

Sorption behavior of amine micropollutants on polyethylene microplastics - Impact of aging and interaction with green seaweed

Thorben Vockenber^{a,b}, *Thomas Wichard*^c, *Nico Ueberschaar*^d, *Marcus Franke*^{a,b}, *Michael Stelter*^{a,b,e}, *Patrick Braeutigam*^{a,b*}

^a Institute of Technical Chemistry and Environmental Chemistry, Faculty of Chemistry and Earth Sciences, Friedrich Schiller University Jena, Jena, Germany

^b Center for Energy and Environmental Chemistry (CEEC Jena), Faculty of Chemistry and Earth Sciences, Friedrich Schiller University Jena, Jena, Germany

^c Institute for Inorganic and Analytical Chemistry, Faculty of Chemistry and Earth Sciences, Friedrich Schiller University Jena, Jena, Germany

^d Mass Spectrometry Platform, Faculty of Chemistry and Earth Sciences, Friedrich Schiller University Jena, Jena, Germany

^e Fraunhofer IKTS, Fraunhofer Institute for Ceramic Technologies and Systems, Hermsdorf, Germany

SI 1.

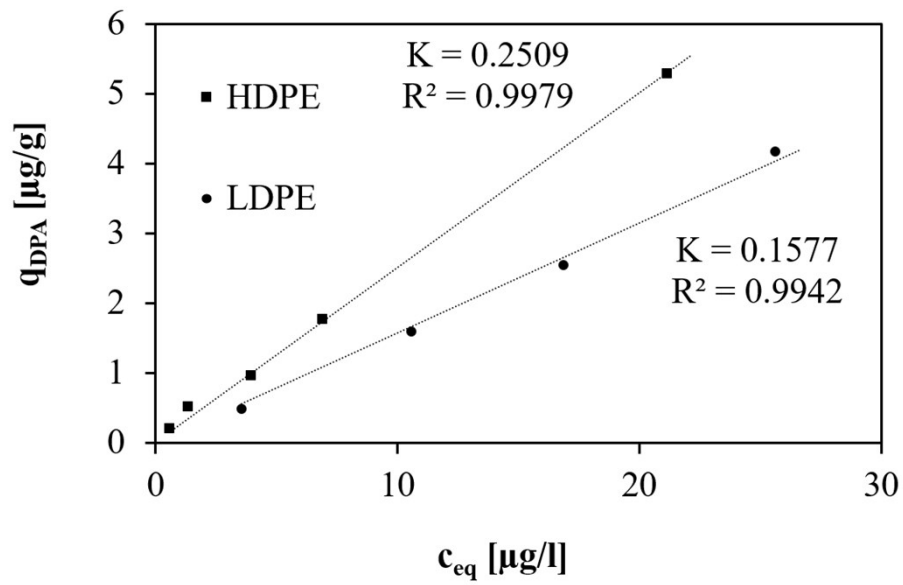
A: Parameter of UHPLC gradient program

retention time [min]	flow [mL/min]	% eluent B	curve
0	0.4	0	-
0	0.4	0	5
0.2	0.4	0	5
1	0.441	15	5
1.5	0.551	55	2
2	0.566	60	6
2.5	0.675	100	8
3.5	0.675	100	5
3.6	0.4	0	5
4.5	0.4	0	1

B: Analytes with UHPLC-HRMS data

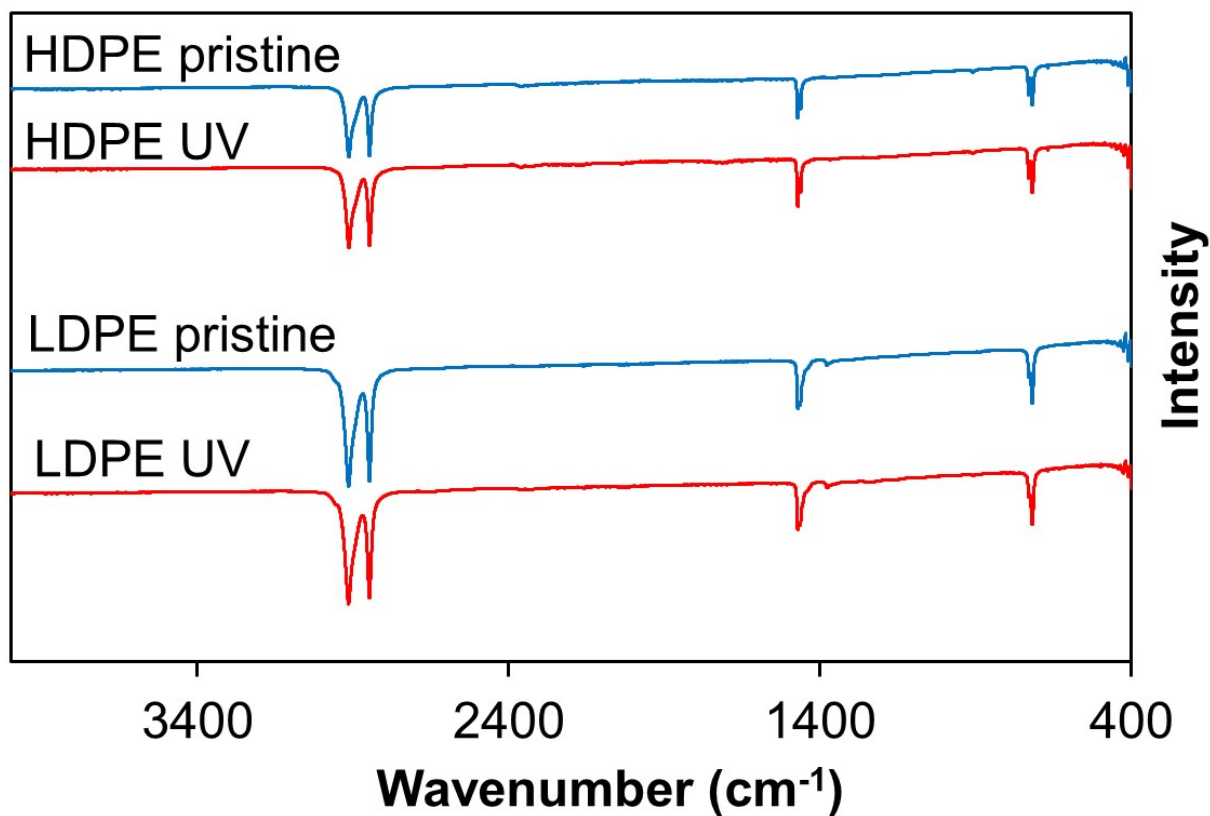
compound	<i>m/z</i> [M + H]⁺	detection time [min]	MS
aniline	94.06513	0.10-1.00	tSIM
aniline-d7	99.09651	0.30-1.25	tSIM
carbamazepine	237.10224	1.80-2.50	tSIM
carbamazepine-d10	247.16501	1.80-2.50	tSIM
diphenylamine	170.09643	1.25-4.00	MS ²
diphenylamine-d10	180.15919	1.25-4.00	MS ²
<i>o</i> -toluidine-d9	108.08078	0.50-1.25	tSIM
<i>o</i> -toluidine-d9	115.12470	0.50-1.25	tSIM

SI 2.



SI 2. Relationship between DPA concentration in equilibrium (c_{eq}) and loading of HDPE/LDPE microplastic in equilibrium state (q_{DPA}) with given slope (K) ($V = 250$ mL; $c_0 = 10^{-6}$ M; fraction size 0.5-1 mm; $t_{max} = \text{equ.}$)

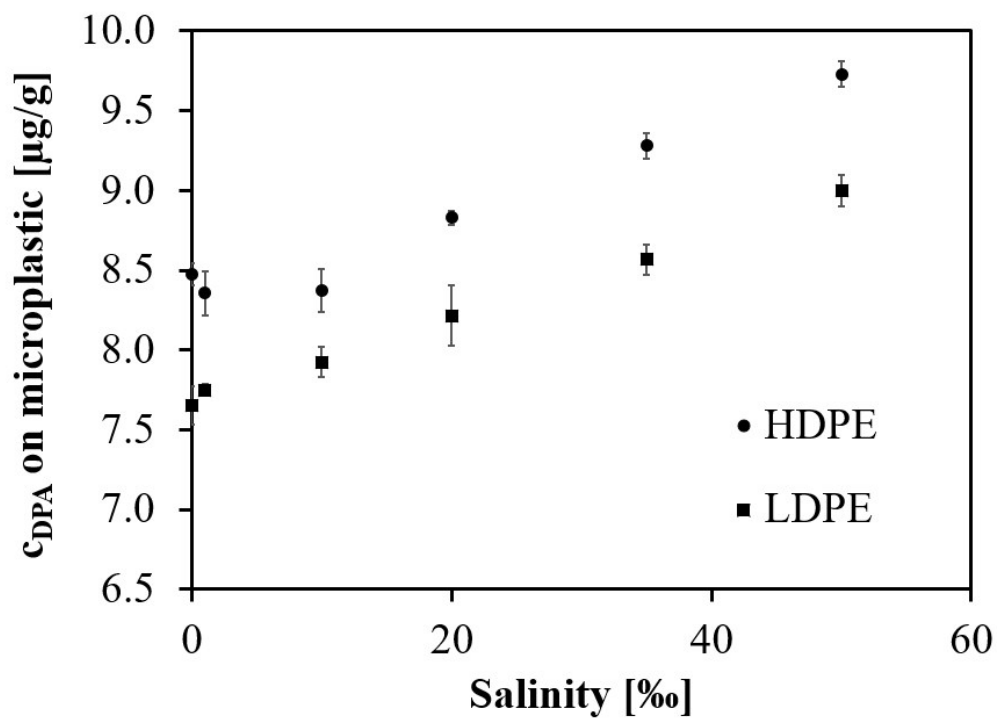
SI 3.



SI 3. IR spectra of pristine and UV aged HDPE / LDPE microplastic (fraction size 0.5-1 mm; $t_{UV} = 10$ h);

Measurements were carried out at a Nicolet™ IS™ FTIR-Spectrometer using an all diamond iD7 ATR accessory and 64 scans min^{-1} . For spectra interpretation Thermo Scientific™ OMNIC™ spectra software was used.

SI 4.



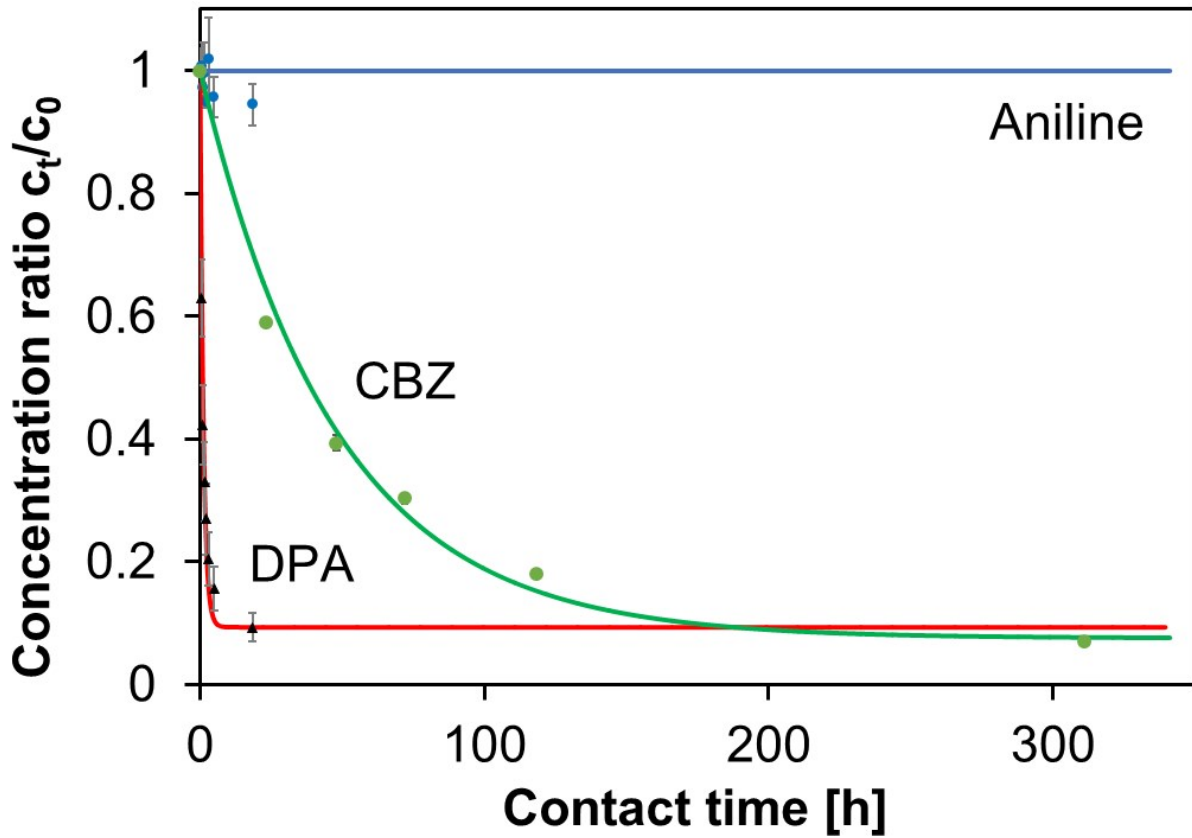
SI 4. Influence of salinity on DPA sorption behavior on HDPE and LDPE ($V = 250$ mL; $c_0 = 10^{-6}$ M; NaCl concentration = 0, 1, 10, 20, 35 and 50‰ (m/m); fraction size 0.5-1 mm; $t = 24$ h)

SI 5.



SI 5. Used LDPE / HPDE microplastic particles float on the water surface. Therefore in all experiments the solution was shaken on a multi-flask shaker VKS-75 (Edmund Bühler, Hechingen, Germany) to hold microplastic and amine pollutants homogenized.

SI 6.



SI 6. Sorption behaviour of aniline, CBZ and DPA on HDPE with time (dots) and overlaying model based on Lagergren (line) ($V = 250$ mL; $c_0 = 10^{-6}$ M; HDPE fraction size 0.5-1 mm; amount 5 g; $t_{\text{aniline, DPA}} = 24$ h, $t_{\text{CBZ}} = 348$ h)

SI 7.

Calculation of the duration of used UV weathering in comparison to natural occurring sunlight was done by measuring the energy output of a 30 cm x 30 cm solar cell:

Energy output of UV lamp (TNN 12/20 (Peschl Ultraviolet, 30 W, 254 nm, 20 cm)): **0.0260 W**

Energy output of sunlight in middle Europe at 1 pm in May 2020 (no clouds), minus the amount of UV-A radiation, which is about 95%: **0.0049 W**

UV weathering is around 5 times stronger than natural aging. Therefore we can conclude, that with a duration of 10 h in the laboratory, we simulate an occurrence in the environment of about 50 h of pure sunlight which corresponds to ~ 5 days. Taking into account parameters such as overlaying water column, shading, clouding etc. we would suggest a simulated time of 1 - 2 weeks compared to the environment.

We are aware of the fact, that this is just a very simplistic calculation which should only help to put our UV treatment duration into perspective to environmental processes.