Supplemental Information

Electrocatalytic Water Treatment of Per- and Polyfluoroalkyl Substances Reduces Adsorbable Organofluorine and Bioaccumulation Potential

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Text S1. Boron-doped Diamond (BDD) electrodes

BDD electrodes used in this study were manufactured by NeoCoat (La Chaux-de-Fonds, Switzerland). The doping thickness is 2 ~ 3 μm, and the boron doping level is 2500 ppm. Rectangle size of 50 × 25 × 1 mm monocrystalline p-Silicon is the substrate for doping. Total resistivity of a BDD electrode is 14 mΩ cm.

Text S2. LC-MS/MS method

Target PFAS for PFOA, PFHxA, PFBA analysis was conducted using an Agilent (Santa Clara, CA) 1290 multisampler liquid chromatograph coupled to a 6460 Triple Quadrupole mass spectrometer (LC-MS/MS) operating in electrospray negative ionization (ESI-) mode. The analytical column used was a Phenomenex (Torrance, CA) Gemini C18 reverse-phased column (3mm × 100mm, 5μm), with a Phenomenex Luna® C18 column (3 mm × 30 mm, 5 μm) serving as the delay column, and an Agilent Zorbax DIOL column (4.6 mm × 12.5 mm, 6 μm) used as the guard column. Mobile phases were consisted of 20mM ammonium acetate (NH_4COOH) dissolved in ThermoFisher Scientific (Hampton, NH) Optima® water as mobile phase A, and 100% LC-MS grade methanol from Honeywell (Charlotte, NC) as mobile phase B. A constant flow rate of 0.8 mL/min was maintained throughout the analysis. The LC system was equipped with a rinsing solution containing 100% HPLC grade acetonitrile from Sigma Aldrich. Internal standards (IS) were prepared using a ^{13}C isotope-labeled methanol-based 24 MPFAS-MXA mixture obtained from Wellington Laboratories (Guelph, ON).

Text S3. LC-MS/MS quality assurance (QA) and quality control (QC)

All samples were spiked with 400 ppt ^{13}C mass labeled internal standard (IS) of each analyte. Calibrations were based on the relative response of target compound over internal standard, and the linear calibration curves containing 8 concentration points between 0.1~100 μg/L were analyzed by 1/x weighting. Concentrations with 3 times signal to noise (S/N) and 10 times S/N were used to determine limit of detection (LOD) and limit of quantification (LOQ), respectively. Double blank was prepared by Optima® Water/methanol 50:50 (v/v). Blank prepared by spiking 400 ppt IS into double blank. A sample with 500 ppt of all the 3 target PFASs from external source was used as QC. Double blank, blank and a QC were inserted every 10 samples to make sure LC-MS/MS equipment was working accurately and consistently. Responses of double blank and blank should be smaller than 1/10 of the response of the lowest standard. Variation of QC responses should be within ±50%.

Text S3: Transil^{XL} assay preparation procedure

The assays were stored at -20 ℃ and thawed at 4 ℃ overnight prior to use. To simplify the procedure and avoid the loss of Transil^{XL} beads and other interferences, we followed an established protocol by adding 20 μL of the sample into each vial of the same column without removing the original phosphate buffer saline (PBS). Transil^{XL} samples were then incubated at room temperature on a plate shaker at 1000 rpm for 12 minutes, a sufficient time to reach partition equilibrium as demonstrated in previous studies. After incubation, the Transil^{XL} samples were settled at 4 ℃ for 3 hours to separate the supernatants and sediments. For target compound analysis, 20 μL of the supernatants were taken and analyzed using LC-MS/MS. Additionally, 100 μL of the supernatants were transferred into a clean CIC boat to the TF in the liquid phase. The remaining 140 μL of

Transil^{XL} sediment in PBS were vortexed to achieve a homogeneous mixture, and 100 µL of this mixture were transferred to the CIC system to measure the combined TF in both the liquid and solid phases.

Text S4: Transil^{XL} assay bioaccumulation potential calculations by LC-MS/MS

Define the following constants:

V_0 : initial PBS volume, 240 µL;

V_1 : volume of sample addition, 20 µL;

V_2 : supernatant volume removed for LC-MS/MS target compound analysis, 20 µL;

V_3 : supernatants volume used for measuring TF_{sup} by CIC, 100 µL;

V_{tot} : total PBS volume after sample addition, $V_{tot} = V_0 + V_1 = 260$ µL.

V_4 : sediment mixture volume, $V_4 = V_{tot} - V_2 – V_3 = 140$ µL;

V_5 : sediment volume taken for measuring TF_{sed} by CIC, 100 µL;

where C_s (µmol PFAS/kg lipid) is the PFAS concentration in lipid, and C_l (µmol PFAS/L) is the aqueous concentration.

Consider the total mass of a single PFAS analyte in the Transil^{XL} assay

$$M_{tot} = M_s + M_l \quad (4.1)$$

$$M_{tot} = C_{ini} \times V_1 \times 10^{-6} \quad (4.2)$$

where M_s (µmol) is total mass in lipid and M_l (µmol) is the total mass in liquid. C_{ini} (µmol/L) is the sample concentration spiked into the Transil^{XL} assay.

The total mass adsorbed onto Transil^{XL} lipid beads is expressed as

$$M_s = C_s \times m_s \times 10^{-6} \quad (4.3)$$

$$m_s = V_s \times \rho_s / 10^3 \quad (4.4)$$

where m_s (μg) is the mass of solid Transil^{XL} lipid beads inside the vial, V_s (μL) is the volume of Transil^{XL} lipid beads, and ρ_s is the bead density.

According to Transil^{XL} product description, V_s from position A to H are 0, 0.048, 0.086, 0.156, 0.281, 0.505, 0.907, and 0 μL. ρ_s = 1.05 kg/L

The total PFAS in the liquid phase is

$$M_l = C_l \times V_{aq} \times 10^{-6} \quad (4.5)$$

C_l (μmol PFAS/L) was measured by LC-MS/MS. V_{aq} is the total liquid volume inside a Transil^{XL} vial after sample addition, and here we have $V_{aq} = V_{tot}$ = 260 μL.

$$C_s = \frac{C_{ini}V_{1-}C_lV_{aq}}{V_s\rho_s} \quad (4.6)$$

The Transil^{XL} membrane affinity coefficient of fluorine, LBP (L/kg lipid), was calculated as the follow:

$$LBP = \frac{C_s}{C_l} \quad (4.7)$$

Substitute (3.6) into (3.7),

$$LBP = \frac{C_{ini}V_{1-}C_lV_{aq}}{C_lV_s\rho_s} \quad (4.8)$$

Take the average value of the LBP of vial B~G provides the final result.

Text S5: Transil assay bioaccumulation potential calculations by CIC

Consider the fluorine mass balance inside a single Transil^{XL} vial:

$$TF_{tot} = TF_s + TF_l \quad (5.1)$$

where TF_{tot} (μmol) is the total fluorine mass inside a Transil^{XL} vial, TF_s (μmol) is the total fluorine mass adsorbed onto Transil^{XL} beads, TF_l (μmol) is the total fluorine mass in liquid.

TF_{sup}(μmol) and TF_{sed} (μmol) refer to the total fluorine measured directly by CIC in Transil^{XL} supernatant and sediment, respectively.

$$TF_{tot} = C_{TF} \times V_1 \times 10^{-6} \quad (5.2)$$

where C_{TF}(μmol/L) is the total fluorine concentration in sample added into the Transil^{XL} vial.

On the solid phase,

$$C_s = \frac{TF_s}{m_s} \quad (5.3)$$

where m_s(μg) is the mass of solid Transil^{XL} lipid beads inside the vial, and can be calculated by equation (4.4)

Fluorine concentration in the liquid phase can be calculated by,

$$C_l = \frac{TF_l}{V_{tot}} \quad (5.4)$$

Also,

$$C_l = \frac{TF_{sup}}{V_3} \quad (5.5)$$

From equation (4.4) and (4.5), we can derive that

$$TF_l = TF_{sup} \times \frac{V_{tot}}{V_3} = 2.6 \times TF_{sup} \quad (5.6)$$

Since the liquid volumes used for TF_{sup} and TF_{sed} are the same, assume no carry over and loss of beads during experimental operation, theoretically, the differences between TF_{sup} and TF_{sed} are resulted from the solids in sediment.

$$TF_s = (TF_{sed} - TF_{sup}) \times \frac{V_4}{V_5} = 1.4 \times (TF_{sed} - TF_{sup}) \quad (5.7)$$

Substitute (5.3) ~ (5.7) into (4.7), the TF concentration in liquid $C_{l,F}$ (μmol F/L) and in solid $C_{s,F}$ (μmol F/kg) are:

$$C_{l,F} = \frac{2.6TF_{sup}}{V_{tot}} \quad (5.8)$$

$$C_{s,F} = \frac{1.4(TF_{sed} - TF_{sup})}{V_s \rho_s} \quad (5.9)$$

So the partition coefficient of total organofluorine is

$$LBP = \frac{C_{s,F}}{C_{l,F}} = \frac{1.4(TF_{sed} - TF_{sup})/(V_s \rho_s)}{2.6TF_{sup}/V_{tot}} = \frac{1.4(TF_{sed} - TF_{sup})V_{tot}}{2.6TF_{sup} V_s \rho_s} \quad (5.10)$$

Take the average value of the K_{MW} of vial B~G as the final result, and calculate the standard deviation.

Text S6. Minimal working concentration

Minimum measurable total fluorine by CIC is:

$$TF_{min} = 2\ \mu g/L \times 5.139 mL = 11\ ng \quad (6.1)$$

In the worst case of vial G, let $TF_{sup} = TF_{min} = 11$ ng, then we have:

$$C_l = \frac{TF_{sup}}{V_2} = \frac{11\ ng}{100\ \mu L} = 0.11\ ppm \quad (6.2)$$

$$TF_l = 2.6 \times TF_{sup} = 2.6 \times 11\ ng = 28.6\ ng \quad (6.3)$$

For PFOA, LBP = 10^3 L/kg was measured by LC-MS/MS, so the TF from 20 μL of PFOA addition is:

$$C_s = LBP\ C_l = 10^3\ L/kg \times 0.11\ ppm = 110\ mg/kg \quad (6.4)$$

$$TF_s = C_s V_s \rho_s = 110\ mg/kg \times 0.907\ \mu L \times 1.05 \times 10^3 g/L = 104.8\ ng \quad (6.5)$$

$$TF_{tot} = TF_s + TF_l = 104.8\ ng + 28.6\ ng = 133.4\ ng \quad (6.6)$$

PFOA concentration from stock solution was at least:

$$C_{PFOA} = \frac{133.4\ ng\ F}{20\ \mu L \times 285\ g\ F/mol} = 23\ \mu mol/L \quad (6.7)$$

Text S7. Quality control and quality assurance of Transil^{XL}

1. The references (A and H) vary no more than 50%.

2. At least 2 data points with Transil^{XL} are available in a series, which means TF_{sed}, TF_{sup} > CIC detection limit, $TF_{sed} - TF_{sup} > 0$

3. The correlation coefficient (R^2) of $logC_s$-$logC_l$ linear fitting above 0.8 is considered as good fitting, between 0.3 to 0.8 is acceptable for CIC data in this study.

Text S8. Explanation TF partition on Transil^{XL} throughout the electrocatalysis period

The changes of fluorine distribution in liquid and solid phase of Transil^{XL} assay are shown in Figure S7, where we can see TF in solid phase decrease by approximately 1 log, while TF in liquid remained almost constant. TF in solid consists exclusively of organofluorine adsorbed onto TransilXL beads and is supposed to decrease over the course of treatment, while TF in liquid include organofluorine that partition into liquid and F^- that do not adhere onto Transil^{XL} and a slight increase is expected but not detected due to sampling size and CIC testing capability. Within the 1st hour, PFOA is the primary content of fluorine in either phase of Transil^{XL} because PFOA take up the highest percentage of fluorine mass balance among all compounds in all samples taken before 1 hour. However, after PFOA is removed after 3 hours, partition of compounds other than PFOA dominates inside Transil^{XL} assay. The reduced LBP could be attributed to the increased portion of compounds with low LBP such as byproducts and F^- as a result of chain shortening and defluorination processes occurred during electrocatalysis.

Table S1. Information of PFAS reagents

Full name	Abbreviation	Molecular weight (g/mol)	Purity	Supplier	CAS
Perfluorobutanioc acid	PFBA	214	98%	Sigma Aldrich	375-22-4
Perfluoro-*n*-hexanoic acid	PFHxA	314	≥ 97%	Sigma Aldrich	307-24-4
Perfluoro-*n*-octanoic acid	PFOA	414	95%	Sigma Aldrich	335-67-1

Table S2. Target PFAS ESI parameters

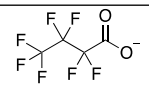
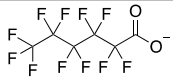
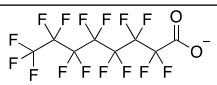
Target PFAS	Molecular structure	Precursor ion (m/z)	Quantifier ion (m/z)	Qualifier ion (m/z)	Collision energy (eV)	Retention Time (min)
PFBA		213	169	n/a	8	2.3
PFHxA		313	269.1	119	8	3.1
PFOA		413	369	169	8	3.8

Table S3. ESI parameters of mass labeled IS

Internal standards	Molecular formula	Precursor ion (m/z)	Quantifier ion (m/z)	Collision energy (eV)	Retention Time (min)	Target analyte
MPFBA	$^{13}C_4F_7O_2$	217	172	8	2.3	PFBA
MPFHxA	$^{13}C_2{}^{12}C_4F_{11}O_2$	315	270	8	3.1	PFHxA
MPFOA	$^{13}C_4{}^{12}C_4F_{15}O_2$	417	372	8	3.8	PFOA

Table S4. LC-MS/MS eluent composition gradient

Time (min)	A (%) [20mM Ammonium Acetate]	B (%) [MeOH]
0.00	95	5
0.75	40	60
4.00	0	100
7.00	0	100
8.00	95	5
10.00	95	5

Table S5. LC-MS/MS electrospray negative ionization (ESI) parameters

Parameter	Value	Unit
Capillary voltage	300	V
Fragmentor voltage	380	V
Drying gas	N_2	-
Gas flow rate	14	L/min
Drying gas temperature	200	°C

Table S6. LC-MS/MS detection limits of 3 target PFAS

PFAS compound	Limits of detection (ng/L)	Limits of quantification (ng/L)
PFBA	11	37
PFHxA	6	19
PFOA	3	10

Table S7. CIC operating parameters

	Value	Unit
Temperature	1050	℃
Combustion time	5	min
Combustion gas	O_2	-
Combustion gas flow rate	300	mL/min
Carrier gas	Ar	-
Carrier gas flow rate	100	mL/min
Injection loop volume	1	mL

Table S8. AOF recovery rates of target PFAS (n = 3)

	pH = 2	pH = 7	pH = 12
PFBA	57.5 ± 20.1	51.3 ± 14.0	35.2 ± 4.17
PFHxA	69.2 ± 11.4	77.6 ± 6.47	104 ± 74.1
PFOA	110 ± 2.9	113 ± 4.84	71.8 ± 33.4

Table S9. LBP (L/kg) of target PFAS

	This study	Previous study[1]
PFBA	1.7 ± 1.9	1.0
PFHxA	2.5 ± 2.3	2.31 ± 0.08
PFOA	3.0 ± 0.2	3.51 ± 0.07

Table S10. Pearson correlation coefficient matrix of PFOA, F^-, AOF and LBP

	PFOA	F^-	AOF	LBP
PFOA	1.000	-0.997	0.985	0.888
F^-	-0.997	1.000	-0.987	-0.899
AOF	0.985	-0.987	1.000	0.863
LBP	0.888	-0.899	0.863	1.000

Figure S1. Setup of the electrocatalysis reactor system

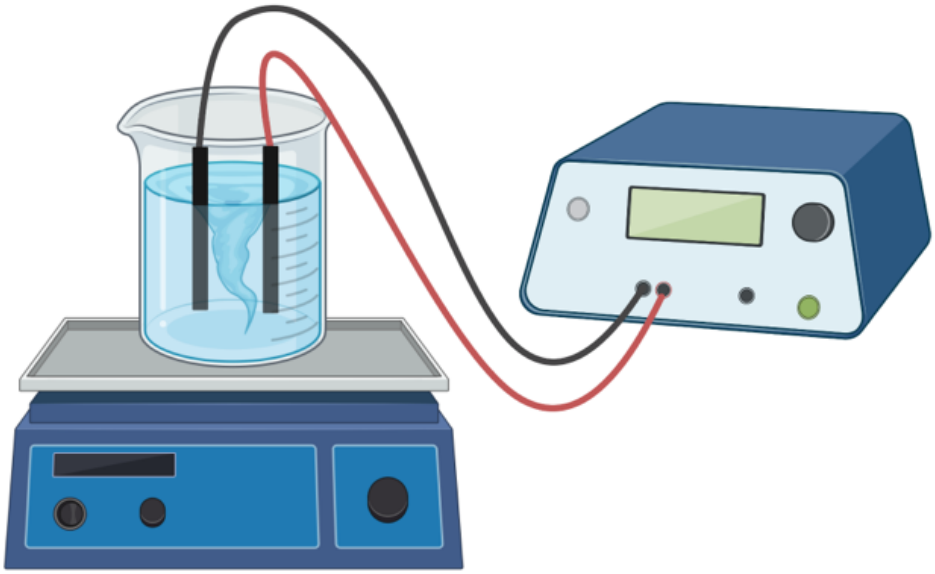


Figure S2. View of a Transil^{XL} kit. Row A and H are references without lipid membrane. B to G contain increased volume of membranes indicated by deeper filling colors.

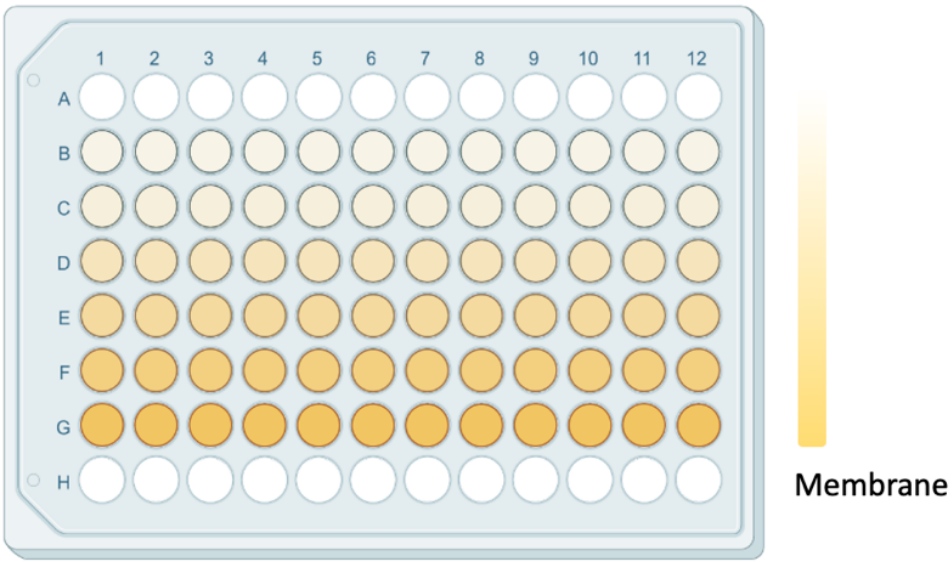


Figure S3. TF during 3 hours of electrocatalysis. Error bars show standard deviation from duplicate measures.

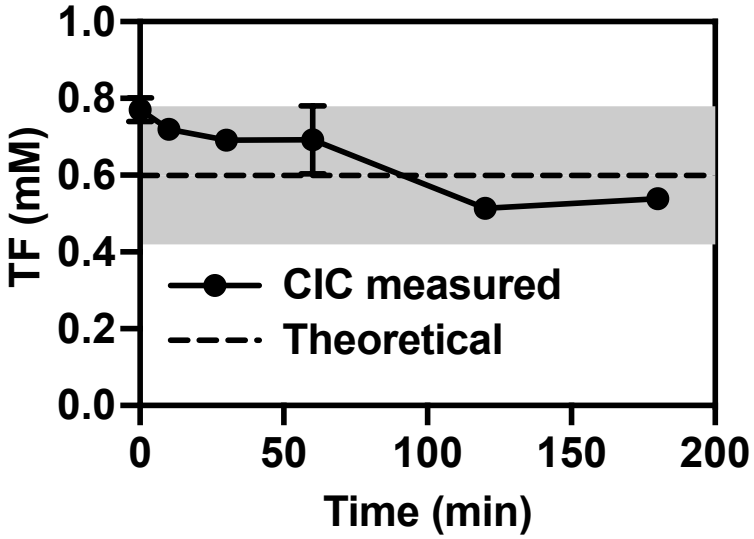


Figure S4. Rescaled TF molecular percentage of PFHxA and PFBA during 3 hours of electrocatalysis.

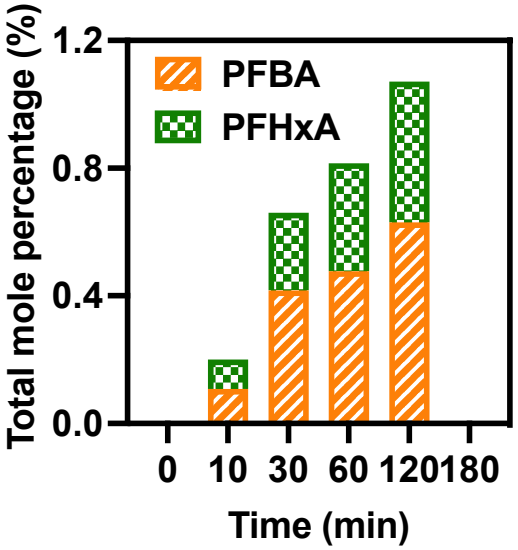


Figure S5. PFBA, PFHxA's partition isotherms between aqueous phase and Transil lipid bilayer beads measured by LC-MS/MS. Solid line shows regressed partition model fitted by LC-MS/MS data. Dashed lines are 95% CI of LC-MS/MS result's regression. LBP of PFBA and PFHxA are $10^{1.03}$ L/kg and $10^{1.63}$ L/kg, respectively.

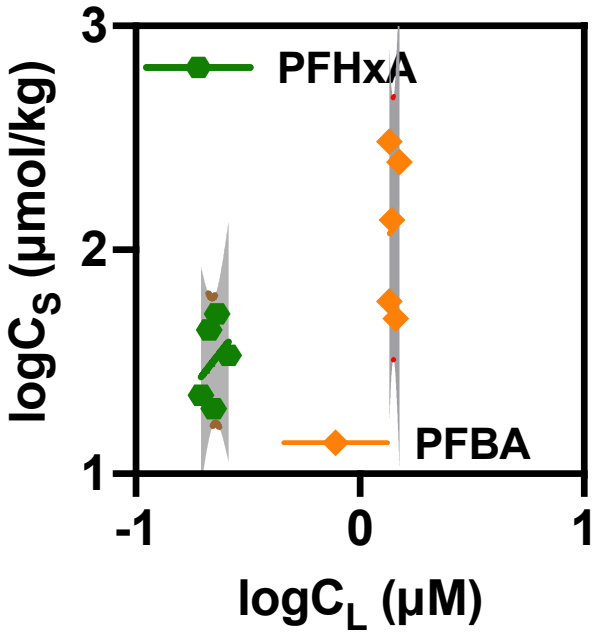
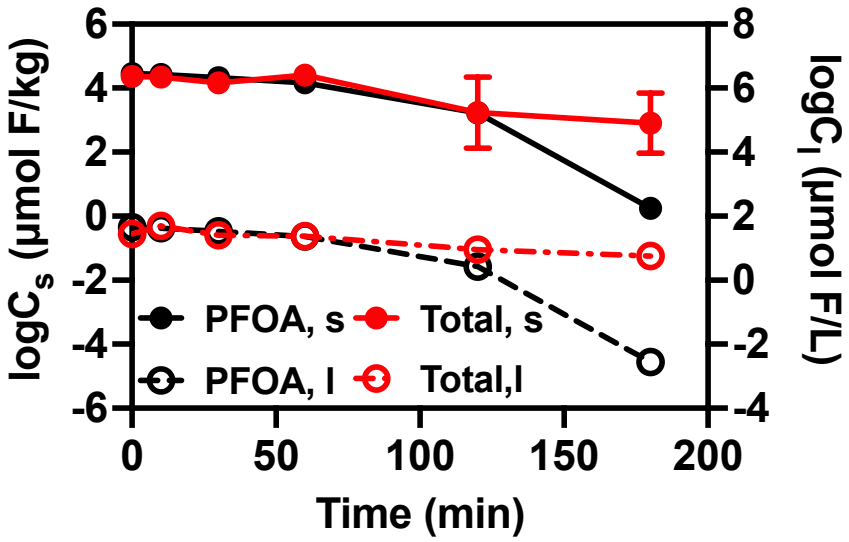


Figure S6. Changes of total fluorine mass balance in Transil^{XL} assay with treatment time. Solid and dashed lines represent solid and liquid phase concentrations, respectively. Red lines stands for total fluorinated compounds (both organofluorine and F^-), black lines refer to PFOA's contribution to total organofluorine. $C_{PFOA,l}$ was measured by LC-MS/MS. $C_{PFOA,s}$ was estimated using $C_{PFOA,l}$ multiply by a K_{MW} value of $10^{2.9}$ L/kg. TF in solid and liquid are measured by CIC.



Reference

1. S. T. J. Droge, *Environ Sci Technol*, 2019, **53**, 760-770.