Interannual variation in summer N\textsubscript{2}O concentration in the hypoxic region of the northern Gulf of Mexico, 1985–2007

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Abstract. Microbial nitrous oxide (N\textsubscript{2}O) production in the ocean is enhanced under low-oxygen (O\textsubscript{2}) conditions. This is especially important in the context of increasing hypoxia (i.e., oceanic zones with extremely reduced O\textsubscript{2} concentrations). Here, we present a study on the interannual variation in summertime nitrous oxide (N\textsubscript{2}O) concentrations in the bottom waters of the northern Gulf of Mexico (nGOM), which is well-known as the site of the second largest seasonally occurring hypoxic zone worldwide. To this end we developed a simple model that computes bottom-water N\textsubscript{2}O concentrations with a tri-linear \(\Delta N\textsubscript{2}O/O_2\) relationship based on water-column O\textsubscript{2} concentrations, derived from summer (July) Texas–Louisiana shelf-wide hydrographic data between 1985 and 2007. \(\Delta N\textsubscript{2}O\) (i.e., excess N\textsubscript{2}O) was computed including nitrification and denitrification as the major microbial production and consumption pathways of N\textsubscript{2}O. The mean modeled bottom-water N\textsubscript{2}O concentration for July in the nGOM was 14.5 \(\pm\) 2.3 nmol L\textsuperscript{-1} (min: 11.0 \(\pm\) 4.5 nmol L\textsuperscript{-1} in 2000 and max: 20.6 \(\pm\) 11.3 nmol L\textsuperscript{-1} in 2002). The mean bottom-water N\textsubscript{2}O concentrations were significantly correlated with the areal extent of hypoxia in the nGOM. Our modeling analysis indicates that the nGOM is a persistent summer source of N\textsubscript{2}O, and nitrification is dominating N\textsubscript{2}O production in this region. Based on the ongoing increase in the areal extent of hypoxia in the nGOM, we conclude that N\textsubscript{2}O production (and its subsequent emissions) from this environmentally stressed region will probably continue to increase into the future.

1 Introduction

Nitrous oxide (N\textsubscript{2}O) has a lifetime of \(\sim\) 120 yr in the atmosphere, where it has two major effects: it contributes to both the greenhouse effect in the troposphere and the depletion of ozone in the stratosphere (IPCC, 2007; Ravishankara et al., 2009). The atmospheric N\textsubscript{2}O concentration has increased rapidly since the 18th century, primarily because of anthropogenic activities (IPCC, 2007; Machida et al., 1995). The oceans are a major source of atmospheric N\textsubscript{2}O, with oceanic emissions of N\textsubscript{2}O accounting for approximately 20% (4–7 Tg N yr\textsuperscript{-1}) of the total annual emissions (16–34 Tg N yr\textsuperscript{-1}) (Nevison et al., 1995; Seitzinger et al., 2000; Bange, 2006). Among identified oceanic sources, coastal oceans account for up to 60% of the total oceanic N\textsubscript{2}O emissions (Bange et al., 1996). The production of N\textsubscript{2}O in coastal oceans is projected to increase worldwide (Bange, 2000; Naqvi et al., 2010), in proportion to the extent and intensity of eutrophication and hypoxia (Diaz and Rosenberg, 2008; Rabalais et al., 2009). The amount of N\textsubscript{2}O produced during nitrification and denitrification, which are the major production processes of N\textsubscript{2}O in the ocean, strongly depends on the prevailing oxygen (O\textsubscript{2}) concentration. N\textsubscript{2}O production is significantly enhanced under low O\textsubscript{2} concentrations (Codispoti, 2010). However, N\textsubscript{2}O consumption occurs as O\textsubscript{2} concentrations decrease toward zero levels (e.g., O\textsubscript{2} < 0.13 mg L\textsuperscript{-1} (\(\approx\) 4 \(\mu\)M)) (Nevison et al., 2003, and references therein).

The northern Gulf of Mexico (nGOM) is widely considered to be a “dead zone” because of extreme eutrophication arising from nutrient loads that enter from adjacent rivers, including the Atchafalaya and Mississippi (Malakoff, 1998;
Justić et al., 2003; Turner and Rabalais, 2004). As a result, the area affected by hypoxia (defined here as an O$_2$ concentration $\leq$ 2 mg L$^{-1}$ ($\approx$ 62.5 µM)) increased to $\sim$ 20 000 km$^2$ during the past two decades (Rabalais et al., 2002) and has likely affected N$_2$O production (subsequent emissions to the atmosphere). Unfortunately, there are only a limited number of measurements of dissolved N$_2$O concentrations from the nGOM hypoxic zone available for September 2007, April, and July–August 2008 (see Visser, 2009, and Walker et al., 2010). According to Visser (2009) and Walker et al. (2010), the nGOM becomes a significant source of atmospheric N$_2$O during the summer with flux densities of 3.3–43.9 µmol N$_2$O m$^{-2}$ d$^{-1}$. At present, the summer nGOM N$_2$O emission rates (0.2–2.3 $\times$ 10$^{-2}$ Tg N$_2$O yr$^{-1}$ extrapolated to an area of $\sim$ 3.24 $\times$ 10$^{10}$ m$^2$) are < 2 % of total N$_2$O emission rates from marine low-oxygen environments (1.5–3.1 Tg N$_2$O yr$^{-1}$, Naqvi et al. (2010) and references therein). However, the magnitudes of the summer nGOM N$_2$O fluxes are comparable to those associated with open-ocean hypoxic zones (2.7–4.5 µmol N$_2$O m$^{-2}$ d$^{-1}$), enclosed anoxic basins (1.6–5.2 µmol N$_2$O m$^{-2}$ d$^{-1}$), and naturally formed continental-margin hypoxic zones (10–50 µmol N$_2$O m$^{-2}$ d$^{-1}$) (Naqvi et al., 2010, and references therein). Despite the fact that the nGOM has received much attention as a notorious “dead zone”, it is not known how N$_2$O emissions from the nGOM have evolved throughout time. Addressing these unknowns will help to establish a modeling framework for the prediction of the future production and release of N$_2$O from the nGOM as well as from other comparable coastal areas throughout the globe. This is especially important in view of the fact that the number of hypoxic areas is increasing worldwide.

Using a simple model framed in terms of measured seawater O$_2$ levels and long-term summer hydrographic data collected from the nGOM, we estimate the evolution of bottom-water N$_2$O concentrations in Texas–Louisiana shelf regions for the month of July from 1985 to 2007.

2 Methods

2.1 Study area and data

The continental shelf area of the nGOM broadly extends seaward, and is shallower than 100 m depth (Fig. 1). The characteristics of nGOM seawater are primarily determined by mixing of Gulf of Mexico saltwater with freshwater discharged from the Atchafalaya and Mississippi rivers (Fig. 1). In our analysis, we used observations (temperature, salinity, dissolved O$_2$, nitrite + nitrate, phosphate and silicate) from Texas–Louisiana shelf-wide surveys regularly conducted in July (approximately 80 stations were occupied during each of the surveys). These July data for the period 1985–2007 (excluding the three years between 1988 and 1990) are available online: http://www.nodc.noaa.gov and http://www.aoml.noaa.gov/ocd/necop/. The websites also provide information concerning the hydrographic cruises and the analytical methods used for nutrient analysis. Nutrients were measured at only two depths (near-surface and near-bottom). Our calculation of N$_2$O concentrations is based on the water samples collected near the shelf bottom.

2.2 A conceptual biogeochemical model for estimating N$_2$O production and consumption

In general, the tracer conservation equation at a fixed position is expressed as

$$\frac{\partial C}{\partial t} = \frac{\partial C}{\partial t}_{advection} + \frac{\partial C}{\partial t}_{diffusion} + J(C),$$

where $C$ is tracer concentration, and $J(C)$ represents the net sources and sinks.

The tracer continuity equation for $\Delta$N$_2$O ($= \text{[N}_2\text{O} \text{estimated}-\text{[N}_2\text{O} \text{equilibrium}]})$ in the bottom layer associated with microbial processes (i.e., nitrification and denitrification by Bacteria and Archaea) is expressed as follows:

$$\Gamma \left( \Delta N_2O \right) = J_{\text{nitrification}} \left( \Delta N_2O \right) + J_{\text{low oxygen}}^{+} \left( \Delta N_2O \right)$$

$$+ J_{\text{low oxygen}}^{-} \left( \Delta N_2O \right),$$

where $J(\Delta N_2O)$ represents the function describing net production (i.e., source) minus consumption (i.e., sink) for each process. $J_{\text{nitrification}} (\Delta N_2O)$ denotes the source term for nitrification, $J_{\text{low oxygen}}^{+} (\Delta N_2O)$ the N$_2$O production during low O$_2$, and $J_{\text{low oxygen}}^{-} (\Delta N_2O)$ the N$_2$O consumption during low O$_2$. $$\Gamma$$
low O\textsubscript{2} (Fig. S1). The operator $\Gamma$ is the transport and time rate of change and is given as

$$\Gamma (C) = \frac{\partial C}{\partial t} + U \cdot \nabla C - \nabla \cdot (V \cdot \nabla C) ,$$

where $C$ is any tracer concentration (here, it is $\Delta$N\textsubscript{2}O\textsubscript{2}), $\nabla$ denotes the gradient operator in the $x$, $y$, and $z$ directions, $U$ is the 3-dimensional velocity field, and $V$ is the eddy diffusivity.

Under low-oxygen conditions, such as suboxic and anoxic conditions, anaerobic ammonium oxidation (anammox) and dissimilatory nitrate reduction to ammonium (DNRA) could be additional sources of N\textsubscript{2}O (Naqvi et al., 2010). However, the pathways and yields of N\textsubscript{2}O production during these two processes are poorly known. Furthermore, measurements of anammox and DNRA in the nGOM are in short supply (Dagg et al., 2007). As a result, we did not explicitly include the N\textsubscript{2}O production by anammox and DNRA in our model. Instead, we assumed that the low oxygen terms ($J_{\text{low oxygen}}$) are determined by denitrification alone.

Since $\Delta$N\textsubscript{2}O\textsubscript{2} is associated with microbial processes, we assume that transport by advection and diffusion is negligible, and, therefore, we drop the second and third terms on the right-hand side of Eq. (3). $\Delta$N\textsubscript{2}O\textsubscript{2} is only determined by nitrification and denitrification. So, Eq. (2) is simplified to

$$\frac{\partial \Delta \text{N}_2\text{O}_2}{\partial t} = J_{\text{nitrification}} (\Delta \text{N}_2\text{O}_2) + J_{\text{low oxygen}}^+ (\Delta \text{N}_2\text{O}_2) + J_{\text{low oxygen}}^- (\Delta \text{N}_2\text{O}_2) \quad (4)$$

Either a numerical or analytical approach can be used to solve the partial derivative Eq. (4). However, to date, exact $J (\Delta \text{N}_2\text{O}_2)$ terms for the right-hand side are not known. Therefore, we assumed a tri-linear $\Delta \text{N}_2\text{O}_2$/$\text{O}_2$ relationship (Fig. S1). The use of a simple tri-linear $\Delta \text{N}_2\text{O}_2$/$\text{O}_2$ relationship may increase the uncertainty of our modeled results, but can be taken as a simple best-guess approach. Using the empirically derived linear relationships, an analytical solution for $\Delta$N\textsubscript{2}O\textsubscript{2} may be derived as

$$\Delta \text{N}_2\text{O}_2 = \alpha \left( \frac{\text{nmol N}_2\text{O}_2}{\mu\text{mol O}_2} \right) \cdot \text{AOU} + \beta \left( \frac{\text{nmol N}_2\text{O}_2}{\mu\text{mol N}_2\text{O}_2} \right) \cdot \Delta \text{N}_\text{deni},$$

where AOU is the apparent oxygen utilization – the difference between the measured O\textsubscript{2} concentration and the O\textsubscript{2} equilibration value, the coefficient of $\alpha$ indicates the relationship between $\Delta$N\textsubscript{2}O\textsubscript{2} and AOU, and the coefficients of $\beta$ and $\gamma$ are the relationships between $\Delta$N\textsubscript{2}O\textsubscript{2} and the amount of denitrification ($\Delta$N\textsubscript{deni}) that is the loss of nitrate (NO\textsubscript{3}) as a consequence of denitrification. Finally, $[\text{N}_2\text{O}]_{\text{est}}$ can be estimated as

$$[\text{N}_2\text{O}]_{\text{est}} = \Delta \text{N}_2\text{O}_2 + [\text{N}_2\text{O}]_{\text{equilibrium}}$$

The values of these coefficients applicable to the nGOM are empirically determined to be 0.048, 0.83, and 0.83 for $\alpha$, $\beta$, and $\gamma$, respectively. The rationale for choosing these values is described in Sect. 3.1. The procedures for estimating bottom-water N\textsubscript{2}O concentrations in the nGOM are schematically presented in Fig. S2.

### 2.3 The O\textsubscript{2} criteria for determining nitrogen (N) processes that dominate N\textsubscript{2}O production and consumption

We used Eq. (6) along with observations to estimate the N\textsubscript{2}O concentrations in the near-bottom waters in the nGOM. The determination of which nitrogen processes (i.e., nitrification and denitrification) dominate N\textsubscript{2}O production/consumption depends primarily on O\textsubscript{2} concentrations. Often hypoxia is defined as $0.14 < \text{O}_2 \leq 2$ mg L\textsuperscript{-1} ($\approx 62.5 \mu$M), suboxia as $0 < \text{O}_2 \leq 0.14$ mg L\textsuperscript{-1} ($\approx 4.5 \mu$M), and anoxia as $\text{O}_2 = 0$ mg L\textsuperscript{-1}, based on O\textsubscript{2} levels (e.g., Naqvi et al., 2010). As little information is available on the O\textsubscript{2} threshold for N\textsubscript{2}O production by denitrification, we deduced $\beta$ and $\gamma$ from the results of Farias et al. (2009) for our analysis. However, it should be kept in mind that these values were based on measurements from the eastern tropical South Pacific Ocean, and thus represent only a rough approximation.

In order to evaluate the O\textsubscript{2} dependence of our N\textsubscript{2}O estimations, we considered two cases (Table 1). Case I characterizes the O\textsubscript{2} conditions as stated in Naqvi et al. (2010). Under oxic conditions, N\textsubscript{2}O is produced by nitrification only, and thus the concentration is calculated as $\alpha \times$ AOU (Yoshinari, 1976; Cohen and Gordon, 1979; Oudot et al., 1990). Recently, Farias et al. (2009) showed net N\textsubscript{2}O production around hypoxic O\textsubscript{2} levels in the eastern tropical South Pacific Ocean (see their Table 1). Under hypoxic conditions, during which nitrification and denitrification are both involved in N\textsubscript{2}O
production (Naqvi et al., 1998; Nevison et al., 2003), N₂O concentrations were calculated as $\alpha \times \text{AOU} + \beta \times \Delta N_{\text{deni}}$. It has been reported that N₂O production occurs at $O_2 < \sim 4 \mu M$ ($\sim 0.13 \text{mg L}^{-1}$) (Nevison et al., 2003, and references therein). Under such suboxic–anoxic conditions, denitrification consumes N₂O (Cohen and Gordon, 1978; Elkins et al., 1978; Yamagishi et al., 2007), and nitrification produces N₂O via nitrite reduction (nitrifier denitrification: $\text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{N}_2\text{O}$) (Poth and Focht, 1985; Wrage et al., 2001). Therefore, under these conditions N₂O concentrations were calculated as $\alpha \times \text{AOU} - \gamma \times \Delta N_{\text{deni}}$.

For Case II the same approach was adopted as for Case I, and different $O_2$ thresholds were applied: (1) oxic conditions defined as $O_2 > 2 \text{mg L}^{-1}$ ($\alpha \times \text{AOU}$), (2) hypoxic–suboxic conditions defined as $0.07 < O_2 < 0.02 \text{mg L}^{-1}$ ($\alpha \times \text{AOU} + \beta \times \Delta N_{\text{deni}}$), and (3) suboxic–anoxic conditions defined as $0 \leq O_2 < 0.07 \text{mg L}^{-1}$ ($\alpha \times \text{AOU} - \gamma \times \Delta N_{\text{deni}}$).

### 2.4 Information of denitrification ($\Delta N_{\text{deni}}$) estimated in the nGOM

The $\Delta N_{\text{deni}}$ term plays a crucial role in the estimation of bottom-water N₂O concentrations (Eq. 5). The $\Delta N_{\text{deni}}$ was estimated using the extended optimum multi-parameter (eOMP) analysis by Kim and Min (2013) with the same summer Texas–Louisiana shelf-wide hydrographic data sets used here. The eOMP analysis is a useful way to quantify physical mixing and biogeochemical processes simultaneously (Karstensen and Tomczak, 1998; Hupe and Karstensen, 2000). It is an inverse method based on an over-determined linear system, and its basic structure is given as

$$A \cdot x - d = R,$$

where the matrix $A$ is composed of the physicochemical characteristics of end-members that participate in physical mixing in the study area, and the Redfield ratios that represent biogeochemical processes. The vector $x$ consists of the unknowns including mixing ratios among different pre-defined water masses, the amount of remineralized phosphate ($\Delta P_{\text{remi}}$), and denitrification ($\Delta N_{\text{deni}}$), whereas the vector $d$ contains the observed values, and the vector $R$ represents the constraint residuals.

The results of this eOMP analysis produced residuals for the mass conservation equations $< \sim 2\%$. Further details can be found in Kim and Min (2013). Here, we used the results of denitrification ($\Delta N_{\text{deni}}$) estimated from the eOMP analysis by Kim and Min (2013) for this study.

### 3 Results and discussion

#### 3.1 Determination of the coefficients $\alpha$, $\beta$, and $\gamma$ in the conceptual model

The coefficients of $\alpha$, $\beta$, and $\gamma$ in Eq. (5) are known to vary as a result of mixing of water masses, changes in the rates of nitrification/denitrification, and variations in the chemical composition of organic matter produced in situ (Cohen and Gordon, 1978; Elkins, 1978; Nevison et al., 2003). This, in turn, implies that the applicability of the three coefficients for estimating N₂O concentrations will vary on a regional scale (Suntharalingam et al., 2000). Walker et al. (2010) measured N₂O in the waters of the nGOM between August 2 and 7,
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2008, when a tropical storm (i.e., Edouard) passed over the nGOM on 4 August. This gave Walker et al. (2010) the opportunity to compare pre-storm with post-storm \( \text{N}_2\text{O} \) production. They reported enhanced \( \text{N}_2\text{O} \) post-storm production, resulting from a reoxygenation of the water column after the storm. The estimated \( \alpha \) values for pre-storm and post-storm conditions based on \( \Delta \text{N}_2\text{O} / \text{AOU} \) relationships were 0.048 and 0.096, respectively (see their Fig. 4). Since the factors known to influence \( \alpha \) in the nGOM are probably at their most extreme immediately following the storm event, it is likely that \( \alpha = 0.096 \) is an upper limit. The data sets used for the present analysis were little influenced by storm/hurricane events (Table S1), which enhance \( \text{N}_2\text{O} \) production only for very short periods. Therefore, we assumed that \( \alpha = 0.048 \) is a representative summertime nGOM coefficient for \( \text{N}_2\text{O} \) production by nitrification.

We assigned a value 0.83 to the coefficient \( \beta \) for the nGOM. This value was derived from an incubation experiment in the eastern tropical South Pacific Ocean (ETSP) (see Fig. 4 of Farías et al., 2009). We adopted this estimate in our modeling because no comparable data from the nGOM are available. During the denitrification process \( \text{N}_2\text{O} \) is also consumed. The amount consumed is quantitatively related to the \( \text{N}_2\text{O} \) available. During the denitrification process \( \text{N}_2\text{O} \) is also consumed. The amount consumed is quantitatively related to the \( \text{N}_2\text{O} \) available. During the denitrification process \( \text{N}_2\text{O} \) is also consumed. The amount consumed is quantitatively related to the \( \text{N}_2\text{O} \) available. During the denitrification process \( \text{N}_2\text{O} \) is also consumed. The amount consumed is quantitatively related to the \( \text{N}_2\text{O} \) available.

We, therefore, have increased the possible range in these values that generated random numbers for \( \alpha \) between 0 and 0.31. We deduced \( \beta \) and \( \gamma \) from the results of Farías et al. (2009), since information on \( \beta \) and \( \gamma \) from other oceanic regions is lacking. We, therefore, have increased the possible range in these values that generated random numbers for \( \beta \) between 0 and 2.5. In the nGOM, Visser (2009) and Walker et al. (2010) directly measured water-column \( \text{N}_2\text{O} \) concentrations during the summer of 2008, and reported that bottom-water \( \text{N}_2\text{O} \) concentrations ranged from 4.25 to 30.02 nmol L\(^{-1} \) (July) and from 5 to 30 nmol L\(^{-1} \) (August). Bottom-water \( \text{N}_2\text{O} \) concentrations were similar in both months, so we used the median of measured values (17–18 nmol L\(^{-1} \)) as the

\( \gamma \) from other oceanic regions is lacking. We, therefore, have increased the possible range in these values that generated random numbers for \( \beta \) between 0 and 2.5. In the nGOM, Visser (2009) and Walker et al. (2010) directly measured water-column \( \text{N}_2\text{O} \) concentrations during the summer of 2008, and reported that bottom-water \( \text{N}_2\text{O} \) concentrations ranged from 4.25 to 30.02 nmol L\(^{-1} \) (July) and from 5 to 30 nmol L\(^{-1} \) (August). Bottom-water \( \text{N}_2\text{O} \) concentrations were similar in both months, so we used the median of measured values (17–18 nmol L\(^{-1} \)) as the

3.2 Sensitivity, uncertainty, and caveat

We assigned 0.048, 0.83, and 0.83 for \( \alpha \), \( \beta \), and \( \gamma \), respectively, to estimate bottom-water \( \text{N}_2\text{O} \) concentrations using the empirical relationship presented in Sect. 3.1. To investigate the validity of chosen values of \( \alpha \), \( \beta \), and \( \gamma \), we used a Monte Carlo technique generating random numbers for individual \( \alpha \), \( \beta \), and \( \gamma \) values within expected ranges looking for those coefficients that produced estimated bottom-water \( \text{N}_2\text{O} \) concentrations within the observed range. The value of \( \alpha \) ranges from 0.048 to 0.31 in various ocean environments, including the nGOM (Suntharalingam and Sarmiento, 2000, and references therein). For our model simulation we generated random numbers for \( \alpha \) between 0 and 0.31. We deduced \( \beta \) and \( \gamma \) from the results of Farías et al. (2009), since information on \( \beta \) and \( \gamma \) from other oceanic regions is lacking. We, therefore, have increased the possible range in these values that generated random numbers for \( \beta \) between 0 and 2.5. In the nGOM, Visser (2009) and Walker et al. (2010) directly measured water-column \( \text{N}_2\text{O} \) concentrations during the summer of 2008, and reported that bottom-water \( \text{N}_2\text{O} \) concentrations ranged from 4.25 to 30.02 nmol L\(^{-1} \) (July) and from 5 to 30 nmol L\(^{-1} \) (August). Bottom-water \( \text{N}_2\text{O} \) concentrations were similar in both months, so we used the median of measured values (17–18 nmol L\(^{-1} \)) as the
acceptable zone, and then applied the random \( \alpha, \beta, \) and \( \gamma \) values to the data sets to estimate N\(_2\)O concentrations. When the mean N\(_2\)O concentration reproduced by random \( \alpha, \beta, \) and \( \gamma \) values fell in the acceptable range (i.e., 17 < mean [N\(_2\)O] < 18), they were saved and averaged. We generated a thousand of random numbers for individual \( \alpha, \beta, \) and \( \gamma \) for each simulation, and performed 10 simulations (Fig. S3). The resulting \( \alpha, \beta, \) and \( \gamma \) coefficients averaged over all the simulations were 0.051 ± 0.003, 1.27 ± 0.15, 1.16 ± 0.16, respectively. The \( \alpha = 0.048 \) obtained from the empirical relationship compared well with the simulated \( \alpha = 0.051 \pm 0.003 \). The \( \beta = 0.83 \) and \( \gamma = 0.83 \) are somewhat lower than the simulated \( \beta = 1.27 ± 0.15 \) and \( \gamma = 1.16 ± 0.16 \). The change of N\(_2\)O concentrations according as \( \alpha, \beta, \) and \( \gamma \) individually change with 0.01 interval was \( \sim 1.3, \sim 0.03, \) and \( \sim 0.001 \) nmol L\(^{-1}\), respectively.

To examine the sensitivity to the threshold O\(_2\) values for N\(_2\)O production/consumption by denitrification (Table 1), Case I estimates were compared with Case II. On average, the N\(_2\)O concentrations estimated for Case I were \( \sim 0.9 \) nmol L\(^{-1}\) lower than those by Case II (Fig. S4). Also, both temporal trends were similar. Thus, the results of Case I are primarily used for our study.
Kim and Min (2013) defined four different water masses (i.e., SUW: Subtropical Underwater, TLCW: Texas–Louisiana Coastal Water, ADW: Atchafalaya Discharge Water, and MDW: Mississippi Discharge Water) for the eOMP analysis in the study area. Unlike the others, SUW is a foreign water mass that only occasionally intrudes into the study area depending on eddy development/circulation patterns. Although it is difficult to estimate preformed N$_2$O concentrations for each water mass from this analysis, because SUW locally occupies the bottom layer and is derived from outside the study area, it is possible to approximate the amount of N$_2$O advected by SUW using a plot of the estimated bottom-water N$_2$O concentrations vs. the mixing ratios of SUW (Fig. S5). Higher mixing ratios of SUW imply that the water properties are close to those of the source water mass, and by using a constraint on SUW mixing ratios of $>90\%$, the N$_2$O concentrations produced through advection of SUW into the nGOM region is estimated to be $13.3 \pm 2.5 \text{nmol L}^{-1}$, which is the mean value averaged from the N$_2$O concentrations for SUW mixing ratios $>90\%$ (Fig. S5). This estimate is close to the overall N$_2$O mean concentration of $14.5 \pm 2.3 \text{nmol L}^{-1}$ for the nGOM. However, SUW is only locally found in the study area (approximately 89.5–92° W and 28.5–29.0° N deeper than ~40 m), and its occurrence in the nGOM bottom waters has been decreasing since ~1998 (Kim and Min, 2013). Therefore, the overall effect of N$_2$O advected by SUW seems to be small.

Our model cannot directly account for possible N$_2$O sediment fluxes, as $\Delta N_{\text{deni}}$ signals estimated by Kim and Min (2013) in the bottom waters cannot be distinguished from those derived from sediments. Therefore, we assumed that the estimated N$_2$O concentrations from this study were resulting from bottom-water and sedimentary processes combined (i.e., benthic coupling processes). In the following section, we quantify the contribution by denitrification to the total N$_2$O concentration.

Here we estimated bottom-water N$_2$O concentrations using the tri-linear relationships between O$_2$ and $\Delta N_{\text{deni}}$ signals estimated by Kim and Min (2013) in the bottom waters cannot be distinguished from those derived from sediments. Therefore, we assumed that the estimated N$_2$O concentrations from this study were resulting from bottom-water and sedimentary processes combined (i.e., benthic coupling processes). In the following section, we quantify the contribution by denitrification to the total N$_2$O concentration.

For the period 1985–2007, the July mean N$_2$O concentration in near-bottom waters of the nGOM is estimated to be $14.5 \pm 2.3 \text{nmol L}^{-1}$ (min: $11.0 \pm 4.5 \text{nmol L}^{-1}$ in July 2000, max: $20.6 \pm 11.3 \text{nmol L}^{-1}$ in July 2002), with large interannual variability (Table 2). The range of bottom-water N$_2$O measurements during the summer (July–August) of 2008 was from 4.5 to 30.0 nmol L$^{-1}$ (Visser, 2009; Walker et al., 2010), and during the spring/fall (September 2007 and April 2008) from 6.5 to 12.0 nmol L$^{-1}$ (Visser, 2009) (Fig. 2). Thus, we conclude that our estimates are in good agreement with the measurements. Comparing the nGOM estimates with those observed in other hypoxic coasts (Table 2b of Naqvi et al., 2010, and references therein), it can be seen that maximum subsurface N$_2$O concentrations in the anthropogenically produced coastal hypoxic systems have a broad range from 9.8 nmol L$^{-1}$ in the Chesapeake Bay to 62.6 nmol L$^{-1}$ in the Changjiang Estuary, to 139 nmol L$^{-1}$ in the Tokyo Bay. Estimates from the nGOM (~30 nmol L$^{-1}$) lie in the middle of this range according to Naqvi et al. (2010). The maximum N$_2$O concentration estimated in our analysis was ~52 nmol L$^{-1}$ (Table 2).

The mean bottom-water N$_2$O concentration for July 1998 ($11.4 \pm 10.7 \text{nmol L}^{-1}$) was relatively low for the study period, but the areal extent of hypoxia in 1998 was relatively large (>12 000 km$^2$) (Fig. 4). This was caused by the fact that the estimated N$_2$O concentrations were significantly influenced by N$_2$O consumption in July 1998 (Fig. 3). In July 2000, the mean bottom-water N$_2$O concentration ($11.0 \pm 4.5 \text{nmol L}^{-1}$) was lower compared to other years. However, in contrast to 1998, the areal extent of the hypoxia in 2000 was smaller (~4400 km$^2$) (Figs. 4 and 5). The following scenario may explain the lower N$_2$O concentration and smaller areal extent of hypoxia found in July 2000. The total freshwater discharge from the Mississippi and Atchafalaya rivers in the period January–July 2000 was less than in the same period in other years (Fig. S6), resulting in decreased production of organic matter through biological productivity (Walker and Rabalais, 2006). This feature is consistent with the interannual variation of mixing ratios of ADW and MDW (Fig. S7). Consequently, the oxidation of organic matter was probably decreased, and the net effect was a reduction in the areal extent of hypoxia in July 2000. Another contrasting example is evident for July 2002. The mean bottom-water N$_2$O concentration was highest ($20.6 \pm 11.3 \text{nmol L}^{-1}$), and the size of the hypoxic zone was largest (~22 000 km$^2$) (Fig. 4). The N$_2$O production by denitrification was also highest in July 2002, and its contribution to the overall N$_2$O production was also significant (Fig. 3). These conditions probably resulted in July 2002 having the highest N$_2$O concentration (Fig. 5). Overall, interannual variation in the estimated bottom-water N$_2$O
concentrations is significantly correlated with the areal extent of hypoxia ($R = 0.59; \ p < 0.05$; Fig. 4).

To identify the primary mechanism(s) of N$_2$O production in the nGOM, we estimate the contribution to N$_2$O concentration of each mechanism: production by nitrification and denitrification, consumption by denitrification, and N$_2$O equilibrium (Fig. 3). Our result indicates that $\sim 44\%$ of the total N$_2$O is produced by nitrification, and $\sim 14\%$ is produced by denitrification. The result also indicates that, with reasonable parameters for denitrification, the N$_2$O sink is small compared to the sources, and represents only a small contribution (approximately 1%) to the total N$_2$O concentration. The results of Visser (2009) showed that N$_2$O consumption can occur in the sediments and reported that the contribution of N$_2$O released from the sediments was negligible in the nGOM. Together, these results imply that water-column processes may be the dominant control for N$_2$O production in the nGOM. The remainder ($\sim 41\%$) is covered by N$_2$O equilibrium. Our study indicates that the nitrification is the major process responsible for the biological production of N$_2$O in the nGOM. This is also supported by the findings that the N$_2$O production by nitrification is significantly correlated with the areal extent of hypoxia (Fig. S8). Moreover, the total N$_2$O production by nitrification and denitrification shows a significant correlation with the amount of remineralized carbon as estimated by Kim and Min (2013) (Fig. S9).

Based on the significance of the correlation between the estimated bottom-water N$_2$O concentrations and the areal extent of hypoxia (Fig. 4), it is expected that the strength of the nGOM as a source of N$_2$O will increase into the future if the expansion of the hypoxic region in the nGOM continues. This is in line with the suggestions by Bange (2000), Naqvi et al. (2000), and Codispoti (2010).

4 Conclusions

The nGOM is receiving ever-increasing loads of nutrients through rivers from anthropogenic activities, and this has led to more intense and widespread hypoxic conditions (Rabalais et al., 2009; Bianchi et al., 2010). As the areal extent of nGOM hypoxia continues to expand, it is expected that N$_2$O production and its subsequent emissions to the atmosphere will be enhanced. In particular, it is expected that this study area will likely be more vulnerable to human-induced events.

Table 2. Mean bottom-water N$_2$O concentrations (nmol L$^{-1}$) during the study period estimated from Eq. (6) using $\alpha = 0.048$, $\beta = 0.83$, and $\gamma = 0.83$. The mean is calculated as $[N_2O]_{\text{mean}} = \frac{\sum_{i=1}^{n}[N_2O]_{\text{est}}}{n}$, where $i$ is the estimate at one station, and $n$ is the number of total estimates. Standard deviations (±) are calculated as $\sqrt{\frac{\sum_{i=1}^{n}(N_2O)_{\text{est}}^2 - [N_2O]_{\text{mean}}^2}{n}}$.

<table>
<thead>
<tr>
<th>Year (for July)</th>
<th>$[N_2O]_{\text{mean}}$</th>
<th>maximum</th>
<th>remark</th>
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<tr>
<td>1985</td>
<td>13.0 ± 7.6</td>
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<td></td>
</tr>
<tr>
<td>1986</td>
<td>16.7 ± 10.0</td>
<td>52.4</td>
<td></td>
</tr>
<tr>
<td>1987</td>
<td>13.6 ± 4.9</td>
<td>32.9</td>
<td></td>
</tr>
<tr>
<td>1988</td>
<td>ND</td>
<td>ND</td>
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<td>1989</td>
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<td>1990</td>
<td>ND</td>
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</tr>
<tr>
<td>1991</td>
<td>13.7 ± 5.6</td>
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<td></td>
</tr>
<tr>
<td>1992</td>
<td>14.3 ± 7.0</td>
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<tr>
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</tbody>
</table>

ND: not determined.
in the future. For these reasons, we need to improve our understanding of N₂O cycles in the nGOM. However, this investigation, as well as previous studies, has been severely limited by a distinct lack of information on the ΔN₂O coefficients (i.e., α, β, and γ). In particular, knowledge of interannual and seasonal variability in these terms would provide a fundamental step forward in our understanding of the nGOM N₂O cycles. Further, an increased number of direct N₂O measurements could improve our knowledge of the ΔN₂O/O₂ relationship allowing an improvement in our modeling approach through a reduction in uncertainties. Our model results indicate that nitrification is the primary process responsible for the microbial N₂O production in the nGOM, implying that N₂O production is mainly controlled by water-column processes. This result suggests that future observational surveys in both the nGOM and perhaps also other coastal oceans can concentrate resources on the water column in an effort to improve the resolution of available time series.

Supplementary material related to this article is available online at http://www.biogeosciences.net/10/6783/2013/bg-10-6783-2013-supplement.pdf.

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