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1	Electronic Supplementary Information
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3	Monitoring microplastic-contaminant sorption processes in real-time using
4	membrane introduction mass spectrometry
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17 Figure S1. Initial sorption kinetics of four aqueous contaminants onto 100 LDPE pellets as

18 determined by two different data treatments: A) converting the signal to concentration based on a

19 five-point, same-day calibration curve, and **B**) normalizing the signal by the initial signal and

20 multiplying the result by the known initial concentration, a one-point calibration curve. The initial

21 concentrations of the analytes were 0.4776  $\mu M$  naphthalene, 0.4687  $\mu M$  pyrene, 0.4716  $\mu M$ 

22 nonylphenol, and 0.1693  $\mu$ M anthracene.





Figure S2. Comparison of analyte depletion (light colours) and sorption to LDPE (dark colours) for pyrene and nonylphenol. A) and B) shows normalized sorption for both analytes, while C) and D) shows the natural logarithm of the normalized signal. The pseudo-first order rate constants associated with each type of experiment are given. Rate constants shown here are for a single replicate (n = 1), while rate constants in Table 1 are an average based on at least three replicates (n23).



Figure S3. The sorption rates of analytes at different concentrations onto 100 LDPE. (n = 1 per

- experiment)



40

Figure S4. Initial sorption kinetics  $(k'_{obs})$  onto 17 LDPE pellets of analytes undergoing solo

sorption and sorption in the presence of the other three contaminants. Experiments were performed

in triplicate, results shown as the average  $k'_{obs}$  with error bars showing the standard deviation. The

sorption rate constants for the different experimental treatments were statistically non-significant.





48 Figure S5. Linearized time dependent sorption onto 100 LDPE pellets for A) anthracene B)

49 nonylphenol C) pyrene and D) naphthalene at different concentrations (0.09  $\mu$ M light shade, 0.2  $\mu$ M

50 medium shade, 0.5  $\mu$ M dark shade). (*n* = 1 per experiment)

51





56 **Figure S6.** Initial sorption of analytes onto 50, 100, and 150 LDPE pellets. (n = 1 per experiment) 57





Figure S7. Comparison of analyte depletion for four analytes at the same initial concentration in the
 40 mL vials used in long-term sorption experiments (dark colours) and the 250 mL vials used in

40 mL vials used in long-term sorption experiments (dark colours) and the 250 mL short-term sorption experiments (light colours) (n = 1 for each type of experiment).





65 Figure S8. The relationship between the rate constants (k'<sub>obs</sub>) of naphthalene, anthracene, and

66 pyrene adsorbing onto LDPE, HDPE, PS, and PP and contaminant hydrophobicity ( $K_{ow}$ ).

67



68

69 Figure S9. Comparison of nonylphenol (blue) and pyrene (yellow) sorption on non-aged (dark

shade) and aged (light shade) LDPE. The observed rate constants  $(k'_{obs})$  are included next to the sorption trace.



75 Figure S10. ATR-FTIR spectra of (top, red) UV-C aged ( $\lambda_{max}$  254 nm, 8 days long), (bottom, blue)

76 UV-B aged ( $\lambda_{max}$  313 nm, 5.5 months long), and (black) pristine non-aged low-density polyethylene

77 used in long-term sorption experiments. Spectra were taken with a Nicolet iS5 FT-IR Spectrometer

78 with a Diamond crystal iD5 ATR accessory (Thermo Fisher Scientific, Madison, WI, USA). Using

79 OMNIC 9.2.86 software, 16 scans were taken per measurement with a data spacing of 0.060 cm<sup>-1</sup>.



83 Figure S11. Photographs of LDPE pellets which were A) pristine B) aged beneath UV-C light for 8

84 days, and C) aged beneath UV-B light for 5.5 months. All pellets were stirred in solution for 21

85 days. Panel D shows all four pristine plastic nurdles (LDPE, HDPE, PP, and PS).

87 Table S1: Properties of plastic pellets

Plastic Type	Approximate Shape	Diameter (cm) <sup>†</sup> $x \pm s$	Weight $(g)^{\dagger}$ x = s	Estimated Surface Area (cm <sup>2</sup> )	Estimated Density (g/mL) $x \pm s$
Low-Density Polyethylene	Sphere	$0.41\pm0.18$	$0.03245 \pm 0.002$	0.54	$0.927\pm0.009$
High-Density Polyethylene	Half-sphere	$\begin{array}{c} 0.38 \pm 0.11 \\ 0.17 \pm 0.047 \end{array}$	$0.01394 \pm 0.0006$	0.16	$0.94\pm0.01$
Polypropylene	Sphere	$0.38\pm0.010$	$0.02451 \pm 0.0002$	0.42	$0.87\pm0.01$
Polystyrene	Sphere	$0.38\pm0.17$	$0.03288 \pm 0.0003$	0.45	$1.049\pm0.001$

88  $\dagger$  n = 10 diameter, n = 3 weight, n = 3 density. Dimensions measured with a dial caliper (0.1 mm,

89 Westward, Switzerland).

90 <sup>††</sup> density calculated gravimetrically by displacement of water. Manufacturer provided densities

91 were 0.925 g/mL (0.9215–0.9255) for LDPE, and 0.9 g/mL for PP.

92

## 93 Table S2: Experiment details

<b>I</b>					
	250 mL Shor	t-Term Experiment <sup>†</sup>	40 mL Long-Term Experiment <sup>†</sup>		
Plastic Type	Pellets Used	Surface Area per Volume (cm <sup>2</sup> /mL) <sup>§</sup>	Pellets Used	Surface Area per Volume (cm <sup>2</sup> /mL) <sup>§</sup>	
Low-Density Polyethylene	100	0.233	17	0.234	
Polypropylene	127	0.232	22	0.237	
Polystyrene	120	0.233	21	0.241	
High-Density Polyethylene	170	0.233	28	0.226	

<sup>94</sup> <sup>†</sup> Solution volume in short and long-term experiments was 230 mL and 39 mL, respectively

95 § e.g., 17 LDPE pellets and 39 mL of solution provided in an estimated 0.234 cm<sup>2</sup>/mL surface area

96 per solution volume ratio, compared to a  $0.233 \text{ cm}^2/\text{mL}$  ratio in the short-term experiment where

97 100 LDPE pellets were added to 230 mL of solution. This plastic/volume ratio was chosen based on

98 the kinetic sorption experiments for LDPE.

Mass Spectrometer	Agilent Technologies 7010B GC/MS Triple Ouad <sup>†</sup>	Agilent Technologies 597: Inert Mass Selective Detector <sup>†</sup>
Gas Chromatograph <sup>§§</sup>	Agilent Technologies 7890B GC System <sup>†</sup>	Agilent Technologies 6890N Network GC System <sup>†</sup>
Ion Source	High efficiency axial CI ion source <sup>†</sup>	EI inert 350 ion source <sup>†</sup>
Filament	Part number G3850- 60021, utilizing a single coiled filament and the extractor plate removed <sup>†</sup>	Part number G7005- 60061 <sup>†</sup>
Solvent Pump	Agilent 1100 series HPLC pump system <sup>†</sup>	Agilent 1100 series HPLC pump system <sup>†</sup>
Helium Flow (mL/min)	0.5	1.0
Transfer Line Heater Temperature (°C)	400	350
Source Temperature (°C)	200	280
Quadrupole Temperature (°C)	Q1: 150, Q2: 150	150
Emission/Filament Current (µA)	50.0	34.6
Insertion Depth into Brass Nut (mm)	3	3
Capillary Liner Insertion Depth into Ion Source (mm)	2	2
Normal Operating Pressure (Torr)	1.40×10-4	1.40×10 <sup>-4</sup>
Ionization Energy (eV)	70	70
Dwell Time (ms)	250††	200
MS Mode	Multiple Reaction Monitoring (MRM)	Selective Ion Monitoring (SIM)
	<b>-</b> · · · /	

100 Table S3: Operational parameters for mass spectrometer
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101 § For additional instrumental details see Vandergrift 2019.<sup>1</sup>

<sup>102</sup> <sup>†</sup>Agilent Technologies Inc.; Santa Clara, CA, USA.
<sup>103</sup> <sup>§§</sup> Used to introduce helium (99.999% purity, Praxair, Mississauga, ON, Canada) to and heat the

104 LEI/CI interface

105 <sup>††</sup> Resolution of MS 1 and MS 2 set to 'wide'

107 Table S4: Tandem mass spectrometry and analytical calibration data for the triple quad MS used
 108 for short-term sorption monitoring experiments <sup>†</sup>

Analyte	Precursor Ion → Product Ion <sup>#</sup> ( <i>m/z</i> )	Collision Energy (eV)	Slope (µg/L)	R <sup>2</sup>	Concen Rar (µg,	tration 1ge /L)	Detection Limit (µg/L) <sup>§</sup>
NAD	$129 \rightarrow 102$	45	11.80	0.9845	10.06	58 61	1.0
	$129 \rightarrow 128$	33	40.11	0.9828	10.90	56.04	0.49
ANT	$179 \rightarrow 152$	50	18.53	0.9359	15.41	27.51	0.52
ANI	$179 \rightarrow 178$	37	81.85	0.9380		57.51	0.21
DVD	$203 \rightarrow 152$	60	2.334	0.9861	17.54	00.00	2.1
PIK	$203 \rightarrow 202$	37	116.5	0.9859	17.34	99.90	0.40
NON	$221 \rightarrow 85$	5	0.6722	0.9721	10.00	06.28	7.4
INUIN	$221 \rightarrow 71$	5	1.210	0.9735	19.90	90.28	5.2

109 <sup>†</sup> 4 point calibration curve based on a multi-component solution in deionized water. 250 mL bottle,

110 stirring at the 300 RPM on a CORNING PC-351 Hot Plate Stirrer.

111 § Detection Limit =  $3 \times$  standard deviation of blanks / calibration curve slope

112 <sup>#</sup> Molecular fragmentations depicted in bold were used here although no difference in the rate

113 constants were observed using either transition.

114

115 **Table S5:** Single quadrupole mass spectrometry and analytical calibration data for single quad MS

116 used for long-term experiments †

Analyte	Selected Ion Monitoring ( <i>m/z</i> )	Slope (µg/L)	R <sup>2</sup>	Concen Ran (µg/	tration Ige (L)	Detection Limit (µg/L)§
NAP	128	0.7902	0.9960	18.80	63.84	3.7
ANT	178	0.8784	0.9934	9.234	31.35	2.9
PYR	202	0.8978	0.9935	28.87	98.03	2.5
NON	107	0.1723	0.9935	31.44	106.7	19

117 <sup>†</sup> 5 point calibration curve based on a multi-component solution in deionized water. 40 mL vial,

118 stirring at 500 RPM on Fisherbrand<sup>™</sup> Ultra Thin Magnetic Stirrer (Fisher Scientific Cat #14-955-

119 150). Long-term adsorption rates were stirred off line at 500 RPM on CORNING PC-351 Hot Plate

120 Stirrer and Fisher Thermix<sup>®</sup> Stirring Hot Plate Model 210T stir plates.

121 § Detection Limit =  $3 \times$  standard deviation of blanks / calibration curve slope

0.1711 $\mu$ MChemicalNaphthaleneSorbate129.0 $\rightarrow$ 102.0 m/z		$\begin{array}{c} 0.1730 \ \mu M\\ \text{Anthracene}\\ 179.0 \rightarrow 152.0 \ m/z \end{array}$		$\begin{array}{c} 0.1735 \ \mu\text{M} \\ \text{Pyrene} \\ 203.0 \rightarrow 152.0 \ \text{m/z} \end{array}$			$0.1806 \ \mu M$ Nonylphenol $221.0 \rightarrow 71.0 \ m/z$						
Plastic Sorbent	n	Slope h <sup>-1</sup>	Sorption Rate µM h <sup>-1</sup>	RSD	Slope h <sup>-1</sup>	Sorption Rate µM h <sup>-1</sup>	RSD	Slope h <sup>-1</sup>	Sorption Rate µM h <sup>-1</sup>	RSD	Slope h <sup>-1</sup>	Sorption Rate µM h <sup>-1</sup>	RSD
LDPE	4	-0.96	0.16	3	-2.0	0.35	3	-2.2	0.38	4	-0.29	0.05	6
UV-C wLDPE	3	-0.98	0.17	10	-2.2	0.38	10	-2.2	0.38	22	-1.2	0.21	21
HDPE	3	-0.65	0.11	5	-1.7	0.29	9	-1.8	0.30	11	-0.19	0.03	7
PS	3	-0.35	0.06	5	-0.64	0.11	11	-1.0	0.18	10	-0.36	0.07	7
PP	3	-0.57	0.10	13	-0.61	0.11	15	-0.72	0.13	22	-0.61	0.11	30

## 124 Table S6: Observed initial sorption rates (µM h<sup>-1</sup>) over the first 10 min

**Table S7:** Observed pseudo-first order rate constants  $k'_{obs}$  (h<sup>-1</sup>)

						005 ( )				
Chemical Sorbate		$0.1711 \ \mu M$ Naphthalene $129.0 \rightarrow 102.0 \ m/z$		$0.1730 \mu M$ Anthracene $179.0 \rightarrow 152.0 m/z$		$\begin{array}{c} 0.1735 \ \mu\text{M} \\ \text{Pyrene} \\ 203.0 \rightarrow 152.0 \ m/z \end{array}$		$0.1806 \ \mu M$ Nonylphenol $221.0 \rightarrow 71.0 \ m/z$		
	Plastic Sorbent	n	Rate Constants (h <sup>-1</sup> )	RSD	Rate Constants (h <sup>-1</sup> )	RSD	Rate Constants (h <sup>-1</sup> )	RSD	Rate Constants (h <sup>-1</sup> )	RSD
	Analyte Depletion $(k_{loss})$	3	0.23	29	0.22	38	0.21	36	0.13	69
	LDPE $(k_{obs})$	4	0.69	19	2.2	10	2.4	11	0.25	84
	UV-C wLDPE (k <sub>obs</sub> )	3	0.73	11	2.3	10	2.5	10	1.1	23
	HDPE $(k_{obs})$	3	0.52	16	1.8	14	1.8	13	0.12	65
	$PS(k_{obs})$	3	0.32	21	0.56	7	0.62	2	0.26	26
	$PP(k_{obs})$	3	0.36	12	0.48	8	0.45	14	0.10	150

Expe	eriment	Percent of Analyte Sorbed to Pellets (%)						
Dl.	D. L'	0.4776 μM	0.1693 μM	0.4687 μM	0.4716 µM			
Plastic	Replicates	Naphthalene	Anthracene	Pyrene	Nonylphenol			
Type	(n)	$x \pm s$	$x \pm s$	$x \pm s$	$x \pm s$			
LDPE	8	$87 \pm 4$	99 ± 1	$100 \pm 1$	81 ± 5			
UV-C	2	<u> 20 ⊥ 1</u>	$08 \pm 2$	$100 \pm 1$	05 + 5			
wLDPE	5	$89 \pm 1$	98 ± 2	$100 \pm 1$	$95 \pm 5$			
HDPE	4	$73 \pm 5$	$96 \pm 2$	$99 \pm 1$	$60 \pm 8$			
PP	3	$56 \pm 9$	$88 \pm 1$	$92 \pm 1$	$39 \pm 3$			
PS	3	$69 \pm 14$	$95 \pm 2$	$95 \pm 3$	$87\pm8$			

Table S8: Extent of chemical sorption to microplastics after three weeks <sup>†</sup>

129 <sup>†</sup> Results represented as the mean and standard deviation of replicate experiments.

130

128

131 **Table S9:** Kinetic limit of analytes using the 8.0 cm membrane CP-MIMS J-Probe<sup>†</sup>

Analyte	Kinetic Limit (min <sup>-1</sup> ) $x^{\pm} s$	Kinetic Limit (h <sup>-1</sup> ) $x \pm s$
Nonylphenol	$0.65\pm0.11$	$39\pm 6$
Naphthalene	$1.27\pm0.05$	$76 \pm 3$
Anthracene	$0.96\pm0.20$	$58\pm12$
Pyrene	$1.03\pm0.04$	$62 \pm 3$

132 TBased on the natural rise time in response to a step function increase in aqueous concentration

133 (*n*=4). The kinetic limit was determined from the slope of the plot of  $\ln(1-S_t/S_{\infty})$  between  $S_t/S_{\infty} =$ 

134 0.1 to 0.9, where  $S_t$  and  $S_{\infty}$  are the MS signals at time t and at steady-state, respectively.<sup>2</sup>

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