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

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Submitted to Biogeosciences (OUTPACE special issue)

16 October 2018

Abstract

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

1. Introduction

Gyres are oceanic deserts similar to those found in continental landscapes spanning an area of several thousands of Km and are characterized by low nutrient content and limited productivity (Raimbault et al., 2008; D'Hondt et al., 2009; Bender et al., 2016; de Verneil et al., 2017, 2018). Moreover, gyres are now considered as the world's plastic dumps (Law et al., 2010; Eriksen et al., 2013; Cozar et al., 2014), whereas their study may us help to understand future climate changes (Di Lorenzo et al., 2008; Zhang et al., 2014) and marine ecosystem functioning (Sibert et al., 2016; Browing et al., 2017). Among the five well-known oceanic gyres the South Pacific gyre, although the world's largest, has been less extensively studied mainly due to its remoteness from the main landmasses. Nonetheless, earlier studies indicated that Western Tropical South Pacific (WTSP) is a hot spot of N_2 fixation (Bonnet et al., 2013; Bonnet et al., 2017; Caffin et al., 2018) and recent studies have shown that there is a gradient of increasing oligotrophy from WTSP to the western part of the Pacific gyre (Moutin et al., 2018). The ultra-oligotrophic regime is reached in the center of the gyre, and then it decreases within the eastern part of the gyre toward the Chilean coast (Claustre et al., 2008) with high residual phosphate concentrations in the center of the gyre (Moutin et al., 2008).

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

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

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

Free monosaccharide concentrations range from 10 to100 nM; they account < 10% of total dissolved neutral sugars (TDNS), and experiments have shown that they are rapidly utilized (minutes to hours) by bacterioplankton and as such they are considered as labile organic matter (Rich et al., 1996; Skoog et al., 1999; Kirchman et al., 2001). Polysaccharide or dissolved combined neutral sugars (DCNS) concentrations range from 200-800 nM; they account for 80-95% of TDNS and experiments have shown that they disappear within time scales of days to months and, as such, they are considered as labile and semi-labile organic matter (Aluwihare and Repeta, 1999; Carlson and Hansell, 2015 and references therein). Other studies have shown that this labile and/or semi-labile organic matter accumulates in the surface ocean and may potentially be exported to depth contributing to the ocean carbon pump (Goldberg et al., 2010; Carlson and Hansell, 2015).

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

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

2. Materials and Methods

2.1 Sampling

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

Discrete seawater samples were collected from 12 L Niskin bottles equipped with Viton O-rings and silicon tubes to avoid chemical contamination. For DOC and DCNS analyses, samples were filtered through two pre-combusted (450°C for 24 h) GF/F filters using a custom-made all-glass/Teflon filtration syringe system. Samples for DOC (SD: 1-15 including LD: A, B ,C) were collected into precombusted glass ampoules (450°C, 6h) that were sealed after acidification with H_3PO_4 (85%) and stored in the dark at 4°C. Samples for DCNS (SD 1, 3-7, 9, 11, 13-15 including LD: C) were collected in 40-mL Falcon vials (previously cleaned with 10% of HCl and Milli-Q water) and frozen at -20°C until analysis.

3. Chemical and microbiological analyses

3.1. Dissolved organic carbon (DOC) determination

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

1999). Typical analytical precision was ± 0.1-0.5 µM C (SD) for multiple injections (3-4) of replicate samples. Consensus reference materials were injected every 12 to 17 samples to ensure stable operating conditions and were in the range 42-45 µM (lot # 07-14; (http://yyy.rsmas.miami.edu/groups/biogeochem/Table1.html).

3.2. Dissolved combined neutral sugars (DCNS) determination

3.2.1. Carbohydrate extraction and isolation

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

3.2.2. Liquid Chromatography

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

3.3. Bacterial production

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

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174 **4. Results**

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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, N_2 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 µM C (mean ±
204 sd: 67 ± 10 µM; n = 136) except at LDB (~85 µM 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 µM C (mean ± sd: 46 ± 4 µM; 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 µM C
210 (mean ± sd: 1.9 ± 0.8 µM; 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 µM 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 µM C) also monitored under stratification conditions (Goldberg
216 et al., 2010). Mesopelagic DCNS concentrations ranged from 0.3 to 2.4 µMC (average ± sd: 1.2 ±
217 0.6 µM; n = 68) (Fig. 4b; Table 1) and concur with previously reported literature values at the
218 ALOHA station (0.2-0.8 µMC; Kaiser and Benner, 2009) or in the Equatorial Pacific (0.8-1 µMC;
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 ± sd: 2.8
226 ± 1.3%; n = 41) and MA (range 0.8-7.0%; average ± sd: 2.8 ± 1.0%; n = 91) areas whereas deeper
227 than 200 m they were 2.4 ± 1.0% (n = 23) and 2.7 ± 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 ± 18%
233 (n = 132) of the DCNS in epipelagic waters and 64 ± 21% (n = 68) in mesopelagic waters (Table 1).
234 Epipelagic glucose concentrations (DCGlc-C) averaged 1.0 ± 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 ±

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

5. Discussion

5.1 DOC and DCNS stocks in relation with biological activity

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

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

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

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

The high stock of DOC_{EX} measured in WGY was also characterized by an elevated residence time ($T_{r\,SL}$) calculated as the ratio of DOC_{EX} / BCD. This ratio is calculated based on the assumption that DOC_{EX} is representative of the DOC_{SL} and the latter pool turnover is at the scale of seasonal mixing (i.e weeks to months) whereas the BP, as determined with leucine technique on short incubation times (1-2 hours), tracks only the ultra-labile to labile organic matter consumption and not DOC_{SL} utilization. Biodegradation experiments (3 experiments, duration 10 days each) 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 ± 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 (αCDOM(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.,

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

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

5.2 DCNS dynamics across the South West Pacific

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

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

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

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

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

6. Conclusions

This study showed a rather uniform distribution of DOC and DCNS concentrations in surface waters across an increasing oligotrophic gradient in the South West Pacific Ocean during the OUTPACE cruise. Nevertheless, our results showed that DOC and DOC_{EX} stocks were by ~40% in WGY than the MA area, accompanied with higher residence times in the WGY area suggesting an accumulation of semi-labile material in the euphotic zone of WGY. Although DCNS accounted a small fraction of DOC_{SL} (~7%) our results showed that DCNS or polysaccharides also exhibited a higher residence time ($T_{r\ DCNS\text{-}C}$) in the WGY than in the MA area indicating that DCNS persist longer in the WGY. This $T_{r\ DCNS\text{-}C}$ is calculated on the basis of many assumptions on DNCS hydrolysis rates that were not practically determined, showing the need to estimate such fluxes in order to better estimate the dynamics of carbohydrates. Glucose was the major monosaccharide in both areas (51 - 55%) and its relative abundance increased with depth along with a decrease of the DCNS yields indicating a preferential removal of the other carbohydrates relative to glucose. Clearly further investigations are warranted to better characterize the semi-labile DOC pool in terms of combined and free amino acids distribution in relation with N_2 fixation.

Acknowledgements

This is a contribution of the OUTPACE (Oligotrophy from Ultra-oligoTrophy PACific Experiment) project lead by T. Moutin and S. Bonnet and funded by the French national research agency (ANR-14-CE01-0007-01), the LEFE-CyBER program (CNRS-INSU), the GOPS program (IRD) and CNES (BC T23, ZBC 4500048836). The OUTPACE cruise (http://dx.doi.org/10.17600/15000900) was managed by the MIO from Marseille (France). The authors thank the crew of the R/V L'Atalante for outstanding shipboard operation. G. Rougier and M. Picheral are thanked for their efficient help in CTD rosette management and data processing. C. Schmechtig is acknowledged for the LEFE CYBER database management. We also thank A. Lozingot for administrative aid for the OUTPACE project. The authors also acknowledge Prof. R. Benner and one anonymous reviewer for valuable comments and fruitful discussions. M.B. was funded by the People Programme (Marie Skłodowska-Curie Actions) of the European Union's Seventh Framework Programme (FP7/2007-2013) under REA grant agreement number 625185. C.P. received support from the PACA region (MANDARINE project, grant number 2008-10372) and Aix Marseille University (ORANGE project, FI-2011).

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Figure and Table captions:

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

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

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

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

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

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

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

Figure 7: Residence time (days) of semi labile DOC ($T_{r\ SL}$) and DCNS-C ($T_{r\ DCNS\text{-}C}$) for MA and WGY areas. * $T_{r\ SL}$ and $T_{r\ DCNS\text{-}C}$ were statistically different between MA and WGY areas (Man-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	

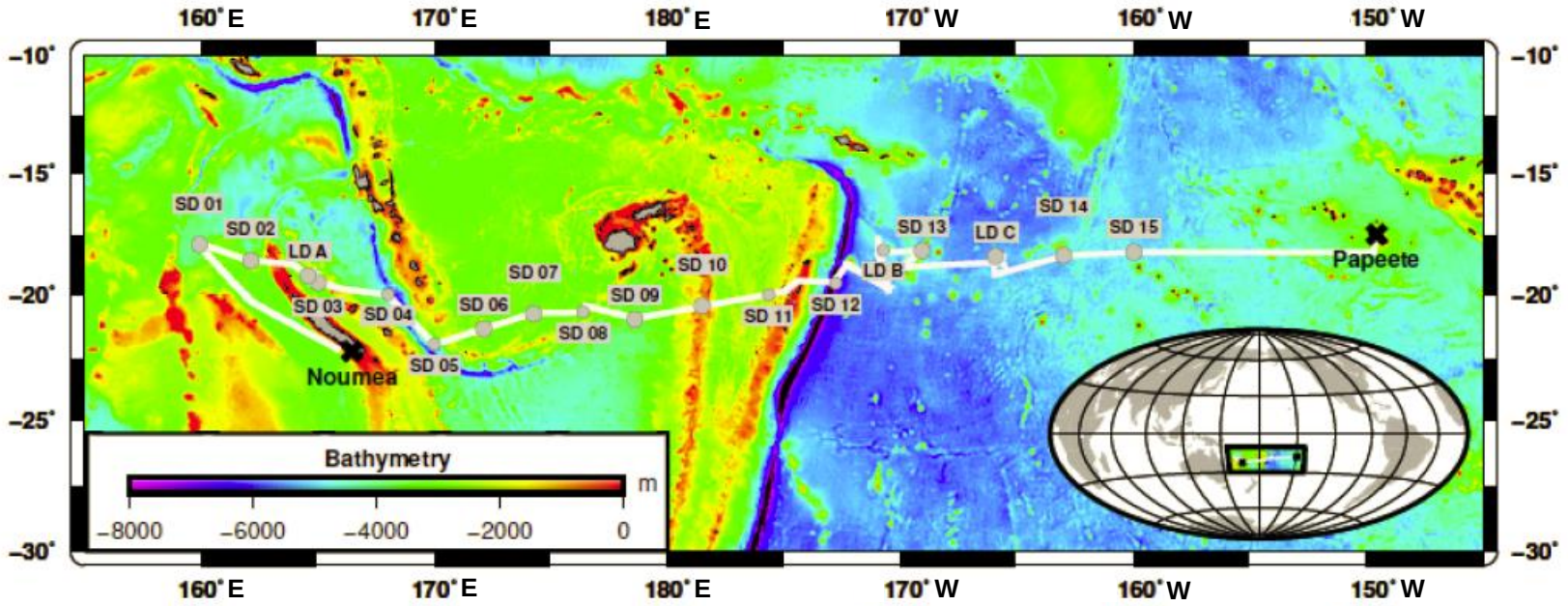
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Figure 1

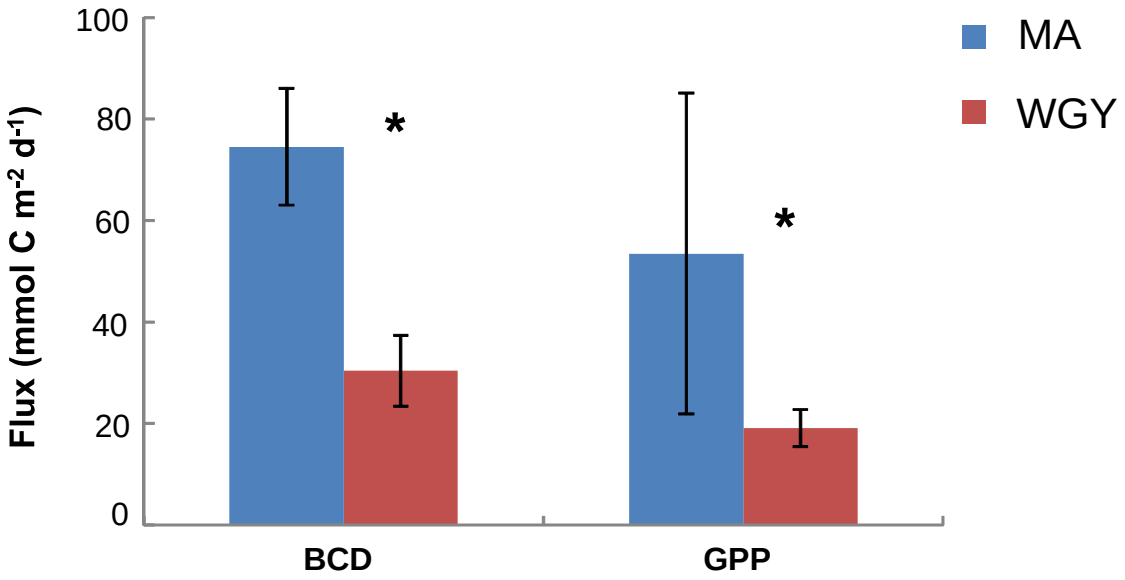
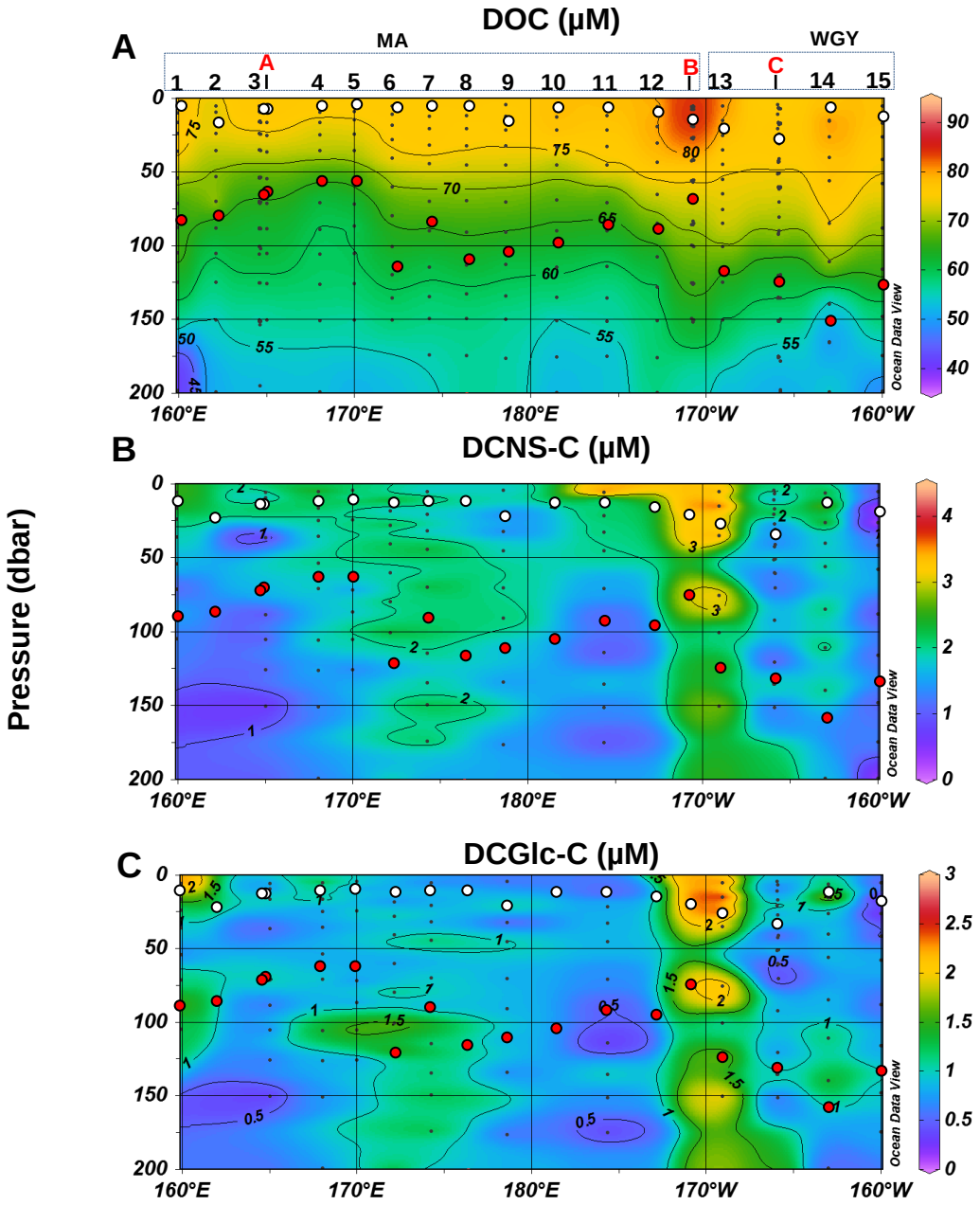


Figure 2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DOC (μM)
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A
B
C
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200
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170°E
180°E
170°W
160°W
Ocean Data View
90
80
70
60
50
40
B
DCNS-C (μM)
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DCGlc-C (μM)
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2.5
2
1.5
1
0.5
0
Pressure (dbar)

Figure 3

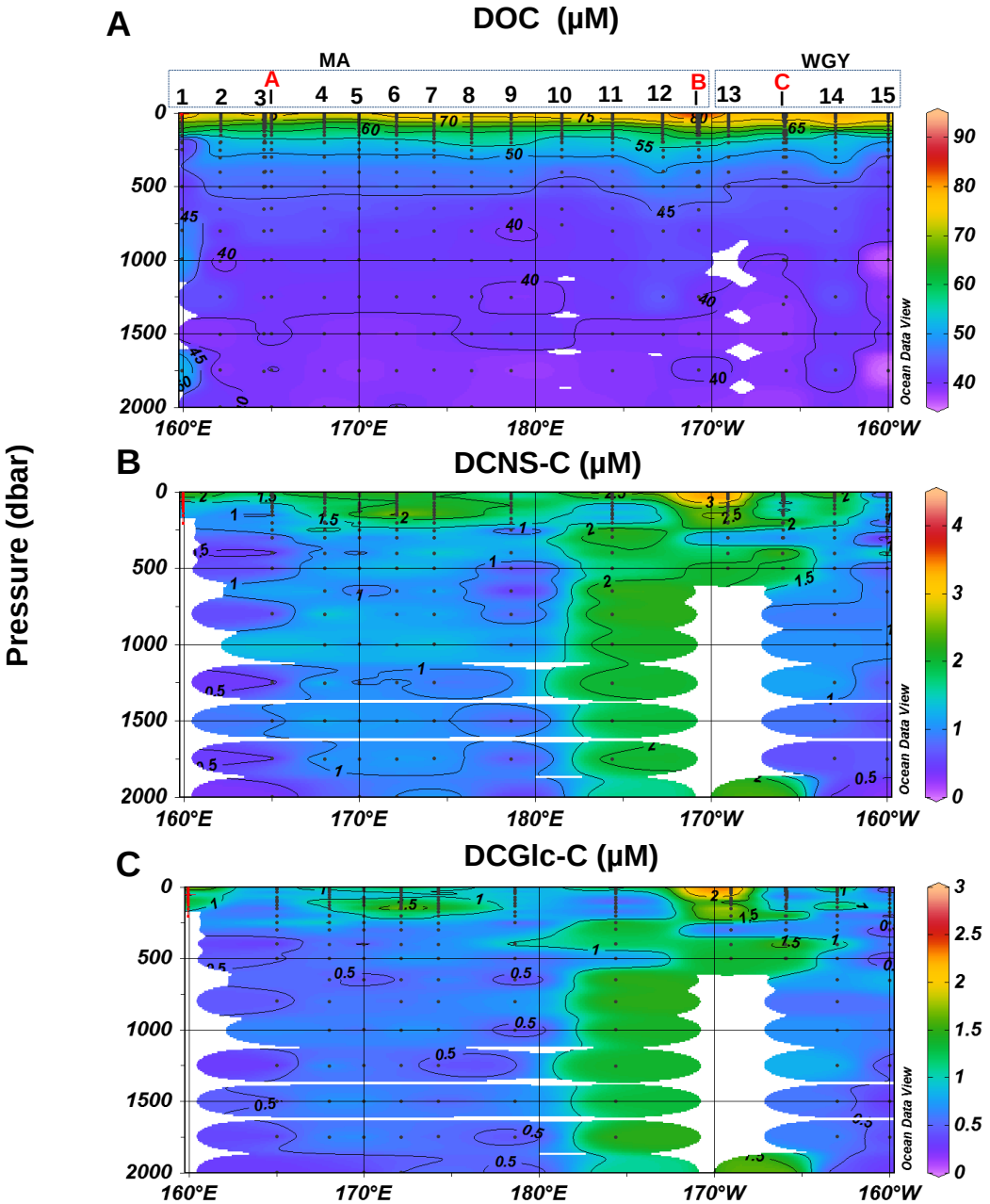
A
DOC (μM)
MA
WGY
A
B
C
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
Pressure (dbar)
0
500
1000
1500
2000
160°E
170°E
180°E
170°W
160°W
Ocean Data View
B
DCNS-C (μM)
C
DCGlc-C (μM)

Figure 4

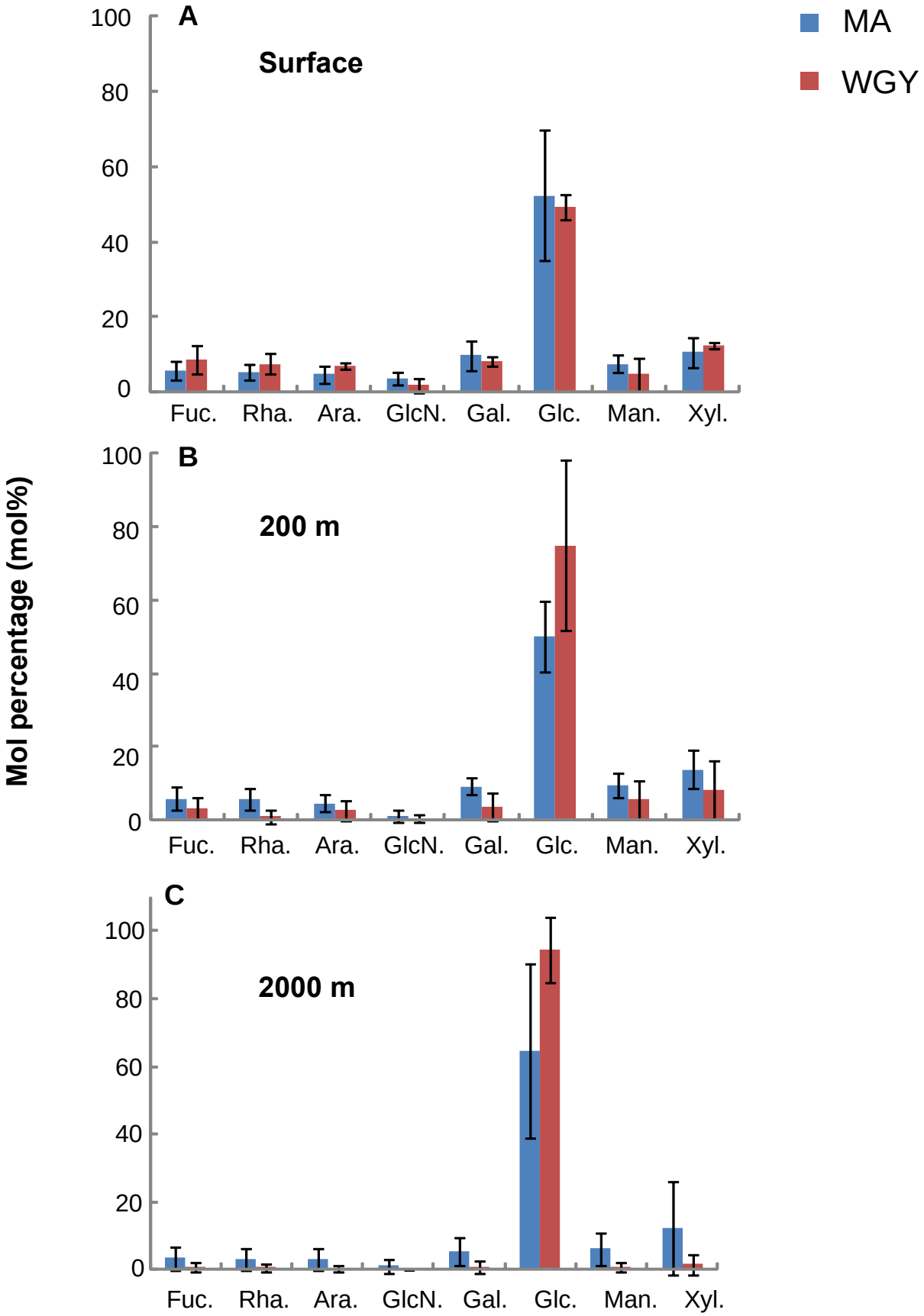
A
Surface
B
200 m
C
2000 m
MA
WGY
Mol percentage (mol%)
100
80
60
40
20
0
Fuc.
Rha.
Ara.
GlcN.
Gal.
Glc.
Man.
Xyl.

Figure 5

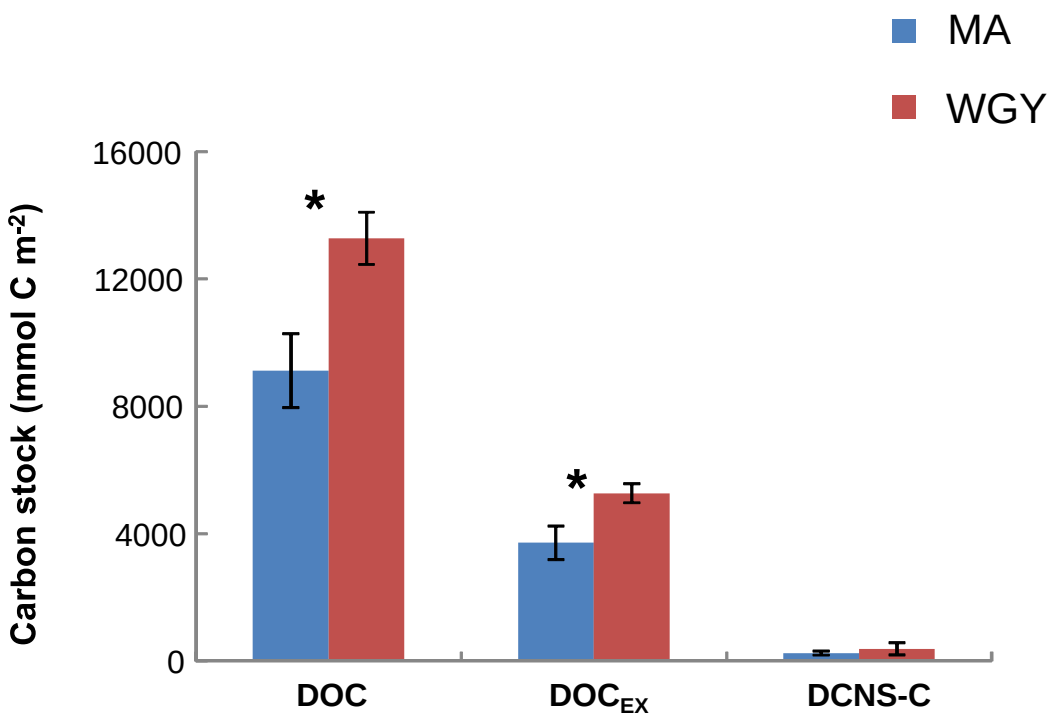
MA
WGY
16000
12000
8000
4000
0
Carbon stock (mmol C m-2)
*
*
DOC
DOCEX
DCNS-C

Figure 6

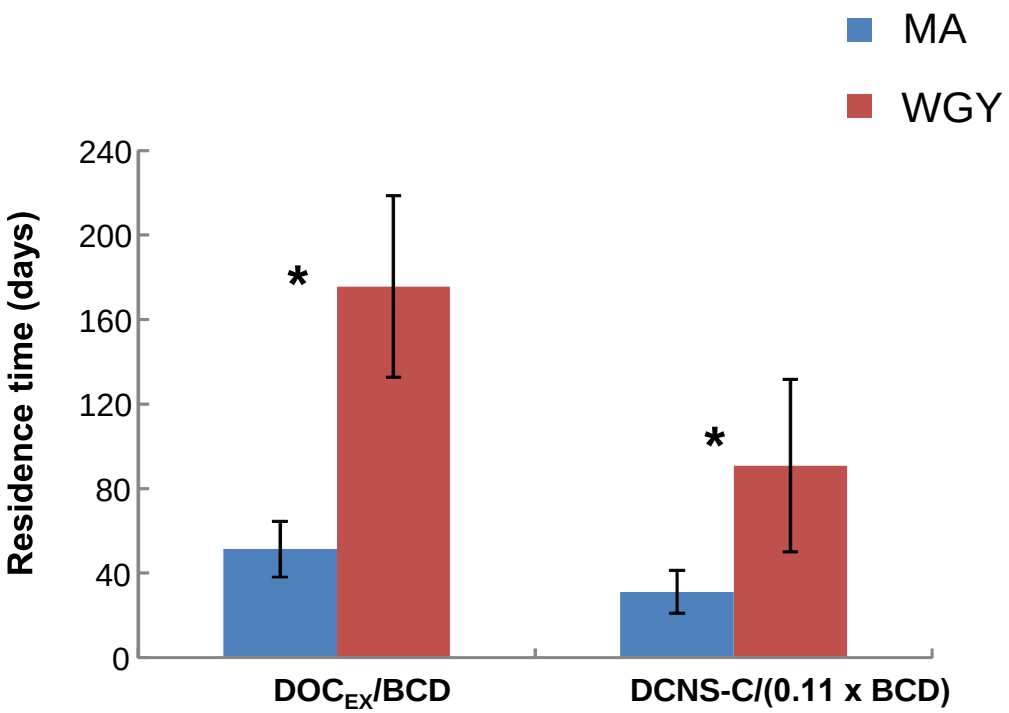
MA
WGY
Residence time (days)
240
200
160
120
80
40
0
*
*
DOC$_{EX}$/BCD
DCNS-C/(0.11 x BCD)

Figure 7

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

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Submitted to Biogeosciences (OUTPACE special issue)

5 October 2018

Abstract

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

1. Introduction

Gyres are oceanic deserts similar to those found in continental landscapes spanning an area of several thousands of Km and are characterized by low nutrient content and limited productivity (Raimbault et al., 2008; D'Hondt et al., 2009; Bender et al., 2016; de Verneil et al., 2017, 2018). Moreover, gyres are now considered as the world's plastic dumps (Law et al., 2010; Eriksen et al., 2013; Cozar et al., 2014), whereas their study may us help to understand future climate changes (Di Lorenzo et al., 2008; Zhang et al., 2014) and marine ecosystem functioning (Sibert et al., 2016; Browing et al., 2017). Among the five well-known oceanic gyres the South Pacific gyre, although the world's largest, has been less extensively studied mainly due to its remoteness from the main landmasses. Nonetheless, earlier studies indicated that Western Tropical South Pacific (WTSP) is a hot spot of N_2 fixation (Bonnet et al., 2013; Bonnet et al., 2017; Caffin et al., 2018) and recent studies have shown that there is a gradient of increasing oligotrophy from WTSP to the western part of the Pacific gyre (Moutin et al., 2018). The ultra-oligotrophic regime is reached in the center of the gyre, and then it decreases within the eastern part of the gyre toward the Chilean coast (Claustre et al., 2008) with high residual phosphate concentrations in the center of the gyre (Moutin et al., 2008).

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

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

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

Free monosaccharide concentrations range from 10 to100 nM; they account < 10% of total dissolved neutral sugars (TDNS), and experiments have shown that they are rapidly utilized (minutes to hours) by bacterioplankton and as such they are considered as labile organic matter (Rich et al., 1996; Skoog et al., 1999; Kirchman et al., 2001). Polysaccharide or dissolved combined neutral sugars (DCNS) concentrations range from 200-800 nM; they account for 80-95% of TDNS and experiments have shown that they disappear within time scales of days to months and, as such, they are considered as labile and semi-labile organic matter (Aluwihare and Repeta, 1999; Carlson and Hansell, 2015 and references therein). Other studies have shown that this labile and/or semi-labile organic matter accumulates in the surface ocean and may potentially be exported to depth contributing to the ocean carbon pump (Goldberg et al., 2010; Carlson and Hansell, 2015).

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

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

2. Materials and Methods

2.1 Sampling

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

Discrete seawater samples were collected from 12 L Niskin bottles equipped with Viton O-rings and silicon tubes to avoid chemical contamination. For DOC and DCNS analyses, samples were filtered through two pre-combusted (450°C for 24 h) GF/F filters using a custom-made all-glass/Teflon filtration syringe system. Samples for DOC (SD: 1-15 including LD: A, B ,C) were collected into precombusted glass ampoules (450°C, 6h) that were sealed after acidification with H_3PO_4 (85%) and stored in the dark at 4°C. Samples for DCNS (SD 1, 3-7, 9, 11, 13-15 including LD: C) were collected in 40-mL Falcon vials (previously cleaned with 10% of HCl and Milli-Q water) and frozen at -20°C until analysis.

3. Chemical and microbiological analyses

3.1. Dissolved organic carbon (DOC) determination

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

1999). Typical analytical precision was ± 0.1-0.5 µM C (SD) for multiple injections (3-4) of replicate samples. Consensus reference materials were injected every 12 to 17 samples to ensure stable operating conditions and were in the range 42-45 µM (lot # 07-14; (http://yyy.rsmas.miami.edu/groups/biogeochem/Table1.html).

3.2. Dissolved combined neutral sugars (DCNS) determination

3.2.1. Carbohydrate extraction and isolation

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

3.2.2. Liquid Chromatography

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

3.3. Bacterial production

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

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

4. Results

4.1 General observations

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

a. Most of the biogeochemical parameters examined in the OUTPACE cruise (chlorophyll *a* concentrations, primary production, BP, BCD, N_2 fixation rates, and nutrient concentrations) showed significantly higher values in the MA area than in the WGY area (Moutin et al., 2018; Van Wambeke et al., 2018; Benavides et al., 2018; Caffin et al., 2018). These differences were also reflected by the distribution of the diazotrophic communities detected in both areas further highlighting the different dynamics across the oligotrophic gradient (Stenegren et al., 2018; Moutin et al., 2017, 2018). The net heterotrophic/autotrophic status of the MA and WGY areas has been discussed in previous investigations by comparing BCD and gross primary production (GPP) (Fig. 2). By using propagation of errors, Van Wambeke et al. (2018) concluded that GPP minus BCD could not be considered different from zero at most of the stations investigated (11 out of 17)

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

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

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

4.2 DCNS yields and composition

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 ± sd: 2.8
226 ± 1.3%; n = 41) and MA (range 0.8-7.0%; average ± sd: 2.8 ± 1.0%; n = 91) areas whereas deeper
227 than 200 m they were 2.4 ± 1.0% (n = 23) and 2.7 ± 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 ± 18%
233 (n = 132) of the DCNS in epipelagic waters and 64 ± 21% (n = 68) in mesopelagic waters (Table 1).
234 Epipelagic glucose concentrations (DCGlc-C) averaged 1.0 ± 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 ±

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

5. Discussion

5.1 DOC and DCNS stocks in relation with biological activity

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

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

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

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

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

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

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

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

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

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

5.2 DCNS dynamics across the South West Pacific

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

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

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

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

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

6. Conclusions

This study showed a rather uniform distribution of DOC and DCNS concentrations in surface waters across an increasing oligotrophic gradient in the South West Pacific Ocean during the OUTPACE cruise. Nevertheless, our results showed that DOC and DOC_{EX} stocks were by ~40% in WGY than the MA area, accompanied with higher residence times in the WGY area suggesting an accumulation of semi-labile material in the euphotic zone of WGY. Although DCNS accounted a small fraction of DOC_{SL} (~7%) our results showed that DCNS or polysaccharides also exhibited a higher residence time ($T_{r\ DCNS\text{-}C}$) in the WGY than in the MA area indicating that DCNS persist longer in the WGY. This $T_{r\ DCNS\text{-}C}$ is calculated on the basis of many assumptions on DNCS hydrolysis rates that were not practically determined, showing the need to estimate such fluxes in order to better estimate the dynamics of carbohydrates. Glucose was the major monosaccharide in both areas (51 - 55%) and its relative abundance increased with depth along with a decrease of the DCNS yields indicating a preferential removal of the other carbohydrates relative to glucose. Clearly further investigations are warranted to better characterize the semi-labile DOC pool in terms of combined and free amino acids distribution in relation with N_2 fixation.

Acknowledgements

This is a contribution of the OUTPACE (Oligotrophy from Ultra-oligoTrophy PACific Experiment) project lead by T. Moutin and S. Bonnet and funded by the French national research agency (ANR-14-CE01-0007-01), the LEFE-CyBER program (CNRS-INSU), the GOPS program (IRD) and CNES (BC T23, ZBC 4500048836). The OUTPACE cruise (http://dx.doi.org/10.17600/15000900) was managed by the MIO from Marseille (France). The authors thank the crew of the R/V L'Atalante for outstanding shipboard operation. G. Rougier and M. Picheral are thanked for their efficient help in CTD rosette management and data processing. C. Schmechtig is acknowledged for the LEFE CYBER database management. We also thank A. Lozingot for administrative aid for the OUTPACE project. The authors also acknowledge Prof. R. Benner and one anonymous reviewer for valuable comments and fruitful discussions. M.B. was funded by the People Programme (Marie Skłodowska-Curie Actions) of the European Union's Seventh Framework Programme (FP7/2007-2013) under REA grant agreement number 625185. C.P. received support from the PACA region (MANDARINE project, grant number 2008-10372) and Aix Marseille University (ORANGE project, FI-2011).

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Figure and Table captions:

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

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

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

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

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

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

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

Figure 7: Residence time (days) of semi labile DOC ($T_{r\ SL}$) and DCNS-C ($T_{r\ DCNS\text{-}C}$) for MA and WGY areas. * $T_{r\ SL}$ and $T_{r\ DCNS\text{-}C}$ were statistically different between MA and WGY areas (Man-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	

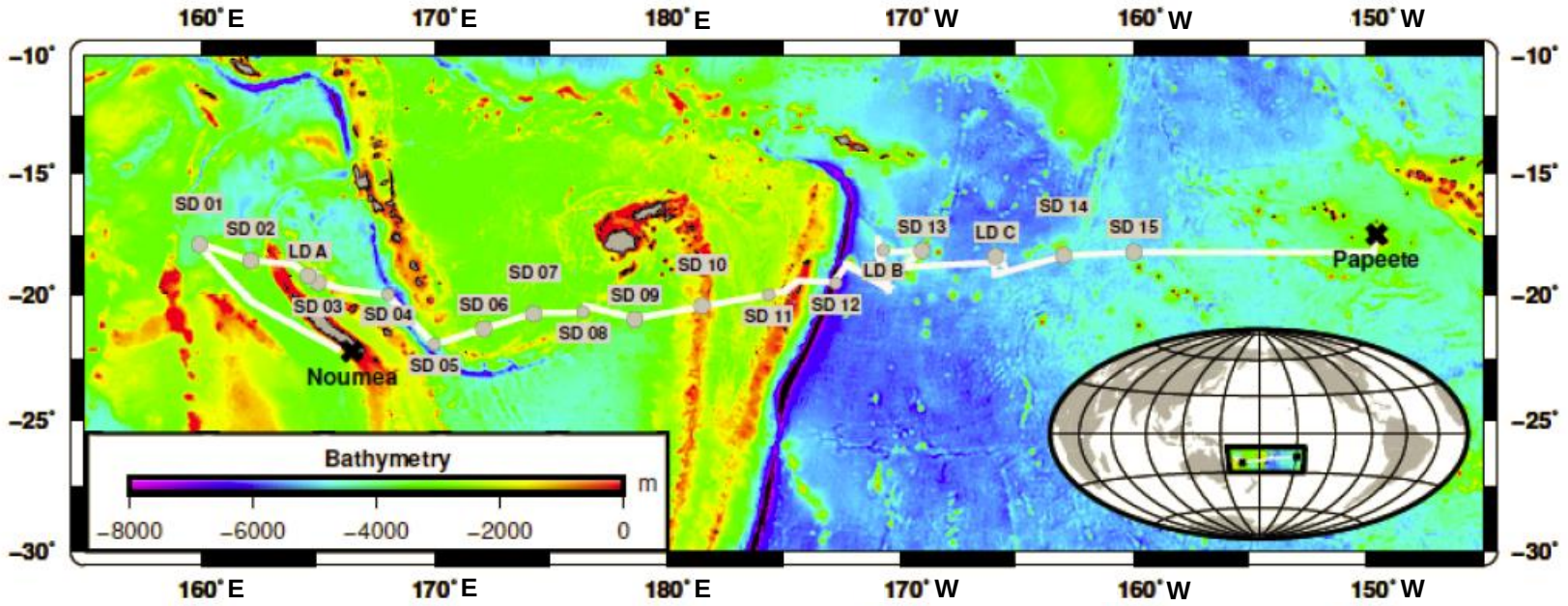
160° E
170° E
180° E
170° W
160° W
150° W
−10°
−15°
−20°
−25°
−30°
SD 01
SD 02
LD A
SD 03
SD 04
SD 05
SD 06
SD 07
SD 08
SD 09
SD 10
SD 11
SD 12
LD B
SD 13
LD C
SD 14
SD 15
Noumea
Papeete
Bathymetry
m
−8000
−6000
−4000
−2000
0

Figure 1

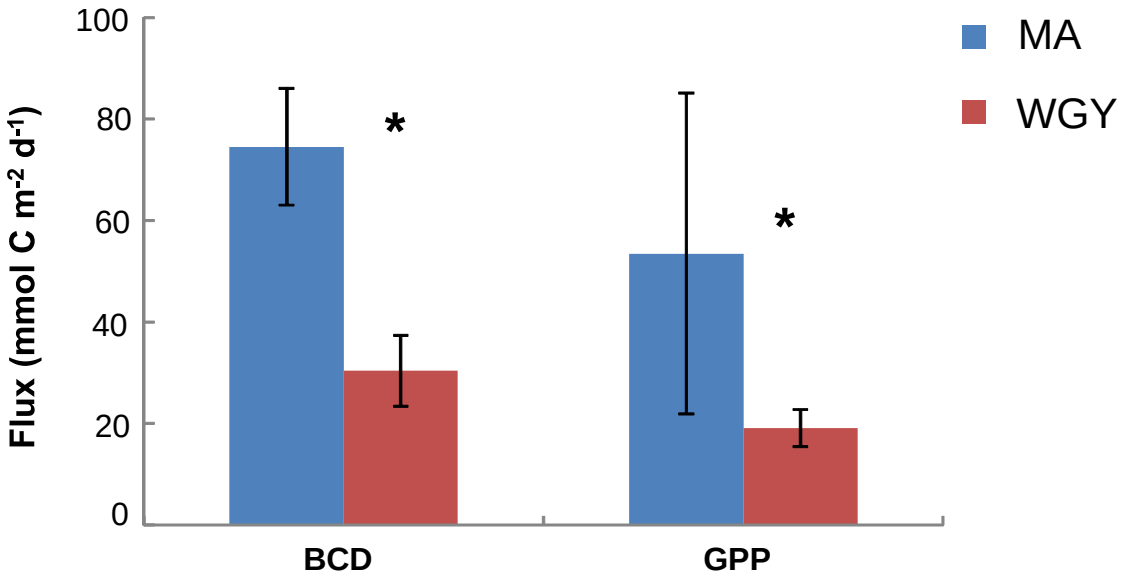

Figure 2

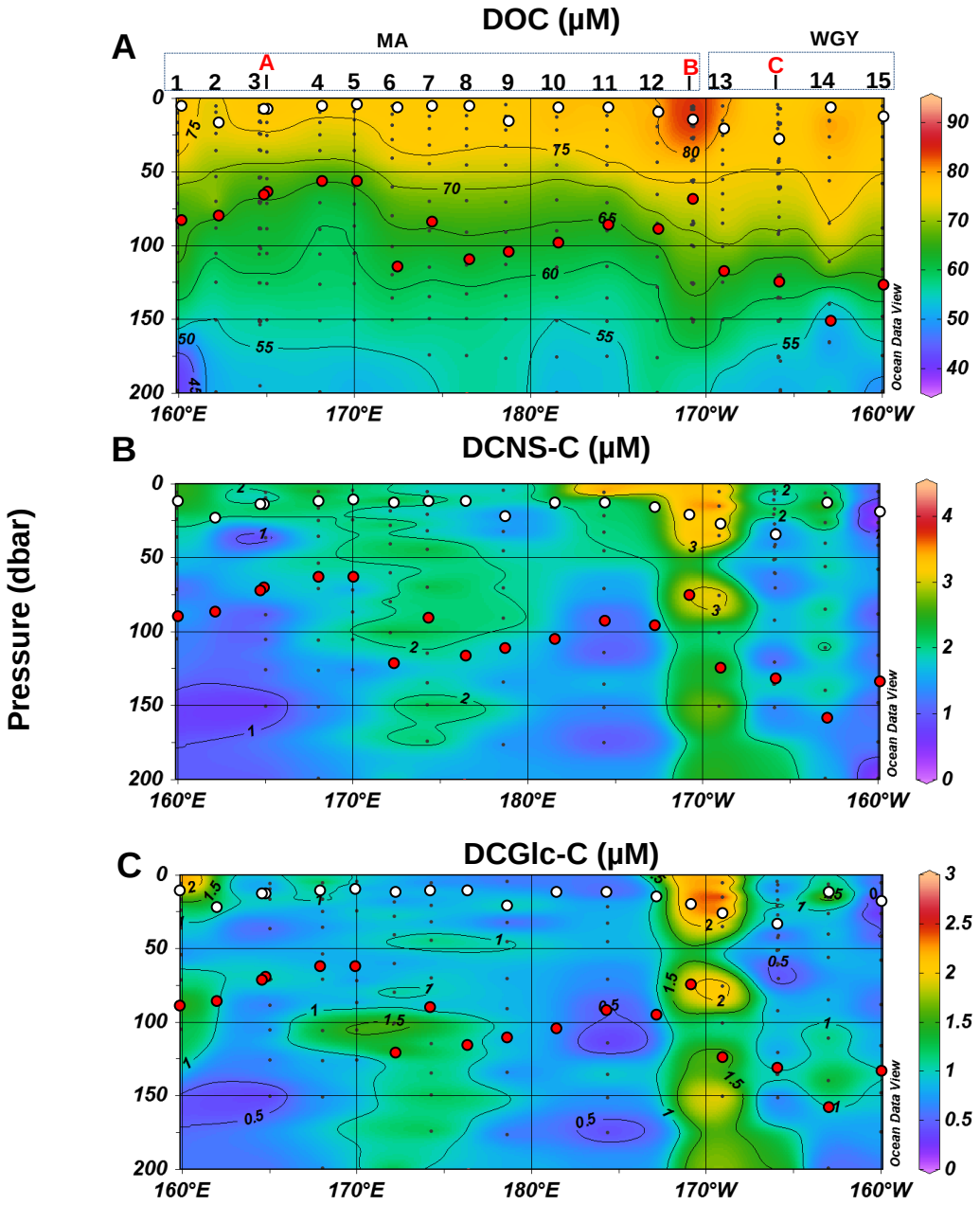
A
DOC (μM)
MA
WGY
A
B
C
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
0
50
100
150
200
160°E
170°E
180°E
170°W
160°W
Ocean Data View
90
80
70
60
50
40
B
DCNS-C (μM)
4
3
2
1
0
C
DCGlc-C (μM)
3
2.5
2
1.5
1
0.5
0
Pressure (dbar)

Figure 3

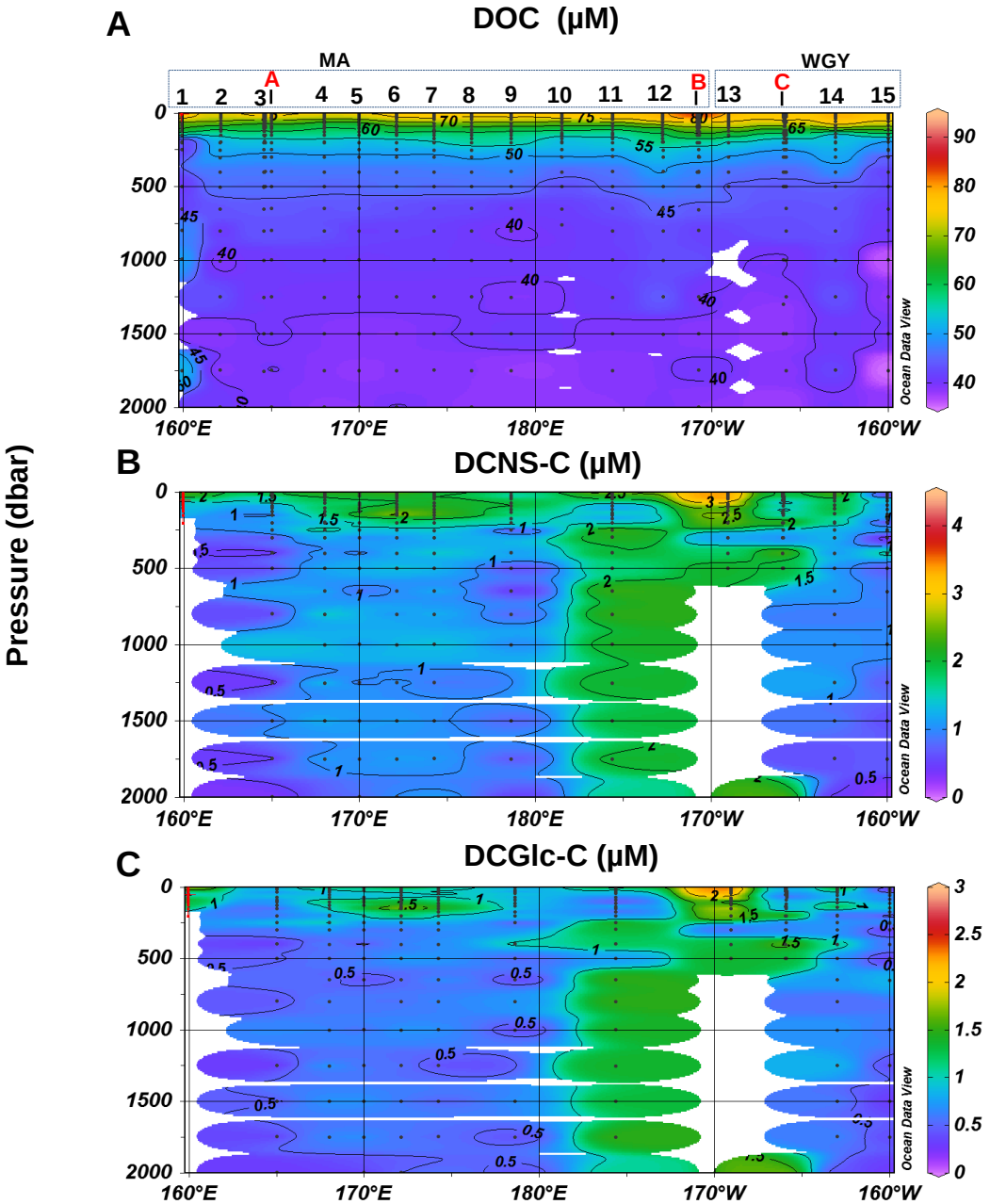
A
DOC (μM)
MA
WGY
A
B
C
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
Pressure (dbar)
0
500
1000
1500
2000
160°E
170°E
180°E
170°W
160°W
Ocean Data View
B
DCNS-C (μM)
C
DCGlc-C (μM)

Figure 4

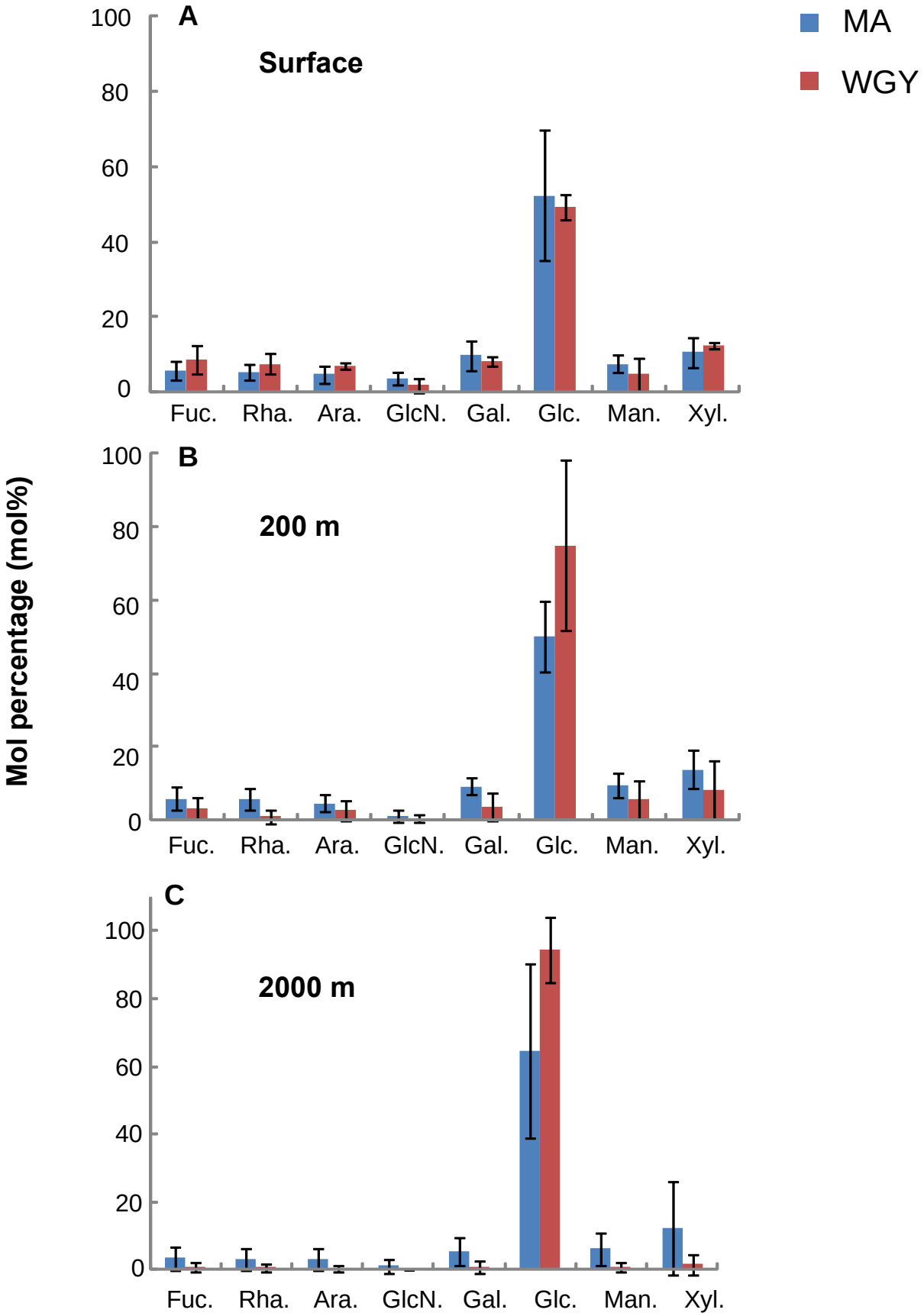
A
Surface
B
200 m
C
2000 m
MA
WGY
Mol percentage (mol%)
100
80
60
40
20
0
Fuc.
Rha.
Ara.
GlcN.
Gal.
Glc.
Man.
Xyl.

Figure 5

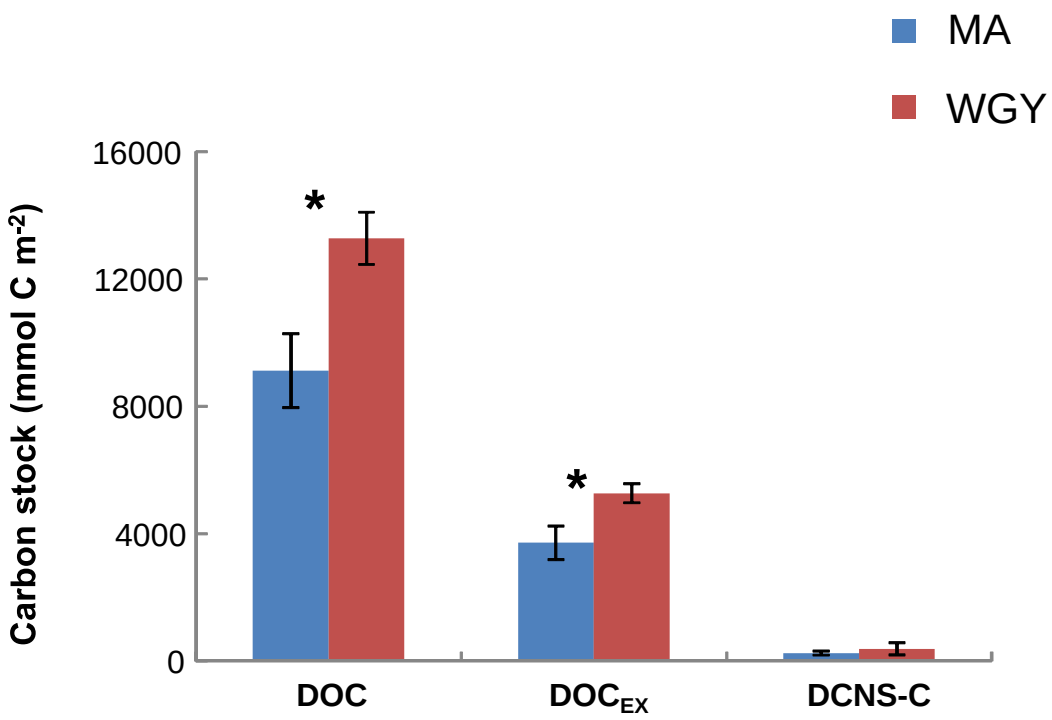
MA
WGY
16000
12000
8000
4000
0
Carbon stock (mmol C m-2)
*
*
DOC
DOCEX
DCNS-C

Figure 6

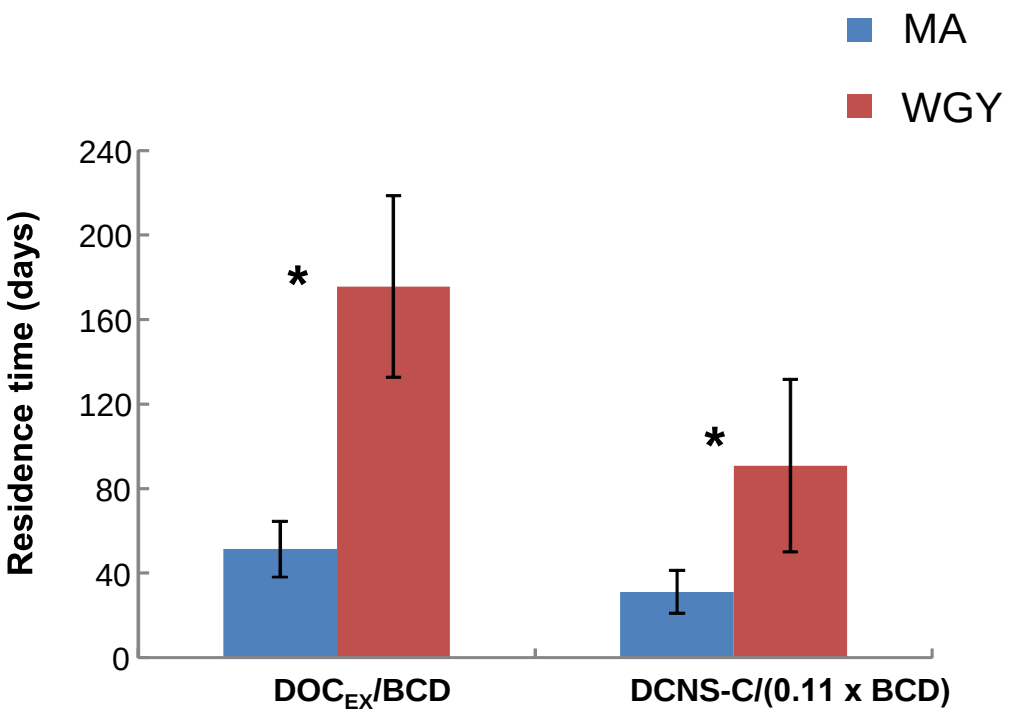
MA
WGY
Residence time (days)
240
200
160
120
80
40
0
*
*
DOC$_{EX}$/BCD
DCNS-C/(0.11 x BCD)

Figure 7