

**This Supporting Information A (SI\_A) contains 11 texts, 33 figures and 4 tables.**

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# Text S1 – Details on consumer products

Four different types of PE-consumer products were selected. PE\_1 (greenhouse cover foil), PE\_2 (sunprotection cover), and PE\_4 (agricultural foil) are produced for outdoor applications. PE\_1 and PE\_2 are advertised as being weather-resistant, therefore increased UV-stability was expected. PE\_3 was a jerrycan (HD-PE), which was also advertised with UV-stable properties.

PET products were selected from the field of electrical applications. Due to the high safety demands, materials for electronic devices are known to contain high additive contents, e.g. of flame retardants [1]. The selected materials are applied as D-SUB plugs (PET\_1) and multipurpose housings (PET\_2). PET\_2 was advertised as chemically resistant and ideal for harsh environments.

Two types of PVC tubing were selected. PVC\_1 is used as a cable housing, so flame retardants were expected in this product, and PVC\_2 is recommended for the transport of foodstuff, which might indicate a comparatively low additive load.

ATR-FTIR spectroscopy was applied to confirm the polymer types of the selected plastic products (Table 1), and in several cases indicated a polymer composition different from that stated by the manufacturer. For Analysos plastic pieces were placed on diamond crystal and analyzed by ATR-FTIR spectroscopy (Alpha I, Bruker Optics, Ettlingen, Germany). Measurements were performed three times with 32 scans and a resolution of 4 cm-1 (wavenumber range: 4000 cm-1 – 400 cm-1).

The respective ATR-FTIR spectra were compared to the siMPle single spectra IR (326 spectra) and automated IR analysis (270 spectra) databases published by Primpke et al. (2020) (https://simple-plastics.eu) using OPUS 7.5 (Bruker Optics) (Primpke et al. 2020). Hereby, the vector-normalized original spectra and their first derivatives were used. A hit quality index (HQI) value was determined for the database comparison of every spectrum. Additionally, IR spectra of UV-treated and DC plastics were compared to those of their respective raw materials (untreated plastics).

Only three of the eight materials could be fully verified as the material declared by the manufacturer based on high HQI values: PE\_1 (transparent greenhouse cover foil), PE\_3 (jerrycan), and PE\_4 (agricultural foil: black and white side). PE\_2 (grey sun protection foil for balconies) exhibited one PE and one PET side. PET\_1 (D-Sub plug housing) was identified as styrene acrylonitrile copolymer (SAN; HQI value: 745/1000; good visual spectral agreement). Although the material is distributed as PET, the clear presence of a nitrile band at 2250 cm-1, amongst others, was observed. In accordance with the dedicated use of the housing material, the similar copolymers acrylonitrile butadiene styrene (ABS) and SAN have an increased relevance for electrical and electronic applications (Plastics Europe 2022). For the IR spectrum of PET\_2 (glass fiber reinforced polyester, Multipurpose housing), no suitable database spectrum could be identified. PVC\_1 (cable housing) could not be assigned to any synthetic polymer type (highest spectral fit with chitin; HQI value: 559/1000).

The spectrum of PVC\_2 (transparent PVC-tubing) showed the highest agreement with the database spectrum of a vinyl chloride, vinyl acetate, and hydroxypropyl acrylate terpolymer (HQI value: 581/1000).

The spectra of the UV-treated and DC materials were also compared to the corresponding original spectra (untreated) to find qualitative differences indicative of UV weathering or alterations due to the rotation and elevated temperature in the weathering chamber for DC (SI\_D slide 16 - 26). In the IR spectrum of the PE side of PE\_2, UV weathering led to the formation of a carbonyl band (SI\_D Slide 19) indicating significant oxidation (Almond et al. 2020; Julienne et al. 2019), while the spectrum of the PET side remained unchanged. The spectrum of UV-weathered PET\_1 showed clear hydroxy and carbonyl bands that were not visible in the spectra of DC and original PET\_1 (SI\_D Slide 25).

The other materials’ spectra did not significantly change during the treatment indicating that no pronounced surface oxidation had occurred (Liu et al. 2019). Nevertheless, ATR-FTIR spectroscopy is not sensitive when it comes to detecting minor chemical changes on the surface or in the bulk of a polymer (penetration depth: several 100 nm).

# Text S2 – Determination of UV-irradiation

This exposure time was calculated from measured UV-irradiation using a PTE-UV-34 luxmeter, as proposed by Gewert et al. (2018) [2].

*rad*Germany (2010 - 2020) 1114 kWh/m²\*a  
*UVrad*Germany (5%): 22.3 kWh/m²\*a

|  |  |  |  |
| --- | --- | --- | --- |
|  | UVC1 | UVC2 | UVC3 |
| *rad*measured [W/m²] | 75 | 60 | 59 |
| *t*run [h] | 249 | 237 | 245 |
| *t*sim | 306 | 232 | 237 |

# Text S3 – More details on LDIR imaging

The used spectral library (Microplastic starter 1.0, Agilent Technologies) was expanded by spectra of environmental particles (confirmed with the µ-ATR-unit of the system). Additionally, the spectra of in-house reference microplastics (expanded polystyrene (EPS), PE, polyethylene terephthalate (PET), PP polystyrene (PS) and polyvinylidene chloride (PVDC; similar IR spectrum to polyvinylchloride (PVC)) and different polymeric materials used in the laboratory were integrated into the library [3]. For particle sensitivity the default setting was used (4/6) enabling time-efficient particle characterization. The particle size range of the LDIR imaging system was set to 20 μm – 5000 μm. Only spectral assignments with a HQI ≥ 0.85 were accepted and considered for the calculation of microplastic concentrations generated during the experiments.

# Text S4 – Details on NTS analytical method

It was equipped with a Biphenyl column (Phenomenex, Kinetex 2.6 µm Biphenyl 100 A 100 x 2.1 mm) with a guard column of the same material. The same chromatographic method was used for positive and negative mode. Water with 0.1% formic acid (FA) was used as eluent A. Methanol with 0.1% FA was applied as eluent B and acetonitrile was used as eluent C. 100 μL of sample were injected with a flow rate of 0.3 mL min-1. The initial column composition was 3% B and 0% C. This was kept for 2 min. Subsequently, %B was increased to 97% in 14 min.

Then %C was increased to 97% and %B was reduced to 0% within 4 min. This composition was kept for another 4 min. The initial column composition was reconstituted in 0.25 min. The column was left to reequilibrate for 4.55 min. The column was flushed with 100% A for 1.2 min, which yielded a total run time of 30 min. Full scan mass resolution was set to 120,000, with a scan range of 80-1200. Tandem mass spectrometry was performed in data-dependent mode using a Top 6 inclusion, applying a dynamic exclusion for 8 sec and an apex detection of 30% of the window. The data was stored in the raw files in profile mode for MS1 and centroid mode for MS2, while centroiding was performed though the conversion to mzml via msconvert of the Proteowizard [4].

# Text S5 – Details on the sample preparation for targeted analysis

A solid-phase extraction (SPE) protocol adapted from Neale et al. (2018) was used [10]. In brief, Chromabond HR-X cartridges (6 mL, 200 mg, 85 µm, Macherey-Nagel) were conditioned with 4 mL ethyl acetate (EtAc), 4 mL methanol (MeOH) and 2 mL MQW before loading 5 mL leachate sample, spiking with a mixture of 12 internal standards (20 ng absolute each) and loading another 5 mL leachate sample. After washing with 6 mL MQW and drying using vacuum for 90 min, the chemicals retained in the cartridges were sequentially eluted into Barkey vials with 2 mL EtAc, 2 mL MeOH, 2 mL MeOH + 1% formic acid, and 2 mL MeOH + 2% ammonia in MeOH. Extracts were concentrated to 150 µL using nitrogen blow-down (Flowtherm Optocontrol evaporator, Barkey, Germany), walls were rinsed thrice with MeOH, and samples were again concentrated to 150 µL before removing 75 µL for analysis by GC-MS/MS (not reported here). The remaining 75 µL were evaporated to dryness and reconstituted in 190 µL MeOH for LC-MS/MS analysis. Samples were transferred to amber auto-injector vials, stored at – 20 °C, and prior to analysis 10 µL injection standard in MeOH (20 ng absolute) and 50 µL MQW were added (final volume = 250 µL). For information on spiked mass-labelled standards see Table S3 in SI\_A.

# Text S6 – Details on the instrumental analysis for targeted analysis

A guard column of the same material as the analytical column was employed. Samples were separated in 27 min with a gradient of MQW (A) and MeOH (B), both with modifiers 2 mM ammonium acetate and 0.1% formic acid. A was held at 95% for 1 min, reduced to 10% over 7 min and further reduced to 1% in the following 10 min. At this point, conditions were kept for 5 min before the starting conditions of 95% A were restored over 2 min and stabilized for further 2 min. The injection volume was 10 µL and the flow rate was 0.2 mL min‑1. MassHunter software v10 was used for data acquisition and evaluation.

# Text S7 – Details on the sample preparation Plastics for ICP-MSMS analysis

Digestions (EasyDigest, monobloc, Analab, Hoenheim, France (*t* = 6 h; *ϑ* = 120 °C) were conducted in 5 mL nitric acid (HNO3; 65% *m*/*m*, Merck-Millipore) and 1 mL hydrochloric acid (HCl) (30% *m*/*m*, Merck- Millipore). P.a. grade HNO3 and HCl were further purified by double sub-boiling in perfluoroalkoxy alkane (PFA) stills (Savillex, Eden Prairie, USA).

Quartz pressure vessels were cleaned (2 ×) in a PTFE/PFA steam cleaner at 90 °C for 8 h (65% HNO3; Easy Trace Cleaner Evolution II, ANALAB, Paris, France). After digestion, the solutions were transferred quantitatively to pre-cleaned 50 mL DigiTUBEs and diluted to a final volume of 50 mL with Milli-Q water (MQW). Subsequently, vacuum-filtration (0.45 µm PTFE filters; SCP Science) with a manifold was applied to remove any remaining undigested particles and herewith prevent blockage of the nebulizer. Type I reagent-grade water (18.2 MΩ cm) was obtained from a Milli-Q Integral water purification system (Merck-Millipore, Darmstadt, Germany) equipped with a Q-Pod Element and a 100 nm endfilter. Tubes and pipette tips (VWR International, Radnor, USA) were pre-cleaned in a two-stage washing procedure using diluted HNO3 (10% *m*/*m* and 1% *m*/*m* respectively).

In every run, triplicates of the certified reference material (CRM) ERM-EC680m (low density polyethylene (LD-PE); JRC, Ispra, Italy) were digested to ensure a quantitative recovery.

# Text S8 – Details on the ICP-MS/MS data evaluation

The instrument settings, measured isotopes and chosen measurement modes were very similar to Hildebrandt et al. (2020) [5]. However, O2 was replaced by N2O as reaction gas according to Klein et al. (2021) [30]. The instrument was tuned in a daily routine using a Li, Co, Y, Ce, Tl solution. Rh and Ir were used as internal normalization standards (Merck-Millipore). An in-house quality control multi-elemental standard solution (Inorganic Ventures, Christiansburg, USA) was rigorously measured at least five times during each measurement batch. Processing of the multi-element raw data was conducted using MassHunter version 4.4 (Agilent Technologies, Tokyo, Japan) in combination with a custom-written Excel© spreadsheet. Limits of detection (*LOD*s) (3×SD), as well as the limits of quantification, (*LOQ*s) (10×SD) of the method were calculated on the basis of procedural blanks (*n*= 6) [7]. Furthermore, expanded uncertainties with a coverage factor of 2 (*U*, *k* = 2) for each element were calculated using a simplified Kragten approach following Reese et al. (2019) [8,9]. For this purpose, the measurement precision of the samples, as well as the reproducibility of multiple digests was considered (Table S1 in SI\_B, *LOD*s and *LOQ*s also provided).

The best suitable detection modes and isotopes were chosen according to recoveries.

Sensitive and interference-minimized quantification of elements contained in the in-house quality control multi-element standard solution (Inorganic Ventures) and the analyzed reference materials was achieved [5].

# Text S9 – Results of the chemical characterization using HRMS for the individual consumer products

Most features were detected in PE\_1 (DC: 164; UV: 539), PE\_2 (DC: 282, UV: 430), PET\_2 (DC: 260; UV: 462) and PVC\_1 (DC: 217; UV: 559). PE\_1 and PE\_2 are intended for outdoor use as greenhouse cover foil and sun protection cover, respectively. The increase of the number of features in the UV-treated samples could imply that the materials may fatigue easily when exposed to natural UV irradiation. This might pose a risk to the environment since degradation of polymers also increases the release of additives [62]. Compared to PE\_3 and PE\_4, the materials seemed less stable towards water regarding the content of chemicals although very little microplastic formation occurred (see section 3.2 and Figure S3). PET\_2 is probably a composite material made of a polyester and a glass fibre matrix (see section S1). Apparently, this mixed material contained many water-soluble compounds and was relatively unstable towards UV irradiation, although it is advertised as “resistant against harsh environments”. As PET\_2 is intended for industrial use, these rough environments might rather refer to, e.g., humidity or acidic fumes, which may also occur indoors, but not during outdoor application. The consumer product PVC\_1 is intended to be applied as a cable housing, which implies required high safety standards and the use of flame retardants. Despite that the group of organic additives contains more than 10,000 different compounds [9], single formulations typically contain only few functional additives. Considering the numbers of characteristic features detected here, this could imply substantial formation of transformation products in all studied materials.

The least features were detected in leachates PET\_1 (DC: 182, UV: 256) and PVC\_2 (DC: 217, UV: 237). PET\_1 was a product for electronic applications, which require extended material safety. Often this is realized by higher flame-retardant contents relative to other product groups [63,64]. PVC\_2 was a tubing for food applications, which demand for relatively clean materials. The UV treatment had minor effects on the number of features though PVC is known to contain high numbers of additives, which are needed as processing aids [65,66].

The here discussed numbers of features match well values reported in literature. Klein et al. (2021) had found an increase of features in UV-treated samples (SPE-extracts) after aqueous leaching for 24 h; PVC pellets contained most features (DC: 618, UV: 2168), followed by PET (DC: 178, UV: 745) and LDPE (DC: 105, UV: 148) [67]. Other studies have also observed higher numbers of features for PVC products compared to PET products [68,69]. This can indicate that PVC products tend to be more highly processed and more diverse materials. The generally higher number of features in the literature can likely be attributed to the fact that concentrated extracts were analyzed instead of directly injected leachates. In general, the experimental design and the selected analytical method strongly determine the number of detections. However, up to two-fold the number of features could be detected, e.g., in PVC-extracts, derived with the same method [70]. Though pristine pellets were investigated, and the leaching period was relatively short, the complexity of plastic leachates is demonstrated.

# Text S10 – Discussion on the results of the spiked mass-labelled standards

The results from the spiked mass-labelled standards indicated complex matrix related challenges for an accurate quantification (Figure S22 in SI\_A). The injection standards, which were added just before analysis, indicated matrix effects and/or instrument drift in positive electro-spray ionization (ESI) and no similar effects in negative ESI (results for BP-d10 and FOSA-13C8, respectively). They further indicated unreliable results for the UV-treated samples of PET\_2 and PVC\_1. In the blank samples, the results of the internal standards generally matched the results of the other samples of the same batch, which indicated loss and/or matrix effects induced by the SPE procedure. Any possible signal enhancement by the plastic leachate matrix was apparently outweighed, since signal intensities across all samples were reduced about equally. The results within the respective batches generally matched, so comparison between e.g. DC and UV-exposed samples of the same consumer product seemed appropriate. Some differences were observed between the different sample batches, with generally lower signal intensities in the first batch, followed by the second batch and then the third batch. This could be due to differences in sample storage or extraction, or instrument drift. These losses resulted in four of the 12 spiked internal standards not detected in most of the samples, which made quantification challenging. This was especially true for negative ESI, where all three internal standards were lost. It was, therefore, decided to only calculate absolute concentrations. To reduce risk of false positive reporting, concentrations were only reported when they exceeded the respective blank’s concentration by at least factor 10.

In conclusion, the here reported results of the targeted analytes provide conservative estimates likely underestimating the true concentrations. Comparison of the DC and UV-exposed samples of a given consumer product appeared appropriate. The results were, thus, discussed accordingly.

# Text S11 – Results of the targeted analysis for the individual consumer products

Four groups of leaching additives were detected, covering plasticizers (*n*=2), antioxidants (*n*=3), flame retardants (*n*=7) and UV stabilizers (*n*=3). PE\_1, a transparent greenhouse cover foil with advertised UV-stability, was found to leach the antioxidant Cyanox 2246 and traces of the flame retardant trimethyl phosphate (TMP), but no targeted UV stabilizers were detected. PE\_2, a protective cover for balcony furniture supposed to be weatherproof, leached the flame retardants diphenylphosphate (DPhP) and tertrabromobisphenol-A (TBBPA) and the antioxidant Irganox 1010. PE\_3, a jerrycan advertised as durable and UV-protected, released the flame retardants tri(butoxyethyl)phosphate (TBEP) and TMP and the antioxidant Irgafos 126, however no targeted UV stabilizers were found. No leached additives were detected for PE\_4, an agricultural foil. PET\_1, a D-sub-case plug housing, leached the most diverse additives with five flame retardants (DPhP, tris-(2-chloroethyl) phosphate (TCEP), triphenyl phosphate (TPhP), bis(2-ethylhexyl)phosphate (HDEHP), TBBPA) and three UV stabilizers (Tinuvin 327, Tinuvin 329 and Tinuvin P) detected. PET\_2, a thick case for various applications advertised as stable against chemicals, was found to leach the flame retardant HDEHP. PVC\_1, a cable tube that was sold as self-extinguishing and as “pollutant free (phthalate 0.1%)”, released the plasticizer diisononylcyclohexane-1,2-dicarboxylate (DINCH) and the flame retardant TCEP. DINCH is a non-phthalate replacement plasticizer that was introduced globally in 2002 and has since been found at increasing rates together with its metabolites in e.g. human urine samples [87,88]. PVC\_2, a transparent tubing for transporting liquids, leached the plasticizer diisononyl phthalate (DINP). Leaching additives detected at high concentration levels far exceeding the calibration curve were the two plasticizers DINP and DINCH and the flame retardants TBBPA (PET\_1) and DPhP (PET\_1). Plasticizers are typically added to PVC products in high quantities [83], so these results indicating high release potential of plasticizers from PVC products seem reasonable. Similarly, considerable leaching of flame retardants has been observed before [85,89].

# Figures

Ein Bild, das Grafiken, Cartoon, Kunst enthält.

Automatisch generierte Beschreibung

Figure S1 Schematic illustration of the UV-chamber.



Figure S2. Pictures of consumer plastics after aging. Left: DC, right: UV-treated sample. A: PE\_1. B: PVC\_2. C: PVC\_1. D: PE\_2. E: PET\_2. F: PET\_1. G: PE\_4. H: Blank. I: PE\_3

**A comparison of a graph

Description automatically generated**

Figure S3 Size distribution of SAN and PET microplastics in leachates resulting from UV treatment. Non-equidistant size classes can lead to strong curve smoothing.

A graph with numbers and a bar

Description automatically generated

Figure S4. Number of features detected in each leachate in the dark control (top) and UV-treated samples (bottom). Only features that exceeded the height of the respective blank by at least factor 10 were considered.

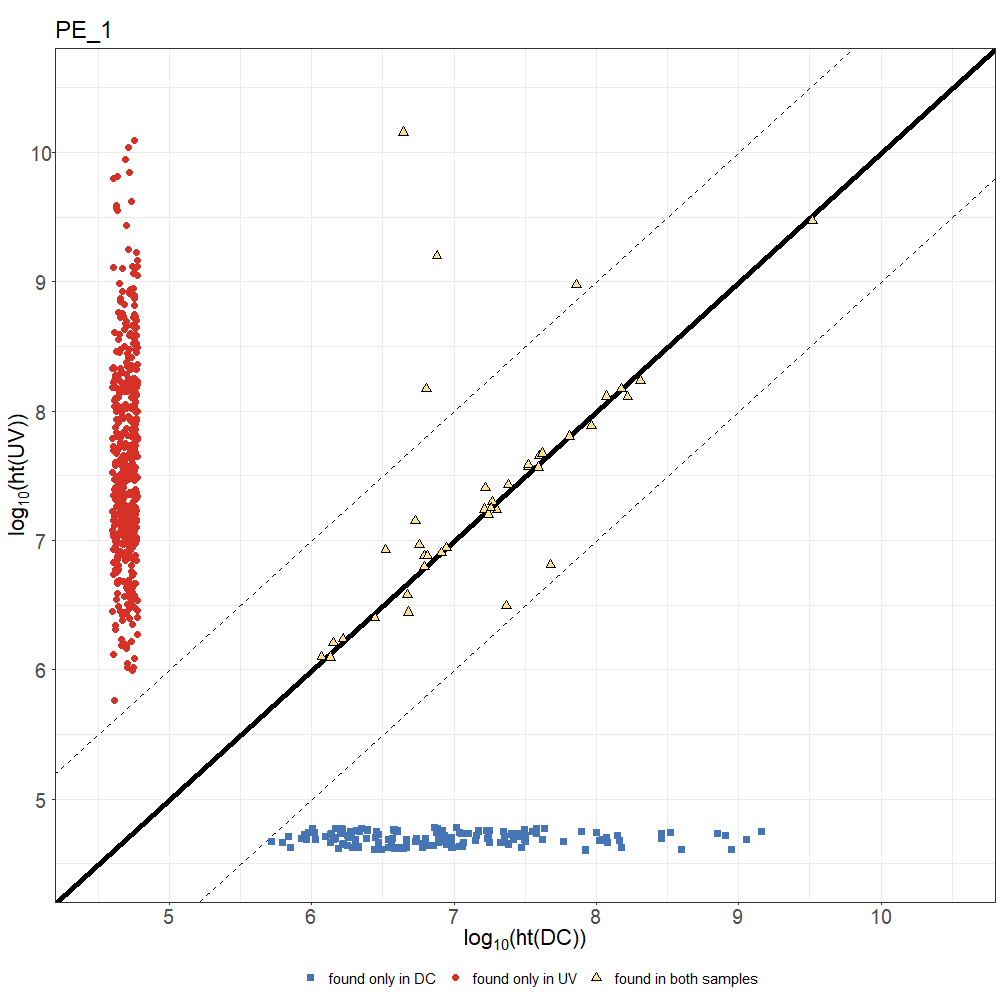


Figure S5. Peak height of UV-treated sample vs dark control (PE\_1). Red dots: Only detected in UV-sample. Blue squares: Only detected in dark control. Yellow triangles: Found in both samples.

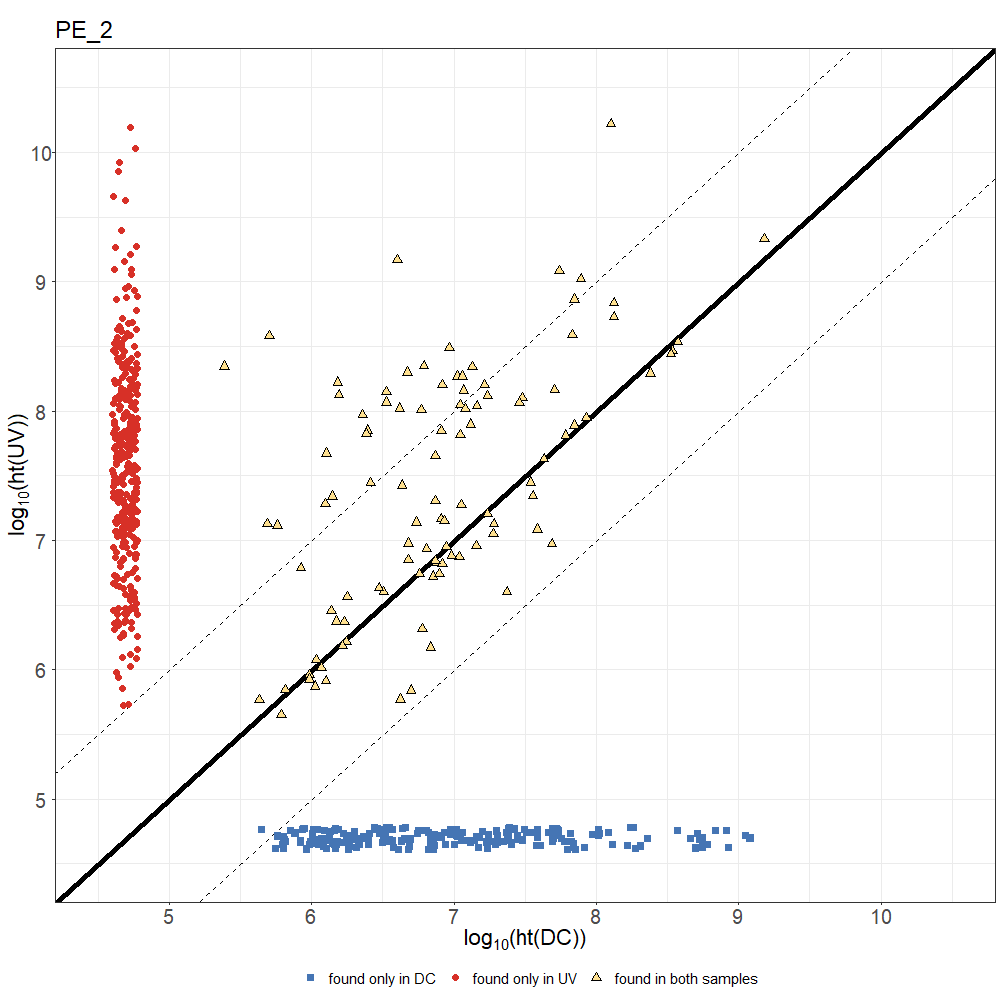


Figure S6. Peak height of UV-treated sample vs dark control (PE\_2). Red dots: Only detected in UV-sample. Blue squares: Only detected in dark control. Yellow triangles: Found in both samples.

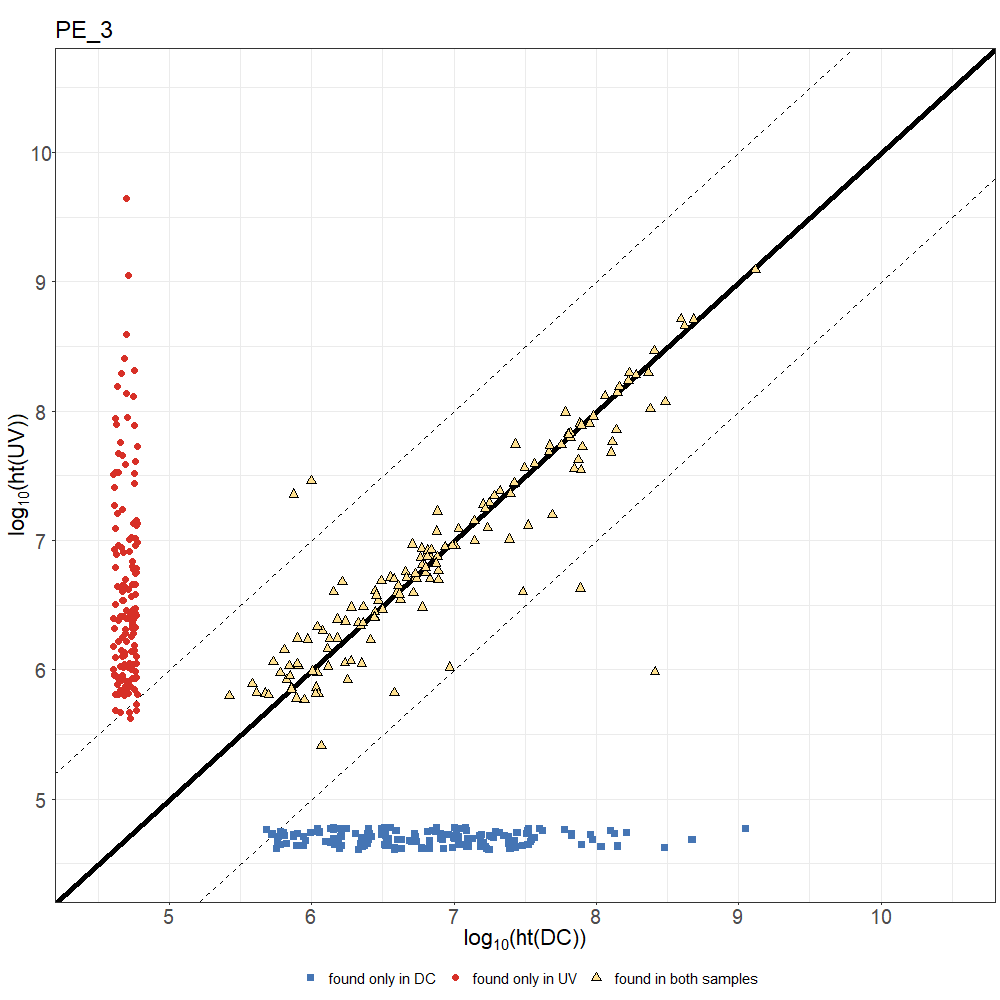


Figure S7. Peak height of UV-treated sample vs dark control (PE\_3). Red dots: Only detected in UV-sample. Blue squares: Only detected in dark control. Yellow triangles: Found in both samples.

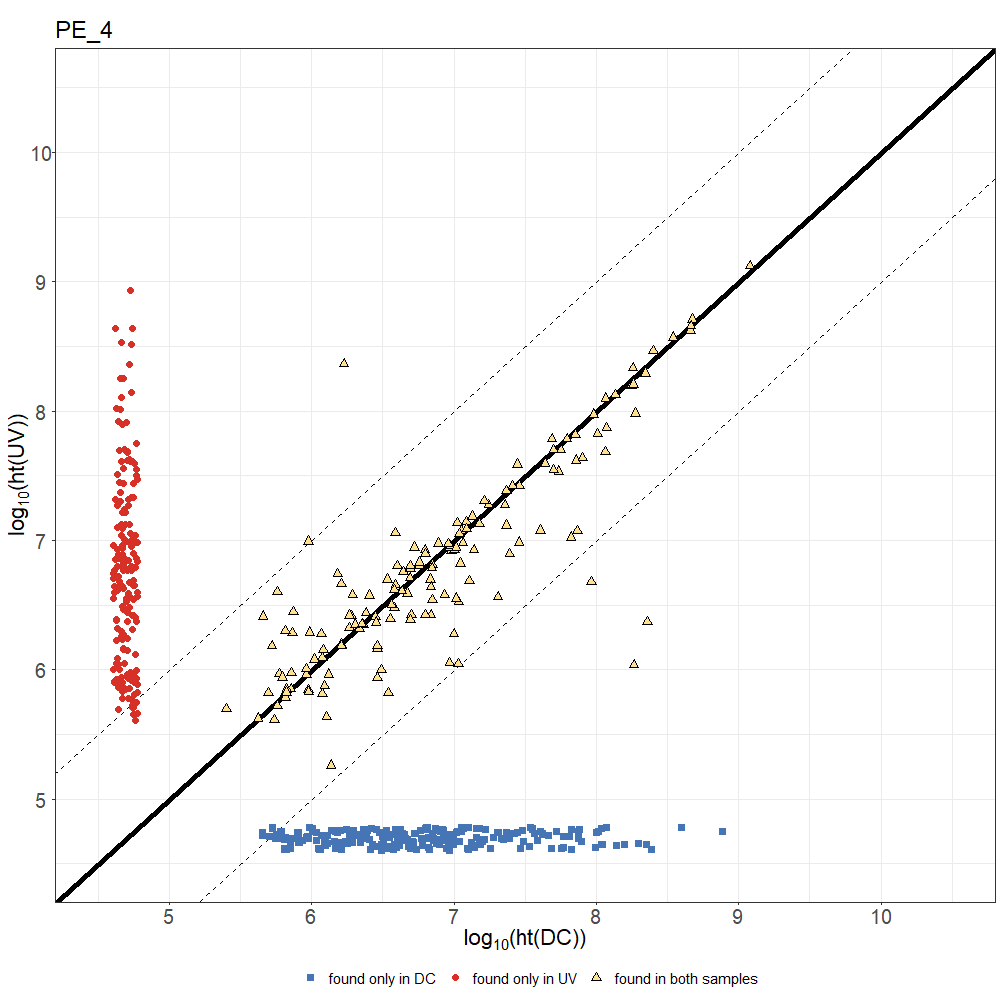


Figure S8. Peak height of UV-treated sample vs dark control (PE\_4). Red dots: Only detected in UV-sample. Blue squares: Only detected in dark control. Yellow triangles: Found in both samples.

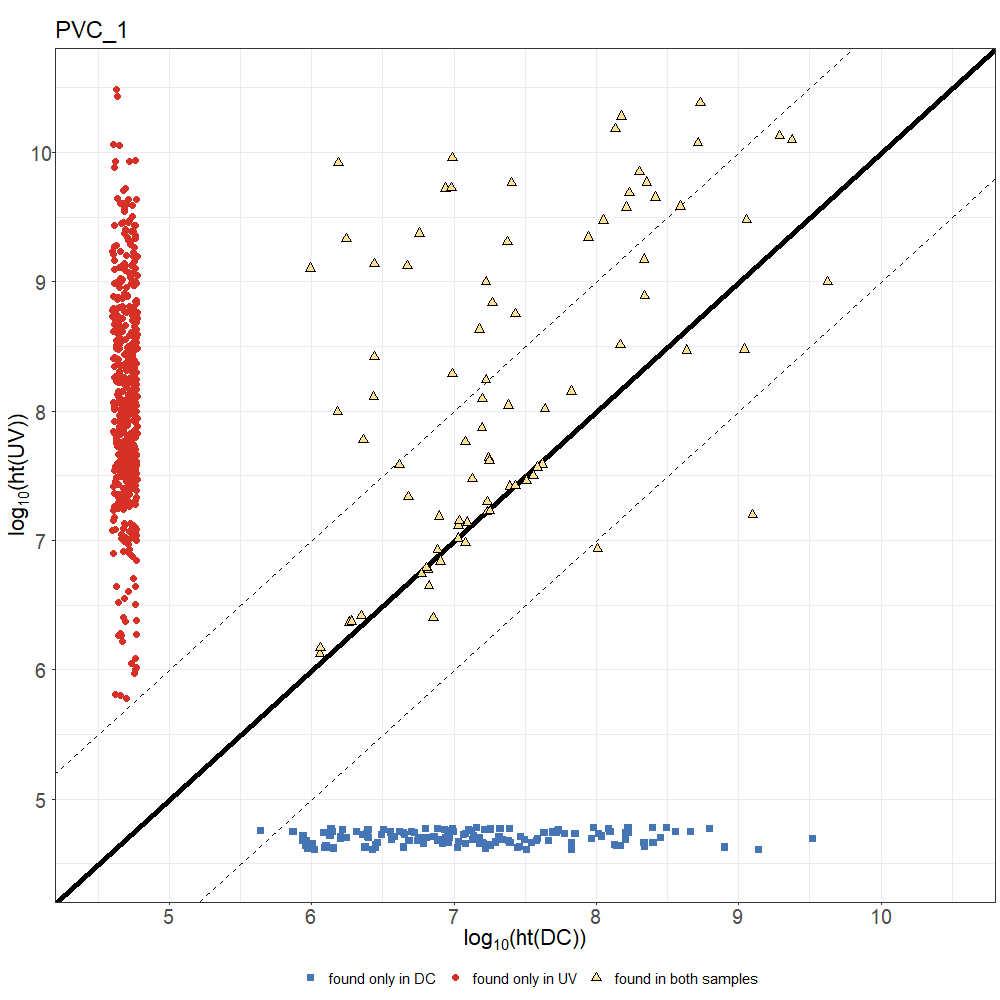


Figure S9. Peak height of UV-treated sample vs dark control (PVC\_1). Red dots: Only detected in UV-sample. Blue squares: Only detected in dark control. Yellow triangles: Found in both samples.

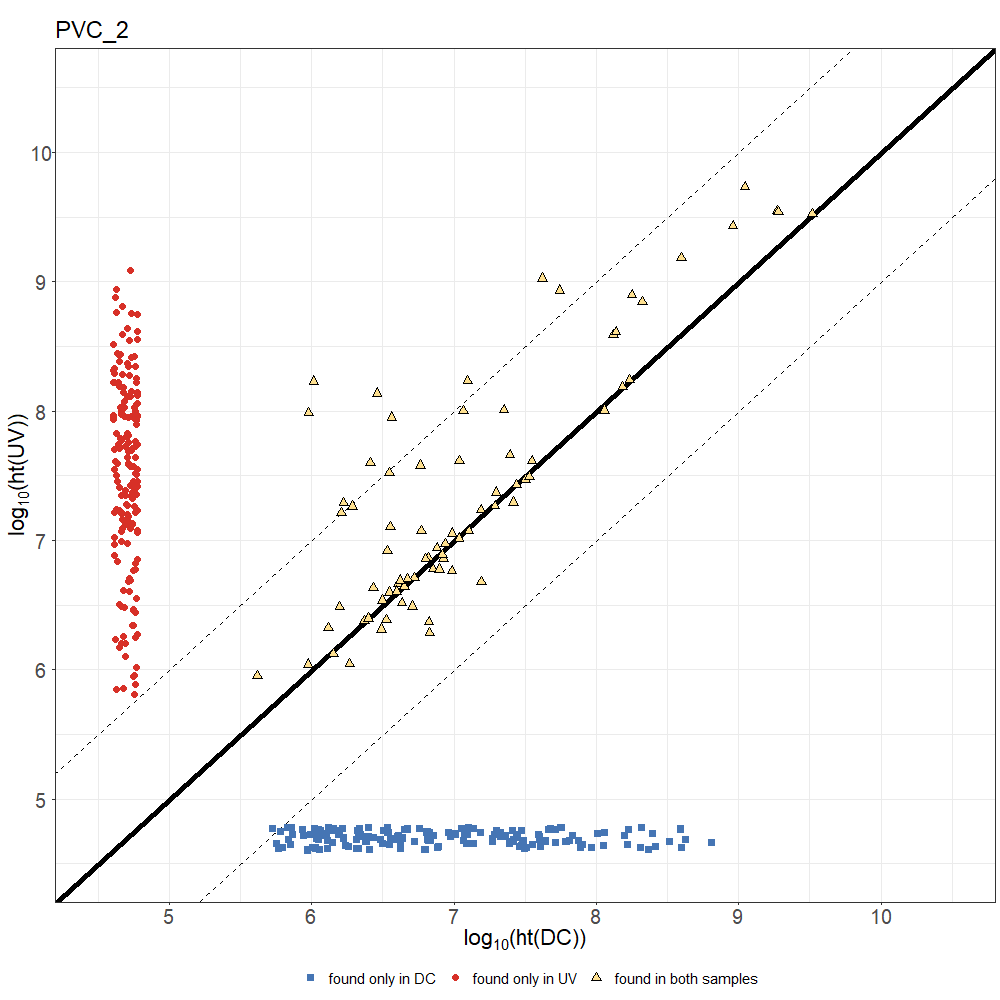


Figure S10. Peak height of UV-treated sample vs dark control (PVC\_2). Red dots: Only detected in UV-sample. Blue squares: Only detected in dark control. Yellow triangles: Found in both samples.

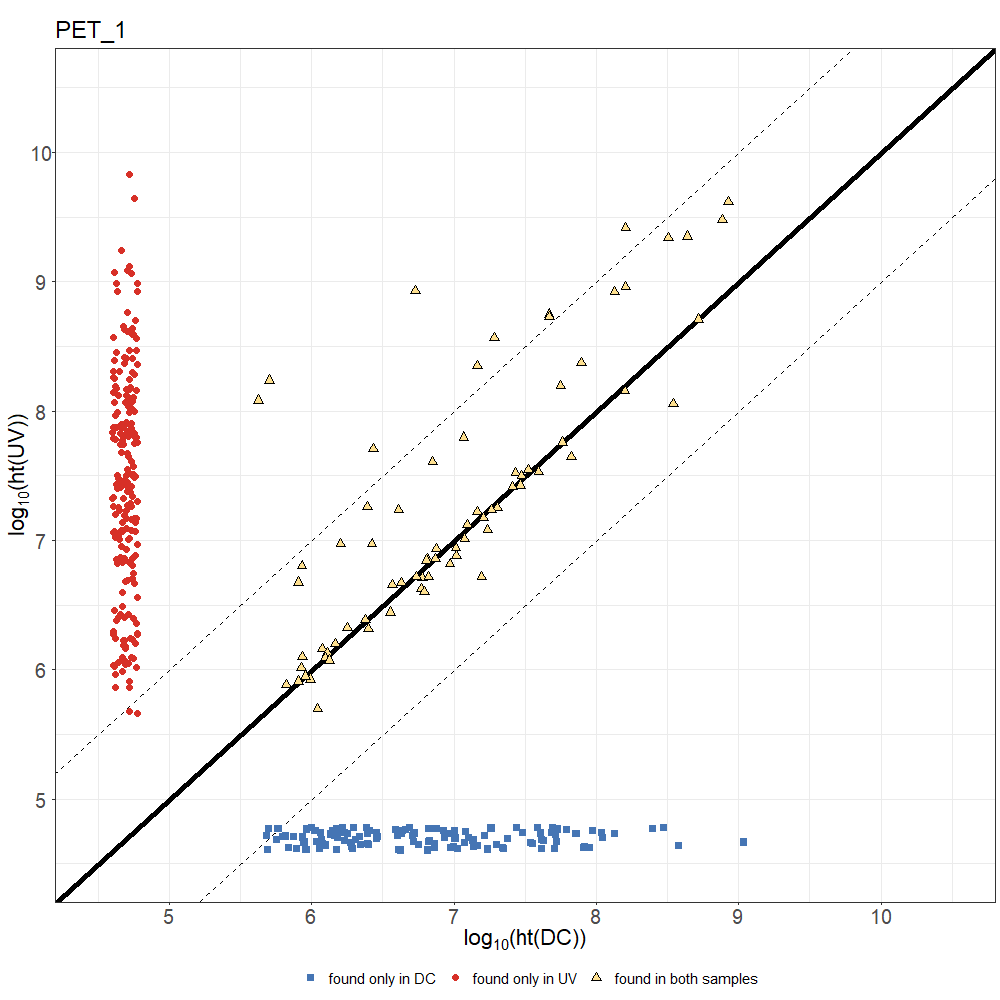


Figure S11. Peak height of UV-treated sample vs dark control (PET\_1). Red dots: Only detected in UV-sample. Blue squares: Only detected in dark control. Yellow triangles: Found in both samples.

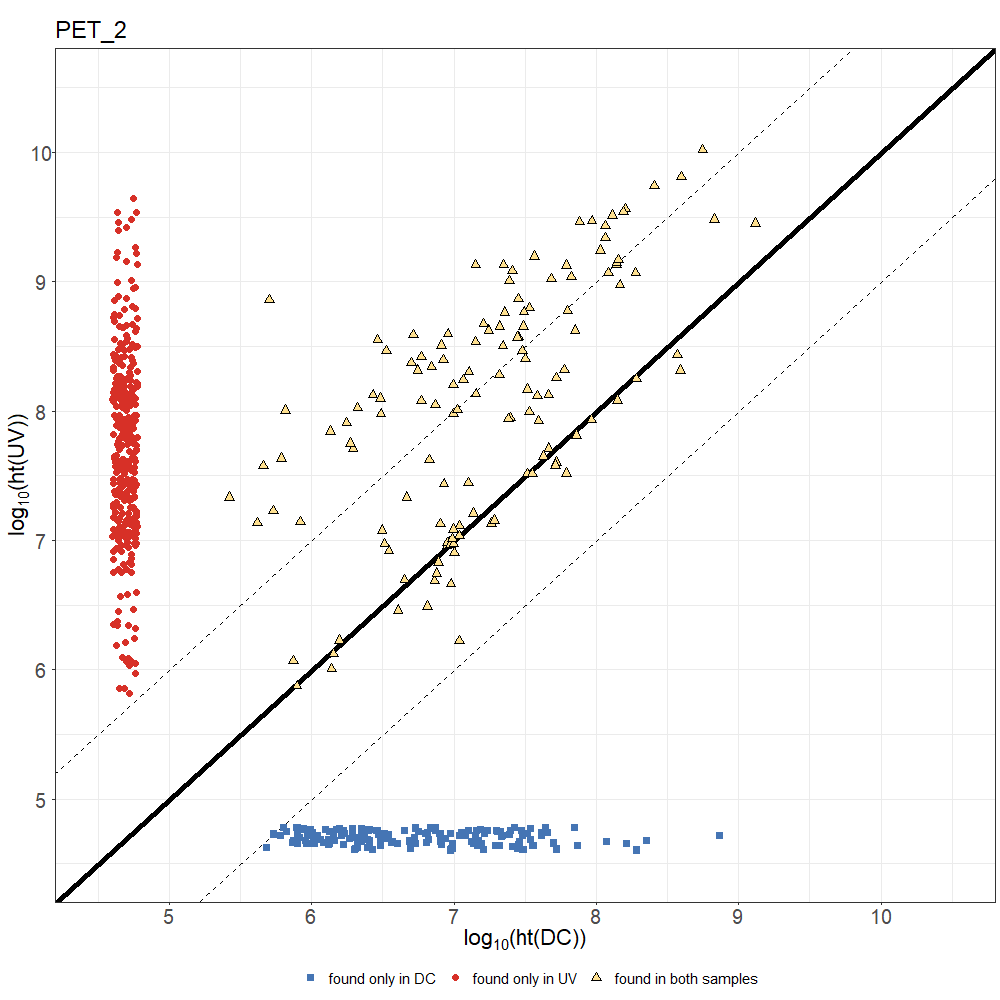


Figure S12. Peak height of UV-treated sample vs dark control (PET\_2). Red dots: Only detected in UV-sample. Blue squares: Only detected in dark control. Yellow triangles: Found in both samples.

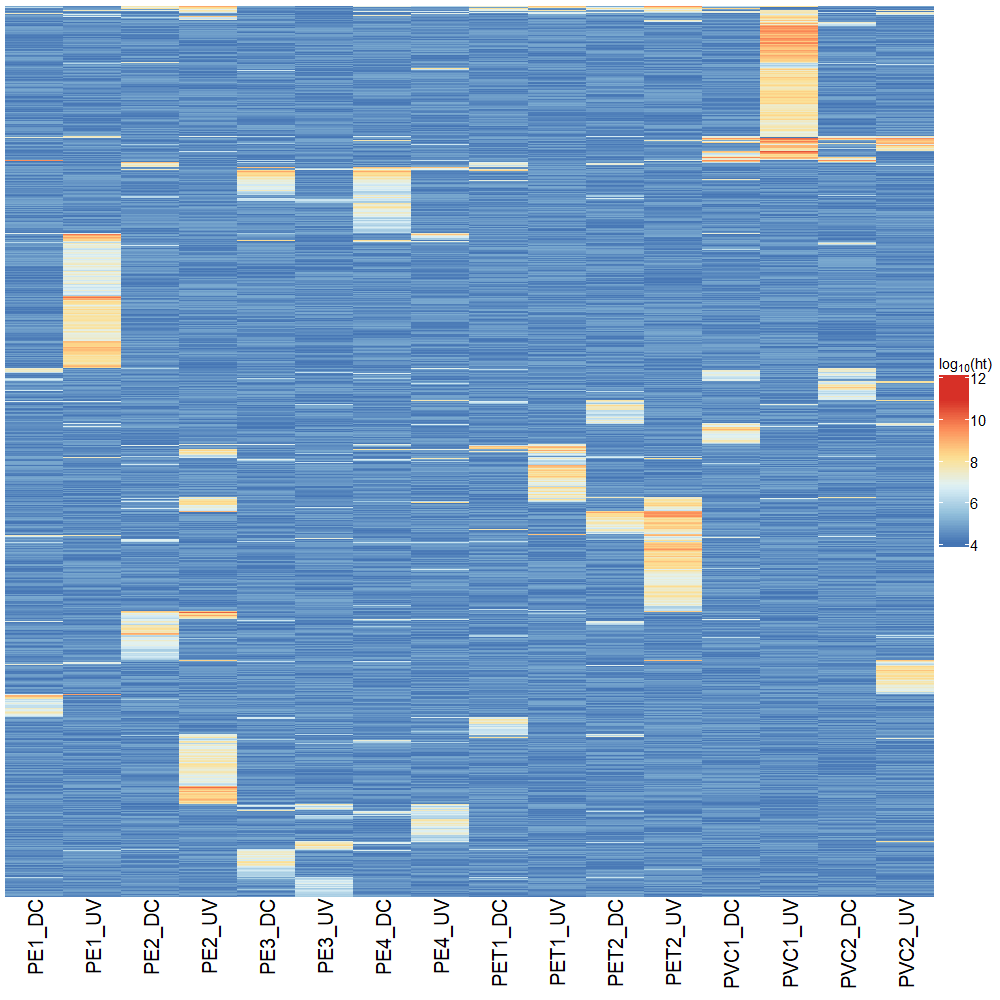


Figure S13. Heatmap of feature heights, sorted by sample. Color-codes represents logarithmic feature height.

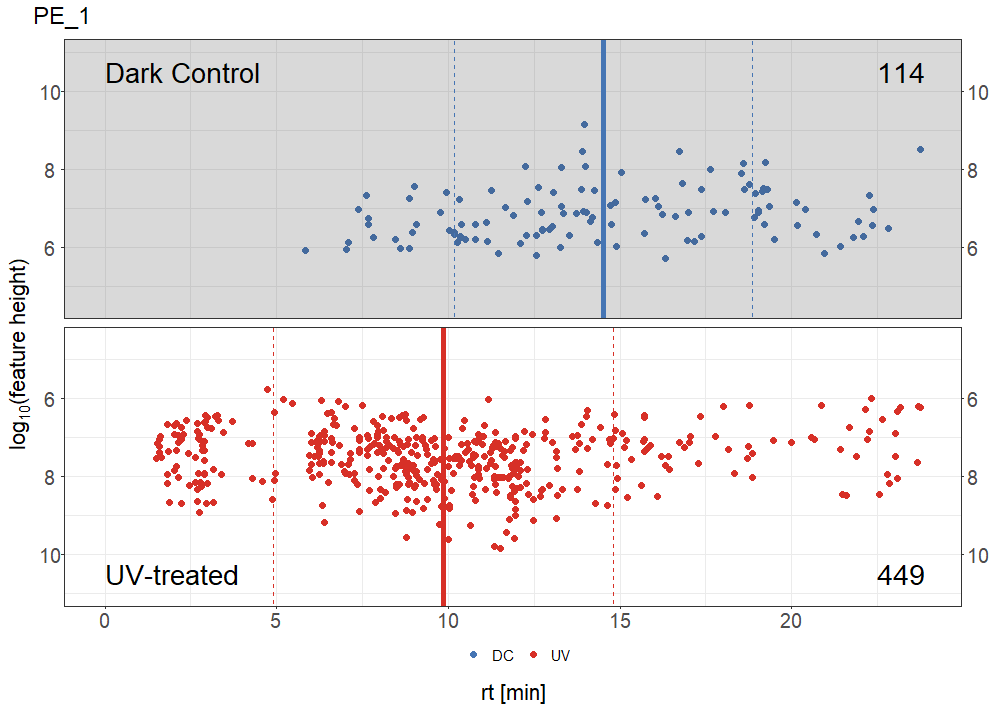


Figure S14. Peak height of UV-treated sample and dark control sorted by retention time (PE\_1). The bold line represents the mean retention time. The dashed lines show the standard deviation.

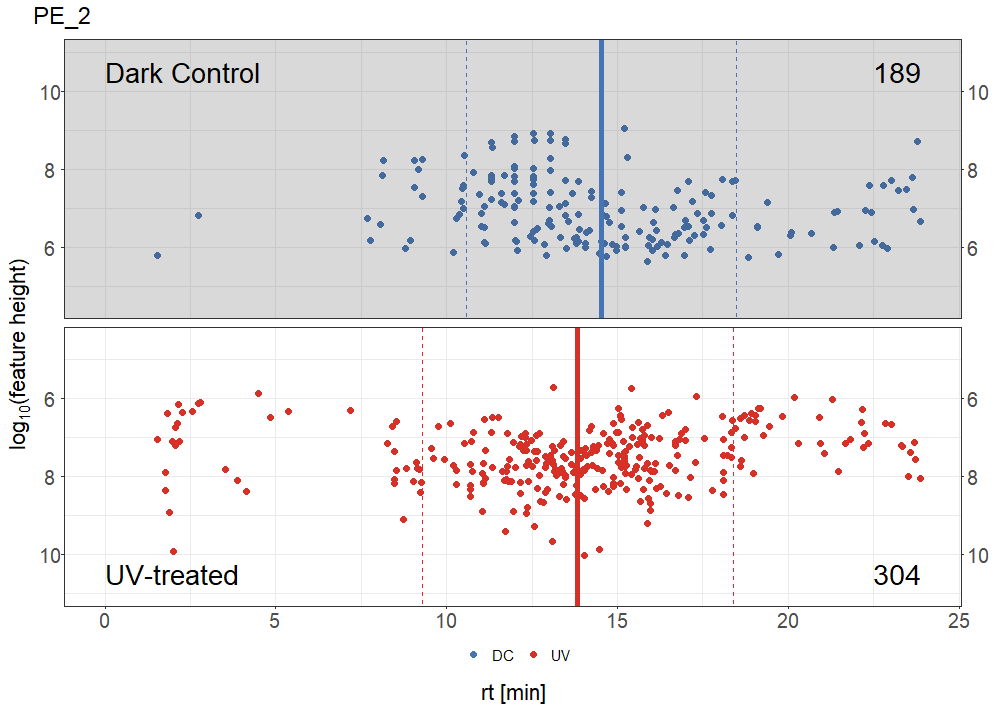


Figure S15. Peak height of UV-treated sample and dark control sorted by retention time (PE\_2). The bold line represents the mean retention time. The dashed lines show the standard deviation.

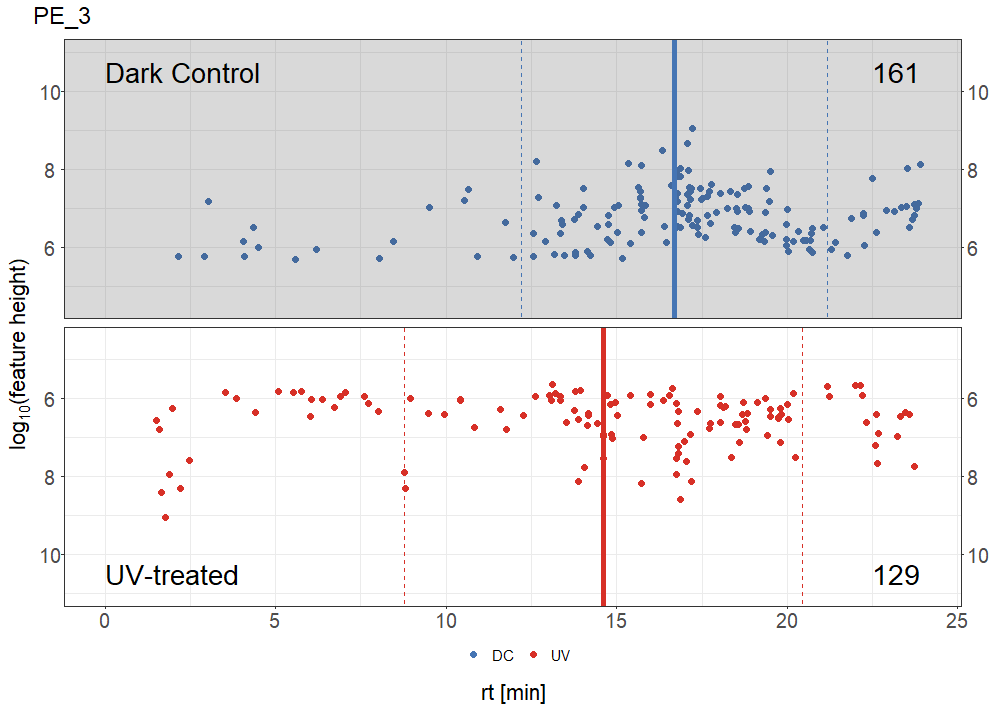


Figure S16. Peak height of UV-treated sample and dark control sorted by retention time (PE\_3). The bold line represents the mean retention time. The dashed lines show the standard deviation.

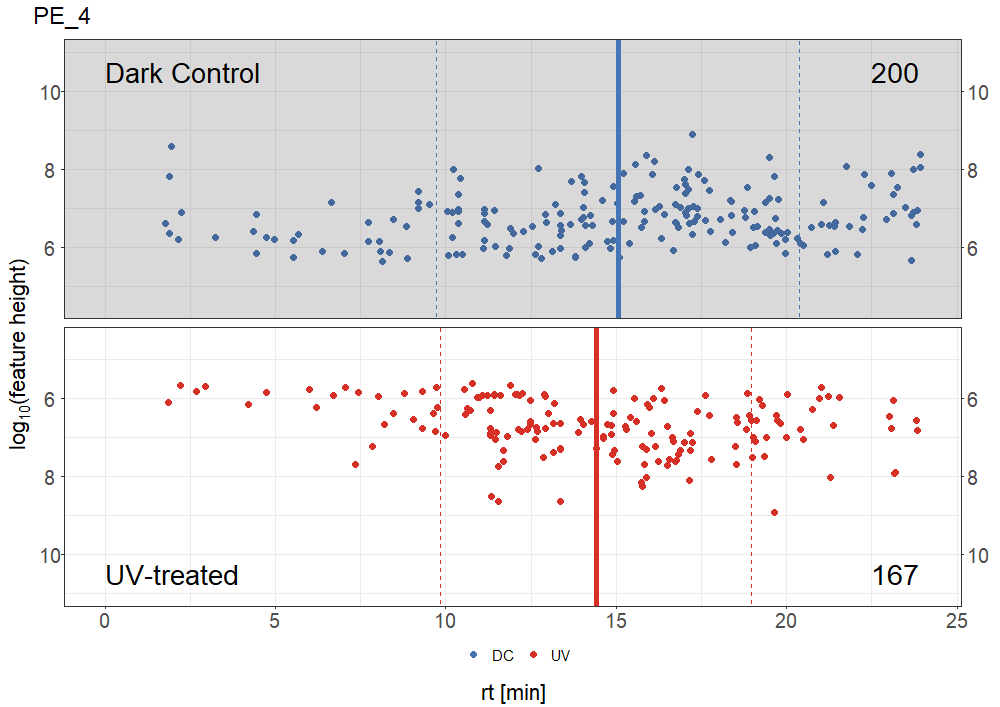


Figure S17. Peak height of UV-treated sample and dark control sorted by retention time (PE\_4). The bold line represents the mean retention time. The dashed lines show the standard deviation.

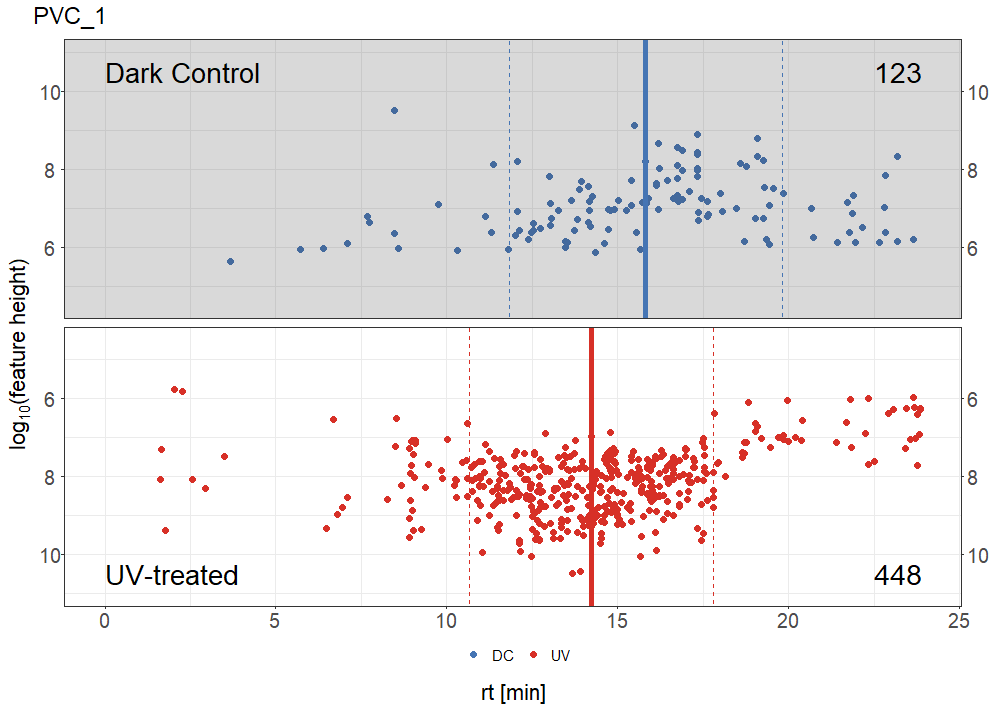


Figure S18. Peak height of UV-treated sample and dark control sorted by retention time (PVC\_1). The bold line represents the mean retention time. The dashed lines show the standard deviation.

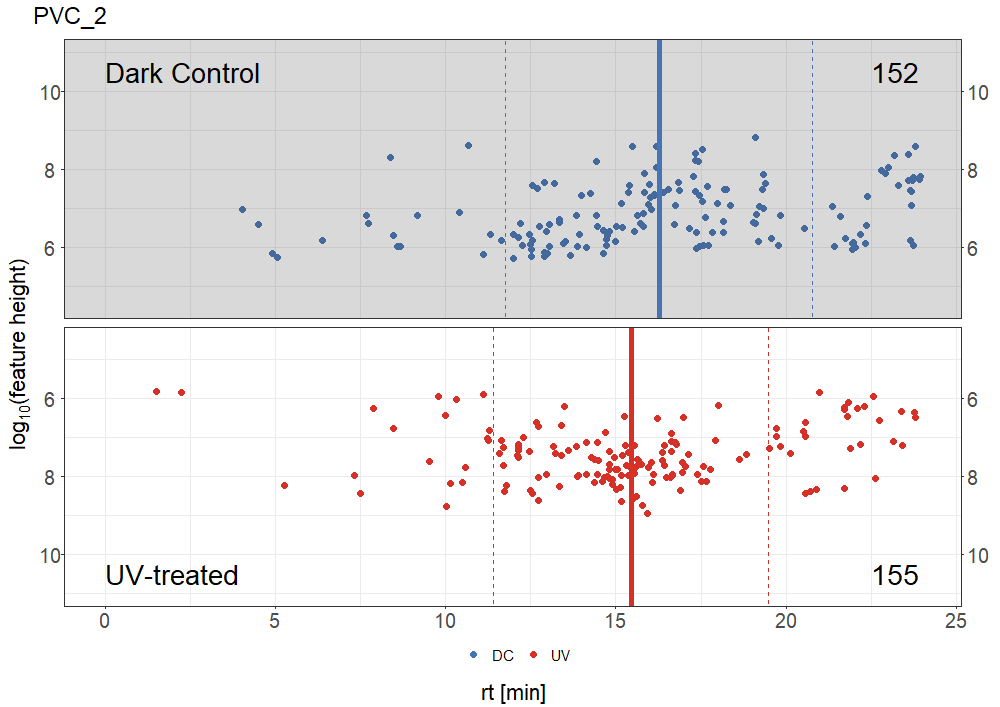


Figure S19. Peak height of UV-treated sample and dark control sorted by retention time (PVC\_2). The bold line represents the mean retention time. The dashed lines show the standard deviation.

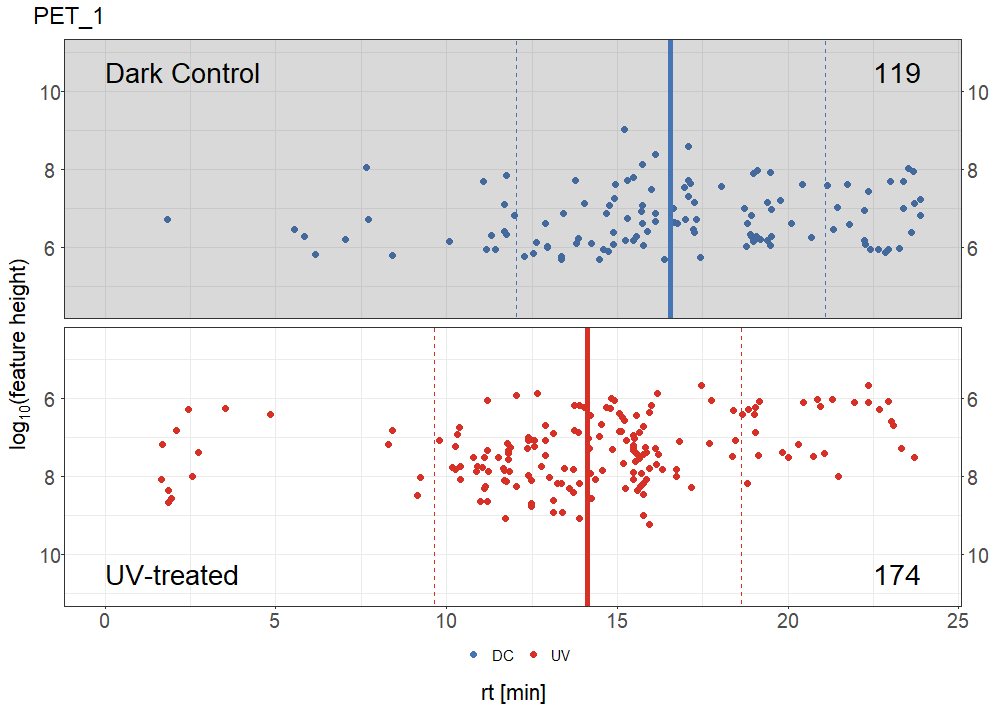


Figure S20. Peak height of UV-treated sample and dark control sorted by retention time (PET\_1). The bold line represents the mean retention time. The dashed lines show the standard deviation.

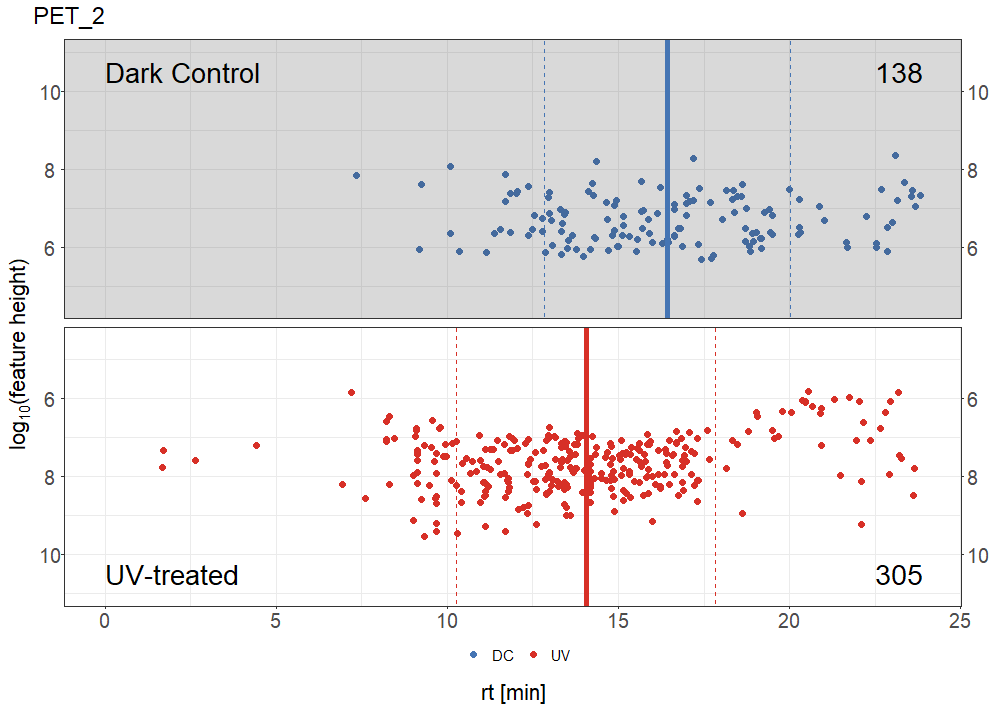


Figure S21. Peak height of UV-treated sample and dark control sorted by retention time (PET\_2). The bold line represents the mean retention time. The dashed lines show the standard deviation.

A screen shot of a graph

Description automatically generated

Figure S22. Responses of spiked mass-labelled internal standards across samples normalized to the overall highest measured area of the respective standard. Calibration points (Cali\_) were followed by the different samples of batches three, two, and one (B3\_, B2\_, and B1\_, respectively). Methanol (MeOH) injections marked red.

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Automatisch generierte Beschreibung

Figure S23 Measured elemental mass fractions of Ba of all consumer plastic products together with the relative leached out share of the dark control and UV treated materials

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Automatisch generierte Beschreibung

Figure S24 Measured elemental mass fractions of Cd of all consumer plastic products together with the relative leached out share of the dark control and UV treated materials

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Figure S25 Measured elemental mass fractions of Cr of all consumer plastic products together with the relative leached out share of the dark control and UV treated materials

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Automatisch generierte Beschreibung

Figure S26 Measured elemental mass fractions of Cu of all consumer plastic products together with the relative leached out share of the dark control and UV treated materials

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Automatisch generierte Beschreibung

Figure S27 Measured elemental mass fractions of Hg of all consumer plastic products together with the relative leached out share of the dark control and UV treated materials

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Automatisch generierte Beschreibung

Figure S28 Measured elemental mass fractions of Sn of all consumer plastic products together with the relative leached out share of the dark control and UV treated materials

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Figure S29 Measured elemental mass fractions of Ti of all consumer plastic products together with the relative leached out share of the dark control and UV treated materials

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Automatisch generierte Beschreibung

Figure S30 Measured elemental mass fractions of U of all consumer plastic products together with the relative leached out share of the dark control and UV treated materials

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Automatisch generierte Beschreibung

Figure S31 Measured elemental mass fractions of V of all consumer plastic products together with the relative leached out share of the dark control and UV treated materials

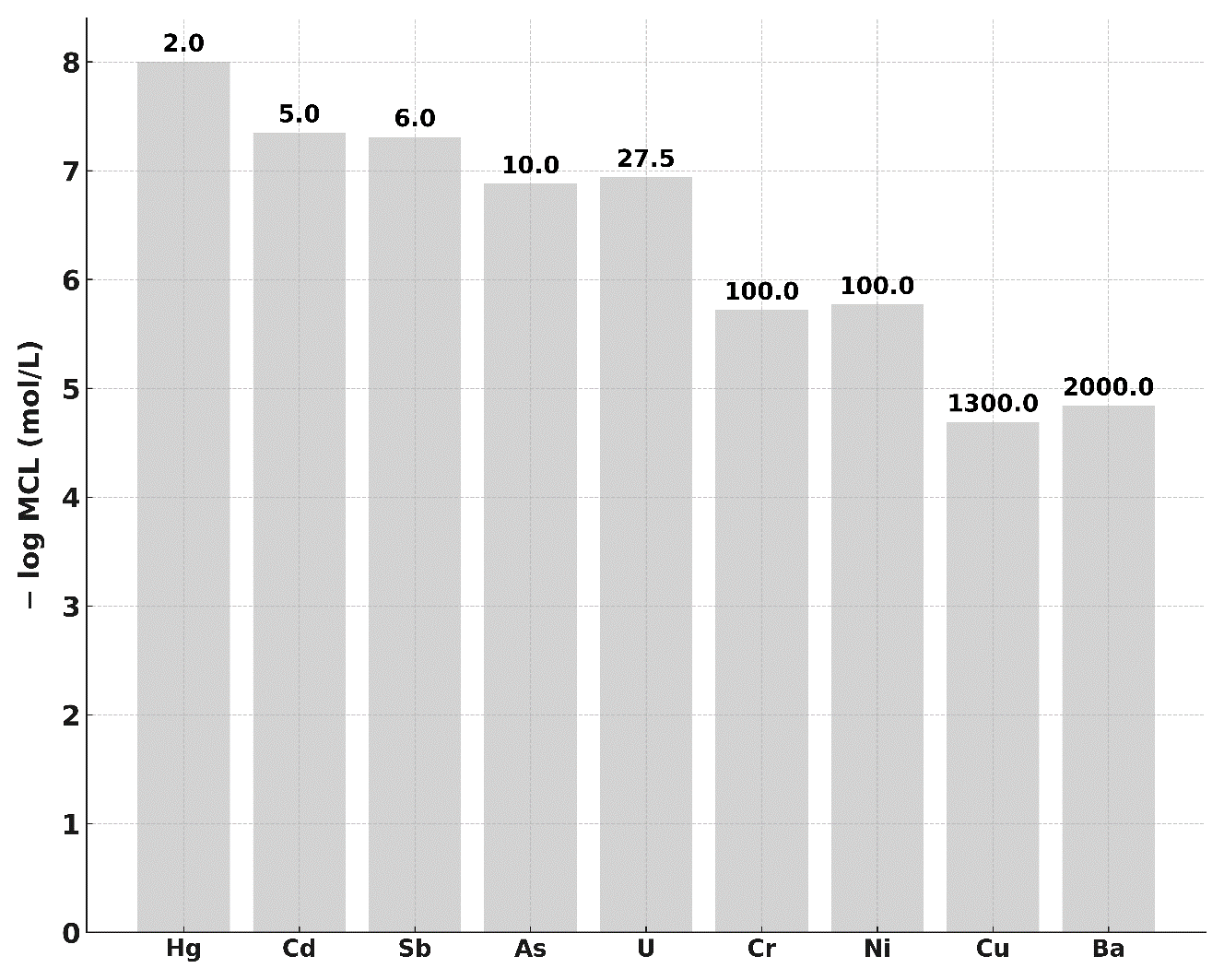


Figure S32: Maximum Contaminant Level (MCL) for metals Mercury (Hg), Cadmium (Cd), Antimony (Sb), Arsenic (As), Uranium (U), Chromium (Cr), Nickel (Ni), Copper (Cu), and Barium (Ba). The annotated values on the bars indicate the MCLs in µg/L, sourced from the ToxVal database, while the bars themselves depict the negative logarithm of the MCL in mol/L. The MCL is defined as the highest permissible level of a contaminant in drinking water, as regulated under the US EPA's National Primary Drinking Water Regulations, ensuring the safety and quality of drinking water.

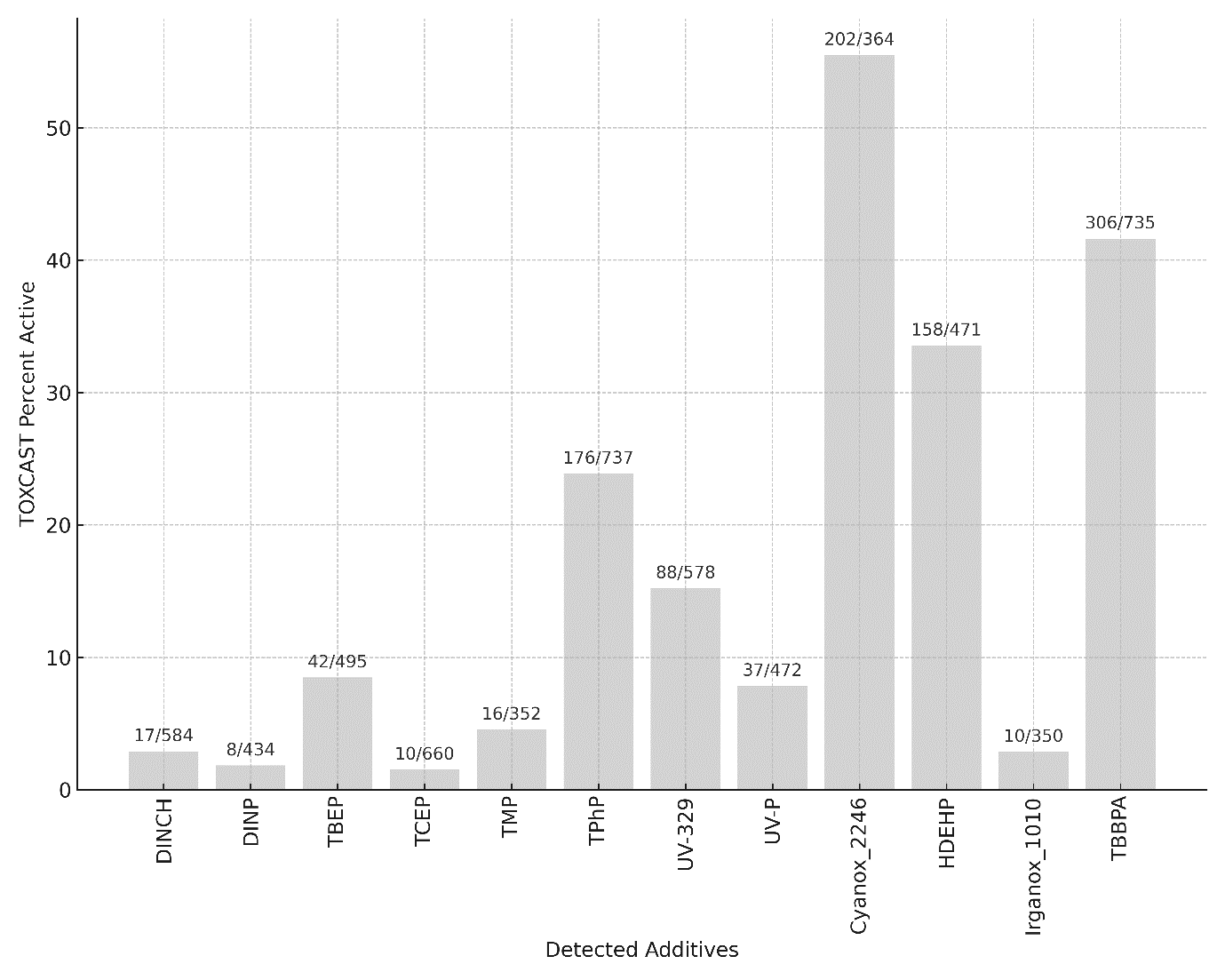


Figure S33: The in vitro bioactivity data for detected organic additives. Out of the 15 detected organic additives, data for 12 were found in the ToxCast assay database. This includes diisononyl phthalate (DINP), diisononylcyclohexane-1,2-dicarboxylate (DINCH), Irganox 1010, Cyanox 2246, tetrabromobisphenol-A (TBBPA), tris-(2-chloroethyl) phosphate (TCEP), triphenyl phosphate (TPhP), trimethyl phosphate (TMP), tri(butoxyethyl)phosphate (TBEP), bis(2-ethylhexyl)phosphate (HDEHP), Tinuvin-329 (UV-329), and Tinuvin-P (UV-P), as retrieved from the ToxCast assay database. Data for di(2-propylheptyl) phthalate (DPhP), Irgafos 126, and Tinuvin-327 (UV-327) were not available in the database. The y-axis displays the percentage of active assays out of the total tested assays. Each bar is annotated with the number of active assays out of the total assays conducted.

# Tables

Table S1: Weighed portions of plastic samples.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **sample** | **m (plastic) / g** | **m (water) / g** | **treatment** | **Experiment** |
| PE\_1 | 25.2 | 200.6 | UV | UVC1 |
| PE\_1 | 30.1 | 199.6 | DC | UVC1 |
| PE\_2 | 20.1 | 200.6 | UV | UVC2 |
| PE\_2 | 20.2 | 201.1 | DC | UVC2 |
| PE\_3 | 30.1 | 199.6 | UV | UVC3 |
| PE\_3 | 29.9 | 206.8 | DC | UVC3 |
| PE\_4 | 23.7 | 200.1 | UV | UVC3 |
| PE\_4 | 23.6 | 205.3 | DC | UVC3 |
| PET\_1 | 31 | 201.2 | UV | UVC2 |
| PET\_1 | 30.5 | 200.9 | DC | UVC2 |
| PET\_2 | 30.6 | 200.4 | UV | UVC2 |
| PET\_2 | 29.8 | 200.2 | DC | UVC2 |
| PVC\_1 | 30.1 | 200.2 | UV | UVC1 |
| PVC\_1 | 25.6 | 201.2 | DC | UVC1 |
| PVC\_2 | 30.3 | 200.0 | UV | UVC1 |
| PVC\_2 | 30.4 | 201.5 | DC | UVC1 |

Table S2: Parameters for mzMine.

|  |  |  |
| --- | --- | --- |
| Step | Parameters | Settings |
| Mass detection | Auto |  |
| ADAP Chromatogram Builder | Scan filters | MS1 |
| Minimum consecutive scans | 4 |
| Minimum intensity for consecutive scans | 5.0 E4 |
| Min absolute height | 1.0E5 |
| *m*/*z* tolerance | 0.002 *m*/*z* or 10.0000 ppm |
| Smooting | Algorithm | Savitzky Golay |
| Local minimum feature resolver | Chromatographic threshold | 90.0% |
| Search minimum in RT range | 0.100 |
| Minimum relative height | 0.0% |
| Minimum absolute height | 1.0E5 |
| Min ratio of peak top/edge | 1.8 |
| Peak duration range (min/mobility) | 0.00 – 3.01 |
| Minimum scans (data points) | 4 |
| m/z tolerance | 0.0015 m/z or 5.0000 ppm |
| Join aligner | Weight of m/z | 3 |
| Retention time tolerance | 0.4 min |
| Weight for RT | 1 |

Table S3: Summary of mass-labelled standards used for target analysis.

|  |  |  |  |
| --- | --- | --- | --- |
| **Abbreviation** | **Name** | **Supplier** | **Purity / %** |
| BP-3-13C6 | Benzophenone-3-13C6 | Cambridge Isotope Laboratories (CIL) | 99.0 |
| BP-8-d3 | Dioxybenzone-d3 | Toronto Research Chemicals | 98.0 |
| DEHP-d4 | Phthalic acid, bis-2-ethylhexyl ester D4 | Dr. Ehrensdorfer GmbH | 98.0 |
| DnBP-d4 | Phthalic acid, bis-butyl ester-d4 | Dr. Ehrensdorfer GmbH | 98.7 |
| EHMC-d15 | Octyl-methoxycinnamate-d15 | Sigma-Alrdich/Fluka | 99.3 |
| OC-d15 | Octocrylene-d15 | Sigma-Aldrich | 99.7 |
| TCEP-d12 | Tris(2-chloroethyl) phosphate-d12 | Wellington Laboratories | >98 |
| TPhP-d15 | Triphenyl phosphate-d15 | Dr. Ehrensdorfer GmbH | 98.0 |
| Tinuvin-327-d20 | 2,4-Di-tert-butyl-6-(5-chloro-2H-benzotriazol-2-yl)phenol-d20 | Toronto Research Chemicals | 96.0 |
| Tinuvin -328-d4 | 2-(2H-Benzotriazol-2-yl)-4,6-di-tert-pentylphenol-d4 | Campro Scientific | 99.4 |
| Tinuvin -360-d8 | Bisoctrizole-d8 | Campro Scientific | 99.6 |
| Tinuvin -P-d4 | 2-(2-Hydroxy-5-methylphenyl)benzotriazole-d4; UV-P-d4 + UV328-d4 | Campro Scientific | 99.4 |
| BP-d10 (inj. Standard) | Benzophenone-d10 | Sigma-Aldrich | 99.0 |
| FOSA-13C8 (inj. Standard) | Perfluoro-1-octanesulfonamide-13C8 | Wellington Laboratories | >99 |

Table S4: Summary table of the findings in this study. If not stated otherwise, observations apply to both the UV and DC sample.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Parameter / Plastic** | **Visual changes** | **Microplastic analysis** | **ATR-FTIR analysis** | **Chemical characterization (HR-MS/MS** | **Metal(loid) analysis** | **Targeted analysis** |
| **PE\_1** | Foam formation | No microplastics | Polymer type confirmed, no changes / oxidation | *More (new) compounds (UV)* | Clean | Low content |
| **PE\_2** | Fibers | 400/3280 microplastic fibers mL-1 (DC/UV) | One PE and one PET side, increased carbonyl band (UV) | *More (new) compounds (UV), higher peaks (UV)* | Sb elevated | Antioxidant (DC) |
| **PE\_3** |  | No microplastics | Polymer type confirmed, no changes / oxidation |  | Low content | Antioxidant and flame retardant (DC) |
| **PE\_4** | Heat formation | No microplastics, | Polymer type confirmed, no changes / oxidation |  | Low content (Cr, Ti elevated) | Clean |
| **PET\_1** | Foam formation, particles | ≥ 2400 microplastic particles mL-1 | Identified as SAN, increased carbonyl band, formation of OH band (UV) | *More (new) compounds (UV)* | As, Ba, Cd, Cr, Ni, Sb, Sn | UV stabilizers, flame retardants (UV > DC) |
| **PET\_2** | Foam formation, turbidity | Interfering precipitate (UV), numerus rubber- and PE-Cl-like spectra (DC) | Polymer type unknown, no changes / oxidation | *More (new) compounds (UV), higher peaks (UV)* | Pb, Ti, U, V, Zn | Antioxidants (DC) |
| **PVC\_1** | Bleaching, particles (UV) | No microplastics,stearate-like spectra (UV) | Polymer type unknown, no changes / oxidation | *More (new) compounds (UV), higher peaks (UV)* | Co, Cr, Ni, Sb, U, V, Zn elevated | High content of plasticizers (replacement), flame retardant |
| **PVC\_2** | Bleaching (UV) | No microplastics | Probably a terpolymer including vinyl chloride, no changes / oxidation | *More (new) compounds (UV)* | Clean | High content of plasticizers (replacement) |

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