Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Supporting Information

Characterizing photochemical ageing processes of microplastic materials using multivariate analysis of infrared spectra

Misha Zvekic[1], Larissa C. Richards[1,2], Christine C. Tong[1], Erik T. Krogh*[1,2]

[1]Applied Environmental Research Laboratories (AERL), Department of Chemistry, Vancouver Island University, 900 Fifth Street, Nanaimo, British Columbia, Canada

[2]Department of Chemistry, University of Victoria, PO Box 1700, Stn CSC, Victoria, British Columbia, Canada

* Corresponding author: Erik T. Krogh, Applied Environmental Research Laboratories, Department of Chemistry, Vancouver Island University, Erik.Krogh@viu.ca

Supporting Information contains 14 pages including Figures S1 – S10 and Tables S1 – S4.

Information includes supplier details on plastics used, spectral distribution and intensities of light treatments, photographs, summary of outdoor sunlight exposure data, assignment of IR spectral features identified by PC loadings, and additional PCA and CI results not included in the main document.

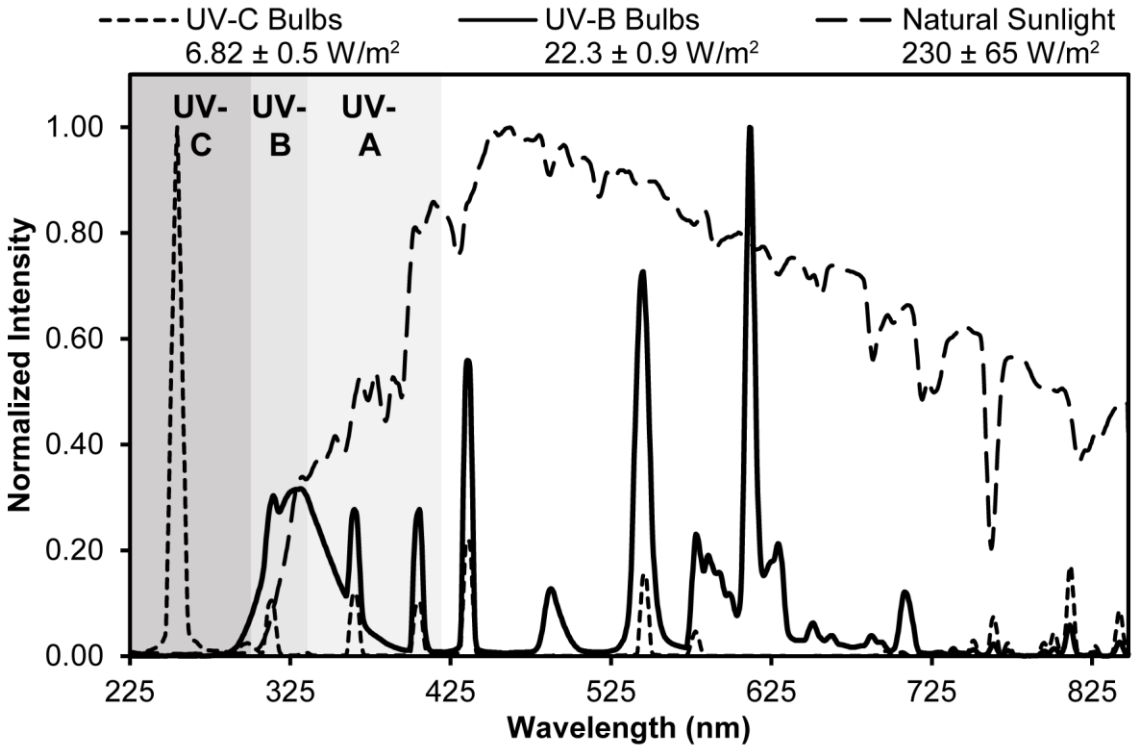

Figure S1. Normalized irradiance spectra and measured irradiance (W/m^2) ($n \geq 4$ measurements) of the three weathering light sources: UV-C (254 nm) mercury vapour bulbs, UV-B bulbs (ExoTerra PT2189), and the outdoor solar spectrum on an overcast day. The measured intensities of the light sources are listed, with the natural sunlight being an average daily value recorded by the Vancouver Island School-Based Weather Station Network (VISN) in Nanaimo (Ecole Hammond Bay Elementary)[1] over the course of the weathering period.

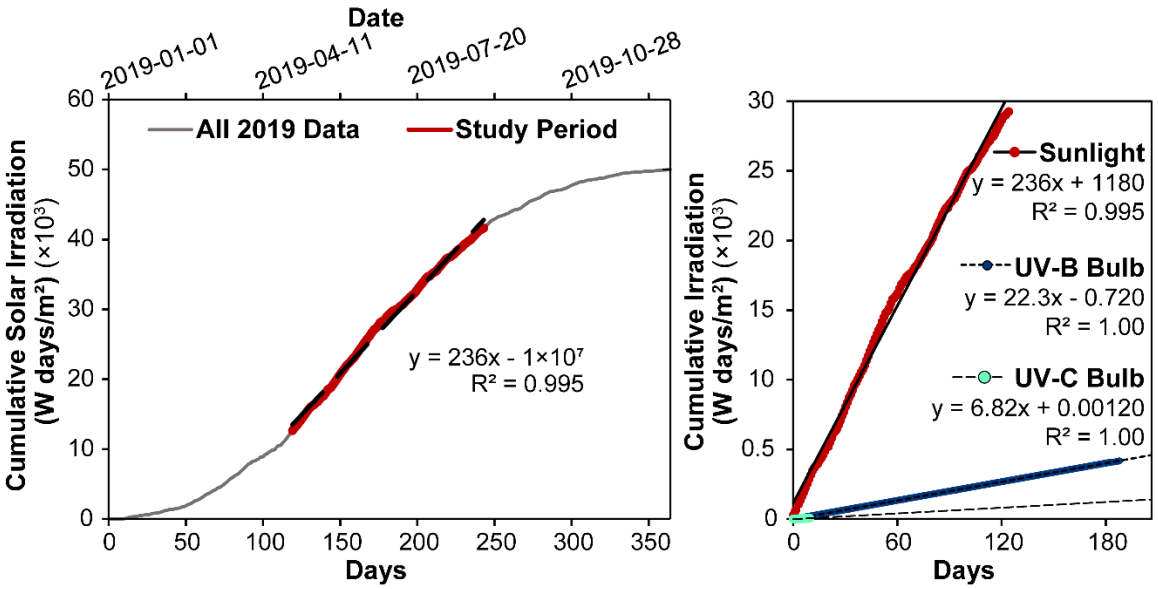

Figure S2. Left – Cumulative solar irradiation (W days/m^2) in Nanaimo as recorded by the VISN (Ecole Hammond Bay Elementary)[1] over the course of 2019 (grey) and during the study period (red). Right – Comparison of cumulative irradiation of sunlight (red) and the artificial UV-B (dark blue) and UV-C (light teal) light sources over the course of their exposure periods in days.

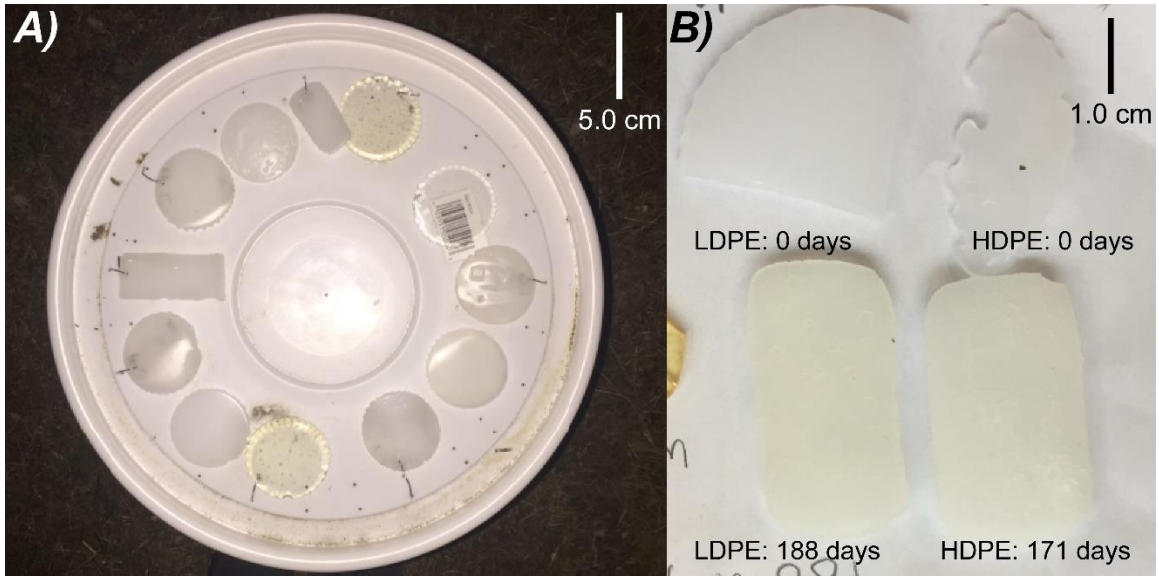

Figure S3. Photos of A) plastics weathering outdoors, and B) comparison of low-density polyethylene (LDPE) and high-density polyethylene (HDPE) before and after UV-B weathering.

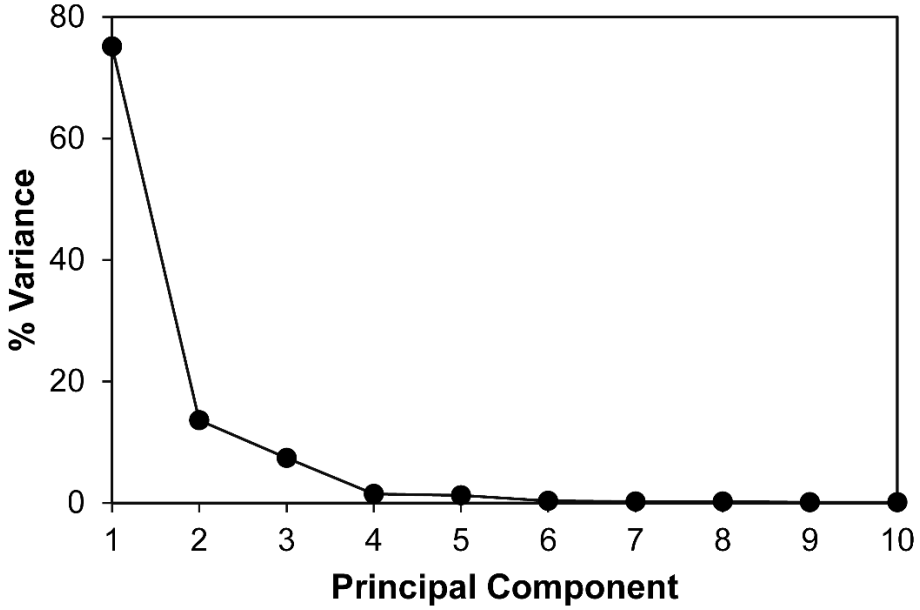

Figure S4. Scree plot illustrating the percent variance described by the first 10 principal components (PCs) in the principal component analysis (PCA). The first 3 PCs account for 96.2% of variance with each subsequent PC describing less than 1.5% of the remaining variance.

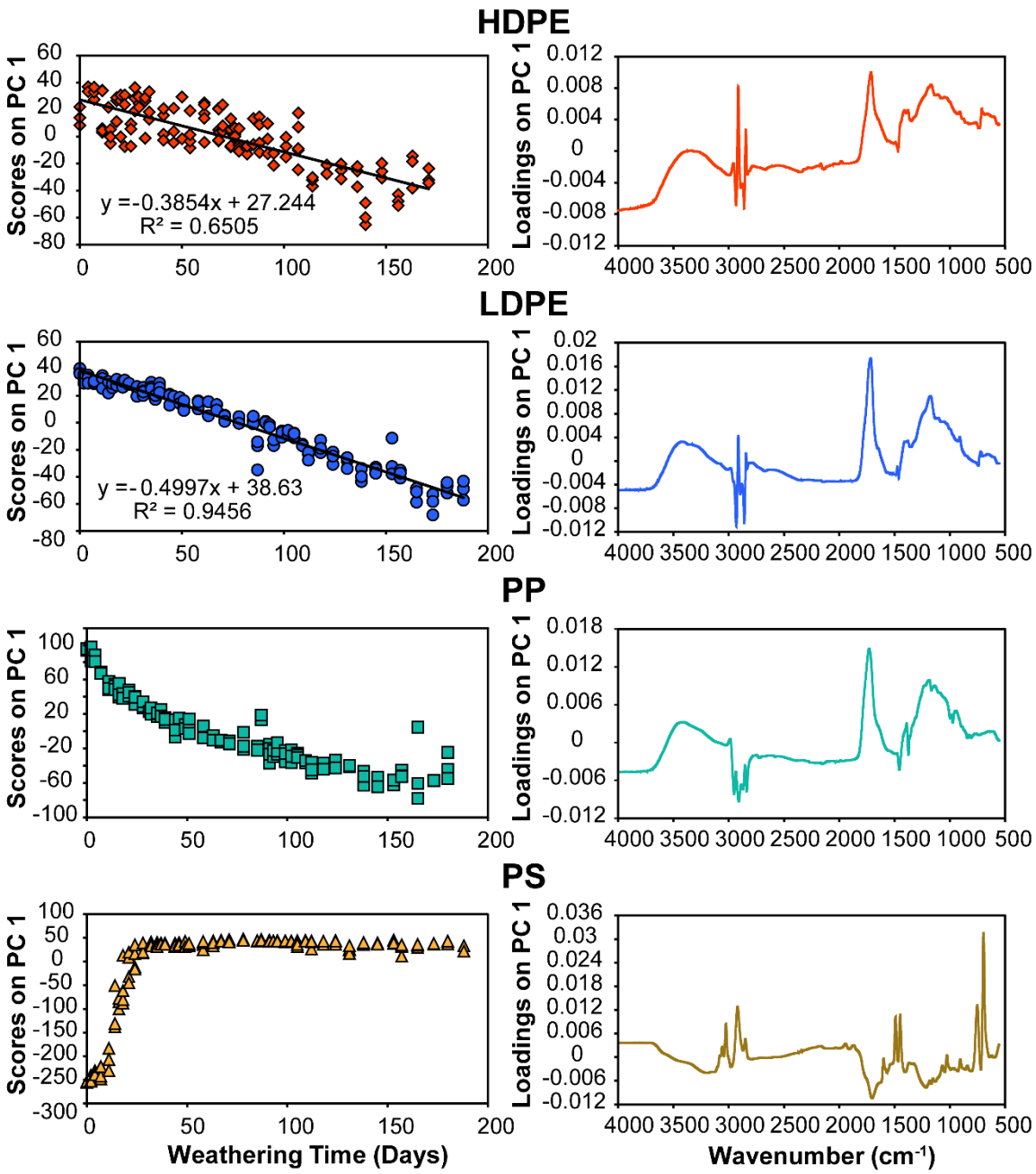

Figure S5. PCA applied to pristine and UV-B weathered spectra individually for each type of plastic; high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), and polystyrene (PS).

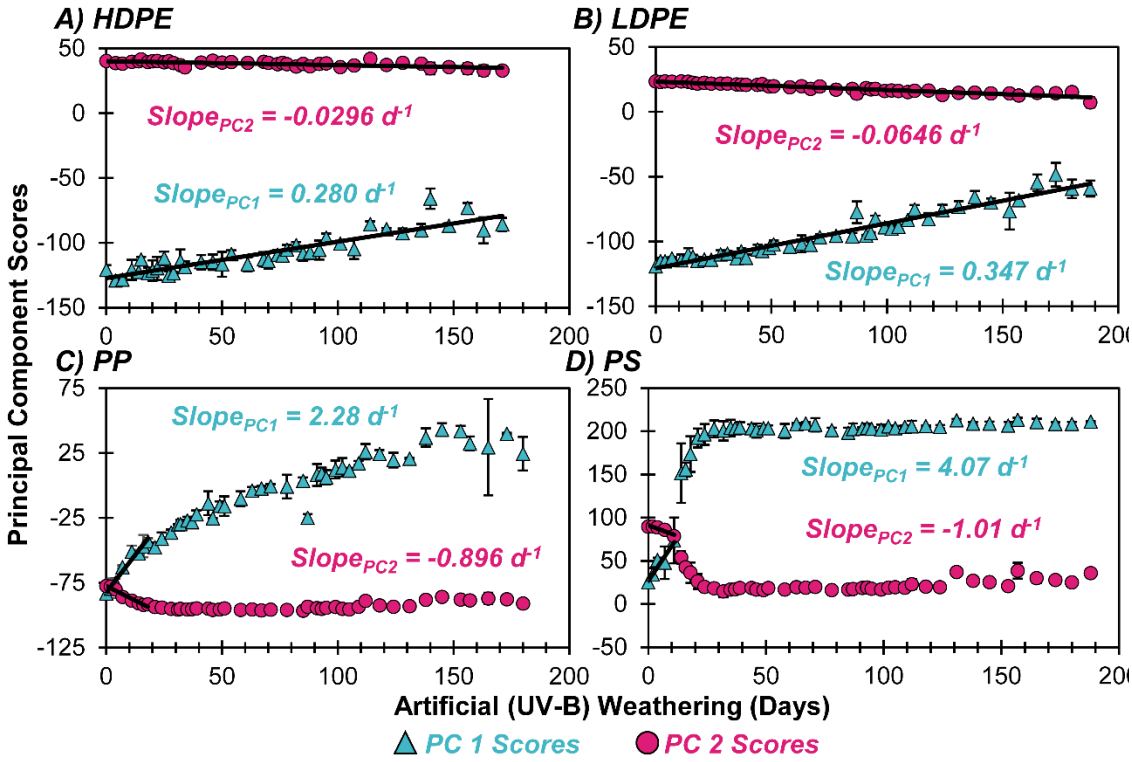

Figure S6. Changes in PC 1 (teal triangles) and PC 2 (pink circles) scores for A) HDPE), B) LDPE, C) PP, and D) PS over *ca.* six months of photochemical ageing under artificial UV-B lights. Equations for the linear fits for LDPE and HDPE over the full course of exposure, PP over the first 18 days, and PS over the first 11 days are included.

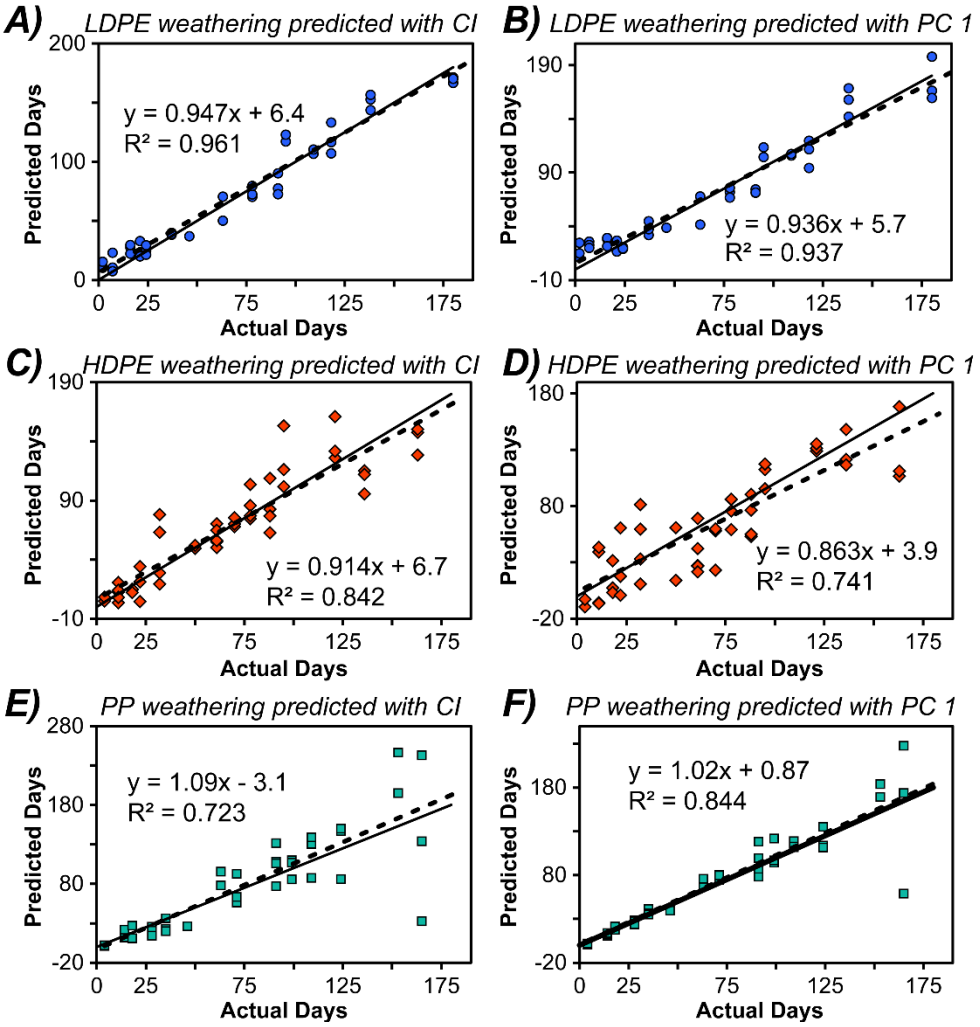

Figure S7. Predicting LDPE (A and B), HDPE (C and D), and PP (E and F) weathering under UV-B lights with CI (left) and PCA (right) by comparing predicted days of UV-B weathering against the actual days of UV-B weathering. The dotted lines represent the trendline through the data and the solid line is the line of equality (x=y).

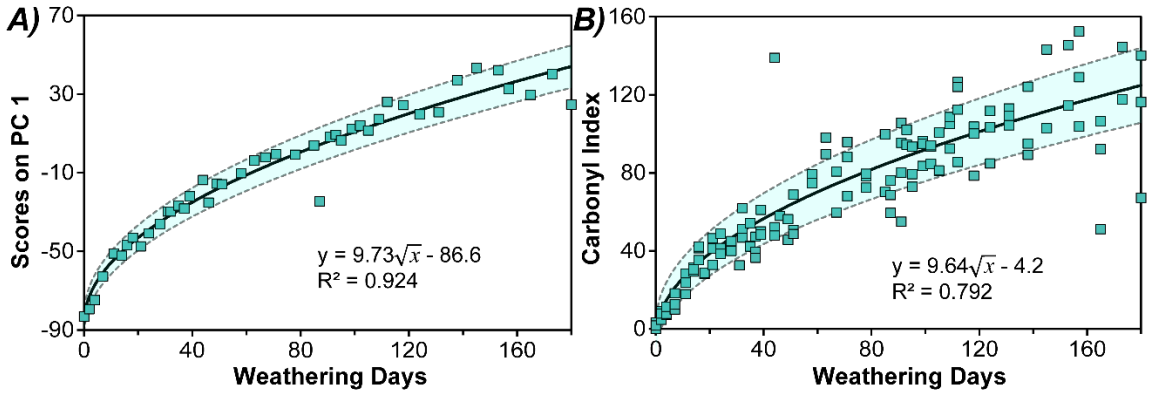

Figure S8. Trendlines through polypropylene scores on PC 1 (A) and carbonyl index (B). The boundaries of the 95% confidence intervals for the trendlines are represented as dashed lines.

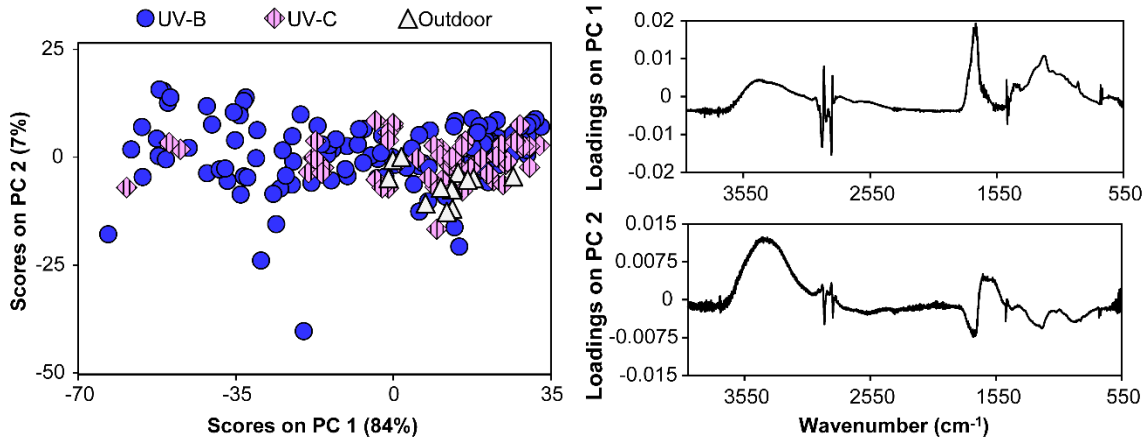

Figure S9. Left – PCA Scores plot for all LDPE samples with different weathering treatments (blue circles UV-B weathered, light grey triangles naturally weathered, pink striped diamonds UV-C weathered). Right – PCA Loadings plots for LDPE samples with all weathering treatments.

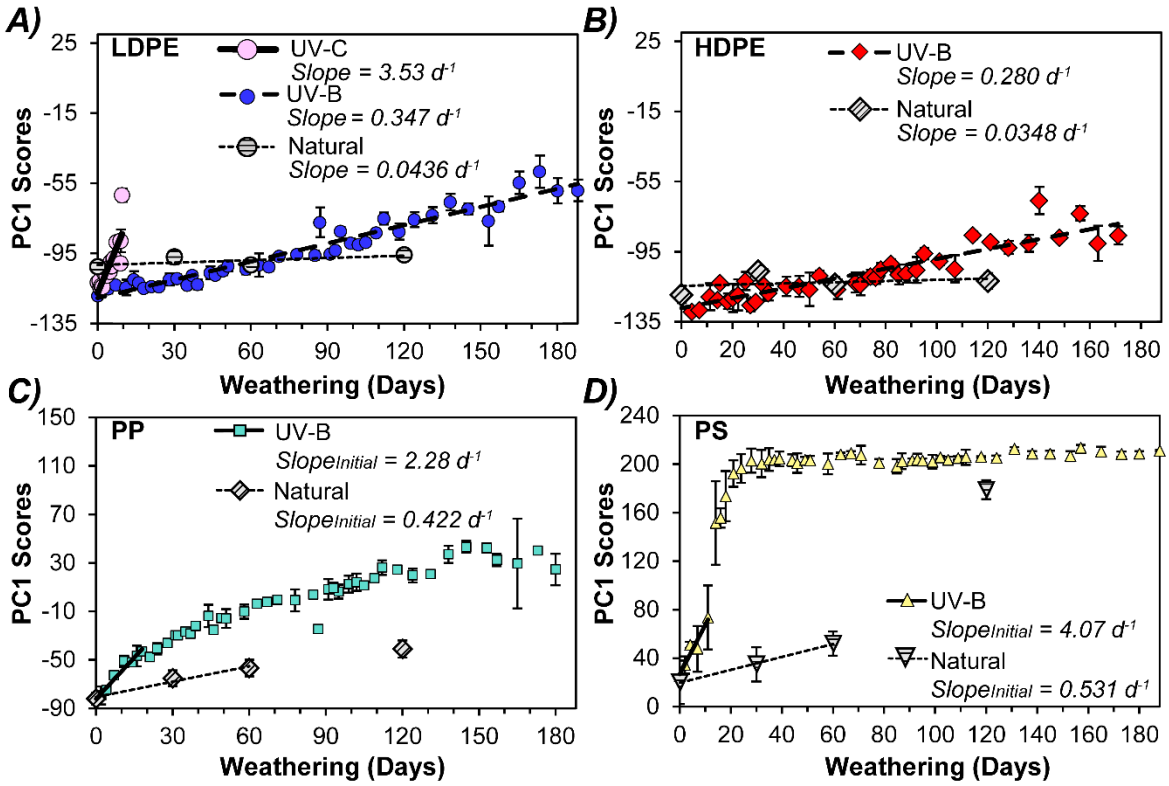

Figure S10. PC 1 scores over time for A) LDPE (blue UV-B weathered, grey striped naturally weathered, light pink UV-C weathered), B) HDPE (red UV-B weathered, grey striped naturally weathered), C) PP (teal UV-B weathered, grey striped naturally weathered), and D) PS (yellow UV-B weathered, grey striped naturally weathered).

Table S1. Manufacturer-provided properties of microplastics

Plastic Type [†]	LDPE	HDPE	PS	Isotactic PP
CAS #	9002-88-4	9002-88-4	9003-53-6	9003-07-0
CAT #	428043	547999	430102	427888
Form	Pellets	Pellets	Beads or Pellets	Pellets
Melt Index (g/10 min)	25 (190 °C/2.16 kg)	2.2 (190 °C/2.16 kg)	6.0-9.0 (200 °C/5 kg)	12 (230 °C/2.16 kg)
Density (g/mL at 25 °C)	0.925 (0.9215 – 0.9255)	---	---	0.9
Softening Point (°C) [§]	93	123	107	---
Melting Point (°C)	116	---	---	160-165
Hardness	---	65 (Shore D, ASTM D 2240)	---	100 (Rockwell R, ASTM D 785-A)
Impact Strength	45.4 J/m (Izod, ASTM D 256, −50 °C)	---	---	---
Average Molecular Weight (Mw)	---	---	~192,000	~250,000
Number Average Molecular Weight (Mn)	---	---	---	~67,000
Refractive Index	---	---	n20/D 1.59	---

[†] Values reported by Sigma Aldrich
[§] Vicat, ASTM D 1525

Table S2. Relative energy and intensity outputs of the light sources employed

Wavelength range	UV-B Bulbs (n = 4) †		UV-C Bulbs (n = 9)		Sunlight (n = 39)	
	Intensity § (%)	Energy §§ (%)	Intensity (%)	Energy (%)	Intensity (%)	Energy (%)
UV-C (225-280 nm)	Not ‡ detected	Not detected	51 ± 2	77 ± 1	Not detected	Not detected
UV-B (280-315 nm)	5.9 ± 0.1	12.1 ± 0.2	5.6 ± 0.6	5.9 ± 0.5	0.18 ± 0.02	0.51 ± 0.04
UV-A (315-400 nm)	27.1 ± 0.2	44.9 ± 0.1	6.4 ± 0.5	5.0 ± 0.4	9.7 ± 0.9	20 ± 1
Visible (400-847.5 nm)	67.0 ± 0.2	42.8 ± 0.3	37 ± 3	12.1 ± 0.5	90 ± 1	79 ± 1

† Values presented are the mean in 'n' replicate measurements ± standard deviation.

§ The relative proportions of the intensity of the different light sources were determined by integrating the intensity of the spectra (Figure S1) over the wavelength using the 'trapz' function in MATLAB.

§§ Similarly, the relative proportions of the energy were determined by integrating the intensity of the spectra over the reciprocal wavelength.

‡ Less than our estimated detection limit of 0.3%.

Table S3. IR assignments of variables identified by principal component 1 loadings

Wavenumbers (cm^{-1})	Contributing Polymer †	Associated Vibrational Mode	Reference
3690-3120	wPS, (wPP, wLDPE, wHDPE)	O-H	2
3079, 3059	pPS	C-H stretching	
3025	pPS	aromatic C-H stretching	3
2914	p/wLDPE, p/wHDPE, (p/wPP)	C-H stretching	3
2847	p/wLDPE, p/wHDPE, (pPS, wPS)	C-H stretching	3
1702	wPS, (wPP, wLDPE, wHDPE)	C=O groups	4,5
1600	wPS, (pPS)	aromatic ring stretching, conjugated C=C stretching	2,3
1490	pPS	aromatic ring stretching	3
1467	p/wLDPE, p/wHDPE	trough between 1462 and 1473 cm^{-1} peaks (CH_2 bending)	3
1411-800	wPS (wPP, wHDPE, wLDPE)		2
1200-1000	(wPP, wLDPE, wHDPE, wPS)	C-O bonds	5
1024	wPS, (pPS)	aromatic CH out-of-plane bending	3
754	wPS, (pPS)		
724	p/wLDPE, p/wHDPE	trough between 719 and 730 cm^{-1} peaks (CH_2 rocking)	3
694	wPS (pPS)	aromatic CH out-of-plane bending	3

† Weathered (w) and pristine (p) plastics. Presence of peaks in infrared (IR) spectra of the four different polymers are used to identify potential contributing polymers for each wavenumber. Polymers whose spectra most greatly resemble the PC loadings are listed first, while plastics which have minor contributions are listed secondarily in brackets.

Table S4. IR assignments of variables identified by principal component 2 loadings

Wavenumbers (cm^{-1})	Contributing Polymer †	Associated Vibrational Mode	Reference
3620-3225	wPP, wLDPE, wHDPE (wPS)	O-H	2
3058	pPS (wPS)		
3025	pPS (wPS)	aromatic C-H stretching	3
2953	p/wPP, wPP	trough between 2949 (C-H stretching) and 2960 cm^{-1}	3
2923	pPS, wPS, (p/wPP, p/wLDPE, p/wHDPE)	C-H stretching	3
2870	p/wPP	trough between 2866 and 2877 cm^{-1}	
2849	pPS, wPS (p/wLDPE, p/wHDPE)	C-H stretching	3
2721	p/wPP	CH bending, CH_3 stretching	6
1735	wPP, wLDPE, wHDPE, (wPS)	C=O groups	4
1598	pPS (wPS)	aromatic ring stretching, conjugated C=C stretching	2,3
1490	pPS (wPS)	aromatic ring stretching	3
1452	pPS, (pPP, wPP, wPS)	CH_2 bending	3,7
1375	p/wPP (p/wLDPE, p/wHDPE)	CH_3 bending	3
1200-1000	(wPP, wLDPE, wHDPE, wPS)	C-O bonds	5
1165	pPP, (wPP)	CH bending, CH_3 rocking, C-C stretching	3
996	p/wPP (wPS)	CH_3 rocking, CH_3 stretching, CH bending	3
972	p/wPP	CH_3 rocking, C-C stretching	3
841	p/wPP	CH_2 rocking, C-CH_3 stretching	3
809	p/wPP	CH_2 rocking, C-C stretching, C-CH stretching	3
753	pPS, (wPS)		
724	p/wLDPE, p/wHDPE	trough between 719 and 730 cm^{-1} peaks (CH_2 rocking)	3
695	pPS, (wPS)	aromatic CH out-of-plane bending	3

† Weathered (w) and pristine (p) plastics. Presence of peaks in IR spectra of the four different polymers are used to identify potential contributing polymers for each wavenumber. Polymers whose spectra most greatly resemble the PC loadings are listed first, while plastics which have minor contributions are listed secondarily in brackets.

References

1 Vancouver Island School-Based Weather Station Network, https://www.victoriaweather.ca/data_summary.php?id=139&year=2019, (accessed November 2021)

2 V. Fernández-González, J. M. Andrade-Garda, P. López-Mahía and S. Muniategui-Lorenzo, Impact of Weathering on the Chemical Identification of Microplastics from Usual Packaging Polymers in the Marine Environment, *Anal. Chim. Acta*, 2021, **1142**, 179–188.

3 M. R. Jung, F. D. Horgen, S. v. Orski, V. Rodriguez C., K. L. Beers, G. H. Balazs, T. T. Jones, T. M. Work, K. C. Brignac, S. J. Royer, K. D. Hyrenbach, B. A. Jensen and J. M. Lynch, Validation of ATR FT-IR to Identify Polymers of Plastic Marine Debris, Including Those Ingested by Marine Organisms, *Mar. Pollut. Bull.*, 2018, **127**, 704–716.

4 M. Hamzah, M. Khenfouch, A. Rjeb, S. Sayouri, D. S. Houssaini, M. Darhouri and V. v. Srinivasu, Surface Chemistry Changes and Microstructure Evaluation of Low Density Nanocluster Polyethylene under Natural Weathering: A Spectroscopic Investigation, *J. Phys.: Conf. Ser.*, 2018, **984**, DOI: 10.1088/1742-6596/984/1/012010.

5 J. Brandon, M. Goldstein and M. D. Ohman, Long-Term Aging and Degradation of Microplastic Particles: Comparing in Situ Oceanic and Experimental Weathering Patterns, *Mar. Pollut. Bull.*, 2016, **110**, 299–308.

6 G. Grause, M. F. Chien and C. Inoue, Changes during the Weathering of Polyolefins, *Polym. Degrad. Stab.*, 2020, **181**, 109364.

7 E. Yousif and R. Haddad, Photodegradation and Photostabilization of Polymers, Especially Polystyrene: Review, *SpringerPlus*, 2013, **2**, 1–32.