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Spatial variability in nutrient concentration and biofilm nutrient limitation in an urban watershed

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Abstract Nutrient enrichment threatens river ecosystem health in urban watersheds, but the influence of urbanization on spatial variation in nutrient concentrations and nutrient limitation of biofilm activity are infrequently measured simultaneously. In summer 2009, we used synoptic sampling to measure spatial patterns of nitrate (NO_3^-), ammonium (NH_4^+), and soluble reactive phosphorus (SRP) concentration, flux, and instantaneous yield throughout the Bronx River watershed within New York City and adjacent suburbs. We also quantified biofilm response to addition of NO_3^-, phosphate (PO_4^{3-}), and $NO_3^- + PO_4^{3-}$ on organic and inorganic surfaces in the river mainstem and tributaries. Longitudinal variation in NO_3^- was low and related to impervious surface cover across sub-watersheds, but spatial variation in NH_4^+ and SRP was higher and unrelated to sub-watershed land-use. Biofilm respiration on organic surfaces was frequently limited by PO_4^{3-} or $NO_3^- + PO_4^{3-}$, while primary production on organic and inorganic surfaces was nutrient-limited at just one site. Infrequent NO_3^- limitation and low spatial variability of NO_3^- throughout the watershed suggested saturation of biological N demand. For P, both higher biological demand and point-sources contributed to greater spatial variability. Finally, a comparison of our data to synoptic studies of forested, temperate watersheds showed lower spatial variation of N and P in urban watersheds. Reduced spatial variation in nutrients as a result of biological saturation may represent an overlooked effect of urbanization on watershed ecology, and may influence urban stream biota and downstream environments.

Keywords Nitrogen · Phosphorus · Stream · Biofilm · Synoptic sampling

Introduction

The addition of anthropogenically-derived nutrients such as nitrogen (N) and phosphorus (P) to the environment threatens the water quality and ecosystem function of rivers and estuaries worldwide (Carpenter et al. 1998; Vitousek et al. 1997). Streams influenced by agricultural and urban watershed land use can have particularly high nutrient concentrations (Mulholland et al. 2008; Paul and Meyer 2001). Although lotic ecosystems have the potential for high rates of biological nutrient uptake (Alexander et al.

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2007), the capacity of stream biota to absorb excess nutrients can be exceeded at the highest concentrations (Bernot et al. 2006; Newbold et al. 2006). Saturation of uptake by stream biofilms increases the likelihood that excess nutrients will be transported downstream to estuarine ecosystems, where nutrient enrichment can cause nuisance algal blooms, changes in algal community composition, hypoxia, and impact fisheries (Kennish 2002). Quantifying factors which control the ability of stream biota to remove nutrients, especially in nutrient-enriched ecosystems such as urban streams, is of major interest for managing the health of riverine and coastal environments.

Multiple interacting environmental drivers control river nutrient concentrations including uptake by aquatic biofilms (Arango et al. 2008), terrestrial vegetation (Bormann and Likens 1979; Roberts et al. 2007), wetlands (Likens and Buso 2006), and hyporheic processes (Valett et al. 1997). In contrast to relatively pristine watersheds, land use patterns in urbanized catchments also contribute to spatial variability of nutrient concentrations from point-source (e.g., waste water effluent) and non-point source (e.g., lawn fertilizer, impervious surface runoff) inputs of anthropogenic solutes (Martí et al. 2004; Paul and Meyer 2001; Zambrano et al. 2009).

As physio-chemical descriptors of water quality (i.e., ecosystem structure), nutrient concentrations do not always indicate biological *activity* (i.e., ecosystem funtion; Lake et al. 2007). Similarly, water quality categories based on “high to low” nutrient concentrations are useful for classifying ecosystem trophic status (Dodds 2006), but they do not measure the ability of stream biofilms (i.e., bacteria, fungi, and algae in an extracellular mucilaginous matrix) to remove nutrients from the water column. For example, stream biofilms can transform biologically reactive nutrients into inert compounds (e.g., denitrification), or incorporate nutrients into biomass and stream food webs (Hall et al. 2000; Mulholland et al. 2008), and either pathway can attenuate downstream nutrient delivery. Understanding how nutrient concentrations influence the ability of biota to remove nutrients from the water column requires measuring the activity of biofilms under ambient and experimentally-enriched conditions (Scrimgeour and Chambers 2000; Tank and Dodds 2003; von Schiller et al. 2007). Manipulation of nutrients available for biofilm growth under in situ conditions at multiple locations in a single watershed could help identify where (i.e., river tributaries or mainstem) and under what conditions (i.e., open or closed canopy) biofilms can most effectively process nutrients at high concentrations.

This research was designed to address the following questions: (1) What is the magnitude of the spatial variation in nutrient concentrations and flux in an urban watershed? (2) How do land-use patterns drive spatial variation in nutrient concentrations throughout an urban watershed? and (3) How does biofilm nutrient limitation vary across multiple sites in an urban watershed? We predicted that urban land-use intensity would increase both the magnitude and spatial variation of nutrient concentrations. We also predicted that biofilm nutrient limitation should decline at locations with high concentrations, and the magnitude of biofilm response to enrichment would decrease with increased metrics of urbanization such as watershed impervious surface cover.

Methods

Study site

The Bronx River watershed is approximately 144 km^2, and flows south from suburban Westchester County (Valhalla, NY) through the Bronx in New York City (NYC) before draining into the East River (a tidal straight; Fig. 1). One major tributary, Grassy Sprain Brook, contributed approximately 25% of total river discharge during the period of our study, and there are about 12 smaller tributaries. Much of the riparian zone is parkland, including the New York Botanical Gardens, the Bronx Zoo and Bronx Park (each in NYC), and the 15.4 km Bronx River Pathway (Westchester County). However, parkland makes up a small portion of the watershed and impervious surface cover (ISC) represents 13–39% of the subwatersheds (Table 1). European colonization started in the 1600s (Sanderson 2009), and the river has a legacy of industrial pollution and urbanization from the 1800s to the present. Because of low dissolved oxygen and presence of pathogens, NY has listed the Bronx River as impaired under section 303(d) of the Clean Water Act (New York State Department of Environmental Conservation 2008).

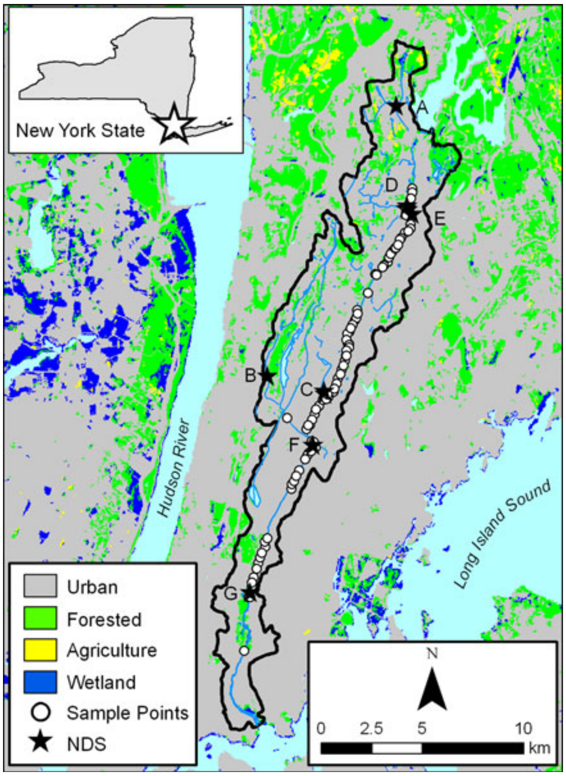


Fig. 1 The Bronx River watershed is located in the Bronx, New York City, and adjacent Westchester County, NY, USA. Synoptic sampling sites are indicated by circles. *Stars* indicate nutrient diffusing substrata (NDS) sites. *A* Davis Brook, *B* Sprain Brook, *C* Troublesome Brook, *D* Manhattan Park Brook, *E* Upper Bronx River, *F* Middle Bronx River, and *G* Lower Bronx River

Synoptic sampling

Synoptic sampling was conducted from August 24–26, 2009. We started at the approximate tidal maximum at 180th St., Bronx, NYC (~4 river km from the East River), and took samples sequentially from downstream to upstream, ending north of White Plains, NY (~33 river km from the East River). Tides have minimal influence on discharge upstream of this site due a 4 m tall spillway south of the Bronx Zoo and just downstream of our most downstream sampling site. Sampling sites were selected at approximately 150 m intervals. However, longer distances between sites occurred at three inaccessible sections where the Bronx River Expressway and MetroNorth Railway flank the river (Fig. 2). Therefore, the average distance between sampling locations was 332 m. At each sampling site in the Bronx River mainstem, we recorded location (Garmin GPSMAP 60Cx, Garmin AT, Salem, OR, USA) and took a 125 ml water sample from the stream thalweg ($n = 85$ sample sites). At the confluence of each tributary with the Bronx River mainstem, three replicate samples of tributary water were collected. Acid-washed HDPE Nalgene bottles were rinsed with filtered stream water three times, and then water was passed through glass fiber filters with 0.7 μm nominal pore size (Whatman GF/F, Whatman, Inc. Piscataway, NJ, USA), and frozen until solute analyses in the laboratory.

We directly measured discharge (Q) at 19 of the 85 sampling locations along the Bronx River mainstem and in each tributary. We placed a meter tape across the width of the stream and recorded depth and water velocity (Marsh McBirney Flo-Mate, Hach Company, Loveland, Colorado, USA) at 10 cm to 1 m intervals, depending upon stream width. Water velocity was measured at a depth of 1/3 of the way from the water surface to the benthos. Discharge was interpolated for sites between locations where Q was directly measured. To do this, we calculated the change in Q m^{-1} between two sites, subtracted for any tributary input, and assumed a constant change in Q m^{-1}.

Bronx River discharge is recorded hourly by a USGS gauging station at the New York Botanical Gardens (USGS Gauge number 01302020). Discharge at the gauging station declined from 2.350 to 1.812 m^3 s^{-1} over the course of the synoptic sampling period as it was in decline from a rain event on August 21 (peak discharge on August 22 of 7.53 m^3 s^{-1}). The declining discharge may have increased solute concentrations as water volume declined in the later portion of the sampling (upstream) if point sources are significant in the watershed. However, the influence of the falling discharge is likely minimal because (1) we did not see a gradual declining trend moving upstream for N or P concentrations (Fig. 2), and (2) the solute concentrations measured during synoptic sampling were consistent with those taken throughout the approximately 2 week incubation period for nutrient limitation measurements (see below).

Nutrient limitation

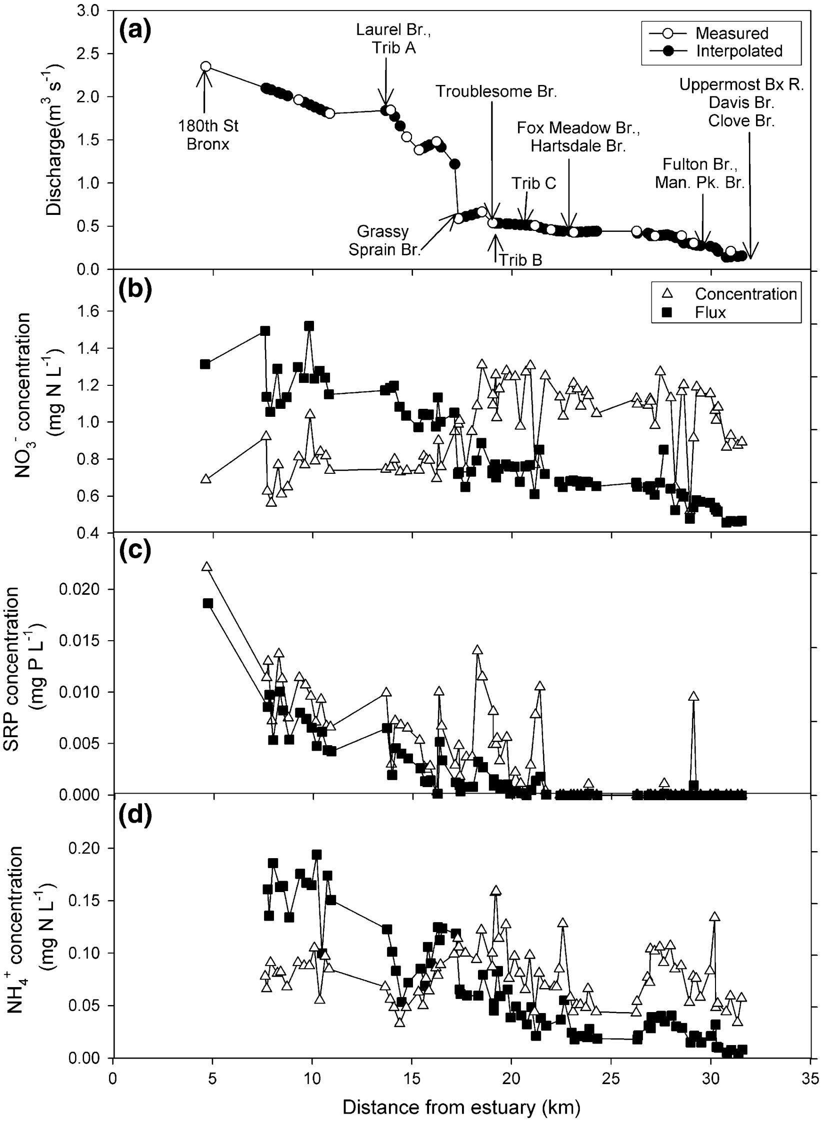
We measured biofilm nutrient limitation using the nutrient diffusing substrata (NDS) technique (Tank et al. 2006). NDS were made of 30 ml plastic cups filled with nutrient-infused agar and capped with

Table 1 Mean (±SD) of physiochemical parameters, nutrient diffusing substrata (NDS) incubation dates, and land-use coverage for the seven study sites in the Bronx River watershed

	Tributaries				River mainstem		
	Davis Brook	Sprain Brook	Troublesome Brook	Manhattan Park Brook	Upper Bronx	Middle Bronx	Lower Bronx
Physiochemical							
Watershed area (km^2)	5.6	4.4	3.7	6.2	50.2	96.5	116.2
Q (m^3 s^{-1})	0.034 (0.006)	0.043 (0.007)	0.045 (0.005)	0.071 (0.009)	0.265 (0.052)	0.975 (0.111)	1.961 (0.162)
Width (m)	2.2 (0.1)	3.4 (0.1)	4.2 (0.2)	4.5 (0.3)	5.9 (0.5)	13.3 (0.7)	14.0 (4.0)
Depth (cm)	7.4 (0.7)	14.1 (0.7)	4.1 (0.3)	15.6 (1.1)	17.3 (1.1)	12.7 (0.8)	13.3 (0.7)
Temperature (°C)	18.7 (0.4)	20.7 (0.6)	23.8 (0.5)	19.8 (0.7)	22.6 (1.5)	22.8 (0.6)	21.8 (0.1)
Canopy cover (%)	78.9 (2.9)	73.7 (5.1)	70.7 (4.7)	47.6 (2.9)	63.0 (13.3)	57.2 (10.2)	31.1 (7.7)
NO_3^- (μg N l^{-1})	967 (81)	704 (31)	886 (58)	1261 (15)	895 (84)	797 (39)	988 (29)
SRP (μg P l^{-1})	<1 (<1)	45 (9)	26 (5)	4 (<1)	15 (12)	6 (2)	17 (1)
NH_4^+ (μg N l^{-1})	85 (27)	94 (10)	51 (26)	41 (5)	45 (14)	97 (39)	94 (10)
Conductivity (μS cm^{-1})	637 (108)	808 (301)	562 (21)	1040 (33)	769 (57)	818 (112)	738 (48)
DO (mg l^{-1})	7.26 (0.38)	7.34 (0.14)	7.22 (0.23)	8.77 (0.23)	7.50 (0.33)	8.30 (0.82)	5.86 (0.35)
DO (%)	79.8 (5.4)	81.3 (1.7)	84.3 (3.5)	92.2 (2.8)	84.3 (3.0)	98.3 (10.1)	66.7 (4.6)
NDS							
Incubation dates ('09)	17 Jul–6 Aug	10 Aug–22 Aug	10 Aug–22 Aug	17 Jul–6 Aug	10 Aug–22 Aug	17 Jul–6 Aug	10 Aug–22 Aug
NDS depth (cm)	8.5 (0.8)	15.4 (1.8)	8.8 (0.5)	31.0 (1.5)	19.9 (1.2)	31.1 (1.7)	42.6 (1.3)
Land-use (%)							
Impervious surface	16.7	12.7	38.3	27.1	19.8	24.7	28.2
Urban	77.8	69.9	97.3	87.2	72.5	83.4	84.7
Forest	21.9	25.3	1.7	12.5	22.8	14.1	12.9
Agriculture	0.2	4.3	0.0	0.3	3.2	1.0	0.9
Wetlands + open water	0.0	0.5	0.9	0.0	1.4	1.4	1.5

Q, discharge; NO_3^-, nitrate; SRP, soluble reactive phosphorus; NH_4^+, ammonium; DO, dissolved oxygen

Fig. 2 Longitudinal patterns in (**a**) discharge, (**b**) nitrate (NO_3^-) concentration and flux, (**c**) soluble reactive phosphorus (SRP) concentration and flux, and (**d**) ammonium (NH_4^+) concentration and flux



fritted glass or cellulose sponge to mimic inorganic and organic surfaces, respectively (Hoellein et al. 2010; Johnson et al. 2009). Nutrients diffuse out of the agar directly into the biofilm that colonizes the substratum surface. Agar in the NDS was enriched with 1 of 4 treatments: nitrate (0.5 M $NaNO_3$), phosphate (0.25 M KH_2PO_4), $NO_3^- + PO_4^{3-}$, or none (control). Phosphate enrichment was lower than N to avoid P inhibition of biofilm growth at 0.5 M, which several studies have recorded (Hoellein et al. 2010; Johnson et al. 2009; Tank and Dodds 2003).

NDS were deployed at three sites in the river mainstem and in four tributaries, representing a gradient of stream nutrient concentrations across the seven sites (Table 1). At each site, we used five replicates of each treatment and substratum ($N = 40$ NDS $site^{-1}$). NDS were attached to a cinderblock and left on the stream benthos for 12–18 days. At the start, middle, and end of the NDS incubation periods we recorded NDS depth, conductivity, dissolved oxygen (DO), temperature, and we took three replicate water samples at each site to measure water column NO_3^-, SRP, and NH_4^+. We measured NDS depth as the mean distance from the water surface to the substrata at four corners and the center. Canopy cover was measured using a spherical densiometer (Forestry Suppliers, Inc. Model A, Jackson MI, USA) in four cardinal directions at each NDS incubation site. Following the incubation period, NDS were collected in 50 ml centrifuge tubes filled with stream water and transported on ice to the laboratory to measure biofilm metabolism.

We measured community respiration (CR) and net primary production (NPP) using the light/dark method (Bott 1996; Johnson et al. 2009). Each centrifuge tube was filled with unfiltered stream water collected at each NDS site and with known DO concentration. We used care to ensure no air bubbles were present in the tubes, and then placed them in an environmental chamber. For all incubations we used three control tubes which contained only site water to account for changes in DO not attributed to NDS biofilms. Conditions in the chamber were constant temperature of 22°C and constant photosynthetically active radiation of 275 μmol m^{-2} s^{-1}. After 2–4 h in the light, we recorded the final DO and time, refilled the tubes with fresh stream water, and left the tubes in the dark for 2–4 h. In many cases, some of the cellulose sponge had decomposed during deployment. We measured the remaining cellulose surface area, by photographing each disk on laminated paper with a 1 cm^2 grid. The area remaining was quantified by counting the portion of sponge filling each 1 cm^2 on a computer screen.

We calculated NPP and CR as change in oxygen per substratum area per time in the light (NPP) and dark (CR), and gross primary production (GPP) as NPP = GPP − CR. Our goal was to document the functional ecosystem response rather than the community response, so we did not measure chlorophyll *a* or identify biofilm taxa. As with many other NDS studies, we did not document how any potential changes in community composition alter ecosystem function. We consider biofilms the primary mechanism for biological nutrient uptake in this river. Although macrophytes and phytoplankton can affect nutrient uptake and release, they were abundant only at impounded sections of the Bronx river. We observed no differences in NO_3^-, SRP, or NH_4^+ concentrations upstream vs downstream of dams, implying a limited role in whole-system nutrient cycling.

Nutrient analyses

We used standard spectrophotometric assays to measure NO_3^- (cadmium reduction; APHA 1998), SRP (antimonyl tartrate; Murphy and Riley 1962), and NH_4^+ (phenol hypochlorite; Solorzano 1969) using an AQ2+ discrete autoanalyzer (Seal Analytical Inc., Mequon, WI, USA). Nutrient concentrations were scaled to nutrient fluxes (mg s^{-1}) by multiplying concentration and discharge, and we calculated instantaneous yield (mg km^{-2} s^{-1}) for each sub-watershed as flux divided by sub-watershed area.

Land use

We imported geographic coordinates of each synoptic sample point into ArcGIS 9.2 (Environmental Systems Research Institute, Redlands, California). We manually digitized the watershed boundary corresponding to each sample point by interpreting 1:250,000 scale 10-m USGS digital elevation models and/or the contours found on 1:24,000 USGS digital raster graphics. After digitizing watershed boundaries, we extracted the corresponding land cover data from the National Land Cover Database (reclassed Landsat Thematic Mapper imagery centered on 2001; Homer et al. 2004). There was nearly a 10-year time lag between the collection of the land cover data and our study, but the watershed has been urbanized for many decades, so there was likely minimal conversion from agricultural or forested to urban land use.

Data analysis

Simple linear regression was used to compare instantaneous yield with percent cover of impervious surface, forest, agriculture, and wetlands in each of the tributary watersheds. Nutrient yield and impervious surface cover were normally distributed, while nutrient concentration, flux, and other land-use categories were log-transformed. We used an ANOVA with two factors, the presence of N or P, to test for nutrient limitation (after Tank and Dodds 2003). To meet ANOVA assumptions, data were log-transformed for normality if needed. Using Tank and Dodds (2003) protocol for NDS analyses, N or P limitation was indicated when NO_3^- or PO_4^{3-} alone increased GPP or CR without a significant interaction term. We recorded co-limitation when N and P independently affected the response variable, or when N + P together significantly increased GPP or CR. We calculated the nutrient response ratio (NRR) as (treatment/control) for each treatment and site, and used linear regression of physiochemical parameters and land-use with the NRR for GPP and CR on both substrata in all streams ($n = 14$; Johnson et al. 2009).

Results

Synoptic sampling

Discharge in the Bronx River mainstem ranged between 0.157 $m^3\ s^{-1}$ at the upstream sampling point to 2.350 $m^3\ s^{-1}$ at the downstream sampling point (Fig. 2a). The greatest increase in discharge was at the confluence with Grassy Sprain Brook (Fig. 2a). Longitudinal patterns of NO_3^-, SRP, and NH_4^+ concentrations differed (Fig. 2b–d). Nitrate concentrations indicated enriched conditions: mean (±SD) $NO_3^- = 0.992$ (±0.247) mg N l^{-1}, however, the coefficient of variation (CV) along the entire river was relatively low at 24.9%. Enriched conditions were also suggested by the mean NH_4^+ concentration of 0.079 (±0.027) mg N l^{-1} (CV = 33.7%; Fig. 2d). In contrast, SRP concentrations indicated oligotrophic conditions: mean (±SD) SRP = 0.004 (±0.005) mg P l^{-1}, and the CV was higher than for either N species at 121.6%. NO_3^- concentration was generally lower downstream of the Grassy Sprain Brook confluence (Fig. 2b). In contrast, SRP concentrations increased with distance downstream (Fig. 2c), and NH_4^+ concentration did not exhibit a clear longitudinal pattern (Fig. 2d). Flux increased with distance downstream for all nutrients.

Variation in NO_3^-–N instantaneous yield among subwatersheds was explained by ISC ($r^2 = 0.503$, $p = 0.015$; Fig. 3a) and coverage of high intensity development ($r^2 = 0.589$, $p = 0.001$; data not shown). NO_3^- flux was unrelated to any land-use category, and NO_3^- concentration was related only to urban land-use ($r^2 = 0.402$, $p = 0.035$; data not shown). Variation in SRP yield was not explained by ISC, and one tributary, Grassy Sprain Brook, had much higher P yield than the other subwatersheds (Fig. 3b). Yield of NH_4^+–N was also unrelated to ISC but exhibited no geographic trend (Fig. 3c). Concentration and flux of SRP and NH_4^+ were not related to any other land-use types.

Nutrient limitation of biofilms on organic and inorganic substrata

Biofilm metabolism on inorganic and organic substrata was net heterotrophic for ecosystem production across all sites and treatments, with the exception of biofilms on fritted glass at the Upper Bronx River site (Figs. 4, 5). The magnitude of GPP and the GPP/CR ratio was always higher for fritted glass than for cellulose, indicating greater presence of autotrophic biofilms on glass despite net heterotrophy. For both substrata, biofilm nutrient limitation of GPP occurred at just one site (Manhattan Park Brook), however, respiration was nutrient limited at multiple sites (Figs. 4, 5). For fritted glass biofilms, respiration was N limited at the Middle Bronx River, N + P limited in Manhattan Park Brook, P limited in Davis Brook (Fig. 4), and not nutrient limited elsewhere. On cellulose sponge, respiration was P limited at three sites (Manhattan Park Brook, Middle Bronx River, and Lower Bronx River), and N + P limited at two sites (Davis Brook and the Upper Bronx River; Fig. 5).

The magnitude of the biofilm response to nutrient enrichment (nutrient response ratio; NRR) was

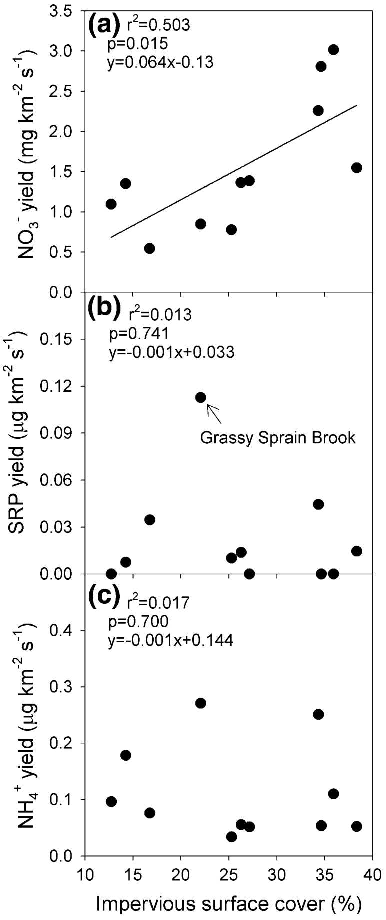


Fig. 3 Impervious surface cover in Bronx River subwatersheds versus instantaneous yield of (**a**) nitrate (NO_3^-–N), (**b**) soluble reactive phosphorus (SRP), and (**c**) ammonium (NH_4^+–N)

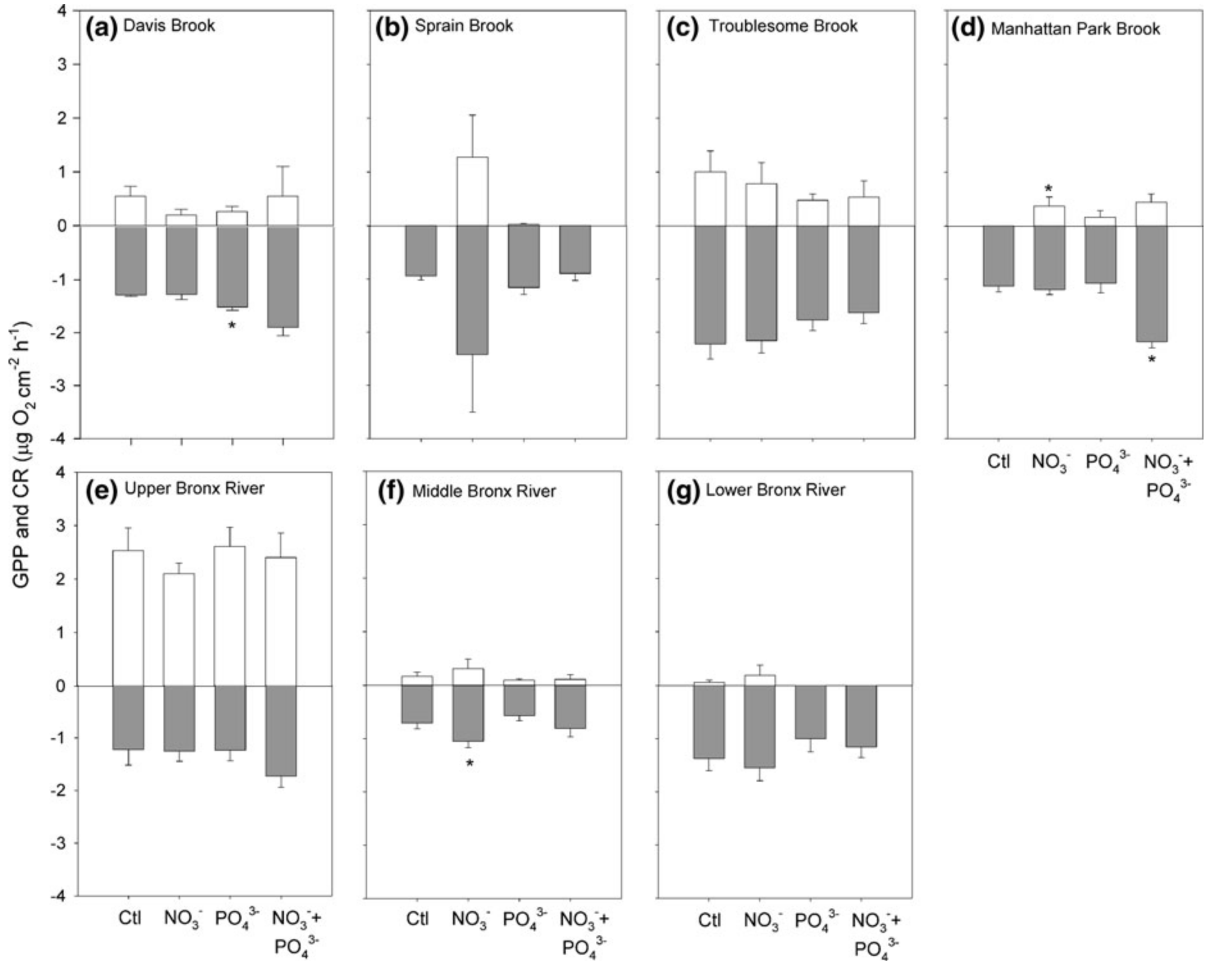


Fig. 4 Gross primary production and community respiration of biofilms on fritted glass enriched with no nutrients (Ctl), nitrate (NO_3^-), phosphate (PO_4^{3-}), and $NO_3^- + PO_4^{3-}$ in (**a**–**d**) four Bronx River tributaries and (**e**–**g**) three locations in the river mainstem. *Indicates significant nutrient limitation, calculated after Tank and Dodds (2003). GPP is shown in *white squares* and CR in *grey*

related to different environmental drivers for each substratum. On cellulose sponge, NRR for respiration on P treatments was significantly related to water column NO_3^- concentration ($r^2 = 0.963$, $p < 0.001$; Fig. 6a). Similarly, the NRR for GPP on N treatments was significantly related to water column SRP ($r^2 = 0.828$, $p = 0.004$; Fig. 6b). While respiration on glass disks was infrequently nutrient limited, the response to P enrichment was negatively related to ISC ($r^2 = 0.710$, $p = 0.017$; Fig. 6c). Finally, even though GPP was only N limited at one site (Figs. 4, 5), the magnitude of the biofilm response to N enrichment was negatively related to canopy cover ($r^2 = 0.941$, $p < 0.001$; Fig. 6d). There were no other relationships between NRR and the potential environmental drivers in Table 1.

Discussion

Longitudinal and spatial variation for N and P

Synoptic sampling and NDS results imply important differences for N and P sources and retention in this watershed. Several results suggest non-point sources and biological saturation of NO_3^-, including lower spatial variation in NO_3^- concentrations relative to SRP and NH_4^+, the positive relationship between

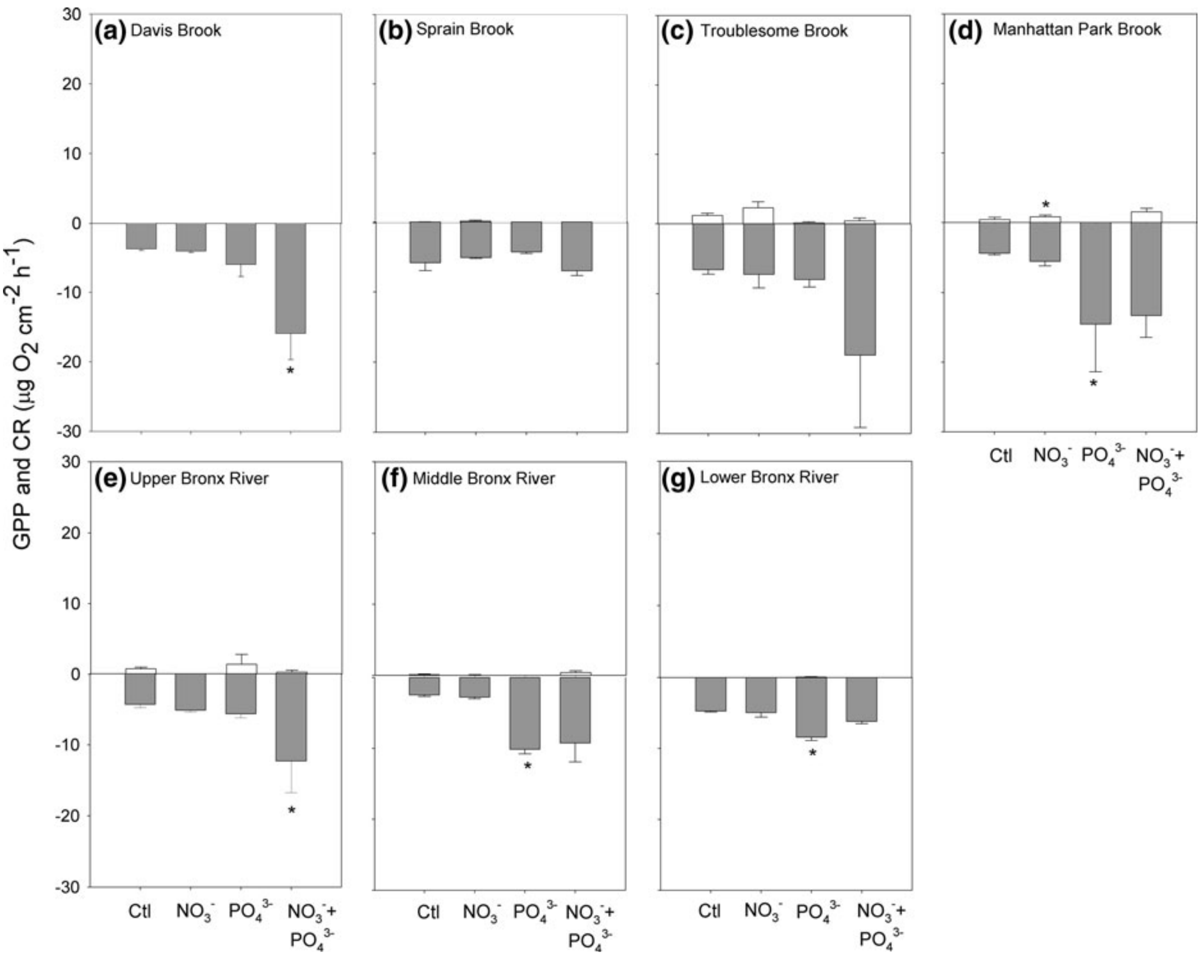


Fig. 5 Gross primary production and community respiration of biofilms on cellulose sponge enriched with no nutrients (Ctl), nitrate (NO_3^-), phosphate (PO_4^{3-}), and $NO_3^- + PO_4^{3-}$ in (**a**–**d**) four Bronx River tributaries and (**e**–**g**) three locations in the river mainstem. *Indicates significant nutrient limitation, calculated after Tank and Dodds (2003). GPP is shown in *white squares* and CR in *grey*

NO_3^- yield and ISC, and infrequent limitation of NDS biofilms by N-alone. Diffuse sources of NO_3^- likely include atmospheric deposition, which is relatively high across NY state (Golden and Boyer 2009), and urban/suburban fertilizer use, as there is little septic tank usage in the watershed. Using a mass balance approach, Groffman et al. (2004) and Sivirichi et al. (2010) also found that urban and suburban streams near Baltimore have high N export rates and are sources of N to downstream ecosystems.

In contrast to NO_3^-, patterns for SRP concentration, instantaneous yield, and NDS results suggest that low SRP frequently limits biofilm activity throughout the watershed, except where one or more point-sources contribute to high SRP. The Grassy Sprain Brook subwatershed had much higher SRP than the other subwatersheds, no PO_4^{3-} biofilm limitation, and none of the land use categories explained spatial variation in SRP. This suggests a point-source of SRP such as construction, lawn care, human or animal waste, or the influence of the Grassy Sprain Reservoir. Hatt et al. (2004) also found a single high P watershed among multiple urban drainages near Melbourne, Australia and postulated a point-source was responsible for the pattern.

There was no clear indication of NH_4^+ sources throughout the watershed as there was no geographic pattern for NH_4^+ yield and no relationships with land-use. This is in contrast to Hatt et al. (2004) who documented a strong positive correlation between

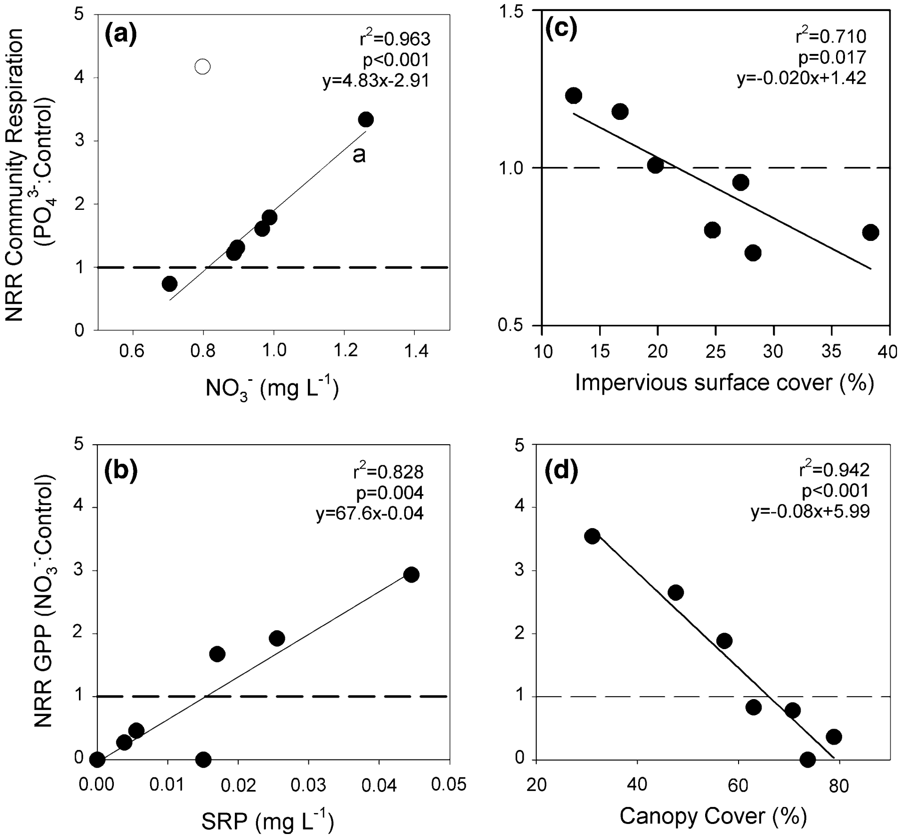


Fig. 6 The nutrient response ratio (NRR) for (**a**) community respiration of phosphate (PO_4^{3-}) enrichment was related to water column nitrate (NO_3^-) on cellulose sponge biofilms. The white circle was removed as an outlier (studentized residual = 14.9, $p < 0.001$; if the point is left in $r^2 = 0.127$, $p = 0.433$), (**b**) gross primary production (GPP) of NO_3^- enrichment on cellulose sponge biofilms was related to water column soluble reactive phosphorus (SRP), (**c**) community respiration of PO_4^{3-} enrichment on fritted glass biofilms was related to nutrient diffusing substrata (NDS) depth, and (**d**) GPP of PO_4^{3-} enrichment on fritted glass biofilms was related to canopy cover

NH_4^+ and ISC at baseflow and storm events in urban streams. Our results may indicate a combination of point and non-point sources of NH_4^+, at least at baseflow when this study was conducted. We might infer low ecosystem NH_4^+ demand from the relatively high concentrations, low spatial variation, and infrequent biofilm N limitation (measured as NO_3^-–N in the NDS experiments), which is consistent with lower NH_4^+ demand with increased urbanization (Meyer et al. 2005) and at sites downstream from waste water outflows (Martí et al. 2004). The drivers of NO_3^- and total N in urban streams have been well studied in Baltimore watersheds (Groffman et al. 2004; Sivirichi et al. 2010), but fewer data have been published for controls on spatial patterns in NH_4^+ in urban systems (Claessens et al. 2010). Clearly more work is needed to clarify how biotic and abiotic processes contribute to spatial patterns of NH_4^+ concentrations in urban stream networks.

Synoptic studies have used the relative values of N and P concentration and spatial variability to imply nutrient limitation, even without measuring limitation directly (Dent et al. 2001; Gardner and McGlynn 2009). For example, Dent et al. (2001) found high concentration and lower spatial variation of P in a desert stream, which when combined with low concentration and high variation of NO_3^- suggested N limitation of the stream ecosystem. Using this logic, because NO_3^- was the highest and least variable of nutrients in the Bronx River, and SRP was lowest and most variable, P limitation is more likely than N limitation in this watershed. We confirmed this pattern with NDS measurements, which showed low frequency of NO_3^- limitation, and higher incidence of P-alone or N + P co-limitation.

Urban watersheds exhibit high temporal variability in discharge and nutrient export due to seasonality of flooding and influence of ISC (Groffman et al. 2004). Nutrient export from urban streams during short periods of high flow can be 50% of annual N export (Groffman et al. 2004). By sampling only during base flow, we may have missed important dynamics of

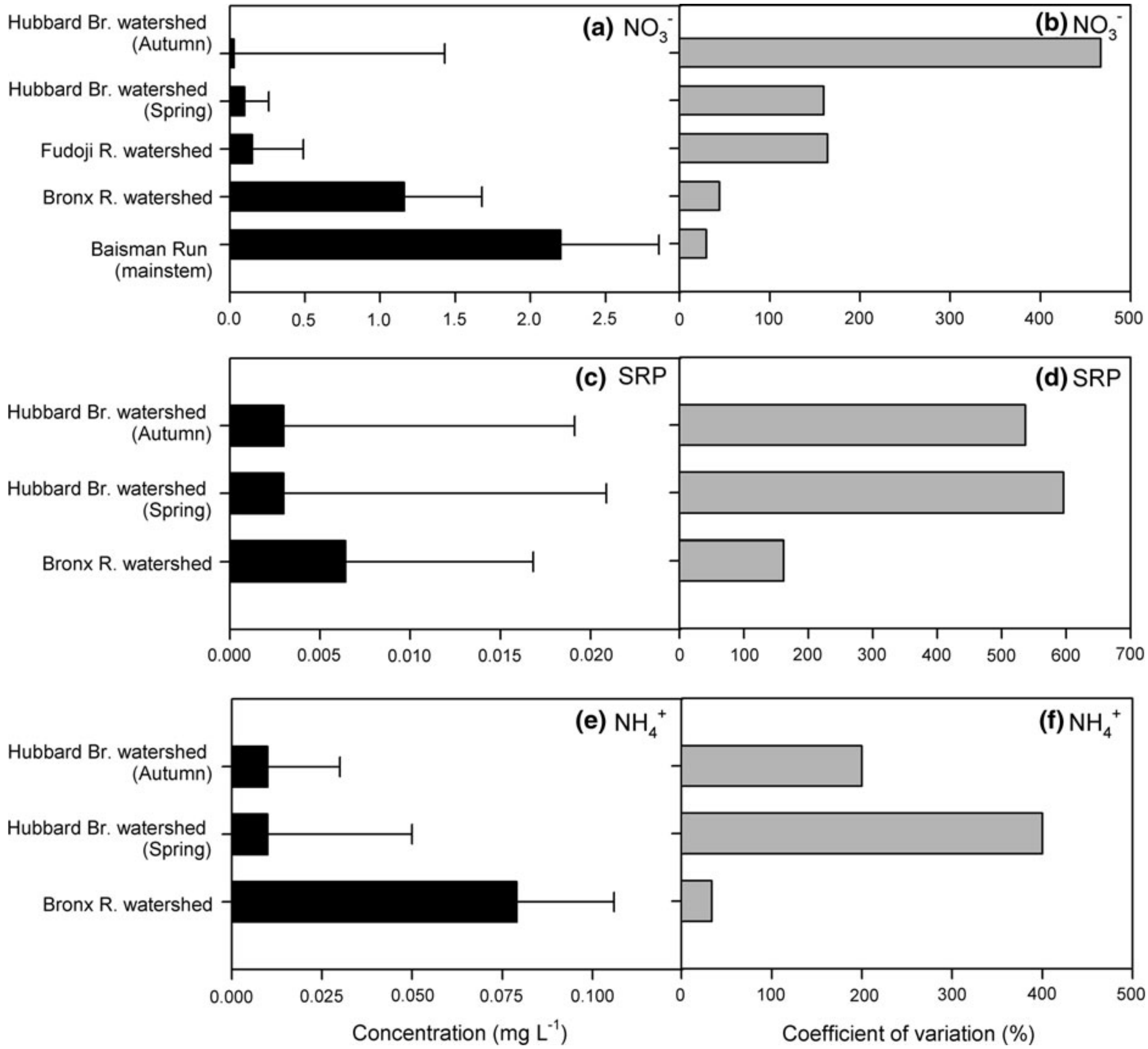


Fig. 7 Mean (±standard deviation) for (**a**) nitrate (NO_3^-) concentration, (**b**) NO_3^- coefficient of variation, (**c**) soluble reactive phosphorus (SRP) concentration, (**d**) SRP coefficient of variation, (**e**) ammonium (NH_4^+) concentration, and (**f**) NH_4^+ coefficient of variation from synoptic sampling in this study and studies of spatial distribution of nutrient concentrations in a forested watershed in New Hampshire, USA (Likens and Buso 2006), a forested watershed in central Japan (Asano et al. 2009), and a suburban Maryland, USA watershed (Claessens et al. 2010)

export and retention in the Bronx River. For example, Gardner and McGlynn (2009) found NO_3^- concentrations declined with increased biological immobilization during summer in a developing watershed, reducing longitudinal variability in NO_3^- concentrations relative to winter. In this context, we note the spatial variation in nutrient concentrations and limitation observed in this study were for a period of low flow during late summer, and the patterns could differ at other times.

Longitudinal variation of N and P in the Bronx River relative to other watersheds

Several studies have used synoptic approaches in streams in desert (Dent et al. 2001), prairie (Dodds and Oakes 2008), alpine (Gardner and McGlynn 2009), and boreal (Scrimgeour and Chambers 2000; Temnerud and Bishop 2005) biomes, and the number of synoptic data sets from urban or suburban sites is growing (Claessens et al. 2010; Gómez et al. 2009;

Sivirichi et al. 2010). Although it is challenging to analyze across studies due to interregional differences in controls on water chemistry and sampling regimes (Clark et al. 2000), we compared longitudinal variation in our data to studies from temperate forested watersheds that represent climatic conditions similar to the Bronx River (Asano et al. 2009; Claessens et al. 2010; Likens and Buso 2006; Fig. 7).

NO_3^- and NH_4^+ concentrations were higher in the Bronx River and Baisman Run (a suburban watershed 15 km from Baltimore, MD) relative to forested catchments, while *variation* in nutrients was lower in the developed watersheds (Fig. 7). The higher nutrient concentrations in the developed watersheds are most likely due to the influence of agriculture (MD) and urbanization (NY and MD). Their lower *variation* in concentration, however, suggests that development simultaneously increases nutrient concentrations and lowers spatial variability, which has not been well documented and could influence stream biota. For example, low spatial variation in elevated nutrient concentrations could reduce biofilm diversity by favoring taxa which grow under enriched conditions throughout the river network, and could thereby affect higher trophic levels (Cross et al. 2007).

We note that reduced variation of nutrient concentrations in developed watersheds in Fig. 7 may also be from differences in the spatial scale of sampling efforts among studies. In the forest streams, the greatest variation in solute concentrations occurred far upstream in seeps, springs, and small headwaters (Asano et al. 2009; Likens and Buso 2006). We were unable to access most tributaries beyond their confluence with the Bronx River mainstem due to highways, major train tracks and stations, private property, fencing, and piped streams. Similarly, the synoptic data from Baisman Run only includes the mainstem and no tributary values (Claessens et al. 2010). It is possible we would have identified discrete point sources and recorded higher variation in concentrations if we had access to longer reaches of the headwater streams. Our reduced variation in nutrients reported in Fig. 7, therefore, may represent a methodological artifact of low tributary data. However, we note the constrained sampling regime accurately represents conditions "on the ground" when conducting research in the Bronx River watershed. Lack of access to headwater reaches in urban environments constricts our ability for extended longitudinal studies in tributaries, and is a challenge for studying network connectivity in urban streams.

Several synoptic studies have shown a convergence in solute concentrations in higher order streams relative to headwaters, as solute concentrations are "homogenized" downstream (Asano et al. 2009; Likens and Buso 2006). Asano et al. (2009) concluded this convergence trend strongly explained spatial variation in solute concentrations across forested subcatchments of the Fudoji River in Japan (Fig. 8a). Despite a lack of access to small headwaters in the Bronx River relative to Asano et al. (2009),

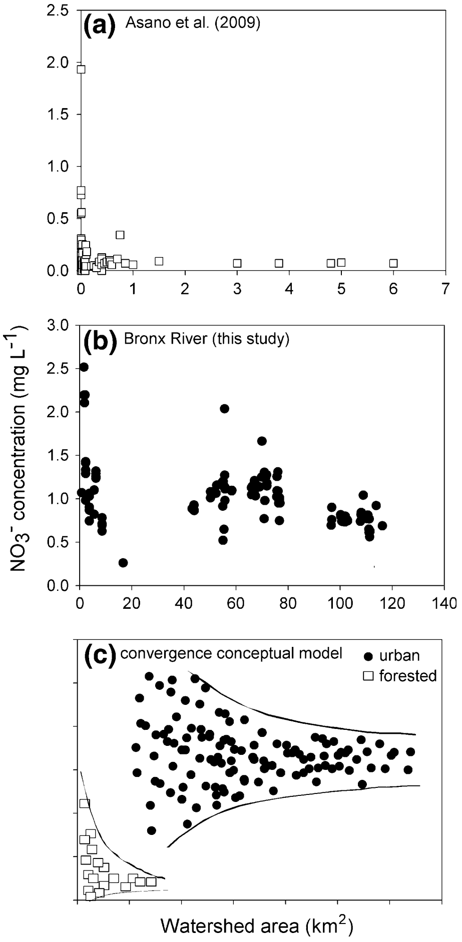


Fig. 8 Nitrate (NO_3^-) concentration and subwatershed size in (**a**) the Fudoji River (Asano et al. 1999) and (**b**) the Bronx River (this study). **c** The convergence model of spatial distribution of solute concentrations, in forested and urban watersheds (modified from Asano et al. 2009) indicates higher nutrient concentrations, lower variation, and larger subwatershed sizes in urban relative to forested watersheds

our NO_3^- concentrations concur with this convergence pattern, although with three important differences in the urban watershed: (1) higher nutrient concentrations, (2) decreased variation, and (3) larger subwatershed sizes (Fig. 8b). We present a conceptual diagram for solute convergence in urban and forested watersheds in Fig. 8c (modified from Asano et al. 2009).

In contrast to NO_3^-, SRP and NH_4^+ concentrations did not show longitudinal patterns of convergence, which we attribute to their biogeochemical properties and origins. A pattern of convergening solute concentration would be expected when diffuse solute sources are primarily influenced by dilution rather than biological or abiotic uptake. Nitrate follows this pattern because it does not sorb to sediments, was infrequently the primary limiting nutrient to stream biofilms, was related to ISC (i.e., diffuse inputs), and remained at high concentrations throughout the watershed. SRP, however, does not exhibit the convergence pattern because it was the primary limiting nutrient, and was found at low concentrations in most places. It is unclear what biotic or abiotic processes controlled NH_4^+ concentrations, but it was also highly variable and does not match the convergence pattern. Additional application of this pattern to urban watersheds will enhance our understanding of landscape level controls on N and P concentrations across gradients of nutrient enrichment and hydrology.

Hydrological modification

A rudimentary water budget from the tributaries and mainstem suggested a large proportion of discharge from the Bronx River watershed to the East River was not accounted for by tributaries. The sum of all measured tributary inputs was 837 $m^3\ s^{-1}$, or between 35 and 46% of the discharge measured at the downstream USGS gauging station. We hypothesize a relatively large portion of discharge entered the river through direct inputs, pipes, and groundwater connections. Historical maps in the region indicate a more complex tidal wetland and watershed ecosystem than exists today (Sanderson 2009), but the proportion of buried, piped, or filled-in streams is unknown. Our data suggests anywhere between 1/3 and 1/2 of the river input is not from surface tributaries, which is consistent with estimates of stream burial in Baltimore ranging from 20–70% (Elmore and Kaushal 2008). Hatt et al. (2004) also found that while impervious surface cover explained NO_3^- export from urban streams, accounting for “effective imperviousness,” or the amount of impervious surfaces directly connected to streams, more strongly explained N patterns. Our land-use quantification could not take into account underground storm-water drainage systems as we could find no geospatial data that accurately characterizes storm-water drainage for the entire area under study. Stream burial and piping represents a major challenge for understanding longitudinal dynamics of nutrient flux in urban rivers, and it likely contributes to the unexplained variability of N and P concentrations in the Bronx River mainstem.

Environmental drivers of biofilm growth limitation operate at multiple spatial scales

Our results indicated clear differences on nutrient limitation between substrata, where biofilms on cellulose were more strongly nutrient-limited than on fritted glass. Previous studies using identical substrata have found that rates of heterotrophic decomposition on cellulose, which selects for a net heterotrophic biofilm community (Johnson et al. 2009), are stimulated by carbon + nutrient availability and warm temperatures. In contrast, autotrophs show preference for fritted glass relative to cellulose and are primarily limited by light availability (Johnson et al. 2009; Hoellein et al. 2010). It appears that during summer, nutrient demand from heterotrophic biofilms may exert a stronger influence on nutrient concentrations than for biofilms on inorganic surfaces.

Light limitation strongly influenced response of GPP to nutrient addition and may have influenced spatial patterns of nutrient concentrations. Light availability, rather than nutrients, is often the primary limiting factor for autotrophic stream biofilms (Hill et al. 2001; Mulholland et al. 2006). In a study of nutrient limitation in 72 streams draining urban, forested, and agricultural watersheds, the sites most likely to show nutrient limitation of GPP had no forest canopy (Johnson et al. 2009). Our data concur with these patterns, as GPP response to N-enrichment was strongly related to low canopy cover, which is also correlated with stream size (Table 1). The lower NO_3^- concentrations observed in the lower mainstem of the river (Fig. 2a) may reflect algal uptake in the wider downstream reaches. Finally, we note N retention via algal growth probably increases during other seasons when stream canopy cover decreases throughout the watershed (Arango et al. 2008; Francoeur et al. 1999; Hoellein et al. 2009).

We expected that nutrient limitation patterns in the three river mainstem sites (i.e., Upper, Middle, and Lower Bronx River) would be more similar to each other than to the tributaries given their direct flowpath connections. However, NDS indicated no limitation at the Upper Bronx site, and different limitation patterns in the Middle and Lower Bronx. Thus, environmental drivers of biofilm nutrient limitation, such as canopy cover and nutrient concentrations, appear to change at spatial scales shorter than the length of river among the three NDS sites (i.e., 7.8 and 14.0 km). Variation in nutrient limitation at different spatial scales has also been reported elsewhere. For example, Pringle (1990) showed variation in substratum type controlled diatom community composition at scales of 100 µm, while in a 155,000 km^2 river system in west-central Canada, Scrimgeour and Chambers (2000) noted alleviation of epilithic nutrient limitation by waste water effluent persisted for an average of 78 km. Despite reduced spatial variation of nutrient concentrations in this urban watershed (i.e., Fig. 7), high spatial variation in drivers of nutrient limitation such as riparian vegetation (Groffman et al. 2003) may directly alter biofilm nutrient limitation status at nearby NDS sites.

Implications for nutrient management in urban streams

The results from both synoptic sampling and NDS suggest opportunities for management of nutrient sources and retention in urban watersheds. For example, synoptic sampling constricted the range of SRP point-sources which could allow for targeted management in Grassy Sprain Brook. Our results suggest reducing NO_3^- inputs from diffuse sources would be helpful, although likely a significant challenge given requirements of watershed-scale approaches including coordinated restoration efforts along the entire stream network. The NDS data show that enhancing biofilm nutrient uptake on organic substrata may be an overlooked strategy to increase watershed nutrient attenuation, especially in summer. This approach would entail techniques such as restoration of debris dams (Entrekin et al. 2008), inundated floodplains or wetlands (Saunders and Kalff 2001), and hyporheic organic matter storage (Valett et al. 1997). Unfortunately, increasing organic matter retention runs counter to the historic strategy of managing urban rivers to reduce flooding by removing retention structures (Paul and Meyer 2001).

Watershed approach in urban environments

The watershed approach to ecosystem science has greatly increased our understanding of nutrient cycling and energy flow through the environment. Application of the watershed approach in urban ecosystems, however, presents several challenges not encountered in rural or undeveloped settings (Groffman et al. 2004). Practical challenges we encountered include vast numbers of private property owners, permitting from multiple local governments (e.g., city, county, township), frequent interactions with representatives from the public and law enforcement, restricted stream access due to major infrastructure (e.g., trains, highways, power lines), and extensive stream burial. Despite this, the synoptic sampling + NDS approach employed in this study will directly inform nutrient management in the Bronx River. Our results will assist in targeting point and diffuse sources of N and P, and suggest mitigation efforts to increase nutrient retention. Overall, our study supports the use of the watershed approach in urban environments to inform management of streams and enhance our understanding of their structure and function.

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References

Alexander RB, Boyer EW, Smith RA, Schwarz GE, Moore RB (2007) The role of headwater streams in downstream water quality. J Am Water Resour Assoc 43(1):41–59

APHA (1998) Standard methods for the examination of water and wastewater, 20th edn. United Book Press, Inc, Baltimore

Arango CP, Tank JL, Johnson LT, Hamilton SK (2008) Assimilatory uptake rather than nitrification and denitrification determines nitrogen removal patterns in streams of varying land use. Limnol Oceanogr 53(6):2558–2572

Asano Y, Uchida T, Mimasu Y, Ohte N (2009) Spatial patterns of stream solute concentrations in a steep mountainous catchment with a homogeneous landscape. Water Resour Res 45:W10432

Bernot MJ, Tank JL, Royer TV, David MB (2006) Nutrient uptake in streams draining agricultural catchments of the midwestern United States. Freshw Biol 51(3):499–509

Bormann FH, Likens GE (1979) Pattern and process in a forested ecosystem. Springer, New York

Bott TL (1996) Primary productivity and community respiration. In: Hauer FR, Lamberti GA (eds) Methods in stream ecology. Academic Press, San Diego, pp 533–556

Carpenter S, Caraco NF, Correll DL, Howarth RW, Sharpley AN, Smith VH (1998) Nonpoint pollution of surface waters with phosphorus and nitrogen. Issues Ecol 1998(3):1–12

Claessens L, Tague CL, Groffman PM, Melack JM (2010) Longitudinal assessment of the effect of concentration on stream N uptake rates in an urbanizing watershed. Biogeochemistry 98:36–74

Clark GM, Mueller DK, Mast MA (2000) Nutrient concentrations and yields in undeveloped stream basins of the United States. J Am Water Resour Assoc 36(4):849–860

Cross WF, Wallace JB, Rosemond AD (2007) Nutrient enrichment reduces constraints on material flows in a detritus-based food web. Ecology 88(10):2563–2575

Dent CL, Grimm NB, Fisher SG (2001) Multiscale effects of surface-subsurface exchange on stream water nutrient concentrations. J N Am Benthol Soc 20(2):162–181

Dodds WK (2006) Eutrophication and trophic state in rivers and streams. Limnol Oceanogr 51(1):671–680

Dodds WK, Oakes RM (2008) Headwater influences on downstream water quality. Environ Manag 41(3):367–377

Elmore AJ, Kaushal SS (2008) Disappearing headwaters: patterns of stream burial due to urbanization. Front Ecol Environ 6:308–312

Entrekin SA, Tank JL, Rosi-Marshall EJ, Hoellein TJ, Lamberti GA (2008) Responses in organic matter accumulation and processing to an experimental wood addition in three headwater streams. Freshw Biol 53(8):1642–1657

Francoeur SN, Biggs BJF, Smith RA, Lowe RL (1999) Nutrient limitation of algal biomass accrual in streams: seasonal patterns and a comparison of methods. J N Am Benthol Soc 18:242–260

Gardner KK, McGlynn BL (2009) Seasonality in spatial variability and influence of land use/land cover and watershed characteristics on stream water nitrate concentrations in a developing watershed in the Rocky Mountain West. Water Resour Res 45:W08411

Golden HE, Boyer EW (2009) Contemporary estimates of atmospheric nitrogen deposition to the watersheds of New York State, USA. Environ Monit Assess 155:319–339

Gómez R, García V, Vidal-Abarca SuárezL (2009) Effect of intermittency on N spatial variability in an arid Mediterranean stream. J N Am Benthol Soc 28(3):572–583

Groffman PM, Bain DJ, Band LE, Belt KT, Brush GS, Grove JM, Pouyat RV, Yesilonis IC, Zipperer WC (2003) Down by the riverside: urban riparian ecology. Front Ecol Environ 1(6):315–321

Groffman PM, Law NL, Belt KT, Band LE, Fisher GT (2004) Nitrogen fluxes and retention in urban watershed ecosystems. Ecosystems 7:393–403

Hall RO, Wallace JB, Eggert SL (2000) Organic matter flow in stream food webs with reduced detrital resource base. Ecology 81(12):3445–3463

Hatt BE, Fletcher TD, Walsh CJ, Taylor SL (2004) The influenc eof urban density and drainage infrastructure on the concentrations and loads of pollutants in small streams. Environ Manag 34(1):112–124

Hill WR, Mulholland PJ, Marzolf ER (2001) Stream ecosystem responses to forest leaf emergence in spring. Ecology 82(8):2306–2319

Hoellein TJ, Tank JL, Rosi-Marshall EJ, Entrekin SA (2009) Temporal variation in substratum-specific rates of N uptake and metabolism and their contribution at the stream-reach scale. J N Am Benthol Soc 28(2):305–318

Hoellein TJ, Tank JL, Kelly JJ, Rosi-Marshall EJ (2010) Seasonal variation in nutrient limitation of microbial biofilms colonizing organic and inorganic substrata in streams. Hydrobiologia 649:331–345

Homer C, Huang C, Yang L, Wylie B, Coan M (2004) Development of a 2001 national landcover database for the United States. Photogramm Eng Remote Sens 70:829–840

Johnson LT, Tank JL, Dodds WK (2009) The influence of land use on stream biofilm nutrient limitation across eight North American biomes. Can J Fish Aquat Sci 66(7):1081–1094

Kennish MJ (2002) Environmental threats and environmental future of estuaries. Environ Conserv 29(1):78–107

Lake PS, Bond N, Reich P (2007) Linking ecological theory with stream restoration. Freshw Biol 52(4):597–615

Likens GE, Buso DC (2006) Variation in streamwater chemistry throughout the Hubbard Brook Valley. Biogeochemistry 78(1):1–30

Martí E, Aumatell J, Gode L, Poch M, Sabater F (2004) Nutrient retention efficiency in streams receiving inputs from wastewater treatment plants. J Environ Qual 33(1):285–293

Meyer JL, Paul MJ, Taulbee WK (2005) Stream ecosystem function in urbanizing landscapes. J N Am Benthol Soc 24(3):602–612

Mulholland PJ, Thomas SA, Valett HM, Webster JR, Beaulieu J (2006) Effects of light on nitrate uptake in small forested streams: diurnal and day-to-day variations. J N Am Benthol Soc 25(3):583–595

Mulholland PJ, Helton AM, Poole GC, Hall RO, Hamilton SK, Peterson BJ, Tank JL, Ashkenas LR, Cooper LW, Dahm CN, Dodds WK, Findlay SEG, Gregory SV, Grimm NB, Johnson SL, McDowell WH, Meyer JL, Valett HM, Webster JR, Arango CP, Beaulieu JJ, Bernot MJ, Burgin

AJ, Crenshaw CL, Johnson LT, Niederlehner BR, O'Brien JM, Potter JD, Sheibley RW, Sobota DJ, Thomas SM (2008) Stream denitrification across biomes and its response to anthropogenic nitrate loading. Nature 452(7184):202–206

Murphy J, Riley JP (1962) A modified single solution method for determination of phosphate in natural waters. Anal Chim Acta 26(1):31–36

New York State Department of Environmental Conservation (2008) New York State Section 303(d) list of impaired/TMDL waters. In: Management WAa (ed). Albany, NY, p 58

Newbold JD, Bott TL, Kaplan LA, Dow CL, Jackson JK, Aufdenkampe AK, Martin LA, Van Horn DJ, de Long AA (2006) Uptake of nutrients and organic C in streams in New York City drinking-water-supply watersheds. J N Am Benthol Soc 25(4):998–1017

Paul MJ, Meyer JL (2001) Streams in the urban landscape. Annu Rev Ecol Syst 32:333–365

Pringle CM (1990) Nutrient spatial heterogeneity: effects on community structure, physiognomy, and diversity of stream algae. Ecology 71:905–920

Roberts BJ, Mulholland PJ, Hill WR (2007) Multiple scales of temporal variability in ecosystem metabolism rates: results from 2 years of continuous monitoring in a forested headwater stream. Ecosystems 10(4):588–606

Sanderson EW (2009) Mannahatta: a natural history of New York City. Abrams, New York

Saunders DL, Kalff J (2001) Nitrogen retention in wetlands, lakes, and rivers. Hydrobiologia 443:205–212

Scrimgeour GJ, Chambers PA (2000) Cumulative effects of pump mill and municipal effluents on epilithic biomass and nutrient limitation in a large northern river ecosystem. Can J Fish Aquat Sci 57:1342–1354

Sivirichi GM, Kaushal SS, Mayer PM, Welty C, Belt KT, Newcomer TA, Newcomb KD, Grese MM (2010) Longitudinal variability in streamwater chemistry and carbon and nitrogen fluxes in restored and degraded urban stream networks. J Environ Monitor 13:288–303

Solorzano L (1969) Determination of ammonium in natural waters by the phenolhypochlorite method. Limnol Oceanogr 14:799–801

Tank JL, Dodds WK (2003) Nutrient limitation of epilithic and epixylic biofilms in ten North American streams. Freshw Biol 48(6):1031–1049

Tank JL, Bernot MJ, Rosi-Marshall EJ (2006) Nitrogen limitation and uptake. In: Hauer FR, Lamberti GA (eds) Methods in stream ecology, 2nd edn. Academic Press, San Diego, pp 213–238

Temnerud J, Bishop K (2005) Spatial variation of streamwater chemistry in two Swedish boreal catchments: implications for environmental assessment. Environ Sci Technol 39(6):1463–1469

Valett HM, Dahm CN, Campana ME, Morrice JA, Baker MA, Fellows CS (1997) Hydrologic influences on groundwater-surface water ecotones: Heterogeneity in nutrient composition and retention. J N Am Benthol Soc 16(1):239–247

Vitousek PM, Mooney HA, Lubchenco J, Melillo JM (1997) Human domination of Earth's ecosystems. Science 277(5325):494–499

von Schiller D, Martí E, Riera JL, Sabater F (2007) Effects of nutrients and light on periphyton biomass and nitrogen uptake in Mediterranean streams with contrasting land uses. Freshw Biol 52(5):891–906

Zambrano L, Contreras V, Mazari-Hiriart M, Zarco-Arista A (2009) Spatial heterogeneity of water quality in a highly degraded tropical freshwater ecosystem. Environ Manag 43:249–263