

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

3 Xinping Hu ^{1,*}, Wei-Jun Cai ², Nancy N. Rabalais ³, Jianhong Xue ⁴

4 1. Department of Physical and Environmental Sciences, Texas A&M University – Corpus
5 Christi, Corpus Christi, TX 78412

6 2. College of Earth, Ocean, and Environment, University of Delaware, Newark, DE,
7 17716

8 3. Louisiana Universities Marine Consortium, Chauvin, LA 70344

9 4. Marine Science Institute – The University of Texas at Austin, Port Aransas, TX 78373

10

11

12 * Corresponding Author (Xinping.Hu@tamucc.edu, Tel 361-825-3395)

13

14 Keywords: carbon cycle, carbon isotopes, hypoxia, oil spills

15

16 Manuscript prepared for Deep-Sea Research II (Editor: Dr. Samantha Joye)

17

18 **Abstract**

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

34 **1. Introduction**

35 Dissolved inorganic carbon (DIC), nutrients (nitrogen and phosphorus), and dissolved
36 oxygen (in the form of “apparent oxygen utilization” or AOU, the difference between
37 saturated oxygen concentration and observed oxygen concentration) have long been used
38 to calculate the composition of the organic matter (or the “Redfield ratio”) undergoing
39 remineralization in the ocean (e.g., Takahashi *et al.*, 1985). Here, AOU in a water mass
40 represents the net consumption of oxygen from the time when the parcel of water was last
41 exposed at the air-sea interface. The “isopycnal method” to examine evolution of
42 chemical species along individual isopycnals (Minster and Boulahdid, 1987; Takahashi *et*
43 *al.*, 1985) or “neutral” surfaces (Anderson and Sarmiento, 1994), as well as water mass
44 mixing models coupled with a multilinear regression approach (Li *et al.*, 2000; Li and
45 Peng, 2002) are appropriate methods used to derive relatively confined ranges of C, N, P
46 ratios in remineralizing organic matter as well as the reaction stoichiometry between the
47 reacting organic matter and dissolved oxygen. Conversely, the Redfield ratio obtained in
48 these studies can be used to calculate the carbon contribution to the seawater DIC pool
49 from organic matter remineralization in order to differentiate this carbon source from the
50 net accumulation of anthropogenic CO₂ in seawater (e.g., Brewer, 1978; Sabine *et al.*,
51 2002). Despite the range of calculated elemental ratios (see a review in Hu and Cai,
52 2011b), oceanographic datasets often yield consistent patterns in the property-property
53 relationship (for example, N vs. P, DIC vs. AOU), indicating the planktonic nature of the
54 remineralizing material.

55 Studies on organic matter remineralizing stoichiometry mostly focused on the open
56 ocean, subsurface and deep waters where water mass compositions are relatively simple

57 and air-sea gas exchange is nil. In the coastal ocean, however, due to the potential
58 complexity in water column hydrodynamics (e.g., mixing with either freshwater or
59 among different coastal water masses) and gas exchange between the atmosphere and the
60 ocean, studies tend not to use the observed AOU-DIC relationship to obtain quantitative
61 information regarding the composition of organic matter being remineralized in the water
62 column. Nevertheless, good AOU-DIC linear correlations have been reported in some
63 recent studies. For example, Catoni *et al.* (2012) observed significant correlation between
64 AOU and DIC in the bottom layer of the Gulf of Trieste, and the regression line agrees
65 well with the Redfield stoichiometry. Similarly, Maske *et al.* (2010) observed a linear
66 relationship between DIC and AOU in the Pacific oxygen minimum zone off Mexico,
67 with the regressed slope consistent with the Redfield stoichiometry.

68 It is rare that other types of organic matter in the marine environment would play a
69 significant role in water column oxygen consumption under natural conditions, except
70 perhaps in places near shallow fossil carbon seepages (for example, Aharon *et al.*, 1992).
71 However, following the catastrophic *Deepwater Horizon* oil spill in 2010, not only oil
72 carbon affected bacterial biomass and entered the planktonic food web (Chanton *et al.*,
73 2012; Graham *et al.*, 2010; Hazen *et al.*, 2010), there were also indications that oil
74 remineralization may have influenced shelf waters in the northern Gulf of Mexico
75 (nGOM) as what we are showing in this work. We based our discussion on a multiyear
76 dataset collected in the nGOM region and suggested the likelihood of petroleum carbon
77 remineralization in the summer of 2010. We compared 2010 data in the same region from
78 before (2006-2009) and after the spill (2011-2012). We also determined whether
79 petroleum carbon contamination remained from data collected in 2011 and 2012.

80 2. Materials and methods

81 We collected the multiyear dataset from 2006 to 2012 (Table 1). The depths of our
82 sampling sites ranged from a few meters close to the shore to over 200 meters near the
83 shelf-slope break. In this data analysis however, we arbitrarily limited the water depth to
84 20-50 meters and the samples were all collected within 1-2 meters above the seabed. The
85 minimum depth boundary (20 m) was selected to limit our discussion on bottom water
86 that had little freshwater influence (Strauss *et al.*, 2012). The deeper boundary 50 m was
87 selected to be consistent with the maximum depth of the annual hypoxia survey carried
88 out by the scientists at Louisiana Universities Marine Consortium.

89 For the 2006-2007 cruises, water column dissolved oxygen (DO) concentration was
90 measured using an YSI® 5000 benchtop dissolved oxygen meter (Murrell and Lehrter,
91 2011). For all other cruises, DO was measured *in situ* using shipboard Conductivity-
92 Temperature-Depth (CTD) sensors. Both the DO meter and the CTD were calibrated
93 using the traditional Winkler titration method. AOU was calculated using the equation of
94 Weiss (1970), and potential temperature (θ) was calculated using salinity, pressure
95 obtained from the CTD, and *in situ* temperature. Bottom water DIC samples were taken
96 using 250 ml ground-neck borosilicate bottles from the shipboard Niskin bottles
97 following the standard procedure in Dickson (2007). Upon collection, these samples were
98 first poisoned using 0.1 ml saturated HgCl_2 solution and stored in dark until further
99 analysis. Usually within one month of sample collection, DIC was analyzed following the
100 procedure in Wang and Cai (2004) on an Appolo® DIC analyzer. 0.5 ml of sample was
101 first acidified by 10% H_3PO_4 and the resultant CO_2 was extracted using N_2 carrier gas
102 and directed to a Li-Cor 7000 CO_2 detector. Total amount of CO_2 was obtained by

103 integrating the area below the CO₂ curve. Certified reference material (CRM) from A. G.
104 Dickson's lab at Scripps Institution of Oceanography was used to obtain standard curves
105 for DIC analysis and ensure analytical accuracy. The precision of DIC analysis was ± 2
106 $\mu\text{mol kg}^{-1}$.

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

117 **3. Results**

118 Both DIC and DO concentrations in the bottom waters of the nGOM shelf exhibited
119 temporal and spatial variations (Figs. 1-2). For example, in early summer (June 2006 and
120 May 2007), DIC concentrations were relatively low compared to those later in the
121 hypoxia season (September 2009 and August 2007, respectively). Even in the same
122 season (i.e., July in 2009-2012), DIC showed significant inter-annual variations.
123 Similarly, DO concentrations demonstrated a similar but reverse pattern as DIC (Fig. 2).
124 Using calculated AOU, however, the multiyear dataset from 2006-2012 generated a
125 consistent relationship between AOU and DIC, except for a few data points ("outliers",

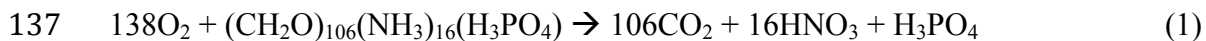
126 Fig. 3) that were collected between Southwest Pass of the Mississippi River and
127 Terrebonne Bay at Stations A5, A7, B9, and C9 in July, 2010 (Fig. 1, the circled area in
128 panel 201007), three months after the initiation of the oil spill.

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

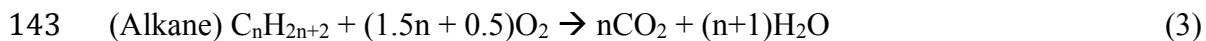
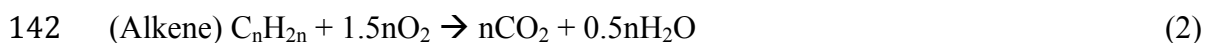
133 4. Discussion

134 4.1. Reaction stoichiometry of different organic matter

135 Based on reaction stoichiometry, algal materials with the Redfield composition would
136 be respired under oxic conditions following Eq. 1:



138 If hydrocarbons were involved in water column remineralization, depending on the
139 type of the hydrocarbon, the reactions would consume different amounts of oxygen per
140 unit of carbon oxidation. Assuming the crude oil is mostly alkane and alkene (Speight,
141 2006):



144 Theoretically, if a hydrocarbon molecule is completely remineralized in the water
145 column, for saturated alkanes ($\text{C}_n\text{H}_{2n+2}$), a major components of crude oils, the C/H ratio
146 would approach 1:2, and the oxygen consumption (AOU) and CO_2 production
147 (AOU/ ΔDIC) ratio would approach ~ 1.5 per carbon as the number of carbon (n) increases
148 (i.e., $(1.5n+0.5)/n$ approaches 1.5 when n is large). A special case for saturated alkane is

149 methane and during methane oxidation two units of oxygen are consumed per unit of
150 carbon oxidation (Eq. 4).



152 Remineralization of alkene (C_nH_{2n}) would yield an AOU/ Δ DIC ratio of 1.5 regardless of
153 the number of carbon atoms in the molecule.

154 Therefore, for complete hydrocarbon oxidation in a closed water parcel that has no
155 gas exchange with the atmosphere, the ratio of AOU and DIC would be 1.5-2.0 (Eqs. 2-
156 5). By comparison, if algal material is the only organic carbon source, the ratio would be
157 ~ 1.3 (Eq. 1).

158 In the marine environment, conversion from petroleum carbon to CO_2 under the
159 presence of O_2 is neither a single step nor an instantaneous reaction (e.g., Joye *et al.*,
160 2011). Petroleum carbon can be incorporated into the microbial biomass and oxygen can
161 be introduced into the organic molecules mediated by enzymes (e.g., Harayama *et al.*,
162 1999). Therefore the remineralization reactions above (Eqs. 2-4) may not be as
163 quantitative as the remineralization of algal materials in marine water column integrated
164 over relatively long time scales (years to decades) in typical oceanographic studies.

165 Furthermore, it is likely the hydrocarbon degradation envelope shown in Fig. 5 needs to
166 be expanded upward to reflect the incomplete organic carbon turnover.

167 Excluding the four outliers from July 2010, a linear regression of the remaining
168 tightly-correlated AOU and DIC data yielded (Table 2):

$$169 \quad \text{AOU} = (0.82 \pm 0.09) \times \text{DIC} - (1646.1 \pm 185.0)$$

170 At $\text{AOU} = 0$, calculated $\text{DIC}_0 = 2019.7 \pm 311.1 \mu\text{mol kg}^{-1}$. Assuming the organic
171 matter degradation occurred in a bottom water starting from a single water mass that has

172 a starting DIC concentration as DIC_0 , a detailed examination of the 2010 data suggested
173 that the four outliers indeed fell into the hydrocarbon remineralization envelope (Fig. 6)
174 while the linear regression of the remaining data yielded a slope (0.82 ± 0.09) that was
175 significantly lower than the Redfield stoichiometry (~ 1.3 , see next section for more
176 detailed interpretation). Therefore, the few exceptions in AOU-DIC property-property
177 plot (Fig. 3) were likely affected by oil remineralization, while all other cruise/station
178 data were consistent with the overall observed AOU-DIC relationships from cruises both
179 before and after 2010. Further, the stations where these data were collected coincided
180 with patches of oil slick observed on the surface during our cruise (Hu, personal
181 observation). In addition, from both the Satellite image taken in May 2010 (c.f. Liu *et al.*,
182 2012) and the ocean circulation model for June 2010 (Liu *et al.*, 2011), surface oil slick
183 did go beyond the Mississippi River Delta and enter the small area between the
184 Terrebonne Bay and the Southwest Pass, consistent with the locations of July 2010
185 outliers. However, water column fluorescence analysis did not always indicate the
186 presence of oil at these stations (Rabalais *et al.*, ms in prep). Further studies on oil
187 degradation coupled oxygen dynamics under controlled conditions are thus necessary.

188 Long-term monitoring of dynamic coastal waters for oxygen and inorganic carbon
189 proved useful for our analyses of potentially-derived hydrocarbon inorganic carbon.
190 Similar multi-parameter datasets would prove useful for identification of any deviations
191 from natural conditions thus is probably more robust than observation of a single
192 parameter (for example dissolved oxygen).

193 *4.2 Deviation of AOU-DIC relationship in nGOM waters from the Redfield stoichiometry*

194 The slopes of AOU-DIC regression from our previous field expeditions are mostly
195 lower than the ideal Redfield ratio 1.3 except the June 2006 dataset, which roughly
196 agreed with the Redfield stoichiometry. The reasons for such deviation were two-folds.

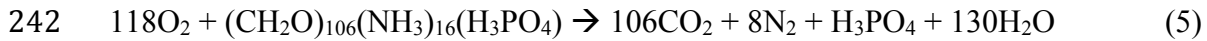
197 First, the underlying assumption in using AOU/DIC property-property plot was that
198 there was no gas-exchange between the stratified bottom water and the atmosphere
199 (Redfield *et al.*, 1963). Thus we needed to examine the validity of AOU usage in coastal
200 ocean. Sharp and Church (1981) were among the first to extend the use of AOU to the
201 coastal waters to explore nitrogen and phosphorous dynamics under the thermocline in
202 the Middle Atlantic Bight region; they justified the use of AOU in these waters based on
203 the slow diffusion of gas across the stratified water column. Further, Sharp *et al.* (1982)
204 and Sharp (2010) proposed that very high rates of both microbial degradation of organic
205 matter or primary production would dwarf the much slower gas exchange rates, therefore
206 the calculated AOU reflects a time-integrated multi-day influence of biological activities
207 when no strong wind is present.

208 For the nGOM region, there are several events that would re-aerate the water column
209 including weather frontal passages, tropical storms, thermal turnover and tidal advection
210 of oxygenated waters; such events could easily overturn the water column and facilitate
211 gas exchange. With adequate freshwater discharge from both the Mississippi and the
212 Atchafalaya Rivers and thermal warming of coastal waters in the summer, water column
213 stratification can resume fairly quickly so that oxygen consumption during organic matter
214 decomposition in the lower water column and at the seabed rapidly outpaces resupply.
215 Unlike the studies that involve oxygen and nutrients (Sharp *et al.*, 1982) that assume
216 minimal air-sea exchange, re-aeration events in coastal waters do affect DIC as high

217 $p\text{CO}_2$ bottom water could degas and release CO_2 into the atmosphere because of high
218 $p\text{CO}_2$ level in the bottom waters. As discussed in Cai *et al.* (2011), the time scales of air-
219 sea equilibration for oxygen and CO_2 are very different. It is about a week for oxygen,
220 although CO_2 needs a few months (Sarmiento and Gruber, 2006). Therefore, a storm may
221 increase (or decrease) $[\text{O}_2]$ (or AOU) rapidly while has a much smaller effect on DIC.
222 Similar to the reasoning in Sharp (2010), we also propose that the bottom water DIC in
223 the nGOM shelf was also subject to relatively longer-term effect (on the order of weeks
224 to month) of biogeochemical (i.e., remineralization) and physical controls (i.e., gas
225 exchange) than DO, and a reduced AOU-DIC slope than the Redfield stoichiometry is
226 thus expected.

227 In addition to the air-sea gas exchange mechanism, sediment-water exchange may
228 also force the AOU - DIC relationship away from the Redfield ratio. Based on reaction
229 stoichiometry (e.g., Hu and Cai, 2011a), all anaerobic remineralization produce only CO_2
230 (or DIC) without directly consuming oxygen. Both diffusion and advection (the latter
231 driven by wave pumping under strong hydrodynamic conditions when it is windy) could
232 drive out the DIC and thus increase bottom water DIC concentration. Theoretically
233 reduced species (such as NH_3 , $\text{Fe}^{2+}/\text{Mn}^{2+}$, and sulfide) could also be brought into the
234 water column along with benthic DIC flux and their reoxidation would consume oxygen.
235 A complete oxidation of these species would be equivalent to direct aerobic oxidation,
236 and essentially these redox elements act as the “electron shuttles” between organic carbon
237 and the ultimate oxidant – DO. However, these complete reoxidation reactions usually do
238 not occur. For example, from the perspective of nitrogen cycling, most of denitrification
239 in continental shelf sediments would occur through coupled nitrification and

240 denitrification pathway with AOU/DIC ratio of 1.1, less than the Redfield stoichiometry
241 1.3 (Eq. 5) (Middelburg *et al.*, 1996):



243 Furthermore, Childs *et al.* (2002) studied denitrification in the nGOM sediments and
244 concluded that dissimilatory nitrate reduction to ammonia (DNRA) rates exceed those of
245 denitrification. The DNRA reaction potential also has a lower AOU/DIC ratio. For
246 anaerobic reactions involving metals and sulfur, the nGOM sediment is known for
247 preservation of reduced sulfur in the forms of pyrite and mackinawite minerals in
248 sediments (Lin and Morse, 1991), the latter metal-sulfur compounds are products of
249 coupled organic carbon remineralization and Fe (III)-sulfate reductions (see Table 1 in
250 Hu and Cai, 2011a) with a net release of DIC without oxygen consumption. Therefore,
251 anaerobic reactions in the sediment can ultimately increase DIC concentration and make
252 the oxygen consumption and DIC production not in proportion to the ideal Redfield
253 stoichiometry.

254 *4.3 The post-spill “normalcy”?*

255 Using the $\text{DIC} \cdot \delta^{13}\text{C}$ vs DIC regression method for the 2011 dataset, we obtained a
256 slope of $-22.0 \pm 0.6\%$ (d.f. = 10). This regression method has been used in a number of
257 studies (Aller and Blair, 2006; Hu and Burdige, 2007; Hu *et al.*, 2010; Martin *et al.*,
258 2000) to obtain the $\delta^{13}\text{C}$ signature of remineralizing organic carbon in marine sediments.
259 However, the examined spatial scales of this method in previous studies are only on the
260 order of tens of centimeters. We examined whether the same approach can be used to
261 examine bottom water in the nGOM region that has a spatial span of hundreds of
262 kilometers.

263 First, the salinity range of the 2011 bottom waters was 34.4-36.3. The high salinity
264 value was consistent with salinity data collected at 20-50 m depths along the Mississippi
265 transect during our 2007 Gulf of Mexico and U.S. East Coast Carbon study (GOMECC,
266 <http://www.aoml.noaa.gov/ocd/gcc/GOMECC/>) (36.3 ± 0.1). Thus the shelf bottom water
267 can be considered “ocean” water. We assumed the low salinity water was caused by river
268 water dilution. Based on mass balance, river water contributed to <5% to the low salinity
269 end of the bottom water. DIC_0 from the regression of all field data (except the 2010
270 outliers) was $2054 \pm 97.5 \mu\text{mol kg}^{-1}$ (Table 2), and this value agreed well with the average
271 DIC concentration ($2040 \pm 24 \mu\text{mol kg}^{-1}$, with $\text{AOU} = -6.2 \pm 13.4 \mu\text{mol kg}^{-1}$) collected
272 from the 20-50 m water column along the Mississippi transect during the GOMECC
273 study. These comparisons indicated that the dominant water mass in the bottom waters at
274 the 20-50 depth interval was from the offshore GOM.

275 Mississippi River DIC had a $\delta^{13}\text{C}$ value of -8.8‰ and Atchafalaya River DIC had a
276 $\delta^{13}\text{C}$ of -9.7‰ based on the data collected from our 2009-2010 GulfCarbon Project (Cai
277 and Hu, unpublished data). Assuming freshwater residence time is approximately one
278 month on the nGOM shelf under examination (cf. Wiseman *et al.*, 1997), we took
279 average discharge and total alkalinity data of both rivers (and here approximate alkalinity
280 to DIC) in June 2011 (<http://nwis.waterdata.usgs.gov/usa/nwis/qwdata>) (Table 3) to
281 represent the freshwater endmember that was mixed into the bottom water. Therefore, a
282 discharge-weighted freshwater DIC concentration was $2339.2 \mu\text{mol kg}^{-1}$ with $\delta^{13}\text{C}$ value
283 of -9.0‰. As will be shown later, effect of freshwater on bottom water chemistry is
284 minimal, thus slight variation in freshwater DIC caused by selection of residence time is
285 insignificant for studying bottom water stable isotope evolution.

286 We assumed the shelf bottom water was a mixture between river water and seawater,
287 then we subtracted the contribution of river water to both bottom water DIC and $\delta^{13}\text{C}$
288 using the following equations:

$$289 \quad \text{DIC}_r = (36.3 - S) / 36.3 \cdot \text{DIC}_{\text{river}} \quad (6)$$

$$290 \quad \text{DIC}' = \text{DIC}_{\text{meas}} - \text{DIC}_r \quad (7)$$

$$291 \quad (\text{DIC}' \cdot \delta^{13}\text{C}') = \text{DIC}_{\text{meas}} \cdot \delta^{13}\text{C}_{\text{meas}} - \text{DIC}_r \cdot \delta^{13}\text{C}_{\text{river}} \quad (8)$$

292 Here subscripts *river*, *r*, and *meas* represent river endmember, river contribution to
293 bottom water through mixing, and measured concentration, respectively. DIC' is bottom
294 water DIC corrected for river DIC contribution. $\delta^{13}\text{C}'$ is unknown, although $(\text{DIC}' \cdot \delta^{13}\text{C}')$
295 can be calculated using the mass balance in Eq. 8. We regressed $(\text{DIC}' \cdot \delta^{13}\text{C}')$ against
296 DIC' , and obtained a slope of $-22.2 \pm 1.5\%$ (dashed line in Fig. 4b), which was essentially
297 the same as the result without a river DIC correction ($-22.0 \pm 0.6\%$), even though
298 statistically the two regressions were significantly different (ANCOVA test, MS =
299 448353, MS error = 41866, F = 10.71, d.f. = 1, 20, P = 0.004). Furthermore, $\delta^{13}\text{C}$ of DIC
300 in the seawater endmember was calculated as $0.8 \pm 0.1\%$ (n=12) using the regressed slope
301 and mass balance. This seawater endmember $\delta^{13}\text{C}$ value was slightly higher than the
302 $\delta^{13}\text{C}_{\text{DIC}}$ value (0.4%) in the upwelled outer shelf water at 60 m in a 2008 cruise (Strauss
303 *et al.*, 2012) but fell in the range of our measured values during the GulfCarbon cruises
304 (Cai and Hu, unpublished data). Therefore the bottom water we examined for the 2011
305 shelfwide cruise did not have significant freshwater influence and DIC evolution was
306 mostly controlled by remineralization of organic carbon that had $\delta^{13}\text{C}$ value of $\sim -22\%$.

307 (Turner and Rabalais, 1994) Based on $\delta^{13}\text{C}$ of the apparent remineralizing organic
308 carbon alone, it was tempting to conclude that algal carbon drove oxygen consumption

309 because typical surface ocean primary production produces organic carbon in the range of
310 -20~-22‰ both in the literature (e.g., Eadie and Jeffrey, 1973) and in any standard stable
311 isotope geochemistry textbook. However, Turner and Rabalais (, 1994) studied stable
312 isotope compositions of sedimentary organic carbon in the Mississippi River Delta. They
313 found that $\delta^{13}\text{C} < -22.2\text{‰}$ near the river mouth indicates terrestrial carbon input and
314 marine carbon has $\delta^{13}\text{C}$ of -20.4 ~21.44‰. Furthermore, Goñi et al. (1997) examined
315 sedimentary organic carbon in the same region and concluded that C_4 plant derived
316 carbon could modify the overall terrestrial carbon $\delta^{13}\text{C}$ and make it indistinguishable
317 from marine carbon. Therefore, it was not possible to ascertain that algal carbon was the
318 only carbon material that was being utilized in the nGOM bottom waters in 2011 without
319 more detailed investigation such as compound-specific analysis and biomarker studies.
320 Nevertheless, it was likely that at least oil degradation was not significant in these waters
321 in 2011, one year after the oil spill, because petroleum carbon found in the GOM area is
322 much more ^{13}C -depleted than both the terrestrial and algal carbon. For example,
323 thermogenic petroleum carbon in the GOM area typically has stable carbon isotope value
324 ($\delta^{13}\text{C}$) of -40~-60‰ (Hu *et al.*, 2010), and that of biogenic methane can reach as low as
325 ~-100‰ (Joye *et al.*, 2010).

326 **5. Summary**

327 Based on the coevolution of bottom water oxygen and dissolved inorganic carbon and
328 the deviation of AOU-DIC relationship in a small area of the nGOM shelf in 2010
329 between the Southwest Pass and the Terrebonne Bay, we concluded that petroleum
330 carbon degradation from the *Deepwater Horizon* oil spill may have influenced four
331 stations in the Louisiana Bight (July, 2010). Therefore, monitoring of bottom-water DO

332 and DIC indeed may provide a potentially useful tool for detecting degradation of
333 petroleum carbon in the water column, and this approach could be used in deeper waters
334 as well.

335 In the next two years post oil spill, the tight correlation between AOU and DIC in the
336 bottom water reappeared and suggested that the nGOM shelf waters were likely free of
337 oil contamination from 2011, one year after the spill. Furthermore, apparent stable
338 isotope composition of the remineralizing organic carbon (derived from $\text{DIC} \cdot \delta^{13}\text{C}$ vs DIC
339 regression) did not indicate significant contribution from petroleum carbon
340 remineralization to bottom water DIC in 2011. However, based on water column DIC
341 data alone we could not ascertain whether it was algal carbon or terrestrial carbon that
342 were being used by the bottom water microbes.

343 The regression of shelf water AOU and DIC, despite their regular tight correlation,
344 did not completely agree with the Redfield reaction stoichiometry. The reasons behind
345 this discrepancy may be caused by air-sea exchange that replenished O_2 faster than to
346 release CO_2 and benthic respiration that released CO_2 in excess of O_2 consumption.

347

348 **Acknowledgements**

349 This study was supported by grants from BP/The Gulf of Mexico Research Initiative,
350 RFP-III award to WJC, XH, and NNR, and RFP-II award to WJC and XH, RFP-I award
351 to NNR, and in part by NOAA Grant No. NA09NOS4780204 from the Center for
352 Sponsored Coastal Ocean Research. XH was also supported by the new faculty startup
353 fund provided by the College of Science and Engineering of Texas A&M University –
354 Corpus Christi. Previous cruises have been supported by NSF, EPA, and NOAA. Many
355 colleagues and students, including YC Wang, WJ Huang, X. Guo, LQ Jiang, J. Hartman,
356 and G Han, participated in the sample collection and helped with sample analyses over
357 the years and we thank them for their invaluable help. Crew of *OSV Bold*, *R/V Cape*
358 *Hatteras*, and *R/V Pelican* are thanked for their assistance during our field expeditions. H.
359 Maske and an anonymous reviewer offered critical comments that helped to improve the
360 quality of this work. Finally, we thank the editor SB Joye for incorporating this study into
361 the DSR II volume.

362 **References**

- 363 Aharon, P., Graber, E.R., Roberts, H.H., 1992. Dissolved carbon and $\delta^{13}\text{C}$ anomalies in
364 the water column caused by hydrocarbon seeps on the northwestern Gulf of
365 Mexico slope. *Geo-Marine Letters* 12, 33-40.
- 366 Aller, R.C., Blair, N.E., 2006. Carbon remineralization in the Amazon–Guianas
367 tropical mobile mudbelt: A sedimentary incinerator. *Continental Shelf*
368 *Research* 26, 2241-2259.
- 369 Anderson, L.A., Sarmiento, J.L., 1994. Redfield ratios of remineralization determined
370 by nutrient data analysis. *Global Biogeochemical Cycles* 8, 65-80.
- 371 Bianchi, T.S., DiMarco, S.F., Cowan Jr, J.H., Hetland, R.D., Chapman, P., Day, J.W.,
372 Allison, M.A., 2010. The science of hypoxia in the Northern Gulf of Mexico: A
373 review. *Science of the Total Environment* 408, 1471-1484.
- 374 Brewer, P.G., 1978. Direct observation of the oceanic CO_2 increase *Geophysical*
375 *Research Letters* 5, 997-1000.
- 376 Cai, W.-J., Hu, X., Huang, W.-J., Murrell, M.C., Lehrter, J.C., Lohrenz, S.E., Chou, W.-C.,
377 Zhai, W., Hollibaugh, J.T., Wang, Y., Zhao, P., Guo, X., Gundersen, K., Dai, M.,
378 Gong, G.-C., 2011. Acidification of subsurface coastal waters enhanced by
379 eutrophication. *Nature Geoscience* 4, 766-770.
- 380 Cantoni, C., Luchetta, A., Celio, M., Cozzi, S., Raicich, F., Catalano, G., 2012. Carbonate
381 system variability in the Gulf of Trieste (North Adriatic Sea). *Estuarine,*
382 *Coastal and Shelf Science*.
- 383 Chanton, J.P., Cherrier, J., Wilson, R.M., Sarkodee-Adoo, J., Bosman, S., Mickle, A.,
384 Graham, W.M., 2012. Radiocarbon evidence that carbon from the Deepwater

385 Horizon spill entered the planktonic food web of the Gulf of Mexico
386 Environmental Research Letters 7, 045303 doi:045310.041088/041748-
387 049326/045307/045304/045303.

388 Childs, C.R., Rabalais, N.N., Turner, R.E., Proctor, L.M., 2002. Sediment denitrification
389 in the Gulf of Mexico zone of hypoxia. Marine Ecology Progress Series 240,
390 285-290.

391 Corbett, D.R., McKee, B., Duncan, D., 2004. An evaluation of mobile mud dynamics in
392 the Mississippi River deltaic region. Marine Geology 209, 91-112.

393 Dickson, A.G., Sabine, C.L., Christian, J.R., 2007. Guide to Best Practices for Ocean CO₂
394 Measurements. PICES Special Publication 3. p. 191.

395 Eadie, B.J., Jeffrey, L.M., 1973. $\delta^{13}\text{C}$ analyses of oceanic particulate organic matter.
396 Marine Chemistry 1, 199-209.

397 Eldridge, P.M., Morse, J.W., 2008. Origins and temporal scales of hypoxia on the
398 Louisiana shelf: Importance of benthic and sub-pycnocline water
399 metabolism. Marine Chemistry 108, 159-171.

400 Goñi, M.A., Ruttenger, K.C., Eglinton, T.I., 1997. Sources and contribution of
401 terrigenous organic carbon to surface sediments in the Gulf of Mexico. Nature
402 389, 275-278.

403 Graham, W.M., Condon, R.H., Carmichael, R.H., D'Ambra, I., Patterson, H.K., Linn, L.J.,
404 Hernandez, F.J., 2010. Oil carbon entered the coastal planktonic food web
405 during the Deepwater Horizon oil spill. Environmental Research Letters 5,
406 045301 doi:045310.041088/041748-049326/045305/045304/045301.

407 Harayama, S., Kishira, H., Kasai, Y., Shutsubo, K., 1999. Petroleum biodegradation in
408 marine environments. *Journal of Microbiology and Biotechnology* 1, 63-70.

409 Hazen, T.C., Dubinsky, E.A., DeSantis, T.Z., Andersen, G.L., Piceno, Y.M., Singh, N.,
410 Jansson, J.K., Probst, A., Borglin, S.E., Fortney, J.L., Stringfellow, W.T., Bill, M.,
411 Conrad, M.E., Tom, L.M., Chavarria, K.L., Alusi, T.R., Lamendella, R., Joyner,
412 D.C., Spier, C., Baelum, J., Auer, M., Zemla, M.L., Chakraborty, R., Sonnenthal,
413 E.L., D'haeseleer, P., Holman, H.-Y.N., Osman, S., Lu, Z., Van Nostrand, J.D.,
414 Deng, Y., Zhou, J., Mason, O.U., 2010. Deep-sea oil plume enriches indigenous
415 oil-degrading bacteria. *Science* 330, 204-208.

416 Hu, X., Burdige, D.J., 2007. Enriched stable carbon isotopes in the pore waters of
417 carbonate sediments dominated by seagrasses: evidence for coupled
418 carbonate dissolution and reprecipitation. *Geochimica et Cosmochimica Acta*
419 71, 129-144.

420 Hu, X., Cai, W.-J., 2011a. An assessment of ocean margin anaerobic processes on
421 oceanic alkalinity budget. *Global Biogeochemical Cycles* 25, GB3003, doi:
422 3010.1029/2010GB003859.

423 Hu, X., Cai, W.-J., 2011b. The impact of denitrification on the atmospheric CO₂ uptake
424 potential of seawater. *Marine Chemistry* 127, 192-198.

425 Hu, X., Cai, W.-J., Wang, Y., Luo, S., Guo, X., 2010. Pore-water geochemistry of two
426 contrasting brine-charged seep sites in the northern Gulf of Mexico
427 continental slope. *Marine Chemistry* 118, 99-107.

428 Joye, S.B., Bowles, M.W., Samarkin, V.A., Hunter, K.S., Niemann, H., 2010.
429 Biogeochemical signatures and microbial activity of different cold-seep

430 habitats along the Gulf of Mexico deep slope. *Deep-Sea Research, Part II:*
431 *Topical Studies in Oceanography* 57, 1990-2001.

432 Joye, S.B., Leifer, I., MacDonald, I.R., Chanton, J.P., Meile, C.D., Teske, A.P., Kostka, J.E.,
433 Chistoserdova, L., Coffin, R., Hollander, D., Kastner, M., Montoya, J.P., Rehder,
434 G., Solomon, E., Treude, T., Villareal, T.A., 2011. Comment on "A Persistent
435 oxygen anomaly reveals the fate of spilled methane in the deep Gulf of
436 Mexico". *Science* 332, 1033.

437 Li, Y.-H., Karl, D.M., Winn, C.D., Mackenzie, F.T., Gans, K., 2000. Remineralization
438 ratios in the subtropical North Pacific Gyre. *Aquatic Geochemistry* 6, 65-85.

439 Li, Y.-H., Peng, T.-H., 2002. Latitudinal change of remineralization ratios in the
440 oceans and its implication for nutrient cycles. *Global Biogeochemical Cycles*
441 16, 1130, doi:1110.1029/2001GB001828.

442 Lin, S., Morse, J.W., 1991. Sulfate reduction and iron sulfide mineral formation in
443 Gulf of Mexico anoxic sediments. *American Journal of Science* 291, 55-89.

444 Liu, Y., Weisberg, R.H., Hu, C., Zheng, L., 2011. Tracking the Deepwater Horizon oil
445 spill: A modeling perspective. *Eos, Transactions American Geophysical Union*
446 92, 45-46.

447 Liu, Z., Liu, J., Zhu, Q., Wu, W., 2012. The weathering of oil after the
448 Deepwater Horizon oil spill: insights from the chemical composition of the oil
449 from the sea surface, salt marshes and sediments. *Environmental Research*
450 *Letters* 7, 035302.

451 Martin, W.R., McNichol, A.P., McCorkle, D.C., 2000. The radiocarbon age of calcite
452 dissolving at the sea floor: estimates from pore water data. *Geochimica et*
453 *Cosmochimica Acta* 64, 1391-1404.

454 Maske, H., Medrano, R.n.C., Castro, A.T.a., Mercado, A.J.n., Jauregui, C.O.A., Castro,
455 G.G., Ochoa, J., 2010. Inorganic carbon and biological oceanography above a
456 shallow oxygen minimum in the entrance to the Gulf of California in the
457 Mexican Pacific. *Limnology and Oceanography* 55, 481-491.

458 Middelburg, J.J., Soetaert, K., Herman, P.M.J., Heip, C.H.R., 1996. Denitrification in
459 marine sediments: a model study. *Global Biogeochemical Cycles* 10, 661-674.

460 Minster, J.-F., Boulahdid, M., 1987. Redfield ratios along isopycnal surfaces--a
461 complementary study. *Deep-Sea Research, Part II: Topical Studies in*
462 *Oceanography* 34, 1981-2003.

463 Morse, J.W., Eldridge, P.M., 2007. A non-steady state diagenetic model for changes in
464 sediment biogeochemistry in response to seasonally hypoxic/anoxic
465 conditions in the "dead zone" of the Louisiana shelf. *Marine Chemistry* 106,
466 239-255.

467 Murrell, M., Lehrter, J., 2011. Sediment and lower water column oxygen
468 consumption in the seasonally hypoxic region of the Louisiana Continental
469 Shelf. *Estuaries and Coasts* 34, 912-924.

470 Rabalais, N.N., Turner, R.E., Sen Gupta, B.K., Boesch, D.F., Chapman, P., Murrell, M.C.,
471 2007. Hypoxia in the northern Gulf of Mexico: Does the science support the
472 Plan to Reduce, Mitigate, and Control Hypoxia? *Estuaries and Coasts* 30, 753-
473 772.

474 Redfield, A.C., Ketchum, B.H., Richards, F.A., 1963. The influence of organisms on the
475 composition of seawater. In: Hill, M.N. (Ed.), *The Sea*, v. II. Interscience
476 Publishers, pp. n/a-n/a.

477 Sabine, C.L., Feely, R.A., Key, R.M., Bullister, J.L., Millero, F.J., Lee, K., Peng, T.-H.,
478 Tilbrook, B., Ono, T., Wong, C.S., 2002. Distribution of anthropogenic CO₂ in
479 the Pacific Ocean. *Global Biogeochemical Cycles* 16, 1083,
480 doi:10.1029/2001GB001639.

481 Sarmiento, J.L., Gruber, N., 2006. *Ocean Biogeochemical Dynamics*. Princeton
482 University Press, Princeton.

483 Sharp, J.H., 2010. Estuarine oxygen dynamics: What can we learn about hypoxia
484 from long-time records in the Delaware Estuary? *Limnology and*
485 *Oceanography* 55, 535-548.

486 Sharp, J.H., Church, T.M., 1981. Biochemical modeling in coastal waters of the Middle
487 Atlantic States. *Limnology and Oceanography* 26, 843-854.

488 Sharp, J.H., Culbertson, C.H., Church, T.M., 1982. The chemistry of the Delaware
489 Estuary: General considerations. *Limnology and Oceanography* 27, 1015-
490 1028.

491 Speight, J.G., 2006. *The Chemistry and Technology of Petroleum*. CRC Press.

492 Strauss, J., Grossman, E.L., DiMarco, S.F., 2012. Stable isotope characterization of
493 hypoxia-susceptible waters on the Louisiana shelf: Tracing freshwater
494 discharge and benthic respiration. *Continental Shelf Research* 47, 7-15.

495 Takahashi, T., Broecker, W.S., Langer, S., 1985. Redfield ratio based on chemical data
496 from isopycnal surfaces. *Journal of Geophysical Research* 90, 6907-6924.

497 Turner, R.E., Rabalais, N.N., 1994. Coastal eutrophication near the Mississippi river
498 delta. *Nature* 368, 619-621.

499 Wang, Z.A., Cai, W.-J., 2004. Carbon dioxide degassing and inorganic carbon export
500 from a marsh-dominated estuary (the Duplin River): A marsh CO₂ pump.
501 *Limnology and Oceanography* 49, 341-354.

502 Weiss, R.F., 1970. The solubility of nitrogen, oxygen and argon in water and
503 seawater. *Deep Sea Research and Oceanographic Abstracts* 17, 721-735.

504 Wiseman, W.J., Rabalais, N.N., Turner, R.E., Dinnel, S.P., MacNaughton, A., 1997.
505 Seasonal and interannual variability within the Louisiana coastal current:
506 stratification and hypoxia. *Journal of Marine Systems* 12, 237-248.

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

Cruise Time	Temperature (°C)	Salinity	Research Vessel
Jun, 2006	20.8-25.6	35.9-36.4	<i>OSV Bold</i>
Sep, 2006	21.2-29.7	35.5-36.5	<i>OSV Bold</i>
May, 2007	20.2-22.9	34.8-36.5	<i>OSV Bold</i>
Aug, 2007	22.2-29.5	34.4-36.9	<i>OSV Bold</i>
Jul, 2009	20.1-28.1	35.7-36.6	<i>R/V Cape Hatteras</i>
Jul, 2010	20.5-29.1	32.6-36.3	<i>R/V Pelican</i>
Jul, 2011	21.8-27.7	34.4-36.3	<i>R/V Pelican</i>
Jul, 2012	21.7-28.7	35.2-36.4	<i>R/V Pelican</i>

508

509

510 Table 2. Results of linear regression for AOU vs. DIC

Cruise Time	Slope	Intercept	DIC ₀ (μmol kg ⁻¹) [#]	R ²	N
Jun. 2006	1.44±0.11	-3009.6±240.2	2088.2±234.0	0.89	23
Sep. 2006	0.79±0.05	-1617.6±118.6	2045.6±206.7	0.88	29
May 2007	1.23±0.07	-2552.4±145.5	2067.0±165.0	0.91	33
Aug. 2007	0.92±0.08	-1889.4±179.0	2047.6±266.4	0.83	27
Jul. 2009	0.81±0.06	-1667.0±129.6	2062.2±222.0	0.94	13
Jul. 2010 [*]	0.82±0.09	-1646.1±185.0	2019.7±311.1	0.83	21
Jul. 2011	0.99±0.07	-2051.2±153.3	2074.7±213.4	0.91	21
Jul. 2012	0.88±0.09	-1788.6±185.3	2028.7±290.5	0.86	17
Overall [*]	0.92±0.03	-1886.0±64.7	2054.3±97.5	0.83	185

511 ^{*} Results for 2010 data were calculated after excluding the four outliers.

512 [#] DIC₀ represent x-the intercept when AOU = 0.

513 Table 3. Average discharge and water chemistry of major freshwater endmembers to the
514 nGOM (Mississippi River and Atchafalaya River) in June 2011.

River endmember	Discharge ($\text{m}^3 \text{s}^{-1}$)	TA ($\mu\text{mol kg}^{-1}$)	$\delta^{13}\text{C}_{\text{DIC}}$ (‰)
Mississippi	24900	2390	-8.8
Atchafalaya	8970	2198	-9.7

515

516 **Figure Captions**

517 Figure 1. Bottom water DIC ($\mu\text{mol kg}^{-1}$) in the 20-50 m depth interval on the nGOM
518 shelf. Note that the actual station depths measured during our cruises did not agree
519 completely with the bathymetry database (TerrainBase global 5-minute digital terrain)
520 used to make the map plots (for example the depth discrepancies in the 2011 and 2012
521 maps). The *Deepwater Horizon* oil spill site (DWH) is marked with a star in panel
522 201007. DIC and DO data in the circled area in July 2010 showed different relationship
523 than all the other years.

524 Figure 2. Bottom water DO ($\mu\text{mol kg}^{-1}$) in the 20-50 m depth interval on the nGOM
525 shelf. DIC and DO data in the circled area in July 2010 showed different relationship than
526 all the other years.

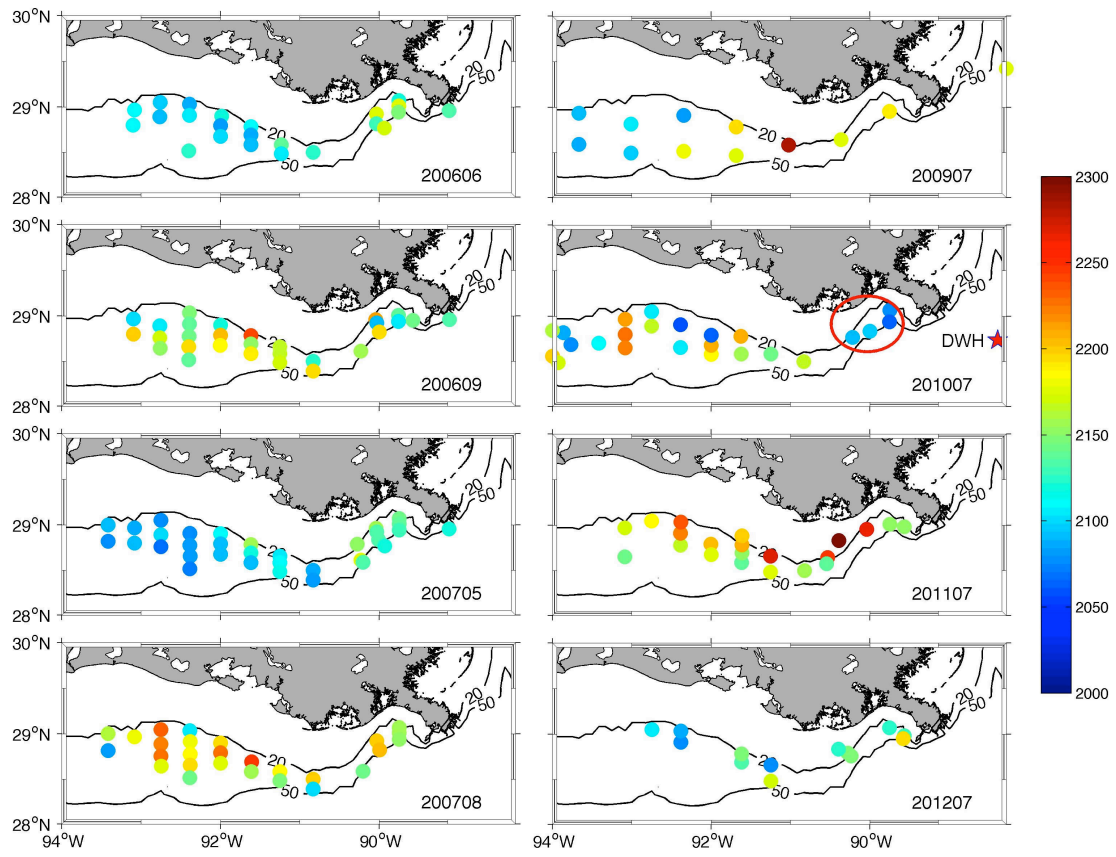
527 Figure 3. A compilation of multi-year AOU-DIC data. The four “outliers” represent the
528 possible influence of oil degradation in the water column and their locations are circled in
529 Figs. 1-2.

530 Figure 4. (a). An inverse correlation between $\delta^{13}\text{C}$ of DIC and DO for the data collected
531 in July, 2011. (b). The linear regression for solving the apparent $\delta^{13}\text{C}$ of the
532 remineralizing organic carbon (i.e., the slope of the regression). The solid circles are
533 collected data and the open squares represent the data after correction for freshwater
534 input (see text in Section 4.3 for details).

535 Figure 5. A conceptual model of different reaction stoichiometry between
536 remineralization of petroleum carbon and that of marine produced algal carbon.

537 Figure 6. AOU-DIC property-property plot based on the 2010 dataset. The four outliers
538 were excluded from the linear regression. The initial bottom water DIC concentration

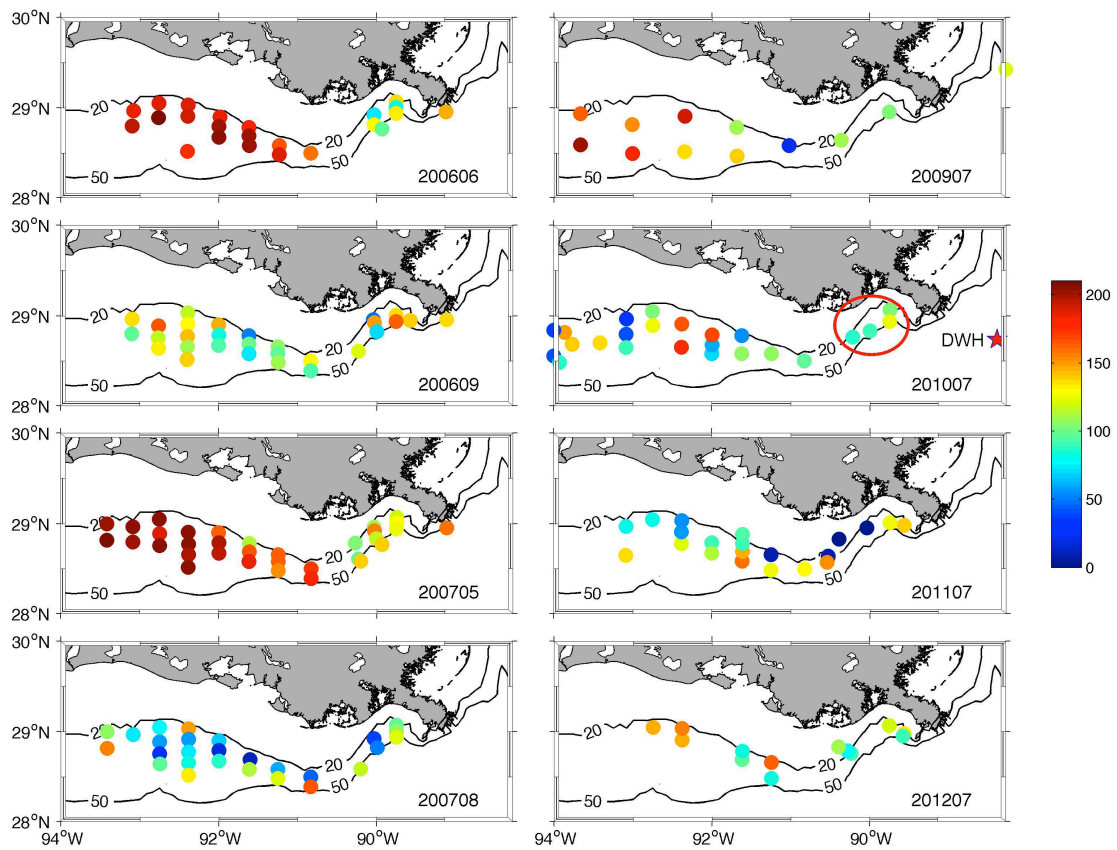
539 ($\text{DIC}_0 = 2019.7 \mu\text{mol kg}^{-1}$) was calculated using the regressed slope and intercept (see
540 text and Table 2 for details). The solid line is the result of the linear regression, the long
541 dashed line represents Redfield reaction stoichiometry, and the short dashed lines enclose
542 the degradation envelope of petroleum carbon as shown in Fig. 5.



543

544 Fig. 1

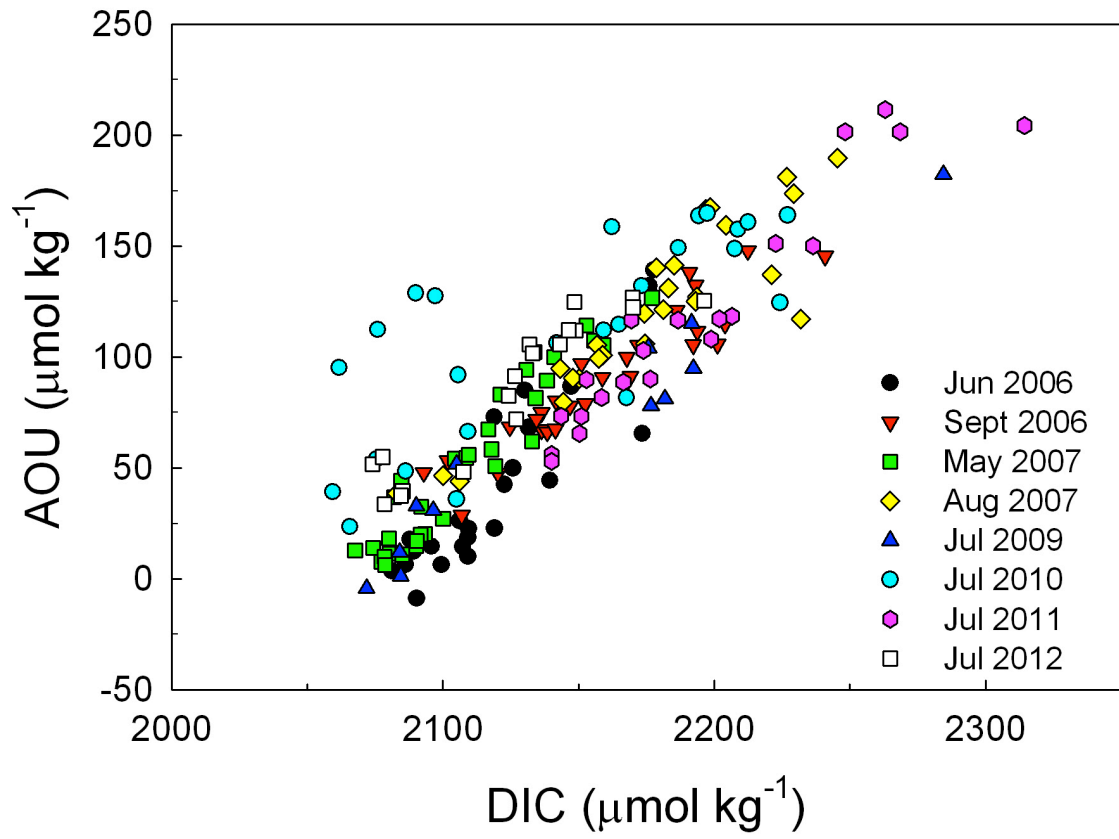
545



546

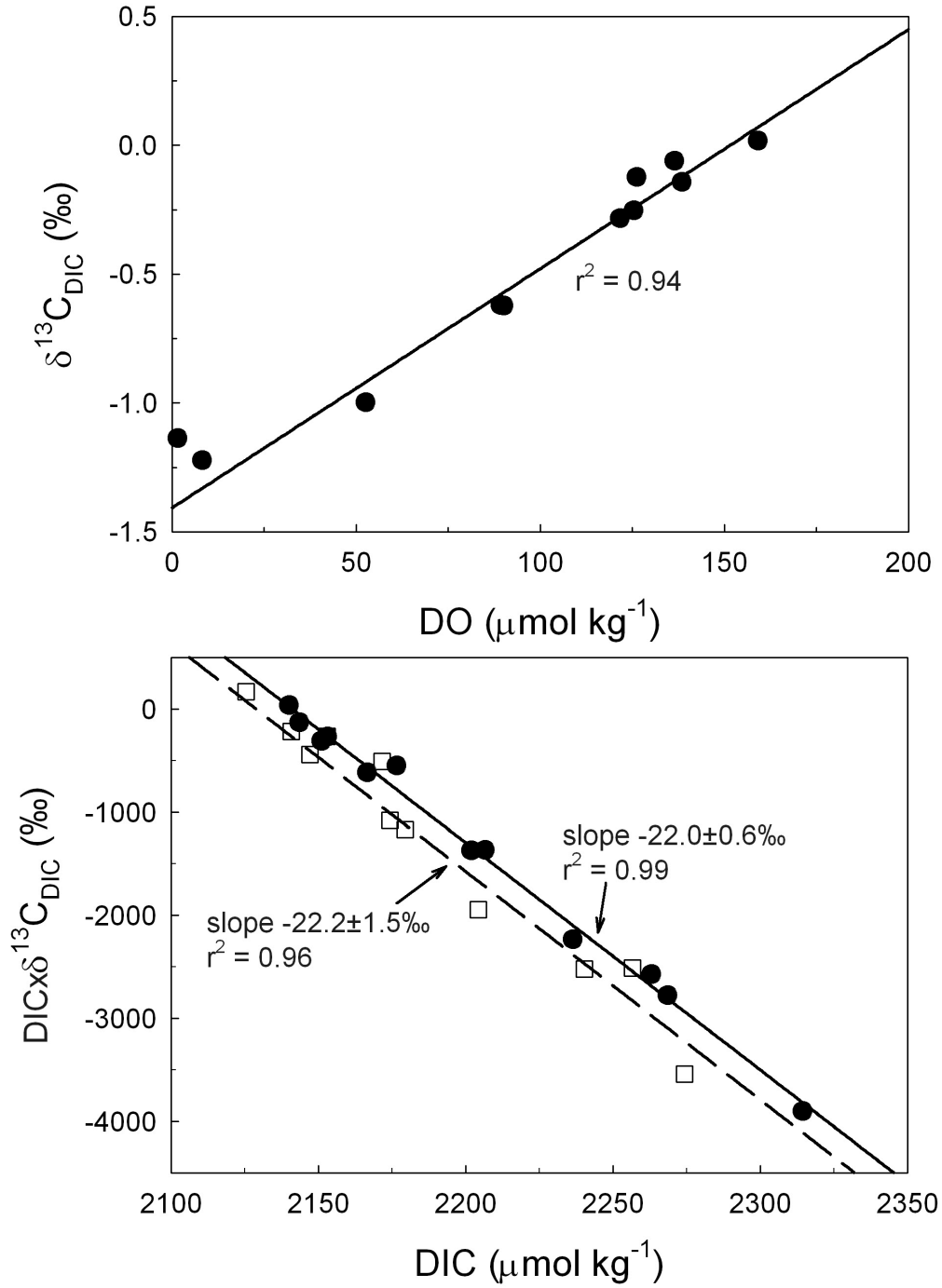
547 Fig. 2

548



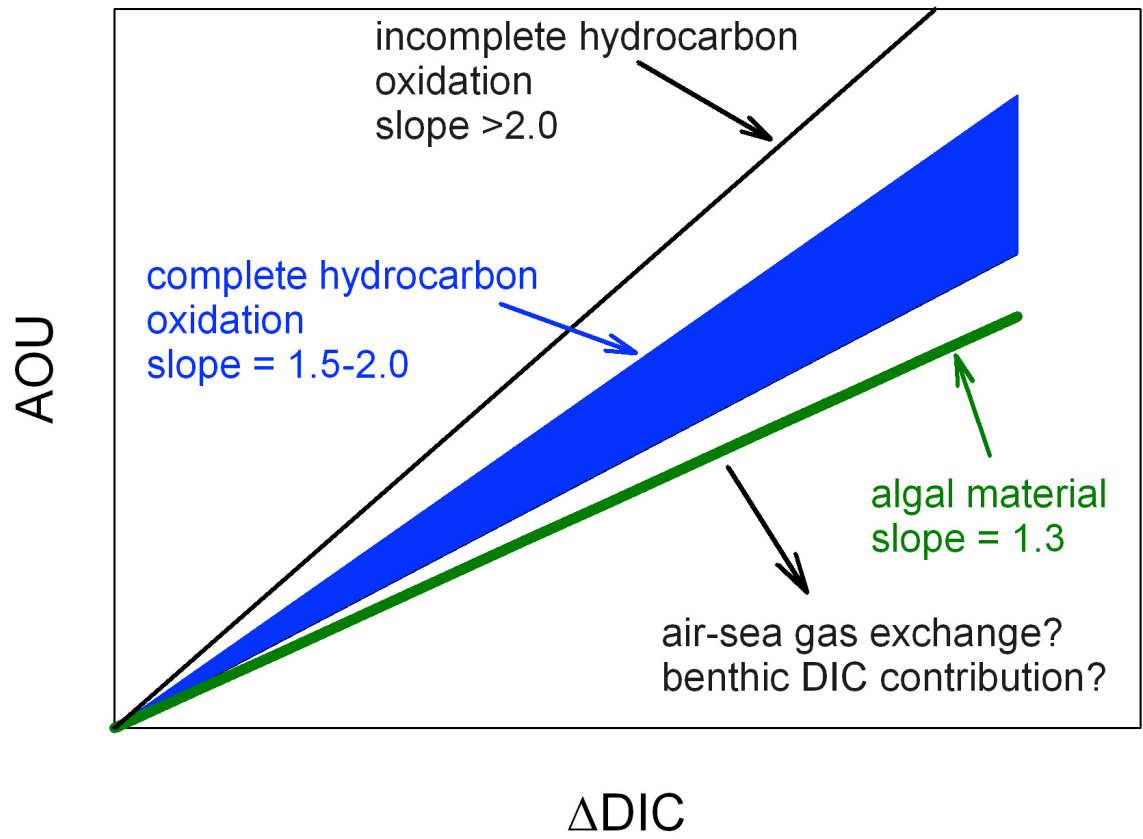
549 Fig. 3
550

551



552

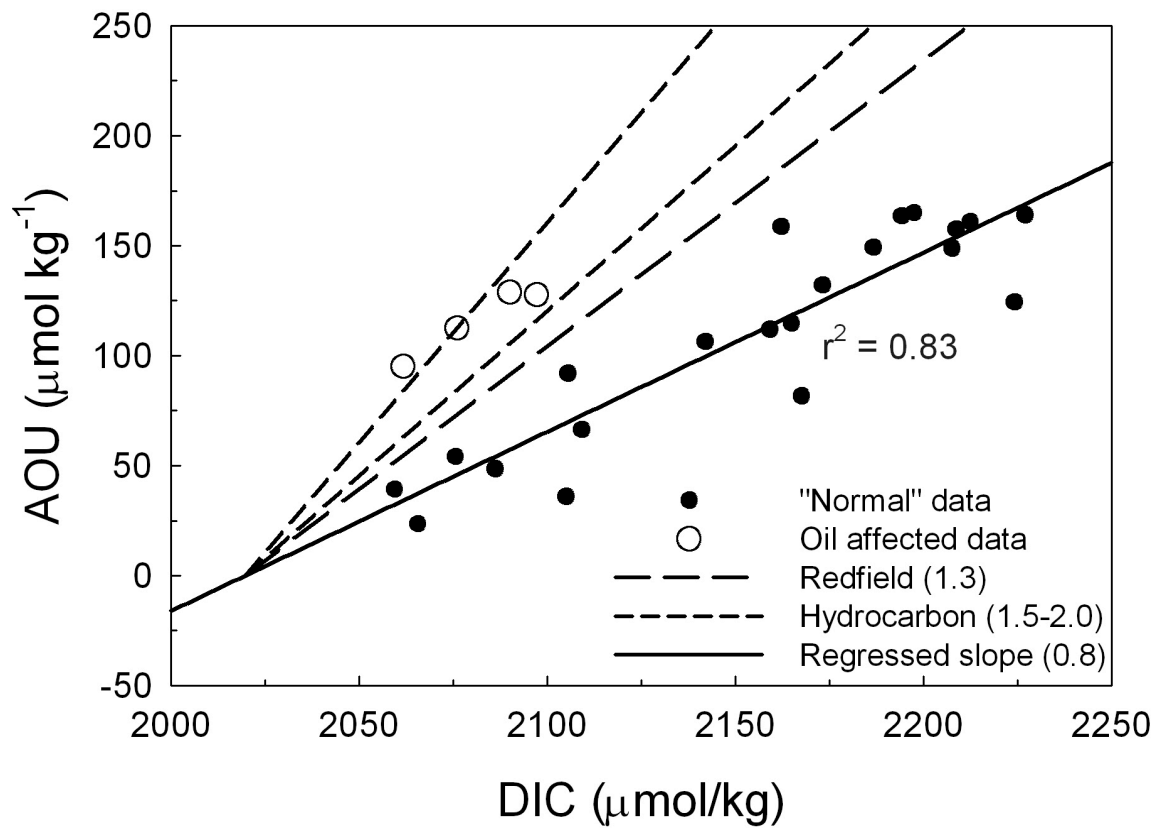
553 Fig. 4



554

555 Fig. 5

556



557

558 Fig. 6