Supplementary Materials

MANUSCRIPT TITLE: Effects of biofouling on the uptake of perfluorinated alkyl acids by organic-diffusive gradients in thin films passive samplers

AUTHORS: Po Wang[a], Jonathan K. Challis[b], Zi-Xuan He[a], Charles S. Wong[a,c] *, and Eddy Y. Zeng[a]

ADDRESS: [a] Guangdong Key Laboratory of Environmental Pollution and Health, School of Environment, Jinan University, Guangzhou 511443, China; [b] Toxicology Centre, University of Saskatchewan, Saskatoon, SK S7N 5B3, Canada; [c] Southern California Coastal Water Research Project Authority, Costa Mesa CA 92626, USA.

NO. OF TABLES: 4

NO. OF FIGURES: 7

NO. OF PAGES: 10

Text S1. Extraction Procedures

o-DGT extraction

The binding gel from exposed o-DGT samples was placed in a 15 mL polypropylene centrifuge tube, then spiked with 20 ng of an internal standard mixture directly onto the gel. The mixture was allowed to soak for 15 min. Separate 3×3 mL aliquots of methanol were added prior to sonication for 5 min between each addition. Extracted aliquots of solvent were combined in a separate tube and evaporated to dryness by nitrogen blowdown. Dried samples were reconstituted in 1 mL of methanol and filtered through 0.2 μm syringe nylon filters (Thermo Scientific, USA) into polypropylene LC amber vials, which was stored at -20 ℃ until instrumental analysis.

Water sample extraction

Before extraction, water samples (500 mL of lake water and 30 mL of spiked lake water) were spiked with 20 ng of the internal standard mixture. Oasis WAX cartridges (3 cc, 60 mg, 30 μm particle size, Waters) were pre-activated with sequential additions of 4 mL 0.1% (v/v) NH_4 OH/methanol solution, 4 mL methanol, and 4 mL Milli-Q water. The water samples were extracted onto WAX cartridges with 4 mL of ammonium acetate buffer (25 mmol L^{-1}), then dried under vacuum for 15 minutes. Elution was done with 4 mL of methanol followed by 4 mL of 0.1% (v/v) NH_4 OH/methanol. The eluate was collected in a 15 mL polypropylene centrifuge tube, then evaporated to dryness under a gentle stream of nitrogen. The remaining extract was processed as above for o-DGT samples.

Table S1. PFAS and internal standards used in this study.

Chemicals	Acronym	CAS number	Molecular formula	Molecular weight (Da)	Log D[a]
Perfluorobutanesulfonic acid	PFBS	375-73-5	$C_4HF_9SO_3$	300.10	-1.56
Sodium perfluoro-1-hexane [$^{18}O_2$] sulfonate	MPFHxS	-	$C_6F_{13}S^{18}O_2{}^{16}ONa$	426.10	-
Perfluorooctanesulfonic acid	PFOS	1763-23-1	$C_8HF_{17}SO_3$	500.13	0.66
Sodium perfluoro-1-[1,2,3,4-$^{13}C_4$] Octanesulfonate	MPFOS	-	$^{13}C_4{}^{12}C_4F_{17}SO_3Na$	526.08	-
Perfluorooctanoic acid	PFOA	335-67-1	$C_8HF_{15}O_2$	414.07	1.82
Perfluoro-*n*-[1,2,3,4-$^{13}C_4$] octanoic acid	MPFOA	-	$^{13}C_4{}^{12}C_4HF_{15}O_2$	418.04	-
Perfluorononanoic acid	PFNA	375-95-1	$C_9HO_2F_{17}$	464.08	2.84
Perfluoro-*n*-[1,2,3,4,5-$^{13}C_5$] nonanoic acid	MPFNA	-	$^{13}C_5{}^{12}C_4HF_{17}O_2$	469.04	-
Perfluorodecanoic acid	PFDA	335-76-2	$C_{10}HO_2F_{19}$	514.08	3.62
Perfluoro-*n*-[1,2-$^{13}C_2$] decanoic acid	MPFDA	-	$^{13}C_2{}^{12}C_8HF_{19}O_2$	516.07	-
Perfluoroundecanoic acid	PFUnDA	2058-94-8	$C_{11}HF_{21}O_2$	564.09	4.23
Perfluoro-*n*-[1,2-$^{13}C_2$] undecanoic acid	MPFUnDA	-	$^{13}C_2{}^{12}C_9HF_{21}O_2$	566.08	-

[a] ACD Labs predicted at pH 7.4.

Table S2. Relative difference between the sampling rates (R_s-mL d^{-1}) of six PFAS into o-DGT in the gel-fouled (A), whole-fouled (B), and control-fouled (C) o-DGT group in the calibration experiment.

Compounds	R_s (mL d^{-1})			Relative Error	
	A	B	C	A *vs* C	B *vs* C
PFBS	4.0 ± 0.3	3.4 ± 0.2	5.2 ± 0.5	23%	35%
PFOS	5.7 ± 0.7	5.2 ± 0.7	8.1 ± 0.5	29%	35%
PFOA	6.2 ± 0.7	5.9 ± 0.8	8.8 ± 1.3	30%	33%
PFNA	6.0 ± 0.4	5.8 ± 0.7	8.5 ± 0.9	29%	32%
PFDA	4.4 ± 0.5	4.7 ± 0.3	6.7 ± 0.5	35%	30%
PFUnDA	2.3 ± 0.4	2.4 ± 0.5	3.4 ± 0.6	33%	31%

Table S3. The mass accumulation (ng) of six PFAS into o-DGT in the gel-fouled (A), whole-fouled (B), and control-fouled (C) o-DGT group in the calibration experiment. Standard deviations (n=3) are given in parentheses.

Compounds	5 d			10 d			15 d			18 d			21 d		
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
PFBS	289 (17.6)	309 (9.1)	386 (8.0)	437 (2.0)	395 (13.7)	599 (16.9)	519 (17.8)	493 (28.1)	693 (38.5)	544 (38.5)	510 (21.9)	709 (26.3)	755 (29.0)	627 (52.8)	952 (51.3)
PFOS	240 (5.2)	284 (11.2)	378 (14.4)	428 (32.4)	417 (16.1)	650 (12.0)	543 (18.9)	587 (22.9)	842 (65.0)	604 (24.7)	643 (13.7)	925 (44.6)	971 (93.7)	821 (56.0)	1260 (31.8)
PFOA	222 (4.1)	255 (7.2)	343 (16.4)	385 (23.8)	390 (9.0)	611 (31.1)	520 (14.8)	550 (33.2)	801 (63.8)	551 (25.7)	623 (22.2)	906 (25.6)	881 (51.6)	815 (82.1)	1170 (36.3)
PFNA	273 (5.8)	320 (13.3)	418 (16.0)	468 (27.3)	485 (11.8)	743 (49.5)	616 (36.8)	681 (41.4)	973 (72.0)	676 (31.8)	755 (15.5)	1080 (30.5)	1050 (94.6)	991 (56.2)	1430 (62.1)
PFDA	225 (0.5)	256 (7.5)	345 (20.0)	383 (33.0)	402 (14.8)	613 (14.1)	499 (10.0)	552 (34.4)	794 (86.2)	538 (13.1)	608 (4.2)	877 (61.2)	806 (63.0)	795 (45.5)	1140 (29.8)
PFUnDA	221 (12.9)	251 (3.5)	323 (16.6)	369 (24.5)	385 (10.2)	582 (31.7)	468 (23.3)	541 (23.8)	751 (51.0)	536 (18.6)	586 (12.2)	820 (45.7)	814 (68.8)	770 (40.3)	1110 (30.7)

Table S4**.** Relative difference between the mass accumulation of six PFAS into o-DGT in the gel-fouled (A), whole-fouled (B), and control-fouled (C) o-DGT group in the calibration experiment.

Compounds	5 d		10 d		15 d		18 d		21 d	
	A *vs* C	B *vs* C	A *vs* C	B *vs* C	A *vs* C	B *vs* C	A *vs* C	B *vs* C	A *vs* C	B *vs* C
PFBS	25%	20%	27%	34%	25%	29%	23%	28%	21%	34%
PFOS	37%	25%	34%	36%	36%	30%	35%	31%	23%	35%
PFOA	35%	26%	37%	36%	35%	31%	39%	31%	25%	31%
PFNA	35%	24%	37%	35%	37%	30%	37%	30%	27%	31%
PFDA	35%	26%	37%	34%	37%	30%	39%	31%	29%	30%
PFUnDA	32%	22%	37%	34%	38%	28%	35%	29%	26%	30%

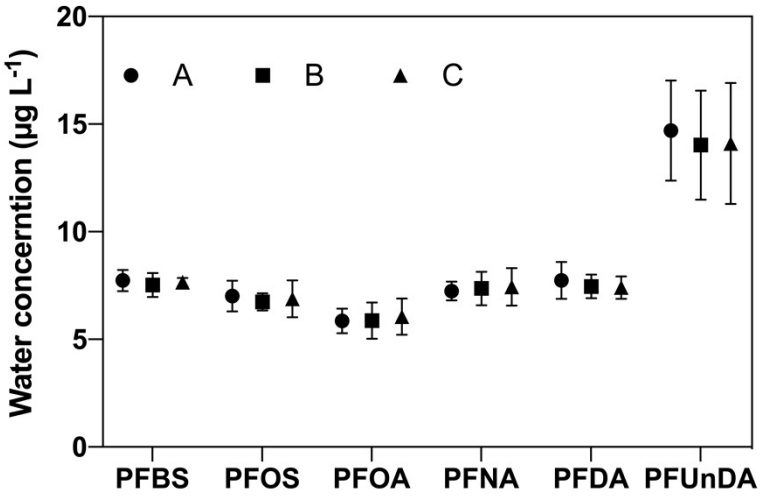

Fig. S1. The exposed water concentrations of six target PFAS throughout the o-DGT calibration experiment. A, B, and C represent gel-fouled, whole-fouled, and control-fouled group, respectively. Errors bars are the standard deviation of the means.

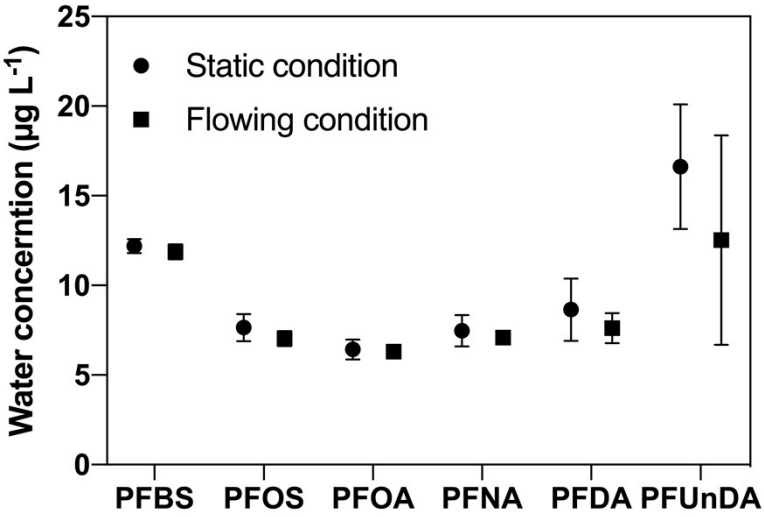

Fig. S2. The exposed initial water concentrations of six target PFAS in the o-DGT biofilm thickness experiment under static and flowing (~ 5.8 cm s^{-1}) conditions. Errors bars are the standard deviation of the means.

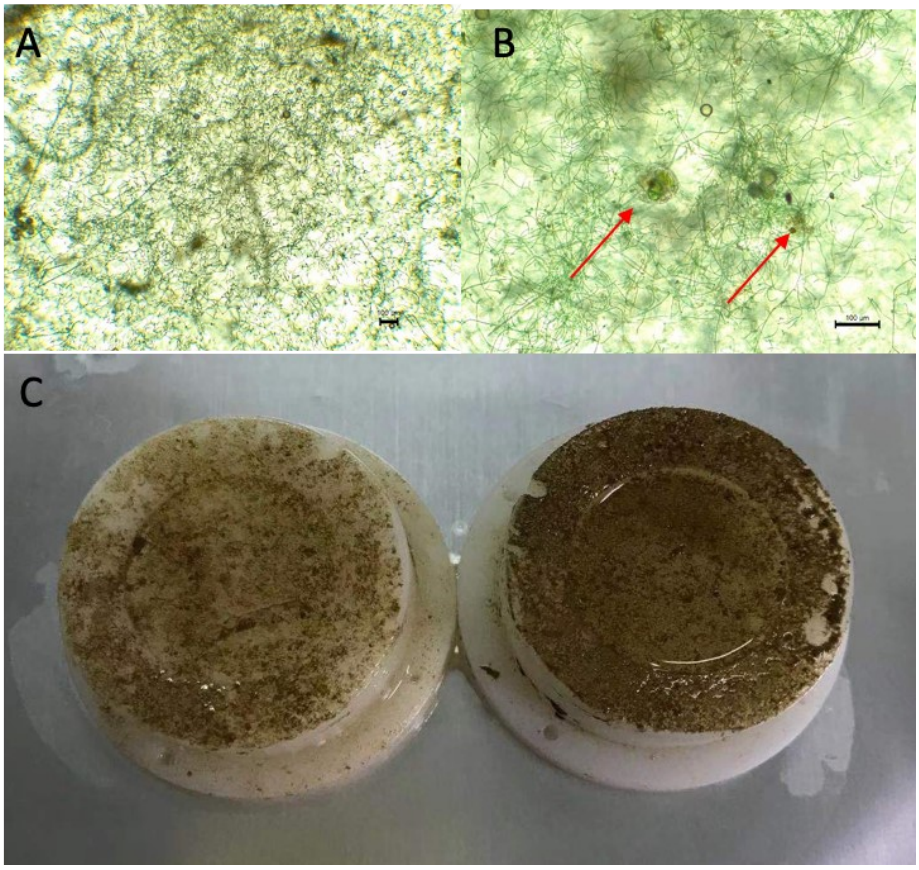

Fig. S3. Photos of biofilm on the surface of polyacrylamide gel (A and B) under an optical microscope (40 X, A and 200 X, B), red arrow indicates live small zooplankton in biofilm; and fouled o-DGT cultured for 10 days in Jing Lake (C), including gel-fouled (polyacrylamide gel and plastic layer, left) and whole-fouled (polyacrylamide gel and WAX binding gel, right).

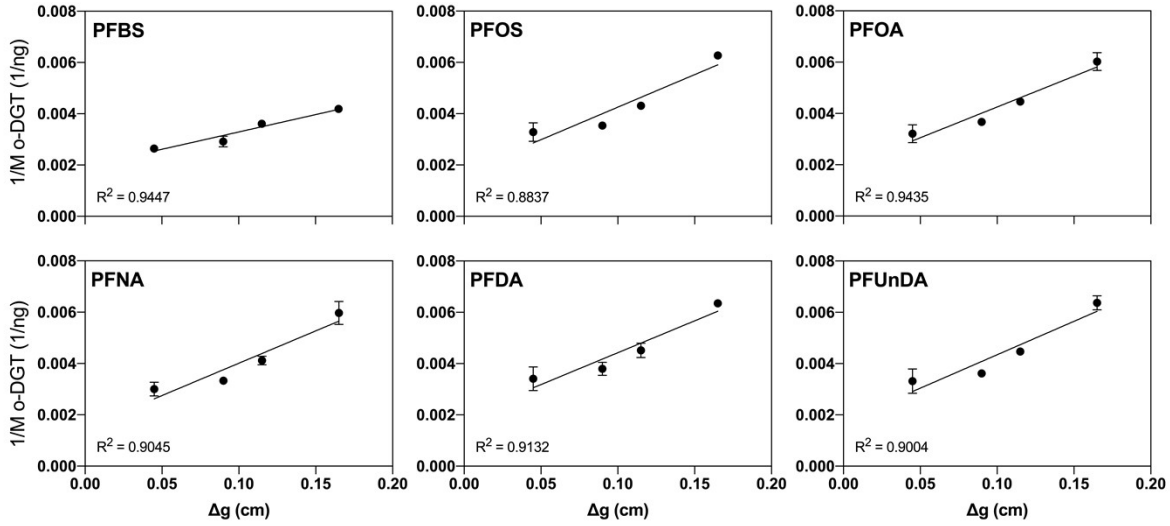

Fig. S4. Plot of 1/mass accumulation in clean o-DGT (1/ng) of six PFAS versus different gel thickness (Δg, cm) under static conditions.

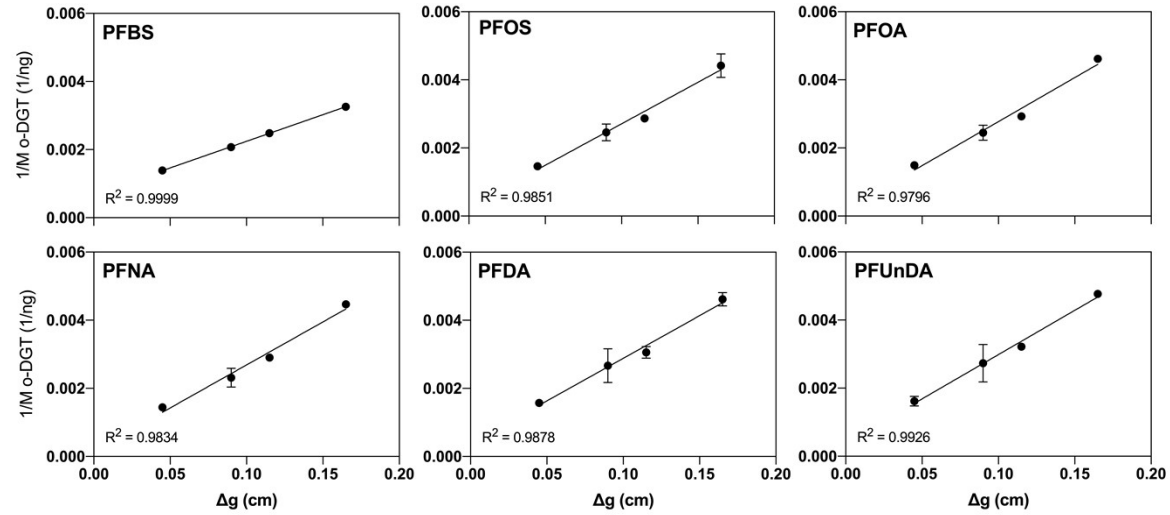

Fig. S5. Plot of 1/mass accumulation in clean o-DGT (1/ng) of six PFAS versus different gel thickness (Δg, cm) under flowing conditions.

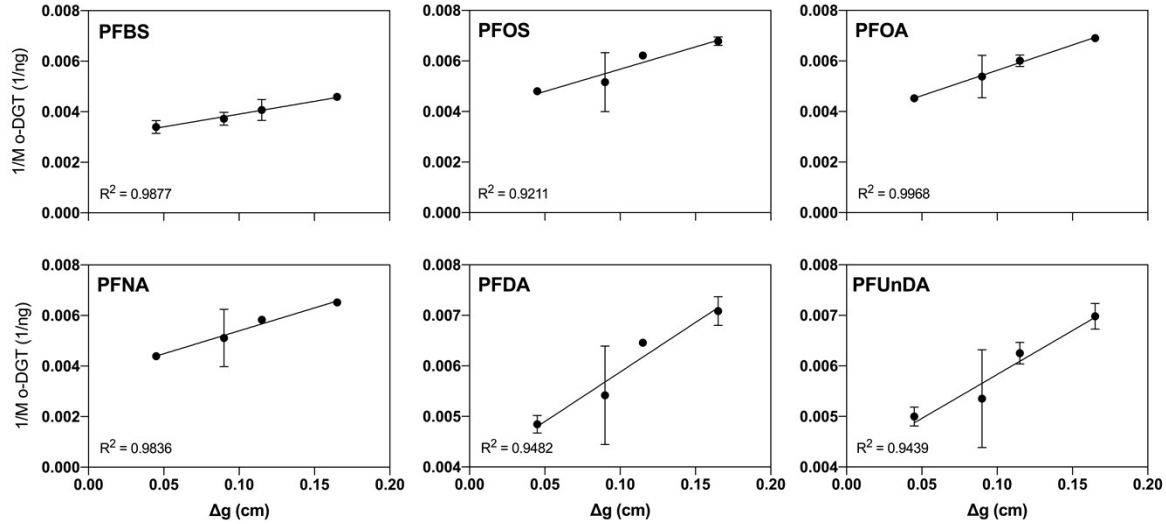

Fig. S6. Plot of 1/mass accumulation in diffusive gel-fouled o-DGT (1/ng) of six PFAS versus different gel thickness (Δg, cm) under static conditions.

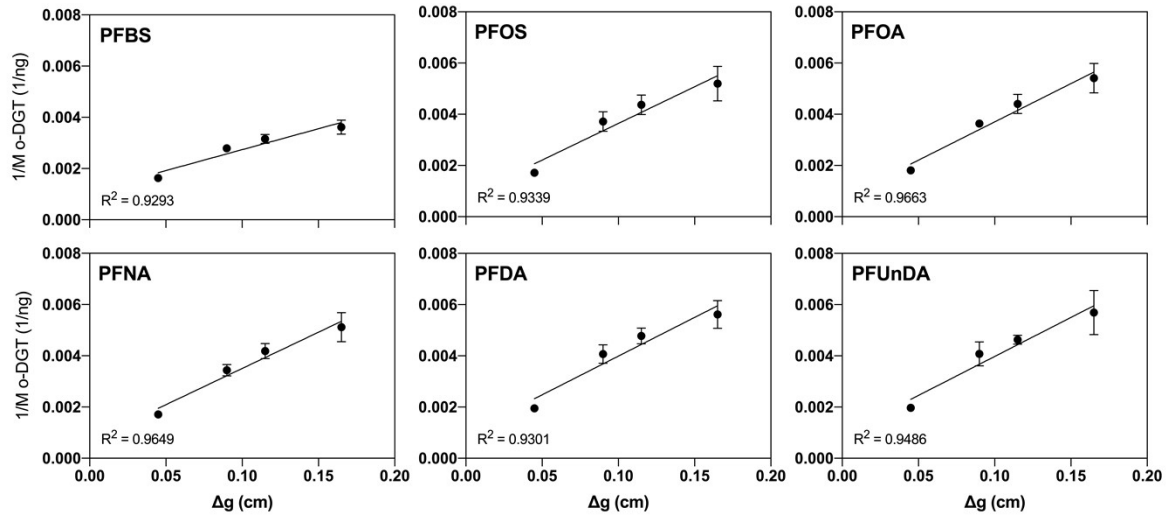

Fig. S7. Plot of 1/mass accumulation in diffusive gel-fouled o-DGT (1/ng) of six PFAS versus different gel thickness (Δg, cm) under flowing conditions.