

INDICATORS OF REDUCTION IN SOIL (IRIS) IN VARIOUS CONDITIONS OF
SATURATION IN SOUTH FLORIDA MARL

BY

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To my husband for his support, patience and love

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
°C	Degrees Celsius
CC	Cubic centimeter
CEC	Cation exchange capacity
CM	Centimeter
DB	Bulk density the weight per volume, typically expressed in grams per cubic centimeter for soils.
DI	Deionized water
DDI	Double deionized water
DPI	Dots per inch, indicating visual quality of a digital image
EC	Electrical conductivity
EDTA	Ethylenediaminetetraacetic acid
EH	Reduction-oxidation potential
FIRIS	Iron oxide coated Indicators of Reduction in Soil
G	Gram
IC	Inorganic carbon
ICP	Inductively coupled plasma — atomic emission spectrometry
IFAS	Institute of Food and Agricultural Science
IRIS	Indicators of Reduction in Soil includes FIRIS and MIRIS
L	Liter
M	Moles per liter, a concentration expressed in units of mol/L
MEQ	Milliequivalent
MG	Milligram
MIRIS	Manganese oxide coated Indicators of Reduction in Soil
ML	Milliliter

MM	Millimeter
MWCO	Molecular weight cut off
NRCS	Natural Resources Conservation Service, a Federal Agency
NSSL	National Soil Survey Laboratory
NTCHS	National Technical Committee for Hydric Soils
NWI	National Wetlands Inventory
OM	Organic matter
P	Pearson's correlation coefficient
PT	Platinum
PVC	Polyvinyl chloride pipe
RPM	Revolutions per minute
SHE	Standard hydrogen electrode
SiL	Silt loam soil texture based on particle size analysis
TREC	Tropical Research and Education Center
UF	University of Florida
US	Micro-siemens
USDA	United States Department of Agriculture
USFWS	United States Fish and Wildlife Service

Abstract of Thesis Presented to the Graduate School
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Marl soils of south Florida lack redoximorphic features traditionally used to determine if anaerobic conditions exist. Soils with anaerobic conditions rely on alternative oxidants, such as manganese oxide (MnO_4) and iron oxide (FeO_3) to facilitate microbial respiration processes. For field investigations of anaerobic soils the platinum (Pt) electrode is a standard tool to measure redox potentials, but is not cost-effective. Indicators of Reduction in Soils (IRIS) were developed as an alternative to Pt electrodes for use in field investigations of hydric soils.

In this study, three marl soil types were extracted to compare anaerobic determination results of Pt electrodes, iron oxide coated IRIS (FIRIS), and manganese oxide coated IRIS (MIRIS). IRIS were installed in the upper 45 cm of the soils and treated with 0 cm, 15 cm and 30 cm water table depths. IRIS tubes were extracted at intervals of 14, 28, and 56 days to quantify metal oxide removal using visual, trace and scan methods.

Results of the study showed FIRIS tubes had $\geq 30\%$ iron oxide removal in the upper part of the soil during the 56 days when inundated to the soil surface. Findings suggest that in high calcareous soils FIRIS need 56 days of installation time to reduce enough iron oxide to reflect anaerobic conditions. Metal oxide removal in saturated conditions from MIRIS averaged just 29% of the amount removed from FIRIS, and MIRIS failed to reflect anaerobic soil conditions

over the 56 day installation. Pt electrode readings indicated anaerobic reduction within seven days, allowing for anaerobic conditions to be determined in as little as 14 days in calcareous marl soils.

CHAPTER 1 INTRODUCTION AND LITERATURE REVIEW

Rationale

Soils with marl deposits at the surface are found in the extreme southern portions of Florida. The marls are taxonomically classified as carbonatic Typic fluvaquents and represent seven soil series located in Miami-Dade, Monroe, Broward and Collier counties in Florida. An inventory of marl soils in south Florida is approximately 500,000 acres including federally owned lands within two national parks and a preserve (Davis et al., 2005; USDA-NRCS, 1998). In protected, natural areas such as Everglades National Park, Biscayne National Park, the Big Cypress Preserve, and other protected coastal wetlands, marl soils exist in functioning wetland systems of inland freshwater prairies and along coastal fringes where seasonally flowing, slow shallow water environs still exist. Many protected species use the marl lands for habitat, most notably is the Cape Sable Seaside Sparrow (*Ammodramus maritimus mirabilis*), the American Alligator (*Alligator mississippiensis*), and a vast array of native and migratory bird species. Although such designated areas are protected, the natural hydroperiod has been altered by water control structures installed during the mid-1900s to drain the Everglades for flood protection.

The term “hydric soil” was first used by Lewis Cowardin of the United States Fish and Wildlife Service (USFWS) in the 1979 publication *Classification of Wetlands and Deep Water Habitats of the United States* to describe soils found in wetland systems. The term has been widely adopted and officially recognized as one identifying characteristic of a wetland along with wetland hydrology and hydrophytic vegetation. To consistently identify, delineate, and regulate wetlands, a formal system of hydric soils classification has been developed and continues to evolve as knowledge expands. Anaerobic conditions and saturation must both exist to support the determination that a soil is hydric.

Once a soil is classified as hydric, it has regulatory connotations relative to land use and management. A hydric soil is defined as having formed in conditions of saturation, flooding or ponding for long enough periods during the growing season to develop anaerobic conditions in the upper part (USDA-NRCS, 2006). During the development of the first national list of hydric soils, the National Technical Committee for Hydric Soils (NTCHS) was formed to oversee the process.

Soils are evaluated according to the criteria, indicators, and test methods approved by the NTCHS. Anaerobic conditions can be documented by either redox potential (Eh) readings, iron reduction on buried iron oxide coated Indicators of Reduction in Soils (FIRIS) tubes, the presence of reduced iron (Fe^{2+}) in the soil, or positive reaction to alpha-alpha-dipyridyl solution. The latter two options can only be used on soils with sufficient iron present, which is not characteristic of marl soils in south Florida. FIRIS and manganese coated (MIRIS) tubes were developed for use by field soil scientists in problem soils that lack readily assessable morphologic indicators of reduction and anaerobic conditions.

Research Goals

This study compares the results obtained using platinum (Pt) electrodes, FIRIS, and MIRIS in determining anaerobic soil conditions in calcareous marl soils. An evaluation of the potential of these tools for use by field soil scientists conducting hydric soil determinations would be helpful. Chemical and physical properties of the three marl soils used in the research can help identify characteristics that may affect anaerobic redox processes. As part of the evaluation of FIRIS and MIRIS, examine how hydric soil determinations might vary by analysis methods used to determine the percent metal oxide removal from Indicators of Reduction in Soil (IRIS) tubes.

Application

IRIS technology has the potential to provide a cost-effective alternative to scientists conducting hydric soil investigations in problem soils, by allowing rapid in-situ assessments with minimal expense for equipment and labor. Hydric soil determinations are a key component in developing interpretive land use limitations and are a requirement of regulatory wetland determinations. IRIS could have potential application in monitoring the progress of wetland restoration, creation, and enhancement projects associated with the Comprehensive Everglades Restoration Plan in south Florida.

Marl Soil Formation and Geographic Extent

To determine where marl soils exist, it is important to understand what marl is, and the differences used to describe marl. In the National Soil Survey Handbook marl is described as a limnic layer that is light colored and reacts with hydrochloric acid (USDA-NRCS, 1997). The two characteristics used to verify marl soils in the field is a moist soil color value of 5 or more and reaction with dilute (1M) HCl to evolve carbon dioxide CO₂ as shown in Equation 1-1.



Limnic materials are used as modifiers of texture to describe either the origin or the material itself. These materials were deposited in water by precipitation, or through the action of aquatic organisms, or derived from plants and organisms (USDA-NRCS, 1997). Marl is primarily calcium carbonate, typically found below the surface of organic soils where the marl formed in a preexisting open water environment (USDA-NRCS, 1999).

Marl soil forms in areas inundated with calm, shallow waters over a limestone substrate. In the 1996 Dade County Soil Survey (USDA-NRCS, 1996) the depth to limestone varies in each of the marl soil series:

- Biscayne marl = limestone bedrock at 1 cm to 51 cm below the soil surface

- Perrine marl = limestone bedrock at 51 cm to 1 m below the soil surface
- Pennsuco marl = limestone bedrock at 1m to 2 m below the soil

Equation 1-2 explains what occurs when periphytic algal mats dominated by cyanobacteria species cause an increase in water pH through respiration, leading to saturation and precipitation of calcium carbonate from the water column. The powder-fine precipitate accumulates on the inundated substrate to form these waterborne soils. The rate at which calcitic marls accumulate is directly related to their spatial extent and productivity (Davis et al., 2005).



Algal and bacterial mats are able to survive the fluctuating hydroperiods in marl prairies and sloughs of the Everglades ecosystem. Wetlands with these abbreviated hydroperiods are dry long enough each year to prohibit the accumulation of organic material through oxidation, preventing the formation of organic soil layers (Davis et al., 2005). With the annual return of the rainy season, around June in south Florida, these periphyton mats are rehydrated in shallow waters that overlay limestone bedrock.

Marl soils are located across the globe where these conditions are or were present at various geologic periods with favorable water levels and alkaline chemistry. The term marl is widely used in English-language geology, while the terms mergel and seekreide are used in European references (Strasser et al., 2008). It is curious that marl soils are not mentioned in areas of the Far East, Russia, Central/South America, or Australia. Soils in parts of the world have not been mapped, or may not identify marl by the same terminology or concepts that are used in the United States.

A search of the Natural Resources Conservation Service's national soils database revealed that in the United States, marl at the soil surface is not common or expansive in spatial distribution. Outside the Everglades, there are lacustrine marl soils of the Great Lakes and in

coastal areas of South Carolina. Figure 1-1 shows the distribution of marls in Florida, which are primarily limited to Miami-Dade, Monroe, Broward and Collier counties associated with the southeastern areas of the greater Everglades ecosystem. In this subtropical environment marls form under shallow surface waters that are seasonally present from 2 to 9 months in duration each year (Davis et al., 2005).

An inventory of the acres of marl soils in south Florida are listed in Table 1-1. The actual acres are significantly higher since federally owned lands within Everglades National Park, Biscayne National Park and Big Cypress National Preserve are not included in the most recent published soil surveys. At least 190,000 hectares of marl prairies surround the Shark River Slough in the heart of Everglades National Park (Davis et al., 2005).

South Florida Hydrologic Alterations

In protected, natural areas of south Florida, such as Everglades National Park, Biscayne National Park, the Big Cypress Preserve and protected coastal wetlands, marl soils often exist in functioning wetland systems. In areas where seasonally, slow flowing, shallow water is present, inland freshwater prairies, sloughs, and coastal fringe ecosystems are sustained. Although many of these designated areas are protected, their natural hydroperiods were either abbreviated or removed by water control structures installed to provide flood protection for developing areas. If the wetland hydrology at a site has been removed, then the wetland functions and values are also altered. An over-simplified relationship of the interdependence of the site characteristics is represented by the formula in Equation 1-3.

$$\text{WETLANDS} = \text{wetland hydrology} + \text{hydric soils} + \text{hydrophytic vegetation} \quad (1-3)$$

Everglades hydrology was significantly altered, beginning at the turn of the 20th Century and peaked during the early 1960s to facilitate the objective of reclaiming swamp land for land uses considered more productive at that time. Drainage projects not only provided flood

protection but also enabled year-round crop production on marl soils that were drained through a vast network of canals and levees. Before the 1960s, the east glades area south of Miami and east of Homestead was used during the dry season (December – April) to produce seasonal truck crops. Post-harvest, these areas were left idle until the following dry season returned and the water table fell below the shallow root systems of these crops.

Before initiation of systematic drainage in south Florida, marl soils had hydroperiods lasting from 2 to 9 months in duration. After drainage canals and pumps were installed, the eastern glades stayed dry for 9 months of the year (Davis et al., 2005). At present, drained marl soils are used for the year-round production of food crops (okra, malanga, bananas, squash, beans, corn), field grown ornamental plants (woody landscape plants and large palms), or container grown ornamental plants (bedding plants, annuals, herbs, orchids and bromeliads).

Hydric Soils Classification

At the Federal Government level, wetland regulations primarily derive from the 1972 Clean Water Act and/or the Swampbuster provisions of the 1985 Food Security Act. In addition, to Federal Legislation there may be state and county level regulations for wetland use and permitting, but varies across the United States from state to state as well as between counties. Hydric soils are an integral component in jurisdictional wetland determinations that affect land use planning and management by individuals and bodies of government.

To assist the USFWS in delineating wetlands for the National Wetland Inventory (NWI) in the late 1970s, the United States Department of Agriculture - Natural Resources Conservation Service (NRCS) was asked to develop a national hydric soils list that would enable the use of remote sensing and existing soil surveys for the production of NWI maps. The culmination of that collaborative effort resulted in the first version of the NTCHS, published in 1985 (Richardson and Vepraskas, 2001). During the development of the first national list of hydric

soils in the early 1980s, there was disagreement among NRCS personnel throughout the country on what criteria and which soils should be included. The NTCHS was formed to oversee the process to be used as well as develop a scientifically sound list that could withstand scrutiny (Tiner, 1999). Marl soils in this research were evaluated according to the criteria, indicators and test methods approved by the NTCHS.

NRCS maintains the official list of hydric soils covering all soil map units delineated throughout the United States and its territories. During the 20th Century, most soils in the United States were mapped on a countywide basis and some have been updated since the original publications were completed. Each map unit in a soil survey is either classified as hydric or non-hydric according to the current criteria of a hydric soil. The list provides a quick indication of whether a specific site may contain hydric soils and/or wetlands.

A soil can be saturated and not anaerobic if the water has a significant amount of dissolved oxygen present. Likewise, fine textured soils can show anaerobic conditions when not saturated if the water holding capacity of the soil matrix excludes O₂, while large macro-pores in the soil structure contain air. Capillary fringe is not always considered to be part of the saturated zone, as its influence above the water table is not easily measured and can be a dynamic property affecting soil-water state (Vepraskas and Sprecher, 1997). Migliaccio et al. (2008) found that capillary rise in Biscayne marl soils had a significant influence on the soil water content in the soil layers above the water table.

Criteria and Field Indicators of Hydric Soils

For a soil series or map unit to be included in the hydric soils list, at least one of the hydric soil criteria in Table 1-2 must be met. Criteria 1, 3 and 4 are also indicators of hydric soils that can be determined in the field. Criteria 2 are used for the purpose of searching the National Soil Information System database in preparation of hydric soil lists and are not field indicators

(USDA-NRCS, 2002). One limitation placed on the criteria is soil temperature, which is not a concern in the Everglades region where soils are warm enough to facilitate year-round biologic activity. An on-site investigation is necessary to determine the soil properties and document any evidence of saturation in the upper 30 cm of the soil. Correct and consistent determinations are necessary if they are to be credible and defensible in a legal context.

Today, an official list of 48 indicators is used to identify and delineate hydric soils in the United States. The indicators are applicable to one or more of the 26 geographically defined Land Resource Regions (LRR) in the United States, which are alphabetically labeled A – Z. Land Resource Regions serve to group regions with similar soils and land uses for broad management of soil survey activities and data management by NRCS. Figure 1-2 shows that most of Florida is in LRR U, Florida Subtropical Fruit, Truck Crop, and Range Region, extending from Key West north to about Gainesville, and encompassing the area of interest in this research. Indicators are alphanumerically coded, with a letter preceding the number to indicate the conditions that each indicator can be applied; A = All soil types, S = Sandy soils, F = Fine textured soils (loamy and clayey), T = Test Indicators. Each LRR has an official list of hydric soil indicators that can be used to identify and delineate hydric soils. Indicator A4, hydrogen sulfide odor, may be present in coastal areas of marl accumulation receiving sulfur rich marine waters. Soils collected in this study do not include marls receiving tidal waters. A soil can have more than one indicator present, which provides additional confidence in a hydric determination. The primary indicator relative to marl soils in LRR U is F10, as follows (USDA-NRCS, 2006):

- All mineral layers above a marl layer must have a color chroma of 2 or less, OR
- F10 is only for use in Land Resource Region U
- The marl layer must have a color value of 5 or more
- The marl layer must start within 10 cm of the soil surface

Evaluating the Hydric Status of Marl Soils

Labeling a soil as marl indicates formation in water from the biogenic process of CaCO_3 precipitation in response to algal respiration. Marls in south Florida are taxonomically classified as carbonatic Typic fluvaquents and represented by 7 soil series in the 4 counties listed in Table 1-1. Some silt loam soils existing in Broward and Collier are not positively identified as marl soils, as it is thought they may have derived from non-biogenic processes of erosion and deposition (H. Yamataki, personal communication, 2010).

In the 1998 Collier County Soil Survey of Florida, the Pennsuco soil series is not labeled as Pennsuco marl, but rather as Pennsuco silt loam. Understanding that it is a marl soil or marl variant requires the reader to review the Pennsuco series description as it occurs in that survey area, which states the soil formed in marl and is associated with wet prairies (USDA-NRCS, 1998). The concern is not simply the marl label itself, but the hydric soil criteria that are applicable once a soil is labeled marl.

In October of 1999 some soils in Collier County, Florida were investigated for hydric soil identification problems. Pennsuco marl was one soil sampled and found to contain 30% CaCO_3 , 7% organic matter, and the balance was quartz sand. Another observation during that investigation is that the F10 field indicator color value of ≥ 5 was not always met, and color values of 3 and 4 were not uncommon. Following that investigation, Wade Hurt with the NTCHS proposed the following considerations to address the problems associated with hydric soil identification in south Florida:

- Marl should be defined to contain a minimum of 60% CaCO_3 , with no secondary carbonates
- Marly mineral materials be allowed using indicator F10, as long as the CaCO_3 content is at least 15%, with no secondary carbonates

- Include colors with a value and chroma of 4/1 in indicator F10

The 2010 update to the Hydric Soil Field Indicators, had none of the proposed changes, or expansion of criteria incorporated into the F10 indicator (USDA-NRCS, 2010).

Morphologic Indicators of Soil Saturation

The most common features of a soil, used in-situ, to evaluate if a soil is saturated for a significant period is the organic matter content, a gleyed matrix, and/or redoximorphic features (Tiner, 1999). Iron reduction can be visibly determined with the change from reddish-brown ferric iron into a grayish ferrous iron; the resulting gray soil matrix is then referred to as “gleyed” (USDA-NRCS, 2010). Gleying is not used as an indicator in marls since the gray color is not derived from the presence of Fe^{2+} , but rather the biogenic formation of calcium carbonates.

When marl occurs beneath organic soil layers, this position indicates a hydroperiod of sufficient duration to allow the accumulation of organic matter at the surface. A review of typical pedon descriptions of marl soils in the 1996 Dade County Soil Survey reveals marls occur at the soil surface and are not overlain by an organic horizon. The color of marl does not change when dried because it contains too little organic matter to coat the carbonate particles. Most of the samples of marl from the United States have organic-matter contents between 4% and 20% (USDA-NRCS, 1999).

In lieu of sufficient organic matter at the soil surface, a gleyed matrix can be used to indicate soil saturation. Oxygen (O_2) is the preferred electron receptor for soil microbes, but in anaerobic conditions microbes will reduce ferric iron (Fe^{3+}) to ferrous iron (Fe^{2+}). In 1999, Chen et al. explored background values of iron and other elements in marl soils from undisturbed sites in Everglades National Park (ENP) and compared these element concentrations with disturbed soils throughout Florida. Iron content in the upper 20 cm of marl soils ranged from 1295 mg/kg

to 100,385 mg/kg. Iron and the other elements were determined to exist in higher concentrations in the ENP marl soils when compared with other soils throughout Florida (Chen et al., 2000).

While investigating the arsenic content of surface soils in Florida, Chen et al. (2002) reported an average CaCO_3 content of 56% in south Florida marls. Since these soils are dominated by calcium carbonates (calcite), they offer little to no morphological evidence of soil processes regarding saturation and anaerobic conditions. Redoximorphic features such as redox concentrations and redox depletions are also visible soil characteristics expressed when a soil contains sufficient iron or manganese, but are not produced in marl soils for the in-situ assessment of anaerobic and saturated soil conditions.

Reduction in Saturated Soil Conditions

Reduction is a measurable process that can be utilized to document anaerobic soil condition, a prerequisite of hydric soils. A lack of dissolved O_2 , an organic food source, and the presence of anaerobic microbes to degrade the organic matter are all necessary for reduction to occur. Microbial respiration then requires an electron acceptor once dissolved. In natural soil environments, electrons are accepted by the oxidants shown in Table 1-3, listed in order of preference. In the absence of dissolved O_2 , NO_3^- would first be utilized and CO_2 would be the last desired acceptor since significant energy must be expended on the part of the microbe to transfer the electron (Mitsch and Gosselink, 2000).

Measurement of Oxidation-Reduction Potentials in Soils

The ability to quantitatively measure energy associated with the electron transfer was discovered during the nineteenth century while studying elements using electricity. The quantity of electrical charge that passes through an electrochemical cell is proportional to the substance produced at the electrode when a redox reaction occurs. Anaerobic conditions can be documented using Pt and reference electrodes to measure the voltage difference and obtain a

redox potential reading. In the presence of free O₂ in the soil, potentials ranging from +400 to +700 mv should be expected. Once saturated, O₂ can be depleted within several hours to several days with values dropping in the range of +400 to -400 mv (Mitsch and Gosselink, 2000).

Measuring the reduction and oxidation potential of a soil by collecting conductance readings between Pt and reference electrodes is an established method (Appendix A). Eh is pH dependent and the standard used to evaluate readings is +175 mV at a pH of 7.0. For each whole pH unit greater than 7 a correction factor of -60 mV is added to the Eh reading; +60 mV is added for each pH unit less than 7. The value of 60 is derived from the Equation 1-4 where a line with a -60 slope is derived when plotting iron redox potentials against pH.

$$Eh_{\text{volts}} = Eh^{\circ} - \frac{0.059}{N} \log \frac{\text{reduced species}}{(\text{oxidized species}) (H)^m} \quad (1-4)$$

Figure 1-3 demonstrates that in anaerobic conditions iron reduction potential is achieved at greater reduction potentials in non-alkaline soils. A query of the NRCS soil survey data base (online at <http://soildatamart.nrcs.usda.gov/>), shows the pH in marl samples at the 25 cm depth in Broward, Collier, Miami-Dade, and Monroe counties ranges from 7.0 to 8.3. Saturated Ag/AgCl electrodes with 4 M KCl electrolyte solution will vary in conductance from temperature fluctuations of just -0.13 mv for each +1^o C (Ansuini and Dimond, 1994). A small temperature correction factor is recommended when using saturated Ag/AgCl electrodes at temperatures that vary from 25^o C. Under climate controlled lab conditions with an ambient air temperature set at 25^o C, correction factors for temperature were not expected to be significant or necessary but were recorded.

Iron Indicators of Reduction in Soil (FIRIS)

Outside of a research lab the Pt electrode method is not practical for routine use by field soil scientists due to the installation of expensive equipment, labor requirements, and exposure to

hazards from weather conditions and wildlife, as well as vandalism or theft. In 2006, Jenkinson and Franzmeier introduced the use of iron coated IRIS tubes as a method to determine reduction in soils (Castenson and Rabenhorst, 2006). FIRIS tubes have been accepted by the NTCHS as an alternative tool for documenting anaerobic soil conditions associated with wetlands and hydric soils. For soils low in iron, FIRIS can serve as a surrogate representing Fe^{3+} , as if naturally present. Most Florida soils, including marls, do not contain sufficient amounts of iron to produce morphologic indicators that allow for rapid identification of anaerobic conditions in the field.

In contrast to electrodes, IRIS tubes have distinct advantages in that they are relatively easy to install and extract, inexpensive, and lightweight enough to carry on-foot to remote locations not accessible by vehicles. Castenson and Rabenhorst (2006) described the construction and methodology used to evaluate FIRIS tubes for investigating soil reducing conditions. The iron coated IRIS tubes are now referred to as FIRIS to differentiate them from the newly developed manganese coated IRIS, or MIRIS. FIRIS tubes for this project were provided courtesy of the United States Department of Agriculture – Natural Resources Conservation Service, National Soil Survey Lab in Lincoln, Nebraska.

Iron transformations in soils supporting rice production found that water soluble/exchangeable iron was dependent more on pH than either iron or organic matter content (Mandal and Mitra, 1982). Soils derived from carbonates can maintain high saturations of siderite (FeCO_3) that do not dissolve due to the extreme buffering capacity of marl soils (Stiles et al., 2010). In high pH, alkaline soils, reduction of Fe^{3+} to Fe^{2+} is suppressed and expected to limit FIRIS usefulness (Stiles et al., 2010).

Manganese Indicators of Reduction in Soil (MIRIS)

Since 2009, MIRIS tubes have been investigated as an alternative to FIRIS to accurately reflect saturated, reduced, soil conditions, in significantly less time than FIRIS reacts in alkaline

soils. Dr. Cynthia Stiles, while at the United States Department of Agriculture (USDA), National Soil Survey Center performed bench testing of the MIRIS before an initial field test was conducted in Alaska during the summer of 2009. In the Brooks Range region of north-central Alaska, FIRIS and MIRIS were installed in a calcareous fen wetland utilizing two sets of 5 MIRIS and one set of 5 FIRIS tubes. The tubes were oriented along a wetland transect with high pH/Eh conditions. To observe manganese oxide transformation in non-hydric soils, one set of MIRIS tubes was installed in a well-drained mid-slope position. Within four days, the wetland MIRIS tubes displayed oxide paint removal. The MIRIS positioned in the well-drained slope did not show significant manganese oxide removal after 7 days, confirming manganese oxide removal in saturated conditions (Stiles et al., 2010).

After 42 days, the five FIRIS tubes that were installed adjacent to the MIRIS had <10% oxide removal on four of the five tubes and a concentration of iron oxide on the upper 10 cm of the tube. Rapid removal of manganese oxide in high pH/Eh conditions supports the idea that MIRIS could be effective in identifying the presence of reducing conditions that are unfavorable for iron reduction (Stiles et al., 2010). Observing IRIS in calcareous, marl soils of south Florida provides a measure of performance to build upon the 2009 investigation by Stiles et al. in Alaska.

MIRIS manufacturing methods at this early stage of development is similar to the methods used for FIRIS manufacture, except manganese oxide paint production and application to the polyvinyl chloride (PVC) tubes are more labor intensive and time consuming. In Appendix B there is a description of the entire process used to produce manganese oxide paint and to fabricate the MIRIS tubes. This research project provided an additional evaluation of the new

MIRIS on calcareous marl soils that are problematic in their inability to reflect changes in soil hydrologic regimes.

Carbonates in South Florida Marl Soils

It has been suggested that marl soils, as a positive indicator of their biogenic origin and classification as marl, should contain no secondary carbonates. The formation of marl in south Florida involves the precipitation of CaCO_3 in shallow water environments fed by water from surficial limestone aquifers. Calcite and dolomite account for 90% of natural carbonates, are known to occur in soils as primary or secondary carbonates (Table 1-4). In soils, the most common carbonates are calcite, dolomite and magnesite (Ming, 2007).

Rabenhorst et al. (1984) were able to use stable C isotopes to differentiate primary and secondary carbonates in limestone soils of Texas. The methodology was based on the assumption that soil CO_2 is incorporated into secondary carbonates, which have more negative C^{13} values than marine limestone (West et al., 1988). Marl soils of south Florida do not fit this model since Florida marls are formed in response to respiration by periphytic algae in shallow freshwater as well as saltwater environs. Morphologic characteristics of pedogenic carbonates often used in arid regions are not present in the humid climate of the Everglades ecosystem with an annual rainfall of approximately 152 centimeters. Segregation of primary from secondary carbonates in soils derived from highly calcareous materials is challenging as current analytical methods cannot identify the Mg as deriving from MgCO_3 or $\text{CaMg}(\text{CO}_3)_2$ (Goh and Mermut, 2008). Soil samples collected from this research will have total soil carbonates determined from the volume of CO_2 gas generated upon dissolution of solid carbonates with HCl acid, using a Scheibler apparatus (USDA, 1993).

Research Objectives

Iron and Manganese are not expected to be present in appreciable amounts in natural systems of the greater Everglades ecosystem to reflect reducing conditions, but can be provided to the soils via FIRIS and MIRIS tubes to simulate redox potentials of soils with naturally sufficient reducible iron and manganese oxides. The newest MIRIS tubes were fabricated and tested against the original FIRIS to see if MIRIS tubes can reflect reduction at a faster and more reliable rate than with the FIRIS, which is known reduce iron oxides at a slow rate in high pH conditions. When reduced, both metals are soluble and move with soil water, so that there is visible evidence of translocation by absence of metal oxides from the tube surfaces.

The first objective of this research was to evaluate the performance of the recently developed FIRIS and MIRIS tubes against the established, conventional Pt and reference electrodes. A comparison of the quantity of metal oxides removed in a time interval allows a comparison of anaerobic soil determinations by each tool. Results can provide guidance on the most appropriate tool for use in high pH, calcareous soils in south Florida.

The second objective was to determine if general soil characteristics of marl might have some influence on redox processes since FIRIS and MIRIS were both developed for use in problem soils. South Florida marls selected for this research are integral components of wetland ecosystems that are being restored as part of the Comprehensive Everglades Restoration Project. Marl soil properties may help in identifying the limits for use of IRIS tools or improve IRIS technology for use in alkaline, problem soils.

The final objective was to analyze results obtained from three methods used to determine the percent metal oxide removal from the surface of IRIS tubes. In keeping with the concept of using trained soil scientists to provide a visual estimate of the percent of oxide removal, the visual estimate would be compared against a digital scan of the tubes. Digital analysis by hand

tracing, as well as direct scanning with a bar/hand scanner will include both techniques currently used.

Table 1-1. Extent of marl soils in Florida

Soil series	Acres in Miami-Dade County	Acres in Monroe County	Acres in Collier County	Acres in Broward County	Total acres by soil series
Biscayne	67,364	--	--	--	67,364
Cudjoe	--	3,410	--	--	3,410
Key West	--	450	--	--	450
Lignumvitae	--	1,360	--	--	1,360
Pennsuco	14,490	--	7,697	1,886	24,073
Perrine	50,362	--	--	276	50,638
Saddlebunch	--	1,140	--	--	1,140
Total acres	132,216	6,360	7,697	2,162	148,435

--Indicates soil series not present in the county. Data compiled from the U.S. Dept. of Agriculture database on official soil series. More info at <https://soilseries.sc.egov.usda/osdquery.aspx> (22 July 2012).

Table 1-2. Criteria for hydric soils

Soil taxonomy	Criteria	Drainage class	Texture in upper 50 cm	Water table depth (cm)	Duration of saturation	Saturation occurrence	Permeability in upper 50 cm
Histels (no Folistels)	1	n/a	n/a	n/a	n/a	n/a	n/a
Histosols (no Folistols)	1	n/a	n/a	n/a	n/a	n/a	n/a
Aquic suborder, greatgroup, or subgroup	2A	Some-what poorly	finer than fine sands	0	n/a	Growing season	n/a
Albolls suborder	2A		n/a	n/a	n/a	n/a	n/a
Historthels greatgroup	2B1	Poorly or very poorly	sands	0	n/a	n/a	n/a
Histoturbel greatgroup	2B1		finer than fine sands				
Cumulic subgroup	2B2			15	n/a	Growing season	≥ 15 cm/hr all layers
Pachic, Andic, and Vitrandic subgroups	2B3			15	n/a	Growing season	< 15 cm/hr any layer
Any	3	n/a	n/a	Ponded	> 7	Growing season	n/a
Any	4	n/a	n/a	Flooded	> 7	Growing season	n/a

* Frequently is more than 50% of the time, † consecutive days; data adapted from: Changes in hydric soils of the United States. USDA - Natural Resources Conservation Service. Federal Register Doc. 02-23683, Vol. 67, No. 181, September 18, 2002.

Table 1-3. Oxidants in soil redox processes, listed in order of preference by reducing bacteria

Oxidized form	Reduced form	Redox potential (mV)
NO ₃ ⁻	N ₂ O, N ₂ , NH ₄ ⁺	+250
Mn ₄ ⁺	Mn ₂ ⁺	+225
Fe ₃ ⁺	Fe ₂ ⁺	+100 to -100
SO ₄ ²⁻	S ₂ ⁻	-100 to -200
CO ₂	CH ₄	< -200

Data adapted from: Mitsch W.J. and J.G. Gosselink, 2000. Wetlands, 3rd Edition. John Wiley and Sons, Inc., Canada. Table 6-2, p. 169.

Table 1-4. Characteristics of soil carbonates

Mineral	Composition	Occurrence	Genesis
Calcite	CaCO_3	soil, limestone, igneous	primary or secondary
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	dolostone	primary or secondary
Siderite	FeCO_3	sediments	primary
Aragonite	CaCO_3	biological (shells, molluscs)	primary
Magnesite	MgCO_3	evaporite	primary
Nesquehonite	$\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$	evaporite	secondary
Soda	Na_2CO_3	evaporite	secondary

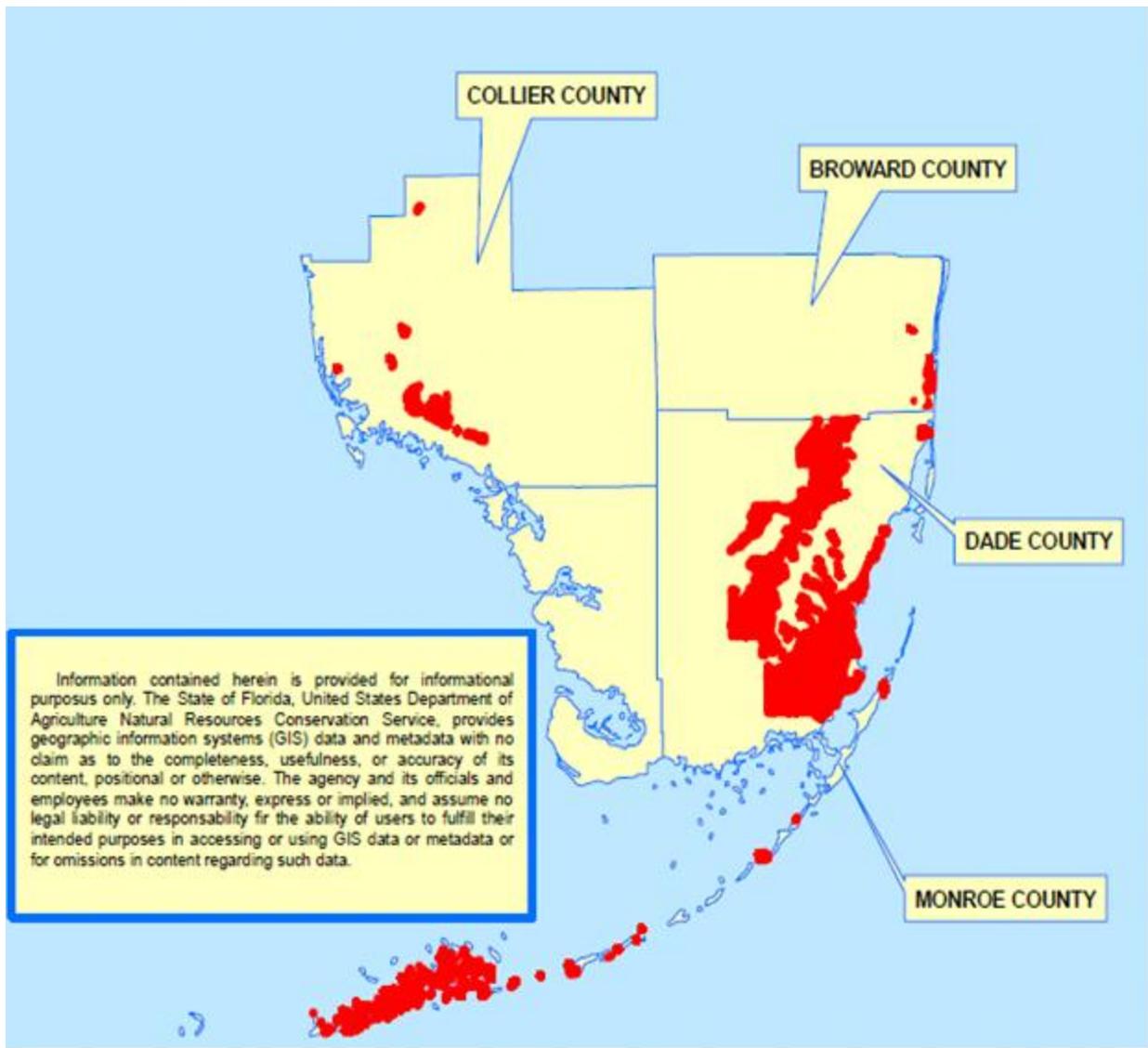


Figure 1-1. Areas mapped as marl in south Florida. Source: Martin Figueroa, Senior Soil Scientist with the United States Dept. of Agriculture-Natural Resources Conservation Service in the Major Land Resource Area 8 office in Ft. Myers, Florida (October 2009).

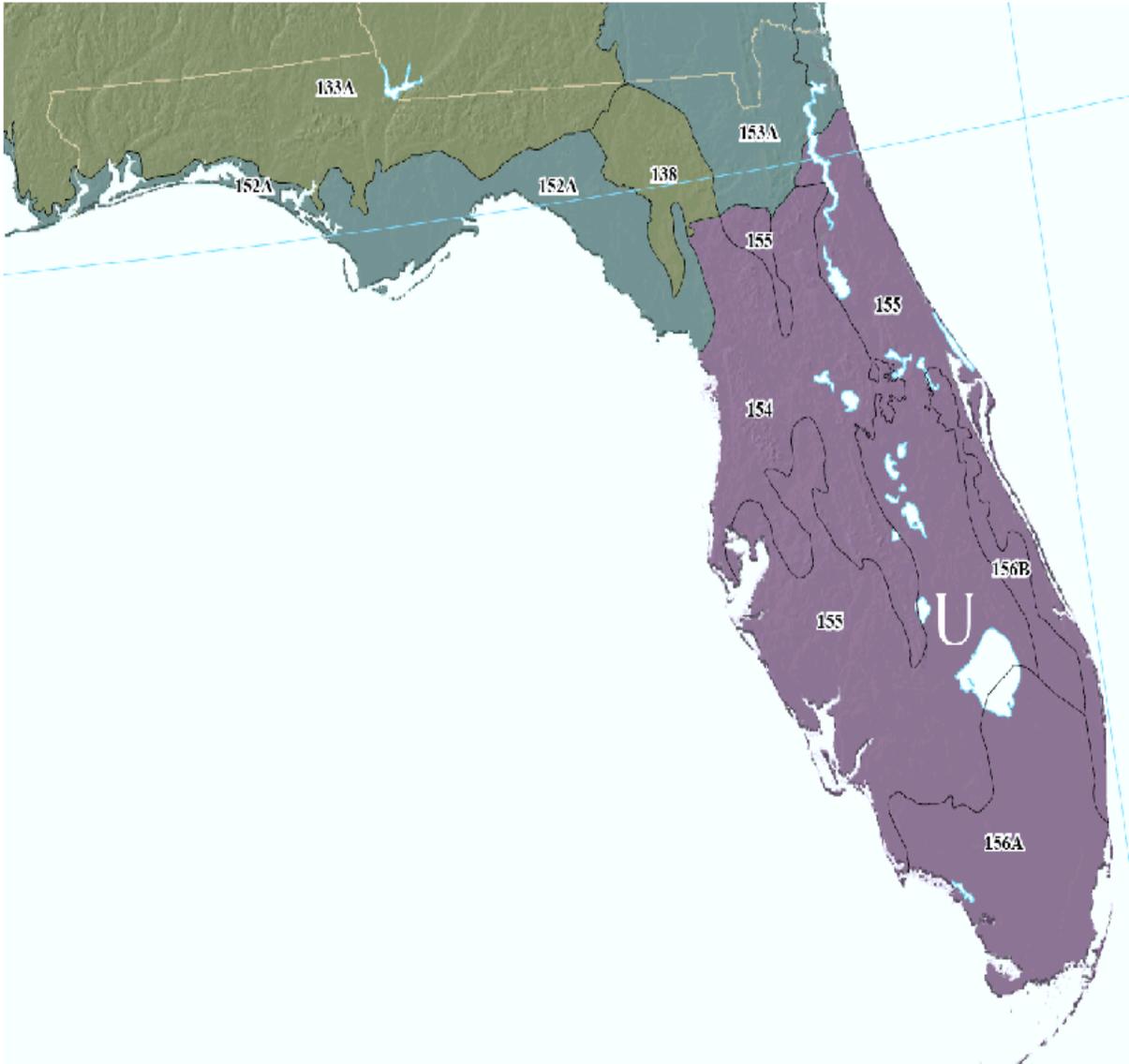


Figure 1-2. Major Land Resource Region U in Florida. Map source: United States Department of Agriculture, Natural Resources Conservation Service. 2006. Land Resource Regions and Major Land Resource Areas of the United States, the Caribbean, and the Pacific Basin. U.S. Department of Agriculture Handbook 296. Online at: http://www.mo15.nrcs.usda.gov/technical/mlra_fl.html (May 2012)

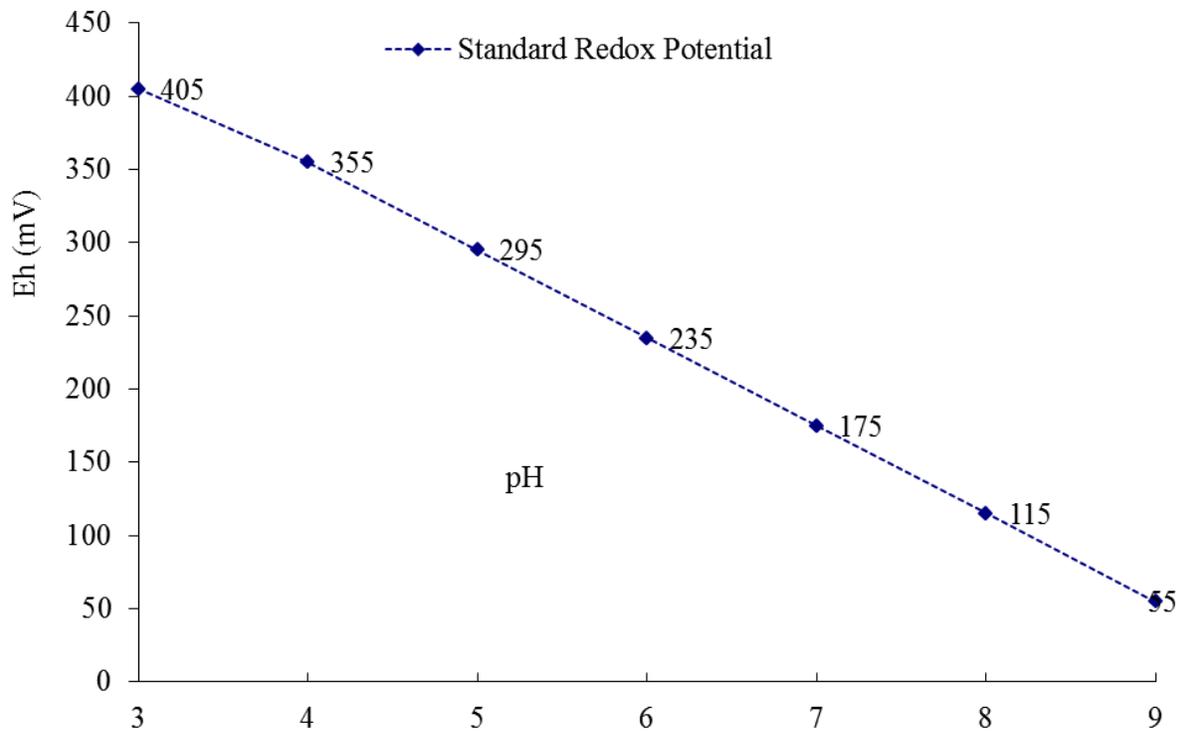


Figure 1-3. Standard redox (Eh)/pH line for determining anaerobic conditions. Adapted from The Hydric Soil Technical Standard 2007, Technical Note 11, p 9. Available at: http://soils.usda.gov/use/hydric/ntchs/tech_notes/index.html

CHAPTER 2 ANAEROBIC SOIL DETERMINATIONS

Introduction

Anaerobic soils incapable of displaying morphologic indicators to allow rapid, in-situ assessments by field scientists in soil mapping, site use limitations, and wetland determinations or delineations are referred to as problem soils (Vepraskas and Sprecher, 1997). Iron Indicators of Reduction in Soil (FIRIS) and manganese Indicators of Reduction in Soil (MIRIS) tubes were recently developed as alternatives for assessing anaerobic soils that lack readily assessable morphologic indicators of reduction and anaerobic conditions. FIRIS tubes have been in use since 2006 and accepted by the National Technical Committee for Hydric Soils (NTCHS) as an alternative to electrodes for determining hydric status of a soil through the verification of sustained anaerobic conditions (NTCHS, 2007).

The performance of FIRIS or MIRIS has not been evaluated in south Florida where alkaline soils and wetlands dominate the landscape. Marl soils of south Florida are considered problem soils. Whether marl soils are oven-dry or saturated they maintain a light grey color, which typically indicates a reduced state in most mineral soils with sufficient iron content. This study provides an additional evaluation of the performance of FIRIS and MIRIS in high pH soils of a different ecological setting than Alaska to see how these recently developed redox tools may be applied. In this research, simultaneous investigations of both the FIRIS and MIRIS tubes abilities to reflect reduction in high pH, saturated calcareous marls will be conducted. As part of this study, a visual method, scan method and trace method were used on select Indicators of Reduction in Soil (IRIS) tubes to compare the percentage of metal oxides that would be calculated by each method.

Materials and Methods

Selection and Extraction of Soil Mesocosms

Three marl soil map units in Miami-Dade County, Florida were selected to represent varying land uses and hydrologic alterations common on undeveloped marl soil areas of south Florida. Depth to limestone contact was 51 centimeters to 1 meter in the Perrine soil, and 1 to 2 meters in the Pennsuco soils (USDA-NRCS, 1996). Additional considerations of site selection included land use and drainage for the possible variances in nutrient content and redox species. To best represent the in-situ soil matrix, horizons/layers were extracted with minimal disturbance to the soil from each of the three sites shown in Figure 2-1.

Pennsuco marl (Soil A) collection site had no compaction and the marl had a loose consistency similar to a powdery snow. 25.4 centimeter diameter polyvinyl chloride (PVC) pipes, 61 centimeters in length and beveled on one end were manually inserted to the 45 centimeter target soil. A 25.4 centimeter diameter pipe gripper was then inserted into the top of the submerged column and expanded to achieve an air-tight seal, preventing the soil core being vacuumed from the bottom of PVC pipe when extracted to the surface. A manually powered lever and fulcrum was constructed of 15 cm x 15 cm beams and heavy-duty chain to extract the soil mesocosm to the surface. Immediately after each extraction, a sand filter, 25.4 centimeter PVC cap, and 1.6 centimeter clear Tygon tube were installed onto the PVC pipe before carrying to the vehicle and placing the rack for transport to the lab.

Perrine marl, drained (Soil B) and the Pennsuco marl, drained (Soil C) mesocosms were collected using a backhoe during the first week of August, 2011. After transporting all twenty seven mesocosms to the Tropical Research and Education Center (TREC) lab, they were left in the rack, under cover, to drain overnight. The following day they were moved into a climate controlled lab, where each PVC column was placed into a custom built wooden cradle to

facilitate installation of plumbing appurtenances and provide structural stability during data and sample collection. The twenty seven soil columns, containing 9 mesocosms from each of the three marl soils, were randomly located throughout the lab space to minimize the impacts of micro-climate variations. Once mesocosms were in the lab, water table levels were maintained approximately 30 centimeters below the surface in each column throughout the next 21 days until treatment water tables were established. Maintaining soil moisture minimized development of surface cracks in the soil from the air conditioning, which could affect redox potentials by allowing oxygen penetration deeper into the soil than would naturally occur

Installation of Equipment for Monitoring Reduction

Platinum electrodes

A Campbell Scientific Data Logger (model CR1000) was utilized to test the platinum (Pt) electrodes before installation into the soil mesocosms. Analog inputs 1 and 2 were wired for differential measurements that would be manually connected to each of the 27 Pt electrodes and the Ag/AgCl reference electrode before to each reading. A laptop was used to interface with the data logger, using Loggernet (version 4.0) software to receive and record the data of each reading, which represented a 10 second average of measured redox potential.

During the last week of August 2011, the water that had been maintained in the bottom of the mesocosms to prevent drying and cracking, was drained for installation of the Pt electrodes and the other redox equipment to be installed. The electrodes were labeled and installed in the center of the soil column by boring to 23 cm depth with a 2.54 centimeter diameter auger. The platinum tip was then inserted into undisturbed soil to the target 25 cm depth, as prescribed for collecting redox readings in fine textured soils (NTCHS, 2007). From the extracted soil, thick slurry was made with deionized water (DI) water, and then poured back into the auger hole to vertically anchor each Pt electrode. The 0 cm and 15 cm water table depths guarantee the Pt

electrode would be submerged and reduction was expected. A water table at 30 cm provided an opportunity to see if the capillary movement in marls is sufficient enough for reducing conditions to occur at the 25cm redox reading depth.

Salt bridges

A KCl salt bridge has shown to be effective in providing consistent electrical conductivity while not influencing redox processes (Veneman and Pickering, 1983). To install the salt bridges, a 2.54 centimeter diameter soil boring was made in the same manner described for installing the Pt electrodes. A soil slurry was made from the extracted soil with DI water and poured around the bridge in each soil mesocosm to secure the bridge position and ensure electrical conductivity. After installation, each salt bridge was labeled and a removable PVC cap was kept on the top of each bridge to keep the exposed agar gel from drying out and shielding the surface from any foreign particles that might alter reference electrode conductance.

Indicators of Reduction in Soil (IRIS)

The FIRIS were stored in climate controlled lab until ready to be installed in order to prevent exposure to moisture. Installation procedures for IRIS are described below and are the same, except that the diameter of the FIRIS tubes was 1.27 centimeters while the MIRIS were 1.91 centimeters. The diameter of the soil boring is important in providing direct contact between the oxide paints on the IRIS tubes and soil, since using soil slurry would alter the soil structure and not best represent the soil in field-site conditions. A soil boring with a diameter smaller than the IRIS tube diameter is also a concern, as there is the potential to remove oxide paints during installation from excessive abrasion.

Three - 1.27 centimeter and three - 1.91 centimeter borings were made to the 45 centimeter depth in each soil column. The extracted soil was collected from three layers from each column, labeled and allowed to air dry for analyses of soil properties. To protect the oxide paint during

insertion into the soil borings, each IRIS tube was enveloped in a clear plastic sleeve before inserting to the 45 centimeter depth. After installed, the protective sleeve was vertically removed to expose the tube surface to the surrounding soil. Due to the size limitations of 25.4 centimeter diameter soil columns, only 3 each of the FIRIS and MIRIS tubes could be placed in each mesocosm to spatially accommodate all the equipment as depicted in Figure 2-2. Each IRIS tube was labeled to identify the soil mesocosm and treatment variables to which each tube would be subject to.

Treatments

Three marl soil series selected from the sites shown in Figure 2-1 had different land uses that could influence the biogeochemistry of each marl soil:

- Pennsuco marl, undrained, from a natural wetland area
- Pennsuco marl, drained, from an ornamental field nursery
- Perrine marl, drained, from an annually tilled, row crop field

Three water table levels were selected to evaluate performance of IRIS in various degrees of soil saturation. The water table treatments at 15 cm and 0 cm provide a simulation of the soils in conditions of saturation and inundation, respectively.

- 30 cm below the soil surface
- 15 cm below the soil surface
- 0 cm - at the soil surface

Three extraction intervals were selected to determine how rapidly the FIRIS vs. MIRIS would reflect the reducing conditions in the soils.

- 14 days after installation
- 28 days after installation
- 56 days after installation

At each time interval, one FIRIS and one MIRIS were extracted from each of the 27 soil mesocosms so that the performance of both types of IRIS could be evaluated within the same

water table and sampling date. Redox readings, ambient air temperature and soil-water pH were collected during the late afternoon/early evening for 56 days from September 1 through October 27, 2011. During the first week, readings were taken 1 time each day; during the 2nd week, readings were taken 1 time every two days; during the 3rd week, readings were taken 1 time every three days; during days 28 through 56, readings were taken every 7 days.

The frequency of the redox readings meets the minimum requirement of no more than 7 days between readings, as specified by the Hydric Soils Technical Standard. If a predominance of reduction continues for at least 14 consecutive days, then anaerobic conditions can be documented by this method (NTCHS, 2007). With the extraction of 9 soil profiles for each of the three marl soils, three replicates were used to evaluate the IRIS tubes. Cumulatively, the replicates would provide 162 IRIS (3 soils x 3 water table treatments x 3 extraction intervals x 6 IRIS per mesocosm = 81 FIRIS and 81 MIRIS) to be evaluated from the 27 soil mesocosms.

Soil Properties and Sampling

Soil samples were collected from each of the 27 soil mesocosms during installation of the IRIS tubes to evaluate soil properties that are known to effect reduction and nutrient availability. Marls soils collected for this research are taxonomically classified as Entisols, are relatively young in their development with only A and C horizons described in the top 45 centimeter of the soil profile (USDA-NRCS, 1996). The Perrine marl, drained soil at the second collection site is annually disk-plowed to a 15.2 centimeter depth and the other two sites were not tilled and had little to no soil horizon development. Soil samples were collected from three layers in each of the 27 soil mesocosms; Layer A = 0 to 15 cm, Layer B = 15 to 30 cm, Layer C = 30 to 45 cm. The 81 samples were placed in soil sampling bags, labeled, air dried for 42 days, and passed through a 2mm mesh screen in preparation of the soil analyses described below. Soil and soil-water

samples were processed at the TREC lab from November 2011 through January 2012, with 3 replicates from each soil series analyzed.

Organic matter measurement by Loss of Ignition (LOI)

The evaluation of organic matter (OM) content by the Loss on Ignition (LOI) American Society for Testing and Materials (ASTM) standard D2974-07, method C by dry combustion was chosen for the ease of use (ASTM, 2000). Ten grams of air dried, sieved soils was processed from each of the 81 soil samples (3 layers x 27 mesocosms) for determination of organic matter using Equation 2-1. Organic carbon was then estimated at 50% of OM content.

$$\frac{\% \text{ OM} = \text{oven dry soil weight} - \text{soil weight after ignition} \times 100}{\text{oven-dry soil weight}} \quad (2-1)$$

Carbonate composition

Eighty-one soil samples were collected from each of the three soil layers (0 to 15 cm, 15 to 30 cm, and 30 to 45 cm depths). Determination of total carbonate content was determined by using a Scheibler apparatus to measure the volume of CO₂ gas generated when the soil carbonates react with 6 M HCl (Dreimanis, 1962). The percent of inorganic carbon was calculated as 12% of the CaCO₃ as prescribed by the procedure used at TREC for determining inorganic carbon in soils.

Soil bulk density (Db)

When adding DI water to replace the water lost from evaporation in the lab, there was a concern that Perrine marl water table might equalize too slowly to maintain the desired water table level and affect redox. A bulk density test was conducted by the ring method to see if the compacted layer below the plowed surface of the Perrine marl might have some influence on soil water movement in the mesocosms. A standard 7.6 centimeter ring could not be used to collect the samples due to the installation of 8 pieces of the redox equipment in each mesocosm. A

smaller ring with an inside diameter of 5.1 centimeters was fabricated from galvanized steel pipe and used successfully. Samples were pulled directly from the soil mesocosms in November 2011, after the 56 days of redox readings were collected and soil disturbance would no longer be an issue. Three mesocosms of each marl soil series, had samples collected from both the surface (0 to 2.5 cm) and subsurface layers (15 to 17.5 cm). A total of 18 samples were weighed for moist weight, oven dried for 24 hours at 95 °C, weighed again for oven-dry weight, and bulk density calculated in g/cc.

Soil particle size

Particle size was determined using a Bouyoucos hydrometer (Gavlak et al., 2003). The hydrometer method removes CaCO₃ with acid before drying the soil samples for particle size analysis. Since marl soils are predominantly composed of CaCO₃, this step was omitted from the process to avoid significant alteration of the marl soils. Three mesocosms from each of the three marl soil series had 500 grams of soil collected from all three layers (0 to 15 cm, 15 to 30 cm and 30 to 45 cm). The 27 soil samples were oven dried for 24 hours at 95°C and passed through a 2 mm sieve to exclude particles larger than very coarse sand. Fine shell fragments ≤ 2 mm were observed in the sieved samples, but without acid dissolution, could not be separated from the similar sized sand particles.

Iron, manganese and calcium content of soils

Total iron, manganese, and calcium of the marl soils were measured by inductively coupled plasma atomic emission spectrometry (ICP) at the Analytical Research Laboratory on the University of Florida main campus in Gainesville, Florida using Environmental Protection Agency standard method 200.7. Metals were acid digested and extracted from 81 soil samples in the Soil and Water Lab at TREC. Twenty seven of the extractions were selected for shipment to

Gainesville. The samples provided three replicates for each of the three layers in each of the three soil types (3x3x3=27).

Cation exchange capacity (CEC)

A method was first described by Polemio and Rhoades in 1977, where Na and Cl were determined by ICP without prior removal of CaCO₃ was used for CEC. The method has two steps using NaOAc – NaCl + 60% ethanol as the saturating solution, then extracted by application of Mg(NO₃)₂ (Wang et al., 2005). The results from ICP were used in Equation 2-2 to calculate CEC in cmol/kg.

$$CEC = (Na_t - Na_{sol}) = Na_t - [Cl_t (Na/Cl)_{sat.sol}] \quad (2-2)$$

Na_t = total sodium
Na_{sol} = soluble sodium
Cl_t = total chloride
Na/Cl_{sat.sol} = ratio of sodium to chloride in the saturating solution

Temperature, pH, and electrical conductivity

Digital and mercury thermometers were used to check and record ambient temperatures when each redox reading was collected. Temperatures in the climate controlled laboratory remained stable at 22.8 to 23.9⁰ C, except on two occasions when the air conditioning unit was not working properly and temperatures rose to 26.7⁰ C and 28.9⁰ C for less than 24 hours. Those temperature increases represent a maximum variance in the redox reading of less than 0.8 mv, having inconsequential effects.

United States Department of Agriculture (USDA) published soil survey data for Miami-Dade County shows pH values form marl soils at the 25 cm depth ranges from 7.4 to 8.4 (USDA-NRCS, 1996). The 25 cm depth corresponds to the depth platinum electrodes were installed to collect redox readings. To document soil pH, 20 ml soil-water samples were

collected from the valve in the bottom of each soil mesocosm before each reading was taken with the data logger.

Water levels in the mesocosms were checked the same time each day to maintain the water table treatment levels at 0 cm, 15 cm or 30 cm depths. If water had been lost to evaporation, then DI water was added after the soil water samples and the redox readings had been taken. The pH of the DI water being added to maintain the water table levels was monitored over the 56 days to identify any possible influence the DI water chemistry may have on redox processes.

Electrical conductivity of the water samples was also checked as an indicator of salinity. The Pennsuco marl, undrained soil collection site was about 2 kilometers west of Biscayne Bay and subject to salt water intrusion as well as windblown salts associated with tropical storms or hurricanes approaching from the eastern Atlantic. A total of 513 soil water samples were collected, filtered and analyzed at the Soil and Water Lab at TREC in October and November 2011. Electrical conductivity and pH were measured using an Accumet Excel SL50 Dual Channel conductivity meter and an Accumet AR60 Dual Channel pH meter.

Methods of Analyzing Oxide Removal from IRIS Tubes

Following removal of IRIS tubes, metal oxide removal can be estimated visually or it can be digitally scanned and analyzed using image analysis software. This latter method of digital analysis can be accomplished with two different techniques. The first technique is to scan the actual IRIS tube, which may require multiple images be cut and pasted together to attain a single seamless image of a round tube. A second technique is to wrap the tube in clear acetate and hand trace the reduced areas, then the acetate sheet can laid flat and scanned as a single image for import into the software. Each of these three techniques was utilized on select IRIS tubes extracted for this study and will be referred to as either the visual method, scan method or trace method when discussed.

After each extraction the IRIS tubes were rinsed under a gentle flow of tap water to remove loose soil particles, and then placed in a test tube rack to dry. Once in a completely aerobic environment, metal oxide reduction ceases preserving the removal pattern on the PVC tubes. After completely dry, each labeled tube was stored into a 6 mil plastic sleeve to prevent further alteration/removal of any remaining oxide paint until analysis could be performed. The initial scope of the research was to only use the visual estimate following the guidelines provided by in the Hydric Soils Technical Standard (NTCHS, 2007). The successful construction of a rotation device that allowed the adaptation of a hand/bar scanner for recording the surface of the IRIS tubes as a single image prompted the desire to compare the results attained from each of three techniques when applied to the same set of IRIS tubes.

Visual method

The first technique used was the visual estimate which required determining if there was any oxide removal within the upper 15 cm of the tube, at what depth removal began, and then what percentage of oxides were removed from a 15 cm long section. Tubes that did not have oxide removal beginning within the upper 15 cm of the soil, were recorded as having 0% removal since deeper depths are not considered in anaerobic determinations (NTCHS, 2007). Over one day, all 162 tubes were visually estimated for oxide removal and 96 were estimated to have 0% removal and 10 showed 30% or more removal of oxides in the upper 30 cm of the tubes. The sets of 3 that each of the 10 IRIS tubes were grouped with in a single mesocosm was selected for further digital analysis unless they were observed to have no oxide removal.

Trace method

The trace method was executed by wrapping a sheet of clear acetate around each IRIS tube, securing with scotch tape, and marking the points of overlap. Each area of oxide removal was outlined with a permanent black magic marker and filled in. For tubes with significant oxide

removal of 30% or more, this can be time consuming. A benefit of this technique is it allows exclusion of any areas of oxide removal that occurred during installation and extraction of the IRIS tubes, rather than by electro-chemical reduction processes. Linear scrapes did occur on a few of the IRIS tubes used in this project and showed up on more MIRIS than FIRIS tubes and could be a consequence of the variability in the two oxide paints regarding adhesion to the PVC tube during manufacture. Scrapes may have occurred at installation from the polycarbonate protective sleeve or by shell fragments in the soil at time of extraction.

Scan method

Direct scanning of the PVC tubes was done at the University of Maryland (Rabenhorst et al., 2009) using a modified flatbed scanner, which required cutting and pasting of multiple images from different sides of the tube. To cut down on the time constraints associated with direct scanning, a rotation device was designed and built to allow the use of a hand/bar scanner to be employed in scanning all 360° of the PVC tube as one continuous image. Belt adjustments between the turning rods allowed the device to scan both the 1.27 cm diameter FIRIS tubes as well as the 1.9 cm diameter MIRIS tubes. The hand scanner used in this study, a VuPoint Magic Wand, captured the images in color at 300 dpi resolution and downloaded as jpeg image files. Two images of each tube were taken to provide an additional option if one image was distorted or blurry.

Results

Properties of Selected Marl Soils

Table 2-1 provides a list of all the measured and observed soil properties for the three marl soils sampled to aid in identifying relationships between soil redox processes and inherent soil properties. The three soils are very similar in most properties, except for % silt, bulk density, OM, electrical conductivity (EC), structure and live macro fauna. Soil A has less silt and more

sand than the other soils, which may be due to the noticeable presence of mollusk shell fragments that did settle out as sand-sized particles in soil texture determinations by the hydrometer method. Dissolution of calcium carbonates before determining soil texture would have dissolved shell fragments, but was not done to prevent the dissolution of the calcitic marl soil itself.

The presence of a plow layer in Soil B prompted the decision to test bulk density (Db) in the top two layers of each soil, with three replicates. The compacted layer (15 to 30 cm) in Soil B had a Db of 1.1 g/cc, compared to 0.65 and 0.89 g/cc in Soils A and C, respectively. All three soils were below the 1.3 g/cc bulk density of a mineral silt loam soils, and Soil A aligned more closely with Db values of 0.5 g/cc measured in organic muck soils used for farming in the northern Everglades (Wright and Inglett, 2009).

Table 2-1 lists Soil A as having 8.3% organic matter, twice the amount measured in Soils B or C, which was unexpected since Soil A had color values of 7 and 6 in the upper 30 cm and sparse vegetation adjacent to the soil sampling site. Soils B and C were noticeably darker in appearance with color values of 5 in the upper 30 cm. One possible explanation of the light color in Soil A is that precipitating CaCO_3 from active marl formation results in organic particles being coated or masked. In the Bahama Banks, 240 kilometers southeast of the study area, researchers used a scanning electron microscope on actively forming calcitic soils to identify 0 to 5% organic materials oriented in thin concentric films with carbonate precipitates in shallow coastal waters (Davies et al., 1978).

EC in Soil A revealed this site to be in the upper end of the slightly saline range of 700 to 2000 uS/cm (Rhoades et al., 1992), which is 2 to 3 times higher than in Soils B and C, respectively. Increased salinity in Soil A is most likely due to its location in a coastal wetland

area subject to saltwater intrusion and windblown salts during tropical storms and hurricane events. The shores of Florida Bay are less than 2 kilometers east of where Soil A was collected, and well within the boundaries of the saltwater intrusion line, which extended 6 kilometers westward from the coast at the time it was delineated (Shonenshine, 1995). Deionized water used to maintain the water table treatments showed no changes in electrical conductivity or pH with time, and did not contribute to any changes within the mesocosms (data not shown).

Examination of the soil from each site revealed that Soil C possessed subangular soil structure, where Soils A and B had no discernible structure (massive). Soil structure provides aeration and allows water to infiltrate and permeate at a faster rate than massive soils lacking structure. Figure 2-3 shows significant burrowing by wireworms in Soil B that excavated tunnels to the soil surface shortly after water table treatments were established at the 15 and 30 cm depths in the mesocosms. Wireworms are controlled in agricultural fields by continuous flooding for 42 or more days (Hall and Cherry, 1993) and were not apparent in mesocosms with water tables maintained at the soil surface. A single mole cricket surfaced in mesocosm B6-4 after establishing the water table at 15 cm and was promptly removed, but had been burrowing below the soil surface since extraction more than 21 days earlier.

Water Table Treatment Effects on Electro-chemical Soil Properties

Electrical conductivity in soils A, B and C increased by 25.6%, 10.9% and 15.1%, respectively as water table depths decreased from 30 cm to 0 cm, as shown in Figure 2-4. Soil A had the largest increase of ~600 uS/cm between the 30 cm and 0 cm water table depths. Higher salinity in Soil A is likely attributed to its close proximity to the saline coastal waters of Biscayne Bay. In contrast, Soil B and C receive in-land freshwater sources derived from an annual rainfall amount of 145cm and irrigation water pumped from the Biscayne aquifer (USDA-NRCS, 1996).

Water table treatment depths had little impact on pH levels (Figure 2-5) with pH variations of +/- 0.1, and within the standard error ranges for all but Soil B. Previously drained, alkaline soils tend to decrease in pH with time due to the build-up of CO₂ gases that produce carbonic acid as a consequence of iron reduction (Mitsch and Gosselink, 2000). Marl soils possess such extreme buffering capacity (Zhang et al., 2002) that small amounts of carbonic acid would have little ability to alter pH in these soils. High pH resulted in requirements for lower reduction potentials to achieve the reduction level set in the Hydric Soils Technical Standard (NTCHS, 2007).

Over 56 days, 18 pH measurements were taken from each of the mesocosms to coincide with the collection of redox readings for comparison against the standard redox potential. A strong correlation (0.21, P<0.01) was identified between pH and soil with time (Table 2-2), but changes in pH were small (between 7.7 and 8.1) during the 56 day time span, regardless of soil type or water table depth (Figure 2-5). The primary effect of high pH was the requirement of standard redox values less than +175 mV (at pH of 7.0) to verify reduced conditions.

Anaerobic Conditions as Determined by Redox Potential

In this study, initial redox readings were taken from the Pt electrodes on the same day water table treatments were established in the soil mesocosms. Even though all soils had been drained of gravitational water 7 days before the experiment began, high variability of the initial redox potential was apparent in all soil mesocosms regardless of soil type. The highest redox potential (Eh) reading on day 0 had a high of +635 mV in Soil C with a 30 cm water table depth to a low of -54 mV in Soil A with water table at the soil surface, revealing a wide range of soil moisture contents before establishing water table treatment depths. Initial readings were taken 6 hours after water tables were established so that other soil properties such as saturated hydraulic

conductivity and capillary water movement (Migliaccio et al., 2008) could have contributed to the wide range of the initial Eh readings.

Eh values dropped ~400 mV in the first 7 days in all soils except Soil C with the 30 cm water table treatment (Figure 2-6). During the first 24 hours Eh in Soil C drops by just less than 200 mV, but by day 2 the Eh rebounds upward slightly until leveling off in a highly aerated zone of +400 mV by day 14. Redox potentials in Soils A and B also dropped quickly once water was applied to the mesocosms to establish a 30 cm water table depth, but unlike Soil C, Soils A and B did not rapidly rebound into the aerobic zone. Following initial establishment of water table depths, small daily additions of DI water were necessary to maintain constant 30cm water table levels. Soils A and B did not come back above the standard redox line to an aerobic state until after 51 and 58 days, respectively.

The presence of subangular soil structure in Soil C is a characteristics that separates Soil C from the other two soils and likely to impact hydraulic conductivity (Table 2-1). Soil C is not in continuous production of field grown ornamental shrubs and trees with a persistent ground cover of grass and herbaceous weeds; all conditions favoring the development and persistence of soil structure. Soils A and B both lacked structure and the ability to drain quickly, but from different conditions. Soil A is still actively forming with ongoing CaCO_3 precipitation and lacking the time necessary for a soil to develop structure. Soil B is annually tilled with heavy equipment resulting in a compacted layer that could explain the lower Eh readings in Figure 2-7 than for Soil A with the same 15 and 30 cm water table treatment depths. Compacted soils or plow pans are known to result in significant reductions in hydraulic conductivity, permeability and air diffusion (Horn et al., 1995).

Figure 2-6 shows all three soils had average redox potentials in the aerobic zone on the day that water tables were established at a 15 cm depth; and all more than 200 mV higher than anaerobic standard lines. Soils A and B both had rapid drops in average Eh and moved into the anaerobic zone with $+81$ mV readings by day 3 for Soil A, and by day 5 for Soil B. Soil C was relatively slow to reach a reduced state with an average redox reading of $+43$ mV after 11 days, then continuing on a slow, steady decline so that by day 44 all three soils coincide around a median Eh of -210 mV.

The platinum electrode collects redox potential readings from a fixed depth of 25 cm, 10 cm below the 15 cm water table treatment depth, where anaerobic conditions were expected to develop. Review of the three 15 cm water table repetitions for Soil C, rather than the average, showed delayed responses of 9, 11 and 22 days before reaching the anaerobic zone. As with the 30 cm water table treatment, soil structure for Soil C provides a likely explanation for the difference in response time to soil saturation. Spaces between soil aggregates in the subangular structure that contained O_2 may have been entrapped by the downward moving DI water, diffusing slowly into the soil water, then utilized as preferential oxidants by soil bacteria.

Figure 2-6 shows a similar response time to saturated conditions for each of the three soils observed in the 0 and 15 cm water table treatment. In flooded conditions, Soil A started out in a reduced state since that soil was kept moist right up until drained 7 days before the water tables treatments depths were applied. Marl soils in field conditions will develop surface cracks from shrinkage as they dry out. Soil B started out at a higher Eh value than Soil C then rapidly dropped 250 mV to reach a reduced state after only 2 days while Soil C took 11 days to drop 280 mV and arrive at a reduced state. A slow, steady reduction occurred in the three soils so they

merged on day 37 at an average Eh of $\bar{228}$ mV and remained there for the final 21 days of monitoring.

At the 0 and 15 cm depth water table treatment depths, all soils were expected to reach a reduced redox value shortly after water tables were established based solely on the corresponding 25 cm depth of platinum electrode tips. Whether the soils would have a reduced redox potential due to the 30 cm water table treatment was questionable since the water table would be maintained just 5 cm below the tip of the Pt electrode, providing an opportunity for O₂ to occupy soil voids adjacent the Pt electrode. Figure 2-8 shows that Soil C with all three water table treatments had the highest redox values of the three soils and maintained aerobic conditions with the 30 cm water table treatment throughout the entire 56 day sampling period. The two soils (A and B) lacking any discernible soil structure displayed their water holding capacities were sufficient to develop saturated soil conditions within 5 days. Once Soils A and B were reduced, these soils maintained that reduced state for more than the 14 consecutive days resulting in positive confirmation of anaerobic soil conditions according to the Hydric Soil Technical Standard (NTCHS, 2007).

Table 2-2 shows strong correlation between redox readings (Eh-Electrode) and soil, water table, and time (days). Figure 2-9 displays the relation between Eh values and water table depths with time for each soil. Soil C shows initial fluctuations in Eh, but then follows a constant, downward movement with time. The 30 cm water table Soil C maintained a high, steady aerobic state during the 56 days, compared to Soils A and B with fluctuations in the reduction pattern during the first 21 days. Reactions of Soils A and B were comparable to each other in terms of initial and final Eh values and the general pattern of Eh fluctuations throughout the 56 days.

Determination of Anaerobic Conditions with FIRIS

FIRIS tubes are currently accepted for use by the NTCHS as an alternative to Pt electrodes for determining anaerobic conditions, a prerequisite to classifying soils as hydric. At present FIRIS tubes are recommended to be installed for 28 days and require that at least 30% of the iron oxides be removed from a 15 cm long section that must start within 15 cm of the soil surface (NTCHS, 2007). In this study, FIRIS were compared to Pt electrode performance as well as MIRIS, which resulted in the selection of three extraction intervals of 14 days, 28 days and 56 days to provide a comparison of each tool at those specific intervals. Unlike Pt electrodes that can continue to collect data for long periods, IRIS tubes can only reflect the soil conditions that exist between initial installation and the day of extraction since they are not reinstalled upon exposure to an aerated environment.

The first extraction of FIRIS tubes after 14 days showed an average of less than 1% iron oxide removal in all soils for both the 15 cm and 30 cm water table treatments (Figure 2-10). FIRIS reaction in flooded conditions with the water table at 0 cm depth during that same time showed measureable oxide removal. The results varied by soil type with Soil A showing 0% removal while Soil C displayed 8% oxide removal on that initial extraction. This gradation of performance between Soils A, B and C continue with the next two extractions at 28 days and 56 days.

Electrical conductivity in Table 2-1 is the only measured soil property that follows the oxide removal pattern across the three soils. Soils A and B are within the slightly saline range of 700 to 2000 uS/cm, while Soil C is < 700 uS/cm and considered non-saline (Rhoades et al., 1992). Table 2-2 shows no significant correlation between FIRIS performance and EC readings. Studies into energy harvested from underwater reduction do show that bacterial species do vary across the salinity of classes of fresh, brackish or saline water bodies (Holmes et al., 2004).

Research into the direct effects of salinity on iron oxide reducing soil bacteria species or their performance was not part of this study nor could research this specific be located, indicating this could be an indirect factor in iron oxide reduction and removal.

The primary difference between FIRIS and Pt electrode performance was that the electrodes captured Eh readings showing favorable conditions for Fe^{3+} reduction allowing the documentation of anaerobic conditions in as little as 14 days in flooded conditions. In Table 2-3, FIRIS in flooded conditions did not meet the minimum 30% oxide removal until sometime between the extraction on day 28 with 24% removal and the final extraction on day 56 with 48.2% oxide removal. Figure 3-11 displays the longer of reaction time of both IRIS tubes as compared with the Pt electrodes that reflected anaerobic Eh values within 7 days. Redox measurements are able to capture reduction potentials immediately but oxide reduction and removal from the PVC tubes takes longer. FIRIS technology did reflect the same redox trend as Pt electrodes, but at a slower rate in the marl soils utilized for this study

Determination of Anaerobic Conditions with MIRIS

MIRIS were developed building upon FIRIS manufacture and research to-date. This study represents the first comprehensive redox investigation to include MIRIS since its development and field test in Alaska during the summer of 2010 (Stiles et al., 2010). At this time the same Hydric Soils Testing Standards listed for FIRIS performance (NTCHS, 2007) will be applied to MIRIS. In Table 1-3, Mn_4^+ reduction is measured to occur before Fe_3^+ reduction at corresponding higher Eh values, indicating a conservative approach in the application of the iron oxide removal standards. If MIRIS technology is expanded and studied further, a set of evaluation standards separate from FIRIS may be prescribed.

MIRIS installed in the 15 cm and 30 cm water table treatments showed the same lack of oxide removal (Figure 2-12) as displayed in the FIRIS installed with the same set of variables.

Based on visual estimates, averages of 0.7% and 0.9% of manganese oxides were removed from the 54 MIRIS installed at the 15 cm and 30 cm water table depths, respectively. Under the flooded soil conditions displayed in Figure 2-13, there is a steady increase in oxide removal with time for each soil type, but only MIRIS installed in Soil C achieved >30% manganese oxide removal by the final extraction on day 56.

Table 2-4 affirms the significant relationship MIRIS has to water table treatment, soil type and the length of reaction time. The response pattern of MIRIS and FIRIS to water table levels and time are almost identical, with a comparative removal ratio of 0.29 manganese oxides for every to 1.0 iron oxide removed, as averaged from the full 56 day period in the 0 cm water table treatment. From the comparative removal ratio, it could be projected that 71% more time is required for manganese oxide removal than iron oxide removal in south Florida marl soils in flooded conditions which would be close to 90 days.

Comparing MIRIS with the standard Pt electrode in Table 2-5 there is low or no significance between these two tools, depending on the analysis method used to calculate the percent oxide removal from the tubes. Figure 2-11 shows manganese oxide removal increases gradually and continually through final extraction on day 56. For that same period, we can see Eh readings drop by an average of 400 mV during the first 14 days, continue to drop slightly, and then level-off by day 29. This pattern show that Pt electrodes are quick to confirm saturated conditions, and when sustained can confirm anaerobic conditions within 14 days.

Looking at Table 2-3 we can see that within the data collection period of 56 days the Pt electrodes verified anaerobic soil conditions across all three water table treatments by maintaining reduced conditions ($< +175$ mV) at the 25 cm depth for least 14 consecutive days. The exception was Soil C with the 30 cm water table treatment, which accounts for the aerobic

Eh readings ($> +175$ mV) in Table 2-3. The IRIS were also able to confirm anaerobic soil conditions within the 56 days, but only for the 0 cm water table treatment with 33% of FIRIS and 4% of MIRIS having $> 30\%$ oxide removal. IRIS installed in soils with 15 and 30 cm water tables did not reflect the anaerobic conditions shown in the Eh readings during the same 56 days. The progressive pattern of reduction conveyed in Figure 2-11 demonstrates that both FIRIS and MIRIS react to reduced conditions in south Florida marl soils, but at very different rates. FIRIS with the same treatments variables of soil, water table and time are able to reduced iron oxides at an average of 3.4 times faster than occurs for manganese oxides reduction and removal from MIRIS tubes.

Comparison of IRIS Analysis Methods

Once tracing and scanning was accomplished, the image was imported into Digimizer 4.0 by MedCalc software for binary image analysis (Figure 2-14). The percentages of areas with data (dark areas) and without (white areas) were calculated to determine the percent oxides removed from 18 IRIS tubes. The areas without data represent areas where oxides were removed from the tube. The three tubes in Figure 2-15 were recorded as having 0% oxide removal, although iron oxide was removed in a zone of inundation below the 30 cm depth, which cannot be included in the anaerobic soil determination.

Table 2-6 shows the 3 MIRIS and 18 FIRIS that met the selection criteria for further analysis by trace and scan digital methods. All IRIS tubes in the Table 2-6 were treated with a 0 cm water table depth, which shows strong correlation in Table 2-2 for all methods, but not as significant for MIRIS tubes estimated by either of the digital analysis techniques. Figure 2-16 shows the lack of manganese oxide removal in all soils but Soil C. A small data set of only three MIRIS tubes were digitally analyzed, so standard error values are more pronounced for the trace

and scan methods. In Figure 2-17 we can see that iron oxide removal is also most abundant for FIRIS installed in Soil C, and to a lesser extent in Soils A and B.

The small data set available for MIRIS tube analysis by digital methods resulted in almost perfect correlation in Figure 2-18, where the three data points come from one Soil C mesocosm with pronounced removal of manganese oxides in flooded conditions. In Figure 2-19 there are 18 data points from seven soil mesocosms representing the three soil types treated with the 0 cm water table. The larger and more diverse sample set for the FIRIS, provides additional confidence in the correlation data shown in Table 2-5. Visual methods have the lowest correlations but the differences were comparatively small and shows that either visual, trace or scan methods can be successfully utilized to provide reliable estimates of oxide removal from IRIS tubes.

Discussion

General characteristics of the marl soils selected for this study were similar in texture, pH, and nutrient content. Land use and ecological setting of each marl soil resulted in moderate variations in physical and chemical properties. Soil salinity of Soil A, adjacent to a coastal wetland system, had an average EC of value of 1777 uS/cm, that places it in the upper end of the slightly saline category with a range of 700 to 2000 uS/cm (Rhoades et al., 1992). Soil B had 53% lower EC readings than in Soil A, but still in the lower end of the slightly saline category. Soil C was classified as freshwater with 71% lower EC value as found in Soil A. There was significant correlation between EC and redox potentials identified from data analyzed by SAS.

Another characteristic of Soil C that set it apart was a subangular soil structure that developed under the production of ornamental trees and shrubs without tillage of the soil. Structure impacts aeration, hydraulic conductivity, and drainage that influence saturation, and redox potentials. The correlation of soil structure and Eh were found to be just as significant as

identified between EC and Eh. In general, Eh increases with salinity and aeration meaning that higher Eh readings in Soils A and C are expected as displayed in Figure 2-7. Vertical capillary water movement and dissolved oxygen content of marl soils are two properties that could explain the redox patterns observed in this study.

Pt electrodes, FIRIS, and MIRIS performance were compared in their ability to reflect redox state of the soil through Eh readings, iron oxide removal or manganese oxide removal. The Pt electrodes performed consistently during the sampled 56 days and displayed the distinct advantage of providing measured redox potentials in real-time, allowing for rapid assessment of reducing and anaerobic conditions. In flooded conditions, Eh readings were able to provide confirmation of anaerobic conditions after just 14 days, which met the Hydric Soils Testing Standards (NTCHS, 2007). A major disadvantage of Pt electrodes is the high cost to purchase or manufacture with platinum. Field installation of electrodes requires significant equipment set up and protection measures, both limit the number of data collection points that can be analyzed at any one time.

FIRIS performed as expected with a delay in iron oxide reduction associated with high pH, calcareous soils. With flooded soil conditions, iron oxides are readily reduced and could be confirmed with the last of three extractions (Figure 2-20), 56 days after installation. When water tables were at the 15 and 30 cm depths, the required 30% removal of oxides from the upper part of the FIRIS did not occur by the end of the 56 days. For use in alkaline soils with pH values of 7.5 to 8.5 the FIRIS require additional time to reduce iron oxides, and 56 days instead of the current 28 day installation time is recommended (NTCHS, 2007).

In 2009, MIRIS tubes were developed for use in high pH alkaline soils where FIRIS tubes are known to perform slowly. A rapid field test in the summer of 2009 in alkaline soils of Alaska

had >30% manganese oxide reduction and removal from MIRIS within one week and comparable results were expected in this study. Of the 81 MIRIS tubes installed in this study, only one had > 30% manganese oxide removal > 30% (54%), with 27 of the 81 tubes installed in soils that were flooded (0 cm water table) throughout the 56 days sampling period. The poor performance of MIRIS in this study is not fully understood from the data collected. During the manufacture of the MIRIS it was obvious that the manganese oxide paint is difficult to apply uniformly and does not adhere to the PVC tube as well as in the FIRIS tubes, but those issues alone do not explain the poor reduction results. Additional microbial studies into the manganese reducing *Geobacter* species could help to determine if manganese reducing bacteria are present in sufficient populations to reduce manganese oxides, as manganese is not present in the natural systems of south Florida.

Once testing of IRIS concluded, the amount of oxide removal was determined using three different techniques. The visual, trace and scan methods were applied to select FIRIS and MIRIS tubes and found to correlate well with similar estimates in oxide removal across all three soils indicating that any of the techniques could be applied to provide reliable estimates of oxide removal. Deciding which IRIS analysis method(s) to use will likely depend on the end use of the data, the number of tubes to be processed and an assessment of oxide removal extent upon extraction.

If processing time or ease of use is a primary concern, then visual estimates should be used. When results are likely to be challenged or to fall close to the 30% removal standard (NTCHS, 2007), then verifying results by more than one method may be desired. Digital analysis can provide quantitative documentation directly from a scan of the IRIS tube surface. Direct scanning can be fast when image editing is not required before analysis. Tubes with linear

scratches or other features that should be edited would benefit from the trace method by selectively excluding unrepresentative features to improve accuracy before binary image analysis proceeds.

Table 2-1. Characteristics of three marl soils selected for this study

Characteristic	Soil A	Soil B	Soil C
Taxonomic class	Typic fluvaquents	Typic fluvaquents	Typic fluvaquents
Map unit name	Pennsuco marl	Perrine marl, drained	Pennsuco marl, drained
% Sand	40.30	34.16	34.45
% Silt	28.11	42.51	41.41
% Clay	31.59	23.34	24.14
Bulk density (g/cm ³)	0.54	0.98	0.82
Structure	Massive	Massive	Subangular blocky
% Organic matter	8.30	3.86	4.60
CEC (meq/100 g)	21.28	14.58	15.47
Total Na (mg/L)	1237.16	850.96	901.13
Total Cl (mg/L)	209.28	146.70	154.12
pH	7.91	7.83	8.12
EC (uS/cm)	1777.00	843.00	517.00
% CaCO ₃	71.51	81.64	82.88
Total Ca (mg/L)	1452.99	1586.79	1555.00
Total N %	0.30	0.13	0.20
Total C%	14.30	13.14	13.46
Total Mn (mg/L)	0.03	0.86	0.17
Total Fe (mg/L)	5.61	7.06	3.53
Soil insects observed	None	Wireworms	None

Table 2-2. Correlation coefficients among water table, time, insects and soil properties

	Soil type	Water table	Days	Soil insects	pH	Electrical conductivity	Structure
Eh-electrode	0.35**	0.44**	-0.31**	0.24**	0.21**	-0.33**	0.41**
FIRIS-visual	0.22*	-0.52**	0.29**	NS	NS	NS	0.23*
FIRIS-trace	NS	-0.57**	0.30**	NS	NS	NS	NS
FIRIS-scan	NS	-0.59**	0.28*	NS	NS	NS	NS
MIRIS-visual	0.25*	-0.39**	0.36**	NS	NS	NS	NS
MIRIS-trace	NS	-0.31*	NS	NS	NS	NS	0.30*
MIRIS-scan	NS	-0.31*	NS	NS	NS	NS	0.30*

* P < 0.05, ** P < 0.01, NS = no significant correlation; Statistical Analysis Software

Table 2-3. Anaerobic conditions determined by platinum electrodes, iron Indicators of Reduction in Soil (FIRIS) and manganese Indicators of Reduction in Soil (MIRIS) in 3 water table treatments

Redox tool§	Water table depth (cm)	Measured property	Time of measurements*			Hydric standard met		
			day 14	day 28	day 56	yes or no	% Tubes◇	% Soils†
Pt electrode	0	Eh (mV)	-121.6	-208.3	-239.6	Yes	-	100
FIRIS	0	Fe removal (%)	5.2	23.8	48.2	Yes	33	-
MIRIS	0	Mn removal (%)	1.2	6.4	17.4	Yes	4	-
Pt electrode	15	Eh (mV)	-156.0	-121.3	-195.7	Yes	-	100
FIRIS	15	Fe removal (%)	0.0	0.0	0.0	No	0	-
MIRIS	15	Mn removal (%)	0.0	0.0	1.4	No	0	-
Pt electrode	30	Eh (mV)	215.3	225.9	355.1	No	-	44
FIRIS	30	Fe removal (%)	0.0	0.0	0.0	No	0	-
MIRIS	30	Mn removal (%)	0.0	0.6	2.1	No	0	-

* Measurement values generated using the average for all three soil repetitions, † percent of soils that remained anaerobic for 2 or more consecutive weeks, ◇ percent of tubes having at least 30% oxide removed, § oxide removal from 81 FIRIS and 81 MIRIS calculated by visual method.

Table 2-4. Analysis of variance

Parameter	Soil type	Soil depth	WT†	Time	Reps	Soil+soil depth	Soil+ WT	Soil+ time	WT+ time	Soil+soil depth+WT+time
Eh	**	-	**	**	**	-	**	NS	**	NS
PeakEh rate	**	-	NS	**	NS	-	NS	NS	-	-
pH	**	-	*	**	**	-	**	**	**	NS
EC	**	-	**	NS	**	-	**	NS	**	NS
CEC	-	-	-	-	-	-	-	-	-	-
OM	**	**	NS	-	*	*	*	-	-	NS
OC	**	**	NS	-	*	*	*	-	-	NS
IC	**	**	NS	-	NS	NS	NS	-	-	NS
Total C	**	*	NS	-	NS	NS	NS	-	-	NS
Total N	**	*	NS	-	NS	NS	NS	-	-	NS
CaCO ₃	**	**	NS	-	NS	NS	NS	-	-	NS
Ca	NS	-	NS	-	NS	-	NS	-	-	-
Mn	**	-	NS	-	NS	-	NS	-	-	-
Fe	**	-	NS	-	NS	-	NS	-	-	-
Sand	NS	NS	NS	-	NS	NS	NS	-	-	NS
Silt	*	NS	NS	-	NS	NS	NS	-	-	NS
Clay	NS	NS	NS	-	NS	NS	NS	-	-	NS
Bulk density	-	-	-	-	-	-	-	-	-	-
Structure	**	NS	**	**	**	NS	**	**	**	**
V-MIRIS	**	-	**	**	NS	-	**	*	**	NS
T-MIRIS	**	-	**	**	**	-	**	**	**	**
S-MIRIS	**	-	**	**	**	-	**	**	**	**
V-FIRIS	**	-	**	**	NS	-	**	NS	**	*
T-FIRIS	**	-	**	**	NS	-	**	NS	**	NS
S-FIRIS	**	-	**	**	NS	-	**	NS	**	NS
Soil insects	**	-	-	-	-	-	-	-	-	-

* P < 0.05, ** P < 0.01, NS = no significant correlation ; - no data, † water table depth; GLM report generated using Statistical Analysis Software

Table 2-5. Correlation coefficients among various methods of determining redox potential

Method	Eh-electrode	FIRIS-visual	FIRIS-trace	FIRIS-scan	MIRIS-visual	MIRIS-trace
Peak Eh rate	NS					
FIRIS-visual	-0.29**					
FIRIS-trace	-0.30**	0.97**				
FIRIS-scan	-0.30**	0.96**	0.99**			
MIRIS-visual	-0.23*	0.82**	0.82**	0.81**		
MIRIS-trace	NS	0.90*	0.90*	0.87**	1.0**	
MIRIS-scan	NS	0.90*	0.90*	0.86**	1.0**	1.0**

* P < 0.05, ** P < 0.01, NS = no significant correlation; Statistical Analysis Software

Table 2-6. Comparison of results using different techniques to estimate oxide removal from FIRIS and MIRIS tubes

IRIS tube label	% Removal - visual method	% Removal - trace method	% Removal - scan method	Median (%)	Average (%)
C0-1_Mn1	1.0	1.0	0.3	1.0	0.8
C0-1_Mn2	16.0	21.0	21.0	21.0	19.3
C0-1_Mn3	54.0	60.0	60.0	60.0	58.0
A0-1_Fe2	16.0	21.0	20.0	20.0	19.0
A0-1_Fe3	30.0	41.0	40.0	40.0	37.0
A0-2_Fe2	10.0	15.0	34.0	15.0	19.7
A0-2_Fe3	40.0	78.0	77.0	77.0	65.0
B0-1_Fe1	5.0	3.0	9.0	5.0	5.7
B0-1_Fe2	10.0	13.0	12.0	12.0	11.7
B0-1_Fe3	60.0	60.0	59.0	60.0	59.7
B0-3_Fe2	5.0	7.0	5.0	5.0	5.7
B0-3_Fe3	33.0	47.0	39.0	39.0	39.7
C0-1_Fe1	15.0	27.0	34.0	27.0	25.3
C0-1_Fe2	80.0	87.0	84.0	84.0	83.7
C0-1_Fe3	85.0	99.0	100.0	99.0	66.7
C0-2_Fe1	4.0	4.0	5.0	4.0	4.3
C0-2_Fe2	15.0	23.0	24.0	23.0	20.7
C0-2_Fe3	50.0	52.0	49.0	50.0	50.3
C0-3_Fe1	5.0	15.0	21.0	15.0	13.7
C0-3_Fe2	60.0	66.0	63.0	63.0	63.0
C0-3_Fe3	99.0	81.0	78.0	81.0	86.0

Alphanumeric labels for IRIS tubes explained: 1st character of the label reveals the soil (A, B, or C); 2nd character is the water table treatment depth (0, 15 or 30 cm); 3rd character is the mesocosm number for the order they were collected in the field (1-9); 4th character indicates the type of IRIS (Fe = iron, or Mn = manganese); the last character indicates the time the tubes were installed in the soil before extracted for analysis (1 = 14 days, 2 = 28 days, and 3 = 56 days).

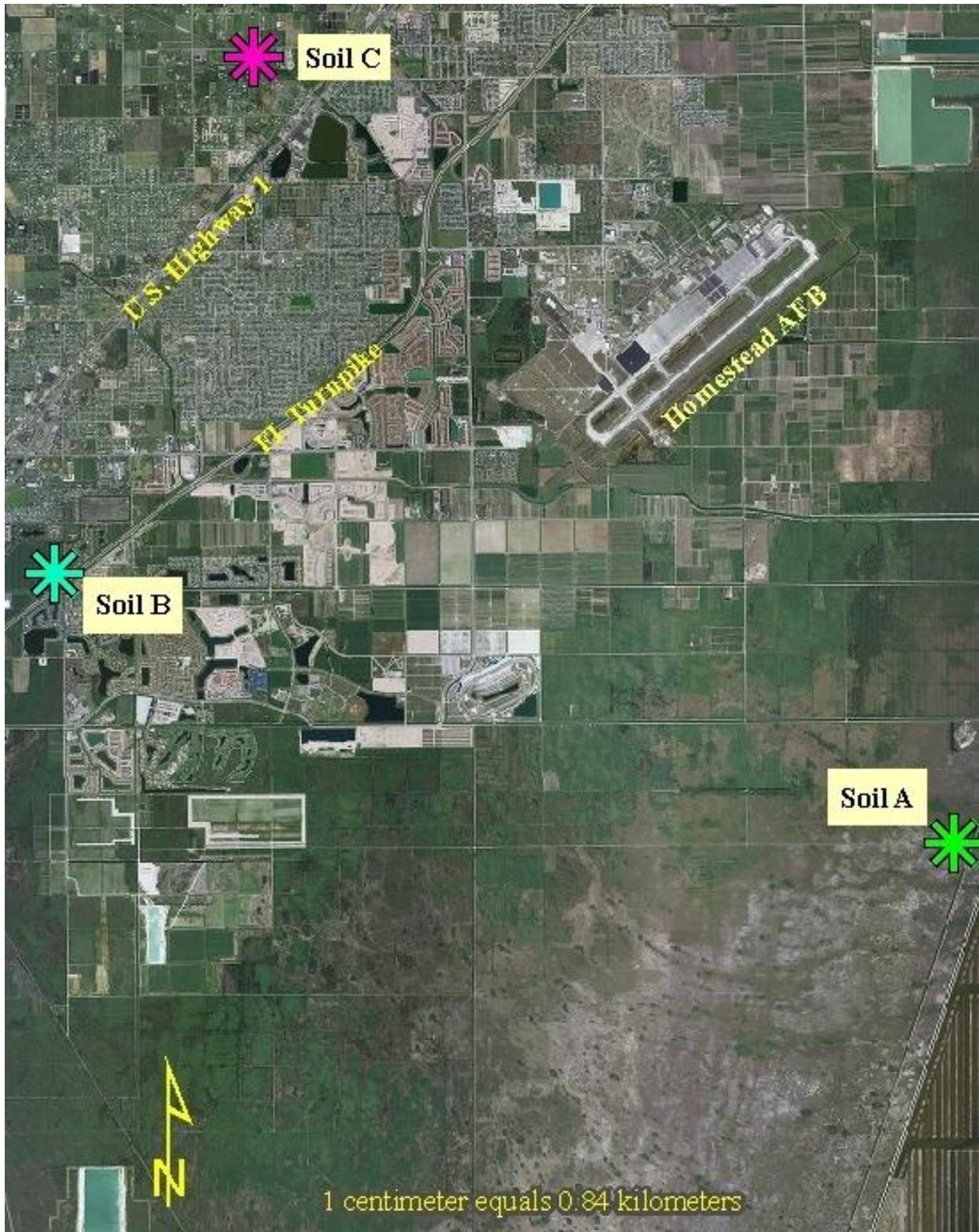


Figure 2-1. Map of soil collection sites in southeastern Miami-Dade County, Florida.

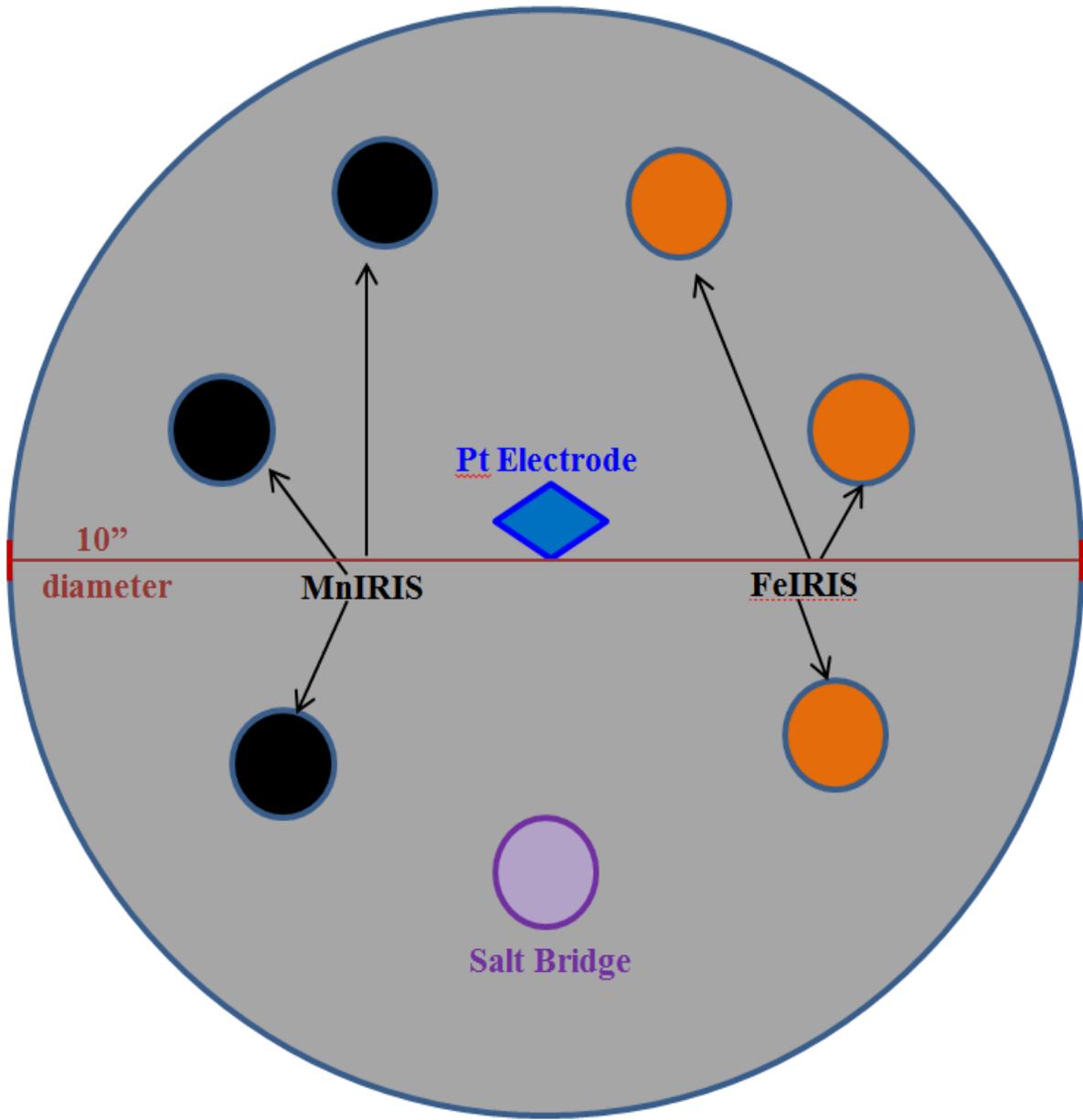


Figure 2-2. Schematic of redox equipment as installed in soil mesocosms.

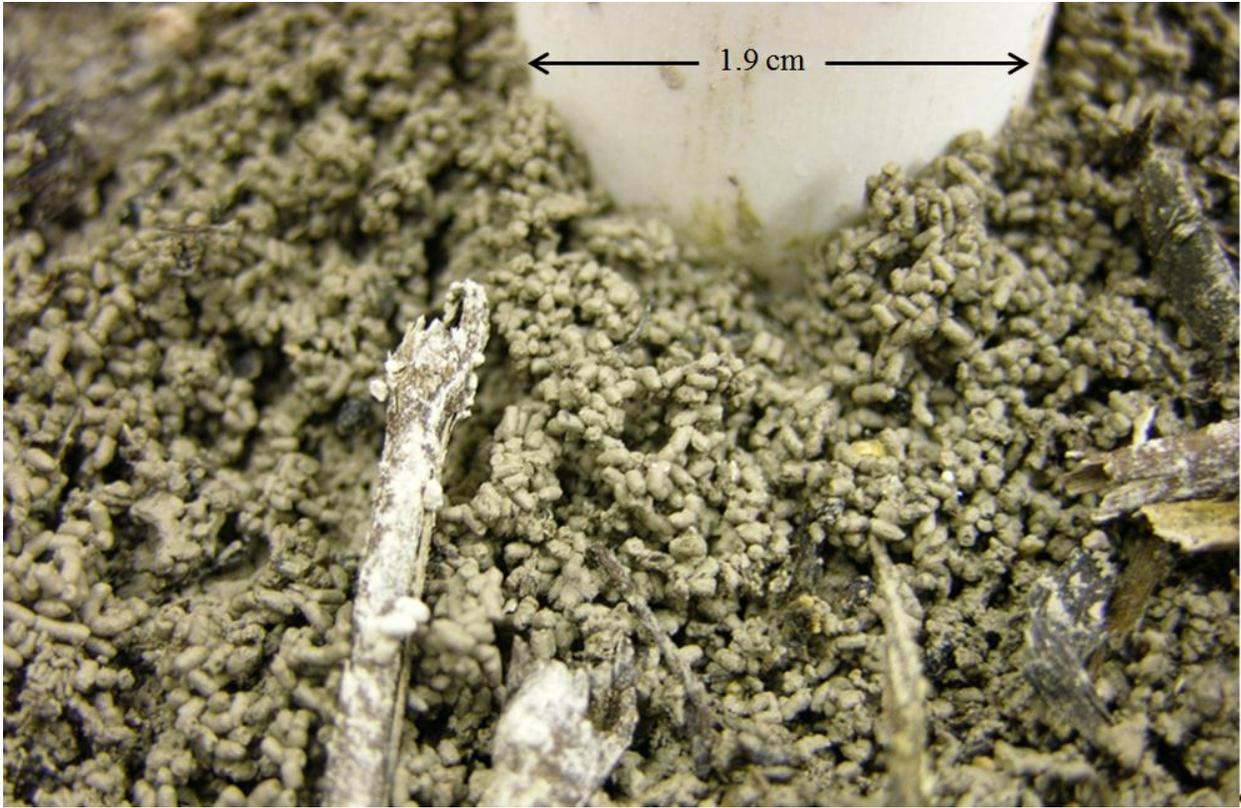


Figure 2-3. Wireworm excavation in Soil B mesocosm

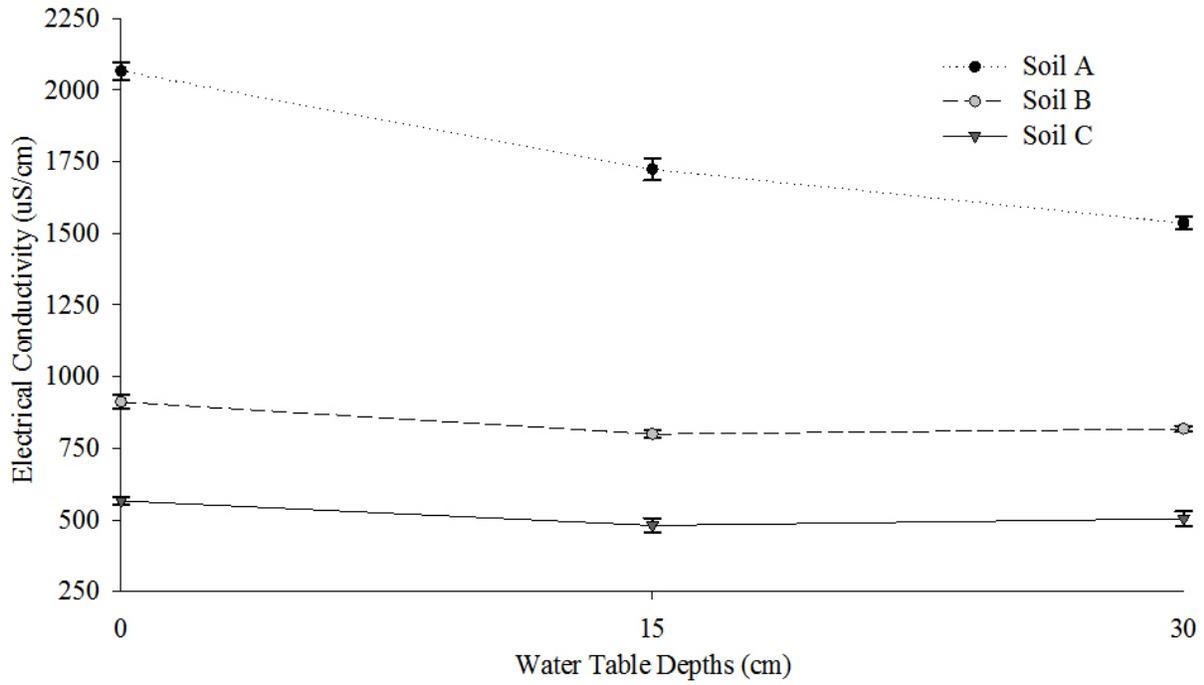


Figure 2-4. Changes in electrical conductivity associated with water table treatments in each marl soil.

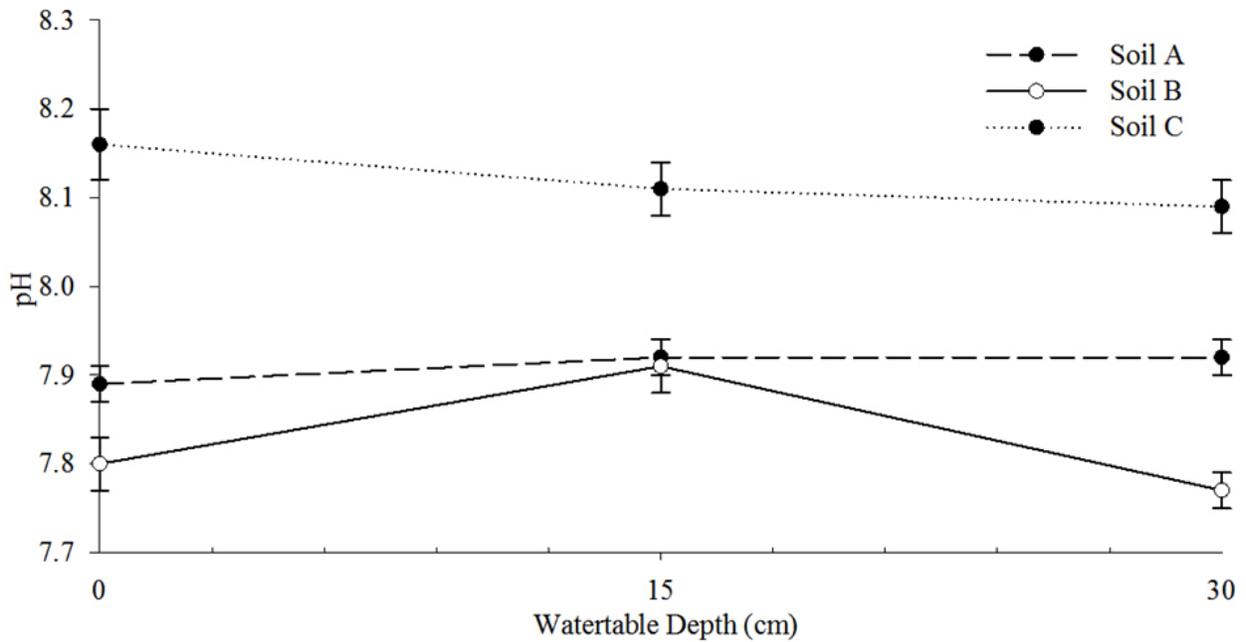


Figure 2-5. Average pH response to water table treatments in three marl soils.

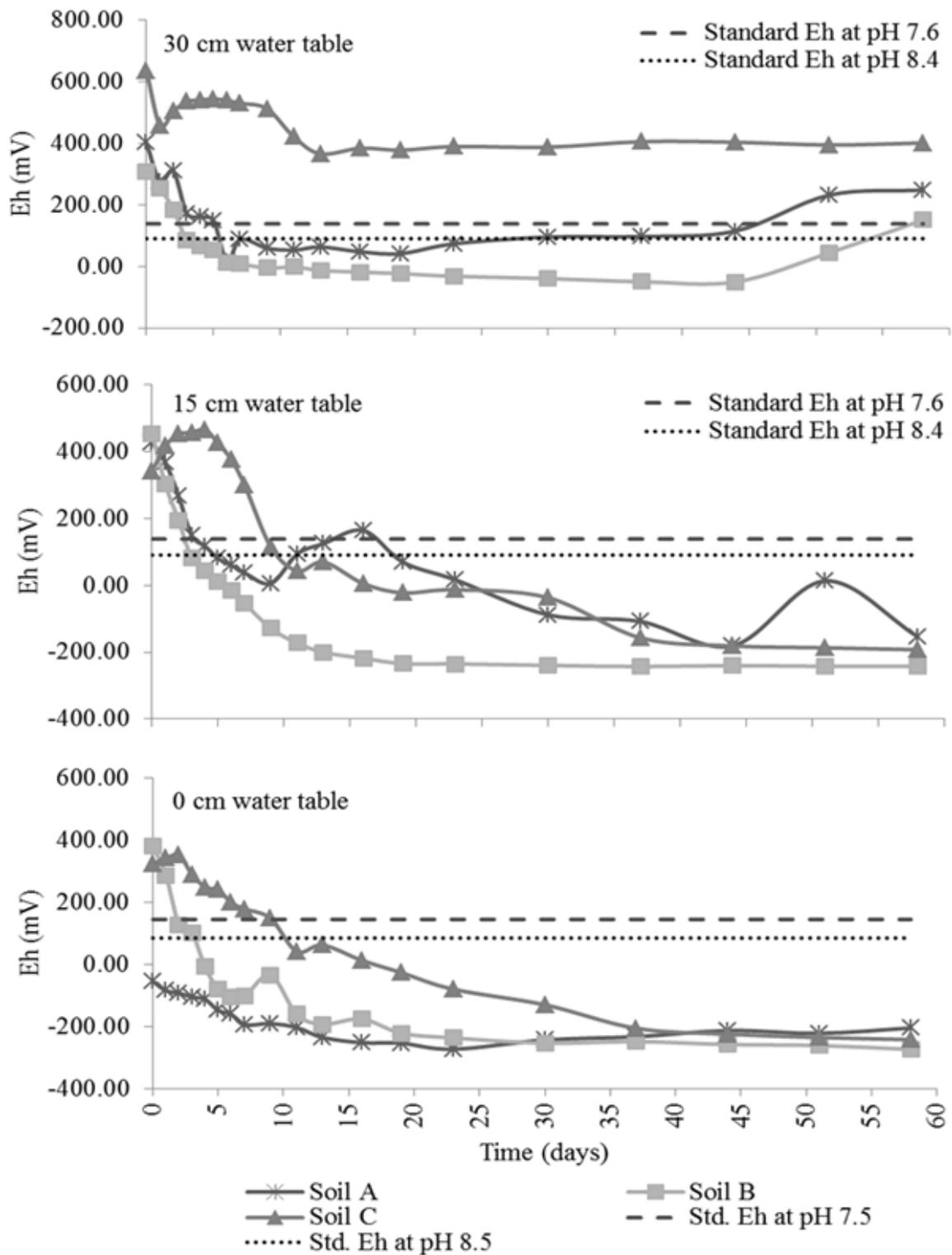


Figure 2-6. Corrected Eh measured by platinum and reference electrodes. Comparison is by water table treatment depths of 0 cm, 15 cm, and 30 cm over 56 consecutive days. Standard redox lines covering the pH range show aerobic conditions above the line or anaerobic when below.

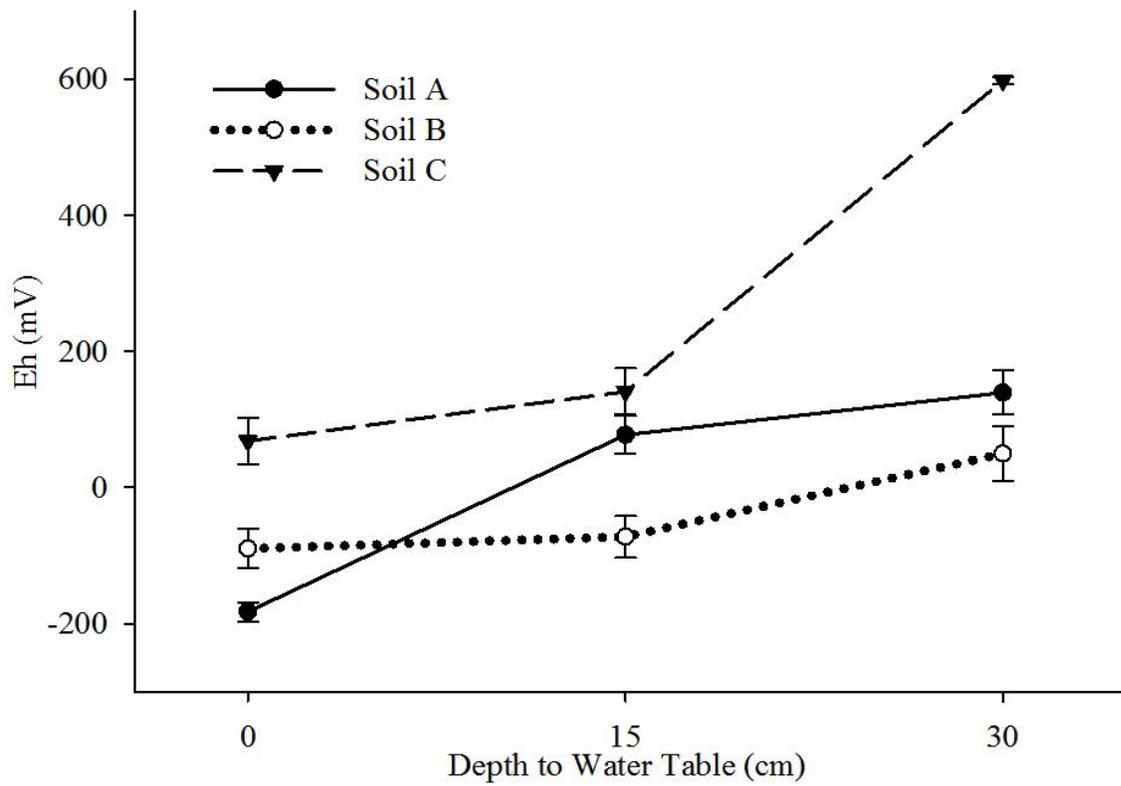


Figure 2-7. Average Eh for each marl soil in varying water table treatment depths

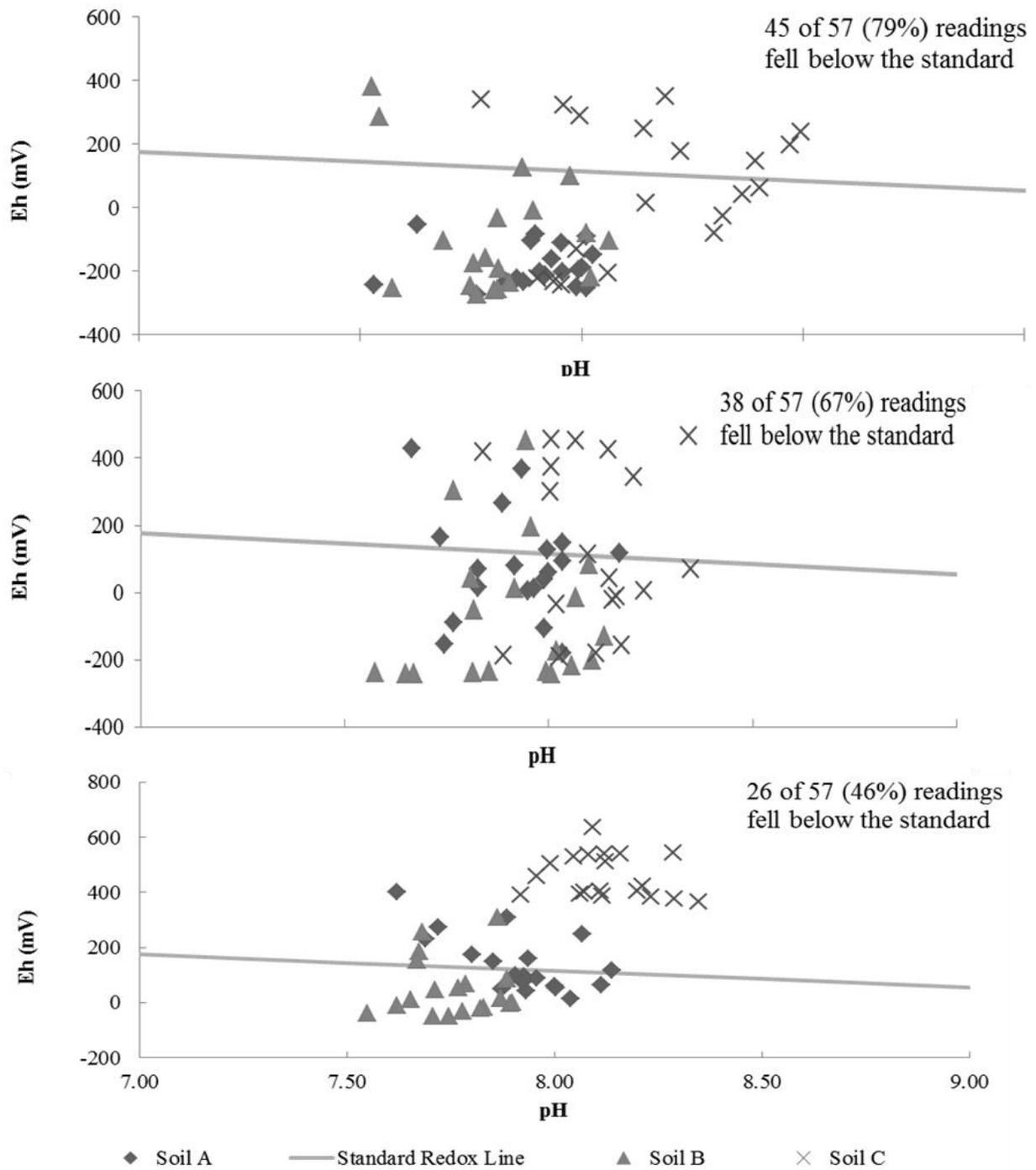


Figure 2-8. Distribution of Eh values above and below the standard redox line (NTCHS, 2007). Three soils were treated with water tables maintained at 0 cm, 15 cm or 30 cm depths for 56 consecutive days.

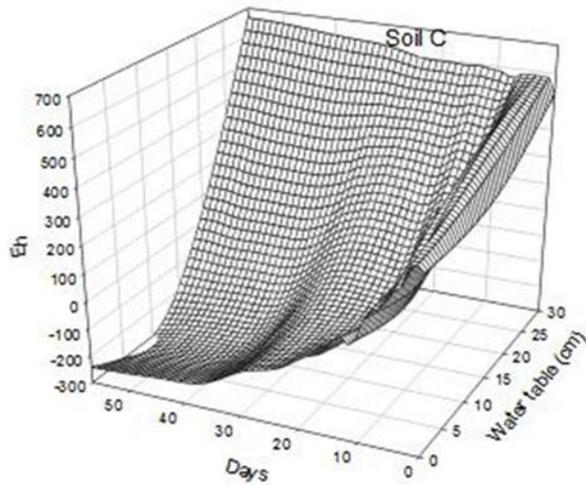
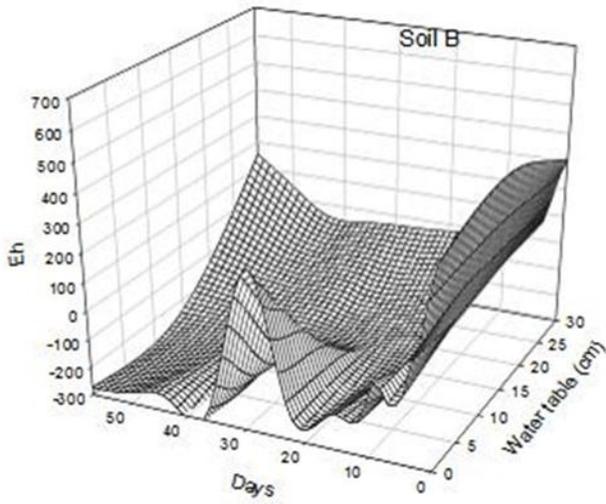
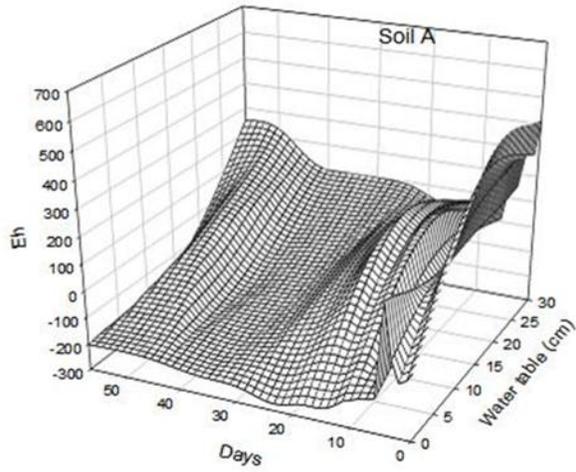


Figure 2-9. Temporal relationship between Eh and degree of saturation in each soil type. Soil A is Pennsuco marl; Soil B is Perrine marl, drained; and Soil C is Pennsuco marl, drained.

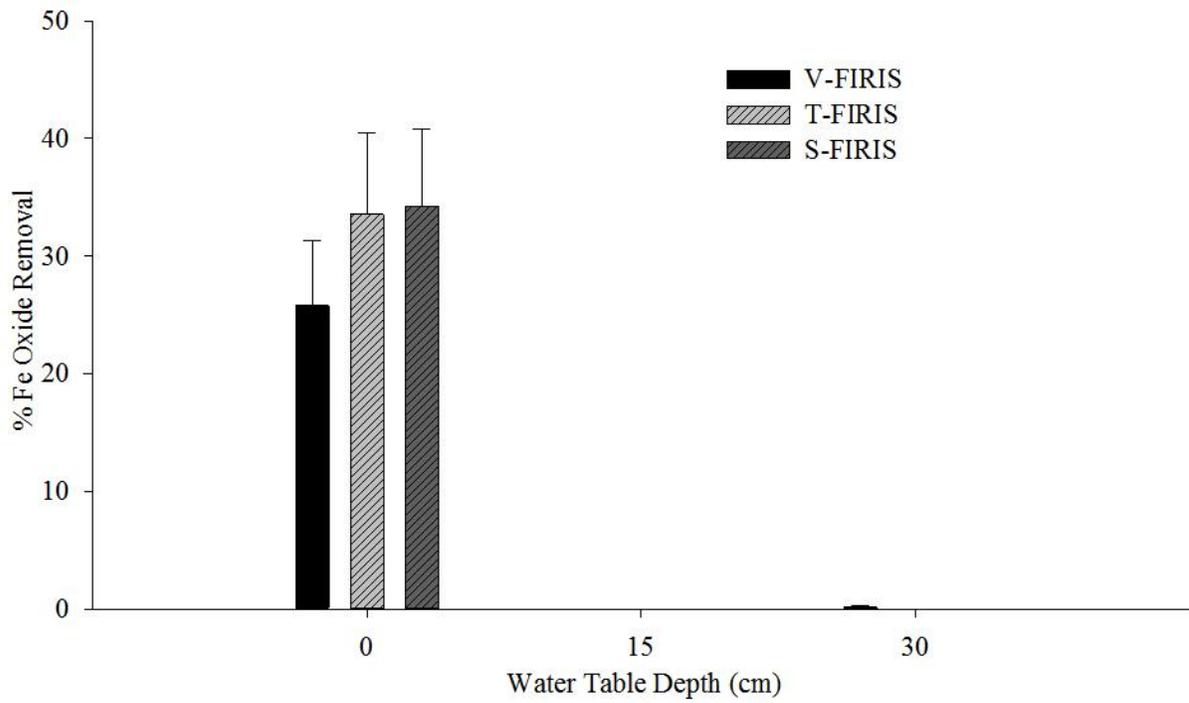


Figure 2-10. Iron oxide removal from Indicators of Reduction in Soil (IRIS) installed in three water table regimes. Estimates by three different methods are noted by the prefix letter on FIRIS labels in the legend: visual estimate (V-), trace method (T-) and scan method (S-) visual estimate.

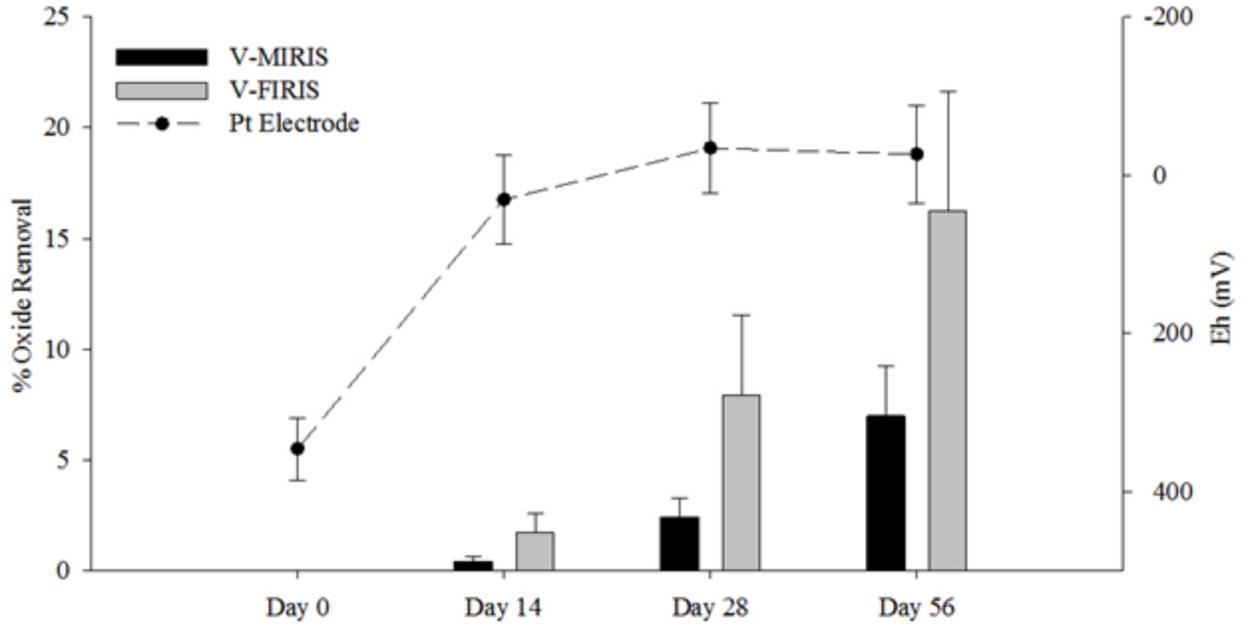


Figure 2-11. The measured response of redox tools to water table treatments with time. Averages were generated from the three soils and the three water table treatment depths. Oxide removal estimate calculated using the visual estimate and notated by the pre-fix letter on IRIS labels in the legend: visual estimate (V-).

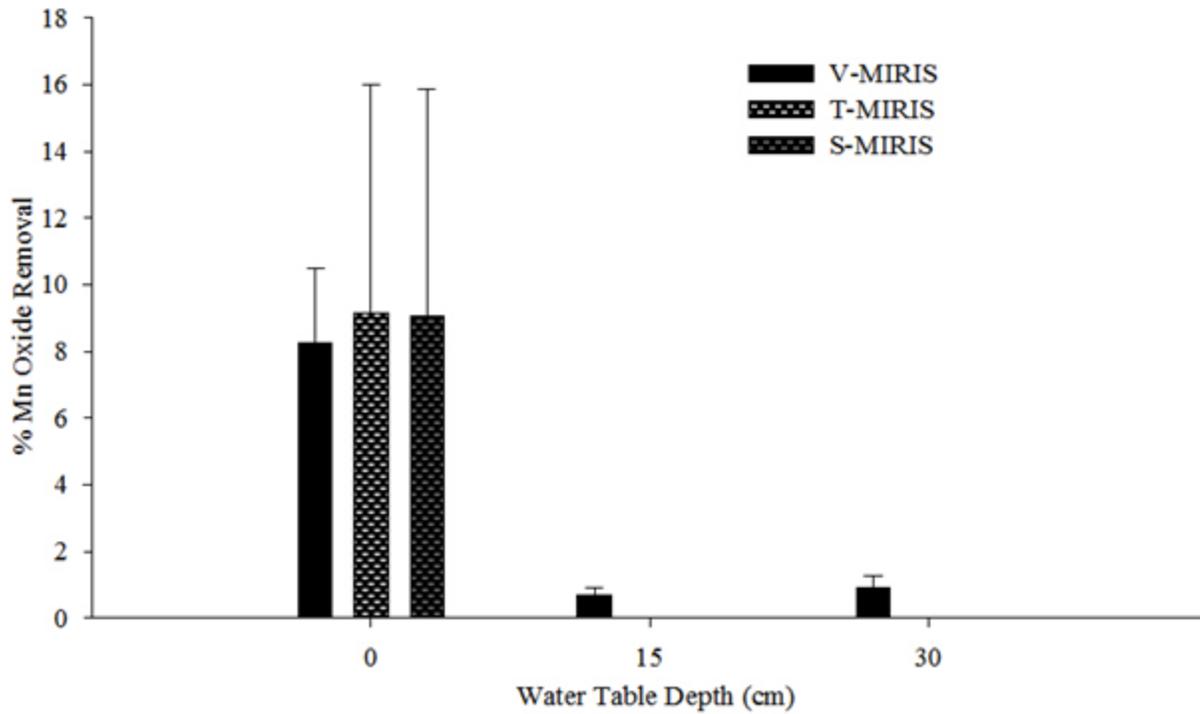


Figure 2-12. Manganese oxide removal from IRIS installed in three water table regimes. Estimates by three different methods are notated by the pre-fix letter on MIRIS labels in the legend: visual estimate (V-), trace method (T-) and scan method (S-) visual estimate.

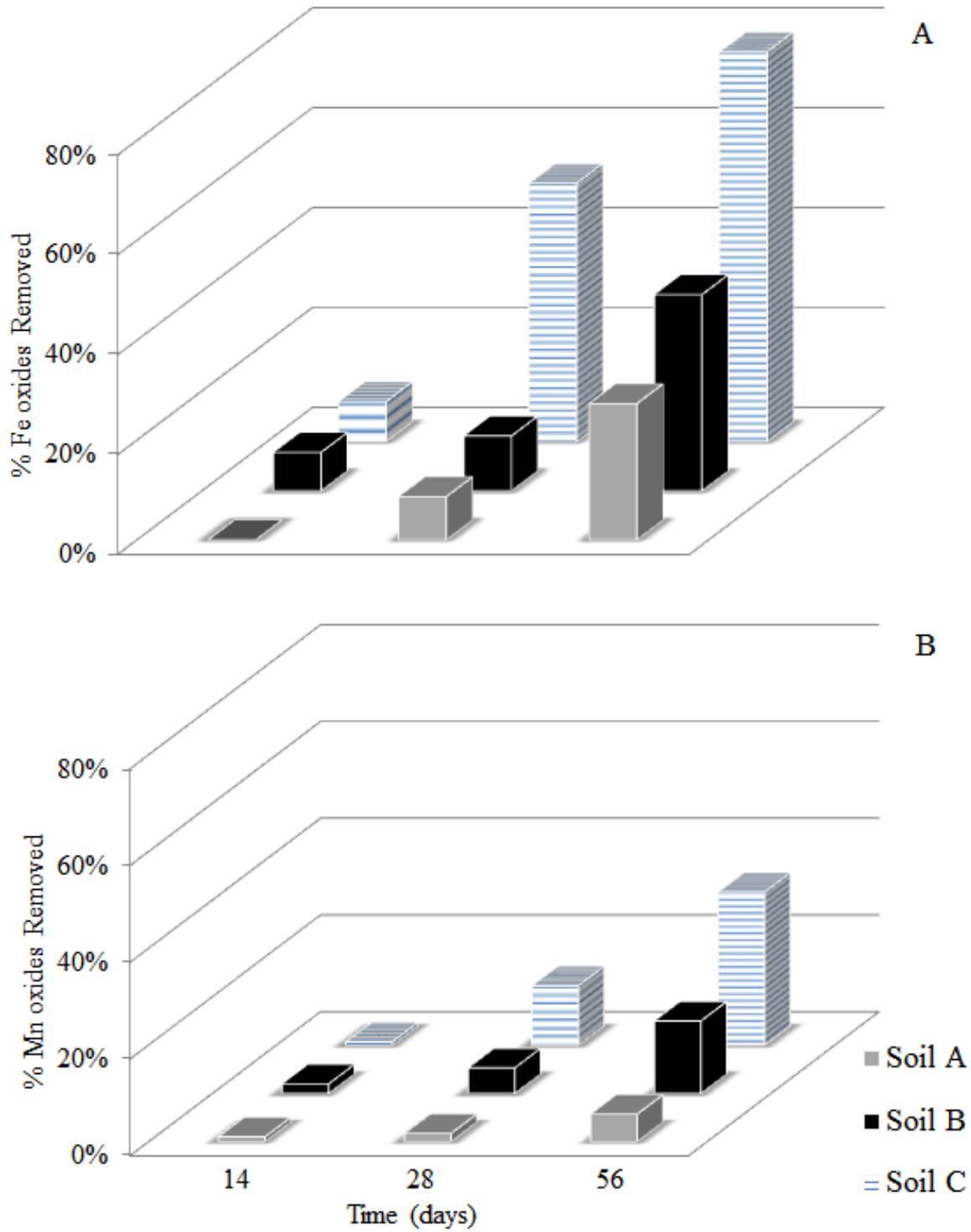


Figure 2-13. IRIS performance in marl soils with flooded conditions. A) FIRIS tubes, B) MIRIS tubes with metal oxide removal calculated from the averages for the three - 0 cm water table treatment repetitions.

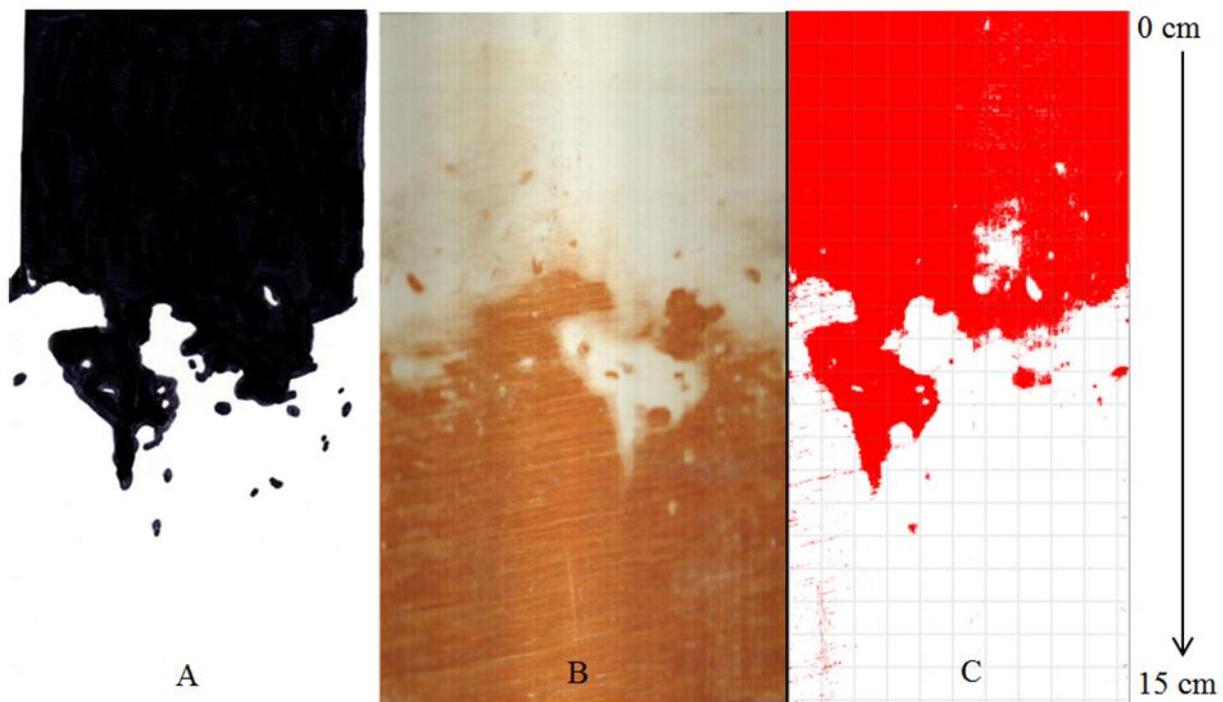


Figure 2-14. Comparison of digital image techniques used to analyze an IRIS tube. A) Traced image using acetate and permanent marker. B) Digitally scanned tube. C) Binarization of the scanned image in preparation for digital analysis. 0-15 cm indicates the zone of removal, which began at the soil surface.



Figure 2-15. Iron oxide removal on IRIS tubes treated with the 30 cm water table. Depth of the water table is indicated by the dashed line, and shows no removal above that line.

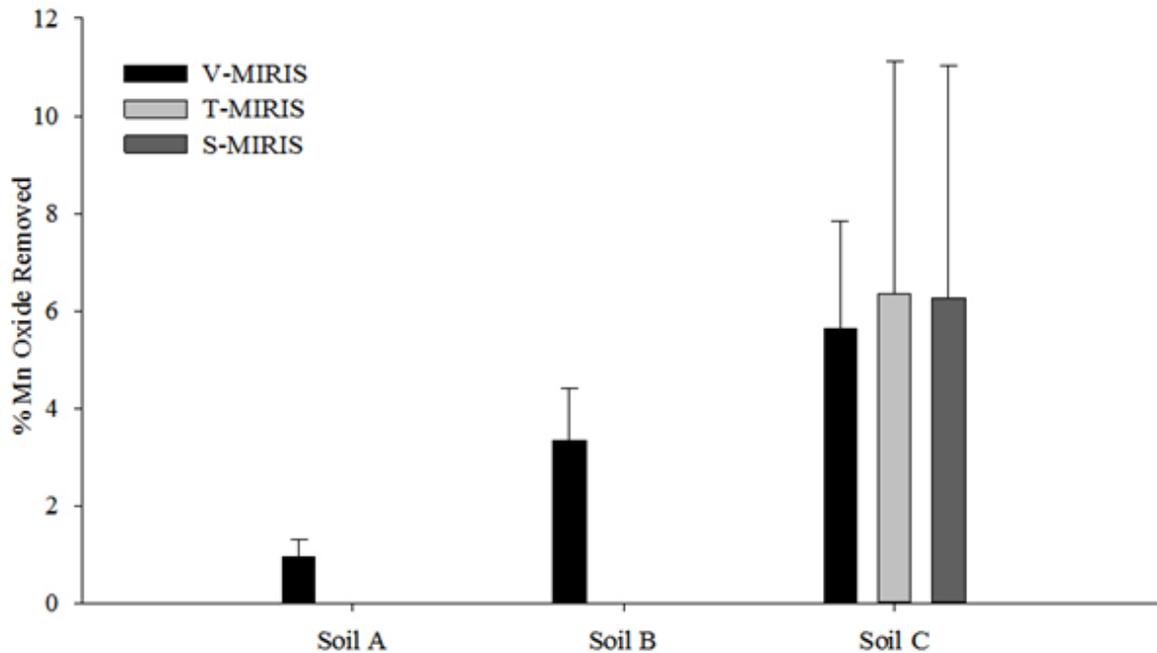


Figure 2-16. Manganese oxide removal from IRIS tubes as estimated by three methods. Method is notated by the pre-fix letter on the MIRIS label in the legend: visual estimate (V-), trace method (T-) and scan method (S-).

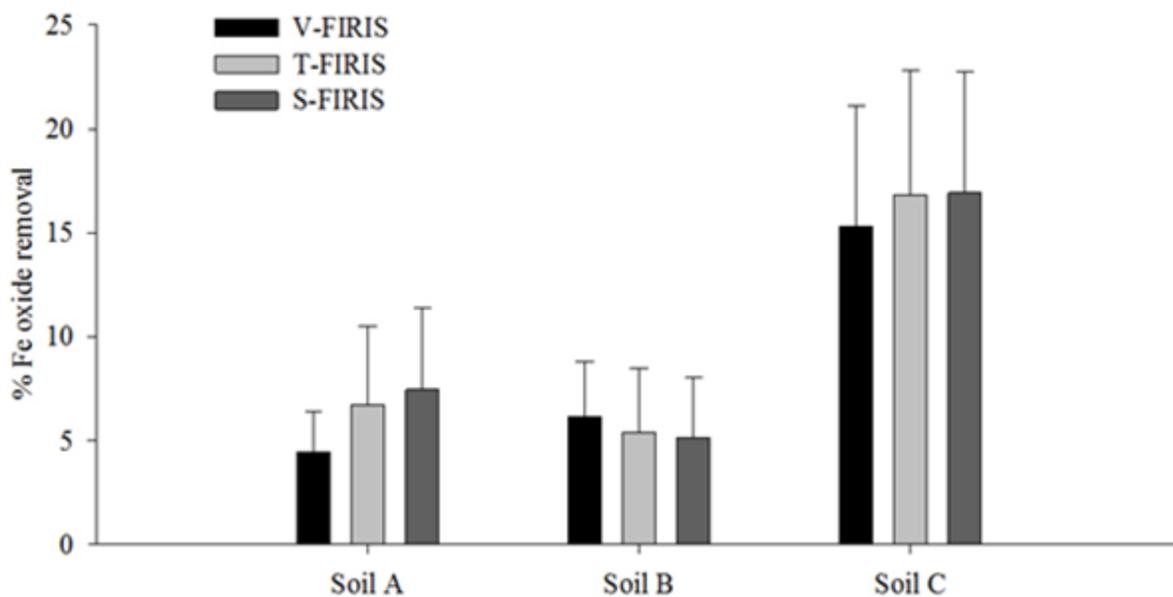


Figure 2-17. Iron oxide removal from IRIS tubes as estimated by three methods. The method is notated by the pre-fix letter on FIRIS label in the legend: visual estimate (V-), trace method (T-) and scan method (S-).

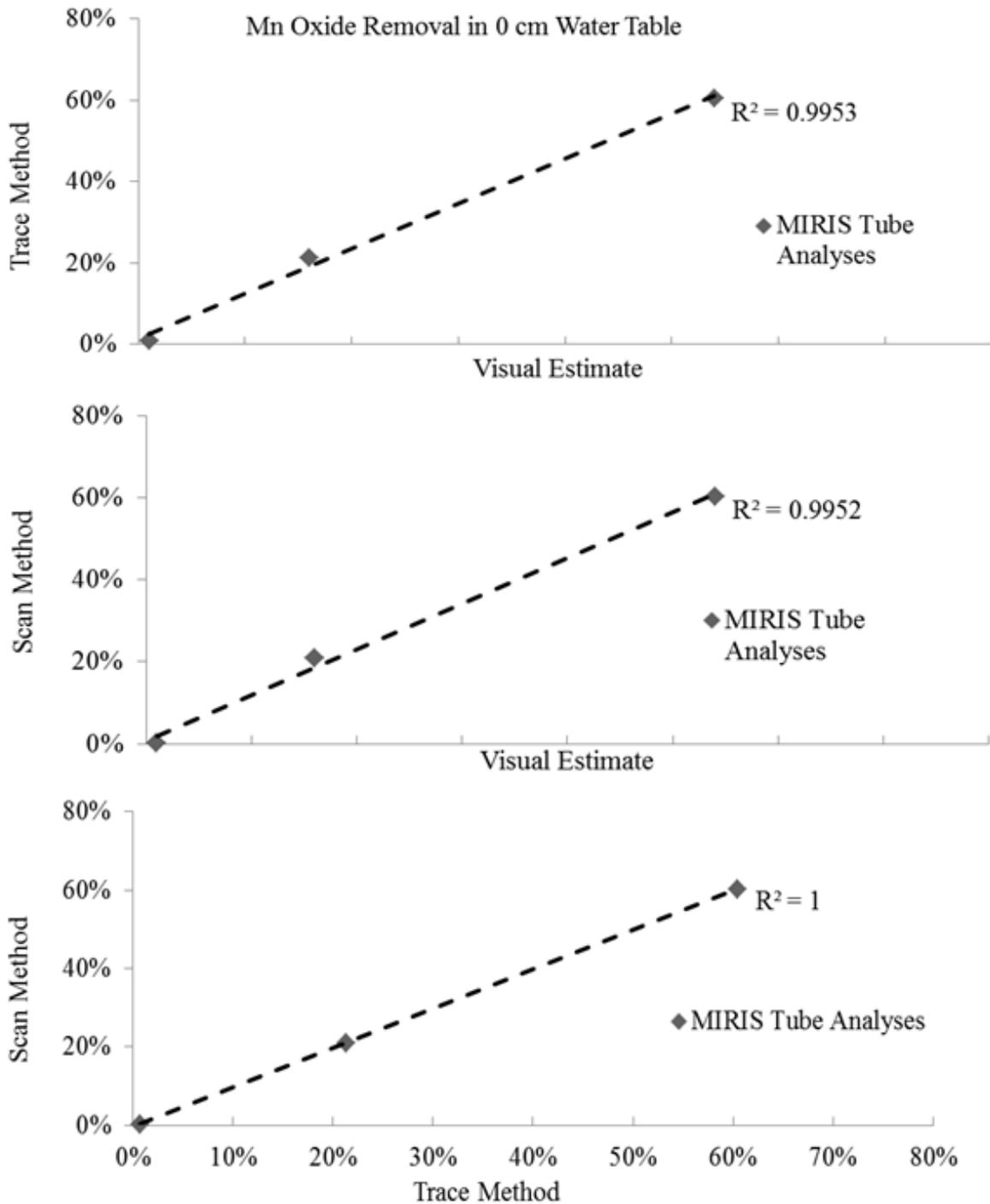


Figure 2-18. Correlation of three methods used to determine manganese oxide removal. MIRIS extracted from a Soil C mesocosm treated with 0 cm water tables maintained for 56 consecutive days are compared. Linear regression line and R^2 values provided. Note: Only one set of manganese tubes had oxide removal in a quantity significant enough to warrant digital analysis by the trace and scan methods.

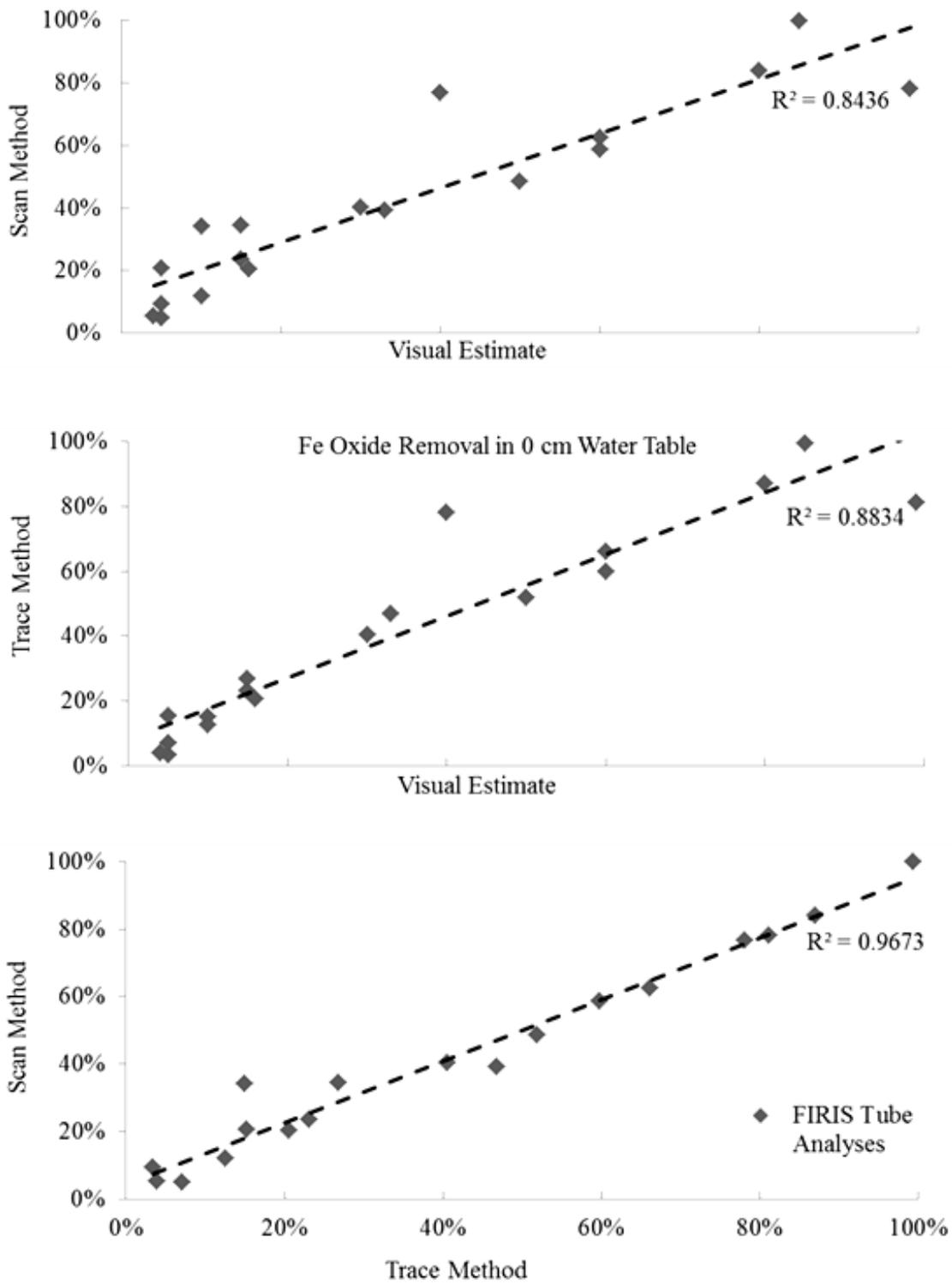


Figure 2-19. Correlation of the three methods used to determine iron oxide removal. FIRIS from the nine soil mesocosms treated with a 0 cm water table and maintained for 56 consecutive days are compared. Linear regression line and R^2 values provided.



Figure 2-20. Iron and manganese coated IRIS tubes after receiving the same treatments. Each set of 3 was installed in a Soil A mesocosm with a 0 cm water table depth.

CHAPTER 3 SUMMARY AND CONCLUSIONS

Introduction

Expectations were that iron coated Indicators of Reduction in Soil (FIRIS) would not reduce within the recommended installation time of 28 days and the manganese coated Indicators of Reduction in Soil (MIRIS) would reduce within 14 days. In this study, the hypothesis was not proven with the iron oxides reducing 3.4 times faster than the manganese oxides. Soil structure and salinity were the two soil properties that had positive correlation to redox potential increases in the data, with the latter potentially impacting anaerobic microbe reduction rates. Results indicate an extended installation time for FIRIS, additional testing of MIRIS, as well as confirmation of the reliability of platinum (Pt) electrodes.

Objective 1

The first objective of this research was to evaluate the performance of the recently developed Indicators of Reduction in Soils (IRIS) tubes against the established, conventional method of measuring the soil redox potential using Pt and reference electrodes. Once flooded conditions were applied (0 cm water table) the Pt electrodes averaged 5.2 days to reflect anaerobic reduction potentials, by dropping below the pH dependent standard reduction line ($+175$ mV at pH 7, -60 slope). Real-time redox readings (Eh) from the Pt electrode were able to verify anaerobic conditions 22.8 days after flooding. With the same treatments, average iron oxide removed from FIRIS was estimated at 5.2% after 14 days, 23.8% after 28 days and 48.2% after 56 days of flooding. Manganese oxide removal from MIRIS was lower than expected at 1.2% after 14 days, 6.4% after 28 days and 17.4% after 56 days of flooding. Applying the Hydric Soil Technical Standard requirement of $\geq 30\%$ iron oxide removal to both types of IRIS,

anaerobic conditions could be verified on FIRIS from the extraction at 56 days; the MIRIS failed to reflect anaerobic conditions during the 56 days with flooding.

The results support the use of FIRIS for inundated conditions with an installation interval of 56 days, which limits the applicability since most hydric soil investigations are on sites saturated below the soil surface. In contrast, < 1% of oxides were removed from the upper part of either FIRIS or MIRIS in the 15 and 30 cm water table treatments, concluding that in high pH, calcareous soils of south Florida, the most reliable method is the Pt electrode although it is not preferred for field investigations. Additional research into MIRIS paint formulation, similar to the work by Dr. M. Rabenhorst et al. on iron oxide paint formulation, may improve reduction rates as well as the adhesion of the manganese oxide paint to polyvinyl chloride tubes during fabrication. Evaluation of MIRIS in other high pH, problem soils would be beneficial to identify use limitations and improve the technology at this early development stage of MIRIS tubes.

Objective 2

Determining what general soil characteristics of marl might influence redox processes was the second objective. Soil structure, electrical conductivity and pH were found to have significant ($P < 0.01$) correlation with Pt electrode readings. Electrical conductivity in this situation was a consequence of the proximity to coastal waters of Biscayne Bay. Higher salinity in Soil A is the one characteristic that can explain the higher Eh readings than found in Soil B with the same water table treatments. The aeration provided by soil structure explains why Soil C quickly rebounded from water applications when the soil water tables were established for each soil mesocosm. Soil C had an average Eh $+212$ mV higher than in Soil A, and $+260$ mV higher than in Soil B, as an average from all water table treatments. The resistance to reduction provided by good soil structure could be promoted through reduced tillage practices and permanent cover crops for low lying areas prone to subterranean flooding or sea level rise.

Research into anaerobic microbial species involved in metal oxide reduction would be beneficial in recognizing how impacts of land use or ecological communities may affect populations of microbes and their respiration rates. Soil salinity impacts to reduction rates in this study showed positive correlation with Eh, resulting in less reduced conditions. The impacts to microbes in brackish and saltwater environments would be helpful to understanding IRIS use limitations in tidally influenced wetland systems.

Objective 3

The final objective was to compare the results obtained from the visual, trace and scan methods of estimating the percent oxide removal from IRIS tubes. Visual estimates of oxide removal were 17% and 20% less than when compared to trace ($R^2 = 0.88$) and scan methods ($R^2 = 0.84$), respectively. The variance between the visual, scan and trace method results, indicate that oxide removal within +/-13% of the $\geq 30\%$ removal criteria could have different anaerobic soil determinations, depending on the method selected for IRIS analysis. The trace and scan digital methods corresponded most closely ($R^2 = 0.97$) with the trace method estimates 4% lower than the scan method

If processing time and ease of use are primary concerns, then visual estimates can be used. If oxide removal results are close to the 30% removal criteria, then evaluation by more than one method may be desired. Digital analysis provides quantitative documentation directly from a scan of the IRIS tube surface. Direct scanning requires less time than the trace method when image editing is not necessary before analysis. The rotation device constructed for this project could be refined to allow portable hand/bar scanners to be readily adapted to scanning round IRIS tubes of variable diameters. The trace method pairs professional judgment with technology for digital analysis. Tubes with linear scratches or other features that require editing would benefit from the trace method by selective exclusion of unrepresentative features.

Deciding which IRIS analysis method(s) to use should be determined by the end use of the data, the number of tubes to be processed, and the extent of oxide removal observed upon extraction. Additional study with IRIS tubes from other problem soils and from a large group of individuals performing visual estimates would be helpful to determine if findings in this study are applicable in other areas where IRIS used. Development of recommendations for oxide removal estimate methods and the various software applications used for image analysis would further the standardization of IRIS technology for research purposes.

APPENDIX A
HYDRIC SOILS TECHNICAL STANDARD

Hydric Soil Testing Methods

The Hydric Soil Technical Standard has been specified and approved for use by the National Technical Committee for Hydric Soils (NTCHS) in investigating the surface hydrology of soils with regard to anaerobic conditions and saturation. Although other methods may exist, the methods discussed here are accepted by the NTCHS for the purposes of evaluating: wetland functions, hydric soil status, or field indicator criteria (NTCHS, 2007). Saturation and anaerobic conditions must both exist to prove a soil is hydric.

Redox potential (Eh) measurements of $< +175$ mV at pH 7 must exist to document anaerobic conditions, and are adjusted for pH on a line with a slope of negative 60 (Figure 1-3). Positive reaction to alpha-alpha-dipyridyl through a pink or red color change reflects the presence of reduced iron in soils with sufficient iron present, but low iron content in marl soils does not provide the indicator reaction necessary to utilize this solution. Soils low in iron, such as marl, can be evaluated for redox potential using iron coated Indicators of Reduction in Soil (FIRIS) tubes. Confirmation of anaerobic conditions in the field by Indicators of Reduction in Soil (IRIS) tubes requires that at least 3 of the 5 buried IRIS tubes have iron removed from at least 30% of a 15 cm long area along the tube, which must start within 15 cm of the soil surface (NTCHS, 2007).

Saturated conditions in-situ can only be proven with piezometer data, which should include site-specific water table data from an open well and site-specific precipitation records. Piezometers must be installed at 25 cm and 100 cm depths and read at least every 7 days. The period of readings should cover a minimum cycle of dry-wet-dry (April through November in

south Florida) or up to one year. If water occurs within 25 cm of the soil surface for at least 14 consecutive days then the saturation criteria for a hydric soil has been met (NTCHS, 2007).

When evaluating hydric soils status, both saturated and anaerobic conditions must occur more than 50% of the time, this timeframe might be >1 in 2 years, >5 in 10 years, etc. The required precipitation data help to determine if the wet period of interest is occurring during a year with low, normal, or high precipitation rates when compared with historical data for a location (Sprecher and Warne, 2000). Historical precipitation data from 1971-2000 are available online from the United States Department of Agriculture-Natural Resources Conservation Service, National Water and Climate Center. In this research, water tables were managed in the laboratory.

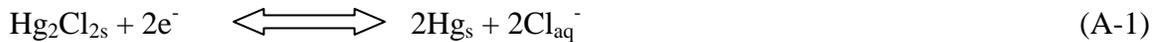
Collection of Oxidation-Reduction Readings with Pt Electrodes

Measuring the reduction and oxidation potential of a soil by taking conductance readings between platinum (Pt) and reference electrodes is an established method used in laboratory and field research. When documenting soil saturation to meet hydric soil criteria, in addition to the electrodes, a salt bridge(s) and a piezometer(s) are needed to document the water table (NTCHS, 2007). Outside of a research lab this method is not practical for routine use by field soil scientists due to the installation of expensive equipment, labor requirements, and exposure of equipment to hazards from weather conditions and wildlife, as well as vandalism or theft.

When the use of Pt electrodes is employed, redox readings need to be collected at least every 7 days, since Eh fluctuates with time. The voltage should be read at a depth of 25 cm from the mineral soil surface in loamy and clayey soils, which categorizes the marl soils in this research. If a predominance of reduction continues for a minimum of 14 consecutive days, then anaerobic conditions can be documented at the location of the electrode. Since Eh varies

spatially, as well as with time, multiple electrodes are installed throughout the study area. Soil pH should be collected at the same time redox readings are taken to determine the corrected Eh.

Figure 1-3 demonstrates that in anaerobic conditions iron reduction potential is achieved at higher Eh values than in non-alkaline soils. Ambient soil temperature to correct the reference electrode based on the type of electrode and the electrolyte used should be recorded at the time redox readings are taken. Interpretations of the readings are based on values obtained from using a standard hydrogen reference electrode (SHE), which is not suitable for field use. More durable electrodes can be used, but must include a correction factor to represent the expected value if a SHE had been used. Calomel or Ag/AgCl reference electrodes are the most common types used with differing correction factors of +250 mV and +200 mV. Equations A-1 and A-2 explain the redox reactions for each of these electrode types. Calomel electrodes contain mercury, which requires careful handling and disposal, so they were not considered for used in this study.



A small temperature correction factor is recommended when using saturated Ag/AgCl electrodes used at temperatures that vary from 25⁰ C. Increase in temperatures above 25⁰ C are corrected by -0.13 mV/°C, while temperatures below 25⁰ C are adjusted using +0.13 mV/°C (Ansuini and Dimond, 1994). Under climate controlled lab conditions with an ambient air temperature set at 25⁰ C, correction factors for temperature were not expected to be significant or necessary but were recorded.

APPENDIX B CONSTRUCTION OF EQUIPMENT

Introduction

Execution of research required 10 months of construction and testing of the equipment and components because similar instruments were not available on the market. Detailed information for constructing components is described in this chapter to assist future research and development of the Indicators of Reduction in Soil (IRIS). The quality of the components used in this research was integral to the quality of the data collected and analyzed.

Platinum Electrodes

Thirty – 45 centimeter platinum electrodes (Pt) were fabricated for the project due to lack of availability and to control costs. Electrodes were constructed with guidance from the methods and materials recommended by Vepraskas and Cox at North Carolina State University. The platinum wire and brass rod were connected using electrical solder as they could not be fused with a propane torch since their melting points are too far apart at 1772 °C and 882 °C, respectively. The quality of the constructed electrodes was tested using an Ag/AgCl reference electrode filled with a 4.0 M saturated KCl solution. A ferrous-ferric buffer solution (Light's Solution) of known conductance was the standard buffer solution with a target reading of +475 mV, and a variance of +/- 20 mV was determined acceptable (Light, 1972). Deionized water (DI) water was also used to check for variance in a non-buffered solution and identify any major variations. Electrodes were tested 5 times throughout 7 months, between initial construction and final installation.

Considering the quality of the redox readings, the meter used to measure conductivity between the electrodes should have an input resistance of at least 20 giga-ohms to minimize electrical feedback to reduce fluctuations in the readings (Rabenhorst et al., 2009). An

inexpensive handheld volt meter (Extech Auto Ranging Digital Multimeter Model: MN36) was used to complete initial bench tests on the electrodes. The day before installation into mesocosms the electrodes were tested using a Campbell Scientific Data Logger (model CR1000), with a resistance rating of 20 giga-ohms.

Salt Bridges

Good conductance between the platinum and reference electrodes is necessary to obtain representative redox readings. One of the three water level treatments to be used in this research will result in a 30 cm deep water table, which is 5 cm below the Pt electrode tip at a 25 cm depth. The other two water level treatments will inundate the 25 cm deep platinum tip. Installation of salt bridges in the mesocosms with the 30 cm water table was desired since the degree of soil saturation above the water table was not known, and variability in conductance could affect the quality of the redox readings.

Installation of salt bridges in all the soil mesocosms, instead of just those with the 30 cm deep water level treatment improved the efficiency and reduced costs of collecting redox readings from the 27 soil mesocosms. Salt bridges eliminated the need to clean the reference electrode between each reading and facilitated the use of a single Ag/AgCl reference electrode for redox readings in all 27 mesocosms, which cut equipment costs by \$2,600.00. An additional benefit to using salt bridges in all the soil mesocosms was that the reference electrode would stay clean, as the need to clean soil from the reference electrode tip between readings was eliminated.

Between July and August of 2011, 30 salt bridges were constructed from 61 centimeter lengths of 1.91 centimeter diameter polyvinyl chloride (PVC) pipe. The bridges were constructed in the lab by dissolving a saturated KCl solution into an agar powder that had been diluted in boiling, deionized water was allowed to cool slightly to form a pourable gel that sets up in the PVC tubes when cooled. To minimize air pockets in the gel, liquid agar was poured at a 45

degree angle in a steady stream to allow the hot, liquid gel to displace air as each tube was filled. To prevent the agar gel from desiccation and cracking, the bridges were stored in a saturated KCl solution until ready for installation. The day before installation the salt bridges were rinsed with DI water and dried to remove external salt deposits from the PVC tubes, and a permanent PVC cap was glued on the bottom of each. Three – 0.3 centimeter diameter holes were drilled around the circumference of the 1.9 centimeter PVC salt bridges at the 25 cm depth to expose the KCl agar gel at the same depth as the Pt electrode tip.

Soil Columns

Soil columns were designed and constructed from PVC irrigation pipe materials for durability, light weight and non-reactive nature of the material. Size of the columns was relatively large for soil mesocosms used in lab analyses, with a length of 61 centimeters and a diameter of 25.4 centimeters. Using a bulk density of 1.41 g/cc for a silt loam soil (marl is typically silt loam) and considering soil-water weight, each soil column weigh approximately 100 pounds. The large size and weight of the soil columns required additional planning of the sampling and transporting from the field to the lab.

A primary concern during field collection would be to extract soil cores to avoid disturbing the soil layers and structure as much as possible. The 25.4 centimeter diameter of the PVC pipe was necessary to accommodate the installation of 8 pieces of equipment into each soil mesocosm; which included 3 iron coated Indicators of Reduction in Soil (FIRIS), 3 manganese coated Indicators of Reduction in Soil (MIRIS), 1 Pt electrode and 1 salt bridge. The 61 centimeter length of the PVC columns allowed for a 45 centimeter soil sample to be collected with enough space left accommodating water above the soil surface, which allowed the addition of water to establish and maintain the specified water table depths. The bottom rim of each PVC

pipe was beveled to reduce soil resistance and allow for more efficient penetration during soil sampling in the field.

A 25.4 centimeter PVC cap was fitted with a PVC drain pipe and ball valve to control water levels in each column and to facilitate collecting water samples from the bottom of the column. A wooden cradle was built for each column to accommodate the plumbing appurtenances coming from the bottom center of each column and to provide access for repairs if any leaks were to develop during the research. To monitor and adjust water levels, a 0.95 centimeter clear poly tube was installed vertically into the side of each column with a sponge filter in the elbow fitting to minimize movement of soil particles between the tube and the PVC pipe. To prevent soil particles from exiting the drain pipe during water sampling, 23 centimeter diameter by 2.54 centimeter thick sand filters were constructed of silica sand that was soaked in 1M HCl for two hours, rinsed with DI water and air dried. The acid-washed sand was placed into 30 fine mesh polyester bags that were fabricated to fit flush inside each PVC cap between the soil sample in the column and the drain pipe in the bottom center of the PVC cap.

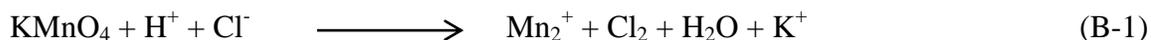
Manganese Oxide Paint

With instruction from Patty Jones and Steve Monteith at the National Soil Survey Lab (NSSL), the manganese oxide paint was manufactured at the Tropical Research and Education Center facility in Homestead from February through May of 2011. Potassium permanganate was first treated with high levels of potassium to form acid birnessite for the final manganese “paint” substance (Stiles et al., 2010). Birnessite is the most common form of mineralized manganese found in soils. It is a poorly crystalline, tetravalent, oxide of manganese ($\delta\text{-MnO}_2$) and readily synthesized in the lab (McKenzie, 1971). Since the process to manufacture the manganese “paint” for the fabrication of the MIRIS tubes is not currently published, the materials and methods below describe the processes. Three batches were produced to ensure enough of the

product would be available since it requires two months after manufactured before the paint is ready for application.

Dialysis tubing was prepared for the leaching of oxides from the manganese paint. Five – 61 centimeter sections of 12,000 to 14,000 molecular weight cut off (MWCO) dialysis tubing was heated to 80⁰C for 30 minutes in a solution of 0.01 mol/L of NaHCO₃ and 0.01 mol/L of sodium ethylenediaminetetraacetic acid (NaEDTA) with enough DI water to equal 1 L. Once cooled, the tubing was transferred into an air tight glass container with a 50% ethanol solution for storage in the refrigerator until ready to be filled with the acid birnessite, produced in the next step.

Acid birnessite was then prepared by dissolving 4.0 moles of potassium permanganate (KMnO₄) into enough DI water to equal 2.5 L of solution. The solution was brought to a boil in a 3.5 L glass flask using a stirrer bar on a hot plate under a fume hood. 163.5 ml of 12 M HCl was added to the boiling permanganate solution, 1 drop at time to prevent boiling. Equation B-1 shows the reduction of potassium permanganate with the addition of the acid (H⁺) and reduction of the chloride ion. Acid solution was cooled overnight, allowing the acid birnessite precipitate to settle. The decanted precipitate was transferred into four 250 ml centrifuge bottles, filled with DI water and centrifuged at 2000 rpm for 30 minutes, decanted; repeated again. After the second and final decanting, DI water was added to the centrifuge bottle and shook for 10 minutes.



Each of the prepared dialysis tube was filled with the contents of the four centrifuge bottles; tubing was secured on each end with plastic clips and immersed in 2 to 3 gallons of DI water. DI water immediately turned a bright violet/purple color on initial immersion in the bath, but this dissipated after the initial soaking. The DI water bath was changed every hour the first

day, and then twice a day until the salts were determined to have completed leaching by use of a silver nitrate indicator solution.

Silver nitrate (AgNO_3) indicator solution was prepared by diluting 9g of AgNO_3 in 500 ml DI water. This was applied with a disposable pipette adjacent to the submerged dialysis tubing to check for completion of salt leaching. If salts are still leaching the indicator solution turns cloudy white. Staff at the NSSL indicated it should take about 7 days to complete leaching, but a negative AgNO_3 test was achieved after the 2nd day for all three batches. This could have been related to the larger quantity of DI water used since the NSSL staff were using only 2 L of DI water, and 2 to 3 gallons of DI water were used each time the water baths were changed for this project due to the large size (49 liters) plastic tubs used for submersion of the dialysis tubes containing the birnessite.

After consulting with Patty Jones at the NSSL on the premature AgNO_3 test I was advised to use observable changes to the dialysis tubing and the precipitate it contained. Swelling of the dialysis tubing, followed by a squeaky, balloon-like texture would develop and finally the precipitate would change from a purple-black color to a dark brown color. Over days 3 to 5 day, these indicators were all observed. Daily testing with the AgNO_3 indicator solution continued to produce no reaction and confirmed the leaching process had completed. Each of the 3 batches was extracted from the dialysis tubes after 6 days in the DI water baths.

The solid adduct remaining in the dialysis tubing was placed into 50 ml centrifuge tubes and processed at 2000 rpm for 5 minutes and decanted. The adduct was rinsed two more times by refilling tubes with DI water, agitating on a shaker for 5 minutes, centrifuged at 2000 rpm for 5 minutes, and decanted. On the final decanting, an equal volume of the liquid to solids was left in the tubes. Each 50 ml centrifuged tube produced between 7.5 to 15 ml of adduct; 81 tubes were

processed. The tubes were then labeled and stored in the refrigerator for 42 days (mid-April to the end of May 2011) to stabilize the manganese paint to ensure the proper conversion of hydrous oxides before fabrication of the actual MIRIS tubes (personal communication with Cynthia Stiles at the NSSL in Lincoln, Nebraska, April 2011).

IRIS Rotation Device for Digital Scanning

After extracting MIRIS and FIRIS tubes the percentage of oxide paint that has been removed from the PVC pipe must be measured. This can be done by two or more sets of human eyes, or the tubes can be scanned and digitally analyzed by an image software application. Flatbed scanners have been used for this purpose, but require taking multiple images from different sides of the tube, which then need to be cropped and merged to produce a single image for analysis (Rabenhorst et al., 2008). Relatively inexpensive, portable, handheld/bar scanners are now widely available and had the potential to be used to analyze the extracted IRIS tubes.

The idea of using a hand scanner for this research was suggested by MIRIS researcher, Ed Dunkinson, in July of 2011, but a device to adapt the scanner was needed. The model available (Magic Wand by VuPoint Solutions; cost \$100.00) for this research had a scanning window 0.5 cm wide that is 1.5 cm from the roller bar. The distance between the scanning window and the roller bar that activates the device to record the image is too far to produce a clear, undistorted image of either the 1.27 centimeter FIRIS or the 1.91 centimeter MIRIS tubes.

To overcome this obstacle, a device with similar mechanics to a lathe was fabricated from wood, screws, a metal rod, and rubber rollers off of a fax machine. An IRIS tube is mounted onto a horizontal dowel that is perpendicular to second roller bar that rotates simultaneously with the dowel, allowing the IRIS tube to be centered in the scanning window while a 360⁰ image of the entire circumference of the tube is recorded. The 25 cm by 3 cm bar scanner is placed in a stationary cradle, centered above the IRIS tube so that the controls of the scanner are easily

accessible. The device could serve as a prototype for a more refined piece of equipment to use with the handheld/bar scanners.

APPENDIX C
DETAILED SOIL DESCRIPTIONS

Pennsuco marl (Soil A), with persistent shallow water above the surface, this site actively produces marl as part of a larger marl prairie ecological community. Vegetation consisted of periphytic algae floating above the soil surface and sparse saw grass inundated with 30 cm of standing water, at the time of collection during the last week of July 2011. Here is a description of the upper 45 centimeters of Pennsuco marl soil profile collected at Latitude 25.4347,

Longitude -80.3555:

- | | |
|-------------|---|
| 0 to 10 cm | 10YR 7/2 clay loam; very small distinct organic bodies ranging in color from 10YR 4/2 to 10YR 2/1 in 15% to 20% of the matrix; common, fine roots; massive structure. |
| 10 to 35 cm | 10YR 6/2 clay loam; organic staining around few and very fine root channels; massive structure. |
| 35 to 45 cm | 10YR 4/2 loam; small shell fragments (< 1 mm) throughout matrix; few medium and fine roots; massive structure. |

Perrine marl, drained (Soil B). The perimeter of the site is drained by field ditches to allow annual production of tilled, irrigated, vegetable crops between December and April each year. Sweet corn had been harvested from the field several months prior to sample collection, which was evident by the remaining corn stubble on the soil surface. Limestone bedrock at the sample site was between 51 centimeters and 56 centimeters below the soil surface and the water table was measured at 71 centimeters below the soil surface on the day of sample collection. Here is a description of the upper 45 centimeters of the Perrine marl profile collected at Latitude 25.4644,

Longitude -80.4616:

- | | |
|-------------|---|
| 0 to 12 cm | 10 YR 5/2 loam; massive structure |
| 12 to 28 cm | 10 YR 5/2 loam; massive structure; dense plow layer from 12 to 22 cm |
| 28 to 35 cm | 10 YR 6/1 loam; CaCO ₃ precipitation as small distinct concretions in 20% of matrix; massive structure |

35 to 45 cm 10 YR 5/2 loam; CaCO₃ precipitation as small distinct concretions in 5% of matrix; massive structure

Pennsuco marl, drained (Soil C). Historically, the site was part of a long, narrow drainage slough (also referred to as a marl finger) at a naturally lower elevation in the landscape. A review of aerial photos showed that during the 1960s the canal was excavated in the center of the drainage slough adjacent to this site, as part of a larger regional flood control project throughout central and south Florida. A 3 to 5% slope away from the canal bank indicates the site received marl spoil when the canal was excavated. Marl is more than 1.8 meters deep at this site, providing ideal conditions for the existing field nursery operation. Vegetation consists of a variety of field grown ornamental plants and palms with a permanent ground cover of volunteer grasses and herbs between the plants and rows. Here is a description of the upper 45 centimeters of the Perrine marl profile collected at Latitude 25.4644, Longitude -80.4616:

0 to 10 cm 10YR 5/2; loam; weak, medium subangular blocky structure
10 to 38 cm 10YR 5/2; loam; weak, very coarse subangular blocky structure
38 to 45 cm 10 YR 4/1; clay loam; moderate, medium subangular blocky structure

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BIOGRAPHICAL SKETCH

Christine Coffin began her interest in soils as an undergraduate at the University of Maryland with an elected course in soils, which sparked a deep interest and ultimately resulted in switching to a major in soil science. In 1991, she served as a Summer Intern with the United States Department of Agriculture – Natural Resources Conservation Service (USDA-NRCS) in Sussex County, Delaware and participated in the University of Maryland Soil Judging Team. After earning a Bachelor of Science degree in 1992, she planned to move to south Florida and work on the conservation of the Everglades, but was offered a career position with USDA-NRCS in Delaware as a field Soil Scientist. In that position, she conducted soil salinity studies, soil survey updates in the coastal plain and piedmont regions of the mid-Atlantic. Extensive survey of both coastal and inland wetlands was the focus of her work in that position, as well as digital cartography and survey manuscript development.

An opportunity to work in the Everglades region became available in 1995, at which time she relocated to Davie, Florida as a District Conservationist (DC) with USDA-NRCS. In 1996, she accepted a DC position in Homestead, Florida, where she continues her career in natural resources conservation. In 2005, she decided to work towards a Master of Science degree through the University of Florida while continuing to work full-time. Soil research in this study was conducted at the University of Florida - Institute of Food and Agricultural Science - Tropical Research and Education Center in Homestead, Florida.