

Water Quality Trends in the Loxahatchee National Wildlife Refuge

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Abstract The Loxahatchee National Wildlife Refuge (Refuge) developed throughout millennia as a system with waters low in nutrients. Today, the Refuge wetlands are impacted by inflows containing elevated nutrient concentrations originating from agricultural sources. Surface water samples were collected monthly at 48 marsh and five canal sites from June, 2004 through May, 2011 and analyzed water quality trends by sampling perimeter, transition, and the interior zones based on distance from the canal towards the Refuge interior. Nutrient, inorganic ion, and C concentrations generally decreased with distance from the canal to the Refuge interior. These water quality parameters also decreased from the canal to the Refuge interior, but less sharply. This finding suggests that there has been less canal water intrusion into the Refuge during the sampling period. The origin of the high Ca and Cl concentrations in canal water is most likely from intrusion of connate seawater into the canal. The reason for the improved water quality from June, 2004 to June 2011 can be attributed to an improved STA1-East performance since 2005. Additionally, canal water that originally 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.

Keywords Refuge · A.R.M. Loxahatchee National Wildlife Refuge · Kendall tau seasonal trend · Tobit trend

Abbreviations

Refuge	A.R.M. Loxahatchee National Wildlife Refuge
STA	Stormwater treatment areas
ALK	Alkalinity
DO	Dissolved oxygen
DOC	Dissolved organic carbon
FTU	Formazin turbidity unit
SpC	Conductivity
TB	Turbidity
TDS	Total dissolved solids
TOC	Total organic carbon
TP	Total phosphorus
TSS	Total suspended sediments
CDdepth	Depth of the clear water column
CSdepth	Depth to consolidated substrate

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 concentration and low conductivity (Davis 1994). The Arthur R. Marshall 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

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content. Refuge surface water is classified by the State of Florida as Class III freshwater with water quality standards established to protect recreation, propagation, and maintenance of a healthy, well-balanced population of fish and wildlife (Section 62–302.400, 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 that no degradation of water quality be allowed to occur other than that allowed in Rule 62–4.242(2) and (3), F.A.C.

Fauna and flora that were native to the Everglades before modern agricultural and urban development are adapted to extremely low P concentrations; therefore ecosystem function changes with only 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). Conversion of sawgrass (*Cladium jamaicense* Crantz.) stands to cattail (*Typha domingensis* Pers.) has also been documented (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 their 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). Outflows are controlled by the US 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; Chang et al. 2009; Wang et al. 2009).

Before 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 sources is treated in STA1-East, whereas stormwater treated in STA1-West originates primarily from the 280,000 ha Everglades Agricultural Area located northwest of the Refuge. Treated water is pumped into the Refuge from STA-

1 East into the eastern L-40 canal and from STA-1 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 exceed 4.57 m National Geodetic Vertical Datum 1929 and inflow rates are greater than $14.18 \text{ m}^3 \text{ s}^{-1}$ (Harwell et al. 2008; Miller and McPherson 2008; Surratt et al. 2008).

Entry (2012a) found that alkalinity (ALK), total dissolved solids (TDS), and concentrations of SpC, Ca, Cl, and SO_4 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 interior zone. Alkalinity, SpC, and TDS values, as well as 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), TOC, TDS, Ca, Cl, 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, whereas total phosphorus (TP) concentrations in the Refuge did not. This finding suggests that excess inorganic N and P are quickly assimilated by nutrient-limited periphyton and plants (Entry 2012a, b). Alkalinity, TDS, TB, and SpC values and Ca, Cl, Si, SO_4 , and TP concentrations decreased from 2005 through 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 through 2009 in the interior zone (Entry 2012b). The objective of this research was to determine if water quality has improved in the Refuge, and whether water quality improved more quickly in areas where marsh water contains a higher concentration of nutrients.

2 Materials and Methods

2.1 Marsh Zones and Delineations

The Refuge was divided into four zones (Fig. 1) delineated as the canal surrounding the Refuge marsh,

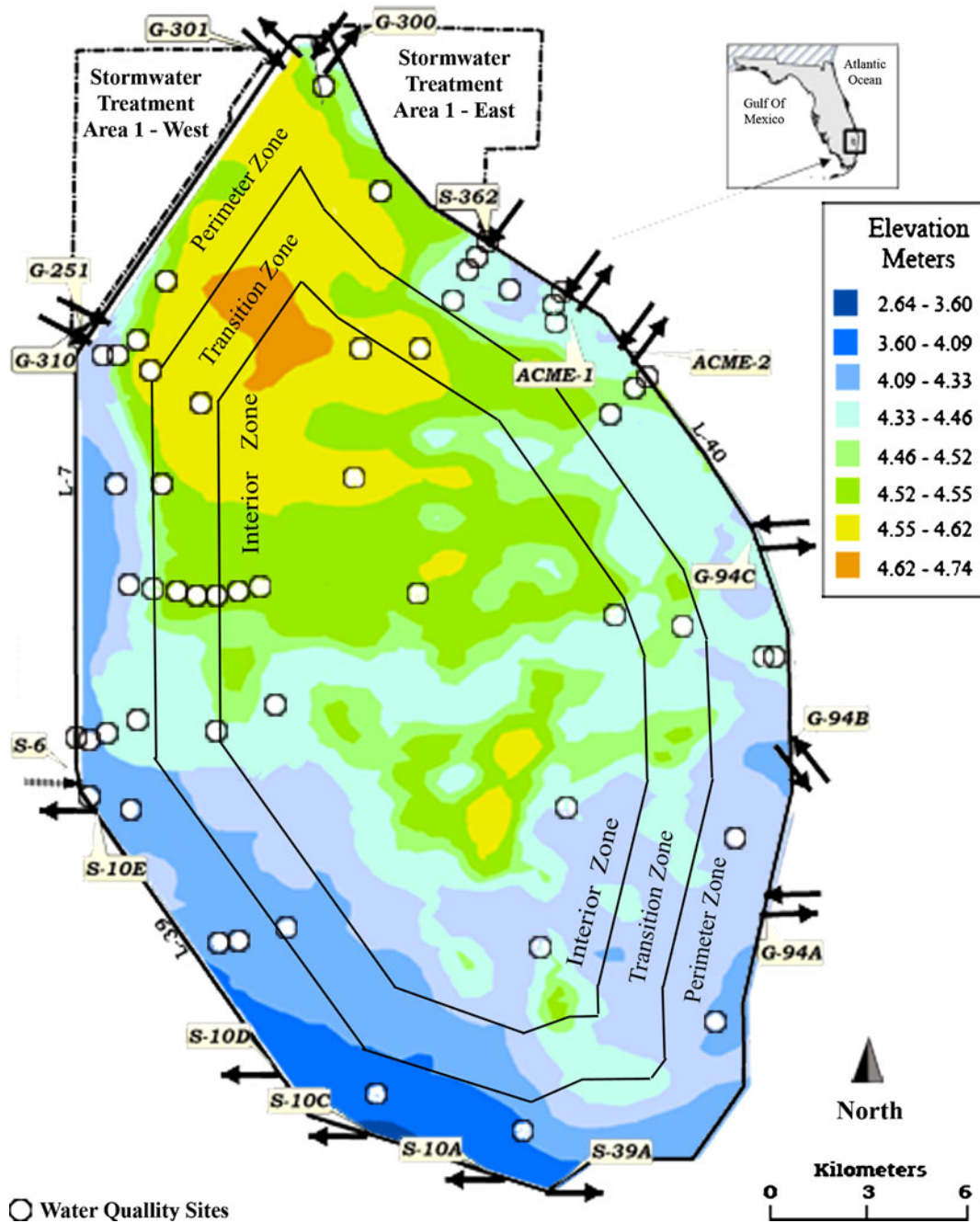


Fig. 1 Water quality sites in the Loxahatchee National Wildlife Refuge Inflow sites are indicated by arrows pointing into the Refuge. Outflow sites are indicated by arrows pointing out of the Refuge. Elevation provided by USGS (2005)

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; Entry 2012a).

2.2 Sample Collection

Surface water samples were collected monthly at 48 marsh and five canal sites from June, 2004 through

May, 2011. Marsh sites were accessed by float helicopter and sampled by wading out into the marsh to collect 0.5 to 3.0 L of undisturbed water, and to make field measurements of SpC, dissolved oxygen (DO), and pH using Hydrolab multiprobe datasondes (Hydrolab, Mini Sonde 4a; Loveland, CO), and depth of the clear water column (CWdepth), and CSdepth (SFWMD 2006). Depths were measured within a 10-m radius of each sampling point. At water levels greater than 20 cm, 3.0 L of water was collected for analysis allowing a full suite of chemical analyses to be performed. Samples were stored on ice at 4 °C, filtered, and preserved within 4 h of collection.

2.3 Laboratory Analysis

All samples collected from June, 2004 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 May, 2011 were analyzed by Columbia Analytical Services (Jacksonville, FL). Total organic carbon (TOC) was determined by thermal combustion as described in the EPA 415.1 method, and measured on a Shimadzu TOC-V_{CHS} carbon analyzer. Dissolved organic carbon and total dissolved solids were measured in water passed through a 0.45- μm filter. TDS was 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. Total suspended solids was measured after the sample was dried at 103 °C and weighed as described in the EPA 160.2 method (APHA 2005). TDS was 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 sub-sample was analyzed for Ca, Cl, and Si using a PerkinElmer 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 acidified ammonium persulfate (APHA 2005).

2.4 Statistical Analysis

Only data with complete records for all parameters measured were analyzed. The data did not have a normal distribution, nor could a normal distribution be achieved using transformations. If there were TP data that were less than the 2 $\mu\text{g TP L}^{-1}$ the limit of detection, we reported that number as one half the detection limit (Schertz et al. 1991; APHA 2005). All other measurements for water quality parameters exceeded above limits of detection. Data from the middle 4 months of each six-month dry (May 1 to October 31) and wet (November 1 to April 30) seasons were subjected to seasonal Kendall tau trend analysis with residuals from locally weighted scatterplot smoothing (LOWESS) curves (Helsel and Hirsch 2002). Tobit trends were analyzed using SAS programs QLIM procedure (SAS 2008). Since <0.1 % of the values in the data set were less than the 2 $\mu\text{g TP L}^{-1}$ limit of detection, the small number of TP values did not invalidate the Kendall tau or Tobit trend analysis (Helsel and Hirsch 2002). Trend analyses for the entire year were based on the center dry season months (June 1 through September 30) and wet season months (December 1 through March 31) because transition months may distort trend analysis (Helsel and Hirsch 2002).

3 Results

When statistically significant, Kendall tau and Tobit TP, total Keldahal nitrogen (TKN), and SO_4 slopes were negative in all zones on an annual basis and in both the wet and dry seasons, indicating that the concentrations of these nutrients in water throughout the Refuge have decreased during since 2004 (Table 1). Although there was some variation, the Kendall tau and Tobit TP, TKN, and SO_4 slopes generally decreased from the canal to the interior zone indicating that the concentrations of these nutrients in water throughout the Refuge have decreased more rapidly in the more impacted canal and perimeter zones than in the less impacted interior zone. In the perimeter, transition, and interior zones the Kendall tau TP, TKN,

Table 1 Seasonal Kendall tau and Tobit trends for total phosphorus, total keldahal nitrogen, and sulfate in four zones during the dry season, wet season, and annually in the Loxahatchee National Wildlife Refuge from June, 2004 through June, 2011

Zone	Season	Total phosphorus				Total Keldahal nitrogen				Sulfate			
		Seasonal Kendall tau		Tobit		Seasonal Kendall tau		Tobit		Seasonal Kendall tau		Tobit	
		<i>p</i>	% Slope year ⁻¹	<i>p</i>	% Slope year ⁻¹	<i>p</i>	% Slope year ⁻¹	<i>p</i>	% Slope year ⁻¹	<i>p</i>	% Slope year ⁻¹	<i>p</i>	% Slope year ⁻¹
Canal	Dry	0.00*	-92.52	0.00*	-12.28	0.38	-0.27	NS	-0.62	0.38	-12.78	0.00*	-25.67
Canal	Wet	0.00*	-117.44	0.00*	-199.71	0.01*	-0.95	NS	-1.10	0.30	-18.32	0.00*	-9.52
Canal	Annual	0.00*	-106.56	0.00*	-175.46	0.01*	-0.60	NS	-1.07	0.18	-14.81	0.00*	-28.56
Perimeter	Dry	0.34	-5.83	0.23	-7.69	0.00*	-0.71	NS	-0.69	0.00*	-5.03	0.00*	-27.25
Perimeter	Wet	0.03*	-8.64	0.00*	-49.70	0.00*	-1.53	NS	-1.83	0.00*	-18.25	0.00*	-53.91
Perimeter	Annual	0.04*	-92.42	0.00*	-34.65	0.00*	-0.95	NS	-1.37	0.00*	-7.31	0.00*	-45.36
Transition	Dry	0.00*	-7.38	NS	-6.90	0.34	-0.20	NS	-0.16	0.02*	-0.51	NS	-1.12
Transition	Wet	0.01*	-10.66	0.00*	-17.83	0.00*	-0.86	NS	-1.07	0.00*	-2.02	NS	-7.94
Transition	Annual	0.00*	-13.34	0.00*	-14.66	0.00*	-0.94	NS	-6.90	0.00*	-5.68	NS	-5.47
Interior	Dry	0.00*	-8.50	0.00*	-7.64	0.34	-0.24	NS	-0.76	0.02*	29.12	NS	-0.21
Interior	Wet	0.09*	-5.70	0.00*	-24.18	0.00*	-1.09	NS	-2.12	0.04*	26.57	NS	-0.56
Interior	Annual	0.00*	-12.77	0.00*	-15.24	0.01*	-0.61	NS	-1.38	0.00*	243.69	NS	-0.38

NS not significant

* $p \leq 0.05$ (Kendall tau trend significant)

and SO₄ slopes in wet season were higher than those in the dry season, indicating that TKN may be intruding into the Refuge interior during wet seasons. Kendall tau slopes for SO₄ increased in the interior zone, indicating that the SO₄ concentration in water in the Refuge interior may have increased during that same period.

When statistically significant, Kendall tau and Tobit Ca, Cl, Si, SpC, and ALK slopes were negative in the perimeter and transition zones on an annual basis and in both the wet and dry seasons, indicating that the concentrations of these elements in these zones have decreased over the past 7 years (Tables 2 and 3). When statistically significant, Kendall tau and Tobit Ca, Si, SpC, and ALK slopes were negative in the canal zone on an annual basis and in both the wet and dry seasons, indicating that the concentrations of these water quality parameters in this zone have decreased since 2004. Both Kendall tau and Tobit Cl slopes were positive in the canal, indicating that the Cl concentration in the canal has increased during the study period. Kendall tau and Tobit slopes for Ca, Cl, and Si slopes

were less negative from the perimeter to the interior zone, indicating that the concentrations of these elements in marsh water throughout the Refuge have decreased more rapidly in the more impacted zones than the less impacted interior zone. Kendall tau and Tobit Si, SpC, and ALK slopes were less negative in the canal than the perimeter zone, indicating that Si, SpC, and ALK has intruded from the canal into the Refuge marsh at least as far as the transition zone. Seasonal Kendall tau trends for pH were not significant when analyzed on an annual basis in the perimeter zone, in the transition during the wet season, and for the interior zone in the dry season. Tobit trends for pH were not significant in wet or dry seasons or annually in all zones. Seasonal Kendall tau slopes for pH were positive in the perimeter and transition zones during the dry season but negative in the perimeter, transition, and interior zones in the wet season and annually.

When statistically significant, Kendall tau and Tobit TOC and DOC slopes were negative in the perimeter, transition, and interior zones on an annual basis

Table 2 Seasonal Kendall tau and Tobit trends for calcium, chloride, and silicon in four zones during the dry season, wet season, and annually in the Loxahatchee National Wildlife Refuge from June, 2004 through June, 2011

Zone	Season	Calcium				Chloride				Silicon			
		Seasonal Kendall tau		Tobit		Seasonal Kendall tau		Tobit		Seasonal Kendall tau		Tobit	
		<i>p</i>	% Slope year ⁻¹	<i>p</i>	% Slope year ⁻¹	<i>p</i>	% Slope year ⁻¹	<i>p</i>	% Slope year ⁻¹	<i>p</i>	% Slope year ⁻¹	<i>p</i>	% Slope year ⁻¹
Canal	Dry	0.00*	-34.70	0.00*	-51.10	0.00*	93.77	0.00*	80.61	0.00*	-12.45	0.00*	-15.21
Canal	Wet	0.00*	-30.10	0.00*	-35.57	0.91	0.00	0.00*	5.83	0.68	-1.87	0.00*	-2.51
Canal	Annual	0.00*	-32.28	0.00*	-43.52	0.02*	42.10	0.00*	40.48	0.00*	-8.65	0.00*	-13.53
Perimeter	Dry	0.00*	-28.65	0.00*	-5.08	0.00*	-61.97	0.00*	-92.28	0.00*	-18.74	0.00*	-23.32
Perimeter	Wet	0.00*	-45.17	0.00*	-63.96	0.00*	-64.07	0.00*	-85.21	0.00*	-13.41	0.00*	-21.03
Perimeter	Annual	0.00*	-32.77	0.00*	-59.48	0.00*	-46.10	0.00*	-88.04	0.00*	-14.19	0.00*	-23.60
Transition	Dry	0.02*	-5.96	NS	-4.50	0.16	-6.49	0.00*	-7.18	0.00*	-15.12	0.00*	-13.80
Transition	Wet	0.00*	-12.22	NS	-17.11	0.00*	-37.66	0.00*	-52.10	0.03*	-5.34	NS	-1.78
Transition	Annual	0.00*	-27.94	NS	-11.52	0.00*	-41.96	0.00*	-30.86	0.00*	-13.82	NS	-12.02
Interior	Dry	0.57	-1.16	NS	-1.27	0.57	-2.56	0.00*	-4.22	0.35	-3.49	NS	-4.06
Interior	Wet	0.22	-3.83	NS	-5.09	0.01*	-17.69	0.00*	-18.06	0.75	-0.90	NS	-6.50
Interior	Annual	0.22	-24.46	NS	-2.88	0.05*	25.60	0.00*	-9.57	0.34	-7.99	NS	-5.29

NS not significant

* $p \leq 0.05$ (Kendall tau trend significant)

Table 3 Seasonal Kendall tau and Tobit trends for conductivity, alkalinity, and pH in four zones during the dry season, wet season, and annually in the Loxahatchee National Wildlife Refuge from June, 2004 through June, 2011

Zone	Season	Conductivity				Alkalinity				pH			
		Seasonal Kendall tau		Tobit		Seasonal Kendall tau		Tobit		Seasonal Kendall tau		Tobit	
		<i>p</i>	% Slope year ⁻¹	<i>p</i>	% Slope year ⁻¹	<i>p</i>	% Slope year ⁻¹	<i>p</i>	% Slope year ⁻¹	<i>p</i>	% Slope year ⁻¹	<i>p</i>	% Slope year ⁻¹
Canal	Dry	0.42	145.79	0.00*	-7.99	0.01*	-76.57	0.00*	-112.14	0.46	-0.12	NS	-0.21
Canal	Wet	0.21	-193.47	0.00*	-180.52	0.01*	-88.04	0.00*	-106.30	0.79	-0.05	NS	-0.10
Canal	Annual	0.79	-29.79	0.00*	-94.85	0.00*	-81.83	0.00*	-101.93	0.47	-0.08	NS	-0.61
Perimeter	Dry	0.00*	-412.89	0.00*	-641.09	0.00*	-96.82	0.00*	-151.82	0.01*	0.50	NS	-0.43
Perimeter	Wet	0.00*	-559.19	0.00*	-770.57	0.00*	-154.62	0.00*	-198.83	0.00*	-0.67	NS	-0.62
Perimeter	Annual	0.00*	-383.15	0.00*	-724.06	0.00*	-107.61	0.00*	-179.49	0.49	-0.10	NS	-0.01
Transition	Dry	0.01*	-90.81	0.00*	-53.73	0.32	-15.73	0.00*	-15.37	0.00*	1.78	NS	-1.63
Transition	Wet	0.00*	-220.62	0.00*	-287.00	0.00*	-47.82	0.00*	-55.13	0.54	-0.21	NS	0.00
Transition	Annual	0.00*	-335.54	0.00*	-179.34	0.00*	-95.74	0.00*	-36.21	0.03*	-0.07	NS	0.71
Interior	Dry	0.12	-46.04	0.00*	-39.20	0.05*	-15.97	0.00*	-19.23	0.77	-0.11	NS	0.26
Interior	Wet	0.06*	-91.20	0.00*	-134.87	0.01*	-29.94	0.00*	-52.20	0.00*	-1.23	NS	-1.22
Interior	Annual	0.02*	-41.89	0.00*	-82.85	0.00*	-65.35	0.00*	-33.89	0.04*	-0.12	NS	-0.35

NS not significant

* $p \leq 0.05$ (Kendall tau trend significant)

and in both the wet and dry seasons, indicating that the TOC and DOC concentrations in Refuge marsh water have decreased since 2004 (Table 4). Both Kendall tau and Tobit TOC and DOC slopes were less negative from the perimeter to the interior zone, indicating that TOC and DOC concentrations in marsh water throughout the Refuge have decreased more rapidly in the more impacted perimeter zone than the less impacted transition and interior zones. The TSS Kendall tau slopes in canal water have decreased, indicating that suspended solids in the canal and possibly in the interior zone have decreased since 2004.

When statistically significant, Kendall tau and Tobit TDS slopes were negative in the perimeter, transition, and interior zones on an annual basis and in both the wet and dry seasons, indicating that the TDS concentration in the Refuge marsh water decreased during the years of this study (Table 5). Tobit TB slopes were not significant on an annual basis and in the dry and wet seasons in any zone. Kendall tau and Tobit TDS slopes were less negative from the perimeter to the interior zone, indicating that the concentration of TDS throughout the Refuge marsh has

decreased more rapidly in the more impacted perimeter and transition zones than the less impacted interior zone. Kendall tau TB slopes were negative in all zones on an annual basis and in both the wet and dry seasons, indicating that the TB concentration in the Refuge marsh water has decreased since 2004. Tobit DO slopes were not significant on an annual basis in the dry and wet seasons for any zone. Kendall tau DO slopes were positive in the canal, perimeter, and transition zones, indicating that the DO concentration has increased in these zones during the years of this study.

4 Discussion

The intrusion of high nutrient concentration 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 most likely the case for the western border of the Refuge

Table 4 Seasonal Kendall tau and Tobit trends for total organic carbon, dissolved organic carbon, and total suspended solids in four zones during the dry season, wet season, and annually in the Loxahatchee National Wildlife Refuge from June, 2004 through June, 2011

Zone	Season	Total organic carbon				Total dissolved carbon				Total suspended solids			
		Seasonal Kendall tau	Tobit	Seasonal Kendall tau	Tobit	Seasonal Kendall tau	Tobit	Seasonal Kendall tau	Tobit				
		<i>p</i>	% Slope year ⁻¹	<i>p</i>	% Slope year ⁻¹	<i>p</i>	% Slope year ⁻¹	<i>p</i>	% Slope year ⁻¹	<i>p</i>	% Slope year ⁻¹	<i>p</i>	% Slope year ⁻¹
Canal	Dry	0.48	1.98	0.02*	-0.13	0.53	0.00	0.06	0.41	0.04*	-3.46	NS	-6.21
Canal	Wet	0.05*	-10.12	0.13	-8.70	0.04*	-10.30	0.17	-8.49	0.00*	-6.13	0.11	-9.33
Canal	Annual	0.41	-1.09	0.14	-6.03	0.36	-1.64	0.14	-5.91	0.00*	-4.78	0.00*	-5.93
Perimeter	Dry	0.00*	-19.42	0.00*	-20.43	0.00*	-20.71	0.00*	-23.24	0.22	0.00	0.00*	3.13
Perimeter	Wet	0.00*	-25.12	0.00*	-29.71	0.00*	-19.97	0.00*	-21.16	0.46	0.00	NS	-0.37
Perimeter	Annual	0.00*	-17.60	0.00*	-25.50	0.00*	-16.45	0.00*	-22.21	0.16	0.00	0.00*	-0.22
Transition	Dry	0.01*	-14.02	0.00*	-9.49	0.00*	-15.19	NS	-9.91	0.73	0.00	NS	-0.31
Transition	Wet	0.00*	-20.04	0.00*	-18.29	0.00*	-17.65	0.00*	-18.07	1.00	0.00	NS	-4.09
Transition	Annual	0.00*	-17.59	0.00*	-15.01	0.00*	-16.52	NS	-12.92	0.81	0.00	NS	-2.55
Interior	Dry	0.59	-0.79	NS	-3.14	0.70	0.00	NS	-3.11	0.18	-0.28	NS	-3.43
Interior	Wet	0.00*	-37.28	0.00*	-34.86	0.06	-0.43	NS	-6.10	0.13	-0.24	0.00*	-62.50
Interior	Annual	0.01*	-2.95	0.00*	-16.57	0.14	-0.18	NS	-0.40	0.04*	-4.29	0.00*	-32.10

NS not significant

**p*≤0.05 (Kendall tau trend significant)

Table 5 Seasonal Kendall tau and Tobit trends for total dissolved solids, turbidity, and dissolved oxygen in four zones during the dry season, wet season, and annually in the Loxahatchee National Wildlife Refuge from June, 2004 through June, 2011

Zone	Season	Total dissolved solids				Turbidity				Dissolved oxygen			
		Seasonal Kendall tau		Tobit		Seasonal Kendall tau		Tobit		Seasonal Kendall tau		Tobit	
		<i>p</i>	% Slope year ⁻¹	<i>p</i>	% Slope year ⁻¹	<i>p</i>	% Slope year ⁻¹	<i>p</i>	% Slope year ⁻¹	<i>p</i>	% Slope year ⁻¹	<i>p</i>	% Slope year ⁻¹
Canal	Dry	0.10	-208.36	0.00*	-0.11	0.00*	-9.29	NS	-12.01	0.00*	5.20	NS	5.67
Canal	Wet	0.07	-179.96	0.00*	-162.14	0.00*	-6.69	NS	-11.54	0.71	-0.37	NS	-0.39
Canal	Annual	0.02*	-191.06	0.00*	-6.85	0.00*	-7.78	NS	-11.12	0.02*	2.29	NS	4.67
Perimeter	Dry	0.00*	-357.66	0.00*	-348.26	0.00*	-0.35	NS	-0.67	0.00*	5.61	NS	4.58
Perimeter	Wet	0.00*	-401.10	0.00*	-514.91	0.00*	-0.99	NS	-1.36	0.00*	2.88	NS	5.31
Perimeter	Annual	0.00*	-332.34	0.00*	-508.33	0.00*	-0.87	NS	-0.59	0.00*	3.52	NS	5.17
Transition	Dry	0.00*	-134.87	0.00*	-120.03	0.01*	-0.45	NS	-0.03	0.00*	8.86	NS	6.52
Transition	Wet	0.00*	-152.49	0.00*	-196.40	0.02*	-0.63	NS	-1.27	0.03*	2.31	NS	2.27
Transition	Annual	0.00*	-302.38	0.00*	-157.29	0.00*	-0.85	NS	-0.84	0.00*	3.55	NS	5.24
Interior	Dry	0.16	-49.56	0.00*	-54.61	0.05*	-0.28	NS	-1.75	0.30	-0.27	NS	-2.12
Interior	Wet	0.00*	-116.93	0.00*	-112.70	0.11	-0.73	NS	-3.87	0.48	-0.10	NS	-0.92
Interior	Annual	0.00*	-155.03	0.00*	-78.86	0.01*	-0.71	NS	-2.74	0.20	0.14	NS	-1.21

NS not significant

* $p \leq 0.05$ (Kendall tau trend significant)

marsh. Substantial ecological changes have been reported downstream of P sources intruding into the Everglades marsh (McCormick et al. 1996; Cooper et al. 1999; Pan et al. 2000; Noe et al. 2001; Gaiser et al. 2005). 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. Entry (2012b) found that in the northern Refuge most water quality parameters measured in the canal and perimeter zone decreased from 2005 through 2009, whereas fewer water quality parameters decreased in the transition and interior zones. The reason for the improved water quality can be attributed to improved STA1-East performance since 2005 and to the fact that canal water that by-passed treatment in STA1-East and STA1-West, and thereby flowed into the L-7 canal through the S-6 pump, is now diverted farther south

into STA2 for treatment (Payne and Xue 2011). In nutrient-enriched areas of the Everglades, plants grow faster and larger, cycling and depositing C, N, and P more rapidly into the soil (Craft and Richardson 1998, 1993a, b). The vast majority of plant roots typically grow to a depth of only 30 cm (Christina et al. 2011; Sampathkumara et al. 2012), and in the Everglades marsh peat accretion rates vary from 1.6 mm year⁻¹ in areas with low soil N and P concentration to 4.0 mm year⁻¹ in areas with high soil N and P concentration. If water containing 10 µg TP L⁻¹ was continuously delivered to the Refuge marsh today, it would take from 100 to 200 years for these nutrients to be buried below 30 cm where roots are unable to rapidly take up and cycle these nutrients back into the ecosystem.

In general the decreasing Ca, Cl, Si, SpC, and ALK slopes from the canal to the Refuge interior suggest that there has been less canal water intrusion into the Refuge during the sampling period. The origin of the high Ca and Cl concentrations in canal water is thought to be from intrusion of connate seawater into the canal. Excavation of canals released saline groundwater,

enabling it to mix with the overlying surface and groundwater in the canals (Craft and Richardson 1993b). Chloride is not a plant macronutrient and is not taken up by periphyton or marsh plants in appreciable quantities. Therefore Cl is an additional ion that can be used as a tracer for canal water diffusion and intrusion into the Refuge marsh. Surratt et al. (2008) used SpC as a tracer of canal water intrusion into the Refuge interior. The decreasing Cl, SpC, TSS, TDS, and ALK slopes and the less negative slopes of these water quality parameters from the canal to the Refuge interior may require more of the sampling sites to be statistically designed and located closer to the canal surrounding the Refuge to be sensitive enough to accurately detect changes. Entry (2012a, b) found that the Consent Decree and Four-Part test monitoring networks were insufficient to adequately characterize Refuge water quality, and that an entirely new water quality sampling network was necessary. Since only 11 monitoring sites are located in the southern third of the Refuge, there may be insufficient data to characterize water quality in this part of the Refuge with confidence. Water flow from the canal into the marsh in the Northern and Southern Refuge may also differ 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 can be expected to 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. In addition, since the elevation in Southern Refuge decreases in a more southerly direction than the Northern Refuge, canal water intrusion into the marsh may follow the direction of this transect more readily than water flow relative to the Northern Refuge.

In general, TOC and DOC slopes were less negative from the canal to the interior zone, indicating that the C concentration in water throughout the Refuge have decreased more rapidly in the more impacted zones than the less impacted interior zone. Using $\delta^{13}\text{C}$ signatures of organic matter pools, Chang et al. (2009) found that C in the top 5 cm of Refuge soil was strongly related to chemical gradients caused by canal water intruding into the Refuge marsh. Detritus $\delta^{13}\text{C}$ signatures near the Refuge perimeter varied fourfold greater than at the most interior sites. Detritus and metaphyton $\delta^{13}\text{C}$ signatures were negatively correlated with SpC and/or soil chemical gradients both at the

perimeter and in the interior (Chang et al. 2009). These results indicate that most of the TOC and DOC in the water column are primarily from canal water intrusion into the Refuge marsh as opposed to litterfall from marsh vegetation.

5 Conclusions

Although the trends were not significant in every analysis and there was a minor amount of variation, Kendall tau and Tobit nutrient and inorganic ion slopes were more negative in the more nutrient-enriched canal and perimeter zones than the less nutrient-enriched transition and interior zones. These results indicate 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.

The origin of the high Ca and Cl concentrations in canal water is most likely from intrusion of connate seawater into the canal. Excavation of canals released saline groundwater, enabling it to mix with the overlying surface and ground water in the canals. Conductivity and ALK can be used as tracers for canal water diffusion and intrusion into the Refuge marsh, and these water quality parameters show that Refuge water quality is slowly improving.

In general, TOC and DOC slopes were also less negative from the canal to the interior zone, indicating that C concentration in water throughout the Refuge have decreased more rapidly in the more impacted zones than the less impacted interior zone. Detritus and metaphyton $\delta^{13}\text{C}$ signatures were negatively correlated with SpC and/or soil chemical gradients both at the perimeter and in the interior (Chang et al. 2009). This shows that TOC and DOC in the water column are primarily from canal water intrusion into the Refuge marsh as opposed to litterfall from marsh vegetation.

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