

ENVIRONMENTAL FACTORS AFFECTING TEMPORAL AND SPATIAL PATTERNS OF SOIL REDOX POTENTIAL IN FLORIDA EVERGLADES WETLANDS

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Abstract: Redox potential impacts wetland ecosystem functions and processes. This study assessed the temporal and spatial patterns and variability of soil redox potential in relation to: 1) hydrology, 2) soil phosphorus (P) enrichment, and 3) dominant vegetation community in an Everglades wetland. Probes installed for 2-week periods required 8 to 10 days for measurements to stabilize, considerably longer than what has been reported in the literature. Probes installed for 1 year yielded more stable measurements and were more useful for ecological analysis. Redox temporal patterns were related to water table fluctuation with redox increasing exponentially as the water table decreased from 5 cm above marsh surface. Large-scale spatial redox patterns were found in relation to P enrichment with higher average redox occurring in moderately-enriched regions (–134 mV) than in highly-enriched or unenriched regions (–185 mV for both). Vegetation community had no effect on redox status. Water level change was the primary driver of small-scale spatial variability (soil profile) with redox measurements varying more near the marsh surface during low water conditions. The degree of redox response to water table fluctuation decreased with increasing soil depth. These findings are important in understanding how altering hydrology can affect soil processes and ecosystem function.

Key Words: cattail, microbial processes, phosphorus, sawgrass, scale, water depth

INTRODUCTION

In wetland ecosystems, the reduction-oxidation (redox) potential of soils is a major indicator of physically and/or biologically driven chemical reactions such as oxygen demand, decomposition, geochemical equilibria, and potential plant stress (ZoBell, 1946; Moore and Reddy, 1994; Newman et al., 1996; Pezeshki et al., 1996; Chabbi et al., 2000). An important geochemical reaction in the Everglades is the release of phosphorus (P) bound to iron (Moore and Reddy, 1994), potentially increasing P availability to plants. The P-limited Everglades is sensitive to increased P availability resulting in plant community changes (Weisner and Miao, 2004) and has profound effects on carbon (C) accumulation and nutrient cycling (Craft and Richardson, 1993). Therefore, temporal and spatial redox dynamics will affect wetland ecosystem functions and processes at multiple scales. Understanding the temporal and spatial patterns of redox in wetland soils is an important step towards understanding critical wet-

lands functions such as plant productivity, decomposition, and ultimately C storage.

Soil redox potential is primarily controlled by microbial activity, which is a function of soil temperature, water levels, and soil C and nutrient supply (Fiedler et al., 2007). Soil temperature governs the rate of chemical reactions as well as microbial activity, which significantly slows at temperatures below 5°C (Megonigal et al., 1996). However, wetland soils in the southeastern United States rarely experience temperatures below this threshold, especially when saturated, and redox potential is not generally affected by temperature (Megonigal et al., 1996; Seybold et al., 2002). Water-level changes have been shown to affect redox potential (de Mars and Wassen, 1999; Seybold et al., 2002; Niedermeier and Robinson, 2007). As water levels decrease below the marsh surface, redox potential increases either linearly or exponentially depending on marsh type and nutrient availability (de Mars and Wassen, 1999; Niedermeier and Robinson, 2007). Soil C and nutrient availability

influence redox through microbial activity. Low C or nutrient availability results in decreased microbial activity, less oxygen demand, and higher redox potential than high C or nutrient availability (de Mars and Wassen 1999).

Water depth as well as soil C and nutrient availability can vary temporally and spatially. Temporally, water level in the Everglades changes with south Florida's wet/dry seasonal cycle and water management activities. The wet season occurs between June and October and water depths can reach over 100 cm. During the dry season between November and May, water depths can decrease below the marsh surface exposing the upper layers of soil to air. This seasonal variation in water depth could therefore result in temporal variability in soil redox potential, especially in the near-surface soils. Spatially, in the northern Everglades, an increase in P availability, leaf litter addition, and decomposition (Craft and Richardson, 1993) has led to the formation of a soil nutrient gradient from highly-enriched regions to non-enriched regions. Given that increased C and nutrient availability should affect redox, Qualls et al. (2001) examined redox potential differences along the northern Everglades nutrient gradient but found no correlation between redox and soil P concentration. However, with permanently installed redox probes, they only measured one root-zone soil depth (12.5 cm). This depth may have been too deep in the soil profile to detect the effect of high C and nutrient supply on microbial activity, which would occur near the soil surface. By measuring redox at more discrete and shallower depth increments, it may be possible to detect both large (within a nutrient and vegetation gradient) and small (along a soil profile) scale spatial patterns.

The redox potential of the soil-depth profile can be affected by both water depth and vegetation. When soils are saturated for long periods, microbes use all available oxygen before using other, less energy-yielding electron acceptors (Fiedler et al., 2007). During drawdown (the lowering of water level), the near-surface soils will drain before the deeper soils, creating a vertical saturation and redox gradient at small spatial scales (Niedermeier and Robinson, 2007). Redox potential of different soil depths is also influenced by rooting depth and growth strategies of different plant species for growing in saturated soils. Some wetland plants, including *Typha domingensis* (cattail), readily lose oxygen through their roots to the rhizosphere, while others, such as *Cladium jamaicense* (sawgrass), have low rates of oxygen diffusion to the surrounding rhizosphere (Chabbi et al., 2000). The differences in oxygen loss between species may create variability in

redox along the soil profile and among plant communities.

Although redox potential can be a valuable indicator of microbial processes and can influence ecosystem function, measurements of redox potential are notoriously variable (Fiedler et al., 2007 and references there in). This variability can arise from both methodological as well as environmental factors. Measurements taken immediately (within a few minutes to a few hours) after probe installation may be skewed by installation disturbance and potential introduction of oxygen to a reduced environment. Long-term measurements (over months) may suffer from probe corrosion and malfunction (Mansfeldt, 2003). Therefore, problems with methodology must be considered when evaluating redox potential variability at the landscape and ecosystem level.

This study is part of a long-term, large-scale, whole-ecosystem project that examines how multiple prescribed fires affect major ecosystem functions and processes and fire's potential use as a tool for accelerating ecosystem recovery from eutrophication in the northern Everglades (Miao et al., 2009). As part of the larger project, this study focused on soil redox potential and habitat characteristics including hydrology, soil nutrient enrichment, and plant species dominance that may affect temporal and spatial (large- and small-scale) redox patterns. We hypothesized that: 1) redox potential would vary with different water depths as oxygen diffuses through water more slowly than in air; 2) redox potential would differ along the soil P gradient as soils with high P concentrations and high C input have higher microbial activity than low P concentration soils; and 3) redox potential would differ between cattail and sawgrass dominated communities, as both species have different adaptive strategies to survive in low oxygen soil conditions. Moreover, the study also examined issues related to redox measurement variability using temporary and permanent probe installations.

METHODS

Site Description and Study Design

This study was conducted between 2006 and 2008 in Water Conservation Area 2A (WCA 2A) (26°20'N, 80°22'W) (Figure 1) of the northern Everglades, Florida, USA. The 447 km² impounded marsh is surrounded by canals and levees constructed in the 1950s. Water enters the marsh from the north through water-control structures in the Hillsboro Canal and generally flows south. Histor-

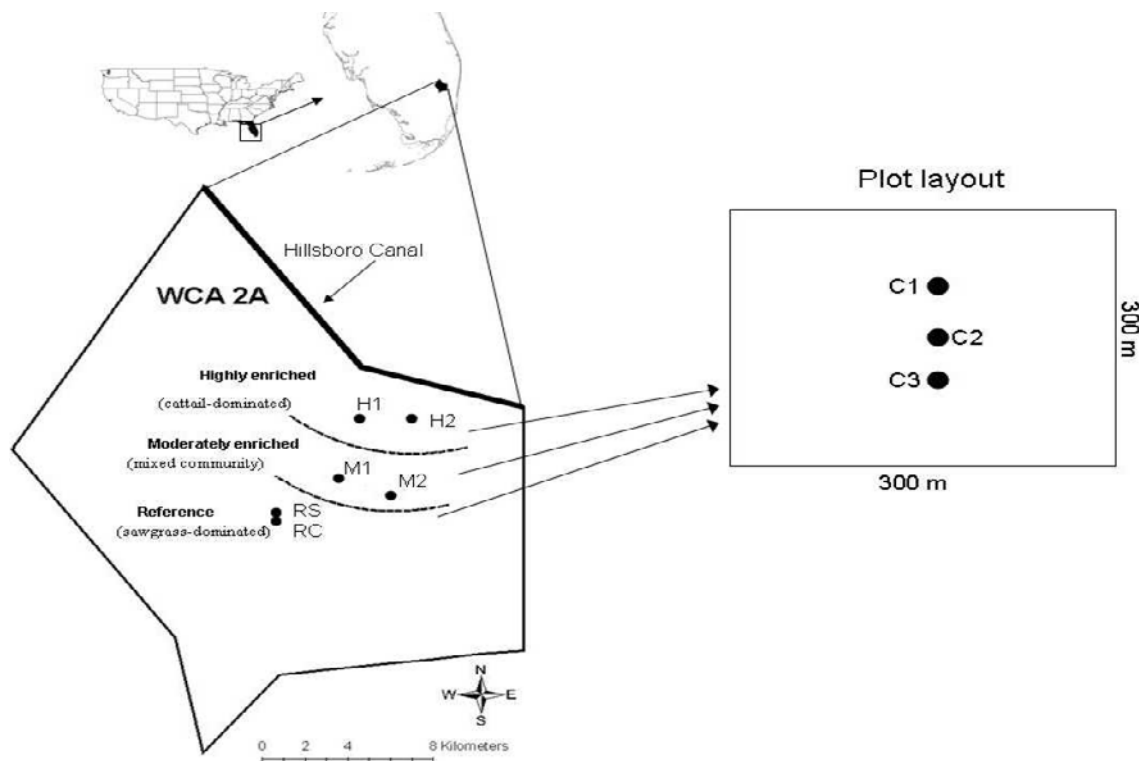


Figure 1. Location of plots used for both temporary and permanent redox probe installations. The H2 and M2 areas were burned in 2006. RS is dominated by sawgrass, while RC is dominated by cattail. The highly-enriched region is dominated by cattail and the moderately-enriched region is a mix of cattail and sawgrass. Each plot is 9 ha and had 3 sampling stations except for the M2 plot, which had 7 sampling stations to capture the variability of its vegetation communities.

ically, the water has had high P and nitrogen (N) concentrations, which in turn has created a soil-nutrient gradient from the northern part of the marsh to the southern interior. This nutrient loading has also resulted in a plant species shift from sawgrass to monotypic stands of cattail. Cattail is a native species of the Everglades that historically was found in small patches, but, with nutrient enrichment, has out-competed sawgrass (Davis, 1989). The marsh can now be divided into three regions; 1) a highly-enriched region with 1000 to 1200 mg P/kg soil that is dominated by cattail; 2) a moderately-enriched region with 600 to 1000 mg P/kg soil and a mix of cattail and sawgrass; and 3) an unenriched reference region with < 600 mg P/kg soil that is dominated by sawgrass with small patches of cattail. This gradient in soil P extends approximately 15 km from the Hillsboro Canal southward to the interior of the marsh (Figure 1). The soil is about 45% organic C and has an accretion rate of 4.0 mm/year in the highly-enriched region and 1.6 mm/year in the reference region (Craft and Richardson, 1993). The differences in C availability and quality affect decomposition rates (Debusk and Reddy, 2005), which may influence redox potential.

Six plots (300 × 300 m each) were selected and grouped in pairs along the P gradient (Figure 1). Two plots were located in the highly-enriched region (H1 and H2), two in the moderately-enriched region (M1 and M2), and two in the reference region (RS, which was sawgrass dominated; and RC, which was cattail dominated). Both the H2 and M2 plots were burned once in 2006, while the other plots served as controls (covariates). In general, each plot had three subplot sampling stations. However, M2 had seven sampling stations to capture the higher spatial variability of the plot (M2 has four subplots in the cattail-dominated areas and three in the sawgrass-dominated areas). The RS and RC plots each had three sampling stations during the temporary probe installations but only one during the permanent probe installations. Each sampling station represented an area 3 ha in size, except at M2 where the sampling stations were closer together and represented an area about 1 ha in size. Each plot totaled 9 ha. For analyzing spatial variability, the regions were defined by soil P concentration and flow path of canal water. The highly-enriched region was 400 ha and the moderately-enriched region was 600 ha. Because of the small number of sampling

stations and the heterogeneity of the area, the reference region was only considered to be 20 ha. However, the total area of the wetland within the flow path was about 10,000 ha.

At each sampling station, multiple probes were installed either temporarily or permanently to measure redox potential from multiple soil depths (see below). The probes were constructed of platinum (Pt) welded to insulated copper wire and then sealed with liquid electrical tape and heat-shrink tubing. Enough copper wire was used so that the tops of the probes would be at least 30 cm above the water surface. Each probe was then tested using Orion ORP Standard for calibration. An Accumet calomel reference electrode was used to complete the circuit, and a +250 mV correction factor was added to the mV measurements made with a Hach Sension 2 portable pH/mV meter. Adjusted readings were within ± 5 mV of the ORP Standard. Field measurements were not corrected for pH because the ranges of pH values were small and circumneutral (Qualls et al., 2001).

Installation of Temporary Probes

From April 2006 to December 2006, five probes per sampling station representing soil depth increments of 2, 5, 10, 20, and 30 cm were installed and removed after 2-week intervals four times at M1, M2, and RS plots; five times at H1 and H2 plots; and eight times at RC plot. The probes were installed by carefully pushing the Pt tip of the probe into the soil until the appropriate depth was reached. The aboveground portions of the probes were then gathered and zip-tied to a vertical PVC pole. The probes at each sampling station were several cm from each other and sampling stations were approximately 50 m apart within a plot. Probes were installed in different areas of the sampling stations for each installation event, thus preventing spurious results from numerous holes in a small area. Water depth was recorded at each sampling station before redox potential was measured. The exposed copper end of each probe was cleaned with sandpaper to remove any corrosion before measurements were taken. To connect the probe to the volt meter, a wire connected to the meter's BNC port was attached to the probe with an alligator clip. The calomel reference electrode was either placed in the soil or water column depending on water depth to complete the circuit. Measurements were taken the day of probe installation and several other days within the 2-week period. Measurements were recorded after mV drift was < 0.1 mV per minute.

Installation of Permanent Probes

In March 2007, a single set of redox probes were installed at each sampling station. Construction was the same as for the temporary probes except that the permanent probes at each sampling station were bundled together using a PVC pipe. Four probes were threaded through the 50-cm-long PVC pipe and exited the pipe through holes drilled 5 cm apart such that the Pt tip of each probe extended from the pipe 2, 5, 10, or 20 cm. The interior of the PVC pipe was filled with aerosol insulation and allowed to dry. Probes were installed by gently pushing the Pt tips into the marsh surface until the PVC pipe lay flush with the peat surface. A t-connector was attached to the end of the PVC pipe to stabilize the pipe as it lay horizontally on the marsh surface with the probes pointing down into the soil. The PVC pipe was then covered by a terra cotta tile. The other ends of the probes were gathered and zip-tied to a separate vertical PVC pipe located approximately 1 m from the horizontal PVC pipe. The 30-cm soil depth was not measured with the permanent probes because of the high variability of measurements at 30 cm from the temporary probes. All probes were placed in areas with dense vegetation cover as opposed to open water areas so that measurements would capture the effect of root activity on soil redox potential.

To allow for a 1-month recovery period after installation of permanent probes, redox potential was first measured at all plots in April 2007. Measurements were then taken monthly for 1 year at each plot as described for the temporary probes. Water depths were noted for each sampling event. Pore water pH was measured using a YSI 600XLM sonde with an attached flow cell. Pore water was pumped into the flow cell from pore water wells installed to 30-cm depth. Pore water samples were collected at approximately the same time as redox measurements were made. Soil temperature was monitored using HOBO temperature loggers installed 5 cm deep in the peat.

Data Analysis

Data were evaluated for goodness-of-fit to a normal distribution. While the data did not fit a normal distribution, no transformation adequately improved fit, and therefore, data were not transformed. Standard deviations were calculated for both the temporary and permanent redox probe measurements for each depth increment at both the small (sampling station and plot) and large (region and wetland) scale for each sampling event to

determine the temporal and spatial variability of redox. Standard deviations were also calculated for data at sampling station, plot, region, and wetland scales to assess how increasing scale influences redox measurement variability. Data from permanent probes were analyzed using both analysis of variance (ANOVA) and analysis of covariance (ANCOVA) to determine the effect of soil phosphorus gradient, dominant vegetation, soil depth, and water depth on redox potential. Redox response to different variables was considered statistically significant at $p \leq 0.05$ and ecologically significant if redox values changed in categorization between oxidizing ($> +400$ mV), weakly reducing ($+400$ to $+200$ mV), moderately reducing ($+200$ to -100 mV), or strongly reducing (< -100 mV) (Mansfeldt, 2003). The data from the temporary probes were not included in any analysis of environmental factors' affect on redox potential. Instead, those data were regressed against "days since probe installation" to determine when measurements stabilized (when the regression line reached a plateau). This was assessed by regressing measurements against days of installation, fitting the best line, and noting when the line stopped decreasing.

RESULTS

Effect of Installation on Measurements from Temporary Probes

Using only redox measurements taken when water levels were above the marsh surface, and therefore not affected by changing hydrology, redox for each soil depth was regressed against days since probe installation to determine the magnitude of probe installation disturbance and the length of time required for probe stabilization and equilibration with the soil. The initial redox measurements immediately following probe installation averaged 200 mV higher than measurements taken 2 weeks later and were as much as 400 mV higher for some sampling events (Figure 2). Redox potential for the 2-cm depth stopped decreasing 8 days after probe installation and days 11, 12, and 13 were significantly lower than day 0 ($p < 0.001$). Measurements at the 5-cm depth, did not stabilize after 13 days even though the range in redox between installation and final day was, on average, low (95 mV) compared with those at the other soil depths that did stabilize. Redox potential stabilized after 9 days for the 10- and 30-cm depths, with days 9 and 11 being significantly lower than day 0 for 10-cm ($p < 0.001$) and day 11 being significantly lower for 30-cm ($p = 0.003$). It took redox potential 10 days to

stabilize at the 20-cm depth with days 11, 12, and 13 being significantly lower than day 0 ($p < 0.001$). Measurements at the 2-cm depth were the most affected by disturbance during installation, with an average difference between initial and final measurements of 157 mV, while the 30-cm depth was the least affected, with an average difference of 80 mV.

Temporal and Spatial Variability of Measurements from Permanent Probes

Temporal Patterns and Variability. Redox measurements were similar over time except for April 2007 (Figure 3). Redox potential was approximately 400 to 700 mV higher in April 2007 than for all following months for the 2-, 5-, and 10-cm soil depths and between 50 and 200 mV higher for the 20-cm depth (Figure 3). This pattern corresponded to low water depths in WCA 2A, when the water table was near or below the marsh surface in April 2007 as opposed to water levels being above the marsh surface the remainder of the sampling period (Figure 4). During drawdown, the water table never dropped below a soil depth of 13 cm. A peak water depth of 80 cm above the marsh surface was reached in October 2007, with the highest water levels in the reference plots. Redox potential did not correspond to changes in pore water pH or soil temperature over time (Figure 4).

During low water conditions, the redox measurement standard deviations ranged from 9 to 412 mV and averaged 220 mV, while during flood conditions, regardless of water level, the standard deviations ranged from 1 to 270 mV and averaged 57 mV (Figure 3 and 4). This indicates that redox variability increases during low water conditions. The increase in variability of redox measurements during low water condition was greatest for the 5-cm depth (standard deviation was 307 mV) and the least for the 20-cm depth (standard deviation was 176 mV).

Spatial Patterns and Variability. The spatial patterns of redox potential were examined along the soil profile (small-scale) and nutrient gradient (large-scale) (Figure 5 and 6). There was no significant difference in redox potential between plots individually. However, when plots were grouped by region, the moderately-enriched region had higher average redox potential (-134 mV) than the highly-enriched or reference regions (-185 mV for both) at all soil depths regardless of water level ($p = 0.027$) (Figure 5).

There were no consistent trends in redox potential moving down the soil profile and no significant

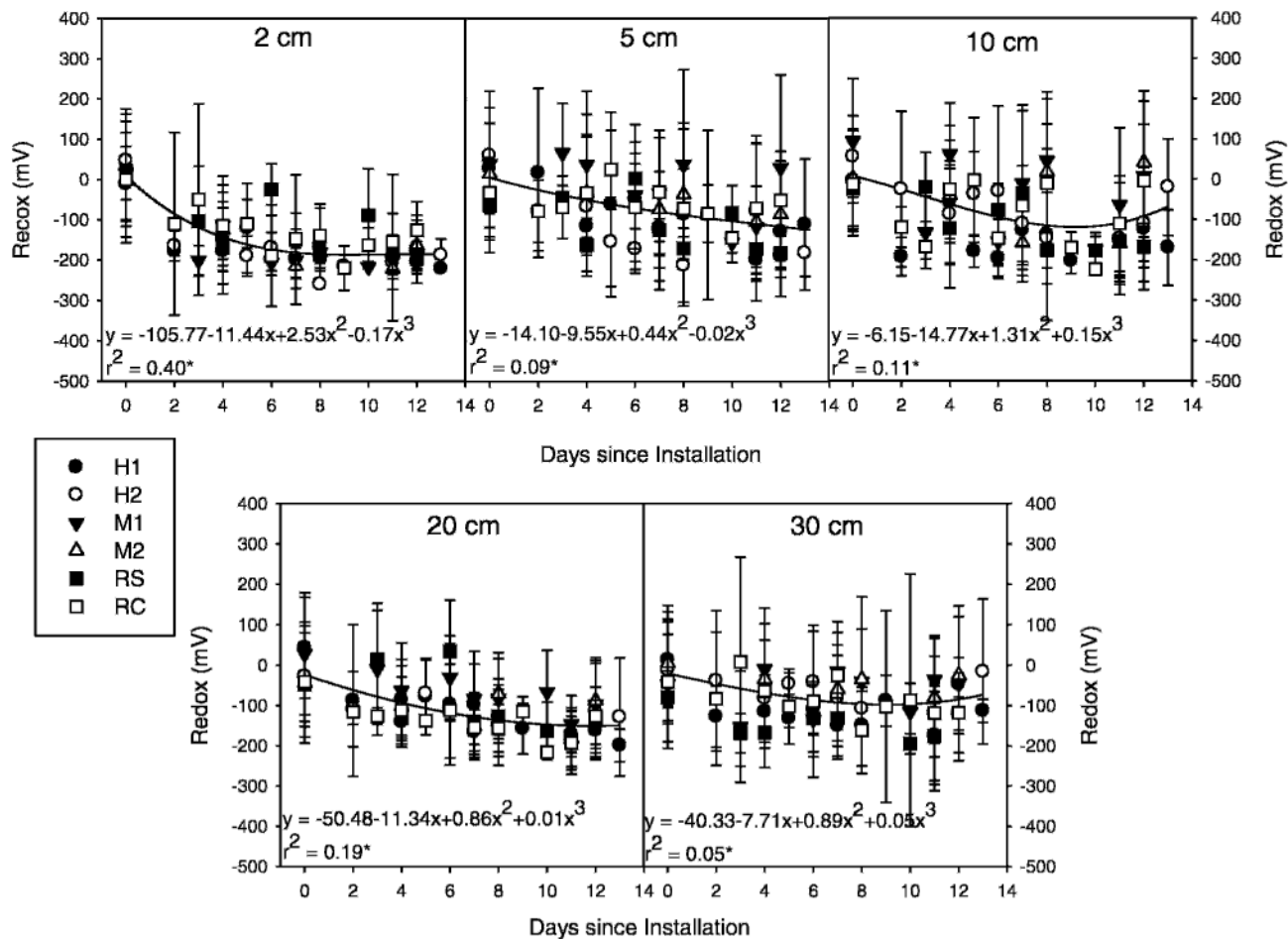


Figure 2. Redox measurements from temporary probes by soil depth and averaged across plots. Redox measurements for each 2 week-installation event between July and December 2006 were categorized by “days of installation” and averaged. April 2006 measurements were not used due to low water conditions. Error bars are one standard deviation. Significant ($\alpha = 0.05$) r^2 values are indicated with an *.

difference in redox at 2-, 5-, and 10-cm soil depth when data were categorized by region, plot, or dominant plant species (Figure 6). However, redox potential decreased at depths > 10 cm below the soil surface, averaging about 30 mV lower for the 20-cm depth than for the 2-, 5-, and 10-cm depths. The average redox potential at 20-cm depth (-168 mV) was significantly lower than redox potential at 2-cm depth (-123 mV) ($p = 0.027$). Redox potential at 20 cm for the reference region was lower than -200 mV, which is in the range where methanogenesis is possibly the dominant microbial process (Atlas and Bartha, 1993). The difference in redox potential with depth at the reference plots may be ecologically significant as it may indicate a shift in the dominant microbial process; however, we did not measure microbial activity during this study.

Spatial variability was assessed for all depths combined and for the 10-cm soil depth only (10 cm was considered representative of the near-surface

depth but less likely to vary with water table fluctuation) for multiple spatial scales including sampling station (3–8 ha), plot (9 ha), region (~500 ha), and total area sampled (~10000 ha). At the sampling-station scale, redox potential at the reference plots was the least variable, followed by the moderately-enriched plots (Figure 7). As the scale increased to the plot level, variability increased for the moderately-enriched plots but decreased for the highly-enriched plots. At the regional and landscape scale, the standard deviation for redox measurements stabilized around 155 mV for values from all depths combined and around 160 mV for values from the 10-cm soil depth. The reference region was significantly less variable than the highly-enriched region ($p = 0.012$ for all depths combined and $p = 0.031$ for 10-cm depths).

Redox variability decreased with soil depth (Figure 6). The 2-cm depth measurements were the most variable, while the 20-cm depth measurements

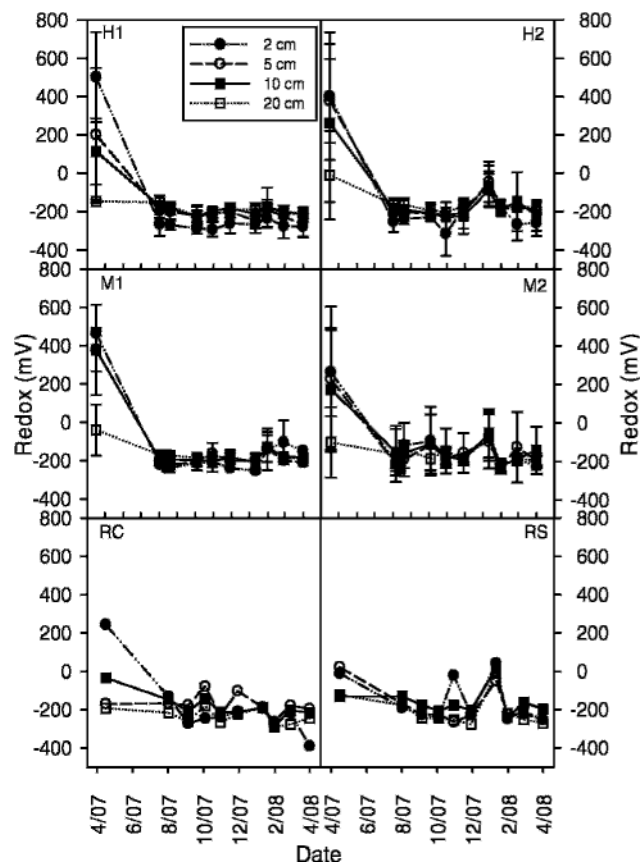


Figure 3. Redox measurements from permanent probes for 2-, 5-, 10-, and 20-cm soil depths at different plots from April 2007 to April 2008. Error bars are one standard deviation.

were the least ($p < 0.001$). There was no significant difference in variability along the soil profile between regions or plant communities.

The standard deviations of redox measurements for both the permanent and temporary probes were also assessed for the small spatial scale (each plot and sampling event) and the large scale (all plots for each sampling event) for measurements taken during flood conditions. The standard deviations were then averaged to assess overall variability. For the permanent probes, standard deviation ranged from 37.4 to 91.4 for the small scale and 53.9 to 108.4 for the large scale (Table 1). The 20-cm soil depth had the least variability in redox measurements but the difference between the soils depths was small. These results were stable compared to those from the temporary probes. For the temporary probes, only the “stabilized” measurements were used for calculating standard deviations, and therefore variability in redox could not be attributed to probe installation disturbance. At the small scale, the redox measurements at 5-cm depth were the most variable (Table 1). Measurements at the 2- and 20-cm depths

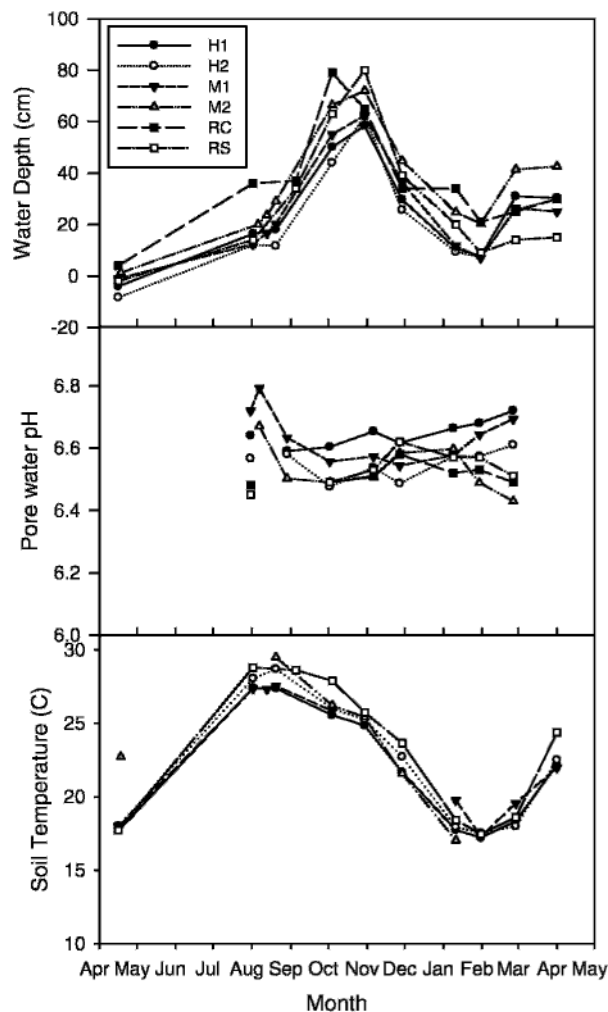


Figure 4. Average water depth in relation to marsh surface, pore water pH, and soil temperature over time for each plot. All measurements were taken from April 2007 to April 2008.

were the least variable. The variability of measurements from the permanent probes was significantly less than from the temporary probes for each depth (Table 1). Because of their high variability, measurements from the temporary probes were excluded from ecological analysis.

Environmental Variables Influencing Redox Potential

Hydrology. When the water levels were at or below the marsh surface, redox potential increased exponentially up to 600 mV for the 2-, 5-, and 10-cm soil depths (Figure 5). At the 20-cm soil depth, which was constantly saturated, redox averaged -92 mV during drawdown and -189 mV during flooded conditions, a significantly smaller redox response to water level changes than for other soil depths ($p =$

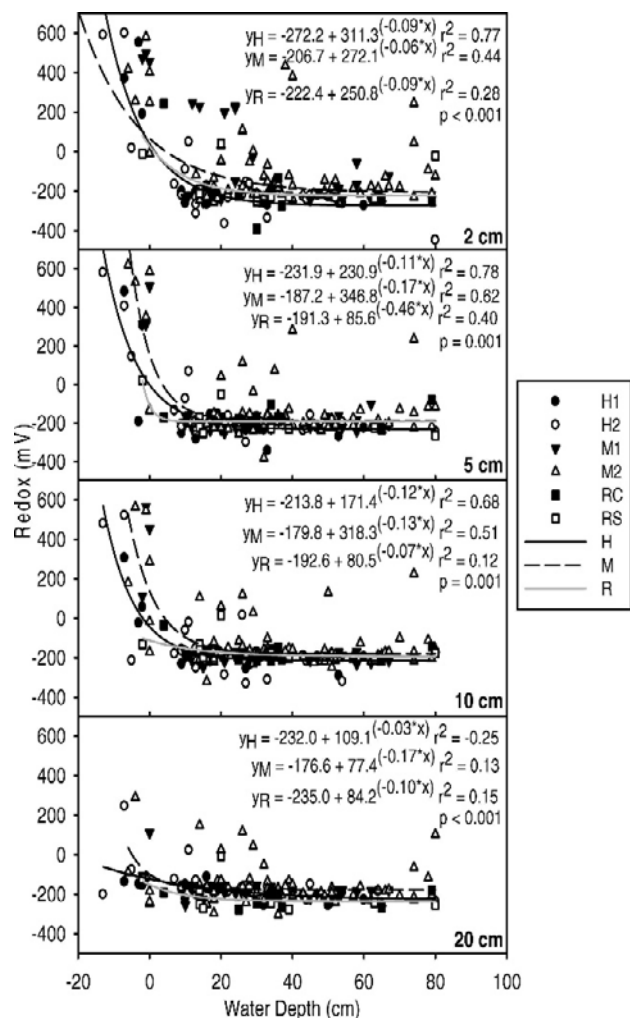


Figure 5. Redox potential at 2-, 5-, 10-, and 20-cm soil depths in relation to water depths (cm). Regression lines are for each region at each depth. Redox potential was measured using the permanent probes from April 2007 to April 2008.

0.05). At water depths > 10 cm, redox potential for each soil depth stabilized around -200 mV. Redox became significantly higher during low water conditions when the water table was at 4 cm for the 2-cm soil depth, 0 cm for the 5-cm soil depth, and -1 cm for the 10-cm soil depth ($p < 0.001$ for all). Water depth had no effect on redox potential at the 20-cm soil depth; however, water levels never dropped more than 13 cm below the marsh surface.

Exponential equations that relate water table depth and redox potential where “a” in the equation $y = a + b(-c^*x)$, represents where redox potential stabilized regardless of how high water levels increase, b represents the average redox during low water conditions, and c is the proportional change in redox as water levels increase (Figure 5). At the 2-cm soil depth the highly-enriched region had a

higher average redox potential during low water conditions than the other regions but as water levels increase, redox potential decreases significantly faster at the highly-enriched region than the other regions ($p = 0.015$). Therefore, the moderately-enriched region had a higher average redox potential ($p = 0.016$). For the other soil depths, the sensitivity of redox potential to changing water depths at the highly-enriched region was insignificantly higher compared to the other regions, while the average redox potential was insignificantly higher for the moderately-enriched region compared to the other regions. However, the equations for each region at each soil depth are significantly different from each other ($p \leq 0.001$ for all) (Figure 5).

Soil P Gradient. During flood conditions, redox measurements for each plot fluctuated around -200 mV regardless of location along the P gradient (Figure 3 and 5). When water levels were below the marsh surface, however, redox potential was higher in the moderately-enriched regions than in the highly-enriched regions (Figure 5). This was especially true for the 5-cm (329 mV and 289 mV, respectively) and 10-cm (280 mV and 188 mV, respectively) depths. The average redox potential in the moderately-enriched region (-134 mV) was significantly higher than in the reference (-184 mV) and highly-enriched regions (-185 mV) ($p < 0.001$) with water depth as a covariate (Figure 5). However, the redox potential at the highly-enriched region was more sensitive to changes in water depth than the other regions at the 2-cm depth (steeper slope ($p < 0.001$)) but the sensitivity decreased with depth (Figure 5). The P gradient had no effect on changes in redox potential at different soil depths (Figure 6). Different soil P fractions (phosphate, calcium-bound P, and iron-bound P) also did not correlate with redox potential, nor did soil C, N, or sulfur concentrations (data not shown). Variability of redox measurements was lowest in the reference region, but there was no consistent difference in variability in the enriched regions (Figure 6).

Vegetation Community. Each sampling station was either dominated by cattail, sawgrass, or a nearly equal mix of the two species. Data from each sampling station were categorized based on the dominant vegetation community to assess whether vegetation influenced redox potential. Redox potential in sawgrass communities was generally higher at all soil depths than cattail or a mixed community (Figure 6) but differences were not significant. Redox potentials in soil dominated by each species were in the range where sulfate reduction is the dominant microbial process. Sawgrass-dominated

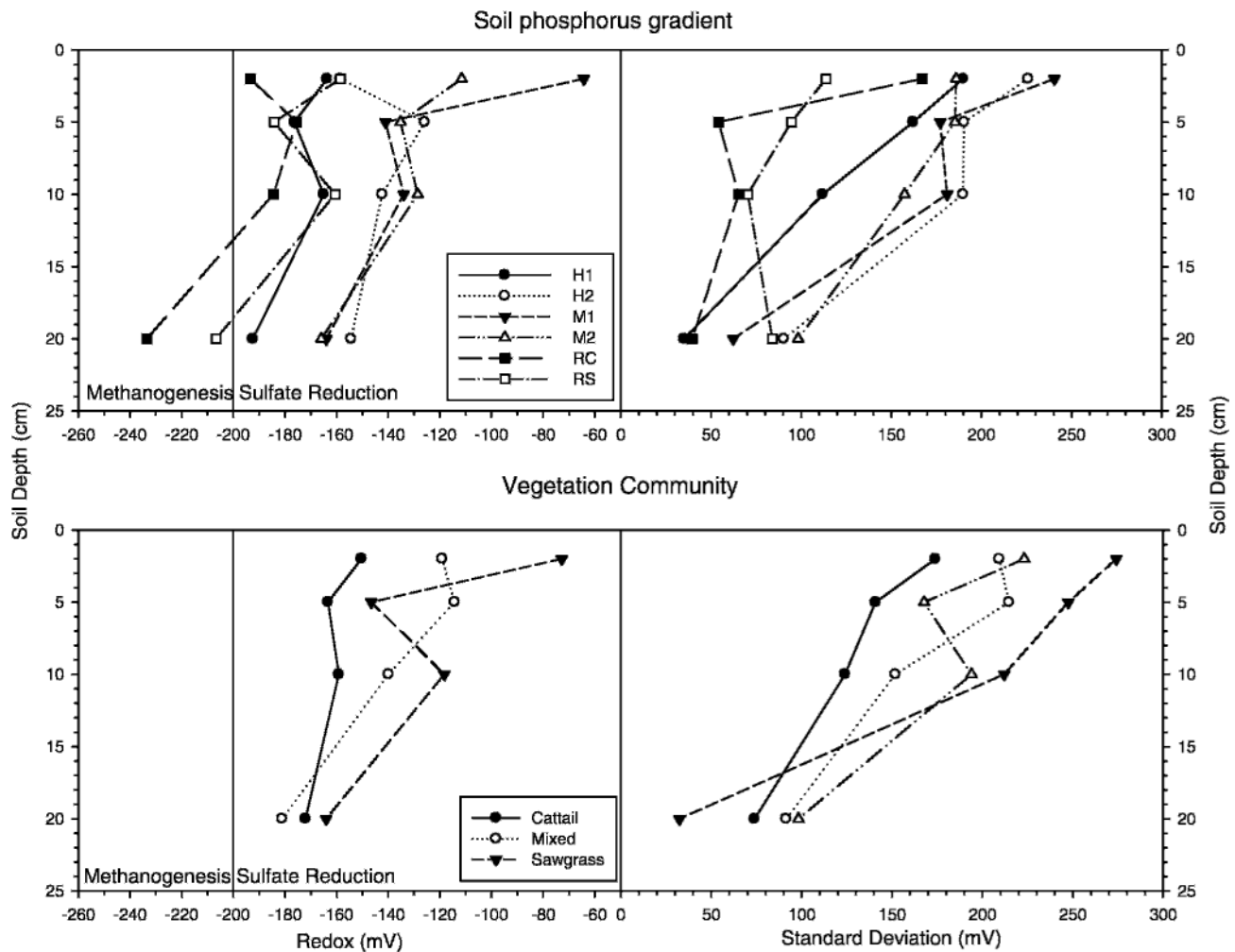


Figure 6. Redox potential at different depths for plots representing a phosphorus gradient and each vegetation community and the standard deviation for those measurements. Redox potential was measured using permanent probes from April 2007 to April 2008.

areas tended to exhibit greater variability in redox measurements than either mixed or cattail-dominated areas, and variability decreased with depth (Figure 6).

DISCUSSION

Temporal Patterns and Variability

Redox potential responded strongly to changes in water level by exponentially decreasing as water levels increased, as hypothesized. Water level is controlled primarily by the wet/dry seasons of south Florida and/or water management needs. Others have also found water levels to be the main variable explaining redox potential in wetlands, although direct comparisons to those studies is not possible due to the differences in environmental conditions (Austin and Huddleston, 1999; Mansfeldt, 2003). The effect of hydrology on soil redox potential is

indirect and results from the reduction in oxygen diffusion through saturated soil (Gambrell and Patrick, 1978). As saturation persists, oxygen is consumed by microbial activity and redox potential decreases. As in our study, de Mars and Wassen (1999) reported nonlinear correlations between water table and redox potential with the degree of nonlinearity depending on marsh type and quality of peat and its influence on capillarity. This was similar to our study, where the soil P gradient influenced how sensitive redox potential was to changing water depths with the redox potential in the highly-enriched region decreasing more rapidly than other regions as water levels increased. We also found that the degree of nonlinear response depended on soil depth. This indicates that the factors that influence redox (decomposition, biological oxygen demand) respond faster to hydrology in near surface highly-enriched soils.

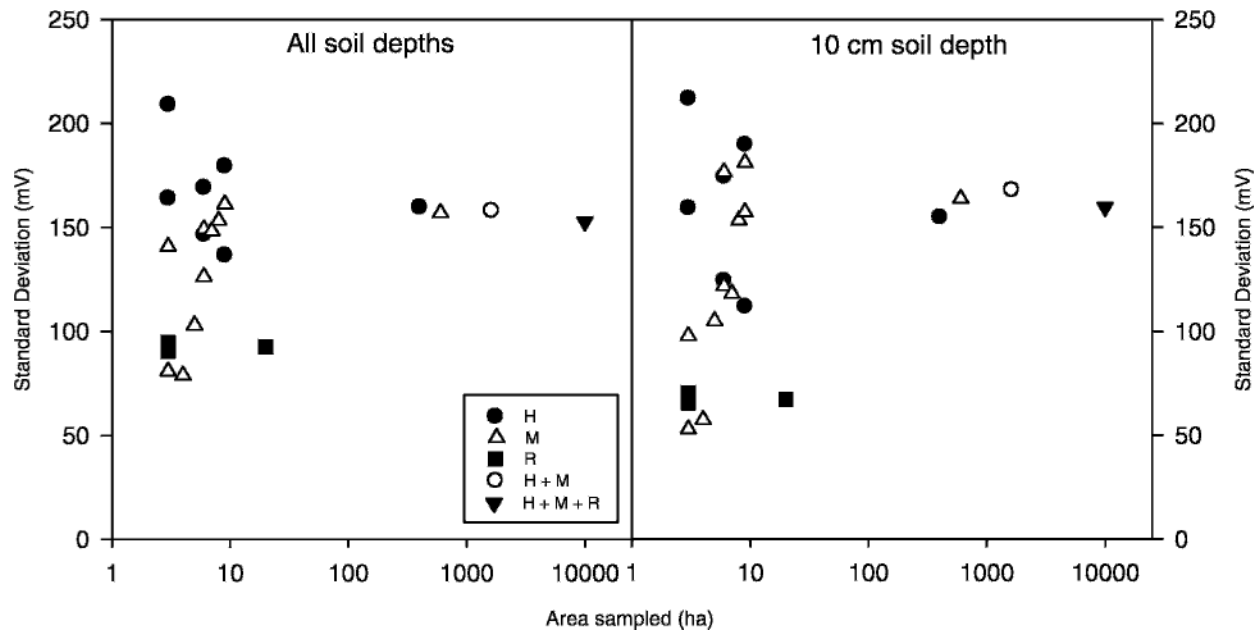


Figure 7. Redox potential standard deviations for different spatial scales for all soil depths together and for 10-cm soil depth only. Redox potential was measured using permanent redox probes from April 2007 to April 2008.

The effect of water level on redox potential is similar in different types of marshes (Table 2). When water levels are high (> 0 cm above marsh surface) and soil is saturated, redox potential ranged between -200 to +100 mV in the root zone. When water levels are low (< 0 cm above marsh surface), redox potential increases and its range also increases from -170 to +750 mV. The changes in water levels in

WCA 2A are based on south Florida’s wet/dry season, with low water in the spring and high water in the fall. In contrast, water levels of tidal marshes fluctuate on a daily or twice-daily basis with an influx of new electron acceptors from the estuary and a removal of microbial metabolic toxins, adding to the complexity of redox measurements (Seybold et al., 2002).

Table 1. Average of Standard Deviations for the temporary and permanent installation of redox probes at different soil depths at each plot separately (small scale) and for all plots together (large scale) for each sampling event. There was no 30-cm probe for the permanent installation.

Soil Depth (cm)	Temporary Installation Standard Deviation	Permanent Installation Standard Deviation	P-value
Small scale			
2	66.5	91.4	0.039
5	117.8	48.6	< 0.001
10	103.2	51.6	< 0.001
20	82.0	37.4	< 0.001
30	115.1		
Large scale			
2	75.9	108.4	0.038
5	135.5	60.2	< 0.001
10	116.7	63.2	< 0.001
20	91.5	53.9	0.002
30	119.1		

According to Mansfeldt (2003), temporal variability in redox measurements were greatest when the water table fluctuated at the marsh surface and were least variable with either continuously aerated or saturated conditions. During low-water conditions, our study found that variability resulted from microtopographic differences between sampling stations within a plot such that water levels varied by several centimeters between sampling stations. As a consequence, near-surface soils had different saturation levels, which increased both the temporal variability and the small-scale spatial variability in redox potential. Overall, temporal patterns and variability of soil redox in wetlands are most closely linked to water levels but the magnitude of response to water level changes is tied to spatial characteristics.

Spatial Patterns and Variability

It is commonly believed that redox measurements are highly variable (Cogger et al., 1992; Eshel and Banin, 2002; Yang et al., 2006; Fiedler et al., 2007). At the large scale, variability is thought to result

Table 2. Redox measurements (mV) in relation to various water depth and nutrient status in different marshes. High water depths refers to water above the marsh surface, while low water depths are below the marsh surface. High nutrient status is either > 1 g P/kg or nitrogen fertilized soil, moderate is 0.6–1 g P/kg soil, and low is < 0.6 g P/kg soil.

Marsh Type	Soil Depth (cm)	Water Depth		Nutrient Status			Source
		High	Low	High	Moderate	Low	
Tidal Saltwater	1			+350		0	Howes <i>et al.</i> , 1981
	5			+25		-75	
	15			-50		-100	
	30			-100		-125	
Impounded Freshwater	12.5	-200 – +100	>+290	-150	-50	-100	Qualls <i>et al.</i> , 2001 This study
	2	-250 – +100	>+250	-150	-120	-175	
	5	-250 – +100	+200 – +250	-150	-135	-180	
	10	-250 – +100	+150 – +200	-150	-130	-170	
	20	-250 – +100	-100 – -50	-175	-165	-220	
	10	-200 – +100	-50 – +750				
Restored Freshwater	30	-200 – +100	-170 – +200				Niedermeier and Robinson, 2007
	20	-200 – +100	-100 – +500				
Tidal Freshwater	50	< -150	< -150				Seybold <i>et al.</i> , 2002
	15	-122	+648				
Freshwater Peatlands							de Mars and Wassen, 1999

from environmental gradients related to C quality and electron acceptor availability (Fiedler *et al.*, 2007). At the small scale, variability is thought to be caused by the heterogeneity of the soil matrix either through root growth or soil textural changes (Yang *et al.*, 2006). However, we found variability of measurements to be small at both spatial scales when the variation due to water depth was removed.

At the large scale, the nutrient status of different regions in WCA 2A affected soil redox potential, as hypothesized. When the effect of water level on redox potential was considered a covariate, the moderately-enriched region had higher redox potentials, while the highly-enriched region was more sensitive to changing water depths (greater decrease in redox potential with same increase in water depth). Qualls *et al.* (2001) did not find any significant difference between these identical regions; however, they only measured at the 12.5 cm depth (Qualls *et al.*, 2001). We found that the biggest differences between regions were in the near surface soil layers, where the addition of leaf litter of different quality and differences in decomposition rates are most pronounced (Qualls *et al.*, 2001). While Howes *et al.* (1981) found a difference in redox potential between a fertilized and unfertilized salt marsh (Table 2), they found higher redox potential with enriched soils. They attributed the difference to the increased vigor of the plants and the greater radial oxygen loss from the roots in the fertilized plot. As part of a separate study, we found root production was greater and decomposition slower in the moderately-enriched region than the highly-enriched region (unpublished data); therefore the combination of slower decay and higher root production may explain why redox potential is highest in the moderately-enriched region.

Differences in redox potential of different soil depths in the present study reflected water table location but not species-specific root dynamics. During saturated conditions, redox potential did not change with soil depth but when the water table was below the marsh surface, a small depth gradient emerged, most likely due to the introduction of oxygen to the upper soil layers. Roots can also influence oxygen availability in the soil. Cattail roots are more porous than sawgrass roots and have greater radial oxygen loss to the rhizosphere (Chabbi *et al.*, 2000). However, near plant roots, oxygen saturation is around 30% (about +250 mV) and decreases to near 0% (< +200 mV) within 100 μ m (Laskov *et al.*, 2006). Therefore the oxidized rhizosphere is confined to a very small area around the roots. The quantity of live roots then becomes an important factor for detecting the increase in redox

associated with radial oxygen loss. In our plots, although differences were small, cattail root growth was greater from 0 to 10 cm below the soil surface, while sawgrass had greater root growth from 10 to 20 cm. The difference in root growth between species did not translate into differences in redox potential at 0 and 20 cm below the soil surface as we had hypothesized. However, the variability of field conditions and our measuring technique may not have allowed us to detect these fine-scale differences between species. When comparing redox potentials between near-cattail and near-sawgrass, Qualls et al. (2001) did not find differences between 0 and 20 cm, but did between 20 to 40 cm soil depths. Litter quality differences between cattail and sawgrass affect decomposition rates (Davis, 1991), which should also affect redox potential, but we did not find this to be the case in this study.

Redox Measurements from Temporary vs. Permanent Probe Installations

Probe installation substantially disturbed the soil, resulting in large increases in redox measurements. Although most researchers recognize this effect of probe installation, they report wide ranges for the time required until redox measurements equilibrate or stabilize (Eshel and Banin, 2002). This study found that readings stabilized within 1 to 2 weeks depending on soil depth but the variability between sampling stations was high. Readings from the permanent probes had much lower variability and were more useful for ecological comparisons than those from the temporary probes.

However, two types of problems can occur with long-term installation: electrode breakdown and corrosion (or poisoning) (Mansfeldt, 2003). Electrode breakdown is caused by electrode rupture or waterproof resin leakage, especially under water-saturated conditions (Mansfeldt, 2003). Probe corrosion can occur in several ways. In oxygen-dominant environments, Pt adsorbs O_2 creating PtO, making the probe act like a hydrogen electrode that measures pH instead of redox (Mansfeldt, 2003). In high sulfide environments, PtS can slowly form on electrodes. PtS results in lower redox measurements and slow electrode response (Mansfeldt, 2003). However, after three years in a high-sulfide environment, electrodes had not developed detectable PtS corrosion in a diked marsh in northern Germany (Mansfeldt, 2003). After five years, Austin and Huddleston (1999) found no evidence of probe corrosion in a freshwater wetland and had only 3% probe failure. Spot checks of our probes revealed no visual evidence of PtS corrosion

nor were any measurements abnormally low. PtO corrosion is also unlikely because the marsh was flooded for most of our study. Only one of our probes began giving suspect measurements toward the end of the study. The suspect measurements were removed from any analysis. Therefore, soil redox variability detected during this study is most likely the result of environmental factors and not probe failure.

CONCLUSIONS

Redox potential increased exponentially as water levels fell below 5 cm above the marsh surface. The degree of redox response to water table changes decreased with increased soil depth, varying more near the marsh surface during low water conditions. Redox potential also varied as a function of soil phosphorus. While the moderately-enriched region had higher redox potentials, the highly-enriched region exhibited a greater decrease in redox potential with same increase in water depth. However, redox potential did not differ between areas dominated by different plant communities, which might be due to our measuring techniques not being sensitive enough to detect radial oxygen loss from roots. The permanent probe installations were better for assessing ecological influences on redox potential than the temporary probe installations because of the lower variability in measurements during each sampling event.

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