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2	Dissolved organic carbon dynamics in the East China Sea and the
3	northwest Pacific Ocean
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Abstract. Oceanic dissolved organic carbon (DOC) represents one of the largest carbon 33 34 reservoirs on Earth, and its distribution and biogeochemical cycles play important roles in carbon cycling and other biogeochemical processes in the ocean. We report the distribution and 35 concentrations of DOC for water samples collected from the shelf-edge and slope regions in 36 the East China Sea (ECS) and the Kuroshio Extension (KE) in the northwestern North Pacific 37 during two cruises in 2014-2015. The DOC concentrations were 45-88 µM in the ECS and 35-38 65 µM in the KE. In addition to biological processes that are estimated to account for 7% and 39 8-20% in shaping the DOC distribution in the ECS and KE regions, respectively, the DOC 40 distribution is largely controlled by hydrodynamic mixing of different water masses. By 41 42 comparing the DOC results with dissolved inorganic carbon (DIC) and dissolved inorganic radiocarbon (Δ^{14} C-DIC) measured from the same water samples, we further demonstrate that 43 the intrusion of the Kuroshio Current could dilute the DOC concentrations at stations in the 44 outer shelf and slope regions of the ECS. The concentrations of DOC in the KE were 45 46 significantly lower in surface waters than in the ECS, and a relatively low and stable DOC level (~40 µM) was found in deep water (below 1500 m) at all stations. Based on the previously 47 reported DIC and Δ^{14} C-DIC values for the stations, the observed spatial variations of DOC in 48 the upper 700 m among the stations in the KE were mainly influenced by mixing of the two 49 water masses carried by the Kuroshio and Oyashio, the two dominant western boundary 50 currents in the region. The hydrodynamic processes are thus important factors in the distribution 51 52 and dynamics of DOC in the KE region. 53

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58 **1 Introduction**

The world's oceans contain the second largest reservoir of carbon on earth, and dissolved 59 organic carbon (DOC) is the largest reduced carbon pool (685 Pg C) in the ocean (Hansell and 60 61 Carlson, 1998; Hansell et al., 2009). The DOC in the ocean consists of a highly diverse organic molecular mixture in which ~20,000 individual molecular formulae have been detected (Riedel 62 and Dittmar, 2014). The concentration and distribution of ocean DOC play significant roles not 63 64 only in the global carbon cycle but also in control and regulation of the microbial community and many biogeochemical processes in the oceans (Azam et al., 1983; Fenchel, 2008; Carlson 65 66 et al., 2010; Nelson and Carlson, 2012). Because ocean DOC is directly linked to the oceanic 67 dissolved inorganic carbon (DIC) system through biological photosynthesis and microbial respiration processes, the DOC pool in the ocean also indirectly contributes to the cycles of 68 atmospheric CO₂ (Druffel et al., 1992; Carlson et al., 1994; Carlson et al., 1998; Hansell and 69 Carlson, 2001; Carlson et al., 2010). 70

In the most recent 20 years, improved precision of DOC concentration analysis via the high-71 72 temperature catalytic oxidation (HTCO) technique has revealed detailed oceanic DOC distributions, such as those generated by the US Climate Variability Repeat (CLIVAR) 73 hydrography program (Sharp et al., 1995; Sharp et al., 2002; Carlson et al., 2010; Hansell et al., 74 2012; Bercovici and Hansell, 2016). In general, biological and physical processes combine in 75 modulating the distribution and dynamics of DOC in open oceans (Hansell and Waterhouse, 76 1997; Ogawa et al., 1999; Hansell et al., 2009; Carlson et al., 2010; Bercovici and Hansell, 77 2016). It has been widely observed that oceanic DOC accumulates in the upper water column 78 (100 m) at elevated concentrations (70-90 µM) compared with its relatively constant values 79 (35-45 µM) in deep water (>1000 m), reflecting biological production of DOC in the euphotic 80 zone and microbial consumption with depth (Hansell et al., 2009). However, many previous 81 82 studies conducted in different coastal and open oceans have shown that the distribution of DOC appeared to depend, to a large extent, on the hydrographical structure and/or horizontal/ vertical
water mixing (Hansell and Waterhouse, 1997; Hansell and Peltzer, 1998; Hung et al., 2007;
Ogawa et al., 2003; Guo et al., 1995) and the secondary biological forcing superimposed on the
physical forcing (Carlson et al., 2010; Wu et al., 2017). Based on a water mixing model, Wu et
al. (2017) also reported that microbial degradation contributed 10% of the DOC removal and
that physical mixing controlled the majority variation of the DOC pool in the northern South
China Sea.

The northwestern North Pacific is a rather special oceanic region where carbon cycling and 90 biogeochemical processes are greatly influenced by two major oceanic western boundary 91 currents: the Kuroshio Current (KC) and Oyashio Current (OC). As one of the largest 92 marginal sea in the northwestern North Pacific, the hydrological characteristics of the East 93 China Sea (ECS) are largely influenced by vigorous exchange between the warm saline 94 95 Kuroshio and cold fresh continental shelf water masses (Hsueh, 2000). Ogawa et al. (2003) reported that the distribution of DOC was primarily controlled by hydrological rather than by 96 97 biological processes around the shelf edge of the ECS. However, few studies have focused on the distribution and dynamics of DOC around the Kuroshio Extension region. DOC ¹⁴C analysis 98 from different North Pacific stations revealed the export of young DOC accompanied by the 99 North Pacific Intermediate Water (NPIW) formation, resulting in an enrichment in the Δ^{14} C-100 DOC values and a reduction in the notably old DOC ¹⁴C-age in the Pacific Ocean interior 101 102 (Druffel et al., 1992; Druffel et al., 2019), but the vertical profiles of DOC were only determined at stations in the subpolar water in the northwestern North Pacific (Hansell et al., 2002). DOC 103 104 observations in the WOCE (World Ocean Circulation Experiment) and CLIVAR cruises were collected at Line P02 stations along a 30° N latitudinal transect, but the distribution of DOC 105 near the KE was not investigated during these cruises. 106

107 Overall, our understanding of DOC dynamics and cycling in the outer shelf and slope regions

of the ECS and KE region is still limited. In this work, we present the results from DOC concentrations measured in the ECS and KE region in the northwestern North Pacific combined with the observations of dissolved inorganic carbon (DIC) concentrations and dissolved inorganic radiocarbon (Δ^{14} C-DIC) values for an evaluation of the roles of the physical mixing process on the distribution of DOC in these two different dynamic oceanic regions.

113 2 Methods

114 **2.1 Study areas**

115 Water samples were collected from two main oceanic regions: the ECS and the KE region in the northwestern North Pacific (Fig. 1). The ECS is one of the largest marginal seas connected 116 to the northwest North Pacific, with a broad continental shelf area of approximately 0.5×10^6 117 118 km² (Gong et al., 2003). In the relatively shallow (<60 m) and wider inner shelf region, oceanic processes are largely influenced by the inputs of the Yangtze and Yellow Rivers, which are the 119 largest and second largest rivers in China, and each delivers 1.58×10^{12} g DOC and 3.20×10^{10} g 120 DOC into the ECS (Wang et al., 2012; Xu et al., 2016). In the outer shelf and slope region of 121 the ECS, the hydrographic characteristics and oceanic processes are affected largely by the 122 123 northward-flowing Kuroshio Current, which impinges on the shelf break; and a branch of the Kuroshio Current enters the ECS across the shelf break (Chen and Wang, 1999; Guo et al., 2006; 124 Hu et al., 2015; Ge et al., 2016). The high primary productivity and intersection of different 125 water masses make the ECS a complex region for studying the ocean carbon biogeochemical 126 cycle. 127

The Kuroshio Extension (KE) in the northwestern North Pacific is an important and highly dynamic region that is largely influenced by the Kuroshio and Oyashio currents. The Kuroshio Current carrying relatively warm and saline waters flows northward along the east coast of Japan, turns eastward near 34° N/140° E, and subsequently flows as the KE into the North

132	Central Pacific (Yasuda et al., 1996; Qiu, 2001; Qiu and Chen, 2011). The southward-flowing
133	Oyashio Current, which carries fresh and cold subarctic water, meets with Kuroshio water at
134	approximately 37° N and forms the Kuroshio-Oyashio inter-frontal zone where the subarctic
135	water mass mixes with the KE water and flows eastward (Yasuda et al., 1996; Qiu and Chen,
136	2011; Hu et al., 2015). The new NPIW is formed in the same region and is a mixture of relatively
137	fresh and recently ventilated Oyashio water and high-salinity Kuroshio water (Yasuda et al.,
138	1996; Talley, 1997; Qiu and Chen, 2011). The mixed water region in the KE has been
139	characterized as an important sink of anthropogenic CO2 in the northwestern North Pacific
140	(Tsunogai et al., 1993), and it is a key area for understanding regional climate and ecosystem
141	variations and biogeochemical cycles (Yasuda, 2003; Wu et al., 2012; Hu et al., 2015; Nishibe
142	et al., 2017).

Table 1. Summary of sampling stations and times in the East China Sea (ECS) and the Kuroshio
Extension (KE) in the northwestern North Pacific (NP).

Station #	Latitude (°N)	Longitude (°E)	Water depth (m)	Sampling Date
<u>ECS</u>				
Stn.1	28.37	126.69	177	12 July 2014
Stn.7	28.30	126.83	265	12 July 2014
Stn.11	28.43	126.53	148	13 July 2014
Z1	28.07	127.13	1078	14 July 2014
Z2	27.93	127.36	1326	14 July 2014
Z4	28.63	127.00	425	14 July 2014
Z3	27.75	126.63	1415	15 July 2014
<u>KE in NP</u>				
K2	25.10	134.02	4100	5 April 2015
B2	37.00	147.00	5586	27 April 2015
B8	30.97	146.99	6000	11-12 April 2015
B9	29.86	146.53	5500	10-11 April 2015
A1-b	32.63	145.95	4800	18 April 2015
A4	34.00	147.80	5800	25 April 2015
A6	34.02	150.04	5800	23 April 2015
A8	34.04	152.02	5500	21 April 2015

147 **2.2 Sample collection**

Water samples for DOC analysis were collected from 7 stations on the shelf-edge and slope 148 region of the ECS during a cruise in July 2014 onboard the Japanese R/V Shinset Maru and 149 150 from 8 deep stations in the KE region and western North Pacific during a cruise in April-May 2015 onboard the Chinese R/V Dongfanghong-2 (Fig. 1). General information on the sampling 151 stations is summarized in Table 1. All water samples were collected using 12 L Niskin bottles 152 153 deployed on a rosette with a calibrated SeaBird CTD (model SBE 911) that recorded the temperature and salinity profiles. The accuracies for temperature and salinity are 0.001°C and 154 155 0.001, respectively.

After collection, water samples from the Niskin bottles were transferred directly into a 1 L pre-combusted (at 550°C for 4 h) glass bottle after rinsing three times with seawater. The water was filtered immediately on board through Whatman GF/F filters with 0.7 μ M pore size (prebaked at 550°C for 4 h). The filtered water samples were acidified with super-high-purity 85% H₃PO₄ (Aladdin[®]) to pH = 2 and preserved in a frozen state at -20°C until chemical analysis.

161 **2.3 Chemical analysis**

Concentrations of DOC were analysed by the high temperature catalytic oxidation (HTCO) 162 method (Sharp et al., 1995; Sharp et al., 2002) using a Shimadzu TOC-L analyser equipped 163 with an ASI-V autosampler. Potassium hydrogen phthalate (KHP) dissolved in high-purity 164 Milli-Q water was used as the DOC standard. The quality assessment for DOC measurements 165 166 was checked against reference low-carbon water and deep-sea water which were analysed every 10 samples (CRM Batch 13 with 41-44 µM DOC concentration, supplied by Hansell 167 Biogeochemical Laboratory at University of Miami, USA). The average value and standard 168 deviation of deep-sea water reference throughout our measuring was 43±1 µM, which was used 169 as an index of our analytical precision. The instrumental blank was subtracted using high-purity 170 Milli-Q water that was analysed between samples (before every sample for deep seawater). The 171

average blank of the DOC measurement was $\leq 5 \mu$ M, and the analytical precision on triplicate injections were $\pm 3\%$. All samples were analysed in duplicate from different vials, and the average values were reported. The standard deviation for DOC ranged in ± 0.1 - 4.0 μ M.

The methods for DIC concentrations and Δ^{14} C-DIC measurements were described in detail 175 in separate papers for the samples collected during the same cruises (Ge et al., 2016; Ding et 176 177 al., 2018). In brief, DIC concentrations were measured using a Shimadzu TOC-L analyser with the total IC mode. Sodium carbonate and sodium bicarbonate dissolved in Milli-Q water were 178 used as the DIC standards, and the concentration values were checked against DIC reference 179 180 materials (deep sea water) for quality assessment (supplied by Dr Dickson at Scripps Institution of Oceanography). The total blanks were approximately < 0.15% of the seawater DIC 181 concentrations, and the analytic precisions were < 3%. For ¹⁴C-DIC measurement, DIC was 182 first extracted as gaseous CO_2 using our modified method with extraction efficiencies > 96% 183 (Ge et al., 2016). The ¹⁴C-DIC values were analysed in the National Ocean Sciences Accelerator 184 185 Mass Spectrometry (NOSAMS) facility at Woods Hole Oceanographic Institution (WHOI). The purified CO₂ was graphed for Δ^{14} C analysis using AMS. The Δ^{14} C values are reported as 186 the modern fraction based on the reference material used (McNichol et al., 1994). The 187 conventional ¹⁴C ages (years before present or yr BP) were calculated following the method of 188 189 Stuiver and Polach (1977). The maximum total uncertainty is 6‰, as tested with a DIC standard (Ge et al., 2016). 190

191 **3 Results**

192 **3.1 Hydrography**

The hydrographic parameters of the sampling stations (temperature and salinity) recorded with the CTD are summarized in Table S1 in the Supporting information, and the depth profiles are plotted in Fig. S1. The hydrology of the water is further described in the T-S diagrams, as plotted in Fig. 2. The physical properties of different water masses in the two oceanic regions
were extracted from literature and corresponded to the temperature and salinity of the water
types in their formation area or the values around the boundaries, which is also included in Fig.
Because our study involved two distinctive oceanic regions, we separately plotted the
hydrographic characters (T-S diagrams) for stations in the ECS (Fig. 2a) and KE (Fig. 2b)
regions.

As shown in Fig. 2a and Fig. S1 for the seven shelf-edge and slope stations in the ECS, the water temperature was higher (26.3-29.3°C) at the surface ($\leq 10 \text{ m}$ and $\sigma_t \leq 22.1$) and decreased rapidly with depth at all stations. The salinity ranged from 33.88 to 34.87 and exhibited a reversed *S*-shape, i.e., lower at the surface, increasing with depth to the maximum at 150 m water depth (23.2-24.9 σ_t), and decreasing again to 500 m (26.4-26.8 σ_t). The salinity (*S*) remained relatively constant below 500 m depth (at $\sigma_t > 26.8$) for the three slope stations (Fig. 2a and Fig. S1).

For Sta. K2 and the seven deep stations in the KE, the temperature (T) of the surface water 209 ranged from 14.7 to 24.4°C, exhibited a rapid decrease and subsequently remained constant for 210 all stations at density levels of $\sigma_t > 27.6$ at ~1500 m depth (Fig. 2b and Fig. S1). The largest 211 temperature variations occurred in the upper 700 m with the highest $T(24.4^{\circ}C)$ observed at Sta 212 213 K2 (end-member value of T in the Kuroshio water) and the lowest $T(14.7^{\circ}C)$ at Sta B2 observed in the surface layer (5 m) (end-member value of T in the Oyashio water) (Fig. 2b). The salinity 214 (S) for these stations was higher at the surface, decreased initially to reach a minimum at the 215 density range of 26.4-26.9 σ_t , and subsequently increased with depth to approximately 2500 m 216 with the density layer of 27.6 σ_t (Fig. 2b). The salinity for all stations remained relatively 217 uniform below 2500 m ($\sigma_t > 27.6$). Similar to T, the largest differences in salinity also appeared 218 in the upper 700 m water column (the density range of 26.4-27.0 σ_t), where low salinity (34.49) 219 was observed at the surface of Sta B2. The salinity decreased to 33.66 near 250 m and 220

subsequently increased to values similar to those of the other stations at 2500 m. The salinity
for the remaining seven stations (Stas. K2, A1-b, A4, A6, A8, B8 and B9) showed less variation
in the surface layers (5 m) (34.76 to 34.98), and Sta K2 had the highest *S* (34.98) at the surface
among all stations (Fig. 2b and Fig. S1) (the typical salinity of Kuroshio water is 34.98 and
33.66 for the Oyashio water).

226 **3.2 Concentrations and distribution of DOC**

227 To examine the distribution of DOC with different water masses in the studied regions, we plotted the depth profiles (Fig. 3) and the T-S-DOC diagrams for the ECS and the KE, as shown 228 in Fig. 4. The concentrations of DOC ranged from 45 to 88 μ M in the ECS and from 35 to 65 229 µM in the KE region (Fig. 3 and Table S1). The concentrations of DOC ranged from 55 to 88 230 μ M for the four shelf-edge stations (Stn. 11, 1, 7 and Z4) and from 45 to 84 μ M for the three 231 232 slope stations (Stas. Z1, Z2 and Z3) in the ECS. As plotted in Fig. 3a and Fig. 4a, the concentrations of DOC showed less variation (71-81 μ M) in the surface water (≤ 10 m and $\sigma_t \leq$ 233 22.1) and decreased rapidly to ~300 m depth for all stations in the ECS. Below 300 m, the 234 235 concentrations of DOC remained relatively constant down to 1000-1400 m depth for Z1, Z2 and Z3 (Fig. 3a). 236

The concentrations of DOC in the KE region were much lower than that in the ECS, and 237 above 1000 m the stations showed large spatial variations (Fig. 3b). The highest DOC value (65 238 μ M) and the lowest DOC level (43 μ M) were measured at the surface at Sta K2 and Sta B2, 239 respectively. In the upper 200 m depth, the concentrations of DOC also showed a notably rapid 240 decrease for most stations. The DOC concentrations were visibly lower at Sta A4 and Sta B2 241 (36-53 μ M) than at the other stations in the upper 700 m depth (at $\sigma_t < 27.0$), whereas the 242 concentrations were slightly higher in the 500-800 m depth at Sta B8 and Sta A8. The T-S-DOC 243 diagrams showed that DOC concentrations decreased to relative low levels (36-44 µM) at all 244 stations at $\sigma_t > 27.5$ (approximately below 1500 m depth) and remained constant in deep waters 245

246 (Fig. 3b and Fig. 4b).

247 **3.3** Concentrations and radiocarbon distribution of DIC

The results of the DIC concentrations and Δ^{14} C-DIC values measured from the same samples 248 have been recently published (Ge et al., 2016; Ding et al., 2018). In this work, we use these data 249 as water mass tracers to support our DOC results. In brief, as shown in Fig. 5a, the DIC 250 concentrations were higher in the four shelf-edge stations (Stn.11, Stn.1, Stn.7 and Z4) than that 251 in the slope stations (Z1 and Z2) at the same depths in the ECS (Fig. 5a). The depth profiles of 252 Δ^{14} C-DIC showed a trend opposite to that of the concentrations of DIC, i.e., higher at the 253 surface and decreasing with depth (Fig. 5b). Higher DIC concentrations had lower Δ^{14} C-DIC 254 values. The Δ^{14} C-DIC values at 138 m for Stn.11 and 413 m for Stn. Z4 were significantly 255 256 lower than the values of the slope stations at the same water depths (Fig. 5b).

The concentrations of DIC were also lower at the surface and increased with depth for the 257 stations in the KE region (Fig. 5c). The large variability in DIC concentrations was observed 258 between 400 and 800 m depths. The Δ^{14} C-DIC values were high at the surface, decreased with 259 depth and showed large variations in the upper 250-1000 m among the stations (Fig. 5d). The 260 Δ^{14} C-DIC values showed a rapid drop within only the upper 500 m of the water column at Sta 261 A4 and in the upper 1000 m depth at Sta B2 and subsequently remained constant below 1000 262 m depth. The Δ^{14} C-DIC profiles for stations K2, A8, and B9 exhibited a similar trend. The 263 surface bomb ¹⁴C signal mixed well down to 600 m and subsequently decreased until 1500 m 264 (1000 m for K2) (Fig. 5d). 265

266 4 Discussion

267 **4.1 Processes that control the DOC distribution in the ECS**

In this study, the concentrations of DOC measured in the shelf-edge and slope waters are comparable to the values reported previously for the ECS (Hung et al., 2003; Ogawa et al.,

2003; Gan et al., 2016). As one of the large river-influenced shallow (~60 m) marginal sea, 270 271 many factors could influence the distribution of DOC. The inputs of the Yangtze and Yellow rivers play important roles affecting the carbon cycling in the ECS. In their study, Wang et al. 272 (2012) and Xue et al. (2017) reported that the Yangtze and Yellow rivers delivered 3.1×10^{12} g 273 and 7.26×10^{10} g terrestrial organic carbon, comprised 45-50% DOC input to the ECS in 2009 274 and 2015. These riverine DOC was derived mainly from pre-aged soil organic matter with ¹⁴C 275 276 ages of around 1,000 years old (Wang et al., 2012; Xue et al., 2017). The observed higher DOC concentrations in the upper layer of the ECS could be caused by the riverine refractory DOC 277 that was cycled in the water for long time and transported offshore. In addition, DOC 278 279 concentration in the shallow shelf region of the ECS could be influenced by relatively high primary production, flux from sediment and bacterial degradation (Ogawa et al., 2003; Wang 280 et al., 2012; Gan et al., 2016). However, export of DOC from the shelf water to the slope 281 282 offshore could be limited because most of the bioavailable DOC had been respired in the shelf waters (Bauer and Bianchi, 2011; Bauer et al., 2013; Ward et al., 2017). In the shelf edge and 283 284 slope region of the ECS, early studies by Hung et al. (2003) and Ogawa et al. (2003) reported that the distribution of DOC was primarily controlled by physical processes rather than 285 production and/or microbial processes. In this respect we observed a statistically significant 286 positive correlation between DOC and water temperature ($R^2 = 0.82$, p < 0.001) for the stations 287 in the ECS (Fig. 6a). A similar pattern has also been found in other marginal seas of the North 288 Pacific (Hung et al., 2007; Dai et al., 2009). In our recent study, we reported that the 289 concentrations of DIC and Δ^{14} C-DIC in the ECS slope and the KE region showed conservative 290 behaviour and could be used as tracers of water mass movement and water parcel 291 homogenization as predicted by the solution mixing model (Ge et al., 2016; Ding et al., 2018). 292 As shown in Fig. 6b, the negative relationship between DOC and DIC ($R^2 = 0.73$, p < 0.001) 293 for the stations further suggests that physical processes (such as horizontal and vertical water 294

mixing) influenced the distribution and variation of DOC in the shelf break and slope region of the ECS. However, since DOC is not conservative in the ocean, the observed strong correlation between DOC and T could involve biological and microbial processes and possibly depth covariation. Using this DOC-T correlation alone, we are not able to drawn conclusion that physical mixing was the controlling factor influencing the distribution of DOC in the ECS.

Although the river inputs play an important role in the ECS, our sampling stations in the slop 300 301 region are unlikely affected directly by freshwater input from the Yangtze River, according to the high salinity without any freshwater dilution signals in Fig. 2a and Fig. S1. The vertical 302 variations of DOC for the shelf-edge and slope stations, as shown in Fig. 3a, followed a typical 303 304 trend similar to the DOC depth profiles observed in open oceans, with higher levels of DOC in the low-density upper waters and low levels of DOC in the high-density deep waters. Around 305 the shelf-edge of the ECS, the vigorous exchange between the warm saline Kuroshio and cold 306 307 fresh continental shelf water masses affect the hydrographical characteristics (Hsueh, 2000). As shown in Fig. 2a, the salinity maximum at the density range of 23.2-24.9 σ_t (near 100-160 m) 308 309 is influenced largely by the northward-flowing Kuroshio Current. Physical models and chemical tracers both supplied clear evidence of the intrusion of upwelled Kuroshio 310 intermediate water (500-800 m) into the ECS shelf region (Yang et al., 2011; Yang et al., 2012; 311 312 Ge et al., 2016). To further demonstrate the influence of different water mass mixing processes on the hydrological properties, Figure 7 compared the latitudinal distributions of salinity, 313 DOC/DIC concentrations and Δ^{14} C-DIC for the seven stations in the ECS. The cross-section 314 salinity plot (Fig. 7a) showed that the water mass in the studied area was composed of mixed 315 Kuroshio and shelf waters. It appeared likely that the influences of Kuroshio intermediate water 316 (500-800 m) on the bottom water at station Z4 and Stn. 11 brought low concentrations of DOC, 317 high concentrations and low Δ^{14} C values of DIC (Fig. 7b-d). This intrusion of Kuroshio 318 intermediate water diluted the DOC at Stn. 11 and Z4. However, it appears that this upwelling 319

intrusion had almost no effect on the surface water (<100 m depth) for the shelf stations. The
intrusion of Kuroshio intermediate water could reflect a smaller-scale or eddy effect rather than
a large-scale influence beyond Stn. 11 and Z4 (Ge et al., 2016).

The calculation based on the Δ^{14} C-DIC mass balance showed that approximately 54-65% of 323 the bottom water in the shelf region of ECS originated from the intrusion of Kuroshio 324 325 intermediate water (Ge et al., 2016). As referred to the water mass analysis on the basis of the assumed conservative variables (potential temperature and salinity) as the characteristics of 326 water type (Catalá, et al., 2015a and 2015b), if we use the same two end-member mixing model 327 328 (Ge et al., 2016) and the corresponding average DOC values for the shelf water (77 μ M) and Kuroshio water (52 μ M), the conservative concentrations of DOC (referred as DOC⁰) could be 329 calculated in the range of 61-64 µM, which is slightly higher but comparable to the observed 330 DOC values in the bottom waters at Stn. 11 and Z4 (56-61 μ M). The negative values of Δ DOC 331 (measured $DOC - DOC^{\theta}$) could represent the biological consumption effects superimposed on 332 the water physical mixing processes around the shelf-edge and in the slope of ECS. Based on 333 334 the calculated ΔDOC and the field-measured DOC, we estimated that the bioavailable fraction 335 of DOC could account for approximately 7% of the total DOC pool in this region. The value is 336 comparable to the results (6.1% and $10\% \pm 5\%$) previously reported for the Kuroshio Current and the shelf-slope region of the South China Sea (Gan et al., 2016; Wu et al., 2017). Clearly, 337 biological processes had a significant influence on DOC but were not the dominant controlling 338 factor on the observed DOC distributions in the ECS. 339

4.2 Processes that influence the DOC profiles in the Kuroshio Extension

In general, the biological and physical processes could both affect the DOC profiles in open oceans (Hansell and Waterhouse, 1997; Ogawa et al., 1999; Hansell et al., 2009; Carlson et al., 2010; Bercovici and Hansell, 2016). Based on a correlation analysis of data collected over ten years in the KE region, Nishikawa et al. (2011) presumed that the shoaling of mixed layer depth

could reduce the nutrient supply from deep layers, resulting in less productivity around the KE 345 346 region in the spring. Low primary production was also observed during the spring time on previous cruises between 2008 and 2011 in the KE region attributed primarily to the low 347 concentration of nitrate and silicic acid (Nishibe et al., 2015). Moreover, notably low levels of 348 available dissolved nitrogen (< 4 μ M) were observed in the region (unpublished data) during 349 the same cruise in spring (April-May 2015). The relatively lower surface DOC concentrations 350 351 (average $57\pm7 \mu$ M) could be due to the low primary production during sampling in the spring season. Despite the low DOC concentrations in the region, we observed the interesting feature 352 of relatively large spatial variations for DOC concentration among these stations, especially in 353 354 the upper 1500 m (Fig. 3b and Fig. 4b). For example, concentrations of DOC in the upper 100 m depth at Stas B2 and A4 located north of and around the KE were significantly lower (average 355 43 ± 5 µM) than those of other stations and were close to the deep water values (ca. 36-44 µM, 356 357 average 39±3 µM), while elevated concentrations of surface DOC (61-65 µM) prevailed at Sta K2 located far south of KE and the other five stations (54-63 µM, Stas A1-b, B8, B9, A6 and 358 A8), with values 28% higher than average. In the KE region, primary production is largely 359 affected by advection along the KE meander and differs among representative areas in spring, 360 i.e., high in the northern edge and around the KE axis (483-630 mg C m⁻² day⁻¹), accompanied 361 362 by high chlorophyll a concentration and high column integrated chlorophyll a values (35-44 mg m⁻²) in April (Nishibe et al., 2015). The relatively high primary production should result in 363 a high level of DOC in the stations located north and around the KE, but the measured DOC 364 concentrations were rather low at Stas B2 and A4. In addition, surface mooring data from the 365 NOAA Kuroshio Extension Observatory (KEO) indicated that physical processes dominate the 366 carbon input to the mixed layer at KEO (Fassbender et al., 2017). Therefore, we speculate that 367 the low DOC levels at Sta B2 and A4 were unlikely directly related to the primary production, 368 and instead, the observed large spatial variations were mainly modulated by the mixing 369

370 dynamics of different water masses rather than biological processes in the region.

371 Hydrodynamic mixing can be directly evaluated by comparing the DOC concentrations with the variables of hydrographic properties. In Figs. 6c and 6d, we examined the correlations of 372 the DOC concentrations with water temperature and DIC concentrations in the KE region, 373 respectively. Overall, a positive relationship exists between the DOC concentrations and 374 temperature in the KE (Fig. 6c, $R^2 = 0.62$, p < 0.001), and a negative correlation exists between 375 the DOC and DIC concentrations (Fig. 6d, $R^2 = 0.51$, p < 0.001). Considering the relatively 376 conservative behaviour of DIC in the open ocean, it could be used as tracers of water mass 377 movement and water parcel homogenization as predicted by the solution mixing model in the 378 379 KE region (Ding et al., 2018). The observed correlations of DOC concentrations and hydrographic variables could thus indicate the physical water mixing played important roles on 380 the DOC distribution in the KE region. To further examine the distribution of DOC with 381 different water masses in the KE region, we plotted the DOC and DIC concentrations and Δ^{14} C-382 DIC values superimposed on the plots of potential temperature (θ) and salinity in Fig. 8. It can 383 be observed that the distributions of DOC, DIC and Δ^{14} C-DIC were clearly associated with 384 different water masses, as identified by the temperature, salinity and potential density (σ_0) in 385 the T-S diagrams (Fig. 8). The denser water mass C with density levels of 26.4-27.1 σ_0 near 386 387 500-800 m (Fig. 8) likely originated from the subarctic gyre, which had low temperature and salinity and was transported by the south-flowing Oyashio Current along the western boundary 388 389 to the KE region. This water is subsequently mixed with the warm saline water mass transported 390 by the northeast-flowing Kuroshio Current (water mass A) corresponding to the six stations 391 (K2, A1-b, A6, A8, B8 and B9) in the south of KE axis.

Many results suggested that hydrodynamic processes, such as the deep water penetration by vertical mixing, possibly affected the DOC concentrations within the surface waters in the high latitude despite high primary production (Ogawa et al., 1999; Ogawa and Tanoue, 2003).

Considering the relatively lower temperature ($< 15^{\circ}$ C) and salinity (< 34.5) in the upper 700 m 395 396 (Fig. 2b and Fig. S1), Sta B2 was mainly affected by the intrusion of cold and fresh subarctic water transported by the southward-flowing Oyashio, which also carried lower concentrations 397 of DOC. In contrast, despite the nutrient-depleted and low primary productivity in the 398 subtropical gyre, physical stability factors such as water column stratification could restrict the 399 vertical mixing of the surface and deep waters, which is beneficial for DOC accumulation in 400 the surface layer. The similar patterns of hydrographic properties and relatively higher DOC 401 levels in the upper 500 m at Sta K2 and other five stations (A1-b, B8, B9, A6 and A8) in the 402 KE region suggested that the Kuroshio water dominated the mixing in the upper 500 m at these 403 404 stations, which are mainly characterized with a subtropical warm and high-salinity water mass, as demonstrated in Fig. 3b and Fig. S1. The regional influences of the two water masses carried 405 by Kuroshio and Oyashio currents can be demonstrated more clearly in Fig. 9, where we plotted 406 the salinity, DOC and DIC concentrations, and Δ^{14} C-DIC values for the five stations (B2, A4, 407 A1-b, B8 and B9) as a cross KE transect from north to south. It can be observed that the 408 Kuroshio, which carries relatively high DOC, dominated stations B9, B8 and A1-b above 500 409 m depth. The latitudinal distributions of salinity could serve as intuitive evidence to show the 410 411 intrusion of Oyashio Current, which resulted in the low salinity near 200-800 m at Sta B2 and other two reference stations at the north and near of 35° N labelled in Fig. 9e (at a density range 412 of 26.4-26.9 σ_t in Fig. 2b). It appeared likely that the Oyashio, which carries low salinity, low 413 DOC but high DIC concentrations, and low Δ^{14} C-DIC values in the subarctic intermediate water, 414 influenced the upper layers (above 1000 m) at Sta B2. The Oyashio water could further intruded 415 416 southward to affect the upper 200-1000 m at Sta A4 and mixed with the Kuroshio water to form the KE water mass flowing eastward, which resulted in low DOC, high DIC and low Δ^{14} C-DIC 417 values. However, it cannot be determined whether this southward intrusion of Oyashio water is 418 seasonal or decadal oscillations (Ding et al., 2018). Previous studies focused on physical 419

oceanography have shown that the unstable mode of the KE could generate active water-mass 420 421 changes around the region, such as the enhanced meso-scale eddies and ocean recirculation (Qiu and Chen, 2005; Qiu and Chen, 2011; Ma et al., 2016). The fresher Oyashio-origin water 422 could be transported southward through the meso-scale eddies (Qiu and Chen, 2011), 423 influencing the chemical and biological processes in the KE region. Using the significantly low 424 Δ^{14} C-DIC values at stations B2 and A4 in the upper 700 m depth in the KE region, we also 425 426 demonstrated the same strong influence of the southward Oyashio-transported subarctic intermediate water mass via meso-scale eddies (Ding et al., 2018). The ratios of Oyashio water 427 428 to Kuroshio water mixing for the five stations (B2, B8, A4, A8 and B9) were obtained by mass balance calculations based on the selected two end-member Δ^{14} C-DIC values (an average of 429 50‰ for the Kuroshio water and -220 ‰ for the North Pacific Intermediate Water of Oyashio) 430 in the Δ^{14} C-DIC Keeling plot analysis (Fig. 10) (Ding et al., 2018). For example, 55-58% 431 Oyashio water could contribute to produce the observed Δ^{14} C-DIC values at the depth of 500 432 m in Stas B2 and B8 and 100% Oyashio water at Sta A4 and 96-100% Kuroshio water at Stas 433 A8 and B9, respectively. If we consider that the distribution of DOC is controlled mainly by 434 435 hydrodynamic mixing in the KE region, the conservative concentrations of DOC could subsequently be calculated using the two water mass mixing model and the corresponding 436 average DOC values for the selected end-member water masses (an average of 57 µM for the 437 Kuroshio water and 40 μ M for the NPIW of Oyashio) derived from the Δ^{14} C-DIC values within 438 the range of 40-56 μ M. The difference between the measured and conservative DOC (DOC⁰) 439 concentrations ($\Delta DOC=DOC_{measured} - DOC^{\theta}$) can represent other biological processes that 440 441 secondarily modulate DOC in the KE region. For example, the positive Δ DOC values (~6 μ M) that accounted for approximately 11% of the measured DOC at Sta B8 indicated a net DOC 442 increase from biological processes, accompanied by the relatively low DIC concentrations 443 shown in Fig. 9c. The recirculation gyre immediately south of the KE has been found to exhibit 444

high production rates in winter-spring season in the North Pacific due to the entrainment of nutrient-rich water during deep winter mixing (Yasunaka et al., 2013; Yasunaka et al., 2014). However, biological consumptions of DOC could account for 8-20% of the total DOC pool based on the negative Δ DOC values (2-8 µM) and the measured DOC at Stas B2 and A4.

449 The concentrations of DOC in deep waters in the KE region were low, in the range of 36-44 µM, comparable to the values reported for the deep North Pacific (Druffel et al., 1992; Hansell 450 451 and Carlson, 1998; Hansell et al., 2009) and the deep South Pacific (34-43 µM) (Doval and Hansell, 2000; Druffel and Griffin, 2015) but slightly lower than the values in the North Atlantic 452 453 (40-48 µM) (Carlson et al., 2010; Druffel et al., 2016). These uniformly low levels of DOC indicate the homogeneous distribution of deep water and the more presumably refractory DOC 454 left behind in deeper waters in the KE and North Pacific (Carlson et al., 2010; Hansell et al., 455 2012; Follett et al., 2014). Radiocarbon measurements of DOC collected in the KE indicate that 456 the ¹⁴C age of DOC in deep water was ~6,200 years (Wang, unpublished data), similar to the 457 458 DOC ages in the deep North Pacific (Druffel et al., 1992), and support the refractory nature of DOC in the deep KE. The lower deep DOC concentrations in the North Pacific relative to the 459 North Atlantic could be due to the general circulation pattern of the world ocean, as proposed 460 by Hansell and Carlson (1998). DOC has been cycled for longer time scales with older ¹⁴C ages 461 (~6,000 years) in the deep North Pacific (Druffel et al., 1992) than DOC (~4,000 years) in the 462 North Atlantic Ocean (Bauer et al., 1992). However, by comparing with the deep DOC results 463 in the slope region of the ECS, it can be observed that the deep DOC level in the KE was 10-464 15 µM lower on average than that in the ECS, implying the possibility of outflow export of 465 466 DOC from marginal seas to the ocean interior and cycling in the deep ocean for a long duration.

467 **5 Summary**

468 The results of our study indicate that the concentration of DOC ranged from 45 to 88 μ M in 469 the outer shelf and the slope region of ECS and from 35 to 65 μ M in the KE region. The distribution of DOC in the shelf-edge and slope region of the ECS was largely influenced by
the physical mixing processes of Kuroshio and ECS shelf waters. The upwelling intrusion of
Kuroshio intermediate water could dilute the DOC concentrations at stations around the shelf
break region of the ECS.

In comparison, the concentrations of DOC in the KE region were significantly lower in the 474 surface layer. The DOC in the deep water of the KE had similar comparable values as those 475 reported for the deep north and south Pacific. The large spatial variations of DOC in the upper 476 700 m among the stations in the KE were influenced primarily by hydrodynamic mixing of two 477 different water masses. The Kuroshio, which carries warm and relatively higher DOC water, 478 479 and the Oyashio, which carries cold and fresh subarctic intermediate water with lower DOC, mix to form KE. These mixing dynamics could have a major influence on primary production 480 and on biogeochemical processes in the KE region. 481

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484 *Data availability.* All data used in this study will be freely available, for scientific use only, 485 upon request. Anyone interested in using this data set for scientific research should contact the 486 corresponding author via e-mail.

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490 Author contributions. Ling Ding is a post-doc working on this project, participated in the cruises, 491 sample analysis and manuscript writing. Tiantian Ge is a laboratory technician participated in 492 all cruises, sampling and sample analysis. Dr. Xuchen Wang is the corresponding author and 493 leading scientist for this study from proposal writing, cruise and sampling planning, and 494 manuscript writing. All authors have read the manuscript and agreed on the authorship.

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498 *Competing interests.* The authors declare that they have no conflict of interest.

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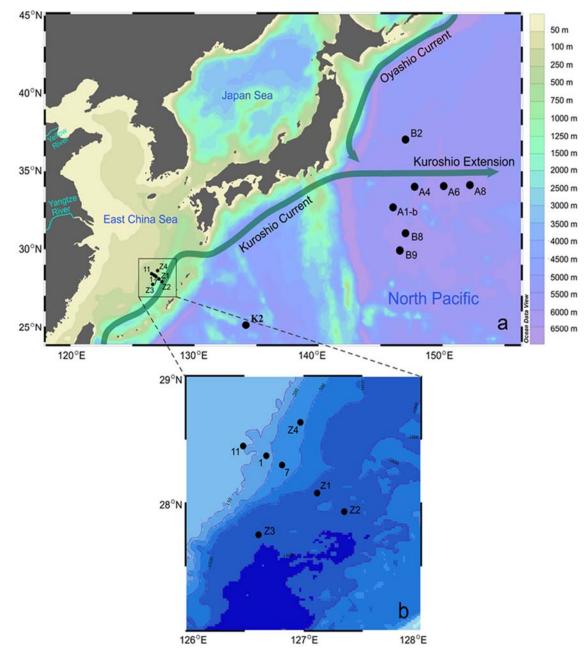
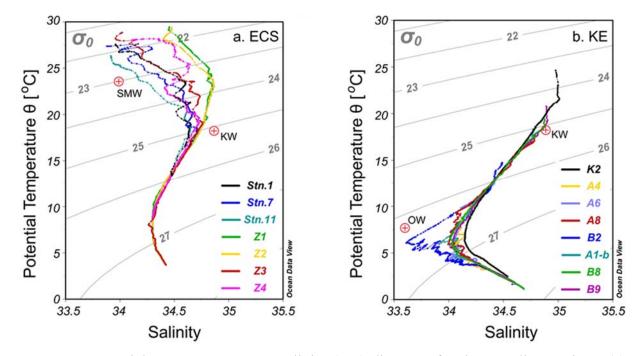


Figure 1. Map showing the study region and the sampling stations in the ECS and the northwestern North Pacific during two cruises in 2014-2015 described in the text. Two major western boundary currents, the northeastward-flowing Kuroshio and southward-flowing Oyashio, meet and form the Kuroshio Extension flowing eastward to the North Central Pacific.



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Figure 2. Potential temperature versus salinity (T-S) diagrams for the sampling stations. (a) 717 Seven shelf-edge to slope stations in the ECS and (b) eight deep stations in the KE region in 718 the northwestern North Pacific. σ_0 isolines are included in the figures. The coloured lines 719 correspond to CTD data, and red dots indicate the potential temperature (θ) and salinity (S) of 720 different water masses. The representative θ and S of these water types referred to previous 721 studies (Yasuda et al., 1996; Chen and Wang, 1999; Hung et al., 2003; Wong et al., 2007) 722 Acronyms used in this figure: SMW-Shelf Mixed Water, KW-Kuroshio Water and OW-Oyashio 723 724 Water.

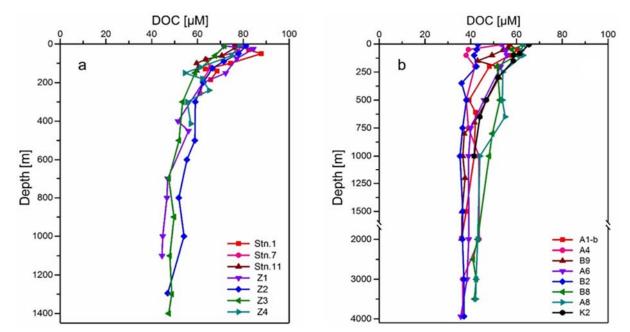


Figure 3. Depth profiles of DOC concentrations measured for the stations in the (a) ECS and
(b) northwestern North Pacific during the two cruises in 2014-2015. Note in panel b that the
depth below 1500 m is on a different scale.

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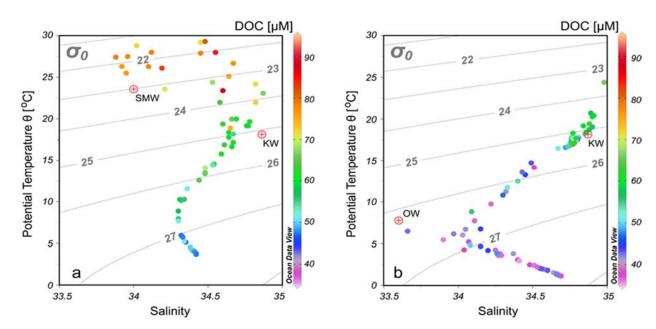


Figure 4. DOC concentrations superimposed on plots of potential temperature versus salinity for the sampling stations in the (a) ECS and (b) Kuroshio Extension in the northwestern North Pacific. σ_0 isolines are included in the figures. Red dots indicate the potential temperature and salinity of the water types, and acronyms of water types as SMW-Shelf Mixed Water, KW-Kuroshio Water and OW-Oyashio Water.

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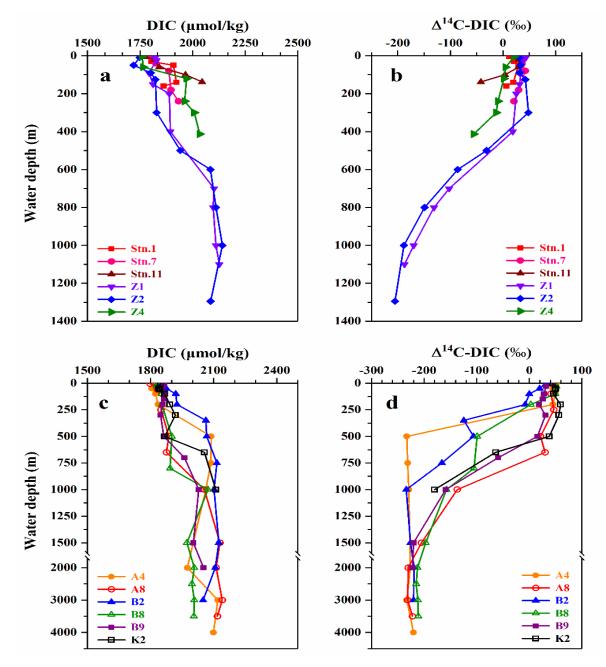


Figure 5. Depth profiles of DIC concentrations and Δ^{14} C-DIC measured for the stations in the (a, b) ECS and (c, d) northwestern North Pacific during the two cruises in 2014-2015. Note in panel c and d that the depth below 1500 m is on a different scale. The plots were adapted from data previously reported in Ge et al. (2016) and Ding et al. (2018).

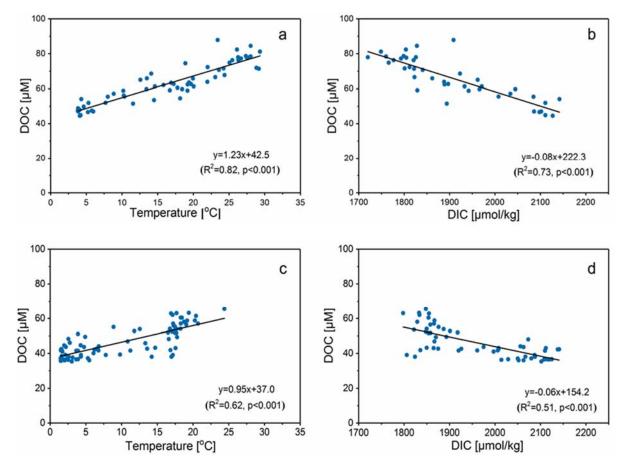
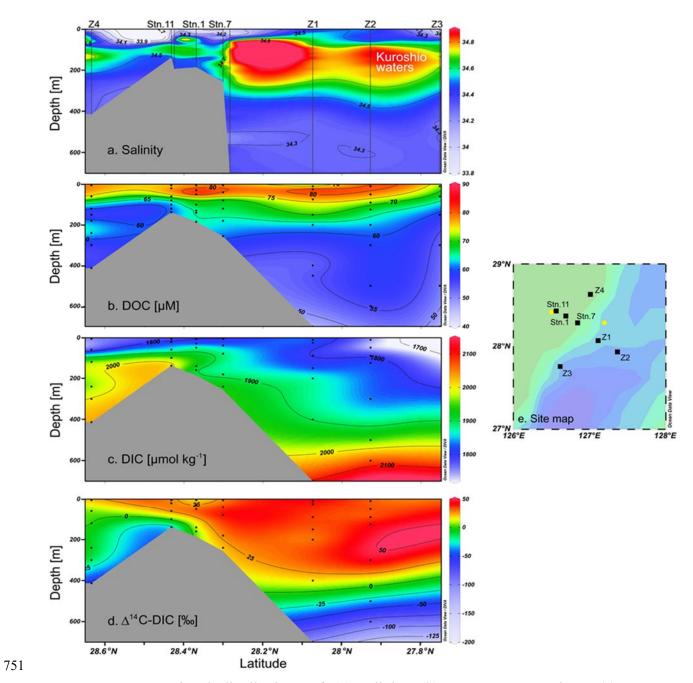




Figure 6. Correlation of DOC concentrations with water temperature and DIC concentrations
for stations sampled in the (a, b) ECS and (c, d) KE. The solid lines denote linear regressions
fit to the data.



752 Figure 7. Transectional distributions of (a) salinity, (b) DOC concentrations, (c) DIC concentrations and (d) Δ^{14} C-DIC values for the (e) sampling stations (black squares) covering 753 the shelf-edge and slope region of ECS during the cruise in July 2014. Black dots indicate the 754 755 depths where samples were collected. Note: (a) The salinity of the other two stations (yellow circles) from the cruise in July 2011 are included to support the spreading of the data. (b-d) The 756 distributions of DOC concentrations include seven stations, whereas DIC concentrations and 757 Δ^{14} C-DIC values are given only for six stations due to the lack of data at Sta. Z3 (Ge et al., 758 2016). 759

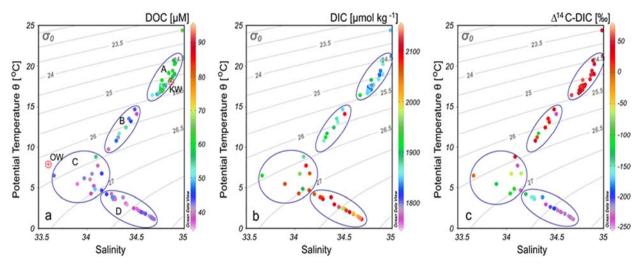
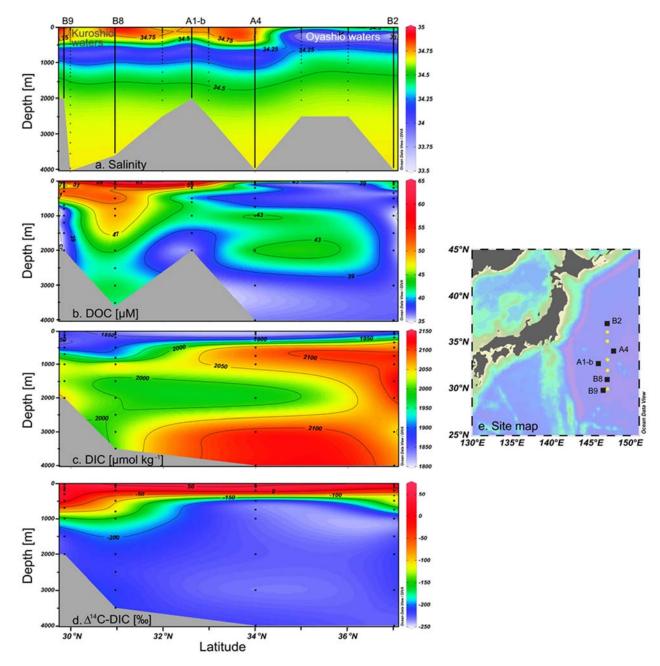


Figure 8. Plot of potential temperature (θ) vs. salinity with (a) DOC concentrations, (b) DIC 762 concentrations and (c) Δ^{14} C-DIC values (indicated as the colours of points) associated with the 763 potential water density (σ_t) for eight stations in the northwestern North Pacific. The circular 764 areas represent different water masses in terms of (A) lower density water in the upper 300 m 765 depth with higher DOC concentration, lower DIC concentration and enriched Δ^{14} C-DIC; (B) 766 mixed upper water in the 300-500 m depth; (C) mixed intermediated water in 500-800 m water 767 depth; and (D) denser North Pacific deep water below 1000 m depth. Higher levels of DOC 768 were associated with lower DIC concentrations, and high Δ^{14} C-DIC values were found in lower 769 density waters ($\sigma_0 < 25.5$, water mass A), while lower levels of DOC were associated with 770 higher DIC concentrations, and low Δ^{14} C-DIC values occurred in denser waters (water mass C 771 and water mass D at $\sigma_0 > 27.1$). Note: DOC concentrations were measured for all stations, 772 whereas DIC results from Ding et al. (2018) were only measured for six stations except Stas. 773 A1-b and A6. Red dots indicate the potential temperature and salinity of the water types, and 774 acronyms of water types as in Fig. 4 are shown. 775



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Figure 9. Transectional distributions of (a) salinity, (b) DOC concentrations, (c) DIC 778 concentration and (d) Δ^{14} C-DIC values for (e) stations (black squares) sampled across the 779 Kuroshio Extension (KE) in the northwestern North Pacific. Black dots indicate depths where 780 samples were collected. Note: (a) The salinity of another five stations (yellow circles) along the 781 35°N transect are included to support the spreading of the data. The hydrographic data for the 782 five reference stations are taken from the Pacific data source in https://www.nodc.noaa.gov/ 783 ocads/. (c-d) DIC concentrations and Δ^{14} C-DIC values are given only for four stations due to 784 the lack of data at Sta. A1-b (Ding et al., 2018). 785

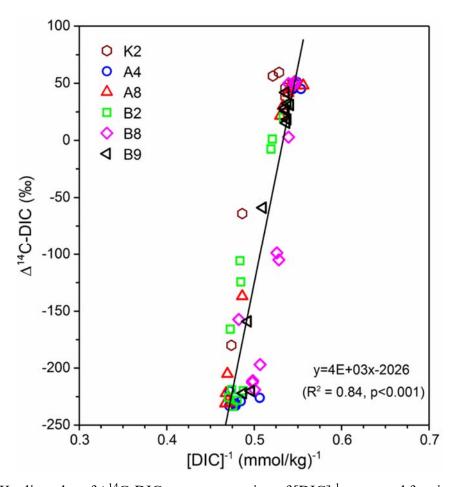


Figure 10. Keeling plot of Δ^{14} C-DIC *vs.* concentration of [DIC]⁻¹ measured for six stations (B9, B8, A4, A8, B2 and K2) in the northwestern North Pacific (data from Ding et al. (2018)). The

790 line indicates the linear regression fit to all data points.