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Preliminary study on tracing ^{14}C in groundwater-derived dissolved organic carbon: transport, transformation, and seawater recirculation in Jeju Island, South Korea

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Submarine groundwater discharge (SGD) is a key but understudied pathway in the terrestrial-oceanic dissolved organic carbon (DOC) cycle. In this study, fresh and saline groundwater samples were collected from two sites on Jeju Island, South Korea: Hwasun and Bangdu Bay on the western and eastern coast, respectively. DOC concentrations in fresh groundwater were extremely low (5 $\pm$ 3 μM), with pre-aged radiocarbon values ranging from −469 to −407‰. In the brackish zone of Bangdu Bay, distinctive spectroscopic signals, elevated DOC concentrations, and enriched $\Delta^{14}C$-DOC values along the groundwater-coastal continuum indicate active recirculation of coastal water. Overall, our findings demonstrate that SGD not only delivers aged terrestrial DOC to coastal waters but is also modified by coastal processes, underscoring its potential significant yet complex role under the influence of coastal pollutions.

KEYWORDS

radiocarbon, dissolved organic carbon, submarine groundwater discharge, coastal water, Jeju island, carbon cycle, chromophoric dissolved organic matter, fluorescent dissolved organic matter

1 Introduction

Submarine groundwater discharge (SGD) is an important pathway for the transport of water, organic matter, nutrients, and trace elements to coastal oceans (Burnett et al., 2006; Luijendijk et al., 2020; Zhu et al., 2025). Globally, approximately 44 million km^3 of groundwater is estimated to be stored within the upper ~10 km of the continental crust (Luijendijk et al., 2020; Ferguson et al., 2021). SGD consists of both fresh groundwater and recirculated seawater, and biogeochemical reactions within the subterranean estuary modifying the chemical composition of the discharging water (Santos et al., 2021). Although fresh SGD to the ocean accounts for only ~1% of the annual river discharge (Taniguchi et al., 2019), the total SGD-derived nutrient fluxes can exceed river inputs (Santos et al., 2021). However, most previous investigations do not distinguish between fresh and saline SGD, despite substantial differences in their nutrient sources, residence times, and biogeochemical signatures (Santos et al., 2021). Therefore, differentiating the chemical characteristics of fresh and saline SGD is essential for understanding mixing processes and nutrient transformation within the subterranean estuary.

SGD has also been proposed as a key component of coastal carbon budgets (Moore, 2010), especially as a recent study have highlighted its role in delivering dissolved organic matter (DOM) and CO_2 to diverse coastal ecosystems (Tomer et al., 2025). Due to prolonged anoxic conditions and limited photodegradation, the degradation of DOM in groundwater systems differs from that in marine or riverine systems (Abarike et al., 2024; Moore et al., 2024). Dissolved organic carbon (DOC), which constitute the major fraction of DOM, plays a critical role in this process. McDonough et al. (2022) estimated that up to 13 Tg of photolabile and biolabile DOC is released from the groundwater systems and can be rapidly degraded in the ocean. Additionally, coastal zones are often characterized by high biological productivity driven by heavy nutrient loading (Oh et al., 2023). Overall, the nutrients and DOM supplied via SGD play a significant role in the coastal ocean carbon cycle.

Jeju Island, located off the southern coast of the Korean Peninsula, provides an ideal natural setting for studying SGD (Figure 1). The island hosts ~1000 artesian springs and wells along its coastline, with fresh groundwater supplying about 90% of the island's total water resources. Due to its volcanic geology, Jeju

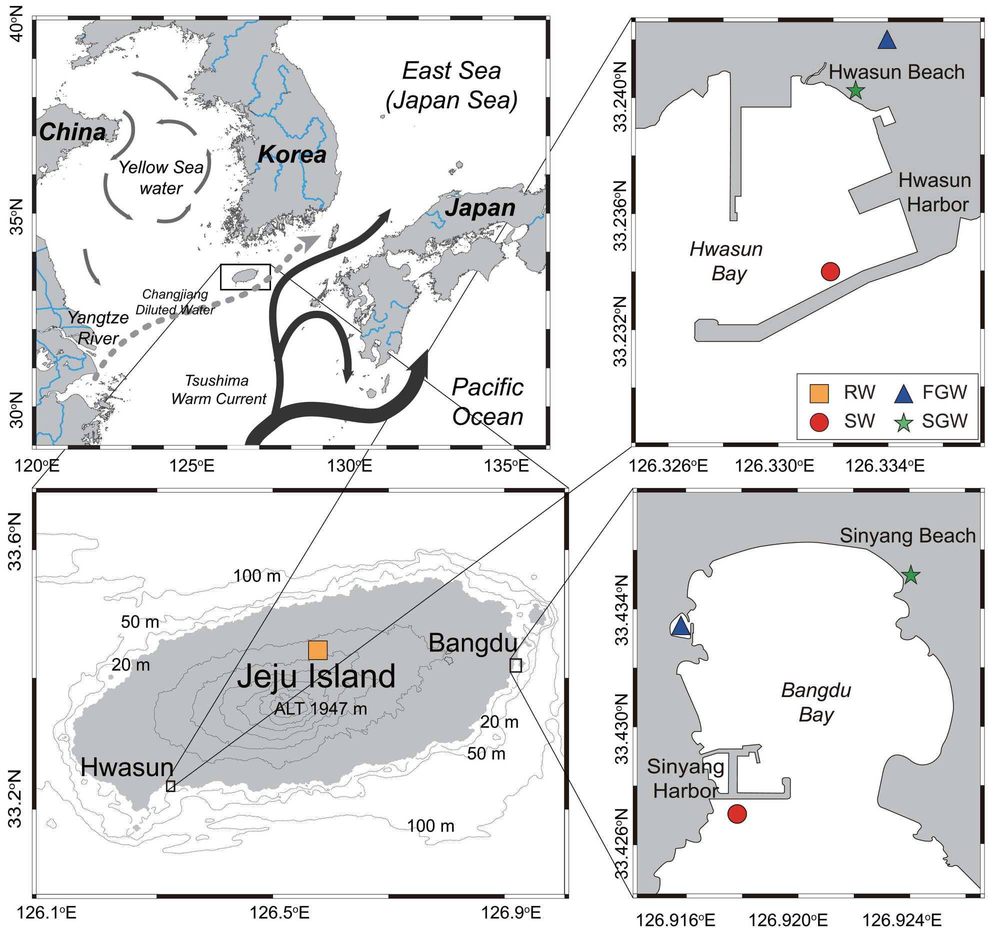

FIGURE 1
(A) Geographic location of Jeju Island. The dash arrow indicates the Changjiang diluted water and solid black arrows indicate the Tsushima Warm Current (modified from Bai et al., 2014). **(B)** Map of Jeju Island with sampling sites indicated. **(C, D)** Enlarged figures of the sampling sites (RW, Rainwater; FGW, Fresh Groundwater; SW, Seawater; and SGW, Saline Groundwater).

Island is characterized by high permeability that facilitating SGD discharge (Kim et al., 2003). Furthermore, Jeju Island has minimal sustained river flow, making SGD a major source of nutrients and DOM to adjacent coastal waters (Hwang et al., 2005; Kim et al., 2011; Kim and Kim, 2017; Kim et al., 2022a). Spatial variability in water optical properties across Jeju Island likely reflect contrasting bedrock and hydrological conditions (Hahn et al., 1997). In the west, coastal groundwater flows directly to the sea through the basal-parabasal zone and is overlain by low-permeability layers (Kwon et al., 2021). In contrast, the east features a more complex aquifer system, where basal groundwater mixes with saline water due to the Seogwipo Formation's low-permeability bedrock being overlain by permeable volcanic rocks, facilitating seawater intrusion (Lee et al., 2023). Therefore, on the eastern coast of Jeju, almost all groundwater discharge is attributed to recirculating seawater, while fresh groundwater contributes about 25% of the total submarine SGD on the western coast of Jeju (Kim et al., 2011).

Understanding the processes and chemical characteristics of DOC in brackish water is thus essential for evaluating the role of SGD in the coastal system. The average DOC concentration in groundwater on Jeju Island (35 ± 13 µM, Song et al., 2018; Kim et al., 2022b) is slightly lower than that in the deep Pacific Ocean (<39 µM, >1000 m water depth; Druffel et al., 1996) and the deep East/Japan Sea (<50 µM, >1000 m water depth; Ryu et al., 2023). Radiocarbon (^{14}C hereafter) in DOM provide valuable insights into the coastal carbon cycle. However, only a limited number of studies have measured ^{14}C in groundwater DOC globally (Wassenaar et al., 1991; Downing and Striegl, 2018; Thomas et al., 2021; McDonough et al., 2022). Most of those studies utilized $\Delta^{14}C$-DOC (where $\Delta^{14}C$ represents the fractionation-corrected $^{14}C/^{12}C$ ratio relative to a standard: Broecker et al., 1959; Stuiver and Polach, 1977) to determine the age of groundwater DOC (Wassenaar et al., 1991). A few studies have reported $\Delta^{14}C$-DOC values in brackish waters, with the results showing significant spatial variation, ranging from an average of −176 ± 102‰ in Korean estuaries (Kang et al., 2024) to 133 ± 74‰ in the York River (Raymond and Bauer, 2001). Notably, Kang et al. (2024) suggested that aged DOC may be exported through groundwater discharge from the Seomjin Estuary in South Korea.

To improve our understanding of submarine groundwater system in Jeju Island, we examined the ^{14}C age and molecular transformation of DOM in the SGD-coastal continuum of Jeju Island. This study presents the first $\Delta^{14}C$-DOC measurements from groundwater on Jeju Island. Here we measured DOC concentration, chromophoric dissolved organic matter (CDOM), fluorescent dissolved organic matter (FDOM), and $\Delta^{14}C$-DOC values in samples of Fresh Groundwater (FGW), Saline Groundwater (SGW) and Seawater (SW) collected from both the western and eastern coast of Jeju Island. The dataset generated in this study contributes to more comprehensive understanding of the role of groundwater in coastal carbon cycling and its potential modification by coastal waters.

2 Materials and methods

2.1 Study site and sample collection

Jeju Island is a dormant volcanic island with an area of ~1830 km^2, located in the southern sea of Korea (Figure 1). The island is primarily composed of permeable basaltic rocks formed by Cenozoic volcanism and includes the Mountain Hallasan shield volcano, which has an elevation of 1950 m. The volcanic bedrock allows rainwater to rapidly penetrate and recharge the groundwater, which is then transported to the coastal region through an aquifer system (Fenta et al., 2020). Jeju Island experiences an East Asian monsoon climate, with most precipitation occurring in the summer (annual rainfall: 1440–1690 mm; Kim et al., 2013).

Details of the sample collection are provided in Kim et al. (2013) and Kim et al. (2022). Briefly, sampling campaigns for FGW, SGW, and SW were conducted in the Hwasun area (southwestern Jeju Island) in April 2023, and in Bangdu Bay (eastern Jeju Island) in September 2023 (Figure 1; Supplementary Table S1). FGW sample from Hwasun area was collected from coastal artesian wells using HDPE bottles, whereas FGW sample from Bangdu Bay was taken directly from a spring outlet located inside the bay. SGW samples were obtained from shallow pits (~50 cm deep) dug into beach sediments. The first two volumes of seeping groundwater were gently discarded using a plastic beaker, and freshly recharged water was collected. A precipitation sample was collected during rainfall in June 2023 from the rooftop of a building at Jeju National University, located near the center region of Jeju Island, approximately 33km from both sampling sites (Figure 1). To minimize the influence of dry deposition, the rainwater sample was taken from the center of the roof, two hours after rainfall began. All samples were collected in Nalgene HDPE bottles pre-cleaned with 10% hydrochloric acid. In total, 7 samples were collected for radiocarbon analysis. Salinity and Oxidation-Reduction Potential (ORP) were measured on-site using a portable YSI Pro Plus sensor (YSI Inc., OH, USA). The measurement accuracies for salinity and ORP were ±0.1 PSU and ± 20 mV, respectively.

2.2 Nutrients analysis

Water samples were vacuum filtered through pre-combusted (550 °C for 4 hours) Whatman GF/F filters (pore size: 0.7 µm; Whatman Inc., NJ, USA) within 1 hour of each sampling campaign. Concentrations of dissolved inorganic nutrients (NO^{3-}, NO^{2-}, NH^{4+}, PO_4^{3-}, and $Si(OH)_4$) were analyzed photometrically using an auto-analyzer (New QuAAtro39, SEAL Analytical, Southampton, UK). Accuracy was verified prior to sample analysis using certified reference materials (Lots CO, CB, and BZ; KANSO Technos Co., Ltd. Japan), and the measured values were consistent with the certified values (within 2%). The detection limits for NO^{3-}, NO^{2-}, NH^{4+}, PO_4^{3-}, and $Si(OH)_4$ were 0.02, 0.04, 0.08, 0.05, and 0.06 µM, respectively.

2.3 DOC and TDN concentrations and Δ^{14}C-DOC analysis

For DOC concentration and radiocarbon analysis, samples were filtered through pre-combusted (500 °C for 5 hours) GF/F filters and transferred to pre-combusted, 1 L Amber Boston Round glass bottles (Fisher Scientific, PA, USA), acidified to pH ~2 using 6 M HCl (Walker et al., 2017) and stored at room temperature. A previous study found no difference in radiocarbon results between acidified and frozen (at −20 °C) samples (Oh et al., 2025). DOC concentrations were determined using high-temperature catalytic oxidation (HTCO) at 680 °C with a total organic carbon analyzer (TOC-L, Shimadzu, Japan) equipped with an ASI-L auto-sampler. Prior to analysis, the system baseline was stabilized with carbon-free distilled water until the signal remained consistently below the detection limit (< 2 µM for DOC and< 3 µM for TDN). Accuracy was verified using deep-sea reference samples (DSR; 41–42 µM for DOC, University of Miami), with results in good agreement with consensus values (within 2%).

For radiocarbon analysis, DOC was converted to CO_2 using high-energy UV oxidization. Each sample was introduced into a quartz reactor, and sparged with high-purity N_2 gas (99.999%) at a steady flow rate for approximately 60 minutes. The samples were then irradiated with UV light (1200 W) for 6 hours. The resulting CO_2 was recovered by continued sparging with N_2 gas, cryogenically purified, quantified by pressure measurement, and sealed in Pyrex tubes. Sample tubes were sent to the Xi'an AMS Center of Institute of Earth Environment, Chinese Academy of Sciences. CO_2 gas samples graphitized offline and radiocarbon measurements were performed on the Mini Carbon Dating System (MICADAS, Ionplus AG) at the Xi'an AMS Center of Institute of Earth Environment, Chinese Academy of Sciences, with a reported precision of 0.2–0.3% and an accuracy of 3–4‰, based on long-term standards (Zhou et al., 2007; Fu et al., 2015). Blanks were determined by oxidizing ultrapure water. To obtain sufficient carbon for blank analysis, three blanks combined for one measurement. All samples were corrected using a process blank (n=9), which contained 11 ± 9 µg C with a Δ^{14}C value of −326 ± 139‰ (n=3). The average difference between the original and blank-corrected Δ^{14}C values was 5 ± 11‰. Notably, the associated uncertainty of fresh groundwater was highly variable due to error propagation (Figure 2A). Conventional ^{14}C age is calculated with the half-life of 5700 years (Godwin, 1962).

A two-endmember ^{14}C mass balance was used to trace the contributions of aged and recently produced DOC, using the following equations:

$$[DOC]_{sample} = [DOC]_{background} + [DOC]_{exce} \quad (1)$$

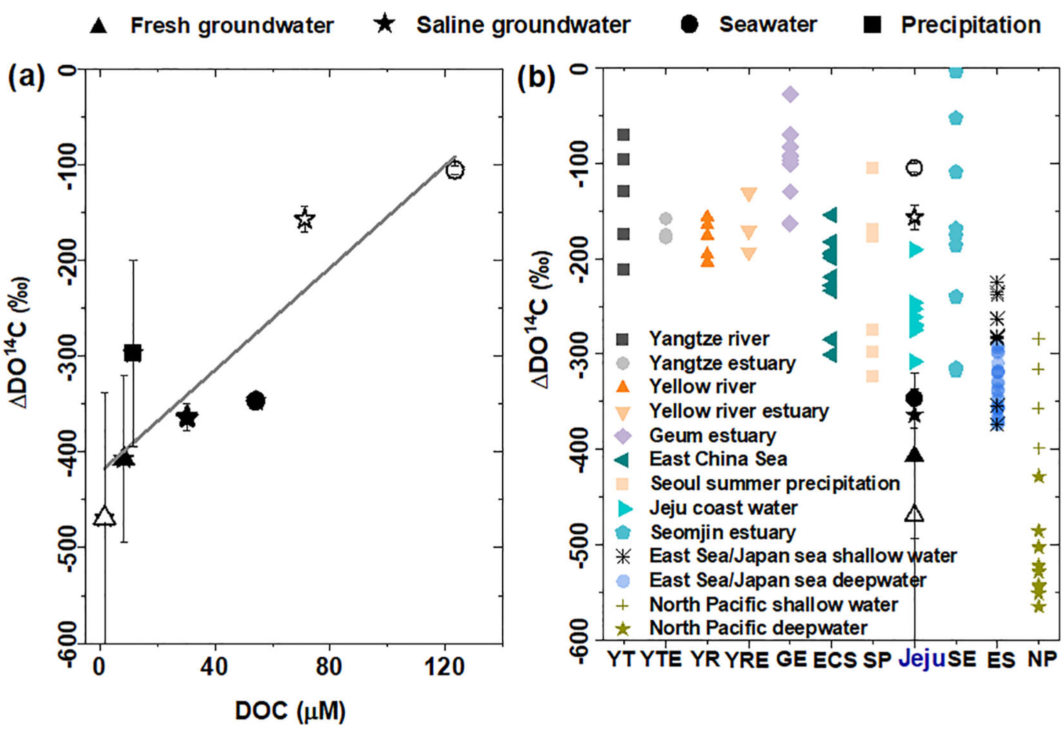

FIGURE 2
(A) Relationship between dissolved organic carbon (DOC) concentration and Δ^{14}C-DOC values. Solid and open symbols represent Hwasun Bay and Bandu Bay, respectively, with the trend line indicating the linear fit. **(B)** Δ^{14}C-DOC values of water from the Yangtze River (YT) and its estuary (YTE, Qi et al., 2020), the Yellow River (YR) and its estuary (YRE, Qi et al., 2020), the Geum Estuary (GE, Kang et al., 2024), the East China Sea (ECS, Han et al., 2022), precipitation in Seoul (SP, Cha et al., 2020), coastal water from Jeju Island (Jeju, Han et al., 2022), the Seomjin Estuary (SE, Kang et al., 2024), the East/Japan Sea (EJS, Ryu et al., 2023), and the North Pacific (Druffel et al., 1996). Error bar is given in gray lines.

$$\Delta^{14}C_{sample} \times [DOC]_{sample}$$
$$= \Delta^{14}C_{background} \times [DOC]_{background} + \Delta^{14}C_{exce} \times [DOC]_{exce} \quad (2)$$

where $[DOC]_{\mathbf{sample}}$, $[DOC]_{\mathbf{background}}$, and $[DOC]_{\mathbf{exce}}$ represent DOC concentrations in sample, the background aged DOC, and added DOC, respectively. $\Delta^{14}C$ values correspond to the radiocarbon measurements for each pool.

2.4 CDOM and FDOM analysis

Samples for CDOM and FDOM analysis were filtered through pre-rinsed polycarbonate filters (Nuclepore™, Whatman Inc., NJ, USA). Absorbance spectra and excitation-emission matrix (EEM) fluorescence were measured on the sampling day using a spectrofluorometer (Aqualog, HORIBA Jobin Yvon, NJ, USA). CDOM absorbance was converted to the Napierian absorption coefficient at 350 nm (a_{350}) following Helms et al. (2008), serves as a proxy for CDOM concentration. Spectral slope coefficients for 250–600 nm ($S_{250-600}$, nm^{-1}), 275–295 nm ($S_{275-295}$), and 350–400 nm ($S_{350-400}$) were derived from the absorption spectra by fitting them to an exponential decay function. The slope ratio (S_R) was calculated as the ratio of the slope in the shorter wavelength region (275–295 nm) to that in the longer wavelength region (350–400 nm). Specific UV absorbance at 254 nm ($SUVA_{254}$, unit: L mg C^{-1} m^{-1}) was determined by normalizing UV absorbance at 254 nm to the DOC concentration.

Fluorescence EEMs were recorded across excitation wavelengths from 250–600 nm with emission at 5 nm intervals. A PARAFAC (PARAllel FACtor) model was applied to four EEM datasets using the Solo+MIA software (Eigenvector Research Inc., WA, USA) and validated through split-half analysis and core consistency diagnostics (Bro and Kiers 2003). The fluorescence index (FI) was calculated as the ratio of emission intensities at 470 nm and 520 nm at an excitation wavelength of 370 nm (Cory and McKnight, 2005). The humification index (HIX) was determined as the ratio of the summed emission intensities from 435–480 nm to the sum of 300–345 nm and 435–480 nm at an excitation of 254 nm (Ohno, 2002). The biological index (BIX) was calculated as the ratio of emission intensities at 380 nm and 430 nm, with an excitation wavelength of 310 nm (Huguet et al., 2009).

3 Results and discussions

3.1 Aged DOC supply coastal water from fresh groundwater

In both the Hwasun and Bangdu areas, the highest DOC concentrations were observed in seawater (54 and 123 µM, respectively), while the lowest were found in fresh groundwater (5 ± 3 µM, n=2; Figure 2A). A linear correlation was found between $\Delta^{14}C$-DOC and DOC concentration (R^2 = 0.79). These results indicate that the DOC concentration and $\Delta^{14}C$ values across the SGD-coastal continuum are influenced by mixing between recently produced DOC in seawater and aged DOC from groundwater (Figure 2A). Corresponding to the low DOC concentrations, the most depleted $\Delta^{14}C$-DOC values (–469 ± 131‰ and –407 ± 87‰) were also observed in fresh groundwater. These values are more depleted than those recorded for the oldest seawater in the Yellow River and East China Sea (Figure 2B). In seawater, $\Delta^{14}C$-DOC ranged from –346 to –105‰ across the two sites, with higher DOC concentrations and $\Delta^{14}C$ values observed in Bandu Bay. A two-endmember ^{14}C mass balance calculation based on Equations 1 and 2 indicates that the added DOC has a modern ^{14}C of ~85‰ (54µM×–346‰+69µM×X =123µM×–105‰, X = 85‰). This estimated value falls within the reported $\Delta^{14}C$-DIC range of 36–132‰ (Ryu et al., 2023), suggesting that the added DOC signal resembles new primary production. This implies that the differences in DOC concentration and $\Delta^{14}C$ values between the sites may be driven by variations in primary production, a conclusion further supported by the observed CDOM distribution pattern (discussed in the following section). Previous studies have also shown that DOC concentrations are higher in summer than spring in Jeju coastal waters due to microbial activity (Song et al., 2023). Recently produced particulate organic matter has been decomposed to DOC during the summer. Therefore, the differences in DOC and $\Delta^{14}C$-DOC values of seawater between the two sites likely reflect seasonal variations. Notably, DOC concentrations in fresh groundwater were generally lower than those in the open ocean, and these values deviated significantly from the regression line of the Keeling plot (Supplementary Figure S1).

In the East/Japan Sea, the lowest $\Delta^{14}C$-DOC value was observed at subsurface depths (–396 ± 31‰; Ryu et al., 2023), whereas in the open ocean, the most depleted values typically occur at greater depths. The subsurface water mass with depleted DOC displayed characteristics of the Tsushima Warm Current (TWC), which originates in the Northwest Pacific (Figure 1). However, the relatively homogeneous $\Delta^{14}C$-DOC signal during photochemical oxidation this region differs from that reported for the North Pacific (Ryu et al., 2023), suggesting the potential contribution of other aged DOC sources.

The $\Delta^{14}C$-DOC values from large rivers, such as the Yellow and Yangtze Rivers show wider variation (–227 to –57‰; Xue et al., 2017; Qi et al., 2020), whereas DOC discharged from major Korean rivers predominantly contains relatively young DOC (–124 to 0.8‰; Lee et al., 2021). During the summer monsoon, slightly more depleted $\Delta^{14}C$-DOC values were observed in precipitation over Seoul, South Korea, ranging from –321 to –106‰ (Cha et al., 2020). Consistent with these findings, our summer precipitation value (–297‰) fell within this range. Overall, the $\Delta^{14}C$-DOC values from riverine and precipitation are higher than those observed in subsurface waters of the East/Japan Sea (Figure 2B), suggesting that groundwater may be a minor but potential source of the depleted DOC.

Despite the remarkably high seepage rate, the overall SGD flux (1.6×10^{10} m^3 yr^{-1}, Kim et al., 2003) is relative low due to its limited spatial extent especially when compared to SGD inputs from the Yellow Sea ($1–6.7\times10^{11}$ m^3 yr^{-1}; Kim et al., 2005) and continental margins of Korea, Russia, and Japan, which have extensive coastlines (Kim et al., 2005; Jung and Yoon, 2025). Accordingly, this rapid groundwater turnover suggests younger DOC (Koh et al., 2005), yet our measurements indicate Jeju exports relatively older, refractory DOC (~6294 to 7431years) compared to surrounding seawater. DOC fluxes are typically estimated based on DOC concentrations and SGD fluxes (Burnett et al., 2006; Webb et al., 2019). The SGD fluxes into Hwasun Bay and Bangdu Bay were estimated to be 8.0×10^8 m^3 yr^{-1} and 5.1×10^7 m^3 yr^{-1}, respectively (Kim et al., 2011). Previous studies indicate that on the eastern coast of Jeju (including Bangdu Bay) all groundwater discharge is attributed to recirculating seawater (Kim et al., 2003, 2011). Using the DOC concentration in saline groundwater of 71 µM, the estimated DOC discharge from Bangdu Bay SGD is approximately of 4.3×10^7 g yr^{-1} (71 µM×5.1×10^7 m^3 yr^{-1}). In contrast, at Hwasun Bay, 25% of SGD is attributed to fresh SGD (Kim et al., 2011). The estimated fresh and saline SGD-derived DOC discharge from Hwasun Bay are $0.5–1.9\times 10^7$ g yr^{-1} and 2.2×10^8 g yr^{-1}, respectively. Although the DOC flux associated with fresh SGD is smaller than that from saline SGD, it may represent an important source of pre-aged DOC to the coastal ocean. Further evidence from Obama Bay on the western coast of Japan also highlight the role of groundwater inflow in supplying DOC to the East/Japan Sea (Cabral et al., 2023). In that region, average DOC concentrations in groundwater (57 ± 13 to 63 ± 61 µM, Cabral et al., 2023) were higher than those at our study sites. If similarly depleted in radiocarbon, this groundwater may represent one of the unknown sources of aged DOC to the subsurface waters of the East/Japan Sea.

3.2 Regional dynamics of brackish water DOM on Jeju Island

Four FDOM components (C1–C4) were identified using the PARAFAC model, based on comparisons with previous studies in the OpenFluor database (Supplementary Figure S2, Supplementary Tables S2, S3; Murphy et al., 2014). Among these, one component was protein-like (C3) and three were humic-like (C1, C2, and C4), as defined by Coble (2007). The optical characteristics of each FDOM component were interpreted based on the location of their fluorescence peaks and literature characterizations (Supplementary Table S2). C1 ($Max_{ex/em}$ = 250/405 nm) and C2 ($Max_{ex/em}$ = 250 (370)/465 nm) were classified as terrestrial humic-like components. A strong correlation between C1 and C2 (R^2 = 0.987) indicates that they are likely to share similar sources and transformation processes. The fluorescence of C3 ($Max_{ex/em}$ = 270/305 nm) aligned with that of the amino acid tyrosine, and corresponds to the B peak (Coble, 2007). The spectral signature of C4 ($Max_{ex/em}$ = 285/350 nm) resembled the marine humic-like of M peak (Coble, 2007).

Analysis of spectral slope and absorption coefficients revealed two distinct subsets based on sampling location (Figure 3). In the Hwasun region, a_{350} values increased from 0.009 m^{-1} to 0.050 m^{-1} due to seawater mixing in the subterranean estuary, while $S_{260-600}$ values decreased (Supplementary Table S2). This suggests the introduction of marine origin CDOM with higher molecular weight organic matter via seawater mixing (Figure 3). FGW from Hwasun exhibited the lowest DOC concentration (8 µM), the highest $S_{260-600}$ value (0.066 nm^{-1}), and the lowest a_{350} value (0.009 m^{-1}) (Figure 3), indicating a reduction in molecular weight likely caused by microbial degradation during aquifer recharge and transit. The depleted Δ^{14}C-DOC values further support potential biodegradation fractionation, aligning with the rapid turnover of the groundwater system on Jeju Island (Koh et al., 2005). Moreover, elevated higher humic-like FDOM and a high HIX (3.22) in FGW from Hwasun Bay suggest that highly decomposed organic matter significantly contributes to the DOC pool. FI values for FGW, SGW, and SW further indicate a dominant input from terrestrial organic matter.

In contrast, absorption parameters in Bangdu Bay were markedly different. The a_{350} values (1.896 ± 0.617 m^{-1}) were substantially higher than those in the Hwasun region (0.029 ± 0.021 m^{-1}), whereas $S_{260-600}$ values were lower (0.013 ± 0.001 nm^{-1}) than in the Hwasun area (0.048 ± 0.016 nm^{-1}). The Bangdu region also exhibited higher BIX (avg: 1.01 ± 0.08) and FI (avg: 1.62 ± 0.19) and lower HIX (avg: 1.89 ± 1.26), indicating greater contribution from recently produced, high molecular weight organic matter. Furthermore, the similarity in $S_{260-600}$ values across FGW, SGW, and SW (0.012–0.014 nm^{-1}) suggests well-mixed conditions within the coastal aquifers of Bangdu Bay.

The findings of this study confirm that, in Jeju Island's coastal aquifers, the characteristics of organic matter in brackish groundwater vary significantly depending on the groundwater properties. The geological features of Bangdu Bay contribute to the presence of brackish groundwater in coastal artesian springs, indicating a strong seawater influence (Figure 4). Additionally, the region's DOC levels may be impacted by algae (e.g., Ulva spp.) that accumulates along the coast of Jeju Island (Kwon et al., 2017). The organic matter from these algae likely enters the aquifer, resulting in similar molecular weights between groundwater and seawater. At Sinyang Beach in Bangdu Bay, where the highest a_{350} value (2.580 m^{-1}) was recorded, the SGW had an ORP of −34.8 mV, suggesting severe organic pollution. Certain areas of Sinyang Beach (Bangdu region) experience seaweed accumulation and significant organic pollution in porewater. Elevated ammonium levels in SGW further suggest anoxic degradation of organic materials and anthropogenic influences (Supplementary Figure S3), such as nearby aquafarms (Samanta et al., 2019), contaminated groundwater inflow (Cho et al., 2019), and reduced circulation due to breakwaters (Choi et al., 2023). This is further supported by the Δ^{14}C-DOC values of coastal seawater. At Hwasun, Δ^{14}C-DOC values in seawater were slightly higher (~18‰) than in saline SGW, whereas at Bangdu, coastal seawater exhibited higher Δ^{14}C-DOC values (~52‰) compared to saline SGW, possibly reflecting the influence of algal blooms (Figure 4).

Seasonal variations in primary production and microbial activity likely account for the observed differences in coastal seawater between the two sites. Fresh SGD shows low DOC concentrations and aged Δ^{14}C-DOC values but lowest a_{350} value in Hwasun Bay, indicating a predominantly terrestrial source. In contrast, saline SGD reflects a strong marine influence, particularly in Bangdu Bay. Nutrient concentrations decrease with increasing

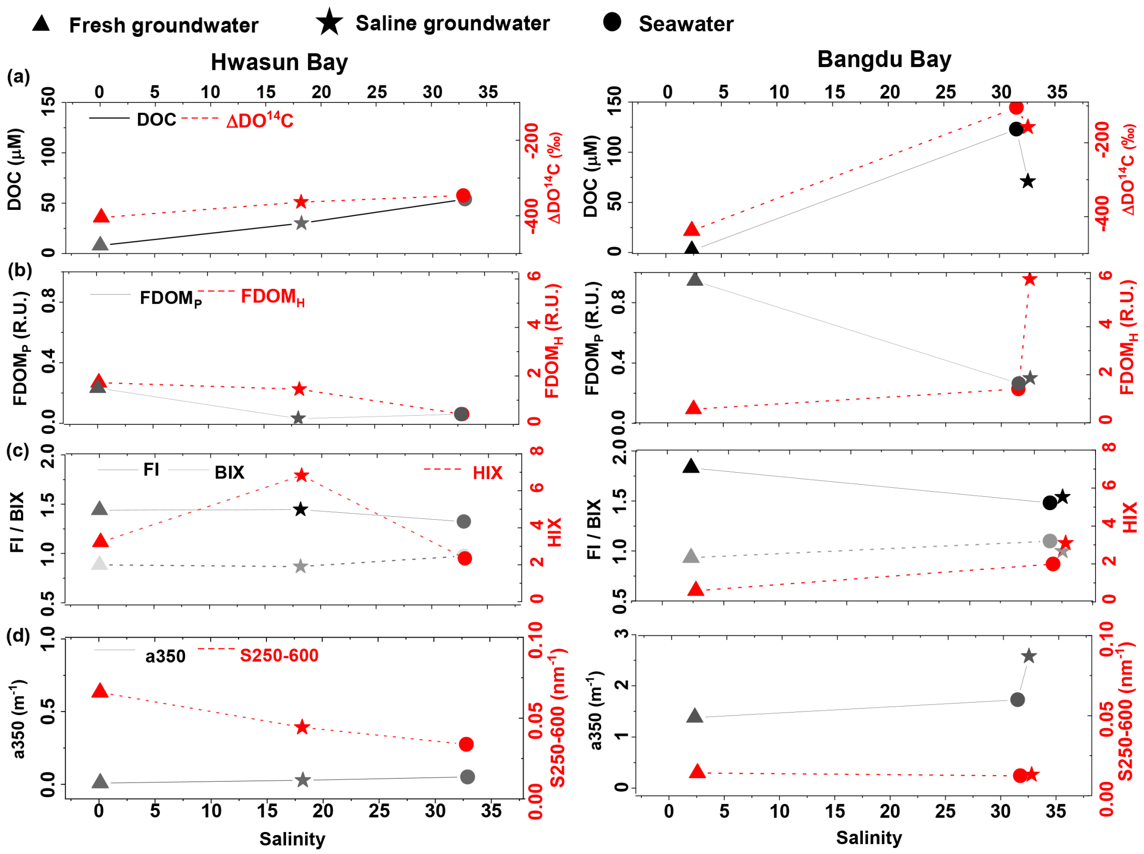

FIGURE 3
Various parameters of water samples from Hwasun Bay and Bangdu Bay, Jeju Island. **(A)** DOC concentrations and Δ^{14}C-DOC values. **(B)** Humic-like fluorescence dissolved organic matter (FDOM) and protein-like FDOM. **(C)** Fluorescence index (FI), biological index (BIX), and humification index (HIX). **(D)** Absorption at 350 nm (a_{350}) and spectral slope ($S_{260-600}$) values.

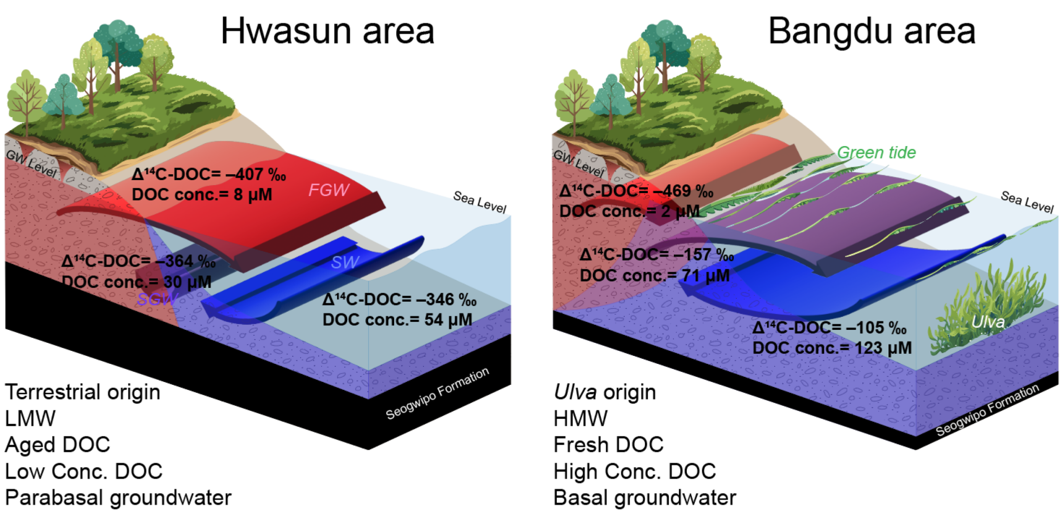

FIGURE 4
A conceptual diagram illustrating the differences between Hwasun Bay and Bangdu Bay areas. In Bangdu Bay, submarine groundwater discharge is significantly influenced by seawater and seaweed blooms.

salinity, whereas DOC concentrations increase (Supplementary Figure S3). The different patterns of nutrients and DOC with salinity likely reflect contrasting biogeochemical process: nutrients primarily result from terrestrial inputs, weathering, and the accumulation of remineralized organic matter, whereas DOC in saline SGD is predominantly of marine origin, especially in Bangdu Bay. The distinct chemical characteristics of brackish waters further highlight the contrasting hydrogeological settings of eastern and western Jeju Island. A larger proportion of recirculated seawater contributed to the SGD on the eastern side of Jeju Island. Due to the highly porous basaltic bedrock and coastal sediments, mixing between fresh groundwater and seawater occurs relatively rapidly. Our results suggest that *in situ* biogeochemical reactions within the subterranean estuary of the Jeju coast are not actively occurring, which likely explains the observed low DOC concentrations. These findings indicate that SGD is not only exports aged DOM and nutrients to the coastal ocean but is also modified by recirculated seawater, particularly along the eastern coast.

4 Conclusion and insights

Previous studies have shown that groundwater discharge plays a crucial role in supplying nutrients and DOM to coastal waters, thereby potentially stimulating biological production. This study demonstrates that groundwater not only serves as a potential source of pre-aged DOC to the adjacent ocean but is also modified by seawater intrusion, particularly in the eastern part of Jeju Island. High concentrations of humic-like FDOM and depleted Δ^{14}C-DOC values in FGW suggest that the discharged DOC is highly degraded and may be preserved as it is transported to the open ocean. In contrast, the Bangdu area, which exhibits highly humic FDOM linked to recently produced DOC, indicates the influence of algal blooms. This seawater recirculation underscores the vulnerability of groundwater system to coastal influence and reinforces the importance of sustained monitoring efforts. However, given the diverse characteristics across Jeju Island, these findings may not fully represent the entire island system. Therefore, more extensive sampling of SGD across different depths and regions is required to better constrain the characteristics and dynamics of groundwater–seawater interactions.

Data availability statement

Data are all available in this paper: Fang, Ling; Kim, Jeonghyun; Kim, Minkyoung (2025), "Aged Dissolved Organic Carbon Supply through Submarine Groundwater Discharge in Jeju Island, South Korea", Mendeley Data, V2, doi: 10.17632/zf7t7cryzv.2.

Author contributions

LF: Data curation, Methodology, Writing – original draft. HK: Data curation, Methodology, Writing – original draft. JK: Data curation, Funding acquisition, Writing – review & editing. PC: Methodology, Writing – review & editing. YR: Software, Writing – original draft. GK: Conceptualization, Writing – review & editing. MK: Conceptualization, Funding acquisition, Writing – review & editing.

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Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fmars.2025.1719001/full#supplementary-material

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