

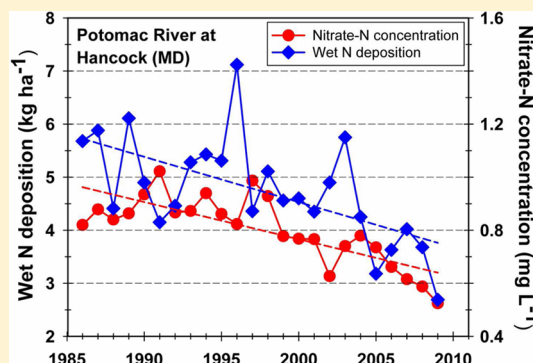
# Surface Water Quality Is Improving due to Declining Atmospheric N Deposition

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**S** Supporting Information

**ABSTRACT:** We evaluated long-term surface water nitrate and atmospheric nitrogen (N) deposition trends for a group of nine predominantly forested Appalachian Mountain watersheds during a recent multidecadal period (1986–2009) in which regional NO<sub>x</sub> emissions have been progressively reduced. Statistical analysis showed unexpected linear declines in both annual surface water nitrate-N concentrations (mean =46.4%) and yields (mean =47.7%) among the watersheds corresponding to comparable declines in annual wet N deposition (mean =34.4%) resulting from U.S. NO<sub>x</sub> emission control programs during the same time period. Nitrate-N concentration trends were robust across a large geographical region and appeared insensitive to watershed size across several orders of magnitude—suggesting that the improvements in water quality are probably propagated to surface and estuarine waters downstream. Surface waters are thus responding to declining atmospheric N deposition in much the same way they responded to declining sulfur deposition—although only one watershed showed a 1:1 relationship. Application of a kinetic N saturation model indicated that all nine forested watersheds are exhibiting signs of N saturation as evidenced by a limited, but variable, efficiency of demand for N. Further reductions in N deposition would be expected to produce additional reductions in streamwater N loads.



## INTRODUCTION

The rate of production of reactive nitrogen (N) on earth has accelerated dramatically over the past century, primarily due to widespread cultivation of N-fixing crops (e.g., legumes), combustion of fossil fuels, and industrial production of fertilizers by the Haber–Bosch process. Rates of N production now exceed rates of removal at all scales—local, regional, and global—causing N accumulation that has significant consequences for air quality, human health, terrestrial productivity, and both acidification and eutrophication of aquatic ecosystems.<sup>1</sup> It is quite understandable that the overwhelming majority of experimental studies has addressed system responses to *increasing* N inputs. Against this backdrop of widespread increasing N, the United States initiated a major atmospheric emission reduction program with passage of the 1990 Clean Air Act Amendments Acid Rain Program (ARP) that called for a 10 million ton reduction in annual sulfur dioxide (SO<sub>2</sub>) emissions and a 2 million ton annual reduction in nitrogen oxide (NO<sub>x</sub>) emissions to reduce acid deposition, primarily by targeting large electrical generation facilities in the eastern United States. Subsequent reductions in NO<sub>x</sub> emissions in the U.S. were mandated through other “cap and trade” programs, including the Ozone Transport Commission NO<sub>x</sub> Budget Trading Program (1999–2002), the NO<sub>x</sub> State Implementation Plan Call (2003), the Clean Air Interstate Rule (CAIR) in 2005, and the Cross-State Air Pollution Rule (2011).<sup>2</sup> Superimposed on these reductions from stationary

sources were national efforts to reduce mobile source NO<sub>x</sub> emissions<sup>3</sup> through improved vehicle emission standards and fleet turnover.<sup>4</sup> It has been estimated that total anthropogenic NO<sub>x</sub> emissions declined 32% between 1997 and 2005 in 20 eastern U.S. states that participated in the NO<sub>x</sub> Budget Trading Program.<sup>2</sup>

Implementation of SO<sub>2</sub> emission controls and reductions in sulfur deposition produced almost immediate declines in surface water sulfate concentrations, especially in the northeastern U.S., Canada, and Europe;<sup>5–10</sup> in some cases, these reductions have also lead to recovery of acid neutralizing capacity of acid-sensitive waters.<sup>11,12</sup> While a few studies have demonstrated long-term decreasing trends in surface water nitrate-N concentrations,<sup>10,11,13</sup> we found only one study<sup>14</sup> that was able to explicitly connect decreasing surface water nitrate-N with decreasing atmospheric N deposition. For the most part, water quality responses to declining N deposition have neither been predicted nor identified, as forested ecosystems are often presumed to exhibit a “nitrogen saturation” behavior<sup>15</sup> that is presumed to complicate the relationship between atmospheric deposition and loads of N discharged from the land to surface waters. It has been posited that some forested systems respond

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rapidly to increasing N deposition through increased export (i.e., load or yield) of nitrate-N to surface waters, while other systems are seemingly unresponsive.<sup>16–19</sup> Data from some of the longest running forest ecosystem studies have failed to produce any significant relationships between N deposition and loads in streamwater.<sup>20,21</sup> Conceptual models of forest N dynamics suggest that responses to N deposition may occur on the time scale of centuries,<sup>10</sup> although N modeling results often bear little resemblance to observed water quality measurements.<sup>22,23</sup> Changes in N dynamics in forests have particular relevance for efforts to restore freshwater and estuarine ecosystems, such as Chesapeake Bay,<sup>23,24</sup> however. While forest nitrate-N loads are not thought to dominate the overall N load to Chesapeake Bay, the fact that about 60% of the watershed is forested increases the need for water quality managers to more accurately account for forest N dynamics in establishing total maximum daily loads.<sup>25</sup> In this paper, we do the following: (1) evaluate long-term atmospheric deposition and water quality trends for a group of nine forested Appalachian Mountain watersheds (Figure 1) during a multidecadal period in which regional NO<sub>x</sub> emissions have been progressively reduced; (2) report on the sensitivity of nitrate-N yields to reductions in atmospheric N deposition through application of a simple, kinetic N saturation model;<sup>19</sup>

and (3) discuss the implications for managing water quality across the entire Chesapeake Bay watershed.

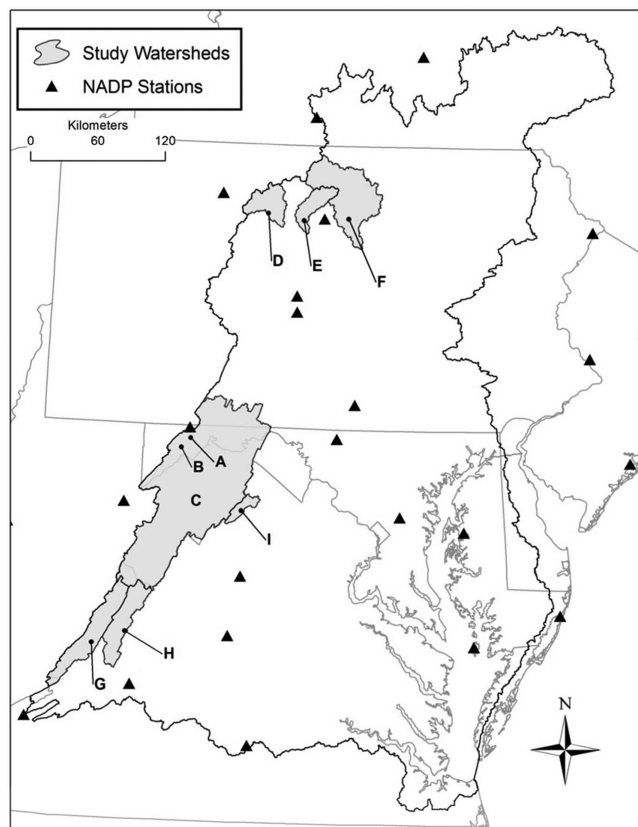
## MATERIALS AND METHODS

Our focus in this study is on water quality in forested watersheds that are either not affected or minimally affected by nitrogen pollution from agricultural or developed lands. We were able to identify nine gaged predominantly forested (i.e., ≥75% forested land use) watersheds within the Chesapeake Bay basin with extensive daily discharge and periodic (monthly or higher frequency) water quality data that are suitable for analysis of long-term nitrate-N load and concentration trends. The nine watersheds are all located along the spine of the Appalachian Mountains from Pennsylvania to southern Virginia (Table 1; Figure 1). Seven of the watersheds are a small subset of more than 100 Chesapeake Bay subwatersheds that were previously identified as having sufficient nutrient and sediment data to enable load computations.<sup>26</sup> Each has been continuously gaged by the U.S. Geological Survey using well-established hydrologic methods, and water samples have been periodically collected at the outlet of these watersheds by state water quality agencies and analyzed for nitrate-N in accredited water quality laboratories. Two western Maryland research watersheds (BIGR and BLAC) have been monitored by the authors using comparable field and laboratory methods. The nine watersheds range in size from 1.62 km<sup>2</sup> (BIGR) to over 10 000 km<sup>2</sup> (POTH). With the exception of the two research watersheds that have somewhat shorter data records, water quality and discharge data for the watersheds were available for the 24 year period from 1 October 1985 through 30 September 2009 (i.e., water years 1986–2009).

Water samples were analyzed for nitrate-N concentration using either ion chromatography (BIGR, BLAC) or a flow injection or segmented flow instrument in which the nitrate ion reacts with sulfanilamide and *N*-(1-naphthyl) ethylenediamine following cadmium reduction; nitrite-N concentrations (measured similarly, but without cadmium reduction) were subtracted to obtain nitrate-N values. We computed continuous daily nitrate-N loads for each station using a standard estimation method (LOADEST) that models the nitrate-N load,  $L_{\text{NO}_3\text{-N}}$ , using a seven-parameter multiple linear regression model calibrated using maximum likelihood estimation:<sup>27,28</sup>

$$\ln(L_{\text{NO}_3\text{-N}}) = a_0 + a_1 \ln Q + a_2 \ln Q^2 + a_3 \sin(2\pi d\text{time}) + a_4 \cos(2\pi d\text{time}) + a_5 d\text{time} + a_6 d\text{time}^2 \quad (1)$$

where  $Q$  is daily discharge and  $d\text{time}$  is a measure of decimal time minus the center of decimal time for the calibration period. Highly predictive ( $0.83 < r^2 < 0.97$ ) multivariate nitrate-N load models were developed using the data (Table S1 and Figure S1, Supporting Information). Some of the LOADEST models failed statistical tests used to assess assumptions about normality and heteroscedastic residual variance, although the residuals exhibited little autocorrelation (Figure S2, Supporting Information) or relationships with any independent variables. More importantly, all of the regression models produced very high Nash–Sutcliffe efficiency indices<sup>29</sup> ( $0.85 < E < 0.97$ ) that we used to evaluate model performance after back-transforming the data from logarithmic to linear scales as has been recommended (Figure S3, Supporting Information).<sup>30</sup> Thus, the results suggest no major issues with model bias. Daily loads (kg) and discharge (m<sup>3</sup>) were aggregated and normalized by watershed area to generate monthly and annual (water year:

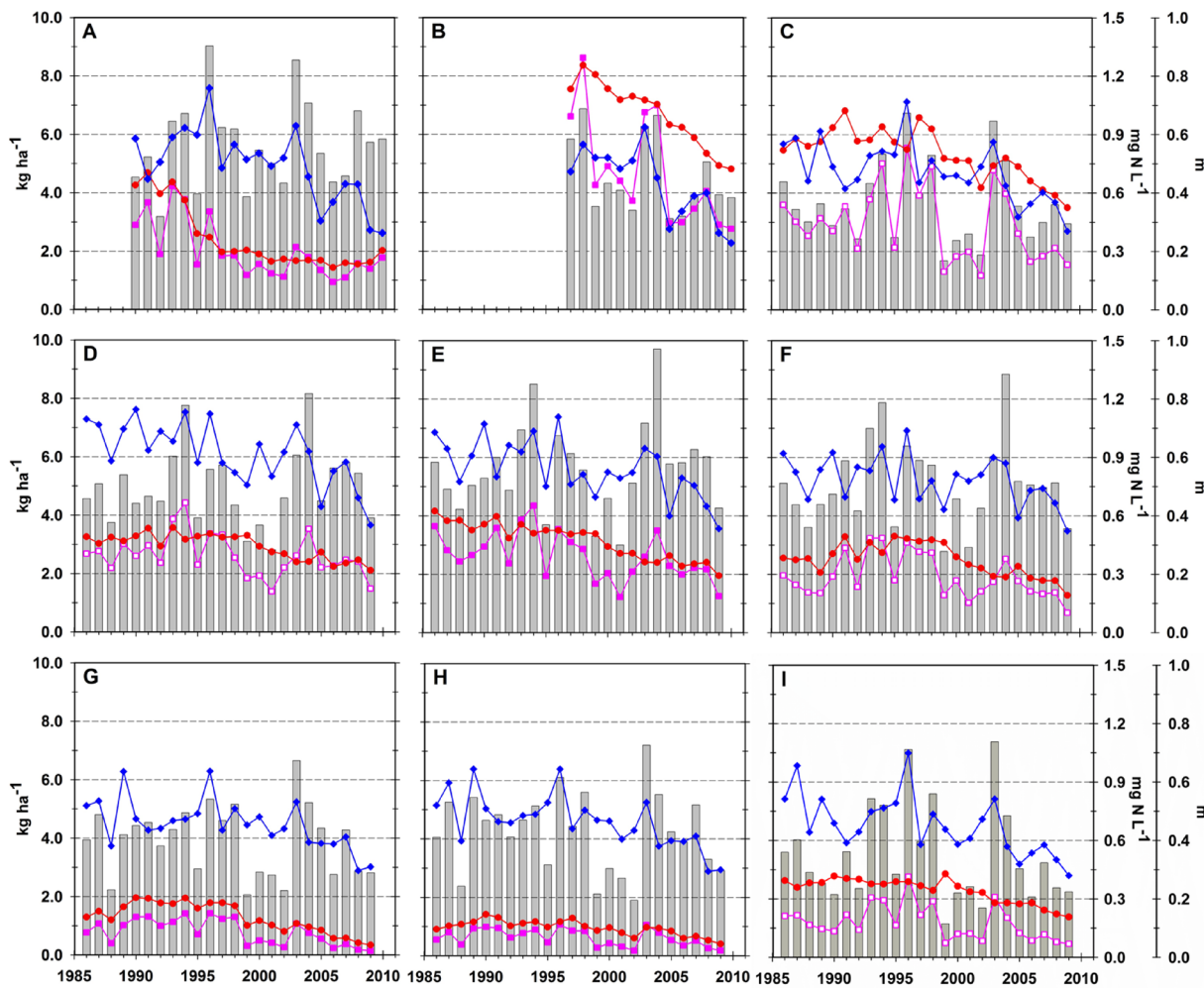


**Figure 1.** Locations of nine predominantly forested Appalachian Mountain watersheds for which long-term trends in water quality were evaluated. The stations (see Table 1 for details) are as follows: (A) Upper Big Run (MD); (B) Black Lick (MD); (C) Potomac River at Hancock (MD); (D) Driftwood Branch Sinnemahoning Creek (PA); (E) Kettle Creek (PA); (F) Pine Creek (PA); (G) Jackson River (VA); (H) Cowpasture River (VA); and (I) Cedar Creek (VA). NADP stations within and surrounding the Chesapeake Bay watershed are also shown.

**Table 1. Site Information for Nine Predominantly Forested Watersheds with Long-Term Data Used in the Current Study**

watershed/station (abbr.) <sup>a</sup>	watershed/station description	water quality station code	USGS station no.	watershed area (km <sup>2</sup> )	% forest
BIGR (1990–2010)	Upper Big Run, MD	BIGR	N/A	1.63	91.7
BLAC (1997–2010)	Black Lick, MD	BLAC	N/A	5.64	78.5
POTH	Potomac River at Hancock, MD	POT2386 <sup>b</sup>	01613000 <sup>c</sup>	10 550	75.4
DBSC	Driftwood Branch Sinnemahoning Creek at Sterling Run, PA	WQN420 <sup>c</sup>	01543000 <sup>c</sup>	704	92.9
KCWP	Kettle Creek near Westport, PA	WQN434 <sup>c</sup>	01545000 <sup>c</sup>	603	94.9
PCLP	Pine Creek below Little Pine Creek near Waterville, PA	WQN410 <sup>c</sup>	01549700 <sup>c</sup>	2440	98.2
JRDC	Jackson River below Dunlap Creek at Covington, VA	2JKS023.61 <sup>d</sup>	02013100 <sup>e</sup>	1590	81.0
CRCF	Cowpasture River near Clifton Forge, VA	2CWP002.58 <sup>d</sup>	02016000 <sup>e</sup>	1190	81.8
CCWV	Cedar Creek near Winchester, VA	1BCDR013.29 <sup>d</sup>	01634500 <sup>e</sup>	267	85.6

<sup>a</sup>Data available for water years 1986–2009 (unless otherwise indicated). <sup>b</sup>Nitrate-N data obtained from Maryland Department of Natural Resources. <sup>c</sup>Nitrate-N data obtained from Pennsylvania Department of Environmental Protection. <sup>d</sup>Nitrate-N data obtained from Virginia Department of Environmental Quality. <sup>e</sup>Continuous daily discharge data downloaded from U.S. Geological Survey website (<http://waterdata.usgs.gov/nwis/sw>).



**Figure 2.** Temporal patterns (1986–2009) in annual (1) nitrate-N yields (kg ha<sup>-1</sup>, pink lines/squares), (2) areal N deposition (kg ha<sup>-1</sup>, blue lines/diamonds), (3) nitrate-N concentrations (mg N L<sup>-1</sup>, red lines/circles), and (4) runoff (m, gray bars) for the nine study; letters correspond to watersheds identified in Figure 1. Time series illustrated with solid symbols produced statistically significant linear trends (see details in Table S2, Supporting Information).

Oct. 1 to Sept. 30) nitrate-N yields (kg ha<sup>-1</sup>) and runoff (m). Annual discharge-weighted nitrate-N concentrations (hereafter referred to simply as nitrate-N concentrations; mg N L<sup>-1</sup>) were readily computed by dividing the computed annual yields by the annual runoff and a unit conversion factor.

We also extracted annual wet inorganic N deposition data for calendar years 1986–2009 for stations that are part of the

National Acid Deposition Program (NADP) network and that surround the Chesapeake Bay basin and our study watersheds, as well as digital maps of areal wet N deposition for the same period from the NADP database (<http://nadp.sws.uiuc.edu/data/>). Annual areal wet N deposition for each of the nine watersheds was extracted from the digital map data using geographic information system software. Watershed wet N

deposition, nitrate-N yields, nitrate-N concentrations, and runoff were analyzed for linear trends using simple regression (Table S2, Supporting Information).

Lovett and Goodale<sup>19</sup> proposed a simple conceptual “kinetic N saturation” model based on *rates* of inputs, outputs, and storages in a forested ecosystem (note that our notation is slightly different for internal consistency):

$$D - V - S = Y + G \quad (2)$$

where  $D$  is N deposition,  $V$  is net incorporation of N into vegetation,  $S$  is net incorporation of N into soil,  $Y$  is the yield or export of N to surface waters, and  $G$  is gaseous N loss. Neglecting the  $G$  term (assumed small relative to  $Y$ ), combining  $V$  and  $S$  into one term ( $A = V + S$ ) representing net vegetation and soil aggradation, respectively, and rearranging, eq 2 is simplified to the following:

$$Y = D - A \quad (3)$$

Since we are interested in applying this model to watersheds that may not be 100% forested (i.e., streams that may have other sources of N such as nonpoint source N pollution derived from agricultural land uses), we added another term ( $Y_0$ ) to the right-hand side of eq 3 to represent this N source:

$$Y = Y_0 + D - A \text{ [subject to constraints} \\ Y, Y_0, D, A, D - A \text{ all } \geq 0] \quad (4)$$

A simple solution to eq 4 can be obtained by making  $A$  a linear function of  $D$ :  $A = aD$  where  $a$  ( $0 \leq a \leq 1$ ) represents the (assumed constant) proportion of  $D$  that is taken up and stored in vegetation and soil. By substituting for  $A$  in eq 4:

$$Y = Y_0 + D - aD \quad (5)$$

and simplifying:

$$Y = Y_0 + (1 - a)D \quad (6)$$

Using paired values of  $D$  (annual wet N deposition,  $\text{kg N ha}^{-1}$ , from NADP) and  $Y$  (annual nitrate-N yield,  $\text{kg N ha}^{-1}$ ) for each of the nine study watersheds, we solved for  $a$  and  $Y_0$  using Sigmaplot Dynamic Fit Wizard (a graph of  $Y$  on  $D$  has a slope of  $1 - a$  and an intercept  $Y_0$ ) subject to constraints that  $Y_0 \geq 0$  and  $0 \leq a \leq 1$ . The effects of neglecting dry N deposition in this analysis were addressed as a separate uncertainty analysis.

There is some empirical evidence (Figure S4, Supporting Information) that, over a wider range in  $D$ , the relationship between  $A$  and  $D$  may be more complex (e.g., a power function,  $A = pD^n$ ). Therefore, we evaluated more complex polynomial representations of the relationship between  $A$  and  $D$  using data from our nine watersheds, but none of these functions produced any better statistical results than eq 6.

## RESULTS AND DISCUSSION

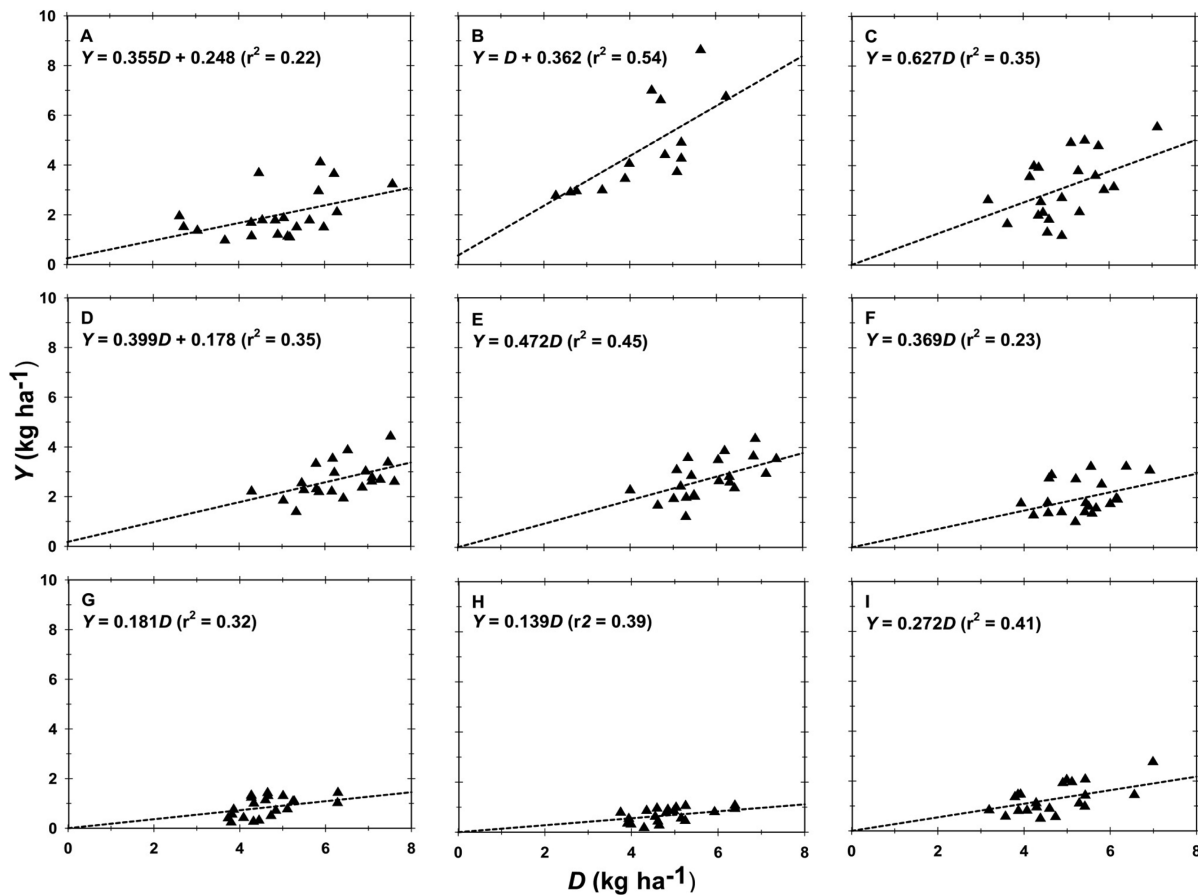
Our results shown in Figure 2 provide strong empirical evidence of decreasing trends in both annual areal wet N deposition and nitrate-N yields for all nine forested watersheds during the study period, although both time series show considerable variability induced by climatic variability (i.e., precipitation and runoff). Statistically significant ( $p \leq 0.05$ ) decreasing trends in areal wet N deposition were observed for all nine watersheds; slopes varied by about a factor of 4 (from  $-0.050 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  at PCLP to  $-0.222 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  at BLAC; Table S2, Supporting Information); the equivalent (unweighted) mean reduction in wet N deposition computed

for these nine stations is 34.4% (range 20.0–50.2%). While changes in dry N deposition were not quantified on a watershed-by-watershed basis, results from the Clean Air Status and Trends Network (CASTNET) indicate that dry N deposition decreased from  $2.5 \text{ kg N ha}^{-1}$  in 1989–1991 to  $1.5 \text{ kg N ha}^{-1}$  in 2007–2009 (~40% reduction) over the entire mid-Atlantic region.<sup>31</sup>

Mean annual nitrate-N yields ranged from 0.63 to  $4.67 \text{ kg N ha}^{-1}$  among the nine watersheds; nitrate-N yields from the three southern-most watersheds ( $0.63$  to  $1.20 \text{ kg N ha}^{-1}$ ) were the lowest among the group (Table S2, Supporting Information). All nine watersheds showed declining yields (slopes ranged from  $-0.019 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  at CRCF to  $-0.295 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  at BLAC), although only five of the watersheds showed statistically significant decreasing linear trends; the equivalent (unweighted) mean reduction in nitrate-N yield computed for these nine stations is 46.4% (range 31.9–72.6%). Aside from the fact that the two western Maryland watersheds (BGR and BLAC) with the greatest declining yields also showed the greatest declines in wet N deposition, there is no obvious geographic explanation for any differences in these trends. The group producing statistically significant trends included the two western Maryland watersheds, one watershed in north-central Pennsylvania (KCWP), and two watersheds in Virginia (JRDC, CRCF).

As expected, annual nitrate-N yields were strongly influenced by interannual variations in runoff, because yield is the product of concentration and runoff. Interannual variation in the nitrate-N yield time series is most easily recognized by the peaks in both N deposition and nitrate-N yield that occurred during high runoff years (e.g., 1996, 2003, and 2004), as well as by troughs that accompanied the drought years from 1999 to 2002 (Figure 2). Annual runoff was highly variable during the 24 year study period, but no significant linear trends were observed at any of the stations (Table S2, Supporting Information). Using long-term (1896–2010) runoff data from the USGS Potomac River at Point of Rocks (MD) station (not one of our load stations, but a station with an extremely long runoff record that is located downstream from many of the study watersheds), the study period produced only slightly greater mean annual runoff ( $0.35 \text{ m}$ ) than the climatic mean ( $0.34 \text{ m}$ ). There was considerably more interannual variability in the most recent period than in the climatic record, however; interestingly, the minimum (2002), maximum (1996), second highest (2003), and third highest (1998) values of annual runoff in the entire 115 year record fell within the 24 year study period. Mean annual runoff from the nine study watersheds actually fell within a very tight range of  $0.35$ – $0.60 \text{ m}$ ; the highest values were observed at the three Pennsylvania watersheds (DBSC, KCWP, and PCLP) and BGR in western Maryland, while the lowest values were observed at the three Virginia watersheds (JRDC, CRCF, and CCWV) and POTH. These observations are reasonably consistent with a latitudinal gradient in evapotranspirative demand.

Statistically significant decreasing linear trends in discharge-weighted nitrate-N concentrations were observed for all nine watersheds over the study period (Figure 2; Table S2, Supporting Information). In contrast to the rather noisy wet N deposition and nitrate-N yield time series, the nitrate-N concentration time series varied much more smoothly and were deemed superior for understanding water quality trends (Figure 2). This can be attributed to the fact that our computational procedure effectively reduces the noise associated with



**Figure 3.** Results from application of a modified kinetic N saturation model for nine study watersheds (see details in Table S3, Supporting Information). Letters correspond to watersheds identified in Figure 1.

interannual climatic variations.<sup>11</sup> The time series for most of the watersheds (except BGR) shows that streamwater nitrate-N concentrations peaked in the late 1990s at about the time that NO<sub>x</sub> emission reductions under the ARP were implemented and have been steadily decreasing thereafter (Figure 2). Overall, slopes in streamwater concentration ranged from  $-0.004$  mg N L<sup>-1</sup> yr<sup>-1</sup> at CRCF to  $-0.039$  mg N L<sup>-1</sup> yr<sup>-1</sup> at BLAC; the equivalent (unweighted) mean reduction in nitrate-N concentration computed for these nine stations is 47.7% (range 27.0–69.5%). Mean annual nitrate-N concentrations varied by about an order of magnitude (0.14 to 1.00 mg N L<sup>-1</sup>) among the watersheds (Table S2, Supporting Information). The nitrate-N yield and concentration time series for BGR were previously interpreted as having been affected by an outbreak of insect defoliations during the mid-1980s (prior to our data collection);<sup>11</sup> we concur with this interpretation but believe that the excessive losses of N that accompanied these disturbances may have contributed to N deficiencies reflected in the more recent data. None of the other time series show this pattern, so we are reasonably confident that we can rule out forest disturbance as the principal driver of the recent nitrate-N dynamics of these systems.

Annual wet N deposition was found to be a reasonably strong predictor of observed annual nitrate-N yield from all nine watersheds (Figure 3) in compartment with application of the modified conceptual model of kinetic N saturation.<sup>19</sup> The calibrated models explained 22–54% of the total variation in nitrate-N yield, with the  $a$  coefficient (a proxy for the efficiency of N demand) varying from 0.0 to 0.86; eight of the nine

estimates of  $(1 - a)$  were statistically significant. The unexplained variation in nitrate-N yield can likely be attributed to several factors, including (1) time lags associated with watershed transport and transformation of atmospherically deposited N (magnified by the fact that our yield estimates were computed for water years, while the wet deposition estimates were computed for calendar years) and (2) interannual variation in terrestrial N processing rates due to hydroclimatological variability and possibly natural disturbances such as insect defoliation.<sup>32</sup> The highest values of  $a$  were found for the three southern-most watersheds, while the lowest values were observed for one of the research watersheds (BLAC) and POTH. It should be noted that the estimated values of  $a$  would have been somewhat higher had dry deposition been explicitly considered, but the inclusion of dry deposition trends would not have changed the overall study conclusions. The fact that dry N deposition in the region has decreased by about the same percentage as wet N deposition has likely contributed to our ability to detect these relationships. As expected, no statistically significant  $y$ -intercept ( $Y_0$ , a proxy for nonforested N in surface water) was identified, suggesting that the proximate source of virtually all of the nitrate-N discharged from these predominantly forested systems is of atmospheric origin (Table S3, Supporting Information). Model testing using data from other watersheds with considerably greater agricultural and urban land use will be needed to evaluate the overall applicability of such a simple conceptual model.

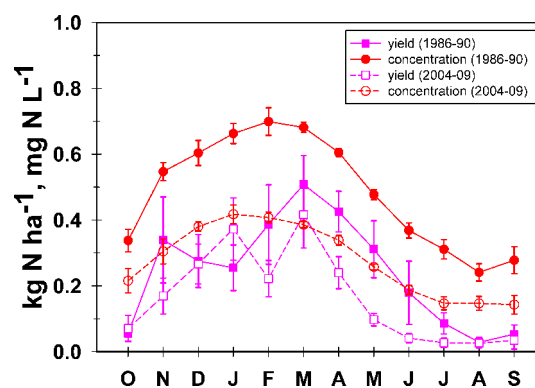
Most studies that have attempted to establish relationships between nitrate-N yield and N deposition in forested

watersheds have relied on space-for-time substitution and the underlying assumptions of that approach.<sup>33–35</sup> With implementation of the ARP and subsequent “cap and trade” programs, the U.S. government has essentially enabled a region-wide natural experiment that can be used to determine how reductions in  $\text{NO}_x$  emissions affect nitrate-N yields derived from forested watersheds using a cross-correlation analysis of time series data. The results of this experiment are uniformly clear: reducing  $\text{NO}_x$  emissions from stationary (and, to a lesser extent mobile) sources caused a regional-scale reduction in atmospheric N deposition that has further caused nitrate-N yields from forested watersheds to decline. Our results (Figure 2) suggest that the decline in yields and streamwater concentrations have occurred with little, if any, obvious lag, as these reductions can be observed in the time series as early as the late 1990s coinciding with implementation of the earliest ARP reductions. Surface waters draining these watersheds have apparently responded to reductions in N deposition in much the same way that they have responded to previous reductions in sulfur deposition, although only one watershed (BLAC) showed a 1:1 relationship. No studies conducted in the U.S. have previously reported on this phenomenon, although a recent study showed declining trends in streamwater nitrate-N in 6 of 11 small, upland-dominated watersheds in south-central Ontario, Canada; trends were attributed to declining N deposition.<sup>14</sup> Much earlier, the reversibility of N saturation was purportedly demonstrated on the basis of results from a small-scale acid-exclusion experiment conducted at Risdalsheia, Norway.<sup>36</sup> Our results appear to provide more widespread confirmation of this phenomenon over a fairly large geographical region of the U.S.

Identified trends were obviously robust under conditions of comparatively high climatic variability, but the long-term yield and concentration trends were also robust inasmuch as they appear largely independent of watershed size. Trends for POTH are strikingly similar to BLAC, despite the fact that the former watershed is 1870 times larger than the latter watershed. The ability to produce observational data that are essentially scale-independent provides additional support for the conclusion that the identified trends are real. Moreover, the results provide compelling evidence that the observed patterns are not confined to small headwater-watersheds, rather the water quality improvements can also be observed in large river basins and propagated downstream to receiving rivers and estuarine systems. Hirsch et al.<sup>37</sup> showed significant improvements in water quality at the Potomac River “RIM” (River Input Monitoring) station over the same period of time as our study, and our results suggest that improvements in water quality downstream can be at least partially explained by improved water quality at the upstream POTH station that we have attributed to reduced N deposition. Improvements in downstream water quality (e.g., of Chesapeake Bay tributaries) should probably be considered a “co-benefit” of past  $\text{NO}_x$  emission control programs, as the primary goal of these controls under ARP was to reduce acid deposition and concentrations of tropospheric ozone and particulate matter, both criteria pollutants under the Clean Air Act.<sup>38</sup> In tributary watersheds with a mix of land uses and a variety of N sources, efficient water quality management will depend on proper evaluation of the cost-effectiveness of any additional emission controls relative to the costs of alternative strategies (e.g., agricultural best management practices, riparian restoration, sewage treatment plant upgrades, etc.) for nutrient control.

What do these results imply about the behavior of N in these forested watersheds? As noted earlier, only one of these systems (BLAC) would be considered “N saturated” if the criterion were a 1:1 relationship between N inputs and outputs (i.e.,  $a = 0$ ). Since our computation neglected the role of dry N deposition, it is likely the case that even BLAC is not exhibiting this 1:1 relationship if dry deposition were taken into account. Regardless of the extent of N saturation, the results are consistent in indicating that streamwater N concentrations can respond very quickly to reductions in N deposition, even in large river basins, with the results providing no evidence of any substantial lags in response (again, the similar responses of BLAC and POTH are most illustrative of this point). This is perhaps the most surprising result of the study. A paradigm of temperate forest biogeochemistry is that annual N deposition rates ( $\sim 10^0\text{--}10^1 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ) are small compared to rates of N mineralization and nitrification ( $\sim 10^1\text{--}10^2 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ) in temperate forest soils,<sup>39–41</sup> so nitrate-N yields are effectively controlled by soil processes/vegetation demand and do not respond very quickly to small changes in deposition.<sup>40</sup> The conceptual model of N saturation first proposed by Aber et al.<sup>15</sup> thus supposes a relatively long period of N deposition during which the N status of the ecosystem increases prior to the occurrence of any measurable changes in surface water nitrate-N. At least during the rapid recovery phase described in this paper, the data seem to suggest that short-term variations in soil and vegetation processes are relatively small and are thus not the major drivers of the observed trends in nitrate-N yields.

It is possible that these two seemingly conflicting models could be reconciled through closer examination of the output data. As an example, mean monthly discharge-weighted nitrate-N loads and concentration data for KCWP for two different time periods illustrate that the dominant portion of the nitrate-N load occurs during the dormant season when the rates of vegetation and soil processing are lower; the result is an intra-annual pattern of higher nitrate-N concentrations during the winter, lower concentrations during the summer, and intermediate concentrations during spring and autumn (Figure 4). The data



**Figure 4.** Mean monthly discharge-weighted nitrate-N concentrations and yields for Kettle Creek (KCWP) for two time periods: water years 1986–1990 and 2004–2009; standard errors also shown.

(particularly the concentration time series) support the interpretation that reductions in N deposition have decreased the amplitude of the intra-annual cycle, consistent with predictions that the earliest impacts of N saturation would occur during the dormant season.<sup>42</sup> Our data suggest that one of the first signs of recovery from N saturation is a decrease in

nitrate-N concentrations during the dormant period. While significant concentration changes were observed during all 12 months, larger (absolute) reductions in nitrate-N concentrations during the winter period (with higher flows) also have a disproportionate impact on the annual nitrate-N load.

Regardless of the mechanism, our results imply a limited, but variable, efficiency of N demand by forested watersheds as measured by the coefficient  $a$  in the kinetic N saturation model. All nine forested Appalachian Mountain watersheds were found to be appreciably responsive to changes in atmospheric N inputs, and we found no evidence of any watershed being nonresponsive to atmospheric N deposition as some have proposed. By using the value of  $a$  as an index of the degree of N saturation, the most highly N saturated systems are located in western Maryland where atmospheric N deposition has historically been comparatively high; the least N saturated forests are the southernmost systems where N deposition has been lower. Thus, our results indicate that, over a considerable range in atmospheric N deposition, Appalachian forests appear to be able to store a substantial quantity of deposited N. Further reductions in N deposition throughout the region would be expected to produce additional proportionate reductions in streamwater N loads, however.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Additional tables and graphs convey the statistical and modeling results of the study in greater detail. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

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### Notes

The authors declare no competing financial interest.

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