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Supplementary Materials for

Legacy nitrogen may prevent achievement of water quality goals in the Gulf of Mexico

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Materials and Methods

S1.0 Relationship Between NO3-N and Total N Loading

Based on a multi-model analysis of the relationship between N loading from the Mississippi River Basin and the areal extent of the hypoxic zone, it has been suggested that an approximately 60% decrease in total N loading may be necessary to meet policy goals (*6*). In our simulations, however, we focus only on prediction of changing NO3-N loads based on the assumption that total N trajectories will mirror temporal changes in NO3-N loads. We believe this assumption to be justifiable based on our analysis of 1980-2016 Mississippi N data, which shows that NO3-N consistently accounts for 65% of total N (±6%) and thus demonstrates a strong linear relationship (R2=0.83) with total N (Fig. S2).

S2.0 The ELEMeNT Model

The ELEMeNT modeling framework couples source-zone N dynamics (the root zone) with a travel time-based approach that accounts for both transport and transformation of N along groundwater pathways, as has been described in detail in Van Meter et al (*4*). The model was created to explicitly account for changing stocks of N within the soil profile and in groundwater pools. Model development was based on the principle that watershed nutrient dynamics at any given time are a function of both current and historical land use and management. ELEMeNT is the only watershed model that can directly simulate the impacts of watershed-scale nutrient legacies.

S2.1 Source Zone Dynamics

To capture long-term patterns of land-use (LU) and management, the model segments the watershed into *s* distinct units corresponding to distinct land-use trajectories, with each being stored within a 2D land-use array, $LU(s,t)$ representing distributions of land use over time, *t*.

$$LU(s,t) = \begin{cases} 2 & s \le A_{crop}(t) & cropland \\ 1 & A_{crop}(t) < s \le [A_{crop}(t) + A_{past}(t)] & pastureland \\ 0 & s > [A_{crop}(t) + A_{past}(t)] & other \end{cases}$$

(1)

where A_{crop} and A_{past} correspond to watershed-scale percent cropland and percent pastureland, respectively (*4*).

S1.2.2 Source Function

Each distinct LU trajectory has a corresponding $J_s(s,t)$, which describes the N mass leaching from the source zone (vadose zone) at any time *t*. Accordingly, the source function, which is the mass of N leaching from the source zone to groundwater, is quantified as the sum of source-zone values across the distribution of all LU trajectories:

$$J_{s_{wshd}}(t) = \sum_{s=1}^{1000} J_s(s,t) \tag{2}$$

Within the soil profile, we consider that all of the annual N surplus cycles through either active or protected soil organic N (SON) pools, with inorganic N then being produced as a function of SON mineralization. Additional details regarding source-zone dynamics can be found in Van Meter et al (*4*).

S2.3 Catchment N loading

ELEMeNT couples a travel time-based approach with source-zone dynamics to predict N loading at the catchment outlet. This approach entails conceptualization of all points on the landscape as corresponding to individual stream tubes, each with its unique travel time to the stream network (*4, 32*). The resulting distribution of travel times then controls NO_3-N mass fluxes at the outlet, $M_{out}(t)$, as described in the following equation:

$$M_{out}(t) = \int_0^{\infty} J_s(t-\tau) f(\tau) e^{-\gamma\tau} d\tau + (1-k_h)W(t) \tag{3}$$

where $J_s(t-\tau)$ is the contaminant input function describing the mass flux of N from the unsaturated zone to groundwater, as discussed in *S2.2*, γ is the denitrification rate constant, and $W(t)$ is human N consumption and k_h the denitrification rate constant for human waste. For additional details, see Van Meter et al (*4*).

S3.0 N Surplus Calculations and Data Sources

A surface N balance approach was used to calculate annual N surplus values, which are the primary input term to the model's source zone function (*4, 33*). Inputs were considered to include N fertilizer application, biological N fixation, livestock manure N, and atmospheric deposition, with crop N uptake as the major output. For further details regarding mass balance calculations and data sources, see Van Meter et al (*4*).

S4.0 Uncertainty Analysis, Sensitivity Analysis, and Model Calibration/Validation

The ELEMeNT model developed for the Mississippi River Basin was subjected to rigorous evaluation to ensure that model predictions were robust. The evaluation process included uncertainty analysis for calculated N surplus values, sensitivity analysis for model parameters, and a calibration/validation approach which included use of mean absolute error values for both measured soil organic N (SON) data and N loading data at the catchment outlet as objective functions. A summary of our approach is provided below, and additional details can be found in Van Meter et al (4).

S4.1 Uncertainty Analysis for N Surplus Trajectories

Monte Carlo simulations were used to characterize uncertainty related to the calculated N surplus trajectories for the watershed. For each parameter used in the mass balance calculations, we assumed a normal distribution of values with a coefficient of variation (CV) value of 0.3. We then carried out 1000 simulations to obtain time-varying median and interquartile range values for the N surplus trajectories for the period 1800-2014.

S4.2 Sensitivity Analysis

For the sensitivity analysis, we utilized the Latin hypercube sampling technique, a form of stratified Monte Carlo sampling (*34*), to generate 1000 parameter sets from designated ranges of values based on literature review and data specific to the MRB. Model simulations were run with these parameter sets, and the evaluated output variables included not only annual N loading at the catchment outlet, but median soil organic N values for soil across the MRB (1950-2015) and soil organic N accumulation (1980-2010). The results of the sensitivity analysis showed that the primary parameters impacting 1950-2010 median SON levels were the mineralization rate constants and humification coefficients for non-cultivated and cultivated land. N loading at the catchment was found to be particularly sensitive to denitrification rate constants in soil and groundwater and the mean travel time through hydrologic pathways, including the shallow subsurface, deeper groundwater, and surface water.

S4.3 Model Calibration

For the model calibration, we selected parameters for optimization based on the results of the sensitivity analysis, as described in *S4.2*. The model was then calibrated to optimize simulation of (1) current levels of SON, based on USDA gridded soil survey data, and (2) N loading at the catchment outlet, as quantified from USGS water quality data (Mississippi River near St. Francisville, Louisiana, and Atchafalaya River at Melville, Louisiana) and discharge data (Mississippi River at Tarbert Landing, Old River Outflow Channel near Knox Landing, Atchafalaya River at Simmesport, Ohio River at Metropolis, and Mississippi River at Thebes). To assess the goodness of fit of the observed data with predicted value, we used as our objective functions mean absolute error values for both stream NO_3-N loading and current soil SON data. Optimization was carried out iteratively, leading to a final selection of the top-performing 10% of parameter sets. Performance was based on goodness of fit to the specified objective function. Median parameter values were extracted for all relevant parameters. For watershed NO_3-N loads, model calibration was carried out for the years 1979-2013, and the period 1955-1970 was used for validation.

Measured data for the period 1979-2013 indicate medianNO_3-N loading of 3.3 kg ha^{-1} yr^{-1} (980 kt yr^{-1}) compared with modeled values of 3.2 kg ha^{-1} yr^{-1}, a difference of only 1.3%. For the 1955-1970 validation period, median measured loading values for the watershed were 1.2 kg ha^{-1} yr^{-1}, while modeled median values were 1.1 kg ha^{-1} yr^{-1}, a statistically insignificant difference.

S5.0 Future Simulations

In the main text, we report the results of our core simulations, which assume constant inputs of N from atmospheric deposition and wastewater treatment plants across the study period. We have also performed a set of secondary simulations which assume predicted changes in these values. Details regarding the two different simulation sets are described below.

S5.1 Core Simulations

In the main text, we present the results of our core simulation scenarios for the MRB. In the business-as-usual (BAU) scenario, we assume that agricultural management practices remain constant; as a result, watershed N surplus values remain at 2016 levels throughout the simulation period. For the other scenarios, we assume simple percent decreases in the agricultural N surplus (ANS) in relation to mean 2010-2015 surplus values. As an example, we have determined that from 2010-2015, the mean N surplus for cropland throughout the MRB was approximately 48.9 kg/ha (2). Under the 25% reduction, the ANS value is reduced to 36.7 kg/ha, and under the 100% reduction scenario it becomes zero. We consider the ANS to include inputs and outputs specific to crop and livestock production. Accordingly, it does not include atmospheric N deposition or wastewater N. Under these scenarios, the changes in watershed management are considered to be immediate, with a start year of 2017.

In all of the core simulations we assume that atmospheric N deposition and wastewater N inputs remain constant over the simulation period. This simplified approach, though not our best prediction of future dynamics, allows us to more clearly evaluate the role of legacy N in driving changes in N loading without the addition of other complicating factors. We have, however, also run a set of simulations that do include such changes, as described in S5.2.

S5.2 Secondary Simulations

In our secondary simulations, we run the BAU and N surplus reduction scenarios, as described in S3.1, but also consider both projected increases in human population and projected decreases in atmospheric N deposition. Population trajectories were obtained from the U.S. Census Bureau, which predicts a 22% increase in population by the year 2060. Trends in atmospheric deposition assume a 22% decrease in N deposition by the year 2022 in response to implementation of tighter air quality standards (*12*).

As seen in Fig. S3, the trends in N loading are quite similar to those under the core simulation scenarios, as shown in Fig. 2 of the main text, but the actual reductions in loading that can be achieved are somewhat greater. Under the secondary BAU scenario, a 16% reduction in N loading is achieved by 2050, as compared with the 11% achieved under the core BAU scenario. Similarly, a 100% reduction in the agricultural N surplus under the secondary scenario provides a 57% reduction in loading by 2050, as compared with a 55% reduction under the core scenario. Under both core and secondary scenarios, however, the lag time to achieving new steady-state loading levels is still approximately 30 years, and it is clear that legacy N still has a strong influence on N loading.

Figures

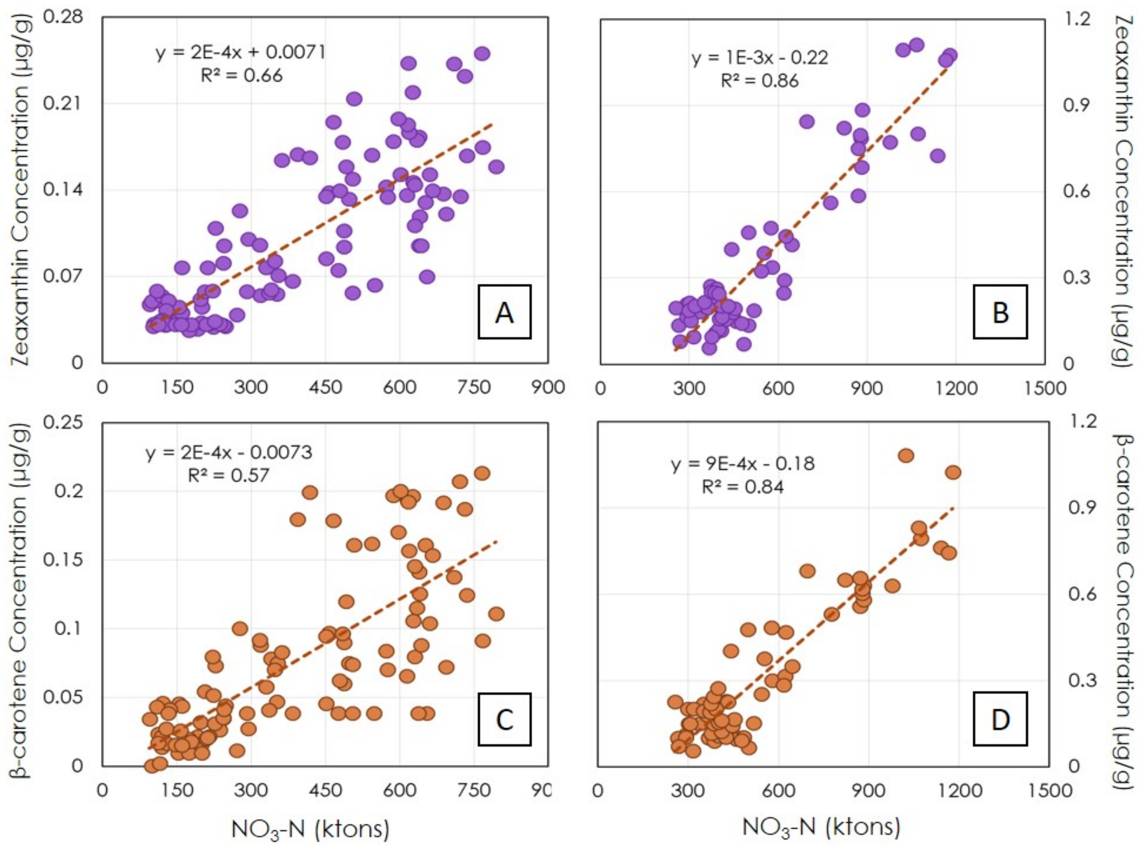

Fig. S1.

Linear correlations between predicted nitrate loads and chloropigment (zeaxanthin and ß-carotene) concentrations in sediment cores obtained from the northern Gulf of Mexico (1). Panels (A) and (C) represent the period from 1820-1930, and panels (B) and (D) that from 1930-1998. All relationships are significant ($p<0.001$)

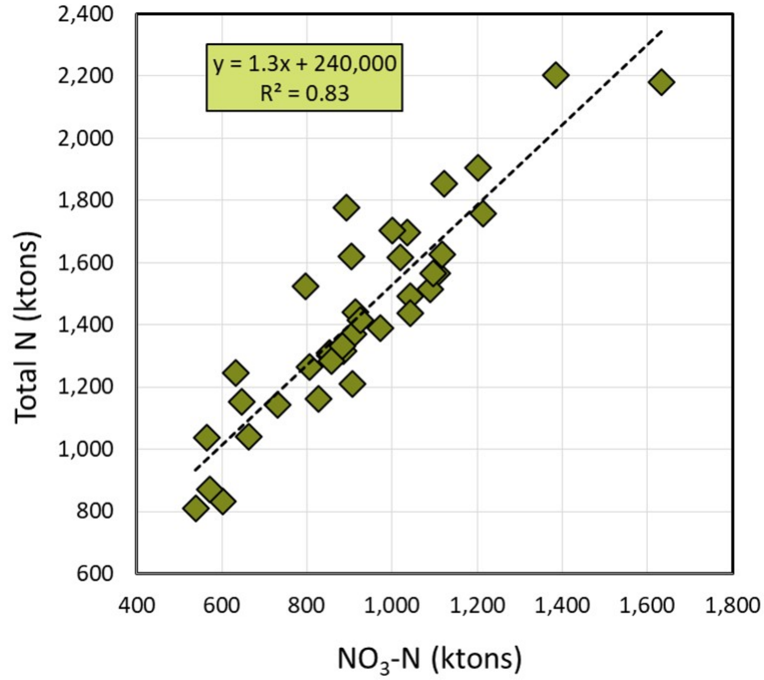

Fig. S2

Strongly linear relationship between NO3-N and total N loads in the Mississippi River Basin, 1980-2016. Loads represent the sum of the mainstem Mississippi River and the Atchafalaya River

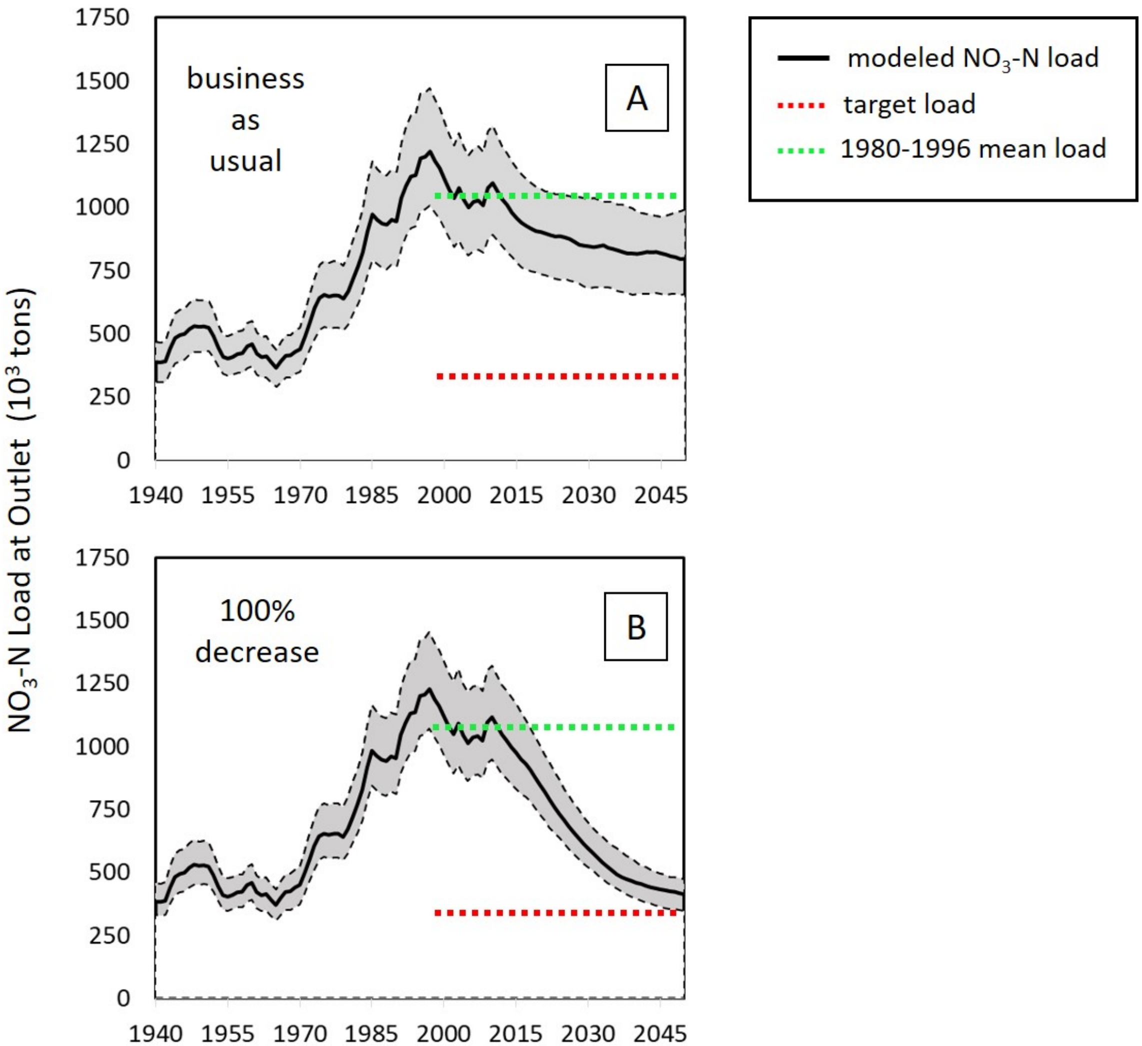

Fig. S3

Catchment-scale NO3-N loading for the Mississippi River Basin, 1940-2050, under two future scenarios: (A) business as usual and (B) a 100% decrease in the agricultural N surplus. The green dashed lines represent mean N loading for the period 1980-1996, and the red dashed lines represent target N loading to achieve an areal reduction in the summer Gulf of Mexico hypoxic zone to 5,000 km2. In these scenarios, we take into account predicted increases in population as well as decreases in atmospheric N deposition. Under these scenarios, our results suggest that reductions in N loading from 16-57% can be achieved.

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