



Supplement of

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

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1 Supporting Information

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4 and nutrients in urban watersheds

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7 **1 Methods**

8 **1.1 Site Description**

9 Red Run (RRN), Powder Mill Run (PMR), and Dead Run (DRN) are all part of
10 the Gwynns Falls watershed, which is monitored by Baltimore Ecosystem Study's Long
11 Term Ecological Research (www.beslter.org). Previous information on runoff and
12 nutrient export in these watersheds can be found elsewhere (Groffman et al., 2004;
13 Kaushal et al., 2008a; Kaushal et al., 2011; Duan et al., 2012). Specific land use and
14 other site characteristics of each watershed are found in Figure S1 and listed in Table S1.

15 Minebank Run is an urban headwater stream located in Towson, MD. The
16 headwater reach of Minebank Run was restored in 1999 and the lower reach in 2005
17 (Doheny et al., 2006). The stream restorations at MBR consisted of bank stabilization,
18 the addition of riffles and meander features with step-pool habitat, a hydrologically
19 connecting streambed and floodplain wetland, and the planting of trees in the riparian
20 zone (Kaushal et al., 2008b).

21 Red Run, located in Owings Mills, MD, has been gauged by UMBC Center for
22 Urban Environmental Research and Education (CUERE) to measure stream flow since

1 2005. RRN is characterized by newer development and relatively high-density
2 stormwater management (SWM) facilities in both residential and commercial
3 development areas within the watershed. The newer residential and commercial
4 developments in RRN watershed have implemented stormwater detention facilities,
5 draining areas of impervious surfaces, such as detention basins, wet ponds, stormwater
6 bioretention facilities, and sand filters. This watershed also has extensive riparian
7 buffers. The outflows of SWM facilities are either connected to a stream or flow into a
8 forested buffer. Red Run is missing discharge data from July 2011 through September
9 2011, due to construction under the bridge where the gauge is located. For daily flow
10 data, we were able to estimate the missing mean daily flow by creating a linear
11 relationship with nearby USGS gauged streams of similar size and discharge ($R^2 > 0.95$).
12 For the real-time data Flashiness estimates, the missing discharge was left out of the
13 calculations. Also, the Red Run flow data has not been through USGS QA/QC and is
14 based on a provisional rating curve.

15 Powder Mill Run and Dead Run are also subwatersheds of the BES LTER site.
16 Dead Run has 6 USGS stream gauging stations along its stream network, and has had
17 weekly stream chemistry sampling since 1998 (Groffman et al. 2004; Kaushal et al.
18 2008a). The Dead Run watershed has been the focus of numerous eco-hydrological
19 investigations and there exists a rich dataset on nitrogen dynamics (e.g. Groffman et al.,
20 2004; Kaushal et al., 2008a; Kaushal et al., 2011; Newcomer et al., 2012), hydrologic
21 characteristics, and water mass balances (Klockner et al., 2009; Ryan et al., 2010; Ryan et
22 al., 2011; Svirichni et al., 2011).

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1 **1.2 Stream Chemistry Analysis**

2 During each stream chemistry sampling, measurements of dissolved oxygen
3 (DO), pH, and temperature were recorded. DO and pH meters were calibrated each day
4 before use in the field. All stream chemistry samples were analyzed using standard EPA
5 methods at the National Risk Management Research Lab (NRMRL) in Ada, OK, USA.
6 Water samples requiring filtration were filtered in the lab within 24 hours using a 47mm
7 (0.45 μm) glass fiber filter, then preserved until analysis. All nitrogen species, except
8 samples for stable isotope analysis, were preserved by acidifying to pH 2 with sulfuric
9 acid and stored frozen in HDPE bottles until analysis. Samples for TOC and DOC were
10 stored in 40 ml glass VOA bottles, preserved by acidifying to pH 2, using phosphoric
11 acid and refrigerated until analysis. NO_3^- isotope samples were filtered and preserved
12 frozen in HDPE bottles. Samples for H_2O isotope analysis were unfiltered and collected
13 for only 1 year during 2010-2011. H_2O isotope samples were unfiltered and collected in
14 a 30 ml glass Qorpak bottle, that was filled and capped under water in the field so that
15 there are no air bubbles or headspace, and then sealed with a Teflon-lined cap. The EPA
16 NRMRL Isotope Ratio Mass Spectrometer (IRMS) lab analyzes the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of
17 water samples following RSKSOP 296. Samples for carbon quality analysis were filtered
18 and saved in amber glass Qorpak vials and kept refrigerated (see further methods below).
19 The rest of the samples were preserved frozen in HDPE bottles until analysis.
20 Fluorescence samples were analyzed within 1-3 weeks. All other samples, besides NO_3^-
21 isotopes samples, were analyzed within 1-2 months.
22 TKN, NH_4^+ , $\text{NO}_3^- + \text{NO}_2^-$, ortho-P and Br^- were measured using Lachat flow
23 injection analyses (Lachat Instruments, Loveland, CO USA). Total organic nitrogen

1 (TON) was calculated as TKN of unfiltered water minus ammonium and dissolved
2 organic nitrogen (DON) was calculated as TKN of filtered water minus ammonium (with
3 TKN being the sum of organic nitrogen plus ammonia/ammonium). Total nitrogen (TN)
4 was calculated as TKN plus $\text{NO}_3^- + \text{NO}_2^-$. NH_4^+ was measured using EPA FIA Method
5 10-107-06-1-A. Br and Iodide were analyzed by EPA FIA Method 10-135-21-2-A. SO_4
6 was analyzed by FIA Method 10-116-10-1-C. Chloride was analyzed by FIA Method 10-
7 117-07-1-B. H_2O isotopes were measured using a high temperature conversion elemental
8 analyzer (tc/ea), a continuous flow unit, and an isotope ratio mass spectrometer (IRMS)
9 (EPA's RSKSOP 296v0). Total organic carbon (TOC) and dissolved organic carbon
10 (DOC) were analyzed using a total organic C analyzer with high-temperature Pt-
11 catalyzed combustion and NDIR detection (Shimadzu TOC-VCPH, Columbia, MD
12 USA). Samples for carbon quality analysis were analyzed on a Fluoromax-4
13 spectrofluorometer (Jobin Yvon Horiba) at the University of Maryland Biogeochemistry
14 Lab.

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16 **1.3 Fluorescence Analysis**

17 On the day of analysis, samples were allowed to warm to room temperature and
18 placed in a 1 cm quartz cuvette for analysis. Each day that samples were run on the
19 spectrofluorometer, a blank sample was also run at the beginning of the day using
20 milli-Q water. Between samples, the cuvette was rinsed three times with milli-Q water
21 and then sample rinsed with the next sample, two times. A fluorescence EEMs was
22 collected for each sample and also collected for Milli-Q water as a blank. A full EEMs
23 was also collected for a quinine sulfate standard (10 ppb in 0.1 N H_2SO_4). This quinine

1 sulfate standard can be used when comparing samples run on different instruments and
2 used to monitor instrument drift over time (Del Vecchio and Blough, 2004; Fellman et
3 al., 2009). A scan rate of 4nm/sec was used and the excitation and emission slit widths
4 were 5 nm. The EEMs were collected under the S1/R1 mode to correct for instrument
5 drift. The standard inner-filter corrections (IFC) were not done on most samples because
6 absorbance measurements were not attained for most samples. However, for the samples
7 where absorbance was collected (using scanning spectrophotometer), the IFC was done
8 and it was found that there is < 5% difference between EEMs with and without IFC.

9 We analyzed fluorescence EEMs for the following indices: the fluorescence
10 index, FI (McKnight et al., 2001) the humification index, HIX (Zsolnay et al., 1999;
11 Huguet et al., 2009), the biological freshness index, BIX (Huguet et al., 2009), and the
12 protein to humic fluorescence intensities ratio (Coble, 1996; Stolpe et al., 2010). FI
13 values are ~ 1.9 for microbial derived fulvic acids and ~1.4 for terrestrial derived fulvic
14 acids sources (McKnight et al., 2001; Cory et al., 2010). BIX values of < 0.7, 0.8 – 1.0,
15 or > 1.0 are associated with terrestrial sourced DOM, algal sourced DOM, or aquatic
16 bacterial sources, respectively (Huguet et al., 2009). HIX was used to distinguish the
17 humic or autochthonous nature of the organic matter in the sample (Zsolnay et al., 1999;
18 Ohno, 2002). Higher HIX values suggest DOM of strong humic character and terrestrial
19 origin, while lower values indicate weaker humic character and higher autochthonous
20 sourced DOM. Further details are described in Pennino et al. (2014). Fluorescence EEM
21 peak intensities at specific excitation and emission wavelengths were also used to
22 determine the relative contribution of protein (at excitation 275 nm and emission 340
23 nm), fulvic (at excitation 310 nm and emission 420 nm) and humic (at excitation 350 nm

1 and emission 480 nm) dissolved organic matter (Coble, 1996; Stolpe et al., 2010) and
2 then used to calculate the protein to humic (P/H) organic matter ratio in each sample.

3 The higher the peak intensity for each of these organic matter types the greater the
4 proportion of that organic matter in the sample

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

	MBR	RRN	PMR	DRN
DOC (mg/L)	1.6 \pm 0.1 ^a	1.7 \pm 0.1 ^a	2.5 \pm 0.3 ^b	3.7 \pm 0.2 ^c
TOC (mg/L)	1.6 \pm 0.1 ^a	1.9 \pm 0.2 ^a	2.9 \pm 0.4 ^b	4.0 \pm 0.2 ^c
NO ₃ ⁻ (mg/L)	1.4 \pm 0.0 ^a	1.3 \pm 0.05 ^b	1.7 \pm 0.1 ^c	1.0 \pm 0.05 ^d
TN (mg/L)	1.7 \pm 0.1 ^a	1.5 \pm 0.05 ^b	1.9 \pm 0.1 ^c	1.3 \pm 0.1 ^d
PO ₄ ⁻³ (μ g/L)	17 \pm 0.6 ^a	17 \pm 0.7 ^a	27 \pm 3.6 ^b	20 \pm 0.8 ^b
TP (μ g/L)	45 \pm 1.9 ^a	51 \pm 2.6 ^{ab}	59 \pm 3.4 ^{bc}	65 \pm 4.2 ^c
Γ (μ g/L)	9.1 \pm 0.3 ^a	8.3 \pm 0.2 ^{ab}	7.6 \pm 0.3 ^b	15 \pm 0.7 ^c
F ⁻ (mg/L)	0.10 \pm 0.01 ^a	0.10 \pm 0.01 ^a	0.20 \pm 0.02 ^b	0.17 \pm 0.02 ^{ab}

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.

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1 Table S2. Flashiness metrics for mean daily carbon, nitrogen, and phosphorus loads
 2 (mean \pm S.E.).

		Minebank Run	Red Run	Powder Mill Run	Dead Run
DOC	Daily Load (g/day)	19 \pm 2 ^a	35 \pm 11 ^a	53 \pm 8 ^b	107 \pm 20 ^c
	CV	1.85 \pm 0.14 ^a	1.64 \pm 0.15 ^a	2.29 \pm 0.13 ^b	2.71 \pm 0.14 ^b
	Mean diff. (g/day)	0.02 \pm 0.00 ^a	0.03 \pm 0.01 ^b	0.07 \pm 0.01 ^c	0.15 \pm 0.03 ^d
	Flashiness Index	1.00 \pm 0.08 ^a	0.73 \pm 0.06 ^b	1.20 \pm 0.07 ^{ac}	1.38 \pm 0.08 ^c
NO ₃ ⁻	Daily Load (g/day)	10.6 \pm 0.85 ^a	10.4 \pm 0.83 ^a	19.0 \pm 1.74 ^b	11.8 \pm 1.26 ^a
	CV	1.23 \pm 0.09 ^a	0.68 \pm 0.07 ^b	1.61 \pm 0.11 ^c	1.88 \pm 0.10 ^d
	Mean diff. (g/day)	0.007 \pm 0.001 ^a	0.004 \pm 0.001 ^b	0.018 \pm 0.002 ^c	0.013 \pm 0.002 ^c
	Flashiness Index	0.74 \pm 0.06 ^a	0.33 \pm 0.03 ^b	0.88 \pm 0.06 ^{ac}	1.02 \pm 0.05 ^c
TN	Daily Load (g/day)	12.4 \pm 0.99 ^a	13.1 \pm 1.23 ^a	27.1 \pm 2.99 ^b	19.4 \pm 2.33 ^{ab}
	CV	1.24 \pm 0.09 ^a	0.82 \pm 0.08 ^b	1.90 \pm 0.13 ^c	2.07 \pm 0.11 ^c
	Mean diff. (g/day)	0.01 \pm 0.00 ^a	0.01 \pm 0.00 ^b	0.03 \pm 0.00 ^c	0.02 \pm 0.00 ^c
	Flashiness Index	0.74 \pm 0.06 ^a	0.39 \pm 0.03 ^b	1.01 \pm 0.06 ^c	1.11 \pm 0.05 ^c
PO ₄ ⁻³	Daily Load (g/day)	0.17 \pm 0.02 ^a	0.22 \pm 0.04 ^a	0.40 \pm 0.05 ^b	0.50 \pm 0.08 ^b
	CV	1.65 \pm 0.13 ^{ab}	1.39 \pm 0.12 ^a	1.96 \pm 0.13 ^b	2.57 \pm 0.13 ^c
	Mean diff. (g/day)	0.0002 \pm 0.00002 ^a	0.0002 \pm 0.00004 ^a	0.0005 \pm 0.0001 ^b	0.0007 \pm 0.0001 ^b
	Flashiness Index	0.91 \pm 0.07 ^a	0.64 \pm 0.05 ^b	1.03 \pm 0.07 ^a	1.32 \pm 0.07 ^c
TP	Daily Load (g/day)	0.4 \pm 0.05 ^a	0.8 \pm 0.21 ^{ab}	0.9 \pm 0.11 ^b	1.0 \pm 0.13 ^b
	CV	1.61 \pm 0.13 ^{ab}	1.41 \pm 0.13 ^a	1.95 \pm 0.13 ^{bc}	2.08 \pm 0.11 ^c
	Mean diff. (g/day)	0.0004 \pm 0.0001 ^a	0.0007 \pm 0.0003 ^a	0.0010 \pm 0.0001 ^b	0.0012 \pm 0.0002 ^b
	Flashiness Index	0.89 \pm 0.07 ^a	0.64 \pm 0.05 ^b	1.03 \pm 0.07 ^{ac}	1.11 \pm 0.05 ^c
I ⁻	Daily Load (g/day)	0.06 \pm 0.003 ^a	0.08 \pm 0.01 ^a	0.07 \pm 0.01 ^a	0.17 \pm 0.02 ^b
	CV	0.94 \pm 0.06 ^a	1.00 \pm 0.10 ^a	1.35 \pm 0.07 ^b	1.79 \pm 0.09 ^c
	Mean diff. (g/day)	0.00 \pm 0.00 ^a	0.00 \pm 0.00 ^a	0.00 \pm 0.00 ^b	0.00 \pm 0.00 ^c
	Flashiness Index	0.60 \pm 0.05 ^a	0.47 \pm 0.04 ^a	0.81 \pm 0.05 ^b	0.98 \pm 0.05 ^c
F ⁻	Daily Load (g/day)	0.5 \pm 0.05 ^a	NA	41.3 \pm 10.09 ^b	1.5 \pm 0.17 ^c
	CV	0.76 \pm 0.06 ^a	NA	3.68 \pm 0.23 ^b	1.63 \pm 0.09 ^c
	Mean diff. (g/day)	0.000 \pm 0.000 ^a	NA	0.07 \pm 0.02 ^b	0.001 \pm 0.000 ^c
	Flashiness Index	0.53 \pm 0.05 ^a	NA	2.22 \pm 0.64 ^b	0.91 \pm 0.04 ^c

3 Different letters (a, b, c, or d) indicate significant differences ($p < 0.05$), based on daily loads.
 4 Values are based on mean monthly data from 2010-2012. CV = Coefficient of Variation; Mean diff. =
 5 mean absolute value of the difference between daily loads; Flashiness Index = absolute value of mean
 6 difference in load between days, divided by the mean load.

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

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

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

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

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1 Table S4. Flashiness metrics for water and nitrate sources (mean \pm S.E.).

		Minebank Run	Red Run	Powder Mill Run	Dead Run
$\delta^2\text{H-H}_2\text{O}$	Mean (‰)	-43.3 \pm 1.74 ^a	-44.9 \pm 2.35 ^a	-43.0 \pm 2.19 ^a	-43.8 \pm 3.22 ^a
	CV	-0.13 \pm 0.06 ^a	-0.14 \pm 0.05 ^a	-0.24 \pm 0.06 ^a	-0.20 \pm 0.06 ^a
	Mean Diff (‰)	5.55 \pm 1.57 ^a	9.21 \pm 2.06 ^a	10.83 \pm 2.09 ^a	10.29 \pm 2.27 ^a
	Flash Index	-0.12 \pm 0.03 ^a	-0.19 \pm 0.03 ^{ab}	-0.24 \pm 0.04 ^b	-0.23 \pm 0.05 ^{ab}
$\delta^{18}\text{O-H}_2\text{O}$	Mean (‰)	-6.7 \pm 0.20 ^a	-7.0 \pm 0.26 ^a	-6.6 \pm 0.27 ^a	-6.7 \pm 0.40 ^a
	CV	-0.11 \pm 0.03 ^a	-0.12 \pm 0.03 ^a	-0.19 \pm 0.04 ^a	-0.16 \pm 0.04 ^a
	Mean Diff (‰)	0.82 \pm 0.15 ^a	1.1 \pm 0.23 ^a	1.3 \pm 0.23 ^a	1.3 \pm 0.27 ^a
	Flash Index	-0.12 \pm 0.02 ^a	-0.15 \pm 0.03 ^a	-0.20 \pm 0.03 ^a	-0.19 \pm 0.04 ^a
$\delta^{15}\text{N-NO}_3^-$	Mean (‰)	7.0 \pm 0.25 ^{ac}	6.2 \pm 0.25 ^a	8.1 \pm 0.13 ^b	7.4 \pm 0.27 ^{bc}
	CV	0.11 \pm 0.03 ^a	0.16 \pm 0.06 ^a	0.15 \pm 0.03 ^a	0.20 \pm 0.04 ^a
	Mean Diff (‰)	0.87 \pm 0.13 ^a	1.0 \pm 0.17 ^a	1.13 \pm 0.13 ^{ab}	1.49 \pm 0.16 ^b
	Flash Index	0.13 \pm 0.02 ^a	0.19 \pm 0.05 ^{ab}	0.14 \pm 0.02 ^{ab}	0.22 \pm 0.03 ^b
$\delta^{18}\text{O-NO}_3^-$	Mean (‰)	4.9 \pm 0.37 ^{ab}	4.1 \pm 0.32 ^a	5.8 \pm 0.51 ^{bc}	7.8 \pm 0.86 ^c
	CV	0.28 \pm 0.06 ^a	0.28 \pm 0.07 ^a	0.34 \pm 0.09 ^a	0.45 \pm 0.07 ^a
	Mean Diff (‰)	2.04 \pm 0.37 ^a	1.65 \pm 0.31 ^a	2.69 \pm 0.59 ^a	4.91 \pm 0.81 ^b
	Flash Index	0.40 \pm 0.07 ^a	0.37 \pm 0.05 ^a	0.39 \pm 0.07 ^a	0.58 \pm 0.08 ^a

2 Different letters (a, b, c, or d) indicate significant differences ($p < 0.05$).
 3 CV = coefficient of variation; Mean Diff = mean absolute value of the difference between biweekly isotope
 4 values; Flashiness Index = mean change in isotope value / mean isotope value.

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

		Minebank Run	Red Run	Powder Mill Run	Dead Run
HIX	Mean	0.88 \pm 0.01 ^a	0.79 \pm 0.05 ^{ab}	0.80 \pm 0.02 ^b	0.83 \pm 0.02 ^{ab}
	CV	0.06 \pm 0.02 ^a	0.02 \pm 0.00 ^a	0.04 \pm 0.01 ^a	0.05 \pm 0.03 ^a
	Mean Diff	0.07 \pm 0.02 ^a	0.09 \pm 0.05 ^a	0.07 \pm 0.01 ^a	0.06 \pm 0.02 ^a
	Flash Index	0.08 \pm 0.02 ^a	0.16 \pm 0.11 ^a	0.09 \pm 0.02 ^a	0.07 \pm 0.02 ^a
BIX	Mean	0.69 \pm 0.08 ^a	0.61 \pm 0.06 ^b	0.71 \pm 0.07 ^a	0.75 \pm 0.08 ^a
	CV	0.03 \pm 0.01 ^a	0.06 \pm 0.02 ^a	0.03 \pm 0.01 ^a	0.09 \pm 0.03 ^a
	Mean Diff	0.14 \pm 0.07 ^a	0.12 \pm 0.06 ^a	0.14 \pm 0.07 ^a	0.19 \pm 0.07 ^a
	Flash Index	0.94 \pm 0.83 ^a	0.56 \pm 0.46 ^a	0.64 \pm 0.54 ^a	0.75 \pm 0.60 ^a
FI	Mean	1.15 \pm 0.10 ^a	1.10 \pm 0.10 ^a	1.12 \pm 0.10 ^a	1.22 \pm 0.07 ^a
	CV	0.03 \pm 0.02 ^a	0.03 \pm 0.01 ^a	0.03 \pm 0.00 ^a	0.10 \pm 0.03 ^a
	Mean Diff	0.19 \pm 0.10 ^a	0.18 \pm 0.10 ^a	0.18 \pm 0.10 ^a	0.22 \pm 0.07 ^a
	Flash Index	0.36 \pm 0.29 ^a	0.38 \pm 0.31 ^a	0.35 \pm 0.27 ^a	0.20 \pm 0.07 ^a
P/H ratio	Mean	0.80 \pm 0.06 ^a	0.73 \pm 0.03 ^a	1.16 \pm 0.08 ^b	0.92 \pm 0.07 ^{ab}
	CV	0.25 \pm 0.08 ^a	0.30 \pm 0.04 ^a	0.23 \pm 0.07 ^a	0.25 \pm 0.09 ^a
	Mean Diff	0.27 \pm 0.05 ^{ab}	0.17 \pm 0.04 ^a	0.41 \pm 0.06 ^b	0.28 \pm 0.10 ^{ab}
	Flash Index	0.34 \pm 0.07 ^a	0.24 \pm 0.05 ^a	0.36 \pm 0.06 ^a	0.28 \pm 0.08 ^a
Protein	Mean	0.09 \pm 0.03 ^a	0.11 \pm 0.04 ^a	0.25 \pm 0.12 ^a	0.26 \pm 0.08 ^a
	CV	0.49 \pm 0.17 ^a	0.50 \pm 0.10 ^a	0.53 \pm 0.10 ^a	0.54 \pm 0.08 ^a
	Mean Diff	0.03 \pm 0.01 ^a	0.06 \pm 0.02 ^a	0.18 \pm 0.11 ^a	0.10 \pm 0.04 ^a
	Flash Index	0.46 \pm 0.13 ^a	0.58 \pm 0.13 ^a	0.74 \pm 0.28 ^a	0.45 \pm 0.10 ^a
Fulvic	Mean	0.14 \pm 0.04 ^a	0.17 \pm 0.06 ^a	0.38 \pm 0.24 ^a	0.40 \pm 0.14 ^a
	CV	0.44 \pm 0.13 ^a	0.48 \pm 0.15 ^a	0.57 \pm 0.12 ^a	0.46 \pm 0.09 ^a
	Mean Diff	0.09 \pm 0.03 ^a	0.13 \pm 0.05 ^a	0.52 \pm 0.29 ^a	0.32 \pm 0.13 ^a
	Flash Index	2.15 \pm 1.68 ^a	2.98 \pm 2.44 ^a	10.08 \pm 9.41 ^a	3.75 \pm 3.31 ^a
Humic	Mean	0.11 \pm 0.03 ^a	0.13 \pm 0.04 ^a	0.23 \pm 0.14 ^a	0.27 \pm 0.09 ^a
	CV	0.43 \pm 0.14 ^a	0.50 \pm 0.18 ^a	0.59 \pm 0.13 ^a	0.48 \pm 0.09 ^a
	Mean Diff	0.06 \pm 0.02 ^a	0.09 \pm 0.03 ^a	0.30 \pm 0.16 ^a	0.19 \pm 0.07 ^a
	Flash Index	1.05 \pm 0.59 ^a	1.28 \pm 0.76 ^a	4.01 \pm 3.33 ^a	1.49 \pm 1.06 ^a

2 Different letters (a, b, c, or d) indicate significant differences ($p < 0.05$).
 3 CV = coefficient of variation; Mean Diff = mean absolute value of the difference between biweekly sample
 4 indices; Flashiness Index = mean change in index value / mean index value.
 5 HIX = humification index; BIX = biological freshness index; FI = fluorescence index; P/H ratio = protein-
 6 to-humic ratio; Protein = protein-like organic matter fluorescence intensity index; Fulvic = fulvic-like
 7 organic matter fluorescence intensity index; Humic = humic-like organic matter fluorescence intensity
 8 index.

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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.

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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.

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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.

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13 Figure S4. Water isotope comparison: $\delta^2\text{H-H}_2\text{O}$ vs. $\delta^{18}\text{O-H}_2\text{O}$ 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).

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18 Figure S5. Seasonal relationship between $\delta^{15}\text{N-NO}_3^-$ vs. $\delta^{18}\text{O-NO}_3^-$ 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.

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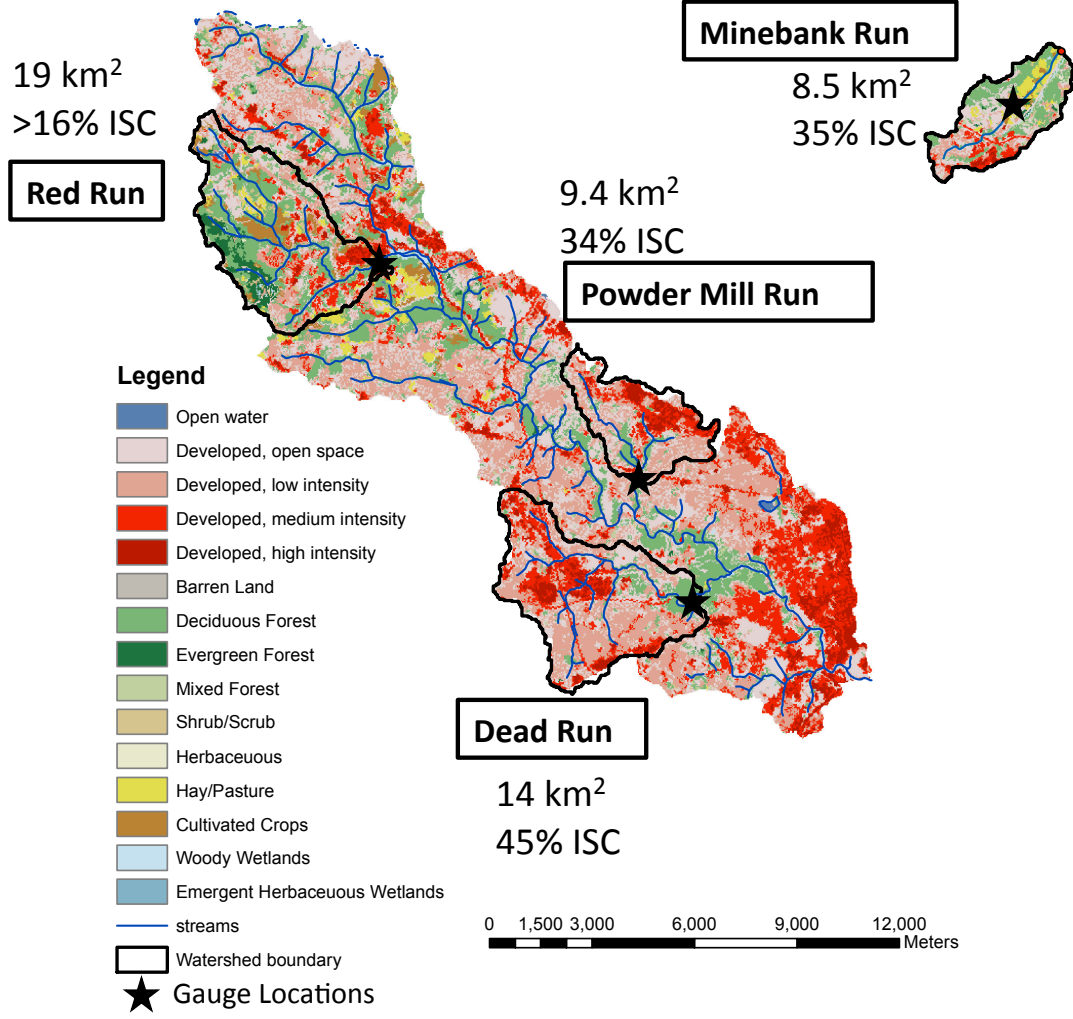
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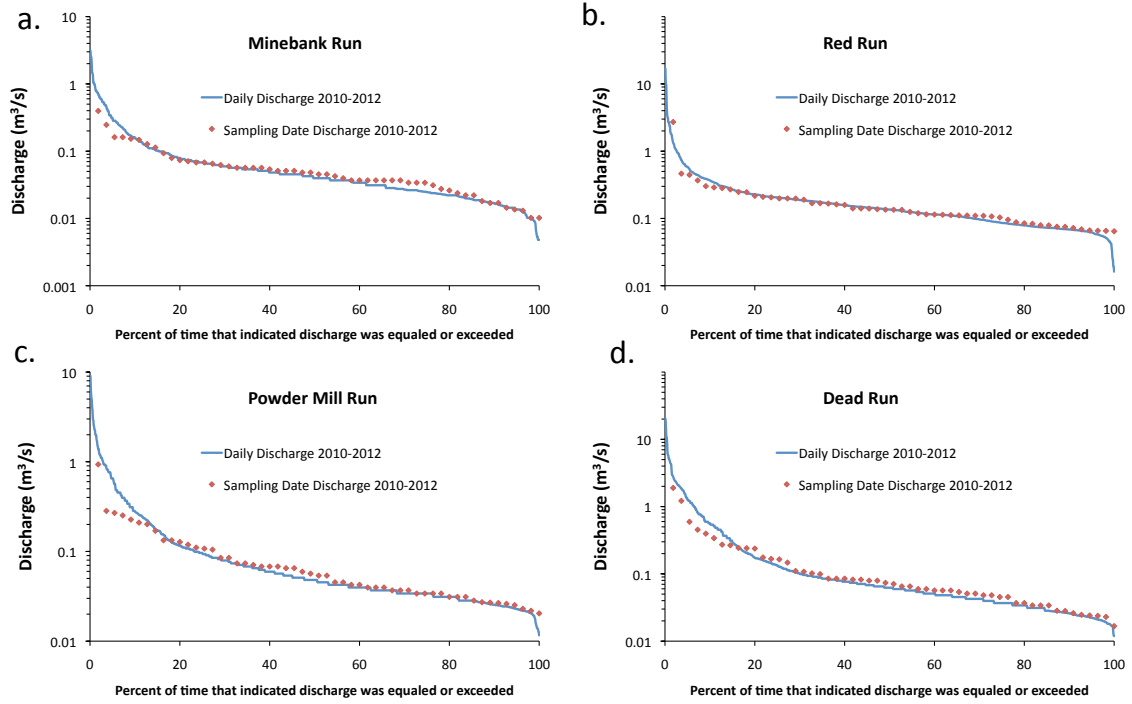
1 Figure S1.

Baltimore, MD Stream Sites



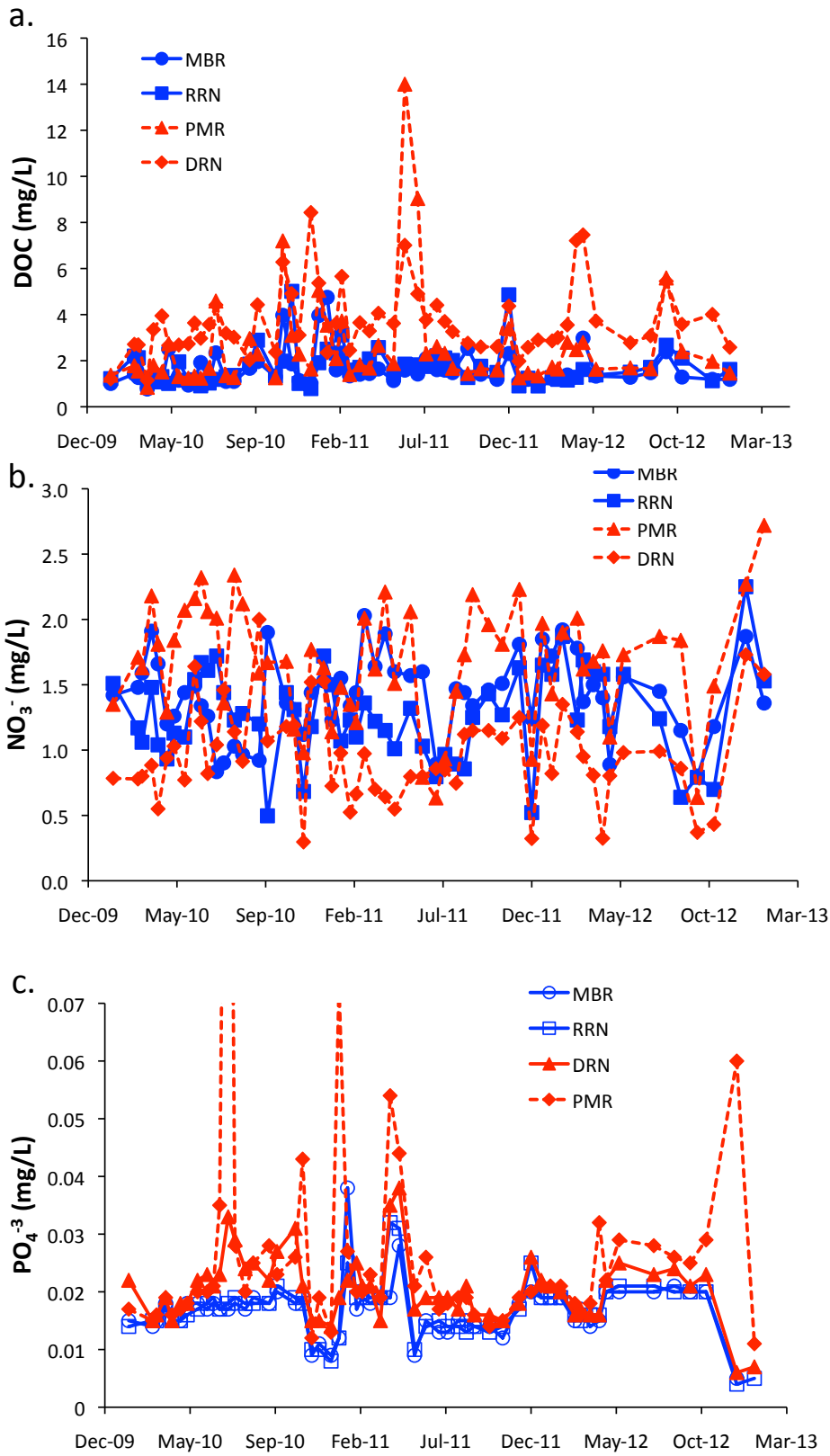
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1 Figure S2.

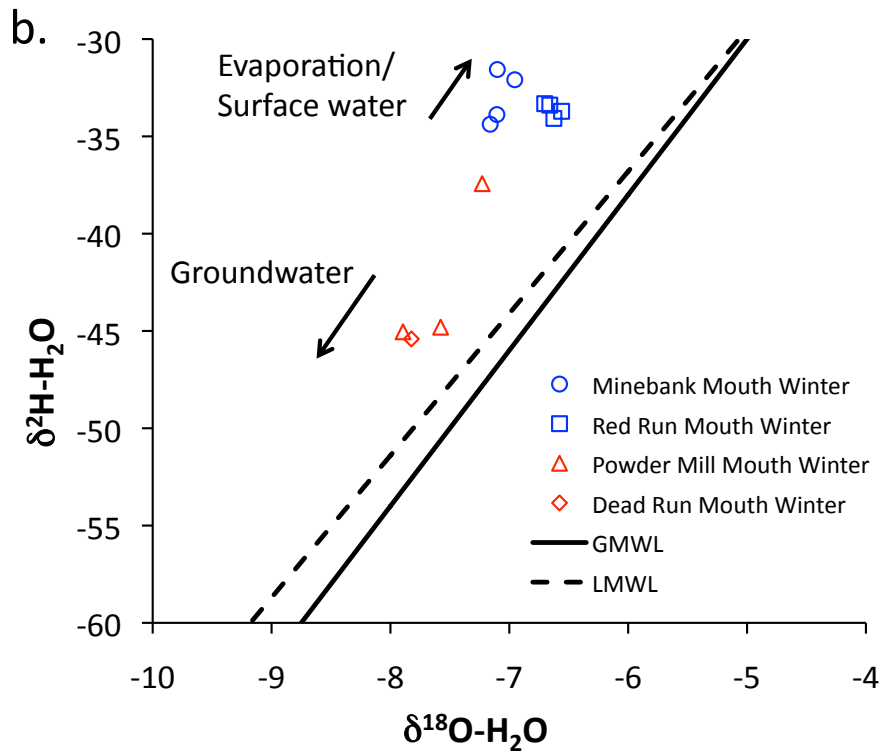
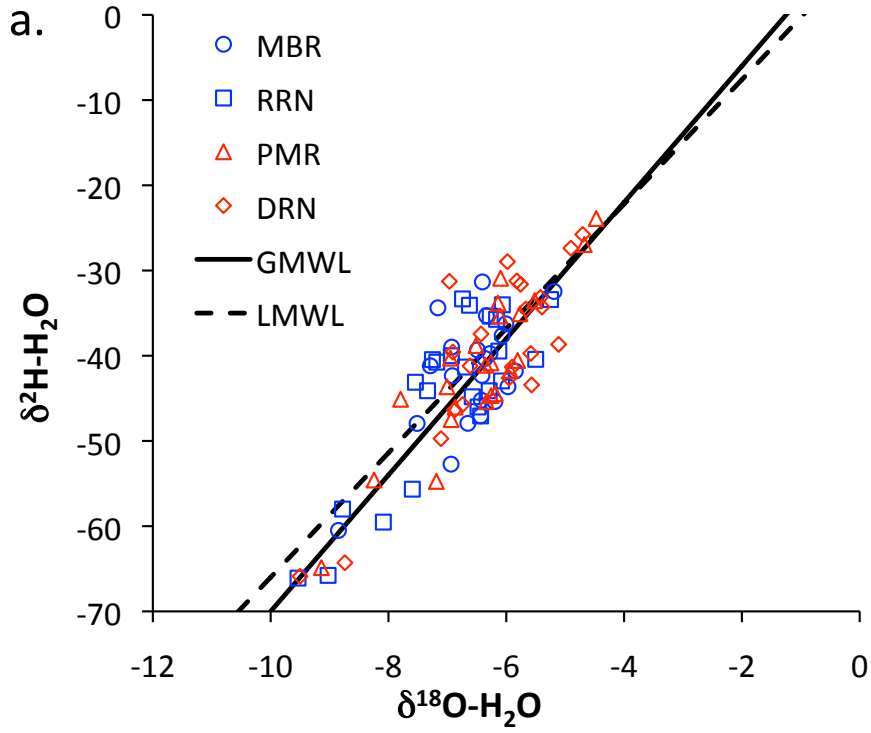


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1 Figure S3.

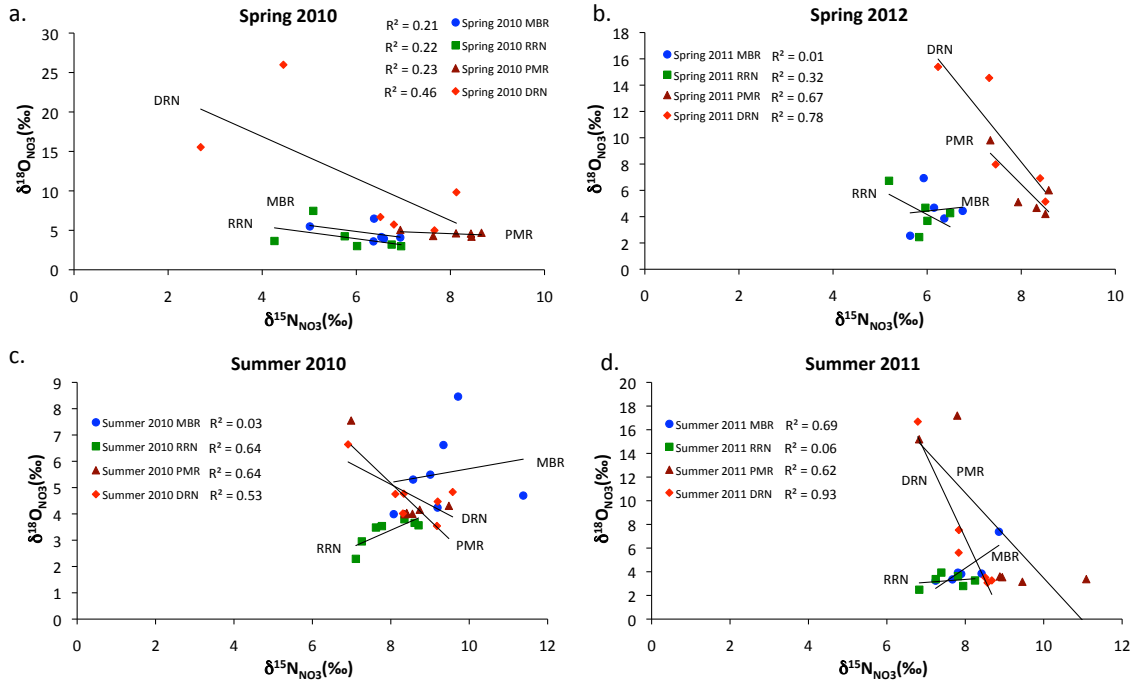


1 Figure S4.



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1 Figure S5.
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