

Longitudinal patterns in carbon and nitrogen fluxes and stream metabolism along an urban watershed continuum

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Abstract An urban watershed continuum framework hypothesizes that there are coupled changes in (1) carbon and nitrogen cycling, (2) groundwater-surface water interactions, and (3) ecosystem metabolism along broader hydrologic flowpaths. It expands our understanding of urban streams beyond a reach scale. We evaluated this framework by analyzing longitudinal patterns in: C and N concentrations and mass balances, groundwater-surface interactions, and stream metabolism and carbon quality from headwaters to larger order streams. 52 monitoring sites were sampled seasonally and monthly along the Gwynns Falls watershed, which drains 170 km² of the

Baltimore Long-Term Ecological Research site. Regarding our first hypothesis of coupled C and N cycles, there were significant inverse linear relationships between nitrate and dissolved organic carbon (DOC) and nitrogen longitudinally ($P < 0.05$). Regarding our second hypothesis of coupled groundwater-surface water interactions, groundwater seepage and leaky piped infrastructure contributed significant inputs of water and N to stream reaches based on mass balance and chloride/fluoride tracer data. Regarding our third hypothesis of coupled ecosystem metabolism and carbon quality, stream metabolism increased downstream and showed potential to enhance DOC lability (e.g., ~4 times higher mean monthly primary production in urban streams than forest streams). DOC lability also increased with

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distance downstream and watershed urbanization based on protein and humic-like fractions, with major implications for ecosystem metabolism, biological oxygen demand, and CO₂ production and alkalinity. Overall, our results showed significant in-stream retention and release (0–100 %) of watershed C and N loads over the scale of kilometers, seldom considered when evaluating monitoring, management, and restoration effectiveness. Given dynamic transport and retention across evolving spatial scales, there is a strong need to longitudinally and synoptically expand studies of hydrologic and biogeochemical processes beyond a stream reach scale along the urban watershed continuum.

Keywords Nitrogen · Carbon · New Watershed Concept · Urban watershed · Nutrient retention

Introduction

Human alteration of the global nitrogen cycle has contributed to increased coastal eutrophication, harmful algal blooms and changes in aquatic food webs (Kemp et al. 2005; Seitzinger and Sanders 1997a, b; Vitousek et al. 1997). In addition, elevated bioavailable organic carbon in streams and rivers can contribute to coastal hypoxia (Mallin et al. 2004; Sickman et al. 2007). Simultaneously, both watershed nitrogen (N) and carbon (C) loads in streams and rivers have been altered due to atmospheric deposition, land-use change, and wastewater inputs (Galloway et al. 2003; Sickman et al. 2007). Although a portion of increased watershed nitrogen and organic carbon loads are exported to coastal waters, a substantial proportion may also be transformed along stream and river networks (Alexander et al. 2000; Galloway et al. 2003). Subsidies of organic C and N from headwaters can alter the metabolic balance of streams and rivers downstream (Howarth et al. 1991; Mulholland et al. 1997; Cole and Caraco 2001; Fellows et al. 2006; Battin et al. 2008), influence coastal eutrophication (Seitzinger and Sanders 1997a, b; Seitzinger et al. 2002a, b; Stepanauskas et al. 2002), and serve as indicators of changes in the regional carbon balance of terrestrial watersheds (Cole et al. 2007; Raymond et al. 2008). We investigated the degree to which an urban

watershed continuum from headwaters to larger order streams can retain and modify organic carbon and nitrogen loads.

Although considerable work has focused on transport and retention of nitrate in streams (e.g., Mulholland et al. 2008), it is increasingly recognized that organic carbon and nitrogen are abundant and can also undergo substantial retention in watersheds and streams (e.g., Kaushal and Lewis 2005; Petrone et al. 2009; Scott et al. 2007; Seitzinger and Sanders 1997a; Wiegner et al. 2006). In particular, bioavailable dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) can constitute a considerable proportion of stream C and N loads and are subject to in-stream retention; bioavailability of DOC and DON is typically defined as uptake over days or weeks (e.g., Bronk et al. 2007; Petrone et al. 2009; Seitzinger and Sanders 1997b; Seitzinger et al. 2002a). These experimental studies and others imply that cycling and retention of DOC and inorganic and organic N can be important across evolving spatial scales along watersheds and stream networks.

Land-use change can alter the quantity and quality of organic C delivered to aquatic ecosystems (Kaushal and Binford 1999), but the effect of urbanization on longitudinal C and N fluxes along urban watersheds is less well known. Along urban watersheds, there can be coupled changes in: carbon and nitrogen cycling, metabolism of organic matter and carbon quality, and groundwater-surface water interactions along broader hydrologic flowpaths and evolving spatial scales (Kaushal and Belt 2012). The capacity for variation in C and N fluxes at the reach scale may be enhanced in urban streams because many of the factors known to stimulate production of DOC and particulate organic matter can be higher than forest streams (e.g., temperature, gross primary production (GPP), ecosystem respiration, microbial activity, etc.) (Claessens et al. 2009; Kaushal et al. 2008b, 2010; Paul and Meyer 2001; Walsh et al. 2005). Furthermore, groundwater-surface water interactions can also shift along watersheds with increasing urbanization due to non-point sources from leaking sanitary infrastructure and chronic groundwater contamination (Kaushal and Belt 2012). It is critical to identify the appropriate spatial scales relevant for retention and modification of watershed C and N loads to improve watershed monitoring, management, restoration strategies (Kaushal et al. 2008b; Mayer et al. 2010; Roberts and

Mulholland 2007), and to better understand drivers of delivery of carbon and nitrogen to receiving waters.

We investigated changes in retention and release of DOC and major nitrogen fractions under typically baseflow conditions along an urban watershed and its stream network located in the Chesapeake Bay region. We use the term “urban watershed continuum” here to describe this evolving spatial scale across stream orders, which include hydrologic flowpaths from small headwater streams to larger order streams (including all tributaries and the mainstem) and underlying shallow ground water. The urban watershed continuum conceptual framework also considers engineered and non-traditional hydrologic flowpaths across watersheds (and several stream orders) and has been previously described (e.g., Kaushal and Belt 2012; www.beslter.org). Our goal was to quantify the longitudinal variation in net in-stream retention and/or release in C and N across land uses and seasons, and to understand what potential factors drive this variation. Potential drivers explored included stream metabolism, changes in dissolved organic matter quality, and groundwater-surface water interactions.

We hypothesized that there are coupled changes in (1) carbon and nitrogen cycling, (2) groundwater-surface water interactions, and (3) ecosystem metabolism and carbon quality from headwaters to larger streams along the urban watershed continuum. We expected urbanization to enhance existing nitrogen sinks and organic carbon production with increasing watershed area via changes in ecosystem metabolism. For example, as urban streams progressively widen downstream, there can be greater opportunity for increased light availability, warmer temperatures, and enhanced in-stream nitrogen retention and production of labile organic carbon by GPP and ecosystem respiration (e.g., Paul and Meyer 2001; Kaushal and Belt 2012; Wollheim et al. 2008). Alternatively, we hypothesized that there can also be coupled biogeochemical and hydrological processes along the urban watershed continuum due to leaky piped infrastructure and groundwater-surface water interactions (e.g., Kaushal et al. 2011; Divers et al. 2013). Overall, we evaluated the importance of retention and release of watershed C and N loads and potential drivers over spatial scales seldom considered for most monitoring, management, and restoration studies.

Table 1 Average reach-scale characteristics for mass balance studies

Reach #	Distance downstream (km)	Reach length (km)	Reach width (m, mean and SE)	Stream reach area (m ²)
1	4.5–5.9	1.4	5.8 ± 0.4	8,173
2	5.9–10.9	5	6.0 ± 0.4	29,767
3	10.9–13.5	2.6	6.9 ± 0.5	17,956
4	13.5–18.4	4.9	8.2 ± 0.3	40,032
5	18.4–19.5	1.1	8.4 ± 0.4	9,232
6	19.5–20.9	1.4	11.2 ± 0.3	15,728
7	20.9–25.5	4.6	13.0 ± 0.2	59,624
8	25.5–30.1	4.6	13.9 ± 0.2	63,844
9	30.1–35.8	5.7	11.9 ± 0.5	67,564

Methods

Study sites

The Baltimore Ecosystem Study (BES) Long-term Ecological Research (LTER) project has collected data since 1998 on major N chemical fractions in a network of streams in the Baltimore metropolitan area (located within the Chesapeake Bay watershed) (e.g., Groffman et al. 2004; Kaushal et al. 2008a) (Table 1). The main study watershed of the Baltimore LTER site is the 17,150 ha Gwynns Falls watershed (76°30′, 39°15′). We focused on understanding fluxes along a nested set of sample sites that occur along a single flow path of the mainstem of the Gwynns Falls (described below), but also sampled the major and minor tributaries along the stream network. The length of the longest flow path over which we sampled was ~36.5 km and was located entirely in the Piedmont physiographic province (Fig. 1). In conjunction with this monitoring strategy, we conducted intensive mass-balance studies of net retention and release of TDN, nitrate, and DOC. The headwaters of the Gwynns Falls watershed begin in suburban Baltimore County and then flow along a land-use gradient into a high-density urban area of Baltimore City. There are no point-source discharges (e.g., domestic or industrial waste water) in the study reaches of the Gwynns Falls watershed, but nonpoint source N pollution from aging sanitary infrastructure has been shown to be a significant source (Kaushal et al. 2011). The fraction of flow contributed by ground water and leaks from

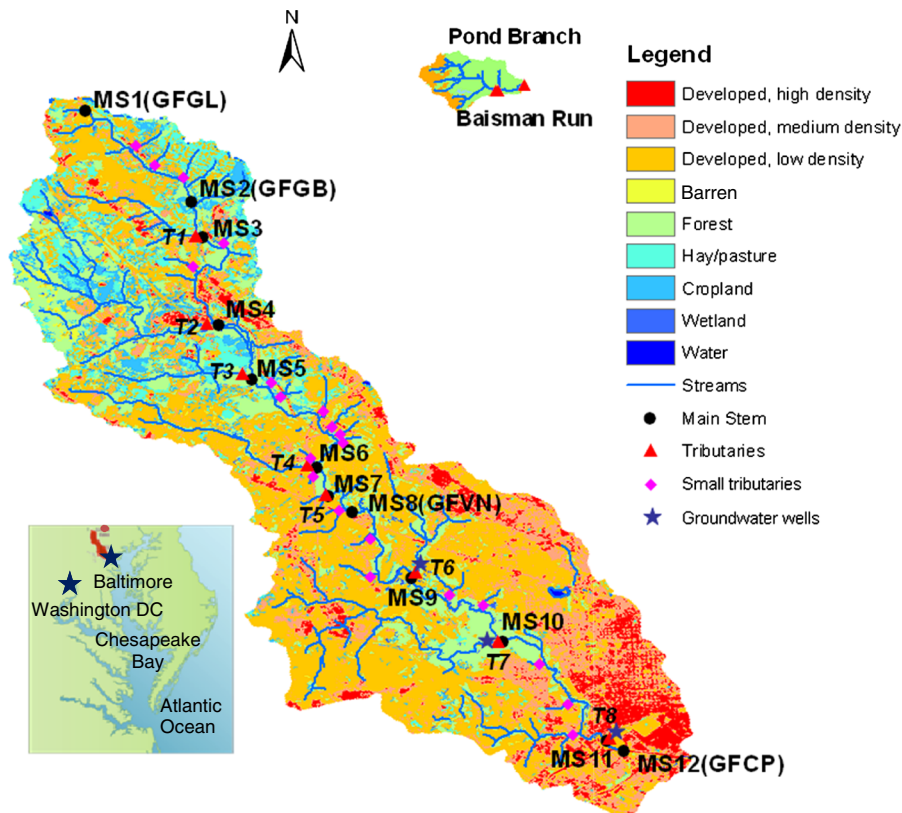


Fig. 1 Sampling locations and watershed land use are shown for the BES LTER site located in Maryland, USA. Sampling for the present study was conducted along the Gwynns Falls mainstem and tributaries extending from suburban headwaters to progressively urban reaches in Baltimore City, Maryland. The

longest hydrologic flow path spanned 36.5 km from headwaters at GFGL to the Gwynns Falls outflow at GFCP. Pond Branch and Baisman Run are reference forested watersheds located in the nearby Gunpowder River watershed

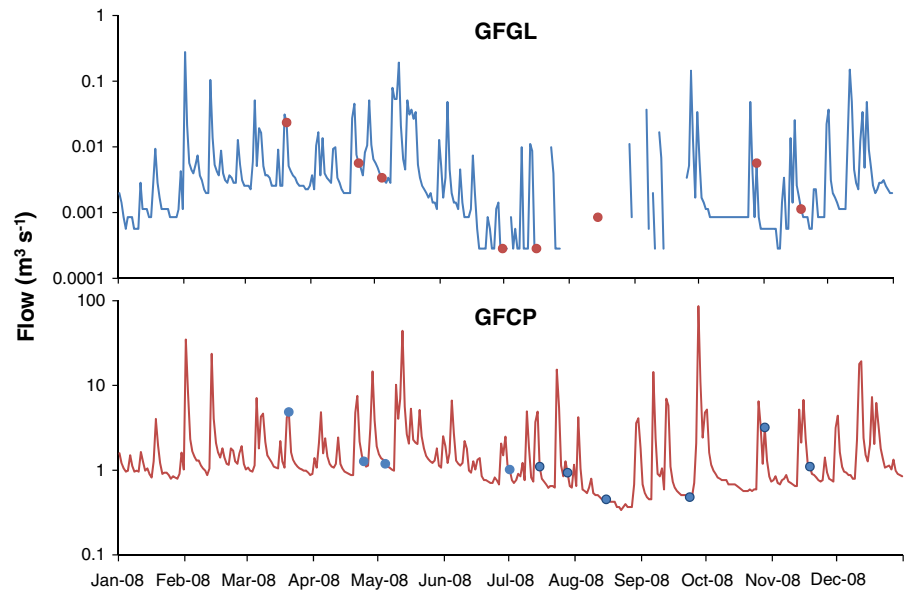
infrastructure in stream reaches of the Baltimore LTER site can be large, as revealed by: (1) detailed water budgets and hydrologic mass balances (Bhaskar and Welty 2012), (2) isotopic source tracking of sanitary sewer leaks (Kaushal et al. 2011), (3) use of fluoride concentrations as a tracer of potable water leaks (Kaushal and Belt 2012), and (4) extensive piezometer networks (Mayer et al. 2010). For example, it was estimated by a U.S. Army Corp of Engineers study that ~65 % of the average flow in the Gwynns Falls stream can be derived from sewage (Kaushal and Belt 2012). Similarly, sewer infiltration and inflow has been shown to account for 41 % of total watershed outflows annually for watersheds in Baltimore City (Bhaskar and Welty 2012). Land use/land cover for the study watersheds has been described elsewhere (e.g., Groffman et al. 2004, Kaushal et al. 2005). Impervious surface cover (ISC) for subwatersheds

was derived from the 2006 National Land Cover Database (NLCD) and Arc GIS.

Seasonal synoptic sampling

Fifty-two synoptic locations were typically sampled during baseflow conditions along the Gwynns Falls watershed during 3 seasons (March 2008, July 2008, and October 2008) to investigate longitudinal variations in C and N concentrations and fluxes. The synoptic sampling typically occurred over 1–2 days at baseflow (there were a few storm events), and the flow conditions for each synoptic sampling can be compared to the rest of the hydrograph during the study period (Fig. 2). We sampled along the length of the Gwynns Falls watershed and 30 of its tributaries spanning various sizes. Specific sampling locations of the 52 synoptic sites for the Gwynns Falls watershed

Fig. 2 Time series of daily average discharge are shown for GFGL and GFCP with sampling dates identified as circles. GFGL drains the suburban headwaters of the Gwynns Falls and GFCP represents the urban outlet of the Gwynns Falls. A few dates with no measurable streamflow at GFGL are not presented



were chosen based on tributary junctions and positioning of BES LTER and USGS gauging stations. Study reaches of the Gwynns Falls watershed were co-located across 4 mainstem USGS gauges (GFGL, GFGB, GFVN, GFCP) that are supported as part of the BES LTER project. Water samples were also collected at the mouth of each tributary and 100 m downstream from the tributary confluence along the mainstem of the Gwynns Falls watershed (to increase the likelihood that the stream was well-mixed). Coordinates for all seasonal synoptic sites were recorded using handheld GPS systems. Our synoptic sampling scheme included discharge measurements using a Marsh McBirney 2000 (Hach Co., Loveland, CO, USA) velocity meter and grab sample collection to measure concentrations of major fractions of N [total dissolved nitrogen (TDN), ammonium, nitrate, DON], DOC, chloride, and fluoride. Real-time discharge data were available at 4 gauging stations along the Gwynns Falls watershed and tributaries. The recession of storm hydrographs from urban streams such as the Gwynns Falls watershed occurs from minutes to days depending upon storm size and watershed position (Shields et al. 2008) and sampling was usually conducted typically 3 days after any rain events (Fig. 2).

Reach-scale mass balances

Sampling for reach-scale mass-balance estimates along the Gwynns Falls watershed was conducted

from March 2008 to November 2008 at 26 sampling locations, at a frequency of bi-weekly or monthly depending on season. Gwynns Falls mainstem and major tributary samples were collected using the same sampling scheme as the seasonal synoptic sampling (e.g., similar methods for discharge measurements and analyses of water chemistry). We defined major tributaries as any tributary contributing 5 % or more of the stream flow at that point along the stream channel. Groundwater concentrations were sampled and analyzed at 3 sites with 5–6 replicate groundwater wells per site representing 16 sampling points along the Gwynns Falls, three times per year (Fig. 1). Samples were collected from mini-piezometers installed 0.5 m below the streambed in the riparian zone, ~0.5–2 m from the stream bank, to characterize water movement into the stream (Sivirichi et al. 2011). Samples were also analyzed for TDN, DOC, and nitrate concentrations in ground water using the same methods as for stream samples.

Mass-balance calculations

Mass-balance calculations were used to determine net retention or release of major nitrogen and carbon fractions per unit area of stream, with each unit consisting of a stream reach ranging from 720 to 5,680 m in length. Fluxes were calculated by multiplying concentration (mg/L) by the stream flow rate

(L/day) to obtain mass transport per day. Differences between upstream and downstream fluxes were then used as an estimate of retention. More information on reach sizes including their mean area can be found in Table 1. No net change in instantaneous fluxes does not imply that N transformations are absent between stations, but that uptake processes balance release processes. Mass balances were calculated for TDN, nitrate, ammonium, and DON, as well as total organic carbon (TOC) and DOC, using Eq. (1):

$$M_D - (M_U + M_T + M_S + M_M) = \Delta M, \quad (1)$$

where M_D is the mg/day at downstream end of reach; M_U is the mg/day at upstream end of reach; M_T is the mg/day of major tributaries; M_S is the mg/day of groundwater seepage; M_M is the mg/day of minor tributaries; ΔM is the mg/day of net change (positive indicates release and negative indicates retention).

Areal net retention or release rates (mg/m²/day) were calculated by dividing ΔM by reach surface area. The surface area was estimated by measuring stream cross sections at 2–3 points along each reach to determine wetted width of the channel and multiplying by the length of each reach (Table 1). A negative ΔM indicated net removal of the constituent (retention), whereas a positive ΔM indicated net generation (release) of the constituent. This approach assumes no change in storage within the reach and no gains or losses via atmospheric exchange (net DOC retention could include mineralization processes, however, when DOC may be transformed into CO₂ and released to the atmosphere). Percent retention or release of a constituent for each reach was calculated using Eq. 2 [(outputs–inputs)/inputs] for 9 reaches in the Gwynns Falls stream network.

$$100 \times [\Delta M / (M_U + M_T + M_S + M_M)] \quad (2)$$

M_S was calculated by combining estimates of seepage (F_S) (F_S is described below in Eq. 3 for the water budget) with water chemistry data from groundwater well samples. M_S discharge was estimated by subtraction using a water budget including all other components of the mass balance for each reach on each sampling date (Eq. 3):

$$F_D - (F_U + F_T + F_M) = F_S \quad (3)$$

where F_D is the m³/day at downstream end of reach; F_U is the m³/day at upstream end of reach; F_T is the

m³/day of major tributaries; F_M is the m³/day of minor tributaries; F_S is the m³/day of seepage,

M_M was determined using discharge and water chemistry data from extensive synoptic seasonal sampling, in which minor tributaries (<5 % of stream flow in the mainstem) were sampled, in addition to the routine sampling scheme that included only major stream tributaries (>5 % of stream flow in the mainstem). Because minor tributaries were such a small proportion (<5 %), stream flow and water chemistry data were only collected once per season and were assumed to remain constant in the mass-balance calculations for each month of that season.

Because groundwater data were only collected seasonally and were not collected in conjunction with each mass-balance sampling, groundwater concentration was estimated using the overall mean concentration over the entire year and across the entire stream network. We estimated medians, means, and ranges for groundwater chemistry during the sampling period to indicate potential variability. The flux of M_S was then estimated for the entire stream network and treated as the flux from “distributed flow” for the mass balance calculations. We use the term “distributed flow” throughout because these contributions could have originated from groundwater seepage and/or subsurface inputs to the stream from leaky piped infrastructure in the watershed (e.g., Bhaskar and Welty 2012; Kaushal and Belt 2012). Groundwater seepage or “distributed flow” on each sampling date was estimated for each reach individually according to Eq. 3.

Using hydrologic mass balances for each of the 9 reaches along with corresponding chemistry measurements, we then determined medians, ranges, and any outliers for all of the 9 reaches on a given sampling date using box and whisker plots to characterize C and N retention/release patterns along the Gwynns Falls. We acknowledge that uncertainty is higher for individual stream reaches than the averages for all 9 study reaches. Given that sampling across the stream network was typically conducted all on the same day and the water in the mainstem was actually in the headwaters some time before that, we made the assumption about being at steady-state conditions (e.g., mass balances are not substantially influenced by water masses moving at different rates through the watershed during baseflow).

Some sources of uncertainty in our mass balances are presented here, in addition to describing use of conservative tracers of chloride and fluoride to check our mass balance approaches. Lack of characterization of deeper groundwater flowpaths due to logistical constraints may have contributed to some uncertainty in the mass balance calculations. For example, while it is difficult to explain a net mass loss between sampling stations in any way other than in-stream retention, it is difficult to differentiate a net mass gain between loadings due to groundwater inputs versus production. Furthermore, we used discharge estimates from 4 USGS gauging stations and field measurements from a current meter for estimating discharge at tributaries without a gauge. We measured cross sectional area of the stream channel and stream velocity at 2/3 depth incrementally along the width of the stream to estimate discharge at sites without gauges typically at >7 points (similar to Kaushal and Lewis 2005). Sources of error in field measurements of discharge using current meters can be related to uncertainties in cross sectional area, determination of mean velocity, computation procedures, systematic errors that bias estimates, and/or other uncertainties (Sauer and Meyer 1992). Previous work indicates that discharge measurements using current meters ranges from 2 to 20 % from ideal conditions due to poor conditions and most discharge measurements have standard errors ranging from ~3–6 % (Sauer and Meyer 1992). Uncertainty due to imprecise discharge measurements in the present study was estimated to be 12 %, by taking repeated measurements of the same cross-section of the stream (Delaney-Newcomb, Unpub. Results), as well as comparing our measurements with streamflow measurements calculated using USGS gauges at the same cross-section of the stream. The flow of groundwater into the stream was measured by difference, and its uncertainty is affected by the uncertainty of discharge measurements of the stream and tributaries, which are used to estimate groundwater input (F_S). For example, using the equation to estimate F_S (Eq. 3 above) in July 2009, each component was: F_D is the 92,970 m³/day at downstream end of reach; F_U is the 3,425 m³/day at upstream end of reach; F_T is the 27,537 m³/day of major tributaries; F_M is the 11,268 m³/day of minor tributaries; F_S is the 50,739 m³/day of seepage.

To estimate the worst case scenario for uncertainty in groundwater seepage or FS, we derived a minimal and maximal estimate of F_S . The minimum estimate of F_S occurs if the upstream and tributary Q is overestimated by 12 % and downstream Q is underestimated by 12 %. The maximum FS occurs if streamflow values for upstream and tributaries are underestimated and downstream is overestimated. For the example shown, these minimum and maximum FS values are 34,500 and 67,000 m³/days, respectively. Sampling was typically conducted at baseflow when uncertainty is likely to be less than the worst case (Harmel et al. 2006), and there were substantial differences in discharge and C and N concentrations between stations (e.g., average streamflow increased from 859 to 86,534 m³/day from headwaters to outflow and corresponding concentrations varied by several mg/L). Therefore, uncertainty in estimation of the seepage contribution from distributed flow was unlikely to impair our ability to detect longitudinal patterns in changes in instantaneous fluxes between stations. As an additional check on the ability of our mass balance to detect changes in retention, we conducted a mass balance of a conservative tracer (chloride) available on 1 sampling date in August 2009 for comparison to C and N. We also analyzed fluoride concentrations during 2 sampling dates on August 2009 and November 2009. Drinking water is fluoridated in the Baltimore metropolitan area to reduce tooth decay, and fluoride can be used to directly detect contributions of wastewater inputs via leaky sanitary sewers or potable water pipes to streams (Kaushal et al. 2011; Kaushal and Belt 2012).

Streamwater chemistry and DOM characterization

All samples were filtered through 0.7-micron glass-fiber filters within 24 h of collection and then frozen until analysis. Nitrate/nitrite and ammonium were analyzed using an enzyme-catalyzed reduction method on an Aquakem (Nutrient Analytical Services, Chesapeake Biological Laboratory). Analyses showed that nitrate/nitrite concentrations were almost entirely nitrate, and we will therefore refer to this fraction as nitrate throughout. TDN and DOC concentrations were measured using a Shimadzu TOC-V CPH/CPN. DON was calculated by subtraction: TDN—(nitrate-N +

ammonium-N) (Kaushal and Lewis 2003; Kaushal et al. 2006); thus, DON was calculated as the difference between two relatively large values (TDN-DIN), which contributes to higher variability.

Fluorescence spectroscopy was also used in characterization of DOC composition and source similar to Duan and Kaushal (2013). These relationships were based on available seasonal synoptic data for all stream sampling that were collected during the August of 2009. Briefly, fluorescence measurements were made on a FluoroMax-4 Spectrofluorometer (Horiba Jobin-Yvon, Edison NJ, USA) using a 1 cm quartz cuvette with slit widths set to 5 nm. Excitation emission matrix scans (EEMs) were obtained by collecting a series of emission wavelengths ranging from 300 to 600 nm (2 nm increments) at excitation wavelengths ranging from 240 to 450 nm (5 nm increments). The calibrated values of fluorescence intensities at excitation/emission = 275/240 and 350/480 nm were recorded as protein-like and humic-like fluorophores (Coble 1996; Stolpe et al. 2010). Relative to the humic-like fluorophore, the intensity of the protein-like fluorophore is generally higher in labile DOC sources [e.g., wastewater; (Hudson et al. 2008)]. The ratio of protein-like to the humic-like fluorophore (P/H) was calculated here as an index for DOC lability and composition.

Stream metabolism

GPP and ecosystem respiration along the urban watershed continuum were estimated by diel oxygen and temperature measurements and the Bayesian metabolic model (BaMM) (Holtgrieve et al. 2010). Dissolved oxygen (DO) YSI sondes were deployed monthly during 2010 for a 24 to 48 h period. Dissolved oxygen and temperature were recorded every 15 min during each deployment for sondes that were calibrated before deployment. The BaMM Bayesian statistical model used inputs such as dissolved oxygen, temperature, and water depth, and the BaMM model for the Gwynns Falls showed that the mean R^2 for observed versus median predicted O_2 values for all sites and dates was 0.89. The BaMM model required an estimate of irradiance, but because PAR was not measured for this study, the model estimated irradiance based on the latitude, longitude, and time of year. There was progressively less shading along

the Gwynns Falls mainstem as the stream widened along the 36.5 km flowpath.

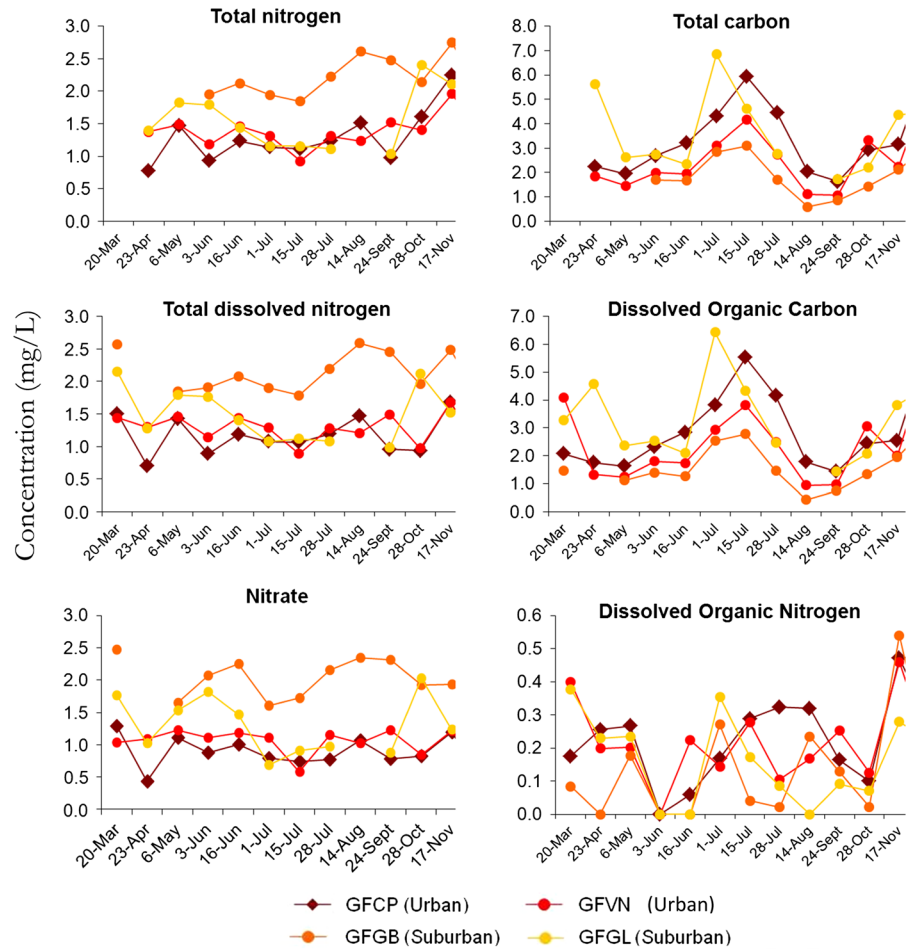
Results

Temporal patterns in water chemistry and fluxes

During 2008–2009, temporal patterns of DOC displayed a considerable range in concentrations, from 0.6 to 6.4 mg/L across all sites. DOC concentrations peaked during summer months (Fig. 3). DON was highly variable throughout the year, with no consistent seasonal or land-use patterns (Fig. 3). DON was calculated as the difference between two relatively large values (TDN-dissolved inorganic N), which contributes to higher variability. Similar to concentrations, TDN and DOC fluxes for individual stations showed distinct temporal and seasonal patterns along the Gwynns Falls (Fig. 4). For example, 4 mainstem sampling stations along the Gwynns Falls (GFGL, GFGB, GFVN, GFCP) showed distinct seasonal patterns in daily runoff, daily TDN flux (mass flux at a station per unit watershed area), and daily DOC flux (mass flux at a station per unit watershed area) (Fig. 4). Daily runoff showed a strong decline during late summer months, and daily TDN flux showed a similar temporal pattern to runoff. Interestingly, daily DOC fluxes at longitudinal sampling stations showed a different temporal pattern than daily runoff and daily TDN fluxes. Daily DOC flux showed 2 pronounced seasonal peaks during early summer and late autumn coinciding with leaf fall (Fig. 4).

Estimates of shallow groundwater concentrations in the Gwynns Falls watershed showed that dissolved organic matter could be a potential source of C and N in shallow groundwater. Shallow groundwater nitrate ranged from 0.00 to 1.41 mg/L with a median of 0.01 mg/L and a mean (\pm SE) of 0.19 ± 0.13 mg/L ($N = 11$). Shallow groundwater TDN ranged from 0.19 to 19.7 mg/L with a median of 1.02 mg/L and a mean (\pm SE) of 2.56 ± 0.63 mg/L ($N = 44$). Shallow groundwater DOC ranged from 0.63 to 16.76 mg/L with a median of 4.47 mg/L and a mean (\pm SE) of 5.01 ± 0.50 mg/L ($N = 44$). Shallow groundwater concentrations of nitrate were lower than streamwater concentrations of nitrate (Fig. 3). Shallow groundwater concentrations of TDN and DOC were similar to streamwater concentrations of TDN and DOC, however (Fig. 3).

Fig. 3 Examples of temporal variations in N and C concentrations for 4 major sampling sites representing land uses ranging from high-density urban (GFCP) to lower-density suburban (GFGL) sites



Longitudinal patterns in streamwater chemistry

Longitudinally, nitrate concentrations generally declined from the headwaters to the outflow of the Gwynns Falls (Fig. 5). DOC and DON concentrations generally increased with distance downstream and then became more variable and/or sometimes decreased at the watershed outlet. Nitrate concentrations were highest in the headwaters whereas DOC concentrations were highest at the outflow of the Gwynns Falls (Fig. 5). There was a significant inverse linear relationship between DOC and nitrate concentrations and DON and nitrate concentrations for samples collected longitudinally along the Gwynns Falls during 3 seasons ($P < 0.05$) (Fig. 6).

Reach-scale mass balances of carbon and nitrogen

From the headwaters to the outflow of the Gwynns Falls watershed, the flow of water increased by two orders of magnitude from an average flow of 859 m³/day at the headwaters to 86,534 m³/day at the outflow (averages for all sampling dates) with pronounced seasonal variability (Fig. 2). The water mass balance of the Gwynns Falls watershed indicated large contributions from the major and minor tributaries that were sampled entering the mainstem, but there were also substantial contributions from distributed flow originating from ground water seepage and leaky piped infrastructure. Across sampling dates, distributed flow comprised between 30 and 64 % of the stream flow, while

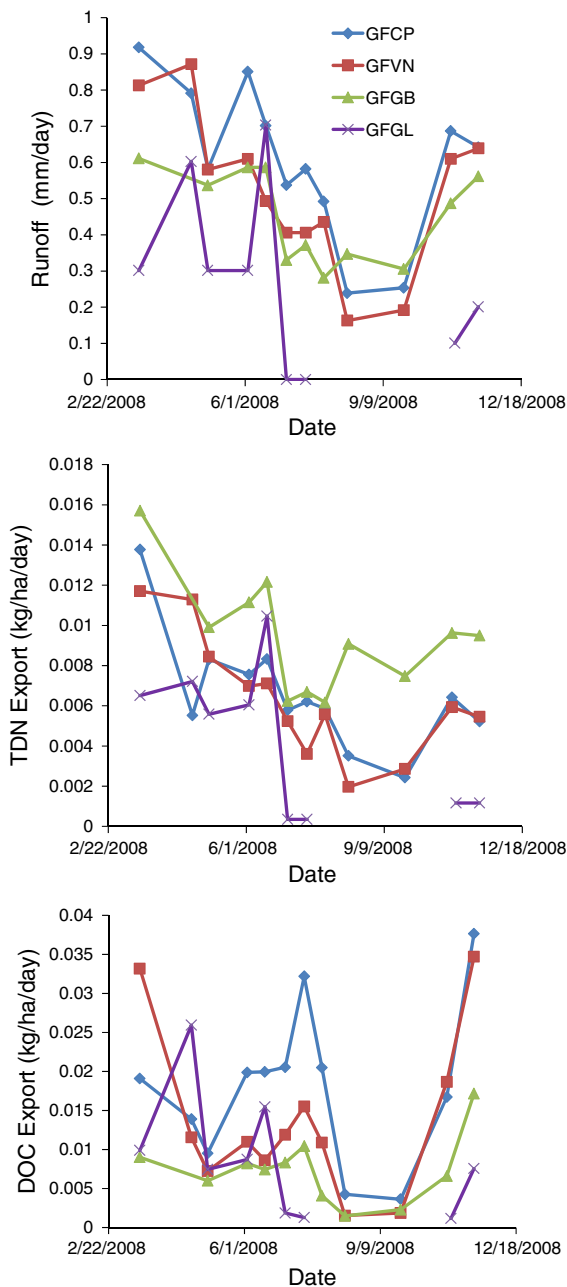


Fig. 4 Seasonal patterns in runoff and daily exports (mass flux at a station per unit watershed area) of DOC and TDN along 4 longitudinal sampling stations of the Gwynns Falls in order from upstream to downstream (GFGL, GFGB, GFVN, GFCP). GFGL drains the suburban headwaters of the Gwynns Falls, GFGB drains the suburban headwaters of the Gwynns Falls, GFVN is located at the suburban/urban boundary of the Gwynns Falls, and GFCP represents the urban outlet of the Gwynns Falls

tributaries comprised 33–71 % of the stream flow of the Gwynns Falls watershed. As a check, the mass balance of chloride showed that <5 % was typically retained along reaches supporting our estimates of groundwater inputs (Table 2). Baseflow was dominated by groundwater inputs, and there were observable differences in concentrations longitudinally due to variations in sources/dilution. Mass balance results for chloride behaved conservatively (minimal retention as an additional conservative tracer due to low biotic uptake) and provide further support for our mass balance approach. Furthermore, increasing fluoride concentrations indicated contributions of sewage and potable water leaks along the Gwynns Falls mainstem. Fluoride concentrations typically increased with distance downstream and progressive watershed urbanization, but concentrations showed variable patterns (Fig. 7).

The C and N mass balance of the Gwynns Falls revealed substantial changes in C and N retention and release relative to inputs, with substantial variability among study reaches (Figs. 8, 9). The Gwynns Falls mainstem typically showed mean net retention of DOC and TDN across all dates (Figs. 8, 9). In contrast, there was mean net generation of nitrate along the mainstem across sampling dates. DON retention showed seasonal variability, but DON showed net retention over most sampling dates (Figs. 8, 9). Ammonium was present in the stream, but the retention rates were at least two orders of magnitude lower than other nitrogen fractions (Figs. 8, 9). The retention rates for ammonium were low because concentrations were low, but retention rates for ammonium were not necessarily low on a percentage basis (Fig. 9). Overall, mass balance results for DOC, TDN, DON, nitrate, and ammonium along the Gwynns Falls showed no clear seasonal patterns (Figs. 8, 9). On average, monthly reach-scale mass balances indicated that considerable proportions (~25–30 %) of TDN and DOC loads could be retained along the Gwynns Falls, however (Fig. 9).

Stream metabolism and dissolved organic matter quality

There appeared to be seasonal patterns in stream metabolism. There was higher GPP during winter months (Fig. 10a), and this was potentially due to

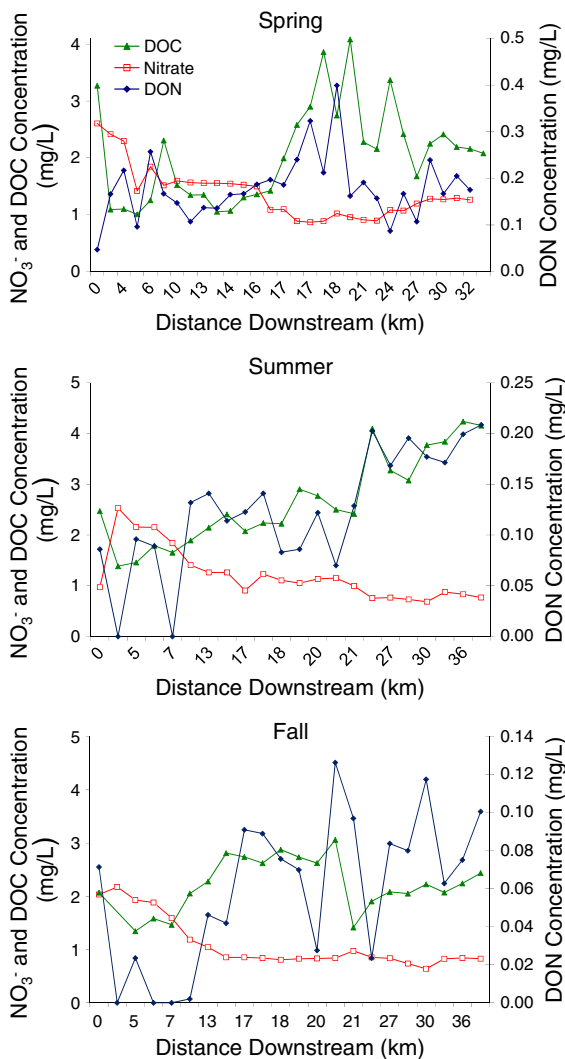


Fig. 5 Longitudinal patterns in DOC concentrations (mg/L), DON concentrations (mg/L), and nitrate concentrations (mg/L) along the Gwynns Falls mainstem across seasons. Please note the differences in scales across seasons due to minor differences in sampling points along synoptics

greater light availability to the stream, when canopy cover was lower. GPP varied significantly among sites using one-way ANOVA ($P < 0.01$) (Fig. 10b). GPP was the lowest for forested sites and highest for the more urbanized sites. There were no statistical differences found for ecosystem respiration using one-way ANOVA ($P = 0.09$), though ecosystem respiration tended to be greater for the more urban sites and lower for the forested and suburban sites (Fig. 10c).

Elevated GPP along the urban watershed continuum coincided with changes in organic matter quality

in urban streams. DOM composition along the Gwynns Falls tributaries and mainstem were significantly related to both land use and distance from headwaters. We observed that the labile fraction of DOC, indicated by protein-like fluorescence (measured by fluorescence spectroscopy), significantly increased with ISC for the Gwynns Falls mainstem and its tributaries ($P < 0.05$). The relationships between protein-like to humic ratio of DOM (an index for DOM lability), and both distance downstream and percent ISC were strong (Fig. 11).

Discussion

Linking increasing stream size with changes in downstream carbon inputs and in-stream processing has been a central question in stream ecology for decades (Vannote et al. 1980; Gregory et al. 1991; Junk 1999). In urban watersheds, there are emerging concepts that describe how extensive hydrologic alteration can contribute to a “syndrome” of water quality impairments at the stream reach scale (Paul and Meyer 2001; Walsh et al. 2005), but concepts across evolving spatial and temporal scales are needed to link cumulative watershed impacts to receiving waters and management activities (Kaushal and Belt 2012). It may be expected that urban watersheds show high spatial heterogeneity and erratic patterns in downstream organic carbon and nitrogen patterns due to nonpoint sources such as storm drain inputs and sewage leaks, as well as in-stream processes. Despite seasonal variability and the importance of tributary inputs, we observed consistent longitudinal patterns in concentrations of DOC and nitrate, GPP, and dissolved organic matter composition as watershed area and urbanization increased. Our results suggest that the urban watershed continuum may not always be best characterized as an inert “pipe” influenced solely by extensive watershed hydrologic alteration, but that it has the potential to also act as a “reactor” modifying carbon and nitrogen export across evolving spatial scales (e.g., del Giorgio and Pace 2008; Kaushal and Belt 2012).

Retention of nitrogen and carbon along the urban watershed continuum

Retention of TDN at the reach-scale was typically observed along the Gwynns Falls watershed. The

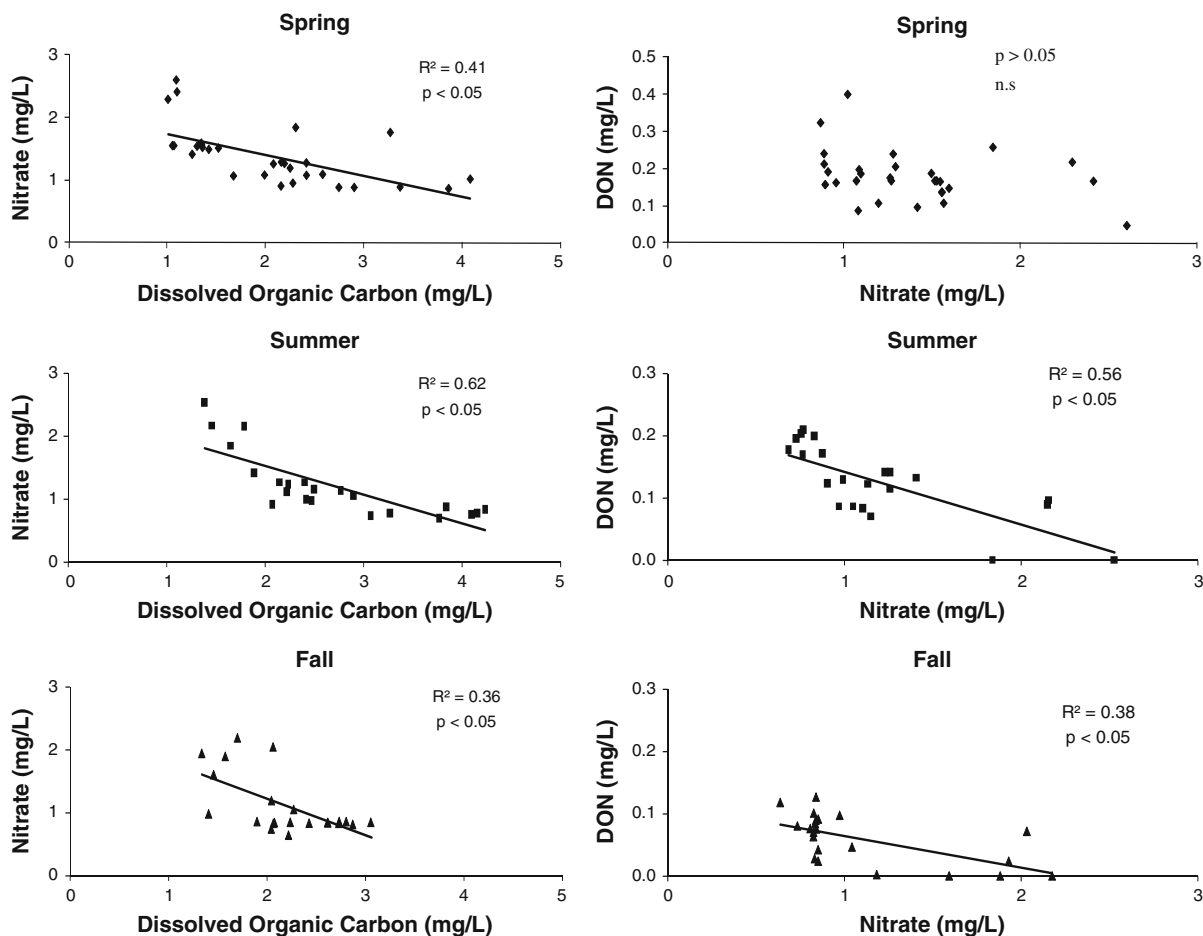


Fig. 6 Relationships between DON and nitrate concentrations and DOC and nitrate concentrations across seasons in the Gwynns Falls. There was no significant relationship between

DON and nitrate during spring, and no regression is shown. Please note the differences in scales across seasons

variability in retention rates of TDN for multiple reaches of the Gwynns Falls watershed were consistent with and fully span the range of N uptake rates for streams found in other studies (e.g., Grimm et al. 2005; Mulholland et al. 2008; Roberts and Mulholland 2007). Grimm et al. (2005) showed a particularly broad range and found that uptake rates of N varied dramatically from 33 to 106,358 mg/m²/day in urban streams of the southwestern United States. Grimm et al. (2005) attributed some of these high N uptake rates to high autotrophic demand and primary production in concrete channels. Other studies have also indicated the importance of in-stream N retention (Alexander et al. 2000; Peterson et al. 2001; Seitzinger et al. 2002b), these include individual streams, river networks, and river mainstems (Burns 1998; Duff

et al. 2008; Pribyl et al. 2005; Sjodin et al. 1997; Smith et al. 2008; Triska et al. 2007). For example, ~50 % of N inputs were retained in an agricultural river network in the western U.S. (Sjodin et al. 1997), 14–32 % in a river draining mixed forest and agricultural watersheds (Triska et al. 2007), and up to 29 % N retention was observed in a mostly forest watershed in the northeastern U.S. (Burns 1998). Furthermore, previous work using modeling approaches have suggested that N retention can be considerable at the river network scale (e.g., Mulholland et al. 2008, Wollheim et al. 2008, Stewart et al. 2011). For example, Wollheim et al. (2008) estimated that 18–71 % of dissolved inorganic nitrogen was removed by assimilation and denitrification in a suburban river network located in the Northeastern U.S., and Stewart et al.

Table 2 Reach-scale mass balances for chloride during August 2009

Distance from headwater (km)	Cl ⁻ input (mg/L)	Cl ⁻ input (kg/d)	Cl ⁻ output (mg/L)	Cl ⁻ output (kg/days)	Cl ⁻ inputs from tributaries (mg/L)	Cl ⁻ inputs from tributaries (kg/days)	Cl ⁻ gain from groundwater (kg/days)	Cl ⁻ loss to groundwater (kg/days)	% Cl ⁻ Retention
5	64.5	189	72.5	613			221	0	-49.4
6	72.5	613	75.8	1,106	85.0	199	151	0	-14.8
11	75.8	1,106	66.8	1,639	82.8	441	184	0	5.3
17	66.8	1,639	66.1	1,669	83.4	9	25	0	0.2
17	66.1	1,669	53.7	1,781	113.7	11	312	0	10.6
18	53.7	1,781	52.8	1,821	32.1	39	7	0	0.3
19	52.8	1,821	52.1	2,040	167.1	7	184	0	-1.4
21	52.1	2,040	45.7	2,108			278	0	9.0
25	45.7	2,108	44.9	1,901	79.0	244	0	263	8.0
27	44.9	1,901	42.3	2,027			221	0	4.5
29	42.3	2,027	41.9	2,350			326	0	0.2
30	41.9	2,350	45.7	3,774	60.0	318	848	0	-7.4
36	45.7	3,774	44.5	3,814			124	0	2.2
								Mean	-2.50 %

For reaches that had more than one tributary, we calculated a flow-weighted concentration by summing the loads from all the tributaries and dividing by the total flow (this applies to the following reaches with distances from headwaters at: 6 km = 4 tributaries, 25 km = 3 tributaries, and 30 km = 2 tributaries). We estimated groundwater concentrations of chloride to be 40 mg/L

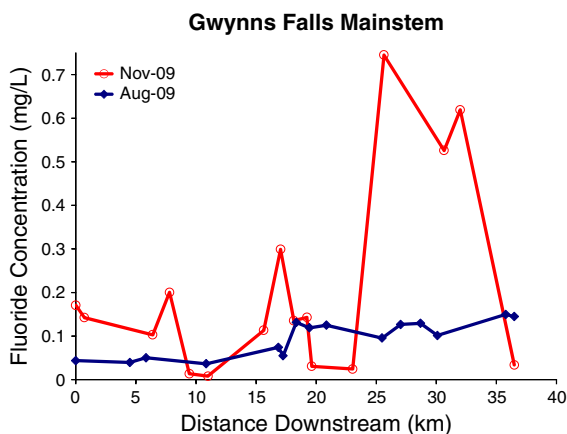


Fig. 7 Comparison of longitudinal patterns in fluoride concentrations (mg/L) along the Gwynns Falls mainstem across two seasons during August 2009 and November 2009. Data from August 2009 was taken from Kaushal and Belt (2012)

(2011) estimated that 38 % of total DIN inputs were removed in the main channel of this same river network during baseflow conditions. Although biological N demand can become “saturated” in streams at the reach scale (Bernot and Dodds 2005), our results suggest that the role of streams in modifying

watershed N loads over evolving spatial scales of kilometers should be considered when anticipating and/or modeling downstream water quality.

We observed substantial organic carbon retention in streams, but there was seasonal variability in DOC retention and uptake rates. For example, there were pronounced seasonal peaks in DOC transport in urban streams seasonally. During summer months, the mainstem of the Gwynns Falls was a net source of DOC, and this may have been due to an imbalance in increased GPP versus ecosystem respiration (exudation of DOC by algae and bacteria) and generation of labile dissolved organic matter (discussed further below). Retention of DOC could have occurred on benthic biofilms, which can be important in influencing DOC fluxes at the reach scale (Battin et al. 1999). The effects of urbanization on DOC and DON uptake rates in streams has been less studied compared to ammonium and nitrate. Net uptake rates of DOC were 1642 ± 505 and 234 ± 125 mg/m²/day for 2 urban stream networks at the Baltimore LTER site (Sivirichi et al. 2011). These rates are comparable to our estimates of DOC retention using mass balances along the Gwynns Falls. Previous work also showed that in-stream uptake of labile DOC (acetate) and DON

(glycine) in urban and agricultural streams can be equivalent or greater than ammonium, which is known to be highly bioreactive (Johnson et al. 2009). Overall, retention of DOC can be important relative to GPP and respiration along the urban watershed continuum, but the capacity for in-stream DOC retention may vary based on seasonal patterns in streamflow and stream metabolism.

Stream metabolism and organic matter quality

Autotrophic production and denitrification both represent important pathways for N retention in urban streams (Groffman et al. 2005; Kaushal et al. 2008b; Klockner et al. 2009). Primary production and denitrification can both increase in urban watersheds as contact time with sediment substrates increases (Arango et al. 2008; Kaushal et al. 2008a). Previous work has found that assimilatory uptake rather than nitrification and denitrification better explains nitrogen retention and downstream export in urban streams (Arango et al. 2008). This is consistent with ^{15}N tracer studies, which have shown that most nitrogen can be retained in autotrophic organic matter with short turnover times in urban streams (Sobota et al. 2012). Differences in GPP between urban and forested streams might have been due to light availability. Forested canopy cover may have reduced light penetration to the stream, which hindered GPP. Urban sites along the Gwynns Falls were considerably less shaded. For example, GFVN and GFCP sites have little riparian cover by virtue of their width and are fairly shallow streams whereas GFGB has a tight canopy as its width is small; GPP appeared to increase along 4 stations of the Gwynns Falls in a downstream direction as the channel widened. Light availability may have contributed to seasonal changes in GPP functions along the Gwynns Falls and differences with forest reference sites (Pennino et al. 2014). Overall, our results suggest that assimilatory N demand due to GPP may be important in N retention along the urban watershed continuum, particularly during baseflow.

We observed significant inverse relationships between DOC and DON concentrations and nitrate concentrations along the Gwynns Falls watershed. Previous studies have also proposed that assimilatory demand by algae and bacteria can contribute to

transformations of nitrate to DON (Bronk and Ward 2005; Kaushal and Lewis 2005). For example, primary producers can assimilate inorganic N and release organic N as waste products (Bronk and Ward 2005). Heterotrophic microbial communities can also assimilate inorganic N and generate organic N in response to increased organic C availability (increased C:N ratio) via microbial DIN immobilization and extracellular leakage of DON; microbes can also mineralize organic N to nitrate based on C:N stoichiometry (Brookshire et al. 2005; Kaushal and Lewis 2005). It is unlikely that the relationship between nitrate and DON in the Gwynns Falls watershed was solely due to in-stream retention by microbial processes, however. There may be alternative hypotheses to explain these patterns. For example, there may have been shifts in watershed C and N loading and differences in hydrologic flowpaths/sources of DOC and DON and nitrate along the stream network. There may have been direct inputs from stormdrains, sewage, and/or residential sources of nitrate and DOC and DON along suburban to urban reaches (Kaushal et al. 2011). Stormdrains can have DOC concentrations several-fold higher than forest streams, and some stormdrains flow when there is no rain due to groundwater inputs into cracks in pipes (discussed further below) (Kaushal and Belt 2012). Based on the bioavailability of sewage DOM, it is also possible that there is also rapid mineralization and nitrification of sewage-derived DON (Kaushal et al. 2011). This would contribute to a positive relationship between DON removal and nitrate production in the stream (i.e. mineralization and nitrification of sewage DON). The inverse relationship between the concentrations of DON and DOC and nitrate may suggest a potential biological mechanism in the stream, but it is difficult to distinguish exact mechanisms in the present study.

Although the mainstem of the Gwynns Falls was a net source of nitrate and net sink of DON, it does not suggest that assimilatory uptake prefers DON over nitrate. Instead, it suggests that nitrate contributions from ground water and leaky sewage infrastructure may overwhelm net nitrate uptake along the Gwynns Falls. Our results suggest that DON is remineralized to nitrate and DON declines while nitrate increases. DON from sewage leaks can be rapidly mineralized and nitrified under oxygenated conditions in streams. Denitrification rates can be considerable in urban

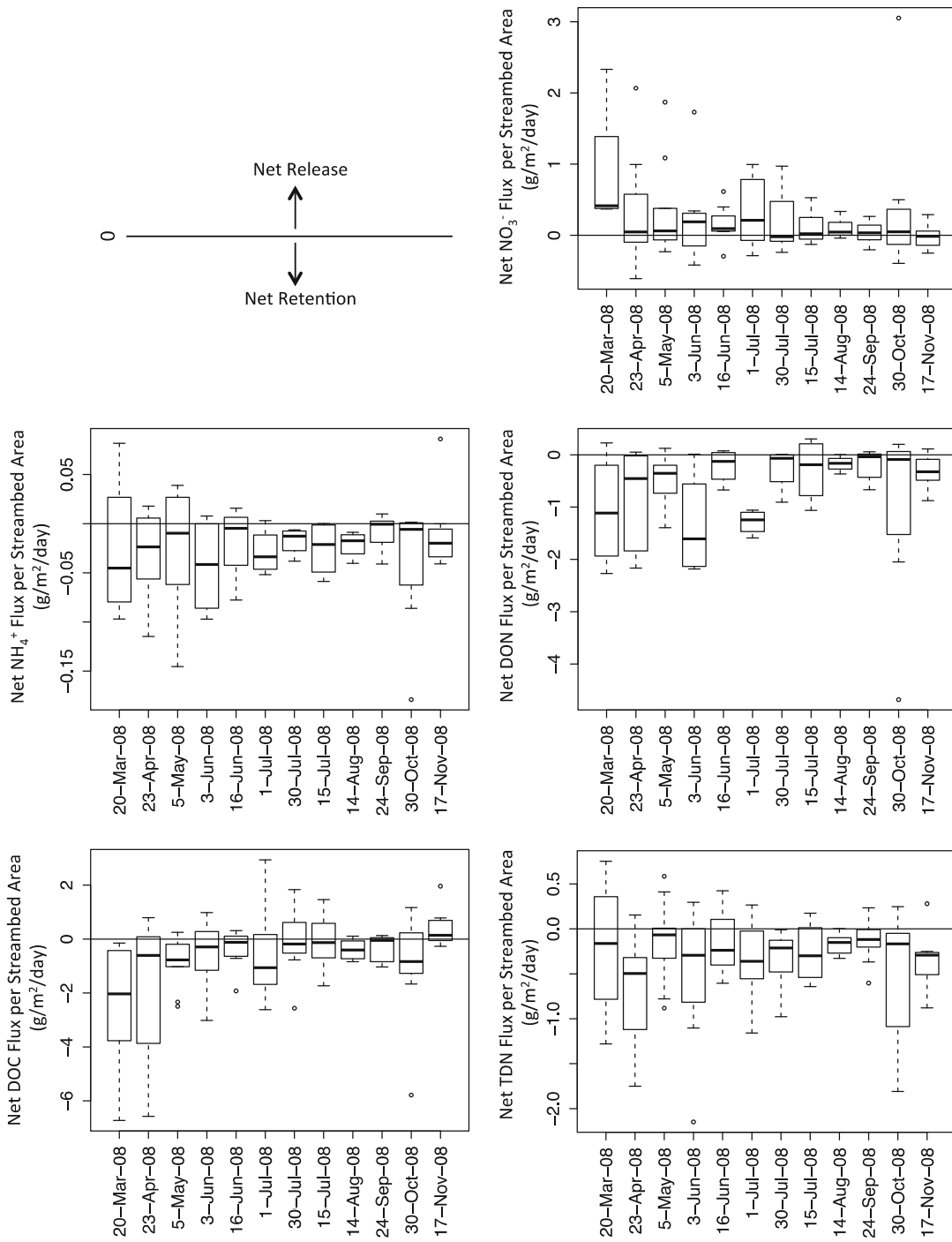


Fig. 8 Variations in net retention and release rates (g/m²/day) for the Gwynns Falls mainstem over time (N = 9 reaches). A positive value indicates net release and a negative value indicates net retention. The center vertical line of the box-and-whisker plot marks the median of the sample. The length of each whisker shows the range within which the central 50% of the values fall. Box edges indicate the first and third quartiles. Open circles represent outside values

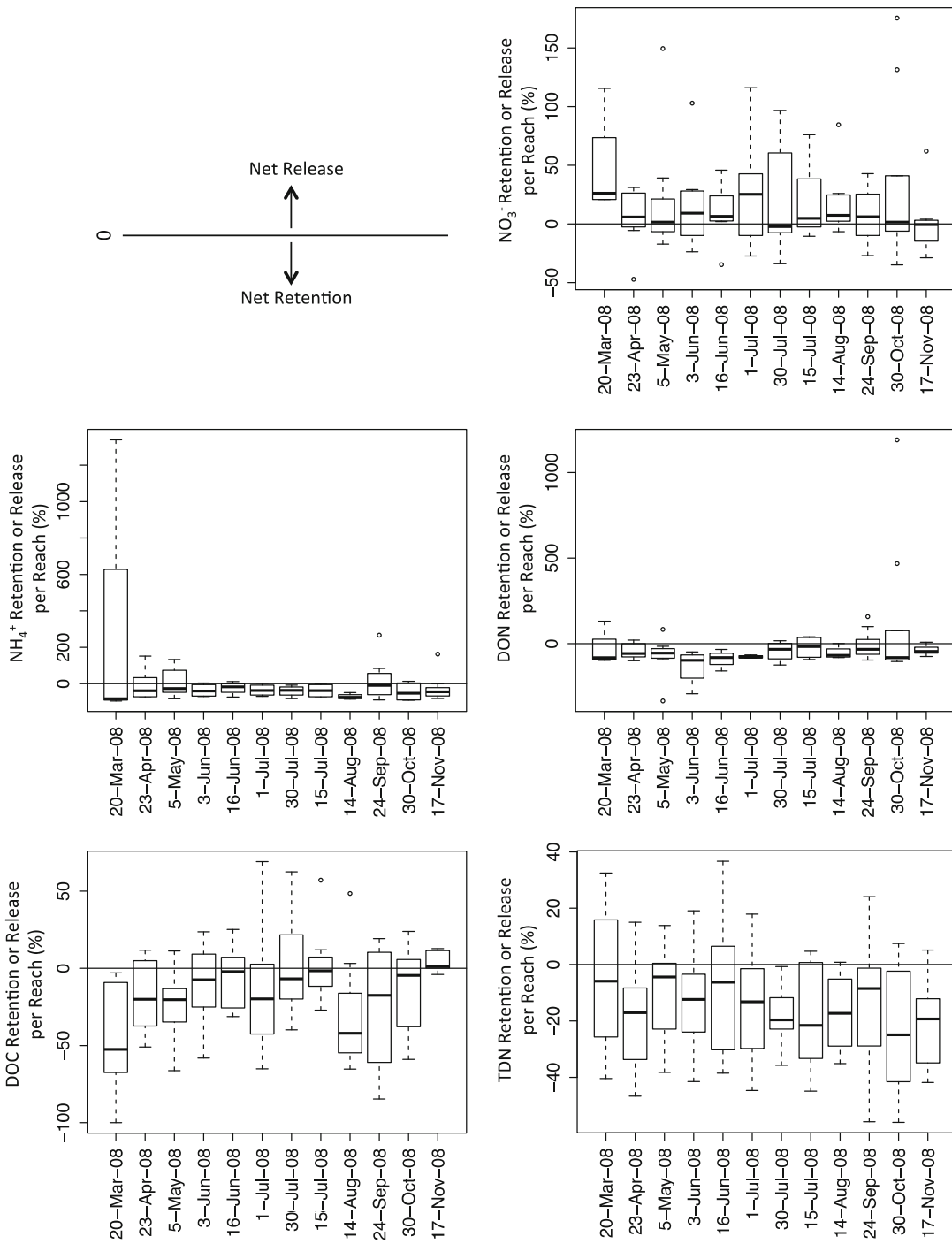


Fig. 9 Variations in net retention and release rates (%) for the Gwynns Falls mainstem over time ($N = 9$ reaches). A positive value indicates net release and a negative value indicates net retention. The center vertical line of the box-and-whisker plot marks the median of the sample. The length of each whisker shows the range within which the central 50 % of the values fall. Box edges indicate the first and third quartiles. Open circles represent outside values

streams of Baltimore, but they may not be able to keep pace with substantial nitrate inputs from chronic groundwater contamination and leaks from aging sanitary infrastructure.

We observed a change in the chemical composition of DOM (protein-like to humic ratio) with increasing watershed urbanization. Changes in DOM fluorescence have previously been related to biochemical oxygen demand in surface waters (Hudson et al. 2008). Our results suggest that urbanization can increase the lability of DOC and DON. Recent work has shown that wastewater inputs from urbanization can alter the chemical composition of dissolved organic matter in streams (Kalschauer et al. 2012). Other work has shown that DOC and DON from urban sources can be bioavailable over relatively short time scales (Seitzinger et al. 2002a; Wiegner and Seitzinger 2004) and that labile organic matter inputs from urban watersheds can contribute to oxygen demand in streams and rivers (Mallin et al. 2006). There are gradients in the isotopic values of carbon in particulate organic matter with land use at the Baltimore LTER site, which suggested shifts in organic matter sources and quality (Kaushal et al. 2011). Other related work at the Baltimore LTER site shows that organic matter in urban streams is different between forest, urban, and restored streams using a combination of lipid biomarkers, stable isotope analyses, and C:N ratios (Newcomer et al. 2012). Given these previously observed changes in the chemical composition of organic matter, it is likely that urbanization enhances DOM quality. There is emerging interest regarding whether organic carbon should be managed in urban and agricultural watersheds due to its potential effects on ecosystem processes and water quality (Newcomer et al. 2012; Stanley et al. 2012). Our results suggest that the amount of GPP and quality of organic matter can be enhanced along the urban watershed continuum with potential downstream impacts on ecosystem function and water quality. Recent work in the Gwynns Falls watershed has found a long-term increase in alkalinity, and this may partially be influenced by mineralization of labile organic matter and production of dissolved inorganic carbon or bicarbonate alkalinity (Kaushal et al. 2013). An increase in labile organic carbon loading along the urban watershed continuum has major downstream implications for water quality, ecosystem metabolism,

CO₂ production and alkalinity, and oxygen demand in receiving waters.

Potential importance of groundwater-surface water interactions: the urban karst

Across sampling dates and detailed sampling of tributaries, delivery of carbon and nitrogen from distributed sources (i.e. not accounted for by tributary inputs) accounted for a considerable portion of the water, carbon, and nitrogen budgets along 9 reaches of the Gwynns Falls. Similarly, we observed that there was consistently net export of nitrate along the Gwynns Falls and this may have been due to: (1) transformation from DON to nitrate as a result of organic matter mineralization and nitrification, (2) nitrate release from N-rich sediment (Duan and Kaushal 2013), and/or (3) the relative importance of groundwater inputs. Over the study period, total input of distributed flow (including inputs from groundwater, leaky piped infrastructure, and unaccounted tributaries) to the Gwynns Falls ranged from 27 to 67 % of baseflow—a consistently major component of the water budget. Increasing fluoride concentrations along the Gwynns Falls mainstem further indicated that leaky piped infrastructure contributed to the flow budgets of urban streams. This complexity and patchiness in urban hydrologic flowpaths known as the “urban karst” has been well documented and explored at the Baltimore LTER site (Kaushal and Belt 2012), and it is likely due to groundwater seepage and inputs from leaky potable water and sanitary infrastructure to streams. Furthermore, our observation of elevated chloride concentrations along the Gwynns Falls (Table 2) was an additional line of evidence regarding the importance of distributed flow. Chloride is stored in soils and ground water from winter road salt applications and can enter streams during summer baseflow conditions (Kaushal et al. 2005). Long-term chloride concentrations in nearby a forest reference stream with no watershed development ranged from 2 to 8 mg/L seasonally (Kaushal et al. 2005), whereas chloride concentrations along the Gwynns Falls during the summer (no road salt applications) were approximately tenfold higher likely from groundwater seepage inputs.

Multiple studies suggest that groundwater-surface water interactions now should be considered in studies

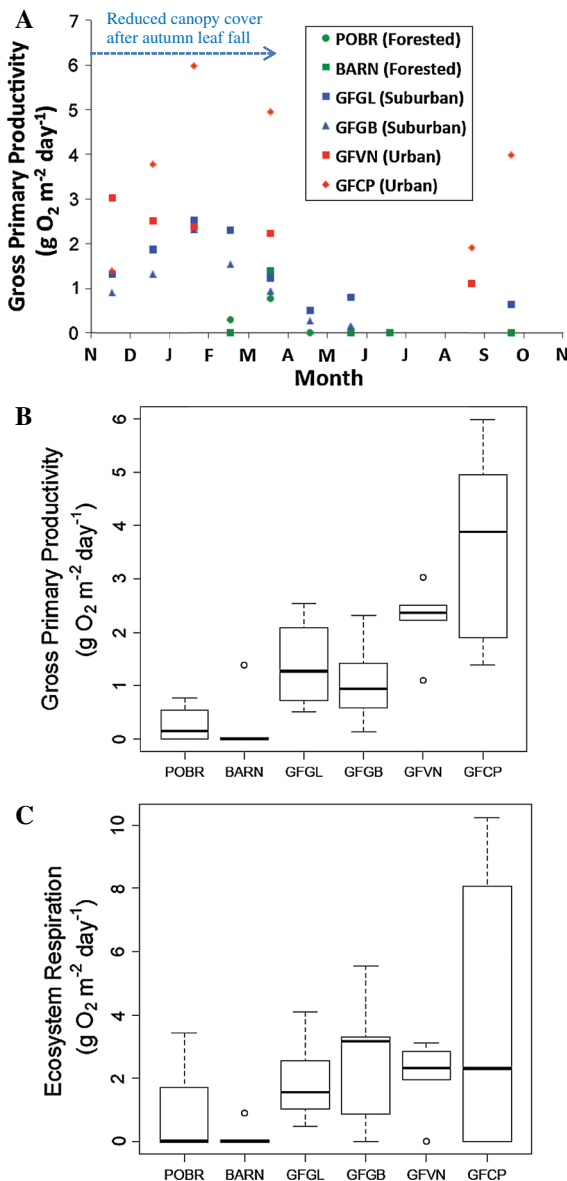


Fig. 10 **a** Monthly estimates of GPP for 4 longitudinal sampling stations along the Gwynns Falls in order from upstream to downstream (GFGL, GFGB, GFVN, GFCP) and two nearby forest reference watersheds of the Baltimore LTER site (POBR, BARN). **b** Estimates of average GPP for all months, **c** estimates of average ecosystem respiration for all months. The *center vertical lines* of the box-and-whisker plots indicate the median of the sample. The length of each whisker shows the range within which the central 50 % of the values fall. *Box edges* indicate the first and third quartiles. *Open circles* represent outside values

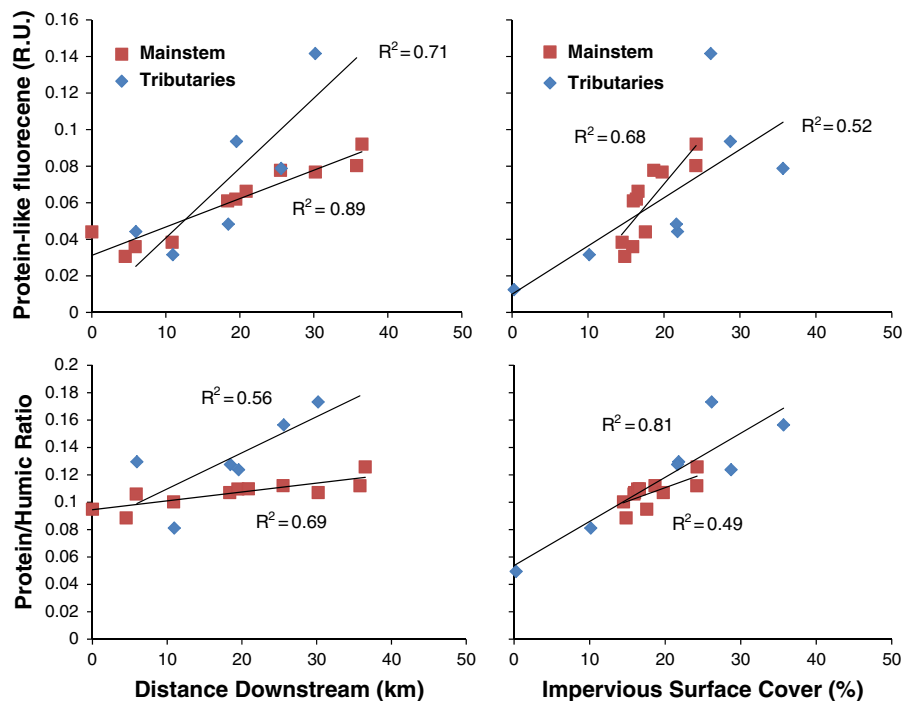
of urban ecosystems (e.g., Mayer et al. 2010; Ryan et al. 2010; Kaushal et al. 2011; Sivirichi et al. 2011; Bhaskar and Welty 2012; Kaushal and Belt 2012).

Similar to our study, distributed flow was found to be important in detailed interannual water budgets from 2001 to 2009 at the Baltimore LTER study sites (Bhaskar and Welty 2012) and nitrate stable isotope source tracking has shown that nearly 100 % of the nitrate-N in streams can originate from leaky sewers and contaminated shallow ground water during base-flow (Kaushal et al. 2011). Finally, research in other U.S. cities has suggested that N source contributions from leaky pipes to streams needs to be considered in urban watershed N mass balance budgets (Divers et al. 2013). More detailed sampling of the chemistry of groundwater, leaky sanitary infrastructure pipes, and leaky potable water pipes along with a sensitivity analysis and elucidation of the role of seepage in hydrologic and N budgets is necessary to accurately reflect subsurface contributions to N export in urbanized watersheds.

The urban watershed continuum: downstream implications

An improved understanding of longitudinal changes in organic matter quality, retention, and export across the urban watershed continuum is critical for predicting downstream alterations of ecosystem functions, and managing bioavailable organic carbon and nitrogen exports to drinking water and sensitive coastal waters (Seitzinger and Sanders 1997a; Sickman et al. 2007; Petrone et al. 2009). Less is known regarding the length of the river that organic matter travels before it is retained and generated and which chemical fractions are most actively modified over broader watershed spatial scales (Kaushal and Lewis 2005; Kaplan et al. 2006, 2008; del Giorgio and Pace 2008). These fluxes and processes regulating DOM may increase from low-residential and suburban headwater areas (where some natural vegetation and riparian zones are intact) to downstream reaches in progressively urban areas (where there are increased subsidies of bioavailable DOC and DON inputs from storm drains, sewage leaks, and algal blooms). Given that urbanization is increasing rapidly in coastal watersheds and globally (Grimm et al. 2008), changes in the fluxes and lability of organic C and N along the urban watershed continuum may be substantial in the future (Kaushal et al. 2014).

Fig. 11 Increases in protein-like fluorescence (labile DOC) and protein-like to humic-like ratio (an index of DOC lability) with increasing ISC and distance downstream at BES LTER sites, which suggest the effect of urbanization on enhancing stream DOC quality. Protein-like fluorescence is expressed in Raman units (RU)



Conclusions

As urbanization increases, N and organic C loads will continue to impact water quality, making urbanized watersheds a priority in future organic matter cycling studies and watershed restoration activities. In particular, the contributions of groundwater-surface water interactions and in-stream processing are lesser known but apparently important components of urban watershed N budgets, and may be important factors in regulating N cycling in urban stream networks (Mayer et al. 2010; Svirichi et al. 2011). This study provides evidence of considerable variability in C and N fluxes along the urban watershed continuum during typically baseflow hydrologic conditions. Due to spatial heterogeneity, monitoring beyond the stream-reach scale is critical for an improved perspective of evaluation of biogeochemical fluxes along the urban watershed continuum and assessing the effectiveness of watershed and stream restoration activities (Svirichi et al. 2011; Newcomer et al. In Review). Our results further suggest that urban streams have the capacity to retain and modify watershed C and N

exports over evolving watershed spatial scales, and that they are not always inert pipes completely influenced by hydrologic alterations in the watershed (del Giorgio and Pace 2008; Kaushal and Belt 2012). Research elucidating the biogeochemical and hydrological role of the urban watershed continuum beyond the individual stream reach scale will help guide proper understanding and management of N and C (Mayer et al. 2010; Svirichi et al. 2011; Kaushal and Belt 2012). Furthermore, it will also allow us to understand how urbanization can enhance organic carbon export and composition via both in-stream production and nonpoint sources such as sewage and stormdrains with downstream implications for water quality, ecosystem metabolism, CO₂ production and alkalinity, and oxygen demand in receiving waters.

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