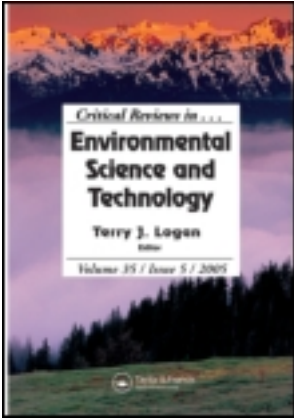


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Water Conservation Area 1: A Case Study of Hydrology, Nutrient, and Mineral Influences on Biogeochemical Processes

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Water Conservation Area 1: A Case Study of Hydrology, Nutrient, and Mineral Influences on Biogeochemical Processes

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At the northern tip of the remnant Everglades, Water Conservation Area 1 is the only remaining softwater peatland in the ecosystem. The spatial pattern of altered hydrology, anthropogenic nutrient, and mineral enrichment is distinct, with biogeochemical processes driven by a north-south hydrologic gradient combined with west-east nutrient and mineral gradients. Hydrology effects on carbon cycling are evident by the 10–20% lower average soil carbon concentrations in the drier oxidizing regions of the north, compared with the ponded environment in the south. Elevated nutrient and mineral inputs also increase carbon loss by causing changes in species composition, substrate quality, and microbial activity. Water management may be optimized to limit mineral intrusion and peat oxidation, while also meeting water depth requirements for habitat and wildlife, such that ecological tradeoffs are minimized.

KEYWORDS: A. R. M. Loxahatchee National Wildlife Refuge, conductivity, ecosystem restoration, Everglades, peat loss, phosphorus enrichment, water management

INTRODUCTION

At the northern extent of the remnant Everglades, Water Conservation Area 1 (WCA-1), encompasses 59,000 hectares and historically received the majority of water from rainfall (Parker et al., 1955). Unlike other areas of the Everglades, where there are distinct point source inputs, surface water generally moves around the marsh edges via the perimeter (L7, L39, and L40)

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canals. As a result of this limited interaction with mineral-rich canal water, WCA-1 is the sole remaining softwater ecosystem in the Everglades. Additionally, this area is unique in that it has the deepest peat layer of any region of the Everglades. In a recent compilation of multiple system-wide surveys, Scheidt and Kalla (2007) documented median peat depths of 2.7 m (8.7 ft), compared with an overall Everglades median soil thickness of 0.70 m (2.3 ft). Combined with an average carbon (C) content of 473–492 g/kg in the top 0–30 cm of soil (Corstanje et al., 2006), WCA-1 is the highest C storage reservoir of the Everglades landscape. As a result, the key to understanding ecosystem biogeochemistry is to examine the factors that drive C cycling.

The biogeochemistry of WCA-1 is driven by three distinct gradients: hydrologic, mineral, and nutrient (Chang et al., 2009). The topography shows ground elevations are highest in the northwest and lowest in the south (Figure 1). It is enclosed within 90 km of levees and canals, with rain accounting for 54–69% of the surface water budget (South Florida Water

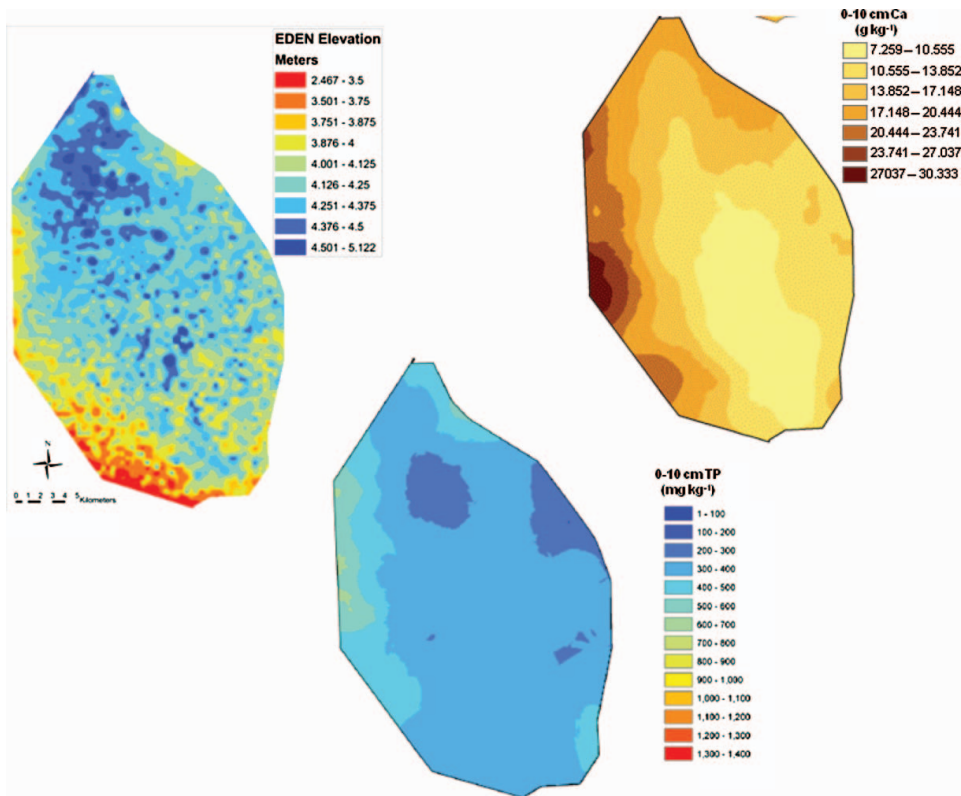


FIGURE 1. Hydrologic, nutrient, and mineral gradients as evident in topography and soil chemistry. Sources: Elevation from the Everglades Depth Estimation Network produced by the U.S. Geological Survey (EDEN; sofia.usgs.gov/eden), TP and Ca (modified from Corstanje et al., 2006). (This figure is available in color online.)

Management District, 1992; Surratt et al., 2008). The combination of topography, confinement within a perimeter levee, and water management results in the northernmost extent of the system experiencing more frequent dry periods, while the southern area ponds extensively.

For the past five decades, phosphorus (P) and mineral-enriched surface waters entered the area via pump station S-5A at the northern tip and S6 from the west. Presently S-5A surface water inflows first pass through constructed wetlands, Stormwater Treatment Area (STA) 1 west and more recently STA-1 east, prior to discharge into the perimeter canal. The S6 no longer discharges into WCA-1 as surface waters are diverted to STA-2. The majority of water exits WCA-1 through a series of water control structures, the S-39 and S-10s, at the southern end. A recent study of 2004–2006 water quality data suggests that perimeter marsh soils with elevations <4.9 m are more likely to experience canal water intrusions (Surratt et al., 2008). The extent of canal water intrusion into the marsh is a function of the relative inflow and outflow rates, the duration of the canal inflows (Surratt et al., 2008) and the relationship between canal and marsh stages. The canal waters are higher in nutrients and minerals than the marsh interior; thus, intrusions into the adjacent marsh have created nutrient and mineral gradients (Figure 1). In this paper we address the influence of these inputs, by (a) providing context to the biogeochemical changes the system has experienced, (b) documenting spatial characteristics, and, because C accumulation is critical to peatland sustainability, we will (c) discuss causative links between these changes and C cycling.

COMPARISON OF WCA-1 WITH REMNANT EVERGLADES

There is strong environmental evidence to suggest that the surface water chemistry of the northern Everglades historically had low mineral and nutrient contents. Prior to drainage, at the start of the 20th century, the major hydrologic sources were precipitation and overland runoff emanating from the watershed, primarily Lake Okeechobee. The ion chemistry of precipitation in South Florida is dominated by low concentrations of sea salt aerosols (<2.0 mg L⁻¹) because of the close proximity to the Atlantic Ocean and Gulf of Mexico (Grimshaw and Dolske, 2002; Guentzel et al., 1998). Present day wet-dry deposition rates are likely reflective of the low historic values (e.g., 690–840 mg sodium m⁻² yr⁻¹ and 1100–1190 mg chloride m⁻² yr⁻¹; Guentzel et al., 1998) based on a rainfall average of 150 cm yr⁻¹ (Duever et al., 1994). In addition, the regional geology of the surrounding watershed likely resulted in runoff low in minerals and nutrients. The mineral chemistry for the tributaries draining into Lake Okeechobee prior to construction of the Central and Southern Florida Flood Control Project (C&SF) project were low (Parker et al., 1955; estimated specific conductivity <100 μ S cm⁻¹)

and continue to remain low today ($<200 \mu\text{S cm}^{-1}$). The ion concentration of the lake during this period was 3 times greater than its tributaries (estimated $<300 \mu\text{S cm}^{-1}$), but it has been suggested that the building of the Herbert Hoover dike around the lake in 1937 may have increased ion concentrations by allowing mineral-rich groundwater to enter the lake (Parker et al., 1955). Alternatively, the ion chemistry of the lake in 1913 is similar to modern-day values suggesting that lake may have always been elevated relative to its tributaries or influence by early drainage efforts (Dole, 1914).

The low ion content of rainfall and upstream sources, in combination with thick peat deposits ($>3 \text{ m}$) isolating much of the peatland from the surficial groundwater system would have sustained a low pH and low mineral marsh chemistry in WCA-1. Whereas nutrient enrichment is coupled with the development of the Everglades Agricultural Area (EAA), mineral enrichment is additionally linked to the construction of canals which exposes the limestone bedrock to accelerated dissolution and increases the discharge of ion rich groundwater (Harvey and McCormick, 2009).

To highlight the present-day unique characteristics of WCA-1, it is essential to place its biogeochemistry in context of other regions in the Everglades. To minimize the effects of water management and compartmentalization effects on biogeochemistry, all regional comparisons are based on sites located within the marsh interior, distant from canal water and areas that do not tend to pond. However, we do recognize that in some regions, water and soil chemistry has been significantly impacted throughout the entire system due to agricultural and urban runoff and the flow of those discharges across the system. For example, since the 1950s, the decadal averages of specific conductivity for WCA-1 have remained low with little variability, $92\text{--}131 \mu\text{S cm}^{-1}$ whereas WCA-2A have been higher and more variable, $621\text{--}1235 \mu\text{S cm}^{-1}$. However, paleoecological data suggest that WCA-2A was historically a softwater wetland (Slate and Stevenson, 2000), so these are not true historical comparisons, but represent present-day differences. The majority of surface waters of the Everglades are buffered at neutral to alkaline pH, on average 7.2; in contrast, WCA-1 is slightly acidic with an average pH of 6.3 (Table 1; Swift and Nicholas, 1987). Associated with lower pH, WCA-1 also has low mineral ion concentrations (Table 1; Hagerthey et al., 2010). With an average concentration of 5.6 mg L^{-1} , calcium (Ca) is an order of magnitude lower in WCA-1 compared to WCA-2A and Everglades National Park (ENP). Organic C levels are intermediate between those in WCA-3 and 2A, while nitrogen (N) values vary as a function of speciation. As expected, because the Everglades is a P-limited ecosystem, P concentrations are low throughout all regions (Table 1).

Soils provide additional evidence for the low mineral content of WCA-1 (Table 2). The high organic nature of WCA-1 is evident with a loss on ignition average of 96%, compared with 81–91% in other regions. Average Ca contents are four- to sevenfold lower than other areas and magnesium

TABLE 1. Means and standard errors for select parameters measured on surface water collected at interior marsh stations throughout the Everglades, 1999–2008

Parameter ^a	Units	WCA-1 (Lox8)	WCA-2 (CA-215)	WCA-3 (CA-315)	ENP (P33)
Spec Cond.	$\mu\text{S cm}^{-1}$	114 ± 4.08	897 ± 14.7	348 ± 6.66	507 ± 12.4
pH		6.3 ± 0.04	7.6 ± 0.02	7.2 ± 0.02	7.5 ± 0.02
NO _x -N	$\mu\text{g L}^{-1}$	7 ± 1.5	5 ± 0.4	5 ± 1	20 ± 2.5
NH ₄ -N	$\mu\text{g L}^{-1}$	15 ± 3.39	37 ± 2.7	26 ± 3.7	51 ± 7.1
TKN	mg L^{-1}	1.4 ± 0.04	2.0 ± 0.03	0.98 ± 0.02	1.3 ± 0.04
SRP	$\mu\text{g L}^{-1}$	3 ± 0.2	2 ± 0.1	2 ± 0.1	3 ± 0.1
TP	$\mu\text{g L}^{-1}$	10 ± 0.3	6 ± 0.2	7 ± 0.2	7 ± 0.3
SiO ₂	mg L^{-1}	3.3 ± 0.21	19 ± 0.47	7.4 ± 0.24	—
Na	mg L^{-1}	13 ± 0.45	85 ± 2.1	18 ± 0.54	33 ± 1.39
K	mg L^{-1}	0.6 ± 0.03	6.7 ± 0.14	2.1 ± 0.06	2.9 ± 0.11
Ca	mg L^{-1}	5.6 ± 0.19	56 ± 0.86	45 ± 0.76	56 ± 0.85
Mg	mg L^{-1}	1.8 ± 0.05	23 ± 0.45	3.9 ± 0.11	9.7 ± 0.31
Cl	mg L^{-1}	22 ± 0.89	123 ± 3.43	28 ± 0.83	49 ± 2.1
TOC	mg L^{-1}	24 ± 0.65	34 ± 0.75	16 ± 0.29	—

^aSouth Florida Water Management District database (DBHydro) from January 1, 1999 through Dec 31, 2008.

(Mg), iron (Fe), and aluminum (Al) contents are lower in WCA-1, with Fe and Al contents an order of magnitude lower than those in ENP. While Fe and Al contents tend to be higher in acidic peatlands, the particularly high Fe contents documented along the eastern boundary of WCA-1 are thought likely due to inputs from the adjacent ACME basin (Corstanje et al., 2006), an area (approximately 3,513 ha) of low-density development with rural residential lots, horse ranches, and plant nurseries.

SPATIAL CHEMICAL CHARACTERISTICS

Nitrogen and P

Following C, N is the most abundant element in WCA-1. Nitrogen contents in interior surface soils average 37 g kg⁻¹ (Table 2), ranging from 17 to 46 g kg⁻¹

TABLE 2. Chemical properties of interior marsh soils (0–10 cm) in different regions of the Everglades

Parameter	WCA-1	WCA-2A	WCA-3A	ENP
Bulk density (g cm ⁻³)	0.06 ± 0.01	0.09 ± 0.01	0.08 ± 0.00	0.14 ± 0.01
Loss on ignition (%)	96 ± 0.51	83 ± 6.88	91 ± 0.39	81 ± 3.65
Total P (mg kg ⁻¹)	372 ± 31	321 ± 34	384 ± 26	401 ± 47
Total N (g kg ⁻¹)	37 ± 1.8	29 ± 2.8	33 ± 1.9	32 ± 1.1
Total C (g kg ⁻¹)	488 ± 5.3	404 ± 28	423 ± 19	409 ± 21
Total Ca (g kg ⁻¹)	8.1 ± 0.91	61 ± 33	29 ± 1.8	32 ± 6.2
Total Mg (mg kg ⁻¹)	816 ± 55	4548 ± 380	1049 ± 55	2118 ± 281
Total Fe (mg kg ⁻¹)	1615 ± 443	2140 ± 160	5215 ± 411	18922 ± 2687
Total Al (mg kg ⁻¹)	1384 ± 211	1811 ± 204	2769 ± 128	1904 ± 5075

Note. Based on $N = 5$ from interior of each region. Data source: Reddy et al., 2005.

(Corstanje et al., 2006). Nitrogen contents are higher in the north and lower in the south and western areas, and show no significant changes with soil depth. Increased mineralization in response to P loading over the last four decades likely explains the lower N values on the western side. Because many C compounds such as proteins, RNA, and DNA contain N within their structure, N and C cycling are tied. The coupled relationship between P and N is supported by studies in WCA-2A that demonstrate N mineralization is directly influenced by P loading (Newman et al., 2004; White and Reddy, 2000). Ecosystem-wide, differences in soil total P (TP) concentrations accounted for 57% of the variability in N content (Sklar et al., 2006). Additionally, P-enriched areas have high N assimilation coefficients, which, combined with low N:P ratios, suggest the ecosystem switched from a P- to a N-limited system (Reddy and DeLaune, 2008). This causative relationship between increased P load and N mineralization is discussed in detail below.

Because of the historically P-limited nature of the Everglades, P is by far the most well studied element in this ecosystem. Numerous studies have documented changes in ecosystem structure (Davis, 1991; Gaiser et al., 2005; McCormick et al., 2002; Rutchey et al., 2008; Sklar et al., 2005) and function (Hagerthey et al., 2010; Newman et al., 2001) in response to elevated P loads. In general, P enriched areas in WCA-1 tend to be restricted to 0.5–1 km from the eastern and 2 km from the western perimeter canals (Childers et al., 2003; Corstanje et al., 2006; Newman et al., 1997), where ground elevations are lower, resulting in greater potential for canal water to intrude into the marsh (Surratt et al., 2008). In 1999, Childers et al. (2003) sampled a transect extending west, from the S6 pump station, east to the L40 canal, resampling sites originally surveyed in 1989 by Doren et al. (1997). While there was not a dramatic change in soil TP within the decade, the density of cattail increased further into the marsh. Chang et al. (2009) noted the isotopic signatures of the microbial pools (i.e., periphyton and detritus) in WCA-1 are more responsive to changes in hydrology and chemistry, while rooted macrophytes respond more slowly following soil changes. A similar response in increased cattail density and extent lagging behind soil TP increases was reported in WCA-2A (Sklar et al., 2005).

In addition to transect sampling, spatially intensive sampling of WCA-1 soils has been conducted. A recent comparison of the 2003 system-wide soil data (Corstanje et al., 2006) with the 1991 soil data (Newman et al., 1997) utilized nutrient and cattail data to examine spatial changes in TP distribution within the surficial 0–10 cm profile (Marchant et al., 2009). The P content gradient from the western perimeter extended further into the marsh in 2003 than 1991 (Figure 2). It should be noted that in 2003 the floc and surface soil were analyzed separately, but this was not the case in 1991. However, the two approaches are comparable, as described for WCA-3 by Bruland et al. (2007). Floc depths are deeper in southern WCA-1 and have elevated floc TP contents that extend further into the marsh interior than in the underlying soils (Corstanje et al., 2006); thus, in areas where floc depth is

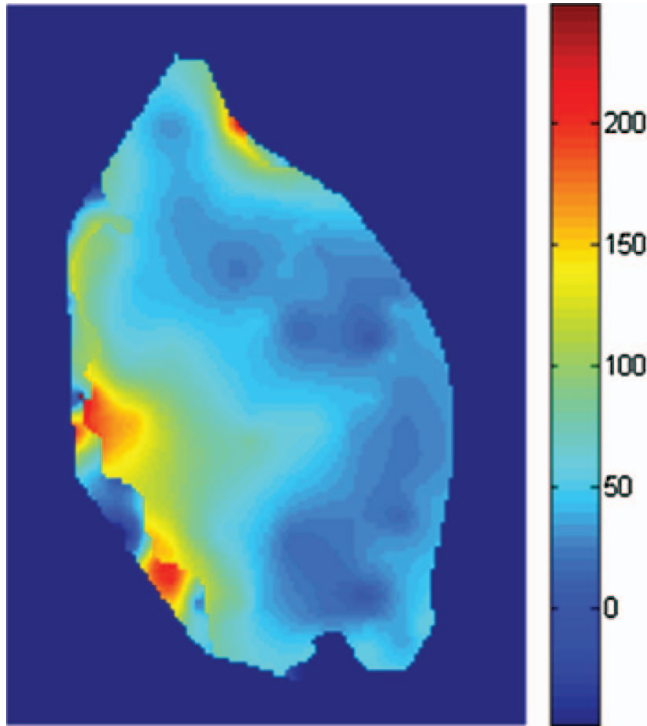


FIGURE 2. Spatial distribution changes in TP content (mg kg^{-1}) from 1991 to 2003. Modified from Marchant et al. (2009). (This figure is available in color online.)

greater than 10 cm, the entire surface layer is comprised of floc. The floc layer is more biologically active than soil and responds more rapidly to changes in external P loads than the underlying soil, with increased concentrations and accumulation rates (Newman et al., 2001), as a result nutrient concentrations in the floc may provide an earlier indicator of biogeochemical change relative to the soil layer (Hagerthey et al., 2008). These differences in distinction of soil layers likely accounts for the disparate conclusions drawn from the spatial study compared to the transect data of Childers et al. (2003), because including floc data results in a different interpretation than if it is excluded and only soils data are used. However, the floc layer is also more variable, specifically in terms of sample composition (e.g., plant detrital or algal origin, degree of decomposition, and highly subjective floc layer delineation). These factors may make the floc layer too insensitive to be used to routinely assess ecosystem responses.

On average, approximately 70% of P stored in Everglades soils is in the organic form (Reddy et al., 1998). In WCA-1, organic P represented 53–68% and 84% of the TP pool near the western perimeter and in the marsh interior, respectively (Reddy et al., 1998). Phosphodiesteres are the dominant form of P found in organic floc and soils along the nutrient and mineral

gradient in WCA-1 (Turner and Newman, 2005). This is significant because phosphodiester esters are also a dominant form of organic P compounds found in plants and microbes. Their dominance in the organic P pool suggests phosphodiester turnover may be a rate limiting step in soil organic matter decomposition.

Phosphodiester esters may be degraded to monoesters, whose subsequent hydrolysis as catalyzed via phosphatase enzymes is one of the most documented biogeochemical processes in organic P cycling. Few studies have measured phosphatase activity in WCA-1 soils (cf. Penton and Newman, 2007), in contrast, phosphatase activity is measured routinely in surface waters of WCA-1. Water column phosphatase activity is inversely related to specific conductivity ($R^2 = .68$; Figure 3) and individual anions and cations. Higher specific conductivity is generally restricted to within 4–5 km of the perimeter canal. Interestingly, despite surface water TP concentrations of $\sim 10 \mu\text{g L}^{-1}$ or less over the last decades, phosphatase activities suggest there is a P enrichment effect because activities are lower within 4–5 km of the perimeter canal than toward the marsh interior. This supports the suggestion that phosphatase activity is a good early warning indicator of P enrichment (Newman et al., 2003) and, similar to periphyton tissue TP content (Gaiser et al., 2004), may be a more sensitive and reliable indicator of P enrichment effects than surface water chemistry alone.

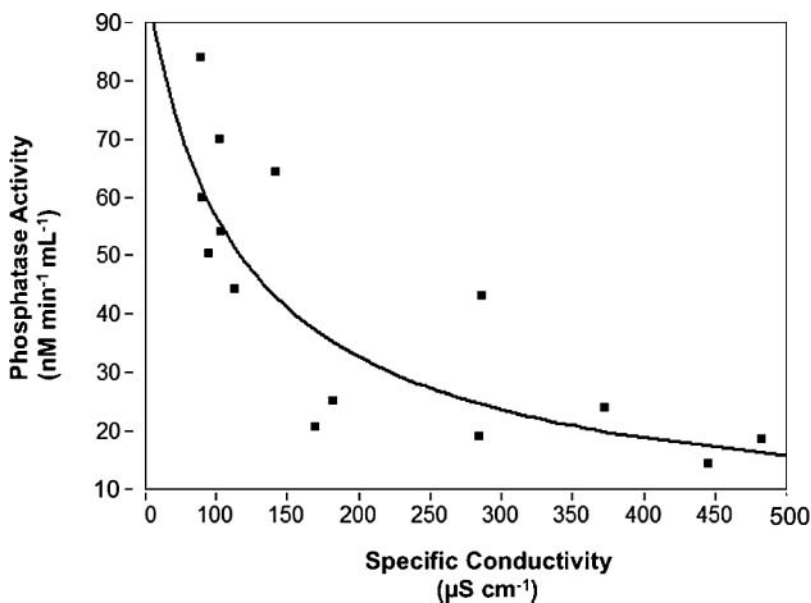


FIGURE 3. Relationship between specific conductivity and phosphatase activity determined from the 14 long-term District water quality monitoring stations.

Mineral Intrusion

A combination of synoptic surveys (Reddy et al., 2005; Sklar et al., 2005) and transect studies (Harwell et al., 2008; McCormick et al., 2011; McCormick et al., 2002; Surratt et al., 2008) have shown that specific conductivity is a good tracer for canal water penetration in WCA-1. However, better resolution may be obtained by examining relationships between individual cations and anions (Harvey and McCormick, 2009).

Compared with P effects, mineral influences penetrate further across the ecosystem, encompassing northern as well as eastern and western regions, thus having a greater ecological impact. Surface water specific conductivities average less than $200 \mu\text{S cm}^{-1}$ (Table 1) and SO_4 concentrations less than 5 mg L^{-1} , generally below detection. The contrast between the fivefold higher specific conductivities in the western perimeter canal (L7) compared to the low values of the interior highlight the isolation of the interior marsh from the chemical influence of the canal system (Figure 4). While short-term effects are evident in periphyton community shifts (Swift and Nicholas, 1987), the longer-term effects of mineral intrusion can be seen in the floc and soil (Corstanje et al., 2006). Calcium contents are two- to fivefold higher along

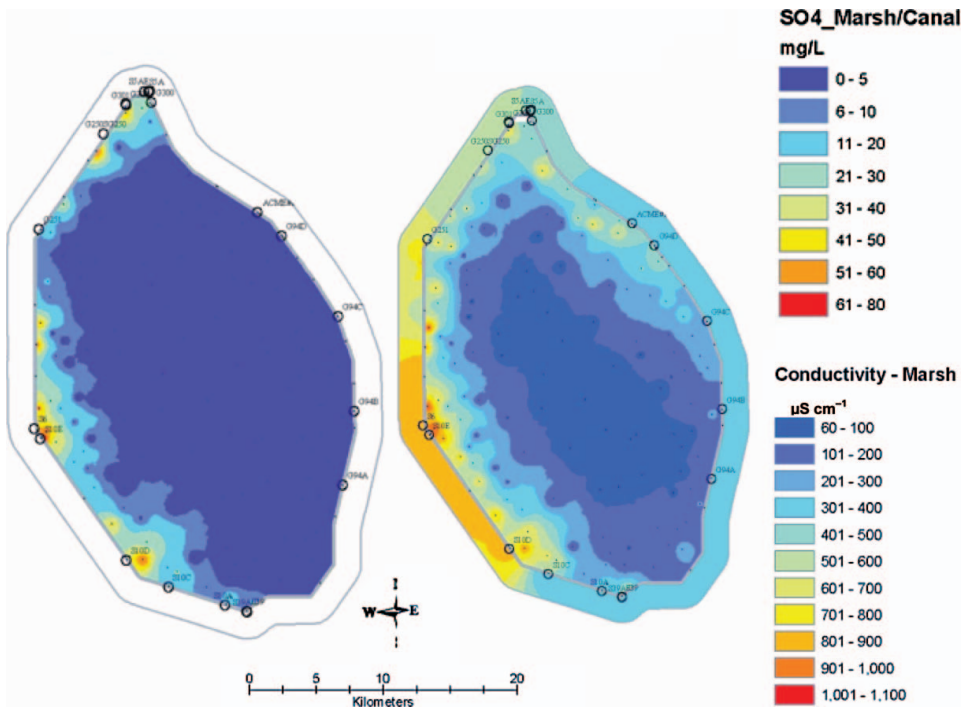


FIGURE 4. Spatial distribution of surface water SO_4 concentrations (left) and specific conductivity in a synoptic survey conducted in February 2004. Note no grab samples were collected for SO_4 analysis from the perimeter canal. (This figure is available in color online.)

the entire west, northwest, and northeast perimeter than the marsh interior (Figure 1). It could be argued that the higher mineral contents in western areas are associated with calcitic seat earth compared to sand-rich seat earth in eastern areas (Sawyer et al., 1987); however, the direct influence of the seat earth, buried below 3 m of peat, on surface soil mineralogy would be limited. In addition, soil mineral contents within fine depth increments of the surficial 35 cm of sediment generally increase in Ca and Mg content toward the sediment/water interface (Reddy et al., 1993a). This supports the influence of mineral enrichment from overland runoff, including the indirect contribution of groundwater influences via surface water inputs, as opposed to direct bedrock effects.

HYDROLOGIC AND BIOGEOCHEMICAL PROCESSES DRIVING C CYCLING

Hydrologic Effects

Overdrainage causes the loss of peat via soil oxidation and may account for the slightly lower, 452 g C kg⁻¹, in the northern half of WCA-1, compared with 504 g C kg⁻¹ (Corstanje et al., 2006) in southern WCA-1, which experiences a longer hydroperiod. Comparisons of aerobic and anaerobic C turnover in WCA-1 soils are limited; however, higher CO₂ release was observed from soils under aerobic conditions compared to anaerobic CO₂ (Wright et al., 2009). Similarly, field and laboratory studies using soils from the WCA-2A nutrient gradient demonstrated that microbial CO₂ production for samples incubated under aerobic conditions were significantly higher than CO₂ production rates under anaerobic conditions (Wright and Reddy, 2001).

A comparison of present and predrainage topography of the Everglades suggests there has been a 20–40% loss of peat in WCA-1, generally occurring in a north-south gradient, with depth reductions up to 0.6–1.5 m (2–5 ft) at the northern end (C. McVoy, personal communication, 2009). Since the 1940s there is no evidence of net peat loss as peat depths measured during the 1995 and 2005 REMAP studies are similar to those reported in 1946 (Scheidt and Kalla, 2007). Average peat accumulation rates estimated from ¹⁴C dating of marsh cores in WCA-1 are 0.05 cm yr⁻¹ (Willard et al., 2001; Willard et al., 2006); thus, the 20–40% loss of peat that has occurred over the last century represents 1000–3000 years of peat development.

While the principal cause of C loss is overdrainage, it should also be noted that there is a natural degradation process that results in peat C concentrations being lower at the soil surface and increasing with soil depth (i.e., age; Reddy et al., 1993b). Few studies have collected deep cores in WCA-1; however, those that have show similar increased C contents with peat

depth. Cores collected to a depth of 61–90 cm had average organic C contents in the surficial layers of 53%, and 61% at the deepest depth (B. Orem, personal communication, 2009). In contrast, percentage of oxygen content decreased from 31% to 25% over the same depth increments. Organic C compounds become less oxidized during decomposition, partly explaining why C concentrations are higher and oxygen concentrations lower in older deeper soils.

Phosphorus Effects

The carbon content of soil is lower in close proximity to the perimeter canal on the western and northeastern extents, in areas of higher P concentrations (Newman et al., 2010). Phosphorus is a limiting nutrient and as such, elevated rates of supply and concentrations have significant effects on C cycling. At higher P inputs there are distinct vegetative community shifts and resultant changes in C quality, while at the lower P enrichment increases in microbial activity are observed.

The most obvious impact of P enrichment on the system is the switch in emergent vegetation communities from ridge and slough to cattail dominated habitat. A recent vegetation mapping effort documented that cattail-dominated communities represent over 5% of WCA-1; however, cattail is present in almost 10% of the area (K. Rutchey, personal communication, 2009). Field and litter bag studies conducted in WCA-2A comparing cattail and sawgrass decomposition rates show that cattail decomposes more rapidly losing more C than sawgrass (Davis, 1991; DeBusk and Reddy, 1998; Qualls and Richardson, 2000), and rates increase in response to P enrichment. Thus, conversion to cattail may, in the long term, not be advantageous to C storage. Compared to other areas of the ecosystem, limited decomposition studies have been conducted in WCA-1. However, a recent study with litterbags containing sawgrass leaves deployed along a west-east gradient demonstrated a decrease in the rate of decomposition with increasing distance from the western canal (McCormick et al., 2011). At sites within the most P-enriched areas, an average 28% mass loss was observed, compared to interior unenriched sites where mass loss averaged 19%.

As noted previously, C turnover in the Everglades is greater under aerobic than anaerobic conditions (Wright and Reddy, 2001; Wright et al., 2009); thus, decomposition rates may also be affected by primary production through the regulation of water column dissolved oxygen (DO) concentrations. The presence of cattail reduces both water column DO, gross primary production (GPP), and respiration (R) by limiting light penetration and subsequently periphyton primary production (Hagerthey et al., 2010). However, P enrichment effects are observable before the transition to dense cattail occurs as low GPP but high R rates relative to the oligotrophic marsh. This is due to a vegetation shift from periphyton to floating and emergent macrophytes.

On a broader scale, a study sampling nutrient gradients throughout the Everglades showed that TP and the relationship between the enzymes involved in C and P mineralization accounted for between 46 and 92% of the variability in measured cellulose decomposition rates (Penton and Newman, 2007). However, P enrichment occurs in conjunction with SO_4 and mineral enrichment, therefore the causal link between P and decomposition cannot be ascertained by only examining the responses along the gradients created within the wetland. Direct evidence of P enrichment on decomposition was obtained from mesocosm dosing experiments conducted within the softwater section of WCA-1 where increased decomposition of cotton strips was observed both within material above and below the soil–water interface in response to P enrichment (Newman et al., 2001).

In highly organic systems such as WCA-1, nutrients are primarily bound in organic matter and the elimination of the limiting nutrient, such as P, can result in release of other parameters as organic matter is processed. Notable examples are porewater NH_4 and Ca. Following P enrichment of WCA-1 mesocosms, there was a significant increase in porewater NH_4 , Ca, and Mg concentrations within 4 months of receiving 1.6–3.2 g P m² yr⁻¹ (Newman et al., 2001). After 2–3 years of P dosing, increased plant growth and uptake reduced NH_4 concentrations below those observed in the controls (Figure 5). Five years after the cessation of P addition, porewater NH_4 concentrations increased to levels observed in controls, providing some evidence for the time frame for recovery from P enrichment on N cycling.

Unlike N, which was actively depleted from the porewater following P enrichment, Ca concentrations remained elevated, though decreased shortly after P loading was stopped. As discussed below, increased Ca concentrations may have significance for plant decomposition, in terms of both subsequent litter quality as well as associated enzyme activity. Treatment effects observed in the porewater lasted far longer than that which would have been suggested by P content of the floc and soil (Figure 5), which while elevated, decreased rapidly relative to the porewater NH_4 concentrations. Thus, a significant effect of P enrichment in this oligotrophic peat system is enhanced nutrient regeneration.

Sulfur Effects on C Cycling

While other chapters specifically discuss the issue of S in the Everglades (Orem et al., this volume), it is worth noting that the spatial intrusion of S into the marsh interior in WCA-1 can have significant influences on C cycling. Several studies have documented that S can act as an alternative electron acceptor and elevated S levels will therefore increase C turnover (Beltman et al., 2000; Smolders et al., 2006). In the Everglades, mesocosm dosing experiments demonstrated that P concentrations increased in the porewater

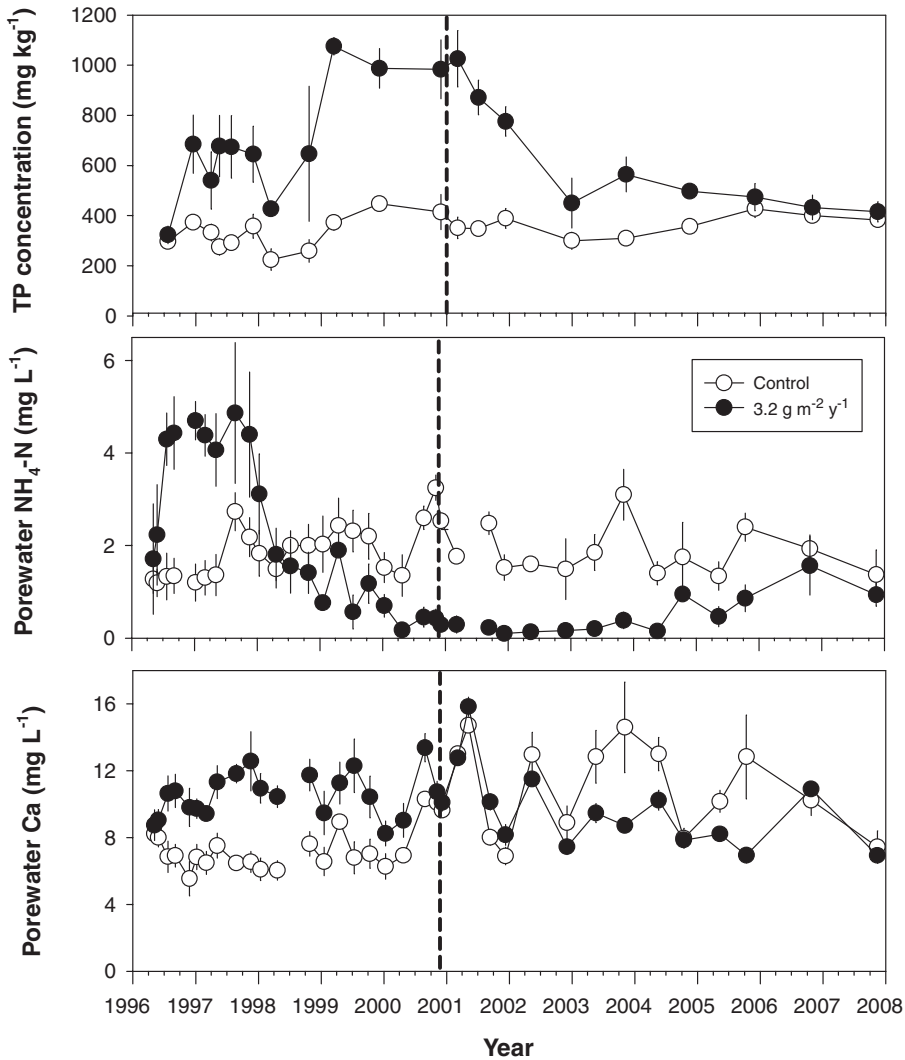


FIGURE 5. Floc and porewater nutrient and mineral concentrations following P enrichment. Symbols to the right of the dashed line are samples that were collected after the cessation of P dosing (expanded from Newman et al., 2001).

following S enrichment and this was attributed to P release following organic C mineralization (Gilmour and Orem, 2007)

Mineral Influences on C Cycling

The dominant contributors to peat C storage are the higher plants via both above- and belowground productivity, with the balance of productivity versus decomposition driving soil accumulation. Decomposition rates of sawgrass litter along the nutrient/mineral gradient in WCA-1 are elevated not

just in areas of high soil P, but also in areas where soil P is low, but minerals concentrations are high (McCormick et al., 2011). Decomposition rates are influenced by a number of factors, including the chemical and physical composition of the organic matter, microbial community composition and productivity, and external nutrient concentrations (Brinson et al., 1981; Rejmánková and Houdková, 2006; Rybczyk et al., 1996; Webster and Benfield, 1986). A comparison of cattail and sawgrass leaf decomposition, using litter packs deployed for over 1 year at a low-P and variable but often low mineral site in WCA-1 to those at a P-poor but mineral-rich site in WCA-2A show significantly higher rates of decomposition for both sawgrass and cattail in WCA-2A (Figure 6). Similarly, comparisons of decomposition rates of sawgrass litter in P-dosed mesocosms in the consistently low mineral interior of WCA-1 demonstrated that on average only 30% of litter weight was lost over the 3-year study period, producing calculated first-order exponential decay rates averaging $0.10\text{--}0.15\text{ yr}^{-1}$ (Newman et al., 2001). In comparison, a range of $0.46\text{--}1.11\text{ yr}^{-1}$ was reported for litter in WCA-2A (DeBusk and Reddy, 1998; Qualls and Richardson, 2000). The range in the mineral-rich interior of WCA-2A is more in line with the average of 1.02 yr^{-1} reported for Cyperaceae (Webster and Benfield, 1986).

There is no evidence to suggest that sawgrass and cattail grown in WCA-1 compared to WCA-2A would be structurally different, but they do have different nutrient contents. As previously discussed, higher nutrients, specifically P, result in increased decomposition rates in the Everglades; however, minerals may also influence decomposition through their effect on substrate quality and enzyme activity. Litter with a high Ca content has been

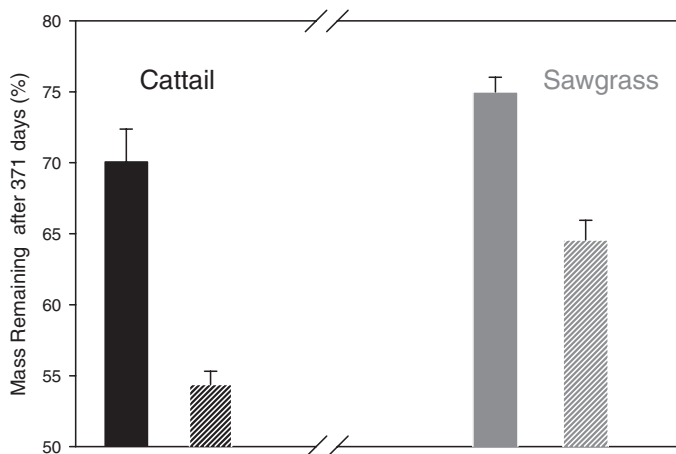


FIGURE 6. Decomposition of sawgrass litter in mineral-poor and mineral-rich surface water environments. Solid bars = litter packs deployed in low-mineral, low-P environment (WCA-1); hatched bars = litter packs deployed in high-mineral, low-P environment (interior WCA-2A). Litter material collected from WCA-1 (Newman et al., unpublished data).

observed to decay faster than Ca-poor litter (Smith et al., 1993). Microbially mediated decomposition is catalyzed by extracellular enzymes, which is considered the rate-limiting step in decomposition (Meyer-Reil, 1991; Sinsabaugh et al., 1993). Phosphatase activity, an important mediator of P availability in P-limited systems, is influenced by several factors, including ionic strength and metal ion concentrations (Jansson et al., 1988). In softwater systems phosphatase activity is inhibited due to the reversible binding of enzymes with humic acid (Wetzel, 1991). In hardwater systems divalent cations bind with the humic acids, thereby suppressing the inhibition of enzyme activity by humic compounds (Wetzel, 1991). In a recent dosing experiment, where different concentrations of a mineral mix, excluding P, were added to mesocosms in the ombrotrophic interior of WCA-1, litter bags did not show significant differences in decomposition rates; however, the highest concentration of minerals generally had higher phosphatase activity after 12 months (Figure 7), providing some support for the interaction between the P and minerals in C cycling (Newman et al., unpublished data).

While C storage is typically attributed to higher macrophytes there is some evidence that periphyton C may also become incorporated into peat. The examination of the diagenesis of Everglades peats using ^{13}C -NMR identified a significant concentration of aliphatic compounds (Orem and Hatcher, 1987). Orem and Hatcher (1987) suggested these compounds were likely algal as opposed to higher plants in origin, and therefore algal remains may be a significant component of the organic matter in Everglades peat. One of the most noticeable effects of mineral enrichment in WCA-1 has been the switch in algal assemblages resulting in three distinct groups: (a)

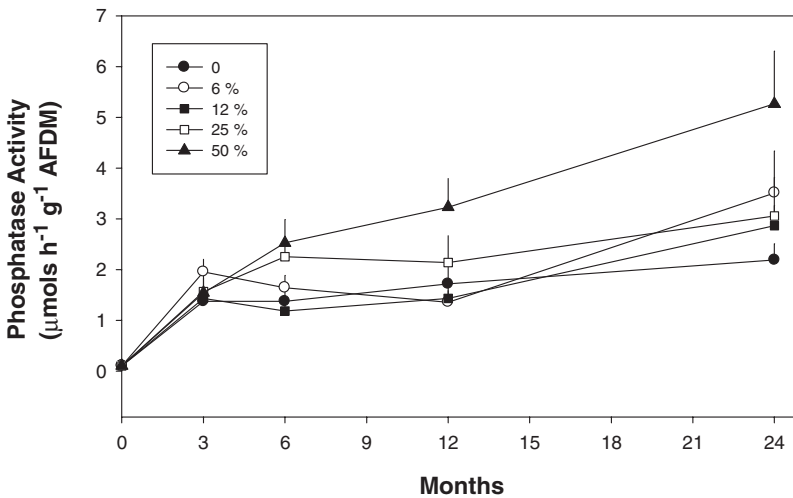


FIGURE 7. Phosphatase activity ($M \pm 1 SE$) measured in litterbags incubated in mesocosms in WCA-1 subject to mineral enrichment treatments (Newman et al., unpublished data).

marsh interior algal assemblages dominated by desmids and diatoms, indicative of low-mineral and low-P waters; (b) cyanobacteria and diatoms assemblages indicative of high-mineral and low-P waters; and (c) cyanobacteria and diatoms assemblages indicative of mineral-rich and high-P waters (Hagerthey et al., 2010; McCormick et al., 2002; Swift and Nicolas 1987). These species shifts may have an effect on C cycling via the carbohydrates they produce. This varies with different assemblages, for example, under a high mineral environment, the extracellular polymeric substances produced by the periphyton are more structural and may be less labile and more likely to be stored in peat upon senescence (see Bellinger et al., in press). The differences in carbon quality associated with the mineral content of macrophytes and algae may extend to water column biogeochemistry. Hagerthey et al. (2010a) found that GPP in the oligotrophic waters of WCA-1 were not influenced by the mineral content of surface waters $99\text{--}111\text{ mmol m}^2\text{ d}^{-1}$; however, R for the ombrotrophic marsh interior ($87\text{ }\mu\text{S cm}^{-1}$) was $181\text{ mmol m}^2\text{ d}^{-1}$ but was over 23% greater ($233\text{ mmol m}^2\text{ d}^{-1}$) for waters with specific conductivities greater than $221\text{ }\mu\text{S cm}^{-1}$.

SUMMARY AND RELEVANCE TO RESTORATION AND FUTURE DIRECTIONS

The biogeochemistry of WCA-1 is highly influenced by topography, which, along with present water management, results in a north-south hydrologic gradient. Nutrient and mineral enrichment also affect spatial and temporal patterns in biogeochemical cycles. The penetration of nutrient- and ion-rich canal water that occurs along the marsh perimeter results in distinct biogeochemical gradients. However, a significant portion of the ecosystem remains rainfall driven therefore WCA-1 has a unique biogeochemistry compared to the remnant Everglades. There is some evidence that WCA-1 may have low decomposition rates compared to other areas of the Everglades because of environmental influences on substrate quality and enzyme activity. Comparing historic with present peat depths, the system has lost up to 40% of the peat it originally accumulated. Changes in biogeochemistry have the potential to exacerbate C losses through increased organic matter decomposition. Due to rapid biological uptake, P effects on the system are restricted to within 2 km of the perimeter canal, though phosphatase activity, which may be a reliable indicator of P impacts, suggest some evidence of biological change prior to any evidence of changes in surface water TP concentrations.

Given the present topographic differences, the only means to limit mineral water intrusion, while not exacerbating hydrologic differences, is to increase water flow from north to south, while minimizing the penetration of water into the marsh interior from the west and east. However, because of the softwater nature of the marsh interior, compared to the hardwater of the

canal system, increased flow will increase the footprint of mineral changes in the region. Because much of the canal water penetration occurs on the western edge, perhaps a first step to restoration is to actively modify the topography of the area to decrease the potential for canal-marsh exchange.

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