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Differences in Phosphorus and Nitrogen Delivery to The Gulf of Mexico from the Mississippi River Basin

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Seasonal hypoxia in the northern Gulf of Mexico has been linked to increased nitrogen fluxes from the Mississippi and Atchafalaya River Basins, though recent evidence shows that phosphorus also influences productivity in the Gulf. We developed a spatially explicit and structurally detailed SPARROW water-quality model that reveals important differences in the sources and transport processes that control nitrogen (N) and phosphorus (P) delivery to the Gulf. Our model simulations indicate that agricultural sources in the watersheds contribute more than 70% of the delivered N and P. However, corn and soybean cultivation is the largest contributor of N (52%), followed by atmospheric deposition sources (16%); whereas P originates primarily from animal manure on pasture and rangelands (37%), followed by corn and soybeans (25%), other crops (18%), and urban sources (12%). The fraction of in-stream P and N load delivered to the Gulf increases with stream size, but reservoir trapping of P causes large local- and regional-scale differences in delivery. Our results indicate the diversity of management approaches required to achieve efficient control of nutrient loads to the Gulf. These include recognition of important differences in the agricultural sources of N and P, the role of atmospheric N, attention to P sources downstream from reservoirs, and better control of both N and P in close proximity to large rivers.

Introduction

Reactive nutrients are accumulating rapidly in the environment in response to population growth and associated activities (*1*), with agriculture and fossil-fuel combustion serving as the primary sources of increasing nutrient loads to watersheds (*2, 3*). Although the increased availability of reactive nutrients benefits society via food and energy production, the environmental consequences are severe (*4*). Concerns over nutrient enrichment are of particular importance in coastal waters, where increased nutrient loads have caused eutrophication and the degradation of estuarine water quality on a global scale (*3, 4*). In the United States, elevated riverine nitrogen has contributed to degradation of the ecosystems in the majority of the estuaries (*5*). This includes the shallow coastal waters of the Louisiana shelf in the northern Gulf of Mexico, where the increased occurrence of seasonal hypoxia has been attributed to the rise in riverine nitrogen flux. A major governmental study (*6*) concluded in 1999 that nitrogen pollution is intrinsically linked to Gulf hypoxia. This led to a management goal (*7*) to reduce point and diffuse nitrogen source inputs to streams in the Mississippi and Atchafalaya River Basins (MARB) by quantities sufficient to achieve a 30% reduction by 2015 in the riverine nitrogen discharge to the Gulf.

There is growing recognition, however, of a need for an expanded and complementary understanding of the sources and transport of both nitrogen and phosphorus and their complex interactions toward developing effective nutrient management plans in coastal waters (*8–12*). Though the importance of nitrogen in controlling eutrophication in Gulf waters is well-known, recent evidence from experimental studies of Louisiana coastal waters (*11, 13*) suggests that phosphorus plays a more important role than previously thought in the occurrence of Gulf hypoxia. The management of nutrients in interstate inland waters also favors phosphorus, which is typically more limiting to primary production in freshwater ecosystems. Excessive phosphorus concentrations in many inland waters of the MARB have contributed to difficulties in meeting State-designated use requirements (*14*). A major limitation in understanding connections between phosphorus sources and management in the MARB and delivery to the Gulf is that most phosphorus research and models have focused on small watersheds**;** the few regional-scale water-quality models of the 3-million-km^2 MARB have emphasized nitrogen (*15–18*). Noteworthy advances have been made in modeling techniques and watershed data (*19*) since the development of earlier MARB models that can greatly improve understanding of nutrient sources and transport.

We developed an improved SPARROW (spatially referenced regression on watershed attributes (*20*)); water-quality model specifically to assess the pollutant sources and the terrestrial and aquatic processes that influence the supply and transport of total phosphorus (TP) and total nitrogen (TN) in the MARB and their delivery to the Gulf. Model advances include enhanced reach-scale flux-accounting methods that support nonlinear in-stream and reservoir nutrient decay functions, an updated spatial infrastructure, based on 30 m land use and 1 km digital topography, and new data on climatic conditions, cropping and artificial-drainage systems, and animal manure nutrients. The resulting model has higher prediction accuracy and greater complexity with improved interpretability of nutrient sources and processes in comparison to prior SPARROW models (*16, 20*). The development of separate models of nitrogen and phosphorus, with similar specifications and stream monitoring data for calibration, enables comparisons among these nutrients that advance understanding of the geography and types of sources and the coupled hydrologic and biogeochemical processes that control their delivery to the Gulf.

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Materials and Methods

The SPARROW water-quality model (*19, 20*) uses a hybrid statistical and process-based approach to estimate nutrient sources, transport, and transformation in the terrestrial and aquatic ecosystems of watersheds under long-term steady-state conditions. The model includes nonconservative transport, mass-balance constraints, and water flow paths defined by topography, streams, and reservoirs, based on a detailed stream reach network (1:500000 scale) with subcatchments (median size = 60 km^2) delineated from 1-km digital elevation models (DEMs; ref *21*); the MARB contains approximately 25000 subcatchments in the SPARROW model. See the Supporting Information (SI) for method details.

We simulate the mean annual flux of TN and TP in streams as a function of 10 nutrient sources (eight for TP), six climatic and landscape factors that influence nutrient delivery to streams (five for TP), and nutrient removal in streams and reservoirs (Table 1). Nutrient sources include atmospheric deposition of nitrogen, urban sources, and nutrients in the runoff and subsurface flow from agricultural and other lands. Agricultural sources are structurally separated into cultivated croplands and pasture/rangelands. Croplands include nutrient inputs from biological N_2 fixation (soybeans, alfalfa, and hay), commercial fertilizer use on seven major crops, and animal manure that is recovered from confined animals on nearby farms and applied to crops as fertilizer. Pasture/rangelands include nutrients from nonrecoverable animal manure-i.e., manure from unconfined animals and manure lost during the collection, storage, and treatment of wastes from confined animals, including concentrated animal feeding operations (*22*). The model assumes that nutrient immobilization and mineralization rates in soils of the MARB are approximately in equilibrium as in prior MARB models (*18, 23, 24*).

The model estimates nutrient delivery to streams in subsurface and overland flow ("land-to-water" delivery) in relation to landscape properties (*19*), including climate, soils, topography, drainage density, and artificial drainage. Aquatic transport is described according to first-order decay functions for streams and reservoirs (see eqs 2 and 3 in the SI; ref *19*). We include estimates (*25, 26*) of the annual rate of nitrogen removal in 24 large "pools", located on the Upper Mississippi River above Clinton, IA.

Model parameters for the sources, land-to-water delivery factors, and aquatic decay terms (Table 1) are statistically estimated using nonlinear methods, based on a calibration to the long-term mean annual load of TN and TP (i.e., the steady-state response variable in the model) at 425 stream monitoring stations in the conterminous U.S. (Figure 1). We included stations outside the MARB to ensure broad coverage of the spatial variability in major nutrient sources and processes and to enhance the statistical sensitivity of the model estimation; MARB-specific model coefficients were evaluated, but were unnecessary (see SI). We report the final models (Table 1) with the highest prediction accuracy in evaluations of alternative specifications of the explanatory variables. Comparisons of the estimated aquatic decay rates (Figure 2) and model predictions of stream nutrient yields with those from the literature also provide partial confirmation of model accuracy (see SI for details).

Long-term mean annual nutrient loads were estimated for each monitoring station prior to SPARROW modeling by applying load estimation methods (*19*) to regularly measured total nutrient concentrations and daily flow measurements for 1975–1995. Generally consistent sampling and analytical methods were used over a 20-year period at these stations (*27*). The mean annual load for each station is *standardized* to the 1992 base year to give an estimate of the mean nutrient load that would have occurred in 1992 if mean annual flow conditions from 1975 to 2000 had prevailed (nutrient source inputs to the model are for 1992). The 1992 base year ensures consistency in the stream-monitoring and nutrient-source data (see SI) and lies within the 1980–1996 baseline (*7*) for tracking future changes in riverine nutrient flux. The use of flow records for 1975–2000 ensures that the nutrient loads in SPARROW mass-balance calculations are representative of long-term hydrologic variability during a contemporaneous time period; this produces robust estimates of the nutrient sources to streams and the processes that govern the mean rates of nutrient removal and transport in watersheds (*19*).

We use the calibrated models to predict the mean annual flux (mass) and yield (mass per unit area) of TN and TP that is delivered to the Gulf of Mexico from nutrient sources in the watersheds in eight regional drainages of the MARB (Figure 1and Table 2; these regions have been used in previous studies *15, 16*). These predictions account for the cumulative effects of terrestrial and aquatic removal processes on nutrient delivery to the Gulf.

Results and Discussion

Model Accuracy and Parameter Estimates. Mean annual nutrient fluxes at the monitoring sites vary over 6 orders of magnitude and yields range over about 3 orders of magnitude (TN: 0.94–5243 kg/km^2/yr, median = 294.8 interquartile range = 95.7–612.1; TP: 0.12–772.9 kg/km^2/yr; median = 22.1, interquartile range = 11.1–47.7). Model R^2 values (Table 1) indicate that the SPARROW models explain about 90% of the spatial variability in the log-transformed values of mean annual flux. The somewhat lower nutrient yield R^2 values adjust for drainage area scaling effects, providing a more informative measure of the model's explanatory power. The prediction accuracy of the mean annual flux in unmonitored reaches is within 55–76% of the mean (RMSE; Table 1). Model prediction errors are 20% lower than those reported for prior SPARROW models (*16, 20*), after accounting for differences in the calibration stations.

The nutrient sources included in the final models (Table 1) are more numerous than in prior SPARROW models (*16, 28*), indicating greater complexity and improved quantification of precursor nutrient sources. We find that similar types of nutrient sources are statistically significant in the TN and TP models. Watersheds with predominantly urban and agricultural sources have the highest predicted nutrient yields, whereas those dominated by forest and shrub lands have the lowest; these compare favorably with literature estimates (see SI). Nutrient sources are statistically estimated in the model, and therefore, include nutrient contributions from all sources that are spatially correlated with the model inputs. For example, the nutrient coefficients associated with urban sources quantify the per capita delivery rates of nutrients to streams. These rates include nutrient contributions from septic systems, industrial and municipal treatment plant wastewaters, and runoff from residential lands. The estimated per capita rates are 50–60% of that for untreated human wastes (*29, 30*); nitrogen falls within the range reported for treated effluent (*31*), whereas phosphorus is about 50% of that for treated effluent (*14*). The nitrogen per capita rate also includes contributions of wet/dry nitrogen deposition from stationary and mobile sources (power plants, vehicles) in urban areas that are spatially correlated with population.

The coefficients for crops (Table 1) quantify the fraction of the nutrient inputs to croplands from commercial and recoverable-manure fertilizers and biologically fixed N_2 that are delivered to streams. These quantities range from 2 to 16% of the nutrient inputs to the crops in Table 1, and implicitly include the effects of nutrient removal in harvested biomass. Nutrient uptake in crops varies in relation to soils and climate (*32*), but represents as much as 50% or more of

TABLE 1. SPARROW Model Statistics for Total Nitrogen and Total Phosphorus

nitrogen parameters	coefficient units	mean coefficient	standard error	*p*-value
sources (β)				
urban and population-related sources	kg^{-1} person yr^{-1}	2.58	0.322	<0.001
atmospheric deposition	dimensionless	0.694	0.144	<0.001
corn and soybeans	dimensionless	0.164	0.024	<0.001
alfalfa	dimensionless	0.083	0.058	0.076
wheat	dimensionless	0.137	0.060	0.011
other crops	dimensionless	0.071	0.030	0.010
pasture/rangeland	dimensionless	0.063	0.055	0.125
forest land	kg ha^{-1} yr^{-1}	1.09	0.347	<0.001
barren/transitional land	kg ha^{-1} yr^{-1}	1.60	1.75	0.180
shrub land	kg ha^{-1} yr^{-1}	0.902	0.418	0.016
land-to-water delivery (α)				
soil permeability	log (cm hr^{-1})	−0.143	0.047	0.003
drainage density	log (km^{-1})	0.186	0.104	0.075
temperature	Deg. C.	−0.071	0.010	<0.001
precipitation	cm	0.014	0.001	<0.001
specific catchment area	log (m)	0.628	0.103	<0.001
artificial drains	percent area	0.006	0.003	0.086
aquatic nutrient removal (*k*)				
streams	m yr^{-1}	17.7	1.94	<0.001
reservoirs	m yr^{-1}	1.4	0.61	0.021
mean square error	0.3054			
root mean square error	0.5526			
number of observations	425			
r-squared flux	0.933			
r-squared yield	0.866			

phosphorus parameters	coefficient units	mean coefficient	standard error	*p*-value
sources (β)				
urban and population-related sources	kg^{-1} person yr^{-1}	0.255	0.050	<0.001
corn and soybeans	dimensionless	0.023	0.012	0.029
alfalfa	dimensionless	0.124	0.080	0.060
other crops	dimensionless	0.026	0.016	0.053
pasture/rangeland	dimensionless	0.138	0.028	<0.001
forest land	kg ha^{-1} yr^{-1}	0.167	0.035	<0.001
barren/transitional land	kg ha^{-1} yr^{-1}	1.35	0.757	0.037
shrub land	kg ha^{-1} yr^{-1}	0.227	0.084	0.004
land-to-water delivery (α)				
soil permeability	log (cm hr^{-1})	−0.404	0.074	<0.001
slope	log (percent)	0.099	0.059	0.092
precipitation	cm	0.006	0.002	<0.001
specific catchment area	log (m)	0.623	0.285	0.030
artificial drains	percent area	0.027	0.008	<0.001
aquatic nutrient removal (*k*)				
streams	m yr^{-1}	12.2	3.2	<0.001
reservoirs	m yr^{-1}	34.0	6.0	<0.001
mean square error	0.581			
root mean square error	0.762			
number of observations	425			
r-squared flux	0.871			
r-squared yield	0.684			

The source coefficients (β), which measure the mean rate of nutrient mass delivery to streams as a function of the source input units, are standardized for the mean of the land-to-water delivery conditions to facilitate comparisons between sources and models; the land-to-water delivery variables are expressed as deviations from their national means. The sources with dimensionless coefficients (β) multiplied by an exponential land-to-water delivery function (i.e., e^{-az}, where z is a vector of land-to-water decay factors) quantify the proportion of available nutrient mass delivered to rivers. The atmospheric source reflects regional nitrogen deposition on all land types, based on wet-nitrate deposition measurements, but also includes the deposition of additional wet and dry nitrogen forms that are spatially correlated with wet-nitrate deposition (see SI for details). Pasture/rangeland estimates reflect nutrients from non-recoverable animal manure from farms with confined or unconfined animals. The other source terms quantify the mass delivered to rivers as a per capita rate (population) or per unit of area (land use). Nutrients from forest, barren, and shrub lands primarily reflect natural background sources, but may include contributions from atmospheric deposition of nitrogen. The land-to-water delivery function is equal to one for the population source. The rate coefficients (*k*) are applied in first-order mass-transfer rate expressions in the model. For streams, the quotient of the rate coefficient and mean water depth quantifies the rate of nutrient loss per unit of water travel time. The reservoir rate coefficient (k^r) and the areal hydraulic load (q^r; ratio of reservoir outflow to surface area) are used in the expression $1/(1 + k^r (q^r)^{-1})$ to quantify the proportion of the nutrient mass transported through impoundments (*19*). The reported *p*-values are one-sided values for the source parameters and two-sided for all other parameters.

the nutrient inputs to soils, with a majority of the harvested nutrients incorporated into animal feed (*33*). Model estimates of nutrient delivery from cropland to streams also include effects of landscape and climatic factors (Table 1). These

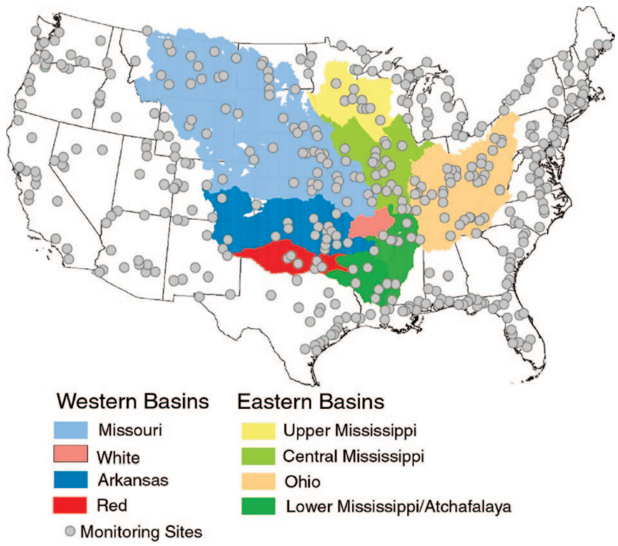

FIGURE 1. Location of the major hydrologic regions of the MARB and stream monitoring stations used to estimate the SPARROW models.

influence transport by controlling water availability, subsurface and surficial flow paths, the residence times of water and nutrients in soils and ground waters, and biochemical processing (e.g., denitrification).

We find that the mean fraction of the nitrogen inputs to corn/soybeans that are delivered to streams (0.164) is 7-fold higher than that for phosphorus (0.023; Table 1). This reflects intrinsic differences in crop nutrient requirements and the chemical forms and transport pathways for nitrogen and phosphorus. The large nutrient requirements for corn and the potential for nitrogen overapplication contribute to the leaching of nitrate-nitrogen, which is highly mobile in soils and groundwater (*2*). Phosphorus is frequently transported in surface runoff, with mobility decreasing as soil–water contact with phosphorus-deficient subsoils increases (*34, 35*). Conservation and reduced tillage, used on nearly 60% of the cultivated lands in the MARB in 1992, and other management practices such as filter strips may limit the transport of phosphorus more than that of nitrogen. Conservation practices are generally effective in increasing water infiltration and removing particulates from runoff, but have little effect on nitrate leaching (*36*), with more mixed results on dissolved forms of phosphorus (*35*). The larger nitrogen delivery coefficient may also reflect small additional contributions of ammonium deposition from volatilized ammonia in animal wastes that are correlated with model inputs of nitrogen to cropland. Total ammonium deposition in the MARB represents less than 10% of the nitrogen inputs to cropland from commercial and manure fertilizers and biologically fixed N_2. Much of the deposition originates from livestock ammonia emissions, which are more than double those from fertilizer (*37*), with about half of the deposition occurring within 50 km of the emission source (*23*). Ammonium deposition was not explicitly included in the model inputs to cropland because of uncertainties in agricultural sources and transport distances (i.e., long-range vs local deposition).

By contrast, the fraction of phosphorus (0.14) delivered to streams from pastures/rangelands (Table 1) is about double that for nitrogen (0.06), with evidence of statistically separable coefficient distributions ($p = 0.11$). These model coefficients describe the fraction of the nutrients in nonrecoverable animal manure that is delivered to streams, including nutrients from seasonally applied fertilizers on pasture/rangelands that are unmeasured, but correlated with animal populations. Differences in nitrogen and phosphorus delivery fractions may be explained, in part, by the enrichment of phosphorus in animal manure as compared to that in commercial fertilizers (nitrogen to phosphorus (N:P) ratio of ~7 vs ~14, respectively) related to the inefficient uptake of phosphorus in feeds by livestock (*38*). Nitrogen losses from ammonia volatilization in animal wastes range from 10 to 40% (*39*) and may also contribute to a smaller nitrogen delivery coefficient. Overland runoff of phosphorus from pastures may be enhanced by animal treading and compaction of soil surfaces in intensely grazed pastures, leading to decreased water infiltration and increased sediment runoff (*35*). The frequent excretion of animal manure and urine on pasture/rangelands may also accentuate nutrient runoff as compared to croplands where commercial fertilizers are applied seasonally.

We find that the rate of nutrient removal declines in streams with increases in water depth and stream size (Figure 2a), and decreases in reservoirs with increases in the water flushing rate (Figure 2b). These inverse relations are consistent with those reported for prior SPARROW models (*16, 20, 28, 40*) and with current understanding of the hydrologic and biogeochemical processes (denitrification, particulate settling, water velocity and depth, water volume to surface area ratios) responsible for nutrient loss in natural waters (*41, 42*). For streams, the TN mass-transfer coefficient (Table 1; 18 m yr^{-1}) gives corresponding reaction rate coefficients (Figure 2a) similar to the literature rates for stream denitrification (*43–47*). The SPARROW reaction rates are generally less than one-half of those estimated for streams in an earlier SPARROW TN model (*16*), although slightly higher rates are estimated for large rivers of the MARB. These differences are explained by the improved model infrastructure and new data on precipitation and terrestrial factors. As compared with earlier models, the current model indicates greater nitrogen loss in the "landscape" (note that the "landscape" component includes the effects of streams smaller than those modeled in the 1:500000 scale network with mean-annual flows >~0.028 m^3 s^{-1}).

The in-stream removal rate for TP is 69% of that for TN and is also smaller than estimated in earlier models (*20, 28*). The TP mass-transfer removal rate for streams (12 m yr^{-1}) is one-third of that estimated for reservoirs (34 m yr^{-1}), a plausible finding given that long-term particulate burial and floodplain storage is likely to be less in lotic ecosystems than in reservoirs. Stream phosphorus removal rates are unavailable in the literature for the large time and space scales examined here. The reservoir TP mass-transfer coefficient (34 m yr^{-1}) is more than an order of magnitude higher than that for TN (1.4 m yr^{-1}); both rates are consistent with those in the literature (*40*). The smaller TN removal-rate coefficient for reservoirs as compared to that for streams is also typically observed in the literature (*2, 40*).

Nutrient Transport and Sources in the MARB. We estimate the percentages of the nutrient load in streams of the MARB that are delivered to the Gulf, based on the mean water velocity in streams and reservoirs and model estimates of the mean rates of aquatic nutrient removal (Figure 3). The delivery percentages generally increase with stream size and display a dendritic spatial pattern (Figure 3). The largest percentages (>90%) occur in the largest mainstem rivers and their tributaries. More than 50–75% of the stream nutrients are delivered from most small to midsized streams in the central and eastern regions, whereas less than 25–50% of the nutrients are delivered from streams in the western regions, where lower flows and longer river distances enhance in-stream removal. The dendritic pattern results from the combined effect of the inverse relation between nutrient removal and stream size (Figure 2) and the positive relation of velocity with stream size as reported in tracer studies (*19*) and applied in SPARROW. Reservoirs cause local- and regional-scale differences in phosphorus delivery as com-

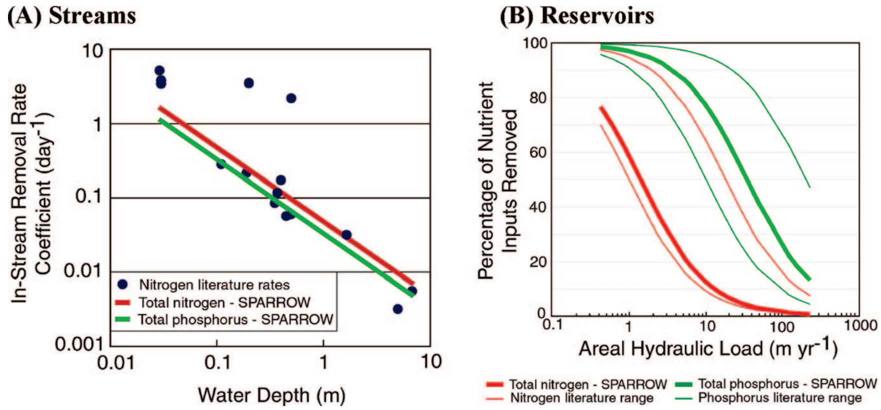

FIGURE 2. Model estimates of the removal of total nitrogen and total phosphorus in: (a) streams; (b) reservoirs.

pared to nitrogen, especially in the Tennessee Basin and portions of the upper, central, and western regions of the MARB (Figure 3b); this relates to the 10-fold higher phosphorus loss-rate coefficient as compared to that for nitrogen. As a result, the phosphorus delivery percentage is less than 50% of that for nitrogen for most MARB reaches. The spatial pattern in nitrogen delivery is similar to that previously reported (*16*); however, we find that larger fractions of the nitrogen in small streams (and somewhat lower fractions in the largest rivers) are delivered to the Gulf than previously reported. In the 1600 smallest streams of the Ohio and Central Mississippi regions (mean flow <1.0 $m^3\ s^{-1}$), a median of 57% (interquartile range = 39–67%) of the mean annual nitrogen flux is delivered to the Gulf.

The dendritic pattern of nutrient delivery (Figure 3) implies that, independent of other factors, reductions in nutrient loads to the Gulf can be most efficiently achieved by targeting nutrient sources near large rivers or near small streams that flow quickly (with short water travel times) to large rivers. For example, the removal of 1 kg of the nutrients in large rivers ("90–100" percent class in Figure 3) would cause a nearly equal reduction in delivery to the Gulf, whereas the removal of 2–4 kg would be required in smaller streams, where higher natural rates of nutrient loss prevail ("25–50" class in Figure 3), to achieve a 1 kg reduction in delivery to the Gulf.

Our summary of the delivered fluxes and source shares for the MARB (Table 2) indicates that agriculture is the predominant nutrient source to the Gulf, although we observe distinct differences in the agricultural land uses that contribute nitrogen as compared to those for phosphorus. We find that 52% of the nitrogen entering the Gulf from sources in the Mississippi River Basin (46% in the Atchafalaya Basin) originates from lands cultivated in corn/soybeans, the largest single contributor among all sources. All other crops contribute only about 14% of the nitrogen, with each crop type contributing less than 8%. Nonrecoverable animal manure from pasture/rangelands contributes even less nitrogen, only about 5%. By contrast, nonrecoverable animal manure from pasture/rangelands is the largest contributor of phosphorus to the Gulf (37–39%), an appreciably larger share than that for nitrogen, whereas phosphorus contributions from corn/soybeans represent from 21 to 25% of the total TP flux to the Gulf (cultivated crops collectively account for 40–43% of the TP flux). In evaluations of the statistical robustness of the nutrient models and source share estimates, we find supporting evidence of these structural differences in agricultural nutrient sources (see SI). Our finding that cultivated crops are a predominant source of nitrogen agrees with previous studies (*15, 16*), including a recent study that identified corn/soybeans as the principle nitrogen source in the MARB (*18*); this study did not include animal manure sources in the model. Our estimate of the phosphorus from animal manure on pasture/rangelands is more than twice as high as previously estimated for the MARB (*15*).

We conclude that the structural differences in the sources of agricultural nutrients delivered to the Gulf are explained by differences in the supply and transport properties of nitrogen and phosphorus as discussed in the previous section. This is related to our finding of appreciable differences in the rates of nitrogen and phosphorus enrichment in the waters delivered to streams from different agricultural land uses. We observe that nitrogen is generally enriched relative to phosphorus in the waters delivered to streams from lands in corn/soybeans, whereas phosphorus is enriched relative to nitrogen in waters delivered to streams from pasture/rangelands. These differences are denoted by changes in the nitrogen to phosphorus ratios from those observed in nutrient inputs (i.e., commercial fertilizers and animal manure) to those estimated by our model for waters entering streams from crop and pasture/range lands. For example, based on ratios of the standardized coefficients reported for the corn/soybean and pasture/rangeland sources in Table 1, the N:P ratios in the waters delivered to streams from corn/soybean cultivation are, on average (0.164/0.023), seven times higher than the N:P ratios for the nutrient inputs to these lands. By contrast, the average ratio for pasture/rangelands (0.063/0.138) indicates that the N:P ratios in delivered waters are about 50% of those for the inputs. A recent study of Iowa lakes (*48*) provides limited confirmation of these findings; however, surprisingly little research has assessed the effects of different agricultural production systems on N:P stoichiometry in runoff and stream waters (*48*). More spatially detailed modeling that includes stream monitoring data from small catchments with diverse agricultural land uses is needed to improve understanding of the explanatory factors. Nevertheless, our findings suggest that future changes in livestock and crop production systems in the MARB could have ecologically important implications for the N:P stoichiometry of the waters delivered to the Gulf, where both nitrogen and phosphorus currently limit algal production (*11*).

We also find that nonagricultural sources are important contributors of nutrients to the Gulf, representing about 20% of the phosphorus and 30% of the nitrogen. A majority of the nitrogen originates from regional atmospheric deposition sources (16–18%) and urban sources (9%) that may include nitrogen from wastewater effluent, septic systems, and local atmospheric deposition from power-plant and vehicular emission sources. Most of the nonagricultural phosphorus originates from urban sources (12%) and forests (8%).

Much of the nitrogen and phosphorus delivered to the Gulf originates from generally similar regions and watersheds of the MARB (Table 2; see SI Figure S6). These include many watersheds in the Central Mississippi and Ohio, which have the highest delivered nutrient yields. These regions contribute nearly 60% of the nitrogen, mostly from corn/soybeans, and

TABLE 2. Nutrient Delivery to the Gulf of Mexico from Regions of the Mississippi and Atchafalaya River Basin (MARB)[a,b,c]

	Share of the Total Nitrogen Flux Delivered to the Gulf of Mexico from MARB Watersheds[a]											
	total river basin share (percent of total flux)				total regional share (percent of regional total flux)							
	Mississippi		Atchafalaya									
nitrogen	mean	90% P.I.[b]	mean	90% P.I.[b]	Upper Mississippi	Missouri	Central Mississippi	Ohio and Tennessee	White	Arkansas	Red	Lower Miss. and Atchafalaya
source												
urban and population-related sources	9.1	6.6–10.8	8.9	6.5–10.6	7.9	5.6	9.3	11.6	6.2	11.3	7.9	5.5
atmospheric deposition	16.2	11.2–25.1	18.0	12.5–27.2	13.4	13.9	9.7	21.2	24.8	21.5	27.7	18.5
corn and soybeans	51.5	42.2–57.4	45.6	37.0–51.2	51.8	52.5	72.2	44.7	13.8	11.3	7.0	39.9
wheat	3.7	1.1–6.0	3.9	1.2–6.3	0.6	4.4	2.0	2.4	3.3	18.1	15.1	6.3
alfalfa	2.9	0–6.6	2.5	0–5.7	10.0	5.0	2.2	2.3	2.0	2.3	1.7	0.1
other crops	7.5	2.3–12.1	10.2	3.2–16.1	5.6	8.8	1.3	5.9	24.0	17.8	20.0	23.0
pasture/ rangeland	5.0	0–13.1	5.6	0–14.2	7.4	7.4	2.9	5.0	11.2	11.8	13.1	2.6
forest	4.1	1.5–5.8	5.2	1.8–7.6	3.5	2.0	1.0	7.0	14.6	5.7	6.9	5.0
shrub lands	0.1	<0.1–0.1	0.1	<0.1–0.1	<0.1	0.4	<0.1	<0.1	<0.1	0.2	0.6	<0.1
barren lands	0.1	<0.1–0.2	0.1	<0.1–0.3	<0.1	0.1	<0.1	0.1	0.1	0.1	0.1	0.2
delivered flux (kg/yr × 10^6)	1,104	428–2,679	357	99–813	90	178	348	503	22	63	14	175
delivered yield (kg km^2 year^{-1})	377	146–914	397	110–905	402	135	1282	959	415	149	109	651
percent of total MARB flux	77		23		7.3	16.2	23.7	36.2	1.4	4.3	0.9	11.3
aquatic loss												
% of inputs	39		40		56	57	36	21	22	53	58	36
% of MARB loss	75		25		11	30	22	14	<1	8	2	12
watershed area (km^2)	2,931111		898293		223059	1,322539	271032	524093	51713	399225	124384	268515
flow-independent change in flux, 1992–2002 (%)[c]												
simulated	−4.9		−4.5		−4.1	5.1	−2.2	−5.9	−4.6	3.8	0.2	
p-value	<0.001		<0.001		0.001	<0.001	0.008	<0.001	0.010	0.060	0.923	
estimated	−7.5		7.6		2.3	−0.8	−2.4	−3.2		−7.5		
p-value	<0.001		0.014		0.326	0.747	0.167	0.077		0.006		

	Share of the Total Phosphorus Flux Delivered to the Gulf of Mexico from MARB Watersheds[a]											
	total river basin share (percent of total flux)				total regional share (percent of regional total flux)							
	Mississippi		Atchafalaya									
phosphorus	mean	90% P.I.[b]	mean	90% P.I.[b]	Upper Mississippi	Missouri	Central Mississippi	Ohio and Tennessee	White	Arkansas	Red	Lower Miss. and Atchafalaya
source												
urban and population-related sources	12.3	6.9–15.4	10.6	6.1–13.6	11.1	7.9	15.7	15.7	3.5	8.1	3.8	5.8
corn and soybeans	25.1	5.9–35.2	20.9	4.8–32.0	18.6	14.0	42.2	23.1	6.5	1.8	1.1	27.3
alfalfa	7.8	0–20.8	6.0	0–16.3	25.2	9.7	9.8	6.9	4.2	2.1	1.3	0.4
other crops	10.2	0.4–17.7	13.1	0.5–21.8	3.0	5.5	3.8	5.6	15.3	9.1	5.5	39.7
pasture/ rangeland	37.0	28.7–50.8	39.4	29.8–52.8	37.2	59.6	26.3	36.4	51.1	68.1	78.6	18.8
forest	7.5	4.9–10.6	9.2	6.1–12.8	4.8	3.1	2.8	12.2	19.0	10.2	8.5	8.2
shrub lands	0.1	<0.1–0.1	0.1	<0.1–0.2	<0.1	0.2	<0.1	<0.1	0.1	0.4	0.7	<0.1
barren lands	0.3	0.1–1.0	0.8	0.2–2.0	0.2	0.1	<0.1	0.5	0.5	0.5	0.7	1.3
delivered Flux (kg/yr × 10^6)	86.9	24.0–284.7	30.6	6.8–81.3	6.0	10.2	23.5	39.4	2.9	5.5	2.1	20.6
delivered yield (kg km^2 year^{-1})	29.7	8.2–97.1	34.1	7.6–90.5	26.9	7.7	85.8	75.1	56.8	13.7	17.1	76.7
percent of total MARB flux	74		26		6.8	16.8	19.0	34.9	2.2	4.3	1.6	15.4
aquatic loss												
% of inputs	51		55		54	68	40	36	48	79	75	40
% of MARB loss	72		28		6	33	12	17	2	15	5	11
watershed area (km^2)	2,931111		898293		223059	1,322539	271032	524128	51713	399313	124384	268515

TABLE 2. Continued

phosphorus	Share of the Total Phosphorus Flux Delivered to the Gulf of Mexico from MARB Watersheds[a]											
	total river basin share (percent of total flux)				total regional share (percent of regional total flux)							
	Mississippi		Atchafalaya									
	mean	90% P.I.[b]	mean	90% P.I.[b]	Upper Mississippi	Missouri	Central Mississippi	Ohio and Tennessee	White	Arkansas	Red	Lower Miss. and Atchafalaya
source												
flow-independent change in flux, 1992–2002 (%)[c]												
simulated	−1.5		−0.88		−9.7	8.9	1.6	−4.7	2.8	11.0	7.2	
p-value	0.487		0.677		0.023	<0.001	0.590	<0.001	0.300	<0.001	<0.001	
estimated	1.8		4.0		−4.5	7.3	0.7	0.2		−0.2		
p-value	0.513		0.445		0.124	0.055	0.781	0.928		0.960		

[a] The river basin source shares for the Mississippi and Atchafalaya are reported separately as a percentage of the nutrient flux delivered to the Gulf of Mexico from the MARB outlets at St. Francisville, LA and Melville, LA, respectively, whereas the regional source shares are reported as a percentage of the delivered flux for the entire MARB (i.e., sum of the delivered flux for the Mississippi and Atchafalaya outlets). The delivered nutrient flux for the intervening drainage of the Central Mississippi watershed is estimated as the difference between the delivered flux for the Mississippi River at Thebes, IL, and the sum of the delivered flux for the Mississippi River at Clinton, Iowa and the Missouri River at Hermann, MS. Delivered flux for the intervening combined drainage of the Lower Mississippi and Atchafalaya watersheds is estimated as the difference between the delivered flux from the MARB outlets and the sum of the delivered flux from upstream tributaries including the Mississippi River at Thebes, IL, the Ohio River at Grand Chain, IL, the Arkansas River below Little Rock, AR, the White River at Newport, AR, and the Red River at Index, AR. Nutrient delivery to the Gulf assumes that the fraction of nutrients diverted to the Atchafalaya River basin from the Lower Mississippi (at river kilometer 506) is identical to that known for streamflow (22 percent). The Atchafalaya River serves as an alternate flowpath to the Gulf of Mexico accounting for a total of 30 percent of the total flow of the two rivers. [b] Prediction intervals (P.I.) for the SPARROW model predictions of nutrient flux, yield, and source shares reflect both parameter variability and model error (i.e., residual error) as estimated from percentiles of the bootstrap distributions (*19*). [c] The "simulated" change in nutrient flux is based on the percentage difference in SPARROW model-based estimates of flux for 1992 and 2002 at the two MARB outlets and the outlets of selected regional basins (the flux at the outlets reflects nutrient contributions for the entire upstream drainage and is not independent of upstream regional drainages as reported for the source shares in the table). Statistical significance is based on bootstrap estimation methods (Schwarz et al. 2006) and reflects uncertainties from parameter variability and model residuals, but assumes that parameters and model errors are constant over time. The "simulated" change in nutrient flux gives a streamflow-independent estimate of the change in stream nutrient flux from 1992 to 2002 in response to changes in population and agricultural sources (animal manure, biological N2 fixation in crops, farm fertilizer use, and crop harvesting). The coefficients of the model are unchanged for 2002 and assume steady-state conditions, based on long-term average streamflow over the 1975−2000 period. Therefore, estimates of the "simulated" change in flux only reflect changes in nutrient sources and are independent of the actual changes in streamflow from 1992 to 2002. The changes in agricultural sources account for changes in the marginal rates of crop production (i.e., harvested biomass relative to nutrient inputs; note that the estimated 1992 base-year model implicitly reflects crop production related to climatic conditions and farm practices and technologies in this year). The simulations do not include the effects of any changes in farm management practices unrelated to crop fertilizer use and production or animal populations (e.g., addition of buffer strips). The "estimated" change in nutrient flux is computed as the percentage difference in the monitoring-based estimates of the flow-adjusted, long-term mean-annual nutrient flux for base years 1992 and 2002 (no base-year adjustment is made for trend in flow for consistency with the model-based estimates). Statistical significance is from the significance levels of the flow-adjusted trend coefficients reported from the flux estimation method (*19*).

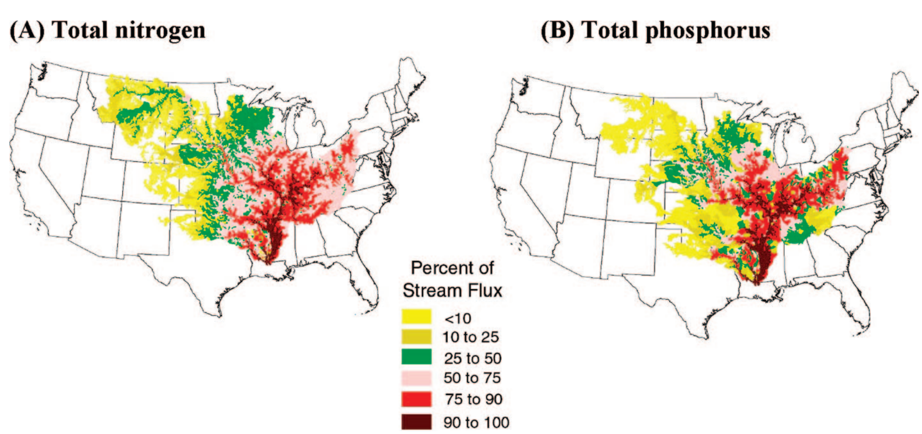

FIGURE 3. Percentage of stream nutrient load delivered to the Gulf of Mexico from the incremental drainage of MARB reaches: (a) total nitrogen; (b) total phosphorus.

54% of the phosphorus primarily from corn/soybeans and nonrecoverable animal manure on pastures; these regions account for less than 30% of the MARB drainage. Atmospheric deposition is the second largest contributor of nitrogen in both regions. The Missouri and the Lower Mississippi/Atchafalaya regions contribute approximately 30% of the phosphorus and nitrogen to the Gulf, mostly from agricultural sources.

The state estimates of nutrient deliveries to the Gulf also show similarities in the geographic origins of both nitrogen and phosphorus, which provides complementary information for managing nutrients in the MARB (see SI Tables S4−S5). We find that although the MARB drains lands from 31 states, nine states (Illinois, Iowa, Indiana, Missouri, Arkansas, Kentucky, Tennessee, Ohio, and Mississippi), with the largest percentage shares of the total nutrient flux delivered to the

Gulf, collectively account for 75% of the nitrogen and phosphorus delivery to the Gulf (also, 69% of the phosphorus from pasture/rangelands and 86% of the nitrogen from corn/soybeans). These states account for only 33% of the MARB drainage area and, thus, have among the highest delivered nutrient yields. The nutrients from these States include contributions from large cities and agricultural lands that border large rivers, which enhance nutrient transport to the Gulf.

The flow-independent measures of stream nutrients changed from 1992 to 2002 by less than 10% in the MARB (Table 2), with similarly small changes in the source shares for the major regions. Thus we conclude that the source contributions to the Gulf in Table 2 are generally robust to changes in major nutrient sources from 1992–2002. The trends in simulated stream nutrient flux display generally similar spatial patterns, including decreases in the Upper Mississippi and Ohio and increases in the Missouri and Arkansas regions. The net result of these changes at the MARB outlets is that nitrogen flux to the Gulf decreased by about 5% ($p < 0.02$), whereas phosphorus changed by <1%. (see SI).

Our study advances understanding of the structural, spatial, and temporal differences in nitrogen and phosphorus sources in the MARB and their nonlinear interactions with the climatic and terrestrial and aquatic processes that control nutrient transport to the Gulf of Mexico. This adds new insight into the diversity of management approaches that may be necessary to achieve efficient reductions in nutrients to the Gulf. This includes recognition of the different effects of agricultural production systems on nitrogen and phosphorus runoff to streams and the nutrient stoichiometry in the waters delivered to the Gulf. Efficient reductions may also be achieved by targeting phosphorus sources downstream from reservoirs and both nitrogen and phosphorus sources in close proximity to large rivers.

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Supporting Information Available

Details are reported on the model form, model estimation methods, and information specific to the MARB application, including descriptions of input data, evaluations of model accuracy, and additional results. This material is available free of charge via the Internet at http://pubs.acs.org.

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