Responses to comments by Referees

We want to thank the Editor and the referees for the constructive and valuable comments on our manuscript. These comments and suggestions helped us to revise our MS and that improved the quality our MS substantially. As suggested, we have changed the title to “Dissolved organic carbon dynamics in the East China Sea and the northwest Pacific Ocean”, and revised the MS accordingly. You will see the attached author’s responses to referees that we tried our best to address the comments of the referees. The lines numbers in this rebuttal refer to the revised version of the manuscript.

Authors corresponding reply to the Referee’s comments.

Referee #1:

Ding et al have adequately addressed my comments and I now find the manuscript suitable for publication in Ocean Science. The English of the manuscript is overall good; however, I noted some minor grammatical issues. I have noted a few instances below, but the manuscript should be read over before final publication. Also, this may just be my own stylistic preference, but I do recommend that the authors reserve the word “significant” for when results are statistically significant (i.e. there is an associated p value).

R: We thank the positive summary of Referee #1 on our revised manuscript and recognition of our work. We have checked the English carefully and corrected these as suggested by the Referee accordingly.

1) Line 167: “…, supplied by the Hansell Biogeochemical Laboratory”.
R: Yes, we replaced “Biogeochemistry” with “Biogeochemical”.

2) Line 172: it should be “analytical precision”, not “analytic precisions”.
R: Yes, corrected as suggested.

3) Line 190: “The maximum total uncertainty is…” instead of “The total uncertainty is…or better”
R: Yes, we have rephrased this sentence as “The maximum total uncertainty is 6‰,”

4) Line 234: “In the upper 1000 m depth” should be replaced with “above 1000 m”.
R: Replaced “in the upper 1000 m depth” with “above 1000 m”.

5) Line 318: “Calculation” should be replaced with “The calculation”.
R: Yes, corrected as suggested.

6) Line 333: Replace “combine in” with “both”. Also, remove “of”.
R: Yes, we have revised this sentence as “the biological and physical processes could both affect the DOC profiles in open oceans as well”.

7) Line 459: “Significantly lower”, not “significant lower”.
R: We have replaced “significant” with “significantly”.

Referee #2:

One major concern I still have is that the authors haven’t fully addressed the comment of inappropriately relying on DOC vs. temperature correlation to support physical mixing. In the response, the authors stated that when they tried excluding surface DOC to derive the correlation or correlating DOC and temperature only at specific depths, correlations were worse. I think this is probably due to the fact that physical mixing is not universally distributed to certain depth across all studied regions, but only to certain locations or different depths at different stations. I think the tones related to physical mixing solely based on DOC vs. temperature correlation should be further softened (for example, line 363-367) and the authors should at least acknowledge somewhere in the text that the correlation itself alone cannot fully support the physical mixing idea since depth co-variation cannot be excluded. And they should highlight that they derive the physical mixing more from the transection distribution plots such as Fig. 7 and Fig. 9.
R: Yes, we agree with the Referee #2 that the discussion of linking DOC distribution to physical mixing is not fully developed in our discussion, especially for the correlation between DOC and temperature. As suggested, we modified the expressions related to the hydrodynamic mixing as the following comment in L39-41. Also, we acknowledged in the manuscript that the
relationship between DOC and temperature could not fully support the physical mixing process since the depth co-variation cannot be excluded, in L308-311. We emphasized the evidence in support of the physical mixing from the discussion of the transection distribution and the calculations for the conservative concentrations of DOC and observed DOC values.

Some other specific comments:

1) Line 24: restructure sentence, for example “In addition to biological processes that are estimated to account for 7%.....respectively, the DOC distribution is largely controlled .....”
R: We agree with the Referee and revised the sentence as suggested.
“In addition to biological processes that are estimated to account for 7% and 8-20% in shaping the DOC distribution in the ECS and KE regions, respectively, the DOC distribution is largely controlled by hydrodynamic mixing of different water masses.”

2) Line 30: delete “In contrast”
R: Yes, we deleted “In contrast” from the sentence.

3) Line 45: “plays” change to “play”
R: Yes, corrected as suggested.

4) Line 122: “which” change to “and”
R: Changed.

R: We have modified this sentence as “and a branch of the Kuroshio Current enters the ECS across the shelf break.” in L138-139.

6) Line 172: delete “each”
R: Yes, deleted.

7) Line 257: “drop in only 300m” change to “drop within only the upper 300m”. Based on the figure, it looks like it is more or less close to 500m. Recheck on this.
R: Clarified the sentence to “drop within only the upper 500 m” in L274.
8) Line 260: “decreased to background value? at 5000m”
R: Replaced “to” with “until” in L277-278.

9) Line 310: sentence confusing, Sta. Z1, Z2, Z3 are more influenced by KC? But above just said Sta. 1, 7 are more affected
R: As combined with the Referee #3’ comments, we feel that there is no sufficient information and obvious trend to better discuss in this part. We therefore deleted this part of the discussion including this sentence.

10) Line 451: Do you mean biological degradation along lateral transport here?
R: We feel sorry for the confusion about this sentence. As also suggested by another Referee, we have modified this part as following, “implying the possibility of outflow export of DOC from marginal seas to the ocean interior” in L472.

Referee #3:
I carefully read the revised version of the paper and the replies by the authors.
I appreciate the efforts made by the authors to follow the reviewer’s suggestions and I think the manuscript is improved, however some of the points that I raised were not addressed and there are still some weak points that hinder the publication of the paper in the present form.
1) As an example, I asked to discuss DOC data from the ECS, since the values are higher than those usually observed in deep oceanic waters, but the authors just added 3 lines (P19, L 448-451), without explaining this finding.
R: We agree with the Referee #3 that we should discuss the DOC in the ECS more because the concentration of DOC was higher in ECS than in the deep ocean. We tried to do so. The ECS is a large river-influenced marginal sea and the geochemical processes and carbon cycle in ECS is different from the deep ocean. The high DOC in the ECS is obvious because many processes such as river input, high PP, flux from sediment can influence DOC. We discussed more on this from L283-293.

2) I asked to include in this paper radiocarbon data on DOC, but the authors replied that “the distribution of Δ14C-DOC values in the northwestern North Pacific would be discussed in
details in another paper.”

R: We are still in the process of $\Delta^{14}$C-DOC measurements and only limited data available at this time. We feel that it would be better to discuss the $\Delta^{14}$C-DOC values in another paper when all measurements are finished. We therefore prefer not to include the $\Delta^{14}$C-DOC data in this paper.

3) The authors state that “there were no chlorophyll data measured by CTD during the same cruise”, but at P13, L313 they write “At Stn. 1 and Z1, the subsurface DOC maximums were not related to the chlorophyll maximum (data not shown)”. This is confounding, are chlorophyll data available or not? In case they are available they should be included in the paper.

R: Since the samples for DOC analysis were collected from two different cruises, the chlorophyll was not measured during the cruise in the KE region and western NP in April-May 2015. The vertical profiles of fluorescence were measured in some stations in the ECS during the cruise in July 2014, however, the chlorophyll data are not available. As the following response, we deleted this discussion including the sentence.

The data are new and interesting and I would like to see them published, but I think the goal of the paper should be changed.

4) I suggest to change the title to “Dissolved organic carbon dynamics in the East China Sea and the northwest Pacific” and to focus the discussion on the main processes affecting DOC dynamics, since I do not think the data they used and the approach they followed are adequate to support the main goal of the paper.

R: Yes. We agree with the Referee and changed the title to “Dissolved organic carbon dynamics in the East China Sea and the northwest Pacific Ocean” and emphasized on the discussions about evidence in support of the physical mixing from the discussion of the latitudinal distribution and the calculations for the conservative concentrations of DOC and observed DOC values.

5) The results section is strongly improved, but the discussion should be deeply reworked, since most of it is not supported by the data. I still think that the authors do not have strong evidences that mixing and hydrodynamic processes are the main processes affecting DOC distribution in the study area. As reported in my previous comments, I do not think that the good linear regression between DOC and temperature can be used to support that mixing affects DOC
distribution, unless data from the same depth range are compared or surface samples are removed from the regression, but, as stated by the authors, in these cases the correlation is lost, supporting that the correlation is mainly driven by the similar shape of the vertical profiles for both parameters.

R: We agree with the Referee #3 that the discussion of linking DOC distribution to physical mixing is not thoroughly developed and supported by our data, especially for based on the correlation between DOC and temperature alone. This is also a comment given by Referee #2. We realized that the hydrodynamic mixing of different water masses is an important process affecting the distribution of DOC in the ocean but could not be a controlling factor for DOC in the ocean. As suggested, we revised the expressions related to the hydrodynamic mixing. Also, we acknowledged in the manuscript that the relationship between DOC and temperature could not fully support the physical mixing process since the depth co-variation cannot be excluded in L308-311, and we emphasized the evidence in support of the physical mixing from the discussion of the transection distribution and the calculations for the conservative concentrations of DOC and observed DOC values.

6) The authors report in many parts of the paper that Kuroshio water is characterized by high-salinity whereas the south-flowing Oyashio Current is characterized by low salinity, salinity would therefore be a better tracer for water masses, why the authors do not use salinity to follow the mixing? Did they look at correlation between DOC and Salinity? Did they try to apply an Optimum MultiParameter (OMP) water mass analysis as done by other authors? (Catalá, et al., 2015, Global Biogeochemical Cycles, DOI: 10.1002/2014GB005048; Catalá, et al., 2015, Nature communication DOI: 10.1038/ncomms6986; Catalá, et al., 2018, Progress in Oceanography, https://doi.org/10.1016/j.pocean.2018.05.002).

R: Yes. We used salinity to follow the different characters of Kuroshio and Oyashio waters in the discussion of the transection distribution across Kuroshio Extension from north to south. We tried to plot the correlation between DOC and salinity, in fact, the correlations were not significant (see the below figures). We agree that the better correlation between DOC and T in the water column does not fully support physical mixing, and we modified the related sentences to be further softened in L308-311 and L388-389.

As suggested, we have read the papers related to the water mass analysis or OMP analysis by other authors. As referred to the water mass analysis on the basis of the assumed conservative variables (potential temperature and salinity) as the characteristics of water type (Catalá, et al., 2015a and 2015b, listed as references), we calculated the proportion of different water masses
and thus the conservative DOC concentrations by using the $\Delta^{14}$C-DIC values. However, the OMP analysis was set by four conservative input variables (Català, et al., 2018), we didn’t further do the OMP analysis due to the lack of other two conservative variables (NO and SiO$_4$) in our data.

7) The authors also state that the good correlation between DOC and temperature, reported in figure S2, is a supporting evidence for their data, but they also report that the four stations used for the correlation were in the same water mass. In my opinion, this correlation clearly shows that temperature along the water column cannot be used as a tracer of the water masses. Density alone cannot be used as a tracer of water masses as well, since it is mostly related to the structure of water column, water masses are usually identified by their salinity and temperature.

R: We agree with the Referee that temperature along the water column cannot be used as a tracer of the water masses and density alone cannot be used as a tracer of water masses as well. We deleted this Figure S2 and discussions.

8) The authors should describe the main water masses found in the study area and they should clearly identify them in the T/S graphs.

R: We have added the red dots in the T-S diagrams (Figure 2) as the representative physical properties of the water types in L209-212 and L730-735, and added the corresponding references in the reference list.

We described the general features of different water masses influenced the two studied regions in Part 2.1 Study areas.

9) I find interesting the use of DIC14 to estimate the concentration of DOC due to conservative mixing, but I suggest to clearly report in the paper how the calculation was done.

R: Yes. We have added the details of calculation in L339-343 and L444-446.

“If we use the same two end-member mixing model (Ge et al., 2016) and the corresponding
average DOC values for the shelf water (77 μM) and Kuroshio water (52 μM),”.
“and the corresponding average DOC values for the selected end-member water masses (an
average of 57 μM for the Kuroshio water and 40 μM for the NPIW of Oyashio)”.  

Some suggestions, specific concerns, and questions are provided below.  
10) ABSTRACT

P1, L18-20 “DOC[...] and its distribution and behavior play important roles in carbon cycling and biogeochemical processes in the ocean.” This sentence is not well written. What does DOC behavior mean?
R: In this sentence, its behavior inferred the biogeochemical cycles of DOC. We have modified the sentence clearly, “Oceanic dissolved organic carbon (DOC) represents one of the largest carbon reservoirs on Earth, and its distribution and biogeochemical cycles play important roles in carbon cycling and other biogeochemical processes in the ocean.” in L33-35.

11) INTRODUCTION

“microbial respiration processes, the DOC pool in the ocean also indirectly contributes to the sink of atmospheric CO2.” Respiration cannot contribute to the sink of atmospheric CO2, in contrast it will represent a source of CO2.
R: Yes, we replaced “sink of” with “cycles of”.

12) METHODS

Information about CRM are still missing. The author should report the average value ± standard deviation and the number of CRM analyzed in the period of the analysis.
R: Yes. The average value and standard deviation of CRM analyzed was 43±1 μM, and the CRM was analysed every 10 samples during the sample analysis.
We have added the CRM information in L179-182.

RESULTS
13) Section 3.1 Hydrography

The physical properties of the main water masses occurring in the study area should be described in this section and the water masses should be identified in the O/S graphs.
R: See the earlier response for general comment, we have added the red dots in the T-S diagrams
(Figure 2) as the representative physical properties of the water types, and added the corresponding references in the reference list.

14) P10, L240 “DOC concentrations decreased to much lower levels ...” Than??
R: Replaced “much lower” with “relative low”.

15) P11, L246 I think Fig. 5c should be cited not 5b.
R: Checked and changed it to “in Fig. 5a”.

16) P12, L272-273, “Export of DOC from the shelf water to the slope was also limited because most of the bioavailable DOC had been respired in the shelf waters and this could be the case, as we observed a statistically positive correlation between DOC and water temperature (R2 = 0.82, p<0.001) for the stations in the ECS (Fig. 6a).” Why and how does the positive correlation between DOC and temperature support that the bioavailable DOC had been respired in the shelf waters?
R: The positive correlation between DOC and temperature could not directly support that the bioavailable DOC was respired in the shelf waters. However, the positive correlation between DOC and temperature is similar with the previous studies which reported that the distribution of DOC was primarily controlled by physical processes rather than production and/or microbial processes. In the revised MS, we modified these sentences to clarify the confusion in L293-300.

17) P13, L296 “To further demonstrate the influence of different water mass mixing processes on the hydrological properties, Figure 7 compared the transectional distributions of density”. Density mainly gives information on the vertical structure of the water column. I think salinity would be more appropriated to trace water mixing. What does “transectional distributions” mean?
R: We replaced density with salinity in Figure 7a, and revised the corresponding parts in the main text in L324-329. Transectional distributions means the latitudinal distribution from north to south, and we changed the “transectional distributions” to “latitudinal distributions’ in L327.

18) P13, L “The cross-section density plot (Fig. 7a) showed that the water mass in the studied area was composed of mixed Kuroshio and shelf waters.” I do not understand how density can show this mixing and there is no information on the figure.
R: As responded to the earlier comment, we have replaced density with salinity in Figure 7a
and revised the corresponding parts in the main text in L324-329.

19) P13, L299-301 “It appeared likely that the influences of Kuroshio intermediate water (500-800 m) on the bottom water at station Z4 and Stn. 11 brought low concentrations of DOC, high concentrations of DIC and low 14C values of DIC. This intrusion of Kuroshio intermediate water diluted the DOC at Stn. 11 and Z4 (Figs. 7b-d).” As above reported, I do not find this information in the figure. What I can see is that DOC accumulates in the mixed layer at all the stations and, as expected, it decreases below the pycnocline.

R: As the earlier comment, we have replaced density with salinity in Figure 7a, and thus the different water masses could be clearly identified by the variations of salinity. Although the depth co-variation cannot be excluded, the degrees of DOC concentrations reduction in the bottom water at Stn. 11 and Z4 could be due to the dilution effects, which could also be the cases for the distribution of DIC concentrations and $\Delta^{14}$C-DIC.

20) P13, L302-302 “However, it appears that this upwelling intrusion had almost no effect on the surface water (<100 m depth) for the shelf stations.” This supports that mixing is not the main driver of DOC distributions at these stations.

R: Yes, the surface distributions of DOC for the shelf stations is not mainly influenced by the mixing process, just like the variation of surface salinity. Discussion of the sentence focused on the surface water (<100 m depth) of the shelf stations.

21) P13, L305-310. This paragraph is not clear to me and as above reported, the information reported in Figure 7 do not support this part of the discussion.

R: We agree with the Referee’s comment. As the Figure 7 has been redrawn, we feel that there is no sufficient information and obvious trend to better discuss in this part. We therefore deleted this part of the discussion.

22) P13, L313 “At Stn. 1 and Z1, the subsurface DOC maximums were not related to the chlorophyll maximum (data not shown) and could not accumulate in the developed stratification water column, as inferred from the $\sigma_t$ distribution (Fig. 7a).” This sentence makes no sense to me. What does “could not accumulate in the developed stratification water column” mean?

R: Since the chlorophyll data are not available in the stations in the ECS during the cruise in
23) P13, L314 What does “fixed sinking POC” mean?
R: As responded to the comment above, we deleted this part of the discussion including these words.

24) P14, L316-317. I do not see any DOC subsurface maximum. Between station 7 and Z3 the pycnocline is deeper, DOC accumulates in the mixed layer and this can easily explain the observed DOC distribution. There is no data supporting the role of POC in this paper.
R: As suggested by the Referee, we deleted the discussion part on the role of POC and the corresponding references.

25) P15, L341-342. How can the authors explain “the relatively large spatial variations for DOC concentration among these stations, especially in the upper 1500 m (Fig. 3b and Fig. 4b).” No hypothesis is reported.
R: In the manuscript, we speculate that the observed large spatial variations were mainly modulated by the mixing dynamics of different water masses rather than biological processes in the region in L378-381.

26) P15, L360-367. As reported in the general comments, this part of the discussion is not supported by the data.
R: We clearly realized that the correlation between DOC and temperature is a major concern for the Referee. We agree with the referee that the correlation of DOC with temperature should not be caused by physical mixing alone. It could be a covariation with depth but there must reasons to cause the change. Biological processes could also influence the distribution changes of DOC. On the other hand, DIC and its $\Delta^{14}C$ values have been used as conservative tracers to study the sources, movement and mixing of different water masses in the ocean, such as in the WOCE and CLIVAR Programs.
As suggested, we modified the statements related to the hydrodynamic mixing as the earlier comment in L388-389. Also, we acknowledged in the revised manuscript that the relationship between DOC and temperature could not fully support the physical mixing process since the depth co-variation cannot be excluded in L308-311, and we reported the evidence in support of the physical mixing from the discussion of the latitudinal distribution and the calculations for
the conservative concentrations of DOC and observed DOC values.

27) P16, L370-371. “It can be observed that the distributions of DOC, DIC and \( ^{14} \text{C-DIC} \) were clearly associated with different water masses, as identified by the potential water density \( (\sigma_0) \). “As reported in the general comments, density alone cannot be used to identify the different water masses.

R: Yes, we clarified this sentence to “as identified by the temperature, salinity and potential density \( (\sigma_0) \) in the T-S diagrams (Fig. 8).”

28) P16, L372-375 “Higher levels of DOC were associated with lower DIC concentrations, and high \( ^{14} \text{C-DIC} \) values were found in lower density waters \( (\sigma_0 < 25.5, \text{water mass A}) \), while lower levels of DOC were associated with higher DIC concentrations, and low \( ^{14} \text{C-DIC} \) values occurred in denser waters \( (\text{water mass C and water mass D at } \sigma_0 > 27.1) \) (Fig. 8).”

As I reported many times this finding can be easily explaining by biological processes and water column stratification. The surface waters (with the lowest density) are characterized by the highest DOC concentration (due to biological production of DOC) low DIC concentration and high \( ^{14} \text{C-DIC} \) values due to the exchanges with the atmosphere. This is something observed everywhere in the oceans.

R: Yes, we removed these sentences from the main text, and added the sentences in Fig. 8 to describe the results.

29) P17, L392-394. “The relatively higher DOC level in the upper 200 m at Sta K2 was influenced by the northeastward-flowing Kuroshio, which carries a subtropical warm and high-salinity water mass in the upper layers, as demonstrated in Fig. 2b and Fig. S1.”. Fig 2b does not show DOC data and looking at table S1, St. K2 is not characterized by DOC concentration higher than at stations A8 and B8.

R: We agree that there is a mistake in the number of figure and Fig 2b was replaced with Fig 3b. We also modified these sentences in L409-413: “The similar patterns of hydrographic properties and relatively higher DOC levels in the upper 500 m at Sta K2 and other five stations (A1-b, B8, B9, A6 and A8) in the KE region suggested that the Kuroshio water dominated the mixing in the upper 500 m at these stations, which are mainly characterized with a subtropical warm and high-salinity water mass, as demonstrated in Fig. 3b and Fig. S1.”.

30) P16-17, L383-412 All this paragraph should be rewritten since it is confusing and not
supported by the data.

R: We feel very sorry that there are some confusions in our statements. We have modified this paragraph to clarify the confusion in L409-432.

31) P17, L402-403. The authors in many parts of the paper state that the Kuroshio water is characterized by high salinity values. I do not therefore understand how they can write “It can be observed that the Kuroshio, which carries relatively high DOC, dominated stations B9, B8 and A1-b from ~200 to 1500 m depth.” Since station B8 and B9 are clearly characterized by a minimum of salinity between 500 and 1000 m.

R: See the earlier comment, we have modified the paragraph including this sentence in L416-418.

32) P17 L403-407. The occurrence of Oyashio water, characterized by low salinity, is visible at St. B2 between ~100 and ~700 m (Fig. 9a), so I do not understand how the authors can state “In contrast, the Oyashio, which carries low salinity, low DOC but high DIC concentrations, and low Δ14C-DIC values in the subarctic intermediate water, influenced the entire water column at Sta B2”.

R: See the earlier comment, we have modified the paragraph including this sentence in L418-426.

33) Figure 2, 4 and 8. I recommend to clearly identify on the Ω/S graphs the water masses occurring in the study area.

R: Yes, we added the descriptions of the water types as red dots in the three Figures.

34) Figure 3 the same x-axis should be used for the graphs

R: Yes, we used the same range for the x-axis in the two subgraphs in Fig. 3.

35) Figure 4, it seems that the correlation between DOC and temperature is investigated taking into consideration all the data, as reported in my general comments this correlation cannot support that mixing and hydrodynamic processes are the main drivers of DOC distribution. This figure should be removed.

R: As response to earlier comments, we agree that the correlation between DOC and T in the water column does not fully support physical mixing, and we modified the related sentences to
be further softened in L308-311 and L388-389. This figure (Figure 6) could show direct- 
viewing information for the correlation, and we have retained it.

36) Figure 7. *Density does not give any information about water masses, I suggest to replace 
density with salinity.*
R: Yes. We have replaced density with salinity in Figure 7a.

37) Figure 7 and 9. *The numbers are really small, as well as the points where data are available. 
I would add the contour lines and the name of the main water masses occurring in the study 
area.*
R: Yes. We have adjusted the font and the points in the figure, and also added the contour lines 
for different parameters and the name of the main water masses.

38) Figure 9 it is not possible to discriminate between black squares and black circles.
R: Yes. We have redrawn the black circles to yellow circles.
Dissolved organic carbon dynamics in the East China Sea and the northwest Pacific Ocean

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Keyword: Ocean carbon cycle, Dissolved organic carbon, East China Sea, North Pacific Ocean, Ocean water mixing
Abstract. Oceanic dissolved organic carbon (DOC) represents one of the largest carbon 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 concentrations of DOC for water samples collected from the shelf-edge and slope regions in the East China Sea (ECS) and the Kuroshio Extension (KE) in the northwestern North Pacific (NP) during two cruises in 2014-2015. The DOC concentrations were 45-88 µM in the ECS and 35-65 µM in the KE. In addition to biological processes that are estimated to account for 7% and 8-20% in shaping the DOC distribution in the ECS and KE regions, respectively, the DOC distribution is largely controlled by hydrodynamic mixing of different water masses. By comparing the DOC results with dissolved inorganic carbon (DIC) and dissolved inorganic radiocarbon ($\Delta^{14}$C-DIC) measured from the same water samples, we further demonstrate that the intrusion of the Kuroshio Current could dilute the DOC concentrations at stations in the outer shelf and slope regions of the ECS. The concentrations of DOC in the KE were 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 reported DIC and $\Delta^{14}$C-DIC values for the stations, the observed spatial variations of DOC in the upper 700 m among the stations in the KE were mainly influenced by mixing of the two water masses carried by the Kuroshio and Oyashio, the two dominant western boundary currents in the region. The hydrodynamic processes are thus important factors in the distribution and dynamics of DOC in the KE region.

1 Introduction

The world’s oceans contain the second largest reservoir of carbon on earth, and dissolved organic carbon (DOC) is the largest reduced carbon pool (685 Pg C) in the ocean (Hansell and 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 and Dittmar, 2014). The concentration and distribution of ocean DOC play significant roles not 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 et al., 2010; Nelson and Carlson, 2012). Because ocean DOC is directly linked to the oceanic 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 atmospheric CO$_2$ (Druffel et al., 1992; Carlson et al., 1994; Carlson et al., 1998; Hansell and Carlson, 2001; Carlson et al., 2010).

In the most recent 20 years, improved precision of DOC concentration analysis via the high-temperature catalytic oxidation (HTCO) technique has revealed detailed oceanic DOC distributions, such as those generated by the US Climate Variability Repeat (CLIVAR) hydrography program (Sharp et al., 1995; Sharp et al., 2002; Carlson et al., 2010; Hansell et al., 2012; Bercovici and Hansell, 2016). In general, biological and physical processes combine in modulating the distribution and dynamics of DOC in open oceans (Hansell and Waterhouse, 1997; Ogawa et al., 1999; Hansell et al., 2009; Carlson et al., 2010; Bercovici and Hansell, 2016). It has been widely observed that oceanic DOC accumulates in the upper water column (100 m) at elevated concentrations (70-90 μM) compared with its relatively constant values (35-45 μM) in deep water (>1000 m), reflecting biological production of DOC in the euphotic zone and microbial consumption with depth (Hansell et al., 2009). However, many previous 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. In the upper ocean, studies have found that the distribution of DOC often displays obvious latitudinal patterns with relatively higher concentrations (65-85 µM) in the subtropical ocean above 100 m, where stratification might restrict vertical water mixing (Abell et al., 2000; Carlson et al., 2010; Pan et al., 2014). However, in high-latitude oceans, DOC concentrations remain at relatively low levels (45-60 µM) as a result of deep water penetration that dilutes DOC concentrations (Ogawa et al., 1999; Abell et al., 2000; Pan et al., 2014). In the deep ocean, a 14 µM decrease in DOC concentrations occurs along the abyssal circulation pathway from the North Atlantic to the North Pacific Ocean due to differences in thermohaline circulation patterns (Hansell and Carlson, 1998). Carlson et al. (2010) later confirmed DOC export by the meridional overturning circulation in the Atlantic Ocean and further estimated the export and decay rates of DOC during this water circulation. In addition, concentrations of DOC in the deep Southern Ocean were similar to those in the North Atlantic deep water (NADW) but were higher than in Pacific deep water, which could result from conservative mixing of deep ocean waters from the Atlantic, Indian and Pacific (Bercovici and Hansell, 2016).

The northwestern North Pacific (NP) is a rather special oceanic region where carbon cycling and biogeochemical processes are greatly influenced by two major oceanic western boundary currents: the Kuroshio Current (KC) and Oyashio Current (OC). As one of the largest marginal seas connected to the northwestern NP, the hydrological characteristics of the East China Sea (ECS) are largely influenced by vigorous exchange between the warm saline 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 biological processes around the shelf edge of the ECS. After exiting the ECS at 30° N/128-129° E, the Kuroshio Current flows northeastward and merges with the southward-flowing Oyashio
Current in the mixed water region off the coast of Japan to finally form the Kuroshio Extension (KE) flowing eastward into the North Central Pacific (NCP) (Yasuda et al., 1996; Talley, 1997; Qiu, 2001). The newly formed North Pacific Intermediate Water (NPIW) in the mixed water region has received attention due to its important role in the ocean circulation systems and its impacts on regional carbon cycle and climate variability (Talley, 1993; Hansell et al., 2002; Yasuda, 2003; Wu et al., 2012; Hu et al., 2015). However, few studies have focused on the distribution and dynamics of DOC around the KE region. DOC analysis from different NP stations revealed the export of young DOC accompanied by the NPIW formation, resulting in an enrichment in the $\Delta^{14}C$-DOC values and a reduction in the notably old DOC $^{14}C$-age in the Pacific Ocean interior, but the vertical profiles of DOC were only determined at stations in the subpolar water in the northwestern NP (Hansell et al., 2002). DOC 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 near the KE was not investigated during these cruises.

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 NP combined with the observations of dissolved inorganic carbon (DIC) concentrations and dissolved inorganic radiocarbon ($\Delta^{14}C$-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.

2 Methods

2.1 Study areas

Water samples were collected from two main oceanic regions: the ECS and the KE region in the northwestern NP (Fig. 1). The ECS is one of the largest marginal seas in the northwest NP,
with a broad continental shelf area of approximately $0.5 \times 10^6$ km$^2$ (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 largest and second largest rivers in China, and each delivers $1.58 \times 10^{12}$ g DOC and $3.20 \times 10^{10}$ g DOC into the ECS (Wang et al., 2012; Xu et al., 2016). In the outer shelf and slope region of the ECS, the hydrographic characteristics and oceanic processes are affected largely by the 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; Hu et al., 2015; Ge et al., 2016). The high primary productivity and intersection of different water masses make the ECS a complex region for studying the ocean carbon biogeochemical cycle.

The Kuroshio Extension (KE) in the northwestern NP 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 Central Pacific (Yasuda et al., 1996; Qiu and Chen, 2011). The southward-flowing Oyashio Current, which carries fresh and cold subarctic water, meets with Kuroshio water at approximately 37° N and forms the Kuroshio-Oyashio inter-frontal zone where the subarctic water mass mixes with the KE water and flows eastward (Yasuda et al., 1996; Qiu and Chen, 2011; Hu et al., 2015). The new NPIW is formed in the same region and is a mixture of relatively fresh and recently ventilated Oyashio water and high-salinity Kuroshio water (Yasuda et al., 1996; Talley, 1997; Qiu and Chen, 2011). The mixed water region in the KE has been characterized as an important sink of anthropogenic CO$_2$ in the northwestern NP (Tsunogai et al., 1993), and it is a key area for understanding regional climate and ecosystem variations and biogeochemical cycles (Yasuda, 2003; Wu et al., 2012; Hu et al., 2015; Nishibe et al., 2017).

Table 1. Summary of sampling stations and times in the East China Sea (ECS) and the Kuroshio

<table>
<thead>
<tr>
<th>Station</th>
<th>Sampling Time</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>ECS</td>
<td>Week 1</td>
<td>0° N, 120° E</td>
</tr>
<tr>
<td>KE</td>
<td>Week 2</td>
<td>30° N, 150° E</td>
</tr>
<tr>
<td>NPIW</td>
<td>Week 3</td>
<td>40° N, 180° E</td>
</tr>
</tbody>
</table>
Extension (KE) in the northwestern North Pacific (NP).

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

2.2 Sample collection

Water samples for DOC analysis were collected from 7 stations on the shelf-edge and slope region of the ECS during a cruise in July 2014 onboard the Japanese R/V Shinset Maru and from 8 deep stations in the KE region and western NP during a cruise in April-May 2015 onboard the Chinese R/V Dongfanghong-2 (Fig. 1). General information on the sampling stations is summarized in Table 1. All water samples were collected using 12 L Niskin bottles 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 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 µM 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.

2.3 Chemical analysis

Concentrations of DOC were analysed by the high temperature catalytic oxidation (HTCO) method (Sharp et al., 1995; Sharp et al., 2002) using a Shimadzu TOC-L analyser equipped with an ASI-V autosampler. Potassium hydrogen phthalate (KHP) dissolved in high-purity Milli-Q water was used as the DOC standard. The quality assessment for DOC measurements 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 Biogeochemical Laboratory at University of Miami, USA). The average value and standard deviation of deep-sea water reference throughout our measuring was 43±1 μM, which was used as an index of our analytical precision. The instrumental blank was subtracted using high-purity Milli-Q water that was analysed between samples (before every sample for deep seawater). The average blank of the DOC measurement was ≤ 5 μM, and the analytical precision on triplicate injections were ± 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 μM.

The methods for DIC concentrations and Δ¹⁴C-DIC measurements were described in detail in separate papers for the samples collected during the same cruises (Ge et al., 2016; Ding et 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 used as the DIC standards, and the concentration values were checked against DIC reference 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 concentrations, and the analytic precisions were < 3%. For Δ¹⁴C-DIC measurement, DIC was first extracted as gaseous CO₂ using our modified method with extraction efficiencies > 96%
(Ge et al., 2016). The $^{14}$C-DIC values were analysed in the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility at Woods Hole Oceanographic Institution (WHOI). The purified CO$_2$ was graphed for $\Delta^{14}$C analysis using AMS. The $\Delta^{14}$C values are reported as the modern fraction based on the reference material used (McNichol et al., 1994). The conventional $^{14}$C ages (years before present or yr BP) were calculated following the method of Stuiver and Polach (1977). The maximum total uncertainty is 6‰, as tested with a DIC standard (Ge et al., 2016).

3 Results

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. 2. 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 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 $\sigma_t$), and decreasing again to 500 m (26.4-26.8 $\sigma_t$). The salinity ($S$) remained relatively constant below 500 m depth (at $\sigma_t >$26.8) for the three slope stations (Fig.
For Sta. K2 and the seven deep stations in the KE, the temperature \((T)\) of the surface water ranged from 14.7 to 24.4°C, exhibited a rapid decrease and subsequently remained constant for all stations at density levels of \(\sigma_t > 27.6\) at \(\sim 1500\) m depth (Fig. 2b and Fig. S1). The largest temperature variations occurred in the upper 700 m with the highest \(T\) (24.4°C) observed at Sta K2 (end \(T\) value of the Kuroshio water) and the lowest \(T\) (14.7°C) at Sta B2 observed in the surface layer (5 m) (end \(T\) values of the Oyashio water) (Fig. 2b). The salinity \((S)\) for these stations was higher at the surface, decreased initially to reach a minimum at the density range of 26.4-26.9 \(\sigma_t\), and subsequently increased with depth to approximately 2500 m with the density layer of 27.6 \(\sigma_t\) (Fig. 2b). The salinity for all stations remained relatively uniform below 2500 m \((\sigma_t > 27.6)\). Similar to \(T\), the largest differences in salinity also appeared in the upper 700 m water column (the density range of 26.4-27.0 \(\sigma_t\)), where low salinity (34.49) was observed at the surface of Sta B2. The salinity decreased to 33.66 near 250 m and 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).

### 3.2 Concentrations and distribution of DOC

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 in Fig. 4. The concentrations of DOC ranged from 45 to 88 µM in the ECS and from 35 to 65 µM in the KE region (Fig. 3 and Table S1). The concentrations of DOC ranged from 55 to 88 µM for the four shelf-edge stations (Stn. 11, 1, 7 and Z4) and from 45 to 84 µM for the three 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 µM) in the surface water (≤10 m and σt ≤ 22.1) and decreased rapidly to ~300 m depth for all stations in the ECS. Below 300 m, the concentrations of DOC remained relatively constant down to 1000-1400 m depth for Z1, Z2 and Z3 (Fig. 3a).

In comparison, the concentrations of DOC in the KE region were much lower (43-65 µM) and showed large spatial variations among the stations above 1000 m (Fig. 3b). The highest DOC value (65 µM) and the lowest DOC level (43 µM) were measured at the surface at Sta K2 and Sta B2, respectively. In the upper 200 m depth, the concentrations of DOC also showed a notably rapid decrease for most stations. The DOC concentrations were visibly lower at Sta A4 and Sta B2 (36-53 µM) than at the other stations in the upper 700 m depth (at σt < 27.0), whereas the concentrations were slightly higher in the 500-800 m depth at Sta B8 and Sta A8. The T-S-DOC diagrams showed that DOC concentrations decreased to relative low levels (36-44 µM) at all stations at σt > 27.5 (approximately below 1500 m depth) and remained constant in deep waters (Fig. 3b and Fig. 4b).

3.3 Concentrations and radiocarbon distribution of DIC

The results of the DIC concentrations and Δ¹⁴C-DIC values measured from the same samples have been recently published (Ge et al., 2016; Ding et al., 2018). In this work, we use these data as water mass tracers to support our DOC results. In brief, as shown in Fig. 5a, the DIC concentrations were higher in the four shelf-edge stations (Stn.11, Stn.1, Stn.7 and Z4) than that in the slope stations (Z1 and Z2) at the same depths in the ECS (Fig. 5a). The depth profiles of Δ¹⁴C-DIC showed a trend opposite to that of the concentrations of DIC, i.e., higher at the surface and decreasing with depth (Fig. 5b). Higher DIC concentrations had lower Δ¹⁴C-DIC values. The Δ¹⁴C-DIC values at 138 m for Stn.11 and 413 m for Stn. Z4 were significantly 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
stations in the KE region (Fig. 5c). The large variability in DIC concentrations was observed between 400 and 800 m depths. The $\Delta^{14}$C-DIC values were high at the surface, decreased with depth and showed large variations in the upper 250-1000 m among the stations (Fig. 5d). The $\Delta^{14}$C-DIC values showed a rapid drop within only the upper 500 m of the water column at Sta A4 and in the upper 1000 m depth at Sta B2 and subsequently remained constant below 1000 m depth. The $\Delta^{14}$C-DIC profiles for stations K2, A8, and B9 exhibited a similar trend. The surface bomb $^{14}$C signal mixed well down to 600 m and subsequently decreased until 1500 m (1000 m for K2) (Fig. 5d).

4 Discussion

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, 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. (2012) and Xue et al. (2017) reported that the Yangtze and Yellow rivers delivered $3.1 \times 10^{12}$ g and $7.26 \times 10^{10}$ g terrestrial OC, comprised 45-50 % DOC to the ECS in 2009 and 2015. These riverine DOC was derived mainly from pre-aged soil OM with $^{14}$C ages 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 influenced by the riverine refractory DOC that was cycled in the water for long time and fluxes offshore. In addition, DOC 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 et al., 2012; Gan et al., 2016). However, export of DOC from the shelf water to the slope 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 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 production and/or microbial processes, as we observed a statistically significant positive correlation between DOC and water temperature ($R^2 = 0.82$, $p < 0.001$) for the stations in the ECS (Fig. 6a). A similar pattern has also been found in other marginal seas of the NP (Hung et al., 2007; Dai et al., 2009). In our recent study, we reported that the concentrations of DIC and $\Delta^{14}$C-DIC in the ECS slope and the KE region showed conservative behaviour and could be used as tracers of water mass movement and water parcel homogenization as predicted by the solution mixing model (Ge et al., 2016; Ding et al., 2018). As shown in Fig. 6b, the negative relationship between DOC and DIC ($R^2 = 0.73$, $p < 0.001$) for the stations further suggests that physical processes (such as horizontal and vertical water 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 co-variation. 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 slope 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 variations of DOC for the shelf-edge and slope stations, as shown in Fig. 3a, followed a typical 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 the shelf-edge of the ECS, the vigorous exchange between the warm saline Kuroshio and cold fresh continental shelf water masses could affect the hydrographical characteristics (Hsueh, 2000). As shown in Fig. 2a, the salinity maximum at the density range of 23.2-24.9 $\sigma_T$ (near
100-160 m) is influenced largely by the northward-flowing Kuroshio Current. Physical models and chemical tracers both supplied clear evidence of the intrusion of upwelled Kuroshio intermediate water (500-800 m) into the ECS shelf region (Yang et al., 2011; Yang et al., 2012; Ge et al., 2016). As mentioned above, the statistically significant positive correlation between DOC and water temperature indicated the hydrodynamic mixing has important influences on DOC distribution. To further demonstrate the influence of different water mass mixing processes on the hydrological properties, Figure 7 compared the latitudinal distributions of salinity, DOC/DIC concentrations and Δ14C-DIC for the seven stations in the ECS. The cross-section salinity plot (Fig. 7a) showed that the water mass in the studied area was composed of mixed Kuroshio and shelf waters. It appeared likely that the influences of Kuroshio intermediate water (500-800 m) on the bottom water at station Z4 and Stn. 11 brought low concentrations of DOC, high concentrations and low Δ14C values of DIC (Fig. 7b-d). This intrusion of Kuroshio intermediate water diluted the DOC at Stn. 11 and Z4. However, it appears that this upwelling 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 Δ14C-DIC mass balance showed that approximately 54-65% of the bottom water in the shelf region of ECS originated from the intrusion of Kuroshio 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 water type (Catalá, et al., 2015a and 2015b), if we use the same two end-member mixing model (Ge et al., 2016) and the corresponding average DOC values for the shelf water (77 μM) and Kuroshio water (52 μM), the conservative concentrations of DOC (referred as DOC0) could be calculated in the range of 61-64 μM, which is slightly higher but comparable to the observed DOC values in the bottom waters at Stn. 11 and Z4 (56-61 μM). The negative values of ΔDOC
(measured DOC – DOC⁰) could represent the biological consumption effects superimposed on
the water physical mixing processes around the shelf-edge and in the slope of ECS. Based on
the calculated ΔDOC and the field-measured DOC, we estimated that the bioavailable fraction
of DOC could account for approximately 7% of the total DOC pool in this region. The value is
comparable to the results (6.1% and 10% ± 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,
biological processes had a significant influence on DOC but were not the dominant controlling
factor on the observed DOC distributions in the ECS.

4.2 Processes influence the DOC profiles in the Kuroshio Extension

In general, the biological and physical processes could both affect the DOC profiles in open
oceans as well (Hansell and Waterhouse, 1997; Ogawa et al., 1999; Hansell et al., 2009; Carlson
et al., 2010; Bercovici and Hansell, 2016). Attributed to the low concentration of nitrate and
silicic acid, primary production during spring was low in the KE region (Nishibe et al., 2015).
Moreover, notably low levels of available dissolved nitrogen (< 4 μM) were observed in the
region (unpublished data) during the same cruise in spring (April-May 2015). The relatively
lower surface DOC concentrations (average 57±7 μM) 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 of relatively large spatial variations for DOC
concentration among these stations, especially in 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 43±5 μM) than those of other stations and
were close to the deep water values (ca. 36-44 μM, 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 A8), with values 28% higher than
average. In the KE region, primary production is largely affected by advection along the KE
meander and differs among representative areas in spring, i.e., high in the northern edge and around the KE axis (483-630 mg C m$^{-2}$ day$^{-1}$), accompanied by high Chl a concentration and high column integrated Chl a values (35-44 mg m$^{-2}$) in April (Nishibe et al., 2015). The relatively high primary production should result in a high level of DOC in the stations located north and around the KE, but the measured DOC concentrations were rather low at Stas B2 and A4. In addition, surface mooring data from the NOAA Kuroshio Extension Observatory (KEO) indicated that physical processes dominate the carbon input to the mixed layer at KEO (Fassbender et al., 2017). Therefore, we speculate that the low DOC levels at Sta B2 and A4 were unlikely directly related to the primary production, and instead, the observed large spatial variations were mainly modulated by the mixing dynamics of different water masses rather than biological processes in the region.

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 the DOC concentrations with water temperature and DIC concentrations in the KE region, respectively. Overall, a positive relationship exists between the DOC concentrations and temperature in the KE (Fig. 6c, $R^2 = 0.62$, $p < 0.001$), and a negative correlation exists between the DOC and DIC concentrations (Fig. 6d, $R^2 = 0.51$, $p < 0.001$). These observed correlations of DOC concentrations and hydrographic variables indicate the physical water mixing played important roles on the DOC distribution in the KE region. To further examine the distribution of DOC with different water masses in the KE region, we plotted the DOC and DIC concentrations and $\Delta^{14}$C-DIC values superimposed on the plots of potential temperature ($\theta$) and salinity in Fig. 8. It can be observed that the distributions of DOC, DIC and $\Delta^{14}$C-DIC were clearly associated with different water masses, as identified by the temperature, salinity and potential density ($\sigma_0$) in the T-S diagrams (Fig. 8). The denser water mass C with density levels of 26.4-27.1 $\sigma_0$ near 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 to the KE region. This water is subsequently mixed with the warm saline
water mass transported by the northeast-flowing Kuroshio Current (water mass A)
corresponding to the six stations (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°C) and salinity (< 34.5) in the upper 700 m
(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
of DOC. In contrast, despite the nutrient-depleted and low primary productivity in the
subtropical gyre, physical stability factors such as water column stratification could restrict the
vertical mixing of the surface and deep waters, which supplied the environment for DOC
accumulation in the surface layer. The similar patterns of hydrographic properties and relatively
higher DOC levels in the upper 500 m at Sta K2 and other five stations (A1-b, B8, B9, A6 and
A8) in the KE region suggested that the Kuroshio water dominated the mixing in the upper 500
m at these 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 by Kuroshio and Oyashio currents can be demonstrated more clearly in Fig. 9,
where we plotted the salinity, DOC and DIC concentrations, and Δ¹⁴C-DIC values for the five
stations (B2, A4, A1-b, B8 and B9) as a cross KE transect from north to south. It can be
observed that the Kuroshio, which carries relatively high DOC, dominated stations B9, B8 and
A1-b above 500 m depth. The latitudinal distributions of salinity could serve as intuitive
evidence to show the intrusion of the fresh 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 of 26.4-26.9 $\sigma_t$ in Fig. 2b). It appeared likely that the Oyashio, which carries low salinity, low DOC but high DIC concentrations, and low $\Delta^{14}$C-DIC values in the subarctic intermediate water, influenced the upper layers (above 1000 m) at Sta B2. The Oyashio water could further intruded 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 $\Delta^{14}$C-DIC values. However, it cannot be determined whether this southward intrusion of Oyashio water is seasonal or decadal oscillations (Ding et al., 2018).

Previous studies focused on physical oceanography have shown that the unstable mode of the KE could generate active water-mass 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 could be transported southward through the meso-scale eddies (Qiu and Chen, 2011), influencing the chemical and biological processes in the KE region. Using the significantly low $\Delta^{14}$C-DIC values at stations B2 and A4 in the upper 700 m depth in the KE region, we also 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 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 $\Delta^{14}$C-DIC values (an average of 50‰ for the Kuroshio water and -220 ‰ for the NPIW of Oyashio) in the $\Delta^{14}$C-DIC Keeling plot analysis (Fig. 10) (Ding et al., 2018). For example, 55-58% Oyashio water could contribute to produce the observed $\Delta^{14}$C-DIC values at the depth of 500 m in Stas B2 and B8 and 100% Oyashio water at Sta A4 and 96-100% Kuroshio water at Stas A8 and B9, respectively. If we consider that the distribution of DOC is controlled mainly by 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 average DOC values for the selected end-member water masses (an average of 57 $\mu$M for the
Kuroshio water and 40 µM for the NPIW of Oyashio) derived from the Δ^{14}C-DIC values within the range of 40-56 µM. The difference between the measured and conservative DOC (DOC^0) concentrations (ΔDOC=DOC^{measured}−DOC^0) can represent other biological processes that secondarily modulate DOC in the KE region. For example, the positive ΔDOC values (~6 µM) that accounted for approximately 11% of the measured DOC at Sta B8 indicated a net DOC increase from biological processes, accompanied by the relatively low DIC concentrations shown in Fig. 9c. The recirculation gyre immediately south of the KE has been found to exhibit 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 ΔDOC values (2-8 µM) and the measured DOC at Stas B2 and A4.

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 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 (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 left behind in deeper waters in the KE and North Pacific (Carlson et al., 2010; Hansell et al., 2012; Follett et al., 2014). Radiocarbon measurements of DOC collected in the KE indicate that the ^{14}C age of DOC in deep water was ~6,200 years old (Wang, unpublished data), similar to the DOC ages in the deep NP (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 North Atlantic could be due to the differences in thermohaline circulation patterns, as proposed by Hansell and Carlson (1998), which presented changes in the deep-ocean DOC concentrations along the abyssal circulation pathway. However, by comparing with the deep DOC results in
the slope region of the ECS, it can be observed that the deep DOC level in the KE was 10-15 µM lower on average than that in the ECS, implying the possibility of outflow export of DOC from marginal seas to the ocean interior and cycling in the deep ocean for a long duration.

5 Summary

The results of our study indicate that the concentration of DOC ranged from 45 to 88 µM in the outer shelf and the slope region of ECS and from 35 to 65 µM 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 surface layer. The DOC in the deep water of the KE had similar comparable values as those reported for the deep north and south Pacific. The large spatial variations of DOC in the upper 700 m among the stations in the KE were influenced primarily by hydrodynamic mixing of two different water masses. The Kuroshio, which carries warm and relatively higher DOC water, 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 and on biogeochemical processes in the KE region.

Data availability. All data used in this study will be freely available, for scientific use only, upon request. Anyone interested in using this data set for scientific research should contact the corresponding author via e-mail.
Author contributions. Ling Ding is a post-doc working on this project, participated in the cruises, sample analysis and manuscript writing. Tiantian Ge is a laboratory technician participated in all cruises, sampling and sample analysis. Dr. Xuchen Wang is the corresponding author and leading scientist for this study from proposal writing, cruise and sampling planning, and manuscript writing. All authors have read the manuscript and agreed on the authorship.

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

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References


Figure 1. Map showing the study region and the sampling stations in the ECS and the northwestern North Pacific (NP) 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 (KE) flowing eastward to the North Central Pacific (NCP).
**Figure 2.** Potential temperature versus salinity plot (T-S) diagrams for the sampling stations. (a) Seven shelf-edge to slope stations in the ECS and (b) eight deep stations in the KE region in the northwestern NP. $\sigma_0$ isolines are included in the figures. The coloured lines correspond to CTD data, and red dots indicate the potential temperature ($\theta$) and salinity ($S$) of different water masses. The representative $\theta$ and $S$ of these water types referred to previous studies (Yasuda et al., 1996; Chen and Wang, 1999; Hung et al., 2003; Wong et al., 2007). Acronyms used in this figure: SMW-Shelf Mixed Water, KW-Kuroshio Water and OW-Oyashio Water.
Figure 3. Depth profiles of DOC concentrations measured for the stations in the (a) ECS and (b) northwestern NP during the two cruises in 2014-2015. Note: The depth scale below 1500 m has been reduced in (b).

Figure 4. Field-observed 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 NP. $\sigma_0$ isolines are included in the figures. Red dots indicate the potential temperature and salinity of the water types, and acronyms of water types as KW-Kuroshio Water, OW-Oyashio Water.
Figure 5. Depth profiles of DIC concentrations and $\Delta^{14}C$-DIC measured for the stations in the (a, b) ECS and (c, d) northwestern NP during the two cruises in 2014-2015. Note: The depth scale below 1500 m has been reduced in (c and d). 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.
Figure 7. Transectional distributions of (a) density (Sigma-t, $\sigma_t$), (b) DOC concentrations, (c) DIC concentrations and (d) $\Delta^{14}$C-DIC values for the (e) sampling stations (black squares) covering the shelf-edge and slope region of ECS during the cruise in July 2014. Black dots indicate the depths where samples were collected. Note: (a) The density of the other two stations (yellow circles) from the cruise in July 2011 are included to support the spreading of the data. (c-d) The distributions of density and DOC concentrations include seven stations, whereas DIC concentrations and $\Delta^{14}$C-DIC values are given only for six stations due to the lack of data at Sta. Z3 (Ge et al., 2016).
Figure 8. Plot of potential temperature ($\theta$) vs. salinity with (a) DOC concentrations, (b) DIC concentrations and (c) $\Delta^{14}C$-DIC values (indicated as the colours of points) associated with the potential water density ($\sigma_t$) for eight stations in the northwestern North Pacific (NP). The circular areas represent different water masses in terms of (A) lower density water in the upper 300 m depth with higher DOC concentration, lower DIC concentration and enriched $\Delta^{14}C$-DIC; (B) mixed upper water in the 300-500 m depth; (C) mixed intermediate water in 500-800 m water depth; and (D) denser NP deep water below 1000 m depth. Higher levels of DOC were associated with lower DIC concentrations, and high $\Delta^{14}C$-DIC values were found in lower density waters ($\sigma_0 < 25.5$, water mass A), while lower levels of DOC were associated with higher DIC concentrations, and low $\Delta^{14}C$-DIC values occurred in denser waters (water mass C and water mass D at $\sigma_0 > 27.1$). Note: DOC concentrations were measured for all stations, whereas DIC results from Ding et al. (2018) were only measured for six stations except Stas. A1-b and A6. Red dots indicate the potential temperature and salinity of the water types, and acronyms of water types as in Fig. 4 are shown.
Figure 9. Transectional distributions of (a) salinity, (b) DOC concentrations, (c) DIC concentration and (d) $\Delta^{14}$C-DIC values for (e) stations (black squares) sampled across the Kuroshio Extension (KE) in the northwestern NP. Black dots indicate depths where samples were collected. Note: (a) The salinity of another five stations (yellow circles) along the 35°N transect are included to support the spreading of the data. The hydrographic data for the five reference stations are taken from the Pacific data source in https://www.nodc.noaa.gov/ocads/. (c-d) DIC concentrations and $\Delta^{14}$C-DIC values are given only for four stations due to the lack of data at Sta. A1-b (Ding et al., 2018).
Figure 10. Keeling plot of $\Delta^{14}$C-DIC vs. concentration of $[\text{DIC}]^{-1}$ measured for six stations (B9, B8, A4, A8, B2 and K2) in the northwestern NP (data from Ding et al. (2018)). The line indicates the linear regression fit to all data points.