
Supplementary information

**Intrinsic physicochemical activity at
microplastic–water interfaces**

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Intrinsic Physicochemical Activity at Microplastic-Water Interfaces

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Table S1. Comparison of interaction energies and hydrogen-bond–related intermolecular distances (Å) between water and PE, PVC, and PMMA. Shown are computed quantities using OPLS-AA/SPC/E, OPLS-AA/C-GeM, and DFT (ω B97X-V/def2-TZVPD). Model systems are constructed from small-molecule analogues: $C_{12}H_{26}$ for PE, $CH_3CH_2CHClCH_3$ for PVC, and methyl heptanoate for PMMA. All geometries are optimized at each level of theory prior to analysis.

Binding energy (kcal/mol)	OPLS-AA/SPC/E	OPLS-AA/C-GeM	DFT (ω B97X-V/def2tzvpd)
PE	-3.43	-3.52	-4.01
PVC	-3.17	-3.18	-4.01
PMMA	-5.81	-6.72	-6.80
H-Bond distance (Å)			
PE(C...O)	3.43	3.52	3.55
PVC(Cl...O)	3.20	3.34	3.24
PMMA(O...O)	2.73	2.72	2.86

Table S2: Densities of simulated plastics compared to experiment. Simulated densities of polymer systems using OPLS-AA compared with experimental values for MPs¹ described in Figure 4. Each system is modeled as a single long chain with a degree of polymerization (DOP, number of repeat units) sufficient to ensure bulk-like behavior; structures are equilibrated using a standard 21-step protocol².

Plastic	DOP	Simulation Density	Exp. Density
PE	13198	0.821	0.855-0.990
PMMA	2700	1.100	1.170-1.200
PVC	6600	1.339	1.332-1.352
PS	2500	1.008	1.040
PP	4400	0.853	0.855-0.864
PET	1800	1.231	1.300-1.400

SUPPLEMENTARY NOTES

Supplementary Note 1. Semi-quantitative estimation of apparent hydroxyl radical production rate at the plastic–water interface

To place the observed interfacial physicochemical activity in a broader physiological and environmental context, we sought to obtain a semi-quantitative estimate of hydroxyl radical ($\cdot\text{OH}$) generation at the plastic-water interface. Because the reaction occurs locally within a confined and heterogeneous interfacial region rather than in bulk solution, direct determination of a true steady-state $\cdot\text{OH}$ concentration is not straightforward. In particular, the effective reactive interfacial volume and the true surface area contributing to radical generation are difficult to define precisely for individual particles. Therefore, our analysis was designed to provide a conservative, lower-bound estimate of the apparent interfacial $\cdot\text{OH}$ production rate rather than an absolute interfacial radical concentration.

1. Extraction of time-dependent surface APF fluorescence

Hydroxyl radical generation was monitored using aminophenyl fluorescein (APF), which becomes fluorescent upon oxidation to fluorescein. For each particle, the APF-derived fluorescence signal localized at the particle surface was tracked over time by confocal imaging. The microplastic surface-associated fluorescence region for each particle was segmented to measure the corresponding fluorescence intensity at each time point.

The surface fluorescence signal increased approximately linearly with time for most particles. Therefore, for each particle, the fluorescence trajectory was fit using a linear model:

$$I(t) = k_I t + b$$

where $I(t)$ is averaged surface fluorescence intensity for each particle at time t , k_I is the fitted rate of fluorescence increase, and b is the intercept.

2. Conversion to apparent fluorescein formation rate

As indicated in **Figure 1e**, APF detects the hydroxyl radical generation by reacting with it to form a fluorescein molecule that produces the measured fluorescence signal. To relate the measured fluorescence increase to product formation, fluorescence calibration curves were acquired in the corresponding solution environment (i.e., PBS, serum, and cell culture medium **Extended Data Figure 1 d-e**).

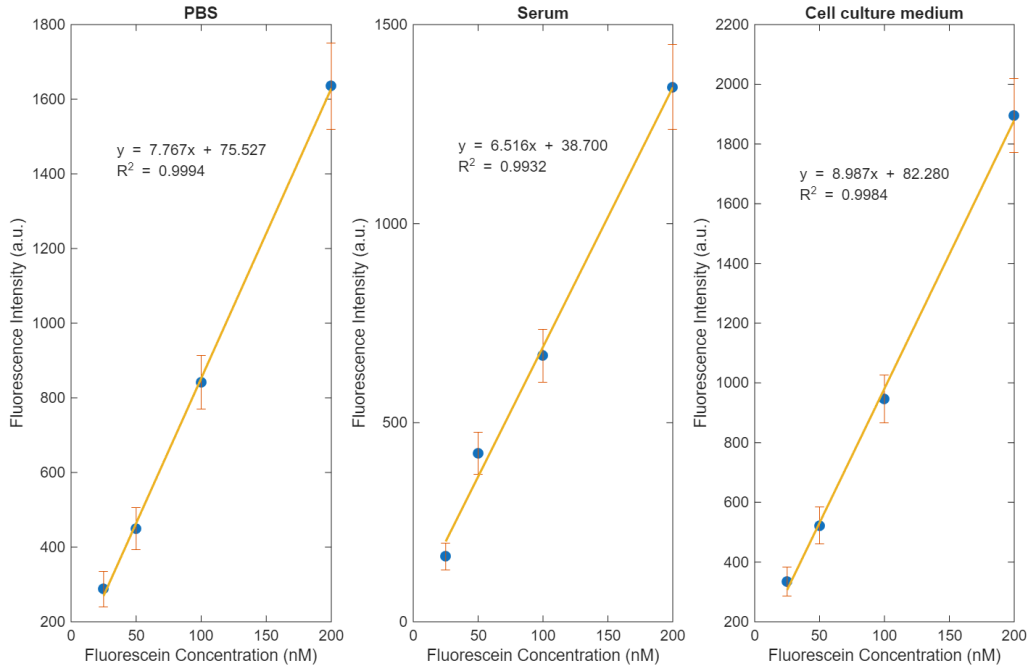


Figure S1 Fluorescein calibration curves in different solution environments.

Fluorescence intensity as a function of fluorescein concentration measured in PBS, serum, and cell culture medium. Data points represent mean $\pm$ s.d. Linear fits are shown as solid lines, with the corresponding fitting equations and R^2 values indicated in each panel.

These calibration curves were used to convert fluorescence intensity into an apparent fluorescein concentration at the interfacial region of microplastics. Thus, the fitted slope k_I for each particle was converted to an apparent fluorescein formation rate:

$$C_{\text{Fl}}^{\text{app}}(t) = k_{\text{Fl}}^{\text{app}} t + b'$$

where $C_{\text{Fl}}^{\text{app}}(t)$ is the apparent fluorescein concentration associated with the surface signal, and $k_{\text{Fl}}^{\text{app}}$ has units of concentration per unit time (for example, nM/min).

3. Lower-bound estimate of the $\cdot\text{OH}$ production rate at the plastic–water interface

Assuming approximate 1:1 conversion of APF to fluorescein upon reaction with $\cdot\text{OH}$,

$$R_{\cdot\text{OH}}^{\text{LB}} \approx k_{\text{Fl}}^{\text{app}}$$

the apparent fluorescein formation rate $k_{\text{Fl}}^{\text{app}}$ at the particle surface derived above was used as an operational readout to estimate a lower bound of $\cdot\text{OH}$ production rate $R_{\cdot\text{OH}}^{\text{LB}}$ at the plastic–water interface. This estimate is intended to provide a semi-quantitative measure of the interfacial oxidative activity captured by the APF assay under our experimental conditions, rather than the true total radical generation rate within the full interfacial region.

Several factors make this estimate inherently conservative. First, fluorescein generated near the particle surface may diffuse away from the segmented interfacial region during the measurement, leading to underestimation of local signal accumulation. Second, fluorescein can undergo photobleaching or other side reactions during imaging, further reducing the measured fluorescence increase. Third, radicals generated at the interface may not be fully captured by the APF sensor but rather consumed by competing reactions with surrounding solutes, biomolecules, or the particle surface before being reported through APF-derived fluorescence. In addition, the interfacial region has inevitable heterogeneity on probe accessibility. Together, these factors mean that the measured fluorescence increase reflects only the fraction of interfacial oxidative activity that is retained and captured within the assay readout. Accordingly, the converted apparent fluorescein increase rate is interpreted here as a lower-bound estimate of the $\cdot\text{OH}$ production rate at the plastic-water interface region, rather than an absolute rate of total radical generation.

Reference:

1. *Polymer Data Handbook: Second Edition*. (Oxford University Press New York, NY, 2009).
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2. Abbott, L. J., Hart, K. E. & Colina, C. M. Polymatic: a generalized simulated polymerization algorithm for amorphous polymers. *Theor Chem Acc* **132**, 1334 (2013).