



1 **The composition and distribution of labile dissolved organic matter across the south west**

2 **Pacific**

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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) spanning from the Melanesian Archipelago (MA) area to the western part of the south  
28 Pacific gyre (WGY), in austral summer, as a part of the OUTPACE project. Our results showed  
29 DOC and DCNS concentrations exhibited little differences among the MA and WGY areas (0-  
30 200m: 55-78  $\mu\text{MC}$  for DOC and 1.5-2  $\mu\text{MC}$  for DCNS), however, a deeper penetration of DOC  
31 was noticeable at 150 m depth at the WGY area. This finding was also reflected to the DOC and  
32 semi-labile DOC ( $\text{DOC}_{\text{SL}}$ ) stocks values (integration 0-200m) for which we found higher values  
33 in the WGY than the MA area. The high excess  $\text{DOC}_{\text{SL}}$  measured in WGY was characterized by  
34 a high residence time ( $130 \pm 31$  days ( $n = 3$ )) about three times higher than the MA region ( $T_r =$   
35  $40 \pm 7$  days ( $n = 8$ )) suggesting an accumulation of the semi-labile DOM in the surface waters of  
36 WGY. DCNS yields ( $\text{DCNS-C} \times \text{DOC}^{-1}$  %) also followed this pattern with higher values  
37 recorded in the WGY ( $3.2 \pm 1.3\%$ ) than MA ( $2.8 \pm 0.8\%$ ) highlighting the presence of semi-  
38 labile dissolved organic material (DOM) in the form of polysaccharides. These polysaccharides  
39 also exhibited a higher residence time in WGY ( $T_r = 8 \pm 4$  days,  $n = 3$ ) than in MA ( $T_r = 3 \pm$   
40 1days,  $n=8$ ) suggesting that this DCNS pool persists longer in the surface waters of the WGY.  
41 The accumulation of  $\text{DOC}_{\text{SL}}$  in the surface waters of WGY is probably due to the very slow  
42 bacterial degradation due to nutrient limitation indicating that biologically produced DOC can be  
43 stored in the euphotic layer for a very long period.

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## 46 1. Introduction

47

48 Gyres are oceanic deserts similar to those found in continental landscapes spanning an area  
49 of several thousands of Km and are characterized by low nutrient content and limited life  
50 (Raimbault et al., 2008; D'Hondt et al., 2009; Bender et al., 2016; de Verneil et al., 2017a, b).  
51 Moreover, gyres are now considered as the worlds plastic dumps (Law et al., 2010; Eriksen et  
52 al., 2013; Cozar et al., 2014) whereas their study may help to understand future climate changes  
53 (Di Lorenzo et al., 2008; Zhang et al., 2014) and marine ecosystem functioning (Sibert et al.,  
54 2016; Browning et al., 2017). Among the five well-known oceanic gyres the South Pacific  
55 subtropical gyre, although the world's largest, has been less studied mainly due to its remoteness  
56 from the main landmasses. Nonetheless, earlier studies indicated that the western part of gyre  
57 (western tropical south pacific; WTSP) is a hot spot of N<sub>2</sub> fixation (Bonnet et al., 2013; Bonnet  
58 et al., 2017; Caffin et al., 2017) and recent studies have shown that there is a gradient of  
59 increasing oligotrophy from WTSP to the south Pacific Gyre (GY) (Moutin et al., 2018).

60 Flowing from the east of the GY, oligotrophy decreases toward the Chilean coast (Claustre et al.,  
61 2008) with high residual phosphate concentrations in the center of the GY (Moutin et al., 2008).

62 Recent studies indicated an efficient DOC export in the subtropical gyres is related with the  
63 inhibition of DOC utilization under low-nutrient conditions (Letscher et al., 2015; Roshan and  
64 DeVries, 2017). Similar observations have also been made for the oligotrophic Mediterranean  
65 Sea (Guyennon et al., 2015). However, little information exists regarding dissolved organic  
66 matter (DOM) dynamics in GY particularly for its labile component (accumulation, export, fate),  
67 which is mainly represented by carbohydrates (Sempéré et al., 2008; Goldberg et al., 2011).

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



69 seawater, carbohydrates are the major components of organic matter in surface and deep waters  
70 accounting 5-10% and < 5% of dissolved organic carbon (DOC), respectively as shown by liquid  
71 chromatography (Benner, 2002; Panagiotopoulos and Sempéré, 2005 and references therein).  
72 The carbohydrate pool of DOC consists of free monosaccharides (i.e. free monomers) and  
73 polysaccharides (i.e. dissolved combined neutral sugars or DCNS), which are generally  
74 measured as their monosaccharide constituents (sum of fucose, rhamnose, arabinose, galactose,  
75 glucose, mannose and xylose) after acid hydrolysis (Aluwihare et al., 1997; Skoog and Benner,  
76 1997; Kirchman et al., 2001; Panagiotopoulos and Sempéré, 2005). Free monosaccharide  
77 concentrations range from 10 to 100 nM, they account < 10% of total dissolved neutral sugars  
78 (TDNS) and experiments have shown that they are rapidly utilized (minutes to hours) by  
79 bacterioplankton and as such they are considered as ultra labile organic matter (Rich et al., 1996;  
80 Skoog et al., 1999; Kirchman et al., 2001). Polysaccharide or dissolved combined neutral sugars  
81 (DCNS) concentrations range from 200-800 nM, they account 80-95% of TDNS and  
82 experiments have shown that they disappear within time scales of days to months and, as such,  
83 they are considered as labile and semi-labile organic matter (Aluwihare and Repeta, 1999;  
84 Carlson and Hansell, 2015 and references therein). Other studies have shown that this labile  
85 and/or semi-labile organic matter accumulates in the surface ocean and may potentially be  
86 exported to depth contributing to ocean carbon pump (Goldberg et al., 2010; Carlson and  
87 Hansell, 2015).

88 In the frame of the OUTPACE project we studied DOM dynamics in terms of DOC and  
89 DCNS composition in relation to N<sub>2</sub> fixation to evaluate the production and fate of organic  
90 matter (including carbon export) which was one of the main goals of the project. The results are  
91 presented and discussed along with heterotrophic prokaryotic production (BP) to better



92 understand the bacterial cycling of dissolved organic matter (DOM) in the area.

93

## 94 **2. Materials and Methods**

### 95 **2.1 Sampling**

96 Sampling took place along a 5500 Km transect spanning from New Caledonia to French  
97 Polynesia in the Western Tropical South Pacific (WTSP) onboard the R/V *L'Atalante* during the  
98 Oligotrophy to Ultraoligotrophy Pacific Experiment (OUTPACE) cruise (19 February-5 April,  
99 2015). Samples were taken from 18 different stations comprising three long duration stations  
100 (LDA, LDB, and LDC; about 7-8 days duration) and 15 short duration (SD1-15) stations (~8 h  
101 duration). Biogeochemical and physical characteristics of these sites as well as the adaptive  
102 strategy are described in detail elsewhere (Moutin et al., 2017). Briefly, the cruise took place  
103 between 18-20°S covering two contrasted trophic regimes with increasing oligotrophy from west  
104 to east (Fig.1).

105 Discrete seawater samples were collected from 12 L Niskin bottles equipped with Viton O-  
106 rings and silicon tubes to avoid chemical contamination. For DOC and DCNS analyses, samples  
107 were filtered through two precombusted (450°C for 24 h) GF/F glass fiber filters using a custom-  
108 made all-glass/Teflon filtration syringe system. Samples for DOC were collected into  
109 precombusted glass ampoules (450°C, 6h) that were sealed after acidification with H<sub>3</sub>PO<sub>4</sub> (85%)  
110 and stored in the dark at 4°C. Samples for DCNS were collected in 40-mL Falcon vials  
111 (previously cleaned with 10% of HCl and Milli-Q water) and frozen at -20°C until analyses.

112

## 113 **3. Chemical and microbiological Analyses**

### 114 **3.1. Dissolved organic carbon (DOC) determination**



115 DOC was measured by high temperature combustion on a Shimadzu TOC-L analyzer  
116 (Cauwet, 1999). Typical analytical precision was  $\pm 0.1\text{-}0.5 \mu\text{M C}$  (SD). Consensus reference  
117 materials (<http://www.rsmas.miami.edu/groups/biogeochem/CRM.html>) were injected every 12  
118 to 17 samples to insure stable operating conditions.

119

## 120 **3.2. Dissolved combined neutral sugars (DCNS) determination**

### 121 *3.2.1. Carbohydrate extraction and isolation*

122 Seawater samples were desalted using dialysis tubes with a molecular weight cut-off of 100-  
123 500 Da (Spectra/Por® Biotech cellulose ester) according to the protocol of Panagiotopoulos et  
124 al. (2014). Briefly, the dialysis tube was filled with 8 mL of the sample and the dialysis was  
125 conducted into a 1 L beaker filled with Milli-Q water at 4°C in the dark. Dialysis was achieved  
126 after 4-5 h (salinity dropped from 35 to 1-2 g L<sup>-1</sup>). Samples were transferred into 40 mL plastic  
127 vials (Falcon; previously cleaned with 10% HCl and Milli-Q water), frozen at -30 °C, and freeze  
128 dried. The obtained powder was hydrolyzed with 1M HCl for 20 h at 100°C and the samples  
129 were again freeze dried to remove the HCl acid (Murrell and Hollibaugh, 2000; Engel and  
130 Handel, 2011). The dried samples were diluted in 4 mL of Milli-Q water, filtered through quartz  
131 wool, and pipetted into scintillation vials for liquid chromatographic analysis. The vials were  
132 kept at 4°C until the time of analysis (this never exceeded 24 h). The recovery yields of the  
133 whole procedure (dialysis and hydrolysis) were estimated using standard polysaccharides  
134 (laminarin, and chondroitine sulfate) and ranged from 82 to 86% (n=3).

135

### 136 *3.2.2. Liquid Chromatography*

137 Carbohydrate concentrations in samples were measured by liquid chromatography according



138 to Mopper et al. (1992) and were modified by Panagiotopoulos et al. (2001, 2014). Briefly,  
139 neutral monosaccharides were separated on an-anion exchange column (Carbopac PA-1,  
140 Thermo) by isocratic elution (mobile phase 19 mM NaOH) and were detected by an  
141 electrochemical detector set in the pulsed amperometric mode (Panagiotopoulos et al., 2014).  
142 The flow rate and the column temperature were set at  $0.7 \text{ mL min}^{-1}$  and  $17^\circ\text{C}$ , respectively. Data  
143 acquisition and processing were performed using the Dionex software Chromeleon. Repeated  
144 injections ( $n = 6$ ) of a dissolved sample resulted in a CV of 12-15% for the peak area, for all  
145 carbohydrates. Adonitol was used as an internal standard and was recovered at a percentage of  
146 80-95%; however, we have chosen not to correct our original data.

147

### 148 **3.3. Bacterial production**

149 Heterotrophic prokaryotic production (BP) was determined onboard with the  $^3\text{H}$ -leucine  
150 incorporation technique to measure protein synthesis (Smith and Azam, 1992). Additional details  
151 are given in Van Wambeke et al. (2018). Briefly, 1.5 mL samples were incubated in the dark for  
152 1-2 h after addition of  $^3\text{H}$  leucine, at a final concentration of 20 nM, with standard deviation of  
153 the triplicate measurements being on average 9%. A factor of  $1.5 \text{ Kg C mol leucine}^{-1}$  was used to  
154 convert leucine incorporation to carbon equivalents. To estimate bacterial carbon demand  
155 (BCD) which is used to calculate semi-labile DOC residence time, we used a bacterial growth  
156 efficiency (BGE) of 8% as determined experimentally during the OUTPACE cruise (Van  
157 Wambeke et al., 2018). BCD was calculated by dividing BP values at each station with BGE.  
158 Trapezoidal 0-200 m integrals were then computed from volumetric rates.

159

160



161 **4. Results**

162

163 4.1 General observations

164

165 The OUTPACE cruise was conducted under strong stratification conditions (Moutin et al.,  
166 2018) during austral summer encompassing a longitudinal oligotrophic gradient starting from the  
167 Melanesian Archipelago (MA) area (stations SD1-SD13 including LDA and LDB stations) and  
168 ending in the western part of the south Pacific gyre (WGY; stations SD14-SD15 including LDC  
169 station; Fig. 1). Additional information on the hydrological conditions of the study area (*i.e.*  
170 temperature, salinity) including water masses characteristics is provided elsewhere (de Verneil et  
171 al., 2017a; Moutin et al., 2018). Two different trends can be noticed in a first approach:

172 a. Most of the biogeochemical parameters examined in the OUTPACE cruise (chlorophyll  $\alpha$   
173 concentrations, primary production and heterotrophic prokaryotic production (BP),  $N_2$  fixation  
174 rates, and nutrient concentrations) exhibited significantly higher values in the MA area than in  
175 the WGY area (Moutin et al., 2018; Van Wambeke et al., 2018; Benavides et al., 2018; Caffin et  
176 al., 2017). These differences were also reflected by the distribution of the diazotrophic  
177 communities detected in both areas further highlighting the different dynamics across the  
178 oligotrophic gradient (Stenegren et al., 2018; Moutin et al., 2017, 2018).

179 b. The bulk of DOM as shown by DOC analysis did not follow the above biogeochemical  
180 pattern and showed little variations on DOC absolute concentrations although a deeper  
181 penetration of DOM was noticeable at 150 m depth at the WGY area (Fig. 2a). As such,  
182 epipelagic (0-200 m) DOC concentrations all over the OUTPACE cruise ranged from 55 to 78  
183  $\mu\text{M C}$  with highest values observed at LDB ( $\sim 85 \mu\text{M C}$ ) probably related to a decaying  
184 phytoplankton bloom (de Verneuil et al., 2017b; Van Wambeke et al., 2018). Mesopelagic (200-





185 1000 m) DOC values varied between 45 to 55  $\mu\text{M C}$  (Fig. 3a) and are in agreement with  
186 previous studies in the South Pacific Ocean (Doval and Hansell, 2000; Hansell et al., 2009;  
187 Raimbault et al. 2008).

188 DCNS concentrations closely followed DOC trends and fluctuated between 1.5-2  $\mu\text{M C}$  (Fig.  
189 2b) in the epipelagic zone. These values are in good agreement to those previously reported for  
190 the central and/or the eastern part of the south Pacific Gyre (1.1-3.0  $\mu\text{M C}$ ; Sempéré et al., 2008)  
191 that were recorded under strong stratification conditions during austral summer (Claustre et al.,  
192 2008). Compared with other oceanic provinces our epipelagic DCNS concentrations fall in the  
193 same range to those reported in the BATS station in the Sargasso Sea (1.0-2.7  $\mu\text{M C}$ ) also  
194 monitored under stratification conditions (Goldberg et al., 2010). Below 200 m depth DCNS  
195 concentrations ranged from 0.5 to 1  $\mu\text{M C}$  (Fig. 3b) and concur with previous reported literature  
196 values (Skoog and Benner, 1997; Amon and Benner, 2003).

197

#### 198 4.2 DCNS yields and composition

199

200 The contribution of DCNS-C to the DOC pool is referred here as DCNS yields and are  
201 presented as a percentage of DOC (*i.e.* DCNS-C  $\times$  DOC<sup>-1</sup> %). Epipelagic (0-200 m) average  
202 DCNS yields were slightly higher in the WGY (average  $\pm$  sd: 3.2  $\pm$  1.3%) than the MA (2.8  $\pm$   
203 0.9%) whereas deeper than 200 m they were 2.6  $\pm$  0.9% and 2.3  $\pm$  0.9% for the WGY and MA,  
204 respectively. These values are in good agreement to those reported for the eastern part of the  
205 gyre (Sempéré et al., 2008) and concur well with the range of values (2-7%) recorded in the  
206 Equatorial Pacific (Rich et al., 1996; Skoog and Benner, 1997).

207 The molecular composition of carbohydrates revealed that glucose was the major



208 monosaccharide at all depths in both the MA and WGY areas accounting for 55-75% of the  
209 DCNS. Glucose concentrations (DCGlc-C) ranged from 0.5 to 1  $\mu\text{MC}$  in both areas (Fig. 2c, Fig.  
210 3c), however, a significantly higher mol% contribution of glucose was recorded in the WGY  
211 than the MA especially at depths > 200 m (Fig. 5). Glucose was followed by xylose (9-12%),  
212 galactose (4-9%) and mannose (5-8%) whereas the other monosaccharides accounted for < 6%  
213 of DCNS (Fig. 5). The same suite of monosaccharides was also reported by Sempéré et al.  
214 (2008) although the latter author also found that arabinose was among the major  
215 monosaccharides. Finally, it is worth noting that the relative abundance of glucose increased by  
216 depth and sometimes accounted 100% of the DCNS especially in the WGY area (Fig. 5).

217

#### 218 4.3 DOC and DCNS stocks calculation

219

220 DOC stocks (integrated values 0-200 m) were calculated in the same stations where  
221 carbohydrate (DCNS) data were available in order to have a better comparison between the MA  
222 (stations: SD3, SD4, SD5, SD6, SD7, SD9, SD11, SD13) and WGY (LDC, SD14, SD15)  
223 stations (Fig. 2a). Semi labile DOC stock ( $\text{DOC}_{\text{SL}}$ ) was calculated by subtracting an average  
224 DOC value (refractory DOC) measured at 1000 m depth from the DOC pool. This DOC value  
225 was 41  $\mu\text{MC}$  ( $40.8 \pm 1.8 \mu\text{MC}$ ,  $n = 11$ ) and was estimated averaging all DOC values at 1000m  
226 from all stations ( $n = 11$ ).  $\text{DOC}_{\text{SL}}$  stock values in the upper 200m averaged  $4494 \pm 520$  ( $n = 8$ )  
227 and  $5121 \pm 400$  ( $n = 3$ )  $\text{mmol C m}^{-2}$  accounting for  $37 \pm 2\%$  ( $n = 8$ ) and  $38 \pm 1\%$  ( $n = 3$ ) of DOC  
228 in the MA and WGY sites respectively. DCNS represented  $9 \pm 5\%$  ( $n = 8$ ) and  $6 \pm 4\%$  ( $n = 3$ ) of  
229  $\text{DOC}_{\text{SL}}$  in the MA and WGY sites, respectively, further suggesting that only a small percentage  
230 of  $\text{DOC}_{\text{SL}}$  can be attributed to DCNS (polysaccharides).



231 **5. Discussion**

232

233 5.1 DOC and DCNS stocks in relation with biological activity

234

235 In terms of absolute stocks, DOC and DOC<sub>SL</sub> were respectively by 4 and 12% higher in the  
236 WGY than in the MA whereas the opposite trend was observed for DCNS (Fig. 4b). DCNS  
237 stocks were by 12% higher in the MA than in the WGY, which agrees with the high primary  
238 production rates measured at MA (Fig. 4a). As DCNS accounted only  $3.2 \pm 1.3\%$  and  $6 \pm 4\%$  ( $n$   
239  $=3$ ) of DOC and DOC<sub>SL</sub> in WGY site, respectively it appears that DCNS cannot explain alone  
240 these differences in organic carbon stocks and that other semi-labile compounds (*i.e.* proteins and  
241 lipids) should be taken under consideration. Unfortunately, proteins (combined amino acids)  
242 were not measured in this study. However, based on concentration kinetics on single amino acids  
243 recent investigations indicated significantly lower <sup>3</sup>H leucine concentrations in the LDC (0.56  
244 nM) than the LDA (1.80 nM) stations (Duhamel et al., 2018). This result may suggest that single  
245 amino acids and perhaps proteins are exhausted in the LDC station reflecting the ultra-  
246 oligotrophic regime of the WGY. On the other hand, DOM exhibited only slightly different C/N  
247 ratios (integrated values 0-70 m) between MA (C/N = 13) and WGY (C/N =14), which does not  
248 suggest differences on DON dynamics in relation with organic matter lability (Moutin et al.,  
249 2018). Clearly more investigations are warranted on combined and free amino acids distribution  
250 in relation with N<sub>2</sub> fixation.

251 The high excess DOC<sub>SL</sub> measured in WGY was also characterized by an elevated residence  
252 time  $T_r$  calculated as the ratio of DOC<sub>SL</sub> / BCD. Our results showed that  $T_r$  in the WGY was in  
253 the order of  $130 \pm 31$  days ( $n = 3$ ), *i.e.* about three times higher than in the MA region ( $T_r = 40 \pm$   
254  $7$  days ( $n = 8$ ) indicating an accumulation of the semi-labile DOM in the surface waters of WGY



255 (Fig. 4c). As suggested by previous studies the accumulation of DOC in the surface waters of  
256 oligotrophic regimes may be related in biotic and/or abiotic factors.

257 Nutrient limitation can prevent DOC assimilation by heterotrophic bacteria and as such  
258 sources and sinks are uncoupled, allowing accumulation (Thingstad et al., 1997; Jiao et al.,  
259 2010). Biodegradation experiments (Van Wambeke et al., 2018) focusing on the determination  
260 of the BGE and the degradation of the labile DOC pool (turning over 10 days) revealed a less  
261 biodegradable DOM fraction and lower degradation rates at the LDC (2.4% labile DOC;  $0.012 \text{ d}^{-1}$ )  
262 than the LDA site (5.3% labile DOC;  $0.039 \text{ d}^{-1}$ ). Other experiments, focusing on the factors  
263 limiting BP by testing the effect of different nutrient additions, showed that BP is limited in a  
264 first place by the availability of labile carbon in the WGY (as tracked with glucose addition, Van  
265 Wambeke et al., 2018). This limitation on BP by labile carbon was also the case in the center of  
266 the GY (Van Wambeke et al., 2008), while N limitation (as tracked by addition of  
267 ammonium+nitrate) was more pronounced in the MA area.

268 Although extensive photodegradation may transform recalcitrant organic matter into labile,  
269 the low content in chromophoric DOM recorded in the surface waters of WGY ( $\alpha\text{CDOM}(350) =$   
270  $0.010\text{-}0.015 \text{ m}^{-1}$ , 0-50 m; Dupouy et al. unpublished results from the OUTPACE cruise) points  
271 toward an already photobleached and thus photodegraded organic material (Tedetti et al., 2007;  
272 Carlson and Hansel, 2015). Notably, the 10% irradiance depths for solar radiations (Z 10%)  
273 clearly showed a higher penetration of UV-R and PAR radiations in the WGY area than in MA  
274 area (Dupouy et al., 2018). These results are in agreement with previous investigations reporting  
275 an intense solar radiation in the south Pacific gyre highlighting an important decrease of  
276 chromophoric dissolved organic matter (CDOM) in the GY (Tedetti et al., 2007).

277 The computation of the C, N, and P budgets in the upper 0-70 m layer by Moutin et al.



278 (2018) suggested that at 70 m the environmental conditions remained seasonally unchanged  
279 during the OUTPACE cruise forming an average wintertime depth of mixed layer. These authors  
280 calculated seasonal (from winter to austral summer) net DOM and POM accumulation based on  
281 such assumptions and found a dominance of DOC accumulation in the MA area (391 to 445  
282  $\text{mmol m}^{-2}$  over 8 months). This DOC accumulation in the MA area was 3.8 to 8.1 times higher  
283 than that of POC accumulation during the same time period whereas, only DOC accumulation  
284 was calculated at WGY, although two times lower than DOC in the MA. The accumulation of  
285 DOC and  $\text{DOC}_{\text{SL}}$  (Fig. 4b) in the WGY may have important implications to the sequestration of  
286 this organic material to the mesopelagic layers. DOC appears to be the major form of export of  
287 carbon in the WGY area and this result agrees with the general feature observed in oligotrophic  
288 regimes (Roshan and Devries, 2017).

289

290 5.2 DCNS dynamics across the south west Pacific

291

292 Previous investigations have employed the DCNS yields along with mol% of glucose to  
293 assess the diagenetically “freshness” of organic matter (Skoog and Benner, 1997; Benner, 2002;  
294 Goldberg et al. 2010). In general freshly produced DOM has DCNS yields >10% and mol%  
295 glucose between 28-71% (Biersmith and Benner, 1998; Hama and Yanagi, 2001). Elevated  
296 mol% glucose (> 25%) does not necessarily mirror fresh material because such values have also  
297 been reported for deep DOM and low molecular weight DOM that are considered as a  
298 diagenetically altered material (Skoog et al., 1997). Our results showed higher DCNS yields in  
299 the surface waters of WGY than the MA area with about a similar contribution of glucose ( $52 \pm$   
300  $17\%$ ,  $n = 8$  vs  $49 \pm 3\%$ ,  $n = 3$ ; Fig. 5a) to the DCNS pool, further confirming the presence of a



301 higher amount of semi-labile organic material in WGY than in the MA. Despite that DCNS  
302 represent a small fraction of semi-labile DOC the higher residence time of DCNS in the WGY  
303 ( $T_r = 8 \pm 4$  days,  $n = 3$ ) than the MA area ( $T_r = 3 \pm 1$  days,  $n=8$ ) clearly shows that the DCNS pool  
304 persist longer in the surface waters of the WGY (Fig. 4c). Moreover, because carbohydrates do  
305 not absorb light these polysaccharides (DCNS) do not seem to be impacted by the high  
306 photochemistry in WGY and potentially may be exported in the Ocean interior.

307 As expected, DCNS yields decreased by depth but remained always higher in WGY than the  
308 MA area. Glucose accounted for 75% and 50% of DCNS in the WGY and MA areas,  
309 respectively (200 m depth), and this percentage increased considerably with depth in both areas  
310 (76% for MA and 96% for WGY at 2000 m depth) indicating a preferential removal of the other  
311 carbohydrates relative to glucose (Fig. 5b; Fig. 5c). The low DCNS yields (~1%) at 2000 m  
312 depth along with the high % mol abundance of glucose clearly suggests the presence of  
313 diagenetically altered DOM and is consistent with previous investigations (Skoog and Benner,  
314 1997; Goldberg et al. 2010; Golberg et al., 2011).

315

## 316 **6. Conclusions**

317

318 This study showed a rather uniform distribution of DOC and DCNS concentrations in surface  
319 waters across an increasing oligotrophic gradient in the south west Pacific Ocean during the  
320 OUTPACE cruise. Nevertheless, our results showed that DOC and  $DOC_{SL}$  stocks were by 4 and  
321 12% higher in WGY than the MA area, respectively accompanied with higher residence times in  
322 the WGY area indicating an accumulation of semi-labile material in the latter area. Although  
323 DCNS accounted a small fraction of  $DOC_{SL}$  (5 – 9%) our results showed that DCNS or



324 polysaccharides also exhibited a higher residence time and higher DCNS in the WGY than in the  
325 MA area indicating that DCNS persist longer in the WGY. Glucose was the major  
326 monosaccharide in both areas (50 - 75%) and its relative abundance increased with depth along  
327 with a decrease of the DCNS yields indicating a preferential removal of the other carbohydrates  
328 relative to glucose. Clearly more investigations are warranted to better characterize this DOC<sub>SL</sub>  
329 material in terms of combined and free amino acids distribution in relation with N<sub>2</sub> fixation.

330

331

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333

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534 **Figure captions:**

535

536 Figure 1: Quasi-Lagrangian Surface Chlorophyll-a concentration ( $\text{mg m}^{-3}$ ) during the OUTPACE  
537 cruise. The satellite data are weighted in time by each pixel's distance from the ship's position for  
538 the entire cruise. The white line shows the vessel route (data from the hull-mounted ADCP  
539 positioning system). Coral reefs and coastlines are shown in black, land is grey, and areas of no  
540 data are left white. The positions of the short (long) duration stations are shown by cross (plus)  
541 symbols. The ocean color satellite products are produced by CLS.

542 Figure courtesy of A. de Verneil (02/06/2017).

543

544 Figure 2: Depth profiles of (A) DOC (B) DCNS and (C) DCGlc in the upper surface layer (0-  
545 300m) of the study area. Abbreviations DCNS: Dissolved combined neutral sugars; DCGlc;  
546 Dissolved combined glucose. DCNS and DCGlc concentration is given in carbon equivalents in  
547 order to have the same unit with DOC. Long duration stations (LDA, LDB and LDC) are also  
548 indicated in each graph. In contrast to DCNS, DOC was also sampled in LDA and LDB  
549 including SD2, SD8, SD10, and SD12 stations and these results are shown in Fig. 2A and Fig.  
550 3A.

551

552 Figure 3: Depth profiles of (A) DOC (B) DCNS and (C) DCGlc in the 0-2000 m layer of the  
553 study area. Abbreviations and comments on DOC sampling are given in Fig. 1. The white  
554 rectangles mask abnormal extrapolation due to the absence of DCNS data.

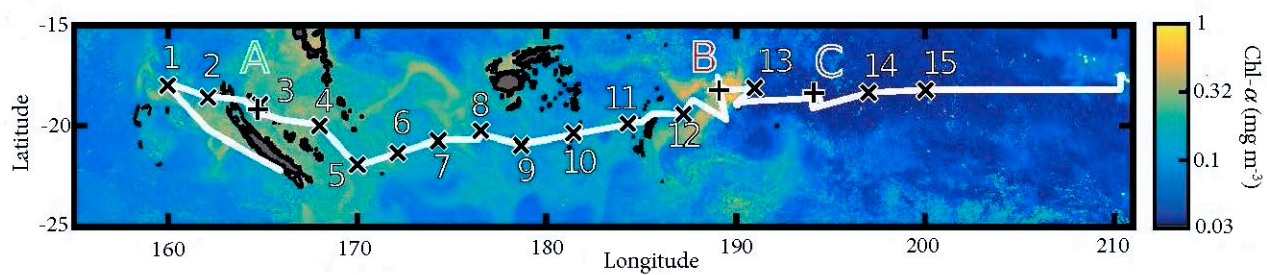
555

556 Figure 4: (A) Integrated (0-200m) BCD and PP fluxes ( $\text{mmol C m}^{-2} \text{d}^{-1}$ ) (B) Carbon stock





557 (mmol C m<sup>-2</sup> d<sup>-1</sup>) and (C) residence time (days) of semi labile DOC and DCNS-C for MA and  
558 WGY. MA comprises the SD2-SD13 stations and WGY comprises the LDC and SD14-SD15.  
559 BCD values are calculated assuming a BGE of 8% according to VanWambeke et al. (2018)  
560 (see material and methods). Error bars correspond to standard deviation of the different stations.  
561  
562 Figure 5: Relative abundance (%) of dissolved monosaccharides at (A) surface, (B) 200 m and  
563 (C) 2000 m depth for MA and WGY. MA comprises the SD2-SD13 stations and WGY  
564 comprises the LDC and SD14-SD15.



26

Figure 1

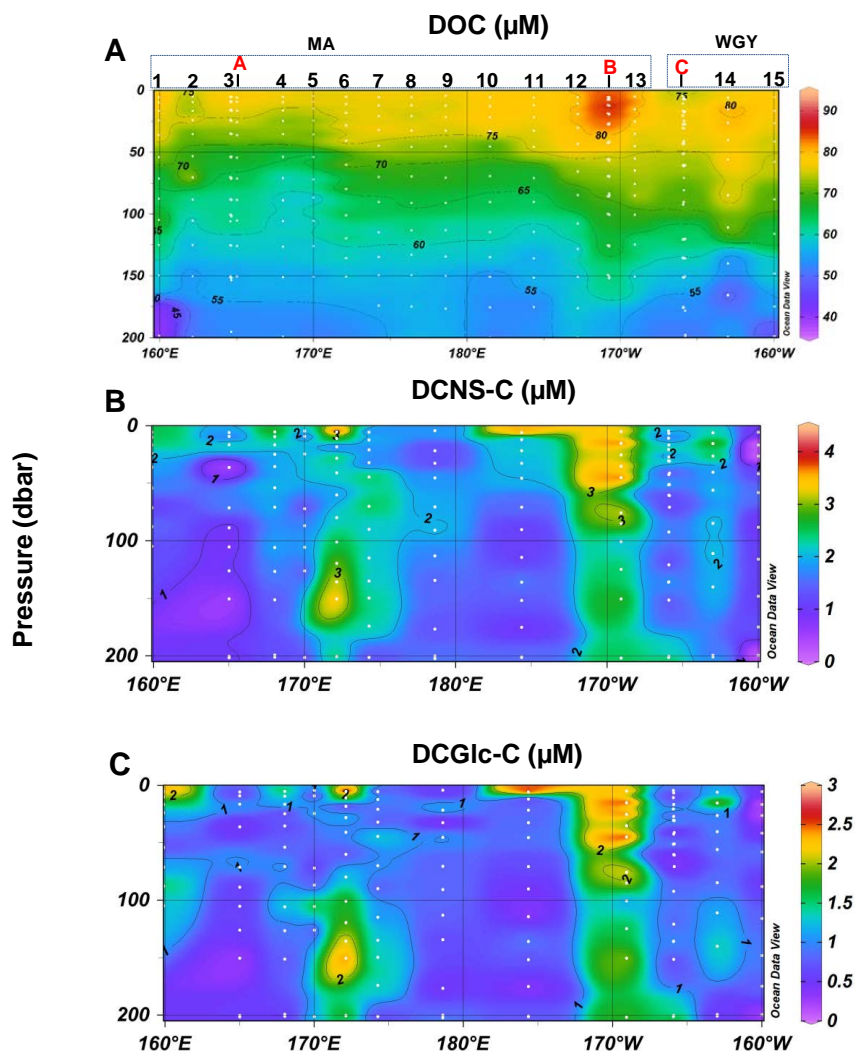


Figure 2

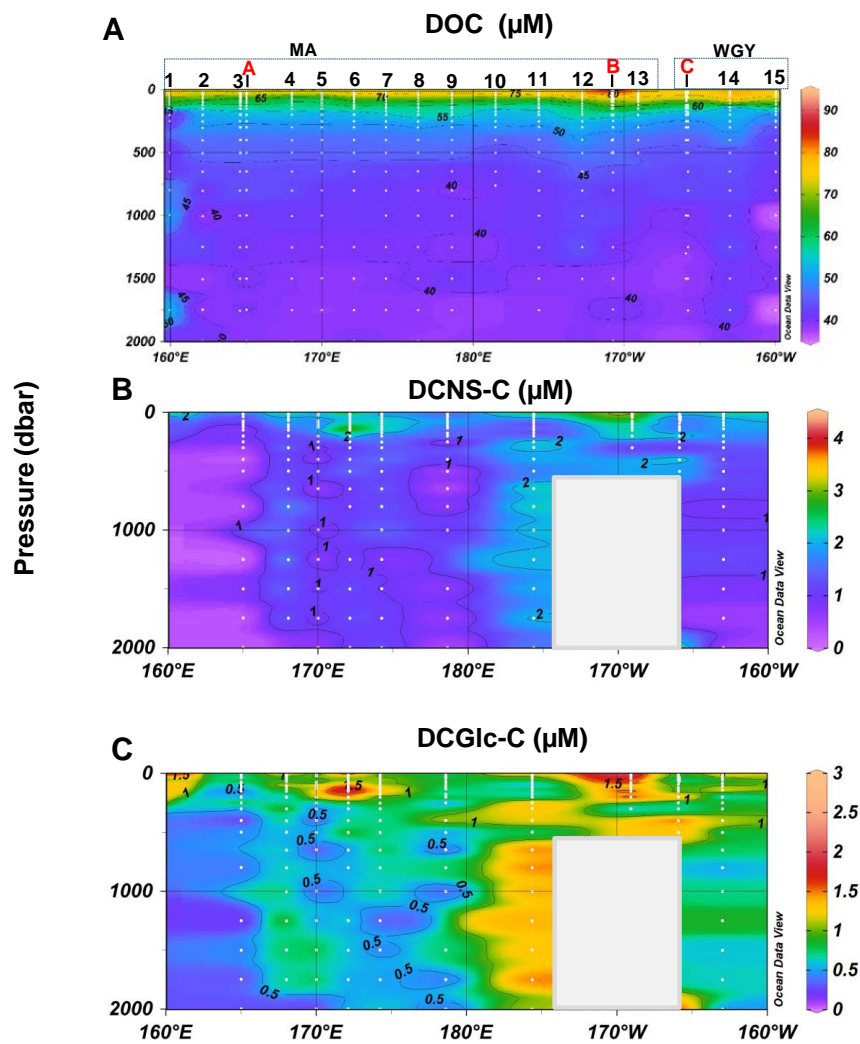


Figure 3

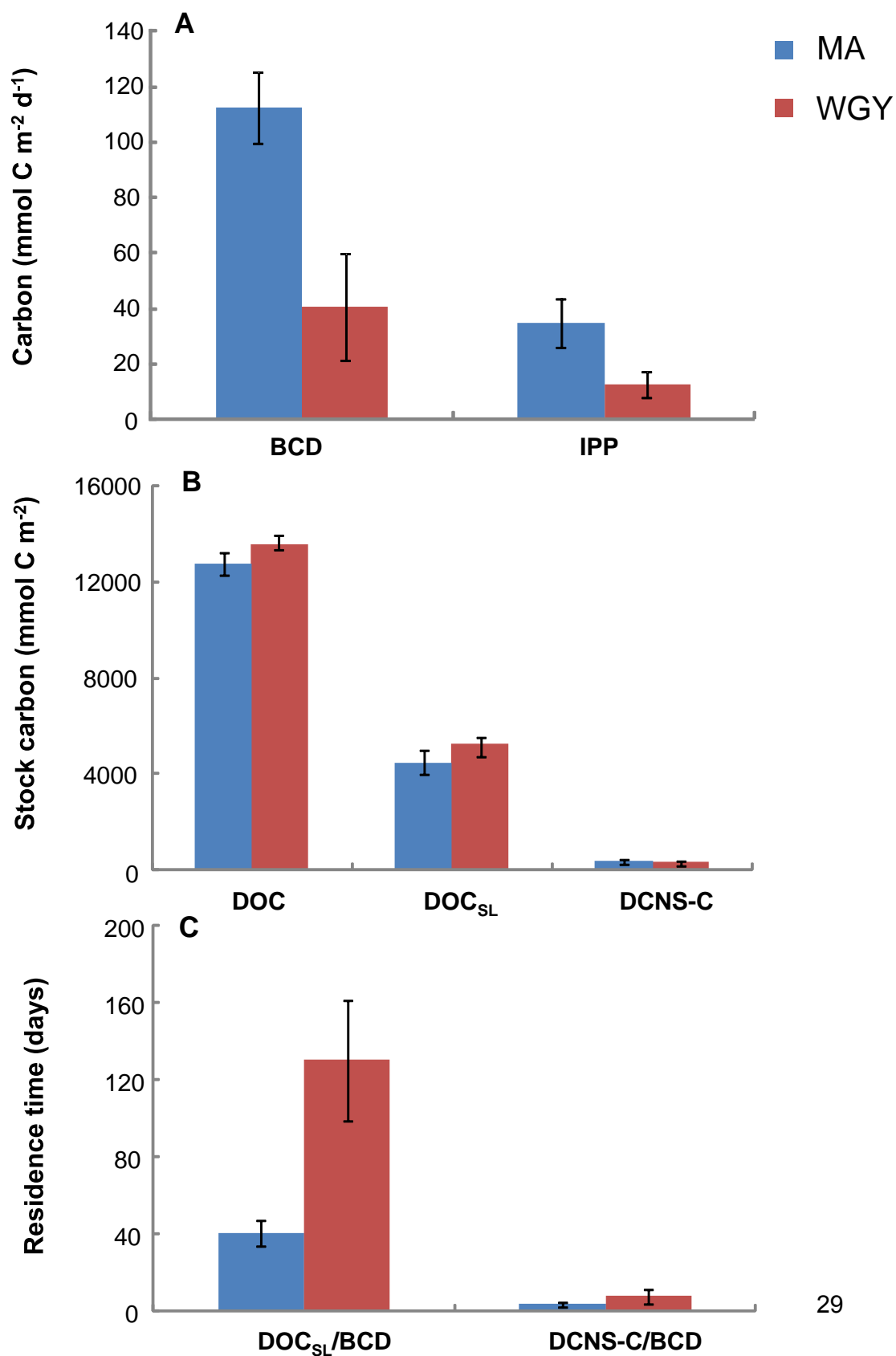


Figure 4

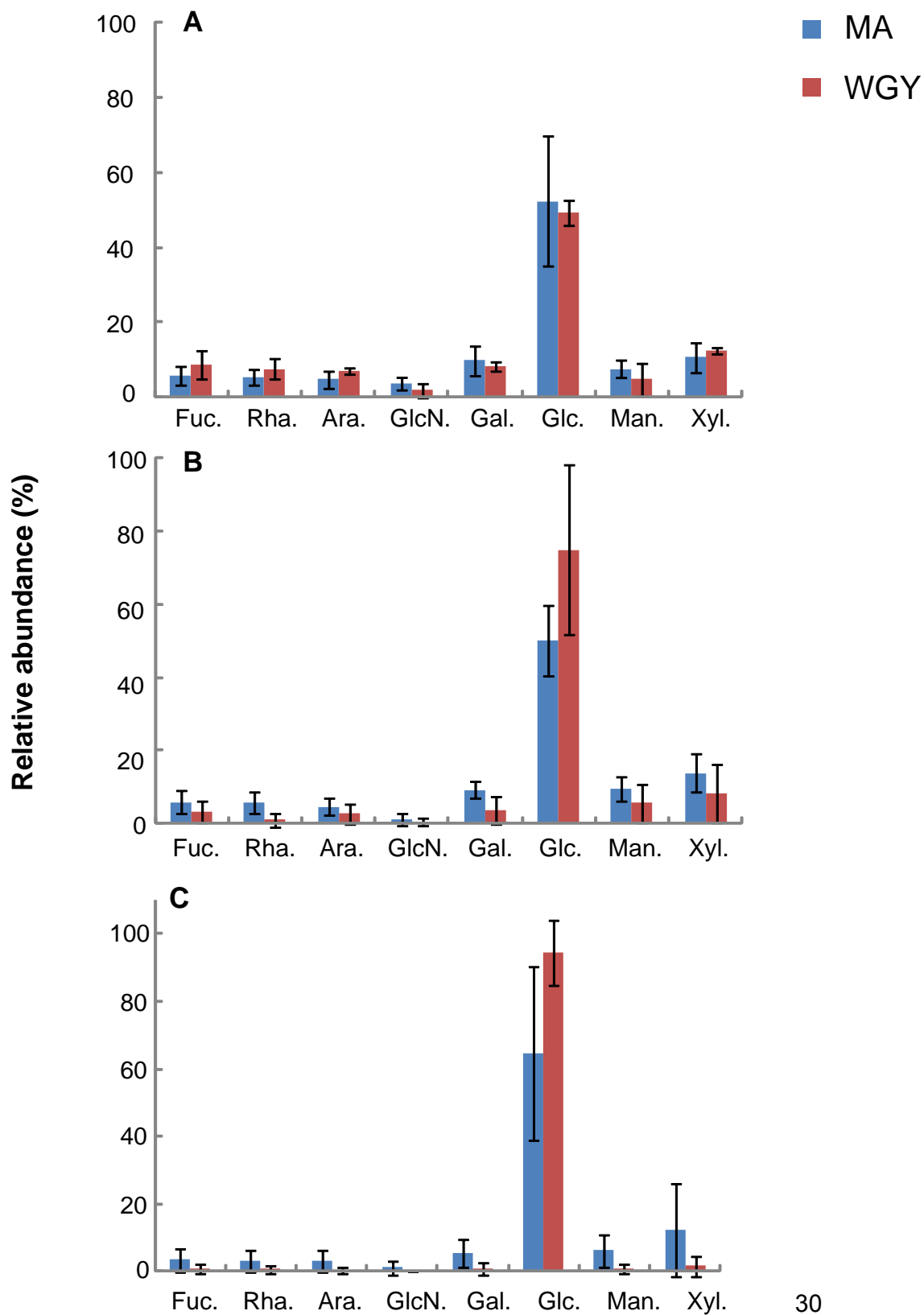


Figure 5