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Beyond best management practices: pelagic biogeochemical dynamics in urban stormwater ponds

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Abstract. Urban stormwater ponds are considered to be a best management practice for flood control and the protection of downstream aquatic ecosystems from excess suspended solids and other contaminants. Following this, urban ponds are assumed to operate as unreactive settling basins, whereby their overall effectiveness in water treatment is strictly controlled by physical processes. However, pelagic microbial biogeochemical dynamics could be significant contributors to nutrient and carbon cycling in these small, constructed aquatic systems. In the present study, we examined pelagic biogeochemical dynamics in 26 stormwater ponds located in southern Ontario, Canada, during late summer. Initially, we tested to see if total suspended solids (TSS) concentration, which provides a measure of catchment disturbance, landscape stability, and pond performance, could be used as an indirect predictor of plankton stocks in stormwater ponds. Structural equation modeling (SEM) using TSS as a surrogate for external loading suggested that TSS was an imperfect predictor. TSS masked plankton–nutrient relationships and appeared to reflect autochthonous production moreso than external forces. When TSS was excluded, the SEM model explained a large amount of the variation in dissolved organic matter (DOM) characteristics (55–75%) but a small amount of the variation in plankton stocks (3–38%). Plankton stocks were correlated positively with particulate nutrients and extracellular enzyme activities, suggesting rapid recycling of the fixed nutrient and carbon pool with consequential effects on DOM. DOM characteristics across the ponds were mainly of autochthonous origin. Humic matter from the watershed formed a larger part of the DOM pool only in ponds with low productivity and low dissolved organic carbon concentrations. Our results suggest that in these small, high nutrient systems internal processes might outweigh the impact of the landscape on carbon cycles. Hence, the overall benefit that constructed ponds serve to protect downstream environments must be weighed with the biogeochemical processes that take place within the water body, which could offset pond water quality gains by supporting intense microbial metabolism. Finally, TSS did not provide a useful indication of stormwater pond biogeochemistry and was biased by autochthonous production, which could lead to erroneous TSS-based management conclusions regarding pond performance.

Key words: dissolved organic matter; extracellular enzyme activity; managed ecosystems; microbial loop; plankton abundance; stormwater ponds; structural equation modeling; urban biogeochemistry.

Introduction

Around half of the world's population live in urban areas today and the number is expected to grow to 70% by 2050 (United Nations 2008). With increased populations, suburban growth, and a tendency of smaller family households, the urban biogeochemical footprint will likely expand dramatically without novel and extensive efforts to increase sustainability with respect to the water, nutrient, and carbon cycles of these areas (Kaye et al. 2006, Luck et al. 2009). Despite the vast ecological knowledge gleaned from natural ecosystems, we continue to poorly understand the biogeochemistry and global importance of these systems. In temperate urban and suburban settings, altered landscapes and increased effective impervious areas lead to reduced surface water infiltration, greater pollutant loading, lower stream base flow, shorter water residence times on the landscape, and flashier and amplified hydrology (Paul and Meyer 2001, Walsh et al. 2005*a*, *b*). To mitigate these impacts, a variety of water quantity and quality control (i.e., best management practices) options are available that vary widely in their cost, sustainability, and effectiveness (Anderson et al. 2002, Crowe et al. 2007, Roy et al. 2008, Collins et al. 2010). Stormwater ponds are one popular option and are an increasingly prominent and conspicuous feature of human settlements (Collins et al. 2010). Yet, we know very little about the ecology and biogeochemistry of stormwater systems. This understanding is central to future applications of these managed ecosystems to enhance urban

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sustainability and their incorporation into urban and global biogeochemical models (Kaye et al. 2006, Cole et al. 2007, Downing 2010).

Small water bodies (<0.02 km^2) have recently been found to play a larger role in global carbon cycles and climate than historically thought (Downing et al. 2006, 2008, Downing 2010). Ponds between 0.001 and 0.01 km^2 make up an important fraction (7–16%) of the global lake land mass (Downing et al. 2006, McDonald et al. 2012). These small systems are generally more active, with greater greenhouse gas emissions and carbon sequestration rates per area, than larger lakes (Tranvik et al. 2009, Downing 2010). Stormwater ponds are small bodies of water, which can occur at similar densities in cities (0.14–0.99 pond/km^2) as would be expected based on the global densities of similarly sized ponds (0.07–0.91 pond/km^2, calculated from Eq. 1 in Downing et al. [2006]). In these anthropogenically disturbed watersheds, the dissolved organic matter (DOM) pool is likely altered rapidly to reflect the high rates of in situ microbial metabolism, which could counterbalance watershed carbon inputs and modify the lability of the DOM pool. Little is known, however, about the biogeochemistry of stormwater ponds, although it appears that they are extremely productive and support complex microbial communities (Sommaruga 1995, Chiandet and Xenopoulos 2010). Given the elevated processing rates that are thought to occur in small ponds (e.g., Downing 2010), the global extent of these systems, and the rapid construction of stormwater ponds, these anthropogenically disturbed systems will likely have a disproportionate impact on global carbon cycles. Therefore, understanding the biogeochemical cycles in stormwater ponds is of paramount importance to fully assess their overall function in cityscapes and global significance.

Urban stormwater ponds are often designed as end of the pipe style practices that intercept runoff prior to its discharge into downstream waters (Roy et al. 2008, Collins et al. 2010). Stormwater ponds can vary considerably in structure, encompassing open, permanently wet, episodically dry, planted wetland, and online with stream basins, where each pond can be made up of a series of basins and water inlet and outlet locations (Anderson et al. 2002, Crowe et al. 2007, Collins et al. 2010). Even with this structural variation, ponds are typically engineered to meet flood control requirements and total suspended solids (TSS) load reduction standards. Pond basins are usually built in size to provide a 24–48 h lag phase during a rain event, which allows TSS to settle out of the pond water column prior to discharge (Olding et al. 2004, Gharabaghi et al. 2006). Sediment accumulation is expected to be high, similar to small ponds in agricultural systems (Downing et al. 2008), but stormwater ponds are periodically dredged to maintain their sediment storage capacity (Anderson et al. 2002). Stormwater ponds could thus provide insight into the ecological function of constructed, shallow aquatic systems across agricultural and urban landscapes, which will lead to a better understanding of aquatic ecosystem stability, disturbance response, and organization.

Functional studies of stormwater ponds have generally focused on each pond's ability to retain solids and urban contaminants as well as provide hydrological storage to delay and reduce the magnitude of peak flow during or after storm events (Anderson et al. 2002, Olding et al. 2004, Hancock et al. 2010). TSS levels in stormwater ponds are used widely to assess engineered pond performance and as the main measure of landscape inputs and disturbance in a pond's sewershed (Olding et al. 2004). Hence, from a management perspective ponds are treated mainly as unreactive settling chambers that allow suspended solids and associated materials to clear from the water column. In fact, Collins et al. (2010) surveyed 51 U.S. state officials that, on average, rated TSS as their top stormwater management concern. It appears that little to no consideration of microbial biogeochemical process has been given in these open, wet ponds (Anderson et al. 2002, Olding et al. 2004, Collins et al. 2010). The current stormwater pond management view omits the idea that these high-nutrient, small-pond systems are expected to be especially productive and suffer from conditions typical of eutrophic lake ecosystems (Downing 2010).

Stormwater ponds, consequently, are engineered to funnel terrestrial and urban material into them for retention purposes. High inputs of dissolved materials could nonetheless support high levels of internal production and potentially lead to greater particulate export. TSS-focused management goals place pond performance on particle mass reduction without consideration of this internal production and alteration of particles. As such, a singular TSS focus might lead to faulty management assessment of pond performance. To fully understand the sustainability of constructed ponds in disturbed habitats, the physicochemical environmental and biogeochemical mechanisms that ultimately control the quality and clarity of water released need to be determined. This information will also allow us to better understand the effects of anthropogenically impacted, small ponds on global greenhouse gas emissions, global carbon and nutrient cycles, and downstream freshwater resources.

The present study examined pelagic biogeochemical dynamics of permanently wet stormwater ponds located in southern Ontario, Canada, during late summer. We used univariate linear regression, Pearson bivariate correlation, and structural equation modeling (SEM) to examine direct and indirect relationships between watershed driver indicators, nutrient levels, plankton abundance and biomass, extracellular enzyme activity, and DOM characteristics. Together, these variables comprise a wide range of ecological and limnological processes that encapsulate pelagic microbial biogeochemical cycles. We tested the feasibility of using TSS as a direct predictor of water column nutrient levels and an indirect predictor of plankton stocks. We predict that biologically produced endogenous particles will cause TSS to fit poorly in the SEM as an external driver of pond resources and plankton dynamics. In addition, we hypothesize that DOM characteristics in stormwater ponds are driven by microbial processes, reflecting the biogeochemical functions akin to eutrophic lakes and ponds rather than more watershed influenced streams and rivers.

Methods

Sampling and site description

Duplicated water samples were collected once from 26 stormwater ponds located in three municipalities (Peterborough, $n = 8$; Richmond Hill, $n = 12$; and Whitby, $n = 6$) of southern Ontario, Canada, between 27 August and 3 September 2009. In general, above average rainfall levels were observed across the study region in July and August 2009. Rain events of >25 mm and >10 mm occurred on 21 August and 29–30 August, respectively, across the study region, indicating that ponds had received new freshwater inputs within one week of sampling. These rainfall conditions suggest that ponds were connected or recently connected to the terrestrial catchment (Chiandet and Xenopoulos 2010) during the time of our sampling. Within each municipality permanent wet ponds were selected along a north to south transect. The oldest ponds were built in the mid-1970s and the most recent in 2007. The design and morphological characteristics varied greatly between ponds in this study. As examples, stormwater ponds had 1–3 basins, 1–3 inlets, 1–2 outlets, length to width ratios that ranged from 1.4:1 to 12.5:1, maximum depths that ranged from 0.3 to 2.6 m. Stormwater ponds were located in primarily residentially developed land use areas with human populations ranging from urban to suburban and little to no industrial use (see Plate 1). Additional information on the characteristics of ponds in this region can be found in Chiandet and Xenopoulos (2010) and McEnroe et al. (2013).

Water samples were collected from the center of each stormwater pond using an inflatable rubber raft that was held in place by land-fixed mooring lines. Using a Van Dorn sampler, whole water was collected from 10 to 20 cm below the surface of the water and from 10 to 20 cm above the surface of the sediment. Water samples were transferred to acid-washed, sample rinsed 1-L polypropylene bottles and stored in the dark and on ice until laboratory processing. All samples were processed for direct measurement or storage and later measurement within 24 hours of collection. In situ dissolved oxygen (mg O_2/L), temperature (°C), and specific conductivity (μS/m) measurements were taken at sampling depths using electronic handheld probes (YSI models 55 DO and 30/10 FT; YSI, Yellow Springs, Ohio, USA). In addition, Secchi depth (z_{sd}; cm) was measured at each site.

Physicochemical and microbial measurements

Once in the laboratory, whole water subsamples from each site were allowed to warm to room temperature and their pH determined using an Accumet Basic AB15 meter (Accumet, Pittsburgh, Pennsylvania, USA). Whole water was filtered through precombusted, preweighed 47 mm diameter 0.7-μm GF/F (Whatman, Mississauga, Ontario, Canada) filters. After passing a known volume through each filter, GF/F filters were dried in an oven at 60°C until constant mass and TSS concentration (mg/L) was determined. The <0.7-μm filtrate was then filtered through a Milli-Q rinsed 0.2-μm polycarbonate membrane filter (Millipore, Billerica, Massachusetts, USA) and the filtrate was used for dissolved organic carbon (DOC), total dissolved nitrogen (TDN), DOM characterization, total dissolved phosphorus (TDP), nitrite, and nitrate analyses. Whole water total phosphorus (TP), TDP, nitrite, and nitrate samples were stored frozen at −20°C in polypropylene bottles until analysis. Samples for DOM, DOC, and TDN were stored at 4°C in precombusted, sample rinsed amber Boston round bottles. Throughout the paper DOM is used when describing optical characteristics of the carbon pool and DOC when describing carbon concentration.

DOC (mg C/L) and TDN (μg N/L) were measured by combustion after acidification using an OI Aurora TOC analytical analyzer (College Station, Texas, USA) with an external nitrogen detector. Nitrite (μg N/L) was measured following the diazotization method from filtered water; nitrite and nitrate were measured as NO_2 after water was passed through a cadmium-reduction column; and nitrate calculated as the difference between $NO_2 + NO_3$ and NO_2 measurements (Wetzel and Likens 2000). TDP and TP (μg P/L) were measured using the molybdate-blue color reagent method (Wetzel and Likens 2000) after autoclaving for 30 minutes at 121.5°C in the presence of 1.7% final concentration persulfate.

Chlorophyll *a* (CHL; μg/L), a measure of phytoplankton biomass, was extracted from particles collected on 25 mm diameter GF/F filters using 95% ethanol incubated in the dark at 4°C for 24 h. Extracts were measured as fluorescence and converted to concentration (μg chl/L) using spinach extract standard and correcting for filtration volume. Free-living heterotrophic bacteria (TBAC; $\times 10^9$ cells/L) and nano- and picophytoplankton (PHYTO; $\times 10^6$ cells/L) abundance was determined by flow cytometry (Beckman Coulter Cytomics FC500; Mississauga, Ontario, Canada). Bacteria were stained with SYBR Green I in the presence of potassium citrate and grouped as low and high nucleic acid (LNA and HNA, respectively) bacteria based on side scatter and relative intensity of NA fluorescence (Jochem 2001). Phytoplankton were enumerated and grouped based on photosynthetic pigment autofluorescence and relative cell size into cyanobacteria (CYANO) and eukaryotic algae (EUK) populations. All cell counts

TABLE 1. Comparison of the seven PARAFAC (parallel factor analysis modeling) components generated in this study with those of published works.

Component	Excitation peak (nm)	Emission peak (nm)	Reference 1	2	3	4	5	Description
C1	260 (360)	482	C7	C4	C1	C1	C1	ubiquitous humic-like
C2	<250 (310)	420 (388)	C10	C3	C2	C3	C3	terrestrial humic-like
C3	<250	440 (468)	C2	C1		C2		terrestrial humic-like
C4	285 (440)	536	C5		C6	C5	C2	soil fulvic-like
C5	360 (260)	424	C9		C4			microbial humic-like
C6	<250 (285)	386	C12	C6		C4	C6	microbial humic-like
C7	280	342 (318)	C8, C13	C7, C8	C5	C7, C8	C4, C8	protein-like

Notes: Primary and, when present, secondary (in parentheses) excitation and emission peaks are given with their suggest source and chemical identity. References are: (1) Cory and McKnight (2005), (2) Stedmon and Markager (2005), (3) Williams et al. (2010), (4) Yamashita et al. (2010), (5) Petrone et al. (2011).

were converted to concentration using flow weight calibrated flow rates and sample measurement time.

Particulate carbon (PC), nitrogen (PN), and phosphorus (PP) concentrations were determined from particles collected onto precombusted 25 mm diameter GF/F filters. Filters were collected in duplicate. For PC and TN, whole filters were compressed inside tin squares and measured by combustion with a CN elemental analyzer (Elementar vario EL III; Palo Alto, California, USA). PP filters were measured in duplicate colorimetrically as free P following persulfate digestion.

Extracellular enzyme activity (EEA) potentials were determined for alkaline phosphatase (AP), leucine-aminopeptidase (AM), and β-glucosidase (βglu) using fluorogenic model substrate analogs (Williams et al. 2012). EEA was measured in the evening on the day of sample collection. Due to logistical constraints, however, EEA could not be determined for Richmond Hill stormwater ponds. For each model substrate, micro-well kinetic assays were incubated at four model substrate concentrations in quadruplicate for four to six hours, depending on substrate. One replicate was sacrificed initially by adding NaOH-glycine buffer to adjust the pH to 10.2. At the end of incubation, buffer was added to the active samples and fluorescence was measured with a BioTek FLx800TB computer-controlled plate reader (BioTek, Winooski, Virginia, USA). Initial fluorescence was subtracted from final fluorescence; fluorescence intensity was converted to concentration using end-product standard curves; and then data were fit to the Michaelis-Menten kinetic model to generate activity potentials (V_{max}).

Optical DOM characteristics

DOM UV-visible absorbance and fluorescence characteristics were determined for Richmond Hill and Peterborough stormwater ponds. Light absorbance was measured from 800 to 230 nm using a lambda 25 spectrophotometer (Perkin Elmer, Waltham, Massachusetts, USA). Molar absorptivity (ε280) was calculated by dividing the absorbance at 280 nm (cm^{-1}) by DOC (μmol C/L). Fluorescence excitation emission matrix (EEM) were measured using a Cary Eclipse fluorometer (Varian, Santa Clara, California, USA) set to scan from 230 to 500 by 5 nm excitation and 270 to 600 by 2 nm emission with a bandwidth of 5 nm and at a scanning interval of 0.25 seconds. EEMs were corrected fully for inner filter effects, Milli-Q background, and instrument bias (Murphy et al. 2010). Corrected EEM fluorescence was converted to Raman units using the area under the Milli-Q scatter peak at 350 nm excitation. From select regions of each EEM, the β:α ratio (freshness index; Wilson and Xenopoulos 2009, Fellman et al. 2010), a humification index (HIX; Ohno 2002), and the fluorescence index (FI; McKnight et al. 2001) were calculated.

Parallel factor analysis (PARAFAC) modeling was used to extract unique components from the EEMs (Stedmon and Bro 2008). PARAFAC was performed using a larger data set of 971 EEMs, which was composed of lake, stormwater pond, stream, and river DOM samples. Prior to modeling, EEMs were trimmed to 250–500 excitation and 300–600 emission, first-order scatter was removed, and outlier EEMs were deleted. The PARAFAC model was validated using split-half analysis and Tucker congruence. From this data set, a valid seven-component model was produced (Table 1; Appendix). C1 to C3 were indicative of terrestrial humic-like DOM features. C4 had a spectrum similar to soil fulvic-like DOM. C5 and C6 were most similar to microbial humic-like DOM. C7 was a protein-like component with a spectral signature that includes both tyrosine- and tryptophan-like optical properties.

Data analysis

Prior to statistical analysis, all data were log- or square-root-transformed to better meet the assumptions of normality and equal variance. Pearson's correlation was used to explore bivariate relationships between variables and create a correlation, sample size, mean, and standard deviation table for use with structural equation modeling (SEM). Univariate linear regression was used to determine environmental and plankton standing stock controls on EEA. Nonmetric multidimensional scaling (MDS) and analysis of similarity (ANOSIM) were used to explore multivariate resemblance between municipalities and sampling location.

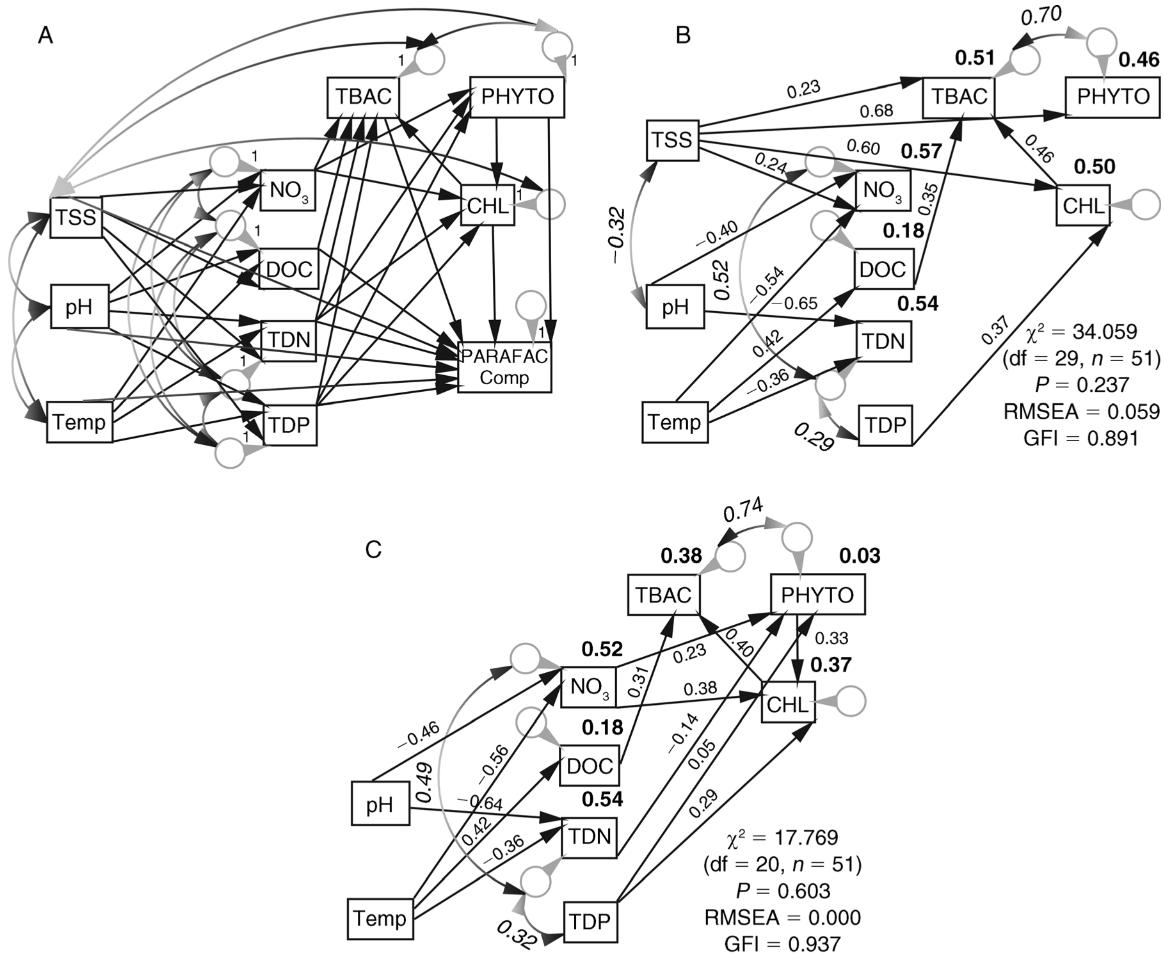

FIG. 1. (A) Hypothesized structural equation model (SEM), (B) best SEM model with total suspended solids (TSS) as an independent variable, and (C) best non-TSS SEM model for the complete data set. Only significant relationships ($P < 0.05$) between variables are included in models B and C. Italic numbers are correlation coefficients, bold numbers are regression coefficients for dependent variables, and normal type numbers are standardized regression weights. Gray outlined circles and arrows with unity coefficient indicate error terms in SEM. See Table 2 for physicochemical terms; other abbreviations are: CHL, chlorophyll *a* concentration; TBAC, total free-living heterotrophic bacteria; PHYTO, nano- and microphytoplankton; PARAFAC, parallel factor analysis modeling; RMSEA, root mean squared error of approximation; GFI, goodness-of-fit index.

Structural equation modeling (SEM)

SEM was used to demonstrate complex pelagic biogeochemical pathways present in stormwater ponds (Schumacker and Lomax 2010). A hypothetical regression SEM model that allowed direct and indirect paths and covariance between select variables and/or variable error was designed using observed variables measured in our study (Fig. 1A). The model was set up in three tiers: (1) watershed influenced (TSS, pH, and temperature), (2) resources (NO_3, TDN, TDP, and DOC), and (3) plankton (TBAC, CHL, and PHYTO). Variables were included in the model based on their importance in pelagic limnological processes and the availability of data. For the full data set ($n = 51$), this hypothesized model with and without TSS was then further restricted by stepwise removal of insignificant ($P > 0.05$) path relationships and covariances. TSS was intentionally included and removed to determine the soundness of using TSS as an externally controlled indicator of pond function. Next, the non-TSS SEM, which appeared to be the most conceptually appropriate model, was extended by adding PARAFAC components as a fourth tier of dependent variables. The DOM SEM was performed on a reduced data set ($n = 33$), which excluded the municipality of Whitby because of missing DOM data. Chi square, goodness-of-fit index (GFI), and root mean squared error of approximation (RMSEA) were used to evaluate the model fit criterion. Chi-square $P > 0.05$, GFI > 0.90, and RMSEA < 0.08 suggested that modeled covariance matrix was acceptable and similar to that of the original samples (Schumacker and Lomax 2010). SEM was performed by maximum likelihood estimation with PASW Statistics and Amos 18 (IBM SPSS, New York, New York, USA) software.

TABLE 2. Physicochemical data for 26 stormwater ponds located in three municipalities of southern Ontario, Canada.

Variable	Mean ± SD	Range
Length to width ratio	4.0 ± 2.5	1.4–12.5
Maximum depth, z_m (cm)	120 ± 70	30–260
Secchi disk depth, z_{sd} (cm)	56 ± 36	10–150
Temperature, temp (°C)	19.6 ± 2.2	16.0–24.8
pH	7.93 ± 0.54	7.16–9.66
Dissolved oxygen (mg O_2/L)	9.1 ± 3.9	1.31–16.86
Specific conductivity (μS/m)	464 ± 351	136–1864
Total suspended solids, TSS (mg/L)	27.4 ± 27.9	1.0–128.8
Total phosphorus (μg P/L)	80.1 ± 46.5	14.5–202.1
Total dissolved phosphorus, TDP (μg P/L)	21.0 ± 13.1	7.7–97.2
Dissolved organic carbon, DOC (mg C/L)	5.5 ± 1.5	3.6–10.7
Total dissolved nitrogen, TDN (μg N/L)	610 ± 302	240–1720
Nitrite (μg N/L)	9.9 ± 12.6	bdl–52.3†
Nitrate (μg N/L)	189 ± 238	1.1–1156.4
molar TDN : TDP ratio	73.1 ± 36.3	19.6–155.4

† Below detection limits (bdl).

RESULTS

Stormwater pond nutrient concentrations and plankton dynamics vary considerably and suggest a wide range in trophic conditions among ponds (Tables 2–4). Water clarity ranged from light reaching the sediment (TSS of a few milligrams/L) to ponds with z_{sd} of tens of centimeters (TSS > 50 mg/L). The DOM pool was composed of moderately humic, low aromatic, terrestrial, and more recently produced microbially derived forms (Tables 1 and 4). The microbial humic-like C6 was the most abundant PARAFAC component followed by a range of terrestrial humic-like components (C1, C2, and C3) and the protein-like C7 (Table 4). In the nano- and picophytoplankton, CYANO tended to numerically dominate, but were much more variable than the EUK population (Table 3). CHL varied from 1 to 140 μg/L and was correlated weakly with PHYTO ($r = 0.38$, $P = 0.006$), suggesting that micro- and macro-sized phytoplankton made up much of the total biomass. On average, LNA bacteria were more abundant than HNA, although there was a strong positive correlation between each group ($r = 0.70$, $P < 0.001$). The percentage of HNA bacteria was weakly and positively correlated with CHL and dissolved nutrient levels. Overall, stormwater ponds did not differ by municipality (global $R = 0.05$, $P = 0.131$), but there was some dissimilarity between near surface and bottom waters across all ponds (global $R = 0.13$ $P = 0.002$; Fig. 2).

TABLE 3. Plankton data for 26 stormwater ponds located in three municipalities of southern Ontario, Canada.

Variable	Mean ± SD	Range
Chlorophyll *a* (μg chl/L)	49.5 ± 38.2	1.0–140.4
<20-μm-sized eukaryotic algae ($\times 10^6$ cells/L)	21.5 ± 19.6	0.5–78.6
<20-μm-sized cyanobacteria ($\times 10^6$ cells/L)	130.9 ± 156.4	6.8–816.7
Heterotrophic bacteria ($\times 10^9$ cells/L)	0.62 ± 0.41	0.10–2.06
High nucleic acid bacteria (%)	40 ± 13	14–64
Particulate C (mg C/L)	3.46 ± 2.38	0.30–10.12
Particulate N (μg N/L)	711 ± 461	92–1773
Particulate P (μg P/L)	73 ± 45	11–188
Particulate molar N:P ratio	22.9 ± 9.1	8.7–41.7
Alkaline phosphatase activity† ($nmol \cdot L^{-1} \cdot h^{-1}$)	216 ± 192	37–749
Aminopeptidase activity† ($nmol \cdot L^{-1} \cdot h^{-1}$)	106 ± 114	24–602
β-glucosidase activity† ($nmol \cdot L^{-1} \cdot h^{-1}$)	11 ± 15	bdl–71‡

† EEA potentials were not determined for Richmond Hill stormwater ponds due to logistical constraints that prevented timely return of kinetic samples to the laboratory.
‡ Below detection limits (bdl).

TABLE 4. Dissolved organic matter characteristics for 17 stormwater ponds located in two municipalities (Richmond Hill and Peterborough) of southern Ontario, Canada.

Variable	Mean ± SD	Range
ε280	177 ± 38	121–259
β:α ratio	0.82 ± 0.04	0.73–0.92
HIX	0.85 ± 0.03	0.79–0.90
FI	1.42 ± 0.03	1.37–1.49
PARAFAC C1 (%)	12.4 ± 1.6	8.6–14.8
PARAFAC C2 (%)	10.9 ± 3.2	3.0–16.9
PARAFAC C3 (%)	19.8 ± 2.1	16.0–24.1
PARAFAC C4 (%)	3.7 ± 0.7	2.0–4.8
PARAFAC C5 (%)	5.2 ± 1.1	2.6–6.6
PARAFAC C6 (%)	39.4 ± 5.3	25.9–51.7
PARAFAC C7 (%)	8.5 ± 2.4	4.9–13.6

Note: Abbreviations are: ε280, molar absorptivity; β:α ratio, freshness index; HIX, humification index; FI, fluorescence index; PARAFAC, parallel factor analysis modeling.

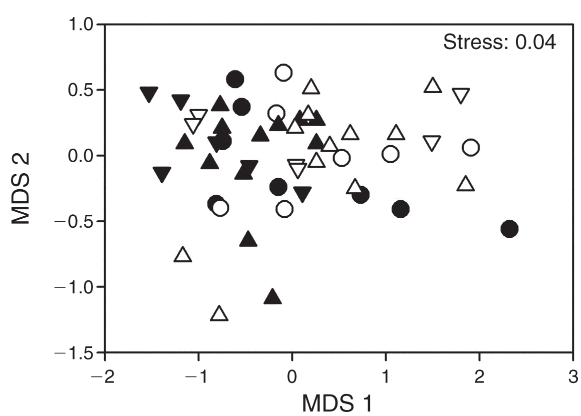

FIG. 2. Nonmetric multidimensional scaling plot (MDS) of environmental and plankton variables measured near the surface (open symbols) and bottom (solid symbols) of stormwater ponds in the municipalities of Peterborough (circles), Richmond Hill (up-triangles), and Whitby (down-triangles), Ontario, Canada. Analysis of similarity results indicate that the multivariate data set was similar among municipalities (global $R = 0.05$, $P = 0.131$), with some dissimilarity between sampling depths (global $R = 0.13$, $P = 0.002$).

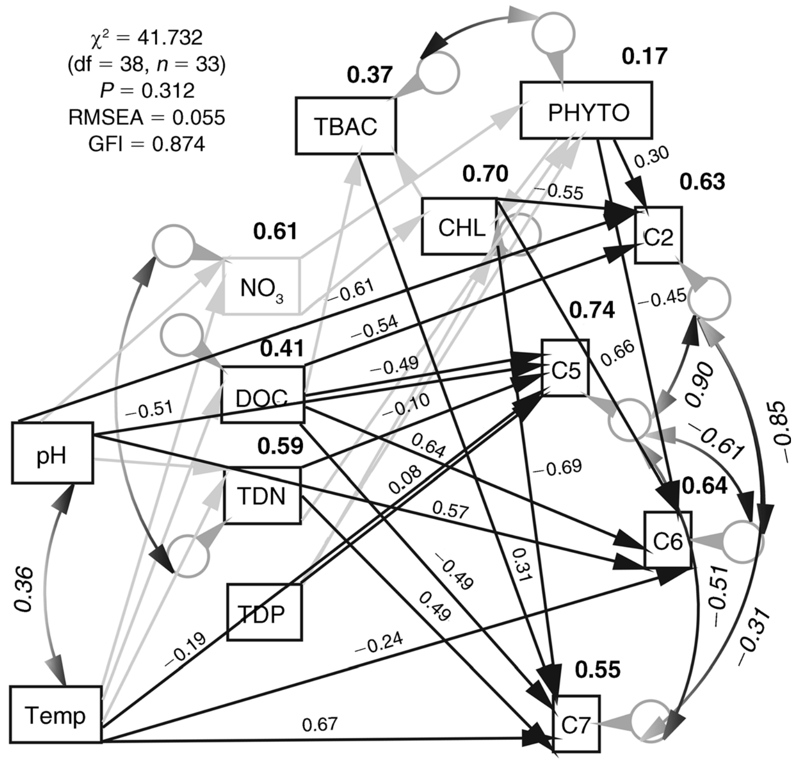

FIG. 3. SEM model incorporating dissolved organic matter (DOM) characteristics into the base non-TSS SEM model (Fig. 1C). PARAFAC model components C2 and C5–C7 are shown in boxes (see Table 1). For simplification, C1 and C3 were omitted from the SEM because they covaried strongly with C2. C4 was omitted because of its low relative abundance among stormwater ponds. Base model weights are not displayed, and paths are displayed in grayscale. Only significant relationships ($P < 0.05$) between variables are included in the model. Italic numbers are correlation coefficients, bold numbers are regression coefficients for dependent variables, and normal-type numbers are standardized regression weights. See Fig. 1 and Table 2 for abbreviations.

Pond maximum depth and length to width ratio, which were expected to function as watershed-influenced variables, did not correlate with the variables measured in the data set and were not considered in the SEM. The hypothesized SEM model without DOM (Fig. 1A) fit the data relatively well (chi-square $P = 0.46$, GFI = 0.971, RMSEA < 0.01), but not all path relationships were significant and a negative regression coefficient was produced for PHYTO, suggesting that some paths were incorrect. With stepwise removal of insignificant regression paths, it became clear that covariance pathways between TSS and the plankton were negatively impacting model estimates and the SEM was adjusted to allow TSS to directly predict these variables (Fig. 1B). The final TSS model was able to explain 51%, 46%, and 50% of the variation in TBAC, PHYTO, and CHL, respectively. TSS, however, was the sole predictor of PHYTO and the dominant weight for CHL, suggesting that much of the suspended solids in the ponds were produced autochthonously. TSS did not act as a useful predictor of watershed inputs and dissolved nutrients.

When TSS was removed from the model (Fig. 1C), the overall predictive power of the SEM was significantly reduced, but the framework better matched the structural organization of pelagic microbial systems (e.g., interactive links between nutrients, DOC, bacteria, and phytoplankton; Jansson et al. 2000). At the front end of the model, temperature and pH explained ~50% of the variation in N but only a small amount of the variation in DOC and could not predict TDP. Direct relationships from NO_3, TDP, and PHYTO explained 37% of the variation in CHL (Fig. 1C). Direct relationships from DOC and CHL with indirect links to NO_3 and TDP explained 38% of the variation in BACT. By removing TSS, the SEM model structure better mimed the pelagic biogeochemical cycles, suggesting feedback loops between bacteria, phytoplankton, and the resource pool.

The non-TSS SEM was then extended to include DOM characteristics for C2, C5, C6, and C7, C1, C2, C3, ε280, and HIX strongly positively correlated with each other and of these only C2 was included in the model. C4 was the least abundant component and not included in the model. The DOM SEM had a reduced sample size of 33 but the model fit was not significantly different than the full sample model (Fig. 1C), although more variance could be explained by the relationships in

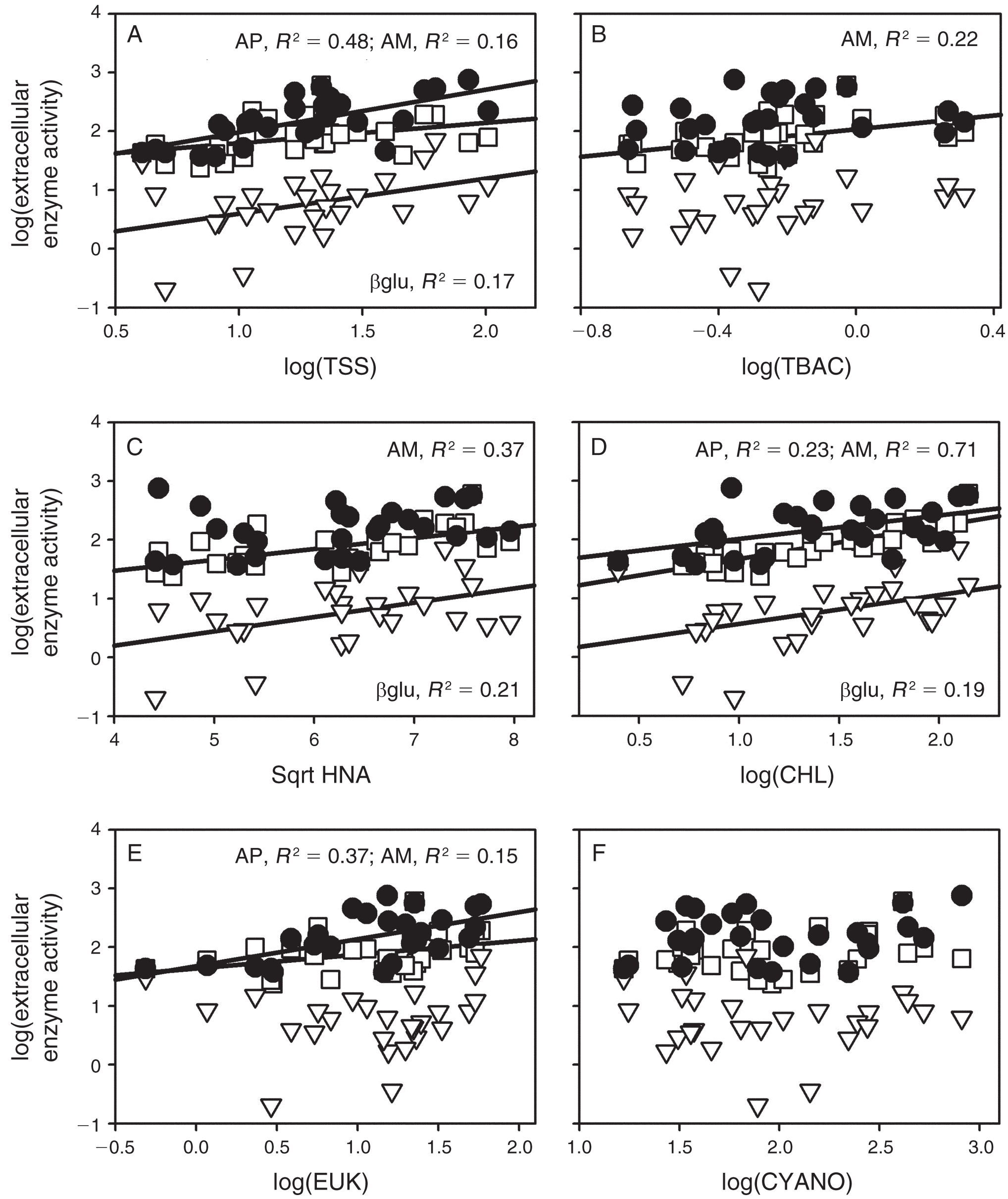

FIG. 4. Relationships between log-transformed values for extracellular enzyme activity potentials (originally measured as nmol·L^{-1}·h^{-1}) for alkaline phosphatase (AP, circles), aminopeptidase (AM, squares), and β-glucosidase (βglu, triangles) and plankton groups. Log-transformed values for the plankton groups were measured as follows: TSS (total suspended solids), mg/L; TBAC (total bacteria), $\times 10^9$ cells/L; CHL, μg/L; EUK, $\times 10^6$ cells/L; CYANO, $\times 10^6$ cells/L; HNA (square-root-transformed), %. Regression coefficients and model fit lines are presented only for significant relationships ($P < 0.05$).

the reduced data set (Fig. 3). The DOM SEM model supported complex networks between physical factors, nutrients, the plankton, and DOM characteristics, explaining 55–74% of the variability in the PARAFAC components. For example, C7 (4.9–13.6% of the DOM pool) was negatively weighted by CHL and DOC but positively weighted by TBAC, TDN, and temperature. C6 was positively associated with factors that correspond to pelagic productivity. This suggested that the dominance of C6 across ponds was due to autochthonous production rather than through transformation of terrestrial material.

As with the other variables, EEA potentials determined in Peterborough and Whitby stormwater ponds varied greatly among ponds (Table 3). CHL and TSS (Fig. 4) and dissolved and particulate nutrients (not shown) were significant positive predictors of all EEA potentials. EUK and %HNA were also positively associated with APA and AMA, but CYANO did not significantly relate to EEA (Fig. 4). When standardized to account for these cell or biomass relationships (data not shown), TBAC-specific AMA correlated positively with TDN ($r = 0.81$, $P < 0.001$), TDP ($r = 0.41$, $P = 0.034$), and PN ($r = 0.47$, $P = 0.013$). TBAC-specific APA correlated only with TDN ($r = 0.46$, $P = 0.016$). CHL-specific AMA correlated negatively with PC ($r = -0.57$, $P = 0.002$), PN ($r = -0.57$, $P = 0.002$), and PP ($r = -0.50$, $P = 0.008$). CHL-specific APA correlated negatively with PN ($r = -0.38$, $P = 0.049$) and TDP ($r = -0.41$, $P = 0.036$). Although limited to Peterborough samples, microbial-like DOM characteristics correlated with normalized EEA. TBAC-specific AMA and APA tended to positively relate to C5 and CHL-specific APA related negatively to C6 and positively to C7.

Discussion

A central focus of urban stormwater management is the retention and storage of total suspended solids (Olding et al. 2004, Collins et al. 2010). While this focus has a well-developed rationale (e.g., development and human activities disturb soils and increase erosion), we found that TSS did not strongly predict pond nutrient concentrations, suggesting that TSS, in and of itself, was not useful as a general measure of external pond nutrient loading. In addition, by focusing on TSS removal, internal pond biogeochemistry and its impact on global climate and carbon cycles are largely omitted from urban design and management practices. We demonstrate that stormwater ponds harbor complex and intense internal processes that seem to allow the development of diverse pond ecologies. DOM characteristics suggest stormwater ponds have a distinct carbon cycle relative to neighboring ecosystems that could have a significant impact on the global carbon emissions from inland waters. The DOM in stormwater ponds largely reflected the interplay of the hydrology, physical environment, light, nutrient levels, allochthonous organic inputs, and autochthonous productivity. During the time of our study, a clear structural scaffold to the biogeochemistry of stormwater ponds was present, which helps explain the fundamental processes of small pond ecosystems embedded in human impacted landscapes.

TSS concentration reduction from inflowing to the pond basin to outflowing waters is used as one performance measure of stormwater pond function (Olding et al. 2004, Gharabaghi et al. 2006). TSS loads have also been linked to impervious surface area in the watershed and other anthropogenic land activities and associated inputs (Paul and Meyer 2001, Walsh et al. 2005*b*). This externally driven notion of TSS, however, is somewhat oversimplified when used for management because this view does not consider, aside from resuspension, allochthonous production of particles within each pond. Small nutrient-rich ponds should be productive (Downing 2010) and, thus, the active biogeochemical cycles within these ponds likely complicate the source of TSS in constructed ponds. Our SEM did not support indirect relationships between TSS and the plankton via resource levels, even when covariance was allowed between TSS and plankton (Fig. 1A). TSS only fit well when allowed to directly predict plankton levels in the SEM (Fig. 1B). Conceptually, this pattern does not work as TSS should not drive plankton but rather act as a surrogate for overland resource inputs to stormwater ponds, which then shape in part plankton dynamics. These findings suggest that using TSS reduction as a sole benchmark of engineered pond performance (see Collins et al. 2010) might fall short of providing an independent assessment of a pond's ability to retain watershed inputs.

Stormwater pond water chemistry and phytoplankton biomass vary widely between ponds (Tables 2 and 3; Chiandet and Xenopoulos 2010, Sanchez et al. 2011; McEnroe et al. 2013). Stormwater ponds tend to be more variable than natural ponds with low levels of anthropogenic impacts (Chiandet and Xenopoulos 2010), but as variable as eutrophic lakes (Sommaruga 1995, Sanchez et al. 2011) and restored and natural wetlands in human impacted watersheds (Stewart and Downing 2008, Hossler et al. 2011). Among natural and constructed urban ponds, although limited information is available, complex microbial food webs have been observed with multiple grazer and prey size classes (Sommaruga 1995, Sanchez et al. 2011, Van Meter et al. 2011). Though planktivore stocks were not determined in our study, non-TSS SEM suggests a significant role for a stormwater pond microbial food web. This was evident through covariance between BACT and PHYTO groups and BACT being driven by DOC and CHL, which served as a conduit for nutrient flow (Fig. 1C).

The structure of pond microbial food webs and nature of biogeochemical cycles can depend on the water residence time of the system and the quality and quantity of external chemical inputs (Sommaruga 1995, Van Meter et al. 2011). During dry periods ponds are isolated, internally driven systems but during wet periods they are open to the watershed and the water column can turn over rapidly (Olding et al. 2004, Chiandet and Xenopoulos 2010). It is reasonable to suspect that during wet periods, ponds should receive more terrestrial derived DOM, which could be diluted with rainfall, and transition toward microbial-like and/or photodegraded DOM during dry periods. The high contribution of microbial-like, low aromatic (e.g., low $\varepsilon 280$), and recently produced DOM would then suggest that ponds were sampled during a dry period in our study. However, rain events capable of producing stormwater pond flows (>10 mm within 24 hours) occurred in the week prior to our sampling, though pond hydrology was not monitored directly. In this case, the late summer conditions of these anthropogenically impacted systems might have influenced pond biogeochemical dynamics more so than hydrologic connectivity

PLATE 1. Researchers carry their vessel down a vegetated slope into a residential stormwater pond located in Whitby, Ontario, Canada. Photo credit: Alison McDonald.

with the landscape. These patterns might change significantly with season. Ponds might reflect better their terrestrial connections during the snow melt and in early spring. These seasonal and hydrology dynamics should, thus, be considered in future studies of engineered or constructed ponds and their biogeochemistry.

Stormwater ponds predominately receive water from surface flow drainage from highly urbanized terrestrial catchments, yet their DOM character during late summer suggested a prevailingly microbial source with smaller but important terrestrial constituents. While watershed features such as buildings, parking lots, roads, lawn surfaces, and drainage infrastructure can have mixed impacts (e.g., some increase and some decrease) on DOC inputs (Paul and Meyer 2001, Walsh et al. 2005*a*, *b*), how this affects DOM quality has not been examined. We found that ponds having low DOC concentration also had higher levels of terrestrial-derived PARAFAC components (C2 in Fig. 3). This pattern is opposite to that observed in developed and mixed land use streams in the area, which have positive relationships between DOC and terrestrial attributes of the DOM pool (Williams et al. 2010). In contrast to streams, stormwater pond DOC and CHL were positive predictors of the most abundant PARAFAC component (C6), suggesting that much of the DOC in these systems is produced autochthonously (Table 4, Fig. 3). One of the least abundant components, C5, was predicted by all physical and resource variables in the SEM and tended to correlate positively with terrestrial derived DOM (Fig. 3). Positive, bivariate correlates between C5 and BACT-specific EEA suggested that C5's presence was associated with microbial transformation of organic matter. In addition, the DOM SEM captured well pathways for microbial production and consumption of the protein-like component, C7, frequently observed in aquatic systems (Fellman et al. 2010, Williams et al. 2010, Petrone et al. 2011).

Ponds with increased connection to the watershed should receive more nutrients and presumably terrestrial inputs than ponds with lower connectivity, yet the stormwater ponds with the most nutrients and presumably most connection with watershed inputs had DOM pools dominated by autochthonous properties. This irregularity held true for particles; ponds with more TSS also had more autochthonously produced particles, which limited greatly the use of TSS as a predictor of overland nutrient inputs (Fig. 1). Hence, stormwater ponds seem to have a distinctive biogeochemistry from what has been reported for other marine and freshwater DOM cycles (Jansson et al. 2000, Williams et al. 2010). Urban landscapes themselves have a unique biogeochemistry as a whole (Kaye et al. 2006), and our results suggest that this holds true at the small scale of urban residential development as well. These findings suggest stormwater ponds function in a manner reminiscent of small constructed agricultural ponds with high rates of internal processing (Downing et al. 2008, Tranvik et al. 2009, Downing 2010). However, to our knowledge the present study is the first to report a DOM response of increased autochthonous material with increased watershed connectivity. The expected pattern found in less impacted ecosystems links terrestrial inputs with higher plant produced and soil (e.g., terrestrial) humic-like DOM and increased heterotrophy (Jansson et al. 2000). Even in urban and agricultural streams, the terrestrial signature of the DOM pool remains strong, though protein- and microbial-like DOM characteristics are relatively more abundant (Wilson and Xenopoulos 2009, Fellman et al. 2010, Williams et al. 2010). Together, our results suggest that stormwater ponds are particularly good reactors in freshwater systems with distinct carbon signatures, which upon discharge could impact carbon cycles of downstream ecosystems (Cole et al. 2007, Tranvik et al. 2009).

At a global scale, stormwater ponds are now placed throughout residential, business, industrial, and transportation landscapes to protect downstream ecosystems and help manage water quality and quantity (Anderson et al. 2002, Roy et al. 2008). We provide a glimpse into the pelagic biogeochemistry and organization in stormwater ponds. We demonstrated that the late summer organic matter pool in stormwater ponds is mainly of an autochthonous nature and that TSS does not function well on its own as a performance predictor. Future work is needed to validate the mechanism by which carbon inputs are taken up, transformed, and buried in these ponds. These mechanisms could be explored by monitoring DOM characteristics from pond inflowing through outflowing water under different seasonal conditions. TSS and possibly other mass reduction based management strategies could fall short of recognizing internal stormwater pond mechanisms that ultimately reveal the broader impacts of these management systems. With further consideration of stormwater pond biogeochemistry, ponds could be designed to meet broader performance goals and their full impact on downstream water bodies and urban footprints could be adequately judged. Based on their density in urbanized landscapes, which is comparable to the global density of similar sized ponds (e.g., Downing et al. 2006), and their high microbial/biogeochemical activity levels, stormwater ponds could play an important role in global climate and carbon cycles, through amplified carbon emission, sequestration, and transformation mechanisms.

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Supplemental Material

Appendix

Seven component PARAFAC model loadings and split-half validation (*Ecological Archives* A023-073-A1).