

1 **The composition and distribution of semi-labile dissolved organic matter across the South**
2 **West Pacific**

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4 Christos Panagiotopoulos^{1*}, Mireille Pujo Pay², Mar Benavides¹, France Van Wambeke¹, and
5 Richard Sempéré¹

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9 ¹ *Aix-Marseille Université, Université de Toulon, CNRS, IRD, Mediterranean Institute of*
10 *Oceanography (MIO), UM 110, 13288, Marseille, France*

11 ² *Laboratoire d'Océanographie Microbienne (LOMIC), Observatoire Océanologique, Sorbonne*
12 *Universités, UPMC Univ. Paris 06, CNRS, 66650 Banyuls/Mer, France*

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15 *Corresponding author e-mail: christos.panagiotopoulos@mio.osupytheas.fr

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24 **Abstract**

25 The distribution and dynamics of dissolved organic carbon (DOC) and dissolved combined
26 neutral sugars (DCNS) were studied across an increasing oligotrophic gradient (-18 to -22°N
27 latitude) in the Tropical South Pacific Ocean, spanning from the Melanesian Archipelago (MA)
28 area to the western part of the South Pacific gyre (WGY), in austral summer, as a part of the
29 OUTPACE project. Our results showed DOC and DCNS concentrations exhibited no statistical
30 differences between the MA and WGY areas (0-200 m: 47-81 μMC for DOC and 0.2-4.2 μMC
31 for DCNS). However, due to a deepening of the euphotic zone, a deeper penetration of DOC was
32 noticeable at 150 m depth at the WGY area. This finding was also observed with regard to the
33 excess-DOC (DOC_{EX}), which was determined as the difference between surface and deep-sea
34 DOC values. Euphotic zone integrated stocks of both DOC and DOC_{EX} were higher in the WGY
35 than the MA area. Considering DOC_{EX} as representative of the semi-labile DOC (DOC_{SL}), its
36 residence time was calculated as the DOC_{SL} to bacterial carbon demand (BCD) ratio. This
37 residence time was 176 ± 43 days ($n = 3$) in the WGY area, about three times longer than in the
38 MA area ($T_r = 51 \pm 13$ days ($n = 8$)), suggesting an accumulation of the semi-labile dissolved
39 organic matter (DOM) in the surface waters of WGY. Average epipelagic (0-200 m) DCNS
40 yields ($\text{DCNS} \times \text{DOC}^{-1}$), based on volumetric data, were roughly similar in both areas,
41 accounting for ~2.8% of DOC. DCNS exhibited a longer residence time in WGY ($T_r = 91 \pm 41$
42 days, $n = 3$) than in MA ($T_r = 31 \pm 10$ days, $n=8$) further suggesting that this DCNS pool persists
43 longer in the surface waters of the WGY. The accumulation of DOC_{EX} in the surface waters of
44 WGY is probably due to the very slow bacterial degradation due to nutrient/energy limitation of
45 heterotrophic prokaryotes indicating that biologically produced DOC can be stored in the
46 euphotic layer of the South Pacific gyre for a long period.

47 **1. Introduction**

48

49 Gyres are oceanic deserts similar to those found in continental landscapes spanning an area of
50 several thousands of Km and are characterized by low nutrient content and limited productivity
51 (Raimbault et al., 2008; D'Hondt et al., 2009; Bender et al., 2016; de Verneil et al., 2017, 2018).
52 Moreover, gyres are now considered as the world's plastic dumps (Law et al., 2010; Eriksen et al.,
53 2013; Cozar et al., 2014), whereas their study may us help to understand future climate changes (Di
54 Lorenzo et al., 2008; Zhang et al., 2014) and marine ecosystem functioning (Sibert et al., 2016;
55 Browning et al., 2017). Among the five well-known oceanic gyres the South Pacific gyre, although
56 the world's largest, has been less extensively studied mainly due to its remoteness from the main
57 landmasses. Nonetheless, earlier studies indicated that Western Tropical South Pacific (WTSP) is a
58 hot spot of N₂ fixation (Bonnet et al., 2013; Bonnet et al., 2017; Caffin et al., 2018) and recent
59 studies have shown that there is a gradient of increasing oligotrophy from WTSP to the western part
60 of the Pacific gyre (Moutin et al., 2018). The ultra-oligotrophic regime is reached in the center of
61 the gyre, and then it decreases within the eastern part of the gyre toward the Chilean coast (Claustre
62 et al., 2008) with high residual phosphate concentrations in the center of the gyre (Moutin et al.,
63 2008).

64 Recent studies indicated that efficient DOC export in the subtropical gyres is related with the
65 inhibition of DOC utilization under low-nutrient conditions (Letscher et al., 2015; Roshan and
66 DeVries, 2017). Similar patterns have been observed for the oligotrophic Mediterranean Sea
67 (Guyennon et al., 2015). However, little information exists regarding dissolved organic matter
68 (DOM) dynamics in the south Pacific gyre particularly for its semi-labile component (accumulation,
69 export, fate), which is mainly represented by carbohydrates (Sempéré et al., 2008; Goldberg et al.,
70 2011; Carlson and Hansell, 2015).

71 Among the three well-identified chemical families (amino acids, lipids and carbohydrates) in

72 seawater, carbohydrates are the major components of organic matter in surface and deep waters
73 accounting for 5-10% and < 5% of dissolved organic carbon (DOC), respectively as shown by
74 liquid chromatography (Benner, 2002; Panagiotopoulos and Sempéré, 2005 and references therein).
75 The carbohydrate pool of DOC consists of free monosaccharides, oligosaccharides and
76 polysaccharides. Major polysaccharides are constituted by dissolved combined neutral sugars
77 (DCNS), which are generally measured as their monosaccharide constituents (sum of fucose,
78 rhamnose, arabinose, galactose, glucose, mannose and xylose) after acid hydrolysis (McCarthy et
79 al., 1996; Aluwihare et al., 1997; Skoog and Benner, 1997; Kirchman et al., 2001; Panagiotopoulos
80 and Sempéré, 2005). Other minor carbohydrate constituents of DOC include the amino sugars
81 (glucosamine, galactosamine and muramic acid; Benner and Kaiser, 2003), uronic acids (glucuronic
82 and galacturonic acids; Hung et al., 2003; Engel and Handel, 2011), methylated and dimethylated
83 sugars (Panagiotopoulos et al., 2013), heptoses (Panagiotopoulos et al., 2013) and sugar alcohols
84 (Van Pinxteren et al., 2012).

85 Free monosaccharide concentrations range from 10 to 100 nM; they account < 10% of total
86 dissolved neutral sugars (TDNS), and experiments have shown that they are rapidly utilized
87 (minutes to hours) by bacterioplankton and as such they are considered as labile organic matter
88 (Rich et al., 1996; Skoog et al., 1999; Kirchman et al., 2001). Polysaccharide or dissolved combined
89 neutral sugars (DCNS) concentrations range from 200-800 nM; they account for 80-95% of TDNS
90 and experiments have shown that they disappear within time scales of days to months and, as such,
91 they are considered as labile and semi-labile organic matter (Aluwihare and Repeta, 1999; Carlson
92 and Hansell, 2015 and references therein). Other studies have shown that this labile and/or semi-
93 labile organic matter accumulates in the surface ocean and may potentially be exported to depth
94 contributing to the ocean carbon pump (Goldberg et al., 2010; Carlson and Hansell, 2015).

95 In the frame of the OUTPACE project we studied DOM dynamics in terms of DOC and DCNS
96 composition and tried to evaluate their residence time. The results are presented and discussed

97 along with heterotrophic prokaryotic production in order to better understand the bacterial cycling
98 of DOM in the region.

99

100 **2. Materials and Methods**

101 **2.1 Sampling**

102 Sampling took place along a 5500 Km transect spanning from New Caledonia to French
103 Polynesia in the WTSP aboard the R/V *L'Atalante* during the Oligotrophy to Ultraoligotrophy
104 Pacific Experiment (OUTPACE) cruise (19 February-5 April, 2015). Samples were taken from 18
105 different stations comprising three long duration stations (LDA, LDB, and LDC; about 7-8 days)
106 and 15 short duration (SD1-15) stations (~8 h). Biogeochemical and physical characteristics of
107 these sites are described in detail elsewhere (Moutin et al., 2017). Briefly, the cruise took place
108 between 18-20°S covering two contrasted trophic regimes with increasing oligotrophy from west to
109 east (Fig. 1).

110 Discrete seawater samples were collected from 12 L Niskin bottles equipped with Viton O-rings
111 and silicon tubes to avoid chemical contamination. For DOC and DCNS analyses, samples were
112 filtered through two pre-combusted (450°C for 24 h) GF/F filters using a custom-made all-
113 glass/Teflon filtration syringe system. Samples for DOC (SD: 1-15 including LD: A, B ,C) were
114 collected into precombusted glass ampoules (450°C, 6h) that were sealed after acidification with
115 H₃PO₄ (85%) and stored in the dark at 4°C. Samples for DCNS (SD 1, 3-7, 9, 11, 13-15 including
116 LD: C) were collected in 40-mL Falcon vials (previously cleaned with 10% of HCl and Milli-Q
117 water) and frozen at -20°C until analysis.

118

119 **3. Chemical and microbiological analyses**

120 **3.1. Dissolved organic carbon (DOC) determination**

121 DOC was measured by high temperature combustion on a Shimadzu TOC-L analyzer (Cauwet,

122 1999). Typical analytical precision was $\pm 0.1-0.5 \mu\text{M C}$ (SD) for multiple injections (3-4) of
123 replicate samples. Consensus reference materials were injected every 12 to 17 samples to ensure
124 stable operating conditions and were in the range 42-45 μM (lot # 07-14;
125 (<http://yyy.rsmas.miami.edu/groups/biogeochem/Table1.html>)).

126

127 **3.2. Dissolved combined neutral sugars (DCNS) determination**

128 *3.2.1. Carbohydrate extraction and isolation*

129 Seawater samples were desalted using dialysis tubes with a molecular weight cut-off of 100-500
130 Da (Spectra/Por® Biotech cellulose ester) according to the protocol of Panagiotopoulos et al.
131 (2014). Briefly, the dialysis tube was filled with 8 mL of the sample and the dialysis was conducted
132 into a 1 L beaker filled with Milli-Q water at 4°C in the dark. Dialysis was achieved after 4-5 h
133 (salinity dropped from 35 to 1-2 g L^{-1}). Samples were transferred into 40 mL plastic vials (Falcon;
134 previously cleaned with 10% HCl and Milli-Q water), frozen at -30 °C, and freeze dried. The
135 obtained powder was hydrolyzed with 1M HCl for 20 h at 100°C and the samples were again freeze
136 dried to remove the HCl acid (Murrell and Hollibaugh, 2000; Engel and Handel, 2011). The dried
137 samples were diluted in 4 mL of Milli-Q water, filtered through quartz wool, and pipetted into
138 scintillation vials for liquid chromatographic analysis. The vials were kept at 4°C until the time of
139 analysis (this never exceeded 24 h). The recovery yields of the whole procedure (dialysis and
140 hydrolysis) were estimated using standard polysaccharides (laminarin, and chondroitine sulfate) and
141 ranged from 82 to 86% (n=3). Finally, it is important to note that the current desalination procedure
142 does not allow the determination of the dissolved free neutral sugars (i.e., sugar monomers present
143 in samples with MW ~ 180 Da) because these compounds are lost/poorly recovered during the
144 dialysis step (Panagiotopoulos et al., 2014).

145

146 *3.2.2. Liquid Chromatography*

147 Carbohydrate concentrations in samples were measured by liquid chromatography according to
148 Mopper et al. (1992) modified by Panagiotopoulos et al. (2001, 2014). Briefly, neutral
149 monosaccharides were separated on an-anion exchange column (Carbopac PA-1, Thermo) by
150 isocratic elution (mobile phase 19 mM NaOH) and were detected by an electrochemical detector set
151 in the pulsed amperometric mode (Panagiotopoulos et al., 2014). The flow rate and the column
152 temperature were set at 0.7 mL min⁻¹ and 17°C, respectively. Data acquisition and processing were
153 performed using the Dionex software Chromeleon. Repeated injections (n = 6) of a dissolved
154 sample resulted in a CV of 12-15% for the peak area, for all carbohydrates. Adonitol was used as an
155 internal standard and was recovered at a percentage of 80-95%; however, we have chosen not to
156 correct our original data.

157

158 **3.3. Bacterial production**

159

160 Heterotrophic prokaryotic production (here abbreviated classically as “bacterial” production
161 or BP) was determined onboard with the ³H-leucine incorporation technique to measure protein
162 synthesis (Smith and Azam, 1992). Additional details are given in Van Wambeke et al. (2018).
163 Briefly, 1.5 mL samples were incubated in the dark for 1-2 h after addition of ³H leucine, at a final
164 concentration of 20 nM, with standard deviation of the triplicate measurements being on average
165 9%. Isotopic dilution was checked and was close to 1 (Van Wambeke et al, 2018), and we therefore
166 applied a conversion factor of 1.5 Kg C mol leucine⁻¹ to convert leucine incorporation to carbon
167 equivalents (Kirchman, 1993). BP was corrected for leucine assimilation by *Prochlorococcus*
168 (Duhamel et al., 2018) as described in Van Wambeke et al. (2018). To estimate bacterial carbon
169 demand (BCD) which is used to calculate semi-labile DOC residence time, we used a bacterial
170 growth efficiency (BGE) of 8% as determined experimentally using dilution experiments during the
171 OUTPACE cruise (Van Wambeke et al., 2018). BCD was calculated by dividing BP values at each

172 station by BGE. Euphotic zone integrals were then computed from volumetric rates.

173

174 **4. Results**

175

176 4.1 General observations

177

178 The OUTPACE cruise was conducted under strong stratification conditions (Moutin et al.,
179 2018) during the austral summer encompassing a longitudinal gradient starting at the oligotrophic
180 Melanesian Archipelago (MA waters; stations SD1-SD12 including LDA and LDB stations) and
181 ending in the ultra-oligotrophic western part of the South Pacific gyre (WGY waters; stations SD13-
182 SD15 including LDC station; Fig. 1). Additional information on the hydrological conditions of the
183 study area (*i.e* temperature, salinity) including water masses characteristics is provided elsewhere
184 (de Verneil et al., 2018; Moutin et al., 2018). Mixed layer depth ranged from 11 to 34 m with higher
185 values recorded in the WGY (Moutin et al., 2018). The depth of the deep chlorophyll maximum
186 ranged from 69 to 119 m and from 122 to 155 m for the MA and WGY areas, respectively. Two
187 different trends can be noticed in a first approach:

188 a. Most of the biogeochemical parameters examined in the OUTPACE cruise (chlorophyll α
189 concentrations, primary production, BP, BCD, N₂ fixation rates, and nutrient concentrations)
190 showed significantly higher values in the MA area than in the WGY area (Moutin et al., 2018; Van
191 Wambeke et al., 2018; Benavides et al., 2018; Caffin et al., 2018). These differences were also
192 reflected by the distribution of the diazotrophic communities detected in both areas further
193 highlighting the different dynamics across the oligotrophic gradient (Stenegren et al., 2018; Moutin
194 et al., 2017, 2018). The net heterotrophic/autotrophic status of the MA and WGY areas has been
195 discussed in previous investigations by comparing BCD and gross primary production (GPP) (Fig.
196 2). By using propagation of errors, Van Wambeke et al. (2018) concluded that GPP minus BCD
197 could not be considered different from zero at most of the stations investigated (11 out of 17)

198 showing a metabolic balance. For the other stations, net heterotrophy was shown at stations SD 4, 5,
199 6 and LDB, and net autotrophy at station SD9 (Van Wambeke et al, 2018).

200 b. The bulk of DOM as shown by DOC analysis did not follow the above biogeochemical
201 pattern and showed little variability on DOC absolute concentrations although a deeper penetration
202 of DOM was noticeable at 150 m depth in the WGY area (Fig. 3a; Table 1). As such, epipelagic (0-
203 200 m) DOC concentrations throughout the OUTPACE cruise ranged from 47 to 81 $\mu\text{M C}$ (mean \pm
204 sd: $67 \pm 10 \mu\text{M}$; $n = 136$) except at LDB ($\sim 85 \mu\text{M C}$) which is probably related to a decaying
205 phytoplankton bloom (de Verneuil et al., 2018; Van Wambeke et al., 2018). Mesopelagic (200-1000
206 m) DOC values varied between 36 to 53 $\mu\text{M C}$ (mean \pm sd: $46 \pm 4 \mu\text{M}$; $n = 67$) (Fig. 4a; Table 1)
207 and are in agreement with previous studies in the South Pacific Ocean (Doval and Hansell, 2000;
208 Hansell et al., 2009; Raimbault et al. 2008).

209 DCNS concentrations closely followed DOC trends and fluctuated between 0.2-4.2 $\mu\text{M C}$
210 (mean \pm sd: $1.9 \pm 0.8 \mu\text{M}$; $n = 132$) in the epipelagic zone (Fig. 3b; Table 1). These values are in
211 good agreement to those previously reported for the central and/or the eastern part of the South
212 Pacific gyre (1.1-3.0 $\mu\text{M C}$; Sempéré et al., 2008) that were recorded under strong stratification
213 conditions during austral summer (Claustre et al., 2008). Compared with other oceanic provinces
214 our epipelagic DCNS concentrations fall within the same range of those reported in the BATS
215 station in the Sargasso Sea (1.0-2.7 $\mu\text{M C}$) also monitored under stratification conditions (Goldberg
216 et al., 2010). Mesopelagic DCNS concentrations ranged from 0.3 to 2.4 $\mu\text{M C}$ (average \pm sd: $1.2 \pm$
217 $0.6 \mu\text{M}$; $n = 68$) (Fig. 4b; Table 1) and concur with previously reported literature values at the
218 ALOHA station (0.2-0.8 $\mu\text{M C}$; Kaiser and Benner, 2009) or in the Equatorial Pacific (0.8-1 $\mu\text{M C}$;
219 Skoog and Benner, 1997).

220

221 4.2 DCNS yields and composition

222

223 The contribution of DCNS-C to the DOC pool is referred to here as DCNS yields and is
224 presented as a percentage of DOC (*i.e* DCNS-C x DOC⁻¹ %). Epipelagic (0-200 m) average DCNS
225 yields, based on volumetric data, were similar between the WGY (range 0.3-5.1%; average \pm sd: 2.8
226 \pm 1.3%; n = 41) and MA (range 0.8-7.0%; average \pm sd: 2.8 \pm 1.0%; n = 91) areas whereas deeper
227 than 200 m they were 2.4 \pm 1.0% (n = 23) and 2.7 \pm 1.3% (n = 43) for the WGY and MA,
228 respectively (Table 1). These values are in good agreement to those reported for the eastern part of
229 the gyre (Sempéré et al., 2008) and concur well with the range of values (2-7%) recorded in the
230 Equatorial Pacific (Rich et al., 1996; Skoog and Benner, 1997).

231 The molecular composition of carbohydrates revealed that glucose was the major
232 monosaccharide at all depths in both the MA and WGY areas accounting on average for 53 \pm 18%
233 (n = 132) of the DCNS in epipelagic waters and 64 \pm 21% (n = 68) in mesopelagic waters (Table 1).
234 Epipelagic glucose concentrations (DCGlc-C) averaged 1.0 \pm 0.6; n = 132 in both areas (Fig. 3c,
235 Table 1), however, a significantly higher mol% contribution of glucose was recorded in the WGY
236 than the MA especially at depths > 200 m (Fig. 5). Glucose was followed by xylose (9-12%),
237 galactose (4-9%) and mannose (5-8%) whereas the other monosaccharides accounted for < 6% of
238 DCNS (Fig. 5). The same suite of monosaccharides was also reported by Sempéré et al. (2008)
239 although the latter author also found that arabinose was among the major monosaccharides. Finally,
240 it is worth noting that the relative abundance of glucose increased with depth and sometimes
241 accounted 100% of the DCNS (Table 1, Fig. 5).

242

243 4.3 DOC and DCNS integrated stocks

244

245 DOC stocks (euphotic zone integrated) were calculated at the same stations where carbohydrate
246 (DCNS) data were available and were compared between the MA (stations: SD 1, 3, 4, 5, 6, 7, 9,
247 11) and WGY (SD13-SD15; LDC) stations (Fig. 6). DOC stock values in the euphotic were 9111 \pm

248 1159 (n = 8) and 13266 ± 821 (n = 4) mmol C m⁻² for the MA and WGY areas, respectively. Excess
249 DOC stock (DOC_{EX}) was calculated by subtracting an average deep DOC value from the bulk
250 surface DOC pool. This DOC value was 40 μMC and was estimated averaging all DOC values
251 below 1000 m depth from all stations (39.6 ± 1.4 μMC, n = 36). DOC_{EX} stock values averaged
252 3717 ± 528 (n = 8) and 5265 ± 301 (n = 4) mmol C m⁻² accounting about 40% of DOC in both areas.
253 DCNS represented 6.7 and 7.1% of DOC_{EX} in the MA and WGY sites, respectively, further
254 suggesting that only a small percentage of DOC_{EX} can be attributed to DCNS (polysaccharides).

255

256 **5. Discussion**

257

258 5.1 DOC and DCNS stocks in relation with biological activity

259

260 Euphotic zone integrated stocks of DOC, DOC_{EX} and DCNS were respectively 46, 42 and 52%
261 higher in the WGY than in the MA (Fig. 6), as opposed to BCD and GPP (Fig. 2). This is a
262 consequence of the deepening of the euphotic zone, because the variability of the volumetric stocks
263 was high, and not statistically different in the euphotic zone between MA and WGY areas. As
264 indicated above DOC_{EX} is calculated as the difference between the bulk surface DOC and deep
265 DOC the latter assumed to be refractory. Thus, DOC_{EX} is often described as “semi-labile” DOC or
266 DOC_{SL} with a turnover on time scales of weeks to months (Carlson and Hansell, 2015). DCNS
267 belong to this semi-labile category of DOC (Biersmith and Benner, 1998; Aluwihare et Repeta,
268 1999; Benner, 2002), and the results of this study showed that DCNS represented a low proportion
269 (~7%) of DOC_{EX}. Because the conditions of the HPLC technique employed in this study does not
270 allow identification and quantification of all the carbohydrate components of DOC (methylated
271 sugars, uronic acids, amino sugars etc) it is possible that the contribution of polysaccharides to the
272 DOC_{EX} is underestimated. Previous investigations on amino sugars and methylated sugars indicated
273 that these monosaccharides account for < 3% of the carbohydrate pool (Benner and Kaiser;

274 Panagiotopoulos et al., 2013) while uronic acids may account for as much as 40% of the
275 carbohydrate pool (Engel et al., 2012) indicating that the latter compounds should at least be
276 considered in future DOM lability studies.

277 Other semi-labile compounds that potentially may contribute to the DOC_{EX} pool are proteins
278 and lipids. Unfortunately, proteins (combined amino acids) were not measured in this study.
279 Nonetheless, previous investigations indicated that total dissolved amino acids represent 0.7-1.1%
280 of DOC in the upper mesopelagic zone of the north Pacific (Kaiser and Benner, 2012) further
281 suggesting a relatively small contribution of amino acids to the DOC_{EX} . During the OUTPACE
282 cruise, assimilation rates of ^3H - leucine using concentration kinetics were determined (Duhamel et
283 al., 2018) and, based on the Wright and Hobbie (1966) protocol, the ambient concentration of
284 leucine was determined. The results showed a lower ambient leucine concentration at the LDC
285 (0.56 nM) than at the LDA (1.80 nM) stations (Duhamel et al., 2018).

286 This result may suggest that single amino acid and perhaps proteins concentrations are very low
287 at the LDC station, reflecting the ultra- oligotrophic regime of the WGY. On the other hand, DOM
288 exhibited only slightly different C/N ratios between MA (C/N = 13) and WGY (C/N =14), which
289 does not suggest differences in DON dynamics in relation with organic matter lability (data from
290 integrated values of 0-70 m; Moutin et al., 2018). Clearly further investigations are warranted on
291 combined and free amino acids distribution in relation with N_2 fixation.

292 The high stock of DOC_{EX} measured in WGY was also characterized by an elevated residence
293 time (T_{rSL}) calculated as the ratio of $\text{DOC}_{\text{EX}} / \text{BCD}$. This ratio is calculated based on the
294 assumption that DOC_{EX} is representative of the DOC_{SL} and the latter pool turnover is at the scale
295 of seasonal mixing (i.e weeks to months) whereas the BP, as determined with leucine technique on
296 short incubation times (1-2 hours), tracks only the ultra-labile to labile organic matter consumption
297 and not DOC_{SL} utilization. Biodegradation experiments (3 experiments, duration 10 days each)
298 performed during the OUTPACE cruise showed that the labile DOC represented only 2.5 to 5% of

299 the DOC pool (Van Wambeke et al., 2018), confirming that the residence time calculated from
300 DOC_{EX} / BCD overestimates the residence time of ultra-labile DOC. The bacterial production and
301 BGEs associated with the use of semi-labile DOC is currently not technically measurable due to
302 long-term confinement artifacts. Our results showed that $T_{r,SL}$ in the WGY was in the order of 176
303 ± 43 days ($n = 3$), i.e. about three times higher than in the MA region ($T_{r,SL} = 51 \pm 13$ days ($n = 8$))
304 indicating an accumulation of the semi-labile DOM in the surface waters of WGY (Fig. 7). As
305 suggested by previous studies the accumulation of DOC in the surface waters of oligotrophic
306 regimes may be related in biotic and/or abiotic factors.

307 Nutrient limitation can prevent DOC assimilation by heterotrophic bacteria and as such
308 sources and sinks are uncoupled, allow accumulation (Thingstad et al., 1997; Jiao et al., 2010; Shen
309 et al., 2016). Biodegradation experiments (Van Wambeke et al., 2018) focusing on the
310 determination of the BGE and the degradation of the labile DOC pool (turning over 10 days)
311 revealed a less biodegradable DOM fraction and lower degradation rates at the LDC (2.4% labile
312 DOC; $0.012 d^{-1}$) than the LDA site (5.3% labile DOC; $0.039 d^{-1}$). Other experiments, focusing on
313 the factors limiting BP by testing the effect of different nutrient additions, showed that over a short-
314 time period, BP is initially limited by the availability of labile carbon in the WGY (as tracked with
315 glucose addition, Van Wambeke et al., 2018). This limitation on BP by labile carbon/energy was
316 also the case at the center of the South Pacific gyre (Van Wambeke et al., 2008), while N limitation
317 (as tracked by addition of ammonium+nitrate) was more pronounced in the MA area.

318 Although extensive photodegradation may transform recalcitrant organic matter into labile, the
319 low content in chromophoric DOM recorded in the surface waters of WGY ($\alpha_{CDOM}(350) = 0.010$ -
320 $0.015 m^{-1}$, 0-50 m; Dupouy et al. unpublished results from the OUTPACE cruise) points toward an
321 already photobleached and thus photodegraded organic material (Tedetti et al., 2007; Carlson and
322 Hansel, 2015). Notably, the 10% irradiance depths for solar radiations (Z 10%) clearly showed a
323 higher penetration of UV-R and PAR radiations in the WGY area than in MA area (Dupouy et al.,

324 2018). These results are in agreement with previous investigations reporting intense solar radiation
325 in the South Pacific gyre highlighting an strong decrease of chromophoric dissolved organic matter
326 (CDOM) in the gyre (Tedetti et al., 2007). Less energy available for heterotrophic prokaryotes
327 should prevent them from degrading such recalcitrant, photo-degraded organic matter.

328 The computation of the carbon, nitrogen, and phosphorus budgets in the upper 0-70 m layer by
329 Moutin et al. (2018) suggested that at 70 m the environmental conditions remained seasonally
330 unchanged during the OUTPACE cruise, forming an average wintertime depth of the mixed layer.
331 These authors calculated seasonal (from winter to austral summer) net DOM and POM
332 accumulation on the basis of such assumptions, and found a dominance of DOC accumulation in
333 the MA area (391 to 445 mmol m⁻² over 8 months). This DOC accumulation in the MA area was
334 3.8 to 8.1 times higher than that of POC accumulation during the same time period. On the other
335 hand, only DOC accumulated at WGY, although the amount was two times lower in magnitude
336 than in the MA (391- 445 vs 220 mmol m⁻²). The accumulation of DOC and DOC_{EX} (Fig. 6) in the
337 WGY may have important implications with regard to the sequestration of this organic material in
338 the mesopelagic layers. DOC appears to be the major form of export of carbon in the WGY area
339 and this result agrees with the general feature observed in oligotrophic regimes (Roshan and
340 Devries, 2017).

341

342 5.2 DCNS dynamics across the South West Pacific

343

344 Previous investigations have employed the DCNS yields along with mol% of glucose to assess
345 the diagenetically “freshness” of organic matter (Skoog and Benner, 1997; Benner, 2002; Goldberg
346 et al. 2010). In general freshly produced DOM has DCNS yields >10% and mol% glucose between
347 28-71% (Biersmith and Benner, 1998; Hama and Yanagi, 2001). Elevated mol% glucose (> 25%)
348 does not necessarily mirror fresh material because such values have also been reported for deep

349 DOM and low molecular weight DOM that are considered as a diagenetically altered material
350 (Skoog et al., 1997).

351 Our results showed that epipelagic DCNS yields were about similar (~2.8%) in both WGY and
352 MA areas (Table 1) further indicating a similar contribution of DCNS to the DOC pool despite the
353 major differences observed for the other biochemical parameters (e.g. deepening of the nitraclines
354 and deep chlorophyll maximum etc) between MA and WGY. As expected, DCNS yields decreased
355 by depth but were always comparable between WGY and MA areas (Table 1). By analogy to the
356 DOC_{SL} , we tried to estimate a DCNS residence time assuming that (a) the ectoenzymatic hydrolysis
357 is a rate-limiting step for bacterial production, ii) the mean contribution of polysaccharides
358 hydrolysis to bacterial production is 11%, based on Pointek et al. (2011), and iii) this 11%
359 correction factor can be propagated to BCD. On the basis of these assumptions, we estimated a
360 DCNS residence time as $DCNS / (11\% \times BCD)$. The results showed that DCNS exhibited a higher
361 residence time in the WGY ($T_{rDCNS-C} = 91 \pm 41$ days, $n = 3$) than the MA area ($T_{rDCNS-C} = 31 \pm 10$
362 days, $n = 8$) which clearly shows that the DCNS pool persist longer in the surface waters of the
363 WGY (Fig. 7). Moreover, because carbohydrates do not absorb light these polysaccharides (DCNS)
364 do not seem to be impacted by the high photochemistry in WGY and potentially may be exported in
365 the Ocean interior during a non-stratification period (e.g. winter time) considering their high
366 residence time at the WGY area. In addition, their slow utilization could also be related to energy
367 limitation by heterotrophic prokaryotes in the WGY area.

368 Glucose accounted for ~50% of DCNS in the MA surface waters which most likely reflects the
369 high abundance of *Trichodesmium* species in that area (Dupouy et al., 2018; Rousset et al., 2018). A
370 roughly similar percentage of glucose was also recorded in surface WGY waters (Fig. 5a) which is
371 probably due to the low utilization of semi-labile organic matter in the form of exopolysaccharides.
372 These exopolysaccharides are probably hydrolyzed by bacteria, but not taken up due to limited
373 nutrient availability. At 200 m depth, glucose accounted for 75% and 50% of DCNS in the WGY

374 and MA areas, respectively (200 m depth), and this percentage increased considerably with depth in
375 both areas (76% for MA and 96% for WGY at 2000 m depth) indicating a preferential removal of
376 the other carbohydrates relative to glucose (Fig. 5b; Fig. 5c). The low DCNS yields (~1%) at 2000
377 m depth along with the high % mol abundance of glucose clearly suggests the presence of
378 diagenetically altered DOM and is consistent with previous investigations (Skoog and Benner,
379 1997; Goldberg et al. 2010; Golberg et al., 2011).

380

381 **6. Conclusions**

382

383 This study showed a rather uniform distribution of DOC and DCNS concentrations in surface
384 waters across an increasing oligotrophic gradient in the South West Pacific Ocean during the
385 OUTPACE cruise. Nevertheless, our results showed that DOC and DOC_{EX} stocks were by ~40%
386 in WGY than the MA area, accompanied with higher residence times in the WGY area suggesting
387 an accumulation of semi-labile material in the euphotic zone of WGY. Although DCNS accounted a
388 small fraction of DOC_{SL} (~7%) our results showed that DCNS or polysaccharides also exhibited a
389 higher residence time ($T_{r\ DCNS-C}$) in the WGY than in the MA area indicating that DCNS persist
390 longer in the WGY. This $T_{r\ DCNS-C}$ is calculated on the basis of many assumptions on DNCS
391 hydrolysis rates that were not practically determined, showing the need to estimate such fluxes in
392 order to better estimate the dynamics of carbohydrates. Glucose was the major monosaccharide in
393 both areas (51 - 55%) and its relative abundance increased with depth along with a decrease of the
394 DCNS yields indicating a preferential removal of the other carbohydrates relative to glucose.
395 Clearly further investigations are warranted to better characterize the semi-labile DOC pool in terms
396 of combined and free amino acids distribution in relation with N₂ fixation.

397

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399

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414

415 **References**

416 Aluwihare, L.I., Repeta, D.J., and Chen, R. F.: A major biopolymeric component to dissolved
417 organic carbon in seawater, *Nature*, 387, 166–167, 1997.

418 Aluwihare, L.I., and Repeta, D.J.: A comparison of the chemical characteristics of oceanic
419 DOM and extracellular DOM produced by marine algae, *Mar. Ecol. Progr. Ser.* 186, 105-117, 1999.

420 Amon, R.M.W., and Benner, R.: Combined neutral sugar as indicators of the diagenetic state
421 of dissolved organic matter in the Arctic Ocean, *Deep-Sea Res., Part I* 50, 151– 169, 2003.

422 Benavides, M., Shoemaker, K.M., Moisander, P.H., Niggemann, J., Dittmar, T., Duhamel, S.,
423 Grosso, O., Pujo-Pay, M., Hélias-Nunige, S., and Bonnet, S.: Aphotic N₂ fixation along an
424 oligotrophic to ultraoligotrophic transect in the Western Tropical South Pacific Ocean.

425 Biogeosciences, 15, 3107-3119, 2018. <https://doi.org/10.5194/bg-15-3107-2018>.

426 Bender, M.L., and Jonsson, B.: Is seasonal net community production in the south Pacific
427 subtropical gyre anomalously low? *Geophys. Res. Lett.* 43, 9757-9763, DOI:
428 10.1002/2016GL070220, 2016.

429 Benner, R.: Chemical composition and reactivity, in: *Biogeochemistry of Marine Dissolved*
430 *Organic Matter*, edited by Hansell, D. and Carlson, C., Academic Press, New York, USA, 59–90,
431 2002.

432 Benner, R., and Kaiser, K.: Abundance of amino sugars and peptidoglycan in marine
433 particulate and dissolved organic matter. *Limnol. Oceanogr.* 48, 118-128.

434 Biersmith A., and Benner, R.: Carbohydrates in phytoplankton and freshly produced
435 dissolved organic matter. *Mar. Chem.*, 63, 131-144, 1998.

436 Bonnet, S., Dekaezemacker, J., Turk-Kubo, K. A., Moutin, T., Hamersley, R. M., Grosso, O.,
437 Zehr, J. P. and Capone, D. G.: Aphotic N₂ Fixation in the Eastern Tropical South Pacific Ocean,
438 *PLOS ONE*, 8(12), e81265, doi:10.1371/journal.pone.0081265, 2013.

439 Bonnet, S., Caffin, M., Berthelot, H. and Moutin, T.: Hot spot of N₂ fixation in the western
440 tropical South Pacific pleads for a spatial decoupling between N₂ fixation and denitrification, *Proc.*
441 *Natl. Acad. Sci.*, 114(14), E2800–E2801, doi:10.1073/pnas.1619514114, 2017.

442 Browning, T.J., Achterberg, E.P., Rapp, I., Engel, A., Bertrand, E.M., Tagliabue, A., and
443 Moore, M.: Nutrient co-limitation at the boundary of an oceanic gyre, *Nature*, 551, 242-246, 2017.

444 Caffin, M., Moutin, T., Foster, R.A, Bouruet-Aubertot, P., Doglioli, A.M., Berthelot, H.,
445 Guieu, C., Grosso, O., Helias-Nunige, S., Leblond, N., Gimenez, A., Petrenko, A.A., de Verneil, A.,
446 and Bonnet, S.: N₂ fixation as a dominant new N source in the western tropical South Pacific Ocean
447 (OUTPACE cruise). *Biogeosciences*, 15, 2565-2585, <https://doi.org/10.5194/bg-15-2565-2018>,
448 2018.

449 Carlson, C.A., and Hansell, D.A.: DOM sources, sinks, reactivity, and budgets, in;

450 Biogeochemistry of marine dissolved organic matter, edited by Hansell, D.A and Carlson, C.A.,
451 Elsevier, Academic Press, 66-109, 2015.

452 Cauwet, G.: Determination of dissolved organic carbon (DOC) and nitrogen (DON) by high
453 temperature combustion, in: Methods of seawater analysis, 3rd edn., edited by: Grashoff, K.,
454 Kremling, K., and Ehrhard, M., 407-420. 1999.

455 Claustre, H., Sciandra, A., and Vaultot, D.: Introduction to the special section bio-optical and
456 biogeochemical conditions in the South East Pacific in late 2004: the BIOSOPE program,
457 Biogeosciences, 5, 679-691, 2008.

458 Duhamel, S., Van Wambeke, F., Lefevre, D., Benavides, M., and Bonnet, S.: Mixotrophic
459 metabolism by natural communities of unicellular cyanobacteria in the western tropical South
460 Pacific Ocean, Environmental Microbiology/Environmental Microbiology Reports., 2018,
461 doi.org/10.1111/1462-2920.14111.

462 Dupouy, C., Frouin, R., Tedetti, M., Maillard, M., Rodier, M., Lombard, F., Guidi, L.,
463 Picheral, M., Duhamel, S., Charrière, B., and Sempéré, R.: diazotrophic *Trichodesmium* influences
464 ocean color and pigment composition in the South West tropical Pacific, Biogeosciences, 15, 5249-
465 5269, <https://doi.org/10.5194/bg-15-5249-2018>, 2018.

466 Cozar, A., Echevarria, F., Gonzalez-Gordillo, J.I., Irigoien, X., Ubeda, B., Hernandez-Leon, S.,
467 Palma, A.T., Navarro, S., Garcia-de-Lomas, J., Ruiz, A., Fernandez-de-Puelles, M.L., and Duarte,
468 C.M.: Plastic debris in the open ocean, Proc. Natl. Acad. Sci. USA, 111, 10239–10244, 2014.

469 de Verneil, A., Rousselet, L., Doglioli, A.M., Petrenko, A.A., and Moutin, T.: The fate of a
470 southwest Pacific Bloom : Gauging the impact of submesoscale vs. mesoscale circulation on
471 biological gradients in the subtropics, Biogeosciences, 14, 3471–3486, doi.org/10.5194/bg-14-
472 3471-2017, 2017.

473 de Verneil, A., Rousselet, L., Doglioli, A. M., Petrenko, A. A., Maes, C., Bouruet-Aubertot,
474 P., and Moutin, T.: OUTPACE long duration stations: physical variability, context of

475 biogeochemical sampling, and evaluation of sampling strategy, *Biogeosciences*, 15, 2125-2147,
476 <https://doi.org/10.5194/bg-15-2125-2018>, 2018.

477 D'Hondt, S., Spivack, A.J., Pockalny, R., Ferderlman, T.G., Fischer, J.P., Kallmeyer, J.,
478 Abrams, L.J., Smith, D.C., Graham, D., Hasiuk, F., Schrum, H., and Stancin, A.M.: Subseafloor
479 sedimentary life in the South Pacific Gyre, *Proc. Natl. Acad. Sci. USA*, 106, 11651–11656, 2009.

480 Di Lorenzo, E., Schneider, N., Cobb, K.M., Franks, P.J.S., Chhak, K., Miller, A.J., Mc
481 Williams, J.C., Bograd, S.J., Arango, H., Curchitser, E., Powell, T.M., and Riviere, P.: North
482 Pacific Gyre Oscillation links ocean climate and ecosystem change, *Geophys. Res. Lett.* 35, 2008,
483 [doi:10.1029/2007gl032838](https://doi.org/10.1029/2007gl032838).

484 Doval, M.D., and Hansell, D.A.: Organic carbon apparent oxygen utilization in the western
485 South Pacific and the central Indian Oceans, *Mar. Chem.* 68, 249-264, 2000.

486 Engel, A., Harlay, J., Piontek, J., and Chou, L.: Contribution of combined carbohydrates to
487 dissolved and particulate organic carbon after the spring bloom in the northern Bay of Biscay
488 (North-Eastern Atlantic Ocean). *Cont. Shelf Res.* 45, 42-53, 2012.

489 Engel, A., and Handel, N.: A novel protocol for determining the concentration and
490 composition of sugars in particulate and in high molecular weight dissolved organic matter (HMW-
491 DOM) in seawater, *Mar. Chem.*, 127, 180–191, 2011.

492 Eriksen, M., Maximenko, N., Thiel, M., Cummins, A., Lattin, G., Wilson, S., Hafner, J.,
493 Zellers, A., and Rifman, S.: Plastic pollution in the South Pacific subtropical gyre, *Mar. Pollut.*
494 *Bull.*, 68, 71–76, 2013.

495 Goldberg, S. J., Carlson, C.A., Bock, B., Nelson, N.B., and Siegel, D.A.: Meridional
496 variability in dissolved organic matter stocks and diagenetic state within the euphotic and
497 mesopelagic zone of the North Atlantic subtropical gyre, *Mar. Chem.*, 119, 9–21, 2010.

498 Goldberg, S.J., Carlson, C.A., Brzezinski, M., Nelson, N.B., and Siegel, D.A.: Systematic
499 removal of neutral sugars within dissolved organic matter across ocean basins, *Geophys. Res. Lett.*

500 38. <http://dx.doi.org/10.1029/2011GL048620> L17606, 2011.

501 Guyennon, A., Baklouti, M., Diaz, F., Palmieri, J., Beuvier, J., Lebaupin-Brossier, C.,
502 Arsouze, T., Béranger, K., Dutay, J.-C., and Moutin, T.: New insights into the organic carbon
503 export in the Mediterranean Sea from 3-D modeling. *Biogeosciences*, 12, 7025–7046, 2015.
504 doi:10.5194/bg-12-7025-2015.

505 Hama T. and Yanagi K. (2001) Production and neutral aldose composition of dissolved
506 carbohydrates excreted by natural marine phytoplankton populations. *Limnol. Oceanogr.* 46,
507 1945–1955.

508 Hansell, D. A., Carlson, C. A., Repeta, D.J., and Schlitzer, R.: Dissolved organic matter in
509 the Ocean: A controversy stimulates new insights, *Oceanography*, 22, 202-211, 2009.

510 Hung, C-C., Guo, L., Santschi, P.H., Alvarado-Quiroz, N., and Haye, J.M.: Distributions of
511 carbohydrate species in the Gulf of Mexico. *Mar. Chem.* 81, 119-135, 2003.

512 Kaiser, K., and Benner, R.: Biochemical composition and size distribution of organic matter
513 at the Pacific and Atlantic time-series stations. *Mar. Chem.* 113, 63-77. 2009.

514 Kaiser, K., and Benner, R.: Organic matter transformations in the upper mesopelagic zone of
515 the North Pacific: Chemical composition and linkages to the microbial community structure. *J.*
516 *Geophys. Res.* 117, C01023, doi:10.1029/2011JC007141, 2012.

517 Kirchman, D. L., Meon, B., Ducklow, H. W., Carlson, C. A., Hansell, D. A., and Steward, G.:
518 Glucose fluxes and concentrations of dissolved combined sugars (polysaccharides) in the Ross Sea
519 and Polar Front Zone, Antarctica, *Deep-Sea Res. Pt. II*, 48, 4179–4197, 2001.

520 Jiao, N., Herndl, G. J., Hansell, D. A., Benner, R., Kattner, G. K., Wilhelm, S. W., Kirchman,
521 D. L., Weinbauer, M. G., Luo, T., Chen, F., and Azam, F.: Microbial production of recalcitrant
522 dissolved organic matter: long-term carbon storage in the global ocean, *Nature Reviews*
523 *Microbiology*, 8, 593–599, 2010.

524 Kirchman, D. L.: Leucine incorporation as a measure of biomass production by heterotrophic

525 bacteria, in: Handbook of methods in aquatic microbial ecology, edited by: Kemp, P. F., Sherr, B.
526 F., Sherr, E. B., and Cole, J. J., Boca Raton, Lewis, 509–512, 1993.

527 Law, K.L., Morét-Ferguson, S., Maximenko, N.A., Proskurowski, G., Peacock, E.E., Hafner,
528 J., and Reddy, C.M.: Plastic accumulation in the North Atlantic subtropical gyre, *Science*, 329,
529 1185-1188, 2010.

530 Letscher, R.T., and Moore, J.K.: Preferential remineralization of dissolved organic
531 phosphorus and non-Redfield DOM dynamics in the global ocean: Impacts on marine productivity,
532 nitrogen fixation, and carbon export. *Global Biogeochem. Cycles*, 29, 325-340, 2015,
533 doi:10.1002/2014GB004904.

534 McCarthy, M., Hedges, J.I., and Benner, R.: Major biochemical composition of dissolved
535 high molecular weight organic matter in seawater. *Mar. Chem.* 55, 281–297, 1996.

536 Mopper, K., Schultz, C., Chevolut, L., Germain, C., Revuelta, R., and Dawson, R.:
537 Determination of sugars in unconcentrated sea-water and other natural waters by liquid
538 chromatography, *Environ. Sci. Technol.*, 26, 133–137, 1992.

539 Moutin, T., Karl, D. M., Duhamel, S., Rimmelin, P., Raimbault, P., Van Mooy, B. A., and
540 Claustre, H.: Phosphate availability and the ultimate control of new nitrogen input by nitrogen
541 fixation in the tropical Pacific Ocean, *Biogeosciences*, 5, 95-109, 2008.

542 Moutin, T., Doglioli, A., de Verneil, A., and Bonnet, S.: The Oligotrophy to the Ultra-
543 oligotrophy PACific Experiment (OUTPACE cruise, 35 Feb. 18 to Apr. 3, 2015), *Biogeosciences*,
544 14, 3207-3220, 2017.

545 Moutin, T., Wagener, T., Caffin, M., Fumenia, A., Gimenez, A., Baklouti, M., Bouruet-
546 Aubertot, P., Pujo-Pay, M., Leblanc, K., Lefevre, M., Helias Nunige, S., Leblond, N., Grosso, O.
547 and de Verneil, A.: Nutrient availability and the ultimate control of the biological carbon pump in
548 the Western Tropical South Pacific Ocean. *Biogeosciences*, 15, 2961-2989,
549 <https://doi.org/10.5194/bg-15-2961-2018>, 2018.

550 Murrell, M.C., and Hollibaugh, J.T.: Distribution and composition of dissolved and
551 particulate organic matter in northern San Francisco bay during low flow conditions, *Estuar. Coast.*
552 *Shelf Sci.*, 51, 75–90, 2000.

553 Panagiotopoulos, C., Sempéré, R., Lafont, R., and Kerhervé, P.: Sub-ambient temperature
554 effects on separation of monosaccharides by HPAEC-PAD. Application to marine chemistry, *J.*
555 *Chromatogr. A.*, 920, 13-22, 2001.

556 Panagiotopoulos, C. and Sempéré, R.: Analytical methods for the determination of sugars in
557 marine samples: A historical perspective and future directions, *Limnol. Oceanogr. Meth.*, 3, 419–
558 454, 2005.

559 Panagiotopoulos, C., Repeta, D.J., Mathieu, L., Ronatani, J-F., and Sempéré, R. : Molecular
560 level characterization of methyl sugars in marine high molecular weight dissolved organic matter.
561 *Mar. Chem.* 154, 34-45, 2013.

562 Panagiotopoulos, C., Sempéré, R., Jacq, V., and Charrière, B.: Composition and distribution
563 of dissolved carbohydrates in the Beaufort Sea Mackenzie margin (Arctic Ocean), *Mar. Chem.*, 166,
564 92-102, 2014.

565 Piontek, J., Händel, N., de Bodt, C., Harlay, J., Chou, L., and Engel, A.: The utilization of
566 polysaccharides by heterotrophic bacterioplankton in the Bay of Biscay (North Atlantic Ocean). *J.*
567 *Plankton Res.* 33, 1719-1735, 2011.

568 Raimbault, P., Garcia, N., and Cerruti, F.: Distribution of inorganic and organic nutrients in
569 the South Pacific Ocean – evidence for long-term accumulation of organic matter in nitrogen-
570 depleted waters, *Biogeosciences*, 5, 281-298, 2008.

571 Rich, J. H., Ducklow, H. W., and Kirchman, D. L.: Concentrations and uptake of neutral
572 monosaccharides along 140 °W in the equatorial Pacific: contribution of glucose to heterotrophic
573 bacterial activity and the DOM flux, *Limnol. Oceanogr.*, 41, 595–604, 1996.

574 Roshan, S., and DeVries, T.: Efficient dissolved organic carbon production and export in the

575 oligotrophic Ocean, *Nature*, 8, 2036, 2017.

576 Sempéré, R., Tedetti, M., Panagiotopoulos, C., Charrière, B., and Van Wambeke, F.:
577 Distribution and bacterial availability of dissolved neutral sugars in the South East Pacific,
578 *Biogeosciences*, 5, 1165-1173, 2008.

579 Shen, Y., Fichot, C.G., Liang, S-K., and Benner, R.: Biological hot spots and the
580 accumulation of marine dissolved organic matter in a highly productive ocean margin, *Limnol.*
581 *Oceanogr.* 61, 1287-1300, 2016.

582 Sibert, E., Norris, R., Cuevas, J., and Graves, L.: Eighty-five million years of Pacific Ocean
583 gyre ecosystem structure: long-term stability marked by punctuated change, *Proc. R. Soc. B*, 283,
584 2016, doi: 10.1098/rspb.2016.0189, 2016.

585 Skoog, A. and Benner, R.: Aldoses in various size fractions of marine organic matter:
586 Implications for carbon cycling, *Limnol. Oceanogr.*, 42, 1803–1813, 1997.

587 Skoog, A., Biddanda, B., and Benner, R.: Bacterial utilization of dissolved glucose in the
588 upper water column of the Gulf of Mexico, *Limnol. Oceanogr.*, 44, 1625–1633, 1999.

589 Smith, D. C. and Azam, F.: A simple, economical method for measuring bacterial protein
590 synthesis rates in sea water using ³H-Leucine, *Mar. Microb. Food Webs*, 6, 107–114, 1992.

591 Stenegren, M., Caputo, A., Berg, C., Bonnet, S., and Foster, R. A.: Distribution and drivers of
592 symbiotic and free-living diazotrophic cyanobacteria in the Western Tropical South Pacific,
593 *Biogeosciences*, 15, 1559-1578, <https://doi.org/10.5194/bg-15-1559-2018>, 2018.

594 Tedetti, M., Sempéré, R., Vasilkov, A., Charrière, B., Nérini, D., Miller, W. L., Kawamura,
595 K., and Raimbault, P.: High penetration of ultraviolet radiation in the south east Pacific waters,
596 *Geophys. Res. Lett.*, 34, L12610, doi:10.1029/2007GL029823, 2007.

597 Thingstad, T. F., Hagstrom, A., and Rassoulzadegan, F.: Accumulation of degradable DOC in
598 surface waters: Is it caused by a malfunctioning microbial loop?, *Limnol. Oceanogr.*, 42, 398–404,
599 1997.

600 Van Pinxteren, M., Muller, C., Iinuma, Y., Stolle, C., and Hermann, H.: Chemical
601 characterization of dissolved organic compounds from coastal sea surface microlayers (Baltic Sea,
602 Germany). *Environ. Sci. Technol.* 46, 10455-10462, 2012.

603 Van Wambeke, F., Bonnet, S., Moutin, T., Raimbault, P., Alarçon G., and Guieu, C.: Factors
604 limiting heterotrophic prokaryotic production in the southern Pacific Ocean, *Biogeosciences*, 5,
605 833–845, 2008.

606 Van Wambeke, F., Gimenez, A., Duhamel, S., Dupouy, C., Lefevre, D., Pujo-Pay, M., and
607 Moutin, T.: Dynamics and controls of heterotrophic prokaryotic production in the western tropical
608 South Pacific Ocean: links with diazotrophic and photosynthetic activity, *Biogeosciences*, 15, 2669-
609 2689, <https://doi.org/10.5194/bg-15-2669-2018>, 2018.

610 Wright, R.R., and Hobbie, J.E. Use of glucose and acetate by bacteria and algae in aquatic
611 ecosystems. *Ecology* 47: 447–464, 1966.

612 Zang, X., Church, J.A., Platten, S.M., and Monselesan, D.: Projection of subtropical gyre
613 circulation and associated sea level changes in the Pacific based on CMIP3 climate models, *Clim.*
614 *Dyn.*, 43, 131-144, 2014.

615

616 **Figure and Table captions:**

617

618 Figure 1: Sampling stations during the OUTPACE cruise. The white line shows the vessel
619 course (data from the hull-mounted ADCP positioning system). Stations and their respective
620 names (SD1-SD15 including LDA, LDB and LDC) are depicted in grey. Figure courtesy of T.
621 Wagener.

622

623 Figure 2: Integrated stocks of bacterial carbon demand (BCD) and gross primary production (GPP)
624 ($\text{mmol C m}^{-2} \text{d}^{-1}$) over the euphotic zone. Data from Van Wambeke et al. (2018). Error bars

625 correspond to standard deviation of the different stations. * BCD and GPP were statistically
626 different between MA and WGY areas (Man-Whitney test, $p < 0.05$).

627

628 Figure 3: Distribution of A: dissolved organic carbon (DOC); B: dissolved combined neutral sugars
629 (DCNS); and C: dissolved combined glucose (DCGlc) in the upper surface layer (0-200 m) of the
630 study area. DCNS and DCGlc concentration is given in carbon equivalents in order to have the
631 same unit as DOC. Long duration stations (LDA, LDB and LDC) are also indicated in each graph.
632 White and red circles indicate the mixed layer depth and deep chlorophyll maximum, respectively
633 for each station.

634

635 Figure 4: Depth profiles of A: DOC; B: DCNS; and C: DCGlc in the 0-2000 m layer of the study
636 area.

637

638 Figure 5: Average Mol percentage (mol %) of dissolved monosaccharides at A: surface; B: 200 m;
639 and C: 2000 m depth for MA and WGY areas. Monosaccharides abbreviations: Fuc.: Fucose;
640 Rha.: Rhamnose; Ara.: Arabinose; GlcN.: Glucosamine; Gal.: Galactose; Glc.: Glucose; Man.:
641 Mannose and Xyl.: Xylose.

642

643 Figure 6: Integrated carbon stocks (mmol C m^{-2}) over the euphotic zone carbon in terms of DOC,
644 DOC_{EX} and DCNS-C. * DOC and DOC_{SL} were statistically different between MA and WGY areas
645 (Man-Whitney test, $p < 0.05$).

646

647 Figure 7: Residence time (days) of semi labile DOC ($T_{\text{r SL}}$) and DCNS-C ($T_{\text{r DCNS-C}}$) for MA and
648 WGY areas. * $T_{\text{r SL}}$ and $T_{\text{r DCNS-C}}$ were statistically different between MA and WGY areas (Man-
649 Whitney test, $p < 0.05$).

650 Table 1: Range and mean values (0-200 m and 200-1000 m) of DOC (μMC), DCNS-C (μMC),
651 DCGlc-C (μMC), DCNS-C/DOC (%) and DCGlc-C/DCNS-C (%) recorded during the OUTPACE
652 cruise. MA comprises the SD2-SD12 stations and WGY comprises the LDC and SD13-SD15.
653 Means of MA and WGY were not statistically different for any of the parameters presented (Man-
654 Whitney test, $p > 0.05$).

655

656

Table 1: Range and mean values (0-200 m and 200-1000 m) of DOC, DCNS-C, DCGlc-C, DCNS-C/DOC and DCGlc-C/DCNS-C recorded during the OUTPACE cruise. MA comprises the SD2-SD12 stations and WGY comprises the LDC and SD13-SD15. Means of MA and WGY were not statistically different for any of the parameters presented (Man-Whitney test, $p > 0.05$).

	All data				MA				WGY			
	Range	mean±sd (n)	Range	mean±sd (n)	Range	mean±sd (n)	Range	mean±sd (n)	Range	mean±sd (n)	Range	mean±sd (n)
DOC (μM)	47-81	67±10 (136)	36-53	46±4 (67)	51-79	66±9 (94)	39-52	46±3 (43)	47-81	68±10 (42)	36-53	46±4 (24)
Depth (m)	0-200		200-1000		0-200		200-1000		0-200		200-1000	
DCNS-C (μM)	0.2-4.2	1.9±0.8 (132)	0.3-2.4	1.2 ±0.6 (68)	0.6-4.2	1.8±0.7 (91)	0.3-2.4	1.2±0.6 (45)	0.2-3.8	1.9±1.0 (41)	0.3-2.0	1.0±0.4 (23)
Depth (m)	0-200		200-1000		0-200		200-1000		0-200		200-1000	
DCGlc-C (μM)	0.2-3.0	1.0±0.6 (132)	0.2-1.6	0.7±0.3 (68)	0.3-3.0	1.0±0.6 (91)	0.2-1.6	0.7±0.4 (45)	0.2-2.7	1.1±0.7 (41)	0.3-1.4	0.7±0.3 (23)
Depth (m)	0-200		200-1000		0-200		200-1000		0-200		200-1000	
DCNS-C/DOC (%)	0.3-7.0	2.8±1.1 (132)	0.56-5.4	2.6±1.2 (66)	0.8-7.0	2.8±1.0 (91)	0.6-5.4	2.7±1.3 (43)	0.3-5.1	2.8±1.3 (41)	0.6-4.7	2.4±1.0 (23)
Depth (m)	0-200		200-1000		0-200		200-1000		0-200		200-1000	
DCGlc-C/DCNS-C (%)	19-100	53±18 (132)	35-100	64±21 (68)	28-100	54±17 (91)	36-100	63±22 (45)	19-100	58±20 (41)	35-100	66±20 (23)
Depth (m)	0-200		200-1000		0-200		200-1000		0-200		200-1000	

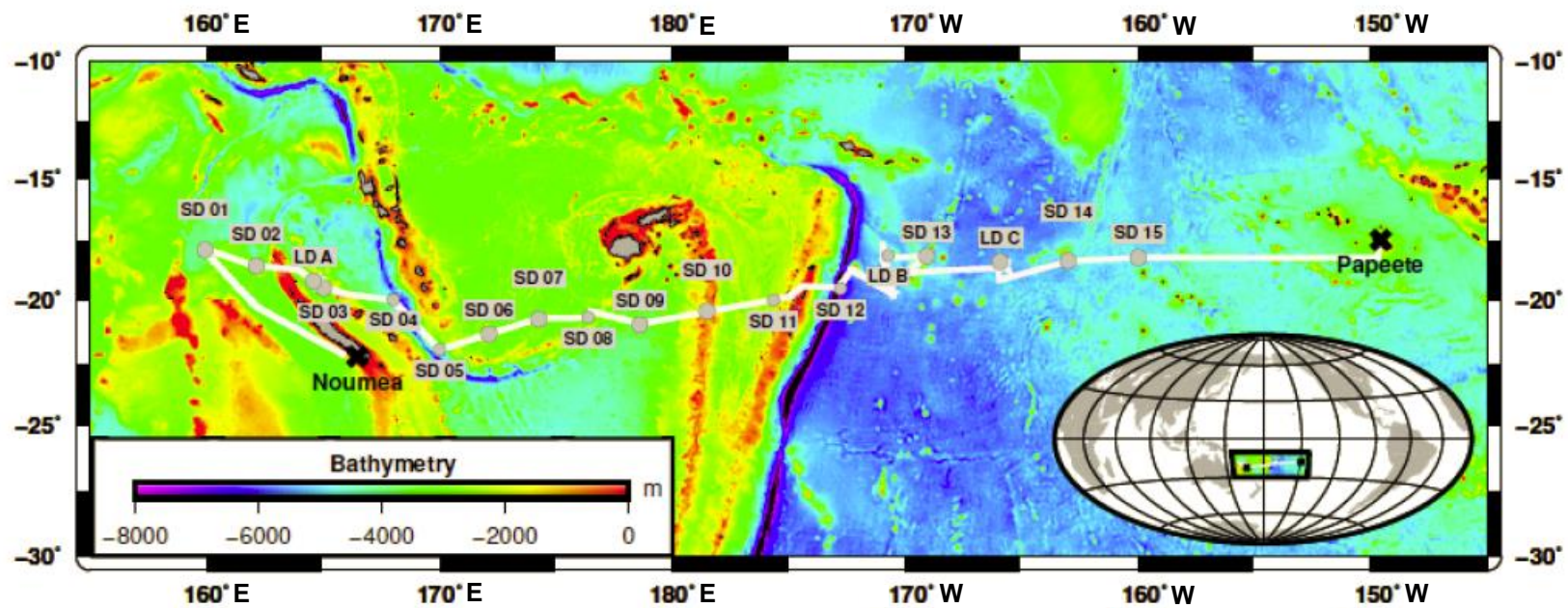


Figure 1

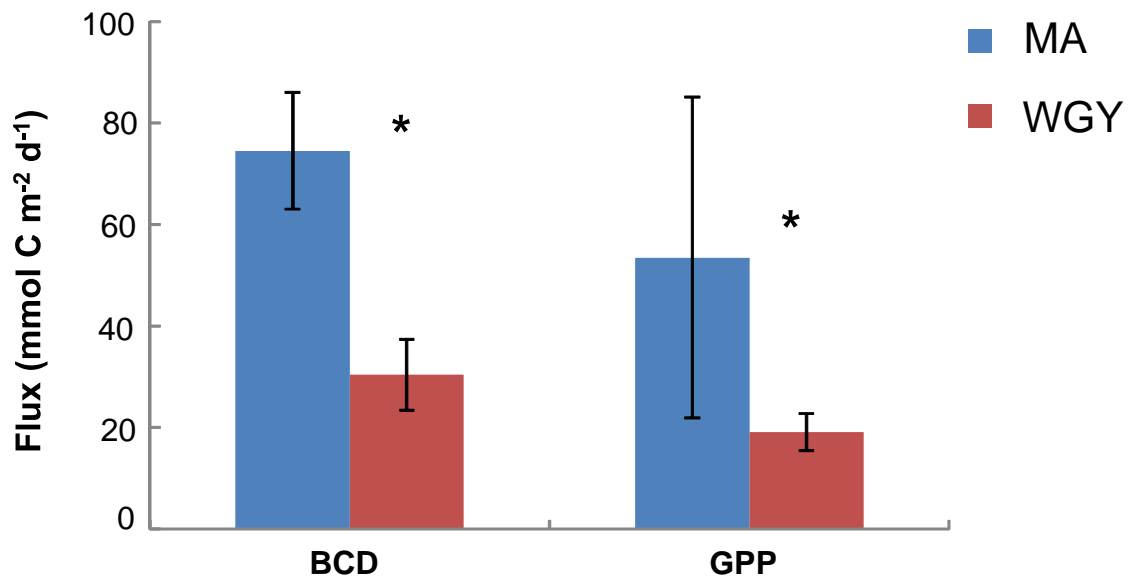


Figure 2

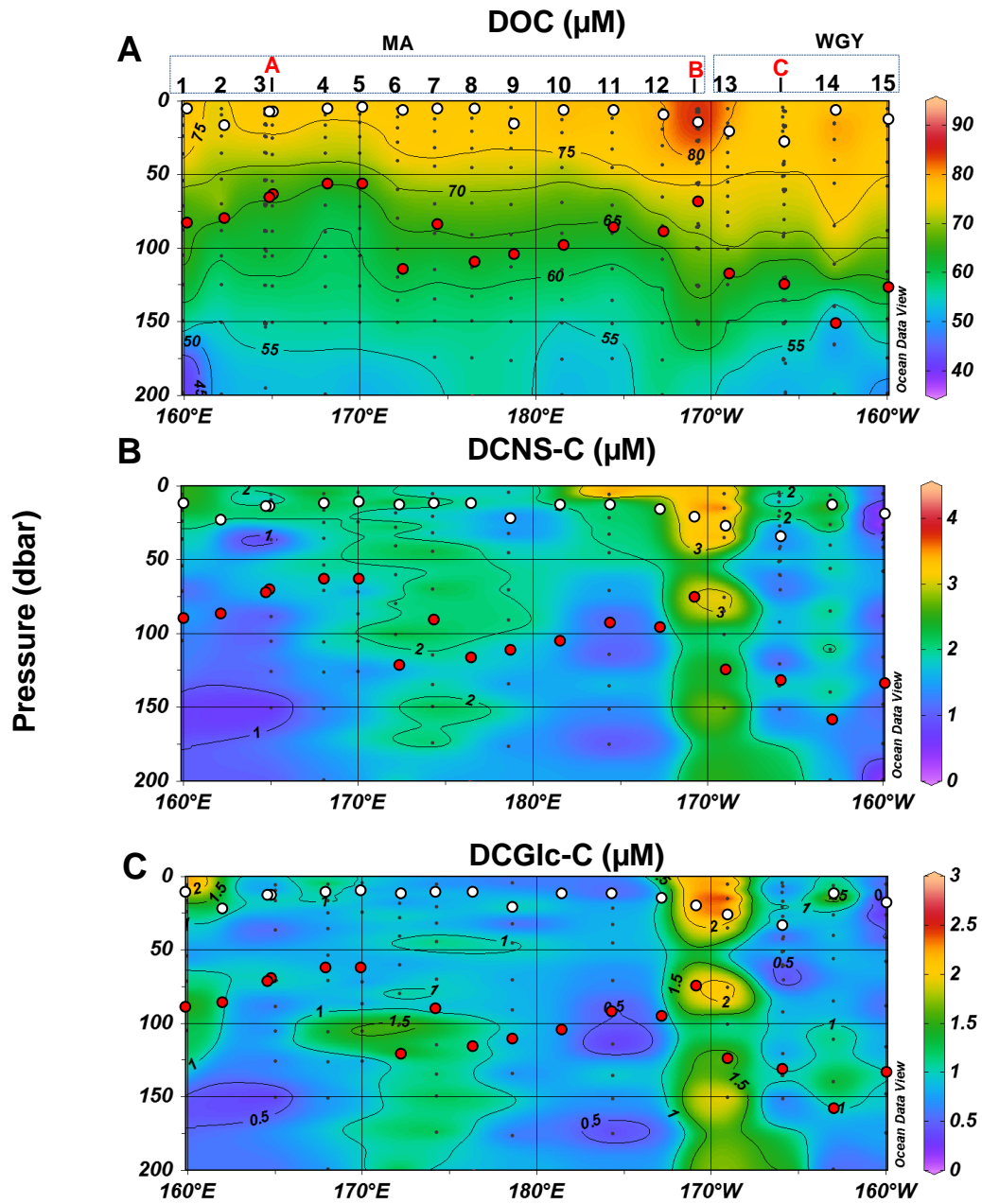


Figure 3

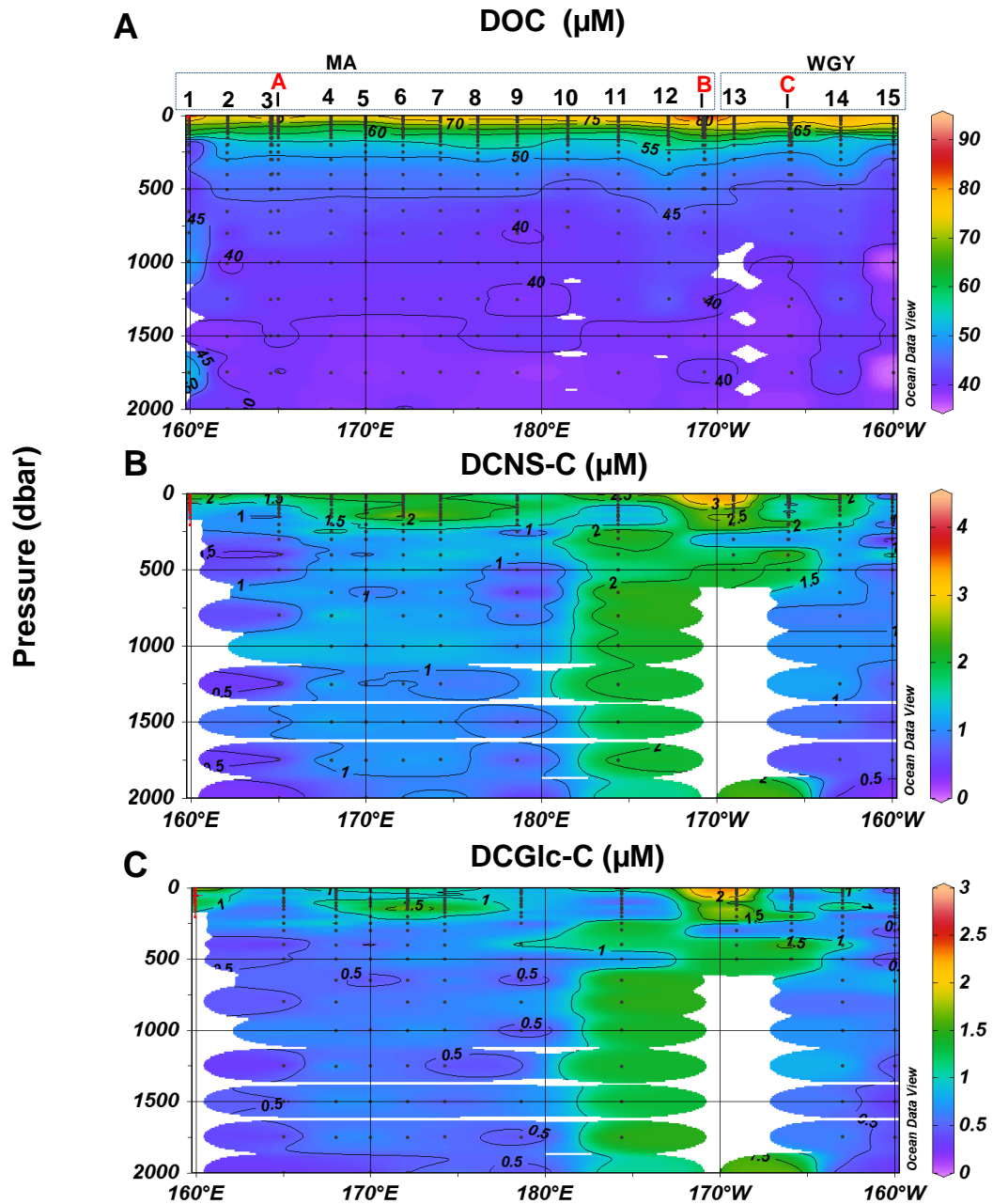


Figure 4

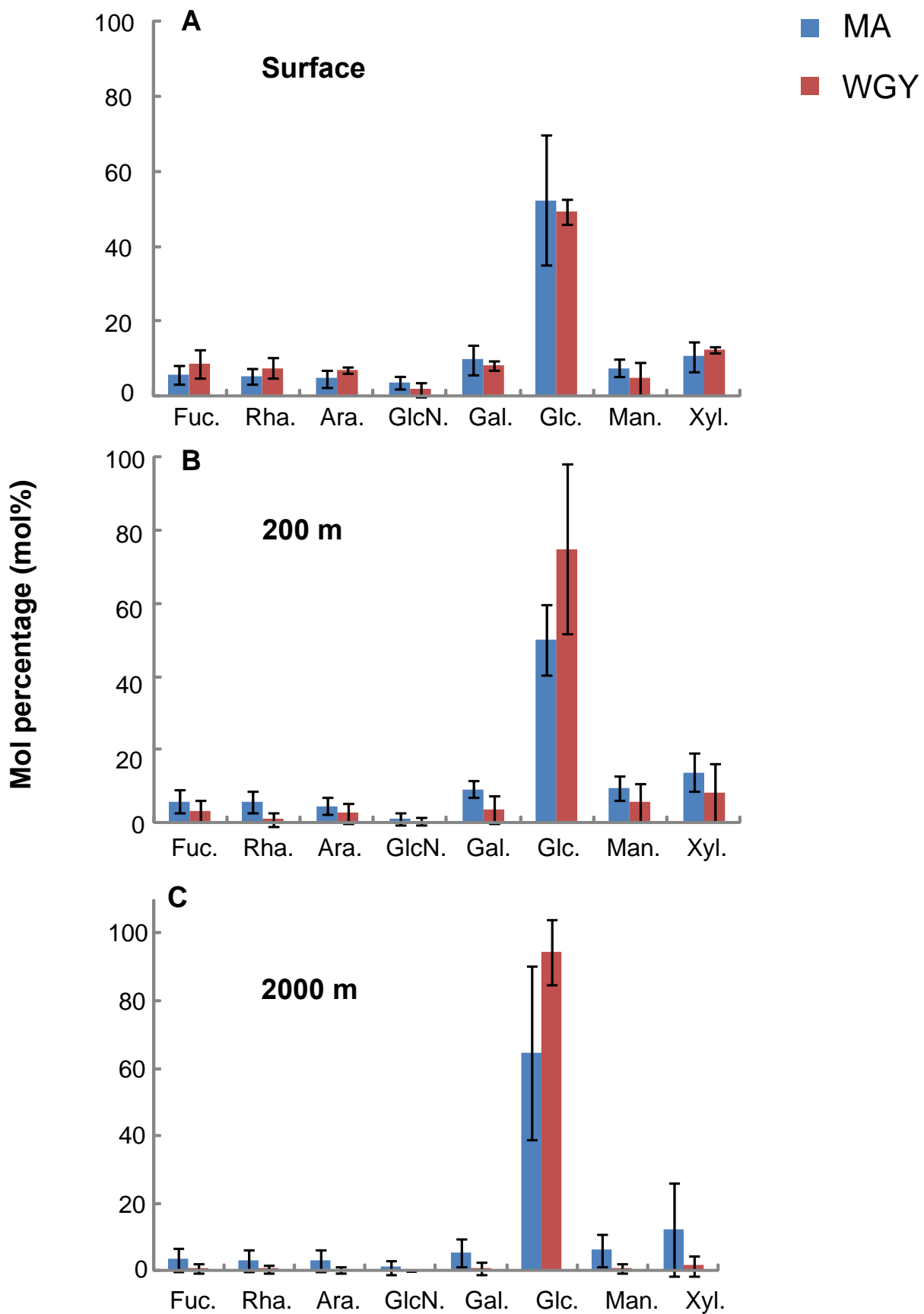


Figure 5

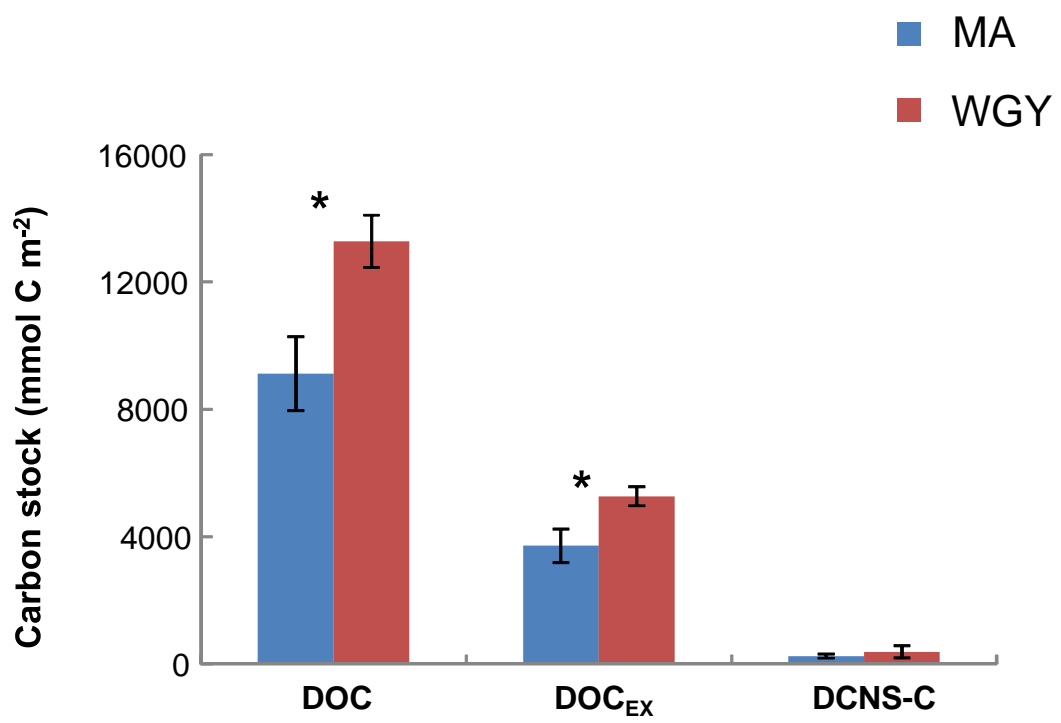


Figure 6

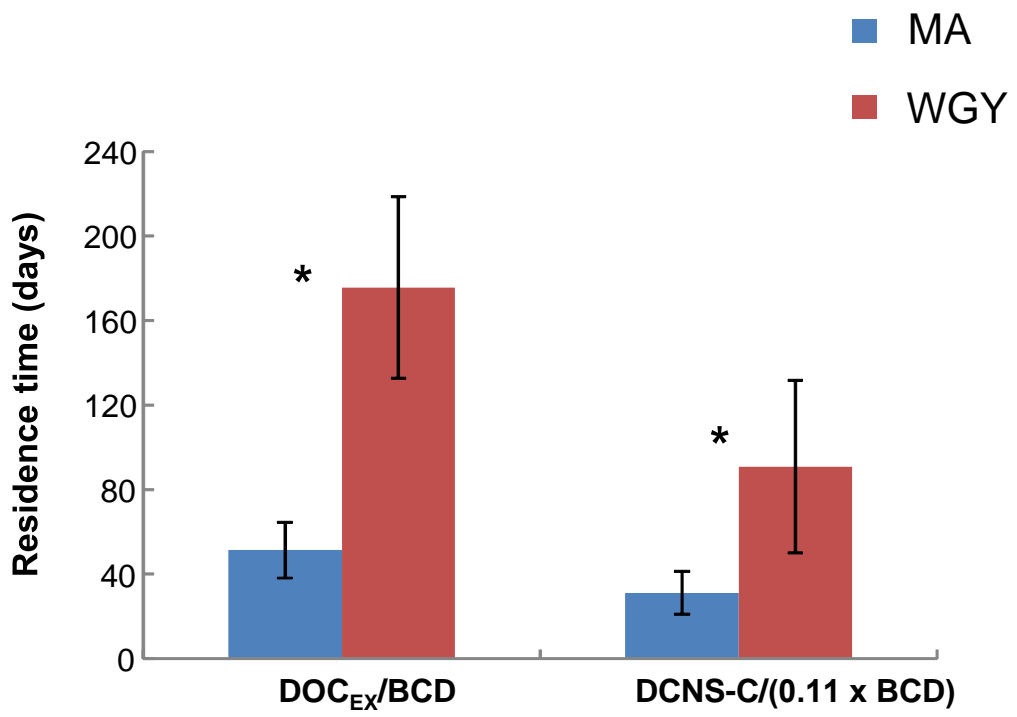


Figure 7