Geophysical Research Letters®

Key Points:

- Radiocarbon ages of dissolved organic carbon (DOC) in the East Sea (Japan Sea) ranged from 2,000 to 3,700 years, exceeding the water turnover time
- The oldest DOC at subsurface depths in the East Sea was transported from the North Pacific via the Tsushima Warm Current
- The aged DOC from the North Pacific is mixed with younger DOC produced in situ and spreads to the deep waters in the East Sea

Supporting Information:

Supporting Information may be found in the online version of this article.

Correspondence to:

J. Hwang,
jeomshik@snu.ac.kr

Author Contributions:

Formal analysis: Yeongjin Ryu, Heejun Han, Taehee Na
Methodology: Yeongjin Ryu, Heejun Han, Taehee Na, Jeomshik Hwang
Writing – original draft: Yeongjin Ryu, Jeomshik Hwang
Writing – review & editing: Yeongjin Ryu, Guebuem Kim, Ellen R. M. Druffel, Jeomshik Hwang

Transport of Aged Dissolved Organic Carbon via the Surface Current Revealed by Radiocarbon

Yeongjin Ryu[1] ⓘ, Heejun Han[1], Taehee Na[1], Guebuem Kim[1] ⓘ, Ellen R. M. Druffel[2] ⓘ, and Jeomshik Hwang[1] ⓘ

[1]School of Earth and Environmental Sciences/Research Institute of Oceanography, Seoul National University, Seoul, South Korea, [2]Department of Earth System Science, University of California, Irvine, CA, USA

Abstract The East Sea (also known as the Japan Sea) is connected to the Northwest Pacific via shallow straits and has independent deep water circulation, as a model miniature ocean. The radiocarbon age of dissolved organic carbon (DOC) in the East Sea ranged from 2,000 to 3,700 years, exceeding the water turnover time (~100 years). The oldest DOC was found in the subsurface layer characterized by the Tsushima Warm Water. Comparison of the radiocarbon content and concentration of DOC in the East Sea to those in the ocean suggests that aged DOC was transported conservatively from the Northwest Pacific to the East Sea via the shallow Tsushima Warm Current. The fractions of DOC released by serial-oxidation of the oldest DOC sample had identical radiocarbon ages, implying that refractory DOC was produced in situ and added to the DOC pool in the East Sea.

Plain Language Summary The East Sea (also known as the Japan Sea) is connected to the Northwest Pacific exchanging surface water only through shallow passages. The radiocarbon age of DOC in the East Sea is old, ranging from 2,000 to 3,700 years. This cannot be explained by DOC production and aging in the East Sea. Instead, it appears that old DOC is transported into the East Sea from the Northwest Pacific. The oldest DOC was found in the subsurface layer instead of the deepest layer. We show that this oldest DOC is a mixture of the old DOC from the North Pacific and modern DOC produced in the East Sea however their characteristics in terms of resistance to oxidation were modified. These findings provide clues for understanding the global DOC cycling especially in the surface ocean.

1. Introduction

Along the deep ocean circulation from the North Atlantic to the North Pacific, the dissolved organic carbon (DOC) concentration in the deep ocean (>1,000 m) decreases by about 29% (Hansell & Carlson, 1998) and the radiocarbon (^{14}C) age increases from about 4,900 to 6,500 years (Druffel et al., 1992, 2016, 2019; Williams & Druffel, 1987). DOC in the deep ocean is thought to repeat the deep ocean circulation several times. Thus, the aged DOC in the deep North Pacific is believed to return to the surface of the North Atlantic to close the loop.

Vertical distribution of the ^{14}C content of DOC (Δ^{14}C; Stuiver & Polach, 1977) can be explained by a two-component mixing model, where DOC is a mixture of aged DOC existing uniformly throughout the water column and freshly-produced, young DOC found mainly in the surface (Beaupré & Aluwihare, 2010; Mortazavi & Chanton, 2004; Williams & Druffel, 1987). For example, the Δ^{14}C value of DOC (−146‰) in surface water of the North Pacific was determined to be a mixture of 44% aged DOC (Δ^{14}C = −525‰) and 56% young DOC (Δ^{14}C = +150‰) (Williams & Druffel, 1987). According to the two-component mixing model, the refractory DOC in the deep North Atlantic is higher in concentration and higher in Δ^{14}C than that in the deep North Pacific. Therefore, young and refractory DOC should be added during the transit from the deep North Pacific to the surface of the North Atlantic. However, DOC of various residence times (hours to thousands of years) co-exist in the surface water (Hansell, 2013). Thus, it is difficult to understand the behavior of the aged DOC in the surface water.

We focused on the linkage of the DOC cycles through the surface current between the Northwest Pacific and the East Sea (also known as the Japan Sea). The East Sea is a marginal sea surrounded by Asia and the Japanese Islands (Figure 1). Its surface is about 1×10^6 km^2 in area and the maximum depth is >3,500 m (Chough et al., 2000). The East Sea is connected to the Northwest Pacific via straits shallower than 150 m (Lee et al., 2009). Surface water input to the East Sea mainly occurs via the inflow of the Tsushima Warm Current, a branch of the
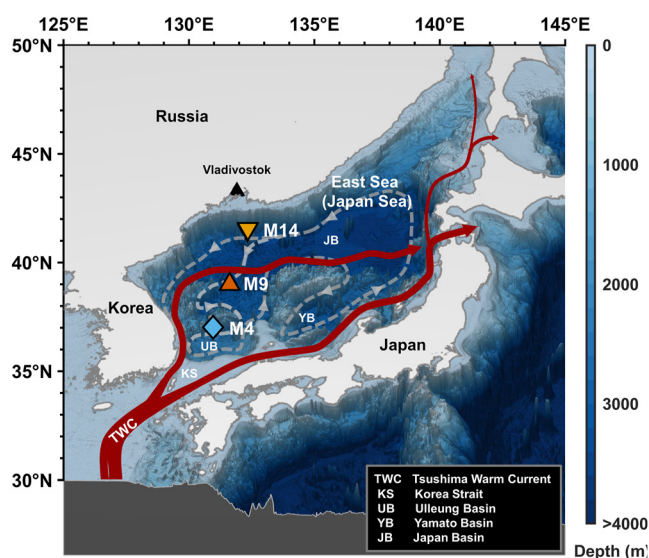
Figure 1. Map of the East Sea (Japan Sea) showing the sampling locations. At the surface, the Tsushima Warm Current, a branch of Kuroshio, flows into the East Sea through the Korea Strait (maximum depth 150 m). A branch of the Tsushima Warm Current flows north to ~40°N along the coast of Korea, then is detached to form the subpolar front (K. Kim et al., 2004). Deep waters generally flow counter-clockwise (gray dashed line; Senjyu et al., 2005) along the three basins: the Japan Basin (JB), Ulleung Basin (UB), and Yamato Basin (YB). Station M4 is located in the UB and Station M14 in the JB. Station M9 is located at the subpolar front region.

Kuroshio, through the Korea Strait in the south (K. Kim et al., 2004). Upon entering the East Sea, the Tsushima Warm Current spreads into the Ulleung Basin, bifurcating into two to three branches, with one of them flowing north along the east coast of Korean Peninsula and another flowing north of Japan. A deep water mass is formed in winter near Vladivostok, driving a rapid, deep overturning circulation with a turnover time of about 100 years (for the layer >1,000 m) (K. R. Kim & Kim, 1996; Kumamoto et al., 1998). Therefore, it is likely that the DOC in the deep East Sea is a mixture of the DOC from the surface water of the Northwest Pacific and the DOC produced in the East Sea.

The previously reported DOC concentration in the deep (>1,000 m depth) East Sea (>50 μM) (T. H. Kim et al., 2015, 2017) is significantly higher than the deep North Pacific (<39 μM) (Hansell et al., 2009) and the high-latitude North Atlantic (~50 μM; the Nordic Sea) (Amon et al., 2003). High primary production (Joo et al., 2016; Yamada et al., 2005) and rapid turnover of the deep waters have been suggested as potential causes (T. H. Kim et al., 2015). However, the causes of the high DOC concentration in the East Sea are not clear. In this study, we measured $\Delta^{14}C$ of the DOC in the East Sea and assessed the connectivity with the Northwest Pacific in DOC cycling. We used the East Sea as if it were a model miniature ocean (K. Kim et al., 2001). Such geological setting offers a chance to explore the mechanisms through which the old DOC found in the water column is circulated to different areas by surface currents.

2. Methods

2.1. Sample Collection

Seawater samples were collected from 26 October to 22 November 2019 aboard the R/V *Akademik Oparin* of the Pacific Oceanological Institute, Russia. Vertical distribution of DOC concentrations and $\Delta^{14}C$ values along with hydrographic properties were measured at three sites from the Ulleung Basin (Station M4, 37°00′N; 130°57′E), the subpolar front region (Station M9, 39°00′N; 131°37′E), and the Japan Basin (Station M14, 41°30′N; 132°20′E) along a meridional transect in the East Sea (Figure 1). Samples from depths shallower than 400 m were filtered directly from Niskin Bottles through pre-combusted (450°C for 4 hr) GF/F (0.7 μm pore size) filters and collected in pre-combusted, 1 L Amber Boston Round glass bottles. Samples from depths deeper than 400 m were not filtered because the concentration of particulate organic carbon (POC) is nominal compared to that of DOC (Druffel et al., 2019). The samples were stored at −20°C until analysis (Walker et al., 2017). Samples for determination of DOC concentration were filtered using pre-combusted GF/F filters and were collected in pre-combusted glass ampules. Samples were acidified with 6 M HCl to pH < 2, flame-sealed, and stored at room temperature (Halewood et al., 2022).

2.2. DOC Concentration

DOC concentration was measured with a total organic carbon analyzer (TOC-L; Shimadzu) following the high-temperature catalytic oxidation method within 2 months of sampling (Dittmar et al., 2006; Halewood et al., 2022). After removing inorganic carbon from the sample by purging ultrapure air (zero grade; 20.5% oxygen in nitrogen), the sample was injected into a combustion tube (720°C) containing a catalyst (Pt-coated Al) to oxidize DOC. The analytical uncertainty estimated by repeated measurements of the deep seawater reference material (DSR; ~43 μM; University of Miami; Hansell Organic Biogeochemistry Lab) was ±2 μM.

2.3. Radiocarbon Analysis of DOC

The oxidation of DOC to CO_2 for ^{14}C measurement was performed following the UV oxidation method (Beaupré et al., 2007). About 600 mL of each thawed sample was transferred to a quartz reactor and acidified with 1 mL

of 85% phosphoric acid (AC grade) to pH < 2. After stripping dissolved inorganic carbon (DIC) with ultrapure nitrogen (400 mL min^{-1} for 90 min), the sample was irradiated with UV (1200 W; mercury arc lamp) for 6 hr. The CO_2 was stripped with nitrogen (120 mL min^{-1} for 90 min), cryogenically purified and quantified manometrically, and flame-sealed in a Pyrex tube. ^{14}C content was measured at the National Ocean Sciences Accelerator Mass Spectrometry Facility at Woods Hole Oceanographic Institution. The standard deviation from five pairs of duplicate Δ^{14}C analysis was $\pm 8‰$. Blank correction was performed by comparison of the Δ^{14}C values of the processed and unprocessed standard materials using glucose (Δ^{14}C = +23‰) and glycine (Δ^{14}C = −1,000‰) standards (Fang et al., 2020; Hwang & Druffel, 2005). The Δ^{14}C values of the processed glucose and glycine standards were +21‰ (n = 1; 483 μg C), and −973 ± 3‰ (n = 2; 421 μg C and 509 μg C), respectively. The blank amount was estimated to be 12.8 ± 1.5 μg C with the Δ^{14}C value of −23 ± 5‰, indicating that most of the blank was air CO_2. The amount of blank correction was smaller than 14‰.

The serial-oxidation experiments were performed on two samples by UV-irradiation for 10, 20, 30, 60, and 240 min with He as a carrier gas (Beaupré & Druffel, 2012; Beaupré et al., 2007). We designed the length of each irradiation so that each step releases ∼20% of the total DOC as CO_2 gas. Increased UV-irradiation is believed to oxidize increasingly more refractory fractions. This experiment was to investigate the Δ^{14}C values of DOC fractions having different resistance to UV-irradiation. A previous study demonstrated that the earlier DOC was oxidized by UV, the higher was the observed Δ^{14}C value, suggesting a relationship between photochemical lability and biological lability (Beaupré & Druffel, 2012). The amount and Δ^{14}C value of the blank for these processes were estimated to be 9.2 ± 2.3 μg C and −476 ± 128‰, respectively, based on the processed Δ^{14}C values of glucose (+11 ± 6‰; n = 2; 419 and 427 μg C) and glycine (−990 ± 5‰; n = 2; 421 and 531 μg C), after 6 hr of UV-irradiation. Thus, this blank correction is probably larger than the actual blank effect, considering the much shorter UV-irradiation times for each step and there is possibility of over-correction. The blank correction was from 6 to 17‰ depending on the amount of recovered CO_2 and Δ^{14}C value.

3. Results and Discussion

3.1. Concentrations and Δ^{14}C Values of DOC in the East Sea

The DOC concentrations were 67–74 μM in the upper 50 m layer. The mean value at ∼200 m depth at all stations was 62 ± 1 μM (n = 3; Figure 2a). It is notable that the DOC concentrations at depths of 75 and 100 m at M4 in the Ulleung Basin were significantly lower than those at adjacent depths. The DOC concentration ranged from 60 to 63 μM between 200 and 500 m, below which values gradually decreased. The mean DOC concentration in the deep layer at all stations was 55 ± 3 μM (n = 11). The DOC concentrations in the surface water of the East Sea were similar to the observed values of the warm tropical and subtropical oceans (65–80 μM) (Hansell & Carlson, 2014), but those in the deep layer of the East Sea were significantly higher than those of the open oceans (34–∼50 μM) (Hansell & Carlson, 1998; Hansell et al., 2009).

The Δ^{14}C values of DOC in the East Sea varied with depth in a similar fashion to the DOC concentration (Figure 2b). The Δ^{14}C values in the upper 50 m of the water column were −284 to −225‰ and decreased to an average of −318 ± 17‰ by 200 m. At 75 and 100 m at Station M4, Δ^{14}C values were −374‰ and −354‰, 50‰–100‰ lower than those at adjacent depths. The Δ^{14}C values decreased from 500 to 1,000 m and were relatively constant below 1,000 m (mean −355 ± 13‰, n = 11) at all stations, showing no significant spatial variation. The lack of spatial variation is consistent with the rapid horizontal circulation in the deep layer, within a decade or less (note that horizontal circulation in the deep layer is much faster than the vertical turnover in the East Sea; M. Kim et al., 2022; Senjyu et al., 2005). The Δ^{14}C values in the deep layer were significantly higher (by 19‰–177‰) than those of the open oceans (Figure 2b).

The mean Δ^{14}C value of the DIC in the deep East Sea (collected in 1999) was −49 ± 14‰ (Sim et al., 2014), and is similar to that of the Atlantic deep waters in 1991 (−71 ± 20‰) (Druffel et al., 1992), indicating young ages and the presence of bomb ^{14}C in the deep waters. The high DOC concentrations together with the high DIC Δ^{14}C values imply that the DOC cycle in the East Sea somewhat resembles that in the North Atlantic. The mean DOC Δ^{14}C value in the deep layer of the East Sea was about 20‰ higher than that in the high-latitude (60°N) North Atlantic in 2013 (−374 ± 8‰) (Druffel et al., 2016). Despite the close proximity, the mean DOC Δ^{14}C value in the deep layer of the East Sea was considerably higher than the mean of −532 ± 15‰ in the North Pacific (Druffel et al., 2018, 2019, 2021). This difference in DOC Δ^{14}C values is caused by the absence of direct
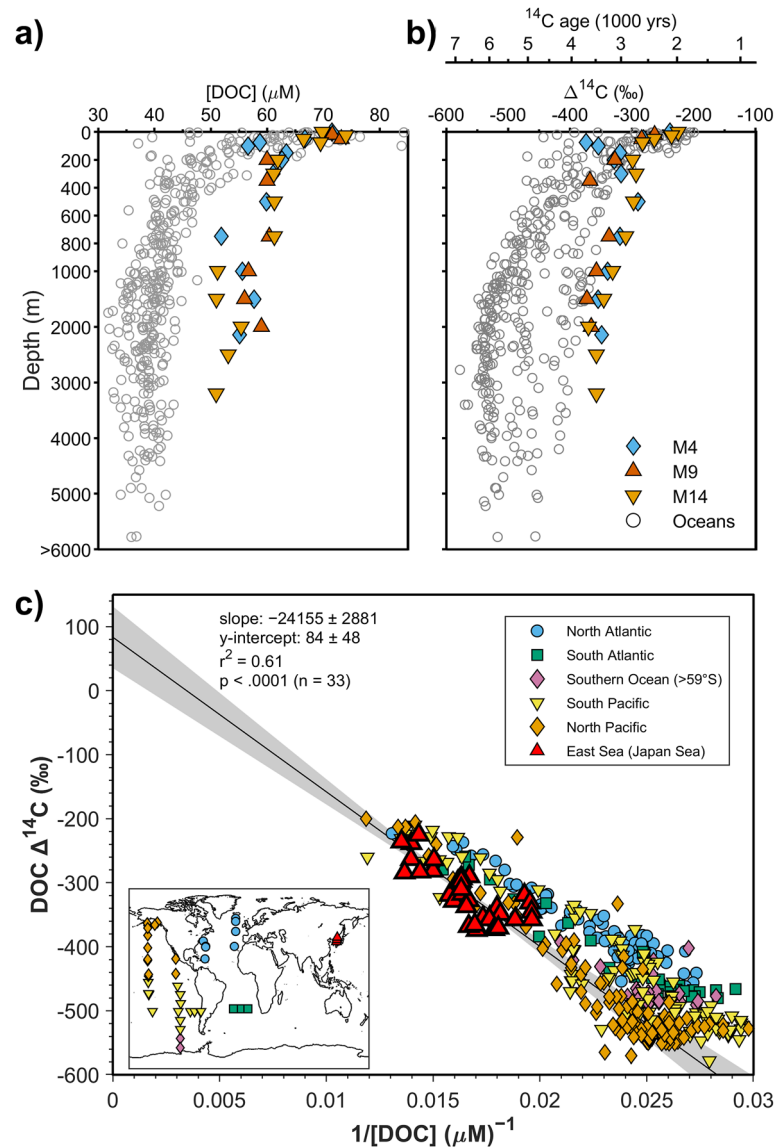
Figure 2. The vertical profiles of (a) the dissolved organic carbon (DOC) concentration and (b) the $\Delta^{14}C$ values and ^{14}C ages of the DOC, and (c) the cross plot of the DOC $\Delta^{14}C$ values and the reciprocal of the DOC concentrations. The data presented in all plots for comparison are from the Atlantic (Druffel et al., 2016), Pacific (Druffel & Griffin, 2015; Druffel et al., 2018, 2019, 2021), and Southern Ocean (Druffel et al., 2021). The regression line in (c), shown as a black line, with gray shading representing the 95% confidence interval, is derived from the East Sea (Japan Sea) data only.

exchange of deep waters between the East Sea and the North Pacific, and also by much faster vertical circulation in the East Sea than the global ocean circulation (Figure 2b and Figure S1 in Supporting Information S1).

The ^{14}C age of DOC in the entire water column of the East Sea ranged from 2,000 to 3,700 years (Figure 2b). The old ^{14}C age of DOC cannot be explained by aging alone during the deep water circulation, given that the turnover time of the deep water is ~100 years (K. R. Kim & Kim, 1996). Although no large rivers drain into the East Sea (Chough et al., 2000), the Yellow River and the Yangtze River, draining into the Yellow Sea and the East China Sea, may supply riverine DOC eventually to the East Sea (Ding et al., 2019; Kwon et al., 2018). The DOC originated from the Yellow River and the Yangtze River are generally old (300–1,700 ^{14}C years) and have low $\delta^{13}C$ values (−32.2‰ to −21.0‰) (Wang et al., 2012, 2016). However, the riverine DOC appears to be degraded quickly and its influence is confined within the close proximity of the mouths of these rivers (Han et al., 2022). The $\delta^{13}C$ values of DOC in the East China Sea (mean = −21.1 ± 1.1‰, n = 21; Han et al., 2022), and the East Sea (−20.4 to −21.7‰; T. H. Kim et al., 2015) indicate a dominant marine source of DOC. Therefore, the

influence of riverine DOC is likely small. DOC concentration and $\Delta^{14}C$ data obtained in water east of Jeju Island and south of the Korea Strait showed that the DOC in this region was a mixture of the subsurface DOC from the Kuroshio water and locally produced DOC (Oh & Hwang, 2023). Another possible source of aged DOC is from the sediment. The $\Delta^{14}C$ values of the surface sediment (core-top, 0–1 cm) in the East Sea ranged from −100‰ to −375‰ (M. Kim et al., 2020; Otosaka et al., 2008). However, Bauer et al. (1995) argued that DOC supplied from the sediments is minor. A more feasible source of the aged DOC is the surface water inflow (Tsushima Warm Current, Figure S2 in Supporting Information S1) from the Northwest Pacific into the East Sea (see below).

According to the two-component mixing model, DOC is a mixture of a recently produced labile DOC and refractory background DOC that is uniformly present in the entire water column (Beaupré & Aluwihare, 2010; Mortazavi & Chanton, 2004; Williams & Druffel, 1987).

$$[DOC]_{total} = [DOC]_{background} + [DOC]_{excess} \tag{1}$$

$$[DOC]_{total} \times \Delta^{14}C_{total} = [DOC]_{background} \times \Delta^{14}C_{background} + [DOC]_{excess} \times \Delta^{14}C_{excess} \tag{2}$$

These two equations can be rearranged to show the relationship between the $\Delta^{14}C_{total}$ and $1/[DOC]_{total}$ as follows:

$$\Delta^{14}C_{total} = \left(\Delta^{14}C_{background} - \Delta^{14}C_{excess}\right)[DOC]_{background}(1/[DOC]_{total}) + \Delta^{14}C_{excess} \tag{3}$$

This plot, known as the Keeling plot, is a straight line, with $(\Delta^{14}C_{background} - \Delta^{14}C_{excess})[DOC]_{background}$ representing the slope (Keeling, 1958; Mortazavi & Chanton, 2004). The y-intercept, $\Delta^{14}C_{excess}$, indicates the $\Delta^{14}C$ value of the DOC added to the mixture.

The crossplot of $1/[DOC]_{total}$ and DOC $\Delta^{14}C$ values in the open ocean reveals a significant linear relationship (Mortazavi & Chanton, 2004). The DOC results in the East Sea also show a significant linear relationship of the crossplot ($r^2 = 0.61$, $n = 33$, $p < 0.0001$; Figure 2c). The y-intercept of the linear regression, $\Delta^{14}C_{excess}$, is $+84 \pm 48‰$, and is within the range of DIC $\Delta^{14}C$ values in the surface water (<200 m) in the East Sea collected in 1999 (63‰–85‰) (Sim et al., 2014). This result demonstrates that the two-component model is valid for the East Sea DOC and the major source of the $\Delta^{14}C_{excess}$ was in situ production of organic matter in the surface water via photosynthesis.

Because the East Sea is connected to the Northwest Pacific through the shallow straits, we compared the East Sea results with those of the open ocean values. The East Sea results were more closely aligned with those of the North Pacific (Figure 2c). This alignment implies that they share the same source of $DOC_{background}$. Also, the linearity argues against significant removal of $DOC_{background}$ during the transport from the Northwest Pacific to the East Sea. The insignificant removal by either photodegradation (Mopper et al., 1991) or microbial degradation (Jiao et al., 2010; Shen & Benner, 2018) of the $DOC_{background}$ in the surface water was likely due to the short travel time of the surface water. Therefore, we hypothesize that the DOC in the deep East Sea is a mixture of DOC similar to the $DOC_{background}$ in the North Pacific and DOC_{excess} produced in the East Sea. The mean concentration and $\Delta^{14}C$ value of deep DOC in the North Pacific were $39 \pm 2\,\mu M$ and $-532 \pm 15‰$, respectively ($n = 59$) (Druffel et al., 2018, 2019, 2021). Using −532‰ and +84‰ as the two end-members, the DOC in the deep East Sea would be 71% aged DOC and 29% newly-produced DOC [$f \times (-532 \pm 15‰) + (1 - f) \times (+84 \pm 48‰) = (-355 \pm 13‰)$, $f = 0.71 \pm 0.11$]. The concentration of the young DOC in the deep layer, $16 \pm 6\,\mu M$, is high (see below).

3.2. Intrusion of Refractory Dissolved Organic Carbon and Its Spread to the Deep Layer of the East Sea

We performed a serial-oxidation experiment on the water sample from 2,500 m depth at Station M9. The result showed a similar decreasing trend in the $\Delta^{14}C$ values from $-299 \pm 23‰$ to $-396 \pm 31‰$ with the increasing UV-irradiation time (Figure 3). The weighted mean $\Delta^{14}C$ value of these fractions was identical to the mean $\Delta^{14}C$ value of all bulk DOC samples in the deep layer ($n = 11$). In contrast to the open ocean data, the lowest $\Delta^{14}C$ value in the East Sea was observed at the subsurface at Station M4 (Figure 2b). The water mass at this depth has the characteristics of the Tsushima Warm Water (TWW, water mass originating from the Tsushima Warm Current), which has a salinity of ∼34.3, a temperature of >10°C (K. Kim et al., 2004), and a low dissolved oxygen concentration of ∼180 μM (Figure S2 in Supporting Information S1). Therefore, it is suspected that the DOC in the TWW represents the refractory DOC introduced to the East Sea from the Northwest Pacific. We performed a serial-oxidation experiment on another sample collected at 100 m depth at Station M9, where similar TWW
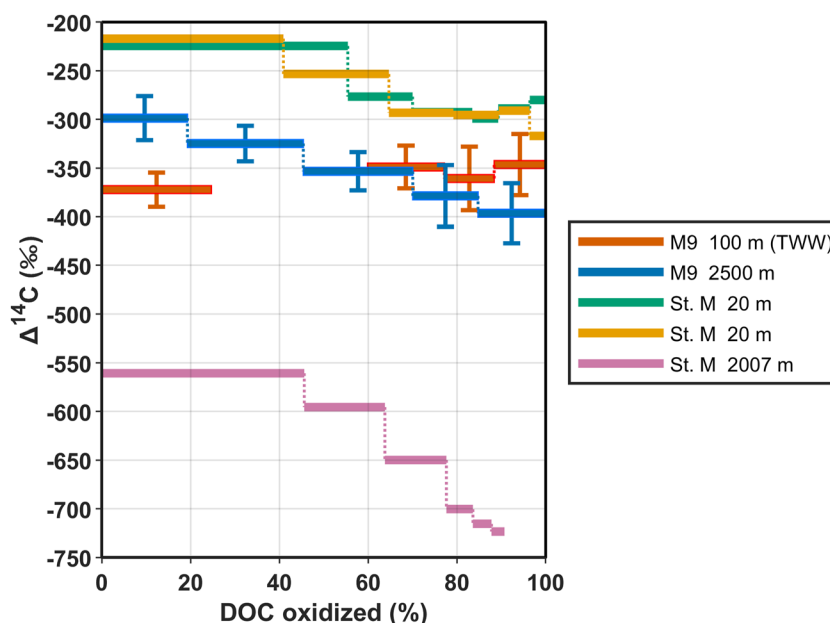
Figure 3. Variation of $\Delta^{14}C$ values of the fractions retrieved by serial-oxidation by UV-irradiation. Each horizontal line indicates the fraction of dissolved organic carbon (DOC) extracted during each oxidation relative to the sum of each extracted fraction. The vertical lines represent the uncertainties. The DOC data in the Pacific Ocean are from Station M (34°50′N; 123°00′W) as published by Beaupré and Druffel (2012) and Beaupré et al. (2007). The second fraction of the Station M9 sample from 100 m depth of the East Sea (Japan Sea) was lost.

characteristics were observed (Figure S2 in Supporting Information S1). Unlike the sample from 2,500 m, the sample from 100 m at Station M9 showed a much smaller variation in $\Delta^{14}C$ value, within the uncertainty, with irradiation time (between $-372 \pm 18‰$ and $-346 \pm 31‰$; Figure 3). This result implies a homogeneous nature of the DOC at 100 m depth in terms of photochemical/biological reactivity, in contrast to that at 2,500 m depth and other samples from the open ocean (Figure 3) (Beaupré & Druffel, 2012).

Considering the serial-oxidation result and the high value of apparent oxygen utilization (AOU, ~75 μmol kg^{-1}; Figure S2 in Supporting Information S1), this DOC (hereafter TWW-DOC; 58 μM, $\Delta^{14}C = -364‰$) could be a biologically refractory fraction that remained after selective degradation of labile and semi-labile fractions. Because the TWW-DOC does not deviate from the trend line on the Keeling plot, the TWW-DOC appears to be a mixture of the background DOC in the deep Northwest Pacific and DOC with modern $\Delta^{14}C$ values. The serial-oxidation results suggest that the modern DOC portion of the TWW-DOC is biologically refractory. Also, the refractory and aged DOC portion was transformed to become more reactive to UV-irradiation. The refractory DOC with modern $\Delta^{14}C$ values is assumed to have been produced in situ in the East Sea by microbial activity (Jiao et al., 2010; Ogawa et al., 2001) and photochemical reactions (Benner & Biddanda, 1998). Alternatively, these processes may have changed the properties of the aged portion. At this point, we do not understand any specific processes to cause the homogeneous nature of TWW-DOC, and necessitates further investigation. TWW-DOC would comprise the oldest fraction of the deep DOC ($\Delta^{14}C = -396 \pm 31‰$; Figure 3) in the East Sea. Subsequent aging (hundreds of years) during deep circulation could partly explain the age difference between the most refractory portions of DOC at 2,500 and 100 m. Selective degradation of younger DOC fraction in the deep layer can also increase the age difference.

The nature of deep DOC in the East Sea in terms of its bioavailability/refractory nature has been assessed by a few different approaches. In general, the DOC:DON molar ratio (hereafter C:N ratio) increases, and the $\Delta^{14}C$ value decreases as the molecular size of dissolved organic matter (DOM) decreases (Amon & Benner, 1994; Benner & Amon, 2015; Walker et al., 2016). The C:N ratios of the DOM in the East Sea were 17 ± 4 and 23 ± 3 in the surface and deep layers, respectively (T. H. Kim & Kim, 2013; T. H. Kim et al., 2017), which are higher than those of the labile DOM (C:N ratio of 10) (Jiao et al., 2010). However, the average contents of total dissolved amino acids relative to DOC content (TDAA yields) in the deep East Sea were $0.8 \pm 0.2\%$ of the DOC (T. H. Kim et al., 2017),

which were similar to those (0.7 ± 0.1% DOC) at the BATS (Bermuda Atlantic Time-series Study) site and were higher than those (0.5 ± 0.1% DOC) at the HOT (Hawaii Ocean Time-series) site (Kaiser & Benner, 2009). Together with the results of serial-oxidation of the deep DOC, the high TDAA yields imply the existence of semi-labile DOC in the deep East Sea. Fast deep water turnover is at least partly responsible for the presence of labile and semi-labile DOC in the deep East Sea. Primary production in the East Sea (~20 molC m^{-2} yr^{-1} annual average) is significantly higher than that in the open ocean (Joo et al., 2016). The export production (the flux of organic carbon from the euphotic zone to the sea interior) is also high (~8 molC m^{-2} yr^{-1}) (Hahm & Kim, 2008). Thus, POC dissolution (Smith et al., 1992) may be another important factor for high DOC concentration in the deep East Sea. The amount of humic fluorescent DOM (FDOM) in the layer >200 m in the East Sea was higher than that in the North Pacific, suggesting the accumulation of FDOM during the repeated renewal of deep water in the East Sea (Tanaka et al., 2014). In summary, the deep DOC in the East Sea appears to contain both refractory DOC transformed by the microbial carbon pump and the semi-labile DOC injected by rapid turnover (Aramaki et al., 2013) and POC dissolution.

4. Summary and Conclusions

We investigated DOC cycling in the East Sea by measuring its radiocarbon content. The Δ^{14}C values were considerably higher than those in the open ocean. On the Keeling plot, the East Sea data formed a straight line, which aligned with that of the Pacific Ocean. These results imply that the background DOC in the East Sea originated from the Pacific, transported via the surface current. The lowest Δ^{14}C value of DOC was observed at subsurface depths, unlike the oceanic data where the lowest values are observed in the deep layer. This water mass has the characteristics of the TWW that originates from the Northwest Pacific. This result is consistent with what the Keeling plot implies, in terms of association with the Pacific in DOC cycling. In the serial-oxidation experiment, this TWW-DOC exhibited homogeneous reactivity to UV-irradiation. Therefore, modern DOC that was added to the refractory DOC pool had a refractory nature, and the refractory background DOC became more reactive to UV-irradiation. The aged DOC introduced from the Pacific is added by modern DOC and spreads into the deep layer along the deep water circulation in the East Sea. Our results in a marginal sea that investigated the linkage in DOC cycling to the Northwest Pacific may provide a clue to the removal of the aged DOC and the addition of modern DOC to the refractory DOC pool during surface water circulation in the oceans.

Data Availability Statement

Total and serially-oxidized DOC Δ^{14}C values and concentrations from the East Sea (Japan Sea) are available at Ryu et al. (2023). Total DOC Δ^{14}C values and concentrations in the Pacific, Atlantic, and Southern Ocean can be found in Druffel and Griffin (2015), Druffel et al. (2016, 2018, 2019, 2021). Serially-oxidized DOC Δ^{14}C values and concentrations from the Pacific are available through Beaupré and Druffel (2012) and Beaupré et al. (2007).

References

Amon, R. M. W., & Benner, R. (1994). Rapid-cycling of high-molecular-weight dissolved organic-matter in the ocean. *Nature*, *369*(6481), 549–552. https://doi.org/10.1038/369549a0

Amon, R. M. W., Budéus, G., & Meon, B. (2003). Dissolved organic carbon distribution and origin in the Nordic seas: Exchanges with the Arctic Ocean and the North Atlantic. *Journal of Geophysical Research*, *108*(C7), 3221. https://doi.org/10.1029/2002JC001594

Aramaki, T., Tanaka, S. S., Kushibashi, S., Kim, Y. I., Kim, C. J., Hong, G. H., & Senjyu, T. (2013). Spatial distribution of radiocarbon in the Southwestern Japan/East Sea immediately after bottom water renewal. *Radiocarbon*, *55*(2–3), 1675–1682. https://doi.org/10.1017/S0033822200048591

Bauer, J. E., Reimers, C. E., Druffel, E. R. M., & Williams, P. M. (1995). Isotopic constraints on carbon exchange between deep-ocean sediments and sea-water. *Nature*, *373*(6516), 686–689. https://doi.org/10.1038/373686a0

Beaupré, S. R., & Aluwihare, L. (2010). Constraining the 2-component model of marine dissolved organic radiocarbon. *Deep Sea Research Part II: Topical Studies in Oceanography*, *57*(16), 1494–1503. https://doi.org/10.1016/j.dsr2.2010.02.017

Beaupré, S. R., & Druffel, E. R. M. (2012). Photochemical reactivity of ancient marine dissolved organic carbon [Dataset]. Geophysical Research Letters, *39*(18), L18602. https://doi.org/10.1029/2012GL052974

Beaupré, S. R., Druffel, E. R. M., & Griffin, S. (2007). A low-blank photochemical extraction system for concentration and isotopic analyses of marine dissolved organic carbon [Dataset]. Limnology and Oceanography: Methods, *5*(6), 174–184. https://doi.org/10.4319/lom.2007.5.174

Benner, R., & Amon, R. M. W. (2015). The size-reactivity continuum of major bioelements in the ocean. *Annual Review of Marine Science*, *7*(1), 185–205. https://doi.org/10.1146/annurev-marine-010213-135126

Benner, R., & Biddanda, B. (1998). Photochemical transformations of surface and deep marine dissolved organic matter: Effects on bacterial growth. *Limnology & Oceanography*, *43*(6), 1373–1378. https://doi.org/10.4319/lo.1998.43.6.1373

Chough, S. K., Lee, H. J., & Yoon, S. H. (2000). *Marine geology of Korean seas*. Elsevier.

Ding, L., Ge, T. T., & Wang, X. C. (2019). Dissolved organic carbon dynamics in the East China Sea and the Northwest Pacific Ocean. *Ocean Science*, *15*(5), 1177–1190. https://doi.org/10.5194/os-15-1177-2019

Dittmar, T., Hertkorn, N., Kattner, G., & Lara, R. J. (2006). Mangroves, a major source of dissolved organic carbon to the oceans. *Global Biogeochemical Cycles*, *20*(1), GB1012. https://doi.org/10.1029/2005gb002570

Druffel, E. R. M., & Griffin, S. (2015). Radiocarbon in dissolved organic carbon of the south Pacific Ocean [Dataset]. Geophysical Research Letters, *42*(10), 4096–4101. https://doi.org/10.1002/2015GL063764

Druffel, E. R. M., Griffin, S., Coppola, A. I., & Walker, B. D. (2016). Radiocarbon in dissolved organic carbon of the Atlantic Ocean [Dataset]. Geophysical Research Letters, *43*(10), 5279–5286. https://doi.org/10.1002/2016GL068746

Druffel, E. R. M., Griffin, S., Lewis, C. B., Rudresh, M., Garcia, N. G., Key, R. M., et al. (2021). Dissolved organic radiocarbon in the eastern Pacific and southern oceans [Dataset]. Geophysical Research Letters, *48*(10), e2020GL091746. https://doi.org/10.1029/2021GL092904

Druffel, E. R. M., Griffin, S., Wang, N., Garcia, N. G., McNichol, A. P., Key, R. M., & Walker, B. D. (2019). Dissolved organic radiocarbon in the central Pacific Ocean [Dataset]. Geophysical Research Letters, *46*(10), 5396–5403. https://doi.org/10.1029/2019GL083149

Druffel, E. R. M., Griffin, S., Wang, N., & Walker, B. D. (2018). Temporal variability of dissolved organic radiocarbon in the deep North Pacific Ocean [Dataset]. Radiocarbon, *60*(4), 1115–1123. https://doi.org/10.1017/RDC.2018.39

Druffel, E. R. M., Williams, P. M., Bauer, J. E., & Ertel, J. R. (1992). Cycling of dissolved and particulate organic-matter in the open ocean. *Journal of Geophysical Research*, *97*(C10), 15639–15659. https://doi.org/10.1029/92JC01511

Fang, L., Lee, S., Lee, S. A., Hahm, D., Kim, G., Druffel, E. R. M., & Hwang, J. (2020). Removal of refractory dissolved organic carbon in the Amundsen Sea, Antarctica. *Scientific Reports*, *10*(1), 1213. https://doi.org/10.1038/s41598-020-57870-6

Hahm, D., & Kim, K. R. (2008). Observation of bottom water renewal and export production in the Japan Basin, East Sea using tritium and helium isotopes. *Ocean Science Journal*, *43*(1), 39–48. https://doi.org/10.1007/BF03022430

Halewood, E., Opalk, K., Custals, L., Carey, M., Hansell, D. A., & Carlson, C. A. (2022). Determination of dissolved organic carbon and total dissolved nitrogen in seawater using High Temperature Combustion Analysis. *Frontiers in Marine Science*, *9*, 15. https://doi.org/10.3389/fmars.2022.1061646

Han, H., Na, T., Cho, H. M., Kim, G., & Hwang, J. (2022). Large fluxes of continental-shelf-borne dissolved organic carbon in the East China Sea and the Yellow Sea. *Marine Chemistry*, *240*, 104097. https://doi.org/10.1016/j.marchem.2022.104097

Hansell, D. A. (2013). Recalcitrant dissolved organic carbon fractions. *Annual Review of Marine Science*, *5*(1), 421–445. https://doi.org/10.1146/annurev-marine-120710-100757

Hansell, D. A., & Carlson, C. A. (1998). Deep-ocean gradients in the concentration of dissolved organic carbon. *Nature*, *395*(6699), 263–266. https://doi.org/10.1038/26200

Hansell, D. A. & Carlson, C. A. (Eds.). (2014). *Biogeochemistry of marine dissolved organic matter*. Academic Press.

Hansell, D. A., Carlson, C. A., Repeta, D. J., & Schlitzer, R. (2009). Dissolved organic matter in the ocean a controversy stimulates new insights. *Oceanography*, *22*(4), 202–211. https://doi.org/10.5670/oceanog.2009.109

Hwang, J., & Druffel, E. R. M. (2005). Blank correction for Delta C-14 measurements in organic compound classes of oceanic particulate matter. *Radiocarbon*, *47*(1), 75–87. https://doi.org/10.1017/S0033822200052218

Jiao, N., Herndl, G. J., Hansell, D. A., Benner, R., Kattner, G., Wilhelm, S. W., et al. (2010). Microbial production of recalcitrant dissolved organic matter: Long-term carbon storage in the global ocean. *Nature Reviews Microbiology*, *8*(8), 593–599. https://doi.org/10.1038/nrmicro2386

Joo, H., Son, S., Park, J. W., Kang, J. J., Jeong, J. Y., Lee, C. I., et al. (2016). Long-Term pattern of primary productivity in the East/Japan sea based on ocean color data derived from MODIS-Aqua. *Remote Sensing*, *8*(1), 25. https://doi.org/10.3390/rs8010025

Kaiser, K., & Benner, R. (2009). Biochemical composition and size distribution of organic matter at the Pacific and Atlantic time-series stations. *Marine Chemistry*, *113*(1–2), 63–77. https://doi.org/10.1016/j.marchem.2008.12.004

Keeling, C. D. (1958). The concentration and isotopic Abundances of Atmospheric carbon dioxide in rural areas. *Geochimica et Cosmochimica Acta*, *13*(4), 322–334. https://doi.org/10.1016/0016-7037(58)90033-4

Kim, K., Kim, K. R., Kim, Y. G., Cho, Y. K., Kang, D. J., Takematsu, M., & Volkov, Y. (2004). Water masses and decadal variability in the East Sea (Sea of Japan). *Progress in Oceanography*, *61*(2–4), 157–174. https://doi.org/10.1016/j.pocean.2004.06.003

Kim, K., Kim, K. R., Min, D. H., Volkov, Y., Yoon, J. H., & Takematsu, M. (2001). Warming and structural changes in the East (Japan) sea: A clue to future changes in global oceans? *Geophysical Research Letters*, *28*(17), 3293–3296. https://doi.org/10.1029/2001GL013078

Kim, K. R., & Kim, K. (1996). What is happening in the East Sea (Japan Sea)? Recent chemical observations during CREAMS 93-96. *Journal of the Korean Society of Oceanography*, *31*(4), 164–172. https://doi.org/10.1007/BF02910222

Kim, M., Hwang, J., Kim, G., Na, T., Kim, T. H., & Hyun, J. H. (2022). Carbon cycling in the East Sea (Japan Sea): A review. *Frontiers in Marine Science*, *9*, 787992. https://doi.org/10.3389/fmars.2022.938935

Kim, M., Kim, Y. I., Hwang, J., Choi, K. Y., Kim, C. J., Ryu, Y., et al. (2020). Influence of sediment resuspension on the biological pump of the Southwestern East Sea (Japan Sea). *Frontiers in Earth Science*, *8*, 538412. https://doi.org/10.3389/feart.2020.00144

Kim, T. H., & Kim, G. (2013). Factors controlling the C: N: P stoichiometry of dissolved organic matter in the N-limited, cyanobacteria-dominated east/Japan sea. *Journal of Marine Systems*, *115*, 1–9. https://doi.org/10.1016/j.jmarsys.2013.01.002

Kim, T. H., Kim, G., Lee, S. A., & Dittmar, T. (2015). Extraordinary slow degradation of dissolved organic carbon (DOC) in a cold marginal sea. *Scientific Reports*, *5*(1), 13808. https://doi.org/10.1038/srep13808

Kim, T. H., Kim, G., Shen, Y., & Benner, R. (2017). Strong linkages between surface and deep-water dissolved organic matter in the East/Japan Sea. *Biogeosciences*, *14*(9), 2561–2570. https://doi.org/10.5194/bg-14-2561-2017

Kumamoto, Y., Yoneda, M., Shibata, Y., Kume, H., Tanaka, A., Uehiro, T., et al. (1998). Direct observation of the rapid turnover of the Japan Sea bottom water by means of AMS radiocarbon measurement. *Geophysical Research Letters*, *25*(5), 651–654. https://doi.org/10.1029/98GL00359

Kwon, H. K., Kim, G., Hwang, J., Lim, W. A., Park, J. W., & Kim, T. H. (2018). Significant and conservative long-range transport of dissolved organic nutrients in the Changjiang diluted water. *Scientific Reports*, *8*(1), 12768. https://doi.org/10.1038/s41598-018-31105-1

Lee, J. Y., Kang, D. J., Kim, I. N., Rho, T., Lee, T., Kang, C. K., & Kim, K. R. (2009). Spatial and temporal variability in the pelagic ecosystem of the East Sea (Sea of Japan): A review. *Journal of Marine Systems*, *78*(2), 288–300. https://doi.org/10.1016/j.jmarsys.2009.02.013

Mopper, K., Zhou, X. L., Kieber, R. J., Kieber, D. J., Sikorski, R. J., & Jones, R. D. (1991). Photochemical degradation of dissolved organic-carbon and its impact on the oceanic carbon-cycle. *Nature*, *353*(6339), 60–62. https://doi.org/10.1038/353060a0

Mortazavi, B., & Chanton, J. P. (2004). Use of Keeling plots to determine sources of dissolved organic carbon in nearshore and open ocean systems. *Limnology & Oceanography*, *49*(1), 102–108. https://doi.org/10.4319/lo.2004.49.1.0102

Ogawa, H., Amagai, Y., Koike, I., Kaiser, K., & Benner, R. (2001). Production of refractory dissolved organic matter by bacteria. *Science*, *292*(5518), 917–920. https://doi.org/10.1126/science.1057627

Oh, S., & Hwang, J. (2023). Radiocarbon content of dissolved organic carbon in the East China Sea. Unpublished results.

Otosaka, S., Tanaka, T., Togawa, O., Amano, H., Karasev, E. V., Minakawa, M., & Noriki, S. (2008). Deep Sea circulation of particulate organic carbon in the Japan sea. *Journal of Oceanography*, *64*(6), 911–923. https://doi.org/10.1007/s10872-008-0075-4

Ryu, Y., Han, H., Na, T., Kim, G., Druffel, E. R. M., & Hwang, J. (2023). Delta carbon-14 and dissolved organic carbon taken by CTD and Niskin bottles from the research vessel Akademik Oparin in the East Sea, Sea of Japan, from 2019-10-27 to 2019-11-05 (NCEI Accession 0280198) [Dataset]. NOAA National Centers for Environmental Information. Retrieved from https://www.ncei.noaa.gov/archive/accession/0280198

Senjyu, T., Shin, H. R., Yoon, J. H., Nagano, Z., An, H. S., Byun, S. K., & Lee, C. K. (2005). Deep flow field in the Japan/East Sea as deduced from direct current measurements. *Deep Sea Research Part II: Topical Studies in Oceanography*, *52*(11–13), 1726–1741. https://doi.org/10.1016/j.dsr2.2003.10.013

Shen, Y., & Benner, R. (2018). Mixing it up in the ocean carbon cycle and the removal of refractory dissolved organic carbon. *Scientific Reports*, *8*(1), 2542. https://doi.org/10.1038/s41598-018-20857-5

Sim, B. R., Kang, D. J., Park, Y. G., & Kim, K. R. (2014). Spatial and temporal variation of dissolved inorganic radiocarbon in the East sea. *Ocean and Polar Research*, *36*(2), 111–119. https://doi.org/10.4217/OPR.2014.36.2.111

Smith, K. L., Baldwin, R. J., & Williams, P. M. (1992). Reconciling particulate organic-carbon flux and sediment community oxygen-consumption in the deep North Pacific. *Nature*, *359*(6393), 313–316. https://doi.org/10.1038/359313a0

Stuiver, M., & Polach, H. A. (1977). Reporting of C-14 data—Discussion. *Radiocarbon*, *19*(3), 355–363. https://doi.org/10.1017/S0033822200003672

Tanaka, K., Kuma, K., Hamasaki, K., & Yamashita, Y. (2014). Accumulation of humic-like fluorescent dissolved organic matter in the Japan Sea. *Scientific Reports*, *4*(1), 5292. https://doi.org/10.1038/srep05292

Walker, B. D., Griffin, S., & Druffel, E. R. M. (2017). Effect of acidified versus frozen storage on marine dissolved organic carbon concentration and isotopic composition. *Radiocarbon*, *59*(3), 843–857. https://doi.org/10.1017/Rdc.2016.48

Walker, B. D., Primeau, F. W., Beaupré, S. R., Guilderson, T. P., Druffel, E. R. M., & McCarthy, M. D. (2016). Linked changes in marine dissolved organic carbon molecular size and radiocarbon age. *Geophysical Research Letters*, *43*(19), 10385–10393. https://doi.org/10.1002/2016GL070359

Wang, X. C., Ma, H. Q., Li, R. H., Song, Z. S., & Wu, J. P. (2012). Seasonal fluxes and source variation of organic carbon transported by two major Chinese Rivers: The Yellow River and Changjiang (Yangtze) River. *Global Biogeochemical Cycles*, *26*(2), GB2015. https://doi.org/10.1029/2011gb004130

Wang, X. C., Xu, C. L., Druffel, E. M., Xue, Y. J., & Qi, Y. Z. (2016). Two black carbon pools transported by the Changjiang and Huanghe Rivers in China. *Global Biogeochemical Cycles*, *30*(12), 1778–1790. https://doi.org/10.1002/2016gb005509

Williams, P. M., & Druffel, E. R. M. (1987). Radiocarbon in dissolved organic-matter in the central north Pacific-ocean. *Nature*, *330*(6145), 246–248. https://doi.org/10.1038/330246a0

Yamada, K., Ishizaka, J., & Nagata, H. (2005). Spatial and temporal variability of satellite primary production in the Japan Sea from 1998 to 2002. *Journal of Oceanography*, *61*(5), 857–869. https://doi.org/10.1007/s10872-006-0005-2

References From the Supporting Information

McNichol, A. P., & Key, R. (2019). DIC-14C data from Cruise 33RO20150525 (exchange version) [Dataset]. CLIVAR and Carbon Hydrographic Data Office (CCHDO). https://doi.org/10.7942/C2RP43

Santinelli, C., Follett, C., Brogi, S. R., Xu, L., & Repeta, D. (2015). Carbon isotope measurements reveal unexpected cycling of dissolved organic matter in the deep Mediterranean Sea. *Marine Chemistry*, *177*, 267–277. https://doi.org/10.1016/j.marchem.2015.06.018

Wanninkhof, R., Bullister, J., & Peltola, E. (2013). Partial pressure (or fugacity) of carbon dioxide, dissolved inorganic carbon, pH, alkalinity, temperature, salinity and other variables collected from discrete sample and profile observations using CTD, bottle and other instruments from NOAA Ship MALCOLM BALDRIGE in the North Atlantic Ocean and South Atlantic Ocean from 1993-07-04 to 1993-08-30 (NCEI Accession 0114997) [Dataset]. DELTA CARBON-14. NOAA National Centers for Environmental Information. https://doi.org/10.3334/cdiac/otg.woce_a16n_1993