducing. Our observations indicate that saturated soils will become reducing even at temperatures below 5°C, which has been cited as biological zero (Rabenhorst, 2005), but require longer periods to do so. Approximately 20 d of saturation were required for the onset of reducing conditions when the soil temperature averaged 3.0°C, whereas approximately 11 and 7 d of saturation were required when the soil temperature averaged 5.1 and 8.0°C, respectively. Many environmental factors, such as water table dynamics and soil organic C content, likely contributed to variability within this field data set. Because this relationship was developed using data from soils on a specific physiographic province and landscape position (Mid-Atlantic Piedmont floodplains), it should not be extrapolated to other areas without further testing.

## ACKNOWLEDGMENTS

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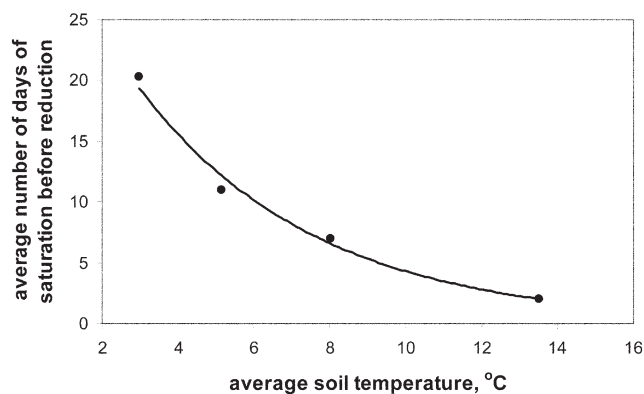
Fig. 5. Summary of the relationship between the average soil temperature and the number of days the soils were saturated before the onset of reducing conditions with respect to ferrihydrite. Soil temperature is inversely proportional to the number of days of saturation required for the reduction of ferrihydrite, but the exponential function illustrates that the effect of temperature is more pronounced at lower temperatures (below 8 to 10°C) and less pronounced when the soil is warmer (above 8 to 10°C).

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