Electronic Supporting Information to:

Photochemical dissolution of polyurethane microplastics produced complex and dynamic mixtures of organic chemicals

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S-1. Chemicals and analytical standards

Magnesium chloride pure (CAS 7786-30-3) and calcium chloride 96% (CAS 10043-52-4) were obtained from ACROS ORGANICS. Sodium chloride, pure (CAS 7647-14-5) and sodium sulfate anhydrous 99% (CAS 7757-82-6) were obtained from Fisher Chemical. Sodium fluoride >99% (CAS 7681-49-4) and potassium bromide >99% (CAS 7758-02-3) were obtained from Mallinckrodt. Boric acid 99.8% (CAS 10043-35-3) was obtained from Merck. Strontium chloride >99% (CAS 7647-14-5) and potassium chloride >99% (CAS 7447-40-7) were obtained from Sigma-Aldrich. Sodium bicarbonate >99% (CAS 144-55-8) was obtained from EMD Chemicals Inc. HPLC-grade methanol was obtained from Fischer Scientific. Adipic acid-13C6 99% and diethylene glycol-D8 98% were purchased from Cambridge Isotope Laboratories. Potassium hydrogen phthalate (CAS 877-24-7) 1000±10ppm in water was purchased from LabChem. Purine 98% (CAS 120-73-0) and hexakis(1H, 1H, 3H-tetrafluoropropoxy)phosphazene 97.5% (CAS 58943-98-9) were purchased from Agilent.

S-2. Microplastics physicochemical properties

The TPU_Ether and TPU_Ester both use divalent aromatic polyol segments that are reacted with a prepolymerised isocyanate to generate non-crosslinked polyurethane chains with the molar mass distributions given in Figure S-2.2. The IR spectra and their aging were recently described for the identical TPU_Ether¹. In contrast, the PU_Hardened is a crosslinked structure generated by the reaction of a triglyceride polyol (based on castor oil) with a prepolymerised isocyanate. A molar mass distribution of PU_Hardened cannot be determined due to the insoluble crosslinked nature. All test materials were cryo-milled as described elsewhere¹ with the resulting particle sizes given in Table S-2.1. The density of all test materials is similar in the range of 1.15 to 1.20 g/cm³ (Table S-2.1).

Material	Particle size distribution	Density
TPU_Ester	Dx(10) 136 μm	1.2 g/cm3
	Dx(50) 273 μm	
	Dx(90) 478 μm	
TPU_Ether	Dx(10) 120 μm	1.16 g/cm3
	Dx(50) 256 μm	
	Dx(90) 464 μm	
PU_Hardened	Dx(10) 122 μm	1.15 g/cm3
	Dx(50) 253 μm	
	Dx(90) 422 μm	

Table S-2.1. Particle size distribution and density of the investigated polymers





S-3. Photoreactor characterization

Figure S-3.1. Irradiated area and irradiance values of UV-A radiation at 340 nm (in μ W cm⁻²). The photo-weathered samples were placed within the area highlighted with a red dashed line.



Figure S-3.2. Light spectrum measured in photoreactor's center area



S-4. TOC analysis method performance

To quantify the dissolved organic carbon generated by photo-oxidation of the microplastics, 8 calibration standards in the range of 1-500 mg/L organic carbon were prepared. The mean area values obtained by triplicate injections were plotted against the theoretical concentrations (Table S-4.1) to obtain a calibration curve (Fig. S-4.1).

Theoretical Concentration	Mean Area (n=3)
(mg/L)	(A.U.)
1	243
5	1174
12.5	3059
25	5246
50	10880
100	19593
250	50691
500	102933

Figure S-4.1. TOC analysis calibration curve



A blank and the lowest calibration standard (1 mg/L) were injected seven times. The mean blank value (*BLK*_{mean}) and the standard deviation of the calibration standard (*STD*_{SD}) shown in Table S-4.2 were used to calculate the limit of detection (LOD) and the limit of quantification (LOQ) according to equation 1 and equation 2, respectively. The method precision was calculated as the relative standard deviation (RSD) of seven injections of the 1 mg/L standard. The method performance is summarized in Table S-4.3.

 $LOD = BLK_{mean} + 3*STD_{SD}$

LOQ =	BLK _{mean}	+	6*	SI	D	SE

Table S-4.2. Data for method performance

		Calculated
Sample	Area	concentration (mg/L)
STD_1ppm_inj_1	209	0.72
STD_1ppm_inj_2	280	1.07
STD_1ppm_inj_3	249	0.92
STD_1ppm_inj_4	232	0.83
STD_1ppm_inj_5	262	0.98
STD_1ppm_inj_6	228	0.81
STD_1ppm_inj_7	241	0.88
Blank_inj_1	64	0.01
Blank_inj_2	97	0.18
Blank_inj_3	74	0.06
Blank_inj_4	72	0.05
Blank_inj_5	68	0.03
Blank_inj_6	99	0.19
Blank_inj_7	103	0.20

LOD	LOQ	Precision	
mg/L	mg/L	RSD (%)	
0.45	0.79	12.8	

(1)

(2)

S-5. Extrapolation of DOC release rates

The DOC release rates expressed as mass of organic carbon released to ambient seawater per cumulative UV dose received by the polyurethane microplastics (mg MJ⁻¹), were extrapolated adapting an approach published by Wohlleben and Neubauer². First, the release of carbon per microplastics surface area (mg m⁻²) was determined. For this purpose, the DOC concentrations (mg L⁻¹) were converted to absolute amounts (mg), as the seawater volume in the samples was known. Subsequently, assuming that the particles were spherical and that the known particle size equaled the sphere diameter, the volume (m³) and area (m²) of a single particle were calculated. This way, the mass of a single particle could be obtained by rearranging the density equation ($\delta = m V^{-1}$). Knowing the total mass of microplastics added to the samples, it was possible to calculate the number of particles in each sample and consequently the total microplastics surface area was assumed. Finally, the release in units of mg m⁻² was divided by the cumulative UV dose integrated across the wavelength range of 300 to 400 nm (MJ m⁻²) to obtain the rates in units of mg MJ⁻¹.

S-6. Nontarget screening workflow script for patRoon

All functions and parameters listed below are explained in detail in Helmus et al. (2021)³.

```
workPath <- "/Volumes/Extreme SSD/PU microplastics /"</pre>
setwd(workPath)
anaInfo <- read.csv("anaInfo.csv")
# ------
# features
# -----
# Find all features.
# NOTE: see manual for many more options
fList <- findFeatures(anaInfo, "openms")</pre>
# Group and align features between analysis
fGroups <- groupFeatures(fList, "openms")</pre>
# Basic rule based filtering
fGroups <- filter(fGroups, preAbsMinIntensity = 1000, absMinIntensity = 20000,</pre>
                 relMinReplicateAbundance = 1, maxReplicateIntRSD = 0.75,
                 blankThreshold = 10, removeBlanks = TRUE,
                 retentionRange = NULL, mzRange = NULL)
 -----
# annotation
# ------
# Retrieve MS peak lists
avgPListParams <- getDefAvgPListParams(clusterMzWindow = 0.005)</pre>
mslists <- generateMSPeakLists(fGroups, "mzr", maxMSRtWindow = 5, precursorMzWindow = 4,</pre>
                              avgFeatParams = avgPListParams, avgFGroupParams = avgPListParams)
# Calculate formula candidates
formulas <- generateFormulas(fGroups, "genform", mslists, relMzDev = 5,</pre>
                            adduct = "[M+H]+", elements = "CHNO",
                            calculateFeatures = T, featThreshold = 0.75)
```

S-7. ATR-FTIR analysis

Figure S-7.1. Microplastics yellowing at t= 60d.



Figure S-7.2. Proposed Mechanisms behind PU yellowing



Figure S-7.2. PU yellowing results from the oxidation of aromatic isocyanate residues to monoquinone imide and diquinone imide when irradiated with UV light at wavelength greater than 340 nm^{4–6}. PU yellowing can also result from photo-Fries rearrangement of the urethane linkage after irradiation with UV light at wavelength lower than 340 nm^{5,7}.

Figure S-7.3. Absorbance spectrum of TPU_Ester



Figure S-7.4. Absorbance spectrum of TPU_Ether





Figure S-7.5. Absorbance spectrum of PU_Hardened

Figure S-7.6. Absorbance band at 814 cm⁻¹ (out-of-plane C–H bending vibration in 1,4-disubstituted aromatic rings)





Figure S-7.7. Absorbance bands of asymmetrical (2856 cm⁻¹) and symmetrical (2941 cm⁻¹) – CH_2 — stretching vibrations

Figure S-7.8. Absorbance bands of amide II (1527 cm⁻¹), quinonic C=C (1597 cm⁻¹) and carbonyl (1704 cm⁻¹) stretching vibrations









Figure S-7.10. Absorbance band at 1100 cm⁻¹ in C—O stretching vibration in ether bonds

S-8. Elemental Analysis Results

The CHNO content in the dark samples matched values expected for raw polyurethanes. The oxygen abundance of the non-irradiated PU microplastics (Fig. S-8.1c) followed the order of the carbonyl index (Manuscript Figure 1): TPU Ester>>TPU Ether>>PU Hardened. The different O mass fraction of the TPU elastomers matched well the chemistry of the flexible segment, whereas the lower values obtained for PU Hardened suggested that possibly shorter polyol precursors were used during manufacture. This was reasonable as short polyols typically result in a more rigid PU structure. Compared to the dark controls, C mass in TPU Ether and TPU Ester had gradually decreased by 2% and 0.9%, respectively by 120d. Likewise, H mass fractions decreased by 0.5% and 0.4% in TPU Ether and TPU Ester, respectively. The mean O mass fraction increased by 0.5% for TPU Ether, but decreased by 0.8% for TPU Ester. The N mass fraction followed the pattern observed for O, although it was considered negligible as it accounted for 0.1% mass change only. In all cases and for all elements, no substantial differences were observed between the results at 90 and 120 days due to overlapping values. Apart from a minor increase in N mass fraction (0.2%), PU Hardened gave ambiguous results due to large deviations between measurements, especially for C content (Fig. S-8.1a), but also in H and O content (Fig. S-8.1b and Fig. S-8.1c) and most notably in dark controls. As mass loss through hydrolysis should be ruled out for this polymer, it was assumed that that the crosslinked PU material was more heterogeneous prior to irradiation.



Figure S-8.1. Elemental Analysis Results of the residual polymer

Figure S-8.1. Carbon (a), hydrogen (b), oxygen (c) and nitrogen (d) mass fractions in the PU microplastics and their variations as function of UV irradiation time (days). Data points and error bars represent the mean and standard deviations, respectively, obtained from three replicate samples. Invisible error bars are smaller than the data marker. The dark control corresponds to 120 days.

S-9. LC-HRMS data



Figure S-9.1. Hexbin chart showing feature density in their respective Van Krevelen space

Figure S-9.2. Van Krevelen space enhanced to display correlation (Spearman's rho) between normalized feature intensity and irradiation time.



References

- Pfohl P, Wagner M, Meyer L, et al. Environmental Degradation of Microplastics: How to Measure Fragmentation Rates to Secondary Micro- and Nanoplastic Fragments and Dissociation into Dissolved Organics. *Environ Sci Technol*. 2022;56(16):11323-11334. doi:10.1021/acs.est.2c01228
- Wohlleben W, Neubauer N. Quantitative rates of release from weathered nanocomposites are determined across 5 orders of magnitude by the matrix, modulated by the embedded nanomaterial. NanoImpact. 2016;1:39-45. doi:https://doi.org/10.1016/j.impact.2016.01.001
- 3. Helmus R, ter Laak TL, van Wezel AP, de Voogt P, Schymanski EL. patRoon: open source software platform for environmental mass spectrometry based non-target screening. *J Cheminform*. 2021;13(1):1. doi:10.1186/s13321-020-00477-w
- 4. Rabek JF. *Polymer Photodegradation*. SPRINGER-SCIENCE+BUSINESS MEDIA, B.V; 1995.
- Xie F, Zhang T, Bryant P, Kurusingal V, Colwell JM, Laycock B. Degradation and stabilization of polyurethane elastomers. *Prog Polym Sci.* 2019;90:211-268. doi:https://doi.org/10.1016/j.progpolymsci.2018.12.003
- Singh RP, Tomer NS, Bhadraiah SV. Photo-oxidation studies on polyurethane coating: effect of additives on yellowing of polyurethane. *Polym Degrad Stab.* 2001;73(3):443-446. doi:https://doi.org/10.1016/S0141-3910(01)00127-6
- 7. Wilhelm C, Gardette J-L. Infrared analysis of the photochemical behaviour of segmented polyurethanes: aliphatic poly(ether-urethane)s. *Polymer (Guildf)*. 1998;39(24):5973-5980. doi:https://doi.org/10.1016/S0032-3861(97)10065-9