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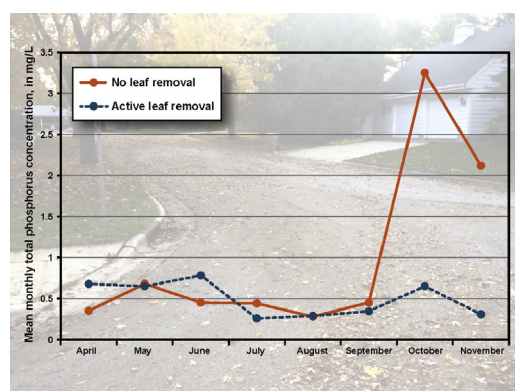
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HIGHLIGHTS

- Leaves are a significant source of phosphorus to urban stormwater.
- Phosphorus and nitrogen were measured in basins with and without leaf removal.
- Nearly 60 percent of the annual phosphorus yield comes from leaf litter in the fall.
- Timely removal of leaf litter can reduce phosphorus concentrations by 80%.
- Leaf removal is one of a few options available to reduce dissolved phosphorus.

GRAPHICAL ABSTRACT



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ABSTRACT

While the sources of nutrients to urban stormwater are many, the primary contributor is often organic detritus, especially in areas with dense overhead tree canopy. One way to remove organic detritus before it becomes entrained in runoff is to implement a city-wide leaf collection and street cleaning program. Improving our knowledge of the potential reduction of nutrients to stormwater through removal of leaves and other organic detritus on streets could help tailor more targeted municipal leaf collection programs. This study characterized an upper ideal limit in reductions of total and dissolved forms of phosphorus and nitrogen in stormwater through implementation of a municipal leaf collection and street cleaning program in Madison, WI, USA. Additional measures were taken to remove leaf litter from street surfaces prior to precipitation events.

Loads of total and dissolved phosphorus were reduced by 84 and 83% ($p < 0.05$), and total and dissolved nitrogen by 74 and 71% ($p < 0.05$) with an active leaf removal program. Without leaf removal, 56% of the annual total phosphorus yield (winter excluded) was due to leaf litter in the fall compared to 16% with leaf removal. Despite significant reductions in load, total nitrogen showed only minor changes in fall yields without and with leaf removal at 19 and 16%, respectively. The majority of nutrient concentrations were in the dissolved fraction making source control through leaf removal one of the few treatment options available to environmental managers when reducing the amount of dissolved nutrients in stormwater runoff. Subsequently, the efficiency, frequency, and timing of leaf removal and street cleaning are the primary factors to consider when developing a leaf management program.

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1. Introduction

Excessive amounts of nutrients in stormwater runoff, such as phosphorus and nitrogen, have long been identified as accelerating the effects of eutrophication in urban streams and lakes (U.S. EPA, 1972; Browman et al., 1979; Schindler, 2006; Smith et al., 2006; Carpenter, 2008; Lusk and Toor, 2014). Unlike an undisturbed terrestrial ecosystem, urban watersheds can dramatically increase the export of phosphorus to receiving waters (Duan et al., 2012). With the conversion of rural to urban landscape comes a proliferation of impervious surfaces creating a directly connected pathway by which pollutants can migrate from source to stream in what has been coined the “urban stream syndrome” (Walsh et al., 2005; Meyer et al., 2005; Wallace et al., 2008). The replacement of natural drainage networks with urban conveyances has dramatically increased streamflows and altered subsidies and fluxes of organic matter creating a complex suite of stressors to downstream receiving waters (Kaushal and Belt, 2012). Duan et al. (2014) recognized the importance of leaf litter in regulating ecological function in headwater forest streams. However, the release of nutrients from leaf litter in hydrologically flashy urban systems is a complex process requiring additional research (Belt, 2012). Increased export of nutrients from the urban landscape to urban lakes and streams can have ecosystem and human health implications by increasing the occurrence of algal blooms which can block sunlight for other aquatic plants, clog the gills of fish and produce toxins that are harmful if ingested. As such, management of nitrogen and phosphorus from urban sources should be considered when developing watershed plans to protect and preserve the ecological function of streams and lakes.

Sources of phosphorus and nitrogen in the urban landscape include anthropogenic (fertilizers, automotive detergents, pet waste) and biogenic (leaves, pollen, grass clippings) materials (Berretta and Sansalone, 2011; Hochmuth et al., 2012). Of these, organic detritus and particulate matter are often considered the primary contributors of nutrients to urban stormwater, especially in areas with high overhead tree canopy (Waller, 1977; Waschbusch et al., 1999). Previous studies have noted the positive correlation between tree canopy and phosphorus and nitrogen loads on streets which vary seasonally and by prevalent tree species (Kalinovsky et al., 2014; Baker et al., 2014). Early research by Cowen and Lee (1973) has shown the concentration of leachable phosphorus from leaves that are subjected to stormwater can vary considerably between tree species. This was also supported by Dorney (1986) who concluded leaf litter was a major source of phosphorus in Milwaukee, WI. Based on laboratory experiments, as much as 9% of total leaf phosphorus leached from leaves within 2 h (Dorney, 1986). Despite past research confirming the high nutrient content of leaves, the potential loading from urban tree canopy is still not fully understood. Using urban tree models, Scheuler et al. (2016) estimated the average load of phosphorus and nitrogen associated with leaf litter in the city of Baltimore to be 2.95 and 28.8 lbs./ac/year, respectively. What is still uncertain, however, is how much of the leaf litter made it to the street gutter where it becomes available for washoff during precipitation events. In a review of studies linking nutrients with plant debris, Hochmuth et al. (2012) concluded that plant debris can be a significant source of nutrients in stormwater. Hochmuth et al. (2012) also noted that the removal of plant debris should be done as soon as possible because stormwater can easily and rapidly extract nutrients from the debris.

While many studies have documented the phosphorus content of leaves and their potential effect on water quality in urban watersheds, few have quantified the potential benefit of their removal on stormwater quality. Templer et al. (2015) estimated reductions in carbon and nitrogen from urban areas in the city of Boston via leaf litter removal during the fall leaf collection period. Their results showed removal of leaves may cause nutrient limitation in vegetation due to diminished nutrient cycling thereby creating spatial heterogeneities of urban ecosystems that are either nitrogen limited or saturated

depending on leaf collection practices; however, the effect of leaf removal on stormwater quality was left unaddressed. Similarly, Kalinovsky et al. (2014) and Law et al. (2008) used material collected by street cleaners to estimate nutrient removal from urban streets. Although they concluded street cleaners were capable of removing an appreciable amount of seasonal organic detritus from streets, their data served only as a proxy for improvements to water quality through nutrient reduction in stormwater runoff. Stack et al. (2013) made a similar conclusion when estimating the nutrient removal benefits of street cleaners, catch basins, and trash nets in Talbot County, MD but also noted additional research was needed to statistically quantify the impact of leaf litter on urban stream nutrient loadings.

Understanding the role of municipal practices such as street cleaning or leaf collection on preventing nutrient release from organic material on impervious surfaces is important in the context of stormwater management (Hobbie et al., 2014). Implementation of structural stormwater control measures (SCMs) may help remove leaves and coarse particulates entrained in stormwater but may do little to remove dissolved nutrients leached from leaves. Furthermore, cities around the Nation are often faced with limited open space available for the construction of new structural SCMs. While the possibility of retrofitting existing areas remains an option for environmental managers, costs may be prohibitive. Improving our knowledge of the potential reduction of nutrients to stormwater through removal of leaves and other organic detritus on streets could help tailor more targeted municipal leaf collection programs.

The purpose of this study was to characterize the potential for a municipal leaf collection and street cleaning program to reduce nutrient concentrations and loads from stormwater runoff. The U.S. Geological Survey, in cooperation with the City of Madison and the Wisconsin Department of Natural Resources, measured concentrations of phosphorus and nitrogen in stormwater from two residential catchments in Madison, WI, USA. One catchment was established as a control in which there was no effort to remove leaf litter and other organic detritus from streets. The second catchment served as the test catchment in which removal of leaf litter was done through a combination of municipal leaf collection, street cleaning, and leaf blowers. Relations were established between nutrient loads from both the control and test catchments during a calibration and treatment period to quantify the effect of leaf removal from streets during precipitation events. This study supports an ongoing effort to identify existing and new methods to reduce nonpoint source pollution from urban areas.

2. Materials and methods

2.1. Site description

This study characterized concentrations of select nutrients in urban stormwater runoff from two residential catchments in Madison, Wisconsin, USA (Fig. 1). The climate in Madison is typical of interior North America, with a large annual temperature range and frequent short-period temperature changes. Months of the year were lumped by season in which leaves were either emerging (spring), mature (summer), or in recession (fall). Spring is defined as April–May, summer as June–September, and fall as October and November, inclusive. Winter months of December through March were not monitored as part of this study. Based on the 30-year normal (1980–2010), annual rainfall for this area is 917 mm of which 25% occurs in the spring, 52% in summer, and 16% in fall (National Oceanic and Atmospheric Administration, 2016). Fig. 2 illustrates measured monthly rainfall during the study period compared to the 30-year normal. Although the fall equinox officially occurs in late September, accumulation of leaf litter does not typically start until shortly after leaf senescence in early October continuing through mid to late November.

Two sites were selected to characterize nutrients in stormwater; the first a 6.47 ha medium-density residential catchment that drained into a



Fig. 1. Location of the control and test catchments with spatial coverage of tree canopy over land and street surfaces.

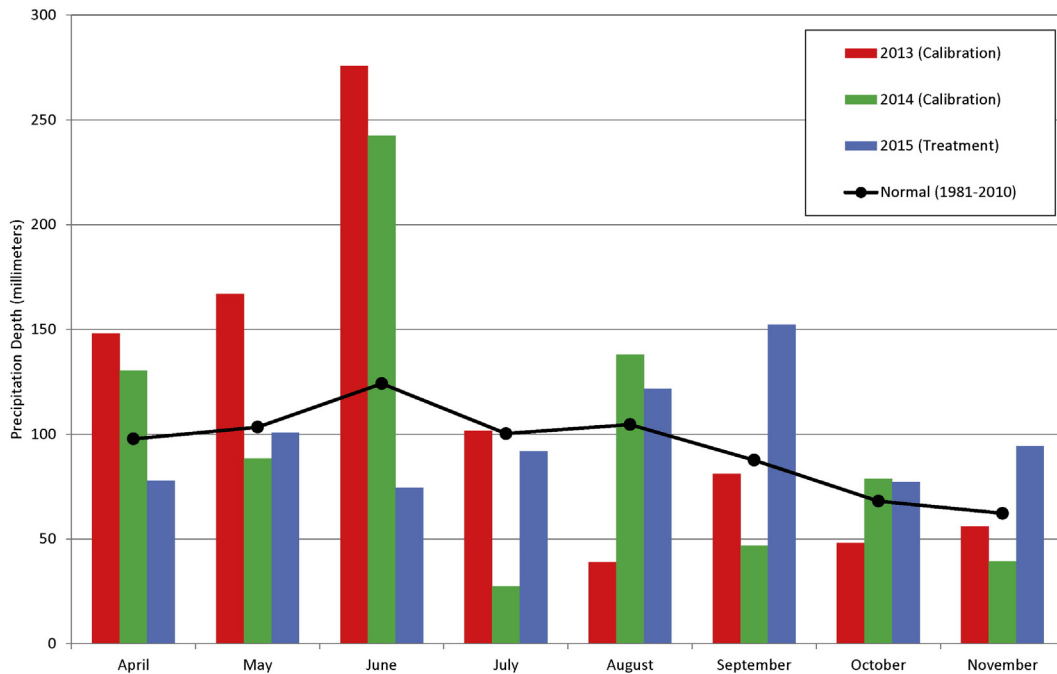


Fig. 2. Monthly precipitation total during the calibration and treatment phase compared to the 30-year normal in Madison, WI. Winter months of December through March were not included in the study.

0.53 m diameter storm sewer, herein referred to as the ‘control’ catchment. The second site collected runoff from 1.21 ha medium-density residential catchment that drained into a 0.38 m diameter storm sewer, herein referred to as the ‘test’ catchment. The curb and guttered streets were approximately 9.75 m wide. There were no catch basins or other storage areas in the storm drain network of either catchment.

The control and test catchments were located within 1.5 km of each other to help reduce variation in storm rainfall patterns (Fig. 1). Selection was based on similarity in physical characteristics, including land use, street condition, overhead tree canopy, topography, and lot size. Despite differences in drainage area, the composition and distribution of source areas were similar (Table 1). The percentage of impervious and pervious surfaces was evenly split with slightly more pervious than impervious (Table 1).

Trees were generally a mix of mature, deciduous hard and softwood species. Estimates of tree canopy were made using a combination of aerial imagery coupled with ArcGIS software and field surveys. A greater percentage of area was covered by tree canopy in the test catchment (64%) than the control (46%). However, the percentage of tree canopy covering streets was the same in each catchment at 17% (Table 1). In addition to geographic location, Fig. 1 shows the spatial extent of tree canopy in each catchment and the portion of canopy extending over street surfaces. >70% of street trees in each catchment were characterized as Norway maple (*Acer platanoides*) or Green Ash (*Fraxinus pennsylvanica*). It should be noted the amount of leachable phosphorus can vary appreciably amongst different tree species. Dorney (1986) reported concentrations of leachable phosphorus from 52 intact tree leaves representing 13 species in Milwaukee, WI ranged from 20 to 411 $\mu\text{g gm}^{-1}$. Therefore, the range of nutrient concentrations reported herein may not be similar to other areas with different tree species.

2.2. Sample collection and measurement of nutrient concentrations

A monitoring station was used to measure flow and collect water samples at the storm sewer outfall of both the control and test catchments. Each monitoring station was equipped with automated stormwater-quality samplers with a sample orifice diameter of approximately 9.5 mm and withdrawal velocity of approximately 0.9 m/s. Low-profile sensors were used to measure water level (calibrated to ± 6 mm) and velocity as a means to compute discharge. Precipitation data were collected by use of a tipping-bucket rain gage calibrated to 0.25 mm per tip. There was no dry weather flow in either the test or control storm drain network.

Sample collection was activated by a rise in water level in the pipe during a precipitation event. Once a water-level threshold was exceeded, typically a depth of 1.2 cm from the pipe floor, the volume of water passing the station was measured and accumulated at 1-minute increments until a volumetric threshold was reached. At that point, a depth-integrated sample arm (DISA) sampler (Selbig et al., 2012) collected a discrete water sample and the volumetric counter was reset. A DISA was used because it collects a water sample from

the entire water column, rather than a single, fixed point thereby limiting concentration bias caused by the stratification of solids in storm sewers (Selbig et al., 2012). The process was repeated until the water level receded below the threshold. All flow-weighted discrete samples collected over the duration of an event hydrograph were combined into a single, composite sample resulting in an event mean concentration (EMC) representing a minimum of 80% of the storm hydrograph. Water-quality samples were typically collected within 24 h after runoff cessation. A Teflon churn splitter was used to composite and split samples into smaller plastic sample containers for delivery to the analytical laboratory. A portion of the composite sample was processed through a 0.45 μm filter for analyses of dissolved constituents. Processed samples were kept in a refrigerator at 4 °C until delivered to the analytical laboratory, usually within 48 h after runoff cessation. Samples were analyzed at the Wisconsin State Laboratory of Hygiene (WSLH), in Madison, Wisconsin, USA. All samples were tested for total and dissolved phosphorus according to USEPA Method 200.7 (USEPA, 2001) and total and dissolved nitrogen according to USEPA Method 353.2 (USEPA, 1993).

2.3. Leaf collection and street cleaning practices

In late September to early October of each year, the city of Madison continuously rotates a fleet of leaf collection vehicles to collect and remove leaf litter and other organic detritus from primarily residential areas. Residents are asked to pile their leaves adjacent to the street to limit excess debris in the street gutter. Upon collection, a vehicle equipped with a modified plow will first transfer any piles of leaves near the curb into the street. The leaves are then pushed into a garbage collection vehicle for removal. A high-efficiency vacuum-assisted street cleaner, similar to that described by Selbig and Bannerman (2007), serviced the area within a few days following leaf collection to remove any residual organic debris from the street and gutter. Leaf collection and street cleaning occurred approximately every 7 days. For the period April through September, weekly street cleaning was the only form of treatment in the test catchment. Leaf collection, in addition to street cleaning, was done in October and November. The control catchment remained without any leaf collection or street cleaning throughout the entire study period.

Despite weekly municipal operations, an appreciable amount of leaves and other organic debris would accumulate on the street surface in a matter of a few hours to a few days. Therefore, in order to characterize a “best case scenario” for municipal operations, USGS personnel were deployed to the test catchment in October and November during the treatment phase of the study to remove all organic detritus from the street prior to a precipitation event. Field crews used high-powered leaf blowers to transfer all debris from the street to an area that was not in the contributing drainage area. While this extra measure of leaf removal exceeds the capabilities of most municipal leaf collection programs, it sets a benchmark for the greatest potential reduction of nutrients in runoff through removal of leaves and other organic detritus from urban streets with high overhead tree canopy.

2.4. Statistical analyses

2.4.1. Paired catchment design

A paired-catchment design was used to help evaluate the effectiveness of leaf collection based on differences in loads of phosphorus and nitrogen in the control and test catchment between calibration and treatment phases of the project. The basis behind the paired catchment approach is that there is a quantifiable relationship between paired water-quality data and that this relationship is valid until a major change (i.e. treatment) is made in one of the catchments (Clausen and Spooner, 1993). At that time, a new relation will develop. The strength of this approach is that it does not require the assumption that the control and test catchments are statistically the same; however, it does

Table 1
Description of source areas and tree canopy in the control and test catchments (rounding applied).

Characteristic	Control	Test
Total drainage area (hectares)	6.47	1.21
Land use (hectares)		
Streets	1.08 (17%)	0.23 (19%)
Driveways	0.39 (6%)	0.05 (4%)
Roofs	1.10 (17%)	0.23 (19%)
Sidewalks	0.33 (5%)	0.04 (3%)
Lawns/open	3.55 (55%)	0.66 (54%)
Other impervious	0.02 (<1%)	0 (0%)
Catchment tree canopy	46%	64%
Street tree canopy	17%	17%

require that the two catchments respond in a predictable manner together and that their relation remains the same over time except for the influence of leaf collection.

The calibration phase occurred in the months of May and September through November in 2013 and April through November in 2014. During this time, paired water-quality samples were collected to develop a relationship between the control and test catchments without leaf collection or street cleaning. In 2015, the treatment phase was implemented in the test catchment which consisted of a leaf collection and street cleaning program (as described in Section 2.3), while the control catchment remained the same. Resulting data were parsed by season (as described in Section 2.1).

Following procedures outlined in Clausen and Spooner (1993), the significance of the relationship between log-transformed paired water-quality data during each phase was confirmed using the analysis of variance (ANOVA, $p = 0.05$). At the end of the treatment phase the significance of the effect of leaf collection and street cleaning was determined using analysis of covariance (ANCOVA) (Clausen and Spooner, 1993). The analysis is a series of steps determining the significance of the treatment regression, the significance of the overall regression which combines the calibration and treatment phase data, the difference between the slopes of the calibration and treatment regressions, and the difference between the intercepts of the calibration and treatment regressions. A change in intercepts but not slopes between the calibration and treatment phase indicates an overall parallel shift in the regression equation. If the treatment regression shifted below that of the calibration phase, the form of treatment (in this case leaf removal) can be considered effective at reducing nutrient loads. No significant change in either the slope or intercept of the treatment regression suggests leaf removal had little to no effect on nutrient loads when compared to the calibration phase. If the results of the ANCOVA test for slope and/or intercept reveal a significant difference between the calibration and treatment regressions, the regression equation representing the calibration period can be used to quantify the degree of load reduction as a result of leaf removal by predicting what average runoff event loads should have been in the test catchment during the treatment phase if leaf removal was not done. The overall reduction due to leaf removal can then be expressed as a percentage change on the basis of the average predicted and observed values during the treatment phase (Clausen and Spooner, 1993).

2.4.2. Computation of seasonal load

Storm event loads were computed by multiplying the EMC by stormwater runoff volumes. For some storm events, EMCs were not determined due to equipment failure, laboratory error, or budgetary constraints. In order to better define the total nutrient load in each study catchment in 2015, estimates of loads for missed storm events were based on predictions using regression-based relations with environmental parameters including Julian day (unitless), leaf area index (unitless), event duration (hours), precipitation depth (inch), 15-minute precipitation intensity (inch/hour), 30-minute precipitation intensity (inch/hour), 60-minute precipitation intensity (inch/hour), 1-day antecedent precipitation depth (inch), 3-day antecedent precipitation depth (inch), event volume (cubic feet), peak discharge (cubic feet per second), preceding dry days (days), cosine of time (hour) and sine of time (hour).

Given the small dataset, the strength of the environmental parameters as predictors of load was first evaluated using Gradient Boosting Regression Trees (GBRT) (Fienen et al., 2016). GBRT is an ensemble technique in which a group of weak predictors - predictors that perform a little better than a random guess (Hastie et al., 2009) - have strong performance when aggregated together. Results of the GBRT analysis were considered acceptable when calibration and validation correlation coefficients were >0.90 and 0.40 , respectively. The GBRT models, built from the environmental parameters, were then used to make forecasts in cases where the environmental parameters were measured but for

which loads were not measured. For months that did not satisfy GBRT validation criteria, an arithmetic mean of measured loads in each corresponding month was used.

3. Results

A total of 71 paired samples were collected over the study period, with 40 and 31 paired samples representing the calibration and treatment phases, respectively. A complete list of paired concentrations, loads, and measured weather parameters can be found in Appendix 1 in the supplemental online material (also available in Selbig, 2016).

3.1. Patterns in mean monthly nutrient concentrations in stormwater by study phase

Fig. 3 shows mean monthly concentrations of measured nutrients from April through November in the control and test catchments during the calibration and treatment phase. Regardless of catchment or phase, the overall pattern of mean monthly concentrations was similar; both the total and dissolved forms of nitrogen were greater than phosphorus. Mean monthly concentrations of phosphorus were generally lowest in summer and highest in fall. Nitrogen was similarly lowest in summer but highest in spring.

3.1.1. Calibration phase

Mean monthly concentrations in both the control and test catchments showed little variation from April through September with only minor increases measured during the month of May (Fig. 3), likely due to the presence of new blossoms, seeds and pollen from emerging vegetation. As leaves matured by early June, concentrations of phosphorus were lower and remained relatively steady through September. During this period of leaf maturation, sources other than seeds and leaves, such as street dirt and grass clippings, were likely the primary contributor to phosphorus and other nutrients in runoff. The maximal amounts of nutrients measured in runoff occurred from senescent leaf litter in the fall where appreciable gains in concentration were observed in October, a period of time when the amount of leaf litter intensified (Fig. 3). The largest gains were observed in dissolved phosphorus with a 979 and 933% increase over average summer (June through September) concentrations in both the control and test catchments, respectively. Nitrogen similarly increased but to a lesser degree. Total phosphorus increased by 702 and 425%, dissolved nitrogen at 91 and 18%, and total nitrogen at 69 and 13% in the control and test catchments, respectively. As fall advanced, fewer leaves were deposited thus reducing sources of nutrients. With the exception of nitrogen in the test catchment during the calibration phase, nutrient concentrations in November declined from October levels but remained above those measured during spring and summer months. This pattern was observed in the control catchment for both study phases as well as the test catchment during the calibration phase, indicating the monthly distribution of nutrients without a leaf collection program was generally repeatable both spatially and temporally. The pattern observed in Fig. 3, especially for phosphorus, suggests the mass of organic detritus accumulated on street surfaces may be correlated to the concentration and partitioning of phosphorus entrained in runoff. While this was qualitatively observed in the field, additional information quantifying the mass of organic detritus on streets is needed to validate this statement.

Nitrogen, unlike phosphorus, appeared to be more erratic and less predictable. Similar to phosphorus, mean monthly concentrations of total and dissolved nitrogen were generally lowest during summer months with higher concentrations observed in May and October (Fig. 3). In contrast to phosphorus, the magnitude of increase in October was less, with concentrations higher than summer levels but lower than those observed in spring. It is unclear why the month of November

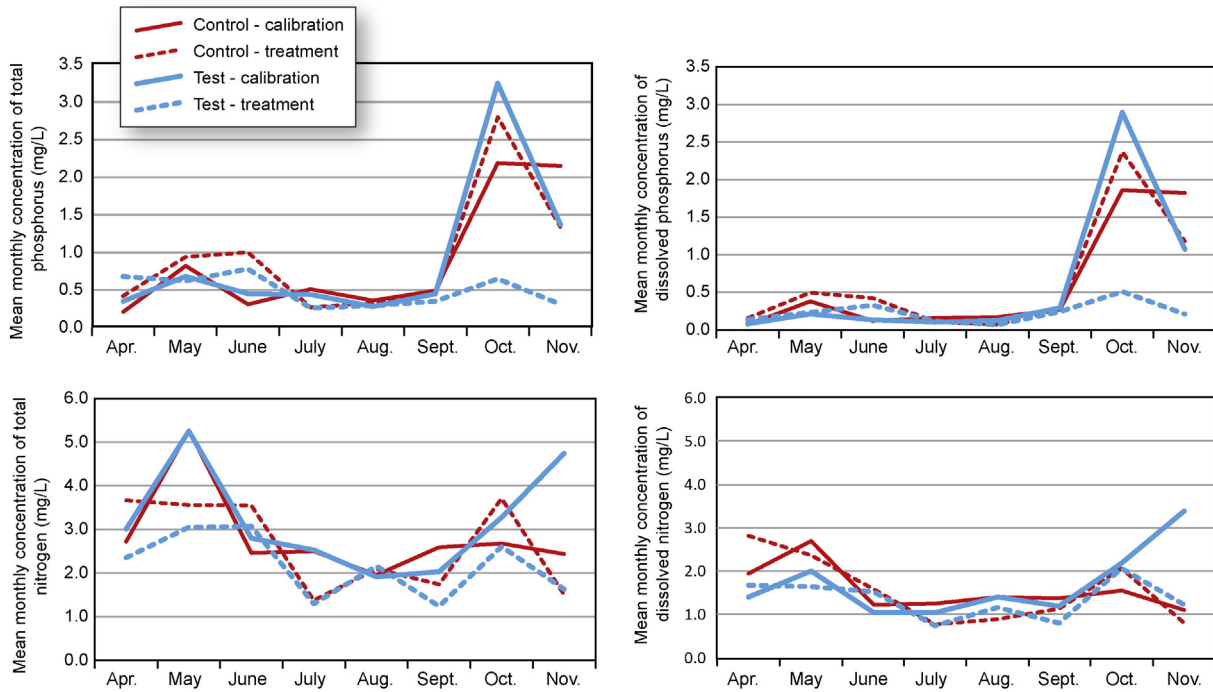


Fig. 3. Mean monthly concentration of nutrients measured in stormwater runoff in the control and test catchments during the calibration and treatment phases.

showed an increase in total and dissolved nitrogen in the control catchment during the calibration phase when all other instances observed a decrease.

3.1.2. Treatment phase

Use of the Mann-Whitney test (Helsel and Hirsch, 2002) showed mean monthly nutrient concentrations in the control catchment during the treatment phase were not significantly different ($p > 0.05$) than the calibration phase since there was no change in leaf collection practices. The test catchment, like the control, also displayed a pattern in nutrient concentrations similar to the calibration phase, but only for the months of April through September. The month of May continued to show slightly higher mean concentrations than the rest of the spring and summer months despite the addition of weekly street cleaning efforts. In contrast, the combination of leaf collection and street cleaning in the months of October and November reduced nutrient concentrations to near summer levels. Compared to the calibration phase, mean October concentrations of total and dissolved phosphorus in the test catchment during the treatment phase decreased by approximately 80%.

3.2. Partitioning of nutrient concentrations by season

Table 2 details the seasonal mean concentrations of the total and dissolved forms of phosphorus and nitrogen. Dissolved phosphorus and nitrogen, as a percentage of the total fraction, is also detailed in Table 2. The partitioning of phosphorus shifted from primarily particulate in the spring and summer to dissolved in the fall. During the calibration phase, fall concentrations of dissolved phosphorus in the control and test catchments were 85% or more of total phosphorus compared to <50% in spring or summer (Table 2). A similar trend was observed during the treatment phase. Nitrogen showed some preference for dissolved fractions during the fall in the test catchment during both phases of the study but was more evenly distributed in the control catchment during the calibration phase and higher in the spring during the treatment phase.

3.3. Changes in nutrient loads as a result of leaf collection and street cleaning

Loads from the control catchment were paired with loads from the test catchment to establish a quantifiable relation using linear

Table 2

Seasonal mean concentrations of phosphorus and nitrogen in the control and test catchment during the calibration and treatment phase. All values are in milligrams per liter except those in parentheses which indicate the dissolved concentration as a percentage of the total.

Season	Control				Test			
	Calibration		Treatment		Calibration		Treatment	
	Total	Dissolved	Total	Dissolved	Total	Dissolved	Total	Dissolved
Phosphorus								
Spring	0.67	0.31 (45%)	0.74	0.37 (50%)	0.60	0.18 (30%)	0.64	0.20 (31%)
Summer	0.41	0.19 (46%)	0.45	0.19 (42%)	0.43	0.19 (44%)	0.38	0.16 (42%)
Fall	2.18	1.85 (85%)	2.17	1.86 (86%)	2.71	2.37 (87%)	0.50	0.38 (76%)
Nitrogen								
Spring	4.7	2.53 (54%)	3.6	2.55 (71%)	4.7	1.86 (39%)	2.8	1.64 (59%)
Summer	2.5	1.3 (53%)	2.0	1.01 (50%)	2.4	1.14 (48%)	1.9	1.0 (54%)
Fall	2.6	1.42 (54%)	2.8	1.53 (55%)	3.7	2.54 (68%)	2.2	1.7 (78%)

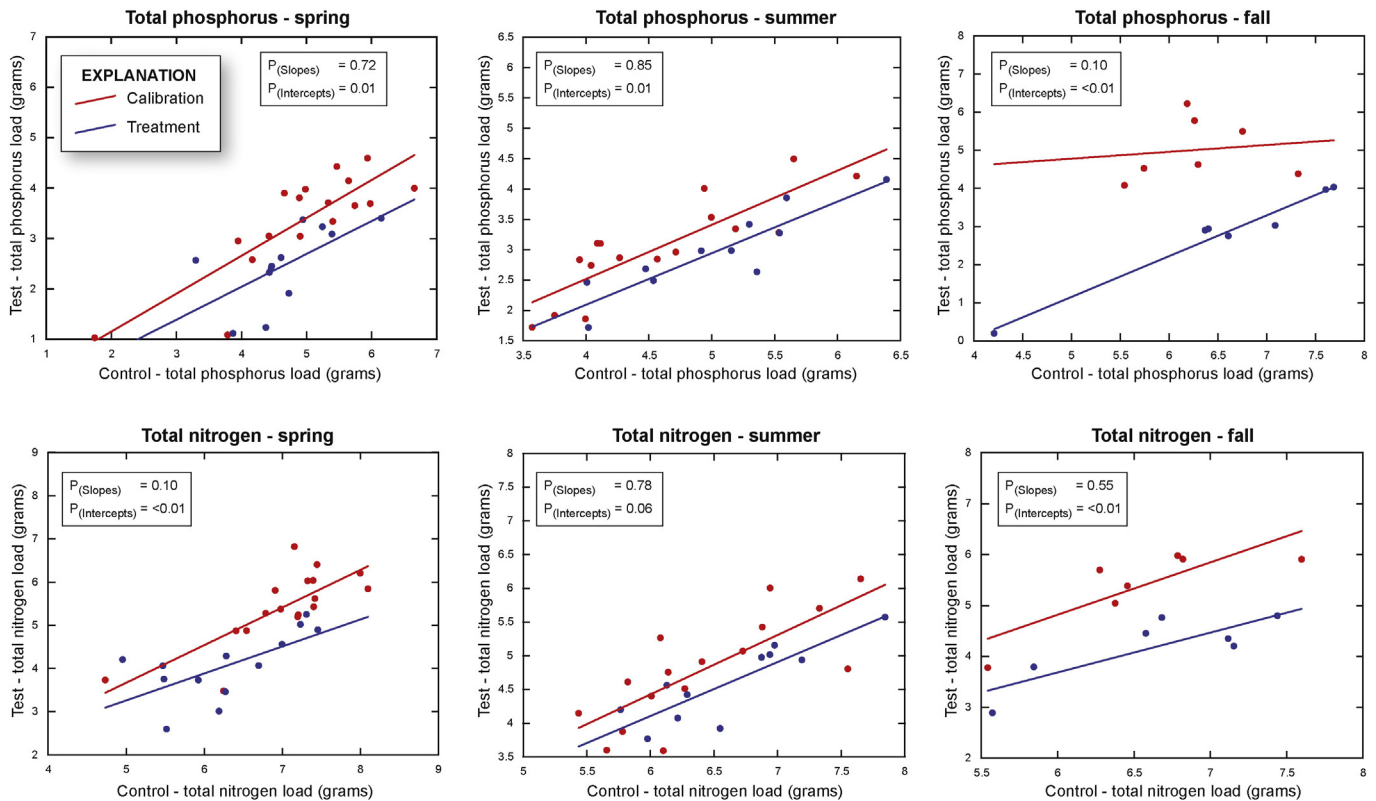


Fig. 4. Log-transformed seasonal loads of total phosphorus and total nitrogen for paired samples collected in the control and test catchment during the calibration and treatment phases of the study. Statistical significance of both slopes and intercepts are indicated by corresponding p values.

regression. Paired loads were grouped into seasonal categories representing spring ($n = 30$), summer ($n = 27$), and fall ($n = 14$). According to the paired-catchment approach, any change in the relation that was established between the control and test catchments during the calibration phase of the study can be attributed directly to leaf collection and/or street-cleaning activity. The magnitude of change is a reflection of the amount of organic material removed from streets by the frequency and method of leaf collection and/or street-cleaning. Fig. 4 represents the relations in seasonal loads of total phosphorus and total nitrogen developed between the control and test catchments during the calibration and treatment phase. Additional figures for the dissolved form of these constituents are available in Appendix 2 in the online supplemental material (also available in Selbig, 2016).

Results of the ANCOVA test are presented in Table 3. Modest reductions in load were observed in spring for total and dissolved phosphorus and nitrogen at the 95% confidence level. With the exception of total phosphorus, results of the ANCOVA test indicated no significant difference in loads between study phases during summer. Therefore, any reduction in loads of dissolved phosphorus and total and dissolved nitrogen as a result of street cleaning was negligible. Street cleaning did, however, show some influence on total phosphorus in summer, reducing loads by 36% (Table 3).

Table 3

Mean seasonal load of nutrients observed in the test catchment during the treatment phase compared to those predicted if treatment was not applied. Values for percent change are statistically significant at the 95% confidence level. Negative values represent percent reduction due to treatment. Numbers have been rounded to the nearest whole value. [g, grams; -, not statistically significant at the 95% confidence level].

Nutrient	Spring			Summer			Fall		
	Observed (g)	Predicted (g)	Change (%)	Observed (g)	Predicted (g)	Change (%)	Observed (g)	Predicted (g)	Change (%)
TP	15	27	-45	24	38	-36	26	161	-84
DP	5	10	-51	13	15	-	21	125	-83
TN	77	158	-52	115	166	-	76	285	-74
DN	42	75	-44	68	87	-	54	186	-71

The addition of leaf collection in the fall significantly reduced loads of all nutrients. Reductions in total and dissolved phosphorus were similar at 84 and 83%, respectively (Table 3). Significant reductions were also observed for total and dissolved nitrogen at 74 and 71%, respectively (Table 3). Fall reductions for both phosphorus and nitrogen were at percentages nearly twice as those observed during spring. The magnitude of the percent change described in Table 3 is a reflection of the amount of organic and inorganic material available for wash off during a precipitation event. A larger amount of leaf litter and other organic detritus would produce higher nutrient concentrations. Although this study used methods to remove detritus from streets that are beyond the capabilities of most municipal programs, it represents the upper boundary of achievable reductions in nutrient concentrations. Other municipal leaf collection programs would likely result in reductions that are less than those presented in Table 3.

3.4. Changes in seasonal contributions to annual nutrient yields

Without the removal of leaf litter, fall concentrations of phosphorus exceed those in spring or summer (Fig. 3, Table 2). In terms of the load delivered to receiving waters, this may not be as much of a concern since the 30-year normal for precipitation shows only 16% occurs in

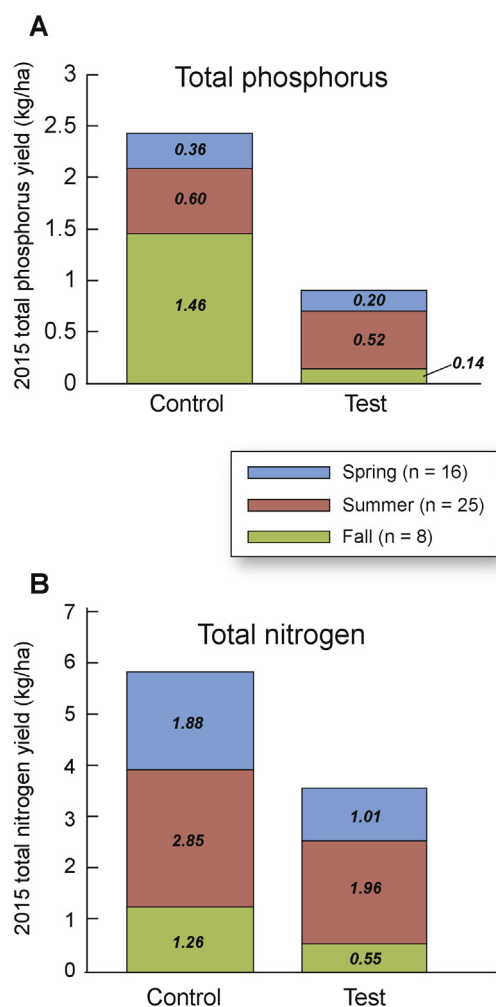


Fig. 5. Seasonal contribution to annual yields of total phosphorus and total nitrogen (winter excluded) in the control and test catchments during the treatment phase (2015).

October and November (National Oceanic and Atmospheric Administration, 2016); however, the magnitude of increase in concentration may overcome the low frequency of precipitation events typically observed for this time of the year, thereby producing greater load with less runoff volume. The relevance of seasonal precipitation is illustrated in Fig. 5 which breaks down the annual yield of total phosphorus and total nitrogen by season for each study catchment during the treatment phase (2015). Winter was excluded from this analysis due to lack of data. Comparison of yield was done since it normalizes differences in concentration and load by the total area of the control and test catchments. Event yields, both measured and estimated, were summed and categorized by season.

Estimates of the annual total phosphorus yield in 2015 showed that, despite having the fewest number of precipitation events ($n = 8$), the highest proportion of annual yields in the control catchment occurred during the fall (56%). Conversely, spring and summer contributed much lower proportions of annual total phosphorus yield at 14 and 30%, respectively, despite having double and triple the number of precipitation events ($n = 16$ and $n = 25$) than observed in the fall. Comparatively, inclusion of leaf removal and street cleaning in the test catchment during the fall resulted in only 16% of the annual total phosphorus yield, much lower than the control at 56%. In this case, the primary seasonal contribution of the annual total phosphorus yield shifted from fall to summer. Little difference in summer yield was observed between the control and test catchments (Fig. 5), suggesting the majority of total phosphorus originated from sources other than

organic debris on streets and these sources were outside the influence of street cleaning. By removing leaf litter in the fall, the seasonal yield of total phosphorus was shifted away from a concentration-based system (fall) to one that is dominated primarily by the frequency of precipitation events (summer). This is important for environmental managers who must evaluate cost-effective strategies to meet pollution reduction goals.

Estimates of total nitrogen yield did not follow the same general pattern as total phosphorus. The differences between mean seasonal concentrations of total nitrogen (Table 2) were not as large as total phosphorus, with fall concentrations only slightly larger than summer but less than spring. As such, estimates of seasonal yields were subsequently controlled by the frequency of precipitation events. Summer, despite having the lowest seasonal mean concentration of total nitrogen, had the largest number of precipitation events ($n = 25$) which produced the greatest percentage of annual yield (53%) in the control catchment. Spring, with fewer precipitation events ($n = 16$) but a greater seasonal mean concentration, produced 28% of the total nitrogen yield in the control catchment followed by fall at 19%. Spring and fall percentages were only slightly shifted downward as a result of leaf collection and street cleaning in the test catchment. Summer was still the largest contributor to annual yields (56%) followed by spring (28%) and fall (16%).

4. Discussion

4.1. Leaves as a source of phosphorus in urban stormwater

Results from this study confirm what others (e.g. Kluesner and Lee, 1974; Waller, 1977; Hochmuth et al., 2012) previously concluded, that in an urban residential area with high overhead street tree canopy (> 15% in this case), leaf litter could be the primary source of phosphorus in stormwater during the fall months (for this study defined as October and November). This study provides additional evidence that significant reductions in loads of the total and dissolved forms of phosphorus and nitrogen can be achieved with removal of leaf litter prior to a precipitation event. The timing of leaf removal is of importance because of the highly leachable nature of leaves. Hobbie et al. (2014) made a similar conclusion based on leaching experiments of leaf litter in urban gutters noting 27 to 88% of initial phosphorus was leachable in the first 24 h of soaking. Wallace et al. (2008) similarly reports the majority of dissolved phosphorus from leaves of certain tree species is leached within the first 48 h. Other studies report only a small percentage of phosphorus in leaves is leachable (Cowen and Lee, 1973; Dorney, 1986); however, these laboratory studies were limited to only a two hour period. Duan et al. (2014) reported leaching of phosphorus over a much longer period of time (> 100 h) with resulting concentrations resembling a first order decay function that initially releases rapidly then slows over time. While these laboratory studies all report an increase in the concentration of leachable phosphorus over time, Hobbie et al. (2014) also reported significant differences between nutrient dynamics in the street to those in the laboratory with unpredictable increases and decreases of the phosphorus content of gutter leaves throughout the year. The increase in phosphorus content was attributed to the uptake of phosphorus by microbes to meet nutritional demands for breaking down and using organic matter as an energy source. Despite these findings, evidence of sharp increases in dissolved phosphorus observed during this study support the notion that the removal of leaves accumulated on streets and in piles near the street curb, can minimize contributions of nutrients to storm drains. Furthermore, most structural practices, such as sumps and screens, are designed to protect receiving waters by trapping coarse particles of organic matter. Unless these devices are equipped with special filters, the dissolved fraction of pollutants is usually left unmitigated (Wallace et al., 2008). Therefore, the physical removal of leaves and other organic debris before they have an opportunity to leach nutrients

into runoff may be the only viable form of management during the fall in urban catchments.

Although leaf litter was a clear source of nutrients in stormwater during the fall, the contribution of urban trees is less pronounced in the spring and minimal in summer. While minor increases in phosphorus were observed in spring, summer concentrations remained consistently low. This is consistent with previous studies characterizing seasonal concentrations of phosphorus in urban environments (Shapiro and Pfannkuch, 1974; Kluesner and Lee, 1974; Weatherbe and Novak, 1977; Baker et al., 2014). The mass of detritus during summer was not enough to overcome natural variability and uncertainty in load measurements, making it difficult to detect a significant reduction through weekly street cleaning alone.

The emergence of vegetation in the spring, on the other hand, did have a measurable effect on nutrient loads. Unless stressed by disease or drought, spring is a time when leaves begin to emerge and remain on a tree. Therefore, contributions of nutrients from trees during the spring likely came from deposition of seeds, blossoms and pollen rather than leaves. The significance of seeds as a source of phosphorus was also addressed by Dorney (1986) who, through laboratory testing, found the amount of leachable phosphorus in seeds was much lower than leaves since seeds were designed to preserve their nutrients for germination. From Table 3, the mean observed load for nutrients was generally lowest in the spring yet the percent removal was greater than summer and approximately one-half of what was measured during the fall. One explanation may be related to the seasonal mass of organic detritus on street surfaces. Summer, having the lowest mass, failed to show significant reductions in load after treatment whereas fall, having the greatest mass, showed the largest reductions after treatment. The mass of organic detritus on streets in the spring is generally greater than in summer but less than fall. Accordingly, load reductions due to treatment followed that same pattern.

4.2. Leaves as a source of nitrogen in urban stormwater

Like phosphorus, summer concentrations of nitrogen were variable but generally lower than spring and fall. Unlike phosphorus, mean concentrations of nitrogen were highest in the spring and did not have the same spike in fall (Fig. 3). Although variability in concentrations can make statistical inferences difficult (Taylor et al., 2005), loads of total and dissolved nitrogen were reduced through a combination of leaf removal and street cleaning in spring and fall during the treatment phase. However, the removal of phosphorus was greater than nitrogen. These two observations suggest sources of nitrogen other than leaves and organic detritus may have contributed to what was measured at the outfall.

One such source may have been the application of lawn fertilizers which contain nitrogen as a nutrient to stimulate root growth. Lawn fertilizer is typically applied in the spring and fall, which coincided with observed increases in concentrations. Fertilizer has long been recognized as an anthropogenic source of nitrogen and phosphorus to urban runoff causing localized “hot spots” from residential land management practices (Cowen and Lee, 1973; Hobbie et al., 2014; Templar et al., 2015). Phosphorus from fertilizers was not a concern for this study since the state of Wisconsin enacted a ban on phosphorus in lawn and turf fertilizer in 2009 (Wisconsin State Legislature, 2016). Nitrogen, however, remains an active ingredient in lawn fertilizers and may have acted as a potential source that would not have been treated by leaf collection and/or street cleaning. Hobbie et al. (2014) made a similar conclusion after discovering periods of nitrogen immobilization (an increase in nitrogen mass) in urban leaf litter followed by release. These periods were assumed to coincide with the application of fertilizer on nearby turf grass.

Previous studies clearly recognize leaf litter as a source of nitrogen (Duan et al., 2014; Hobbie et al., 2014), but also report large uncertainties in measurements, especially in hydrologically flashy systems

(Belt, 2012). Statistically significant reductions of total nitrogen for all monitored seasons suggest that uncertainty and variability in measured nitrogen concentrations were overcome by the combined effect of street cleaning in spring and leaf collection in the fall. Vaze and Chiew (2004) attribute the readily removable nature of total nitrogen in stormwater from a street surface to its association with sediment ranging between 11 and 150 μm . This suggests the resulting concentrations of total nitrogen in stormwater runoff are source limited where the amount of total nitrogen washed off a street is limited by the available load on the street surface (Miguntanna et al., 2013). This phenomenon is observed during the fall when appreciable gains in street load through the addition of leaf litter coincide with a larger percent removal of total nitrogen.

Elevated concentrations of dissolved nitrogen may also have been related to the rapid transfer of nitrogen from streets to storm drain during a precipitation event. The directly connected nature of streets and storm sewers decreases detention time thereby limiting the opportunity for nutrient cycling and thus increasing levels of dissolved nitrogen (Galloway et al., 2003).

4.3. Implications for effective leaf management programs

Understanding the seasonal contribution of nutrients from leaf litter and other organic detritus can help environmental managers assess the most effective way to limit their source and delivery to receiving water bodies. Leaf management and street cleaning through an individual municipal program, or combined with modifications to homeowner behaviors, may not necessarily result in reduced concentrations and loads in stormwater runoff. While a paucity of available data has left interpretation of the water-quality benefits of various leaf collection programs inconclusive, many studies have evaluated the benefits of street cleaning. Some studies (e.g. Baker et al., 2014) conclude that street cleaning can be an effective tool for nutrient management in urban areas based on the evaluation of material collected in the hopper; however, many other studies have shown street cleaning, while efficient at removing an appreciable amount of solids and other debris from street surfaces, are largely ineffective at improving the quality of stormwater runoff (Selbig and Bannerman, 2007; Law et al., 2008; Sorenson, 2012). The results from these studies suggest removal of organic debris from a street surface may be insufficient to overcome natural variability of nutrient concentrations measured at the end of a pipe. However, based on results from this study, the connection between the mass of leaves and other organic matter on streets and concentrations measured in the storm drain suggests otherwise. Unlike Baker et al. (2014), the other street cleaning studies ceased before autumn leaf fall when the mass of debris, both organic and inorganic, is generally the highest. If the amount of material removed was large enough to overcome natural variability, a detectable change in concentration would become more likely.

The methods used to remove organic material from streets during this study exceed what most municipal programs are capable of implementing and therefore represent maximal reductions in nutrient concentrations as a result of treatment. Additional research is needed to quantify the range and frequency of existing municipal leaf collection programs such as vacuum mulching or bagging. Beyond municipal efforts, more work needs to be done quantifying nutrient reductions through changes in homeowner behavior such as on-site mulching or composting. Regardless of the leaf removal method, municipal or otherwise, concentrations of phosphorus and nitrogen in urban stormwater become a function of the cleanliness of streets prior to a precipitation event. Subsequently, the efficiency, frequency, and timing of leaf removal are the primary factors when tailoring a leaf management program.

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