Supporting information

Screening of textile finishing agents available on the Chinese market: an important source of per- and polyfluoroalkyl substances to the environment

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Text S1. Material and Method Details

Chemicals and reagents

Methanol (HPLC grade) was purchased from Duksan Pure Chemicals Co., Ltd. (Gyeonggi-do, Korea). Ammonium hydroxide (HPLC grade) was purchased from Aladdin (Shanghai China. Acetic acid (HPLC grade) was bought from Kanto chemicals (Tokyo, Japan). The P-WAX cartridges (150 mg, 30 μm) for purification and extraction of samples were obtained from Waters Corporation (Milford, MA). The ultrapure water (UPW; 18 MΩ·cm, Millipore, MA, USA) was used for the rinsing, pre-treatment and final analysis.

Sample pretreatment

Calculated volume of pure textile finishing agent (TFA) was diluted with UPW (50 mL final volume) and subjected to solid phase extraction (SPE) column. The SPE cartridges were preconditioned with 4 mL of 0.5 % ammonium methanol, 4 mL of methanol and 4 mL of ultrapure water sequentially. The sample was loaded into the column at a rate of 1 drop per second. After loading the sample, the cartridges were washed with sodium acetate buffer (25 mM, pH=4) and dried for 30 minutes. Target PFASs were firstly eluted with 4 mL of methanol and then with 4 mL of ammonium methanol (0.5%). The extract was concentrated by nitrogen stream evaporation to the final volume of 0.25 mL. Subsequently, the concentrated sample was further diluted with 0.25 mL of UPW and then spiked with 50 µL of mass labeled internal standard. After filtration through 0.22 µm filter, the sample was stored in polypropylene vials (1 mL volume) at -18°C.

Corresponding QA/QC

To calculate the recovery for ionic and volatile compounds, selected sample (FA3) was spiked at 200 ng/mL with the native standards, the samples were pretreated and recovery was assessed. Meanwhile, in order to ensure accuracy, samples were also spiked with mass labeled internal standard (C^{13}-PFOA; 0.5 μg/mL). The calculated recovery of internal standard varied between 50 and 150 %.

Estimating unidentified precursors

The unidentified precursors were quantified by difference between the oxidation products (i.e. total PFCAs) and the identified precursors (i.e. FTOH). Total concentration of PFASs was estimated by summing the concentrations of PFCAs (by EPA method), PFSAs (by EPA method), FTOH and unidentified precursors (Houtz et al., 2012; Houtz et al., 2013; Houtz et al., 2016).

In figure 6, the concentrations of PFCAs and PFSAs were obtained by direct quantification (EPA method). The measured precursors substantially correspond to FTOH, and the unidentified precursors are the additional PFCAs generated upon oxidation (compared to those originally present) subtracted by those originated by identifiable precursors (i.e. FTOH). Hence, unidentified precursors can be estimated by the following equation:

$$\text{Unidentified precursors} = \text{PFCAs upon TOP assay} - (PFCAs\ by\ EPA\ method\ + measured\ precursors\ (FTOH)$$

These calculations were performed on molar basis, so results are reported as molar fractions.

Table S1

Detailed sampling information

No.	Sample name	Components	Vendors	Sampling year
Telomerization technology based TFAs				
FA 1	PHOBOL CP-SLA	C6	Shanghai Lutong	2017
FA 2	LT-EC601	C6		
FA 3	LT-710	NA		
FA 4	AGE-7800	C6		
FA 5	LT-A05	C6		
FA 6	FSJ	C6		
FA 7	LG-630	NA		
Electrochemical fluorination based TFAs				
FA 8	S34	C6	Hubei Hengxin;	2013
FA 9	S35	C4		
FA 10	S42	C6	Wuhan Fengfan surface engineering co., Ltd	
FA 11	S43	C6		
FA 12	S44	C4		

*C4 and C6 belong to short-chain technology; NA (not available)

Table S2

Analyte acronyms with corresponding IS

Compounds	Acronym	Formula	Corresponding IS
Perfluorobutanoate	PFBA	$CF_3(CF_2)_2COOH$	M4-PFBA
Perfluoropentanoate	PFPeA	$CF_3(CF_2)_3COOH$	M5-PFPeA
Perfuorohexanoate	PFHxA	$CF_3(CF_2)_4COOH$	M2-PFHxA
Perfluoroheptanoate	PFHpA	$CF_3(CF_2)_5COOH$	M4-PFHpA
Perfluorooctanoate	PFOA	$CF_3(CF_2)_6COOH$	M4-PFOA
Perfluorononanoate	PFNA	$CF_3(CF_2)_7COOH$	M5-PFNA
Perfluorodecanoate	PFDA	$CF_3(CF_2)_8COOH$	M2-PFDA
Perfluoroundeconoae	PFUnDA	$CF_3(CF_2)_9COOH$	M2-PFUnA
Perfluorododeconoate	PFDoDA	$CF_3(CF_2)_{10}COOH$	M2-PFDoA
Perfluorobutane sulfonate	PFBS	$CF_3(CF_2)_3SO_3H$	M3-PFBS
Perfluoropentane sulfonate	PFPeS	$CF_3(CF_2)_4SO_3H$	M3-PFHxS
Perfluorohexane sulfonate	PFHxS	$CF_3(CF_2)_5SO_3H$	M3-PFHxS
Perfluoroheptane sulfonate	PFHpS	$CF_3(CF_2)_5SO_3H$	M3-PFHxS
Perfluorooctane sulfonate	PFOS	$CF_3(CF_2)_7SO_3H$	M4-PFOS
4:2 Fluortelomer alchole	4:2 FTOH		M_2FOET
6:2 Fluortelomer alchole	6:2 FTOH		M_2FOET
8:2 Fluortelomer alchole	8:2 FTOH		M_2FOET

10:2 Fluortelomer alchole	10:2 FTOH	M_2FOET
Internal standard		
Perfluoro-n-[13C4]butanoate	MPFBA	-
Pfluoro-n-[13C5]pentanoate	M5PFPeA	-
Perfluoro-n-[1,2,3,4,6-13C2]hexanoate	M2-PFHxA	-
Perfluoro-n-[1,2,3,4-13C4]heptanoate	M4-PFHpA	-
Perfluoro-n-[1,2-13C2]octanoate	M2-PFOA	-
Perfluoro-n-[$^{13}C_8$]octanoate	M8-PFOA	-
Perfluoro-n-[$^{13}C_5$]nonanoate	M5-PFNA	-
Perfluoro-n-[1,2-$^{13}C_2$]decanoate	M-PFDA	-
Perfluoro-n-[1,2-13C2]undecanoate	M2-PFUdA	-
Perfluoro-n-[1,2-13C2]dodecanoate	M2-PFDoA	-
Sodium perfluoro-1-[2,3,4-13C3]butanesulfonate	M3-PFBS	-
Sodium perfluoro-1-[1,2,3-13C3]hexanesulfonate	M3-PFHxS	-
Sodium perfluoro-1-[1,2,3,4-$^{13}C_4$]octanesulfonate	M4-PFOS	-
2 perfluorooctyl-[1,2-$^{13}C_2$]-etanol	M_2FOET	-

*IS: Internal standard

Table S3

Directly quantified PFASs concentration (mg/L) in textile finishing agents

Compounds	Telomerization							Electrochemical fluorination				
	FA1	FA2	FA3	FA4	FA5	FA6	FA7	FA8	FA9	FA10	FA11	FA12
	SLA	601	710	7800	A05	FSJ	LG630	S34	S35	S42	S43	S44
PFBA	0.03	0.01	0.01	0.02	0.00	0.11	0.03	0.97	7.92	0.34	1.61	3.70
PFPeA	0.03	0.01	0.02	0.03	0.01	0.10	0.03	0.49	0.06	0.14	0.60	0.04
PFHxA	0.13	0.07	0.06	0.07	0.01	0.43	0.16	5.75	0.06	1.71	9.84	0.04
PFHpA	0.05	ND	0.03	0.03	0.00	0.09	0.06	0.02	0.02	0.01	0.02	0.01
PFOA	0.69	ND	0.28	0.23	ND	0.43	0.42	<LOQ	<LOQ	ND	ND	<LOQ
PFNA	0.05	ND	0.01	0.02	ND	0.03	0.04	ND	<LOQ	ND	ND	<LOQ
PFDA	0.71	ND	0.03	0.11	ND	0.07	0.14	<LOQ	<LOQ	ND	0.01	<LOQ
PFUnDA	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFBS	ND	ND	ND	ND	ND	0.00	0.00	0.28	2.81	0.01	0.01	1.44
PFPeS	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFHxS	ND	ND	ND	ND	ND	ND	ND	1.14	0.30	0.49	5.93	0.10
PFHpS	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFOS	0.16	ND	ND	ND	ND	0.09	0.06	0.07	1.21	0.07	0.11	0.44
PFNS	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFDS	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
4:2 FTOH	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
6:2FTOH	1.18	298.42	20.89	6.23	141.91	75.85	ND	ND	ND	0.15	ND	ND
8:2FTOH	0.49	0.85	38.79	426.67	ND	2.59	1145.56	ND	ND	ND	ND	ND
10:2FTOH	ND	ND	1309.88	112.72	ND	ND	ND	ND	ND	ND	ND	ND

Table S4

Observed perfluoroalkyl carboxylates upon oxidative treatment in UPW

	Spiked concentration (μM)*	**Generated PFCAs products (μM percentages)**							
		PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	Total PFCAs
8:2 FTOH	0.054	5% ± 2	27% ± 3	36 ± 4%	17% ± 4%	12% ± 0%	-	-	97 ± 4%
10:2 FTOH	0.044	11% ± 1%	31%	34%	2% ± 2%	12% ± 1%	13 ± 4%	1%	102 ± 3%

*25 ng/mL (as mass concentration)

Table S5

Concentrations of perfluoroalkyl carboxylates generated by total oxidizable precursor assay (mg/L)

Compounds	Telomerization							Electrochemical fluorination				
	FA1 SLA	FA2 601	FA3 710	FA4 7800	FA5 A05	FA6 FSJ	FA7 LG 630	FA8 S34	FA9 S35	FA10 S42	FA11 S43	FA12 S44
PFBA	43.63	89.93	52.29	21.50	283.57	276.79	38.36	252.50	242.50	20.93	213.00	74.69
PFPeA	96.25	132.50	118.57	30.50	659.64	700.36	69.57	537.50	6.035	8.35	9.98	158.75
PFHxA	287.75	155.00	290.36	98.93	1964.29	1960.71	151.43	2570.00	ND	28.98	ND	975.00
PFHpA	562.50	ND	363.21	119.29	225.36	218.21	293.57	ND	ND	ND	ND	ND
PFOA	980.00	ND	467.50	253.93	ND	ND	571.43	ND	0.009	ND	ND	ND
PFNA	284.00	ND	115.00	32.14	ND	ND	79.29	ND	ND	ND	ND	ND
PFDA	141.00	ND	61.54	2.49	ND	ND	46.86	ND	ND	ND	ND	ND
PFUnDA	14.50	3.04	1.45	4.10	ND	ND	2.27	1.67	ND	0.56	ND	ND

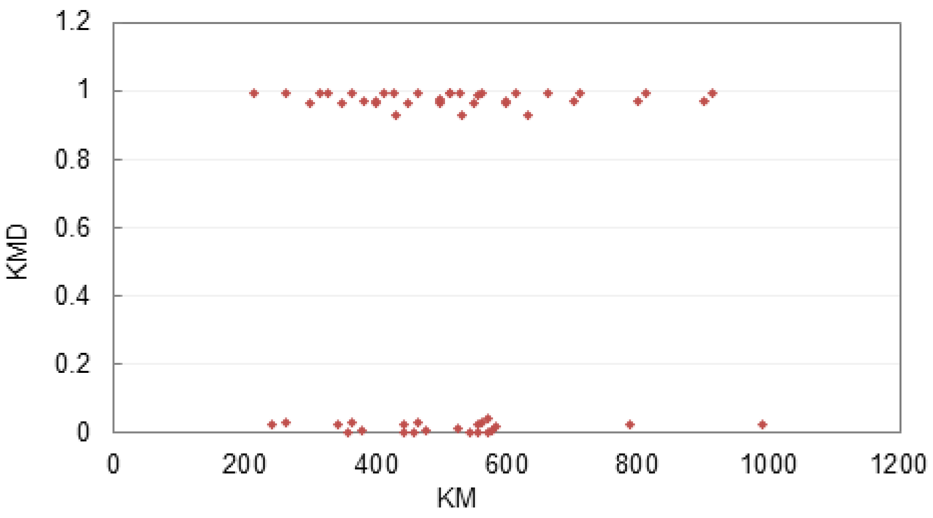

Fig. S1 Theoretically compute KMD for 58 PFASs (above 0.8 corresponds to PFCAs and PFSAs, and range between 0-0.1 corresponds to some precursors; few precursors also exist above 0.8)

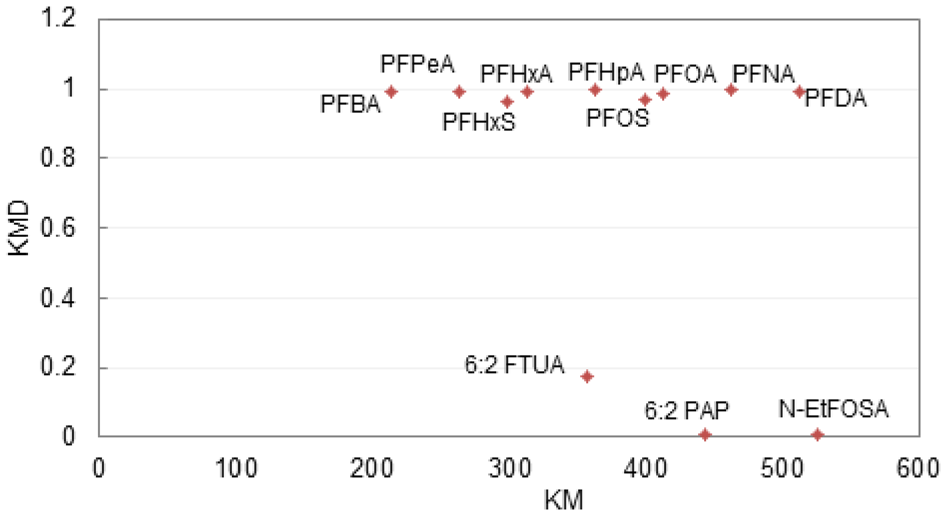

Fig. S2 KMD against KM plot for the entire mass spectrum in FA8

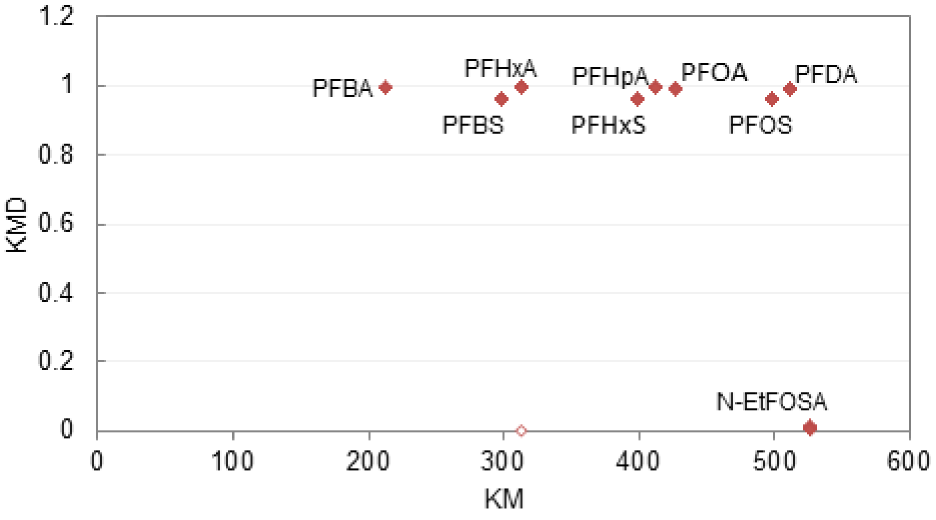

Fig. S3 KMD against KM plot for the entire mass spectrum in FA9

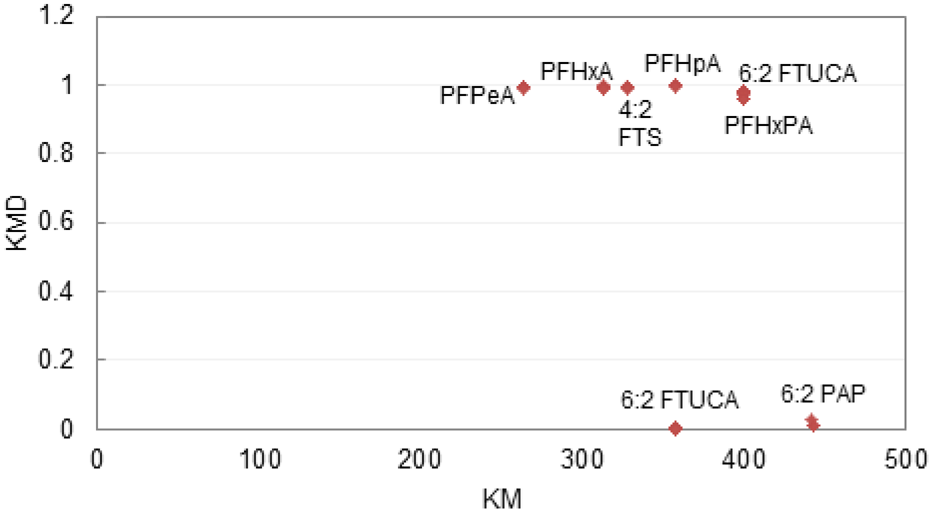

Fig. S4 KMD against KM plot for the entire mass spectrum in FA11

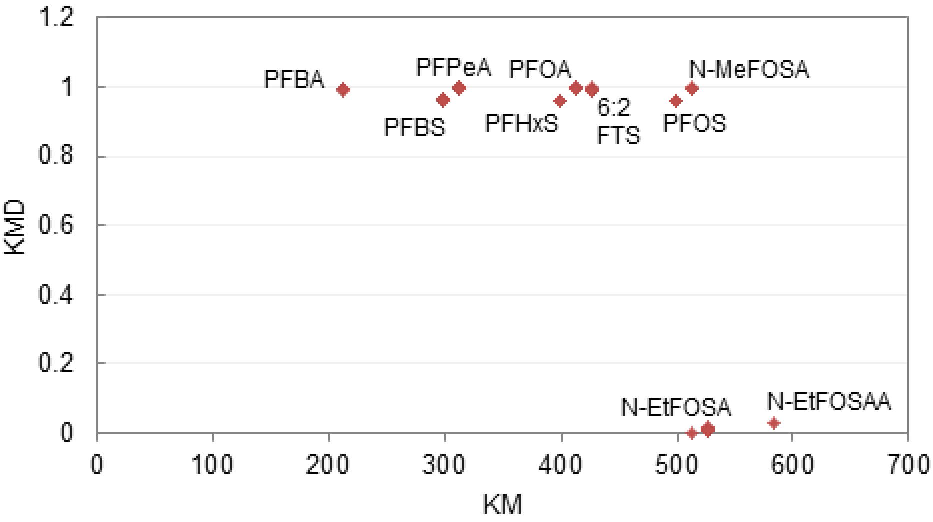

Fig. S5 KMD against KM plot for the entire mass spectrum in FA12

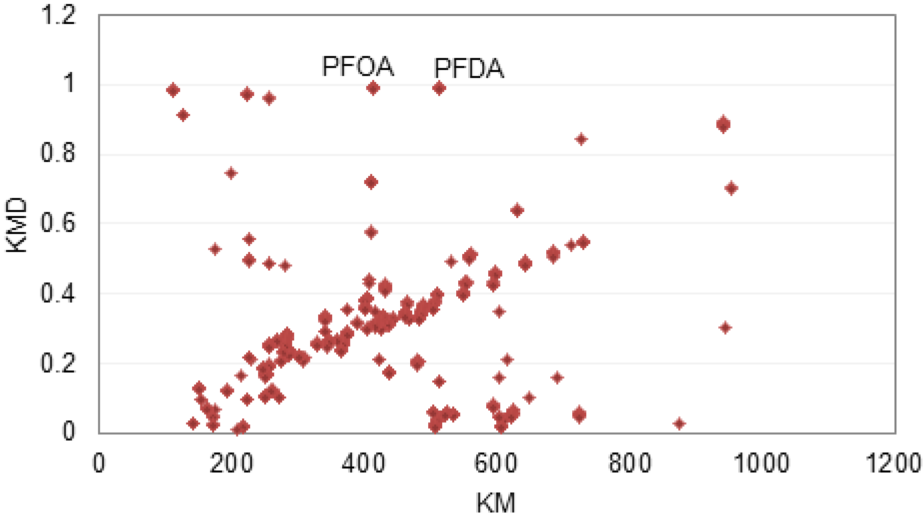

Fig. S6 KMD against KM plot for entire mass spectrum in FA1

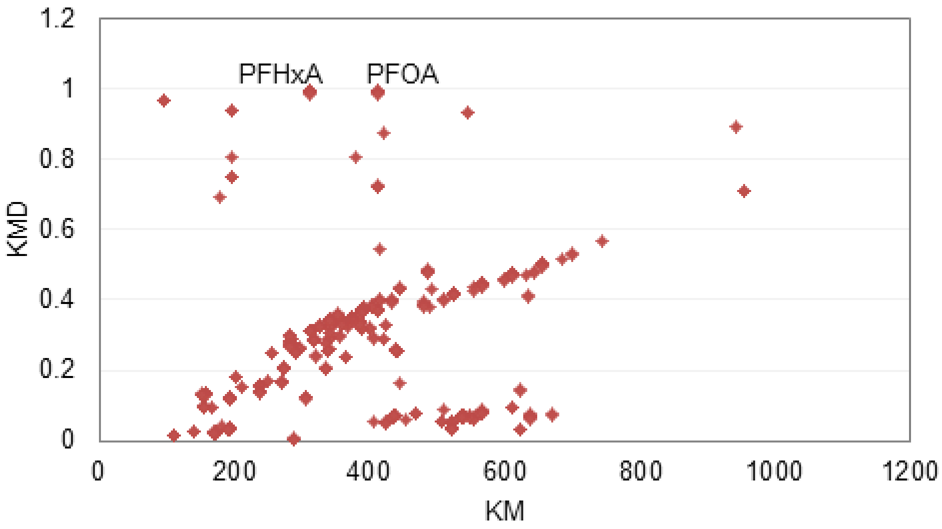

Fig. S7 KMD against KM plot for entire mass spectrum in FA6

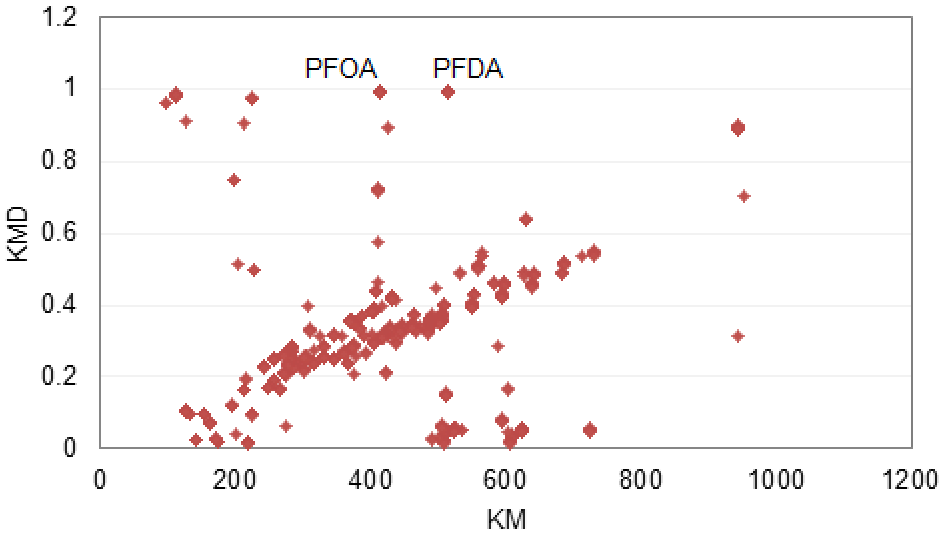

Fig. S8 KMD against KM plot for all the mass spectrum in FA7

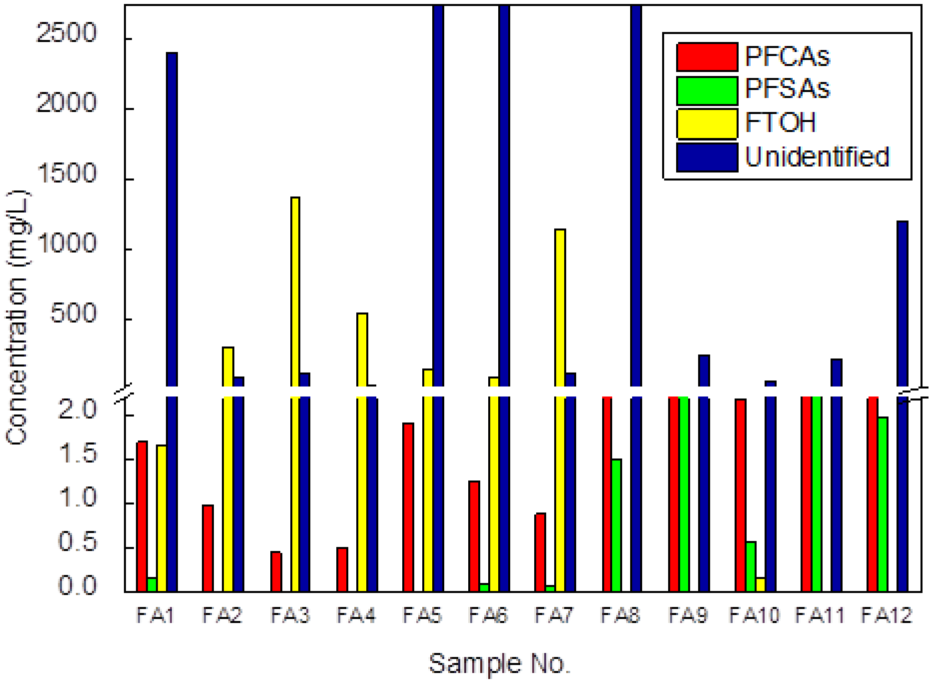

Fig. S9 Total PFASs concentration mg/L (It corresponds to sum of perfluoroalkyl carboxylates (PFCAs), perfluoroalkane sulfonates (PFSAs), measured fluorotelomer alcohol and unidentified precursor- observed increase in PFCAs profile upon oxidative treatment)

References

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