

Benthic Anaerobic Respiration Enhances Bottom-water Acidification in the northern Gulf of Mexico

Hongjie Wang¹, John Lehrter², Kanchan Maiti³, Katja Fennel⁴, Arnaud Laurent⁴, Nancy Rabalais³, Najid Hussain¹, Qian Li¹, Baoshan Chen¹, K. Michael Scaboo¹ and Wei-Jun Cai^{1,*}

1. School of Marine Science and Policy, University of Delaware, Newark, Delaware 19716, USA.
2. Department of Marine Sciences, University of South Alabama, and Dauphin Island Sea Lab, Dauphin Island, Alabama 36528, USA
3. Department of Oceanography and Coastal Sciences, Louisiana State University, Baton Rouge, Louisiana 70803, USA
4. Department of Oceanography, Dalhousie University, Halifax, Nova Scotia, B3H 4R2, Canada

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*Corresponding to Dr. Wei-Jun Cai (wcai@udel.edu)

Key points

1. The observed pH and Ω in hypoxic bottom water are less than the ~~predicted~~^{estimated} values from anthropogenic CO₂ intrusion and aerobic respiration in northern Gulf of Mexico;
2. The additional pH and Ω declines in hypoxic water of northern Gulf of Mexico are caused by sediment benthic anaerobic respiration, and are positively correlated to ~~correlated to modeled time-integrated~~ hypoxic area.
- ~~3. The additional pH and Ω decline in hypoxic water is caused by sediment anaerobic respiration.~~

Abstract

In coastal oceans affected by nutrient delivery from the land, surface water eutrophication enhances ocean acidification in bottom waters. Based on an ~~eleven~~^{ten}-year collection of summer data from the northern Gulf of Mexico hypoxic zone, we show substantially lower pH (-0.03 ± 0.06 , up to 0.14~~up to 0.14~~) and aragonite saturation state Ω (-0.17 ± 0.39 , up to 0.9) in years

of extensive hypoxia than those ~~predicted-estimated~~ from water column aerobic respiration, anthropogenic CO₂ increase, and their known additive effect. Severe hypoxic or even anoxic conditions, which correspond to longer water residence times, favor the accumulation of benthic anaerobic respiration products, leading to additional pH and Ω reductions. Our findings on aerobic and anaerobic processes that contribute acidification in bottom waters provide new insights on the sensitivity of coastal acidification to hypoxia under current and future climate and anthropogenic change scenarios.

Plain Language Summary

The ongoing decrease in seawater pH (the base 10 logarithm of the molar concentration of hydrogen ions) as a result of uptake of anthropogenic carbon dioxide (CO₂) from the atmosphere is known as ocean acidification, which can be enhanced by the ~~water column~~-aerobic respiration in the water column. Meanwhile, regions of coastal hypoxia (dissolved oxygen < 2 mg L⁻¹) has increased in size and number during the last several decades because of water column eutrophication. In this study, we report that the bottom-water acidification is more severe in hypoxic water than ~~predicted-estimated~~ from anthropogenic CO₂ intrusion and water column organic carbon respiration in northern Gulf of Mexico. More specifically, we found that the organic matter respiration in sediment ~~can~~ further decreases the buffer capacity in hypoxic bottom waters. To our knowledge, this is the first study that uses data from multiple years and systematically examines the role of benthic fluxes on ocean acidification in eutrophic coastal bottom waters. The finding has significant implications for similar coastal systems ~~that where the~~ eutrophication-induced bottom ocean acidification is likely more severe than we thought.

1. Introduction

Ocean deoxygenation and ocean acidification (OA) resulting from natural and anthropogenic activities, are threatening marine ecosystem health (Doney, 2010; Gruber, 2011). Global warming decreases oxygen solubility and increases stratification, and thus is likely to further increase low-oxygen areas (Breitburg et al., 2018; Brewer & Peltzer, 2016). Biogeochemical models for the northern Gulf of Mexico predict that the hypoxia area (dissolved oxygen, or DO < 62.5 $\mu\text{mol L}^{-1}$) will increase by 26% between 2005-2010 and ~2100 (Laurent et al., 2018) and that the duration of hypoxia that occurs over an annual cycle will increase (Lehrter et al.,

2017). At the same time, increasing nutrient runoff is triggering eutrophication, which enhances both inorganic carbon removal in surface water, and production of more organic carbon in the water column (Smith, 2003). While eutrophication reduces surface-water acidification resulting from the anthropogenic CO₂ intrusion (Borges & Gypens, 2010; Laruelle et al., 2018; Wang et al., 2017), the respiration of organic carbon in both water column and sediment releases CO₂ back to the bottom water and accelerates bottom-water acidification (Berelson et al., 2019; Cai et al., 2011; Feely et al., 2010; Hagens et al., 2015; Wallace et al., 2014). Excess nutrient loadings have also led to the development of bottom-water hypoxic or anoxic conditions (DO=0 μmol L⁻¹), which may further draw down local pH (pH<7.5) due to benthic flux and subsequent oxidation of reduced chemicals (Cai et al., 2017). Meanwhile, the change of riverine alkalinity and dissolved inorganic carbon input from watersheds may either increase or decrease the buffering capacity in coastal systems (Duarte et al., 2013; Salisbury et al., 2008; Van Dam & Wang, 2019). Understanding the interactions among the above processes is crucial to understanding regional coastal acidification states and impacts on ecosystem service.

Eutrophication has resulted in increased accumulation of labile organic carbon in the surface sediment of the northern Gulf of Mexico (nGoM) based on the distribution of biomarkers in the sediment (Turner et al., 2004). This is likely happening in coastal oceans on a global scale (Dell'Anno et al., 2002; Turner & Rabalais, 1994; Zhao et al., 2015; Zimmerman & Canuel, 2000). As a result, Turner et al. (2008) hypothesized that benthic DO consumption has increased through time, in step with an increase in nutrient loading from the Mississippi River watershed. A coupled physical-biological model has also shown that the hypoxia formation in the nGoM is sensitive to benthic DO consumption driven by the vertical flux of organic matter from surface waters (Fennel et al., 2013). In general, the contribution of benthic DO consumption to total bottom-water DO consumption is negatively related to the hypoxic-layer depth (Fennel & Testa, 2019). For example, on average, the benthic consumption accounts for about 20~33% of the oxygen consumption in the hypoxic layer in the nGoM where the hypoxic-layer depth is only ~4 m above the sea bed (Fennel & Testa, 2019; Murrell & Lehrter, 2011). In comparison, the benthic consumption only contributed 3% to the total oxygen consumption in East China Sea where has a much thicker hypoxic-layer depth (~25 m). Therefore, in shallow waters and in waters where there is a pycnocline near the bottom, the bottom DO concentration is more

sensitive to the benthic respiration and physical processes of the bottom boundary layer (Kemp et al., 1992; Laurent et al., 2017; Yu et al., 2015).

Benthic respiration not only consumes DO and generates CO₂, but also affect total alkalinity (TA) depending on the dominant redox processes at a [given](#) site, e.g., reduction of NO₃⁻, Mn⁴⁺, Fe³⁺, and SO₄²⁻ generates TA while oxidation of NH₃, reduced Mn²⁺ and Fe²⁺, and H₂S consumes TA (Krumins et al., 2013; Van Cappellen & Wang, 1996). The ratio of benthic TA flux and DIC flux is less than 1 in shallow water (Hu & Cai, 2011), while the TA/DIC ratio in the water column is generally greater than 1.1. Therefore, benthic processes have the potential to further decrease bottom-water pH (Berelson et al., 2019), yet the observational evidence to verify this prediction has not yet been reported. Recently, Hu et al. (2017) simulated the bottom-water pH change based on two benthic DIC flux rates that were reported by Rowe et al. (2002) and a global model-derived TA/DIC of 0.25 (Krumins et al., 2013). However, benthic flux measurements in the nGoM carried out in summer 2011, under strong hypoxia, showed an average TA/DIC of 0.8 (Berelson et al., 2019). Nevertheless, Hu et al.'s (2017) simulation supports a strong implication that the bottom-water pH is sensitive to benthic anaerobic respiration products. The data from Hu et al. (2017) were collected in late July 2010, three months after the initiation of the Deepwater Horizon oil spill in mid-April, within a month after above average discharge of the Mississippi River in May and June, and shortly after tropical storm Bonnie. It is unclear whether the lowest pH values (~7.6) within the 20-m isobath close to the Louisiana-Texas border in 2010 is a recurring event or simply an isolated condition in summer 2010.

The objective of this study is to synthesize the effect of benthic processes on bottom-water pH in the nGoM from 2006 to 2017. Observations of water column carbonate chemistry, benthic fluxes, and results from a biogeochemical model are used to analyze the underlying mechanisms of any pH and Ω variability. We propose that the physical processes that support the development and maintenance of hypoxia also favor the accumulation of benthic respiration products, leading to further reductions in pH and Ω under prolonged low-oxygen concentrations.

2. Data and Methods

2.1 Seawater Carbonate Chemistry

We report the inorganic carbon data (DIC and TA) collected from 2006 to 2017 on summer cruises (Fig. S1, Table S1), when hypoxia occurs on the Louisiana shelf. pH and DO data from 2006-2010, and 2017 have been published in prior studies (Cai et al., 2011; Hu et al., 2017; Jiang et al., 2019). DIC data that were used to calculate pH and Ω from 2011 to 2016 were published in Wang et al. (2018).

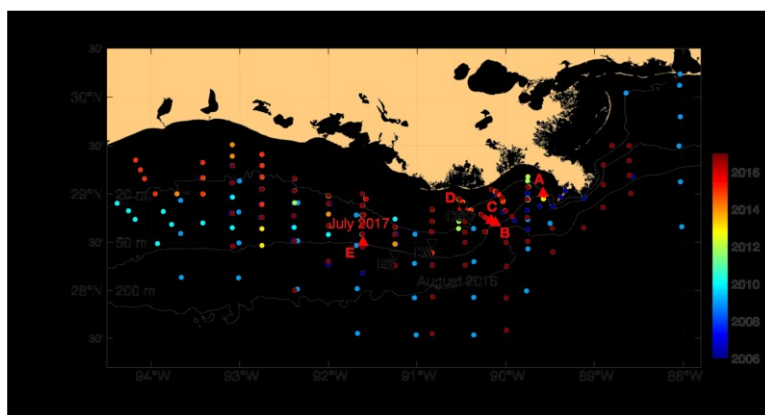


Fig. 1. The sampling locations in June, July, August, and September from 2006 to 2017 in the northern Gulf of Mexico. Upward-pointing and downward-pointing triangles represent the stations with sediment incubation in August 2016, and July 2017, respectively. Color map shows the sampling locations in different years as in Maintext (from 2006 to 2017). The grey contour or the shaded area shows the frequency of summer bottom-water hypoxia. Date source: N. Rabalais.

Briefly, Details of routine sampling and analytical methods are given in SI. water samples were taken from Niskin bottles into 250-mL borosilicate glass bottles and were poisoned with 100 μ L saturated HgCl_2 . The samples were kept at 4°C until being analyzed in the laboratory. DIC was measured with an infrared CO_2 detector-based DIC analyzer (AS-C3 Apollo Scitech). TA was measured with the open-cell Gran titration method using a temperature-controlled, semi-automated titrator (AS-ALK2 Apollo Scitech). Certified Reference Materials were analyzed for DIC and TA for quality control. The precisions for both DIC and TA are within 2 $\mu\text{mol kg}^{-1}$ ($\pm 0.1\%$). Spectrophotometric pH (pHspec; Liu et al. (2011)) was collected in year 2009, 2010 and 2012-2017 (Fig. 1, Table S1). We also calculated pH ($\text{pH}_{(\text{TA}, \text{DIC})}$) and aragonite saturation state (Ω) using CO2SYS program by choosing measured DIC and TA as the input pair (van Heuven, 2011). Silicate and phosphate concentrations was assigned as 0. The coefficients for pH

and Ω calculation were selected as: K_1 and K_2 value from Lueker et al. (2000); K_{HF} was from Dickson & Riley (1979); K_{HSO_4} was from Dickson (1990) and B_T (total boron) was from Uppström (1974). DO was measured by Winkler titration. Note, all the data listed in this study are from the warm season (June, July, August and September).

To determine how pH evolves because of anthropogenic CO_2 intrusion (from 2006 to 2017) and organic carbon respiration, we did simulations following the method reported in Cai et al. (2011). This study used the same representative surface water conditions as in Cai et al. (2011), which were collected from the July 2007 Gulf of Mexico and East Coast Carbon Cruise (GOMECC-1) in the Gulf of Mexico ($S = 36.3$, $t = 25^\circ C$, $TA = 2398.1 \mu mol\ kg^{-1}$). For example, for summer 2006, the dried air xCO_2 in 2006 was 381.9 ppm (<https://www.esrl.noaa.gov/gmd/ccgg/trends/>), so the equilibrated pCO_2 for this water mass was 370.2 μatm . The balanced DIC could be calculated as 2057.2 $\mu mol\ kg^{-1}$ by inputting the TA and equilibrated pCO_2 to CO_{2sys} . Using the same method, the balanced DIC was 2071.1 $\mu mol\ kg^{-1}$, with dry $xCO_2 = 406.5$ ppm in 2017 by assuming all other parameters constant (Cai et al., 2011). Aerobic respiration adds DIC or removes TA following the Redfield ratio (DO: DIC: TA = -138: 106: -17) based on the anthropogenic CO_2 equilibrated water. $pH@ 25^\circ C$ and $\Omega@ 25^\circ C$ was recalculated with CO_{2sys} by choosing the new pair of DIC and TA. With the same method, the pH-DO and Ω -DO evolutions were also simulated for each sampling year, pre-industrial era and year of 2100. When considering the benthic impact on bottom pH or Ω , we added benthic DO, DIC and TA flux on basis of water column DO, DIC and TA concentration. Eventually, another set of $pH@ 25^\circ C$ and $\Omega@ 25^\circ C$ can be recalculated with CO_{2sys} .

2.2 Benthic Flux Incubation

Sediment-water exchange rates of DO, DIC and TA were observed at five stations in August 2016 and July 2017 (Fig. S1). At each station, sediments were collected using either a multicorer or a 0.25-m² box corer that was subsampled in triplicate with Plexiglas cylindrical chambers (10-cm ID x 40 cm). The overlying water column inside the core incubations collected via multicorer were adjusted to a constant height of 25 cm using custom design lids that can be positioned at any height inside the core tube. For samples collected by box corer, the cores tubes were manually inserted into the box corer sample. Immediately after collection, three incubation cores per station were immersed in a temperature-controlled recirculating water bath incubator

adjusted to the recorded bottom-water temperature. Each core was carefully filled with bottom water with minimum disturbance to the sediment-water interface and closed to ensure no visible headspace or air bubbles at the top. All cores were attached to a reservoir containing bottom water for gravity driven replenishment of water inside the cores during sampling so as not to introduce any air bubbles. The core incubation and volumetric corrections was carried out by following the method outlined by (Ghaisas et al., 2019; Steingruber et al., 2001), where, sediment consumption alone decreased the DO inside these otherwise airtight core tubes.

All sediment incubations were carried out in the dark and lasted for 18-30 hours, depending on the final DO concentrations. Water samples in the incubation tubes were collected at regular intervals. DO was measured at each sampling point using temperature-compensated microoptodes. Samples for DIC and TA were collected in 12-ml exetainers, fixed with saturated HgCl_2 and stored at 5°C until final analysis. DIC and TA were measured with the same method as for water samples. Sediment DO consumption rates and benthic fluxes ($\text{mmol m}^{-2} \text{ d}^{-1}$) of DIC and TA were calculated by linear regression of constituent concentrations and time. Regression p-values were used to determine if flux rates were significantly different from zero ($\alpha=0.2$). In cases where p was higher than 0.2, a value of zero was assigned. Benthic flux rates were corrected for water column processes by subtracting rates measured in control core tubes with only bottom water. Positive sediment benthic fluxes indicated a net flux out of the sediments to the bottom water, whereas negative fluxes indicated a net flux from the bottom water into the sediments. The detail sediment sampling and incubation methods are given in SI. Note that the measured benthic DO flux at Station C6 in July 2017 only was not representative of *in situ* flux because the overlying water used for the incubation was collected at mid-depth instead of at the bottom. However, as TA and DIC gradients in sediment porewater develop over a much longer long-time-scale than oxygen, these sites' benthic TA and DIC fluxes are considered to be unaltered, less likely to be disturbed.

2.3 Modelled Time-integrated Low Oxygen Area

In order to scale benthic flux over the entire hypoxic region, we adopted the time-integrated low-oxygen area from a coupled physical-biogeochemical model that is configured for the nGoM (Laurent et al., 2018). The model is an implementation of a Regional Ocean Modeling System (Shepovetkin & McWilliams, 2005), which includes a hydrological module and a

DO, which is defined as the year-integrated area where bottom DO drops below a certain level. For our analysis, we defined two levels of low bottom-water DO: hypoxia ($DO < 62.5 \mu\text{mol L}^{-1}$) and severe hypoxia ($DO < 30 \mu\text{mol L}^{-1}$). For example, the modeled time-integrated hypoxic area was estimated to be $\sim 1,932 \times 10^3 \text{ km}^2 \cdot \text{yr}$ for 2017 (i.e. the area under the curve in Fig S12). Time-integrated areas of low bottom-water DO represent the cumulative impact of all processes from both water column and sediment before the low DO water was abated by loss of stratification or lateral advection of normoxic waters.

3. Results

3.1 Interannual Variability of Bottom-water pH and Ω

We compared pH calculated from DIC and TA with the measured spectrophotometric pH (pH_{spec}) from a subset of cruises and found that the calculated pH was close to the pH_{spec} (Fig. S3S2). The difference between the two methods is 0.00 ± 0.02 , which is within the uncertainty of the pH calculation (Woosley et al., 2017). Therefore, this study adopted the calculated pH and Ω to ensure the longest data record. Further, we only used data points with salinity > 32 and depth between 12 m and 50 m to achieve spatial consistency across the summer cruises (Cai et al., 2011; Hu et al., 2017).

Water column pH decreases with declining DO concentration (Fig. 4a2a). Consistent with a previous study (Cai et al., 2011), water column pH generally followed the trends predicted estimated by anthropogenic CO_2 intrusion and aerobic respiration when DO was still relatively high ($DO > 150 \mu\text{mol L}^{-1}$) (Fig. 4a2a, detailed method to derive the prediction-estimation curves is in SI). However, additional pH decline in the hypoxic condition is -0.03 ± 0.06 (mean $\pm$ stdev), with a maximum up to 0.14 unit lower than the predicted-estimated curve lines values caused by anthropogenic CO_2 intrusion and aerobic respiration (Fig. 4b2b), in contrast to pH in higher DO conditions, which is close to the predicted-estimated lines (0.00 ± 0.04 , Fig. 1a). Ω is also positively correlated with DO but there is more curvature at low DO condition in the relationship (Fig. 4e2c), which is consistent with a previous study (Feely et al., 2018). Additional Ω decline in hypoxic conditions is -0.17 ± 0.39 , with a maximum up to 0.90 unit lower than the predicted estimated curve (Fig. 4e2d).

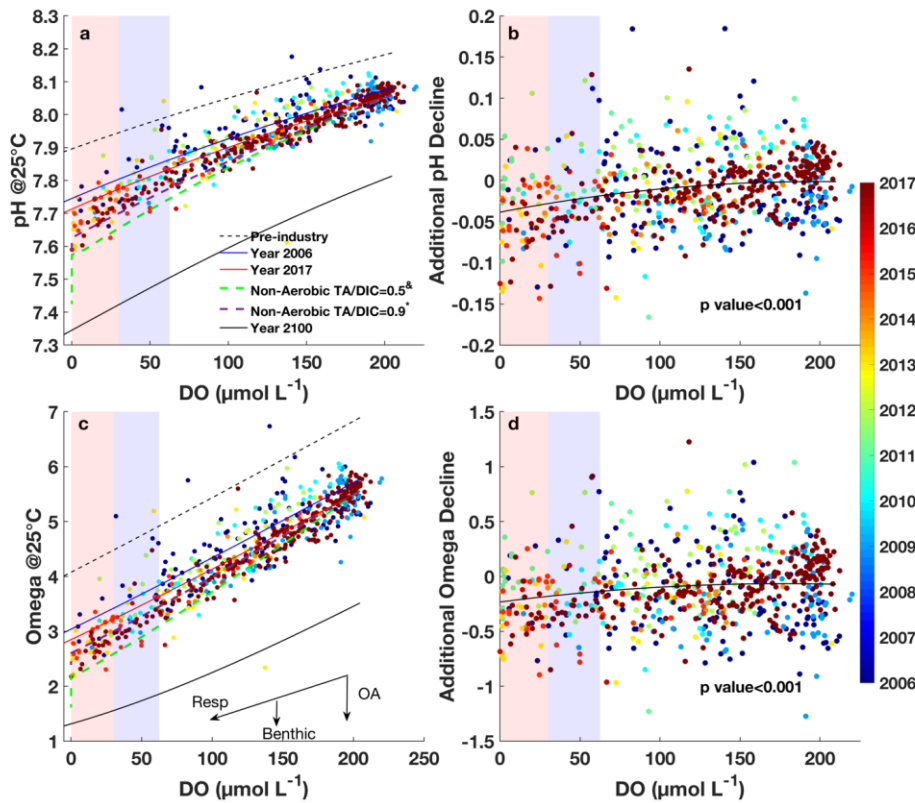


Fig. 4. (a). Relationship between pH and DO from summer 2006 to 2017 in northern Gulf of Mexico. All data presented here are with salinity > 32 and water depth between 12 m and 50 m. The black dashed, blue, red, and black solid lines represent the pH in the pre-industrial era, 2006, 2017, and 2100 with anthropogenic CO_2 intrusion and aerobic respiration. The green dashed lines represent the simulation based on our August 2016 cruise (R). The purple line denotes the simulation with results from Berelson et al. (2019)*. The method to derive the prediction-estimation curve is in SI. The extensions of the green and purple dashed lines are along the zero-oxygen line (y-axis) by assuming a ten days' anoxic conditions. (b) Relation between additional pH decline and DO concentration. Note, additional pH decline is defined as the difference between measured values and predicted-estimated ones from aerobic respiration of organic carbon and anthropogenic CO_2 intrusion in water column. The straight line represents the

second ~~order~~ polynomial fit. All notes are the same for panel (c, d) except they are for Ω @25°C, and all panels share the same color bar. pH and Ω changes due to increasing atmospheric CO₂, organic carbon ~~aerobic~~ respiration and benthic process are marked as OA, Resp (respiration), and Benthic in the insert panel c. The ~~patched-shaded~~ areas represent hypoxic conditions (DO<62.5 $\mu\text{mol L}^{-1}$), while red highlights the severe hypoxic (DO<30 $\mu\text{mol L}^{-1}$) to anoxic (DO=0 $\mu\text{mol L}^{-1}$) conditions.

The ~~eleven-ten~~ years of summer pH and Ω observations (Figs. ~~24~~a, c) indicate strong year-to-year variability. The observed pH and Ω values for DO <62.5 $\mu\text{mol L}^{-1}$ tend to be lower than the ~~predicted-estimated~~ curves, for example, in summer 2017, when the largest ever recorded hypoxic area occurred (Fig. ~~4a2a~~, https://gulfhypoxia.net/research/shelfwide-cruise/?y=2017&p=press_release). Hereafter, we refer to the difference between observed pH (or Ω) and ~~predicted-estimated~~ pH (or Ω) caused by anthropogenic CO₂ intrusion and aerobic respiration as “additional pH decline” or “additional Ω decline.” After combining all these yearly efforts, both declines were found to be significantly related to DO concentration (Figs. ~~4b2b~~, d, $p<0.001$).

3.2 Benthic Flux

During August 2016, the five benthic incubation stations extended from the river mouth to the open ocean (Fig. ~~S1~~, Table 1). Among them, Stations A and E were the closest and farthest station from river mouth, respectively. Station A was dominated by aerobic respiration (DO concentration was 144.7 $\mu\text{mol L}^{-1}$, Table 1). At Station E, used as a control station outside the regular hypoxic zone, bottom DO was as high as 150.3 $\mu\text{mol L}^{-1}$. Its negative TA flux indicated the dominance of aerobic respiration in sediment at this location. Station B was located at the edge of the regular hypoxic zone, while stations C and D were within the core of the hypoxic zone. Thus, we will assume hereafter that the mean DO, DIC and TA flux at Stations C and D (Table 1 and Table S2) are representative of the hypoxic zone and use those to estimate the impact of benthic respiration on bottom-water inorganic carbon system. The benthic DIC and TA flux at hypoxic station (Station C6) in July 2017 was 24.9 and 10.1 $\text{mmol m}^{-2} \text{d}^{-1}$, respectively. Overall, the DIC/TA ratios from 2016 and 2017 fall within the ranges of other studies in the

nGoM (Table 1) and are consistent with an earlier study that found the TA/DIC flux ratio to be always less than 1 within the 100-m water depth (Hu & Cai, 2011).

3.3 Benthic Impact Simulations

DO consumption rate in the water column was not measured in August 2016, but previous shelfwide study data indicated that the average water column DO consumption is $6.8 \mu\text{mol L}^{-1} \text{d}^{-1}$ (Murrell & Lehrter, 2011). At this rate, water column aerobic respiration alone should decrease bottom-water pH (or Ω) from 8.06 to 7.71 (or 5.56 to 2.86). Using the average hypoxic layer depth above the sea bed (3.9 m, Obenour et al. (2013)), the average measured DO flux from stations C and D in August 2016, and average DO consumption rate in the water column, it would take 21 days to deplete the saturated DO. The bottom-water residence time in nGoM is variable but likely longer than 30 days (Fennel & Testa, 2019; Rabouille et al., 2008). Therefore, bottom water has enough time to be impacted by benthic processes. Using the measured benthic DIC and TA flux from Station C and D in August 2016, the total DIC (or TA) production below the thermocline is $13.7 \mu\text{mol L}^{-1} \text{d}^{-1}$ (or $1.6 \mu\text{mol L}^{-1} \text{d}^{-1}$), leading to bottom pH and Ω under oxygen free conditions decreases to 7.57 and 2.20, respectively. In other words, with this benthic simulation, benthic respiration can further decrease bottom pH and Ω by 40% and 24% of water column aerobic respiration (Fig. 42, green dashed line).

The water column DO conditions in our shipboard incubation may not be fully representative of the *in situ* near-bottom conditions (see Method). Using an *in situ* benthic chamber technique, Berelson et al. (2019) determined that the average benthic DO, DIC and TA fluxes across the nGoM were -5.1, 41.5, and $32.4 \text{ mmol m}^{-2} \text{d}^{-1}$ in August 2011. With this new set of fluxes, smaller pH and Ω decreases to 7.63 and 2.63, respectively, (Figs. 4a2a, c, purple line) are comparable to the simulation with our own benthic data (Figs. 42a, c, green line).

3.4 Relationship between Bottom-water Ocean Acidification and Hypoxic Area

Both modeled hypoxic and anoxic areas vary annually (Fig. 23). The mean additional pH and Ω decline in hypoxic conditions is inversely related to the modeled time-integrated hypoxic area ($r=0.76\sim0.86$, Fig. 2b3b). Based on the second order polynomial fitting between time-integrated hypoxic area and additional pH decline, the time-integrated hypoxic area should be less than $1,163 \times 10^3 \text{ km}^2$ to maintain a zero-pH deviation. The annual mean additional pH decline

(-0.04±0.00, Fig. 2a3a) from 2014 to 2017 is lower than the value from 2010 to 2012 (0.00±0.01), which is related to a greater modelled time-integrative hypoxic and anoxic area from 2014 to 2017. Similarly, the annual mean additional Ω decline from 2014 to 2017 was -0.24±0.03, which is more negative than the values from 2010 to 2012 (-0.06±0.10).

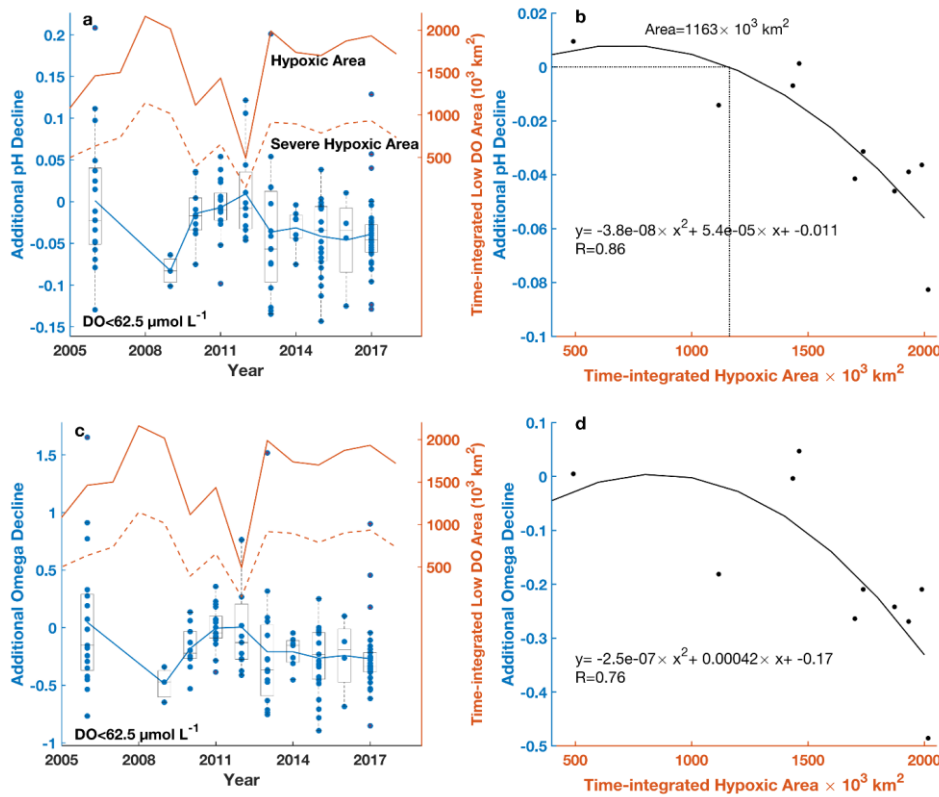


Fig. 23. (a) Distribution of observed additional pH decline at DO<62.5 μmol L⁻¹ condition (blue points), modelled time-integrated hypoxic area (<62.5 μmol L⁻¹, straight-connected orange line), and time-integrated severe hypoxic area (<30 μmol L⁻¹, dashed orange line) over time. The light-gray boxplots show the distribution of observed additional pH decline in hypoxic water (<62.5 μmol L⁻¹) in each year. The blue line connects the mean additional pH decline in each year. (b) relationship between mean additional pH decline at DO<62.5 μmol L⁻¹ and modelled

time-integrated hypoxic area. The inserted text shows the best-fit second [order](#) polynomial equation. All notes in (c, d) are the same as panel (a, b) except they are for additional Ω decline. Note, additional pH or Ω decline means the difference between measured values and ~~predicted~~ [estimated](#) values from organic carbon respiration and anthropogenic CO₂ intrusion in water column.

4. Discussion

4.1 Benthic Processes Affecting Bottom-water pH and Ω

Benthic fluxes of DO, DIC and TA are a net result of aerobic and anaerobic processes, which are not homogeneously distributed in the nGoM. Among them, the benthic DO flux rate covaries strongly with bottom-water DO concentration with rates approaching zero when the overlying DO is depleted (Cai & Sayles, 1996; Lehrter et al., 2012; Morse & Eldridge, 2007; Nunnally et al., 2013; Rowe et al., 2002). Under DO-rich conditions, aerobic respiration dominates the benthic organic [carbon](#) respiration, which can lead to a much lower benthic TA/DIC ratio. For example, the TA and DIC flux at station B in August 2016 is 1.0 mmol m⁻² d⁻¹ and 33.3 mmol m⁻² d⁻¹, when the benthic DO flux is -24.6 mmol m⁻² d⁻¹. Aerobic respiration stops in both water column and sediment when DO is near zero. Under this condition, benthic anaerobic respiration takes over according to the early diagenetic reaction sequence, i.e., denitrification, manganese and iron reduction, and sulfate reduction. The combination of aerobic and anaerobic consumption of DO, such as denitrification, can increase the TA and DIC addition to sediment porewater at a ratio derived from the Redfield ratio (i.e., -0.16) to 0.94 with decreasing DO concentration. However, the denitrification rates are much lower compared to rates of manganese and iron reduction, which are the dominant anaerobic processes across the nGoM (Devereux et al., 2015; Devereux et al., 2019). Anaerobic respiration processes increase TA at a faster rate than DIC (Berelson et al., 2019). In addition, CaCO₃ dissolution contributes to a TA:DIC ratio of 2:1. All these processes can be the reason for a higher TA/DIC ratio than aerobic respiration in sediment.

Even though the anaerobic process could increase TA in sediments, the subsequent re-oxidation of the reduced species (diagenetic byproducts such as NH₄⁺ and H₂S) by O₂ should release H⁺ and eliminate the additional TA increase with a net result equivalent to the aerobic respiration (Canfield et al., 1993a). However, the two processes can be decoupled spatially and

temporally forming pH maximum and minimum zones in sediment porewater (Cai et al., 2006). This can be further complicated when there is FeS and FeS₂ formation, which can be buried in sediments without readily being re-oxidized by O₂. It is possible there may be periods, such as summer, when anaerobic processes dominate, and reduced species build up in the sediments (Devereux et al., 2015). These reduced species may not be re-oxidized until fall/winter when DO is replenished (Eldridge & Morse, 2008), so there would be a period when TA is being generated, and then later being consumed. In summary, the combination of denitrification, oxidation of reduced species and iron sulfide precipitation may all be important for maintaining an observed benthic TA/DIC ratio (<1). More detail is provided in SI.

To circumvent the difficulty of not knowing exactly how much of the benthic O₂ flux is caused by aerobic respiration and how much is by the re-oxidation of reduced species, we separate benthic flux into “Net-aerobic” and “Non-Aerobic” parts for the purpose to quantify the impact of benthic flux on the water column pH vs DO curve. We defined “Net-Aerobic” flux as the sum of aerobic respiration and re-oxidation of reduced species generated from anaerobic processes (Canfield et al., 1993a). The “Net-Aerobic” part of benthic respiration could be integrated with the water column aerobic respiration, because they share the same amount of DIC addition and TA removal with every mole of DO consumption (at a change ratio of 106/-17/-138). Thus, the net impact of benthic respiration on pH vs DO or Ω vs DO curve depends on the remaining fraction (“Non-Aerobic” part which includes the anaerobic respiration and CaCO₃ dissolution, Table S2), which alters water column DIC and TA concentration but not DO concentration. The “Non-Aerobic” part of the TA/DIC ratio (Table S2) in August 2016 and August 2011 was 0.5, and 0.9, respectively. The lower “Non-Aerobic” TA/DIC ratio in August 2016 sediment flux led to a weaker water column buffer capacity, consequently, a higher pH reduction was predicted (Fig. 24, green line). In addition, water exchange affects the absolute time to reach hypoxia, but the pH vs DO curve remains the same as long as the water mass at the sampling location and surrounding region is impacted by the same processes (see detailed discussion in SI).

In summary, the combination of “Net-Aerobic” and “Non-Aerobic” flux can increase the benthic TA/DIC ratio from the Redfield ratio of -17/106 to a reasonably high value (<1) under a reduced DO in bottom water and near-zero DO inside the sediment. Selectively using one benthic flux under a particular DO concentration can either underestimate or overestimate the

benthic impact on bottom pH and Ω . However, the current limited sediment flux observation summarized in Table 1 is not sufficient to derive a reliable empirical equation to predict a benthic TA/DIC ratio because most of early studies did not reported benthic TA flux in the nGoM. To overcome this limitation, we did two simulations in Fig. 4 with higher and lower benthic DO flux conditions (-13.8 vs -5.1 mmol m⁻² d⁻¹). In other words, instead of exploring a single realistic scenario, our strategy was to estimate the possible ranges of benthic respiration impact on bottom-water pH and Ω (Figs. 4a, c). Overall, the additional pH decline caused by observed benthic DO, DIC and TA flux is smaller than the range (up to 0.2) reported by Hu et al. (2017), where a TA/DIC ratio of 0.25 derived from a global model was applied.

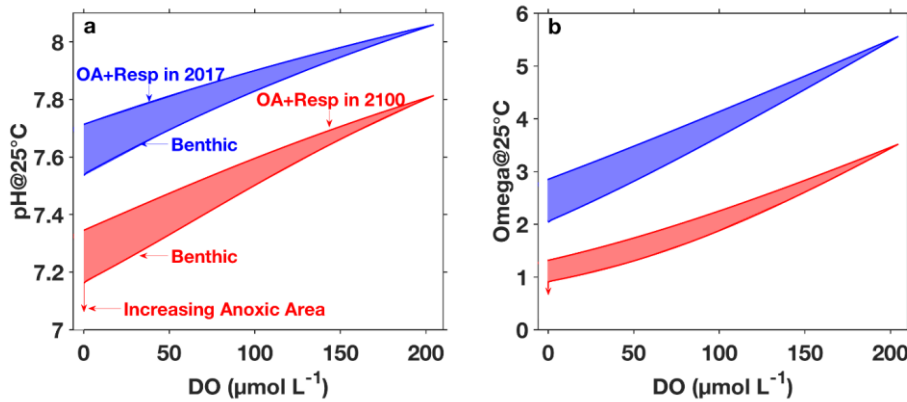
Laurent et al. (2018) used a coupled physical-biogeochemical model that calculated a negative-additional pH decline in low-DO conditions (Figure 4b in Laurent et al., 2018), which was only attributed to the weaker buffering capacity of acidified waters because they did not have anaerobic TA flux included in the benthic parameterization. The novelty of our study is to demonstrate how the benthic anaerobic process, especially, the “Non-Aerobic” fraction impacts bottom-water OA. This is likely happening in other coastal oceans that suffer seasonal or persistent hypoxic conditions. Clearly, further study is needed to develop a more comprehensive picture of benthic respiration products under different DO condition to better refine and constrain future models of OA dynamics.

4.2 Implication for Future Coastal Bottom-water Ocean Acidification

Models by Laurent et al. (2018) predict that hypoxia in the Gulf of Mexico is likely to increase by ~ 26% by 2100 because the decreasing oxygen solubility and increasing stratification caused by climate change. This study demonstrates that as the time-integrated extent of hypoxia increases in the Gulf of Mexico, the accumulation of benthic respiration products is favored.
~~Under the RCP8.5 scenario, the extent of hypoxia in the Gulf of Mexico is projected to increase by 26% by 2100. This is due to a combination of factors, including decreasing oxygen solubility and increasing stratification caused by climate change. The study shows that as the time-integrated extent of hypoxia increases, the accumulation of benthic respiration products is favored, leading to a further decline in pH and Ω .~~
 anthropogenic CO₂ intrusion and organic carbon respiration (Fig. 34).

The increased duration of severe hypoxia and anoxia (Laurent et al., 2018; Lehrter et al., 2017) under a future scenario would further decrease bottom pH, because of the accumulation of benthic DIC and TA in bottom water (Fig. 42). The simulation based on August 2016 (Fig. 42, green dash line) indicates that an additional ten days of anoxic condition will results in further pH and Ω decrease-decline from 7.57 to 7.41, and 2.20 to 1.58, respectively (at DO=0, Fig.1).

414 This prediction shows the importance of anoxic duration on pH or Ω decrease. The exact amount
 415 of the additional pH (or Ω) declines by 2100 is difficult to predict, but the maximum pH (or Ω)
 416 decrease would be over 0.14 (or 0.90). These decreases are compounded by the expected pH (or
 417 Ω) decrease of 0.47 (or 2.2) due to water column aerobic respiration, anthropogenic CO₂ increase
 418 in the atmosphere, and their synergistic effects (Cai et al., 2011). Even though bottom-water Ω is
 419 still expected to be above 1 in the coming few decades, the dissolution threshold ($\Omega \sim 1$) would
 420 occur sooner in bottom hypoxic waters than expected from the combined impact from
 421 anthropogenic CO₂ intrusion and aerobic respiration (Fig. 34).



422
 423 Fig. 34. Relationships between (a) pH, (b) Ω and DO in summer bottom water of the
 424 northern Gulf of Mexico. Relationships are calculated for present (year 2017, blue) and future
 425 (year 2100, red) simulations. The shades are the impact of benthic respiration on bottom pH
 426 based on August 2016 sediment dissolved oxygen, dissolved inorganic carbon, and alkalinity
 427 flux (non-aerobic benthic TA and DIC ratio is 0.5). The vertical red arrow along DO=0 shows
 428 the impact of ten days of anoxic condition on bottom water (a) pH and (b) Ω . pH changes due to
 429 increasing atmospheric CO₂ intrusion, organic carbon respiration and observed benthic processes
 430 are marked as OA, Resp and Benthic in panel a. All notes are applicable to Ω change in panel b.
 431 Note, we used August 2016 benthic flux to simulate pH and Ω change under the future scenario.

433 5. Conclusion

434 The interannual variability of additional pH and Ω decrease is positively related to decreased
 435 bottom DO concentration. The extensive and prolonged hypoxic or anoxic conditions can

amplify the benthic effects on bottom pH and Ω decreases. The additional pH and Ω decrease can be alleviated only if the modeled time-integrated hypoxic area hypoxia condition is well under control (i.e., $< 1.16 \times 10^6 \text{ km}^2$ modeled time-integrated hypoxic area in the GoM in Fig. 23). This is likely happening to other shallow bottom water systems, such as Chesapeake Bay and Pearl River estuary. High resolution sediment profiles have confirmed a net H^+ flux from sediment to bottom water in Long Island Sound sediments (Fig. 7d in Zhu et al. (2006)). The benthic impact, which is known as a eutrophication legacy concerning oxygen consumption, can also enhance bottom-water OA. This research adds another mechanism to the big picture linking eutrophication and bottom-water OA.

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Table 1. Summary of DO, DIC and TA flux from the northern Gulf of Mexico. Positive flux is defined as from sediments into the bottom water.

	Date	Depth (m)	T (°C)	S	DO ($\mu\text{mol L}^{-1}$)	Benthic DO flux ($\text{mmol m}^{-2} \text{d}^{-1}$)	Benthic DIC flux ($\text{mmol m}^{-2} \text{d}^{-1}$)	Benthic TA flux ($\text{mmol m}^{-2} \text{d}^{-1}$)	TA/DIC
Station A#	August 2016	19.5	29.64	31.81	144.7	-13.5 $\pm$ 0.2	33.0 $\pm$ 2.1	-3.3 $\pm$ 13.2	-0.1
Station B#	August 2016	45.5	24.05	36.32	161.2	-24.6 $\pm$ 13.8	33.3 $\pm$ 4.2	1.0 $\pm$ 3.6	0.03
Station C#	August 2016	35.5	25.80	35.92	132.5	-13.7 $\pm$ 0.6	39.9 $\pm$ 13.3	15.4 $\pm$ 21.1	0.39 [•]
Station D#	August 2016	17.5	27.51	33.77	45.0	-13.8 $\pm$ 0.6	26.3 $\pm$ 6.9	3.7 $\pm$ 9.2	0.14 [•]
Station E#	August 2016	49.5	24.43	36.08	150.3	-10.9 $\pm$ 1.0	84.5 $\pm$ 10.5	-15.5 $\pm$ 27.8	-0.18
Station C6	July 2017	18.4	16.98	35.12	26.7	-	24.9	10.1	0.41
Station D5	July 2017	31.4	25.23	36.08	173.4	-	16.0	0.6	0.04
Station E6	July 2017	55.1	22.53	36.21	135.8	-	5.4	2.2	0.40
Shelf nGoM [§] (Rowe et al, 2002)	July 1991	17.0~21.0 (19.0 $\pm$ 1.8)	25.2~26.8 (26.2 $\pm$ 0.7)	-	6~83 (26.5 $\pm$ 37.7)	-18.4~-0.82 (-9.73 $\pm$ 7.2)	-	-	-
	August 1994	12.0~25.0 (20.7 $\pm$ 7.5)	27.2~28.6 (28.1 $\pm$ 0.8)	-	0~14 (8 $\pm$ 7)	-1.9~-56.4 (-25.0 $\pm$ 28.2)	24~55 (39.0 $\pm$ 15.5)	-	-
	March 2005 to August 2007	5.0~22.0 (13.5 $\pm$ 8.3)	20.0~30.0	>35	58.7~125.5 (100 $\pm$ 29)	-23.9~0 (-10 $\pm$ 6)	7.9~21.5 (17.2 $\pm$ 2.4)	-	-
Shelf nGoM [*] (Lehrter et al., 2012)	August 2007	18.0~23.0	22.6~29.2	25.2~35.8	0~160	-11.8~0	24.8~58.9	24.2~49.1	0.57~0.98
Shelf nGoM [*] (Berelson et al., 2019)	August 2011	(21.5 $\pm$ 2.4)	(25.7 $\pm$ 2.7)	(32.7 $\pm$ 5.0)	(53 $\pm$ 73)	(-5.1 $\pm$ 4.9)	(41.5 $\pm$ 14.0)	(32.4 $\pm$ 11.7)	(0.80 $\pm$ 0.2) [•]

Note, # Ebner (2019); [§] flux data without Station 1 (see details in Rowe et al. (2002)); [&]There were no DIC flux measurement in March 2005 (see details in Lehrter et al. (2012)); ^{*}Flux data from entire Gulf of Mexico shelf after excluding Station 8 (see details in Berelson et al. (2019)); [•]TA/DIC ratio we used to simulate benthic impact on bottom-water pH and Ω (See details in text). The hypoxic stations are highlighted in bold.