Supplemental material for
Future riverine nitrogen export to US coastal regions: prospects for improving water quality

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There are 7 parts to this Supplemental Material:

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2: Description of NEWS2 model calibration and evaluation

3: Description of atmospheric nitrogen deposition and fertilizer inputs for future scenarios

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1. Description of NEWS2\textsubscript{US-DIN} and NEWS2\textsubscript{US-DON} Models

Dissolved inorganic nitrogen export model

The basic structure of NEWS2\textsubscript{US-DIN} is:

\[
DIN = FE_{riv} \times ((TN_{sew} \times FE_{pmt}) + (TN_{diff} \times FE_{ws}))
\]  

(1)

where \(DIN\) is the modeled annual yield per basin, \(TN_{sew}\) is TN (total nitrogen) in effluent from wastewater treatment facilities, \(FE_{pmt}\) is the portion (0-1) of \(TN_{sew}\) that is DIN, and \(TN_{diff}\) represents diffuse sources of TN that are available to be transported to the river network (all in kg N km\(^{-2}\) y\(^{-1}\)). The portion (0-1) of diffuse sources that leaches from soils to rivers is \(FE_{ws}\) and the portion (0-1) of point and diffuse sources exported by the river to the basin mouth as DIN is \(FE_{riv}\) (Table 1). Diffuse N sources include fertilizer, livestock manure, agricultural and non-agricultural N-fixation, and atmospheric deposition (Dumont, et al., 2005, Mayorga, et al., 2010).

The portion of TN in sewage effluent emitted to rivers as DIN is estimated as:

\[
FE_{pmt} = (1 - F_{hwrem})
\]  

(2)

where \(F_{hwrem}\) is the portion of N in human waste removed by wastewater treatment. Primary, secondary, and tertiary waste treatment removes 10%, 35%, and 80% of N, respectively (Van Drecht, et al., 2009). The portion of the US population connected to sewage systems and served by different levels of waste treatment was obtained from the USEPA’s Clean Watersheds Needs Survey (2008).

The portion of diffuse N sources that is transported from soils to the river network \((FE_{ws})\) is modeled as a function of runoff:

\[
FE_{ws} = b(R^a)
\]  

(3)

where \(R\) is annual runoff (m y\(^{-1}\)) and \(a\) and \(b\) are calibrated parameters that define the shape of the relationship between \(R\) and \(FE_{ws}\).
The portion of diffuse and point N sources that are transported by rivers to the coastal zone is:

\[ F_{ERV} = (1-F_{deN})(1-F_{Qrem})(1-F_{res}) \]  

(4)

where riverine sinks are denitrification \( F_{deN} \), consumptive water use \( F_{Qrem} \), and retention in reservoirs \( F_{res} \). We estimated DIN removal through denitrification \( F_{deN} \) as a function of basin area (Dumont, et al., 2005, Seitzinger, et al., 2002):

\[ F_{deN} = (m \times \ln(A) - n) \]  

(5)

where \( A \) is basin area (km\(^2\)), and \( m \) and \( n \) are fitted parameters (0.0605 and 0.0443, respectively) that were determined previously (Dumont, et al., 2005).

Nitrogen associated with water removed from rivers for irrigation or industrial uses consumptive water use is treated as permanently removed from the river system. The portion of river discharge removed for consumption \( F_{Qrem} \) is estimated as:

\[ F_{Qrem} = (Q_{nat} - Q_{wd})/Q_{nat} \]  

(6)

where \( Q_{nat} \) is modeled “natural” river discharge (Fekete, et al., 2010) and \( Q_{wd} \) surface water removed for agriculture and industry (Kenny, et al., 2009) (both in km\(^3\) y\(^{-1}\)).

Retention of DIN in reservoirs \( F_{res} \) is modeled as:

\[ F_{res} = 0.8845 \times (h/\tau)^{0.3677} \]  

(7)

where \( h \) is mean reservoir depth (meters) and \( \tau \) is the water residence time (years) for the each reservoir in the National Inventory of Dams (USACE, 2007). The aggregated \( F_{res} \) is estimated as the average retention of all reservoirs in each basin. Retention in individual basins is capped at a maximum of 0.965 as in Dumont, et al. 2005.
Dissolved Organic Nitrogen Export Model

Building on Harrison, et al. (2005), the equation for annual DON export in NEWS2US-DON is:

\[
DON = FE_{riv} \times \left( (TN_{sew} \times FE_{pnt}) + (TN_{diff} + EC_N) \times FE_{ws} \right)
\]

(8)

where \(DON\) is the modeled annual yield per basin (kg N km\(^{-2}\) y\(^{-1}\)), \(TN_{sew}\) is TN in effluent from wastewater treatment facilities, \(FE_{pnt}\) is the portion (0-1) of \(TN_{sew}\) that is DON, \(TN_{diff}\) represents diffuse sources, and \(EC_N\) is a calibrated parameter that represents background DON sources (all in kg N km\(^{-2}\) y\(^{-1}\)). Diffuse N sources for the DON model differ from that of the DIN model and include fertilizer and livestock manure minus N that is removed by plant uptake and harvest. The portion (0-1) of diffuse sources that leaches from soils to rivers is \(FE_{ws}\) and the portion (0-1) of point and diffuse sources exported by the river to the basin mouth as DON is \(FE_{riv}\) (Table 1). \(FE_{pnt}\) for DON is 0.14 as used in previous models (Mayorga, et al., 2010).

As for NEWS-DIN, the portion of diffuse sources that is transported from soils to the river network (\(FE_{ws}\)) as DON is modeled as a function of runoff using the same form as for DIN (Eq. 3), however, separate estimates of \(FE_{ws}\) were made for the DIN and DON.

The portion of DON transported by rivers to the coast is:

\[
FE_{riv} = 1-F_{Qrem}
\]

(9)

where \(F_{Qrem}\) is the portion of river discharge removed for irrigation or industry. \(F_{Qrem}\) is the same for both the DIN and DON models (Eq. 6).

Source Contributions of Riverine Export

Multiple natural and anthropogenic sources contribute to the export of nutrients at river mouths. NEWS estimates the contributions of agriculture, atmospheric deposition, biological N fixation (BNF) from non-agricultural sources, and sewage. Attribution to diffuse N sources
(agriculture, non-agricultural BNF, and atmospheric deposition) is calculated as the product of
(1) landscape-level input of each source (as in Eqs 1 and 8), (2) the land-to-water export
coefficient \( FE_{ws} \), Eq. 3), and (3) the river-system export coefficient \( FE_{riv} \), Eqs. 4 and 9).
Background DON leaching \( EC_N \) is classified as agricultural sources in proportion to the percent
cover of agricultural land in each basin. Agricultural land cover is estimated from the 2006
National Land Cover Dataset (Fry, et al., 2011). For example, if agriculture occupied 35% of
catchment, 35% of \( EC_N \) was allocated to agriculture and 65% was included with BNF in non-
agricultural areas for purposes of source attribution. Agricultural contributions to DIN and DON
reflected the removal of N by plant uptake and harvest. For example, landscape-level inputs
attributable to agriculture for DON (kg N y\(^{-1}\)) are estimated as fertilizer plus manure, minus N
removed in harvest, plus the product of \( EC_N \) and % agriculture cover. Attribution to sewage is
calculated as the product of (1) land-based sewage inputs \( TN_{sew} \), (2) the export coefficient for
sewage treatment \( FE_{pnt} \), Eq. 2), and (3) the river-system export coefficient \( FE_{riv} \), Eqs. 4 and 9).
Source contributions for DIN and DON are estimated separately and then summed and reported
as TDN for the categories of agriculture, background, atmospheric deposition, and sewage.

NEWS2 model code and user documentation are available at:
http://www.marine.rutgers.edu/globalnews/GNE/.
Model Notation

$A$  
Basin area, km$^2$

$a$  
Coefficient defining the relationship between runoff and $FE_{ws}$ (0–1)

$b$  
Coefficient defining the relationship between runoff and $FE_{ws}$ (0–1)

$DIN$  
Dissolved inorganic nitrogen yield (DIN) yield, kg N km$^{-2}$ y$^{-1}$

$DON$  
Dissolved organic nitrogen yield (DON) yield, kg N km$^{-2}$ y$^{-1}$

$EC_N$  
Calibrated parameter representing background sources of DON leaching, kg N km$^{-2}$ y$^{-1}$

$F_{deN}$  
Portion of DIN lost in the basin river network due to denitrification (0–1)

$F_{hwrem}$  
Portion of N removed from effluent by sewage treatment

$FE_{pnt}$  
Portion of $TN_{sew}$ exported by rivers as DIN (0–1)

$FE_{riv}$  
Portion of total point and nonpoint DIN or DON inputs to the river that is exported as DIN or DON, respectively, (0–1)

$FE_{ws}$  
Portion of N from diffuse sources in the watershed that leaches to the river as DIN or DON.

$F_{Qrem}$  
Portion of DIN or DON retained owing to the anthropogenic removal of (DIN- or DON-containing) river water (0–1)

$F_{res}$  
Portion of DIN retained in dammed reservoirs (0–1)

$h$  
Reservoir depth, m

$m$  
Fitted parameter in relationship between basin area (A) and river network retention ($F_{deN}$); in NEWS2US-TDN is set to equal 0.0605

$Mod_{i}$  
Modeled TDN yield, kg N km$^{-2}$ y$^{-1}$ for the $i$th basin

$n$  
Fitted parameter in relationship between basin area (A) and river network retention ($F_{deN}$); in NEWS2US-TDN is set to equal 0.0443

$Obs_{i}$  
Observed TDN yield, kg N km$^{-2}$ y$^{-1}$ for the $i$th basin

$NSE$  
Nash-Sutcliffe Efficiency, (-∞ to 1)

$Q_{act}$  
Basin discharge, km$^3$ y$^{-1}$

$Q_{nat}$  
Basin discharge prior to the construction of dams, km$^3$ y$^{-1}$

$R$  
Basin runoff, m y$^{-1}$

$\tau$  
Reservoir water residence time, y.

$TN_{diff}$  
N from diffuse water sources that is mobilized from the watershed soils and sediments, kg N km$^{-2}$ y$^{-1}$
2. Description of NEWS2 Model Calibration and Evaluation

For calibration basins, we used long-term average measured discharge and concentrations to represent 2005 conditions. Measured data were obtained from the US Geological Survey’s National Water information System (2013) from the most downstream monitoring station (Table 1, Fig. 1a). We used LoadRunner v1.2b (Booth, et al., 2007) to estimate mean annual export from measured discharge and concentration data that were collected between 1980 and 2010. Because export from the Mississippi River is one to three orders of magnitude greater than other rivers in the dataset (Table 1), there was potential for this one data point to influence model calibration. To calibrate the DIN and DON models, we used the measured data for the Arkansas-Red, Ohio-Tennessee, Missouri, and Upper Mississippi sub-basins (which together account for 95% of TDN export for the Mississippi River) from the US Geological Survey’s “Hypoxia in the Gulf of Mexico Studies” (USGS, 2013). Mean annual export for these basins is estimated using LOADEST (Runkel, et al., 2004) and data from sampling stations located at the sub-basin mouth. For rivers in the calibration dataset, long-term average runoff is estimated as long-term average discharge (km$^3$ y$^{-1}$) multiplied by catchment area (km$^2$). For all other basins, runoff and discharge estimates for year 2005 were obtained from the Water Balance Model (WBM$^{plus}$) (Fekete, et al., 2010). Both year 2030 scenarios used the same data input as year 2005 because our focus is exploring how changes in land-based N inputs, not hydrology, influence N export.

We calibrated the DIN and DON models separately using a resampling approach where 80% of the basins in the dataset were randomly selected and the best-fit parameters $a$, $b$, and $EC_N$ (Eqs. 3 and 10) were determined by maximizing Nash-Sutcliffe Efficiency (NSE). NSE is a measure of how well the linear relationship of observed and modeled data conform to unity (Nash and Sutcliffe, 1970):
\[ NSE = 1 - \frac{\sum_{i=1}^{t} (Obs_i - Mod_i)^2}{\sum_{i=1}^{t} (Obs_i - \bar{Obs}_i)^2} \]  

where \( Mod_i \) and \( Obs_i \) are the model-predicted and measurement-based estimates, respectively, for the \( i \)th basin. In contrast to the coefficient of determination \( (r^2) \), NSE values can range between negative infinity and 1. NSE values between 0 and 1 indicate model predictions are better than simply using the mean of measurements to predict export and 1 reflects perfect agreement between measurements and model estimates. The resampling routine was repeated 250 times and the final parameters were determined as the mean of the resampling iterations (Table S1). For all basins, TDN yield (kg N km\(^{-2}\) y\(^{-1}\)) and load (kg N y\(^{-1}\)) is the sum of DIN and DON yield and load, respectively (Table S1). Calibration was performed in MATLAB (MathWorks, 2007). Other analyses were performed in R (R Core Team, 2013, Zambrano-Bigiarini, 2013).
3: Description of Atmospheric Nitrogen Deposition and Fertilizer Inputs for Future Scenarios

Atmospheric Nitrogen Deposition

Rates of atmospheric N deposition resulting from fossil-fuel combustion were obtained for year 2002 from the Community Multiscale Air Quality (CMAQ) model, which estimates deposition of oxidized (NO$_x$) and reduced (NH$_y$) inorganic N (USEPA, 2013). Total inorganic N deposition is comprised of NO$_x$ (78%) and NH$_y$ (22%). To account for deposition of organic N compounds, we increased CMAQ-derived values by 30% as recommended by Sobota et al. (2013). For year 2030, estimated NO$_x$ deposition originating from electric power generation (accounting for 24% of total NO$_x$ emissions) was reduced by 48% for both BAU and AMB in a manner consistent with currently enacted provisions of the Clean Air Interstate Rule (USEPA, 2005). Under AMB, year 2030 mobile NO$_x$ emissions decreased 40% from 2005 levels in a manner consistent with proposed, but not yet adopted regulations aimed at controlling motor vehicle pollution (76% of total NO$_x$ emissions) as suggested by the Science Advisory Board (SAB) of the USEPA (2011). In addition, the SAB identified opportunities to reduce NH$_y$ emissions from livestock by 30% through improved manure management (SAB, 2011).

Examples of some practices include the installation of storage covers for manure storage tanks, lagoons, and pits or mixing sawdust litter with swine manure.

Nitrogen Fertilizer Inputs

We obtained historical data for consumption of nitrogen fertilizers (1990-2010) from the Economic Research Service of the US Department of Agriculture (USDA-ERS, 2011) (Fig. S1a).

We obtained historical US grain production for the same periods from the USDA Economic Research Service (USDA-ERS, 2014). Bushels of corn, barley, oats, and sorghum were
converted to weights using standard conversion factors (USDA-ERS, 1992). We evaluated the logarithmic relationship between grain production and fertilizer consumption using Sigma Plot (Systat Software Inc., 2011) (Fig. S1b). The logarithmic model explained ~60% of the variation in the data:

\[ N_{Fertilizer} = 0.36 \times \ln(Production) - 1.9 \]  
(11)

where \( N_{Fertilizer} \) is fertilizer consumption (Tg N y\(^{-1}\)) and \( Grain\ Production\) is Tg y\(^{-1}\) of grain produced.

We used year 2030 scenarios developed by the International Food Policy Research Institute (IFPRI) to estimate the percentage growth in grain production between 2005 and 2030 (Msangi and Rosegrant, 2011) and then applied these estimates to Eq. 11 to estimate N fertilizer usage. IFPRI’s modeling approach considers population growth, dietary preferences, food prices, and international trade. The base scenario (used for BAU) estimated a 45% increase in grain production to support a 7% increase in meat consumption by Americans and export of grain products to other regions (for example to China, where meat consumption increases 50% between 2000 and 2030). Under the low-meat diet scenario (used for AMB), meat consumption decreases by half in the US because of broad adoption of healthier diets. Under this scenario, year 2030 meat consumption in the US still remains >50% greater than global average per capital consumption. US grain production increases 37% in this scenario, reflecting export to meet demand for feed grains in India and China, where meat consumption increases by more than 70% between 2000 and 2030. Under IFPRI’s scenarios, N fertilizer usage for BAU and AMB increases by 6% and 5%, respectively, between 2005 and 2030. In the past few decades, rates of fertilizer use have grown more slowly than grain production rates (Fig S1b) due to improved crop nutrient use efficiencies (Cassman, et al., 2002).
4. References for Supplemental Materials


MathWorks. 2007. MATLAB 7.5.0. Natick, MA, USA.


Systat Software Inc. 2011. Sigmaplot 12. San Jose, CA, USA.


## 5. Calibrated parameters for NEWS2\textsubscript{US-DIN} and NEWS2\textsubscript{US-DON} models

Table S1. Values are mean and standard error (S.E.) that were calculated from 250 resampling iterations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>NEWS2\textsubscript{US-DIN}</th>
<th>S.E.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>0.70</td>
<td>0.01</td>
</tr>
<tr>
<td>$b$</td>
<td>0.42</td>
<td>0.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>NEWS2\textsubscript{US-DON}</th>
<th>S.E.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>0.48</td>
<td>0.01</td>
</tr>
<tr>
<td>$b$</td>
<td>0.06</td>
<td>0.00</td>
</tr>
<tr>
<td>$EC_N$</td>
<td>2,386</td>
<td>54</td>
</tr>
</tbody>
</table>
6. Results of sensitivity analysis

Table S2. Values are the mean % change in modeled TDN yield for all US basins resulting from increasing and decreasing individual model components by 5% and 10%. Model components are common to both the NEWS-DIN and NEWS-DON sub-models unless denoted “(DIN)" or “(DON)".

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Mean % change in TDN yield</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10%</td>
</tr>
<tr>
<td><strong>Model Inputs</strong></td>
<td></td>
</tr>
<tr>
<td>Runoff</td>
<td>4.2</td>
</tr>
<tr>
<td>Fertilizer</td>
<td>3.4</td>
</tr>
<tr>
<td>N removed in crop harvest</td>
<td>-2.1</td>
</tr>
<tr>
<td>Atmospheric deposition</td>
<td>1.8</td>
</tr>
<tr>
<td>Crop BNF</td>
<td>1.5</td>
</tr>
<tr>
<td>Per capita N in sewage</td>
<td>1.5</td>
</tr>
<tr>
<td>Background BNF</td>
<td>1.1</td>
</tr>
<tr>
<td>Manure</td>
<td>0.7</td>
</tr>
<tr>
<td><strong>Retention Factors</strong></td>
<td></td>
</tr>
<tr>
<td>(F_{riv})</td>
<td>10.0</td>
</tr>
<tr>
<td>(F_{ws} ) (DIN)</td>
<td>5.2</td>
</tr>
<tr>
<td>(F_{ws} ) (DON)</td>
<td>3.4</td>
</tr>
<tr>
<td>(F_{DeN} ) (DIN)</td>
<td>-2.4</td>
</tr>
<tr>
<td>(F_{Qrem})</td>
<td>-1.1</td>
</tr>
<tr>
<td>(F_{pnt} )</td>
<td>0.8</td>
</tr>
<tr>
<td>(F_{res} ) (DIN)</td>
<td>-0.3</td>
</tr>
<tr>
<td><strong>Calibrated Parameters</strong></td>
<td></td>
</tr>
<tr>
<td>(b ) (DIN)</td>
<td>5.2</td>
</tr>
<tr>
<td>(a ) (DIN)</td>
<td>-3.8</td>
</tr>
<tr>
<td>(b ) (DON)</td>
<td>3.4</td>
</tr>
<tr>
<td>(EC_N ) (DON)</td>
<td>2.1</td>
</tr>
<tr>
<td>(a ) (DON)</td>
<td>-1.9</td>
</tr>
</tbody>
</table>
7. Development of model inputs for fertilizer

Figure S1. a. Trends in US fertilizer consumption and grain production (1990-2010). b. Logarithmic regression to estimate future fertilizer use based on estimated grain production (solid line is regression for period 1990-2010, dashed line is estimated future condition).