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Seasonally decoupled dynamics of dissolved organic carbon and fluorescent dissolved organic matter in continental shelf waters

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Abstract. We investigated seasonal variations in dissolved organic carbon (DOC) and humic-like fluorescent dissolved organic matter ($FDOM_H$) in the Yellow Sea and East China Sea to better understand the factors shaping dissolved organic matter (DOM) dynamics in continental shelf waters. Multi-year observations revealed that DOC concentrations increased with Radium based water residence time, whereas $FDOM_H$ showed no corresponding accumulation across seasons. This contrasting behavior was particularly evident during summer, when strong solar radiation may promote preferential degradation of photo-labile $FDOM_H$, while a relatively more photo-resistant DOC remains in shelf waters, indicating a seasonal decoupling between DOC and $FDOM_H$. The persistent increase in DOC with water residence time suggests that a fraction of DOC can accumulate in shelf waters despite ongoing degradation processes. Based on the observed relationship between DOC and water residence time, we estimated a net DOC accumulation flux of 1.1±0.2 Tg C yr^{-1}, comparable in magnitude to annual riverine DOC inputs in this region. Our findings highlight the contrasting dynamics of DOC and $FDOM_H$ and suggest that prolonged water residence and selective DOM transformation may contribute to DOC persistence in continental shelf waters, potentially supporting the export of persistent DOC to the open ocean.

1 Introduction

The marine dissolved organic matter (DOM), mostly composed of dissolved organic carbon (DOC), is known as the largest reservoir of reduced carbon (~662 Pg C) in the Ocean (Hansell et al., 2009). This carbon pool comprises a complex mixture of organic compounds such as proteins, carbohydrates, lignin, and other biomacromolecules (Repeta, 2015). Marine DOM can be classified into labile, semi-labile, and refractory DOC based on its reactivity. Labile and semi-labile fractions are enriched in the surface layer due to biological production (autochthonous) and various external sources (allochthonous). DOC is subsequently transformed and degraded through either microbial or photochemical processes (Hansell, 2013; Miller and Moran, 1997). A large fraction of DOM pool is resistant to rapid microbial degradation and persists as refractory DOC (RDOC) over long timescales. The radiocarbon age of RDOC in the deep ocean is typically estimated to be approximately 4,000 to 6,000

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years, highlighting its long-term persistence in the ocean. Recent studies have shown that the measured ages of DOC depend on the mixture of DOC with a wide range of ages, from modern to 12,000 years, in the ocean (Follett et al., 2014). Therefore, founding the behavior, production, and removal mechanisms of marine DOM is essential for understanding marine environments, climate systems, and the global carbon cycle. However, the mechanisms that control the production and long-term persistence of refractory DOC remain largely unknown.

The optically reactive portion of marine DOM, known as colored DOM (CDOM), protects aquatic organisms by absorbing ultraviolet and visible light in the surface layer (Coble, 2007). A fraction of CDOM that emits fluorescence after absorbing light is referred to as fluorescent DOM (FDOM) (Coble, 2007). CDOM and FDOM have been widely used as powerful tracers for identifying sources, molecular compositions, and transformations of DOM in aquatic environments due to their conservative behavior (Stedmon et al., 2003; Catala et al., 2015; Yamashita and Tanoue, 2008; Helms et al., 2008; Hansen et al., 2016). In general, CDOM and FDOM are derived from allochthonous (terrestrial sources) and autochthonous (biological production) inputs and removed by photochemical and microbial degradation (Carlson and Hansell, 2015). CDOM and FDOM components exhibit relatively conservative behavior during water transport and mixing, making them useful tracers of DOM dynamics,

Continental shelves, which cover only about 7% of the global ocean surface, serve as major reservoirs of organic matter, contributing more than 20% of the ocean's total organic matter production (Barron and Duarte, 2015). The Bohai Sea (BS), Yellow Sea (YS), and East China Sea (ECS) together form one of the largest continental shelf systems in the world, covering approximately 1 million km^2. The BS, located in the northwestern part of the YS, is characterized by relatively low salinity and pronounced seasonal variability in water mass structure, with a residence time of approximately 3–4 years (Chen, 2009). Similarly, the water residence time in the YS can reach up to five years (Nozaki et al., 1991; Kim et al., 2005; Men and Liu, 2015). This shelf system receives substantial inputs of organic matter from the Changjiang River (Wang et al., 2012), and an equivalent amount of DOC is produced within the shelf water column (Han et al., 2022). Radium (Ra) isotopes have been widely used as tracers of water mass transport and residence time in coastal and shelf waters (Moore, 2000; Moore, 2007). In particular, the distribution of Ra isotopes can provide information water exchange and residence time, which are important for understanding the accumulation and transformation of DOM in shelf waters. The combination of substantial terrestrial and in situ organic matter inputs with relatively long water residence times make this extensive shelf system an ideal setting for investigating the sources, transformation, accumulation, and removal of DOC and FDOM in continental shelf waters.

This study aims to investigate the complex seasonal dynamics of DOM in relation to water residence time in the northwestern Pacific marginal seas based on a multi-year dataset covering all four seasons. By examining the relationships among DOC, $FDOM_H$, and Ra-derived water residence time, we evaluate the contrasting accumulation patterns of these DOM components

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in continental shelf waters. We further characterize seasonal variations in DOM optical properties to explore the potential role of photochemical transformation in shaping DOM dynamics.

2 Materials and Methods

2.1 Study site

This study was conducted in the northwestern Pacific marginal seas, including the YS and ECS, during four different seasons (Fig. 1). The continental shelf of the YS and northern ECS has an average depth of 50 m (Wang et al., 2000; Ichikawa and Beardsley, 2002; Chen, 2009). The major water masses in this region include the Bohai Sea Central Water (BSCW), Bohai Sea Coastal Water (BSCoW), Changjiang diluted water (CDW), Kuroshio Current water (KCW), Kuroshio subsurface water (KSSW), and Yellow Sea bottom cold water (YSBCW), with their relative contributions varying seasonally (Ichikawa and Beardsley, 2002; Hur et al., 1999; Chen, 2009; Chang and Isobe, 2003; Wang et al., 2014) (Fig. 2). In this region, the Changjiang River plays a significant role in supplying approximately 80% of the freshwater and delivering large amounts of terrestrial materials to the adjacent seas (Wang et al., 2012; Ichikawa and Beardsley, 2002).

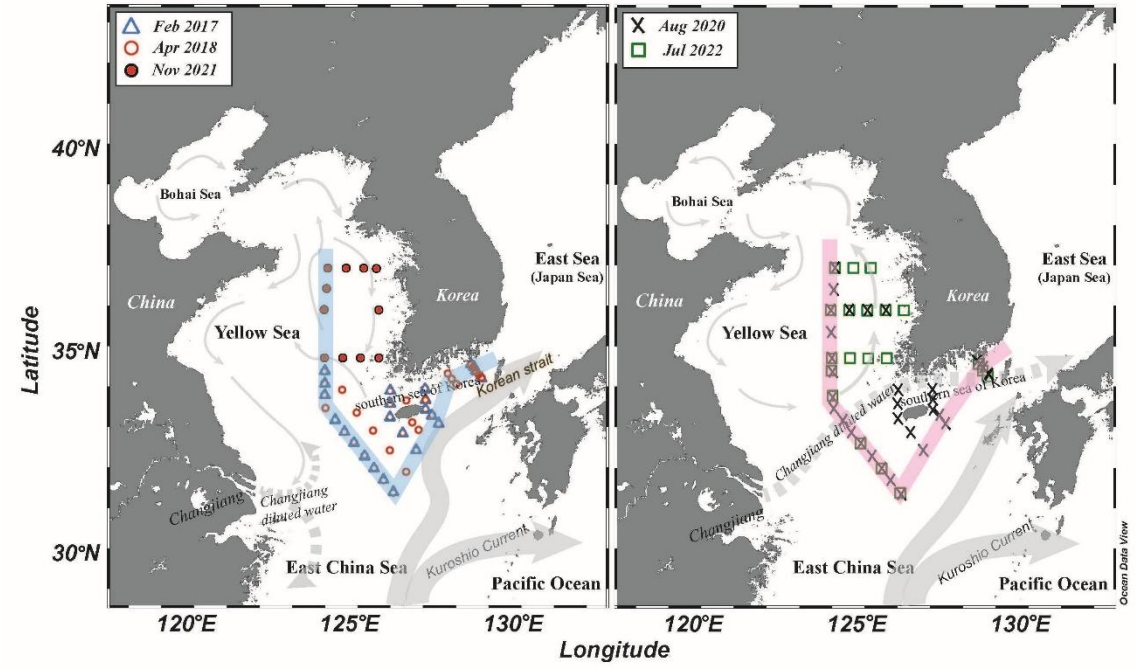


Figure 1: Maps of sampling stations and schematic patterns of the surface current sin the northwestern Pacific marginal seas during the sampling periods. The bold color lines (blue in winter and spring; pink in summer) indicate the transect used in this study.

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In the northern part of the study region, the Bohai Sea (BS) is a semi-enclosed marginal sea that is strongly influenced by freshwater inputs from several large rivers, including the Yellow River, one of the largest and most sediment-dominated rivers in the world (Ren and Shi, 1986). The Bohai Sea waters, including BSCW and BSCoW, are characterized by relatively low salinity (29–30) and high organic matter contents. The water residence time of the BS has been estimated to be approximately 3–4 years (Liu et al., 2012; Luo et al., 2021). The BS water flows southward into the YS, a productive shallow marginal sea, while in the southern part of the ECS, a branch of the Kuroshio Current transports saline, warm, and oligotrophic water into the region (Chen, 2009). Previous studies have estimated that the residence times of the ECS shelf and YS waters to be approximately 2–3 and 5–6 years, respectively, based on the distributions of ^{210}Pb, ^{210}Po, and radium isotope (Nozaki et al., 1991; Kim et al., 2005; Men and Liu, 2015). These hydrographic features provide an important physical framework for understanding the distribution and transformation of DOM in this region.

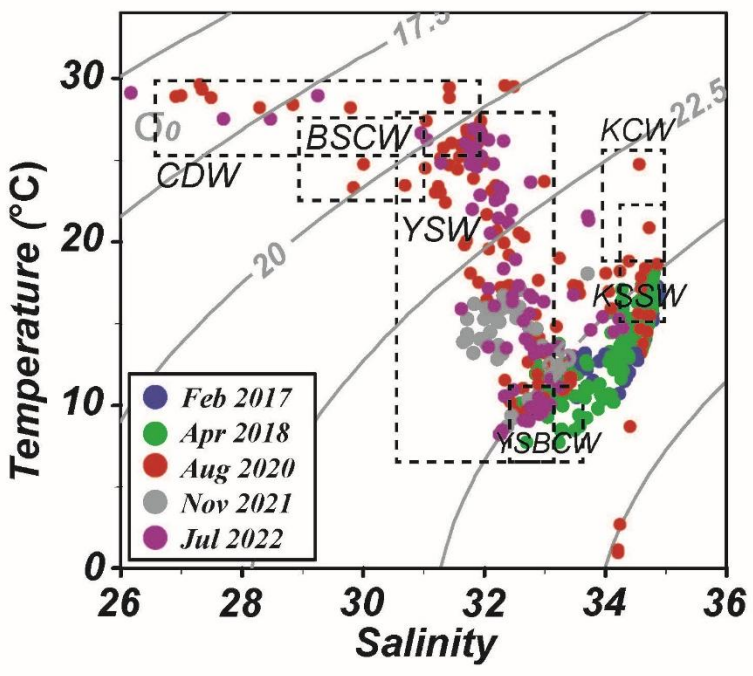


Figure 2: T-S diagram in different sampling periods. Dashed boxes indicate different water masses in this region: Changjiang diluted water (CDW), Kuroshio Current Water (KCW), Kuroshio subsurface water (KSSW), Yellow Sea Water (YSW), Yellow Sea bottom cold water (YSBCW), and Bohai Sea coastal water (BSCW).

The hydrographic characteristics of this region exhibited clear seasonal variations associated with changes in water mass contributions (Hur et al., 1999; Chen, 2009; Han et al., 2023) (Fig. 2). During summer, CDW was mainly distributed in the southwestern part of the study area, while the KCW (salinity >34) was observed in the southernmost region (Fig. 1–2). In

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summer, water masses primarily consisted of the CDW, YSW, and YSBCW, whereas KCW and YSBCW were dominant during colder seasons, including early spring, winter, and fall (Fig. 2). In the central YS, relatively low-salinity waters (30.5–32.5) persisted throughout all seasons (Fig. S1–S5). In winter, the BS is strongly influenced by winter monsoon winds, which drive water toward the Bohai Strait and into the YS (Wu et al., 2025). Overall, the composition and spatial distribution of water masses showed pronounced seasonal variability, providing a dynamic hydrographic framework \for interpreting the observed variations in DOM.

2.2 Sampling

The water samples were collected aboard the *R/V Onnuri* of the Korea Institute of Ocean Science and Technology (KIOST) in July 2022 (summer; n=99) and November 2021 (fall; n=57). Seawater samples were collected using Niskin bottles mounted on a rosette sampler equipped with a CTD (SBE911-plus, Sea-Bird Electronics). The samples were immediately filtered through pre-combusted GF/F glass microfiber filters (500°C for 5 h; 0.7 μm, Whatman) and stored in glass containers. Data from February 2017 (winter; n=125), April 2018 (spring; n=193), and August 2020 (summer; n=161) were obtained from Han et al. (2022; 2023). We included the study by Han et al. (2022) to strengthen our argument regarding seasonal variations.

2.3 Biogeochemical analysis

DOC concentrations were measured using a TOC analyzer (TOC-L, Shimadzu). Prior to analysis, the system blank was minimized until the signal from ultrapure water showed a consistent value at the detection limit (< 1 μM). The instrument was calibrated with a titration curve derived from the analysis of potassium hydrogen phthalate aqueous solutions. To ensure accuracy, a deep-seawater reference material (~46 μM; Hansell Laboratory) was analyzed with every sample batch run (Hansell, 2005). The precision, based on the measurements of the reference material, was within 2% of the DOC concentration.

The absorbance spectra and fluorescence excitation-emission matrices were measured using a spectrofluorometer (Aqualog, HORIBA). The absorbance data were blank-corrected, and a baseline correction was applied at 600 nm, assuming negligible CDOM absorption at that wavelength. The CDOM absorbance at 350 nm was converted into the Napierian absorption coefficient (a_{350}, unit: m^{-1}). Here, a_{350} served as the primary indicator of CDOM quantity (Son et al., 2024). The spectral slope coefficients between 275 and 295 nm ($S_{275–295}$, unit: nm^{-1}) and between 350 and 400 nm ($S_{350–400}$, unit: nm^{-1}) were calculated as the linear regression slopes of the log-transformed absorption data (Helms et al., 2008). The spectral slope ratio (S_R), an indicator of the molecular weight and composition of DOM, was determined as the ratio of the slope at shorter wavelengths ($S_{275–295}$) to that of the longer wavelength ($S_{350–400}$) (Hansen et al., 2016). The specific UV absorbance ($SUVA_{350}$, unit: L mg C^{-1} m^{-1}), an indicator of the aromatic content of DOM, was calculated using the UV absorbance at 350 nm and DOC concentration (Helms et al., 2008).

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The fluorescence analysis was conducted using emission wavelengths scanned from 211.2 to 617.4 nm at 3.2 nm intervals and excitation wavelengths from 240 to 600 nm at 3 nm intervals. All EEM processing and the parallel factor analysis (PARAFAC) model were performed using Solo software (Eigenvector). Blank subtraction, Raman and Rayleigh scattering signals, and the inner-filter effect were corrected. The fluorescence intensities of the samples were normalized daily using the Raman peak area of pure water at 350 nm and reported in Raman Units (R.U.) (Lawaetz and Stedmon, 2009).

The PARAFAC model identified three components. Component 1 (C1; $Max_{ex/em}$ = 355/472 nm) was defined as a terrestrial humic-like component ($FDOM_H$), representing terrestrial organic matter composed of high molecular weight (HMW) organic compounds, commonly identified as peak C. Component 2 (C2; $Max_{ex/em}$ = 280/337 nm) was characterized as a protein-like (tryptophan-like) component ($FDOM_P$), representing amino acid-like DOM associated with freshly produced autochthonous DOM in the surface water, identified as peak T. Component 3 (C3; $Max_{ex/em}$ = 310/400 nm) was classified as a marine humic-like component ($FDOM_{H2}$), produced by microbial remineralization of marine organic matter and identified as peak M (Kowalczuk et al., 2009; Yamashita et al., 2010; Jørgensen et al., 2011). The fluorescence spectra were also compared with the OpenFluor spectral database (Murphy et al., 2014), yielding statistical matches with 48, 44, and 12 previous studies, respectively, at a confidence level of >98%.

For radium isotope measurements, 100 L of water were passed through a column of acrylic fiber impregnated with MnO_2 (Mn-fiber) at a flow rate of <1 L min^{-1} by gravity (Moore, 1976). The Mn-fiber samples were washed with deionized water and ashed in a muffle furnace at 820°C for 16 h. The ashed fiber was transferred to a gamma vial for the measurement of ^{228}Ra and ^{226}Ra using a high-purity germanium well-type detector (CANBERRA). Counts for ^{228}Ra and ^{226}Ra were determined using the ^{228}Ac peak (911 keV) and the ^{214}Pb peak (351.9 keV), respectively. The measurement efficiency of the gamma counter was calculated using standard materials with three different heights.

3 Results

3.1 DOC distribution

The concentration of DOC (47–122 μM) showed significant seasonal and spatial variations, reflecting differences in water mass contributions (Fig. S1–S6). In summer, the highest DOC concentrations were observed in the central YS (avg. 97 ± 12 μM) and in the CDW region (avg. 85 ± 13 μM) (Fig. S3, S5, S6b). In winter and spring, relatively higher DOC concentrations were observed in the YSBCW (avg. 91 ± 8 μM and 83 ± 5 μM, respectively) near the central YS region (Fig. S1, S2, S4, S6b). In fall, relatively higher DOC concentrations were observed in the central YS region (avg. 81 ± 8 μM) (Fig. S5, S7b). In all seasons, relatively high DOC concentrations (>90 μM) were found in the central YS region, and the concentrations gradually decreased toward the Korean Strait (Fig. S1−S5).

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The vertical distributions of DOC showed clear seasonality (Fig. S6b). In summer, the vertical distribution exhibited higher DOC concentrations with a wide range in the surface layer, decreasing with increasing depth. In winter and fall, DOC concentrations were nearly constant at all depths, presumably due to active vertical mixing. DOC concentrations across the entire water column were lowest in winter. In spring, DOC concentrations were intermediate between those in winter and summer.

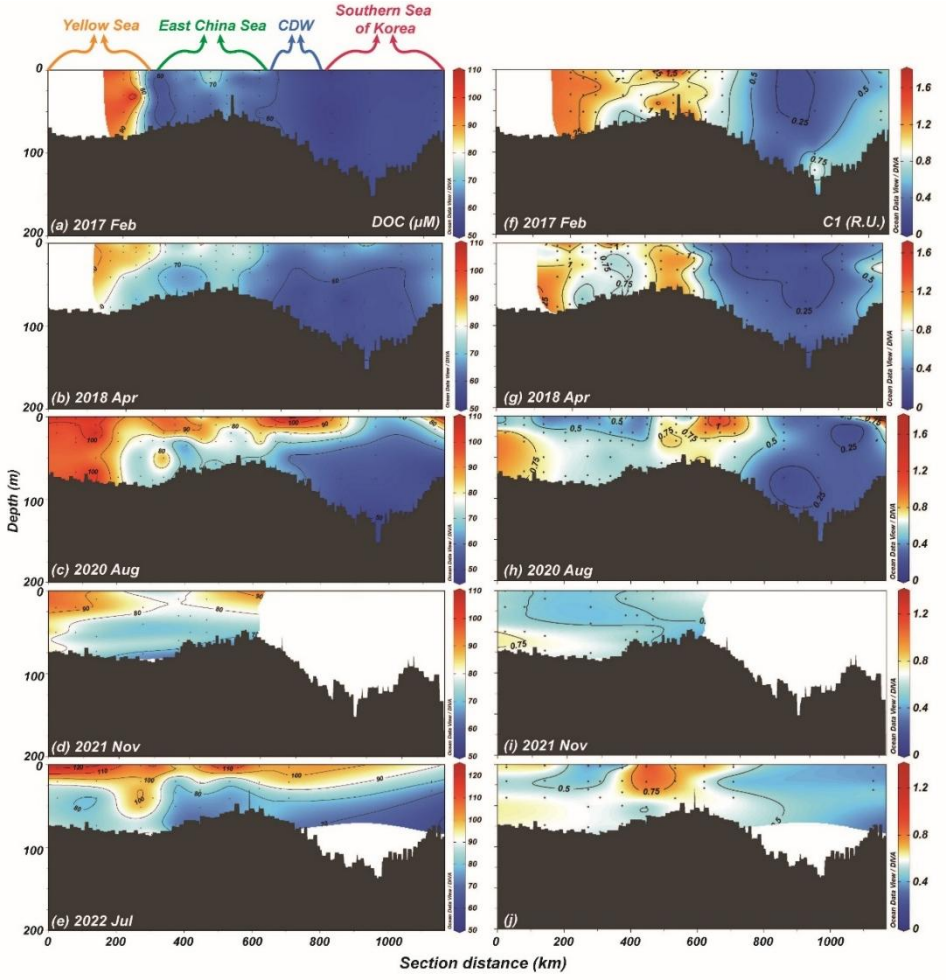


Figure 3: Vertical distributions of (a, b, c, d, e) DOC and (f, g, h, i, j) $FDOM_H$ in different sampling periods along the transect shown in Figure 1. The geographical regions indicated along the upper x-axis correspond to those shown in Figure 1, while CDW was labelled separately to indicate the region influenced by Changjiang Diluted Water.

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3.2 Optical properties of DOM

Similar to the DOC distribution, relatively higher $FDOM_H$ concentrations were found near the central YS region in winter and spring (Fig. S1, S2, S4, S6c). However, higher $FDOM_H$ concentrations were observed in the CDW during summer (Fig. S3, S5, S6c). In contrast to DOC, the vertical distributions showed that the highest average $FDOM_H$ concentration occurred during winter at all depths (avg. 0.73 ± 0.37 R.U.), whereas the lowest average $FDOM_H$ concentration was observed during summer (avg. 0.54 ± 0.18 R.U.) (Fig. S6c).

The $SUVA_{350}$ values, an indicator of aromatic carbon content, showed the highest average values during summer (0.46 ± 0.15 L mg C^{-1} m^{-1}) in low-salinity waters, while the lowest values were observed during winter (0.24 ± 0.25 L mg C^{-1} m^{-1}) (Fig.S1–S5, and Table S1).

The average S_R values, a common index of molecular weight, decreased in the order of winter > spring > fall > summer (Table S1). High S_R values were mostly found in high-salinity waters derived from the KCW, whereas low S_R values were observed near the CDW region (Fig. S1–S6d).

4 Discussion

4.1 Origins of DOM

The seasonal distributions of DOC and $FDOM_H$ differed significantly, indicating distinct DOM sources and/or compositions across seasons in this region (Fig. 3). DOC and $FDOM_H$ concentrations were negatively correlated with salinity in all seasons, and each component exhibited two distinct slopes, suggesting that they originated from two different sources (Fig. 4a–b). All observed DOC concentrations were higher than the conservative mixing line (black dotted line in Fig. 4a) between the Changjiang River endmember (salinity = 0; DOC = 180 μM) (Shi et al., 2016; Zhao and Gao, 2019) and the KCW endmember (salinity = 34.40; DOC = 55 μM; this study), indicating the presence of additional sources besides the riverine input (Fig. 3a). Here, the elevated DOC concentrations (92–109 μM), mainly observed during summer in low-salinity waters (salinity = 26–28), were attributed to active biological production fueled by riverine nutrient inputs in the estuarine mixing zone (Gao et al., 2020; Kim et al., 2020). The higher DOC concentrations (100–122 μM) observed in the central YS region (salinity = 31–33) suggest contributions from shelf-borne DOC, produced in both shelf sediments and the water column during water residence in the YS (Han et al., 2022; Ryu et al., 2026) (Fig. S3, S5).

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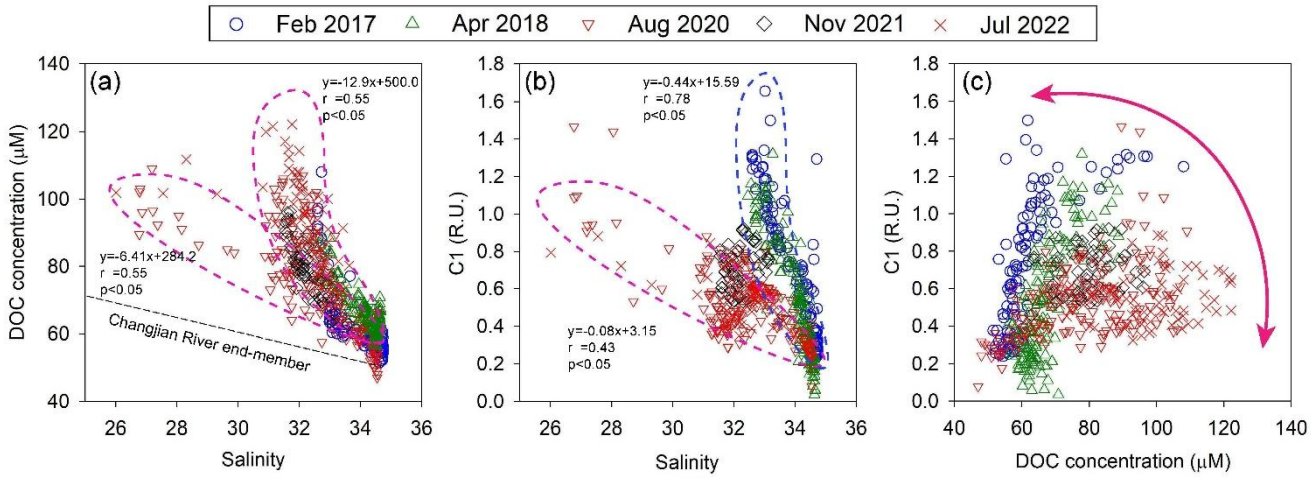


Figure 4: Correlations between the salinity and the concentrations of (a) DOC, (b) C1 ($FDOM_H$), and (c) between the DOC concentrations and C1 component during the sampling periods. The black dotted line in (a) indicates the end-member mixing line between the Changjiang river and the KCW. The pink dotted lines indicate the summer samples, while the blue dotted lines indicate the cold season samples. The pink arrow in (c) illustrates the contrasting patters of DOC and C1, indicating a shift in their relative contributions.

To further constrain the sources and transformations of DOM, we examined the optical properties of $FDOM_H$ and CDOM. Higher $FDOM_H$ (C1) concentrations were observed in winter and spring in relatively high-salinity waters (salinity = 31–33) in the YS, whereas elevated values in low-salinity waters (salinity = 26–28), were mainly observed during summer (Fig. 3b, S1, S2, S4). DOM composition also exhibited clear seasonal patterns, as shown in the a_{350} versus $S_{275–295}$ plot (Fig. 5a). In summer, a wide range of a_{350} value (an indicator of CDOM quantity) combined with low $S_{275–295}$ value (indicative of HMW-DOM) suggests mixing between riverine HMW-DOM and degraded LMW-DOM from the innermost region in BS (Chen et al., 2013; Yang et al., 2020; Zhao et al., 2021). In addition, relatively high S_R values, which increase with solar irradiation, were observed near the YS during summer, indicating the presence of highly photo-exposed DOM (Fig. S3, S5). In contrast, low a_{350} values combined with high $S_{275–295}$ values indicate the predominance of LMW-DOM, likely associated with enhanced contributions from shelf-derived $FDOM_H$ during winter (Helms et al., 2008; Son et al., 2024) (Fig. 4a). These optical signatures support the interpretation that DOM sources change seasonally, reflecting varying contributions from riverine input, in situ production, and bottom sediments. Previous studies have similarly suggested that the Changjiang River is a major source of $FDOM_H$ in summer, whereas bottom sediments dominate as a source in winter (Han et al., 2022; Kim et al., 2018; Bai et al., 2013).

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In addition, this region is highly influenced by BS water, facilitating the exchange of water masses and associated materials. The BS is characterized by relatively high DOC concentrations (avg. 226±75 μM) (Chen et al., 2013) and low CDOM values indicative of low-molecular-weight material (Yang et al., 2020). The transport of BS-derived water may therefore contribute to shaping the distinct DOM characteristics of this region (Ji et al., 2022).

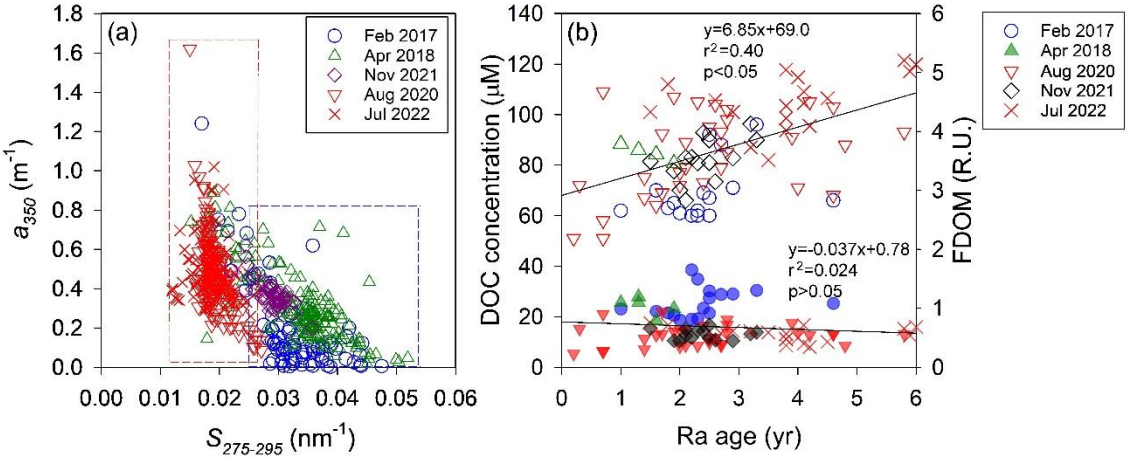


Figure 5: Correlations between the (a) a350 and $S_{275–295}$ and (b) Ra age and DOC concentrations during the sampling periods. Red dotted square in (a) consists of summer samples (Aug 2020 and Jul 2022) and blue dotted square consists of winter, spring, and fall season samples (Feb 2017, Apr 2018, and Nov 2021). Black solid lines indicate the regressions lines in (b). Closed symbols are $FDOM_H$ and opened symbols are DOC samples in (b).

4.2 Decoupled patterns of DOM distribution

The seasonal distributions of DOC and $FDOM_H$ differed markedly, likely due to their distinct behaviors in this shelf environment (Fig. 3a, 3b). In general, DOC and $FDOM_H$ show contrasting vertical profiles with increasing depth in the open ocean, whereas in coastal and marginal regions, DOC and $FDOM_H$ exhibit similar behavior influenced by common source inputs (Yamashita and Tanoue, 2008). In this study, the relationship between $FDOM_H$ and DOC exhibited significant seasonal variations, with a steeper slope observed in winter and a gentler slope in summer (Fig. 3c). Selective additional DOM sources could potentially explain these patterns; however, isotopic and radiocarbon evidence and water mass contributions from previous studies (Bao et al., 2016; Guo et al., 2018; Han et al., 2022; Han et al., 2023; Ryu et al., 2026) suggest that the seasonal decoupling between DOC and $FDOM_H$ observed in summer and winter is unlikely to be attributed to the input of a new DOM source. The stable carbon isotope ($\delta^{13}C$) values of both the water column and bottom sediments in this region consistently indicate a marine origin (–22 to –18‰) (Han et al., 2022; Fu et al., 2022; Chen et al., 2021). While this region is indeed influenced by different water masses seasonally (Hur et al., 1999; Chen, 2009; Han et al., 2023) – with the CDW dominating in summer and the Kuroshio Current in winter – the semi-enclosed nature of the YS results in a relatively long water residence time of approximately five years (Nozaki et al., 1991; Kim et al., 2005; Men and Liu, 2015), along with contributions from BS water from the innermost region (Luo et al., 2021). If water mass influences were the primary driver of this DOM variability,

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the relationships between Ra-derived water mass age and DOC and $FDOM_H$ concentrations would likely exhibit distinct slopes or non-linear patterns, rather than the consistent trends observed in Fig. 5b. Although microbial activity can contribute to the formation of FDOM (Lønborg et al., 2015), microbially derived FDOM is generally more susceptible to photodegradation (Arai et al., 2017) and is therefore likely to be rapidly degraded under intense solar radiation, particularly during summer. Thus, the reduced slope of $FDOM_H$ relative to DOC observed during summer is likely attributable to the preferential removal of $FDOM_H$ through processes such as photodegradation (Hansen et al., 2016; Gao et al., 2020; Arai et al., 2017; Moran et al., 2000) (Fig. 3b). In addition, $FDOM_H$ originating from Bohai Sea Central Water exhibits a gradual decrease in concentration with increasing water residence time, likely reflecting the effects of degradation and mixing processes (Yang et al., 2020). Such intense solar radiation likely inhibits the accumulation of $FDOM_H$ by enhancing photochemical degradation during summer.

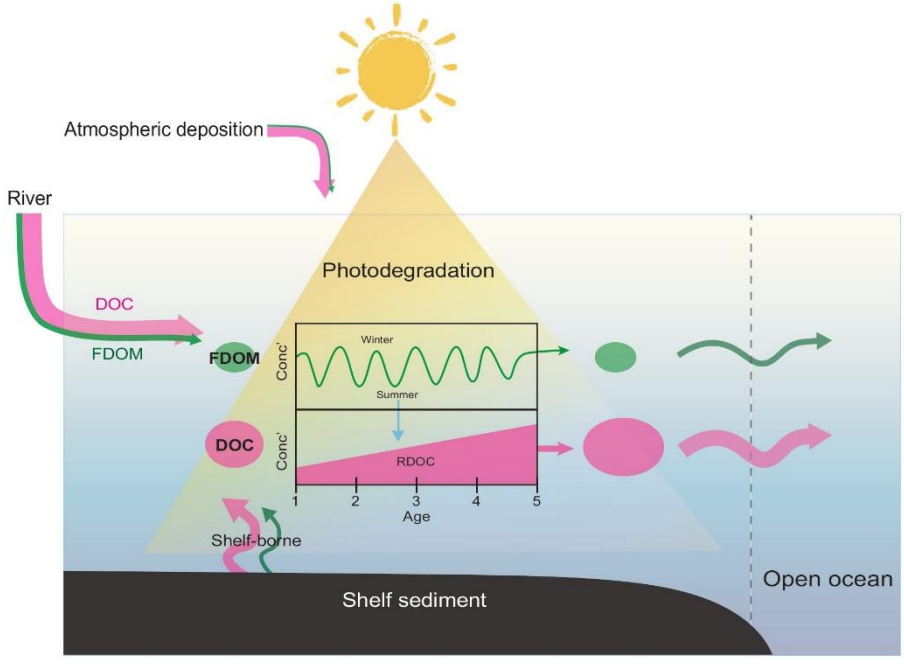


Figure 6: Schematic figure of the photodegradation of FDOM and the accumulation of refractory DOC over water residence time in a continental shelf water.

In contrast, DOC concentrations increased with water residence time in the shelf region (Fig. 4a), showing a significant correlation (Supplementary; r^2=0.5; $p<0.05$) and suggesting DOC accumulation during prolonged water residence in shelf waters (Fig. 6). Our findings demonstrate that within this time scale (~5 years), DOC and FDOM undergo different biogeochemical processes and exhibit different behaviors.

A previous study has shown that photodegradation removes approximately 46% of terrigenous DOC, whereas marine DOC produced through biological activity remains largely unaffected by irradiation (Obernosterer and Benner, 2004). Our results

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are also consistent with those reported in previous laboratory incubation experiments (Moran et al., 2000; Obernosterer and Benner, 2004). Photochemical transformation of terrigenous DOM led to an approximately 7% increase in biodegradable DOC, whereas irradiated marine DOM showed no increase in biodegradable DOC (Lønborg et al., 2015; Arai et al., 2017). Also, previous study has demonstrated the presence of RDOC in shelf waters, highlighting the potential role of shelf regions in the cycling and retention of aged carbon (Ryu et al., 2026). Our findings further suggest that DOC resistant to photochemical degradation may be preferentially retained and accumulated with increasing water residence time in the shelf region.

FDOM has been widely applied as a source tracer for DOC in marine environments. However, in shelf waters, photodegradation may preferentially remove the labile fraction of DOM, while relatively photo-resistant DOC is retained and accumulates with increasing water residence time (Fig. 5). Consequently, $FDOM_H$ may remain relatively constant due to continuous photodegradation, whereas photo-resistant DOC progressively accumulates during shelf-water residence (Nozaki et al., 1991; Kim et al., 2005; Men and Liu, 2015). This photo-resistant fraction may represent a relatively refractory component of DOC that persists in shelf water and is potentially exported to the open ocean.

We further estimated the flux of DOC accumulated in the shelf water using the flowing equation:

$$DOC_{accunulated}\ Flux = \frac{(DOC_{YSW} - DOC_{Ra=0yr}) \times V_{YSW}}{\tau_{YSW}}$$

where DOC_{YSW} is the end-member value (101±11 μM) described in previous study (Han et al., 2022) and $DOC_{Ra=0yr}$ is the DOC end-member value, when Ra-based water mass age is 0, described in Figure 5b (69±7 μM). The flux of DOC accumulated in the shelf water to be approximately 1.1±0.2 Tg C yr^{-1} (Fig. 5b), based on a water residence time (5–6 years) (Fig. 6; Supplementary). This estimate is comparable to the previous reported total DOC export flux for this shelf region (1.9±0.8 Tg C yr^{-1}; Han et al., 2022). Our estimate suggests that approximately 1.1±0.2 Tg C yr^{-1} of this total DOC export may represent DOC accumulated during prolonged residence in shelf waters, potentially reflecting a relatively refractory fraction that persists despite ongoing degradation processes. This accumulated DOC flux is also comparable in magnitude to the annual DOC discharge from the Changjiang River (1.6 Tg C yr^{-1}; Wang et al., 2012), highlighting the importance of internal DOC accumulation in shelf carbon cycling. These results further suggest that previous estimates of FDOM fluxes from shelf sediments (Kim et al., 2018) may not fully capture the overall DOM flux, particularly when the contribution of photoreactive DOM is considered.

5 Conclusion

Our findings underscore the pivotal role of photodegradation in decoupling cycling of DOM in shelf waters. Preferential removal of photo-labile DOM ($FDOM_H$) may promote the relative accumulation and persistence of photo-resistant DOC during prolonged water residence. Given the uncertainties surrounding the production and fate of refractory DOM in the ocean, our

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results provide insights into the potential persistence of relatively refractory DOM in shelf waters and its role in the global carbon cycle. Further laboratory experiments and isotopic analyses are needed to validate the persistence of this DOC fraction and reduce uncertainties in flux estimates.

Code and data availability

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

Supplement link

The supplement related to this article is available on-line.

Author contributions

HH and GK conceptualized the study. HH, H-MC, and HL conducted the field observation, formal analysis, data curation, and investigation. GK and JH supervised the research. HH wrote the original manuscript (original draft and preparation). All authors contributed to review and editing the manuscript.

Competing interests

The authors declare there are no conflicts of interest for this manuscript.

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Review statement

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