



Supplement of

Stream restoration and sewers impact sources and fluxes of water, carbon, and nutrients in urban watersheds

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1 1 Methods

2 **1.1 Site Description**

3 Red Run (RRN), Powder Mill Run (PMR), and Dead Run (DRN) are all part of 4 the Gwynns Falls watershed, which is monitored by Baltimore Ecosystem Study's Long 5 Term Ecological Research (www.beslter.org). Previous information on runoff and 6 nutrient export in these watersheds can be found elsewhere (Groffman et al., 2004; 7 Kaushal et al., 2008a; Kaushal et al., 2011; Duan et al., 2012). Specific land use and 8 other site characteristics of each watershed are found in Figure S1 and listed in Table S1. 9 Minebank Run is an urban headwater stream located in Towson, MD. The 10 headwater reach of Minebank Run was restored in 1999 and the lower reach in 2005 11 (Doheny et al., 2006). The stream restorations at MBR consisted of bank stabilization, 12 the addition of riffles and meander features with step-pool habitat, a hydrologically 13 connecting streambed and floodplain wetland, and the planting of trees in the riparian 14 zone (Kaushal et al., 2008b). 15 Red Run, located in Owings Mills, MD, has been gauged by UMBC Center for 16 Urban Environmental Research and Education (CUERE) to measure stream flow since 17 2005. RRN is characterized by newer development and relatively high-density 18 stormwater management (SWM) facilities in both residential and commercial 19 development areas within the watershed. The newer residential and commercial 20 developments in RRN watershed have implemented stormwater detention facilities, 21 draining areas of impervious surfaces, such as detention basins, wet ponds, stormwater 22 bioretention facilities, and sand filters. This watershed also has extensive riparian

1	buffers. The outflows of SWM facilities are either connected to a stream or flow into a
2	forested buffer. Red Run is missing discharge data from July 2011 through September
3	2011, due to construction under the bridge where the gauge is located. For daily flow
4	data, we were able to estimate the missing mean daily flow by creating a linear
5	relationship with nearby USGS gauged streams of similar size and discharge ($R^2 > 0.95$).
6	For the real-time data Flashiness estimates, the missing discharge was left out of the
7	calculations. Also, the Red Run flow data has not been through USGS QA/QC and is
8	based on a provisional rating curve.
9	Powder Mill Run and Dead Run are also subwatersheds of the BES LTER site.
10	Dead Run has 6 USGS stream gauging stations along its stream network, and has had
11	weekly stream chemistry sampling since 1998 (Groffman et al. 2004; Kaushal et al.
12	2008a). The Dead Run watershed has been the focus of numerous eco-hydrological
13	investigations and there exists a rich dataset on nitrogen dynamics (e.g. Groffman et al.,
14	2004; Kaushal et al., 2008a; Kaushal et al., 2011; Newcomer et al., 2012), hydrologic
15	characteristics, and water mass balances (Klocker et al., 2009; Ryan et al., 2010; Ryan et
16	al., 2011; Sivirichi et al., 2011).
17	

1.2 Comparison of Pre- and Post-Restoration Hydrologic Response

Estimating the relationship between effective precipitation (Ppt) and effective peak
discharge (Q_{pk}). 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

1 electronically every 5 minutes, and discharge data were available online, and the high 2 temporal resolution weather data were made available via a request to the USGS. The 3 discharge data were transformed from the original cubic feet per second (cfs) to cubic 4 meters per second (cms) and precipitation was transformed from inches to millimeters. 5 In order to determine effective precipitation and the associated effective 6 discharge, we first removed dates without measureable precipitation or discharge. Of the 7 2283 dates in the study period (2001 - 2008) with data, approximately 800 dates had 8 precipitation. Based upon the remark codes, dates were removed when either 9 precipitation or discharge were estimated leaving 679 dates. An additional series of data 10 were removed for days where less than 1.27 mm (0.05 inches) of precipitation was 11 measured. At this precipitation depth there was no identifiable discharge response, even 12 for cloudbursts with the entire 1.27 mm occurring in a 5 minute period. It was assumed 13 that much of this precipitation was intercepted and could be classified as the initial 14 abstraction. 15 Five (5) storms were found to be multi-day events (meaning that they occurred at 16 night and fell into two calendar days) and were then combined into a single day event. 17 Data for the hydrographs where the peak discharge for a storm was on the falling limb of 18 a precipitation event on the previous day were also removed. Because of low intensity 19 precipitation, 33 storms were removed from the analysis, these were low precipitation 20 intensity drizzle events and a distinct discharge response could not be identified at the 5minute data interval. There were also 20 dates where there were multiple storms during 21 22 that 24-hour period/calendar day. Therefore, the first peak on the hydrograph was

23 selected, along with the associated precipitation occurring up till the peak discharge.

2 **1.3 Stream Chemistry Analysis**

3 During each stream chemistry sampling, measurements of dissolved oxygen 4 (DO), pH, and temperature were recorded. DO and pH meters were calibrated each day 5 before use in the field. All stream chemistry samples were analyzed using standard EPA 6 methods at the National Risk Management Research Lab (NRMRL) in Ada, OK, USA. 7 Water samples requiring filtration were filtered in the lab within 24 hours using a 47mm 8 $(0.45 \,\mu\text{m})$ glass fiber filter, then preserved until analysis. All nitrogen species, except 9 samples for stable isotope analysis, were preserved by acidifying to pH 2 with sulfuric 10 acid and stored frozen in HDPE bottles until analysis. Samples for TOC and DOC were 11 stored in 40 ml glass VOA bottles, preserved by acidifying to pH 2, using phosphoric 12 acid and refrigerated until analysis. NO_3^{-1} isotope samples were filtered and preserved 13 frozen in HDPE bottles. Samples for H₂O isotope analysis were unfiltered and collected 14 for only 1 year during 2010-2011. H₂O isotope samples were unfiltered and collected in 15 a 30 ml glass Qorpak bottle, that was filled and capped under water in the field so that 16 there are no air bubbles or headspace, and then sealed with a Teflon-lined cap. The EPA 17 NRMRL Isotope Ration Mass Spectrometer (IRMS) lab analyzes the δ^2 H and δ^{18} O of 18 water samples following RSKSOP 296. Samples for carbon quality analysis were filtered 19 and saved in amber glass Qorpak vials and kept refrigerated (see further methods below). 20 The rest of the samples were preserved frozen in HDPE bottles until analysis. 21 Fluorescence samples were analyzed within 1-3 weeks. All other samples, besides NO₃⁻ 22 isotopes samples, were analyzed within 1-2 months. Samples for nitrate isotope analysis

were all analyzed on the same date, resulting in the samples being stored frozen from
 seven months to 2 years and 7 months.

3	TKN, NH4 ⁺ , NO3 ⁻ + NO2 ⁻ , ortho-P and Br ⁻ were measured using Lachat flow
4	injection analyses (Lachat Instruments, Loveland, CO USA). Total organic nitrogen
5	(TON) was calculated as TKN of unfiltered water minus ammonium and dissolved
6	organic nitrogen (DON) was calculated as TKN of filtered water minus ammonium (with
7	TKN being the sum of organic nitrogen plus ammonia/ammonium). Total nitrogen (TN)
8	was calculated as TKN plus $NO_3^- + NO_2^-$. NH_4^+ was measured using EPA FIA Method
9	10-107-06-1-A. Br and Iodide were analyzed by EPA FIA Method 10-135-21-2-A. SO ₄
10	was analyzed by FIA Method 10-116-10-1-C. Chloride was analyzed by FIA Method 10-
11	117-07-1-B. H ₂ O isotopes were measured using a high temperature conversion elemental
12	analyzer (tc/ea), a continuous flow unit, and an isotope ratio mass spectrometer (IRMS)
13	(EPA's RSKSOP 296v0). Total organic carbon (TOC) and dissolved organic carbon
14	(DOC) were analyzed using a total organic C analyzer with high-temperature Pt-
15	catalyzed combustion and NDIR detection (Shimadzu TOC-VCPH, Columbia, MD
16	USA). Samples for carbon quality analysis were analyzed on a Fluoromax-4
17	spectrofluorometer (Jobin Yvon Horiba) at the University of Maryland Biogeochemistry
18	Lab.

19

20 **1.4 Fluorescence Analysis**

21 On the day of analysis, samples were allowed to warm to room temperature and 22 placed in a 1 cm quartz cuvette for analysis. Each day that samples were run on the 23 spectrofluoromometer, a blank sample was also run at the beginning of the day using

1	milli-Q water. Between samples, the cuvette was rinsed three times with milli-Q water
2	and then sample rinsed with the next sample, two times. A fluorescence EEMs was
3	collected for each sample and also collected for Milli-Q water as a blank. A full EEMs
4	was also collected for a quinine sulfate standard (10 ppb in 0.1 N H ₂ SO ₄). This quinine
5	sulfate standard can be used when comparing samples run on different instruments and
6	used to monitor instrument drift over time (Del Vecchio and Blough, 2004; Fellman et
7	al., 2009). A scan rate of 4nm/sec was used and the excitation and emission slit widths
8	were 5 nm. The EEMs were collected under the S1/R1 mode to correct for instrument
9	drift. The standard inner-filter corrections (IFC) were not done on most samples because
10	absorbance measurements were not attained for most samples. However, for the samples
11	where absorbance was collected (using scanning spectrophotometer), the IFC was done
12	and it was found that there is $< 5\%$ difference between EEMs with and without IFC.
13	We analyzed fluorescence EEMs for the following indices: the fluorescence
14	index, FI (McKnight et al., 2001) the humification index, HIX (Zsolnay et al., 1999;
15	Huguet et al., 2009), the biological freshness index, BIX (Huguet et al., 2009), and the
16	protein to humic fluorescence intensities ratio (Coble, 1996; Stolpe et al., 2010). FI
17	values are ~ 1.9 for microbial derived fulvic acids and ~1.4 for terrestrial derived fulvic
18	acids sources (McKnight et al., 2001; Cory et al., 2010). BIX values of $< 0.7, 0.8 - 1.0$,
19	or > 1.0 are associated with terrestrial sourced DOM, algal sourced DOM, or aquatic
20	bacterial sources, respectively (Huguet et al., 2009). HIX was used to distinguish the
21	humic or autochthonous nature of the organic matter in the sample (Zsolnay et al., 1999;
22	Ohno, 2002). Higher HIX values suggest DOM of strong humic character and terrestrial
23	origin, while lower values indicate weaker humic character and higher autochthonous

1	sourced DOM. Further details are described in Pennino et al. (2014). Fluorescence EEM
2	peak intensities at specific excitation and emission wavelengths were also used to
3	determine the relative contribution of protein (at excitation 275 nm and emission 340
4	nm), fulvic (at excitation 310 nm and emission 420 nm) and humic (at excitation 350 nm
5	and emission 480 nm) dissolved organic matter (Coble, 1996; Stolpe et al., 2010) and
6	then used to calculate the protein to humic (P/H) organic matter ratio in each sample.
7	The higher the peak intensity for each of these organic matter types the greater the
8	proportion of that organic matter in the sample
9	
10	

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39	

	MBR	RRN	PMR	DRN
DOC (mg/L)	1.6 ± 0.1^a	1.7 ± 0.1^{a}	2.5 ± 0.3^{b}	3.7 ± 0.2^{c}
TOC (mg/L)	1.6 ± 0.1^a	1.9 ± 0.2^a	2.9 ± 0.4^{b}	4.0 ± 0.2^{c}
NO3 ⁻ (mg/L)	1.4 ± 0.0^{a}	1.3 ± 0.05^{b}	1.7 ± 0.1^{c}	1.0 ± 0.05^d
TN (mg/L)	1.7 ± 0.1^{a}	1.5 ± 0.05^{b}	1.9 ± 0.1^{c}	1.3 ± 0.1^{d}
PO ₄ -3 (µg/L)	17 ± 0.6^{a}	17 ± 0.7^{a}	27 ± 3.6^{b}	20 ± 0.8^{b}
TP (µg/L)	45 ± 1.9^{a}	51 ± 2.6^{ab}	59 ± 3.4^{bc}	65 ± 4.2^{c}
I ⁻ (μg/L)	9.1 ± 0.3^a	8.3 ± 0.2^{ab}	7.6 ± 0.3^{b}	15 ± 0.7^{c}
F⁻ (mg/L)	0.10 ± 0.01^a	0.10 ± 0.01^a	0.20 ± 0.02^{b}	0.17 ± 0.02^{ab}

1 Table S1. Comparison of carbon and nutrient concentrations (mean \pm S.E.).

2 MBR = Minebank Run, RRN = Red Run, PMR = Powder Mill Run, DRN = Dead Run.

3 Different letters (a, b, c, or d) indicate significant differences (p < 0.05), based on pairwise

4 comparisons of three years of routinely sampled data.

1 Table S2. Flashiness metrics for mean daily carbon, nitrogen, and phosphorus loads

2 (mean \pm S.E.).

				Powder Mill	
		Minebank Run	Red Run	Run	Dead Run
DOC	Daily Load (g/day)	19 ± 2^a	35 ± 11^a	53 ± 8^b	107 ± 20^{c}
	CV	1.85 ± 0.14^a	1.64 ± 0.15^{a}	2.29 ± 0.13^{b}	2.71 ± 0.14^{b}
	Mean diff. (g/day)	0.02 ± 0.00^a	0.03 ± 0.01^{b}	0.07 ± 0.01^{c}	0.15 ± 0.03^{d}
	Flashiness Index	1.00 ± 0.08^a	0.73 ± 0.06^{b}	1.20 ± 0.07^{ac}	1.38 ± 0.08^{c}
NO ₃ -	Daily Load (g/day)	10.6 ± 0.85^a	10.4 ± 0.83^{a}	19.0 ± 1.74^{b}	11.8 ± 1.26^{a}
	CV	1.23 ± 0.09^a	0.68 ± 0.07^b	1.61 ± 0.11^{c}	1.88 ± 0.10^{d}
	Mean diff. (g/day)	0.007 ± 0.001^{a}	0.004 ± 0.001^{b}	0.018 ± 0.002^c	0.013 ± 0.002^{c}
	Flashiness Index	0.74 ± 0.06^a	0.33 ± 0.03^{b}	0.88 ± 0.06^{ac}	1.02 ± 0.05^{c}
TN	Daily Load (g/day)	12.4 ± 0.99^{a}	13.1 ± 1.23^{a}	27.1 ± 2.99^{b}	19.4 ± 2.33^{ab}
	CV	1.24 ± 0.09^{a}	0.82 ± 0.08^{b}	1.90 ± 0.13^{c}	2.07 ± 0.11^{c}
	Mean diff. (g/day)	0.01 ± 0.00^a	0.01 ± 0.00^{b}	0.03 ± 0.00^c	$0.02 \pm 0.00^{\rm c}$
	Flashiness Index	0.74 ± 0.06^a	0.39 ± 0.03^{b}	1.01 ± 0.06^c	1.11 ± 0.05^{c}
PO_4^{-3}	Daily Load (g/day)	0.17 ± 0.02^{a}	0.22 ± 0.04^{a}	0.40 ± 0.05^{b}	0.50 ± 0.08^{b}
	CV	1.65 ± 0.13^{ab}	1.39 ± 0.12^{a}	1.96 ± 0.13^{b}	2.57 ± 0.13^{c}
		$0.0002 \pm$	$0.0002 \pm$	$0.0005 \pm$	$0.0007 \pm$
	Mean diff. (g/day)	0.00002^{a}	0.00004 ^a	0.0001 ^b	0.0001 ^b
	Flashiness Index	0.91 ± 0.07^a	0.64 ± 0.05^{b}	1.03 ± 0.07^a	1.32 ± 0.07^{c}
TP	Daily Load (g/day)	0.4 ± 0.05^{a}	0.8 ± 0.21^{ab}	0.9 ± 0.11^{b}	1.0 ± 0.13^{b}
	CV	1.61 ± 0.13^{ab}	1.41 ± 0.13^a	1.95 ± 0.13^{bc}	2.08 ± 0.11^{c}
		$0.0004~\pm$	$0.0007 \pm$	$0.0010 \pm$	$0.0012 \pm$
	Mean diff. (g/day)	0.0001 ^a	0.0003 ^a	0.0001 ^b	0.0002^{b}
	Flashiness Index	0.89 ± 0.07^a	0.64 ± 0.05^{b}	1.03 ± 0.07^{ac}	1.11 ± 0.05^{c}
I-	Daily Load (g/day)	0.06 ± 0.003^a	0.08 ± 0.01^a	0.07 ± 0.01^a	0.17 ± 0.02^{b}
	CV	0.94 ± 0.06^a	1.00 ± 0.10^a	1.35 ± 0.07^b	1.79 ± 0.09^{c}
	Mean diff. (g/day)	0.00 ± 0.00^a	0.00 ± 0.00^a	$0.00\pm0.00^{\mathrm{b}}$	$0.00\pm0.00^{\rm c}$
	Flashiness Index	0.60 ± 0.05^a	0.47 ± 0.04^a	0.81 ± 0.05^{b}	0.98 ± 0.05^c
F-	Daily Load (g/day)	0.5 ± 0.05^{a}	NA	41.3 ± 10.09^{b}	1.5 ± 0.17^{c}
	CV	0.76 ± 0.06^a	NA	3.68 ± 0.23^b	1.63 ± 0.09^{c}
	Mean diff. (g/day)	0.000 ± 0.000^{a}	NA	0.07 ± 0.02^{b}	0.001 ± 0.000^{c}
	Flashiness Index	0.53 ± 0.05^a	NA	2.22 ± 0.64^b	0.91 ± 0.04^{c}

Different letters (a, b, c, or d) indicate significant differences (p < 0.05), based on daily loads.

mean absolute value of the difference between daily loads; Flashiness Index = absolute value of mean

3 4 5 6 difference in load between days, divided by the mean load.

7

Values are based on mean monthly data from 2010-2012. CV = Coefficient of Variation; Mean diff. =

		Minebank		Powder Mill	
		Run	Red Run	Run	Dead Run
DOC	Mean (mg/L)	1.6 ± 0.09^{a}	1.8 ± 0.10^{a}	2.5 ± 0.24^{b}	3.6 ± 0.19^{c}
	CV	0.36 ± 0.06^{a}	0.25 ± 0.06^a	0.40 ± 0.08^{a}	0.31 ± 0.04^{a}
	Mean diff. (mg/L)	0.68 ± 0.09^{a}	0.67 ± 0.12^{a}	1.40 ± 0.27^{ab}	1.26 ± 0.16^{b}
	Flashiness Index	0.40 ± 0.05^a	0.38 ± 0.06^a	0.48 ± 0.06^a	0.34 ± 0.04^{a}
NO ₃ -	Mean (mg/L)	1.4 ± 0.05^{a}	1.2 ± 0.06^{b}	1.7 ± 0.07^{c}	1.0 ± 0.06^d
	CV	0.11 ± 0.02^a	0.15 ± 0.04^a	0.25 ± 0.04^b	0.28 ± 0.06^{ab}
	Mean diff. (mg/L)	0.28 ± 0.03^a	0.35 ± 0.05^{ab}	0.44 ± 0.05^b	0.34 ± 0.06^{ab}
	Flashiness Index	0.20 ± 0.02^a	0.30 ± 0.05^a	0.30 ± 0.06^a	0.36 ± 0.06^a
TN	Mean (mg/L)	1.7 ± 0.07^{a}	1.4 ± 0.06^{b}	1.9 ± 0.08^{c}	1.4 ± 0.06^{b}
	CV	0.09 ± 0.02^a	0.11 ± 0.02^{ab}	0.18 ± 0.03^{ab}	0.19 ± 0.04^{b}
	Mean diff. (mg/L)	0.38 ± 0.08^a	0.34 ± 0.05^a	0.56 ± 0.06^{b}	0.34 ± 0.06^a
	Flashiness Index	0.22 ± 0.03^a	0.24 ± 0.04^a	0.44 ± 0.16^a	0.26 ± 0.04^a
PO4-3	Mean (µg/L)	17 ± 0.8^{a}	17 ± 0.9^{a}	27 ± 3.0^{b}	20 ± 1.0^{b}
	CV	0.14 ± 0.04^a	0.12 ± 0.03^a	0.31 ± 0.08^a	0.16 ± 0.04^a
	Mean diff. (µg/L)	3.6 ± 1.0^a	2.9 ± 0.7^a	14 ± 5.1^{b}	4.0 ± 0.6^{b}
	Flashiness Index	0.29 ± 0.11^a	0.29 ± 0.14^a	0.44 ± 0.14^a	0.25 ± 0.09^a
TP	Mean (µg/L)	47 ± 2^a	51 ± 3^{ab}	60 ± 4^{bc}	66 ± 4^{c}
	CV	0.18 ± 0.03^a	0.22 ± 0.06^a	0.23 ± 0.06^a	0.31 ± 0.05^a
	Mean diff. (µg/L)	10.5 ± 1.1^{a}	15.3 ± 2.5^a	18.9 ± 3.6^{ab}	26.1 ± 4.2^{b}
	Flashiness Index	0.24 ± 0.03^a	0.31 ± 0.05^a	0.33 ± 0.06^a	0.40 ± 0.05^a
I-	Mean (µg/L)	9.1 ± 0.36^{a}	8.0 ± 0.28^{b}	7.5 ± 0.34^{b}	14.4 ± 0.69^{c}
	CV	0.18 ± 0.03^{ab}	0.11 ± 0.02^{a}	0.20 ± 0.04^{ab}	0.31 ± 0.05^{b}
	Mean diff. (µg/L)	1.99 ± 0.28^a	1.17 ± 0.20^{b}	1.71 ± 0.20^{a}	5.25 ± 0.51^{c}
	Flashiness Index	0.22 ± 0.03^a	0.15 ± 0.03^{b}	0.25 ± 0.04^a	0.42 ± 0.06^c
F	Mean (mg/L)	0.11 ± 0.02^a	0.10 ± 0.02^{ab}	0.18 ± 0.02^{b}	0.17 ± 0.04^{ab}
	CV	0.51 ± 0.12^a	0.31 ± 0.23^a	0.39 ± 0.07^a	0.42 ± 0.10^a
	Mean diff. (µg/L)	0.08 ± 0.02^a	$0.04\pm NA^{a}$	0.08 ± 0.01^a	0.17 ± 0.05^a
	Flashiness Index	0.72 ± 0.14^a	$0.31 \pm \mathrm{NA}^\mathrm{a}$	0.41 ± 0.06^b	0.95 ± 0.24^{ab}

1 Table S3. Flashiness metrics for routine sample concentrations (mean \pm S.E.).

Different letters (a, b, c, or d) indicate significant differences (p < 0.05).

2 3 4 CV = coefficient of variation; Mean diff. = mean absolute value of the difference between routine sample concentrations; Flashiness Index = mean change in concentration / mean concentration.

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				Powder Mill		
		Minebank Run	Red Run	Run	Dead Run	
$\delta^2 H - H_2 O$	Mean (‰)	$\textbf{-43.3} \pm 1.74^{a}$	-44.9 ± 2.35^a	-43.0 ± 2.19^{a}	-43.8 ± 3.22^a	
	CV	$\textbf{-0.13} \pm 0.06^a$	-0.14 ± 0.05^{a}	$\textbf{-0.24} \pm 0.06^a$	$\textbf{-0.20} \pm 0.06^a$	
	Mean Diff (‰)	5.55 ± 1.57^a	9.21 ± 2.06^a	10.83 ± 2.09^a	10.29 ± 2.27^a	
	Flash Index	-0.12 ± 0.03^{a}	-0.19 ± 0.03^{ab}	-0.24 ± 0.04^{b}	$\textbf{-0.23} \pm 0.05^{ab}$	
δ^{18} O-H ₂ O	Mean (‰)	-6.7 ± 0.20^{a}	-7.0 ± 0.26^{a}	-6.6 ± 0.27^{a}	-6.7 ± 0.40^{a}	
	CV	-0.11 ± 0.03^{a}	-0.12 ± 0.03^{a}	-0.19 ± 0.04^{a}	-0.16 ± 0.04^{a}	
	Mean Diff (‰)	0.82 ± 0.15^a	1.1 ± 0.23^a	1.3 ± 0.23^a	1.3 ± 0.27^a	
	Flash Index	$\textbf{-0.12}\pm0.02^a$	$\textbf{-0.15} \pm 0.03^a$	-0.20 ± 0.03^a	$\textbf{-0.19} \pm 0.04^a$	
δ^{15} N-NO ₃ -	Mean (‰)	7.0 ± 0.25^{ac}	6.2 ± 0.25^a	8.1 ± 0.13^{b}	7.4 ± 0.27^{bc}	
	CV	0.11 ± 0.03^a	0.16 ± 0.06^a	0.15 ± 0.03^a	0.20 ± 0.04^a	
	Mean Diff (‰)	0.87 ± 0.13^a	1.0 ± 0.17^a	1.13 ± 0.13^{ab}	1.49 ± 0.16^b	
	Flash Index	0.13 ± 0.02^a	0.19 ± 0.05^{ab}	0.14 ± 0.02^{ab}	0.22 ± 0.03^b	
δ^{18} O-NO ₃ -	Mean (‰)	4.9 ± 0.37^{ab}	4.1 ± 0.32^{a}	5.8 ± 0.51^{bc}	7.8 ± 0.86^{c}	
5	CV	0.28 ± 0.06^{a}	0.28 ± 0.07^a	0.34 ± 0.09^{a}	0.45 ± 0.07^a	
	Mean Diff (‰)	2.04 ± 0.37^a	1.65 ± 0.31^a	2.69 ± 0.59^a	4.91 ± 0.81^b	
	Flash Index	0.40 ± 0.07^a	0.37 ± 0.05^a	0.39 ± 0.07^a	0.58 ± 0.08^a	
Different letters	(a, b, c, or d) indi	cate significant di	fferences ($p < 0.0$	5).		
CV = coefficier	CV = coefficient of variation; Mean Diff = mean absolute value of the difference between biweekly isotope					

1	Table S4.	Flashiness	metrics for	water and	nitrate sources	$(\text{mean} \pm S.E.)$
-	14010 0 11	I ICOIIIICOO	Incures ion	. mater and	intrate boarees	(mean - o.e

values; Flashiness Index = mean change in isotope value / mean isotope value.

		Minebank		Powder Mill	
		Run	Red Run	Run	Dead Run
HIX	Mean	0.88 ± 0.01^a	0.79 ± 0.05^{ab}	0.80 ± 0.02^{b}	0.83 ± 0.02^{ab}
	CV	0.06 ± 0.02^a	0.02 ± 0.00^a	0.04 ± 0.01^a	0.05 ± 0.03^a
	Mean Diff	0.07 ± 0.02^a	0.09 ± 0.05^a	0.07 ± 0.01^a	0.06 ± 0.02^a
	Flash Index	0.08 ± 0.02^a	0.16 ± 0.11^a	0.09 ± 0.02^a	0.07 ± 0.02^a
BIX	Mean	0.69 ± 0.08^a	0.61 ± 0.06^{b}	0.71 ± 0.07^a	0.75 ± 0.08^a
	CV	0.03 ± 0.01^a	0.06 ± 0.02^a	0.03 ± 0.01^a	0.09 ± 0.03^a
	Mean Diff	0.14 ± 0.07^a	0.12 ± 0.06^a	0.14 ± 0.07^a	0.19 ± 0.07^a
	Flash Index	0.94 ± 0.83^a	0.56 ± 0.46^a	0.64 ± 0.54^a	0.75 ± 0.60^a
FI	Mean	1.15 ± 0.10^{a}	1.10 ± 0.10^{a}	1.12 ± 0.10^{a}	1.22 ± 0.07^{a}
	CV	0.03 ± 0.02^{a}	0.03 ± 0.01^{a}	0.03 ± 0.00^{a}	0.10 ± 0.03^{a}
	Mean Diff	0.19 ± 0.10^{a}	0.18 ± 0.10^{a}	0.18 ± 0.10^{a}	0.22 ± 0.07^{a}
	Flash Index	0.36 ± 0.29^a	0.38 ± 0.31^{a}	0.35 ± 0.27^a	0.20 ± 0.07^a
P/H ratio	Mean	0.80 ± 0.06^{a}	0.73 ± 0.03^{a}	1.16 ± 0.08^{b}	0.92 ± 0.07^{ab}
1/11/1410	CV	0.25 ± 0.08^{a}	0.30 ± 0.04^{a}	0.23 ± 0.07^{a}	0.25 ± 0.09^{a}
	Mean Diff	0.22 ± 0.00 0.27 ± 0.05^{ab}	0.17 ± 0.04^{a}	0.23 ± 0.07 0.41 ± 0.06^{b}	0.28 ± 0.10^{ab}
	Flash Index	0.34 ± 0.07^{a}	0.24 ± 0.05^{a}	0.36 ± 0.06^{a}	0.28 ± 0.08^{a}
Protein	Mean	0.09 ± 0.03^{a}	0.11 ± 0.04^{a}	0.25 ± 0.12^{a}	0.26 ± 0.08^{a}
Tiotem	CV	0.09 ± 0.03 0.49 ± 0.17^{a}	0.11 ± 0.04 0.50 + 0.10 ^a	0.23 ± 0.12 0.53 ± 0.10 ^a	0.20 ± 0.00^{a}
	C v Mean Diff	0.49 ± 0.17 0.03 ± 0.01^{a}	0.06 ± 0.10^{a}	0.33 ± 0.10 0.18 ± 0.11 ^a	0.04 ± 0.00 0.10 ± 0.04^{a}
	Flash Index	0.05 ± 0.01 0.46 ± 0.13^{a}	0.58 ± 0.13^{a}	0.13 ± 0.11 0.74 ± 0.28^{a}	0.45 ± 0.10^{a}
Euluia	Maan	0.14 ± 0.04^{a}	0.17 ± 0.06^{a}	0.28 ± 0.24^{a}	$0.40 + 0.14^{a}$
FUIVIC	Mean CV	0.14 ± 0.04 0.44 + 0.12 ^a	0.17 ± 0.00 0.48 ± 0.15 ^a	0.38 ± 0.24 0.57 ± 0.12 ^a	0.40 ± 0.14
		0.44 ± 0.13	0.46 ± 0.13	0.37 ± 0.12	0.40 ± 0.09
	Fleeh Index	0.09 ± 0.03	0.13 ± 0.03	0.32 ± 0.29	0.52 ± 0.15 2.75 + 2.21 ^a
	Flash Index	2.13 ± 1.08	2.98 ± 2.44	10.08 ± 9.41	5.75 ± 5.51
Humic	Mean	0.11 ± 0.03^{a}	0.13 ± 0.04^{a}	0.23 ± 0.14^a	0.27 ± 0.09^a
	CV	0.43 ± 0.14^a	0.50 ± 0.18^a	0.59 ± 0.13^a	0.48 ± 0.09^a
	Mean Diff	0.06 ± 0.02^a	0.09 ± 0.03^a	0.30 ± 0.16^a	0.19 ± 0.07^a
	Flash Index	1.05 ± 0.59^a	1.28 ± 0.76^a	4.01 ± 3.33^{a}	1.49 ± 1.06^{a}

1 Table S5. Flashiness metrics for carbon source metrics (mean \pm S.E.).

Different letters (a, b, c, or d) indicate significant differences (p < 0.05).

2345678 CV = coefficient of variation; Mean Diff = mean absolute value of the difference between biweekly sample indices; Flashiness Index = mean change in index value / mean index value.

HIX = humification index; BIX = biological freshness index; FI = fluorescence index; P/H ratio = protein-

to-humic ratio; Protein = protein-like organic matter fluorescence intensity index; Fulvic = fulvic-like organic matter fluorescence intensity index; Humic = humic-like organic matter fluorescence intensity

index.

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I Figure Capitons	1	Figure	Captions
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3	Figure S1. Site map of study streams in the Baltimore Metropolitan Region showing land
4	cover characteristics.
5	
6	Figure S2. Flow duration curves for each site: (a) Minebank Run, (b) Red Run (c),
7	Powder Mill Run, and (c) Dead Run, showing the range of flows and also at what flows
8	the 3 years of regular sampling took place.
9	
10	Figure S3. Comparison of (a) DOC, (b) NO_3^- and (c) PO_4^{-3} concentration vs. time, from
11	routine samples collected at each of the four stream gage sites.
12	
13	Figure S4. Water isotope comparison: δ^2 H-H ₂ O <i>vs</i> . δ^{18} O-H ₂ O for (a) all samples from the
14	gauge locations and (b) samples taken from the mouth of each stream during the winter
15	2010. GMWL = Global Meteoric Water Line, LMWL = Local Meteoric Water Line
16	(Craig, 1961; Kendall and Coplen, 2001) (Craig 1961; Kendall & Coplen 2001).
17	
18	Figure S5. Seasonal relationship between δ^{15} N-NO ₃ ⁻ vs. δ^{18} O-NO ₃ ⁻ for (a) spring 2010,
19	(b) spring 2011, (c), summer 2010, and (d) summer 2011, for routine samples at each of
20	the four stream sites.
21 22 23 24 25 26	

1 Figure S1.



1 Figure S2.



1 Figure S3.



1 Figure S4.



1 Figure S5.



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