Supporting Information

Discovery of a Novel Polyfluoroalkyl Benzenesulfonic Acid around Oilfields in Northern China

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Purification process of OBS. OBS authentic standard was purified from commercial OBS product using Autopurification HPLC system (Waters 2767, Milford, Massachusetts, American). The analytes were separated on the Xbridge Prep C18 column (19mm×250mm, 5μm). The mobile phase composed 0.1% ammonium bicarbonate in water (m/m, eluent A) and acetonitrile (eluent B) running in the gradient mode. The solvent gradient started at 20% B and then ramped to 65% B by 12.0 min, and then linearly increased to 100% by 25.0 min. The flow rate was set at 20 ml/min. Product solution was prepared at 140 mg/ml, and 500 μL was injected in each separation cycle. The single-quadruple MS detector was used to direct the fraction collection. White solid crystals were obtained after they were lyophilized. The structure were further validated by an nuclear magnetic resonance spectrometer (19F-NMR, Bruker AVANCE III 400Hz, as shown in Figure S3).

Table S1. Experimental conditions used for electrospray tandem mass spectrometry.

Curtain gas pressure: 25 psi; collision gas pressure: 3 psi; ion spray voltage: -2000 V;

Source temperature: 400°C; gas 1: 50 psi; and gas 2: 40 psi

Compound	Parent ion (Q1)	Daughter ion (Q3)	Dwell time (ms)	Declustering Potential (V)	Entrance Potential (V)	Collision Cell Ent. Potential (V)	Collision Energy (eV)	Collision Cell Exit Potential (V)
PFBA	212.8	168.8	15	-26	-2.3	-7.0	-11	-8
PFPeA	262.8	218.9	15	-26	-2.5	-8.5	-10	-9.5
PFHxA	312.8	269.0	15	-26	-2.6	-10	-10.5	-7
PFHpA	362.8	319.0	15	-27	-3.3	-12	-12	-8
PFOA	412.8	369.0*	15	-22	-4.0	-35	-21	-15
	412.8	169.0	15	-25	-4.0	-8.0	-21	-8
PFNA	462.8	419.1	15	-30	-3.8	-14	-13	-10
PFDA	512.8	469.1	15	-27	-4	-16	-14	-18
PFUnDA	562.8	519.1	15	-28	-4.3	-17	-14.5	-20
PFDoDA	612.8	569.0	15	-29	-5	-37	-24	-23
PFTrDA	662.8	619.0	15	-31	-4.8	-20	-16	-24
PFTeDA	712.8	669.0	15	-40	-5.0	-18	-18	-20

PFBS	298.8	79.9*	15	-58	-4.5	-13	-55	-8.5
	298.8	99.0	15	-57	-5.5	-13	-42	-7.5
PFHxS	398.8	79.9*	15	-64	-9.5	-15	-75	-9
	398.8	99.0	15	-62	-9	-14	-51	-8
PFOS	498.8	79.9*	15	-80	-9	-20	-90	-10
	498.8	99.0	15	-78	-8.5	-19	-68	-9
OBS	603.1	172.0*	15	-120	-10	-15	-45	-9
	603.1	465.0	15	-120	-10	-15	-50	-15
13C4 PFBA	216.9	171.9	15	-25	-2.4	-7.5	-11	-8
13C4 PFOA	416.8	372.1	15	-26	-3.5	-36	-21	-15
13C2PFDoDA	614.8	570.0	15	-32	-5	-19	-15	-22
13C4 PFOS	502.8	79.9	15	-80	-9	-19	-90	-10

*quantification ion

Table S2. The whole method performance for OBS and legacy PFASs, including extraction efficient, recovery, MLD, MLQ and RSD

Compound	Internal standard	Extraction Efficient (%,mean±SD, n=5)	Recovery (%, mean±SD, n=5)	MLD (ng/L)	MLQ (ng/L)	RSD (%)
PFBA	$^{13}C_4$ PFBA	86±5.6	96±5.9	0.09	0.27	6.5
PFPeA	$^{13}C_4$ PFBA	104±5.4	110±5.5	0.22	0.65	5.2
PFHxA	$^{13}C_4$ PFOA	117±4.5	106±7.0	0.05	0.14	3.8
PFHpA	$^{13}C_4$ PFOA	120±5.2	105±4.7	0.02	0.05	4.3
PFOA	$^{13}C_4$ PFOA	119±3.7	98±7.0	0.14	0.42	3.1
PFNA	$^{13}C_4$ PFOA	114±4.0	89±7.3	0.12	0.35	3.5
PFDA	$^{13}C_4$ PFOA	101±5.5	99±4.9	0.08	0.23	5.5
PFUnDA	$^{13}C_2$PFDoDA	93±4.0	91±1.8	0.09	0.28	4.3
PFDoDA	$^{13}C_2$PFDoDA	85±5.4	101±7.9	0.06	0.12	6.4
PFTrDA	$^{13}C_2$PFDoDA	80±4.0	93±9.7	0.06	0.19	5.0
PFTeDA	$^{13}C_2$PFDoDA	70±4.1	80±9.1	0.05	0.16	5.9
PFBS	$^{13}C_4$ PFOS	110±5.0	107±6.4	0.05	0.15	4.5

PFHxS	$^{13}C_4$ PFOS	108±4.2	109±6.1	0.02	0.06	3.9
PFOS	$^{13}C_4$ PFOS	101±2.8	98±4.7	0.02	0.06	2.8
OBS	$^{13}C_4$ PFOS	89±7.5	86±3.7	0.32	0.96	8.4
$^{13}C_4$ PFBA	/	86±5.7	/	/	/	6.7
$^{13}C_4$ PFOA	/	118±6.0	/	/	/	5.1
$^{13}C_2$PFDoDA	/	83±5.4	/	/	/	6.5
$^{13}C_4$ PFOS	/	101±5.8	/	/	/	5.8

Table S3. Summary statistics of OBS and legacy PFASs concentrations in surface water (unit: ng/L)

		OBS	PFOS	PFBS	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA
BC	Min	<MLQ	<MLQ	<MLQ	7.7	0.73	1.4	2.4	2.2	0.68
	Max	19	24	9.6	86	40	15	14	46	11
	Mean	6.9	3.7	3.0	31	12	5.0	5.4	12	2.3
	Median	5.5	0.23	2.0	18	4.1	3.8	3.6	5.5	1.0
NOF	Min	9.9	0.07	<MLQ	11	1.7	2.1	2.3	4.0	0.99
	Max	1.1×10^2	4.4	0.55	80	52	7.7	8.2	13	3.2
	Mean	50	0.81	0.11	27	11	4.6	4.5	6.8	2.1
	Median	57	0.37	0.06	21	3.7	4.7	3.5	5.2	2.0
OOF	Min	10	0.65	<MLQ	3.0	0.67	1.6	1.9	2.7	0.58
	Max	3.2×10^3	1.5×10^2	19	2.4×10^2	1.8×10^2	42	23	28	5.2
	Mean	5.6×10^2	14	5.0	37	23	9.2	6.6	12	2.4
	Median	2.3×10^2	2.3	1.4	20	7.3	4.3	4.2	9.6	2.1

Table S4. Deaths (cumulative mortality) of Zebrafish and Tadpoles exposed to each concentrations of OBS and LC50 for Zebrafish and Tadpoles

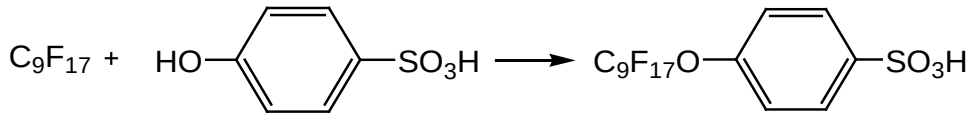
Group (mg/L)	Time (h)	**Zebrafish (n=30)**	**Tadpoles (n=30)**
		Deaths (Mortality / %)	Deaths (Mortality / %)
0(0)*	24	0 (0)	0 (0)
	48	0 (0)	0 (0)
	72	0 (0)	0 (0)
	96	0 (0)	0 (0)
11.3 (13.7)	24	0 (0)	0 (0)
	48	0 (0)	0 (0)
	72	0 (0)	0 (0)
	96	0 (0)	0 (0)
14.5 (19.2)	24	0 (0)	0 (0)
	48	0 (0)	0 (0)
	72	0 (0)	0 (0)
	96	0 (0)	0 (0)
18.9 (26.9)	24	0 (0)	10 (33.3)
	48	0 (0)	12 (40)
	72	0 (0)	13 (43.3)
	96	0 (0)	18 (60)
24.6 (37.6)	24	6 (20)	30 (100)
	48	8 (26.7)	30 (100)
	72	9 (30)	30 (100)
	96	9 (30)	30 (100)
32 (52.7)	24	30 (100)	30 (100)
	48	30 (100)	30 (100)
	72	30 (100)	30 (100)
	96	30 (100)	30 (100)
LC 50 (mg/L)		25.5	28.4

*exposed concentrations for Zebrafish (Frog tadpoles)

Table S5. The degradation half-lives of OBS obtained from EPI Suite software

	Half-life in air (h)	Half-life in water (h)	Half-life in soil (h)	Half-life in sediment (h)	Persistence time
OBS-Na	4.21	4.32×10^{3}	8.64×10^{3}	3.89×10^{4}	9.98×10^{3} h
OBS-H	4.19	4.32×10^{3}	8.64×10^{3}	3.89×10^{4}	9.61×10^{3} h
PFOS-Na	1.83×10^{5}	4.32×10^{3}	8.64×10^{3}	3.89×10^{4}	8.65×10^{3} h
PFOS-H	1.83×10^{3}	4.32×10^{3}	8.64×10^{3}	3.89×10^{4}	4.04×10^{3} h

[1] Synthesis 1:



[1, 2] Synthesis 2:

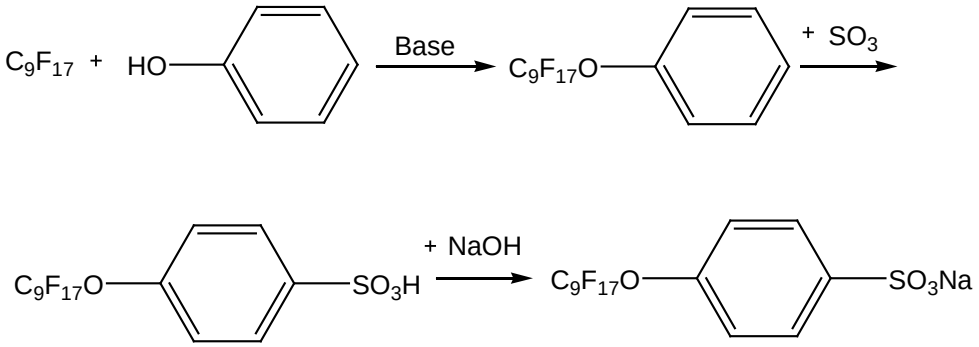
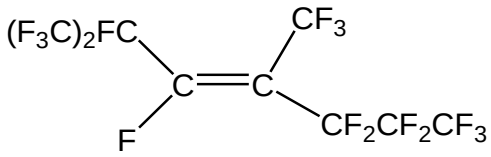
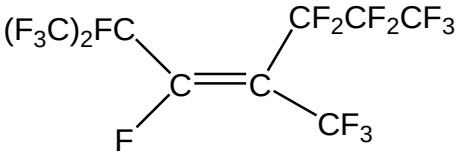


Figure S1. The synthesis process of OBS



HFPT-a'



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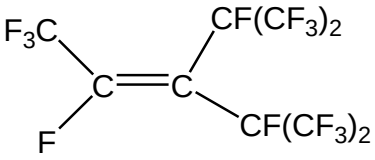
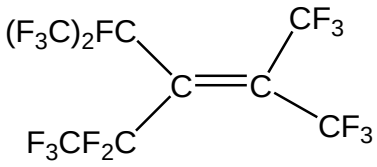
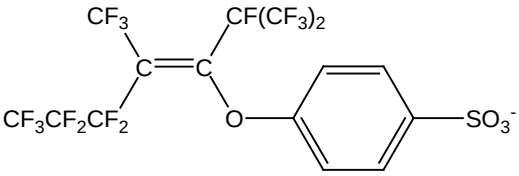


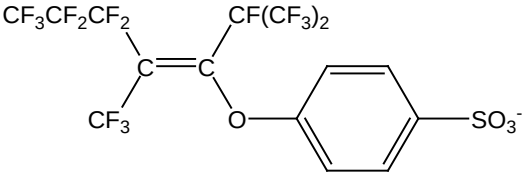
HFPT-c'



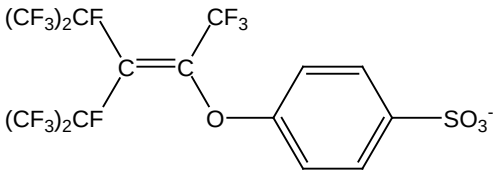
HFPT-d'



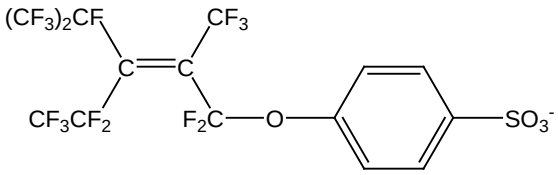
OBS-a



OBS-b



OBS-c



OBS-d

Figure S2. The structure of HFPT and OBS isomers

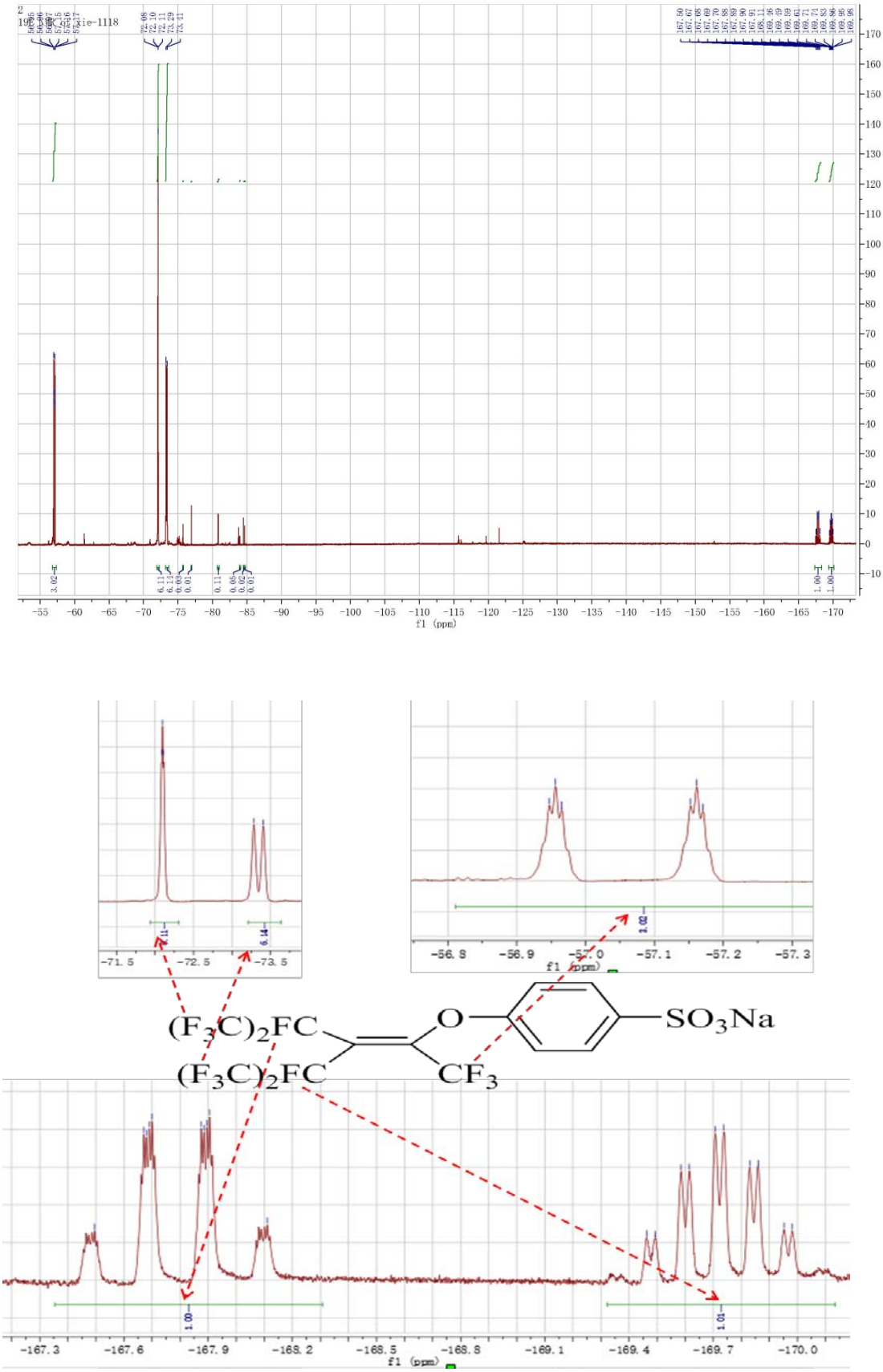


Figure S3. 19F-NMR spectrometry of OBS standard solution

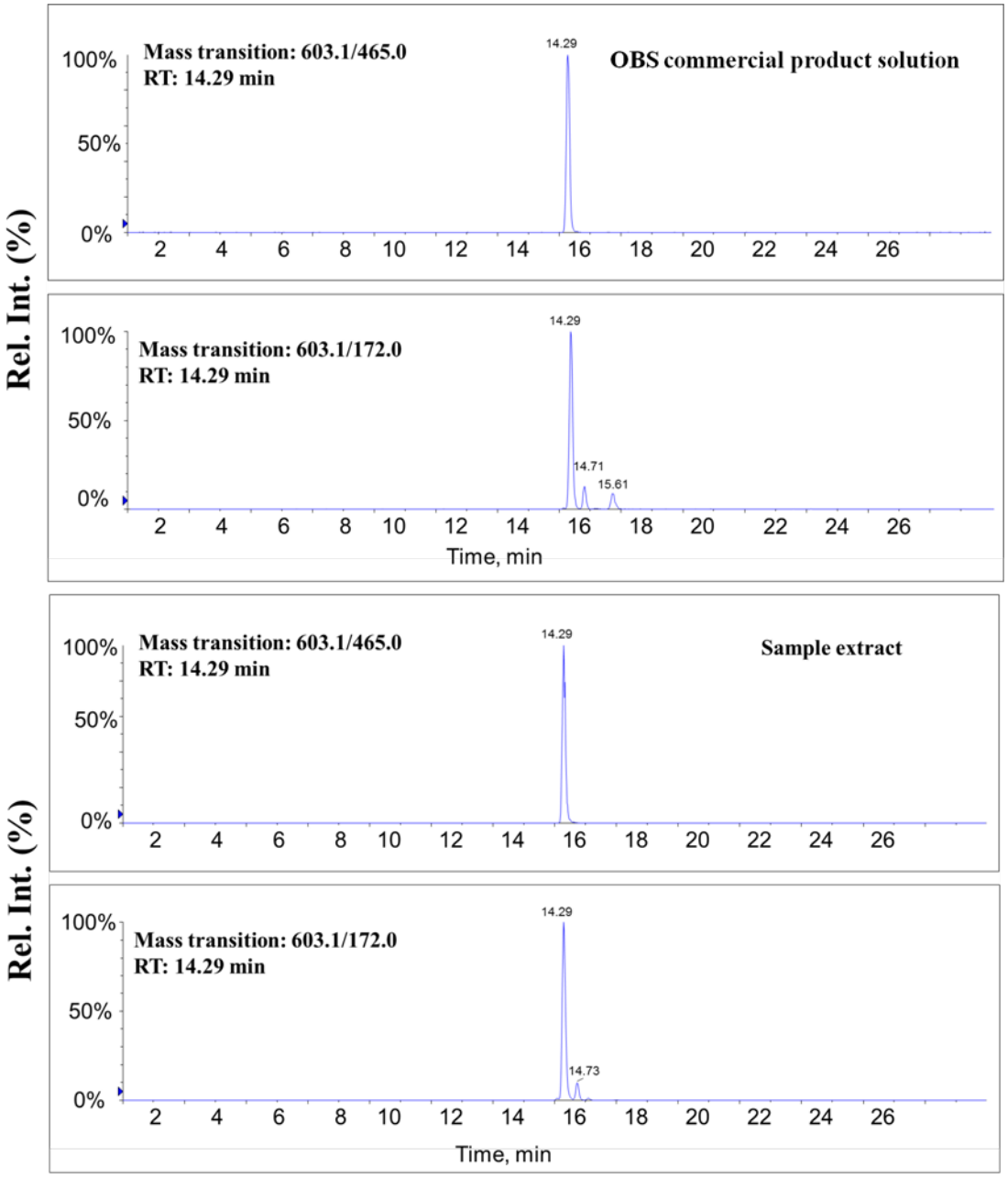


Figure S4. The chromatograms of OBS commercial product solution and surface water extract on PFP column

Reference:

1. Chen, L.; Shi, H.; Wu, H.; Xiang, J. Synthesis and combined properties of novel fluorinated anionic surfactant, *Colloi. Surface. A* **2011,** 384, 331-336

2. Sha, M.; Xing, P.; Jiang, B. Strategies for synthesizing non-bioaccumulable alternatives to PFOA and PFOS, *Chinese Chem. Lett.* **2015,** 26, 491-498