Electronic Supplementary Material (ESI) for Analytical Methods.

Electronic Supporting Information

Microplastics analysis in environmental samples – Recent pyrolysis-gas chromatography-mass spectrometry method improvements to increase the reliability of mass related data

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Supplement content: 15 pages (cover page included), 6 tables, 5 figures, 1 text paragraphs

Pyrolysis-GCMS/Thermochemolysis

Table S1 Conditions for Pyrolysis-GCMS/Thermochemolysis measurements

Micro furnace pyrolyzer	**EGA/PY-3030D (FrontierLabs)**
carrier gas	Helium
curie temperature	590°C
transfer line temperature	320°C
Gas chromatograph	**7890B (Agilent)**
injector	split/split less
mode	split 15:1
temperature	300°C
column	DB5 (J&W); 30 m x 0.25 mm ID, film thickness 0.25 µm
flow (const.)	0.8 ml/min
temperature program	35°C (2 min) → 310 °C (30 min) at 3°C/min
transfer line temperature	280°C
Mass spectrometer	**MSD 5977A (Agilent)**
ionization energy	70 eV
scan rate	2.48 scans/s
scan range	50-650 amu

Table S2 List of polymers and their respective specific indicator ions

Polymer	Abbre-viation	Characteristic decomposition product(s)	RI [a]	M (*m/z*)	Indicator ions (*m/z*)
Polyethylene	PE	Alkanes (e.g. C_{20})	2000	282	85
		α-Alkenes (e.g. C_{20})	1994	280	**83**
		α,ω-Alkenes (e.g. C_{20}**)**	1987	278	**82**
Polypropylene	PP	**2,4-Dimethylhept-1-ene**	832	126	126, **70**
		2,4,6,8-Tetramethyl-1-undecenes[b]	1306	210	100, 69
		2,4,6,8-Tetramethyl-1-undecenes[c]	1315	210	100, 69
		2,4,6,8-Tetramethyl-1-undecenes[d]	1323	210	100, 69
Polystyrene	PS	Styrene	890	104	104
		2,4-Diphenyl-1-butene	1720	208	91
		2,4,6-Triphenyl-1-hexene	2440	312	**91**
Polyvinyl chloride	PVC	**Benzene**	738	78	**78**
		Chlorobenzene	840	112	112
Poly(methyl methacrylate)	PMMA	Methylacrylate	726	86	55
		Methyl methacrylate	775	100	**100**, 69
Polyamide	PA6	**ε-Caprolactam**	1257	113	**113**
		***N*-methyl caprolactam**[e]	1224	127	**127**
Polyethylene terephthalate	PET	**Dimethyl terephthalate**[e]	1504	194	**163**
Polycarbonate	PC	*p*-Methoxy-tert-butylbenzene[e]	1240	242	149, 164
		2,2-Bis(4'-methoxy-phenyl)propane[e]	2065	256	256**, 241**
MDI-Polyurethane	MDI-PUR	4,4'-Methylenbis(*N*-methylaniline)[e]	2330	226	226
		N,N-Dimethyl-4-(4-methylamino)benzylanilin[e]	2341	240	240
		4,4'-Methylenbis(*N,N*-dimethylaniline)[e]	2354	254	253, **254**

[a] RI = Retention index calculated after Van Den Dool 1963, DB-5 column; M = molecular ion, m/z = mass to charge ratio; [b] Isotactic.
[c] Heterotactic. [d] Syndiotactic. [e] Only after TMAH treatment; bold: indicator ions used for calibration

Polymer Standards

Table S3 Table of all plastic standards used for quantification.

Polymer standard	Abbre-viation	Characteristics	Use (examples)	Source of supply
Polyamide 6 (K891), Akulon® K222-D	PA6	Low viscosity	Consumer durables, convoluted tubes	Ter Hell GmbH, Hamburg, Germany
Polycarbonate, Makrolon 2558	PC	SM (solvent method) PC	Households products/ Consumer Goods (Toys),	Bayer Material Science
Polyethylene, Lupolen 4261 AG UV	HDPE	High density	injection molding	LyondellBasell
Polyethylentereph-thalate, NEOPET 80	PET			Neogroup
Polymethylmeth-acrylate, PLEXIGLAS® 7N	PMMA	Thermoplast	Optical waveguides	Plexiglas
Polypropylene, HL508FB	PP	Homopolymer, isotactic	for medical devices, secondary packaging, infusion bags	Borealis
Polystyrene, TOTAL PS impact 7240	PS	High impact PS for extrusion industry	Dairy sheets, dairy pots	Ter Hell GmbH, Hamburg, Germany
Polystyrene, Styrolution PS 158N/L	PS	Raw material	Packaging material, foams	IINEOS Styrosolution
Polyurethane	PUR	MDI - Thermoplast		GEBA
Polyvinylchloride, Vinnolit S 3268	PVC	Hard PVC, raw material	Extruding mass	Vinnolit

Table S4 Indicator compounds and indicator ions used for quantification with *S/N*-ratio of the smallest calibration point.

Polymer	Indicator compound used for quantification	Indicator ion	low. calibration point	*S/N*
		m/z	µg	
PE	*n*-C_{16-26}-alkadienes	82	0.5	>83
PP	2,4-Dimethylhept-1-ene	70	0.3	478
PET	dimethyl terephthalate	163	0.6	32
PS	2,4,6-Triphenyl-1-hexene	91	0.8 0.01 (LOD 0.03)*	38
PVC	benzene	78	0.3	167
PC	dimethyl bisphenol-A	241	0.9	inf
PMMA	methyl methacrylate	100	0.8	392
PA6	ε-Caprolactame + *N*-Methyl-Caprolactame	113 + 127	0.5	30
PUR	4,4'-Methylenbis (*N,N*-dimethylaniline)	254	1.4	94

*LOD calculated from dissolved PS

Figure S1 CP-pyrolysis targets & MF-pyrolysis cups

Text section S1

Calibration and internal standardization of the pyrolysis process. Py-GCMS measurements of the samples were conducted in different measurement campaigns. For each measurement campaign a new calibration was performed (cf. Table S5a-i). The internal standardization of the pyrolytic process was successively developed and adapted during these measurement campaigns. Firstly, anthracene-d^{10} and androstane were added. In the following the polar cholanic acid, which acid-group will be methylated during the performed on-line derivatization and 9-Dodecyl-1,2,3,4,5,6,7,8-octahydro anthracene (DOHA), which has aromatic as well as aliphatic features and is not plain as anthracene-d10 were added to the mixture. In the last measurement campaigns the relatively poor performing anthracene-d^{10} and androstane were replaced with 9-Tetradecyl-1,2,3,4,5,6,7,8-octahydro anthracene (TOHA), which is very similar to DOHA and was added in lower concentrations (0,01 µg/µL in *n*-hexane instead of 0,02 µg/µl).

Text section S2

Process standard deviation. The process standard deviation s_{x0} is an absolute quality criterion of the precision of an analytical process. It is calculated by dividing the residual standard deviation of a linear regression with the slope (Reichenbächer and Einax, 2011).

$$s_{x0} = \frac{\sqrt{\frac{1}{n-2}\left(Q_{yy} - \frac{Q_{xy}^2}{Q_{xx}}\right)}}{b}$$

S_{x0} process standard deviation

n number of calibration points

Q Sum of Squares

b slope

Table S5 a Calibration parameter PE

CP-Py-GCMS		**Area**				
	m	3.21E+05				
	b	-5.03E+06				
	r^2	0.9				
	S_{x0}	22.4				
	n	7				
MF-Py-GCMS		**Area**				
(Sediment A & B)	m	-9.18E+04				
	b	1.46E+05				
	r^2	0.97				
	S_{x0}	5.1				
	n	10				
MF-Py-GCMS	ISTDpy	Area			Anthr.	**Andros.**
(Sediment C)	m	8.13E+04			-5.01E-03	3.82E-02
	b	-2.39E+03			1.24E-02	3.67E-02
	r^2	0.87			0.59	1.00
	S_{x0}	6.2			13.2	0.8
	n	4			4	4
MF-Py-GCMS	ISTDpy	**Area**	Cholan.	**DOHA**	Anthr.	Andros.
(Salt I)	m	2.16E+04	2.12E-02	2.76E-02	1.20E+00	-3.50E-01
	b	6.65E+04	3.36E-02	-2.03E-02	1.36E-01	2.68E-01
	r^2	0.97	0.98	0.99	0.73	0.98
	S_{x0}	2.9	2.1	1.3	9.8	2.0
	n	6	6	6	6	6
MF-Py-GCMS	ISTDpy	**Area**	Cholan.	**DOHA**	Anthr.	Andros.
(Salt II)	m	-1.08E+05	-1.13E-01	2.47E-02	2.77E+00	1.28E+00
	b	1.27E+05	7.44E-02	5.08E-02	7.19E-02	1.86E-01
	r^2	0.999	0.996	0.99	0.07	0.55
	S_{x0}	0.5	1.4	1.5	75.9	18.9
	n	4	4	4	4	4
MF-Py-GCMS	ISTDpy	Area	Cholan.	**DOHA**	TOHA	
(Sediment D)	m	3.32E+04	-1.74E-02	-2.67E-02	-8.32E-03	
	b	-4.69E+02	1.82E-02	1.29E-02	1.98E-02	
	r^2	-0.22	0.95	0.98	0.96	
	S_{x0}	70.0	5.2	3.4	4.6	
	n	7	7	7	7	
MF-Py-GCMS	ISTDpy	Area	Cholan.	DOHA	**TOHA**	
(Seawater)	m	-2.55E+05	1.45E-02	4.51E-02	-7.42E-02	
	b	1.15E+05	4.12E-02	3.53E-02	6.55E-02	
	r^2	0.99	0.99	0.999	0.9998	
	S_{x0}	1.5	1.6	0.5	0.3	
	n	4	4	4	4	

Anthr. = Anthracene-d^{10}; Andros. = Androstane; Cholan. = Cholanic acid methyl ester, DOHA = 9-dodecyl-1,2,3,4,5,6,7,8-Octahydro anthracene; TOHA = 9-Tetradecyl-1,2,3,4,5,6,7,8-octahydro anthracene. Bold $ISTD_{py}$ were used for quantification.

Table S5 b Calibration parameter PP

CP-Py-GCMS		**Area**				
	m	8.35E+04				
	b	7.07E+03				
	r^2	0.96				
	S_{x0}	32				
	n	17				
MF-Py-GCMS		**Area**				
(Sediment A & B)	m	1.07E+06				
	b	3.04E+05				
	r^2	0.99				
	S_{x0}	3.5				
	n	10				
MF-Py-GCMS	ISTDpy	Area			**Anthr.**	Andros.
(Sediment C)	m	1.83E+06			-3.75E-01	3.54E-01
	b	-8.58E+04			1.04E-01	3.21E-01
	r^2	0.88			0.95	0.42
	S_{x0}	2.7			0.6	12.9
	n	5			5.00	5.00
MF-Py-GCMS	ISTDpy	**Area**	Cholan.	**DOHA**	Anthr.	Andros.
(Salt I)	m	2.19E+05	1.77E-01	1.07E-01	5.56E+00	-8.64E-01
	b	2.57E+05	1.30E-01	-1.90E-02	5.28E-01	1.04E+00
	r^2	0.99	0.99	0.99	0.72	0.98
	S_{x0}	2.1	2.0	2.3	11.8	2.9
	n	6	6	6	6	6
MF-Py-GCMS	ISTDpy	**Area**	Cholan.	**DOHA**	Anthr.	Andros.
(Salt II)	m	3.55E+04	-1.07E-01	1.53E-01	4.53E+00	2.52E+00
	b	3.08E+05	1.79E-01	1.25E-01	3.17E-01	5.23E-01
	r^2	0.999	0.99	0.999	0.19	0.62
	S_{x0}	0.8	2.2	0.7	42.0	15.6
	n	5	5	5	5	5
MF-Py-GCMS	ISTDpy	Area	Cholan.	**DOHA**	TOHA	
(Sediment D)	m	6.86E+05	-1.37E-01	-3.33E-01	8.95E-02	
	b	-1.09E+04	2.95E-01	2.06E-01	3.20E-01	
	r^2	0.09	0.90	0.96	0.91	
	S_{x0}	54.0	5.5	3.2	5.2	
	n	7	7	7	7	
MF-Py-GCMS	ISTDpy	Area	Cholan.	DOHA	**TOHA**	
(Seawater)	m	-6.28E+05	-3.70E-02	-4.68E-02	-2.75E-01	
	b	3.73E+05	1.39E-01	1.23E-01	2.18E-01	
	r^2	0.99	0.99	0.996	0.996	
	S_{x0}	1.5	1.9	1.0	1.0	
	n	6	6	6	6	

Anthr. = Anthracene-d^{10}; Andros. = Androstane; Cholan. = Cholanic acid methyl ester, DOHA = 9-dodecyl-1,2,3,4,5,6,7,8-Octahydro anthracene; TOHA = 9-Tetradecyl-1,2,3,4,5,6,7,8-octahydro anthracene. Bold $ISTD_{py}$ were used for quantification.

Table S5 c Calibration parameter PET

CP-Py-GCMS		Area				
	m	2.99E+07				
	b	2.07E+06				
	r^2	0.9				
	S_{x0}	31				
	n	12				
MF-Py-GCMS		**Area**				
(Sediment A & B)	m	9.82E+05				
	b	2.08E+06				
	r^2	0.9671				
	S_{x0}	2.0				
	n	8				
MF-Py-GCMS	ISTDpy	Area			**Anthr.**	Andros.
(Sediment C)	m	2.49E+06			-2.13E+00	-7.68E-01
	b	-4.40E+04			6.58E-01	1.21E+00
	r^2	0.05112			0.97531	0.89557
	S_{x0}	49.0			1.8	3.2
	n	6.00			6.00	6.00
MF-Py-GCMS	ISTDpy	**Area**	Cholan.	**DOHA**	Anthr.	Andros.
(Salt I)	m	-2.43E+06	-8.03E-01	6.94E-01	6.27E+00	-4.01E+00
	b	2.08E+06	1.01E+00	-4.22E-01	5.47E+00	6.33E+00
	r^2	0.95	0.97	0.99	0.8	0.97
	S_{x0}	1.8	1.4	0.7	3.9	1.2
	n	6	6	6	6	6
MF-Py-GCMS	ISTDpy	**Area**	Cholan.	**DOHA**	Anthr.	Andros.
(Salt II)	m	1.64E+06	6.83E-01	9.60E-01	4.58E-01	2.33E+00
	b	1.65E+06	9.17E-01	6.92E-01	4.31E+00	4.34E+00
	r^2	0.98	0.99	0.97	0.38	0.59
	S_{x0}	1.2	0.8	1.5	10.3	6.7
	n	5	5	5	5	5
MF-Py-GCMS	ISTDpy	Area	Cholan.	**DOHA**	TOHA	
(Sediment D)	m	3.92E+05	-5.56E-01	-4.85E-01	-5.23E-01	
	b	-9.97E+03	4.35E-01	3.00E-01	4.88E-01	
	r^2	0.02	0.984	0.975	0.931	
	S_{x0}	39.6	0.8	1.0	1.7	
	n	6	6	6	6	
MF-Py-GCMS	ISTDpy	Area	Cholan.	DOHA	**TOHA**	
(Seawater)	m	2.89E+05	6.06E-01	3.71E-01	2.53E-01	
	b	1.51E+06	5.79E-01	5.29E-01	9.10E-01	
	r^2	0.998	0.93	0.95	0.98	
	S_{x0}	0.3	1.8	1.5	0.9	
	n	6	6	6	6	

Anthr. = Anthracene-d^{10}; Andros. = Androstane; Cholan. = Cholanic acid methyl ester, DOHA = 9-dodecyl-1,2,3,4,5,6,7,8-Octahydro anthracene; TOHA = 9-Tetradecyl-1,2,3,4,5,6,7,8-octahydro anthracene. Bold $ISTD_{py}$ were used for quantification.

Table S5 d Calibration parameter PS

CP-Py-GCMS		Area				
	m	-1.27E+05				
	b	3.61E+04				
	r^2	0.95				
	S_{x0}	46				
	n	18				
MF-Py-GCMS		Area				
(Sediment A & B)	m	-8.59E+06				
	b	1.45E+06				
	r^2	0.95115				
	S_{x0}	6.5				
	n	9				
MF-Py-GCMS	ISTDpy	Area			Anthr.	Andros.
(Sediment C)	m	-1.64E+05			-1.32E+00	-3.34E+00
	b	5.85E+04			6.49E-01	1.27E+00
	r^2	0.99			0.99985	0.99593
	S_{x0}	1.5			0.2	1.1
	n	4.00			4.00	4.00
MF-Py-GCMS	ISTDpy	**Area**	Cholan.	**DOHA**	Anthr.	Andros.
(Salt I)	m	-1.34E+05	-2.70E-01	-2.08E-01	4.88E+00	2.90E+00
	b	6.98E+05	4.13E-01	2.98E-01	5.71E-01	1.07E+00
	r^2	0.95	0.96	0.95	0.18	0.7
	S_{x0}	1.6	1.5	1.7	15.9	4.9
	n	8	8	8	8	8
MF-Py-GCMS	ISTDpy	**Area**	Cholan.	**DOHA**	Anthr.	Andros.
(Salt II)	m	2.61E+05	-1.17E-01	1.94E-01	3.83E+00	2.78E+00
	b	7.14E+05	3.65E-01	2.71E-01	4.64E-01	1.51E+00
	r^2	0.9468	0.89117	0.95364	0.17932	0.57313
	S_{x0}	2.0	2.9	1.8	17.8	7.2
	n	7	7	7	7	7
MF-Py-GCMS	ISTDpy	Area	Cholan.	**DOHA**	TOHA	
(Sediment D)	m	6.56E+05	-6.85E-01	-8.00E-01	-5.33E-01	
	b	-1.68E+04	7.14E-01	5.12E-01	7.77E-01	
	r^2	0.03	0.99	0.96	0.97	
	S_{x0}	43.1	0.8	1.6	1.4	
	n	6	6	6	6	
MF-Py-GCMS	ISTDpy	Area	**Cholan.**	DOHA	TOHA	
(Seawater)	m	5.24E+04	1.30E-01	1.13E-01	6.53E-02	
	b	4.04E+05	1.47E-01	1.30E-01	2.35E-01	
	r^2	0.96	0.98	0.95	0.97	
	S_{x0}	1.8	1.4	1.6	1.6	
	n	5	5	5	5	

Anthr. = Anthracene-d^{10}; Andros. = Androstane; Cholan. = Cholanic acid methyl ester, DOHA = 9-dodecyl-1,2,3,4,5,6,7,8-Octahydro anthracene; TOHA = 9-Tetradecyl-1,2,3,4,5,6,7,8-octahydro anthracene. Bold $ISTD_{py}$ were used for quantification.

Table S5 e Calibration parameter PVC

CP-Py-GCMS		Area				
	m	1.20E+06				
	b	2.55E+04				
	r^2	0.94				
	S_{x0}	92				
	n	29				
MF-Py-GCMS		Area				
(Sediment A & B)	m	-1.16E+06				
	b	2.44E+05				
	r^2	0.96548				
	S_{x0}	6.3				
	n	6				
MF-Py-GCMS	ISTDpy	Area			Anthr.	Andros.
(Sediment C)	m	1.01E+06			-7.31E-01	4.60E-01
	b	4.10E+03			2.37E-01	4.26E-01
	r^2	0.25997			0.99534	0.99987
	S_{x0}	61.1			2.5	0.4
	n	4.00			4.00	4.00
MF-Py-GCMS	ISTDpy	Area	Cholan.	DOHA	Anthr.	Andros.
(Salt I)	m	3.64E+05	2.07E-01	6.79E-03	4.57E+00	-5.90E-01
	b	1.78E+05	9.00E-02	7.56E-02	3.46E-01	7.40E-01
	r^2	0.88	0.92	0.98	0.6	0.98
	S_{x0}	6.7	5.5	2.6	14.9	2.6
	n	5	5	5	5	5
MF-Py-GCMS	ISTDpy	Area	Cholan.	DOHA	Anthr.	Andros.
(Salt II)	m	-5.11E+05	-5.44E-01	-2.23E-01	1.87E+00	1.71E+00
	b	2.45E+05	1.39E-01	9.85E-02	1.81E-01	4.08E-01
	r^2	0.98701	0.95799	0.98391	0.17725	0.61151
	S_{x0}	2.1	3.7	2.3	38.7	14.3
	n	7	7	7	7	7
MF-Py-GCMS	ISTDpy	Area	Cholan.	DOHA	**TOHA**	
(Sediment D)	m	3.52E+05	8.21E-02	3.15E-03	1.32E-01	
	b	-4.68E+03	8.96E-02	6.66E-02	9.62E-02	
	r^2	0.06	0.98	0.99	0.99	
	S_{x0}	78.0	2.8	2.0	1.5	
	n	5	5	5	5	
MF-Py-GCMS	ISTDpy	Area	Cholan.	DOHA	**TOHA**	
(Seawater)	m	7.60E+05	5.04E-01	3.91E-01	5.12E-01	
	b	1.53E+05	5.35E-02	4.86E-02	8.87E-02	
	r^2	0.97	0.79	0.82	0.91	
	S_{x0}	3.5	10.0	9.0	6.2	
	n	5	5	5	5	

Anthr. = Anthracene-d^{10}; Andros. = Androstane; Cholan. = Cholanic acid methyl ester, DOHA = 9-dodecyl-1,2,3,4,5,6,7,8-Octahydro anthracene; TOHA = 9-Tetradecyl-1,2,3,4,5,6,7,8-octahydro anthracene. Bold $ISTD_{py}$ were used for quantification.

Table S5 f Calibration parameter PC

CP-Py-GCMS		Area				
	m	1.24E+07				
	b	1.64E+06				
	r^2	0.95689				
	S_{x0}	8.0				
	n	14				
MF-Py-GCMS		Area				
(Sediment A & B)	m	4.08E+07				
	b	3.60E+06				
	r^2	0.93072				
	S_{x0}	9.4				
	n	6				
MF-Py-GCMS	ISTDpy	Area			Anthr.	Andros.
(Sediment C)	m	1.65E+07			-9.62E+01	-6.34E+01
	b	6.00E+05			1.11E+01	2.10E+01
	r^2	0.36269			0.95789	0.86122
	S_{x0}	30.51			4.80	9.20
	n	6.00			6.00	6.00
MF-Py-GCMS	ISTDpy	Area	Cholan.	DOHA	Anthr.	Andros.
(Salt I)	m	5.30E+06	2.67E+00	-3.32E+00	1.09E+01	-4.07E+01
	b	-4.52E+06	-1.83E+00	2.23E+00	2.89E+01	2.20E+01
	r^2	0.98	0.99	0.97	0.7	0.95
	S_{x0}	0.7	0.4	1.0	3.7	1.2
	n	5	5	5	5	5
MF-Py-GCMS	ISTDpy	Area	Cholan.	DOHA	Anthr.	Andros.
(Salt II)	m	-6.24E+05	-1.11E+00	5.91E-01	1.63E+01	8.28E+00
	b	3.53E+06	2.04E+00	1.42E+00	4.82E+00	6.68E+00
	r^2	0.99699	0.98632	0.97716	0.18812	0.53068
	S_{x0}	0.36	0.77	0.99	13.5	6.11
	n	5	5	5	5	5
MF-Py-GCMS	ISTDpy	Area	Cholan.	DOHA	TOHA	
(Sediment D)	m	1.38E+06	-3.01E+00	-1.58E+00	-4.84E+00	
	b	6.30E+05	3.29E+00	1.98E+00	4.50E+00	
	r^2	0.52	0.86	0.88	0.81	
	S_{x0}	3.6	1.48	1.4	1.8	
	n	5	5	5	5	
MF-Py-GCMS	ISTDpy	Area	Cholan.	**DOHA**	TOHA	
(Seawater)	m	-2.48E+06	6.74E-01	3.66E-01	-8.82E-01	
	b	5.47E+06	2.07E+00	1.84E+00	3.24E+00	
	r^2	0.99	0.97	0.96	0.99	
	S_{x0}	0.76	1.14	1.25	0.76	
	n	6	6	6	6	

Anthr. = Anthracene-d^{10}; Andros. = Androstane; Cholan. = Cholanic acid methyl ester, DOHA = 9-dodecyl-1,2,3,4,5,6,7,8-Octahydro anthracene; TOHA = 9-Tetradecyl-1,2,3,4,5,6,7,8-octahydro anthracene. Bold $ISTD_{py}$ were used for quantification.

Table S5 g Calibration parameter PMMA

CP-Py-GCMS		Area				
	m	3.96E+05				
	b	1.97E+05				
	r^2	0.9				
	S_{x0}	14				
	n	22				
MF-Py-GCMS		Area				
(Sediment A & B)	m	1.69E+06				
	b	7.09E+05				
	r^2	0.93459				
	S_{x0}	9.28				
	n	7				
MF-Py-GCMS	ISTDpy	Area			Anthr.	Andros.
(Sediment C)	m	3.08E+04			-2.11E+00	1.57E+01
	b	1.05E+05			1.22E+00	3.34E+00
	r^2	0.99824			0.99769	0.53836
	S_{x0}	1.25			1.40	27.50
	n	5.00			5.00	5.00
MF-Py-GCMS	ISTDpy	Area	Cholan.	DOHA	Anthr.	Andros.
(Salt I)	m	-1.37E+06	-7.13E-01	-7.74E-01	-1.17E+01	2.87E+00
	b	7.11E+05	3.65E-01	2.92E-01	3.86E+00	-8.70E+00
	r^2	0.97	0.97	0.92	0.53	0.92
	S_{x0}	1.2	1.3	2.3	7.3	2.4
	n	6	6	6	6	6
MF-Py-GCMS	ISTDpy	Area	Cholan.	DOHA	Anthr.	Andros.
(Salt II)	m	-1.74E+06	-1.07E+00	-4.71E-01	4.26E+00	6.08E-01
	b	6.06E+05	3.86E-01	2.40E-01	4.09E-01	8.92E-01
	r^2	0.9235	0.99976	0.92619	0.2298	0.8797
	S_{x0}	3.06	0.199	3	19.45	3.93
	n	5	5	5	5	5
MF-Py-GCMS	ISTDpy	Area	Cholan.	DOHA	TOHA	
(Sediment D)	m	1.24E+06	-7.59E+00	-4.36E+00	-8.49E+00	
	b	1.53E+03	2.14E+00	1.25E+00	2.49E+00	
	r^2	0.00	0.89	0.89	0.85	
	S_{x0}	478.8	1.94	1.89	2.3	
	n	5	5	5	5	
MF-Py-GCMS	ISTDpy	Area	Cholan.	**DOHA**	TOHA	
(Seawater)	m	-1.45E+06	-3.32E-01	-3.22E-01	-7.79E-01	
	b	9.51E+05	3.51E-01	3.09E-01	5.54E-01	
	r^2	0.99	0.99	0.998	0.996	
	S_{x0}	0.88	0.95	0.49	0.63	
	n	5	5	5	5	

Anthr. = Anthracene-d^{10}; Andros. = Androstane; Cholan. = Cholanic acid methyl ester, DOHA = 9-dodecyl-1,2,3,4,5,6,7,8-Octahydro anthracene; TOHA = 9-Tetradecyl-1,2,3,4,5,6,7,8-octahydro anthracene. Bold $ISTD_{py}$ were used for quantification.

Table S5 h Calibration parameter PA6

CP-Py-GCMS		Area				
	m	-5.03E+06				
	b	3.21E+05				
	r^2	0.86				
	S_{x0}	22.4				
	n	7				
MF-Py-GCMS	ISTDpy	Area			Anthr.	Andros.
(Sediment C)	m	1.32E+06			4.29E-02	2.20E+00
	b	1.28E+04			5.41E-02	2.10E-01
	r^2	0.00229			0.90371	0.21022
	S_{x0}	207.10			3.24	19.25
	n	5.00			5.00	5.00
MF-Py-GCMS	ISTDpy	Area	Cholan.	DOHA	Anthr.	Andros.
(Salt I)	m	-2.21E+05	-1.47E-02	-3.32E-01	7.80E+00	-4.52E+00
	b	3.87E+05	1.95E-01	1.65E-01	7.43E-01	1.61E+00
	r^2	0.99	0.99	0.99	0.8	0.98
	S_{x0}	2.1	1.0	1.9	9.1	2.7
	n					
MF-Py-GCMS	ISTDpy	Area	Cholan.	DOHA	Anthr.	Andros.
(Salt II)	m	-4.84E+05	-1.34E+00	-2.35E-01	8.43E+00	8.99E+00
	b	5.87E+05	3.51E-01	2.38E-01	3.81E-01	8.47E-01
	r^2	0.99676	0.96243	0.98517	0.10368	0.54054
	S_{x0}	1.03	3.58	2.23	53.33	16.72
	n	6	6	6	6	6
MF-Py-GCMS	ISTDpy	Area	Cholan.	DOHA	TOHA	
(Sediment D)	m	-6.65E+04	-5.23E-03	-1.84E-02	3.22E-02	
	b	1.64E+04	2.60E-02	1.82E-02	2.75E-02	
	r^2	0.34	0.97	0.96	0.87	
	S_{x0}	28.93	3.69	3.98	7.9	
	n	5	5	5	5	
MF-Py-GCMS	ISTDpy	Area	Cholan.	DOHA	TOHA	
(Seawater)	m	-7.76E+05	-4.16E-02	-3.35E-02	-3.20E-01	
	b	4.62E+05	1.72E-01	1.51E-01	2.69E-01	
	r^2	0.99	0.99	0.997	0.997	
	S_{x0}	1.65	1.94	1.22	1.26	
	n	6	6	6	6	

Anthr. = Anthracene-d^{10}; Andros. = Androstane; Cholan. = Cholanic acid methyl ester, DOHA = 9-dodecyl-1,2,3,4,5,6,7,8-Octahydro anthracene; TOHA = 9-Tetradecyl-1,2,3,4,5,6,7,8-octahydro anthracene. Bold $ISTD_{py}$ were used for quantification.

Table S5 i Calibration parameter PUR

MF-Py-GCMS	ISTDpy	Area			Anthr.	Andros.
(Sediment C)	m	3.84E+03			-1.79E-03	-4.84E-02
	b	1.88E+01			1.74E-03	9.84E-03
	r^2	0.61128			0.84908	0.77053
	S_{x0}	16.47			8.70	11.30
	n	4.00			4.00	4.00
MF-Py-GCMS	ISTDpy	Area	Cholan.	DOHA	Anthr.	Andros.
(Salt I)	m	2.05E+04	1.04E-02	8.69E-03	4.00E-02	-2.68E-01
	b	-2.49E+04	-1.02E-02	-2.17E-02	3.27E-01	8.50E-02
	r^2	0.96	0.98	0.96	0.72	0.95
	S_{x0}	3.2	2.4	3.3	10.1	3.8
	n	5	5	5	5	
MF-Py-GCMS	ISTDpy	**Area**	Cholan.	**DOHA**	Anthr.	Andros.
(Salt II)	m	-4.61E+04	-5.94E-02	1.12E-02	1.33E+00	7.00E-01
	b	6.08E+04	3.56E-02	2.44E-02	4.20E-02	9.17E-02
	r^2	0.9849	0.99328	0.97752	0.07484	0.46527
	S_{x0}	2.27	1.77	3.27	75.68	23.1
	n	4	4	4	4	4
MF-Py-GCMS	ISTDpy	**Area**	Cholan.	**DOHA**	TOHA	
(Sediment D)	m	9.11E+04	-9.59E-01	-7.77E-01	-9.65E-01	
	b	-1.44E+03	9.88E-02	7.33E-02	1.07E-01	
	r^2	0.09	0.98	0.97	0.97	
	S_{x0}	57.3	2.4	3	3.4.	
	n	4	4	4	4	
MF-Py-GCMS	ISTDpy	Area	Cholan.	DOHA	TOHA	
(Seawater)	m	2.31E+04	4.51E-02	5.27E-02	3.82E-02	
	b	2.37E+04	8.01E-03	6.84E-03	1.32E-02	
	r^2	0.92	0.85	0.84	0.91	
	S_{x0}	5.28	7.37	7.70	5.78	
	n	4	4	4	4	

Anthr. = Anthracene-d^{10}; Andros. = Androstane; Cholan. = Cholanic acid methyl ester, DOHA = 9-dodecyl-1,2,3,4,5,6,7,8-Octahydro anthracene; TOHA = 9-Tetradecyl-1,2,3,4,5,6,7,8-octahydro anthracene. Bold $ISTD_{py}$ were used for quantification.

Table S6 MP contents in the analysed samples

	PE	PP	PET	PS	PVC	PC	PMMA	PA6	PUR
	TOHA	TOHA	DOHA	-	TOHA	-	DOHA	-	-
seawater	4.3	1.9	1.4	<LOD	5.8	<LOD	5.8	<LOD	<LOD
	Area	Area	Area	-	Area	-	Area	-	-
seawater	5.1	2.3	1.8	<LOD	6.5	<LOD	5.9	<LOD	<LOD
	DOHA	DOHA	DOHA	DOHA	-	-	-	-	DOHA
salt I	2.0	19.6	0.7	<LOD	<LOD	<LOD	<LOD	<LOD	2.7
salt II	9.8	26.6	4.1	0.5	<LOD	<LOD	<LOD	<LOD	<LOD
	Area	Area	Area	Area	Area	Area	Area	Area	Area
salt I	1.7	19.8	1.3	<LOD	<LOD	<LOD	<LOD	<LOD	1.3
salt II	13.3	29.3	5.9	0.1	<LOD	<LOD	<LOD	<LOD	<LOD
	Area	Area	Area	Area	Area	Area	Area	Area	Area
sediment A	18.5	<LOD	14.5	7.4	<LOD	<LOD	13.1	<LOD	<LOD
sediment B	26.6	<LOD	5.0	19.3	10.7	<LOD	6.1	<LOD	<LOD
	Andros.	-	Anthr.	Anthr.	Anthr.	Andros.	Anthr.	-	-
sediment C	23.5	12.5	0.2	5.0	7.2	<LOD	<LOD	<LOD	<LOD
	DOHA	DOHA	DOHA	DOHA	DOHA	DOHA	DOHA	-	-
sediment D	29.9	11.5	11	13.2	80.9	0.9	19.5	<LOD	<LOD

Anthr. = Anthracene-d^{10}; Andros. = Androstane; Cholan. = Cholanic acid methyl ester, DOHA = 9-dodecyl-1,2,3,4,5,6,7,8-Octahydro anthracene; TOHA = 9-Tetradecyl-1,2,3,4,5,6,7,8-octahydro anthracene

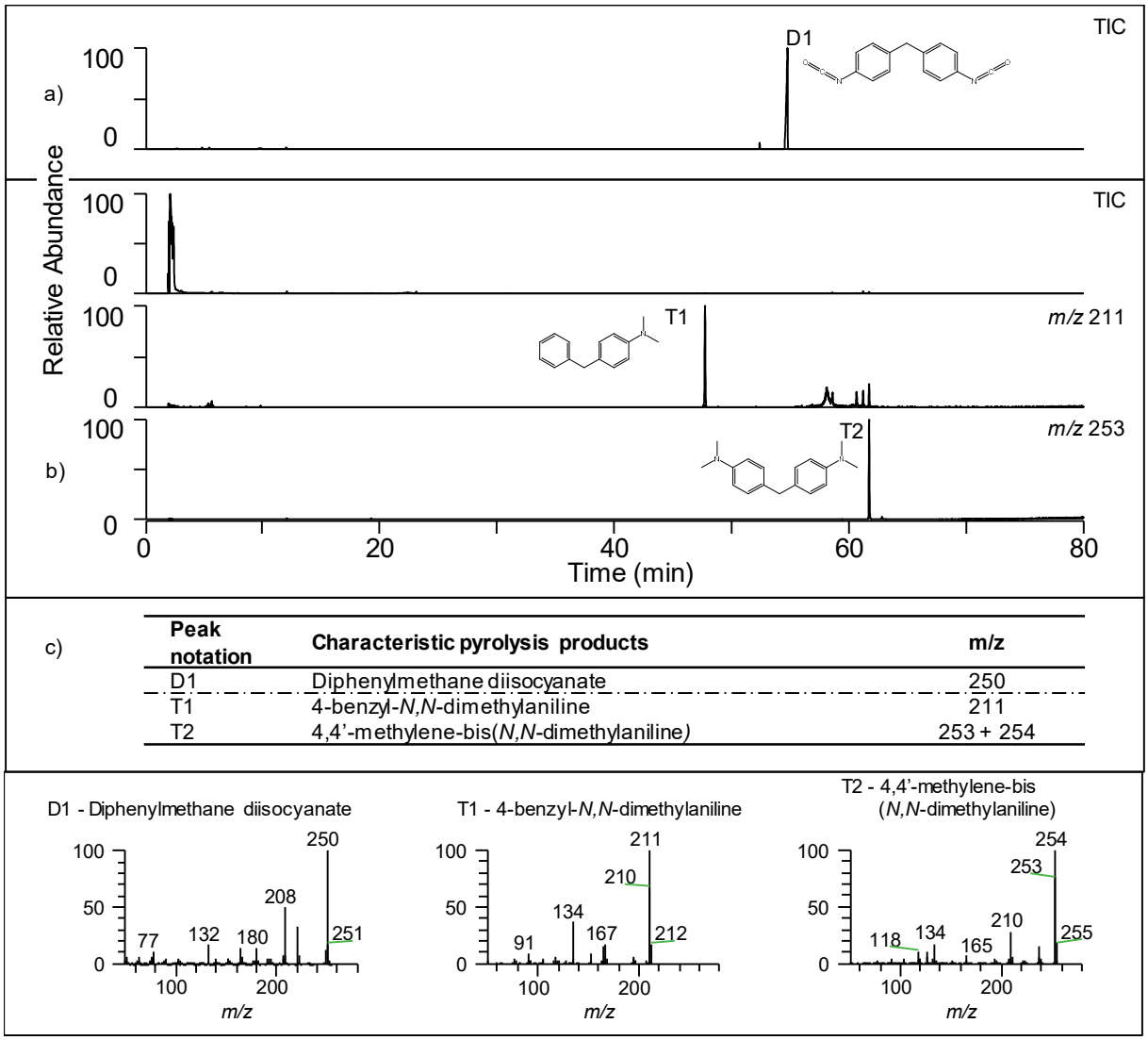

Figure S2 MDI-PUR; a) pyrogram (TIC) of direct pyrolysis and b) pyrogram (TIC and selected ion chromatograms) of thermochemolysis of selected indicator compounds; c) table of characteristic pyrolysis products with d) mass spectra of these products.

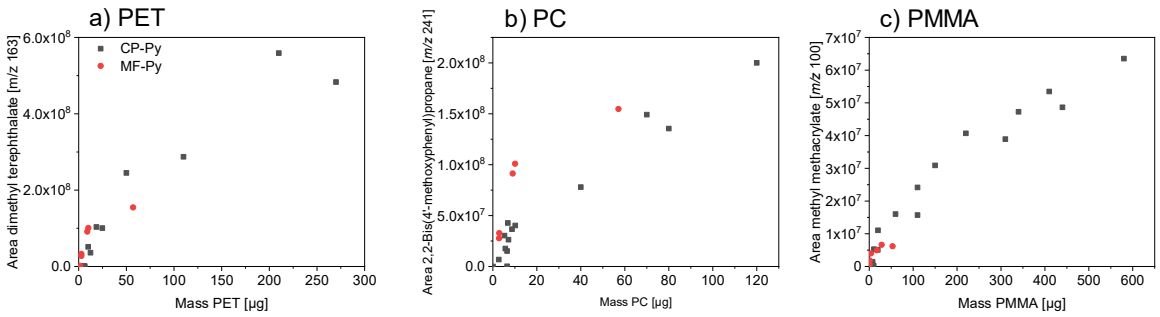

Figure S3 Examples of calibration curves of CP-PyGCMS (black squares) and MF-PyGCMS (red dots) with higher polymer amounts outside the linearity range

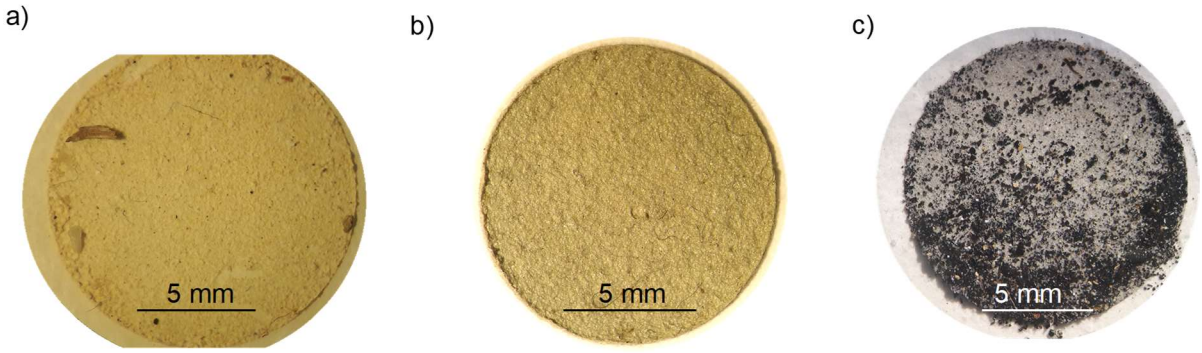

Figure S4 Preconcentrated samples on glass fibre filters: a) salt sample, b) seawater sample, c) sediment sample.

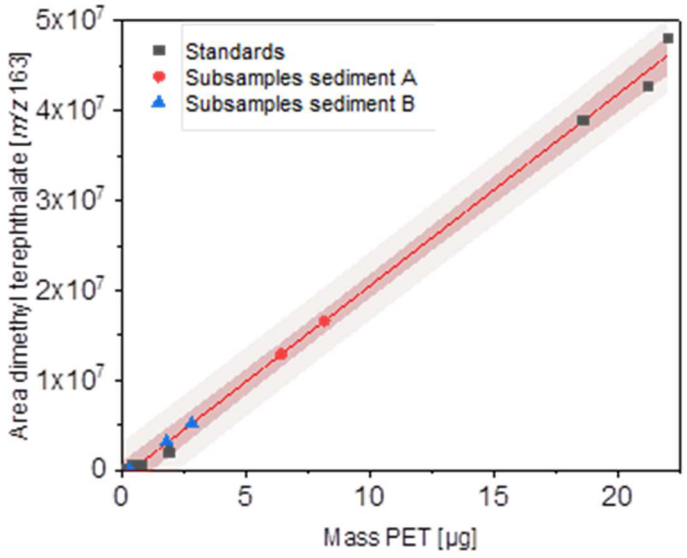

Figure S5 Example of calibration curve (PET) for evaluation of sediments without addition of $ISTD_{py}$, sediment sub-samples are visualized by red dots and blue triangles.

References

Reichenbächer, M., Einax, J.W., 2011. Challenges in Analytical Quality Assurance. Springer, Berlin Heidelberg. doi:DOI 10.1007/978-3-642-16595-5