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Water Quality Gradients in the Northern Florida Everglades

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Abstract The Loxahatchee National Wildlife Refuge (Refuge) developed as a system with waters low in nutrients. Today, the Refuge wetlands are impacted by inflows containing elevated nutrient concentrations originating from agricultural sources. We analyzed water quality sampled at 54 sites in the Refuge. The Refuge was divided into northern, central, and southern latitudinal areas and then perimeter, transition, and the interior zones based on distance from the canal towards the Refuge interior. In the perimeter zone, total dissolved solids (TDS), silicon (Si), and total phosphorus (TP) concentrations in water were higher in the northern than the central area and TDS, Si, SO_4, and TP concentrations in water were higher in the central than the southern area. In general TDS, Ca, Cl, Si, SO_4, and TP loads in the northern perimeter, transition, and interior zones decreased from 2005 to 2009. The decrease is less pronounced in the central and southern areas than the northern area. As water flowed southward for over 30 km from the northern to the southern area in the perimeter zone, most water quality parameters analyzed were reduced in the water column. However, large amounts of Ca and Cl were added to the water column indicating that canal water is continually diffusing and intruding into the Refuge in all zones. In the perimeter zone, and to a lesser degree in the transition zone, the Refuge has accumulated substantial amounts of Ca, Si, SO_4, and TP in vegetation and soils during the sampling period.

Keywords Everglades · Water quality · Latitude · Water flow · Canal water intrusion

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1 Introduction

The Northern Everglades developed as a rainfall-driven system with surface waters low in nutrients and inorganic ions and is characterized as an oligotrophic ecosystem with low dissolved mineral concentrations and low conductivity (Davis 1994). The Loxahatchee National Wildlife Refuge (Refuge) contains the last major remnant of the Northern Everglades ecosystem that continues to be characterized by relatively low conductivity and mineral contents. Refuge surface water is classified by the State of Florida as class III freshwater with corresponding water quality standards established to protect recreation, propagation, and maintenance of a healthy, well-balanced population of fish and wildlife (section 62-302.400, Florida Administrative Code (F.A.C.). The Refuge is also classified as Outstanding Florida Waters (section 62-302.700, F.A.C.) which, beyond the class III water quality standards, requires no degradation of water quality other than that allowed in rule 62-4.242(2) and (3), F.A.C.

Pre-development Everglade's fauna and flora are adapted to extremely low P concentrations. Therefore, ecosystem function changes with very small increases in this nutrient. Water containing elevated nutrients flowing into the Everglades ecosystems has been associated with altered ecosystem structure and function (DeBusk et al. 1994; 2001; Davis et al. 2003; Noe et al. 2003; Childers et al. 2003; King et al. 2004; Liston and Trexler 2005; Hagerthey et al. 2008) including conversion of sawgrass (*Cladium jamaicense* Crantz.) stands to cattail (*Typha domingensis* Pers.) (Debusk et al. 1994, 2001; Doren et al. 1997; Stewart et al. 1997; Lorenzen et al. 2000; Miao et al. 2001; 2000; McCormick et al. 2009). Since completion of construction in the early 1960s, the Refuge wetland has been surrounded by perimeter levees and associated canals encircling the wetland on the interior side of the levees. Inflows into this impounded system are controlled by the South Florida Water Management District (SFWMD) and outflows are controlled by the U.S. Army Corps of Engineers, the SFWMD, and local drainage districts (USFWS 2000). Areas of pristine Refuge wetlands have been impacted by canal water intrusion containing elevated concentrations of nutrients and minerals (Childers et al. 2003; Harwell et al. 2008; Surratt et al. 2008; Wang et al. 2009; Chang et al. 2009).

Prior to discharge into the Refuge, most pumped inflows are first treated in large constructed wetlands called stormwater treatment areas (STAs) adjacent to the Refuge northern boundary (Fig. 1). Untreated water is also discharged to the northern Refuge, but at a much lower frequency, rate, and volume (USFWS 2007a, b). Stormwater originating from urban, agricultural, and horticultural lands is treated in STA1-East while stormwater treated in STA1-West originates primarily in the 280,000-ha Everglades Agricultural Area located northwest of the Refuge. Treated water is pumped into the Refuge from STA1-East into the eastern L-40 canal and from STA1-West into the western L-7 canal forming a perimeter around the Refuge (Ivanoff and Chen 2012). Once discharged to the canals surrounding the Refuge wetland, these waters mix and tend to move into the marsh when water levels are high (>4.57 m) and inflow rates are moderate to high (>14.18 $m^3 s^{-1}$) (Harwell et al. 2008; Miller and McPherson 2008; Surratt et al. 2008). Harwell et al. (2008) classified the Refuge into four separate zones based on surface water conductivity. Specific conductivity (SpC), a tracer of canal water movement, declined across each zone from the canal toward the Refuge interior. The perimeter zone was from the canal to 2.5 km into the marsh, the transition zone was from 2.5 to 4.5 km into the marsh, and the interior zone was comprised of sites located greater than 4.5 km into the marsh.

Entry (2012a) found that alkalinity (ALK) total dissolved solids (TDS) values, and SpC and Ca, Cl, and SO_4 concentrations were greater in the perimeter than in transition and interior zones. Alkalinity and SpC values and SO_4 concentrations were greater in the transition than in the interior zone. Alkalinity, SpC, and TDS values and Ca, SO_4, and Cl concentrations correlated in negative curvilinear relationships with distance from the canal. Entry (2012b) found that the perimeter zone contains higher ALK, TDS, TB, and SpC values and dissolved organic carbon (DOC), total organic carbon (TOC), TDS, Ca, Cl, silicon (Si), and SO_4 concentrations relative to the interior zone. The transition zone is moderately impacted by higher ALK and SO_4 concentrations relative to the interior zone. Alkalinity, SpC, TDS, Ca, Cl, and SO_4 concentrations all decreased in negative curvilinear relationships with distance from the canal toward the Refuge interior, while total phosphorus (TP) concentrations in the Refuge did not, suggesting that excess inorganic N and P are quickly assimilated by nutrient limited periphyton and plants (Entry 2012a; c). Alkalinity, TDS, TB, and SpC values and Ca, Cl, Si, SO_4, and TP concentrations decreased from 2005 to 2009 in the perimeter zone; TDS, total suspended solids (TSS), TB, and SpC and SO_4 and TP concentrations decreased in the transition zone; TDS, TSS, and TB and SO_4 concentrations decreased from 2005 to 2009 in the interior zone (Entry 2012c, d). The Refuge was divided into northern, central, and southern latitudinal areas and three zones which were the perimeter, transition, and interior zones to characterize water quality by zone as it flowed southward in the Refuge. While water is flowing southward in the Refuge marsh, high nutrient canal water can intrude toward the marsh interior when water levels are high and STA inflow rates are moderate to high. The objective of this research was to determine if: (1) water quality varies as water flows southward in the Refuge, (2) the amount of nutrients

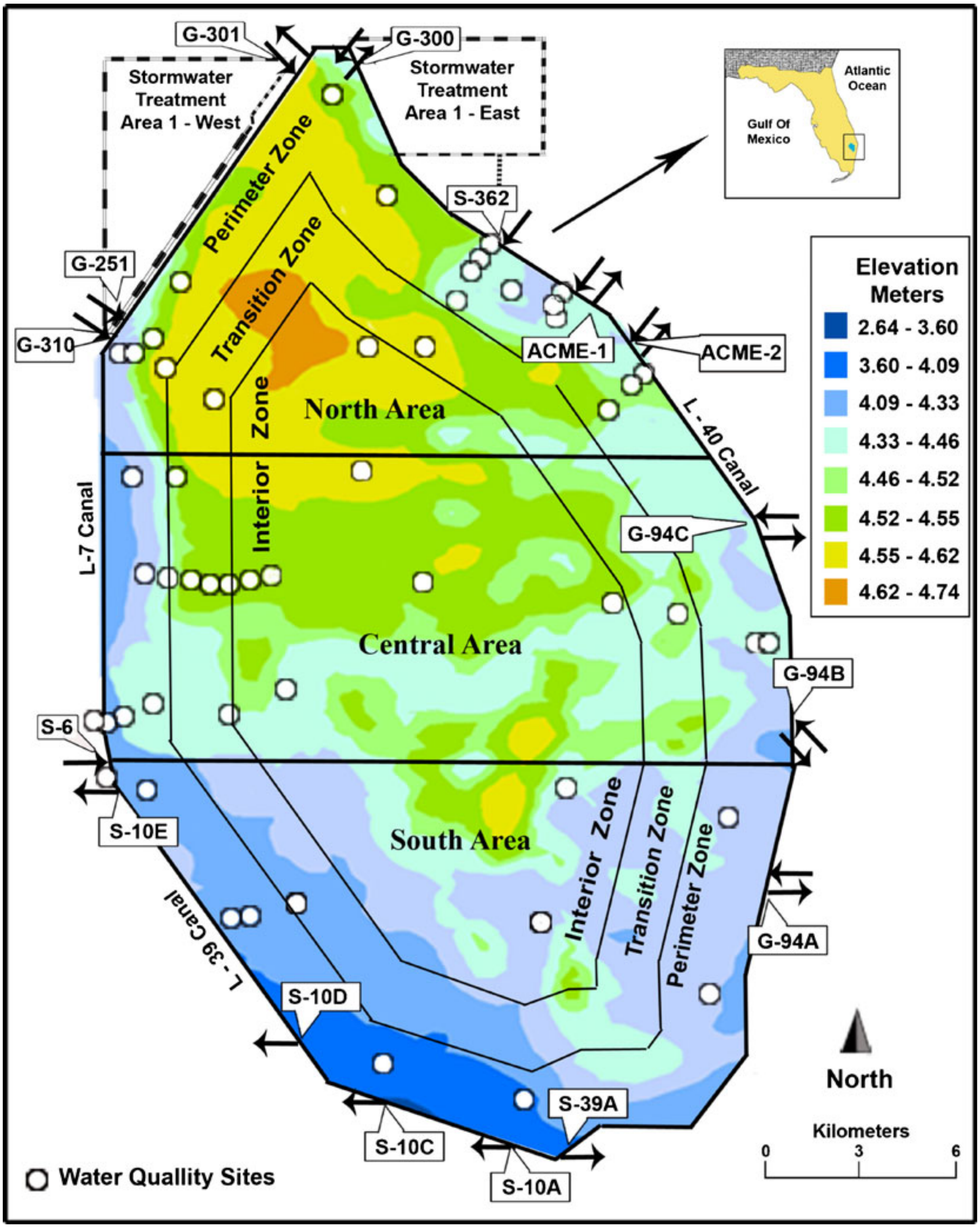

Fig. 1 Water quality sites in the A.R.M. Loxahatchee National Wildlife Refuge classified by latitude (northern, central, and southern areas) and zones (canal, perimeter, transition, and interior) and northern and southern areas. Inflow sites are indicated by *arrows* pointing into the Refuge. Outflow sites are indicated by *arrows* pointing out of the Refuge. Elevation was provided by USGS (2005)

(load) in each zone differs with latitude, and (3) the nutrient load removed as the water flows southward through the Refuge marsh can be used to further develop the understanding of the effect of canal water intrusion on nutrient concentrations and loads in the Refuge.

2 Materials and Methods

2.1 Marsh Zones and Delineations

The Refuge was divided into northern, central, and southern areas reflecting sites that were farther from STA1-East and STA1-West inflow pumps and may be less affected by canal water intrusion. The Refuge was also divided into four zones delineated as the canal surrounding the Refuge marsh, the perimeter zone (0 to 2.5 km into the Refuge marsh), the transition zone (2.5 to 4.5 km into the marsh), and the interior zone (>4.5 km into the marsh) (Harwell et al. 2008) (Fig. 1).

2.2 Sample Collection

Surface water samples were collected monthly at 49 marsh and 5 canal sites from January 2005 through December 2009. Marsh sites were accessed by float helicopter and sampled by wading out into the marsh to collect 0.5 to 3 L of undisturbed water and measure depth of the clear water column and depth to consolidated substrate (SFWMD 2012). Depths were measured within a 10-m radius of each sampling point. At water levels greater than 20 cm, 3 L of water was collected allowing a full suite of chemical analyses to be performed. Samples were stored on ice at 4 °C and then filtered and preserved within 4 h of collection.

2.3 Laboratory Analysis

All samples collected from January 2005 through May 2006 were analyzed by the SFWMD chemistry laboratory in West Palm Beach, Florida. Samples collected from the Consent Decree Network from January 2005 through December 2006 were analyzed by the SFWMD chemistry laboratory in West Palm Beach, Florida. Samples from the Refuge's Enhanced Network collected from June 2006 to December 2009 were analyzed by Columbia Analytical Services (Jacksonville, FL) (Entry 2012a, c).

TOC was determined by thermal combustion as described in the EPA 415.1 method and measured on a Shimadzu TOC-V_{CHS} carbon analyzer. DOC and total dissolved solids (TDS) defined above already were measured in water passed through a 0.45 μm filter. TDS were measured using a thermal combustion Shimadzu TOC-V_{CHS} carbon analyzer. Turbidity was measured on a Hach 2100 AN turbidimeter following the EPA 160.2 method (APHA 2005) and is expressed as a formazin turbidity unit. TSS were measured after the sample was dried at 103 °C and weighed as described in the EPA 160.2 method (APHA 2005). TDS were measured by weighing filters which were dried at 90 °C and fixed at 180 °C (APHA 2005). Sulfate was determined by the EPA 300.1 method using a Dionex DX 500 ion chromatograph (APHA 2005). After water samples were filtered through a 0.45-μm filter, a 2.0-mL subsample was analyzed for Ca, Cl, and Si using a Perkin Elmer Optima 4300 DV inductively coupled plasma emission spectrometer (SM 3120.B method; APHA 2005). Total P was determined by digesting water aliquots in an autoclave at 103.5 kPa and 121 °C for 60 min with 4.0 mL of acidified ammonium persulfate (APHA 2005).

2.4 Statistical Analysis

Only data sets with complete records for all parameters measured were analyzed. In the northern area, data were subjected to a two-way general linear model (GLM) analysis (Snedecor and Cochran 1994; Kirk 1995) using Statistical Analysis Software programs (SAS Institute Inc. 2008). Significance of treatment means was determined at $p \leq 0.05$ with the least square means test. After values were log-normal transformed, residuals were normally distributed with constant variance (Snedecor and Cochran 1994; Kirk 1995). Statistical comparisons in the GLM model showed that all interactions for parameters were significant for area (northern, central, and southern) × zone (perimeter, transition, and interior) at $p < 0.05$. Therefore, results are discussed with respect to area and zone (Snedecor and Cochran 1994; Kirk 1995).

3 Results

3.1 Concentration

In the perimeter zone, TDS, Cl, Si, SO_4, and TP concentrations in water were higher in the northern than the southern area (Table 1). Total dissolved solids, Si, and TP concentrations in water were higher in the northern than the central area. Total dissolved solids, Si, SO_4, and TP concentrations in water were higher in the central than the southern area. In the

Table 1 Dissolved organic carbon, total organic carbon, total dissolved solids, total suspended solids, Ca, Cl, Si, SO_4, and total phosphorus concentrations in the northern, central, and southern areas in the Loxahatchee National Wildlife Refuge from 2005 to 2009

Zone	Area	DOC mg L^{-1} water	TOC mg L^{-1} water	TSS mg L^{-1} water	TDS mg L^{-1} water	Ca mg L^{-1} water	Cl mg L^{-1} water	Si mg L^{-1} water	SO_4 mg L^{-1} water	TP mg L^{-1} water
Perimeter	Northern	24.18 a	24.70 a	2.29 c	261.92 a	30.55 a	52.44 a	11.81 a	10.91 a	0.031 a
	Central	21.28 a	21.40 a	1.11 c	230.27 b	25.09 ab	45.03 a	10.62 b	11.24 a	0.018 b
	Southern	19.25 a	19.51 a	2.19 c	195.52 c	22.58 b	49.75 a	7.27 c	7.34 b	0.012 c
Transition	Northern	20.68 a	21.08 a	2.24 c	106.13 e	7.60 d	21.60 b	6.54 c	0.67 b	0.011 c
	Central	17.47 b	17.83 b	3.38 b	103.54 e	8.34 d	17.50 b	7.60 c	0.89 b	0.010 c
	Southern	16.43 b	16.45 b	1.81 c	134.04 d	13.02 c	27.82 b	6.86 c	0.87 b	0.010 c
Interior	Northern	20.09 a	20.41 a	4.86 a	97.38 a	5.20 d	17.65 b	4.01 d	0.13 c	0.009 c
	Central	20.81 a	21.00 a	1.00 d	110.51 e	6.15 d	22.49 b	4.52 d	0.11 c	0.010 c
	Southern	18.36 b	18.52 b	0.77 d	100.17 e	6.92 d	19.62 b	3.20 d	0.06 c	0.008 c

In each column, values followed by the same letter are not significantly different as determined by the least square means test ($p \leq 0.05$; $n \geq 51$). Statistical comparisons in the GLM model showed that all interactions for parameters were significant for area (northern, central, and southern) × zone (perimeter, transition, and interior) at $p<0.05$. Therefore, results are discussed with respect to area and zone (Snedecor and Cochran 1994; Kirk 1995)

DOC dissolved organic carbon, *TOC* total organic carbon, *TDS* total dissolved solids, *TSS* total suspended solids, *TP* total phosphorus

transition zone, DOC, TOC, TDS, and Ca concentrations in water were higher in the northern than the southern area. Dissolved organic carbon and TOC concentrations in water were higher in the northern than the central area. Total suspended solids and TSS in water were higher in the central than the southern area. In the interior zone, DOC, TOC, TSS, and TDS concentrations in water were higher in the northern than the southern area. Total suspended solids and TDS concentrations in water were higher in the northern than the central area. Dissolved organic carbon and TOC concentrations in water were higher in the central than the southern area.

3.2 Nutrient Load

In the perimeter zone, the DOC, TOC, TSS, TDS, Ca, and Cl loads were lower in the northern than the southern area (Table 2). Only the TDS and Ca loads were lower in the northern than the central area. The DOC, TOC, TSS, TDS, Ca, and Cl loads were lower in the central than the southern area. In the transition zone, DOC, TOC, TDS, Ca, Cl, Si, and TP loads were lower in the northern than the southern area. The DOC, TOC, TSS, TDS, Ca, Cl, Si, and TP loads were lower in the northern than the central area. The DOC, TOC, TSS, TDS, Ca, Cl, and Si loads were lower in the central than the southern area. In the interior zone, DOC, TOC, TDS, Ca, Cl, Si, and TP loads were lower in the northern than the southern area. The DOC, TOC, TSS, TDS, Ca, Cl, Si, and TP loads were lower in the northern than the central area. The DOC, and TOC loads were higher in the central than the southern area.

In the northern area perimeter zone, the TSS load was greater in 2005 than in 2006 through 2009 (Table 3). The TP load was greater in 2005 and 2007 than in 2006, 2008, and 2009. The TDS, and Cl loads were greater in 2005 and 2006 than in 2007 through 2009. The Ca load was greater in 2006 through 2008 than in 2009. In the northern area transition zone, the TDS, Ca, Cl, and SO_4 loads were greater in 2005 and 2006 than in 2007 through 2009. The Si load was greater in 2005 through 2007 than in 2008 and 2009. In the northern area interior zone, the TDS, Cl, and Si loads were greater in 2005 through 2007 than in 2008 and 2009. The Ca load was greater in 2005 than in 2006 through 2009. The SO_4 and TP loads were greater in 2005 and 2006 than in 2007 through 2009. In the central area perimeter zone, TOC and Si loads were greater in 2005 through 2007 than in 2008 and 2009 (Table 4). The TDS, Ca, and SO_4 loads were greater in 2005 and 2006 than in 2007 through 2009. The TP load was less in 2009 than in 2005 through 2008. In the central area transition zone, TDS load was greater in 2005 through 2007 than in 2008 and 2009. In the central area transition zone, Si and SO_4

Table 2 Dissolved organic carbon, total organic carbon, total dissolved solids, total suspended solids, Ca, Cl, Si, SO_4, and total phosphorus load in the northern, central, and southern areas in the Loxahatchee National Wildlife Refuge from 2005 to 2009

Zone	Area	Size ha	Depth m	DOC kg	TOC kg	TSS kg	TDS kg	Ca kg	Cl kg	Si kg	SO_4 kg	TP kg
Perimeter	Northern	6,519.72	0.45	709.8 b	724.8 b	67.2 c	786.2 d	896.5 b	1,539.0 b	346.6 a	320.1 a	0.54 a
	Central	6,180.98	0.53	700.6 b	705.0 b	115.7 c	7,583.5 b	826.1 b	1,482.8 b	349.8 a	370.1 a	0.58 a
	Southern	7,779.55	0.73	1,099.6 a	1,115.0 a	125.2 b	11,170.9 a	1,920.3 a	2,271.1 a	415.3 a	419.2 a	0.66 a
Transition	Northern	3,441.97	0.40	282.6 d	288.1 d	30.6 d	1,450.7 d	103.9 e	295.2 c	89.3 d	9.21 b	0.15 c
	Central	5,306.83	0.49	450.2 c	459.4 c	87.0 b	2,667.7 c	214.9 d	451.0 c	195.7 c	22.9 b	0.25 b
	Southern	4,786.79	0.85	669.7 b	670.5 b	74.1 b	5,462.7 b	530.5 c	1,133.9 b	268.0 b	35.6 b	0.39 b
Interior	Northern	1,972.10	0.41	162.1 e	164.8 d	39.2 d	786.1 d	41.9 d	142.5 c	32.4 e	1.0 c	0.08 d
	Central	14,399.26	0.41	1,227.9 a	1,238.9 a	211.8 a	6,519.8 b	362.7 c	1,327.0 a	266.9 b	6.7 c	0.59 a
	Southern	3,956.75	0.55	401.9 d	405.2 c	43.9 d	2,192.2 c	151.5 e	429.3 c	70.0 d	1.3 c	0.18 c

In each column, values followed by the same letter are not significantly different as determined by the least square means test ($p \leq 0.05$; $n \geq 58$). Statistical comparisons in the GLM model showed that all interactions for parameters were significant for area (northern, central, and southern) × zone (perimeter, transition, and interior) at $p<0.05$. Therefore, results are discussed with respect to area and zone (Snedecor and Cochran 1994; Kirk 1995)

DOC dissolved organic carbon, *TOC* total organic carbon, *TDS* total dissolved solids, *TSS* total suspended solids, *TP* total phosphorus

loads were greater in 2005 and 2006 than in 2008 and 2009. In the central area interior zone, the TSS load was greater in 2005 than in 2006 through 2009. The TDS, Si, and SO_4 loads were greater in 2005 and 2006 than in

Table 3 Amount of dissolved organic carbon, total organic carbon, total dissolved solids, total suspended solids, Ca, Cl, Si, SO_4, and total phosphorus concentrations in the in the perimeter zone, transition, and interior zones in the northern area in the Loxahatchee National Wildlife Refuge from 2005 to 2009

Year	Area	Zone	DOC kg	TOC kg	TSS kg	TDS kg	Ca kg	Cl kg	Si kg	SO_4 kg	TP kg
2005	Northern	Perimeter	752.0 a	759.8 a	85.1 a	8,229.6 a	973.0 a	1,789.4 a	320.2 a	326.0 a	0.61 a
2006	Northern	Perimeter	715.9 a	706.3 a	62.2 b	8,516.3 a	962.4 a	1,765.8 a	347.8 a	351.7 a	0.27 b
2007	Northern	Perimeter	666.6 a	679.1 a	67.9 b	6,230.1 b	689.5 a	1,139.9 b	308.7 ab	141.0 b	0.44 a
2008	Northern	Perimeter	672.9 a	683.8 a	55.6 b	6,592.8 b	831.1 a	1,444.8 b	312.7 ab	274.4 a	0.32 b
2009	Northern	Perimeter	679.7 a	683.9 a	60.2 b	6,149.5 b	710.8 b	1,304.2 b	268.2 b	195.7 a	0.39 b
2005	Northern	Transition	297.3 b	297.3 b	41.0 c	1,597.5 c	128.7 c	382.9 c	144.7 c	10.8 b	0.18 c
2006	Northern	Transition	275.3 b	279.2 b	35.5 c	1,778.8 c	159.3 c	437.8 c	124.0 c	15.4 b	0.40 b
2007	Northern	Transition	301.9 b	309.4 b	30.1 c	1,411.5 cd	91.2 d	260.9 d	101.0 c	3.2 c	0.11 c
2008	Northern	Transition	265.2 b	273.4 b	26.2 c	1,105.1 d	80.1 d	225.1 d	74.8 d	2.6 c	0.09 dc
2009	Northern	Transition	271.4 b	275.3 b	33.2 c	1,343.4 d	93.3 d	246.0 d	87.7 d	1.3 c	0.11 c
2005	Northern	Interior	137.2 c	139.9 c	15.0 d	731.8 e	56.5 e	165.5 e	37.1 e	2.2 c	0.11 c
2006	Northern	Interior	199.1 c	199.1 c	12.9 d	842.2 e	40.9 f	133.2 e	40.8 e	2.9 c	0.07 c
2007	Northern	Interior	177.6 c	178.9 c	17.4 d	875.8 e	40.6 f	154.7 e	47.1 e	1.1 d	0.06 d
2008	Northern	Interior	150.5 c	151.9 c	20.5 d	725.7 e	37.4 f	124.3 f	26.3 f	0.5 d	0.06 d
2009	Northern	Interior	141.3 c	133.2 c	16.1 d	565.0 f	41.6 f	100.9 f	23.0 f	0.2 d	0.04 d

In each column, values followed by the same letter are not significantly different as determined by the least square means test ($p \leq 0.05$; $n \geq 58$). Statistical comparisons in the GLM model showed that all interactions for parameters were significant for area (northern, central, and southern) × zone (perimeter, transition, and interior) at $p<0.05$. Therefore, results are discussed with respect to area and zone (Snedecor and Cochran 1994; Kirk 1995)

DOC dissolved organic carbon, *TOC* total organic carbon, *TDS* total dissolved solids, *TSS* total suspended solids, *TP* total phosphorus

Table 4 Amount of dissolved organic carbon, total organic carbon, total dissolved solids, total suspended solids, Ca, Cl, Si, SO_4, and total phosphorus concentrations in the perimeter, transition, and interior zones in the central area in the Loxahatchee National Wildlife Refuge from 2005 to 2009

Year	Area	Zone	DOC kg	TOC kg	TSS kg	TDS kg	Ca kg	Cl kg	Si kg	SO_4 kg	TP kg
2005	Central	Perimeter	735.8 b	735.8 b	127.6 c	9,287.3 a	1,056.3 a	1,833.7 a	342.4 a	483.3 a	0.57 b
2006	Central	Perimeter	736.2 b	734.1 b	75.4 d	9,765.0 a	1,090.9 a	1,928.9 a	424.1 a	532.1 a	0.47 b
2007	Central	Perimeter	731.1 b	726.7 b	173.2 b	7,466.9 b	774.1 b	1,452.8 a	375.7 a	224.3 b	0.91 a
2008	Central	Perimeter	611.5 b	630.2 c	142.9 e	4,996.0 c	511.9 c	964.5 a	281.0 b	215.4 b	0.50 b
2009	Central	Perimeter	662.9 b	665.8 c	45.0 e	5,201.9 c	552.0 c	1,041.4 a	294.4 b	115.4 c	0.29 c
2005	Central	Transition	409.0 c	420.3 d	256.0 b	2,905.0 d	248.5 e	484.2 b	166.5 c	29.3 d	0.35 c
2006	Central	Transition	417.4 c	407.1 d	64.4 e	2,813.5 d	234.5 e	461.7 b	184.0 c	22.4 d	0.21 c
2007	Central	Transition	501.2 c	491.9 d	49.7 e	3,075.4 d	225.8 e	484.8 b	343.1 b	12.0 e	0.53 b
2008	Central	Transition	471.8 c	490.4 d	50.5 e	2,334.8 e	181.4 e	384.3 b	153.7 c	13.5 e	0.15 d
2009	Central	Transition	441.7 c	447.2 d	45.8 e	2,239.7 e	192.3 e	418.5 b	183.5 c	5.9 f	0.16 d
2005	Central	Interior	1,137.7 a	1,157.4 a	776.5 a	6,857.3 b	363.4 d	1,284.4 a	298.5 b	13.0 e	0.85 a
2006	Central	Interior	1,467.2 a	1,467.2 a	94.4 c	7,905.2 b	464.5 cd	1,732.9 a	296.6 b	11.1 e	0.55 b
2007	Central	Interior	1,215.9 a	1,206.1 a	101.9 c	6,141.9 c	338.9 d	1,172.0 a	133.5 c	5.7 f	0.82 a
2008	Central	Interior	1,099.4 a	1,140.6 a	118.2 c	5,820.7 c	315.7 d	1,237.6 a	211.6 c	3.0 g	0.45 b
2009	Central	Interior	1,295.7 a	1,282.6 a	122.1 c	5,888.5 c	350.9 d	1,234.5 a	281.1 c	1.4 g	0.59 b

In each column, values followed by the same letter are not significantly different as determined by the least square means test ($p \le 0.05$; $n \ge 58$). Statistical comparisons in the GLM model showed that all interactions for parameters were significant for area (northern, central, and southern) × zone (perimeter, transition, and interior) at $p < 0.05$. Therefore, results are discussed with respect to area and zone (Snedecor and Cochran 1994; Kirk 1995)

DOC dissolved organic carbon, *TOC* total organic carbon, *TDS* total dissolved solids, *TSS* total suspended solids, *TP* total phosphorus

2007 through 2009. In the southern area perimeter zone, the TDS, Ca, Cl, and SO_4 loads were greater in 2005 and 2006 than in 2007 through 2009 (Table 5). The TSS and TP loads were greater in 2005 than in 2006 through 2009. In the southern area transition zone, Ca, Cl, Si, and SO_4 loads were greater in 2005 through 2007 than in 2008 and 2009. In the southern area interior zone, the SO_4 load was greater in 2005 and 2006 than in 2007 through 2009.

3.3 Nutrients Removed in the Refuge Marsh

As water flowed southward in the Refuge marsh, more DOC, TOC, and TP and less TSS were removed from clear water in the perimeter zone than the transition zone, and more of these same parameters were removed in the transition zone than the interior zone (Table 6). As water flowed southward in the Refuge marsh from the northern to the southern area in the perimeter zone, substantial amounts of DOC, TOC, TSS, TDS, Ca, Si, SO_4, and TP were removed from the water column. As water flowed southward in the Refuge marsh from the northern to the southern area in the perimeter zone, large amounts of Cl were added to the water column. As water flowed southward in the Refuge marsh from the northern to the central area in the perimeter zone, SO_4 was added to the water column. As water flowed southward in the Refuge marsh from the central to the southern area in the perimeter zone, TSS and Cl were added to the water column. As water flowed southward in the Refuge marsh from the northern to the southern area in the transition zone, large amounts of DOC, TOC, TSS, and TP were removed from the water column. As water flowed southward in the Refuge marsh from the northern to the southern area in the transition zone, DOC, TOC, TSS, and TP were removed from the water column, while large amounts of TDS, Ca, Cl, Si, and SO_4 were added to the water column. As water flowed southward in the Refuge marsh from the northern to the central area in the transition zone, substantial amounts of DOC, TOC, TDS, Cl, and TP were removed from

Table 5 Amount of dissolved organic carbon, total organic carbon, total dissolved solids, total suspended solids, Ca, Cl, Si, SO_4, and total phosphorus concentrations in the in the perimeter zone, transition, and interior zones in the southern area in the Loxahatchee National Wildlife Refuge from 2005 to 2009

Year	Area	Zone	DOC kg	TOC kg	TSS kg	TDS kg	Ca kg	Cl kg	Si kg	SO_4 kg	TP kg
2005	Southern	Perimeter	1,127.6 a	1,157.7 a	160.9 a	12,280.6 a	1,508.3 a	2,635.3 a	445.5 a	471.4 a	0.70 a
2006	Southern	Perimeter	1,163.4 a	1,165.2 a	101.8 b	12,737.2 a	1,459.0 a	2,776.7 a	374.6 a	409.5 a	0.46 b
2007	Southern	Perimeter	1,054.4 a	1,070.0 a	107.5 b	10,805.1 b	1,183.5 b	1,976.3 b	378.7 a	280.3 b	0.55 b
2008	Southern	Perimeter	968.4 a	978.9 a	115.8 b	8,100.5 b	904.8 b	1,538.0 b	319.0 b	193.8 c	0.45 b
2009	Southern	Perimeter	1,120.4 a	1,135.7 a	109.8 b	9,796.2 b	1,198.4 b	2,050.4 b	464.4 a	308.0 b	0.53 b
2005	Southern	Transition	667.4 b	672.5 b	65.2 c	5,512.1 c	605.2 c	1,135.0 c	271.5 b	50.4 d	0.33 c
2006	Southern	Transition	700.1 b	700.1 b	65.2 c	5,991.0 c	609.7 c	1,210.4 c	357.7 a	40.8 d	0.28 c
2007	Southern	Transition	716.1 b	716.1 b	65.2 c	6,060.8 c	519.3 c	1,070.1 c	260.2 b	31.4 d	0.34 c
2008	Southern	Transition	573.3 b	570.6 b	91.1 bc	4,064.4 c	356.4 d	891.4 d	198.3 c	11.2 e	0.29 c
2009	Southern	Transition	656.6 b	661.1 b	83.8 bc	4,030.2 c	417.1 d	822.8 d	233.5 c	8.0 e	0.39 c
2005	Southern	Interior	393.9 c	404.9 c	47.1 d	2,344.4 d	146.6 e	429.2 e	65.2 c	2.1 f	0.15 d
2006	Southern	Interior	446.1 c	441.1 c	35.0 d	2,410.7 d	177.3 e	512.3 e	40.9 c	1.8 f	0.16 d
2007	Southern	Interior	372.0 c	379.3 c	35.0 d	2,321.6 d	151.7 e	407.8 e	50.8 c	1.1 g	0.15 d
2008	Southern	Interior	365.1 c	365.1 c	49.5 d	1,990.6 d	135.6 e	394.3 e	85.9 c	0.8 g	0.15 d
2009	Southern	Interior	417.8 c	419.8 c	50.1 d	2,108.9 d	143.0 e	400.5 e	97.2 c	0.2 g	0.14 d

In each column, values followed by the same letter are not significantly different as determined by the least square means test ($p \leq 0.05$; $n \geq 58$). Statistical comparisons in the GLM model showed that all interactions for parameters were significant for area (northern, central, and southern) × zone (perimeter, transition, and interior) at $p < 0.05$. Therefore, results are discussed with respect to area and zone (Snedecor and Cochran 1994; Kirk 1995)

DOC dissolved organic carbon, *TOC* total organic carbon, *TDS* total dissolved solids, *TSS* total suspended solids, *TP* total phosphorus

the water column, while TSS, Ca, Si, and SO_4 were added to the water column. As water flowed southward in the Refuge marsh from the central to the southern area in the transition zone, DOC, TOC,

Table 6 The amount of dissolved organic carbon, total organic carbon, total dissolved solids, total suspended solids, Ca, Cl, Si, SO_4, and total phosphorus removed from clear water (without floc) annually in the perimeter, transition, and interior zones as water flowed southward in the A.R.M. Loxahatchee National Wildlife Refuge from 2005 to 2009

Zone	Area	Distance km	DOC mg m^{2}yr^{-1}	TOC mg m^{2}yr^{-1}	TSS mg m^{2}yr^{-1}	TDS mg m^{2}yr^{-1}	Ca mg m^{2}yr^{-1}	Cl mg m^{2}yr^{-1}	Si mg m^{2}yr^{-1}	SO_4 mg m^{2}yr^{-1}	TP mg m^{2}yr^{-1}
Perimeter	Northern to central	13	1,262	1,436	514	13,776	2,376	3,225	518	−144	5.66
Perimeter	Central to southern	17	797	742	−424	13,689	986	−18,745	1,316	1,532	2.36
Perimeter	Northern to southern	30	2,160	2,179	89	27,465	3,362	−15,520	1,834	1,388	8.02
Transition	Northern to central	13	1,397	1,415	−497	1,127	−322	1,785	−461	−96	0.44
Transition	Central to southern	17	409	542	617	−11,981	−1,838	−4,054	291	8	0
Transition	Northern to southern	30	1,806	1,957	121	−10,853	−2160	−2,269	−172	−88	0.44
Interior	Northern to central	13	−313	−257	1,680	−5,715	−413	−2,107	−222	9	−0.44
Interior	Central to southern	17	962	974	90	4,062	−302	1,127	519	20	0.79
Interior	Northern to southern	30	649	717	1,770	−1,653	−716	−979	297	28	0.35

Each value n=192. In the Everglades ecosystem, average solute velocity in surface water is 0.34 cm s^{-1}, which is 8.8 km month^{-1} (Harvey et al. 2005)

DOC dissolved organic carbon, *TOC* total organic carbon, *TDS* total dissolved solids, *TSS* total suspended solids, *TP* total phosphorus

TSS, Si, and SO_4 were removed from the water column, while large amounts of TDS, Ca, and Cl were added to the water column. As water flowed southward in the Refuge marsh from the northern to the southern area in the interior zone, DOC, TOC, TSS, Si, SO_4, and TP were removed from the water column, while TDS, Ca, and Cl were added to the water column. As water flowed southward in the Refuge marsh from the northern to the central area in the interior zone, only TSS and SO_4 were removed from the water column, while DOC, TOC, TDS, Ca, Cl, Si, and TP were added to the water column. As water flowed southward in the Refuge marsh from the central to the southern area in the interior zone, DOC, TOC, TSS, TDS, Cl, Si, SO_4, and TP were removed from the water column, while Ca was added to the water column.

4 Discussion

In the perimeter zone, DOC, TOC, TSS, and Cl concentrations in water did not differ as water flowed southward through the Refuge marsh. Scheidt and Kalla (2007) found that in general, TP, organic carbon, N, and Cl concentrations in water decreased as water flowed southward through the Everglades ecosystem from the northern Refuge through Everglades National Park. However, these decreasing TP, organic carbon, N, and Cl concentrations in water that flowed through the Everglades ecosystem were dramatically affected by canal water intrusion into the marsh. Entry (2012a) found that in the perimeter zone, the Refuge marsh has an exponential decrease in TDS, Ca, Cl, and SO_4 concentrations from the canal through the perimeter zone resulting in an approximately 60–90 % reduction of the values found in the canal. The exponential decrease of these parameters and elements with distance from canal suggests that canal water is continually intruding toward the Refuge interior with inorganic P being quickly assimilated by plants and algae in the northern Everglades system. Nutrients, especially P, in this oligotrophic ecosystem are quickly assimilated by primary producers (Noe et al. 2001, 2003; Childers et al. 2003; Gaiser 2009). The intrusion of high nutrient canal water into the Refuge perimeter zone over decades may be responsible for the transition of sawgrass to cattail communities, which are adapted to higher soil P concentrations (Miao et al. 2000, 2001; Debusk et al. 2001; Asaeda and Hung 2007; Hagerthey et al. 2008; McCormick et al. 2009). Such a transition was the case for the western border of the Refuge marsh. Substantial ecological changes have been reported downstream of P sources intruding into the Everglades marsh (McCormick et al. 2009; Cooper et al. 1999; Pan et al. 2000; Noe et al. 2001; Gaiser et al. 2006). Periphyton mats comprise a substantial portion of the Everglades biomass contributing to a large portion of net primary production (Noe et al. 2003; Gaiser et al. 2004; 2006). In the Everglades ecosystem, increasing nutrient concentrations can decrease periphyton biomass (Davis 1994; McCormick and Stevenson 1998) and shift the periphyton community structure (Sklar et al. 2005; McCormick et al. 2009) ultimately impacting plant communities. In the transition and interior zones, DOC, TOC, TDS, and Ca concentrations in water were higher in the northern than in the southern area indicating that canal water has not intruded into these zones as often as it does into the perimeter zone.

In general, the amounts of TDS, Ca, Cl, Si, SO_4, and TP in the northern, perimeter, transition, and interior zones have decreased from 2005 to 2009. These decreases are much less pronounced in the central and southern areas. Although the trends were not significant in every analysis and there was a minor amount of variation, nutrient and inorganic ion trends were more negative in the more nutrient-enriched canal and perimeter zones than the less nutrient-enriched transition and interior zones (Entry 2012b). Entry (2012c) also found that that nutrient and ion concentrations in Refuge water have decreased more rapidly in the more nutrient-enriched zones near the canal than the less nutrient-enriched zones and that nutrients have been cycling more rapidly in the more enriched zones than in the less enriched zones. Entry (2012d) found that in the northern Refuge, most water quality parameters measured in the canal and perimeter zone decreased from 2005 to 2009, while fewer water quality parameters decreased in the transition and interior zones. The reason for the improved water quality can be attributed to an improved STA1-East performance since 2005 and that canal water, which by-passed treatment in STA1-East and STA1-West and flowed into the L-7 canal through the S-6 pump, is now diverted farther south into STA2 for treatment (Germain and Pietro 2011; Ivanoff and Chen 2012). These results indicate that the amount of TDS, Ca, Cl, Si, SO_4, and TP in the Refuge water has decreased from 2005 to 2009. If the Refuge ecosystem is to be preserved, decreases in the amount of these nutrients in the Refuge water need to be improved until canal water has the same water quality as the interior zone.

As water flowed southward for over 30 km in the Refuge marsh from the northern to the southern area in the perimeter zone, most water quality parameters were removed from the water column. However, a large amount of Cl was added to the water column indicating that there is canal water continually intruding into the marsh along the entire zone. As water flowed southward in the Refuge marsh from the northern to the southern perimeter zone, only SO_4 was added to the water column indicating that there is most likely an amount of plant biomass in the northern perimeter zone which is rapidly accumulating nutrients when canal water intrudes into this zone. These results also indicate that unlike the other nutrients analyzed, the quantity of SO_4 added to the northern perimeter zone is greater than the ability of the periphyton and plants to remove the nutrient from the water column. As water flowed southward for over 30 km in the Refuge marsh from the northern to the southern area in the transition zone, large amounts of TDS, Ca, Cl, Si, and SO_4 were added to the water column indicating that there is canal water continually intruding as far as 4.5 km into the marsh along the entire zone. As water flowed southward in the Refuge marsh from the northern to the central area in the transition zone, TSS, Ca, Si, and SO_4 were added to the water column indicating that periphyton and plants growing in the northern transition zone are unable to accumulate these ions as quickly as canal water intrusion deposits them into the central and southern transition zones. As water flowed southward for over 30 km in the Refuge marsh from the northern to the southern area in the interior zone, some TDS, Ca, and Cl were added to the water column indicating that there is canal water continually intruding as into the Refuge interior and that the entire Refuge is affected by canal water intrusion. As water flowed southward in the Refuge marsh from the northern to the central area in the Refuge interior, DOC, TOC, TDS, Ca, Cl, Si, and TP were added to the water column indicating that periphyton and plants in the Refuge interior are unable to accumulate these ions as quickly as canal water intrusion deposits them. As water flowed southward in the Refuge marsh from the central to the southern area in the Refuge interior, only Ca was added to the water column indicating that there is less canal water intruding into the southern than the northern Refuge interior. Water flow from the canal into the marsh in the Northern and Southern Refuge differs because water is deeper in the southern Refuge and on an area basis contains a greater volume of water than the northern Refuge. Canal water containing a higher concentration of nutrients intruding into the southern Refuge should become diluted and dispersed more rapidly because it is intruding into a greater volume of nutrient-poor water than when intruding into the northern Refuge.

Surratt et al. (2008) found that the most frequent canal water intrusion was on the west side of the Refuge. In general, canal water intruded between 0.1 and 5 km into the Refuge from the canal into the Refuge marsh and that canal–marsh stage difference influenced the movement of water in and out of the marsh, and high inflow rates to the canal tended to increase intrusion. Areas with sediment elevation lower than 4.5 m were the most vulnerable to canal water movement in or out of the Refuge. These results agree with the findings of Surratt et al. (2008) that there is frequent and persistent intrusion of canal water as far as 5.0 km into the Refuge marsh. Richardson et al. (1990) reported on the change in species composition in relation to water quality in the Refuge; however, data for nutrient loads in soil and plant biomass on an area basis are lacking. A study documenting nutrient uptake, storage, and cycling in relation to water quality in the Refuge and throughout the entire Everglades ecosystem is necessary in order to make informed management decisions. In addition, Entry (2012c, d) found that both the consent decree and four-part test monitoring network are insufficient to detect water quality changes in the Refuge marsh because of the sparseness and location of sampling sites. The number and placement of monitoring sites in the Refuge require optimization based on flow patterns, distance from contaminant sources, and water volumes to fully understand the effect of canal water intrusion on water quality.

Other than TSS and TOC, these results are confined to ions dissolved in water without appreciable concentrations of suspended particles. Fluxes of suspended sediment in the Everglades ecosystem are controlled by vegetation, water flow, and wind (Noe et al. 2007, 2010). Vegetation decreases water velocity (Leonard and Luther 1995; Leonard and Reed 2002; Leonard et al. 2002), decreases turbulence intensity (Leonard and Luther 1995; Leonard et al. 2002), and can trap suspended particulates (Saiers et al. 2003; Palmer et al. 2004). These vegetation-induced changes can result in lower concentrations of suspended particulates (Braskerud 2001; Leonard and Reed 2002), greater sediment deposition rates, or decreased resuspension of sediments in densely vegetated portions of wetlands (Braskerud 2001; Noe et al. 2007, 2010). Transport and retention of suspended particles play a major role in ecosystem cycling of the Everglades wetlands (Noe et al. 2007, 2010). Therefore, the TSS results show that an investigation of nutrients attached to suspended particulates is necessary to complete our understanding of the transport of nutrients in the Refuge. Although vegetation will affect water flow through the Refuge marsh, dissolved ions are not as readily deposited or resuspended by changes in water velocity and turbulence.

5 Conclusions

In the perimeter zone, and to a lesser degree in the transition zone, the Refuge has accumulated substantial amounts of Ca, Si, SO_4, and TP in vegetation and soils during the sampling period. In the perimeter zone, TDS, Si, and TP concentrations in water were higher in the northern than the central area and TDS, Si, SO_4, and TP concentrations in water were higher in the central than the southern area. Dissolved organic carbon, TOC, TSS, and Cl concentrations in water did not differ as water flows southward through the Refuge marsh; however, in the transition and interior zones, DOC, TOC, TDS, and Ca concentrations in water were higher in the northern than in the southern area indicating that canal water has not intruded into these two zones as often as in the perimeter zone. In general, the TDS, Ca, Cl, Si, SO_4, and TP loads in the northern area's perimeter, transition, and interior zones have decreased from 2005 to 2009. This decrease is much less pronounced in the central and southern areas. As water flowed southward for over 30 km in the Refuge marsh from the northern to the southern area in the perimeter zone, most water quality parameters were removed from the water column. However, a large amount of Cl was added to the water column indicating that the northern perimeter zone canal water is continually intruding into the marsh along the entire zone.

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