Divergent effects of biological and physical processes on dissolved oxygen and dissolved inorganic carbon dynamics on a eutrophied and hypoxic continental shelf

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ABSTRACT

Dissolved oxygen (DO) and dissolved inorganic carbon (DIC) represent reciprocal sides of aquatic metabolism. In closed systems, absolute DO and DIC changes follow a $\sim 1 : 1$ ratio, but in open systems coupling depends on mixing, air–sea gas exchange, and anaerobic respiration. To quantify DO–DIC controls in coastal waters, we evaluated their concentrations and stable isotopes together with water quality and physical conditions across the hypoxic zone off the Louisiana continental shelf in July 2002 and July 2003. This area is characterized by high yet variable productivity and strong seasonal changes in vertical stratification and river discharge. Prior to 2003, this area was impacted by two tropical systems that could impact vertical stratification and mixing with offshore waters. The relationship between DO and DIC displayed three patterns: (1) In bottom waters, DO and DIC showed similar (opposing) trends in concentrations and stable isotopes in both years, largely associated with nutrients and algal biomass. (2) In 2002, DO and DIC concentrations in surface waters followed similar spatial patterns (reflecting algal biomass, salinity, and nutrients). However, due to different atmospheric gas exchange, DIC depletion exceeded DO supersaturation sixfold. Accordingly, short-term (DO) and long-term productivity (DIC) were on the same trajectory. (3) In 2003, DO and DIC were decoupled in surface waters. High DO concentrations correlated with algal biomass (recent production) while DIC concentrations followed salinity (past production). Understanding challenges and opportunities of using DO and DIC individually or combined is critical for quantifying metabolic patterns and capturing impacts of natural variability and climate change on eutrophic continental shelfs.

The concentrations of dissolved oxygen (DO) and dissolved inorganic carbon (DIC) are good proxies for metabolic processes in aquatic systems. The absolute changes in concentrations of these metabolic gases depend on the rates of

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production (P) and respiration (R), their ratio, and on physical processes such as atmospheric gas exchange and water mass mixing. The relative importance of the various biological and physical processes are keys to understanding how climate change may affect oxygen and carbon dynamics on continental shelves. Future climate-induced changes, such as higher water temperatures, ocean acidification, altered riverine freshwater discharge, or the frequency and intensity of tropical storms, will occur within the context of eutrophication and the often-consequential formation of low-oxygen (hypoxic) zones that exist throughout the world's coastal oceans (Huang et al. 2015; Bourgeios et al. 2016; Breitburg et al. 2018).

The coupling of O_2 production and CO_2 uptake during photosynthesis follows molar P : R of 1.0–1.2, with larger values indicating nitrate or protein as N-source instead of ammonium (Oviatt et al. 1986; Williams and Robertson 1991). Likewise, the respiratory quotient (RQ) varies between 0.8 and 1.1, depending on organic matter stoichiometry (Oviatt

et al. 1986; Robinson and Williams. 1991). Environmental processes can also decouple DO and DIC dynamics, such as anaerobic respiration, nitrification, air–sea gas exchange, and physical mixing (Guo et al. 2012; Hu et al. 2016; Jiang et al. 2019a). Anaerobic respiration can be linked to NO_3 and SO_4 reduction in sediments, and a corresponding generation of CO_2, N_2, and H_2S (Sørensen et al. 1979). Nitrification consumes 1.5 mol O_2 for every mol NO_3 produced and can act as an additional DO sink (Knowles and Lean 1987). Furthermore, atmospheric gas exchange is much faster for O_2 than for CO_2 (Weiss 1970; Cole and Caraco 1998). In productive alkaline waters, this can lead to continued seasonal DIC drawdown (Lorenz and Cai 2006; Fry et al. 2014), while the concentration of DO generally corresponds to diurnal or short-term (days) patterns rather than seasonal changes of P : R (Quiñones-Rivera et al. 2007; Wissel et al. 2008). Physical mixing can affect the DO–DIC coupling when combining waters with P : R larger and smaller than 1. This mixing can occur in the coastal ocean when inshore or offshore waters enter continental shelves, or when storms or cold fronts weaken or break up stratification.

The stable isotope values of DO and DIC (respectively, expressed in the delta notation as $\delta^{18}O$ and $\delta^{13}C$, with a unit of ‰; Craig 1961) change as a function of P : R because isotope values vary with the relative importance of photosynthesis and respiration. In a purely physical system in equilibrium with the atmosphere the $\delta^{18}O$ value of DO is 24.2‰, whereas photosynthesis adds isotopically depleted (light) oxygen to the existing pool with a value equivalent to that of ambient water (Guy et al. 1989, 1993), which is around 0‰ for seawater (Gröning 2004). Respiration removes relatively light oxygen from the existing pool with a fractionation factor (preferential uptake; ε) of about −20‰ to −22‰ (Kroopnick 1975; Quay et al. 1995; Hendricks et al. 2004), which increases the $\delta^{18}O$ of the remaining DO pool. The stable isotope values of DIC also fluctuate in a similar, but inverse manner. In alkaline coastal waters in equilibrium with the atmosphere, the $\delta^{13}C$ value of DIC is approximately 1‰ (Vogel et al. 1970; Mook et al. 1974; Keeling et al. 2005). Respiration adds CO_2 from ambient organic matter to the DIC pool without fractionation (Farquhar et al. 1982; Lin and Ehleringer 1997), with organic matter values around −20‰ to −22‰ in the coastal ocean (Peterson and Fry 1987; Wissel et al. 2008; Wang et al. 2018). The DIC uptake during photosynthesis is associated with a fractionation factor of about −20‰ (Kroopnick 1975), increasing $\delta^{13}C$ values of the remaining DIC pool. Thus, combining measurements of DO and DIC concentrations and stable isotopes can provide insights into how DIC vs. DO dynamics differentially integrate metabolic processes.

The northern Gulf of Mexico continental shelf is a well-suited system to make these measurements because of its high yet variable metabolic activity and variant physical mixing that is dependent on river discharge, seasons, weather patterns and tropical cyclone activity (Rabalais et al. 2014). It is also the site of the world's 2nd largest human-caused coastal hypoxic zone whose average spatial extent regularly exceeds management goals (Rabalais and Turner 2019), leading to severe ecological (e.g., water quality, biological integrity) and socioeconomic impacts (e.g., loss of fisheries revenue; Huang et al. 2012, Smith et al. 2010). Summertime hypoxia in this region develops as a synergistic product of the high productivity that is fueled by the Mississippi River nutrient loading (manifested in a high carbon flux to the sediments) and strong water column stratification that prevents re-oxygenation of bottom waters (Rabalais et al. 2014).

Mississippi River discharge generally determines the magnitude of nutrient delivery to these coastal waters, although nutrient loads are also mediated by the seasonal variations in riverine nutrient concentrations. For example, the load of nitrogen (NO_3) is a good predictor of the areal extent of hypoxic bottom-waters in the summer (Turner et al. 2012). During high-flow years, a strong pycnocline that develops during late spring and early summer prevents re-oxygenation of bottom waters, allowing respiration to deplete DO in the lower water column. Late summer conditions are also characterized by a DIC drawdown in surface waters associated with prolonged periods of high primary production (Guo et al. 2012; Fry et al. 2014; Hu et al. 2016). Severe weather events, such as tropical storms, hurricanes, and frontal disturbances, however, can cause physical mixing of stratified shelf waters (Rabalais et al. 2007), bringing low-DO, high-DIC bottom waters in contact with the atmosphere. Quantifying the similarities and discrepancies of DO and DIC as metabolic proxies is critical for predicting the potential impacts of climate change (e.g., acidification, storms, river discharge) on eutrophic coastal waters. Hence, a more comprehensive understanding of the DO–DIC coupling is needed that includes the temporal and spatial dynamics of algal biomass, primary production and respiration, and their respective biological and physical controls. We tested how environmental conditions impact the coupling of DO and DIC, by determining DIC and DO concentrations and their stable isotope values across the northern Gulf of Mexico hypoxia region during two summers of differing environmental conditions. Spring and early summers of 2002 and 2003 were both characterized by high river discharges and nutrient inputs that promoted high surface productivity and bottom water hypoxia across the continental shelf. But during 2003, Tropical Storm Bill and Hurricane Claudette passed over the study area 4 and 2 weeks, respectively, before sampling in late July. These storm events created a natural experiment that allowed us to test to what extent physical disturbances affect DO and DIC as productivity indicators. We hypothesized that during prolonged calm

conditions DO and DIC would have similar patterns and are subject to the same environmental controls, while the tropical systems would decouple DO–DIC dynamics in surface and bottom waters.

Methods

Field sampling

The sampling grid consisted of 14 transects aligned perpendicular to shore on the Louisiana shelf from the Mississippi River birdfoot delta westwards past the Texas–Louisiana border (Fig. 1). Each transect extended 40 to 60 km offshore and included 4–10 stations ranging in depth from 5 to 50 m. Surface and bottom (~1 m above the sediments) water samples were collected at 47 stations in July 2002, and at 88 surface and 45 bottom stations in July 2003. Surface waters were collected by bucket and bottom waters were collected from a Niskin bottle deployed within 0.5 m of the sediment surface. There were 38 surface and 32 bottom stations that overlapped between years, representing the core area of the continental shelf where hypoxia occurs.

All water samples were analyzed for indicators of algal biomass (μg L^{-1} chlorophyll *a* [Chl *a*] and phaeopigments) and dissolved forms (μmol L^{-1}) of nitrogen (NO$_3$, NH$_4$), phosphate (PO$_4$), and silicate (DSi). Water samples for Chl *a* analyses were filtered through GF/F filters (0.7 μm) that were then fixed in 5 mL of dimethyl sulfoxide–90% acetone (40 : 60 by volume). Chl *a* was extracted for at least 2 h in the dark (Lohrenz et al. 1999), and extracts were measured on a Turner Model 10 fluorometer before and after acidification with 10% HCl (Parsons et al. 1984).

We kept unfiltered water samples frozen until determination of the concentration of dissolved nutrients. Analyses were conducted with a Lachat Quick-Chem 8000 Flow Injection Analyzer using U.S. Environmental Protection Agency (USEPA) approved methods. To determine concentrations of particulate organic carbon (POC), samples were collected on precombusted (450°C, 6 h) GF/F filters which were kept frozen until return to the laboratory where they were dried overnight at 60°C. The analyses were conducted using an elemental analyzer (Carlo Erba 1500) that was coupled to a Finnigan Thermoquest Delta plus XP isotope ratio mass spectrometer (*see* Wissel et al. 2005 for details).

Vertical profiles of temperature, salinity, sigma *t*, and pH were measured at all stations using a Hydrolab multiprobe (Hach Instruments). The DO and DIC concentrations (μmol L^{-1}) were measured as part of DO and DIC stable isotope analyses (*see* below). Given the strong temporal and spatial gradients in DO and DIC, the combined measurement of DO and DIC concentrations and stable isotope values from the same parcel of water was critical to properly assess their coupling. Wind speed readings were taken from station BURL1 (NOAA National Data Buoy Center; https://www.ndbc.noaa.gov/station_history.php?station=burl1) near the Mississippi River Southwest Pass. Average wind speeds (km h^{-1}) over the preceding 48 h were calculated for each sampling date. Secchi depth (m; black and white disc, 25 cm diameter) was measured between 6 h before and after apparent noon and used to evaluate potential light penetration that could have affected bottom water DO and DIC dynamics, which was negligible (Quiñones-Rivera et al. 2007).

Stepwise multiple linear regressions (using data from all available surface and bottom samples for each year) identified environmental parameters that had significant correlations with DO and DIC dynamics. For surface samples, parameters included in the regressions were Chl *a*, POC, molar C/N, NO$_3$, NH$_4$, PO$_4$, DSi, salinity, delta sigma *t*, pH, temperature (°C), and wind speed. Wind speed and POC (not measured) were excluded from the analysis of bottom water samples. Independent variables that were not normally distributed (Chl *a*, POC,
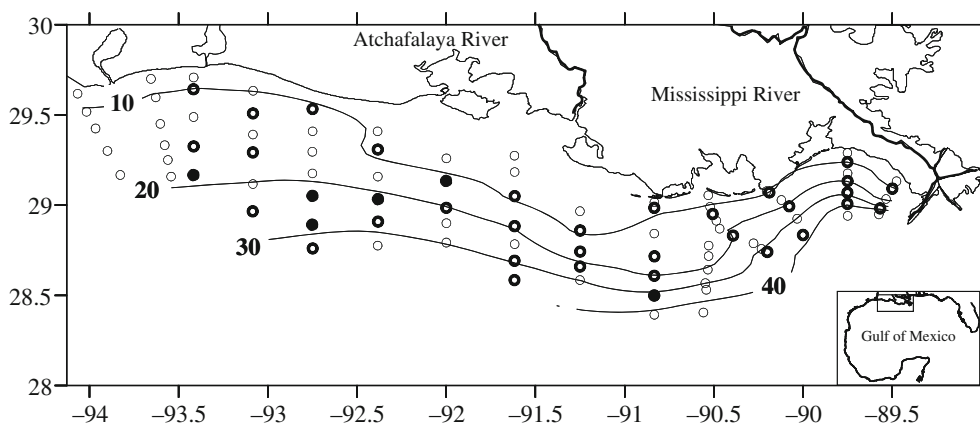
Fig. 1. Station grid across the Louisiana continental shelf. Insert (lower right corner shows study area within the Gulf of Mexico. Bolded circles (open and solid ◐, ●) represent surface water stations that were sampled in both years (*n* = 38). Open bolded circles (◐) represent bottom water stations that were sampled in both years (*n* = 32). Regular circles (○) represent stations that were visited only in 1 yr. Isolines indicate water depth in meters.

and delta sigma t) were log10-transformed. The *p*-values for variable inclusion and retention during stepwise regressions were 0.05 and 0.10, respectively. We used independent *t*-tests to compare average conditions between 2002 and 2003 summer cruises for selected environmental variables (surface, bottom). These between-year comparisons were limited to data from surface or bottom stations that were sampled in both years to avoid confounding impacts, such as water depth and distance from shore. We also performed Analysis of Covaraince (ANCOVA) with salinity as covariate to test if salinity gradients had a statistical influence on the between-year comparisons. Because *t*-tests and ANCOVAs generated the same conclusions, we relied on the more easily interpretable *t*-tests for subsequent analyses. All statistical analyses were performed using IBM SPSS Statistics, version 25.

Isotope analyses

We used a 5-liter Niskin sampler to collect bottom water samples, and a 20-liter plastic bucket for surface water. For surface samples, the bucket was filled passively to avoid intrusion of atmospheric oxygen into the sample water due to turbulent mixing. Bottom samples were collected within 1 m of the sediment. Subsequently, 160-mL Wheaton glass bottles were filled using plastic Tygon tubing attached to the Niskin sampler (bottom samples), or the water was siphoned directly from the bucket (surface samples). Bottles were allowed to overflow twice their volume to exclude air bubbles. The filled bottles were immediately sealed with heavy rubber stoppers (Bellco Glass, 20 mm, Wassenaar and Koehler 1999) fitted with a syringe needle that allowed excess water to escape. The needle was then removed and the stopper was crimped with an aluminum cap. Samples were poisoned with 1.0 mL 6 N HCl (Miyajima et al. 1995; Quiñones-Rivera et al. 2007) and stored in the dark. This procedure prevented the potential loss of CO_2 to the atmosphere from acidified samples, significantly reducing the measurement error (± 1 SD) from 45 (acidification before stopper) to 15 mmol DIC m^{-3} (acidification after stopper).

After return to the laboratory, samples were analyzed using headspace equilibration (Wassenaar and Koehler 1999; Quiñones-Rivera et al. 2007). Ten milliliters of ultrapure helium were injected into inverted bottles while allowing 10 mL of sample water to drain out through a small needle. Samples were stored in the dark at 5°C for up to 4 weeks before analysis.

For equilibration of dissolved gases with the headspace, samples were placed in a shaker (100 rpm, room temperature) for 12 h before analyses (Quiñones-Rivera et al. 2007). A 3-mL headspace-sample was injected through a septum (Thermogreen LB-2, 6 mm; 20651) into the sample stream. Two gas chromatograph columns (GCC) were used simultaneously by employing an eight-port valve on a GasBench II (ThermoFinnigan). The 1st GCC was upstream of the switching valve and the 2nd GC column was in a loop that could be switched in and out of the main flow. While out of the main flow, the 2nd GC was flushed

by helium. The CO_2 was retained on the first upstream column, while the other two gases (O_2 and N_2) passed onto the 2nd, downstream column. Flow paths were changed to achieve optimal elution of all three gases (for details, *see* Wissel et al. 2008).

The concentrations of dissolved O_2, CO_2, and N_2 (mmol m^{-3}) were calculated based on the IRMS chromatograms of masses 32, 44, and 28, respectively. The relationship between peak areas and gas amounts were calibrated using air-equilibrated artificial sea water (*see* below). The isotope values of oxygen ($\delta^{18}O$ in ‰ relative to Standard Mean Ocean Water, SMOW) and carbon ($\delta^{13}C$ in ‰ relative to Vienna-Pee Dee Belemnite, VPDB) were determined using a Finnigan Thermoquest Delta plus XP IRMS. We used air as a primary standard (Dole et al. 1954) with a known $\delta^{18}O$ value of 23.5‰ (± 0.14‰ SD, $n = 128$), and artificial sea water as a procedural standard. The oxygen and nitrogen-saturated artificial sea water gave the expected $\delta^{18}O$ value of 24.2‰ (± 0.17‰ SD for $\delta^{18}O$, $n = 113$) as well as accurate DO and N_2 gas concentrations (Weiss 1970) using the known temperature and salinity values. The artificial sea water contained little background CO_2, hence the concentration for CO_2 in the procedural standard was set to 2000 mmol m^{-3} by adding 0.848 kg m^{-3} of Na_2CO_3. The $\delta^{13}C$ value of Na_2CO_3 was 1.8‰ (± 0.2 SD), which was determined by combustion. We collected replicate samples ($n = 41$) to investigate the precision of our analyses. The average differences for oxygen concentrations and $\delta^{18}O$ values were 0.08 mg L^{-1} (± 0.12 SD) and 0.05‰ (± 0.04 SD), respectively.

Carbon fluxes and regulation

The DIC uptake and production (ΔDIC) were assessed based on the deviations of DIC from conservative mixing lines (Fry et al. 2014). The DIC conservative mixing lines for July 2002 and 2003 (Supporting Information Fig. S2) connected the respective endmember values for the zero-salinity Mississippi River (2580 and 2450 μmol L^{-1}) and high-salinity offshore waters (2150 and 2100 μmol L^{-1}). Respective net DIC removal and production is indicated when ΔDIC values fall below and above the mixing line (mostly surface and bottom samples, respectively). We applied the same conceptual model to calculate deviations from conservative mixing values for $\delta^{13}C$ of DIC ($\Delta\delta^{13}C_{DIC}$), where positive and negative values indicate dominance of respiration and production, respectively. The $\Delta\delta^{13}C_{DIC}$ values were based on weighted averages to account for the different DIC concentration and $\delta^{13}C$ values of endmembers. The 2002 and 2003 $\Delta\delta^{13}C_{DIC}$ endmember values for Mississippi River and offshore water were -10.1‰ and 1.2‰ vs. -10.1‰ and 1.0‰, respectively.

In contrast to our approach, Huang et al. (2012) and Jiang et al. (2019*b*) proposed a three-endmember mixing model to also account for the different (generally lower) DIC values of the Atchafalaya River. Yet, the results of Fry et al. (2014) indicated that applying a three-endmember model had only a small effect of the calculation of DIC removal from surface

waters. In addition, for the time periods preceding our 2002 and 2003 cruises, DIC values were not available for the Atchafalaya River (Gomez et al. 2020). Nevertheless, applying the long-term (1979–2015) DIC difference between the Mississippi and Atchafalaya Rivers ($\sim$400 μmol L^{-1}; Gomez et al. 2020), DIC removal in surface waters west of the Atchafalaya River would be underestimated by up to 20%, assuming zero contribution of Mississippi River water to this shelf region (Wissel, unpubl. data). Given the relatively small potential effect and high degree of data uncertainty, we decided to proceed with the two-endmember mixing model that was previously applied to this area (Fry et al. 2014).

The concentrations (mmol C m^{-3}), partial pressure (pCO$_2$) and chemically enhanced flux of CO$_2$ (mmol C m^{-2} d^{-1}) (hereafter referred to as flux) were calculated for surface samples from the DIC concentrations (mg C L^{-1}), pH and average wind speed (m s^{-1}) over the past 48 h (station BURL1, NOAA National Data Buoy Center), after correcting for ionic strength and water temperature by using equations for marine ecosystems (Millero 2007) as detailed in Finlay et al. (2009). In brief, pCO$_2$ (Pa) was estimated by using Henry's Law constant and accounted for changes in temperature (Kling et al. 1992). Chemically enhanced CO$_2$ flux was calculated for each sampling date in accordance with the boundary layer equations Cole and Caraco (1998):

$$\text{net daily CO}_2\,\text{flux} = \alpha k \left([\text{CO}_2]_{\text{water}} - [\text{CO}_2]_{\text{sat}}\right),$$

where [CO$_2$]$_{\text{water}}$ is the concentration of CO$_2$ in the surface water (μmol L^{-1}), [CO$_2$]$_{\text{sat}}$ is the concentration of CO$_2$ at equilibrium with the atmosphere (μmol L^{-1}), α is the chemical enhancement of CO$_2$ flux at high pH (Hoover and Berkshire 1969), and was calculated from the equations in Wanninkhof and Knox (1996), and k is piston velocity (cm h^{-1}) determined from eq. (5) in Cole and Caraco (1998) relating k to wind speed and accounting for temperature (Wanninkhof 1992).

Results

Surface water conditions during 2002 vs. 2003

July 2002 sampling occurred during an extended period of calm summer conditions with strong stratification and well-established bottom hypoxia (Quiñones-Rivera et al. 2010). The spatial patterns of surface salinity indicate the strongest freshwater influence to the west of the Mississippi and Atchafalaya River deltas (Fig. 2). Similar spatial patterns were observed for [POC], δ^{18}O$_{\text{DO}}$ and [ΔDIC] (Fig. 2), with r^2 values among these parameters ranging from 0.56 to 0.68 ($p < 0.001$). Salinity was significantly and inversely correlated with [NO$_3$], [PO$_4$] and [DSi] ($r^2 = 0.24$, 0.55, and 0.46, respectively; $p < 0.01$) (Supporting Information Table S1; Fig. S1). Furthermore, [POC] was a good indicator of algal biomass (r^2 with Chl $a = 0.79$). Therefore, during 2002, high riverine nutrient inputs (low salinity) resulted in increased algal biomass (high POC) with simultaneous increase

in DO concentration (low δ^{18}O$_{\text{DO}}$) and DIC uptake (negative ΔDIC; and positive $\Delta\delta^{13}$C$_{\text{DIC}}$, not shown) (Fig. 2, left panels). The study area had high productivity (P : R > 1, DO-based; Quiñones-Rivera et al. 2010) and acted as a CO$_2$ sink (Fig. 3; top panel) with spatial patterns of C flux matching those of salinity, [POC], δ^{18}O$_{\text{DO}}$, and [ΔDIC] (r^2 ranging from 0.55 to 0.85; $p < 0.001$) (Table 1).

In 2003, continental shelf waters were exposed to Tropical Storm Bill and Hurricane Claudette, which passed over the study area 4 and 2 weeks, respectively, before the July 2003 cruise. Also, stronger localized winds occurred just before the July 2003 cruise (Quiñones-Rivera et al. 2010). Concurrently, the spatial pattern of salinity was decoupled from those of [POC] and δ^{18}O$_{\text{DO}}$ ($r^2 < 0.05$; $p > 0.05$) but was still similar to that of [ΔDIC] (Fig. 2; $r^2 = 0.29$; $p < 0.001$) (Supporting Information Table S1). Yet, the spatial distributions of POC and δ^{18}O$_{\text{DO}}$ were similar ($r^2 = 0.52$; $p < 0.001$), with the highest [POC] and lowest δ^{18}O$_{\text{DO}}$ closer to shore, respectively. Despite a P : R > 1 (DO-based, Quiñones-Rivera et al. 2010) and regions of high DIC uptake, the study area acted as a CO$_2$ source to the atmosphere during July 2003 (Fig. 3; lower panel).

In July 2002, the continental shelf experienced significantly warmer, fresher surface waters with stronger stratification, and elevated productivity (based on [Chl a], [POC], [DO], [ΔDIC], pH) compared to July 2003 (Table 1). NH$_4$ and DSi concentrations were slightly higher in 2002 that in 2003, with no significant between-year differences for [PO$_4$] and [NO$_3$]. Total organic carbon (TOC) removal from surface waters (Eq. 1) was higher and less variable during 2002 than 2003. For both years, the respective total range of C removal from surface waters (40–180 μmol L^{-1}) was similar to the DIC addition/DO depletion ranges in bottom waters (35–196 μmol L^{-1}). In addition, C removal during both years was negatively correlated with salinity ($p < 0.006$).

$$\text{TOC removal} = \Delta\text{DIC} - \text{POC} - \text{DO}_{\text{sat}}, \qquad (1)$$

all converted to μmol L^{-1}, with ΔDIC = DIC depletion, total seasonal uptake of DIC by algae; POC = current algal biomass, recent production still in surface waters; and DO$_{\text{sat}}$ = DO supersaturation as DIC equivalent, instantaneous primary production.

The multiple linear regression analyses of δ^{18}O$_{\text{DO}}$, $\Delta\delta^{13}$C$_{\text{DIC}}$, and POC varied between years in strength (r^2) and significant parameters. For 2002-POC, the best model explained 85% of the variability and included temperature, δ^{18}O, DSi, and C : N (Supporting Information Table S2), with salinity and $\Delta\delta^{13}$C$_{\text{DIC}}$ also having zero-order correlations > |0.7|. For 2003-POC, the regression was weaker ($r^2 = 0.56$), and it was associated with δ^{18}O, salinity, PO$_4$, and temperature. For this and all other 2003 regressions, none of the parameters had zero-order correlations > |0.7|. For 2002-δ^{18}O$_{\text{DO}}$, the best model included POC, C : N, and pH
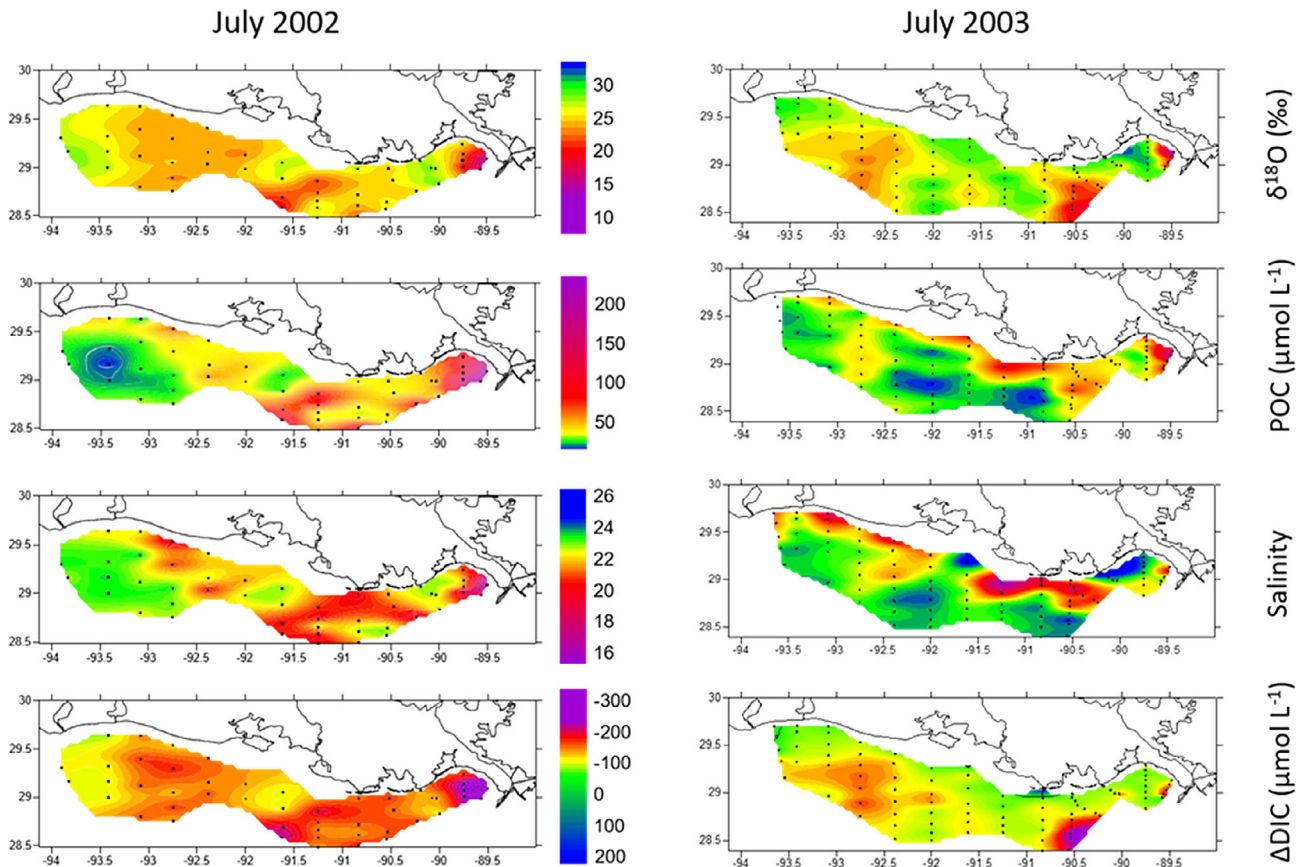
July 2002   July 2003

Fig. 2. July 2002 and 2003 surface distributions of δ^{18}O (‰), POC (μmol L^{-1}), salinity (psu) and ΔDIC (μmol L^{-1}) in surface waters. For δ^{18}O, values above 24.2‰ (orange, reds, and purple) represent dominance of primary production (P : R > 1). Negative ΔDIC values show DIC depletion due to primary production.

(r^2 = 0.74), with salinity, DSi and Δδ^{13}C$_{DIC}$ also having zero-order correlations > |0.7|. For 2003-δ^{18}O$_{DO}$, POC, temperature, and salinity were incorporated into the model and the r^2 value

(0.41) was lower than that for 2002. The Δδ^{13}C$_{DIC}$ values from 2002 were correlated with temperature, salinity, pH, and POC (r^2 = 0.85), with δ^{18}O$_{DO}$ also having a zero-order correlation

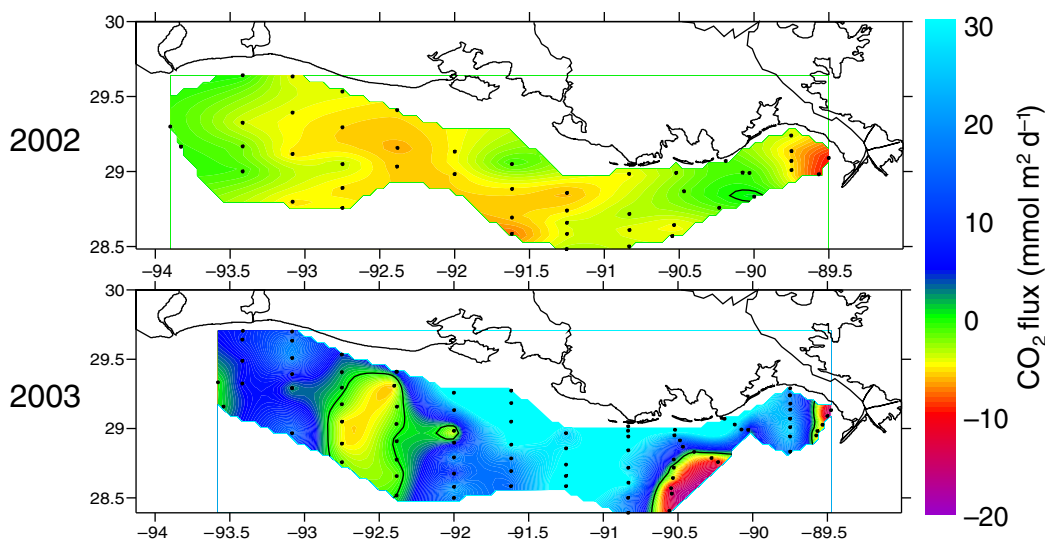**Fig. 3.** July 2002 and 2003 surface distributions of CO$_2$ flux (mmol m^2 d^{-1}) in surface waters. Negative values (largely 2002) designate net CO$_2$ flux from the atmosphere into surface waters, and positive values (largely 2003) indicate that surface waters act as a carbon source to the atmosphere.

Table 1. Average ($\pm$ SD) environmental conditions in surface and bottom water samples across the Louisiana continental shelf during July 2002 and July 2003. Only stations that were sampled during both years ($n = 38$ for surface and 32 for bottom) are included in the analyses. Significance was tested using an independent *t*-test. Non-significant results ($p > 0.05$) are indicated as "ns."

	Surface			Bottom		
	2002	**2003**	*p*-value	**2002**	**2003**	*p*-value
Wind speed (m s^{-1})	3.3 (1.8)	4.7 (2.4)	0.005			
Stratification (Δ sigma-*t*)	8.24 (2.9)	7.36 (4.6)	0.008			
Depth (m)	21.2 (9.5)	21.0 (13.0)	ns	20.1 (9.8)	21.6 (9.7)	ns
pH	8.35 (0.10)	8.13 (0.12)	0.000	7.89 (0.12)	7.85 (0.14)	ns
Temperature ($^{\circ}$C)	31.2 (0.87)	29.1 (0.70)	0.000	27.4 (1.6)	25.5 (2.6)	0.001
Salinity (psu)	24.9 (2.9)	26.7 (3.9)	0.005	33.9 (1.8)	34.2 (2.2)	ns
pCO$_2$ (μatm)	197 (41)	366 (108)	0.000			
POC (μmol L^{-1})	51.5 (47)	36.9 (28)	0.026			
Chl a (μg L^{-1})	3.43 (4.8)	2.04 (2.4)	0.025	2.60 (3.0)	1.5 (1.3)	0.035
δ^{18}O (‰)	21.5 (1.7)	22.3 (1.8)	0.006	30.6 (6.2)	29.4 (5.4)	ns
O$_2$ (%)	105.9 (9.1)	102.0 (10.3)	0.006	29.1 (25.0)	47.8 (24.5)	0.004
Δ δ^{13}C (‰)	1.80 (0.59)	1.09 (0.74)	0.000	-1.4 (0.73)	-1.0 (0.64)	0.029
DIC - DO (μmol L^{-1})	75 (58)	112 (75)	0.000			
C removed (μmol L^{-1})	128.3 (31)	75.6 (82)	0.000			
NH$_4$ (μmol L^{-1})	0.68 (0.30)	0.46 (0.21)	0.000	3.20 (4.64)	0.96 (0.69)	0.009
NO$_3$ (μmol L^{-1})	0.66 (0.80)	0.54 (0.35)	ns	9.64 (5.07)	5.99 (4.59)	0.004
PO$_4$ (μmol L^{-1})	1.1 (0.14)	0.54 (0.34)	0.000	1.90 (0.73)	1.13 (0.27)	0.000
DSi (μmol L^{-1})	9.51 (9.7)	7.62 (4.4)	ns	35.9 (14.6)	19.1 (9.0)	0.000

> |0.70|. For 2003, $\Delta\delta^{13}C_{DIC}$ was best predicted by salinity, NH$_4$, and temperature ($r^2 = 0.55$).

Bottom water conditions during 2002 vs. 2003

Hypoxic conditions in bottom waters were frequently encountered in both years, characterized by low oxygen concentrations, excess-DIC, low pH, low temperature, and high salinity (Fig. 4; Table 1). However, bottom waters were significantly warmer, had higher algal biomass (Chl *a*, phaeophytin), lower DO saturation, more DIC addition, and higher nutrient concentrations in 2002 than in 2003 (Table 1).

Multiple linear regressions for $\delta^{18}O_{DO}$, and $\Delta\delta^{13}C_{DIC}$ varied between years in strength (r^2) and parameters included (Supporting Information Table S2). For 2002, the best $\delta^{18}O_{DO}$ model included Chl *a*, DSi and $\Delta\delta^{13}C_{DIC}$ ($r^2 = 0.58$), with no other parameters having zero-order correlations > |0.5|. For 2003, the best $\delta^{18}O_{DO}$ model included $\Delta\delta^{13}C_{DIC}$, salinity, DSi temperature and Chl *a* and the r^2 value was 0.79. The $\Delta\delta^{13}C_{DIC}$ for 2002 were correlated with pH, DSi, temperature, and Chl *a* ($r^2 = 0.85$), with $\delta^{18}O_{DO}$, PO$_4$, and NH$_4$ also having a zero-order correlation > |0.50|. For 2003, $\Delta\delta^{13}C_{DIC}$ was best predicted by salinity, DSi, $\delta^{18}O_{DO}$, temperature, Chl *a*, and pH ($r^2 = 0.96$), with PO$_4$ also having a zero-order correlation > |0.50|.

DO–DIC coupling during 2002 vs. 2003

The DO and DIC dynamics in bottom waters were tightly coupled during 2002 and 2003 ($r^2 = 0.58$; $p < 0.001$ and

$r^2 = 0.72$; $p < 0.001$, respectively). Respiration-related depletion of DO (ΔDO; deviation from saturation in μmol L^{-1}) and addition of DIC (ΔDIC) fell along the 1 : 1 line (Fig. 5a and b), with the expected respiratory quotient ~1. The main difference between years was that the absolute values of ΔDO and ΔDIC during 2002 were larger than in 2003 (i.e., more respiration). A decoupling of DO–DIC in bottom waters only occurred at those stations in 2002 where DO was completely depleted and DIC continued to accumulate, indicating the presence of anaerobic respiration in bottom waters and/or the sediment.

The 2002 DO and DIC concentrations in surface waters were closely coupled, but the values departed from the 1 : 1 line two-fold (Fig. 5a). First, there was an offset of about 130 μmol DIC for DO samples that were close to 100% saturation (0–0 intercept, Fig. 5a), which was equivalent to the average C removal rate from surface waters in 2002 (Table 1). Second, the slope of the DIC : DO line was much larger than 1.0 (average of 6, ranging from 2 to 10), reflecting larger DIC depletion relative to DO supersaturation. Finally, both DO and DIC values of surface and bottom samples were completely separated, with all respective surface and bottom samples showing simultaneous DO production/depletion and DIC depletion/production and (Fig. 5a, lower right and upper left quadrants, respectively).

Surface DO–DIC dynamics during 2003 differed strongly from those observed in 2002. For most samples DO values were close to saturation levels, while DIC depletion had a 2.5-fold range in 2003 compared to 2002 (~500 vs.
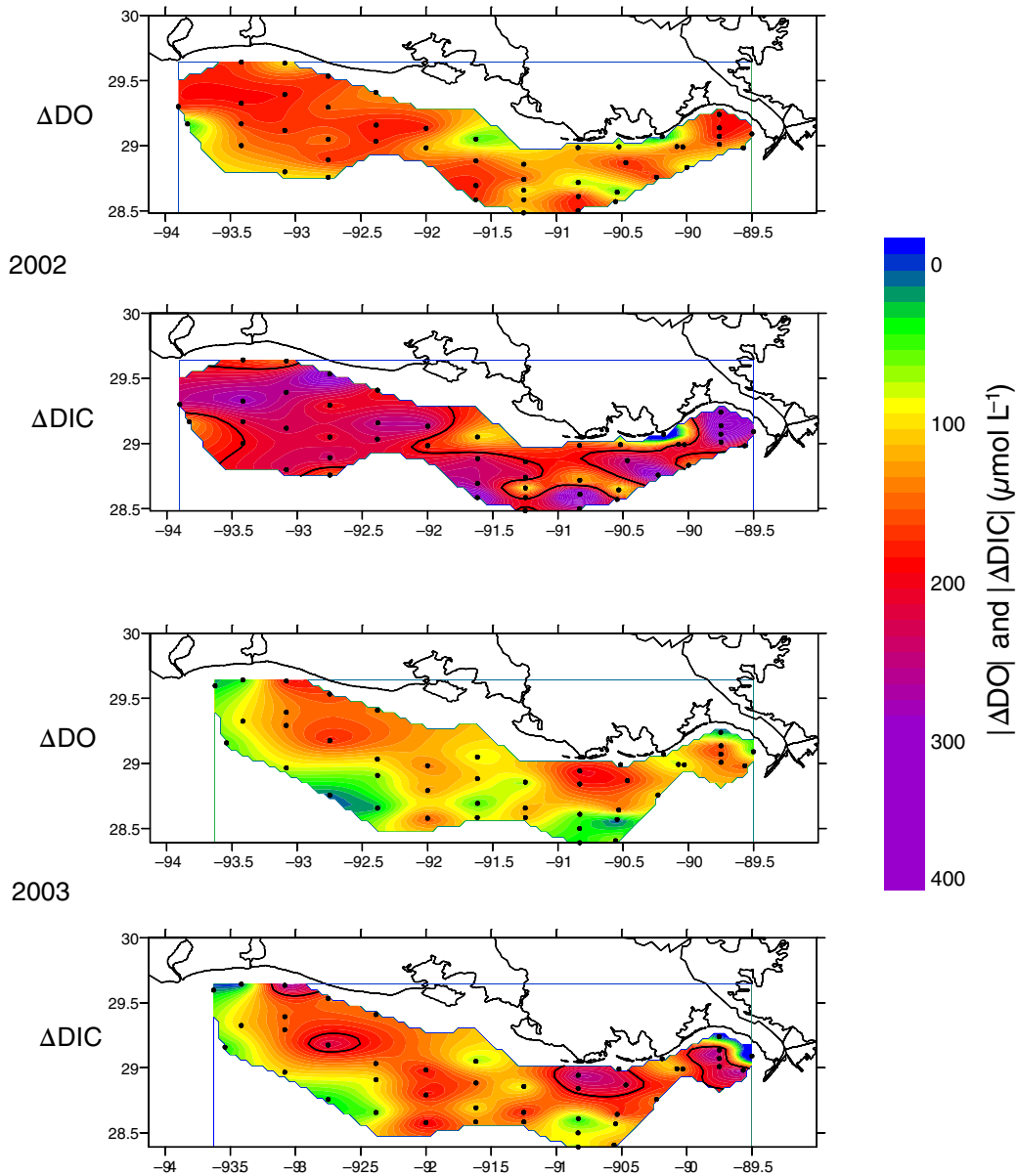
Fig. 4. July 2002 and 2003 bottom distributions of ΔDO and ΔDIC (both in μmol L^{-1}) in bottom waters. True ΔDO and ΔDIC are negative (DO depletion) and positive (DIC addition), respectively.

< 200 μmol L^{-1}). Neither the DIC offset (C removal, *see* 2002 above) nor the strong correlation between DO and DIC were observed in 2003. In addition, both DO and DIC values overlapped between surface and bottom samples, including conditions where DO and DIC were simultaneously depleted (Fig. 5b, lower left quadrant) or increased relative to saturation levels (Fig. 5b, upper right quadrant). Consequently in 2003, the estimates of P : R that were based on DO vs. DIC showed conflicting results. For example, for samples in the lower left quadrant (Fig. 5b), P : R is lower than 1.0 based on DO (negative ΔDO = respiration), but larger than 1.0 based on DIC (negative Δ DIC = production).

Discussion

Nutrients/salinity as ultimate (higher-level, indirect) and POC/algal biomass as proximate (immediate, direct) causes for changes in DO and DIC were strongly linked in July 2002, following an extended period of calm weather conditions. Despite strong metabolic coupling of DO and DIC in surface waters, the absolute changes in DIC exceeded those of DO by a factor of six (range 2–10) due to their different atmospheric gas exchange rates. Accordingly, DO and DIC integrated productivity over different time scales, with DO representing production over days and DIC production over weeks to months.
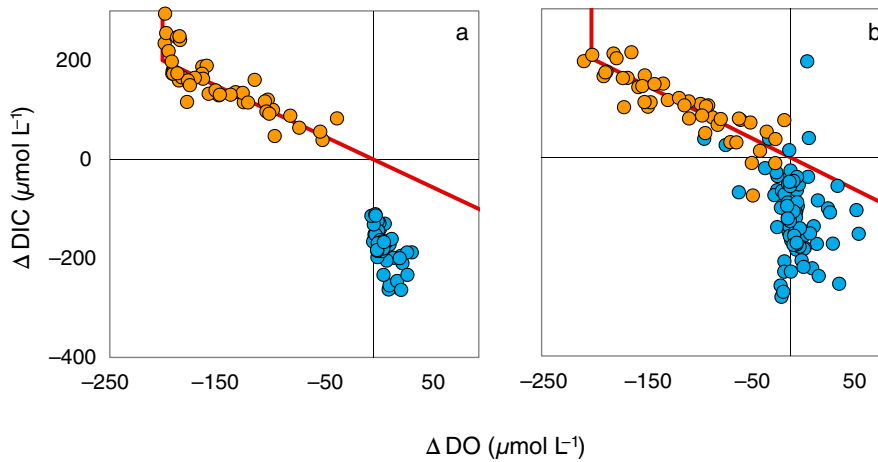
Fig. 5. 2002 (**a**, left) and 2003 (**b**, right) ΔDO and ΔDIC (both in μmol L^{-1}) in surface (blue) and bottom (orange) waters. The zero–zero intercept indicates no deviation from atmospheric equilibrium. Data points in the upper left and lower right quadrants represent dominance of respiration and primary production, respectively. The red line represents a 1 : 1 relationship between ΔDO and ΔDIC. At complete depletion of DO the red line deviates from the 1 : 1 relationship showing DIC addition under anaerobic conditions.

In contrast, following the passage of two tropical systems weeks before 2003 sampling, DO and DIC dynamics were decoupled, at least in surface waters. The POC patterns were associated with salinity (an ultimate cause) reflecting past production, while DO was related to POC (a proximate cause) representing recent productivity. Hence, DO and DIC in surface waters were decoupled both temporally and spatially during 2003, while during 2002 decoupling was limited to temporal effects. Based on salinity and temperature patterns during 2003, the tropical systems likely caused intrusions of inshore and offshore waters and temporary weakening of stratification, rather than complete vertical mixing and breakup of stratification.

The concentrations and associated stable isotope values of DO and DIC in bottom waters were tightly coupled in both years, despite the different histories of tropical storm activity preceding the cruises and wind speeds before/during sampling. With absolute changes in DO and DIC following a 1 : 1 line, the bottom water DO and DIC dynamics predominantly reflected metabolic activity. Yet, physical factors, such as vertical mixing and offshore water intrusions, might have also contributed to the observed patterns.

Environmental conditions during 2002 vs. 2003

Despite similarities during early summer (Quiñones-Rivera et al. 2010), environmental conditions during July 2002 and 2003 sampling differed substantially. Significantly lower temperatures in both surface and bottom waters after the respective passages of Tropical Storm Bill and Hurricane Claudette in early and mid-July of 2003 indicated cooling of the entire water column. Further evidence for this cooling effect comes from 2002 surface-water temperatures along transect C, which increased by more than 2°C between June and July (Quiñones-Rivera et al. 2010). However, during the same time

period in 2003 surface temperatures decreased by ~1°C. Bottom water temperatures in 2002 along transect C also increased by about 2°C from June to July, while during 2003 bottom temperatures remained largely unchanged (Quiñones-Rivera et al. 2010). This so-called "cold wake" has been described previously for tropical systems and is commonly attributed to heat flux to the atmosphere and vertical mixing with cooler bottom waters (Cione and Uhlhorn 2003; D'Asaro et al. 2007). Heat flux is usually only a minor factor and unlikely accounted for the ~2°C cooling of the entire water column (D'Asaro et al. 2007). Yet, vertical mixing of ambient surface and bottom waters was probably also less relevant because surface and bottom water temperatures decreased simultaneously. Likewise, complete vertical mixing would have increased surface salinity and decreased bottom salinity, but only the former was the case.

It is more likely that the differences in temperature and salinity between years were caused by the intrusion of colder, more saline, oxygen-rich offshore waters during the 2003 storms that subsequently, together with oxygen-poor, DIC-rich ambient bottom waters, impacted surface water conditions. This scenario is supported by the fact that salinity increased in surface waters but remained unchanged in bottom waters (no measured impact expected as bottom water and offshore salinities were similar). Further evidence is provided by the sudden increase of bottom water oxygen at station C6b (continuous DO measurement) from hypoxia to ~5 mg L^{-1} during the passage of Hurricane Claudette, followed by an instantaneous return to hypoxic conditions within 24 h (Rabalais et al. 2009). Ultimately, a weaker stratification was apparent in 2003 as a consequence of the lower temperatures and a lower salinity gradient between surface and bottom water. In addition to storm-related impacts on upwelling, mixing, and stratification, there were significantly

higher wind speeds in 2003 during the time of sampling compared to 2002 (4.7 ± 2.4 m s^{-1} in 2003 vs. 3.3 ± 1.8 m s^{-1} in 2002; Table 1). Higher wind speeds in 2003 potentially further exacerbated mixing-related processes such as DO/DIC air–sea gas exchange and intrusion of deeper, more oxygenated waters.

DO and DIC as a productivity indicator

The dynamics of DO and DIC are good proxies for primary production, particularly when used in combination with their stable isotopes (Wissel et al. 2008). In coastal waters, DO has been used to quantify P : R in surface waters and the importance of benthic respiration in bottom waters (Quay et al. 1995; Ostrom et al. 2005; Quiñones-River et al. 2009). Similarly, DIC dynamics have been proven critical for assessing carbon dynamics, ranging from productivity estimates, identifying carbon sources, and studying the impacts of oil spills and ocean acidification (Feeley et al. 2004; Guo et al. 2012; Hu et al. 2016). Nevertheless, few of these studies have explored the combined analyses of DO and DIC to assess their respective characteristics as metabolic indicators (Jiang et al. 2019b) and, to our knowledge, nobody has tested the impacts of tropical storms and hurricanes and associated mixing of stratified coastal waters on the coupling of DO and DIC dynamics.

Here, we identified three patterns of DO–DIC coupling. First, DO and DIC concentrations in bottom waters were tightly coupled, with DO-depletion equaling excess-DIC (RQ close to 1.0), irrespective of the impact of two tropical systems preceding the 2003 cruise. Regression analyses indicated that both DO and DIC patterns were associated with similar environmental parameters, that is, Chl *a*, nutrients, temperature, as well as the reciprocal metabolic gas (DO for DIC and DIC for DO). In addition, the strong associations between DO and DIC and their respective stable isotope values both followed the inverse patterns expected for metabolic processes (Kroopnick 1975; Farquhar et al. 1982; Wissel et al. 2008). Accordingly, respiration of organic material from warmer surface waters appears to be the dominant factor controlling DO and DIC dynamics in bottom waters. The regression analyses also indicated that respiration: (1) was elevated in warmer bottom waters, and (2) resulted in an accumulation of nutrients (DSi). Increased DSi concentrations with more intense respiration were likely the result of DSi mineralization and efflux from the sediments at low DO concentrations (Danielson 2014). In addition, the concentrations of PO$_4$ and NH$_4$ (2002 only) were also significantly, positively correlated with Δδ^{13}C, but did not enter the multiple linear regression once DSi was selected. The lack of association of NH$_4$ with respiration in 2003 may be the result of overall higher DO concentrations in bottom waters and quick oxidation of released NH$_4$.

Anaerobic (sediment) respiration, however, was more pronounced during calm conditions in 2002, which was indicated by a continued DIC generation at stations that experienced complete oxygen depletion (Fig. 5a). In support of this

conclusion, 2002 was also characterized by overall higher sediment respiration relative to water-column respiration (81% in 2002 vs. 60% in 2003; Quiñones-Rivera et al. 2010). Even though metabolic processes were clearly linked to the observed patterns in DO and DIC, we cannot rule out the intrusion of offshore bottom water, particularly during 2003. Offshore bottom waters would likely have had a weaker respiration signal but DO and DIC (and their stable isotopes) would still be expected to be coupled (Fig. 5a). Hence, mixing bottom shelf waters with offshore waters should result in a somewhat weakened respiration signal while maintaining a strong DO–DIC coupling (which occurred in 2003 relative to 2002).

The second DO–DIC pattern was observed in surface waters during calm conditions in 2002, when DO and DIC were both strongly related to algal biomass, but the magnitude of response differed several-fold (range of 2–10, which was not significantly associated with any measured environmental variables). Excess DO (supersaturation) as a result of intense primary production diffuses fairly quickly into the atmosphere due to a high air–sea gas exchange rate (Weiss 1970). Yet, diurnal patterns of DO-δ^{18}O in surface waters in response to changes in light intensity during multiday cruises were not apparent, likely due to the confounding effect of different intensities of primary production across the study area (Quiñones-Rivera et al. 2007). Hence, DO dynamics are more representative of short-term, recent (days) primary production across the Louisiana continental shelf. DIC has a much lower gas exchange rate than DO (Wanninkhof 1992) and therefore high primary production can result in a significant drawdown of DIC in surface waters (often exceeding 200 μmol L^{-1}, Fig. 2), because diffusion cannot compensate for algal DIC uptake. The extent of the DIC drawdown (and consequential increase in absolute difference between ΔDO and ΔDIC) depends on the intensity of primary production, duration of calm conditions, and CO$_2$-influx from the atmosphere. Potentially, primary production could be integrated over longer (seasonal) time periods based on ambient DIC-deficit and calculated CO$_2$-flux, with all required parameters being fairly easy to attain (Justić et al. 2002). If the CO$_2$-flux from the atmosphere and respective time-period were better constrained, then the total summer primary production could be estimated for the Louisiana coastal shelf. The average offset between excess-DO and DIC-depletion in 2002 was equivalent to the average C-removal rate (ΔDIC – POC – DO) of ~130 μmol C L^{-1}. This indicates that DIC depletion was in the same range as past POC production, whereby this value is likely a lower estimate because it does not include any resupply of DIC due to diffusion from the atmosphere.

The third DO–DIC pattern was the decoupling of DO and DIC dynamics in surface waters in 2003. In contrast to the strong correlations among DO, DIC, salinity, and POC in 2002, DO was most strongly associated with POC (algal biomass), while the patterns in DIC concentration resembled

those of salinity (original nutrient source). Similarly in 2002, P : R (>/< 1.0) followed the expected patterns of DO super/undersaturation and concurrent DIC depletion/addition, respectively. Yet during 2003, many stations were characterized by simultaneous DO and DIC supersaturation (or undersaturation), which is in contrast to the expected negative association between DO and DIC. This created opposing conclusions with respect to autotrophy vs. heterotrophy of the water mass. An extension of this argument is that the continental shelf acted as a C source in 2003 while DO-based P:R estimates were >1.0. Hence, if DO is a proxy for short-term productivity and DIC represents long-term productivity patterns, then only the combined DO–DIC analysis can identify and characterize recent vs. seasonal productivity of the same water parcel, and the continental shelf in general.

As a caveat, our study focused on the effects of metabolic processes on DO–DIC coupling and diverging patterns were assumed to be related to different air-sea gas exchange of O_2 and CO_2 and/or mixing. Yet, $CaCO_3$ precipitation and dissolution can also impact the coupling of DO and DIC. Nevertheless, it has been shown that metabolic processes are dominating DO–DIC dynamics during productive summer conditions across the LA continental shelf (Guo et al. 2012; Jiang et al. 2019*b*; Huang et al. 2021).

Implications for DO- vs. DIC-based metabolic estimates

This study demonstrates that there are at least three possible scenarios depending on whether DO or DIC are used as proxies for metabolic activities. The implications are fairly small for bottom waters, with the exception that only DIC-based analyses can identify anaerobic respiration (DIC build-up beyond complete DO depletion). A build-up of reduced compounds such as NH_4, H_2S, and CH_4 also creates an additional DO deficit because they need to be oxidized before any free O_2 is available again (Bedard and Knowles 1989; Di Toro et al. 1990).

In order to characterize metabolic processes in surface waters it is critical to identify if short-term (DO dynamics) and/or long-term (DIC dynamics) productivity information is needed. While this concept seems novel within the context of quantifying aquatic metabolism, it is well known in stable-isotope based food-web applications where carbon, nitrogen and sulfur stable isotopes of muscle, liver, and blood integrate past diet over days to months (Vander Zanden et al. 2015).

Finally, physical disturbances, such as tropical storms and hurricanes may be infrequent, but nevertheless represent critical events in coastal areas (Halper and Schroeder 1990; Guo and Subrahmanyam 2020). In such situations, a dual analysis of DO and DIC dynamics can capture contrasting short- and long-term productivity patterns in surface waters. This study showed that if during 2003 we had relied exclusively on DO concentration changes, then the continental shelf would have been characterized as autotrophic (P : R > 1), while relying on the DIC analysis alone would have led to the erroneous conclusion of overall heterotrophic conditions (acting as a CO_2 source). Understanding

and accounting for these differences will be particularly important in studies that use DO as primary proxy with subsequent elemental ratios to convert the results into carbon dynamics. We understand that it will not be always possible to simultaneously measure DO and DIC, but this work points out that it is important to carefully choose the better suited indicator and to be aware of its advantages and limitations.

Relevance for climate change studies

A better understanding of metabolic patterns and their environmental controls is critical for predicting how future climate-induced changes will impact continental shelves by means of ocean acidification, increased water temperatures, altered riverine freshwater discharge, or change in the frequency and intensity of tropical storms (Justić et al. 1996; Rabalais and Turner 2019). In terms of DO vs. DIC impacts, acidification will only affect DIC whereas a lower pH will shift inorganic carbon speciation toward free CO_2, which could reduce the potential for DIC to characterize past production. Nevertheless, seawater pH would have to drop to circumneutral values (~ 7) to have a strong impact on DIC concentrations and speciation (CO_2 vs. HCO_3^- vs. CO_3^{-2}), which is not anticipated in the foreseeable future. Changes in the Mississippi River discharge and nutrient load will directly impact primary production in surface waters across the Louisiana continental shelf. We do not expect these factors to cause DO and DIC productivity proxies to differ during calm conditions, beyond their abilities to integrate metabolic activity at different time scales. Finally, an increase in the frequency and severity of tropical storms and hurricanes in the northern Gulf of Mexico (Mousavi et al. 2011) would most likely result in strong differences in the inferences that would be drawn from DO vs. DIC analyses. Under those circumstances, only the combined analyses of DO and DIC would guarantee that both long- and short-term productivity patterns, and ultimately carbon dynamics, are accurately captured.

Data availability statement

Data will be available upon request from the corresponding author.

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Conflict of Interest

All authors declare that they have no conflicts of interest.