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Declining nitrate-N yields in the Upper Potomac River Basin: What is really driving progress under the Chesapeake Bay restoration?

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HIGHLIGHTS

- U.S. NO_x emission control programs were shown to be the primary driver of improving water quality across most of the UPRB.
- The MKNSM explained large proportions of the variation in annual nitrate-N yield through time and among the watersheds.
- The MKNSM allowed the annual nitrate-N yield to be separated into "responsive" and "non-responsive" components.
- NO_x emission controls have rapidly reversed nitrogen saturation across most of the UPRB.

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ABSTRACT

Reducing nutrient pollution of surface and coastal waters in the U.S. and elsewhere remains a major environmental and engineering challenge for the 21st century. In the case of the Chesapeake Bay restoration, we still lack scientific proof that watershed-based management actions have been effective at reducing nonpoint-source nutrient loads from the land to this estuary in accordance with restoration goals. While the conventional wisdom is that implementation of best management practices (BMP's) and wastewater treatment have turned the tide against nutrient pollution, we examined long-term (1986-present) nitrate-N trends in streams and major tributaries of the Upper Potomac River Basin (UPRB) and found that: 1) dramatic reductions in annual discharge-weighted mean nitrate-N concentrations and yields across the UPRB can be almost universally attributed to reductions in atmospheric N deposition as opposed to on-the-ground management actions such as implementation of BMP's; 2) observed water quality changes generally comport with a modified kinetic N saturation model (MKNSM); 3) the MKNSM can separate the nitrate-N yield that is responsive to atmospheric deposition from a "non-responsive" yield; and 4) N saturation from atmospheric N deposition appears to be an inherently reversible process across most of the landscape. These unanticipated region-wide water quality benefits can be attributed to NO_x emission controls brought about by the 1990 Clean Air Act Amendments (and subsequent U.S. NO_X control programs) and reflect a water quality "success story" in the Chesapeake Bay restoration.

1. Introduction

Reducing nutrient pollution of streams, rivers, lakes, and coastal waters in the U.S. and elsewhere remains a major environmental and engineering challenge for the 21st century (NRC, 2000; Howarth et al., 2000, 2002). In the U.S., the Clean Water Act passed in 1972 and amended in 1977 and 1987 established water pollution control regulations, provided funding for water treatment systems, and created a federal-state administrative program that has significantly reduced some types of water pollution—especially wastewater from municipal and industrial point source discharges (Dzombak, 2011). Controlling nonpoint source pollution (e.g., nutrient pollution from agricultural and urban runoff), has proven to be a much more vexing problem, however, due at least in part to a lack of regulatory and enforcement actions that can be used under the Clean Water Act (Dzombak, 2011). Perhaps nowhere in the U.S. has solving this nutrient pollution problem been more challenging than in the Chesapeake Bay—the nation's largest estuary—which has been plagued by excessive nutrient pollution and widespread hypoxic conditions that developed over many decades. Now on the third iteration of a state/federal agreement and partnership to restore this valuable ecosystem by dramatically reducing nutrient

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pollution through implementation of a total maximum daily load (TMDL) allocation process, and nearly thirty years of water monitoring and scientific study, progress has been frustratingly slow (NRC, 2011). In the case of the Chesapeake Bay restoration, we still lack scientific proof that watershed-based management actions have been effective at reducing nonpoint-source nutrient loads from the land to this estuary in accordance with the restoration goals. It has been suggested that improvements in nitrogen use efficiency resulting from implementation of agricultural best management practices (BMP's) combined with advanced municipal wastewater treatment are primarily responsible for observed declining nitrogen yields in some Chesapeake rivers (Shenk and Linker, 2013), despite the fact that some of the greatest percentage declines in N yields have been observed in predominantly-forested watersheds (Eshleman et al., 2013).

The availability of long-term water quality datasets, however, allows us to take a different tack that focuses more explicitly on the analysis of water quality trends in streams and major tributaries of Chesapeake Bay to determine whether the water quality improvements might be explained by drivers that have been largely overlooked or not properly accounted for in previous modeling efforts (e.g., Shenk and Linker, 2013). Our particular interest is in understanding watershed responses to atmospheric N deposition which was first implicated as a contributor to riverine nitrogen loads to Chesapeake Bay in the 1990's (Fisher and Oppenheimer, 1991; Jaworski et al., 1992, 1997). In the early 2000's, some researchers concluded that reducing N emissions and associated atmospheric N deposition was not an effective management tool for reducing total N loads to estuaries in the eastern U.S (Castro and Driscoll, 2002; Whitall et al., 2003). Recently, the role of atmospheric N deposition has been more accurately accounted for using the NANI (i.e., net anthropogenic nitrogen input) concept, but this approach has been used exclusively to examine spatial (rather than temporal) variability in N inputs and responses (Howarth et al., 2012; Hong et al., 2013). Chesapeake Bay Program data indicate that steep declines in atmospheric N inputs to the Chesapeake Bay watershed brought about through federal NO_x emission controls dwarf any declines in inputs of agricultural N sources (e.g., manures and fertilizers), but the possibility that declining atmospheric N deposition might *by itself* provide a universal explanation for recent improvements in water quality in both forested and mixed land use watersheds has not been fully assessed (Shenk and Linker, 2013; Linker et al., 2013; Boyer et al., 2002).

The research we report on here focuses on an issue of great importance to scientists and watershed managers alike by addressing two questions: 1) have controls on atmospheric N deposition reduced N yields from the land to surface waters (and, if so, how and by how much); and 2) will future reductions in atmospheric N deposition result in additional water quality improvements? Our previous work on these questions focused exclusively on nine predominantly-forested (i.e., >75% forest cover) watersheds located in the mountainous headwaters of the Chesapeake Bay basin (Eshleman et al., 2013). The study provided evidence that reductions in atmospheric N deposition—brought about through controls on NO_x emissions from stationary sources under the Acid Rain Program (ARP) of the Clean Air Act Amendments of 1990 (and subsequent federal air quality regulatory actions that reduced both stationary and mobile NO_x sources)—had produced dramatic (~40%) reductions in nonpoint-source nitrate-N yields during the period from the mid-1990's to the present. Our results also provided support for the application of a kinetic N saturation model—based on the simple concept of a watershed N mass balance—that attributed long-term changes in nitrate-N yields from forests to changes in atmospheric N deposition (Eshleman et al., 2013). The specific focus of this follow-up study is on the Upper Potomac River Basin (UPRB)—after the Susquehanna River, the 2nd largest source of freshwater to Chesapeake Bay—although we believe that the methods are relevant to understanding N dynamics throughout the larger Chesapeake Bay watershed.

We evaluate long-term changes in nitrate-N yields across the UPRB using monitoring data from 12 subwatersheds and the mainstem station at Washington, DC (POTW); data from five other Chesapeake Bay watersheds (not located in the UPRB, but analyzed previously by Eshleman et al., 2013) are also included in the present analysis. The data are used to test the following hypotheses: 1) reductions in annual nitrate-N concentrations and yields across the entire UPRB, including watersheds dominated by non-forested land, can be attributed to reductions in atmospheric N deposition; and 2) the observed water quality changes comport with a conceptual model of kinetic N saturation.

In our previous analysis (Eshleman et al., 2013), we interpreted empirical relationships between annual nitrate-N yield (Y) and annual wet N deposition (D) as evidence of a process of kinetic forest N saturation first suggested by Lovett and Goodale (2011):

$$Y = D - A - G \quad (1)$$

where A is the net annual incorporation of N into forest vegetation and soil organic matter and G are gaseous N losses. A simple solution to Eq. (1) was obtained by: 1) neglecting G; and 2) making A a linear function of D: $A = aD$ where a ($0 \leq a \leq 1$) represents the proportion of D that is taken up and stored in forest vegetation and soil (i.e., a is a forest N retention factor) and the y-intercept ($Y_0 \geq 0$) provides a measure of the (assumed constant) annual nitrate-N yield from non-forested land considered to be non-responsive to changes in atmospheric N deposition (Eshleman et al., 2013):

$$Y = Y_0 + (1 - a)D \quad (2)$$

For cases where $Y_0 = 0$, it is easily shown that $a = A/D = 1 - Y/D$ where a is a forest N retention factor (i.e., the average proportion of atmospheric N retained by a forest system in a year) which can be readily measured in watershed input-output studies (e.g., Grigal, 2012). In the present analysis of data from both predominantly forested and mixed land use watersheds, we test whether there is statistical support for a more general, *modified* kinetic N saturation model (MKNSM) in which Y increases exponentially with increasing atmospheric N deposition such that:

$$Y = Y_0 exp[kD] \quad (3)$$

where Y = annual watershed nitrate-N yield (kg N ha^{-1}); Y_0 is a baseline annual watershed nitrate-N yield (kg N ha^{-1}) that is considered non-responsive to changes in atmospheric N deposition; and k is a constant (ha kg^{-1}). Exponential relationships between N outputs and inputs have been observed in several other studies (Howarth et al., 2006, 2012; Gao et al., 2014), but our analysis is the first to examine such relationships using long-term, temporal datasets for individual watersheds. In testing this relationship for mixed land use watersheds in particular, we are effectively assuming that other non-atmospheric N inputs to these systems (i.e., N from point sources and nonpoint sources) are static and independent of D.

2. Materials and methods

We supplemented our own long-term data from two UPRB watersheds by obtaining nitrate-N concentration records from state water quality databases or USEPA STORET (http://www.epa.gov/storet) and stream/river discharge data from U.S. Geological Survey (http://waterdata.usgs.gov/nwis/sw) for 16 additional stations;

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annual wet atmospheric N (both nitrate-N and ammonium-N) deposition data were downloaded from the National Atmospheric Deposition Program (NADP, 2015: http://nadp.isws.illinois.edu/NTN/maps.aspx). We followed the same methods as those described by Eshleman et al. (2013), except that for the present analyses: 1) all wet N deposition and nitrate-N yield (and concentration) data were aggregated on a calendar year (as opposed to a water year) basis; 2) long-term records for all of the stations that remained active were extended through calendar year 2012; 3) the load estimation model, LOADEST (Cohn et al., 1989; Runkel et al., 2004; Stets et al., 2015), was recalibrated using the extended records; and 4) we made the explicit assumption that total annual N (nitrate plus ammonium) deposition = 2 × annual wet N deposition based on the data extracted from NADP (i.e., areal-weighted mean values) to account for the role of dry N deposition. This has been a very common assumption in N deposition modeling where detailed data on dry deposition are typically unavailable (Lovett and Lindberg, 1993; Boyer et al., 2002; Grigal, 2012).

The 12 UPRB watersheds and the entire UPRB are shown in Fig. 1 with descriptive data for all 18 study watersheds are provided in Table 1). We evaluated the efficacy of the MKNSM by parameterizing the model using annual Y and D data for each of the 18 watersheds using linear regression; a graph of lnY vs. D has a y-intercept of lnY_0 and slope k. Further, combining Eq. (1) and Eq. (3):

$$\alpha = 1 - \frac{Y_0 exp[k\overline{D}]}{\overline{D}} \quad (4)$$

where $0 \leq \alpha \leq 1$, $\overline{D}$ is the average N deposition, and α is defined as a long-term average atmospheric N retention factor for the entire watershed (representing forested and non-forested land). This is a useful modification of our original model, because it allows us to examine N responses as a function of land cover type for eight systems that we characterize as "mixed land use watersheds". As in the previous study, long-term trends (annual nitrate-N yields, nitrate-N concentrations, total N deposition, and runoff) were evaluated using linear regression (with $p \leq 0.05$ used as the criterion of statistical significance). We also used two-segment, piecewise linear regression (SigmaPlot for Windows 10.0) to examine whether nitrate-N concentrations and N deposition trends exhibited evidence of a break in slope from a constant value during the study period by iteratively varying the breakpoint (year) over the range of annual observations. We determined a breakpoint for a particular watershed from a statistically significant model that both maximized r^2 (relative to all competing breakpoint models) and increased r^2 relative to the linear model. We developed regression models to explain the interannual variations in a (= $1 - Y/D$ computed from annualized data) and used National Land Cover Data (NLCD) to explore whether among-watershed differences in k, α, and Y_0 could be explained by differences in land cover (i.e., differences in the percentage of forested land).

3. Results

Our analyses revealed nearly universal improvement in water quality across the UPRB and at the five ancillary stations. All 18 stations showed decreasing annual discharge-weighted mean nitrate-N concentrations over the periods of record (15–26 years), with 16 of the stations showing statistically significant ($p \leq 0.05$) linear trends. Decreasing annual nitrate-N yields were observed at 17 of 18 stations, although only five of the stations showed statistically significant trends. Yield trends are inherently "noisy" due to the effect that temporal variability in runoff has on the data, since yield is the product of concentration and runoff. The estimated slopes of the concentration trends (from linear regression) ranged over nearly an order of magnitude (from −0.004 mg N L^{-1} yr^{-1} at CRCF to −0.035 mg N L^{-1} yr^{-1} at BLAC) with a median value of −0.02 mg N L^{-1} yr^{-1}. The rate of change in nitrate-N concentration

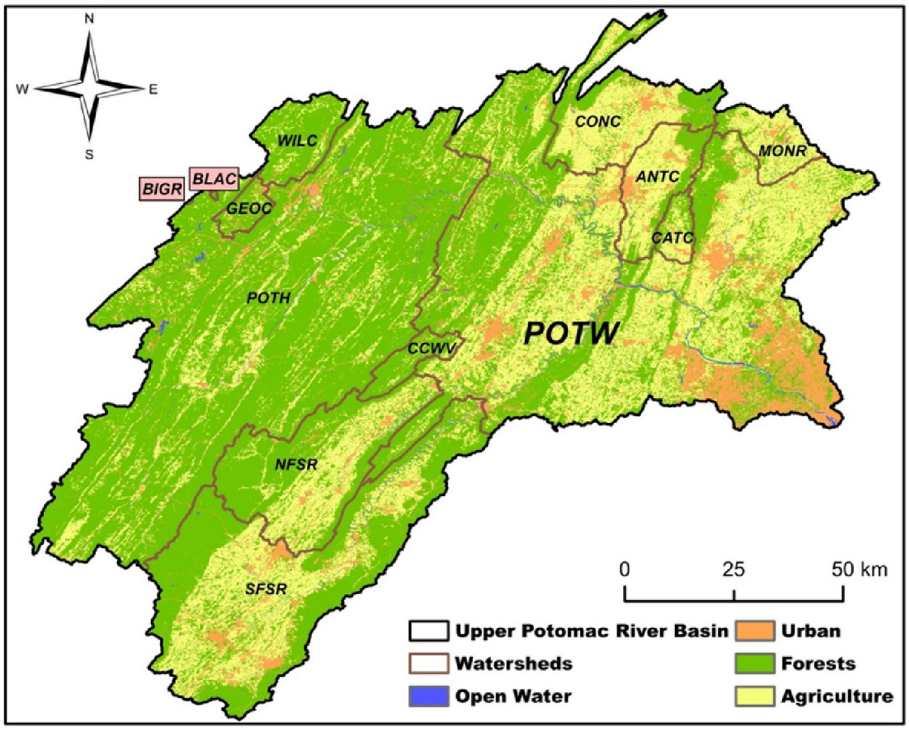

Fig. 1. Map of the Upper Potomac River Basin (UPRB) with land cover; 13 subwatersheds with long-term data for estimating annual nitrate-N yields are also shown (see Table 1 for site descriptions). Five study watersheds located outside the UPRB are not shown.

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Table 1
Site information for study watersheds used in the analysis of long-term trends.

Watershed name	Site code	Years of data	Watershed area (km^2)	Forested area (%)
Upper Potomac River Basin watersheds				
Upper Big Run, MD	BIGR	1990–2012	1.63	91.7
Black Lick, MD	BLAC	1997–2012	5.64	78.5
Georges Creek at Franklin, MD	GEOC	1986–2012	187	79.9
Wills Creek near Cumberland, MD	WILC	1986–2012	639	74.5
Potomac River at Hancock, MD	POTH	1986–2012	10,550	75.4
Cedar Creek near Winchester, VA	CCWV	1986–2008	267	85.6
Conococheague Creek at Fairview, MD	CONC	1986–2012	1280	41.1
Antietam Creek near Sharpsburg, MD	ANTC	1986–2012	727	32.2
North Fork Shenandoah River near Strasburg, VA	NFSR	1986–2012	1990	52.2
South Fork Shenandoah River at Front Royal, VA	SFSR	1986–2012	4230	52.5
Catoctin Creek near Middletown, MD	CATC	1986–2012	173	51.5
Monocacy River at Bridgeport, MD	MONR	1986–2012	448	19.7
Potomac River near Washington, DC	POTW	1986–2012	29,930	57.9
Other watersheds				
Driftwood Branch Sinnemahoning Creek at Sterling Run, PA	DBSC	1986–2012	704	92.9
Kettle Creek near Westport, PA	KCWP	1986–2012	603	94.9
Pine Creek below Little Pine Creek near Waterville, PA	PCLP	1986–2008	2440	98.2
Jackson River below Dunlap Creek at Covington, VA	JRDC	1986–2008	1590	81.0
Cowpasture River near Clifton Forge, VA	CRCF	1986–2008	1190	81.8

at POTW was −0.023 mg N L^{-1} yr^{-1} for a total change of −0.59 mg N L^{-1} over the 26-year monitoring period. In percentage terms, the mean decrease in nitrate-N concentration among the 18 stations was 37% with a median decline of 41%; the basin-wide decrease in nitrate-N concentration measured at POTW was 33.6%—very close to the median value of the other 17 stations. The mean decrease in nitrate-N yield was 31% with a median decrease of 35%; the basin-wide decrease in nitrate-N yield for the entire river basin (i.e., using data for POTW) was 30% (Table 2, Fig. 2). No statistically significant trends in runoff were observed (data not shown).

We also found very strong concurrence between improving water quality trends and declining atmospheric N deposition. Annual N deposition declined at all 18 stations (14 of the 18 stations showed statistically significant trends); estimated slopes from linear regression varied about thirty-fold (from −0.012 kg N ha^{-1} yr^{-1} at MONR to −0.360 kg N ha^{-1} yr^{-1} at BLAC). The rate of change in N deposition for the entire UPRB was −0.14 kg N ha^{-1} yr^{-1} for a total decrease of 3.64 kg N ha^{-1} (10.9×10^6 kg N) over the 26-year study period. In percentage terms, the mean decrease in annual N deposition to the 18 stations was 34% with a median decline of 43%; the basin-wide percentage decrease was 31% (Table 2, Fig. 2).

To illustrate spatial variations in N deposition trends across the UPRB, we produced a map displaying temporal changes between two time periods (1986–1988 and 2010–2012). Decreasing N deposition is apparent over nearly the entire basin with the greatest reductions (>4 kg N ha^{-1}) found in the western and southwestern parts of the basin and at the highest elevations (i.e., on the divides between the major watersheds, where some locations showed reductions that exceeded 6 kg N ha^{-1}). Lesser (<2 kg N ha^{-1}) reductions were observed in the northeastern part of the UPRB including large portions of the three watersheds (MONR, ANTC and CONC) for which N deposition trends were not statistically significant; more than half of the MONR watershed actually experienced a slight increase in N deposition (Fig. 3).

Table 2
Statistical results from linear trend analyses (slopes, absolute changes, and percentage changes) of annual nitrate-N yields, nitrate-N concentrations, runoff, and N deposition for the 18 study watersheds for the time periods shown in Table 1.[a] Breakpoint (BP) results based on the two-segment, piecewise linear regression are also shown.

Site code	Nitrate-N yield (kg N ha^{-1})				Nitrate-N concentration (mg L^{-1})							N deposition (kg N ha^{-1})						
	Slope (yr^{-1})	Δ (abs)	Δ (%)	r^2	Slope (yr^{-1})	Δ (abs)	Δ (%)	r^2	BP slope (yr^{-1})	BP (yr)	BP r^2	Slope (yr^{-1})	Δ (abs)	Δ (%)	r^2	BP slope (yr^{-1})	BP (yr)	BP r^2
Upper Potomac River Basin watersheds																		
BIGR	**−0.090**	**−1.97**	**−67**	**0.428**	**−0.019**	**−0.41**	**−74**	**0.634**	N/A	N/A	N/A	**−0.256**	**−5.63**	**−44**	**0.488**	**−0.332**	**1996**	**0.563**
BLAC	**−0.192**	**−2.88**	**−49**	**0.320**	**−0.035**	**−0.52**	**−49**	**0.919**	N/A	N/A	N/A	**−0.360**	**−5.40**	**−47**	**0.538**	N/A	N/A	N/A
GEOC	−0.070	−1.83	−34	0.086	**−0.026**	**−0.66**	**−48**	**0.896**	N/A	N/A	N/A	**−0.216**	**−5.60**	**−44**	**0.510**	**−0.328**	**1996**	**0.586**
WILC	−0.108	−1.67	−39	0.117	**−0.022**	**−0.57**	**−39**	**0.744**	N/A	N/A	N/A	**−0.202**	**−4.42**	**−42**	**0.463**	**−0.304**	**1996**	**0.517**
POTH	−0.064	−2.80	−44	0.139	**−0.019**	**−0.50**	**−47**	**0.731**	**−0.035**	**1998**	**0.926**	**−0.170**	**−5.26**	**−39**	**0.425**	**−0.259**	**1996**	**0.489**
CCWV	−0.024	−0.53	−36	0.073	**−0.007**	**−0.16**	**−37**	**0.717**	**−0.012**	**1998**	**0.910**	**−0.158**	**−3.47**	**−32**	**0.308**	**−0.205**	**1996**	**0.352**
CONC	0.125	3.26	22	0.027	−0.009	−0.24	−6	0.073	N/A	N/A	N/A	−0.077	−2.00	−16	0.090	N/A	N/A	N/A
ANTC	−0.003	−0.09	−1	0.000	**−0.031**	**−0.80**	**−16**	**0.544**	N/A	N/A	N/A	−0.087	−2.25	−19	0.106	N/A	N/A	N/A
NFSR	−0.008	−0.20	−4	0.001	−0.000	−0.00	−0	0.000	**−0.110**	**2006**	**0.347**	**−0.146**	**−3.79**	**−39**	**0.339**	**−0.222**	**1996**	**0.390**
SFSR	**−0.114**	**−2.95**	**−50**	**0.155**	**−0.028**	**−0.73**	**−44**	**0.776**	**−0.037**	**1994**	**0.868**	**−0.146**	**−3.80**	**−37**	**0.393**	**−0.221**	**1996**	**0.447**
CATC	−0.020	−0.53	−7	0.002	**−0.014**	**−0.36**	**−19**	**0.314**	N/A	N/A	N/A	**−0.126**	**−3.27**	**−35**	**0.185**	N/A	N/A	N/A
MONR	−0.058	−1.50	−13	0.012	**−0.028**	**−0.71**	**−26**	**0.280**	**−0.084**	**2002**	**0.432**	−0.012	−0.32	−3	0.002	N/A	N/A	N/A
POTW	−0.071	−1.85	−30	0.047	**−0.023**	**−0.59**	**−34**	**0.626**	**−0.047**	**1999**	**0.854**	**−0.140**	**−3.64**	**−32**	**0.359**	**−0.214**	**1996**	**0.416**
Other watersheds																		
DBSC	**−0.048**	**−1.25**	**−40**	**0.223**	**−0.009**	**−0.26**	**−46**	**0.701**	**−0.015**	**1997**	**0.863**	**−0.210**	**−5.45**	**−37**	**0.525**	N/A	N/A	N/A
KCWP	−0.040	−1.05	−34	0.139	**−0.010**	**−0.27**	**−45**	**0.875**	N/A	N/A	N/A	**−0.145**	**−3.77**	**−29**	**0.324**	N/A	N/A	N/A
PCLP	−0.027	−0.59	−26	0.061	**−0.006**	**−0.14**	**−31**	**0.286**	**−0.013**	**1998**	**0.633**	−0.073	−1.61	−14	0.109	N/A	N/A	N/A
JRDC	**−0.033**	**−0.72**	**−62**	**0.251**	**−0.008**	**−0.18**	**−63**	**0.583**	**−0.012**	**1996**	**0.827**	**−0.118**	**−2.59**	**−25**	**0.260**	**−0.196**	**1998**	**0.356**
CRCF	−0.016	−0.36	−44	0.119	**−0.004**	**−0.08**	**−43**	**0.533**	**−0.005**	**1996**	**0.709**	**−0.150**	**−3.29**	**−30**	**0.369**	**−0.200**	**1996**	**0.444**

[a] Slopes and associated changes shown in bold are statistically significant at $p \leq 0.05$ level; N/A = not applicable.

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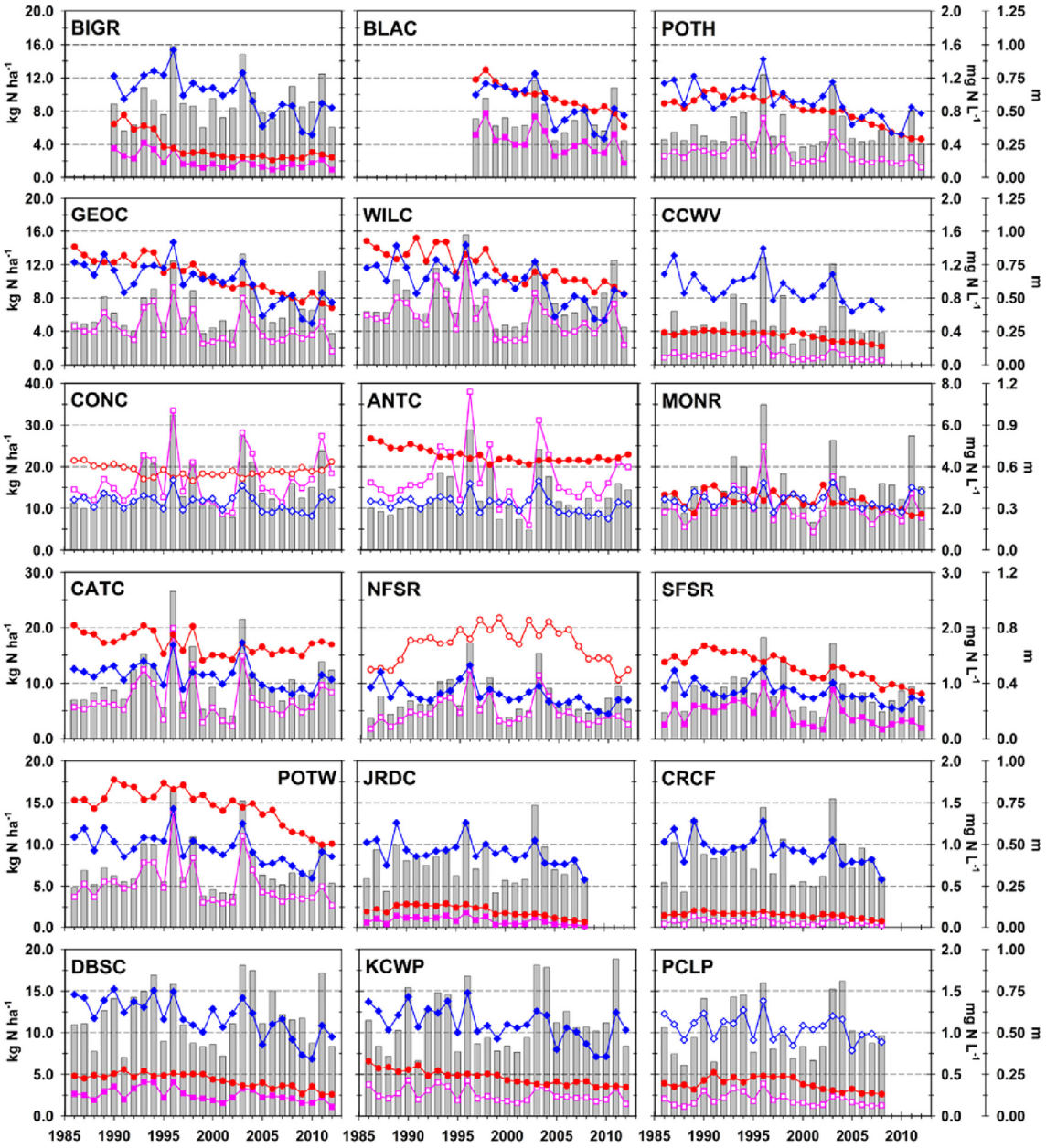

Fig. 2. Temporal variations in annual nitrate-N yields (pink squares), discharge-weighted mean nitrate-N concentrations (red circles), total N deposition (blue diamonds), and runoff (gray bars) for the 18 study watersheds. Linear trends of plots shown as solid symbols are statistically significant at $p < 0.05$ level (see Table 2 for trend results). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Of the 14 watersheds that exhibited statistically significant decreasing linear trends in annual N deposition, 10 produced statistically significant breakpoint models, 3 (CATC, DBSC, and KCWP) showed no statistical evidence of a breakpoint, and one (BLAC) lacked a sufficiently long record to identify a break in slope; for the 10 stations showing a break, 9 showed that the break occurred in the same year (1996) and one (JRDC) showed a break in 1998. Of the 4 stations showing no trend in N deposition, none showed a break. Of the 16 watersheds that showed statistically significant declining nitrate-N concentrations, 9 showed statistical evidence of a breakpoint, 5 showed no breakpoint, and the record for BLAC was again deemed too short; one watershed (NFSR) that did not show a declining linear trend in nitrate-N concentration produced a statistically significant breakpoint model. Among the group showing a breakpoint in nitrate-N concentration, breakpoint years ranged from 1994 to 2006 (median of 1998). Three watersheds (BIGR, WILC, and GEOC) showed evidence of a breakpoint in N deposition but not one in nitrate-N concentration, while three watersheds (MONR, DBSC, and PCLP) showed the opposite pattern. Only two watersheds (SFSR, JRDC) exhibited nitrate-N concentration breakpoints that preceded their corresponding N deposition breakpoint year (Table 2).

In general, the results were strongly supportive of the proposed exponential relationship between Y and D that underpins the MKNSM. We identified two-parameter, exponential relationships (i.e., Eq. (3)) for all 18 watersheds including the entire UPRB (station POTW); k and Y_0 values were statistically significant ($p \leq 0.05$) in all 18 models and these "local" models explained 14–61% of the total variation in Y. Mean k values for the 11 forested watersheds and 7 mixed land use watersheds were very similar (0.15 and 0.13 ha kg^{-1},

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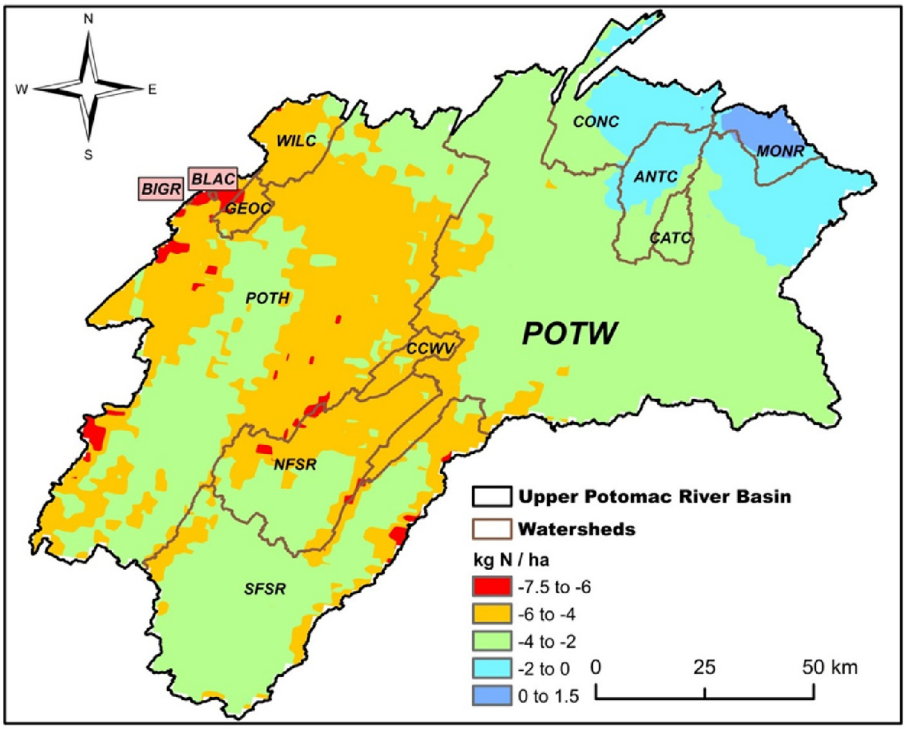

Fig. 3. Map showing computed changes in annual total (wet + dry) atmospheric N deposition to the UPRB study watersheds between 1986–1988 and 2010–2012 based on NADP/PRISM data and assuming wet and dry N deposition are equivalent in magnitude. See Table 1 for watershed names and site codes.

Table 3
Statistical results from testing of MKNSM.

Site code	Results from Eq. (3)			Results from Eq. (4)		Regression of a on annual runoff (R): $a = b_1R + b_0$		
	k (ha kg^{-1})	Y_0 (kg N ha^{-1})	r^2	$\overline{D}$ (kg N ha^{-1})	α	b_0	b_1	r^2
Upper Potomac River Basin watersheds								
BIGR	0.1116	0.59	0.404	9.97	0.820	0.874	−0.125	0.081
BLAC	0.1210	1.42	0.542	8.78	0.532	0.758	−0.580	0.410
GEOC	0.1047	1.44	0.364	9.89	0.590	0.851	−0.718	0.631
WILC	0.0987	2.00	0.302	9.89	0.463	0.835	−0.872	0.566
POTH	0.1514	0.67	0.551	9.22	0.707	0.887	−0.556	0.665
CCWV	0.1743	0.22	0.560	9.20	0.881	0.953	−0.228	0.800
CONC	0.0965	5.18	0.335	11.51	−0.367	0.312	−1.685	0.637
ANTC	0.1002	5.34	0.303	11.01	−0.462	0.289	−2.203	0.684
NFSR	0.0895	2.15	0.143	7.91	0.417	0.802	−1.482	0.573
SFSR	0.1734	0.92	0.394	8.39	0.530	0.900	−1.239	0.745
CATC	0.1388	1.30	0.403	11.40	0.445	0.822	−1.059	0.795
MONR	0.1258	2.15	0.483	12.07	0.187	0.565	−0.925	0.586
POTW	0.1535	1.11	0.472	9.54	0.497	0.828	−1.015	0.820
Other watersheds								
DBSC	0.1078	0.66	0.573	11.87	0.800	0.898	−0.181	0.471
KCWP	0.1203	0.65	0.594	11.09	0.777	0.885	−0.207	0.577
PCLP	0.1539	0.36	0.439	10.58	0.827	0.928	−0.214	0.441
JRDC	0.3040	0.03	0.561	9.09	0.948	1.000	−0.218	0.525
CRCF	0.2320	0.06	0.609	9.35	0.944	0.995	−0.144	0.808

respectively), while mean Y_0 values (0.7 and 2.6 kg N ha^{-1}, respectively) were quite different. With just two exceptions, α values computed using Eq. (4) fell in the presumed range between 0 and 1, thus supporting the general applicability of the MKNSM. Results for two stations (ANTC and CONC) produced negative α values that are inconsistent with the model; these two stations were thus treated as "outliers" in all subsequent analyses (Table 3).

Linear regression analysis revealed that the best predictor of the interannual variation in α for the individual watersheds was annual runoff (R). We observed statistically significant negative linear relationships between α and R for 17 of the 18 watersheds with the models explaining 41–82% of the total variation in α. Data for one watershed, BIGR, a small forested watershed in western Maryland that experienced extensive gypsy moth defoliation in the late 1980's that dramatically altered the temporal pattern of nitrate-N yield in the years following disturbance (Eshleman et al., 1998), showed the same relationship, but it was only statistically significant at the 0.2 level (Table 3).

The percentage of forested land within a watershed was found to be an excellent predictor of α (r^2 = 0.69) based on linear

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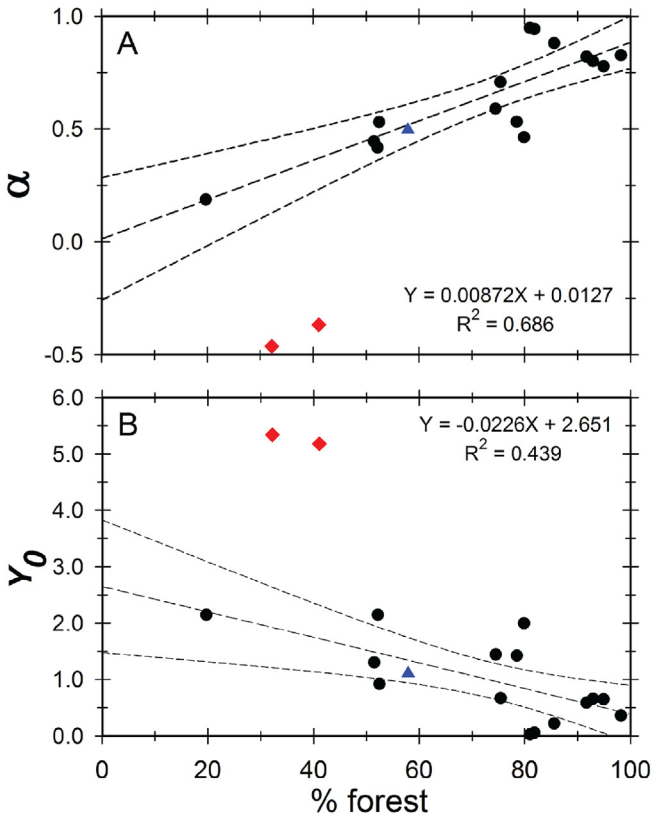

Fig. 4. Relationship between (A) α; and (B) Y_0 estimated using the MKNSM vs. % forest for 15 watersheds (black circles) from linear regression; error bars are 95% confidence intervals. Results for outliers ANTC and CONC (red diamonds) and POTW (blue triangles) are shown, but were not used in the regressions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

regression. For 15 of the 18 watersheds (not including ANTC and CONC which we discuss separately and station POTW that was not used in the regression), the linear model predicts that a watershed that is 100% forested would be expected to have an α value of 0.88, while a watershed that is 0% forested should have a value of 0.01 (Fig. 4A). This model is our "regional MKNSM" that is applicable to predicting the region-wide response of watersheds to decreasing annual N deposition; the model also showed very good agreement between predicted (0.52) and observed (0.50) values of α for POTW. Further, %forest was also a good predictor of Y_0 for the same 15 watersheds ($r^2 = 0.44$); watersheds that are 100% forested are predicted to have a Y_0 value of 0.4 kg N ha^{-1}, while watersheds that are 0% forest are predicted to have a Y_0 value of 2.7 kg N ha^{-1}. For POTW, the model predicts a Y_0 of 1.3 kg N ha^{-1} compared to the observed value obtained from the local model of 1.1 kg N ha^{-1}, again suggesting reasonably good agreement (Fig. 4B).

4. Discussion

Nitrate-N yields from both non-forested and forested lands across most of the UPRB have apparently declined in response to decreasing atmospheric N deposition, although extreme interannual variability owing to hydroclimatic variation makes it difficult to use yield trends as the sole indicator of improving water quality. At most of the UPRB watersheds (except two mixed land use watersheds located in the Ridge and Valley province) and at the five ancillary forested sites, our results showed contemporaneous declines in total N atmospheric deposition, nitrate-N yields, and discharge-weighted mean nitrate-N concentrations in streamwater during the study period (Table 2, Fig. 2). Annual average discharge-weighted mean nitrate-N concentrations provide a superior, robust indication of water quality improvement and our analyses suggest that decreases in N deposition and surface water nitrate-N concentrations began at about the same time (mid-1990's). The graphical results and iterative piecewise regression analysis indicate that atmospheric N deposition began to decline in most of these systems (and in the UPRB as a whole) in 1996—the same year that ARP NO_x emission limits on coal-fired boilers were first put into effect. At the national scale, USEPA estimated 100% compliance with the NO_x limits in 1996 for a total emission reduction of 33% relative to 1990 levels, although it's likely that some NO_x emission reductions actually began a year or so earlier as some electric utilities effectively "overcomplied" with the new regulations (USEPA, 1997). Additional NOx emission reductions under ARP, reinforced by the Clean Air Interstate Rule (CAIR), continued after 1996 (Butler et al., 2011). While only a small number of watersheds showed clear breakpoints in both N deposition and nitrate-N concentrations, the decrease in nitrate-N concentration in these systems generally lagged the decline in N deposition by several years or more; over the entire UPRB, results for station POTW indicate a lag of three years from the onset of declining N deposition (Table 2). Overall, we interpret the results as providing relatively strong evidence that decreasing trends in N deposition, surface water nitrate-N yields, and concentrations throughout most of the UPRB and in neighboring basins reflect a systematic response to national air quality regulations.

Perhaps counterintuitively, the results indicate that non-forested land has been considerably more responsive to decreasing N deposition than forested land, presumably because it is inherently less retentive of atmospheric N inputs due to sparser vegetation and greater N loads from non-atmospheric sources (e.g., fertilizers, manures, etc.). Our results can be interpreted using an end-member model in which the end-members are 100% forest (i.e., $\alpha_F = 0.885$) and 100% non-forest (i.e., $\alpha_{NF} = 0.012$). The regional MKNSM thus indicates that a decline in atmospheric N deposition onto non-forested land produces about a 1:1 decline in annual nitrate-N yield, while the same decline in N deposition onto forested land produces a decline in nitrate-N yield that is about 1/9th (i.e., $[1-\alpha_F]/[1-\alpha_{NF}] = 0.116$) as large. Therefore, estimated α values can be interpreted as area-weighted averages of α end-members. For the POTW station as an example, the two end-members can be used to predict the area-weighted α value using known relative areas of forest (57.9%) and non-forest (42.1%) and the end-member values (i.e., $[\alpha_F][0.579] + [\alpha_{NF}][0.421] = [0.885][0.579] + [0.012][0.421] = 0.52$); the computed value is nearly identical to the estimated value from the field data of 0.50 (Fig. 4A, Table 3). The same approach can be used to predict the area-weighted Y_0 values. For POTW: $[Y_{0,F}][0.579] + [Y_{0,NF}][0.421] = [0.39][0.579] + [2.65][0.421] = 1.34$, which is within 20% of the estimated value (1.11) from the field data (Fig. 4B, Table 3). The fact that the modeled values are very close to the field-based values not only supports the general concept of the regional MKNSM, but also demonstrates that the model can be successfully scaled and aggregated to larger river basins. The model also predicts that 86% (i.e., $100 \times [1-\alpha_F][0.579]/\{[1-\alpha_F][0.579] + [1-\alpha_{NF}][0.421]\}$) of the computed reduction in nitrate-N yield for POTW attributable to atmospheric N reduction was associated with non-forested land compared to 14% for forested land. Even for predominantly-forested POTH, the non-forested atmospheric N yield reduction is nearly three times greater than the reduction on forested land (74% vs. 26%). Similarly, for all of the watersheds, the model predicts that Y_0 (i.e., the non-responsive or "baseline" portion of the nitrate-N yield) is dominated by the non-forested

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component; using POTW and POTH as examples, the non-forested portions of Y_0 were estimated as 83% and 69% of the total baseline yield, respectively.

While some previous work has suggested that a N deposition threshold may exist below which nitrate-N leaching does not occur (Dise and Wright, 1995; Aber et al., 1989), more recent evidence suggests that there is no threshold atmospheric N deposition value below which nitrate-N yields remain completely unaffected (Grigal, 2012). The evidence presented here showing that a continuous, two-parameter exponential function can represent the relationship between Y and D for individual systems is consistent with the observation that no such threshold exists. Further, the baseline annual watershed nitrate-N yield, Y_0, provides a straightforward approach to separating the portion of the nitrate-N yield that does not respond to changing N deposition. As noted previously, Howarth et al. (2012) observed similar relationships between riverine N yields and N deposition for a group of selected U.S. watersheds, but their analysis involved substitution of space for time. Their estimated y-intercept of 117.7 kg N km^{-2} (= 1.2 kg N ha^{-1}) and k of 0.0024 km^2 kg^{-1} (= 0.24 ha kg^{-1}) fell near the middle of our observed ranges for these parameters (0.03–2.15 kg N ha^{-1} and 0.09–0.30 ha kg^{-1}; Table 3), respectively, excluding results for ANTC and CONC as we have done throughout. The relatively good agreement was found despite that fact that the approach of Howarth et al. (2012) explicitly neglected ammonium-N deposition which our analysis included.

Interestingly, our regional forest N retention factor ($\alpha_F = 0.89$) is very close to the value (0.85) determined by Grigal (2012) making the same assumption about wet and dry N deposition being equal. Campbell et al. (2004) analyzed data for 24 small forested watersheds in the northeastern U.S. and found a mean N retention of 69% (including dry N deposition would have brought their value much closer to ours). It is well established that non-forested land in the Chesapeake Bay watershed is significantly less retentive of N inputs than forested land (Jaworski et al., 1992; Groffman et al., 2004), but no studies that we are aware of have been able to separately quantify the retention of atmospheric N by agricultural, urban, and suburban land uses from retention of other N inputs (e.g., fertilizer); our work is a step in that direction, although our current method only allows a separation of retention between forested and non-forested land uses.

Our results suggesting that non-forested land uses may provide minimal net retention of atmospheric N deposition (i.e., the nitrate-N yield is roughly equal to N deposition when both are expressed in the same units)—is in sharp disagreement to the conclusion of Linker et al. (2013) that “most of the [Chesapeake Bay] watershed atmospheric nitrogen deposition loads are attenuated by plant uptake, denitrification, and other loss mechanisms”. Some input-output results have suggested significant net retention of atmospheric N by non-forested land uses in eastern Maryland: 75% retention by a suburban watershed and 77% retention by an agricultural watershed (compared to 95% retention by a forested watershed; Groffman et al., 2004). Our results suggest that such analyses are effectively overestimating the retention of atmospheric N deposition because atmospheric and fertilizer N inputs are simply lumped together in making the calculation. It seems much more reasonable to consider that the majority of atmospheric N in mixed land use watersheds is deposited onto: 1) impervious surfaces (year-round); 2) unvegetated agricultural soils (especially during the dormant season); and 3) vegetated agricultural soils (during the growing season) that have been heavily fertilized. Under these conditions, it might be expected that atmospheric N retentiveness would be very low (or nearly zero) as our results suggest. Jaworski et al. (1992) speculated that retention of N added in fertilizer to agricultural lands should differ from retention of atmospherically-deposited N, but they did not have the data in the form of a long time series to explicitly test that hypothesis.

We also observed that atmospheric N retentiveness (a) generally varied as a linear function of annual runoff, R (Table 3)—illustrating the important role of interannual hydroclimatologic variability as a driver of nitrate-N yields in these watersheds; as others have shown, greater proportions of N inputs are typically exported in years with higher precipitation and runoff (Han et al., 2009; Howarth et al., 2012; Huang et al., 2014). The fact that a linear model can explain most of the variation in annual N retentiveness is consistent with an interpretation that greater runoff is primarily driven by greater “quickflow” (i.e., subsurface stormflow or overland flow) along preferential hydrologic pathways in upland watersheds, thus enabling greater nitrate-N export. To the extent that a significant portion of the N retention in these systems can be attributed to denitrification in wetlands and hydric soils, the proportion of nitrate that can be removed would expectedly be directly related to hydrologic residence time (Howarth et al., 2006).

Although the MKNSM explained large proportions of the interannual variation in both α and Y_0 for 16 of the 18 watersheds, the model broke down when we applied it to ANTC and CONC; computed α values for these watersheds were negative and Y_0 values were extremely high (>5 kg N ha^{-1})—suggesting that a significant portion of the present annual nitrate-N yield from these watersheds can perhaps be attributed to a legacy of nitrate contamination of groundwater by agricultural practices. Both watersheds are highly agricultural and are located in the northeastern part of the UPRB where atmospheric N deposition reductions have been much lower than in the western portion of the basin; as importantly, these watersheds are located in the Ridge and Valley physiographic province that is dominated by unconfined, carbonate-rock aquifers comprised of karstic, Paleozoic-age limestone and dolomite formations (Lindsay et al., 2009), relatively long (1–232 yr) groundwater residence times based on dating using chlorofluorocarbons (Focazio et al., 1998), and groundwater flowpaths and in which flow is mostly through connected solution conduits for distances that range from thousands of feet to miles (Trapp and Horn, 1997). As water moves downgradient from recharge areas, it tends to be concentrated in ever-larger conduits until it typically discharges to a stream from a large spring (Trapp and Horn, 1997). Where recharge occurs under agricultural areas, nitrate contamination by fertilizers or animal wastes is quite common (Focazio et al., 1998; Lindsay et al., 2009), effectively swamping out any declines in nitrate associated with atmospheric N reduction. Long subsurface flowpath lengths and groundwater residence times may also be physically “decoupling” nitrate-N yields from atmospheric N deposition in ANTC and CONC and perhaps elsewhere in the Ridge and Valley Province.

Are the decreased yields at the POTW station between 1986 and 2012 realistic? Over the entire UPRB, our results indicate that a 32% reduction in total annual atmospheric N deposition (3.64 kg N ha^{-1} or 10.9×10^6 kg N) produced a 34% reduction in annual nitrate-N yield (2.11 kg N ha^{-1} or 6.31×10^6 kg N) at the basin outlet. Linker et al. (2013) recently examined N deposition for the 21-year period from 1985 to 2005 and reported about a 30% reduction over the entire Chesapeake Bay watershed and used a dynamic, process-based, watershed model (USEPA, 2010; Shenk and Linker, 2013) to estimate the response of various Bay watersheds (including the UPRB) to this reduction; they estimated that total N delivered to the UPRB outlet (i.e., POTW) declined from 34.9 million kg N in 1985 to 31.5 million kg N in 2010 (~10% decrease of 3.4 million kg N). Thus, their modeled decline in total N yield is only about half as large as the value we obtained for the nitrate-N yield reduction by applying the regional MKNSM to POTW, and their annual N yield reduction of 10% is less than a third as large as the value (34%) we obtained

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from the long-term analysis of nitrate-N trends. Since Linker et al. (2013) did not provide any comparison of their simulations with observations, it is difficult to evaluate how much confidence one should have in these results or their conclusion that atmospheric N deposition loads are fully attenuated. Our results strongly suggest that atmospheric N deposition loads to the UPRB are not fully attenuated, thus making possible the dramatic improvements in water quality described here. These improvements have also occurred despite the fact that the ARP and subsequent U.S. NO_x emission controls never anticipated the region-wide water quality benefits demonstrated in the present study. Nonetheless, even if these water quality improvements should be properly considered "co-benefits" of a regulatory program that has been focused exclusively on acid-sensitive waters and human health effects, we believe that these results reflect one of a very few water quality "success stories" for the Chesapeake Bay restoration program—albeit one that was ironically driven by air quality rather than by water quality control efforts.

What are the implications of our interpretation of these results for the Chesapeake Bay restoration? While interannual variability in nitrate-N yields often obscured long-term trends, the results taken as a whole provide a compelling case that atmospheric N deposition controls have likely been the primary driver of recent reductions in nitrate-N yield throughout much of the UPRB (excluding portions of the Ridge and Valley province where our model broke down). With the exception of one other watershed (MONR) for which the rate of decline in annual atmospheric N deposition was lowest across the basin, the estimated change in atmospheric N deposition during the period 1986–2012 was of sufficient magnitude to explain the *entire* change in total nitrate-N yield at the same stations (Table 2). The effect of other management actions (i.e., implementation of BMP's, point source reductions, etc.) noted by others appear to be of secondary importance at the scale of the entire UPRB, consistent with the fact that inorganic fertilizer and manure N inputs to the UPRB show no long term decline. We suspect that land use changes (i.e., conversion of agricultural to suburban land use), shifts in agricultural production (i.e., increasing poultry production), and wastewater treatment plant upgrades may be secondary drivers of water quality changes, especially in some of the mixed land use basins (e.g., MONR, CATC, and NFSR). Additional work will be needed to explicitly account for these drivers that our current approach effectively discounts. Our results also appear to refute other studies (Castro and Driscoll, 2002; Whitall et al., 2003; Linker et al., 2013) that may have seriously underestimated the role of N emissions and deposition reduction as a tool in achieving watershed N loading targets. It is also possible that decreasing nitrate yield trends reported for other Chesapeake Bay subbasins (Hirsch et al., 2010; Zhang et al., 2013) can be mostly explained by this common driver. Our results thus have obvious ramifications for managing water quality in the entire Chesapeake Bay watershed—particularly through the 2017 "midpoint assessment" that is part of the latest Chesapeake Bay Watershed Agreement. If the land-based management actions being undertaken now are not having the presumed water quality effects, then a strong argument can be made that resources should be deployed more efficiently to achieve desired future water quality goals.

What about the future? Our results confirm that the long-term decline in atmospheric N deposition onto the UPRB is sufficient to explain the decreasing nitrate-N yields and concentrations at most UPRB surface water monitoring stations (and at the basin outlet), but interannual variations in nitrate-N yields are also controlled by hydroclimatological variations, especially runoff, as others have suggested (Howarth et al., 2006; Kaushal et al., 2008; Han et al., 2009; Howarth et al., 2012; Huang et al.,, 2014). Our conceptualization of the watershed using the MKNSM based on the long-term data and relationships between Y and D suggest that—with the exception of some Ridge and Valley subwatersheds—N saturation appears to be inherently reversible with a negligible lag (owing to relatively short hydrologic residence times) across most of the UPRB. While it can be dangerous to extrapolate these results into the future, the model would clearly predict that future declines in N deposition brought about by additional NO_x emission reductions across the UPRB airshed would be expected to produce more improvements in water quality (although the exponentially decreasing relationship between Y and D means that future improvements will continue to "decay" over time). Further, the MKNSM projects that future declines in nitrate-N yield will be moderated by the fact that as N deposition declines, a greater proportion of the yield will be attributed to the non-responsive ("baseline") portion (i.e., Y_0). As an example (Fig. 5), using POTW, the MKNSM results suggest that Y declined by an estimated 2.31 kg N ha^{-1} from 5.64 kg N ha^{-1} (41%) between 1996 and 2012 due to a decline in D of 3.43 kg N ha^{-1} (32%); using $Y_0 = 1.1$ kg N ha^{-1} to account for the portion of the load that is non-responsive, the model suggests that the responsive portion of Y decreased by about 51% as of 2012, however. An additional decline in D of 3.43 kg N ha^{-1} in the future would be predicted to cause an additional decline in Y of 1.36 kg N ha^{-1}—only 59% as large as the present reduction—illustrating an important impact of the exponential relationship. Given the likely future replacement of relatively old, inefficient, coal-fired electrical generating facilities in the airshed by newer renewable (e.g., wind turbines, solar, etc.) and high efficiency coal- and natural gas-fired generating facilities with lower NO_x emissions per kWh of power generated (Jaramillo et al., 2007), we consider it likely that the UPRB will see some additional improvements in water quality within the next decade and perhaps beyond—but the nitrate-N yield improvements will be subjected to an apparent "law of diminishing returns" as the terrestrial ecosystem becomes increasingly dominated by non-responsive N sources. One cautionary note is that the apparent reversibility of the process means that future increases in atmospheric N deposition due to any relaxation in air quality regulation would be expected to cause an immediate reversal in the direction of watershed N yield trends across the basin.

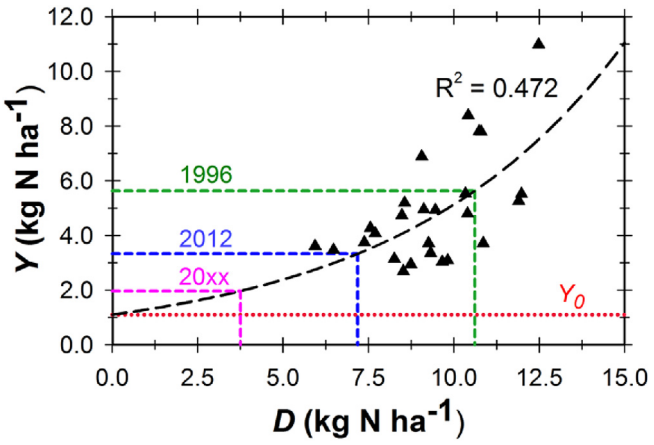

Fig. 5. Conceptual diagram of the parameterized MKNSM for POTW illustrating changes in annual nitrate-N yield (Y) in response to declining atmospheric N deposition (D). Dashed lines correspond to reference D values in 1996 and 2012 based on our breakpoint model (Table 3) and in a hypothetical future year (20xx) at which time it is assumed that an additional reduction in D has occurred that is of equal magnitude (3.43 kg N ha^{-1}) as the total reduction that occurred between 1996 and 2012.

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5. Conclusions

- Reductions in atmospheric N emissions and deposition under the 1990 U.S. Clean Air Act Amendments and subsequent NO_x emission control programs were shown to be the primary driver of improving water quality across most of the UPRB.
- For most of the watersheds examined, the overall improvement in water quality (i.e., the decline in surface water nitrate-N concentrations) was shown to vary as a function of the decline in N deposition and a model parameter (α) representing the average N retentiveness of the watershed.
- The use of the MKNSM, based on a two-parameter exponential relationship between Y and D, explained large percentages of the variation in the nitrate-N yield data and effectively allowed the yield to be separated into "responsive" and "non-responsive" components.
- Nitrogen saturation—brought on through excessive additions of N both from atmospheric deposition and other sources—has been significantly and rapidly reversed across most of the UPRB (with the exception of some of the Ridge and Valley portion of the basin).

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