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Carbon cycle of an urban watershed: exports, sources, and metabolism

Rose M. Smith · Sujay S. Kaushal

Abstract Rivers transport and transform significant quantities of carbon to coastal zones globally. Urbanization and climate change impact the transport and transformation of carbon by altering hydrology, water temperatures, and in-stream metabolism rates. Changes in exports, sources, and metabolism of carbon influence ecosystem processes, food webs, and greenhouse gases. We characterized exports, sources, and metabolism of carbon in four urban watersheds using a combination of discrete stream chemistry measurements and continuous water-quality sensors. Over three years, watershed DOC exports in the Baltimore-Washington D.C. metropolitan area ranged from 9 to 23 kg ha^{-1} year^{-1}. DIC exports ranged from 19 to 59 kg ha^{-1} year^{-1}. Daily contributions from in-stream metabolism varied between −65 and 90 % of DIC export depending on stream size and streamflow conditions. Negative contributions from metabolism occurred on days when streams were autotrophic. All streams were heterotrophic during 60 to 87 % of each year, but showed significant peaks in autotrophy during spring and summer. Differences in the timing and magnitude of peaks in springtime net ecosystem productivity were likely driven by varying light availability across streams of different sizes and riparian shading. CO_2 was consistently over-saturated with respect to the atmosphere on all sampling dates and was 0.25–2.9 mg C L^{-1}. Exports, sources, and metabolism of DOC and DIC showed strong predictable patterns across streamflow. Thus, we present a new conceptual model for predicting carbon transport and transformation across changing streamflow and light availability (with impacts on sources and fluxes of DOC, DIC, and CO_2). Overall, our results and conceptual model suggest that urbanization accelerates the transition of streams from transporters to transformers of carbon across streamflow, with implications for timing and magnitude of CO_2 fluxes, river alkalinization, and oxygen demand in downstream waters.

Responsible Editor: C. T. Driscoll.

R. M. Smith (✉) · S. S. Kaushal
Department of Geology, University of Maryland, College Park, MD 20742, USA
e-mail: rsmith24@umd.edu

R. M. Smith · S. S. Kaushal
Earth System Science Interdisciplinary Center, College Park, MD 20740, USA

Introduction

Carbon transported by rivers provides a major source of energy for aquatic food webs, and is a significant

component of the global carbon cycle (Perdue and Ritchie 2003; Cole et al. 2007; Battin et al. 2008; Moens et al. 2002; Middelburg and Nieuwenhuize 1998). Approximately 2.7 Pg of carbon is exported from terrestrial to aquatic ecosystems globally. However, only 0.9 Pg of carbon reaches the ocean, while 1.2 Pg is respired as CO_2, and 0.6 Pg is stored in sediments (Regnier et al. 2013). Changes in human activities related to agricultural liming, increased soil erosion, chemical weathering, and urban wastewater inputs have contributed significantly to accelerated transport of carbon from the land to ocean (e.g., Daniel et al. 2001; Raymond and Cole 2003; Cole et al. 2007; Tank et al. 2010; Kaushal et al. 2013; Regnier et al. 2013). Furthermore, riparian vegetation removal and nutrient loading from urban and agricultural landscapes may increase autochthonous carbon production (Mulholland et al. 2001; Bernot et al. 2010; Griffiths et al. 2013). Warming from climate change and urban heat islands has the potential to increase rates of organic carbon breakdown in rivers and estuarine sediments (Neal et al. 1998; Daniel et al. 2001; Raymond and Cole 2003; Barnes and Raymond 2009; Kaushal et al. 2014a). Here, we investigate how hydrologic variability and urbanization can alter the sources and metabolism of carbon exported by rivers.

Over decades, carbon cycling has been studied extensively in forested watersheds (e.g., McDowell and Fisher 1976; Sobczak and Findlay 2002). Controls on carbon export from forest watersheds can include climate, topography, soil carbon content, and the presence of wetlands (Hopkinson et al. 1998; Aitkenhead et al. 1999; Perdue and Ritchie 2003). These studies indicate that the quantity and quality of dissolved organic carbon (DOC) are important drivers of the ecological function of forest streams (Vannote et al. 1980; Hopkinson et al. 1998). Streams naturally contain a mix of terrestrial (allochthonous) and in-stream (autochthonous) sources of dissolved organic matter (DOM), which contribute to watershed DOC export as particulate organic matter is leached or decomposed. Sources of terrestrial DOM include leachates or decomposed soil organic matter and leaf detritus. Autochthonous sources of DOM consist primarily of decomposed or leached algal, bacterial, and fungal biomass (Sinsabaugh et al. 1997; Webster and Meyer 1997). Previous studies have shown that hydrologic variability (e.g., Raymond and Saiers 2010) and stream metabolism (e.g., Tank et al. 2010)

alter the relative proportions of terrestrial and in-stream-derived carbon in rural watersheds. However, impact of urbanization on exports, sources, and metabolism of terrestrial vs. in-stream sources of DOM remains unclear.

Urbanization increases the quantity of both natural (e.g., soil, leaves, algae) and anthropogenic (e.g., sewage, grass clippings) sources of organic matter, which may be leached into DOM in streams and soils (Daniel et al. 2001; Newcomer et al. 2012; Kaushal et al. 2014a; Duan et al. 2014). Frequent flooding can increase inputs of natural particulate organic matter from riparian vegetation and soil erosion (Raymond and Saiers 2010; Imberger et al. 2011; Fraley et al. 2009), which also contribute to the DOM pool downstream through leaching and decomposition. Nutrient loading and tree canopy removal (which increases light availability) can stimulate autochthonous productivity (Mulholland et al. 2001). This contributes to the autochthonous DOM pool as this biomass decomposes over daily or seasonal timescales. Wastewater-derived DOM and nutrient inputs can enter streams via point sources such as wastewater treatment plant outfalls (e.g., Daniel et al. 2001; Barnes and Raymond 2009; Aitkenhead-Peterson et al. 2009; Edmonds and Grimm 2011) and nonpoint sources such as diffuse sewage pipe leakage and septic systems (Sickman et al. 2007; Kaushal et al. 2011). In addition, rising stream temperatures and salinization may influence rates of DOM leaching from soils and benthic sediments (e.g., Kaushal et al. 2005; Aitkenhead-Peterson et al. 2009; Kaushal et al. 2010, Duan and Kaushal 2015). For instance, Duan and Kaushal (2013) found that warming increased DOC fluxes from streambed sediments, and previous studies have shown that road salt additions increases DOM leaching from soils through sodium dispersion and pH suppression (Green et al. 2008, Duan and Kaushal 2013).

Dissolved inorganic carbon (here we define DIC = carbonate + bicarbonate + CO_2) is the dominant form of carbon exported from many rivers and streams globally (Meybeck 2003). Annual riverine DIC fluxes are comparable in magnitude to the terrestrial carbon sink (Cole et al. 2007). Several studies have shown that alkalinity of running waters, largely controlled by bicarbonate, is currently increasing in many watersheds (Raymond and Cole 2003; Kaushal et al. 2013). Recent work suggests that long-

term alkalinization of streams and rivers can be an indicator of evolving water quality in cities over time due to human activities (Kaushal et al. 2014c, 2015). Potential drivers of river alkalinization include agricultural liming, weathering of urban building materials, and a time-lag response of increased weathering due to acid rain (Raymond and Cole 2003; Kaushal et al. 2013; Hossler and Bauer 2013). Patterns of DIC and alkalinity in urban watersheds warrant further study due to its potential role in buffering coastal ocean acidification, aquatic primary production, and global aquatic carbon budgets (Cole et al. 2007; Kaushal et al. 2013). DIC in streams and rivers is produced by several processes that offset terrestrial carbon storage, including mineral weathering, terrestrial soil and root respiration, and in-stream DOC mineralization (e.g., Berner et al. 1983; Meybeck 1987, Hotchkiss et al. 2015). Dissolved CO_2 from terrestrial (soil and root) respiration contributes to the in-stream DIC pool via groundwater or shallow soil flowpaths (Jones and Mulholland 1998). Bicarbonate is produced when carbonate rocks dissolve in the presence of carbonic (or other) acid and when carbonic acid interacts with silicate rocks (Berner et al. 1983; Schnoor and Stumm 1986). The rates of various terrestrial processes vary widely with climate, vegetation, and underlying geology (Meybeck 2003). In-stream DIC (including CO_2) production via ecosystem respiration (ER = heterotrophic + autotrophic respiration) also varies widely in streams and is largely controlled by temperature, organic carbon loading, stream biota, and nutrients (e.g. Mulholland et al. 2001; Bernot et al. 2010; Tank et al. 2010). Urbanization has been suggested to increase export of DIC from anthropogenic sources such as building materials and wastewater treatment plant effluent (Daniel et al. 2001; Barnes and Raymond 2009; Zeng et al. 2010; Hossler and Bauer 2013). Urbanization may also influence production of DIC via in-stream ER through heat island effects and increased DOC loading (Tank et al. 2010; Kaushal et al. 2014b). As DIC fluxes from streams and rivers continue to change globally, we seek to understand how urbanization alters sources and fluxes. In the current paper, we investigated how light availability, temperature, streamflow conditions influence DIC sources and export in urbanized watersheds. We also estimated the relative contribution of stream metabolism and terrestrial (soil/root respiration + weathering)

processes to total DIC export from three watersheds on daily time scales over three years.

The impacts of urbanization on export, sources, and metabolism of carbon can evolve over time as watershed development practices alter hydrologic flow paths (Kaushal et al. 2014c). For example, urbanization often dramatically increases hydrologic response and peak streamflow conditions during storms due to impervious surfaces, riparian development, and subsurface drainage systems (e.g., Paul and Meyer 2001; Walsh et al. 2005; Kaushal and Belt 2012). The net effect of all these hydrologic alterations raises questions about the relative influence of in-stream vs. terrestrial controls on carbon quantity and quality. The objectives of this study were (1) to quantify inter-annual and intra-annual fluxes of DIC and DOC, and DOM sources from urban watersheds, (2) identify key environmental variables influencing carbon fluxes using a combination of in situ sensor and discrete measurements, and (3) to propose a conceptual model integrating the hydrologic and biological controls on C cycling in urban watersheds across streamflow. An improved understanding of the processes controlling transport, and transformation of carbon in urban watersheds across annual streamflow cycles is necessary to anticipate changes brought on by climate and land cover changes.

Our overarching hypothesis was that urban streams shift from carbon transformers to transporters as streamflow increases, with resulting impacts on sources and fluxes of DOC, DIC, and CO_2. Based on this hypothesis, we tested the following specific predictions: (a) urbanized watersheds export more DOC than minimally disturbed watersheds in similar climatic zones, (b) gross primary productivity (GPP) in nutrient-loaded and un-shaded streams would be elevated, causing dissolved matter quality to resemble recent autochthonous inputs more than terrestrial carbon sources, and (c) in-stream respiration contributes a significant portion of daily DIC fluxes compared with terrestrial sources. Based on our analysis, we also developed a new conceptual model illustrating how streamflow and light availability can influence in-stream vs. terrestrial controls on transport and transformation of DIC, DOC, and CO_2. An improved understanding of anthropogenic impacts on the sources, fluxes, and metabolism of carbon is essential for management of the coastal carbon cycle, organic nutrient cycling, contaminant transport, and

increased river alkalinization (e.g., Raymond and Cole 2003; Stanley et al. 2012; Kaushal et al. 2013, 2014c; Middelburg and Nieuwenhuize 1998).

Methods

We investigated the hydrologic and metabolic controls on carbon cycling in an urban watershed over three years using a combination of stream chemistry measurements and continuous water quality sensor data. We used discrete chemistry samples to characterize the sources and export of carbon in streams. We used high-frequency sensor data to model continuous stream ecosystem metabolism and CO_2 fluxes from streams. Unless otherwise noted, all analyses were carried out using the programming language, R (R Core team 2014).

Site description

The Anacostia River is a major tributary of the Potomac River, with a watershed draining 176 km^2 of the Piedmont and Coastal Plain geographic provinces in southeastern Maryland, USA and the northeastern portion of Washington D.C. (Fig. 1). Widespread clearing of forests and draining of wetlands for agriculture occurred between the 1700s and mid-1800s (Washington Council of Governments 2010), and urban land use spread quickly after the 1950s, with a major increase during the 1970s. The current land use distribution of the overall Anacostia watershed is: 45 % residential, 30 % undeveloped, 16 % commercial or institutional, 4 % agricultural, 4 % industrial, and 1 % mining (Fig. 1) (Fry et al. 2011). Efforts to reduce sediment and nutrient loads, biochemical oxygen demand, fecal coliform bacteria, trash, heavy metals, and organic contaminants are currently in progress as part of a comprehensive restoration initiative for the Anacostia. These efforts also contribute to progress toward meeting total maximum daily loads (TMDLs) for each sub-basin of the Chesapeake Bay (Maryland Department of Environment 2015). Numerous studies have taken place in this watershed evaluating nutrient dynamics and geochemistry (e.g., Huanxin et al. 1997; Langland et al. 2012; Miller et al. 2013; Connor et al. 2014), sediment sources (Devereux et al. 2010), suspended sediment loads (Yorke and Herb 1978; Miller et al. 2013), bacterial abundance (Miller et al. 2013), and organic contaminants (Foster et al. 2000).

We characterized sources and exports of carbon in four non-tidal tributaries of the Anacostia watershed in Maryland, which comprise 98 % of river's flow at its convergence with the Potomac River. These tributaries include Paint Branch (PBCP), Sligo Creek (SLIGO), Northwest Branch (NWHV), and the Northeast Branch (NERP). Paint Branch is nested within the Northeast Branch, and Sligo Creek is nested within the Northwest Branch. Sampling sites were co-located with continuous flow and water quality monitoring stations maintained by the U.S. Geological Survey (USGS). USGS maintains continuous flow data at all four sites, and water quality sensors at three of the four (SLIGO, PBCP, and NERP), which include dissolved oxygen, pH, specific conductivity, turbidity, temperature. Water quality sensor measurements are collected at 5 or 15-min intervals, and are continuously updated and available online (http://waterdata.usgs.gov/nwis). Details about sensor data collection, maintenance, and calibration are outlined in Miller et al. (2013). A summary of watershed characteristics is provided in Table 1.

Water chemistry measurements

We collected discrete stream chemistry samples every 2 weeks between October 2011 and October 2014. We collected samples in acid-washed 500-mL high-density polyethylene bottles. Field samples were transported on ice to the laboratory where they were filtered through a pre-combusted Whatman 0.7-micron glass fiber filter. A subset of filtered water to be analyzed for optical properties of dissolved organic matter (DOM) was stored into a pre-combusted glass amber vial and refrigerated until analysis within two weeks.

Analyses of DOC, DIC, and total dissolved nitrogen (TDN) were performed on a Shimadzu Total Organic Carbon Analyzer (TOC-272V CPH/CPN; Shimadzu, Columbia, Maryland, USA). We ran samples for DIC immediately after filtering following the Shimadzu IC method. We analyzed DOC and TDN following the Shimadzu NPOC (nonpurgeable organic carbon) and TN methods respectively (e.g., Kaushal and Lewis 2005). We selected the NPOC rather than the alternative TC-IC method because it is not sensitive to variations in DIC and thus less prone to significant overestimation of DOC than TC-IC (Findlay et al. 2010).

Fig. 1 Map of the Anacostia watershed, located northeast of Washington D.C. Prominent *red* colors signify medium to high intensity urban cover, which dominates the lower reaches of the watershed. *Greens* and *yellow* signify forested and agricultural land. *Stars* denote the four U.S. Geological Survey gages sampled. Land cover data is from the 2006 National Land Cover Database (Fry et al. 2011)
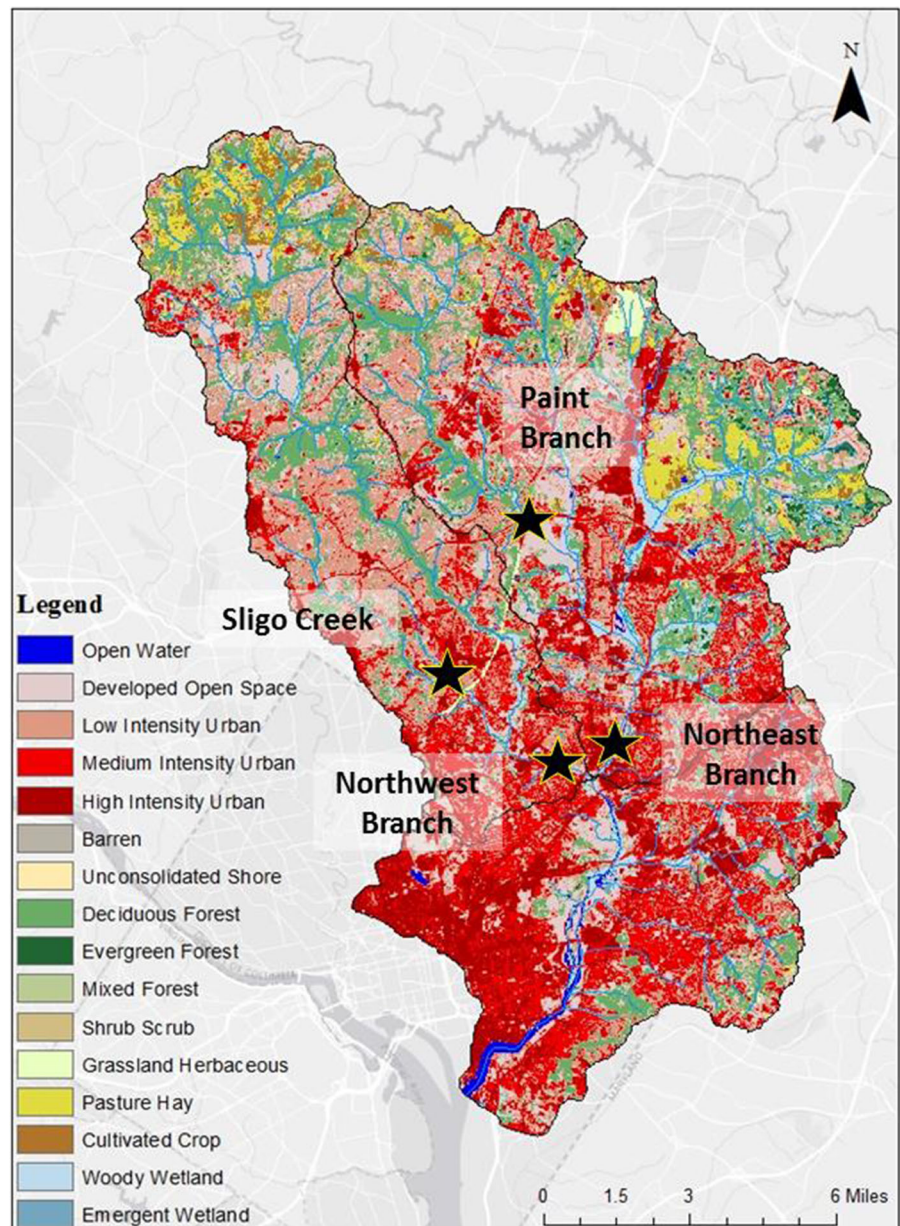
Dissolved inorganic carbon speciation

We used CO2SYS, a model of the inorganic carbonate system in freshwater and marine waters (Pierrot et al. 2006), to determine the abundance of individual dissolved inorganic carbon species (HCO_3^-, CO_3^{2-}, CO_2, OH^-, and alkalinity) using measured values of DIC, pH, and temperature.

Estimation of dissolved carbon and nitrogen exports

Discrete samples for DOC, DIC, and TDN concentrations were collected across a broad range of streamflow conditions in each stream during three years. Relationships between discrete concentration measurements and continuous discharge were optimized

Table 1 Study sites including U.S. Geological Survey gage number, watershed name with 4-letter abbreviation below, watershed area, and percentage of each land use based on NLCD 2006 data (Fry et al. 2011)

USGS station ID	Station name	Watershed area (km^2)	Urban	Agriculture	Forest	Wetland
01649190	Paint Branch (PBCP)	21.1	57	7.1	33	2.1
01649500	Northeast Branch (NERP)	117.2	63	5.6	26	4.8
01651000	Northwest Branch (NWHV)	79.5	66	7.6	24	1.5
01650800	Sligo Creek (SLIGO)	10.3	88	0	12	0.29

Watershed area and gage information can be found at http://waterdata.usgs.gov/nwis

using a FORTRAN-based program, LOADEST, developed by (Runkel et al. 2004). This approach allowed estimation of daily, monthly, and annual watershed exports (kg ha^{-1} year^{-1}) for each solute.

Characterization of dissolved organic matter sources

We measured optical properties of stream water in order to evaluate the contributions of terrestrial and aquatic sources of DOM. Upon filtering, samples were stored in pre-combusted amber vials at 4 °C for up to two weeks prior to optical measurements. Many naturally occurring DOM compounds will fluoresce, or emit low-energy light following excitation by a higher energy light source. The emission spectra produced in response to a range of excitation wavelengths can be used to evaluate the relative abundance of DOM with terrestrial origin (humic soil/plant) and aquatic origin (periphyton/algae) (Zsolnay et al. 1999; Ohno 2002; Huguet et al. 2009). We used a FluoroMax-4 Spectrofluorometer (Horiba Jobin–Yvon, Edison NJ, USA) to measure excitation-emission matrices (EEMs) of each sample. We then calculated the humification (HIX) and recent autochthonous contribution (BIX) indices of DOM quality from the EEM of each sample. HIX is defined as the ratio of emission intensity of the 435–480 nm region of the EEM to the emission intensity of the 300–345 nm region of the EEM at the excitation wavelength of 254 nm (Zsolnay et al. 1999; Ohno 2002). BIX is defined as the ratio of fluorescence intensity at the emission wavelength 380 nm to the intensity emitted at 430 nm at the excitation wavelength of 310 nm (Huguet et al. 2009). HIX and BIX are both used to differentiate between DOM with more humic/terrestrial character and DOM of more autochthonous character. HIX varies from 0 to 1, with higher values

signifying high-molecular weight DOM molecules characteristic of humic terrestrial sources. Lower HIX values are driven by low molecular weight DOM of bacterial or aquatic origin (Zsolnay et al. 1999). Conversely, BIX values (<0.7) represent terrestrial sources, and higher BIX (0.8 to 0.1 and >0.1) represent algal or bacterial sources (Huguet et al. 2009). HIX and BIX are calculated for each sample EEM after correcting the EEM for (1) emissions from a blank sample, (2) inner-filter effects from Raman scattering, and (3) absorbance of wavelengths 200–800 nm. Analyses of fluorescence indices were carried out using Matlab (version R 2012a).

Estimating continuous ecosystem metabolism

We estimated continuous ecosystem metabolism on a daily time-step using a Bayesian oxygen mass-balance model (BaMM) developed by Holtgrieve et al. (2010). The model is based on the principle that the amount of dissolved oxygen in a stream is a result of three main processes: (1) GPP, (2) ER, and (3) reaeration/gas exchange with the atmosphere (Odum 1956). Continuous monitoring of dissolved oxygen over diurnal cycles allows for estimation of daily stream metabolism based on the general mass-balance model of oxygen described by the following equation

$$\frac{dO_2}{dt} = \frac{\left[k\left([O_{2,sat}] - [O_2]\right) - R + P\right]}{D} \qquad (1)$$

where O$_{2,sat}$ is the oxygen concentration at equilibrium with the atmosphere (mg O$_2$ m^{-3}) and O$_2$ is the measured O$_2$ concentration. R and P are respiration and photosynthesis rates respectively (mg O$_2$ m^{-2} h^{-1}), k is gas transfer velocity (m h^{-1}) and D is water depth (m). GPP rates are modeled based on O$_2$ saturation data and light availability, and ER is based on O$_2$ under-saturation and temperature over diurnal periods.

Model input data included continuous measurements of dissolved oxygen, temperature, and discharge made available by USGS at the SLIGO, PBCP, and NERP gaging stations. Model time steps varied from 5 to 15-min increments across sites. Photosynthetically active radiation (PAR) data was measured at the nearby USDA Beltsville Agricultural Research Center (USDA Agricultural Research Service 2014). Daily rates of GPP, ER, and net ecosystem production (NEP = GPP-ER) were converted to g C m^{-2}day^{-1} using respiration quotient of 1. Several studies have made this assumption in order to infer connections between carbon and oxygen cycling in stream metabolism studies (Jones and Mulholland 1998; Hall and Tank 2003; Demars et al. 2011).

Gaseous and dissolved inorganic carbon fluxes

Multiple processes at both the stream channel and watershed-scale contribute to the total DIC flux, which we estimated at daily and annual time steps (described above). In-channel processes include GPP, ER, and exchange of CO_2 between the water surface and atmosphere. DIC from dissolution of carbonate minerals (e.g. calcite, aragonite) as well as soil and root respiration in upland soils are delivered to the stream via soil and groundwater flowpaths. We describe a simplified mass-balance model of inorganic carbon fluxes from watersheds as follows:

$$WS - NEP * A = CO_{2F} * A + DIC_F \qquad (2)$$

where WS is the total flux of watershed sources (soil respiration + weathering) into the stream (grams/day), NEP is GPP-ER (g C m^{-2} day^{-1}). A is stream surface area (m^2) above each stream gage. CO_{2F} is the flux of CO_2 from stream to atmosphere (g C m^{-2} day^{-1}). DIC_F is the daily DIC flux (g C day^{-1}) modeled using LOADEST. We estimated NEP, CO_{2F}, and DIC_F using measured data, and determined WS by difference. We estimated A based on flow lines using the EPA WATERS dataset (EPA WATERS 2015), and measured mean wetted width from Google Earth imagery (Google Earth, 2015). We calculated the daily net consumption (or production) of DIC by NEP (g C stream^{-1} day^{-1}) by assuming that NEP rate was spatially consistent within the stream channel upstream of each gage. Positive daily NEP signified net DIC production and negative NEP (or net

respiration) signified net DIC production over a diurnal cycle. CO_{2F} (g C m^{-2} day^{-1}) was calculated using Eq. 3

$$CO_{2F} = K_{CO_2}\left(CO_{2w} - CO_{2eq}\right) \qquad (3)$$

where CO_{2w} is the CO_2 concentration in the water column (CO_2 g C m^{-3}) and CO_{2eq} is the CO_2 concentration in water if it were in equilibrium with the atmosphere. We estimated daily mean CO_{2w} concentration by running the LOADEST model separately with mean daily DIC concentration estimates. Then, we used the CO2SYS model to estimate mean daily CO_{2w} with modeled DIC and measured daily temperature, depth and pH from each gaging station (Pierrot et al. 2006). We determined mean daily CO_{2eq} using equations in Weiss (1974) assuming barometric pressure of 1 atm and atmospheric mixing ratio of 350 ppm CO_2. K_{CO2} is the gas exchange velocity, with units of m day^{-1} for CO_2 at ambient stream temperature. We estimated daily average gas exchange of oxygen at 20C (K_{20}) using the BaMM model (Holtgrieve et al. 2010). We corrected daily oxygen K_{20} values for differences in solubility between CO_2 and O_2 using the ratio of their Schmidt numbers (Wanninkhof 1992),

$$K_{CO_2} = K_{O_2}(Sc_{CO_2}/Sc_{O_2})^n \qquad (4)$$

where Sc_{CO2} and Sc_{O2} are Schmidt numbers for CO_2 and O_2 respectively. The exponent, n is set to $-2/3$ because this value corresponds to smooth (rather than -1/2 for choppy) water surfaces (Wanninkhof 1992). We converted K_{20} to K_T based on relationships described in Elmore and West (1961).

$$K_T = K_{20} * (1.0241)^{T-1} \qquad (5)$$

Our estimates of CO_2 flux is likely conservative because CO_2 is based on DIC measured during daytime hours and do not account for diurnal lows in GPP. An unknown portion of CO_2 from nighttime respiration may be lost to the atmosphere and thus unaccounted for with this analysis. In this case, we would also under estimate the contribution of DIC from watershed sources in the mass balance model (Eq. 2). Another assumption we made was that CO_2 concentrations and flux rates estimated at each gage were representative of the total stream surface upstream of that point. We also acknowledge that a

small amount of CO_2 may have been lost prior to DIC analysis during filtration.

Results

Streamflow variability

Study sites varied in mean annual discharge. Mean annual discharge across the three study years was lowest at SLIGO, with a range of 0.19–0.22 m^3 s^{-1} during the study period, followed by PBCP (0.31–0.38 m^3 s^{-1}), then NWHV (1.22–1.57 m^3 s^{-1}), and NERP (2.00–2.76 m^3 s^{-1}). Baseflow varied significantly among seasons ($p < 0.05$), with the annual minimum occurring in early fall and maximum occurring during late winter/early spring, due to seasonal fluctuations in the water table with evapotranspiration (Fig. 2).

Annual exports of carbon and nitrogen

Carbon export varied widely across sites and years. The range of DIC export for all four sites and three years was 22–84 kg C ha^{-1} $year^{-1}$, and the range of DOC exports was 8–40 kg C ha^{-1} $year^{-1}$ (Table 2). TDN export was less variable, with a range of 2.8–9.0 kg N ha^{-1} $year^{-1}$. TDN export was also less responsive to changes in runoff (Fig. 3a) compared to DIC and DOC. PBCP had the lowest annual exports of: DIC (22–37 kg C ha^{-1} $year^{-1}$), DOC (8–16 kg C ha^{-1} $year^{-1}$), and TDN (3–6 kg N ha^{-1} $year^{-1}$). SLIGO had the highest annual DIC export in all years (50–84 kg C ha^{-1} $year^{-1}$). DOC exports were variable across years for all sites. SLIGO had the highest DOC export in two out of three years. Concentrations of DOC and DIC were significantly correlated with mean daily discharge at three out of four sites (p values = 2×10^{-7} to 1×10^{-3}, r^2 = 0.11–0.38). DOC

Fig. 2 Time-series of continuous measurements of streamflow and Gross Primary Production (GPP) for Sligo Creek, Northeast Branch, and Paint Branch. Both streamflow and GPP show seasonal variability with leaf-out processes. Seasonal variations in GPP are driven by light availability during leaf-out and seasonal changes in discharge are driven by evapotranspiration following leaf-out
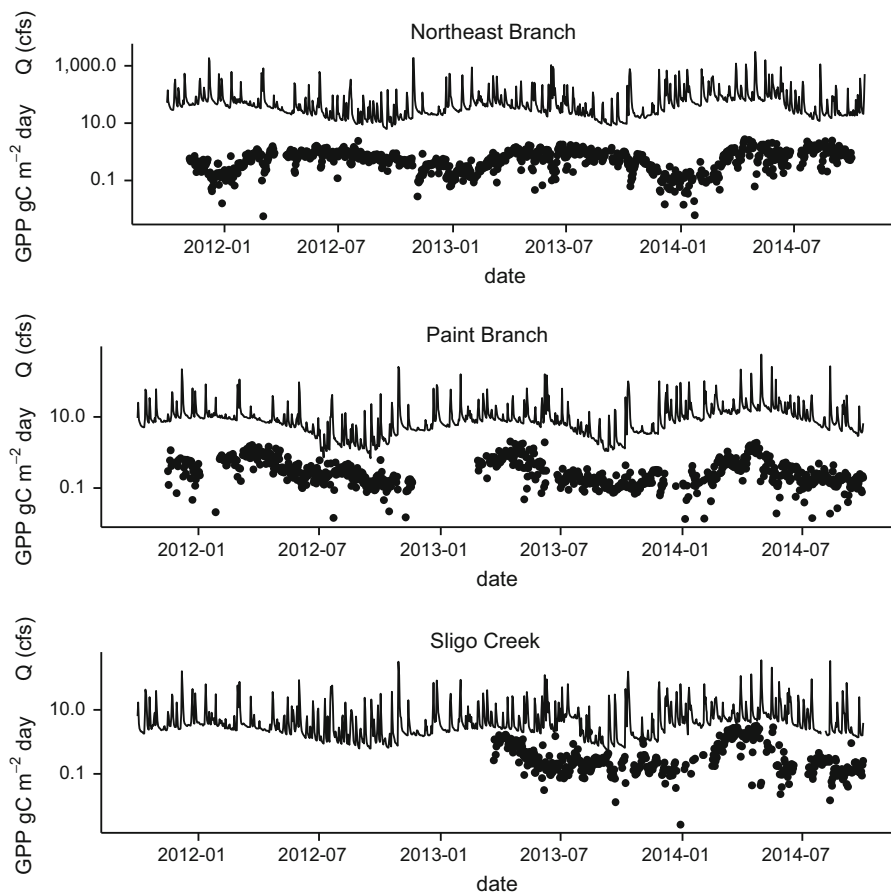
Table 2 Annual area-normalized export (kg ha^{-1} year^{-1}) of dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), and total dissolved nitrogen (TDN) by water year for four stream sites in the Anacostia watershed

Site	Water year	DIC	DOC	TDN
PBCP	2011–2012	22.5	8.4	3.3
	2012–2013	23.2	12.3	2.9
	2013–2014	37.7	17.0	6.0
SLIGO	2011–2012	50.1	17.3	3.9
	2012–2013	57.4	24.1	4.2
	2013–2014	83.6	40.1	9.0
NWHV	2011–2012	28.5	13.8	3.1
	2012–2013	43.3	23.2	3.8
	2013–2014	64.3	38.8	6.6
NERP	2011–2012	25.3	19.4	2.8
	2012–2013	30.9	21.7	2.8
	2013–2014	48.2	38.9	5.8

showed a positive log-linear relationship with discharge, whereas DIC showed a log-linear negative relationship at three of the four sites (Fig. 3b).

Carbonate system

Thirty estimates of DIC speciation between carbonate, bicarbonate, and CO_2 were made at three sites (SLIGO, PBCP, and NERP) between 2012 and 2014. These estimates were calculated from DIC, pH, and temperature measurements. Mean DIC concentrations at SLIGO, PBCP, and NERP were 16.8, 8.1, and 10.7 mg C L^{-1} respectively, and CO_2 concentrations were 0.97, 0.84, and 1.02 mg C L^{-1} (pCO$_2$: 2201, 1537, and 2003 µatm). The majority of DIC was present as bicarbonate (HCO$_3^-$), in which the average (and total range) was 89 % (60–94 %), 94 % (88–97 %), and 90 (81–97 %) of total DIC at NERP, SLIGO, and PBCP, respectively. CO_3^{2-} was less than 1 % of DIC on all sampling occasions. CO_2 contributed the remaining DIC (varying from 0.1 and 40 % of DIC across sites and sampling dates), with an average of 5, 10, and 11 % at SLIGO, NERP, and PBCP, respectively.

CO_2 concentration was negatively correlated with TDN at SLIGO and positively correlated with DOC and SLIGO and NERP. CO_2 concentration was also positively correlated with temperature at SLIGO ($p < 0.01$, $r^2 = 0.30$). GPP and NEP were both negatively correlated with CO_2 concentration at SLIGO ($p < 0.01$, $r^2 = 0.58$ and 0.61), but not at the

other two sites (PBCP, NERP). CO_2 concentration was not correlated with discharge at any site.

Spatial and temporal variability in dissolved organic carbon sources

The index of recent autochthonous inputs (BIX) was negatively correlated with discharge at all sites (p values = 1.2×10^{-6} to 2.0×10^{-3}, $r^2 = 0.14–0.43$), which suggests a shift from aquatic to terrestrial organic matter with increasing streamflow (Fig. 3b). The humification index (HIX) and SUVA$_{254}$ were not correlated with discharge at any site, however. BIX was also significantly different among sites, with the highest values at SLIGO and lowest median value at PBCP. Higher values of BIX (>1) are expected to be indicative of aquatic production, and low values (0.6–0.7) are expected to be indicative of terrestrial organic matter sources (Huguet et al. 2009). BIX values in this study mainly fell within the terrestrial range, with a minimum value of 0.52 and a maximum of 0.85 (Fig. 3b).

Continuous stream ecosystem metabolism

Daily metabolism rates were estimated for 466 days at SLIGO (between March, 2013 and October, 2014), 785 days at PBCP (between October, 2011 and October, 2014), and 953 days at NERP (between October, 2011 and October, 2014). Mean daily GPP estimates for the entire period at SLIGO, PBCP, and NERP were 0.49, 0.38, and 0.66 g C m^{-2} day^{-1}, respectively. Mean daily ER (negative sign convention) estimates were −0.76 (SLIGO), −0.73 (PBCP), and −0.88 g C m^{-2} day^{-1} (NERP). NEP was <0 for 75 % of measured days at SLIGO, 84 % of measured days at PBCP, and 71 % of measured days at NERP. Peaks in GPP were evident at all sites, resulting in periods of autotrophy (NEP > 0) during the spring and early summer (Fig. 2). Seasonal variability in GPP was primarily influenced by day length and light availability (Fig. 4). GPP was related to streamflow in a parabolic fashion, with the highest GPP rates corresponding with medium discharge conditions at each site (Fig. 5). There were short-term declines in GPP following storms including Hurricane Sandy, a major hydrologic event during the study period (Fig. 6); but day length and riparian shading availability appeared to be more important over longer seasonal and annual time scales (Fig. 4). The duration of springtime peaks in GPP were
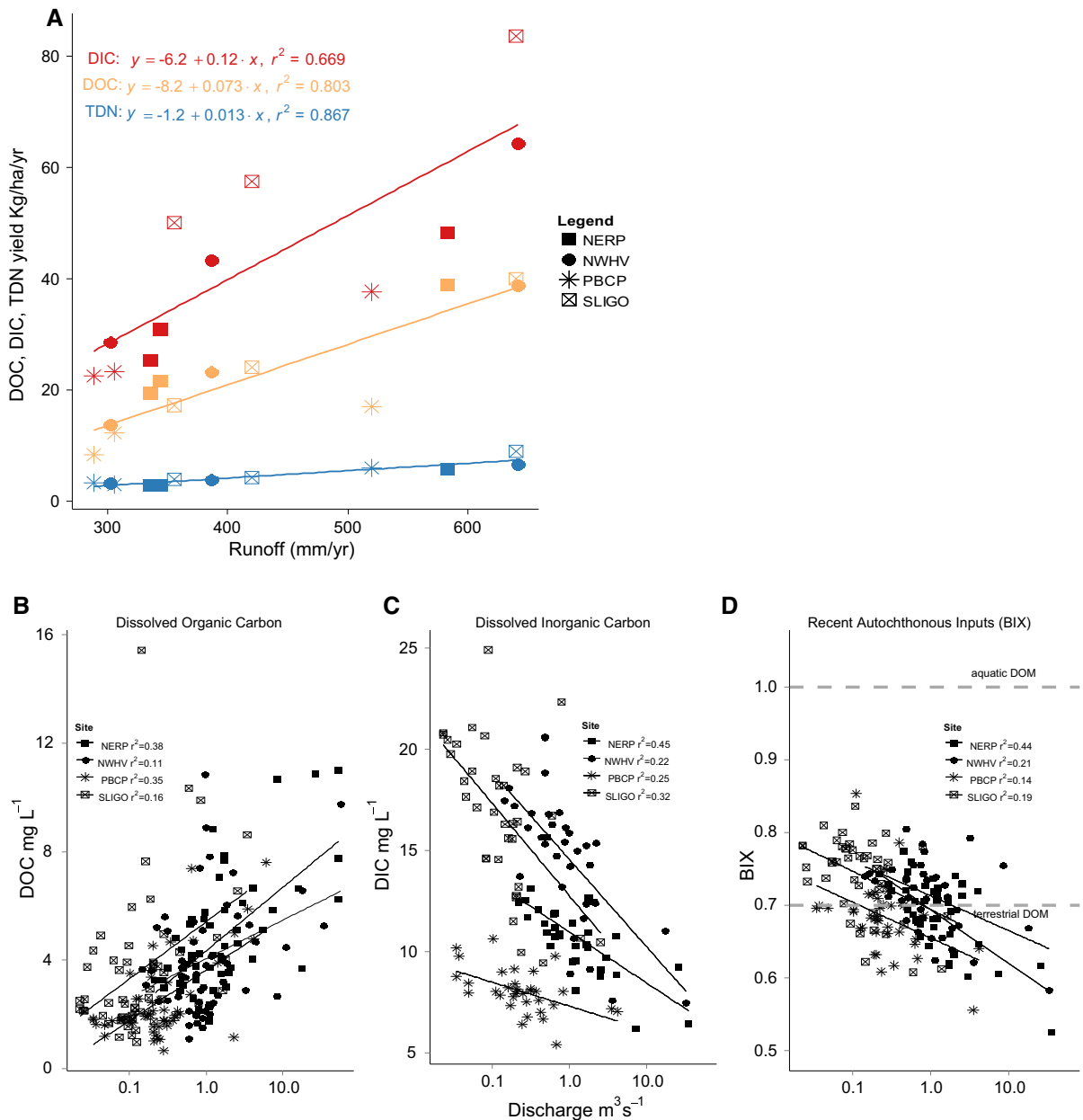
Fig. 3 Scatterplots showing relationships between **a** DOC and DIC export (kg ha^{-1} year^{-1}) vs. total annual runoff (p < 0.01 for all sites) and **b** mean daily discharge vs. DOC, DIC, and Index of Recent Autochthonous Inputs (BIX)

greatest in the stream with a large, open channel (NERP) and lower in the two more narrow streams, which had greater riparian vegetation cover (SLIGO and PBCP) (Fig. 3). ER was primarily influenced by seasonal variations in temperature and GPP (Fig. 7).

Daily GPP rates were positively correlated with TDN at two of the three sites (PBCP and SLIGO:

p < 0.001, r^2 = 0.37, n = 21; and p < 0.001, r^2 = 0.76, n = 9 respectively). ER was also positively correlated with TDN at SLIGO (p < 0.001, r^2 = 0.47, n = 9). DIC and DOC did not show significant relationships with GPP or ER for sampling dates with coinciding chemistry measurements and ecosystem metabolism (n = 19).

Fig. 4 Continuous Gross Primary Production vs. day length for three stream sites. *Orange* and *yellow* colors show data from smaller shaded stream sites (SLIGO, PBCP), and *purple lines* are from open-channel river site (NERP)
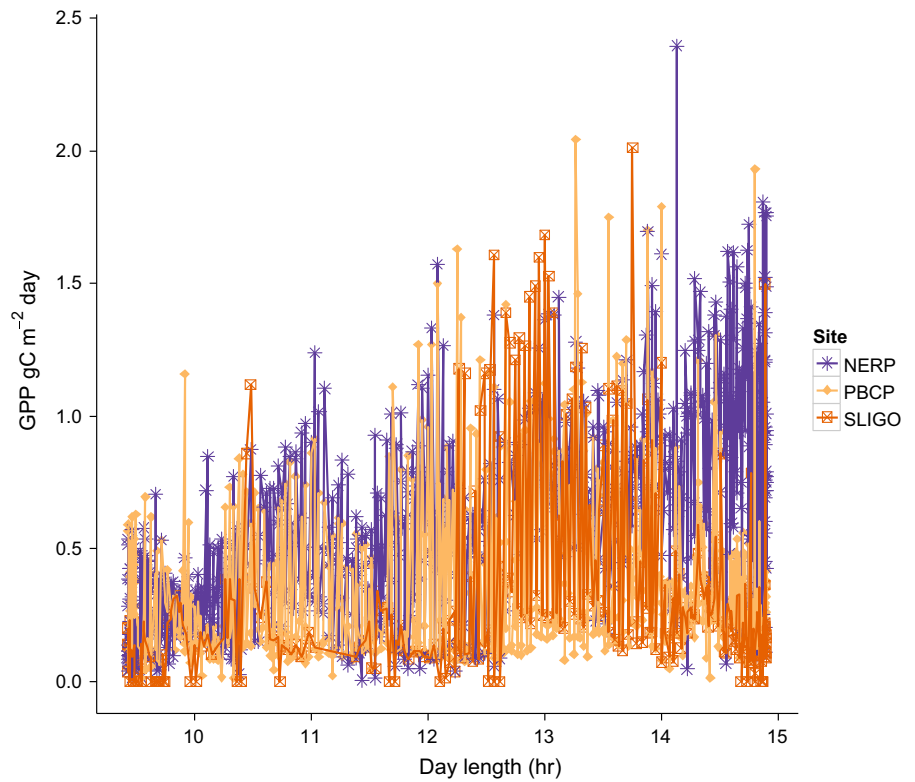

Fig. 5 Relationships between Gross Primary Production (GPP) and streamflow across four seasons at three sites. Sligo Creek and Paint Branch are small streams with significant riparian shading, and the Northeast Branch is a larger, channelized tributary of the Anacostia River

GPP before, during, after Hurricane Sandy at NERP
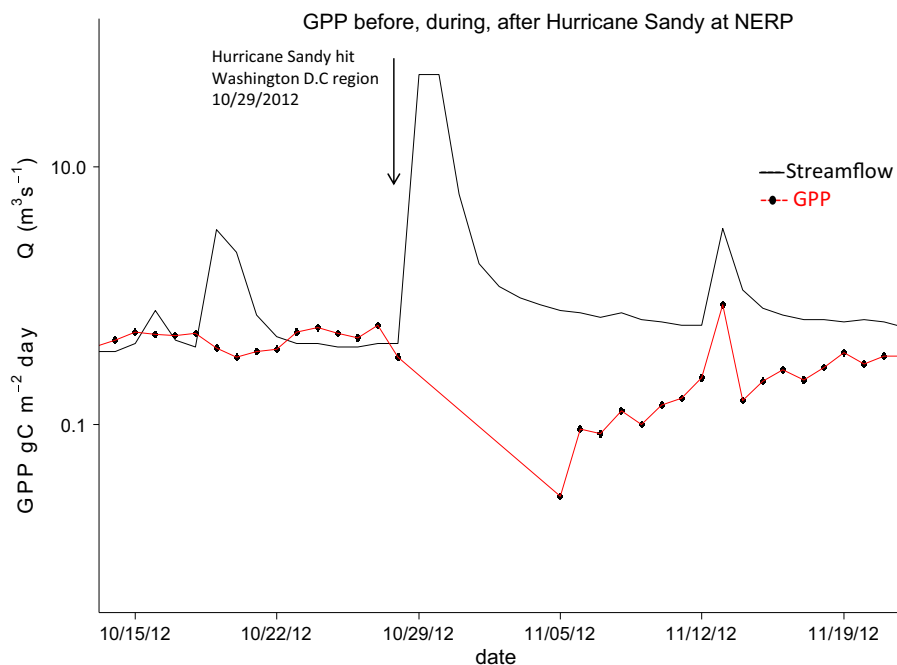
Gaseous and dissolved inorganic carbon fluxes

Using a simplified mass balance model of the stream/
watershed DIC budget, we separated DIC inputs to the
water column into two categories: 'net stream respi-
ration' and 'watershed sources' (Eq. 2). In this model,
we defined 'net stream respiration' as ER-GPP, or
-NEP. Net stream respiration accounted for less than
0 % of DIC inputs on days when NEP was positive,
and thus watershed inputs account for more than
100 % of total export (downstream DIC + CO_2
emissions). The percent contribution of total DIC
inputs from net stream respiration varied from -65 to
90 % across streams and dates, and the percent
contribution from watershed inputs also varied widely
(10 to 165 %). The mean percentage of inputs from net
stream respiration across PBCP, SLIGO, and NERP
were 13.4, 13.2, and 3.4 % respectively. Percent
inputs by net stream respiration had a significant
negative, log-linear relationship with streamflow at
both PBCP and SLIGO (r^2 = 0.22, 0.23; p values
<0.01) (Fig. 8). No such relationship existed at
NERP, and NEP was generally positive during low-
flow conditions at this site.

We also estimated the percent of inorganic C
outputs from gaseous (CO_2) and fluvial (DIC) fluxes
from the stream network. Daily fluxes were dominated

by fluvial DIC export which contributed between 93
and 102 % of total export on all dates. Fluvial export
exceeding 100 % signifies dates when NEP > 0. The
range of areal CO_2 fluxes was −2.67 to 25 g C m^{-2}
day^{-1} across sites and dates, where negative values
signifies uptake of CO_2 by the water column. These
fluxes comprised the remainder of total inorganic
carbon output (−2 to 7 %) from the stream network.

Discussion

Urban streams as transporters vs. transformers
of carbon across streamflow

The role of urban streams as biologically active
ecosystems vs. passive hydrologic transporters of
carbon and nutrients is an active source of investiga-
tion (Kaushal and Belt 2012). Urban streams have
historically been characterized hydrologically by their
flashy and frequent 'transporting' flow events (e.g.
Leopold 1968; Paul and Meyer 2001). However, a
growing body of work has shown that urban streams
are also dynamic biological systems which transform
watershed carbon and nutrient inputs (Newcomer et al.
2012, Duan et al. 2014; Kaushal et al. 2014b).
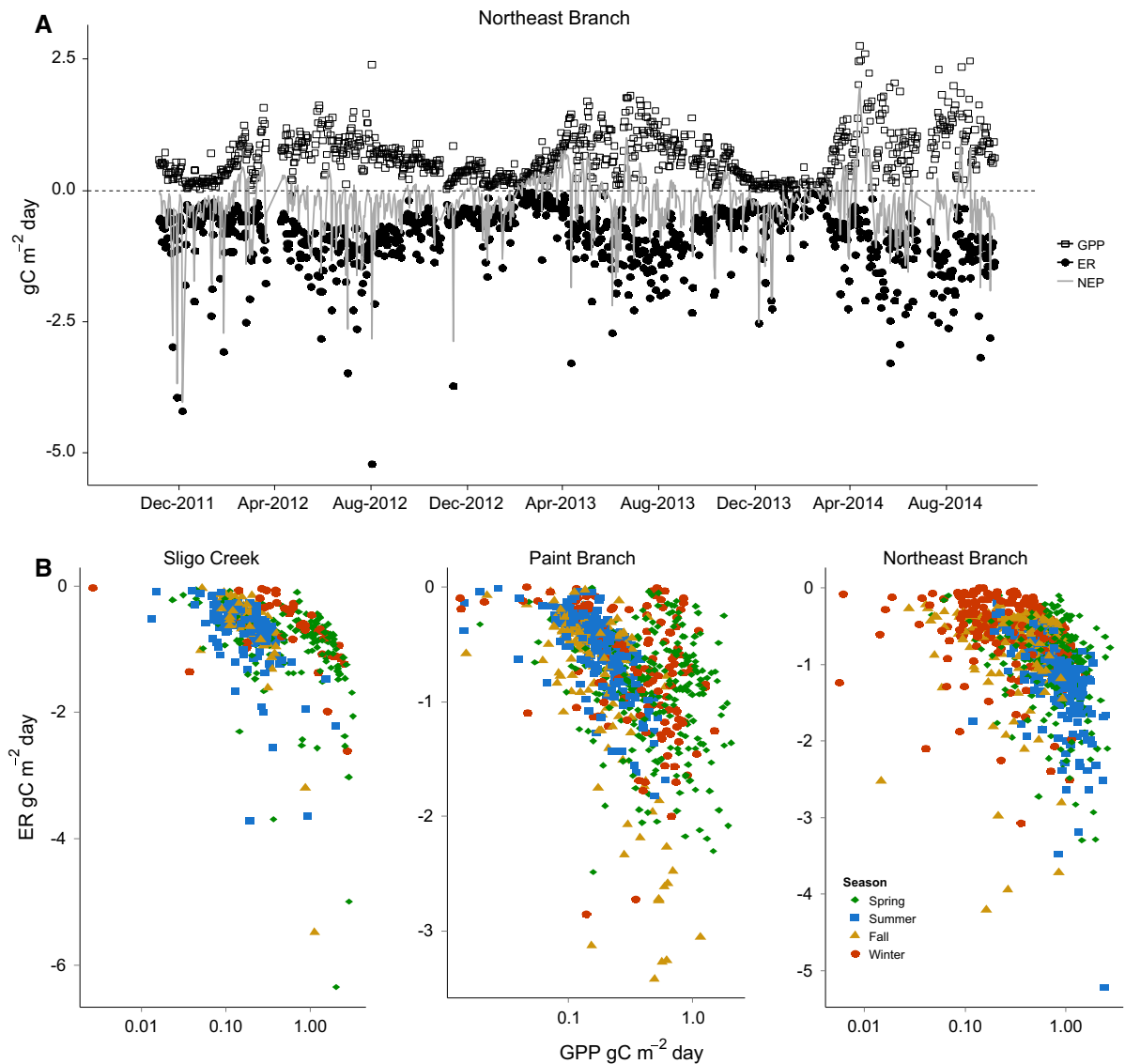Globally, river and stream ecosystems act as both

Fig. 7 **a** An example of time-series of gross primary production (GPP), ecosystem respiration (ER), and net ecosystem production (NEP) for the Northeast Branch. **b** GPP vs. ER for Sligo Creek, Paint Branch, and Northeast Branch in the Anacostia Watershed

transporters of terrestrial organic matter to coastal areas (Middelburg and Nieuwenhuize 1998), and bioreactors that transform organic matter into CO_2 along their hydrologic flowpaths (del Giorgio and Pace 2008). As population growth continues, the extent to which urban aquatic ecosystems transform terrestrial organic matter inputs has direct implications for global and regional carbon budgets (Cole et al. 2007; Aufdenkampe et al. 2011), as well as water quality and ecosystem processes (Stanley et al. 2012; Newcomer et al. 2012).

Streamflow variability was the primary driver of carbon transport from urban watersheds in this study. Light availability also influenced the timing of peaks in net ecosystem production (NEP) and net stream respiration (−NEP). Based on our empirical results, we developed a new streamflow-based conceptual. This conceptual model demonstrates the ways in which organic and inorganic carbon exports, sources, and metabolism can vary with streamflow across an urban watershed (Fig. 9). The model illustrates how the concentration of DOC increased and DIC decreased

Fig. 8 Daily estimates of terrestrial vs. in-stream DIC sources across variations in flow conditions. Source contributions are based on daily measurements of net respiration, CO_2 fluxes, and DIC load estimates. Three separate colors signify three different study sites across the Anacostia watershed
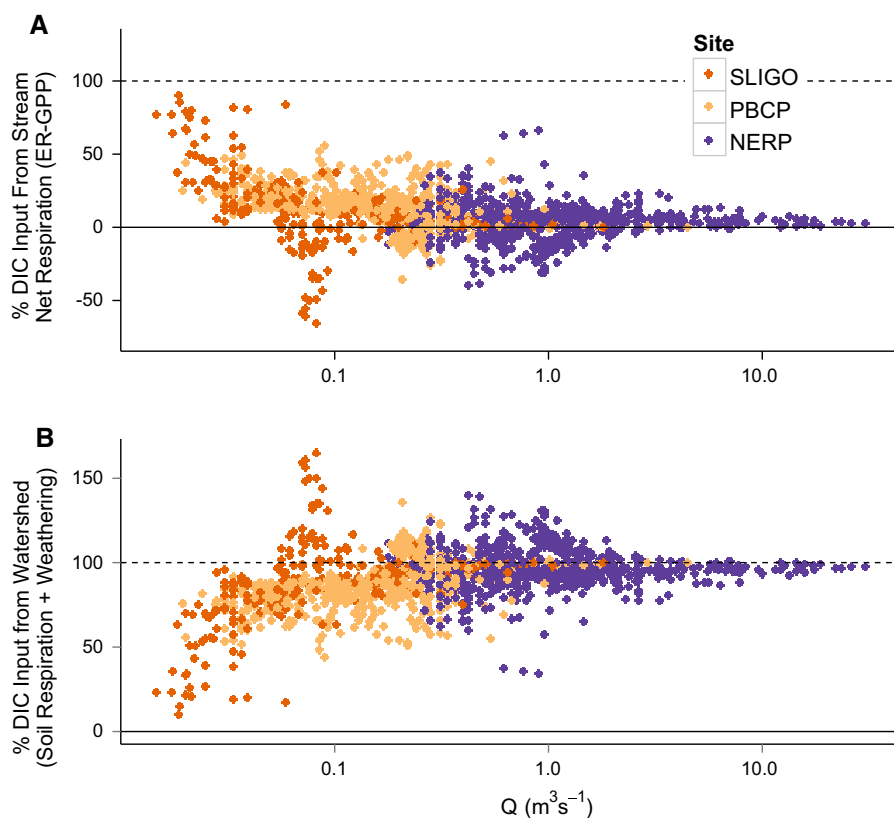
with increasing streamflow. The conceptual model demonstrates how dominant sources of DIC and DOC transition from in-stream to terrestrial sources at moderate to high flow conditions. Additionally, we show how GPP varies with season and streamflow as periods of high GPP (corresponding with positive NEP) occur during low to moderate streamflow conditions. GPP and ER were both at their lowest during high streamflow in all streams. In smaller streams with riparian canopies, GPP was also low during summer baseflow. Low streamflow conditions are driven in part by seasonal evapotranspiration by riparian trees and thus correspond with shading and reduced in-stream GPP (Fig. 9).

Urban streams as transporters: terrestrial inorganic carbon contributions

DIC was the dominant form of carbon exported in this study, which originated primarily from watershed sources (terrestrial weathering + soil respiration). Urbanization has been shown to influence terrestrial DIC loading to streams from both natural and

anthropogenic sources (Barnes and Raymond 2009; Lu et al. 2014). Natural sources include dissolved CO_2 from soil respiration and products of chemical weathering. Novel anthropogenic sources may include building materials and wastewater. In our study, the range in mean DIC concentrations (8, 10, 16 mg C L^{-2}) from streams draining predominantly silicate-based lithology (quartz-feldspar schist) of the Atlantic Piedmont is high compared to pristine streams draining non-carbonate lithology (Dicken et al. 2005; Meybeck 2003). Small portions of the Northeast Branch of the Anacostia watershed drain the Atlantic Coastal Plain, which may constitute additional DIC sources from carbonate deposits to downstream portions at the Northeast Branch site. Urbanization may also play a role in elevating DIC sources from the landscape through human-accelerated weathering of building materials and nonpoint sewage sources (Kaushal et al. 2013, 2014c). Several studies using carbon isotope tracers have shown correlations between urban land cover and DIC from bedrock (Zeng et al. 2010; Connor et al. 2014; Barnes
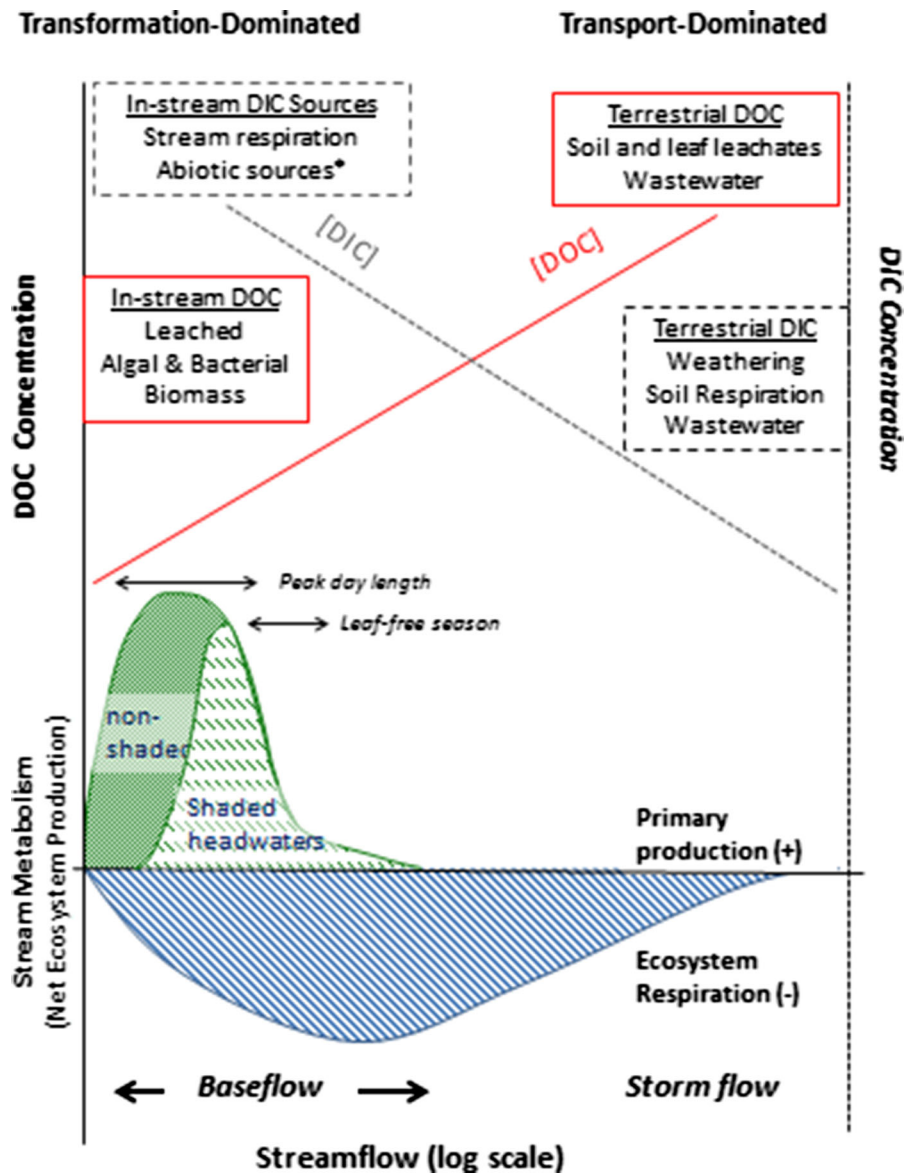
Fig. 9 Streamflow-based conceptual model of processes that mediate carbon transport and transformation in urban streams. Streamflow is on the x-axis, and the y-axis is shared between the *top*: DOC (*left*) and DIC (*right*) concentrations, and bottom: Stream metabolism (GPP and ER). As streamflow increases, [DOC] increases and [DIC] decreases. In-stream metabolism dominates DIC sources at baseflow, and may contribute significantly to DOC as well, as seen during peaks in GPP. The proportion of each (DOC and DIC) contributed from terrestrial sources (vs. in-stream) increases with streamflow. Peaks in GPP are more pronounced and occur during a wider range of flow conditions in larger non-shaded rivers. GPP in smaller streams peaks during seasonal periods of intermediate baseflow in early spring. We hypothesize that this is the case because leaf-out corresponds to riparian shading and baseflow drawdown. Carbon export processes measured in this study include dissolved and gaseous fluxes. Gaseous CO_2 export from the stream network (not pictured) was very low compared with fluvial DIC (mean = 0.33 %, SD = 0.28 %) with the majority of inorganic carbon export (including CO_2) leaving the watershed in dissolved form

and Raymond 2009; Lu et al. 2014; Hossler and Bauer 2013), which suggest that urbanization may mobilize of older, previously stable carbon reservoirs. For

instance, Lu et al. (2014) found that DIC in urban headwater streams of Virginia originated primarily from older bedrock weathering, compared to DIC in

forested watersheds (which represented more recent primary production). Numerous studies have also shown that wastewater treatment plants contribute to watershed DIC fluxes (e.g. Hossler and Bauer 2013). Our study and others show that DIC can be elevated in urban streams without WWTPs as well, however. Additionally, previous work has shown long-term increasing alkalinity trends in the Anacostia watershed and other nearby urban watersheds, where there are minimal natural carbonate sources suggesting the importance of anthropogenic DIC sources (Kaushal et al. 2013; Prasad et al. 2013).

Urban streams as transporters: terrestrial organic carbon contributions

Streamflow has a major influence on DOC concentrations and sources in both forested and urban watersheds (McDowell and Likens 1988; Yeakley and Hook 2005; Raymond and Saiers 2010; Stanley et al. 2012; Kaushal et al. 2014a). Forested streams often have positive concentration *vs.* discharge (C: Q) relationships as saturated soil and leaf leachates are delivered to the stream during precipitation events (Inamdar et al. 2013). We found positive C: Q relationships at our study streams as well as a decreased signal for 'recent autochthonous inputs index' (BIX) within increased flow. These patterns together suggest that terrestrial sources of DOC become more important with increasing streamflow, whereas in-stream organic matter may be more important at low streamflow. Impervious surfaces and storm drains may have an important role in delivery of terrestrial organic matter to urban streams. Yeakley and Hook (2005) found significantly higher DOC concentration in stormflow (median 3.5 mg C L^{-1}) vs. baseflow (median 2.0 mg C L^{-1}) in an urban stream in Portland, OR and estimated that 26 to 30 % of DOC during came from storm drains. Additionally, Hope et al. (2004) found significant DOC loading from paved surfaces in Arizona, following long periods of accumulation between rainfall events. In temperate watersheds, storm drains and gutters may be significant sources of organic matter (Kaushal and Belt 2012). Hobbie et al. (2013) found that this 'gutter subsidy' of leaf detritus contributes significantly to stormwater N and P loads in St. Paul, Minnesota. Our results show evidence to support a similar mechanism in the Anacostia River, warranting further study on the role of storm drains as flowpaths impacting terrestrial carbon export from urban watersheds.

The processes that increase vs. decrease DOC fluxes from wastewater, soil, and vegetation management vary across cities. Fluxes and sources also vary spatially within watersheds along the continuum of light availability between headwaters and large open channels (Vannote et al. 1980; Kaushal et al. 2014b), and over time with changing streamflow conditions (Daniel et al. 2001; Duan et al. 2014). Currently, few studies have estimated DOC exports over annual timescales in urban watersheds. DOC exports in our study varied from 8.4 to 40.1 kg C ha^{-1} $year^{-1}$, which is within the typical range estimated in temperate forests (i.e., 5–57 kg C ha $year^{-1}$) (e.g., McDowell and Likens 1988; Fahey et al. 2005; Raymond and Saiers 2010 (and citations within); Hossler and Bauer 2013). Conversely, Sickman et al. (2007) found significant increases in TOC (DOC + POC) export (10–121 kg C ha^{-1} $year^{-1}$) with urbanization in the Sacramento River watershed. Their study attributed 60 % of urban C export to WWTP effluents, which were absent from our study sites. Sickman et al. (2007) also attributed the remaining 40 % of urban C sources to leaching of older soils in urban areas. Similarly, Aitkenhead-Peterson et al. (2009) reported exceptionally high mean annual DOC concentrations (20 to 52 mg C L^{-1}) in urban streams with and without WWTP effluent in Texas, and attributed elevated DOC to soil leachates from irrigated turf grass. These studies suggest that urban soils contribute significantly to urban DOC loads, regardless of wastewater inputs. Compared with other urban watersheds, the relatively low annual DOC concentrations and exports that we report may be partially explained by the lack of WWTP outfalls.

Stream metabolism: shifts in urban streams from transporters to transformers

The relative contribution of in-stream vs. terrestrial or anthropogenic sources to organic carbon fluxes is highly variable across watersheds of differing biomes and urban land cover (Hopkinson et al. 1998; Tank et al. 2010). In temperate forested streams, terrestrial sources often dominate DOM export (Fisher and Likens 1973), while in-stream processes have been

shown to dominate DOM export in arid (Jones 1997) and grassland streams (Young and Huryn 1996). In the present study, indices of in-stream organic matter (BIX) decreased with streamflow, which suggests that terrestrial sources became more dominant more as streamflow increased. Our metabolism measurements show peaks of autotrophy during periods of seasonal light availability, suggesting that in-stream organic matter sources may be significant during low to moderate flow conditions. Nutrient enrichment and vegetation removal influence autotrophic productivity in urban streams (Taylor et al. 2004; Catford et al. 2007), and leached or decomposing algae may contribute to increased overall lability of the DOM pool. Duan et al. (2014) found this to be the case, as leached bacterial and algal-based carbon dominated the DOM pool of channelized urban streams in Texas. Even at high streamflow, Duan et al. (2014) found that channelized streams had reduced terrestrial organic matter loads due to the combination of increased autotrophic productivity and reduced hydrologic connectivity with floodplain soils and vegetation. Newcomer et al. (2012) also found significant differences in diatom biomarkers and C: N ratios of DOM between nutrient-enriched urban streams and a forested reference in Baltimore, Maryland. Similarly, Kaushal et al. (2014b) also found that export of protein-like DOM was correlated with increasing GPP. Empirical data from the present study and others suggest that in-stream productivity can contribute significantly to DOM export annually in urban streams with elevated nutrients and light availability.

One way to evaluate shifting contributions from in-stream vs. terrestrial organic matter sources is to compare DOC export to NEP. This comparison does not take into account time lags between primary production and biomass turnover, leaching, or biomass export in particulate form over annual timescales. However, it allows us to compare the magnitude of these two watershed carbon fluxes on a daily basis. Stream metabolism is defined as the capture of energy as GPP and release of heat by ER, which is commonly measured in units of dissolved oxygen production (GPP) and consumption (ER) in the water column (Odum 1956). Stream metabolism can also be evaluated in units of carbon uptake and production by assuming a constant ratio of O_2 consumption to CO_2 production during photosynthesis and aerobic respiration. By assuming that this ratio (respiratory

quotient, RQ) was 1, we compared the magnitude net CO_2 uptake from daily stream metabolism with DOC export across a range of streamflow conditions. Berggren et al. (2012) tested the RQ assumption by measuring side-by-side CO_2 and O_2 production and consumption in 52 lakes and showed that RQ varies from 0.5 to 2 on average (depending largely on the most abundant carbon substrate being mineralized). Here, we proceed with our RQ = 1 assumption with the caveat that this value is likely to vary in space and time. Additional assumptions used to scale NEP to the watershed-scale for comparison with DOC export are outlined in the 'Gaseous and Dissolved Fluxes' subset of the methods section. NEP rates in our streams varied from -4.4 to 1.0 g C m^2 day^{-1}, within the high and low end of metabolism rates reported in the literature by single-day (Acuña et al. 2004; Bernot et al. 2010) and continuous methods (Izagirre et al. 2008; Beaulieu et al. 2013). Out of 1557 daily NEP measurements across three streams, NEP was positive on 22 % of days and greater than daily DOC flux on 13 % of days when NEP was positive. On average, daily NEP was lower than DOC by a factor of 0.66 with a minimum of 14.7 times lower and 3.3 times higher than DOC. Despite potentially significant time lags between autotrophic productivity and leaching/DOC production, this comparison shows that productivity is near equal to DOC flux on a substantial portion of the year. Of the days when NEP > 0, NEP is only greater than DOC during low to moderate streamflow conditions. Given the inter-annual importance of autotrophy in these urban streams, there was considerable potential for stream ecosystems to function as transformers of carbon.

Urban streams as transformers: gross primary production across streamflow

Continuous sensor measurements allowed us to investigate environmental controls on stream metabolism across a variety of timescales and environmental conditions. These include storm events, seasonal light and temperature regimes, and varying carbon and nutrient loads. We found short-term decreases in GPP following major storms, similar to previous studies (Uehlinger 2006; Roberts and Mulholland 2007; Beaulieu et al. 2013). Storm events caused GPP to decrease by approximately half, with a two-to three-week recovery period (Fig. 6). These effects are seen in both urban/suburban settings (Beaulieu et al. 2013)

and non-urban streams (Acuña et al. 2004; Uehlinger 2006; Roberts and Mulholland 2007). Because urban areas tend to have greater flood frequency and intensity, it is possible that high streamflow events have a substantial effect on in-stream productivity (Beaulieu et al. 2013). One leading hypothesis explaining temporary decreases in GPP following storms is the scouring of in-stream benthic periphyton communities.

While storms influence GPP over shorter (weekly) timescales, other factors such as light availability appear to play a larger role across seasons. Light availability varied with stream size and adjacent vegetation, and these changes influenced the timing and magnitude of seasonal peaks in GPP and NEP. Across three streams of differing widths and shading in the Anacostia watershed, we found similar daily rates of GPP during the peak season. However, there were notable differences in the timing and duration of seasonal peaks in GPP between the two smaller, shaded streams (PBCP, SLIGO) and the larger non-shaded NERP. These variations contributed to overall differences in annual NEP for each stream (Fig. 4). While the importance of light availability for GPP is well established, the influence of riparian vegetation, stream size, and shading on annual GPP and NEP varies widely across stream reaches, watersheds, and biomes (Mulholland et al. 2001; Bernot et al. 2010). Our results highlight implications for the importance of spatial heterogeneity in riparian cover and stream order for influencing annual GPP rates, as well as potential management implications for reducing summer algal blooms by increased riparian shading.

Along with light availability, nutrients can also be a limiting factor for in-stream productivity in streams (e.g., Mulholland et al. 2001; Bernot et al. 2010). We found significant (p < 0.001) correlations between TDN concentrations and GPP at two sites (SLIGO, PBCP). These relationships suggest that nitrogen is limiting, compared to phosphate, which showed no relationship with GPP (data not shown). However, these relationships are based only on a small subset (9 and 21) of days when metabolism and bi-weekly chemistry data coincide. More work is required to experimentally evaluate potential N limitation in these streams. Several studies have shown that coupling between nutrient (N and P) cycles and metabolism is highly variable. For instance, linkages between nutrient availability and GPP have been reported where

large gradients in these variables exist as a result of: (1) large regional comparisons (Mulholland et al. 2001; Bernot et al. 2010), (2) sharp contrasts in land cover in small watersheds (Kaushal et al. 2014b), or (3) over very long (15-year) records of pollution reduction (Uehlinger 2006). Alternatively, several studies of nutrient uptake and ecosystem metabolism have shown tight coupling between these processes both in pristine (Hall and Tank 2003; Roberts and Mulholland 2007; Heffernan and Cohen 2010; Cohen et al. 2013) and nutrient enriched streams (Pennino et al. 2014; Beaulieu et al. 2014). This suggests that stream ecosystem metabolism influences nutrient fluxes to some degree as well, particularly in urban streams with increased light availability and elevated GPP (Kaushal et al. 2014b).

Urban streams as transformers: ecosystem respiration across streamflow

Stream metabolism in urbanized rivers can contribute significantly to increased DIC production and export (Martinelli et al. 1999; Daniel et al. 2001; Barnes and Raymond 2009; Andrade et al. 2011). Few studies have simultaneously evaluated variations in terrestrial and in-stream sources of DIC across variable stream-flow conditions. However, the longstanding assumption that terrestrial sources dominate DIC export merits testing in urban areas. A recent study by Hotchkiss et al. (2015) estimated that 28 % of CO_2 emissions from running waters in the U.S. are produced by stream metabolism, with the remainder from terrestrial or abiotic in-stream processes. In the present study, we found that on average, terrestrial sources of DIC (including CO_2) were greater than in-stream sources. Our results show that daily net respiration across three streams only contributed between 3.4 and 13 % of total daily DIC inputs on average. Variability around these mean values was great, however, and DIC inputs from stream metabolism were often nearly 50 % and approached 100 % during low and moderate streamflow (Fig. 8). Along with streamflow, variation in DIC production from net-respiration is also driven by temperature and organic matter substrate.

Although, we found significant relationships between ER and temperature, there was no relationship with DOC. This does not necessarily preclude a causal relationship between respiration and organic

carbon, given that the bulk of stream respiration may take place in benthic sediments with particulate organic carbon rather in the water column. Additionally, growing evidence from previous studies suggests that lability of organic matter may be a stronger driver of metabolic rates and pathways than bulk DOC loading (Ballester et al. 1999; Martinelli et al. 1999). For instance, Newcomer et al. (2012) found that labile algae and grass leachates had a stronger effect on denitrification than leaf leachates in urban streams of Baltimore, Maryland. Similarly, Kaushal et al. (2014b) reported correlations between lability of organic matter and ecosystem respiration in similar sites. Additionally, Ballester et al. (1999) found that sewage inputs shifted riverine conditions from aerobic to anaerobic in a Brazilian river. Labile organic carbon sources can include decomposing microbial or phytoplankton biomass, urban wastewater inputs, or photo-oxidation of complex organic matter (Moran and Zepp 1997 Jarvie et al. 1997, Martinelli et al. 1999; Zhang et al. 2009). These studies provide evidence that a small rapidly cycling fraction of the overall DOC pool may be the main source of organic carbon mineralized within streams (Mayorga et al. 2005; Hall and Beaulieu 2013; Hofmann et al. 2008; Van den Meersche et al. 2009).

While stream metabolism has been shown to contribute to DIC fluxes in several cases (Jones and Mulholland 1998; Acuña et al. 2004), our results demonstrate that the magnitude of metabolic contributions vary across streamflow conditions. By assuming that daily in-stream DIC production was synonymous with net respiration (ER-GPP, or NEP*−1), we found that in-stream DIC contributed significantly to total inorganic carbon exports during low baseflow conditions. GPP and ER are tightly coupled across all sites throughout the year, which suggests that much of ER is attributable to autotrophic respiration and/or mineralization of recently produced algal biomass (Hall and Beaulieu 2013). We observed negative NEP on the majority of days in our study, signifying heterotrophic conditions. By converting metabolism measurements to units of CO_2 uptake and production, we equated heterotrophic conditions with DIC production. While autotrophic respiration makes up a significant portion of ER, continuously heterotrophic conditions such as those measured in our streams require outside inputs of organic matter. Microbial mineralization of terrestrial organic carbon

inputs is especially apparent when ER exceeds GPP (negative NEP), given that autotrophic respiration cannot exceed GPP. Heterotrophic conditions are common in shaded forest streams, where GPP is light-limited and terrestrial inputs are high. However, many open-canopied streams are autotrophic due to high light availability and lower terrestrial inputs (Bernot et al. 2010; Demars et al. 2011). Urban watersheds, such as the Anacostia have a mixture of shaded and open channels, and this drives spatial and temporal variability in NEP. One common pattern found in forested streams is an autumnal spike in ER, driven by pulses of labile carbon from fallen leaves (Mulholland et al. 2001; Stelzer et al. 2003). Despite the prevalence of terrestrial organic matter, we did not find a clear pulse of ER or a seasonal drop in NEP during the fall. This pulse of ER was also absent in agricultural streams measured by Griffiths et al. (2013), and suburban streams measured by Beaulieu et al. (2013). In the former, the lack of riparian trees may reduce autumnal leaf litter inputs. In the latter, the authors suggest that scouring of banks during frequent storms reduced the availability of in-channel storage of labile organic C from riparian trees.

Conclusions

Urban and agricultural land use has contributed to significant increases in DOC, DIC, and CO_2 export by streams and rivers globally (Raymond and Cole 2003; Barnes and Raymond 2009; Zhang et al. 2009; Andrade et al. 2010; Bianchi et al. 2013; Kaushal et al. 2013, 2014a). As urbanization increases globally, it is critical to understand the factors that influence transformations and transport of carbon in nutrient-enriched streams and rivers. In the present study, we found that transport and transformation are both significant processes that influence the carbon cycle in urban streams. We documented the importance of streamflow variability on exports, sources, and metabolism of carbon over annual periods. DIC was the predominant form of carbon transported from these urban watersheds. There were major shifts between carbon transport and transformation and net ecosystem carbon production across variable streamflow conditions, which can impact river alkalinization and biological oxygen demand in downstream receiving waters. Future work is necessary to test hypotheses

regarding transport and transformation of carbon across hydrologic variability in order to better understand and manage stream ecosystem functions such as denitrification and primary production and water quality issues related to river alkalinization and oxygen demand.

Compliances with ethical standards

Conflict of interest The authors do not claim any conflicts of interest.

Ethical approval The present study was conducted without the involvement of human participants and/or animals. The following is a summary of all funding sources that contributed to this project. We do not claim any potential conflicts of interest.

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