Chemical and toxicological characterization of chemicals released from plastic polymers under ultraviolet light

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Chemical and toxicological characterization of chemicals released from plastic polymers under ultraviolet light

Hypothesis

Plastic polymers themselves are the source of chemical contaminants that could pose a risk to the environment

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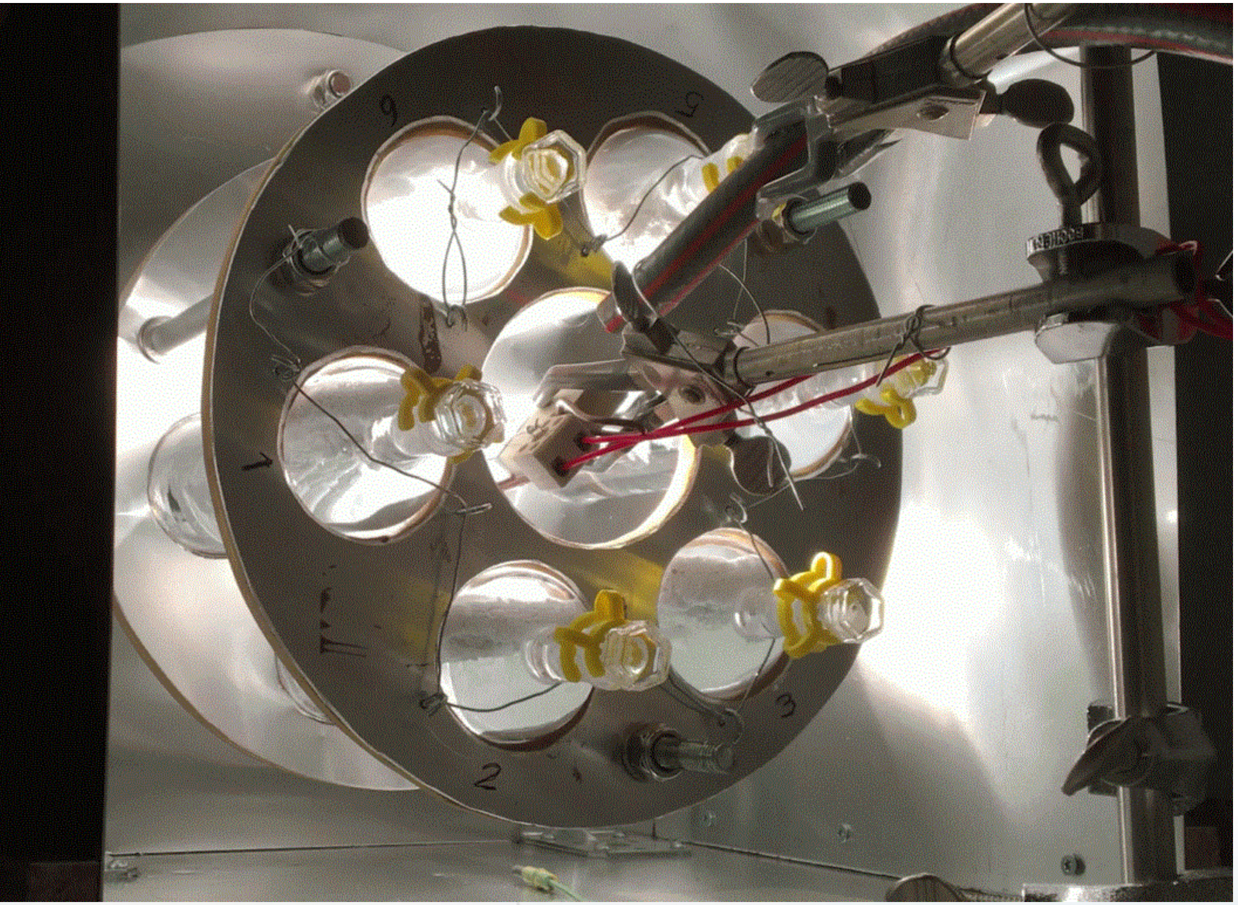
Chemical and toxicological characterization of chemicals released from plastic polymers under ultraviolet light

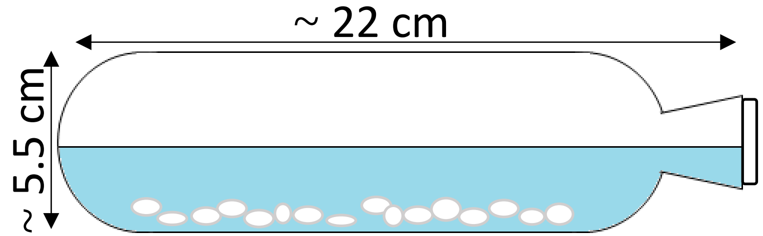
Goals

1. Develop a lab procedure to artificially weather plastics under UV-light
2. Identify chain-scission degradation products of different polymers
3. Screen leachates from weathering plastics for toxicity & compare to pristine plastic

1. Artificial weathering of plastic



- The “weathering wheel”
- Air-cooled UV lamp in center
- 5 g of plastic material & 250 mL water
- 5 days → ~ 510 days of sunlight
- Blank samples & dark controls



2. Identifying Polymer Chain-Scission Products in Leachates

- Solid phase extraction (SPE) of water
- Analysis via LC-HRMS
  - **LC:** C18 column run with a gradient of H_2O and ACN
  - **HRMS:** Q Exactive HF Orbitrap
  - Full scan mode + data dependent MS2 fragmentation
- **Data processing:** Compound Discoverer 2.1
  - Peak picking and alignment between samples
  - Molecular formula prediction

2. Identifying Polymer Chain-Scission Products in Leachates

Signals detected in leachates of pre-production polyethylene (Goodfellow, Gmbh)

965

2. Identifying Polymer Chain-Scission Products in Leachates

Workflow

1 Molecular formula:
$C_xH_yH_z$
≤ 5ppm

Signals detected in leachates of pre-production polyethylene (Goodfellow, Gmbh)

965

256

2. Identifying Polymer Chain-Scission Products in Leachates

Workflow

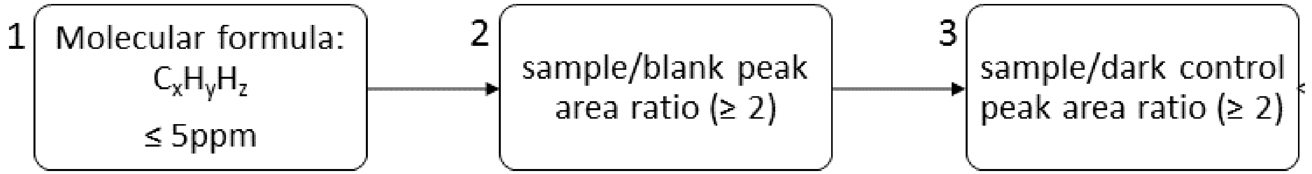
1 Molecular formula: $C_xH_yH_z$ ≤ 5ppm → 2 sample/blank peak area ratio (≥ 2)

Signals detected in leachates of pre-production polyethylene (Goodfellow, Gmbh)

965 256 75

2. Identifying Polymer Chain-Scission Products in Leachates

Workflow



Signals detected in leachates of pre-production polyethylene (Goodfellow, Gmbh)

965 256 75 68

2. Identifying Polymer Chain-Scission Products in Leachates

Workflow

1 Molecular formula: $C_xH_yH_z$ ≤ 5ppm → 2 sample/blank peak area ratio (≥ 2) → 3 sample/dark control peak area ratio (≥ 2) → 4a Homologous series of monomers / 4b Literature research → Tentatively identified degradation products

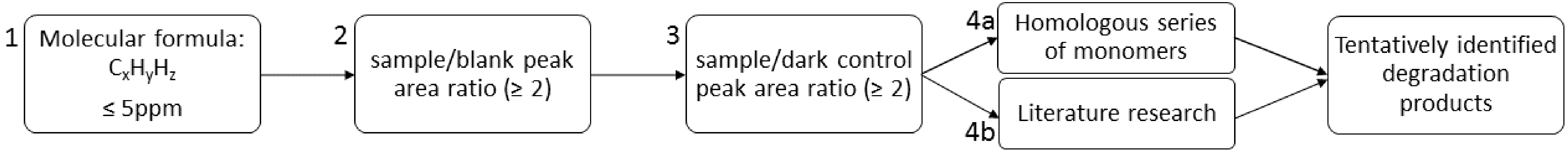
Signals detected in leachates of pre-production polyethylene (Goodfellow, Gmbh)

965	256	75	68	6 compounds tentatively identified

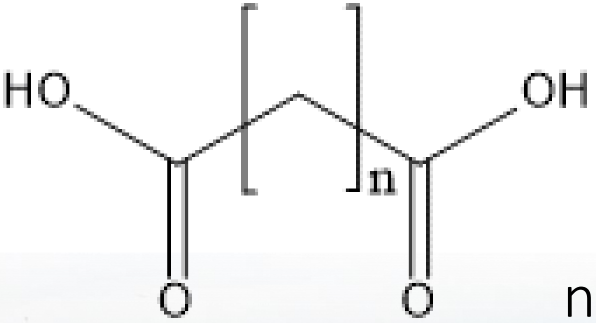
3 confirmed by reference standard

2. Identifying Polymer Chain-Scission Products in Leachates

Workflow



Signals detected in leachates of pre-production polyethylene (Goodfellow, Gmbh)



n = 6,7,8,9,10 & 12

6 compounds tentatively identified

3 confirmed by reference standard

Environmental Science & Technology Letters

Letter

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Identification of Chain Scission Products Released to Water by Plastic Exposed to Ultraviolet Light

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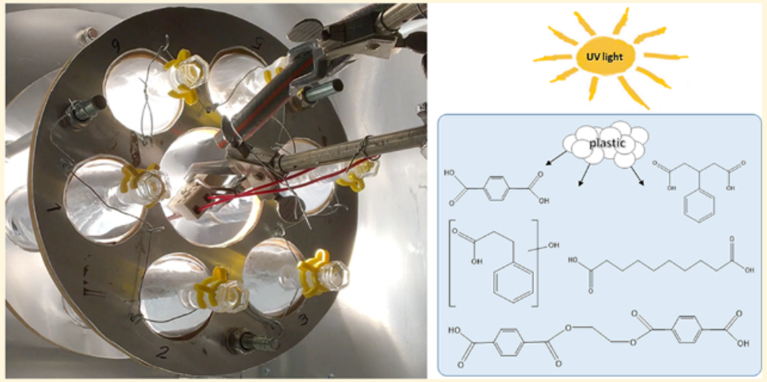
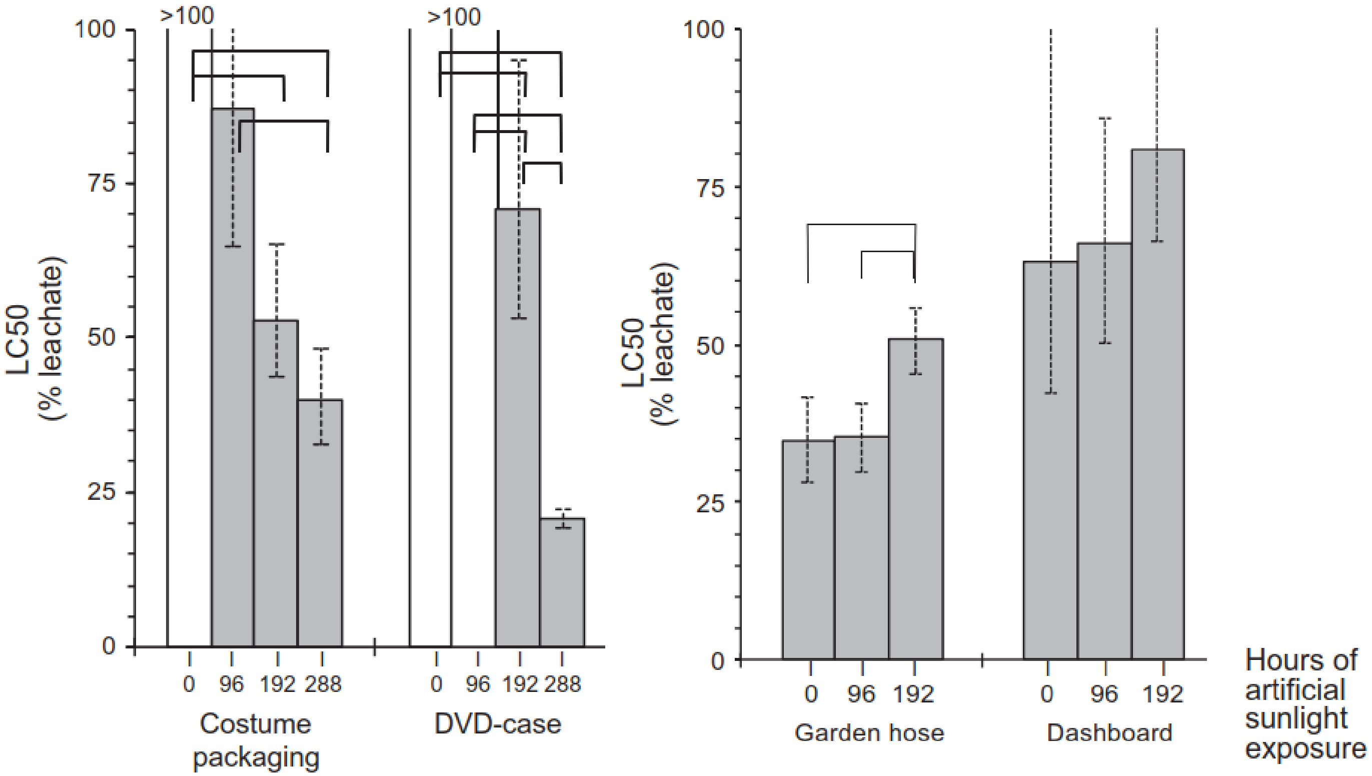
Supporting Information

ABSTRACT: Buoyant plastic in the marine environment is exposed to sunlight, oxidants, and physical stress, which may lead to degradation of the plastic polymer and the release of compounds that are potentially hazardous. We report the development of a laboratory protocol that simulates the exposure of plastic floating in the marine environment to ultraviolet light (UV) and nontarget analysis to identify degradation products of plastic polymers in water. Plastic pellets [polyethylene, polypropylene, polystyrene, and poly(ethylene terephthalate)] suspended in water were exposed to a UV light source for 5 days. Organic chemicals in the water were concentrated by solid phase extraction and then analyzed by ultra-high-performance liquid chromatography coupled to high-resolution mass spectrometry using a nontarget approach with a C18 LC column coupled to a Q Exactive Orbitrap HF mass spectrometer. We designed a data analysis scheme to identify chemicals that are likely chain scission products from degradation of the plastic polymers. For all four polymers, we found homologous series of low-molecular weight polymer fragments with oxidized end groups. In total, we tentatively identified 22 degradation products, which are mainly dicarboxylic acids.



- 22 chain-scission degradation products of polyethylene, polystyrene and polyethylene terephthalate identified.
- Mostly dicarboxylic acids.
- 515 additional possible degradation products of these polymers identified by exact mass and molecular formula CxHyOz.

3. Screening leachates from weathering plastics for toxicity



- Exploratory experiments with artificial weathering of diverse plastic materials

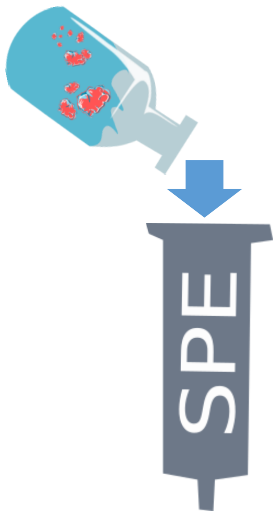
- Toxicity of leachates to *nitrocra spinipes* could either increase of decrease as a result of weathering

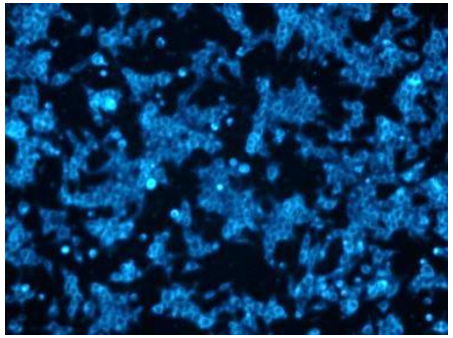
Bejgarn, MacLeod, Bogdal, Breitholtz. Toxicity of leachates from weathering plastics: An exploratory study. *Chemosphere*. 132 114-119 **2015**.

3. Screening leachates from weathering plastics for toxicity

Cell-based bioassays

Department of bioanalytical ecotoxicology, Helmholtz Centre for Environmental Research – UFZ, Leipzig





recombinant cells

High-throughput bioassays

Assay	Endpoint
AhR	Xenobiotic metabolism
AREc32	Antioxidant response element
PPARγ	Peroxisome proliferating activity

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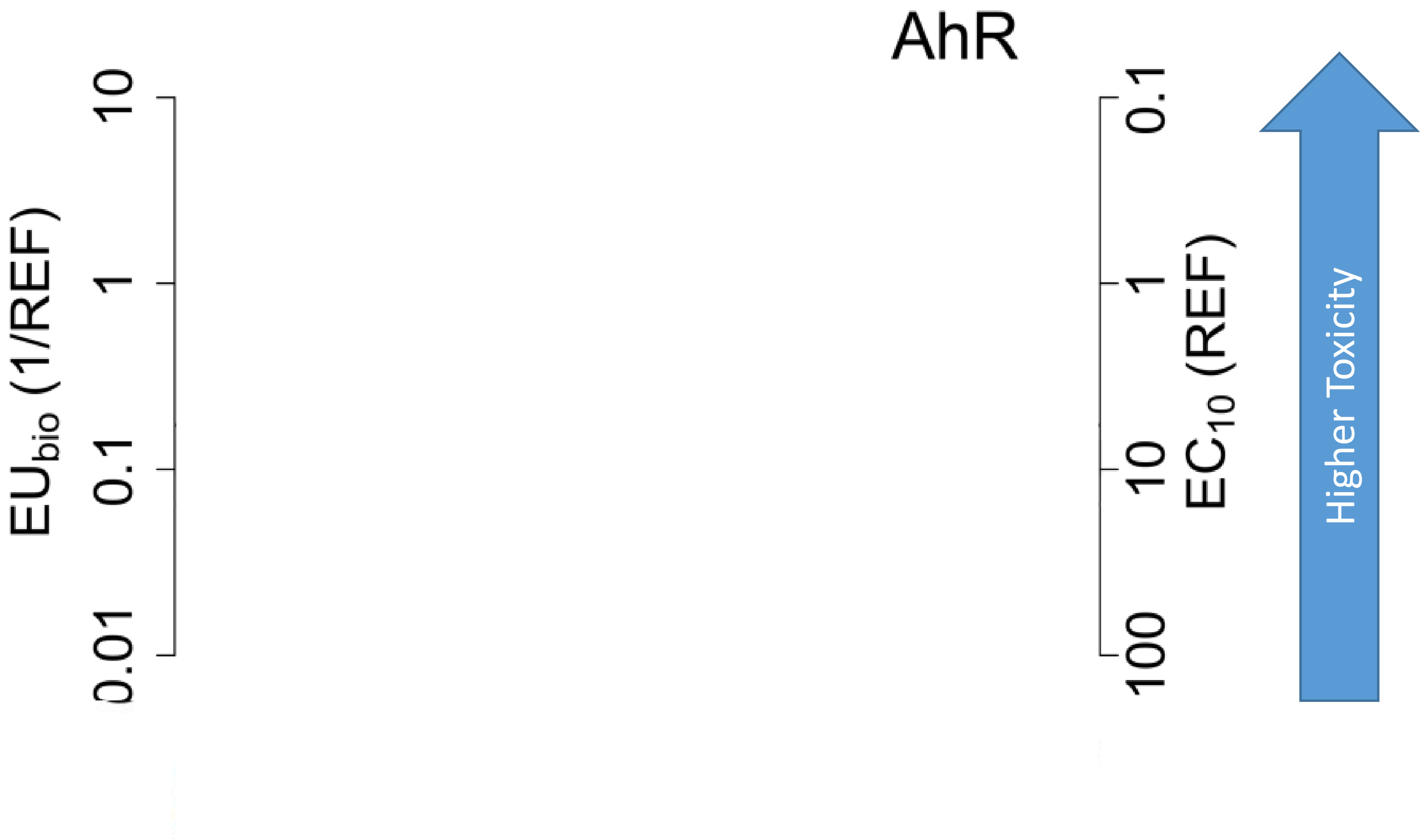
3. Screening leachates from weathering plastics for toxicity



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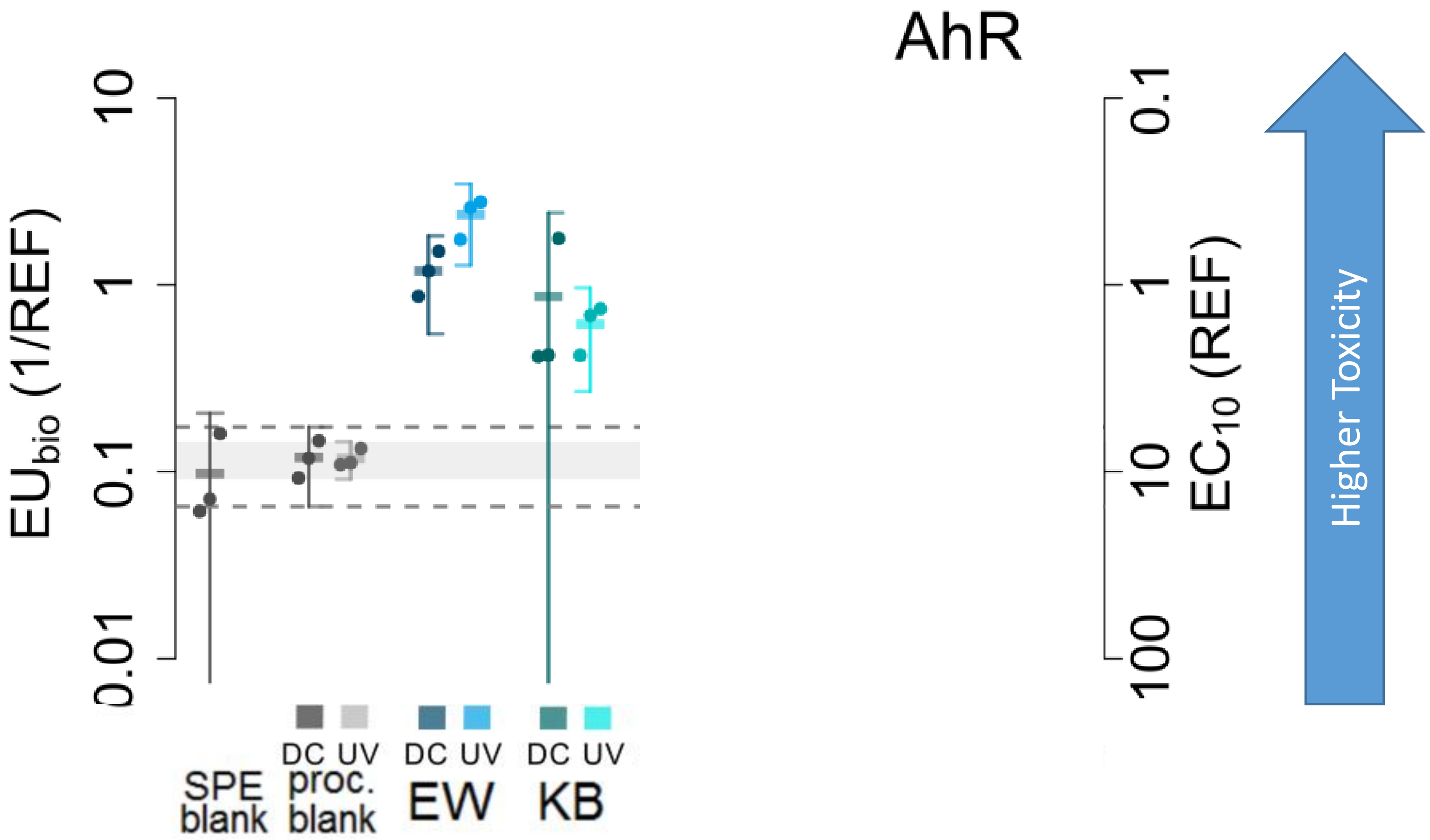

Blanks & positive controls

EW – E-Waste
KB – New keyboard

DC – Dark control
UV – UV weathered

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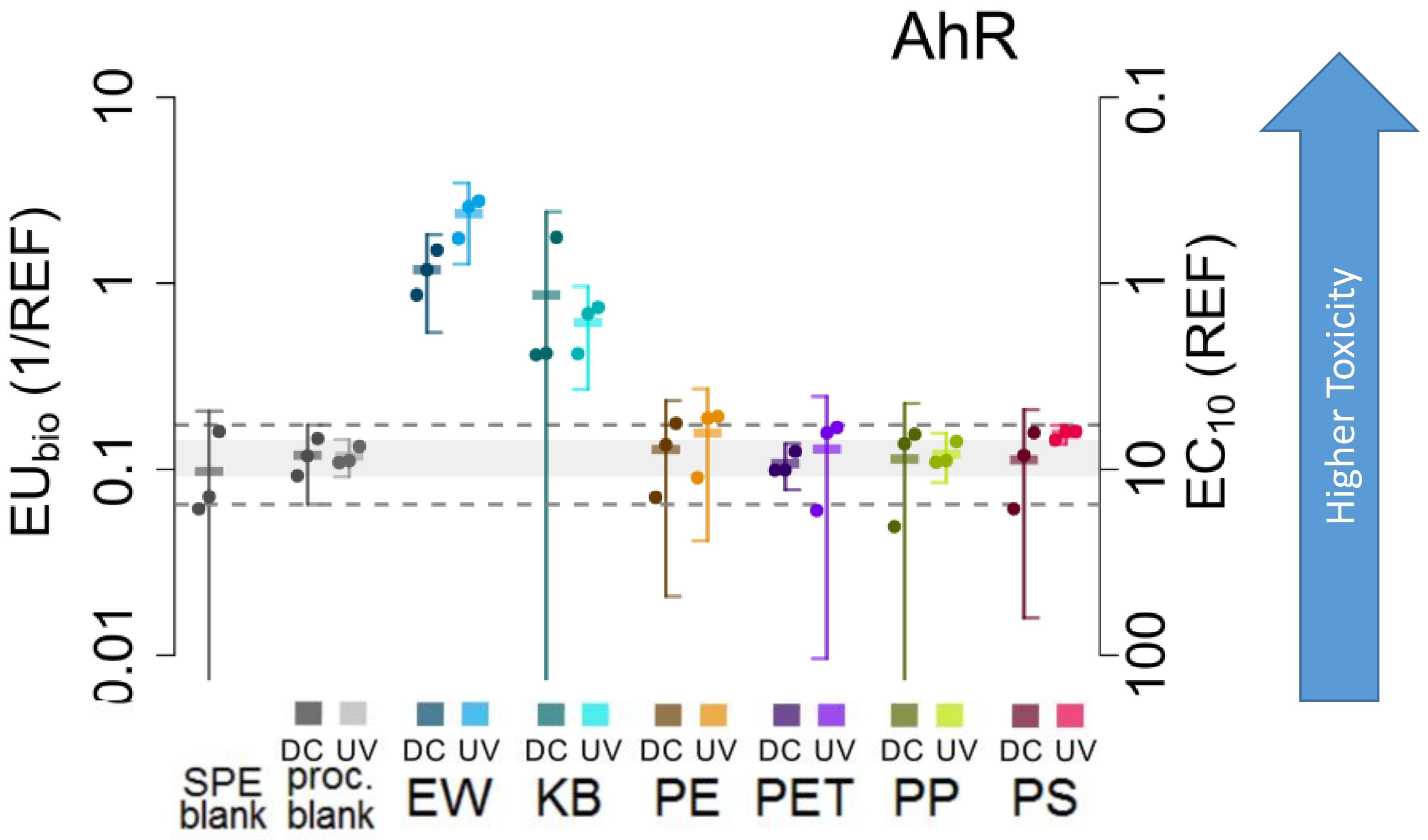
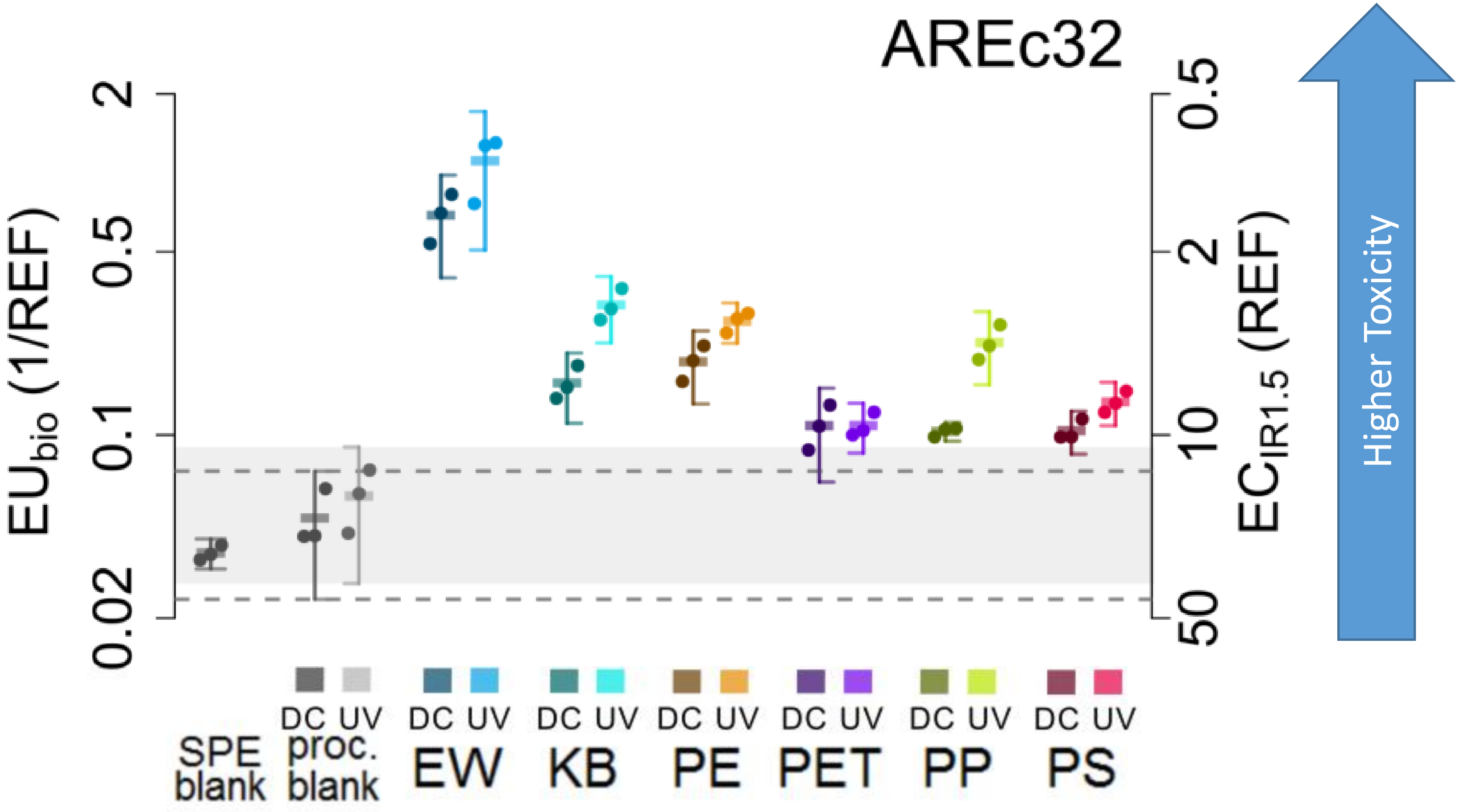
3. Screening leachates from weathering plastics for toxicity



- Positive AhR response (xenobiotic metabolism) for the Ewaste and keyboard controls
- No response for the pre-production plastics

3. Screening leachates from weathering plastics for toxicity



- Antioxidant response from all leachates
- Stronger for UV-weathered material
- Strongest (non-positive control response) for weathered polyethylene and polypropylene.

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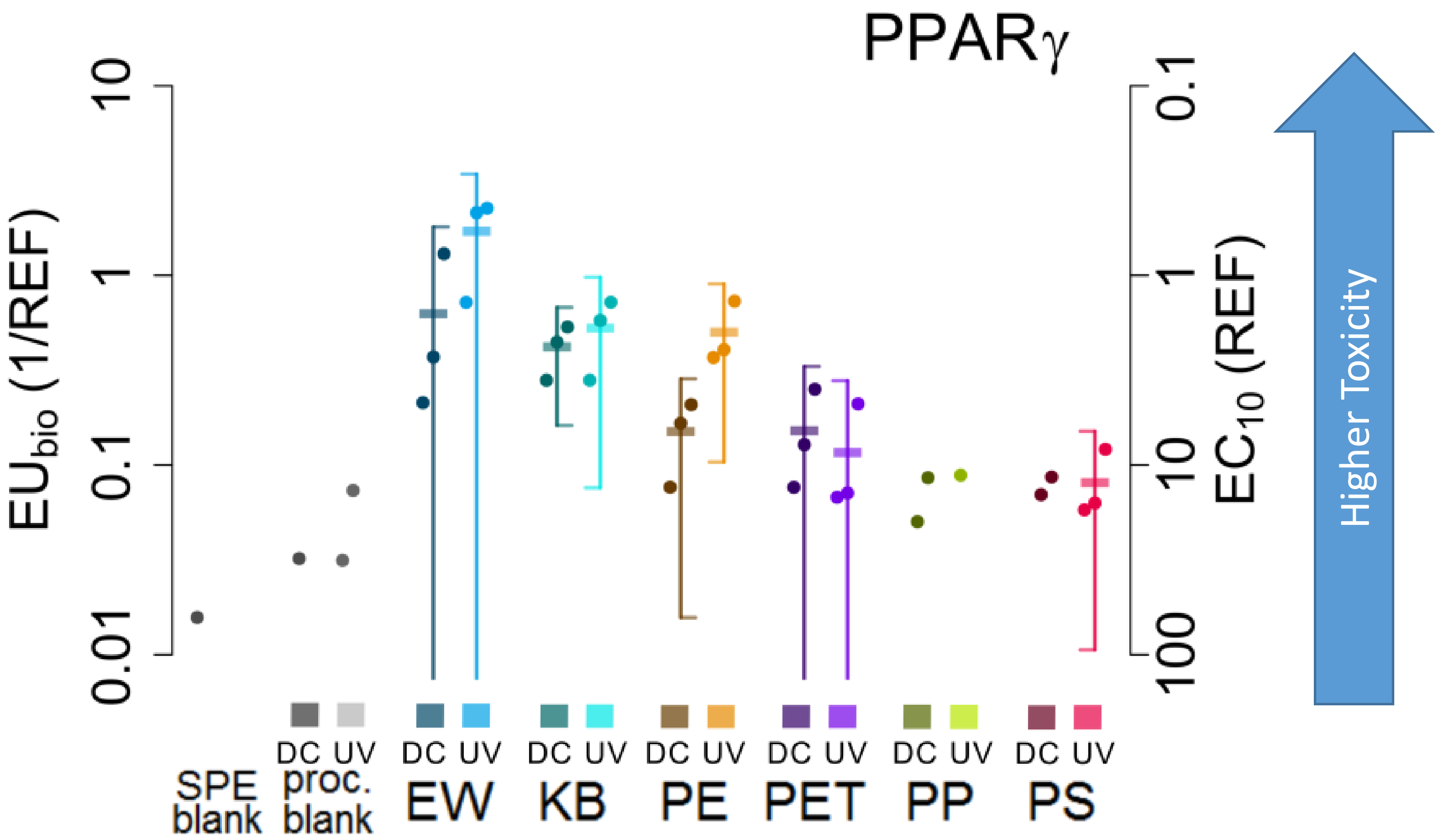
3. Screening leachates from weathering plastics for toxicity



- Peroxisome proliferating response for all leachates
- Strong response for UV-weathered polyethylene.

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References

Pathways for degradation & identification of chain scission products

Gewert, B.; Plassmann, M.; MacLeod, M., Pathways for degradation of plastic polymers floating in the marine environment. *Environmental Science: Processes & Impacts* **2015** 17 (9) 1513-1521.

Gewert, B.; Plassmann, M.; Sandblom, O.; MacLeod, M. Identification of chain scission products released to water by plastic exposed to ultraviolet light. *Environmental Science & Technology Letters* **2018**, *5* (5), 272–276.

Toxicity in-vivo and in cell-based bioassays

Bejgarn, S.; MacLeod, M.; Bogdal, C.; Breitholtz, M., Toxicity of leachate from weathering plastics: An exploratory screening study with *Nitocra spinipes*. *Chemosphere* **2015** 132 114-119.

Rummel, C. D.; Escher, B. I.; Sandblom, O.; Plassmann, M. M.; Arp, H. P. H.; MacLeod, M.; Jahnke, A. Effects of leachates from UV-weathered microplastic in cell-based bioassays. *Environmental Science & Technology* **2019**, *53* (15), 9214–9223.

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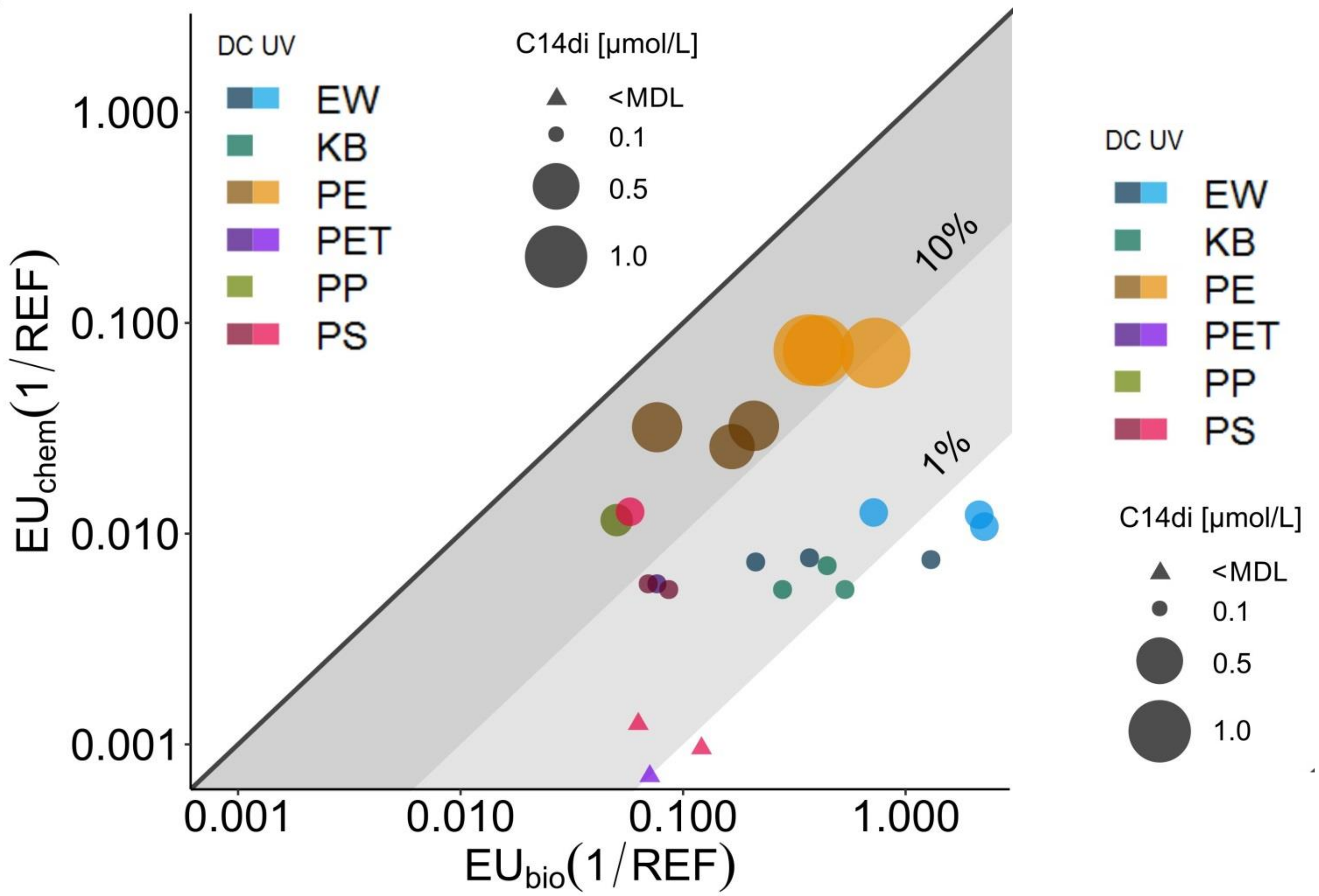

- ”Iceberg modeling” of the PPARγ response
- Response of pure linear mono- and di-carboxylic acids explains up to 42% of the response for UV-weathered polyethylene

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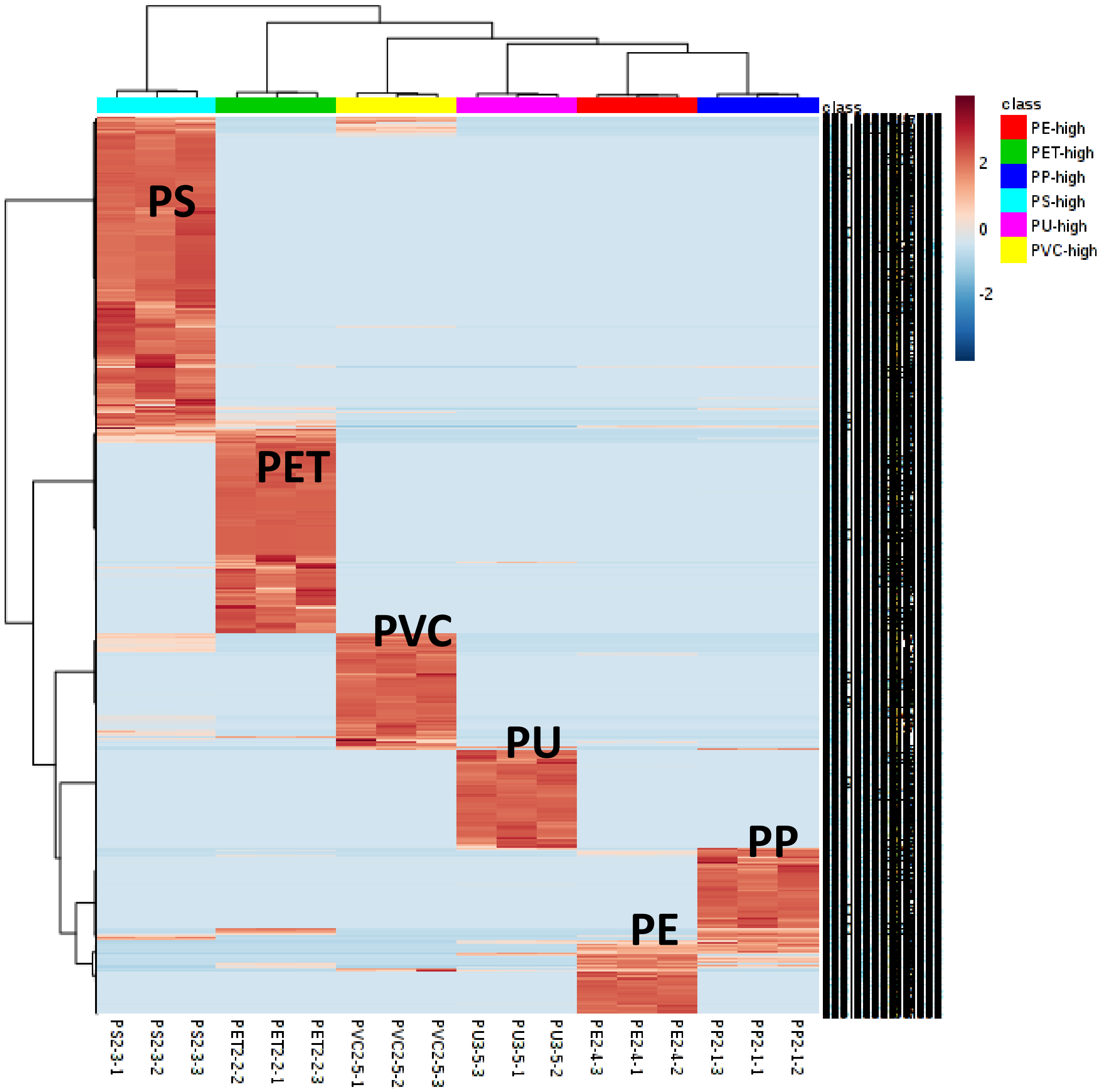
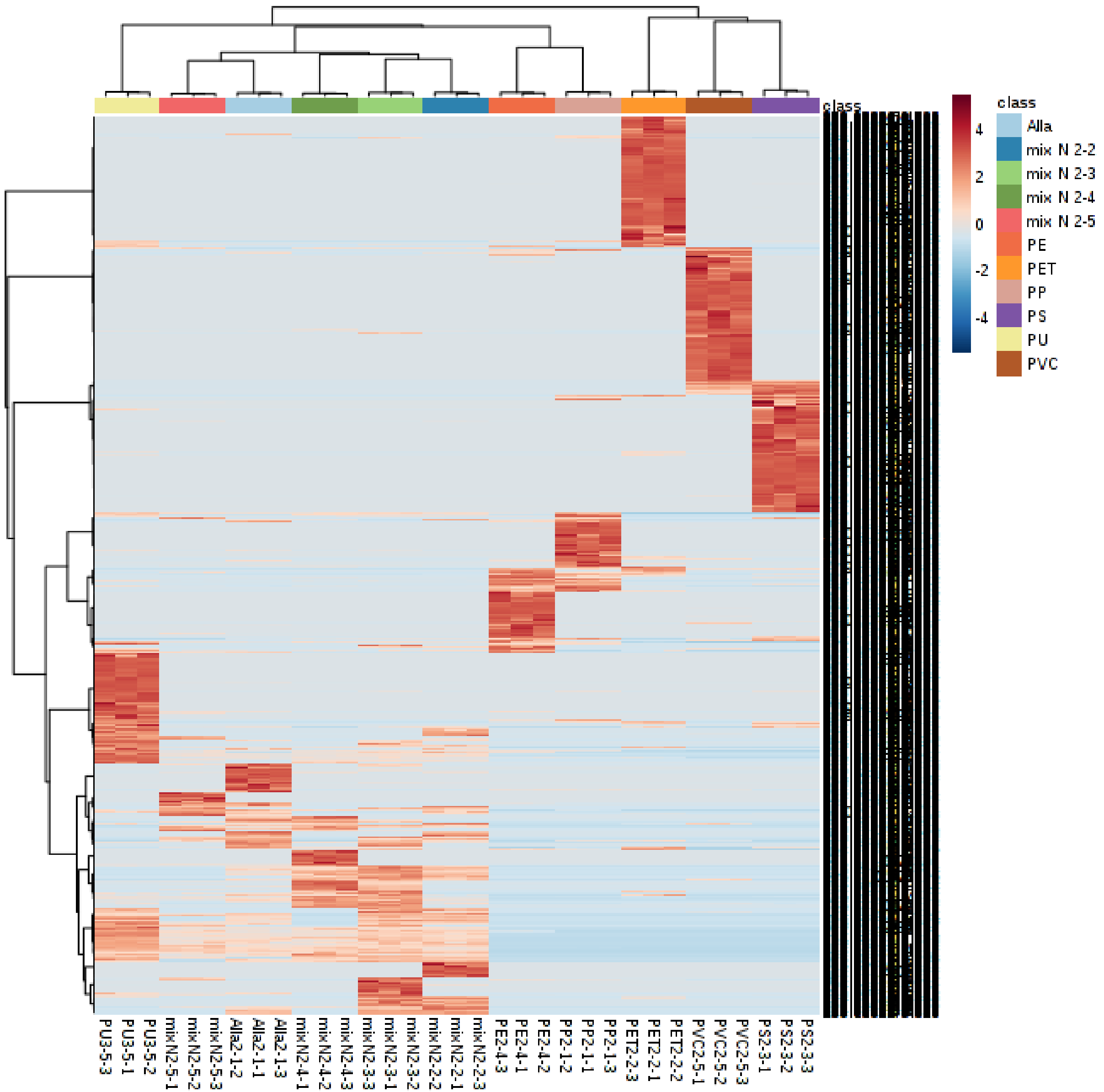
Pure samples of reference plastic materials have distinct fingerprints



But in experiments with mixtures of pure plastics we cannot find the same ”fingerprint”!



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IF YOU CAN DODGE A WRENCH YOU CAN DODGE IMPACTS OF GLOBAL POLLUTION

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