Supporting Information for:

Precipitation Dominates Interannual Variability of Riverine Nitrogen Loading across the Continental United States

Eva Sinha*,†,‡ and Anna M. Michalak†,‡

†Department of Earth System Science, Stanford University, Stanford, California 94305, USA

‡Department of Global Ecology, Carnegie Institution for Science, Stanford, California 94305, USA

* Correspondence to: E. Sinha (esinha@stanford.edu)

Consisting of 4 sections, 3 tables and 9 figures within 15 pages

S1 Prediction Interval for Multiple Linear Regression Model

Estimates of regression coefficients ($\widehat{\boldsymbol{\beta}}, k\times1$) in eq 1 and 4 were obtained by multiple linear regression:

$$\widehat{\boldsymbol{\beta}} = (\mathbf{X}^{\mathbf{T}}\mathbf{X})^{-\mathbf{1}}\mathbf{X}^{\mathbf{T}}\mathbf{y} \quad \text{(S1.1)}$$

the mean squared error of residuals ($\boldsymbol{s_\epsilon}$) was calculated as follows:

$$s_\varepsilon^2 = \frac{(\boldsymbol{y} - \widehat{\boldsymbol{y}})^T(\boldsymbol{y} - \widehat{\boldsymbol{y}})}{m-2} \quad \text{(S1.2)}$$

and the standard error of the fit for particular values of the predictor variables ($\mathbf{x}_{\boldsymbol{h}}$) was defined as:

$$s_{\hat{y}} = \sqrt{s_\varepsilon^2(\mathbf{x}_h^T(\mathbf{X}^{\mathbf{T}}\mathbf{X})^{-\mathbf{1}}\mathbf{x}_h)} \quad \text{(S1.3)}$$

and the standard error of the prediction of $\ln(Q_{\mathrm{TN}})$ (Eq. 4) was defined as:

$$s_{PI} = \sqrt{s_\varepsilon^2 + s_{\hat{y}}^2} \quad \text{(S1.4)}$$

where all other variables are as defined in section 2.2.

The 95% prediction interval for Q_{TN} [kg - N/(km^2 yr)] for each HUC8 watershed and year was estimated through a Monte Carlo approach by generating 10,000 samples of $\ln(Q_{\mathrm{TN}})$ from a normal distribution with mean $\ln(Q_{\mathrm{TN}})$ and standard deviation $\boldsymbol{s_{PI}}$; taking the exponential of each of the samples to yield sampled values of Q_{TN}; and calculating the 2.5th and 97.5th percentiles from these 10,000 sampled values.

The mean and 95% prediction interval for TN load [kg - N/yr] for any given year for an aggregated region composed of multiple HUC8 watersheds was estimated by multiplying the aforementioned 10,000 sampled values of Q_{TN} for each of the HUC8 watersheds within the aggregated region by the corresponding watershed area to obtain 10,000 sampled of TN load for each watershed; summing the loads across the HUC8 watersheds to yield 10,000 sampled values of TN load for the region; and calculating the mean as well as the 2.5th and 97.5th percentiles from the 10,000 sampled values of spatially-aggregated TN loads.

The mean and 95% prediction interval for average TN load over the 21 year period for an aggregated region was estimated by repeating the process outlined in the last paragraph, but generating sampled values for each of the 21 years, and ultimately summing the sampled load in both space and time.

The uncertainties calculated in this way account for the uncertainty of the multiple linear regression model but do not explicitly consider uncertainty in the auxiliary data and the response variable used for model build.

S2 Use of National Atmospheric Deposition Program (NADP) Data for Atmospheric N Deposition

Whereas the NANI toolbox uses atmospheric deposition estimates from the Community Multiscale Air Quality (CMAQ) model, atmospheric deposition was estimated here from the National Atmospheric Deposition Program. This is because atmospheric deposition outputs from the Community Multiscale Air Quality (CMAQ) model used in the NANI toolbox are available only starting in 2002. The National Trends Network (NTN) operated by NADP measures wet deposition of various chemicals including NO_3^- on a weekly basis at over 200 sites across the US. In keeping with the methodology used in the NANI toolbox, only the oxidized form of nitrogen (NO_X) was included in the atmospheric deposition estimate.[1–4] NADP monitoring data were utilized for estimating wet NO_X deposition, and dry deposition was assumed to be 0.7 times that of wet.[5] A comparison of CMAQ and NADP estimates of NOx deposition for 2002-2006 showed a high correlation between the two datasets, but revealed that NADP estimates are lower than CMAQ estimates for overlapping years (Figure S9). A sensitivity analysis where NADP estimates were scaled according to the regression in Figure S9, however, showed no impact on the overall conclusions, as that scaling was largely offset by a corresponding adjustment in the overall model drift coefficients (eq 4).

S3 Lagged NANI, Tile-drainage, and Temperature

NANI for preceding years, used to represent lagged impacts of NANI on TN loading, did not improve model fit sufficiently to justify its inclusion in the model based on BIC. This is not to say that residual NANI is not an important factor for some specific watersheds or years, but rather that it did not provide substantial explanatory power across the large range of catchments and period considered here. Its influence is therefore implicitly included in the residual term of the model, and thus in the reported uncertainties.

Temperature and tile drainage were not included in the final model. Although annual temperature was selected via BIC in addition to the five variables listed in Eq. 4 for the calendar year analysis, the improvement in R^2 was minor (ΔR^2=0.008). In addition, temperature was not selected when running a sensitivity test using water-year loading in place of calendar year loading. The converse is true for tile drainage. Tile drainage was not selected as a key variable in the calendar-year analysis. For the water-year sensitivity test, tile drainage was selected, but the improvement in explanatory power was again very small (ΔR^2=0.006). Therefore, in the interest in presenting a conservative and parsimonious model, neither variable was included in the final model (eq 4). Here again, this result does not imply that temperature and tile drainage are not important factors for some specific watersheds or years, but rather that they did not provide substantial explanatory power across the large range of catchments and period considered here. Their influence is therefore implicitly included in the residual term of the model, and thus in the reported uncertainties. Additional sensitivity tests (results not shown) confirmed that including these variables in the model yielded only marginal changes to estimates.

S4 Comparison of TN Load Estimates for Large Regions

The average annual nitrogen loading for the CONUS of 4.12±0.03 Tg - N/yr for 1987–2007 is largely in line with two existing estimates of CONUS coastal nitrogen discharge to coastal regions: an earlier estimate of 5.0 Tg - N/yr[6] for 1997 based on an assumption that nitrogen export is a fixed percentage of NANI, and an earlier estimate of 4.8 Tg - N/yr[7] using the SPARROW model applied to long-term average hydrologic conditions and 2002 NANI. For reference, our estimate for 1997 is 4.64±0.26 Tg - N/yr, while that for 2002 is 4.19±0.12 Tg - N/yr. Note that the numbers for 2002 are not directly comparable, however, as those from the SPARROW model are based on long-term average hydrologic conditions.

For the MARB, our 21-year average estimate (2470 Gg - N/yr) is consistent with an analysis of non-decayed load based on SPARROW (2530 Gg - N/yr[8]). For the CBB, our average estimate (122 Gg - N/yr) is lower than the non-decayed load based on SPARROW (160 Gg - N/yr[9]), but the corresponding delivered load estimate from SPARROW (132 Gg - N/yr[9]) overestimates the average measured load delivered to the CBB for calendar years from 1987–2007 (97 Gg - N/yr[10]), suggesting that the estimate obtained here is more likely to be representative of the actual loading relative to the SPARROW estimate. For the CRB, an estimate of the non-decayed load is not available from SPARROW, but the estimate of the delivered load (50 Gg - N/yr[11]) is inconsistent with the average measured load for water years from 1993-2007 (109 Gg - N/yr[12]) and suggests that our estimate of non-decayed loading of 122 Gg - N/yr is realistic. Neither SPARROW estimates nor an observation-based estimate are available for the entire SSRB.

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Table S1. Predictor variables evaluated

Category	Variable(s) considered	Variable description(s)	Number of variables: Considered	Number of variables: Allowed	Selected variables
Nitrogen inputs (current year)	$NANI$; f_{NANI}	Net anthropogenic nitrogen input (NANI) [kg - N/km^2 yr] and inverse hyperbolic sine of NANI (asinh(NANI/2)) for current year.	2	1	f_{NANI}
Nitrogen inputs (previous years)	$NANI_{-1}$; $f_{\mathrm{NANI},-1}$; $NANI_{-2}$; $f_{\mathrm{NANI},-2}$; $NANI_{-1\&-2}$; $f_{\mathrm{NANI},-1\&-2}$	NANI and inverse hyperbolic sine of NANI for prior year (-1), two year prior (-2), and cumulative over two prior years (-1&-2).	6	2[1]	-
Annual precipitation	P_{annual}	Total annual precipitation [mm]	1	1	P_{annual}
Seasonal precipitation	P_{MAM}	Total precipitation in the months of March, April and May [mm]	1	1	-
Extreme precipitation	$n_{\mathrm{P>10mm}}$; $n_{\mathrm{P>20mm}}$	Number of days with precipitation greater than 10 or 20 mm [days]	2	1	$P_{\mathrm{MAM},p>0.95}$
	$P_{p>0.90}$; $P_{p>0.95}$; $P_{p>0.99}$	Total precipitation on days with precipitation above the 90th, 95th or 99th percentile[2] (calculated based on 30 years of daily precipitation amounts from 1981-2010) [mm]	3		
	$n_{\mathrm{MAM,P>10mm}}$; $n_{\mathrm{MAM,P>20mm}}$	Number of days in March, April and May with precipitation greater than 10 or 20 mm [days]	2		
	$P_{\mathrm{MAM},p>0.90}$; $P_{\mathrm{MAM},p>0.95}$; $P_{\mathrm{MAM},p>0.99}$	Total precipitation (mm) in March, April & May on days with precipitation greater than 90th, 95th or 99th percentile (calculated based on 30 years of daily precipitation from 1981-2010)	3		
	$P_{\mathrm{MAM},p(\mathrm{MAM})>0.90}$; $P_{\mathrm{MAM},p(\mathrm{MAM})>0.95}$; $P_{\mathrm{MAM},p(\mathrm{MAM})>0.99}$	Total precipitation (mm) in March, April & May on days with precipitation greater than 90th, 95th or 99th percentile (calculated based on 30 yrs of daily precipitation in March, April & May from 1981-2010)	3		
Temperature	T_{Annual}; T_{MAM}	Average annual (Annual) and March, April, and May (MAM) temperature [°C]	2	1	-
Land use	LU_{D}; LU_{C}; LU_{F}; LU_{SH}; LU_{W}; $LU_{\mathrm{D,C}}$; $LU_{\mathrm{D,F}}$; $LU_{\mathrm{D,SH}}$; $LU_{\mathrm{D,W}}$; $LU_{\mathrm{C,F}}$; $LU_{\mathrm{C,SH}}$; $LU_{\mathrm{C,W}}$; $LU_{\mathrm{F,SH}}$; $LU_{\mathrm{F,W}}$; $LU_{\mathrm{SH,W}}$; $LU_{\mathrm{D,C,F}}$; $LU_{\mathrm{D,C,SH}}$; $LU_{\mathrm{D,C,W}}$; $LU_{\mathrm{D,F,SH}}$; $LU_{\mathrm{D,F,W}}$; $LU_{\mathrm{D,SH,W}}$; $LU_{\mathrm{C,F,SH}}$; $LU_{\mathrm{C,F,W}}$; $LU_{\mathrm{C,SH,W}}$; $LU_{\mathrm{F,SH,W}}$; $LU_{\mathrm{D,C,F,SH}}$; $LU_{\mathrm{D,C,F,W}}$; $LU_{\mathrm{D,F,SH,W}}$; $LU_{\mathrm{D,C,SH,W}}$; $LU_{\mathrm{C,F,SH,W}}$	Percentage of land use classified as Developed (D), Cultivated (C), Forest (F), Shrubland & Herbaceous (SH) and Wetlands (W) and various combinations of two, three and four land use categories [%]	30	4[3]	LU_{W}; $LU_{\mathrm{F,SH}}$
Tile drainage	L_{TD}	Percentage of land with tile drainage	1	1	-
TOTAL			**56**	**12**	**5**

[1] Nitrogen input variables from previous years only allowed if at least one variable from Nitrogen input current year is included.
[2] 90th, 95th and 99th percentile were defined during wet days in the 1981-2010 time-period. In this study wet days were defined as days with precipitation greater than 1.0 mm.
[3] Any single land use category can only be represented once in the model either as an individual or binned category and a maximum of four-land use categories can be represented either as single or binned categories.

Table S2. Land-cover Level I classes and included Level II classes based on National Land Cover Database (NLCD) 2006[13]

NLCD Class Level I	NLCD Class Level II
Developed	Developed, Open Space Developed, Low Intensity Developed, Medium Intensity Developed, High Intensity
Planted/Cultivated	Pasture/Hay Cultivated Crops
Forest	Deciduous Forest Evergreen Forest Mixed Forest
Wetlands	Woody Wetlands Emergent Herbaceous Wetlands
Shrubland & Herbaceous	Shrub/Scrub Grassland/Herbaceous

Table S3. Percentage of HUC8 watersheds where given predictor variables are the primary drivers of spatial variability, interannual variability, and extreme loading based on estimated loading for 1987–2007 and a sensitivity test using only agricultural census years (1987, 1992, 1997, 2002, 2007). Shaded cells represent variables for which temporal variability is not considered.

	Spatial variability		Temporal variability		Extreme loading	
	1987–2007	1987, 1992, 1997, 2002, 2007	1987–2007	1987, 1992, 1997, 2002, 2007	1987–2007	1987, 1992, 1997, 2002, 2007
P_{annual}	2%	2%	62%	48%	45%	68%
$P_{\mathrm{MAM},p>0.95}$	0	0	24%	32%	48%	56%
f_{NANI}	81%	81%	14%	20%	16%	34%
$LU_{\mathrm{F,SH}}$	16%	16%				
LU_{W}	1%	1%				

Figures

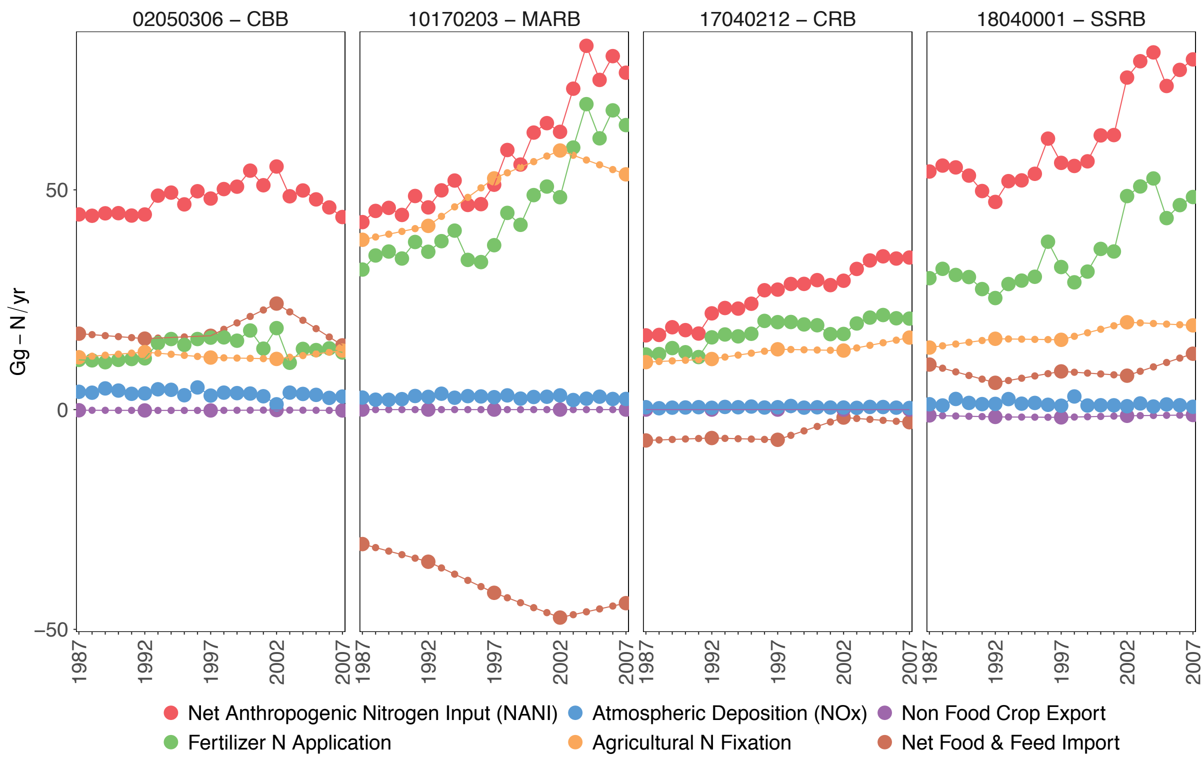

Figure S1. Time series for NANI and its components for four representative HUC8 watersheds, one within each of the regions upstream of the major nutrient delivery points shaded in Figure 1. Larger symbols represent years for which data are available, while values estimated based on linear interpolation are shown using smaller symbols. The Non Food Crop Export represents nitrogen leaving the watershed and its value is subtracted from NANI while all other components are added to estimate NANI. Here we have reversed the sign on Non Food Crop Export such that all NANI components as shown can be added to obtain NANI for the whole watershed.

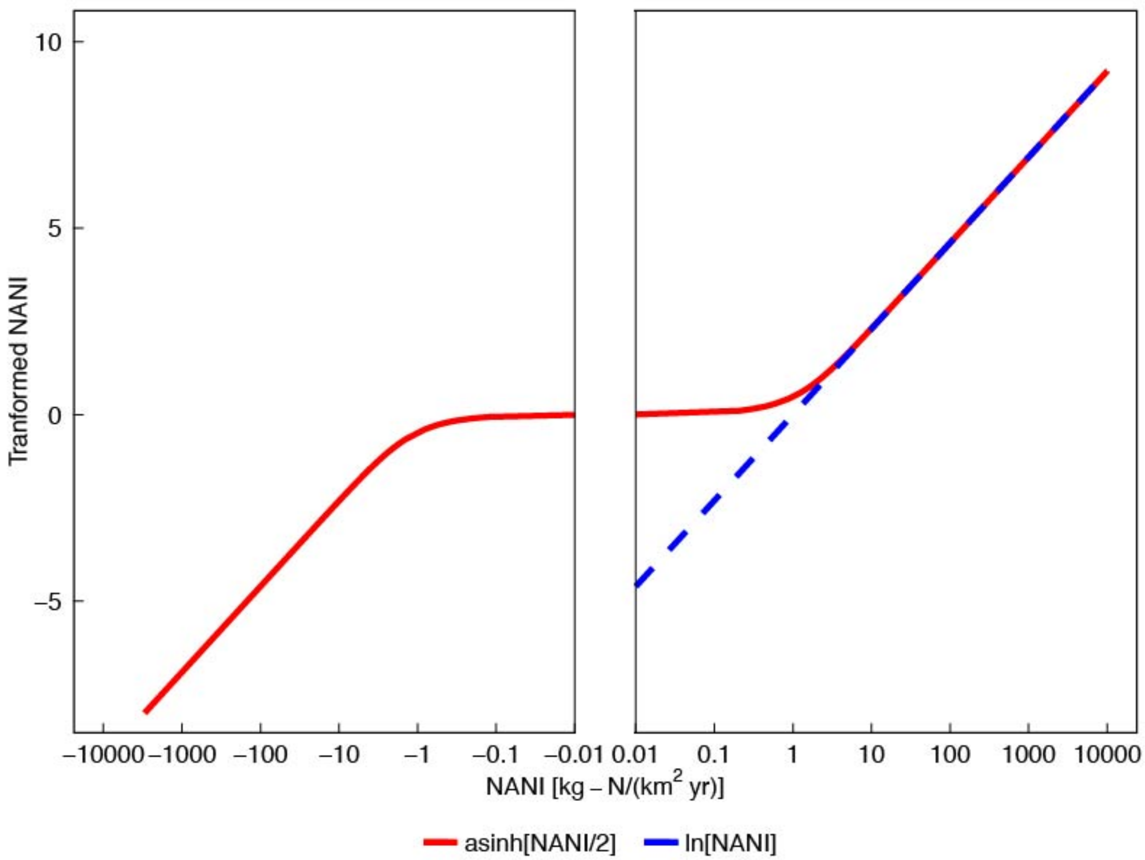

Figure S2. NANI vs. natural log of NANI (blue) and inverse hyperbolic sine of NANI (red). For reference, the full range of NANI values for HUC8 watersheds over the study period is -2,980 kg - N/km^2 yr to 29,677 kg - N/km^2 yr.

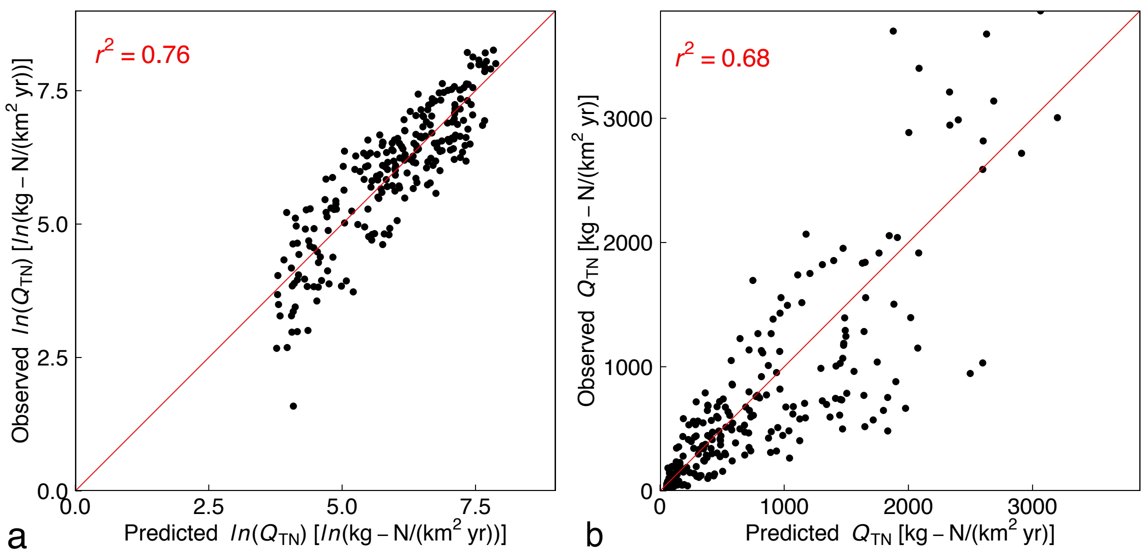

Figure S3. Scatterplot of predicted vs. observed annual TN flux (Q_{TN}) for the USGS gages and years used in the model build, on a log-transformed scale (a) and the original scale (b). The red line represents the 1:1 line. Predicted Q_{TN} is based on the statistical model in Eq. 4.

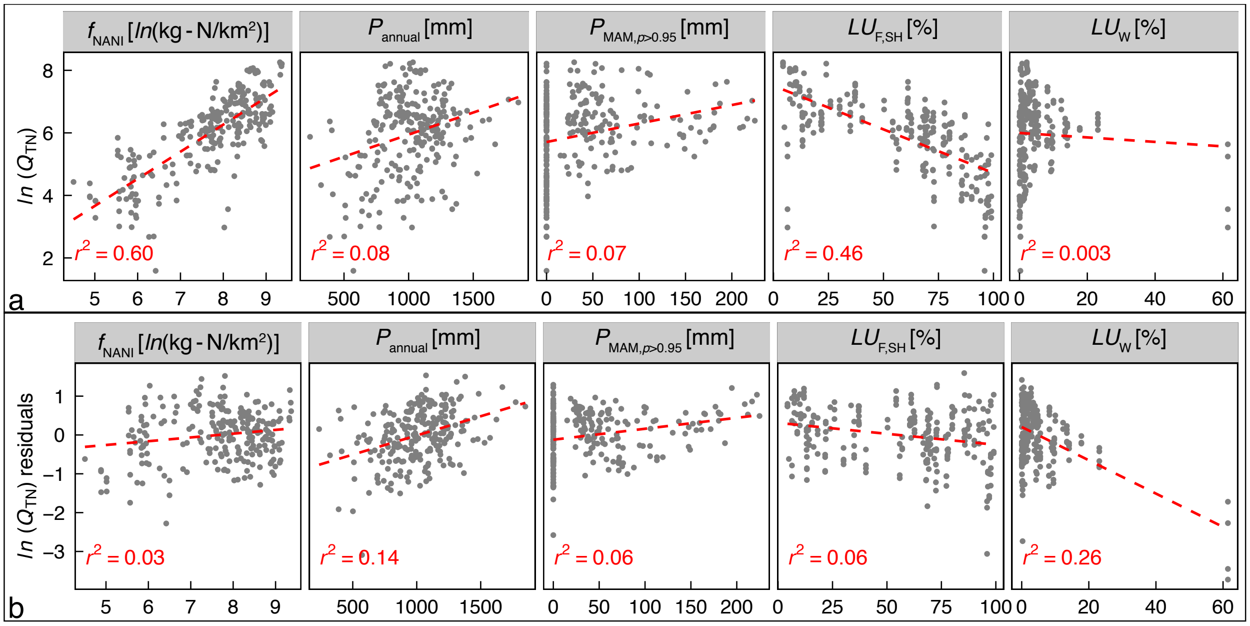

Figure S4. (a) Scatterplots of natural log transformed annual TN flux ($\ln(Q_{TN})$) and selected predictor variables, and (b) scatterplots of residuals from final multiple linear regression with one variable removed and this individual variable. All variables are as defined in SI Table 1.

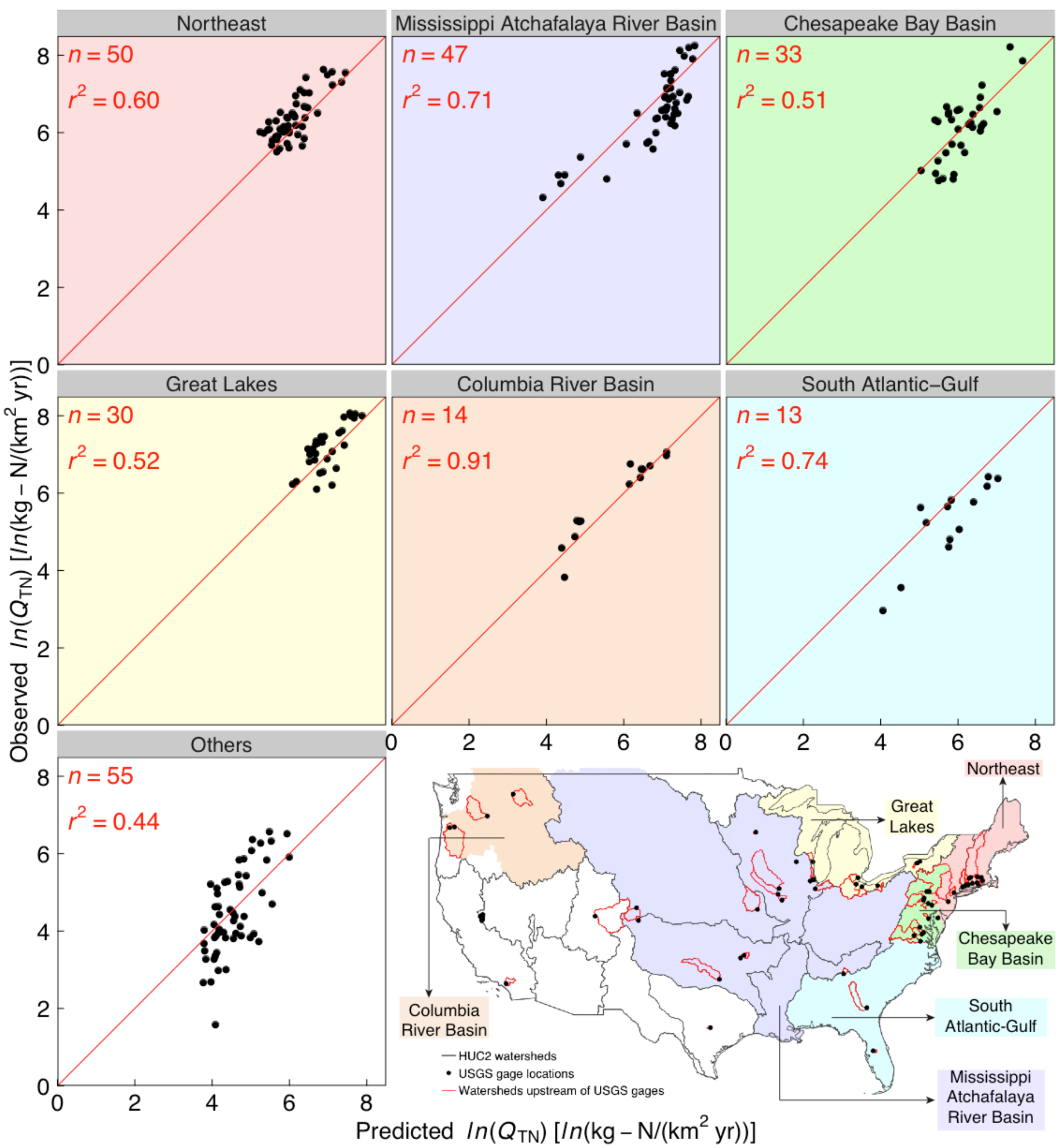

Figure S5. Same as Figure S3a, but with catchment-years broken out by the regions shaded in the inset map. Predicted Q_{TN} for all regions is based on the statistical model in eq 4. The model explains a high fraction of observed variability across all regions. Note that observations are limited in some regions (e.g. Columbia River Basin, South Atlantic-Gulf).

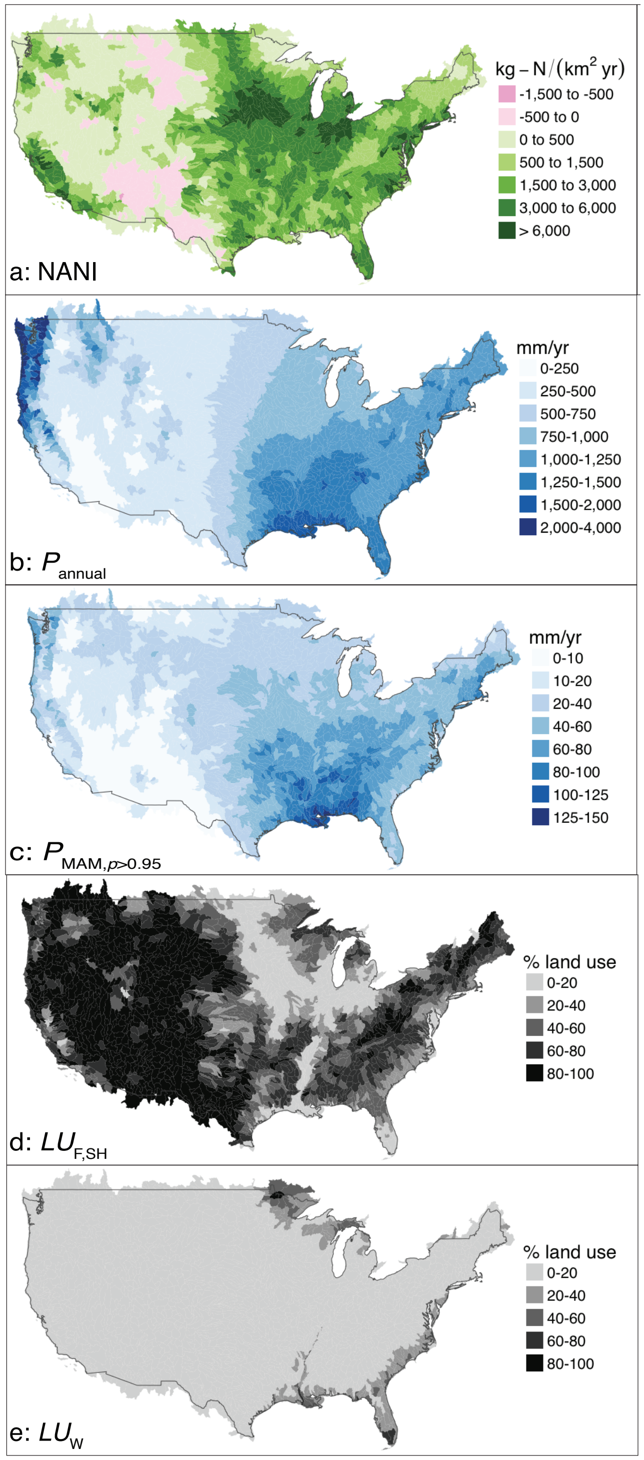

Figure S6. Selected predictor variables averaged over the 21 year (1987−2007) study period, including (a) average net anthropogenic nitrogen input (NANI); (b) average annual precipitation (P_{annual}); (c) average precipitation in March, April, and May on days with precipitation greater than 95th percentile ($P_{MAM,p>0.95}$); (d) the percentage of land use classified as forest and shrubland & herbaceous ($LU_{F,SH}$); and (e) the percentage of land use classified as wetlands (LU_W).

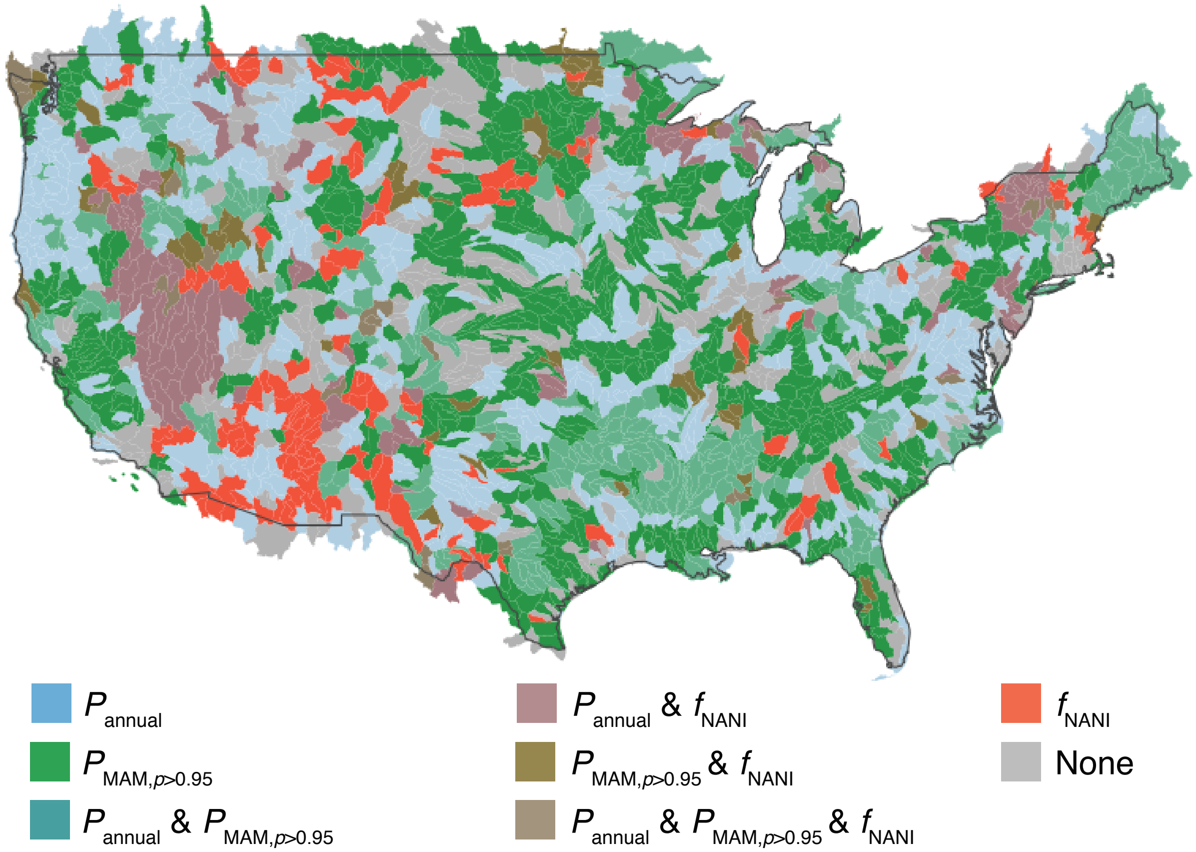

Figure S7. Primary drivers of extreme loading for HUC8 watershed. All variables are defined in SI Table 1.

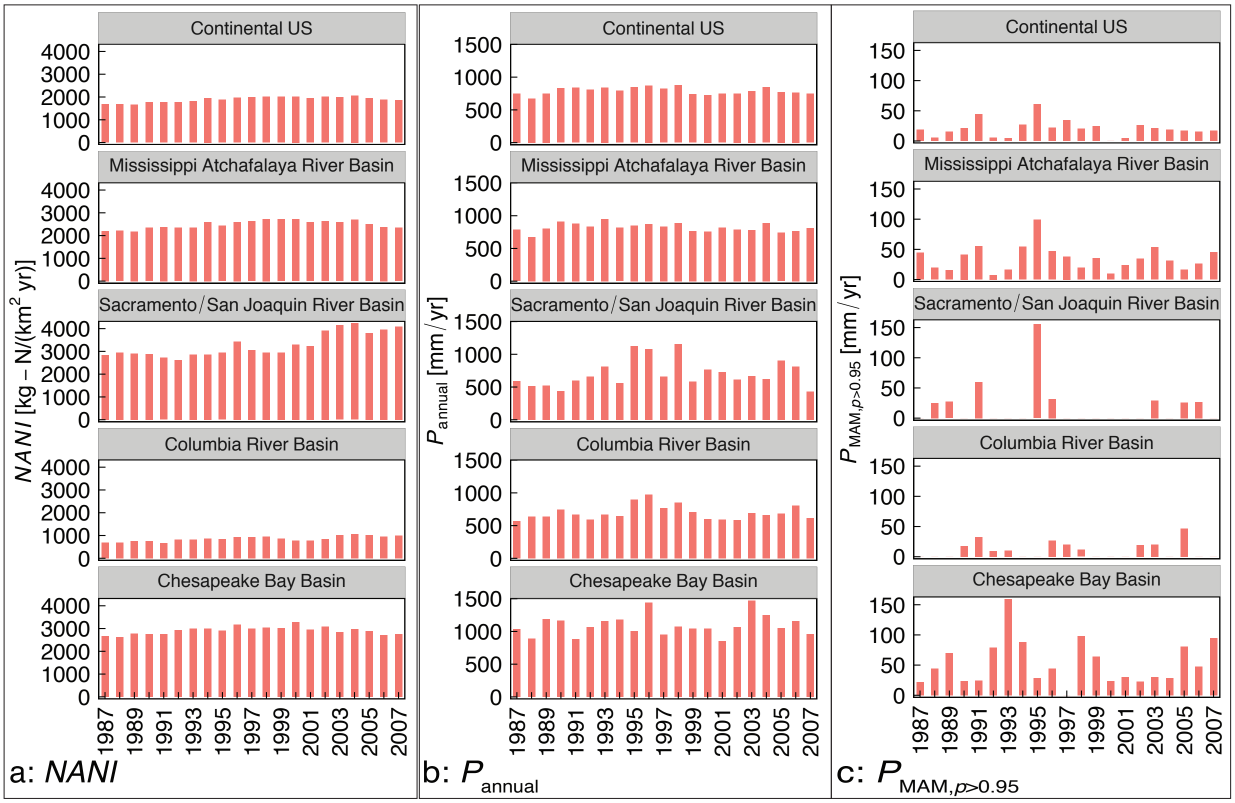

Figure S8. Spatially-averaged NANI, P_{annual}, and $P_{MAM,p>0.95}$ for watersheds draining to major nutrient delivery point to the coastal oceans. The annual predictor variables were estimated by aggregating annual predictor variables for HUC8 watersheds corresponding to each nutrient delivery point (Figure 1).

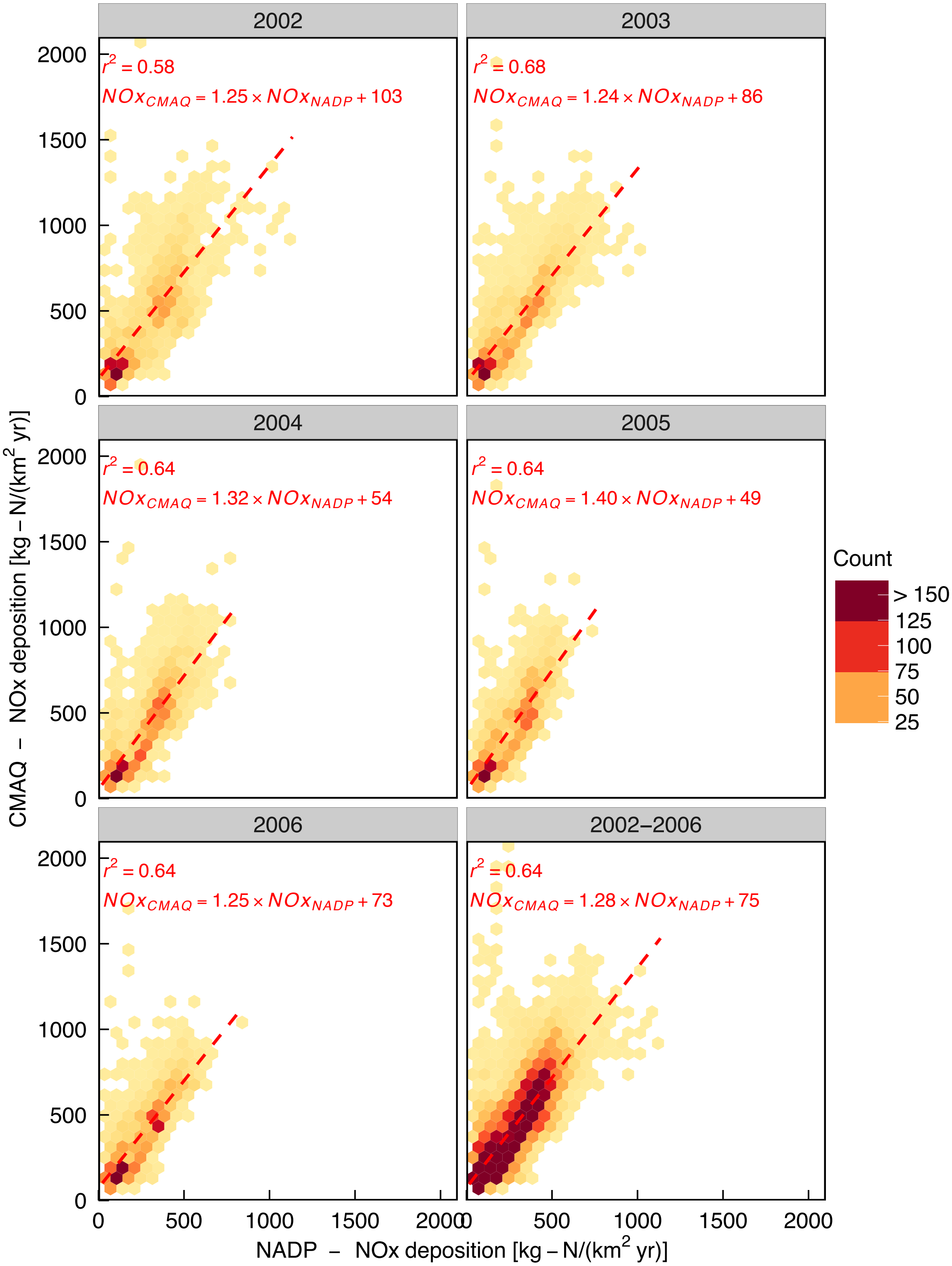

Figure S9. Comparison of estimated NOx deposition for all HUC8 watersheds within the CONUS based on data from NADP versus CMAQ.