1 Size distribution of absorbing and fluorescing DOM in Beaufort Sea, 2 Canada Basin

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7 **Abstract.** The molecular weight (MW) of dissolved organic matter (DOM) is considered as an important factor affecting the
8 bioavailability of organic matter and associated chemical species. Colored DOM (CDOM) MW distribution was determined,
9 for the first time, in the Beaufort Sea (Canada Basin) by asymmetrical flow field-flow fractionation (AF4) coupled with
10 online diode array ultra violet-visible photometer and offline fluorescence detectors. The apparent MW ranged from 1.07
11 kDa to 1.45 kDa, congruent with previous studies using high performance size exclusion chromatography and tangential
12 flow filtration. Interestingly, a minimum in MW was associated with the Pacific Summer Waters (PSW), while higher MW
13 was associated with the Pacific Winter Waters (PWW). The Arctic Intermediate Waters (AIW) did not show any significant
14 change in MW and fluorescence intensities distribution between stations, suggesting homogeneous DOM composition in
15 deep waters. Three fluorescence components including two humic-like components and one protein-like component were
16 PARAFAC-validated. With the increase of MW, protein-like fluorescence component became more dominant while the
17 majority remained as marine/microbially derived humic-like components. Overall, it is concluded that water mass origin
18 influenced DOM MW distribution in the Arctic Ocean.

19

20 **Keywords.** DOM, Asymmetrical flow field-flow fractionation (AF4), Molecular weight (MW), PARAFAC-EEM

21 **1 Introduction**

22 Dissolved organic matter (DOM), usually measured as dissolved organic carbon (DOC), is a major carbon pool in
23 aquatic systems (Amon and Benner, 1994; Benner et al., 1992; Jiao et al., 2010). DOM serves as a source of food for
24 microorganisms (Cole et al., 2006), contributing to the food web and energy transport (Baylor and Sutcliffe Jr, 1963). DOM
25 also plays an important role in regulating the speciation and distribution of trace metals such as Cu, Hg, Fe and Zn (Hirose,
26 2007; De Schamphelaere et al., 2004; Yamashita and Jaffé, 2008). Previous studies showed that increased Cu-binding
27 affinity was observed with increasing DOM molecular weight (MW) in natural waters (Midorikawa and Tanoue, 1998; Wu
28 and Tanoue, 2001). High MW DOM complexation was favoured by metals with high binding strength while low MW DOM
29 was preferentially bound by weak binding strength metals (Wu et al., 2004). Besides affecting metal binding affinity, DOM
30 MW could influence uptake by microorganisms (Guo and Santschi, 2007; Sun et al., 1997). For example, high MW oceanic
31 DOM was favoured by bacterial utilization (Amon and Benner, 1996), boosting growth rates of some bacterial group and
32 algae (Tulonen et al., 1992).

33 The heterogeneous nature of DOM requires the use of complementary analytical techniques. The absorbance and
34 fluorescence properties of DOM have been increasingly used in differentiating allochthonous and autochthonous DOM
35 sources (Stedmon et al., 2003) and tracing riverine supply into the ocean system (Fichot et al., 2013; Fichot and Benner,
36 2012; Guéguen et al., 2011, 2012a; Nelson et al., 2010; Stedmon et al., 2011). The ultraviolet-visible absorbance properties
37 of chromophoric dissolved organic matter (CDOM) have been used as molecular size and aromaticity proxies (Guéguen and
38 Cuss, 2011; Helms et al., 2008). emission matrix (EEM; Coble, 1996) technique coupled to parallel factor analysis
39 (PARAFAC; Murphy et al., 2008) have been used to facilitate the identification and quantification of independent
40 fluorescent classes such as protein-like, microbially derived and terrestrial humic-like in marine studies (e.g. Dainard and
41 Guéguen, 2013; Guo et al., 2011; Murphy et al., 2008). Asymmetrical flow field-flow fractionation (AF4) is a
42 chromatographic-like method that has been recently applied to investigate the sources and dynamics of DOM in aquatic
43 systems (Boehme and Wells, 2006; Guéguen and Cuss, 2011; Lin et al., 2016; Stolpe et al., 2010, 2014). For example, Lin et
44 al., (2016) showed that the 1-10kDa CDOM fraction was influenced by terrestrial input. Stolpe et al., (2014) concluded that

45 the small MW DOM (2-3nm) in surface northern Gulf of Mexico originated from terrestrial sources whereas the larger MW
46 DOM (>6 nm) was protein-rich and freshly produced.

47 The Arctic regions are undergoing rapid changes in air temperatures, river discharge, sea ice extent and permafrost
48 integrity (Frey and McClelland, 2009; Overland and Wang, 2013; Peterson et al., 2002; Schuur et al., 2009; Shimada et al.,
49 2006). Continued climate change will likely have profound effect on carbon cycle. Documenting the composition and
50 distribution of DOM (i.e. MW and optical properties) could provide valuable insights into the biogeochemical carbon cycle.

51 In this study, DOM samples were collected at four sites and five water masses in Beaufort Sea: Arctic Surface Water
52 (ASW), Pacific Summer Water (PSW), Pacific Winter Water (PWW) and Arctic Intermediate Waters (AIW) including Fram
53 Strait Branch (FSB) waters and Barents Sea Branch (BSB) water (Carmack et al., 2015; McLaughlin et al., 2011; 2004;
54 Rudels et al., 2012; Woodgate et al., 2005). The DOM MW distribution in the Arctic Ocean was assessed, for the first time,
55 using asymmetrical flow field-flow fractionation (AF4) coupled with online diode array ultra-violet/visible photometer and
56 offline fluorescence detectors.

57

58 **2 Methods**

59 **2.1 Sampling Sites**

60 A total of 88 samples, including 20 samples for MW analysis, were collected at 4 sites (CB28b, CB29, CB50 and CB51;
61 Fig. 1) in Beaufort Sea in September 2014 as part of the Joint Ocean Ice Studies cruise. Water samples were collected at
62 depths ranging from 5 m to 1000 m at each site using Niskin bottles mounted on a rosette together with a conductivity –
63 temperature – depth profiler and immediately filtered using pre-combusted (450 °C for 4 h) 0.7 µm glass fiber filters (GF/F,
64 Whatman) and stored in the dark at 4 °C in pre-combusted amber glass vials until measurement. The AF4 based MW
65 distribution was carried out on samples collected at 10 m, sub-chlorophyll maximum (i.e. 50 - 68 m), salinity 33.1 (i.e. 148 -
66 161 m) and temperature maximum (i.e. 414 – 433 m) and 1000 m at each site (Fig. 1). High-resolution vertical profiles of
67 humic-like fluorescent DOM (FDOM), primarily derived from terrestrial sources, were also acquired using a WET Labs
68 probe (WETStar Ex/Em 370/460 nm) at each site.

69

70 2.2 Asymmetrical Flow Field-Flow Fractionation

71 MW distribution was assessed using an asymmetrical flow field-flow fractionation (AF4) system within 10 days of
72 collection to avoid MW alteration (Guéguen and Cuss, 2011). AF4 is carried out using an AF2000 Focus fractionation
73 system (Postnova Analytics, Landsberg, Germany) which includes two PN1130 HPLC pumps to control the axial and focus
74 flows, a PN1610 syringe pump to control the crossflow rate, and a PN7505 degasser to remove gas from the carrier solution
75 prior to introduction to the pumps (Guéguen and Cuss, 2011). Absorbance scan was recorded from 270 nm to 700 nm, using
76 an on-line diode array ultra-violet/visible photometer (Shimadzu SPD-M20A). The fractionation system is equipped with a
77 300 Da polyethersulfone membrane (Guéguen and Cuss, 2011; Guéguen et al., 2013; Zhou and Guo, 2015). It should be
78 noted that DOM smaller than 300 Da will not be retained on the AF4 membrane and thus not measured. The pH and
79 conductivity of the NaCl carrier solution matched that of the Arctic samples (20 mS/cm, pH 7.9) to preserve the native
80 chemical environment of DOM.

81 The AF4 system was operated under the following conditions: detector flow rate at 0.35 mL/min, focusing at 0.15
82 mL/min focus flow rate for 7 min, elution at 2.20 mL/min cross flow rate for 13 min. MQ blank were performed under the
83 same operating conditions between each DOM sample to avoid any cross contamination. In order to get accurate MW
84 distribution, the AF4 system was calibrated at 254 nm using a log-log calibration based on four macromolecules (laser grade
85 rhodamine B (479 Da), bromophenol blue (692 Da), cytochrome C (12,400 Da) and lysozyme (14,300 Da) twice a day, at
86 the beginning and the end of each day (Guéguen and Cuss, 2011). The simultaneous multi wavelength measurements of the
87 online absorbance detector allow us to accurately determine each of the four macromolecules in a single injection. The
88 retention time at 254 nm was used to estimate the CDOM MW at peak maximum intensity (Guéguen and Cuss, 2011; Lin et
89 al., 2016; Stolpe et al., 2010, 2014). For example, a typical calibration recorded at 254 nm was $\log(\text{Time}) = (0.1634 \pm$
90 $0.0086) * \log(\text{MW}) + (0.4831 \pm 0.0228)$ ($r^2 = 0.999$). The smallest and largest macromolecules, rhodamine-B and
91 lysozyme, respectively, were eluted at 8.680 ± 0.165 (n = 10) and 14.759 ± 0.503 min (n = 10), respectively. It can be noted
92 that the retention time (i.e. MW) of the Beaufort samples was 4.8% higher (n = 20) at 350 nm than at 254 nm, confirming the
93 higher MW of aromatic CDOM (Cuss and Guéguen, 2013). A typical chromatogram (Fig. 2) showed a very sharp peak
94 representing the void peak with unfocused and small MW materials and a smooth peak containing the focused and eluted

95 material. The AF4 fractions corresponding to the material eluted after the void peak (Fig. 2) were collected using a fraction
96 collector (Varian ProStar 701).

97 In terms of repeatability, MW of bromophenol blue sodium salt (Sigma-Aldrich) was measured daily ($n = 10$) and was
98 within 6% of the recommended MW (669 Da). The relative standard deviation of MW of Suwannee River natural organic
99 matter ($n = 5$) was 3% (or 85 Da). Similar precision was reported in earlier work (Guéguen and Cuss, 2011).

100

101 **2.3 Chromophoric dissolved organic matter (CDOM) and Fluorescent DOM (FDOM)**

102 Chromophoric dissolved organic matter (CDOM) samples were allowed to warm to room temperature before analyzing
103 on a Shimadzu UV 2550 spectrophotometer. Milli-Q water was measured between each samples to avoid carry-over. A slit
104 width of 0.5 nm was applied, with an absorbance acquisition interval of 1 nm. The measured absorbance at wavelength λ was
105 converted to absorption coefficient a (m^{-1}) as following Eq (1):

$$106 \quad a_{\lambda} = 2.303A_{\lambda}/l \quad (1)$$

107 where a_{λ} is the absorption coefficient at wavelength λ , A_{λ} is the instrumental absorbance signal, l is the path-length of
108 the optical cell in meters (i.e. 10 cm). Absorbance coefficient at 254 nm (a_{254}) and 355 nm (a_{355}) were used as indicator for
109 CDOM concentration in natural samples (Chen et al., 2004; Dainard and Guéguen, 2013; Granskog et al., 2007; Penru et al.,
110 2013).

111 Three dimensional excitation-emission fluorescence matrices (EEMs) were generated by measuring fluorescence
112 intensity across excitation wavelengths ranging from 250 to 500 nm and emission wavelengths ranging from 300 to 600 nm
113 through successive scans with a Fluoromax-4 Jobin Yvon spectrofluorometer. Excitation and emission slit widths were set to
114 5 nm. Blank Milli-Q EEMs were measured daily to correct background and scatter peak. Before loading samples, a cuvette
115 was rinsed to avoid cross contamination and scanned at excitation 270 nm and emission 280 – 500 nm for confirmation. All
116 EEMs were normalized to Raman units (R.U.) by dividing the signal at all Ex/Em pairs by the integrated area under the
117 Raman water peak at excitation 350 nm using a daily acquired Milli-Q blank EEM (Lawaetz and Stedmon, 2009).
118 Absorption spectra were obtained for all natural seawater samples to make sure the intensity were within the linear range
119 ($A_{250} < 0.05$).

120 Parallel factor analysis (PARAFAC) was carried out on 88 EEMs (20 AF4 fractions and 68 bulk) in Matlab using the
121 DOMFluor (Stedmon and Bro, 2008) and DrEEM toolboxes (Murphy et al., 2013). The model was constrained to
122 nonnegative values and run for three to ten components. The appropriate number of components was determined by split-
123 half and Tucker congruence coefficient analyses. Percent fluorescence was calculated as follows:

$$124 \quad C1\% = \frac{C1}{(C1+C2+C3)} \quad (2)$$

125

126 **3 Results and Discussion**

127 **3.1 Hydrographical parameters**

128 Five main water masses were found based on the temperature/salinity (T/Sp) diagram (Fig. 3A): Arctic surface waters
129 (ASW) in the top 50 m ($Sp < 30$ and $-1.5\text{ }^{\circ}\text{C} < T < -0.5\text{ }^{\circ}\text{C}$) were influenced by river runoff (Cory et al., 2007; Pegau, 2002;
130 Walker et al., 2009), primary production (Fouilland et al., 2007; Hill and Cota, 2005), sea ice formation and melt
131 (Logvinova et al., 2016; Walker et al., 2009), and photobleaching (Bélanger et al., 2006); Pacific summer waters (PSW, $30 <$
132 $Sp < 32$) were characterized by a temperature maximum ($T \sim -0.8\text{ }^{\circ}\text{C}$; Steele et al., 2004); Pacific winter water (PWW, $Sp \sim$
133 33.1) was characterized by a temperature minimum ($T \sim -1.4\text{ }^{\circ}\text{C}$; McLaughlin et al., 2004) and a terrestrial humic-like
134 maximum (Fig. 3B) (Guéguen et al., 2012b); Deeper layers ($> 400\text{ m}$) were dominated by Atlantic-derived Arctic
135 intermediate water (AIW). A temperature maximum near 400 m characterized Fram Strait Branch waters (FSB; $Sp \sim 34.8$, T
136 $\sim 0.6\text{ }^{\circ}\text{C}$) while lower temperature characterizes the Barents Sea Branch waters (BSB; $Sp \sim 34.8$, $T \sim 0\text{ }^{\circ}\text{C}$) (McLaughlin et
137 al., 2004; Woodgate et al., 2005).

138

139 **3.2 Molecular weight depth distribution**

140 Natural marine CDOM MW ranged from 1.07 kDa to 1.45 kDa (Fig. 4), congruent with previous studies on DOM MW
141 using AF4, high performance size exclusion chromatography and tangential flow filtration (Beckett et al., 1992; Everett et
142 al., 1999; Guéguen and Cuss, 2011; Huguet et al., 2010; Landry and Tremblay, 2012; Penru et al., 2013; Stolpe et al., 2010).

143 For example, colloidal DOM MW averaged 1.4 ± 0.4 kDa in Northern Gulf of Mexico (Stolpe et al., 2010). Higher MWs
144 ($1.62\text{--}2.52$ kDa) were reported for colloidal DOM in Chukchi Sea (Lin et al., 2016). The average MW reported in Beaufort
145 Sea agreed with values reported for fulvic acids (Beckett et al., 1987; Guéguen and Cuss, 2011), confirming that fulvic acids
146 are good proxy for marine DOM (Tipping et al., 2015).

147 Average CDOM MW (1.37 ± 0.01 kDa) in ASW was remarkably consistent across the study area. This contrasts with
148 the halocline complex and deeper layers where significant MW differences were found (Fig. 4). Compared to ASW, the
149 CDOM MW in PSW was lower, likely due to the influence of sea ice melt waters rich in low MW DOM (Logvinova et al.,
150 2016). CDOM MW increased again in PWW, which resulted from the interactions with C-rich shelf bottom sediment
151 (Moore et al., 1983) remobilizing high MW DOM (Skoog et al., 1996). Below the halocline complex, lower MW CDOM
152 (~ 1.21 kDa) was found with the saline Atlantic waters. The BSB MW was relatively consistent (1.27 ± 0.06 kDa),
153 confirming the CDOM homogeneity in deeper layer.

154

155 3.3 Optical properties

156 The a_{254} and a_{355} values (Fig. 5A-B) compared well with previous Arctic studies (Dainard and Guéguen, 2013; Spencer
157 et al., 2009). Relatively low a_{254} and a_{355} values (2.444 and 0.2014 m^{-1} , respectively) were found in ASW likely due to
158 photobleaching (Guéguen et al., 2016; Logvinova et al., 2015) and/or sea ice melt (Logvinova et al., 2015) in surface waters.
159 Similar trends were previously observed (Dainard and Guéguen, 2013; Stedmon et al., 2011). The PSW-PWW waters were
160 characterized by high CDOM values (Fig. 5A-B), congruent with previous studies. As proxy for molecular size and
161 aromaticity (Guéguen and Cuss, 2011; Helms et al., 2008), $S_{275-295}$ ranged from 0.018 to 0.033 nm^{-1} (Fig. 5C), congruent
162 with previous Arctic DOM studies (Fichot et al., 2013). Although $S_{275-295}$ was not significantly correlated with AF4-based
163 MW in this study, the increase in $S_{275-295}$ (i.e. decrease in MW) from PSW to deeper waters was consistent with the overall
164 vertical decrease in AF4-based MW (Fig. 4).

165 Three fluorescent components (Fig. 6) were PARAFAC-validated and reported in previous studies (Dainard and
166 Guéguen, 2013; Kowalczuk et al., 2009; McIntyre and Guéguen, 2013; Singh et al., 2010; Stedmon and Markager, 2005;
167 Walker et al., 2009). Component C1 displayed a maximum excitation wavelength at 305 nm and emission wavelength at 410

168 nm, similar as to peak M (Coble, 1996), representing marine humic-like component or biological and microbial origin DOM
169 (Shimotori et al., 2012; Yamashita et al., 2008). This component was widely found in both freshwater and marine systems
170 (Dainard and Guéguen, 2013; Kowalczyk et al., 2009; McIntyre and Guéguen, 2013; Singh et al., 2010; Walker et al., 2009).
171 Component C2 showed a maximum excitation wavelength at < 280 nm and emission wavelength at 330 nm, which was
172 similar to peak T, traditionally considered as protein-tryptophan-like component (Coble, 1996). Tryptophan-like component
173 was linked to biological production (Coble et al., 1998) and commonly found among different aquatic systems (Dainard and
174 Guéguen, 2013; McIntyre and Guéguen, 2013; Stedmon and Markager, 2005). Component C3 had maximum excitation
175 wavelengths at < 270 nm and 365 nm and a maximum emission wavelength at 465 nm. This component was comparable to
176 peaks A and C (Coble, 1996). Despite of its terrestrial origin, similar components have been reported along a large salinity
177 scale (Dainard and Guéguen, 2013; Kowalczyk et al., 2009; Stedmon and Markager, 2005; Walker et al., 2013).

178 Total fluorescence intensity (TF=C1+C2+C3) as well as the fluorescent component (C1, C2 and C3) intensities (Fig. 7)
179 were within the ranges reported earlier (Dainard and Guéguen, 2013; Guéguen et al., 2014; Walker et al., 2009). TF was
180 relatively stable within each water mass except in ASW likely due to the influence of biological activities and sea ice melt.
181 Maximum TF and humic-like intensities (C1 and C3) were associated with PWW (150 m; Fig. 7A-B, D), consistent with
182 CDOM distribution (Fig. 5). Similar distributions were found in previous studies (Dainard et al., 2015; Guéguen et al., 2007,
183 2012b; Nakayama et al., 2011). Low TF in ASW is likely due to enhanced photobleaching (Dainard et al., 2015; Guéguen et
184 al., 2016; Logvinova et al., 2016) associated with a greater influence of DOM-poor sea ice melt waters (Belzile et al., 2002)
185 in surface waters. The prominent FDOM (and CDOM; Fig. 5) maximum at PWW was due to humic-rich materials brought
186 by injection of cold saline shelf waters (Guéguen et al., 2007; Moore et al., 1983; Woodgate et al., 2005). No significant
187 difference in humic-like fluorescence intensities was found in FSB and BSB between sites (0.0137 ± 0.0014 r.u. for C1;
188 0.0090 ± 0.0010 r.u. for C3), suggesting homogeneous humic-like intensity in deeper layers. Protein-like C2 intensity
189 maximum (Fig. 7C) was associated with the highly productive (Arrigo et al., 2008; Fouilland et al., 2007; Hill and Cota,
190 2005) ASW, confirming the biological origin of protein-like component. Lower C2 intensities were associated with the
191 PSW-PWW complex and Atlantic-derived waters. Homogeneous distribution ($p > 0.05$) was observed in AIW.

192

193 3.4 Relationship between fluorescence properties and MW

194 Despite a 40% difference in TF (0.042 vs 0.060 r.u., $p < 0.05$; Fig. 8), ASW and PWW showed similar average CDOM
195 MW values (1.37 vs 1.38 kDa) (Fig. 8). PWW was largely associated with the increase in aromatic CDOM (low $S_{275-295}$; Fig.
196 5C) and humic-like FDOM (Fig. 7) due to sediment interactions (Guéguen et al., 2007; Moore et al., 1983). Although
197 FDOM concentration and composition did not significantly influence MW in ASW and PWW, the significant decrease in
198 MW from PWW and AIW was associated with a dramatic decrease in humic-like intensities ($p < 0.05$). Similarly, PSW and
199 BSB displayed comparable mean MW values (1.27 kDa in both water masses) but a 39 % reduction ($p < 0.05$) in TF in BSB.
200 Together these results showed that a change in AF4 based MW does not necessarily mean a change in TF. This contrasts
201 with previous studies where higher TF, and particularly higher humic-like intensities, was generally associated with higher
202 MW material (Cuss and Guéguen, 2013; Huguet et al., 2010). Because the PARAFAC-validated components cannot be
203 attributed to pure compounds but to a group of compounds sharing similar fluorescence properties, it is possible that a
204 change in the concentration and/or nature of fluorescing compounds affects the fluorescence efficiency and therefore FDOM
205 signal without changing MW. Furthermore, Stolpe et al. (2014) showed that protein-like fluorescence (275/340 nm) in
206 marine waters had a size distribution that was very different from the size distribution of CDOM measured at 254 nm.
207 Further studies should be carried out to assess the influence of absorbing and fluorescing DOM composition on MW.

208 In terms of fluorescence composition in bulk samples (Fig. 9A-C), humic-like C1% and C3% decreased with increasing
209 MW ($r^2 = 0.38$ and 0.40 , respectively). This contrasts with protein-like C2% which was more abundant at higher MW ($r^2 =$
210 0.41 ; Fig. 9D). The change in size distribution between protein- and humic-like FDOM was also found in the northern Gulf
211 of Mexico (Stolpe et al., 2014) where humic-like components dominated small size marine DOM while protein-like DOM
212 was enriched in larger MW DOM. Similarly, increase in protein-like component was observed with decreasing $S_{275-295}$ (i.e.
213 increase in MW) in North Pacific seawater studies (Helms et al., 2013). Despite of variation in $S_{275-295}$, humic-like
214 components were found to be dominant ($> 50\%$) throughout the study area (Dainard and Guéguen, 2013).

215

216 4 Conclusions

217 For the first time, asymmetrical flow field-flow fractionation system was applied in the Arctic Ocean to assess CDOM
218 MW distribution in relation with optical properties and water masses. The CDOM MW ranged from 1.07 to 1.45 kDa,
219 consistent with earlier works. The vertical distribution of CDOM MW and optical properties showed some water-mass
220 related distribution pattern. DOM in Arctic surface waters displayed similarity in MW and fluorescence intensity across the
221 study area. PWW formed in from ice formation and freshwater injection, showed higher MW CDOM associated with higher
222 fluorescence intensity. Protein-like fluorescence became more dominant as MW increased, but humic-like components
223 remained dominant throughout the water column.

224

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235

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441

442 Figure Captions

443 Figure 1: Sampling locations in Beaufort Sea, Canada Basin

444

445 Figure 2: AF4 fractograms of CB29 (400m depth; black) and CB28b (1000m depth; gray)

446

447 Figure 3: A) Potential temperature and B) FDOM as a function of salinity (S_p) at the four study sites (Figure1). ASW -

448 Arctic surface waters, PSW – Pacific summer water, PWW – Pacific winter water, FSB – Fram Strait Branch water, BSB –

449 Barents Sea Branch water

450

451 Figure 4: MW depth profiles in Beaufort Sea

452

453 Figure 5: Depth distribution of A) a_{254} , (B) a_{355} , and (C) $S_{275-295}$

454

455 Figure 6: Individual components identified by PARAFAC (A- marine humic-like C1, B- protein-like C2 and C- terrestrial

456 humic-like C3)

457

458 Figure 7: Depth distribution of A) Total Fluorescence Intensity (TF), B) marine humic-like C1, C) protein-like C2 and D)

459 terrestrial humic-like C3

460

461 Figure 8: Change in TF vs CDOM MW

462

463 Figure 9: Correlation between MW and fluorescence components (A) C1; (B) C2; (C) C3; (D) Change in fluorescence

464 abundance with increasing DOM MW

Fig01

Fig02

Fig03

Fig04

Fig05

Fig06

Fig07

Fig08

Fig09