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The Effectiveness of an Artificial Floating Wetland to Remove Nutrients in an Urban Stream: A Pilot-Study in the Chicago River, Chicago, IL USA

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Abstract: Ever expanding urbanized landscapes are increasingly impacting streams that run through them. Among other stressors, urban streams often are host to elevated concentrations of nutrients, salts, and heavy metals. The pollutants, coupled with high temperatures, are drivers of ecosystem degradation in urban streams. The installation of artificial floating wetlands (AFWs) has been successful in mitigating the effects of urbanization in lakes and wastewater treatment ponds, but rarely have they been tested in streams. This pilot-study examined the ability of an AFW to improve water quality in an urban stream. The small, 90 m^2 AFW was installed to improve the aquatic habitat and aesthetics of a small section of the Chicago River, Chicago, IL USA. Water samples and in-situ measurements were collected from the surface and at 0.3 m depth of upstream and downstream of the AFW. Samples were analyzed for nitrate-as-nitrogen, phosphate, chloride, and heavy metals. Comparison of upstream and downstream waters showed that the AFW lowered the concentrations of nitrate-as-nitrogen and phosphate during the growing season by 6.9% and 6.0%, respectively. Nitrate was also removed during the dormant season; however, phosphate was not removed during that time. Plant or microbial uptake of the nutrients are believed to be the dominant mechanisms in the growing season with denitrification serving as the primary pathway in the dormant season. Despite not having a measurable effect on the water temperature, the AFW was an effective means to reduce concentrations of nitrate and phosphorus, decreasing the potential for eutrophication.

Keywords: artificial floating wetland; nitrate; phosphate; Chicago River; heavy metals

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1. Introduction

Urban stream syndrome is defined as the "consistently observed ecological degradation of streams draining urban land" [1]. Further work has refined the urban stream syndrome designation to include the alteration of chemistry, ecology, and/or hydrology in urban streams as a result of urban land-use and urban runoff [2–6]. Attributed to point- and nonpoint-sources, specific symptoms include higher temperatures, lower dissolved oxygen (DO), loss of aquatic habitat [3,7], and elevated concentrations of heavy metals, nutrients (i.e., nitrogen and phosphorus), and salts (i.e., chloride) [2,8–11]. Nutrient, chloride, and heavy metal concentrations in urban streams are documented to increase as the footprint of urbanization grows landscapes [6,12–15].

Nitrogen and phosphorus, are key nutrients for plant growth and development of many photosynthetic organisms, and elevated concentrations of both contribute to eutrophication and hypoxic conditions in waterways [16–18]. Notorious algal blooms, such as the ones witnessed in Lake Erie [19], frequently occur at the mouths of waterways that drain urban and agricultural lands. Mitigating and preventing eutrophication requires the reduction of nutrients from the waters before algal growth can begin to negatively impact the proper functioning of ecosystems [20,21].

High concentrations of chloride in urban streams negatively affects all manner of aquatic life in different ways [22]. At concentrations above 1770 mg/L, the water flea, *C. dubia*, was unable to reproduce and mortality occurred at concentrations above 2420 mg/L. Freshwater minnows, such as *P. promelas*, suffered from reduced weight, and possible death, when concentrations reached 2920 mg/L. Heavy metals are also considered a priority pollutant of watersheds and can cause adverse effects to the ecosystems they pollute [23]. Primarily industrial pollutants, metals such as aluminum (Al), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), manganese (Mn), and zinc (Zn), can be detrimental to both the environment and human health [23–26]. While at some levels some heavy metals such as Cu, Mn, and Cr are essential for human health, excess amounts can be toxic [23,27].

A watershed dominated by urban land uses, the Chicago River (Chicago, IL, USA) is a classic example of an impaired waterway experiencing urban stream syndrome [28]. As Chicago's footprint has expanded, runoff and drainage patterns for the river have been significantly altered, resulting in a dramatic increase in the rate and volume of stormwater runoff and a reduction in groundwater recharge into the river. Wastewater discharge from the Metropolitan Water Reclamation District of Greater Chicago (MWRDGC), storm runoff and combined sewage overflows (CSOs) can cause spikes of salts, nutrients, and heavy metals [29,30]. Between 1974 and 1995, nitrate was the dominant N species measured in the river water [31]. Additionally, nitrate (NO_3^-) showed an increase in concentrations while ammonia (NH_4^+) and Total Kjeldahl Nitrogen (TKN) experienced declining concentrations during the two decades. Between 2002 and 2004 as the City of Chicago began to focus on lessening urban impacts on the river, nitrate concentrations exhibited temporal variability, ranging between 4 and 9 mg/L [32].

The MWRDGC operates several wastewater treatment plants in the Chicago region, including one of the largest facilities in the country at the Stickney treatment plant. Overall, urban discharge contributes an estimated 175,000 metric tons of salt per year to the Chicago region [33]., with an additional 140,000 tons of deicing salts (primarily NaCl) applied to Chicago roadways [34]. Highly soluble, an estimated 35 to 55% of deicing chloride is transported via urban runoff into water bodies, negatively affecting biota and entire ecosystems [35]. Repeated water-quality measurements of the Chicago River document high chloride concentrations (>400 mg/L) in the winter with lower concentrations (<200 mg/L) in the summer [36,37]. Within the urbanized Chicago River watershed, the primary sources of heavy metal pollution are from the drainage of impervious areas, domestic wastewater, and industrial wastewater [24,38,39]. The accumulation of road dusts within urban areas can deposit inorganic minerals such as Cu, Cd, Cr, Pb, and Zn on the impermeable surfaces of roads and roofs within the city [40].

A means to remedy the symptoms of urban stream syndrome is the installation of an artificial floating wetland (AFW). AFWs are an ecosystem created with a buoyant substrate that support plants and allow them to grow hydroponically, with their roots dangling down into the water column [41]. The typical focus of an AFW design is to provide low cost, low maintenance water purification, but AFWs can also protect shorelines, beautify, and create structure and habitat for riverine flora and fauna [42–45]. As the primary driver of ecosystems, plants alter the pH, temperature, and the dissolved oxygen (DO) of the waters [46], remove nutrients and heavy metals from the water column via root uptake [42,43,47–51], and prevent eutrophication [46,52,53]. While plant uptake is a direct pathway for nutrient reduction, microbial biofilms that colonize on underwater structures, such as the root systems of the plants on AFWs, can also transform or remove N species [48,54–56].

The utility of AFWs to improve water quality has been explored, but the studies have been primarily microcosm/mesocosm experiments [47–49,57–59] or system modeling [41]. Few studies have examined AFWs in open water systems [60]. Additional limitations are that the majority of work has focused on the effects during only the summer and chosen species tend to be of limited diversity and are, in many instances, cut back regularly to improve the plant uptake potential by stimulating more plant growth [51,59]. While plants are most active during the summer, the role of nitrate abatement by plants in the winter has been observed in other environments, i.e., a saturated buffer [61]. The year-round presence of microbial biofilms could potentially provide an assimilation of the denitrification pathway even when the plants are dormant.

Several studies have proven that AFWs are effective on stagnant waters in removing nitrogen, phosphorus, and heavy metals from ponded water [8,50,62]. Many previous studies conducted on AFWs did so in different ecosystems and employed different species to act as phytoremediators, but it is significant to note that they unanimously observed the effects of AFWs in controlled systems. The present study will provide insight into the benefits of AFWs on flowing rivers. This work investigated the effectiveness of a small (pilot) AFW to remediate an urban stream in a small section of the Chicago River. The pilot AFW was designed to improve the aquatic habitat and enhance the aesthetics of the stream segment. However, we examined whether an AFW provided any in-situ benefits by addressing the following questions: (1) Does the AFW decrease nutrient concentrations, nitrate and phosphate, within the water column? (2) Are chloride concentrations of waters upstream from the AFW greater than chloride concentrations of waters downstream from the AFW? (3) Are heavy metal concentrations of waters upstream from the AFW greater than heavy metal concentrations of waters downstream from the AFW? (4) Are there seasonal differences in the effectiveness of an AFW to remove dissolved solutes?

2. Materials and Methods

2.1. Study Location

This study site was located in a side canal on the north branch of the Chicago River flowing adjacent to Goose Island in Chicago, Illinois, USA (Figure 1). The canal was constructed in the 1870s and for over a century hosted heavy industry along its banks. The commercial and industrial value of the canal meant it had undergone periods of channelization, widening, dumping, and dredging. Because of restrictions of commercial boat traffic and deprioritization by the Army Corps of Engineers, dredging of the canal has stopped, and several meters of fine, loose sediment sit atop a hard clay bed. The canal ranges from 1 m deep at the northern end to 2.5 m deep at the southern end and has a width of 24–37 m. In the portion of the Chicago River located around Goose Island, impermeable areas of urban landscape drain directly into the river. Two CSO outfalls near the north (upgradient) end of the canal can discharge into the canal during high rainfall events, sometime occurring with as little as a few centimeters of rain in the area.

Along the eastern edge of the canal, around 90 m^2, approximately 3 m by 30 m, of AFWs were installed in 2017, hosting roughly 2000 plants representing 50 unique species native to Illinois (Figure 1B,C). Installed to improve aquatic habitat and the aesthetics of the canal, the AFWs were constructed from interconnected tubes of coconut husk that provide a buoyant substrate for various plant species (Table 1; Figure 2). While some roots extended greater than 1 m into the water column, most roots grew to a depth of 0.5 m (Figure 1D). The gardens were anchored to the eastern bank, which is entirely cement and steel lined. The bank opposite is mixed, with steel seawall and concrete riprap intermingled with natural banks with trees and plants growing along the riparian zone. Water typically enters the canal from the northwest, branching off from the river, and flowing to the southeast until it rejoins the north branch approximately 1.5 km south. Based upon the last 67 years of water data collected by the USGS, the canal has a mean discharge of 0.88 m^3/s. The primary purpose of these AFWs is to assess improvement in aquatic habitat and species as the artificial habitat will provide an ecosystem for aquatic life and introduces both allochthonous and autochthonous organic matter to the river.

2.2. Water Chemistry

River water was collected upstream of the garden and downstream of the garden at two depths during sample events: at the surface and at 0.3 m below the surface. The

0.3 m depth was selected to capture waters that flowed through the root zone. From each depth, two samples were collected with a horizontal sampler before being filtered through a 0.4-μm membrane filter and transferred into acid washed 30 mL sample bottles. Samples to be processed for heavy metals were acidified to a pH of 2 with concentrated sulfuric acid. All samples were frozen prior to analysis. In-situ measurements of dissolved oxygen (DO) (mg/L), temperature (°C), and specific conductance (SpC) (μS/cm) were recorded using a YSI-85.

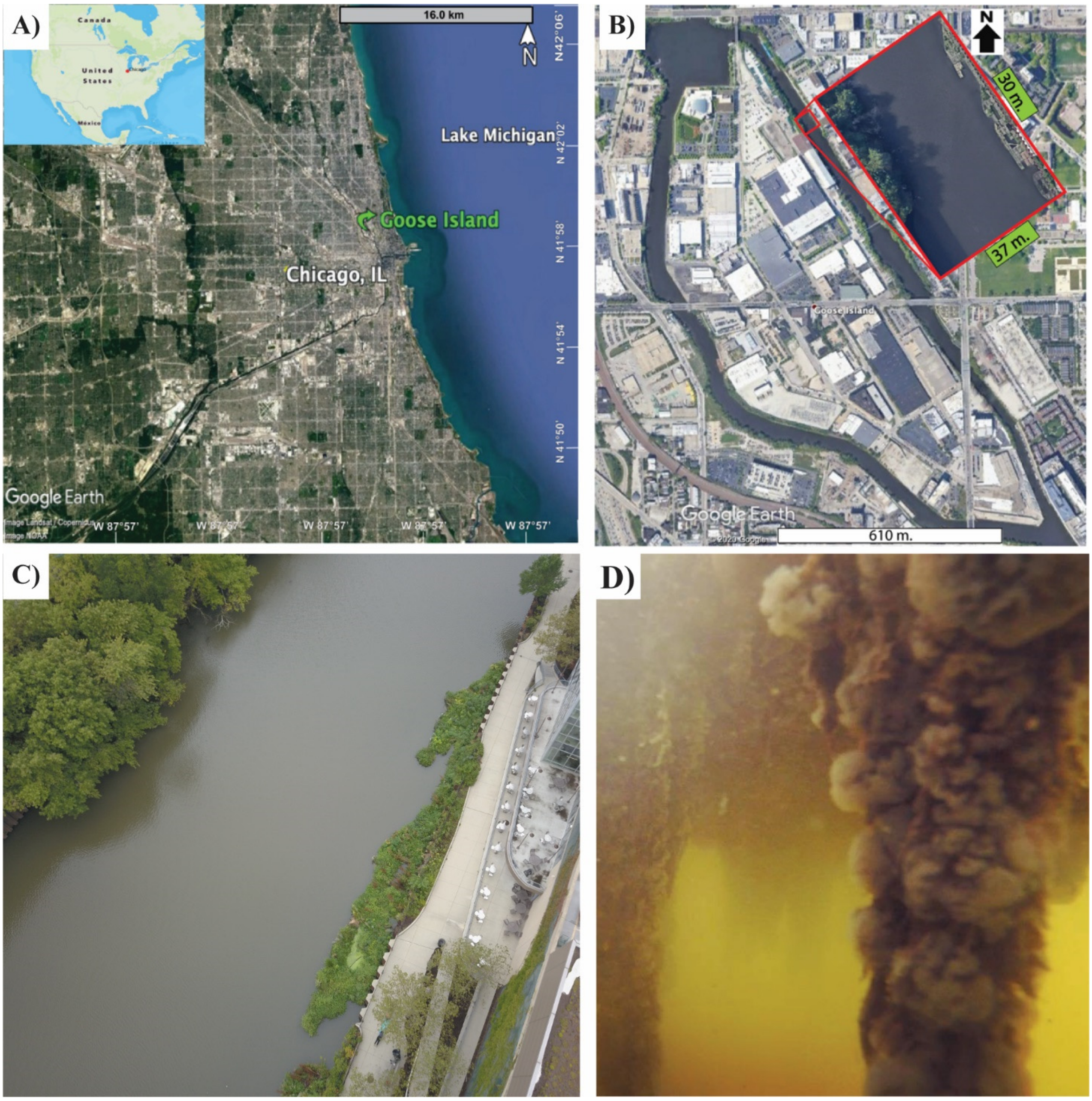

Figure 1. Location of the AFW along Goose Island Canal. (**A**) General location within Chicago, Illinois, USA (base image from Google Earth). (**B**) AFW location on the eastern edge of Goose Island Canal of the Chicago River. The general location is outlined in red. The inset shows the garden (3 m × 30 m) in relation to the river (37 m × 30 m) (**C**) An overhead image of the AFW. (**D**) Image of the system of roots within water column underlying the AFW.

Major anions (Cl^-, Br^-, NO_3^--N, PO_4^{3-}, SO_4^{2-}) were measured on a Dionex ICS-1100 Ion Chromatograph (US EPA method 300.1 [63]. Heavy metal concentrations (Al, As, Be, Cd, Cr, Cu, Pb, Mn, Se, Zn) were quantified using a PerkinElmer Optima 8300 Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). Quality assurance (QA) and quality control (QC) was maintained during analysis of each sampling event by running blank, duplicate, and replicate samples. The analytical error was less than 3%.

Table 1. Plant species that have experienced successful growth in the AFWs.

Species Name	Common Name
Acorus calamus	Sweet flag
Caltha palustris	Marsh-marigold
Carex bromoides	Brome sedge
Carex comosa	Bristly sedge
Carex stricta	Tussock sedge
Decodon verticillatus	Waterwillow
Filipendula rubra	Queen of the prairie
Hibiscus moscheutos	Rose mallow
Iris virginica var. shrevei	Southern blue flag
Juncus effusus	Common rush
Justicia americana	American water-willow
Rumex altissimus	Pale dock
Saururus cernuus	Lizards tail
Scirpus cyperinus	Woolgrass
Verbena hastata	Blue vervain

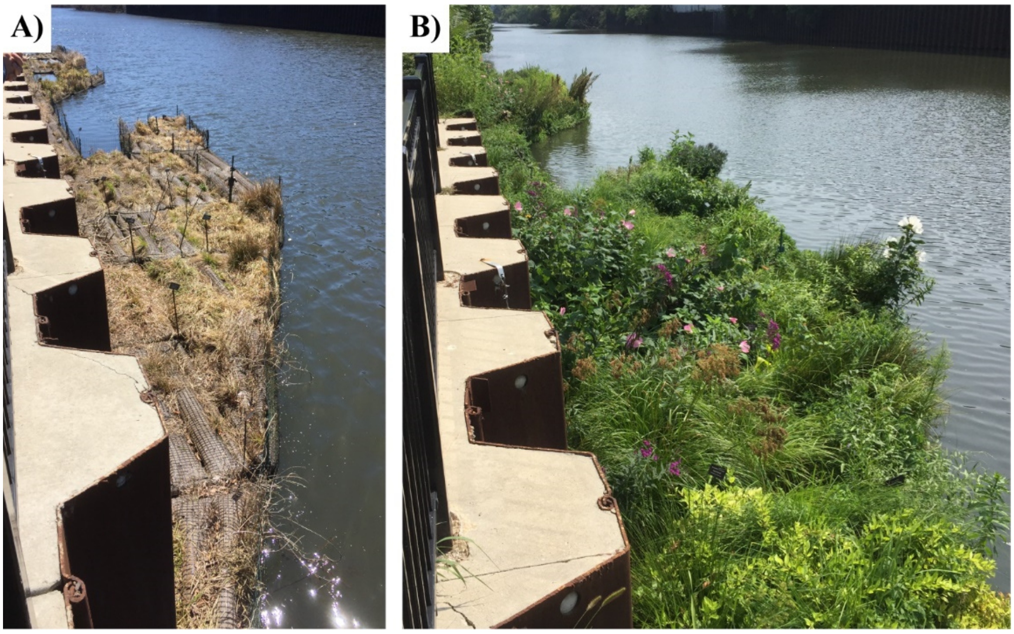

Figure 2. (**A**) AFWs during the dormant period (April 2019). (**B**) AFWs during the growing period (August 2019).

One-sided paired *t*-tests, $\alpha = 0.05$, were used to assess the null hypothesis that upstream concentrations (or temperature) were equal to the downstream concentrations (or temperature) for the given ion, i.e., the difference in concentration will be zero (0). The alternative hypothesis was that the upstream ion concentration was larger than the downstream ion concertation. Statistical analyses were conducted on a complete data set and for the time periods representing the growing season (May–August) and the non-growing season (September–April).

3. Results

Between 29 April 2018, and 19 November 2019, 39 sampling events were completed. Of the 39 sampling events, 21 occurred during the growing season and 18 were completed during the non-growing season. The data that support the findings of this study are openly available (as a csv file) in Faculty Publications–Geography, Geology, and the Environment at https://ir.library.illinoisstate.edu/fpgeo/3 [64].

3.1. Nutrients

Nutrients, nitrate as nitrogen (NO_3-N) and phosphate (PO_4^{3-}) were observed in the Chicago River waters (Figure 3). Upstream of the AFWs, measured NO_3-N concentrations in the surface waters ranged from 2.14 to 10.72 mg/L ($\bar{x}$ = 5.28 mg/L), while concentrations in the surface waters downstream of the AFW ranged from 0.23 to 10.4 mg/L ($\bar{x}$ = 4.92 mg/L). Temporal variation of the concentrations created the range of observed concentrations (Figure S1). For the entire period of study, a significant difference was observed between the upstream ($\bar{x}$ = 5.21 mg/L, SD = 1.76 mg/L) and downstream ($\bar{x}$ = 4.92 mg/L, SD = 1.86 mg/L) surface NO_3-N concentrations; t(41) = 3.08, $p < 0.01$. A significant difference was also noted for 0.3 m depth; the upstream NO_3-N concentrations ($\bar{x}$ = 5.08 mg/L, SD = 1.73 mg/L) were larger than the downstream concentrations ($\bar{x}$ = 4.75 mg/L, SD = 1.77 mg/L); t(30)= 2.09, $p = 0.02$. Statistical differences were also noted between the seasons. For the growing season, the surface NO_3-N concentrations upstream ($\bar{x}$ = 4.53 mg/L, SD = 1.46 mg/L) were greater than the downstream ($\bar{x}$ = 4.22 mg/L, SD = 1.71 mg/L), t(22) = 1.95, $p = 0.03$. The dormant season witnessed higher concentrations entering the AFW at both the surface ($\bar{x}$ = 6.03 mg/L, SD = 1.78 mg/L) and the 0.3 m depth (m = 5.82 mg/L, SD = 1.84 mg/L) than in the waters downstream at surface ($\bar{x}$ = 5.76 mg/L, SD = 1.71 mg/L) and at the 0.3 m depth (m = 5.45 mg/L, SD = 1.58 mg/L), $t_{surface}$ (18) = 4.15, $p < 0.01$ and $t_{0.3\ m}$ (11) = 2.05, $p = 0.03$, respectively.

Phosphate concentrations in the waters entering the garden varied between 1.16 and 9.91 mg/L ($\bar{x}$ = 4.12 mg/L) with the waters exiting the garden having concentrations between BDL and 10.00 mg/L ($\bar{x}$ = 3.89 mg/L). Higher concentrations of phosphate entered the AFW than exited ($\bar{x}_{growing}$ = 2.78 mg/L and $\bar{x}_{dormant}$ = 4.87 mg/L) during both the growing season ($\bar{x}_{growing}$ = 2.95) and the dormant season ($\bar{x}_{dormant}$ = 5.19 mg/L). A statistical difference was observed for only the surface waters during the growing season; concentrations entering the AFW at the surface ($\bar{x}$ = 2.95 mg/L, SD = 1.12 mg/L) were significantly greater than at the downstream surface ($\bar{x}$ = 2.77 mg/L, SD = 1.31 mg/L) $t_{surface}$(20) = 1.85, $p = 0.4$. No other statistically significant differences were observed for phosphate.

3.2. Chloride

Chloride concentrations exhibited strong seasonal variability (Figure 3). During the growing season, upstream surface water concentrations ranged from 54.04 to 190.64 as compared to downstream concentrations between 46.32 and 188.97 mg/L. The dormant season experienced high concentrations, with the upstream waters fluctuating between 47.21 and 296.55 mg/L as compared to the downstream waters ranging between 40.73 to 301.31 mg/L. Statistically significant differences between the upstream waters and the downstream water were observed at the 0.3 m depth for both the dormant season and the collective data. In the dormant season, the 0.3 m upstream concentrations ($\bar{x}$ = 150.93 mg/L, SD = 39.80 mg/L) were higher than the downstream concentrations ($\bar{x}$ = 145.52 mg/L, SD = 45.37 mg/L); t(11) = 2.09, $p = 0.03$. With the data as a whole, the upstream 0.3 m chloride concentrations ($\bar{x}$ = 135.69 mg/L, SD = 37.03 mg/L) were higher than the downstream concentrations ($\bar{x}$ = 129.93 mg/L, SD = 38.67 mg/L); t(30) = 2.28, $p = 0.01$.

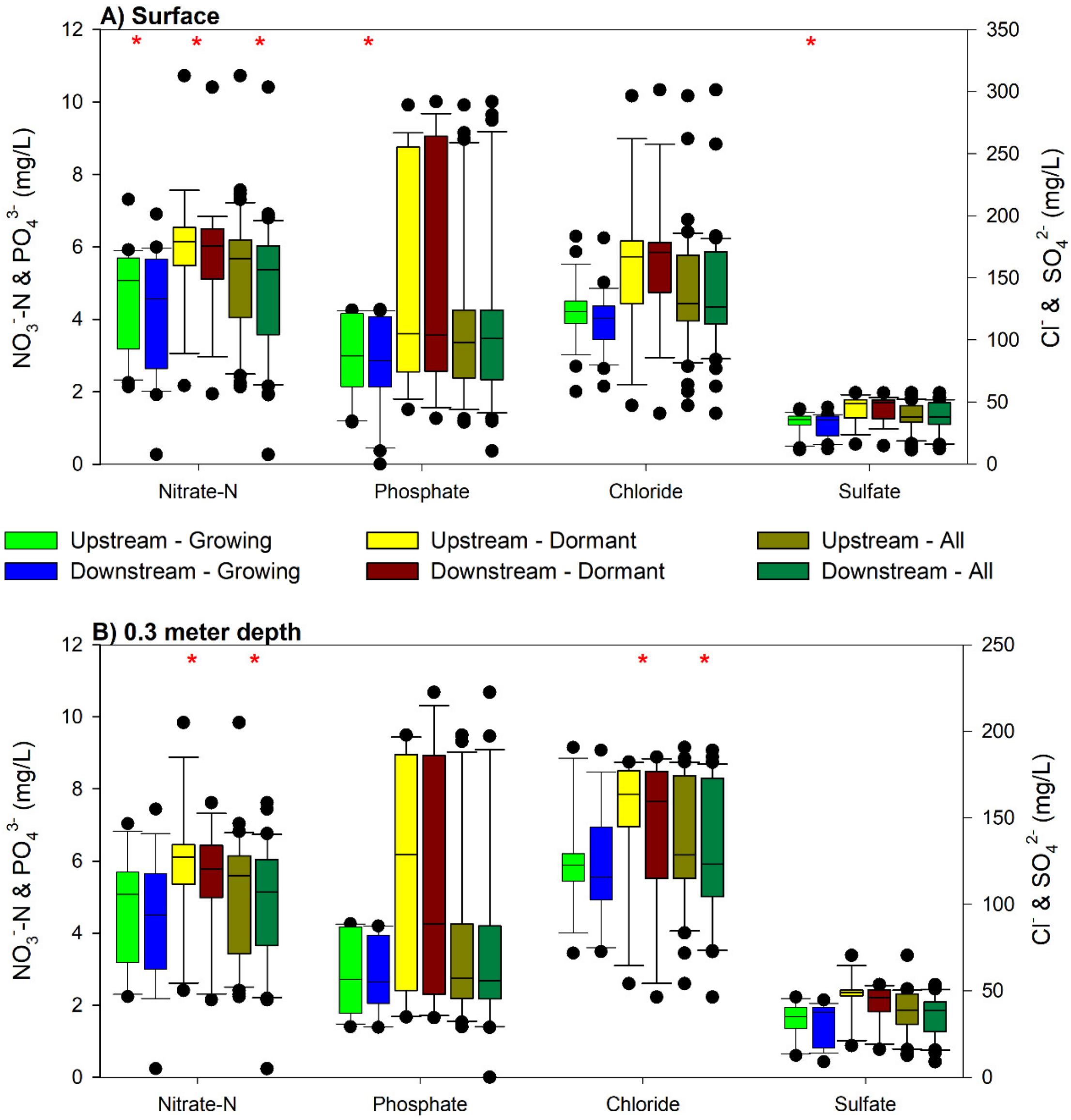

Figure 3. Measured anion concentrations in the waters upstream and downstream of the AFW differentiated by season (growing or dormant) and collectively (all) for (**A**) surface waters and (**B**) waters at a 0.3 m depth. The red asterisk (*) signifies statistically significant differences between the upstream concentration and the downstream concentration for the given anion.

3.3. Heavy Metals

For all of the heavy metals analyzed, we observed BDL concentrations, which were below the United States Environmental Protection Agency (USEPA) maximum contaminant levels (MCL) and the secondary maximum contaminant levels (SMCL) for the metals [65] (Table 2). Thus, the concentrations for Cu, Pb, and Zn detected in this study were lower than what was found by Komínková, et al. [66] at combined sewage overflow sites, which implies that the four CSO locations on the canal are not significantly contributing to heavy metal contamination to this section of the Chicago River. The absence of such metals in the Chicago River could be influenced by the chemistry of the river itself, the chemistry of the individual metals, or the surface area and surface charge of sediments in the river. In the neutral to alkaline waters of the Chicago River, the solubility of metals is low. These metals may precipitate onto either sediments or suspended particles in the water [67], which could help to explain the absence of dissolved phases of the metals in the water. The metal concentrations measured for this work are consistent with those reported by the

Chicago Metropolitan Water Reclamation District (CMWRD). The CMWRD has collected heavy metal and chloride data monthly at locations 3.2 km upstream on the North Branch of the Chicago River and 4.8 km downstream on the South Branch of the Chicago River of the canal. In 2018, monthly heavy metal concentrations for As, Cd, Cr, Cu, Pb, Mn, Se, and Zn were less than 2 μg/L on both the North and South Branches of the Chicago River. The lack of heavy metals in the river water is a positive; however, the role of the AFWs in the concentration of heavy metals at this section of the river could not be assessed.

Table 2. Heavy metal analysis–detection limits of ICP-AES and either the United States Environmental Protection Agency (USEPA) maximum contaminant level (MCL) or secondary maximum contaminant level (SMCL) for each metal [65].

Analyte	ICP-AES Detection Limit	MCL	SMCL
	μg/L	μg/L	μg/L
Al	1		50
As	1	10	
Be	0.09	4	
Cd	0.1	5	
Cr	0.2	100	
Cu	0.4		1300 *
Mn	0.1		50
Pb	1	0	15 *
Se	2	50	
Zn	0.2		500

*—Action level defined by US EPA.

3.4. Dissolved Oxygen

During the growing season, the mean DO concentrations in the surface waters upstream and downstream were 4.09 mg/L (42.6%) and 3.90 mg./L (41.0%), respectively. During the dormant season, the mean upstream and downstream surface water concentrations were 5.68 mg/L (47.3%) and 5.63 mg/L (46.0%), respectively (Figure 4). The results of the paired *t*-test indicate that there were no statistically significant differences in DO concentrations in surface waters upstream as compared to the downstream during either the growing ($p = 0.05$) or dormant ($p = 0.35$) season. At the 0.3 m depth, no significant differences were detected in DO concentration between the upstream ($\bar{x} = 3.68$ mg/L, SD = 0.65 mg/L) and the downstream water ($\bar{x} = 3.33$ mg/L, SD = 1.01 mg/L) during the growing season; $t(18) = 1.36$, $p = 0.10$. Similarly in the dormant season, DO concentration at the 0.3 m depth upstream ($\bar{x} = 5.21$ mg/L, SD = 1.31 mg/L) and downstream ($\bar{x} = 5.14$ mg/L, SD = 1.39 mg/L) were similar: $t(20) = 0.64$, $p = 0.27$.

3.5. Temperature

For the growing season, the mean upstream and downstream surface water temperatures were 22.5 °C and 22.4 °C, respectively. For the dormant season, the upstream and downstream mean temperatures were 11.5 °C and 11.5 °C, respectively (Figure 4). No statistical difference was noted in the surface water temperatures during either season: growing ($p = 0.09$) or dormant ($p = 0.24$). At the 0.3 m depth, the mean temperatures upstream, 22.1 °C, and downstream, 22.1 °C, were not different (=0.36) during the growing season. Similarly, in the dormant season no difference was noted between the mean temperatures upstream, 11.5 °C and downstream, 11.5 °C.

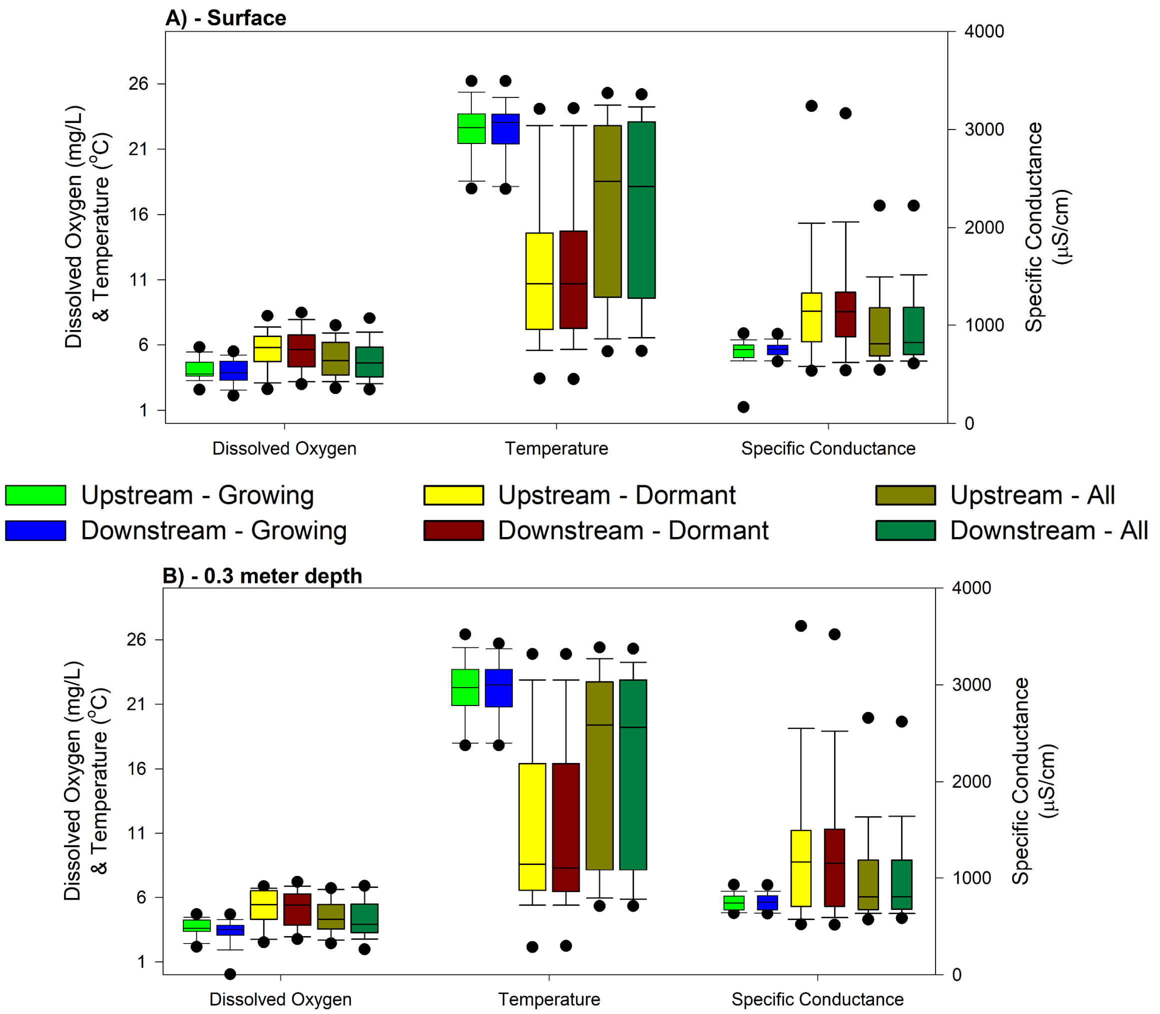

Figure 4. Measured in-situ parameters in the waters upstream and downstream of the AFW presented by season (growing or dormant) and collectively (all) for (**A**) surface waters and (**B**) waters at a 0.3 m depth.

4. Discussion

The importance of plants and photosynthesis to nutrient reduction have been well documented in wetlands [68,69], in the hyporheic zone [70–73], in riparian forests [74–77], and in saturated buffer zones [61,78]. AFWs have been introduced into lake and stream systems to provide aquatic habitat, to enhance the aesthetics of aquatic systems, and to improve water quality [42–45]. The hydroponic nature of the AFWs provides a unique treatment mechanism; the combination of plant uptake and microbial transformations by biofilms on the roots that can contribute to decreases in nutrient concentrations [41–43,47–49]. In an AFW, the structural floating pontoons and plant root systems reduce the velocity of the water, allowing for extended interaction with the roots and the biofilms growing on the roots [47,79,80]. As the AFW matures, an extensive network of roots and attached biofilms develop within the water column [41–43,49].

While the primary purposes of the pilot garden on the Chicago River was to enhance aquatic habitat and the aesthetics of a formerly industrial canal, the presence of the AFW had a positive impact on the water quality. The AFW reduced the nitrate and phosphate concentrations during the growing seasons and the nitrate concentrations during the dormant season. During the growing season, downstream nitrate concentrations in the surface water were 6.9% lower than the upstream concentrations, while the phosphate concentrations were reduced 6.0%. In the dormant season, the waters at 0.3 m exhibited a significant decrease of 6.8% in nitrate, while the loss of nitrate in the surface water was smaller, at 4.2%. The observed reduction rates were much lower than rates observed in other AFW, 36.9% and 64.5% for nitrate and phosphate, respectively [81], but this may be a function of the residence time of the water within the root network of the garden or other factors specific to any study's particular materials and methods. In stream ecosystems, the loss of nitrate via uptake, denitrification, or microbial assimilation is thought to occur disproportionately in zones with long residence times that facilitate contact of reactive solutes with high biotic capacity for biogeochemical processing [82,83].

Despite a surface area of only 90 m^2, the AFWs exhibited the ability to reduce nitrate and phosphate, which can limit eutrophication [52,53]. However, the residence time of the water within the root network is limited, and the footprint of the AFWs was small compared to the volume of water passing through as indicated by the minimal impact on the water temperature and the dissolved oxygen of the waters. Studies in systems with longer residence times for waters in the root system observed decreases in water temperature, up to 2 °C [45,84]. With an average discharge of 0.88 m^3/s and a cross-sectional area of 60 m^2, the velocity for the Chicago River calculates to 0.015 m/s. With a length of 30 m, the waters would interact with the garden a minimum of 2000 s (33.3 min). The calculated residence time is a conservative estimate given that the roots will provide resistance, decreasing the velocity. The velocity coupled with the mass and heat capacity of the water limit the effectiveness of the garden to ameliorate the effects of urban heating on the stream waters. Increasing the size of the AFW would increase the residence time, which would further enhance the nutrient reduction and may allow for enhanced shading to decrease the water temperature.

Seasonally, the difference between upstream and downstream nitrate concentrations in the growing season, 6.8%, was slightly higher than during the dormant season, 4.2%, and a significant difference in phosphate uptake was only noted during the growing season. The higher reduction rates in the summer are consistent with those reported by [81], which they attributed to a combination of plant uptake and denitrification. Studies agree, however, that denitrification and vegetation uptake can occur simultaneously or independently depending on environmental conditions that may change within or between seasons [76,85,86]. However, the concomitant reductions in both nitrate and phosphate coupled with DO concentrations above levels suitable for dentification, suggest plant or microbial uptake as the primary mechanism of nutrient reduction. Seasonal changes in solar radiation influence growth of aquatic plants and algae by controlling photosynthesis [70,71,87]. While photosynthesis creates a complex set of interactions, the highest rates of plant and algal NO_3-assimilation are reported during periods of greater sunlight [61,88], which occur during the growing season. Denitrification is also dependent upon the temperature of the environment [89]. The optimum temperature for denitrification is 30 °C, which was close to the average water temperature in the growing season at the pilot-scale site. Colder temperatures do not preclude denitrification from occurring but do tend to decrease microbial activity [90]. Denitrification has been observed during winter months in soils [75,91,92] and in groundwater [61,85]. The observed losses of nitrate during the dormant season for the AFW suggest that the biofilms on the roots may provide microsites suitable for denitrification despite the DO concentrations above 4.5 mg/L.

Chloride concentrations at the study site did not experience significant changes upstream or downstream during either season. However, seasonal differences were detected with the concentration increasing from 117.9 mg/L to 124.8 mg/L in the growing season to 165.8 mg/L to 171.2 mg/L in the dormant season. Snow events and freezing temperatures occurred during the week of 5 November 2019 and road salt application took place throughout the city, contributing to the seasonal increase in Cl^- concentrations. While some plants may incorporate Cl^- [93], the lack of a significant decrease in Cl^- during the growing season suggests that the plants are not removing the Cl^-. However, the lower Cl^- concentrations observed in the water exiting the AFW in the dormant season indicate some type of uptake is occurring, but the identifying the pathway is beyond the scope of this work.

5. Conclusions

A small, 90 m^2 AFW installed on the Chicago River reduced the concentrations of nitrate by 6.9% and phosphate by 6.0% in the river waters during the growing season. While phosphate was not removed in the dormant season, nitrate and chloride both exhibited reductions in concentration, 6.8% and 3.6%, respectively. The AFW was not effective in regulating the temperature of the water, but this may be a function of limited shading, approximately 30 min, as the waters travel below the garden for approximately 30 min. Despite the primary design of the AFW being to improve the aquatic habitat and the aesthetic, the AFW showed promise in improving water quality.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/hydrology8030115/s1, Figure S1: Time series data for (A) Nitrate as nitrogen, (B) Phosphate, and (C) Chloride.

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