

ABSTRACT

ZELASKO, AMANDA JEAN. Soil Reduction Rates Under Water Saturated Conditions in Relation to Soil Properties (Under the direction of D.L. Hesterberg and M.J. Vepraskas).

The success of wetland restoration projects depends in part on the length of time that a soil is in a reduced redox state. This time depends on how quickly reduction occurs following saturation with water, and is termed the reduction rate. The relationship between reduction rate and various soil chemical and mineralogical properties is poorly understood, but such properties might be manipulated to improve the success of wetland restoration projects. The goals of this research were to determine soil properties that predict the rate at which soils undergo reduction when saturated, and to determine the roles of electron donors and acceptors on reduction rates. Sixteen soil samples were collected at various depths from two wetland sites, a Carolina bay (Juniper Bay) and a wetland catena (Frog Level). Samples were incubated in specially designed redox incubators to monitor reduction rates, changes in soil properties, and soil solution chemistry. Samples were subjected to three cycles of oxidation and reduction during the course of 36 d. Soil reduction rates were determined from the slopes of linear regression models fit to data for redox potential (Eh) over time. Reduction rates varied among soils from 1.2 to 46.2 mV h⁻¹, and were significantly greater in soils with total organic carbon (TOC) ≥ 27 g kg⁻¹ than in soils with TOC < 27 g kg⁻¹. Increasing amounts of dissolved Fe(II) were found at Eh values below 500 mV for pH between 4.5 and 5.1. Reduction rates were best correlated to amount of TOC using a linear plateau model where reduction rate increased up to a TOC level of 27

g kg⁻¹ and stabilized at 38.7 mV h⁻¹ ($r = 0.82$). A multiple linear regression model including TOC and initial soil pH ($R^2 = 0.49$) also showed promise in predicting soil reduction rates. The linear plateau model between reduction rate and TOC, or the multiple linear regression model, can be used along with hydrologic data to predict the frequency and duration that soils meet hydric criteria.

SOIL REDUCTION RATES UNDER WATER SATURATED CONDITIONS IN RELATION TO SOIL PROPERTIES

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DEDICATION

I would like to dedicate this thesis to my wonderful fiancé, Perry Morris who has helped support me throughout my endeavors as a student. Your encouragement has been the driving force behind my success in life. Most importantly you helped me to maintain a healthy balance of work and play by making sure I enjoyed my weekends and vacations. I would also like to dedicate this thesis to my family in Southern Illinois. All of you have been supportive toward my education despite your desires for me to be closer to home. Lastly, I would like to dedicate this to my grandpa who puts an extra plate out for me every week for his Wednesday morning family breakfast despite my absence. No matter where my life journey takes me, Southern Illinois will always be my home.

BIOGRAPHY

Amanda Jean Zelasko, daughter of Robert and Mary Zelasko, was born and raised on a small family farm near DuBois Illinois. Amanda has one older brother, Ben Zelasko, who currently resides in Illinois and plans to take over the family farming business. Amanda's favorite activities growing up as a child included fishing, hunting, four-wheeler riding, volleyball, and helping out on the farm. At an early age she learned agricultural concepts that sparked her future interest in soil science. In high school Amanda participated in many activities including FFA, Band, Volleyball and various scholastic clubs. After graduation she attended Southern Illinois University in Carbondale where she studied plant and soil science with a soil science specialization. In college Amanda was active in Sigma Sigma Sigma sorority, Alpha Zeta Fraternity, Collegiate FFA, Agriculture Future of America, and a member of the university honors program. While at SIUC, Amanda worked in the soybean pathology lab under the direction of Dr. Jason Bond. Through her work she decided to continue her education in soil science. After taking a wetland ecology course, Amanda was determined to study wetland soils. Amanda graduated with honors from SIUC in May 2005. Following the completion of her BS degree, she went on to pursue her masters degree in soil science at North Carolina State University where her interest in soil chemistry and environmental soil issues grew. Amanda plans to continue her education at NCSU by studying reductive dissolution of soil phosphorous while pursuing her Ph.D.

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LIST OF ABBREVIATIONS

Total organic carbon (TOC)	7
Microbial Biomass carbon (MBC)	8
Dissolved organic carbon (DOC)	21

CHAPTER ONE: GENERAL INTRODUCTION

GENERAL INTRODUCTION

Rationale

Wetlands are among the most important ecosystems in the world. They are valuable sources, sinks, and transformers of a multitude of chemical, biological and genetic materials (Mitsch and Gosselink, 2000). It has been estimated that 53% of the original wetlands in the United States have been lost (Dahl 1990). In the 1970's, efforts were made to preserve and protect wetland environments. Due to these efforts, wetland restoration has taken on a very important role in ensuring that these ecosystems persevere.

For an area to be considered a jurisdictional wetland it must possess three parameters: hydrology, hydric soils, and hydrophytic vegetation (Environmental Laboratory, 1987);. The aim of wetland restoration is to create areas that function as natural wetlands, as well as meet the jurisdictional definition of a wetland. The research presented here focused on the hydric soil aspect of wetland delineation and restoration.

Soil Redox Potential

Hydric soils are defined as “soils that formed under conditions of saturation, flooding, or ponding long enough during the growing season to develop anaerobic conditions in the upper part” (USDA, Soil Conservation Service, 1987). The redox potential of the soil can be monitored to determine if anaerobic conditions occur. Platinum electrodes are commonly employed in the field to measure electrode redox potential (Eh). The redox potential of an aqueous chemical system is a measure of the electron availability or potential. In theory, the platinum electrode transfers electrons either to or from the soil but does not react chemically with the soil (Ponnamperuma, 1972).

Poor reproducibility, due mainly to lack of poisoning of the redox systems, is one of the main limitations of redox potential. Because soils and other biological systems are rarely at redox equilibrium, redox potential measurements cannot be used to accurately predict the activity of specific oxidized and reduced components of the system (Patrick et al., 1996). According to McBride (1994), Pt electrodes respond quickly to some redox couples such as Fe(III) - Fe(II), but not to others such as $O_2 - H_2O$. Although redox potential cannot be relied on to reflect the thermodynamic reaction potentials, it can be used as a general guide to redox reactions taking place in the soil.

The National Technical Committee for Hydric Soils (NTCHS) developed the technical standard for identifying hydric soils. Smith (2004) used equation 1 to determine the Eh required for anaerobic conditions (Figure 1.1). Equation 1 was developed based on the slope of the thermodynamically predicted oxygen line (Figure 1.2), but was lowered to extend through the $Fe(OH)_3 : Fe^{2+}$ line at pH 7 to ensure the equation represented anaerobic conditions for most soils. Many factors can affect the rate of reduction in wetland soils, including the amount and forms of organic matter, amount and forms of Fe, microbial activity, and concentrations of NO_3 and Mn (Ponnamperuma, 1972).

$$Eh \text{ (mV)} = 595 - 60 \text{ (pH)} \quad (1)$$

Effect of pH on redox potential

As noted in Equation 1, pH directly affects soil redox potential. As pH decreases, the Eh for a soil to be considered anaerobic increases (Figure 1.1). The pH affects the Eh differently in soils than in solutions because the pH can be buffered by silicates, carbonates,

and insoluble oxyhydroxides that are not involved in redox reactions (Bohn, 1969). During reduction a general increase in pH occurs. Because most soils contain more Fe(III)-oxides than any other oxidant under O₂ free conditions, reduction of Fe(III) is mainly responsible for the increase in soil pH upon reduction. (Ponnamperuma, 1972).

Iron Chemistry

The reduction of Fe(III) has been termed the most important chemical change that takes place in the development of anaerobic soils (Ponnamperuma, 1972). Iron is responsible for the typical red and yellow colors of soils. When Fe(III) is reduced to Fe(II), it becomes soluble and moves through the soil, altering the soils color. This process ultimately produces discrete features of contrasting coloration called redoximorphic features, which are used to identify hydric soils.

The form of Fe in the soil has also been shown to affect the time to reduction significantly. Thermodynamics predicts that more soluble Fe-oxides such as ferrihydrite provide more energy upon reduction than crystalline Fe-oxides (Lindsay, 1979). Lowe et al. (2000) suggested that in a salt marsh, poorly crystalline Fe(III) oxyhydroxides are the main terminal electron acceptors for microbial Fe(III) reduction. Lovley (1991) found that hydroxylamine-extractable Fe(III) oxides were strongly correlated to microbial Fe(III) reduction in soils. The hydroxylamine-extractable Fe(III) contains organically bound Fe and some poorly crystalline Fe, indicating that these forms are the primary source of reducible Fe(III). Roden (2003) found that the surface area of Fe(III) oxides determined which types of Fe were more reducible in soils. His research showed that rates of reduction were higher on synthetic ferrihydrite than on synthetic goethite.

A study conducted by Weiss et al. (2004) found that rhizosphere soil became abiotically reduced more quickly than non-rhizosphere soil, and that 75% of the Fe in the rhizosphere became reduced compared to 23% in the non-rhizosphere soil during a four hour time period. In this case, differences persisted despite additions of organic carbon, reducing bacteria, and an electron-shuttling compound, indicating that Fe-oxide mineralogy contributed strongly to differences in the Fe(III) reduction potential of the two pools. The Fe in the root zone was in the form of more poorly crystalline oxide-minerals compared to that of the bulk soil. Weiss et al. (2004) hypothesized that organic carbon from decomposing roots and root exudates may help stabilize rhizosphere derived Fe(III) after it transitions to the non-rhizosphere soil Fe pool. Thus cycles of new root growth, poorly crystalline Fe(III) deposition, root death, and Fe plaque dissolution may cumulatively influence the Fe mineralogy of the entire root zone. A likely reason that iron was less crystalline in the rhizosphere soil is that it oxidizes quickly and forms crystals of small size. Oxygen released by plant roots creates microaerophilic zones that can oxidize Fe(II), but also creates conditions suitable to the activity of Fe(II)-oxidizing bacteria. According to Taiz and Zeiger (2002), plant roots have developed several mechanisms that increase iron solubility, including soil acidification, reduction of ferric iron to ferrous iron, and the release of iron chelators.

Although one of the earliest studies on microbial Fe(III) reduction, by Starkey and Halvorson (1927) concluded that Fe(III) reduction was abiotic, no other studies have demonstrated that Fe(III) can be abiotically reduced by changes in dissolved oxygen or pH (Lovely, 1991). Recent studies have shown that in anaerobic, nonsulfidogenic environments in which Fe(III) reduction is most important, dissimilatory Fe(III) reducers enzymatically

catalyze nearly all of the Fe(III) reduction (Lovley 1991,1993). The mechanisms by which electrons are transported from microorganisms to Fe(III) have been studied extensively (Nevin & Lovley, 2002). Previously it was thought that Fe(III)-reducing microorganisms must come into direct contact with Fe(III) oxides in order to reduce them. Recent studies have suggested that electron-shuttling compounds and/or Fe(III) chelators may alleviate the need for direct contact between Fe(III)-reducing microorganisms and Fe(III) oxides (Nevin et al., 2002). It is evident when looking at various research reports that different Fe(III)-reducing microorganisms may reduce Fe(III) using different mechanisms. Nevin and Lovley (2002) demonstrated that the *Shewanella* alga strain *Bry* may release a compound that permits electron transport to Fe(III) oxides that are not in direct contact with the microorganisms. This was the first evidence presented indicating that electron transport could take place via an electron shuttling compound and/or a Fe(III) chelator produced by Fe(III)-reducing microorganisms.

The amount of Mn and nitrate in the soil may have a significant effect on the time it takes for Fe(III) to be reduced under anaerobic conditions (Ponnamperuma, 1972). The reduction of elements in submerged soils proceeds in a sequence predicted by thermodynamics. Oxygen is the first component to be reduced, followed by nitrate, then Mn(IV)-oxide minerals, then Fe(III)-oxides, then sulfate, and finally carbon dioxide (Figure 1.2). High levels of Fe(III) can suppress the amount of methane formed in wetland soils. According to Lovley (1991), net Fe(III) reduction does not occur in the presence of Mn(IV) and nitrate. The suppression of net Fe(III) reduction in the presence of Mn(IV) has been attributed to the rapid Mn(IV) oxidation of Fe(II) and a lower concentration of electron donors, such as organic matter, in the presence of Mn(IV) (Lovley & Phillips, 1998). Native

or added Mn(IV) retards the decrease in Eh of flooded soils and prevents the buildup of high concentrations of Fe(II) and other reduction products (Ponnamperuma, 1972). Because Fe(II) reduction and movement of Fe(II) contributes to redoximorphic features used as hydric soil indicators, Mn(IV) and NO₃ can retard the development of the visible features in soils.

Soil Organic Matter and Nitrogen

According to Lovley (1993), Fe(III) is one of the most abundant potential electron acceptors for organic matter decomposition in many aquatic sediments and subsurface environments. It has been found that the redox potential in wetland soils low in organic matter content may take longer to reach a level that is characteristic of reduced conditions (Smith, 2004; Scott et al., 1998; Ponnamperuma, 1972; Ugwuegbu et al., 2001). In submerged soils the decomposition of organic matter is almost entirely the work of facultative and obligate anaerobes. Since anaerobic bacteria operate at a much lower energy level than aerobic organisms, both OM decomposition and assimilation are slower in submerged soils than in aerobic soils (Ponnamperuma 1972). Smith (2004) found that soils with > 30 g kg⁻¹ of total organic carbon (TOC) took less time to develop anaerobic conditions than soils having < 30 g kg⁻¹ TOC (Figure 1.3). Smith's (2004) trend was found using soils from a Carolina bay, Juniper Bay, as well as two other soils.

Studies have also shown that the time to reduction in wetland soils is correlated to the amount and/or forms of organic matter that is present in the soil (Nevin & Lovley, 2002; Smith, 2004; Lovley & Phillips, 1998; Pracht et al., 2001). One theory indicates that rates of organic-matter oxidation and Fe(III) reduction are faster in the presence of OM than in their absence because of electron shuttling by humic substances found in OM, alleviating the need

for Fe(III) reducing microorganisms to contact insoluble Fe(III) oxides (Nevin and Lovley, 2002). Humic substances may further aid Fe(III) reduction by augmenting the reduction of forms of Fe(III) otherwise inaccessible to Fe(II) reducing microorganisms. For example, reduction of the crystalline Fe(III) oxides goethite and hematite has been shown by Lovley & Phillips (1998) to be accelerated in the presence of humic substances.

It is possible that the chemical composition of organic matter in the soil could also be an important factor regarding the rate of reduction in wetland soils. Research conducted by Pracht et al. (2001) showed that phenolic substances with two hydroxyl groups in the ortho position or at least one hydroxyl group and a methoxy group can be abiotically oxidized to CO₂ while Fe(III) is reduced. Humic substances are known to be more resistant to decomposition than fresh plant materials. According to Brady and Weil (2002), fulvic acid is the humic substance most susceptible to microbial attack followed by humic acid and then humin. D'Angelo and Reddy (1999) hypothesized that the amount of labile carbon may affect the rate of reduction more than TOC, after observing that one of their samples having received wastewater showed higher reduction rates than other soils having similar TOC without wastewater treatment.

Microbial biomass carbon has been shown to correlate with TOC content in soils. D'Angelo and Reddy (1999) found that microbial biomass carbon (MBC) was also correlated with reduction rates in saturated soils. Lower amounts of MBC led to longer lag times to methane production in the soils studied. MBC in D'Angelo and Reddy's (1999) study also correlated well with TOC, indicating that microbial populations are likely to be higher in soils having higher amounts of organic matter.

The carbon to nitrogen ratio (C/N) could also affect the rate of reduction in wetland soils. Microbial reduction was shown to increase with decreasing C/N ratios (Gaunt et al., 1997). Nitrogen is more limiting when C/N ratios are high, which decreases microbial activity. Gaunt et al. (1997) found that a greater rate of reduction corresponded to a narrower C/N ratio in the labile carbon enriched fraction of the soils studied. Generally stabilized organic matter has a greater C/N ratio than fresh organic matter. Wetland plants typically have a C/N ratio > 50, and as plant matter decays in the soil, CO₂ is evolved while N is retained causing the C/N ratio to decrease (stabilizing at 15-25) instead of increase with age (Nair et al., 2001).

Temperature

Temperature has also been found to affect the rate of reduction. According to Yao and Conrad (2000), the optimum temperature for Fe(III) reduction is between 32 and 41° C. At temperatures above and below this range, time to reduction is slower. This effect was more noticeable in soils that had low contents of organic matter, indicating a relationship between the two parameters.

Combined Soil Properties

Research has shown that soil reduction rate is not simply related to one factor, but a combination of several. Soils high in nitrate (> 275 mg L⁻¹) have positive redox potentials for several weeks after submergence, and soils low in organic matter (< 1.5%) or high in Mn (> 0.2%) maintain positive redox potentials even 6 months after submergence. Soils low in active Mn, Fe, and with > 3% TOC attained Eh values of -200 mV to -300 mV within 2 weeks of submergence (Ponnamperuma, 1972).

Past research has generally focused on only one or two variables affecting soil reduction. Additional research is needed to establish how relationships between multiple soil properties and reduction rates can be applied toward wetland delineation and restoration. The application of these results could lead to improving the methods currently used to identify hydric soils.

In summary, the following soil properties are expected to increase rates of reduction after aerobic soils become water saturated: 1. High TOC 2. High MBC 3. Low C/N ratio 4. Low concentrations of NO_3 , and Mn(III,IV)-oxides 5. Increasing poorly crystalline Fe(III) – oxide minerals.

Objectives

The goal of this research is to quantitatively determine relative relationships of various soil properties to reduction rates in water-saturated soils in order to predict soil reduction rates for wetland restoration. The objectives of this study were to (i) measure rates of reduction under water-saturated conditions for soil samples collected from different topographic settings and varying in redox-related properties. (ii) determine whether reduction rate is related to soil properties, including concentrations and forms of organic matter, C/N ratio, MBC, and concentrations and forms of electron acceptors (O_2 , NO_3 , Fe(II), SO_4).

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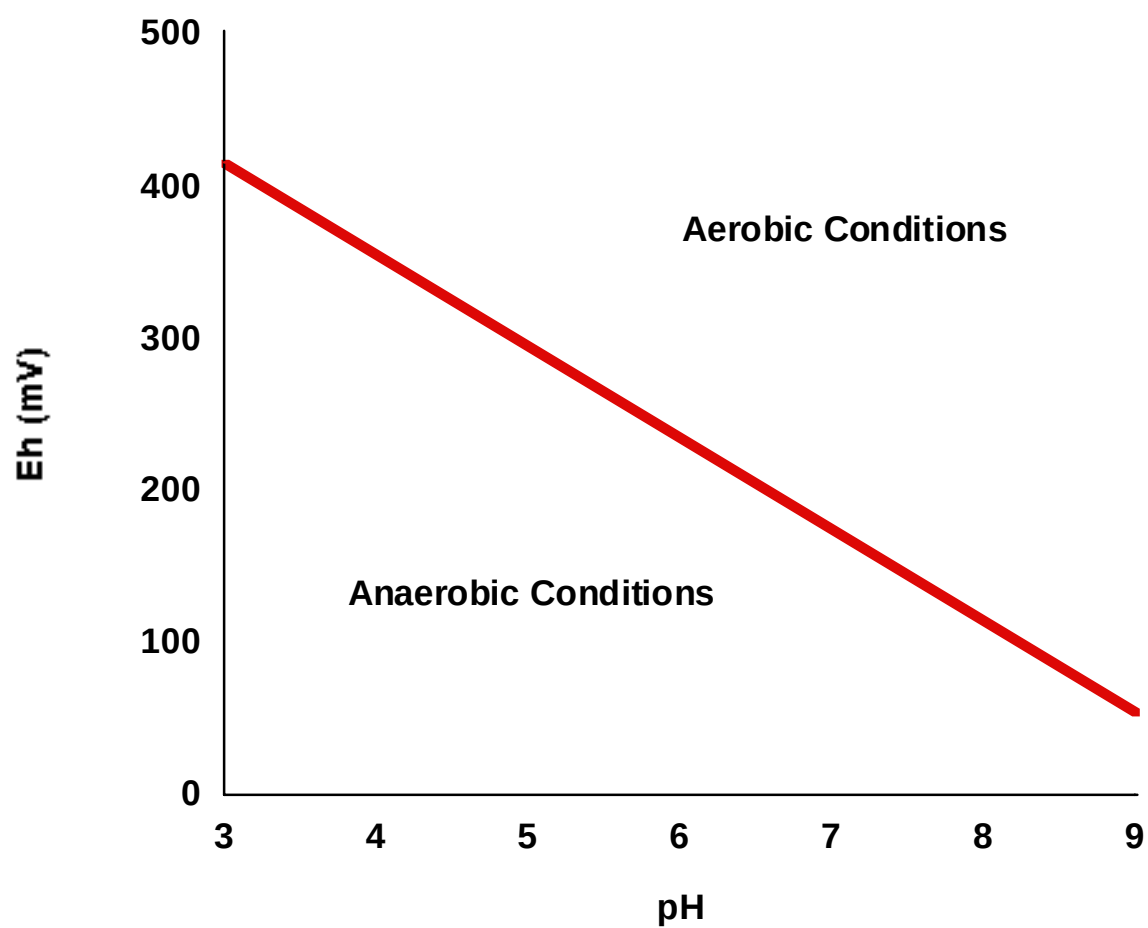


Figure 1.1: Electrode potential (Eh) needed for a soil to be considered anaerobic as a function of pH [$Eh(mV) = 595 - 60 (pH)$].

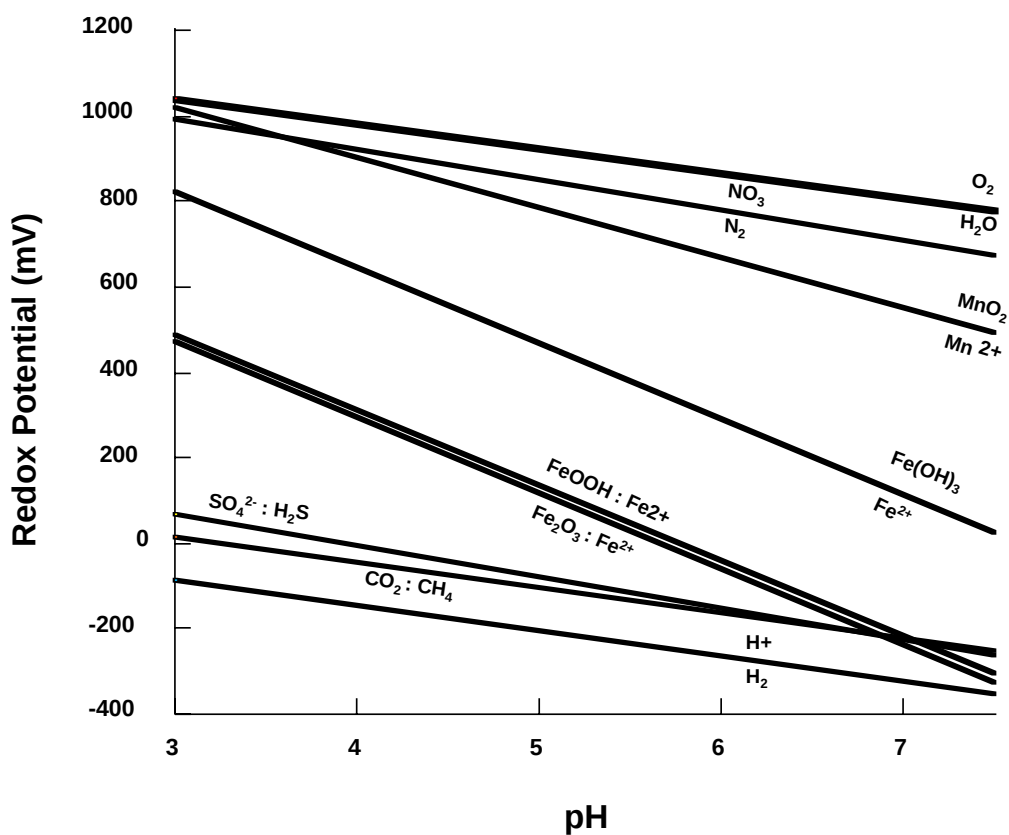


Figure 1.2: An Eh-pH phase diagram for reducing reactions, reproduced from Richardson and Vepraskas (2001), pg. 4.1. The lines were computed for the following conditions: dissolved species were assumed to have an activity of 10^{-5} M, partial pressures for O_2 and CO_2 were 0.2 and 0.8 atm, respectively, and partial pressures of the remaining gasses were assumed to be 0.001 atm.

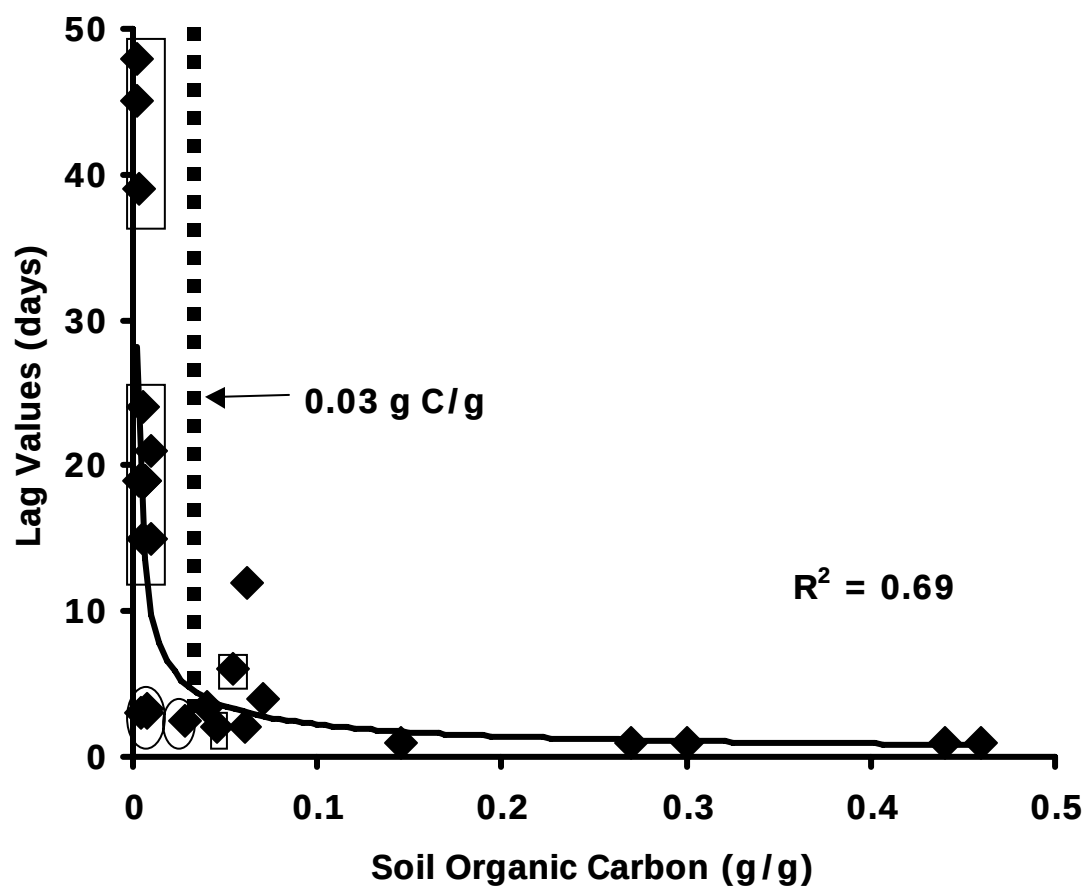


Figure 1.3: Relationship of reduction time to total organic carbon (TOC) at Juniper Bay and two other soils to the number of days after saturation that the soil took to become reduced (L_a). The circled points have low soil organic carbon and short L_a values reproduced from Smith, (2004).

**CHAPTER 2: SOIL REDUCTION RATES UNDER WATER
SATURATED CONDITIONS IN RELATION TO SOIL
PROPERTIES**

ABSTRACT

Predicting the time required to develop hydric soils following water saturation provides an important wetland restoration and management tool. The objective of this research was to determine rates of soil reduction under water-saturated conditions in relation to redox-related soil properties. Samples of sixteen soils with different drainage, chemical, mineralogical, and microbial characteristics were collected at a Carolina bay and a wetland catena. Soils were incubated for 36 d under alternating water saturated and unsaturated conditions, and soil solution chemistry was monitored. Redox potential began to decrease in most columns within 12 h of saturation with rate of reduction varying between soil samples. Similarly, dissolution of Fe(II) varied between soil samples and was correlated to soil reduction rate ($r = 0.45$). Reduction rates were best correlated to amount of total organic carbon (TOC) using a linear plateau model where reduction rate increased up to $\text{TOC} = 27 \text{ g kg}^{-1}$ and stabilized at 38.7 mV h^{-1} ($r = 0.82$). A multiple linear regression model including TOC and initial soil pH ($R^2 = 0.49$) also showed promise in predicting soil reduction rates. The linear plateau model of reduction rate and TOC, or the multiple linear regression model involving TOC and pH, can be used in order to predict the frequency and duration that soils meet hydric criteria when combined with hydrologic data.

INTRODUCTION

More than half of the original wetlands in the United States have been destroyed or otherwise lost (Dahl, 1990). Wetlands are valuable sources, sinks, and transformers of a multitude of chemical, biological and genetic materials (Mitsch and Gosselink, 2000), and therefore must be managed as an environmental resource. Wetland restoration has become an important issue for maintaining the current land area of wetlands under the U.S. Wetland Reserve Program. According to the U.S. Army Corps of Engineers Wetland Delineation Manual (1987), if an area meets the criteria of hydrology, hydric soils, and hydrophytic vegetation; it is considered a Jurisdictional wetland. Hydric soils are defined as soils that formed under conditions of saturation, flooding, or ponding long enough during the growing season to develop anaerobic conditions in the upper part (USDA, Soil Conservation Service, 1987). Oxygen, as O_2 , is the main electron acceptor for heterotrophic microbial metabolism of organic carbon in aerobic soils. When soils are water saturated for extended periods, anaerobic conditions develop as O_2 becomes depleted during organic matter oxidation, and alternative electron acceptors such as NO_3 , $Mn(IV)$, $Fe(III)$, and SO_4 are used. The length of time required for soils to become anaerobic varies, but the controlling factors are poorly understood. Accordingly, soil properties that are expected to affect redox reactions include water content, organic matter quantity and quality, and abundance of electron acceptors. Microbial ecology and temperature can also affect reduction rates given that they are microbially mediated processes.

Soil organic matter serves as the main energy source for microbial respiration. Research has shown that the length of time required for a soil to become anaerobic can

depend on soil organic matter contents. Christensen et al. (1990) observed that a lag period of five days preceded increased denitrification rates in saturated soil cores after injection of particulate organic matter. Smith (2004) found that soils having total organic carbon (TOC) $< 30 \text{ g kg}^{-1}$ took more time to become anaerobic than soils with TOC $> 30 \text{ g kg}^{-1}$. He et al. (2003) showed that the time required to significantly reduce Fe(III) after saturation in the field varied from 2 to 48 d. Ponnampetuma (1972) indicated that soils with low organic matter concentration ($< 15 \text{ g kg}^{-1}$) or high Mn concentration ($> 390 \text{ mmol kg}^{-1}$ soil) could maintain redox potentials $> 0 \text{ mV}$ for 6 months or more following saturation.

With regard to carbon sources, dissolved organic carbon (DOC) is one component that serves as a source of energy for microbial respiration (Johnson and Ward, 1996; Mann and Wetzel, 1996). In three limesink wetlands and one riparian wetland, an increase in the amount of DOC and a decrease in the proportion of aromatic carbon was noted during water inundation (Opsahl, 2005). Evidence from Hill et al. (2000) suggested that oxidized forms of N were depleted in reducing environments with high concentrations of DOC. Anaerobic conditions have been observed across a riparian zone in conjunction with DOC concentrations of 5 mg L^{-1} or higher (Vidon and Hill, 2004). Methane emissions were found to correlate to DOC concentrations in rice paddies (Lu et al., 2000). Despite correlations between DOC and soil reduction processes, Opsahl (2005) found that DOC was not a quantitative indicator of bioavailability of organic matter in all wetlands. Decreases in DOC with increasing bacterial abundances and biomass indicate that DOC stimulates microbial production (Johnson and Ward, 1996).

D'Angelo and Reddy (1999) found that microbial biomass carbon (MBC) correlated with TOC concentration in soils, and that inorganic N and MBC were the most reliable

indicators of heterotrophic activity in all wetland soils studied. Lower amounts of MBC ($< 25 \mu\text{g g}^{-1}$) led to longer lag times for methane production in those soils.

The reduction of Fe(III) has been termed the most important chemical change that takes place in the development of anaerobic soils (Ponnamperuma, 1972). Iron is responsible for the typical red and yellow colors of soils. When Fe(III) is reduced to Fe(II), it becomes soluble and moves through the soil, altering its color. This process ultimately produces discrete features of contrasting coloration called redoximorphic features, which are used to identify hydric soils.

The course, rate, and magnitude of decreasing Eh in saturated soils also depends on the nature and content of electron acceptors (Ponnamperuma, 1972). Thermodynamics shows that more soluble Fe-oxides such as ferrihydrite provide more energy upon reduction than crystalline Fe-oxides (Lindsay, 1979). Lowe et al. (2000) suggested that poorly crystalline Fe(III) oxyhydroxides were the main terminal electron acceptors for microbial Fe(III) reduction in a salt marsh. Lovley (1991) found that hydroxylamine-extractable Fe was strongly correlated to microbial Fe(III) reduction in soils. The hydroxylamine-extractable Fe presumably contains organically-bound Fe and some poorly crystalline Fe-oxides, indicating that these forms are the primary source of reducible Fe(III) (Lovley, 1991). Roden (2003) found that the surface area of synthetic Fe(III) oxides dictated which types of Fe were more reducible, with rates of reduction being greater for ferrihydrite than goethite.

The reduction of submerged soils proceeds following a sequence of electron acceptors predicted by thermodynamics. Typically, O_2 is the first component to be reduced, followed by NO_3 , Mn(IV)-oxides, Fe(III)-oxides, SO_4 , and finally CO_2 (Ponnamperuma, 1972). Therefore, the amounts of reducible Mn and NO_3 in soil can have a significant effect

on the rate of Fe(III) reduction under anaerobic conditions (Lovley and Phillips, 1998). According to Lovley (1991) net Fe(III) reduction does not occur in the presence of Mn(IV) and NO₃. The net suppression of Fe(III) reduction by Mn(IV) has been attributed to rapid oxidation of Fe(II) by Mn(IV), and a lower concentration of electron donors like organic matter in the presence of Mn(IV) (Lovley & Phillips, 1998). Native or added Mn(IV) poises Eh of flooded soils and suppresses the buildup of aqueous Fe(II) and other reduction products (Ponnamperuma, 1972). Soils with very elevated concentrations of nitrate (> 275 mg L⁻¹) have also been shown to maintain higher soil Eh values for longer time periods than soils with less nitrate (Ponnamperuma, 1972).

Soil carbon to nitrogen (C/N) ratio has also been related to soil reduction rates. Gaunt et al. (1997) concluded that the C/N ratio of organically-enriched soil fractions controlled the rate of reduction upon flooding, with greater rates corresponding to lower C/N ratios. Wetland plants typically have a C/N ratio > 50, and as plant matter decays in the soil, CO₂ is evolved while N is retained. In this case, C/N ratio decreases to a stable level of 15 to 25 instead of increasing with age (Nair et al., 2001).

In essence, the rate at which soils become reduced following water saturation depends on the availability of degradable organic carbon sources, and on the concentrations and chemical or mineralized forms of various electron acceptors (O₂, NO₃, Fe(III), SO₄, CO₂). The objectives of this study were to (i) measure rates of soil reduction under water-saturated conditions for samples collected from different topographic settings and varying in redox-related properties, and (ii) determine whether reduction rate is related to soil properties, including concentrations and forms of organic matter, C/N ratio, MBC, and concentrations and forms of electron acceptors (O₂, NO₃, Fe(II), SO₄).

MATERIALS AND METHODS

Soil Sample Collection

Soil samples were collected from two different wetland sites, a Carolina bay named Juniper Bay located in Robeson County North Carolina (Fig 2.1) and a topographic wetland catena in Pitt county North Carolina (Fig 2.2). At Juniper Bay, soil samples were taken at two depths, 20 to 30 cm and 56 to 66 cm from three locations representing two soil series - Ponzer (a loamy, mixed, dysic, thermic, Terric Haplosaprists) and Leon (a sandy, siliceous, thermic, Aeric Alaquod). Soil profile descriptions for soils from Juniper Bay are given in Smith (2004). The wetland catena site was located approximately 5.1 km southwest of Greenville near Highway 13/264A at the Frog Level crossroads, 35° 34' 10" latitude and 77° 26' 26" longitude (Hayes and Vepraskas, 1998). Four sampling sites representing four different soil series were sampled: a moderately well-drained Goldsboro soil (fine-loamy, siliceous, subactive, thermic, Aquic Paleudult), a somewhat poorly drained Lynchburg soil (fine-loamy, siliceous, semiactive, thermic, Aeric Paleaquult), a poorly-drained Rains soil (fine-loamy, siliceous, semiactive, thermic Typic Paleaquult), and a very poorly drained Pantego soil (fine-loamy, siliceous, semiactive, thermic, Umbric Paleaquult). Different soil horizons were sampled at each location down to a maximum depth of 30 cm. Soil profile descriptions were conducted while sampling.

Soil Characterization

Moist soil samples were sieved through a 2 mm sieve and stored moist in 2 mil polyethylene bags at 4°C to maintain partially aerobic conditions (Bartlett and James, 1993).

The initial pH of the samples was taken within two weeks of sampling using a 1 to 1 soil to deionized-water ratio (Thomas, 1996).

Moist soil samples were analyzed for Fe and Al using citrate-bicarbonate-dithionite (CBD), sodium-pyrophosphate, and oxalate (dark) extractions. CBD and oxalate extractions were performed as described by Jackson et al. (1987). Sodium pyrophosphate extraction was performed as described by Loeppert and Inskeep (1996). All extracts were filtered through 0.2 μm Isopore polycarbonate filter membranes (Millipore Corp., Bedford, MA). Iron and Al in the CBD and oxalate extractions and Fe in the Na-pyrophosphate extractions were measured using flame atomic absorption spectrometry (FAAS) and reported on an oven dried (110 °C) basis.

Amounts of total organic carbon (TOC) and nitrogen were determined using a Perkin Elmer model PE 2400 CHNS elemental analyzer. Soil samples were oven dried at 110 °C for 24 h, ground, and passed through a 2 mm sieve prior to analysis. The C/N ratios ($\text{g C} - \text{g}^{-1} \text{N}$) were calculated from these measurements.

Fractionation of humic substances was carried out according to Swift (1996), using 10 to 20 g of moist soil. The humic acid and soil plus humin fractions were freeze dried and weighed to determine the total concentrations of humic acid and fulvic acid (by difference). Sample microbial biomass carbon (MBC) concentrations were measured using 15 g moist soil just prior to setting up the reduction incubation experiment (described below), and immediately following the experiment using the chloroform extraction method described by Vance et al. (1987).

Redox Incubation Design

Incubation experiments were performed to monitor soil reduction and re-oxidation rates during saturation and drainage, and change in soil porewater chemistry after saturation. Incubation systems consisted of 600 mL Buchner funnels with fritted glass plates and handmade polycarbonate lids (Fig. 2.3). A reference electrode (Ag/AgCl) and two handmade Pt tip electrodes (Wafer et al., 2004) were inserted into each column and connected to a Campbell Scientific CRX-10 data logger. The data logger measured Eh every 0.167 h, and averaged the six readings taken every hour. Eh measurements from both Pt tip electrodes in each column were averaged together for data analysis. Pore water samples were taken only under saturated conditions using 5 cm long Rhizon Flex Pore water samplers. Samplers were buried in the columns 1.5 cm to 6.5 cm from the column rim (Item # 19.21.26, Rhizosphere Research Products, Dolderstraat 62, NL 6706JG Wageningen, The Netherlands), and sampled water was replaced with distilled, deoxygenated H₂O.

The Pt tip electrodes were constructed as described by Wafer et al. (2004), using 12.7 cm of brass brazing rod. At the start of the incubation experiment Pt electrodes and reference electrodes were cleaned with steel wool and rinsed with DI water before testing with pH buffered quinhydrone solutions (pH 4 and 7) (Patrick et al., 1996), and a standard ferrous-ferric solution (Light, 1973). All electrodes produced Eh readings within 20 mV of the expected value. Pt tip electrodes were inserted 3.5 cm into the soil after packing and lid placement.

Salt bridges were constructed using 100 MPa round bottom straight wall ceramic cups purchased from Soil Moisture Equipment (#0652XO7-B01M1). Salt bridges were prepared by combining 20 mL of saturated KCl solution with 0.6 g of granular laboratory grade agar

while continuously stirring and heating. After boiling, the hot agar mixture was transferred into the porous cups. The salt bridge was allowed to cool before inserting into the soil column. An Ag-Ag/Cl reference electrode was placed into each salt bridge after placing the lids securely onto the columns.

Following construction of the salt bridge, field moist soils were packed around the pore water samplers in the columns to a specified bulk density, 0.5 g cm⁻³ (Ponzer Oa-1, Oa-2 and Oa2-2), 0.9 g cm⁻³ (Pantego A), 1.2 g cm⁻³ (Goldsboro A, B, E, Rains A, E, Ponzer Oa2-1, Leon A/E, Bhir) and 1.5 g cm⁻³ (Lynchburg E, B, Pantego B, Rains B), depending on soil texture and assumed particle density of 1.3 g cm⁻³ for organic (Caldwell et al., 2007), and 2.65 g cm⁻¹ for mineral soils.

Several precautions were taken in order to seal columns. Rubber gaskets were placed between funnel lids and the funnel and rubber stoppers were placed around Pt electrodes and pore water sampler. Silicon gel was placed around all devices on column lids to ensure lids were impervious to gas.

Incubation of Soil Samples

To aerate soil columns at the beginning of the experiment or following reduction cycles, a vacuum was placed on the bottom of the Buchner funnel and laboratory grade air (National Welders, Charlotte NC) was flushed across the headspace above the soil surface. Initial aeration was not applied to the first set of eight samples, but all results were similar so data was integrated. When Eh was ≥ 500 mV, anaerobic conditions were initiated by saturating with water. Saturation of columns was achieved by placing a vacuum in the headspace of each column while a constant head reservoir supplied water through the bottom

of the funnel (Fig. 2.3). After soils were saturated, N_2 (g) was flushed across water ponded in the headspace of the columns. Two replications of soils underwent saturation and drainage three times for five or more days each cycle. During the last saturation phase, columns remained saturated until all samples became reduced. Soil columns were drained before removing soil for final storage and analysis, and an aerated state was maintained during storage.

Water samples were collected on days 1, 2, 3 and 5 of each 5-day reduction cycle. Samples were collected using 50 mL evacuated serum bottles with rubber stoppers that connected to the embedded pore water samplers through a lure lock valve and syringe needle. Vacuum bottles were weighed prior to and following water sampling to obtain sample masses. Sampled water was replaced with the same amount of de-oxygenated water to maintain a constant water volume in the soil columns.

The pH and concentrations of Fe(II) in water samples were analyzed immediately in most cases, and no longer than 48 h after sampling. Colorimetric determination of Fe(II) was conducted by adding 0.1 mL of concentrated HCl, 1 mL of 0.1% 1,10-phenanthroline, 0.5 mL of ammonium acetate, and 1 mL of deionized water (Clesceri et al., 1989; Olson and Ellis, 1982). Dissolved Al, Fe, SO_4 , and NO_3 were measured using optical emission spectrometry and ion chromatography analysis. At the conclusion of the incubation experiment, soils were stored as described earlier (Bartlett and James, 1993), and final MBC was measured within two weeks.

Statistical Analysis

Three replications were performed for all initial soil analysis. The incubations, measurement of MBC, and Fe(II) were performed in duplicate. To quantify the rate at which soils reduced, zero order rate coefficients calculated from the slope between points within the most linear portion of each reduction phase were used. Analysis of variance and Fishers protected least significant difference tests were used to determine if groups of data were significantly different. Multiple linear regression analysis estimated relationships between reduction rate and all initial soil properties measured on both mineral and organic soils.

RESULTS AND DISCUSSION

Soil Properties

Selected soil properties for all soil samples are shown in Table 2.1. Initial pH of soil samples ranged from 3.7 to 5.4 while final pH ranged from 3.7 to 5.5. Total organic carbon ranged from 2.7 g kg⁻¹ in mineral soils to 560 g kg⁻¹ in organic soils, and C/N ratio ranged from 28 g g⁻¹ to 60 g g⁻¹ or greater. Extractable Fe varied among soil types, ranging from 5.3 mmol kg⁻¹ to 182 mmol kg⁻¹ for CBD extractable Fe, from 0.4 to 41.4 mmol kg⁻¹ for oxalate extractable Fe, and from 0.6 to 47 mmol kg⁻¹ for pyrophosphate extractable Fe. The CBD extractable Fe was always greater than oxalate and sodium-pyrophosphate extractable Fe. CBD-extractable Al varied from 5.3 to 200.1 mmol kg⁻¹. The temperature in the room used for soil incubation ranged from 24 to 27° C with a mean of 25.7 ± 1.03° C (n = 22).

Incubation Experiment

Thirteen of the 16 soil samples were successfully incubated in duplicate. The Eh began to decrease in most incubation systems, as predicted by thermodynamics, within 12 h of water saturation. The rate of decreasing Eh was dependent on soil type and pH (Fig. 2.4). Reduction rates, calculated over the linear portion of each reduction cycle as denoted by “X” in Fig. 2.4, were consistently slower than oxidation rates. As illustrated in Fig 2.4, reduction rates varied between consecutive cycles, and Eh typically stabilized at different values (Fig. 2.4). One mineral soil did not drain well and remained reduced following flushing with air. None of the organic soils could be re-oxidized after initial saturation, although two organic soil incubations did show increases and decreases up to ± 300 mV in Eh with imposed aeration and saturation.

The averaged reduction rates for each soil sample and cycle are shown in Fig. 2.5. Reduction rates from the upland soils from the Greenville site (Goldsboro and Lynchburg) showed reduction rates that tended to decrease with consecutive reduction cycles, while lowland soils (Rains and Pantego) showed reduction rates that tended to increase with consecutive reduction cycles. Juniper Bay soils showed no consistent trends between consecutive reduction cycles. Variance between replications was high for many soils especially during the first reduction cycle. Reduction rates were also calculated using a polynomial model. Although trends in data were similar, significance or results was much lower than when using the linear method.

Manual Eh readings typically followed the same trend and were within ± 20 mV from the data logger Eh readings (data not shown), although discrepancies can occur between Eh readings taken using a data logger (Bochove et al., 2002). In the first and third replications

of the experiment data logger readings were significantly different (> 20 mV) from manual readings for the third reduction cycle only. When data logger readings were continuously different than manual readings, reduction rates were calculated from manual readings. Differences between the data logger and manual readings were most likely due to drift when the redox stability of the systems was low (Bochove et al., 2002). The mean of all three reduction cycles for each sample were used to relate reduction rate to soil properties. Comparisons between measured soil properties and reduction rates were performed using mineral soils only due to problems with re-oxidizing organic soils. Eleven soil samples were compared in duplicate, yielding 22 different experimental average reduction rates.

Table 2.2 shows correlation results between reduction rate and selected soil properties, and summarizes the best fit multiple linear regression models when using all three reduction cycles to determine reduction rate. Soil properties significantly correlated to reduction rate included TOC, average DOC, and dissolved Fe(II). The strongest correlation found was between reduction rate and TOC using a linear plateau model ($r = 0.82$; Figure 2.6). It was evident that the first reduction cycle in each incubation differed from the second two (Figure 2.5). For this reason, reduction rate was also calculated using only the second two reduction cycles (Table 2.3). Correlations were very similar and generally less significant than when using all three reduction cycles to calculate reduction rates (Table 2.3).

Figure 2.6, displaying TOC in relation to reduction rate, shows that reduction rate in soils with $\text{TOC} < 27 \text{ g kg}^{-1}$ increased with increasing TOC, while reduction rate in soils with $\text{TOC} \geq 27 \text{ g kg}^{-1}$ was not dependent on TOC. When only the second and third reduction cycles were used (Figure 2.7) the linear plateau model increased up to $\text{TOC} = 16.6 \text{ g kg}^{-1}$ and stabilized at $\text{TOC} = 16.6 \text{ g kg}^{-1}$. A plot with reduction rate compared to TOC using un-

averaged data can be found in Appendix A, Figure A1.3. Further analysis showed that soils with $\text{TOC} \geq 27 \text{ g kg}^{-1}$ had nearly three times the reduction rate (mV h^{-1}) than soils with $\text{TOC} < 27 \text{ g kg}^{-1}$ supporting this observation (Table 2.4). Soils with $\text{TOC} \geq 27 \text{ g kg}^{-1}$ included the Ponzer horizons, the Leon A/E horizon, the Goldsboro A horizon, the Rains A horizon, and the Pantego A horizon. Soils with $\text{TOC} < 27 \text{ g kg}^{-1}$ included the Goldsboro E and B horizons, the Lynchburg E and B horizons, the Rains E and B horizons the Pantego B horizon, and the Leon Bhir horizon (Table 2.1). These findings are consistent with field measurements of Smith (2004) which indicated that time to reduction was slower in soils with $\text{TOC} < 30 \text{ g kg}^{-1}$ than those with $\text{TOC} > 30 \text{ g kg}^{-1}$.

When combined with TOC in a multiple linear regression model, pH was a significant variable correlated with soil reduction rates (Table 2.2). The increase in solution pH during the first saturation cycle was nearly three times larger ($p\text{-value} = 0.16$) for soils that released high amounts of Fe(II) than in soils that released very little to no Fe(II) during saturation, corresponding with previous research that the increase in pH of acid soils is largely due to the reduction of iron (Ponnamperuma, 1972). Initial and final pHs in redox incubation experiments were not significantly different (Table 2.4), although findings have shown that when an aerobic soil is submerged, its pH decreases during the first few days, reaches a minimum, and then increases asymptotically to a fairly stable value (Ponnamperuma, 1972).

Our measurements of DOC showed an increase from day 0 to day 1 and 2 for all soils likely due to anaerobic microbial activity (Johnson and Ward, 1996; Mann and Wetzel, 1996; Hill et al., 2000; Vidon and Hill, 2004). DOC was correlated with reduction rate ($r = 0.47$; $p = 0.02$; Table 2.2) although DOC was not significantly different between soils with $\text{TOC} \geq 27 \text{ g kg}^{-1}$ and soils with $\text{TOC} < 27 \text{ g kg}^{-1}$ (Table 2.4). Previous research indicated that DOC

can indicate the bioavailability of organic matter in some wetlands, but not all (Opsahl, 2005).

Dissolved Fe(II) typically increased with decreasing Eh (Fig. 2.8) and was significantly correlated with reduction rate ($r = 0.45$), as predicted by thermodynamics. Three groups of soils were distinguishable when comparing dissolved Fe(II) relative to Eh (Figure 2.8). One group showed a high increase in dissolved Fe(II) with decreasing Eh (up to 23 Fe(II) mg L⁻¹), and included the Pantego A and B horizons, the Goldsboro A horizon and the Rains A horizon. The second group showed a moderate increase in dissolved Fe(II) with decreasing Eh (up to 6 Fe(II) mg L⁻¹), and included the Rains B horizon, and the Lynchburg E horizon. The remaining soil samples showed little to no increase in dissolved Fe(II) with decreasing Eh. The amount of Fe(II) dissolved decreased between consecutive reduction cycles (Fig. A2.3, A2.4).

When grouped, soils with TOC ≥ 27 g kg⁻¹ had nearly three times the oxalate to CBD Fe ratio as soils with TOC < 27 g kg⁻¹ ($p < 0.05$) (Table 2.4), supporting previous findings that less crystalline Fe minerals are more soluble than more crystalline Fe minerals. The rate of bacterial Fe(III) reduction has been shown to depend on the surface area of Fe minerals (Roden, 2003). Our results are consistent with previous findings showing that soils with high amounts of poorly crystalline Fe-oxides reduce more quickly than soils with low amounts of poorly crystalline Fe-oxides (Lovely, 1991; Roden, 2003).

The C/N ratio was higher for organic soils collected from Juniper Bay than for mineral soils collected from the wetland catena, and was correlated to reduction rate ($r = 0.41$, $p\text{-value} < 0.10$). It was logical that the C/N ratio would be different between wetland sites because Juniper Bay had been in agriculture production and fertilized for several years,

while the catena site had been forested. The C/N ratio was not significantly different between soils with $\text{TOC} \geq 27 \text{ g kg}^{-1}$ and soils with $\text{TOC} < 27 \text{ g kg}^{-1}$ (Table 2.4).

Initial MBC varied from 74.6 to 13200 mg kg^{-1} over all samples, while final MBC varied from 117 to 1410 mg kg^{-1} (Table 2.5). The initial MBC measurements taken in this experiment were very high (Table 2.5) and often exceeded 3% of the TOC. The high measurements indicate a possible error in laboratory technique. Final MBC measurements were much lower and closer to expected values. In this research TOC was correlated to final MBC ($r = 0.76$, $p < 0.0001$) as predicted by previous research (D'Angelo and Reddy, 1999).

Concentration of dissolved Mn never exceeded $0.005 \text{ mmol L}^{-1}$ indicating that levels of Mn did not greatly influence reduction rates in this experiment (Table A2.5). Similarly, concentrations of $\text{NO}_3 > 4.4 \text{ mmol L}^{-1}$ could prevent reduction of Fe(III) (Ponnamperuma, 1972). Concentrations of NO_3 were monitored in the soils and never exceeded 0.15 mmol L^{-1} (Table A2.8).

Concentrations of dissolved SO_4 were typically low, and never exceeded concentrations of $0.68 \text{ mmol SO}_4 \text{ L}^{-1}$ (Table A2.9). Average SO_4 was correlated to TOC ($r = 0.80$, $p\text{-value} < 0.05$). No strong correlation was found between concentration of SO_4 and soil redox potential. The saturation period of five days was likely too short to reach SO_4 reduction following Fe(III) reduction.

Application of Results

Multiple soil properties appeared to affect soil reduction rates (Table 2.2) so a multiple linear regression was conducted to develop an equation that could be used to predict soil reduction rates. Of all soil properties evaluated, the best two variable model for mineral

soils included pH and TOC ($R^2 = 0.49$, $p < 0.05$) (Table 2.2, Figure 2.9). Three or more variables could not be used due to inter-correlations between TOC and other soil properties such as MBC and C/N ratio. The regression model, listed in Table 2.2 could be used along with hydrologic data to predict reduction rates prior to water saturation.

As further refinement of regression analysis, soils were divided into two groups of $\text{TOC} < 27 \text{ g kg}^{-1}$ and $\text{TOC} \geq 27 \text{ g kg}^{-1}$, and multiple linear regressions analysis was done on each group to determine if a stronger relationship could be found to predict soil reduction rates. For soils with $\text{TOC} < 27 \text{ g kg}^{-1}$, TOC and average DOC fit best into a two variable model to predict reduction rate ($R^2 = 0.48$; $p < 0.05$; Figure 2.11). For soils with $\text{TOC} \geq 27 \text{ g kg}^{-1}$, dissolved Fe(II) and TOC gave the best model ($R^2 = 0.54$; $p > 0.25$; Figure 2.10). The multiple linear regression model for $\text{TOC} \geq 27 \text{ g kg}^{-1}$ (Table 2.2) was produced using only six data points (Figure 2.10) resulting in a non-significant model. Results by Smith (2004) showing that time to reduction was faster when $\text{TOC} > 30 \text{ g kg}^{-1}$ correspond to these results.

Results from multiple linear regressions could be applied, along with hydrologic data, in wetland restoration and delineation as an easy, inexpensive method for determining the length of time soils are hydric. Data in Figure 2.12 showing water table fluctuations with time was taken from Juniper Bay and can be used to determine the length of time the soil is saturated in the upper part. Using figure 2.12 in conjunction with figure 2.13, which shows the time required for soil Eh to drop by 500 mV compared to TOC, allows us to predict the frequency and duration of reduced conditions by comparing how long a soil is saturated in the upper part to how long it would take for the soil to become reduced under saturated conditions. An easy method of predicting the frequency and duration that soils meet hydric criteria is very important for large scale wetland delineation because installing redox

monitoring systems can be very expensive. Using this linear plateau model in conjunction with water table data could be an easy inexpensive alternative to installing several redox monitoring systems.

Based on our data, TOC along with hydrologic data would provide the best overall estimate for how quickly soils will reduce once saturated (Figure 2.6). Both pH and TOC are readily available or easily measured soil properties, however, different models could be used based on the availability of soil information at restoration sites. Predicting soil reduction rate can serve as a valuable tool for ensuring success of wetland restoration projects.

CONCLUSIONS

Redox potential measurements in incubated soils showed a rapid (typically < 12 h) decline following saturation with water. The reduction rate varied among soil types, indicating variations in soil properties affected reduction rates. Reduction rate was significantly correlated to TOC, DOC, Fe(II) and C/N ratio, but showed the greatest correlation with TOC using a linear plateau model ($r = 0.82$). Amount of humic acid, DOC, TOC, oxalate to CBD extractable Fe ratio, and C/N ratio were significantly different between soils with $\text{TOC} < 27 \text{ g kg}^{-1}$ and soils with $\text{TOC} \geq 27 \text{ g kg}^{-1}$, suggesting that all of these variables in part affected soil reduction rates. A model using TOC and pH ($R^2 = 0.49$) was determined using multiple linear regression analysis. The relationships found between soil properties and reduction rates can be used along with hydrologic data to predict reduction rates for wetland delineation and restoration purposes. The linear plateau model using TOC to predict reduction rate would serve as the most accurate method, although other models such as the multiple linear regression using TOC and pH could be used. Predicting the time

to reduction without installing expensive equipment over long time periods can be beneficial to the success and speed of wetland delineation.

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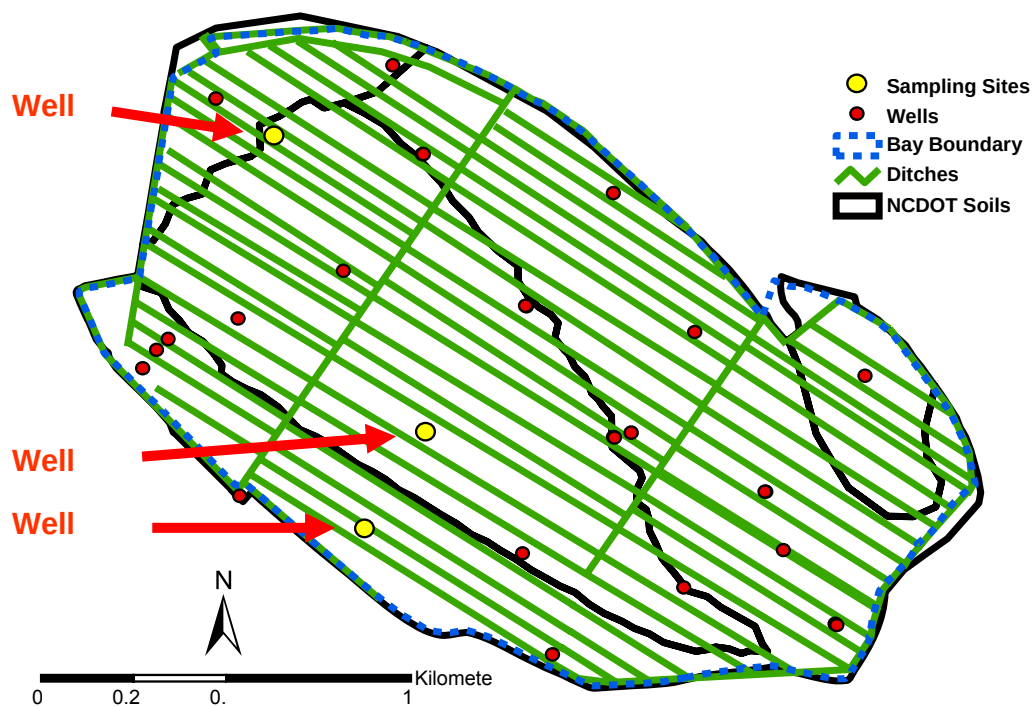


Figure 2.1: Map of Juniper Bay located in Robeson County, NC showing three soil sampling locations.

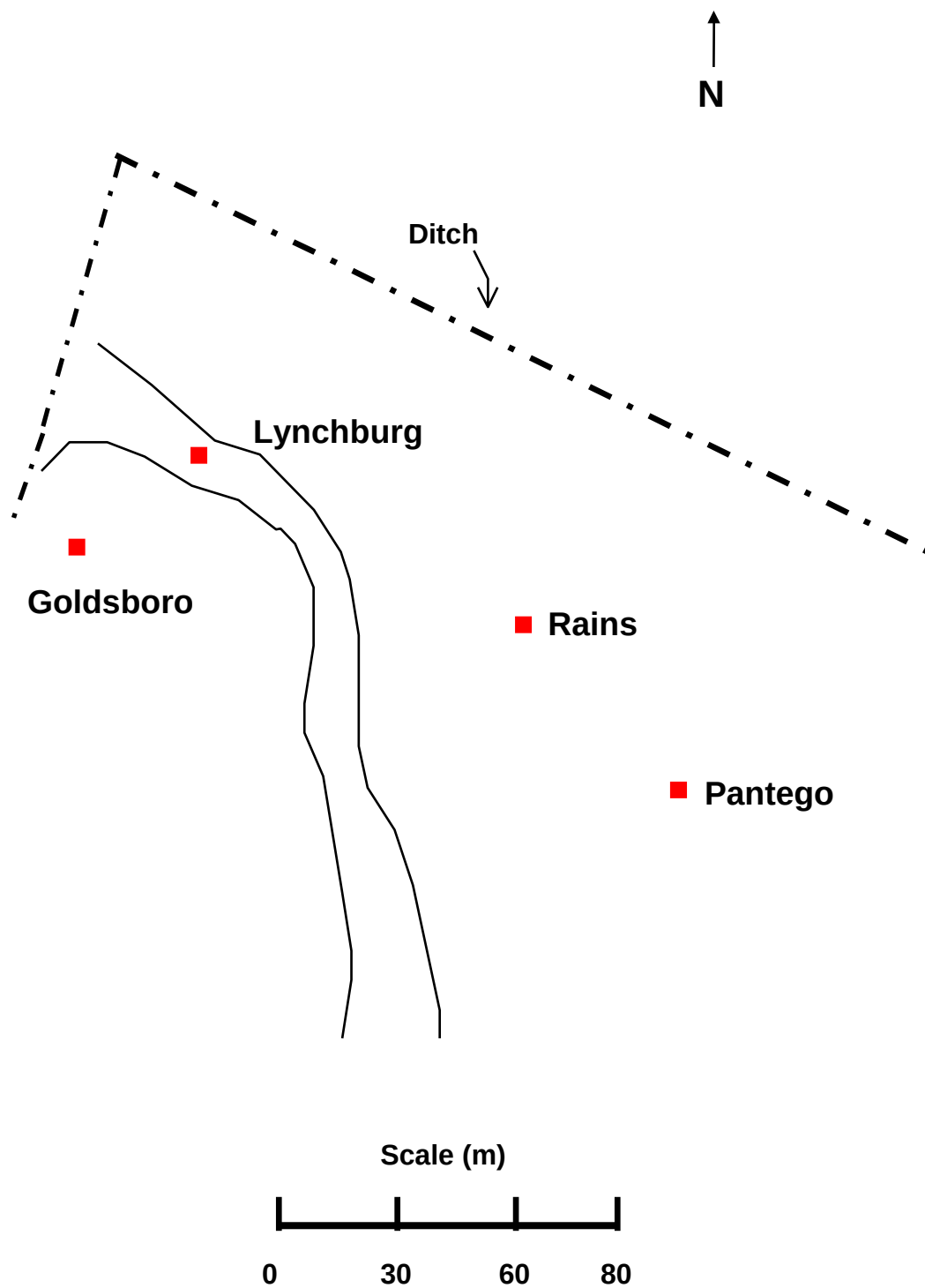


Figure 2.2: Map of the Greenville catena located near Greenville NC in Pitt County, showing four soil sampling locations (modified from Hayes and Vepraskas, 2000).

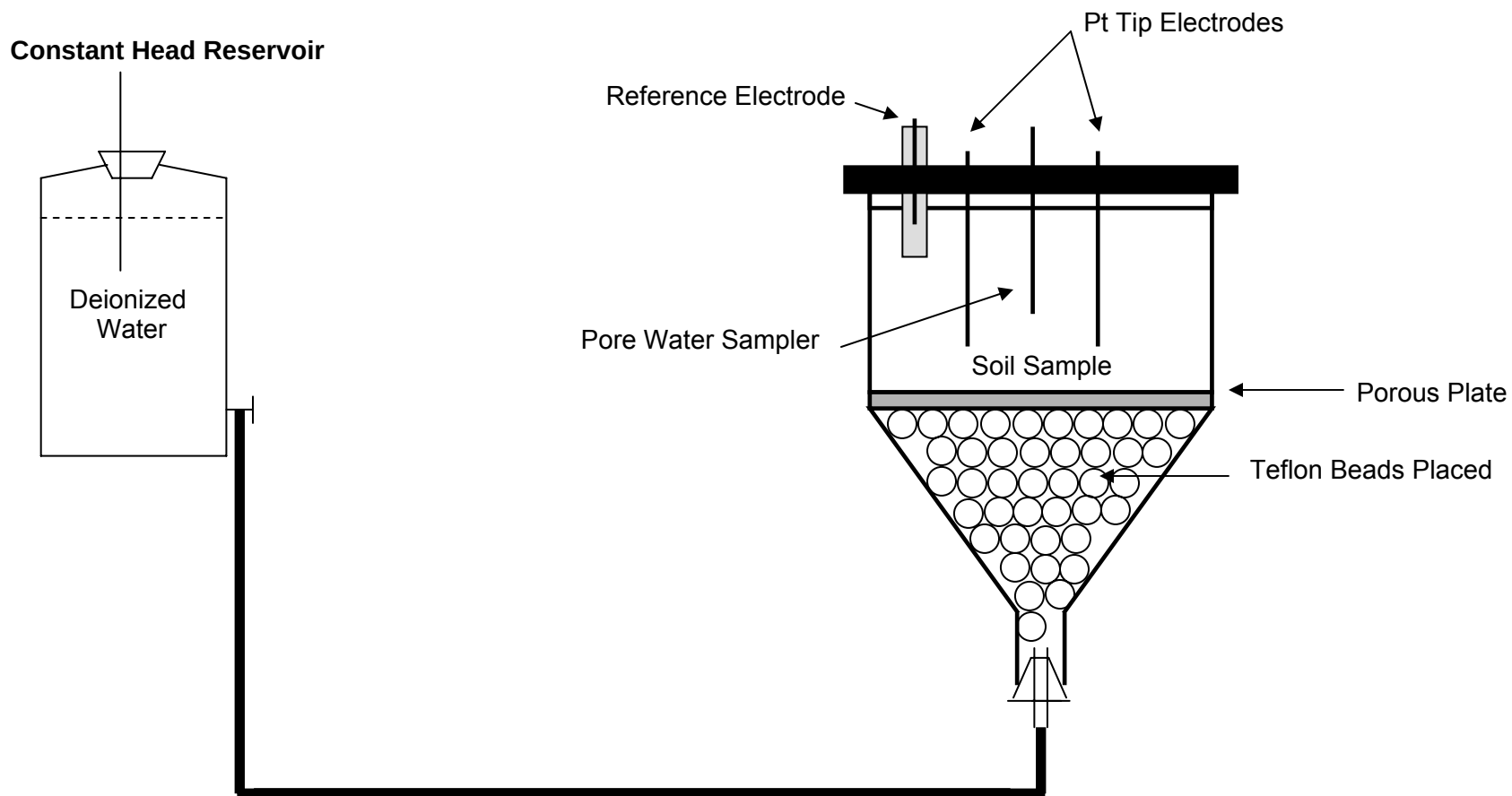


Figure 2.3: Redox incubation system depicting Buchner funnel on right with Pt tip electrodes, reference electrode, pore water sampler and salt bridge. Soil was packed above the porous plate and teflon beads were placed below to minimize the amount of water during incubation. A constant head reservoir (left) was used to saturate columns from the bottom upward.

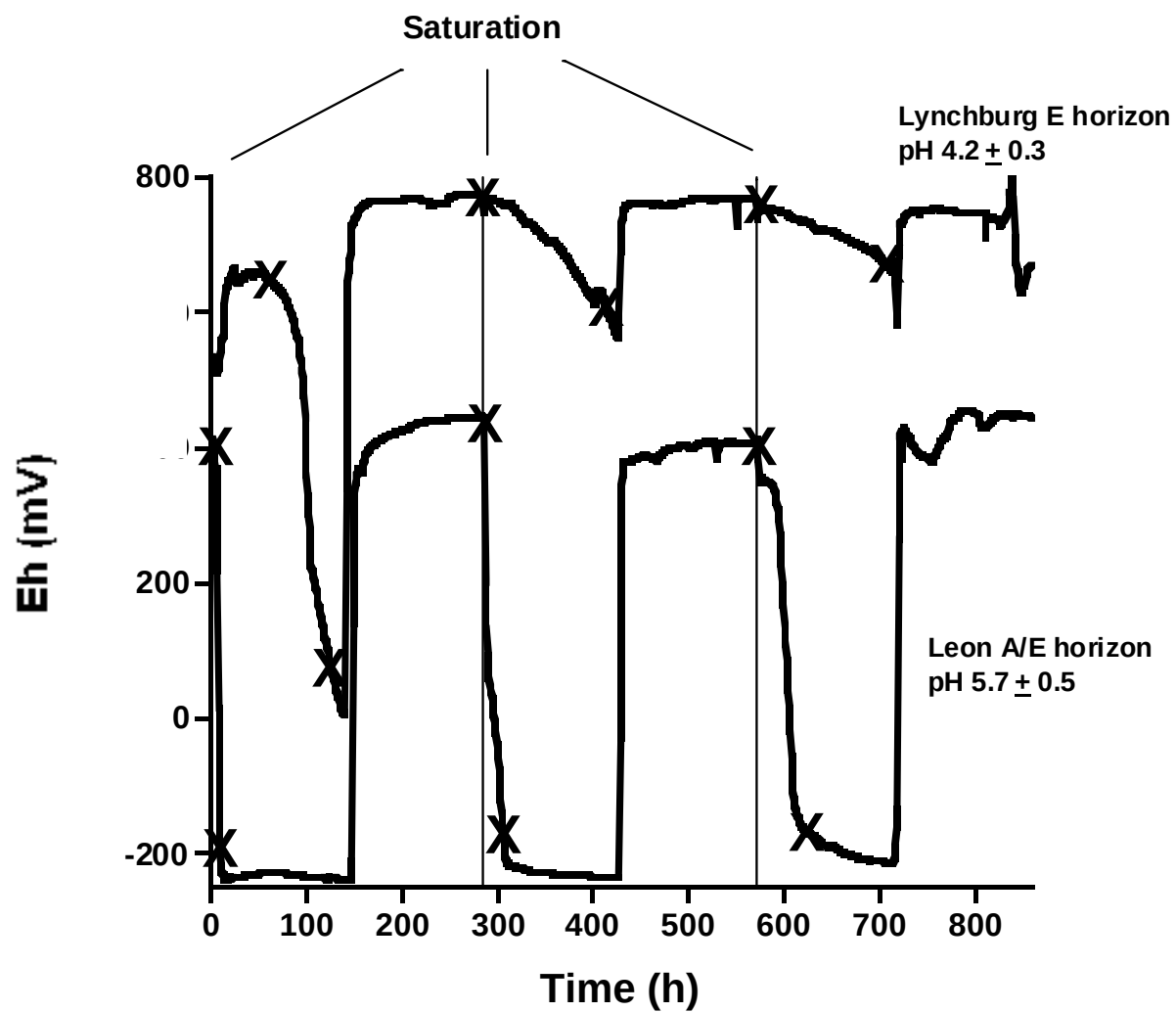


Figure 2.4: Three reduction-oxidation cycles of one replication of two different soil samples: the Lynchburg E horizon, and the Leon A/E horizon. The Y axis and the black vertical lines denote times where the water level was raised to saturate soils. “X” represents the endpoints of data used in the linear regression used to determine reduction rate.

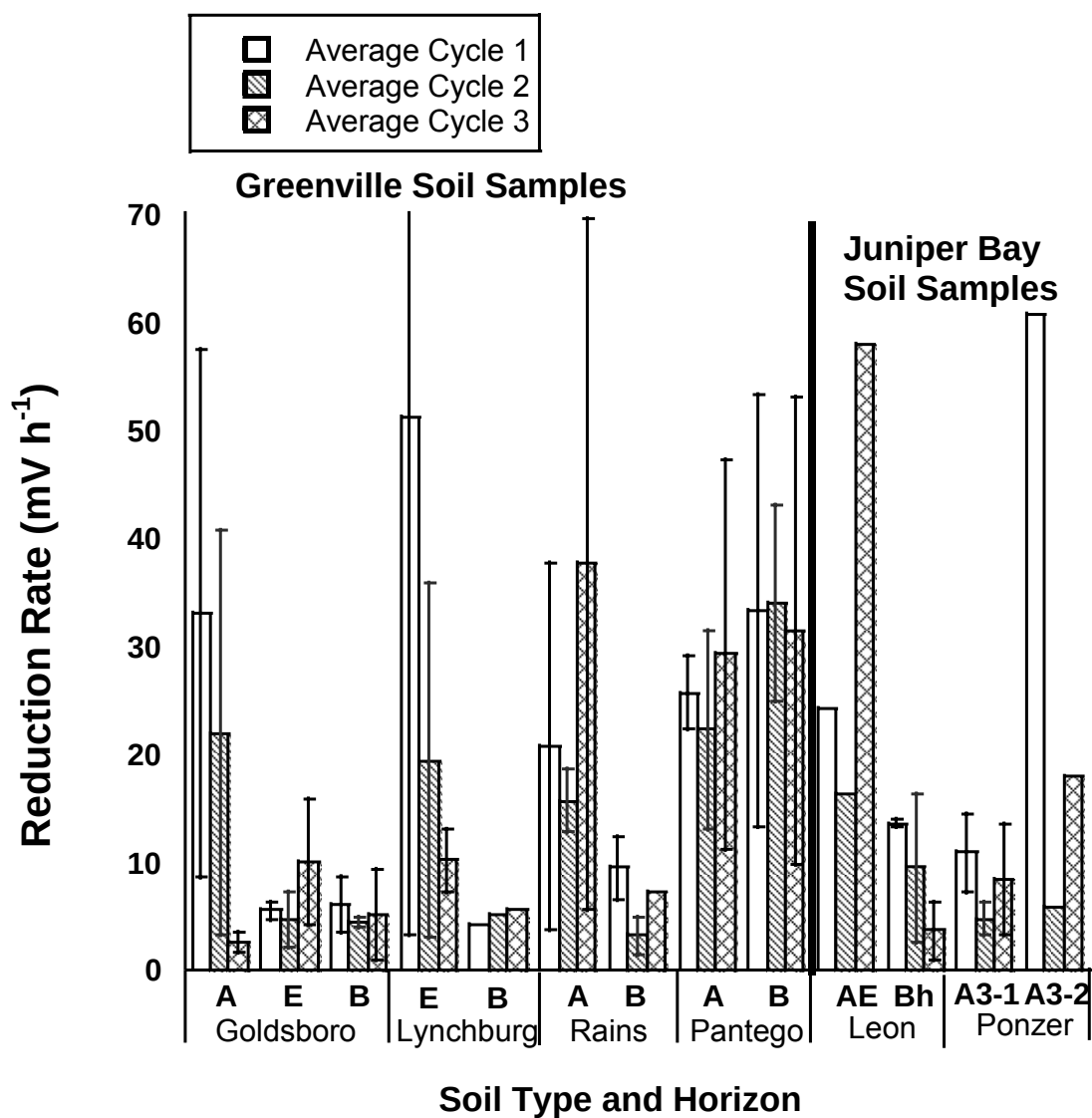


Fig 2.5: Average reduction rates for different soil samples in duplicate. The X axis is arranged by soil series, horizon, location, and landscape position (highest landscape position to left, lowest landscape position to right). Reduction rate was variable in many columns between cycles.

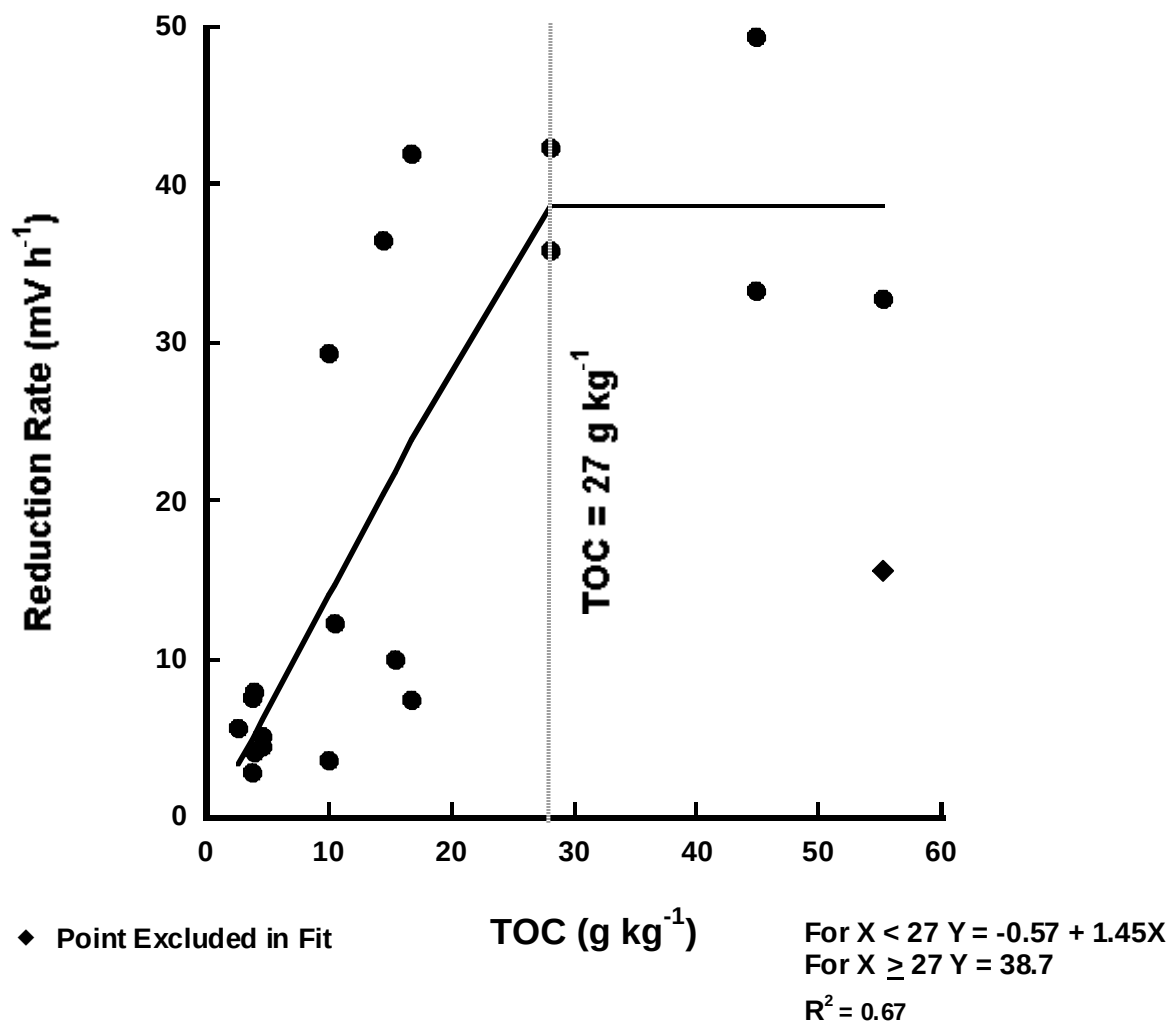


Figure 2.6: Total organic carbon (TOC) concentration is shown in relation to reduction rate. A linear plateau model was used to fit the data and shows increasing reduction rate with increasing TOC up until TOC = 27 g kg^{-1} . One outlying point, pictured as a diamond, was excluded from the fit.

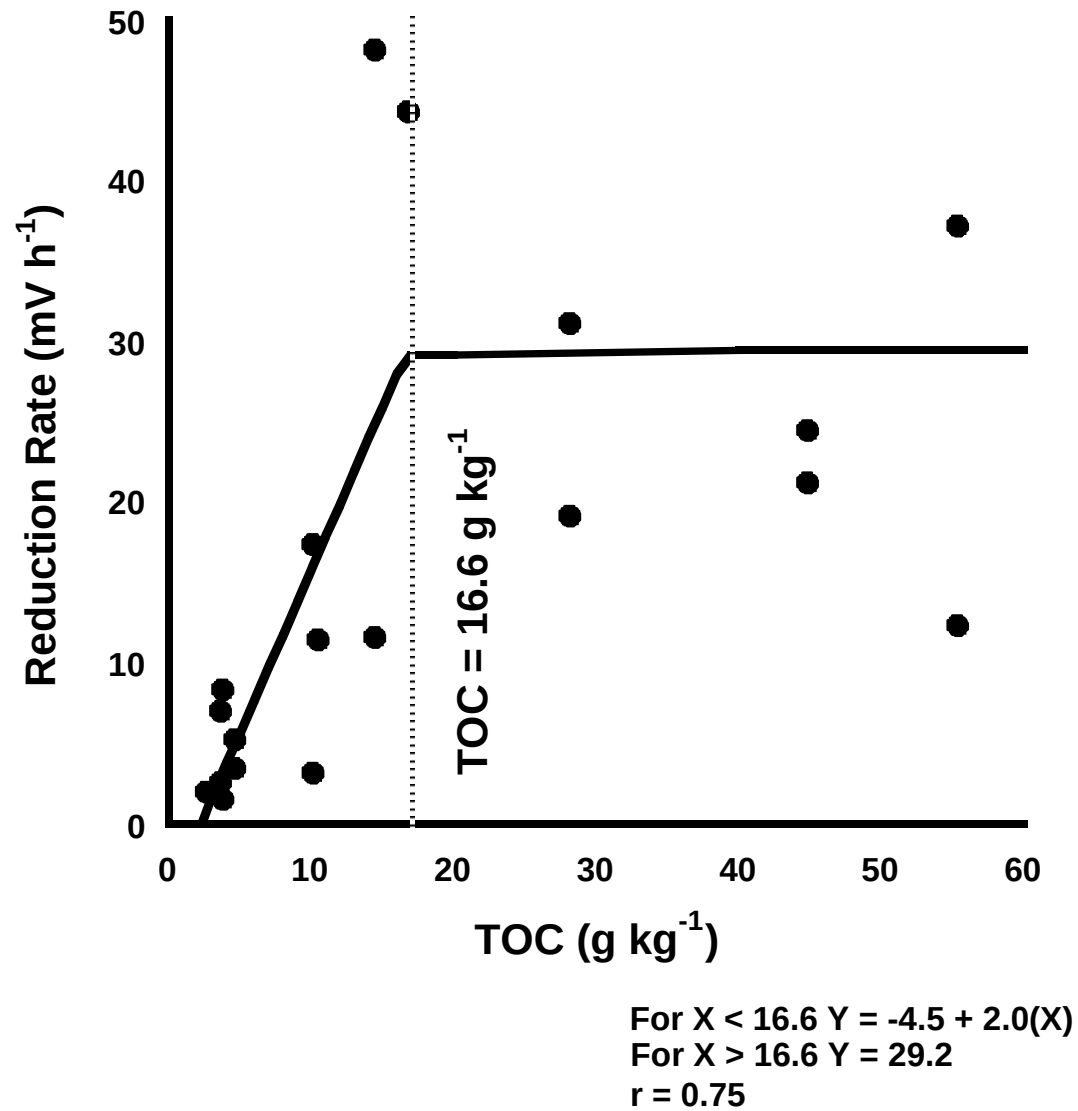


Figure 2.7: Total organic carbon (TOC) concentration shown in relation to average reduction rate using only the second and third reduction cycles. A linear plateau model was used to fit the data and shows increasing reduction rate with increasing TOC up until TOC = 16.6 g kg⁻¹.

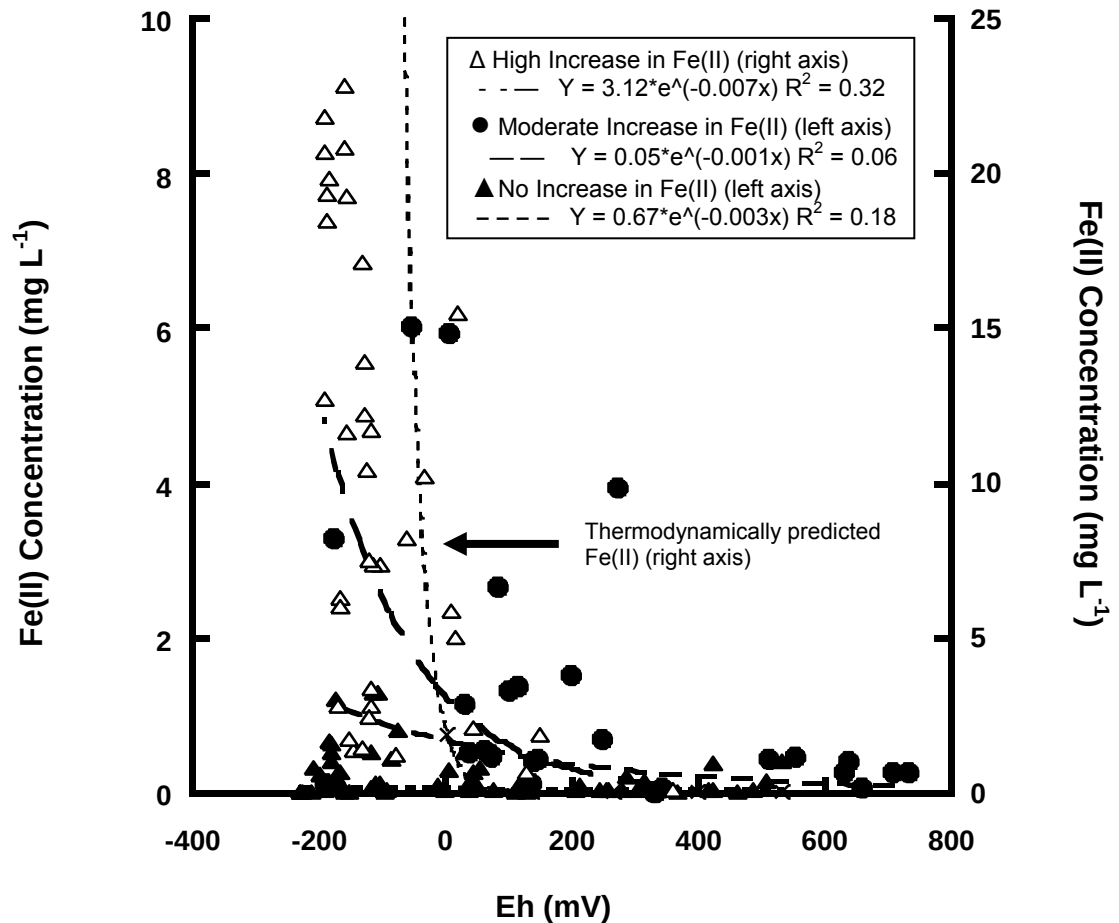


Figure 2.8: Dissolved Fe(II) (mg L⁻¹) vs. Eh for redox incubations. Three groups were denoted: those with high increases in Fe(II) (Pantego A and B horizons, Goldsboro A horizon, and Rains A horizon – right Y axis), those with moderate increases in Fe(II), (Rains E and B horizons, Lynchburg E horizon – left Y axis), and those with no increase in Fe(II), (remaining soils – left Y axis). The smooth curve corresponds to the thermodynamically predicted rate of Fe(II) dissolution from goethite, (right y axis).

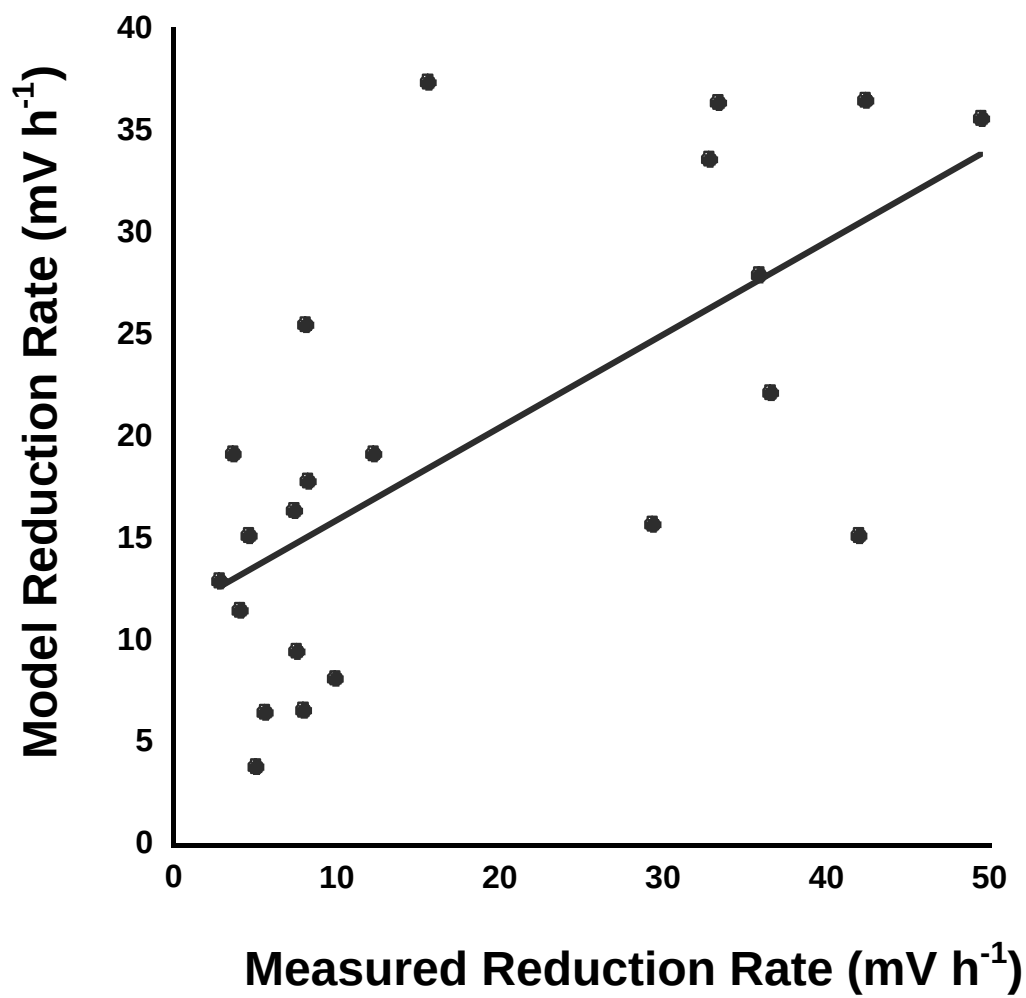


Figure 2.9: Measured reduction rate (mV h⁻¹) compared to multiple linear regression model for mineral soils. $RR = -57.0 + 0.55(\text{Total organic carbon}) + 13.7(\text{Initial pH})$.

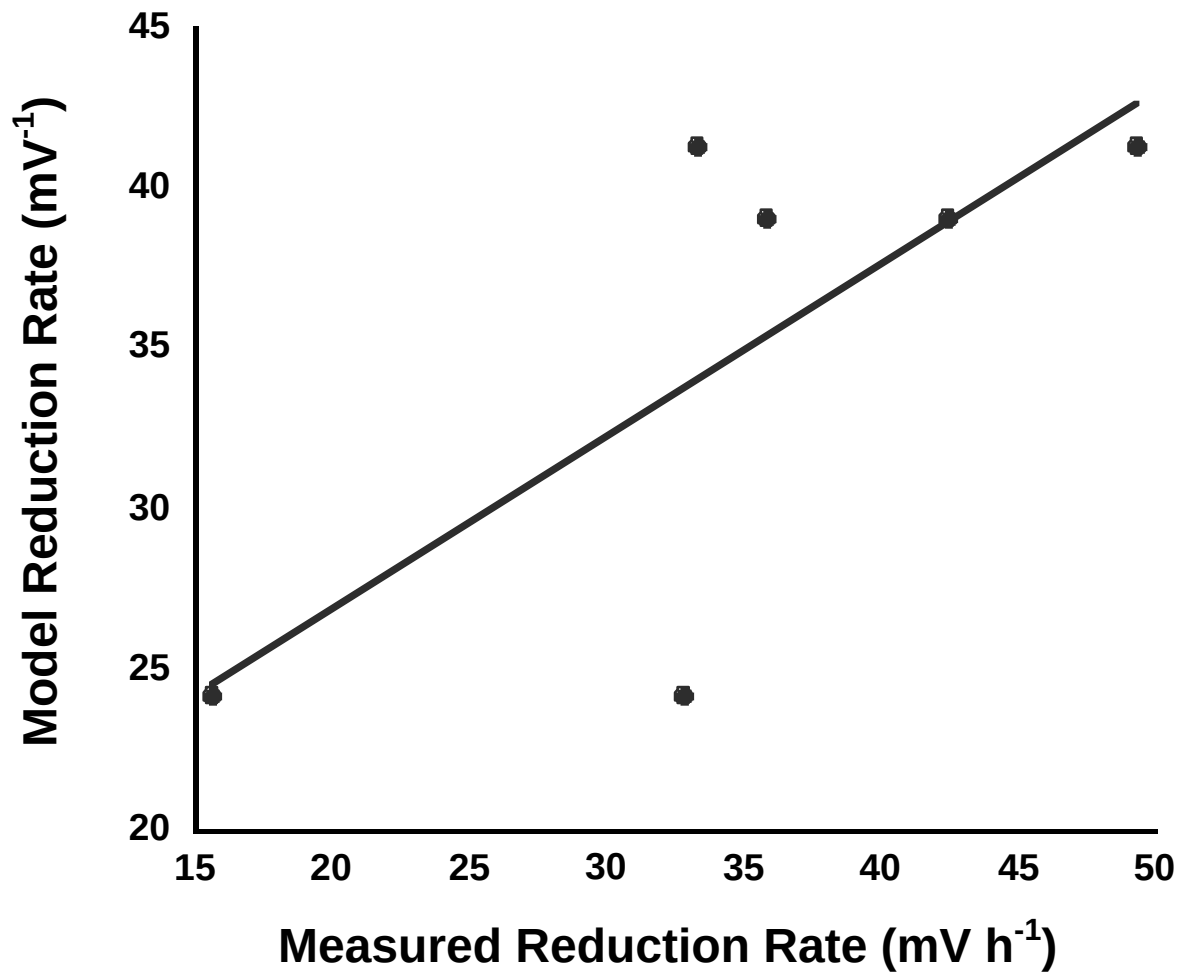


Figure 2.10: Measured reduction rate (mV h⁻¹) compared to multiple linear regression model for soils with total organic carbon (TOC) ≥ 27 g kg⁻¹. Reduction rate = $47.1 - 0.55(\text{TOC}) + 41.5$ (oxalate to CBD extractable Fe)

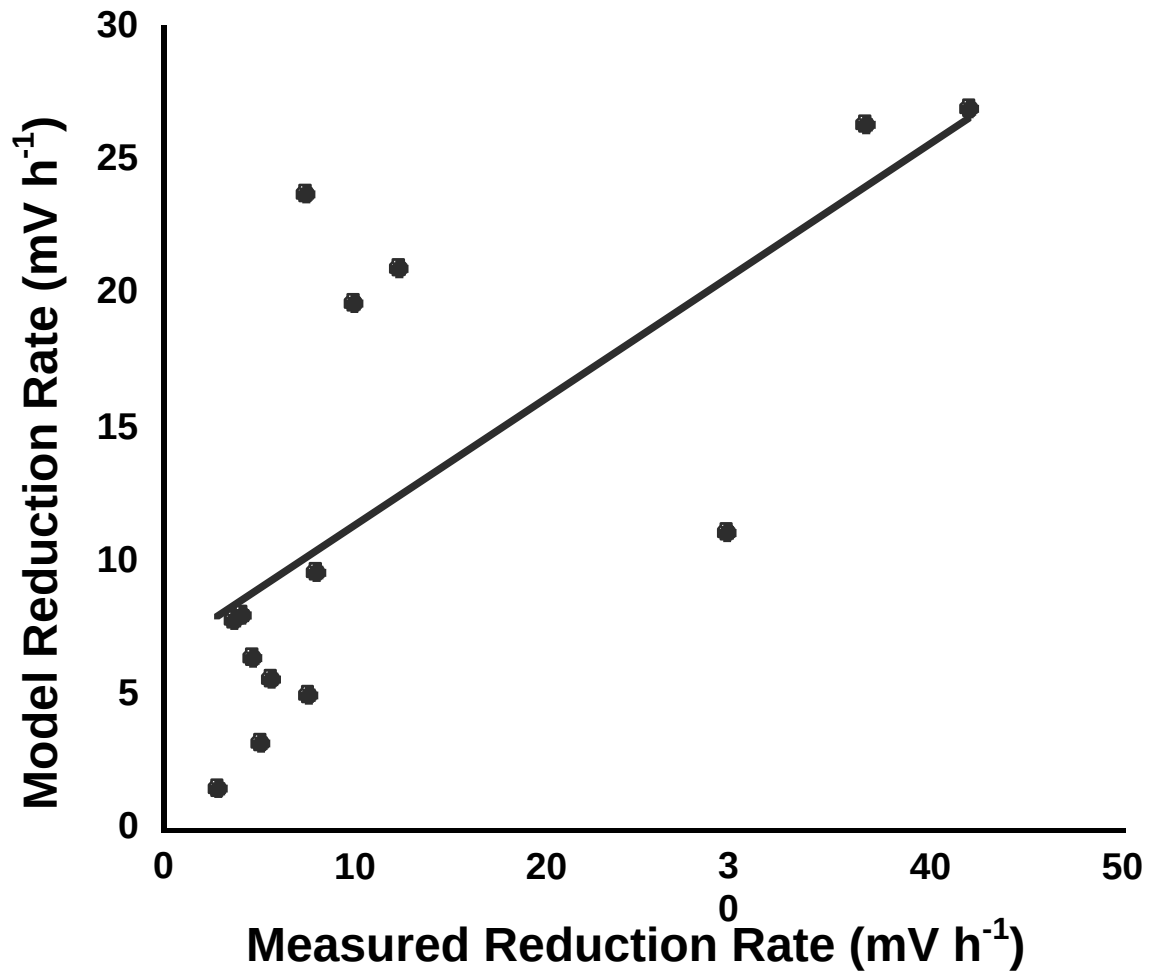


Figure 2.11: Measured reduction rate (mV h⁻¹) compared to multiple linear regression model for soils with total organic carbon (TOC) < 27 g kg⁻¹. Reduction rate = - 2.89 + 0.30(Dissolved organic carbon) + 0.92(TOC)

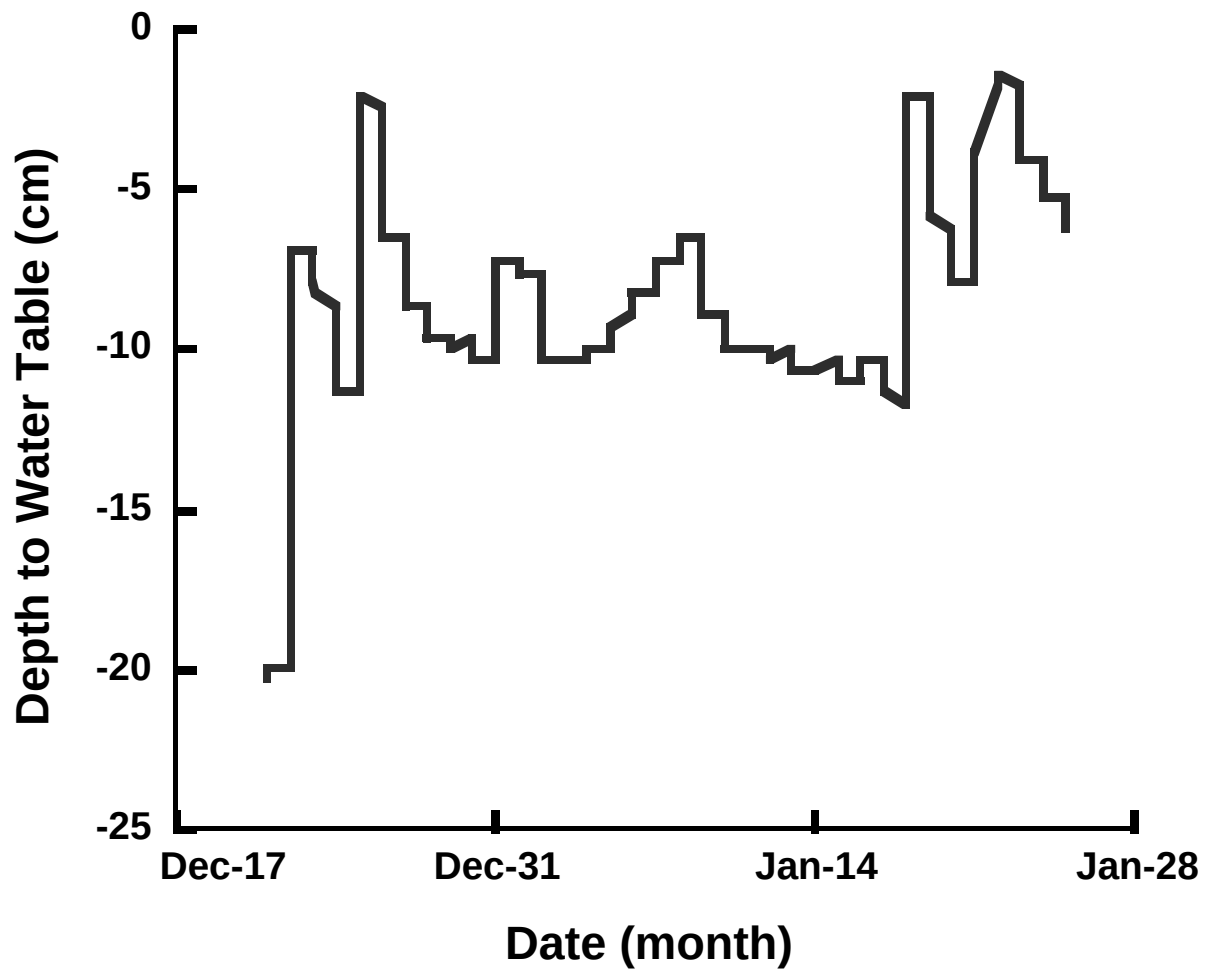


Figure 2.12: Example of water table fluctuation with time collected from Juniper Bay.

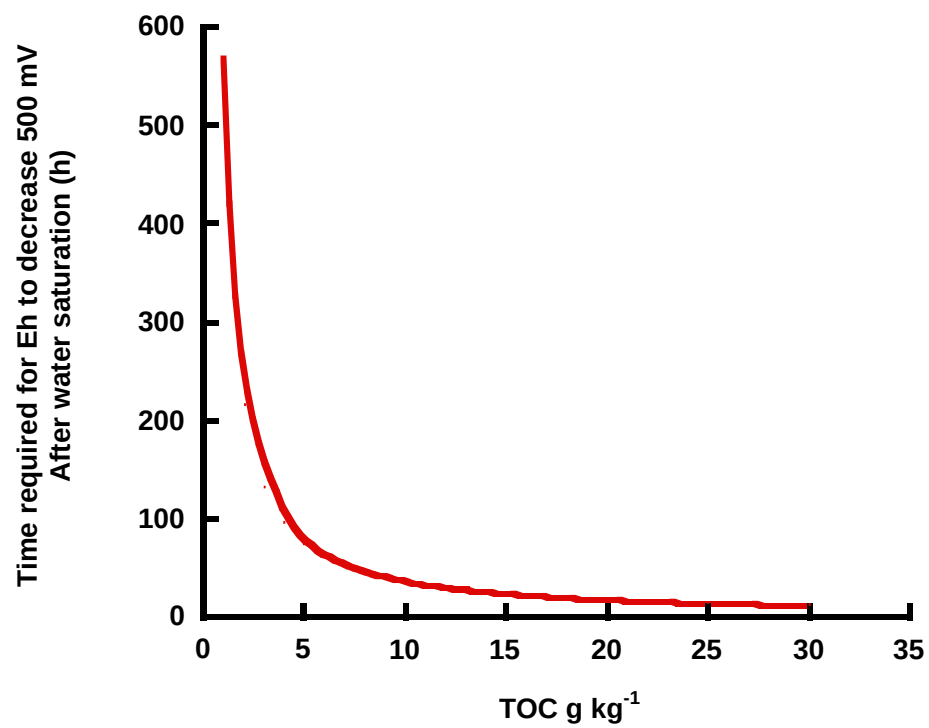


Figure 2.13. Total organic carbon (TOC) compared to the amount of time it would take for soil Eh to decrease by 500 mV after water saturation.

Table 2.1: Selected properties of soil samples used in this study.

Soil	Initial pH	TOC [†] -----g kg ⁻¹ -----	Total N [§] -----g C g N ⁻¹ -----	C/N Ratio g C g N ⁻¹	Fe _{pyr} [*] -----mmol kg ⁻¹ -----	Fe _{ox} [‡] -----mmol kg ⁻¹ -----	Fe _{CBD} [¶] -----mmol kg ⁻¹ -----	Fe _{ox} /Fe _{CBD} [¥] -----	Al _{CBD} [±]	Final pH
Ponzer Oa-1	4.2 ± 0.1	330 ± 24	5.5 ± 0.4	60	11.4 ± 0.8	9.8 ± 1.5	62.9 ± 3.4	0.16	130.7 ± 3.3	4.0 ± 0.04
Ponzer Oa-2	3.7 ± 0.0	560 ± 3.8	10.5 ± 0.4	53	10.4 ± 3.3	12.6 ± 1.8	64.5 ± 3.0	0.20	200.7 ± 9.1	3.8 ± 0.04
Ponzer Oa2-1	4.2 ± 0.3	38 ± 8.5	0.8 ± 0.3	48	1.2 ± 0.1	0.8 ± 0.6	10.0 ± 0.5	0.08	33.5 ± 1.1	4.3 ± 0.03
Ponzer Oa2-2	3.9 ± 0.2	390 ± 16	5.9 ± 0.3	66	3.9 ± 0.2	1.78 ± 0.73	28.1 ± 2.9	0.06	197.0 ± 9.6	3.7 ± 0.08
Leon A/E	5.4 ± 0.3	28 ± 2.2	1.0 ± 0.2	28	4.1 ± 0.3	4.9 ± 0.8	27.1 ± 1.6	0.18	15.0 ± 0.9	5.5 ± 0.3
Leon Bhir	4.9 ± 0.2	11 ± 0.3	0.3 ± 0.0	37	0.6 ± 0.1	0.8 ± 0.3	5.3 ± 0.7	0.15	9.7 ± 1.3	5.4 ± 0.2
Goldsboro A	5.0 ± 0.0	45 ± 5.2	1.5 ± 0.2	30	47.1 ± 0.3	41.4 ± 0.1	90.9 ± 0.4	0.46	105.6 ± 3.6	4.9 ± 0.05
Goldsboro B	4.8 ± 0.1	3.7 ± 0.3	≤0.2 ± 0.1	≥19	26.5 ± 1.3	6.2 ± 1.2	182.8 ± 5.7	0.03	130.4 ± 1.4	5.0 ± 0.03
Goldsboro E	5.0 ± 0.1	10 ± 1.1	0.3 ± 0.1	33	28.5 ± 1.3	17.3 ± 0.4	35.5 ± 1.9	0.49	92.6 ± 4.0	5.0 ± 0.8
Lynchburg B	4.7 ± 0.2	2.7 ± 0.2	≤0.2 ± 0.0	≥14	10.0 ± 1.5	3.8 ± 1.3	150.5 ± 1.1	0.03	102.6 ± 2.1	4.4 ± 0.2
Lynchburg E	4.7 ± 0.4	4.6 ± 4.5	≤0.3 ± 0.0	≥15	27.8 ± 1.0	7.6 ± 0.7	118.8 ± 3.5	0.06	84.8 ± 5.8	4.4 ± 0.04
Rains A	4.02 ± 0.4	50 ± 1.2	1.5 ± 0.1	33	9.2 ± 0.3	11.6 ± 2.0	56.3 ± 3.6	0.21	40.4 ± 1.4	4.2 ± 0.1
Rains B	4.7 ± 0.2	3.9 ± 0.5	≤0.2 ± 0.0	≥20	0.8 ± 0.5	0.4 ± 0.2	9.2 ± 1.5	0.04	5.3 ± 0.9	5.0 ± 0.3
Rains E	4.6 ± 0.1	17 ± 1.1	0.4 ± 0.1	43	4.5 ± 0.3	5.0 ± 1.4	33.0 ± 5.3	0.15	21.5 ± 1.9	4.7 ± 0.1
Pantego A	4.5 ± 0.1	55 ± 6.8	1.5 ± 0.1	37	7.4 ± 0.3	6.5 ± 1.6	35.7 ± 3.8	0.18	35.9 ± 0.9	4.2 ± 0.1
Pantego B	4.7 ± 0.5	15 ± 1.0	0.5 ± 0.00	30	3.1 ± 1.6	2.7 ± 0.6	17.5 ± 1.7	0.15	21.0 ± 1.1	4.4 ± 0.2

† Total Organic Carbon determined with Perken Elmer PE 2400 CHN elemental analyzer

§ Total Nitrogen determined by a Perken Elmer PE 2400 CHN elemental analyzer

* Sodium Pyrophosphate extractable Fe (Loeppert and Inskeep 1996).

‡ Oxalate extractable Fe (Jackson et al. 1987)

¶ Citrate Bicarbonate Dithionate extractable Fe (Jackson et al. 1987)

¥ Ratio of Oxalate extractable Fe to Citrate Bicarbonate Dithionate extractable Fe

± Citrate Bicarbonate Dithionate extractable Al (Jackson et al. 1987)

Table 2.2 Summary of regression models relating reduction rate (RR) to soil properties

Linear Correlation Results			
Variable	-----Regression Equations-----		
Mineral Soils	Intercept	Coefficient	r
TOC ⁺	8.00	0.58	0.62 [*]
Average DOC ^a	8.59	0.32	0.47 [*]
Fe(II) [§]	13.65	1.66	0.45 [*]
C:N Ratio ^Δ	-7.40	1.02	0.41 ^{**}
Humic Acid	30.38	-2.37	0.41 ^{**}
Initial pH	-42.9	12.7	0.34 ^{***}
Soils with TOC < 27 g kg ⁻¹			
Average DOC	0.006	0.50	0.40 [*]
TOC	-0.51	1.54	0.40 [*]
Soils with TOC ≥ 27 g kg ⁻¹			
TOC	55.5	-0.48	0.27 ^{ns}
C:N Ratio	-19.75	2.04	0.19 ^{ns}
Linear Plateau Mode			
	-----Regression Equation-----		r
TOC < 27 g kg ⁻¹	RR = -0.57 + 1.45(TOC)		0.82 [*]
TOC ≥ 27 g kg ⁻¹	RR = 38.7		
Multiple Linear Regression Results			
Mineral Soils	-----Regression Equation-----		R ²
TOC and Initial pH	RR=-57.0 + 0.55(TOC) + 13.7(pH)		0.49 [*]
TOC < 27 g kg ⁻¹	RR = -2.89+ 0.30(DOC) +0.92(TOC)		0.48 [*]
DOC and TOC			
TOC ≥ 27 g kg ⁻¹	RR = 47.1 + TOC(-0.55) + 41.5(OX: CBD)		0.54 ^{ns}
TOC and OX: CBD [@]			

+ Total organic carbon determined with Perkin Elmer PE 2400 CHN elemental analyzer

a Dissolved organic carbon in soil pore water samples

§ Mean dissolved Fe(II) in soil pore water samples

Δ Carbon to nitrogen ratio (g g⁻¹)

* p-value < 0.05

** p-value < 0.10

*** p-value < 0.25

@ Oxalate extractable Fe to citrate bicarbonate dithionite extractable Fe (mmol kg⁻¹)

ns p-value > 0.25

Table 2.3 Summary of regression models relating reduction rate (RR) to soil properties using only second 2 reduction cycles to calculate average RR.

Linear Correlation Results			
Variable	-----Regression Equations-----		
Mineral Soils	Intercept	Coefficient	r
TOC ⁺	8.00	0.58	0.50 [*]
Average DOC ^a	8.59	0.32	0.60 [*]
Fe(II) [§]	13.65	1.66	0.45 [*]
C:N Ratio ^Δ	-7.40	1.02	0.42 ^{**}
Humic Acid	30.38	-2.37	0.47 [*]
Initial pH	-42.9	12.7	0.25 ^{ns}
Soils with TOC < 27 g kg ⁻¹			
Average DOC	-3.15	0.67	0.76 [*]
TOC	-3.85	1.90	0.68 [*]
Soils with TOC ≥ 27 g kg ⁻¹			
TOC	45.2	-0.41	0.50 ^{ns}
C:N Ratio	67.36	-1.48	0.36 ^{ns}
Linear Plateau Mode			
	-----Regression Equation-----		r
TOC < 17 g kg ⁻¹	RR = -4.5 + 2.0(TOC)		0.75 [*]
TOC ≥ 17 g kg ⁻¹	RR = 29.2		
Multiple Linear Regression Results			
Mineral Soils	-----Regression Equation-----		R ²
TOC and Initial pH	RR=-60.80 + 0.39(DOC) + 13.4(Initial pH)		0.46 [*]
TOC < 17 g kg ⁻¹	RR = 40.0+ 0.67(DOC) -10.5 (Average pH [~])		0.63 [*]
DOC and TOC			
TOC ≥ 17 g kg ⁻¹	RR = 40.37 + 0.18(DOC) - 5.35(Humic Acid)		0.059 ^{ns}
TOC and OX:CBD [@]			

+ Total organic carbon determined with Perkin Elmer PE 2400 CHN elemental analyzer

a Dissolved organic carbon in soil pore water samples

§ Mean dissolved Fe(II) in soil pore water samples

Δ Carbon to nitrogen ratio (g g⁻¹)

~ pH averaged from initial column set up through final take down

* p-value < 0.05

** p-value < 0.10

*** p-value < 0.25

@ Oxalate extractable Fe to citrate bicarbonate dithionite extractable Fe (mmol kg⁻¹)

ns p-value > 0.25

Table 2.4: Selected soil incubation properties divided into low total organic carbon (TOC) (< 27 g kg⁻¹) and high TOC (≥ 27 g kg⁻¹) for mineral soil incubations.

	Reduction Slope		Dissolved Fe(II) [§] mg L ⁻¹		Final MBC ^Δ		DOC [¥] (mg kg ⁻¹)		Oxalate to CBD Fe ratio ⁺		C/N Ratio [£]		Initial pH		Humic Acid %(g HA / g soil)	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Low TOC [‡]	12.7	39.2	2.7	14.0	60.6	119	25.4	49.5	0.10	0.17	24.8	24.8	4.80	1.1	5.3	9.9
High TOC ^a	34.9	33.7	4.2	10.9	214.3	499	51.3	88.6	0.27	0.28	26.8	26.8	5.0	1.3	4.1	3.2
Difference [@]	-22.2		-1.5		-153.7		-25.9		-0.17		-2.0		-0.2		1.7	
LSD [*]	12.5		3.92		110.6		28.6		0.11		6.00				2.34	
P – Value	< 0.05		0.05		<0.05		< 0.05		< 0.05		< 0.05		0.97		0.13	

⁺Oxalate to CBD Fe ratio represents poorly crystalline to total Fe in soils.

[‡] Low total organic carbon (< 27 g kg⁻¹)

^a High total organic carbon (≥ 27 g kg⁻¹)

[¥] Total dissolved organic carbon measured from water samples

[£] Carbon to nitrogen ratio gC gN⁻¹

⁺Oxalate to citrate bicarbonate dithionate Fe ratio represents poorly crystalline to total Fe in soils.

^Δ Final microbial biomass carbon

[§] Average dissolved Fe(II) measured from water samples

[@] Difference between means

^{*}Fishers protected least significant difference,

Table 2.5: Average initial microbial biomass carbon (MBC) and average final MBC for all soil samples.

Soil	Initial MBC*	Final MBC
	-----mg C / kg soil-----	
Ponzer Oa-1	946 $\pm$ 56.1	312 $\pm$ 189
Ponzer Oa-2	86.9 $\pm$ 41.9	141 $\pm$ 53.0
Ponzer Oa2-1	13200 $\pm$ 5980	1410 $\pm$ 546
Ponzer Oa2-2	270 $\pm$ 135	492 $\pm$ 196
Leon A/E	74.6 $\pm$ 13.9	117 $\pm$ 29.8
Leon Bhir	306 $\pm$ 116	56.0 $\pm$ 21.0
Goldsboro A	2820 $\pm$ 1160	373 $\pm$ 116
Goldsboro B	873 $\pm$ 372	21.6 $\pm$ 6.19
Goldsboro E	176 $\pm$ 13.8	147 $\pm$ 50.2
Lynchburg B	1035 $\pm$ 433	31.7 $\pm$ 3.56
Lynchburg E	179 $\pm$ 12.3	182 $\pm$ 32.4
Rains A	597 $\pm$ 89.0	545 $\pm$ 193
Rains B	465 $\pm$ 181	85.5 $\pm$ 35.7
Rains E	686 $\pm$ 291	118 $\pm$ 32.0
Pantego A	2971 $\pm$ 1220	795 $\pm$ 108
Pantego B	220 $\pm$ 13.3	225 $\pm$ 40.2

* MBC was higher than feasible (> 3% total organic carbon) for initial MBC measurements indicating experimental error.

APPENDICIES

APPENDIX A

General Soil Properties

General soil properties are depicted in Tables A1.1-A1.6. Soil descriptions for all Juniper Bay soils were conducted by Ewing (2003). Descriptions for the Greenville catena site were performed when samples were taken by Gary Kreiser.

Construction of Incubation Set up

Incubation lids were constructed using ½ inch thick polycarbonate sheeting cut to measure 13.3 X 13.3 cm squares. Holes for the pore water sampler, Pt tip electrodes, reference electrode, gas inlet, gas outlet, and anchoring were drilled as pictured in Fig. A1.1. Columns were designed to be anchored into a rack by using screws extending from a wooden base through each of the four corners of the incubation lid. The bottom of each funnel extended below the wooden base so that saturation and drainage could be achieved easily. The rack was originally designed by the NCSU soil physics department for use when determining soil moisture release curves.

Water samples were taken over the course of six hours using 50 mL vacuum bottles and a lure-lock valve with syringe connected to pore water samplers. Water samples were collected over the course of six hours. A picture of the incubation system while water samples were being taken can be seen in figure A1.2.

Table A1.1: Profile description of Pantego soil, a Umbric Paleaquult

Horizon	Depth (in)	Matrix	Texture	Structure	Comments
Ap	0-5	10 YR 2/1	L	Weak Fine GR	Gradual Wavy Boundary
Btg	5-12	10 YR 5/1	SCL	Weak Fine SAB	Fe Masses Common 10 YR 5/6

Table A1.2: Profile description of Lynchburg soil, a Aerobic Paleaquult

Horizon	Depth (in)	Matrix	Texture	Structure	Comments
Ap	0-5	10 YR 3/2	LS	Weak Fine GR	Gradual Wavy Boundary
E	5-11	7.5 YR 3/2	LS	Weak Fine SAB	
Bt	11-16+		SCL	Weak Fine SAB	Fe Masses Few 5YR 5/4

Table A1.3: Profile description of Rains soil, a Typic Paleaquult

Horizon	Depth (in)	Matrix	Texture	Structure	Comments
O	0-3				
A	3-8	10YR 3/1	SL	Weak Fine GR	Clear Boundary
Eg	8-11	10YR 6/2	SL	Weak Fine GR	
Btc1	11-+	10YR 6/1	SCL	Weak Moderate SAB	Fe Masses Few 10YR 5/6

Table A1.4: Profile description for Goldsboro soil, a Aquic Paleudult

Horizon	Depth (in)	Matrix	Texture	Structure	Comments
O	0-1				Root Mat Wood Chips
Ap	1-4	10YR 5/2	LS	Weak Moderate GR	Clear Boundary
E	4-10	10 YR 6/4	LS	Weak Moderate SAB	
BE	10-12	10 YR 5/6	SL	Weak Fine SAB	Clear Boundary
Bt	12 +	10 YR 5/6	SCL	Weak Fine SAB	

Table A1.5: Profile description of Ponzer soil, a Terric Haplosaprists

Horizon	Depth (cm)	Matrix	Texture	Structure	Comments
Ap	0-10	10YR 2/2	SL	Moderate Medium Granular	Abrupt Boundary
Oa	10-20	N 2.5/0	sm	Moderate Fine Granular	Abrupt Boundary
OA1	20-51	10YR 2/1	mSiL	Weak Very Course Prismatic	Clear Boundary
OA2	51-61	10YR 2/2	mSiL	Weak Course Prismatic	25% Charcoal
OA3	61-68	10YR 3/3	mfSL	Very Weak Course Prismatic	Clear Boundary

Table A1.6: Profile description of Leon soil, a Aeris Alaquod

Horizon	Depth (cm)	Matrix	Texture	Structure	Comments
Ap	0-17	10YR 2/1	SL	Weak Medium Granular	Clear Boundary
A/E	17-33	10YR 2/1	LS	Weak Medium Sub-angular Blocky	25% light gray sand
Bhir	33-50	10YR 3/3	LS	Weak Medium Sub-angular Blocky	5% light gray sand, Gradual boundary
Bt1	50-78	10YR 4/4	SL	Weak Very course Prismatic	Gradual Boundary

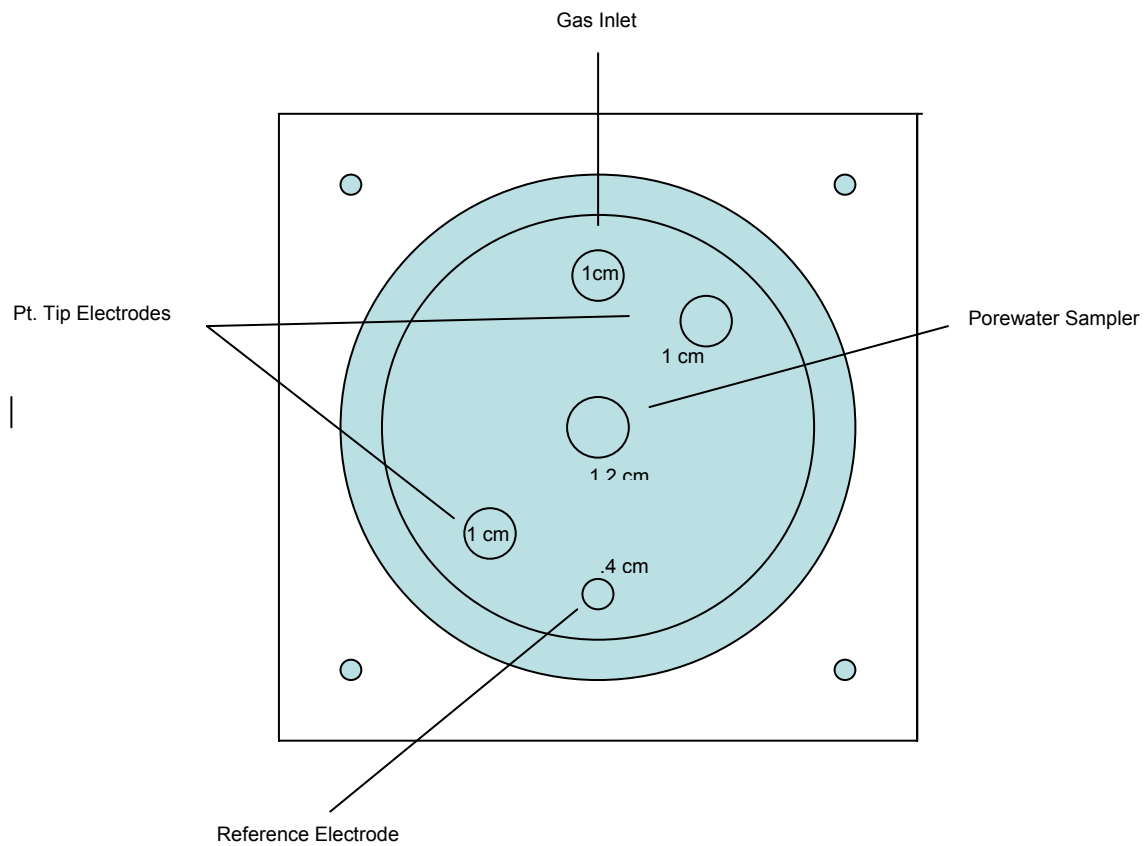


Figure A1.1: Incubation lid design is pictured. Lids were constructed from $\frac{1}{2}$ in. thick polycarbonate sheeting measuring 13.3 by 13.3 cm square.

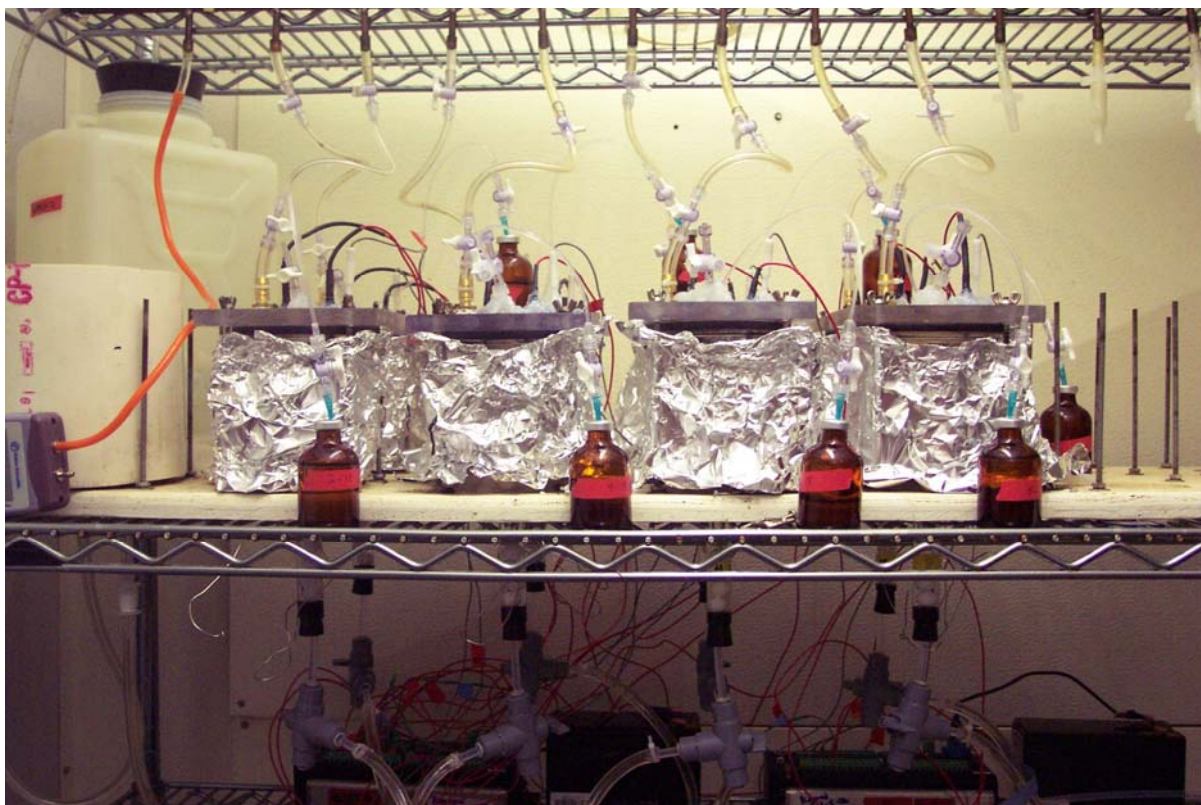
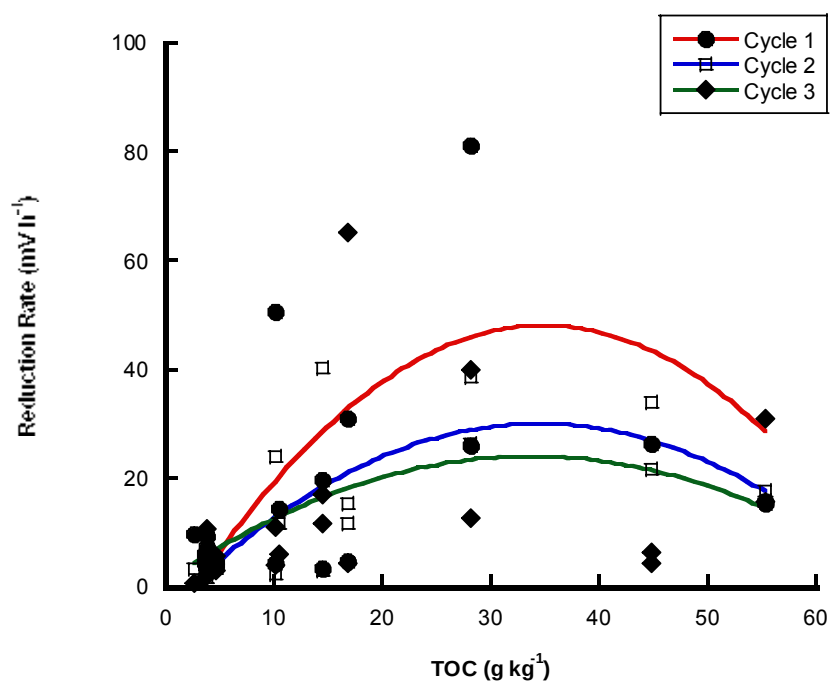


Figure A1.2: Picture of incubation system while water samples are being taken. Water samples were collected in 50 mL vacuum bottles over the course of 6 hours.



Y = M0 + M1*x + ... M8*x ⁸ + M9*x ⁹	
M0	-8.8461
M1	3.2602
M2	-0.046727
R ²	0.36811

Y = M0 + M1*x + ... M8*x ⁸ + M9*x ⁹	
M0	-4.3743
M1	1.994
M2	-0.028908
R ²	0.58844

Y = M0 + M1*x + ... M8*x ⁸ + M9*x ⁹	
M0	0.81445
M1	1.3738
M2	-0.020372
R ²	0.16305

Figure A1.3: Total organic carbon compared to reduction rate for mineral soils using un-averaged reduction rates from each reduction cycle. Although similar, the trends between cycles had different magnitudes.

APPENDIX B: Water Sample Data

Table A4.1: Water sample pH data for all incubations.

Rep 1

Soil Type	Day												
	Initial pH	0	1	2	3	5	13	14	15	17	25	26	27
	pH												
Rains B	4.85	3.93	4.31	4.09	4.24	4.26	5.01	5.01	5.01	5.00	5.19	5.06	5.43
Lynchburg E	5.09	4.59	4.00	4.15	4.12	3.88	4.21	4.21	4.04	4.01		3.87	4.13
Pantego B	5.20	4.49	4.06	3.88	3.93	3.78	4.09	4.09	3.96	3.89	3.91	3.95	4.28
Pantego A	4.67	4.66	4.63	4.03	3.83	3.62	3.94	3.94	3.90	3.93	3.80	3.9	4.11
Ponzer OA3-2	4.07	4.23	4.11	3.67	3.61	3.45	3.73	3.73	3.59	3.58		3.46	3.71
Ponzer OA1-1	4.29	3.71	3.76	3.66	3.77	3.69	4.01	4.01	3.92	3.82	3.69	3.70	3.98
Leon AE	5.70	5.48	4.95	4.95	5.22	5.12	6.32	6.32	6.16	5.94	6.20	6.20	6.45
Lynchburg B	4.78	4.23	4.15	3.9	3.94	3.75	4.03	4.03	3.84	3.86	3.70	3.77	3.98

Rep 2

Soil Type	Day												
	Initial pH	0	1	3	4	5	13	14	16	17	25	27	28
	pH												
Ponzer OA1-2	3.76	3.43	3.57	3.59	3.46	3.74	3.68	3.69	3.58	3.73	3.65	3.76	
Goldsboro B	4.96	4.22	4.29	4.19	4.05	4.28	4.31	4.29	4.21	4.37	4.41	4.59	4.5
Rains E	4.69	3.43	3.74	3.86	3.80	4.05	4.20	4.26	4.27	4.42	4.30	4.49	4.45
Rains A	4.43	3.46	3.74	3.74	3.62	3.88	3.81	3.88	3.81	3.86	3.92	4.04	3.92
Goldsboro A	5.02	4.20	4.37	4.41	4.23	4.48	4.33	4.33	4.41	4.56	4.42	4.73	4.74
Ponzer OA3-1	4.51	3.58	3.42	3.84	3.72	4.01	4.00	4.05	3.98	4.11	4.08	4.24	4.14
Goldsboro E	5.16	4.12	4.35	4.39	4.25	4.59	4.49	4.55	4.49	4.67	4.66	4.80	4.72
Leon Bh	5.14	4.79	5.00	4.67	4.49	4.62	4.86	4.93	4.86	4.86	5.04	5.19	5.1

Rep 3

Soil Type	Day												
	Initial pH	0	1	2	3	5	13	14	15	17	25	27	32
	pH												
Rains E	4.60	3.36	3.36	3.38	3.44	3.48	3.65	3.73	3.83	3.91	4.02	3.96	3.93
Goldsboro B	4.71	3.65	3.79	3.83	3.88	3.82	4.00	4.04	4.04	4.15	3.99	3.88	3.80
Ponzer OA1-2	3.69	3.42	3.37	3.37	3.37	3.31	3.45	3.47	3.54	3.52	3.56	3.46	3.48
Lynchburg B	4.53	3.94	3.85	3.77	3.68	3.55	3.93	3.86	3.85	3.91	3.80	3.58	3.96
Goldsboro A	4.96	4.14	3.99	3.90	3.85	3.85	4.08	4.06	4.22	4.31	4.18	3.88	4.23
Rains B	4.49	3.51	3.54	3.59	3.66	3.66	4.30	4.32	4.39	4.49	4.53	4.45	4.60
Pantego A	4.4	4.17	3.67	3.54	3.53	3.53	3.65	3.67	3.76	3.77	3.79	3.79	3.65
Goldsboro E	4.91	4.00		4.00	4.00	3.86	4.23	4.22	4.31	4.38	4.04	3.72	4.64

Rep 4

Soil Type	Day												
	Initial pH	0	1	2	3	5	13	14	15	17	25	26	31
	pH												
Ponzer OA1-1	4.04	3.71	3.69	3.75	3.71	3.68	3.64	3.76	3.77	3.76	3.87	3.83	3.87
Ponzer OA3-2	3.76	3.24	3.24	3.36	3.39	3.25	3.62	3.55	3.60		3.68	3.66	4.23
Lynchburg E	4.26	3.62	3.66	3.82	3.72	3.57	3.97	3.75	3.96	3.95	4.14	4.06	4.25
Ponzer OA3-1	3.95	3.39	3.27	3.46	3.49	3.41	3.88	3.84	3.93	3.90	4.09	4.10	4.21
Leon Bh	4.75	4.58	4.35	4.28	4.24	3.78	4.45	4.43	4.50	4.49	4.54	4.50	4.69
Leon AE	5.08	4.78	4.33	4.43	4.62	4.23	4.86	4.86	5.0	5.30	5.43	5.33	5.75
Rains A	3.61	3.28	3.25	3.33	3.34	3.40	3.61	3.57	3.65	3.62	3.64	3.66	3.75
GGE	4.14	3.41	3.51	3.60	3.60	3.48	3.77	3.78	3.74	3.85	3.89	4.05	4.17

Table A2.2: Water sample DOC for all incubated soils.

Rep 1

Soil Type	Day														
	0	1	2	3	5	13	14	15	17	18	24	25	26	27	30
	mg C kg soil ⁻¹														
Rains B	42.6	26.6	51.3	35.6	34.6	18.2	19.7	20.1	23.4	13.0	17.4	16.8	21.7	18.0	11.6
Lynchburg E	15.2	57.6	37.2	32.4	33.1	10.8	9.69	9.24	7.98	4.10	8.64	7.68	8.80	8.84	5.00
Pantego B	28.8	105	119	122	112	42.6	43.0	40.6	45.9	16.9	26.8		21.7	18.9	3.78
Pantego A	19.7	156	127	109	102	36.2	35.6	37.8	44.6	13.8	36.7	36.7	49.1	64.5	23.4
Ponzer OA3-2	115	124	104	85.5	77.5	63.3	66.4	69.4	68.5	39.6	66.1		82.4	83.0	16.5
Ponzer OA1-1	152	225	237	221	213	188	187	187	198	71.2	138	202	219	230	71.9
Leon AE	14.1	34.3	56.3	57.6	52.5	39.7	44.6	41.9	62.3	25.3	36.3	16.2	43.4	47.6	45.5
Lynchburg B	45.2	16.1	53.5	49.6	43.2	17.8	19.6	17.8	15.0	11.8	12.4		15	11.8	6.75

Rep 2

Soil Type	Day											
	0	1	3	4	5	13	14	16	17	25	27	28
	mg C kg soil ⁻¹											
Ponzer OA1-2	201	261	276	252	255	226	228	243	238	239	245	
Goldsboro B	9.11	6.83	6.02	5.06	4.66	2.58	2.55	2.20	2.17	1.71	1.63	1.46
Rains E	24.7	25.2	27.4	30.5	33.4	28.3	35.3	48.1	51.6	39.6	47.9	48.4
Rains A	57.0	73.0	77.7	66.3	59.3	69.3	69.7	65.8	74.0	47.6	57.3	59.6
Goldsboro A	24.3	30.0	35.0	35.3	37.7	22.7	25.1	32.2	33.8	25.2	33.1	5.73
Ponzer OA3-1	101	101	107	101.7	106	126	124	147.2	154	170.4	182	192
Goldsboro E	7.15	7.79	7.37	6.05	4.16	3.62	3.74	3.77	3.75	3.45	3.64	3.60
Leon Bh	35.4	52.9	39.5	32.2	30.3	42.8	45.6	51.1	54.1	52.3	60.9	68.7

Rep 3

Soil Type	Day													
	0	1	2	3	5	13	14	15	17	18	25	26	27	32
	mg C kg soil ⁻¹													
Rains E	44.6	49.4	77.8	40.6	47.2	30.11	31.8	35.4	35.0	32.8	49.4	54.7	59.4	76.3
Goldsboro B	35.0	44.2	30.3	24.5	18.8	9.09	8.00	7.47	7.67	12.3	6.31	10.1	5.21	4.68
Ponzer OA1-2	256	295	286	277	282	279	285	313	282	249	274	281	289	307
Lynchburg B	9.20	19.0	27.7	29.3	30.1	11.0	10.3	8.93	111	11.8	8.05	8.04	8.04	5.91
Goldsboro A	24.8	31.4	33.3	41.8	50.3	29.3	31.8	36.7	44.1	20.0	28.3	36.2	40.5	55.6
Rains B	33.3	52.9	44.3	34.6	28.4	23.5	26.5	27.3	28.1		23.5	22.5	26.4	24.0
Pantego A	39.9	108.2	92.2	87.5	96.1	120	127	132	133	19.6	145	149	149	190
Goldsboro E	25.8		34.5	27.9	23.2	11.1	10.8	10.5	11.1	15.4	9.96	9.24	8.22	8.61

Rep 4

Soil Type	Day										
	0	1	2	3	5	13	14	15	17	18	31
	mg C kg soil ⁻¹										
Ponzer OA1-1	248	316	310	291	279	237	240	290	263	213	301
Ponzer OA3-2	35.9	55.1	66.6	48.7	54.5	50.6	53.9	61.3		61.3	85.9
Lynchburg E	9.01	7.65	5.68	5.01	5.36	9.53	8.49	5.00	6.13	4.63	3.47
Ponzer OA3-1	74.7	67.5	63.5	69.1	77.1	28.5	122	127	133	99.9	215
Leon Bh	37.7	31.9	34.4	34.8	34.2	97.3	50.5	48.9	42.9	33.8	40.18
Leon AE	21.6	27.2	25.2	28.9	29.8	50.3	25.8	29.1	24.4	16.6	35.5
Rains A	60.9	68.4	35.5	77.0	76.7	97.3	108	93.9	113	43.5	122
Goldsboro E	25.1	30.3	122	23.2	22.3	22.2	23.4	24.7	33.2	14.0	15.2

Table A2.3: Water sample Fe(II) for all incubated soils.

Rep 1

Soil Type	Day													
	0	1	2	3	5	13	14	15	17	18	25	26	27	30
	$\mu\text{mol Fe L}^{-1}$													
Rains B	1.36	1.45	2.33	8.06	23.30	0.00	0.54	1.02	1.25	1.09	0.00	0.36	0.36	0.00
Lynchburg E	1.61	1.59	8.78	19.71	51.97	1.79	2.33	15.41	32.26	3.76	0.00	3.41	4.30	0.00
Pantego B	84.23	250.9	304.66	286.74	286.74	100.4	100.4	123.7	197.1	4.66	0.00	23.3	28.67	4.12
Pantego A	21.51	0.00	0.00	0.00	0.00	118.3	118.3	152.3	159.5	37.6	34.1	60.9	69.89	12.01
Ponzer OA3-2	1.97	0.00	0.00	0.00	0.00	0.72	1.16	1.02	1.97	1.09	0.00	0.41	0.00	0.00
Ponzer OA1-1	5.91	2.87	4.66	5.38	9.68	10.22	10.57	17.92	21.51	0.00	1.97	8.24	0.00	1.97
Leon AE	1.97	1.25	1.79	3.94	0.00	1.43	1.97	0.00	0.00	1.29	0.00	1.79	0.00	2.69
Lynchburg B	2.87	1.97	5.38	2.15	3.58	0.00	0.50	1.06	0.90	0.00	0.00	0.27	0.66	0.00

Rep 2

Soil Type	Day											
	0	1	3	4	5	13	14	16	17	25	27	28
	$\mu\text{mol Fe L}^{-1}$											
Ponzer OA1-2	0.00	1.97	4.66	9.14	4.84	14.16	6.81	13.62	17.03	9.32	23.30	0.00
Goldsboro B	0.72	0.36	0.54	1.79	0.36	6.45	0.00	0.00	0.23	0.00	0.00	0.54
Rains E	8.06	69.89	100.36	89.61	86.02	7.89	6.45	16.31	17.92	0.63	9.86	8.60
Rains A	232.97	376.34	322.58	304.66	304.66	215.05	197.13	197.13	164.87	91.40	103.94	43.01
Goldsboro A	1.97	134.41	179.21	232.97	268.82	21.51	57.35	127.24	127.24	6.45	43.01	23.30
Ponzer OA3-1	2.51	1.43	1.97	1.79	0.90	7.17	0.00	0.90	1.11	0.00	0.00	0.00
Goldsboro E	0.90	0.36	1.79	3.23	0.54	5.73	0.00	0.00	0.00	0.54	0.75	0.00
Leon Bh	2.15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Rep 3

Soil Type	Day													
	0	1	2	3	5	13	14	15	17	18	25	26	27	32
	$\mu\text{mol Fe L}^{-1}$													
Rains E	155.9	233.0	232.97	358.42	340.5	2.15	15.05	26.88	41.22	28.67	0.84	1.09		11.47
Goldsboro B	0.00	0.36	0.54	0.18	1.97				0.77	3.05				
Ponzer OA1-2	1.79	3.58	3.58	5.73	13.26	5.20	10.22	14.52	19.71	13.08	3.23	4.12		10.57
Lynchburg B		0.54	2.69	3.05	8.60				2.87	1.45				
Goldsboro A	1.25	116.5	232.97	358.42	358.4	111.1	197.1	215.1	322.6	197.1	14.5	39.4	59.1	121.9
Rains B	1.43	1.08	1.08	2.51	32.26					0.50				
Pantego A										80.65				
Goldsboro E	1.43		3.05	3.05	8.60	0.00	1.08	5.91	19.71	25.09				7.17

Rep 4

Soil Type	Day											
	0	1	2	3	5	13	14	15	17	18	25	26
	μmol Fe L ⁻¹											
Ponzer OA1-1	1.40	2.69	4.66	0.00	0.00	6.99	9.50	5.73		1.97		
Ponzer OA3-2	0.23	0.95	1.25	0.52	1.67	0.00	1.08	1.74		1.97	0.70	1.29
Lynchburg E	0.18	0.84	1.77	2.15	10.39	0.00	0.52	1.18	3.41	0.20	0.90	0.65
Ponzer OA3-1	0.34	1.25	1.00	0.77	10.22	0.00	1.02	1.22	0.00	1.74		
Leon Bh	0.00	1.15	0.34							0.95		
Leon AE	0.50	0.73	1.42	1.43	1.72	0.00	1.08	0.97	0.34	0.30	2.15	
Rains A	340.50	376.34	376.34			232.97	394.27	394.27		227.60		
Goldsboro E	173.84	340.50	376.34	358.42	232.97	232.97	268.82	232.97	197.13	0.00	12.90	8.60

Table A2.4: Total Fe ($\mu\text{mol Fe L}^{-1}$) in incubation water samples**Rep 1**

Soil Type	Day											
	0	1	2	3	5	13	14	15	17	25	26	27
	$\mu\text{mol Fe L}^{-1}$											
Rains B	1.25	1.79	0.90	13.62	48.03	1.43	1.43	1.61	1.97	0.00	0.00	0.00
Lynchburg E	0.00	1.25	15.23	35.84	100.90	3.05	12.01	25.81	55.56	0.00	0.00	0.00
Pantego B	37.46	1474.9	1810.0	1657.71	1383.5	198.92	245.52	213.26	35.30	0.00	37.46	60.57
Pantego A	0.00	64.52	327.96	623.66	897.85	224.01	299.28	267.03	295.70	70.97	97.85	127.24
Ponzer OA3-2	0.00	0.00	0.00	0.00	14.34	0.90	0.00	0.00	0.00	0.00	0.00	0.00
Ponzer OA1-1	22.58	12.72	9.14	11.29	23.30	20.79	28.67	31.72	39.43	1.25	0.00	0.00
Leon AE	1.79	8.06	17.74	1.79	20.61	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Lynchburg B	3.58	3.76	3.76	6.81	12.01	4.66	5.02	4.48	3.94	0.00	2.69	2.87

Rep 2

Soil Type	Day											
	0	1	3	4	5	13	14	16	17	25	27	28
	$\mu\text{mol Fe L}^{-1}$											
Ponzer OA1-2	0.00	1.79	0.00	12.54	17.92	6.81	0.00	21.51	26.88	16.13	27.24	0.00
Goldsboro B	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.08	0.00	0.00	0.00
Rains E	13.26	131.54	198.92	11.65	139.78	4.66	0.00	25.09	27.24	0.00	12.54	0.00
Rains A	417.56	440.86	630.82	661.29	0.00	374.55	293.91	206.09	238.35	152.33	133.33	154.12
Goldsboro A	3.76	105.73	324.37	417.56	453.41	27.24	86.02	175.63	172.22	0.00	0.00	0.00
Ponzer OA3-1	0.00	0.00	8.96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Goldsboro E	0.00	0.00	2.33	3.58	1.08	0.00	0.00	4.48	5.56	0.00	1.08	1.08
Leon Bh	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Rep 3

Soil Type	Day												
	0	1	2	3	5	13	14	15	17	25	26	27	32
	$\mu\text{mol Fe L}^{-1}$												
Rains E	5.56	9.50	24.37	20.97	24.91	34.41	19.00	84.59	112.54	93.91	58.78	120.97	109.68
Goldsboro B	345.88	648.75	745.52	702.51	659.50	31.72	49.46	13.26	18.10	3.41	2.87	1.25	2.51
Ponzer OA1-2	5.91	6.63	7.89	37.99	55.20	8.96	39.43	42.29	137.10	103.23	106.45	90.32	95.16
Lynchburg B	16.85	23.48	31.18	7.89	12.72	37.99	9.14	10.22	6.09	2.15	1.97	1.79	2.69
Goldsboro A	3.76	3.41	50.00	38.71	81.72	4.66	50.00	32.26	57.35	62.90	74.19	74.19	72.58
Rains B	11.65	227.60	82.26	259.86	331.54	243.73	37.46	101.61	125.81	4.66	74.19	22.22	198.92
Pantego A	249.10	806.45	718.64	630.82	953.41	51.61	48.39	43.55	40.32	7.89	0.00	0.00	0.00
Goldsboro E	0.90	0.00	49.10	65.05	67.03	59.68	41.22	45.16	38.53	55.20	22.22	20.25	15.95

Rep 4

Soil Type	Day											
	0	1	2	3	5	13	14	15	17	18	25	26
	$\mu\text{mol Fe L}^{-1}$											
Ponzer OA1-1	193.55	2625.45	5745.52	6267.03	46.77	5976.70	4765.23	4021.51	3668.46	419.35	0.00	218.64
Ponzer OA3-2	0.00	1.08	1.43	0.00	2.33	2.15	2.69	3.05	0.00	6.27	0.00	46.77
Lynchburg E	0.00	0.00	1.08	0.00	2.15	0.00	0.00	1.08	2.69	6.99	0.00	0.00
Ponzer OA3-1	3.76	1.43	22.58	8.96	16.85	0.00	0.00	12.90	58.06	0.00	0.00	0.00
Leon Bh	37.10	27.42	25.81	20.97	25.81	0.00	0.00	0.00	0.00	5.91	0.00	0.00
Leon AE	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.23	0.00	0.00
Rains A	22.58	132.26	93.55	14.52	11.29	0.00	0.00	0.00	0.00	5.02	30.65	0.00
Goldsboro E	86.56	124.91	138.89	140.68	137.10	120.07	112.37	98.39	95.88	4587.81	68.82	573.48

Table A2.5: Total Mn ($\mu\text{mol Mn L}^{-1}$) in incubation water samples**Rep 1**

Soil Type	Day											
	0	1	2	3	5	13	14	15	17	25	26	27
	$\mu\text{mol Mn L}^{-1}$											
Rains B	1.28	1.28	1.09	0.91	0.55	0.36	0.36	0.36	0.00	0.00	0.00	0.00
Lynchburg E	0.55	1.46	2.19	2.37	2.73	1.46	1.46	1.46	0.91	0.91	0.00	0.00
Pantego B	0.00	1.82	1.82	1.82	0.00	1.09	0.00	0.00	0.00	0.00	0.36	0.55
Pantego A	0.00	7.29	3.64	5.46	5.46	2.37	2.19	1.64	1.46	0.91	0.73	0.00
Ponzer OA3-2	1.82	3.64	3.64	5.46	5.46	3.10	3.64	3.64	1.82	0.00	0.00	1.82
Ponzer OA1-1	4.37	4.55	5.10	4.55	3.64	3.10	2.91	3.10	1.82	1.82	0.00	1.82
Leon AE	0.91	3.28	3.83	3.64	3.10	0.00	2.91	3.10	1.82	1.82	0.00	1.82
Lynchburg B	0.91	0.91	1.09	1.46	1.46	0.91	0.91	1.09	0.55	0.00	0.55	0.36

Rep 2

Soil Type	Day											
	0	1	3	4	5	13	14	16	17	25	27	28
	$\mu\text{mol Mn L}^{-1}$											
Ponzer OA1-2	5.46	4.74	3.64	3.64	3.64	3.46	3.64	3.64	3.64	1.82	0.00	0.00
Goldsboro B	0.73	1.09	1.46	1.64	1.46	1.09	1.09	0.73	0.73	0.55	0.36	0.36
Rains E	1.82	1.46	1.09	1.09	0.00	0.73	0.00	0.00	0.00	0.00	0.00	0.00
Rains A	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Goldsboro A	1.28	2.19	2.37	1.82	1.82	2.19	1.82	0.00	0.00	0.00	0.00	0.00
Ponzer OA3-1	1.82	3.64	3.64	3.64	1.82	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Goldsboro E	2.91	4.37	6.74	6.56	3.46	4.37	3.46	3.46	2.73	1.64	1.64	1.64
Leon Bh	0.00	1.82	0.00	1.82	1.82	1.82	1.82	0.00	0.00	0.00	0.00	0.00

Rep 3

Soil Type	Day													
	0	1	2	3	5	13	14	15	17	18	25	26	27	32
	$\mu\text{mol Mn L}^{-1}$													
Rains E	0.00	4.37	0.36	13.48	12.20	12.57	6.92	23.32	23.32	0.00	21.86	5.83	11.48	9.84
Goldsboro B	2.91	3.10	2.19	1.64	1.28	0.73	0.73	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ponzer OA1-2	2.00	2.73	2.55	10.20	10.93	1.46	5.10	4.37	8.20	0.00	4.92	4.92	3.28	3.28
Lynchburg B	4.55	5.83	5.83	1.09	1.28	4.19	0.73	0.91	0.36	0.00	0.18	0.18	0.18	0.18
Goldsboro A	0.55	0.73	9.84	5.10	5.10	0.55	6.56	2.19	2.19	0.00	3.28	3.28	1.64	3.28
Rains B	1.46	3.28	0.55	1.28	1.09	3.64	3.64	0.55	0.36	0.00	0.00	0.00	0.00	0.00
Pantego A	19.67	18.03	14.75	13.11	9.84	3.28	1.64	3.28	0.00	0.00	2.19	0.00	0.00	0.00
Goldsboro E	0.36	0.00	0.36	0.36	0.55	0.36	0.36	0.36	0.18	0.00	1.09	0.00	0.00	0.18

Rep 4

Soil Type	Day											
	0	1	2	3	5	13	14	15	17	18	25	26
	$\mu\text{mol Mn L}^{-1}$											
Ponzer OA1-1	9.84	8.20	13.11	14.75	11.48	13.11	11.48	6.56	4.92	0.55	0.00	3.28
Ponzer OA3-2	0.18	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.00	2.00	0.00	1.64
Lynchburg E	3.46	4.01	3.28	2.73	2.73	1.64	1.82	2.00	0.36	1.64	0.00	0.00
Ponzer OA3-1	1.28	1.64	14.75	1.28	1.46	13.11	9.84	9.84	6.56	0.36	0.00	0.55
Leon Bh	32.79	44.26	39.34	29.51	22.95	0.00	0.00	0.00	0.00	0.55	0.00	0.00
Leon AE	0.00	0.00	0.36	0.36	1.64	0.00	0.00	0.00	0.00	0.55	4.92	0.00
Rains A	1.64	27.87	19.67	3.28	3.28	0.00	0.00	0.00	0.00	0.91	11.48	0.00
Goldsboro E	0.18	0.36	0.36	0.18	0.18	0.00	0.00	0.00	0.00	6.56	0.00	0.00

Table A2.6 Total Al ($\mu\text{mol Al L}^{-1}$) in incubation water samples**Rep 1**

Soil Type	Day											
	0	1	2	3	5	13	14	15	17	25	26	27
	$\mu\text{mol Al L}^{-1}$											
Rains B	976.65	476.65	325.06	148.63	57.82	27.06	28.91	30.02	30.02	0.00	0.00	0.00
Lynchburg E	121.94	503.34	930.32	1002.59	1137.51	593.77	611.56	459.60	352.48	250.56	59.30	85.25
Pantego B	88.95	441.07	526.32	315.05	196.44	183.47	100.07	77.84	0.00	0.00	28.17	26.32
Pantego A	0.00	133.43	103.78	103.78	92.66	53.00	49.30	42.99	41.51	34.10	11.49	0.00
Ponzer OA3-2	63.01	74.13	74.13	92.66	92.66	89.70	70.42	63.01	0.00	0.00	0.00	0.00
Ponzer OA1-1	164.94	149.37	151.96	150.48	133.43	139.73	131.21	131.21	92.66	77.84	0.00	70.42
Leon AE	10.38	12.60	14.08	0.00	12.97	0.00	0.00	0.00	0.00	129.73	0.00	0.00
Lynchburg B	494.44	461.45	1582.28	1475.91	1456.63	908.08	937.73	770.94	507.78	0.00	326.91	242.40

Rep 2

Soil Type	Day											
	0	1	3	4	5	13	14	16	17	25	27	28
	$\mu\text{mol Al L}^{-1}$											
Ponzer OA1-2	159.38	240.92	222.39	196.44	203.85	187.55	185.32	159.38	189.03	181.62	147.89	0.00
Goldsboro B	29.28	111.19	124.91	132.69	114.90	41.14	41.14	16.31	25.57	7.04	1.85	2.59
Rains E	371.02	217.94	95.26	78.58	55.60	54.86	48.18	55.60	63.38	59.30	63.01	0.00
Rains A	70.42	0.00	48.18	43.74	0.00	44.48	48.18	0.00	44.85	29.65	0.00	40.77
Goldsboro A	57.82	73.02	80.06	48.18	55.60	57.45	29.65	33.36	0.00	29.65	0.00	0.00
Ponzer OA3-1	122.31	148.26	118.61	122.31	122.31	133.43	119.72	137.14	147.89	163.08	177.91	192.74
Goldsboro E	86.73	117.49	107.49	81.91	22.24	23.35	18.53	10.01	9.27	3.34	4.08	3.71
Leon Bh	29.65	55.60	44.48	37.06	22.24	48.18	51.89	55.60	59.30	35.21	63.01	77.84

Rep 3

Soil Type	Day											
	0	1	2	3	5	13	14	15	17	25	26	27
	$\mu\text{mol Al L}^{-1}$											
Rains E	14.83	563.38	14.46	571.53	396.59	317.3	100.07	296.52	225.6	203.1	31.13	30.65
Goldsboro B	1374.7	1223.13	712.01	408.45	194.22	80.06	68.57	9.64	13.71	13.34	14.46	2.87
Ponzer OA1-2	1026.7	1230.54	754.26	2225.4	1630.8	138.3	433.65	336.55	641.2	250.2	203.5	46.77
Lynchburg B	243.14	277.61	278.72	50.78	55.60	217.6	43.74	42.62	22.61	20.01	20.76	9.68
Goldsboro A	307.64	533.73	7390.66	3621.9	3484.1	270.6	2513.0	1023.0	889.6	900.7	808.0	361.3
Rains B	83.02	149.74	20.39	50.41	28.17	112.7	5.93	13.34	15.20	4.08	40.03	4.66
Pantego A	17324	16701.3	10500.4	7272.1	3024.5	263.5	283.54	323.57	350.3	139.4	23.35	64.52
Goldsboro E	9.27	0.00	11.12	11.12	9.27	10.01	7.78	10.01	10.38	21.13	10.01	4.66

Rep 4

Soil Type	Day											
	0	1	2	3	5	13	14	15	17	18	25	26
	$\mu\text{mol Al L}^{-1}$											
Ponzer OA1-1	36.69	2687.18	4607.12	3906.6	5652.3	2988.9	2235.0	1226.8	767.23	83.02	16.68	90.07
Ponzer OA3-2	16.31	18.53	19.27	18.90	18.90	15.94	15.57	15.57	0.00	132.0	2.97	156.9
Lynchburg E	107.12	114.16	90.07	75.24	75.24	51.89	57.08	55.97	13.71	54.48	0.00	4.08
Ponzer OA3-1	796.89	1041.51	8013.34	638.62	638.62	5174.2	3117.1	2838.8	1908.8	151.6	26.69	433.7
Leon Bh	2416.60	3128.24	2309.12	1357.7	1356.6	76.72	110.08	116.75	103.41	120.1	0.00	183.5
Leon AE	2.22	4.08	6.67	23.35	23.35	30.02	33.36	33.36	0.00	38.18	900.7	133.4
Rains A	110.08	163.45	66.72	0.00	0.00	0.00	0.00	0.00	0.00	10.75	530.0	200.2
Goldsboro E										574.5		
	12.60	14.46	13.34	10.38	10.38	6.30	7.78	7.41	5.56	0	5.93	6.30

Table A2.7: Total P ($\mu\text{mol P L}^{-1}$) in incubation water samples**Rep 1**

Soil Type	Day											
	0	1	2	3	5	13	14	15	17	25	26	27
	$\mu\text{mol P L}^{-1}$											
Rains B	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Lynchburg E	0.00	0.00	1.29	2.27	2.27	2.59	2.59	2.91	2.91	0.65	0.00	0.00
Pantego B	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pantego A	0.00	3.24	0.00	3.24	3.24	1.29	1.62	1.62	2.59	0.65	0.65	0.00
Ponzer OA3-2	12.94	25.89	13.27	13.59	10.36	10.68	14.89	12.30	9.71	0.00	0.00	0.00
Ponzer OA1-1	15.53	11.00	14.24	13.92	19.09	16.18	17.48	19.74	20.06	9.71	13.59	13.92
Leon AE	10.03	6.15	6.47	10.68	7.12	14.56	12.30	9.39	9.71	0.00	0.00	9.71
Lynchburg B	1.94	1.62	3.88	5.50	5.50	5.18	6.15	6.47	4.85	9.71	2.59	2.59

Rep 2

Soil Type	Day											
	0	1	3	4	5	13	14	16	17	25	27	28
	$\mu\text{mol P L}^{-1}$											
Ponzer OA1-2	9.71	17.48	12.94	12.94	16.18	17.80	12.94	22.65	16.18	19.42	30.74	0.00
Goldsboro B	0.00	0.00	0.00	0.00	0.00	0.97	0.00	0.65	0.00	0.00	0.32	0.32
Rains E	0.32	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.24	0.00
Rains A	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	6.47
Goldsboro A	0.00	0.00	0.00	0.00	0.00	0.65	0.00	0.00	0.00	3.24	0.00	0.00
Ponzer OA3-1	0.00	9.71	0.00	0.00	0.00	6.80	0.00	6.47	0.00	9.71	12.94	12.94
Goldsboro E	0.00	0.00	0.00	0.00	0.00	0.97	0.00	0.00	0.00	0.32	0.32	0.32
Leon Bh	3.24	6.47	0.00	0.00	0.00	4.53	0.00	6.47	6.47	12.30	12.94	12.94

Rep 3

Soil Type	Day													
	0	1	2	3	5	13	14	15	17	18	25	26	27	32
	$\mu\text{mol P L}^{-1}$													
Rains E	0.65	0.97	0.65	0.65	0.65	0.97	0.97	2.59	2.59	0.00	12.94	0.00	0.00	1.88
Goldsboro B	1.62	1.29	1.62	0.97	0.97	0.65	0.65	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ponzer OA1-2	1.29	1.29	0.97	5.18	3.88	0.65	2.59	2.59	5.83	0.00	2.91	0.00	0.00	0.00
Lynchburg B	20.39	22.01	21.36	3.88	4.53	21.04	4.53	4.53	2.27	0.00	2.59	2.27	0.73	0.83
Goldsboro A	0.65	1.29	14.56	7.77	9.06	1.29	14.56	5.18	5.18	0.00	5.83	5.83	1.88	1.88
Rains B	0.00	4.85	0.00	0.00	0.32	0.97	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pantego A	5.83	14.56	5.83	5.83	5.83	0.00	0.00	2.91	0.00	0.00	0.00	0.00	0.00	0.00
Goldsboro E	0.00	0.00	0.00	0.00	0.65	0.32	0.32	0.65	0.32	0.00	1.62	0.32	0.10	0.21

Rep 4

Soil Type	Day											
	0	1	2	3	5	13	14	15	17	18	25	26
	$\mu\text{mol P L}^{-1}$											
Ponzer OA1-1	0.00	49.51	40.78	29.13	14.56	14.56	8.74	8.74	8.74	1.29	14.56	5.83
Ponzer OA3-2	3.88	2.27	16.50	2.27	1.94	1.62	1.94	1.94	0.00	23.30	1.29	20.39
Lynchburg E	15.53	13.59	13.59	12.94	13.59	11.65	13.27	12.62	1.94	23.95	1.62	1.29
Ponzer OA3-1	2.91	1.94	14.56	3.56	1.62	14.56	14.56	11.65	5.83	8.74	14.56	0.00
Leon Bh	133.98	99.03	90.29	87.38	84.47	11.65	5.83	8.74	8.74	29.13	0.00	8.74
Leon AE	7.44	2.59	3.88	1.94	14.56	17.48	17.48	14.56	14.56	16.50	11.65	14.56
Rains A	320.39	131.07	52.43	11.65	2.91	14.56	11.65	8.74	11.65	18.45	154.37	14.56
Goldsboro E	0.00	0.00	0.00	0.00	0.32	0.65	0.32	0.32	0.32	291.26	0.00	2.91

Table A2.8: Total NO₃ N, (μmol N L⁻¹) in incubation water samples**Rep 1**

Soil Type	Day											
	0	1	2	3	5	13	14	15	17	25	26	27
	μmol N L ⁻¹											
Rains B	20.00	22.14	22.14	0.00	0.00	17.14	14.29	31.43	5.71	9.29	43.57	50.00
Lynchburg E	29.29	7.86	7.86	0.00	5.71	0.00	7.14	0.00	7.86	0.00	0.00	0.00
Pantego B	0.00	5.00	10.71	7.14	0.00	5.71	0.00	0.00	0.00	5.71	0.00	0.00
Pantego A	0.00	0.00	4.29	0.00	3.57	0.00	0.00	11.43	0.00	0.00	0.00	0.00
Ponzer OA3-2	5.71	25.00	6.43	0.00	0.00	3.57	7.86	10.71	0.00	4.29	0.00	5.71
Ponzer OA1-1	177.14	9.29	6.43	5.71	5.00	0.00	0.00	7.14	0.00	0.00	0.00	0.00
Leon AE	67.86	518.57	635.00	276.43	8.57	25.71	6.43	6.43	3.57	25.00	0.00	57.86
Lynchburg B	16.43	22.14	22.86	11.43	3.57	0.00	27.86	5.71	0.00	0.00	127.14	0.00

Rep 2

Soil Type	Day											
	0	1	3	4	5	13	14	16	17	25	27	28
	μmol N L ⁻¹											
Ponzer OA1-2	388.57	0.00	0.00	0.00	25.71	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Goldsboro B	13.57	12.14	8.57	6.43	4.29	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Rains E	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	14.29	0.00	0.00
Rains A	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Goldsboro A	8.57	7.14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ponzer OA3-1	594.29	551.43	282.86	80.00	120.00	134.29	100.00	0.00	0.00	85.71	0.00	0.00
Goldsboro E	33.57	34.29	5.00	0.00	0.00	23.57	12.14	0.00	0.00	87.14	69.29	48.57
Leon Bh	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	25.71	54.29	22.86

Rep 3

Soil Type	Day													
	0	1	2	3	5	13	14	15	17	18	25	26	27	32
	$\mu\text{mol N L}^{-1}$													
Rains E	0.00	0.00	12.14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	8.57	0.00	0.00	0.00
Goldsboro B	27.86	25.00	10.00	6.43	0.00	0.00	0.00	0.00	0.00	8.57	0.00	0.00	0.00	5.00
Ponzer OA1-2	408.57	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	34.29	0.00	0.00	0.00	0.00
Lynchburg B	32.14	6.43	5.71	0.00	0.00	0.00	0.00	35.00	0.00	0.00	0.00	0.00	0.00	0.00
Goldsboro A	11.43	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Rains B	75.71	72.14	40.00	0.00	3.57	10.71	29.29	29.29	0.00	7.14	80.71	94.29	81.43	89.29
Pantego A	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.29	0.00	22.14	0.00	31.43
Goldsboro E	74.29	0.00	5.71	30.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Rep 4

Soil Type	Day											
	0	1	2	3	5	13	14	15	17	18	25	26
	$\mu\text{mol NL}^{-1}$											
Ponzer OA1-1	190.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5.71	6.43
Ponzer OA3-2	12.14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Lynchburg E	80.71	76.43	54.29	30.71	7.14	5.00	0.00	0.00	0.00	0.00	7.86	0.00
Ponzer OA3-1	654.29	582.14	478.57	55.00	152.86	53.57	51.43	10.00	30.00	30.71	63.57	68.57
Leon Bh	5.71	14.29	10.00	5.00	0.00	12.86	3.57	0.00	0.00	0.00	7.86	65.00
Leon AE	45.71	1092.86	1557.14	921.43	907.14	154.29	213.57	217.14	128.57	107.14	33.57	0.00
Rains A	0.00	0.00	0.00	0.00	0.00	0.00	16.43	0.00	0.00	4.29	0.00	0.00
Goldsboro E	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table A2.9: Total SO₄ (mmol SO₄ L⁻¹) in incubation water samples

Rep 1

Soil Type	Day											
	0	1	2	3	5	13	14	15	17	25	26	27
	mmol SO ₄ L ⁻¹											
Rains B	0.15	0.03	0.13	0.08	0.07	0.05	0.06	0.05	0.02	0.02	0.02	0.02
Lynchburg E	0.03	0.10	0.03	0.07	0.03	0.02	0.02	0.02	0.02	0.02	0.03	0.03
Pantego B	0.00	0.01	0.03	0.07	0.06	0.01	0.01	0.01	0.00		0.01	0.01
Pantego A	0.00	0.03	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00
Ponzer OA3-2	0.20	0.22	0.21	0.18	0.21	0.15	0.14	0.13	0.15		0.11	0.11
Ponzer OA1-1	0.41	0.55	0.59	0.55	0.55	0.32	0.24	0.23	0.20	0.13	0.13	0.12
Leon AE	0.01	0.11	0.19	0.16	0.13	0.01	0.02	0.02	0.02	0.02	0.01	0.01
Lynchburg B	0.02	0.02	0.04	0.03	0.03	0.03	0.03	0.02		0.01	0.02	0.02

Rep 2

Soil Type	Day											
	0	1	3	4	5	13	14	16	17	25	27	28
	mmol SO ₄ L ⁻¹											
Ponzer OA1-2	0.52	0.61	0.56	0.46	0.48	0.40	0.20	0.48	0.47	0.44	0.32	0.23
Goldsboro B	0.04	0.02	0.01	0.01	0.01	0.05	0.01	0.02	0.02	0.02	0.03	0.03
Rains E	0.18	0.19	0.17	0.15	0.15	0.11	0.09	0.10	0.15	0.08	0.10	0.08
Rains A	0.02	0.08	0.01	0.01	0.05	0.01	0.01	0.05	0.02	0.01	0.01	0.19
Goldsboro A	0.20	0.21	0.08	0.19	0.10	0.12	0.16	0.06	0.27	0.10	0.19	0.05
Ponzer OA3-1	0.28	0.37	0.27	0.10	0.20	0.17	0.19	0.11	0.10	0.10	0.08	0.06
Goldsboro E	0.04	0.03	0.01	0.02	0.03	0.03	0.06	0.04	0.05	0.04	0.07	0.09
Leon Bh	0.01	0.03	0.04	0.05	0.04	0.05	0.05	0.05	0.06	0.08	0.03	0.03

Rep 3

Soil Type	Day													
	0	1	2	3	5	13	14	15	17	18	25	26	27	32
	mmol SO ₄ L ⁻¹													
Rains E	0.13	0.11	0.09	0.07	0.01	0.12	0.09	0.09	0.09	0.07	0.03	0.02	0.09	0.10
Goldsboro B	0.02	0.02	0.02	0.02	0.00	0.01	0.01	0.02	0.02	0.03	0.03	0.00	0.03	0.05
Ponzer OA1-2	0.54	0.58	0.55	0.46	0.45	0.10	0.38	0.13	0.11	0.30	0.22	0.21	0.24	0.20
Lynchburg B	0.05	0.01	0.04	0.01	0.01	0.02	0.03	0.05	0.03	0.02	0.03	0.03	0.03	0.05
Goldsboro A	0.24	0.19	0.17	0.13	0.13	0.09	0.10	0.03	0.13	0.09	0.13	0.04	0.16	0.19
Rains B	0.15	0.15	0.11	0.02	0.08	0.02	0.05	0.05	0.04	0.01	0.03	0.03	0.03	0.03
Pantego A	0.01	0.01	0.00	0.03	0.00	0.01	0.01	0.01	0.46	0.00	0.01	0.00	0.01	0.02
Goldsboro E	0.03	0.00	0.00	0.02	0.02	0.01	0.03	0.01	0.02	0.04	0.08	0.09	0.10	0.14

Rep 4

Soil Type	Day											
	0	1	2	3	5	13	14	15	17	18	25	26
	mmol SO ₄ L ⁻¹											
Ponzer OA1-1	0.65	0.75	0.68	0.68	0.11	0.15	0.39	0.07	0.00	0.30	0.43	0.35
Ponzer OA3-2	0.15	0.17	0.14	0.13	0.11	0.08	0.09	0.08	0.00	0.09	0.13	0.02
Lynchburg E	0.06	0.05	0.04	0.04	0.03	0.03	0.03	0.03	0.05	0.00	0.05	0.00
Ponzer OA3-1	0.28	0.33	0.32	0.05	0.24	0.10	0.09	0.02	0.08	0.06	0.02	0.05
Leon Bh	0.01	0.04	0.06	0.08	0.08	0.07	0.06	0.08	0.06	0.03	0.05	0.06
Leon AE	0.01	0.11	0.24	0.17	0.17	0.02	0.03	0.05	0.05	0.03	0.02	0.03
Rains A	0.00	0.01	0.02	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00
Goldsboro E	0.02	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.01

APPENDIX C: Data Logger Program

The data logger program that was used for the CR10X data logger developed to measure redox potential every 10 min. and average the 10 min. readings every hour.

```
;{CR10}
*Table 1 Program
  01: 600.0000 Execution Interval (seconds)

1: Batt Voltage (P10)
  1: 1      Loc [ battv      ]

2: Do (P86)
  1: 10     Set Output Flag High

3: Set Active Storage Area (P80)
  1: 1      Final Storage Area 1
  2: 10     Array ID

4: Real Time (P77)
  1: 1220   Year,Day,Hour/Minute (midnight = 2400)

5: Sample (P70)
  1: 1      Reps
  2: 1      Loc [ battv      ]

6: Volt (SE) (P1)
  1: 2      Reps
  2: 25     2500 mV 60 Hz Rejection Range
  3: 1      SE Channel
  4: 2      -- Loc [ ONE      ]
  5: 1.0    Mult
  6: 200    Offset

7: Sample (P70)
  1: 2      Reps
  2: 2      Loc [ ONE      ]

8: Volt (SE) (P1)
  1: 2      Reps
  2: 25     2500 mV 60 Hz Rejection Range
  3: 3      SE Channel
  4: 4      Loc [ TWO      ]
  5: 1.0    Mult
  6: 200    Offset

9: Sample (P70)
  1: 2      Reps
  2: 4      Loc [ TWO      ]

10: Volt (SE) (P1)
  1: 2      Reps
  2: 25     2500 mV 60 Hz Rejection Range
  3: 5      SE Channel
  4: 6      Loc [ THREE     ]
  5: 1.0    Mult
```

```

6: 200      Offset
11: Sample (P70)
1: 2        Reps
2: 6         Loc [ THREE      ]

12: Volt (SE) (P1)
1: 2         Reps
2: 25        2500 mV 60 Hz Rejection Range
3: 7         SE Channel
4: 8         Loc [ FOUR_1     ]
5: 1.0       Mult
6: 200      Offset

13: Sample (P70)
1: 2         Reps
2: 8         Loc [ FOUR_1     ]

14: Volt (SE) (P1)
1: 1         Reps
2: 25        2500 mV 60 Hz Rejection Range
3: 9         SE Channel
4: 10        Loc [ FIVE_1     ]
5: 1.0       Mult
6: 200      Offset

15: Sample (P70)
1: 2         Reps
2: 10        Loc [ FIVE_1     ]

16: Volt (SE) (P1)
1: 2         Reps
2: 25        2500 mV 60 Hz Rejection Range
3: 11        SE Channel
4: 12        Loc [ SIX_1      ]
5: 1.0       Mult
6: 200      Offset

17: Sample (P70)
1: 2         Reps
2: 12        Loc [ SIX_1      ]

18: If time is (P92)
1: 0         Minutes (Seconds --) into a
2: 60        Interval (same units as above)
3: 10        Set Output Flag High

19: Set Active Storage Area (P80)
1: 1         Final Storage Area 1
2: 60        Array ID

```

20: Real Time (P77)
1: 1220 Year,Day,Hour/Minute (midnight = 2400)

21: Average (P71)
1: 2 Reps
2: 2 Loc [ONE]

22: Average (P71)
1: 2 Reps
2: 4 Loc [TWO]

23: Average (P71)
1: 2 Reps
2: 6 Loc [THREE]

24: Average (P71)
1: 2 Reps
2: 8 Loc [FOUR_1]

25: Average (P71)
1: 2 Reps
2: 10 Loc [FIVE_1]

26: Average (P71)
1: 2 Reps
2: 12 Loc [SIX_1]

27: Do (P86)
1: 20 Set Output Flag Low

*Table 2 Program
01: 60.0000 Execution Interval (seconds)

*Table 3 Subroutines

End Program

-Input Locations-

1 battv	1 1 1
2 ONE	5 2 1
3 ONE_2	17 2 1
4 TWO	5 2 1
5 TWO_2	17 2 1
6 THREE	5 2 1
7 THREE_2	17 2 1
8 FOUR_1	5 2 1
9 FOUR_2	17 2 1
10 FIVE_1	1 2 1
11 FIVE_2	1 2 0
12 SIX_1	5 2 1
13 SIX_2	17 2 1
14 _____	0 0 0
15 _____	0 0 0
16 _____	0 0 0

17	_____	0	0	0
18	_____	0	0	0
19	_____	0	0	0
20	_____	0	0	0
21	_____	0	0	0
22	_____	0	0	0
23	_____	0	0	0
24	_____	0	0	0
25	_____	0	0	0
26	_____	0	0	0
27	_____	0	0	0
28	_____	0	0	0
60	_____	0	0	0

-Program Security-
0000

0000

0000

-Mode 4-

-Final Storage Area 2-
0