

# Acidification of subsurface coastal waters enhanced by eutrophication

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**Human inputs of nutrients to coastal waters can lead to the excessive production of algae, a process known as eutrophication. Microbial consumption of this organic matter lowers oxygen levels in the water<sup>1–3</sup>. In addition, the carbon dioxide produced during microbial respiration increases acidity. The dissolution of atmospheric carbon dioxide in ocean waters also raises acidity, a process known as ocean acidification. Here, we assess the combined impact of eutrophication and ocean acidification on acidity in the coastal ocean, using data collected in the northern Gulf of Mexico and the East China Sea—two regions heavily influenced by nutrient-laden rivers. We show that eutrophication in these waters is associated with the development of hypoxia and the acidification of subsurface waters, as expected. Model simulations, using data collected from the northern Gulf of Mexico, however, suggest that the drop in pH since pre-industrial times is greater than that expected from eutrophication and ocean acidification alone. We attribute the additional drop in pH—of 0.05 units—to a reduction in the ability of these carbon dioxide-rich waters to buffer changes in pH. We suggest that eutrophication could increase the susceptibility of coastal waters to ocean acidification.**

Excessive biological production of organic matter (OM) in coastal ocean surface waters induced by human inputs of nutrients (that is, eutrophication) and the subsequent development of hypoxia ( $[O_2] < 62.5 \mu M$ ) in subpycnocline waters (that is, the lower part of a stratified water column) due to respiration of the sinking OM have been reported with increasing frequency. This process has received global attention because of the negative impact of eutrophication and hypoxic events on coastal ecosystems<sup>1–3</sup>. The same respiratory processes, however, also release carbon dioxide ( $CO_2$ ), lowering the pH (that is, increasing acidity) of subsurface waters in these regions.

Ocean acidification, resulting from dissolution of atmospheric anthropogenic  $CO_2$  in oceanic waters<sup>4</sup>, represents an additional emerging global threat to the health of marine ecosystems<sup>2,5</sup>. Coastal ocean waters undergo natural pH fluctuations on daily, seasonal, and even inter-annual scales; however, the atmospheric  $CO_2$  increase has also caused long-term increases in sea surface  $CO_2$  concentration, resulting in decreases in pH (refs 6–8). Such a trend is predicted to alter patterns of biogenic carbonate formation

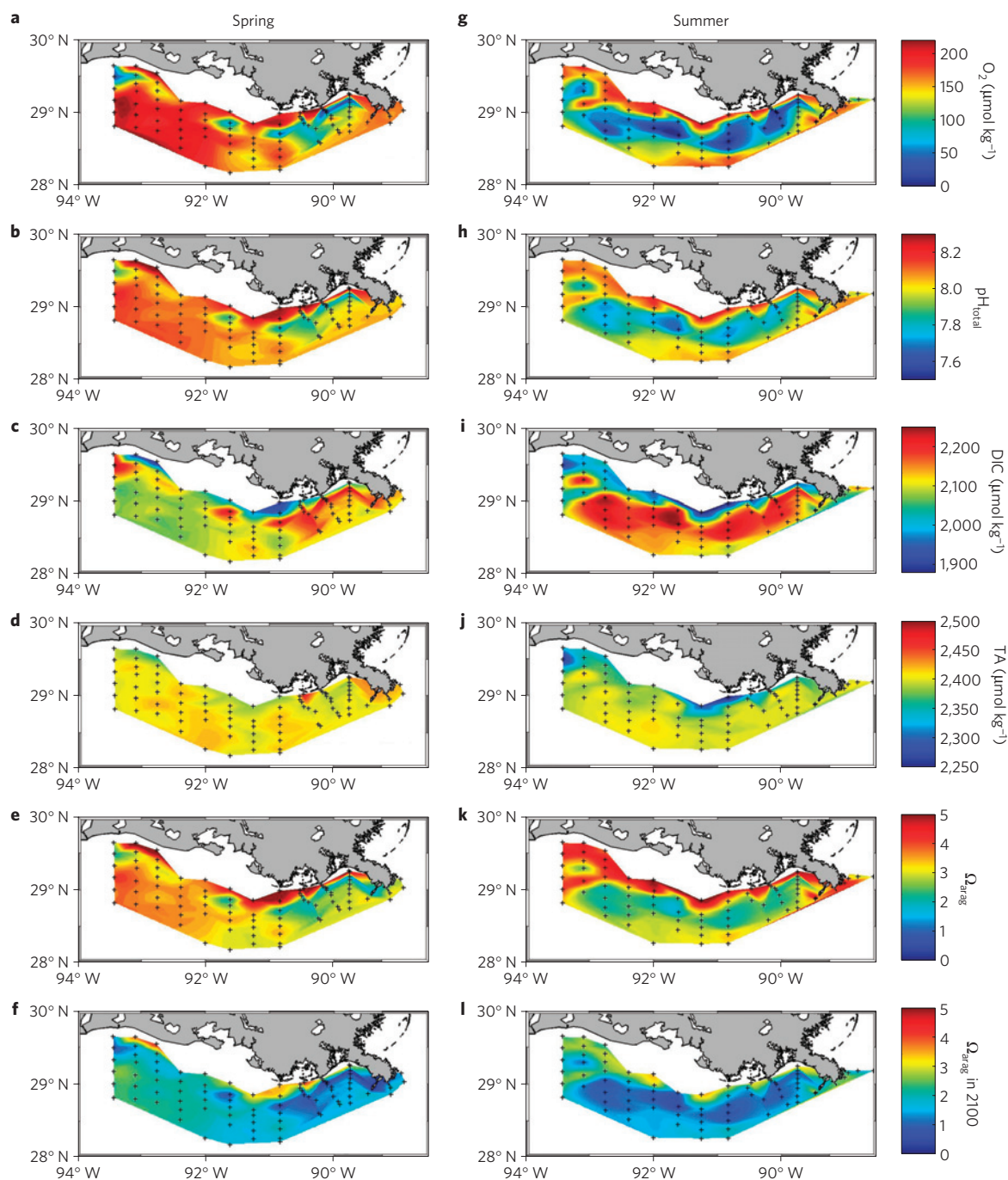
and may also significantly affect other ocean biogeochemical cycles<sup>2,4,5,7,9–11</sup>. In spite of these potentially important consequences, at present there is only limited understanding of the interactions between coastal eutrophication and global ocean acidification.

The interaction between atmospheric  $CO_2$  uptake and coastal eutrophication may be demonstrated in continental shelf waters of the northern Gulf of Mexico (nGOM) and the East China Sea (ECS). Although these systems have distinct characteristics, both the nGOM and ECS are shallow stratified continental shelf environments that receive massive loads of fresh water, nutrients, and organic and inorganic carbon from two of the world's largest rivers, both of which are subject to the effects of human development<sup>12–14</sup>. The Mississippi River has experienced a tripling in nitrate loading between the 1950s and 1980s due to increased use of agricultural fertilizers<sup>13</sup>. Similarly, nitrate loading from the Changjiang River has increased fourfold over the past 40 years<sup>15</sup>. In both systems, hypoxia develops from spring to late summer<sup>3,13</sup> in subpycnocline waters beneath and downstream of the river plumes (salinity  $< 32$ ) in shelf areas less than 50 m deep. The predominant cause of  $O_2$  consumption in both systems is respiration of OM produced and exported from the plume<sup>3,13,16–18</sup>. It is suggested that future climate and land use changes may result in even more extensive eutrophication and hypoxia on river-dominated ocean margins<sup>12,17,19</sup>.

We have conducted multiple surveys in the nGOM and ECS which consistently showed a very low partial pressure of  $CO_2$  ( $p_{CO_2}$ ) in the river plumes during spring and summer. Observed low  $p_{CO_2}$  (refs 20–22), high chlorophyll *a*, and high net primary production<sup>16,18</sup> were consistent with strong biological uptake of  $CO_2$  and nitrate in surface waters of both systems (Supplementary Fig. S1).

This surface water eutrophication was accompanied by development of hypoxia and acidification in subpycnocline waters on the shelves. The development of hypoxia in the nGOM started in spring when water column stratification started (Fig. 1a). Accompanying this early season hypoxia, we observed limited areas of low pH (Fig. 1b), high dissolved inorganic carbon (DIC) (Fig. 1c) and low carbonate saturation state (Fig. 1e). By the summer, widespread hypoxia had developed (Fig. 1g), coinciding with an extensive area of low pH (Fig. 1h) and low carbonate saturation state in near-bottom waters (Fig. 1k). The hypoxia is attributed to local

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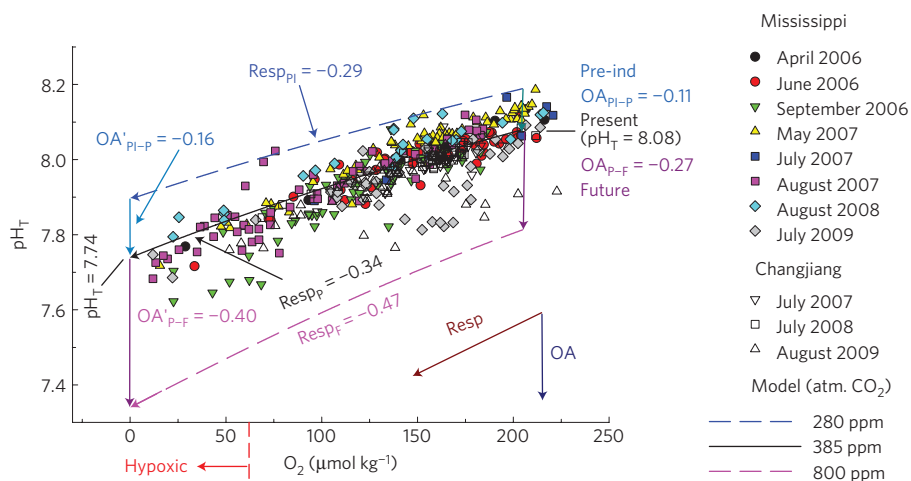
**Figure 1 | Spatial distributions of near-bottom water properties in May 2007 and August 2007 from the nGOM. a–l, Dissolved O<sub>2</sub> (a,g), pH<sub>T</sub> or  $-\log(\text{total hydrogen ion concentration})$  (b,h), DIC (c,i), TA (d,j), seawater saturation state with respect to the mineral aragonite,  $\Omega_{\text{arag}}$ , for the present day (e,k), and predicted values for 2100 with minor hypoxia (f), as in May 2007, and with severe hypoxia (l), as in August 2007. Here  $\Omega_{\text{arag}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]/K_{\text{sp}}$ , where  $[\text{Ca}^{2+}][\text{CO}_3^{2-}]$  is the ion concentration product of the two species and  $K_{\text{sp}}$  is the  $\text{CaCO}_3$  mineral solubility constant.**

OM remineralization and limited ventilation, as evidenced by the increase in DIC in the hypoxic water (Fig. 1i). The total alkalinity (TA), a quasi-conservative tracer of water mixing, was similar between spring and summer (Fig. 1d,j). Subsurface water DIC increase and O<sub>2</sub> decrease were also well correlated as is expected during OM mineralization (Supplementary Fig. S2).

In addition, analysis of all data collected in the nGOM revealed a significant positive correlation between subsurface water pH and O<sub>2</sub> concentration (Fig. 2) ( $r = 0.87$  and  $p < 0.0001$  for the pooled data), further linking the intensified subpycnocline acidification to oxygen consumption via OM oxidation. Data from the ECS

impacted by the Changjiang plume show a similar relationship between pH and O<sub>2</sub> concentrations ( $r = 0.72$  and  $p < 0.0001$  for the pooled data), supporting the generality of our observations from the nGOM.

As illustrated in the conceptual model (Fig. 3), vertical decoupling between the locations of primary production (surface) and respiration (subsurface) is largely responsible for the observed correlation between pH and [O<sub>2</sub>] in shelf waters impacted by a large river plume. Riverine nutrients support elevated phytoplankton carbon fixation in the surface water (which raises pH and lowers  $p_{\text{CO}_2}$ ). Subsequent sinking and respiration of this OM below

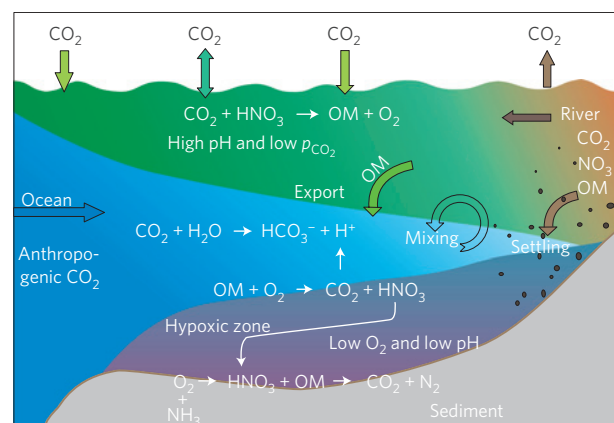


**Figure 2 | Relationships between subsurface water pH and  $O_2$  concentration from the nGOM and ECS shelves and model simulations.** All data points with  $S > 32$  and depth  $> 12$  m are presented. The 2007 pH from the ECS were calculated from published DIC and TA data<sup>21</sup>. Superimposed on the measured data are three model simulations with the blue (dash), black (solid) and pink (dash) lines representing atmospheric  $CO_2$  levels at 280 (pre-industrial or PI), 385 (present day or P), and 800 ppm (future year 2100 or F), respectively (see Supplementary Methods). pH changes due to increasing atmospheric  $CO_2$  or OM respiration are marked as OA (ocean acidification) and Resp (respiration), respectively.

the pycnocline introduces additional  $CO_2$  into subsurface waters, thereby reducing the pH and seawater carbonate saturation state. When  $O_2$  is available, the most important respiration process is aerobic or via  $O_2$  consumption, that is,  $(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138O_2 \rightarrow 106CO_2 + 16HNO_3 + H_3PO_4 + 122H_2O$ . Note that on hydration  $CO_2$  becomes carbonic acid and is part of the DIC pool but has no effect on TA while the production of a small amount of the strong acid,  $HNO_3$ , only plays a minor role in reducing pH and TA. When  $[O_2]$  is sufficiently low, such as at the sediment–water interface, coupled nitrification and denitrification can occur. However, as the proton produced during nitrification is consumed during denitrification, the net result on  $CO_2$  parameters is similar to aerobic respiration<sup>23,24</sup> (Fig. 3 and Supplementary Discussion). A model calculation incorporating aerobic respiration simulates the observed decrease in pH well (black solid line in Fig. 2).

Oceanic uptake of anthropogenic  $CO_2$  from the atmosphere since the 1800s has caused pH in surface waters to decrease by about 0.10 units globally<sup>4</sup>. We assume that the offshore water, which is the source for inner and middle shelf waters, has been in equilibrium with the atmosphere, and thus reflects the increase of the atmospheric  $CO_2$ , as was observed in the North Sea<sup>6</sup> and the South China Sea<sup>8</sup>. When this water, with a higher DIC, is advected onshore and mixed with inshore waters, it lowers pH below that expected from pre-industrial times. Moreover, DIC in this water can be increased further by OM respiration (Fig. 3). Consequently, a model comparison of present conditions in the  $O_2$ -depleted subpycnocline waters of the nGOM shelf with a hypothesized state during pre-industrial and pre-eutrophication conditions revealed a pH decrease of as much as 0.45 units (Fig. 2). Contributing to this pH drop are  $CO_2$  uptake from the atmosphere by oxygenated offshore source waters (0.11 units) and  $CO_2$  produced *in situ* by OM oxidation (0.29 units). The additional drop of 0.05 pH units is a consequence of the decreased buffering capacity of  $CO_2$ -enriched waters.

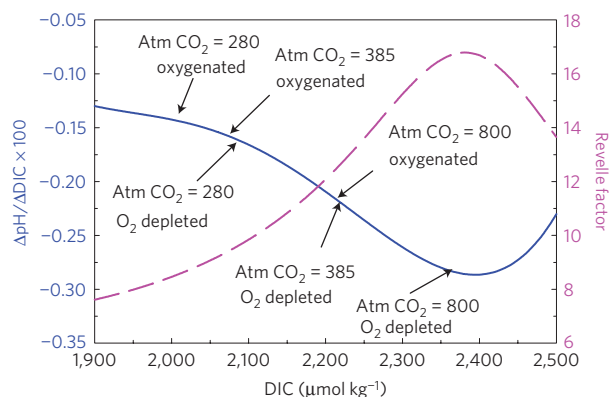
The buffering capacity of sea water is reduced as DIC increases (that is, for a given increase in DIC, a larger decrease in pH occurs or the Revelle factor<sup>25</sup> becomes greater at higher DIC, see Fig. 4). Importantly, the pH and carbonate saturation state of sea water are controlled by the ratio of DIC to TA (ref. 25). For a pure carbonate solution, we have  $TA - DIC = [CO_3^{2-}] - [CO_2]$ , and that  $pH = -(1/2)\log(K_1K_2) - (1/2)\log([CO_2]/[CO_3^{2-}])$ ,



**Figure 3 | A conceptual model for a large river plume eutrophication and subsurface water hypoxia and acidification.** See the main text for explanation.

where  $K_1$  and  $K_2$  are dissociation constants of the carbonic acid. Therefore, at the point where  $DIC = TA$  (that is,  $[CO_3^{2-}] = [CO_2]$ ), a slight increase in  $[CO_2]$  and the associated decrease in  $[CO_3^{2-}]$  will cause a large decrease in pH. In other words, the marine carbonate system has a weakened buffering capacity near this point<sup>26,27</sup>. The resulting highly nonlinear pH change may have a profound implication on how ocean acidification interacts with biogeochemical processes in coastal eutrophication–hypoxia zones and other similar environments where net respiration of OM contributes additional  $CO_2$  to the DIC pool.

The above result can be viewed as a greater pH decrease caused by atmospheric anthropogenic  $CO_2$  input into  $O_2$ -depleted and  $CO_2$ -enriched water (0.16 pH units, Fig. 2) than into  $O_2$ -rich and  $CO_2$ -poor water (0.11 units). We call this effect ‘enhanced ocean acidification’, emphasizing the biological amplification of the originally defined ‘ocean acidification’ concept<sup>4,28</sup>. Consequently, in a future scenario where atmospheric  $pCO_2$  increases to 800 parts per million (ppm) by the end of this century<sup>29</sup>, buffering capacity of waters subjected to eutrophication-induced hypoxia will be reduced further, resulting in an overall pH drop of 0.74 units between oxygenated offshore water today and oxygen-depleted subpycnocline water in the future. In this scenario, uptake of



**Figure 4 | Seawater buffering capacity as a function of CO<sub>2</sub> addition.** The rate of pH decrease (per 100  $\mu\text{mol kg}^{-1}$  addition of CO<sub>2</sub> into the system) increases from 0.1 to 0.3 units, indicating a decreased seawater buffering capacity, as DIC in subsurface waters increases from 1900 to 2400  $\mu\text{mol kg}^{-1}$ . The Revelle factor, defined as the ratio of  $(\Delta p_{\text{CO}_2}/p_{\text{CO}_2})$  to  $\Delta[\text{DIC}]/[\text{DIC}]$ , also reflects, inversely, the system's buffer capacity (note that a higher Revelle factor means a lower buffer capacity). DIC concentrations corresponding to various atmospheric  $p_{\text{CO}_2}$  levels and subsurface [O<sub>2</sub>], discussed in the main text, are marked.

anthropogenic CO<sub>2</sub> contributed to a pH drop of 0.27 units, OM oxidation contributed 0.34 units, and decreased buffering capacity contributed an additional 0.13 units (Fig. 2). Again, the additional pH drop represents a biological enhancement of 'ocean acidification' (from 0.27 to 0.40 pH units, Fig. 2).

Alternatively, the above 'enhanced ocean acidification' can also be interpreted as a greater decrease in pH caused by respiration of a fixed amount of OM in water that is initially in equilibrium with a high atmospheric  $p_{\text{CO}_2}$  versus that with a low atmospheric  $p_{\text{CO}_2}$  (that is, for a given amount of O<sub>2</sub> consumption, the pH-drop increases from 0.29 to 0.34 and to 0.47 units for pre-industrial, present day, and future scenarios, respectively, see model lines in Fig. 2). Again, this is due to decreased buffering capacity under high  $p_{\text{CO}_2}$  scenarios. Overall, the consequences of global ocean acidification will become more acute in the coastal zone as atmospheric CO<sub>2</sub> continues to increase unless eutrophication is greatly reduced.

Decreased pH of subpycnocline waters may have profound implications for biological communities and biogeochemical processes in coastal waters associated with large nutrient-laden rivers and other low O<sub>2</sub> zones in coastal oceans<sup>5,9,11,19,30</sup>. As shown here, such environments would acidify more readily and approach carbonate mineral undersaturation (for example,  $\Omega_{\text{arag}} < 1$ , see Fig. 1 legend) faster than other parts of the world's upper ocean. The acidification observed in the nGOM is approaching, but has not yet reached, carbonate undersaturation (Fig. 1k) because of the overall higher TA in the nGOM than some other marginal seas<sup>7</sup>. However, simulations based on future scenarios, assuming no change in eutrophication status, predict widespread carbonate undersaturation at the nGOM seafloor within this century (Fig. 1f and l, and Supplementary Fig. S3). A recent global synthesis reported that long-term trends in O<sub>2</sub> concentrations indicated faster O<sub>2</sub> consumption in coastal waters than in the open ocean<sup>3</sup>, which supports a trend of increasing eutrophication and hypoxia, and hence biological enhancement of ocean acidification in coastal ocean subpycnocline waters. However, if human actions (for example, agriculture practices) can be taken to reduce eutrophication<sup>13</sup>, seafloor carbonate mineral undersaturation may be less severe (Fig. 1f).

In summary, CO<sub>2</sub> production during the decomposition of OM produced in and settled from eutrophicated river plumes, such as the Mississippi and Changjiang, has already enhanced

the acidification of coastal subsurface waters. Under future scenarios with higher atmospheric CO<sub>2</sub> and the current levels of eutrophication, we predict dramatic increases in acidification of subpycnocline waters that could inhibit biogenic carbonate precipitation, thus making these ecosystems most vulnerable to ecological and biogeochemical perturbations. As a result, these highly productive ecosystems, which support extensive fin- and shellfish fisheries, are at increased risk of suffering the negative effects of ocean acidification.

Analytical methods for determination of DIC, TA and pH are given in the Supplementary Information. Analytical uncertainties for DIC and TA are  $\pm 2\text{--}4 \mu\text{mol kg}^{-1}$  and  $\pm 0.01$  unit for pH. To estimate how much DIC has been and will be added to shelf subsurface water from the industrial revolution to the present, and from the present to the future, we used the chemistry of current offshore surface water (upper 50 m) of the Gulf of Mexico as a starting point. We reduced or increased DIC of this water, while keeping TA and other conditions constant, to obtain a dry CO<sub>2</sub> fraction of 280, 385 and 800 ppm. Then we add CO<sub>2</sub> derived from aerobic oxidation of OM at Redfield ratios (C:O<sub>2</sub> = 106:138) to these waters to obtain the three modelled pH curves in Fig. 2. See Supplementary Methods for details and model parameters. If the offshore source water is 15 ppm off the designated atmospheric value, the model-simulated pH will be off systematically by 0.018, 0.014 and 0.007 units respectively in the 280, 385 and 800 ppm cases.

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### Author contributions

W.-J.C., X.H., W.-J.H., X.G., and Y.W. are responsible for CO<sub>2</sub> and pH data collection in the nGOM and W.-C.C., W.Z., and M.D. for those in the ECS. J.C.L., M.C.M., S.E.L. and K.G. are responsible for O<sub>2</sub> and nutrient data collection in the nGOM and W.Z. and G.-C.G. for those in the ECS. All authors discussed the results and commented on the manuscript.

### Additional information

The authors declare no competing financial interests. Supplementary information accompanies this paper on [www.nature.com/naturegeoscience](http://www.nature.com/naturegeoscience). Reprints and permissions information is available online at <http://www.nature.com/reprints>. Correspondence and requests for materials should be addressed to W.-J.C.