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Discussions

Stream restoration and sanitary infrastructure alter sources and fluxes of water, carbon, and nutrients in urban watersheds

M. J. Pennino[1], S. S. Kaushal[2], P. M. Mayer[3], R. M. Utz[4], and C. A. Cooper[5]

[1]Princeton University, Department of Civil and Environmental Engineering, Princeton, NJ, USA
[2]University of Maryland, Department of Geology and Earth Systems Science Interdisciplinary Center, College Park, MD, USA
[3]US EPA, Office of Research and Development, National Health and Environmental Effects Research Laboratory, Western Ecology Division, Corvallis, OR, USA
[4]Chatham University, Falk School of Sustainability, Pittsburgh, PA, USA
[5]Washington Department of Ecology, Environmental Assessment Program, Olympia, WA, USA

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Correspondence to: M. J. Pennino (mpennino@princeton.edu)

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Abstract

An improved understanding of sources and timing of water and nutrient fluxes associated with urban stream restoration is critical for guiding effective watershed management. We investigated how sources, fluxes, and flowpaths of water, carbon (C), nitrogen (N), and phosphorus (P) shift in response to differences in stream restoration and sanitary infrastructure. We compared a restored stream with 3 unrestored streams draining urban development and stormwater management over a 3 year period. We found that there was significantly decreased peak discharge in response to precipitation events following stream restoration. Similarly, we found that the restored stream showed significantly lower monthly peak runoff ($9.4 \pm 1.0\,\mathrm{mm\,d^{-1}}$) compared with two urban unrestored streams (ranging from 44.9 ± 4.5 to $55.4 \pm 5.8\,\mathrm{mm\,d^{-1}}$) draining higher impervious surface cover. Peak runoff in the restored stream was more similar to a less developed stream draining extensive stormwater management ($13.2 \pm 1.9\,\mathrm{mm\,d^{-1}}$). Interestingly, the restored stream exported most carbon, nitrogen, and phosphorus loads at relatively lower streamflow than the 2 more urban streams, which exported most of their loads at higher and less frequent streamflow. Annual exports of total carbon ($6.6 \pm 0.5\,\mathrm{kg\,ha^{-1}\,yr^{-1}}$), total nitrogen ($4.5 \pm 0.3\,\mathrm{kg\,ha^{-1}\,yr^{-1}}$), and total phosphorus ($161 \pm 15\,\mathrm{g\,ha^{-1}\,yr^{-1}}$) were significantly lower in the restored stream compared to both urban unrestored streams ($p < 0.05$) and similar to the stream draining stormwater management. Although stream restoration appeared to potentially influence hydrology to some degree, nitrate isotope data suggested that $55 \pm 1\,\%$ of the nitrate in the restored stream was derived from leaky sanitary sewers (during baseflow), similar to the unrestored streams. Longitudinal synoptic surveys of water and nitrate isotopes along all 4 watersheds suggested the importance of urban groundwater contamination from leaky piped infrastructure. Urban groundwater contamination was also suggested by additional tracer measurements including fluoride (added to drinking water) and iodide (contained in dietary salt). Our results suggest that integrating stream restoration with restoration of aging sanitary infrastructure can be critical to more effectively minimize

watershed nutrient export. Given that both stream restoration and sanitary pipe repairs both involve extensive channel manipulation, they can be considered simultaneously in management strategies. In addition, ground water can be a major source of nutrient fluxes in urban watersheds, which has been less considered compared with upland sources and storm drains. Goundwater sources, fluxes, and flowpath should also be targeted in efforts to improve stream restoration strategies and prioritize hydrologic "hot spots" along watersheds where stream restoration is most likely to succeed.

1 Introduction

Urbanization significantly increases impervious surface cover (ISC), alters hydrologic regimes, and contributes to elevated organic carbon and nutrient loads in streams and rivers (e.g. Paul and Meyer, 2001; Walsh et al., 2005; Kaushal and Belt, 2012). The growing impacts of urbanization on watershed nutrient exports have contributed to coastal eutrophication and hypoxia both regionally and globally (Nixon et al., 1996; Petrone, 2010). However, urban watersheds can differ significantly in carbon and nutrient sources and fluxes, and there are major questions regarding the potential influence of stream restoration and stormwater management (SWM) to alter sources and fluxes of nutrients (e.g. Bernhardt et al., 2005; Passeport et al., 2013; McMillan and Vidon, 2014). Here, we characterize changes in streamflow variability pre and post restoration in an urban stream. We also compare sources and timing of fluxes of water, carbon, and nutrients in the urban restored stream with several unrestored urban streams of varying levels of upland stormwater management and impervious surface cover.

Given the increasing interactive effects of land use and climate change, there is a substantial need to explore the biogeochemical response of different urban watersheds to hydrologic variability (Kaushal et al., 2014b). It is well known that hydrologically connected impervious surfaces in urban watersheds creates hydrologic regimes characterized by flow events with higher peaks, quicker time to peak, and shorter falling limbs – hereafter referred to as a "flashy" system (Konrad et al., 2005; Walsh et al., 2005; Meierdiercks et al., 2010; Sudduth et al., 2011; Smith et al., 2013; Loperfido et al., 2014). Yet, more work is necessary to characterize variability in fluxes of carbon and nutrients among urban watersheds, particularly for "pulses" (large changes in concentrations and fluxes over relatively short time scales) in restored and managed streams (Kaushal et al., 2014b). Pulses in carbon and nutrient exports can be influenced by the degree of hydrologic connectivity with impervious surfaces, sanitary and stormwater infrastructure, and stream restoration features (e.g. Kaushal et al., 2014a; Newcomer et al., 2014). Although stream restoration research is growing, the effects of certain restoration features such as hydrologically connected floodplains, oxbow wetlands, stream-wetland complexes and stormwater management on minimizing pulses of water, carbon, and nutrient exports is still not clearly understood (Filoso and Palmer, 2011; Harrison et al., 2014; Newcomer et al., 2014).

One key to improved management of urban watersheds is a better understanding of contaminant sources and how they can shift across hydrologic variability in restored and unrestored streams. Knowledge of the sources of chemical fluxes in urban restored streams is particularly lacking, even though stream restoration is currently a billion dollar industry in the US (Bernhardt et al., 2005). In order to characterize contaminant sources, various biogeochemical and hydrologic tracers have been employed in other urban degraded watersheds. For example, recent studies have utilized N and O stable isotopes to determine sources of NO_3^- (e.g. wastewater, atmospheric, or nitrification) (Kendall et al., 2007; Burns et al., 2009; Kaushal et al., 2011). Tracking NO_3^- can be improved when used in conjunction with additional tracers such as anions like fluoride and iodide (Kaushal et al., 2014a), where fluoride is applied as an additive to drinking water (Dean et al., 1950) and iodide is used in table salt (Waszkowiak and Szymandera-Buszka, 2008); therefore, their presence in streams may be considered an indicator of contamination by wastewater. Others have used fluorescence spectroscopy to determine dissolved organic matter sources and quality (e.g. labile vs. recalcitrant) (Baker, 2001; Cory et al., 2010), and to trace wastewater sources. Finally, stable isotopes of water have been used to characterize groundwater vs. surface water flowpaths (Gat, 1996; Harris et al., 1999; Kendall and Coplen, 2001). The present study is unique in that it uses multiple tracers of contaminates to assess the effects of hydrologic variability on sources and fluxes of carbon and nutrients.

The objectives of this study were to characterize sources and timing of water, carbon, and nutrient fluxes in four urban watersheds with varying urban development and water management, including one site with extensive stream restoration. Our first objective was to compare the hydrologic response of the restored stream to precipitation events pre and post restoration. Our second objective was to compare metrics of hydrologic flashiness, and sources and timing of chemical fluxes in this restored stream with 3 urban unrestored streams (draining varying stormwater management and urbanization) over a 3 year period. Research was conducted in watersheds that are part of the Baltimore Long-Term Ecological Research (BES LTER) project, which is described further below and elsewhere (www.beslter.org) (e.g. Groffman et al., 2004; Meierdiercks et al., 2010; Ryan et al., 2010; Kaushal et al., 2011; Lindner and Miller, 2012).

2 Methods

2.1 Site descriptions

All watersheds were located in the metropolitan region of Baltimore, Maryland, USA in the Chesapeake Bay watershed (Fig. 1). Impervious surface cover (ISC) was calculated for each watershed using ArcGIS and based on averaging the ISC values obtained from the 2006 National Land cover Database (NLCD), a two meter satellite imagery obtained from the University of Vermont, and a roads and buildings polygon layer for Baltimore County. The amount of stormwater management (SWM) within each watershed was calculated, using ArcGIS, as the percentage of watershed drainage area that is managed by stormwater management facilities. Data on the locations of SWM facilities and the drainage area controlled by each SWM facility was provided by the

Baltimore County, Maryland Department of Environmental Protection and Sustainability (BCMDEPS).

The most urban watershed, Dead Run (DRN), with 45.7 % ISC, has the second highest percent stormwater management (32.5 % SWM), and was the third oldest in terms of average year built for development (1963). The second most urban site, Powder Mill Run (PMR), with 44.3 % ISC, has virtually no stormwater management (0.7 % SWM), and the oldest average age of development (circa 1954). The third most urban site, Minebank Run (MBR) has moderate impervious surface cover and minimal stormwater management (29.4 % ISC, 17.8 % SWM), but the entire mainstem of the stream from headwaters to mouth is greater than 95 % restored (∼ 5700 linear meters were restored, BCMDEPS), with the headwaters restored in 1998–1999 and the lower portion (directly above and below the stream gauge) restored in 2004–2005. The MBR watershed has the second oldest year of development (circa 1959). Restoration features at MBR include oxbows, redesigned channels, armoring, low connected floodplains, increased sinuosity, and step pools (Kaushal et al., 2008b; Harrison et al., 2011). The least urban site, Red Run (RRN), has 20.5 % ISC, the greatest level of stormwater management (40.4 % SWM), and is the most recently developed watershed (circa 1998) (BCMDEPS). The stormwater management at RRN is primarily in the lower portion of the watershed and includes detention ponds, wet ponds, bioretention, and sand filters, with its headwaters containing a quarry and low-density development on septic systems. DRN has stormwater management mainly in a portion of its headwaters, with primarily detention ponds (Fig. 1, Table 1, Smith et al., 2015). RRN and MBR have broader undeveloped downstream riparian zones than either DRN or PMR. Discharge was measured continuously at all of the 4 study watersheds: Minebank Run, Powder Mill Run, and Dead Run are gauged by the US Geological Survey (USGS gage numbers 0158397967, 01589305, and 01589330, respectively), while Red Run is gauged by the University of Maryland, Baltimore County Center for Urban Environmental Research and Education. Further details on stream site characteristics and the methods described below are in Supplement.

2.2 Comparison of pre and post restoration hydrologic response

In order to examine the hydrologic response of an urban stream to restoration, the relationship between effective precipitation (Ppt) and effective peak discharge (Q_{pk}) was estimated for Minebank Run pre and post restoration, from 2001 to 2008. Discharge and precipitation data are from the US Geological Survey (USGS) National Water Information System. Data were accessed online (http://waterdata.usgs.gov/nwis) or through requests made to the Maryland Water Science Center Water-Data inquiries link between May 2008 and July 2011. Data were collected electronically every 5 min, and discharge data were available online, and the high temporal resolution weather data were made available via a request to the USGS. The discharge data were transformed from the original cubic feet per second (cfs) to cubic meters per second (cms) and precipitation was transformed from inches to millimeters.

In order to determine effective precipitation and the associated effective discharge, we first removed dates without measureable precipitation or discharge. Of the 2283 dates in the study period (2001–2008) with data, approximately 800 dates had precipitation. Based upon the remark codes, dates were removed when either precipitation or discharge were estimated leaving 679 dates. An additional series of data were removed for days where less than 1.27 mm (0.05 inches) of precipitation was measured. At this precipitation depth there was no identifiable discharge response, even for cloudbursts with the entire 1.27 mm occurring in a 5 min period. It was assumed that much of this precipitation was intercepted and could be classified as the initial abstraction.

Five (5) storms were found to be multi-day events (meaning that they occurred at night and fell into two calendar days) and were then combined into a single day event. Data for the hydrographs where the peak discharge for a storm was on the falling limb of a precipitation event on the previous day were also removed. Because of low intensity precipitation, 33 storms were removed from the analysis, these were low precipitation intensity drizzle events and a distinct discharge response could not be identified at the 5 min data interval. There were also 20 dates where there were multiple storms during that 24 h period/calendar day. Therefore, the first peak on the hydrograph was selected, along with the associated precipitation occurring up till the peak discharge.

There were 195 pre-restoration and 221 post-restoration dates used in the effective Ppt-Q_{pk} analysis (where the designation of effective is used to specifically identify data that meets the assumptions of a measureable mechanism between precipitation leading to a discharge response). Regression lines were created in Minitab (Release 14.2, Minitab, Inc. State College, PA, USA) using the data developed for the pre-restoration and the post-restoration for the effective storm precipitation and the effective peak discharge. Slope and intercept of these developed regression lines were compared using a General Linear Model in Minitab (ID 1248).

2.3 Water quality sampling and analyses

Water samples were collected at the MBR, RRN, DRN, and PMR stream gauge locations every 2 to 4 weeks (called "routinely sampled" water quality data from this point on) for 3 calendar years (2010–2012) and longitudinally at 8–12 sampling points (300–1000 m apart) from mouth to headwaters of each stream network during 4 different seasons: 2 winter (January 2010 and December 2010), one spring (April 2010), and one summer (June 2011). Samples were analyzed for total organic C (TOC), dissolved organic C (DOC), total Kjeldahl nitrogen (TKN), nitrate + nitrite ($NO_3^- + NO_2^-$), total phosphorus (TP), orthophosphate (PO_4^{3-}), iodide (I^-), fluoride (F^-), stable water isotopes (δ^2H-H_2O and δ^{18}O-H_2O, details below), C quality characterization (described further below), and NO_3^- stable isotopes (δ^{15}N-NO_3^- and δ^{18}O-NO_3^-, details below). All samples were analyzed using standard Environmental Protection Agency (EPA) methods by the U.S. EPA National Risk Management Research Laboratory in Ada, Oklahoma, USA.

2.4 Nitrate and water stable isotope analyses and mixing models

Surface samples for δ^{15}N-NO_3^- and δ^{18}O-NO_3^- isotopes of dissolved NO_3^- were filtered (0.45 µm), frozen, and shipped to the UC Davis Stable Isotope Facility (SIF) for analysis. The isotope composition of nitrate was measured following the denitrifier method (Sigman et al., 2001; Casciotti et al., 2002). Briefly, denitrifying bacteria were used to convert nitrate in water samples to N_2O gas, which was then analyzed by a mass spectrometer for stable isotopic ratios of N and O of nitrate ($^{15}N/^{14}N$ and $^{18}O/^{16}O$). Values for δ^{15}N-NO_3^- and δ^{18}O-NO_3^- are reported as per mil (‰) relative to atmospheric N_2 ($\delta^{15}N$) or VSMOW ($\delta^{18}O$), according to $\delta^{15}N$ or $\delta^{18}O$ (‰) = $[(R)\text{sample}/(R)\text{standard} - 1] \times 1000$, where R denotes the ratio of the heavy to light isotope ($^{15}N/^{14}N$ or $^{18}O/^{16}O$). For data correction and calibration, UC Davis SIF uses calibration nitrate standards (USGS 32, USGS 34, and USGS 35) supplied by NIST (National Institute of Standards and Technology, Gaithersburg, MD). The long-term standard deviation for nitrate isotope samples at UC Davis SIF is 0.4 ‰ for δ^{15}N-NO_3^- and 0.5 ‰ for δ^{18}O-NO_3^-. Previous studies (Kendall et al., 2007; Kaushal et al., 2011) indicate that the relative amounts of δ^{15}N-NO_3^- and δ^{18}O-NO_3^- can be used to determine specific sources of nitrate (i.e. fertilizer, atmospheric, or sewage derived nitrate).

Stable nitrate isotope data was used to create a three-endmember isotope mixing model to determine the percent contribution of different potential nitrate sources: wastewater, nitrification, or atmospheric derived nitrate (Phillips, 2001; Kaushal et al., 2011), where:

$$f_{\text{wastewater}} = \frac{(\delta^{15}N_N - \delta^{15}N_A)(\delta^{18}O_S - \delta^{18}O_A) - (\delta^{18}O_N - \delta^{18}O_A)(\delta^{15}N_S - \delta^{15}N_A)}{(\delta^{15}N_N - \delta^{15}N_A)(\delta^{18}O_W - \delta^{18}O_A) - (\delta^{18}O_N - \delta^{18}O_A)(\delta^{15}N_W - \delta^{15}N_A)} \quad (1)$$

$$f_{\text{Atmospheric}} = \frac{(\delta^{15}N_S - \delta^{15}N_N)(\delta^{18}O_W - \delta^{18}O_N) \times f_{\text{wastewater}}}{\delta^{18}O_A - \delta^{18}O_N} \quad (2)$$

$$f_{\text{nitrification}} = 1 - f_{\text{wastewater}} - f_{\text{atmospheric}} \quad (3)$$

and $f_{\text{wastewater}}$, $f_{\text{atmospheric}}$, and $f_{\text{nitrification}}$ = the fraction of nitrate from wastewater, atmospheric, or nitrification sources, respectively (also equivalent to % wastewater NO_3^-, % atmospheric NO_3^-, and % nitrification NO_3^-) and $\delta^{15}N_S$ or $\delta^{18}O_S$ is the value (‰) for the nitrate sample, $\delta^{15}N_N$ or $\delta^{18}O_N$ is the endmember value (‰) for nitrification, $\delta^{15}N_A$ or $\delta^{18}O_A$ is the endmember value (‰) for atmospheric nitrate, and $\delta^{15}N_W$ or $\delta^{18}O_W$ is the endmember value (‰) for wastewater nitrate. End-member values for $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ for nitrification (−3 and 0, respectively) and atmospheric nitrate (−0.2 and 80, respectively) were obtained from an average of the values in Kendall et al. (2007). The wastewater $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ end-member value (35.4 and 13.3, respectively) was based on averaging the highest effluent nitrate isotope values measured from the Blue Plains waste water treatment plant in Washington D.C. (for monthly samples collected 2010–2011).

Water isotope ($\delta^2H\text{-}H_2O$ and $\delta^{18}O\text{-}H_2O$) samples were collected from August 2010 to October 2011 and analyzed using a high temperature conversion elemental analyzer (TC/EA), a continuous flow unit, and an isotope ratio mass spectrometer (IRMS). A two end-member mixing model (Williard et al., 2001; Buda and DeWalle, 2009; Kaushal et al., 2011) was created using $\delta^{18}O\text{-}H_2O$ to distinguish between groundwater and atmospheric water sources, where:

$$\%\ \text{groundwater} = \frac{\delta^{18}O_S - \delta^{18}O_R}{\delta^{18}O_G - \delta^{18}O_R} \times 100 \quad (4)$$

% rainwater = 100− % groundwater, and $\delta^{18}O_S$ is the value (‰) for the stream water sample, $\delta^{18}O_R$ is the endmember value (‰) for rain water, and $\delta^{18}O_G$ is the endmember value (‰) for ground water. End-member values for $\delta^2H\text{-}H_2O$ and $\delta^{18}O\text{-}H_2O$ from rain water (−22.41 and −5.23, respectively) and groundwater (−44.02, and −7.995, respectively) were obtained from Kendall and Coplen (2001).

2.5 Fluorescence analyses for dissolved organic matter characterization

The lability (e.g. protein or humic-like) and sources (e.g. allochthonous or autochthonous) of dissolved organic matter were characterized using fluorescence excitation emission matrices (EEMs) (Cory and McKnight, 2005; Cory et al., 2010), using a Fluoromax-4 spectrofluorometer (Horiba, Jobin Yvon). Water samples were analyzed with an excitation range of 240–450 nm at 10 nm increments and an emission range of 290–600 nm at 2 nm increments. Fluorescence EEMs were instrument-corrected, blank-subtracted, and normalized by the water Raman signal following Cory et al. (2010). Standard inner-filter corrections (IFC) were not performed on samples because absorbance measurements were not obtained for most samples (however, for a subset of samples absorbance was collected using a Scanning Spectrophotometer, the inner-filter corrections were done, and it was found that there is < 5 % difference in the EEM metric results, with and without IFC). We analyzed fluorescence EEMs for the following indices: fluorescence index, FI (McKnight et al., 2001), humification index, HIX (Zsolnay et al., 1999; Huguet et al., 2009), biological freshness index, BIX (Huguet et al., 2009), and protein-to-humic fluorescence intensities ratio, P/H ratio (Coble, 1996; Stolpe et al., 2010).

2.6 Estimation of annual watershed carbon, nutrient, and anion exports

Routinely sampled concentration data, mean daily discharge, and the USGS FORTRAN program LOADEST (Runkel et al., 2004) were used to calculate the annual loads of all stream chemistry variables at each site. Various methods have been employed for estimating annual nutrient loads (e.g. Cohn, 1995; Schwartz and Naiman, 1999). However, we chose LOADEST because it uses a multiple parameter regression model that accounts for bias, data censoring, and non-normality to minimize difficulties in load estimation (Qian et al., 2007). LOADEST uses three different statistical approaches to estimate export: Adjusted Maximum Likelihood Estimation (AMLE), Maximum Likelihood Estimation (MLE), and Least Absolute Deviation (LAD). As suggested by Runkel et al. (2004), AMLE was chosen when the calibration model errors (residuals) were normally distributed, while LAD was chosen when residuals were not normally distributed. LOADEST produced load estimates for daily nutrient loads and annual exports were calculated by summing daily export for each year and dividing by watershed area. Through analyses of model residuals and a comparison of the observed and estimated loads, none of the constituents where found to have bias in the LOADEST output (Runkel, 2013). Based on the mean daily runoff and estimated daily loads, flow duration and nutrient curves were quantified for each stream similar to previous studies (Shields et al., 2008; Sivirichi et al., 2011; Duan et al., 2012). Following Shields et al. (2008), we also calculated the F75 metric for each nutrient load, which is the runoff at which 75 % of each nutrient is exported annually. Additionally, 95 % confidence intervals were estimated for annual loads using a simplified bootstrap resampling approach similar to Efron and Tibshirani (1986) and Rustomji and Wilkinson (2008).

Samples were collected over a range of streamflow conditions. However, the largest flows were not sampled due to adherence to a random sampling scheme and logistic feasibility (see Table 1, Fig. S2 in the Supplement). Flow duration records, based on mean daily flow for 2010–2012 show that the majority of samples were collected during low to intermediate flows (Fig. S2). As a result, the daily load estimates from LOADEST may not accurately reflect flows higher than the highest flows sampled. Also, because mean daily discharge data was used instead of instantaneous discharge, there is likely increased uncertainty in the daily load estimates during storm event peak flow periods. However, Carey et al. (2014) found no difference in annual load estimates in an urban watershed when using daily vs. instantaneous records of flow and nitrate concentration, though it was a significantly larger suburbanizing watershed. There are also likely differences in the effects of storms on C, N, and P concentrations, since NO_3^- is generally diluted during storms whereas particulate organic nitrogen and P generally increases during storms (Bowes et al., 2005; Kaushal et al., 2008a). Additionally, when comparing the years sampled (2010–2012) to the full discharge record at each site (starting in 2001 for MBR, 2008 for RRN, 2005 for PMR, and 1998 for DRN), the range of streamflow during 2010–2012 contains 5 of the 10 highest flows recorded at all sites. Our sampling period also included streamflow equal to the lowest streamflow ever recorded at these gauges, indicating that 2010–2012 encompasses the full range of flows.

2.7 Characterizing hydrologic flashiness and pulses of C, N, and P exports

Metrics of hydrologic flashiness were calculated using daily- and instantaneous discharge and precipitation data. Metrics consisted of the following variables: (1) average peak runoff, (2) hydrograph duration, (3) high-flow event frequency (monthly frequency of peaks above 3× monthly median) (Utz et al., 2011), (4) mean monthly peak flow coefficient of variation, and (5) mean lag-time (time between rainfall centroid and peak runoff) (Smith et al., 2013). Additionally, mean daily discharge data were used to calculate the Flashiness Index (average daily change in mean daily streamflow, per month, divided by the mean monthly flow) (Poff et al., 2006; Sudduth et al., 2011), which is identical to the R-B index (Baker et al., 2004). Peak flow runoff is the only metric that accounts for watershed size. These metrics were chosen to provide a sense of how variability in urbanization affect typical stormflow characteristics and the variability in hydrologic response to storm events. Precipitation data used for lag-time calculations were 15 min interval rainfall data obtained from the National Atmospheric and Ocean Administration (NOAA) National Climatic Data Center (NOAA, 2014).

We also quantified the variability of routinely sampled carbon and nutrient source and concentration data and the daily load data from USGS LOADEST by calculating (1) mean monthly coefficient of variation, (2) mean difference (absolute value of change between consecutive daily loads or routinely sampled nutrient concentrations), and (3) the Flashiness Index (described above). These metrics were chosen to determine how differences in urbanization affect the variability or pulsing of C and nutrient sources, concentrations, and loads over time.

2.8 Statistical analyses

In order to compare all time-series data (routinely sampled nutrient concentrations, stable isotopes, carbon quality indices, and monthly flashiness metrics at each stream site), we used a repeated measures ANOVA and post-hoc pairwise comparisons for each site with the Wilcox test (also called the Mann–Whitney test). This is a non-parametric rank sum test considered better suited for censored and skewed data (Helsel and Hirsch, 1992; Cooper et al., 2014; Lloyd et al., 2014). We used 95 % confidence intervals for pairwise annual load comparisons. Analysis of covariance (ANCOVA) was performed to test for differences in regression slopes. Statistical analysis of trends were examined using Sen's Slope Estimator and a Mann–Kendall test (Gilbert, 1987; Helsel and Hirsch, 2002). The Mann–Kendall test is a linear regression zero slope test of time-ordered data over time (Gilbert, 1987). Statistical analysis was performed using the software R (R Development Core Team, 2013) or Minitab (Release 14.2, Minitab, Inc. State College, PA, USA) and MATLAB 8.1.0 (MATLAB and Statistics Toolbox Release R2012a Student) was used for estimating hydrologic flashiness metrics in each stream for the period 2010–2012.

3 Results

3.1 Pre-restoration and post-restoration hydrologic analysis

Data from the analysis of the effective precipitation-peak discharge relationship in MBR are shown in Fig. 2, for both the pre- and post-restoration periods (data during the restoration were not included in the analysis). The median storm depth was 7.6 mm during the pre-restoration period ($n = 195$) and 6.1 mm in the post-restoration period ($n = 221$). The median storm peak discharge was 0.7 cms in the pre-restoration period ($n = 195$) and 0.4 cms in the post-restoration period ($n = 221$). However, since there appears to be more of a skew to smaller storms in the pre-restoration period, of the largest 50 precipitation events, the median storm depth was 24.3 mm in the pre-restoration period ($n = 50_{\text{largest}}$) and 22.4 mm in the post-restoration period ($n = 50_{\text{largest}}$). Associated with the 50 largest precipitation events, the median storm peak discharge was 3.4 cms in the pre-restoration period ($n = 50_{\text{largest}}$) and 2.5 cms in the post-restoration period ($n = 50_{\text{largest}}$).

Regression lines and lines representing the 95 % confidence bands were developed for both the pre-and post-restoration periods. The lower confidence band for the pre-restoration data is nearly identical to the upper confidence band for the post-restoration data. The pre-restoration line has a slope of 0.136 with an R^2 of 0.74 Eq. (5) whereas the post-restoration line has a slope of 0.117 with an R^2 of 0.67 Eq. (6) (Fig. 2).

$$\text{pre}-Q_{\text{peak}} = -0.073 + 0.136(\text{PPT}_{\text{pre}}) \tag{5}$$

$$\text{post-}Q_{\text{peak}} = -0.0596 + 0.117(\text{PPT}_{\text{post}}) \tag{6}$$

Comparison of the slopes and intercepts of the above equations using a General Linear Model found that the intercepts were not significantly different but the slopes were significantly different ($p = 0.019$). Therefore, the different slopes indicate that regression lines are different between the pre- and post-restoration effective precipitation – effective peak discharges relationship.

3.2 Sources of water, carbon, and nitrogen exports among urban watersheds

Routinely sampled stable deuterium (δ^2H) and δ^{18}O water isotopes were not significantly different between sites, including the restored stream, MBR ($p > 0.05$) (Table 2), and there was also no separation when plotting δ^{18}O-H_2O vs. δ^2H-H_2O (Fig. 3a). Water isotope mixing model results also indicate no difference in the percent contribution of groundwater or rainwater sources to the stream between sites (Table 2). However, longitudinal data indicate that watersheds with higher % ISC (PMR and DRN) had significantly higher ($p < 0.05$) δ^{18}O-H_2O isotope values in the headwaters than RRN and higher δ^2H-H_2O isotopes ($p = 0.03$ for PMR and $p = 0.057$ for DRN) in the headwaters than MBR (Fig. 3a) during one winter sampling, indicative of greater evaporation of surface water at the more urban streams.

Fluorescence analyses indicated that the watersheds with greater % ISC (PMR and DRN) transported more labile organic matter than the less urban site, RRN, as suggested by trends in the biological freshness index (BIX, $p < 0.05$) and protein-to-humic (P/H) ratio ($p < 0.05$, Fig. 3b, Table 2), while MBR, the restored stream, was not different than the more urban sites (Fig. 3b, Table 2).

Only one of the more urban unrestored streams (PMR) had greater δ^{15}N-NO_3^- and contributions of NO_3^- from wastewater than the restored stream (MBR) and the least developed stream with SWM (RRN, $p < 0.05$); the most urban stream (DRN) was not significantly different than the other streams (Fig. 3c, Table 2). The percent contribution of NO_3^- from atmospheric sources, however, was greater in the watershed with the highest % ISC (DRN) compared to the watershed with the lowest % ISC (RRN) ($p < 0.05$, Table 2), but not different than the restored stream (MBR). Additionally, all sites showed a significant decline in δ^{15}N-NO_3^- with increasing runoff, and the two least urban sites (RRN and MBR), including the restored stream MBR showed steeper slopes than PMR and DRN ($p < 0.05$, Fig. 4a). Also, the more urban sites (PMR and DRN) showed pulses in δ^{18}O-NO_3^-, during rain events (Fig. 4b), which suggests that atmospheric NO_3^- contributions increase with runoff.

Longitudinally, after a spring rain event the wastewater nitrate signal (based on δ^{15}N-NO_3^- values) declines from the headwater to the mouth in the more urban watershed (DRN), while the δ^{15}N-NO_3^- values are relatively constant at the restored stream, MBR, and least urban watershed, RRN (Fig. 5a). Conversely, during summer baseflow, the δ^{15}N-NO_3^- values are relatively steady at all four sites, but with the more urban streams (PMR and DRN) having consistently higher δ^{15}N-NO_3^- values (Fig. 5b). The contribution of atmospheric nitrate (based on δ^{18}O-NO_3^- values) during the spring high flow period generally increased downstream for the more urban unrestored streams, but decreased for the restored stream, MBR, and stayed the same longitudinally for the less urban watershed with SWM (RRN, Fig. 5c). There was little difference in the δ^{18}O-NO_3^- values longitudinally for summer (Fig. 5d).

3.3 Carbon, nutrient, and anion exports among urban watersheds

Among watersheds, annual DOC export showed up to a 5-fold difference and there was up to a 2-fold difference in annual TP exports. The most urban stream DRN exhibited the highest and the restored stream MBR, exhibited the lowest annual TOC and TP exports (Table 3, $p < 0.05$ for DRN vs. MBR). The restored stream and the least urban stream draining SWM, RRN, also exhibited lower annual total N (TN) exports compared to the more urban streams ($p < 0.05$, Table 3). Annual NO_3^- exports were not significantly different between the restored stream and the most urban unrestored stream, DRN (Table 3). Annual exports of wastewater indicator anions (fluoride and iodide) showed up to 3-fold differences among watersheds, with DRN exhibiting the highest and the restored stream MBR, the lowest annual exports (Table 3, $p < 0.05$ for DRN vs. MBR).

3.4 Flashiness of water, carbon, and nutrient exports among urban watersheds

The sites with greater % ISC (PMR and DRN) had significantly higher monthly peak runoff, mean coefficient of variation of peak runoff, and flashiness index ($p < 0.05$, Table 4, Fig. 6a and 7a) than RRN and the restored stream MBR. RRN (the site with lowest % ISC) also had lower frequency of peak flow runoff events above 3× median monthly runoff and longer hydrograph duration than the other sites (Table 4). Hydrologic lag-time was not significantly different among sites (Table 4).

The two most urban streams (PMR and DRN) showed more variable and pulsed runoff and loads, based on the time series of daily loads for C, N, and P (Fig. 6) and the flashiness index (Fig. 7). Typically, loads of C, N, P, and wastewater indicator anions (F^- and I^-), showed a lower flashiness index (less variable or pulsed) for sites with lower % ISC including the restored stream (MBR and RRN; Fig. 7b–d). Based on nutrient duration curves, the unrestored sites with higher % ISC (PMR and DRN) exported more C, N, and P during higher flows, while the restored stream MBR and the less urban sites with SWM (RRN) exported more during lower flows (Fig. 8). Similarly, the F75 metric showed that 75 % of NO_3^-, TN, PO_4^{-3}, F^-, and, I^- export occurred for the sites with restoration (MBR) or with lower % ISC and more SWM (RRN) typically at lower runoff than in higher %ISC sites PMR and DRN (Table 5).

4 Discussion

Our results show that watershed urbanization increases the hydrologic flashiness and pulses in exports of carbon, nutrients, and atmospheric nitrate sources. From a management perspective, our results suggest that integrating stream restoration with sanitary infrastructure restoration has the potential to minimize sources, fluxes, and flowpaths of nutrients. Overall, impervious surface cover appeared to be an important indicator of timing of fluxes from the watersheds. Watersheds with older sanitary infrastructure and higher ISC showed significant differences in NO_3^- sources and C, N, and

P exports than the stream restoration site (MBR) and the less urban stream with SWM (RRN). Below, we discuss potential effects of stream restoration and sanitary infrastructure on sources, fluxes, and flowpaths of nutrients across a broader range of sites and urban development.

4.1 Pre-restoration and post-restoration hydrologic analysis

Restoration had subtle but statistically significant impacts on hydrology by decreasing peak discharges during storm events in this flashy system. In urban settings, imperious surfaces are identified as the primary mechanism for the flashy hydrology and the stream channel degradation (Leopold, 1968; Paul and Meyer, 2001; Walsh et al., 2005; Doheny et al., 2006). Small increases in impervious surfaces elicit disproportionately large reductions in water quality and biotic integrity (Brabec et al., 2002). Therefore, even small reductions in flashiness may be important benefits of restoration.

The Ppt-Q_{pk} regressions method for urban stream analysis used readily available data sources that are potentially applicable where there have been management changes but typical rainfall–runoff metrics do not apply (i.e. curve numbers). A clear understanding of statistically significant effects (i.e. decreased peak discharges) due to restoration are necessary to support decisions to enhance restoration beyond simple channel reconfigurations and make more active use of flooplains and/or synergistically integrating stormwater management in the uplands. The proposed Ppt-Q_{pk} approach, however, does not quantify change, but only indicates if a change in the peak discharge has occurred. Also, this regression method may not be applicable to larger basins which have different routing pathways and processes that may not occur at the same rate as in a smaller basin (Ziemer and Lisle, 1998). Further study is needed to evaluate the effects of stream restoration on hydrologic responses in larger basins and different climates. The wide availability of high-resolution precipitation data and discharge data make this a potentially useful method to evaluate management effects.

4.2 Sources of water, carbon, and nitrogen exports among urban watersheds

All 4 watersheds showed no significant differences in water isotope signatures, potentially due to complex mixing of surface water with groundwater and leaky urban water infrastructure, which is common among urban watersheds of the Baltimore LTER site (Kaushal and Belt, 2012; Kaushal et al., 2014a; Newcomer et al., 2014). Previous work has suggested that urban watersheds receive considerable inputs of water from a combination of ground water and leaky urban water infrastructure (Bhaskar and Welty, 2012; Kaushal and Belt, 2012; Kaushal et al., 2014a). Recent evidence suggests that the urban stream corridor can be an important nonpoint source (or sink) of some pollutants due to leaky sanitary infrastructure, groundwater contributions, and also instream production of labile organic carbon (Divers et al., 2013; Kaushal et al., 2014a; Newcomer et al., 2014).

The more urbanized watersheds (PMR and DRN), as well as the restored stream, MBR, contained more labile dissolved organic matter than the more recently developed and less urban watershed with SWM (RRN). The higher BIX, P/H ratio, and protein-like organic matter in the restored stream MBR, as well as the more urban watersheds (PMR and DRN), is likely due to leaky sanitary sewers typically found in older urban watersheds (Kaushal et al., 2011). Leaky sanitary sewers contribute more labile protein-like organic matter in wastewater (Hudson et al., 2008). More labile organic matter found in urban streams may also be due to lack of a riparian zone, and more light availability, typical of unrestored urban streams (Goetz et al., 2003), which promotes autotrophic growth and more biologically labile DOM (McKnight et al., 2001; Huguet et al., 2009; Petrone et al., 2011; Pennino et al., 2014). DOM derived from autochthonous production also tends to be more labile than DOC derived from terrestrial organic matter leaching, which is usually more recalcitrant and humified (McKnight et al., 2001; Huguet et al., 2009; Petrone et al., 2011). Consequently, the elevated humification index in the less urban watershed, RRN, with SWM could have resulted from increased allochthonous inputs of recalcitrant terrestrial organic matter (Duan et al., 2014).

Differences in NO_3^- sources among urban watersheds likely result from differences in age of development and extent of % ISC and less likely due to restoration or management. NO_3^- from wastewater was highest in one of the more urban sites (PMR), indicating greater NO_3^- contributions from leaky sanitary sewers (Kaushal et al., 2011); yet all sites showed wastewater as the greatest source of NO_3^-. Nitrification was the second highest source for NO_3^- at all sites, and contributed more NO_3^- in the restored stream (MBR) and the least urban stream with SWM (RRN). The greater atmospheric NO_3^- during high flows in PMR and DRN is a result of the higher impervious surface cover at these sites, allowing for the more direct connection of rainfall to the stream corridor (Silva et al., 2002; Buda and DeWalle, 2009; Burns et al., 2009). Furthermore, the inverse relationship between δ^{15}N-NO_3^- and δ^{18}O-NO_3^- at all sites indicated mixing of sewage and atmospheric NO_3^- to varying degrees among these urban watersheds (Kaushal et al., 2011). The downstream increase in δ^{18}O-NO_3^- after a spring rain event shows how the more urban streams maintain atmospheric NO_3^- throughout their stream length. The restored stream only showed atmospheric sourced NO_3^- in its headwaters (which is more developed), but not further downstream. The least urban watershed with SWM, RRN, showed minimal or no atmospheric NO_3^- signal throughout its entire stream length, corresponding with it having no directly connected ISC. Conversely, during summer baseflow, there were no differences in the atmospheric NO_3^- signal along the stream length for all four watersheds.

4.3 Variability in carbon and nutrient exports among urban watersheds

The higher C exports in the urban watersheds with greater % ISC compared to the restored stream and the least urban stream with SWM may be due to increased autochthonous C production (described above) and leaky sanitary sewers (Kaushal and Belt, 2012). Inputs of leaves and other organic materials from street trees and organic

Title Page
Abstract Introduction
Conclusions References
Tables Figures
◀| |▶
◀ ▶
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

matter delivered by storm drains from impervious surfaces likely also contributed to higher C exports in urban watersheds (Kaushal and Belt, 2012). Differences may have also stemmed from altered in-stream processing and elevated gross primary production in more urbanized, unrestored streams (Kaushal et al., 2014a). Previous work at nearby sites suggests that labile C export from urban watersheds has the potential to increase oxygen demand, alkalinity, and denitrification (Newcomer et al., 2012; Kaushal et al., 2014a). Relatively less work has quantified exports of organic C from urban watersheds (Bullock et al., 2011; Worrall et al., 2012). The C exports of the urban watersheds in the present study, ranging from 6 to 57 $\mathrm{kg\,ha^{-1}\,yr^{-1}}$, were within the range or higher than nearby forested watersheds in North America and elsewhere, which range from 10 to 100 $\mathrm{kg\,ha^{-1}\,yr^{-1}}$ (e.g. Mulholland and Kuenzler, 1979; Tate and Meyer, 1983; Hope et al., 1994; Dillon and Molot, 1997; Aitkenhead-Peterson et al., 2005).

The TN exports in this study, which ranged from 3 to 8 $\mathrm{kg\,ha^{-1}\,yr^{-1}}$, were generally equal to or higher than other urbanized watersheds, which range from 0.2 to 9 $\mathrm{kg\,ha^{-1}\,yr^{-1}}$ (Lewis and Grimm, 2007; Sobota et al., 2009; Petrone, 2010). The TN exports in the present study were lower than some urban watersheds (e.g. Line et al., 2002), which ranged from 20 to 30 $\mathrm{kg\,ha^{-1}\,yr^{-1}}$. TN exports in this study were also similar to the exports estimated in some of the same urban watersheds at the Baltimore LTER site during similar annual runoff (Kaushal et al., 2008a; Shields et al., 2008). Previous work has shown that annual runoff is a strong predictor of annual N exports in the Baltimore LTER watersheds (Kaushal et al., 2008a, 2011), and the relationship between runoff and N export rate varies significantly across a broad range of sites based on the degree of watershed urbanization (Kaushal et al., 2014b). The higher TN exports in the more urban sites (PMR and DRN) compared to the restored stream may be due to various reasons, such as greater N inputs from leaky sanitary sewers in the more urban and older watersheds and/or greater N removal in the restored stream due its hydrologically connected floodplains and alluvial wetlands (Kaushal et al., 2008b; Harrison et al., 2011). There were also higher peakflows and a greater proportion of nutrient exports at higher flows, as indicated by the F75 metric for the more urban sites (PMR and DRN). The lower TN exports in the stream with SWM (RRN) may be due to an extensive undeveloped riparian buffer (Mayer et al., 2007) and from its SWM (Bettez and Groffman, 2012), which both can enhance N removal.

Relatively few studies of P exports in urban watersheds exist compared to those addressing N exports. P exports from the present study, which ranged from 0.14 to 0.54 $\mathrm{kg\,ha^{-1}\,yr^{-1}}$, were similar to those reported elsewhere (e.g. Petrone, 2010). Urban watersheds have been previously reported to export P ranging from 0.027 to 2.11 $\mathrm{kg\,ha^{-1}\,yr^{-1}}$ (Hill, 1981). Watershed P exports were also within the range reported by Duan et al. (2012) for Baltimore LTER watersheds, where the less urban, more managed watersheds typically showed lower TP and soluble reactive phosphorus exports. The higher exports of TP and $\mathrm{PO_4^{-3}}$ at the more urban watersheds (PMR and DRN) may indicate greater inputs from leaky sanitary sewers and possibly from erosion of the stream channel due to flashier hydrology at these sites (Paul and Meyer, 2001). Higher $\mathrm{F^-}$ and $\mathrm{I^-}$ concentrations and loads in the older, more urban, and less managed sites further suggest that there are water inputs from leaky drinking water pipes and sanitary sewers. More work is necessary to trace sources of P in urban watersheds.

4.4 Flashiness of water, carbon, and nutrient exports among urban watersheds

As expected, the streams with greater % ISC (PMR and DRN) showed more flashy hydrology and evidence that overland-flow or storm drain inputs were a significant flow-path (as supported by the water and nitrate isotope mixing model results). In-stream restoration features of MBR may have contributed somewhat to dampening flood pulses by promoting floodplain reconnection, however, the inconsistently lower hydrologic flashiness metrics for MBR compared to the more urban streams (PMR and DRN) may indicate stream restoration has little or no hydrologic impact (e.g. Emerson et al., 2005; Sudduth et al., 2011) depending on the storm size or specific features of the stormwater management. At RRN, the lower % ISC, higher % SWM, and larger watershed size likely contributed to reduced hydrologic flashiness by disconnecting impervious surfaces and promoting infiltration (Meierdiercks et al., 2010; Baltimore County, Maryland Department of Environmental Protection and Sustainability).

The significantly more pulsed C and nutrient exports in the more urban watersheds (PMR and DRN) can be attributed to hydrologic variability. Dissolved C, N, P, F^-, and I^- loads in the more urban watersheds could have also been more variable due to runoff from impervious surfaces and/or increased contributions from the stream corridor (i.e. sewage leaks) during storms. We also found pulses in atmospheric NO_3^- sources (as indicated by $\delta^{18}O\text{-}NO_3^-$) during storms in the more urban watersheds, similar to Kaushal et al. (2011).

Based on the nutrient duration curves and the F75 metrics, the more urban watersheds (PMR and DRN) had greater exports of N, P, and wastewater indicator anions (F^-, I^-) during higher flows compared to sites with lower % ISC and greater stormwater management (RRN) or stream restoration (MBR). Other studies also show elevated nutrient exports during higher flows in urban watersheds (Shields et al., 2008; Duan et al., 2012; Kaushal et al., 2014b). Consequently, reducing the hydrologic flashiness of streams can likely reduce the amount and variability of C, N, and P export from watersheds (Jordan et al., 1997; Kaushal et al., 2008a; Petrone, 2010).

5 Conclusions

Our results demonstrate that stream restoration and urban water infrastructure influence the local variability of C and nutrient sources and fluxes among urban watersheds within the same city. Urban piped water infrastructure also influences sources, fluxes, and flowpaths of water, carbon, and nutrients over time and should explicitly be considered as part of the urban hydrologic cycle (Kaushal et al., 2014c, 2015). NO_3^- isotopes and C quality data suggest that sources of N and C within the stream corridor, such as leaky sanitary sewers and storm drain inputs, strongly influence the amount and timing of exports. Previous work has focused on upland stormwater management, but additional consideration of nonpoint sources in close proximity to streams such as urban water infrastructure is also warranted in stream restoration strategies. Consequently, effective management of urban streams may require upgrading or repairing leaks in sanitary infrastructure in the stream corridor to reduce these major sources, in conjunction with stream restoration or stormwater management strategies for dampening flashy hydrology and minimizing connected impervious surfaces in the watershed. Potential stream restoration strategies to reduce C and nutrient export include reducing the velocity of water and allowing overbank flow, increasing retention of groundwater, providing sustainable sources of labile organic C, reducing imperviousness in the watershed, or daylighting streams. More research is needed to assess the effectiveness of stormwater retrofits in older urban watersheds on mitigating stream degradation and improving water quality. Managing C and nutrient export from aging urban watersheds will require better knowledge of contaminant sources and pulses across hydrologic variability, particularly within the stream corridor itself.

Details on the Supplement

- additional details on methods
- additional site information and site map
- table of mean annual C and nutrient concentrations for each watershed
- table of flashiness metrics for mean daily carbon, nitrogen, and phosphorus loads
- table of flashiness metrics for routinely sampled concentrations
- table of flashiness metrics for water and nitrate sources
- table of flashiness metrics for carbon source metrics
- flow duration curves for each site
- comparison of nutrient concentrations over time at each site

- water isotope comparison
- seasonal relationship between δ^{15}N-NO_3^- vs. δ^{18}O-NO_3^-

The Supplement related to this article is available online at doi:10.5194/hessd-12-13149-2015-supplement.

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References

Aitkenhead-Peterson, J. A., Alexander, J. E., and Clair, T. A.: Dissolved organic carbon and dissolved organic nitrogen export from forested watersheds in Nova Scotia: identifying controlling factors, Global Biogeochem. Cy., 19, GB4016, doi:10.1029/2004gb002438, 2005.

Baker, A.: Fluorescence excitation-emission matrix characterization of some sewage-impacted rivers, Environ. Sci. Technol., 35, 948–953, 2001.

Baker, D. B., Richards, R. P., Loftus, T. T., and Kramer, J. W.: A new flashiness index: characteristics and applications to midwestern rivers and streams, J. Am. Water Resour. As., 40, 503–522, doi:10.1111/j.1752-1688.2004.tb01046.x, 2004.

Bernhardt, E. S., Palmer, M. A., Allan, J. D., Alexander, G., Barnas, K., Brooks, S., Carr, J., Clayton, S., Dahm, C., Follstad-Shah, J., Galat, D., Gloss, S., Goodwin, P., Hart, D., Hassett, B., Jenkinson, R., Katz, S., Kondolf, G. M., Lake, P. S., Lave, R., Meyer, J. L., O'Donnell, T. K., Pagano, L., Powell, B., and Sudduth, E.: Ecology – synthesizing US river restoration efforts, Science, 308, 636–637, doi:10.1126/science.1109769, 2005.

Bettez, N. D. and Groffman, P. M.: Denitrification potential in stormwater control structures and natural riparian zones in an urban landscape, Environ. Sci. Technol., 46, 10909–10917, doi:10.1021/es301409z, 2012.

Bhaskar, A. S. and Welty, C.: Water balances along an urban-to-rural gradient of metropolitan Baltimore, 2001–2009, Environ. Eng. Geosci., 18, 37–50, doi:10.2113/gseegeosci.18.1.37, 2012.

Bowes, M. J., House, W. A., Hodgkinson, R. A., and Leach, D. V.: Phosphorus-discharge hysteresis during storm events along a river catchment: the River Swale, UK, Water Res., 39, 751–762, doi:10.1016/j.watres.2004.11.027, 2005.

Brabec, E., Schulte, S., and Richards, P. L.: Impervious surfaces and water quality: a review of current literature and its implications for watershed planning, J. Plan. Lit., 16, 499–514, doi:10.1177/088541202400903563, 2002.

Buda, A. R. and DeWalle, D. R.: Dynamics of stream nitrate sources and flow pathways during stormflows on urban, forest and agricultural watersheds in central Pennsylvania, USA, Hydrol. Process., 23, 3292–3305, doi:10.1002/hyp.7423, 2009.

Bullock, S. H., Escoto-Rodriguez, M., Smith, S. V., and Hinojosa, A.: Carbon flux of an urban system in Mexico, J. Ind. Ecol., 15, 512–526, doi:10.1111/j.1530-9290.2011.00341.x, 2011.

Burns, D. A., Boyer, E. W., Elliott, E. M., and Kendall, C.: Sources and transformations of nitrate from streams draining varying land uses: evidence from dual isotope analysis, J. Environ. Qual., 38, 1149–1159, doi:10.2134/jeq2008.0371, 2009.

Carey, R. O., Wollheim, W. M., Mulukutla, G. K., and Mineau, M. M.: Characterizing storm-event nitrate fluxes in a fifth order suburbanizing watershed using in situ sensors, Environ. Sci. Technol., 48, 7756–7765, doi:10.1021/es500252j, 2014.

Casciotti, K. L., Sigman, D. M., Hastings, M. G., Bohlke, J. K., and Hilkert, A.: Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method, Anal. Chem., 74, 4905–4912, doi:10.1021/ac020113w, 2002.

Coble, P. G.: Characterization of marine and terrestrial DOM in seawater using excitation emission matrix spectroscopy, Mar. Chem., 51, 325–346, doi:10.1016/0304-4203(95)00062-3, 1996.

Cohn, T. A.: Recent advances in statistical methods for the estimation of sediment and nutrient transport in rivers, Rev. Geophys., 33, 1117–1123, doi:10.1029/95rg00292, 1995.

Cooper, C., Mayer, P. M., and Faulkner, B.: Effects of road salts on groundwater and surface water dynamics of sodium and chloride in an urban restored stream, Biogeochemistry, 121, 149–166, doi:10.1007/s10533-014-9968-z, 2014.

Cory, R. M. and McKnight, D. M.: Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinones in dissolved organic matter, Environ. Sci. Technol., 39, 8142–8149, doi:10.1021/es0506962, 2005.

Cory, R. M., Miller, M. P., McKnight, D. M., Guerard, J. J., and Miller, P. L.: Effect of instrument-specific response on the analysis of fulvic acid fluorescence spectra, Limnol. Oceanogr.-Meth., 8, 67–78, 2010.

Dean, H. T., Arnold, F. A., Jay, P., and Knutson, J. W.: Studies on mass control of dental caries through fluoridation of the public water supply, Public Health Rep., 65, 1403–1408, doi:10.2307/4587515, 1950.

Dillon, P. J. and Molot, L. A.: Effect of landscape form on export of dissolved organic carbon, iron, and phosphorus from forested stream catchments, Water Resour. Res., 33, 2591–2600, doi:10.1029/97wr01921, 1997.

Divers, M. T., Elliott, E. M., and Bain, D. J.: Constraining nitrogen inputs to urban streams from leaking sewers using inverse modeling: implications for Dissolved Inorganic Nitrogen (DIN) retention in urban environments, Environ. Sci. Technol., 47, 1816–1823, doi:10.1021/es304331m, 2013.

Doheny, E. J., Starsoneck, R. J., Striz, E. A., and Mayer, P. M.: Watershed Characteristics and Pre-Restoration Surface-Water Hydrology of Minebank Run, Baltimore County, Maryland, water years 2002–04, USGS Scientific Investigations Rep. 2006–5179, USGS, Reston, VA, 2006.

Duan, S. W., Kaushal, S. S., Groffman, P. M., Band, L. E., and Belt, K. T.: Phosphorus export across an urban to rural gradient in the Chesapeake Bay watershed, J. Geophys. Res.-Biogeo., 117, G01025, doi:10.1029/2011jg001782, 2012.

Duan, S. W., Delaney-Newcomb, K., Kaushal, S. S., Findlay, S. E. G., and Belt, K. T.: Potential effects of leaf litter on water quality in urban watersheds, Biogeochemistry, 121, 61–80, doi:10.1007/s10533-014-0016-9, 2014.

Efron, B. and Tibshirani, R.: Bootstrap methods for standard errors, confidence intervals, and other measures of statistical accuracy, Stat. Sci., 1, 54–75, 1986.

Emerson, C. H., Welty, C., and Traver, R. G.: Watershed-scale evaluation of a system of storm water detention basins, J. Hydrol. Eng., 10, 237–242, doi:10.1061/(asce)1084-0699(2005)10:3(237), 2005.

Filoso, S. and Palmer, M. A.: Assessing stream restoration effectiveness at reducing nitrogen export to downstream waters, Ecol. Appl., 21, 1989–2006, 2011.

Gat, J. R.: Oxygen and hydrogen isotopes in the hydrologic cycle, Annu. Rev. Earth Pl. Sc., 24, 225–262, doi:10.1146/annurev.earth.24.1.225, 1996.

Gilbert, R. O.: 6.5 Sen's nonparametric estimator of slope, in: Statistical Methods for Environmental Pollution Monitoring, John Wiley and Sons, Canada, 217–219, 1987.

Goetz, S. J., Wright, R. K., Smith, A. J., Zinecker, E., and Schaub, E.: IKONOS imagery for resource management: tree cover, impervious surfaces, and riparian buffer analyses in the mid-Atlantic region, Remote Sens. Environ., 88, 195–208, doi:10.1016/j.rse.2003.07.010, 2003.

Groffman, P. M., Law, N. L., Belt, K. T., Band, L. E., and Fisher, G. T.: Nitrogen fluxes and retention in urban watershed ecosystems, Ecosystems, 7, 393–403, doi:10.1007/s10021-003-0039-x, 2004.

Harris, C., Oom, B. M., and Diamond, R. E.: A preliminary investigation of the oxygen and hydrogen isotope hydrology of the greater Cape Town area and an assessment of the potential for using stable isotopes as tracers, Water Sa, 25, 15–24, 1999.

Harrison, M. D., Groffman, P. M., Mayer, P. M., Kaushal, S. S., and Newcomer, T. A.: Denitrification in alluvial wetlands in an urban landscape, J. Environ. Qual., 40, 634–646, doi:10.2134/jeq2010.0335, 2011.

Harrison, M. D., Miller, A. J., Groffman, P. M., Mayer, P. M., and Kaushal, S. S.: Hydrologic controls on nitrogen and phosphorous dynamics in relict oxbow wetlands adjacent to an urban restored stream, J. Am. Water Resour. As., 50, 1365–1382, doi:10.1111/jawr.12193, 2014.

Helsel, D. R. and Hirsch, R. M.: Statistical Methods in Water Resources, Elsevier, Amsterdam, Netherlands, ISBN: 978-0-444-88528-9, 1992.

Helsel, D. R. and Hirsch, R. M.: Statistical methods in water resources, in: Techniques of Water-Resources Investigations of the United States Geological Survey Book 4, Hydrologic Analysis and Interpretation, Book 4, chapter A3. U.S., Geological Survey, 522 pp., 2002.

Hill, A. R.: Stream phosphorus exports from watersheds with contrasting land uses in southern Ontario, Water Resour. Bull., 17, 627–634, 1981.

Hope, D., Billett, M. F., and Cresser, M. S.: A review of the export of carbon in river water – fluxes and processes, Environ. Pollut., 84, 301–324, doi:10.1016/0269-7491(94)90142-2, 1994.

Hudson, N., Baker, A., Ward, D., Reynlds, D. M., Brunsdon, C., Carliell-Marquet, C., and Browning, S.: Can fluorescence spectrometry be used as a surrogate for the Biochemical Oxygen Demand (BOD) test in water quality assessment?, An example from South West England, Sci. Total Environ., 391, 149–158, doi:10.1016/j.scitotenv.2007.10.054, 2008.

Huguet, A., Vacher, L., Relexans, S., Saubusse, S., Froidefond, J. M., and Parlanti, E.: Properties of fluorescent dissolved organic matter in the Gironde Estuary, Org. Geochem., 40, 706–719, doi:10.1016/j.orggeochem.2009.03.002, 2009.

Jordan, T. E., Correll, D. L., and Weller, D. E.: Relating nutrient discharges from watersheds to land use and streamflow variability, Water Resour. Res., 33, 2579–2590, doi:10.1029/97wr02005, 1997.

Kaushal, S. S. and Belt, K. T.: The urban watershed continuum: evolving spatial and temporal dimensions, Urban Ecosyst., 15, 409–435, doi:10.1007/s11252-012-0226-7, 2012.

Kaushal, S. S., Groffman, P. M., Band, L. E., Shields, C. A., Morgan, R. P., Palmer, M. A., Belt, K. T., Swan, C. M., Findlay, S. E. G., and Fisher, G. T.: Interaction between urbanization and climate variability amplifies watershed nitrate export in Maryland, Environ. Sci. Technol., 42, 5872–5878, doi:10.1021/es800264f, 2008a.

Kaushal, S. S., Groffman, P. M., Mayer, P. M., Striz, E., and Gold, A. J.: Effects of stream restoration on denitrification in an urbanizing watershed, Ecol. Appl., 18, 789–804, doi:10.1890/07-1159.1, 2008b.

Kaushal, S. S., Groffman, P. M., Band, L. E., Elliott, E. M., Shields, C. A., and Kendall, C.: Tracking nonpoint source nitrogen pollution in human-impacted watersheds, Environ. Sci. Technol., 45, 8225–8232, doi:10.1021/es200779e, 2011.

Kaushal, S. S., Delaney-Newcomb, K., Findlay, S. E. G., Newcomer, T. A., Duan, S., Pennino, M. J., Sivirichi, G. M., Sides-Raley, A. M., Walbridge, M. R., and Belt, K. T.: Longitudinal patterns in carbon and nitrogen fluxes and stream metabolism along an urban watershed continuum, Biogeochemistry, 121, 23–44, doi:10.1007/s10533-014-9979-9, 2014a.

Kaushal, S. S., Mayer, P. M., Vidon, P. G., Smith, R. M., Pennino, M. J., Duan, S., Newcomer, T. A., Welty, C., and Belt, K. T.: Land use and climate variability amplify carbon, nutrient, and contaminant pulses: a review with management implications, J. Am. Water Resour. As., 50, 585–614, 2014b.

Kaushal, S. S., McDowell, W. H., and Wollheim, W. M.: Tracking evolution of urban biogeochemical cycles: past, present, and future, Biogeochemistry, 121, 1–21, doi:10.1007/s10533-014-0014-y, 2014c.

Kaushal, S. S., McDowell, W. H., Wollheim, W. M., Johnson, T. A. N., Mayer, P. M., Belt, K. T., and Pennino, M. J.: Urban evolution: the role of water, Water, 7, 4063–4087, doi:10.3390/w7084063, 2015.

Kendall, C. and Coplen, T. B.: Distribution of oxygen-18 and deuterium in river waters across the United States, Hydrol. Process., 15, 1363–1393, doi:10.1002/hyp.217, 2001.

Kendall, C., Elliott, E. M., and Wankel, S. D.: Tracing anthropogenic inputs of nitrogen to ecosystems, in: Stable Isotopes in Ecology and Environmental Science, 2nd edn., Blackwell Publishing Ltd, Oxford, UK, 375–449, doi:10.1002/9780470691854.ch12, 2007.

Konrad, C. P., Booth, D. B., and Burges, S. J.: Effects of urban development in the Puget Lowland, Washington, on interannual streamflow patterns: consequences for channel form and streambed disturbance, Water Resour. Res., 41, W07009, doi:10.1029/2005wr004097, 2005.

Leopold, L. B.: Hydrology for Urban Land Planning: a Guidebook on the Hydrologic Effects of Urban Land Use, U.S. Geological Survey Circular 554, U.S. Geological Survey, Washington, DC, 1968.

Lewis, D. B. and Grimm, N. B.: Hierarchical regulation of nitrogen export from urban catchments: interactions of storms and landscapes, Ecol. Appl., 17, 2347–2364, doi:10.1890/06-0031.1, 2007.

Lindner, G. A. and Miller, A. J.: Numerical modeling of stage-discharge relationships in urban streams, J. Hydrol. Eng., 17, 590–596, doi:10.1061/(asce)he.1943-5584.0000459, 2012.

Line, D. E., White, N. M., Osmond, D. L., Jennings, G. D., and Mojonnier, C. B.: Pollutant export from various land uses in the upper Neuse River Basin, Water Environ. Res., 74, 100–108, doi:10.2175/106143002x139794, 2002.

Lloyd, C. E. M., Freer, J. E., Collins, A. L., Johnes, P. J., and Jones, J. I.: Methods for detecting change in hydrochemical time series in response to targeted pollutant mitigation in river catchments, J. Hydrol., 514, 297–312, doi:10.1016/j.jhydrol.2014.04.036, 2014.

Loperfido, J. V., Noe, G. B., Jarnagin, S. T., and Hogan, D. M.: Effects of distributed and centralized stormwater best management practices and land cover on urban stream hydrology at the catchment scale, J. Hydrol., 519, 2584–2595, doi:10.1016/j.jhydrol.2014.07.007, 2014.

Mayer, P. M., Reynolds, S. K., McCutchen, M. D., and Canfield, T. J.: Meta-analysis of nitrogen removal in riparian buffers, J. Environ. Qual., 36, 1172–1180, doi:10.2134/jeq2006.0462, 2007.

McKnight, D. M., Boyer, E. W., Westerhoff, P. K., Doran, P. T., Kulbe, T., and Andersen, D. T.: Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity, Limnol. Oceanogr., 46, 38–48, 2001.

McMillan, S. K. and Vidon, P. G.: Taking the pulse of stream restoration practices: moving towards healthier streams, Hydrol. Process., 28, 398–400, doi:10.1002/hyp.10092, 2014.

Meierdiercks, K. L., Smith, J. A., Baeck, M. L., and Miller, A. J.: Analyses of urban drainage network structure and its impact on hydrologic response, J. Am. Water Resour. As., 46, 932–943, doi:10.1111/j.1752-1688.2010.00465.x, 2010.

Mulholland, P. J. and Kuenzler, E. J.: Organic-carbon export from upland and forested wetland watersheds, Limnol. Oceanogr., 24, 960–966, 1979.

Newcomer, J. T. A., Kaushal, S. S., Mayer, P. M., Groffman, P. M., and Grese, M.: Effects of integrated stormwater management and stream restoration on nitrogen uptake and denitrification in streams, Biogeochemistry, 121, 81–106, doi:10.1007/s10533-014-9999-5, 2014.

Newcomer, T. A., Kaushal, S. S., Mayer, P. M., Shields, A. R., Canuel, E. A., Groffman, P. M., and Gold, A. J.: Influence of natural and novel organic carbon sources on denitrification in forest, degraded urban, and restored streams, Ecol. Monogr., 82, 449–466, doi:10.5061/dryad.4gk00, 2012.

Nixon, S. W., Ammerman, J. W., Atkinson, L. P., Berounsky, V. M., Billen, G., Boicourt, W. C., Boynton, W. R., Church, T. M., Ditoro, D. M., Elmgren, R., Garber, J. H., Giblin, A. E., Jahnke, R. A., Owens, N. J. P., Pilson, M. E. Q., and Seitzinger, S. P.: The fate of nitrogen and phosphorus at the land sea margin of the North Atlantic Ocean, Biogeochemistry, 35, 141–180, doi:10.1007/bf02179826, 1996.

NOAA: The National Atmospheric and Ocean Administration's National Climatic Data Center, available at: http://www.ncdc.noaa.gov/cdo-web (last access: 6 June 2014), 2014.

Passeport, E., Vidon, P., Forshay, K. J., Harris, L., Kaushal, S. S., Kellogg, D. Q., Lazar, J., Mayer, P., and Stander, E. K.: Ecological engineering practices for the reduction of excess nitrogen in human-influenced landscapes: a guide for watershed managers, Environ. Manage., 51, 392–413, doi:10.1007/s00267-012-9970-y, 2013.

Paul, M. J. and Meyer, J. L.: Streams in the urban landscape, Annu. Rev. Ecol. Syst., 32, 333–365, doi:10.1146/annurev.ecolsys.32.081501.114040, 2001.

Pennino, M. J., Kaushal, S. S., Beaulieu, J. J., Mayer, P. M., and Arango, C. P.: Effects of urban stream burial on nitrogen uptake and ecosystem metabolism: implications for watershed nitrogen and carbon fluxes, Biogeochemistry, 121, 247–269, doi:10.1007/s10533-014-9958-1, 2014.

Petrone, K. C.: Catchment export of carbon, nitrogen, and phosphorus across an agro-urban land use gradient, Swan-Canning River system, southwestern Australia, J. Geophys. Res.-Biogeosciences, G01016 doi:10.1029/2009jg001051, 2010.

Petrone, K. C., Fellman, J. B., Hood, E., Donn, M. J., and Grierson, P. F.: The origin and function of dissolved organic matter in agro-urban coastal streams, J. Geophys. Res.-Biogeo., 116, G01028, doi:10.1029/2010jg001537, 2011.

Phillips, D. L.: Mixing models in analyses of diet using multiple stable isotopes: a critique, Oecologia, 127, 166–170, doi:10.1007/s004420000571, 2001.

Poff, N. L., Bledsoe, B. P., and Cuhaciyan, C. O.: Hydrologic variation with land use across the contiguous United States: geomorphic and ecological consequences for stream ecosystems, Geomorphology, 79, 264–285, doi:10.1016/j.geomorph.2006.06.032, 2006.

Qian, Y., Migliaccio, K. W., Wan, Y. S., and Li, Y. C.: Trend analysis of nutrient concentrations and loads in selected canals of the southern indian river lagoon, florida, Water Air Soil Pollut., 186, 195–208, doi:10.1007/s11270-007-9477-y, 2007.

R: A Language and Environment for Statistical Computing, available at: http://www.R-project.org (last access: 9 September 2014), 2013.

Runkel, R. L.: Revisions to LOADEST, available at: http://water.usgs.gov/software/loadest/doc (last access: 9 September 2014), 2013.

Runkel, R. L., Crawford, C. G., and Cohn, T. A.: Load Estimator (LOADEST): a FORTRAN program for estimating constituent loads in streams and rivers, in: Techniques and Methods Book 4, U.S. Geological Survey, Reston, Virginia, 75 pp., 2004.

Rustomji, P. and Wilkinson, S. N.: Applying bootstrap resampling to quantify uncertainty in fluvial suspended sediment loads estimated using rating curves, Water Resour. Res., 44, W09435, doi:10.1029/2007wr006088, 2008.

Ryan, R. J., Welty, C., and Larson, P. C.: Variation in surface water-groundwater exchange with land use in an urban stream, J. Hydrol., 392, 1–11, doi:10.1016/j.jhydrol.2010.06.004, 2010.

Schwartz, S. S. and Naiman, D. Q.: Bias and variance of planning level estimates of pollutant loads, Water Resour. Res., 35, 3475–3487, doi:10.1029/1999wr900107, 1999.

Shields, C. A., Band, L. E., Law, N., Groffman, P. M., Kaushal, S. S., Savvas, K., Fisher, G. T., and Belt, K. T.: Streamflow distribution of non-point source nitrogen export from urban-rural catchments in the Chesapeake Bay watershed, Water Resour. Res., 44, W09416, doi:10.1029/2007wr006360, 2008.

Sigman, D. M., Casciotti, K. L., Andreani, M., Barford, C., Galanter, M., and Bohlke, J. K.: A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater, Anal. Chem., 73, 4145–4153, doi:10.1021/ac010088e, 2001.

Silva, S. R., Ging, P. B., Lee, R. W., Ebbert, J. C., Tesoriero, A. J., and Inkpen, E. L.: Forensic applications of nitrogen and oxygen isotopes in tracing nitrate sources in urban environments, Environ. Forensics, 3, 125–130, doi:10.1006/enfo.2002.0086, 2002.

Sivirichi, G. M., Kaushal, S. S., Mayer, P. M., Welty, C., Belt, K. T., Newcomer, T. A., Newcomb, K. D., and Grese, M. M.: Longitudinal variability in streamwater chemistry and carbon and nitrogen fluxes in restored and degraded urban stream networks, J. Environ. Monitor., 13, 288–303, doi:10.1039/c0em00055h, 2011.

Smith, B. K., Smith, J. A., Baeck, M., Villarini, L. G., and Wright, D. B.: Spectrum of storm event hydrologic response in urban watersheds, Water Resour. Res., 49, 2649–2663, doi:10.1002/wrcr.20223, 2013.

Smith, B. K., Smith, J. A., Baeck, M. L., and Miller, A. J.: Exploring storage and runoff generation processes for urban flooding through a physically based watershed model, Water Resour. Res., 51, 1552–1569, doi:10.1002/2014wr016085, 2015.

Sobota, D. J., Harrison, J. A., and Dahlgren, R. A.: Influences of climate, hydrology, and land use on input and export of nitrogen in California watersheds, Biogeochemistry, 94, 43–62, doi:10.1007/s10533-009-9307-y, 2009.

Stolpe, B., Guo, L., Shiller, A. M., and Hassellov, M.: Size and composition of colloidal organic matter and trace elements in the Mississippi River, Pearl River and the northern Gulf of Mexico, as characterized by flow field-flow fractionation, Mar. Chem., 118, 119–128, doi:10.1016/j.marchem.2009.11.007, 2010.

Sudduth, E. B., Hassett, B. A., Cada, P., and Bernhardt, E. S.: Testing the Field of Dreams Hypothesis: functional responses to urbanization and restoration in stream ecosystems, Ecol. Appl., 21, 1972–1988, 2011.

Tate, C. M. and Meyer, J. L.: The influence of hydrologic conditions and successional state on dissolved organic-carbon export from forested watersheds, Ecology, 64, 25–32, doi:10.2307/1937325, 1983.

Utz, R. M., Eshleman, K. N., and Hilderbrand, R. H.: Variation in physicochemical responses to urbanization in streams between two Mid-Atlantic physiographic regions, Ecol. Appl., 21, 402–415, doi:10.1890/09-1786.1, 2011.

Walsh, C. J., Roy, A. H., Feminella, J. W., Cottingham, P. D., Groffman, P. M., and Morgan, R. P.: The urban stream syndrome: current knowledge and the search for a cure, J. N. Am. Benthol. Soc., 24, 706–723, doi:10.1899/0887-3593(2005)024[0706:tussck]2.0.CO;2, 2005.

Waszkowiak, K. and Szymandera-Buszka, K.: Effect of storage conditions on potassium iodide stability in iodised table salt and collagen preparations, Int. J. Food Sci. Tech., 43, 895–899, doi:10.1111/j.1365-2621.2007.01538.x, 2008.

Williard, K. W. J., DeWalle, D. R., Edwards, P. J., and Sharpe, W. E.: O-18 isotopic separation of stream nitrate sources in mid-Appalachian forested watersheds, J. Hydrol., 252, 174–188, doi:10.1016/s0022-1694(01)00459-0, 2001.

Worrall, F., Davies, H., Bhogal, A., Lilly, A., Evans, M., Turner, K., Burt, T., Barraclough, D., Smith, P., and Merrington, G.: The flux of DOC from the UK – predicting the role of soils, land use and net watershed losses, J. Hydrol., 448, 149–160, doi:10.1016/j.jhydrol.2012.04.053, 2012.

Ziemer, R. R. and Lisle, T. E.: Chapter 3. Hydrology, in: River Ecology and Management: Lessons from the Pacific Coastal Ecoregion, edited by: Naiman, R. J. and Robert, E. Bilby, Springer-Verlag, New York, 43–68, 1998.

Zsolnay, A., Baigar, E., Jimenez, M., Steinweg, B., and Saccomandi, F.: Differentiating with fluorescence spectroscopy the sources of dissolved organic matter in soils subjected to drying, Chemosphere, 38, 45–50, doi:10.1016/s0045-6535(98)00166-0, 1999.

Table 1. Site characteristics for the four urban watersheds.

Site	Status	Median Year of Development*	Stream Length (km)	Area (km^2)	ISC (%)	Range of Flows Sampled ($L s^{-1}$)	Range of Flows ($L s^{-1}$)	Drainage area controlled by SWM (%)
Minebank Run (MBR)	Older Urban Restored	1959	4.6	5.3	29.4	10–396	4.8–3115	17.8
Red Run (RRN)	Newer Urban with SWM	1998	7.7	19.1	20.5	65–2714	17–16 930	40.4
Powder Mill Run (PMR)	Older Urban with No Management	1954	4.8	9.4	44.3	15–934	12–9061	0.7
Dead Run (DRN)	Older Urban with SWM	1963	8.0	14.3	45.7	17–1897	12–20 274	32.5

Land use Data from NLCD 2001, ISC = Impervious surface cover; %ISC is averaged from the 2001 National Land cover Database (NLCD), a two meter satellite imagery obtained from the University of Vermont, and a roads and buildings polygon layer for Baltimore County; SWM = stormwater management.

[*] Median Year of Development is based on the median year built for houses within each watershed. Further information on land use can be found in the Supplement.

Table 2. Comparisons of water, carbon, and nitrate sources (mean ± SE) among the four urban watersheds.

	MBR	RRN	PMR	DRN
Water Isotopes (‰)				
δ^2H-H_2O	-43 ± 1.8^{a}	-44 ± 2.0^{a}	-43 ± 2.5^{a}	-43 ± 3.0^{a}
δ^{18}O-H_2O	-6.7 ± 0.2^{a}	-6.9 ± 0.2^{a}	-6.6 ± 0.3^{a}	-6.6 ± 0.4^{a}
% Groundwater	50 ± 5^{a}	57 ± 6^{a}	47 ± 6^{a}	40 ± 7^{a}
% Rainwater	50 ± 5^{a}	43 ± 6^{a}	53 ± 6^{a}	60 ± 7^{a}
Carbon Quality				
HIX	0.87 ± 0.01^{a}	0.81 ± 0.02^{b}	0.80 ± 0.01^{c}	0.83 ± 0.02^{ab}
BIX	0.73 ± 0.04^{a}	0.64 ± 0.03^{b}	0.75 ± 0.04^{a}	0.78 ± 0.04^{a}
FI	1.20 ± 0.05^{a}	1.15 ± 0.05^{bc}	1.16 ± 0.05^{ac}	1.26 ± 0.05^{ac}
P/H Ratio	0.73 ± 0.07^{ab}	0.66 ± 0.06^{a}	1.11 ± 0.10^{c}	0.89 ± 0.10^{b}
Nitrate Isotopes (‰)				
δ^{15}N-NO_3^-	7.0 ± 0.2^{ab}	6.3 ± 0.2^{a}	8.1 ± 0.2^{c}	7.5 ± 0.2^{bc}
δ^{18}O-NO_3^-	5.0 ± 0.4^{a}	4.0 ± 0.3^{b}	5.9 ± 0.6^{a}	8.0 ± 0.9^{c}
% Wastewater	53 ± 1.0^{a}	51 ± 1.1^{a}	56 ± 1.2^{b}	52 ± 1.8^{ab}
% Atmospheric	8.7 ± 1.0^{ab}	7.6 ± 1.0^{a}	9.4 ± 1.7^{ab}	15 ± 2.5^{b}
% Nitrification	38 ± 0.7^{a}	41 ± 0.5^{b}	34 ± 0.7^{c}	33 ± 0.9^{c}

MBR = Minebank Run, RRN = Red Run, PMR = Powder Mill Run, DRN = Dead Run.
Different letters (a, b, or c) indicate significant differences ($p < 0.05$), based on pairwise comparisons on three years of routinely sampled data. HIX = Humification Index; BIX = Biological Freshness Index; FI = Fluorescence Index; P/H Ratio = Protein-to-Humic Ratio.

Table 3. Annual runoff, C, N and P loads (mean ± 95 % confidence intervals) for 2010, 2011, and 2012 calendar years.

	Year	MBR	RRN	PMR	DRN
Runoff (mm yr^{-1})					
	2010	522 ± 72	325 ± 23	497 ± 83	625 ± 117
	2011	647 ± 88	504 ± 114	639 ± 110	851 ± 176
	2012	412 ± 75	382 ± 61	498 ± 105	564 ± 164
	MEAN	527 ± 45^{a}	404 ± 44^{b}	545 ± 58^{ac}	680 ± 89^{c}
Carbon (kg ha^{-1} yr^{-1})					
DOC	2010	6.7 ± 1.3	6.2 ± 0.8	15 ± 3	28 ± 7
	2011	9.1 ± 1.6	22 ± 8	27 ± 5	57 ± 15
	2012	5.7 ± 1.5	11 ± 3	17 ± 4	33 ± 12
	MEAN	7.2 ± 1^{a}	13 ± 3^{b}	20 ± 2^{c}	39 ± 7^{d}
TOC	2010	NA	NA	NA	NA
	2011	8.1 ± 1.2	26 ± 11	40 ± 11	45 ± 11
	2012	5.1 ± 1.1	14 ± 5	26 ± 9	30 ± 10
	MEAN*	6.6 ± 0.5^{a}	20 ± 4^{b}	33 ± 5^{c}	38 ± 5^{c}
Nitrogen (kg ha^{-1} yr^{-1})					
NO_3^-	2010	4.1 ± 0.3	3.7 ± 0.2	6.6 ± 0.9	4.1 ± 0.6
	2011	4.6 ± 0.4	4.1 ± 0.4	8.0 ± 1.1	5.3 ± 0.8
	2012	2.9 ± 0.3	3.7 ± 0.2	6.3 ± 1.1	3.6 ± 0.7
	MEAN	3.9 ± 0.2^{a}	3.8 ± 0.2^{a}	7.0 ± 0.6^{b}	4.3 ± 0.4^{a}
TN	2010	4.8 ± 0.4	4.4 ± 0.3	9.1 ± 1.5	6.7 ± 1.2
	2011	5.4 ± 0.5	5.4 ± 0.7	11.6 ± 2.1	8.8 ± 1.6
	2012	3.4 ± 0.5	4.6 ± 0.7	9.1 ± 2.1	5.9 ± 1.6
	MEAN	4.5 ± 0.3^{a}	4.8 ± 0.3^{a}	9.9 ± 1.1^{b}	7.1 ± 0.9^{c}
Phosphorus (g ha^{-1} yr^{-1})					
PO_4^{-3}	2010	60 ± 9	58 ± 6	134 ± 22	167 ± 37
	2011	75 ± 11	120 ± 29	172 ± 30	255 ± 62
	2012	47 ± 10	66 ± 11	134 ± 33	122 ± 40
	MEAN	61 ± 6^{a}	81 ± 11^{b}	147 ± 17^{c}	181 ± 28^{c}
TP	2010	138 ± 19	160 ± 17	290 ± 51	330 ± 60
	2011	202 ± 29	431 ± 136	379 ± 72	454 ± 92
	2012	143 ± 30	314 ± 89	298 ± 66	306 ± 76
	MEAN	161 ± 15^{a}	302 ± 54^{b}	322 ± 37^{b}	363 ± 45^{b}
Wastewater Indicator Anions (g ha^{-1} yr^{-1})					
F^-	2010	230 ± 11	b.d.	$2.1 \times 10^4 \pm 1.0 \times 10^4$	726 ± 87
	2011	235 ± 10	b.d.	$1.8 \times 10^4 \pm 5.5 \times 10^3$	606 ± 91
	2012	67 ± 5	b.d.	$5.4 \times 10^3 \pm 3.5 \times 10^3$	281 ± 45
	MEAN	177 ± 5^{a}		$1.5 \times 10^4 \pm 4.0 \times 10^{3b}$	583 ± 45^{c}
I^-	2010	19 ± 1	21 ± 1	20 ± 2	50 ± 7
	2011	29 ± 2	41 ± 8	39 ± 4	85 ± 13
	2012	16 ± 1	24 ± 4	22 ± 2	46 ± 8
	MEAN	21 ± 1^{a}	29 ± 3^{b}	27 ± 2^{b}	60 ± 6^{c}

MBR = Minebank Run, RRN = Red Run, PMR = Powder Mill Run, DRN = Dead Run.
Different letters (a, b, c, or d) indicate significant differences ($p < 0.05$), based on daily loads.
DOC = dissolved organic C; TOC = total organic C; TN = total nitrogen; TP = total phosphorus.
b.d. = below detection. *Note that this range is from 2011–2012, unlike the others.

Table 4. Hydrologic Flashiness Metrics (mean ± SE).

	Water-shed area (km^{2})	% ISC	Mean peak flow runoff (mm d^{-1})	Monthly CV (%) of Peak Runoff	Freq. peaks per month > 3 × monthly median *Q*	Mean Hydrograph Duration (h)	Mean Lag Time (h)	Avg. Monthly Flash Index
MBR	5.3	21.9	9.4 ± 1.0^{a}	92 ± 6^{ab}	5.7 ± 0.4^{ac}	40 ± 1.7^{a}	4.7 ± 0.3^{a}	0.9 ± 0.1^{a}
RRN	19.1	14.6	13.2 ± 1.9^{b}	63 ± 8^{b}	2.2 ± 0.3^{b}	64 ± 2.4^{b}	4.5 ± 0.4^{a}	0.5 ± 0.0^{b}
PMR	9.4	35.5	55.4 ± 5.8^{c}	104 ± 7^{a}	5.3 ± 0.5^{a}	30 ± 1.4^{c}	5.1 ± 0.3^{a}	1.0 ± 0.1^{a}
DRN	14.3	39.3	44.9 ± 4.5^{c}	116 ± 7^{a}	7.0 ± 0.5^{c}	50 ± 1.5^{d}	4.7 ± 0.2^{a}	1.2 ± 0.1^{c}

MBR = Minebank Run, RRN = Red Run, PMR = Powder Mill Run, DRN = Dead Run.
Different letters (a, b, c, or d) indicate significant differences ($p < 0.05$) based on pairwise comparisons of three years of mean monthly flashiness metrics.
ISC = Impervious Surface Cover; CV = Coefficient of Variation; *Q* = discharge; Lag Time = time between rainfall centroid and peak runoff; Flash Index = average daily change in mean daily streamflow, per month, divided by the mean monthly flow.

Table 5. F75 metric: the runoff below which 75 % of nutrients are exported.

Site	F75 DOC $(\mathrm{mm\,d^{-1}})$	F75 TOC $(\mathrm{mm\,d^{-1}})$	F75 NO_3^- $(\mathrm{mm\,d^{-1}})$	F75 TN $(\mathrm{mm\,d^{-1}})$	F75 PO_4^{-3} $(\mathrm{mm\,d^{-1}})$	F75 TP $(\mathrm{mm\,d^{-1}})$	F75 I^- $(\mathrm{mm\,d^{-1}})$	F75 F^- $(\mathrm{mm\,d^{-1}})$
MBR	16.1	15.1	6.9	7.3	12.4	12.4	4.6	2.8
RRN	34.1	44.5	2.2	3.1	11.7	23.7	7.1	NA
PMR	22.8	38.1	14.0	20.5	20.8	20.8	8.6	34.0
DRN	57.3	37.4	25.9	28.3	39.3	29.8	17.9	16.5

MBR = Minebank Run, RRN = Red Run, PMR = Powder Mill Run, DRN = Dead Run.
DOC = dissolved organic C; TOC = total organic C; TN = total nitrogen; TP = total phosphorus; similar to Shields et al. (2008, Table 3).

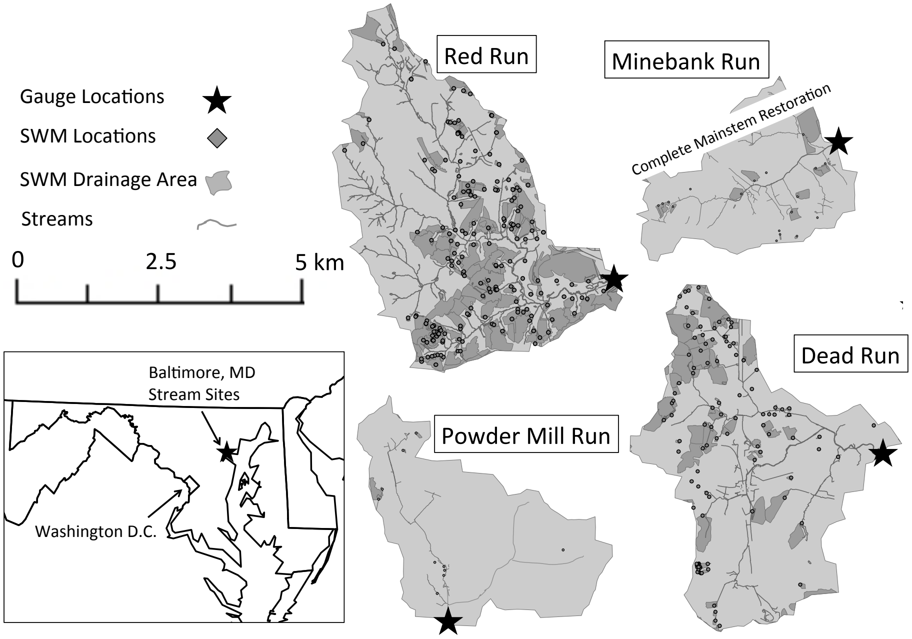

Figure 1. Site map showing the four stream sites in the Baltimore, MD region and the stormwater management (SWM) locations within each watershed. SWM features are based on 2009 data from the Baltimore County Department of Environmental Protection and Sustainability.

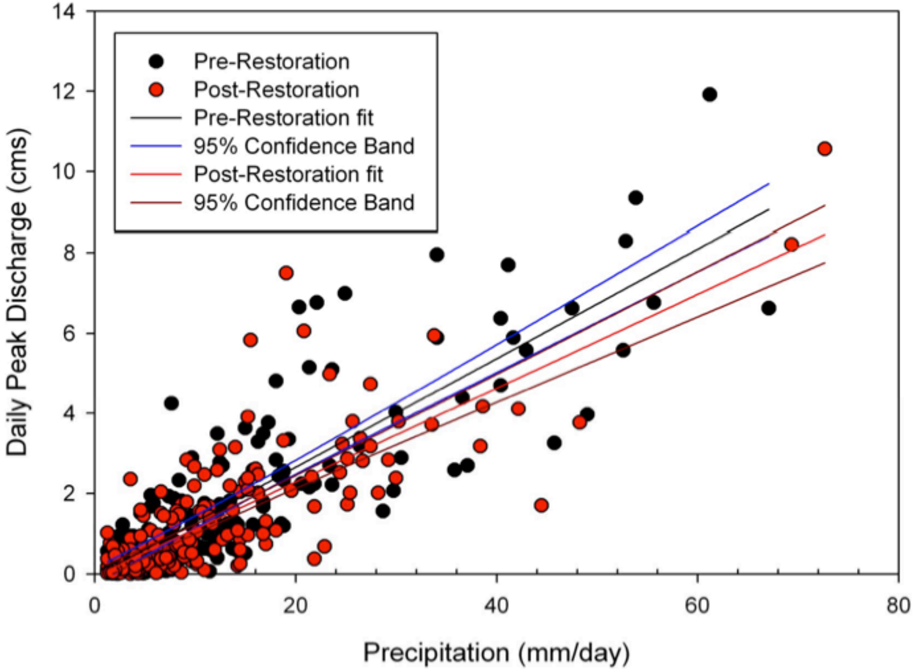

Figure 2. Effective precipitation and effective discharge for Minebank Run. Best-fit regression lines and 95 % confidence lines included.

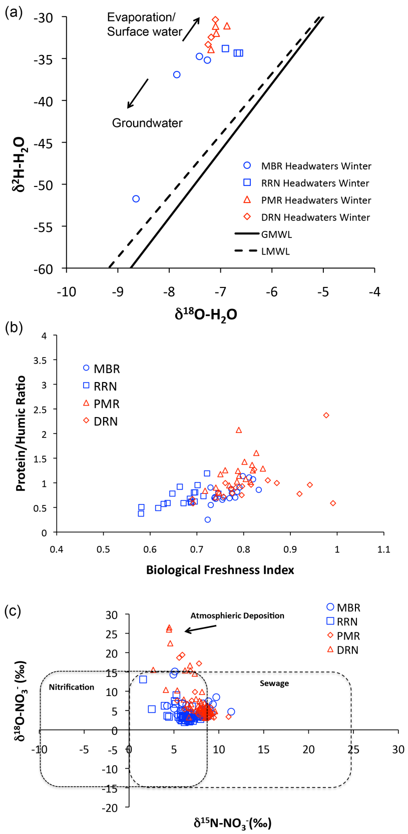

Figure 3. Comparison of **(a)** water isotopes (δ^2H-H$_2$O vs. δ^{18}O-H$_2$O), **(b)** C quality metrics (Biological Freshness Index vs. Protein-to-Humic Ratio), and **(c)** nitrate isotopes (δ^{15}N-NO$_3^-$ vs. δ^{18}O-NO$_3^-$). GMWL = Global Meteoric Water Line, LMWL = Local Meteoric Water Line (Craig, 1961; Kendall and Coplen, 2001).

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◀| |▶
◀ ▶
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

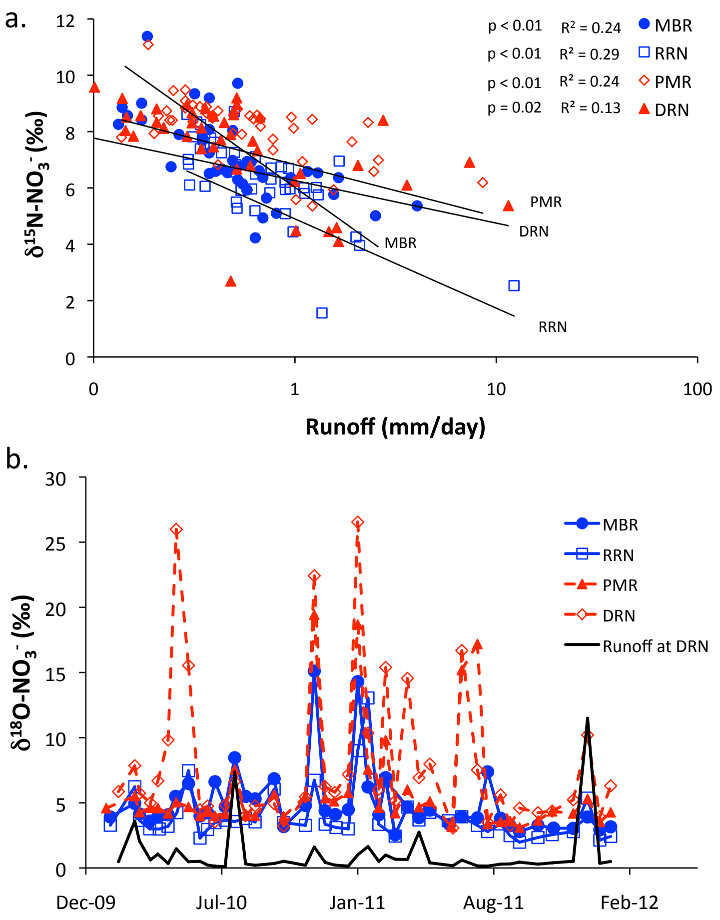

Figure 4. A comparison of **(a)** runoff vs. δ^{15}N-NO$_3^-$ and **(b)** runoff and δ^{18}O-NO$_3^-$ vs. time.

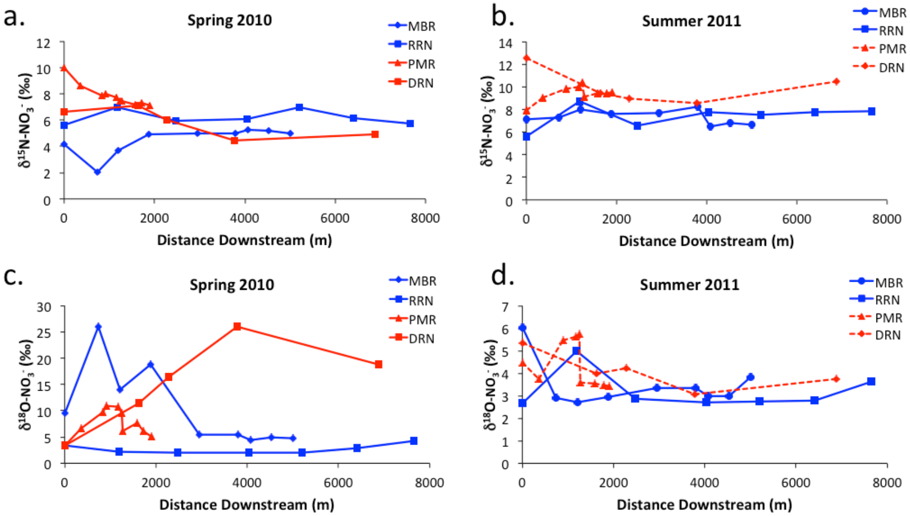

Figure 5. Longitudinal patterns in δ^{15}N-NO$_3^-$ and δ^{18}O-NO$_3^-$ during spring **(a, c)** and summer **(b, d)** seasons.

Title Page
Abstract
Introduction
Conclusions
References
Tables
Figures
◀◀
▶▶
◀
▶
Back
Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

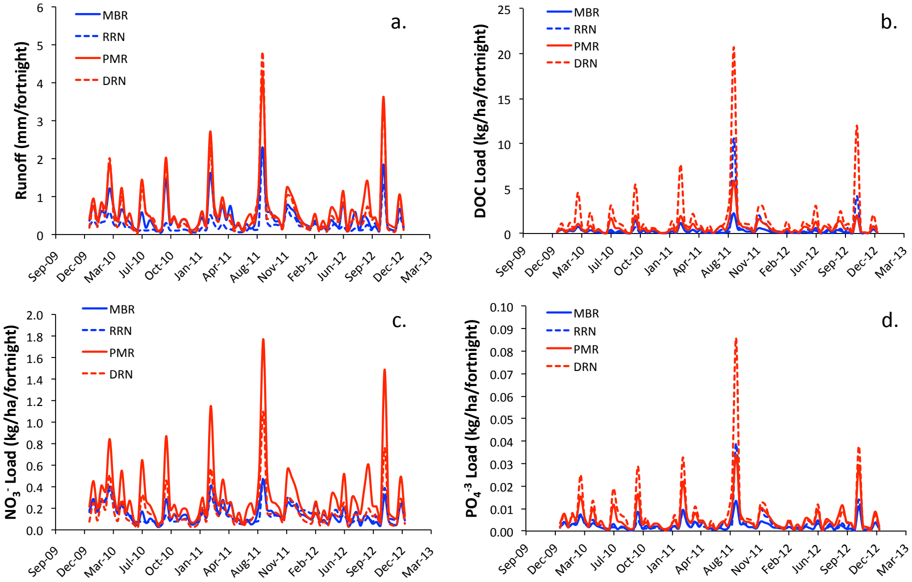

Figure 6. Routinely sampled **(a)** runoff, **(b)** DOC loads, **(c)** NO_3^- loads, and **(d)** PO_4^{-3} loads over time.

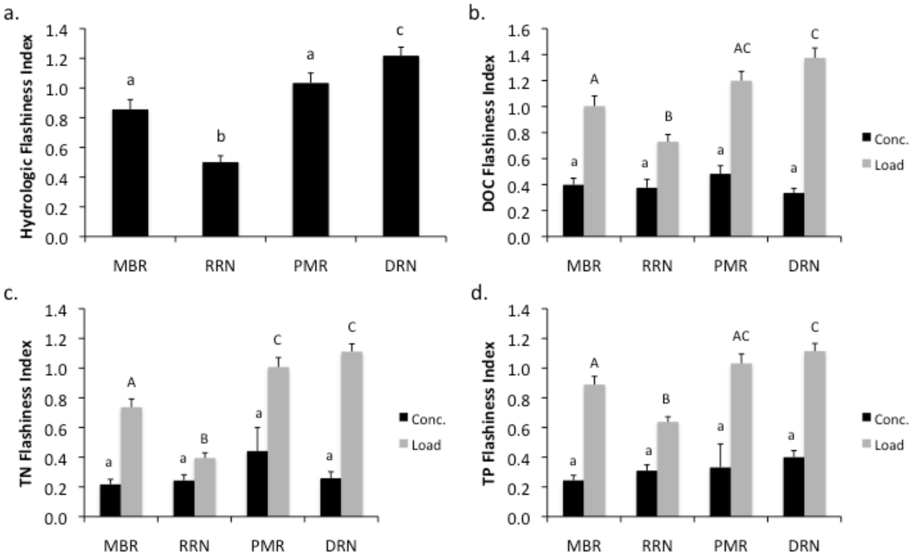

Figure 7. Comparison of the Flashiness Index for **(a)** runoff, **(b)** dissolved organic carbon (DOC) concentration and load, **(c)** Total nitrogen (TN) concentration and load, and **(d)** Total phosphorus (TP) concentration and load. Conc. = Concentration. Error bars are standard errors of the mean. $N = 36$, from averaging the monthly flashiness index over 3 years. Flashiness Index = average change in daily load or routinely sampled concentration per month, divided by the mean monthly load or concentration per month.

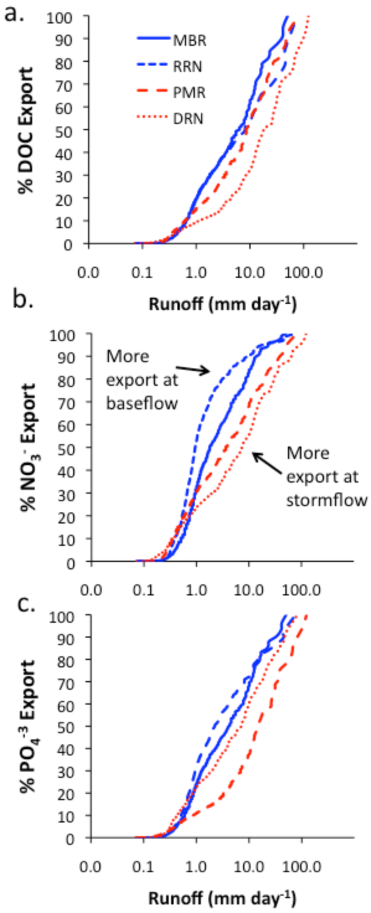

Figure 8. Nutrient duration curves for percent **(a)** DOC, **(b)** NO$_3^-$, and **(c)** PO$_4^{-3}$ daily export.