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Contrasting influences of stormflow and baseflow pathways on nitrogen and phosphorus export from an urban watershed

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Abstract Eutrophication of urban surface waters from excess nitrogen (N) and phosphorus (P) inputs remains a major issue in water quality management. Although much research has focused on understanding loading of nutrients from storm events, there has been little research to understand the contribution of baseflow, the water moving through storm drains between rainfall events. We investigated the relative contributions of baseflow versus stormflow for loading of water and nutrients (various forms of N and P) by the storm drain network in six urban sub-watersheds in St. Paul, MN, USA. Across sites, baseflow made substantial contributions to warm season (May–October) water yields (27–66 % across sites), total N yields (31–68 %), and total P yields (7–32 %). These results show that while P was predominantly delivered by stormflow, N loading was similar between baseflow and stormflow. We found that baseflow was dominated by groundwater inputs, likely caused by interception of shallow groundwater by storm drains, but also that variability in N and P among sites was related in part to the connectivity of the storm drains to upstream lakes and wetlands in some watersheds. The substantial loading by groundwater-dominated baseflow, especially for N, implies that N management may require a broader focus on N source reduction, perhaps through improved land management, in order to prevent contamination of shallow groundwater via infiltration.

Keywords Urban biogeochemistry · Nitrogen · Phosphorus · Baseflow · Storm drains · Urban hydrology

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Introduction

Nonpoint nitrogen (N) and phosphorus (P) pollution contributes substantially to the eutrophication of urban surface waters, and remains a major obstacle in the sustainable management of urban watersheds (Carpenter et al. 1998; Moore et al. 2003; Dubrovsky et al. 2010). Recent studies have shown that export of nonpoint source N and P from urban watersheds far exceeds that from forested watersheds (e.g., Groffman et al. 2004; Wollheim et al. 2005; Petrone 2010), and even approaches export rates from some agricultural watersheds, particularly for P (Dubrovsky et al. 2010; Duan et al. 2012). High nutrient export in urban

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watersheds is caused by the large nutrient inputs these watersheds receive from external sources, including atmospheric deposition, fertilizer, human food, and pet food (Bernhardt et al. 2008; Baker and Brezonik 2007; Fissore et al. 2012), and by human modification of the land surface and drainage network that promotes rapid drainage (Pouyat et al. 2007; Kaushal and Belt 2012).

Storm drains, which are a characteristic feature of the urban drainage network, shorten natural flow paths and often disconnect riparian zones from the drainage network, offering less opportunity for capture and transformation of nutrients in surface runoff (Bernhardt et al. 2008; Kaushal et al. 2008). Simultaneously, storm drains closely link downstream waters with surrounding impervious surfaces, which serve as collectors and conveyances of nutrients from a variety of sources. Previous research has related runoff volumes or nutrients with climate or land cover variables (e.g., Driver and Troutman 1989; Brezonik and Stadelmann 2002), and quantified nutrient loads from urban headwater elements such as roads (e.g., Vaze and Chiew 2002; Davidson et al. 2010), parking lots (e.g., Passeport and Hunt 2009), and lawns (e.g., Garn 2002; Soldat et al. 2009). While results of individual studies vary considerably, surface runoff from storm events has been shown to be high in both sediment and nutrients, and as a result, current stormwater control measures (e.g., detention ponds, infiltration basins, and rain gardens) typically target surface runoff for reduction of water volumes and removal of sediment and particulate nutrients.

Urban land cover is highly heterogeneous but for individual cities is dominated by residential land use that may vary substantially in age, condition, population density, and other characteristics (e.g., Nowak et al. 1996; Hammer et al. 2004). However, the underlying drainage network can be even more complex than the surface land use. As land is developed, networks of storm, sanitary, and water supply pipes are constructed, creating or modifying existing flow paths that may be further altered as infrastructure ages and becomes leaky. This matrix, sometimes referred to as "urban karst" (Sharp et al. 2003; Kaushal and Belt 2012), may dramatically change watershed connectivity and accelerate groundwater movement in watersheds with high water tables that allow groundwater seepage into drains. Furthermore, the burial and entombment of streams during urban development can create enhanced flow paths and alter watershed connectivity (Elmore and Kaushal 2008; Lookingbill et al. 2009). The resulting connection of a diversity of surface and groundwater sources to downstream waters by drainage networks is referred to by Kaushal and Belt (2012) as the "vertical" dimension of the urban watershed continuum (a framework for studying urban watersheds that considers hydrologic connectivity of both natural and man-made systems across multiple spatial and temporal scales), and they note in particular the need to explore the significance of these connections and the potential impacts on nutrient export, especially during baseflow.

Storm drain baseflow is the water flowing through the storm drain network between rainfall events from groundwater intrusion and outflow from connected surface water bodies. Baseflow has a high potential to impact receiving waters because the increased groundwater connectivity provided by urban drainage networks may enhance movement of dissolved nutrient species (Pouyat et al. 2007; Welty et al. 2007; Kaushal and Belt 2012). Elevated concentrations of dissolved nutrients in urban groundwater, especially nitrate but also dissolved organic components of N (Nolan and Stoner 2000; Cole et al. 2006; Kroeger et al. 2006), enhance the potential importance of baseflow. Nutrient loading by baseflow in urban storm drains has rarely been addressed directly by previous studies (but see Taylor et al. 2005; Rosenzweig et al. 2011), though a few studies from a wide range of urban watersheds have included data from baseflow periods (e.g., Hook and Yeakley 2005; McLeod et al. 2006; Petrone 2010). A need therefore exists to evaluate stormflow versus baseflow in nutrient loading by storm drains in urban watersheds.

In this paper we present an analysis of extensive monitoring efforts in seven urban watersheds located in St. Paul, Minnesota, USA aimed at elucidating: (1) the relative importance of baseflow versus stormflow for nutrient loading of various forms of N and P in large urban drainage networks, (2) sources of water and nutrients during baseflow periods, and (3) the influence of land cover on stormwater nutrients.

Study background and methods

Study watershed

Our study sites are contained within the Capitol Region Watershed (CRW), which is located in southeastern

Minnesota, USA, encompassing sub-watersheds primarily in the city of St. Paul and in parts of surrounding cities. The highly urbanized watershed has an area of 106 km^2, with a total imperviousness of approximately 45 % (CRWD 2011). A variety of land uses are present, including parks and several natural lakes, as well as dense residential, commercial, and industrial development. Most of the land surface is connected to a storm drain network that outlets to the Mississippi River at dozens of locations along the southern border of the watershed (CRWD 2011).

Several features enhance the interest in the storm drain network of the CRW with respect to surface vs. subsurface pathways and urban nutrient sources. Several natural lakes are present, the two largest of which, Como Lake (surface area = 29 ha, volume = 65 ha m; CRWD 2002) and Lake McCarrons (surface area = 33 ha, volume = 218 ha m; Myrbo and Shapley 2006), are connected to the storm drain network. Much of the northeastern half of the watershed drains through a system of buried streams, which were converted to storm drains beginning in the late 1800s by city engineers to alleviate flooding and enable development in the Trout Brook and Phalen Creek watersheds (Brick 2008). The water table is shallow, especially in the vicinity of these buried streams and near lakes (Barr Engineering 2010; Kanivetsky and Cleland 1992), and some portion of the CRW storm drain network is located beneath the water table (unpublished data). Soils in the surface aquifer are primarily coarse sand and gravel from glacial outwash (Meyer 2007).

Separation of the storm drain network from the sanitary sewers was completed in 1996 to eliminate combined sewer overflows to the Mississippi River from the Minneapolis-St. Paul metropolitan area. The city of St. Paul has worked to replace or line older portions of the sanitary sewers and disconnect remaining rain leaders from rooftops, in an effort to reduce infiltration and inflow to sanitary sewers and eliminate illicit connections to the storm drains (City of Saint Paul 2010). Storm drain monitoring by the Capitol Region Watershed District (CRWD; http://capitolregionwd.org) has detected only one major illicit connection over the study period (CRWD 2011). In addition, there are very few remaining septic systems in the CRW.

The CRWD has conducted extensive monitoring of storm drains and surface water in the CRW since 2005. CRWD monitoring sites located at the outlet of six sub-watersheds were selected for analysis in our study (Fig. 1): St. Anthony Park (SAP), East Kittsondale (EK), Phalen Creek (PC), Trout Brook—West Branch (TBWB), Trout Brook—East Branch (TBEB), and Trout Brook Outlet (TBO). A much smaller site located at the inlet to an underground stormwater vault, Arlington-Hamline Underground (AHUG), was included only in the analysis of the stormflow data because no baseflow is observed at this site. TBO receives outflow from TBEB and TBWB as well as from a large area downstream of the two branch watersheds, and thus is not an independent monitoring site. Overflows from Como Lake and Lake McCarrons drain into TBWB, and the Sarita Wetland in SAP detains runoff from roughly one-fourth of that watershed for small rainfall events. EK and PC have very little surface water, but a large number of ponds are located in SAP, TBWB, and in particular TBEB (Table 1); their connectivity to the storm drains is unknown.

Excluding AHUG, the monitored sub-watersheds range in size from 3.27 (TBEB) to 31.4 km^2 (TBO), and all are dominated by single-family residential land use. Accordingly, land cover is similar among sub-watersheds (Table 1), with total impervious area ranging from 37 at TBWB to 59 % at PC, while street area (11–17 % across sub-watersheds), tree canopy (22–34 %), and grass/shrub cover (17–25 %) are more uniform. Aerial photography, high-resolution satellite imagery, and LiDAR data (0.5 m spatial resolution) were used by the Department of Forest Resources at the University of Minnesota (UMN) to map and classify land cover in 2009 for the watershed (Kilberg et al. 2011). Spatial data provided by CRWD was used to refine estimates of the street, roof, and other impervious areas, and to calculate the fraction of street covered by canopy as well as street density (total length of streets in the watershed normalized by watershed area, in km/km^2).

Additional computed watershed characteristics include pond density (estimated from aerial photography), spatially averaged depth to water table (using water table elevations from Barr Engineering 2010), connected impervious area (estimated from a line fit to rainfall and runoff data for each watershed per Boyd et al. 1993), and population density (United States Census Bureau 2010). Note that runoff coefficients (seasonal total runoff depth normalized by

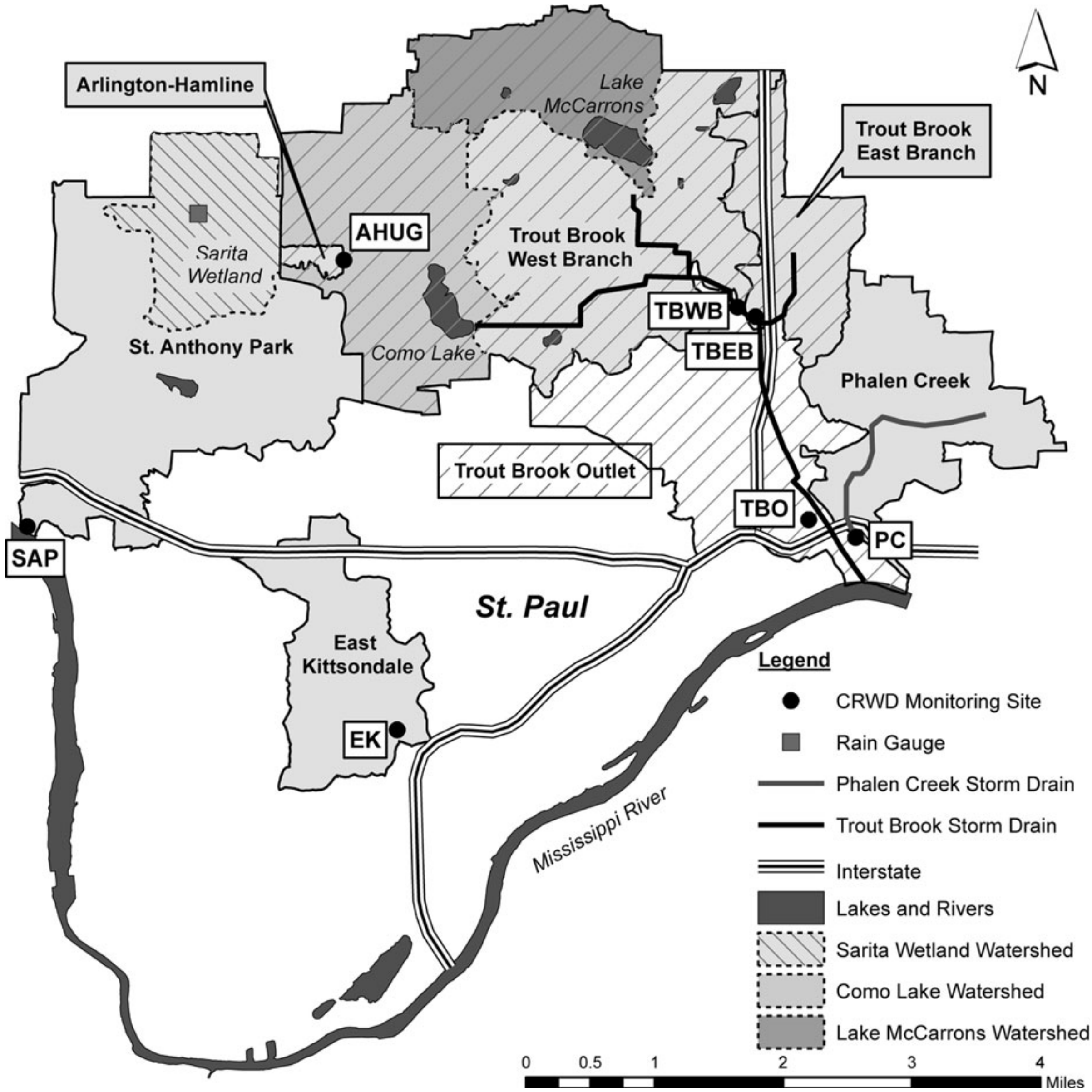


Fig. 1 Capitol Region Watershed, showing monitored sub-watersheds and sampling sites. Note that the Trout Brook Outlet (TBO) sub-watershed includes both the Trout Brook East Branch (TBEB) and the Trout Brook West Branch (TBWB) sub-watersheds, as well as the downstream area. The Como Lake and Lake McCarrons watersheds are included in both TBWB and TBO. Also shown are the main trunks of the Trout Brook and Phalen Creek Storm Drains, which were both constructed in buried stream channels

corresponding rainfall depth), connected impervious area, and land cover characterizations include drainage areas upstream of large lakes or wetlands (i.e., Como Lake and Lake McCarrons in TBWB and TBO, and the Sarita Wetland in SAP).

Data collection

Water quality sampling for baseflow and storm events was conducted by CRWD using ISCO automatic samplers (Model 6712; Lincoln, NE) equipped with

Table 1 (**a**) Land cover types, and (**b**) derived watershed characteristics for the main sub-watersheds

(a) Sub-watershed	Area (km^2)	Percentage of land cover type							Composite land cover (%)	
		Tree	Grass/shrub	Open	Water	Roof	Street	Other imp.	TIA	Veg
Arlington-Hamline (AHUG)	0.17	27	22	0.3	0.0	25	13	13	51	49
East Kittsondale (EK)	4.52	27	17	0.3	0.0	22	16	18	56	43
Phalen Creek (PC)	5.80	24	17	0.5	0.0	22	17	19	59	41
St. Anthony Park (SAP)	13.84	22	19	3.3	0.6	17	12	26	55	41
Trout Brook Outlet (TBO)	31.35	30	23	0.6	3.1	14	13	16	43	53
Trout Brook E Branch (TBEB)	3.27	30	25	0.1	0.4	14	16	15	45	55
Trout Brook W Branch (TBWB)	20.97	34	24	0.5	4.6	13	11	13	37	58

(b) Sub-watershed	Runoff coefficient	Street density (km/km^2)	Street canopy fraction	Connected impervious fraction	Population density (no/km^2)	Pond density (no/km^2)	Depth to water table (m)
Arlington-Hamline (AHUG)	0.16	13.03	0.356	0.154	3628	0.00	16.8
East Kittsondale (EK)	0.35	15.26	0.299	0.280	2438	0.22	30.5
Phalen Creek (PC)	0.26	14.78	0.274	0.202	3176	1.03	20.4
St. Anthony Park (SAP)	0.15	10.60	0.198	0.181	1356	0.94	13.4
Trout Brook Outlet (TBO)	0.17	10.99	0.236	0.132	1881	2.93	10.1
Trout Brook E Branch (TBEB)	0.20	13.15	0.225	0.222	2958	4.28	9.2
Trout Brook W Branch (TBWB)	0.16	9.63	0.294	0.125	1774	2.86	11.1

Areas upstream of major lakes and wetlands are included. 'Other Imp.' cover type includes all non-street and non-roof impervious areas, 'TIA' is total impervious area (sum of Street, Roof, and Other Imp. percentages), 'Veg' is vegetated area (sum of Tree and Grass/Shrub). Runoff coefficient is determined from all warm season rainfall and runoff, 'Street Density' is the total length of streets normalized by sub-watershed area, 'Street Canopy Fraction' is the fraction of street area covered by trees, and depth to water table is spatially averaged over the sub-watershed. Note that both TBEB and TBWB are located within TBO

area-velocity modules (ISCO Model 750) to continuously record water depth and velocity in the storm pipes at 10-min intervals. Flow rates were calculated from these data using storm pipe geometry. The autosamplers were programmed to collect multiple samples during each runoff event or baseflow sampling period, with successive samples drawn on a volumetric basis rather than on a set time interval (CRWD 2011). Volume intervals were selected for each site individually such that all sample bottles would be filled (48 or 96 total samples, depending on autosampler size) for a typical 2.54 cm rainfall event for storms, or during an approximately 24-h period for baseflow, rates of which did not vary much seasonally at most sites and which were smaller than stormflow rates by an order of magnitude or more on average.

Sampling was conducted from early April through early November of each year, with a total of 526 baseflow samples and 702 storm event samples collected from 2006 to 2011 across all sites. A storm event was defined as flow occurring while the water depth in the pipe exceeded some threshold (specific to each site) that was greater than any depth associated with normal baseflow fluctuations (CRWD 2011). Most storm events occurring during the monitoring period were sampled, with some smaller events discarded during wetter seasons, resulting in 15–20 sampled events at each site per season. Conditions were slightly dry but variable during the study period, as mean May–October rainfall measured at the Minneapolis-St. Paul Airport over the study period (49.4 cm) was slightly lower than the 25-year (1987–2011) average of 53.8 cm, with one season among the five wettest seasons and two seasons among the five driest. Median and mean rainfall event size over the study period were 0.81 and 1.3 cm, respectively, as measured by an automatic rain gauge at UMN (St. Paul, MN campus) in the SAP watershed.

Sample bottles were removed by CRWD staff as soon as possible after storms and baseflow events (usually within 24 h) as samples were not pre-acidified or refrigerated in the field, though they were transported to the lab in coolers. A single composite sample was created for each event by combining an identical volume from each filled sample bottle for the event, resulting in a volume-weighted average for the event. Baseflow samples were collected roughly every 2 weeks during dry periods and composited similarly to the storm samples. All samples were delivered to a laboratory for processing the same day of retrieval from the samplers.

Methods and data analysis

Water samples collected by CRWD were analyzed for concentrations of total phosphorus (TP), soluble reactive phosphorus (SRP), total Kjeldahl nitrogen (TKN), ammonium-N (NH_4-N), nitrate–nitrite-N (NO_3-N), and chloride (Cl^-) by the Metropolitan Council Environmental Services (MCES) in St. Paul, Minnesota. Analytical methods follow U.S. Environmental Protection Agency specifications (MCES 2011).

During the 2011 sampling season, CRWD provided sub-samples of composite samples from the main sites, which we supplemented with grab samples from additional sites. All samples were analyzed for water source tracers, including dissolved inorganic carbon (DIC) and oxygen isotope ratio of water ($\delta^{18}O$), as well as additional nutrient forms, including particulate phosphorus (PP), total dissolved phosphorus (TDP), particulate nitrogen (PN), and total dissolved nitrogen (TDN).

Analyses were carried out in laboratories at the University of Minnesota (UMN). Dissolved nutrients were obtained from filtration using pre-ashed 0.7 µm Whatman GF/F filters. TDN samples were acidified with 2 N HCl to pH 2 and refrigerated until analysis with a Shimadzu TOC Vcpn analyzer (Shimadzu Scientific Instruments, Columbia, MD), which was also used to analyze DIC samples. DIC samples were stored with headspace in the vials, and therefore dissolved CO_2 was likely in equilibrium with laboratory air before processing. TDP was analyzed by molybdate colorimetry of SRP after persulfate digestion. For particulate analyses, samples were obtained from filtering through pre-ashed 0.7 µm Whatman GF/F filters. PP was analyzed from the filters using molybdate colorimetry, similar to TDP, while PN was determined using near infrared spectroscopy (NIRS) on the filters (Hood et al. 2006). A subset of PN filters were analyzed using a Perkin Elmer CHN analyzer (Perkin Elmer, Waltham, MA) to update NIRS calibration ($R^2 = 0.93$ and slope = 1.07 for a fit of the two methods). $\delta^{18}O$ was measured using infrared spectroscopy (DLT-100 Liquid Water Analyzer, Los Gatos Research, Inc., Mountain View, CA). Six replicates were run per sample, and $\delta^{18}O$ was determined relative to Vienna Standard Mean Ocean Water with precision of ±0.25 ‰. These 2011 analyses are referred to as "UMN data" hereafter to distinguish this data set from the long-term monitoring data collected from 2006 to 2011 by CRWD, which is referred to as the "CRWD data."

Total organic nitrogen (TON) was calculated as TKN–NH_4-N (CRWD data) or as TDN–NO_3-N–NH_4-N + PN (UMN data). The UMN analyses also allowed for calculation of dissolved organic phosphorus (DOP) as TDP–SRP, and dissolved organic nitrogen (DON) as TDN–NO_3-N–NH_4-N.

Flow and concentration data were used to calculate yields of nutrients from all monitored watersheds. Flow data were manually divided into baseflow and stormflow intervals by CRWD staff from comparison of hydrographs to baseflow rates during known dry periods (B. Suppes, personal communication). Unsampled storm or baseflow intervals were assigned a volume-weighted monthly mean concentration, determined from the entire observation record for a given site, to provide a continuous estimate of loading. Monthly concentrations were used in order to take into account seasonal variability of nutrient concentrations that existed at some sites, and because flow- and volume–concentration relationships were generally very poor. Water and nutrient loads for each site were normalized by total watershed area to produce yields (cm for water, and kg/km^2 per season for nutrients) that allowed comparison across sites. Lake and wetland drainage areas in TBWB, TBO, and SAP were included in the watershed areas for calculation of yields, as these areas are connected by drains to the monitored sub-watersheds and thus influence baseflow, and to a lesser extent stormflow.

Potential relationships of stormflow and baseflow nutrient concentrations to land cover characteristics were explored using linear regression. Variables including warm season mean concentrations and yields of N forms (TON, NO_3-N, NH_4-N, and TN) and P forms (SRP and TP) at all sites were regressed against nine imagery-derived land cover percentages as well as street density, pond density, population density, street canopy fraction, and water table depth (Table 1). AHUG was included for analysis of stormwater nutrients (providing a total of $n = 6$ sites), but not for baseflow as the site lacks baseflow (thus $n = 5$ for baseflow regressions). TBO was excluded from both sets of analyses as it contains both the TBEB and TBWB sub-watersheds in its drainage area and is thus not independent of these sub-watersheds.

Summary statistics (mean, median, minimum, maximum, and standard error) for nutrient concentration data are shown in Online Resource 1. Significant differences among sites in nutrient concentrations were assessed using a Tukey HSD post hoc analysis on an ANOVA of log-transformed data (to meet conditions of normality). Relationships were considered significant at $p < 0.05$. All statistical analyses were performed using Excel and R.

Results

Water yields

The range of mean warm season (May 1–Oct 31) water yields across sub-watersheds (19.6–42.6 cm) was driven primarily by variation in baseflow (Fig. 2). Baseflow yields were substantial, contributing greater than 60 % of total seasonal flow in four of the six main sub-watersheds. Warm season water yields were more variable across sites in baseflow (7.3 cm at EK to 28.2 cm at PC) than in stormflow (8.3 cm at SAP to 19.6 cm at EK). Within sites, baseflow variability was low (smaller SE values than stormflow at most sites) due to relatively steady baseflow rates.

Water yields determined from year-round flow observations available during 2010 and 2011 in five sub-watersheds (EK, PC, TBEB, TBWB, and TBO) show that baseflow was an even greater proportion of the total annual yield, ranging from 44 (EK) to 70 % (PC) of combined annual flow (Table 2). This was due primarily to the scarcity of rainfall events during winter (resulting in very little stormwater runoff), combined with relatively constant baseflow rates throughout the year at most sites. The warm season accounted for 74–86 % of annual stormflow yield, 49–63 % of annual baseflow yield, and 56–66 % of

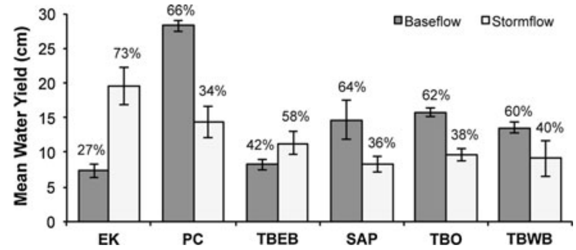


Fig. 2 Mean and standard error of warm season (May 1–Oct 31) stormflow and baseflow water yields (cm) by sub-watershed, averaged over 2006–2011. Sites are arranged *left* to *right* in order of increasing surface water area (Table 1). The portion of each component as a percentage of combined (baseflow + stormflow) yield is shown above the *columns*

the combined (stormflow and baseflow) water yield across sites.

Hydrologic response to rainfall-runoff events also varied among sub-watersheds, as illustrated using a 1.52-cm rainfall event produced by a fast-moving, spatially-extensive storm (Fig. 3). Antecedent conditions were relatively dry, with 0.28 cm of rainfall in the previous 7 days. EK, PC, and SAP had early runoff peaks and relatively short hydrographs typical of urban areas with dense storm drain networks. The Trout Brook sub-watersheds had later runoff peaks and longer, flatter hydrographs, likely reflecting greater surface water connections to lakes and ponds that can slow the movement of water through the system via storage and release. The high post-storm peak flow rates at PC and TBEB may indicate prevalence of shallow groundwater in baseflow of these sub-watersheds.

Nutrient concentrations and yields from long-term monitoring

In the long-term monitoring (CRWD) data set, stormflow nutrient concentrations (Online Resource 1) were consistent with data assembled from previous studies of stormwater across the Minneapolis-St. Paul metropolitan area (Brezonik and Stadelmann 2002). Concentrations and proportions of the various forms of N were similar among all sub-watersheds for stormflow (NO_3-N and NH_4-N concentrations in particular showed no significant differences among sites at $p < 0.05$). By contrast, baseflow N was more variable among sites (for TN and NO_3-N especially) though SE values were lower than in stormflow for most forms of N (Fig. 4). For P, variability of concentrations was

Table 2 Annual water yields at five sub-watersheds averaged over 2010–2011, expressed as depth (cm) and as a percentage of the combined (baseflow + stormflow + snowmelt) yield

Sub-watershed	Mean annual yield (cm)				Warm season Yld. as % of annual Yld.		
	Baseflow (%)	Stormflow (%)	Snowmelt (%)	Combined	Baseflow	Stormflow	Combined
East Kittsondale (EK)	20.8 (43)	23.0 (48)	4.1 (9)	47.8	54	85	65
Phalen Creek (PC)	60.0 (70)	21.8 (25)	4.4 (5)	86.3	49	86	56
Trout Brook E. Branch (TBEB)	17.4 (47)	17.5 (47)	2.0 (6)	36.9	56	82	65
Trout Brook W. Branch (TBWB)	24.2 (54)	18.3 (41)	2.2 (5)	44.7	58	83	66
Trout Brook Outlet (TBO)	22.4 (51)	16.1 (36)	6.0 (14)	44.3	63	74	59

Warm season (May–Oct) yield for each component (baseflow, stormflow) and for the combined yield is expressed as a percentage of the annual yield for that particular component

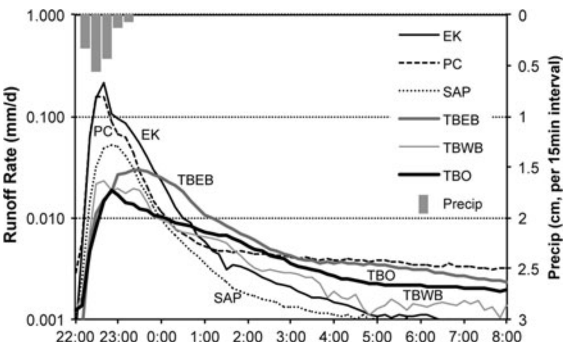


Fig. 3 Hydrographs from the monitored sub-watersheds for a 1.52 cm rainfall event occurring on July 31, 2009. Note that flow rates (mm/d) are plotted on a log scale. Rainfall was measured at a gauge on the St. Paul, MN campus of the University of Minnesota (Fig. 1)

greater in stormflow than in baseflow, with more significant differences present among sites for both TP and SRP (Fig. 5). These results suggest that transport of N and P are affected differently by the dominant hydrologic pathways, and that sources may vary across sub-watersheds, especially for baseflow.

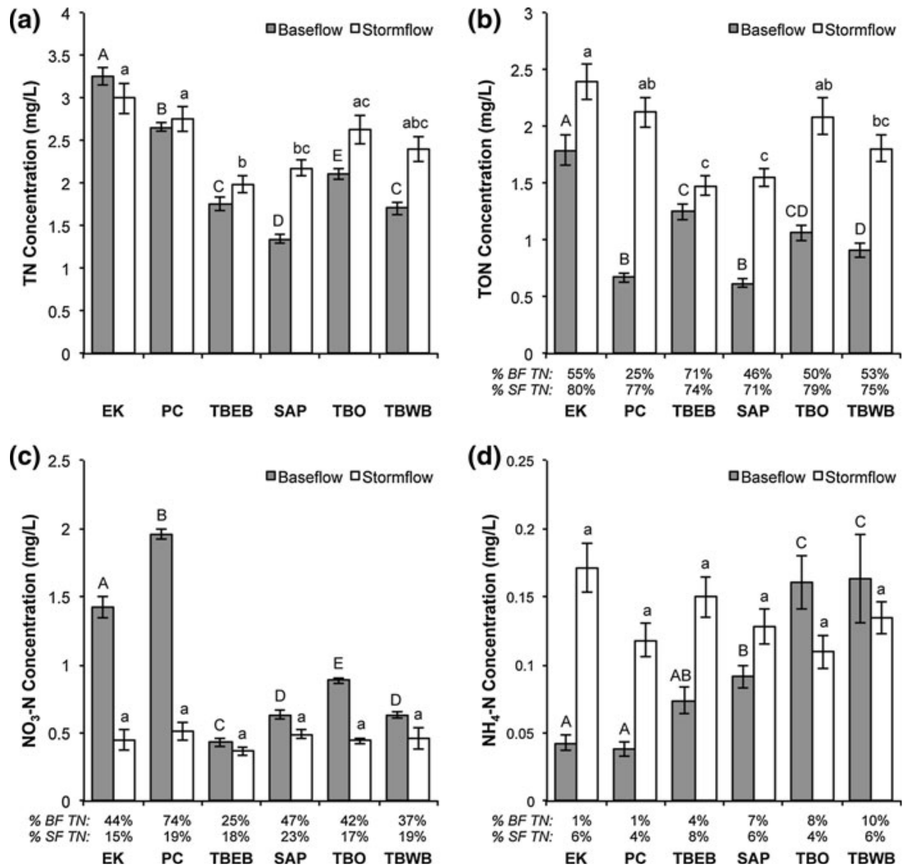
Although TN concentrations were similar between stormwater and baseflow (with a mean percent difference of 21 % across sites), the dominant forms of N contributing to TN differed (Fig. 4). NO_3-N was higher in baseflow than in stormwater at all sites, with the greatest differences at EK (1.42 mg/L in baseflow vs 0.45 mg/L in stormflow) and PC (1.96 mg/L in baseflow versus 0.51 mg/L in stormflow). In contrast, TON was the dominant form in stormwater at all sites, ranging from 71 to 80 % of TN. TON also contributed a large but variable fraction of baseflow (25–71 % of baseflow TN). NH_4-N concentrations were slightly higher in stormflow than in baseflow at most sites, but made up 10 % or less of TN in baseflow or stormflow.

In contrast with TN, baseflow TP concentrations were much lower than in stormwater for all sub-watersheds, ranging from 13 to 28 % of mean stormwater TP (Fig. 5). Most phosphorus was present as PP + DOP (i.e., TP–SRP), comprising from 69 to 95 % of observed stormflow TP and from 54 to 86 % of observed baseflow TP across sub-watersheds. SRP concentrations were generally much lower in baseflow than stormflow (22 to 81 % of stormflow SRP), except at SAP, where mean SRP in stormflow and baseflow were identical (0.014 mg/L).

The range of warm season nutrient yields among sites was similar to that of water yields for both baseflow and stormwater, with the largest nutrient yields observed for the sites with the largest water yields (Figs. 2, 6, 7). The relative importance of baseflow vs. stormflow for TN and TP loading across sites is illustrated in Fig. 8. The proportion of combined (stormflow + baseflow) nutrient yield due to baseflow increases linearly with baseflow water yield for both TN and TP, suggesting that while nutrient concentrations were variable across sites, hydrology had an overriding influence on nutrient loading.

Baseflow also delivered a much greater proportion of warm season nutrient yields for N than for P (Fig. 8), contributing from 31 (EK) to 68 % (PC) of combined TN yield (Fig. 6), including the bulk of the NO_3-N yield (from 52 % at TBEB to 91 % at PC) and

Fig. 4 Warm season (May 1–Oct 31) mean and standard error of concentrations (mg/L) of **a** TN, **b** TON, **c** NO_3-N, and **d** NH_4-N measured in baseflow and stormflow at the main CRWD monitoring sites from 2006 to 2011 ('CRWD data'). Sites are arranged *left* to *right* in order of increasing surface water area (Table 1). The portion of each form as a percentage of TN in baseflow (% BF TN) and in stormflow (% SF TN) is shown along the bottom. Means at sites with different *letters* (uppercase for stormflow and lowercase for baseflow) are statistically different at $p < 0.05$ by Tukey's HSD. Note that $TN = TON + NO_3$-$N + NH_4$-N, and differences in vertical scales among plots



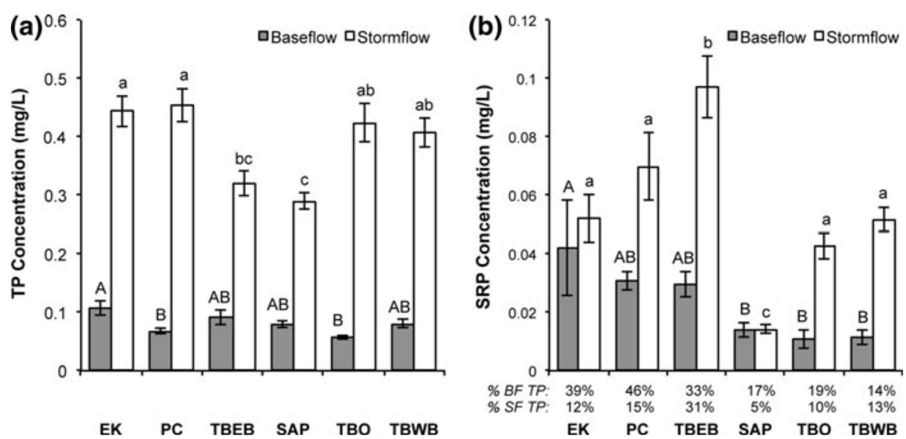
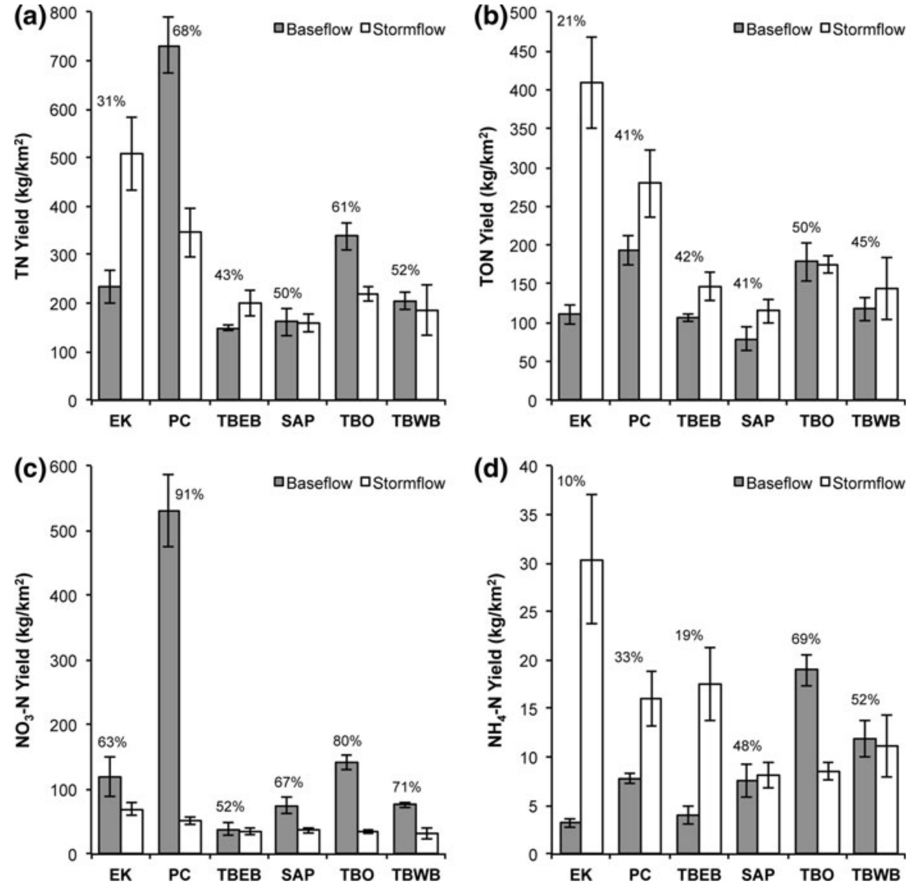


Fig. 5 Warm season (May 1–Oct 31) mean and standard error of concentrations (mg/L) of **a** TP and **b** SRP measured in baseflow and stormflow at the main CRWD monitoring sites from 2006 to 2011 ('CRWD data'). Sites are arranged *left* to *right* in order of increasing surface water area (Table 1). The portion of each form as a percentage of TP in baseflow (% BF TP) and in stormflow (% SF TP) is shown along the *bottom*. Means at sites with different *letters* (uppercase for stormflow and lowercase for baseflow) are statistically different at $p < 0.05$ by Tukey's HSD. Note differences in vertical scales between plots

a large portion of the combined TON yield (from 21 % at EK to 50 % at TBO). NH_4-N loading was small, contributing less than 10 % of either baseflow or stormflow TN yields. By contrast with TN, the contribution of baseflow to TP loading was much lower than its contribution to water yields and to TN

Fig. 6 Warm season (May 1–Oct 31) mean and standard error of yields (km/km^2) of **a** TN, **b** TON, **c** NO_3-N, and **d** NH_4-N in baseflow and stormflow at the main CRWD monitoring sites from 2006 to 2011 ('CRWD data'). Sites are arranged *left* to *right* in order of increasing surface water area (Table 1). The percentage above the set of columns for each site is the portion of the combined (baseflow + stormflow) nutrient yield at the given site due to baseflow. Note differences in vertical scales among plots



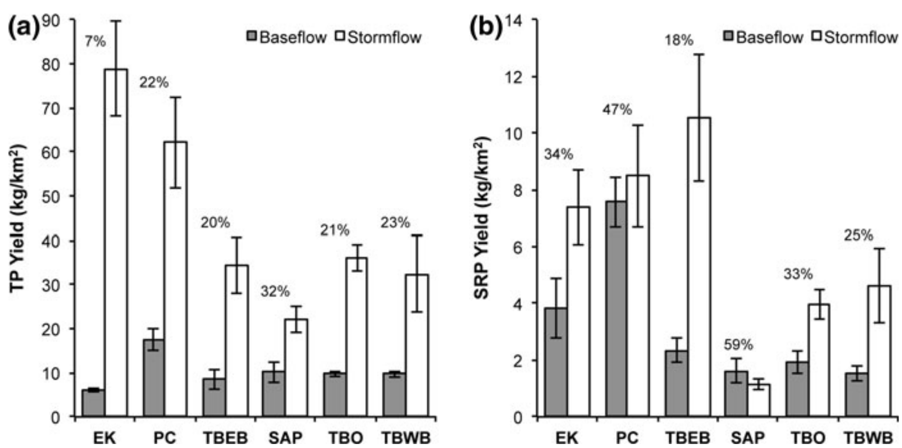


Fig. 7 Warm season (May 1–Oct 31) mean and standard error of yields (km/km^2) of **a** TP and **b** SRP in baseflow and stormflow at the main CRWD monitoring sites from 2006 to 2011 ('CRWD data'). Sites are arranged *left* to *right* in order of increasing surface water area (Table 1). The percentage above the set of columns for each site is the portion of the combined (baseflow + stormflow) nutrient yield at the given site due to baseflow. Note differences in vertical scales between plots

yields, ranging from 7 (EK) to 32 % (SAP) of combined TP yield (Fig. 7), reflecting the much higher relative TP concentrations in stormflow. Baseflow SRP contributions were slightly larger, with 18 (TBEB) to 59 % (SAP) of the combined SRP yield due to baseflow.

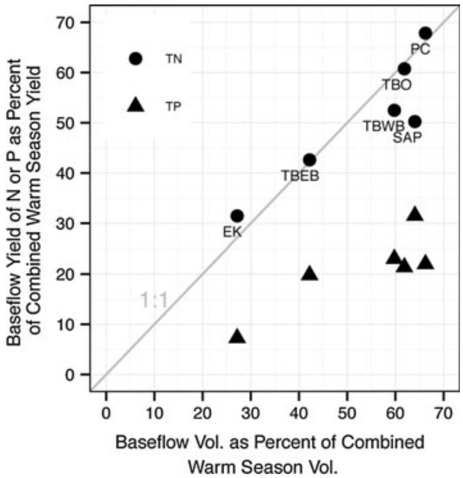


Fig. 8 Baseflow yield of N or P as a percent of the combined (baseflow + stormflow) warm season nutrient yield versus the baseflow water volume as a percent of the combined warm season (May–Oct) water volume, by sub-watershed. Values are an average over the study period (2006–2011)

Dissolved organic and particulate nutrient fractions

N concentrations measured by UMN for 2011 (Table 3) were mostly consistent with observations from the CRWD data set from 2006 to 2011 (Fig. 4), though large differences (~40 %) were present for NO_3-N and TON concentrations. However, these differences were likely related to inter-annual variability (rather than analytical errors), as concentrations from the UMN data were within 10 % of corresponding forms in the CRWD data from 2011. In stormflow, PN was the largest component of TN in all sub-watersheds, ranging from 35 to 62 % of TN. DON, which was similar in baseflow and stormflow, ranged from 0.27 (TBEB) to 0.40 mg/L (EK) in baseflow and from 0.39 (EK) to 0.67 mg/L (SAP) in stormflow. DON contributed 16–31 % of stormwater TN and 12–26 % of baseflow TN, exceeding the contribution of PN in baseflow in all sub-watersheds.

In the UMN data set, P concentrations in baseflow were much smaller than in stormflow (30–56 % of stormflow P on average, depending on form), similar to the long-term monitoring (CRWD) data. Composition of P varied among sites (Table 3): TP was primarily in dissolved form at EK and PC (roughly 70 % of baseflow P in both sub-watersheds), whereas PP dominated baseflow in the remaining sub-watersheds, comprising 64–70 % of baseflow TP at TBEB, SAP, and TBWB. In contrast, PP was the dominant form in stormflow, comprising from 63 (TBEB) to 82 % (EK) of stormflow TP (Table 3). DOP, which was observed in lower concentrations in baseflow (0.015 mg/L on average across sites) than in stormflow (0.029 mg/L on average), constituted a substantial but variable fraction of TP, for baseflow in particular: 40 and 24 % of observed baseflow TP at EK and PC, respectively, and from 8 to 12 % in the other sub-watersheds. In stormflow, DOP concentrations ranged from 7 to 12 % of TP.

Ratios of N to P were calculated for all N and P forms in order to highlight differences in baseflow and stormflow nutrient composition. N to P ratios were generally much higher in baseflow than in stormflow for all forms, illustrating the N dominance of baseflow in the CRW (Table 4). Mean molar TN:TP was very consistent across sites in stormflow, ranging from 13.2 to 18.8 in the UMN data (13.5–18.4 in the more extensive CRWD data). By contrast, baseflow TN:TP was much higher and more variable, ranging from 29.9 to 158 in the UMN data (46.1–136 in the CRWD data), due in part to NO_3-N dominance of dissolved N in baseflow. Despite concentrations of particulate N and P that were much higher (6 times on average) in stormflow than in baseflow, PN:PP ratios in stormflow (11.7 to 17.3 across sites) were similar to those in baseflow (6.5 to 18.9 across sites), suggesting that storm-deposited particulates are being moved through the storm drains during baseflow periods, although at much lower rates than during storms.

Land cover regression analysis

The effectiveness of an analysis of land cover effects on nutrient sources and transport was limited by the low number of sites ($n = 6$ for stormflow, $n = 5$ for baseflow), and by the small ranges and uneven distributions of values of the land cover variables due to the relative uniformity of land cover (predominantly low-density residential) in the monitored sub-watersheds. In addition, the presence of lakes and wetlands in several of sub-watersheds increases travel time of stormwater and allows for nutrient transformation to occur. As a result, linear regression analysis revealed very few statistically significant relationships ($p < 0.05$) between land cover variables (Table 1) and seasonal mean nutrient concentrations in stormflow or baseflow. One exception was street canopy fraction,

Table 3 Summary of nitrogen (N) and phosphorus (P) concentration (mg/L) data from analysis of stormflow and baseflow samples collected during May–October of 2011 ('UMN Data')

	Baseflow					Stormflow			
	EK	PC	TBEB	SAP	TBWB	EK	TBEB	SAP	TBWB
n=	9	8	12	9	11	4	5	5	7
Total phosphorus (TP), mg/L									
Mean	0.062	0.070	0.116	0.100	0.091	0.327	0.264	0.241	0.254
SE	0.011	0.006	0.021	0.013	0.013	0.015	0.031	0.052	0.042
Particulate phosphorus (PP), mg/L									
Mean	0.016	0.024	0.078	0.064	0.064	0.245	0.165	0.198	0.178
SE	0.002	0.002	0.021	0.013	0.008	0.014	0.038	0.032	0.035
% of TP	25	35	67	64	70	75	63	82	70
Dissolved organic phosphorus (DOP), mg/L									
Mean	0.025	0.017	0.013	0.008	0.011	0.038	0.028	0.017	0.031
SE	0.011	0.005	0.002	0.003	0.004	0.013	0.005	0.002	0.005
% of TP	40	24	11	8	12	12	11	7	12
Soluble reactive phosphorus (SRP), mg/L									
Mean	0.021	0.028	0.025	0.028	0.016	0.045	0.071	0.026	0.045
SE	0.006	0.004	0.003	0.012	0.006	0.009	0.009	0.006	0.010
% of TP	34	41	21	28	17	14	27	11	18
Total nitrogen (TN), mg/L									
Mean	2.98	2.71	1.21	1.56	1.51	2.46	1.82	2.39	1.93
SE	0.25	0.17	0.08	0.12	0.06	0.26	0.25	0.49	0.27
Particulate nitrogen (PN), mg/L									
Mean	0.12	0.10	0.14	0.23	0.33	1.53	0.64	1.06	0.98
SE	0.02	0.02	0.03	0.05	0.08	0.23	0.10	0.28	0.20
% of TN	4	4	12	15	22	62	35	45	51
Dissolved organic nitrogen (DON), mg/L									
Mean	0.40	0.31	0.27	0.34	0.39	0.39	0.57	0.67	0.42
SE	0.32	0.15	0.06	0.15	0.06	0.08	0.07	0.24	0.04
% of TN	13	12	22	22	26	16	31	28	22
Nitrate-Nitrite N (NO_3-N), mg/L									
Mean	2.43	2.26	0.72	0.92	0.69	0.29	0.35	0.49	0.37
SE	0.10	0.12	0.06	0.12	0.05	0.06	0.04	0.18	0.04
% of TN	82	84	60	59	46	12	19	21	19
Ammonium-N (NH_4-N), mg/L									
Mean	0.04	0.03	0.08	0.08	0.09	0.24	0.26	0.16	0.16
SE	0.01	0.00	0.01	0.01	0.02	0.07	0.07	0.06	0.04
% of TN	1	1	7	5	6	10	15	7	9

Mean, standard error (SE), and number of samples are included for various forms of N and P at all sites, as well as the percentage of TN or TP. Note that no stormflow data was available for PC due to equipment problems at the site

which was a significant predictor of stormflow TP concentration ($R^2 = 0.70$, $p = 0.037$).

By contrast, for stormflow, impervious cover explained a majority of variation in water and nutrient transport in stormflow. Water yield was significantly and positively correlated with both connected impervious area ($R^2 = 0.74$, $p = 0.027$) and street density ($R^2 = 0.66$, $p = 0.049$), while street density was a

Table 4 Mean nitrogen-to-phosphorus ratios (molar) for stormflow and baseflow, determined from samples collected at 5 sub-watersheds during the 2011 monitoring season ('UMN Data'), as well as from 6 sub-watersheds in the CRWD data (2006–2011)

Baseflow							
Sub-watershed	UMN Data					CRWD Data	
	n	DON:DOP	TDN:TDP	PN:PP	TN:TP	*n*	TN:TP
East Kittsondale (EK)	9	6.8	314.0	18.9	157.9	97	135.5
Phalen Creek (PC)	8	91.4	162.1	10.1	97.1	93	105.3
St. Anthony Park (SAP)	9	49.5	151.0	9.9	45.6	89	46.1
Trout Brook E. Branch (TBEB)	12	56.0	76.5	6.5	29.9	87	61.4
Trout Brook W. Branch (TBWB)	11	114.0	156.6	10.6	45.5	90	58.5
Trout Brook Outlet (TBO)	–	–	–	–	–	70	97.0
Stormflow							
Sub-watershed	UMN data					CRWD data	
	n	DON:DOP	TDN:TDP	PN:PP	TN:TP	*n*	TN:TP
East Kittsondale (EK)	4	26.0	30.1	13.8	16.8	130	15.9
Phalen Creek (PC)	–	–	–	–	–	101	14.8
St. Anthony Park (SAP)	5	59.4	70.3	12.1	18.8	125	18.4
Trout Brook E. Branch (TBEB)	5	53.6	35.7	17.3	18.1	97	14.8
Trout Brook W. Branch (TBWB)	7	34.5	31.7	11.7	13.2	92	13.5
Trout Brook Outlet (TBO)	–	–	–	–	–	82	15.0

n is the number of samples comprising the mean

significant predictor of mean seasonal stormflow yields of TP ($R^2 = 0.71$, $p = 0.036$), TN ($R^2 = 0.67$, $p = 0.043$), and TON ($R^2 = 0.67$, $p = 0.046$). Connected impervious area was also a strong predictor of NO_3-N yield ($R^2 = 0.75$, $p = 0.026$). No statistically significant relationships were found for stormflow yields of any other nutrient forms, nor for baseflow yields of any nutrient forms. These results suggest that surface hydrology is controlling the loading of major nutrients in stormflow, with street density (a surrogate for drainage density) being especially important. Baseflow loading, by contrast, is likely controlled by sub-surface hydrologic features that were not accounted for in our statistical analysis.

Baseflow water sources in the CRW

Measurements of DIC, $\delta^{18}O$, NO_3-N, and Cl^- were used to infer water sources in baseflow. NO_3-N is highly mobile in groundwater, and DIC is normally found in higher concentration in groundwater compared to surface water as a result of chemical weathering of soil and rock (Myrbo and Shapley 2006). $\delta^{18}O$ tends to be higher in warm season precipitation than in cool season precipitation, and thus should be higher in surface water than in groundwater (Krabbenhoft et al. 1994). Cl^-, a conservative tracer, is an input to the CRW landscape primarily in the form of NaCl, which is applied as a winter road deicer and may infiltrate to groundwater (Novotny et al. 2009).

Groundwater appears to be the primary component of baseflow at all sites in the CRW, as suggested in particular by concentrations of Cl^- and DIC, which were higher in baseflow than in stormflow across all sites (especially for Cl^-), and by $\delta^{18}O$, which was consistently low among sites and similar to values for CRW springs (Table 5). DIC concentrations in springs across CRW ranged from 50.7 to 87.4 mg/L and were higher than observed in the outlets of several lakes in and around CRW (20.5 mg/L on average); a similar contrast between lakes and springs was also seen in $\delta^{18}O$ and NO_3-N (Table 5), the latter of which is likely the result of NO_3-N uptake in lakes during summer. Concentrations of NO_3-N were also much higher in baseflow than in stormflow, and together with the other results imply that CRW groundwater may be enriched in NO_3-N.

The considerable variation of NO_3-N, DIC, and Cl^- among sites suggests that groundwater chemical

Table 5 Mean dissolved inorganic carbon (DIC) and chloride (Cl^-) concentrations and $\delta^{18}O$ of water (‰) in stormflow and baseflow at main monitoring sites, as well as mean and range of DIC and nitrate (NO_3-N) concentrations and mean $\delta^{18}O$ measured in 4 lake outlets and 5 springs located in and around the CRW in 2011

Sub-watershed	*n*	DIC (mg/L)	*n*	Cl (mg/L)	*n*	$\delta^{18}O$ (‰)
Main sites, stormflow						
East Kittsondale (EK)	4	4.9	130	19.5	–	–
Phalen Creek (PC)	–	–	101	16.2	–	–
St. Anthony Park (SAP)	5	13.5	125	22.5	–	–
Trout Brook E. Branch (TBEB)	5	11.9	97	54.8	–	–
Trout Brook W. Branch (TBWB)	7	9.0	92	18.4	–	–
Trout Brook Outlet (TBO)	–	–	82	44.3	–	–
Main sites, baseflow						
East Kittsondale (EK)	9	68.1	97	422.0	5	−8.6
Phalen Creek (PC)	8	67.8	93	175.6	4	−8.0
St. Anthony Park (SAP)	9	55.7	89	102.4	4	−7.8
Trout Brook E. Branch (TBEB)	12	71.1	87	350.7	5	−8.3
Trout Brook W. Branch (TBWB)	11	33.3	90	83.3	6	−7.0
Trout Brook Outlet (TBO)	–	–	70	135.9	–	–

Site	*n*	DIC (mg/L)	*n*	NO_3-N (mg/L)	*n*	$\delta^{18}O$ (‰)
Other sites, baseflow						
Lakes (4)	19	20.5 (0.83–54.6)	20	0.011 (BDL-0.101)	8	−4.8
Springs (5)	21	69.6 (50.7–87.4)	24	2.08 (BDL-6.11)	10	−8.0

DIC and $\delta^{18}O$ were measured at 5 sub-watersheds during the 2011 monitoring season ('UMN Data'), and Cl^- was determined from the CRWD data from 6 sub-watersheds (2006–2011). *n* is the number of samples comprising the mean; 'BDL' denotes concentrations below the detection limit of the analysis

composition and source were not uniform across sub-watersheds. For Cl^- in particular, sub-watersheds with known connections to surface water (TBWB, TBO, and SAP) had the lowest Cl^- concentrations. This suggests that road salt-contaminated groundwater, if present, may have been diluted by upstream surface water, the chemical composition of which is highly influenced by Cl^--poor warm season rainfall. By contrast, extremely high concentrations of Cl^- at EK (422 mg/L) and TBEB (351 mg/L), along with the presence in the lower portions of these sub-watersheds of interstate highways that are heavily treated with deicer during winter, indicate Cl^- contamination of shallow groundwater from road salt.

Discussion

Studies of urban storm drainage typically focus on surface runoff resulting from storms (e.g., Hatt et al. 2004; Toran and Grandstaff 2007). However, the work described here shows that baseflow also contributed significantly to warm-season water and nutrient yields in an urban area, and delivered nutrients in substantially different forms and with different N:P ratio compared to stormflow. Baseflow, which was dominated by groundwater, was more important for loading of N than of P, suggesting that N and P move via somewhat separate surface and sub-surface transport pathways. Variation in baseflow N and P among our study sites was related in part to the degree of connectivity of the storm drains to surface and groundwater sources. These sources in turn may be influenced by water table depth, construction of drains in buried streams, and presence of ponds and wetlands or outlets from major lakes.

Hydrologic pathways of urban drainage in the CRW

The magnitude of water and nutrient yields during stormflow in the CRW was determined primarily by runoff from impervious surfaces, as water yield was related to both street density and connected impervious surface area. In addition, street density was a significant predictor of yields of major nutrient forms (TP, TN, and TON), as expected given the role of roadways in collecting and transporting nutrients through urban areas (e.g. Kayhanian et al. 2007; Davidson et al. 2010).

Baseflow in CRW storm drains could be attributed to two primary hydrologic pathways: (1) groundwater, which infiltrates into pipes located below the water table, and (2) surface water, which flows from lakes, ponds, and wetlands connected to the storm drains. Surface water inputs influenced baseflow at some sites (TBWB, TBO, and SAP) where lakes, ponds, and wetlands were more prevalent in the watersheds. However, baseflow in all sites was dominated by groundwater, as suggested by water chemistry and isotope data ($\delta^{18}O$, DIC, and Cl^- in particular), and by the fact that some portion of the storm drain networks in all major watersheds are below the water table, especially near surface water and buried streams (unpublished data). The combination of groundwater and surface water inputs to baseflow is similar to that of a surface stream, and may be expected given the shallow groundwater present in much of the CRW.

The storm drain network of the CRW has replaced nearly all natural surface channels in the watershed, increasing the drainage density of the system far beyond that of pre-settlement conditions (Walsh et al. 2005). Stream burial is common in older, urbanized watersheds like the CRW, though its effect on hydrology and nutrient processing is not well understood (Elmore and Kaushal 2008; Roy et al. 2009). Buried streams may play a role in determining the importance of sub-surface pathways in the study watershed, as the highest baseflow water yields were observed in the two major converted streams in the CRW, Trout Brook and Phalen Creek. The two sites also contrast sharply in terms of water table depth (Table 1) and connectivity to upstream surface water (i.e., PC has no upstream lakes). These differences may be due to potential discrepancies between the groundwatershed and the sewershed for PC, which historically drained a much larger watershed than at present (Capitol Region Watershed District (CRWD) 2010). This uncertainty emphasizes the difficulty in understanding the hydrologic connectivity of the urban drainage network (Roy et al. 2009; Kaushal and Belt 2012).

Nutrient sources to stormwater

Potential sources of N and P to urban landscapes and to storm drains during runoff events are diverse and may include atmospheric deposition, fertilizer, litterfall (e.g., leaves and grass clippings), and pet waste (Baker et al. 2007, Bernhardt et al. 2008). In a study of household landscapes in the Minneapolis-St. Paul metropolitan area, which included the CRW, Fissore et al. (2012) estimated that fertilizer was the primary N input to lawns (nearly an order of magnitude greater than pet waste or atmospheric deposition), whereas pet waste was the largest source of P (fertilizer was a minor P input due to a 2005 Minnesota law restricting the use of P in lawn fertilizer; MDA 2007). These results are particularly relevant to the current study due to the prevalence of low-density residential land use in the monitored watersheds.

Stormflow nutrient sources may be relatively homogenous among watersheds in this study. Stormflow TN:TP ratios were especially similar among sites, and stormwater nutrient concentrations were poorly correlated with land cover variables in the linear regression analysis, likely reflecting the small ranges in most of the land cover metrics among watersheds. These findings may be the result of similar land use across watersheds (predominantly low-density residential), but also suggest the dominance of a source that is relatively spatially uniform (e.g., atmospheric deposition).

Stormwater N and P in the CRW were dominated by dissolved organic and particulate forms (TON and DOP+PP), with particulates comprising the majority of N and P at all sites. Sources of particulate P could include soils and vegetation as well as pet waste. For both N and P, litterfall from trees appears to be an important source of particulate and organic nutrient forms. Lawns and well-established tree canopies are present along streets in much of the low-density residential land use that dominates the CRW, and street canopy fraction was a significant predictor of TP concentration. In addition, tree litter has been shown in recent work in the Minneapolis-St. Paul region to represent a major input of N and P to stormwater (Hobbie et al. 2013), and among tree species in that study, TN:TP ratios (roughly 10.0 on average) were not much lower than TN:TP in stormflow in our study, but were substantially lower than in baseflow.

Atmospheric deposition may be an appreciable source of inorganic N to stormwater in the CRW, as

NO_3-N and NH_4-N concentrations in stormwater were not statistically different among sites, suggesting a spatially uniform source. The significant relationship between NO_3-N yield and connected impervious area indicates that impervious areas may be especially important as collectors and conveyors of deposition, and is consistent with a recent study observing higher deposition of NO_3-N and NH_4-N near roadways (Bettez et al. 2013). However, warm season stormflow DIN (NO_3-N + NH_4-N) concentrations were roughly 40 % of those measured in wet deposition at the Cedar Creek site of the National Atmospheric Deposition Program located 40 km north of the CRW (~1.50 mg/L on average during June–November of 2006–2011; http://nadp.sws.uiuc.edu/data/ntndata.aspx). Lower DIN in CRW stormflow suggests that sources more dilute than deposition (e.g., fertilizer or pet waste) may also be contributing to stormflow DIN, perhaps being transported by runoff from land adjacent to streets.

The restriction on P in lawn fertilizer may have decreased the contribution of SRP to stormwater TP in the CRW. Fertilizer and fertilized soils have been shown to contribute disproportionately to export of total dissolved P from a mixed land use watershed (Easton et al. 2007), while potential P loss from fertilized soils may decrease rapidly after fertilization (Soldat and Petrovic 2008). Accordingly, SRP was a minor component of warm season stormwater TP in the CRW, and concentrations were much lower than reported for urban watersheds across the US (Pitt et al. 2005) and in Wisconsin (Bannerman et al. 1996).

Nutrient sources to baseflow

Potential inputs of N and P to groundwater include leaching and downward movement of surface sources as well as sewage inputs from illicit connections to storm drains or from leakage of sanitary sewers and septic systems (Cole et al. 2006). However, there is strong evidence that sewage is not a major source of N and P in the CRW despite its prevalence in some other urban watersheds (e.g., Kroeger et al. 2006; Duan et al. 2012). In addition to the rarity of septic systems and illicit connections in the monitored watersheds of the CRW, we also did not observe the very low N:P ratios (ca 3:1; Gackstatter et al. 1978) that are characteristic of raw sewage. Furthermore, elevated Cl^- concentrations at several sites, which could indicate sewage contamination, exhibit peaks in winter and early spring (data not shown); this seasonality suggests that road deicer is a source rather than sewage.

Variability in the forms and concentrations of baseflow N and P among sites reflected the balance between hydrologic pathways (i.e., surface water and groundwater) in baseflow of the monitored watersheds. The highest baseflow concentrations and fractions of particulate N and P were observed at the sites with known connections to surface water (SAP and TBWB), consistent with a larger contribution of surface features to particulates (e.g., from suspended sediment, algae, or plant matter) compared to groundwater. Conversely, dissolved N and P (NO_3-N, SRP and DOP) were highest at the sites (EK and PC) with very little surface water influence (i.e. low pond density and no connections to upstream lakes). These sites also had the lowest water tables (Table 1), thus high NO_3-N losses at these sites could also be due to nitrification, which may be enhanced by well-drained soils and low water tables (Groffman et al. 2002; Ullah and Moore 2009).

The high amount of particulate N and P in baseflow at most sites in the CRW suggests that drain connections to surface water were not the only source of particulates to storm drains. As mentioned previously, illicit sanitary connections were an unlikely source, and stream bank erosion, a source of P cited in previous studies (e.g. Easton and Petrovic 2008; Duan et al. 2012), was negligible due to the lack of open channels in the drainage network. A more likely source was re-suspension by baseflow of storm-deposited particulates, as suggested by the similarity of PN:PP between baseflow and stormflow among sites.

Importance of baseflow nutrient loading in the CRW

This study shows that baseflow can play a substantial role in movement of nutrients to waters downstream of urban areas. The importance of baseflow to nutrient loading has seldom been directly addressed in previous studies of urban storm drains (Taylor et al. 2005), although some studies have collected data during baseflow periods (e.g., Hook and Yeakley 2005; McLeod et al. 2006; Petrone 2010). In addition, baseflow transport of nutrients differed for N and P, as baseflow contributed 51 % of the warm season N yield across sites, but only 21 % for P. The greater importance of baseflow for N loading was due in part to the prevalence of dissolved N forms, DIN (or NO_3-N) especially, as mean seasonal baseflow concentrations were similar to or higher than observed in urban streams across the US (Brett et al. 2005; Wollheim et al. 2005; Pellerin et al. 2006).

Loading of N and P by CRW storms drains was comparable to that of streams in urban watersheds of previous studies. For example, warm-season combined (stormflow and baseflow) DIN yields in the CRW were roughly half of those reported by Wollheim et al. (2005) for an urban Massachusetts stream, though year-round persistence of baseflow in the CRW implies that actual annual combined yields by CRW drains were higher and could approach those of that study. Warm-season combined yields of TN and TP in CRW storm drains were similar to corresponding annual yields in urban streams in Baltimore, MD (Groffman et al. 2004; Shields et al. 2008; Duan et al. 2012) and Perth, Australia (Petrone 2010), likely due to the higher baseflow water yields in the CRW. Relative to other managed lands, CRW baseflow was less important for nutrient export, as the proportion of warm-season N and P loading delivered by baseflow in the CRW was less than observed in streams of agricultural watersheds (Caruso 2000; Schilling and Zhang 2004; Hively et al. 2005). The variability in reported nutrient yields among previous studies, and the lack of annual data in our study, prevents a more complete comparison of CRW drains with urban streams.

The substantial contribution of organic and particulate forms to N yields contrasts with previous studies of urban streams in which NO_3-N was the dominant fraction of TN (e.g., Brett et al. 2005; Kaushal et al. 2011). The considerable PN has implications for studies of N retention in urban watersheds, as a few studies have focused solely on the dissolved forms of N or concluded that particulate N is not an important fraction of N export in their study watersheds (e.g. Groffman et al. 2004; Wollheim et al. 2005). Since PN comprised 4–22 % of baseflow TN (26 % to 38 % of combined stormflow and baseflow TN) in our watershed, neglecting particulate N could introduce considerable error in estimating N exports. This potential importance of PN suggests that it warrants inclusion in future work, as only a few previous studies in urban drains and streams have included PN (e.g., Taylor et al. 2005; Rosenzweig et al. 2011).

Conclusions

We hypothesize that the combination of drain-connected surface water, storm drain construction in buried streams, and shallow groundwater in the CRW led to the substantial contributions of baseflow to total nutrient yields. The complexity of the sub-surface drainage network more strongly affected variation in water chemistry than the relatively uniform surface land use in the watersheds. This study therefore contributes to recent work (e.g., Lookingbill et al. 2009; Kaushal and Belt 2012) emphasizing the structure and connectivity of the urban drainage network as key factors in determining the transport of nutrients from urban landscapes to downstream receiving waters. We suggest that baseflow in particular should not be overlooked in development of water quality management strategies or in studies of urban nutrient cycles.

Our study also identifies likely differences in transport pathways between N and P. While P was delivered primarily in stormflow, a substantial amount of N was transported by baseflow due to the abundance of dissolved N in groundwater. High N in groundwater implies that deliberate infiltration of stormwater, a common practice for reduction of particulates and runoff volume, could potentially lead to groundwater pollution and export of dissolved pollutants via storm drains that intercept shallow groundwater. Highly mobile NO_3 and Cl^- may be especially susceptible to export by groundwater, as well as dissolved organic N and P, which may be bioreactive (e.g., Seitzinger et al. 2002) but are rarely targeted by management practices. The fate of N especially in urban infiltration areas is poorly known (Bettez and Groffman 2012). Management of dissolved nutrients, and N in particular, may therefore require different strategies than for P (Taylor et al. 2005; Collins et al. 2010). Such strategies may include redesigning existing stormwater control measures such as wetlands to promote mineralization, nitrification, and denitrification as appropriate (e.g., Gerke et al. 2001; Harrison et al. 2011), or reducing inputs of N to the land surface by (for example) decreasing N fertilization to levels that reduce NO_3 leaching, reducing pet wastes left on lawns, repairing sanitary sewers or disconnecting them from storm drains, and eliminating septic systems (Bernhardt et al. 2008; Kaushal et al. 2011; Fissore et al. 2012).

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