

Geophysical Research Letters[®]

RESEARCH LETTER

10.1029/2025GL120193

Key Points:

- Dissolved organic nitrogen accumulates in summer while phosphorus declines, driving a seasonal shift in surface ocean elemental ratios
- Use of dissolved organic phosphorus supports enhanced summer nitrogen fixation; over half of the new nitrogen enters the dissolved pool
- Stoichiometric flexibility allows dissolved organic matter to buffer nutrient supply, sustaining productivity in the oligotrophic ocean

Supporting Information:

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

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Citation:

Zhang, L., Wen, Z., Hong, H., Kang, S., Jiang, P., Lin, S., et al. (2026). Seasonal shift of dissolved organic matter stoichiometry in the surface North Pacific subtropical gyre: Regulation by enhanced N_2 fixation and DOP utilization. *Geophysical Research Letters*, 53, e2025GL120193. <https://doi.org/10.1029/2025GL120193>

Received 28 OCT 2025

Accepted 12 FEB 2026

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Seasonal Shift of Dissolved Organic Matter Stoichiometry in the Surface North Pacific Subtropical Gyre: Regulation by Enhanced N_2 Fixation and DOP Utilization

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Abstract Dissolved organic matter (DOM) pool acts as both nutrient source and sink in the oligotrophic surface ocean. However, the drivers of seasonal variations in DOM stoichiometry and their relationship to nutrient cycling remain poorly understood. Here, we present a seasonal synthesis of dissolved organic nitrogen (DON) and phosphorus (DOP) distributions across the surface North Pacific Subtropical Gyre (NPSG) with associated biogeochemical measurements. In the central NPSG, summer exhibited elevated DON and depleted DOP, coinciding with a fourfold increase in N_2 -fixation rates compared with winter. This seasonal shift reflects preferential DOP utilization and accumulation of DON via N_2 -fixation. Mass and isotopic balance models confirm that DOP can supply about 40%–100% of summer phosphorus demand while about 50% of fixed nitrogen partitions into DON. These findings demonstrate that seasonal DOM stoichiometric flexibility encode dynamic nutrient cycling, highlighting the fundamental role of DOM transformation in regulating ocean biogeochemical processes.

Plain Language Summary Dissolved organic matter (DOM) in the ocean acts like a vast buffering pool, storing and releasing carbon and nutrients that are vital for the marine surface ecosystem. By studying the surface waters of the North Pacific across seasons, we found that the balance of nitrogen and phosphorus in DOM changes dramatically. In summer, the amount of dissolved organic nitrogen rises while dissolved organic phosphorus drops, shifting the ratio from 19:1 to 25:1. This shift coincides with a fourfold increase in the rate of nitrogen fixation—a process where specialized organisms convert atmospheric nitrogen into a usable form. Our study reveals that summer's intense nitrogen fixation not only drives the preferential consumption of dissolved organic phosphorus but also adds new nitrogen to the DOM pool. These results highlight that the elemental composition of DOM is a sensitive indicator of the dynamic nutrient cycling in the ocean.

1. Introduction

Subtropical oceans, which encompass approximately 26% of the global ocean area, are characterized by persistent stratification and remoteness from terrestrial inputs, resulting in oligotrophic surface waters historically termed marine “biological deserts” (Dai et al., 2023). These regions contribute significantly to global biogeochemical cycles, accounting for ~15% of oceanic CO_2 uptake (Iida et al., 2021) and ~8.2% of global net primary production (Behrenfeld & Falkowski, 1997). Evidence from the ongoing Hawaii Ocean Time-series research program has established dinitrogen fixation (N_2 -fixation) as a major source of new nitrogen in the North Pacific subtropical gyre (NPSG), potentially supplying up to half of the particulate nitrogen (PN) export from the euphotic zone (Dore et al., 2002; Karl et al., 1997). Nevertheless, the drivers behind the pronounced seasonal and stochastic variations in N_2 -fixation rates—particularly the supply of limiting nutrients such as phosphorus and iron—remain poorly constrained. This knowledge gap stems partly from insufficient spatial and temporal sampling coverage within the NPSG (Karl, 1999; Karl et al., 1995; Wen et al., 2022). Consequently, most biogeochemical models and data synthesis studies focus on the annual climatological estimations of N_2 -fixation rates, introducing uncertainties into its contribution to global carbon cycling due to unresolved mechanistic drivers (Shao et al., 2023; Shen & Wang, 2025).

Dissolved organic matter (DOM) is a key component of nutrient cycling in the oligotrophic surface ocean, serving both as a sink for primary production and as a nutrients source through regeneration and direct assimilation

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(Bronk et al., 1994, 2007; Glibert & Bronk, 1994; Jin et al., 2024; Liang et al., 2025). The dissolved organic phosphorus (DOP) pool exhibits dynamic variations on monthly to nearly decadal scales that contributing to export production in regions such as Station ALOHA (Karl et al., 1997). Global distributions of N:P stoichiometry indicate net utilization of DOP in oligotrophic subtropical regions, such as the Western Pacific and North Atlantic gyres, where it may alleviate phosphorus limitation for N₂-fixation (Liang et al., 2023). Inverse biogeochemical modeling further suggests that neglecting direct DOP utilization and preferential remineralization could lead to a 9% underestimation of global N₂-fixation rates, particularly in subtropical gyres (Shen & Wang, 2025). Newly fixed nitrogen enters surface ocean nitrogen cycling, with a variable fraction (3%–90%) partitioning into the dissolved organic pool depending on different methodological approaches and spatiotemporal scales (Bonnet, Berthelot, Turk-Kubo, Cornet-Barthaux, et al., 2016; Bonnet, Berthelot, Turk-Kubo, Fawcett, et al., 2016; Glibert & Bronk, 1994; Hu et al., 2025; Konno et al., 2010; Mulholland & Bernhardt, 2005). Unlike subsurface nutrient supply, which exhibits relatively constrained elemental ratios, N₂-fixation can drive significant variability in DOM stoichiometry through DOP utilization and DON accumulation (Karl et al., 1997). However, few field observations have quantitatively linked temporal variations in N₂-fixation with corresponding shifts in organic matter stoichiometry, leaving this coupling poorly constrained.

Pronounced seasonal N₂-fixation variability is documented at Station ALOHA, peaking in the summer months under elevated water temperature and reduced vertical mixing (Böttjer et al., 2017; Church et al., 2009; Dore et al., 2002). Unicellular diazotrophic cyanobacteria dominate summer assemblages, consistent with the partitioning of fixed nitrogen into smaller (<10 μm) microbial size fractions (Church et al., 2009). However, the nutrient sources sustaining enhanced summer N₂-fixation remain enigmatic. Although mesoscale eddies have been hypothesized to deliver nutrients to surface waters (Church et al., 2009), turbulent mixing processes transport subsurface waters with near-Redfield stoichiometry rather than selectively supplying phosphorus (Karl, 1999). Consequently, phosphorus and iron ultimately become co-limiting during periods of intense N₂-fixation due to disproportionate nitrogen input (Grabowski et al., 2008; Moore et al., 2009; Sohm et al., 2011). Understanding the drivers of seasonal N₂-fixation variability and its coupling with carbon export is essential for constraining biological pump efficiency in subtropical oligotrophic gyres.

In this study, we present the seasonal and spatial distributions of dissolved organic carbon (DOC), DON and DOP coupled with N₂-fixation rates within the NPSG region through two basin-scale sampling campaigns. The utilization of DOP to sustain N₂-fixation was estimated based on the seasonal drawdown of DOP concentrations relative to the increase in N₂-fixation rates. By combining DON concentration measurements with δ¹⁵N-DON analysis, we quantified the fraction of diazotroph-derived nitrogen released into the DON pool. Our findings support a mechanistic link between the stoichiometric shift in DOM and the seasonal variation in N₂-fixation, underscoring the fundamental role of DOM dynamics in ocean nutrient cycling.

2. Materials and Methods

2.1. Site Location and Sampling

As shown in Figure 1, sampling was conducted during two research cruises on board R/V Tan Kah Kee in the NPSG region (KK2003: 3 July–23 August 2020 and KK2007: 23 December 2020–7 February 2021). Surface seawater (5 m depth) was continuously collected using an underway sampling system. Continuous seawater temperature and salinity measurements were acquired using a shipboard Sea-Bird SBE21 thermosalinograph integrated with the underway sampling system. DOC samples were collected in pre-combusted (450°C, 5 hr) amber glass bottles and stored at –20°C. Samples for DON and DOP were collected in pre-acid-washed HDPE bottles and stored at –20°C. Samples for nutrients and Chlorophyll analysis, and N₂-fixation experiments were collected in parallel (Yu et al., 2024).

2.2. DOC Measurements

Following thawing at room temperature (20°C), samples were acidified with 40 μL of 85% H₃PO₄ to a pH of 2. DOC concentrations were determined using a Shimadzu TOC-VCPH analyzer (Li et al., 2018). Calibration employed potassium hydrogen phthalate standards. Quality assurance included analytical blanks (Milli-Q water) every 8 samples and Deep Seawater Reference (DSR: 43.4 ± 1.0 μmol L⁻¹) as consensus reference materials (Hansell Laboratory, University of Miami).

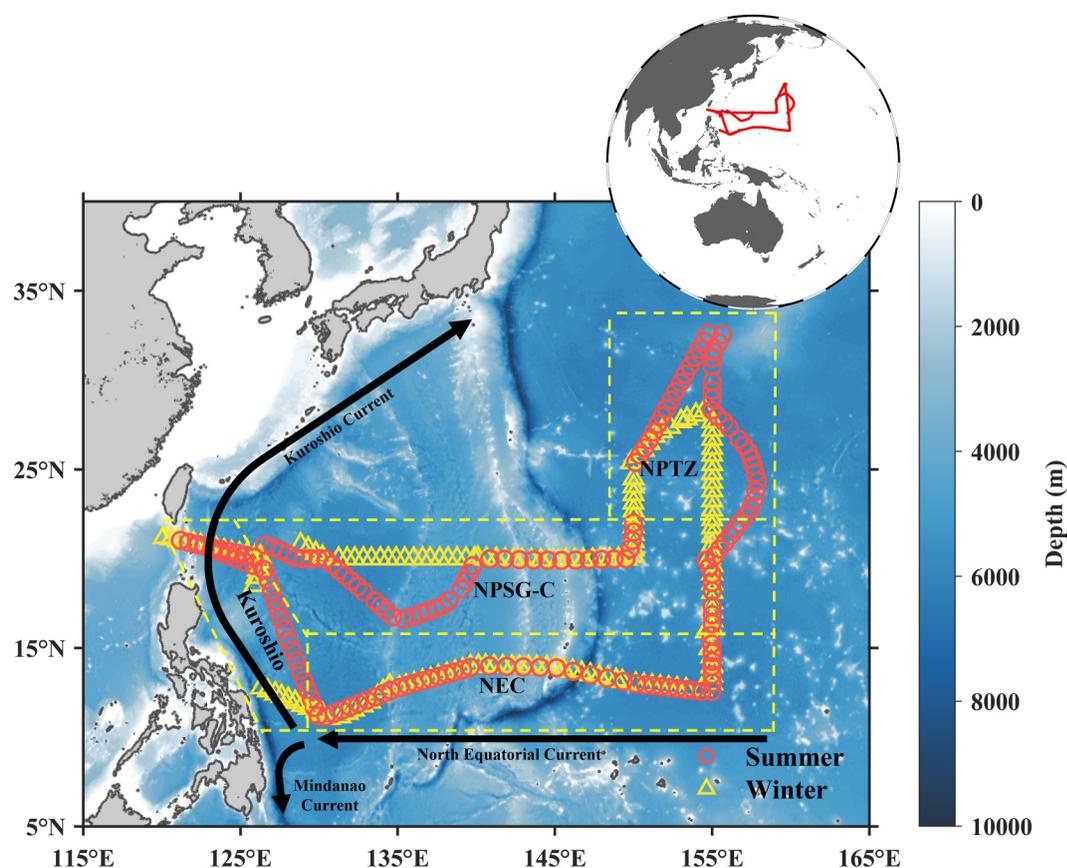


Figure 1. Distribution of surface seawater sampling stations in the North Pacific Subtropical Gyre (NPSG). Red circles denote summer (July–August 2020) sampling locations ($n = 181$); yellow triangles denote winter (December 2020 to February 2021) sampling sites ($n = 167$). The study area was divided into four regions separated by dashed lines based on geographic location and potentially influencing water masses: the Kuroshio Current impacted region (Kuroshio), the North Equatorial Current impacted region (NEC), the North Pacific Transition Zone, and the central region of NPSG (NPSG-C). Black arrows represent surface current directions.

2.3. DON, $\delta^{15}\text{N}$ -DON, and DOP Measurements

DON and DOP concentrations were determined following modified ultraviolet photo-oxidation method (Foreman et al., 2019). Briefly, 20 mL aliquots were transferred to pre-combusted (450°C, 5 hr) quartz vials. For total dissolved nitrogen (TDN) determination, 50 μL of 30% H_2O_2 was added followed by 8-hr oxidation. For total dissolved phosphorus (TDP) determination, an extra of 9 μL of 5 mol L^{-1} H_2SO_4 was added prior to 4-hr oxidation process. Oxidized samples were transferred to acid-washed 15 mL polypropylene centrifuge tubes and stored at -20°C . TDN and TDP were measured using a four-channel continuous flow autoanalyzer (Technicon AA3, Bran-Luebbe GmbH), with detection limits of 0.1 $\mu\text{mol L}^{-1}$ for TDN and 0.08 $\mu\text{mol L}^{-1}$ for TDP. DON and DOP concentrations were calculated by subtracting dissolved inorganic nitrogen (DIN, nitrate and nitrite) from TDN, and dissolved inorganic phosphorus (DIP, also typically reported as soluble reactive phosphorus, SRP) from TDP, respectively. The DIN and DIP concentrations were analyzed by the nanomolar analytical methods, and the achieved detection limits were 5.2 nmol L^{-1} for DIN and 2.5 nmol L^{-1} for DIP (Yuan et al., 2023).

In the oligotrophic surface ocean, $\delta^{15}\text{N}$ of DON approximates $\delta^{15}\text{N}$ of TDN due to negligible DIN concentrations ($\leq 0.02 \mu\text{mol L}^{-1}$). Neglecting the DIN term introduced propagated errors of $\leq 0.03\text{‰}$ in $\delta^{15}\text{N}$ measurements. Isotopic analyses employed the bacterial denitrifier method coupled to a GasBench II interface and isotope ratio mass spectrometer (Delta V Advantage, Thermo Scientific) (Sigman et al., 2001). International isotopic standards were used for calibration (USGS34, $\delta^{15}\text{N} = -1.80\text{‰}$, IAEA3, $\delta^{15}\text{N} = 4.70\text{‰}$, and an in-house standard,

$\delta^{15}\text{N} = 13.8\text{‰}$). Analytical accuracy was better than $\pm 0.3\text{‰}$ for 20 nmol N injections, determined through repeated standard measurements.

2.4. N_2 -Fixation Rate Measurements

N_2 -fixation rates were determined using the modified $^{15}\text{N}_2$ gas dissolution method (Mohr et al., 2010; White et al., 2020). Surface seawater was first degassed using a membrane contactor (Sterapore, Mitsubishi Rayon). $^{15}\text{N}_2$ gas (98.9 atom%, Cambridge Isotope Laboratories) was dissolved in degassed seawater to prepare $^{15}\text{N}_2$ -enriched seawater (Shiozaki et al., 2015). For incubations, 100 mL of $^{15}\text{N}_2$ -enriched seawater was added to 4.5 L polycarbonate bottles containing sample seawater. Triplicate bottles were incubated on-deck for 24 hr under natural sun light with in situ temperature maintained by continuous flow-through surface seawater. Particulate matter was collected onto pre-combusted GF/F filters (450°C, 4 hr) before and after incubation. Filters were analyzed for PN content and $^{15}\text{N}/^{14}\text{N}$ ratios using an elemental analyzer coupled to an isotope ratio mass spectrometry (EA-IRMS). N_2 -fixation rate was calculated following Montoya et al. (1996). The detection limit was $0.173 \pm 0.047 \text{ nmol N L}^{-1} \text{ d}^{-1}$. Detail information about calculated N_2 -fixation rates are archived in Yu et al. (2024).

3. Results

3.1. Seasonal Hydrographic and Biochemical Distributions

Sampling stations spanned the western sector of the NPSG, encompassing gyre boundaries including the Kuroshio Current, North Equatorial Current (NEC), and North Pacific Transition Zone (NPTZ) as well as the central gyre region (NPSG-C, Figure 1, Table S1 in Supporting Information S1). Surface waters exhibited distinct thermal regimes, with significantly higher temperatures ($p < 0.0001$, Text S1 in Supporting Information S1) in the NPSG-C, Kuroshio, and NEC regions (summer: $30.1 \pm 0.4^\circ\text{C}$; winter: $27.7 \pm 1.1^\circ\text{C}$) compared to the NPTZ (summer: $29.1 \pm 0.4^\circ\text{C}$; winter: $25.4 \pm 1.4^\circ\text{C}$), where intensified vertical mixing entrains subsurface water (Figure S1 in Supporting Information S1). Seasonal warming during summer cruises averaged $\Delta T = 2.6^\circ\text{C}$ relative to winter across all regions. Salinity distributions showed maximal values in the central NPSG-C (34.80 ± 0.20) and NPTZ (34.98 ± 0.22), in contrast to the lower salinity in the NEC (34.24 ± 0.21) and Kuroshio (34.37 ± 0.30) boundary regions during both seasons (Figure S1 in Supporting Information S1).

Persistent stratification maintained low DIN concentrations in the NPSG-C (summer: $5.9 \pm 3.1 \text{ nmol L}^{-1}$, winter: $7.1 \pm 2.6 \text{ nmol L}^{-1}$) comparing to the gyre boundaries during both seasons (Figure S1, Table S2 in Supporting Information S1). In the NPSG-C, 37% (summer) and 67% (winter) of DIN measurements were below the detection limit (5.2 nmol L^{-1}) (Figure S1, Table S2 in Supporting Information S1). Distributions DIP concentrations exhibited analogous spatial patterns with lower values in the NPSG-C (summer: $23.8 \pm 13.0 \text{ nmol L}^{-1}$, winter: $22.3 \pm 15.3 \text{ nmol L}^{-1}$) (Figure S1, Table S2 in Supporting Information S1). Chlorophyll-a concentrations displayed no consistent spatial gradient but were significantly higher in winter ($0.11 \pm 0.06 \mu\text{g L}^{-1}$) than in summer ($0.07 \pm 0.02 \mu\text{g L}^{-1}$; $p < 0.001$) across all regions. N_2 -fixation rates exhibited strong regional and seasonal variations (Yu et al., 2024). During summer, significant higher rates occurred in the Kuroshio ($5.81 \pm 5.47 \text{ nmol N L}^{-1} \text{ d}^{-1}$) and NPSG-C ($4.99 \pm 3.01 \text{ nmol N L}^{-1} \text{ d}^{-1}$), exceeding values in the NEC ($1.34 \pm 1.30 \text{ nmol N L}^{-1} \text{ d}^{-1}$) and NPTZ ($2.10 \pm 3.58 \text{ nmol N L}^{-1} \text{ d}^{-1}$) values. During winter, the Kuroshio region maintained relatively elevated rates ($2.39 \pm 2.05 \text{ nmol N L}^{-1} \text{ d}^{-1}$), whereas the NPSG-C, NPTZ, and NEC showed lower values (0.98 ± 1.11 , 1.35 ± 1.73 , and $1.12 \pm 1.70 \text{ nmol N L}^{-1} \text{ d}^{-1}$, respectively). Basin-wide, summer N_2 -fixation rates ($3.58 \pm 3.42 \text{ nmol N L}^{-1} \text{ d}^{-1}$) significantly exceeded winter rates ($1.33 \pm 1.64 \text{ nmol N L}^{-1} \text{ d}^{-1}$; $p < 0.001$), with the most pronounced seasonal contrast in the NPSG-C where summer rates were more than four times higher than winter rates (4.99 ± 3.01 vs. $1.17 \pm 1.11 \text{ nmol N L}^{-1} \text{ d}^{-1}$; Figure 2, Table S2 in Supporting Information S1). The relatively lower N_2 fixation rates observed in the western NPSG compared to those around the Hawaiian Islands may be attributed to a combination of factors: a deeper pycnocline, differing iron supply regimes, and a lower sampling frequency in the open gyre versus the more intensively sampled island region (Boyle et al., 2005; Dai et al., 2023; Hashihama et al., 2020).

3.2. Seasonal DOC, DON, and DOP Distributions

Elevated concentrations of DOC, DON, and DOP were observed in the NPSG-C compared to the NPTZ and NEC regions during both seasons (Figure 2, Table S2 in Supporting Information S1). DOC concentrations showed no

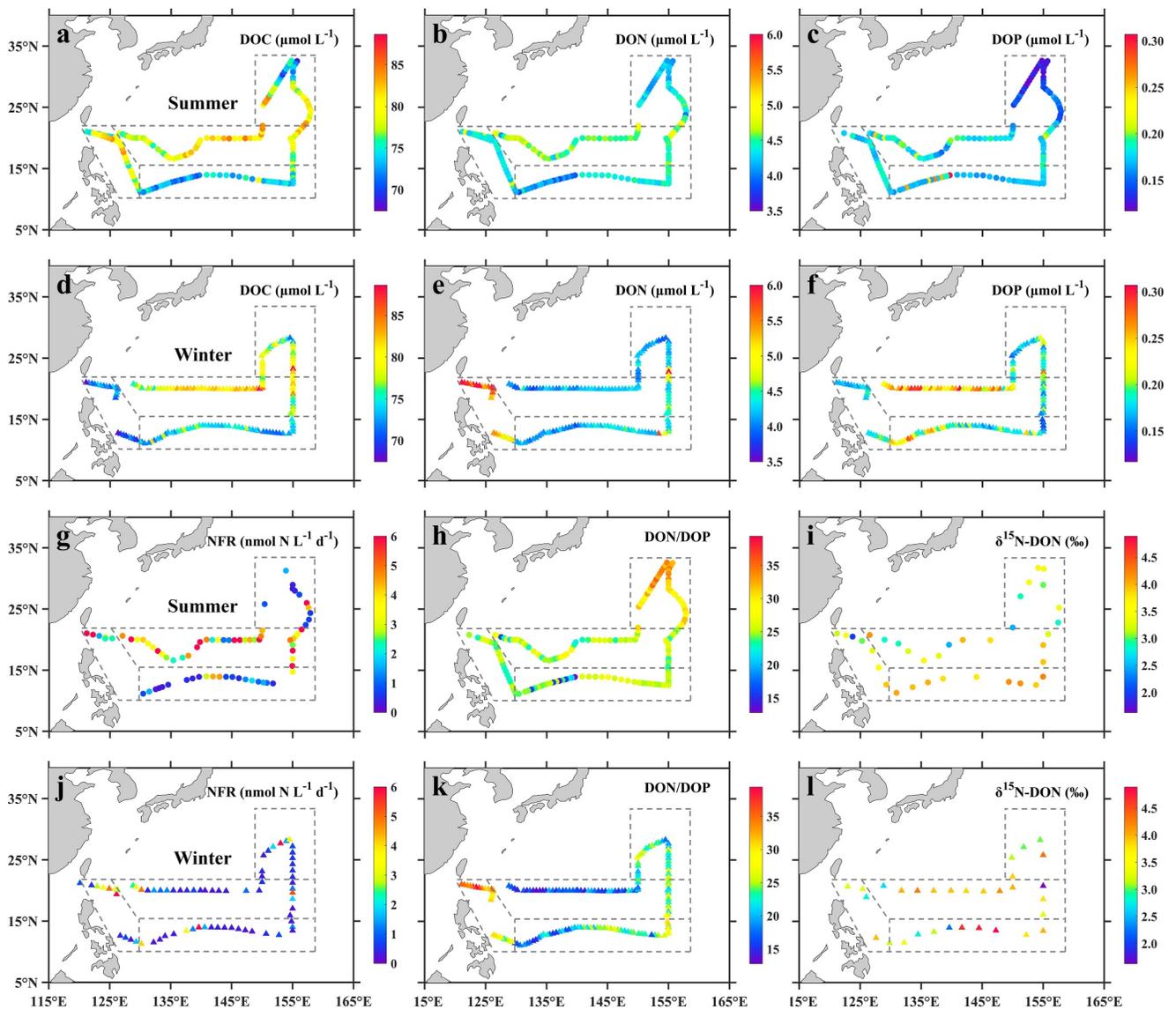


Figure 2. Spatial distributions of dissolved organic matter (DOM) parameters in the North Pacific Subtropical Gyre during summer (upper panels) and winter (lower panels) cruises: (a, d) dissolved organic carbon (DOC, $\mu\text{mol L}^{-1}$), (b, e) dissolved organic nitrogen (DON, $\mu\text{mol L}^{-1}$), (c, f) dissolved organic phosphorus (DOP, $\mu\text{mol L}^{-1}$), (g, j) N_2 -fixation rate (NFR, $\text{nmol N L}^{-1} \text{d}^{-1}$), (h, k) DOM N:P stoichiometry (molar ratio) and (i, l) $\delta^{15}\text{N-DON}$. Symbols represent individual measurements: circles denote summer sampling (July–August 2020); triangles denote winter sampling (December 2020–February 2021). Gray dashed lines indicate subregion boundaries. NFR data from Yu et al. (2023).

significant seasonal differences in NPSG-C (summer: $79.7 \pm 2.5 \mu\text{mol L}^{-1}$; winter: $80.2 \pm 2.8 \mu\text{mol L}^{-1}$), NPTZ ($77.3 \pm 4.1 \mu\text{mol L}^{-1}$; $78.3 \pm 3.1 \mu\text{mol L}^{-1}$), or NEC ($73.7 \pm 2.0 \mu\text{mol L}^{-1}$; $74.0 \pm 2.0 \mu\text{mol L}^{-1}$) ($p > 0.05$). However, the Kuroshio exhibited significantly higher summer DOC ($78.3 \pm 3.3 \mu\text{mol L}^{-1}$) than winter ($71.4 \pm 1.9 \mu\text{mol L}^{-1}$; $p < 0.001$). Pronounced seasonal shifts of DON and DOP occurred in NPSG-C: DON accumulated in summer ($4.59 \pm 0.19 \mu\text{mol L}^{-1}$) relative to winter ($4.23 \pm 0.23 \mu\text{mol L}^{-1}$; $p < 0.001$), while DOP showed opposite trend, with higher concentrations in winter ($0.23 \pm 0.04 \mu\text{mol L}^{-1}$) than in summer ($0.18 \pm 0.02 \mu\text{mol L}^{-1}$; $p < 0.001$). Kuroshio region displayed contrasting DON seasonality, with higher concentrations in winter ($4.23 \pm 0.23 \mu\text{mol L}^{-1}$) than in summer ($3.91 \pm 0.18 \mu\text{mol L}^{-1}$; $p < 0.001$).

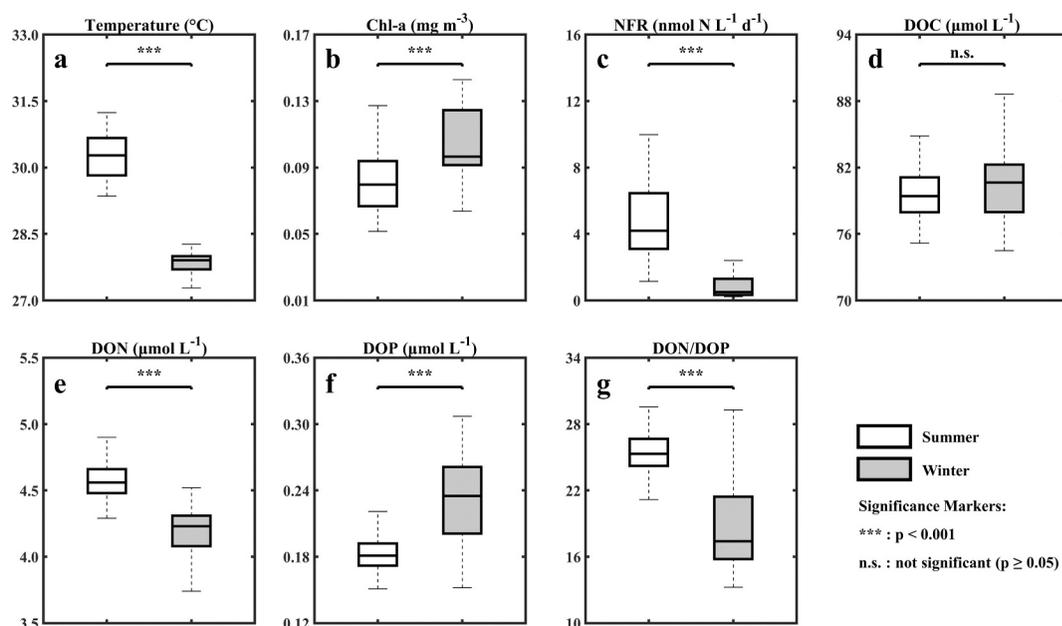


Figure 3. Seasonal comparison of biogeochemical parameters in the central North Pacific Subtropical Gyre (NPSG-C) presented as box-and-whisker plots: (a) sea surface temperature ($^{\circ}\text{C}$), (b) chlorophyll a concentration (mg m^{-3}), (c) N_2 -fixation rates (NFR, $\text{nmol N L}^{-1} \text{d}^{-1}$), (d) dissolved organic carbon (DOC, $\mu\text{mol L}^{-1}$), (e) dissolved organic nitrogen (DON, $\mu\text{mol L}^{-1}$), (f) dissolved organic phosphorus (DOP, $\mu\text{mol L}^{-1}$), and (g) Dissolved organic matter N:P ratio (molar). The boxes are demarcated by the 25th and 75th percentiles, with an internal line representing the median. The whiskers extend to 1.5 times the interquartile range.

4. Discussion

4.1. Comparison of Current Ultraviolet Photo-Oxidation (UV-PhOx) Method With Previous Measurements

This study utilized a newly developed UV-PhOx method with inline colorimetric analyses for the determination of TDN with nitrate and nitrite and TDP with DIP (Foreman et al., 2019). The VelaCure12 UV light system demonstrated consistent performance over 2,600 hr of operation, with irradiation stability monitored across UV-A bandwidths by a calibrated radiometer (Figure S2 in Supporting Information S1). Oxidation durations were optimized to 8 hr for TDN and 4 hr for TDP based on irradiation time-series experiments conducted with surface seawater from the South China Sea (SCS; Figure S3 in Supporting Information S1). Full-depth profiles of DON and DOP from the SCS (Figure S4 in Supporting Information S1) confirmed that the UV-PhOx method offers improved analytical reproducibility and marginally higher recovery of TDN and TDP compared to conventional high-temperature combustion and wet persulfate oxidation (PS-ox) methods, respectively, agreeing with previous report (Forman et al., 2019). A key advantage of this method is its minimal chemical addition, which reduces contamination and providing a cleaner background for subsequent isotopic analysis of DON. Our DOM distributions were compared with existing data sets from the north Pacific: the DOM Data Compilation (Hansell et al., 2021) for DOC and DON, and DOP data from Knapp et al. (2023). The results not only fill key spatial and seasonal gaps in the western NPSG but also show strong agreement at comparable latitudes (Figure S5 in Supporting Information S1).

4.2. Seasonal Enhancement of N_2 -Fixation Supported by the Preferential Utilization of DOP

In the central North Pacific Subtropical Gyre (NPSG-C; see Figure 1), significantly lower chlorophyll-a concentrations were observed during summer, coinciding with significantly higher N_2 fixation rates in the same region (Figure 3). This seasonal pattern in chlorophyll-a aligns with observations at Station ALOHA (Karl, 1999) and is likely driven by photoacclimation: stronger solar radiation and more stable stratification in summer favor photosynthetic efficiency, leading to a reduction in cellular chlorophyll-a content per unit biomass (Lian et al., 2024; Signorini et al., 2015). Consistent with this mechanism, photosynthetically active radiation

levels were notably elevated in summer relative to winter in our observations (Yu et al., 2024). In contrast, the peak in N_2 -fixation during summer is driven by conditions that specifically favor diazotrophs, including optimal sea surface temperatures (Fu et al., 2014) and access to essential nutrients (e.g., phosphorus and iron) that meet the high metabolic demand of nitrogen fixation. Our concurrent measurements of physical and biogeochemical parameters reveal a tight seasonal coupling between N_2 -fixation and DOP dynamics in the center of NPSG (Figures 2 and 3). Consistent with long-term observations at Station ALOHA (Church et al., 2009), N_2 -fixation rates in the central gyre (NPSG-C) were approximately fourfold higher in summer ($4.99 \pm 3.01 \text{ nmol N L}^{-1} \text{ d}^{-1}$) than in winter ($1.17 \pm 1.38 \text{ nmol N L}^{-1} \text{ d}^{-1}$). This seasonal peak coincided with elevated sea surface temperatures and depleted DIN concentrations, with over 63% of summer samples below the detection limit (5.2 nmol L^{-1})—conditions that facilitate diazotroph growth, particularly of unicellular cyanobacteria (Church et al., 2009; Yu et al., 2024). While DIP concentrations remained consistently low across seasons in the central gyre (summer: $23.8 \pm 13.0 \text{ nmol L}^{-1}$; winter: $22.3 \pm 15.3 \text{ nmol L}^{-1}$), we observed a significant basin-wide drawdown of DOP during summer (Figure 3). This pattern suggests that DOP utilization may help alleviate phosphorus limitation during periods of enhanced N_2 -fixation. To quantify the associated phosphorus demand, we estimated seasonal P requirements based on measured N_2 -fixation under two scenarios: an N:P ratio of 16:1 (Redfield Ratio) and the ratio of 6:1 (indicative of P-replete conditions; Chen et al., 2025). The observed seasonal DOP drawdown, representing approximately 20% of DOP pool, fell within the estimated range of P demand (shaded area; Figures 4a and 4b; Text S2 in Supporting Information S1), potentially supporting 42% to over 100% of the required phosphorus under the N:P = 16 and N:P = 6 scenarios, respectively. This provides basin-scale evidence of a seasonal DOP cycle that can partially to fully sustain the phosphorus demand of enhanced N_2 -fixation in summer. These findings align with previous studies highlighting DOP as a key phosphorus source for primary producers (Karl et al., 1997; Torres-Valdés et al., 2009; Yamaguchi et al., 2019). A C-N-P budgetary analysis by Hashihama et al. (2021) in the similar region concluded that upward mixing and atmospheric deposition alone cannot support net community production, underscoring the importance of rapid internal phosphorus recycling within the euphotic zone. Furthermore, shallow lateral transport of DOP from productive gyre margins has been shown to be an important nutrient source for central gyre productivity over interannual timescales (Letscher et al., 2016; Letscher & Moore, 2015). Therefore, the phosphorus demand associated with enhanced summer N_2 -fixation can be partially to fully met by the DOP reservoir, which is replenished through a combination of lateral transport and vertical nutrient exchanges (Gupta et al., 2022; Letscher & Moore, 2015).

4.3. Seasonal Shifts in DOM N:P Stoichiometry and Their Influence on Nutrient Cycling in the Surface NPSG

DOM stoichiometry exhibits significant seasonal variation in the NPSG, with important implications for nutrient cycling. Unlike DOP, DON concentrations in NPSG-C were significantly higher during summer ($4.59 \pm 0.19 \text{ } \mu\text{mol L}^{-1}$) than in winter ($4.23 \pm 0.23 \text{ } \mu\text{mol L}^{-1}$; $p < 0.001$). This divergence resulted in a substantial shift in DOM N:P ratios, with average values of 25 ± 2 in summer compared to 19 ± 4 in winter (Figure 2, Table S2 in Supporting Information S1), consistent with the seasonal range previously observed at Station ALOHA (Karl et al., 2001). The summer accumulation of DON coincides with enhanced N_2 -fixation, suggesting that a considerable portion of newly fixed nitrogen enters the DON pool. Previous studies across various ocean regions have reported that 3%–90% of gross newly fixed nitrogen may be released as DON (Bonnet, Berthelot, Turk-Kubo, Cornet-Barthaux, et al., 2016; Bonnet, Berthelot, Turk-Kubo, Fawcett, et al., 2016; Glibert et al., 1994; Hu et al., 2025; Konno et al., 2010; Mulholland et al., 2005), implying that traditional rate measurements may underestimate total N_2 -fixation by neglecting this pathway. In this study, we developed two independent approaches to quantify the fraction of N_2 -fixation released as DON in the NPSG-C across seasons. First, mass balance calculations indicated that an average of 53% of fixed N enters the DON pool, with most observations falling within the 10%–90% range (Figure 4c). Second, a steady-state isotopic model, based on measured N_2 -fixation rates, observed $\delta^{15}\text{N-DON}$ values fall in the range of predictions when assuming 10%–90% partitioning of fixed nitrogen into DON, yielding a similar average release fraction of 40% (Figure 4d). Notably, our field-based estimates integrate processes occurring over seasonal timescales, such as grazing, viral lysis, and community succession which are not captured by short-term (4–48 hr) incubation experiments (Berthelot et al., 2017; Riemann et al., 2009).

The seasonal dynamics of DOM stoichiometry reflect fundamental patterns in nutrient cycling that influence carbon export in oligotrophic oceans. While new nitrogen inputs from N_2 -fixation can enhance productivity, they

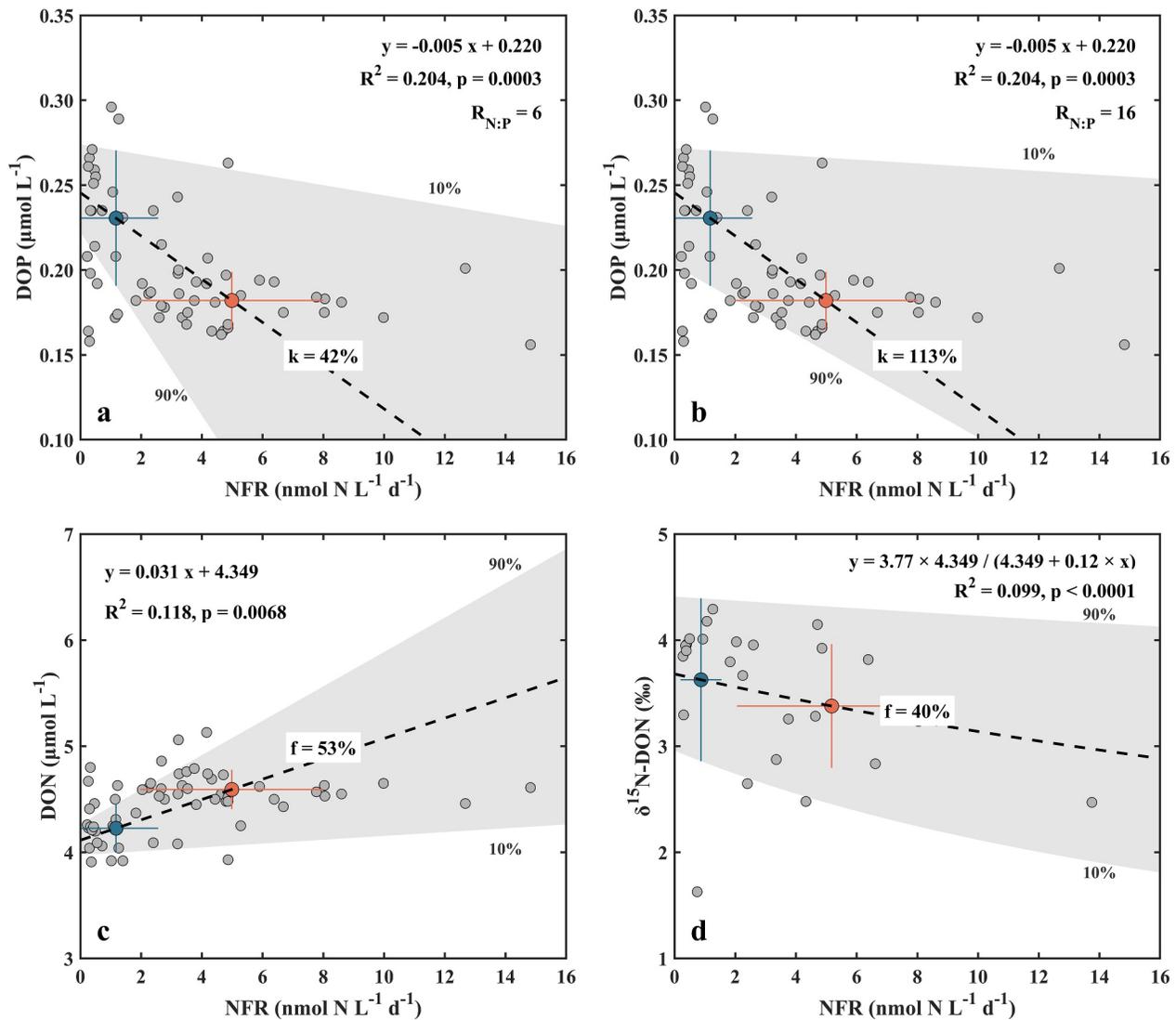


Figure 4. Relationships between N_2 -fixation rates and dissolved organic matter parameters in the central North Pacific Subtropical Gyre (NPSG-C): (a, b) dissolved organic phosphorus (DOP, $\mu\text{mol L}^{-1}$), (c) dissolved organic nitrogen (DON, $\mu\text{mol L}^{-1}$), and (d) $\delta^{15}\text{N-DON}$ (%). Gray points represent all individual measurements from summer and winter campaigns. Seasonal mean values ($\pm\text{SD}$) are shown as red circles (summer) and blue circles (winter). Panels a and b show estimated phosphorus requirements for N_2 fixation under two scenarios: (a) $N:P = 6$ (phosphorus repletion) and (b) $N:P = 16$ (Redfield ratio). The shaded areas represent the range of 10%–90% of phosphorus demand supported by DOP drawdown. Panels c and d show estimates of fixed nitrogen partitioning into the dissolved organic pool, with shaded areas representing 10%–90% release ranges. Black dashed lines in panels c and d show the estimated percentage of newly fixed nitrogen released into the DON pool. Note: For the $\delta^{15}\text{N-DON}$ versus N_2 -fixation rate (NFR) plot, we used the extended NFR data set corresponding to the $\delta^{15}\text{N-DON}$ measurements (see Table S3 in Supporting Information S1 for detailed data).

may ultimately be constrained by the availability of other nutrients (e.g., phosphorus and iron), leading to decoupled nutrient cycling. Our findings suggest that in the NPSG, the DOM pool acts as a biogeochemical buffer—supplying phosphorus during summer when N_2 -fixation rates are high and being replenished during winter when vertical nutrient supply intensifies. This study provides novel insights into seasonal DOM dynamics based on consecutive summer and winter observations. Future research should focus on the drivers of monthly and stochastic variation in N_2 -fixation, its connection to export fluxes, and the mechanisms maintaining stoichiometric balance in the surface ocean.

5. Conclusions

This study provides the first basin-scale assessment of DOM stoichiometry in the NPSG across consecutive seasons, filling critical spatial and temporal gaps in surface ocean DOM distributions. By combining high-resolution field measurements with mass and isotopic balance models, we quantify the role of DOP utilization in supporting seasonal N₂-fixation and demonstrate that a significant fraction of newly fixed nitrogen is released into the DON pool. Our findings emphasize DOM as a dynamic biogeochemical buffer that regulates nutrient cycling in the oligotrophic ocean, with stoichiometric flexibility enabling it to sustain productivity amid shifting nutrient demands.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

The nitrogen fixation data supporting this study are available from Yu et al. (2023). All data related to dissolved organic matter and associated parameters, including the station locations and sampling dates, are available from the Figshare repository via Zhang et al. (2025).

Acknowledgments

This work was supported by the National Key Research and Development Program of China (Grant 2023YFF0805001) and the National Natural Science Foundation of China (Grants 42276034 and 41890801). We thank all scientists and crews of the R/V Tan Kah Kee for their assistance with the sampling and experiments in the field. We sincerely thank Junhui Chen, Lifang Wang, Tao Huang, Weifang Chen, Jing Xu in Xiamen University for their help with Sampling and sample analysis.

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