Comparative assessment of microplastics in water and sediment

of a large European river

- Supplementary data -

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S1 Supplementary Materials and methods

S.1.1 Sampling sites: Background information on collected samples

Tab. S1: Analysed volume/mass of water and sediments (wet and dry weight) and sediment densities for each sampling site along the Elbe river

Site (abbreviation)	Water samples	Sediment samples				
	Filtered water volume [m ³]	Wet weight of total sample [g]	Dry weight of total sample[g]	Dry weight of sediment fraction 20- 125µm [g]	Sediment density [g cm ⁻³]	Volume of total (dry) sample [m³]
Wittenberg (WB)	6.2	1,200	576	63.4	2.16	0.000267
Dessau (DS)	3.2	213 (2,500)*	85.2 (1,000)*	n.a. (97.6)*	1.42 1.42	0.000704 0.000060
Havelberg (HB)	32.7	1,100	385	125.9	1.82	0.000212
Wittenberge (WE)	12.1	1,000	520	33.3	2.34	0.000222
Dömitz (DM)	3.7	1,500	570	152.2	2.14	0.000266
Geesthacht (GH)	12.5	1,066.7 (803)*	326.4 (266)*	n.a. (62.0)*	1.97 1.97	0.000166 0.000135
Elbstorf (ET)	-	623.5 (364)*	257.5 (161)*	n.a. (41.0)*	2.18 2.18	0.000118 0.0000739
Hafenstraße (HS)	14.8	1,128.9	949.4	54.6	2.54	0.000374
Lühemündung (LM)	15.8	2,641	1,357.5	709.9	2.24	0.000606
Hollerwettern (HW)	10.7	1,000	780	14.1	2.63	0.000297
Vogelsand (VS)	16.4	1,020	847.62	7.9	2.39	0.000355

* The sediment fraction 20–125 µm from Dessau, Geesthacht and Elbstorf were lost in the first wet-sieving process and therefore wet-sieving was repeated with a second sample to obtain the 20–125 µm fraction. Numbers in brackets refer to wet and dry weights from the second wet sieving. Wet and dry weights without brackets instead refer to the first wet-sieving from which the sediment fraction 125–5,000 µm was obtained and further processed. n.a. = not analyzed

S1.2 MP extraction from sediment samples

Microplastic (MP) extraction from the Elbe sediments included four processing steps: (I) Dry weight analysis, (II) Wet sieving, (III) Density separation and (IV) Acid digestion. The extracted MPs were identified and characterised (V) via visual sorting, Attenuated total reflection-Fourier-transform infrared spectroscopy (ATR-FTIR) and pyrolysis GC-MS (pyr-GC-MS, Fig. S1).



Fig. S1: Overview of the MP extraction methodology

(I) Dry weight determination

Dry weight content was quantified for each sediment sample by drying a subsample of 200 g (WW) over five days (d) at 55 °C and weighing the samples afterwards again. The ratio of dry weight to wet weight equalled the dry weight content [%].

(II) Wet sieving

MP extraction was facilitated by separating the sediment samples into following size classes using wet-sieving: < 20 μ m, 20–63 μ m, 63–125 μ m, 125–500 μ m, 500–1,000 μ m and > 1,000 μ m. The very fine particle fraction (< 20 μ m) was discarded. For wet-sieving, we used a vibratory sieve shaker (Retsch Technology, AS 200 basic, vibration intensity: 80 %) with five stacked sieves (Retsch Technology, Test Sieve ISO 3310-1, *ø*: 200 mm, height: 50 mm, pore size: 20, 63, 125, 500, 1,000 μ m). Throughout the sieving process, the sample was washed with distilled water until the run-off water appeared to be particle-free. Depending on the percentage of tone and silt, wet-sieving time ranged from 20 to 80 min.

The resulting sieve retentions were rinsed off with distilled water into 500 mL beakers and united in following three fractions: $20-125 \mu m$, $125-1,000 \mu m$ and > 1,000 μm . The sediments > 1,000 μm were directly transferred on glass microfibre filters (GE Healthcare Life Sciences, Whatman, GF/D Cat. No. 1823-047, diameter: 47 mm, pore size: 2.7 μm), while all other fractions

were stored in beakers at 4°C in the dark until further processing. Particles > 5,000 μ m were not included.

(III) Density separation with the Munich Plastic Sediment Separator

The volume of the $125-1,000 \,\mu\text{m}$ sediment fraction was further reduced by ZnCl_2 density separation in a replicate of the stainless-steel Munich Plastic Sediment Separator (MPSS, Fig. S2, Imhof et al. 2012).



Fig. S2: Replica of the Munich Plastic Sediment Separator (MPSS) originally published by Imhof et al. (2012). Overview of the MPSS (A), sediment chamber (B), dividing chamber and filtration unit attached to the standpipe (C), interior of the sediment chamber (D), standpipe (E), dividing chamber (left) and filtration unit (right) which are connected by a bayonet joint (front, F).

For density separation, the sediment chamber (\emptyset : 30 cm, height: 25 cm) of the MPSS was filled with ZnCl₂ solution (ρ = 1.6–1.8 g cm⁻³) and the wet-sieved sediment sample (125–1,000 µm). After attaching the standpipe (\emptyset _{bottom end}: 30 cm, \emptyset _{upper end}: 10.4 cm, height: 50.9 cm) as well as the dividing chamber (height: 23.1 cm), the system was further filled with ZnCl₂, until the sample chamber was almost completely loaded with ZnCl₂ (approximately 38 L). Finally, the filtration unit with the filter holder was attached to close-off the system. The filter holder was equipped with a glass microfibre filter (GE Healthcare Life Sciences, Whatman, GF/D Cat. No. 1823-047, diameter: 47 mm, pore size: $2.7 \,\mu$ m) to allow direct and contamination-free filtration of the sample in the sample chamber after density separation.

The solution of ZnCl_2 and sediments was stirred for 3 h (14 rpm) by a rotor with an external control unit (Siemens, Sinamics G110) at the bottom of the sediment chamber, followed by a 24 h resting phase. Then, the dividing chamber was closed off, rotated 180° degrees and attached to a vacuum filter flask to filter off the retained ZnCl_2 solution. The remaining ZnCl_2 in the sediment chamber and standpipe was removed and recycled for reuse by vacuum-filtrating through a glass microfibre filter (VWR, Type 696, Cat. No. 516-0879, size: 125 mm, pore size: 1.5 µm).Due to hydrophobicity, MPs also attached to the interior of the standpipe and the dividing chamber. Therefore, the inner surface of the standpipe and the dividing chamber were rinsed with distilled water and the rinse water was also vacuum filtrated on glass microfibre filters (GE Healthcare Life Sciences, Whatman, GF/D Cat. No. 1823-047, diameter: 47 mm, pore size: 2.7 µm) for further analysis.

Due to a limited sediment quantity for the sampling site DS, density separation was performed in a 2 L separating funnel instead of the MPSS to minimise particle loss. After intensively mixing the sediment with $ZnCl_2$, the solution remained in the separating funnel for 24 h before the deposited particles were removed and the remaining sample was transferred on glass microfibre filters (GE Healthcare Life Sciences, Whatman, GF/D Cat. No. 1823-047, diameter: 47 mm, pore size: 2.7 μ m).

(IV) Acid digestion

After density separation, the organic content in the separated samples was further reduced by acid digestion. Samples were transferred from the glass microfibre filters into 500 mL Schott bottles with 50–200 mL of a 10:1 mixture of 30 % H_2O_2 and 10 % H_2SO_4 . The acid solutions were incubated for 5 d at 55 °C on an orbital shaker and afterwards filtered on glass microfibre filters (GE Healthcare Life Sciences, Whatman, GF/D Cat. No. 1823-047, diameter: 47 mm, pore size: 2.7 µm). Filters were stored in covered Petri dishes at 4 °C until being analysed.

S1.3 Determination of Elbe sediment densities

The volume of the sediment samples was calculated based on its mass and densities. Sample densities were determined by weighing in up to 90 g of dried sediment into volumetric flasks (100–500 mL) and filling up the remaining volume with ultrapure water. We allowed sediments to settle and air bubbles to escape before we filled up the flask to the gauge mark. Densities were calculated as:

Density $[kg/m^3] = (Sediment mass [kg]) / (Flask volume [m^3]-Volume of ultrapure water [m^3])$

S1.4 Details on ATR-FTIR analysis

We identified a subsample of the visually identified tentative MPs by ATR-FTIR spectroscopy (Spectrum 2 with software: v10.03.09, Perkin Elmer, Waltham, MA, USA). Spectra were acquired with the range set to 450–4,000 cm⁻¹ (resolution: 4 cm⁻¹, total number of scans: 4, peaks referring to CO₂ and H₂O were suppressed). Resulting spectra were compared to a self-prepared reference data base which included spectra of the most common polymer types (PE-LD, PE-HD, PE-X, PP, PS, PVC, PET, PMMA, ABS, PA, PU).

Acid digestion is able to change the chemical surface of MPs. Therefore, we could not exclude the possibility that acid digestion had changed the surface characteristics of the tentative MP particles in our sediment samples. Therefore, we added also spectra of the "digested form" of the reference polymers to the spectra data base. Digestion was performed in an equal way compared to the sediment samples (10:1 mixture of 30 % H_2O_2 and 10 % H_2SO4 , 5 d, 55 °C; compare S1.2).

S1.5 Details on pyrolysis GC-MS methodology

S1.5.1 Pyrolysis GC-MS analysis of the MP content in the Elbe sediments

For quantification of the polymers, characteristic pyrolysis products were monitored. These indicator compounds were specific for the certain polymer (Tab. S2). For the coarser sediment fraction (ground filters with the 125–1,000 µm sediment fraction), 1 g of sediment sample was weighed and for the fine sediment fraction (20–125 µm), the entire sample was used. Extraction was done using 10 mL extraction cells and an ASE-350 (Dionex, Sunnyvale, CA, USA). After a preextraction with methanol, the polymers were extracted using tetrahydrofuran at 185 °C and 100 bar (Dierkes et al. 2019). Extracts were collected in 60 mL vials containing 200 mg calcined silica gel (600 °C, 2 h). After extraction, 10 μ L of Polystyrene-d₅ (270 μ g mL⁻¹ in dichloromethane) were spiked as internal standard and the solvent was subsequently evaporated. The silica gel was ground and 20 mg weighed into a pyrolysis cup. Pyr-GC-MS analysis was performed using a Multi-Shot Pyrolyzer (Frontier Laboratories, Saikon, Japan) and an Auto-Shot Sampler (Frontier Laboratories, Saikon, Japan) at 600 °C. The pyrolyzer was attached to an Agilent 7890B gas chromatograph (Santa Clara, CA, USA) equipped with an Ultra ALLOY UA-5(MS/HT) metal capillary separation column (Frontier Laboratories, Saikon, Japan). Column dimensions were 30 m length, $250 \,\mu$ m inner diameter and $0.25 \,\mu$ m film thicknesses. Chromatographic separation was performed by the following temperature program: hold at 40 °C for 2 min, increased with 20 °C min⁻¹ to 320 °C and hold for 13 min. For detection, an Agilent MSD 5977B in scheduled selected ion monitoring (SIM) modus was used.

Polymer	Pyrolysis product	Indicator ion	t _R [min]
Polypropylene	2,4-dimethylhept-1-ene	126ª	4.89
		70	
Polyethylene	1,14-Pentadecadiene	81ª	10.29
Polyethylene	1-Pentadecene	97 ^a	10.32
Polystyrene	Styrene	104 ^a	5.54
		91	
Polystyrene d ₅	styrene-d ₅	109 ^a	5.50

Tab. S2: Indicator compounds and selected ions (a = used for quantification)

A calibration standard was produced for each analysed polymer type (PE, PP, PS) by diluting the polymers in calcined sea sand (600 °C, 1 h) as inert matrix. For that, the polymers were ground in a cryomill (Retsch, Haan, Germany) into a fine powder. Approximately 30 mg of each polymer were exactly weighed in and the mixture of polymers was hence mixed with 10 g calcined sea sand (ChemSolute, No. 804.9025). This polymer/sand mixture was homogenised in a planet mill (Fritsch, Idar-Oberstein, Germany). To obtain calibration curves, the stock mixture was serial diluted in sand by mixing 1–2 g mixture and 8–9 g sand, respectively. The mixture was homogenised in a planet mill (Fritsch, Idar-Oberstein, Germany) after each dilution step. Calibration ranged from 0.005 to 10 mg polymer g⁻¹ sand. Calibration samples were analysed in the same way as the other samples. Calibration curves were fitted by the Mass Hunter Quantitative Analysis tool (Agilent, Santa Clara, CA, USA) using 1/x weighting. Pyr-GC-MS results on the MP content in the Elbe sediments are summarized in chapter S2.3.

S1.5.2 Pyrolysis GC-MS analysis of the MP spheres collected at Dessau

Selected spheres from the water phase of a sampling campaign in Dessau (2019) were placed into a cup and flash pyrolyzed at 600°C using the same method as described in S1.5.1. Mass spectrometer was operated in full-scan mode (45–500 amu). Results for the pyr-GC-MS analysis of the MP spheres collected at the site Dessau are included in chapter S2.4.

S2 Supplementary Results

S2.1 Quality controls

S.2.1.1 Quality controls for the visual MP analysis of the water samples

The three processing blanks from the water sample analysis contained in average 3.67 (~4) tentative MP particles of which 81.82 % were fibres and 18.18% fragments. The majority of the particles were black (45.45 %) and blue (36.36 %). The corresponding sorting blanks included in average 2.33 (~2) MP particles (only black (71.43 %) and blue (28.57 %) fibres).

S.2.1.2 Quality controls for the visual MP analysis of the sediment samples

The three processing blanks for the sediment samples obtained in average 23.33 (~23) tentative MP particles (80.77 % fibres, 17.95 % fragments and 1.28 % foils). The most dominant colours were blue (48.72 %) and grey (21.79 %). MP abundance on sorting blanks for the sediment samples varied between 0 and 13 tentative MP particles (detailed results in Tab. S3). Particles on the sediment sorting blanks were mostly fibres (94.59 %; fragments: 4.05 %, foils: 1.35 %). The most common MP colours on the sorting blanks were blue (51.35 %), grey (18.92 %), transparent (9.46 %), purple and red (both 5.41 %).

S.2.2 Tentative MP in the water and sediment samples (visual analysis)

S.2.2.1 Summary of tentative MP abundances, particles shapes and size distributions

Tab. S3: Abundance and shape of tentative MP (water: $150-5,000 \mu$ m, sediment: $125-5,000 \mu$ m) in the water and sediment samples of the Elbe, n.a. = not analysed. For site abbreviations, see Tab. S1.

		WB	DS	HB	WE	DM	GH	ET	HS	LM	HW	VS
	Total counts	40	43	137	106	55	17	n.a.	76	21	65	24
	Processing blank	4	4	4	4	4	4	n.a.	4	4	4	4
	Sorting blank	2	2	2	2	2	2	n.a.	2	2	2	2
-	Blank-corrected counts	34	37	131	100	49	11	n.a.	70	15	59	18
Water phase	Concentration [MP m ⁻³ water]	5.48	11.56	4.01	8.26	13.24	0.88	n.a.	4.73	0.95	5.51	1.10
	Fibres [%]	52.50	39.53	25.55	40.57	40.00	58.82	n.a.	32.89	52.38	60.00	62.50
	Fragments [%]	32.50	18.60	37.96	21.70	32.73	17.65	n.a.	18.42	9.52	10.77	29.17
-	Spheres [%]	10.00	32.56	24.82	20.75	23.64	11.76	n.a.	36.84	23.81	18.46	0.00
-	Foils [%]	5.00	9.30	11.68	16.98	3.64	11.76	n.a.	11.84	14.29	10.77	8.33
	Total counts	535	1389	678	191	1330	488	103	74	96	45	36
_	Processing blank	23	23	23	23	23	23	23	23	23	23	23
	Sorting blank	12	6	9	0	7	13	10	5	5	2	5
-	Blank-corrected counts	500	1360	646	168	1300	452	70	46	68	20	8
Sediment	Concentration [MP m ⁻³ sediment]	1,873,737	22,684,527	3,059,633	757,284	4,872,632	2,723,849	592,578	123,018	111,962	70,917	22,557
phase	Concentration [MP kg ⁻¹ sediment]	868	15,962	1,678	323	2,281	1,385	272	48	50	27	9
	Fibres [%]	12.34	1.22	9.73	22.51	8.57	28.89	33.98	14.86	51.04	33.33	19.44
	Fragments [%]	28.22	3.74	37.76	21.99	10.53	21.11	47.57	50.00	21.88	55.56	77.78
	Spheres [%]	52.90	93.38	1.33	48.69	78.87	49.59	15.53	21.62	26.04	0.00	0.00
_	Foils [%]	6.54	1.66	51.18	6.81	2.03	0.41	2.91	13.51	1.04	11.11	2.78

S.2.2.2 Tentative MP particle shapes



Fig. S3: Particle shape classification. Examples for (a) spheres (sampling site: Dömitz), (b) fragments (sampling site: Dömitz), (c) foils (sampling site: Hafenstraße) and (d) fibres (sampling site: Geesthacht).

S.2.2.2 Tentative MP size distribution at the separate sampling sites



Fig. S4: Size distribution of tentative MP particles (visual analysis) in the water (a) and sediment (b) samples of the eleven sampling sites along the Elbe river. Particle size data was fitted with GraphPad Prism[®] (fit: One-phase decay). For comparability reason, only particles with a size of 150–5,000 μ m were included in the size distribution analysis (leaving out 125–150 μ m MPs from the sediments). Bin width: 200 μ m, first bin centre: 250 μ m. For site abbreviations, see Tab. S1.



S.2.2.3 Coloration of tentative MPs

Fig. S5: Colour distribution of tentative MP particles (visual analysis) in the water (a) and sediment (b) samples of the eleven sampling sites along the Elbe river. For site abbreviations, see Tab. S1.

S.2.3 Mass concentration in water and sediment samples (pyrolysis GC-MS)

S2.3.1 Polymer content (originating from 125-5,000 µm MPs) in the sediment samples

Tab. S4: Polyethylene (PE), polypropylene (PP) and polystyrene (PS) content in the sediment samples [mg MP (125–5,000 μ m particles) m⁻³ or kg⁻¹ sediment (dry weight)] from the river Elbe. For details on the analysed volume/mass, see Tab. S1 (ratios were calculated based on the volume/mass of the total sediment sample, not just of the 125–5,000 μ m sediment fraction). For site abbreviations, see Tab. S1.

	Со	oncentration [mg	Concent	tration [mg N	∕IP kg ⁻¹ sed	liment]		
Sites	PE	РР	PS	Total	PE	РР	PS	Total
WB	2.99×10 ⁴	9.43×10 ²	4.03×10 ³	3.48×10^{4}	13.83	0.44	1.86	16.13
DS	1.11×10 ⁴	1.07×10 ³	1.51×10 ³	1.37×10^{4}	7.81	0.75	1.06	9.62
HB	4.53×10 ⁴	2.75×10 ³	1.20×10 ³	4.92×10 ⁴	24.87	1.51	0.66	27.04
WE	1.81×10 ⁴	8.49×10 ²	9.98×10 ²	1.99×10^{4}	7.72	0.36	0.43	8.51
DM	3.88×10 ⁴	1.53×10 ³	3.87×10 ³	4.42×10 ⁴	18.12	0.72	1.81	20.65
GH	2.11×10 ⁴	1.96×10 ³	3.86×10 ³	2.69×10 ⁴	10.70	1.00	1.96	13.66
ET	3.65×10 ⁴	1.62×10 ³	4.36×10 ³	4.25×10 ⁴	16.77	0.75	2.00	19.51
HS	9.31×10 ²	43.22	0	9.75×10 ²	0.37	0.02	0	0.38
LM	1.66×10 ³	2.14×10 ²	1.62×10 ²	2.03×10 ³	0.74	0.10	0.07	0.91
HW	3.21×10 ²	2.41×10 ²	1.29×10 ²	6.92×10 ²	0.12	0.09	0.05	0.26
VS	0	13.66	0	13.66	0	0.006	0	0.006

S2.3.2 Polymer content (originating from 20-125 µm MPs) in the sediment samples

Tab. S5: Polyethylene (PE), polypropylene (PP) and polystyrene (PS) content in the sediment samples [mg MP (20–125 μ m particles) m⁻³ or kg⁻¹ sediment (dry weight)] from the river Elbe. For details on the analysed volume/mass, see Tab. S1 (ratios were calculated based on the volume/mass of the total sediment sample, not just of the 20–125 μ m sediment fraction). For site abbreviations, see Tab. S1.

	Concentration [mg MP kg ⁻¹ sediment]							
Sites	PE	РР	PS	Total	PE	РР	PS	Total
WB	6.86×10 ⁴	8.08×10 ³	0	7.67×10 ⁴	31.75	3.74	0	35.49
DS	3.72×10 ⁴	3.51×10 ³	0	4.07×10 ⁴	26.21	2.47	0	28.68
HB	9.60×10 ⁴	1.14×10^{4}	0	1.07×10^{5}	52.76	6.26	0	59.02
WE	1.18×10 ⁵	1.03×10 ⁴	0	1.28×10 ⁵	50.46	4.39	0	54.85
DM	6.94×10 ⁴	7.73×10 ³	0	7.71×10 ⁴	32.41	3.61	0	36.03
GH	6.99×10 ⁴	1.41×10 ³	2.46×10 ⁵	3.17×10 ⁵	35.50	0.71	124.72	160.93
ET	1.38×10 ⁵	3.43×10 ³	3.41×10 ⁵	4.82×10 ⁵	63.38	1.57	156.29	221.24
HS	3.07×10 ⁴	1.10×10^{4}	84.78	4.18×10 ⁴	12.08	4.32	0.03	16.44
LM	7.27×10 ³	3.29×10 ³	0	1.06×10 ⁴	3.24	1.47	0	4.72
HW	8.55×10 ³	6.84×10 ³	0	1.54×10^{4}	3.25	2.60	0	5.85
VS	4.74×10 ³	5.90×10 ³	0	1.06×10^{4}	1.98	2.47	0	4.45

S2.4 Pyrolysis GC-MS analysis of the polymer spheres at the sampling site Dessau



Fig. S6: Chromatogram of PS-DVB spheres at the sampling site Dessau (A) and a PS reference material (B).

Peak list PS-		Peak list	
DVB		PS	
Retention	Substance	Retention	Substance
time		time	
4.00	Toluene	3.90	Toluene
5.50	Styrene	5.50	Styrene
6.43	Alpha-methylstyrene	6.44	Alpha-methylstyrene
7.40	m-ethylstyrene		
7.47	p-ethylstyrene		
7.65	m-divinylbenzene		
7.76	p-divinylbenzene		
10.70	Bibenzyl	10.71	Bibenzyl
10.89	Benzene, 1,1'-(1-methyl-1,2-	10.90	Benzene, 1,1'-(1-methyl-1,2-
	ethanediyl)bis-		ethanediyl)bis-
11.50	Benzene, 1,1'-(1,3-propanediyl)bis-	11.50	Benzene, 1,1'-(1,3-
			propanediyl)bis-
11.90	3-butene-1,3-diyldi-benzene	11.90	3-butene-1,3-diyldibenzene
	(styrene dimer)		(styrene dimer)
12.84	2,5-diphenyl-1,5-hexadiene	12.85	2,5-diphenyl-1,5-hexadiene
13.00	Hybrid dimer of styrene and		
	divinylbenzene		
13.04	Hybrid dimer of styrene and		
	divinylbenzene		
15.45	5-hexene-1,3,5-triylbenene (styrene	15.45	5-hexene-1,3,5-triylbenene
	trimer)		(styrene trimer)

Tab. S6: Peak list of PS-DVB and PS for measurements of Fig. S6.

S3. Supplementary literature

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S4. References for Figure 6

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