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Phosphorus Retention in Stormwater Control Structures across Streamflow in Urban and Suburban Watersheds

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Abstract: Recent studies have shown that stormwater control measures (SCMs) are less effective at retaining phosphorus (P) than nitrogen. We compared P retention between two urban/suburban SCMs and their adjacent free-flowing stream reaches at the Baltimore Long-Term Ecological Study (LTER) site, and examined changes in P retention in SCMs across flow conditions. Results show that, when compared with free-flowing stream reaches, the SCMs had significantly lower dissolved oxygen (%DO) and higher P concentrations, as well as lower mean areal retention rates and retention efficiencies of particulate P (PP). In all the SCMs, concentrations of total dissolved phosphorus (TDP) consistently exhibited inverse correlations with %DO that was lower during summer base flows. Particulate phosphorus (PP) concentrations peaked during spring high flow period in both streams and in-line pond/SCMs, but they were also higher during summer base flows in suburban/urban SCMs. Meanwhile, PP areal retention rates and retention efficiencies of the SCMs changed from positive (indicating retention) during high flows to negative (indicating release) during low flows, while such changes across flow were not observed in free-flowing stream reaches. We attribute the changing roles of SCMs from a PP sink to a PP source to changes in SCM hydrologic mass balances, physical sedimentation and biogeochemical mobilization across flows. This study demonstrates that in suburban/urban SCMs, P retained during high flow events can be released during low flows. Cultivation of macrophytes and/or frequent sediment dredging may provide potential solutions to retaining both P and nitrogen in urban SCMs.

Keywords: phosphorus; stormwater control measures; urbanization; nutrient management; green infrastructure

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1. Introduction

Excessive phosphorus (P) inputs from urban and agricultural land use are a major cause of freshwater and coastal eutrophication [1–3]. Reducing nonpoint sources of P-rich sediments from urban and suburban watersheds via best management practices (BMPs) including various stormwater control measures (SCMs), and stream restoration designs [4–8], are among the top choices for restoration strategies in the Chesapeake Bay and other coastal watersheds [9–11]. Ignoring land costs, constructed wetlands and ponds were the least expensive to construct and maintain among the six stormwater SCMs investigated [12]. However, recent studies have shown that ponds and stormwater wetlands were less efficient at P retention than at retaining nitrogen (N) [5,6,13]. In some cases (e.g., in [7,13,14]), the SCMs were actually net sources of P to streams or rivers.

The relatively lower retention rates of P compared to N were likely due to differences in the biogeochemical cycling of these elements in constructed wetlands and ponds. Nitrate nitrogen can be permanently removed from these environments via microbial denitrification, a process that requires establishment of anaerobic conditions [15] and ample organic carbon [16,17]. In contrast to nitrate, soluble reactive P (SRP) cannot be removed via degassing. Instead, SRP can be retained via biological uptakes, mineral precipitation or sorption onto surfaces of Fe/Mn-oxides in suspended particles and bed sediments, which can be buried and retained within stream networks [18,19]. However, the retained SRP may be remobilized with particulate P (PP) during storm events via erosive streamflow, or desorbed from particles under anaerobic conditions when Fe/Mn-oxides are reduced to soluble Fe^{2+} and Mn^{2+} [20]. Thus, the roles of constructed wetlands and ponds in retaining N and P may be highly related to anaerobic conditions of these SCMs, dependent on availability of ample organic carbon and stream flow conditions.

The overall objectives of this study were to estimate P retention in the SCMs (e.g., stormwater ponds and wetlands) and restored streams in urban and suburban watersheds, and investigate how the rate and efficiency of P retention in SCMs and restored streams varies with flow conditions. Relative to free-flowing stream reaches, SCMs are generally less dynamic environments with more organic matter [21] and less DO [22]. We expected that the anaerobic conditions of SCMs would cause P release and thereby decrease the efficiency of P retention. Moreover, because exchange of oxygen between aquatic environments and the atmosphere is dependent on the degree of stirring and mixing [23], the occurrence of anaerobic conditions in SCMs may change with flow conditions. Thus, we further hypothesized that the role of SCMs changes from a sink during high flows (due to particle sedimentation), to a source during low flows (due to P release from sediments under anoxic conditions). These hypotheses were tested by conducting P mass balances in two urban/suburban streams at the U.S. National Science Foundation funded Baltimore Long-Term Ecological Research (LTER) site (www.beslter.org). At each site, a pond (at the forest site) or SCM (at urban and suburban sites) and a free-flowing stream reach were selected for comparison. Retention of all P fractions was examined but we focused on PP in this study because it was the main form of P observed in these systems [24]. We also examined DO and water temperature in order to examine to what extent they played a role as controlling factors for P transformations. This work builds on previous N and carbon (C) mass balances at the same locations [25] and other studies at the Baltimore LTER site evaluating the role of hydrology [26], N and C transformations [27], organic C quality [17,28], nonpoint P sources [24], and temperature on P dynamics in urban streams [29]. A better understanding of P dynamics in stormwater management can contribute to urban evolution of future nutrient management strategies considering N and P retention and avoiding unanticipated consequences of management [30].

2. Materials and Methods

2.1. Site Descriptions and Sampling Design

Our study sites were located within the Chesapeake Bay watershed (Figure 1a), where water quality impairments have created interest in reducing downstream nutrient delivery to sensitive coastal waters [9]. We compared P retention in two urban/suburban stream networks and a forested reference watershed at the Baltimore LTER site (Figure 1b). The three selected watersheds have been described in detail in [25]. In brief, Spring Branch (SPBR) is a restored, low-order stream with a drainage area of 407 ha in Baltimore County, MD (Table 1). The SPBR watershed has 18.6% impervious surface cover, 6.37 km of stream channel, and 37.8 km of sewer lines [31]. The headwaters originate from a storm drain in a medium-density residential neighborhood, and the stream passes through confined areas of residential development into Loch Raven reservoir, a major source of drinking water for Baltimore, MD. Development occurred during the 1950s–1970s before current stormwater regulations were in place, and the entire watershed is served by public sewer [31]. Approximately 61% of the watershed drains directly to storm drains and only 7.2% of the watershed is served by stormwater management [31]. SPBR has a relatively low drainage density (1.57 km of stream/km^2 of drainage area) because some sections were straightened and other sections were buried in underground pipes [31]. The stream restoration project repaired leaking infrastructure, removed 0.5 km of concrete channel liner, created a series of step pools, and planted trees and shrubs for bank stabilization [32].

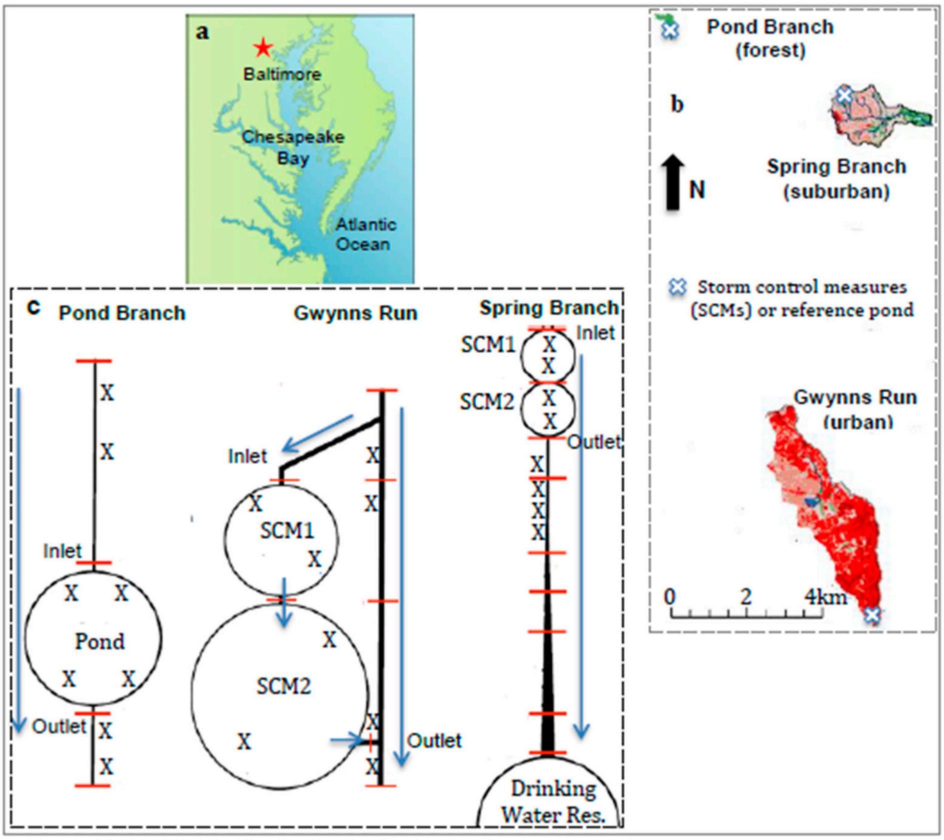

Figure 1. (**a**) Location of LTER site; (**b**) land use of study watersheds; and (**c**) conceptual diagram of stream water and groundwater sampling in the Spring Branch, Gwynns Run, and Pond Branch watersheds. Green, pink and red colors in (**b**) represent forest, suburban and urban land use, respectively, and the positions of these sites are in relationship to one another. Red lines in (**c**) indicate locations of monthly surface water chemistry and discharge measurements. "X"s indicate locations of mini-piezometer wells used for seasonal groundwater monitoring. Arrows indicate flow direction. Pond in Pond Branch and SCMs in Spring Branch are inline while SCMs in Gwynns Run are oxbow type.

Gwynns Run (GFGR) is a highly urbanized stream with a drainage area of 557 ha and the stream has been heavily impacted by sewage leaks (Table 1) [33]. GFGR watershed is highly urbanized (68.1% residential and 16.2% commercial) [34] with an impervious surface coverage of 61.2% [25]. The majority of the stream network was buried in underground pipes during development. This site has a long history of industrial use and pollution, and was identified by Baltimore City as one of its two most degraded streams [35]. In 2003, Baltimore City was required by Civil Action No. Y-97-4185 to construct Gwynns Run Pollution Control Facility, a lowland oxbow SCM system, at a cost of US$1.7 million. The purpose of the lowland oxbow SCMs was to reduce downstream transport of suspended solids, metals, oil, grease, N, and P. The lowland oxbow SCMs were completed in 2004 and consisted of a reinforced concrete flow diverter, forebay (an artificial pool of water in front of a larger body of water), oxbow wetland (SCM 1), and wet pond (SCM 2; Figure 1). The SCMs were designed to treat 40% of flow during 1.4–3.2 cm rain events (capacity of 7380 m^3). However, we have observed that smaller amounts of precipitation generated sufficient runoff to enter the lowland oxbow SCMs. The lowland oxbow SCMs transitioned between wetlands and ponds and were filling with sediment and progressing towards a more wetland state during the study period.

Table 1. Characteristics of Pond Branch, Spring Branch, and Gwynns Run watersheds.

					Land Use (%)			
Site	**Location**	**Context**	**Drainage Area (ha)**	**Impervious Cover (%)**	**Forested**	**High-Density Residential**	**Low and Medium-Density Residential**	**Commercial**
Pond Branch	39°28′49″ N 76°41′16″ W	Forest	37	0	100	0	0	0
Spring Branch *	39°26′43.9″ N 76°37′12.9″ W	Sub-urban	407	18.6	6.7	3.7	87.8	0
Gwynns Run **	39°16′41.3″ N 76°39′07.2″ W	Urban	557	61.2	1.6	68.1	0	16.2

Notes: * Data from Baltimore County Department of Environmental Protection and Resource Management (DEPRM) 2008 [31]. Spring Branch Subwatershed—Small Watershed Action Plan; Addendum to the Water Quality Management Plan for Loch Raven Watershed); ** Data from the Parks & People Foundation 1999 [34].

We also made comparisons with Pond Branch (POBR), a reference stream with an in-line engineered pond at the Baltimore LTER site. POBR is a completely forested, 1st-order stream with a watershed area of 37 ha located within Oregon Ridge State Park in the Maryland Piedmont physiographic province (Table 1, Figure 1). This watershed has no impervious surfaces and has been widely used as the reference watershed for Baltimore Ecosystem Study [17,36].

2.2. Water Collection, Discharge Monitoring and Water Quality Analysis

We conducted monthly monitoring of P concentrations, water temperature, DO, and discharge measurement at Spring Branch, Gwynns Run, and Pond Branch for over 2 years (from April 2008 to August 2010) at multiple longitudinal points along each stream network (Figure 1). Water temperature, DO, and dissolved P were measured over one year (half a year for water temperature, DO, total dissolved P, and SRP in Pond Branch) to examine hydrological variability. At Spring Branch, we initially sampled from Site 1 to Site 5 from April 2008 to September 2008, and extended the study area downstream to the drinking water reservoir. We sampled on all sampling dates along seven longitudinal points at Gwynns Run and along four longitudinal points at Pond Branch, respectively. During the study period, samples spanned a range of flow conditions (from base flow to big storms) according to flow duration curves [25], but three extreme storm events were missed (data not shown), as we expected.

We collected grab samples for streamwater chemistry using High Density Polyethylene (HDPE) bottles rinsed five times with streamwater, and measured water discharge with a Marsh–McBirney 2000 flow meter (Hach Co., Loveland, CO, USA) using the 60% depth method with a 5-s averaging interval [32]. In the field, DO (%) and temperature (°C) were measured using a YSI 550A (YSI Inc., Yellow Springs, OH, USA). Water samples were filtered through pre-combusted glass fiber filters within 24 h of collection, and the filters and filtrates were frozen until further analysis. The filters were used for determinations of total PP and NaOH extractable particulate phosphorus (NaOH-PP). This NaOH-extracted fraction represented the PP that was loosely adsorbed onto iron and aluminum hydroxides. Particles on the filter were digested following EPA acidic persulfate method (ESS Method 310.2) [37]. The filters with particles were submersed in 15 mL persulfate solution (10 g·L^{-1}) amended with 0.25 mL H_2SO_4 in 20 mL Wheaton Glass scintillation vials. The vials were then sealed with caps and digested in a Tuttnauer autoclave (Tuttnauer, New York, NY, USA) at 121 °C and pressure of 98–137 kPa for one hour. The cooled solutions were then neutralized with 5 M NaOH with 1 drop (0.05 mL) of phenolphthalein indicator before analysis as soluble reactive phosphorus. At the same time, suspended particles on another set of filters were extracted with 50 mL 0.1 N NaOH solutions for NaOH-PP using the method of [38]. The extraction lasted for 17 h while being shaken on a shaker table.

The solutions were decanted into tested tubes for centrifugation at 8000 RPM and the supernatant collected and neutralized with concentrated HCl before SRP analysis. Meanwhile, the filtrates were analyzed for total dissolved and soluble reactive phosphorus (TDP and SRP). TDP in water was digested with persulfate solution in a similar method to that of PP except that no acid was added. SRP was measured colorimetrically on a Lachat QuickChem FIA system (Lachat Instruments, Milwaukee, WI, USA), using the ascorbic acid-molybdate blue method [29,39].

2.3. Mass Balances in Ponds and Stream Reaches

Longitudinal surface water sampling was conducted for each stream network as described above (Figure 1). Surface water chemistry was used in conjunction with groundwater chemistry and hydrologic data to estimate monthly mass balances of PP and TDP for the SCMs/pond and adjacent free-flowing stream reaches. Mass-balance calculations were used to determine net retention or net release of PP and TDP per unit area of stream for each unit. Fluxes were calculated by multiplying concentration ($mg \cdot L^{-1}$) by the stream flow rate ($L \cdot day^{-1}$) to obtain mass transport per day ($mg \cdot day^{-1}$). Differences between upstream and downstream fluxes were then used as an estimate of retention/release.

We calculated mass balances for PP and TDP using Equation (1) modified from [25]:

$$(MU + MS) - MD = \Delta M, \tag{1}$$

where MD = $mg \cdot day^{-1}$ at downstream end of reach, MU = $mg \cdot day^{-1}$ at upstream end of reach, MS = $mg \cdot day^{-1}$ from groundwater seepage, and ΔM = $mg \cdot day^{-1}$ of net transformation [net retention if (+); net release if (−)].

Rates of net flux per streambed area ($mg \cdot m^{-2} \cdot day^{-1}$) were calculated by dividing ΔM by reach surface area. Surface area was estimated by measuring stream cross sections at 2–3 points along each reach to determine wetted width of the channel and multiplying by the length of each reach. A positive transformation (ΔM) indicated net removal of the constituent (retention), whereas a negative ΔM indicated net generation (release) of the constituent. Percent retention or release of a constituent for each reach was calculated using Equation (2) [(outputs–inputs)/inputs]:

$$100 \times \Delta M/(MU + MS) = \%\,\text{retention}\,(+)\,\text{or release}\,(-), \tag{2}$$

Groundwater seepage (MS; $mg \cdot day^{-1}$) was calculated by combining estimates of groundwater TDP concentrations ($\mu g \cdot L^{-1}$) with groundwater discharge ($L \cdot day^{-1}$). Each longitudinal site had eight mini-piezometer wells that were installed 0.5 m below the stream surface (during baseflow) in hydrologically connected floodplains and 0.3 m below the surface in the SCMs/pond (Figure 1). To calculate P mass balance, we used average TDP concentrations from our groundwater samples. Rates of net groundwater input for each stream were determined based on the differences in flow from each sampling point to the next, according to Equation (3):

$$FD - FU = FS, \tag{3}$$

where FD = $m^3 \cdot day^{-1}$ at downstream end of reach, FU = $m^3 \cdot day^{-1}$ at upstream end of reach, and FS = $m^3 \cdot day^{-1}$ of groundwater seepage. We focused solely on stream sections without tributary inputs in order to reduce the likelihood of errors in our mass balance (Pond Branch: section 0–119 m and Gwynns Run: section 0–138 m; Figure 1). No mass balances were completed for free-flowing stream reaches of Spring Branch because of the presence of unsampled tributaries.

2.4. Statistical Analyses

Statistical analyses were performed using SPSS 10 (IBM Corporation, New York, NY, USA). P concentrations and water quality parameters were reported in mean and standard errors. Differences in P concentrations and water quality parameters between free-flowing stream reaches and SCMs/pond (or between study sites) were evaluated using One-Way ANOVA. Before performing One-Way ANOVA, the data were analyzed to determine if they were normally distributed. If not, the data were logarithmically transformed or outliers were discarded in order to make the data normally distributed. We used Pearson's correlation analysis to check for collinearity among P concentrations, stream flow, water temperature, and DO. We considered correlation coefficients significant when p values were above 0.05. Areal retention rates and retention efficiencies were reported in descriptive statistics (median, minimum and maximum), because there were a few extremely high outliers. An average of areal retention rate or retention efficiency did not make sense because we had both P release (negative value) and retention (positive values). P areal retention rates and retention efficiencies were regressed linearly with flow or water storage (with a significance level $p < 0.05$), thereby taking into consideration temporal variability. If the relationships were not linear ($p > 0.05$), exponential, logarithmic or power non-linear regressions were used (dependent on R value). In this study, high and low flows were operatively defined as flow one standard deviation above or below than average flows.

3. Results

3.1. Spatial Variability of Water Temperature, %DO, and P Concentrations

Within watersheds, water temperatures were slightly higher in stream than in the SCMs at the suburban site SPBR but higher in oxbow SCMs than in the stream at the urban site GFGR (Table 2), but the differences were not significant. In general, P concentrations and %DO at these suburban and urban watersheds differed significantly between the SCMs and the free-flowing restored stream reaches, although the differences were not significant at the forest site POBR (Table 2). For example, %DO in the SCMs was significantly lower than that in the free-flowing restored streams at both watersheds (One-Way ANOVA, $F = 19.1$ and 54.9, $p < 0.05$), suburban SPBR (81% ± 3% vs. 106% ± 2%) and urban GFGR watersheds (59% ± 7% vs. 77% ± 2%; Table 2). In contrast, concentrations of PP, NaOH-PP, TDP and SRP were usually significantly higher in the SCMs than in the free-flowing stream reaches at the suburban site and urban sites (One-Way ANOVA, $F = 5.5$–84.2, $p < 0.05$; Table 2). Moreover, %DO decreased from near saturation (96.6% ± 1.4%) in the pond at the forested watershed POBR, to under saturation (80.7% ± 2.8%) in the SCMs at of the suburban watershed SPBR and even more under saturation (58.7% ± 6.5%) in the SCMs of the urban watershed GFGR (Table 2). The concentrations of PP, NaOH-PP, TDP and SRP, however, consistently increased across this rural–urban land use gradient (POBR to SPBR to GFGR) (Table 2).

Table 2. Means (standard errors) of water temperature (t), dissolved oxygen saturation (%DO), and concentrations of phosphorus forms (PP, NaOH-PP, TDP and SRP) of the free-flowing stream reaches and pond/SCMs in the study watersheds.

Watersheds	**POBR (Forested)**		**SPBR (Suburban)**		**GFGR (Urban)**	
Site Types	**Stream**	**Inline Pond**	**Stream**	**Inline SCMs**	**Stream**	**Oxbow SCMs**
t (°C)	14.0 (1.1) ^{NS}	13.5 (1.3)	15.4 (0.7) ^{NS}	14.0 (1.0)	15.9 (0.6) ^{NS}	17.2 (1.4)
DO (%)	95.8 (1.1) ^{NS}	96.6 (1.4)	104.1 (2.3) *	80.7 (2.8)	76.9 (1.9) *	58.7 (6.5)
PP ($\mu g \cdot L^{-1}$)	26.7 (2.7)^{NS}	22.3 (1.9)	30.1 (2.4)*	58.1 (4.5)	120.1 (6.1) *	212.2 (12.3)
NaOH-PP	5.8 (0.6) ^{NS}	5.3 (0.4)	8.7 (0.7) *	20.5 (1.8)	36.8 (1.0) *	42.3 (2.2)
TDP ($\mu g \cdot L^{-1}$)	7.6 (0.4) ^{NS}	7.9 (0.4)	15.2 (1.3) ^{NS}	18.7 (2.7)	17.1 (1.8) *	44.9 (6.7)
SRP ($\mu g \cdot L^{-1}$)	4.5 (0.3) ^{NS}	4.2 (0.2)	7.1 (0.5) *	10.3 (0.9)	7.2 (0.4) *	13.1 (1.6)

Notes: Values of streams and pond/SCMs were for measurements of all sites of each stream network, and outlier were not included in calculating means and standard errors. Measurements of PP and NaOH-PP were over two-year (April 2008–August 2010), while the data for water temperatures, dissolved oxygen, TDP and SRP covered around one year period (at SPBR and GFGR sites) or less (e.g., at POBR site); ^{NS} indicates no significant difference and * indicates that water quality parameters differed significantly ($p < 0.05$) between stream and SCM treatment within an ecosystem type.

The changes in PP concentrations from the inlet to the outlet of the suburban/urban SCMs or the forest pond varied with stream flow (Figure 2). For instance, concentrations of PP at the POBR forest pond were always lower at the outlet than at the inlet (ΔPP > 0) when stream flows was >2 L·s^{-1}, although the changes were not consistent usually when stream flows were <2 L·s^{-1} (Figure 2a). For the in-line SCMs at the suburban watershed SPBR, concentrations of PP were usually (13 to 16 times) higher at the outlet (ΔPP < 0) when flows were <0.5 L·s^{-1}) (Figure 2b). For the oxbow SCMs at the urban watershed GFGR, PP concentrations were almost all higher at the outlet (ΔPP < 0) except for two highest flows (6.8 and 7.9 L·s^{-1}) (Figure 2c).

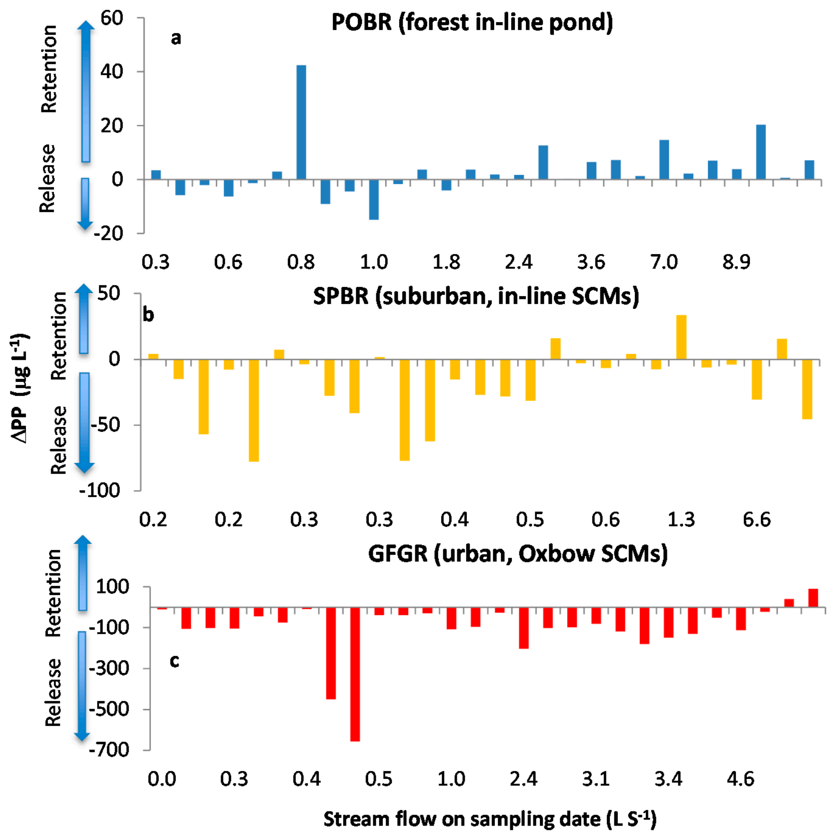

Figure 2. Changes in PP concentrations from inlet to outlet (Δ = inlet − outlet) of (**a**) the POBR forest, in-line pond; (**b**) the SPBR suburban in-line SCMs and (**c**) GFGR urban oxbow SCMs across stream flows (from lowest to highest).

3.2. Temporal Changes in Water Temperature, Flow, %DO and P Concentrations

Water temperatures all exhibited pronounced seasonality (highest in summer and lowest in winter) across sites (Figure 3a–c). Flow varied inversely to water temperature except in the oxbow SCM at the urban watershed GFGR, which had a flow peak during March–May 2010 (Figure 3d–f; Table 3). %DO of streams and in-line pond/SCMs was generally highest during winter high flows (e.g., flows one standard deviation higher than average) (Figure 3g–i), and, at some sites (e.g., SPBR SCMs and GFGR free-flowing stream), %DO of SCMs was negatively correlated with temperature but positively correlated with flow (Table 3). The %DO seasonal pattern at the urban oxbow SCMs was highest in April 2010 followed by extremely low values during summer (Figure 3i).

TDP concentrations were generally higher in summer low flow (June to August) when DO was low, and TDP of all the pond/SCMs (and one free-flowing stream) varied inversely with %DO (Figure 3j–l, $p < 0.05$, Table 3). Although the trend of SRP followed that of TDP, seasonality of SRP was more complex (Figure 3m–o), and a significant correlation was found with DO only in the forest pond

(Table 3). PP concentrations in all streams and the in-line pond/SCM at forest site POBR and suburban site SPBR were highest during December–January (Figure 3p–r), and positively correlated with flow (Table 3). In contrast, PP concentrations of the urban oxbow SCM were highest during summer (Figure 3r) following that of TDP and SRP; such a PP peak was also found in the suburban in-line SCM (Figure 3q). Seasonal changes in NaOH-PP and PP concentration were positively correlated at the forest and suburban sites but not at the urban site (Figure 3s–u and Table 3).

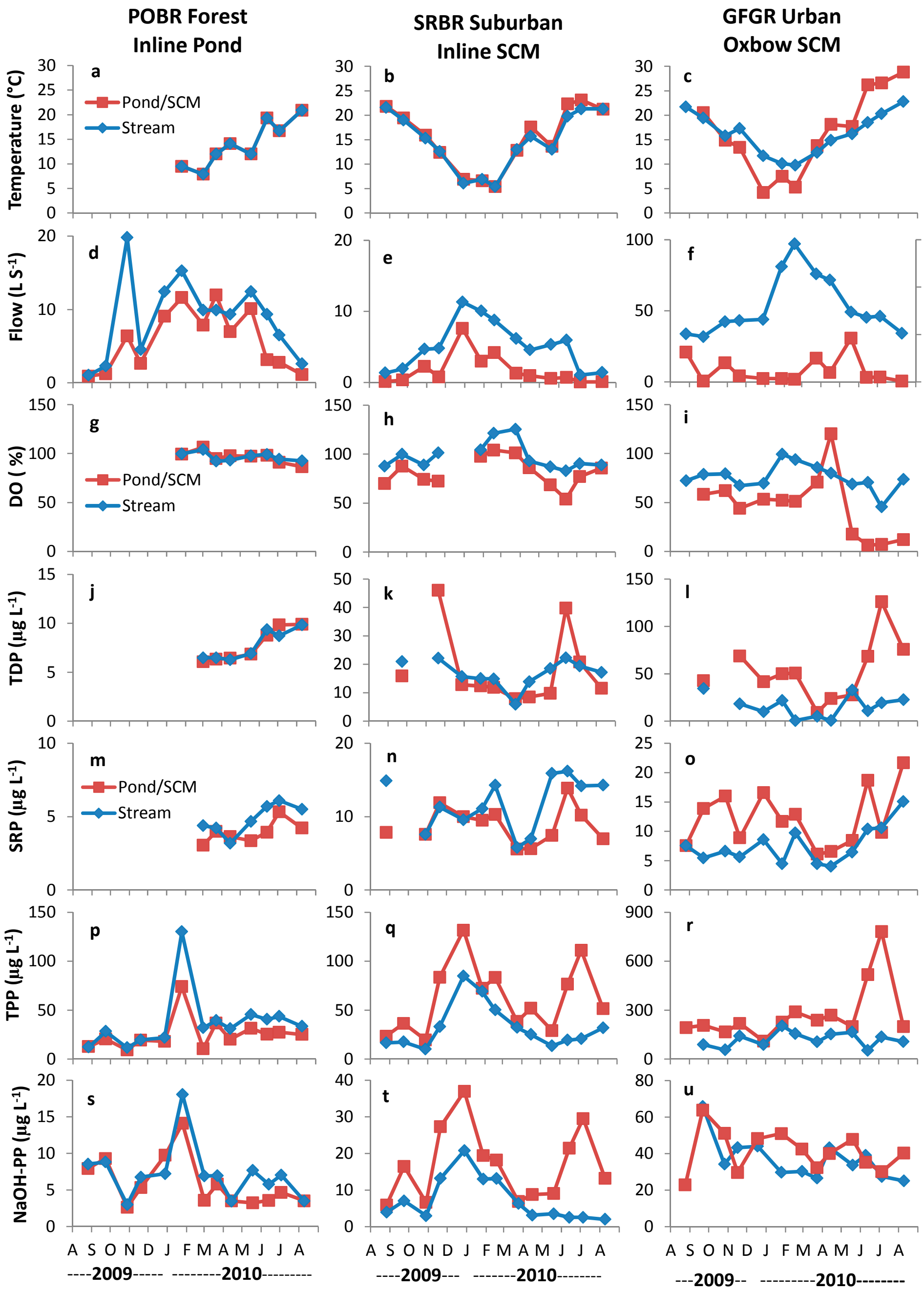

Figure 3. Monthly changes in (**a**–**c**) water temperature; (**d**–**f**) flow; (**g**–**i**) dissolved oxygen saturation (%DO), and concentrations of (**j**–**l**) total dissolved P (TDP); (**m**–**o**) soluble reactive P (SRP); (**p**–**r**) total particulate phosphorus (PP) and (**s**–**u**) NaOH extractable PP (NaOH-PP) at the pond/SCMs outlets and adjacent free-flowing stream reaches. Capital letters on *x*-axis are the first letter of months representing months of the two years in a chronological sequence. Data of water temperature, DO, TDP and SRP of the forest inline pond were not collected during April–July 2009.

Table 3. Correlations between water quality parameters (dissolved oxygen (%DO), water temperature (t) or flow) and concentrations of P forms in the stream or pond/SCMs within an ecosystem type.

Watersheds	PDBR (Forest)		SPBR (Suburban)		GFGR (Urban)	
Site Types	Stream	In-Line Pond	Stream	In-Line SCM	Stream	Oxbow SCM
Flow vs. t (°C)	−0.76	−0.77	−0.92	−0.77	−0.77	
%DO vs. t (°C)		−0.82	−0.68	−0.62	−0.65	
%DO vs. flow				−0.57	−0.67	
TDP vs. %DO		−0.75	−0.69	−0.67		−0.67
SRP vs. %DO		−0.74				
PP vs. flow	−0.44	−0.41	−0.49	−0.40		
NaOH-PP vs. PP	−0.70	−0.56	−0.89	−0.91		

Note: Only values for significant correlation are listed.

3.3. P Retention in SCMs/Pond and Free-Flowing Stream Reaches

Areal retention rate (mg·m^{-2}·day^{-1}) and retention efficiency (%) of PP and TDP were highly variable in both the SCMs/pond and streams (Table 4), and showed no significant difference between sites or between pond/SCMs and free-flowing stream. Median PP areal retention rates in the SCMs were negative (indicating release) at the suburban and urban sites (−0.6 and −3 mg·m^{-2}·day^{-1}), while the values were positive (indicating retention) at the forest site (1 mg·m^{-2}·day^{-1}). Moreover, median areal retention rates of pond/SCMs were lower than that of corresponding free-flowing stream reaches at the forest site (1 vs. 5 mg·m^{-2}·day^{-1}) and the urban site (−3 vs. 26 mg·m^{-2}·day^{-1}). Median PP retention efficiencies of the pond/SCMs for the whole study period were 16%, −10% and −2% for forest, suburban and urban sites, respectively and retention efficiencies of the pond/SCMs were lower than that of the corresponding free-flowing streams at the forest (16% vs. 36%) and urban sites (−2% vs. 13%). The ranges of TDP retention rates in the SCMs/pond and free-flowing stream sections were all much smaller than that of PP (Table 4). Unlike PP, areal retention rates and retention efficiencies of TDP in the SCMs were not always lower than in the corresponding free-flowing stream sections.

Table 4. Ranges (median) of PP and TDP areal retention rates and retention efficiency (ΔPP/total PP inputs × 100%) of the pond/SCMs and free-flowing stream reaches of the three selected watersheds. Positive and negative values refer to retention and release, respectively.

Retention	Site Types	POBR (Forest)	SPBR (Suburban)	GFGR (Urban)
		PP		
Net retention rate	SCMs/pond	−9 to 19 (1)	−22 to 782 (−0.6)	−22 to 238 (−3)
(mg·m^{-2}·day^{-1})	Streams	−12 to 184 (5)	NA *	−136 to 203 (26)
Retention efficiency	SCMs/pond	−389 to 62 (16)	−850 to 75 (−10)	−31 to 36 (−2) **
(%)	Streams	−63 to 80 (36)	NA *	−69 to 51 (13)
		TDP		
Net retention rate	SCMs/pond	−0.2 to 5.2 (0.3)	−4 to 15 (0.4)	−2.9 to -0.1 (−0.5)
(mg·m^{-2}·day^{-1})	Streams	−1.3 to 1.6 (0.6)	NA *	−26 to 33 (−3)
Retention efficiency	SCMs/pond	−8 to 74 (4)	−70 to 38 (8)	−1 to −20 (−5)
(%)	Streams	−8 to 10 (2)	NA *	−47 to 14 (−3)

Notes: The values for PP were from April 2008–August 2010, while the values of TDP were from September 2008–August 2009. * The values for SPBR stream were not calculated due to a lack of tributary data; ** Calculated by dividing PP transformation with total inputs to GFGR stream and SCMs in order to compare relative contributions of the oxbow SCM and free-flowing stream reaches to the stream PP flux.

PP areal retention rates of the SCMs/pond showed consistent changes with streamflow across sites. In general, PP retention rates (mg·m^{-2}·day^{-1}) were negative (indicating PP release) during low flows, and the values increased to positive (indicating PP retention) as streamflow increased (Figure 4a–c). The increases with stream flow were linear at the forest site, while the increases at the urban and suburban SCMs were largely affected by two highest values. Without the two highest values in Figure 4b,c, there would be no linear relationship between delta PP and flow. Retention efficiencies (%) of the pond/SCMs also showed consistent increases with streamflow across sites (Figure 4d–f). In contrast to the pond/SCMs, areal rate and efficiency of PP retention of the free-flowing stream reaches (POBR 0–119 m and GFGR 0–138 m) generally exhibited no trend with stream flow except for retention rate at POBR (Figure 5).

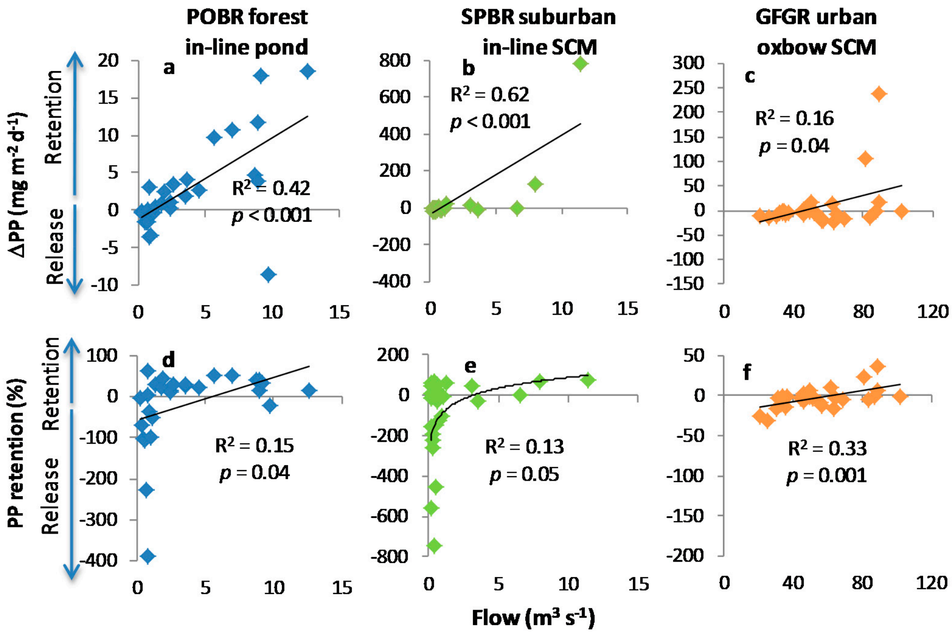

Figure 4. Changes in (**a**–**c**) areal retention rates and (**d**–**f**) retention efficiency of particulate phosphorus (PP) (ΔPP/total PP input × 100%) with increasing stream flow in the forest pond and the suburban/urban SCMs.

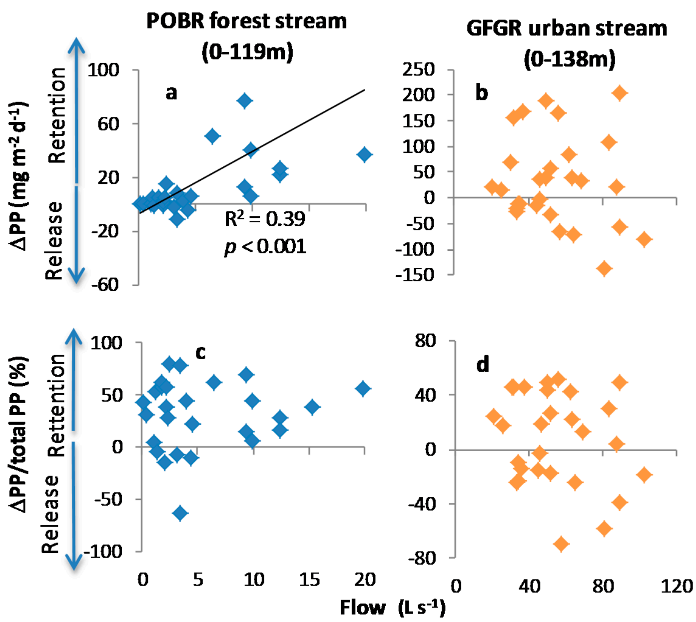

Figure 5. Changes in (**a**,**b**) areal retention rates and (**c**,**d**) retention efficiency of particulate phosphorus (PP) with increasing stream flow in the free-flowing stream reaches of the forest (POBR 0–119 m) and urban stream (GFGR 0–138 m). Mass balances for the suburban stream (SPBR) were not conducted due to the presence of unsampled tributaries.

PP retention efficiencies in all three pond/SCMs were positively correlated with percent stream water storage (r^2 = 0.53–0.83, $p < 0.05$; Figure 6a–c). The slopes of the regression lines were all >1, and the values were generally below 1:1 line, indicating larger PP release relative to stream water storage. PP retention efficiencies of the free-flowing stream reaches of the forest site POBR were also positively correlated with percent streamwater storage, but the slope of the regression line was <1 (Figure 6d). PP retention efficiencies of stream reaches at the urban site GFGR were not correlated with percent water storage (Figure 6e).

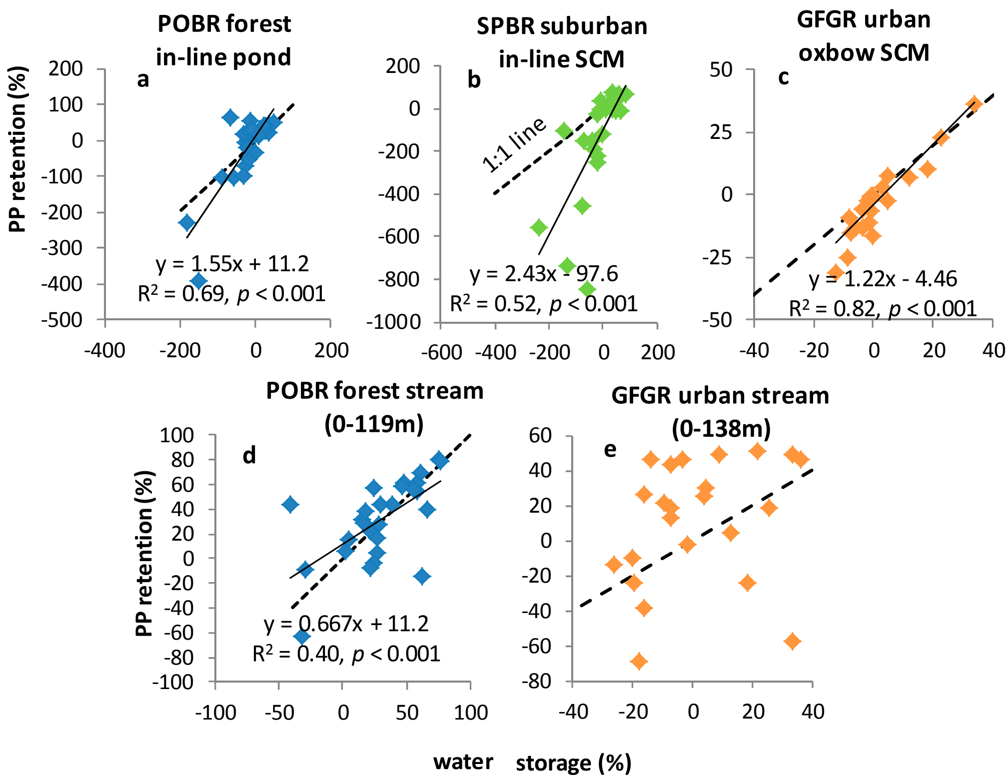

Figure 6. Linear regression of particulate phosphorus (PP) retention efficiency with percent stream water storage in (**a**–**c**) the three pond/SCMs and (**d**,**e**) two free-flowing stream reaches (POBR 0–119 m and GFGR 0–138 m). A 1:1 line was added to each panel to show the deviation of PP from stream water mass balance. The slopes of the regression lines were all >1 and the values were generally below 1:1 line, indicating larger PP release relative stream water storage.

4. Discussion

4.1. Roles of Stormwater Control Structures in P Retention

It is generally accepted that that P, which is tightly bound with particles, can be removed within constructed ponds and wetlands of urban watersheds by particle sedimentation followed by sediment burial, due to reduced flow velocity in these environments. The underlying assumption of this expectation is that P bonded on particles was almost inert after burial and little of the buried P can be recycled and released back into stream ecosystem. However, results of this study suggest that that P buried in constructed ponds and wetlands could be active and SCMs were not always a nutrient sink for streams and rivers, as we expected. Current design of urban SCMs warrants further improvements if the object is P management.

This study, by examining retention areal rates and retention efficiencies of SCMs in two suburban/urban watersheds across the full range of flow regime [25], showed much larger variability in PP retention efficiencies (−850% to 75%; Table 3) than previous studies (−87% to 133%) [5,40,41], suggesting that P retention in SCMs is far more complicated than expected. More importantly, we found that urban constructed ponds and wetlands can be a source of P to streams, especially during low flow conditions (Figure 4). This conclusion can also be inferred from the fact that PP concentrations at outlets of the SCMs were usually higher than at inlets during low flow conditions (Figure 2). Additional evidence for SCMs as P source was that concentrations of all P forms in the suburban/urban SCMs were significantly higher than the corresponding free-flowing stream reaches (Table 2). All above evidence indicated occurrence of P recycling and release with the SCMs. Probably, as a result of the P recycling and release, median areal retention rates and retention efficiencies of the SCMs/pond were lower than that of corresponding stream reaches (Table 4). Because wetlands and ponds could be at a disadvantage compared to streams on an areal base on comparing PP retention rate, we recalculated PP retention per stream length. Results showed that the median retention rates of the pond or SCMs were still lower than that of the corresponding free-flowing stream sections (16 vs. 20 $mg \cdot m^{-1} \cdot day^{-1}$ at forest site and -69 vs. 576 $mg \cdot m^{-1} \cdot day^{-1}$ at urban site GFGR), supporting above conclusion.

The low PP retention rates and efficiency in the pond/SCMs of this study was consistent with previous literature suggesting SCMs (ponds and wetlands) rich in organic matter are not efficient for P retention. For example, Kieckbusch and Schrautzer [14] reported that organic-rich peatland in Norway was a source of TP over a period of three years (up to 105%). Net P release was also reported in two restored riparian wetlands inundated with agricultural drainage water [13]. In the same watershed as our study, Harrison et al. [7] reported that relict oxbow wetlands were a net source of SRP to the adjacent stream during storm events. Although the suburban/urban SCMs in our study were not as rich in organic matter as the previously mentioned peatlands and wetlands, they were still significantly lower in %DO relative to adjacent free-flowing stream reaches (Table 2), likely due to in situ organic inputs [25] and the isolated state of the SCMs. As a result, SRP was released under anoxic conditions, and P (both dissolved and particulate) retention of the SCMs was consequently low. Conversely, in the free-flowing stream reaches, there was less P release likely because of higher DO levels (Table 2) and less organic matter [21]. We also found that median PP areal retention rates and retention efficiencies of the forested pond were higher than that of the suburban and urban SCMs (Table 4); the values were positive (meaning retention) at forest and negative (meaning release) at urban and suburban site. This difference was consistent with significant lower %DO at the urban/suburban sites, which also supports our hypothesis that anaerobic conditions of SCMs will decrease the efficiency of P retention. The lower DO in the suburban and urban SCMs can be ascribed to more organic carbon from algae or wastewater sources at these sites [27,29]. Meanwhile, the urban or suburban SCMs were far richer in P relative to the forest pond (Table 4), probably also reducing P retention.

4.2. Possible Physical Controls on PP Retention in SCMs

We observed increases in PP areal retention rates and retention efficiencies of SCMs with stream flow, and SCMs changed from a PP sink during high flows to a PP source during low flows (Figure 4). Our data suggest that the changing role of SCMs across stream flow was likely a result of physical controls. For example, SCMs or ponds, can act as buffers by temporarily storing runoff during storm events [42], later releasing stored runoff slowly back into the stream. Our stream water mass balance results revealed similar patterns, and showed positive correlation between PP retention efficiencies and river water storage in both the forested pond and suburban/urban SCMs (Figure 6a–c), suggesting that there was hydrological control on the retention pattern of PP retention in SCMs across streamflow. However, we found that PP retention efficiencies of SCMs were generally lower than that of stream water storage (indicated as the 1:1 line) and the difference from stream water storage increased with negative storage (Figure 6a–c). Thus, SCMs hydrologic mass balances can explain only part of the story regarding the changing role of pond/SCMs in regulating stream PP across stream flows, leaving the remainder explained by other processes such as sedimentation and biogeochemical transformations.

Sediment dynamics also are a driver influencing PP retention. As shown in previous river studies [43], PP transport during floods shows a different behavior than discharge, with a high mobilization especially at the beginning or during the flood. In this study, we also found that the peaks of PP concentrations at the free-flowing streams were at the same month (forest site POBR and suburban site SPBR) or one month ahead of flow peak (urban site GFGR) (Figure 3) and PP concentration were positively correlated with streamflow, suggesting the influence of sedimentation. It should be pointed out that our discussion here is based on the relationship between PP concentration and stream flow, and conclusions regarding control of sediment dynamics warrant future measurements on sediment concentration. Relative to free-flowing streams, SCMs (or pond) usually have lower average stream velocity and likely more sedimentation [42]. Thus, we observed that PP concentrations decreased from the inlet to the outlet (ΔPP > 0) during high flows (Figure 2). However, sedimentation cannot explain the downstream PP increases (ΔPP < 0) in the urban/suburban SCMs during low flows (Figure 2) or summer low-flow PP concentration peaks in the SCMs (Figure 3). Possible reasons for these spatiotemporal changes (e.g., SRP release and transformations) will be discussed later.

4.3. Possible Biogeochemical Controls PP Retention in SCMs

As predicted, PP was released from the suburban and urban SCMs during low flows (Figure 4), due to biological mobilization of dissolved SRP from sediments under anaerobic conditions. It is known that, during high flows, water is mixed and oxygen is exchanged with the atmosphere. In contrast, low flow conditions are generally characteristic of lower velocity and longer residence time. Thus, anoxic conditions or oxygen deficits are more likely to occur due to stratification (lack of disturbance) and organic matter decay [23]. We found that %DO levels were lower during summer low flows and were positively correlated with stream flow in suburban in-line SCMs (Figure 4d–f), supporting coupling between anaerobic conditions and stream flow. Meanwhile, previous studies have also shown that SRP adsorbed on Fe or Mn hydroxides was released when Fe or Mn hydroxides were reduced under anoxic conditions, a process influenced by redox potential and water temperature [20,29,44]. Potentially, SRP can be mobilized from sediments of suburban and urban SCMs during low flows due to Fe/Mn hydroxides reduction under anaerobic conditions.

This study did not show coupling between SRP and %DO (Figure 4h,i), but we observed a negative correlation between TDP and %DO in the forest pond and the urban/suburban SCMs. We propose that a fraction of the released SRP were transformed to dissolved organic phosphorus (DOP; included in TDP). That is, a fraction of SRP released from sediments under anaerobic conditions was immediately adsorbed onto negatively-charged colloids. Cai and Guo [45] reported that a large fraction of DOP in river water was in colloidal size due to SRP adsorption onto colloids, supporting the likelihood of this P transformation.

SRP released from anaerobic sediment can also be transformed to PP. According to previous studies, P transformations from SRP to PP can be obtained via two processes, abortive absorption and biological assimilation. On one hand, the released SRP can be adsorbed onto clay-size particles and become NaOH-PP, which keeps SRP at very low levels [46]. On the other hand, the released SRP can also be rapidly assimilated by stream algae or microbial organism and become organic PP (as a fraction of non-NaOH-PP), because P is a limiting nutrient in fresh waters [47]. The completion of these two processes for SRP depends on availability of suspended clay-size particles and growth of algae, which is a function of flow condition, nutrients, and intensity of sunlight [46,48]. PP releases and spatiotemporal changes in PP concentration during summer low flows in the suburban/urban SCMs can be attributed to either adsorption or assimilation. PP concentration peaks during summer low flows were not observed in the free-flowing stream reaches, suggesting this elevated PP was produced from in situ sources rather from watershed sources. Instead, PP concentration peaks occurred almost at the same period of TDP and SRP (June–July; Figure 3), suggesting the same P sources (sediment release) or/and transformation. Although more work is needed, we speculate that the transformation in the suburban headwater inline SCM was dominated by abiotic sorption while the biological assimilation was the dominating process in the large oxbow SCMs. This is based on the same seasonal pattern of NaOH-PP (SRP sorbed onto fine particles) as PP in the former SCMs as well more light availability in the later SCMs (personal observation). As a result of abiotic adsorption and biological assimilation, PP concentrations in the urban/suburban SCMs increased longitudinally from inlet to outlet (Figure 2) and suburban/urban SCMs became a net source of PP during low-flow conditions (Figure 4).

5. Conclusions and Management Implications

There is considerable interest in managing P leaving watersheds and entering lakes and coastal zones [9]. Urban stormwater is one of the fastest growing forms of P pollution in many fresh and marine waters globally [49,50]. Our results show that although urban/suburban stormwater control measures (SCMs) are a net sink of upstream PP, the retention rates and efficiencies were lower than that of stream reaches, and SCMs were actually a source of PP during low flow conditions. PP release from the SCMs during low flows was likely a result of SRP release from anaerobic sediments followed by subsequent adsorption onto clay particles or uptake by phytoplankton (Figure 7). SCMs cannot always be a sink to P from watershed stormwater, as occurring during high flows (Figure 7). Actually, P retention in suburban/urban SCMs during high flows may be partially offset by P mobilization during low flows, potentially leading to net increases in downstream P loads.

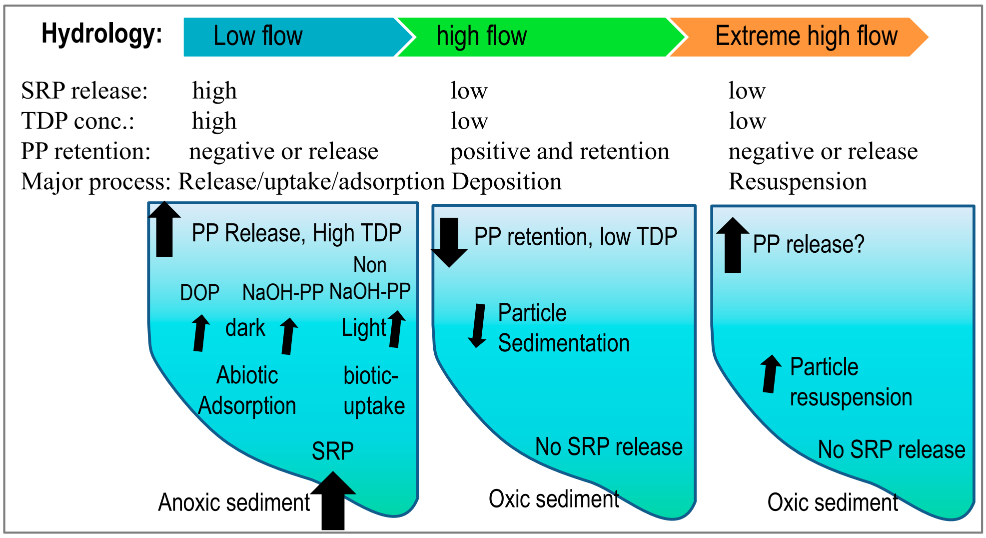

Figure 7. A conceptual diagram showing dominant physical and biogeochemical processes and possible effect on P retention in urban SCMs during across stream flows.

We found that urban/suburban SCMs do not have the same effect on N and P retention because N and P cycles are controlled by different processes. In general, N retention seems to occur mainly during low flow, likely due to longer residence time and subsequent biological transformation during anoxic conditions which favor denitrification. Inputs of labile organic C from in situ sources during low flows may further stimulate N removal [17]. Our results parallel other studies showing that conditions that stimulate denitrification during low flows (e.g., in situ labile organic carbon, low DO, and longer residence time) may also stimulate P mobilization and release from sediments of SCMs [7,13,14]. Therefore, management to remove N and P by SCMs in urban/suburban watersheds may represent a trade-off where establishing conditions for managing N may exacerbate P pollution and vice versa. Like Mallin et al. [51], we suggest that SCMs be designed to support macrophyte growth because roots of macrophytes can oxygenate soil thereby enhance P immobilization. Effective SCM maintenance (e.g., more frequent sediment dredging) is also critical. For example, our results showed that P retention in suburban/urban SCMs during high flows can be partially mobilized during low flows. Thus, if sediments containing retained PP during spring storm events are removed before P release during summer base flows, the chance for P to be released from sediment would thus decrease. This study missed extreme storm events, and the roles of SCMs in retaining P and N during these extreme events warrant further investigation (Figure 7).

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Author Contributions: Tamara Newcomer-Johnson and Sujay Kaushal conceived and designed the experiments; Shuiwang Duan and Tamara Newcomer-Johnson performed the experiments and analyzed the data Shuiwang Duan, Tamara Newcomer-Johnson, Paul Mayer and Sujay Kaushal contributed to writing the manuscript and editing.

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

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