Supplementary Information (SI) for Environmental Science: Processes & Impacts.

Supporting Information

Text

S1. DOC Concentration Measurement of MPs-DOM

In this study, the dissolved organic carbon (DOC) concentration of microplastic leachates was quantified using a total organic carbon analyzer (TOC; Elementar, Germany). The standard curve was constructed via the subtraction method, and the external standard method was employed for concentration determination. Samples intended for DOC analysis were collected in pre-cleaned glass vials and acidified with 1 M HCl to a pH of approximately 2. This step was performed to minimize potential interferences caused by pH fluctuations and metal binding. A standard stock solution of potassium hydrogen phthalate (KHP) was used for daily calibration of DOC measurements. The relative analytical accuracy was determined to be less than 2%.

S2. EEM Measurements and PARAFAC Analysis of MPs-DOM

The fluorescent groups and molecular compounds in the leachate of microplastics (MPs) before and after photoaging were characterized using a three-dimensional fluorescence spectrometer (3D-EEM, FS5, UK). The 3D-EEM parameters were configured as follows: Pure water was used as the reference with an excitation wavelength range of 200-500 nm (incremented by 10 nm), an emission wavelength range of 250-550 nm (incremented by 5 nm), and both the excitation and emission slits set to 10 nm. The scanning rate was set to 1200 nm/min. All 3D-EEM data were processed and visualized using Origin 2021 software, while parallel factor analysis (PARAFAC) and validation were performed using the DOM Fluor toolbox in Matlab.

The component concentration was quantified based on the fluorescence intensity of the highest fluorescence peak, denoted as Fmax (R.U.). Notably, leachate samples aged under UV+H_2O conditions for 80 and 120 days required a fivefold dilution prior to analysis.

The EEM combined with parallel factor analysis (PARAFAC) was used to statistically reduce the three-way data into trilinear terms and a residual array (Equation S1)[1, 2].

$$x_{ijk} = \sum_{n=1}^{N} a_{in} b_{jn} c_{kn} + e_{ijk}, i = 1,2,...; j = 1,2,...; k = 1,2,..., K \quad \text{(S1)}$$

where x_{ijk} is the intensity of the i*th* sample measured at k*th* Ex and j*th* Em wavelengths. Parameters a, b, c, N, and n represent the concentration, Em spectra, Ex spectra, number of components and individual component, respectively. ε_{ijg} is the variability unexplained by model. The reliability of the model results was verified by performing stability analysis and semi-split analysis and stability analysis using the DOM Fluor toolbox in Matlab.

S3. FTIR Measurements of MPs-DOM

Infrared spectroscopy (FTIR, PerkinElmer, USA) was employed to analyze the MPs leachate before and after photoaging. Specifically, 10 mL of filtered leachate samples were mixed with 100 mg of KBr powder (Sigma Aldrich, FTIR grade) and freeze-dried for further analysis. Clean KBr particles, dried at 105 °C for 2 hours, served as blanks. Baseline corrections were applied to each FTIR spectrum after blank subtraction, and the scanning wavenumber range was set to 400-4000 cm^{-1}.

S4. GC-MS Measurements of MPs-DOM

The organic compounds in the leachate of microplastics (MPs) before and after photoaging were analyzed using gas chromatography-mass spectrometry (GCMS-QP2020, Shimadzu, Japan). Specifically, 10 mL of the leachate was transferred into a headspace vial, sealed with a diaphragm cap, and maintained at 75 ℃ for 25 minutes to extract volatile organic compounds released by each test sample. The leaching solution was subsequently loaded onto a 65 μm PDMS/DVB (Fused Silica 24Ga) manual solid-phase microextraction (SPME) fiber head for further analysis. Non-target screening of the MPs leachate extract was performed using gas chromatography (GC) with pulsed splitles injection at 250 ℃. Separation was achieved using an SH-Rxi-5si1 MS chromatographic column (30 m length, 0.25 mm inner diameter, 0.25 μm film thickness). Helium was used as the carrier gas at a constant flow rate of 1.0 mL/min. The temperature program for the column oven was as follows: initial temperature of 40 ℃ held for 1 minute, increased at 6 ℃/min to 130 ℃ (no holding time), and then increased at 10 ℃/min to 220 ℃ (held for 1 minute). Two full scan acquisitions of the quadrupole detector were conducted within the mass range of m/z 35 – 500. The transmission line and ion source temperatures were set at 250 ℃ and 200 ℃, respectively, with a solvent delay of 1 minute.

S5. Quality assurance and quality control

All glassware was sequentially rinsed with propan-2-ol, acetone, and ultrapure water. Non-volumetric glassware was heated at 450°C for 8 hours before use. Non-glass items were cleaned with acetone. Plastic samples were handled with gloves and stored in aluminum trays or foil to minimize contamination.

For quality control, blank samples (ultrapure water) were analyzed in triplicate alongside microplastic leachates. System blanks and solvent blanks were included in each batch. A quality control standard (5 ng/mL) was injected every 8 samples to monitor instrument performance during GC-MS analysis. Helium carrier gas flow and column temperature programs were verified before each run. SPME fiber conditioning and blank checks were performed regularly to avoid carryover contamination.

Figures

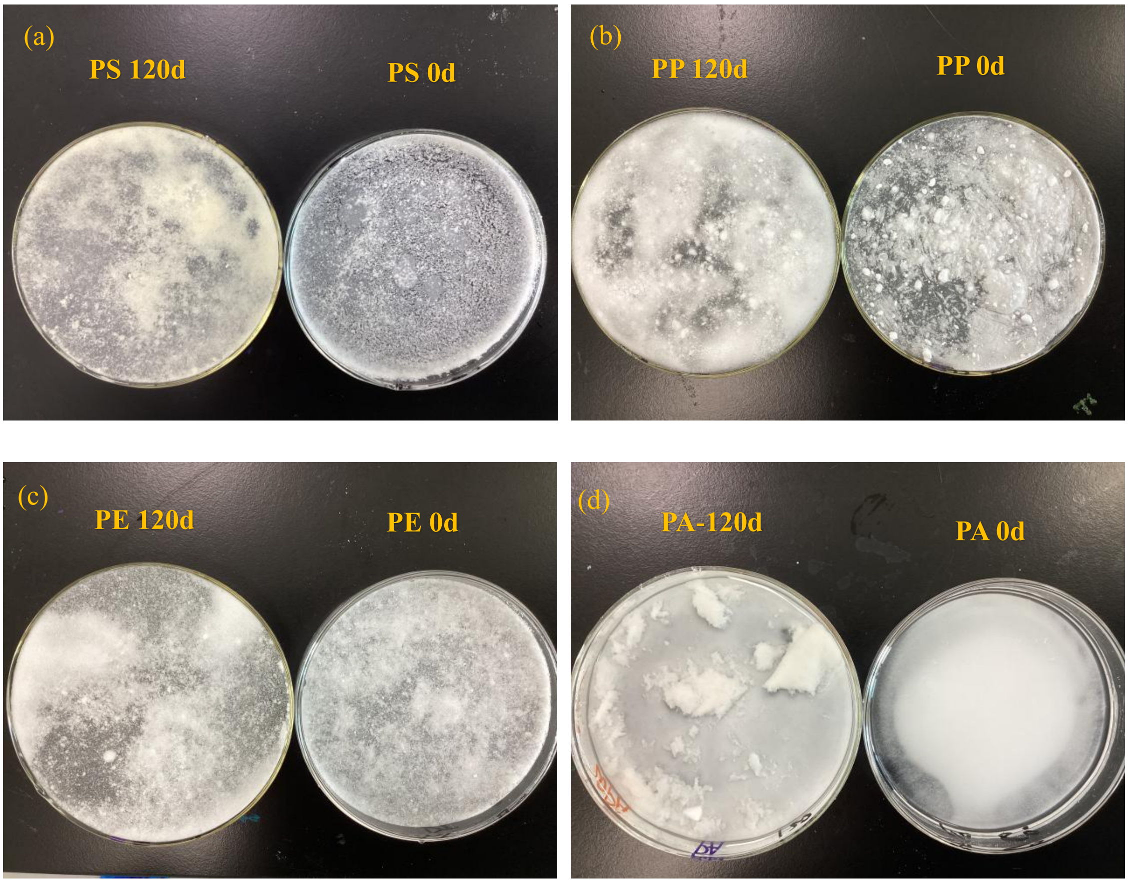
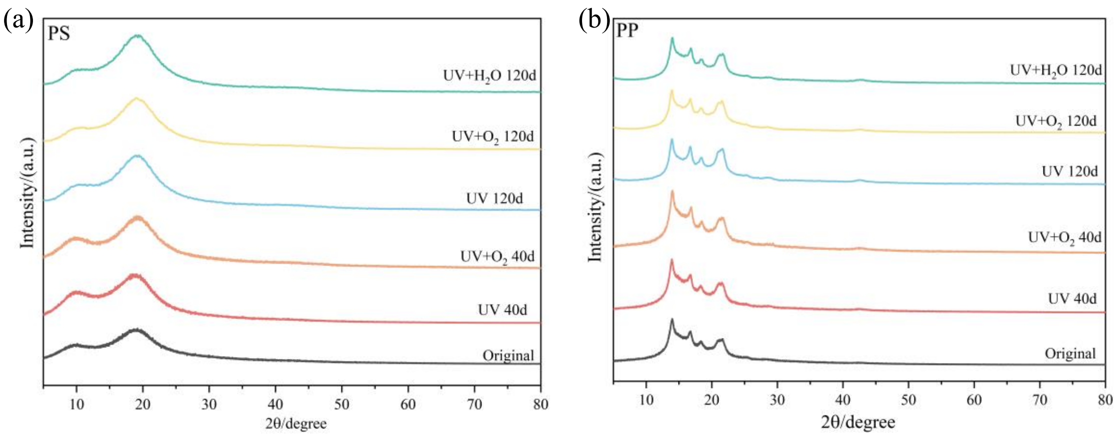


Fig. S1. Morphology of MPs in water (UV+H_2O 120d / UV+H_2O 0d).



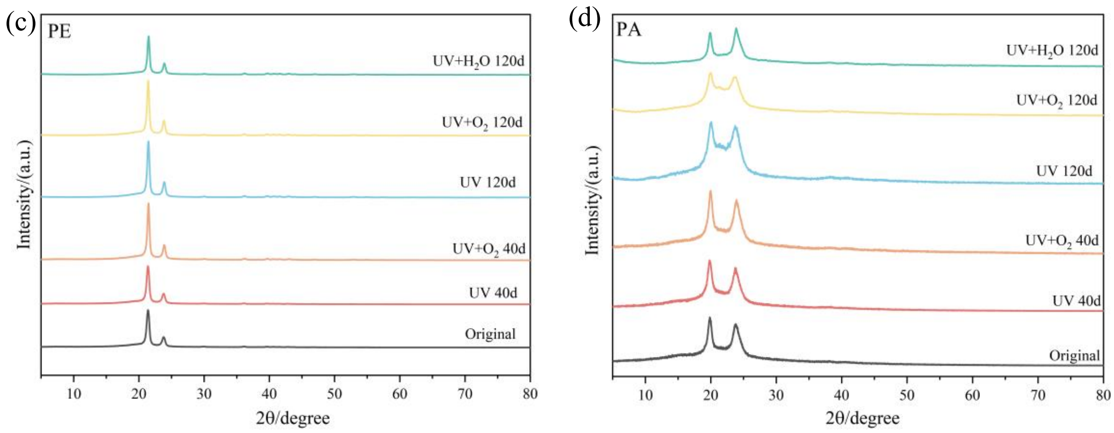


Fig. S2. XRD spectra of the initial sample of MPs-MP and the sample after 40d and 120d aging under different aging conditions: (a) PS; (b) PP; (c) PA; (d) PE. (Note: 1/2/3 represents aging time 40d/80d/120d, respectively; O/E/W stands for UV+O_2/UV/+UV+H_2O conditions respectively)

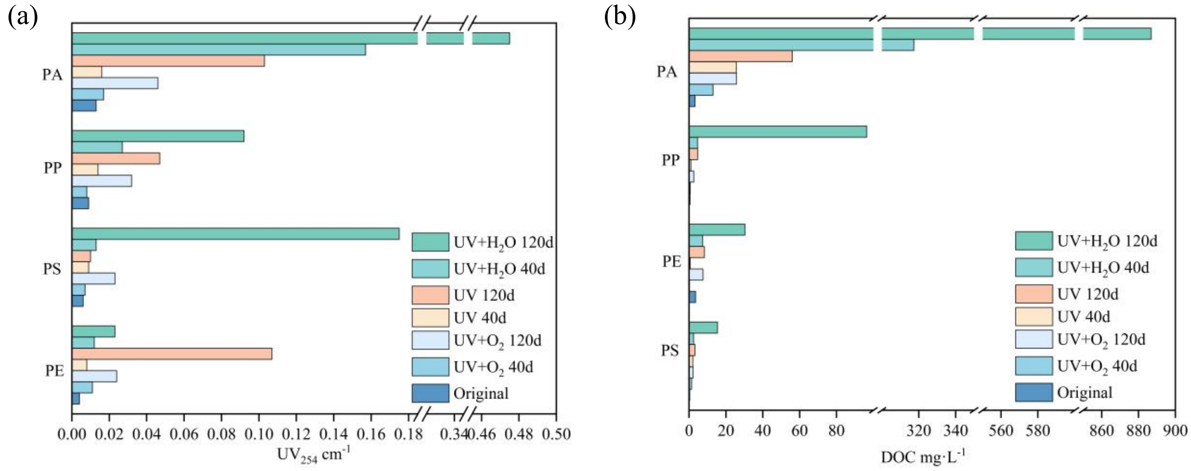


Fig. S3. Changes in organic matter content of four microplastics at different time points under three aging conditions. (a) Ultraviolet absorbance (UV254, cm^{-1}). (b) Dissolved organic concentration (DOC, mg·L^{-1}).

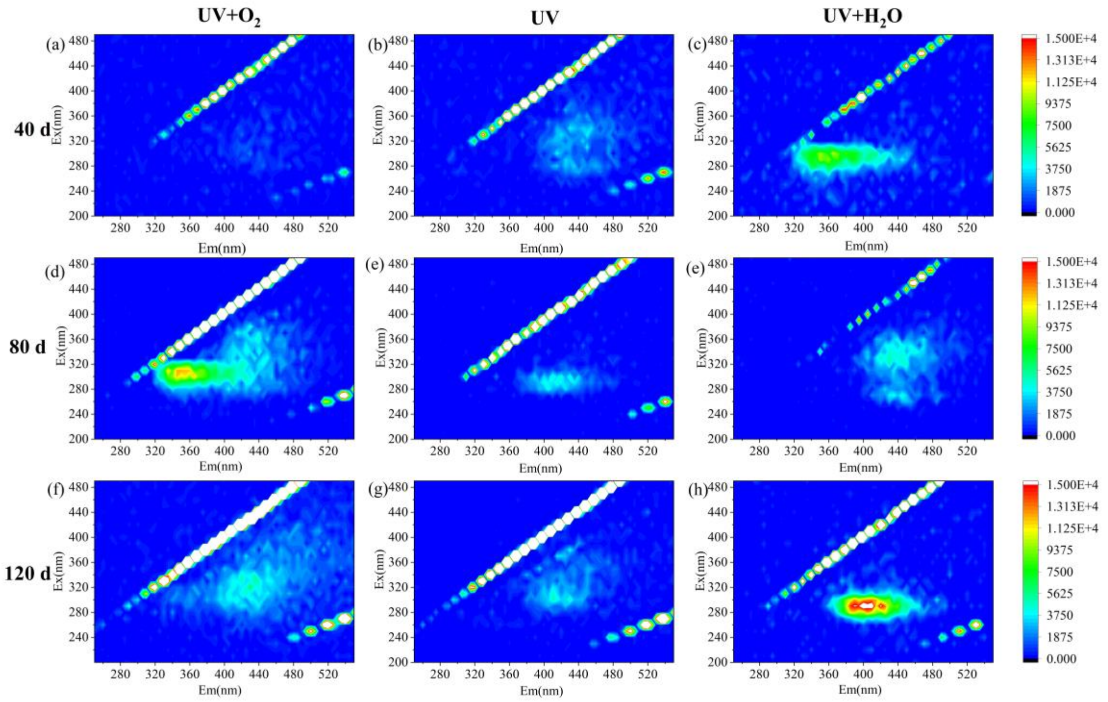


Fig. S4. EEM spectra of MP-DOM of PS under three different aging conditions (UV; UV+O_2; UV+H_2O) for three stages of aging (40d; 80d; 120d)

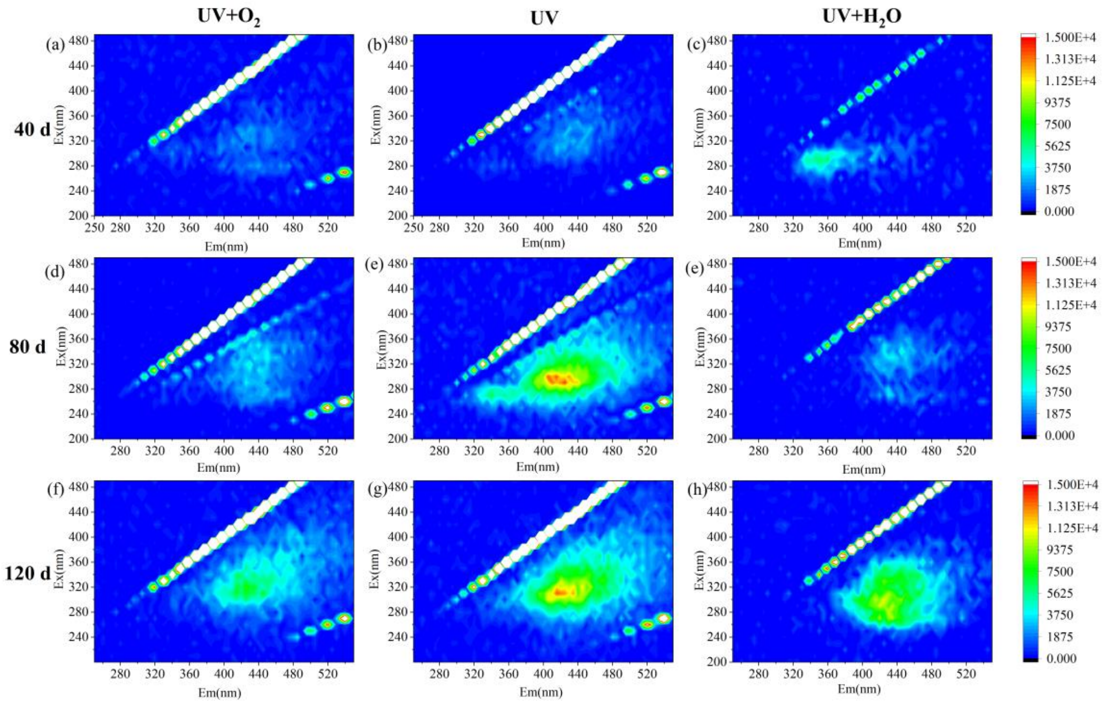


Fig. S5. EEM spectra of MP-DOM of PP under three different aging conditions (UV; UV+O_2; UV+H_2O) for three stages of aging (40d; 80d; 120d)

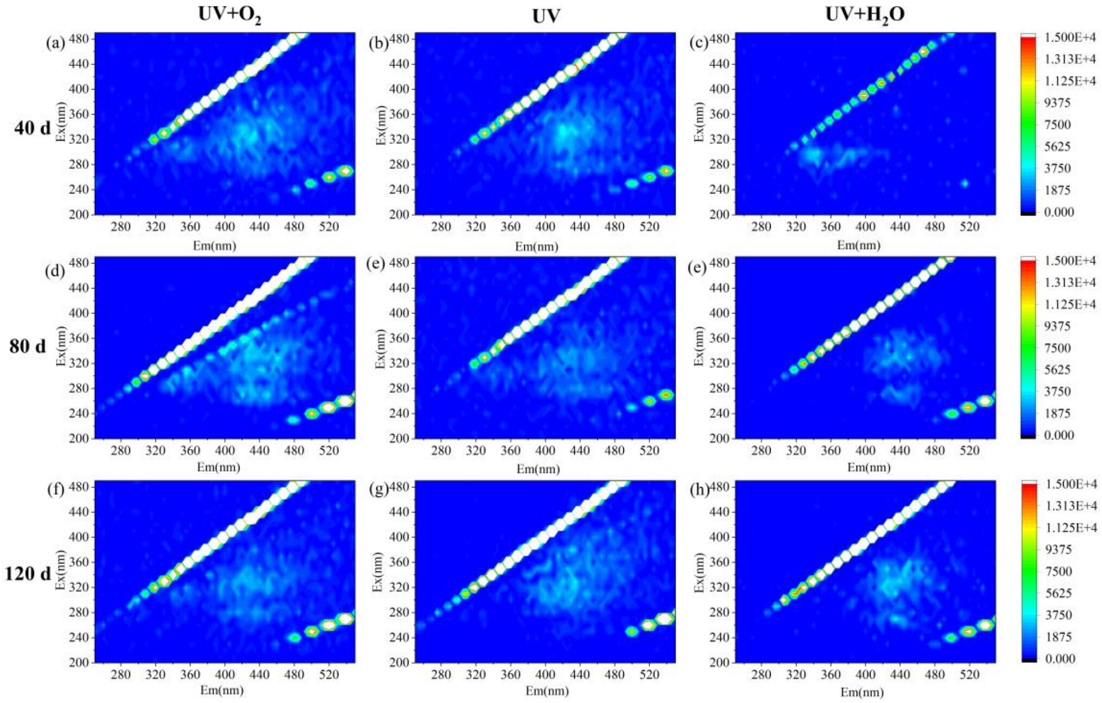


Fig. S6. EEM spectra of MP-DOM of PE under three different aging conditions (UV; UV+O_2; UV+H_2O) for three stages of aging (40d; 80d; 120d)

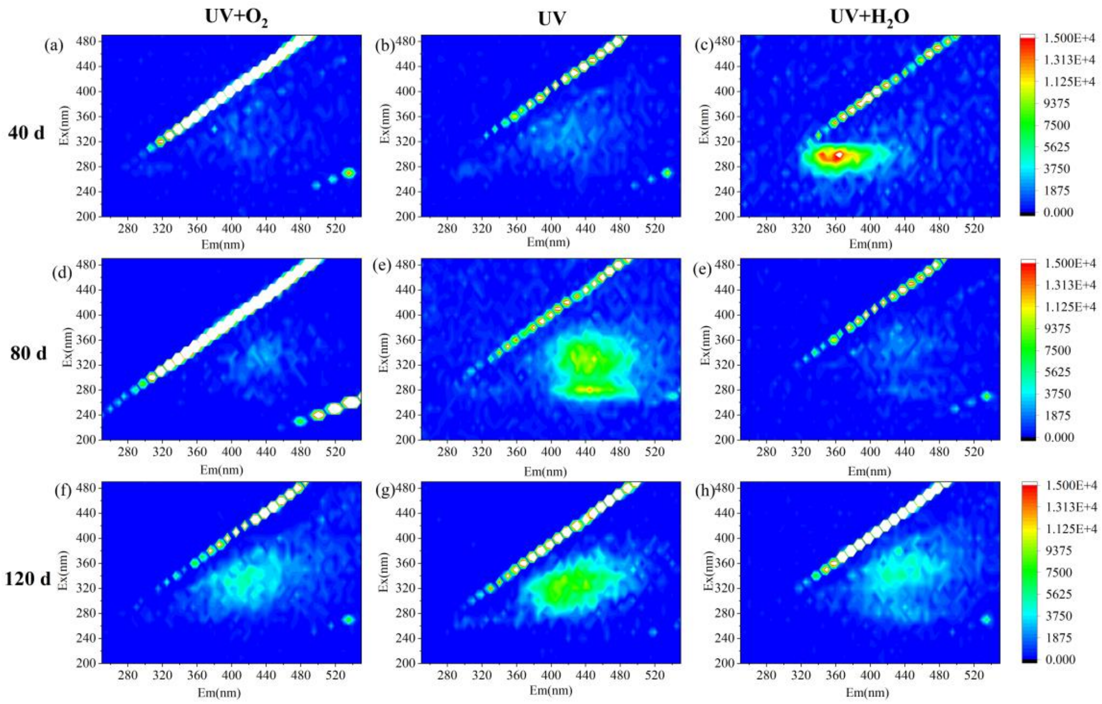


Fig. S7. EEM spectra of MP-DOM of PA under three different aging conditions (UV; UV+O_2; UV+H_2O) for three stages of aging (40d; 80d; 120d)

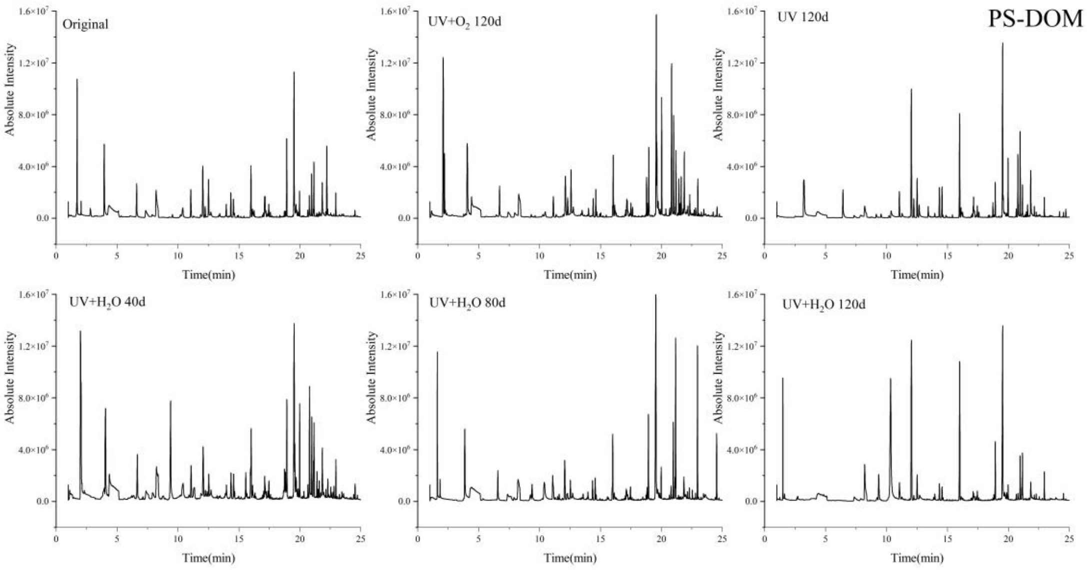


Fig. S8. Total ion chromatogram of PS-DOM: (a) original; (b) UV+O_2 120d; (c) UV 120d; (d) UV+H_2O 40d; (e) UV+H_2O 80d; (f) UV+H_2O 120d.

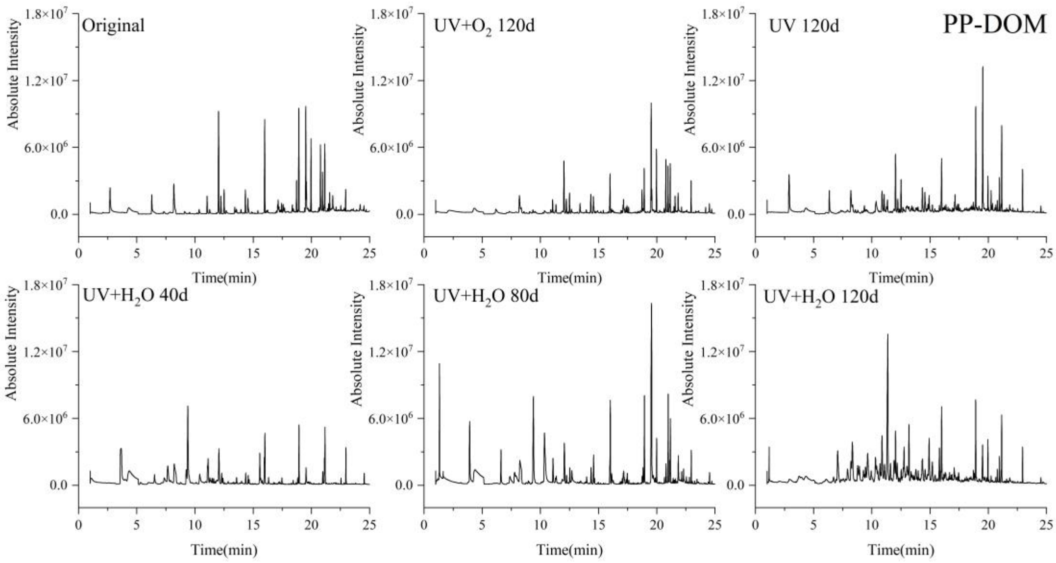


Fig. S9. Total ion chromatogram of PP-DOM: (a) original; (b) UV+O_2 120d; (c) UV 120d; (d) UV+H_2O 40d; (e) UV+H_2O 80d; (f) UV+H_2O 120d.

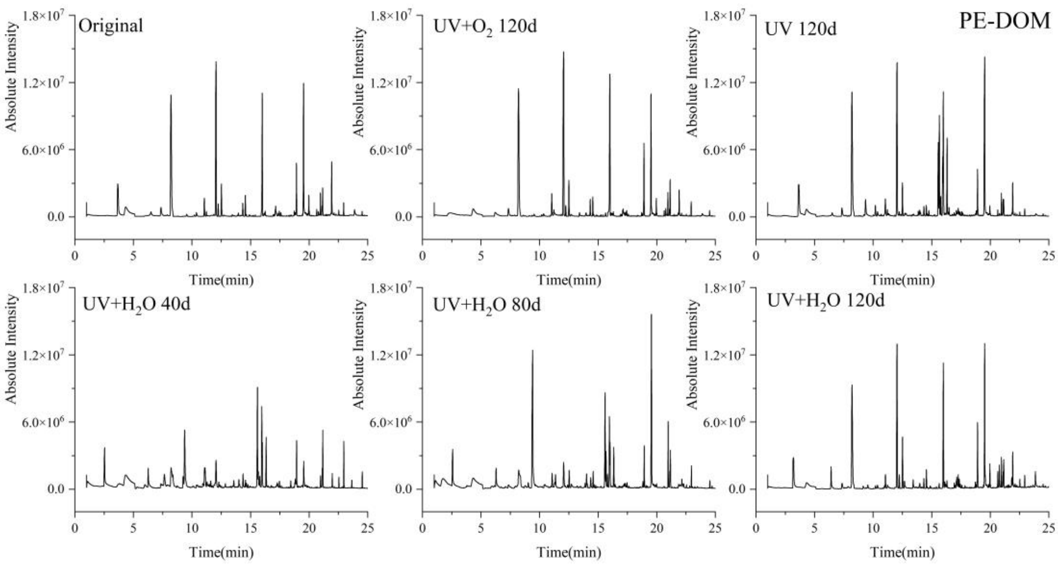


Fig. S10. Total ion chromatogram of PE-DOM: (a) original; (b) UV+O_2 120d; (c) UV 120d; (d) UV+H_2O 40d; (e) UV+H_2O 80d; (f) UV+H_2O 120d.

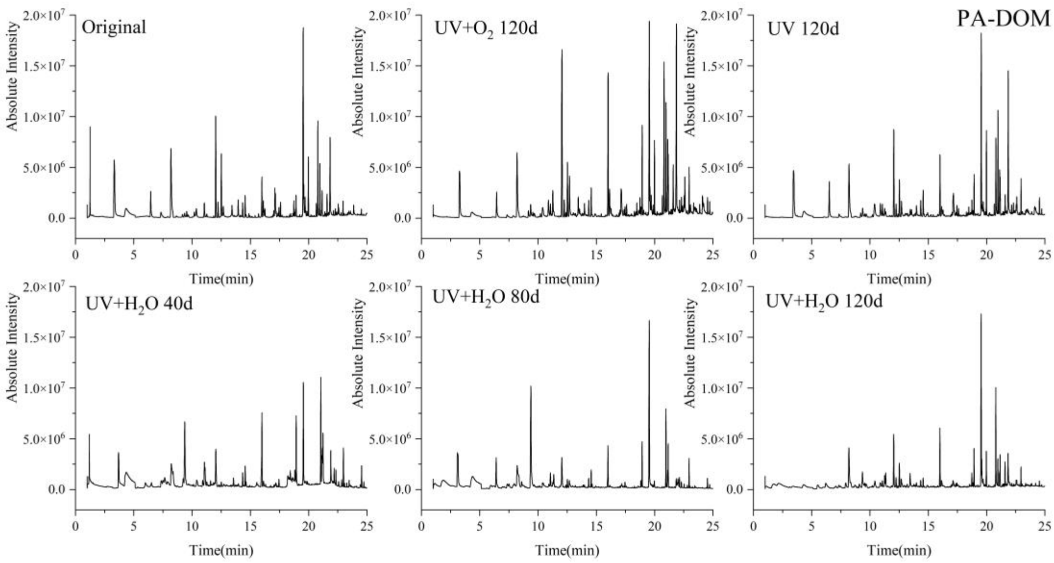


Fig. S11. Total ion chromatogram of PA-DOM: (a) original; (b) UV+O_2 120d; (c) UV 120d; (d) UV+H_2O 40d; (e) UV+H_2O 80d; (f) UV+H_2O 120d.

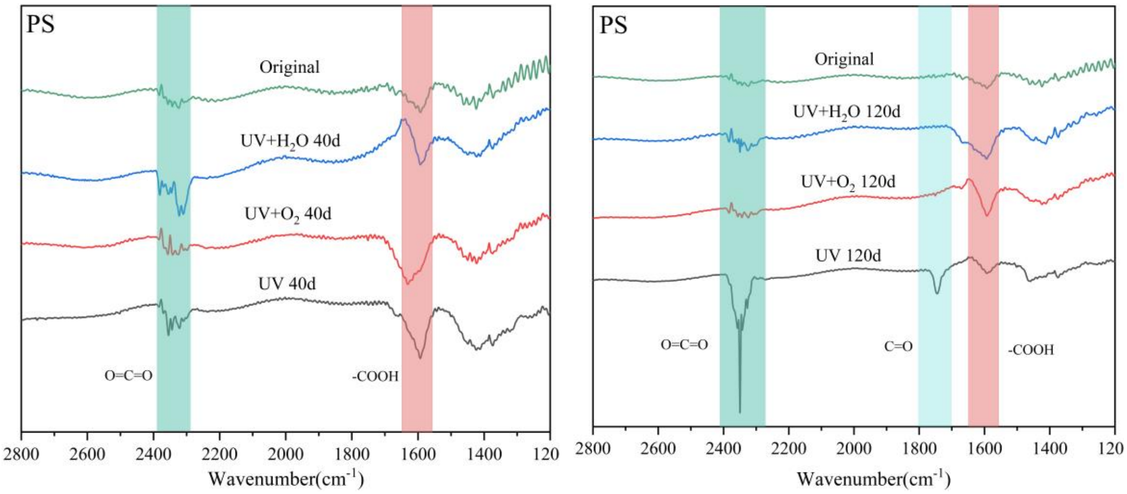


Figure S12. FTIR spectra of the original PS-MP leachate and the leachate samples aged for 40 days and 120 days under different aging conditions ((L1) PS 40d, (L2) PS 120d).

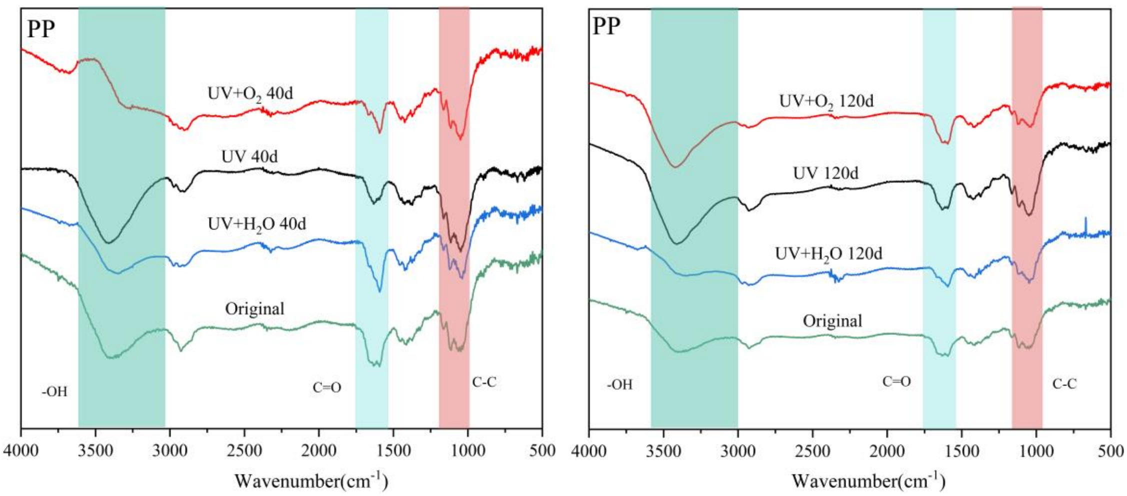


Fig. S13. FTIR spectra of the original PP-MP leachate and the leachate samples aged for 40 days and 120 days under different aging conditions ((L1) PP 40d, (L2) PP 120d).

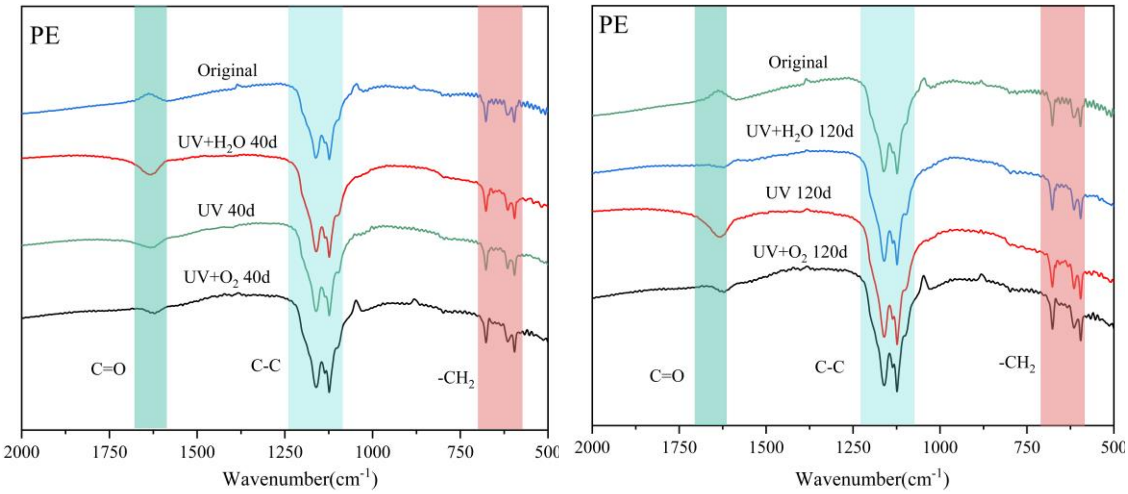


Fig. S14. FTIR spectra of the original PE-MP leachate and the leachate samples aged for 40 days and 120 days under different aging conditions ((L1) PE 40d, (L2) PE 120d).

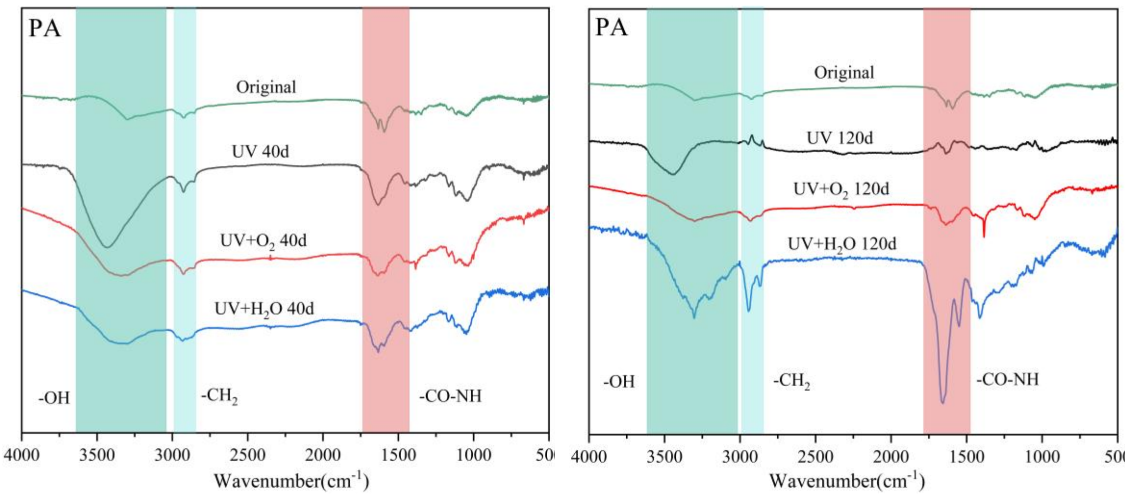


Fig. S15. FTIR spectra of the original PA-MP leachate and the leachate samples aged for 40 days and 120 days under different aging conditions ((L1) PA 40d, (L2) PA 120d).

Tables

Table S1. Properties of microplastics (MPs).

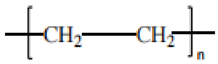
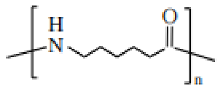
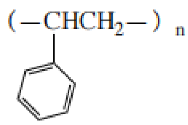
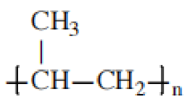
Microplastics polymer	Abbreviations	Density (g/cm3)	Crystallinity (%)	Chemical formula	Molecular structure
Polyethylene	PE	0.91~0.96	35.0[3]	$(C_2H_4)n$	
Polyamide	PA	1.12~1.15	36.6[3]	$(C_6H_{11}NO)n$	
Polystyrene	PS	1.03~1.07	3.7[3]	$(C_8H_8)n$	
Polypropylene	PP	0.89~0.93	38.4[3]	$(C_3H_6)n$	

Table S2. DOC concentration of pristine and aged microplastics leachate ($mg \cdot L^{-1}$)

Microplastics	Original	$UV+H_2O$ 40d	$UV+H_2O$ 80d	$UV+H_2O$ 120d	$UV+O_2$ 40d	UV 40d	$UV+O_2$ 120d	UV 120d
PS	3.554	7.351	3.914	30.278	1.357	2.044	2.157	3.258
PE	0.352	2.491	1.617	15.446	0.255	0.642	7.591	8.312
PP	0.553	4.656	3.365	96.359	0.683	1.028	2.607	4.694
PA	3.237	317.403	572.045	886.835	12.966	25.623	25.734	55.994

Table S3. UV254 of leachate under pristine and aged microplastics (AU/cm)

Microplastics	Original	$UV+O_2$ 40d	UV 40d	$UV+O_2$ 120d	UV 120d	$UV+H_2O$ 40d	$UV+H_2O$ 80d	$UV+H_2O$ 120d
PS	0.006	0.007	0.009	0.023	0.064	0.013	0.126	0.175
PE	0.004	0.011	0.008	0.024	0.107	0.012	0.086	0.057
PP	0.009	0.008	0.014	0.032	0.047	0.027	0.070	0.274
4PA	0.013	0.017	0.016	0.046	0.103	0.157	0.331	0.475

Table S4. Surface element contents of four MPs before and after aging under different aging conditions

Microplastics	C/%	O/%	N/%	O/C	(O+N)/C
PE- Original	99.24	0.76	0.00	0. 008	---
PE-$UV+O_2$ 40d	98.35	1.65	0.00	0. 017	---
PE-UV 40d	98.46	1.54	0.00	0. 016	---
PE-$UV+O_2$ 120d	98.25	1.75	0.00	0. 018	---
PE-UV 120d	98.35	1.65	0.00	0. 017	---
PE-$UV+H_2O$ 40d	97.36	2.64	0.00	0. 027	---
PE-$UV+H_2O$ 80d	97.82	2.18	0.00	0. 022	---
PE-$UV+H_2O$ 120d	96.51	3.49	0.00	0. 036	---
PA- Original	76.09	11.77	12.14	0. 155	0. 314
PA-$UV+O_2$ 40d	74.15	12.61	13.24	0. 170	0. 349
PA-UV 40d	75.41	11.92	12.67	0. 158	0. 326
PA-$UV+O_2$ 120d	76.45	12.90	10.64	0. 169	0. 308
PA-UV 120d	76.98	12.20	10.81	0. 158	0. 299
PA-$UV+H_2O$ 40d	76.10	13.22	10.69	0. 174	0. 314
PA-$UV+H_2O$ 80d	74.86	13.78	11.35	0. 184	0. 336

Microplastics	C/%	O/%	N/%	O/C	(O+N)/C
PA-UV+H_2O 120d	74.69	13.44	11.87	0. 180	0. 339
PP- Original	98.30	1.70	0.00	0. 017	---
PP-UV+O_2 40d	98.00	2.00	0.00	0. 020	---
PP-UV 40d	98.27	1.73	0.00	0. 018	---
PP-UV+O_2 120d	97.42	2.58	0.00	0. 026	---
PP-UV 120d	97.69	2.31	0.00	0. 024	---
PP-UV+H_2O 40d	97.31	2.69	0.00	0. 028	---
PP-UV+H_2O 80d	96.30	3.70	0.00	0. 038	---
PP-UV+H_2O 120d	94.53	5.47	0.00	0. 058	---
PS- Original	98.94	1.06	0.00	0. 011	---
PS-UV+O_2 40d	97.20	2.80	0.00	0. 029	---
PS-UV 40d	98.68	1.32	0.00	0. 013	---
PS-UV+O_2 120d	93.62	6.38	0.00	0. 068	---
PS-UV 120d	93.85	6.15	0.00	0. 066	---
PS-UV+H_2O 40d	95.85	4.15	0.00	0. 043	---
PS-UV+H_2O 80d	94.37	5.63	0.00	0. 060	---
PS-UV+H_2O 120d	93.99	6.01	0.00	0. 064	---

Table S5. Excitation and emission wavelength ranges corresponding to three-dimensional fluorescence spectroscopy analysis

Area	Organic compound type	Excitation wavelength (Ex) nm	Emission wavelength (Em) (nm)
I	Tyrosine proteins	200–250	280–330
II	Tryptophan proteins	200–250	330–380
III	Fulvic acids	200–250	380-550
IV	Soluble microbial metabolites	250–450	280-380
V	Humic acid-like	250–450	380-550

Table S6. Analysis of PS-DOM by GC-MS. The similarity (SI) of the selected compounds in the table is ⩾80%

ageing condition	original（0d）	UV+H_2O (40d)	UV+H_2O (80d)	UV+H_2O (120d)	UV (120d)	UV+O_2 (120d)
	$C_4H_{10}O_3$	$C_4H_{10}O_3$	$C_4H_{10}O_3$	$C_4H_{10}O_3$	$C_{28}H_{46}O_2$	$C_9H_{16}N_4O_6$
	C_7H_6O	$C_7H_{14}O_3$	C_3H_9OP	$C_6H_{10}O$	$C_{14}H_{18}O_2$	$C_7H_{16}O_4$
	$C_{28}H_{46}O_2$	$C_3H_6ClNO_2$	$C_3H_6ClNO_2$	$C_8H_{18}O$	$C_9H_{18}O$	$C_8H_9NO_2$
	$C_{13}H_{26}O_2$	$C_8H_9NO_2$	$C_{28}H_{46}O_2$	$C_{11}H_{14}O$	$C_{19}H_{38}O_2$	$C_3H_4N_2$
	$C_{12}H_{24}O_3$	$C_3H_4N_2$	$C_{14}H_{18}O_2$	$C_9H_{18}O$	$C_{12}H_{24}O_3$	$C_{14}H_{18}O_2$
	$C_{14}H_{22}O$	$C_8H_{11}N_3$	$C_6H_{10}O$	$C_8H_8O_2$	$C_{19}H_{30}O_3$	$C_6H_{13}NO_3$
	$C_{16}H_{30}O_4$	C_3H_9OP	$C_8H_{18}O$	$C_{19}H_{38}O_2$	$C_{16}H_{30}O_4$	$C_9H_{18}O$
	$C_{15}H_{26}O$	$C_3H_3BrF_2$	$C_{10}H_{18}O$	$C_{12}H_{24}O_3$	$C_{15}H_{26}O$	$C_{10}H_{16}O$
	$C_{14}H_{22}O_2$	$C_{28}H_{46}O_2$	C_8H_8O	$C_{15}H_{24}$	$C_{14}H_{22}O_2$	$C_{19}H_{38}O_2$
	$C_{14}H_{18}O_2$	$C_7H_{16}O$	$C_{12}H_{22}O$	$C_{14}H_{22}O$		$C_{12}H_{24}O_3$
		$C_8H_9NO_2$	$C_9H_{16}O$	$C_{15}H_{24}O_2$		$C_{14}H_{22}O$
		$C_7H_{12}O_2$	$C_{11}H_{24}O$	$C_{16}H_{30}O_4$		$C_{16}H_{30}O_4$
		$C_8H_{16}O$	$C_{10}H_{20}O$	$C_{14}H_{22}O_2$		$C_{15}H_{26}O$
		$C_8H_{18}O$	$C_8H_{16}N_2$			$C_{14}H_{22}O_2$
		$C_7H_{16}O$	$C_7H_{12}N_2O$			
		$C_6H_{13}NO_3$	$C_{16}H_{30}O_4$			
Molecular formula		$C_{12}H_{24}$	$C_{12}H_{24}O_3$			
		$C_{11}H_{14}O$	$C_{15}H_{24}$			
		$C_8H_{10}O_2$	$C_{14}H_{22}O$			
		$C_9H_{18}O$	$C_{15}H_{26}O$			
		$C_{14}H_{20}O_3$	$C_{14}H_{22}O_2$			
		$C_{10}H_{16}O$				
		$C_{10}H_{20}O$				
		$C_8H_{16}N_2$				
		$C_7H_{12}N_2O$				
		$C_{15}H_{26}O_6$				
		$C_{16}H_{30}O_4$				
		$C_{12}H_{24}O_3$				
		$C_8H_{16}O_2$				
		$C_{15}H_{24}$				
		$C_{14}H_{22}O$				
		$C_{19}H_{30}O_3$				
		$C_8H_{16}O$				
		$C_{15}H_{26}O$				

Table S7. Analysis of PP-DOM by GCMS. The similarity (SI) of the selected compounds in the table is ≥80%

ageing condition	original（0d）	UV+H_2O (40d)	UV+H_2O (80d)	UV+H_2O (120d)	UV (120d)	UV+O_2 (120d)
Molecular formula	$C_{14}H_{18}O_2$	$C_{28}H_{46}O_2$	$C_4H_{10}O_3$	$C_9H_{18}O_6$	$C_9H_{16}O$	$C_9H_{16}O$
	$C_9H_{18}O$	$C_8H_9NO_2$	$C_8H_9NO_2$	$C_8H_{14}O$	$C_{13}H_{20}O$	$C_8H_{18}O$
	$C_{19}H_{38}O_2$	$C_{17}H_{30}O_4$	C_7H_6O	$C_7H_{16}O$	$C_8H_{18}O$	$C_{10}H_{18}O$
	$C_{12}H_{24}O_3$	$C_6H_{10}O$	$C_8H_6O_2$	$C_8H_{16}O$	$C_{10}H_{18}O$	$C_8H_{10}O_2$
	$C_{14}H_{22}O$	$C_8H_{18}O$	$C_{10}H_{20}O_2$	$C_9H_{20}O$	$C_9H_{14}O_2$	$C_9H_{18}O$
	$C_{12}H_{22}O_4$	C_7H_{14}	$C_6H_{14}O_2$	C_7H_6O	$C_8H_{10}O_2$	$C_{10}H_{16}O$
	$C_{14}H_{22}O$	C_8H_{16}	$C_8H_{18}O$	$C_7H_8O_2$	$C_{14}H_{24}O_2$	$C_{12}H_{22}O$
	$C_{16}H_{30}O_4$	$C_{11}H_{24}O$	$C_9H_{18}O_2$	$C_{10}H_{18}O_2$	$C_9H_{18}O$	$C_{12}H_{24}O$
	$C_{15}H_{26}O$	$C_{10}H_{20}$	$C_8H_8O_2$	$C_8H_{14}O_3$	$C_{15}H_{22}O_4$	$C_{19}H_{38}O_2$
	$C_{16}H_{22}O_4$	$C_{10}H_{20}O$	C_8H_8O	$C_9H_{12}O$	$C_{10}H_{16}O$	$C_{12}H_{24}O_3$
		$C_{10}H_{16}O$	$C_9H_{18}O$	$C_8H_{18}O$	$C_8H_8O_3$	$C_{12}H_{22}O_4$
		$C_{14}H_{17}NO_4$	$C_{10}H_{16}O$	$C_{18}H_{36}O$	$C_9H_{12}O_2$	$C_{14}H_{22}O$
		$C_8H_{16}O_2$	$C_{16}H_{30}O_4$	$C_{12}H_{26}$	$C_{11}H_{18}O_2$	$C_{16}H_{30}O_4$
		$C_9H_{16}O$	$C_{12}H_{24}O_3$	C_8H_8O	$C_{13}H_{26}O$	$C_{15}H_{26}O$
		$C_{10}H_{18}O_2$	$C_{15}H_{24}$	$C_{10}H_{18}$	$C_{12}H_{22}O$	$C_{14}H_{22}O_2$
		$C_7H_{12}N_2O$	$C_{14}H_{22}O$	$C_8H_{10}O_2$	$C_{11}H_{20}O_3$	
		$C_{15}H_{26}O$	$C_{16}H_{30}O_4$	$C_{15}H_{22}O_4$	$C_{13}H_{22}O_3$	
		$C_{18}H_{26}O$	$C_{15}H_{26}O$	$C_8H_8O_2$	$C_{19}H_{38}O_2$	
			$C_{14}H_{22}O_2$	$C_9H_{12}O_2$	$C_{12}H_{24}O_3$	
				$C_8H_{12}O_2$	$C_{14}H_{26}O_3$	
				$C_{15}H_{30}O_2$	$C_{12}H_{22}O_4$	
				$C_{11}H_{16}O_2$	$C_{14}H_{22}O$	
				$C_{14}H_{26}O_3$	$C_{14}H_{18}O$	
				$C_{11}H_{14}O$	$C_{11}H_{20}O$	
				$C_{16}H_{30}O_4$	$C_{16}H_{30}O_4$	
				$C_{12}H_{24}O_3$	$C_{15}H_{26}O$	
				$C_9H_{16}O_2$	$C_{14}H_{22}O_2$	
				$C_{14}H_{22}O$	$C_{20}H_{42}$	
				$C_{11}H_{20}O$		
				$C_8H_{12}O_3$		
				$C_8H_{14}O_2$		

Table S8. Analysis of PE-DOM by GCMS. The similarity (SI) of the selected compounds in the table is ≥80%

ageing condition	original（0d）	UV+H_2O (40d)	UV+H_2O (80d)	UV+H_2O (120d)	UV (120d)	UV+O_2 (120d)
Molecular formula	$C_{28}H_{46}O_2$	$C_5H_{12}O_2$	$C_4H_{10}O_3$	$C_8H_{18}O$	$C_8H_{18}O$	$C_{28}H_{46}O_2$
	$C_{19}H_{38}O_2$	$C_{28}H_{46}O_2$	$C_7H_{16}O$	$C_{10}H_{20}O$	$C_{13}H_{28}$	$C_8H_{18}O$
	$C_{12}H_{24}O_3$	$C_8H_9NO_2$	$C_8H_9NO_2$	$C_{11}H_{20}O_4$	$C_{10}H_{20}O$	$C_9H_{18}O$
	$C_{15}H_{24}$	$C_8H_{16}O$	$C_9H_{20}O$	$C_9H_{18}O$	$C_{10}H_{16}O$	$C_{19}H_{38}O_2$
	$C_{14}H_{22}O$	$C_{17}H_{30}O_4$	$C_8H_{18}O$	$C_{19}H_{38}O_2$	$C_9H_{16}O$	$C_{12}H_{24}O_3$
	$C_{19}H_{30}O_3$	$C_7H_{14}O$	$C_9H_{18}O_2$	$C_{12}H_{24}O_3$	$C_{13}H_{26}O$	$C_{14}H_{22}O$
	$C_{16}H_{30}O_4$	$C_6H_{10}O$	$C_{10}H_{20}O$	$C_{14}H_{30}$	$C_{10}H_{18}O_2$	$C_{16}H_{30}O_4$
	$C_{15}H_{26}O$	$C_8H_{18}O$	$C_{13}H_{28}O$	$C_{15}H_{24}$	$C_{12}H_{24}$	$C_7H_{12}N_2O$
	$C_{16}H_{22}O_4$	$C_9H_{18}O_2$	$C_9H_{18}O$	$C_{14}H_{20}O_2$	$C_{16}H_{30}O_4$	
		$C_{10}H_{20}O$	$C_{10}H_{16}O$	$C_{17}H_{36}$	$C_{12}H_{24}O_3$	
		$C_9H_{18}O$	$C_{16}H_{32}O_2$	$C_{14}H_{22}O$	$C_{15}H_{24}$	
		$C_{12}H_{24}O$	$C_{12}H_{22}O_2$	$C_{15}H_{24}O_2$	$C_8H_9NO_2$	
		$C_{10}H_{18}O_3$	$C_7H_{12}N_2O$	$C_{16}H_{30}O_4$	$C_7H_{12}N_2O$	
		$C_{10}H_{20}$	$C_{13}H_{26}O$	$C_{15}H_{26}O$	$C_8H_{16}N_2$	
		$C_{10}H_{14}O_2$	$C_8H_{16}N_2$	$C_{14}H_{22}O_2$	$C_{12}H_{18}N_4O_4$	
		$C_{15}H_{24}$	$C_{10}H_{18}O_2$	$C_{20}H_{42}$	$C_7H_{12}N_2O$	
		$C_8H_{13}NO_2$	$C_{11}H_{20}O$	$C_{21}H_{44}$		
		$C_{14}H_{22}O$	$C_{16}H_{30}O_4$	$C_{30}H_{62}$		
		$C_{16}H_{30}O_4$	$C_{12}H_{24}O_3$	$C_{18}H_{36}O$		
		$C_{15}H_{26}O$	$C_{10}H_{14}O_2$	$C_{16}H_{22}O_4$		
		$C_{15}H_{26}O$	$C_{15}H_{24}$			
			$C_{14}H_{22}O$			
			$C_{10}H_{18}O_3$			
			$C_{16}H_{30}O_4$			
			$C_{15}H_{26}O$			

Table S9. Analysis of PA-DOM by GCMS. The similarity (SI) of the selected compounds in the table is ≥80%

ageing condition	original（0d）	UV+H_2O (40d)	UV+H_2O (80d)	UV+H_2O (120d)	UV (120d)	UV+O_2 (120d)
Molecular formula	$C_{28}H_{46}O_2$	$C_5H_{12}O_2$	$C_4H_{10}O_3$	$C_6H_{14}O$	$C_8H_9NO_2$	$C_7H_{13}NO_4$
	$C_8H_9NO_2$	$C_6H_{14}O_4$	$C_3H_6O_4$	$C_8H_9NO_2$	$C_6H_{13}NO_3$	$C_8H_9NO_2$
	$C_{13}H_{28}$	$C_4H_{10}O_3$	$C_3H_4N_2$	$C_7H_{14}O$	$C_8H_{18}O$	$C_8H_{11}N_3$
	$C_{13}H_8N_2O_2$	$C_8H_9NO_2$	$C_7H_6N_4O$	$C_7H_{16}O$	$C_8H_{10}O_2$	$C_8H_{18}O$
	$C_8H_{18}O$	$C_9H_{16}O_{20}$	$C_5H_{11}NO$	$C_9H_{16}O_2$	$C_{10}H_{18}O$	$C_{14}H_{30}$
	$C_{17}H_{36}$	$C_7H_{14}O$	$C_{28}H_{46}O_2$	$C_8H_{16}O$	$C_9H_{18}O$	$C_{10}H_{12}$
	$C_{15}H_{32}$	$C_{17}H_{30}O_4$	$C_7H_{14}O$	$C_{12}H_{24}$	$C_8H_{16}O_2$	$C_8H_{10}O_2$
	$C_9H_{18}O$	$C_7H_{16}O$	$C_9H_{16}O_2$	C_8H_{16}	$C_{10}H_{16}O$	$C_9H_{18}O$
	$C_{14}H_{20}O_3$	$C_8H_{16}O$	C_8H_{16}	$C_8H_{14}O$	$C_9H_{12}O_2$	$C_{10}H_{16}O$
	$C_{10}H_{16}O$	$C_8H_{16}O_2$	$C_8H_{14}O$	$C_8H_{18}O$	$C_9H_{12}O_2$	$C_{10}H_{22}O$
	$C_{19}H_{38}O_2$	$C_6H_{10}O$	$C_8H_{18}O_2$	$C_8H_{17}N$	$C_{10}H_{18}O$	$C_{10}H_{18}O$
	$C_{12}H_{24}O_3$	$C_8H_{18}O$	$C_8H_{12}O_3$	$C_{10}H_{18}O$	$C_{11}H_{18}O_2$	$C_{10}H_8$
	$C_{15}H_{24}$	C_9H_{20}	$C_8H_{18}O$	$C_9H_{18}O$	$C_{10}H_{20}O$	$C_{11}H_{18}O_2$
	$C_{14}H_{20}O_2$	$C_{12}H_{24}O$	$C_{10}H_{18}O$	$C_{10}H_{16}O$	$C_{13}H_{22}O_3$	$C_{10}H_{20}O$
	$C_{14}H_{22}O$	$C_9H_{18}O_2$	$C_{11}H_{22}O$	$C_{11}H_{22}$	$C_{12}H_{24}O_3$	$C_{12}H_{20}O_2$
	$C_{16}H_{30}O_4$	$C_9H_{20}O$	$C_{13}H_{26}O$	$C_{11}H_{18}O_2$	$C_{18}H_{34}O_4$	$C_7H_{12}N_2O$
	$C_{15}H_{26}O$	$C_{12}H_{24}O$	$C_9H_{18}O_2$	$C_{10}H_{20}O$	$C_{13}H_{26}O$	$C_{13}H_{28}$
	$C_{14}H_{22}O_2$	$C_9H_{18}O$	$C_{11}H_{19}NO_2$	$C_9H_{16}O_2$	$C_{15}H_{24}$	$C_{19}H_{38}O_2$
	$C_{16}H_{22}O_4$	$C_7H_{12}N_2O$	$C_{10}H_{20}O$	$C_{15}H_{22}O_3$	$C_{12}H_{22}O_4$	$C_{12}H_{24}O_3$
		$C_{12}H_{24}O_3$	$C_{11}H_{22}O$	$C_{19}H_{38}O_2$	$C_{12}H_{26}O$	$C_{18}H_{34}O_4$
		$C_{15}H_{24}$	$C_{10}H_{16}O$	$C_{12}H_{24}O_3$	$C_{14}H_{22}O$	$C_{14}H_{30}$
		$C_{14}H_{22}O$	$C_9H_{20}O$	$C_{12}H_{22}O_3$	$C_{16}H_{30}O_4$	$C_{12}H_{24}O$
		$C_{16}H_{30}O_4$	$C_{16}H_{30}O_4$	$C_{14}H_{28}O$	$C_{18}H_{32}O$	$C_{15}H_{24}$
		$C_{18}H_{32}O$	$C_{12}H_{24}O_3$	$C_{15}H_{24}$	$C_{15}H_{26}O$	$C_{12}H_{22}O_4$
		$C_{15}H_{26}O$	$C_{15}H_{24}$	$C_{11}H_{20}O_2$	$C_{24}H_{50}$	$C_{15}H_{24}O_2$
		$C_{18}H_{26}O$	$C_{11}H_{18}$	$C_{13}H_{22}O$	$C_{15}H_{30}O$	$C_{12}H_{26}O$
		$C_{16}H_{22}O_4$	$C_{14}H_{22}O$	$C_{10}H_{16}O_2$	$C_{23}H_{44}O_3$	$C_{14}H_{22}O$
			$C_{18}H_{26}O$	$C_{14}H_{22}O$	$C_{21}H_{42}O$	$C_{16}H_{30}O_4$
				$C_{16}H_{30}O_4$	$C_{18}H_{36}O$	$C_{18}H_{32}O$
				$C_{15}H_{26}O$	$C_{16}H_{22}O_4$	$C_{15}H_{26}O$
				$C_{14}H_{22}O_2$	$C_{16}H_{34}O$	$C_{20}H_{42}$
				$C_{15}H_{20}O$		$C_{18}H_{36}O$
				$C_{18}H_{26}O$		$C_{27}H_{56}$
				$C_{16}H_{22}O_4$		$C_{21}H_{42}O$
				$C_{15}H_{24}O_2$		$C_{18}H_{26}O_4$
						$C_{16}H_{34}O$
						$C_{16}H_{22}O_4$

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