Supplementary Information for
"Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico"

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Additional details of the spatial model and results were not included in the letter "Effect of stream channel size on the delivery of nitrogen Gulf of Mexico", and are provided here.

Model calibration

The spatial regression model of in-stream total nitrogen flux (TN_i) is developed for a set of 374 monitoring stations in watersheds of the United States containing a defined set of stream reaches to which stream monitoring data and data on nitrogen inputs and watershed characteristics are spatially referenced. Watersheds for the stations range in size from 80 to 2.9 million square kilometers (median=11,700) with mean streamflow ranging from one to 18,500 cubic meters per second (median=63). Data on the source inputs and terrestrial characteristics, available for approximately 20,000 land-surface polygons, were referenced to 60,000 stream reaches in a digital stream network of nearly one million kilometers of channel using conventional spatial analytical methods in a geographic information system (Smith *et al.* 1997). The median watershed size of the stream reaches is 82 km^2 with an interquartile range of 40 to 150 km^2. In-stream flux at the downstream end of a given monitored reach *i* is expressed as the sum of all monitored and unmonitored sources of nitrogen in the set of upstream reaches denoted by *J(i)*. The defined set of upstream reaches for the given reach *i* accounts for nested watersheds in the monitoring network such that the set excludes reaches that are either located above or include monitoring stations upstream of reach *i*. An estimable expression is written as

$$\mathrm{TN}_i = \left\{ \sum_{n=1}^{N} \sum_{j \in J(i)} S_{n,j} \beta_n \exp(-\alpha' \mathrm{Z}_j) \exp(-k' T_{i,j}) \right\} \varepsilon_i \qquad (1)$$

where $S_{n,j}$ is nitrogen mass from source *n* in the drainage of reach *j*, β_n is a source-specific coefficient, $\exp(-\alpha' Z_j)$ is a factor affecting the proportion of available nonpoint-source nitrogen mass delivered to reach *j* as a function of land-to-water delivery coefficients (defined by vector α) and associated terrestrial characteristics, Z_j, in the drainage to reach *j*, $\exp(-k' T_{i,j})$ is the proportion of nitrogen mass in reach *j* transported to downstream reach *i* as a function of a first-order loss process related to water time of travel ($T_{i,j}$) and a loss rate (k) defined as a vector of four discrete classes of channel size, and ε_i is a multiplicative error term assumed to be independent and identically distributed across independent sub-basins in the intervening drainage between stream monitoring sites. The land-to-water exponential delivery function is equal to one for point source inputs. Coefficient estimation was performed on the log transforms of the summed quantities in equation (1) using non-linear least-squares estimation according to a robust bootstrap procedure (Smith *et al.* 1997). The in-stream loss coefficients for the two largest stream classes were constrained in the bootstrap estimation method to be positive for the iterations where small, negative values were initially obtained (fewer than 10% of the 200 iterations for k_3 and fewer than 50% for k_4). The calibrated model explains 88 percent (r-squared) of the spatial variability in the stream monitoring estimates of TN flux. Model residuals are approximately normal with relatively constant variance. The magnitude of model prediction errors for the calibration and validation data sets is reported in table 1 of the accompanying paper.

Explanation of sources

Five major classes of nitrogen sources (fertilizer, livestock wastes, point sources, atmospheric deposition, and runoff from nonagricultural lands; table 1) were statistically significant in the model calibration. In the case of the nonpoint sources, the product of the source coefficients and the land-to-water function (which includes the α coefficients) quantifies the land-to-water delivery fractions of the specified source inputs. Examples of these land-to-water fractions were previously published for selected regions of the United States in Smith *et al.* (1997). The land-to-water delivery fractions may include contributions from additional sources (e.g., dry deposition, fixation by crops, crop imports, and groundwater) and the effects of terrestrial removal processes (e.g., soil denitrification, crop exports, climate, conservation tillage, and storage in vegetation, soils, and the subsurface). In addition to direct runoff of applied fertilizers, the "fertilizer" source may include fixed nitrogen in leguminous crop residues and other soil nitrogen from cropland, including nitrogen mineralized from soil organic matter. In modeling atmospheric nitrogen inputs, we used wet-deposition measurements of inorganic nitrate-nitrogen (Smith *et al.* 1997), and excluded ammonia deposition data to minimize the double accounting of agricultural sources of nitrogen (Howarth *et al.* 1996). Deposition measurements were detrended to reflect conditions for the base year 1987 under long-term average precipitation (i.e., precipitation adjusted). The land-to-water delivery fraction for wet nitrate deposition (product of the deposition coefficient and the exponential land-to-water delivery function) exceeds unity for many watersheds, and is consistent with our assumption that the atmospheric source includes additional nitrogen contributions (i.e., wet deposition of ammonium and organic N and dry deposition of inorganic N) not reflected by the input variable. Available estimates of total deposition (dry plus wet oxidized forms) in the United States range from 2 to 3 times the nitrogen in wet deposition (Fisher and Oppenheimer, 1991). Nonagricultural sources include nitrogen inputs scaled for nonagricultural land area and quantified by the model coefficient. This term includes nitrogen that is not directly accounted for by the other source terms in the model, such as nitrogen entering streams from runoff and groundwater associated with urban, range, and forested lands. The less-than-unity point-source coefficient (to which the land-to-water delivery function is not applied) likely reflects model adjustments for declines in effluent loads (see Smith *et al.* 1997) from the late 1970's (the time period of the input data) to 1987 (the base year for estimating stream flux). Moreover, some point-source facilities discharge to streams that are tributaries to those contained in our river reach network, and thus, aquatic losses from these facilities would likely be included in the point-source coefficient.

Limited confirmation of the model predictions for sources were obtained through literature comparisons (see table 2). Model predictions of TN yield (mass per unit area per time) for small reach-level watersheds with relatively homogenous land cover are found to lie well within the range of nitrogen yields reported for North American watersheds with similar land-cover types (Beaulac and Reckhow, 1982; Ritter, 1988; Frink, 1991). Watersheds dominated by urban sources and agriculture (crop and pasture land) have the largest nitrogen yields, whereas the quantities of nitrogen exported from watersheds with forest and range lands are one-tenth to one-quarter of these yields.

Table 2. SPARROW estimates of total nitrogen (TN) export from major land types in the United States in comparison to literature estimates. SPARROW estimates are reported for TN exported from watersheds associated with individual stream reaches as defined by the digital river network for the conterminous United States.

Watershed Land-Cover Type	**Distribution of TN Yield Exported from Sparrow Watersheds[a] (kg/ha/yr)**							**Literature Exports[b] (kg/ha/yr)**
	Number of Watersheds	**10th**	**25th**	**Median**	**75th**	**90th**	**Range of Values**	**Range of Values**
Crops	203	12.1	17.4	22.2	29.3	35.5	2.2 – 42.5	0.8 – 79.6
Pasture	19	9.5	14.4	16.8	19.2	20.3	8.5 – 20.8	0.1 – 30.8
Forest	17	1.8	3.6	4.5	6.1	7.4	1.8 – 11.2	0.1 – 10.8
Range	58	1.3	2.1	2.9	4.0	5.4	0.4 – 7.4	1.5 – 6.8
Urban	22	4.6	20.0	31.6	87.0	95.2	3.6 – 175	1.6 – 38.5

[a] The land-cover types represent the following percentages of the land area in Sparrow watersheds: crops (>90%), pasture (>85%), forest (>95%), range (100%), urban (>75%).

[b] Total nitrogen export taken from ranges reported in literature reviews (Beaulac and Reckhow, 1982; Frink, 1991; Ritter, 1988). The export reported for "range" is for grasslands in Oklahoma, U.S. (Ritter, 1988).

Model predictions of the nitrogen contributions from diffuse sources assume that the in-stream flux estimates, based on monitoring records for 1978-92, reflect contributions from sources under long-term average conditions as described by 1987 inputs. Although these data reflect past sources of nitrogen in older groundwater, estimates of the age of surface waters, based on a recent application of tritium dating techniques to selected U.S. streams, indicates that younger waters (<1 year in age) constitute an average of about one half of total streamflow [mean=56%; range=35 to 80% for six tritium monitoring sites (Michel, 1992)]. Moreover, source inputs for 1987 are representative of average conditions over at least the past two decades. Increases in N inputs and stream flux in the Mississippi Basin occurred prior to the early 1980s; changes since that time display no significant trends (Goolsby *et al.*, 1999; CEQ, 1989; NASS, 1998; Alexander and Smith, 1990; Battaglin and Goolsby, 1994). In addition, nitrogen diffuse source inputs for 1987 are no more than 3 to 14% higher than mean nitrogen inputs for the 20-year period prior to 1987 (CEQ, 1989; NASS, 1998; Alexander and Smith, 1990; Battaglin and Goolsby, 1994). The relative stability of mean diffuse inputs of nitrogen over the 10 to 20 year period prior to 1987, a period inclusive of the estimated mean residence times of older waters in the streamflow at recently studied U.S. stream sites [mean=12.5 years; range = 10 to 20 years (Michel, 1992; Focazio *et al.* 1997)], provides evidence of the general validity of our steady state assumption.

Percent delivery of TN export to the Gulf from interior watersheds

Table 3 accompanies figure 3 in the letter and presents the distribution of delivery percentages for watersheds within the major regional drainages of the Mississippi River Basin described in figure 1. The dendritic pattern of nitrogen transport noted in figure 3 leads to widely varying delivery percentages in each of the major regional drainages. As shown for the Central and Eastern regions in table 3, these percentages range from more than 90 percent from watersheds on the largest rivers to substantially less than 40 percent from watersheds on small streams. This wide variation is evident despite similarities of the distances of interior watersheds from the Gulf of Mexico within each regional drainage. Nitrogen delivery percentages from many arid watersheds in the western Mississippi basin, including portions of the Missouri and Arkansas/Red regions, are uniformly small because of the effect of the typically shallow rivers with high nitrogen loss rates and the lengthy water travel times to the Gulf.

Although both the first-order loss rate and water travel time per unit channel length (i.e., water velocity) affect the total quantities of nitrogen removed in streams, the dominant effect at the basin scale comes from changes in the loss rate. In the Mississippi Basin, the change in nitrogen loss per unit channel length due to changes in the loss rate coefficient is approximately three times greater than the change in loss due to changes in travel time per unit channel length. Water travel time per unit channel length changes by only a factor of about 32 (velocities range from ~0.076 to 2.4 m s^{-1}) in comparison to a factor of 90 in the loss rate coefficients over the range of streams sizes in the river network of the Mississippi River Basin.

Table 3 Percentage of the nitrogen export from interior watersheds delivered to the Gulf (see explanation in fig. 3 in the accompanying letter).

		Distribution of the Percentage of Stream Total Nitrogen Delivered to the Gulf of Mexico (kilometers to the Gulf from watershed outlets)				
Regional Watershed	**Number**	**Min.**	**25th Percentile**	**Median**	**75th Percentile**	**Max.**
Central Watersheds						
Upper Mississippi	59	8.9	46.9	61.3	84.7	92.2
		(2,514)	(2,880)	(3,107)	(3,234)	(3,539)
Central Mississippi	72	1.8	59.1	76.7	92.9	95.9
		(1,617)	(2,102)	(2,359)	(2,537)	(2,897)
Lower Mississippi	44	39.9	90.0	96.9	98.1	99.9
		(0)	(737)	(1,100)	(1,286)	(1,593)
Eastern Watersheds						
Ohio/Tennessee	152	44.6	67.7	84.2	92.3	95.9
		(1,617)	(2,189)	(2,578)	(2,950)	(3,611)
Western Watersheds						
Missouri	301	<0.1	<0.1	4.0	34.9	94.9
		(1,943)	(3,165)	(3,837)	(4,913)	(5,939)
Arkansas/White	114	<0.1	<0.1	18.8	70.2	96.6
		(1,112)	(1,697)	(2,169)	(2,576)	(3,094)
All Watersheds	742	<0.1	2.4	53.3	83.5	99.9
Standard error[a]		<0.1	0.5	6.4	9.4	17.9

[a] Estimates of the standard error are based on bootstrap estimates of uncertainty in the in-stream loss coefficients.

Estimates of TN delivery to the Gulf from interior watersheds and sources

Combining the estimates of mean total nitrogen flux at the 123 stream locations (fig. 1) with the loss rate coefficients in table 1 and river network data on channel size (i.e., streamflow) and water travel time (i.e., reciprocal water velocity), we computed the quantities of nitrogen delivered to the Gulf of Mexico from the drainage areas above each monitoring site. These estimates were refined by determining the quantities of nitrogen originating in the intervening area between monitoring sites as the difference between the delivered TN flux for each site and the sum of delivered fluxes for the most immediate upstream sites. Expressing the delivered TN flux per unit area of the intervening drainage (i.e., yield) adjusts for differences in basin sizes. The resulting estimates of delivered TN yield (fig. 4) vary over a wide range from <0.1 to 88 kg ha^{-1} yr^{-1} (median=2.2 kg ha^{-1} yr^{-1}; interquartile range of 0.2 to 6.5 kg ha^{-1} yr^{-1}), reflecting spatial variations in the supply of nitrogen and internal processing of nitrogen on the landscape and in the rivers of the Mississippi basin. The highest nitrogen deliveries to the Gulf originate in the northeastern and north central portions of the Mississippi basin, areas containing large amounts of corn and soybean acreage, livestock, atmospheric deposition, and municipal wastes. At the regional scale, the Central Mississippi and Ohio/Tennessee regions (fig. 1) deliver more than two to four times as much nitrogen per unit area (i.e., delivered TN yield) to the Gulf as the quantities delivered from other regional watersheds

Table 4. Total nitrogen (TN) delivered to the Gulf of Mexico from the major regional watersheds and nitrogen sources in the Mississippi River Basin. Source contributions for "All Watersheds" are expressed as a percentage of the mean TN flux (2,931 x 10^3 kg day^{-1}) at the Mississippi River outlet to the Gulf. Source contributions for the regional watersheds are expressed as a percentage of the mean TN flux delivered to the Gulf from each source category.

	Share of the Source TN Flux Delivered to the Gulf of Mexico [a] (mean in bold and 90% confidence interval, in percent)						
Nitrogen Source	**All Watersheds**	**Upper Mississippi**	**Missouri**	**Central Mississippi**	**Ohio and Tennessee**	**Arkansas and White**	**Lower Mississippi**
Point sources	**6.0**	**3.9**	**5.3**	**24.2**	**42.0**	**3.5**	**21.2**
	2.6 – 9.6	3.3 – 4.5	4.7 – 6.0	19.6 – 28.8	38.0 – 45.8	3.1 – 4.0	16.8 – 27.2
Fertilizer use	**48.7**	**9.5**	**12.9**	**31.0**	**30.0**	**4.5**	**12.1**
	38.2 – 59.5	8.2 – 10.8	11.3 – 14.5	28.7 – 33.6	27.9 – 32.1	3.9 – 5.0	9.7 – 14.5
Livestock wastes	**15.3**	**16.7**	**15.7**	**22.0**	**31.6**	**11.4**	**2.6**
	5.3 – 26.2	15.5 – 18.0	14.1 – 17.2	21.2 – 22.9	30.1 – 33.1	10.5 – 12.3	2.3 – 2.9
Atmosphere	**17.7**	**7.0**	**11.7**	**15.0**	**49.4**	**8.3**	**8.6**
	6.3 – 28.2	6.3 – 7.6	10.7 – 12.7	14.3 – 15.6	47.8 – 51.0	7.7 – 8.8	7.6 – 10.0
Nonagricultural nonpoint sources	**12.4**	**9.2**	**12.4**	**8.0**	**47.1**	**13.1**	**10.3**
	9.0 – 15.8	7.9 – 10.2	9.1 – 16.3	7.5 – 8.4	44.0 – 49.7	12.2 – 14.0	8.8 – 12.2
TN yield delivered to Gulf (kg km^{-2} day^{-1}) [b]	**0.98**	**1.15**	**0.25**	**3.88**	**2.00**	**0.26**	**0.82**
Watershed area (km^2)	**2,984,100**	**221,700**	**1,357,700**	**267,800**	**526,000**	**461,400**	**149,500**

[a] Estimates of the source shares (mean and 90% confidence intervals) are determined according to statistical bootstrap methods (see Smith et al. 1997). Uncertainty estimates reflect both variability in the estimated rates of nitrogen supply and attenuation and unexplained variability in the observed stream flux data. Each source's share of the unexplained variability in the observed data (i.e., residual model error) was assumed to be proportional to the mean of the source contributions. Point sources are computed as the sum of industrial and municipal sources.

[b] The mean TN yield for each region gives the quantity of nitrogen per unit area delivered to the outlet of the Lower Mississippi, location of the monitoring station at Belle Chasse, Louisiana, according to estimates of water time of travel and in-channel losses of nitrogen. Delivered flux for the intervening drainage of the Central Mississippi watershed is estimated as the difference between the delivered TN flux for the Mississippi R at Thebes, Illinois and the sum of the delivered TN flux for the Mississippi R at Clinton, Iowa and the Missouri R at Hermann, Missouri. Delivered flux for the intervening drainage of the Lower Mississippi watershed is estimated as the difference between the delivered TN flux for the Mississippi R at Belle Chasse, Louisiana and the sum of the delivered TN flux from upstream tributaries including the Mississippi R at Thebes, Illinois, Ohio R at Grand Chain, Illinois, Arkansas R below Little Rock, Arkansas, and White R at Newport, Arkansas. We assumed that the fraction of nitrogen diverted to the Atchafalaya River basin from the Lower Mississippi (at river kilometer 506) is identical to that known for streamflow (i.e., 22 percent). The Atchafalaya River serves as an alternate flowpath to the Gulf accounting for a total of 30 percent of the total flow of the two rivers.

(see table 4). Collectively, these regions account for 71 percent of the nitrogen delivered to the Gulf although they contain only 27 percent of the total area of the Mississippi basin. By contrast, the Missouri and the Arkansas/White regions contribute only 16 percent of the nitrogen exported to the Gulf although these regions contain 61 percent of the total area of the Mississippi basin.

We quantified the relative contributions to the Gulf of major point and diffuse sources in the intervening watersheds of the 123 monitoring stations (see fig. 5) and in the major regional basins (see table 4) by applying the model coefficients in table 1 to local data on nitrogen sources and landscape and stream characteristics. We assume that the in-stream attenuation of nitrogen is identical for all sources. The estimates of source shares for the entire Mississippi Basin (table 4) indicate that agricultural sources (i.e., fertilizer and livestock wastes) collectively contribute a majority (63%) of the nitrogen delivered to the Gulf, with fertilizer-related sources alone accounting for nearly half (49%) of the nitrogen exported from the basin. Atmospheric sources account for 50 percent of the remaining fraction of nitrogen delivered to the Gulf or 18 percent of the total delivered nitrogen. Municipal and industrial wastes (point sources) represent the smallest fraction (6%) of the nitrogen delivered to the Gulf. The ninety percent confidence intervals for the estimates of point-source and fertilizer-related shares indicate that the relative importance of these sources can be clearly distinguished from the relative contributions of other sources. The relative contributions of the atmospheric, livestock wastes, and non-agricultural nonpoint sources are very similar in magnitude, and cannot be separately ordered because of the overlapping confidence intervals on the mean estimates. Estimates of the regional shares of source contributions to the Gulf (table 4) have narrow 90% confidence intervals (i.e., the shares are estimated with high reliability) because the instantaneous rates of in-stream loss are estimated with high precision and because the regional export of nitrogen is directly measured. The regional results indicate that the Ohio/Tennessee and Central Mississippi regions collectively contribute 53 to 66 percent of the nitrogen delivered to the Gulf from each of the sources. For the interior watersheds in these regions, agriculture represents the dominant source of the nitrogen delivered to the Gulf (see fig. 5a; upper class of 2.0 to 32 kg ha^{-1} yr^{-1}). Atmospheric sources are largest in the eastern portions of the Ohio/Tennessee region where many watersheds have high values of delivered yield (the highest category, 2.0 to 22 kg ha^{-1} yr^{-1}, in fig. 5b). Despite the presence of intensively cultivated areas in the Lower Mississippi region, agriculture (fertilizer and livestock wastes) contributes less than 15 percent of the total agricultural nitrogen delivered to the Gulf (table 4). The Lower Mississippi region contributes about 20 percent of the point source nitrogen, an amount that represents only 1.3 percent of the total mass of nitrogen delivered to the Gulf. Although point sources contribute little of the total nitrogen mass delivered to the Gulf of Mexico (6%), selected highly populated watersheds, including the Chicago metropolitan area (Upper Illinois River), the St. Louis metropolitan area (Central Mississippi region), and the mainstem of the upper Ohio River extending downstream from the Pittsburgh metropolitan area, are identified in figure 5c as areas having high delivered yields (2.0 to 10 kg ha^{-1} yr^{-1}).

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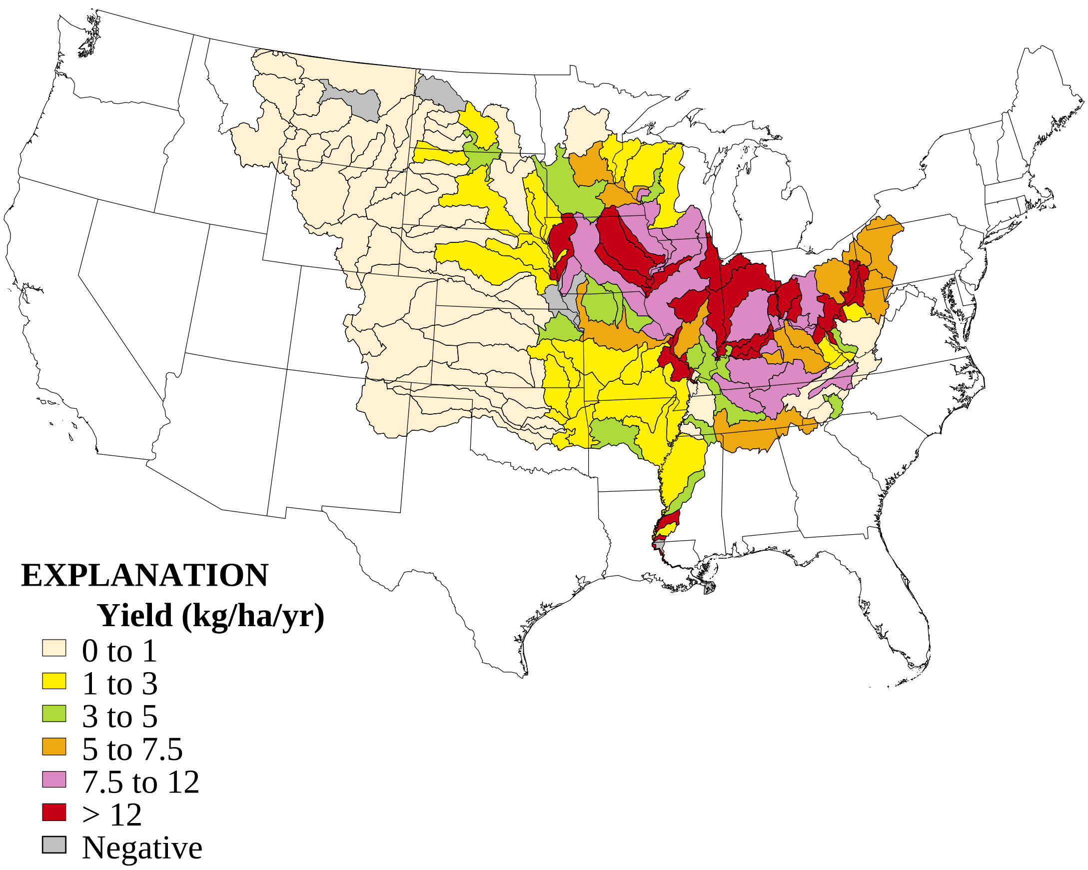

Figure 4. Yield of total nitrogen delivered to the Gulf of Mexico from the incremental drainage areas of monitoring stations in the Mississippi River basin.

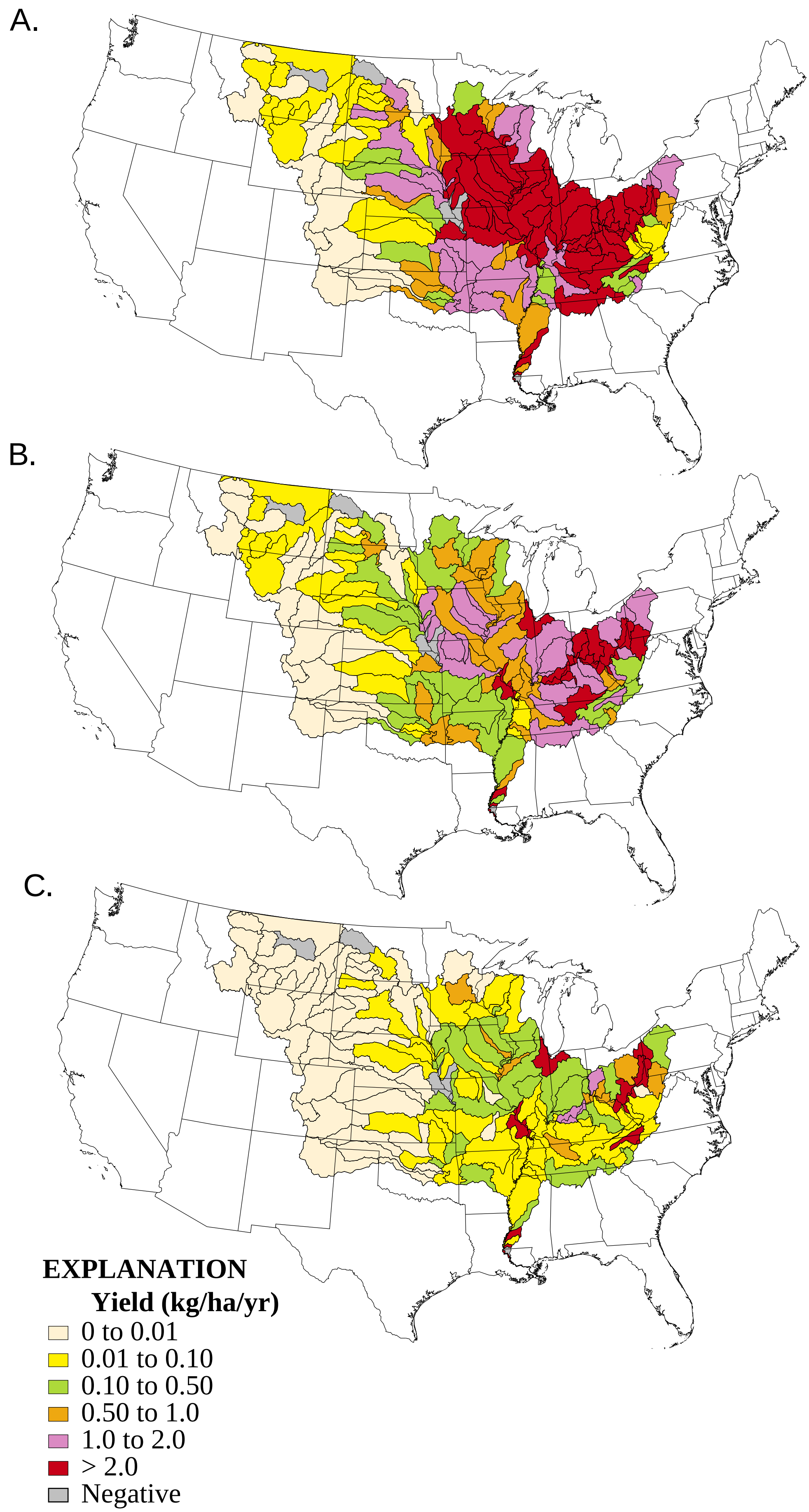

Figure 5. Yield of total nitrogen delivered to the Gulf of Mexico from major sources in the incremental drainage areas of monitoring stations in the Mississippi River basin: (a) agriculture (sum of fertilizer and livestock wastes), (b) atmosphere, (c) industrial and municipal point sources.