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Stormflow dynamics of dissolved organic carbon and total dissolved nitrogen in a small urban watershed

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Abstract. We examined patterns of dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) loading to a small urban stream during baseflow and stormflow. We hypothesized that lower DOC and TDN contributions from impervious surfaces would dilute natural hydrologic flowpath (i.e., riparian) contributions during storm events in an urban watershed, resulting in lower concentrations of DOC and TDN during storms. We tested these hypotheses in a small urban watershed in Portland, Oregon, over a 3-month period during the spring of 2003. We compared baseflow and stormflow chemistry using Mann–Whitney tests (significant at $p < 0.05$). We also applied a mass balance to the stream to compare the relative significance of impervious surface contributions versus riparian contributions of DOC and TDN. Results showed a significant increase in stream DOC concentrations during stormflows (median baseflow DOC = 2.00 mg l^{-1} vs. median stormflow DOC = 3.46 mg l^{-1}). TDN streamwater concentrations, however, significantly decreased with stormflow (median baseflow TDN = 0.75 mg l^{-1} vs. median stormflow TDN = 0.56 mg l^{-1}). During storms, remnant riparian areas contributed 70–74% of DOC export and 38–35% of TDN export to the stream. The observed pattern of increased DOC concentrations during stormflows in this urban watershed was similar to patterns found in previous studies of forested watersheds. Results for TDN indicated that there were relatively high baseflow nitrogen concentrations in the lower watershed that may have partially masked the remnant riparian signal during stormflows. Remnant riparian areas were a major source of DOC and TDN to the stream during storms. These results suggest the importance of preserving near-stream riparian areas in cities to maintain ambient carbon and nitrogen source contributions to urban streams.

Introduction

Many lines of evidence illustrate the ecological importance of dissolved organic carbon (DOC) and soluble nitrogen in watersheds. DOC flux partially controls ecological and chemical processes in soils (Lal et al. 1998) through roles in the denitrification process (Brye et al. 2001), the mobility of toxic metals (Schlesinger 1997) and organopollutants (Moore 1998), and as an energy source for microbial activity (Beyer et al. 1995; Neff and Asner 2001). Soluble nitrogen is often a limiting nutrient for autotrophic production in watersheds and in streams (Vitousek and Howarth 1991; Duff and Triska 2000). DOC is a significant energy source for microbial communities in forested streams (Meyer 1994) and hyporheic sediments (Findlay et al. 1993). The dissolved C:N ratio was a good predictor of bacterial growth in a study of leachate from native vegetation in the Pacific Northwest (McArthur and Richardson 2002). Energy and biomass derived from DOC and total dissolved nitrogen (TDN) and assimilated into bacteria are significant to the food web in forested headwater streams (Hall and Meyer 1998; Sanzone et al. 2001). In forested watersheds, stormflow fluxes of DOC and TDN have stimulated metabolic activity of stream microbial communities (Stepanauskas et al. 2000; Buffam et al. 2001).

At least three major factors contribute to fate and transport dynamics of DOC and TDN in forested watersheds. (1) Vegetation biomass in a watershed governs input of DOC and TDN (Kalbitz et al. 2000) while also playing a role in dissolved nitrogen removal via uptake (Yeakley et al. 2003). (2) Biological and physical properties of soils control transformation, retention, and transport or removal of the constituents (Heathwaite et al. 1996; Moore 1998). (3) Dominant hydrologic flowpaths through upper soil and litter layers to the stream determine contact time of the constituents with plant roots, the microbial community, and soil particles (Hedin et al. 1998; Michalzik et al. 2001). Hydrology is particularly important to DOC and TDN transport during stormflow. Surface water DOC has been correlated with increased discharge during stormflow for many forested watersheds (Meyer and Tate 1983; McDowell and Likens 1988; Hinton et al. 1997; Correll et al. 2001). Streamwater TDN can also increase with stormflow in forested watersheds (Peters 1994; Wondzell and Swanson 1996; Campbell et al. 2000) and in agricultural watersheds (Vanni et al. 2001). Studies that have examined both DOC and TDN concentrations during flood events or stormflows in forested watersheds have also found increases in both constituents with increased discharge (Mulholland et al. 1981; Frank et al. 2000; Stepanauskas et al. 2000; Buffam et al. 2001).

In forested watersheds, a mechanism explaining increased DOC and TDN during stormflow was a flushing of DOC- and TDN-rich upper soil and litter horizons in the riparian ecotone (Hornberger et al. 1994; Frank et al. 2000; Kaplan and Newbold 2000). In multiple low-order forested watersheds when the dominant hydrologic flowpath was through riparian areas, there was greater DOC export to the stream during stormflows (Hinton et al. 1998). A recent study found that riparian areas were a major source of stormflow DOC and concluded that timing and connections of hydrologic flowpaths were a major control on stormflow DOC concentrations and mass export (McGlynn and McDonnell 2003).

Human influences on ecosystems can be extreme and are increasingly pressing in the conversion of land cover to urban and suburban uses (Vitousek et al. 1997). The extent of urban areas has increased recently (Lopez and Hynes 2003) and the Pacific Northwest is one of the fastest developing regions of North America (Naiman et al. 2000). The hydrology of an urban watershed differs from that of forested watersheds primarily because of increased impervious area (Leopold 1968) and engineered stormwater systems that route precipitation more directly to surface waters (Booth and Jackson 1997). Further, higher levels of soil compaction in urban areas (Jim 1998) reduce soil porosity and infiltration rates (Bhuju and Ohsawa 1997). Urbanization also results in an overall reduction of vegetation biomass. In urban areas of western Oregon, a 56% loss of tree cover due to urbanization occurred during 1972–2000 (American Forests 2001). Riparian tree cover was reduced by 1% per year during the 1990s due to new construction in the Portland metropolitan region (Ozawa and Yeakley, 2004). The overall effect of urban alterations to hydrology is increased surface runoff volume from individual precipitation events, higher peak flows, steeper rising limbs of hydrographs, and quicker baseflow recession (Rose and Peters 2001). Although studies have shown that urbanization can increase total inorganic nitrogen loading to streams (Peters and Donohue 2001), and that urban water infrastructure can dramatically increase DOC levels in surface waters (Westerhoff and Anning 2000) few studies have examined carbon and nitrogen dynamics in urban streams that lack combined sewer systems.

Urbanization is expected to produce at least two distinct impacts on dissolved carbon and nitrogen fluxes in watersheds. First, increased impervious area diverts water normally destined for soils directly to streams. Second, vegetation removal reduces the amount of overall organic matter and lowers the vegetative transpiration potential. These effects lower inputs of DOC and TDN and make more water available for runoff. The combination, then, of increased impervious area and loss of evapotranspiration potential should combine to dilute the riparian component of DOC and TDN loading during stormflows in an urban watershed.

Our objective was to examine patterns of DOC and TDN loading to a stream under baseflow and stormflow conditions in a small urban watershed. We addressed the following questions: Do DOC and TDN concentrations and exports change with stormflow in a small urban watershed? What are the relative contributions of DOC and TDN from areas of upland impervious surface runoff and from remnant riparian areas during stormflows and baseflow in a small urban watershed? We hypothesized that: (1) Stormflow concentrations of DOC and TDN are lower than baseflow concentrations in a small urban watershed; (2) During baseflow conditions, remnant riparian areas are the major contributor of DOC and TDN; and (3) During stormflows, the contribution of the upland impervious areas dilutes the remnant riparian contribution and is primarily responsible for observed concentrations of DOC and TDN.

Study area

The study area was a small urban watershed (32 ha) drained by a tributary to Johnson Creek, in southeast Portland, Oregon (Figure 1). Land use in the

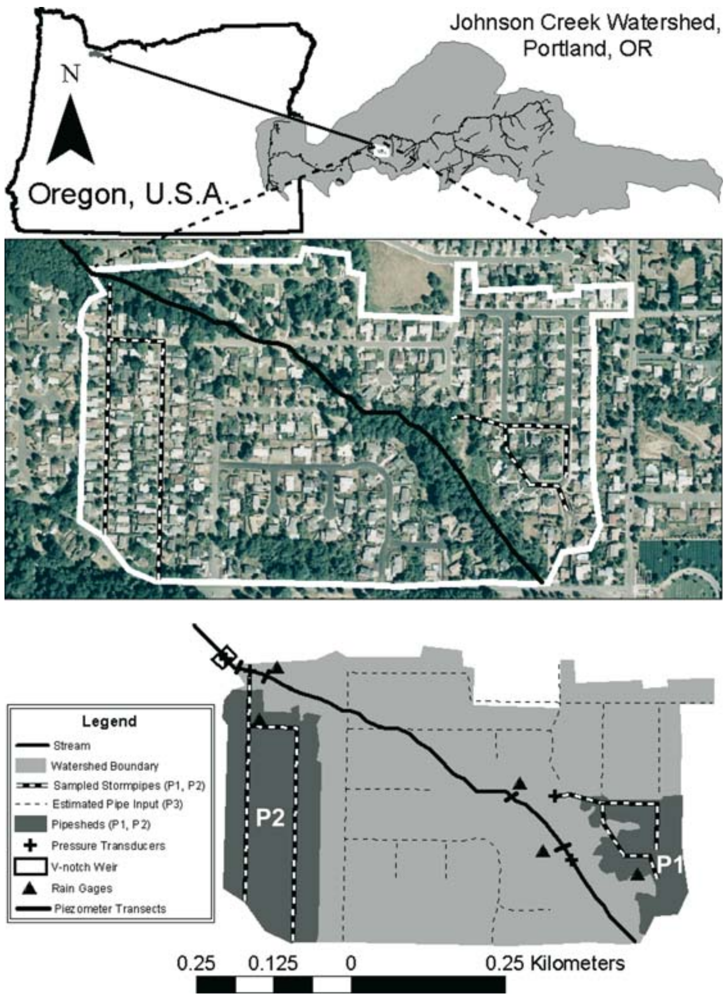

Figure 1. Study area and sampling instrumentation (aerial photo from Metro 2002).

watershed was dominated by single family residential dwellings with a remnant riparian greenspace along the majority of the stream (Figure 1) (Metro 2002). The houses in the watershed are connected to the City of Portland sewer system (Metro 2002). The Johnson Creek watershed covers an area of 140 km^2 and encompasses both agricultural and urban land uses (Sonoda et al. 2001). The study site lies on the Troutdale Gravel aquifer that dates back to the Pleistocene, ranges from 20 to 120 m thick, and generally is composed of a consolidated sandy gravel layer (Sonoda et al. 2001). Average annual precipitation for the Johnson Creek watershed is 937 mm (Clark 1999).

Instrumentation in the watershed included pressure transducers with data loggers (model WL-15, 2001, Global Water Inc.) that were located at all surface water sample sites (Figure 1) (Sonoda 2002). There were five rain gages (model 1001-091, 2001, Rickly Hydrological Company) in the watershed used to collect precipitation chemistry samples (Figure 1); two gages were in open areas and three were under forested riparian canopy. Four piezometer transects, a portable pump sampler (Masterflex E/S^{TM}, model 07571-05, 2001, Cole-Parmer Instrument Co.) and a bailer (Model 101M Mini Water Level Meter, 2001, Solinst Inc.) allowed for shallow subsurface water chemistry sampling (sample wells depth = 61 cm) and measurement of the shallow subsurface water table depth (open wells depth = 100 cm) (Figure 1) (Sonoda 2002). Hourly precipitation data were obtained from a City of Portland HYDRA tipping bucket rain gage (0.25 mm/tip) located within 1000 m of the watershed boundary. The rain gage elevation was 61 m and the mean watershed elevation was 125 m (Metro 2002).

The V-notch weir was located where the stream gradient was shallow enough to ensure a horizontal pool upstream of the weir (Figure 1) (Sonoda 2002). The headwaters sample point was selected upstream of the stormpipe network (Figure 1) and was free of impervious surface area contribution yeilding a direct measurement of remnant urban riparian area contribution. At the headwaters sample point, a short reach of the stream was routed through a culvert allowing for measurement of discharge without the aid of a weir (Sonoda 2002). The stormpipe sample points, P_1 and P_2, were selected for measurement of impervious surface contribution to the stream (Figure 1). The remaining impervious area input, P_3 (Figure 1), was estimated based on measured values of P_1 and P_2 weighted by the pipeshed areas. The stormpipe signal is dominated by runoff from impervious surfaces yet the measurements likely include runoff from pervious surfaces such as lawns and gardens during storm events. The pipesheds were determined from City of Portland stormpipe network maps combined with digitization and interpretation of aerial photographs using ESRI ArcGIS^{TM} software. P_1, the upstream pipe, drained an area that included 0.27 ha of streets and 0.92 ha of roofs and driveways for a total impervious area (TIA) of 57% (Table 1). P_2 collected water from impervious surfaces totaling 0.76 ha of streets and 1.97 ha of roofs and driveways for a TIA of 50% (Table 1). P_3 incorporated 3 distinct stormpipe networks and collected water from impervious surfaces with a street area of 2.47 ha and a roof and driveway area of 5.67 ha for a TIA of 50% (Table 1). Overall the watershed contained a TIA of 37%, well above a 10% TIA threshold for

Table 1. Watershed and pipeshed percent total impervious area.

Location	Total area (ha)	Total impervious area (%)
Pipeshed 1	2.1	57
Pipeshed 2	5.5	50
Pipeshed 3	16.3	50
Remnant riparian area	8.2	0
Watershed	32.2	37

unstable stream channels in urban areas provided in the literature (Booth and Jackson 1997).

Methods

This study was conducted during the spring of 2003 (April–June), a seasonally rainy period at the beginning of the growing season. Surface water samples for this study were collected daily for baseflow, on a 15-min interval for storm rising limbs, and on a 1-h interval for recession limbs. Precipitation chemistry was sampled once at the end of each storm. Shallow subsurface water chemistry was sampled daily for baseflow. During storms, one set of subsurface water samples was collected shortly after peak flow and a second set of subsurface samples was collected during the recession limb, corresponding to slow-stormflow associated with subsurface pathways in urban streams (Solo-Gabriele and Perkins 1997). Water chemistry samples were collected in acid washed 250 ml HDPE Nalgene bottles after rinsing with sample water (Sonoda et al. 2002). Samples were immediately placed on ice for transport to the laboratory and were vacuum-filtered through combusted GF/F filters to remove particulates (Wetzel and Likens 2000). The filtrate was preserved at pH $\leq$ 2.0 and stored at 4 °C in the dark prior to analysis (Wetzel and Likens 2000). Concentrations of DOC and TDN in samples were measured with a Shimadzu 5000A Total Carbon Analyzer equipped with a Total Nitrogen Module (Shimadzu, Kyoto, Japan, 2002). If three of five injections did not produce a standard deviation below 0.1 or a coefficient of variation less than 2.0%, the sample was rejected (Willey et al. 2000). Rejected samples were run a second time. Of the more than 1000 samples analyzed in this study, only four failed to meet reproducibility standards after two runs and were omitted.

A rating curve for the weir was determined by linear regression to convert pressure transducer readings to head measurements ($p < 0.001$, $R^2 = 0.996$). Head measurements for a 90° V-notch were related to discharge according to the empirical equation: $Q = 1.34\ H^{2.37}$, where Q (m^3 sec^{-1}) is discharge and H (m) is the head measurement (Brater et al. 1996). Direct discharge measurements were applied to calibrate the weir using containers ranging in volume from 12 to 51 l ($p < 0.001$, $R^2 = 0.99$). Rating curves were also developed for the three measured input points (Headwaters, P_1, P_2) using direct discharge measurements (containers with volumes ranging from 3 to 29 l). For the headwaters pressure transducer, a piecewise rating curve was developed with a break point at 4 l s^{-1} (low flow: exponential fit, $R^2 = 0.97$; high flow: linear fit, $p < 0.001$, $R^2 = 0.86$). Baseflow rating curves for the two stormpipes were linear (P_1: $p < 0.01$, $R^2 = 0.89$; P_2: $p < 0.001$, $R^2 = 0.97$). Stormflow pressure transducer readings from the stormpipes were highly variable; therefore stormflow rating curves were developed from data collected during (and only applied to) the two intensively sampled storms (5/4/03 and 5/16/03) that were examined in the export analysis. Two rating curves were developed for stormflow at each pipe (high flow, P_1: $p < 0.01$, $R^2 = 0.75$; P_2: $p < 0.1$, $R^2 = 0.45$; recession limb, P_1: $p = 0.17$, $R^2 = 0.40$; P_2: $p = 0.23$, $R^2 = 0.43$). The high flow curves were used for all time intervals in export calculations until discharge $< 2.0\ \mathrm{l\ s^{-1}}$ after which the receding limb rating curves were applied. Based on a review of all storm hydrographs during this study and due to the flashy response of the stream to precipitation input, stormflow was considered to end in the stream 6 h after measurable rainfall, and 4 h after rainfall in the stormpipes. All samples were assigned to stormflow and baseflow groups according to the above criteria.

A mass balance approach was used to compare the relative contributions of DOC and TDN from upland impervious areas via stormpipes and from remnant riparian areas during both stormflows and baseflow:

$$I_{\mathrm{RIP}} = O - (I_{\mathrm{H}} + I_{\mathrm{W}} + I_{\mathrm{P}}), \tag{1}$$

where O = output at the weir, I_{H} = input from the headwaters, I_{W} = input from intercepted precipitation ($I_{\mathrm{W}} = 0$ during baseflow), I_{P} = input from the stormpipes, and I_{RIP} = input from the remnant riparian areas. The assumptions of this mass balance approach included: all impervious surface contribution was via stormpipes; the riparian contribution integrated multiple hydrologic flowpaths through the remnant riparian areas (i.e., soilwater and shallow groundwater); and no significant in-stream uptake or release occurred within this relatively short (840 m) first-order stream reach. The total contributing impervious area of a pipeshed was assumed to be directly related to discharge measured at the pipe outlet. The impervious surface contributing areas were assumed to provide similar amounts of DOC and TDN among pipesheds. The riparian contribution was so termed because we assumed that the majority of DOC and TDN input from the remnant riparian patches was via recognized riparian hydrologic flowpaths (ie. shallow subsurface flow, and near-stream soil water contribution). However, the DOC and TDN loading that occurred via the remnant riparian areas was undoubtedly affected by urbanization, and the riparian term is not intended to represent a DOC and TDN signal that would exist in the absence of urbanization.

The mass balance approach was completed by calculating DOC and TDN mass export for each measured term in Equation (1) and solving for the mass export from the riparian areas. Substituting export equations into the mass balance equation for the stream (Equation (1)) yields:

$$\begin{aligned} I_{\mathrm{RIP}} = {} & \sum (Q_{\mathrm{o}} \times C_{\mathrm{o}} \times \Delta T) \\ & - \left\{ \sum (Q_{\mathrm{H}} \times C_{\mathrm{H}} \times \Delta T) + I_{\mathrm{W}} + \sum (Q_{\mathrm{P}} \times C_{\mathrm{P}} \times \Delta T) \right\}, \end{aligned} \tag{2}$$

where I_{RIP} = input from the remnant riparian areas, Q = discharge at the subscripted sample site ($\mathrm{l\ s^{-1}}$), C = concentration of either DOC or TDN at the subscripted site ($\mathrm{mg\ l^{-1}}$), ΔT = time interval (s), O = output at the weir, H = input from the headwaters, I_{W} = precipitation input ($I_{\mathrm{W}} = 0$ during baseflow), and P = input from the stormpipes. Note that

$$\sum(Q_{\mathrm{P}} \times C_{\mathrm{P}} \times \Delta T) = \sum(Q_{\mathrm{P1}} \times C_{\mathrm{P1}} \times \Delta T) + \sum(Q_{\mathrm{P2}} \times C_{\mathrm{P2}} \times \Delta T) + I_{\mathrm{P3}}$$

and

$$I_{\mathrm{P3}} = 2.175 \times \left[0.5 \times \left(\sum(Q_{\mathrm{P1}} \times C_{\mathrm{P1}} \times \Delta T) + \sum(Q_{\mathrm{P2}} \times C_{\mathrm{P2}} \times \Delta T)\right)\right]$$

(i.e., the contribution from P_3 was averaged from the two measured pipes, P_1 and P_2, and weighted by P_3 pipeshed area). The sum of the export quantities (i.e., sigma notation in (2)) from each 5-min time interval calculation was found for a 5-h period for the two storms and for a week long time scale for baseflow. The precipitation term for storm export calculations, I_W, was estimated by calculating total precipitation volume and multiplying by the concentration of the constituent to obtain a mass of DOC or TDN input to the stream. Precipitation volume was estimated as the product of stream length, stream width, and precipitation depth.

For baseflow conditions, the period-weighted method was used to obtain a concentration value for export calculations (Dann et al. 1986). A combination of the sample-interpolation and regression-based methods described by Hinton et al. (1997) was used to obtain concentration values for each time interval in the storm export calculations. The sample-interpolation method (Hinton et al. 1997) was most appropriate for this dataset because discharge was measured on a short, regular interval, and multiple chemistry samples were collected during both the rising and falling limbs of both storms. To avoid unrealistic extrapolations in our data, we used a linear equation from a regression of all measurements of concentration and discharge when a local minimum or maximum in discharge was encountered.

An error analysis was performed to assess the uncertainty associated with each component of the mass balance (1). Baseflow concentration error was the coefficient of variation of the mean. The error associated with the measured stormflow concentration values was the coefficient of variation from chemical analysis. The uncertainty associated with the interpolated values was derived by propagating the discharge error through the function used to obtain each value. Discharge uncertainty was estimated as the standard error for each value (i.e., the ordinate in rating curve equations) (Zar 1984). The concentration and discharge errors were propagated through the export equations for each time interval as a simple sum (Taylor 1982). Uncertainties calculated for each measured term in the mass balance equation were assumed to be independent and were propagated through the mass balance as a quadratic sum to estimate the uncertainty associated with the unmeasured remnant riparian area term (Taylor 1982).

Summary of hypothesis testing

The first hypothesis was examined by grouping DOC and TDN samples into baseflow and stormflow populations. The groups were compared using the

Mann–Whitney rank sum test. The second hypothesis was tested by sampling the watershed in a manner that allowed for comparison of the relative significance of DOC and TDN contributing areas. Export values were calculated for both DOC and TDN at each sample point. The export values were combined in a mass balance approach and the relative contribution of upland impervious areas and remnant riparian areas were determined and compared relative to the total export from the stream.

Results

Of the 33 observed storm events, seven were sampled for DOC and TDN analyses. We applied the mass balance on two of those storm events for which we were able to sample intensively both the rising and falling limbs of the storms (5/4/03 and 5/16/03) (Figure 2). The 5/4/03 and 5/16/03 were similar to the seasonal average for precipitation input but were two of the four most intense storms observed during the study, and both resulted in relatively high peak flow (Figure 2, Table 2). Precipitation tapered off after mid May 2003 and, consequently, water table depth dropped and baseflow receded (Figure 2). The lag time between precipitation input and streamflow response was short, generally less than 15 min depending on the intensity of the rain event. Peak

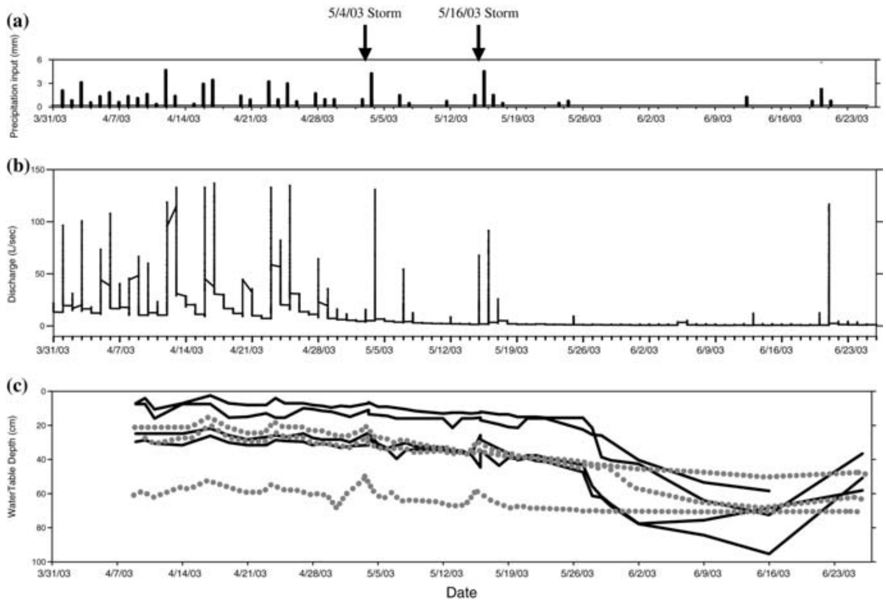

Figure 2. Hydrologic context of study period. Daily hyetograph (a), hydrograph (b), and time-series plot of measured water table depth at seven wells (c) for the study period. Panel (c) solid lines represent wells in the upper watershed, and dotted lines represent wells in the lower watershed.

Table 2. Seasonal storm characteristics.

Storm	Total precipitation input (mm)	Average intensity (mm h^{-1})	Peak intensity (mm h^{-1})	Duration of precipitation (h)	Peak stream flow (l s^{-1})	15-Day antecedent precipitation total (mm)
5/4 Storm	5.8	1.5	4.1	4.0	131	41.1
5/16 Storm	4.3	4.3	4.3	1.0	91	17.5
Seasonal average	3.3	0.8	1.7	4.0	66	27.1
Seasonal maximum	16.5	4.3	5.3	16.0	138	1.3
Seasonal minimum	1	0.3	0.5	1.0	17.3	61.7

flows were reached quickly; for example, during the 5/4/03 and 5/16/03 storms peak flows occurred within 25 min of the onset of stormflow.

The general patterns observed for DOC and TDN were determined from comparison of 34 days of baseflow samples compared to 46 stormflow samples collected during seven discrete storm events. Baseflow and stormflow DOC and TDN concentrations differed significantly for all surface water sample sites (Figure 3). DOC concentrations increased with stormflow for all four surface water sample points, with median DOC concentrations generally doubling. TDN concentrations increased with stormflow at the headwaters input. TDN concentrations decreased with stormflow, however, at all three sample sites that received input from impervious surfaces including the output at the weir. Baseflow TDN concentrations in the stormpipes were very high (Figure 3). Diluted stormflow concentrations in the pipes were still greater than baseflow TDN concentrations in the stream. Further, baseflow TDN concentrations increased from the headwaters to the output while there was no change over the same reach for DOC (Figure 3). Shallow subsurface water concentrations of both constituents, however, did not differ between baseflow and stormflow (median DOC concentrations: baseflow = 1.95 mg l^{-1}, stormflow = 2.00 mg $^{-1}$, p = 0.52; median TDN concentrations: baseflow = 0.36 mg l^{-1}, stormflow = 0.39 mg l^{-1}, p = 0.32).

The sample interpolation plots for DOC show that although stream concentrations generally increased with discharge, there was also an apparent dilution effect at the highest flows (Figure 4: Weir). TDN concentration change during storms also displayed a dilution effect in the stream and at the stormpipes (Figure 5: Weir, P_1, and P_2). The headwaters, without impervious contribution, did not display the dilution effect that was observed at the weir for either DOC or TDN (Figures 4 and 5). The 5/16/03 storm showed an increase over median baseflow TDN concentrations (at the weir from 0.73 to $\sim$1.00 mg l^{-1}) during the storm recession (Figure 5). Further, the TDN concentration increase at the headwaters was large for the 5/16/03 storm corroborating the observed increase late in the hydrograph at the weir (Figure 5).

On average nearly as much DOC was exported from the stream during 5 h of stormflow as was exported during 168 h (1 week) of baseflow (Table 3). DOC flux during storms ranged from 152.8×10^{-4} to 231.4×10^{-4} kg ha^{-1} h^{-1} while average baseflow flux was only 6.7×10^{-4} kg ha^{-1} h^{-1} (Table 4). Remnant riparian areas supplied a large portion of the overall DOC export during both baseflow and stormflow conditions. During baseflow, the majority (90%) of the DOC export was derived from the riparian and headwaters terms (Table 4). During the two storms a large majority of DOC export (70–75%) also originated in the remnant riparian areas Table 4, riparian and headwater terms). Stormpipes also provided DOC during storm events evidenced by increased relative contribution during storms (Tables 3 and 4). DOC input from intercepted precipitation was over an order of magnitude lower than other inputs and therefore was not presented in Tables 3 and 4.

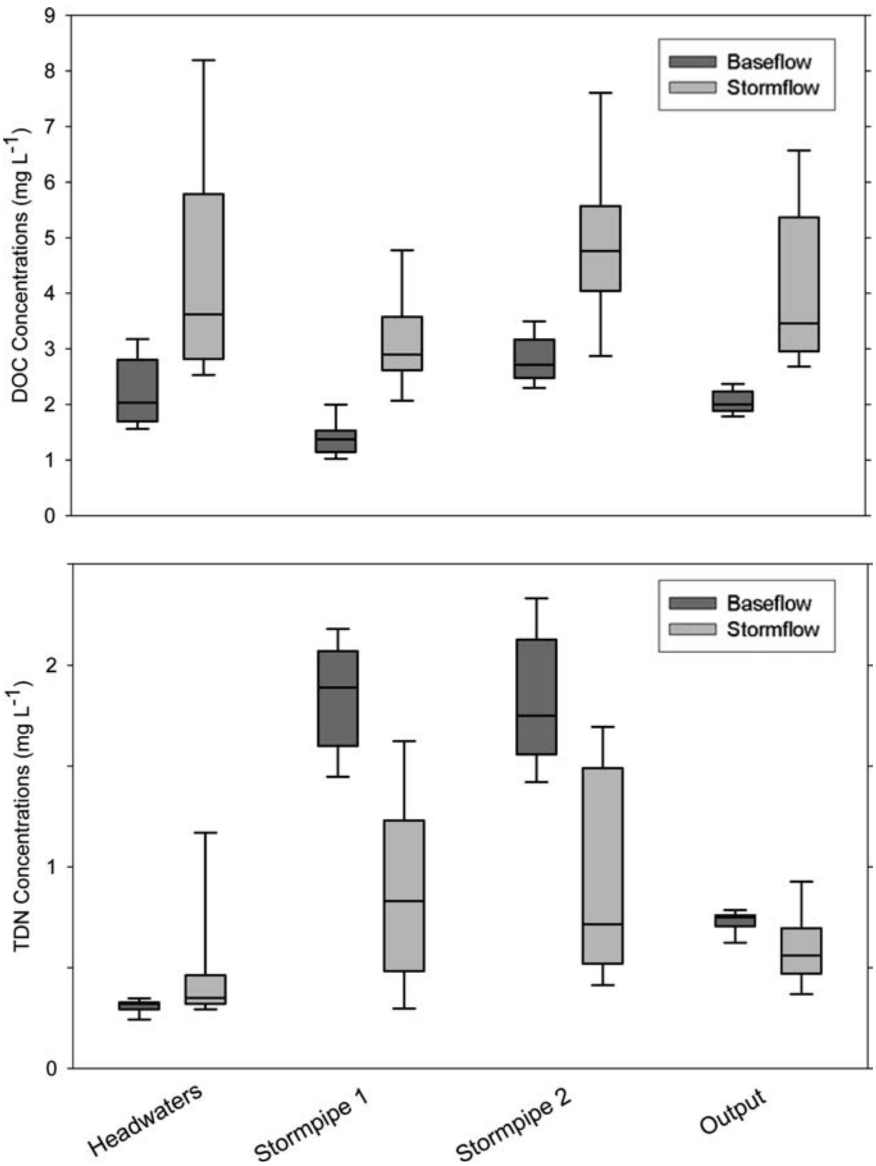

Figure 3. Median DOC and TDN Concentrations. Dark gray boxes show baseflow concentrations and light gray boxes depict stormflow concentrations for the sample sites listed along the *x*-axis. All pairs were determined to be significantly different ($p < 0.001$) by Mann–Whitney rank sum tests.

Roughly four times as much TDN was exported during a week of baseflow than was exported during 5 h of stormflow (Table 3). TDN flux during storms ranged from 11.8×10^{-4} to 23.0×10^{-4} kg ha^{-1} h^{-1} while average baseflow flux was only 2.4×10^{-4} kg ha^{-1} h^{-1} (Table 4). The urbanized

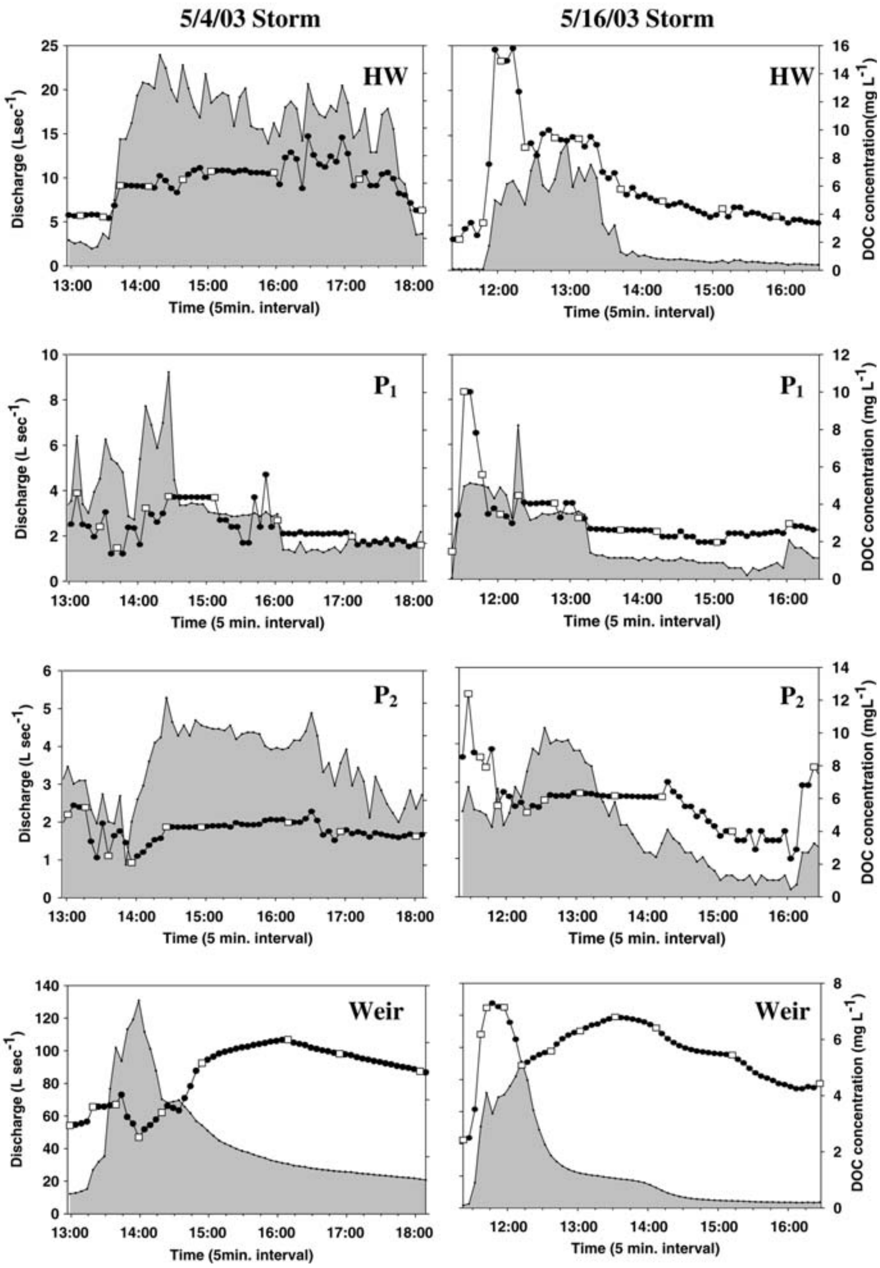

Figure 4. DOC stormflow concentration dynamics. HW panels depict the headwaters sample site, P1 and P2 depict the first and second stormpipe sample sites, respectively and Weir depicts the integrated stream response as measured at the output weir during two storm events labeled at the top of the columns. On each panel the gray area represents the hydrograph, the open squares represent measured concentrations values and the closed circles represent interpolated concentration values.

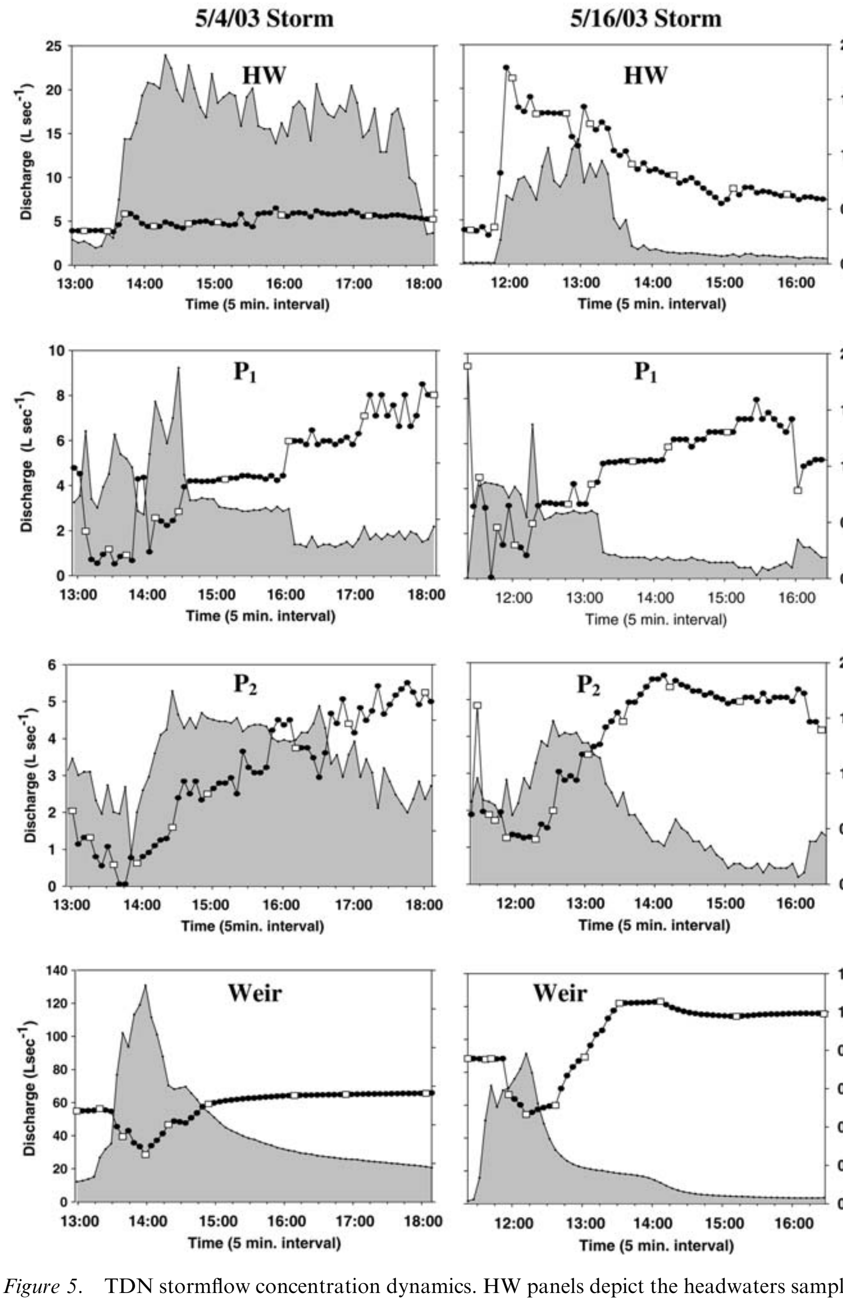

Figure 5. TDN stormflow concentration dynamics. HW panels depict the headwaters sample site, P1 and P2 depict the first and second stormpipe sample sites, respectively and Weir depicts the integrated stream response as measured at the output weir during two storm events labeled at the top of the columns. On each panel the gray area represents the hydrograph, the open squares represent measured concentrations values and the closed circles represent interpolated concentration values.

Table 3. Export and mass balance results.

Flow condition, constituent	Headwaters (I_H+)	Pipe 1 (P_1+)	Pipe 2 (P_2+)	Pipe 3* (P_3=)	$\sum(I_H + P_1 + P_2 + P_3)$	Output	Riparian contribution output $\sum(I_H + P_1 + P_2 + P_3)$
Average weekly baseflow DOC (kg)	1.03 ± 0.56	0.07 ± 0.05	0.11 ± 0.04	0.20 ± 0.23	1.41	3.65 ± 0.80	2.25 ± 1.01
5/4 Storm DOC (kg)	1.85 ± 0.11	0.19 ± 0.04	0.28 ± 0.09	0.51 ± 0.29	2.83	3.73 ± 0.02	0.89 ± 0.32
5/16 Storm DOC (kg)	0.66 ± 0.16	0.13 ± 0.04	0.22 ± 0.12	0.38 ± 0.35	1.40	2.46 ± 0.02	1.06 ± 0.40
Average weekly baseflow TDN (kg)	0.15 ± 0.04	0.09 ± 0.04	0.07 ± 0.02	0.17 ± 0.15	0.48	1.31 ± 0.21	0.83 ± 0.26
5/4 Storm TDN (kg)	0.12 ± 0.01	0.04 ± 0.01	0.07 ± 0.02	0.12 ± 0.08	0.35	0.37 ± 0.002	0.02 ± 0.09
5/16 Storm TDN (kg)	0.09 ± 0.01	0.02 ± 0.01	0.04 ± 0.03	0.07 ± 0.10	0.22	0.29 ± 0.002	0.07 ± 0.10

Total export in kilograms (±95% confidence interval) for average baseflow export and two intensively sample storms. Pipe 3* indicates estimated pipe contribution.

Table 4. Relative Contributions of DOC and TDN source areas.

Flow condition, constituent	Flux (kg ha^{-1} h^{-1})	Headwaters % contribution	Riparian % contribution	$\sum$ Pipes % contribution
Average weekly baseflow DOC	6.7×10^{-4}	28 ± 15%	62 ± 27%	10 ± 9%
5/4 Stormflow DOC	231.4×10^{-4}	50 ± 3%	24 ± 11%	26 ± 11%
5/16 Stormflow DOC	152.8×10^{-4}	27 ± 7%	43 ± 16%	30 ± 20%
Average weekly baseflow TDN	2.4×10^{-4}	12 ± 3%	63 ± 20%	25 ± 16%
5/4 Stormflow TDN	23.0×10^{-4}	32 ± 3%	6 ± 25%	62 ± 32%
5/16 Stormflow TDN	11.8×10^{-4}	31 ± 3%	24 ± 34%	45 ± 48%

Flux values were converted from the total stream export (output) provided in Table 3. The percent values represent the portion of the total export. The uncertainty term associated with each value represents the 95% confidence interval expressed as a portion of the total export (i.e. there is a 95% probability that the true percentage lies between the value ± the uncertainty).

portion of the watershed was a large contributor of TDN during both baseflow and stormflow (Table 4). Remnant riparian areas in this urban watershed also provided TDN to the stream during storms as shown by the headwaters site which provided 31–32% of the total TDN stream export during storms (Table 4). TDN input from intercepted precipitation was over an order of magnitude lower than other inputs and therefore was not presented in Tables 3 and 4.

Discussion

Dissolved organic carbon

In this urban watershed DOC concentration increased with stormflow, as has been observed in previous studies of forested systems (Meyer and Tate 1983; McDowell and Likens 1988; Hinton et al 1997; Buffam et al. 2001; Correll et al. 2001). Moreover, the DOC concentration increase observed in this urban watershed during storms was within the range of concentration increases found in the literature (Table 5). We hypothesized that DOC concentrations would decrease during stormflow due to dilution by runoff from DOC-poor impervious surfaces. For the two intensively sampled storms, that pattern was observed only on a very short time scale during the peak stormflow and concentrations were not diluted to levels below average baseflow concentration (Figure 4).

We demonstrated that impervious areas can provide DOC during stormflows adding to the increased streamwater concentration rather than diluting it. An explanation for our result draws on pollutant build-up and washoff literature that has shown transport from impervious surfaces to be controlled more by rain and runoff energy terms than by the buildup time (Barbe et al. 1996). We observed that the initial spike in concentration was higher for the

Table 5. DOC and TDN baseflow/stormflow concentrations from previous studies.

Constituent	Flow condition	Concentration (mg l^{-1})	Citation
DOC	Baseflow	0.8	Buffam et al. (2001)
	Stormflow	2.0	
DOC	Baseflow	1.8	McDowell and Likens (1988)
	Stormflow	3.1	
DOC	Baseflow	2.0	This study
	Stormflow	4.1	
DOC	Baseflow	4.2	Hinton et al. (1997)
	Stormflow	6.6	
TDN	Baseflow	0.03	Wondzell and Swanson (1996)
	Stormflow	0.06	
TDN	Baseflow	0.15	Buffam et al. (2001)
	Stormflow	0.32	
TDN	Baseflow	0.73	This study
	Stormflow	0.59	
TDN	Baseflow	3.5	Vanni et al. (2001) (agricultural land use)
	Stormflow	8.4	

Mean concentrations from this study are shown in context of values obtained from the literature on forested watersheds (except as indicated).

second storm than the first in both pipes and that the average and peak precipitation intensities were higher for the second storm (Table 2). Further, the importance of raindrop energy in pollutant washoff is thought to decrease during storms (Vaze and Chiew 2003) and the peak intensity of the first storm occurred during the final hour of precipitation input. Our explanation of the pattern observed in this study is that increased concentrations during stormflow in the stormpipes were due to a first flush of urban sources of DOC washing off the impervious surfaces. Urban sources of DOC that could accumulate on impervious surfaces include petroleum products (e.g., motor oils), soaps, latex based products (e.g., paints), and domestic animal feces. Allochthonous DOC input as dust during dry depositional periods in an arid region has also been shown to produce a first flush effect with concentrations 3 times higher during the first minutes of a storm event (Westerhoff and Anning 2000).

Our third hypothesis was that impervious contribution of DOC would primarily govern stream concentrations during stormflow in this urban watershed. Our results do not support this hypothesis for DOC. The majority of DOC export during stormflow in this urban stream was provided by remnant riparian areas (Table 4, riparian and headwater values). For both storms, moreover, stream DOC concentrations were consistently higher after peak flow (Figure 4). Our findings for DOC show the importance of near-stream remnant riparian areas in maintaining DOC stormflow flux in urban streams while simultaneously demonstrating that impervious surfaces can provide DOC flux during storms in an urban watershed.

Total dissolved nitrogen

The study area produced a more variable TDN response to stormflow than for DOC. For example the pattern of TDN stormflow dynamics in the headwaters was the opposite of the downstream TDN stormflow pattern. Further, while DOC baseflow concentrations were similar from the top of the stream to the output, TDN baseflow concentrations doubled over the same reach (Figure 3). TDN concentrations in the lower watershed were between relatively low levels observed in forested watersheds and higher concentrations recorded in an agricultural watershed where anthropogenic sources of TDN were extreme (Vanni et al. 2001) (Table 5). A potential explanation for the variable TDN response is that the lower reaches of this stream experienced high dissolved nitrogen loading from a deeper groundwater source that was unaffected by the stormflow. Baseflow in the stormpipes occurred because the stormpipes were not closed systems. The high TDN concentrations in the stormpipes during baseflow and the increase in TDN from headwaters to output suggest that a groundwater source rich in dissolved nitrogen was leaking into the stormpipes and into the stream itself. This pathway of dissolved nitrogen loading did not appear to be forced into the stream during stormflows, or at least was not observed on the timescale measured for this study.

A second line of reasoning that could contribute to the high TDN levels in the lower watershed is that nitrogen uptake by vegetation was low at the watershed scale due to the overall reduction of vegetation biomass in this urban watershed. This explanation assumes a high inorganic to organic nitrogen ratio in this urban stream. Evidence for this assumption comes from a study of small coastal watersheds that found elevated nitrate concentrations and nitrate:dissolved organic nitrogen ratios in urban streams compared to reference forested streams (Tufford et al. 2003). Additional support for the contention that there was unusually high nitrogen loading in the lower watershed comes from the HJ Andrews Experimental Forest in the Oregon Cascade Mountains where western conifer forests tend to exhibit nitrogen limitation and therefore low nitrogen output (Sollins et al. 1980).

Our results support the contention that urban riparian areas can provide TDN to the stream (Konohira et al. 2001; Groffman et al. 2002). TDN stormflow concentration increased at the headwaters site and the change was of similar magnitude to the results from studies of forested watersheds (Wondzell and Swanson) (Figure 3, Table 5). The headwaters site results are particularly conclusive considering that the TDN pattern was similar to that of DOC stormflow response in this stream and, moreover, there were low uncertainties associated with those estimates (Table 4). We suggest that elevated TDN concentrations in the lower reaches of the stream masked the remnant riparian area stormflow contribution of TDN that was observed at the headwaters site and likely occurred throughout the watershed (Figure 5).

A pattern of consistently higher concentrations of both constituents during the second storm at the headwaters and at the output was observed (Figures 4 and 5). An explanation for this pattern is that the second storm produced higher peak and average precipitation intensities suggesting that the intensity of a storm may affect the transport of DOC and TDN from near-stream soil water to the stream in remnant urban riparian areas (Table 2). A second possible explanation of the observed pattern is that the near-stream soil water became more concentrated in DOC and TDN due to lower antecedent precipitation and therefore drier conditions prefacing the second storm (Table 2).

Conclusions

Our study demonstrated that urban impacts on hydrology do not necessarily alter patterns of DOC and TDN fluxes to a stream during storm events. The hydrology of this urban watershed was similar to descriptions of other urban watersheds in the literature (Paul and Meyer 2001) particularly regarding the flashy response of the stream to precipitation input, yet the hypothesized response of decreased concentrations during stormflow was not observed for DOC. We observed other important differences from watersheds without commensurate human impact. For example, the two constituents (DOC, TDN) behaved differently in response to storms, whereas in the literature on forested systems both tend to respond similarly (Mulholland et al. 1981; Stepanauskas et al. 2000; Buffam et al. 2001; Qualls et al. 2002). Further, we found that remnant riparian patches in an urban watershed can provide DOC and TDN to a stream during storms as observed in forested watersheds yet other processes unique to urban areas also contributed to the patterns observed in this stream. The buildup and subsequent washoff of DOC from impervious surfaces may have contributed to the flux of DOC in this urban stream, while elevated TDN levels in urban groundwater may have masked the signal from remnant riparian areas. Our findings support the current literature that contends that riparian areas are important contributors of DOC and TDN to streams during storms (Cirmo and McDonnell 1997; McGlynn and McDonnell 2003).

Our work was an initial attempt to assess these ecological patterns in an urban watershed and represents a single season of data collection. A study of a local forested watershed has shown that dissolved organic nitrogen fluxes, which dominate nitrogen export in those streams, are highest during the fall season, not during the spring (Vanderbilt et al. 2002) suggesting that our observed pattern could be different for fall storms in this urban watershed. Additional steps including fractionation of TDN and DOC, isotope analysis, or ultra-violet absorbance and fluorescence analyses would help to elucidate sources of the two constituents and therefore also the underlying processes.

Finally, our study contributes to the growing body of knowledge regarding the ecology of cities by describing patterns of DOC and TDN stormflow dynamics and providing information about sources of dissolved carbon and nitrogen to streams in urban watersheds. The findings of this study begin to address questions regarding how urbanization affects the function of riparian zones, an understudied area in the urban ecology literature (Groffman et al. 2003). This study demonstrates the importance of preserving near-stream remnant riparian areas in cities to maintain patterns of carbon and nutrient fluxes in urban streams.

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