Supporting Information for

Sources and Transformations of Anthropogenic Nitrogen along an Urban River-Estuarine Continuum

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Introduction

The supporting information contains additional details on the methods used for this study and additional description of specific results and analysis of the data used in this study. This supporting information also contains data to validate the box model analysis used in the study and additional results that support the findings of the paper.

Text S1. Methods

Text S1.1 Site Description

The Potomac River drains water from both Maryland and Virginia and forms the border between these two states. The entire Potomac River basin has a total drainage of approximately 38,000 km^2 and is comprised of 16% cropland, 12% Pasture, 55% forest, 5% water and wetlands, 10% urban, and 3% other (Boynton et al. 1995). The upper Potomac is freshwater and drains rural and agricultural areas above Washington D.C., while the Potomac River Estuary begins as tidal freshwater and salinity starts to increases 30 to 50 km downriver (Jaworski et al. 1992). The upper Potomac River Basin is classified as 48% forested, 38% agricultural, and 14% urban (Karrh et al. 2007).

Sources of both nitrogen to the Potomac River include wastewater treatment effluent (e.g. the Blue Plains Wastewater Treatment Plant), urban and agricultural runoff, and atmospheric deposition. For the entire Potomac, the sources above the fall-line are 11.3% point, 84.6% diffuse, while the sources below the fall-line are 76.7% point, 15.4% diffuse, and 5.4% atmospheric (Boynton et al. 1995). The study by Jaworski et al. (1992) indicates that for the upper Potomac River, total nitrogen (TN) inputs are 27.5% atmospheric deposition, 42.65% animal waste, 11.6% fixation and adsorption, 16% fertilization, and 2.16% wastewater. The N outputs include 17.2% from river export, 17.1% from crop harvest, and 65.6% from other sinks and storage. Boynton et al. (1995) also estimates that internal losses of TN for denitrification rates above the fall-line are 5.5% point, 16.3% diffuse of total inputs and losses, while the sources below fall-line are 19.9% point, 19.6% diffuse of inputs and losses.

Text S1.2 Water Sampling and Analysis

Three sets of routine sampling along the Lower Potomac were carried out (See Figure 1). First, surface water was collected by small boat during seven separate months between September 2009 through January 2011 above and below the Blue Plains Wastewater Treatment Plant outfall (within 12 km). On each small boat cruise, 3-5 samples were collected longitudinally within 6 km above the wastewater outfall, one sample was collected in the estuary at the Blue Plains effluent outfall, and 4-6 samples were collected longitudinally within 12 km below the outfall. Monthly effluent samples were also taken from the wastewater treatment plant before emptying into the estuary. Second, monthly surface water samples were collected from nine Maryland Department of Natural Resources sampling stations, located longitudinally down the Potomac River Estuary, all the way to the Chesapeake Bay (from April 2010 to March 2011). Thirdly, there were two larger multi-depth sampling cruises from 24 sampling stations along the entire Lower Potomac River Estuary (August 2010 and May 2011). Samples were taken at surface, middle and bottom depths during theses two larger intensive sampling cruises. See Table S1 for site coordinates for the sampling stations.

At each sampling location, a 1-liter plastic amber HPDE bottle (cleaned in 10% HCl and distilled water) was used to take estuarine water samples. The surface water samples were collected using a pump and hose on the boat at 0.5-meter depth. The 1-liter bottle was then stored in a cooler, on icepacks until returning to the lab, where water was stored in the refrigerator, until filtered within 24 hours.

Water was filtered through 47 mm/0.45 µm glass fiber filter. The filtered water was then partitioned into two bottles: one 30 ml Nalgene bottle, one 60 mL glass amber

Quorpak bottle. The 30 mL Nalgene bottle was frozen and saved for nitrate isotope analysis. The 60 mL amber bottle was stored in a refrigerator (at 4°C), to be analyzed for fluorescence within 3-weeks. For quality assurance, blank samples and replicates were taken. The concentration of all total and dissolved forms of N, P, C were measured by Nutrient Analytical Services Laboratory (NASL) at Chesapeake Biological Laboratory (CBL).

Text S1.3 Salinity vs. Nitrate Concentration and Isotope Mixing Plots

The following equations from (Middelburg and Nieuwenhuize 2001) were used for calculating the mixing lines. End member values for these equations were based on the salinity, nitrate concentration, and nitrate isotope values found at the furthest up-estuary sampling station and furthest down-estuary sampling station (Table S2).

$$S = f \times Sm + (1 - f) \times Sr \quad (1)$$

$$f = \frac{S - Sr}{Sm - Sr} \quad (2)$$

$$N = f \times Nm + (1 - f) \times Nr \quad (4)$$

$$\delta^{15}N = \frac{(\delta^{15}Nm \times f \times Nm + \delta^{15}Nr \times (1 - f) \times Nr)}{N} \quad (5)$$

Where,

S = salinity of sample

Sr = salinity of freshwater endmember

Sm = Salinity of marine endmember

f = seawater fraction

N = Nitrate concentration of sample

15N = 15N nitrate of the sample

15Nr = 15N nitrate of freshwater endmember

15Nm = 15N nitrate of marine endmember

Table S1. Potomac River Estuary sampling locations and coordinates.

Shorter intensive synoptic surveys

Site	Distance (km)	Latitude	Longitude
TF2.1	12.1	38°42'23.91"N	77°02'55.54"W
TF2.2	17.8	38°41'26.43"N	77°06'40.00"W
TF2.3	29.6	38°36'29.52"N	77°10'26.04"W
TF2.4	41.4	38°31'48.36"N	77°15'55.44"W
RET2.1	55.6	38°24'12.60"N	77°16'08.76"W
RET2.2	64.0	38°21'09.00"N	77°12'18.36"W
RET2.4	87.9	38°21'45.36"N	76°59'26.27"W
LE2.2	130.1	38°09'27.36"N	76°35'52.80"W
LE2.3	156.6	38°01'17.40"N	76°20'51.72"W

Monthly extensive synoptic surveys

Site	Distance (km)	Latitude	Longitude
PR1	-6.6	38°52'22.65"N	77°02'12.28"W
PR2	-5.4	38°51'44.88"N	77°01'57.52"W
PR3	-6.1	38°51'52.86"N	77°00'32.14"W
PR4	-4.2	38°51'04.71"N	77°01'19.83"W
PR5	-2.7	38°50'18.55"N	77°01'35.62"W
PR6	-1.8	38°49'48.63"N	77°01'45.26"W
PR7	-0.8	38°49'15.85"N	77°01'50.84"W
PR8	-0.4	38°48'49.46"N	77°01'54.32"W
PR9	0	38°48'51.32"N	77°01'39.79"W
PR10	0.26	38°48'43.10"N	77°01'39.62"W
PR11	0.58	38°48'33.04"N	77°01'39.61"W
PR12	1.1	38°48'19.45"N	77°01'55.69"W
PR13	2.0	38°47'17.81"N	77°02'10.81"W
PR14	3.5	38°46'57.39"N	77°01'50.51"W
PR15	5.2	38°46'04.78"N	77°02'04.56"W
PR16	8.0	38°44'33.36"N	77°02'10.33"W
PR17	11.6	38°42'38.33"N	77°02'27.29"W

Seasonal extensive synoptic surveys

Site	Distance (km)	Latitude	Longitude
POTN28	-5.6	38°54'36.00"N	77°05'60.00"W
POTN27	-5.9	38°52'48.00"N	76°58'12.00"W
POTN26	-3.5	38°51'00.00"N	77°01'12.00"W
POTN25	1.2	38°49'48.00"N	77°01'48.00"W
POTN24	0.7	38°48'37.62"N	77°02'02.16"W
POTN23	11.8	38°42'30.96"N	77°02'40.32"W
POTN22	20.6	38°40'03.90"N	77°07'52.68"W
POTN21	20.6	38°40'16.86"N	77°08'01.86"W
POTN20	37.3	38°34'16.50"N	77°14'29.76"W
POTN19	48.7	38°28'32.04"N	77°16'50.94"W
POTN18	52.3	38°26'48.60"N	77°18'09.66"W
POTN17	59.0	38°23'33.78"N	77°16'09.54"W
POTN16	63.5	38°21'35.88"N	77°14'16.26"W
POTN15	76.8	38°24'22.26"N	77°06'46.44"W
POTN14	74.6	38°23'23.28"N	77°07'11.52"W
POTN13	85.0	38°26'49.02"N	77°01'50.58"W
POTN12	82.0	38°24'33.72"N	77°02'26.64"W
POTN11	93.8	38°19'38.34"N	76°58'41.52"W
POTN10	95.8	38°17'56.16"N	77°00'21.60"W
POTN09	110.1	38°20'52.02"N	76°51'12.48"W
POTN08	111.8	38°18'35.64"N	76°50'24.96"W
POTN07	112.8	38°14'25.02"N	76°49'04.32"W
POTN06	115.8	38°11'24.90"N	76°49'16.86"W
POTN05	136.8	38°11'45.78"N	76°34'46.32"W
POTN04	135.8	38°09'38.10"N	76°36'01.86"W
POTN03	153.5	38°05'00.36"N	76°25'16.56"W
POTN02	156.7	38°02'24.60"N	76°25'11.94"W
POTN01	158.4	38°00'41.58"N	76°25'45.00"W

***Distances are along the Potomac River, relative to the location of the Blue Plains wastewater treatment plant, at location 0 km.**

Table S2. Endmember values for salinity vs. nitrate concentration and isotope mixing lines

	Winter	Spring	Summer	Fall
Sr =	0.11	0	0	0
Sm =	15.8	11.0	14.2	16.7
Nr	1.44	1.09	0.3	0.83
Nm	0.0507	0.35	0.008	0.01
15Nr =	9.85	11.0	15.1	16.8
15Nm =	11.5	7.19	10.3	8.2
18Or	7.15	7.51	7.5	7.5
18Om	14.17	8.23	-5.4	-6.1

Table S3. Comparison between box model (this study) and Chesapeake Bay Model results.

Season	Distance (km)	Box Model Flux (kg/day)	Bay Model Flux (kg/d)	Factor Difference	% Difference	Correlation Coefficient
Winter	30	49,752	66,708	1	25	0.97
Winter	49	34,410	56,333	2	39	
Winter	95	19,844	26,926	1	26	
Spring	30	116,848	97,924	1	19	0.99
Spring	49	120,809	94,732	1	28	
Spring	95	68,431	55,274	1	24	
Summer	30	9,411	21,919	2	57	0.73
Summer	49	5,971	8,851	1	33	
Summer	95	4,853	15,496	3	69	
Fall	30	11,347	19,855	2	43	0.85
Fall	49	5,867	9,707	2	40	
Fall	95	(1,613)	9,790	(6)	116	

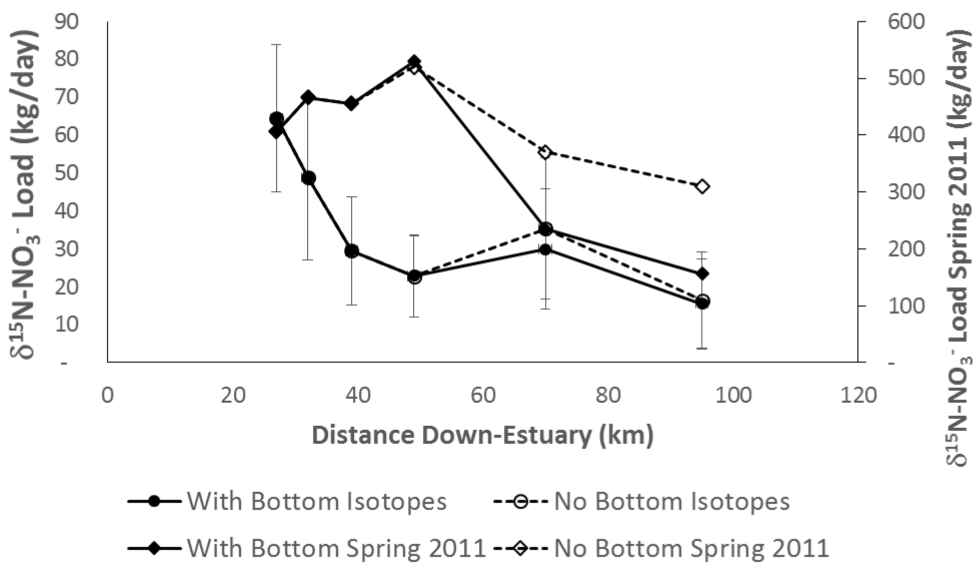

Figure S1. Comparison of nitrate isotope box model results when using bottom $\delta^{15}N$-NO_3^- isotope value from (Horrigan et al. (1990), which reported the bottom water $\delta^{15}N$-NO_3^- value to be ~ 10‰.

References

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