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Closing the gap between small and smaller: Towards a framework to analyse nano- and microplastics in aqueous environmental samples

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Supporting Information

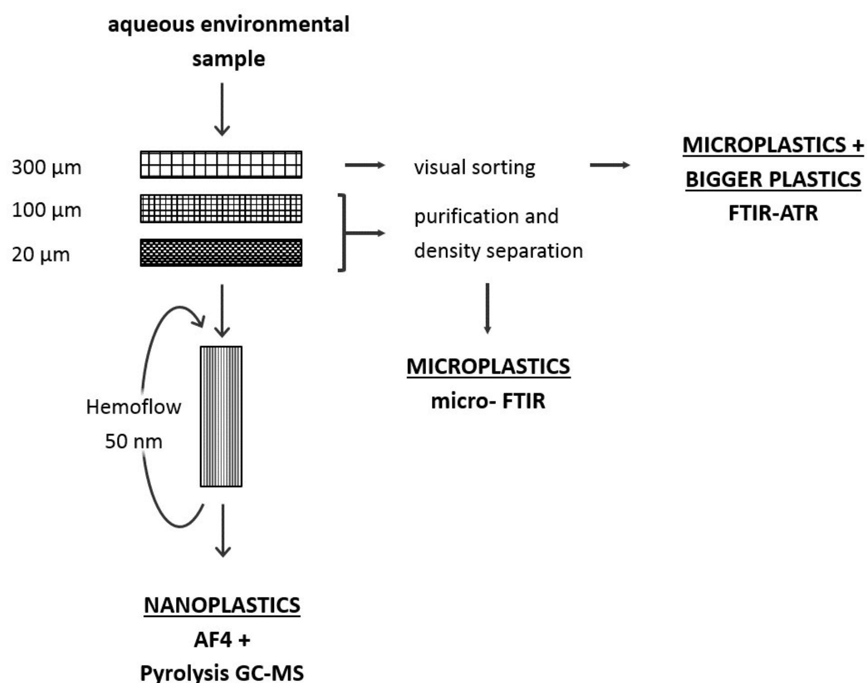


Figure S 1: Scheme of combined techniques to sample and analyse nano- and microplastics.

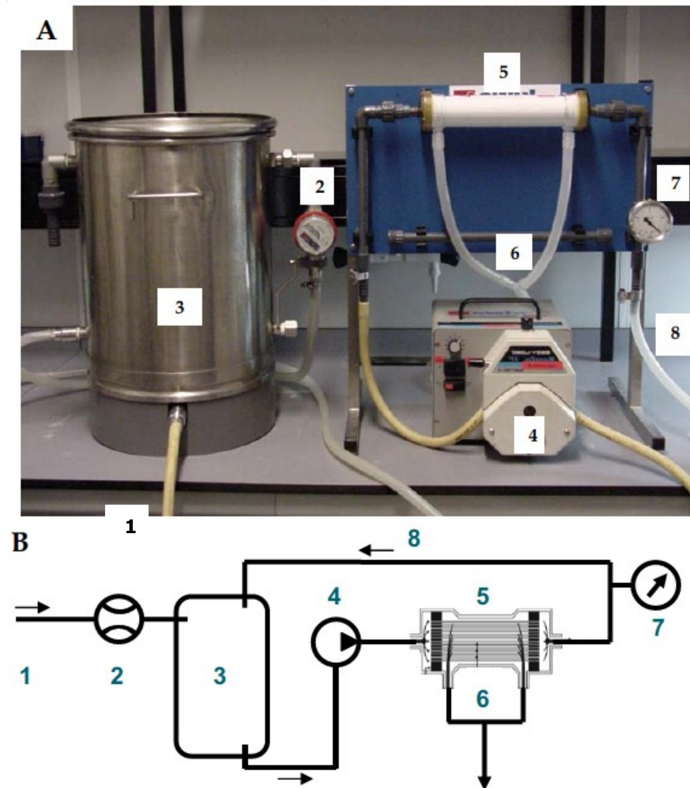


Figure S 2: Schematic presentation of the Hemoflow crossflow ultrafiltration. 1 = water inflow, 2 = water meter, 3 = tank with float valve, 4 = pump, 5 = Hemoflow filter, 6 = permeate, 7 = pressure gauge, 8 = concentrate, circulation back into (3) tank (Source: Veenendaal and Brouwer-Hanzens [1]).

Table S 1: Settings used at the AF4. For the separation of a NP mixture different crossflows were tested.

	Tested Settings (membrane & carrier liquid)	**Applied Settings**
Membrane	Reg. cellulose (RC) 10 kDa Polyethersulfone (PES) 10 kDa	RC
Carrier liquid	Milli-Q 0.01% SDS 0.01% TWEEN	0.01% SDS
Spacer thickness	250 µm	250 µm
Detector flow	1.0 ml min^{-1}	1.0 ml min^{-1}
Split flow	0 ml min^{-1}	0 ml min^{-1}
Cross flow	1.5 ml min^{-1} (0-11 min) 1.5-0 ml min^{-1} (11-50 min, exp. 0.2) 0 ml ml min^{-1} (50-65 min)	1 ml min^{-1} (0-8 min) 1-0 ml min^{-1} (8-28 min, exp. 0.2) 0 ml min^{-1} (28-33 min)
Focusing flow	2.3 ml min^{-1}	1.8 ml min^{-1}
Injection flow	0.2 ml min^{-1}	0.2 ml min^{-1}
Injection time	6 min	4 min
Injection volume	30 µl (monodispersed) (10 µl PS polydispersion)	50 µl

Table S 2: Settings to run the pyrolysis of the samples.

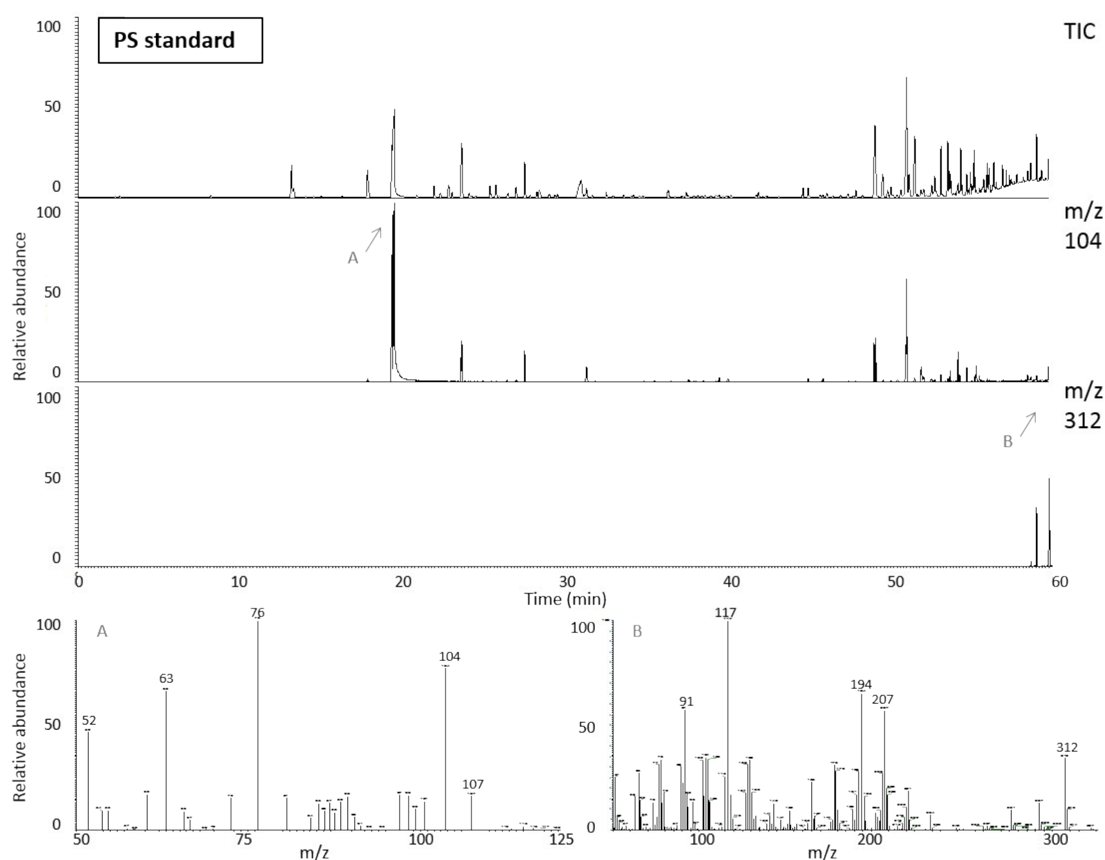
General timing:	
Clean time	20.0 s
Clean time #2	60.0 s
Delay time	0.0 min
Equilibration time	20.0 s
Standby Temperature	
Head temperature	150.0 °C
Offset AS	50.0 °C
Default Parameters	
Temperature	150.0 °C
Pyro Time	10.0 s
Table	single
Pyrolysis Cup	560 °C

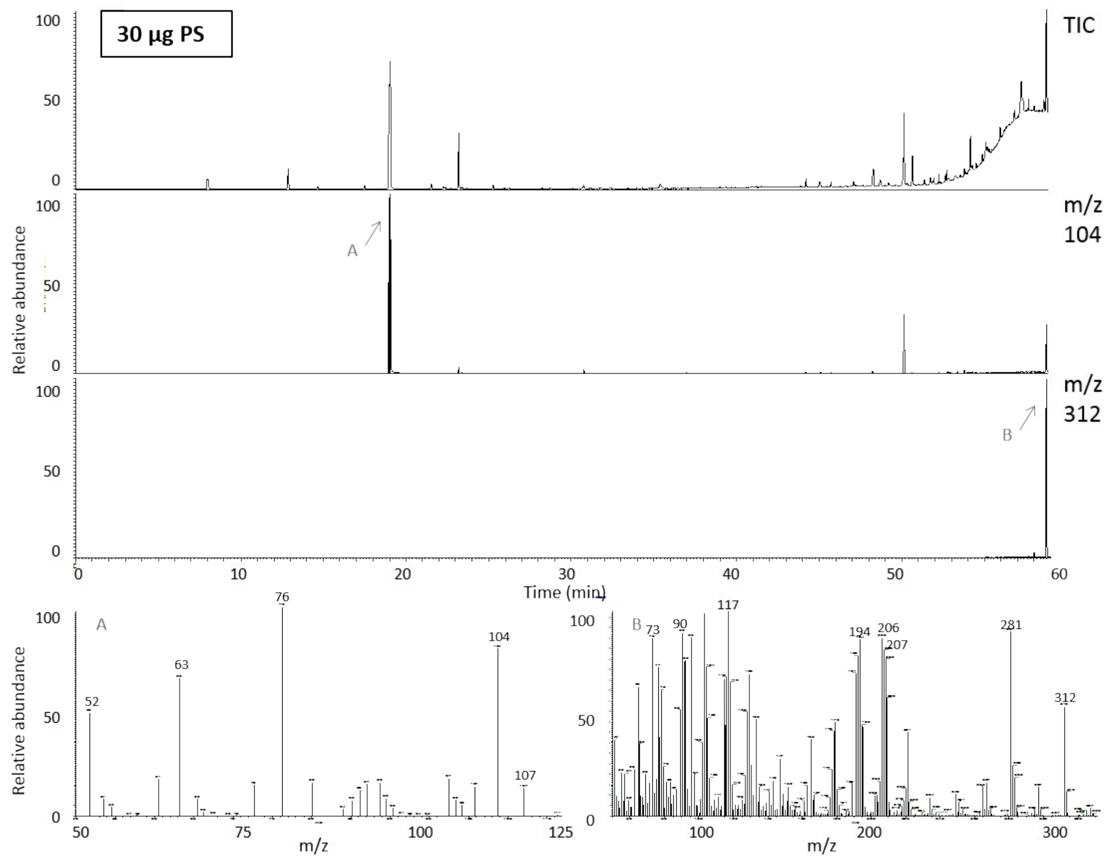
Table S 3: Settings to run the GC-MS.

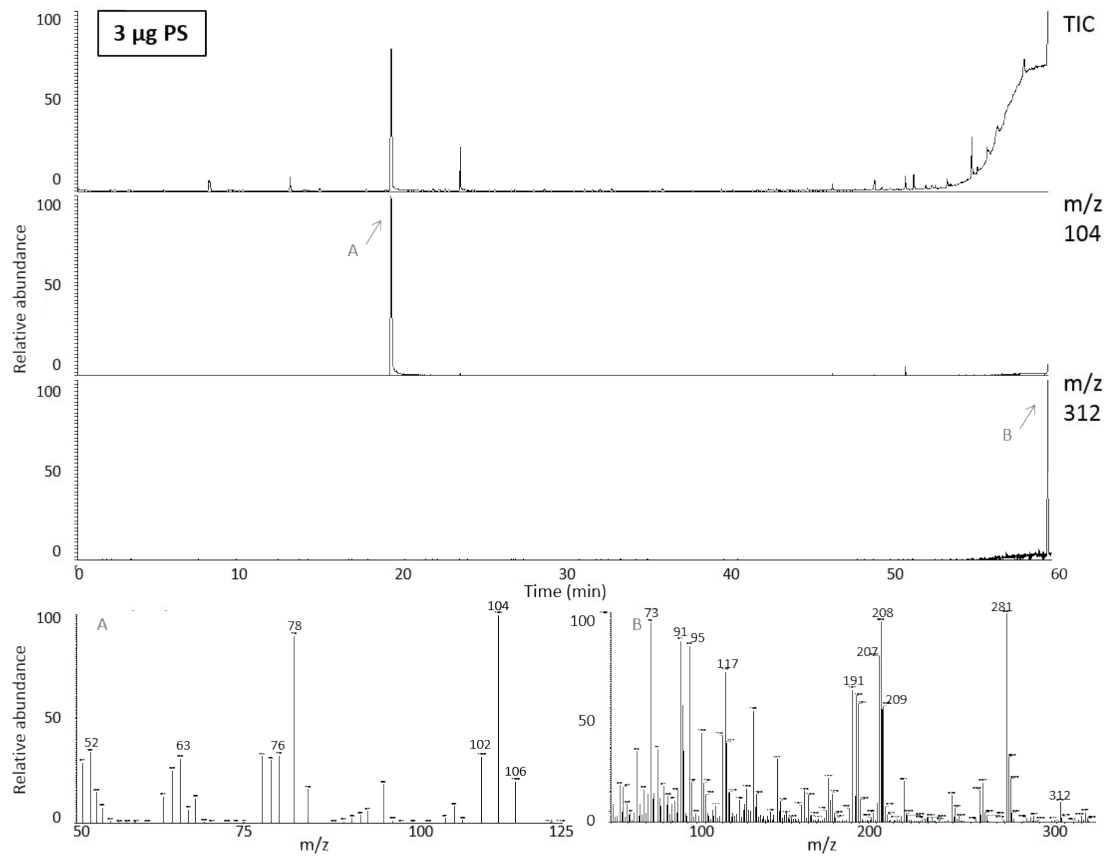
Oven	
Initial Temperature	40 °C
Initial Time	4.00 min
Number of Ramps	2
Rate #1	4.0 °C/min
Final Temperature #1	230 °C
Hold Time #1	0.00 min
Rate #2	20.0 °C/min
Final Temperature #2	325 °C
Hold Time #2	5.00 min
Maximum Temperature	350 °C
Prep Run Timeout	10.00 min
Equilibration Time	0.50 min
Inlet	
Mode	split
Base Temperature	200 °C
Split Flow	40 ml/min
Split ratio	10
Carrier	
Mode	Constant flow
Initial Value	4.00 ml/min
Detector	
Mode	Full scan
Mass Range	50 – 1000 amu
Time Range	0 – 59 min
Peak Format	Centriod
Scan Time	0.40 s
Multiplier	600 V
Ionisation Mode	EI+
Source Temperature	200 °C
Interface Temperature	280 °C

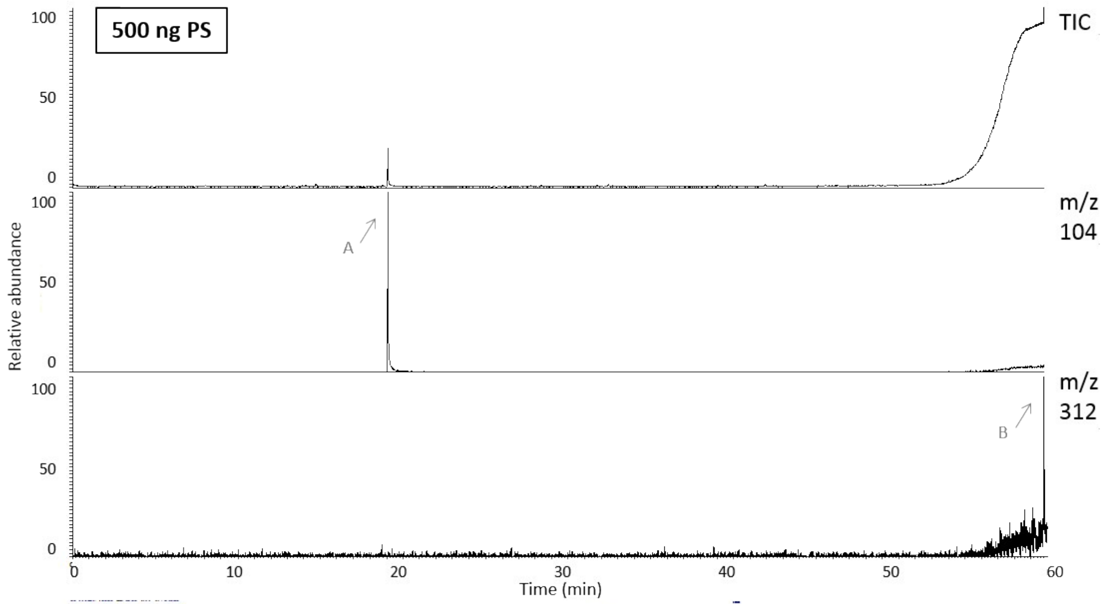
Table S 4: Separation efficiency for various AF4 membrane/ carrier liquid combinations. The fractionation of mono- and polydispersed solutions was concerned successful (marked with an “Y”) when resulting in clear distinct peaks.

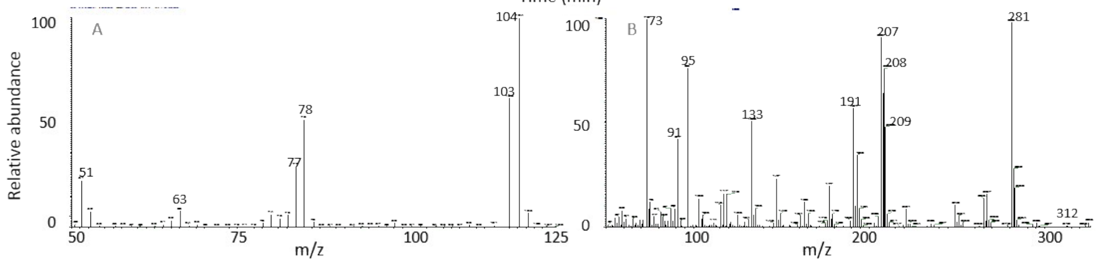
	50 nm	500 nm	fractionation of mixture
PES & Milli-Q	y	y	-
PES & SDS	-	-	-
PES & TWEEN	-	-	-
RC & Milli-Q	(y)	y	-
RC & SDS	y	y	y
RC & TWEEN	-	-	-

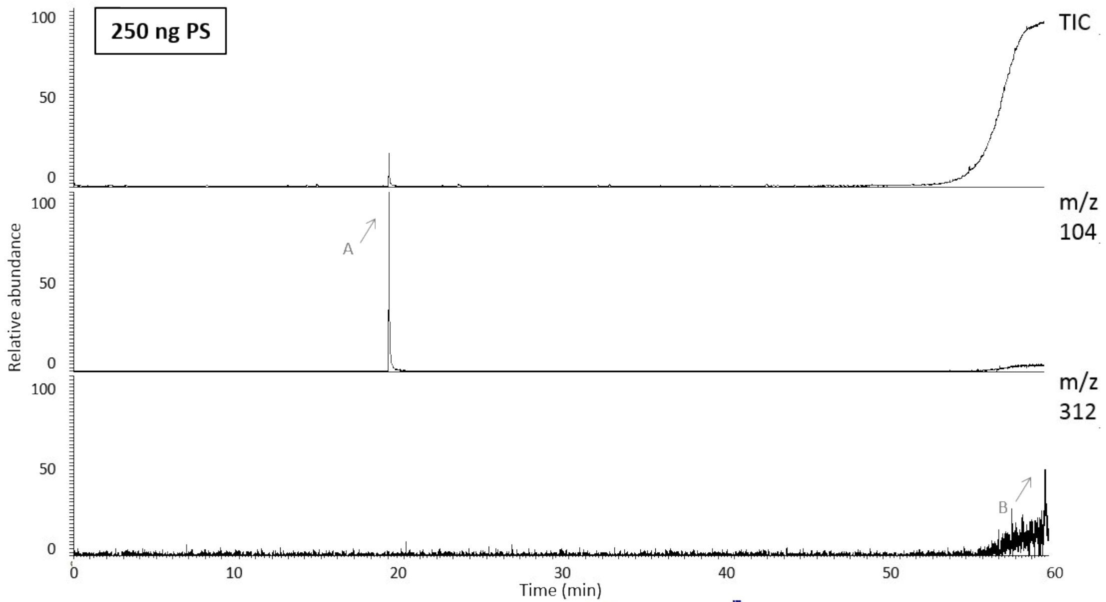


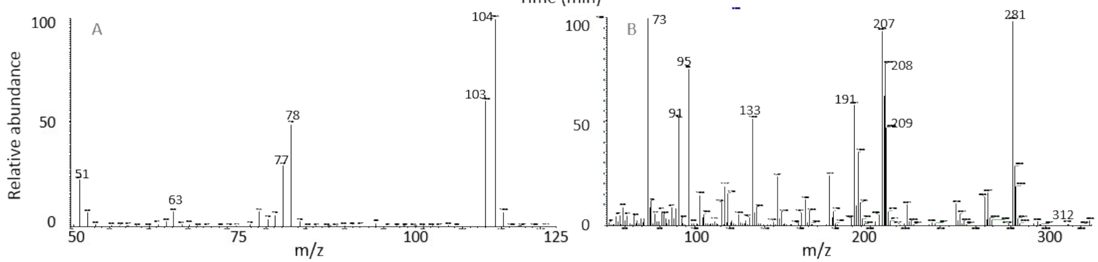

30 µg PS
TIC
m/z
104
m/z
312
A
B
Relative abundance
Time (min)
m/z
76
104
63
52
107
73
90
117
194
206
207
281
312

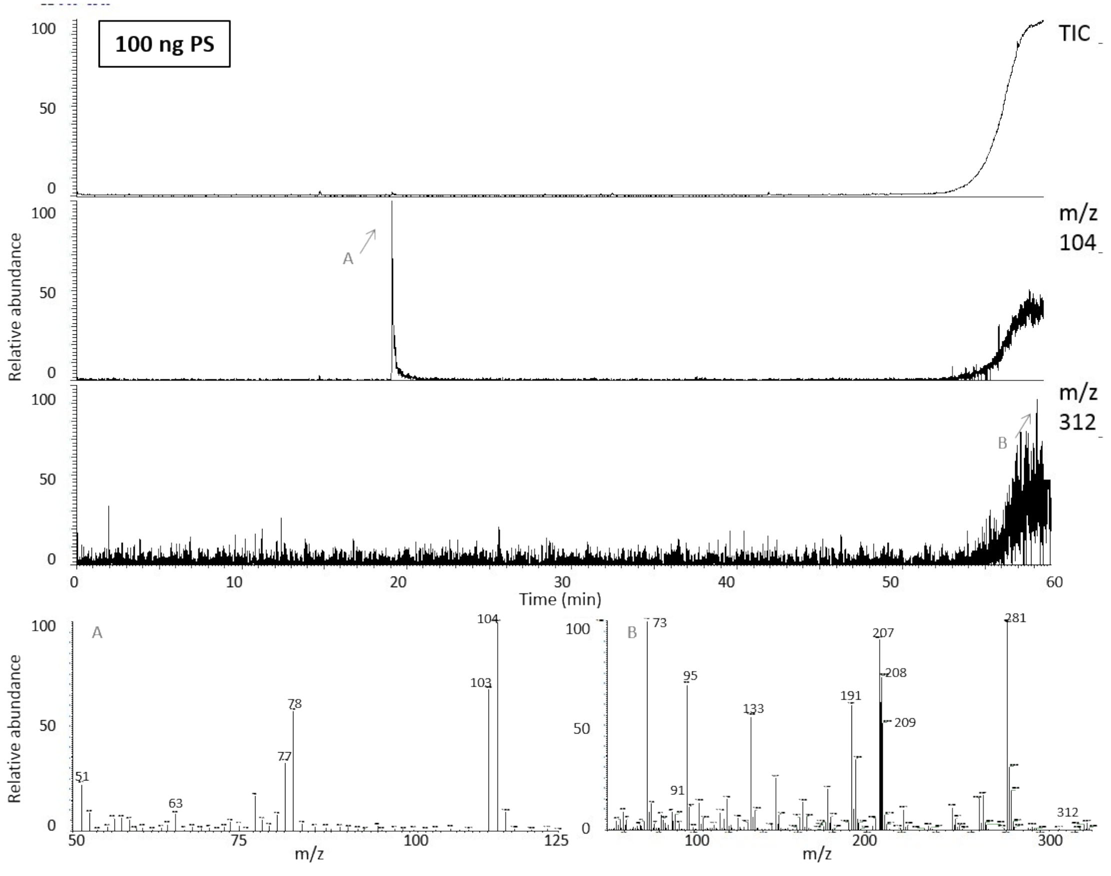

3 µg PS
TIC
m/z
104
m/z
312
A
B
Relative abundance
Time (min)
m/z
104
78
52
63
76
102
106
73
91
95
117
208
207
191
209
281
312

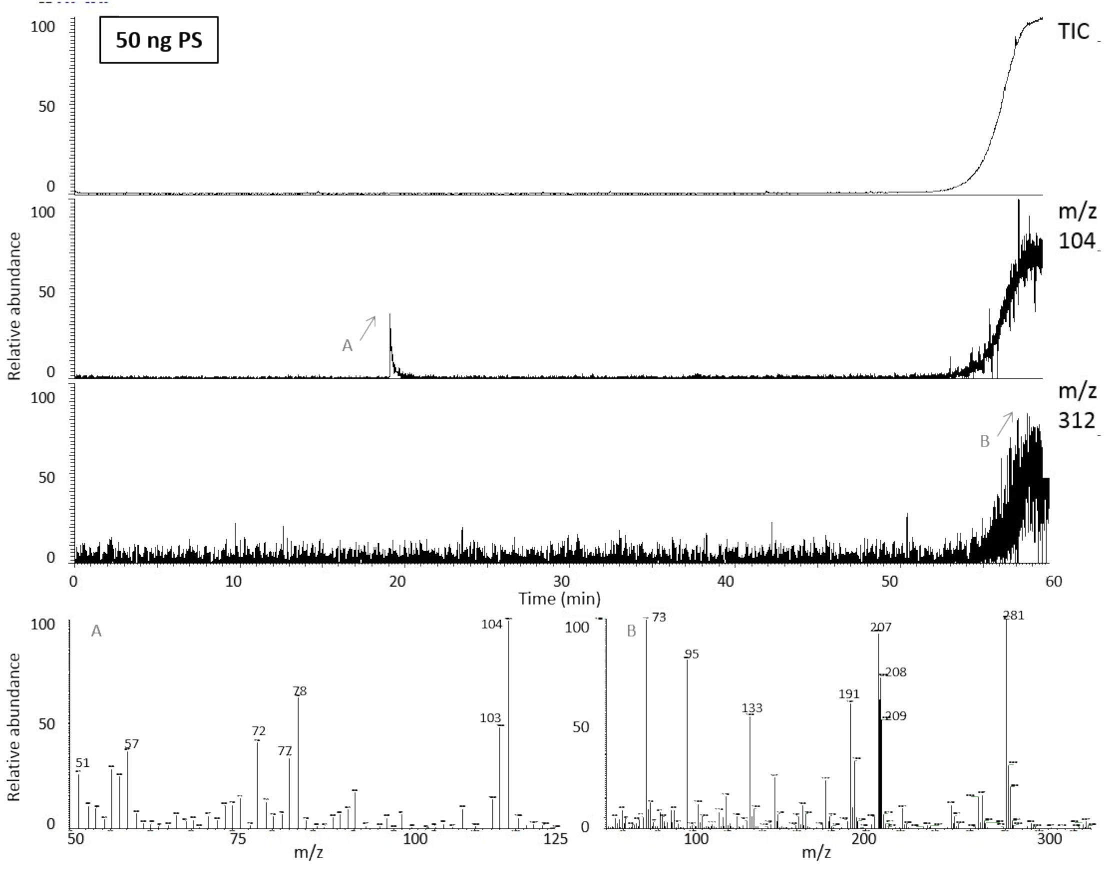

500 ng PS
TIC
m/z 104
m/z 312
Relative abundance
A
B
Time (min)


A
B
Relative abundance
m/z
104
103
78
77
51
63
73
95
91
133
191
207
208
209
281
312


250 ng PS
TIC
m/z 104
m/z 312
Relative abundance
A
B
Time (min)


A
B
Relative abundance
m/z
104
103
78
77
51
63
73
95
91
133
191
207
208
209
281
312


100 ng PS
TIC
m/z 104
m/z 312
Relative abundance
Time (min)
A
B
104
103
78
77
51
63
73
95
133
191
207
208
209
281
91
312
m/z


50 ng PS
TIC
m/z 104
m/z 312
Relative abundance
Time (min)
A
B
104
103
78
77
72
57
51
73
95
133
191
207
208
209
281
m/z

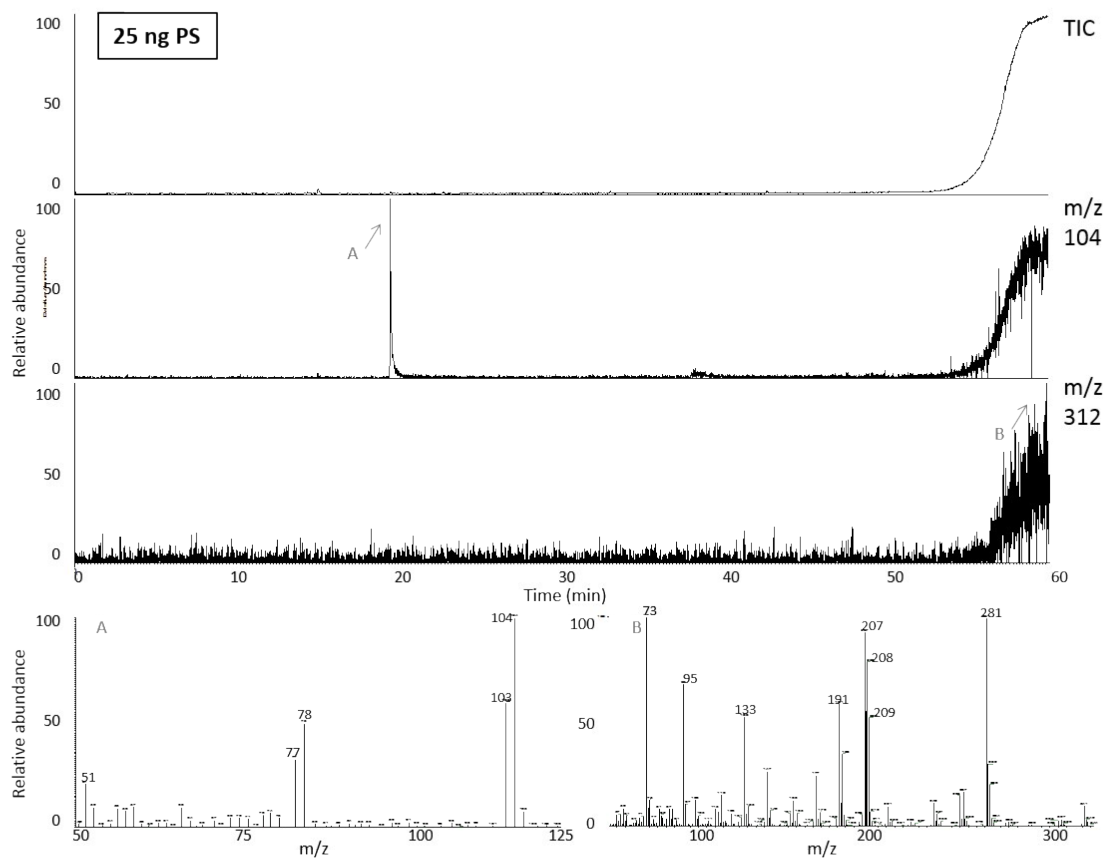


Figure S3: The pyrograms of a PS standard, and of PS (30 µg to 25 ng) that was added to surface water samples after analysis with Pyrolysis GC-MS. Each showing the total ion current (TIC), the chromatogram of selected masses (styrene m/z 104; tri-styrene m/z 312) and the mass spectra of selected peaks (A, B).

References

1. H. R. Veenendaal and A. J. Brouwer-Hanzens, *A method for the concentration of microbes in large volumes of water*, 2007.