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# Estimating "Mean-State" July (1985–2007) $N_2O$ Fluxes in the Northern Gulf of Mexico Hypoxic Region: Variation, Distribution, and Implication

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Along the Texas-Louisiana continental shelf in the northern Gulf of Mexico (nGOM) is a region frequently referred to as the "Dead Zone" due to severe oxygen depletion caused by eutrophication. Owing to its characteristics, it is expected to be an oceanic source region for nitrous oxide ($N_2O$) emissions to the atmosphere during the hypoxic events. However, there is little known about whether the nGOM is source or sink region for atmospheric $N_2O$. Here, we estimate "mean-state" July (1988-2007) $N_2O$ fluxes from the nGOM, using simple modeling approach. The estimated mean $N_2O$ fluxes for July across the air-sea interface ranged from $+0.9 \pm 11.7$ to $+14.3 \pm 15.0$ μmol $N_2O$ $m^{-2}$ $d^{-1}$ with a mean value of $+6.1 \pm 9.0$ μmol $N_2O$ $m^{-2}$ $d^{-1}$ (+: sea → air). Our estimates were in reasonable agreement with the few available summer measurements, and suggested that the nGOM hypoxic region acts as a source of atmospheric $N_2O$ during the month of July between 1985 and 2007. Local regions influenced by the Mississippi and Atchafalaya Rivers showed higher $N_2O$ fluxes to the atmosphere than other regions. If the area affected by nutrient loading and the resulting hypoxia expands, the nGOM may become an even stronger oceanic $N_2O$ "hot spot" source region. Therefore, future study, based on *in-situ* observations, is necessary to elucidate $N_2O$ dynamics in the nGOM hypoxic region.

**Keywords: the northern Gulf of Mexico, $N_2O$, hypoxia, positive climate feedback, air-sea exchange**

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## INTRODUCTION

One of the most important nitrogen cycle processes directly linked to climate change is nitrous oxide ($N_2O$) production, owing to its strong greenhouse effect and high ozone depletion potential (IPCC, 2013). Atmospheric $N_2O$ concentrations rapidly increased during the Anthropocene (~1760 to present) due to human activities (Weiss, 1981; Machida et al., 1995; Battle et al., 1996). Additionally, while land-based sources are important, the oceans are one of the most important sources for atmospheric $N_2O$ (Nevison et al., 1995, 2003; Seitzinger et al., 2000; Bange, 2006; Hirsch et al., 2006) accounting for ~35% (3.8 Tg N $yr^{-1}$) of the total production from natural sources (11.0 Tg N $yr^{-1}$) (IPCC, 2013). Although small in area, coastal regions are responsible for a significant fraction of the total oceanic $N_2O$ emissions (Bange et al., 1996; IPCC, 2013).

The northern Gulf of Mexico (nGOM) along the Texas-Louisiana continental shelf area (**Figure 1**) is frequently referred to as a "Dead Zone" due to severe oxygen depletion caused by eutrophication via river inputs (i.e., the Atchafalaya and Mississippi rivers), leading to high biological production and fast remineralization rates (Justić et al., 1995; Turner and Rabalais, 2004). As a result, hypoxia (i.e., $[O_2] \leq 2\,mg\ L^{-1} \approx 63\,\mu M$) develops every summer season over extensive regions of the nGOM (Dagg et al., 2007). The limited dissolved $N_2O$ concentrations measurements available in the nGOM (available for September 2007, April, July, and August 2008 to date) have shown the area to be a significant source of atmospheric $N_2O$ (Visser, 2009; Walker et al., 2010). Since microbial $N_2O$ production is enhanced during hypoxic conditions and the hypoxic area has extended during recent years (Diaz and Rosenberg, 2008; Rabalais et al., 2009; Codispoti, 2010; Naqvi et al., 2010), the nGOM is assumed to be an oceanic source region for $N_2O$ emissions to the atmosphere. However, little is known about the temporal evolution of $N_2O$ fluxes in the nGOM hypoxic region. Further, the limited available observation records may be insufficient to reach conclusions about whether the nGOM is a net source region for atmospheric $N_2O$ because coastal oceans tend to display a high degree of variability (Gruber, 2015). High variability and limited observations are issues faced widely throughout the coastal oceans research community.

Recently, Kim et al. (2013) developed a simple model that estimates bottom-water $N_2O$ concentrations using an empirically based tri-linear $\Delta N_2O$ (i.e., excess $N_2O$, which is mainly determined by nitrification and denitrification as the major microbial production and consumption pathways) relationship associated with dissolved oxygen ($O_2$) concentrations and presented the evolution of bottom-water $N_2O$ concentrations in the nGOM for the month of July between 1985 and 2007. However, they did not extend to the $N_2O$ flux study to determine whether the nGOM is a source (+: ocean→ atmosphere) or sink (−: atmosphere→ ocean) for atmospheric $N_2O$. The way that the model data (i.e., the bottom-water $N_2O$ concentrations estimated for July 1985–2007) were combined along with the application of some further reasonable assumptions provides an opportunity to reconstruct a time-series of the $N_2O$ fluxes to the atmosphere from the nGOM. Therefore, the main purpose of this study was to (1) present an estimate of the temporal evolution of July $N_2O$ fluxes from the nGOM, and (2) determine whether the nGOM is a net source or sink region for atmospheric $N_2O$ for the month of July from 1985 to 2007. Note that our study is an extension of Kim et al. (2013) with a focus on July $N_2O$ flux dynamics in the nGOM.

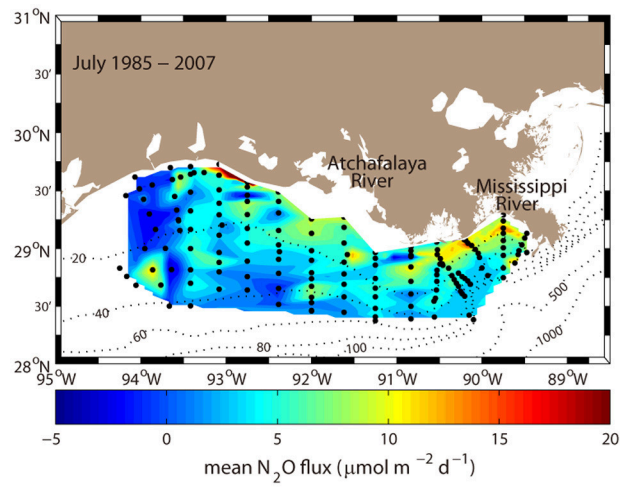


**FIGURE 1 |** Spatial distribution of the July mean $N_2O$ flux averaged from 1985 to 2007 (excluding 1988–1990) with the bathymetry contours (black dotted lines; unit of meters) in the nGOM. Black dots indicate the hydrographic stations used in our analysis.

# METHODS

## Data, Approach, and Limitation

Recently, Kim et al. (2013) estimated the summer (July) bottom-water $N_2O$ concentrations using a conceptual $N_2O$ biogeochemical model, based on the summer Texas-Louisiana shelf-wide hydrographic datasets observed for the month of July between 1985 and 2007 (excluding July 1988-1990 due to lack of available data). The bottom-water $N_2O$ concentrations ($[N_2O]_{est}^{bottom}$) were estimated using an empirically derived $\Delta N_2O/O_2$ relationship as follows:

$$[N_2O]_{est}^{bottom} = \Delta N_2O + [N_2O]_{eq}^{(T,S)}, \quad (1)$$

$$\Delta N_2O = \alpha\left(\frac{nmol\,N_2O}{\mu mol\,O_2}\right)\cdot AOU + \beta\left(\frac{nmol\,N_2O}{\mu mol\,N}\right)\cdot \Delta N_{deni} - \gamma\left(\frac{nmol\,N_2O}{\mu mol\,N}\right)\cdot N_{deni}, \quad (2)$$

where $\Delta N_2O$ is the concentration determined by microbial processes (i.e., nitrification and denitrification by bacteria and archaea), $[N_2O]_{eq}^{(T,S)}$ is the $N_2O$ atmospheric equilibrated value with atmosphere (details in Equation 4 below), AOU is the apparent oxygen utilization—the difference between the measured $O_2$ concentration and the $O_2$ equilibration value (i.e., $[O_2]_{eq}^{(T,S)} - [O_2]_{measured}$), the α coefficient indicates the relationship between $\Delta N_2O$ and $AOU$, and the $\beta$ and $\gamma$ coefficients are the relationships between $\Delta N_2O$ and the amount of denitrification ($\Delta N_{deni}$) that is the loss of nitrate ($NO_3^-$) as a consequence of denitrification. More information about the estimation of bottom-water $N_2O$ concentrations can be found in Kim et al. (2013).

To evaluate whether the nGOM is a net source or sink for atmospheric $N_2O$ during the month of July, we calculated the $N_2O$ fluxes for July from 1985 to 2007 from the nGOM using the July surface-water $N_2O$ concentrations derived from the results of bottom-water $N_2O$ concentrations simulated by Kim et al. (2013) in conjunction with the $N_2O$ exchange rates obtained from the air-sea gas formulations. The summer Texas-Louisiana shelf-wide hydrographic datasets used in our analysis are available at http://www.nodc.noaa.gov and http://www.aoml.noaa.gov.

During the summer, hypoxic conditions develop over extensive regions in the nGOM implying that the water-column stratification is strong. Visser (2009) reported that the mean surface and bottom $N_2O$ concentrations were 6.3 ± 0.9 and 11.0 ± 7.0 nmol $L^{-1}$ in July 2008 (max bottom depth < ~30 m), respectively, indicating a large difference in the $N_2O$ concentration between the surface and bottom waters (i.e., ~57% less in surface waters compared to bottom waters). In this study, we estimated the surface $N_2O$ concentrations ($[N_2O]_{est}^{surface}$) as follows:

$$[N_2O]_{est}^{surface} = [N_2O]_{est}^{bottom} \times 0.57, \quad (3)$$

where $[N_2O]_{est}^{bottom}$ is the estimated bottom-water $N_2O$ concentration by Kim et al. (2013).

Implicit in our approach is that the constant was uniformly applied to generate the surface-water $N_2O$ concentrations. In spite of this approach, our results may provide a baseline for future $N_2O$ studies in the nGOM, where is expected to be a significant $N_2O$ source (sea to air) region due to the extending/strengthening the hypoxic area (Rabalais et al., 2009; Visser, 2009). Therefore, we emphasize that here, the July $N_2O$ fluxes estimated from the following section are the mean values averaged from the hydrographic stations (i.e., $\frac{\sum_{i=1}^{n}[N_2O\ flux]_{est}^{i}}{n}$, where $i$ is the July estimate at one station, and $n$ is the number of total estimates for individual year from 1985 to 2007), and thus could be roughly considered as an upper limit of the $N_2O$ fluxes for July in the nGOM. Although the measurements were collected during a different time window, our estimates were validated by comparing the available summer measurements in the study area to date (see **Figure 2**).

## Estimation of $N_2O$ Flux

We used the air-sea gas exchange equation to estimate the $N_2O$ flux as follows:

$$N_2O\ flux = k_w \left([N_2O]_{est}^{surface} - [N_2O]_{eq}^{(T,S)}\right), \quad (4)$$

where $k_w$ is the gas transfer velocity (cm $h^{-1}$), and $[N_2O]_{eq}^{(T,S)}$ is the concentration of $N_2O$ in equilibrium with the atmosphere and is calculated as:

$$[N_2O]_{eq}^{(T,S)} = x' \times \beta \times P, \quad (5)$$

where $x'$ is the mean atmospheric $N_2O$ dry mole fraction (ppb) for July, $\beta$ is the $N_2O$ Bunsen solubility (mol $L^{-1}$ $atm^{-1}$) that is determined from the seawater temperature and salinity relationship (Weiss and Price, 1980), and $P$ is the ambient pressure which was set to 1 atm. As further information, the atmospheric $N_2O$ dry mole fractions (i.e., $x'$) during the study

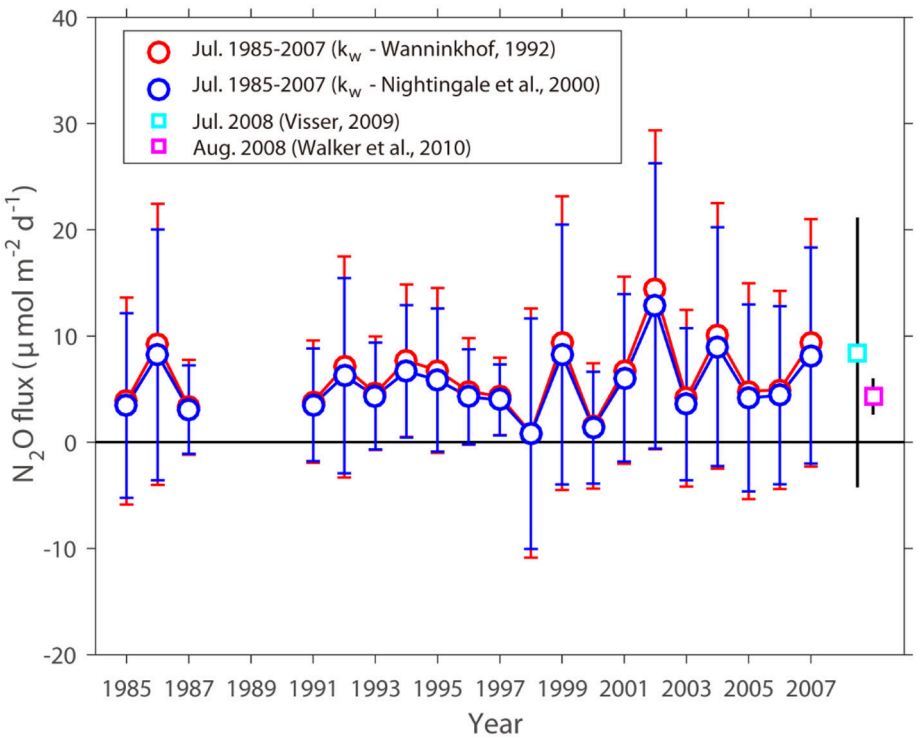


**FIGURE 2 |** Temporal variation of the estimated July $N_2O$ flux during the 1985–2007 study period (excluding 1988–1990) in the nGOM. Red circles are the estimated July $N_2O$ fluxes from this study using the gas transfer velocity ($k_W$) of Wanninkhof (1992), blue circles are the estimated $N_2O$ fluxes from this study using $k_W$ of Nightingale et al. (2000), the cyan square is the measured $N_2O$ fluxes in July 2008 by Visser (2009), and the pink square is the measured $N_2O$ flux in August 2008 by Walker et al. (2010). Error bars indicate the standard deviations from the mean.

period (July 1985–2007) specific to the nGOM did not exist, and therefore the mean atmospheric $N_2O$ dry mole fractions observed during this period over the full northern hemisphere NOAA/ESRL halocarbons program were used instead (http://www.esrl.noaa.gov/).

Several model approaches have been published to estimate the gas transfer velocity ($k_w$) from wind speed (e.g., Liss and Merlivat, 1986; Wanninkhof, 1992; Wanninkhof and McGillis, 1999; Nightingale et al., 2000). To facilitate the comparison of our results with the previous studies, we follow the approach of Visser (2009) and Walker et al. (2010) who used the Wanninkhof (1992) and Nightingale et al. (2000) air-sea exchange models ($k_w^{W1992}$ and $k_w^{N2000}$, respectively) as follows:

$$k_w^{W1992} = 0.31 \times U_{10}^2 \times (Sc/660)^{-0.5}, \quad (6)$$

$$k_w^{N2000} = \left(0.333 \cdot U_{10} + 0.222 \cdot U_{10}^2\right) \times (Sc/600)^{-0.5}, \quad (7)$$

both $k_w$ models require estimates of the wind speed at a 10 m height ($U_{10}$) and Schmidt numbers ($Sc$). The $Sc$ number was calculated as the kinematic viscosity of seawater (Siedler and Peters, 1986) divided by the diffusion coefficient of $N_2O$ in seawater (Rhee, 2000). The $U_{10}$ wind speeds were not measured during the Texas-Louisiana shelf-wide hydrographic cruises. Instead, the mean wind speeds for each July from 1987 to 2007 were obtained for the nGOM from the NOAA Blend Sea Winds product database (BSW, http://www.ncdc.noaa.gov/). Using data from the BSW, we also computed a 20-year mean July $U_{10}$ of 4.9 $\pm$ 0.5 m $s^{-1}$ that was used for July 1985 and 1986 because no data were available from the BSW for these months.

The mean difference in the estimated July $N_2O$ flux between the two models was 0.7 μmol $N_2O$ $m^{-2}$ $d^{-1}$ (**Table 1**). The resulting July $N_2O$ flux estimates, which are discussed in the next section, satisfactory display the "mean-state" spatial distribution and temporal variation in the nGOM (**Figures 1**, **2**) despite the strong variability expected in a coastal region and the potentially high degree of uncertainty due to implicit in our approach. The estimated $N_2O$ fluxes for the month of July 1985-2007 are summarized in **Table 1**.

**TABLE 1 |** Summary of July mean wind speeds ($U_{10}$; m $s^{-1}$) and estimated mean $N_2O$ fluxes for July in the nGOM.

| Year | $U_{10}$ | $N_2O$ flux (μmol $N_2O$ $m^{-2}$ $d^{-1}$) | |
|---|---|---|---|
| (July) | (m $s^{-1}$) | $k_W$ (Wanninkhof, 1992) | $k_W$ (Nightingale et al., 2000) |
| 1985 | *4.89 ± 0.53 | 3.90 ± 9.70 | 3.50 ± 8.70 |
| 1986 | *4.89 ± 0.53 | 9.20 ± 13.2 | 8.20 ± 11.8 |
| 1987 | 4.08 ± 0.58 | 3.30 ± 4.50 | 3.10 ± 4.20 |
| 1988 | 5.20 ± 0.46 | ND | ND |
| 1989 | 5.45 ± 0.84 | ND | ND |
| 1990 | 4.40 ± 0.61 | ND | ND |
| 1991 | 4.29 ± 0.66 | 3.80 ± 5.70 | 3.50 ± 5.30 |
| 1992 | 5.11 ± 0.62 | 7.10 ± 10.4 | 6.30 ± 9.20 |
| 1993 | 3.95 ± 0.72 | 4.60 ± 5.30 | 4.30 ± 5.00 |
| 1994 | 5.51 ± 0.68 | 7.70 ± 7.20 | 6.70 ± 6.20 |
| 1995 | 5.55 ± 0.79 | 6.80 ± 7.80 | 5.90 ± 6.70 |
| 1996 | 4.88 ± 0.53 | 4.80 ± 5.00 | 4.30 ± 4.50 |
| 1997 | 4.32 ± 0.64 | 4.30 ± 3.60 | 4.00 ± 3.30 |
| 1998 | 4.23 ± 0.49 | 0.90 ± 11.7 | 0.80 ± 10.8 |
| 1999 | 5.06 ± 0.28 | 9.30 ± 13.8 | 8.30 ± 12.2 |
| 2000 | 4.87 ± 0.48 | 1.50 ± 5.90 | 1.40 ± 5.30 |
| 2001 | 4.84 ± 0.51 | 6.80 ± 8.80 | 6.10 ± 7.90 |
| 2002 | 4.83 ± 0.52 | 14.3 ± 15.0 | 12.8 ± 13.4 |
| 2003 | 5.74 ± 0.43 | 4.10 ± 8.30 | 3.60 ± 7.20 |
| 2004 | 4.74 ± 0.49 | 10.0 ± 12.5 | 9.00 ± 11.2 |
| 2005 | 5.57 ± 0.51 | 4.80 ± 10.2 | 4.20 ± 8.80 |
| 2006 | 4.75 ± 0.50 | 4.90 ± 9.30 | 4.40 ± 8.40 |
| 2007 | 5.40 ± 0.54 | 9.40 ± 11.6 | 8.20 ± 10.2 |
| Mean | 4.89 ± 0.53 | 6.10 ± 9.00 | 5.40 ± 8.00 |
| 2008 | | †8.50 ± 12.7 | ‡4.30 ± 1.70 |

*The mean was calculated as* $\frac{\sum_{i=1}^{n}[N_2O\ flux]_{est}^{i}}{n}$*, where i was the July estimate at one station, and n was the number of total estimates for an individual year from 1985 to 2007. Errors (±) indicate the standard deviations from the mean.*

**The mean $U_{10}$ value averaged from 1987 to 2007 is used for 1985 and 1986.*

*†The $N_2O$ flux measured in July 2008 by Visser (2009).*

*‡The $N_2O$ flux measured in August 2008 by Walker et al. (2010).*

*ND: not determined.*

## RESULTS AND DISCUSSION

### Spatial and Temporal Dynamics of $N_2O$ Flux

To determine whether the nGOM is a net source or sink of atmospheric $N_2O$ during the summer, we reconstructed the temporal variation of the nGOM $N_2O$ fluxes for July 1985-2007 and included for comparison recent estimates based on direct measurements of dissolved $N_2O$ by Visser (2009) (+8.5 ± 12.7 μmol $N_2O$ $m^{-2}$ $d^{-1}$ in July 2008) and Walker et al. (2010) (+4.3 ± 1.7 in August 2008) (**Figure 2**). Additionally, Visser (2009) also reported $N_2O$ fluxes measured in September 2007 (+66.4 ± 46.7 μmol $N_2O$ $m^{-2}$ $d^{-1}$) and April 2008 (−5.2 ± 4.0 μmol $N_2O$ $m^{-2}$ $d^{-1}$). The estimated $N_2O$ fluxes for July across the air-sea interface ranged from +0.9 ± 11.7 (July 1998) to +14.3 ± 15.0 μmol $N_2O$ $m^{-2}$ $d^{-1}$ (July 2002) with a mean value of +6.1 ± 9.0 μmol $N_2O$ $m^{-2}$ $d^{-1}$ using $k_w^{W1992}$ (+0.8 ± 10.8 to +12.8 ± 13.4 μmol $N_2O$ $m^{-2}$ $d^{-1}$ with the mean value of +5.4±8.0 μmol $N_2O$ $m^{-2}$ $d^{-1}$ using $k_w^{N2000}$) (**Table 1**), equivalent to ∼0.04–0.6 Gg $N_2O$ $July^{-1}$ (G: Giga, $10^9$) extrapolated to the size of study area (≈ $3.24\times10^{10}$ $m^2$). Our July estimates were in reasonable agreement with the measured Visser (2009) and Walker et al. (2010) summer nGOM values (i.e., +8.5 ± 12.7 and +4.3 ± 1.7 μmol $N_2O$ $m^{-2}$ $d^{-1}$ in July and August 2008, respectively) (**Figure 2** and **Table 1**). None of the July estimates were as large as the Visser (2009) September 2007 value (i.e., +66.4 ± 46.7 μmol $N_2O$ $m^{-2}$ $d^{-1}$) and only one (i.e., −5.2 ± 4.0 μmol $N_2O$ $m^{-2}$ $d^{-1}$) indicated the possibility of a sink for spring as suggested by Visser (2009).

Under low oxygen conditions, denitrification ($NO_3^- \rightarrow NO_2^- \rightarrow N_2O/N_2$), which is a dissimilatory process that uses nitrate as an electron acceptor instead of oxygen (Brandes et al., 2007), acts as a source (i.e., production under hypoxic condition: $0.14<O_2\leq2$ mg $L^{-1}$) or a sink (i.e., consumption under suboxic-anoxic condition: $0\leq O_2\leq0.14$ mg $L^{-1}$) depending on the $O_2$ concentrations (Naqvi et al., 2010; Kim et al., 2013). In July

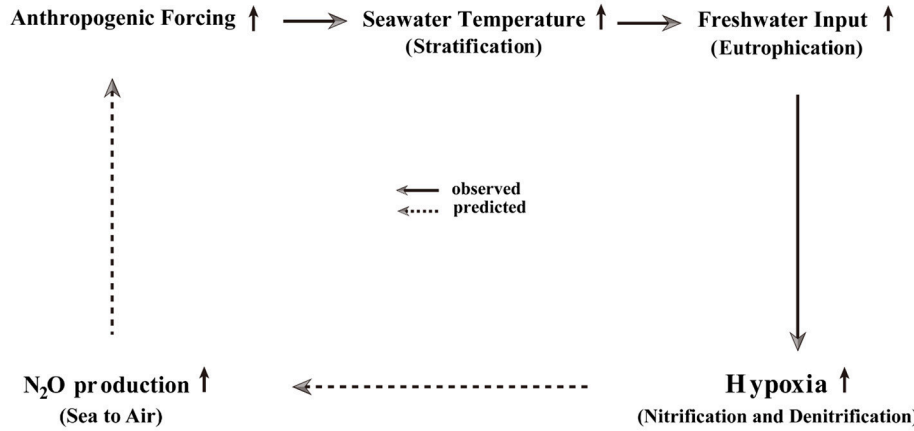


**FIGURE 3 |** A conceptual feedback scheme for future $N_2O$ emission in the nGOM, based on physical changes currently occurring in the nGOM.

1998, $N_2O$ consumption from denitrification was significant (Kim et al., 2013), therefore, the estimated $N_2O$ flux was the lowest during the study period (**Figure 2** and **Table 1**). In July 1987 ($3.3 \pm 4.5$ μmol $N_2O$ $m^{-2}$ $d^{-1}$ using $k_w^{W1992}$) and 2000 ($1.5 \pm 5.9$ μmol $N_2O$ $m^{-2}$ $d^{-1}$ using $k_w^{W1992}$), the estimated $N_2O$ fluxes were relatively low compared to other years (**Figure 2** and **Table 1**). These features may be explained by the magnitude of the remineralization (i.e., primary source for $N_2O$ production via nitrification process) in 1987 and 2000 that was lower than other study years (Kim and Min, 2013; Kim et al., 2013), due to the low biological production driven by less discharges from the Atchafalaya-Mississippi Rivers (sum of January to July) (Walker and Rabalais, 2006). For example, the total river discharge in 1987 and 2000 was 0.15 and 0.12 *Sverdrup* (*Sv*, which is a unit of water volume transport and is given as $10^6$ $m^3$ $s^{-1}$), respectively, and was lower than the mean $0.19 \pm 0.04$ *Sv* Value. As a result, the sizes of hypoxia in July 1987 ($6.7 \times 10^9$ $m^2$) and 2000 ($4.4 \times 10^9$ $m^2$) were smaller compared to the mean value ($14.4 \pm 5.1 \times 10^9$ $m^2$) averaged during the study periods (July 1985–2007) (https://gulfhypoxia.net/). In July 2002, the estimated $N_2O$ flux was highest value during the study periods (**Figure 2** and **Table 1**). In contrast to 1998, denitrification acted as a source for $N_2O$ production in 2002, and also the size of hypoxia ($22 \times 10^9$ $m^2$) was the largest during the study periods, indicating that the magnitude of remineralization was high (Kim and Min, 2013). In addition, the total river discharge was relatively high (0.20 *Sv*). Overall, these conditions might have driven the highest estimated $N_2O$ flux in July 2002.

Further these nGOM July $N_2O$ flux estimates were comparable to those published for other marine $O_2$-deficient systems (i.e., open-ocean hypoxic zones: 2.7–4.5 μmol $N_2O$ $m^{-2}$ $d^{-1}$, naturally-formed continental-margin hypoxic zones: 10–50 μmol $N_2O$ $m^{-2}$ $d^{-1}$, anthropogenically-formed hypoxic zones: 3.3–17.1 μmol $N_2O$ $m^{-2}$ $d^{-1}$, enclosed anoxic basins: 1.6–5.2 μmol $N_2O$ $m^{-2}$ $d^{-1}$) [see Table 3 of (Naqvi et al., 2010), and references therein]. The estimated July $N_2O$ fluxes suggest that the nGOM hypoxic region acts as a source of atmospheric $N_2O$ in July with a mean of $6.1 \pm 9.0$ μmol $N_2O$ $m^{-2}$ $d^{-1}$ using $k_w^{W1992}$ ($5.4 \pm 8.0$ μmol $N_2O$ $m^{-2}$ $d^{-1}$ using $k_w^{N2000}$) (**Table 1**).

A contour map illustrating the spatial distribution of the mean July nGOM $N_2O$ fluxes averaged from 1985 to 2007 (excluding 1988–1990 due to the lack of available data) was used to investigate the spatially homogeneity (**Figure 1**). Relatively high $N_2O$ fluxes ($> \sim$10 μmol $N_2O$ $m^{-2}$ $d^{-1}$) were distributed along inshore regions ($< \sim$20 m isobaths), whereas relatively low $N_2O$ fluxes ($< \sim$10 μmol $N_2O$ $m^{-2}$ $d^{-1}$) occupied a wider offshore area ($> \sim$20 m isobaths). It is noted that the regions influenced by the Atchafalaya and Mississippi Rivers displayed particularly high $N_2O$ fluxes compared to other areas of the nGOM (**Figure 1**). Nutrient loading from river inputs stimulates phytoplankton blooms in these inshore areas downstream of the inflow (Walker and Rabalais, 2006). The anthropogenically supported blooms eventually lead to hypoxia through remineralization processes (Pakulski et al., 2000; Dagg and Breed, 2003; Fry et al., 2015). Remineralization (i.e., nitrification processes) is primarily responsible for the $N_2O$ production ($> \sim$90%) (Kim et al., 2013), therefore, the distribution of the $N_2O$ fluxes largely reflect the magnitude of oxygen consumption in the nGOM.

## Future $N_2O$ Emissions From the nGOM: A Potential Positive Climate Feedback Loop

A multitude of changes that are occurring in the nGOM may directly and/or indirectly influence prediction of future $N_2O$ emissions from the nGOM (**Figure 3**). Summer surface and bottom water temperatures have increased significantly in the study area over the period of 1985–2007 (Kim and Min, 2013). These increases in seawater temperature have enhanced stratification in the water column. Freshwater inflows have also increased into the nGOM (Justić et al., 2003, 2005), leading to coastal eutrophication due to increased nutrient loading. As a consequence of the increases in both stratification and eutrophication, the hypoxic layer thickness in the nGOM has increased (Obenour et al., 2013). The resulting nitrification and denitrification strengthening processes (Kim et al., 2013) that are yielding higher $N_2O$ concentrations under hypoxic

conditions, may lead to further increases in $N_2O$ outgassing from the nGOM. The results presented here suggest that the nGOM is a net summertime source region (i.e., +: sea → air) for atmospheric $N_2O$ (**Table 1**) as a strong greenhouse gas. Based on a significant correlation between $N_2O$ production and the size of the hypoxic region (Kim et al., 2013), we expect that in the future, if the areas affected by nutrient loading and the resulting hypoxia expand, the nGOM may be even more effective oceanic $N_2O$ "hot spot" source region. Therefore, we suggest that regular surveys of dissolved $N_2O$ measurements in the nGOM are needed to improve $N_2O$ flux estimates from the nGOM and to decipher the production pathways.

## SUMMARY

We estimated "mean-state" July (1988–2007) $N_2O$ fluxes from the nGOM and investigated whether the nGOM is a net source (+: sea to air) or a net sink (–: air to sea) for atmospheric $N_2O$, using simple modeling approach. The estimated mean $N_2O$ fluxes for July across the air-sea interface ranged from $+0.9 \pm 11.7$ to $+14.3 \pm 15.0$ μmol $N_2O$ $m^{-2}$ $d^{-1}$ with a mean value of $+6.1 \pm 9.0$ μmol $N_2O$ $m^{-2}$ $d^{-1}$ using $k_w^{W1992}$ ($+0.8 \pm 10.8$ to $+12.8 \pm 13.4$ μmol $N_2O$ $m^{-2}$ $d^{-1}$ with the mean value of $+5.4 \pm 8.0$ μmol $N_2O$ $m^{-2}$ $d^{-1}$ using $k_w^{N2000}$) suggesting that the nGOM hypoxic region acts as a source of atmospheric $N_2O$ during July. Spatially, local regions influenced by the Mississippi and Atchafalaya Rivers showed higher $N_2O$ fluxes to the atmosphere than other regions. If the area affected by hypoxia expands (due to enhanced nitrification/denitrification processes), the nGOM may become an even stronger oceanic $N_2O$ "hot spot" source region. Although the present study results have some caveats, it behooves us to pay attention to future $N_2O$ dynamics in the nGOM.

## AUTHOR CONTRIBUTIONS

The author confirms being the sole contributor of this work and approved it for publication.

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