Coupled oxygen and dissolved inorganic carbon dynamics in coastal ocean and its use as a potential indicator for detecting water column oil degradation

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ABSTRACT

Following the disastrous 2010 Deepwater Horizon oil spill, numerous studies have been carried out to investigate the impact of the oil spill on a variety of environments. However, it is currently unknown whether the spilled oil transported to the coastal ocean has caused any discernible perturbation to the inorganic chemistry of the water column. In this work we compared and contrasted a multiyear dataset (2006–2012) collected in the northern Gulf of Mexico continental shelf, an area subject to frequent summer hypoxia. Before and after the oil spill, apparent oxygen utilization (AOU) and dissolved inorganic carbon (DIC) in bottom water samples all showed consistent relationship that was close to Redfield reaction stoichiometry. However, we observed a possible oil degradation signal in the bottom waters during a July 2010 cruise as manifested by a significant deviation from all other years in the relationship between AOU and DIC. Based on stable carbon isotope analysis of bottom water DIC from a July 2011 cruise in the same region, oil carbon degradation in the water column was likely negligible and the shelf water had returned to the pre-spill conditions.

1. Introduction

Dissolved inorganic carbon (DIC), nutrients (nitrogen and phosphorus), and dissolved oxygen (in the form of "apparent oxygen utilization" or AOU, the difference between saturated oxygen concentration and observed oxygen concentration) have long been used to calculate the composition of the organic matter (or the "Redfield ratio") undergoing remineralization in the ocean (e.g., Takahashi et al., 1985). Here, AOU in a water mass represents the net consumption of oxygen from the time when the parcel of water was last exposed at the air–sea interface. The "isopycnal method" to examine evolution of chemical species along individual isopycnals (Minster and Boulahdid, 1987; Takahashi et al., 1985) or "neutral" surfaces (Anderson and Sarmiento, 1994), as well as water mass mixing models coupled with a multilinear regression approach (Li et al., 2000; Li and Peng, 2002) are appropriate methods used to derive relatively confined ranges of C, N, P ratios in remineralizing organic matter as well as the reaction stoichiometry between the reacting organic matter and

dissolved oxygen. Conversely, the Redfield ratio obtained in these studies can be used to calculate the carbon contribution to the seawater DIC pool from organic matter remineralization in order to differentiate this carbon source from the net accumulation of anthropogenic CO_2 in seawater (e.g., Brewer, 1978; Sabine et al., 2002). Despite the range of calculated elemental ratios (see a review in Hu and Cai, 2011b), oceanographic datasets often yield consistent patterns in the property–property relationships (for example, N vs. P, DIC vs. AOU), indicating the planktonic nature of the remineralizing material.

Studies on organic matter remineralizing stoichiometry mostly focused on the open ocean, subsurface and deep waters where water mass compositions are relatively simple and air–sea gas exchange is nil. In the coastal ocean, however, due to the potential complexity in water column hydrodynamics (e.g., mixing with either freshwater or among different coastal water masses) and gas exchange between the atmosphere and the ocean, previous studies tend not to use the observed AOU–DIC relationship to obtain quantitative information regarding the composition of organic matter being remineralized in the water column. Nevertheless, good AOU–DIC linear correlations have been reported in some recent studies. For example, Cantoni et al. (2012) observed significant correlation between AOU and DIC in the bottom layer of

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the Gulf of Trieste, and the regression line agrees well with the Redfield stoichiometry. Similarly, Maske et al. (2010) observed a linear relationship between AOU and DIC in the Pacific oxygen minimum zone off Mexico, with the regressed slope consistent with the Redfield stoichiometry.

It is rare that other types of organic matter in the marine environment would play a significant role in water column oxygen consumption under natural conditions, except perhaps in places near shallow underwater fossil carbon seepages (for example, Aharon et al., 1992). However, following the catastrophic *Deepwater Horizon* oil spill in 2010, not only did oil carbon affect bacterial biomass and enter the planktonic food web (Chanton et al., 2012; Graham et al., 2010; Hazen et al., 2010), there were also indications that oil remineralization may have influenced shelf waters in the northern Gulf of Mexico (nGOM) as what we are showing in this work. We based our discussion on a multiyear dataset collected in the nGOM region and suggested the likelihood of petroleum carbon remineralization in the summer of 2010. We compared 2010 data in the same region from before (2006–2009) and after the spill (2011–2012). We also determined whether petroleum carbon contamination remained from data collected in 2011 and 2012.

2. Materials and methods

We collected the multiyear dataset from 2006 to 2012 (Table 1). The depths of our sampling sites ranged from a few meters close to the shore to over 200 m near the shelf-slope break. In this data analysis however, we arbitrarily limited the water depth to 20–50 m and the samples were all collected within $1-2$ m above the seabed. The minimum depth boundary (20 m) was selected to limit our discussion on bottom water that had little freshwater influence (Strauss et al., 2012). The deeper boundary 50 m was selected to be consistent with the maximum depth of the annual hypoxia survey carried out by the scientists at Louisiana Universities Marine Consortium.

For the 2006–2007 cruises, water column dissolved oxygen (DO) concentration was measured using an YSI® 5000 benchtop dissolved oxygen meter (Murrell and Lehrter, 2011). For all other cruises, DO was measured *in situ* using shipboard conductivity–temperature–depth (CTD) sensors. Both the DO meter and the CTD were calibrated using the traditional Winkler titration method. AOU was calculated using the equation of Weiss (1970), and potential temperature (θ) was calculated using salinity, pressure obtained from the CTD, and *in situ* temperature. Bottom water DIC samples were taken using 250 ml ground-neck borosilicate bottles from the shipboard Niskin bottles following the standard procedure in Dickson et al., (2007). Upon collection, these samples were first poisoned using 0.1 ml saturated $HgCl_2$ solution and stored in dark until further analysis. Usually within one month of sample collection, DIC was analyzed following the procedure in Wang and

Cai (2004) on an Appolo® DIC analyzer. 0.5 ml of sample was first acidified by 10% H_3PO_4 and the resultant CO_2 was extracted using N_2 carrier gas and directed to a Li-Cor 7000 CO_2 detector. Total amount of CO_2 was obtained by integrating the area below the CO_2 curve. Certified reference material (CRM) from A. G. Dickson's lab at Scripps Institution of Oceanography was used to obtain standard curves for DIC analysis and ensure analytical accuracy. The precision of DIC analysis was ± 2 μmol kg^{-1}.

Selected bottom water samples from 2011 were sub-sampled into 2-ml serum vials from the DIC sampling bottles after DIC analysis and then crimped-sealed. The $\delta^{13}C$ analysis was done in J. Brandes's stable isotope lab at Skidaway Institute of Oceanography using a Delta V Plus mass spectrometer with dual inlet and reported relative to Pee Dee Belemnite (PDB). The precision of the isotope analysis was $\pm 0.1‰$. Bottom water samples from July 2012 were also selected for $\delta^{13}C$ analysis. Probably due to prolonged storage at room temperature (~ 5 months), DIC concentrations measured using the isotope ratio mass spectrometer correlated weakly with the results obtained using our method and a linear regression produced $r^2 = 0.31$ (data not shown). Therefore these data were not reported here.

3. Results

Both DIC and DO concentrations in the bottom waters of the nGOM shelf exhibited temporal and spatial variations (Figs. 1 and 2). For example, in early summer (June 2006 and May 2007), DIC concentrations were relatively low compared to those later in the hypoxia season (September 2009 and August 2007, respectively). Even in the same season (i.e., July in 2009–2012), DIC showed significant inter-annual variations. Similarly, DO concentrations demonstrated a similar but reverse pattern as DIC (Fig. 2). Using calculated AOU, however, the multiyear dataset from 2006 to 2012 generated a consistent relationship between AOU and DIC, except for a few data points ("outliers", Fig. 3) that were collected between the Southwest Pass of the Mississippi River and Terrebonne Bay at Stations A5, A7, B9, and C9 in July, 2010 (Fig. 1, the circled area in panel 201007), three months after the initiation of the oil spill.

The 2011 bottom water DIC $\delta^{13}C$ data showed a strong inverse relationship with respect to DO concentration ($r = 0.97$, Fig. 4a). Moreover, a plot of $\delta^{13}C \cdot DIC$ vs. DIC concentration showed a nearly perfect linear correlation ($r = 0.99$). A regression of these data produced an intercept of $-22.0 \pm 0.6‰$ (Fig. 4b).
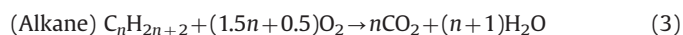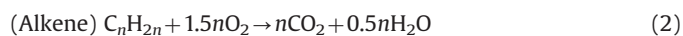
4. Discussion

4.1. Reaction stoichiometry of different organic matter

Based on reaction stoichiometry, algal materials with the Redfield composition would be respired under oxic conditions as follows:

$$138O_2 + (CH_2O)_{106}(NH_3)_{16}(H_3PO_4) \rightarrow 106CO_2 + 16HNO_3 + H_3PO_4 \quad (1)$$
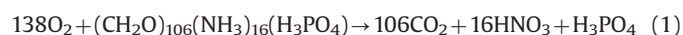
If hydrocarbons were involved in water column remineralization, depending on the type of the hydrocarbon, the reactions would consume different amounts of oxygen per unit of carbon oxidation. Assuming the crude oil is mostly alkane and alkene (Speight, 2006):

$$\text{(Alkene) } C_nH_{2n} + 1.5nO_2 \rightarrow nCO_2 + 0.5nH_2O \quad (2)$$

$$\text{(Alkane) } C_nH_{2n+2} + (1.5n+0.5)O_2 \rightarrow nCO_2 + (n+1)H_2O \quad (3)$$

Theoretically, if a hydrocarbon molecule is completely remineralized in the water column, for saturated alkanes (C_nH_{2n+2}), a

Table 1
Cruise time and bottom water parameters during 2006–2012.

Cruise time	Temperature (°C)	Salinity	Research vessel
June 2006	20.8–25.6	35.9–36.4	*OSV* Bold
September 2006	21.2–29.7	35.5–36.5	*OSV* Bold
May 2007	20.2–22.9	34.8–36.5	*OSV* Bold
August 2007	22.2–29.5	34.4–36.9	*OSV* Bold
July 2009	20.1–28.1	35.7–36.6	*R/V* Cape Hatteras
July 2010	20.5–29.1	32.6–36.3	*R/V* Pelican
July 2011	21.8–27.7	34.4–36.3	*R/V* Pelican
July 2012	21.7–28.7	35.2–36.4	*R/V* Pelican