Adsorption of contaminants of emerging concern (CECs) on macro- and microplastic polyvinyl chloride, polyethylene, and polystyrene: kinetics and potential mechanisms

Linda Y. Tseng [1,2,*], ChanJu You [2], Cecilia Vu [1], Matthew K. Chistolini [3], Catherine Y. Wang [1], Kristen Mast [2,4],
Florence Luo [5], Pitiporn Asvapathanagul [6], Phillip B. Gedalanga [7], Anna Laura Eusebi [8], Stefania Gorbi [9],
Lucia Pittura [9] and Francesco Fatone [8]

1 Environmental Studies Program, Colgate University, Hamilton, NY 13346, USA; cvu@colgate.edu (C.V.); cwang@colgate.edu (C.Y.W.)
2 Department of Physics and Astronomy, Colgate University, Hamilton, NY 13346, USA; cy-ou1@colgate.edu (C.Y.); kmast@colgate.edu (K.M.)
3 Department of Mathematics, Colgate University, Hamilton, NY 13346, USA; mchistolini@colgate.edu
4 Department of Chemistry, Colgate University, Hamilton, NY 13346, USA
5 Department of Psychological and Brain Science, Colgate University, Hamilton, NY 13346, USA; fluo@colgate.edu
6 Department of Civil Engineering and Construction Engineering Management, California State University, Long Beach, CA 90840, USA; pitiporn.asvapathanagul@csulb.edu
7 Department of Public Health, California State University, Fullerton, CA 92834, USA; pgedalanga@exchange.fullerton.edu
8 Department of Science and Engineering of Materials, Environment and Urban Planning-SIMAU,
Marche Polytechnic University, 60131 Ancona, Italy; a.l.eusebi@staff.univpm.it (A.L.E.); f.fatone@staff.univpm.it (F.F.)
9 Department of Life and Environmental Sciences, Marche Polytechnic University, 60131 Ancona, Italy; s.gorbi@univpm.it (S.G.); l.pittura@pm.univpm.it (L.P.)
* Correspondence: ltseng@colgate.edu

SUPPORTING INFORMATION

Content

Preliminary experiments to determine experimental time 3

Table S1. Analyte masses monitored in gas chromatography-mass spectrometry (GC/MS) selected ion mode (SIM) (LOD, limit of detection; LOQ, limit of quantitation). 4

Table S2. Extraction recovery from the experimental procedure. 5

Table S3. Surface information of the plastics studied. 6

Table S4. Initial concentrations of plastic additives in the plastics studied..... 7

Table S5. The pseudo-second order rate constant, k_2 (μg^{-1} d^{-1}) for each of the CECs on the plastics..... 8

Figure S1. The lathe was used to produce coil shavings of polyvinyl chloride (PVC) pipes..... 9
Figure S2. Macro- and microplastics in solution. 10

Figure S3. Scanning electron microscope (SEM) images of the macro- and microplastics..... 11
Figure S4. Preliminary adsorption study of CECs on macro-PVC..... 12
Figure S5. Preliminary adsorption study of CECs on micro-PE. 13
Figure S6. Preliminary adsorption of CECs on micro-PS. (* denotes the chemicals that were not added in the starting working chemical solution). 14
Figure S7. Macro- and micro-PVC adsorption experiment with selected CECs..... 15
Figure S8. Additional adsorption experiment performed with the ATN solution in glass serum bottles for 24 hours. 16
Figure S9. Macro- and micro-PE adsorption experiment with selected CECs..... 17
Figure S10. Macro- and micro-PS adsorption experiment with selected CECs..... 18
Figure S11. Fraction of mass of CECs on PVC, PE, and PS vs. time and their pseudo-first order fit. 19
Figure S12. Concentration of CECs on PVC, PE, and PS vs. time and their pseudo-second order fit. 20
Figure S13. Sorption concentration normalized to surface area and volume plotted against specific surface area or pore area, pore volume or intrusion volume, and porosity. 21
Figure S14. A schematic of potential adsorption mechanisms involved in this study. 22

Preliminary experiments to determine experimental time

Initial preliminary experiment on macro-PVC showed that after 7 days there were consistent detectable ACE and MBT on macro-PVC (SI Fig. 2). However, our results of plastic additives in macro-PVC from sonication extraction showed that macro-PVC had similar MBT concentration before being exposed to CECs in the adsorption experiment, thus MBT was probably not transferred from the solution to the macro-PVC. The detectable ACE concentration on the macro-PVC was low and seemed to be immediately retained by macro-PVC. The adsorption of ACE also seemed to reach equilibrium quickly. Overall, there was one of the six CECs investigated with some retention by macro-PVC within 7 days.

Prior to the preliminary experiment on micro-PE, micro-PE was found to also have undetectable BPA, nNP, and DEHP, but it was found to contain 10.09±0.61 ppm (w/w) MBT. The results from the preliminary experiment on micro-PE (SI Fig. 3) suggested that micro-PE may be able to retain DCF, ATN, ACE, and BPA on its surface, and equilibrium was reached around day 7. However, we were not able to determine the rate of adsorption of CECs with 3 time points, and the IBP added into the solution was low and mostly below detection. The difference between the preliminary result and the experimental result may be due to different micro-PE with different size used for the preliminary experiment (micro-sized PE particles with size range 100-250 μm were obtained from Dr. Stefania Gorbi from the Polytechnic University of Marche, Italy). Nonetheless, the retention of DCF and BPA was consistent and equilibrium was reached quickly within 7 days.

The preliminary chemical adsorption on micro-PS was performed on micro-PS provided by Dr. Stefania Gorbi. Prior to the experiment, the micro-PS (100-250 μm) was found to have undetectable BPA and nNP, but it was found to contain 19.75±2.08 ppm (w/w) MBT and 0.67±0.40 ppm (w/w) DEHP. Similar to PVC, the results for MBT showed that MBT was unlikely adsorbed during the experiment (SI Figs. 2 and 4). The IBP added to the solution was also low and mostly below detection. However, all the other chemicals seemed to be able to adsorb onto the plastic. This preliminary experiment also showed that for micro-PS, equilibrium was reached within 7 days.

Table S1. Analyte masses monitored in gas chromatography-mass spectrometry (GC/MS) selected ion mode (SIM) (LOD, limit of detection; LOQ, limit of quantitation).
Bolded masses are the highest peaks.

Chemical		m/z	Retention time (min)	LOD (mg L^{-1})	LOQ (mg L^{-1})
Diclofenac	DCF	**214**, 242, 277	14.73	0.251	0.836
Atenolol	ATN	**56**, 107, 161	17.06	2.296	7.654
Ibuprofen	IBP	91, 107, **161**	8.26	2.144	7.145
4-acetamidophenol	ACE	80, 109, **151**	9.35	0.502	1.673
Bisphenol A	BPA	119, **213**, 228	14.80	0.182	0.606
4-*n*-nonylphenol	nNP	77, **107**, 220	11.81	0.045	0.151
2-mercaptobenzothiazole	MBT	69, 108, **135**	12.93	0.162	0.542
Bis-2(ethylhexyl)phthalate	DEHP	57, **149**, 167	11.94	0.057	0.189
Anthracene-d_{10}	ANT-d_{10}	80, 94, **188**	17.06	0.464	1.548

Table S2. Extraction recovery from the experimental procedure.
Percent recovery from both chemicals remaining in solution and post-sonication.

CEC	log K_{ow}	Recovery (%)
DCF	4.51	81 ± 28
IBP	3.97	98 ± 31
BPA	3.32	83 ± 23
MBT	2.41	92 ± 41
ACE	0.46	112 ± 21
ATN	0.16	80 ± 17

Table S3. Surface information of the plastics studied.

	Method	**Diameter (µm)**	**Specific surface area (m^2 g^{-1})**	**BJH pore volume 1.7-300 nm (cm^3 g^{-1})**	**BJH average pore diameter 1.7-300 nm (nm)**	**% porosity**
Macro-PVC	Mercury intrusion porosimetry	-	(total pore area) 18.37	(total intrusion volume) 0.29	(volume median pore diameter, µm) 76.09	27.1
Micro-PVC	BET N_2 gas	178±26	0.46	0.0008	6.74	-
Macro-PE	Mercury intrusion porosimetry	-	(total pore area) 23.80	(total intrusion volume) 0.44	(volume median pore diameter, µm) 67.18	29.9
Micro-PE	BET N_2 gas	947±87	0.07	0.0001	29.28	-
Macro-PS	BET N_2 gas	-	0.28	0.002	15.11	-
Micro-PS	Mercury intrusion porosimetry	414±102	(total pore area) 22.96	(total intrusion volume) 0.13	(volume median pore diameter, µm) 28.48	12.6

Table S4. Initial concentrations of plastic additives in the plastics studied.
In an effort to understand the initial plastic additives in the plastics, we extracted four selected plastic additives (bisphenol A [BPA], 4-*n*-nonylphenol [nNP], 2-mercaptobenzothiazol [MBT], and bis(2-ethylhexyl) phthalate [DEHP]) from 1.000 g of the plastics we used in the experiment, macro- and micro-PVC, polystyrene (PS), and polyethylene (PE)) after 15-min sonication.

	PVC		PS		PE	
	Macro	Micro	Macro	Micro	Macro	Micro
BPA (mg L^{-1})	BDL	BDL	BDL	BDL	BDL	BDL
nNP (mg L^{-1})	BDL	BDL	BDL	BDL	BDL	BDL
MBT (mg L^{-1})	BDL	BDL	BDL	BDL	BDL	BDL
DEHP (mg L^{-1})	3.63 ± 0.28	BDL	4.12±0.28	BDL	3.70±0.60	BDL

Table S5. The pseudo-second order rate constant, k_2 (μg^{-1} d^{-1}) for each of the CECs on the plastics.
None of the pseudo-second order fits was significant using the chi-squared test. The CECs that were most likely sorbed onto the plastic are shaded in gray. Some rate constants could not be determined (NA).

CEC	log K_{ow}	Control	Macro-PVC	Micro-PVC	Macro-PE	Micro-PE	Macro-PS	Micro-PS
DCF	4.51	NA	-0.0023	-0.0087	-0.0131	-0.0076	-0.0045	-0.0085
IBP	3.97	NA	0.0017	NA	-0.0018	0.0066	-0.0004	0.0029
BPA	3.32	NA	0.0000	NA	-0.0301	0.0000	-0.0001	NA
MBT	2.41	NA	-10.6617	NA	NA	NA	-0.0045	NA
ACE	0.46	NA	-0.0002	NA	NA	0.0078	-0.0996	NA
ATN	0.16	NA	0.0402	-0.0482	NA	0.0809	-0.0621	-0.0464

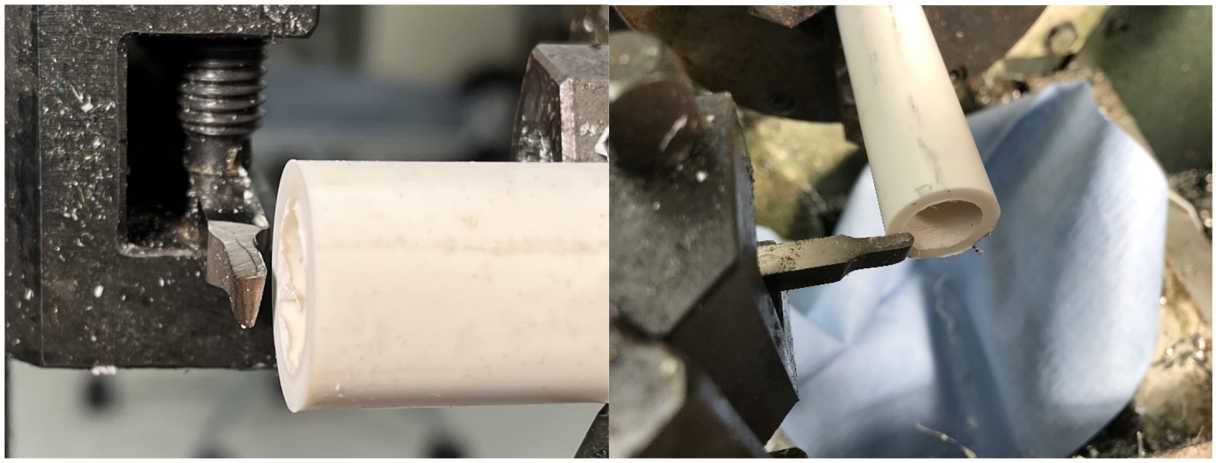

Figure S1. The lathe was used to produce coil shavings of polyvinyl chloride (PVC) pipes.

Figure S2. Macro- and microplastics in solution.

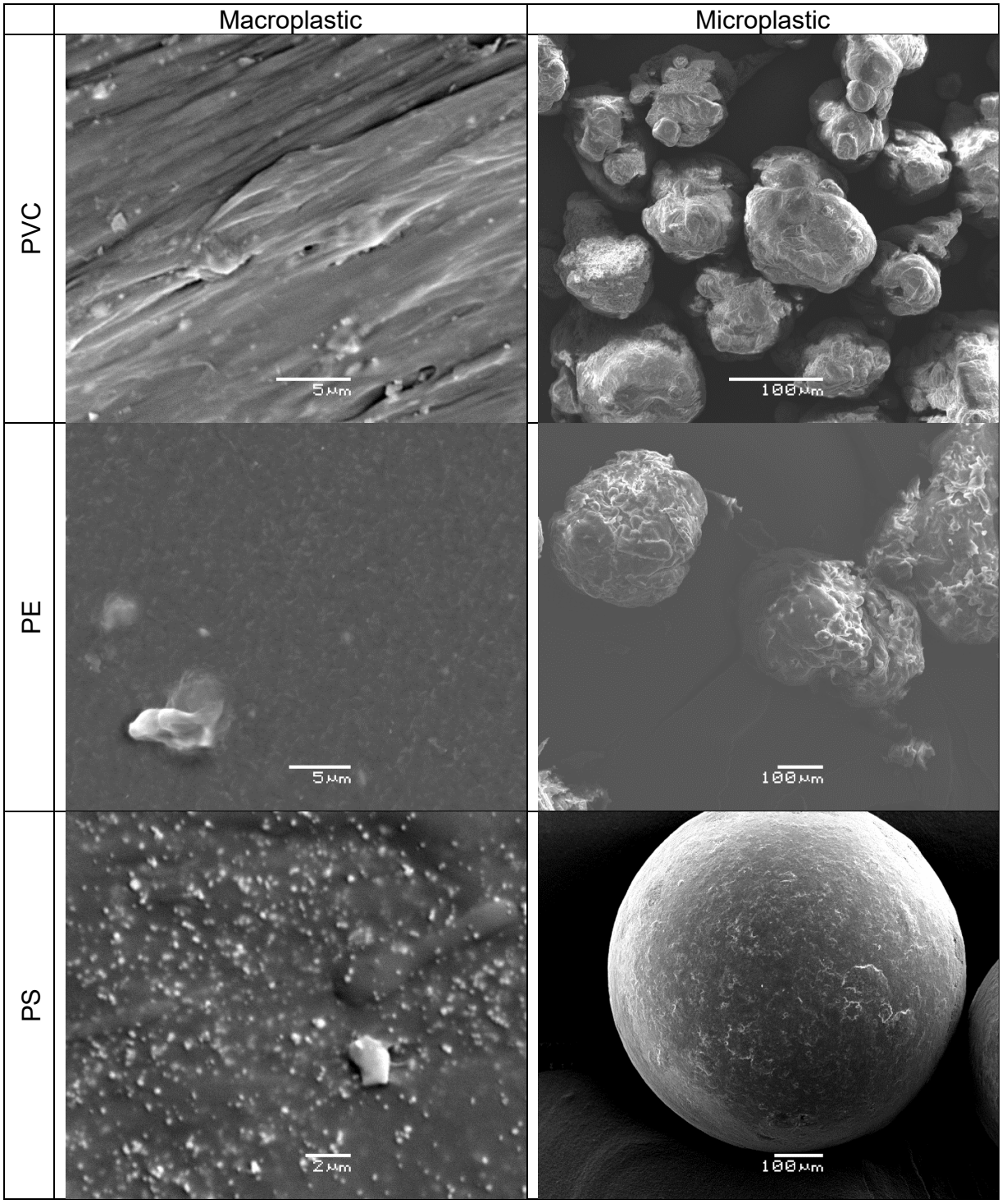

Figure S3. Scanning electron microscope (SEM) images of the macro- and microplastics.

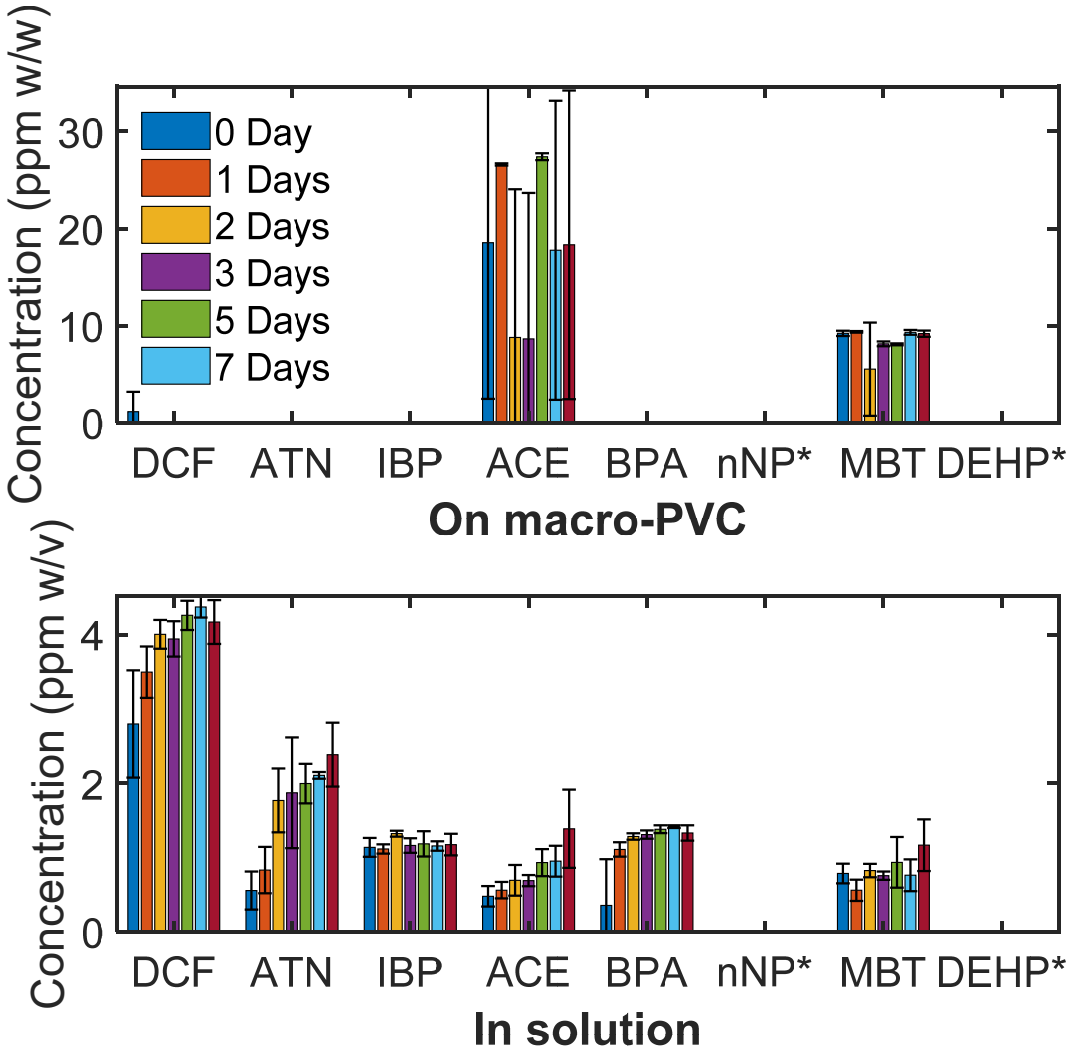

Figure S4. Preliminary adsorption study of CECs on macro-PVC.
The adsorption of chemicals on the macro- PVC pipe shavings after diluting 130 µl working solution in 1 L. The chemicals that were detectable on the PVC were ACE and MBT. However, MBT is present in PVC, at about 13.59±0.97 ppm (w/w), thus MBT at the level detected on the PVC about 8.4 ppm (w/w) likely did not come from adsorption. The concentration of ACE found on the PVC was low but consistently at around 18.0 ppm (w/w) suggests that the adsorption of ACE probably happened immediately on PVC (* denotes the chemicals that were not added in the starting working chemical solution).

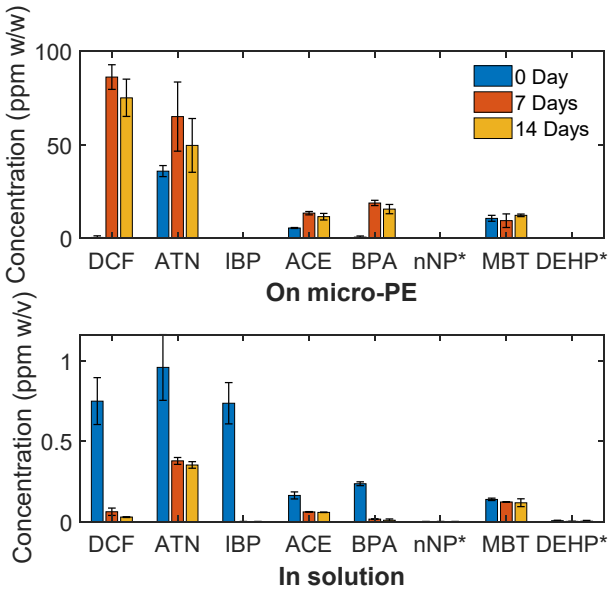

Figure S5. Preliminary adsorption study of CECs on micro-PE.
(* denotes the chemicals that were not added in the starting working chemical solution).

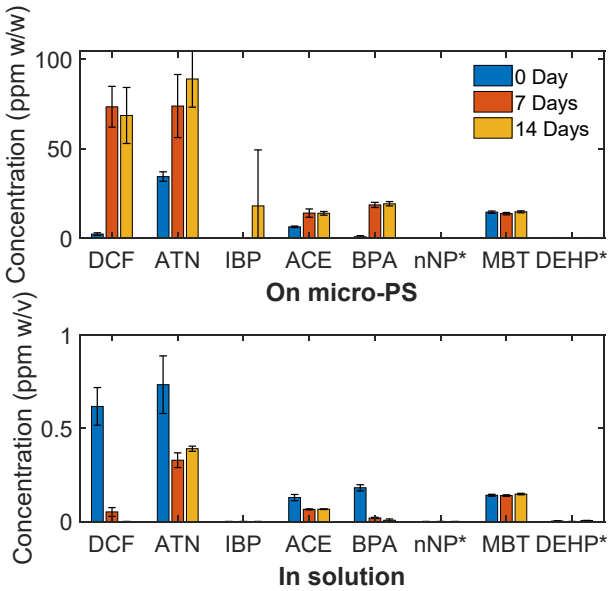

Figure S6. Preliminary adsorption of CECs on micro-PS.
(* denotes the chemicals that were not added in the starting working chemical solution).

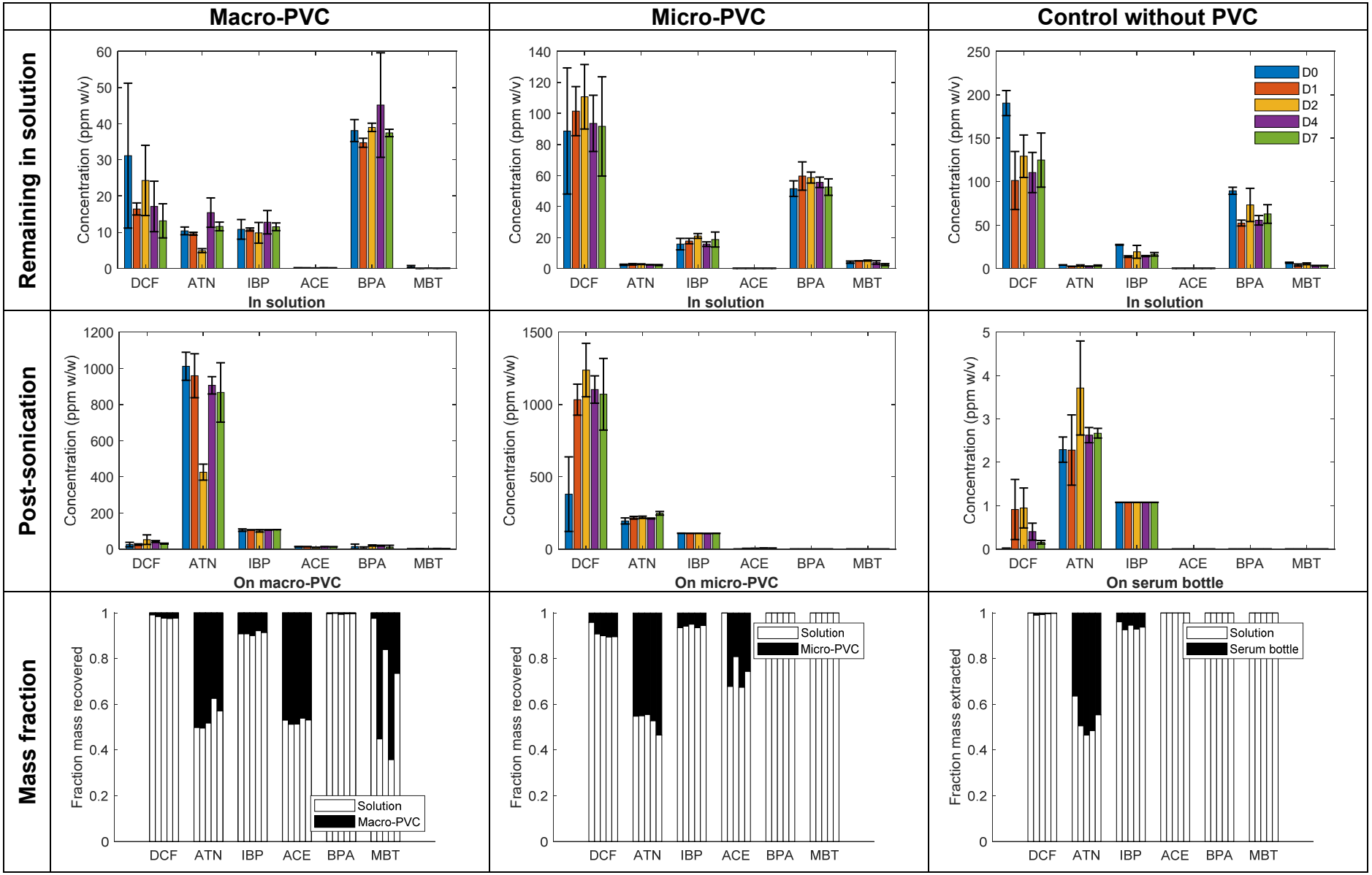

Figure S7. Macro- and micro-PVC adsorption experiment with selected CECs.

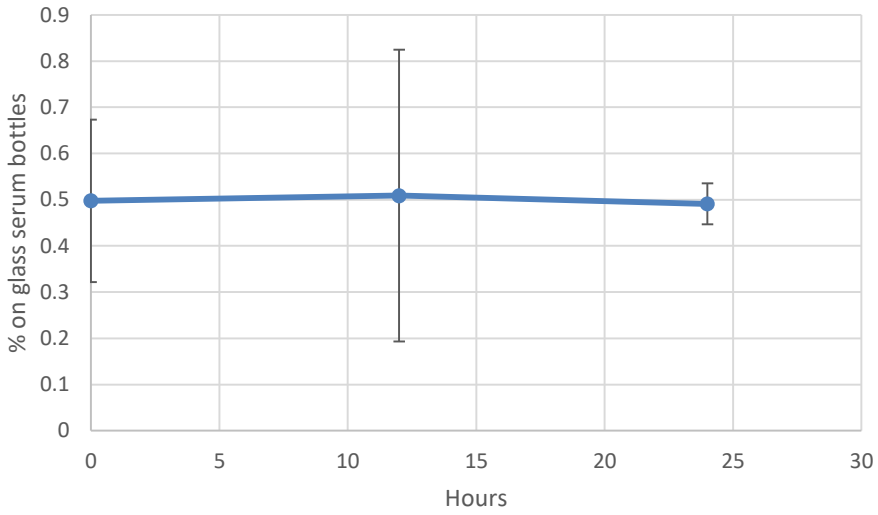

Figure S8. Additional adsorption experiment performed with the ATN solution in glass serum bottles for 24 hours.

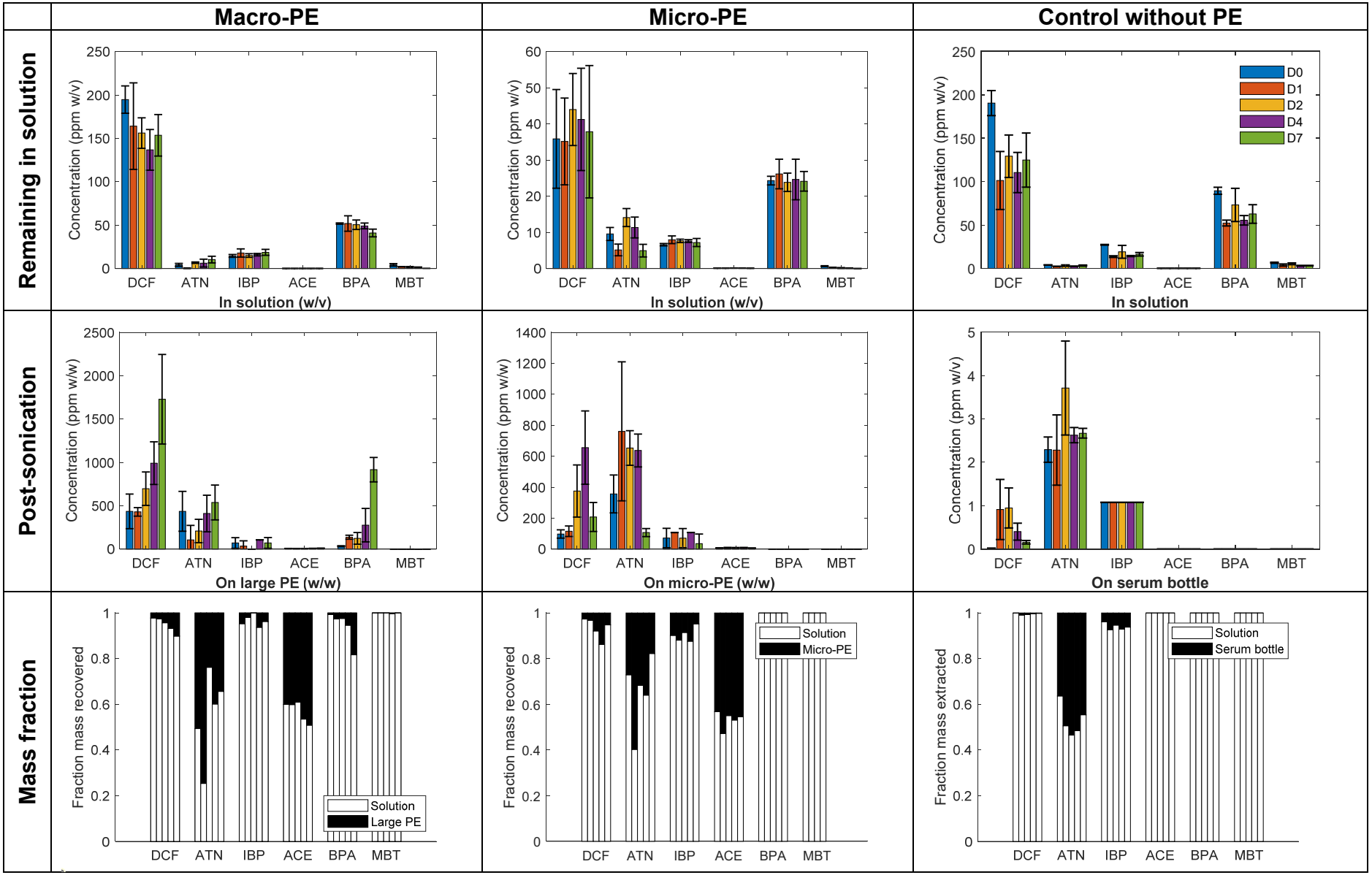

Figure S9. Macro- and micro-PE adsorption experiment with selected CECs.

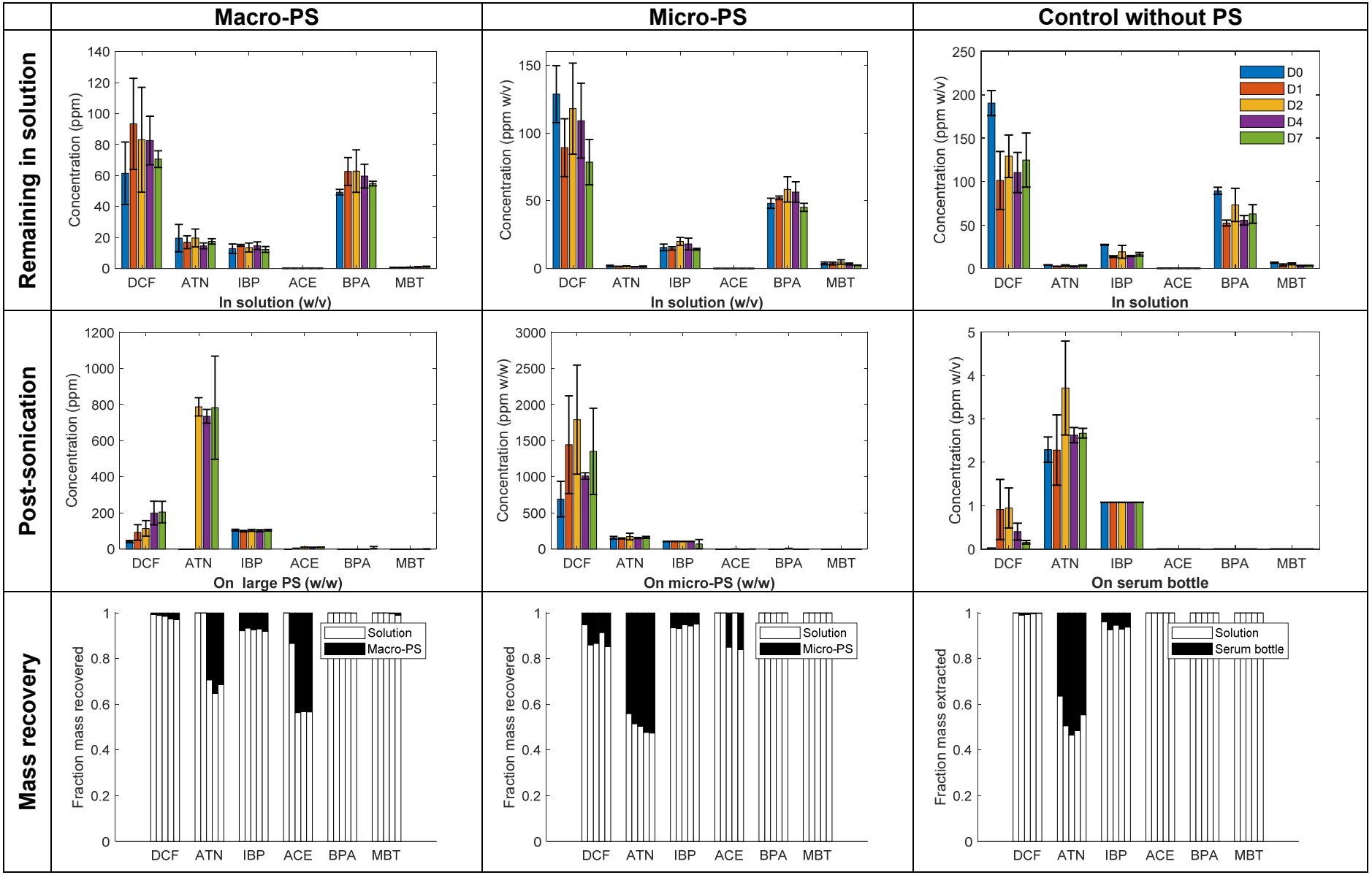

Figure S10. Macro- and micro-PS adsorption experiment with selected CECs.

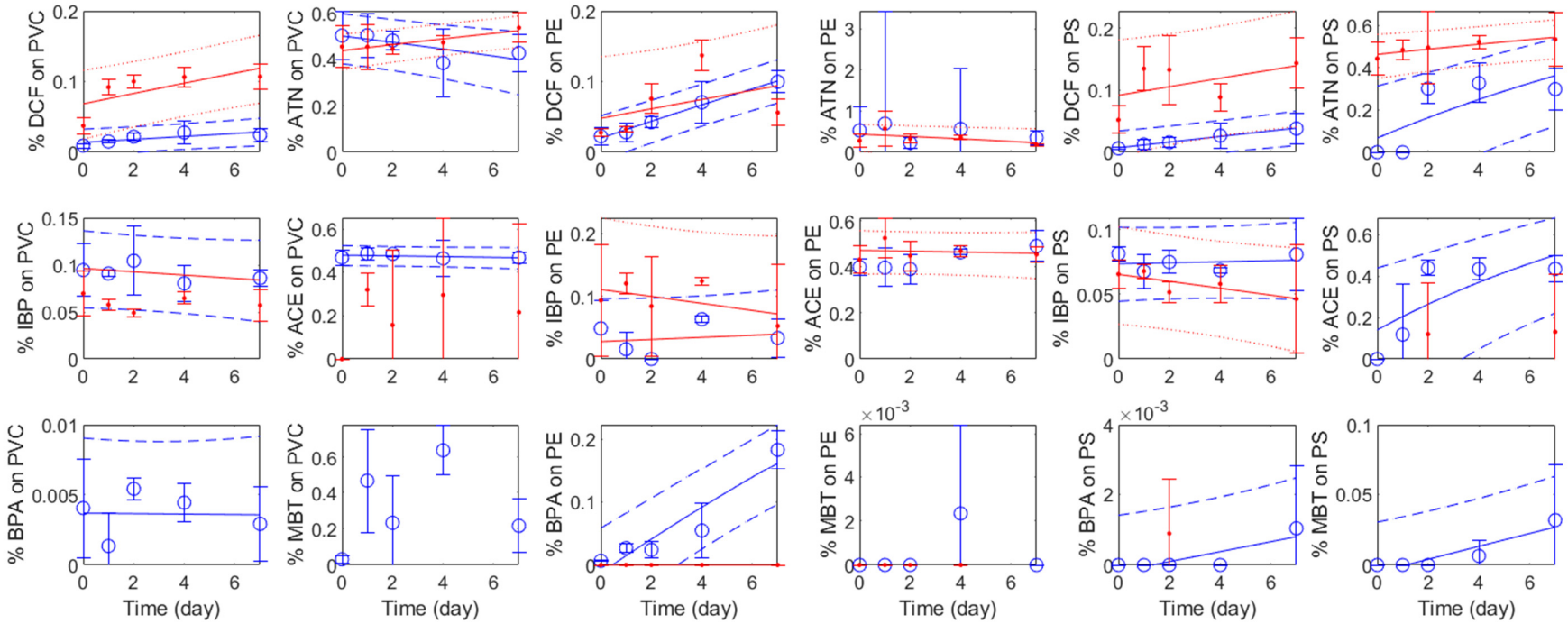

Figure S11. Fraction of mass of CECs on PVC, PE, and PS vs. time and their pseudo-first order fit.
Macro-sized plastics are plotted with blue open circles (○) and micro-sized plastics are plotted with red dots (•), dashed lines contain 95% confidence interval for macro-sized plastics and dotted lines contain 95% confidence interval for micro-sized plastics.

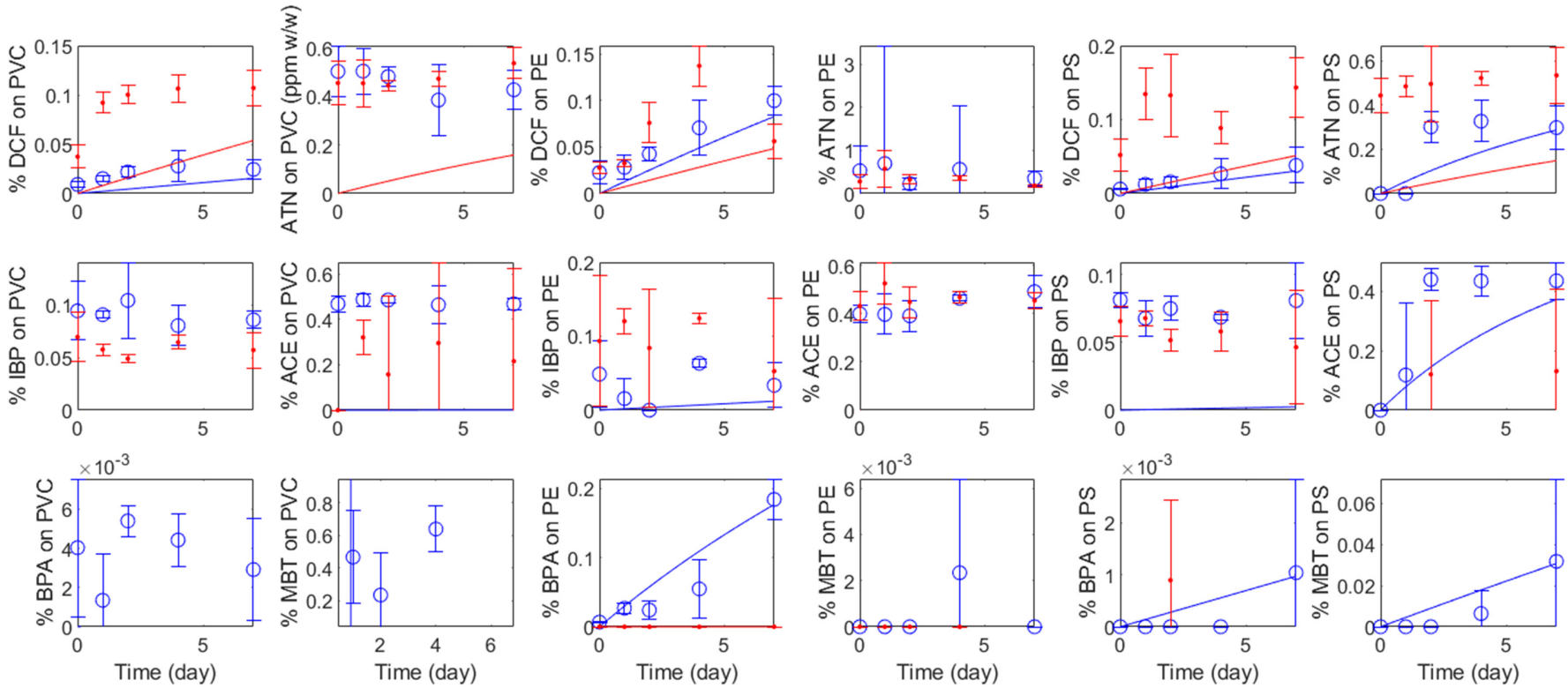

Figure S12. Concentration of CECs on PVC, PE, and PS vs. time and their pseudo-second order fit.
Macro-sized plastics are plotted with blue open circles (○) and micro-sized plastics are plotted with blue dots (•).

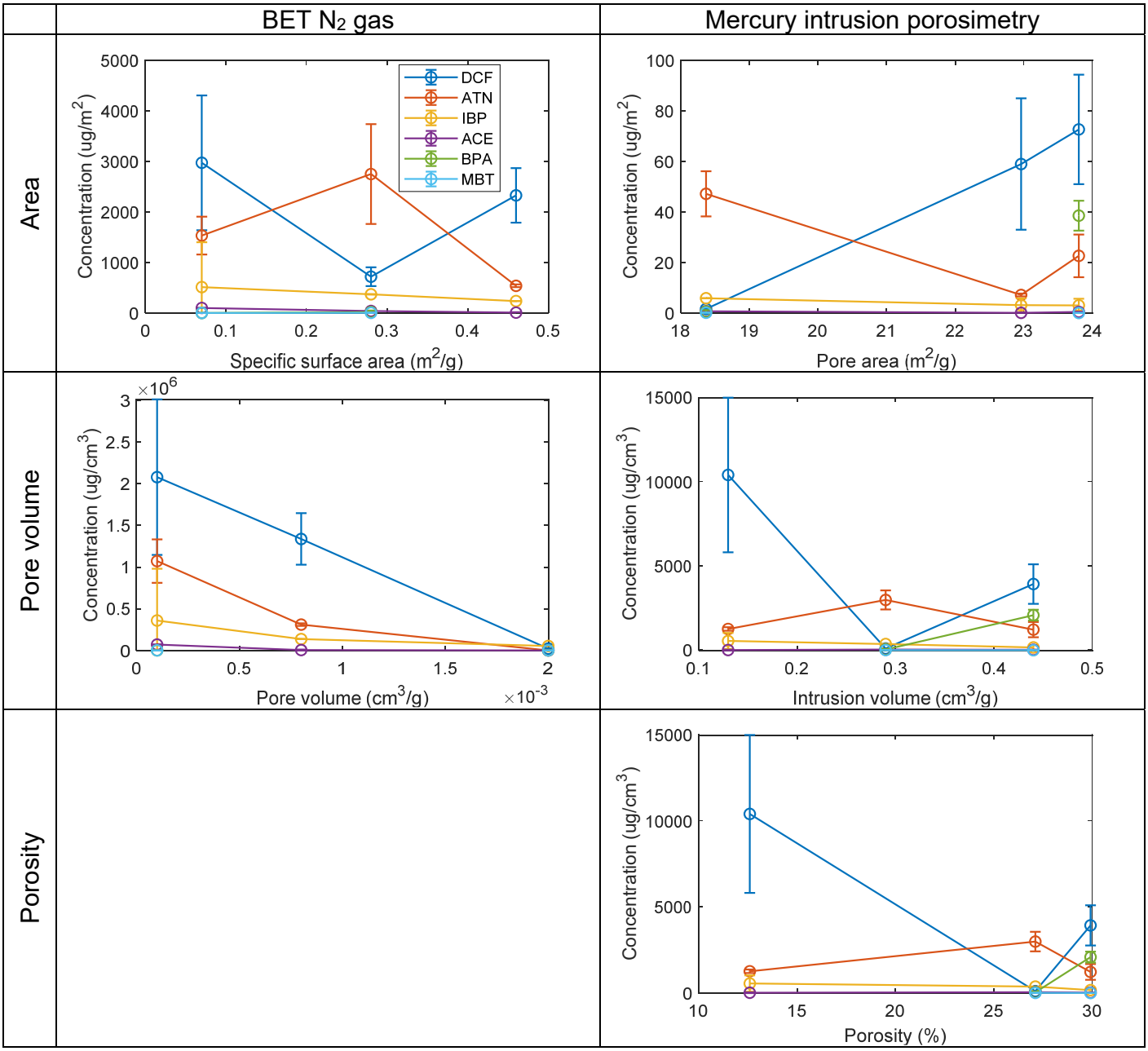

Figure S13. Sorption concentration normalized to surface area and volume plotted against specific surface area or pore area, pore volume or intrusion volume, and porosity.

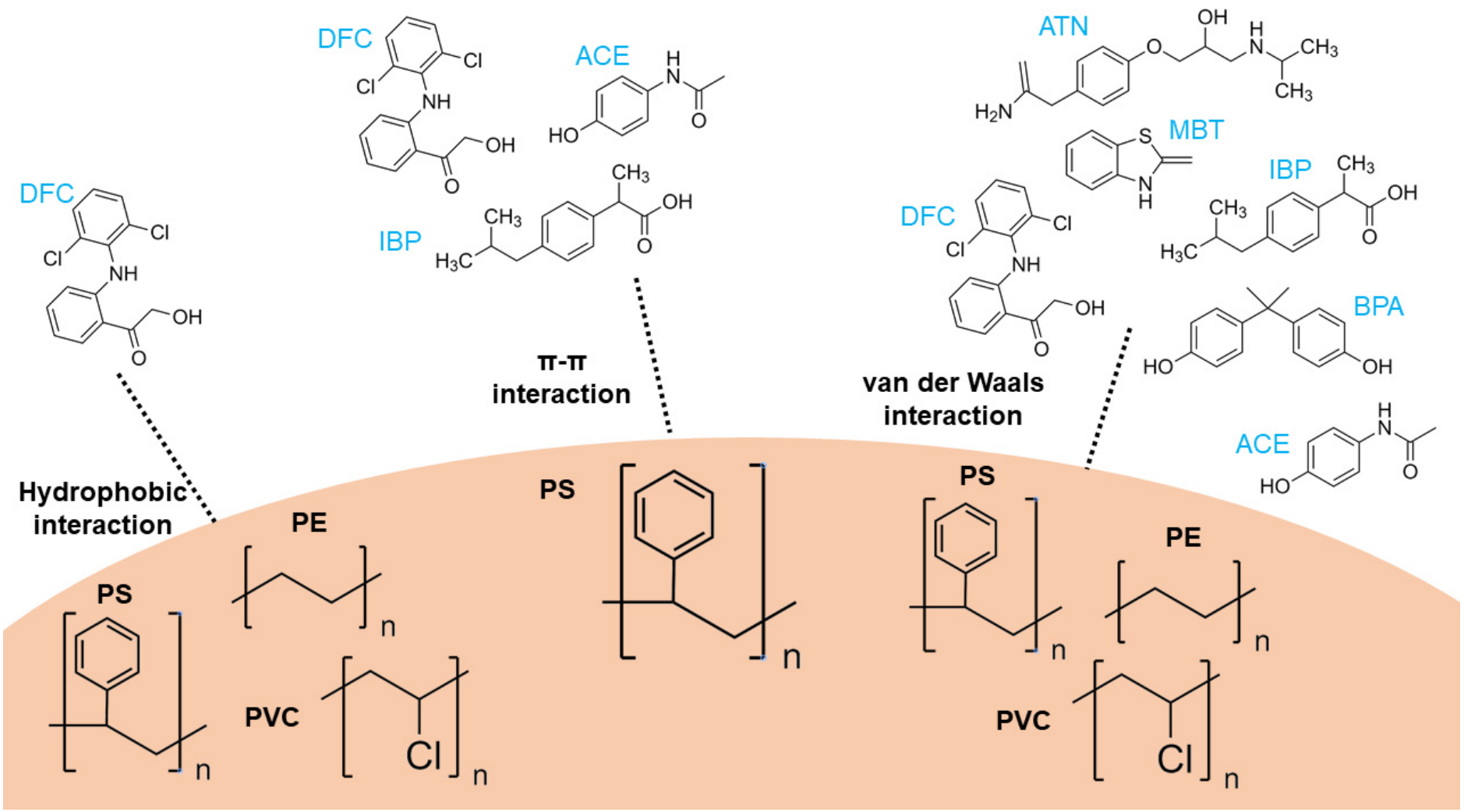

Figure S14. A schematic of potential adsorption mechanisms involved in this study.