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Warming exponentially stimulates photobleaching of dissolved organic matter from multiple microplastics

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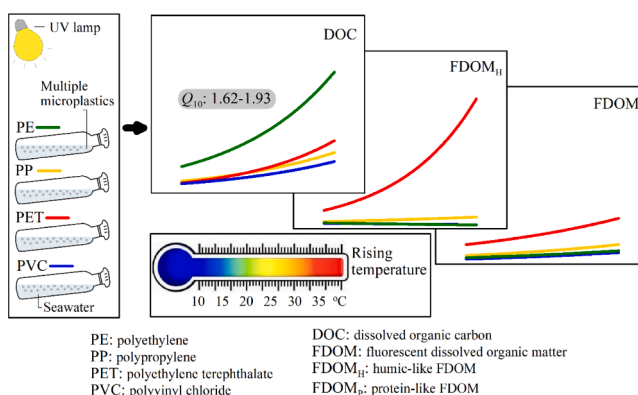
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HIGHLIGHTS

- Microplastic (MP) type affects photobleaching rates of MP-DOC.
- Photobleaching rates of MP-DOC increased with rising temperature ($Q_{10}=1.62-1.93$).
- Four MPs showed contrasting rates for photobleaching of DOC and fluorescent DOM.
- Humification and biological indices can distinguish MP-DOM from natural DOM.

GRAPHICAL ABSTRACT



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ABSTRACT

The substantial release of microplastics (MPs) into the marine environment is now deeply integrated into Earth's carbon cycle. However, the mechanisms by which warming regulates the release of MP-leached dissolved organic matter (MP-DOM) in seawater media remain highly uncertain. This work considers four typical MPs that enter the ocean (polyethylene, PE; polypropylene, PP; polyethylene terephthalate, PET; and polyvinyl chloride, PVC) over 1-week experiments under UV light and dark conditions at a narrow temperature interval of 5 °C between 10–35 °C. The results indicate that different MPs have variable photobleaching rates of dissolved organic carbon (MP-DOC, 0.06 ± 0.01 – 0.61 ± 0.07 mg-C/(g-MP/week)) and fluorescent DOM (MP-FDOM). An unexpected inconsistency emerged in the photobleaching of MP-DOC and MP-FDOM, with dominant MP-DOC release for PE, PP and PVC, while PET showed substantial release of both. The humification index and biological index pair is a useful indicator to distinguish MP-DOM versus natural DOM. The Q_{10} values, which reflect the temperature

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sensitivity of MP-DOM photobleaching, ranged from 1.62 (PVC) to 1.93 (PET) indicating an exponential increase in MP-DOM leaching rates with rising temperature. These findings highlight the need for incorporating ocean warming into predicting the effects of plastic pollution on the marine carbon cycle.

1. Introduction

Plastic pollution has emerged as a critical global issue since the 1950s [1,2]. As a substantial artificial carbon source, plastics entering the environment have greatly influenced Earth's carbon cycle along with unknown ecosystem and human-health consequences. The future carbon content of plastics in oceans is projected to reach levels comparable to the carbon storage in coastal ecosystems (~14 Pg-C) by 2035 and global bacterial biomass (~70 Pg-C) by 2095, making it an important component of the Earth's carbon cycle [3]. Research attention is increasingly focusing on the interconnections between plastic debris, micro(nano)-plastics (1 μm –5 mm and <1 μm , respectively) and the biogeochemical cycles of carbon and other biogenic elements in ecological systems [4–8]. Consequently, assessing the impact of plastic debris and microplastics (MPs) on the marine carbon cycle is crucial to understanding these emergent geomaterials on marine biogeochemistry.

Growing amounts of plastic waste are transported into the oceans through various pathways (expected to rise to 92.8–247.5 million metric tons by 2025) [9], accumulating in marine areas worldwide, from coastal regions to the open ocean, and from tropical to polar regions [10–13]. Most plastics float on the surface of the ocean, where they are subjected to transformations by sunlight, waves, etc., leading to their aging and the formation of plastic debris, MPs and dissolved components [14]. Human activities also produce MPs directly that finally entering the sea through riverine inputs and atmospheric transport/deposition.

Plastic debris and especially MPs can release dissolved organic matter (DOM) through various degradation pathways [15,16]. These degradation products provide anthropogenic sources of organic carbon in addition to natural organic matter (NOM) in the marine environment [17–20], thereby altering the marine carbon cycle (e.g. the microbial loop and biological pump) [21]. It is estimated that up to 10 % of DOM in the sea-surface microlayer originates from degradation of plastic debris [22]. Pfohl et al. [23] identified the leaching of DOM as a major contributor to the mass loss of MPs. Many plastic polymers and their additives contain aromatic structures, which can release DOM through photochemical degradation [24–27]. Current research on the release of MP-derived DOM into marine environments primarily focuses on factors such as MP type and aging degree, and on the bioavailability of MP-DOM. For example, expanded polystyrene (PS) releases dissolved organic carbon (DOC) more quickly than polypropylene (PP), whereas polyethylene (PVC) exhibits the greatest resistance to photodegradation [28]. Moreover, aged MPs typically release more DOC under irradiation than fresh plastics [29]. MP-DOM can stimulate microbial growth in the ocean and influence microbial abundance [30,31]. The utilization of MP-DOM by microorganisms differs greatly among coastal ecosystems, possibly related to differences in their microbial communities and nutrient levels [32]. However, the environmental conditions surrounding MPs in marine settings can vary greatly, and our understanding remains limited concerning the effects of key environmental variables, such as temperature and salinity, on the release of MP-DOM.

The warming of Earth's climate has accelerated the rise in ocean temperatures in 21st century [33]. Between 2011 and 2020, the global average ocean temperature increased by 0.88 °C [34]. By 2100, climate models project a likely increase in mean global ocean temperature, from roughly 1.4–4.4 °C above pre-industrial levels depending on greenhouse gas emission scenarios [34]. Coastal regions are among the most affected; for example, the East China Sea's winter surface temperature rose by nearly 2 °C from 1958 to 2014 at a rate far exceeding the global average [35]. Climate change has also increased the frequency of marine heatwaves (i.e. anomalous warm seawater events), with both the

intensity and duration of these extreme events rising substantially [36]. For example, in August 2016, the East China Sea experienced a record-breaking marine heatwave, with average sea surface temperatures exceeding 28.7 °C [37]. Given the substantial seasonal and latitudinal variations in global ocean temperature, MPs experience varying temperature gradients in the marine environment. Hence, investigating the temperature sensitivity (i.e., Q_{10} value) of MP-DOM release is critical to assessing its biogeochemical effects, particularly in relation to its response to ocean warming.

Similar to NOM, MP-DOM contains unsaturated groups, and thus its composition and properties can be characterized by ultraviolet and fluorescence spectroscopy [17,26,29]. The specific ultraviolet absorbance at 254 nm (SUVA_{254}) can be used as an indicator for aromaticity of MP-DOM [27,38]. Excitation-emission matrix (EEM) spectroscopy as pioneered by Coble (1996) [39] has been widely used to investigate the distribution and optical characteristics of NOM [40,41]. Fluorescent MP-DOM exhibits signals in the protein-like and humic-like region, but its EEM spectra largely differ from those of NOM. Lee et al. [42] identified the C4 component (excitation/emission (Ex/Em): 270/309 nm) in MP-DOM released from PVC as a fluorescent marker for tracking MP-DOM containing bisphenol A additives. The ratio of peaks in the protein-like region (P peak) and humic-like region (H peak and L peak) of MP-DOM, specifically (H+P)/L, has also been proposed as a possible indicator to differentiate MP-DOM from NOM [43]. These studies typically assessed MP-DOM release in experiments at 25 °C. However, whether the MP-DOM released from different plastic types under different temperature conditions exhibits variable and unique spectral characteristics, and whether there is a better spectral indicator for distinguishing MP-DOM from marine NOM remain topics for further investigation.

PE, PP, polyethylene terephthalate (PET), and PVC are among the most widely produced types of plastics [3], accounting respectively for 36 %, 23 %, 10 %, and 12 % of total plastic production between 2002 and 2014 [44]. These plastics also comprise the most common types of plastic debris and MPs entering the marine environment [3,45]. In this study, we focused on the release of DOC and fluorescent dissolved organic matter (FDOM) from MPs composed of PE, PP, PET and PVC over 1 week in seawater media under irradiated and dark conditions. We set a narrow temperature interval of 5 °C within the dominant temperature range (10–35 °C) of marine environments to assess Q_{10} values. The main objectives of this study were to: (1) examine the effects of MP types on the photobleaching rates of DOC and FDOM and the humification index and biological index pair (HIX-BIX) of the four MP types; (2) estimate the temperature sensitivity of DOC and FDOM release from the four MPs by calculating Q_{10} values; (3) identify a general and comprehensive spectral indicator to differentiate MP-DOM from NOM; and (4) evaluate the potential impact of MP-DOM on the marine carbon cycle as the global ocean temperature increases.

2. Materials and methods

2.1. Preparation of MPs

Commercial MP sheets of PE (high density, $(\text{C}_2\text{H}_4)_n$), PP $(\text{C}_3\text{H}_6)_n$, PET $(\text{C}_{10}\text{H}_8\text{O}_4)_n$, and PVC $(\text{C}_2\text{H}_3\text{Cl})_n$ with dimensions of 5 × 5 mm and a thickness of 0.3 mm were purchased from Qianlisi (Dongguan, China). The MPs were pretreated following the method described by Zhu et al. [28]. Briefly, the samples were rinsed three times with ultrapure water, and subsequently ultrasonically treated (SB-5200D, Xinzhi, Ningbo, China) in ultrapure water for 10 min. The MPs were then

immersed in a 1 % H₂O₂ solution for 2 h to sterilize and clean, followed by rinsing with ultrapure water and a second ultrasonic treatment for 5 min to further clean. Finally, they were washed three times with ultrapure water and allowed to dry in the dark at room temperature before experimental use.

2.2. Preparation of artificial seawater and experimental equipment

To avoid interference from natural DOM on determination of MP-DOM signals, artificial seawater (salinity: 30 PSU) was prepared following oceanographic specifications for leaching experiments [46]. Specifically, 133.55 g NaCl (GR, Aladdin, USA) and 42.75 g MgSO₄·7 H₂O (GR, Aladdin, USA) were dissolved in ultrapure water, diluted to a final volume of 5.0 L, and stored in glass bottles. A total of 30.0 L artificial seawater was prepared and autoclaved at 121 °C for 20 min [31]. Then it was exposed to ultraviolet light for 1 week until the DOC concentration was below the detection limit (~0.01 mg/L).

All equipment used in the experiments adhered to trace-cleaning protocols for DOC in marine studies [47]. Plastic bottle caps were soaked overnight in an acidic solution (6 N HCl: ultrapure water, V:V, 1:9), and then rinsed three times with ultrapure water before drying. All quartz tubes, sample bottles and stainless-steel filter holders were cleaned with ultrapure water and dried, and then together with GF/F filter membranes (0.7 μm, Whatman), subjected to combustion in a muffle furnace at 550 °C for 6 h prior to use.

2.3. MP-DOM leaching experiment

Leaching experiments were conducted on the four commercial MPs under UV light and dark conditions using a narrow temperature interval of 5 °C between 10–35 °C, which cover the temperature range for the majority of global ocean. Each MP group at each temperature contained 3 replicate samples. The prepared MPs (~0.1 g) were added to 100 mL artificial seawater in 144 quartz tubes. Due to the difference in MP density, 0.1 g of PE, PP, PET, and PVC corresponded to 14, 13, 10, and 10 sheets, respectively, with a surface area of 7.84, 7.28, 5.60, and 5.60 cm², respectively. After sealing the quartz tubes with quartz stoppers, both UV irradiated and dark (wrapped in aluminum foil) incubations were simultaneously conducted for 1 week in photochemical incubators (GLD-350UVA-B, Ningbo Ledian, China) at 10, 15, 20, 25, 30 or 35 °C (± 1 °C). The 1-week incubation period was selected because 1) the incubation time was comparable to previous studies (Table S1); and 2) in a 4-week pre-experiment, the DOC leaching rate at 4 weeks was comparable to that of the first week (Fig. S1), showing no obvious aging effect over the 4-week incubation period.

Ultraviolet (UV) LED lamps simulating natural near-earth UV exposure were positioned above the quartz tubes (at ~35 cm distance), providing an irradiation intensity of approximately 2000 μW/cm². Exposure at this irradiation intensity for 24 h was slightly higher than the photochemical exposure of one solar day in subtropical ocean surface waters [28,48]. All quartz tubes were inclined at a 10° angle to increase the UV exposure area.

After the one-week incubation, the solution was filtered through GF/F filters to isolate the leachates. MP-DOC samples were collected in 40-mL brown glass bottles, acidified to pH 2, stored at -20 °C, and analyzed within 14 days. Samples for MP-CDOM and MP-FDOM were collected in 60-mL brown glass bottles, stored at 4 °C, and analyzed within 24 h.

2.4. Analysis of MP-DOC

MP-DOC samples were analyzed with a TOC-L analyzer equipped with an autosampler (ASI-L, Shimadzu, Japan) using a high-temperature catalytic oxidation method. A potassium hydrogen phthalate standard solution was used for the calibration curve, and ultrapure water served as the blank. All measurements were replicated three times, with a relative analytical error of less than 2 % [49].

2.5. Analysis of MP-CDOM and MP-FDOM

Absorption spectra for MP-CDOM were measured using a UV-vis spectrophotometer (Lambda 950, PerkinElmer, USA). A 10-cm quartz cuvette with ultrapure water served as the blank [50]. The wavelength range was set as 200–800 nm, with a scanning interval of 1 nm. SUVA₂₅₄ was calculated as the ratio of the absorbance at 254 nm to the DOC concentration [51]. Higher SUVA₂₅₄ values indicate a higher degree of aromaticity of MP-DOM [27,38].

Three-dimensional EEM spectra for MP-FDOM were obtained using a F-7100 fluorescence spectrophotometer (Hitachi, Japan). The excitation wavelength range was 240–450 nm with a 5-nm interval, while the wavelength range for emission detection was 280–600 nm with a 2-nm interval. For each sample, the EEM was corrected using the ultrapure water blank, and the fluorescence intensity was normalized using the Raman peak of ultrapure water excited at 350 nm, expressed in Raman units (R.U.) [52].

The EEMs of all MP-FDOM samples were modeled using the DOM-fluor toolbox in Matlab R2020a, and the number of fluorescent components was determined by parallel factor analysis (PARAFAC) through split-half analysis [53,54], a method that has been widely used for the identification of fluorescent components [49,50,55–57]. The spectral properties of MP-FDOM were compared with those of NOM using two fluorescence indices. The humification index (HIX) is the ratio of the integrated fluorescence intensity at emission wavelengths of 435–480 nm to that at 300–345 nm when excited at 254 nm [58]. The biological index (BIX) is the ratio of fluorescence intensity at 380 nm to that at 430 nm when excited at 310 nm [59]. With respect to NOM, a higher HIX represents an increasing degree of humification, while a higher BIX reflects a greater contribution from autochthonous sources.

2.6. Calculation of temperature sensitivity(Q₁₀)

The Q₁₀ value was calculated to evaluate temperature sensitivity for the leaching rates of DOC and FDOM during photobleaching of MPs. This factor reflects the increase in leaching rate for each 10°C increase in temperature [60]. The relationship between the rate of MP-DOC or MP-FDOM and temperature is represented by an exponential function as:

$$R(T) = R(T_0) \times e^{kT} \quad (1)$$

where k is the temperature coefficient, and $R(T)$ and $R(T_0)$ are the rates of MP-DOC or MP-FDOM at temperatures T and T_0 , respectively. The Q₁₀ value is derived as [60]:

$$Q_{10} = e^{10k} \quad (2)$$

2.7. Statistical analysis

Statistical analysis was conducted using SPSS version 20.0. Pearson correlation analysis assessed relationships between treatment group pairs. Analysis of variance (ANOVA) evaluated significant differences among multiple groups, with a p -value of < 0.05 being considered statistically significant. Results are reported as mean ± SD from triplicate samples unless otherwise noted.

3. Results

3.1. EEM spectra of MP-FDOM

The EEM spectra of FDOM from each MP polymer type under UV exposure did not vary with temperature, but the different MPs did show notable distinctions, allowing them to be categorized into two types (Fig. S2). Type I MP-FDOM included PE, PP and PVC, which all exhibited

four fluorescence peaks: two protein-like peaks (T_1 : Ex/Em at 270–285/308–338 nm; T_2 : Ex/Em at 240/342–360 nm) and two humic-like peaks (A: Ex/Em at 240/398–420 nm; M: Ex/Em at 290–310/404–418 nm). In contrast, Type II MP-FDOM originating from PET exhibited only three fluorescence peaks: T_2 (Ex/Em = 240/330–332 nm), A (Ex/Em = 240/434–438 nm), and M (Ex/Em = 315/430–434 nm). Compared with Type I MP-FDOM, the T_2 emission peak for PET-FDOM was blue-shifted, whereas the A and M peaks were red-shifted.

The EEM spectra for each MP-FDOM polymer type under dark incubation did not vary with temperature (Fig. S2), but displayed a feature (labeled Type III) distinct from that of the UV-irradiated group (Fig. S3). The fluorescence intensities of the protein-like peaks T_1 and T_2 were more pronounced, whereas the humic-like peaks A and M exhibited weak signals. In the dark group, PE- and PP-FDOM displayed only a T_1 peak, whereas PVC-FDOM exhibited both T_1 and T_2 peaks with comparable fluorescence intensities. The PET-FDOM in the dark group exhibited both T_1 and T_2 peaks, in contrast to the presence of only a T_2 peak in the corresponding UV-irradiated group.

The PARAFAC model identified four fluorescent components for all MP-FDOM polymer types: two protein-like (C2 and C3) and two humic-like (C1 and C4; Fig. 1). The C2 and C3 peaks occurred at Ex/Em wavelengths less than 240/338 and 275/308 nm, respectively, showing some overlap with the T_1 and T_2 peaks. The maximum intensities for C1 and C4 were at Ex/Em wavelengths of (245, 315)/436 and 295/406 nm, corresponding to the A and M peaks, respectively.

3.2. Leaching of MP-DOC and MP-FDOM as a function of temperature

3.2.1. MP-DOC leaching

The rates of MP-DOC released from the UV-irradiated groups varied from 0.06 ± 0.01 – 0.61 ± 0.07 mg-C/g-MP/wk across the 10–35 °C range (Fig. 2a and S4; Table S2). The lowest DOC leaching rate was for PVC at 10 °C and the highest for PE at 35 °C. At a given temperature, the DOC leaching rate from PE was always the highest, followed by PET, PP and PVC ($p < 0.01$). For example, the DOC leaching rate for PE at 35 °C was 1.8, 3.2 and 4.1 times that of PET, PP and PVC, respectively (Table S2). Photobleaching rates of DOC for all MP types increased significantly with increasing temperature across the temperature gradient ($p < 0.01$; Fig. 2a, S4, Table S3). For the UV-irradiated groups, the MP-DOC leaching rates at 35 °C were 2.6–4.1 times higher than those at 10 °C.

In the dark group, PET and PVC showed consistently low DOC leaching rates at all temperatures (< 0.01 mg-C/g-MP/wk), whereas PP and PE showed substantially higher DOC leaching (0.01 ± 0.01 – 0.12 ± 0.02 mg-C/g-MP/wk; Fig. 2b and S4). DOC leaching in the dark was considerably lower than that under UV irradiation. For example, the DOC leaching rate of PP under UV irradiation at different temperatures was 2–7 times higher than in the dark, whereas the comparable values for PE were between 13 and 18.

3.2.2. FDOM leaching

The four MP types under UV irradiation released variable intensities of humic-like (FDOM_H; C1 + C4) and protein-like FDOM components (FDOM_P; C2 + C3; Fig. 2c, e). At a given temperature, PET had the highest FDOM_H leaching rate. For example, the PET-FDOM_H leaching rate at 35 °C (0.094 R.U.) was 16.8, 53.2 and 53.6 times that of PP, PE and PVC, respectively. The PET-FDOM_P leaching rate at 35 °C (0.025 R.U.) was also the highest among the MP types and was 2.8, 4.2 and 5.9 times that of PP, PE and PVC, respectively. Comparing between the two FDOM types, the intensity of FDOM_H released by PET under UV irradiation was consistently higher (1.1–3.8 times) than the intensity of FDOM_P released at any given temperature. In contrast, the other MP types released comparable intensities of FDOM_H and FDOM_P. Notably, the photobleaching of FDOM_H and FDOM_P was not consistent with the photobleaching of DOC. For instance, although PE produced the highest DOC (Fig. 2a), its FDOM leaching rate was quite low (Fig. 2c).

Variations in FDOM_H and FDOM_P photobleaching with temperature were also MP types dependent (Fig. 2c, e). Leaching of PET-FDOM_H and PET-FDOM_P did not change appreciably at low temperatures (10–20 °C), but increased markedly at higher temperatures (25–35 °C). PET-FDOM_H and PET-FDOM_P intensities at 35 °C were 6.3 and 2.3 times higher than those at 10 °C. The other three MPs exhibited overall low fluorescent intensities and thus a smaller overall effect from temperature. Finally, the intensities of FDOM_H and FDOM_P at 35 °C were 0.8–1.7 and 1.7–2.3 times higher than those at 10 °C.

The dark groups showed low intensities for FDOM_H in the leachates from all four MP types (0.004–0.006 R.U.), which were generally below the levels for the equivalent irradiated groups (Fig. 2d). In contrast, the intensities of FDOM_P from the dark groups were consistently higher than the corresponding values for the UV-irradiated groups (Fig. 2f), with the value for PE (0.025–0.044 R.U.) significantly exceeding the values for the other three MPs (0.006–0.016 R.U.) ($p < 0.01$). The intensity of

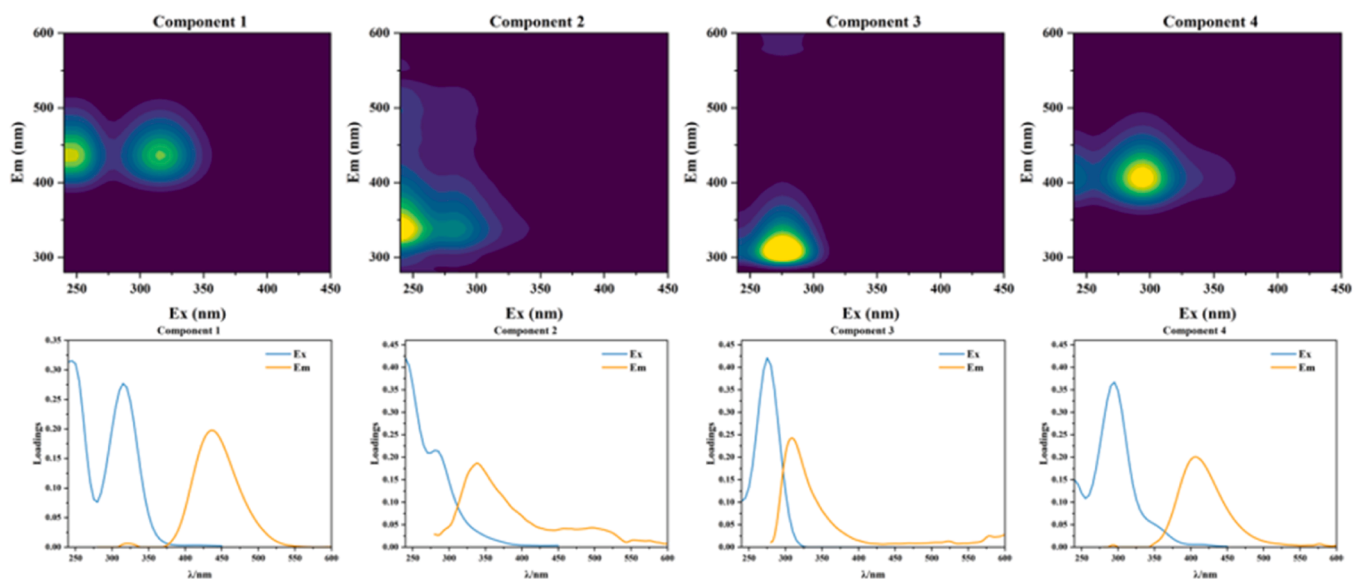


Fig. 1. Four fluorescent components were identified for all UV irradiation and dark incubation EEMs by the PARAFAC model (top) with the corresponding Ex/Em spectra (bottom).

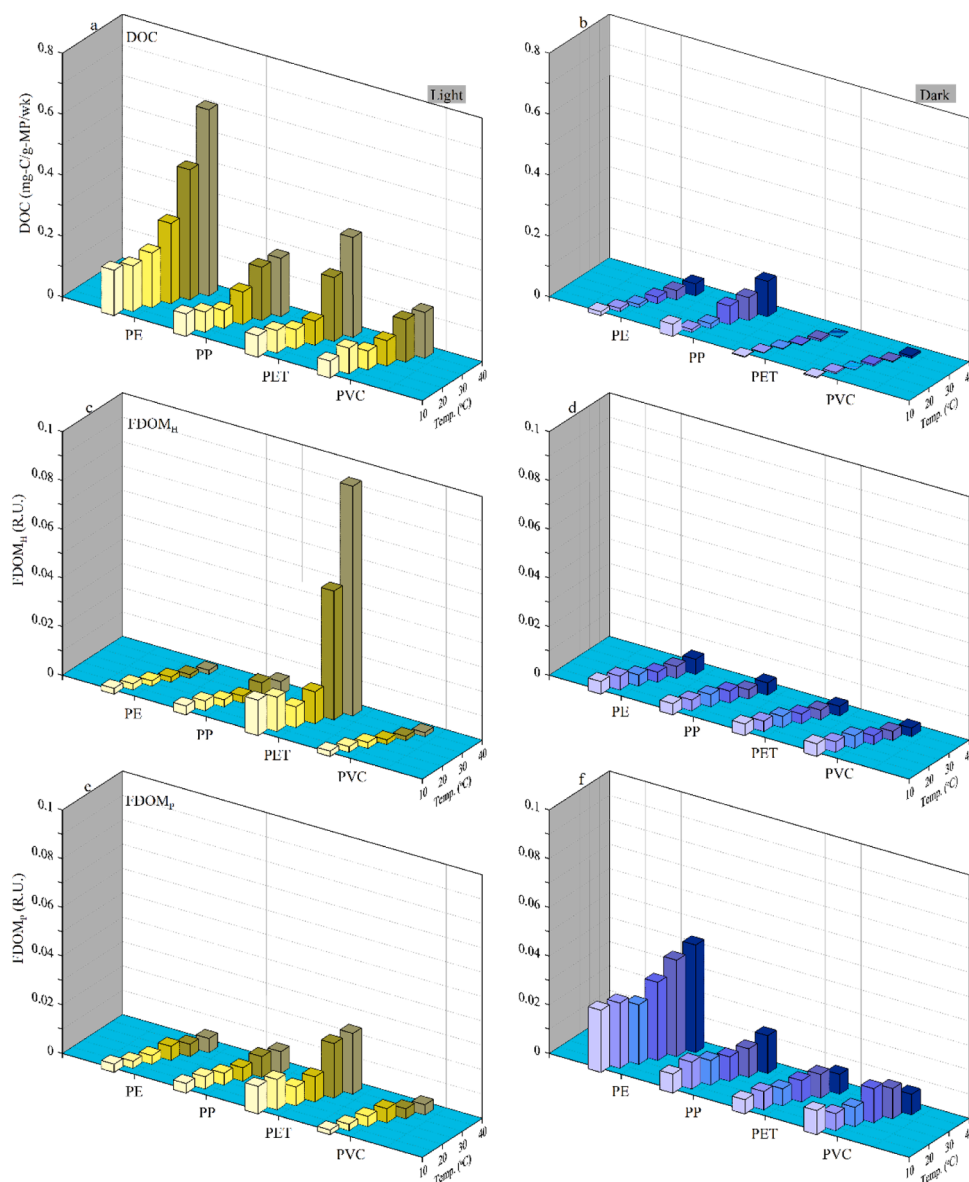


Fig. 2. Leaching of DOC (a, b), FDOM_H (c, d) and FDOM_P (e, f) from PE, PP, PET, and PVC MPs after one week of UV irradiation (left) and dark incubation (right) at 10, 15, 20, 25, 30 and 35 °C.

FDOM_P from PE in the dark at 35 °C was 1.9 times that at 10 °C. In the dark, more FDOM_P than FDOM_H (1.2–8.1 times) was consistently released at all temperatures, which was opposite to the trend observed for UV irradiation.

3.3. Spectral indices (HIX, BIX, SUVA₂₅₄) of MP-FDOM

HIX values for FDOM from the four MP polymer types exposed to UV irradiation ranged from 0.35 ± 0.01 – 0.77 ± 0.01 (Table 1), whereas values for the dark group were 0.22 ± 0.00 – 0.49 ± 0.01 (Table S4). HIX values for the UV-irradiated samples were consistently higher than those for the corresponding dark groups ($p < 0.001$). Conversely, the mean BIX values for the dark groups were higher than those for the corresponding UV-irradiated groups ($p < 0.001$). BIX values for MP-FDOM ranged from 0.11 ± 0.01 – 0.94 ± 0.11 for the UV-irradiated groups versus 0.85 ± 0.06 – 1.09 ± 0.12 for the dark groups (Table S4). BIX values for FDOM with or without UV-irradiation followed PE>PVC>PP>PET.

SUVA₂₅₄ of MP-FDOM at different temperatures varied considerably, from 0.39 ± 0.08 to 10.21 ± 1.34 (Table 1). At a given temperature,

PET-FDOM showed the highest SUVA₂₅₄, followed by PVC, PP and PE, indicating a strong effect of MP type on leachate aromaticity. For a specific MP type, the SUVA₂₅₄ was 1.2–3.1 times higher at low temperatures (10–20 °C) than at elevated temperatures (25–35 °C).

4. Discussion

4.1. Differences in photobleaching of DOC and FDOM from different MPs

In this study, commercial PE and PP subjected to UV irradiation ($\sim 2000 \mu\text{W}/\text{cm}^2$) in artificial seawater at 25 °C, resulted in average DOC leaching rates of 0.26 ± 0.02 and 0.11 ± 0.01 mg-C/g-MP/wk, respectively (Table S2). Previous photobleaching tests of MP-DOC from PE and PP at room temperature (~ 25 °C) showed similar results. For example, Lee et al. [42] investigated commercial PE and PP in deionized water at 25 °C under irradiation of 3553 – $4201 \mu\text{W}/\text{cm}^2$, reporting average DOC leaching rates of 0.24 ± 0.01 and 0.23 ± 0.01 mg-C/g-MP/wk, respectively. Zhu et al. [28] examined commercial PE and PP in natural seawater at room temperatures under irradiation of $\sim 1400 \mu\text{W}/\text{cm}^2$, determining average DOC leaching rates of up to 0.14 ± 0.03 and 5.07

Table 1

DOM spectral indices for HIX, BIX and SUVA₂₅₄ from the four MP types after a one-week UV irradiation across a temperature gradient of 10–35 °C (mean ± SD, n = 3).

Parameters	Temp. (°C)	PE	PP	PET	PVC
HIX	10	0.51	0.53	0.56	0.47
		± 0.02	± 0.03	± 0.01	± 0.01
	15	0.59	0.51	0.53	0.47
		± 0.04	± 0.02	± 0.01	± 0.01
	20	0.46	0.46	0.49	0.42
		± 0.02	± 0.01	± 0.02	± 0.05
	25	0.37	0.39	0.55	0.41
		± 0.05	± 0.02	± 0.02	± 0.04
	30	0.37	0.43	0.70	0.43
		± 0.02	± 0.02	± 0.02	± 0.03
	35	0.35	0.41 ±	0.77	0.41
		± 0.01	< 0.01	± 0.01	± 0.03
BIX	10	0.79	0.63	0.21	0.74
		± 0.06	± 0.02	± 0.02	± 0.02
	15	0.78	0.62	0.21	0.76
		± 0.02	± 0.01	± 0.02	± 0.06
	20	0.84	0.75	0.24	0.84
		± 0.07	± 0.07	± 0.02	± 0.16
	25	0.87	0.78	0.21	0.90
		± 0.05	± 0.01	± 0.02	± 0.08
	30	0.94	0.59	0.14	0.83
		± 0.11	± 0.06	± 0.02	± 0.02
	35	0.87	0.69	0.11 ±	0.92
		± 0.07	± 0.03	< 0.01	± 0.10
SUVA ₂₅₄	10	1.69	3.08	9.60	2.68
		± 0.53	± 0.58	± 1.87	± 1.44
	15	1.50	3.57	9.44	4.42
		± 0.43	± 0.72	± 0.58	± 3.10
	20	1.69	5.18	10.21	7.62
		± 0.96	± 2.76	± 1.34	± 2.22
	25	0.78	1.88	8.57	2.46
		± 0.15	± 0.13	± 1.52	± 0.66
	30	0.39	1.34	6.47	1.35
		± 0.08	± 0.22	± 0.08	± 0.24
	35	0.43	1.99	5.89	1.76
		± 0.13	± 0.84	± 0.41	± 0.80

± 0.04 mg-C/g-MP/wk, respectively. Moreover, we found DOC leaching rates of PE under UV irradiation at different temperatures were 13–18 times higher than in the dark. This is consistent with previous work that found DOC leaching rates from four PE shopping bags under UV irradiation at 25 °C to be 3–80 times that in the dark [61]. These data indicated that our DOC leaching rates were comparable to previous investigations.

The obtained results indicate appreciable differences in the photobleaching of MP-DOC and MP-FDOM from the four contrasting MP types (Fig. 3). The photobleaching of DOC was highest in PE leachate, whereas those of FDOM_H and FDOM_P were low. While PET had the second highest DOC leaching rates, PET produced the highest FDOM_H and FDOM_P intensities, both of which were positively correlated ($p < 0.01$) with PET-DOC (Fig. 3a, c). Consequently, PET-DOM showed the highest specific fluorescence intensity among the four MPs. In contrast, PP demonstrated lower DOC leaching, which was positively correlated with FDOM_P ($p < 0.01$) and FDOM_H ($p < 0.05$). The specific fluorescence intensity of PP-FDOM_P was approximately half that of PET-FDOM_P, whereas that of PP-FDOM_H was an order of magnitude lower than that of PET-FDOM_H. Photobleaching from PVC was particularly low for both DOC and FDOM.

To date, little research has systematically investigated differences in photobleaching of DOC and FDOM from plastics [29]. A study found that leachate from photo-aged commercial PET, contains a higher proportion of unsaturated aromatic components compared with PE and PP [62], which is consistent with the highest SUVA₂₅₄ observed for PET-DOM across all temperatures in this study (Table 1). This suggests that the commercial PET used in our experiments has strong photoreactivity,

allowing for rapid synchronous release of DOC, FDOM_H, and FDOM_P components [26]. This is consistent with PET being the only structure with an aromatic ring among the four contrasting MP types [3]. In contrast, commercial PE and PP contain higher proportions of saturated aliphatic components, primarily alkanes [62], which results in significantly lower ($p < 0.01$) SUVA₂₅₄ values for PP-DOM and PE-DOM compared to PET-DOM. Therefore, the chemical structure and composition of PE and PP plastics is the dominant factor contributing to their lower rates of FDOM_H and FDOM_P leaching.

We observed that PE exhibited a higher DOC leaching rate than PP, with higher PE/PP ratios for DOC leaching rates observed at higher temperatures (20–35 °C: 2.44–3.19) versus lower temperatures (10–15 °C: 2.03–2.24). Prior studies have reported DOC leaching rates from PE to be significantly higher than those from PP in marine [31] and freshwater [63] environments. These findings suggest that despite the similar chemical properties of the two materials, PE with ester bond demonstrates greater photoreactivity than PP [3], whereas the tertiary carbon bonds of PP provide increased resistant to photooxidation [64–66]. Although the SUVA₂₅₄ value for PVC-DOM was not the lowest among the MPs (Table 1), its low carbon content (38 %) and low photoreactivity [3] result in low rates for both DOC and FDOM leaching [38]. Thus, the differences in photobleaching rates for MP-DOC and MP-FDOM are not only related to the differing backbone structures and carbon contents of the MPs but also to their varying degrees of photoreactivity [3].

4.2. Temperature sensitivity of MP-DOM leaching rates

There were significant differences in the rates of MP-DOC leaching from the UV-irradiated samples at different temperatures ($p < 0.01$; Table S3). The relationship between MP-DOC photobleaching rate and temperature was exponential rather than instead of linear (Fig. 4). The temperature sensitivity of biogeochemical reaction rates is commonly expressed using Q_{10} values [60,67,68]. While several mathematical functions for calculating Q_{10} values have been proposed, we used the exponential formula expressed in Eq. 1 [60] to determine the temperature coefficient (k ; Fig. 4). Correspondingly, Q_{10} values for DOC leaching rates of the four MPs followed PET (1.93) > PE (1.84) > PP (1.63) > PVC (1.62), indicating differences in the temperature sensitivity of their DOC photobleaching. In contrast, there was a much lower temperature sensitivity for the photobleaching of FDOM_P, with Q_{10} values following PET (1.41) > PP (1.39) ≈ PVC (1.39) > PE (1.34) (Fig. S5). Finally, Q_{10} values for the photobleaching of FDOM_H were highly variable: PET (2.18) > PP (1.22) > PVC (0.88) ≈ PE (0.84) (Fig. S5). The Q_{10} values being less than 1.0 for FDOM_H leaching could result from photodegradation rates exceeding photobleaching rates [27]. It should be noted that although PE consistently showed the highest DOC leaching rate at all temperatures, PET exhibited the greatest sensitivity to temperature for its DOC leaching rate. In contrast, PET showed the highest leaching rates and temperature sensitivity for both FDOM_H and FDOM_P, whereas PVC displayed lower leaching rates and temperature sensitivity for DOC and FDOM. Overall, there was considerable variability in the temperature sensitivity of DOC and FDOM leaching among the different MP types.

In the dark groups, DOC concentrations from PP and PE exhibited non-linear responses to temperature (Fig. 2), with their Q_{10} values of 2.08 and 1.87 being slightly higher than the corresponding values for irradiated samples. Under dark conditions, MPs primarily leached FDOM_P, with Q_{10} values for FDOM_P leaching from PP, PE and PET of 1.23, 1.27, and 1.17, respectively, which were slightly lower than those of the corresponding UV-irradiated samples. In contrast, the Q_{10} values for FDOM_H release from PET and PVC in the dark were less than 1 (0.93 and 0.86, respectively), indicating slight decreases in FDOM_H release with increasing temperature. This behavior was similar to that observed for PE and PVC under UV irradiation conditions.

Few studies have explored temperature effects on MP photobleaching.

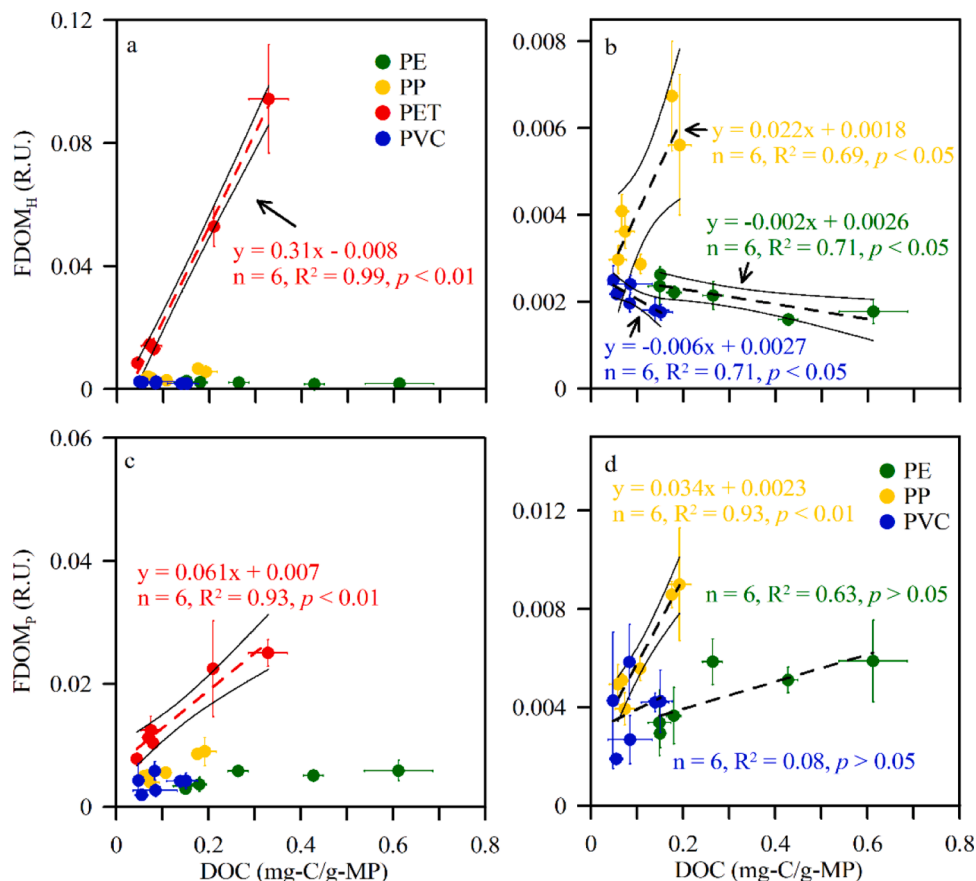


Fig. 3. Correlation analysis of average DOC (mg-C/g-MP) with FDOM_H (R.U.) and FDOM_P (R.U.) for the four MP leachates after incubation under UV irradiation for 1 week.

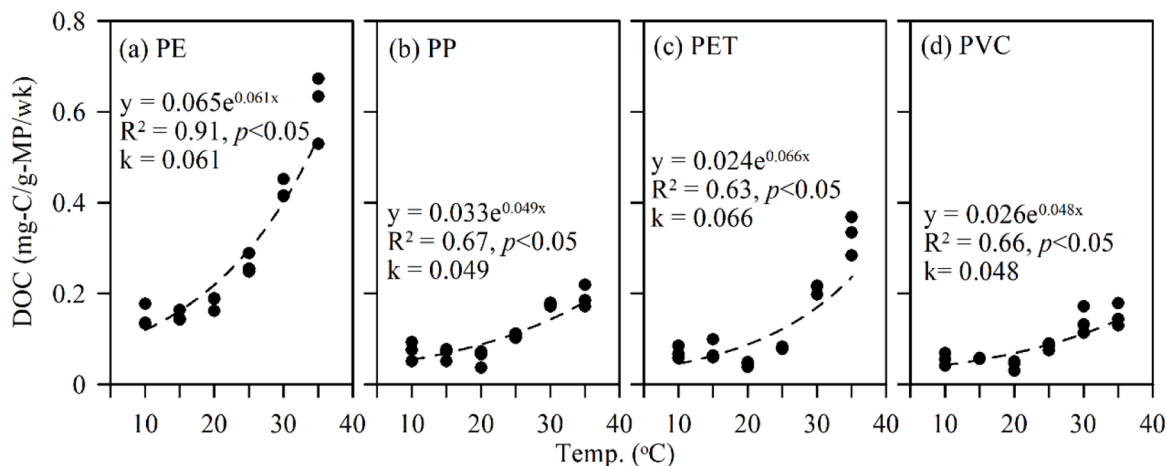


Fig. 4. Temperature sensitivity of DOC leaching rates from microplastics (PE, PP, PET, and PVC) after a 1-week incubation under UV irradiation.

Ward et al. [69] reported a 25 % increase in the photobleaching of PS-DOC with a temperature increase of 10 °C. Similarly, Wu et al. [70] reported an increase of PS-DOC release from a 20 °C increase (from 10 to 30 °C) after a 7-day UV-light incubation. As PS is a major plastic type entering the marine environment, it can be concluded that the temperature effect for MP-DOM photobleaching could be a common phenomenon among the dominate marine MPs.

DOC in natural environments also show temperature-dependent release rates. DOC release in peat and forest soils is highly sensitive to temperature [71,72], with Q_{10} values varying with soil moisture and

oxygen conditions [73,74]. In marine environments, the degradation of labile, semi-labile and refractory DOC pools exhibits large temperature sensitivity, with Q_{10} values increasing from 1.7–1.8–4–8 as the degree of lability decreased. Overall, temperature is a key determinant for the source and sink dynamics of both natural and plastic derived DOM in natural ecosystems.

4.3. Using the HIX-BIX index pair to differentiate MP-DOM from NOM

The EEM spectra for MP-DOM and NOM differed notably, suggesting

that they could be differentiated based on fluorescence characteristics. Lee et al. (2021) designated the protein-like fluorescence peaks in MP-FDOM as P peaks and the humic-like peaks as H and L peaks; they correspond to the T₂, M, and A peaks identified in this study, respectively [43]. According to the (H + P)/L index proposed by Lee et al. [43], DOM from PE, PP and PVC in this study can be distinguished from NOM (Fig. S6). However, the index cannot sufficiently differentiate PET-FDOM. To explore a universal spectral indicator for distinguishing all types of MP-FDOM from NOM, we developed an additional NOM dataset from a continuum of water samples including rivers, estuaries, marginal sea and open ocean [74]. These surface water samples covered a complete natural salinity gradient, thereby providing a comprehensive and representative dataset for natural DOM (Fig. S7).

HIX and BIX are often used to assess the spectral characteristics of NOM [58,59,75]. Fig. 5 shows that riverine and nearshore NOM predominantly had BIX values > 0.7 and HIX > 0.6. There was an increase of BIX and decrease of HIX for offshore NOM samples, especially for NOM in the open Pacific. Overall, the values of HIX + BIX for all NOM samples were above 1.5. The BIX values of MP-FDOM from the dark group were comparable to or even exceeded those of riverine and nearshore NOM, whereas their HIX values were lower (Table S4). The dark group of MP-FDOM samples generally showed HIX + BIX values of 1.3–1.5, except for some overlap with NOM from the South China Sea. In contrast, DOM from UV-irradiated MPs exhibited lower BIX + HIX values (<1.3) than the dark group and NOM (Fig. 5). Therefore, the HIX-BIX pair could clearly differentiate MP-FDOM produced under UV irradiation from NOM and MP-FDOM generated under dark conditions (Fig. 5). This method is particularly powerful for identifying PET-FDOM. Under UV irradiation, PET-FDOM_H was predominantly released, whereas under dark conditions the leaching of PET-FDOM_P was most prevalent (Fig. 2). Consequently, the UV-irradiated PET-FDOM showed significantly higher HIX and lower BIX values than the dark group, especially at higher temperatures (30–35 °C) ($p < 0.01$).

The notable differences in the HIX-BIX index pair between MP-derived and natural FDOM indicates that the so-called “humic-like” and “protein-like” components of MP-FDOM are distinctly different from those found in NOM [76], despite large overlaps in the regions of their fluorescence peaks [77]. The fluorescence moieties of MP-FDOM originate from diverse and complex sources. Fluorescent signals from plastic impurities, such as polycyclic aromatic hydrocarbons, or additives with phenolic structures, can generate B and T peaks ($E_m < 380$ nm) [78]. The A and M humic-like peaks from MP-FDOM are derived from photolytic products [26], and the regions of peaks A and M ($E_m > 380$ nm)

may also be associated with functional groups such as oxidized quinones and aromatic ketones [79]. While the terms “humic-like” and “protein-like” are used to describe NOM properties, they are also commonly used for convenience in the literature to describe MP-FDOM characteristics. However, it should be emphasized that their meanings differ fundamentally from the same terms used for describing NOM. Future studies using pyrolysis GC/MS and other molecular-level analysis (e.g. FT-ICR-MS) are warranted to better characterize the complex and heterogeneous composition of these plastic-derived fluorescent components [42].

4.4. Implications

This study revealed that temperature is a key environmental factor regulating the leaching rate and composition of MP-FDOM in the marine environment, regardless of whether the plastic is irradiated or under dark conditions. Given seasonal variations and latitudinal differences in ocean temperatures, these new findings provide valuable insights for assessing the impact of DOM release from plastic debris and MPs on marine carbon cycle. During summer, with its accompanying heavy rain in many terrestrial watersheds from tropical to temperate regions, there may be an increased flux of plastic debris and MPs into the ocean due to frequent flooding [80,81]. High temperatures and increased solar irradiation in the warm season will enhance the photodegradation of plastics [69,82]. The combined effect could make summer the season with the greatest release potential of plastic-derived DOM into marine environments. Given the variations of temperature and solar irradiation with latitude, tropical and subtropical regions have greater potential for release of plastic-derived DOM than temperate regions.

In summary, the combination trends of projected global warming and an increasing flux of plastic debris and MPs into the oceans [83] will undoubtedly lead to a continuous increase in the release of plastic-derived DOM in marine environments. This is of particular concern to areas with high plastic density, such as estuaries, coastal regions, and oceanic garbage patches [28]. This is especially important considering that plastics can persist in marine environment on the scale of years to centuries [28,64,82]. In the early 21st century, regions experiencing extreme heatwaves have expanded to encompass approximately 25 % of Earth's oceans [84], making these areas likely hotspots for plastic-derived DOM release. For example, coastal mariculture zones are localized marine areas with high plastic usage [85]. Heatwaves can increase surface water temperature by 2 °C in the East China Sea and 4 °C in the Tasman Sea [36,86]. This magnitude of temperature increase would increase MP-FDOM release rates, based on the calculated Q_{10} values for different MPs (1.62–1.93) in this study, by an estimated 10–14 % to 21–30 %, respectively. This raises concerns about potential negative impacts on mariculture, as research has indicated that MP-FDOM can exhibit toxic effects on various organisms [87–89]. Thus, the risks associated with the temperature sensitivity of microplastic degradation in mariculture environments warrant further investigation.

Our study also found that the temperature sensitivity of DOM release varied among the different MP types. Therefore, a clear understanding of the percentage distribution of plastic debris and MP polymer types is essential to assessing the impact of plastic-derived DOM release on the regional marine carbon cycle [5,90,91]. For example, PP, PE, PS, and PVC are primarily found in European waters, whereas PET, polyacrylonitrile, and polyurethane are the main types in Asian waters [45]. Previous studies have found that MP-FDOM may reshape microbial communities in marine environments and different MP-FDOM compositions showed variable microbial utilization efficiency and transformation pathway [28,29,32]. Thus, the regional differences in the distribution of plastic debris and MPs may restructure different interrelationships between MP-FDOM and the microbiome, thereby imposing potential consequences on marine trophodynamics and biogeochemical cycling [92].

There are some limitations in our study that deserve future

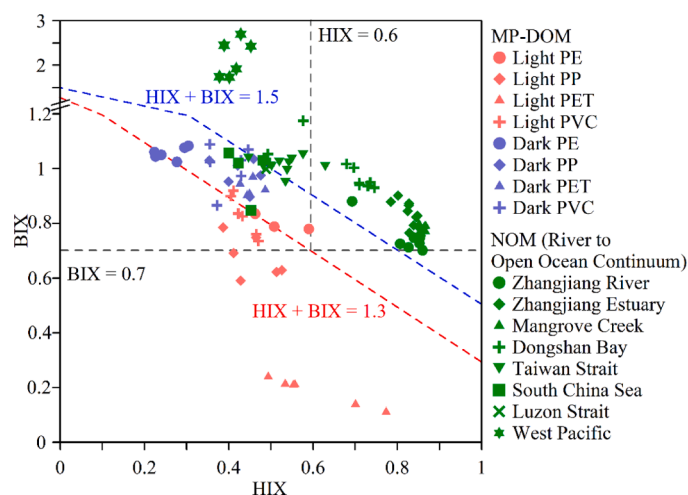


Fig. 5. Plots of HIX and BIX for MP-FDOM incubated under UV light (red symbols) in the dark (blue) and for NOM from various sources along a salinity continuum from rivers to the open ocean (green, Fig. S7, [74]). All MP-FDOM data are the average of triplicate incubations.

considerations. First, the utilization of artificial seawater may neglect the potential interactions between MP-DOM and NOM or the microbial communities present in natural waters. Second, using a fixed UV intensity does not fully account for latitudinal variations in solar radiation. Future studies are warranted to address synergistic effects among multiple degradation-related factors (e.g., temperature, salinity, pH, UV light intensity) is warranted as they are critical for understanding the complexity of real-world DOM cycling. Finally, our experiments focused only on the photodegradation pathway. Future research should evaluate interacting degradation pathways, such as incorporating biodegradation and mechanical forces by waves. In particular, as aged plastics may release DOC at levels two orders-of-magnitude higher than fresh plastics [29], it is also crucial to investigate the role of plastic aging in marine environment over longer time periods. Conducting field-based enclosure experiments with aged plastics can better simulate the release kinetics of plastic-derived DOM under realistic marine conditions, thereby improving the assessment of the long-term impacts of plastic-derived DOM on marine carbon storage and ecosystems.

5. Conclusions

Our experiments assessed the release of DOC and FDOM from four MPs (PE, PP, PET, and PVC) in seawater at six temperatures (10–35 °C). Rates of DOC release from UV-irradiated samples ranged from 0.06 ± 0.01 to 0.61 ± 0.07 mg-C/g-MP/wk. At a given temperature, MP polymer types predominantly affected the MP-DOC rate, following an order of PE>PET>PP>PVC. The PARAFAC model identified the distinct components of FDOM as similar to two humic-like components (C1 and C4) and two protein-like components (C2 and C3). The fluorescent components of MP-DOM differed from those of NOM from rivers to the open ocean, which can be distinguished by using the HIX-BIX spectral index pair. The photobleaching of MP-FDOM contrasted with that of MP-DOC, which may be attributed to the varying backbone structures, carbon contents, and photoreactivity of the different MP types. Temperature gradient experiments (10–35 °C) confirmed temperature as a key factor regulating the photobleaching of MP-DOC, with DOC leaching rates increasing exponentially with rising temperature. Warming affected the DOC leaching rate from PET most strongly, followed by PE, and had the smallest effect on DOC leaching from PVC. With continued oceanic warming, the release of DOM from plastic debris and MPs into the oceans are predicted to rise. This is especially true in areas with high plastic densities, such as estuaries, coastal regions, oceanic garbage patches, and areas prone to marine heatwaves, which are likely to become hotspots for plastic-derived DOM release.

Environmental implication

Plastic pollution is a critical international concern in the global oceans. The substantial release of microplastics (MPs) into the marine environment is now deeply integrated into Earth's carbon cycle. This study reveals that different MPs have variable photobleaching rates of dissolved organic carbon (MP-DOC) and fluorescent dissolved organic matter (MP-FDOM). Warming exponentially increases photobleaching of MP-DOC and MP-FDOM. These findings highlight the need for incorporating ocean warming and frequent heatwaves into predicting the effects of plastic pollution and degradation on the marine carbon cycle and ecosystems, particularly in estuarine, coastal and oceanic garbage patch regions.

CRediT authorship contribution statement

Yan Li: Writing – review & editing, Conceptualization. **Randy A. Dahlgren:** Writing – review & editing, Conceptualization. **Liyin Qu:** Writing – review & editing. **Dezhong Wang:** Software, Methodology, Data curation. **Xiaoxia Cai:** Writing – original draft, Validation, Software, Methodology, Investigation, Data curation, Conceptualization.

Xinhong Wang: Writing – review & editing. **Xufeng Xie:** Software, Methodology, Formal analysis, Data curation. **Weidong Guo:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2025.139079.

Data Availability

Data will be made available on request.

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