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Seasonal organic matter dynamics in the Great Barrier Reef lagoon: contribution of carbohydrates and proteins

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Abstract

Organic matter (OM) plays a fundamental role in sustaining the high productivity of coral reef ecosystems. Carbohydrates and proteins constitute two of the major chemical classes identified in the OM pool and are used as indicators of bioavailability due to their fast turn-over. We conducted three cruises across the southern shelf of the Great Barrier Reef (GBR) during the early dry, late dry and wet seasons in 2009-2010 to 1) assess the relative bioavailability of particulate (POM) and dissolved (DOM) organic matter, 2) track the temporal and spatial variability in the carbohydrate and protein contribution to the OM pool, and 3) assess factors influencing protein and carbohydrate fractions of the OM pool.

Generally, higher concentrations of particulate carbohydrates were found during the wet season, while similar concentrations of particulate protein were found during the three seasons. Both the dissolved carbohydrates and proteins had highest levels during the early dry season and lowest during the wet season, suggesting seasonal variations in the chemical composition of the DOM pool. Spatially, carbohydrates showed higher concentrations at the inshore stations, while no clear spatial pattern was found for the protein concentrations. On average carbohydrates and proteins accounted for a similar fraction (13 ± 5 and 12 ± 6% respectively) of POM, while carbohydrates accounted for a smaller fraction of the DOM than the proteins (6 ± 3 and 13 ± 10 %). This suggests that the POM bioavailability was similar between seasons, while the DOM bioavailability varied seasonally with highest levels during the early dry season. This demonstrates that carbohydrates and proteins in the GBR have temporal and spatial variations. Our statistical analysis showed that 1) both carbohydrates and proteins were related with the POM and DOM C:N:P stoichiometry, demonstrating that estimates provide useful measures of OM

bioavailability in the GBR and 2) the carbohydrates and proteins levels were controlled by the amount of nutrients and POM, which in this system is mainly of plankton origin.

Overall this study shows that the POM and DOM pools contain highly bioavailable compounds and that carbohydrate and proteins could play an important role in sustaining the productivity of the GBR.

Keywords: particulate organic matter; dissolved organic matter; carbohydrates; proteins; tropical; Great Barrier Reef.

1. Introduction

Organic matter (OM) in marine systems is a highly heterogeneous pool, consisting of millions of different compounds which vary in chemical composition, molecular weight and biological accessibility (Benner, 2002). Due to this complexity, OM is often divided into size fractions for convenience. The OM retained on a filter (pore-size between 0.2 to 0.7 μm) is known as particulate (POM), whereas the filterable material is named dissolved (DOM). POM is a mixture of living biomass (e.g. phytoplankton) and non-living detritus (e.g. fecal pellets), while the DOM pool is mainly lifeless (Hedges, 2002). The ocean OM inventory shows that 97% of all the organic carbon is in the DOM fraction, while the POM presents the remaining 3% (Hedges, 2002). In general it is assumed that the POM fraction is less degraded and more bioavailable to degradation than DOM, but both pools contain a labile pool with short turnover times (from hours to days), a semi-labile pool with longer turnover times (from weeks to months) and a recalcitrant background pool (Hansell, 2013).

Carbohydrates and proteins constitute two of the major chemical classes identified in marine biomass (Fraga, 2001) and the bulk of the biomolecules characterized within the DOM pool (Benner, 2002). In coastal waters many potential internal sources (autochthonous) have been identified, such as plankton organisms (Nagata, 2000), macroalgae (Wada et al., 2008), macrophytes, (Søndergaard, 1981), and sediments (Burdige et al., 2000), but external (allochthonous) sources, including submarine groundwater discharge (Santos et al., 2012) and rivers (Panagiotopoulos et al., 2014) are also important.

Some studies have shown that both internally and externally derived OM can be utilized by marine microbes, with the bioavailability depending on the microbial community composition, molecular size and chemical composition (Benner and

Opsahl, 2001; Amon and Benner, 1996; Moran and Hodson, 1990). Carbohydrates and proteins constitute an important source of carbon and nitrogen for heterotrophic bacteria (e.g., Simon and Rosenstock, 2007), and generally both are rapidly degraded, although carbohydrates are less bioavailable than proteins (Lønborg et al., 2010). Nonetheless, a sub-fraction of the carbohydrates and proteins can accumulate in the dissolved pool for weeks to years, due to factors such as physical protection from degradation and inorganic nutrient limitation (Nagata and Kirchman, 1996; Borch and Kirchman, 1999). Despite the range in bioavailability, the proportional contribution of carbohydrates and proteins to the POM and DOM pools (known as % yield of POM or DOM) have been shown to decrease with ongoing microbial degradation. Therefore, they have been used as proxies to trace the bioavailability, or the relative 'freshness', of the ambient OM (Skoog and Benner, 1997; Amon et al., 2001), with higher yields indicating a fresher and more bioavailable pool.

Tropical coastal waters receive roughly one order of magnitude more input of terrestrial derived carbon, nitrogen and phosphorus compared to temperate and Arctic regions (Brunskill 2010). Despite the large inputs, the surface waters of tropical oceans are characterized by low dissolved nutrient (both organic and inorganic) concentrations and plankton biomass (Epply et al., 1973). Nearly all of the terrestrial material, combined with the OM produced in tropical coastal waters, is degraded within the continental shelf, suggesting that only very recalcitrant material is exported from these waters to the adjacent ocean. This intensive microbial degradation is promoted by factors such as elevated temperatures (typically between 20 and 30ºC) and sunlight levels (Alongi and McKinnon, 2005; Bouillon and

Connolly, 2009). This recycling of OM can greatly modify the bioavailability, quantities and composition of the OM pools over temporal and spatial scales.

Coral reefs are primarily found in tropical coastal waters, where they physically shape the ecosystems, mainly by their ability to produce large calcium carbonate structures. Traditionally, coral reef ecosystems have been viewed as self-sufficient systems (Odum and Odum, 1955), but more recently this view has been challenged with coral reefs now considered open systems acquiring OM and nutrients from the surrounding ocean, which is recycled or accumulated within the system, or exported (Hatcher, 1997). As such these highly productive ecosystems are adapted to the oligotrophic oceans, but it still remains to be understood the importance of different sources of energy and nutrients to maintain their productivity (e.g., Alldredge et al., 2013). While the fundamental role of OM as a food web driver, which controls the transfer of energy and nutrients, is thought to sustain the productivity, few studies have investigated changes in the nutritional quality and chemistry of pelagic OM in coral reef ecosystems.

In this study we analysed the temporal and spatial variability of particulate and dissolved carbohydrates and proteins over a comprehensive cross-shelf gradient in the southern section of the Great Barrier Reef (GBR), Australia. The objectives of this work were to 1) measure the relative bioavailability of POM and DOM, 2) track the temporal and spatial distribution and contribution of carbohydrates and proteins to the OM pool , and 3) determine factors which might affect the variability in particulate and dissolved carbohydrates and proteins in this system. As carbohydrates and proteins are useful indictors of the OM pool bioavailability this data will help us better understand how important these chemical classes are for sustaining the productivity of tropical coastal waters.

2. Materials and Methods

2.1. Study area

The Great Barrier Reef (GBR) is situated on the continental shelf and slope of Australia's north-eastern coast ranging between 9 and 24˚S. The GBR has a width of up to 330 km and extends over a total area of 344,000 km^2 (Fig. 1). Around seven percent of this area is covered by coral reefs (total of ~ 3700 reefs) which are mainly located offshore; with the open water body separating the reef matrix from the mainland known as the GBR lagoon. This lagoon has a water depth of about 10-20 m close to shore increasing to 40 m towards the reefs, representing a total area of approx. 238,700 km^2. Within the central part of the lagoon, currents are primarily northward, driven by the predominant south-easterly trade wind regime from March through October (Austral winter), and winds are more variable during the austral summer (Wolanski 1994). Over the continental slope, the East Australian Current flows poleward and enters onto the shelf and outer lagoon by passages between reefs (Benthuysen et al., 2016) (Fig. 1). Cross-shelf exchange from upwelling contributes to the onshore flux of nutrients from the Coral Sea (Andrews and Gentien, 1982). The GBR region has a typical monsoonal climate, characterized by a wet summer season (December–March) and a dry winter season, with more than 60% of the annual rainfall occurring in the wet season. This strong seasonality closely couples the rainfall with river runoff. The river inputs together with surface and deep water inflow from the Coral Sea, nitrogen fixation and rain water are thought to represent the largest external sources of nutrients entering the system (Furnas et al., 2011). But as the magnitude of different sources, sinks and cycling of nutrients (both inorganic and organic) in the GBR is poorly understood, it is not

150 possible to confidently state which of these sources are the most important at any
151 given time and place.
152 In this study we conducted cross-shelf measurements of carbohydrates and
153 proteins in the southern section of the GBR sampled in the early (April 2009) and
154 late dry (September 2009) season, and the subsequent wet season (February 2010).
155 The sampled area has several characteristics such as: 1) the largest number of
156 individual reefs on the GBR shelf, 2) relatively high POM and DOM concentrations,
157 partly due to elevated plankton primary production rates and to terrestrial material
158 entering the southern GBR (Furnas et al., 2005), 3) strong turbulent mixing
159 controlled by a large tidal prism (Wolanski, 1994), and 4) a gradient in the
160 phytoplankton community composition over the cross-shelf transect (Revelante and
161 Gilmartin, 1982). Figure 1 shows the 12 stations included in the coast to reef
162 transect, with stations representing inshore (Station: 1 and 2), mid-shelf (Station: 3
163 and 4), mid-shelf reef lagoon (Station: 5), outer lagoon (Station: 6, 7 and 8), open
164 ocean (Station: 9 and 10) and shelf break (Station: 11 and 12) sites.
165
166 *2.2.Sample collection*
167 Full-depth continuous conductivity-temperature-depth (CTD) profiles were
168 recorded (Seabird SBE19Plus) at each sampling site between 0800 and 0930 h local
169 time in order to determine water depths for subsequent biological sampling. The
170 CTD salinity was calibrated with water samples collected with the Niskin bottles and
171 analysed in the base laboratory with a Portasal Model 8410A. Following the CTD
172 cast, Niskin bottle samples were collected at 2-3 depths for the analysis of
173 chlorophyll *a* (chl *a*), dissolved inorganic nutrients (NH_4^+, NO_3^-/NO_2^- , HPO_4^{2-} and
174 $Si(OH)_4$), particulate organic carbon (POC), nitrogen (PN) and phosphorus (PP),

dissolved organic carbon (DOC), total dissolved nitrogen (TDN) and phosphorus (TDP), and particulate (p-CHO and p-Prot) and dissolved (d-CHO and d-Prot) carbohydrates and proteins. The filtration and processing of the water samples started immediately after collection. Chl *a* samples were collected by filtering between 100 and 200 mL of the sampled water through precombusted (450°C, 4 h) GF/F filters (pore size ~ 0.7 µm), which were frozen (-20°C) until analysis. Suspended matter was collected under low-vacuum on precombusted GF/F filters for particulate organic matter (250 mL), p-CHO (250 mL) and p-Prot (500 mL) analysis. All filters were kept frozen (-20°C) until analysis. The samples for the dissolved phase (inorganic nutrients, DOC, TDN, TDP, d-CHO and d-Prot) were immediately filtered through a 0.45 µm filter cartridge (Sartorius MiniSart) into acid-washed 10-50 mL HDPE plastic containers. Duplicate water samples for inorganic nutrients, TDN, TDP, d-CHO and d-Prot were kept frozen (-20ºC) until analysis. 10 mL sub-samples for DOC were collected in duplicate and preserved by adding 100 µL 32% AR-grade HCl and stored in the dark at 4°C until analysis.

2.3. Samples measurements

Chl *a* was determined with a Turner Designs 10 AU fluorometer (excitation: 300-500 nm; Emmision > 665nm) after 90% acetone extraction (Yentsch and Menzel, 1963). Inorganic nutrients (NO_3^-/NO_2^-, HPO_4^{2-} and $Si(OH)_4$) were determined using standard segmented flow analysis (Hansen and Koroleff, 1999). To avoid contamination during transport and storage, NH_4^+ concentrations were determined manually immediately after sample collection using the OPA fluorometric method (Holmes et al., 1999). The precisions of replicate samples were ± 0.01 µmol L^{-1} for

199 NH_4^+, ± 0.1 µmol L^{-1} for NO_3^-/NO_2^-, ± 0.02 µmol L^{-1} for HPO_4^{2-} and ± 0.05 µmol L^{-1}
200 for $Si(OH)_4$.

201 Particulate organic carbon and nitrogen content (POC and PN) were measured by
202 high temperature combustion (950ºC) using a Shimadzu TOC-V carbon analyser
203 fitted with a SSM-5000A solid sample module, after the inorganic carbon on the
204 filters (e.g. $CaCO_3$) had been removed by acidification of the sample with 2M HCl
205 (Nieuwenhuize et al., 1994). The analyser was calibrated using AR Grade EDTA for
206 the 5 point standard curve (conc. range; 0- 40 µmol L^{-1} for POC; 0- 4 µmol L^{-1} for
207 PN). Particulate phosphorus (PP) was determined spectrophotometrically as
208 inorganic P after digesting the particulate matter in 5% potassium persulphate. The
209 method was standardised using orthophosphoric acid as the standard for the 4 point
210 calibration curve (conc. range; 0- 20 µmol L^{-1}). We compared peak areas of the filter
211 blanks and standard solutions to ensure consistency between runs with no major
212 deviations found.

213 Dissolved organic carbon (DOC) concentrations were measured by high
214 temperature combustion (680°C) using a Shimadzu TOC-5000A carbon analyser.
215 Concentrations were determined by subtracting a Milli-Q blank and dividing by the
216 slope of a daily 4 points standard curve (conc. range; 0- 200 µmol L^{-1}) made from
217 potassium hydrogen phthalate and glycine. The consistency between runs was
218 verified by comparing peak areas of standard solutions with no major deviations
219 found. Analyses of total dissolved nitrogen (TDN) and phosphorus (TDP) were
220 determined by oxidation (121°C, 70 min) in alkaline conditions by persulphate
221 digestion of water samples (Valderrama, 1981), which were then analysed for
222 inorganic nutrients, as described above. Dissolved organic nitrogen (DON)
223 concentrations were calculated as the difference between TDN and dissolved

224 inorganic nitrogen (DIN; NH_4^++ NO_3^-/NO_2^-) (DON = TDN – DIN) and Dissolved
225 organic phosphorus (DOP) as the difference between TDP and dissolved inorganic
226 phosphorus (DIP: HPO_4^{2-})(DOP = TDP – DIP).
227 Particulate (p-CHO) and dissolved (d-CHO) carbohydrates were determined by
228 oxidation of the reduced sugars with 4,6-tripyridyl-s-triazine (TPTZ) to produce a
229 coloured product which can be measured as the absorption at 595 nm (Myklestad et
230 al., 1997). Briefly described, the filtered material (250 mL) or 50 mL of sample water
231 were hydrolysed with 0.1 M HCl at 100°C in sealed glass ampoules for 20 – 22 h and
232 then neutralised with 2 mL 0.1 M NaOH. Total carbohydrates were thereafter
233 measured from hydrolysed particulate or dissolved samples. Standards for the
234 analysis were made from D-glucose, with the CHO concentrations calculated using a
235 4 points calibration curve (conc. range; 0- 30 µmol L^{-1}) and subtraction of a blank
236 value. The consistency of the measurements was verified by comparing blanks and
237 standards between runs, with no major changes found. The p-CHO samples from
238 the early dry season were unfortunately defrosted upon return to the base laboratory
239 and were therefore not determined.
240 For the analysis of particulate proteins (p- Prot), the material collected (500 mL)
241 was extracted in Milli-Q water followed by addition of 0.1 M NaOH and beads
242 (zirconia beads). This was followed by a sonication step using a probe sonicator (40
243 sec.) and a centrifugation step (2800 x g for 5 min at 4°C) to collect extracted
244 proteins (Tanoue 1995). The extraction process was repeated with 0.1 M NaOH and
245 the filtrates were combined in the same collection tube. The combined filtrates were
246 finally clarified by centrifugation (5250 x g for 5 min at 4°C) prior to measurement.
247 The 50 mL dissolved proteins (d-Prot) samples were firstly sonicated using a probe
248 sonicator for 1 min followed by the addition of 2% sodium deoxycholate and

incubation at 4°C for 30 min. The d-Prot were thereafter precipitated by the addition of 5 mL 100% trichloroacetic acid followed by mixing and incubation at 4°C overnight. Precipitated proteins were concentrated by centrifugation (5250 x g for 15 min at 4°C), and the resulting pellet was washed twice with ice-cold acetone and resuspended in 1 mL bicinchoninic acid working reagents. Both p-Prot and d-Prot concentrations were measured using the micro bicinchoninic acid method (Thermo, VIC, Australia) and using bovine serum albumin, which had been subjected to the same treatment as the samples, as standards in a 4 points calibration curve (conc. range; 0- 30 μmol L^{-1}).

2.4. Statistical Analysis

Linear mixed models (Pinheiro and Bates, 2006; Demidenko, 2013) were used to estimate the relationships between stoichiometry and other explanatory variables (e.g. inorganic nutrients) with particulate and dissolved concentrations and yields of carbohydrates and proteins. The explanatory variables were ranked according to their importance in predicting each of the response variables via Random Forest (Breiman, 2001). This covariate variable ranking was combined to select a set of models which were firstly combined with models based on expert knowledge and then compared using the Akaike information criterion to select the final models (Akaike, 1974). The Akaike information criterion examines not only the model's goodness of fit but also their complexity, and it thereby considers a trade-off between both. Finally, bootstrap percentile confidence intervals for the fixed effects model parameters were computed based on 500 bootstrap samples (Davison and Hinkley, 1977). Conditional R square values measuring the proportion of the total variance explained together by the fixed and random effects were also calculated. All the

274 statistical analyses were carried out using R software version 3.2.1 (R Core Team,
275 2016) and packages Random-Forest (Liaw and Wiener, 2002) and lme4 (Bates et al,
276 2015) with all the explanatory variables being log10 transformed and then centred.
277 Details on the fitted models together with the parameters confidence intervals are
278 provided in the supplementary material.
279

280 **3. Results**

281 *3.1. Hydrographic, biological and chemical characteristics*

282 The main seasonal periods (early dry, late dry and wet season) in the GBR were
283 covered during our cruises. Salinity varied from 32.6 to 36.1 (average ± standard
284 deviation; 34.9 ± 0.4), and was lowest close to shore and during the wet season
285 (Supplement Fig. 1a-c). The temperature varied between 19.1 and 28.8ºC (26.4 ±
286 2.0ºC), and was highest during the wet season when a marked thermocline was
287 detected between 60 and 100 m at the offshore stations (Supplement Fig. 1d-f). The
288 salinity and temperature data indicated a slight freshening/river influence near the
289 coast during the early dry and wet seasons, and that the water column was well-
290 mixed over the shelf during the late dry and wet seasons. Along the slope,
291 Subtropical Lower Water is found at depth in all seasons and provides a source for
292 waters onto the shelf through upwelling and/or when changes in the East Australian
293 Current occur.

294 Chl *a* concentrations varied between 0.03 and 2.39 µg L^{-1} (0.57 ± 0.43 µg L^{-1}),
295 with highest levels closer to shore and at mid-shelf during the wet season (Fig. 2a-c).
296 The concentrations of DIN and $Si(OH)_4$ varied between values below the detection
297 limit up to 7.26 µmol L^{-1} (0.48 ± 1.03 µmol L^{-1}) and 12.3 µmol L^{-1} (1.4 ± 1.7 µmol L^{-1})
298 respectively (Fig. 2d-f and j-l), while DIP concentrations varied between 0.04 and

299 0.64 μmol L^{-1} (0.12 ± 0.09 μmol L^{-1}) (Fig. 2g-i). Generally, the dissolved inorganic
300 nutrient concentrations of surface waters (down to 100m) were close to the detection
301 limits of the standard methods (~0.01 μmol L^{-1}) but with elevated levels found in the
302 early dry season closer to shore ($Si(OH)_4$)) and the late dry season at depths below
303 ~ 80 m (DIN and DIP) (Fig. 2d-l).

304 POC concentrations varied between 1.9 and 33.8 μmol L^{-1} (8.5 ± 5.1 μmol L^{-1})
305 (Fig. 3a-c), while PN and PP ranged from 0.24 to 3.17 μmol L^{-1} (1.08 ± 0.52 μmol L^{-1})
306 and from 0.01 to 0.41 μmol L^{-1} (0.08 ± 0.06 μmol L^{-1}), respectively (Fig. 3d-i).
307 Generally, higher average levels of particulate matter were observed in surface
308 waters (above 50 m), during the wet season and closer to shore (Table 1a; Fig. 3).
309 The coefficient of variation (C.V.) over the whole period was 60% for POC, 48% for
310 PN and 74% for PP, showing that the degree of variation was highest for the PP
311 followed by POC and PN. In this work we did not differentiate between sinking and
312 non-sinking particles. The C:N:P stoichiometry of the particulate fraction was on
313 average 117:16:1, which is close to the Redfield ratio (106:16:1, Redfield et al.
314 1963), suggesting a predominantly plankton origin of this material (Álvarez-Salgado
315 et al., 2006). The POC/PN ratios did not vary spatially or temporally, while the
316 POC/PP and PN/PP showed generally higher levels during the early dry season but
317 with no clear spatial pattern (Table 1a).

318 Higher levels of DOM were generally observed in surface waters during the wet
319 season and closer to shore (Table 1b; Fig. 4), with concentrations varying between
320 50 and 185 μmol L^{-1} (70 ± 17 μmol L^{-1}) for DOC (Fig. 4a-c), 4.6 and 17.1 μmol L^{-1}
321 (9.2 ± 2.7 μmol L^{-1}) for DON (Fig. 4d-f) and 0.01 to 0.37 μmol L^{-1} (0.10 ± 0.05 μmol L^{-1})
322 for DOP (Fig. 4g-i). The C.V. over the whole period was largest for DOP (55%)
323 followed by DON (29%) and DOC (25%). In our dataset we did not obtain any

significant linear relationships between the three DOM pools (DOC, DON and DOP). The average C:N:P stoichiometry of the DOM pool was 701:93:1, which was greater than the Redfield ratio. The DOC/DON ratios did not show any clear spatial or temporal differences, while the DOC/DOP and DON/DOP showed generally higher levels during the wet season and at the inshore stations (Table 1b).

3.2. Carbohydrate and protein dynamics

Particulate (p-CHO) and dissolved (d-CHO) carbohydrates concentrations varied between 0.3 to 3.1 μmol L^{-1} (1.0 ± 0.6 μmol L^{-1}) and 0.4 to 9.4 μmol L^{-1} (4.3 ± 1.9 μmol L^{-1}), respectively (Table 1, Fig. 5a-e). The C.V. was larger for p-CHO (56%) than d-CHO (44%). Although p-CHO was not measured during the early dry season, concentrations were slightly higher at inshore stations and during the wet season (Table 1a; Fig. 5a,b). d-CHO concentrations showed higher levels in the early dry season and at stations closest to shore (Table 1a, Fig. 5c-e). The p-CHO yields (% p-CHO) showed no clear spatial pattern but higher levels were found during the wet (15 ± 5%) than the late dry season (11 ± 4%) (Table 1a; Fig. 5f-g). Spatially d-CHO yields (% d-CHO) did not show any clear differences, but slightly higher levels were found during the early dry (10 ± 2%) and lowest during the wet season (4 ± 2%) (Table 1b; Fig. 5h-j). The % d-CHO showed a higher coefficient of variation (47%) compared with the % p-CHO (38%). Our statistical analysis found significant relationships between p-CHO with POC and TDN and d-CHO with POC (Table 2). The % p-CHO could be explained by DIP and TDN, while %d-CHO was best described by TDN and chl *a* (Table 2). The statistical analysis also revealed that changes in p-CHO and d-CHO concentrations and yields followed the overall changes in POM and DOM stoichiometry (Supplement Table 1).

The particulate (p-Prot) and dissolved (d-Prot) proteins reached concentrations between 0.2 and 2.3 μmol L^{-1} (0.9 ± 0.4 μmol L^{-1}; C.V. of 43%) and 0.2 and 22.5 μmol L^{-1} (8.2 ± 5.9; 71%), respectively (Table 1; Fig. 6a-f). The average yields of p-Prot (% p-Prot) and d-Prot (% d-Prot) (12 ± 6% and 13 ± 10%) were equal, but the levels varied seasonally (Table 1; Fig. 6g-l). Spatially and temporally the p-Prot concentrations were quite equal, while the yields showed higher levels at the more offshore stations and during the early dry season (Table 1a; Fig. 6). The d-Prot had elevated average concentrations (15.3 ± 6.0 μmol L^{-1}) and yields (25 ± 6 %) in the early dry season at the most offshore stations and lowest levels in the wet season (4.5 ± 3.6 μmol L^{-1}; 6 ± 5%), (Table 1b; Fig. 6). On average carbohydrates and protein yields accounted for a similar fraction of POC (13 ± 5 % and 12 ± 6 %), while proteins accounted for a larger fraction of the DOC pool than carbohydrates (13 ± 10 % and 6 ± 3 %) (Table 1; Fig. 5 and 6). Our statistical analysis found significant relationships between p-Prot with PN and DIN, and that d-Prot could be explained by TDN and PN (Table 2). The % p-Prot could not be explained by any of the measured variables, while % d-Prot was best described by DIP and TDN (Table 2). Our statistical analysis furthermore showed that the p-Prot concentration could be explained by the POM stoichiometry and both the d-Prot concentrations and yields followed changes in the DOM stoichiometry (Supplement Table 1).

4. Discussion

The major chemical classes identified in both particulate and dissolved organic matter are carbohydrates and proteins (Fraga, 2001; Benner, 2002). To our knowledge this study provides the first seasonal dataset of particulate and dissolved carbohydrates and proteins in a coral reef ecosystem. Our study showed that their

374 seasonal variation is closely connected with changes in total nutrient availability
375 (inorganic and organic) and Chl *a*, generally following the same patterns as found
376 for the particulate (POM) and dissolved organic matter (DOM) pools. The
377 carbohydrates and proteins normalized yields furthermore suggest that the POM
378 bioavailability is similar between seasons, while the DOM bioavailability varies
379 seasonally with highest levels during the early dry season.
380
381 4.1 *Estimates of organic matter bioavailability from carbohydrates and proteins*
382 Carbohydrates (CHO) and proteins (Prot) are abundant components of POM and
383 DOM, yet information on seasonal variation in tropical coastal waters is limited
384 (Benner, 2002). The POM pool is a mixture of plankton and detritus with different
385 elemental (C, N, P) and biochemical (CHO, Prot) composition, with newly produced
386 POM being richer in CHO and Prot and older material having a higher lipid content
387 (Ríos et al. 1998; Volkman & Tanoue 2002). The majority of CHO and Prot are very
388 rapidly consumed (hours to days) and they fuel a large fraction of bacterial
389 production in marine systems (e.g. Rich et al., 1997, Kirchman et al., 2001), but due
390 to factors such as physical protection and inorganic nutrient limitation a portion of
391 CHO and Prot withstands degradation over longer timescales (Meon and Kirchman,
392 2001). The contribution of CHO and Prot to the POC and DOC pools, here referred
393 to as the normalized yields, has been used as a molecular indicator of the relative
394 “freshness” or microbial bioavailability of the organic matter (OM). Higher yields
395 indicate recently produced and more bioavailable material (e.g. Benner, 2002).
396 The CHO and Prot concentrations (average conc. ; p-CHO: 1.0 ± 0.5 μmol L^{-1}; d-
397 CHO: 4 ± 2 μmol L^{-1}; p-Prot: 0.9 ± 0.4 μmol L^{-1}; d-Prot: 8 ± 6 μmol L^{-1}) and yields
398 (average yields; % p-CHO: 13 ± 5 %; % d-CHO: 6 ± 3 %; % p-Prot: 12 ± 6 %; % d-

399 Prot: 13 ± 10 %) are comparable or in some instances even higher (d-Prot in early
400 dry season; 27 μmol L^{-1}) than found previously for other coastal and shelf systems
401 (e.g. Borch and Kirchman, 1997; Skoog and Benner, 1997; Yang et al., 2010). This
402 demonstrates that the bioavailability of OM in this oligotrophic system is similar to
403 other coastal waters. However, as tropical waters have elevated temperatures and
404 sunlight levels, it leads to most bioavailable material being degraded within the
405 continental shelf and only a minor part is therefore exported to adjacent waters
406 (Bouillon and Connolly, 2009). Another approach often used to determine the POM
407 and DOM bioavailability is to study their C:N:P stoichiometry, with more C rich
408 compounds considered less bioavailable due to the preferential degradation of N and
409 P rich compounds (Álvarez-Salgado et al., 2006; Lønborg & Álvarez-Salgado 2012).
410 Our statistical analysis showed that both CHO and Prot were related with OM
411 stoichiometry, demonstrating that both bulk estimates (stoichiometry) and specific
412 compounds (CHO and Prot) provide useful measures of OM bioavailability in the
413 GBR. Furthermore, our observations show that CHO and Prot contribute equally to
414 the POC (13 and 12%), while Prot accounted for a larger fraction of DOC (6 and
415 12%). The higher yields within the particulate fraction suggest that these organic
416 compounds are more recently produced and more bioavailable than the dissolved
417 fraction (Cowie and Hedges, 1994). As the DOM pool is partly a productiof POM
418 dissolution and/or degradation, these results align well with previous studies showing
419 a decreasing CHO and Prot content in more degraded OM (Rios et al., 1998). The
420 equal contributions of CHO and Prot to the POM pool is contrary to the study by
421 Crossman et al., (2001), which found that Prot dominated the POM pool at mid-shelf
422 reefs in the northern GBR. These samples were only collected during the wet season
423 within the coral reef matrix, which often have higher concentrations of suspended

POM. In contrast, we in this study sampled over the whole water column over different seasons and across the shelf, which may partly explain these differences. In addition, as Crossman et al., (2001) only measured starch concentrations as an indicator of carbohydrates and furthermore used high-performance liquid chromatography (HPLC) to determine the Prot content, the difference could also be due to differences in the methods used.

4.2. Temporal and spatial variability in carbohydrates and proteins

During the three seasons we found stable levels of p-CHO and p-Prot , which is most likely connected with that the particulate matter pool was predominantly fresh plankton material with a similar C:N:P stoichiometry (117:16:1) between seasons, not different to the Redfield ratio (106:16:1, Redfield et al., 1963). The CHO and Prot content in the DOM pool indicated higher yields and bioavailability during the early dry season. Highest primary production rates and inputs of river material to the GBR are normally found during the wet season (Furnas et al., 2011).

The highest d-CHO and d-Prot yields were found during the early dry season suggesting that the production of d-CHO and d-Prot might not be directly linked to primary production and river input. As we did not detect any link between d-CHO and d-Prot with salinity and our study area is mainly net autotrophic (gross primary production exceeds respiration) (McKinnon et al. 2013), it suggests that rivers are not directly impacting the CHO and Prot levels and that internal production pathways are the likely source of this material. This is in line with the detailed statistical analysis showing CHO and Prot levels following the same seasonal pattern as the organic carbon pools and the availability of nutrients (DIN, DIP and TDN). A uncoupling between the magnitude of plankton primary production and d-CHO and

d-Prot levels could have several possible explanations. It could be linked with: 1) changes in seasonal plankton community structure which influences the release of dissolved compounds (Lomas and Bates, 2004), 2) changes in the chemical composition due to varying impacts of viral lysis and predation (Lønborg et al., 2013; Nagata, 2000), and/or 3) possible resistance in degradation by d-CHO and d-Prot over longer timescales meaning that production and degradation are not necessarily coupled (Goldberg et al., 2009). As data on these processes are unavailable, we are not able to assess which is the most likely explanation.

Spatially, CHO showed higher concentrations at the inshore, while no clear patterns were found for the yields. For Prot no spatial difference was found in the concentrations, but generally higher yields were found at the offshore stations (up to 42 %). Higher CHO levels found closer to shore could have several potential sources such as macrophytes and sediment release, increased plankton growth due to riverine input of nutrients and/or direct riverine input (Burdige et al., 2000; Panagiotopoulos et al., 2014; Søndergaard, 1981). The higher Prot yields at the more offshore stations, especially during the early dry season, may be due to : 1) release of OM by coral reefs into the surrounding water (Ducklow and Mitchell, 1979; Wild et al., 2010), 2) turbulent mixing and upwelling of deep nutrient rich water from the Coral Sea (both processes have previously been shown to fuel short lived phytoplankton blooms; Andrews and Gentien, 1982; Furnas and Mitchell, 1996) and/or 3) a strong vertical mixing leading to resuspension of benthic material (Alongi et al., 2015). Elevated levels of Prot were not measured at the reef stations, suggesting that coral release is not a likely source, but as direct data on the release is unavailable we cannot exclude this as a possible source. The salinity and temperature profiles showed that the water column at the most offshore stations

474 were well mixed during the dry seasons, suggesting that production over the shelf
475 fuelled by turbulent mixing and/or upwelling could be a potential source of elevated
476 Prot levels. But it might also be linked with tidal driven mixing which could lead to
477 increases in resuspension of benthic organic matter and nutrients (Alongi et al.,
478 2015).

479 Organic matter is thought to play a fundamental role in providing energy and
480 nutrients to support the high productivity of coral reef ecosystems. In this study we
481 demonstrate that CHO and Prot in the GBR have temporal and spatial variations with
482 overall levels being comparable to other coastal systems. The CHO and Prot yields
483 suggest that the POM bioavailability was similar between seasons, while the DOM
484 bioavailability showed seasonal differences with highest levels during the early dry
485 season. Furthermore, the CHO and Prot yields show that POM and DOM pools
486 contain highly bioavailable compounds, which play an important role in sustaining
487 the productivity of the GBR. In this study the sources, sinks and cycling of CHO and
488 Prot were not determined specifically, but the statistical analysis suggests that the
489 levels are controlled by the nutrient availability (DIN and DIP,TDN) and the amounts
490 of POM. Future studies should therefore combine a more detailed biological and
491 chemical characterization, including production and degradation measurements to
492 accurately understand the cycling of organic matter. Such approaches would not
493 only increase our currently fragmented knowledge of the transport and degradation
494 of organic C, N and P in the GBR, but would also provide much needed
495 understanding of tropical coastal waters in general.

496

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Table 1: Average water column concentrations of a) particulate and b) dissolved organic carbon (POC, DOC), nitrogen (PN, DON) phosphorus (PP), stoichiometry (POC/PN, POC/PP, PN/PP, DOC/DON, DOC/DOP, DON/DOP), carbohydrate and protein concentrations (p-CHO, p-Prot, d-CHO, d- Prot) and yields (% p-CHO, % p- Prot, % d-CHO, % d- Prot) shown for the early dry, late dry and wet season. Values are averages ± standard error; n.d – not determined.

Region	Season	POC µmol l^{-1}	PN µmol l^{-1}	PP µmol l^{-1}	POC/PN	POC/PP	PN/PP	p-CHO µmol l^{-1}	% p-CHO	p-Prot µmol l^{-1}	% p-Prot
Inshore	Early dry	17 ± 1	2.8 ± 0.5	0.16 ± 0.02	6 ± 1	107 ± 11	17 ± 1	n.d	n.d	1.3 ± 0.3	8 ± 1
(St.1 and 2)	Late dry	17 ± 3	2.0 ± 0.2	0.16 ± 0.05	8 ± 1	109 ± 20	14 ± 4	1.6 ± 0.2	10 ± 1	0.9 ± 0.2	5 ± 2
	Wet	25 ± 7	2.3 ± 0.8	0.29 ± 0.12	12 ± 3	95 ± 29	8 ± 1	2.0 ± 1.2	11 ± 9	1.2 ± 0.4	6 ± 4
Mid-shelf	Early dry	13 ± 6	1.8 ± 0.7	0.07 ± 0.02	7 ± 1	217 ± 144	31 ± 20	n.d	n.d	1.1 ± 0.1	10 ± 3
(St. 3 and 4)	Late dry	8 ± 2	0.8 ± 0.3	0.05 ± 0.01	10 ± 2	146 ± 43	15 ± 7	0.6 ± 0.1	10 ± 1	0.3 ± 0.1	4 ± 1
	Wet	7 ± 1	1.1 ± 0.2	0.07 ± 0.01	7 ± 1	104 ± 19	16 ± 3	1.2 ± 0.4	11 ± 9	0.9 ± 0.4	13 ± 6
Reef lagoon	Early dry	11 ± 1	1.1 ± 0.2	0.07 ± 0.02	10 ± 3	174 ± 50	17 ± 2	n.d	n.d	1.5 ± 0.3	13 ± 3
(St. 5)	Late dry	6 ± 1	0.8 ± 0.1	0.05 ± 0.01	8 ± 1	128 ± 21	16 ± 3	0.7 ± 0.1	12 ± 2	0.6 ± 0.1	10 ± 1
	Wet	12 ± 1	0.9 ± 0.1	0.10 ± 0.01	13 ± 1	121 ± 18	9 ± 1	1.5 ± 0.3	13 ± 2	0.9 ± 0.2	8 ± 1
Outer lagoon	Early dry	9 ± 2	1.2 ± 0.2	0.08 ± 0.01	7 ± 1	112 ± 21	15 ± 3	n.d	n.d	1.2 ± 0.2	14 ± 4
(St. 6, 7 and 8)	Late dry	5 ± 1	0.7 ± 0.1	0.05 ± 0.01	7 ± 1	101 ± 24	15 ± 2	0.5 ± 0.1	11 ± 3	0.8 ± 0.4	17 ± 9
	Wet	7 ± 2	1.2 ± 0.2	0.08 ± 0.02	6 ± 1	88 ± 22	15 ± 2	1.1 ± 0.2	15 ± 3	0.8 ± 0.2	11 ± 2
Open ocean	Early dry	6 ± 2	1.0 ± 0.4	0.08 ± 0.01	7 ± 2	84 ± 34	14 ± 6	n.d	n.d	1.1 ± 0.1	21 ± 12
(St. 9 and 10)	Late dry	6 ± 1	0.8 ± 0.3	0.05 ± 0.02	8 ± 1	127 ± 55	17 ± 8	0.5 ± 0.1	8 ± 2	0.6 ± 0.1	11 ± 4
	Wet	8 ± 4	0.9 ± 0.3	0.07 ± 0.01	8 ± 4	109 ± 50	14 ± 4	0.9 ± 0.6	12 ± 2	0.8 ± 0.1	12 ± 4
Shelf break	Early dry	5 ± 1	0.8 ± 0.2	0.04 ± 0.02	7 ± 1	172 ± 120	26 ± 23	n.d	n.d	0.7 ± 0.2	13 ± 4
(St. 11 and 12)	Late dry	7 ± 1	0.8 ± 0.2	0.05 ± 0.01	9 ± 2	130 ± 22	15 ± 4	0.9 ± 0.6	14 ± 8	0.9 ± 0.5	13 ± 7
	Wet	7 ± 2	0.8 ± 0.2	0.08 ± 0.02	9 ± 2	94 ± 16	11 ± 2	1.3 ± 0.4	18 ± 4	1.3 ± 0.5	18 ± 7

a)

Region	Season	DOC µmol l^{-1}	DON µmol l^{-1}	DOP µmol l^{-1}	DOC/DON	DOC/DOP	DON/DOP	d-CHO µmol l^{-1}	% d-CHO	d- Prot µmol l^{-1}	% d-Prot
Inshore	Early dry	76 ± 3	10.8 ± 0.5	0.21 ± 0.02	7 ± 1	366 ± 118	52 ± 7	8 ± 1	11 ± 1	13 ± 1	16 ± 1
(St.1 and 2)	Late dry	76 ± 4	8.5 ± 0.2	0.19 ± 0.12	9 ± 1	493 ± 184	55 ± 21	6 ± 1	8 ± 2	6 ± 4	8 ± 5
	Wet	129 ± 32	10.8 ± 2.6	0.09 ± 0.06	12 ± 4	2234 ± 1647	175 ± 107	4 ± 1	3 ± 1	6 ± 2	5 ± 3
Mid-shelf	Early dry	61 ± 7	10.9 ± 2.1	0.19 ± 0.02	6 ± 1	325 ± 47	57 ± 10	6 ± 1	9 ± 1	15 ± 2	25 ± 5
(St. 3 and 4)	Late dry	66 ± 3	7.3 ± 1.4	0.14 ± 0.04	9 ± 1	510 ± 138	56 ± 16	4 ± 1	6 ± 1	7 ± 10	13 ± 17
	Wet	94 ± 38	9.0 ± 2.3	0.07 ± 0.03	11 ± 3	2374 ± 3472	286 ± 524	2 ± 1	3 ± 1	4 ± 4	6 ± 7
Reef lagoon	Early dry	70 ± 6	9.2 ± 1.2	0.06 ± 0.03	8 ± 1	1346 ± 553	176 ± 71	6 ± 1	9 ± 2	15 ± 3	21 ± 5
(St. 5)	Late dry	60 ± 4	6.3 ± 0.9	0.12 ± 0.05	10 ± 1	541 ± 132	56 ± 11	5 ± 2	8 ± 3	2 ± 1	3 ± 1
	Wet	90 ± 6	12.3 ± 1.4	0.07 ± 0.03	7 ± 1	1407 ± 662	189 ± 82	4 ± 1	4 ± 1	7 ± 7	8 ± 8
Outer lagoon	Early dry	73 ± 18	12.8 ± 5.2	0.11 ± 0.05	6 ± 1	793 ± 387	134 ± 61	6 ± 2	9 ± 2	14 ± 2	21 ± 4
(St. 6, 7 and 8)	Late dry	61 ± 3	6.4 ± 1.1	0.09 ± 0.04	10 ± 1	1153 ± 1653	125 ± 184	4 ± 1	6 ± 2	6 ± 3	10 ± 6
	Wet	68 ± 8	11.2 ± 3.0	0.06 ± 0.03	6 ± 2	1466 ± 1320	244 ± 241	2 ± 1	3 ± 1	5 ± 1	7 ± 2
Open ocean	Early dry	54 ± 4	8.5 ± 0.5	0.11 ± 0.02	6 ± 1	509 ± 94	79 ± 13	6 ± 1	11 ± 1	17 ± 2	32 ± 4
(St. 9 and 10)	Late dry	64 ± 6	6.7 ± 1.8	0.10 ± 0.06	10 ± 1	1011 ± 959	106 ± 100	3 ± 1	5 ± 1	7 ± 3	10 ± 5
	Wet	76 ± 10	12.4 ± 4.4	0.08 ± 0.04	7 ± 2	1513 ± 1473	241 ± 223	3 ± 2	3 ± 2	4 ± 4	6 ± 5
Shelf break	Early dry	61 ± 7	9.0 ± 0.9	0.10 ± 0.04	7 ± 1	653 ± 222	96 ± 32	6 ± 1	10 ± 2	18 ± 1	32 ± 1
(St. 11 and 12)	Late dry	69 ± 8	6.8 ± 1.3	0.08 ± 0.05	10 ± 3	1846 ± 2815	203 ± 354	4 ± 1	5 ± 1	11 ± 7	17 ± 10
	Wet	65 ± 6	11.9 ± 1.2	0.09 ± 0.05	5 ± 1	1368 ± 1910	232 ± 283	3 ± 1	5 ± 2	2 ± 1	3 ± 2

682

b)

683 **Table 2:** Models using physical and biogeochemical variables which explain most of
684 the variability in particulate and dissolved carbohydrates (CHO) and proteins (Prot)
685 concentrations and yields. In brackets are listed the random effects considered in
686 each model. Model degrees of freedom (df), Akaike information criterion (AICc) and
687 conditional R^2 are also presented.

Models	df	AICc	Cond. R^2
p-CHO = clogPOC + clogTDN + (1|Season)	5	18.95	0.60
%p-CHO= clogTDN + clogChla + (1|Season)	5	109.44	0.54
d-CHO = clogPOC + (1|Season)	4	108.80	0.81
%d-CHO = clogDIP + clogTDN + (1|Season)	5	133.61	0.84
p-Prot = clogPN + DIN + (1|Season)	5	29.06	0.40
d-Prot = clogTDN + ClogPN + (1|Season)	5	163.87	0.82
%d-Prot = clogDIP + clogTDN + (1|Season)	5	193.44	0.84

688

689 **Figure legends**

690 **Figure 1.** Map showing the sampling stations (●) where samples were collected
691 during cruises aboard R/V *Cape Ferguson* in early (April 2009) and late dry
692 (September 2009), and the wet seasons (February 2010). The dark arrows
693 indicate the main currents in the study area.

694 **Figure 2.** Distribution of a), b), c) chlorophyll a (Chl *a*), d), e), f) dissolved inorganic
695 nitrogen (DIN) and g), h), i), phosphorus (DIP), and j), k), l) silicate (SiO_4) during
696 the early dry, late dry and wet season plotted as a function of depth in meters (y-
697 axis) from station 1 to 12 starting at the most inshore station (stn. 1) (x-axis). Dots
698 represent sampling points and colour the parameter values.Images created using
699 Ocean Data View (Schlitzer, 2015).

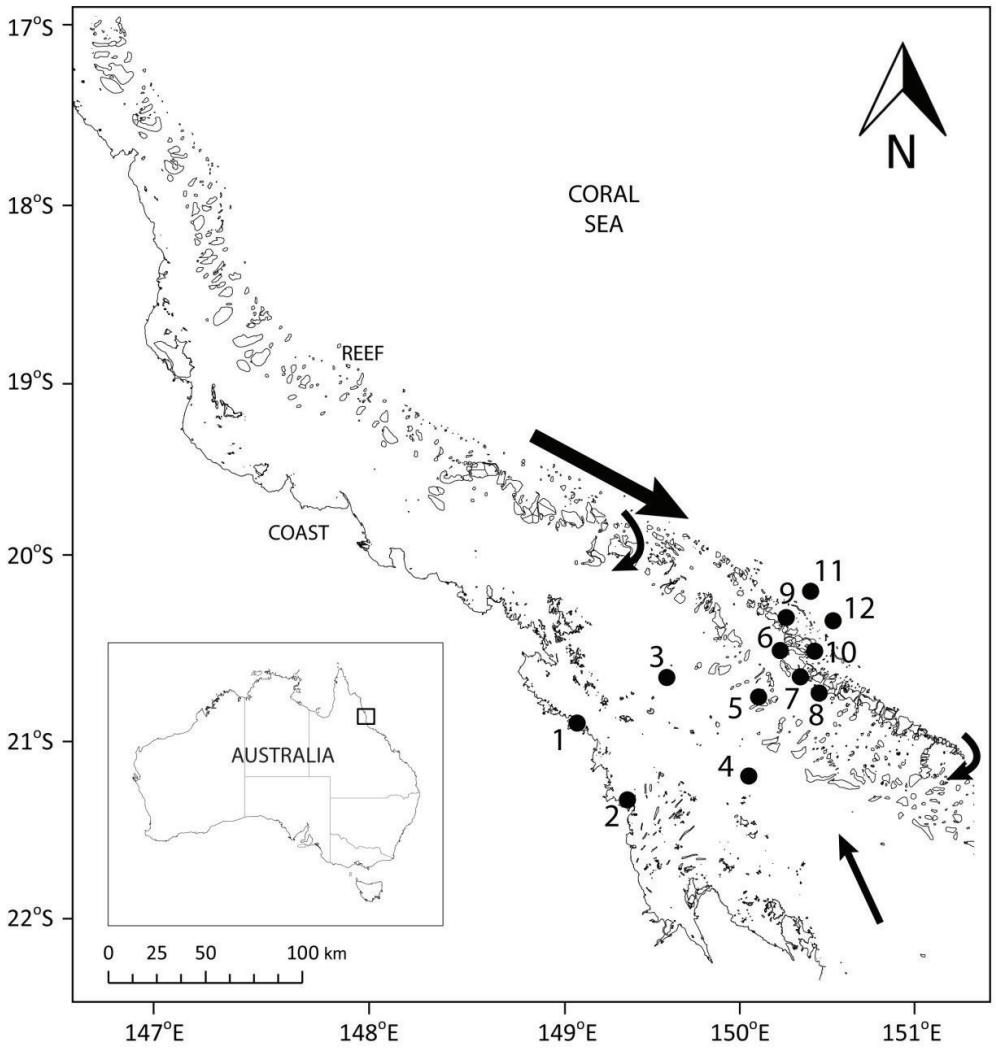
700 **Figure 3.** Distribution of a), b), c) particulate organic carbon (POC), d), e), f) nitrogen
701 (PON) and g), h), i) phosphorus (POP) during the early dry, late dry and wet
702 season plotted as a function of depth in meters (y-axis) from station 1 to 12
703 starting at the most inshore station (stn. 1) (x-axis). Dots represent sampling
704 points and colour the parameter values.Images created using Ocean Data View
705 (Schlitzer, 2015).

706 **Figure 4.** Distribution of a), b), c) dissolved organic carbon (DOC), d), e), f) nitrogen
707 (DON) and g), h), i) phosphorus (DOP) during the early dry, late dry and wet
708 season plotted as a function of depth in meters (y-axis) from station 1 to 12
709 starting at the most inshore station (stn. 1) (x-axis). Dots represent sampling
710 points and colour the parameter values. Images created using Ocean Data View
711 (Schlitzer, 2015).

712 **Figure 5.** Distribution of a), b) particulate (p-CHO) and c), d), e), dissolved
713 carbohydrate concentrations (d-CHO), carbohydrate normalized to f), g)

714 particulate (%p-CHO) and j), h), i) dissolved organic carbon concentrations (%d-
715 CHO) are also shown for the early dry, late dry and wet season plotted as a
716 function of depth in meters (y-axis) from station 1 to 12 starting at the most
717 inshore station (stn. 1) (x-axis). Dots represent sampling points and colour the
718 parameter values. Images created using Ocean Data View (Schlitzer, 2015).

719 **Figure 6.** Distribution of a), b),c) particulate (p-Prot) and d), e), f) dissolved protein
720 concentrations (d- Prot), protein normalized to g), h), i) particulate (%p- Prot) and
721 j), k), l) dissolved organic carbon concentrations (%d- Prot) are also shown for
722 the early dry, late dry and wet season plotted as a function of depth in meters (y-
723 axis) from station 1 to 12 starting at the most inshore station (stn. 1) (x-axis).
724 Dots represent sampling points and colour the parameter values. Images
725 created using Ocean Data View (Schlitzer, 2015).



726

727 **Figure 1. Lønborg et al.**

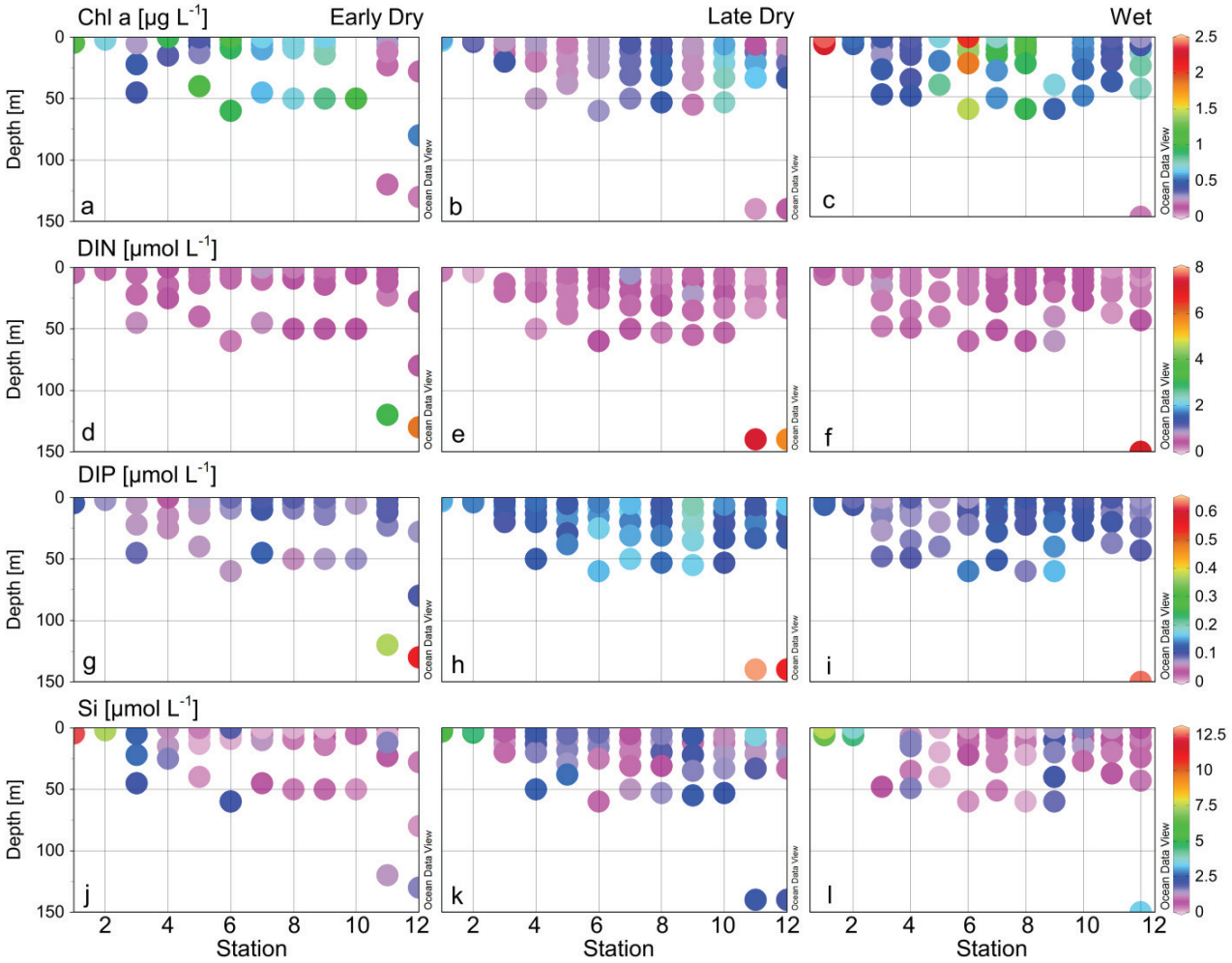


Figure 2. Lønborg et al.

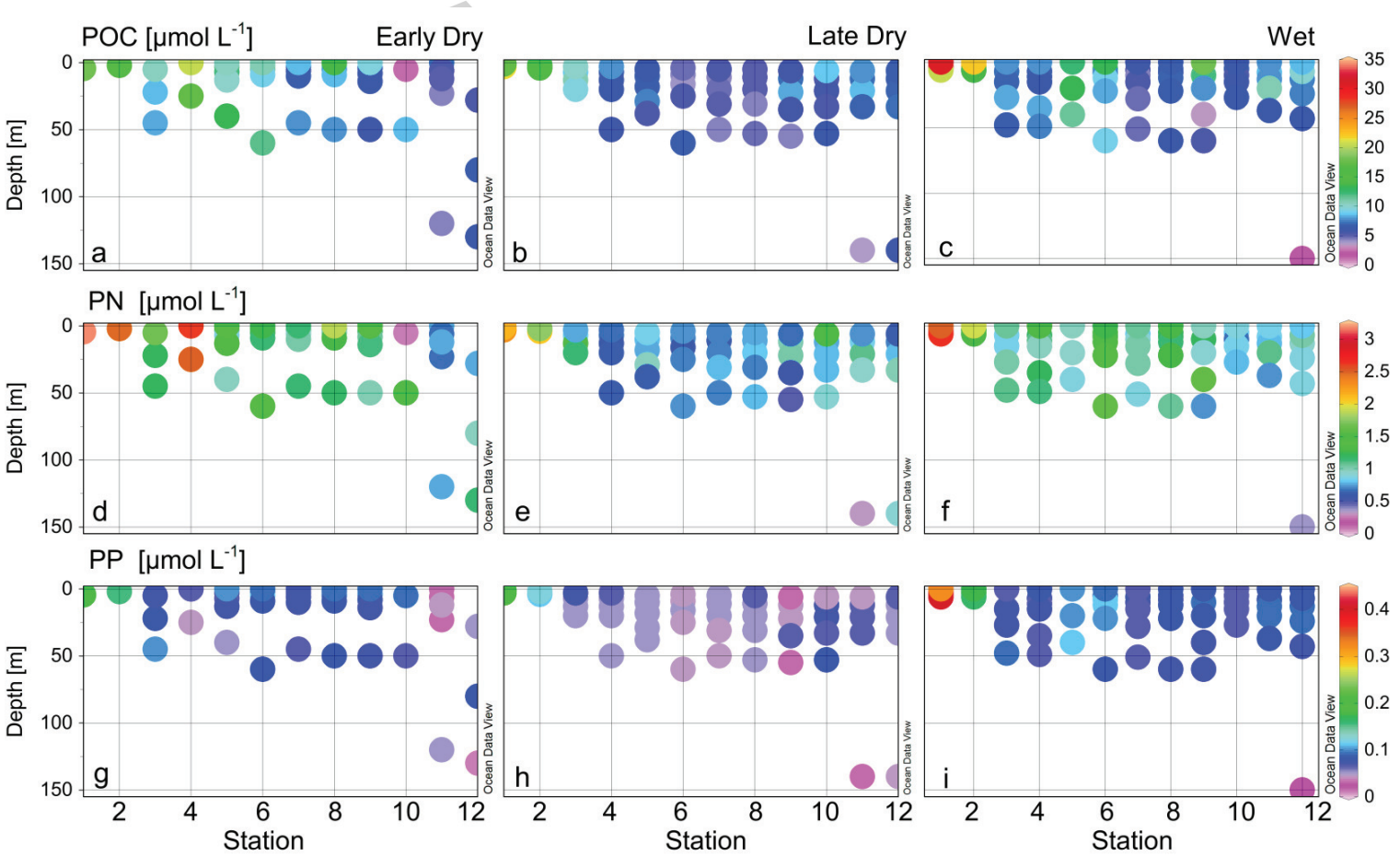


Figure 3. Lønborg et al.

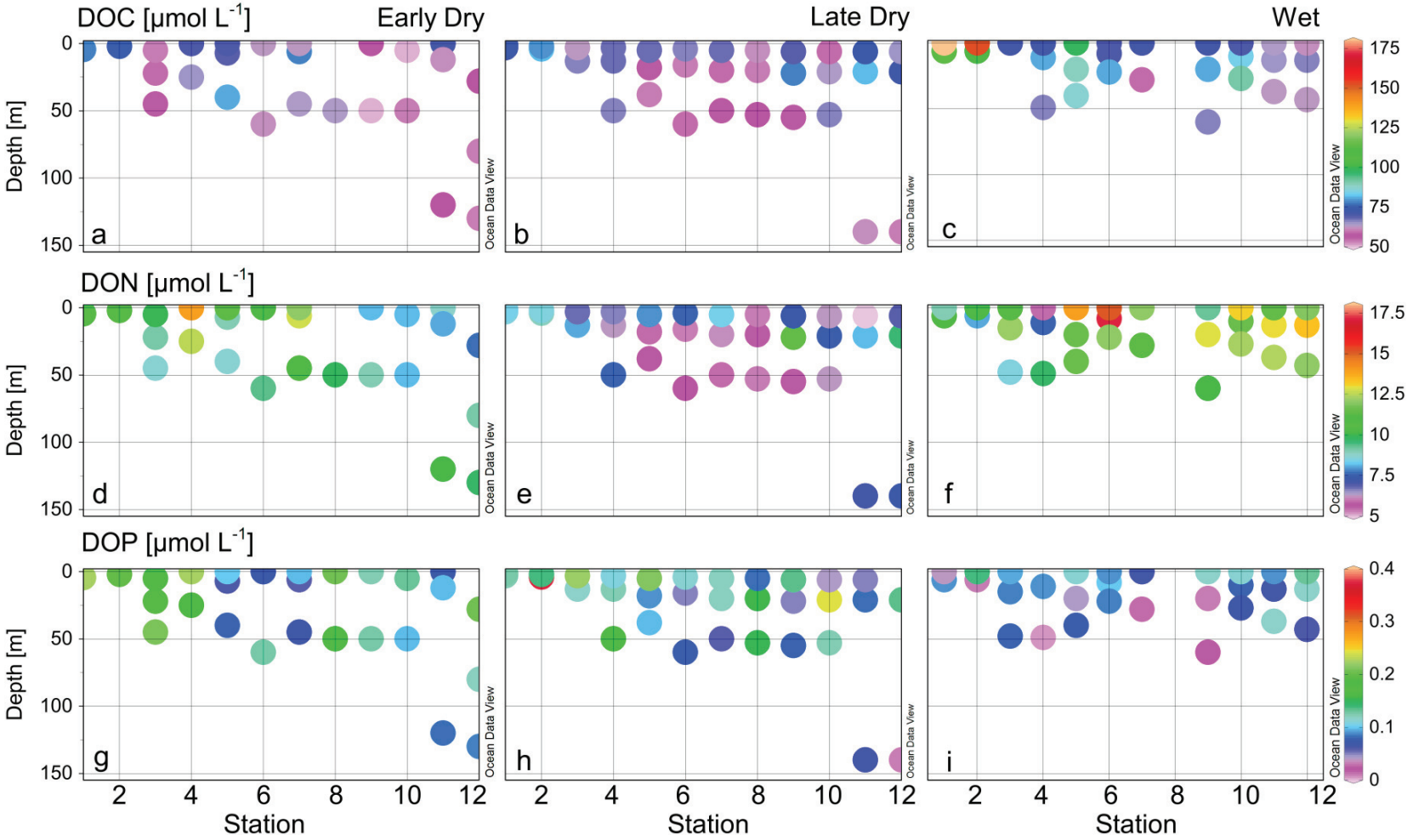


Figure 4. Lønborg et al.

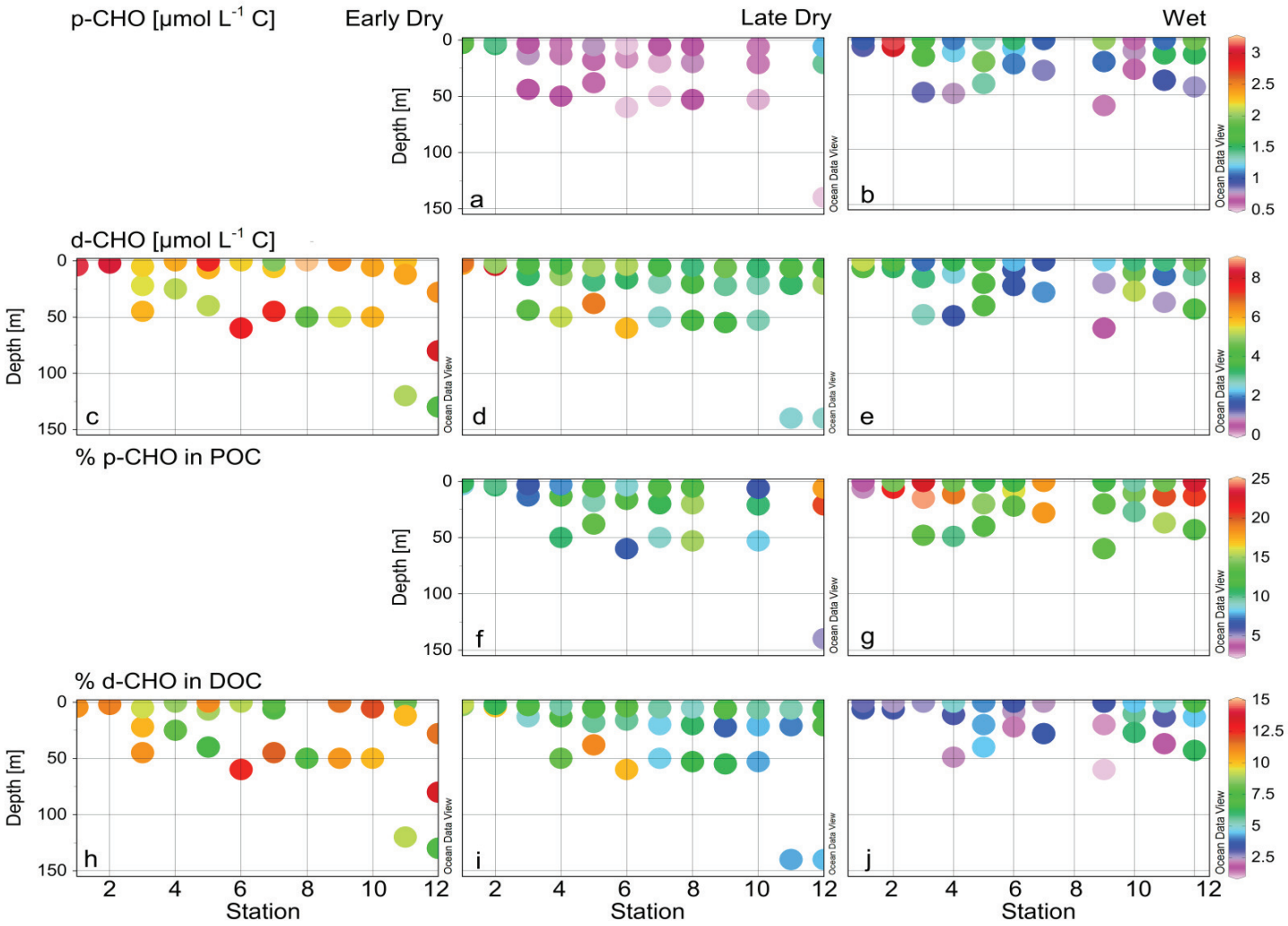


Figure 5. Lønborg et al.

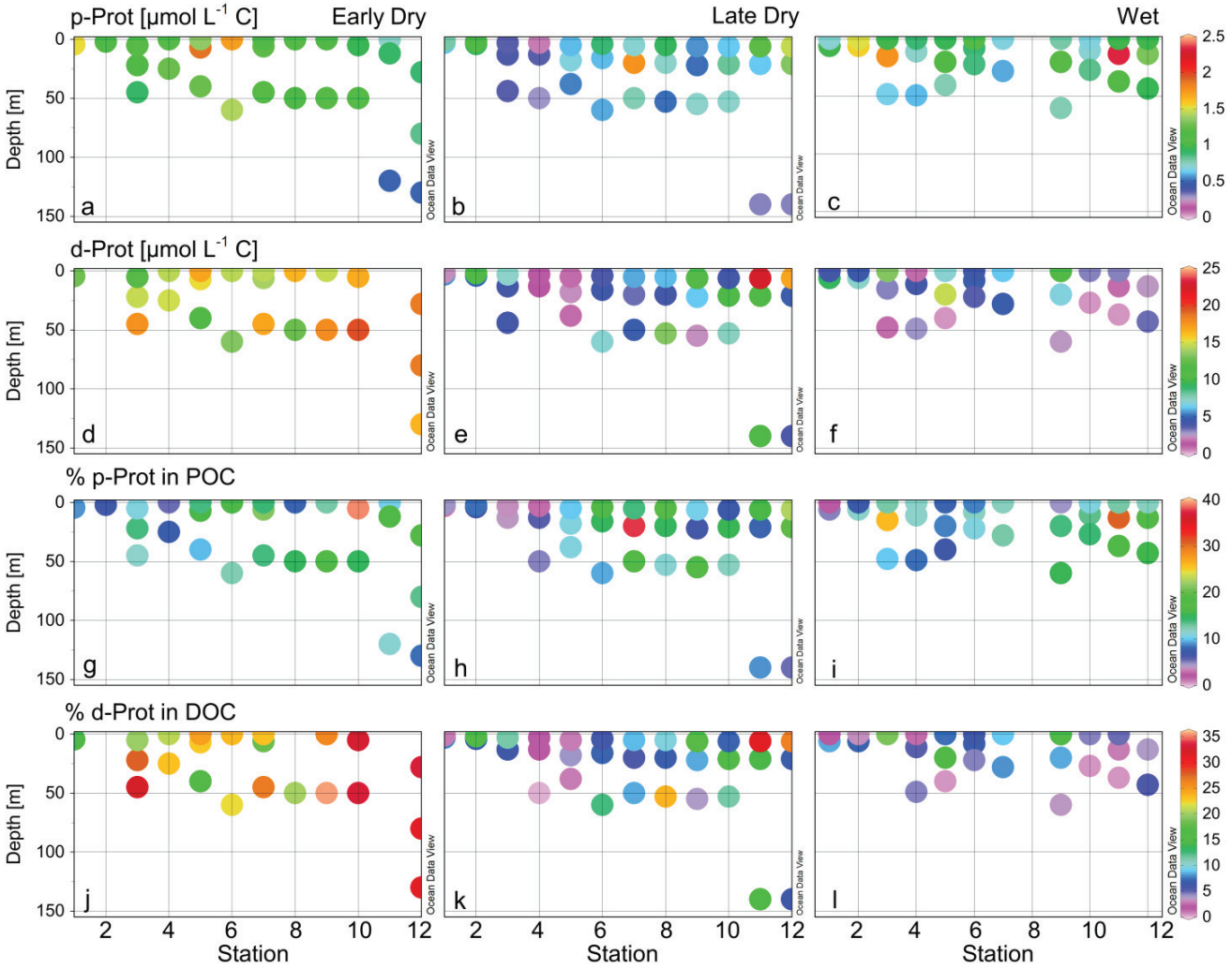


Figure 6. Lønborg et al.

Highlights

- Carbohydrates and proteins account for a similar part of POM, while proteins account for a larger fraction of DOM.
- The variations in carbohydrates and proteins appear to be controlled by inorganic nutrient availability and POM.
- POM bioavailability was similar between seasons, while the DOM bioavailability showed seasonal differences.
- Carbohydrates and proteins play an important role in sustaining the productivity of coral reef ecosystems.