Seasonal Water Quality Changes in On-Farm Water Storage Systems in a South-Central U.S. Agricultural Watershed

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The objective of this study was to investigate the ability of on-farm water storage (OFWS) systems to mitigate off-site nutrient movement in a south-central U.S. agricultural watershed. We examined the seasonal water quality changes in an OFWS system by measuring several physical and chemical constituents at multiple sampling points throughout the system. Water quality sampling occurred every three weeks during the growing season and every six weeks during the dormant season from February 2012 to December 2014. The collected data were grouped into four seasons and then analyzed using boxplots along with the Wilcoxon and Kruskal-Wallis rank-sum tests for detecting changes in nutrient concentrations. Significant water quality changes were observed in the OFWS system by season and nutrient species, indicating a variation in downstream nutrient reduction with season. The in-ditch median removal efficiency, from the center of the tailwater recovery ditch to the outlet, was 54% during winter and 50% during spring for $\text{NO}_3\text{-N}$; 60% during spring for $\text{NH}_3\text{-N}$; 26% during autumn and 65% during winter for ortho-P; and 31% during winter and 10% during spring for TP. The in-pond median concentration removal efficiency was ~77% during summer for $\text{NO}_3\text{-N}$, while the concentration remained stable during winter, spring and autumn; 53% from winter to spring and 58% from spring to summer for $\text{NH}_3\text{-N}$; 70% from winter to spring for ortho-P, while remaining stable during the other seasons; and 28% from winter to spring and 55% from spring to summer for TP. Our results support the hypothesis that OFWS systems could mitigate downstream nutrient-enrichment pollution, especially during spring. The results obtained from this study offer a better insight into the behavior of OFWS systems and help enhance the management of agroecosystems from an ecological and hydrological perspective for water quality pollution control and water resource conservation.

KEYWORDS: On-Farm Water Storage Systems, Tailwater Recovery Ditch,
Agricultural Runoff, Nutrient Reduction, BMP

1. Introduction

It is widely accepted that agricultural practices have become a significant contributor of pollutants that adversely alter the natural cycle of nutrients, especially for nitrogen and phosphorus (Schlesinger, 1991; Vitousek et al., 1997; Smith et al., 1999). This alteration is derived in large part from the dramatic increase in the use of fertilizers needed to maintain agricultural profitability and higher yields, which is required to feed a growing global population (i.e., roughly 77 million individuals per year according to the US Census Bureau, 2015). In 2012, the world consumption of fertilizers reached nearly 120 and 46.5 million tons of nitrogen and phosphorus per year, respectively (FAO, 2015). The increasing use of fertilizers could be detrimental to aquatic ecosystems as a substantial portion of the nutrient inputs is transported from croplands to groundwater *via* percolation and to adjacent waterbodies *via* surface and irrigation runoff (Ongley, 1996; Carpenter et al., 1998; Sims et al., 1998; Hollinger et al., 2001; Rabalais et al., 2002b), often reaching coastal ecosystems (Nixon, 1995; Rabalais, 2002; Seitzinger et al., 2002). The over enrichment of nutrients in waterbodies stimulates eutrophication, which is the most common leading factor in the deterioration of aquatic ecosystems. Additional nutrients result in the excessive growth of phytoplankton, macrophytes, and toxic algal blooms, and dissolved oxygen is consumed and depleted as bacteria decompose carbon in the dead plant material. The depletion of oxygen can cause hypoxia and as a consequence a shift in the benthic population and its related food chain, resulting in fish kills, loss of aquatic biodiversity, and many other adverse ecological effects (Carpenter et al., 1998; Smith, 1999; Smith, 2009).

Agriculture in the southern United States, specifically in the Mississippi Delta region (MDR), faces two major challenges to maintain a high level of productivity while preserving the surrounding ecosystem's health: (1) off-site movement of nutrients contributing to the development of the hypoxic zone in the northern Gulf of Mexico, especially during the spring season, and (2) the declining groundwater levels in the Mississippi River Valley Alluvial Aquifer (MRVAA). According to Rabalais et al. (2002a), an average of roughly 1 million metric tons per year of nitrate, 67% of which originates from agricultural sources, are released into the Gulf of Mexico, causing devastating ecological effects such as “the dead zone” due to hypoxia phenomenon. Similarly, phosphorus has also been suggested as a major contributor to the Gulf hypoxia problem (USEPA, 2007; Sylvan et al., 2006). In addition, the overuse of groundwater from the MRVAA is, on average, nearly $530 \text{ m}^3 \text{ ha}^{-1} \text{ yr}^{-1}$ (Kebede et al., 2014; Massey, 2010; Wax et al., 2008). To address these complex environmental issues, stakeholders and the scientific community have been promoting control measures such as the implementation of Best Management Practices (BMPs) at the field and watershed scale. One of these BMPs is the on-farm water storage (OFWS) system, which has been gaining popularity in agriculturally-dominated regions such as the MDR. By combining tail-water recovery (TWR) ditches and on-farm reservoirs, an OFWS system becomes a structural BMP that collects and stores surface runoff and irrigation tail water from farmed lands. Because of its inherent features, researchers have suggested that OFWS systems have the potential of (1) reducing nutrients exported from agricultural watersheds to receiving waterbodies and (2) providing an alternative source of water for the irrigation of cropped fields.

Over the past decade, many researchers have investigated the role of ditches as an individual structural BMP because of their crucial function of linking agricultural

watersheds to external ecosystems (Herzon and Helenius, 2008; Ahiablame et al., 2010). Dollinger et al. (2015) collated the vast majority of scientific contributions focused on the benefits of implementing ditches for agroecological management. Their study classified these benefits into waterlogging control, soil erosion prevention, water quality improvement, flood control, aquifer recharge, and biodiversity conservation. While several studies have addressed the role of ditches in nutrient movement, little attention has been paid to the combined effect of TWR ditches and on-farm reservoirs (i.e., an OFWS system) or their performance as a BMP on agricultural lands. Popp et al. (2004) cited increased profitability and reduced dependence on groundwater when using on-farm reservoirs and tail-water recovery systems in conjunction with other BMPs. Later, preliminary results from Carruth et al. (2014) and Pérez-Gutiérrez et al. (2015) indicated that OFWS could reduce nutrient runoff from farms and also that the stored water could be used for irrigation needs. In a recent study, Moore et al. (2015) observed no statistical differences in water quality among sampling points in an intensively used on-farm storage reservoir and its surrounding ditches in the Northeast Arkansas Delta. While these investigations examined OFWS systems, there are still many questions regarding the systems' nutrient removal effectiveness and seasonal water quality variation, which are helpful for making better agricultural management decisions. Therefore, it is important to monitor and analyze the water quality changes in these systems to improve our understanding of how this emerging BMP impacts the environment in terms of downstream nutrient control and water conservation.

The objective of this study was to investigate the mitigation of nutrient runoff from a south-central U.S. agricultural watershed implementing an OFWS system, by examining the spatial and temporal variations of water quality occurring at sampling points located

throughout the system. With the goal of measuring downstream nutrient reduction, we tested the hypothesis of water-quality statistical differences between the sampling points by season, using a suitable non-parametric approach.

2. Materials and Methods

2.1. Study Area

The monitored OFWS system is implemented on a farm located in the central portion of the MDR within the headwater region of the Porter Bayou watershed (PBW; Figure 1), north of Indianola, Mississippi. The PBW extends from latitude 33°26'41" to 33°51'40" north and longitude 90°48'54" to 90°31'34" west, covering nearly 506.2 km², most of which are cultivated, producing mainly soybeans and corn (MDEQ, 2012). The topography of PBW is relatively flat with elevations ranging from 90 to 150 m. From 2012 to 2014, the observed total monthly precipitation ranged from about 200 to 600 mm and primarily occurred from early autumn to late spring (Figure 2), when the runoff was usually high. The monthly average temperature ranged from 16.7 °C during winter to 26.7 °C during summer (Figure 2). More information about the watershed can be found at MDEQ (2008; 2012).

~ Figure 1

~ Figure 2

The soils on the 110-ha fields surrounding the monitored system are comprised of several soil types namely, Alligator silty clay loam (24.1%), Forestdale silty clay loam (21.1%), Dowling overwash phase (17.9%), Forestdale silt loam (14.9%), and Dowling clay (13.9%). The soils are exposed during the dormant season, and a soybean-corn crop rotation with conventional and non-tillage practices covered the farm during the growing

season for the monitoring period. Typically, nitrogen was applied during early spring, while phosphorus was applied during the fall.

2.2. Field Sampling and Analytical Techniques

For water quality data acquisition, an edge-of-field monitoring network was established in 2012 in the OFWS system at our study site (Figure 1). The network consists of four sampling points within the system: (1) the inlet, M1; (2) TWR ditch, M2; (3) the outlet, M3; and (4) the pond, MP. Table 1 provides the main characteristics of the monitored OFWS system. Sample collection was conducted from March 2012 to December 2014 every three weeks during the growing season (March to October) and every six weeks during the dormant season.

~ Table 1

Manual samples were collected in high density polyethylene bottles according to EPA Method 600/4-82-029 (USEPA, 1982). Samples were analyzed *in situ* for potential of hydrogen, pH (pH units); electrical conductivity, EC ($\mu\text{S cm}^{-1}$); dissolved oxygen, DO (mg L^{-1}); temperature, T ($^{\circ}\text{C}$); and *ex situ* for nitrate nitrogen, $\text{NO}_3\text{-N}$ (mg L^{-1}); ammonia nitrogen, $\text{NH}_3\text{-N}$ (mg L^{-1}); orthophosphate, ortho-P (mg L^{-1}); total phosphorus, TP (mg L^{-1}); total kjeldahl nitrogen, TKN (mg L^{-1}); and total suspended solids, TSS (mg L^{-1}). *In situ* parameters were measured using a Thermo Scientific Orion Star A329 Portable Multiparameter meter (Thermo Fisher Scientific Inc., Waltham, MA). Before conducting field measurements, all sensors (i.e., Thermo Scientific Orion Ross Ultra pH/ATC Triode for pH, DuraProbe[®] 4 cell Conductivity Electrode Graphite for EC and T, and Thermo Scientific Orion RDO[®] Rugged Dissolved Oxygen Sensor for DO) were calibrated relative to their corresponding standard. Field conditions were recorded in a logbook, and samples were immediately stored at 4°C in an ice-filled cooler for transport to the Agricultural and

Biological Engineering Water Quality Laboratory at Mississippi State University for analysis. Samples were analyzed for TSS using EPA Method 160.2 (USEPA, 1979). TNT plus™, a prepackaged vial chemistry technique (Hach® Loveland, CO), was used for nutrient analyses, and measurements were automatically read by the Hach® DR 2800™ portable spectrophotometer. For the ortho-P analysis, raw samples were filtered through 0.45-µm pore diameter binderless borosilicate glass microfiber filters. Table 2 summarizes the methods used for chemical analyses and their corresponding EPA compliance monitoring code. Samples were subsequently preserved by adding 2 mL of concentrated H₂SO₄ per liter of raw sample and immediately transferred to the Mississippi State Civil and Environmental Engineering Laboratory for TKN analysis, following EPA Method 351.4 (USEPA, 1979).

~ Table 2

2.3. Water Quality Data Analysis

Water quality data were grouped into four seasons: winter, Wi (December 22 – March 20); spring, Sp (March 21 – June 21); summer, Su (June 22 – September 22); and autumn, Au (September 23 – December 21). To detect water quality changes, we used graphical and statistical analyses. For the graphical analysis, box-and-whisker plots, or boxplots, were used at the seasonal scale for each sampling point and water quality constituent. This type of approach is useful for comparison between data sets and for a visual determination of whether data fit the assumptions of a statistical test procedure (USGS, 1989). A boxplot summarizes the distribution of data by displaying the median, the variability, the skewness, and the non-typical values. In this study, boxplots were set at 90th (the upper whisker), 75th (the upper quartile), 50th (the median), 25th (the lower quartile), and 10th (the lower whisker) percentiles. Outliers were considered those observations 1.5 times beyond the 25th

and 75th percentiles. The statistical analyses were conducted to test the significance of the detected changes in the water quality at the sampling points throughout the OFWS system. In this study, these changes were examined using the median because it is a resistant measure of the center of frequency in the presence of outliers. Therefore, the nonparametric Wilcoxon (Wilcoxon, 1945) and Kruskal-Wallis (Kruskal and Wallis, 1952) rank-sum tests were applied.. The former is a test for whether the medians of independent samples of two data sets are similar or not. The latter extends the Wilcoxon rank-sum principle to three or more data sets. These two methods are appropriate when normality assumptions are violated and censored data are present in the data distributions (Helsel, 2012). P-values $\leq$ 0.1 were considered statistically significant. MATLAB[®] and the Statistical Toolbox[™] (The MathWorks, Inc., Natick, MA) were used to perform all mathematical and statistical calculations.

3. Results and Discussion

3.1. Seasonal Variability of Nitrogen Species

3.1.1. Nitrate Nitrogen

Figure 3a shows the seasonal variability of the OFWS nitrate nitrogen concentration. In general, we found that the median NO₃-N concentration increased from winter to spring, decreased from spring to summer, increased from summer to autumn, and remained fairly stable from autumn to winter. We also found that the summer concentrations were close to 0.23 mg L⁻¹ and did not change spatially or temporally. These findings suggest that the changes in NO₃-N concentration might greatly depend on the current hydrologic and hydrodynamic characteristics of the system. The movement of pollutants through the ditch from late autumn to early spring may be governed by a combination of advective and diffusive transport processes, primarily driven by the rainfall occurring during that time

frame. In contrast, diffusive processes could have dominated during summer and early autumn when precipitation was minimal. This shifting from semi-lotic to shallow lentic conditions, which ultimately would increase the system's residence time, in conjunction with the summer warmer temperatures may have stimulated biogeochemical transformations of nutrients (Lillebø et al., 2007). Such transformations might predominantly occur on the system's bottom sediments and biofilms (Peterson et al., 2001). A study conducted by Moore et al. (2015) in an on-farm storage system in the northeast Arkansas Delta noted no statistical differences in water quality between the ditches or between the two ditches and the reservoir, which compared well with the results that were obtained for summer in this study. In contrast, we found statistical evidence of higher $\text{NO}_3\text{-N}$ concentrations during winter, spring, and autumn in the Mississippi OFWS system. Although the study conducted by Moore et al. (2015) was limited by the number of samples analyzed, we do not know why there is a discrepancy for three seasons. However, we can infer that the spatial similarities in summer $\text{NO}_3\text{-N}$ concentrations for the Arkansas and Mississippi studies might be due to plant uptake and decreased $\text{NO}_3\text{-N}$ concentrations as a result of little rainfall.

The inlet (M1 location) showed, on average, the same median $\text{NO}_3\text{-N}$ concentration throughout the winter, spring, and autumn seasons (i.e., around 0.45 mg L^{-1} ; $p = 0.34$). In spite of such similarities, spring and autumn reported a larger variability ($0.23 - 4.53 \text{ mg L}^{-1}$ and $0.23 - 2.82 \text{ mg L}^{-1}$, respectively) than winter ($0.023 - 1.71 \text{ mg L}^{-1}$). Summer concentrations showed little variation and remained close to the median (0.03 mg L^{-1}). Compared with the M1 location, median concentrations in the TWR ditch (M2) were (i) slightly over fourfold higher during winter and spring ($p < 0.01$), (ii) the same during summer ($p = 0.08$), and (iii) twofold larger during autumn ($p = 0.1$). At the M2 location,

the 90th percentile concentration occurred during spring, which was slightly higher than 5 mg L⁻¹. These results suggest that higher amounts of NO₃-N may have entered the system *via* surface runoff from the fields that drain into the TWR ditch, especially during the rainy season. This result was expected as roughly 40% of the total annual precipitation across the study area occurred from March to June during the period of sampling (Figure 2), and the dominant soil series are classified as having a very high runoff potential under the runoff class property. In addition, according to Randall et al. (1997), under continuous corn and corn-soybean rotation, the evapotranspiration rate is limited relative to cover crop systems, leading to higher runoff along with major nutrient losses, conditions that could likely be mirrored in our system.

The M3 location, the outlet of the system, exhibited a similar median NO₃-N concentration (about 0.9 mg L⁻¹; $p = 0.58$) during winter, spring, and autumn. Although the NO₃-N concentration varied considerably through autumn, results showed the maximum concentration during spring exceeding that from autumn by a factor of 1.6. When compared with M2, the median NO₃-N concentration at M3 was reduced by 54% during winter (although it was statistically significant only at $p = 0.17$) and 50% during spring ($p < 0.01$), likely due to potential biological assimilation and denitrification processes (Peterson et al., 2001). Our results are in agreement with those from Fu et al. (2014), who investigated the nutrient mitigation capacity of two agricultural ditches (constructed and traditional) in China. Results from that study reported removal efficiencies of 57% and 21% for the NO₃-N concentrations in a constructed and traditional ditch, respectively. Both ditches were hydro-geomorphically similar in length, width, and slope; however, the constructed ditch was enhanced with geogrid, geotextile, and fine and coarse gravel. Another similar study conducted by Littlejohn et al. (2014) found a 25% reduction

in the median NO_3 load in a ditch containing low-grade weirs for nutrient removal. They attributed this low removal percentage to potential high nitrification rates overwhelming the $\text{NO}_3\text{-N}$ concentration reduction in the system studied. In an earlier investigation, Moore et al. (2010) compared the nutrient reduction potential of a vegetated and non-vegetated agricultural ditch in the Mississippi Delta. Under a simulated storm event, they reported $\text{NO}_3\text{-N}$ load reductions up to 74% and 78% in the vegetated and non-vegetated ditch, respectively. In a more recent investigation conducted in planted mesocosms, Taylor et al. (2015) reported a 68% and 61% reduction in $\text{NO}_3\text{-N}$ load in the vegetated and non-vegetated treatment, respectively. Several researchers have found similar nitrate removal efficiencies in wetlands that drain agricultural areas (Fink and Mitsch, 2007; Jordan et al., 2011; Reddy et al., 1982; Woltemade, 2000).

At the pond sampling point, MP, there were no significant differences among the median $\text{NO}_3\text{-N}$ concentrations (slightly higher than 1 mg L^{-1} ; $p = 0.98$) during winter, spring, and autumn. Summer $\text{NO}_3\text{-N}$ concentrations remained fairly stable and close to the detection limit (0.23 mg L^{-1}). Consistent with results from Moore et al. (2015), we found that the median $\text{NO}_3\text{-N}$ concentration in the pond during autumn was significantly higher (by a factor of ~ 4 ; $p < 0.01$) than during summer. While winter and spring $\text{NO}_3\text{-N}$ concentrations showed similar variability at the MP location, higher concentrations were more frequent during winter (close to 2 mg L^{-1}). When comparing median concentrations over seasons, results from this study show that the pond's removal efficiency for $\text{NO}_3\text{-N}$ was more than 77% during summer. We not only hypothesize that the sediment denitrification rates in the pond could be higher during summer, as noted in other studies (David et al., 2006), but we also believe that primary production might have been a contributing factor as well, controlling the in-pond inorganic nitrogen during the warmer

months (Figure 2). Conversely, during the cooler months, these two biogeochemical sinks for $\text{NO}_3\text{-N}$ might be minimal so that the $\text{NO}_3\text{-N}$ remained primarily in the water column.

3.1.2. Ammonia Nitrogen

Figure 3b shows the seasonal variability of ammonia nitrogen concentrations throughout the OFWS system. At M1, the variability of the $\text{NH}_3\text{-N}$ concentration was relatively similar among seasons, except during autumn, when the variability covered a broader interval ($0.015 - 0.213 \text{ mg L}^{-1}$, the 10th and the 90th percentile concentrations, respectively). The median $\text{NH}_3\text{-N}$ concentrations showed no significant changes during winter, summer, and autumn (0.06 mg L^{-1} ; $p = 0.96$). In contrast, the median $\text{NH}_3\text{-N}$ concentration during spring was significantly lower ($p = 0.09$), which might be explained by dilution processes. A marginal decrease in the median $\text{NH}_3\text{-N}$ concentration was observed from winter to spring (by a factor ~ 3), and a modest increase was seen later during summer and autumn (by a factor 2.8). The highest 90th percentile $\text{NH}_3\text{-N}$ concentration occurred during autumn, reaching levels up to 0.213 mg L^{-1} . At M2, the highest median $\text{NH}_3\text{-N}$ concentration occurred during spring (0.224 mg L^{-1}), followed by autumn and winter (around 0.1 mg L^{-1}). These results indicate that the main source of $\text{NH}_3\text{-N}$ likely entered the system from the fields draining to the TWR ditch, similar to the pattern observed with $\text{NO}_3\text{-N}$ concentrations. We also found a marked decline, as much as 79%, between spring and summer $\text{NH}_3\text{-N}$ concentrations. During summer, the $\text{NH}_3\text{-N}$ concentrations exhibited negligible variability over a narrow interval ($0.015 - 0.098 \text{ mg L}^{-1}$, the lower and the upper quartile concentrations). As discussed by Dodds et al. (1991), ammonium is energetically preferable to nitrate in photosynthetic and heterotrophic assimilation. Thus, we hypothesized that the aggregated effect of biological assimilation, sorption to sediments, nitrification, and high solar radiation may have been responsible for

the low $\text{NH}_3\text{-N}$ concentrations observed in the OFWS system during late spring, summer, and early autumn. We also observed that the median concentration of $\text{NH}_3\text{-N}$ increased by a factor of 2.2 from summer to autumn, which could be attributed to the sorbed and regenerated $\text{NH}_3\text{-N}$ released to the water column from the stream bottom (Peterson et al., 2001) and to the remaining portion of fertilizers flushed by runoff from the field after harvest.

At M3, the outlet of the system, the median $\text{NH}_3\text{-N}$ concentration was fairly constant (around 0.11 mg L^{-1} ; $p = 0.46$) throughout winter, spring, and autumn; whereas, the summer median concentration was nearly twice as low. During the spring season, the $\text{NH}_3\text{-N}$ concentration largely varied, reaching a maximum value of 0.423 mg L^{-1} . When compared with M2, the median $\text{NH}_3\text{-N}$ concentration at M3 showed a reduction of 60% during spring ($p = 0.03$). This measured reduction was high relative to previous studies in a constructed ecological and traditional soil ditch in China (49% and 12% on average, respectively (Fu et al., 2014)). However, our result was lower than the 71% reduction efficiency reported by Moore et al. (2010) after a single simulated runoff event conducted on a non-vegetated ditch in the MDR. The 60% $\text{NH}_3\text{-N}$ reduction efficiency in this study is also slightly lower than the estimated 67% reduction observed by Littlejohn et al. (2014) in a terraced ditch within the Lower Mississippi Alluvial Valley. Moore et al. (2010) also studied the $\text{NH}_3\text{-N}$ reduction efficiency in a vegetated ditch, finding the same order of magnitude that we found in our study. When comparing the spring seasonal removal efficiencies for $\text{NO}_3\text{-N}$ (50%) and $\text{NH}_3\text{-N}$ (60%) in the TWR ditch, we had better results for $\text{NH}_3\text{-N}$. This particular finding is likely due to higher nitrification rates during spring and early summer. The resulting $\text{NO}_3\text{-N}$ is more water-soluble and thus, more mobile and may have been readily transported downstream (Bernot and Dodds, 2005). Bernot et al. (2006)

also noted this finding when conducting studies in agriculturally influenced streams of the Midwestern US. By measuring the nutrient length uptake (S_w) (i.e., the mean distance a nutrient molecule will travel before being removed from the water column; Stream Solute Workshop, 1990), they found that the $\text{NH}_3\text{-N } S_w$ was lower than the $\text{NO}_3\text{-N } S_w$. Peterson et al. (2001) reported similar findings by examining nitrogen dynamics in 12 headwater streams across the US.

At the MP location, we found similar variability during winter and spring; however, the median $\text{NH}_3\text{-N}$ concentration during winter was twofold higher than in the spring, and the highest concentration slightly rose over 0.25 mg L^{-1} during the spring season. The median $\text{NH}_3\text{-N}$ concentration was reduced by 53% from winter to spring and by 58% from spring to summer (although no statistical difference was detected from winter to spring, $p = 0.37$; or from spring to summer, $p = 0.34$); however, median $\text{NH}_3\text{-N}$ concentrations were almost fivefold higher during autumn than summer ($p = 0.01$) in the pond. These results are consistent with the results observed for the $\text{NO}_3\text{-N}$ concentration at the MP location confirming that the temperature might be a controlling factor for the in-pond nitrogen species.

~ Figure 3

3.2. Seasonal Variability of Phosphate Species

3.2.1. Orthophosphate

Figure 4a shows the seasonal variability of the orthophosphate concentrations through the OFWS system. At the OFWS inlet (M1), the median ortho-P concentrations were low during summer (0.074 mg L^{-1}), high during spring (0.235 mg L^{-1}), and remained moderate during winter and autumn (around 0.2 mg L^{-1} ; $p > 0.9$). The variability of the ortho-P

concentrations increased from winter to spring when the concentration reached a peak value of 0.5 mg L⁻¹. The median concentration dropped by a factor of 3.2 from spring to summer ($p < 0.01$), followed by an increase by a factor of 2.7 from summer to autumn ($p < 0.01$). The maximum median ortho-P concentration throughout the system (slightly more than 0.913 mg L⁻¹) occurred at M2 during winter. In addition, we observed a marked variability from 0.164 to 0.913 mg L⁻¹ in the TWR ditch during the winter season. At M2, the median ortho-P concentration during spring was (i) less than the winter by a ratio of 1:3 ($p < 0.01$), and (ii) higher than the summer and autumn by a factor of ~2 ($p = 0.02$). These results suggest that in-ditch biotic processes were enhanced by warmer temperatures and light availability. Median ortho-P concentrations were stable around 0.1 mg L⁻¹ ($p = 0.2$) during summer and autumn. In addition, the distribution of ortho-P concentrations during summer was within a narrow range (0.063 – 0.163 mg L⁻¹). During the autumn, concentrations were more variable (between 0.068 and 0.206 mg L⁻¹). When compared with M1, the median ortho-P concentration was reduced by 49% at M2 ($p = 0.05$) and by 26% at M3 ($p = 0.09$) during the autumn. Also, when compared with M2, we found that the median ortho-P concentration was reduced by 65% at M3 ($p = 0.03$) during the winter. Previous research in the MDR observed lower percentages of ortho-P reduction (i.e., ~14%) in a 500 m-length ditch (Littlejohn et al., 2014). The higher ortho-P removal efficiencies found in this study might be due to the greater in-ditch residence time and concentrations of Ca, Mg, Fe, and Al, which result in a higher rate of P adsorption and precipitation processes (Penn et al., 2007). In a vegetated drainage ditch, Kröger et al. (2008) found a 44% Dissolved Inorganic Phosphorus (DIP) reduction, which is similar to what was observed in the current study. Other studies have observed much higher removal

efficiencies for ortho-P. For instance, Moore et al. (2010) reported a 98% reduction, on average, in DIP load under a simulated storm event conducted on vegetated and non-vegetated drainage ditches in the MDR, which is also similar to the findings of Penn et al. (2007).

The median ortho-P concentration at the M3 location was similar during winter and spring (around 0.2 mg L^{-1} ; $p = 0.88$), and marginally lower during summer and autumn (around 0.15 mg L^{-1} ; $p = 0.33$). Median ortho-P concentrations were more variable at M3 during the spring season, when we observed the maximum 90th percentile concentration of 0.46 mg L^{-1} . These findings reflect the impact of rainfall runoff from the agricultural landscape on the adjacent ditch (Figure 2).

While having similar low values close to the detection limit during spring, summer, and autumn, the median ortho-P concentration was higher during the winter season ($p < 0.01$) at the MP location. This suggests that the pond could act as a sink for P species (observed removal efficiency of more than 70%; $p = 0.03$) during the warmer seasons, likely due to sorption of P to the in-pond sediments and P biological uptake.

3.2.2. Total Phosphorus

Figure 4b shows the seasonal variability of the total phosphorus concentrations through the monitored OFWS system. The inlet sampling point, M1, showed that the median TP concentration increased from winter to spring ($p = 0.12$), decreased from spring to summer ($p = 0.14$), and remained fairly stable throughout the summer and autumn ($p = 0.83$). The M1 TP concentrations largely varied in spring (from $0.113 - 0.82 \text{ mg L}^{-1}$), and while lower, concentrations were also variable during the winter ($0.015 - 0.43 \text{ mg L}^{-1}$) and summer ($0.107 - 0.523 \text{ mg L}^{-1}$). During autumn, TP concentrations ranged from $0.23 - 0.3 \text{ mg L}^{-1}$.

At the M2 sampling point in the TWR ditch, we found that the highest median TP concentrations occurred during winter and spring (around 0.675 mg L^{-1} ; $p = 0.62$), whereas the minimum median concentrations occurred during summer (0.228 mg L^{-1}) and autumn (0.295 mg L^{-1}). At M3, the outlet of the system, the median TP concentrations showed an increase by a factor of 1.6 from winter to spring, while the median TP concentrations during summer and autumn were almost twofold lower than the spring median concentration. The M3 sampling point had the highest variability of TP during the spring ($0.347 - 1.6 \text{ mg L}^{-1}$; $p < 0.01$), which had a median concentration of 0.564 mg L^{-1} . The other three seasons exhibited almost the same median TP concentration around 0.3 mg L^{-1} ($p = 0.16$), with no statistically significant differences. We found that from the M2 sampling point in the ditch to the M3 point at the outlet, the median TP concentration was reduced 31% during winter ($p = 0.03$) and 10% during spring ($p = 0.1$). Moore et al. (2010) reported 95% and 86% TP reduction when examining non-vegetated and vegetated ditches, respectively, in the MDR, which are greater than the reductions measured in this study. However, our results are in the 12% to 73% range of TP removal by plant uptake observed by Reddy and Debusk (1985) and Silvan et al. (2004).. The TP reductions measured in this study are in line with the findings of Fu et al. (2014), who noted a removal efficiency of 26% in a constructed ditch in Tai Lake Basin, China. Fu et al. (2014) concluded that the physical settlement, plant uptake, and adsorption/desorption of P species could be the most important mechanisms for P removal.

At MP, the median TP concentration was reduced by 28% from winter to spring ($p = 0.04$), and by 55% from spring to summer ($p < 0.01$). The highest 90th percentile TP concentration of 1.5 mg L^{-1} in the pond was observed during winter. Also, no significant

differences were detected between the median TP concentrations during spring and autumn (0.35 mg L⁻¹; $p = 0.75$). Again, the median TP concentration during summer was the lowest among seasons (0.16 mg L⁻¹). However, the median TP concentration was almost twofold higher during autumn than during summer ($p < 0.01$). In addition to the movement of P *via* soil erosion during runoff experienced at times of high rainfall in late autumn and winter, these results were expected as the P dynamics might have been enhanced by in-pond shallowness and higher solar radiation during late spring, summer, and early autumn. The results of our study indicate that the downstream nutrient reduction can vary with season.

~ Figure 4

4. Summary and Conclusions

This study examined the water quality changes occurring in the OFWS system implemented at a farm within the PBW, an agricultural watershed in the MDR. Our results provide evidence of significant seasonal water quality changes among the different points monitored throughout the OFWS, and more importantly, highlight downstream nutrient reduction. Our study showed a 54% and 50% reduction in NO₃-N concentration in the TWR ditch during winter and spring, respectively. When comparing median concentrations over seasons, our results showed that the pond's removal efficiency for NO₃-N was more than 77% during summer. A 60% reduction in NH₃-N concentration was measured in the TWR ditch during spring, whereas NH₃-N removal percentages of 53% were observed from winter to spring and 58% from spring to summer in the pond. Orthophosphate concentrations in the ditch were reduced by 49% at M2 and 26% at M3 during autumn, as measured from M1. During winter, the ortho-P concentration was reduced by 65% from M2 to M3. The in-pond ortho-P concentrations removal efficiency was observed to be

approximately 70% from winter to spring, remaining stable through the other seasons. Total phosphorus in the ditch, as measured from M2 to M3, was reduced by 31% and 10% during winter and spring, respectively. From winter to spring, the in-pond TP concentration was reduced by 28% and from spring to summer by 55%. The results of this study indicate that the downstream nutrient reduction can vary with season, with significant reductions possible during spring. This variation is of special interest when targeting the effect of nutrient runoff from agricultural fields into the Gulf of Mexico as the dead zone is mainly observed during spring. Our results provide support in favor of the hypothesis that OFWS systems could mitigate downstream nutrient-enrichment pollution. However, enhanced top-of-the-field agricultural management is required in combination with OFWS to decrease nutrient loading downstream, especially during soil-exposed periods when high nutrient runoff is likely to occur. This study provides better insight into the behavior of OFWS systems and helps to improve the management of agroecosystems for water quality pollution control and water resource conservation.

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Table 1. Hydro-geometric characteristics of the monitored OFWS system

Hydro-Geometric Feature	Value	Units
<i>TWR Ditch (Trapezoidal shape)</i>		
Length	818.8	m
Side slope	1.5:1	-
Channel bed slope	0	-
Bottom width	3.6	m
Flow depth	1.8	m
Freeboard	0.3	m
Storage volume	13,320	m ³
<i>On-farm Reservoir</i>		
Depth	2.4	m
Side slope	3:1	-
Surface area	4.45	ha
Bottom width	3.6	ha
Storage volume	114,700	m ³

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Table 2. Analytical methods used in the nutrient-related chemical analyses at the laboratory scale

Constituent	Chemical Method	Hach® Code	TNT plus™ number	EPA Compliance Monitoring
NO ₃ -N	Dimethylphenol	10206 - Low Range: 0.23-13.5 mg.L ⁻¹	835	40 CFR 141
NH ₃ -N	Salicylate	10205 - Ultra Low Range: 0.015 to 2.0 mg.L ⁻¹	830	EPA 350.1
Ortho-P	Ascorbic Acid	10209 - Low Range: 0.05-1.5 mg.L ⁻¹	843	EPA 365.1, 365.3
TP		10210 - Low Range: 0.05-1.5 mg.L ⁻¹		

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Figure Captions

Figure 1. Location of the edge-of-field water quality monitoring network at the study site in the Porter Bayou watershed, relative to the Mississippi Delta Region

Figure 2. Total monthly precipitation and monthly average temperature observed during 2012 to 2014 at the study site. Source: PRISM Climate Group

(<http://www.prism.oregonstate.edu/explorer/>)

Figure 3. Seasonal variability of (a) $\text{NO}_3\text{-N}$ and (b) $\text{NH}_3\text{-N}$ in the monitored OFWS system (M1: the inlet; M2: TWR ditch; M3: the outlet; MP: the pond; DL: detection limit; Wi: winter; Sp: spring; Su: summer; Au: autumn; Outliers are shown as red circles; The number of samples (n) for each grouped dataset is shown below the X axes)

Figure 4. Seasonal variability of (a) Ortho-P and (b) TP in the monitored OFWS system (M1: the inlet; M2: TWR ditch; M3: the outlet; MP: the pond; DL: detection limit; Wi: winter; Sp: spring; Su: summer; Au: autumn; Outliers are shown as red circles; The number of samples (n) for each grouped dataset is shown below the X axes)

Figure 1.

Figure 2.

Figure 3.

Figure 4.