



## Article

# Chemical Fractionation of Sediment Phosphorus in Residential Urban Stormwater Ponds in Florida, USA

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**Abstract:** Stormwater ponds collect and transform pollutants (including nutrients, such as nitrogen and phosphorus) in urban runoff and are often hydrologically connected to downstream waters, making it important to maximize their pollutant retention efficiency. A key mechanism for phosphorus (P) removal in stormwater ponds is sedimentation. However, sediment P in stormwater ponds may be present in several chemical forms with varying bioavailability and potential to move from sediments into the overlying water column. The purpose of this study was to characterize the chemical fractions of sediment P in residential urban stormwater ponds, with the goal of better understanding expected movement of P from sediments to water. We used a chemical fractionation scheme to separate sediment P into the following pools: loosely adsorbed and readily available P, Fe- and Al-bound P, Ca- and Mg-bound P, NaOH-exchangeable organic P, and refractory P. From six stormwater ponds in the Tampa Bay, Florida urban area, we found the pool of readily available P was less than 3% of total sediment P, and the refractory P pool was 28–40% of Total P. However, both Fe/Al-bound and Ca/Mg-bound P each accounted for about 18% of total sediment P. These latter pools may become available under anoxic or low pH (<6) conditions, respectively, demonstrating that a change in environmental conditions could cause internal P loading from sediments to pond water.

**Keywords:** phosphorus fractionation; urban stormwater; stormwater ponds; sediments



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## 1. Introduction

Stormwater ponds collect and convey stormwater and its associated sediment, nutrient, and other pollutant loads. Often, ponds are hydrologically connected to downstream waters, making ponds potential sources of pollutants to receiving waterbodies [1]. Stormwater ponds receive urban runoff from adjacent impervious surfaces and temporarily store the water before gradual discharge to a receiving water body, thus ameliorating the potential harmful effects of rapid pulses of stormwater that may flood urban areas. While stormwater ponds are constructed primarily for flood control, they are often expected to perform some level of pollutant removal as well [2]. Urban runoff contains numerous pollutants, including sediments, heavy metals, pathogens, and nutrients [3–5], and these pollutants can accumulate in stormwater pond water and sediments. If not held by the pond or transformed by processes that utilize and/or remove them (such as denitrification to convert nitrate-nitrogen in water to N<sub>2</sub>O gas that escapes to the atmosphere), these pollutants can move onward to downstream water bodies.

Stormwater ponds are especially susceptible to problems associated with excess nutrient loads [6,7]. As nutrients from urban runoff accumulate in stormwater ponds, it is not uncommon for the ponds to become highly eutrophic and support dense populations of aquatic vegetation and planktonic and filamentous algae. At the same time, these ponds—because they are such common features of urban residential landscapes—are often highly visible to people, sometimes even marketed by real estate agents as water features that increase the property values of nearby homes [8]. Hence, when the ponds become covered with algae or dense aquatic vegetation, homeowners often seek chemical pesticide

treatments to remove the algal growth and restore a “pristine” appearance to the pond water. Treatments such as copper sulfate can be used as algaecides, but these treatments may result in the accumulation of potentially-toxic copper in pond sediments and shoreline vegetation [9].

In Florida, USA, there are an estimated 76,000 stormwater ponds associated with the state’s urban and rapidly urbanizing areas [10]. The state also has hundreds of impaired waterbodies, and excess nutrients—primarily nitrogen (N) and phosphorus (P)—are one of the leading causes of water quality degradation in the state, often leading to harmful algal blooms and fish kills in both coastal and inland waters [11,12]. A growing body of research shows that stormwater ponds offer little protection of downstream waters from the nutrient loads of stormwater because they are poor removers of both N and P [13–17]. Outflows of stormwater ponds were shown in Florida to be one source of N and P loading to streams and other surface waters [13], and watershed-scale implementation of urban stormwater ponds in coastal North Carolina failed to prevent nutrient enrichment of receiving streams [1]. Yazdi et al. [7] reported that a stormwater pond in coastal Virginia reduced P export by only 10% in both cold and warm seasons and was a net N exporter in cold seasons. Likewise, Lusk and Toor, 2016 [14], showed that urban stormwater ponds may be net exporters of dissolved N when particulate organic N from runoff accumulates in pond sediments and is later converted to dissolved inorganic N via mineralization and nitrification.

Understanding the biogeochemical processes that transform N and P is crucial to constraining and predicting the nutrient removal efficacy of urban stormwater ponds. Nitrogen is primarily removed by denitrification, the process by which nitrate is microbially reduced to the N gases NO, N<sub>2</sub>O, and N<sub>2</sub>, which are then lost to the atmosphere. The P cycle, however, has no gaseous component, and P removal in ponds is dependent on adsorption by sediment particles and precipitation. Though there are few studies on P biogeochemistry in urban stormwater ponds, there is general agreement that they are poor sinks for P in urban ecosystems [1,18]. Reasons for stormwater ponds having low retention efficiency of P include release of dissolved P after breakdown of organic P in sediments, as well as variable reactivity of multiple P forms (dissolved vs. particulate and organic vs. inorganic), which limits P immobilization by microbes and its subsequent retention in pond sediments [19,20]. Particulate P, likely associated with soil particles and leaf litter, was the dominant form of water column P in a Virginia stormwater pond [7], but sedimentation processes were insufficient in preventing pond P outflows from being nearly equal to P inflow concentrations. In the Yazdi et al. [7] study, organic matter decomposition and release of dissolved P from sediments offset P removal and sedimentation, leading to a net P removal efficiency of only 10% during warm summer months.

The redox state of the overlying water column is generally thought to be a major driver of internal P loading from pond sediments, with low oxygen conditions at the water–sediment interface often resulting in increased P release from sediments [21]. This is only true, however, when P is bound to Fe in sediments, and other forms of P can be released from sediments regardless of oxygen concentrations in the water column. For example, Frost et al. [22] found that dissolved organic P was highly mobile in stormwater pond sediments and was released to the water column under a wide range of redox conditions. In the Frost et al. [22] study and others by Song et al. [23,24], it was found that the dissolved organic P (DOP) fraction of stormwater ponds was mostly made up of phosphodiester compounds, which were also shown to be readily released from stormwater pond sediments under a variety of redox conditions. In this case, ameliorating low-oxygen conditions through pond additions such as aerators may be insufficient to avoid release of P from organic sediments. Therefore, management practices such as pond aerators that attempt to eliminate P release from sediments by keeping the water column well-oxygenated may have variable efficacy, ranging from low if appreciable levels of pond P are in organic forms but likely higher if there is a large pool of Fe-bound P.

In addition to having different levels of expected mobility, the various P forms also have different expected lability. Inorganic P extracted with a 1 M KCl solution represents the most labile P fraction, followed in order by Fe- and Al-bound inorganic P, Ca- and Mg-bound inorganic P, and then refractory P often referred to as residual P and that is held to not be bioavailable [25]. There is also a fraction of organic P associated with humic and fulvic acids that is reported to have variable lability [24,25]. Given that the different forms of sediment P vary in mobility and lability, it is clear that simply measuring Total P (TP) in pond sediments will be a poor predictor of P mobility and microbial utilization in stormwater ponds. We need more detailed investigations that fractionate sediment P into inorganic and organic forms if we are to better predict and manage the internal loading of P within the ponds. The objective of this paper is to identify the chemical fractions of P in six stormwater ponds in an urban residential area, with the goal of inferring P mobility and lability in the ponds. We use a P fractionation scheme outlined by Richardson and Reddy [26] to separate sediment P into operationally-defined forms, including (i) labile inorganic P, which is loosely absorbed; (ii) Fe- and Al-bound inorganic P; (iii) Ca- and Mg-bound inorganic P; (iv) alkali-extractable organic P associated with humic and fulvic acids; and (v) residual organic P. From a large body of work characterizing sediment P fractions in wetlands and natural ponds as well as a growing body of work doing the same for stormwater ponds, we compare what is known about the above P fractions to our data. We present the results of the sediment P fractionation and discuss the implications for P mobility in stormwater ponds and potential availability of P in the ponds for water quality deterioration through algal proliferation.

## 2. Materials and Methods

We selected 6 stormwater ponds in a residential neighborhood in Pasco County, Florida, which is part of the Tampa Bay metropolitan area (Figure 1). The neighborhood and its stormwater ponds were constructed in the 1980s to late 1990s. The region is characterized by a subtropical climate, with a distinct wet season from June to September every year, followed by an October to May dry season. Our samples were collected in October, and weather data showed that no rainfall (and hence no stormwater runoff) had entered the ponds for 14 consecutive days. Total annual rainfall in the study area is approximately 140 cm, with about 60% of that occurring in the annual wet season. We used aerial photographs of the neighborhood and the i-Tree Canopy tool (itreetools.org accessed on 3 October 2019) to determine that tree canopy coverage in the neighborhood is 63%, with the dominant tree type being southern live oak (*Quercus virginiana*). The neighborhood has >40% impervious cover.



**Figure 1.** Location of ponds A–F in the study neighborhood, in Pasco County, Florida, USA.

The stormwater ponds are designed as wet detention ponds, or permanently wet basins that collect and store runoff until a threshold volume is reached, after which pond overflows are directed via a network of pipes to Cypress Creek, a tributary of the Hillsborough River and part of the Tampa Bay watershed. Runoff enters the ponds via concrete culverts that collect runoff from curb inlets throughout neighborhood streets. All of the ponds are similar in design and shape, with no forebays for sediment trapping and no pond aerators. They are relatively shallow (<2 m) and surrounded by turfgrass lawns (Figure 1, Table 1).

**Table 1.** Pond morphological features and water chemistry at time of sampling.

Pond ID	Pond Morphology			Mean Surface Water Chemistry	
	Area, m <sup>2</sup>	Year Constructed (Age at Sampling)	Depth, m	pH	Surface DO (% Saturation)
A	1796	1999 (20)	1.2	8.3	72
B	3882	1999 (20)	1.8	8.3	88
C	2801	1999 (20)	1.8	7.9	69
D	5662	1987 (31)	2.0	7.7	101
E	4423	1987 (31)	1.8	7.6	73
F	8284	1987 (31)	1.4	7.8	86

### 2.1. Sediment and Water Sampling

At each of the 6 ponds, we collected 3 water and sediment samples in October 2019. The samples were taken at random locations within 0.9 m of the pond inflows. These sampling points near pond inflows represent areas where runoff converges and where we expect to have the greatest accumulation of sediments. Water samples were collected into 250 mL HDPE bottles, and then placed in ice for immediate transport back to the lab, where they were analyzed for TP and orthophosphate (OP) within 24 h by US EPA Method 365.1. In brief, 2 subsamples of the unfiltered water were used. The first subsample was reacted with ascorbic acid and ammonium molybdate to produce a blue color, which was then analyzed calorimetrically for OP concentration in the water. The second subsample was digested to convert all P forms in the water (including condensed phosphate and organic phosphate) to orthophosphate, followed by analysis for OP by the ascorbic acid method above. Measurements of water pH, dissolved oxygen (DO), and electrical conductivity (EC) were taken in situ at the time of sampling with a YSI multimeter probe. Sediment samples were collected at a depth of 0 to 15 cm, placed in plastic bags with the floodwater to maintain anaerobic conditions, stored at 4 °C, and analyzed for sediment P fractions within 15 days.

### 2.2. Stormwater Pond P Fractionation Analysis

P forms were measured by a sequential fractionation scheme that involved extraction of field wet soils with KCl, followed by NaOH and then HCl at a soil:solution ratio of 1:100 (*w/v* basis). In this procedure, 0.2 g dry-weight equivalent soil was extracted with 1 M KCl over a period of 2 h and with continuous shaking on a mechanical shaker. The solution was then filtered through a 0.45 µm filter paper and the filtrate acidified to pH <2 and analyzed for soluble reactive P (SRP) via US EPA Method 365.1, and the result represents inorganic P extracted by KCl (KCl-Pi).

After extraction with 1 M KCl, the residual soil was next extracted with 0.1 M NaOH over a period of 17 h and continuous shaking on a mechanical shaker. The solution was then filtered as above and analyzed for SRP and TP by EPA Method 365.1. In this part of the fractionation, the SRP represents NaOH-extractable inorganic P (NaOH-Pi). The TP accounted for in this step is notated as NaOH-TP. The difference between NaOH-TP and NaOH-Pi is assumed to be organic P associated with humic and fulvic acids (NaOH-Po).

Next, the residual soil left over from the above step was extracted with 0.5 M HCl over a period of 24 h and filtered and analyzed as above for SRP. This fraction represents

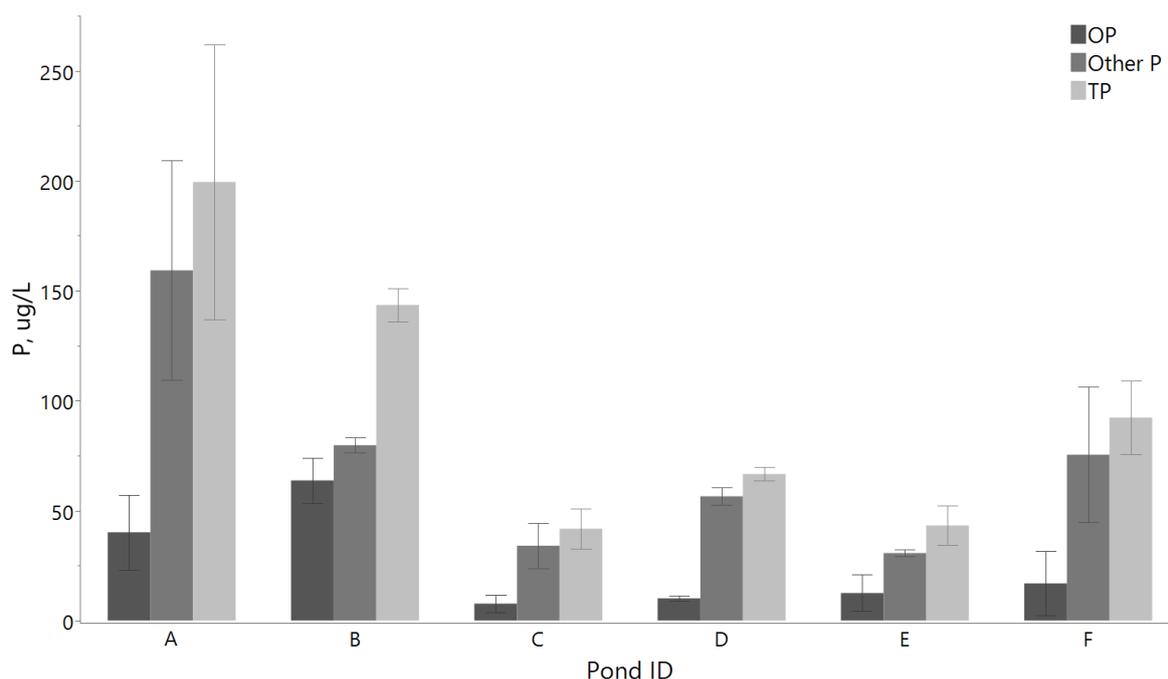
the inorganic P extracted by HCl (HCl-Pi), which is assumed to be Ca- and Mg-bound P. The residual soil left after HCl extraction was combusted at 550 °C for 4 h, after which the ash was dissolved in 6 M HCl to obtain the residual P fraction by EPA Method 365.4. This final fraction is notated as Residue P and is taken to be the organic refractory P pool.

Total inorganic P was taken as the sum of KCl-Pi + NaOH-Pi + HCl-Pi. Total organic P was taken as the sum of NaOH-Po + Residue P.

### 3. Results and Discussion

#### 3.1. Pond Water Column Phosphorus

Across all six stormwater ponds, water column TP ranged from 24.3 to 306.7  $\mu\text{g L}^{-1}$  (Figure 2; Table S1 see the Supplementary Materials). Water column OP across the six ponds ranged from 1.8 to 84.4  $\mu\text{g L}^{-1}$  (Figure 2). While Ponds A and B had the highest P concentrations in their water columns, it was beyond the scope of this study to investigate the mechanistic reasons for the observed variability in dissolved water column P concentrations among ponds. Differences among ponds in TP concentrations could reflect differences in incoming stormwater, different P fractions in sediments, and/or differences in pond structural features that could affect water residence time and phosphorus settling. We expect that stormwater entering all ponds was similar, as the ponds all collected water from similar residential areas, but we did not test this assumption. Likewise, the ponds had similar sizes and shapes, so we do not expect that pond morphology played a large role in supporting different water column P concentrations among ponds.

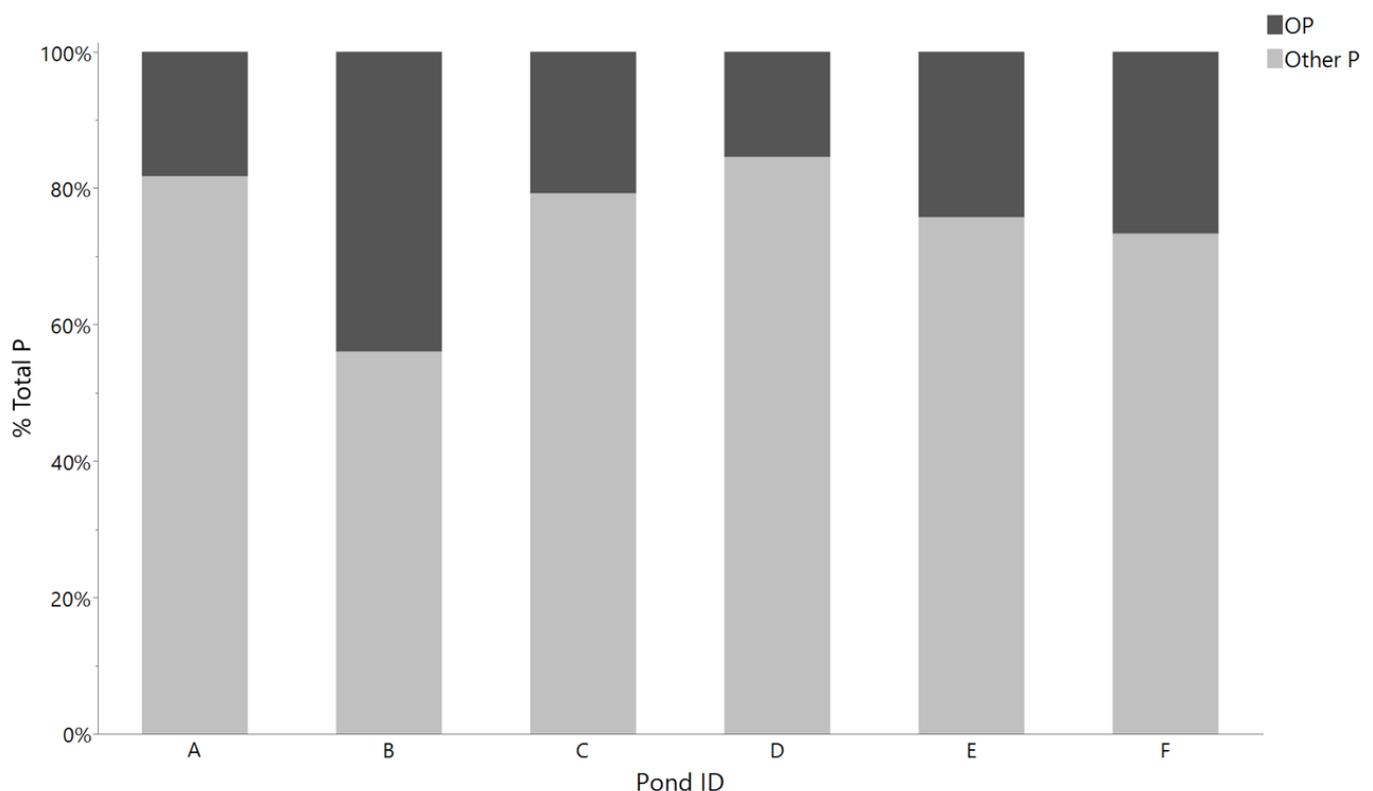


**Figure 2.** Mean and standard errors for orthophosphate (OP), Other P, and Total P (TP) in the water columns of stormwater ponds A–F.

The TP concentrations in this study are in line with the low end of pond TP concentrations in another study in Virginia, where TP concentrations in a stormwater pond measured regularly over 1 year ranged from 200 to > 600  $\mu\text{g L}^{-1}$  [7]. Values for TP and OP concentrations in our study's ponds, however, are lower than mean concentrations in residential urban runoff in another Florida study [27], where mean runoff TP and OP were 430 and 250  $\mu\text{g L}^{-1}$ , respectively. In other US studies, TP in urban runoff has been reported in a similar range of 320 to 370  $\mu\text{g L}^{-1}$  [3]. We expect these runoff TP concentrations are indicative of expected runoff in our study area, since we were focused on an urban residential area in the same geographic setting as the aforementioned Florida study [27]. In

this way, the lower P concentrations in the stormwater ponds of our study may be due to settling of particulate P in stormwater runoff and an indication that this particulate P was not driving internal dissolved OP production at least during our sampling time (October 2019). Anecdotally, we did observe sediment accumulating in the neighborhood stormwater curbs leading to the ponds in this study. These sediments came from lawns with bare patches of exposed soil due to poor turfgrass quality and likely carried appreciable loads of particulate P to the stormwater ponds [28,29]. The observation that P concentrations in our study's ponds were likely lower than those in runoff and the observation that there was a large pool of refractory P in our pond's sediments (see sediment discussion, below) leads us to hypothesize that for this study area and time, an appreciable pool of the runoff P was retained in pond sediments.

In all ponds, the water column TP was mostly made up of "Other P," or non-orthophosphate molecules including condensed phosphates and organic phosphate (Figure 3). The mean OP fraction ranged from 20 to 45% of water column TP in the six ponds (Figure 3). Orthophosphate is the most biologically available P form in aquatic systems and has been linked to rapid algal growth in numerous freshwater bodies [30]. Sources of OP to urban stormwater and stormwater ponds include soils, organic matter, turfgrass fertilizers, and internal release from sediments. In our study area (Pasco County, FL, USA), P-bearing fertilizers are not recommended for turfgrass because soils are naturally P-rich [31], and P-bearing turfgrass fertilizers are not readily available to homeowners because they are not sold in the area. Therefore, OP pools in the water of our study ponds are most likely derived from sediments, soils and organic matter mineralization during the breakdown of materials such as leaves and grass clippings that were mobilized by stormwater runoff [27].



**Figure 3.** Mean proportions of orthophosphate (OP) and Other P in the Total P pools of water columns for ponds A–F.

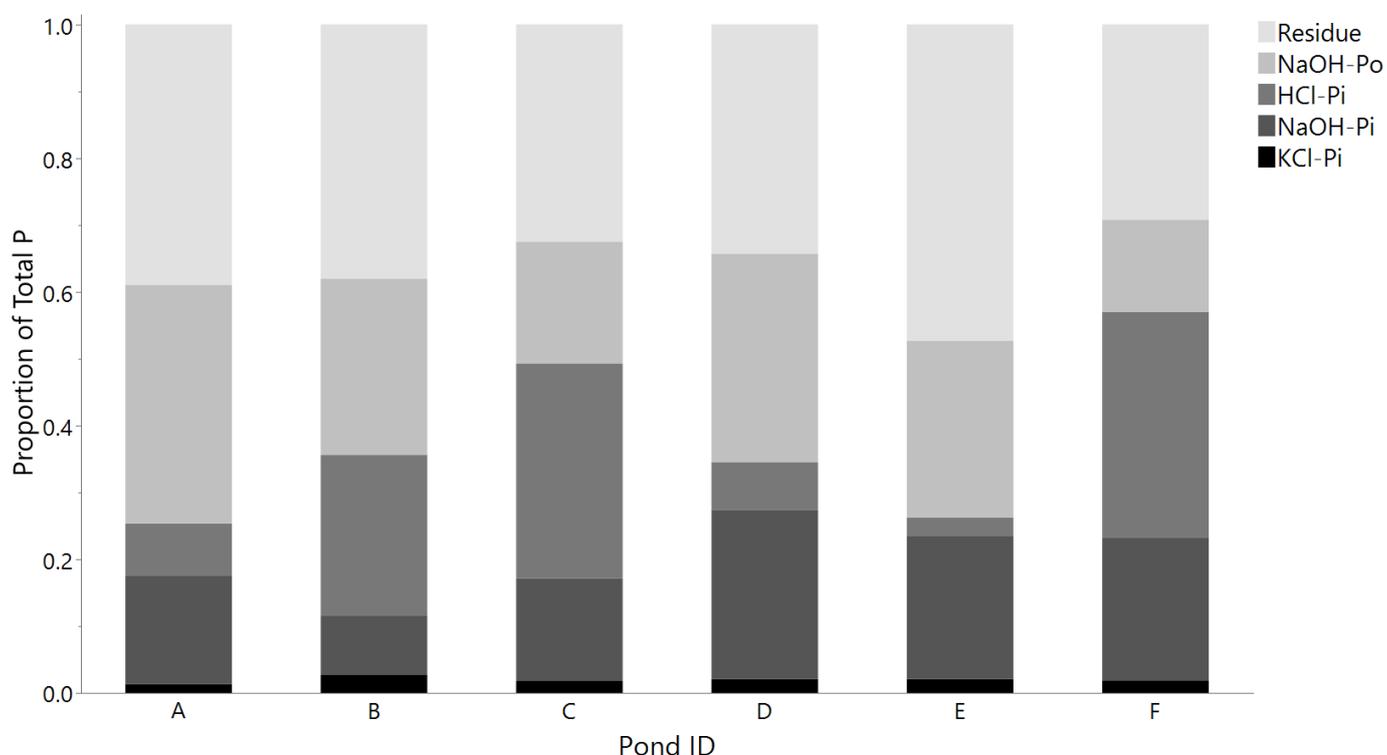
### 3.2. Phosphorus Fractions in Stormwater Pond Sediments

The fractionation scheme used in this study identified the following pools of inorganic P in stormwater pond sediments: (i) labile P, (ii) Fe- and Al-bound P, and (iii) Ca- and Mg-bound P. The sediment P fraction that is extracted by 1 M KCl is the labile, or readily

bioavailable P. It is loosely adsorbed P that can be released to the overlying water column or the P in interstitial waters [24,32]. The KCl-Pi fraction (labile P) was consistently the smallest of all sediment P fractions in this study's ponds (Table 2, Figure 4), making up only 1 to 3% of the sediment TP. This is in line with Frost et al. [22] and Song et al. [24] who also observed that the labile sediment P pool was smaller than other sediment P fractions in stormwater ponds. Although this fraction was relatively small, it does indicate that there is some sediment P that will contribute to water column P in these ponds.

**Table 2.** Mean ( $\pm$ standard deviation) pools of P in the top 15 cm of sediment from stormwater ponds A–F.

P Forms	A	B	C	D	E	F
$\text{mg kg}^{-1}$						
Inorganic P						
KCl-Pi (labile P)	0.99 (0.42)	2.01 (0.57)	1.79 (0.93)	2.70 (2.3)	1.38 (0.25)	2.18 (0.69)
NaOH-Pi (Fe/Al P)	12.53 (1.3)	6.28 (0.72)	15.37 (6.8)	27.88 (9.2)	14.18 (3.3)	26.56 (2.4)
HCl-Pi (Ca/Mg P)	6.05 (1.0)	26.9 (32.8)	65.1 (94.4)	12.6 (17.5)	1.94 (1.2)	57.2 (44.7)
Total Pi	19.57 (2.2)	32.3 (32.9)	82.2 (92.5)	43.2 (28.4)	17.49 (2.5)	85.9 (43.0)
Organic P						
NaOH-Po	28.27 (7.3)	17.91 (3.7)	18.00 (5.6)	40.2 (28.8)	18.28 (6.6)	19.98 (7.7)
Residue P	30.54 (3.6)	32.1 (15.2)	34.9 (14.6)	41.1 (22.4)	31.98 (2.1)	42.0 (15.2)
Total Po	58.8 (11.0)	50.0 (11.6)	52.9 (20.0)	81.3 (51.3)	50.3 (8.7)	62.0 (22.3)
Total P	78.4 (10.2)	85.3 (41.5)	135 (96.6)	125 (79.7)	67.8 (6.2)	148 (65.0)



**Figure 4.** Proportions of the chemical P fractions in sediments of stormwater ponds A–F.

The sediment P fraction that is extracted by 0.1 M NaOH is Fe- and Al-bound inorganic P [33]. The mean Fe/Al-P across all ponds was  $17.1 \text{ mg kg}^{-1}$  and ranged from 6.3 to  $27.9 \text{ mg kg}^{-1}$  (Table 2). The sediment P fraction extracted by 0.5 M HCl is the Ca- and

Mg-bound inorganic P (Table 2). The mean Ca/Mg-P across all ponds was  $28.3 \text{ mg kg}^{-1}$  and ranged from 1.9 to  $65.1 \text{ mg kg}^{-1}$  (Table 2). The Fe/Al-P and Ca/Mg-P each contributed approximately 10–30% of TP in pond sediments (Figure 4). Of these two fractions, the Fe/Al-P is generally held to be the more available [26], but the release of any P in this fraction associated with Fe minerals is dependent on redox conditions. Inorganic P in sediments can be readily sorbed to iron hydroxide ( $\text{FeOH}_3$ ) in aquatic sediment under aerobic conditions. When pond sediments become anoxic, iron III is reduced to iron II, increasing its solubility and releasing inorganic P sorbed to  $\text{FeOH}_3$  [34].

The Ca/Mg-P fraction was consistently the largest inorganic P fraction in pond sediments (Figure 4). The HCl-Pi fraction was likely associated with Ca that entered pond sediments from erosion of the concrete culverts that deliver stormwater to the ponds. Though we did not measure Ca in our samples, another concomitant study in the same neighborhood confirmed that Ca is being transported by neighborhood stormwater infrastructure [35], and other researchers have noted that concrete stormwater infrastructure can contribute Ca ions to stormwater flows [36,37]. The Ca potentially contributed by concrete infrastructure may accumulate in stormwater ponds and retain some fraction of incoming P. This Ca-bound P fraction is expected to remain relatively immobile as long as pond pH is not acidic. At pH values less than about 6.0, Ca/Mg-P is likely released to the overlying water column [38]. It should be noted that our sediment samples were all taken within 0.9 m of the inflow pipes to the stormwater ponds, where deposition of Ca-enriched stormwater would be highest. Therefore, it is likely that sediment samples taken farther away from the pond inflows may have lower relative amounts of Ca/Mg-P. In treatment wetlands, Ca/Mg-P has been shown to decrease with distance from incoming drainage water that contained Ca and Mg in addition to P [39]. It was beyond the scope of our study to investigate spatial gradients in sediment P fractions within the ponds, but future studies on this would aid in better constraining expected P mobility from large ponds or those with forebays that encourage initial sedimentation.

Total organic P in pond sediments is the sum of NaOH-Po and the Residue P. Combined, these two organic forms were the dominant P form in pond sediments (Table 2, Figure 4). Consistent with our data here, Frost et al. [22] also observed that organic and Ca-bound P were the dominant sediment fractions for stormwater ponds in Ontario, Canada. The high proportion of organic P in sediments indicates that P-rich organic matter is entering and accumulating in the stormwater ponds in this study. Sources of this organic matter include urban grass clippings and leaf litter, which were observed collecting on neighborhood streets and that have been shown to carry appreciable loads of P [40]. In this way, urban stormwater ponds are in contrast to natural lakes, where labile inorganic and Fe-bound P usually dominate over organic forms of P [41]. Urban stormwater ponds in a Minnesota, USA study also had surface sediments dominated by labile organic P, which likely played a role in those ponds having high levels of OP in the water columns [42]. Of total organic P in our study, however, about 40% or more of it was made up of Residue P, which is generally held to be refractory P not readily bioavailable [26]. The remainder of the organic P was made up of NaOH-Po, which is P bound to humic substances and its relative stability is understudied but likely variable [39].

### 3.3. Implications for Stormwater Monitoring and Management

Stormwater ponds can be thought of as junctions in the built environment that connect urban landscapes to natural downstream waterbodies. They collect runoff and transform its chemical constituents before its eventual conveyance via piped infrastructure to a receiving stream, creek, or other body of water. They are only protective of downstream water quality inasmuch as they are sinks for runoff pollutants. For nutrients, including P, stormwater ponds often have limited performance as sinks and may instead be transformers that merely alter the chemical forms of N and P before downstream conveyance [14]. The Residue P fraction in this study's ponds was nearly half or more of all sediment P (Figure 4) and represents a refractory pool of P unlikely to move into the water column. However,

the remaining sediment P pools in these ponds are in forms that have varying expected lability. This means that there is some pool of labile P that can move from sediments to the water column, reducing the efficiency of these ponds as P removers. A key implication of this is that management practices aimed at reducing P inputs into the ponds may not result in immediate improvements in water quality, if internal P loading from sediments keeps a supply of dissolved P moving from sediments to the overlying water [42]. If released P is bioavailable, it may be removed from the ponds by microbial communities and subsequently deposited back into sediments. However, in this study, the sediment P fraction with the highest expected bioavailability (KCl-Pi) was less than 3% of total sediment P. A larger fraction of NaOH-Po is present in all ponds in this study, and this organic P form has expected lower bioavailability and microbial utilization than inorganic sediment P, meaning that its release from sediment may increase P concentrations in the water column and increase P export from the ponds. In this way, the ponds cannot be thought of as simply “black boxes” that retain P loads from the watershed. Instead, we must consider that the various chemical fractions of P demonstrated here mean that internal loading and variable microbial utilization of dissolved P from the sediments is possible.

A second key implication of this work comes from the fact that sediment P was found in multiple chemical forms known to be affected by environmental conditions such as oxygen status at the sediment/water interface and pH. A change in either of these could result in release of sediment Fe/Al-P or Ca/Mg-P. In our study area, which has a subtropical climate, heavy summer rains often drive high levels of organic matter into stormwater ponds. As this organic material decomposes and consumes oxygen during the summer rainy season, ponds may become anoxic, which could promote the release of Fe-bound NaOH-Pi. On the other hand, adding pond management features such as an aerator could reduce the release of Fe-bound NaOH-Pi by keeping the pond well-oxygenated. However, given that Fe-bound P in our study was less than 20% it is unclear how much this pool may actually contribute to pond water columns. In addition, any environmental change that lowers the pH of the pond sediments could promote release of Ca- and Mg-bound HCl-Pi. Release of Ca- and Mg-bound P can occur when sediment pH drops  $< 6$  [43] but may not be a realistic concern for stormwater ponds that receive primarily residential runoff from calcareous (concrete) urban surfaces.

Our study was conducted in Florida, where a sub-tropical climate results in a distinct wet and dry season and seasonal variations in stormwater flows to ponds. Future research should examine P fractions in stormwater ponds of other climates and other hydrological and temperature conditions not observed in this study. Future work should also focus on the mechanistic drivers of P forms and concentrations in stormwater pond water columns and investigate relationships between this and sediment P fractions under a variety of environmental conditions. For example, we observed variability in P concentration among pond water columns, and future work could more closely investigate how properties such as pH and redox could be driving variable P release from pond sediments. Finally, we also recommend future study on spatial gradients in P fractionation in stormwater ponds. Our study focused only on sediments accumulated at pond inlets, but future work should characterize sedimentation gradients within ponds to assess overall P variability.

#### 4. Conclusions

Stormwater ponds are a type of stormwater control measure aimed at mitigating floods associated with urban runoff and are often expected to also perform some level of pollutant removal role. Because stormwater ponds are increasingly being found to have limited capacity to remove nutrient pollution from stormwater, it is important to identify the biogeochemical processes that transform and convey N and P in urban stormwater ponds. This study is important because it demonstrates that P in stormwater sediments was in multiple chemical forms with different expected lability and potential to move into the water column, especially if environmental conditions change such as during heavy summer rains that cause anoxic conditions and the release of Fe-bound P from sediments.

We recommend future studies that characterize the chemical fractions of P in stormwater sediment over different seasons or across different spatial scales, as well as studies that connect sediment P chemistry in stormwater ponds to downstream water quality.

**Supplementary Materials:** The following are available online at <https://www.mdpi.com/article/10.3390/urbansci5040081/s1>, Table S1: Raw Data.

**Author Contributions:** M.G.L.: conceptualization, data curation, formal analysis, funding acquisition, methodology, project administration, writing—original draft; K.C.: data curation, investigation, visualization, writing—review and editing. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

## References

- Gold, A.; Thompson, S.; Piehler, M. Water quality before and after watershed-scale implementation of stormwater wet ponds in the coastal plain. *Ecol. Eng.* **2017**, *105*, 240–251. [[CrossRef](#)]
- Collins, K.A.; Lawrence, T.J.; Stander, E.K.; Jontos, R.J.; Kaushal, S.S.; Newcomer-Johnson, T.; Grimm, N.B.; Ekberg, M.L.C. Opportunities and challenges for managing nitrogen in urban stormwater: A review and synthesis. *Ecol. Eng.* **2010**, *36*, 1507–1519. [[CrossRef](#)]
- Yang, Y.-Y.; Lusk, M.G. Nutrients in Urban Stormwater Runoff: Current State of the Science and Potential Mitigation Options. *Curr. Pollut. Rep.* **2018**, *4*, 112–127. [[CrossRef](#)]
- Sidhu, J.; Hodgers, L.; Ahmed, W.; Chong, M.; Toze, S. Prevalence of human pathogens and indicators in storm-water runoff in Brisbane, Australia. *Water Res.* **2012**, *46*, 6652–6660. [[CrossRef](#)] [[PubMed](#)]
- Brown, J.N.; Peake, B.M. Sources of heavy metals and polycyclic aromatic hydrocarbons in urban stormwater runoff. *Sci. Total Environ.* **2006**, *359*, 145–155. [[CrossRef](#)] [[PubMed](#)]
- Jani, J.; Lusk, M.G.; Yang, Y.-Y.; Toor, G.S. Wet season nitrogen export from a residential stormwater pond. *PLoS ONE* **2020**, *15*, e0230908. [[CrossRef](#)] [[PubMed](#)]
- Yazdi, M.N.; Scott, D.; Sample, D.J.; Wang, X. Efficacy of a retention pond in treating stormwater nutrients and sediment. *J. Clean. Prod.* **2021**, *290*, 125787. [[CrossRef](#)]
- Persaud, A.; Alsharif, K.; Monaghan, P.; Akiwumi, F.; Morera, M.C.; Ott, E. Landscaping practices, community perceptions, and social indicators for stormwater nonpoint source pollution management. *Sustain. Cities Soc.* **2016**, *27*, 377–385. [[CrossRef](#)]
- Lusk, M.G.; Chapman, K. Copper concentration data for water, sediments, and vegetation of urban stormwater ponds treated with copper sulfate algaecide. *Data Brief* **2020**, *31*, 105982. [[CrossRef](#)]
- Sinclair, J.S.; Reisinger, A.J.; Bean, E.; Adams, C.R.; Reisinger, L.S.; Iannone, B.V., III. Stormwater ponds: An overlooked but plentiful urban designer ecosystem provides invasive plant habitat in a subtropical region (Florida, USA). *Sci. Total Environ.* **2020**, *711*, 135133. [[CrossRef](#)] [[PubMed](#)]
- Phlips, E.J.; Badylak, S.; Nelson, N.G.; Havens, K.E. Hurricanes, El Niño and harmful algal blooms in two sub-tropical Florida estuaries: Direct and indirect impacts. *Sci. Rep.* **2020**, *10*, 1–12. [[CrossRef](#)]
- Accoroni, S.; Totti, C.; Romagnoli, T.; Giulietti, S.; Glibert, P.M. Distribution and potential toxicity of benthic harmful dinoflagellates in waters of Florida Bay and the Florida Keys. *Mar. Environ. Res.* **2020**, *155*, 104891. [[CrossRef](#)]
- Harper, H.H.; Baker, D.M. *Evaluation of Current Stormwater Design Criteria within the State of Florida*; Environmental Research & Design, Inc.: Orlando, FL, USA, 2007.
- Lusk, M.G.; Toor, G.S. Biodegradability and Molecular Composition of Dissolved Organic Nitrogen in Urban Stormwater Runoff and Outflow Water from a Stormwater Retention Pond. *Environ. Sci. Technol.* **2016**, *50*, 3391–3398. [[CrossRef](#)] [[PubMed](#)]
- Gold, A.C.; Thompson, S.P.; Piehler, M.F. Nitrogen cycling processes within stormwater control measures: A re-view and call for research. *Water Res.* **2019**, *149*, 578–587. [[CrossRef](#)] [[PubMed](#)]
- Williams, C.J.; Frost, P.C.; Xenopoulos, M.A. Beyond best management practices: Pelagic biogeochemical dynamics in urban stormwater ponds. *Ecol. Appl.* **2013**, *23*, 1384–1395. [[CrossRef](#)] [[PubMed](#)]

17. Rosenzweig, B.R.; Smith, J.A.; Baeck, M.L.; Jaffe, P.R. Monitoring Nitrogen Loading and Retention in an urban stormwater Detention Pond. *J. Environmental Qual.* **2011**, *40*, 598–609. [[CrossRef](#)] [[PubMed](#)]
18. Sønderup, M.J.; Egemose, S.; Hansen, A.S.; Grudinina, A.; Madsen, M.H.; Flindt, M.R. Factors affecting retention of nutrients and organic matter in stormwater ponds. *Ecology* **2016**, *9*, 796–806. [[CrossRef](#)]
19. Sinke, A.J.C.; Cornelese, A.A.; Keizer, P.; VAN Tongeren, O.F.R.; Cappenberg, T.E. Mineralization, pore water chemistry and phosphorus release from peaty sediments in the eutrophic Loosdrecht lakes, The Netherlands. *Freshw. Biol.* **1990**, *23*, 587–599. [[CrossRef](#)]
20. Song, K.; Burgin, A.J. Perpetual Phosphorus Cycling: Eutrophication Amplifies Biological Control on Internal Phosphorus Loading in Agricultural Reservoirs. *Ecosystems* **2017**, *20*, 1483–1493. [[CrossRef](#)]
21. Duan, S.; Newcomer-Johnson, T.; Mayer, P.; Kaushal, S. Phosphorus Retention in Stormwater Control Structures across Streamflow in Urban and Suburban Watersheds. *Water* **2016**, *8*, 390. [[CrossRef](#)]
22. Frost, P.C.; Prater, C.; Scott, A.B.; Song, K.; Xenopoulos, M.A. Mobility and Bioavailability of Sediment Phosphorus in Urban Stormwater Ponds. *Water Resour. Res.* **2019**, *55*, 3680–3688. [[CrossRef](#)]
23. Song, K.; Xenopoulos, M.A.; Marsalek, J.; Frost, P.C. The fingerprints of urban nutrients: Dynamics of phosphorus speciation in water flowing through developed landscapes. *Biogeochemistry* **2015**, *125*, 1–10. [[CrossRef](#)]
24. Song, K.; Winters, C.; Xenopoulos, M.A.; Marsalek, J.; Frost, P.C. Phosphorus cycling in urban aquatic ecosystems: Connecting biological processes and water chemistry to sediment P fractions in urban stormwater management ponds. *Biogeochemistry* **2017**, *132*, 203–212. [[CrossRef](#)]
25. Cavalcante, H.; Araújo, F.; Noyma, N.; Becker, V. Phosphorus fractionation in sediments of tropical semi-arid reservoirs. *Sci. Total Environ.* **2018**, *619*, 1022–1029. [[CrossRef](#)]
26. Richardson, C.J.; Reddy, K. Methods for Soil Phosphorus Characterization and Analysis of Wetland Soils. *Methods Biogeochem. Wetl.* **2013**, *10*, 603–638. [[CrossRef](#)]
27. Yang, Y.-Y.; Toor, G.S. Sources and mechanisms of nitrate and orthophosphate transport in urban stormwater runoff from residential catchments. *Water Res.* **2017**, *112*, 176–184. [[CrossRef](#)]
28. Ma, J.; Ying, G.; Sansalone, J.J. Transport and distribution of particulate matter phosphorus fractions in rain-fall-runoff from roadway source areas. *J. Environ. Eng.* **2010**, *136*, 1197–1205. [[CrossRef](#)]
29. Arias, M.E.; Brown, M.T.; Sansalone, J.J. Characterization of Storm Water–Suspended Sediments and Phosphorus in an Urban Catchment in Florida. *J. Environ. Eng.* **2013**, *139*, 277–288. [[CrossRef](#)]
30. Harrison, J.A.; Bouwman, A.; Mayorga, E.; Seitzinger, S. Magnitudes and sources of dissolved inorganic phosphorus inputs to surface fresh waters and the coastal zone: A new global model. *Glob. Biogeochem. Cycles* **2010**, *24*. [[CrossRef](#)]
31. Badruzzaman, M.; Pinzon, J.; Oppenheimer, J.; Jacangelo, J.G. Sources of nutrients impacting surface waters in Florida: A review. *J. Environ. Manag.* **2012**, *109*, 80–92. [[CrossRef](#)] [[PubMed](#)]
32. Fytianos, K.; Kotzakioti, A. Sequential fractionation of phosphorus in lake sediments of Northern Greece. *Environ. Monit. Assess.* **2005**, *100*, 191–200. [[CrossRef](#)]
33. Olila, O.; Reddy, K.; Harris, W. Forms and distribution of inorganic phosphorus in sediments of two shallow eutrophic lakes in Florida. *Hydrobiologia* **1995**, *302*, 147–161. [[CrossRef](#)]
34. Amirbahman, A.; Lake, B.A.; Norton, S.A. Seasonal phosphorus dynamics in the surficial sediment of two shallow temperate lakes: A solid-phase and pore-water study. *Hydrobiologia* **2013**, *701*, 65–77. [[CrossRef](#)]
35. Si, Q.; Lusk, M.; Inglett, P. Inorganic Nitrogen Production and Removal along the Sediment Gradient of a Stormwater Infiltration Basin. *Water* **2021**, *13*, 320. [[CrossRef](#)]
36. Grella, C.; Wright, I.A.; Findlay, S.J.; Jonasson, O.J. Geochemical contamination of urban water by concrete stormwater infrastructure: Applying an epoxy resin coating as a control treatment. *Urban Water J.* **2016**, *13*, 212–219. [[CrossRef](#)]
37. Vadas, T.M.; Smith, M.; Luan, H. Leaching and retention of dissolved metals in particulate loaded pervious concrete columns. *J. Environ. Manag.* **2017**, *190*, 1–8. [[CrossRef](#)]
38. Jin, X.; Wang, S.; Pang, Y.; Wu, F.C. Phosphorus fractions and the effect of pH on the phosphorus release of the sediments from different trophic areas in Taihu Lake, China. *Environ. Pollut.* **2006**, *139*, 288–295. [[CrossRef](#)]
39. Reddy, K.R.; Wang, Y.; DeBusk, W.F.; Fisher, M.M.; Newman, S. Forms of Soil Phosphorus in Selected Hydrologic Units of the Florida Everglades. *Soil Sci. Soc. Am. J.* **1998**, *62*, 1134–1147. [[CrossRef](#)]
40. Janke, B.D.; Finlay, J.C.; Hobbie, S.E. Trees and Streets as Drivers of Urban Stormwater Nutrient Pollution. *Environ. Sci. Technol.* **2017**, *51*, 9569–9579. [[CrossRef](#)]
41. Søndergaard, M.; Jensen, J.P.; Jeppesen, E. Role of sediment and internal loading of phosphorus in shallow lakes. *Hydrobiologia* **2003**, *506–509*, 135–145. [[CrossRef](#)]
42. Taguchi, V.J.; Olsen, T.A.; Natarajan, P.; Janke, B.D.; Gulliver, J.S.; Finlay, J.C.; Stefan, H.G. Internal loading in stormwater ponds as a phosphorus source to downstream waters. *Limnol. Oceanogr. Lett.* **2020**, *5*, 322–330. [[CrossRef](#)]
43. Kim, I.; Choi, E.; Stenstrom, M.K. Sediment characteristics, phosphorus types and phosphorus release rates between river and lake sediments. *Chemosphere* **2002**, *50*, 53–61. [[CrossRef](#)]