Interannual variation in summer N$_2$O concentration in the hypoxic region of the northern Gulf of Mexico, 1985–2007

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Abstract

We present evidence of temporal variation in nitrous oxide (N\textsubscript{2}O) concentrations in the bottom waters of the northern Gulf of Mexico (nGOM) hypoxic zone. The analysis is based on a conceptual model simulating N\textsubscript{2}O biogeochemical processes in conjunction with water-column O\textsubscript{2} levels, derived from summer Texas–Louisiana shelf-wide hydrographic data for twenty Julys between 1985 and 2007. The mean modeled nGOM N\textsubscript{2}O concentration was 7.7 ± 6.7 nmol L\textsuperscript{-1}, and was significantly correlated with the areal extent of hypoxia. Our modeling analysis indicates that the nGOM is a persistent summer source of N\textsubscript{2}O, and nitrification is a primary factor leading to its 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 emission from this environmentally stressed region will continue to increase into the future contributing to the global increase in greenhouse gases.

1 Introduction

Nitrous oxide (N\textsubscript{2}O) has a lifetime of ~120 yr in the atmosphere, where it has two major effects: it contributes to greenhouse effects in the troposphere, and destroys 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 TgN yr\textsuperscript{-1}) of the total annual emissions (16–34 TgN 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 (Fig. 1), which are the major
production processes of $N_2O$ in the ocean, strongly depends on the prevailing oxygen ($O_2$) concentration. $N_2O$ production is significantly enhanced under low (i.e. hypoxic or suboxic) $O_2$ concentrations (Codispoti, 2010).

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 $\leq 2 \text{ mg L}^{-1}$) increased to $\sim 20,000 \text{ km}^2$ during the past two decades (Rabalais et al., 2002) and has likely been emitting increasing quantities of $N_2O$ to the atmosphere. The limited measurements of dissolved $N_2O$ concentrations made in the nGOM hypoxic zone (available only for April and July–September 2008) show the area to be a significant source of atmospheric $N_2O$ (Visser, 2009; Walker et al., 2010). However, it is not known how nGOM $N_2O$ emissions have evolved. More importantly, cause and effect associations remain unclear between variations in the strength of $N_2O$ emissions and the degree of hypoxia in the nGOM. Addressing these unknowns will help to establish a modeling framework for the prediction of the evolving release of $N_2O$ from the nGOM as well as other coastal areas throughout the globe. Such prediction is important because in the future these regions are expected to become more vulnerable to hypoxia as eutrophication continues to increase with population and development.

Using a simple conceptual model framed in terms of measured seawater $O_2$ levels, and long-term summer hydrographic data collected from the nGOM, we simulate the evolution of seawater $N_2O$ concentrations in Texas–Louisiana shelf waters for the month of July from 1985 to 2007. The model used in the present study incorporates all biogeochemical processes known to be involved in the production and consumption of $N_2O$ in seawater.
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. 2). 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. 2). In our analysis, we used observations (temperature, salinity, dissolved O$_2$, nitrite + nitrate, phosphate and silicate) from summer Texas–Louisiana shelf-wide surveys (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 website also provides information concerning the hydrographic cruise 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 simulating N$_2$O production and consumption

In the ocean environment, N$_2$O is produced during nitrification ($\alpha$), and is produced ($\beta$) and consumed ($\gamma$) during denitrification (Bange et al., 2010). Specific microbes are involved in the production and consumption of N$_2$O, and their activities are sensitive to the seawater O$_2$ concentration (Bianchi et al., 2012). Therefore, our conceptual model, which simulates the production and consumption of N$_2$O, is based on seawater O$_2$ concentrations (Fig. 1), and is formulated as follows:

$$[N_2O]_{est} = \alpha \left[ \frac{\Delta N_2O}{\Delta O_2} \right] \times \text{AOU} + \beta \left[ \frac{\Delta N_2O}{\Delta N_{deni}} \right] \times \Delta N_{deni} - \gamma \left[ \frac{\Delta N_2O}{\Delta N_{deni}} \right] \times \Delta N_{deni}$$

(1)
where $\Delta N_2O$ is the difference between the measured $N_2O$ concentration and the equilibrium value. AOU is the apparent oxygen utilization (the difference between the measured $O_2$ concentration and the equilibrium value), and $\Delta N_{\text{deni}}$ is the loss of nitrate ($NO_3^-$) as a consequence of denitrification. The coefficient $\alpha$ indicates the relationship between $\Delta N_2O$ and AOU, and the coefficients $\beta$ and $\gamma$ indicate the relationships between $\Delta N_2O$ and the rate of denitrification. The values of these coefficients applicable to the nGOM are empirically determined to be 0.048, 0.7, and 0.7 for $\alpha$, $\beta$, and $\gamma$, respectively. The rationale for choosing these values is described below.

We use Eq. 1 with the observations to estimate the $N_2O$ concentration in the near-bottom waters of the nGOM (approximately 1 m above the sediment-water interface) based on the $O_2$ concentration, and characterized the condition as: (1) oxic ($O_2 > 2 \text{ mg L}^{-1}$), (2) hypoxic-suboxic ($0.13 < O_2 \leq 2 \text{ mg L}^{-1}$), and (3) suboxic-anoxic ($O_2 \leq 0.13 \text{ mg L}^{-1}$) (Naqvi et al., 2010). Under oxic conditions, $N_2O$ is produced by nitrification only, and thus the concentration is calculated as $\alpha \times \text{AOU}$ (Yoshinari, 1976; Cohen and Gordon, 1979; Oudot et al., 1990). Under hypoxic-suboxic conditions, during which nitrification and denitrification are both involved in $N_2O$ production (Naqvi et al., 1998; Nevison et al., 2003), the $N_2O$ concentration is calculated as $\alpha \times \text{AOU} + \beta \times \Delta N_{\text{deni}}$. Under suboxic-anoxic conditions, nitrification produces $N_2O$ via nitrite reduction (nitrifier denitrification: $NH_4^+ \rightarrow NO_2^- \rightarrow N_2O$) (Poth and Focht, 1985; Wrage et al., 2001), but the competing process (denitrification) consumes $N_2O$ (Cohen and Gordon, 1978; Elkins et al., 1978; Yamagishi et al., 2007). As a result, the $N_2O$ concentration is calculated as $\alpha \times \text{AOU} – \gamma \times \Delta N_{\text{deni}}$, where $\Delta N_{\text{deni}}$ was estimated using extended optimum multi-parameter (eOMP) analysis. The basic structure for the eOMP analysis 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 unknowns including
mixing ratios among different pre-defined water masses, the amount of remineralized phosphate, and denitrification ($N_{\text{deni}}$); the vector $\mathbf{d}$ contains the observed values, and the vector $\mathbf{R}$ represents the constraint residuals. Further details can be found in Kim (2012). Here, we used the results of denitrification ($N_{\text{deni}}$) estimated from the eOMP analysis by Kim (2012) for this study.

The procedures for estimating $N_2O$ concentrations in the nGOM are schematically presented in Fig. S1. A contribution of $N_2O$ released from the underlying sediments is expected to be negligible (Visser, 2009) and was, therefore, not accounted for in our model.

3 Results and discussion

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

The coefficient $\alpha$ in Eq. (1) is known to vary as a result of intrusions of foreign water masses into the nGOM, changes in the rate of nitrification, and variations in the chemical composition of organic matter produced in situ (Cohen and Gordon, 1978; Elkins, 1978; Nevison et al., 2003). In our analysis, $\alpha$ is derived using $\Delta N_2O$ and AOU data for both pre-storm and post-storm periods observed during August 2008 according to Walker et al. (2010). The values of $\alpha$ applicable to the nGOM were determined to be 0.048 (pre-storm) and 0.096 (post-storm). Implicit in chosen value of $\alpha$ is the assumption that $\alpha$ only reflects changes in $\Delta N_2O$ and AOU associated with biological processes (i.e. nitrification). However, physical processes in the marine environment can also affect $\alpha$ by modifying the solubilities of $N_2O$ and $O_2$.

We therefore explored the possibility that the $\alpha$ difference between pre- and post-storm periods (0.048) could have been a consequence of changes in the physical properties of the water that occurred during the transition from pre-storm to post-storm period. During this transition, changes in the properties (temperature, salinity, and $O_2$ concentration) of near-bottom water masses in the nGOM had a negligible influence
on the solubility of $N_2O$ but considerable, disproportional influence on the solubility of $O_2$, thereby increasing the value of $\alpha$ (Table 1). Our sensitivity test of the variability of $\alpha$ associated with changes in water mass properties indicates that the value of $\alpha$ for the post-storm period ($\alpha_{\text{post-storm}}$) could be as much as a factor of $\sim 1.7$ higher than the value for the pre-storm period ($\alpha_{\text{pre-storm}}$), close to the measured post-storm $\alpha$ (0.096) (Fig. 3). It also indicates that the use of the pre-storm $\alpha_{\text{pre-storm}} = 0.048$ is probably a more suitable value for the nGOM. One line of evidence supporting the use of this value is that all the data used were related to the summer months, during which there were no or few hurricanes or storm events (Table S1). We therefore use $\alpha_{\text{pre-storm}} = 0.048$ to simulate the summer $N_2O$ concentration in the nGOM, and assume that the resulting value is valid for all summer periods included in this study. It will not be possible to evaluate the validity of this assumption until multi-year measurements are available for the nGOM and other coastal areas. Such measurements made in the future will enable more accurate calculation of $\alpha$. It is assumed that it is reasonable to set $\alpha = 0.096$ as an upper limit, because the factors known to influence $\alpha$ in the nGOM are probably at their most extremes immediately following the storm event.

We assign a value 0.7 to the coefficient $\beta$ for the nGOM. This value was derived from an incubation experiment in the eastern tropical South Pacific (ETSP) (see Fig. 4 of Farías et al., 2009). We adopt this estimate in our modeling because (i) no comparable data from the nGOM are available and (ii) the nitrogen cycle in oxygen minimum zone of the ETSP is comparable to that in the nGOM hypoxic zone. During the denitrification process $N_2O$ is also consumed. The amount consumed is quantitatively related to the $O_2$ level. Farías et al. (2009) varied the ratio of $N_2O$ production vs. consumption from 0.36 to 6.55 according to oxygen levels in the ETSP (see Fig. 5 of Farías et al., 2009). It was determined that the ratio under suboxic-anoxic conditions is 1 on average. Here, we assign $\gamma \approx \beta$ for the purpose of our modeling exercise. The choice of values for the coefficients $\beta$ and $\gamma$ is less critical than the choice of $\alpha$, because $N_2O$ production
associated with $\beta$ and $\gamma$ typically represents less than $\sim 25\%$ of the total production (Fig. 4).

### 3.2 Mechanisms of $N_2O$ production and consumption in the nGOM

For the period 1985–2007, the July mean $N_2O$ concentration in near-bottom waters of the nGOM is estimated to be $7.7 \text{ nmolL}^{-1}$ (min: $3.7 \text{ nmolL}^{-1}$, max: $13.5 \text{ nmolL}^{-1}$), with considerable associated interannual variability ($\sigma = \pm 6.7 \text{ nmolL}^{-1}$, where $\sigma$ is the standard deviation) (Fig. 5 and Table 2). This estimate appears reasonable as measured bottom $N_2O$ concentrations in July–August 2008 in the nGOM typically ranged from $\sim 4$ to $15 \text{ nmolL}^{-1}$ (Visser, 2009; Walker et al., 2010), although higher concentrations of up to $30 \text{ nmolL}^{-1}$ were also detected. Our estimated nGOM $N_2O$ concentrations are comparable to those observed in other hypoxic-anoxic areas, including Chesapeake Bay, and the Baltic and Black Seas ($6–20 \text{ nmolL}^{-1}$) (Naqvi et al., 2010).

The $N_2O$ concentrations for July 1996 and 1998 (4.5 and $3.7 \text{ nmolL}^{-1}$, respectively) were lower during the study periods, but the areal extents of hypoxia were relatively high ($> 12,000 \text{ km}^2$) (Fig. 5). It was because the estimated $N_2O$ concentrations were somewhat influenced by $N_2O$ consumption For July 1996 and 1998 (Fig. 4). July 2000 $N_2O$ ($\sim 5.1 \text{ nmolL}^{-1}$) was also relatively low compared to other years, however in contrast to 1996 and 1998, the areal extent of hypoxia was smaller ($\sim 4400 \text{ km}^2$) (Figs. 5 and 6). The following scenario may explain the lower $N_2O$ 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, resulting in decreased production of organic matter through biological productivity (Walker and Rabalais, 2006). 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 the month of July 2002. The mean $N_2O$ concentration was highest ($\sim 13.1 \text{ nmolL}^{-1}$) and the size of the hypoxic zone was largest ($\sim 22,000 \text{ km}^2$) (Fig. 5). The production
of N\textsubscript{2}O during denitrification was also highest in July 2002, and its contribution to the overall N\textsubscript{2}O production was significant (Fig. 4). These conditions probably resulted in July 2002 having the highest N\textsubscript{2}O concentration (Fig. 6). Overall, interannual variation in the estimated N\textsubscript{2}O concentrations is significantly correlated with the areal extent of hypoxia ($R = 0.52; p < 0.05$; Fig. 5).

To identify the primary mechanism(s) of N\textsubscript{2}O production in the nGOM, we estimate the contribution to N\textsubscript{2}O concentration of each mechanism: production by nitrification and denitrification, and consumption by denitrification (Fig. 4). Our result indicates that $\sim 75\%$ of the total N\textsubscript{2}O is produced under oxic and hypoxic-suboxic conditions during nitrification, and the remainder ($\sim 20\%$) is produced under hypoxic-suboxic conditions during denitrification. The result also shows that N\textsubscript{2}O is consumed exclusively under suboxic-anoxic conditions during denitrification, but this makes only a small contribution to the N\textsubscript{2}O concentration (approximately $5\%$ of total N\textsubscript{2}O production). Our study indicates that the nitrification is the major process responsible for the production of N\textsubscript{2}O in the nGOM.

Based on the significance of the correlation between the estimated N\textsubscript{2}O concentrations and the areal extent of hypoxia (Fig. 5), it is expected that the strength of the nGOM as a source of N\textsubscript{2}O will increase into the future, with the expansion in the hypoxic region (Bange, 2000; Naqvi et al., 2000; Codispoti, 2010).

4 \textbf{Summary}

The implications of our modeled results are profound. 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\textsubscript{2}O emissions will be enhanced. This study area is particularly vulnerable to human-induced catastrophic events. A prime example is the recent “Deep-Water Horizon” oil spill, which may greatly increase the areal extent of hypoxia in the nGOM.
Acknowledgements. We sincerely thank all scientists and crew who contributed to the summer Texas–Louisiana shelf-wide hydrographic dataset. The preparation of the manuscript was supported by the Mid-career Research Program of the Korea National Research Foundation (No. 2012R1A2A1A01004631) and by Polar Academy Program of the Korea Polar Research Institute. Partial support was also provided by the project titled “Long-term change of structure and function in marine ecosystems of Korea” funded by the Ministry of Land, Transport and Maritime Affairs. Support for Macdonald was provided through NSF Grant no. OCE-0926651.

References


Kim, I.-N.: Ocean biogeochemistry in the northern Gulf of Mexico, the East/Japan Sea, and the South Pacific with a focus on denitrification, Ph. D. thesis, Dep. of Mar., The Univ. of Texas, Austin, Texas, USA, 2012.


Table 1. Mean surface and bottom temperature, salinity, DO, AOU and $\Delta N_2O$ values for pre-storm and post-storm periods based on Walker et al. (2010) used to simulate $\alpha$ variability due to changes in physical environment. Since the pre-storm and post-storm $N_2O$ differences are small within the standard deviations (see their Fig. S1), we used the fixed values of mean surface and bottom $N_2O$ concentrations for the simulation.

<table>
<thead>
<tr>
<th>condition</th>
<th>T</th>
<th>S</th>
<th>DO</th>
<th>AOU (µmolL$^{-1}$)</th>
<th>$\Delta N_2O$ (nmolL$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2O = 8$ nmolL$^{-1}$ at surface</td>
<td>29</td>
<td>23</td>
<td>200</td>
<td>11.7</td>
<td>1.9</td>
</tr>
<tr>
<td>pre-storm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>post-storm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$N_2O = 16$ nmolL$^{-1}$ at bottom</td>
<td>24</td>
<td>36</td>
<td>40</td>
<td>171.7</td>
<td>9.4</td>
</tr>
<tr>
<td>pre-storm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>post-storm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$AOU = $[O_2]_{\text{saturation}}(T, S) - [O_2]_{\text{observed}}$.

$^b$$\Delta N_2O = [N_2O]_{\text{observed}} - [N_2O]_{\text{saturation}}(T, S)$.
Table 2. $N_2O$ concentrations (nmol L$^{-1}$) during the study period estimated from the Eq. (1) using $\alpha=0.048$, $\beta=0.7$, and $\gamma=0.7$. Standard deviations ($\pm$) indicate spatial variability within the study area.

<table>
<thead>
<tr>
<th>Year (for July)</th>
<th>$[N_2O]_{est}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1985</td>
<td>6.5 ± 8.0</td>
</tr>
<tr>
<td>1986</td>
<td>10.1 ± 8.7</td>
</tr>
<tr>
<td>1987</td>
<td>7.3 ± 4.5</td>
</tr>
<tr>
<td>1988</td>
<td>ND</td>
</tr>
<tr>
<td>1989</td>
<td>ND</td>
</tr>
<tr>
<td>1990</td>
<td>ND</td>
</tr>
<tr>
<td>1991</td>
<td>7.5 ± 4.9</td>
</tr>
<tr>
<td>1992</td>
<td>7.6 ± 6.2</td>
</tr>
<tr>
<td>1993</td>
<td>8.5 ± 6.2</td>
</tr>
<tr>
<td>1994</td>
<td>7.9 ± 4.5</td>
</tr>
<tr>
<td>1995</td>
<td>6.6 ± 6.1</td>
</tr>
<tr>
<td>1996</td>
<td>4.5 ± 6.4</td>
</tr>
<tr>
<td>1997</td>
<td>6.9 ± 4.8</td>
</tr>
<tr>
<td>1998</td>
<td>3.7 ± 12.2</td>
</tr>
<tr>
<td>1999</td>
<td>10.0 ± 8.4</td>
</tr>
<tr>
<td>2000</td>
<td>5.1 ± 4.3</td>
</tr>
<tr>
<td>2001</td>
<td>8.4 ± 6.4</td>
</tr>
<tr>
<td>2002</td>
<td>13.5 ± 9.8</td>
</tr>
<tr>
<td>2003</td>
<td>6.2 ± 4.3</td>
</tr>
<tr>
<td>2004</td>
<td>11.0 ± 8.7</td>
</tr>
<tr>
<td>2005</td>
<td>6.1 ± 5.8</td>
</tr>
<tr>
<td>2006</td>
<td>7.8 ± 7.1</td>
</tr>
<tr>
<td>2007</td>
<td>9.5 ± 6.3</td>
</tr>
</tbody>
</table>

ND: not determined.
1. under oxic conditions \((O_2 > 2 \text{mg L}^{-1})\),
Nitrification: \(\text{NH}_4^+ \rightarrow (\text{N}_2\text{O}) \rightarrow \text{NO}_2^- \rightarrow (\text{N}_2\text{O}) \rightarrow \text{NO}_3^-\) 
\(\rightarrow [\text{N}_2\text{O}]_{\text{est}}\)

2. under hypoxic-suboxic conditions \((0.13 < O_2 \leq 2 \text{mg L}^{-1})\),
Nitrification: \(\text{NH}_4^+ \rightarrow (\text{N}_2\text{O}) \rightarrow \text{NO}_2^- \rightarrow (\text{N}_2\text{O}) \rightarrow \text{NO}_3^-\) 
\(+\)
Denitrification: \(\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{N}_2\text{O}\) 
\(\rightarrow [\text{N}_2\text{O}]_{\text{est}}\)

3. under suboxic-anoxic conditions \((O_2 \leq 0.13 \text{mg L}^{-1})\),
Nitrification: \(\text{NH}_4^+ \rightarrow (\text{N}_2\text{O}) \rightarrow \text{NO}_2^- \rightarrow (\text{N}_2\text{O}) \rightarrow \text{NO}_3^-\) 
\(-\)
Denitrification: \(\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2\) 
\(\rightarrow [\text{N}_2\text{O}]_{\text{est}}\)

**Fig. 1.** A conceptual model of the processes affecting production and consumption of \(\text{N}_2\text{O}\) in near-bottom waters of the study area.
Fig. 2. The study area map showing the summer Texas–Louisiana shelf-wide cruise stations (red dots) during July 1985–2007 with bathymetry contours (black dotted-lines) in the northern Gulf of Mexico.
Fig. 3. A simple simulation of $\alpha$ ($= \Delta N_2O/AOU$) variability using the pre-and post-storm information found in Table 1.
Fig. 4. The individual contributions of nitrification (red squares, production), denitrification (blue circles, production), and denitrification (black diamonds, consumption) to the net N₂O concentrations in the nGOM from July 1985 to 2007.
Fig. 5. Interannual variations in summer (July) N\textsubscript{2}O concentration (nmol L\textsuperscript{-1}, red squares) and the areal extent of hypoxia (km\textsuperscript{2}, blue circles). The estimated N\textsubscript{2}O concentrations were significantly correlated with the areal extent of hypoxia ($R = 0.52$, $p < 0.05$ with $n = 20$). Data concerning the areal extent of hypoxia is available at http://www.gulfhypoxia.net/Research/Shelfwide%20Cruises/ (Data source: N.N. Rabalais, Louisiana Universities Marine Consortium, R.E. Turner, Louisiana State University).
Fig. 6. Distributions of bottom O$_2$ and estimated N$_2$O concentrations in July 2000 and 2002, which are min and max hypoxic area during the study periods, respectively. (a) and (b) bottom O$_2$ and N$_2$O spatial distributions in July 2000, (c) and (d) bottom O$_2$ and N$_2$O spatial distributions in July 2002.