Impact of Biofuel Crop Production on the Formation of Hypoxia in the Gulf of Mexico

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Received April 15, 2009. Revised manuscript received July 21, 2009. Accepted August 3, 2009.

Many studies have compared corn-based ethanol to cellulosic ethanol on a per unit basis and have generally concluded that cellulosic ethanol will result in fewer environmental consequences, including nitrate (NO₃⁻) output. This study takes a system-wide approach in considering the NO₃⁻ output and the relative areal extent of hypoxia in the Northern Gulf of Mexico (NGOM) due to the introduction of additional crops for biofuel production. We stochastically estimate NO₃ loading to the NGOM and use these results to approximate the areal extent of hypoxia for scenarios that meet the Energy Independence and Security Act of 2007's biofuel goals for 2015 and 2022. Crops for ethanol include corn, corn stover, and switchgrass; all biodiesel is assumed to be from soybeans. Our results indicate that moving from corn to cellulosics for ethanol production may result in a 20-percent decrease (based on mean values) in NO₃⁻ output from the Mississippi and Atchafalaya River Basin (MARB). This decrease will not meet the EPA target for hypoxic zone reduction. An aggressive nutrient management strategy will be needed to reach the 5000 km² areal extent of hypoxia in the NGOM goal set forth by the Mississippi River/Gulf of Mexico Watershed Nutrient Task Force even in the absence of biofuels, given current production to meet food, feed, and other industrial needs.

Introduction

There is growing concern that the use of agricultural products for liquid transportation fuels (biofuels) will result in an unacceptable increase in the negative aspects of agricultural activity. Agriculture is currently responsible for 76% of the

nitrous oxide (N₂O) generated within the U.S. (1), is a large source of nutrient and pesticide runoff to water bodies, is responsible for carbon dioxide (CO₂) emissions from soils when land is disturbed either directly or indirectly, and leads to soil erosion and loss of habitat (2). Nutrient runoff, particularly reactive nitrogen such as nitrate (NO₃⁻), can lead to eutrophication and ultimately to hypoxic (dissolved oxygen <2 mg/L) conditions in waterbodies. The hypoxic zone in the northern Gulf of Mexico (NGOM) occurs annually due to anthropogenic activities in early spring/summer disrupting the natural functioning of the ecosystem and reducing fish, crab, and shrimp catches within the zone (3, 4). Evidence of hypoxia was not observed before 1900 (3). Nitrate loading increased significantly after 1950 due to deforestation, navigation channelization, wetland draining for cropland, loss of riparian zones, and large increases in fertilizer application, particularly nitrogen (3). The Mississippi River/ Gulf of Mexico Watershed Nutrient Task Force (MR/GOM WNTF) established a goal to reduce the hypoxic zone size to 5000 km² by 2015 as compared to the current five-year running average (2003–2007) of 14,600 km² (5, 6). To date there has been little evidence of progress toward this goal and there is concern that increased agricultural production may further hinder achievement of hypoxic zone reduction.

Formation of the hypoxic zone is dependent on two conditions: stratification of the water column and an abundance of decomposing organic matter (3, 7). Increased nutrients, specifically nitrogen (N) and phosphorus (P), are associated with increased phytoplankton community productivity leading to increased organic matter which sinks to bottom waters where it is decomposed by aerobic bacteria causing oxygen depletion (3, 7). Nitrogen, specifically NO₃⁻, has been noted as one of the principal causes of increased organic matter and thus the hypoxic zone (7–9). Phosphorus may play a more significant role in the formation of hypoxia than previously thought (4, 10). However, it has been suggested that P is only limiting now due to increased nitrogen loads during the 1970s and 1980s (11). Fertilizers are applied in large quantity within the Mississippi and Atchafalaya River Basin (MARB), and corn cultivation is responsible for the majority of nitrogen fertilizer use in the U.S. (12). The majority of U.S. corn and soybean production (over 80% by weight) occurs within the MARB (13) and accounts for just over 51%of the total nitrogen (TN) load to the NGOM (10). Other sources of nitrogen and phosphorus to the NGOM are noted in the Supporting Information (SI). While phosphorus plays an important role in the formation of hypoxia, this paper focuses solely on characterizing N loadings.

The 2007 Energy Independence and Security Act (EISA) calls for the production of 36 billion gallons (Bgal) of biofuels by 2022 of which 15 Bgal is corn ethanol and 21 Bgal is "advanced biofuel" (14). Advanced biofuels are assumed to be 20 Bgal of ethanol that is derived from switchgrass or stover and one Bgal of biodiesel derived from soybeans. Achieving these goals may result in a significant increase in demand for agricultural products. Simultaneously as populations increase so will demand for food/feed products. A pressing question to answer is how will an increase in agricultural activity impact nutrient loading to the NGOM and ultimately the size of the hypoxic zone (9, 15)?

Grasses, e.g., switchgrass, are a promising potential cellulosic feedstock because they reduce losses of N and P to the environment compared to monocrops, e.g., corn. N and P loss is reduced because the land is not tilled and the grass density slows runoff and increases infiltration (16). Further, nutrient application for grass production is roughly half that of corn

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TABLE 1. Scenario Summary Table^a

scenario		production in	MARB (billion kg^b)	ethanol (Bgal)				
	corn	soy ^c	stover ^d	swg	corn	stover	swg	total
2015corn/stover	300	76	34 (11%)	_	15	4.5	_	19.5
2015corn/swg				30	15	_	4.5	
2015stover/swg	200		96 (49%)	44	_	12.8	6.7	
2015swg			<u> </u>	128	_	_	19.5	
2015no fuel		59	_	_	_	_	_	_
2022corn/stover	320	81	149 (47%)	_	15	20	_	35
2022corn/swg			_	131	15	_	20	
2022stover/swg	220		105 (49%)	137	_	14.1	21.9	
2022swg			_	229	_	_	35	
2022no fuel		64	_	_	_	_	_	_

^a swg = switchgrass. ^b Billion kg of crop including: corn grain, soybeans, dry mass of stover, and switchgrass. Production values represent production within the MARB only. The percentage of each state's area within the MARB was used to approximate crop production within the MARB; 82% of corn, 83% of soy, and 72% of switchgrass (Supporting Information). ^c Soy production values include soy required to produce 1 Bgal of biodiesel. ^d Percent of stover removal is in parentheses following production value.

(17). Many authors suggest that replacement of conventional crops with grasses can improve water quality (2, 4, 18, 19). On a per-unit basis (e.g., per gallon or acre) cellulosic crop cultivation results in less nutrient, pesticide, and sediment runoff compared to corn cultivation (20). It is unclear whether an overall benefit to water quality will occur when cellulosics are considered within the entire MARB system. Donner and Kurcharik examined the impact of meeting EISA mandated ethanol production via corn ethanol on the release of inorganic N and concluded that production of 15 Bgal of corn ethanol would reduce the likelihood of reaching the target set for hypoxia reduction (21). In this paper we consider the nitrogen loading to the MARB and the resulting areal extent of the hypoxic zone under various cropping scenarios that more closely follow the EISA mandates, including the use of cellulosic ethanol, as a means to compare the system-wide impact of selecting one crop over another for biofuels production.

Method

Scenario Description. Scenarios were created that consider potential crop mixes to meet EISA goals as well as production required for food, feed, and other nonfuel demands (see Table 1). NO₃⁻ output was quantified and the resulting size of the hypoxic zone in the NGOM was estimated for years 2015 and 2022. In 2015 corn-derived ethanol is assumed to reach maximum production of 15 Bgal as outlined in EISA. In 2022 the ethanol production goal of 35 Bgal is assumed to be reached. In addition, each scenario also includes sufficient corn and soy production to meet future nonfuel demands projected by the United States Department of Agriculture (22). Two scenarios in each year (2015corn/stover, 2015corn/ switchgrass, 2022corn/stover, 2022corn/switchgrass) include sufficient corn to produce 15 Bgal of ethanol with the remaining ethanol production, 4.5 and 20 Bgal in 2015 and 2022, respectively, derived from stover and/or switchgrass. Because the majority of corn and soy production currently occurs within the MARB, it was assumed that the majority of additional corn and soy production as well as cellulosic crops such as switchgrass, will also occur within the MARB. Potentially achievable conversion rates of 3 gallons (gal)/ bushel corn (23) and 100 gal/metric ton (mt) dry cellulosic material, i.e., switchgrass and stover, were used (24).

Scenarios 2015stover/switchgrass, 2015switchgrass, 2022stover/switchgrass, and 2022switchgrass represent scenarios where no corn is grown to produce biofuels. Scenarios including stover, 2015stover/switchgrass and 2022stover/ switchgrass, consider maximum ethanol production from stover based on removal assumptions, with the remaining ethanol production goal met through switchgrass. It is assumed that stover is collected from corn producing acres throughout the MARB. Scenarios 2015switchgrass and 2022switchgrass consider only production of switchgrass to meet ethanol goals. Finally, scenarios 2015no fuel and 2022no fuel consider the scenario where crops are cultivated only for nonfuel purposes. Aside from these production goal scenarios, there are several additional options modeled, as described below.

Stover Removal. Stover, the agricultural residue (i.e., stalks and leaves) left in the field after corn grain harvest, is a cellulosic feedstock. Maximum stover removal rates are an issue of debate. In general, if no-till methods are used stover might be removable at higher rates than under conventional tillage. Sheehan et al. (25) suggest a removal rate of 40% on conventionally tilled fields and 70% removal rate on no-till fields in Iowa and also report that 58% of cornfields practice conventional tillage, 26% practice moderate or mulch tillage, and 16% practice no-till cultivation. These values were used to generate a weighted average removal rate of 49%, the maximum removal modeled in this study. To account for the nitrogen lost to soil due to stover removal it was assumed that the nitrogen content within the stover would be replaced one for one with additions of synthetic fertilizer. This approach is consistent with Sheehan et al. (25) and Hoskinson et al. (26).

Nutrient Management Using Vegetative Buffer Strips. Vegetative buffer strips (VBS) are one management technique shown to reduce nutrient, pesticide, and sediment loads to waterways (27). Runoff is intercepted by the VBS and nitrate is mitigated through denitrification and nutrient uptake by plants. Limitations to effectiveness of VBS include depth to groundwater, topography, climate, and hydrology, i.e., conditions that reduce the interception and residence time of water above or below ground (28). Precipitation can drastically influence the effectiveness of VBS. In general, the reduction in NO₃⁻ concentration due to the VBS is lower when precipitation is high due to reduced retention time within the buffer system (29). Steep topography can result in rapid water flow through the buffer zone, particularly during high precipitation events (28, 30).

Due to the variety of climates and topography found within the MARB, it is unclear how much runoff within the MARB can be effectively treated with VBS. Tomer et al. (30) found that roughly 50% of the riparian zones were suitable for VBS installation in a 49,000-acre Iowan watershed, with 90% of area cultivated for corn and soy cultivation. Given the lack of information about the ability to treat all watersheds within the MARB this analysis considered two VBS options: (1) a best case scenario in which all runoff is intercepted by a VBS and subject to reductions in $\mathrm{NO_3}^-$ concentration, i.e., 100%

Buffer, and (2) a scenario in which 50% of the runoff is intercepted and NO_3^- concentration reduced, i.e., 50% Buffer.

Model Description. The model developed to approximate $\mathrm{NO_3}^-$ output for each scenario builds on the model created by Miller et al. (31), which uses a stochastic approach to generate a probable range of output for nitrogen species in generic watersheds using a linear fractionation of input variables. Only $\mathrm{NO_3}^-$ output is considered in this paper. Monte Carlo Analysis (MCA) was used to generate a range of probable $\mathrm{NO_3}^-$ output for each scenario and crop using variable input parameters and the equations found below. MCA is commonly used in risk assessments to quantify the full range of possible outcomes including the most likely as well as extreme scenarios that are unlikely to occur.

Nitrogen inputs were related to nitrogen outputs based on crop-specific data and relationships between nitrogen, crops, and the environment. Nitrogen input parameters include fertilizer, nitrogen fixation, and mineralized nitrogen. Other inputs to the model include crop yield and output factors. Input parameters are assigned distributions based on data and values reported in the literature to capture the most likely value as well as the full range of possible values. Additional details and references can be found in the SI. Distributions incorporate the inherent variability found in agricultural systems due to regional differences in climate, geology, geography, and management practices.

Nitrate output is commonly estimated as a fraction of fertilizer application. Nitrate output varies considerably from 3% to 80% of applied fertilizer depending on soil, climate, and fertilizer application rates (32). Only a small fraction of soybeans, roughly 25%, is fertilized annually (12); this was accounted for in the MCA (SI Table S1). It was assumed that mineralized nitrogen from soybeans would result in output similar to that of fertilizer and thus the same fractionation parameter is used (eqs 4 and 5) (31). A large factor in the variability of NO₃⁻ output is precipitation, because NO₃⁻ builds up in soils during droughts and can be released in large quantities during high rain events (15, 33). Therefore, it is not always possible to associate fertilizer application and soil mineralization of nitrogen to output that occurs in the same year.

Mitigation scenarios, via 50% and 100% Buffer, were modeled as vegetative buffer strips, as described above. Seventy field measurements of $\mathrm{NO_3}^-$ concentration reductions of water entering versus exiting a buffer were collected for a wide variety of VBS designs implemented across the United States and in Europe (27, 34–38). The probability distribution function for $\mathrm{NO_3}^-$ concentration reduction, r from eq 8, generated from these values is skewed toward the right with a mean value of 75%. In the 50% Buffer scenario 50% of the runoff passes through a VBS, and nitrate concentration is reduced according to the distribution r for an overall mass reduction of 35% (\pm 14) and 68% (\pm 27) in the case of the 100% Buffer scenario.

Model Equations and Input Parameters

mass N in grain:
$$N_{grain} = (H \times f_{grain}) \times A$$
 (1)

mass N in residue:
$$N_{residue} = (H \times HI \times f_{residue}) \times A$$
 (2)

mass N fixed (soy only):
$$N_{fix} = f_{fix} \times (N_{grain} + N_{residue}) \times A$$
(3)

mass NO
$$_{3}^{-}$$
 from fertilizer: $N_{NO_{\overline{3}},f}=(N_{f}\times f_{NO_{\overline{3}}})\times A$ (4

mass NO₃ from mineralization (soy only):

$$N_{NO_{\overline{3}},m} = (N_{min} \times f_{NO_{\overline{3}}}) \times A$$
 (5)

mass stover removal:

$$H_{ST} = ((\%stover_removal) \times H_{corn} \times HI_{corn}) \times A$$
 (6)

additional fertilizer required due to stover removal:

$$N_{f,ST} = (H_{ST} \times f_{residue}) \times A$$
 (7)

mass NO_3^- reduction from riparian buffers:

$$R_{NO_{3},f} = (N_{NO_{3},f} + N_{NO_{3},m}) \times r \times M$$
 (8)

total nitrogen loading to the MARB:

$$N_{tot_MARB} = (N_{NO_{\overline{3}},f} + N_{NO_{\overline{3}},m} - R_{NO_{\overline{3}}}) \times 0.53 \times 1.33 \times 1.49$$
(9)

where N_{grain} = nitrogen exported via grain (kg N); H = grain harvested, i.e., yield (kg grain or biomass/ha); f_{grain} = nitrogen fraction of harvested grain (kg N/kg grain or biomass); N_{residue} = nitrogen exported via residue (kg N); HI = harvested index (mass residue/mass grain); $f_{\rm residue}$ = nitrogen fraction of residue (kg N/kg dry residue); $N_{\rm fix}$ = nitrogen fixed via biological nitrogen fixation (kg N/ha); f_{fix} = fraction of total plant nitrogen obtained through biological nitrogen fixation (%); N_{NO3-} = nitrogen runoff as NO_3^- , subscript f - from fertilizer, subscript m - from mineralization (kg N); $N_{\rm f}$ = rate of fertilizer application (kg N/ha); f_{NO3-} = fraction of fertilizer to NO₃ runoff (%); N_{\min} = mineralized nitrogen from soil and crop residue (kg N/ha); A = area cultivated with a particular crop (ha); R_{NO3} = reduction in nitrate output due to vegetative buffers (%) note this term is zero in base case scenarios; r = percent concentration reduction due to vegetative buffer (%); M = percentage of total area assumed to be managed for nitrate output using vegetative buffers 50 or 100% Buffer; $N_{\text{tot_MARB}}$ = total nitrogen load to the NGOM (kg N). Equation 9 converts modeled nitrate output within the basin to TN load reaching the NGOM, additional details are provided below. Equations 1-5 are adapted from Miller et al. (31).

Crop Yields. Data from 1997 to 2007 were used in this analysis to ensure that the distributions included observed annual variability. Area, *A*, required to meet production goals was determined by dividing the static production value (entered into the model) by the crop yield distribution, *H*, creating a range of required area. Yields are projected to increase in the future due to increases in management and technology while fertilization rates are expected to remain fairly constant, consistent with observed trends over the past thirty years (39). Increases in corn and soybean yield, as projected by the USDA and historical state yield data were used to generate yield distributions for 2015 and 2022 (*22*).

The switchgrass yield distribution is based on 260 yield values collected from field trials over 1992 to 2001 (17, 40–42). Each collected value was increased annually by 3.2% for 8 and 15 years for 2015 and 2022, respectively. New distributions were generated to reflect the higher yields. Projected switchgrass yields were modeled using assumptions provided by the Energy Information Administration as cited in Wakeley et al. (43).

Relationship Between Nitrate Runoff and Areal Extent of the Hypoxic Zone. The areal extent of the hypoxic zone is estimated using a dissolved oxygen model driven by nitrogen load and a simple parametrization of ocean dynamics developed by Scavia et al. (44, 45). This model is assumed to be steady state and ignores longitudinal dispersion.

$$D = [a/(b-a)]B_o[e^{-ax/v} - e^{-bx/v}]$$
 (10)

where B_o is oxygen demand at the point source (mg/L); a is first-order rate constant for organic matter decomposition (day⁻¹); b is first-order rate constant for oxygen flux (day⁻¹); D is dissolved oxygen deficit (mg/L); x is distance downstream

TABLE 2. Summary of Modeled Scenario Nitrate Output (1000 t)

	no nutrient management				50% buffer mitigation				100% buffer mitigation			
scenario	mean	SD	(10%-	90%)	mean	SD	(10%-	90%)	mean	SD	(10%-	90%)
2015corn/stover	1,860	700	1,100	2,750	1,220	540	660	1,920	590	590	16	1,410
2015corn/swg	1,830	690	1,080	2,700	1,200	530	650	1,880	580	580	15	1,390
2015stover/swg	1,600	620	960	2,360	1,050	470	570	1,640	510	510	13	1,210
2015swg	1,520	600	900	2,260	1,000	460	540	1,570	480	490	12	1,160
2015no fuel	1,250	500	720	1,890	820	380	440	1,300	400	400	10	960
2022corn/stover	2,010	720	1,220	2,940	1,330	560	740	2,050	640	630	17	1,520
2022corn/swg	1,860	670	1,130	2,730	1,220	520	670	1,900	580	580	15	1,400
2022stover/swg	1,680	610	1,020	2,450	1,100	470	610	1,700	530	530	14	1,250
2022swg	1,560	600	930	2,320	1,030	460	560	1,610	490	500	13	1,180
2022no fuel	1,260	490	740	1,880	830	370	440	1,300	400	400	10	950

from the point source, i.e., the length of the hypoxic zone (km); and ν is net downstream advection of subpycnoclinal waters, i.e., below the layer in which density increases rapidly with depth (km/day). The ν term is also used as a calibration term to capture all unmodeled processes and associated uncertainties including the many interactions among buoyant river plume, tidal currents, the Louisiana costal current, northward excursions of the Loop Current and its eddies, wind-driven circulation, and hurricanes (44, 45). Typical values for v are between 0.5 and 1 km/day with a mean value of 0.56 km/day (\pm 0.20) (44). Nitrogen load is converted to algal carbon by the Redfield ratio (5.67 C g⁻¹ N), which is related to oxygen consumption using a respiratory quotient of 0.77 (3.47 g O_2 g⁻¹ C), and an estimate that 50% of surface algal production settles beneath the pycnocline (44). Areal extent is related to the downstream distance by a linear regression forced through the origin of observed hypoxic area and length: Area = 33.13x (44).

Total nitrogen delivered to the NGOM is required to approximate the size of the hypoxic zone. The MCA estimates the total amount of $\mathrm{NO_3}^-$ generated within the MARB, however, only 53% of the $\mathrm{NO_3}^-$ output is transported to the NGOM (46). Nitrate accounts for approximately 75% of the TN reaching the NGOM (7). Nitrogen from corn and soy cultivation in the MARB accounts for roughly 51% of the TN load to the NGOM; the remaining 49% is the result of other activities (10). This information was used to approximate TN loading to the NGOM from $\mathrm{NO_3}^-$ output (eq 9). Adjustments were made to approximate spring/early summer loading (SI).

To validate this approach, agricultural production of corn and soy from 1986 to 2002 were used to model the NO_3^- output and daily May/June TN load to the NGOM. The TN and May/June results compared well to those reported by the USGS (SI) (47). The TN load was split between the Mississippi River and the Atchafalaya River assuming a ratio of 2.95:1 and x was determined using eq 10 for each point source (44).

Results

The nitrate output ranges from the MARB for the scenarios described above are summarized in Table 2. Example output distributions are included in the SI. The areal extent of the hypoxic zone based on mean NO₃⁻ output values and mean values for the terms in eq 10 for 2022 scenarios with No Buffer and 50% Buffer are shown in Figure 1. The inputs to the model do not result in the formation of hypoxic conditions for the 2022no fuel and 50% Buffer scenario or the 100% Buffer scenarios (Additional details in SI Section 8). For the model, using the assumptions described above, to result in the formation of a hypoxic zone greater than 5000 km², the modeled NO₃⁻ must be approximately 980,000 t. It is important to note that 100% interception of runoff by buffers from agricultural fields is unlikely and this idealized scenario is included to illustrate the need for aggressive nutrient management within the MARB.

Consistent with previously published literature the results demonstrate that NO_3^- output for corn-derived ethanol will

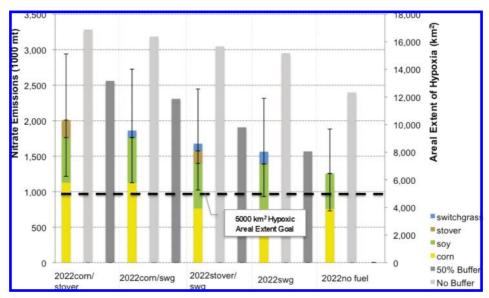


FIGURE 1. Nitrate output within the MARB (colored bars, lefthand y-axis) and mean areal extent of hypoxia in the NGOM with "No Buffer" and "50% Buffer" (gray scale bars, righthand y-axis). Nitrate output columns represent mean values and the 80% credible intervals from MCA modeling. The horizontal dashed line represents the MR/GOM WNTF 5000 km² goal set for 2015.

be higher on average than output for switchgrass- or stover-derived ethanol (2, 4, 19). There is a decrease in mean $\mathrm{NO_3}^-$ output between the scenarios inclusive of corn production for ethanol and those that use only cellulosics for ethanol production (Scenarios 2022corn/stover and 2022corn/switchgrass vs 2022stover/switchgrass and 2022switchgrass). The 80% credible intervals of the modeled scenarios overlap considerably indicating that nitrate mass reductions due to replacement of cellulosics for corn may not be realized in any specific year. While it is true that cellulosics result in lower $\mathrm{NO_3}^-$ output on a per unit basis compared to corn (e.g., one gallon ethanol or one acre), the decrease is insufficient to reduce the hypoxic zone below the EPA's 5000 km² target.

The nitrate output in 2015 and 2022 associated with corn and soy are roughly the same because yield gains are expected to keep up with nonfuel demand increases and biofuel demand for these crops does not change between these years. As demand for cellulosic crops increases from 45 billion kg (4.5 Bgal) in 2015 to 200 billion kg (20 Bgal) in 2022, the NO_3^- output does not increase proportionally. This is particularly true for switchgrass because annual yield increases are expected to be almost 2% greater than that of corn. For these reasons the total NO_3^- output for 2022 scenarios increases only 2–8% over the 2015 scenarios despite an additional 15.5 Bgal of ethanol production.

Figure 1 shows that switchgrass has lower nitrate output than stover for an equivalent amount of ethanol production, which may not seem intuitive given that the nitrogen fertilizer required to replace removed nutrients for stover is on average half that required for switchgrass, i.e., 35 kg/ha versus 74 kg/ha mean values, respectively. The NO₃⁻ output factor, f_{NO3-} , for stover is assumed to be equal to that of corn, and is roughly twice the switchgrass NO₃⁻ factor based on mean values. In 2015 the mean removable stover rate is 4800 kg/ha and mean switchgrass yield is 19,000 kg/ha, in 2022 yields are 5,100 kg stover/ha and 23,400 kg switchgrass/ha. Therefore, the mean kg NO_3^- output per kg biomass in 2015 is 1.75 \times 10⁻³ and 5.06 \times 10⁻⁴ for stover and switchgrass, respectively. Due to yield gains the mean kg NO₃⁻ per kg biomass in 2022 decreases to 1.67 \times 10^{-3} and 4.1 \times $10^{-4},$ or a decrease in $\mathrm{NO_{3}^{-}}$ intensity of approximately 5% and 23%, for stover and switchgrass, respectively.

Discussion

Miscanthus × giganteus (Miscanthus), a perennial grass popular in Europe for cellulosic biofuel production, has received attention as potentially preferable to switchgrass (48). Heaton et al. (49) reported average 3-year postsenescence yields over three locations in the Midwest USA of 29.2 (± 1.8) dry mt/ha for *Miscanthus* versus 10.4 dry mt/ha for switchgrass. In the Heaton et al. study nitrogen fertilizer was applied once in the 4-year study at a rate of 25 kg/ha, roughly one-third of the average annual value used for switchgrass in this study. While Miscanthus was not modeled because data are currently lacking, the nitrate output would fall between "no fuel" scenarios (i.e., no additional fertilizer application and the assumption that there is no release of nitrate through the process of nitrogen mineralization) and Scenarios 2015swg and 2022swg. Miscanthus should be included in future studies as data become available regarding the feasibility of production at a commercial scale.

The sensitivity analysis showed that nitrate output for both corn and switchgrass are most sensitive to the $\mathrm{NO_3}^-$ fractionation variable, fertilization rates, and yield (in descending order). The nitrate output for soybeans is most sensitive to the mineralized nitrogen variable, the $\mathrm{NO_3}^-$ fractionation variable, percent of crop fertilized, and crop yields (in descending order). Mineralized nitrogen is the

largest source of $\mathrm{NO_3}^-$ output due to soybean cultivation. The nitrate output for stover is most sensitive to the nitrate fractionation variable (same value used for corn), the residue fraction, and the fertilization rate. This sensitivity is not surprising given the large range of the $\mathrm{NO_3}^-$ fractionation variable. Yield is important because this variable determines the area required to produce the specified production amount (Table 1), A, which is used to scale up nitrate output to the MARB. Further information and sensitivity charts are provided in the SI.

An important consideration with respect to nitrate output associated with various biofuel mixes is the change in areal extent of the hypoxic zone in the NGOM. Our goal is not to precisely predict the size of the hypoxic zone, but rather to show the relative changes under identical conditions. Historical observations of the size of the hypoxic zone over 1985-2002 are generally within the range of modeled hypoxic zone size, details are provided in the SI. To approximate the areal extent of hypoxia for future scenarios the mean value for the calibration term, v, in eq 10 was used. While the calibration term, v, in eq 10 may vary in a given year due to various climatic and hydrologic conditions, the mean values provide a comparable baseline from which to assess the relative extent of hypoxia. The size of the hypoxic zone in 2015 and 2022 decreases by approximately 1200 km², based on mean NO₃⁻ output, if corn-ethanol (represented by scenarios 2015corn/stover and 2015corn/switchgrass) is replaced with cellulosic-ethanol (2015stover/switchgrass and 2015switchgrass). The results are shown in the SI. No future scenarios, including those with no crops for biofuels, reach the hypoxic areal extent goal of 5000 km². In many cases the zone reaches roughly three times that size. Results for all Scenarios and additional discussion are included in the Supporting Information.

There is uncertainty associated with the model (eqs 9 and 10) used to predict the size of the hypoxic zone that is not explicitly included in modeled results. For example, the contribution of corn and soy cultivation to TN delivered to the NGOM ranges from 42.2 to 57.4% (90% prediction intervals) (10). The amount of N in the MARB delivered to the NGOM has also been estimated at 65% as opposed to 75% used herein. Inclusion of these sources of variability was not deemed necessary because forecasting the climatic factors in the NGOM is difficult and the range of variability in the other factors is not significant enough to change the overall results (see SI for additional information).

In summary, the results of modeling hypoxic area indicates that meeting the biofuel goals set forth by EISA will likely increase the occurrence of hypoxia in the NGOM, regardless of the selection of crops. This work also suggests that aggressive nutrient management is needed even in the absence of energy crops or stover use. There are a number of options to consider for mitigating nitrogen loading from agricultural activities, including wetland construction, vegetative buffers, tillage management, and precision fertilizer application (28). In this paper mitigation of nitrate output was modeled using vegetative buffer strips and their associated nitrate concentration reduction rates. The nitrate mitigation potential due to the use of vegetative buffer strips is considerable, though given the various siting limitations even the 50% implementation described here may overestimate their effectiveness. The intent of modeling aggressive mitigation scenarios was not to suggest that vegetative buffers alone could improve water quality in the NGOM, but rather to highlight the need for aggressive and significant management of nutrient runoff within the MARB.

The results presented here suggest that only when all of the nitrogen runoff associated with the production of corn, soy, and switchgrass is reduced will the EPA goal be met. This is an oversimplification since the approximation of the areal extent of the hypoxic zone includes unmitigated output from all other N sources within the MARB, i.e., other agricultural crops, wastewater treatment facilities, etc. Any aggressive management strategy aimed at reducing nutrient sources within the MARB will likely target these other sources as well.

The EPA Science Advisory Board suggests that a regime shift has occurred in the NGOM (4). In the event of a regime shift it is possible that a threshold is passed such that incremental nutrient load reductions may not result in similarly sized reductions in the extent of hypoxia. This suggests that nutrient load reductions may have to be reduced to a point below where the regime shift occurred (4). The potential implication is that the longer nutrient loadings go unreduced, the larger future reduction requirements may be (50).

The presented results demonstrate that using cellulosic crops for biofuel production will decrease TN loading to the NGOM relative to corn but overall TN loading will still increase as the goals of the EISA are met, adding to the need for aggressive nitrogen mitigation strategies.

Acknowledgments

We thank the National Science Foundation for support from a Materials Use: Science, Engineering, and Society (MUSES) Grant (0628084) and the Philip and Marsha Dowd Engineering Seed Fund. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation. We also thank Robert Smith at EIA for kindly providing the EIA data set.

Supporting Information Available

Additional information regarding data used in the MCA, MCA output, modeling areal extent of hypoxia, and sensitivity analyses. This information is available free of charge via the Internet at http://pubs.acs.org/.

Literature Cited

- (1) U. S. Environmental Protection Agency. *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990–2006*; Washington, DC, 2008; http://www.epa.gov/climatechange/emissions/usgginv_archive.html.
- Mann, L.; Tolbert, V. Soil sustainability in renewable biomass plantings. Ambio 2000, 29 (8), 492–498.
- (3) Rabalais, N. N.; Turner, R. E.; Wiseman, W. J., Jr. Gulf of Mexico hypoxia, a.k.a. "The Dead Zone". Annu. Rev. Ecol. Syst. 2002, 33, 235–263.
- (4) EPA Science Advisory Board. Hypoxia in the Northern Gulf of Mexico: An Update by the EPA Science Advisory Board; U.S. Environmental Protection Agency: Washington, DC, 2007.
- (5) Mississippi River/Gulf of Mexico Watershed Nutrient Task Force. Gulf Hypoxia Action Plan 2008 for Reducing, Mitigating, and Controlling Hypoxia in the Northern Gulf of Mexico and Improving Water Quality in the Mississippi River Basin; Washington, DC, 2008.
- (6) Mississippi River/Gulf of Mexico Watersshed Nutrient Task Force. Action Plan for Reducing, Mitigating, and Controlling Hypoxia in the Northern Gulf of Mexico; Washington, DC, 2001.
- (7) Goolsby, D. A.; Battaglin, W. A. Nitrogen in the Mississippi Basin - estimating sources and predicting flux to the Gulf of Mexico; USGS Fact Sheet 135-00; U.S. Geological Survey, 2000.
- (8) Rabalais, N. N.; Turner, R. E.; Justić, D.; Dortch, Q.; Wiseman, W. J., Jr. Characterization of Hypoxia: Topic 1 Report for the Integrated Assessment on Hypoxia in the Gulf of Mexico. NOAA Coastal Ocean Program Decision Analysis Series No. 15; National Oceanic and Atmospheric Administration (NOAA), Coastal Ocean Program: Silver Spring, MD, 1999; p 167.
- (9) National Research Council: Committee on Water Implications of Biofuels. Water Implications of Biofuels Production in the United States, NRC: Washington, DC, 2008; p 86.
- (10) Alexander, R. B.; Smith, R. A.; Schwarz, G. E.; Boyer, E. W.; Nolan, J. V.; Brakebill, J. W. Differences in phosphorus and nitrogen delivery to the Gulf of Mexico from the Mississippi River Basin. *Environ. Sci. Technol.* 2008, 42, 822–830.

- (11) Scavia, D.; Donnelly, K. A. Reassessing hypoxia forecasts for the Gulf of Mexico. Environ. Sci. Technol. 2007, 41 (23), 8111–8117.
- (12) USDA, Economic Research Service. U.S. Fertilizer Use and Price; http://www.ers.usda.gov/Data/FertilizerUse/.
- (13) USDA. Data and Statistics; http://www.nass.usda.gov/Data_and_ Statistics/Quick_Stats/index.asp.
- (14) Energy Independence and Security Act of 2007; H.R. 6; 110th United States Congress, 2007.
- (15) Powers, S. E. Nutrient loads to surface water from row crop production. Int. J. Life Cycle Assess. 2007, 12 (6), 399–407.
- (16) Parrish, D. J.; Fike, J. H. The biology and agronomy of switchgrass for biofuels. *Crit. Rev. Plant Sci.* **2005**, *24* (5), 423–459.
- (17) McLaughlin, S. B.; Kszos, L. A. Development of switchgrass (*Panicum virgatum*) as a bioenergy feedstock in the United States. *Biomass Bioenergy* 2005, 28, 515–535.
- (18) Babcock, B. A.; Gassman, P. W.; Jha, M.; King, C. Adoption subsidies and environmental impacts of alternative energy crops; Briefing Paper 07-BP 50; 2007; www.card.iastate.edu/ publications/DBS/PDFFiles/07bp50.pdf.
- (19) Perlack, R. D.; Wright, L. L.; Turhollow, A. F.; Graham, R. L.; Stokes, B. J.; Erbach, D. C. Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply; ORNL/TM-2005/66; Oak Ridge National Laboratories: Oak Ridge, TN, 2005.
 (20) Nelson, R. G.; Ascough, J. C. II.; Langemeier, M. R. Environmental
- (20) Nelson, R. G.; Ascough, J. C. II.; Langemeier, M. R. Environmental and economic analysis of switchgrass production for water quality improvement in northeast Kansas. *J. Environ. Manage.* 2006, 79, 336–347.
- (21) Donner, S. D.; Kurcharick, C. J. Corn-based ethanol production compromises goal of reducing nitrogen export by the Mississippi River. Proc. Natl. Acad. Sci. 2008, 105, 4513–4518.
- (22) United States Department of Agriculture. USDA Agricultural Projections to 2017; Office of the Chief Economist, World Agricultural Outlook Board, U.S. Department of Agriculture; Prepared by the Interagency Agricultural Projections Committee; Long-term Projections Report OCE-2008-1, 2008; p. 104; http:// www.ers.usda.gov/Publications/OCE081/.
- (23) National Corn Growers Association. How Much Ethanol Can Come From Corn?; Chesterfield, MO, 2007.
- (24) Granda, C. B.; Zhu, L.; Holtzapple, M. T. Sustainable liquid biofuels and their environmental impact. *Environ. Prog* 2007, 26 (3), 233–250.
- (25) Sheehan, J.; Aden, A.; Paustian, K.; Killian, K.; Brenner, J.; Walsh, M.; Nelson, R. Energy and environmental aspects of using corn stover for fuel ethanol. J. Ind. Ecol. 2004, 7 (3–4), 117–146.
- (26) Hoskinson, R. L.; Karlen, D. L.; Birrell, S. J.; Radtke, C. W.; Wilhelm, W. W. Engineering, nutrient removal, and feedstock conversion evaluations of four corn stover harvest scenarios. *Biomass Bioenergy* 2007, 31 (2–3), 126–136.
- (27) Dosskey, M. G. Profile: Toward quantifying water pollution abatement in response to installing buffers on crop land. *Environ. Manage.* 2001, 28 (5), 577–598.
- (28) Mitsch, W. J.; Day, J. W., Jr.; Gilliam, J. W.; Groffman, P. M.; Hey, D. L.; Randall, G. W.; Wang, N. Reducing Nutrient Loads, Especially Nitrate-Nitrogen, to Surface Water, Ground Water, and the Gulf of Mexico: Topic 5 Report for the Integrated Assessment on Hypoxia in the Gulf of Mexico; NOAA Coastal Ocean Program Decision Analysis Series No. 19; NOAA Coastal Ocean Program: Silver Spring, MD, 1999; p 111.
- (29) Lee, K.-H.; Isenhart, T. M.; Schultz, R. C. Sediment and nutrient removal in an established multi-species riparian buffer. J. Soil Water Conserv. 2003, 58 (1), 1–7.
- (30) Tomer, M. D.; James, D. E.; Isenhart, T. M. Optimizing the placement of riparian practices in a watershed using terrain analysis. J. Soil Water Conserv. 2003, 58 (4), 198–206.
- (31) Miller, S. A.; Landis, A. E.; Theis, T. L. Use of Monte Carlo analysis to characterize nitrogen fluxes in agroecosystems. *Environ. Sci. Technol.* 2006, 40 (7), 2324–2332.
- (32) Howarth, R. W.; Boyer, E. W.; Pabich, W. J.; Galloway, J. N. Nitrogen use in the United States from 1961–2000 and potential future trends. *Ambio* 2002, 31 (2), 88–96.
- (33) Goolsby, D. A.; Battaglin, W. A.; Lawrence, G. B.; Artz, R. S.; Aulenbach, B. T.; Hooper, R. P.; Keeney, D. R.; Stensland, G. J. Flux and Sources of Nutrients in the Mississippi-Atchafalaya River Basin: Topic 3 Report for the Integrated Assessment on Hypoxia in the Gulf of Mexico; NOAA Coastal Ocean Program Decision Analysis Series No. 17; NOAA Coastal Ocean Program: Silver Spring, MD, 1999; p 130.
- (34) Lee, K.-H.; Isenhart, T. M.; Schultz, R. C.; Mickelson, S. K. Nutrient and sediment removal by switchgrass and cool-season grass filter strips in Central Iowa, USA. *Agroforest. Syst.* **1999**, *44*, 121–132.

- (35) Lowrance, R.; Altier, L. S.; Newbold, J. D.; Schnabel, R. R.; Groffman, P. M.; Denver, J. M.; Correll, D. L.; Gilliam, J. W.; Robinson, J. L.; Brinsfield, R. B.; Staver, K. W.; Lucas, W.; Todd, A. H. Water quality functions of riparian forest buffers in Chesapeake Bay Watersheds. *Environ. Manage.* 1997, 21 (5), 687–712.
- (36) Osbourne, L. L.; Kovacic, D. A. Riparian vegetated buffer strips in water-quality restoration and stream management. *Freshwater Biol.* 1993, 29, 243–258.
- (37) Schoonover, J. E.; Willard, K. W. J. Ground water nitrate reduction in Giant Cane and forest riparain buffer zones. J. Am. Water Resour. Assoc. 2003, 347–354.
- (38) Vought, L. B. M.; Pinay, G.; Fuglsang, A.; Ruffinoni, C. Structure and function of buffer strips from a water quality perspective in agricultural landscapes. *Landscape Urban Plan.* **1995**, *31*, 323–331.
- (39) Fixen, P. E.; West, F. B. Nitrogen fertilizers: meeting contemporary challenges. *Ambio* **2002**, *31* (2), 169–176.
- (40) Schmer, M. R.; Vogel, K. P.; Mitchell, R. B.; Perrin, R. K. Net energy of cellulosic ethanol from switchgrass. *Proc. Natl. Acad.* Sci. 2008, 105 (2), 464–469.
- (41) Lemus, R.; Brummer, E. C.; Moore, K. J.; Molstad, N. E.; Burras, C. L.; Barker, M. F. Biomass yield and quality of 20 switchgrass population in southern Iowa, USA. *Biomass Bioenergy* 2002, 23, 433–442.
- (42) Fike, J. H.; Parrish, D. J.; Wolf, D. D.; Balasko, J. A.; Green, J. T., Jr.; Rasnake, M.; Reynolds, J. H. Long-term yield potential of switchgrass-for-biofuel systems. *Biomass Bioenergy* 2006, 30, 198–206.

- (43) Wakeley, H. L.; Hendrickson, C. T.; Griffin, W. M.; Matthews, H. S. Economic and environmental transportation effects of large-scale ethanol production and distribution in the United States. *Environ. Sci. Technol.* 2009, 42, 2323–2327.
- (44) Scavia, D.; Rabalais, N. N.; Turner, R. E.; Justic, D.; Wiseman, W. J., Jr. Predicting the response of Gulf of Mexico hypoxia to variations in Mississippi River nitrogen load. *Limnol. Oceanogr.* 2003, 48 (3), 951–956.
- (45) Scavia, D.; Donnelly, K. A. Reassessing hypoxia forecasts for the Gulf of Mexico. Environ. Sci. Technol. 2007, 41 (23), 8111–8117.
- (46) Alexander, R. B.; Smith, R. A.; Schwarz, G. E. Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico. *Nature* **2000**, *403*, 758–761.
- (47) USGS. Total Mississippi River Basin Nutrient Flux to the Gulf of Mexico (through 2005); 2009; http://toxics.usgs.gov/hypoxia/ mississippi/previous/index.html.
- (48) Heaton, E. A.; Flavell, R. B.; Mascia, P. N.; Thomas, S. R.; Dohleman, F. G.; Long, S. P. Herbaceous energy crop development: recent progress and future prospects. *Curr. Opin. Biotechnol.* 2008, 19, 202–209.
- (49) Heaton, E. A.; Dohleman, F. G.; Long, S. P. Meeting US biofuel goals with less land: the potential of Miscanthus. *Glob. Change Biol.* **2008**, *14*, 2000–2014.
- (50) Turner, R. E.; Rabalais, N. N.; Justic, D. Gulf of Mexico hypoxia: Alternate states and a legacy. *Environ. Sci. Technol.* 2008, 42, 2323–2327.

ES9011433