Supplementary Material

Additives and polymer composition influence the interaction of microplastics with xenobiotics

Darius Hummel,[A] Andreas Fath,[B] Thilo Hofmann[C,D] and Thorsten Hüffer[C,D,E]

[A]Department of Soft Matter Science and Dairy Technology, Institute of Food Science and Biotechnology, University of Hohenheim, Garbenstrasse 21, 70599 Stuttgart, Germany.

[B]Department of Medical and Life Sciences, Furtwangen University, Jakob-Kienzle-Strasse 17, 78054 VS-Schwenningen, Germany.

[C]Department of Environmental Geosciences, Center for Microbiology and Environmental Systems Science, University of Vienna, Althanstrasse 14, 1090 Vienna, Austria.

[D]Research Platform Plastics in the Environment and Society (PLENTY), University of Vienna, Althanstrasse 14, 1090 Vienna, Austria.

[E]Corresponding author. Email: thorsten.hueffer@univie.ac.at

S-1: Further experimental details on the confocal microscopy

<u>Reference samples</u>

Reference samples for fluorescence experiments were prepared (see: Confocal fluorescence microscopy). Pictures were acquired in reflectance mode at 580 nm emission and detection wavelength. For excitation and detection settings see: Confocal fluorescence microscopy. Pictures acquired in reflectance mode are depicted in gray-scale. Fluorescence is depicted in a range from white (highest intensity), over yellow (decreased intensity) to red (lowest intensity). Both channels were merged to obtain one picture.
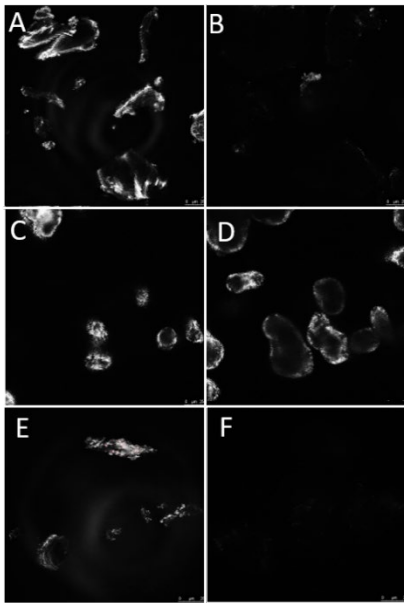

Figure S1: Images of reference samples of PA-6 (1 μm (A) and 15 μm (B) penetration depth), PA- (1 μm (A) and 15 μm (B) penetration depth) and plasticized PVC particles(1 μm (A) and 15 μm (B) penetration depth).

<u>Click-Experiment</u>

Estradiol-Glow shows significant differences in molecular structure compared to the probe molecules (EE2, E1, Nor) utilized for quantitative sorption experiments. Since sorption behavior is governed by molecular structure of the sorbate and the sorbent, results of qualitative sorption experiments could be expected to differ to quantitative experiments. To check whether there are differences in sorption sites, sorption experiment with PA-6 and EE2 were carried out. Subsequently, fluorescence labeling with 3-azido-7-hydroxy-coumarine was performed applying click-chemistry. Consequently, fluorescence intensity of the synthetized molecule is increased, compared to unbound 3-azido-7-hydroxy-coumarine. (Du et al. 2010)

Click reagents (Jena Bioscience, Jena, Germany) were added to a control sample containing PA-6 and aqueous CaCl2 solution, as well as to a sample containing EE2, additionally. Click reagents were added after expected equilibrium time for sorption of EE2 to PA-6 (see sorption experiments). Samples were prepared as in section confocal fluorescence microscopy, replacing E-Glow by EE2. The click experiment was conducted as suggested by the manufacturer.
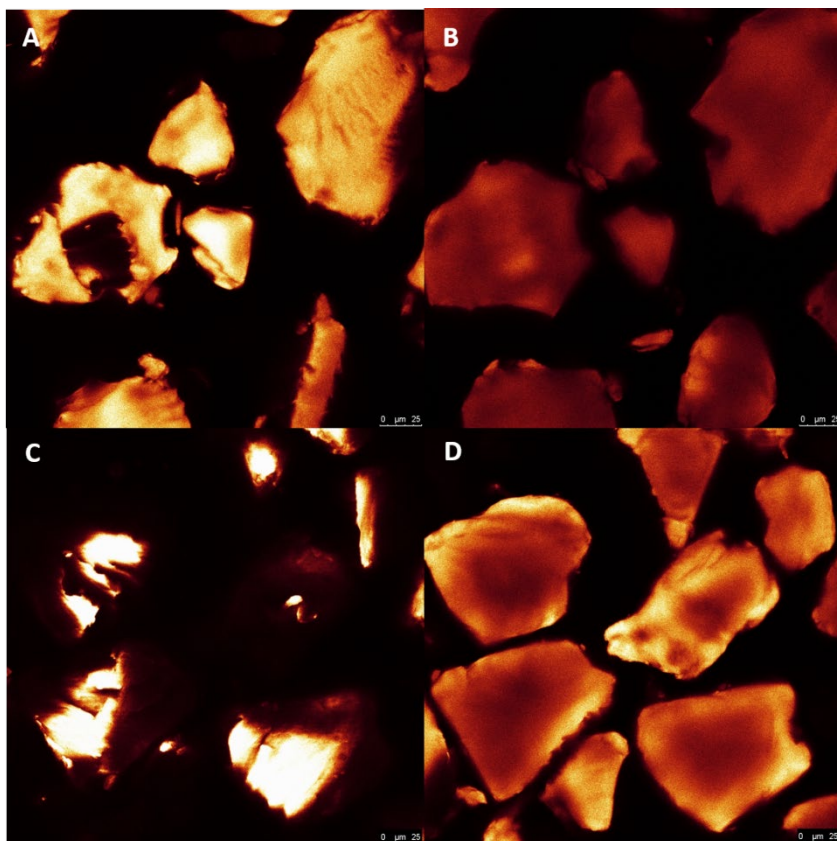
Figure S2: Reference image of PA-6 particles in aqueous CaCl2 solution with click reagents and 3-azido-7-hydroxycoumarine at 1 µm (A) and 15 µm (B) penetration depth and sample of PA-6 particles in aqueous CaCl2 solution containing EE2 with click reagents and 3-azido-7-hydroxycoumarine at 1 µm (C) and 15 µm (D) penetration depth

Samples containing EE2 show increased fluorescence intensity at the particle surface as well as in outer regions of the inner bulk polymer (Figure S2). Increased fluorescence intensity is based on the aforementioned covalent binding of 3-acido-7-hydroxycoumarine to EE2. Distribution of fluorescence throughout the cross-sectional area of the particle is similar to the fluorescence pattern of Estradiol-Glow and PA-6.

S-2: Fitting parameters

Table S1: Fitting parameters ± standard errors, standard error of estimates (SEE), and Akaike's Information Criterion (AIC) for three non-linear sorption model fits to the experimental isotherm data of E1 by the two polyamide sorbents.

Freundlich Model (FM)

Sorbent	K_F	n	SEE	AIC	N
PA6	1.33E+02 ± 1.13E+01	0.8772 ± 0.0168	0.0583	-65.08	13
PA12	3.15E+02 ± 3.57E+01	0.9076 ± 0.0235	0.1133	-56.46	13

Langmuir Model (LM)

Sorbent	Q_{max}	K_L	SEE	AIC	N
PA6	1.61E+05 ± 3.55E+04	1.99E+03 ± 4.84E+02	0.0937	-58.92	13
PA12	4.49E+05 ± 1.31E+05	2.00E+03 ± 6.34E+02	0.2304	-47.22	13

Polanyi-Manes Model (PMM)

Sorbent	log Q_{max}	a	d	SEE	AIC	N
PA6	6.24 ± 0.03	-1.33E-02 ± 1.21E-02	1.19 ± 0.18	0.0523	-63.04	13
PA12	6.56 ± 0.43	-8.10E-02 ± 1.05E-02	1.29 ± 0.26	0.0998	-54.64	13

N: number of data points.

Table S2: Fitting parameters ± standard errors, standard error of estimates (SEE), and Akaike's Information Criterion (AIC) for three non-linear sorption model fits to the experimental isotherm data of EE2 by the two polyamide sorbents.

Freundlich Model (FM)

Sorbent	K_F	n	SEE	AIC	N
PA6	3.97E+03 ± 1.97E+02	0.9151 ± 0.0119	0.0253	-75.90	13
PA12	2.44E+04 ± 1.65E+03	0.8688 ± 0.0177	0.0224	-47.97	9

Langmuir Model (LM)

Sorbent	Q_{max}	K_L	SEE	AIC	N
PA6	2.12E+07 ± 1.13E+07	5.69E+03 ± 3.08E+03	0.0670	-63.28	13
PA12	7.92E+06 ± 1.90E+06	4.60E+02 ± 1.24E+02	0.0819	-36.30	9

Polanyi-Manes Model (PMM)

Sorbent	log Q_{max}	a	d	SEE	AIC	N
PA6	7.93 ± 0.32	-1.08E-02 ± 9.20E+03	1.26 ± 0.17	0.0270	-71.64	13
PA12	7.93 ± 0.85	-4.10E-03 ± 1.25E-02	1.42 ± 0.60	0.0305	-40.38	9

N: number of data points.

Table S3: Fitting parameters ± standard errors, standard error of estimates (SEE), and Akaike's Information Criterion (AIC) for three non-linear sorption model fits to the experimental isotherm data of NOR by the two polyamide sorbents.

Freundlich Model (FM)

Sorbent	K_F	n	SEE	AIC	N
PA6	9.91E+01 ± 9.30E+01	0.6364 ± 0.1485	1.014	-75.90	9
PA12	7.56E+02 ± 9.74E+01	0.8723 ± 0.0203	0.0724	-62.28	13

Langmuir Model (LM)

Sorbent	Q_{max}	K_L	SEE	AIC	N
PA6	2.22E+04 ± 1.24E+04	1.50E+03 ± 1.11E+03	1.803	-8.470	9
PA12	2.71E+06 ± 7.20E+05	7.10E+03 ± 2.10E+03	0.1311	-54.56	13

Polanyi-Manes Model (PMM)

Sorbent	log Q_{max}	a	d	SEE	AIC	N
PA6	4.77 ± 2.44	-2.50E-03 ± 5.02E-02	1.52 ± 4.39	0.5742	-13.97	9
PA12	7.64 ± 0.69	-8.39 E-02 ± 1.12E-01	0.85 ± 0.26	0.0620	-60.83	13

N: number of data points.

References

Du, Lupei; Ni, Nanting; Li, Minyong; Wang, Binghe (2010): A Fluorescent Hydrogen Peroxide Probe Based on a 'Click' Modified Coumarin Fluorophore. In: Tetrahedron letters 51 (8), S. 1152–1154. DOI: 10.1016/j.tetlet.2009.12.049.