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Temporal and Spatial Patterns of Internal Phosphorus Recycling in a South Florida (USA) Stormwater Treatment Area

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Large constructed wetlands, known as stormwater treatment areas (STAs), have been deployed to remove phosphorus (P) in drainage waters before discharge into the Everglades in South Florida, USA. Their P removal performance depends on internal P cycling under typically hydrated, but with occasionally desiccated, conditions. We examined the spatial and temporal P removal capacity under different hydrologic conditions along a STA flow path. While inflow soils are P enriched, the outflow region of the wetland contained P-unsaturated soils with minimal net recycling of bound soil P to the water column as plant-available P. The outflow-region soils were characterized by low porewater soluble reactive P (SRP) (≤40 μg L^{-1}) and high total sulfide (TS) (2–9 mg L^{-1}) concentrations, and total ammoniacal nitrogen (TAN) and SRP flux rates that averaged 1.51 and 0.002 mg m^{-2} d^{-1}, respectively. Pronounced increases in porewater and surface-water concentrations of SRP, dissolved organic P (DOP), and TAN were observed immediately after rehydration of the cell after an extended drought. Elevated total P concentrations persisted at the outfall of the cell for several months thereafter, resulting in an annual outflow total P concentration nearly threefold higher than the long-term mean. Relative to processes that can occur during extended periods of inundation, such as sulfate-enhanced P release from organic matter mineralization or iron sulfide formation, aerobic oxidation of organic matter during prolonged dryout periods is a more significant biogeochemical process in compromising soil P retention in STAs.

Six large (913–6695 ha) treatment wetlands, called stormwater treatment areas (STAs), have been constructed to remove phosphorus (P) from Lake Okeechobee discharges and agricultural drainage waters (ADW) before being released into the Everglades (Chimney and Goforth, 2001). Phosphorus precipitation with calcium (Ca^{2+}) to form metastable Ca-P compounds, or P adsorption onto calcite ($CaCO_3$), have been invoked as one of the major P removal mechanisms in the nutrient-enriched canals and zones of the STAs and Water Conservation Areas (WCAs) in South Florida (Diaz et al., 1994; Dierberg et al., 2002). Soil P fractionations support the concept of a central role for Ca-P removal mechanisms because nonlabile P usually composes a significant percentage of the soil total P (TP) content (Reddy et al., 1998).

While high dissolved Ca^{2+} concentrations are considered to aid in the removal of P from the water column, elevated sulfate (SO_4^{2-}) concentrations have been shown to mobilize P stored in soils and sediments as either bound P within organic matter or associated with iron (Fe)-P minerals (Lamers et al., 2002; Smolders et al., 2006). Based on these studies, it may be anticipated that the high SO_4^{2-} loadings to STAs and WCAs would a priori result in mobilization of soil P to the water column. However, anaerobic laboratory incubations of SO_4^{2-}–amended soil slurries from one STA and two WCAs did not show a P mobilization effect (Dierberg et al., 2011).

Draining and subsequent reflooding of organic soils also influences wetland nutrient retention, usually resulting in an increase in nitrogen (N) and P fluxes into the water column (Newman and Pietro, 2001; White et al., 2004, 2006). These processes can affect outflow concentrations of a treatment wetland because soil-to-water column fluxes can influence water column constituent concentrations (Reddy and DeLaune, 2008).

The primary goal of this investigation is to compare the P mobilization potential of two prominent biogeochemical processes that occur within STAs: aerobic oxidation of organic matter during episodic dryout periods vs. SO_4^{2-} and Fe reduction during hydrated conditions that occur over longer

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Abbreviations: ADW, agricultural drainage waters; DO, dissolved oxygen; DOP, dissolved organic phosphorus; ISE, ion-selective electrode; ORP, oxidation–reduction potential; PES, polyethersulfone; PP, particulate phosphorus; SFWMD, South Florida Water Management District; SRP, soluble reactive phosphorus; STA, stormwater treatment area; TAN, total ammoniacal nitrogen; TDP, total dissolved phosphorus; TP, total phosphorus; TS, total sulfide; WCA, Water Conservation Area.

durations. The objective was to relate the P mobility along a STA flow path after 8 yr of operation to the spatial and temporal soil, surface water, and porewater chemical concentrations and nutrient diffusion rates. We infer from these data which biogeochemical processes are more or less important in recycling soil P during extended periods of flooding and immediately after a prolonged drought. Based on previous research, our hypothesis was that organic matter oxidation as a consequence of dryout has a more profound impact on P internal loading than other biogeochemical processes such as SO_4^{2-} and Fe reduction, or Ca-P desorption/dissolution, which occur when a STA is continually hydrated. The findings of this research have significant management implications based on the relative contributions of these biogeochemical processes in releasing and sequestering P in these wetlands.

Materials and Methods

Site Selection and Description

For this effort, we evaluated surface- and porewater concentrations of nutrients and minerals collected on three occasions during a 15-mo period in a flow path of one of the STAs (Cell 1 of STA-2). Unlike most of the STA acreage, STA-2 Cell 1 was never farmed, but rather was a natural marsh that for years was subject to intermittent draining and flooding. In relation to the other Everglades STAs, STA-2 Cell 1 (26°24′ N, 80°37′ W) (Supplemental Fig. S1) received moderate TP (mean = 108 μg L^{-1}; Chimney, 2011), high SO_4^{2-} (mean = 78 mg L^{-1}; Pietro et al., 2006, 2007, 2008, 2009), and high Ca^{2+} (mean = 94 mg L^{-1}; South Florida Water Management District [SFWMD] DBHydro Environmental Database, http://www.sfwmd.gov/, accessed 22 Nov. 2010) inflow concentrations from 1 May 2004 to 30 Apr. 2008. It is dominated by emergent vegetation (mixed cattail [*Typha domingensis* Pers.] and sawgrass [*Cladium jamaicense* Crantz]), although at the time of sampling, dense water hyacinth [*Eichhornia crassipes* (Mart.) Solms] occurred in the northwest corner of the cell. Cell 1 is shaped like a parallelogram (5.5 km long by 1.8 km wide) and has a treatment area of 728 ha (1798 acres) out of a total STA-2 treatment area of 3335 ha (8240 acres) (Pietro et al., 2010). STA-2 Cell 1 was flooded in June 1999, and flow-through operations commenced in August 2000. Water flow is from north to south along the length of the cell (Supplemental Fig. S1).

Cell 1 is the only one of the four cells within STA-2 that has attained the outflow TP target of 10 μg L^{-1} for several years (flow-weighted mean TP from May 2005 to April 2007), despite having similar P loadings (1.1–2.2 g P m^{-2} yr^{-1}) and inflow P concentrations (94–151 μg L^{-1}) to Cell 3 of STA-2 (Chimney, 2011). It has been noted that non–previously farmed flow paths often provide more effective P removal than those treatment wetlands developed on farmlands (Juston and DeBusk, 2006), but the mechanism for this is unknown.

Field Sampling

Hydrology

Mean daily flow rates and stage levels were downloaded from SFWMD (DBHydro Environmental Database, http://www.sfwmd.gov/, accessed 27 Apr. 2010). Daily flows and stages were time-weighted averages of 15-min recordings.

Surface Waters

Water samples were collected at each of the nine stations (three transects 0.5, 2.5, and 5.0 km distant from the inflow and each transect with three equidistant [~0.65 km] stations) within STA-2 Cell 1 (Supplemental Fig. S1) on three occasions: 3 Dec. 2008, 19 June 2009, and 3 Mar. 2010. Dissolved oxygen (DO) concentrations in the bottom waters at the same stations (plus at the outflow structure) were determined in situ with a YSI Model 550 meter and probe on 3 Mar. 2010. A single grab sample was collected at each station by gently immersing a 125-mL polyethylene bottle to 10 cm below the water surface and filling it to capacity, being certain that particles associated with the nearby vegetation communities were excluded from the sample. Water pH and temperature were immediately measured within the bottle with a Hach Platinum Series pH electrode with temperature probe (Part no. 51910-00) and Hach SensION2 pH/ion-selective electrode (ISE) meter. Total sulfide (TS), which is equal to the sum total of all the dissolved sulfide species (i.e., $H_2S + HS^- + S^{2-}$), was subsampled first for later analysis in the laboratory. It was the only analyte where the preservative (zinc acetate + NaOH) was already present in the sample vials. Filtration through a 0.45-μm polyethersulfone (PES) syringe filter (Whatman PES) occurred in the field before preserving with concentrated sulfuric acid (pH < 2) for total dissolved P (TDP) and total ammoniacal nitrogen (TAN) analyses, or concentrated nitric acid for Ca^{2+} and Fe analyses (pH < 2); sample aliquots for SO_4^{2-} and soluble reactive P (SRP) were also filtered but remained unpreserved and on ice. Aliquots for TS, alkalinity, and TP (sulfuric acid preserved) were unfiltered. Thorough mixing of the 125-mL collection bottle contents between the subsampling of aliquots ensured a homogeneous suspension of particles and a uniform distribution of solutes. All preserved and unpreserved samples were kept cold (4°C) until analyzed within accepted holding times found in the references cited in the Analytical section below, except those for SRP analysis, which were frozen for a maximum of 2 wk, and then analyzed within 1 d after thawing.

Porewaters

Porewater was collected by means of dialysis samplers, or porewater equilibrators ("peepers") (Fisher and Reddy, 2001; DBE, 2010), which are designed to collect a vertical profile of dissolved chemical constituents throughout discrete intervals of the water and soil columns. Porewater equilibrators are constructed from Plexiglas (48 by 14.4 by 2.5 cm), and contain thirty-five 11-mL cells, equally spaced at 1-cm intervals. These equilibrators were deployed at each station on three occasions: 19 Nov. to 3 Dec. 2008; 2 to 19 June 2009; and 17 Feb. to 3 Mar. 2010.

Each equilibrator cell was filled with deoxygenated (by bubbling with N_2 gas) deionized water and covered with a 0.2-μm Supor-200 (Whatman PES) membrane followed by a protective polyurethane (0.6-cm-thick) coarse air conditioner filter (Frost King). The entire equilibrator was then placed in a storage case with deoxygenated deionized water and bubbled with N_2 gas overnight. Equilibrators were transported to the field in the storage case the following day, taken from the case, and quickly

placed into the soil at each site, leaving approximately the same number of cells above and below the soil–water interface.

The equilibrators were retrieved after an equilibration period of 14 to 17 d and immediately processed on-site. We rinsed the outside of each equilibrator with distilled water to remove residual soil, followed by blotting with a paper towel to absorb traces of remaining distilled water. The porewater volume was then withdrawn by piercing the outer protective filter and inner membrane with a syringe needle. The contents of two consecutive cells (~22 mL), which represented a vertical resolution of 2 cm in the water column or soil profile, were composited within the syringe.

The chemical species most sensitive to oxidizing conditions (Fe, SRP, TS) plus oxidation–reduction potential (ORP), temperature, and pH were subsampled first from porewater withdrawn from the equilibrators. Temperature, ORP, and pH were analyzed in the field. For the remaining analytes, we followed the same sample preservation and filtration procedure as previously described for the surface waters.

The ORP was measured with a Hach Platinum Series ORP electrode (Part no. 51937-00) and a Hach sensION2 pH/ISE meter. Calibration of the Pt electrode (referenced to an Ag/AgCl electrode in saturated KCl) was accomplished by measuring the potential of a Light's solution (Light, 1972). Electrode potentials of the samples were subsequently adjusted to a standard hydrogen electrode and for deviations in temperature from 25°C.

Soils

Cores (one per station) were retrieved on 17 Feb. 2010, after 9 mo of continuous inundation in the cell. The coring device consisted of a 1.08-m-long by 10-cm-diameter aluminum pipe where the 0.5-cm-thick wall was beveled at the leading edge while the upper end had handles welded to the main core barrel. Soil cores were sectioned into 0- to 4-, 4- to 10-, and 10- to 30-cm intervals in the field. The soils were placed under an N_2 blanket within 6 d of retrieval in the field before processing for TP, inorganic P, and bulk density. The soils can be characterized as peaty muck overlain with flocculent detrital material and are composed of organic carbon >29% and Ca >7.5% in the 0- to 10-cm soil interval (Dierberg et al., 2011).

Analytical

Surface Water and Porewater

Filtered surface water and porewater samples from equilibrators were analyzed according to SM4500P-F (APHA, 1992) or EPA 365.2 (USEPA, 1979) for TDP following digestion, and for SRP on undigested samples by SM4500P-F (APHA, 1992). Unfiltered surface water samples were analyzed for TP via SM4500P-F after digestion. Surface- and porewater dissolved organic P (DOP) concentration was calculated by the difference between the measured TDP and SRP concentrations, while the particulate P (PP) concentration (surface water only) was obtained by the difference between the TP and TDP concentrations. Sulfate was analyzed according to SM 4110 B (APHA, 1992), while TS was measured with an ISE according to a modification of the SM4500S-G method (APHA, 1998). Dissolved Fe was determined using a modified bathophenanthroline procedure (Nürnberg, 1984). The TAN, alkalinity, and dissolved Ca^{2+} were analyzed according to EPA Methods 350.1, 310.1, and 215.1, respectively (USEPA, 1979). Specific conductance was measured in the lab with a Corning 311 conductivity meter on unfiltered and unpreserved samples by EPA 120.1 (USEPA, 1979).

Soil

Soil samples from 0- to 4-, 4- to 10-, and 10- to 30-cm depths were analyzed for TP using a wet digestion procedure followed by measurement of SRP in the digestate (3-227 [Plumb, 1981] and USEPA Method 365.2 [USEPA, 1979]). Inorganic P was determined by a separate HCl-extraction procedure, in which a 0.5-g subsample of finely ground dry soil was extracted with 25 mL of 1 M HCl for 3 h at room temperature on an orbital shaker at 150 rpm, then filtered through a 0.45-μm-pore-size membrane, and measured for SRP (DeBusk et al., 1994). Soil bulk density, which is the mass per unit volume dry soil, was analyzed according to ASA 13 (Klute, 1986).

Quality Assurance

One of the nine internal stations (A2.5 in Supplemental Fig. S1) was selected for retrieving field duplicates within 2 to 3 m for each sample matrix (surface and porewaters and soils) on each sampling event. The purpose was to assess the proximate spatial variance. In addition, a field blank was analyzed on all water samples. Method blanks, spikes of known concentrations, internal check standards, high and low secondary standards, and laboratory duplicates were performed on all analytes. The results of the field and laboratory quality assurance program and method detection limits are presented in the Supplemental Information provided online (Supplemental Table S1 and S2).

Flux Rate Calculations

Flux rates for SRP and TAN were calculated according to Fick's First Law after determining porosities, diffusion coefficients, and tortuosity factors:

$$F_i = \Phi D_i^{\circ} \theta^{-2} \partial c_i / \partial x \quad [1]$$

where F_i is the flux of the dissolved species i per unit area and time; Φ is porosity of the soil at the sampling location (volume of water/volume of soil at 0–4 cm); D_i° is the diffusion coefficient of the species (i) in particulate-free water; θ is the tortuosity factor; c_i is the concentration of the ith species; and x is the sedimentary depth (cm) measured positively downward. The concentration gradient ($\partial c_i / \partial x$) across the soil–porewater interface was represented by the interval from 2 cm below to 2 cm above the interface.

Because TAN and SRP represent diprotic and polyprotic species, respectively, each of which has different diffusion mobilities (Li and Gregory, 1974), the diffusion coefficients for those species represent a composite diffusion coefficient to account for the relative importance of each species (e.g., $H_2PO_4^-$ and HPO_4^{2-}). The free-solution ionic diffusion coefficient (D_i°) of each species was corrected to field-measured temperatures according to linear correlations found in Boudreau (1997). For this approach, we averaged two or three weekly in situ surface-water temperature measurements taken between 0900 and 1200 h (SFWMD DBHydro Environmental Database, http://www.sfwmd.gov/, accessed 11 May 2010) during equilibrator deployment (14–17 d). We assumed porosities for the upper 2 cm of the soils to be comparable to the difference in wet and dry weights (60°C) of

known soil volumes in the 0- to 4-cm layer of cores retrieved at each of the equilibrator deployment locations.

We could not measure tortuosity (θ) directly, so we employed the following regression equation reported by Boudreau (1997) for fine-grained sediments in determining θ^2 from porosity (ϕ):

$$\theta^2 \approx 1 - 2\ln(\phi) = 1 - \ln(\phi^2), r^2 = 0.65 \quad [2]$$

As the flux of a solute is a vector quantity, it has both a magnitude and a direction (Boudreau, 1997). We have chosen to represent all P fluxes from the soil to the overlying water column (i.e., release rates) as positive values.

Statistical Analyses

Statistical analysis was performed using Statistica (Statsoft, 2010). Whenever a normal distribution (according to a Kolmogorov–Smironov test) was not found for the raw data, we log-transformed the data. In most cases, this fit a normal distribution. Whenever the raw concentration data were below the detection limit, which was limited to SRP, TAN, and dissolved Fe, we used one-half of their method detection limits, which were 2 $\mu g\ L^{-1}$, 0.02 $mg\ L^{-1}$, and 0.025 $mg\ L^{-1}$, respectively. We tested for homogeneity of the variances (homoscedasticity) by the Bartlett chi-square test. One-way analysis of variance (ANOVA) tests for temporal and spatial differences were performed on those data sets that were normally distributed and with variances that were homoscedastic. If the data set was heterogeneous, we still proceeded with a one-way ANOVA as long as the means were not correlated with variances (StatSoft, 2011). Whenever the ANOVA was found to be significant, a post hoc Tukey HSD test determined which means of the comparisons were significantly different. For nonnormal data sets, which were few in number, we used nonparametric procedures for testing significant difference(s) between distributions of two (Mann–Whitney) or three (Kruskal–Wallis) independent samples. If the ANOVA was significant in the Kruskal–Wallis test, then we tested for significant differences among the mean ranks. Pearson product-moment correlation coefficients among porewater constituents were tested for significance using the Student's t distribution for a one-tailed test. The level of significance (α) was 0.05 for normality, homoscedasticity, correlation coefficients, and means comparison tests.

Results

Hydrologic Trends During the Study Period

The STAs are managed by the SFWMD to be flooded as long as possible. This is usually accomplished by an active pumping schedule where water from Lake Okeechobee and ADW from farm fields are delivered to the STAs. However, during the dry season, the lack of precipitation reduces the amount of water pumped to the STAs, and the water levels decrease. The seasonal dry period can be prolonged by occasional regional droughts, one of which occurred during this study (Fig. 1).

Whereas the stage was above mean ground elevation for >5 mo before the first and third deployments of porewater equilibrators in STA-2 Cell 1, the second deployment was preceded by an extended dry period of 6.5 mo (Fig. 1). This was a time when the cell did not receive inflow or rainfall, which led to the absence of standing water during the last 3.6 mo of the 6.5-mo dry period. Installation of the second set of equilibrators occurred 2 wk after the cell had been hydrated and contained standing water.

Soil Characterization

Soil dry bulk density was rather consistent among the nine stations in STA-2 Cell 1 for a given soil layer (data not shown). Bulk density increased with soil depth, reflecting the more compact nature of the soil as a result of compression and organic matter mineralization (Zak et al., 2010). Mean (± 1 SE; $n = 9$) dry weight bulk densities at 0- to 4-, 4- to 10-, and 10- to 30-cm depth intervals were 0.03 (± 0.003), 0.08 (± 0.011), and 0.16 (± 0.005) g cm^{-3}, respectively, reflecting the flocculent nature of the organic particles that have accrued since construction of the wetland.

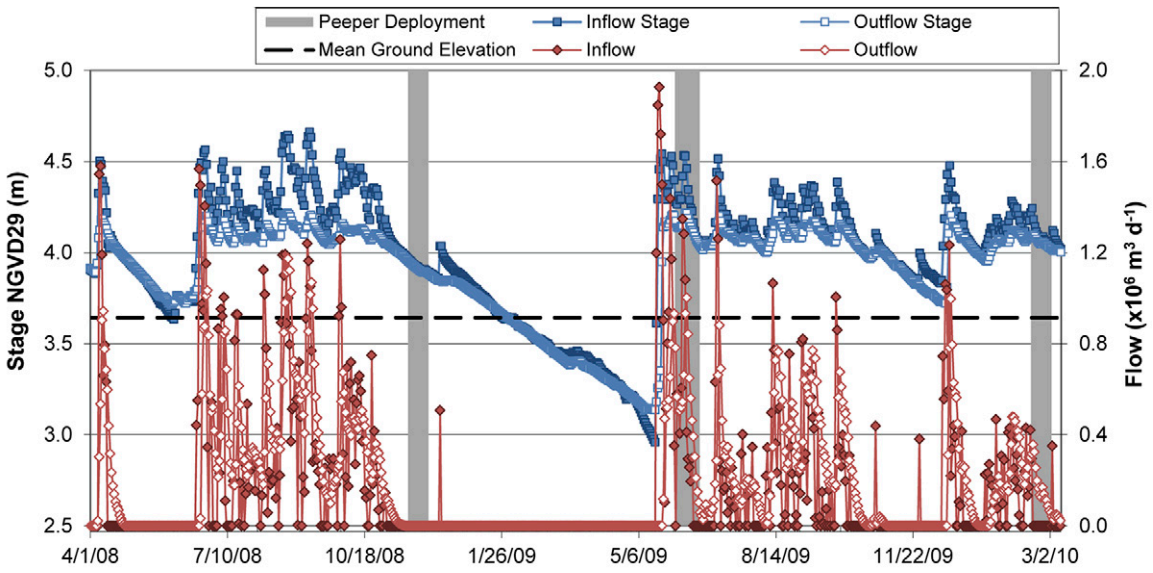

Fig. 1. Stage height and flow characteristics in Cell 1 of STA-2 before, during, and after the deployment of porewater equilibrators ("peepers") from 19 Nov. to 3 Dec. 2008, 3 to 19 June 2009, and 17 Feb. to 3 Mar. 2010. The periods of deployment are shown by the vertical background shading in gray. Source of data: South Florida Water Management District DBHydro Environmental Database, http://www.sfwmd.gov/, accessed 27 Apr. 2010.

Soil at stations located along the inflow (A) and mid (E) transects contained TP concentrations that averaged ≥1000 μg P g^{-1} dry for both the 0- to 4- and 4- to 10-cm soil layers (Table 1). The 0- to 4-cm layer at the outflow transect (J) still exhibited TP concentrations >1000 μg P g^{-1} dry, but decreased to 641 μg P g^{-1} dry (range of 532–704 μg P g^{-1} dry) within the 4- to 10-cm soil layer. The 10- to 30-cm soil layer at all stations contained <500 μg P g^{-1} dry, with the lowest measured mean value (263 μg P g^{-1} dry) along the outflow transect. Based on historical concentrations for unimpacted Everglades soils of <500 μg P g^{-1} dry (DeBusk et al., 1994), the 10- to 30-cm soil layer likely intercepted the pre-STA soil that existed before the cell came online in June 1999.

The pattern of total inorganic P distribution in the soil was similar to that of TP (Table 1). Soil inorganic P was 503 and 240 μg g^{-1} dry for the 0- to 4- and 4- to 10-cm soil depths, respectively, along the outflow transect. In contrast, higher inorganic P levels (873 and 574 μg g^{-1} dry for the 0- to 4- and 4- to 10-cm soil depths, respectively) were measured for the soil near the inflow of the cell. The mid transect soils were more variable in their inorganic P contents, with one station (E2.5) exhibiting concentrations similar to levels associated with the inflow soils, while another station (E1) had an inorganic P content that was more typical of the soil near the outflow (see Supplemental Fig. S1 for station locations). Nevertheless, the average for the three stations at the mid transect was closer to the outflow than inflow transect means for both soil depths (Table 1).

Table 1. Mean ± 1 SE (n = 3) soil total phosphorus (TP) concentrations for the 0- to 4-, 4- to 10-, and 10- to 30-cm, and inorganic P concentrations for the 0- to 4- and 4- to 10-cm soil layers at three locations along each of the three transects within STA-2 Cell 1 on 17 Feb. 2010. See Supplemental Fig. S1 for station locations.

Parameter	Soil layer	Inflow	Mid	Outflow
	cm	μg P g^{-1} dry		
TP	0–4	2010 ± 346	1341 ± 259	1133 ± 35
	4–10	1322 ± 42	1000 ± 250	641 ± 55
	10–30	345 ± 51	357 ± 43	263 ± 13
Inorganic P	0–4	873 ± 109	544 ± 159	503 ± 21
	4–10	574 ± 34	306 ± 105	240 ± 32

Surface Water Quality

Dissolved Ca^{2+} concentration in Cell 1 inflow averaged 97 mg L^{-1} (median = 100 mg L^{-1}) with a range of 63 to 124 mg L^{-1} during the April 2008 to August 2010 period, compared to an average outflow concentration of 86 mg L^{-1} (median = 87 mg L^{-1}) and range of 50 to 111 mg L^{-1} (SFWMD, DBHydro Environmental Database, http://www.sfwmd.gov/, accessed 24 Sept. 2010). Sulfate concentration for STA-2 inflow stream averaged 67 mg L^{-1} (median = 68 mg L^{-1}) during the same 2.3-yr period, and ranged from 37 to 110 mg L^{-1} (SFWMD, DBHydro Environmental Database, http://www.sfwmd.gov/, accessed 24 Sept. 2010). Routine monitoring of SO_4^{2-} was not performed at the Cell 1 outflow, thus long-term data were not available for this parameter.

Inflow TP concentration, as measured by SFWMD at the inflow structure, varied considerably during the study period (Fig. 2). The overall mean and median inflow TP values from April 2008 through mid-August 2010 were 65 and 43 μg L^{-1}, respectively, and the overall range of measured values was 16 to 280 μg L^{-1}. Outflow TP concentration, measured at the discharge structure, was much lower on average, and generally less variable (Fig. 2), indicating efficient P removal in Cell 1. Mean and median outflow TP values during this period were 21 and 14 μg L^{-1}, respectively, with a range of 6 to 195 μg L^{-1} reported for the period. Outflow TP concentrations during the equilibrator deployment periods were typically <20 μg L^{-1}, with higher concentrations observed only during and immediately following the drawdown in Cell 1 in early 2009. For example, outflow TP concentration (37 μg L^{-1}) in June 2009 was four times higher than for either the first (3 Dec. 2008) or third (3 Mar. 2010) sampling events (Fig. 3).

Measuring spatial concentration gradients within the cell defined the inflow region as having higher TP concentrations ($p \leq 0.05$) than either the mid or outflow regions during the first two sampling events (3 Dec. 2008 and 19 June 2009). As a result of the dryout–reflood that occurred immediately before the second sampling (19 June 2009), TP concentrations at the inflow and mid transects on that date were significantly higher ($p \leq 0.05$) than TP concentrations during the more extended flooded period preceding the 3 Dec. 2008 and 3 Mar. 2010 sampling dates.

Data collected during the three spatially intensive sampling events on 3 Dec. 2008, 19 June 2009, and 3 Mar. 2010, indicated that SRP was effectively removed along the Cell 1 inflow–outflow surface-water gradient ($p \leq 0.05$ for the first two sampling events). The DOP and PP species were also removed during transit through Cell 1, although not as effectively as the removal of SRP (Fig. 3). Compared to the first and third monitoring periods, higher concentrations of all P species along all transects and at the

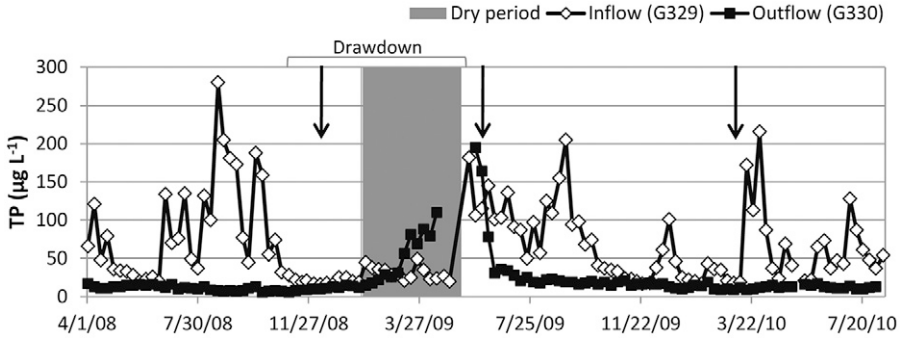

Fig. 2. Total phosphorus (TP) concentrations in the inflow and outflow of STA-2 Cell 1 from 1 Apr. 2008 to 12 Aug. 2010. The drawdown period, defined as the time when there was no inflow, lasted 6.5 mo. There was no standing water (dry period) in the cell for 3.6 mo of the drawdown period. Data points represent weekly grab samples. The days marking the installation for each of the equilibrator deployments are indicated by the arrows. Source of data: South Florida Water Management District DBHydro Environmental Database, http://www.sfwmd.gov/, accessed 22 Nov. 2010.

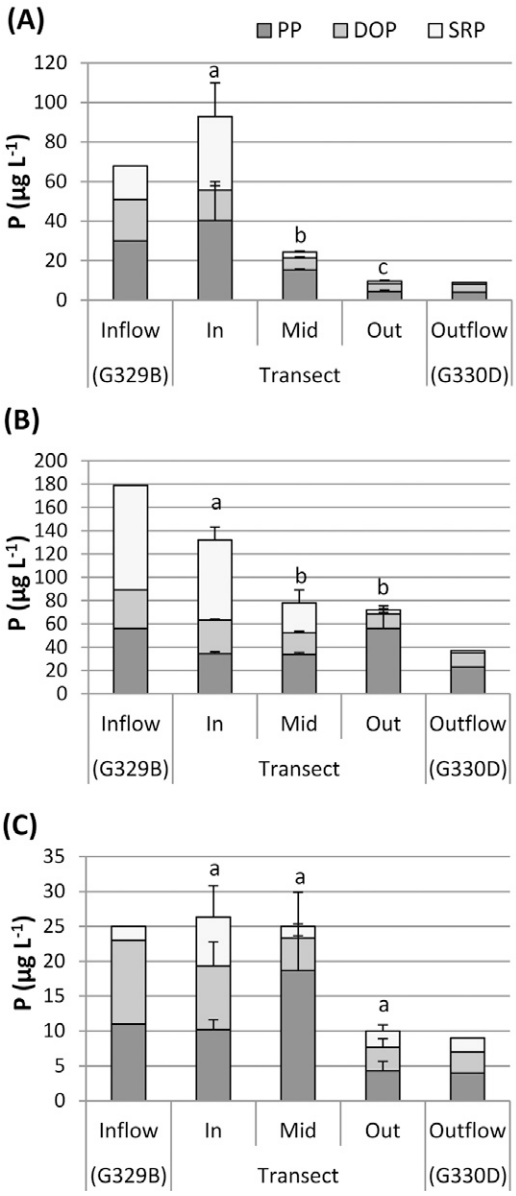

Fig. 3. Surface-water concentrations for soluble reactive (SRP), dissolved organic (DOP), and particulate (PP) phosphorus measured in the inflow and outflow, and along three internal transects, in STA-2 Cell 1 on (A) 3 Dec. 2008, (B) 19 June 2009, and (C) 3 Mar. 2010. The sum of the SRP, DOP, and PP concentrations represent the total phosphorus (TP) concentration. Different lowercase letters (a, b, c) above the bars indicate significantly different TP means between transect locations ($p \leq 0.05$; one-way ANOVA test followed by post hoc Tukey HSD). Each internal transect had three stations that were sampled. Error bars represent +1 SE of the mean ($n = 3$). See Supplemental Fig. S1 for transect locations and Fig. 1 for hydrologic conditions before sampling date. Note the differences in the scale for the *y* axes.

inflow and outflow of Cell 1 occurred on the second sampling (19 June 2009), a likely consequence of the prior extended drawdown and subsequent reflooding just before our sample collection (Fig. 1). Also during June 2009, elevated SRP levels ($p \leq 0.05$) were observed in the middle of the wetland (see Supplemental Information for further details). Such a deep penetration of SRP downstream of the inflow did not occur during the other two sampling periods under extended hydrated conditions.

On 3 Dec. 2008 and 3 Mar. 2010, the two deployments when stage levels in the cell were maintained above ground elevation for 5 mo or more, little to no variations between inflow and outflow stations, and among the internal transects, were observed for pH and electrical conductivity, and concentrations of TAN, SO_4^{2-}, alkalinity, and dissolved Fe and Ca^{2+} (Table 2).

In contrast, during June 2009, TS concentrations increased to 3.0 mg L^{-1} at inflow transect A. A noticeable decrease occurred in the concentration of TAN throughout the cell on that date; SO_4^{2-} concentrations increased along the flow path (Table 2). Compared to the two other sampling dates when the cell had been inundated for 5 mo or more, dissolved Fe concentrations and pH were higher and lower, respectively, during rehydration on 19 June 2009 (Table 2). These changes along the flow path on 19 June 2009 were linked to the dry antecedent conditions with subsequent rehydration before our sampling event (Fig. 1).

Porewater Profiles

We utilized porewater equilibrators to monitor major water quality constituents in the bottom water column and soil pore spaces. This approach enabled us to examine the concentration gradients at a spatial resolution of 2 cm, integrate porewater concentrations for the 0- to 10-cm soil depth, and also calculate SRP and TAN diffusion fluxes according to Fick's First Law [Eq. 1].

Data obtained from the porewater equilibrators revealed distinct concentration gradients of SRP, DOP, TAN, ORP, SO_4^{2-}, and TS across the soil–water interface (Fig. 4 and 5). The vertical concentration gradients for alkalinity and dissolved Fe and Ca^{2+} concentrations were less obvious (Supplemental Fig. S2). Constituent concentrations were lowest in the bottom waters and increased with greater soil depths, except for SO_4^{2-} (Fig. 4), ORP (Fig. 4), and pH (Supplemental Fig. S2).

The SRP interstitial and bottom waters along the inflow, mid, and outflow transects during June 2009, immediately following the drawdown and rehydration, were consistently higher than the corresponding depth interval measured during the November 2008 and February 2010 deployments (Fig. 4). Stations along the inflow transect typically had the highest SRP concentrations on all three deployments ($p \leq 0.05$). Porewater SRP for the 0- to 10-cm soil interval averaged from 190 to 333 µg L^{-1} at the inflow transect to 3 to 32 µg L^{-1} at the outflow transect, with the mid transect (excluding the June 2009 deployment) concentrations (2–113 µg L^{-1}) closer to the outflow than inflow concentrations (means of each deployment for all stations [$n = 3$] along a transect). Porewater SRP concentrations at the mid transect were greater than those from the outflow transect during the first two deployments in 2008 and 2009 ($p \leq 0.05$), but not in the 2010 deployment. The inflow transect porewater SRP concentrations were higher than porewater SRP concentrations along the outflow transect ($p \leq 0.05$) for all three deployments.

The deployment period was also a significant factor in accounting for porewater SRP concentrations within a transect location. For the inflow transect, the only significant ($p \leq 0.05$) difference among the three deployments was between 2009 and 2010. However, significant differences existed among all paired year-by-year comparisons (2008 vs. 2009, 2008 vs. 2010, and 2009 vs. 2010) at the mid transect. For the outflow transect, significant differences existed between 2008 vs. 2010 and between 2009 vs. 2010, but not between 2008 vs. 2009.

Whereas the bottom waters during the last deployment (3 Mar. 2010) were oxygenated (Table 2), the ORP (Eh) values for the porewaters indicated anoxia in the soil profiles. The ORP

decreased below the soil–water interface during the three porewater equilibrator deployments (Fig. 4). The lowest mean porewater ORPs, which were from the 0- to 10-cm soil layer at all three transects, occurred during the second deployment on 2–19 June 2009, immediately following rehydration after drawdown.

Likely due to microbial SO_4^{2-} reduction, SO_4^{2-} concentrations decreased with depth at all transects and for all dates except for the mid transect after rehydration in June 2009, which was highly variable among the three stations (Fig. 4). Corresponding bottom water column and porewater depth interval SO_4^{2-} concentrations were very consistent among the three sampling dates at the inflow transect. This consistency in concentration within a depth interval continued at the mid and outflow stations 5 mo prior (19 Nov. to 3 Dec. 2008 deployment) and 9 mo after (17 Feb. to 3 Mar. 2010 deployment) the extended drawdown, but not immediately following rehydration of the wetland in June 2009.

With exceptions of the TS concentration profiles at the inflow and mid transects immediately after cell rehydration on 2 to 19 June 2009, the direction of the concentration gradient for TS was the opposite of that for SO_4^{2-} (i.e., TS concentrations increased with depth; Fig. 5). Lower TS concentrations were observed in the 0- to 10-cm soil layer along the inflow transect (0.81–4.04 mg L^{-1}) and mid (0.83–3.30 mg L^{-1}) than along the outflow (2.38–4.23 mg L^{-1}) transects during the three deployments. The highest average (0- to 10-cm soil depth) porewater TS concentrations among all transects occurred 9 mo after rehydration during the February 2010 deployment date; the lowest concentrations were measured immediately after rehydration in June 2009 (Fig. 5).

Contrary to the hypothesis that SO_4^{2-} reduction leads to soil P mobilization, SRP and TS concentrations were inversely correlated within each of the three zones in Cell 1, with statistical significance ($p \leq 0.05$) observed only at the mid transect (Supplemental Table S3). Statistically significant positive correlations with the SRP concentration occurred for DOP (all transects), TAN (inflow and mid transects), and dissolved Ca^{2+} and alkalinity (mid transect) concentrations (Supplemental Table S3). Excluding DOP, there were no statistically significant correlations between SRP and any of the other measured constituents at the outflow region porewaters.

Besides SRP, porewater TAN concentrations exhibited a positive correlation ($p \leq 0.05$) with porewater concentrations of DOP, dissolved Ca^{2+}, alkalinity, and dissolved Fe; pH and SO_4^{2-} were the only significant negative correlations with TAN (Supplemental Table S3). Porewater TAN concentrations (0- to 10-cm depth layer) averaged across time ($n = 3$) ranged from 1.65 to 3.54 mg L^{-1} at the inflow transect compared with the averages of 0.95 to 4.31 mg L^{-1} at the mid and 0.41 to 1.58 mg L^{-1} at the outflow transects. As observed for SRP profiles, the June 2009 deployment immediately after rehydration of the cell from the extended drawdown resulted in the highest porewater TAN concentrations ($p \leq 0.05$) compared to 6 mo prior (December 2008) or 8.5 mo later (March 2010) when the cell had been hydrated for at least 5 mo (Fig. 5). As noted for SRP, the inflow and mid transect porewater TAN concentrations were each greater than the outflow transect porewater concentrations during all three deployments (Fig. 5).

Like TAN, the DOP concentration profiles (Fig. 5) closely followed those of SRP (Fig. 4), and the three nutrient species were

Table 2. Mean (± 1 SE) values for selected surface water parameters measured at the inflow (G-329) and outflow (G-330) structures, and along the inflow (A) and outflow (J) region internal transects, in STA-2 Cell 1 on 3 Dec. 2008, 19 June 2009, and 3 Mar. 2010. Each internal transect had three stations that were sampled. Data for mid (E) transect not shown. See Supplemental Fig. S1 for transect locations and Fig. 1 for hydrologic conditions before sampling date.

Parameter†	3 Dec. 2008				19 June 2009				3 Mar. 2010			
	Inflow	A	J	Outflow	Inflow	A	J	Outflow	Inflow	A	J	Outflow
SO_4^{2-}, mg L^{-1}	48	44 ± 1	56 ± 6.1	59	80	52 ± 3.3	65 ± 2.2	68	55	47 ± 2.2	50 ± 2.3	57
Dissolved Ca^{2+}, mg L^{-1}	99	60 ± 30	101 ± 3	99	103	98 ± 3.2	89 ± 1.2	89	86	84 ± 4.3	81 ± 2.1	86
Dissolved Fe, mg L^{-1}	0.049	0.034 ± 0.008	0.031 ± 0.003	0.042	0.089	0.072 ± 0.009	0.046 ± 0.004	0.050	0.013	0.032 ± 0.010	0.013 ± 0.000	0.013
TS, mg L^{-1}	0.032	0.240 ± 0.091	0.194 ± 0.146	0.042	0.036	3.02 ± 0.956	0.166 ± 0.035	0.141	0.023	0.054 ± 0.013	0.028 ± 0.002	0.023
TAN, mg L^{-1}	0.050	0.076 ± 0.026	0.050 ± 0.0236	0.038	0.122	0.136 ± 0.015	0.039 ± 0.003	0.031	0.029	0.054 ± 0.027	0.050 ± 0.029	0.023
Electrical conductivity, µS cm^{-1}	1216	1267 ± 52	1253 ± 15	1165	1077	1090 ± 2.9	1017 ± 9.8	1034	1260	1226 ± 36	1200 ± 30	1264
Alkalinity, mg $CaCO_3$ L^{-1}	372	336 ± 16	349 ± 9.8	356	310	316 ± 3.8	273 ± 2.9	272	302	307 ± 10	286 ± 3	298
pH	7.76	7.41 ± 0.01	7.63 ± 0.16	7.69	7.04	7.39 ± 0.08	7.61 ± 0.03	7.59	8.10	7.38 ± 0.16	7.62 ± 0.05	7.86
Temperature, °C	18.6	15.3 ± 0.93	12.7 ± 0.82	14.7	n/a‡	n/a	n/a	n/a	12.6	13.1 ± 0.81	15.5 ± 0.03	16.2
DO, mg L^{-1}	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	2.8 ± 0.5	2.9 ± 0.24	4.53

† TS, total sulfide; TAN, total ammoniacal nitrogen; DO, dissolved oxygen.

‡ n/a = not measured.

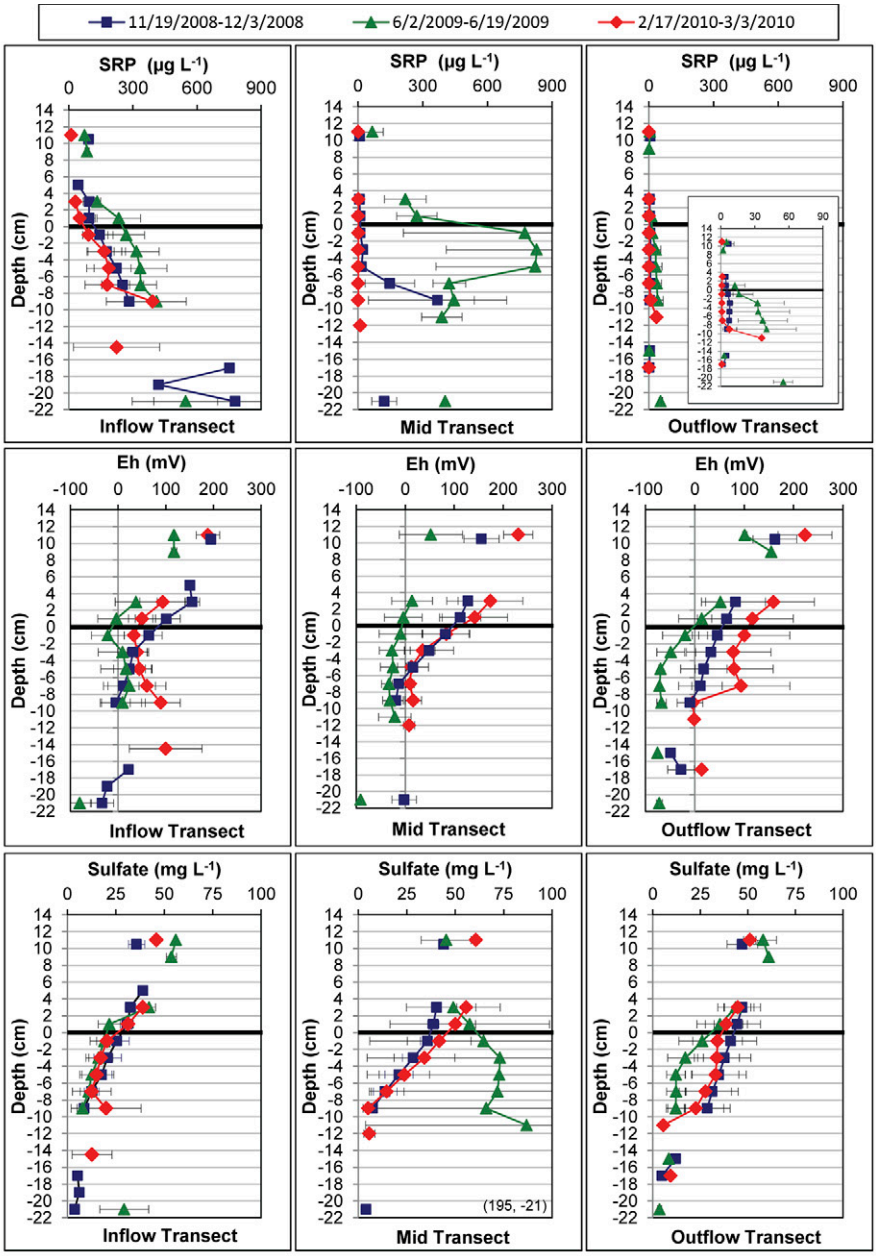

Fig. 4. Vertical profiles of soluble reactive phosphorus (SRP) concentrations, oxidation–reduction potential (Eh), and sulfate (SO_4^{2-}) concentrations collected from the bottom waters and porewaters at three transects in STA-2 Cell 1 on three occasions. Error bars represent ±1 SE of the mean of three stations along each transect. The thick horizontal line signifies the soil–water interface. See Supplemental Fig. S1 for station locations.

significantly intercorrelated ($p \leq 0.05$) at all of the transects, except for TAN vs. SRP and TAN vs. DOP at the outflow transect. This indicates that factors controlling temporal porewater TAN, DOP, and SRP concentrations were similar throughout the flow path, and likely originated from a common process, such as organic matter decomposition.

Dissolved Fe concentrations were consistently low (<0.3 mg L^{-1}) in the porewaters on all sampling occasions. The dissolved Fe concentrations were not significantly correlated ($p > 0.05$) with SRP or TS concentrations (Supplemental Table S3), suggesting the immobilization of reduced Fe by TS was not a prominent mechanism in controlling porewater SRP concentrations in this cell.

As a likely result of microbial respiration, the pH within the porewaters declined with depth on all occasions and along all transects. An average decline of 0.2, 0.3, and 0.3 pH units occurred for all deployments between the 0- to 2-cm and 8- to 10-cm soil layers at the inflow ($p > 0.05$), mid ($p \leq 0.05$), and outflow ($p \leq 0.05$) transects, respectively. The average pH of the 0- to 10-cm porewater interval ranged from 7.4 to 7.5 at the inflow, 7.0 to 7.4 at the mid, and 7.4 to 7.6 at the outflow transects (Supplemental Fig. S2).

Dissolved Ca^{2+} and total alkalinity concentrations increased slightly with depth at most transects and for most of the deployments (Supplemental Fig. S2). The lower pH values in the porewater profile generated enough acidity to dissolve $CaCO_3$, which contributed to the elevated Ca^{2+} and alkalinity concentrations observed in the porewater, compared to the water column. The highest porewater Ca^{2+} and alkalinity concentrations were measured at the inflow and mid transects after wetland rehydration in June 2009, implying that rehydration mobilized the ions released by the dissolution of $CaCO_3$. As expected, correlations among dissolved Ca^{2+}, alkalinity, and pH were statistically significant ($p \leq 0.05$) at all three transects (Supplemental Table S3).

Soluble Reactive Phosphorus and Total Ammoniacal Nitrogen Diffusive Fluxes

Although statistically insignificant due to the variability among the three stations along each transect, higher SRP and TAN diffusive flux rates, as determined by porewater equilibrators, were nevertheless observed for soils situated closer to the inflows than for those at the mid and outflow transects (Table 3). The inflow SRP and TAN diffusion rates averaged 0.06 and 2.85 mg m^{-2} d^{-1}, respectively, whereas the corresponding rates were 0.003 and 0.58 mg m^{-2} d^{-1} at the outflow soils along the J transect. An exception to the decreasing rates along the flow path was at the mid transect during the 2–19 June 2009 deployment when the cell had been rehydrated for only 2 to 4 wk after 6.5 mo of an extended drawdown.

Discussion

Inflow to Outflow Nutrient Concentration and Diffusion Gradients

Well-defined porewater concentration and diffusion gradients existed along the flow path. Porewater (0- to 10-cm soil depth) SRP concentrations (Fig. 4) from soil at the inflow region of the cell were 31, 10, and 63 times greater than for the outflow region soils during the first (after 5 mo of continu-

ous inundation), second (after a 6.5-mo drought), and third (8.9 mo of continuous inundation) porewater equilibrator deployments, respectively; SRP diffusion rates were 10- to >50-fold higher at the inflow than at the outflow region (Table 3). Mean porewater DOP and TAN concentrations in the inflow were 6.5 to 11, and 2.2 to 4 times, respectively, greater than concentrations in the outflow (Fig. 5).

Although soluble inorganic P and N concentration gradients and fluxes commonly occur within areas of the Everglades that receive ADW, the magnitude of SRP diffusion flux rates for the soils nearest the inflows were higher in other studies than what we report in Table 3. Koch and Reddy (1992) and Fisher and Reddy (2001) reported higher SRP diffusive flux rates from P-impacted soils (>500 μg P g^{-1} dry; DeBusk et al., 1994) in nearby WCA-2A than the rates we measured from the inflow region soils of Cell 1: 0.05 to 0.07 mg P m^{-2} d^{-1} (Table 3) vs. −0.71 (indicating influx) to 0.78 mg P m^{-2} d^{-1}. We attribute the higher P efflux rates in the impacted areas of WCA-2A to a longer duration (40+ yr) of receiving P-enriched discharges than the 9-yr operational history of STA-2 Cell 1, and to the lower P loadings to STA-2 Cell 1 as a result of on-farm best management practices (Daroub et al., 2009).

Our measured SRP diffusive flux rates at the back end (mid and outflow regions) of Cell 1 (0.000–0.006 mg P m^{-2} d^{-1}) compare more favorably with the rates reported by Koch and Reddy (1992) and Fisher and Reddy (2001) for the unimpacted regions of WCA-2A: range from −0.007 (indicating SRP uptake by the soil) to 0.02 mg P m^{-2} d^{-1}. The significance of this comparison is that the SRP diffusive flux rates of the mid (with the exclusion of postdrawdown/reflood period in 2009) and outflow regions of STA-2 Cell 1 are representative of unimpacted soils, and thus the back half of Cell 1 has been unaffected by P loading to the cell. This was also true for TAN diffusive fluxes at the outflow region of Cell 1: rates of 0.09 to 1.36 mg N m^{-2} d^{-1} (Table 3) were similar to the 0.14 to 0.42 mg N m^{-2} d^{-1} measured for the unimpacted area of WCA-2A by Koch and Reddy (1992).

Focusing on only the flux rates of outflow region soils, and assuming that the daily rates (Table 3) prevail throughout the year, our porewater profiles suggest that STA-2 Cell 1 exports 0.001 g SRP m^{-2} yr^{-1} and 0.21 g TAN m^{-2} yr^{-1} via soil efflux. This represents 87% of the average annual TAN mass exported from the cell over an 8-yr period. By contrast, only 2.2% (3.6% excluding the high outflow P discharge in 2009; Fig. 2) of the mass of SRP exported from the cell could be attributed to diffusive SRP fluxes. This illustrates the more conservative nature of porewater SRP than TAN in the P-limited downstream portions of the cell. To determine the total internal P loading for the wetland, these diffusive flux rates would need to be added to other sources of P effluxes, such as advective forces caused by groundwater recharge, resuspension, and bioturbation (Fisher and Reddy, 2001; Lewandowski et al., 2002), as well as biological recycling within the water column.

The stability of the soil P in the mid to outflow regions, along with the effective upstream P removal as indicated by the surface water gradients in Fig. 3, contribute to the exemplary P removal performance of the cell. Wetland cells in other STAs have not

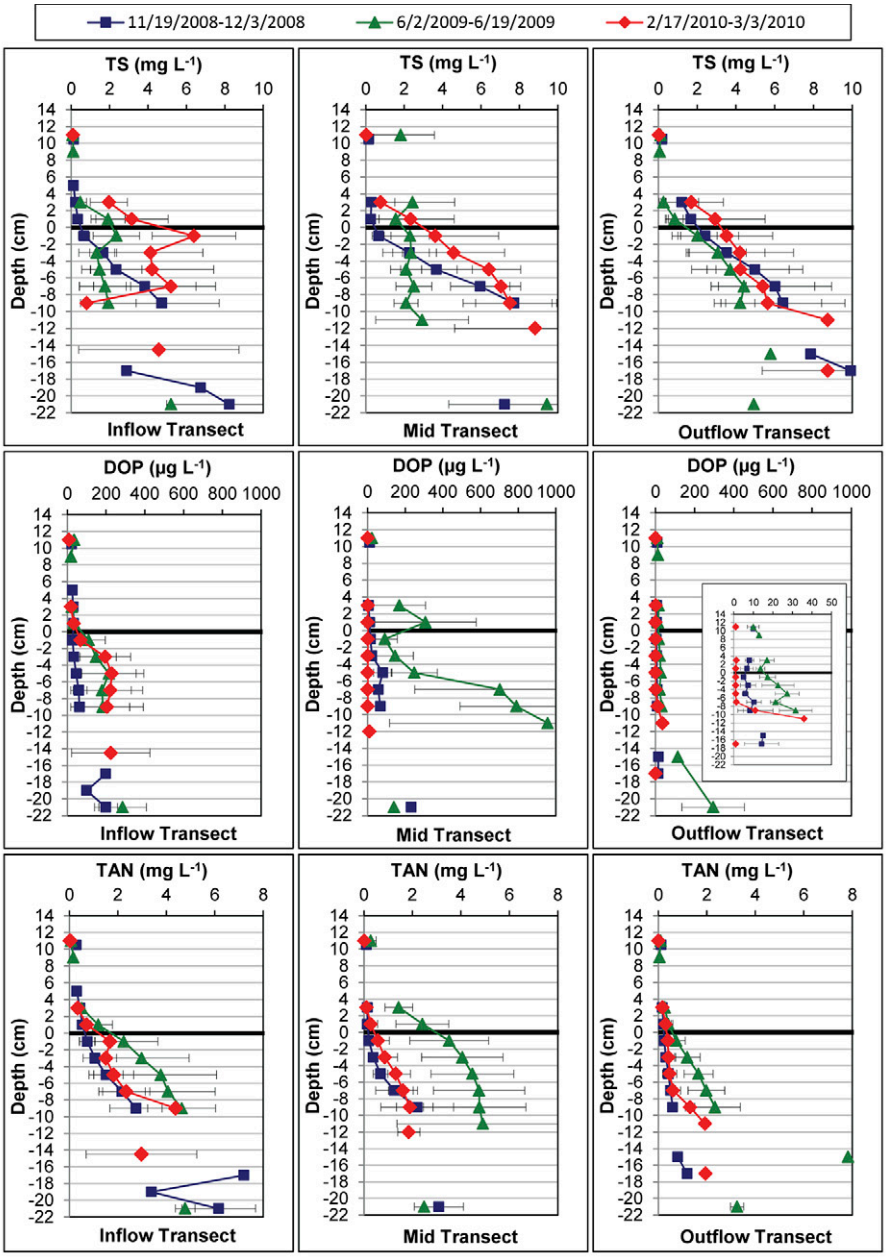

Fig. 5. Vertical profiles of the total sulfide (TS), dissolved organic phosphorus (DOP), and total ammoniacal nitrogen (TAN) concentrations collected from the bottom waters and porewaters at three transects in STA-2 Cell 1 on three occasions. Error bars represent ±1 SE of the mean of three stations along each transect. The thick horizontal line signifies the soil–water interface. See Supplemental Fig. S1 for station locations.

typically exhibited such a high P removal performance (Juston and DeBusk, 2006).

Phosphorus Release after a Prolonged Drawdown and Desiccation

The effects of the 6.5-mo drought-induced drawdown, which included 3.6 mo when standing water was absent, on surface and porewater nutrient concentrations were pronounced (Fig. 2–5). Porewater TAN, SRP, and DOP concentrations more than doubled at most stations after the onset of rehydration compared to hydrologic conditions when the cell remained flooded for at least 5 mo. Drawdown in wetlands introduces oxygen into the soil, and decomposition rates under aerobic conditions are significantly higher than under anaerobic conditions (Wright and Reddy, 2001; DeBusk and Reddy, 2003). DeBusk and Reddy (1998) found that anaerobic mineralization of wetland soils was one-third the rate of aerobic soils, a finding in accordance with aerobic and anaerobic mineralization rates for a Florida wetland outside of the Everglades reported by Corstanje and Reddy (2004). The end result is that rapid P turnover rates and cycling under oxygenated conditions can contribute bioavailable P to the water column and influence downstream water quality following rehydration after a drawdown.

Using smaller platforms (outdoor mesocosms and laboratory containers), shorter time scales, excavated soil, and artificially induced dryout methods, most investigations on the effects of soil desiccation on P mobilization in the Everglades have also reported enhanced P release after reflooding. White et al. (2004, 2006) found that the diminished effectiveness of TP removal in vegetated mesocosms containing soils originating from the outflow region of an STA lasted 3 to 4 wk following two 1-mo drawdowns that were separated by 16 wk of inundation. Based on lab incubations of homogenized detrital material from an STA, Pant and Reddy (2001) reported different SRP release rates for different periods of drying at 30°C. As the drying period extended up to 30 d, the P flux from the detritus to the water column decreased on reflooding; however, the flux increased after 60 d of drying. To the contrary, Fisher and Reddy (2001) did not find an enhancement effect on P release from reflooding dried soils in WCA-2A.

After an initial flush of P immediately on rehydration in our study, it took several months before the wetland treatment capability (with respect to P removal) recovered (Fig. 2), which resulted in an extraordinarily high P mass and concentration leaving the cell (Table 4). The prolonged release from the dried detritus and soil after reflooding the cell resulted in nearly a fourfold increase in the outflow TP concentration (compared to the annual outflow concentrations for the previous 7 yr), which included 4 yr when the annual outflow concentrations were ≤10 μg L^{-1} (Table 4). For the 7 yr before water year 2010, when drawdowns were of shorter duration, the average annual inflow and outflow TP concentrations were 96 (range: 49–151) μg L^{-1} and 11 (range: 7–12) μg L^{-1} (Chimney, 2011). Thus, the cell drawdown, desiccation, and reflooding in 2009 resulted in an increase in the long-term (8 yr) outflow TP concentration from 11 to 15 μg L^{-1}. While shorter periods of drawdown and desiccation of 1 to 2 mo in a STA can also produce an elevated P outflow concentration on reflooding, the effect will be short-lived, lasting approximately 1 mo (Juston and DeBusk, 2006).

The flush of P from the onset of rehydration of the cell notwithstanding, the porewater constituents, as well as the SRP and TAN diffusion rates, returned to background levels within approximately 9 mo after rehydration. It is possible that the effects of higher nutrient discharge after a hydrologic disturbance such as drawdown/reflood may be mitigated somewhat if the initial rehydration waters are held in the wetland for a period of time before being released. Surface and porewater sampling, such as the approach used in this study, should be repeated in the future, since it will help verify the long-term sustainability of P removal by this treatment wetland, which is one of the more efficient flow paths within the STAs.

Phosphorus Release under Extended Flooded Conditions

The hydrologic status of the STAs is usually one of continued hydration, principally by means of pumping activities performed by the SFWMD. As such, oxygen is depleted in the soil, and alternate electron acceptors serve in oxidizing organic matter. The largest pool of potential electron acceptors in the STAs for anaerobic decomposition is SO_4^{2-}.

Sulfate reduction to sulfide occurs if SO_4^{2-} serves as the electron acceptor during organic matter oxidation, and SO_4^{2-}

Table 3. Mean diffusive total ammoniacal nitrogen (TAN) and soluble reactive phosphorus (SRP) flux rates for transects located along the flow path of STA-2 Cell 1. Each transect consisted of three stations. Deployment 1: 19 Nov. to 3 Dec. 2008; Deployment 2: 2 to 19 June 2009; Deployment 3: 17 Feb. to 3 Mar. 2010.

Transect location	Deployment	Flux rate	
		TAN	SRP
		mg m^{-2} d^{-1}	
Inflow	First	0.723	0.070
Mid	First	0.186	0.000
Outflow	First	0.089	0.003
Inflow	Second	4.52	0.061
Mid	Second	4.68	0.951
Outflow	Second	1.36	0.006
Inflow	Third	3.30	0.050
Mid	Third	0.940	0.001
Outflow	Third	0.291	0.000

Table 4. Total phosphorus (TP) mass loading and export, and inflow and outflow concentrations, for STA-2 Cell 1 over eight consecutive years. The drought-induced drawdown and soil desiccation occurred in water year (WY) 2010. Water year = 1 May through 30 April. Data from Chimney (2011).

Water year	TP mass		TP concentration	
	Loading	Export	Inflow	Outflow
	g P m^{-2} yr^{-1}		μg L^{-1}	
WY2003	0.419	0.077	49	14
WY2004	0.832	0.108	73	14
WY2005	1.107	0.092	99	10
WY2006	1.157	0.066	94	7
WY2007	1.527	0.067	151	9
WY2008	1.157	0.111	89	12
WY2009	0.952	0.084	118	10
WY2010	1.176	0.446	118	39
Mean WY2003–2010	1.040	0.131	99	15

reduction has been found to be an important process in controlling the availability of soil P. This occurs principally by means of iron sulfide (FeS_x) formation, which liberates Fe-bound P, and/or by enhanced anaerobic decomposition of P-containing organic matter (Gächter and Müller, 2003; Smolders et al., 2006). Thus, sulfate reduction may be important in Cell 1 of STA-2 since it is an SO_4^{2-}–rich environment (Table 2).

However, the findings of our porewater sampling indicate that SO_4^{2-} reduction is not a prominent biogeochemical process in mobilizing soil P. For example, the high TS concentrations (2–9 mg L^{-1}) in the soil porewaters at the outflow region of the cell were associated with SRP concentrations that averaged only 4 μg L^{-1} from 9 Apr. 2008 to 12 Aug. 2010 in surface waters at the outflow structure (G-330) of the cell (SFWMD DBHydro Environmental Database, http://www.sfwmd.gov/, accessed 17 Sept. 2010) and ≤40 μg L^{-1} in the porewaters (Fig. 4). We also found negative, instead of positive, correlations between porewater SRP and TS concentrations within the three regions of the cell (Supplemental Table S3), indicating the likelihood that SO_4^{2-} reduction is uncoupled from SRP release in the soils. Other investigators, working in nearby WCA-2A, have found a lack of correlation between SO_4^{2-} concentration or SO_4^{2-} consumption and P concentration or flux in soils (Koch-Rose et al., 1994; Fisher and Reddy, 2001). Taken collectively, these data and previous lab investigations (Dierberg et al., 2011) indicate that SO_4^{2-} does not serve as a major electron acceptor in the oxidation of organic matter, and this anaerobic pathway is a minor one in mobilizing soil P in Cell 1.

Besides organic matter mineralization, another biogeochemical process associated with SO_4^{2-} reduction is its effect on Fe chemistry. Iron-phosphate mineral solubility has long been known to be a common regulator of soluble P in Fe-rich anoxic environments, and TS can remove dissolved Fe by the formation of insoluble FeS_x complexes (Hasler and Einsele, 1948). Thus, a proximate control on the availability of P in anoxic porewaters is the Fe-to-SRP ratio. Molar ratios of dissolved Fe:SRP greater than ~3.0 to 3.5 have been reported in the literature as indicative that Fe can control the availability of SRP (Zak et al., 2004, 2010; Geurts et al., 2008). Sulfate reduction and subsequent FeS_x formation is a common process whereby the Fe:SRP ratio is lowered (Gächter and Müller, 2003; Geurts et al., 2008). In our study, Fe:SRP ratios in porewater along the three transects were <3.0 (except along the mid and outflow transects during the March 2010 deployment), suggesting that Fe chemistry was unimportant in regulating SRP concentrations, even near the Cell 1 inflow where SRP concentrations were highest. This is further substantiated by porewater TS and Fe concentration profiles. Porewater TS concentrations tended to increase with depth (Fig. 5), while dissolved Fe concentrations remained low and unvarying during all three deployments and at all transects (Supplemental Fig. S2). This indicates that the more soluble inorganic sources of Fe [e.g., siderite ($FeCO_3$), vivianite ($Fe_3(PO_4)_2$)], and all the organic-derived Fe, have been converted into insoluble FeS_x complexes, where the Fe exists in an irreversible state as long as the soil remains sulfidic (Gächter and Müller, 2003). Consequently, Fe was permanently removed as a reactive partner from the Fe-P-S system, even after rehydration of the cell in June 2009 when amorphous ferric oxyhydroxides, a known P removal substrate, would have been present due to the oxidation of FeS_x during the preceding dry period (DeGroot and VanWijck, 1993; Zak et al., 2010). Instead, surface-water (Fig. 3) and porewater (Fig. 4) SRP concentrations were the highest of all three deployments. Thus, the majority of the released SRP and DOP in June 2009, which were elevated due to the oxidation of organic matter, stayed in an unbound (soluble) form, which we measured in the surface and porewaters.

If SO_4^{2-} reduction is not a significant pathway for porewater SRP accumulation, and Fe is in short supply for regulating SRP in such a dissolved Fe-limited system, then other processes must be more important in causing the elevated porewater SRP concentrations at the inflow stations, where sediments are more enriched with P and are more labile during extended inundation periods. We point to two probable candidates. The first is that organic matter decomposition is still a source of porewater SRP, but electron acceptors (oxygen [O_2], nitrate [NO_3^-]) other than SO_4^{2-} are responsible for oxidizing the organic matter. Porewater TAN concentrations suggest organic matter decomposition is occurring, since TAN originates from organic matter decomposition and is less likely to be assimilated biologically under the P-limited conditions in the STAs (Tezuka, 1989; White and Reddy, 2000). The high porewater correlations between TAN and SRP concentrations at the inflow and mid regions of the cell (Supplemental Table S3) indicate that decomposition of organic matter was likely the major source of the interstitial SRP, but the negative correlations between TS and SRP (Supplemental Table S3) indicate SO_4^{2-} was not serving as the principal terminal electron acceptor. Although ORP in the bottom waters and upper soil porewaters indicated potentials lower than those associated with O_2 and NO_3^- reduction, those electron acceptors can still be supplied into these anoxic zones where they would be consumed (reduced), but at a faster rate than they are being resupplied. Although SO_4^{2-} reduction may be responsible for poising the ORP in soils, this does not preclude more preferred oxidants, like O_2, from being responsible for most of the decomposition of organic matter, especially in the surficial soil layers where O_2 is likely to penetrate from the water column. Photosynthesis by periphyton or submerged vegetation within the water column would be a potential source of DO to the soil layer (DeBusk and Reddy, 2003), along with the introduction of DO in canal waters through the inflow culverts. The DO concentrations (2–4.5 mg L^{-1}) measured in the surface waters of the cell on 3 Mar. 2010 indicated an oxygenated water column, but given the dense stands of emergent vegetation, the DO concentrations were likely close to anoxia near the soil–water interface (Chimney et al., 2006). The ORPs of the bottom waters (0–4 cm above soil–water interface) were lower than those measured in the water column 10 to 12 cm above the soil–water interface (Fig. 4), indicating the existence of an ORP gradient within the water column.

The second source for the porewater SRP concentrations observed in the inflow region is the dissolution of Ca-P or $CaCO_3$ solid phases when respiration lowers the pH (Dittrich et al., 2000; Pant and Reddy, 2003; Harris, 2011). Diaz et al. (1994) noted that ~50% of the calcium phosphate formed in agricultural drainage canal water in south Florida was rapidly

dissolved as the pH decreased to below 8.0 after having been maintained at pH 10 or 11 for 48 h. Given that (i) SRP and dissolved Ca^{2+} concentrations were significantly correlated for soils at the mid transect (Supplemental Table S3), (ii) the pH values in the pore spaces of STA-2 Cell 1 were usually between 7.0 and 7.5, (iii) a large fraction of the soil TP existed as inorganic P (Table 1), and (iv) porewater dissolved Ca^{2+} and pH were significantly correlated in all three regions of the cell (Supplemental Table S3), P associated with $CaCO_3$ may be a secondary source of P to porewaters during diagenesis along these transects. Further studies would help quantify the role of sorption, precipitation, and dissolution of Ca-P minerals on P cycling in these soils.

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