

# Corn-based ethanol production compromises goal of reducing nitrogen export by the Mississippi River

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**Corn cultivation in the United States is expected to increase to meet demand for ethanol. Nitrogen leaching from fertilized corn fields to the Mississippi–Atchafalaya River system is a primary cause of the bottom-water hypoxia that develops on the continental shelf of the northern Gulf of Mexico each summer. In this study, we combine agricultural land use scenarios with physically based models of terrestrial and aquatic nitrogen to examine the effect of present and future expansion of corn-based ethanol production on nitrogen export by the Mississippi and Atchafalaya Rivers to the Gulf of Mexico. The results show that the increase in corn cultivation required to meet the goal of 15–36 billion gallons of renewable fuels by the year 2022 suggested by a recent U.S. Senate energy policy would increase the annual average flux of dissolved inorganic nitrogen (DIN) export by the Mississippi and Atchafalaya Rivers by 10–34%. Generating 15 billion gallons of corn-based ethanol by the year 2022 will increase the odds that annual DIN export exceeds the target set for reducing hypoxia in the Gulf of Mexico to >95%. Examination of extreme mitigation options shows that expanding corn-based ethanol production would make the already difficult challenges of reducing nitrogen export to the Gulf of Mexico and the extent of hypoxia practically impossible without large shifts in food production and agricultural management.**

Gulf of Mexico | hypoxia | nitrogen cycling | biofuels | agriculture

Last year, U.S. farmers planted >90 million acres of corn for the first time in 60 years because of rising corn prices and the demand for ethanol (1). Corn-based ethanol production has risen faster than recent U.S. Department of Agriculture (USDA) projections and has already surpassed the year 2012 target of 7.5 billion gallons per year set in the 2005 Energy Policy Act (2). The most recent U.S. Energy Bill set a target of 36 billion gallons of renewable fuels by the year 2022, of which 15 billion gallons can be produced from corn starch (3). U.S. corn cultivation may continue to increase in the coming years to meet such fuel production targets (2).

Fertilizer applied to corn in the U.S. Midwest is a primary source of nitrogen exported to the Gulf of Mexico by the Mississippi and Atchafalaya Rivers (4). The flux of nitrogen, largely in the form of the nitrate, and fresh water promote the development of extensive seasonal hypoxia on the continental shelf each summer (5, 6). In recent years, this “Dead Zone” has reached >20,000 km<sup>2</sup> in size and has contributed to benthic mortality and the risk of fisheries decline (6). The Mississippi Basin/Gulf of Mexico Task Force set a goal of reducing nitrogen export by the Mississippi and Atchafalaya Rivers by 30% in hopes of reducing the annual spatial extent of hypoxia to <5,000 km<sup>2</sup> (7). Recent research suggests that nitrogen export may need to be reduced by up to 55% to achieve the hypoxia-reduction goal because of annual climate-driven variability in nitrogen flux and annual variability in ocean dynamics (8, 9).

In this study, we use an agricultural version of the Integrated Biosphere Simulator (IBIS), a process-based dynamic ecosystem model, and the Terrestrial Hydrology Model with Biogeochemistry (THMB) to investigate how increasing corn cultivation to meet ethanol production goals will affect nitrogen export to the Gulf of Mexico. The models have been thoroughly tested and applied together to simulate the sensitivity of terrestrial nitrogen, carbon,

and water cycling and downstream transport of nitrogen and water across the Mississippi–Atchafalaya River Basin to agricultural land use practices and climate variability (4, 10–16). First, we used USDA data to generate a series of spatially explicit land use scenarios including a control case (based on 2004–2006 mean land use and land cover); a representation of 2007 land management based on the projected plantings from the spring (1); three scenarios designed to meet the ethanol production goals in the recent Energy Bill (3); and an extreme mitigation scenario (Table 1). Second, we used the control scenario to validate the ability of the models to simulate nitrogen cycling across the Mississippi–Atchafalaya River Basin and nitrogen export to the Gulf of Mexico. Third, we evaluated the effect of the alternative land cover scenarios on nitrogen export to the Gulf of Mexico and the goal of reducing the extent of the seasonal hypoxic zone.

## Results

The study focuses on the 3.2 million-km<sup>2</sup> Mississippi–Atchafalaya River Basin, where >80% of the total U.S. corn and soybean acreage is cultivated. The smaller Atchafalaya Basin is included in this analysis because the Old Water Control Structure north of New Orleans redistributes the combined flow of the Mississippi River and the Atchafalaya River. Because the ethanol production goals are national, the land use scenarios were developed for the entire U.S. The land-cover maps displayed are restricted to the Mississippi–Atchafalaya Basin.

The land use scenarios were generated by simulating decisions by farmers in each county to plant corn on other croplands depicted in the control case or on conservation reserve lands, where yields are expected to be lower (Table 1). The models were driven with the different scenarios to simulate the effect of altered cultivation on terrestrial nitrogen leaching and downstream nitrogen export. Crop management is assumed to be the same in each scenario; for example, the state-level fertilizer application rates for each of the simulated crops (corn, soybean, and three varieties wheat) are the same across all scenarios.

Nitrogen export by the Mississippi and Atchafalaya Rivers has been shown to vary not just with land use and land cover but with annual variability in rainfall and river discharge (8). To account for the role of climate variability, the models were forced with the same 1981–2000 monthly mean 0.5° × 0.5° transient climate data from the Climate Research Unit (CRU) TS2.1 dataset in each scenario (17). This method allows the models to represent the range of nitrogen export that should be expected in each land cover scenario, given climate variability. Therefore, the model output for the control case, based on 2004–2006 mean land use and land cover, does not represent the exact nitrogen export for that period but the range of

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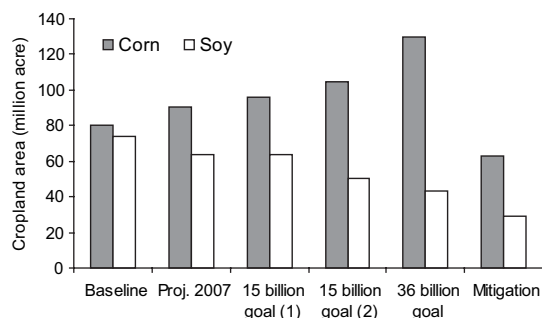
**Table 1. Description of land use scenarios**

Scenario	Objective	Description
Control	2004–2006 mean crop plantings by county	Describes area of corn, soybean, winter wheat, and spring wheat in each grid cell for 2004–2006
Projected 2007	State-level projected plantings for 2007	A fraction of land in corn-growing counties that is planted in soybeans is shifted to corn
15 billion gallon (1)	Meets the goal for nonadvanced biofuels in year 2022	The 2007 land use change plus conversion of some CRP land in corn-growing counties to corn
15 billion gallon (2)	Meets the goal for nonadvanced biofuels in year 2022	A higher fraction of land planted in soybeans shifted to corn (than in 2007)
36 billion gallon	Meets Energy Policy Act goal for all biofuels in year 2022	Aggressive planting of corn on both CRP land and land planted in soybeans in pursuit of 2022 goal
Mitigation	Meets 15 billion gallon goal and achieves nitrogen reduction	A 50% reduction in red meat production reduces land required for feed crops; riparian wetlands constructed adjacent to corn and soybean fields

nitrogen export that could occur with 2004–2006 mean land cover, given typical recent (1981–2000) climate variability.

**Land Use Scenarios.** The total land area in the US devoted to corn production in the scenarios ranges from 44 million acres in the “mitigation” scenario to the 130 million acres in the “36 billion gallon” scenario (Fig. 1). The “projected 2007” scenario is based on state-level projected plantings of corn and soybeans published in the spring of 2007 (1). An iterative process was used to simulate the conversion of soybeans to corn in each county that best matched the state projected planting data for 2007. The area prediction error ( $[A_{\text{USDA}} - A_{\text{scenario}}]/A_{\text{scenario}}$ ) across the 10 major producing states that comprise 80% of the U.S. corn cultivation ranges from  $-4\%$  to  $10\%$ . The greatest increase in corn production occurs across Illinois, Iowa, Nebraska, and Indiana (Fig. 2). Nationally, the area of corn cultivation in 2007 matched the USDA projection for the year 2016 (2).

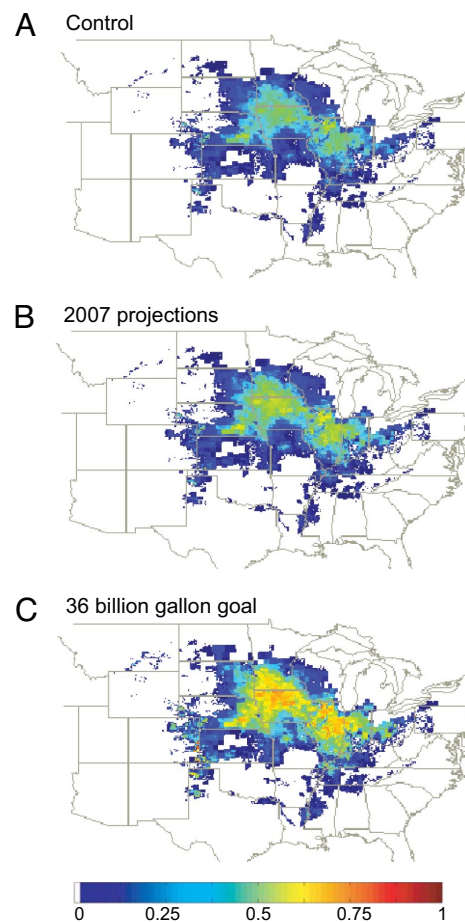
The land use changes required to meet the goals of 15 billion gallons or 36 billion gallons of corn-based ethanol by the year 2022 (3) were generated by using a simple Monte Carlo optimization procedure and assumptions about the use of ethanol coproducts, the increase in corn yields over time, and the increase in the corn-to-ethanol conversion rate over time (see *Materials and Methods*). Corn cultivation is increased by farmers’ decisions to plant corn on land otherwise planted in soybean, as occurred in 2007, or on land currently enrolled in the Conservation Reserve Program (CRP). With the long history of industrial agriculture in the U.S., it is unlikely that any “new” croplands will be brought into production; the total area of land devoted to crops in the U.S. has remained relatively constant in recent decades (18). The only “surplus” cropland that may be available for new corn cultivation is other existing croplands and CRP land in corn-growing regions. Shifting land from soybean to corn can be straightforward for producers because corn and soybean are often grown in rotation on



**Fig. 1.** Area of the Mississippi–Atchafalaya Basin planted in corn and soybeans in each land use scenario.

the same fields (1). The use of CRP land is speculative; because CRP contracts last for 10 years, every farmer will at least have the opportunity to switch their CRP land to corn cultivation before 2022.

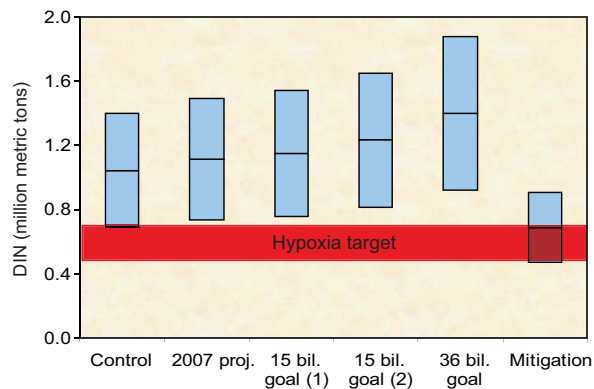
The land use analysis resulted in two different scenarios that could achieve the goal of 15 billion gallons of conventional corn-based ethanol production by 2022 (Fig. 1). In the first or optimistic scenario, the goal is reached by combining the 2007 land use shift with planting corn on some CRP land in corn-growing counties. Presuming crop yields continue to increase by  $1\% \cdot \text{yr}^{-1}$  (2) and the



**Fig. 2.** Fractional area of each  $5' \times 5'$  grid cell planted in corn in the 2004–2006 control (A), the 2007 projections (B), and the 36 billion gallon goal scenario (C). The area is expressed as a fraction of the total grid cell area.







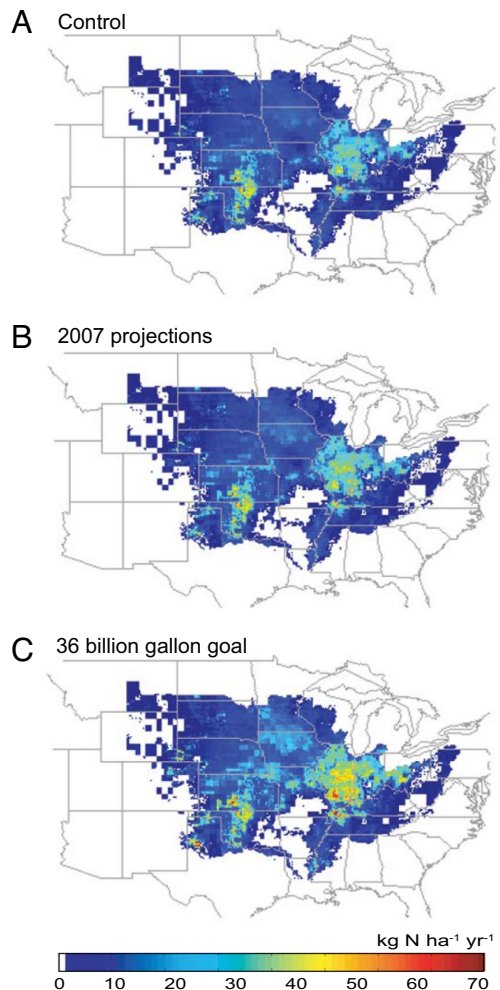
**Fig. 4.** Simulated annual DIN export by the Mississippi and Atchafalaya Rivers to the Gulf of Mexico in the 2004–2006 control and the five ethanol production scenarios. The blue box represents the 5–95% confidence interval range of annual DIN export based on 1981–2000 climate variability (the horizontal line represents the annual mean). In red is the estimated level of DIN export required to achieve the federal goal of reducing the hypoxic zone to  $<5,000$  km<sup>2</sup>; the upper bound is the federally recommended 30% reduction in mean DIN flux (7), and the lower bound is the 55% reduction in mean DIN flux thought necessary to account for variability in climate and ocean dynamics (8, 9).

the rate of change in corn yields ( $0\text{--}1\%$  year<sup>-1</sup>) and the corn-ethanol conversion efficiency ( $2.7\text{--}3.0$  gal·bu<sup>-1</sup>). In these scenarios, the mean DIN export would grow to 39–43% greater than the federal hypoxia reduction target (7) and 58–62% greater than the lower target recommended by ref. 8, which considers variability in climate and ocean dynamics. The DIN export in the more pessimistic production scenario would exceed both the federal and lower hypoxia targets even during the driest or lowest (5th percentile) export years (Fig. 4). In both cases, as in the 2007 scenario, the increase in DIN originates largely from the Corn Belt states.

If the entire 36 billion gallon target for 2022 was met by using corn-based ethanol, even assuming highly efficient corn-ethanol conversion (equivalent to  $3.3$  gal·bu<sup>-1</sup>) and a  $1\%$ ·year<sup>-1</sup> increase in crop yields, the models indicate mean DIN export would be 34% greater than in the control scenario. The annual mean DIN export would reach twice the federal hypoxia target; the annual DIN export would exceed the control case mean in 75% of the years. The Corn Belt would be increasingly dominated by corn and responsible for a substantially larger fraction of the DIN loading to rivers and streams across the Mississippi–Atchafalaya Basin (Fig. 5). Nitrogen entering the river system in southern Ohio, Indiana, Illinois, and Iowa is more likely to reach the Gulf of Mexico than nitrogen entering rivers in the drier western half of the Basin, because greater use of artificial drainage (27) and shorter river travel times result in fewer opportunities for denitrification (14). Therefore, in an extreme corn-based ethanol production scenario, the Corn Belt is even more disproportionately responsible for the nitrogen reaching the Gulf of Mexico than, for example, would be reflected in a map of nitrogen loading to land.

The model results for the optimistic 15 billion gallon scenario and the 36 billion gallon scenario could be considered conservative because of the assumptions made in constructing the scenarios. In both cases, we have assumed a high annual rate of change in crop yields over the next 15 years, without any change in the rates of fertilizer application. Moreover, we have assumed in the optimistic 15 billion gallon scenario and the 36 billion gallon scenario that corn grown on CRP lands will achieve the same yields as corn grown on croplands elsewhere in the particular county. In reality, farmers tend to enroll their most marginal croplands in the CRP program. These lands may also be more susceptible to erosion, runoff, and nutrient leaching losses.

To accommodate the increased planting of corn in the future,



**Fig. 5.** Simulated dissolved inorganic nitrogen leaching ( $\text{kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ ) from land across the Mississippi–Atchafalaya River Basin in the 2004–2006 control (A), the 2007 projections (B), and the 36 billion gallon goal scenario (C).

farmers may shift from the currently common corn–soybean rotations simulated in THMB to either (i) more continuous corn cropping and less corn–soybean or (ii) more use of longer rotations like corn–corn–soybean. We tested the effect of lengthening crop rotations on DIN export in each scenario by using a new THMB algorithm that distributes corn and soybean in each grid cell into the combination of continuous, corn–soybean and corn–corn–soybean (that is algebraically possible). Additional model simulations showed that implementing a longer rotation strategy causes only a minor reduction (1–2%) in DIN flux to the Gulf in each of the land use scenarios.

We estimated the effect of model biases in the Arkansas/Red and the other four major Mississippi subbasins on these results through normalizing the simulated subbasin DIN export by the ratio of the simulated mean DIN flux in the control runs and the 1981–2000 USGS data for each subbasin. A small fraction of the increase in DIN flux to the Gulf between the ethanol scenarios and the control run occurs in the Arkansas/Red subbasin (e.g.,  $<1\%$  in the projected 2007 scenario and the 15 billion gallon scenarios), where model bias is expected to be the highest. The relative change in DIN flux to the Gulf between the ethanol scenarios and the control run increases by only one to four percentage points if the DIN flux from the Arkansas/Red is normalized; the increase in DIN flux to the Gulf is 8% rather than 7% in the 2007 scenario and 38% rather than 34% in the 36 billion gallon scenario. The results are similar if the

DIN flux is also normalized in the other four major Mississippi subbasins because the model biases in the other subbasins are small and balance one another. The higher predicted increase in DIN flux between the ethanol scenarios in the control run after correcting for model biases could be considered the upper bound for the model results.

**Mitigation Scenario.** The ethanol production scenarios demonstrate that achieving the twin goals of corn-based ethanol production and reduced nitrogen export would require dramatic increases in nitrogen-fertilizer use efficiency, restoration of riparian wetlands, and reductions in animal feed or exports, the primary other uses of corn (16, 28). Model simulations of the mitigation scenario show that combining this hypothetical shift in food production and diet with construction of riparian wetlands adjacent to all corn and soybean lands would achieve a 34% decrease in annual mean DIN flux (Fig. 4). Normalizing the DIN flux in each subbasin to account for model biases suggests the decrease in annual mean DIN flux in this scenario could be as high as 42%. The annual mean DIN flux would achieve the level recommended by the Mississippi River/Gulf of Mexico Task Force to reduce the hypoxic zone to <5,000 km<sup>2</sup> in size but not the greater reduction required to account for climatic and oceanographic variability (8). This scenario, although arguably not realistic or politically feasible, could be considered the maximum nitrogen mitigation possible while reaching the 2022 biofuel production goals without sacrificing total food production or altering on-farm management practices.

The nitrogen savings in this scenario are smaller than might be expected, given the construction of riparian wetlands that can remove 35% of DIN leaching from corn and soybean land (20, 21). Because the area of corn and soybean production in the scenario decreases relative to wheat to support a less meat-dominated diet, the construction of engineered riparian wetlands across the Mississippi Basin in this mitigation scenario would result in less nitrogen savings than would occur in the other scenarios or the control case. Therefore, even with the decrease in total corn planting and nitrogen-fertilizer use on corn, and the construction of riparian wetlands, widespread adoption of on-farm nitrogen mitigation practices and precision farming would be necessary to meet the higher hypoxia-reduction goal.

## Conclusions

The results of this study suggest that the projected expansion of corn-based ethanol production could make the already challenging goal of reducing nitrogen export by the Mississippi and Atchafalaya Rivers to the Gulf of Mexico practically impossible without radical shifts in feed production, diet, and agricultural land management. At minimum, a continuation of 2007 land use practices will increase mean annual nitrogen export above previous levels and increase the likelihood of extensive hypoxia in the Gulf of Mexico. Producing 15 billion gallons or more of corn-based ethanol from conventional methods by 2022, without any change in cultivation practices, will require either a large reduction in the use of corn for feed and exports or a large increase in corn cultivation and, in turn, nitrogen loading to the river system.

Greater nitrogen savings could occur by planting corn on land otherwise planted in another nitrogen fertilizer-intensive crop, like cotton or, in some states, wheat rather than soybeans (1). However, cotton currently covers <5% of the croplands in the Mississippi–Atchafalaya Basin, and the corn yields tend to be lower in the drier, western wheat-producing states. A number of research programs are investigating the feasibility of perennial or other warm-season grass crops for biofuel production (29–31). These developments, although promising, will take several years and possibly changes in agricultural policy before becoming widespread practice. It is also likely that, to maximize production, biofuel crops like switchgrass will be treated with moderate-to-high levels of nitrogen fertilizer (30, 31).

The future production estimates in the scenarios and, in turn, the simulations of nitrogen export are contingent on the common assumption that crop yields will continue at 2004–2006 levels or continue the upward trend of recent decades (2, 19). Future crop yields, however, may be impacted by changes in climate, management, atmospheric CO<sub>2</sub>, and ground-level ozone (32–35), making it difficult to project with high certainty the spatial distribution of future crop productivity. One analysis of recent trends in U.S. agricultural yields concluded that corn yields could decline by 17% for every degree of future warming (32). Adaptive measures to combat lower than expected productivity due to global warming could lead to greater land requirements or greater diversion of corn grain from other uses to meet the biofuel production goals.

The land cover analysis in this study raises questions about the availability of land to radically increase ethanol or other biofuel production. Reaching the proposed biofuel production goals will lead to trade-offs between cropland demands for food, feed, and fuel, even when the use of ethanol coproducts as feed is considered. The mitigation scenario demonstrates that reducing the cultivation of animal feed, the majority domestic use of corn and soybeans (2), is one way of attaining the croplands necessary for biofuel production. A sharp reduction in feed cultivation and animal production in the U.S. is purely hypothetical; it would require a substantial change in culture and the reduction of an industry that provides income and employment to a large number of Americans. However, given the probable ceilings on cropland area, grain yields and use of ethanol coproducts as animal feed, a gradual decrease in use of corn and soybeans for animal feed may be a necessary consequence of the projected increase in demand for biofuels.

This study shows that even with reductions in other uses of corn, the construction of efficient riparian wetlands adjacent to fertilized croplands and the implementation of on-farm nitrogen management practices will be necessary to achieve the large reduction in nitrogen loading required to meet the hypoxia target. A massive national wetland restoration project, on the order of 22,000 km<sup>2</sup> of wetlands (22), and/or widespread adoption of efficient nitrogen management practices (28), like a change in diet and meat production, would not be trivial to implement (6). Given these limitations, the expansion of corn-based ethanol production is likely to jeopardize efforts to minimize nitrogen loading to the Mississippi–Atchafalaya River system and the extent of hypoxia in the Gulf of Mexico.

## Materials and Methods

**Land Use and Ethanol Production.** The six land use scenarios were generated by using USDA county-level data on the area and yields of corn, soybeans, and the three varieties of wheat. The 2004–2006 mean county-level planted area and yield of corn, soybeans, wheat, and the eight other most common crops in the U.S. was obtained from the USDA online National Agricultural Statistics Service (available at [www.nass.usda.gov](http://www.nass.usda.gov)). The most recent data on CRP land in each county was obtained from USDA Farm Service Agency online data (available at [www.fsa.usda.gov](http://www.fsa.usda.gov)).

The land cover converted to corn cultivation in pursuit of the ethanol production goal for each scenario was determined from the availability of suitable croplands in each grid cell. Beginning with the 2007 scenario, a simple Monte Carlo optimization procedure was used to develop a universal “rule”—a realistic farmer decision about the conversion of noncorn lands in the 2004–2006 control run land cover distribution to corn cultivation—that allows the country to meet the overall national corn-based ethanol production goal for that scenario. The optimization procedure considered the suitability of the land to corn cultivation, measured as the fraction of total crop area (in each grid cell) devoted to corn, the area of soybean land, and, in some scenarios, the area of CRP land, as constraints on crop conversion. In the projected 2007 scenario, the optimization indicated that a conversion of 20% of soybean lands to corn in grid cells where corn represented at least one-third of all croplands best fit the predicted corn plantings by state (1). The verified conversion for the 2007 scenario then provided a baseline for the larger crop conversions in the other scenarios. Therefore, although the results for each county are speculation, the scenarios represent probable distributions of corn and soybean cultivation across the Mississippi–Atchafalaya Basin necessary to meet each production goal.



In each scenario, the range of total corn production in 2022 is estimated from the planted corn area in the scenario ( $A_i$ , in hectares), the 2004–2006 average yield ( $Y_{br,i}$ , in  $\text{bu}\cdot\text{ha}^{-1}$ ), and an assumption about the rate of increase in corn yields ( $c = 0 - 1.0\%\cdot\text{yr}^{-1}$ ). We assume all corn production in excess of the 2004–2006 mean will be used to produce ethanol, thus adding to the 11% of the 2004–2006 mean that has been used annually to produce ethanol (2). Therefore, total ethanol production ( $E$ , in gallons) is:  $E = r \times (P - 0.89 \times P_{\text{control}})$ , where  $P = \sum A_i \times [Y_i \times (1 + c)^{15}]$ .

We assume the ethanol conversion rate ( $r$ , in  $\text{gal}\cdot\text{bu}^{-1}$ ) to range between the current value of 2.7 and the projected future value of 3.0 (2). A further increase, to  $3.3\text{ gal}\cdot\text{bu}^{-1}$ , could occur but only with the additional conversion of nonstarch plant materials to ethanol (19). Any diversion of other corn grain required to meet the ethanol production goal is estimated assuming a 20% savings because of the use of ethanol coproducts as animal feed (2).

For the mitigation scenario, the area of corn, soybean, wheat, sorghum, oats, and barley production used in the production of feed for beef cattle was estimated by using USDA data on feed use (2) and typical conversion rates (36). The total area of each crop in the U.S. was calculated as the control run area minus that required to generate 50% of the red meat produced from U.S. croplands plus that required to support lacto-ovo vegetarian diets. The methods and parameters are described in detail in ref. 16. The fractional change in the area of each crop was assigned then evenly to each county. The additional corn land required, by county, to meet the 15 billion gallon target, assuming  $1\%\cdot\text{year}^{-1}$  increase in crop yields, was determined by using the method developed for the other scenarios.

For each scenario,  $5' \times 5'$  latitude–longitude spatial resolution ( $\approx 7 \times 9\text{ km}$ ) maps of the planted area of the crops were made by integrating the county-level maps with a satellite-based dataset of total cropland area (37). The area of each crop type is distributed within the county by using the satellite-derived  $5' \times 5'$  pattern of total crop area in the county (38).

**Model Simulations.** In this study, we used an advanced version of the IBIS biosphere model (referred to as Agro-IBIS) that is capable of simulating managed and natural ecosystems (crops, grasslands, and forests) across North America (4, 12). Agro-IBIS was developed by adapting version 2.6 of the global IBIS model (10) to explicitly model corn, soybean, and wheat crop systems across the U.S. (12). Besides modeling short time-scale carbon, nitrogen, and water balance and vegetation structure of natural and managed ecosystems, Agro-IBIS simulates crop transitions through key phenological stages during development (emergence, grain fill, senescence), characterizes seasonal shifts in carbon allocation to specific crop carbon pools (i.e., leaf, stem, root, and grain), and quantifies nitrogen fixation. The model uses algorithms based on 10-day running mean maximum and minimum temperatures to determine the optimal planting date for corn, soybeans, and spring and winter wheat in each grid cell (4, 12). Another algorithm uses the average number of growing degree days (GDD) accumulated

during the period from April through September (base  $0^\circ\text{C}$  for wheat,  $8^\circ\text{C}$  for corn, and  $10^\circ\text{C}$  for soybean) for the previous 5 years of climate data to choose a generic hybrid for planting; these hybrids vary solely in the number of GDD that are needed to reach flowering, silking, heading, and physiological maturity.

Canopy and land surface processes in Agro-IBIS are based on the key differences in C3 and C4 crop physiology, daily phenology, and carbon allocation so that coupled carbon–water exchange is responsive to agricultural management (e.g., irrigation, fertilizer application, planting date) and environmental stresses (e.g., climate and water and nitrogen limitations). Agro-IBIS is continually being evaluated at the individual field scale by using the AmeriFlux network of eddy covariance field sites, including those established over the past decade in corn–soybean rotations near Bondville, IL, and Mead, NE (39).

Agro-IBIS was executed a total of 16 times, with each simulation assuming that the Mississippi Basin was covered by natural vegetation or by the most common 2- and 3-year crop rotations (including corn, soybeans, unfertilized soybeans, winter wheat, and spring wheat). Annual rates of nitrogen fertilizer use on corn, soybean, and wheat (in  $\text{kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ ), and the fraction of that crop treated with nitrogen fertilizer for each state were derived from 2001–2005 USDA state-level agricultural chemical use surveys published online ([www.ers.usda.gov/Data/FertilizerUse](http://www.ers.usda.gov/Data/FertilizerUse)). The surveys are conducted in the major producing states for each crop in most years; a 5- rather than 3-year average is used because the surveys are less comprehensive than crop production data (e.g., no corn nitrogen-use data are available for 2004). The rate of total nitrogen deposition across the Mississippi Basin was adapted from the National Atmospheric Deposition Program data, assuming dry deposition is equal to 50% of wet deposition (4).

For each scenario, the monthly simulated runoff, subsurface drainage, and DIN leaching from Agro-IBIS is integrated with  $5' \times 5'$  resolution crop cover data to determine the inputs to THMB. This method allows for conducting multiple experiments without repeating the more computer-intensive Agro-IBIS simulations each time. THMB is a transport model that simulates the flow, storage, and removal of water and nitrogen over time in rivers, wetlands, lakes, and human-made reservoirs at  $5' \times 5'$  spatial resolution based on upstream inputs, local inputs of surface runoff, subsurface drainage and nitrogen leaching, precipitation and evaporation over surface waters, and topography (11, 40). Here, THMB simulates the transport of all DIN, rather than  $\text{NO}_x$  and  $\text{NH}_3$  separately, because 96% of DIN reaching the Gulf of Mexico is in the form of  $\text{NO}_x$  (22). As in previous studies, the only process permanently removing nitrogen from the river system is denitrification, or reduction of  $\text{NO}_3$  to  $\text{N}_2$  and  $\text{N}_2\text{O}$ . The denitrification function in THMB is described in detail in ref. 14; the only change here is that the upper limit on the denitrification rate parameter in large rivers was removed, based on ref. 41. THMB was executed twice for each scenario, once each by using the different crop rotation systems described in the results.

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