



Characteristics of microplastic polymer-derived dissolved organic matter and its potential as a disinfection byproduct precursor

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ARTICLE INFO

Article history:

Received 29 November 2019

Received in revised form

27 February 2020

Accepted 28 February 2020

Available online 4 March 2020

Keywords:

Microplastics

Dissolved organic matter

Polymers

Molecular size distribution

Trihalomethanes (THMs)

ABSTRACT

Although there are numerous studies concerning the occurrence of microplastics (MP) in the environment and its impact on the ecosystem, dissolved organic matter (DOM) leached from MP (MP-DOM) has received little attention, and its characteristics have been rarely examined. It is presumed that the DOM leaching from plastics could be accelerated when plastics lost their protective additives during their transport and weathering processes in aquatic systems. In this study, two additive-free MPs (or micro-sized plastic polymers) were leached in artificial freshwater under UV irradiation and dark conditions. The leached DOM was characterized by typical analyses for naturally occurring DOM (N-DOM) such as dissolved organic carbon (DOC), size exclusion chromatography (SEC), and Fourier-transform infrared spectroscopy (FTIR). The potential to generate trihalomethanes (THMs), a well-known environmental impact of N-DOM, was also explored for the DOM with plastic origins for the first time. The leaching results demonstrated that UV irradiation promoted the leaching of DOM from the plastic polymers with an amount corresponding to ~3% of the total mass of the polymers. The leached amounts were much greater than those previously reported using commercial plastics which presumably contained protective additives. The SEC results revealed that, different from typical aquatic N-DOM, MP-DOM is mostly composed of low molecular weight fractions <350 Da. For the two polymer types (polyethylene and polypropylene), the MP-DOM exhibited a high potential to form THMs upon chlorination, which was comparable to those of typical aquatic N-DOM. This study highlighted an overlooked contribution of UV irradiation to the DOM leaching from additive-free plastics and the potential risk of MP-DOM to produce toxic disinfection byproducts (DBPs) upon chlorination.

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1. Introduction

The massive production of plastics poses serious risks for the environment and the global ecosystems due to the limited recycling and improper disposal. Approximately 270,000 tons of plastics and more than 5 trillion plastic pieces are currently floating in the world's oceans (Eriksen et al., 2014). During its transport to the ocean through rivers or coastal systems, most disposed plastics are subjected to natural abiotic degradation processes involving chemical and mechanical reactions, which are collectively called weathering, leading to the fragmentation of the plastics (Weinstein et al., 2016; Song et al., 2017). Plastic particles with the size of <5 mm, the so-called microplastics (MPs), have received

tremendous attention in recent years (Law and Thompson, 2014; Jambeck et al., 2015; Siegfried et al., 2017). These small-sized plastic debris are ubiquitous in natural aquatic systems such as freshwater, coastal systems and open oceans (Wagner et al., 2014; Eerkes-Medrano et al., 2015; Su et al., 2016; Alimi et al., 2018; Li et al., 2018), as well as in water treatment facilities (Mason et al., 2016).

In addition to the main polymer chains, commercial plastics commonly contain various types of plasticizers and/or antioxidants, termed additives, that protect the principal polymeric chain from breakdown caused by irradiation and weathering. The additives also help to improve the product quality, like ductility and structural stability. It was previously reported that when plastics are in long contact with water, the additives plus the oligomers or monomers from the main polymer chains could be released to the aquatic media (Suhrhoff and Scholz-Böttcher, 2016). Furthermore, with the progress of the fragmentation of plastics, the more production of such nano-sized materials and the more leaching of

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dissolved organic substances from plastics could occur (Lambert and Wagner, 2016). Chemical modifications promoted by UV irradiation may produce structural damage to plastic materials, accelerating the release of dissolved organic compounds (i.e., additives and/or polymer-derived organic substances) (Potthoff et al., 2017). Previous studies have demonstrated the vulnerable property of polymer chains containing low or zero amount of antioxidant additives by tracking the changes in the infrared spectra of the plastic after photo-oxidation (Gardette et al., 2013) or through the mechanical tension test (Ojeda et al., 2011).

To date, most MP studies have focused on particle counting without paying much attention to its potential leaching capacity. Romera-Castillo et al. (2018) have provided a new insight into the overlooked phenomenon by demonstrating that substantial amounts of dissolved organic matter (DOM) were leached from MPs in ambient seawater. It is easily presumed that microplastic-derived DOM (MP-DOM) can be widespread in natural and engineered aquatic systems, while much still remains unknown about the characteristics of the leached DOM and the environmental impacts. It was previously reported that a substantial amount (65 million particles per day) of MPs were released from one treatment facility through effluent water everyday (Murphy et al., 2016). Moreover, there is a possibility that the actual occurrence of MP-DOM could be more pronounced than presumed from the observed number of the MP particles remaining in treatment facilities because weathering of MPs followed by the release of DOM might already take place prior to the removal of MP particles in the treatment systems.

Chlorine is the most widely used disinfection agent in water treatment processes around the world due to its high effectiveness and affordability for the control of pathogens. Many wastewater treatment plants operate a chlorine disinfection treatment prior to the final discharge (Krasner et al., 2008). However, the formation of toxic disinfection byproducts (DBPs) following chlorination of treated water/wastewater is an unavoidable consequence and, arguably, constitutes one of the most critical risks of DOM to aquatic ecosystems and human health. While the DBP formation potentials of naturally occurring DOM (N-DOM) from different origins have been much studied and well documented (Wang et al., 2017; Zhai et al., 2017), no effort has been made to examine the potential of MP-DOM to form DBPs upon chlorination. In addition, considering that MP-DOM co-exist with N-DOM, in the aquatic environment, it is an intriguing question whether or not MP-DOM would behave similarly with aquatic N-DOM in terms of DBP formation potential.

To answer all the questions, this study aimed at characterizing the DOM leached from MP polymers under different environmental settings and the formation potential of DBPs. To the best of the authors' knowledge, there has not been any previous study that examined the DOM derived from additive-free MPs (i.e., MP polymers). The specific tasks of this study were to (1) compare the amounts of DOM leached from MP polymers under dark and UV irradiation conditions, (2) characterize the MP-DOM using the analytical tools for N-DOM including Fourier-transform infrared spectroscopy (FTIR) and size exclusion chromatography with organic carbon detection (SEC-OCD), and (3) explore the possibility of MP-DOM serving as a precursor of trihalomethanes (THMs) upon chlorination.

2. Materials and methods

2.1. Microplastic polymers

Two types of plastic polymers (or additive-free plastics) were used for this study. They are based on polyethylene (PE) and

polypropylene (PP) materials, which were obtained from Sigma Aldrich and Polyscience companies (Asia Pacific, Inc., Taiwan Branch), respectively. Two particle sizes were selected for each MP polymer as 40–48 μm for PE, and 25–85 μm for PP. The choice of the plastic polymers used in this study is based on the previous report of the highest consumption/discharge rate in the world (Geyer et al., 2017) (PE-36%, PP-21%). Furthermore, the two materials have been widely used in the refined forms for many polymer studies (Beckingham and Ghosh, 2017; Paço et al., 2017).

2.2. Microplastic polymer leaching experiments

Three different factors, which might affect the leached amounts of DOM from the two polymers, were taken into account for the leaching experiments. They were i) the mass of MP per water volume (0.1–2.0 g-MP L^{-1}), ii) contact time with water or leaching time (1 h–14 days), and iii) UV irradiation.

The applied amounts of the plastic polymers, which are expressed by the mass per water volume, were referred to the observed ranges previously reported in relevant studies (Suhrhoff and Scholz-Böttcher, 2016). Since this study aimed to characterize the DOM leached from plastic polymers, the added amounts of MP were intentionally designed to be higher than the values reported in natural water environment (Alimi et al., 2018). For the experiments, an aqueous solution was prepared to have the ion composition similar to a typical freshwater, which consists of NaHCO_3 (96 mg L^{-1}), CaSO_4 (47.4 mg L^{-1}), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (122.86 mg L^{-1}), and KCl (4 mg L^{-1}), according to the U.S. Environmental Protection Agency (EPA) protocol (EPA-821-R-02-013) (Edition, 2002). The MP polymers were added in powder-like form to 50 mL of the artificial freshwater in sterilized glass vials ($n = 237$), which were autoclaved at 120 $^\circ\text{C}$ for 15 min. The vials were placed in the dark on a shaker at 150 rpm and each vial was sacrificed for sampling at designated contact times during the 14 days of the leaching test. Controls were also prepared following the same procedure without the addition of the polymers. The mixing solution with the suspended particles was filtered through a pre-ashed Whatman GF/F filter to obtain the MP-DOM. In the filtration step, a glassware vacuum filtration device was used instead of a syringe filter to minimize further contact with other plastic materials. All the experiments were performed in triplicate.

For a UV irradiation setup, 50 mL of the artificial freshwater solution containing 50 mg of PE or PP polymers with $<100 \mu\text{m}$ particle diameter were prepared in 14 autoclaved cylindrical quartz tubes (125 mL) with an inner diameter of 4.5 cm and a height of 8 cm. A stirrer was placed in the bottom of each quartz tube to achieve continual mixing throughout the 14-day leaching test. The tubes were placed in the middle of a close cabinet surrounded inside by six 8W-UVA lamps with the characteristic wavelengths at 320–400 nm (Sankyo Denki, F8T5BL) as light sources (Fig. S1). The light intensity in the closed cabinet was equivalent to that of natural solar light at noon time in May (Seoul, South Korea) (Lee et al., 2018b), which was approximately 4000 $\mu\text{W cm}^{-2}$ based on an ultraviolet UV meter (Model 850009, Sper Scientific). The reactor temperature was maintained at $25 \pm 3 \text{ }^\circ\text{C}$ by circulating cooling air with fans attached to the system (Phong and Hur, 2015).

2.3. Analytical measurements

2.3.1. FTIR spectroscopy

Fourier transform infrared spectroscopy (FTIR) (Nicolet iS10, Thermo Scientific) was used to confirm the MP origins of the DOM samples obtained from the leaching experiments. The FTIR analysis for this study was based on the procedure previously described in Chen et al. (2018). Briefly, 10 mL of the filtered DOM sample was

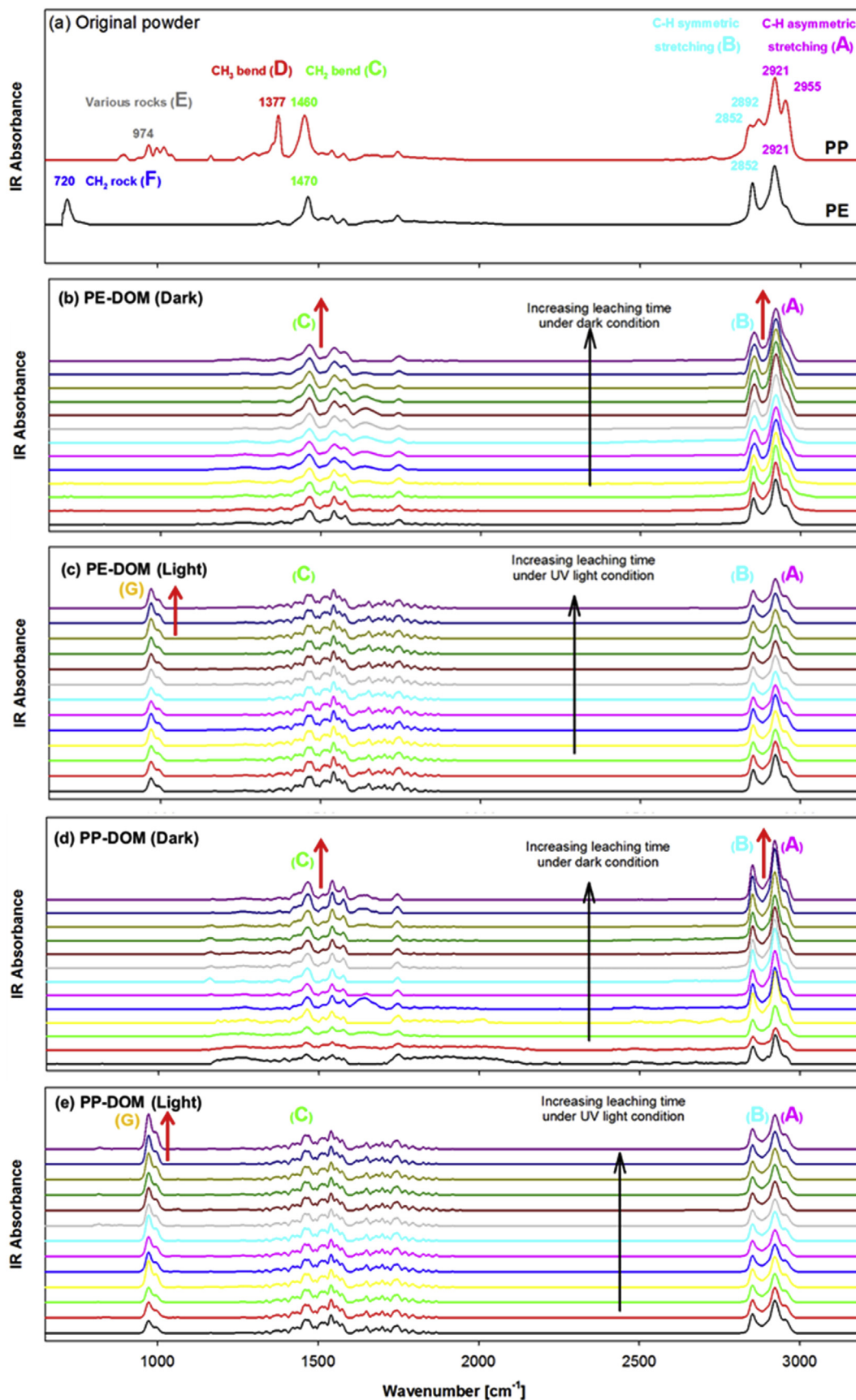


Fig. 1. FTIR absorbance spectra of: (a) the original microplastic polymers. (b–e) Variations of the DOM from PE (PE-DOM) and PP (PP-DOM) polymers with leaching time for dark (b and d) and light treatments (c and e). The letters represent the main absorption bands (cm⁻¹) used to identify PP and PE plastic structures in Table S1. The detailed spectra between 1200 and 2000 cm⁻¹ are shown in Fig. S2.

mixed with 100 mg of KBr powder (Sigma Aldrich, FT-IR grade) and freeze-dried for further analysis. As a blank, clean KBr pellets were prepared after a drying step at 105 °C for 2 h. The blank was corrected with a clean KBr pellet and the scanned wavenumber range was set at 650 to 4000 cm^{-1} . Each FTIR spectrum was corrected for baseline shifts and was smoothed using Origin 9.0 software (12 point, Savitzky-Golay method). FTIR peak intensities were normalized by the summed value of all peaks (Yang et al., 2015).

2.3.2. Dissolved organic carbon (DOC) determination

DOC concentrations were determined based on five measurements of each sample using a TOC analyzer (Shimadzu L-series, TOC-CHP, Japan). Samples for DOC analyses were collected in pre-combusted 40 mL glass vials. They were acidified with 1 M HCl solution to a pH of ~2.0 and stored at 4 °C until analysis. A standard stock solution using potassium hydrogen phthalate (KHP) for DOC measurements was prepared at a low concentration (i.e., 1.06 mg KHP L^{-1} or ~0.5 mg C L^{-1}) and tested daily. The relative analytical accuracy was determined to be <2%.

2.3.3. Determination of DOM molecular size distributions

Different size fractions of MP-DOM samples were quantified by a high-performance liquid chromatography system (S-100, Knauer, Berlin, Germany) equipped with an organic carbon detector (OCD) and a size exclusion column (250 mm \times 20 mm, TSK HW 50S). The detailed analytical procedure is available elsewhere (Huber et al., 2011; Chen et al., 2016). In brief, DOM samples were further filtered through 0.45 μm PES-filter (Sartorius, Germany, #16357) before they were passed through the column filled with a mobile phase consisting of a purified phosphate buffer (pH 6.85, 2.5 g $\text{KH}_2\text{PO}_4 + 1.5 \text{ g Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ in 1L) at a flow rate of 1.1 mL min^{-1} . The assignments and the quantification of five different size fractions, which include biopolymer (BP), humic substances (HS), building blocks (BB), low molecular weight acids (LMWA), and low molecular weight neutrals (LMWN), were based on an established procedure (Huber et al., 2011) and the in-built software. The SEC analysis was performed on one representative sample for the three replicates.

2.4. Trihalomethanes formation potential (THMFP) measurement for MP-DOM

The trihalomethanes (THM) formation potentials (THMFP) of MP-DOM samples were determined following the standard methods (5710B, 6232B, and 6251B) but with some modifications (Lee et al., 2018a). The MP-DOM samples obtained under UV irradiation condition were diluted with ultrapure water to have a constant DOC concentration (i.e., 1 mg-C L^{-1}), while those under dark condition were used as they were because of the low concentrations. The pH was adjusted to 7.0 with the addition of 1 mL of phosphate buffer per 50 mL of sample. Chlorination was performed by adding sodium hypochlorite to the DOM samples to achieve a sufficient chlorine dosage (NaOCl , Sigma Aldrich, 6–14% available chlorine) of 5 $\text{mg-Cl}_2 \text{ mg-C}^{-1}$. The samples were incubated head space-free at 25 °C in the dark for 72 h. The THMs were operationally defined as four species (Cl_3CH , Cl_2BrCH , ClBr_2CH , and Br_3CH) formed upon chlorination. The THM species were extracted using liquid-liquid extraction based on methyl tert butyl ether with 1,3 dipropomopropane (200 $\mu\text{g L}^{-1}$) added as an internal standard. The concentrations of extracted THMs were determined using a gas chromatography (Agilent 7890A, USA) with a micro electron capture detector in accordance with modified versions of US EPA methods 551.1 and 552.3, following the method described in Park et al. (2016).

3. Results and discussion

3.1. Identification of the origins of MP-DOM

Infrared spectroscopy is a proven and reliable analytical technique for identifying the polymeric composition of MPs (Gorassini et al., 2016; Jung et al., 2018). The two MP polymers used in this study presented distinct spectral features with the appearance of A, B, C, and F peaks for PE, and A, B, C, D, and E peaks for PP in the FTIR spectra (Fig. 1a and Table S1). A, B, and C peaks, which originate from the carbon chains of repeating $-\text{CH}_2-$ units, were commonly observed for the spectra of both MP polymers. Meanwhile, structural differences were found between PE and PP, which were characterized by the exclusive presence of D (i.e., CH_3 band) and F (i.e., CH_2 rock band) peaks for PP and PE, respectively.

The FTIR spectra of the DOM samples from leaching experiments evidenced the origins of the two MP polymers (Fig. 1 and S2). Regardless of the polymer type, the C–H bands were observed in the DOM samples with a slight increasing trend of the peak intensity with leaching time under the dark condition (Fig. 1b–d). The same approach using FTIR spectra for the identification of MP-DOM has been adopted in a previous study using polymer powders (Jung et al., 2018). For this study, unlike the polymers presenting distinct spectral features between PE and PP, the MP-DOM did not exhibit any obvious difference between the IR spectra of the two polymer types. These results indicate that the carbon structures of the MP-DOM might be similar despite the different plastic origins (or polymer types).

According to a previous report on the photo-chemically induced oxidation of polyolefin (Bracco et al., 2018), UV irradiation is likely to induce various modifications on polymer structures such as cross linking, chain branching, and oxidative degradation. In this study, peaks A, B, and C were observed in the MP-DOM samples after UV irradiation as well as in the dark treatments, even though the peaks were less prominent than those in the dark. The most striking difference in the FTIR spectra between the two treatments was the unique appearance of Peak G, consisting of the vinyl unsaturated bands at 973 and 996 cm^{-1} , in the irradiated samples. Peak G showed an increasing trend with irradiation time, indicative of its association with UV irradiation. The observation can be attributed to the generation of photolytic byproducts from the MP polymers by photochemical cleavage (Fig. 1c–e), or the so-called Norrish reactions (Gardette et al., 2013). However, there were no notable changes in the range of double bonds (H peak, 1640–1780 cm^{-1} , ketones, carboxylic acids, esters, and lactones) of the MP-DOM along the irradiation time even though the bands have been reported to be related to typical routes of the Norrish reactions (Figs. S2b and S2d) (Gardette et al., 2013; Bracco et al., 2018). Further studies are warranted to examine the exact photochemical reactions involving the DOM leaching under UV irradiation.

3.2. Factors affecting the amounts of MP-DOM

3.2.1. Effects of MP dose, polymer type, and leaching time

DOM leaching behavior under dark condition was evaluated in terms of MP concentration and different polymer types (Fig. S3). The released DOM amounts showed a general increasing trend with a higher dose of plastic. For example, the DOC concentrations of the MP-DOM changed from 66.5 to 390.4 $\mu\text{g-C L}^{-1}$ with increasing dose from 0.1 g L^{-1} to 2.0 g L^{-1} of the PE polymer after 7 days of leaching. The enhancing effect of MP dose on DOM leaching was further supported by the significant correlations between the DOC concentrations and the doses of the MP polymers with the R^2 values of 0.871 ($p < 0.001$, $n = 20$) for PE and 0.784 ($p < 0.001$, $n = 20$) for PP (Fig. S3). The average released amounts of MP-DOM after 7 days of

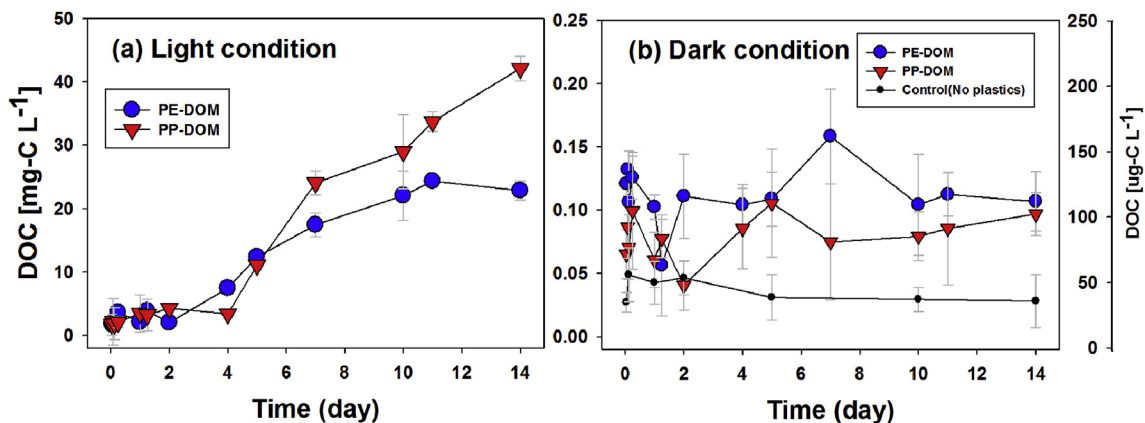


Fig. 2. Changes in dissolved organic carbon (DOC) concentrations of DOM leached from PE and PP microplastic polymers (1 g-MP L⁻¹, <100 μm in diameter), and the control samples (i.e., no microplastics added) during leaching experiments under (a) UV irradiation and (b) dark conditions. The error bars represent the standard errors based on three replicate samples.

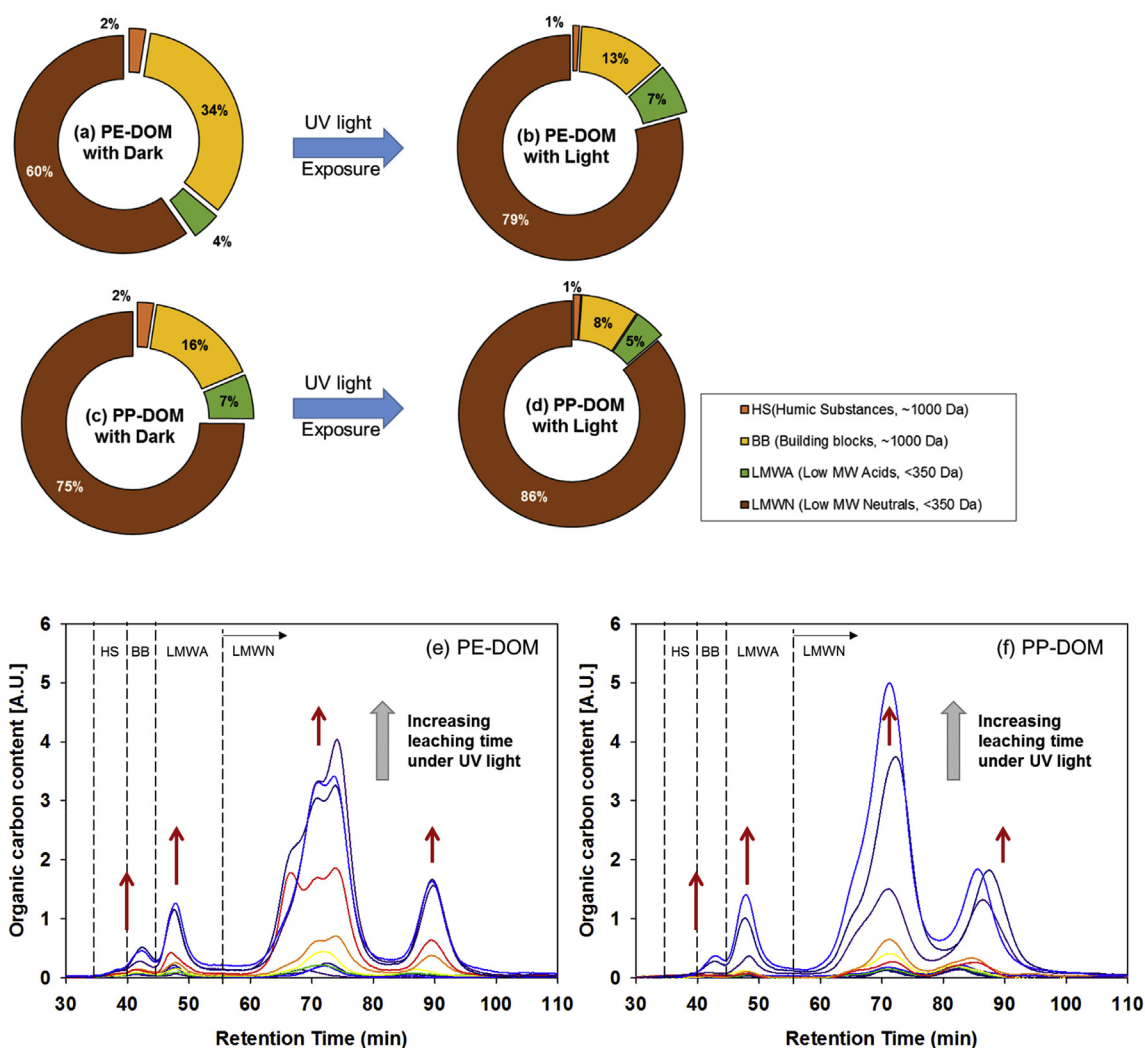


Fig. 3. Relative abundances (%) of four different size fractions of the DOM from PE polymer (PE-DOM) under (a) the dark and (b) the UV irradiation conditions, and those from PP polymer (PP-DOM) under (c) the dark and (d) the UV irradiation conditions. The percent areas in the pie charts are based on the median values of the different size fractions in the MP-DOM obtained after 14 days of leaching. Changes in the SEC chromatograms of MP-DOM with leaching time for (e) PE-DOM and (f) PP-DOM under the UV irradiation condition.

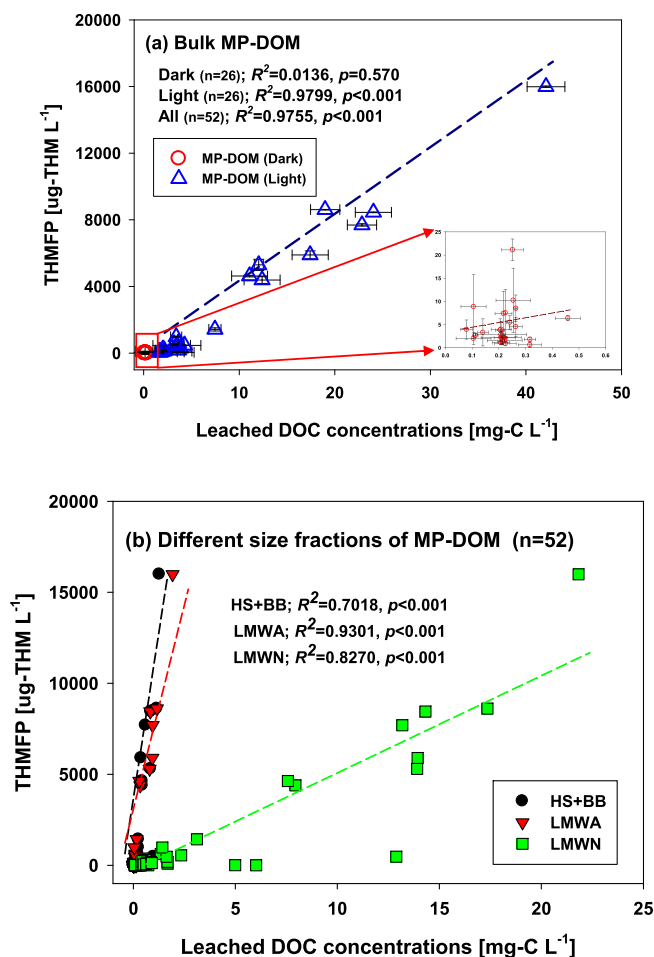


Fig. 4. (a) Correlation between total THM formation potentials and the DOC concentrations of the bulk leached MP-DOM; (b) the DOC concentrations of three individual size fractions (HS + BB, LMWA, and LMWN) of leached MP-DOM. The error bars indicate the standard deviations of the values.

leaching were $368 \pm 17 \mu\text{g-C g}^{-1}$ for PE ($n = 10$) and $93 \pm 4 \mu\text{g-C g}^{-1}$ ($n = 10$) for PP, in DOC per gram of polymers, which were equivalent to $\sim 0.03\%$ of the total mass of the MP polymers used. Although the leached amount is very small per MPs, it cannot be neglected considering the tremendous occurrence of MPs in the aquatic environments. Romera-Castillo et al. (2018) have reported that globally up to 23,600 metric tons of DOC might be leached from plastic entering the ocean per year. Meanwhile, the released DOC concentrations from PE (i.e., PE-DOM) was nearly four times higher than those from PP (i.e., PP-DOM) at all polymer doses (Fig. S3), suggesting the DOM leaching concentrations are highly dependent upon the polymer types. The PE chains appear to be more vulnerable in a water environment than the PP chains. This trend agreed well with a previous report (Romera-Castillo et al., 2018), in which low density PE (LDPE) and high density PE (HDPE) released higher concentrations of DOC (between 2.79 and 8.92 $\mu\text{g-C cm}^{-2}$) than PP (1.61 $\mu\text{g-C cm}^{-2}$) in the dark.

For both polymer types, leaching time (or contact time) was not likely to be a critical factor to influence the amounts of MP-DOM released, since no significant difference (Paired t -test, $p = 0.07$, $n = 40$) were observed in the leached DOC concentrations after an instantaneous contact with water versus a 7-days contact. For example, the instantaneously leached DOC concentrations were

equivalent to 84–90% of the total amounts leached after 7 days (Fig. S3). The same trend was also reported in a previous study (Romera-Castillo et al., 2018), which demonstrated that instantaneously leached DOM amounts from commercial plastics corresponded to $60 \pm 26\%$ of those after 7 days. In some cases, the immediately released DOC concentration was even higher than that observed after 7 days of leaching (e.g., 302.8 $\mu\text{g-C L}^{-1}$ versus 226.1 $\mu\text{g-C L}^{-1}$ when 1 g of the PE polymer per liter was used). The reversed DOC concentration trend for longer time of contact between MPs and water might be explained by the adsorption of the initially released DOC onto the surface of the MPs (Bakir et al., 2014; Curran and Strlič, 2015).

3.2.2. Effect of UV irradiation

In contrast to the dark treatment, changes in the MP-DOM concentrations with leaching time was more obvious and dramatic under UV irradiation (Fig. 2), which indicates the stimulating effect of UV light on the production of MP-DOM from the two polymers. After 14 days of irradiation, the DOC concentrations of the MP-DOM became nearly 100-times greater than those under the dark condition (Fig. 2a versus 2b), suggesting that UV irradiation might play a role in changing the MP polymers into more vulnerable structures to dissolution. The released amounts of MP-DOM after 7 days of leaching were 22.8 mg-C g^{-1} for PE and 42.1 mg-C g^{-1} for PP (in DOC per gram of polymers), which were equivalent to an average of 3.2% of the total mass of the MP polymers. Similar structural instability of the polymer materials under UV light was previously reported in a study that documented substantial changes in the IR spectra of polymer film after direct UV irradiation (Gardette et al., 2013).

For this study, the additional MP-DOM leaching upon UV irradiation was more pronounced for the PP- versus the PE-polymer with the leached concentrations corresponding to $\sim 42.1 \text{ mg-C L}^{-1}$ (PP-DOM) versus $\sim 22.9 \text{ mg-C L}^{-1}$ (PE-DOM) at the end of the irradiation (i.e., 14 days). Song et al. (2017) also demonstrated the similar trend in the fragmentation of plastics, establishing a higher rate for PP versus PE materials under UV exposure lasting for 12 months. The difference was attributed to the presence of alkyl groups on the PP polymer as alkyl radicals are more likely to be formed from the polymers with longer alkyl chains under UV irradiation (Aslanzadeh and Haghghat Kish, 2010; Rajakumar et al., 2012). It is notable that such a UV irradiation-stimulated MP-DOM leaching was not previously reported for additive-containing plastics (Suhrhoff and Scholz-Böttcher, 2016). It is likely that the antioxidants, serving as the main component of the additives in commercial plastics, might protect the basic polymer chains from being broken down by the UV light. The accelerated MP-DOM leaching under UV irradiation in this study strongly imply that the absence or partial loss of additives from MPs could promote the production of MP-DOM in aquatic systems under UV irradiation. Since commercial plastics contain 20 additives on average, which constitutes $<1\%$ – 60% of the total mass of the plastic material (Bilitewski et al., 2012), the released amounts of MP-DOM per mass of plastic could be highly variable across different types of plastics.

3.3. Molecular size characteristics of MP-DOM

Three different size fractions were identified in the MP-DOM from the polymers (Fig. 3), which included operationally defined HS, BB, LMWA, and LMWN size fractions. Irrespective of the polymer type and the experimental conditions (i.e., dark/light), LMWN ($<350 \text{ Da}$) was the predominant fraction, constituting 61–87% of the total leached DOM (Fig. S5). This observation was in contrast with a typical pattern of aquatic N-DOM characterized by a lower distribution of LMWN (Suwannee River NOM: 14%, Paldang Lake:

Table 1

Comparison of specific (or DOC-normalized) THMF values of MP-DOM with those of typical aquatic natural organic matter (NOM) in previous reports.

Sources	Condition (Chlorination) [mg-Cl mg-C ⁻¹]	Condition (Contact time, Temperature) [Day], [°C]	SUVA	Specific THMFP	Literatures	
			[L/mg-C/m]	[µg-THM mg-C ⁻¹]		
MP	PE-DOM (Dark)	5	3, 25	0.50–5.29	3.8–84.0	In this study
	PE-DOM (Light)			1.66–9.25	40.3–439.8	
	PP-DOM (Dark)			0.68–7.04	1.9–109.6	
	PP-DOM (Light)			5.32–10.62	29.2–453.3	
Rivers	2–4	7, 25		1.8–11.4	108–192	(Kraus et al., 2010)
	1–4	7, 25		3.1 ± 0.4	72.1 ± 12.7	Engelage et al. (2009)
	1 ± 0.4	1, 25		2.2–5.0	25.8–42.2	Zhang et al. (2011)
	4	3, 25 ± 1		1.83–2.03	13.0–71.3 ^a	Hao et al. (2017)
	1.5	7, n.m.		4.55–17.82	37.3–71.3 ^a	Alver et al. (2018)
Lake/Reservoir	1 ± 0.4	1, 25		1.7	35.5	Lake Zhang et al. (2011)
	1 ± 0.4	1, 25		0.9–2.7	9.4–36.5	Reservoir Zhang et al. (2011)
	5	7, 25		1.5–7.1	80–400 ^a	Reservoir Brooks et al. (2015)
	5	1, 25		3.14–5.11	~132.2 ^a	Reservoir Padhi et al. (2019)
Other sources	1–4	7, 25		3.4 ± 0.4	68.7 ± 10.7	Agricultural drain Engelage et al. (2009)
	1–4	7, 25		3.2 ± 0.5	80.9 ± 14.8	Wetland Engelage et al. (2009)
	5	7, 25		4.2 ± 0.2	121 ± 10	Water Treatment Plant (WTP) Gough et al. (2014)
	5	7, 25		0.53–9.17	3.2–312.7	Water Treatment Plant (WTP) Golea et al. (2017)
	20 [mg-Cl ₂ L ⁻¹]	3, n.m.		1.6–2.3	32.9–61.0 ^a	Effluent water Meng et al. (2016)

n.m.: Not mentioned.

^a The specific THMFP values were calculated by dividing the reported total THM values with the corresponding DOC concentrations.

38%, Han River: 29%) versus HS fraction (Fig. S4). The SEC result of the MP-DOM was in line with a previous study using mass spectroscopy that detected the occurrence of homogeneous *n*-alkanes (between C₁₂ and C₃₂) in an aqueous phase when commercial PE was placed in contact with water (Suhroff and Scholz-Böttcher, 2016). These chains represent low-molecular weight oligomers (Simoneit et al., 2005). Under UV irradiation, the concentrations of all identified size fractions increased with the irradiation time for both PP-DOM and PE-DOM. (Fig. 3e and f). The most pronounced increasing trend was observed in the LMWN fraction, which led to changes in the proportion of the LMWN from 61% to 80%, for PE-DOM, and from 77% to 87%, for PP-DOM, over 14 days of leaching. Correspondingly, the larger molecular size fraction (i.e., HS + BB) exhibited slowly decreasing trends in their relative abundance with irradiation time (Figs. S5a and S5b). These results suggest that among the identified fractions, the LMWN one might be the most associated with the structures of plastics which are vulnerable to photo-oxidation. The large sized molecules (e.g., HS + BB fraction), particularly from PE-DOM, seem to undergo partial degradation to smaller size species under UV irradiation, as indicated by a strong negative correlation between HS + BB (%) and LMWN (%) ($R^2 = 0.9259$, $p < 0.001$, $n = 26$) (Fig. S5c). This explanation is consistent with many prior studies that reported that UV radiation preferentially attacked double-bonded structures of organic matters and ultimately altered large sized molecules into smaller fractions (Sanly et al., 2007; Choi and Choi, 2010; Maizel and Remucal, 2017). The relatively greater abundance of LMWN fractions in DOM from reservoirs and wetland versus rivers has been ascribed to strong photo-degradation of large sized DOM molecules in the shallow and transparent freshwater environments (Liu et al., 2010).

3.4. Potential impacts about MP-DOM as DBPs precursor

In this study, THMFP of the MP-DOM was examined for the first time and the measured values were compared with those of aquatic N-DOM previously reported. This investigation deserves special attention because MPs are ubiquitous in substantial quantities in many aquatic systems including water/wastewater treatment

facilities (Carr et al., 2016; Murphy et al., 2016). It was surprising to observe substantial levels of THMs detected upon chlorination of the MP-DOM independently of whether the polymers were previously irradiated or not (Fig. 4). Chloroform (CHCl₃) was the only THM species detected from the MP-DOM. Furthermore, similar to the trends of DOC, the THMFP values were much higher for the MP-DOM under the UV irradiation versus the dark condition. After 14 days of irradiation, the THMFP values became $\sim 7697 \pm 75$ µg-THM L⁻¹ for PE-DOM and $\sim 15,990 \pm 42$ µg-THM L⁻¹ for PP-DOM, while the values under the dark condition were $\sim 21 \pm 2$ µg-THM L⁻¹ for PE-DOM and $\sim 22 \pm 4$ µg-THM L⁻¹ for PP-DOM at the same leaching time.

The leached DOC obtained under UV irradiation, either with PE or PP, presented a strong positive correlation with the total THMFP ($R^2 = 0.9799$, $p < 0.001$, $n = 26$) (Fig. 4a). In contrast, there was no significant correlation between the two parameters in the dark treatments ($p = 0.570$), which can be attributed in part, to the very low DOC concentrations and the large uncertainties associated with the values (Fig. 4a). These results indicate that UV irradiation can play a critical role in raising the risk associated with DBP formation from MP-DOM. Such positive linear relationships for the total THMFP were also observed for the individual size fractions of MP-DOM (i.e., HS + BB, LMWA, and LMWN) (Fig. 4b, Table S2). Among the size fractions, the LMWA exhibited the strongest correlation between the leached DOC and the total THMFP ($R^2 = 0.9301$, $p < 0.001$, $n = 52$). Interestingly, a similar trend has also been reported in a previous study based on aquatic N-DOM, which showed that the LMW fractions of river DOM obtained using ultra filtration (<500 Da) produced more THMs than other larger size MW fractions did (Zhao et al., 2006).

The DOC-normalized THM formation potential (or specific THMFP) of the MP-DOM were compared with those of other aquatic N-DOM in previous literatures (Table 1). Under a similar chlorination condition (i.e., 5 mg-Cl mg-C⁻¹ for a 3-day incubation at 25 °C), and irrespective of the leaching conditions (i.e., light or dark) the MP-DOM, presented comparable or even greater potentials towards THM formation per DOC than those of typical aquatic N-DOM independently of whether they were sourced from rivers or from lakes (Hao et al., 2017). The MP-DOM obtained under UV irradiation

exhibited a higher range of THMFPS per DOC than those under dark conditions (40.3–440 vs. 3.8–84 $\mu\text{g-THM mg-C}^{-1}$ for PE-DOM and 29.2–453.3 vs. 1.9–109.6 $\mu\text{g-THM mg-C}^{-1}$ for PP-DOM) (Paired *t*-test, $p = 0.001$). The result suggests that the organic byproducts from the photochemical breakdown of the MP polymers probably have a strong tendency to form THMs upon chlorination. Meanwhile, no significant differences were found in the specific THMFPS between the two MP polymers (Paired *t*-test, $p = 0.109$), signifying no discrimination between the polymer types in the THMFP.

3.5. Environmental implications

This study highlights the critical protective role of plastic additives in DOM leaching from plastic materials under UV irradiation as indicated by the higher leaching under UV irradiation versus dark condition. The finding is significant because plastics may lose their additives due to physical and chemical abrasion during their transport in aqueous environments. UV irradiation condition can be a common feature of sunlit freshwater systems such as lake and wetland or water treatment systems employing UV irradiation.

This study is the first report quantifying the DBPFP of MP-DOM, which revealed a range of values comparable to those of aquatic N-DOM. This novel finding underscores the need to critically evaluate potable water sources or wastewaters that might contain substantial amounts of MPs prior to the disinfection step. The undesirable generation of DBPs can be even more serious when UV irradiation processes are involved for MPs-containing water. On the other hand, this new finding calls for a re-evaluation of the DBPFP previously attributed to pure N-DOM in the aquatic systems in long contact with plastics under UV light.

This study provided a new insight into the unique characteristics of DOM from MP polymers and raised awareness of the environmental risk associated with the formation of DBPs upon disinfection in treatment facilities. However, to generate more concrete evidence for the reported results, comparative leaching experiments are warranted in future studies with identical settings as reported in this study but using physically or chemically weathered commercial MPs. This effort would further clarify the differences in the degree of the DOM leaching from MPs with versus without additives, and in the related environmental impacts.

4. Conclusions

Leaching behaviors of PE and PP plastic polymers were examined under UV light and dark conditions and the leached MP-DOM was characterized in terms of DOC concentrations, functional groups, molecular size distributions, and THMFPS. The characteristics were compared with those of typical aquatic N-DOM. The following main conclusions can be drawn based on the results of this study.

- (1) UV irradiation accelerated the DOM leaching from two common plastic polymers. The vulnerable property to UV light was more pronounced for PP versus PE polymer.
- (2) Irrespective of polymer type, UV irradiation-induced MP-DOM exhibited the presence of a unique functional group related to vinyl unsaturated bond in the structure, which showed an increasing trend with irradiation.
- (3) MP-DOM was characterized by a predominant distribution of LMWN size fraction (<350 Da) and small presence of HS + BB fraction, which contrasts with the typical feature of aquatic N-DOM with prevailing distribution of large size molecules. Among the three size fractions, the LMWN was the most

associated with the production of MP-DOM molecules accelerated by UV irradiation.

- (4) MP-DOM exhibited a high potential to generate THMs and the DOC-normalized THMFP was comparable to those of aquatic N-DOM reported in the literature, suggesting that MP-DOM can act as a significant precursor of DBPs upon chlorination. The specific THMFP values tended to be higher for MP-DOM produced under UV irradiation compared to those under dark conditions.

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.

Acknowledgements

This work was supported by grants from the National Research Foundation of Korea funded by the Korean government (2020R1A2C2007248, 2020R1A4A2002823, and NRF-2017-Fostering Core Leaders of the Future Basic Science Program/Global Ph.D. Fellowship Program). C.R.-C. thanks ComFuturo Program from Fundación General CSIC. We are also especially grateful to Dr. Ikechukwu A. Ike for his careful English proofreading.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.watres.2020.115678>.

References

- Alimi, O.S., Farner Budarz, J., Hernandez, L.M., Tufenkji, N., 2018. Microplastics and nanoplastics in aquatic environments: aggregation, deposition, and enhanced contaminant transport. *Environ. Sci. Technol.* 52, 1704–1724.
- Alver, Alper, Baştürk, Emine, Kılıç, Ahmet, 2018. Disinfection By-Products Formation Potential Along the Melendiz River, Turkey; Associated Water Quality Parameters and Non-Linear Prediction Model. *Int. J. Environ. Res.* 12, 909–919.
- Aslanzadeh, S., Haghghat Kish, M., 2010. Photo-oxidation of polypropylene fibers exposed to short wavelength UV radiations. *Fibers Polym.* 11, 710–718.
- Bakir, A., Rowland, S.J., Thompson, R.C., 2014. Transport of persistent organic pollutants by microplastics in estuarine conditions. *Estuar. Coast Shelf Sci.* 140, 14–21.
- Beckingham, B., Ghosh, U., 2017. Differential bioavailability of polychlorinated biphenyls associated with environmental particles: microplastic in comparison to wood, coal and biochar. *Environ. Pollut.* 220, 150–158.
- Bilitewski, B., Darbra, R.M., Barcelo, D., 2012. Global Risk-Based Management of Chemical Additives I: Production, Usage and Environmental Occurrence. Springer Science & Business Media.
- Bracco, P., Costa, L., Luda, M.P., Billingham, N., 2018. A review of experimental studies of the role of free-radicals in polyethylene oxidation. *Polym. Degrad. Stab.* 155, 67–68.
- Brooks, Emma, Freeman, Christopher, Gough, Rachel, Holliman, Peter J., 2015. Tracing dissolved organic carbon and trihalomethane formation potential between source water and finished drinking water at a lowland and an upland UK catchment. *Sci. Total Environ.* 537, 203–212.
- Carr, S.A., Liu, J., Tesoro, A.G., 2016. Transport and fate of microplastic particles in wastewater treatment plants. *Water Res.* 91, 174–182.
- Chen, M., He, W., Choi, I., Hur, J., 2016. Tracking the monthly changes of dissolved organic matter composition in a newly constructed reservoir and its tributaries during the initial impounding period. *Environ. Sci. Pollut. Control Ser.* 23, 1274–1283.
- Chen, W., Ouyang, Z.-Y., Qian, C., Yu, H.-Q., 2018. Induced structural changes of humic acid by exposure of polystyrene microplastics: a spectroscopic insight. *Environ. Pollut.* 233, 1–7.
- Choi, Y., Choi, Y.-j., 2010. The effects of UV disinfection on drinking water quality in distribution systems. *Water Res.* 44, 115–122.
- Curran, K., Strlic, M., 2015. Polymers and volatiles: using VOC analysis for the conservation of plastic and rubber objects. *Stud. Conserv.* 60, 1–14.
- Edition, F., 2002. Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms.
- Eerkes-Medrano, D., Thompson, R.C., Aldridge, D.C., 2015. Microplastics in freshwater systems: a review of the emerging threats, identification of knowledge gaps and prioritisation of research needs. *Water Res.* 75, 63–82.

- Engelage, Samantha K, Stringfellow, William T, Letain, Tracy, 2009. Disinfection byproduct formation potentials of wetlands, agricultural drains, and rivers and the effect of biodegradation on trihalomethane precursors. *J. Environ. Qual.* 38, 1901–1908.
- Eriksen, M., Lebreton, L.C., Carson, H.S., Thiel, M., Moore, C.J., Borerro, J.C., Galgani, F., Ryan, P.G., Reisser, J., 2014. Plastic pollution in the world's oceans: more than 5 trillion plastic pieces weighing over 250,000 tons afloat at sea. *PLoS One* 9, e111913.
- Gardette, M., Perthue, A., Gardette, J.-L., Janecska, T., Földes, E., Pukánszky, B., Therias, S., 2013. Photo-and thermal-oxidation of polyethylene: comparison of mechanisms and influence of unsaturation content. *Polym. Degrad. Stabil.* 98, 2383–2390.
- Geyer, Roland, Jambeck, Jenna R, Law, Kara Lavender, 2017. Production, use, and fate of all plastics ever made. *Sci. Adv.* 3 (7), e1700782.
- Golea, DM, Upton, Andrew, Jarvis, Peter, Moore, G, Sutherland, S, Parsons, SA, Judd, SJ, 2017. THM and HAA formation from NOM in raw and treated surface waters. *Water Res.* 112, 226–235.
- Gorassini, A., Adami, G., Calvini, P., Giacomello, A., 2016. ATR-FTIR characterization of old pressure sensitive adhesive tapes in historic papers. *J. Cult. Herit.* 21, 775–785.
- Gough, Rachel, Holliman, Peter J, Willis, Naomi, Freeman, Christopher, 2014. Dissolved organic carbon and trihalomethane precursor removal at a UK upland water treatment works. *Sci. Total Environ.* 468, 228–239.
- Hao, R., Zhang, Y., Du, T., Yang, L., Adeleye, A.S., Li, Y., 2017. Effect of water chemistry on disinfection by-product formation in the complex surface water system. *Chemosphere* 172, 384–391.
- Huber, S.A., Balz, A., Abert, M., Pronk, W., 2011. Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography–organic carbon detection–organic nitrogen detection (LC-OCD-OND). *Water Res.* 45, 879–885.
- Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, T.R., Perryman, M., Andrady, A., Narayan, R., Law, K.L., 2015. Plastic waste inputs from land into the ocean. *Science* 347, 768–771.
- Jung, M.R., Horgen, F.D., Orski, S.V., Rodriguez, V., Beers, K.L., Balazs, G.H., Jones, T.T., Work, T.M., Brignac, K.C., Royer, S.-J., 2018. Validation of ATR FT-IR to identify polymers of plastic marine debris, including those ingested by marine organisms. *Mar. Pollut. Bull.* 127, 704–716.
- Krasner, S., Westerhoff, P., Chen, B., Amy, G., Nam, S., Chowdhury, Z., Sinha, S., Rittmann, B., 2008. Contribution of Wastewater to DBP Formation. Water Environment Research Foundation.
- Kraus, Tamara EC, Anderson, Chauncey A, Morgenstern, Karl, Downing, Bryan D, Pellerin, Brian A, Bergamaschi, Brian A, 2010. Determining sources of dissolved organic carbon and disinfection byproduct precursors to the McKenzie River, Oregon. *J. Environ. Qual.* 39 (6), 2100–2112.
- Lambert, S., Wagner, M., 2016. Characterisation of nanoplastics during the degradation of polystyrene. *Chemosphere* 145, 265–268.
- Law, K.L., Thompson, R.C., 2014. Microplastics in the seas. *Science* 345, 144–145.
- Lee, M.-H., Ok, Y.S., Hur, J., 2018a. Dynamic variations in dissolved organic matter and the precursors of disinfection by-products leached from biochars: leaching experiments simulating intermittent rain events. *Environ. Pollut.* 242, 1912–1920.
- Lee, M.-H., Osburn, C.L., Shin, K.-H., Hur, J., 2018b. New insight into the applicability of spectroscopic indices for dissolved organic matter (DOM) source discrimination in aquatic systems affected by biogeochemical processes. *Water Res.* 147, 164–176.
- Li, J., Liu, H., Chen, J.P., 2018. Microplastics in freshwater systems: a review on occurrence, environmental effects, and methods for microplastics detection. *Water Res.* 137, 362–374.
- Liu, S., Lim, M., Fabris, R., Chow, C.W., Drikas, M., Korshin, G., Amal, R., 2010. Multi-wavelength spectroscopic and chromatography study on the photocatalytic oxidation of natural organic matter. *Water Res.* 44, 2525–2532.
- Maizel, A.C., Remucal, C.K., 2017. Molecular composition and photochemical reactivity of size-fractionated dissolved organic matter. *Environ. Sci. Technol.* 51, 2113–2123.
- Mason, S.A., Garneau, D., Sutton, R., Chu, Y., Ehmann, K., Barnes, J., Fink, P., Papazissimos, D., Rogers, D.L., 2016. Microplastic pollution is widely detected in US municipal wastewater treatment plant effluent. *Environ. Pollut.* 218, 1045–1054.
- Meng, Yingjie, Wang, Yan, Han, Qi, Xue, Nan, Sun, Yangyang, Gao, Baoyu, Li, Qilin, et al., 2016. Trihalomethane (THM) formation from synergic disinfection of biologically treated municipal wastewater: Effect of ultraviolet (UV) irradiation and titanium dioxide photocatalysis on dissolve organic matter fractions. *Chem. Eng. J.* 303, 252–260.
- Murphy, F., Ewins, C., Carbonnier, F., Quinn, B., 2016. Wastewater treatment works (WwTW) as a source of microplastics in the aquatic environment. *Environ. Sci. Technol.* 50, 5800–5808.
- Ojeda, T., Freitas, A., Birck, K., Dalmolin, E., Jacques, R., Bento, F., Camargo, F., 2011. Degradability of linear polyolefins under natural weathering. *Polym. Degrad. Stabil.* 96, 703–707.
- Padhi, RK, Subramanian, Suja, Mohanty, AK, Satpathy, KK, 2019. Comparative assessment of chlorine reactivity and trihalomethanes formation potential of three different water sources. *J. Water Process Eng.* 29, 100769.
- Park, K.-Y., Choi, S.-Y., Lee, S.-H., Kweon, J.-H., Song, J.-H., 2016. Comparison of formation of disinfection by-products by chlorination and ozonation of wastewater effluents and their toxicity to *Daphnia magna*. *Environ. Pollut.* 215, 314–321.
- Paço, A., Duarte, K., da Costa, J.P., Santos, P.S., Pereira, R., Pereira, M., Freitas, A.C., Duarte, A.C., Rocha-Santos, T.A., 2017. Biodegradation of polyethylene microplastics by the marine fungus *Zalerion maritimum*. *Sci. Total Environ.* 586, 10–15.
- Phong, D.D., Hur, J., 2015. Insight into photocatalytic degradation of dissolved organic matter in UVA/TiO₂ systems revealed by fluorescence EEM-PARAFAC. *Water Res.* 87, 119–126.
- Potthoff, A., Oelschlägel, K., Schmitt-Jansen, M., Rummel, C.D., Kühnel, D., 2017. From the sea to the laboratory: characterization of microplastic as prerequisite for the assessment of ecotoxicological impact. *Integrated Environ. Assess. Manag.* 13, 500–504.
- Rajakumar, K., Sarasvathy, V., Chelvan, A.T., Chitra, R., Vijayakumar, C., 2012. Effect of iron carboxylates on the photodegradability of polypropylene. II. Artificial weathering studies. *J. Appl. Polym. Sci.* 123, 2968–2976.
- Romera-Castillo, C., Pinto, M., Langer, T.M., Álvarez-Salgado, X.A., Herndl, G.J., 2018. Dissolved organic carbon leaching from plastics stimulates microbial activity in the ocean. *Nat. Commun.* 9, 1430.
- Sanly, M. Lim, Chiang, K., Amal, R., Fabris, R., Chow, C., Drikas, M., 2007. A study on the removal of humic acid using advanced oxidation processes. *Separ. Sci. Technol.* 42, 1391–1404.
- Siegfried, M., Koelmann, A.A., Besseling, E., Kroeze, C., 2017. Export of microplastics from land to sea. A modelling approach. *Water Res.* 127, 249–257.
- Simoneit, B.R., Medeiros, P.M., Diddy, B.M., 2005. Combustion products of plastics as indicators for refuse burning in the atmosphere. *Environ. Sci. Technol.* 39, 6961–6970.
- Song, Y.K., Hong, S.H., Jang, M., Han, G.M., Jung, S.W., Shim, W.J., 2017. Combined effects of UV exposure duration and mechanical abrasion on microplastic fragmentation by polymer type. *Environ. Sci. Technol.* 51, 4368–4376.
- Su, L., Xue, Y., Li, L., Yang, D., Kolandhasamy, P., Li, D., Shi, H., 2016. Microplastics in taihu lake, China. *Environ. Pollut.* 216, 711–719.
- Suhrhoff, T.J., Scholz-Böttcher, B.M., 2016. Qualitative impact of salinity, UV radiation and turbulence on leaching of organic plastic additives from four common plastics—a lab experiment. *Mar. Pollut. Bull.* 102, 84–94.
- Wagner, M., Scherer, C., Alvarez-Muñoz, D., Brennholt, N., Bourrain, X., Buchinger, S., Fries, E., Grosbois, C., Klasmeier, J., Marti, T., 2014. Microplastics in freshwater ecosystems: what we know and what we need to know. *Environ. Sci. Eur.* 26, 12.
- Wang, X., Zhang, H., Zhang, Y., Shi, Q., Wang, J., Yu, J., Yang, M.J. E.S., 2017. New insights into trihalomethane and haloacetic acid formation potentials: correlation with the molecular composition of natural organic matter in source water. *Environ. Sci. Technol.* 51, 2015–2021.
- Weinstein, J.E., Crocker, B.K., Gray, A.D., 2016. From macroplastic to microplastic: degradation of high-density polyethylene, polypropylene, and polystyrene in a salt marsh habitat. *Environ. Toxicol. Chem.* 35, 1632–1640.
- Yang, L., Han, D.H., Lee, B.-M., Hur, J., 2015. Characterizing treated wastewaters of different industries using clustered fluorescence EEM-PARAFAC and FT-IR spectroscopy: implications for downstream impact and source identification. *Chemosphere* 127, 222–228.
- Zhai, H., He, X., Zhang, Y., Du, T., Adeleye, A.S., Li, Y.J.C., 2017. Disinfection byproduct formation in drinking water sources: a case study of Yuqiao reservoir. *Chemosphere* 181, 224–231.
- Zhang, Junzhi, Yu, Jianwei, An, Wei, Liu, Juan, Wang, Yongjing, Chen, Youjun, Tai, Jia, Yang, Min, 2011. Characterization of disinfection byproduct formation potential in 13 source waters in China. *J. Environ. Sci.* 23 (2), 183–188.
- Zhao, Z.-Y., Gu, J.-D., Fan, X.-J., Li, H.-B., 2006. Molecular size distribution of dissolved organic matter in water of the Pearl River and trihalomethane formation characteristics with chlorine and chlorine dioxide treatments. *J. Hazard Mater.* 134, 60–66.

Supporting Information:

Water Research

**Characteristics of microplastic polymer-derived dissolved organic matter
and its potential as a disinfection byproduct precursor**

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2 tables: Tables S1-S2

5 figures: Figs. S1-S5

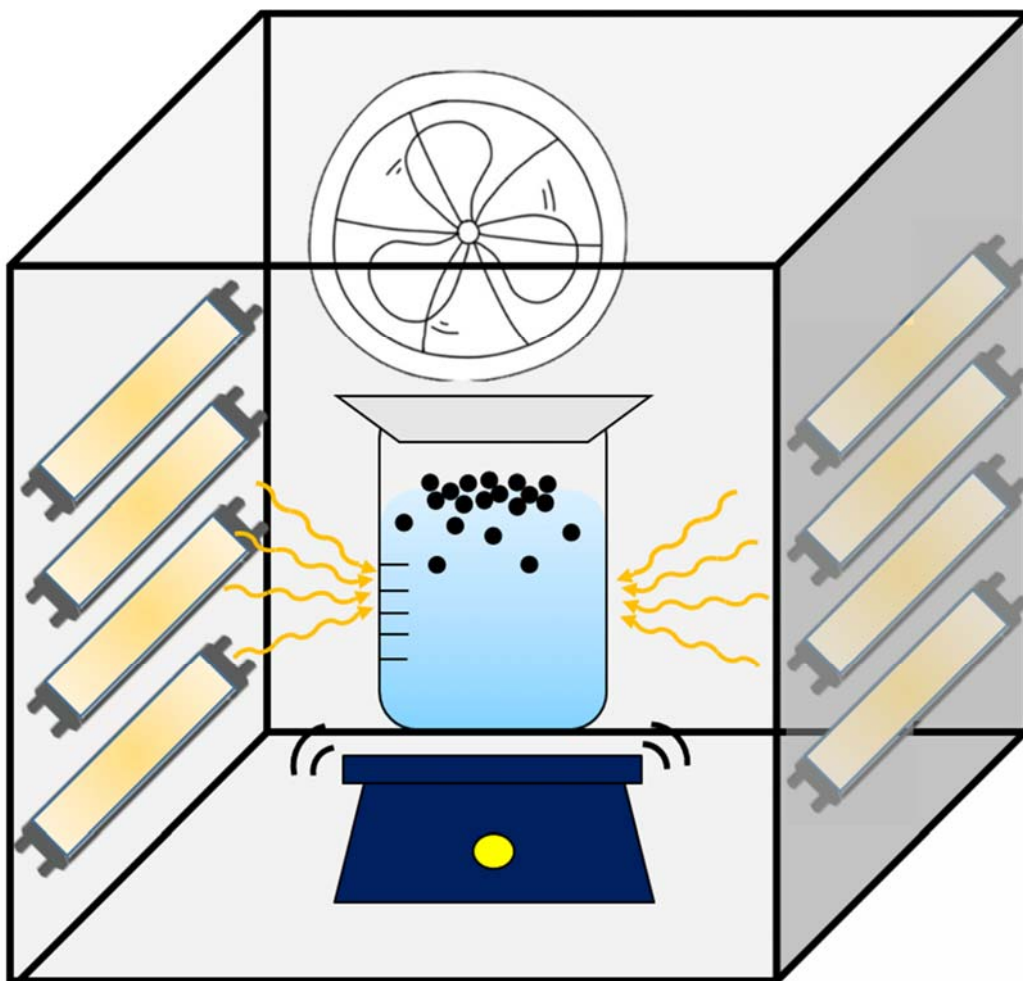


Figure S1. Schematic diagram of the UV irradiation system used in this study. The system is the same as that employed in previous studies (Phong and Hur, 2015; Lee et al., 2018).

Table S1. Main absorption bands of polyethylene (PE) and polypropylene (PP) in the IR regions and their identifying assignment groups.

Assignment band groups used for identification	Absorption Band [cm ⁻¹]	Literature for comparison
A Asymmetric C-H stretching 2951-2915	2951	(Gorassini et al. 2016) -PP
	2950	(Jung et al. 2018)-PP
	2919	(Gulmine et al. 2002)-PE
	2918	(Rajandas et al. 2012)
	2917	(Gorassini et al. 2016) -PP
	2915	(Jung et al. 2018)-PE, PP
B Symmetric C-H stretching 2871-2837	2871	(Gorassini et al. 2016) -PP
	2868	(Gorassini et al. 2016) -PP
	2851	(Gulmine et al. 2002) (Rajandas et al. 2012)-PE
	2849	(Llamas and Talamantes 2014)-PP
	2845	(Jung et al. 2018)-PE
	2839	(Llamas and Talamantes 2014)-PP
	2838	(Jung et al. 2018)-PP
2837	(Gorassini et al. 2016) -PP	
C CH ₂ band 1473-1455	1473	(Gulmine et al. 2002) -PE
	1468	(Rajandas et al. 2012)
	1467	(Jung et al. 2018)-PE
	1463	(Gulmine et al. 2002) -PE
	1462	(Jung et al. 2018)-PE
	1457	(Llamas and Talamantes 2014)-PP
D CH ₃ band 1377-1373	1455	(Jung et al. 2018)-PP
	1377	(Jung et al. 2018) -PE, PP
	1375	(Gorassini et al. 2016) -PP
	1376	(Llamas and Talamantes 2014)-PP
E Various rock related with PP 1166-808	1373	(Gulmine et al. 2002) (Rajandas et al. 2012) -PE
	1166	(Jung et al. 2018) -PP (CH ₃ rock, CH bend, C-C stretch)
	1165	(Gorassini et al. 2016) -PP (CH ₃ rock, CH bend, C-C stretch)
	997	(Jung et al. 2018) -PP (CH ₃ rock)
	996	(Gorassini et al. 2016) -PP (CH ₃ rock)
	972	(Gorassini et al. 2016) (Jung et al. 2018) -PP (CH ₃ rock, C-C stretch)
	840	(Gorassini et al. 2016) (Jung et al. 2018) -PP (CH ₂ rock, C-CH ₃ stretch)
808	(Jung et al. 2018) -PP (CH ₂ rock, C-C stretch)	
F CH ₂ rock related with PE 731-717	731-720	(Gulmine et al. 2002) -PE
	717	(Jung et al. 2018) -PE
	718	(Rajandas et al. 2012)-PE
	730	(Jung et al. 2018) -PE
G Related with photo-oxidized polymer (1) 991-888	965	Vinylene (CH=CH)
	909, 991	Vinyl (CH ₂ =CHR)
	888	Vinylidene (CH ₂ =CR ₂)
H Related with photo-oxidized polymer (2) 1780-1640	1780	Lactones (Gardette et al. 2013)-PE
	1735	Esters
	1720	Ketones
	1713	Carboxylic acids
	1640	Double bonds

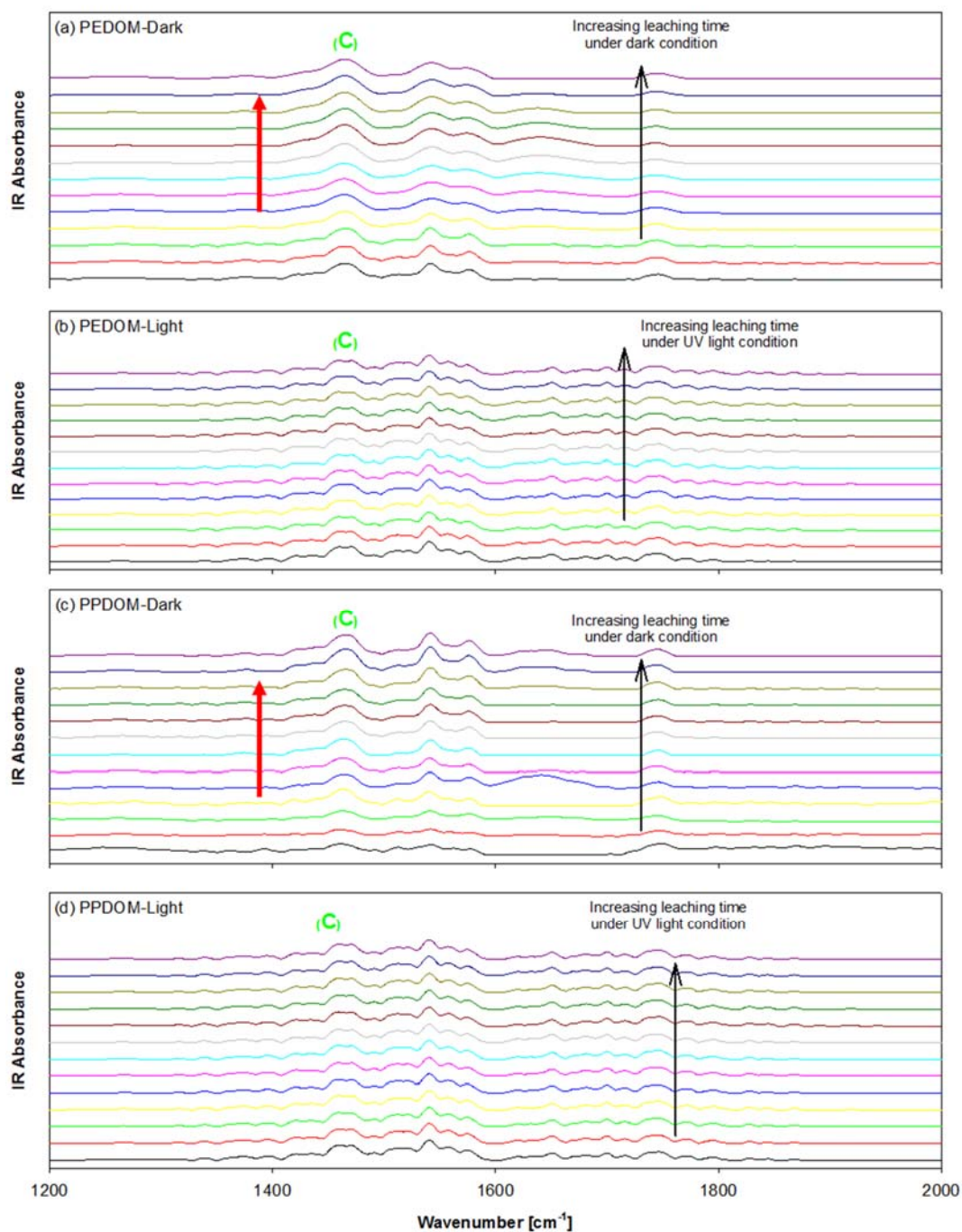


Figure S2. FTIR absorbance spectra between 1200 and 2000 cm^{-1} of: (a-d) Variations of the DOM from PE (PE-DOM) and PP (PP-DOM) polymers with leaching time for dark (a and c) and light treatments (b and d). The letters represent the main absorption bands (cm^{-1}) used to identify PP and PE plastic structures in Table S1.

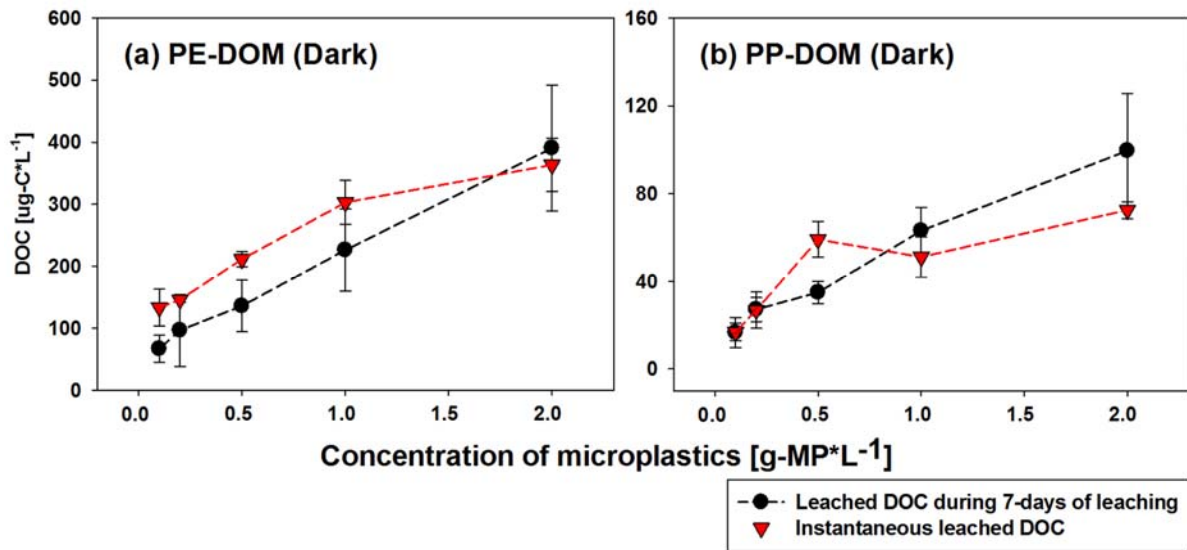


Figure S3. Changes in dissolved organic carbon (DOC) concentrations of DOM leached from PE (a) and PP (b) microplastic polymers with increasing polymer doses from 0.1 to 2.0 g L⁻¹ under dark condition. The error bars represent the standard errors based on three replicate samples. The instantaneously leached DOC refers to the concentrations measured for the samples collected immediately after the addition of the microplastics polymer to artificial freshwater solutions. The total leached DOC represents the amount of DOM measured after the full leaching time period of 7 days.

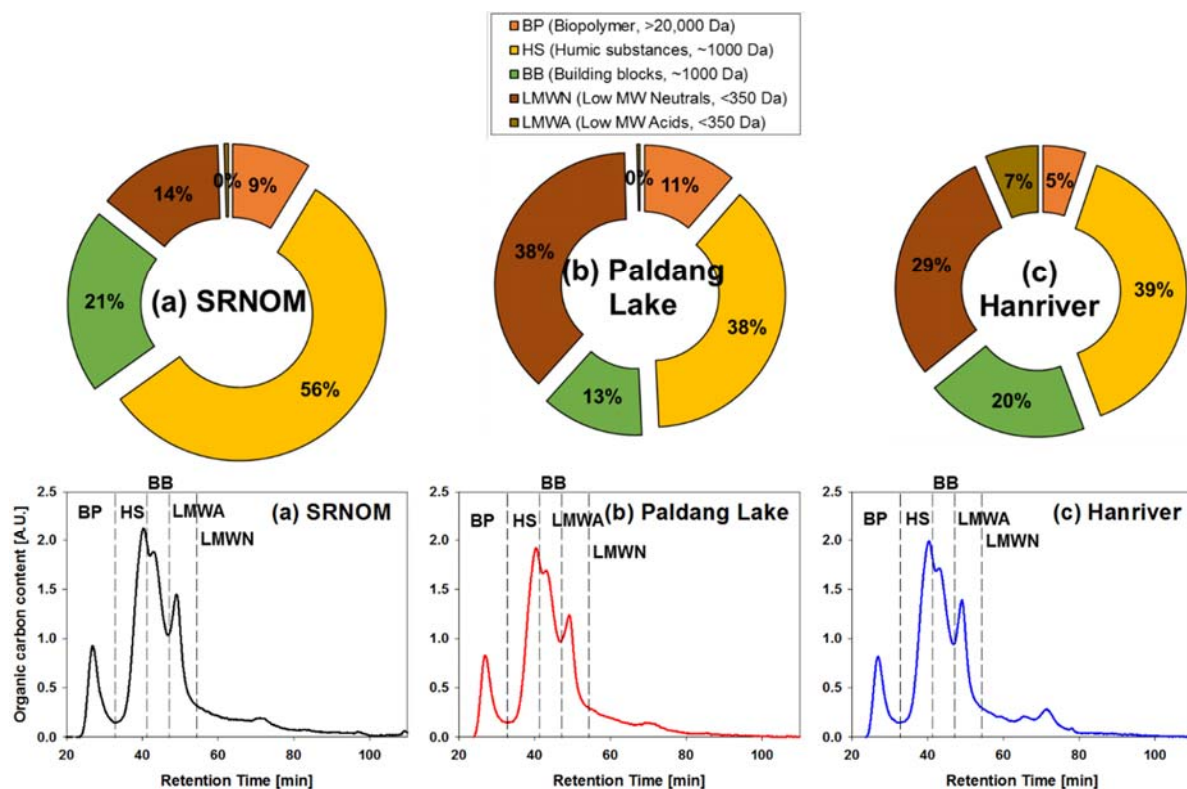


Figure S4. Relative abundances (%) of five different size fractions of aquatic NOM samples from (a) Suwannee River NOM, (c) Paldang Lake, (f) Han River. The corresponding SEC chromatograms: (b) Suwannee River NOM, (d) Paldang Lake, (e) Han River.

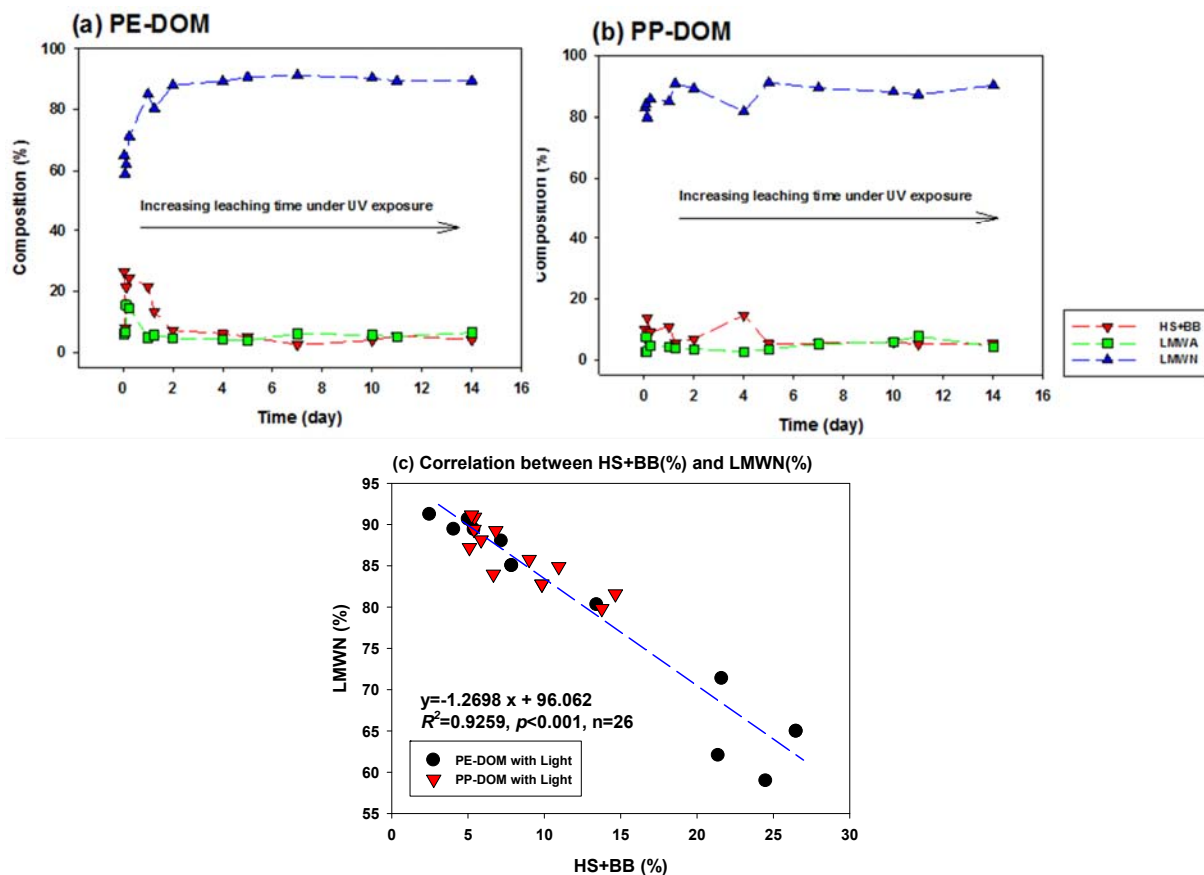


Figure S5. Compositional changes in the different size fractions (%) of the MP-DOM leached from (a) PE and (b) PP polymers (1 g-MP L⁻¹, <100 μm in diameter) by leaching experiments for 14 days under UV irradiation. (c) Correlation between HS+BB (%) and LMN (%) of the leached MP-DOM under the light conditions.

Table S2. Coefficients of determination (R^2) and correlation (r) between DOC concentrations of bulk MP-DOM or three individual size fractions (HS+BB, LMWA, and LMWN) produced under light and dark conditions and the total trihalomethanes formation potentials (THMFPs).

R^2 (r)		Dark (n=26)	Light (n=26)	All (n=52)
		THMFP † [$\mu\text{g-THM L}^{-1}$]	THMFP † [$\mu\text{g-THM L}^{-1}$]	THMFP † [$\mu\text{g-THM L}^{-1}$]
DOC [mg-C L^{-1}]		0.0136 (+0.1166)	0.9799 ** (+0.9899)	0.9755 ** (0.9877)
Molecular size results	HS+BB [$\mu\text{g-C L}^{-1}$]	0.0387 (-0.1968)	0.6834 ** (+0.8359)	0.7018 ** (+0.8378)
	LMWA [$\mu\text{g-C L}^{-1}$]	0.0526 (-0.2294)	0.9203* (+0.9593)	0.9301 ** (+0.9644)
	LMWN [$\mu\text{g-C L}^{-1}$]	0.0226 (-0.1502)	0.8280 ** (+0.9099)	0.8270 ** (+0.9094)

† The dilution factor is taken into account for the samples with relatively high DOC concentrations ($> 1 \text{ mg-C L}^{-1}$) by multiplying the corresponding DOC to the measured THMFP values.

* $p < 0.05$, ** $p < 0.01$.

References

- Gardette, M., A. Perthue, J.-L. Gardette, T. Janecska, E. Földes, B. Pukánszky, and S. Therias. 2013. Photo-and thermal-oxidation of polyethylene: comparison of mechanisms and influence of unsaturation content. *Polymer degradation and stability* **98**:2383-2390.
- Gorassini, A., G. Adami, P. Calvini, and A. Giacomello. 2016. ATR-FTIR characterization of old pressure sensitive adhesive tapes in historic papers. *Journal of Cultural Heritage* **21**:775-785.
- Gulmine, J., P. Janissek, H. Heise, and L. Akcelrud. 2002. Polyethylene characterization by FTIR. *Polymer Testing* **21**:557-563.
- Jung, M. R., F. D. Horgen, S. V. Orski, V. Rodriguez, K. L. Beers, G. H. Balazs, T. T. Jones, T. M. Work, K. C. Brignac, and S.-J. Royer. 2018. Validation of ATR FT-IR to identify polymers of plastic marine debris, including those ingested by marine organisms. *Marine pollution bulletin* **127**:704-716.
- Llamas, R., and M. C. Talamantes. 2014. An analytical study of polypropylene as a support for paint layers. From concept to material in contemporary art. *Journal of Cultural Heritage* **15**:136-143.
- Rajandas, H., S. Parimannan, K. Sathasivam, M. Ravichandran, and L. S. Yin. 2012. A novel FTIR-ATR spectroscopy based technique for the estimation of low-density polyethylene biodegradation. *Polymer Testing* **31**:1094-1099.